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, CO₂ 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-

![Inorganic C System Diagram](image)

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$_2$CO$_3$ 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$_{2_{aq}}$ to H$_2$CO$_3$ 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)

$$\frac{dpH}{dt} = \frac{dCO_2}{dt} \cdot \frac{dpH}{dCO_2}. \quad (1)$$

The rate of change of CO$_2$, $\frac{dCO_2}{dt}$, is described in Equation (2), which considers the significant kinetic parameters that affect the addition and removal of aqueous CO$_2$.

$$\frac{dCO_2}{dt} = K_p - K_r - K_g + k_1 (CO_2) + k_2 (OH^-) (CO_2) - K_{-1} (H_2CO_3) - K_{-2} (HCO_3^-), \quad (2)$$

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)

$$\frac{dCO_2}{dt} = K_p - K_r - K_g. \quad (3)$$

The change in pH as CO$_2$ changes, $\frac{dpH}{dCO_2}$, 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 $\frac{dpH}{dCO_2}$.