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dynamics in lakes

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A CHEMICAL MODEL TO DESCRIBE NUTRIENT DYNAMICS IN LAKES

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Abstract

Chemical equilibria play an important role in nutrient cycling in Dutch lakes. Phosphorus behaviour and bottom-water exchange are influenced by chemical equilibrium reactions. Since non-equilibrium processes (or slow reactions) are important too, a model is used where both processes are included. A description of the model equations is given, and results of two calculations are discussed. These two calculations show the importance of total system modelling (as is done with this chemical model) and the effect of equilibrium processes on nutrient behaviour.

Introduction

Two reasons were decisive in choosing a chemical model for the description of nutrient fluxes in hypertrophic shallow ecosystems.

1. Phosphorus dynamics is pH dependent, since adsorption and subsequent sedimentation is pH dependent. pH modelling requires at least inorganic carbon modelling, which is impossible without introducing chemical equilibria.
2. Bottom-water exchange processes, which can be very important in hypertrophic shallow lakes, are E_h and pH dependent, which again requires chemical modelling.

An advantage of a chemical model is, that the whole system can be modeled (more state-variables can be included), which make such a

model especially suitable for proposing and testing hypotheses; there is however, a disadvantage too: a massive amount of input data is needed, and it has to be coupled to an algal model for making predictions. The present study is a part of the WABASIM-project (WAter BASIn Models), a joint project of the Delta Department of Rijkswaterstaat and the Delft Hydraulics Laboratory. A detailed report about the chemical model will be published by the Delft Hydraulics Laboratory in 1980.

Structure of the model

The model consists of two modules; an equilibrium module and a slow reaction module.

The equilibrium module

The equilibrium part of the model is based on the chemical equilibrium model developed by the Rand Corporation (Clasen, 1965, Shapley et al., 1970, Shapley et al., 1968). This model is well described and documented, so only a short description will be given here.

The objective of the model is to calculate the concentrations of chemical species in a system, when total amounts of chemical constituents (components) are given, and the relative stability (Gibbs free energy) af all species is known.

The model uses two kinds of equations:

1. Mass-balance equations (in terms of components)

2. Mass-action law equations (in terms of minimization of Gibbs free energy).

Mathematical notations are:

1. Mass balance:

$$\sum_j x_j \cdot a_{i,j} = b_i \text{ (for every } i) \tag{1}$$

2. Mass action low: find minimum of function F, where

$$F = \sum_j x_j \cdot (c_j + \log(\hat{x}_j)) \tag{2}$$

Definition of symbols:

x_j : number of moles of species $_j$
b_i : number of moles of component $_i$
a_{ij}: coefficient of component $_i$ in species $_j$
c_j : Gibbs free energy for species $_j$
$\hat{x}_j$: mole fraction of species $_j$
   (number of moles of a species divided by the total number of moles in a phase)

An example of the use of these equations is given below:

1 kilogram of H₂O

species: H⁺, OH⁻, H₂O
components: H⁺, OH⁻.

Matrix of coefficients:

	species/components	
	H⁺	OH⁻
H⁺	1	
OH⁻		1
H₂O	1	1

Since the number of moles in 1 kilogram of water is 55.51, the mass balance equations are:

H⁺ + H₂O = 55.51
   (number of moles H⁺ component)
OH⁻ + H₂O = 55.51
   (number of moles OH⁻ component).

The mass balance gives two equations, and we have three unknowns. The third equations is given by the mass action law, or minimization of Gibbs free energy. One of the advantages of this model formulation is, that the Jacobian matrix with partial derivatives is directly available, when the solution of the chemical problem is found.

In the model as it is used now, the formulation of the mass-action law is extended to include temperature and ionic-strength dependency of the Gibbs free energy:

$$c_j = c_j^0 + f(T) + f \text{ (ionic strength)} \tag{3}$$

in which c_j^0 is the Gibbs free energy at 25°C and zero-ionic strength.

The slow-reaction module

All processes which are not equilibrium processes belong to the slow-reaction module.

The slow-reaction module calculates the progress of slow reactions, (or the change in amount of slow reactant), and recalculates the mass balance for the equilibrium module (add or remove amounts of components).

All slow processes are written as chemical reactions.

The general equation for slow processes is:

$$\frac{dx}{dt} = k(AV_{(t)} - EV) \tag{4}$$

in which: x = the amount of slow reactant
   k = a constant or a function of variables (such as temperature), which are supposed to be constant during a time step
   AV = the actual value of a variable such as mole fraction
   EV = the equilibrium value of a variable.

In equation (4) AV and EV can be zero for some processes.

Examples of slow reaction reaction formulations are given below:
—diffusion of O₂ between air and water
   slow reactant: O₂ air
   process/reaction: O₂ air ⇒ O₂ water
   AV: mole fraction of O₂ water
   EV: mole fraction of O₂ water in equilibrium with air
   k: function of temperature and wind velocity.
—Growth of algae
   Slow reactant: algae
   process/reaction: algae ⇒ 1 CO₂ + 0.14 NO₃⁻ ···
            etc.

AV: none
EV: none
k: time-step dependent input parameter.

The solution of the set of differential equations derived from these processes can only be found after some approximations, since the value of some of the variables in this set of equations depends on the outcome of the equilibrium module, which on its turn depends on the slow reaction module. The following approximations are made:

1. Linearization of equation (4)

$$\Delta x = \Delta t \cdot k \cdot (AV_{(t)} - EV) \qquad (5)$$

2. The value of $AV_{(t)}$ is approximated with a first-order Taylor expansion:

$$AV_{(\Delta t)} = AV_{(0)} + \frac{d(AV)}{dt} \cdot \Delta t \qquad (6)$$

3. A variation in time in an equilibrium system is produced by progress of slow processes:

$$\frac{d(AV)}{dt} \cdot \Delta t = \sum_i \frac{d(AV)}{dx_i} \cdot \Delta x_i$$

where x_i is slow reactant i

$\dfrac{d(AV)}{dx_i}$ is the change in a variable

in the equilibrium system, caused by adding or removing amounts of component by means of progress of the slow process, and this expression can be calculated from the Jacobian matrix from the equilibrium module.
The result of these approximations is a set of linear equations which can be solved easily.

An example of the resulting equations is given below:
Suppose there are two processes influencing the oxygen budget, growth of algae and diffusion of O_2:

1. $\dfrac{d(\text{algae})}{dt} = k_1$

2. $\dfrac{d(O_2\text{air})}{dt} = k_2 \cdot (\hat{x}_{O_2\text{water}} - \hat{x}_{O_2\text{water equil}})$

The resulting equation for O_2 diffusion is:

$$\Delta(O_2\text{air}) = \Delta t \cdot k_z \Big(\hat{x}_{O_2\text{water}(t=0)}$$
$$+ \tfrac{1}{2}\Big(\frac{d\hat{x}_{O_2}}{d(O_2\text{air})} \, \Delta(O_2\text{air}) + \frac{d\hat{x}_{O_2}}{d(\text{algae})} \cdot \Delta(\text{algae}) \Big)$$
$$- \hat{x}_{O_2\text{equil}} \Big)$$

and for algae growth is: $\Delta(\text{algae}) = \Delta t \cdot k_1$.

Equilibrium species and slow processes included in the model

The model contains all important equilibrium species in the system H, O, Ca, P, N, Si, C.
Slow processes which are modeled are:
—diffusion of O_2 and CO_2 between air and water
—C, P, N, Si, and O uptake and release by algae compartments (these processes are input for the model; for the method of calculation of these fluxes one is referred to the report of F. J. Los, Delft Hydraulics Laboratory, to be published in 1980)
—inflow/outflow of all components
—denitrification and nitrification
—sedimentation of suspended material and precipitates
—flux of all components from the bottom.

The input of the model consists of:
—initial composition
—for each time step:
  —all important loadings
  —uptake and release of components by biological processes
  —(for the present version) interstitial bottom-water composition
  —temperature and wind speed.
The output consists of the value of all state variables and fluxes in each time step.

Calculations

The model is used to study processes in a storage reservoir near Dordrecht, in which three butyl-rubber enclosures are placed, in open contact with air and bottom and with a diameter of 46 m. In order to keep the enclosures at the same depth (4 to 5 m) and residence time (about 150 days), as the reservoir itself, water is pumped into and out of them through pipelines. The input source is

Rhine-water. One of the enclosures is untreated, one is dosed with Fe^{2+} (10 mg Fe^{2+}/liter inlet-water), one with Al^{3+} (60 mg AVR/liter inletwater). This experiment, carried out by the National Institute of Drinking water Supply and the Delta Department of Rijkswaterstaat, to test in-water dephosphatizing, started in 1974, and is accompanied by an extensive measuring campaign since 1975 for the overlying water, and since 1976 for the sediment and interstitial water too.

Sampling and measuring methods are described in Al, et al. 1967. As an example of studying processes and formulating hypotheses with the model, the results of two calculations will be given.

Calculations 1977 Al-dosed

The model was calibrated on the dataset of the Al-dosed enclosure 1977. Fig. 1 gives the measurements of the algae biomass (which were input for the model), Figs 2–5 give a comparison of measurements and calculations of some of the important state variables (O_2, pH, NO_3^-, total P); the + signs are measurements, the × signs connected by the drawn line represent the calculations.
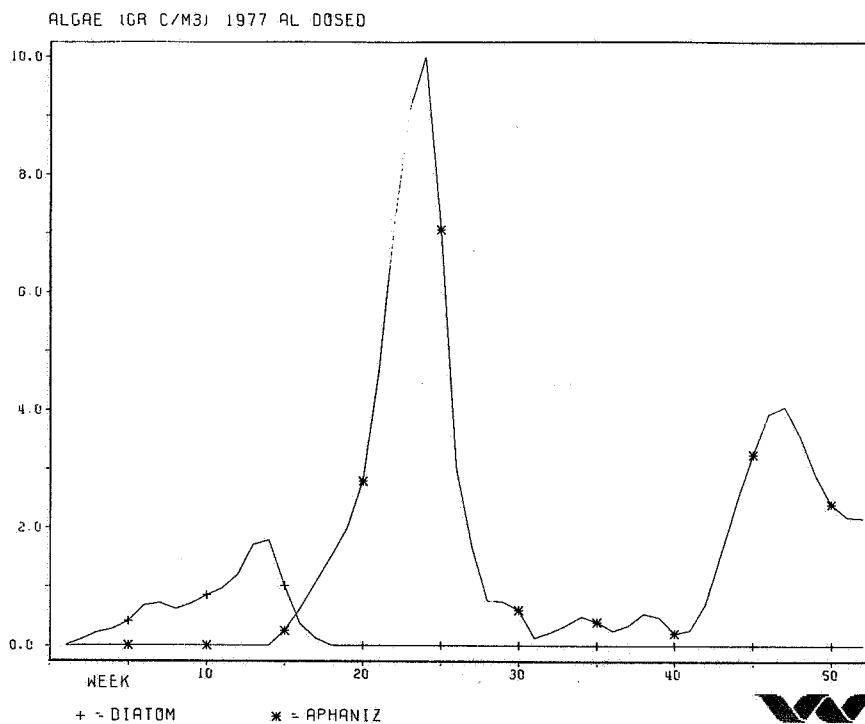
Figure 6 gives the measured phosphorus load to the system from the incoming water and the calculated sedimentation flux of phosphorus adsorbed at $Al(OH)_3$. The rapid fluctuations are due to the fluctuations in the intake of water, but nevertheless, it can be seen that between week 10 and 25, the load is higher than the sedimentation, which between week 20 and 25 even drops to zero. This is partly due to the uptake of P by algae and partly due to the high pH (see Fig. 3), caused by the increase of biomass, which disfavours the adsorption of P at $Al(OH)_3$. The result is an increase of total P concentration (see Fig. 5). After the collapse of the bloom, the pH drops and consequently the adsorption of P at $Al(OH)_3$ and the sedimentation increase; now sedimentation is higher than the external load. The result is a decrease of total P concentration in the water.

Figure 7 shows a comparison of the calculated inorganic sedimentation of P (+ signs) and the calculated flux form the bottom (× signs). This figure shows the importance of bottom fluxes for determining the in-lake concentration, especially during summer where the bottom acts as a net source for P.
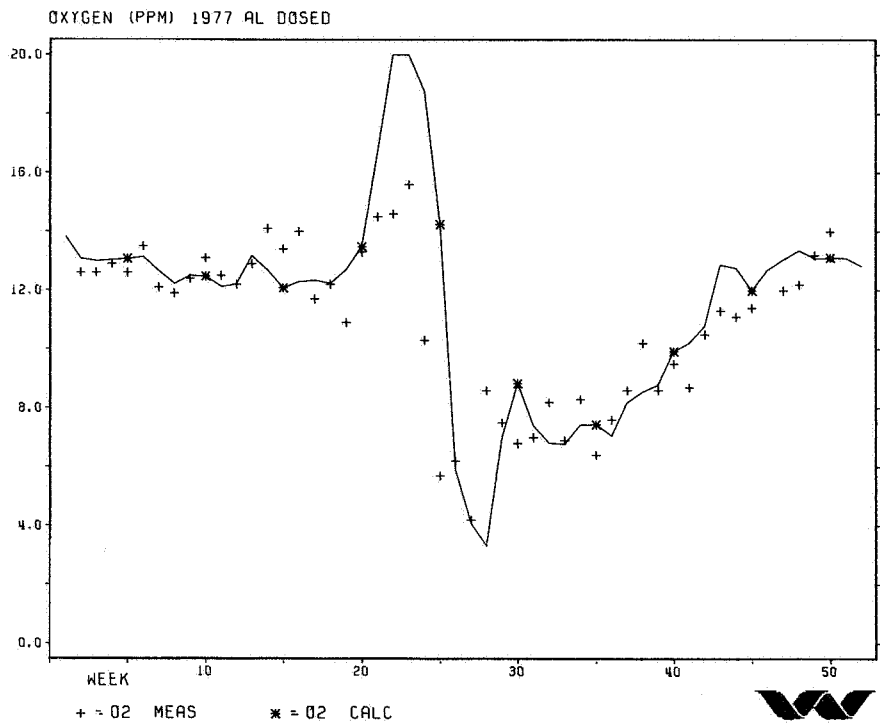
ALGAE (GR C/M3) 1977 AL DOSED

Fig. 1. Measured algae biomasses.

OXYGEN (PPM) 1977 AL DOSED

WEEK   10   20   30   40   50

+ = O2 MEAS   * = O2 CALC

Fig. 2. Measured and calculated oxygen concentration.

PH   1977 AL DOSED

WEEK   10   20   30   40   50

+ = PH MEAS   * = PH CALC

Fig. 3. Measured and calculated pH.

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NITRATE (PPM N) 1977 AL DOSED

+ = NO3 MEAS   * = NO3 CALC
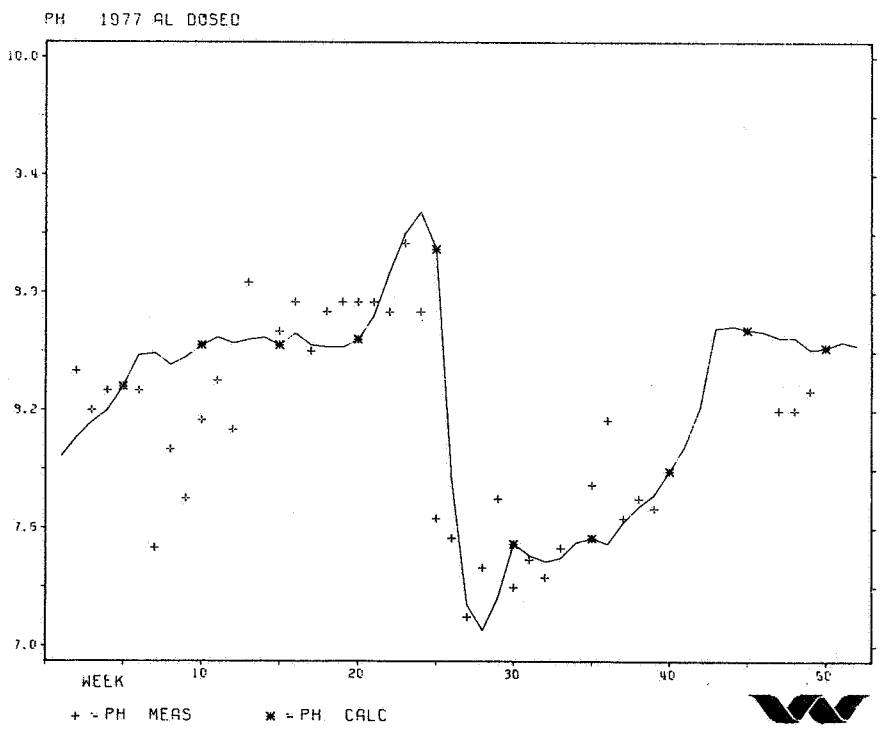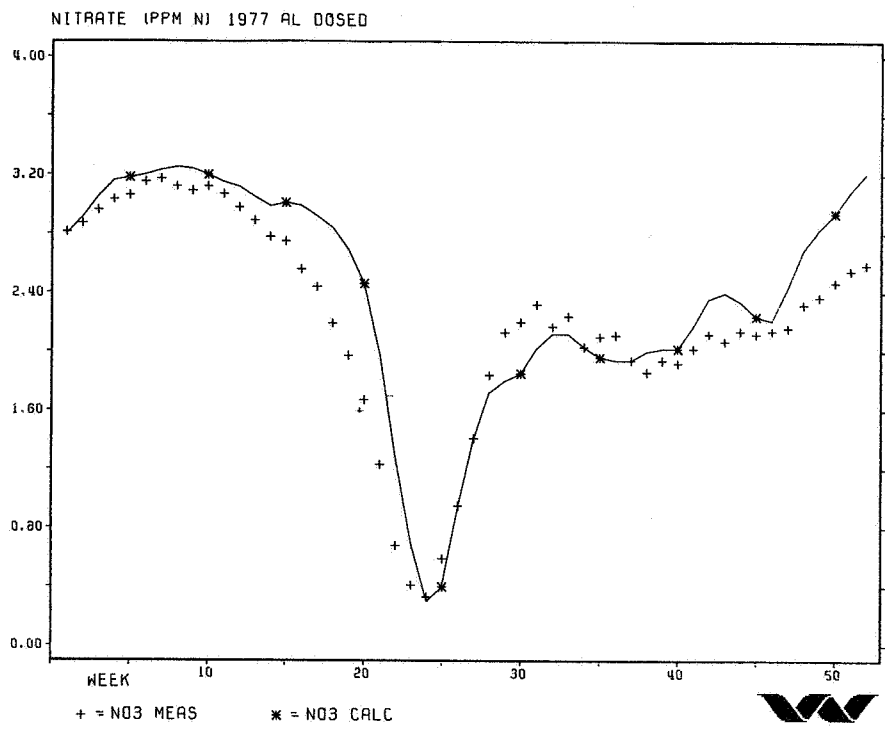
Fig. 4. Measured and calculated NO$_3^-$.

P TOT (PPM P) 1977 (AL DOSED)

+ = PT MEAS   * = PT CALC

Fig. 5. Measured and calculated total phosphorus.

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PHOSPH. FLUXES (GR/M2.WEEK(×100)) 1977 AL DOSED

+ = SEDIM P   × = LOAD P
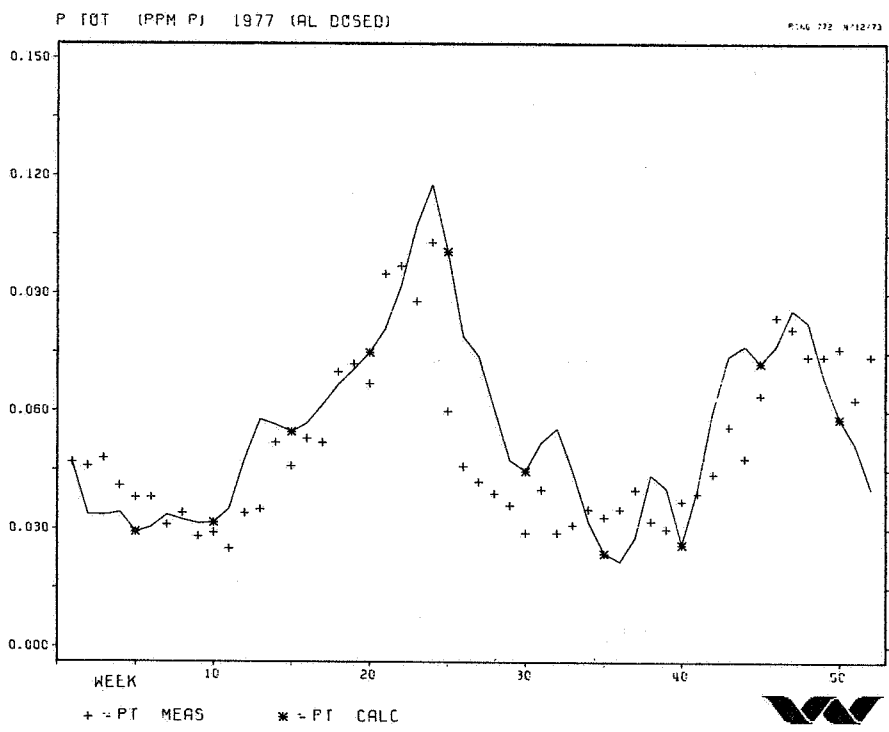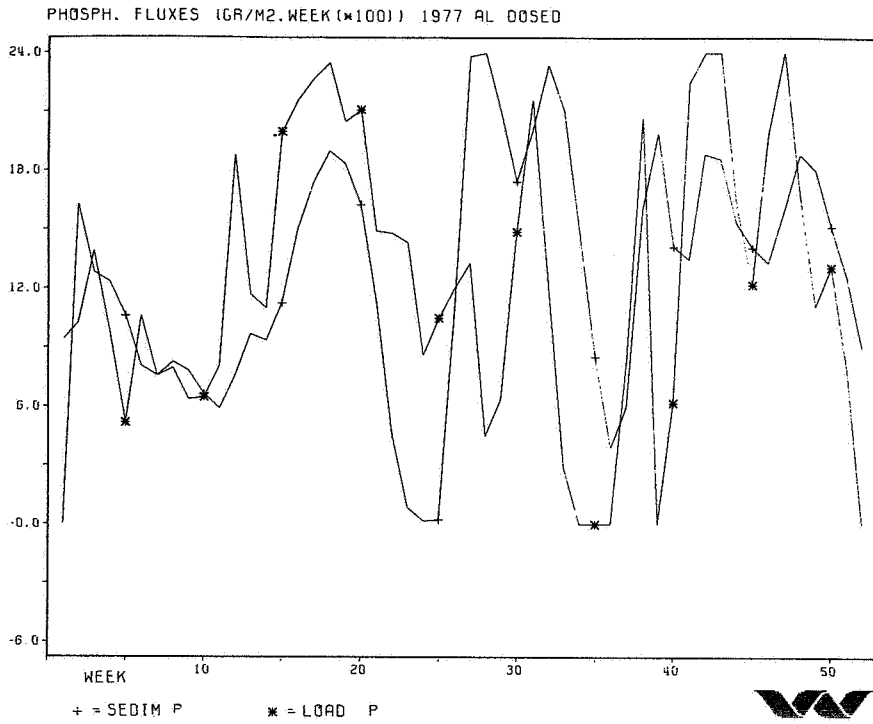
Fig. 6. Measured load and calculated flux of sedimentation of total phosphorus.

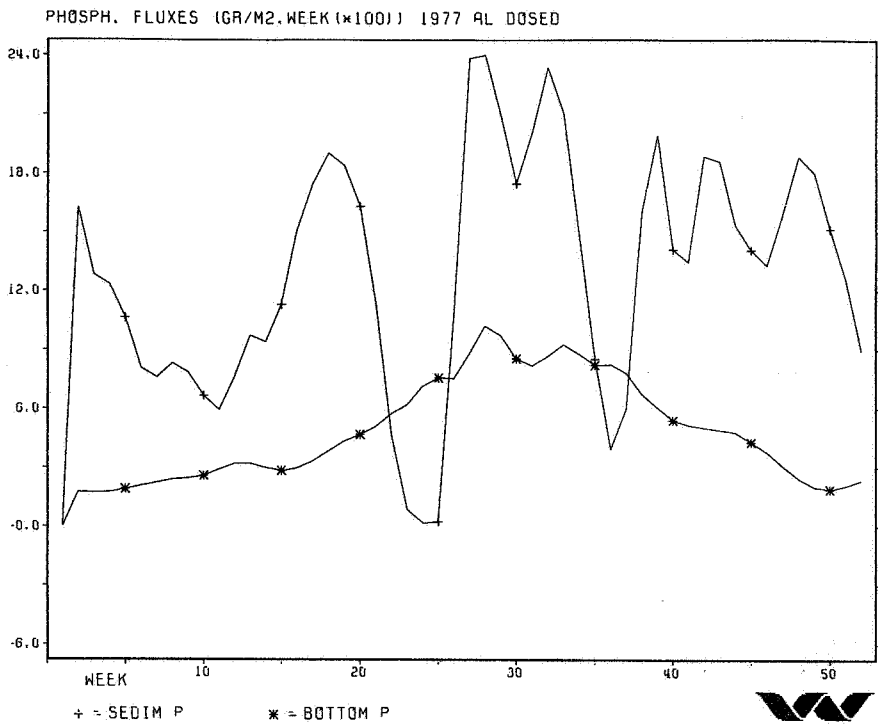PHOSPH. FLUXES (GR/M2.WEEK(×100)) 1977 AL DOSED

+ = SEDIM P   × = BOTTOM P

Fig. 7. Calculated fluxes to (sedimentation) and from (bottom) the bottom of total phosphorus.

Table I.

Phosphorus fluxes 1977 Al-dosed (in $gr/m^2/year$)

loadings external	6.50	77%
loadings internal (bottom)	1.94	23%
	Total 8.44	
outflow (organic + inorganic)	.79	9%
inorganic sedimentation	6.35	75%
organic (algae) sedimentation	1.30	16%
	Total 8.44	

Table I gives the yearly P fluxes calculated by the model except the external load which is measured, from which it is also clear that the internal load (from the bottom) forms a substantial part of the total load.

Table II gives the yearly N fluxes calculated by the model except the external load which is measured.

This example shows the importance of equilibrium calculations, in describing P behaviour in a system where adsorption is important. It also explains why an in-water treatment with Al is not effective in preventing high algae blooms.

Table II.

Nitrogen fluxes 1977 Al-dosed (in $gr/m^2/year$)

loadings external	71.5	84%
loadings internal (bottom)	13.1	16%
	Total 84.6	
outflow (organic + inorganic)	36.2	43%
denitrification (in the bottom)	27.6	33%
organic (algae) sediment	20.8	24%
	Total 84.6	

Calculations 1976 untreated

The model was validated with data of the 1976 untreated enclosure. The measured algae biomass is shown in Fig. 8. A comparison of calculations and measurements of some of the state variables is given in Figs 9–12, from which it is clear that the validation failed for the second half of the year. It is supposed that this miscalculation is due to the fact that a process is going on which is not included in the model formulation.

The nature of this process could be determined from the deviations between calculations and measurements, and the measurements of the interstitial bottom waters. The interstitial bottom waters contain no O_2, no or low NO_3^-, and compared to the overlying water, shows high P, Si, Ca and alkalinity contents. Moreover the sediment itself contains high amounts of adsorbed P.

A mixing process between bottom, interstitial water and overlying water, could be responsible for the deviations between calculation and measurement.

Such a process could occur when $Fe(OH)_3$ coatings dissolve, which bind the sediment particles together. The sediment looses its consistency and mixes very well with the overlying water. This $Fe(OH)_3$ reduction and dissolution is already described by Mortimer (1941), although he studied a stratified lake. In a non-stratified lake, this reduction of Fe^{3+} can only occur, when the amount of oxydator supply (as O_2 and NO_3^-) from the overlying water is less than the use of oxydator by decomposition of organic material. Factors which favour such a process are low NO_3^- concentration in the overlying water (NO_3^- was zero in week 30) and a high decomposition rate of organic material, for instance caused by high temperatures (the summer of 1976 was hot).

Since the oxidation of organic material by O_2 proceeds much faster than by NO_3^-, only NO_3^- is capable of keeping the top layer oxidized. Support for this hypothesis can be found in the results of the experiments of L. Leonardson (1979) and W. Ripl (1979).

Conclusions

Although the model at this moment is not capable of making predictions, since it is not yet coupled
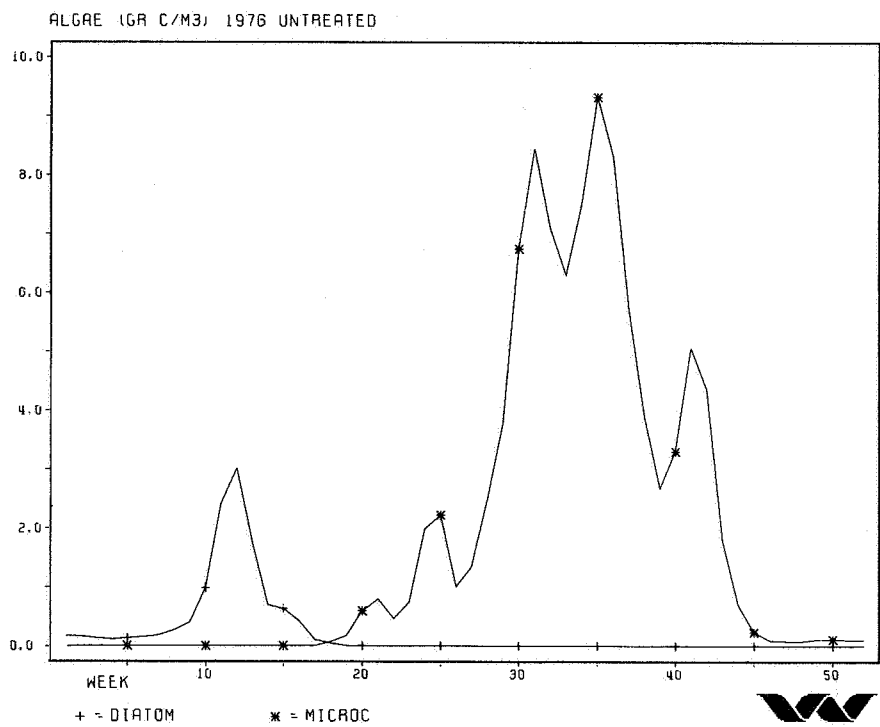
ALGAE (GR C/M3) 1976 UNTREATED
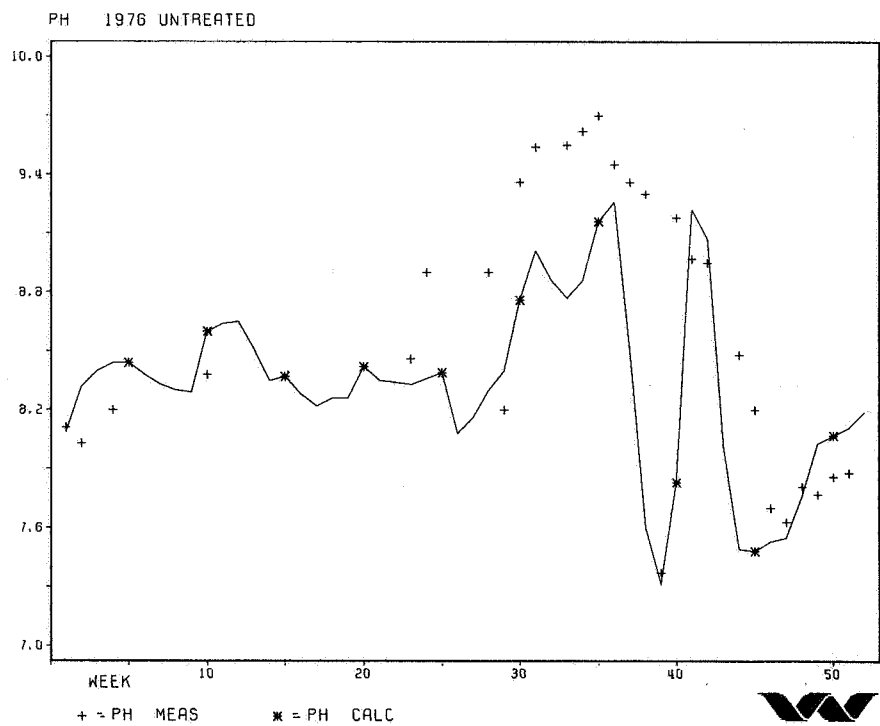

Fig. 8. Measured algae biomasses.

PH   1976 UNTREATED

Fig. 9. Measured and calculated pH.

OXYGEN (PPM) 1976 UNTREATED
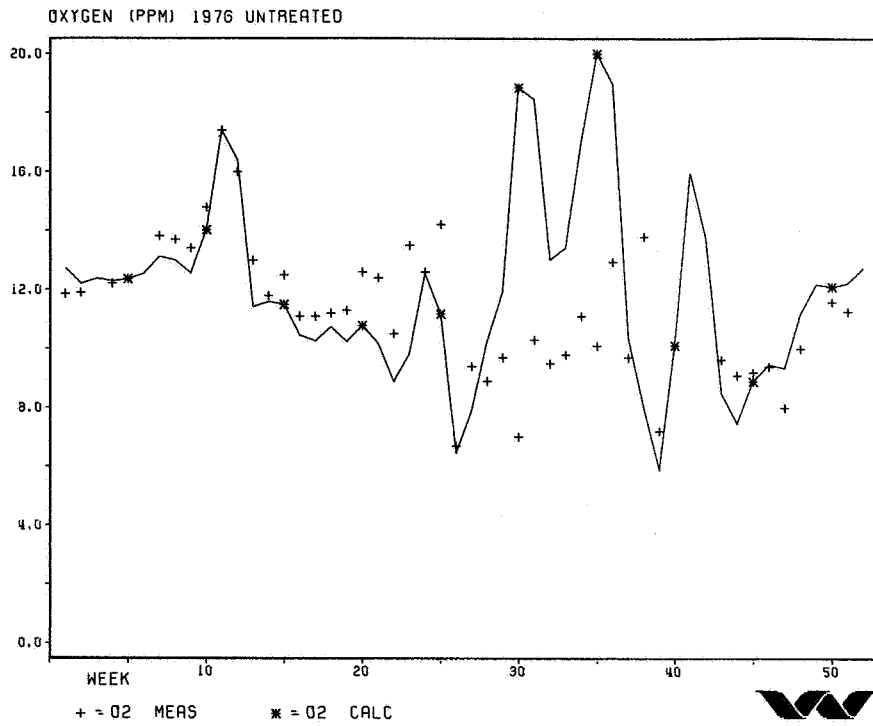
Fig. 10. Measured and calculated O₂.

SI (PPM SI) 1976 UNTREATED

Fig. 11. Measured and calculated Si.

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P TOT (PPM P) 1976 (UNTREATED)
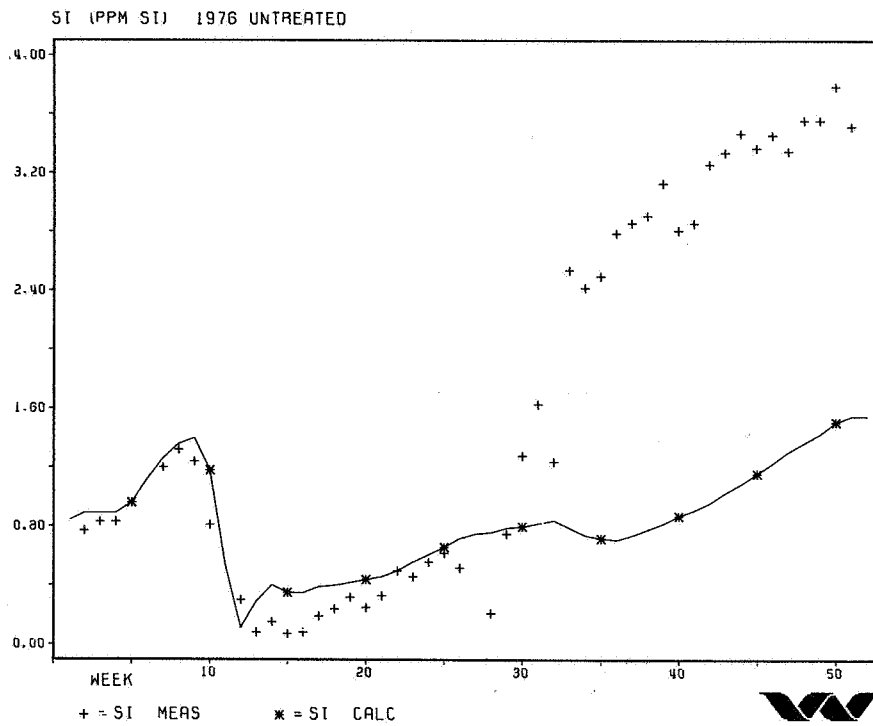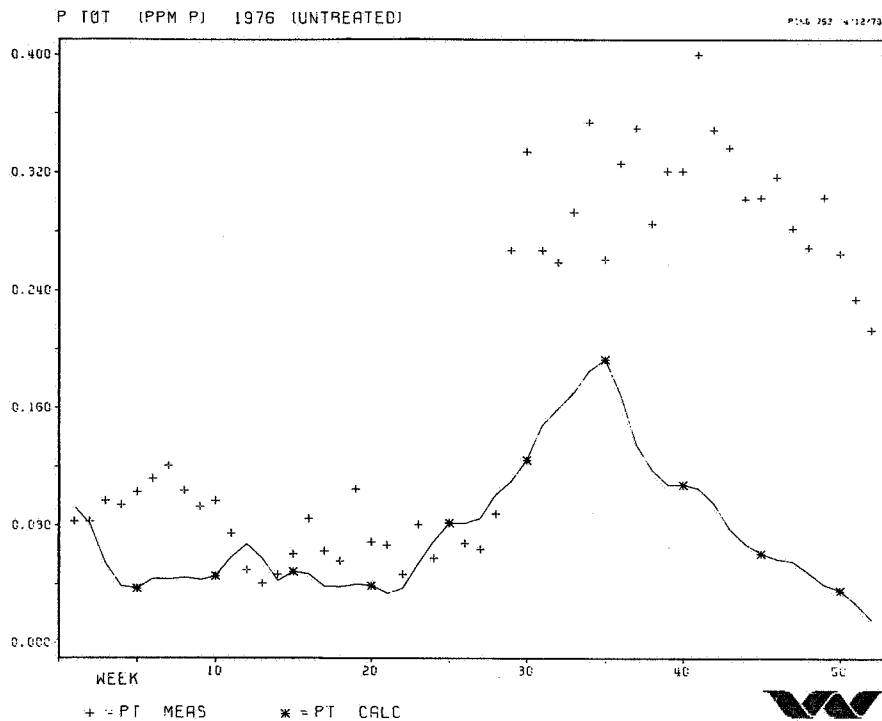

Fig. 12. Measured and calculated total phosphorus.

to an algal calculation model, and the calculations of bottom-water composition are not yet included, it can already be used to study natural systems.

The first example showed the importance of equilibrium calculations, since the model was capable to explain the increase and decrease of total P.

Before the model calculations for the 1976 untreated case, it was clear that something peculiar had happened, but the deviations between measurements and calculations were very helpful in developing a hypothesis, which can and will be tested with this model, especially because of the large amount of state variables, which showed deviations in a certain direction, from which Ca^{2+}, HCO_3^-, $SO_4^=$ and Kjeld. nitrogen were not shown here, a hypothesis can be easier formulated.

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