A MODEL OF INORGANIC CARBON LIMITATION IN NATURAL WATERS

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Abstract. A mathematical model based on the chain rule for partial derivatives was developed in order to predict the situations in which inorganic carbon limits algal productivity. Given data on gross primary productivity, algal-bacterial respiration rates, CO_2 gas transfer rates, temperature, alkalinity, initial pH, and the depth of the epilimnion, the model calculates the theoretical magnitude of dpH/dt in the water body during the photosynthetic period.

Based on sample calculations under various chemical, physical, and biological conditions, it appears that a dpH/dt of something greater that 2.0 units is necessary for inorganic C limitation to occur. Although this value has not been confirmed, the results suggest that C limitation of total planktonic algal growth would be rare in most natural waters. It is possible that C limitation could occur in low alkalinity water which would influence the species of algae present.

1. Introduction

As a means of understanding the role of inorganic C in the eutrophication of natural waters, a mathematical model was constructed that would predict whether or not inorganic C limits the planktonic algal productivity in a given body of water. This paper discusses the development of this model and its application and implications.

2. Theoretical Considerations

The approach of the mathematical model is similar to that developed by Di Toro *et al.* (1970) for working with the conservation of mass principle with respect to algal dynamics. The model depends on the ability to account for changes in the concentra-

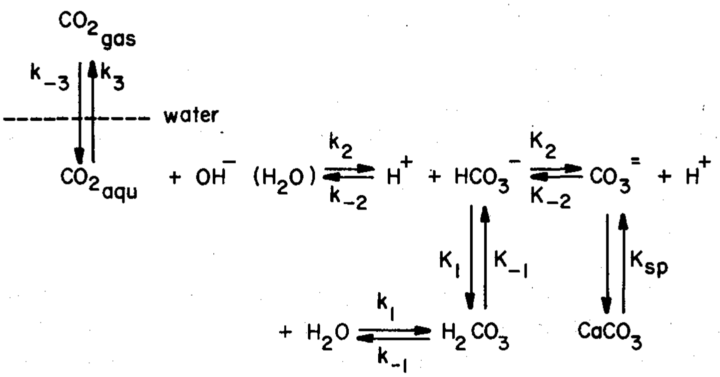

Fig. 1. The inorganic C system, where *k* is a rate constant and *K* is an equilibrium constant.

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tions of inorganic C species, and in particular, aqueous CO_2, based on chemical, physical, and biological processes.

Inorganic carbon distribution in natural waters is both thermodynamically and kinetically controlled. The inorganic C system, including both rate constants and equilibrium constants, is presented in Figure 1. It shows that the sources of aqueous CO_2 include atmospheric CO_2, the conversion of HCO_3^- and H_2CO_3 to CO_2, and solid $CaCO_3$. Other sources of aqueous CO_2 include the bacterial degradation of organic matter and the respiration of both bacteria and aquatic plants. The removal of aqueous CO_2 from the system is controlled by algal and bacterial photosynthesis, CO_2 transfer from the water body to the atmosphere, and the conversion of $CO_{2\mathrm{aqu}}$ to H_2CO_3 and HCO_3^-.

The basis of the mathematical model is the application of the chain rule for partial derivatives, with the rate of change of pH being calculated as the product of the rate of change of CO_2 and the change in pH as CO_2 changes, as shown in Equation (1)

$$\frac{\mathrm{dpH}}{\mathrm{d}t} = \frac{\mathrm{dCO_2}}{\mathrm{d}t} \cdot \frac{\mathrm{dpH}}{\mathrm{dCO_2}}. \tag{1}$$

The rate of change of CO_2, $\mathrm{dCO_2}/\mathrm{d}t$, is described in Equation (2), which considers the significant kinetic parameters that affect the addition and removal of aqueous CO_2.

$$\begin{aligned}\frac{\mathrm{dCO_2}}{\mathrm{d}t} = {} & K_p - K_r - K_g + k_1(\mathrm{CO_2}) + k_2(\mathrm{OH^-})(\mathrm{CO_2}) - \\ & - K_{-1}(\mathrm{H_2CO_3}) - K_{-2}(\mathrm{HCO_3^-}),\end{aligned} \tag{2}$$

where

K_p = gross primary productivity, in g C m^{-2} day^{-1},
K_r = algal-bacterial respiration rate, in g C m^{-2} day^{-1},
K_g = CO_2 gas transfer rate, in g C m^{-2} day^{-1},
k_1 = hydration rate constant,
k_{-1} = dehydration rate constant,
k_2 = $CO_2 + OH^- \rightarrow HCO_3^-$ rate constant,
k_2 = $HCO_3^- \rightarrow CO_2 + OH^-$ rate constant.

Equation (2) can then be reduced to Equation (3) since the rates of conversion of the carbonic acid species into aqueous CO_2 are several orders of magnitude more rapid than the uptake of aqueous CO_2 by planktonic algae (James, 1973)

$$\frac{\mathrm{dCO_2}}{\mathrm{d}t} = K_p - K_r - K_g. \tag{3}$$

The change in pH as CO_2 changes, $\mathrm{dpH}/\mathrm{dCO_2}$, is determined by considering the thermodynamics of the inorganic C system. It is evaluated empirically by a log-log plot of H^+ in mol l^{-1} vs CO_2 in mg l^{-1}, given the pH, alkalinity, and temperature (James, 1973). From this plot, Equation (4) was derived for $\mathrm{dpH}/\mathrm{dCO_2}$.

$$\frac{\mathrm{dpH}}{\mathrm{d}t} = \frac{0.95 \log_{10} \dfrac{\mathrm{CO}_{2_{\mathrm{initial}}}}{\Delta \mathrm{CO}_2}}{\log_{10} \mathrm{alkalinity}}, \tag{4}$$

where

$$\mathrm{CO}_{2_{\mathrm{initial}}} = \mathrm{mg\ l^{-1}\ CO}_{2_{\mathrm{initial}}},$$

$$\Delta \mathrm{CO}_2 = \frac{\mathrm{dCO_2/d}t(\mathrm{g\ C\ m^{-2}\ day^{-1}})}{\text{euphotic zone depth (m)}},$$

and alkalinity = $\mathrm{mg\,l^{-1}}$ as $\mathrm{CaCO_3}$.

Combining Equations (3) and (4) the final expression for dpH/dt is obtained as presented in Equation (5).

$$\frac{\mathrm{dpH}}{\mathrm{d}t} = K_\mathrm{p} - K_\mathrm{r} - K_\mathrm{g} \times \frac{0.95 \log_{10} \dfrac{\mathrm{CO}_{2_{\mathrm{initial}}}}{\Delta \mathrm{CO}_2}}{\log_{10} \mathrm{alkalinity}}. \tag{5}$$

3. Methods

Given the necessary chemical, physical and biological data, Equation (5) is used for calculating the theoretical rate of change of pH during the photosynthetic period. However, in order to apply the model, the following assumptions must be made:

(a) That there is some upper pH limit at which the algae will be C limited, and this limit is determined by the algal species, the alkalinity, and the temperature. The model arbitrarily assumes that a pH $\geqslant 10$ will cause inorganic C limited algal growth.

(b) That all essential growth elements except for C, N and P, are present in quantities not limiting the algal growth. In order for C to be a potentially limiting element, N and P must be present in sufficiently large concentrations relative to C compared to organism requirements. Given that a typical blue-green algal C:N:P mass ratio is 40:7:1, if C:N is less than 40:7 or if C:P is less than 40:1 in the water, inorganic C could be limiting the algal growth and Equation (5) can be applied to evaluate this possibility. In the C:N:P mass ratio, C is to be taken as the available inorganic C, including $\mathrm{CO_2}$–C and $\mathrm{HCO_3^-}$–C, N is the available inorganic nitrogen, including $\mathrm{NH_4^+}$–N and $\mathrm{NO_3^-}$–N, and P is the available orthophosphorus, $\mathrm{H_2PO_4^-}$–P, $\mathrm{HPO_4^=}$–P, and $\mathrm{PO_4^{\equiv}}$–P.

(c) That blue-green algae are the dominant algal species, with the result that $\mathrm{HCO_3^-}$–C, as well as $\mathrm{CO_2}$–C, is considered to be an available inorganic C form.

(d) That the lake is thermally stratified, with the epilimnion corresponding with the photosynthetic zone for the blue-green algae.

(e) That the kinetics of the transformations between inorganic C species are not limiting the availability of inorganic C.

(f) That the buffer capacity of the water is adequately represented by the alkalinity.

(g) That the water temperature and the alkalinity do not change to any great degree during the photic period.

4. Results

Table I shows the magnitude of dpH/dt predicted by the model for two natural bodies of water as well as a hypothetical lake. The Vermont lake is an unproductive soft water lake with an alkalinity of 5 mg l^{-1} as $CaCO_3$ in the epilimnion; western Lake Erie is a more productive body of water with an alkalinity of about 80 mg l^{-1} as $CaCO_3$; and the hypothetical lake, with conditions favoring C limitation, is a low alkalinity lake, with sufficient nutrient concentrations so that N and P do not limit algal productivity. The dpH/dt predicted by Table I ranges from 0.65 to 2.38 units, with the more highly buffered Lake Erie water having the smallest predicted pH change during the photosynthetic period, even though it has the greatest productivity. The hypothetical lake, with a gross productivity about one half that of Western Lake Erie, has a predicted pH change about four times as great, showing the importance of the buffering capacity of the carbonate system with respect to pH fluctuations.

TABLE I

dpH/dt predicted by the model

Given condition	Vermont Lake (after Allen, 1956)	Western Lake Erie (after Verduin, 1956)	Hypothetical Lake
Gross productivity g C m^{-2} day^{-1}	0.600	6.14	3.00
Respiration rate g C m^{-2} day^{-1}	0.060	3.07	0.20
Gas transfer rate g C m^{-2} day^{-1}	0	0.18	0
Alkalinity mg l^{-1} as $CaCO_3$	5	80	10
Epilimnion depth m	10	5	10
Initial pH	5	8.0	7.0
Temperature °C	20	20	20
Calculations			
dCO_2/dt	0.540	2.89	2.80
dpH/dCO_2	4.40	0.227	0.835
dpH/dt	2.38	0.65	2.34

Table I also shows that a pH change of 2.34 units would occur in the hypothetical lake during the photosynthetic daylight hours. With an initial pH of 7.0, a maximum pH of 9.34 would be predicted. With an alkalinity of 10 mg l^{-1} as $CaCO_3$, there are 1.55 g HCO_3^-–C m^{-3} and 0.002 g CO_2–C m^{-3} available to the algae, which convert to 15.5 g C m^{-2} and 0.02 g C m^{-2}, respectively, if a 10 m epilimnion is assumed. With a net productivity of 2.80 g C m^{-2} day^{-1}, C limitation would occur in about

5.4 days if all of the available CO_2 and HCO_3^- were utilized by the algae and no inputs of inorganic C were to occur.

In order to maximize the possibility of inorganic C limitation in the hypothetical lake, a negligible gas transfer rate was assumed. In actuality, CO_2 gas transfer from the atmosphere could supply a significant amount of aqueous CO_2. In fact, Schindler *et al.* (1971), working on an oligotrophic Canadian Shield Lake, found a CO_2 invasion rate ranging from 0.06 to 0.18 g C m^{-2} day^{-1}, while the productivity was about 0.20 g C m^{-2} day^{-1}. Since the lake contained less then 0.6 mg l^{-1} C of dissolved inorganic C, and since this value did not fluctuate much during the experiment, CO_2 gas transfer could be a significant source of inorganic C in low alkalinity lakes.

If conditions in the hypothetical lake are changed so that there is more available inorganic C, it is likely that the algae will become limited by either N or P. With an alkalinity of 100 mg l^{-1} as $CaCO_3$, and a pH of 8, a total available inorganic carbon concentration of 25.27 mg l^{-1} C would be present. Using the 40:7:1 mass ratio for C:N:P that is typical for blue-green algae, an aqueous inorganic N concentration of at least 4.45 mg l^{-1} N and an orthophosphorus concentration of at least 630 μg l^{-1} P would be necessary for C to be potentially limiting. These sorts of N and P concentrations are uncommon in natural waters, even when sewage effluent is being discharged into the water body. In cases where large amounts of sewage effluent are being discharged into small bodies of water, it is possible that bacterial metabolism of the residual BOD could supply enough CO_2 to prevent C limitation of the algal community.

In situations where the dominant algal species present utilizes only CO_2 as a photosynthetic C source, C limitation of that species could result in a shift to a dominant algal species that is able to utilize HCO_3^- as well as CO_2. Under this type of condition there may be no noticeable change in total algal biomass.

In any case, C limitation of algal productivity is rare in natural bodies of water. This conclusion is similar to that reached by Goldman and his associates (Goldman *et al.*, 1972) in a review paper on the effect of C on algal growth. They concluded that C limits the productivity of algae only under well-defined conditions that occur infrequently in nature, such as sewage lagoons, already eutrophic lakes, laboratory flasks with artificial media, or special situations affecting the amounts of available inorganic C. It is interesting to note that even though the approach used by Goldman *et al.* (1972) is different from the approach in this study, the conclusions are the same.

An important basic assumption in the mathematical model used in this investigation is that both CO_2 and HCO_3^- are available to the algae as a C source. It is known, however, while this may be generally true for the blue-green algae, it may not be true for other types of algae such as green algae. It is conceivable, therefore, that based on theoretical considerations used in the model proposed in this paper that the type of algae present in a body of water could be significantly influenced by the amount and forms of inorganic C present. In low alkalinity-high pH waters, blue-green algae could tend to be favored over green algae and other algae which are obligate CO_2 users. Shapiro (1973) has independently developed a somewhat similar conclusion based on some