

# Modelling of a relationship between phosphorus, pH, calcium and chlorophyll-a concentration

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## Abstract

The influence of algal growth on phosphate concentration in water was qualitatively simulated by means of a mathematical model. Phytoplankton, by carbon uptake through photosynthesis, decreases the carbonate concentration which results in equilibrium shifts through several connected chemical reactions that increase the supply of phosphorus to the phytoplankton. This internal cycling mechanism probably serves as a substantial source of P during the development of an algal bloom.

Based on these shifts, the developed mathematical model shows that, depending on the phytoplankton biomass, the phosphate ( $\text{PO}_4\text{-P}$ ) concentration in the water could increase, remain more or less the same, and/or decrease during an algal bloom. The proposed mathematical model suggests that calcium concentration, pH and chlorophyll-*a* concentration may play an important role in the solubility of phosphate in aquatic ecosystems.

## Introduction

The three major environmental variables that control photosynthesis in water bodies are light, temperature and nutrient availability (Peterson et al., 1987), and there is a general correlation between the nutrient status of a body of water and its primary productivity (Riley and Prepas, 1985). Almost all studies on eutrophication emphasise the importance of nitrogen (N) and phosphorus (P) as major causes of excessive algal growth (e.g. OECD, 1982).

Several studies show a limiting effect of P for phytoplankton growth in temperate lakes and reservoirs (Boström et al., 1982), but in certain tropical regions, N seems to be a critical nutrient (Henry et al., 1984). The conventional wisdom is that inorganic N is generally limiting in the oceans while inorganic P limits phytoplankton growth in freshwater environments (Harris, 1986). The major conclusion of the Co-operative Programme on Eutrophication (OECD, 1982) is that phosphorus availability controls algal biomass (chlorophyll-*a*) concentration in most of the lakes studied.

A significant positive correlation between average chlorophyll-*a* concentration and average total phosphorus (TP) has been documented by numerous investigators (e.g. OECD, 1982; White, 1989; Roos, 1992). Several authors have shown that the summer chlorophyll-*a* concentration in lakes is closely correlated to the concentration of winter TP or TP at spring overturn (e.g. Edmondson, 1969; Riley and Prepas, 1985; Golterman, 1988).

TP occurs in aquatic systems in three different components, namely:

- soluble reactive phosphorus (SRP) or phosphate, the form thought most likely to represent the phosphorus directly available to algal growth;
- soluble non-reactive phosphorus, which is largely organic and at least partially available to algal growth through enzymatic hydrolysis; and

- particulate phosphorus, which is stored in living cells, present in organic detritus, and adsorbed on abiotic particulate surfaces (Auer et al., 1986).

In water, phosphorus usually occurs in the oxidised state, either as inorganic orthophosphate ions or in organic, largely biogenic, compounds (Reynolds, 1984).

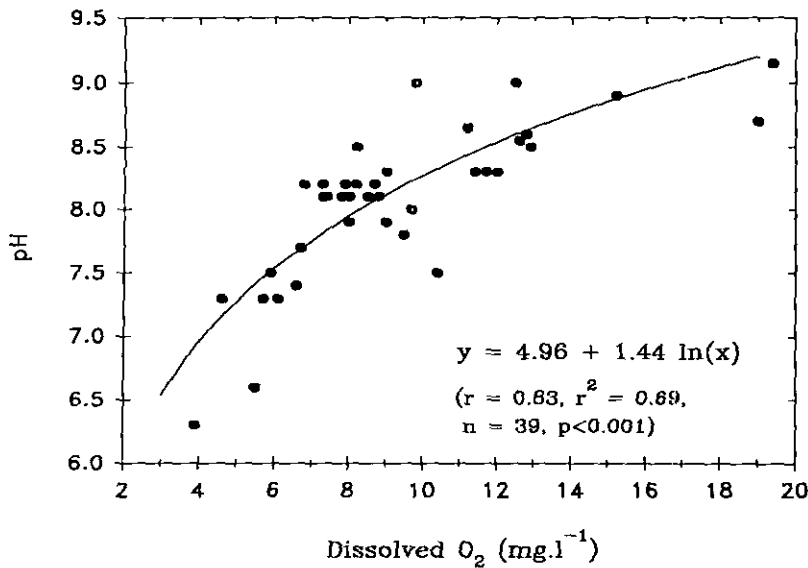
The relationship between chlorophyll-*a* concentration and phosphate phosphorus is, however, not clear. It has often been stated that phosphorus limits phytoplankton growth in lakes because the concentration of phosphate (SRP) is very low (Harris, 1986). Phosphate phosphorus limitation of algal growth or production has been reported in several streams (Newbold, 1992). In all cases the supposedly limiting concentrations of phosphate were equal or less than  $15 \mu\text{g}\cdot\text{L}^{-1}$  and frequently less than  $5 \mu\text{g}\cdot\text{L}^{-1}$ , but a direct measurement of phosphate in water rarely gives an accurate measure of the phosphorus available to algae (Fogg, 1980; Reynolds, 1984; Harris, 1986). Determining the concentration of a nutrient (i.e. a state variable) is not necessarily an indication of whether or not it is limiting. What one needs to know is the pool size and the rate of turnover, i.e. the rate variable (Harris, 1986). For example, Boström et al. (1982) showed that lake sediments (as a nutrient pool) play an important role in the overall phosphorus metabolism in lakes. Caraco et al. (1992) indicated that the P supply to Mirror Lake (USA) by surface runoff and precipitation accounted for less than 19% of calculated algal demand. They suggested that a possible explanation for this phenomenon is that recycling of nutrients in surface water provides almost the entire requirement for phytoplankton growth. Additional interacting factors are the mechanisms that algae have developed to overcome phosphorus deficiency. These include luxury consumption, the ability to use phosphate at low levels and alkaline phosphatase production (Goldman and Horne, 1983).

However, it has been generally observed that blooms of planktonic algae appear in freshwater when concentrations of phosphate and nitrate are at their lowest (Fogg, 1980; Eriksson and Forsberg, 1992; Istvanovics et al., 1992). This happens because assimilable forms of N and P decrease simultaneously with the increase of biomass. For example, Edmondson (1969) demonstrated

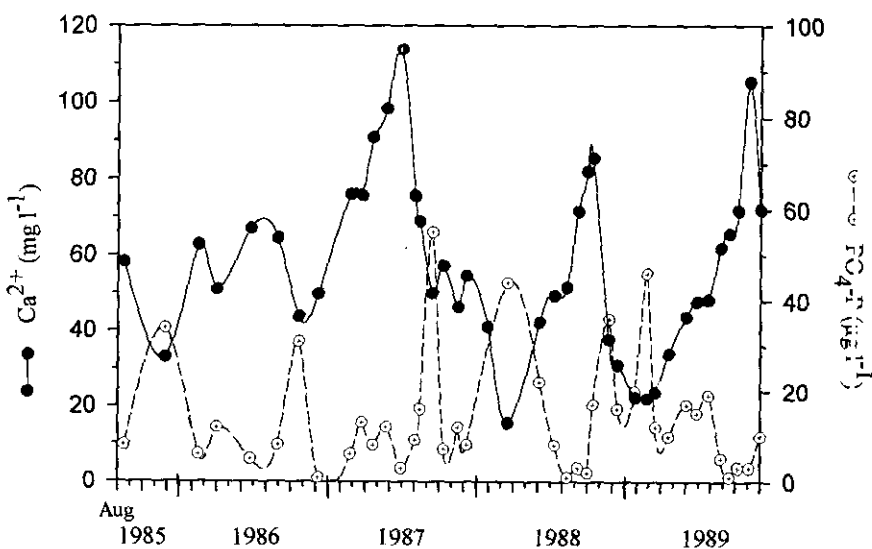
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**Figure 1**  
Relationship between dissolved oxygen concentration and pH in the Vaal River at Balkfontein (August 1985 to November 1989)



**Figure 2**  
Seasonal variation in calcium ( $\text{Ca}^{2+}$ ) and phosphate phosphorus ( $\text{PO}_4\text{-P}$ ) concentration in the Vaal River at Balkfontein (August 1985 to November 1989). A significant inverse correlation was demonstrated ( $r = -0.56$ ,  $n = 40$ ,  $p < 0.001$ )

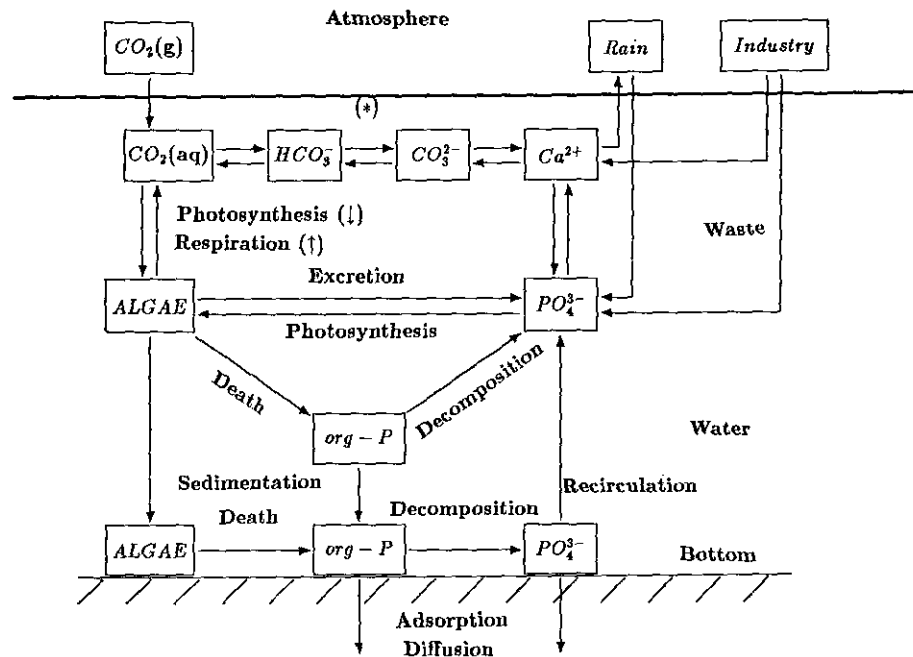
that the growth of *Oscillatoria rubescens* in Lake Washington decreased phosphate concentrations from spring to summer, and maximum algal concentration was reached at a time when phosphate concentration was at its minimum. Roos (1992) showed no significant correlation between chlorophyll-*a* concentration and phosphate in the Vaal River at Balkfontein (South Africa) for the period 1986 to 1989. Instead, an inverse tendency was demonstrated, because low phosphate concentrations usually occur in the river during the annual spring phytoplankton bloom. Golterman (1988) indicated, by plotting chlorophyll-*a* to phosphate ratios in 18 Friesian lakes, that a cloud of points was obtained from which no conclusion could be drawn. In temperate lakes, a large fraction of the annual primary production generally occurs in surface waters during summer, but many of these lakes experience little decrease in P in the surface waters during summer stratification (see Caraco et al., 1992). On the other hand, Pieterse and Toerien (1978) demonstrated a significantly positive correlation between the average chlorophyll-*a* and  $\text{PO}_4\text{-P}$  concentrations in Roodeplaat Dam (South Africa).

It is clear that contradictory results have been reported in the literature on the chlorophyll-phosphate relationship, i.e. positive,

negative or no correlation. An important difference, however, between the aquatic systems can be found in the chlorophyll-*a* concentration levels. Therefore, the purpose of this study is to provide qualitative information about the chlorophyll-phosphate interaction at different chlorophyll concentrations and to suggest a modified conceptual model that can possibly explain these apparently conflicting results from other studies.

Caraco et al. (1992) reported that the outputs of P exceeded the inputs in the epilimnetic P budget of Mirror Lake (USA). Caraco and co-workers concluded that this imbalance indicated that a P source was unaccounted for which could be extremely important for the overall processes in the lake. Istvanovics et al. (1992) concluded that a combination of internal P loading and enhanced P regeneration is necessary to sustain high primary production during exponential growth in Lake Erken, Sweden. We hypothesise that the "internal" cycle, where P transfer mechanisms are biologically mediated, plays an important role in the supply of phosphate to phytoplankton in a water body. Results from an ecological research programme on the Vaal River system provided valuable information concerning this subject (Roos and Pieterse, 1995a; b) that led to the development of a simple mathematical

**Figure 3**  
Simplified diagram of P-cycling showing the interrelationships between algae, inorganic carbon and dissolved phosphate concentration in a water body



model to explain the relationship between phytoplankton biomass and variations in phosphate concentration.

### The model: General concepts

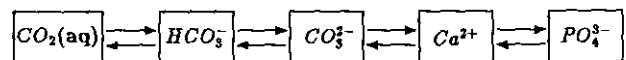
There are two broad groups of processes involved in the P cycling within aquatic ecosystems: the "internal" cycle where P transfer is biologically mediated and the "external" cycle dealing with physico-chemical complexation and release reactions (Golterman, 1975). In this model we focus only on the "internal" cycle.

The  $\text{CO}_2$ -pH-Ca- $\text{PO}_4$  interaction system (Fig. 4) is used as the basis for the model that will now be described in more detail. The components of the carbon dioxide-bicarbonate-carbonate system are interrelated by equilibria, and can provide  $\text{CO}_2$  to photosynthesising algae in a situation where the rate of  $\text{CO}_2$  uptake exceeds the replenishment rate of  $\text{CO}_2$  from the atmosphere (Prins and Elzenga, 1989; Shapiro, 1990). It is known that dense populations of phytoplankton tend to reduce the carbon dioxide concentration in natural waters, with an associated increase in pH (Wetzel, 1983). Because algae, by their photosynthetic activity, influence the dissolved oxygen and pH of the water, a statistically significant correlation may be demonstrated between pH and  $\text{O}_2$  concentration in the Vaal River at Balkfontein (Fig. 1; from Roos and Pieterse, 1995a). On the other hand, inorganic phosphates are known to form complexes, chelates and insoluble salts with a number of metal ions (Stumm and Morgan, 1970). In most of the rivers, however, only the calcium (Ca) will reach concentration levels sufficiently high to interfere with the solubility of phosphates (Golterman, 1975; Roos and Pieterse, 1995b). Stumm and Morgan (1970) calculated hypothetically that, in a water body with a calcium concentration of  $40 \text{ mg}\cdot\text{L}^{-1}$  and pH of 7, the total soluble phosphate is limited to approximately  $10 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ . This interference of Ca with phosphate concentration in the Vaal River (at the Balkfontein site), was supported by a significant inverse correlation between calcium and phosphate (Fig. 2; from Roos and Pieterse, 1995b). Likewise, for the Rhine River (Golterman, 1975), the inverse correlation between dissolved calcium and orthophosphate concentrations was characterised by a solubility product of the form:

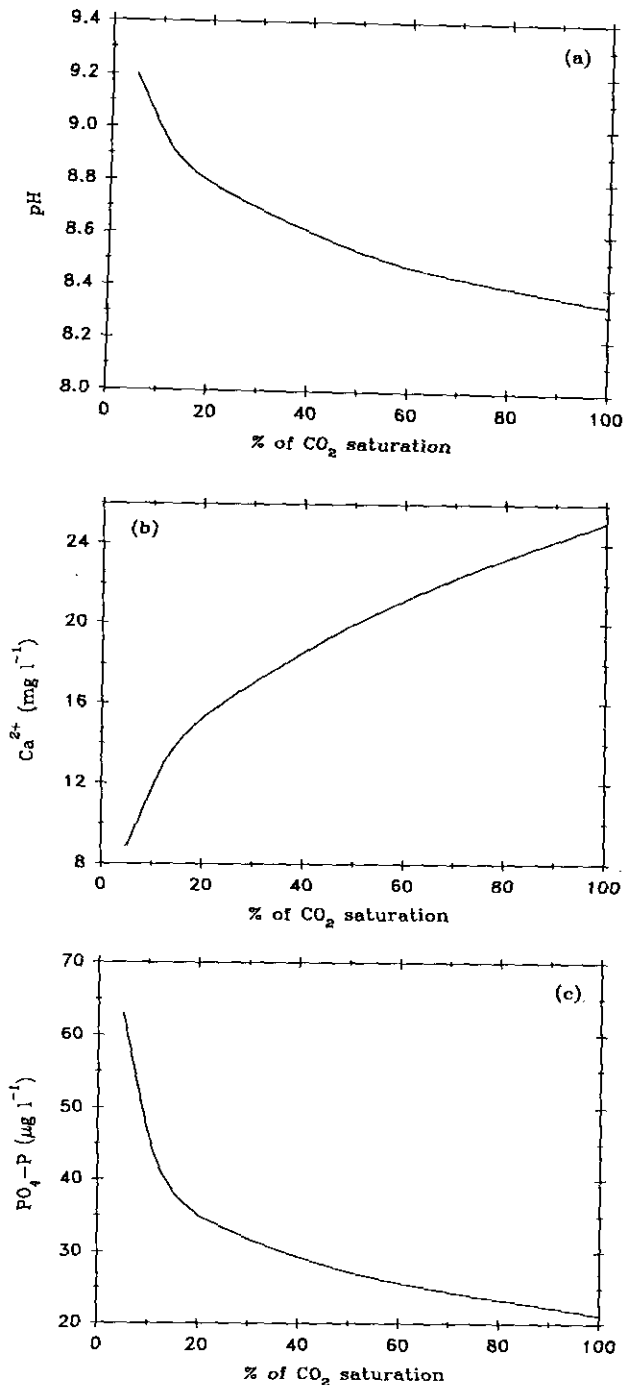
$$[\text{Ca}^{2+}]^{10}[\text{PO}_4^{3-}]^6[\text{OH}^-]^2 = K_{\text{apatic}}$$

where  $K_{\text{apatic}}$  is an equilibrium constant, possibly a function of the temperature. A synthesis of the different interactions governing the  $\text{CO}_2$ -pH-Ca- $\text{PO}_4$  system suggests that, due to algal growth, the variation of dissolved phosphorus concentration in the water could be described by means of a P cycle mechanism that is represented schematically in Fig. 3.

The existence of an indirect effect between dissolved  $\text{CO}_2$  and  $\text{PO}_4$  concentrations (see "\*" in Fig. 3) in the scheme, describing the interaction between algal photosynthesis (in the form of carbon assimilation) and phosphorus concentrations, may be fundamental to the understanding of the nutrient recycling process and could provide an explanation for the apparently contradictory results obtained from different studies referred to in the introduction. Indeed, if all chemical reactions in Fig. 4 are assumed to be of first order kinetics and the equilibrium constants,  $k_i$ 's, are those available in the literature (see for example, Garrels and Christ, 1965; Stumm and Morgan, 1970; Cole, 1975), numerical computations show that the uptake of dissolved carbon dioxide by algae is shifting the equilibrium concentrations in such a manner that the natural equilibrium concentration of dissolved phosphate in the river may increase. This result is in agreement with the work of Boström et al. (1982) who concluded that an increase in pH decreases the phosphorus binding capacity of iron and aluminium compounds, primarily due to ligand exchange reactions where hydroxide ions replace phosphate.



**Figure 4**  
Relationship between algal concentration and dissolved  $\text{PO}_4$ -P. A simple schematic representation of the equilibrium reactions of the carbon dioxide-phosphate system used in the model



**Figure 5**

- (a) Change in the pH value as a function of dissolved CO<sub>2</sub>
- (b) The same as (a) but for the ionic concentration of Ca<sup>2+</sup>
- (c) Theoretical chemical equilibrium dissolved phosphate concentration as a function of CO<sub>2</sub>. CO<sub>2</sub> concentration is expressed as the fraction of dissolved CO<sub>2</sub> in equilibrium with the atmosphere and a temperature of 15°C is considered

The results of numerical simulations for various concentrations of dissolved carbon dioxide are given in Figs. 5a to c. During these simulations, we took:

$$K_{\text{apatite}} = 10^{-81},$$

which is a typical (high) value observed for the equilibrium constant for the solubility of apatite, in the Vaal River context (Roos and Pieterse, 1995b).

These diagrams (Figs. 5a to c) show clearly that the decrease in the dissolved CO<sub>2</sub> concentration is coupled with an increase in the pH value (Fig. 5a) and a decrease in the concentration of Ca<sup>2+</sup> ions in solution (Fig. 5b). The net result of these two opposite mechanisms is a decrease in the product

$$[\text{Ca}^{2+}]^{10}[\text{OH}^{-}]^2$$

which, in turn, leads to an increase in the ionic concentration of PO<sub>4</sub> in solution (Fig. 5c).

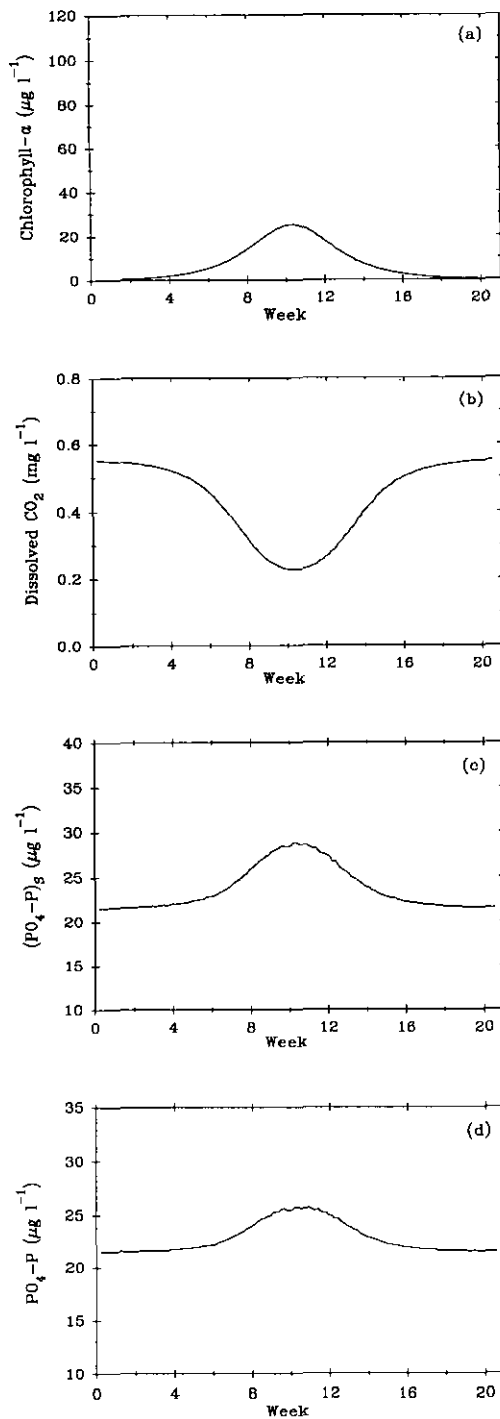
In order to investigate the qualitative effects on the dissolved phosphate concentration resulting from the competition between the uptake rate of phosphate and the recycled production of phosphate, initiated by algal population, we drastically reduced the scheme described in Fig. 3. Assuming that essential parameters such as temperature and flow remain constant and that no source (or sink) of dissolved phosphorus is active during the simulation period, the mechanism described in Fig. 3 can be represented by means of a simple dynamic system which can be written formally as:

$$\frac{d\text{CO}_2}{dt} = k_{\text{prod}}^{\text{CO}_2} (\text{CO}_{2s} - \text{CO}_2) - (k_{\text{up}}^{\text{CO}_2} - k_{\text{resp}})x(t) \quad (1)$$

$$\frac{d\text{PO}_4}{dt} = k_{\text{prod}}^{\text{PO}_4} (\text{PO}_{4s}(\text{CO}_2) - \text{PO}_4) - k_{\text{up}}^{\text{PO}_4}x(t) \quad (2)$$

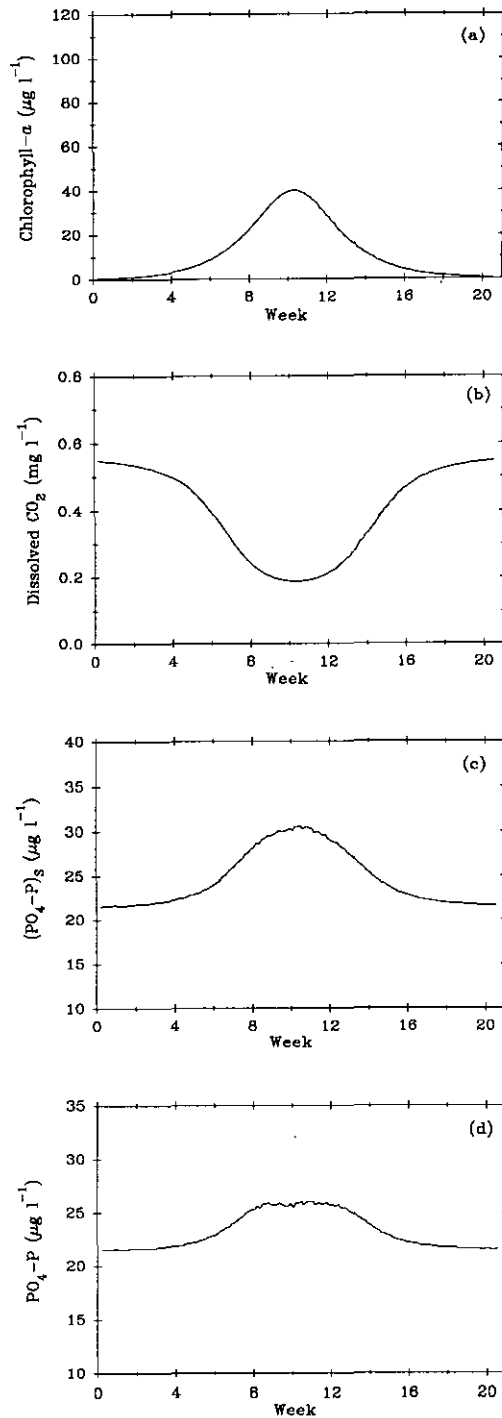
where CO<sub>2</sub> and PO<sub>4</sub> are the time-dependent concentrations of dissolved carbon dioxide and phosphate respectively, while CO<sub>2s</sub> and PO<sub>4s</sub> represent the theoretical equilibrium concentration effect observable in the river in the absence of any algal perturbation. The coefficients  $k_{\text{prod}}^i, k_{\text{up}}^i$  (where  $i = \text{CO}_2$  or PO<sub>4</sub>), represent the production and uptake rates of element "i", respectively. Finally,  $k_{\text{resp}}$  represents the respiration rate of the algae which have an  $x(t)$  concentration at time "t".

Note that it would be incorrect to represent the uptake rate of CO<sub>2</sub> through photosynthesis and the CO<sub>2</sub> release through respiration by means of one global component, because the photosynthesis and respiration processes exhibit different behavioural patterns with regard to the variation of, amongst others, algal concentration level, and light dependence, and with respect to the saturation effects.



**Figure 6A**

- (a) Variation in the chlorophyll-a concentration. A maximum of  $25 \mu\text{g Chl-a}\cdot\text{t}^{-1}$  is considered
- (b) Computed values of the dissolved  $\text{CO}_2$  concentration in the water body
- (c) Computed values of the theoretical chemical equilibrium  $\text{PO}_{4s}$  concentration
- (d) Computed values of the simulated dissolved phosphate concentration in the water body. Note the relationship between  $\text{CO}_2$  and  $\text{PO}_4$



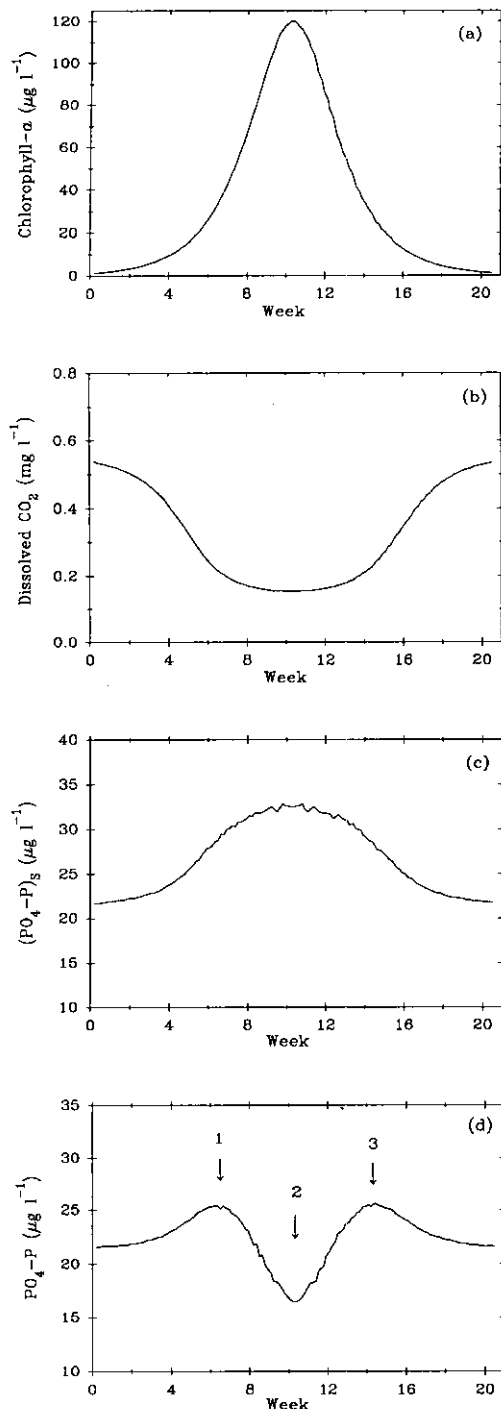
**Figure 6B**

- (a) Variation in the chlorophyll-a concentration. A maximum of  $50 \mu\text{g Chl-a}\cdot\text{t}^{-1}$  is considered
- (b) Computed values of the dissolved  $\text{CO}_2$  concentration in the water body
- (c) Computed values of the theoretical chemical equilibrium  $\text{PO}_{4s}$  concentration
- (d) Computed values of the simulated dissolved phosphate concentration in the water body. Note the relationship between  $\text{CO}_2$  and  $\text{PO}_4$

## Numerical results and discussions

The following values, for the different coefficients of the model (Eqs. 1 and 2), were used (Table 1).

TABLE 1 PARAMETER SET FOR THE COMPUTATION OF EQS. (1) AND (2)	
T	: 20(°C)
$k_{\text{prod}}^{\text{CO}_2}$	: 0.05(h <sup>-1</sup> )
$k_{\text{prod}}^{\text{PO}_4}$	: 1.5(h <sup>-1</sup> )
$k_{\text{upmax}}^{\text{CO}_2}$	: 0.004(mg CO <sub>2</sub> (μg Chl-a-h) <sup>-1</sup> )
$k_{\text{upmax}}^{\text{PO}_4}$	: 0.2 (μg PO <sub>4</sub> (μg Chl-a-h) <sup>-1</sup> )
$k_{\text{resp}}$	: 0.003 (mg CO <sub>2</sub> (μg Chl-a-h) <sup>-1</sup> )



**Figure 6C**

- (a) Variation in the chlorophyll-a concentration. A maximum of 120 μg Chl-a·t<sup>-1</sup> is considered
- (b) Computed values of the dissolved CO<sub>2</sub> concentration in the water body
- (c) Computed values of the theoretical chemical equilibrium PO<sub>4s</sub> concentration
- (d) Computed values of the simulated dissolved phosphate concentration in the water body. Note the relationship between CO<sub>2</sub> and PO<sub>4</sub>. See text for explanation of 1, 2 and 3

The kinetics of the solutions contained in the dynamic CO<sub>2</sub>-PO<sub>4</sub>-Ca system were investigated by assuming that the time-dependent development of the algal concentration  $x(t)$  was given by a hat function whose maximum amplitude,  $x_{max}$ , i.e. the maximum observable algal concentration, was kept as a free parameter. Assuming then that the carbon dioxide and phosphate concentrations were at their chemical equilibrium values, at the onset, the solution of the model, was computed over a wide range of maximum algae concentrations (Figs 6a to c).

The chlorophyll-a concentration in the Vaal River ranged between 8 and an exceptionally high 360 μg·t<sup>-1</sup> with the average at 67 μg·t<sup>-1</sup> (Roos, 1992). Therefore, chlorophyll-a concentrations of 25 μg·t<sup>-1</sup> (weak bloom), 50 μg·t<sup>-1</sup> (moderate bloom) and 120 μg·t<sup>-1</sup> (intense bloom) were used in the simulation. The result of these simulations (Figs. 6a to c) indicates that, due to variations in algal concentration, 3 kinds of reaction were exhibited by the CO<sub>2</sub>-PO<sub>4</sub> system depending on the amplitude of the algal bloom under consideration. Whenever the algal bloom was weak, i.e. the maximum chlorophyll-a concentration observed in the water was 25 μg·t<sup>-1</sup>, a positive correlation between the development of chlorophyll-a concentration and phosphate was observed (see Fig. 6a). In that case, through the increase of carbon dioxide uptake by the algal population, the potential dissolved phosphate concentration, PO<sub>4s</sub>, increased to such an extent that the internal P transfer production of phosphorus in the environment exceeded the nutrient uptake rate and an increase in dissolved phosphorus concentration followed. When a moderate algal bloom was simulated, i.e. at a maximum chlorophyll-a concentration of 50 μg·t<sup>-1</sup>, the recycled production and uptake rates were of the same order of magnitude and balanced each other out in such a way that no drastic increase or decrease in the dissolved phosphate concentration was observable during the algal bloom. This is illustrated in Fig. 6b. On the other hand, during an intense algal bloom, leading to chlorophyll-a concentrations of 120 μg·t<sup>-1</sup>, a depletion of dissolved phosphorus (Fig. 6c) was observed. The reason for this qualitative change in behaviour can be found in the non-linear character of the dynamic system under consideration. Once the algal concentration increased, the carbon dioxide concentration in the water decreased, promoting the internal P transfer production of dissolved phosphorus (see 1 in Fig. 6c). However, the non-linearities implied by the dynamic

nature of the system led to a saturation process which restricted the increase of the phosphate production rate. Should the algal concentration increase above a critical level a bifurcation occurs in the system where the uptake rate of phosphorus by algae becomes greater than the recycled production by chemical reactions so that a decrease in nutrient concentration follows (see 2 in Fig. 6c). Finally, when the algal bloom collapses, the recycled production of phosphate exceeds the uptake and the phosphate concentration increases again (see 3 in Fig. 6c). Note that Caraco et al. (1992) also indicated a slight increase, not a decrease, in dissolved P concentration of surface waters during summer stratification when new biomass production exerted a large demand on P. Results from Lake Erken (Istvanovics et al., 1992) also showed an initial increase in phosphate concentration in the epilimnion with an increase in phytoplankton production, followed by a decrease in phosphate at high phytoplankton biomass. In the light of these results it appears that for a given alga, in specific water conditions, and depending on the intensity of the algal bloom, 3 different kinds of kinetics can be observed for the dissolved phosphorus concentration. Although contradictory at first glance, these different kinds of kinetics may be explained within the framework of a single mechanism. Therefore, the contradictory assertions made by various authors on the subject (see the introductory paragraphs) are unlikely. It may even be possible that during one particular study period, in a given water body, more than one pathway of dissolved phosphorus could be observed. This recycled production of phosphate is in accordance with the predicted changes in Figs. 6a and b.

## Conclusions

The model developed in the present study, based on chemical equilibrium reactions, shows that algae, by their photosynthetic activity, may enhance the recycled production of phosphorus in the water body. This mechanism probably plays an important role in the P supply, which fuels primary production during the development of an algal bloom. The above observations suggest that calcium concentration, pH and chlorophyll-*a* in the river water play an important role in the solubility, and thus concentration, of phosphate in a river. Apparently contradictory results from many other field studies could possibly be explained - at least partially - by this chlorophyll-*a*-phosphate interrelationship mechanism which is described in this investigation.

However, much research remains to be done concerning the quantification of the pathways of the different components involved. This aspect of the problem should be investigated by considering a more complex and complete level of mathematical modelling.

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