



Phosphorus in a Biogeochemical Lake Model

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*Cover picture: Lake Östra Ringsjön.
Photo by Charlotta Pers*

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Abstract/Sammandrag <p>BIOLA is a biogeochemical lake model within the VASTRA research programme. The model's main purpose is to predict the ecological responses to changed nutrient loads. The phosphorus simulations were not satisfactory and the sediment was thought to be the critical part. The aim of this work was to improve the phosphorus simulations. Therefore a new sediment approach has been developed. Three main changes of the sediment processes were carried through:</p> <ul style="list-style-type: none">➤ Resuspension of sediments from erosion and transportation bottoms was added➤ The sediments were divided into an upper, aerobic, and a lower, anaerobic, layer➤ The relation between sorbed and dissolved phosphorus in the sediments was described by Langmuir isotherms, with a sorption 2.5 times higher at aerobic compared to anaerobic conditions <p>The modelling of total phosphorus and blue-green algae was improved. Especially the timing of high concentration peaks was much better. One problem still lingering is the modelled oxygen levels, which were much higher than the observed levels. Therefore the model has not been tested for anaerobic conditions. Average release rates from the sediments were 2.5 mg P d⁻¹ during the summer, which is reasonable. A 20-year simulation of step-response was run with increased and decreased nutrient loads. Roughly four years after the change, the model had reached a new equilibrium.</p>		
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1 Introduction

Phosphorus is a macronutrient which is much too quickly consumed by the human society. Most phosphorus comes from mining of mineral phosphorus in USA, Morocco and Russia (NE, 1991). As fertiliser it is added in large amounts to arable land, and through food and household detergents it comes to the sewage treatment plants. When it reaches the streams and lakes it is a key element in the primary production and a cause of lake eutrophication. Eventually the phosphorus is deposited on the sea bottom.

Eutrophication is one of the largest lake management problems today. Lakes which turn from clear blue to a thick greenish soup of algae deprive us of recreational value, and the whole ecosystem of the lake changes, to the harm of the biological diversity and sometimes the fish population.

The evident and fundamental remedy to lake eutrophication is to decrease the inflow of phosphorus and other critical nutrients. In many cases, this will not result in a fast recovery of the lake, partly because of the phosphorus stored in the bottom sediments. There are several methods of lake restoration that can contribute to a fast recovery; however, these methods are expensive and not always successful. Part of the problem is the lack in knowledge about lake nutrient dynamics and the difficulties in predicting the effects of lake restoration programmes. Here models come in as a useful tool for the simulation of different scenarios and to further increase the knowledge about the nutrient dynamics.

In 1998, the Swedish water management research program VASTRA was initiated. Its main goal is to develop catchment-based water management strategies that are sustainable from ecological, economical and social perspectives. It involves researchers and professionals from different universities, institutes and governmental bodies in Sweden, and is funded by the MISTRA foundation. As part of the VASTRA research program, the biogeochemical lake model BIOLA was developed at SMHI during 2000-2001. It will be used for predicting ecological response in individual lakes when the nutrient load changes (VASTRA, 1998a, 1998b).

The aim of this study was to improve the simulation of the phosphorus cycle in the biogeochemical lake model BIOLA. The task was carried out during a 20-weeks Master Thesis work for a degree of Civil Engineering of Water and Environment at Uppsala University. The study focused on sediment dynamics, which was thought to be the crucial factor.

1.1 Eutrophication

Eutrophication is the over-enrichment of receiving waters with mineral nutrients (Correll 1998). It started after the World War II, when increased productivity was noted in many natural waters close to urban areas. Research on eutrophication started in the 1960's and 1970's and during the late 1960's, chemical treatment of municipal wastewater was introduced in Sweden as a remedy. This effectively reduced the phosphorus load from urban areas (Rydin, 1999). A still lingering intricate problem is the phosphorus loading from diffuse sources, such as leaching and particle-mediated transports from agricultural areas, and the contribution from households not connected to municipal wastewater treatment plants.

With an increase in the cultivated areas in the beginning of the 20th century, and in the use of commercial fertilisers in the end of the same century, the phosphorus load from agriculture now comprises 20 % of the total load to the Baltic Proper. Since the 1980's, the amounts of phosphorus applied to the soil through fertilisers relative to the amounts removed by harvests have been reduced (SNV, 1993).

Phosphorus is often the cause for eutrophication of freshwater systems. The lakes' trophic state can change due to this, but many lakes are naturally eutrophic and a slow eutrophication process is natural. However, anthropogenic supply of phosphorus speeds up the process (Horne and Goldman, 1994). The lake ecosystem is disturbed and typically there is a shift in the algae population towards a larger amount of blue-green algae, some of which can produce toxins. In hypertrophic lakes, the underwater vegetation may disappear, which makes the lake unattractive for waterfowl. Another negative effect is that stands of the reed *Phragmites australis* can spread to cover big parts of the lake.

There are several methods for lake restoration, which have been used with varying results. Usually the aim is to restore the lake as a centre of outdoor activities such as swimming and fishing, by reducing the phytoplankton biomass. Al- or Fe-chemicals can be added to immobilise phosphorus as a precipitate, the bottom can be dredged to remove phosphorus-rich sediments or the bottom water can be oxygenated or replaced with nutrient-poor, well oxygenated water. Implantation of herbivorous fish and biomanipulation through fish removal are also used. The methods can also be combined. The treatment may need to be repeated, especially if the external load is not sufficiently reduced (Pettersson and Wallsten, 1990).

Lake Trummen, outside Växjö in southern Sweden, is an example of a successfully restored lake. Problems with algae blooms and dying fish appeared already in the 1950s. The external load was reduced in 1959, with no significant recovery. During 1970 to 1971 the bottom was dredged and vegetation removed. The cyprinid fish population was reduced 1976 to 1979. The effect of the fish population reduction lasted only a short period, while the dredging reduced the nitrogen and phosphorus levels significantly for 15 years (Pettersson and Wallsten, 1990).

1.2 Lake Ringsjön

Lake Ringsjön is a shallow lake in Scania, Southern Sweden, consisting of three basins (Figure 1). The Lake Sätöftasjön basin and Lake Östra Ringsjön basin have contact through a shallow sound, and from Lake Östra Ringsjön a canal leads to Lake Västra Ringsjön basin. Lake Sätöftasjön has five tributaries, Lake Östra Ringsjön seven and Lake Västra Ringsjön has two tributaries. The lake is drained through the river Rönne å, which discharges to Kattegatt (the sea) by Ängelholm town (Hansson *et al.*, 1999).

Morphometric and hydraulic data of the basins are shown in Table 1. Östra Ringsjön is the deeper basin, with a mean depth of 6.1 m, while Sätöftasjön and Västra Ringsjön are shallow with a mean depth of 3.0 and 3.1 m (Ringsjökommittén, 1991). Lake Ringsjön is regulated. In 1883 the lake surface was lowered by 1.5 m, and further regulations have been carried out to facilitate drinking water withdrawal (Ringsjökommittén, 1991).

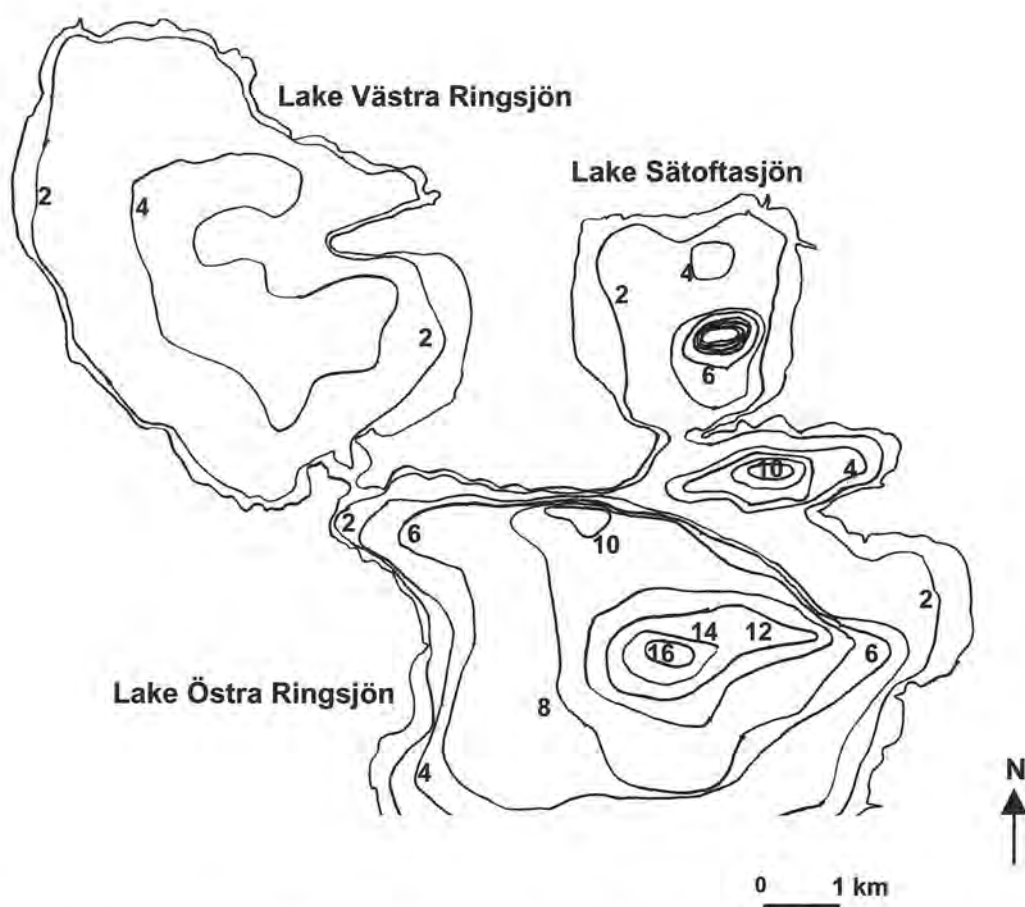


Figure 1. Lake Ringsjön. Depth isoline values are in meters. After Hansson et al., (1999).

Table 1. Morphometric and hydraulic data of Lake Ringsjön and its basins. From Ringsjökommittén (1991)

Lake basin	Lake area (km ²)	Max.depth (m)	Mean depth (m)	Water volume (m ³ * 10 ⁶)	Residence time (year)
Sätöftasjön	4.23	17.5	3.0	12.8	0.30
Östra Ringsjön	20.50	16.4	6.1	124.8	0.84
Västra Ringsjön	14.84	5.4	3.1	46.6	0.30
Lake Ringsjön	39.75	17.5	4.7	184.2	1.05

The summer means of total phosphorus concentrations have decreased from sometimes over 0.25 mg l⁻¹ in the seventies to less than 0.10 mg l⁻¹ in the 1990s. During the same period, summer means of total nitrogen concentrations have decreased from around 2.5 mg l⁻¹ to 1.5 mg l⁻¹. Secchi depth has also improved and was 1-1.5 m during the nineties. pH is usually high, between 7.5 and 9. The yearly peak phytoplankton biomass has decreased from more than 100 mg WW l⁻¹ in the 1980's to 15-20 mg WW l⁻¹ during 1997-1999. The phytoplankton blooms are dominated by blue-green algae (Bergman, 1999; data from the water investigation program by the local interest organisation Ringsjökommittén). The total phosphorus and total nitrogen concentrations are classified

as very high ("mycket höga"), and the phytoplankton biomass as very large ("mycket stor") by the Swedish environmental protection agency (SNV) (SNV, 1999a, 1999b).

The eutrophication of Lake Ringsjön has caused algae blooms, which have made the lake unsuitable for swimming. It has also changed the fish population, and decreased the number of waterfowl and other recreational values. In the 1960s, the water transparency decreased to about 1 m. There were heavy blooms of blue-green algae and cattle drinking from the water got ill and died from algae toxins. The recreational fishing, which had been very high with up to 40 000 licences sold per year, decreased. In 1987, the three cities Helsingborg, Landskrona and Eslöv were forced to stop using Lake Ringsjön as main drinking water source as a result of its bad water quality (Hansson *et al.*, 1999).

The external load was reduced in the 1970s, with no large effects on the water quality. Therefore, the new method of biomanipulation through cyprinid fish reduction was used. Fish was removed from all three basins of the lake during 1988-1992 (Hansson *et al.*, 1999). Although the fish reduction program did not result in an increase in the zooplankton biomass as expected, the phytoplankton biomass decreased and the water transparency increased (Bergman *et al.*, 1999).

When the external loading was decreased, budget calculations reveal that the lake around the year 1980 entered a phase of net phosphorus export, probably originating from the sediments. The last years, Lake Ringsjön has started to act as a net phosphorus sink again (Granéli, 1999).

1.3 Phosphorus in Lakes

In the middle of the 20th century, phosphorus was identified as a key factor limiting algae growth (Rydin, 1999, and references therein). Phosphorus is considered the main limiting nutrient for primary production in most freshwater ecosystems, although deficiencies in nitrogen, silica, carbon dioxide and some metals, e. g. iron and molybdenum, also can limit the plant growth. Phosphorus is needed in smaller amounts than nitrogen, silicon and carbon. It is present in low concentrations in lake water but is recycled faster than nitrogen or silicon (Horne and Goldman, 1994). A common N:P ratio in algae under reasonably good conditions is about 15:1 (Correll, 1998). Thus, the phosphorus loading on a freshwater system is critical for its trophic state (nutrient and productivity status, as defined in Horne and Goldman, 1994). Willén found, as is reviewed in Håkanson (1995), that data from 327 Swedish lakes show a strong ($r^2 = 0.76$) linear relationship between the logarithm of total phosphorus concentrations as a mean value from March to October, and the logarithm of maximum total volume of phytoplankton. McCauley on the other hand found that data from 1041 lakes showed a sigmoid relationship between log chlorophyll *a* vs. log summer total phosphorus, that tended to flatten out at very high total phosphorus concentrations (Correll, 1998).

Phosphorus reaches the lake via tributaries, diffuse runoff from the adjacent land areas and atmospheric deposition (Figure 2). Fractionation to determine the amounts of phosphorus of different forms is performed after special phosphorus fractionation schemes, see for example Rydin (1999) and Reddy *et al.* (1999). The division is made after the bioavailability and degradability of the material. In most aquatic environments, total particulate phosphorus is present in much larger quantities than soluble phosphorus (Horne and Goldman, 1994). Total particulate phosphorus includes phosphorus sorbed to organic and inorganic compounds, as well as bacteria, plankton and detritus. The only directly

bioavailable form of phosphorus, i. e. available for assimilation by bacteria, algae and plants, is orthophosphate (PO_4^{2-}), hereafter called phosphate (Correll, 1998). However, loosely adsorbed phosphorus and phosphorus in easily degradable organic material are potentially available. Phosphate in lakes is often present in amounts close to detection limit (Horne and Goldman, 1994), and even total phosphorus is difficult to measure with high accuracy.

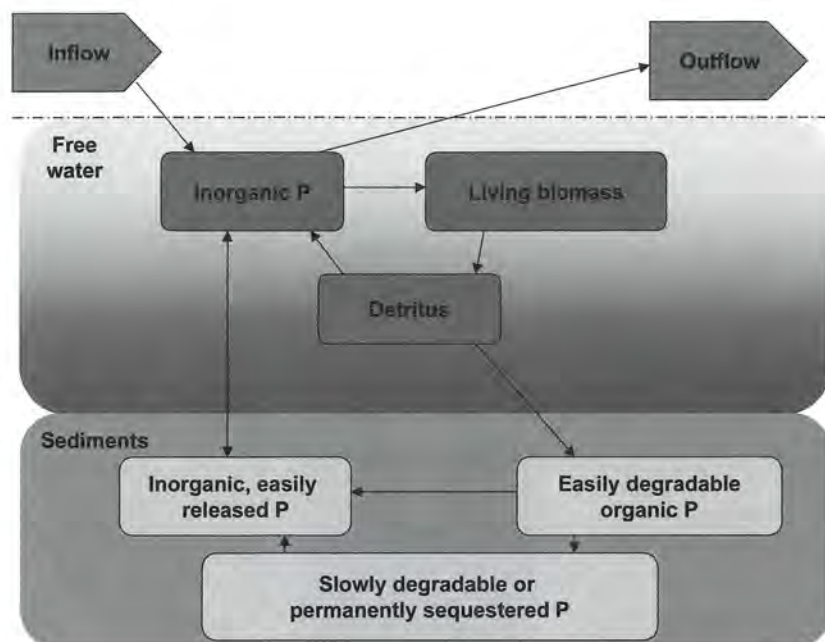


Figure 2. Main phosphorus pools and flows in a lake.

Phytoplankton and periphyton (attached algae) have in the summer in a typical temperate lake at least an order of magnitude larger biomass than any other group of organisms. In the winter they have about the same biomass as herbivorous (feeding on plants) fish and zooplankton (Horne and Goldman, 1994). Bacteria constitute an important part of plankton. They are also important in the bottom microorganism fauna, together with for example Chironomid larvae. The bottom microorganisms feed on the settled organic material and each other.

Phytoplankton take up inorganic nutrients, and sometimes they release nutrients-rich substances, such as enzymes. The phytoplankton and bacteria are grazed by zooplankton, which in their turn are eaten by larger zooplankton and fish. Not all food eaten is assimilated, but some is lost due to imperfect feeding. Some phytoplankton and zooplankton are not eaten, but die and sink slowly as detritus towards the bottom. Alive phytoplankton can also sink towards the bottom. On the way, dead material may be partly mineralised and some phosphate is then released to the water. When they reach the bottom, they are either mineralised or sequestered (permanently immobilised). Some of the phosphate produced by mineralisation is released directly back to the water. Of the phosphate retained in the sediments some can be released later and again take part in the bioproduction.

1.4 Sediment phosphorus dynamics

Lake sediments can be seen as a storage and buffer for lake phosphorus. The exchange of phosphorus between the sediments and the free water is a key factor for the seasonal dynamics as well as over the whole life span of the lake. The capacity of the upper sediments for phosphorus storage is usually large, and in most cases the amounts of phosphorus stored in the upper sediments greatly exceeds that of other compartments of the lake-water system (Figure 3) (Boström *et al.*, 1982; Lijklema, 1993). This implies that if phosphorus is released from the sediment, it constitutes a vast potential nutrient source for the lake.

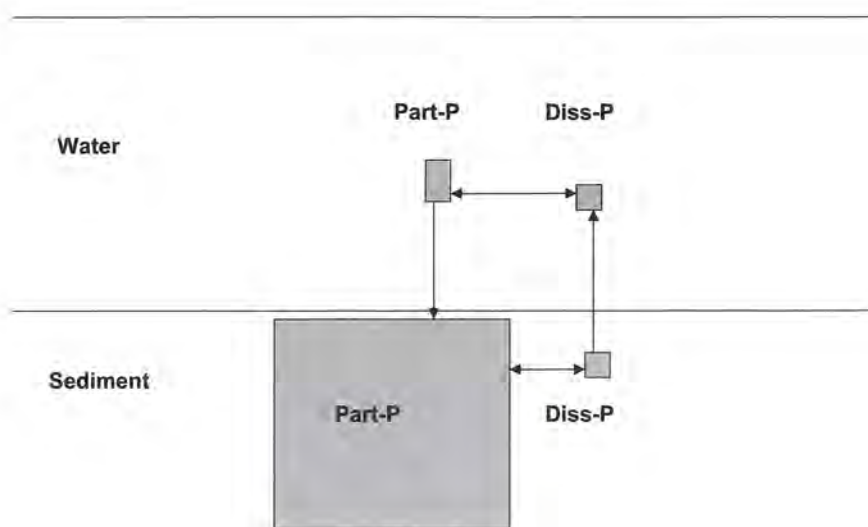


Figure 3. Size of major phosphorus pools in a lake water-sediment system. Hypothetical example assuming a lake with: mean depth = 10 m, "active" sediment layer = 0.1 m, total-P in lake water = $50 \mu\text{g l}^{-1}$, total-P in sediments = 2 mg g^{-1} dry weight, water content of the sediments = 90 %. After Boström *et al.* (1982).

In temperate areas, sediments of oligotrophic lakes are usually a net sink for phosphorus. But in eutrophic lakes, the sediments can periodically release enough phosphorus to be a net source. This phenomenon is called internal loading. When a lake is subjected to an increase in nutrient load, it tends to take up and store much of the surplus phosphorus. Later, if the load is decreased, the sediments may release the stored phosphorus. In modelling Lake Södra Bullaren, Sweden, Håkanson and Carlsson (1995) found that 4-5 % of the phosphorus in the active sediments layer could reach the productive surface waters in a year. The internal loading can be up to 4 times larger than the external loading on an annual basis (Boström *et al.*, 1988). The phosphorus released from the sediments can enhance the primary production (Boström *et al.*, 1982).

The accumulation of phosphorus is nicely illustrated by the experimental lake fertilisation program, which was carried out on two shallow, polymictic, and one deeper thermally stratified lake in Northern Sweden. The lakes were fed with phosphorus up to amounts of $0.51 \text{ g m}^{-2} \text{ year}^{-1}$ for one to four years and for different periods also with nitrogen. 42 to 47 % of the added phosphorus was accumulated in the sediments (Jansson, 1984).

The transport of phosphorus from the sediments occurs as resuspension of phosphorus-carrying sediment particles and from the dissolved phase in the pore water. The overall release from the pore water includes two steps: first, the phosphorus is released from the sediment particles, second, the dissolved phosphorus is transported to the overlying water. The pore water concentrations are commonly 5-20 times higher than the water concentrations in most lakes, and it reflects the trophic status of the lake (Boström *et al.*, 1982). Total phosphorus in the upper 2 cm of the sediments in the naturally eutrophic Lake Erken, Sweden, varied from 2050 to 1450 $\mu\text{g P (g DW)}^{-1}$ in one year, with the highest concentrations during April to June, and the lowest in September to October (Rydin and Brunberg, 1998).

1.4.1 Phosphorus sorption capacity

The phosphorus sorption capacity of the sediments is strongly dependent on the grain size and sediment type – a sediment of fine grains and a large proportion clay will have a high phosphorus retention capacity (Boström *et al.*, 1982). Grain size distributions and sediment materials are dependent on the hydrological flow patterns, the topography and soil type in the catchment area. Moreover, the energy input from winds, river inflow, and atmospheric heating influences the sediment. In very large lakes, gravity and surface barometric pressure are important (Håkanson and Jansson, 1983).

An often-used method for assessment of the sediment dynamics of a lake is the dividing of the bottom into erosion, transportation, and accumulation areas. Erosion bottoms are most common in shallow parts and on the side of the lake most exposed to winds. No deposition of fine materials occurs there. Accumulation bottoms, on the other hand, usually comprise the deepest parts of the lake. The materials deposited there are usually fine and have a high content of water and organic material. If the lake is very shallow and wide, there might not be any accumulation bottom. Transportation bottoms have periods of accumulation interrupted with erosion periods. The extent of the different bottom types is determined by the influence of wind and waves, the form (“topography”) of the lake and the slope of the bottom (Håkanson and Jansson, 1983).

The iron-phosphorus quotient (Fe:P by weight) can be used to assess the sink/source properties of the sediment. If the quote is higher than a critical quote, the sediments has buffer capacity left to retain more phosphorus, but if the quote is lower than the critical number, the sediments is saturated with phosphorus and there is a risk it may act as a phosphorus source. The critical quote of Fe:P by weight is 15 according to Jensen *et al.* (1992) and Rydin and Brunberg (1998).

Lake Finjasjön has a high sediment iron content, average 61-76 mg Fe g^{-1} , which makes the phosphorus dynamics iron-governed (Eckerröt and Pettersson, 1993). Lake Ringsjön has on average a sediment iron content of 23-42 mg Fe g^{-1} (Enell, 1983). The iron-coupled phosphorus-retention is influenced by the redox conditions, as explained below. If Fe is bound in FeS, the phosphorus sorption capacity is reduced (Boström *et al.*, 1988).

Calcareous lakes are different from non-calcareous lakes regarding phosphorus sorption capacity and dynamics. When eight lakes in Wisconsin, USA, were investigated, Williams *et al.* (1970) found that calcareous sediments generally retained and sorbed less phosphorus than non-calcareous lakes (Boström *et al.*, 1988). Jacobsen (1977) found the same, while Boström *et al.* (1988) state that calcium carbonate affects phosphorus sedimentation in a dual way.

Lake sediments rich in clays usually have a large phosphorus sorption capacity. Humic material probably gives the same effect (Boström *et al.*, 1982)

There may be a difference between the phosphorus retention capacities of marine and freshwater sediment. In a study of data from 24 marine and brackish and 25 freshwater systems, Caraco *et al.* (1990) discovered that during aerobic conditions, marine systems did not retain phosphorus, whereas freshwater sediments immobilised about 70 % of the phosphorus released from decomposition. High sulphate reduction and formation of FeS, which reduces the phosphorus sorption capacity, is suggested as an explanation. Gunnars and Blomqvist (1997) suggest the same.

1.4.2 Release and immobilisation of phosphorus

The factors considered to regulate the dissolution and sorption of phosphorus are numerous and of geological, chemical and biological character. The most commonly considered are:

- Oxygen concentration in bottom-near waters
- pH in bottom-near waters
- Nitrate concentration in bottom-near waters
- Sulphur reactions in the sediment
- Temperature
- Bioturbation
- Gas convection
- Other mechanical disturbance
- Calcium carbonate in water and sediment
- Microorganisms

Oxygen. Einsele and Mortimer launched this classical theory during 1936 to 1942 (Boström *et al.*, 1988). It says that oxygenated sediments retain phosphorus through binding it to iron(III). Reduced sediments release phosphorus by reduction of iron and following dissolution of iron-phosphorus complexes (Mortimer, 1941, 1942; Boström *et al.*, 1988). Iron(III) is reduced at a redox potential of about 200 mV, corresponding to O₂-concentrations of 0.1 mg l⁻¹ (Boström *et al.*, 1982). The lower the oxygen concentration, the lower the redox potential.

Deep stratified lakes more often have a redox-controlled phosphorus release than shallow unstratified lakes (Boström *et al.*, 1988). Anaerobic micro-layers can be formed and give a release of P, even when the main water column is well-oxygenated (Eckert and Pettersson, 1993). Anaerobic microsites can form on lake bottoms, (Boström *et al.*, 1988), and on marine bottoms (Maher and DeVries, 1993) giving locally low redox potentials. Enell (1983) found variations in oxygen concentrations over the bottom of Lake Ringsjön from 0.8 to 10.8 mg l⁻¹, which support the idea of microsites. It is also possible that phosphorus mobilisation from living cells contribute to phosphorus release from anaerobic sediments (Boström *et al.*, 1988).

An increase in phosphorus release at anaerobic conditions has been observed in many lakes (Furumai and Ohgaki, 1989; Istvánovics, 1994; Boström *et al.*, 1982). Surface sediments from Lake Erken, Sweden, released double amounts of phosphorus at anaerobic conditions compared to aerobic (Rydin, 1999). Sediments from Granfjärden and Östhammarsfjärden, the Baltic Sea, typically released 30 % of the total phosphorus content at aerobic experimental conditions and 50 % at anaerobic experimental conditions (Persson, 1997). In a study of marine sediments, phosphate was released at anaerobic conditions (Sundby *et al.*, 1986).

Even at aerobic conditions, P can be released in amounts as large as at anaerobic conditions (Eckerrot and Pettersson, 1993; Boström *et al.*, 1988; Jensen and Andersen, 1992; Ramm and Scheps, 1997). In Lake Kasumigaura, Japan, the phosphorus sorption capacity is even higher under anaerobic than under aerobic conditions (Furumai and Ohgaki, 1989). Caraco *et al.* (1990) studied North American- and other lakes and found that in 10 lakes, anaerobic conditions did not induce phosphorus release, but in eight lakes phosphorus was released. There was no significant explanatory difference between the lakes.

pH. An increased pH can result in a release of phosphorus (Eckerrot and Pettersson, 1993; Boström *et al.*, 1988; Istvánovics, 1994). However, in calcareous lakes, the effect may be the opposite (Boström *et al.*, 1988). Maximum release has been found at pH between 9 and 10.5 (Andersen, 1975; Drake and Heaney, 1987; Jacobsen, 1978; Furumai *et al.*, 1989). On the other hand, in the calcareous Lake Neusiedlersee, Austria, the release was at its minimum at pH 9 (Gunatilaka, 1982). Phosphorus release was only significantly influenced by pH in one out of four shallow Danish lakes in an experiment by Jensen and Andersen (1992). In marine systems, pH variations are smaller and of minor importance due to the well-buffered sea water (Jansson, 2001).

Nitrate. Nitrate has been found to have a dual effect on phosphorus release (Jensen and Andersen, 1992; Boström *et al.*, 1988). The phosphorus release was significantly influenced by nitrate in four shallow Danish lakes (Jensen and Andersen, 1992). Nitrate inhibited phosphorus release to anaerobic hypolimnetic water of 31 Danish lakes, probably through buffering the redox potential from getting too low. However, nitrate could possibly also increase the total mineralisation rate, by stimulating the microorganism growth and increase the release (Boström *et al.*, 1988).

Sulphur. If Fe is bound in FeS, the iron-mediated phosphorus sorption capacity is reduced (Boström *et al.*, 1988). This happened in Lake Onondaga in 1989-1990, after anoxia developed (Driscoll *et al.*, 1993).

Temperature. An increased temperature results in increased microbial activity, with an increased oxygen consumption and resulting low redox potential (Boström *et al.*, 1988). The phosphorus release was significantly influenced by temperature in four shallow Danish lakes (Jensen and Andersen, 1992). But mineralisation of phosphorus-containing organic material does not always result in an increased phosphorus release (Boström *et al.*, 1988).

Bioturbation. Bioturbation is the stirring of sediments through the activities of burrowing animals, for example Chironomid larvae. Usually the effect is an increase in the phosphorus release (Boström *et al.*, 1988).

Gas convection. Gases like methane, carbon dioxide and nitrogen gas are formed in the sediments and on their way up induce vertical currents, which can carry substances to the

sediment surface. This mechanism is important in highly eutrophic lakes (Boström *et al.*, 1988).

Other mechanical disturbance, e. g. by waves and bottom currents. Mechanical disturbance can increase, but might also decrease, the phosphorus release (Boström *et al.*, 1988). Brinkman and van Raaphorts found that resuspension from bottom sediments was responsible for almost 50 % of internal P load in a shallow Dutch lake (Bloesch, 1995). Weyhenmeyer (1998) refers to six publications where resuspension has been shown to result in increased lake water phosphorus and two publications where resuspension did not increase lake water phosphorus.

Calcium carbonate. Phosphorus cycling in calcareous lakes differs from non-calcareous lakes. CaCO_3 precipitation affects phosphorus sedimentation in different ways (Boström *et al.*, 1988). In Lake Onondaga, calcium, rather than iron, most likely controls the phosphorus release (Driscoll *et al.*, 1993).

Microorganisms. Many of the factors discussed above are thought to affect the sediment microorganisms, which in their turn store and can release considerable amounts of phosphorus (Rydin, 2001; Lijklema, 1993). Anaerobic conditions in the sediments can cause bacteria to release phosphorus (Rydin, 2001). The P- and Fe-release in Lake Finjasjön is mainly governed by sediment bacteria (Eckerrot and Pettersson, 1993).

1.5 Lake Modelling

One of the earliest lake models was the one that Vollenweider proposed in 1976. It was simple and related the algae biomass to total phosphorus input rates, mean depth of the lake, and outflow per unit lake area. It did fit to data from most lakes and reservoirs studied in the world and gave a strong support for the importance of phosphorus in eutrophication (Correll, 1998). In year 1982 the OECD model came, which gave a better prediction for many lakes. It was based on the same driving variables (Håkanson, 1995).

These models are conceptual and are good tools for lake management on a large scale. However, they do not account for storage of phosphorus, nor do they give any information about the internal processes in the lakes. Many dynamic and mechanistic models have been developed since, which can fulfil these requirements and give more precise results for individual lakes.

1.6 Uncertainty and sensitivity analysis

To know the reliability of model results, the model should be thoroughly tested. There are errors from imprecisely known input parameters, which determine the upper limit of how good modelling can be made. These errors can be estimated through uncertainty analysis. Unfortunately for phosphorus modelling, total phosphorus concentration in tributaries is one of the most variable parameters for lake eutrophication models (Håkanson, 1999a). Thus, the uncertainty of phosphorus models is always large.

The present model is built on many parameters, each contributing to the errors of modelling. To investigate the magnitude of such errors, a sensitivity analysis can be carried out. There the contribution of each parameter is tested (Helton, 1993).

The most common tool for uncertainty sensitivity analysis is Monte Carlo analysis. The distribution and range of each input variable is selected and probabilistic samples are generated from the input variables. Then, the model is run with the different samples of input parameters and uncertainty and sensitivity is evaluated from the different results (Helton, 1993).

2 Material and methods

2.1 The Biogeochemical Lake Model BIOLA

BIOLA is a BIOgeochemical LAke model, developed within the VASTRA research programme. Its main purpose is to predict the ecological responses of individual lakes when the nutrient load changes (VASTRA, 1988a, 1988b). It can be applied to eutrophic lakes with low amounts of humic substances (Pers, pers. comm.).

BIOLA simulates the fluxes and amounts of carbon, nitrogen and phosphorus in one or several water basins. The biogeochemical part is coupled to a physical model. It is based on the equation solver PROBE, which solves the transport equation (1) for the 1D situation.

$$\frac{\partial C}{\partial t} + v \cdot \nabla C = \frac{1}{A} \frac{\partial}{\partial z} \left(Ak \frac{\partial C}{\partial z} \right) + \Phi + \phi \quad (1)$$

where C is the concentration, t time, v the horizontal velocity, A the area of the cell, z vertical co-ordinate, k exchange coefficient, Φ source terms and ϕ sink terms.

For benthic variables and macrophytes, which are attached to the bottom, advection and diffusion is zero, and the equation is reduced to

$$\frac{\partial C}{\partial t} = \Phi + \phi \quad (2)$$

PROBE was written by Urban Svensson and others (Svensson, 1998) at SMHI Norrköping. BIOLA was developed by Charlotta Pers during 2000-2001 (Pers, 2002). It has many features in common with SCOBI, a biogeochemical model for marine environments, developed at SMHI by Eleonor Marmefelt and others (Marmefelt *et al.*, 2000). The programmes are written in Fortran77 with some Fortran90 extensions.

The main differences between SCOBI and BIOLA are:

- BIOLA does not differentiate between nitrate and ammonium in the water, but summarises it in one state variable, DIN
- In BIOLA all state variables are measured as carbon, including phytoplankton, detritus and zooplankton
- Makrophytes and fish are included in BIOLA
- In BIOLA, the sediment parameters are “area-concentrations” (g m^{-2}), but in most versions of SCOBI, they are standard volume-concentrations (g m^{-3})
- In BIOLA, the sediment organic material is mineralised into inorganic nutrients, which are explicitly modelled in the sediment. In SCOBI the organic material is broken down

and part of the nutrients are returned to the water by a formulation depending on oxygen concentration the water, among other things

The water basins of BIOLA are vertically discretised in N-2 cells, numbered from 2 at the bottom to N-1 at the surface. Each cell is assumed to be horizontally homogenous, and consists of a water part and a sediment part (Figure 4). The state variables belonging to the water are “volume concentrations”, in units mg l^{-1} or g m^{-3} . The sediment state variables are “areal concentrations”, in units g m^{-2} .

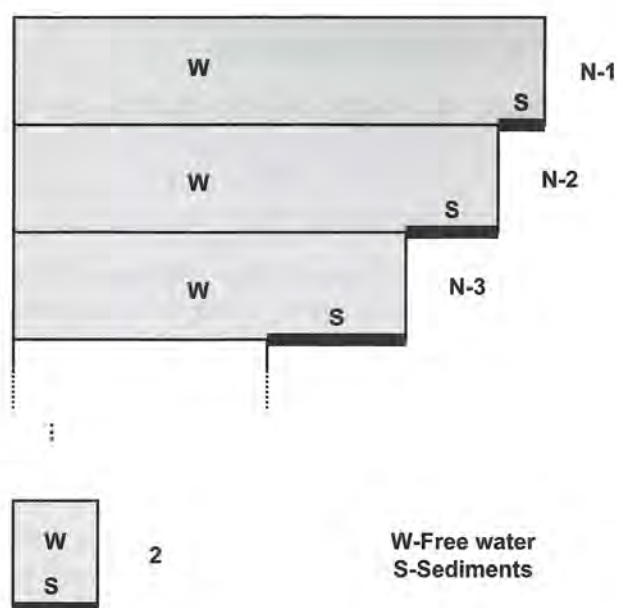


Figure 4. Discretisation of a water basin.

There are 14 state variables in the original BIOLA model. They are listed in Table 2. Relevant processes are modelled (Figure 5). They give the fluxes between the state variables (Table 3). PROBE solves the biogeochemical equations and applies the physical processes such as in-and outflows, boundary conditions, advection, diffusion and mixing.

Table 2. State variables of the original BIOLA model

Inorganic variables	Symbol	Unit	Living organic variables	Symbol	Unit
Phosphate	PO4	mg P l^{-1}	Phytoplankton	PHY	mg C l^{-1}
Dissolved inorganic nitrogen	DIN	mg N l^{-1}	Blue-green algae	ANF	mg C l^{-1}
Oxygen	OXY	mg l^{-1}	Zooplankton	ZOO	mg C l^{-1}
Inorganic P in sediments	BIP	g P m^{-2}	Planktivorous fish	FA	mg C l^{-1}
Dissolved NH_4 in sediment	BNH	g N m^{-2}	Piscivorous fish	FB	mg C l^{-1}
Dissolved NO_3 in sediment	BNO	g N m^{-2}	Macrophyte	MAC	mg C l^{-1}
			Dead organic variables	Symbol	Unit
			Detritus	DET	mg C l^{-1}
			Sediment organic matter	SED	g C m^{-2}

Table 3. *Modelled processes and their links to the state variables*

Process	Sink (ϕ) of	Source (Φ) of
Phytoplankton growth	PO4, DIN	PHY, O2
Blue-green algae growth	PO4, DIN	ANF, O2
Macrophyte growth	BIP, BNH4, PO4, DIN	MAC, OXY
Macrophyte mortality	MAC	SED
Blue-green algae mortality	ANF	DET
Zooplankton grazing on phytoplankton and blue-green algae	PHY, ANF	ZOO, DET
Zooplankton mortality	ZOO	DET
Fish predation on zooplankton	ZOO	FA, DET
Fish predation on fish	FA	FB, DET
Piscivorous fish mortality	FB	SED
Detritus mineralisation	DET, OXY	PO4, DIN
Denitrification	BNO, DIN	BNH, BIP, DIN, PO4
Nitrification	OXY, BNH	BNO
Sediment mineralisation	SED, OXY	BNH, BIP
Exchange of nutrients between water and sediment	BIP, PO4, BNH, BNO, DIN	BIP, PO4, BNO, DIN
Sinking and sedimentation of phytoplankton, blue-green algae and detritus	PHY, ANF, DET	PHY, ANF, DET, SED

In BIOLA, the phytoplankton, PHY and ANF, grow and take up nutrients from DIN and PO4. Zooplankton, ZOO, graze on phytoplankton. Not all of the phytoplankton eaten are assimilated; the rest is ends up in the detritus pool, DET. Fish FA eat zooplankton, and are in their turn eaten by piscivorous fish, FB. At each step in the foodchain some organic material is lost by the incomplete assimilation and included in detritus. Blue-green algae and zooplankton die and are then incorporated in detritus. Detritus and phytoplankton except blue-green algae sink to the bottom and are incorporated in the sediment organic material, SED. Some of the detritus is mineralised in the water and turned into inorganic nutrients again. Fish-eating fish die, and so do macrophytes, and are incorporated in the sediment organic material.

The sediment organic material is mineralised to phosphate and ammonium, BIP and BNH. Ammonium is turned into nitrate, BNO, through nitrification. Denitrification uses a never-ending carbon source, producing phosphate and ammonium, and turns nitrate into nitrogen gas, which leaves the system. Denitrification also takes place in the free water, if the oxygen concentration is below zero. Inorganic nutrients in the sediments are by diffusion transported to the inorganic nutrients in the free water; or, if the concentration in the water is high, the transport may be from the free water to the sediment. Macrophytes take up nutrients from the sediments and from the water. Inflows, outflows and atmospheric deposition are not modelled as sink and source processes but handled by PROBE.

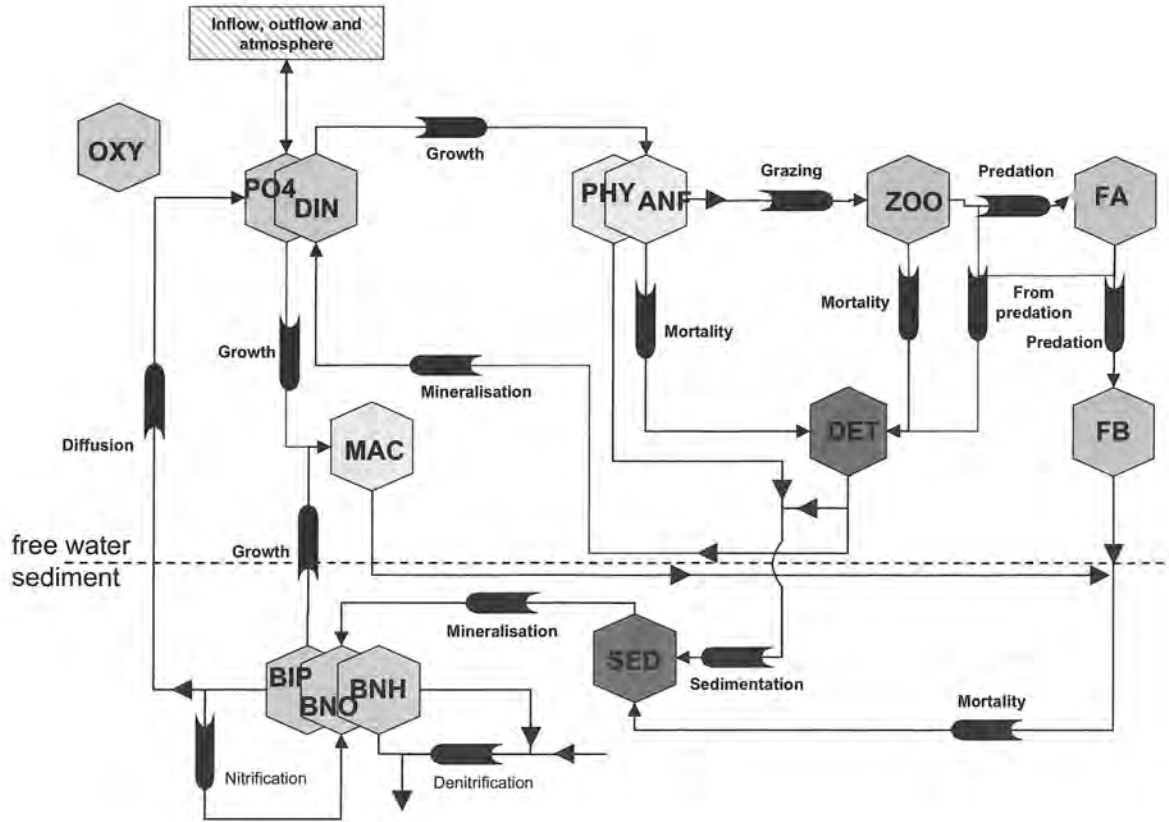


Figure 5. The original BIOLA model. State variables and flows. State variables of inorganic nutrients are grouped; arrows to and from them often indicate processes concerning more than one of grouped state variables. Denitrification in the free water and sequestering are not shown, because they usually equal zero. After Pers, (2002).

2.1.1 Exchange of nutrients between sediments and water

The formulation is simple. Nitrate, ammonium and phosphate are exchanged by diffusion, described by Fick's first law. If the water by the sediment surface is aerobic, that is contains oxygen, all sediment phosphate is assumed to be sorbed. The concentration of dissolved phosphate in the sediments is then assumed to be zero, so phosphate will only be transported from the water to the sediment. If the water by the sediment surface is anaerobic, all phosphate is regarded as dissolved and the diffusion works as usual (3).

$$\phi_{BIP} = -k_{diff} * \frac{\left(\frac{BIP * (1 - h(O_2))}{d_{sed}} - PO_4 \right)}{d_{sed}} \quad (3)$$

where $h(O_2)$ is the Heaviside's step function, $h(O_2) = \begin{cases} 1 & [O_2] > 0 \\ 0 & [O_2] \leq 0 \end{cases} \quad (4)$

k_{diff} is the sediment diffusion coefficient ($1 * 10^{-9} \text{ m}^2 \text{ s}^{-1}$) and d_{sed} is the thickness of the active sediment layer (0.1 m).

2.1.2 Setup requirements

The required indata for a model setup are

- Hypsographs of the basins, i. e. the depth-volume distribution
- Meteorological data, i. e. air temperature, wind speed, wind direction, cloudiness and relative humidity
- Tributary water inflow and concentration of nutrients
- Secchi depth to calculate light attenuation

Atmospheric deposition is optional.

2.2 Model setup for Lake Ringsjön

In this work, a BIOLA setup for Lake Ringsjön, Scania, Sweden was used. The study was concentrated on Lake Östra Ringsjön, with some considerations taken of Sätöftasjön. Lake Östra Ringsjön was considered more representative of eutrophic lakes, as it is deeper than Lake Västra Ringsjön and larger than Lake Sätöftasjön. At previous model development, Lake Sätöftasjön had been difficult to simulate.

The hypsograph was obtained from SMHI SVAR (Svenskt VattenARKiv). Cloudcover and relative humidity were taken from the Barkåkra weather station, air temperature from Bredåkra weather station and wind speed and direction from Falsterbo weather station, SMHI. The data were compared with data from Sturup weather station, which seems to have the best data, but only available for 1990-1995. The meteorological data were then corrected with a factor to give similar monthly averages as data from Sturup. Tributary inflow was obtained from the SMHI water flow measures of Hörbyån at Heåkra. The inflow from the other tributaries was assumed proportional to the Heåkra flow, estimated from the relation between catchment areas. Tributary nutrient concentrations were obtained from the regular water monitoring program for Lake Ringsjön, administrated by Ringsjökommittén, Sweden. The outflow was assumed to equal the inflow, i. e. the water surface level was constant.

The basins were vertically divided in 20 (Lake Sätöftasjön and Lake Östra Ringsjön) and 14 (Lake Västra Ringsjön) cells. The time step can vary, but in this work it was 10 minutes. A 10 years simulation of the three basins of Lake Ringsjön needed one hour to complete on a Pentium III PC, 733 MHz clock frequency, 260 MB RAM memory in Windows.

Chemical and biological data were obtained from the yearly reports of the regular water monitoring program for Lake Ringsjön. The phytoplankton data were kindly provided by the Department of Limnology, University of Lund, Sweden. Water for analysis of water chemistry and phytoplankton was sampled over the deepest point of the basin as an integrated sample from the surface and 2 m down. Samples for zooplankton were taken integrated over the whole water column over the deepest point of the lake.

Later during the model development thickness of aerobic and anaerobic sediment layers were obtained from Enell (1983), who estimated the total active sediment layer in Lake Ringsjön to 20 cm. It was then divided into an aerobic part of 3 cm and an anaerobic of 17 cm, similar to the layer thicknesses found in Lake Vänern by Rosenberg *et al.* (1999).

2.3 Model Development

The original model was studied and literature considered. The aim was to improve the simulation of phytoplankton biomass in the summer and, as far as possible, also the concentration of total phosphorus over the year. Total phosphorus was preferred over phosphate, which in surface waters often is turning over every few minutes and thus is a less meaningful parameter (Correll, 1998).

The sediment processes have by many authors been emphasised as critical for the lake trophic level (Boström *et al.*, 1982; Soetart *et al.*, 2000). They were considered the possibly most rewarding factor to improve at this stage. Three major changes to the sediment processes were carried through:

- Resuspension of sediments from erosion and transportation bottoms was added
- The sediments was divided into an upper, aerobic, and a lower, anaerobic, layer
- The relation between sorbed and dissolved phosphorus in the sediments was described by oxygen-dependent Langmuir isotherms

2.3.1 Resuspension of sediments from erosion and transportation bottoms

The percentage of erosion and transportation bottoms, was calculated after Håkanson and Jansson, (1983) as

$$a_{ET} = 100 - a_A = 25 * (\sqrt{a} / \bar{D}) * 41^{0.061 * \bar{D} / \sqrt{a}} \quad (5)$$

where a_{ET} is the percentage of erosion and transportation bottoms

a_A is the percentage of accumulation bottoms, A

a is the lake surface area, (km²) and

\bar{D} is the mean depth (m)

A subroutine that calculated the depth of the borderline between the erosion and transportation and the accumulation bottoms from the lake hypsograph was added to the program. If the depth to the borderline is already known from investigations of the lake it can be used. The calculations above are not needed then.

The resuspension rate can, according to (Håkanson, 1999b; Malmaeus and Håkanson, manuscript) be described by

$$R_{RES} = \frac{0.693}{12} * \left(\frac{mw}{3.27} \right)^2 \quad (6)$$

where R_{RES} is the part of the active sediment material which is resuspended during a month (1/month) and

mw is the mean wind speed for the present month (m s⁻¹)

This formula (6) is empirical and has been found to give good simulations in Cs-models (Malmaeus, pers. com.). It is used in the LEEDS lake phosphorus model (Malmaeus and Håkanson, manuscript). The formula was adjusted for 10 minutes timesteps and corrected

for the wind data being 3h mean wind instead of 1 month mean wind. The correction factor between 3h mean wind squared and 1 month mean wind squared was 0,778 for wind data 1990-1999. The formula which was used in the program was

$$R_{RES} = 9.5866 * 10^{-7} * (3h - wind)^2 \quad (7)$$

where R_{RES} is the part of the active sediment material which is resuspended during 10 minutes (1/10 minutes) and

$3h-wind$ is the mean wind speed for the previous ten minutes period ($m s^{-1}$)

It was assumed that the organic material in the upper sediment layer could represent the resuspendable active sediment material. The process resuspension was then represented by a flux from the organic material in the upper sediment layer to the detritus in the water column. There was no resuspension at the accumulation bottoms.

$$\phi_{SED} = -R_{RES} * SED \quad (8)$$

$$\Phi_{DET} = -\phi_{SED} * \frac{A_{bottom}}{A_{cell} * \Delta z_{cell}} \quad (9)$$

where A_{bottom} is the bottom area of the specific cell (m^2)

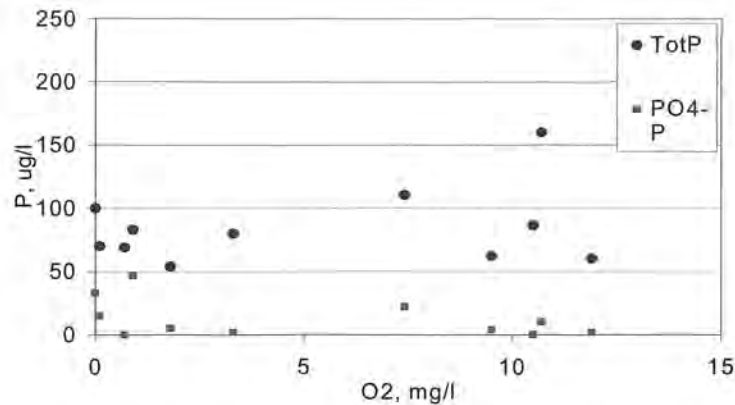
A_{cell} is the area of the specific cell (m^2)

Δz_{cell} is the thickness of the specific cell (m)

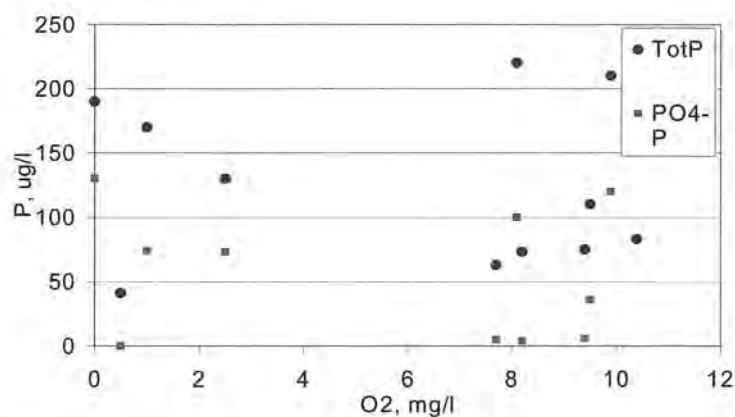
2.3.2 Aerobic and anaerobic sediment layer

There are different approaches to the sediments in biogeochemical water ecosystem modelling. The simplest approach is to completely disregard the bottom and treat the ecosystem as having no coupling to the benthic (bottom) processes. If the sediments are vertically resolved concerning e. g. redox conditions, the approach is more complex. The more simple approaches, where sediment concentrations or fluxes are imposed, have problems in resolving e. g. retention capacity of sediments and long-term effects. If the sediments are vertically resolved, much computer strength is needed. The most rewarding concept considering computer strength and data requirements of the model is usually to treat the sediments as vertically integrated (Soetart *et al.*, 2000). This is the approach used for example here in BIOLA, in SCOB1 (Marmefelt *et al.*, 2000) and by Savchuk and Wulff (1996) in modelling of the Baltic Sea, and also in the LEEDS lake model (Håkanson and Carlsson, 1995).

The redox potential is well known as an important factor for the sediment's phosphorus sorption capacity in many lakes. Lake Ringsjön is a rather calcareous lake, although probably not enough to eliminate the possibility of redox-regulated phosphorus sorption (Rydin, pers. comm.). Scatterplots were made of the phosphorus concentrations and the oxygen concentrations in the bottom water (Figure 6). There was no significant relationship between oxygen level and phosphorus level.



a. Lake Sätöftasjön



b. Lake Östra Ringsjön

Figure 6 a-b. Concentrations of total phosphorus and phosphate at different oxygen concentrations at 15 m depth. Data from June to September 1997-1999 for Sätöftasjön and Östra Ringsjön.

If the phosphorus levels would be higher for low oxygen concentrations, one could suspect that the phosphorus was released because of the low redox potential. But, "Because decomposition both consumes oxygen and liberates P, P in bottom waters (from sediment P release) would be expected to be greater when oxygen had been depleted than when oxygen was still abundant whether or not the binding of P to sediments decreased under anoxia" (Caraco *et al.*, 1991). Increased phosphorus levels in anaerobic bottom waters do consequently not necessarily indicate that anoxia caused phosphorus release.

Caraco *et al.* (1991) further reason that if there is much more phosphorus released than nitrogen, compared to what would be expected from the molar ratio of N:P of the sediment organic material, one could conclude that phosphorus release was indeed increased because of the low oxygen level. In Lake Sätöftasjön and Lake Östra Ringsjön, there was no significant difference between nitrogen and phosphorus release patterns at different oxygen levels, so no evidence of redox-initiated phosphorus release could be found. However, the samples were taken one meter or more from the lake bottom. Mixing of the lake could also have caused a dilution of phosphorus-rich bottom water, obscuring peaks in phosphorus release. The question of whether or not phosphorus release from the sediments of Lake Ringsjön is increased at low redox potentials remains open.

It was decided to try a redox-depending formulation of phosphorus sorption capacity. pH and nitrate dependence could also have been considered, but pH was not included in the modelling and the effects of pH- and nitrate-changes varies between lakes, see above.

DiToro (2001) suggests a two-layer sediment model to deal with the redox dependency of phosphorus release (Figure 7). Lijklema (1993) also suggests a model of an aerobic layer on top of an anaerobic. In DiToro's suggestion, there is a lower, anaerobic sediment layer, and an upper, aerobic layer.

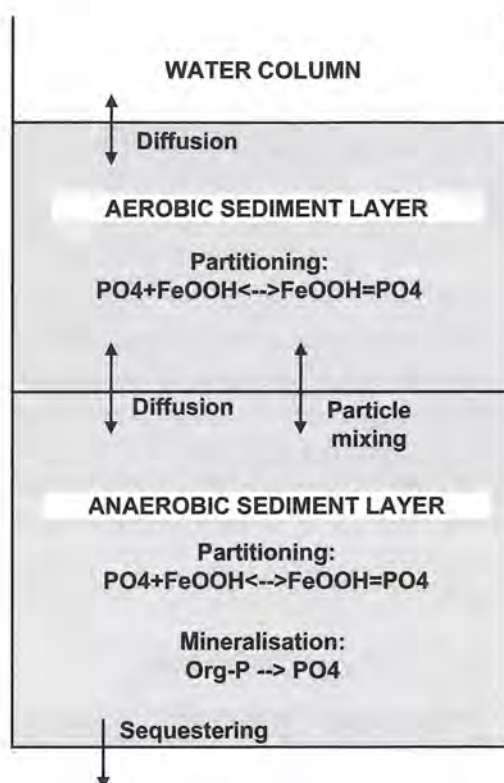


Figure 7. Phosphorus flux model proposed by DiToro (2001).

Organic material is transported between the layers by “particle mixing”, representing the effect of burrowing benthic fauna. He suggests mineralisation only in the anaerobic layer. Phosphate is transported by diffusion between the sediment layers and between the aerobic sediment layer and the free water. A part of the phosphate is sequestered (permanently immobilised). One difference between the layers is in the coefficient regulating the partitioning, i. e. how much of the phosphate is dissolved and how much is sorbed.

The two-layer models seemed attractive because it resembles the reality with the always anaerobic lower sediment layer, see for example Rosenberg *et al.* (1999) and Boström *et al.* (1982). A sediment approach resembling reality was thought more likely to have processes which co-ordinate in realistic way and give reasonable results. It also seemed to give the possibility of slow response, as the material in the anaerobic sediment has a longer way to the water column and thus should have a slower response. So, DiToro's (2001) suggestion was used, with four alterations:

- A mineralisation process was added in the aerobic sediment

- The aerobic layer was supposed to be truly aerobic when the oxygen concentration was above a critical level, and anaerobic when the oxygen concentration was below this level. This required an oxygen-dependent partitioning in this layer, see below on Langmuir isotherms.
- The resuspension process was added for exchange between the aerobic sediment layer and the water, as described above
- The partitioning was described as a sorption-desorption process as a sum of all sorption mechanisms, instead of just sorption by iron-oxid-hydroxids.

Mineralisation is thought to take place in the whole active part of the sediments, so it was added to the upper sediment (Smits and van der Molen, 1993). The oxygen-dependency of the partitioning was suggested by DiToro (2001), but the Langmuir isotherm description was used to improve the partitioning at high phosphorus concentrations. Resuspension was thought to be an important process, and to regard the partitioning as a sum of all sorption mechanisms is an extension of definition in order to describe different lake sediment conditions.

The final sediment module is shown in Figure 8. The limit between the aerobic and the anaerobic layer represents the depth where the oxygen concentration dissolved in the pore water equals zero. Macrophytes took phosphate for growth from the anaerobic sediment layer. The organic material in the aerobic sediment layer was refilled by the sedimentation of phytoplankton, detritus and dead macrophytes. The nitrogen cycle was extended in analogy with the phosphorus cycle. The only new thing for nitrogen was that as the lower sediment layer was anaerobic, there was neither nitrification nor denitrification there.

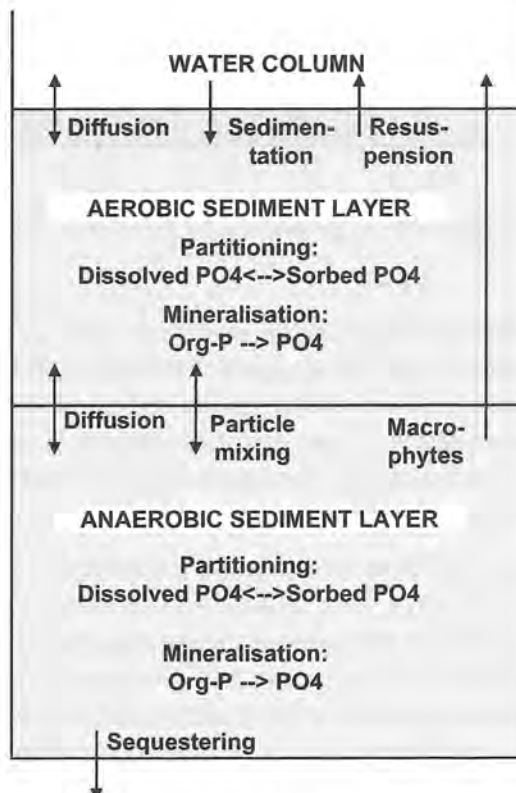


Figure 8. Sediment module for phosphorus and organic material used in the new BIOLA.

The mineralisation rate depended only on temperature. In reality, denitrification is part of the mineralisation process. Here mineralisation means all mineralisation except denitrification, which was calculated separately. The total sink for sediment organic matter in the model was therefore the effect of mineralisation plus denitrification, in addition to resuspension.

$$\phi_{SED} = -\max(k_{sm} * \theta^{T-T_{ref}} * SED + \phi_{SED}(denitr), 0) \quad (10)$$

$$\phi_{SEDAN} = -k_{sm} * \theta^{T-T_{ref}} * SEDAN \quad (11)$$

$$\Phi_{BIP,BIPAN} = -C_{PC} * \phi_{SED,SEDAN} \quad (12)$$

$$\Phi_{BNH,BNHAN} = -C_{NC} * \phi_{SED,SEDAN} \quad (13)$$

$$\phi_{O_2} = -C_{OC} * \phi_{SED,SEDAN} \quad (14)$$

where k_{sm} is the mineralisation rate in the aerobic and anaerobic sediment layer (0.02 d⁻¹ and 0.01 d⁻¹, respectively)

θ is the general temperature coefficient in the aerobic and anaerobic sediment layer (1.5 and 1.1, respectively)

T_{ref} is the general reference temperature in the aerobic and anaerobic sediment layer (20°C for both)

T is the actual water temperature above the bottom (°C)

$\phi_{SED}(denitr)$ is the sink for organic matter through denitrification

C_{PC} is the stoichiometric ratio between phosphorus and carbon in organic matter (0.0244 mg P (mg C)⁻¹)

C_{NC} is the stoichiometric ratio between nitrogen and carbon in organic matter (0.176 mg N (mg C)⁻¹)

C_{OC} is the stoichiometric ratio between oxygen use and carbon in mineralisation of organic matter (2.667 mg O₂ (mg C)⁻¹)

Diffusion was supposed to follow Fick's law. The diffusion rate depended on the concentration gradient. The nutrients were assumed to have an even distribution in each sediment layer. The diffusion was also covering the effect of benthic fauna stirring the sediment and effects from turbulence. Positive diffusion is upwards.

$$\phi_{BIP} = -k_{diffP} * \frac{\left(\frac{disBIP}{h_{AR}} - PO4 \right)}{(h_{AR})} \quad (15)$$

$$\Phi_{PO4} = -\phi_{BIP} * \frac{A_{bottom}}{A_{cell} * \Delta z_{cell}} \quad (16)$$

$$\phi_{BIPAN} = -k_{diffPAN} * \frac{\left(\frac{disBIPAN}{h_{AN}} - \frac{disBIP}{h_{AR}} \right)}{\left(\frac{h_{AN} + h_{AR}}{2} \right)} \quad (17)$$

$$\Phi_{BIP} = -\phi_{BIPAN} \quad (18)$$

where k_{diffP} , $k_{diffPAN}$ are the diffusion constants for phosphorus between the aerobic sediment layer and the free water, and between the two sediment layers, respectively ($1 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and $1 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$)

$disBIP$, $disBIPAN$ are the dissolved parts of BIP and BIPAN, respectively, calculated in the model (g P m^{-2})

h_{AR} , h_{AN} are the thicknesses of the two sediment layers (0.03 and 0.17 m, respectively)

Particle mixing was introduced in the new BIOLA version. The formulation was similar to diffusion after DiToro (2001), equation 6.1b with the value of w in Table 6.1.

$$\phi_{SEDAN} = -w * \left(\frac{SEDAN}{h_{AN}} - \frac{SED}{h_{AR}} \right) \quad (19)$$

$$\Phi_{SED} = -\phi_{SEDAN} \quad (20)$$

where w is particle mixing velocity (0.0012 m d^{-1})

Sequestering of organic material was proportional to the amount of organic material in the anaerobic layer. A sequestering rate of zero was used, but rates between 0 and 0.25 d^{-1} have been used for marine waters (Marmefelt *et al.*, 2000).

$$\phi_{SEDAN} = -k_s * SEDAN \quad (21)$$

where k_s is the sequestering rate (0.0 d^{-1})

A sequestering rate of zero can be motivated by the difference between organic material in reality and in BIOLA. Through mineralisation, real organic material is enriched in carbon as the “tastier” substances are broken down quicker. The sequestered material thus has a lower proportion of nitrogen and phosphorus than fresh organic material, so that a small amount of nitrogen and phosphorus is permanently immobilised. In BIOLA, the proportion of nitrogen and phosphorus in organic material was always constant. If as much organic material as in reality would be sequestered in the model, much too much nitrogen and phosphorus would be lost. Compared to other flows of nitrogen and phosphorus, sequestering was assumed to be negligible.

Macrophytes took up nutrients from the anaerobic layer. If the nutrient demand was higher than the amount of inorganic nutrients available, nutrients were also taken up from the water. Sedimentation included phytoplankton, both blue-green and other, detritus and also dead macrophytes.

Diffusion in the model covers both diffusion and the effect of bioturbation. The mechanisms were assumed to be similar, as “the net effect of bioturbation on phosphorus exchange across the sediment-water interface depends on the prevailing chemical equilibria” (Boström *et al.*, 1988). Thus they could be lumped into a “diffusion” process.

This is of course a simplification, for example as bioturbation can be modelled as temperature dependent (Lijklema, 1993).

The thickness of the aerobic layer varied between 3 and 15 mm in four shallow Danish lakes during 1987 (Jensen and Andersen, 1992). In the new BIOLA, the aerobic layer thickness was 3 cm and the anaerobic 17 cm, following estimations of active sediment depth by Enell (1983) and of aerobic layer thickness in Lake Vänern (Rosenberg *et al.*, 1999).

2.3.3 Langmuir isotherms

The phosphate in the sediment layers was divided into dissolved and sorbed phosphate. Only the dissolved phase is subject to diffusion. The dissolved phase is dissolved in the pore water, which is directly exchangeable with the free lake water (Boström *et al.*, 1988). The relationship between the two fractions has been investigated and found to fit both Freundlich and Langmuir isotherms. Isotherms are used much in Soil Science to describe relationships at equilibrium between the dissolved and sorbed phase of a substance. The term "isotherm" originally refers to the requirement of constant temperature during the analysis. Freundlich isotherms are exponential, so there is no upper limit to how much substance can be sorbed to an amount of soil, whereas Langmuir isotherms have a maximum sorption capacity.

Langmuir isotherms are described by:

$$SP_{C_e} = PSC * \frac{C_e}{k_L + C_e} - NAP \quad (22)$$

and Freundlich isotherms by:

$$SP_{C_e} = K_F * (C_e)^P - NAP \quad (23)$$

where SP_{C_e} is the phosphate that has become sorbed at equilibrium (g P m^{-3})
 C_e is the equilibrium phosphate concentration in the solution (g P m^{-3})
 NAP is the native adsorbed phosphate (g P m^{-3})
 PSC is the phosphate sorption capacity (g P m^{-3})
 k_L is the half-saturation constant (g P m^{-3}) and
 K_F and P are constants for the Freundlich isotherm

Jacobsen (1977) compared the two isotherm descriptions and found that the sorption of phosphate by eight Danish lakes is best described by Langmuir isotherms during aerobic conditions. During anaerobic conditions Freundlich isotherms are more fitting. Langmuir isotherms have been found to well describe the phosphate sorption in four other Danish lakes (Jensen and Andersen, 1992), the Kis-Balaton Reservoir, Hungary (Istvánovics, 1994), Lake Neusiedlersee, Austria (Gunatilaka, 1982) and Lake Kasumigaura, Japan (Furumai and Ohgaki, 1989). On four locations in the Southern and Eastern North Sea, Freundlich isotherms can be used (Slomp *et al.*, 1998).

Jacobsen defines sorption as the sum of chemisorption and adsorption (Boström *et al.*, 1982, and references therein). The Langmuir isotherm is a good choice when the sorption is a chemisorption to for example iron-oxid-hydroxids, because the maximum number of

sorption sites is well described by the maximum sorption capacity. Freundlich isotherms describe adsorption well, so sorption to clay particles and inorganic surfaces are well described by this isotherm (Jacobsen, 1977).

Langmuir isotherms were chosen for the new BIOLA, since it seemed to fit data from many different lakes. The sorption was also assumed to be more chemisorption than adsorption. The sorption processes consist of one fast and one slow process (Furumai *et al.*, 1989, Slomp *et al.*, 1998). Equilibrium in experiments on sediments from Lake Kasumigaura is reached within one hour (Furumai *et al.*, 1989, Furumai and Ohgaki, 1989). On experiments on sediments from eight Danish lakes, equilibrium is reached after 10-15 hours (Jacobsen, 1977). However, the slow process reaches equilibrium after days or months (Rydin, 2001). The changes in the sediments between timesteps are usually small in BIOLA, so it was assumed that the sediments was near equilibrium with its pore water. Thus, the isotherms, which describe the relations at equilibrium, could be used.

Values of the parameters were taken from the eight Danish lakes and Lake Kasumigaura, since the amount of total phosphate in their sediments was similar to that of Lake Ringsjön. The Danish lakes had a total phosphate content of 1.0-2.7 mg P (gDW)⁻¹ in the uppermost 5 cm (Jacobsen, 1977), Lake Kasumigaura had a total phosphate level of 0.8-1.7 mg P (g DW)⁻¹ in the upper 20 cm (Furumai and Ohgaki, 1989). In Lake Ringsjön the amounts were 1.7-2.7 mg P (g DW)⁻¹ in the upper 20 cm (Enell, 1983).

In BIOLA, the PSC at anaerobic conditions was 2.5 times the PSC at aerobic conditions, estimated from Jacobsen (1977). The PSC of anaerobic layer was fixed, but the PSC of the upper, "aerobic" sediment layer varied between aerobic and anaerobic PSC by a formulation from DiToro (2001; eq. 6.19-6.21). The final formulation used was

$$SP_{c_e}^{Tot} = PSC * \frac{C_e}{k_L + C_e} \quad (24)$$

$$PSC_{aerobic} = PSC_{anaerobic} * K_A \quad O_2 > O_{2_{crit}} \quad (25)$$

$$PSC_{aerobic} = PSC_{anaerobic} * (K_A)^\beta \quad O_2 \leq O_{2_{crit}} \quad (26)$$

$$\beta = \frac{O_2}{O_{2_{crit}}} \quad (27)$$

where K_A is the ratio between aerobic and anaerobic PSC (2.5)

$SP_{c_e}^{Tot}$ is the total amount of sorbed phosphate at equilibrium

$$(SP_{c_e}^{Tot} = SP_{c_e} + NAP)$$

PSC is the phosphate sorption capacity in the aerobic and anaerobic sediments (130 g P m⁻³ and 52 g P m⁻³, respectively)

k_L is the half-saturation constant and (0.65 g P m⁻³)

The oxygen limit for reduction of Fe³⁺ to Fe²⁺ is 0.1 mg l⁻¹ (Boström *et al.*, 1982; Håkanson and Jansson, 1983). However, this is the condition at the sediment surface. The model parameter was the oxygen concentration in the water cell, which was assumed to be higher than the concentration at the sediment surface. Therefore a critical oxygen concentration of 1.0 mg l⁻¹ was assumed.

With this formulation, phosphorus can be released from the bottom at both aerobic and anaerobic conditions. This is different from the original model.

2.4 Other changes to BIOLA

The temperature simulation was evaluated for Lake Östra Ringsjön during four days in the year 1999. The wind data gave a too large mixing of the lake water. Different factors were tried, and finally it was found that if the wind data was multiplied by 0.84, it gave a good fit to observed temperature data for this basin. The temperature profiles with original and changed wind speed are shown in Appendix A.

The inflow was changed so that the inflowing inorganic nitrogen was incorporated in the DIN state variable, organic nitrogen and total phosphorus was put in detritus pool, DET, as far as the proportion of nitrogen and phosphorus in organic matter allowed. If there was nitrogen remaining, it was dismissed, and if the leftover was phosphorus, it was incorporated in the dissolved phosphate pool, PO₄.

The fish state variables and flows which were present in the original BIOLA were turned off, since they were not functioning very well and the fluxes were small anyway. They were 1/1000 of the fluxes for zooplankton, which have the second lowest fluxes (Pers, pers. comm.). It is an advantage in modelling to have as few variables as possible (Håkanson, 1999a). In a later step of model development, fish state variables can be included. The change in results, tried on the original version, was negligible.

The printout time of results was changed so that it was in the middle of the day, as most observations were made in the middle of the day.

The diffusion constant was parted in four – one for phosphate and one for nitrate and ammonium in the aerobic sediment layer, and one set for the lower sediment layer.

Values of some parameters concerning sediment processes were changed. These are listed above in the vicinity of the equations. Some other parameter values and of course initial values were changed during the calibration process; the parameters are listed in Appendix B.

2.5 The new BIOLA

There were additional state variables and processes in the new BIOLA. Some state variables were removed with their processes, and a few processes were changed. The flowchart is shown in Figure 9, the state variables are listed in Table 4 and the processes in Table 5. The values of new and changed parameters are listed in Appendix B.

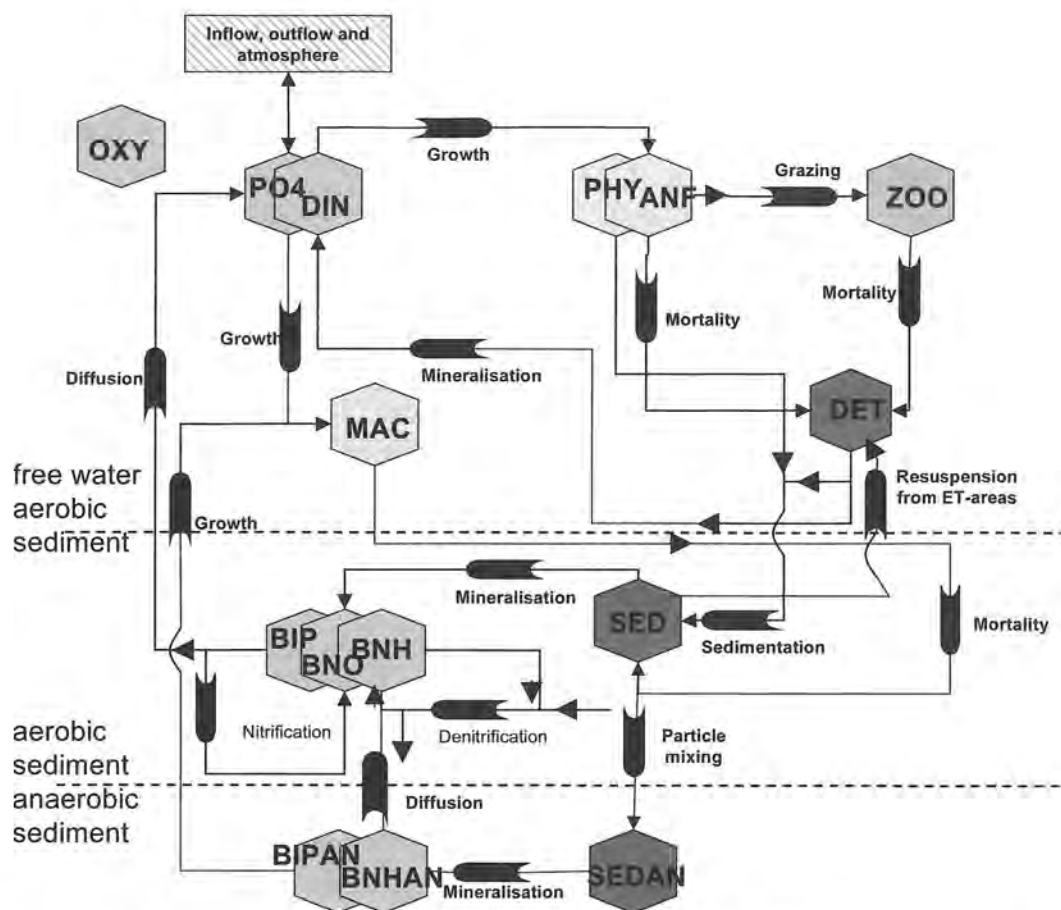


Figure 9. The new BIOLA model. State variables and flows. State variables of inorganic nutrients are grouped; arrows to and from them often indicate processes concerning more than one of grouped state variables. Denitrification in the free water and sequestering are not shown, because they usually equal zero.

Table 4. State variables included in the new BIOLA model

Inorganic variables	Symbol	Unit	Living organic variables	Symbol	Unit
Phosphate	PO4	mg P l ⁻¹	Phytoplankton	PHY	mg C l ⁻¹
Dissolved inorganic nitrogen	DIN	mg N l ⁻¹	Blue-green algae	ANF	mg C l ⁻¹
Oxygen	OXY	mg l ⁻¹	Zooplankton	ZOO	mg C l ⁻¹
Inorganic P in aerobic sediments	BIP	g P m ⁻²	Macrophyte	MAC	mg C l ⁻¹
Dissolved NH4 in aerobic sediment	BNH	g N m ⁻²	Dead organic variables	Symbol	Unit
Dissolved NO3 in aerobic sediment	BNO	g N m ⁻²	Detritus	DET	mg C l ⁻¹
Inorganic P in anaerobic sediment	BIPAN	g P m ⁻²	Sediment organic matter in aerobic sediment	SED	g C m ⁻²
Dissolved NH4 in anaerobic sediment	BNHAN	g N m ⁻²	Sediment organic matter in anaerobic sediment	SEDAN	g C m ⁻²

Table 5. Modelled processes and their links to the state variables for the new BIOLA model

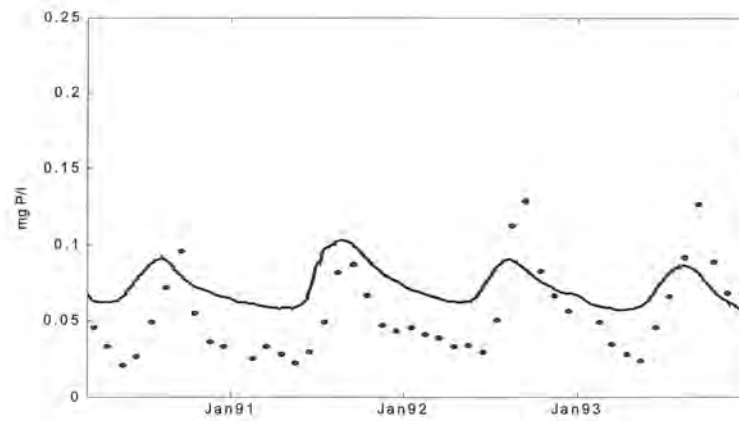
Process	Sink (ϕ) of	Source (Φ) of
Phytoplankton growth	PO ₄ , DIN	PHY, OXY
Blue-green algae growth	PO ₄ , DIN	ANF, OXY
Macrophyte growth	BIPAN, BNHAN, PO ₄ , DIN	MAC, OXY
Macrophyte mortality	MAC	SED
Blue-green algae mortality	ANF	DET
Zooplankton grazing on phytoplankton and blue-green algae	PHY, ANF	ZOO, DET
Zooplankton mortality	ZOO	DET
Detritus mineralisation	DET, OXY	PO ₄ , DIN
Denitrification in free water	DIN	DIN, PO ₄
Denitrification in aerobic sediment layer	BNO	BNH, BIP
Nitrification	OXY, BNH	BNO
Sediment mineralisation in aerobic sediment layer	SED, OXY	BNH, BIP
Sediment mineralisation in anaerobic sediment layer	SEDAN, OXY	BNHAN, BIPAN
Sinking and sedimentation of phytoplankton, blue-green algae and detritus	PHY, ANF, DET	PHY, ANF, DET, SED
Resuspension of sediments from erosion and transportation bottoms	SED	DET
Diffusive exchange of nutrients between water and sediment	BNH, BNO, DIN, BIP, PO ₄	BNH, BNO, DIN, BIP, PO ₄
Diffusive exchange of nutrients between aerobic and anaerobic sediment layer	BNHAN, BNH, BIPAN, BIP	BNHAN, BNH, BIPAN, BIP
Particle mixing between aerobic and anaerobic sediment layer	SED, SEDAN	SED, SEDAN
Sequestering	SEDAN	

2.6 Calibration

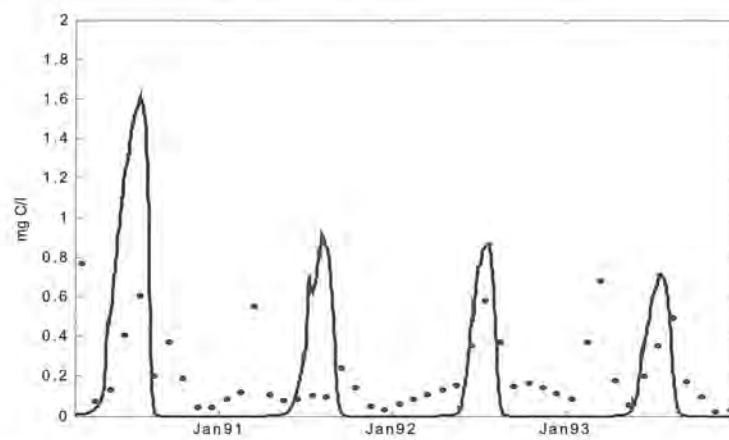
Calibration was carried out for Östra Ringsjön for the period March 1990 to December 1993. During this period, observation data were available for every year. The model was calibrated for total phosphorus and phytoplankton biomass. Reasonable concentrations of phytoplankton biomass were required, as well as steady state for annual averages of all state variables.

Parameters were tuned and initial values of the state variables were changed. The final parameters are listed in Appendix B. The results of a run with the best set of parameters are shown in Figure 10.

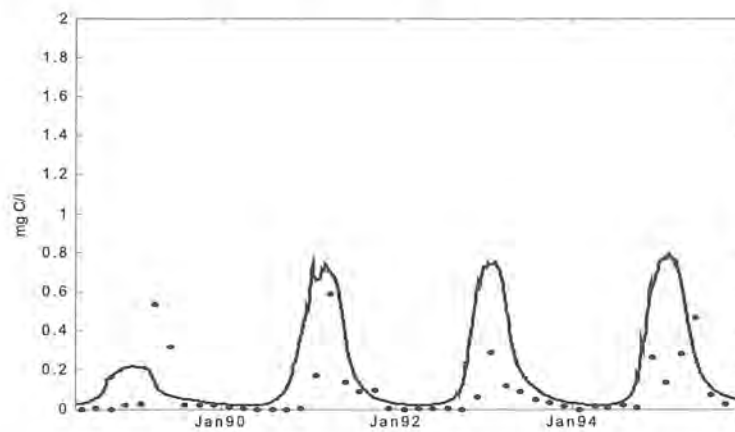
Steady state for annual averages was achieved for almost all state variables, except for ammonium and phosphate concentration in the lower, anaerobic, sediment layer. The drifting is shown in Figure 11.



a. Total phosphorus



b. Phytoplankton except blue-green algae



c. Blue-green algae

Figure 10 a-c. Calibration results from Lake Östra Ringsjön, years 1990-1993. The dots represent observations and the line the modelled concentrations.

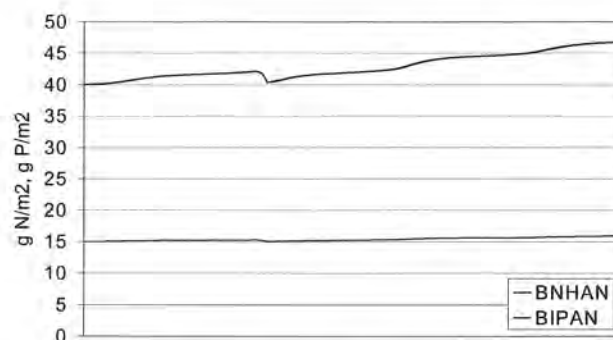


Figure 11. Drifting of state variables during 1990-03-01 to 1994-12-31, Lake Östra Ringsjön.

3 Results

3.1 Model Evaluation

3.1.1 Validation

The new model was run for ten years with the calibrated parameter values and the results were compared with observation data. Data from Lake Östra Ringsjön for the period 1994-1999 and Lake Sätöftasjön for 1990-1999 were used for evaluation. The results for Lake Östra Ringsjön and Lake Sätöftasjön are shown in Figure 12-17, together with the results of the original model for Lake Östra Ringsjön.

The original model was calibrated for phosphate, inorganic nitrogen and phytoplankton in Lake Västra Ringsjön, not for total phosphorus in Lake Östra Ringsjön. It would probably give better results for total phosphorus if it was calibrated for that.

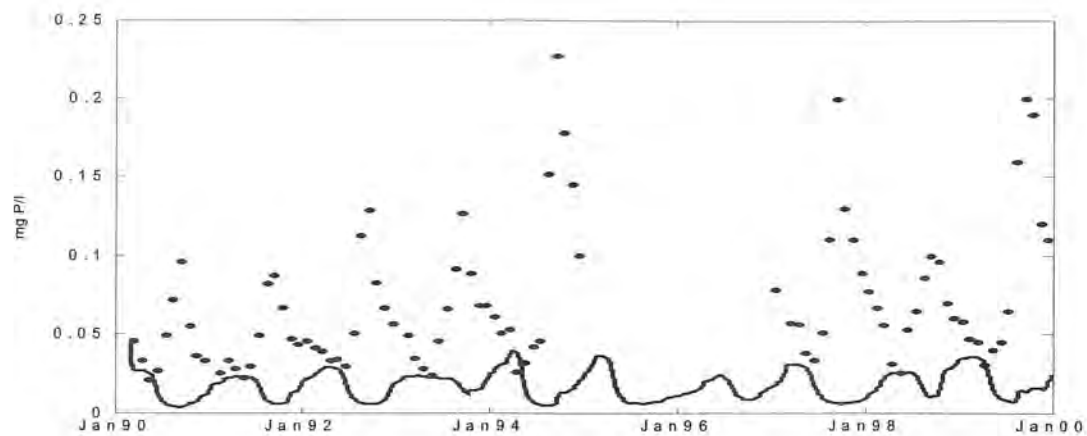
The dynamics of the total phosphorus has improved compared to the original BIOLA model (Figure 12). The peaks for Lake Östra Ringsjön came in the right time and were sharper than for the original model. The amplitude was still too low though. The average concentration also improved. For Lake Sätöftasjön, the simulation fit even better to the observations with about the same amplitude as the observations.

The phosphate average concentration was better modelled with the new BIOLA, but the dynamics have not improved and the peaks are not reproduced at the right time (Figure 13).

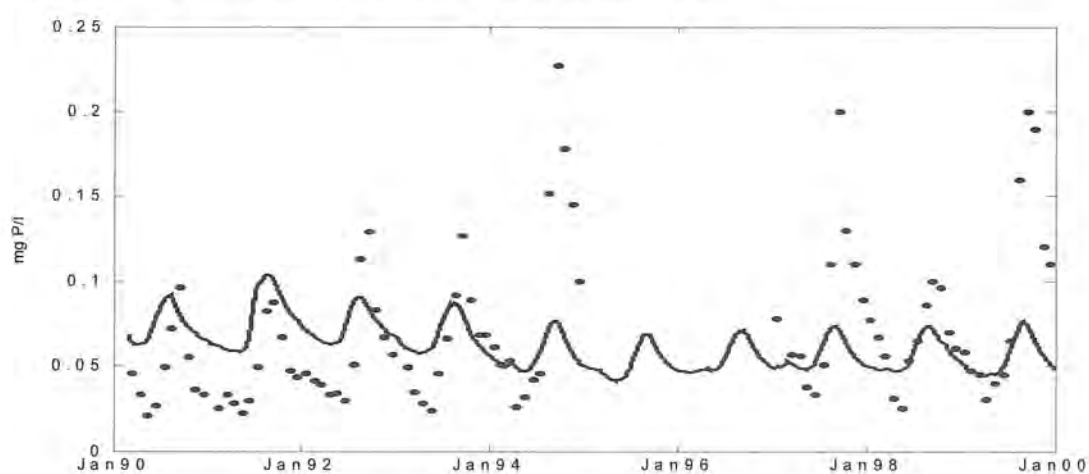
For phytoplankton except blue-green algae, the new model had too high levels for Lake Östra Ringsjön, but the dynamics were slightly improved compared to the original model (Figure 14). The model peaks for Sätöfta were also too high. Both the original and the new model gave too low phytoplankton concentrations during winter.

Blue-green algae were well simulated for Lake Östra Ringsjön with the new model (Figure 15). The biomass was low during winter, which the original model failed to simulate. The model fit for Lake Sätöftasjön was worse, with too low peak concentrations.

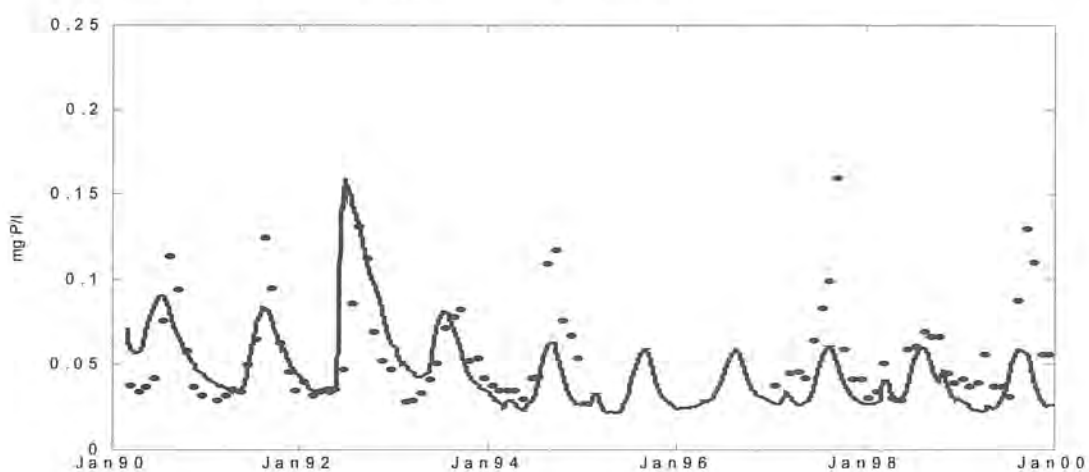
The dynamics for total nitrogen were right in time, but the amplitude was too low (Figure 16). For zooplankton there were only observations for year 1994 in the validation period (Figure 17). The simulation was very similar between years.



a. Lake Östra Ringsjön. The original BIOLA

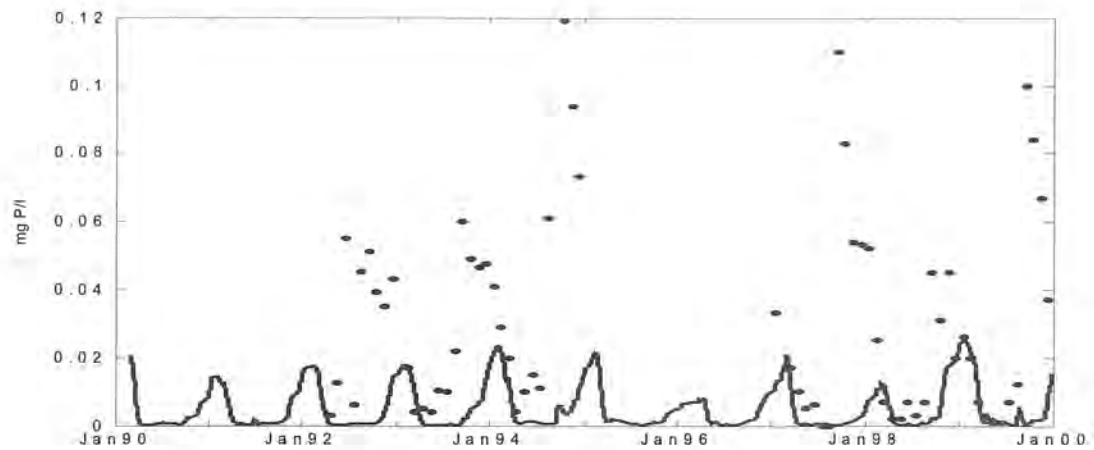


b. Lake Östra Ringsjön. The new BIOLA

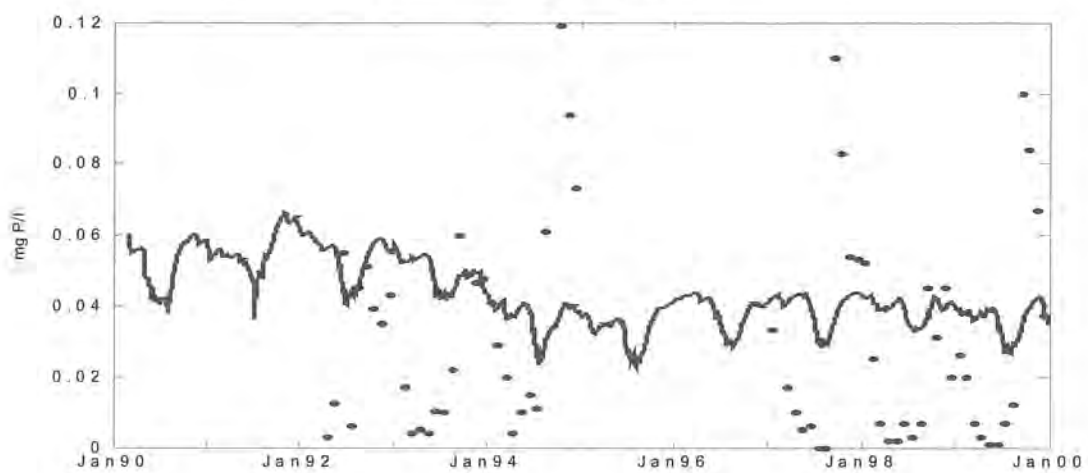


c. Lake Sätöftasjön. The new BIOLA

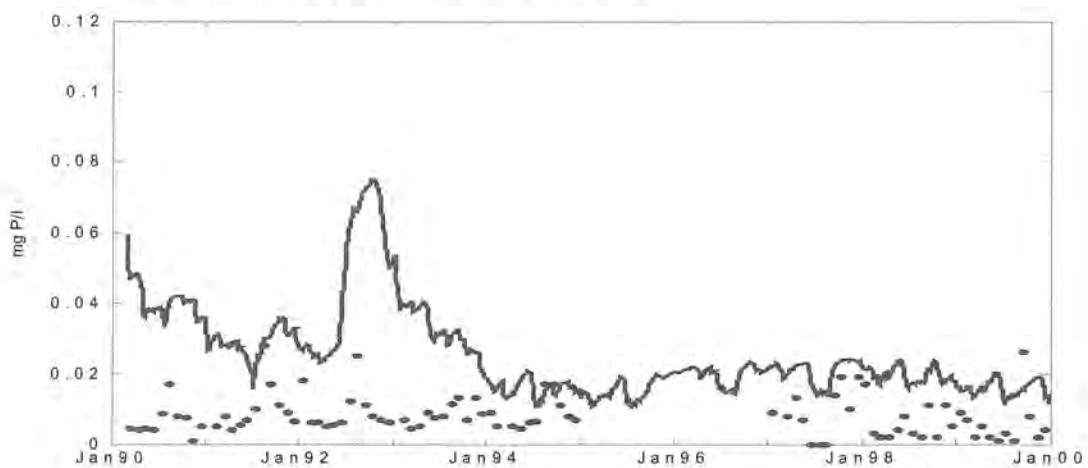
Figure 12 a-c. Total phosphorus concentrations in simulations with the original and the new BIOLA model. Years 1990-1999. Observations were not available for 1995-1996. The dots represent observations and the line the modelled concentrations.



a. Lake Östra Ringsjön. The original BIOLA

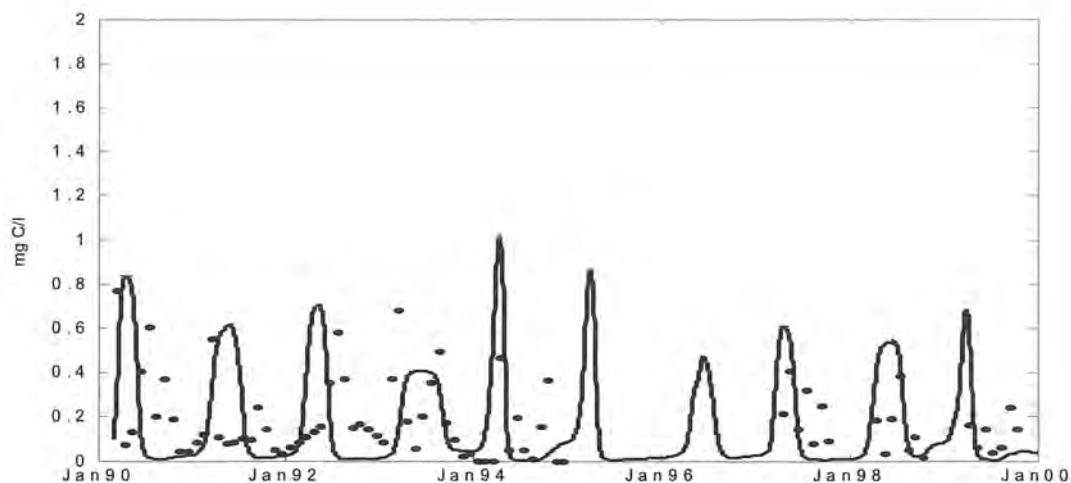


b. Lake Östra Ringsjön. The new BIOLA

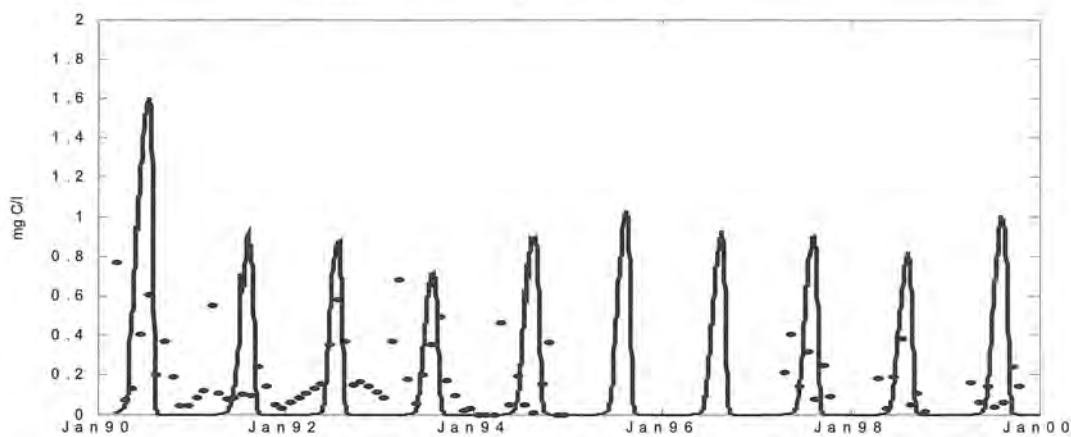


c. Lake Sätöftasjön. The new BIOLA

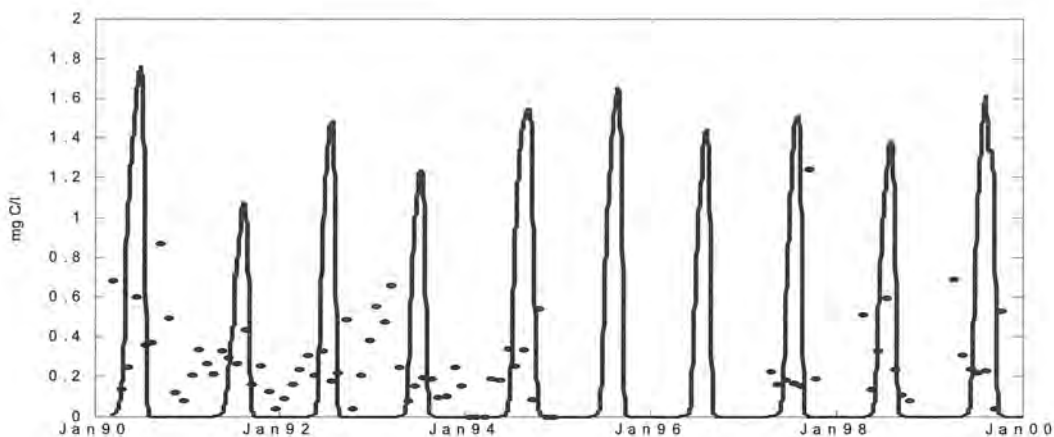
Figure 13 a-c. Phosphate in simulations with the original and the new BIOLA model. Years 1990-1999. The dots represent observations and the line the modelled concentrations. Observations were not available for 1995-1996.



a. Lake Östra Ringsjön The original BIOLA

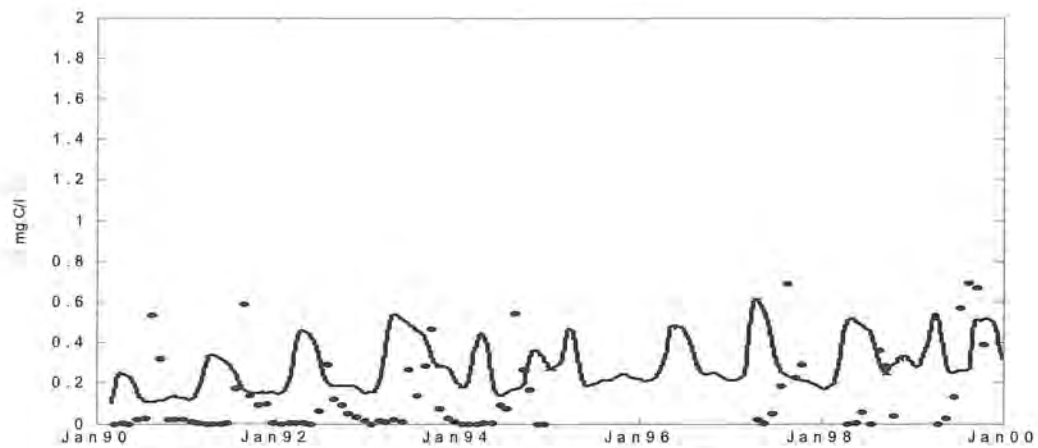


b. Lake Östra Ringsjön The new BIOLA

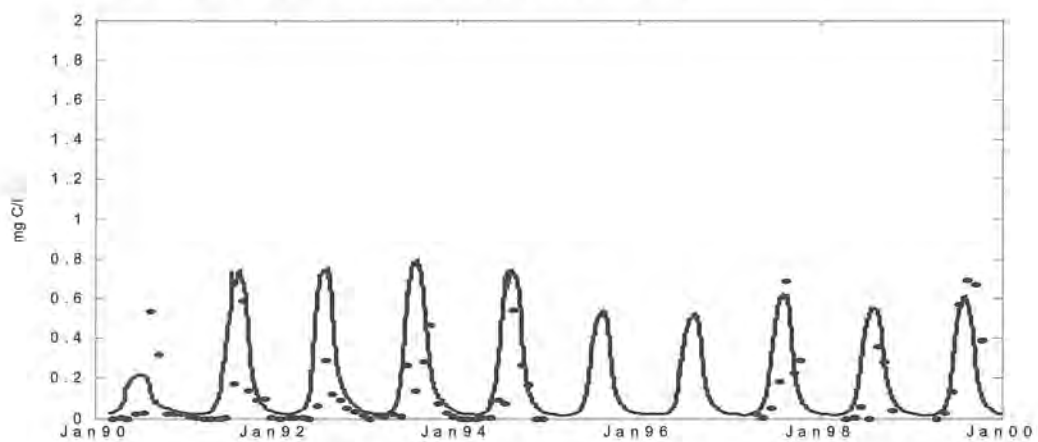


c. Lake Sätöftasjön. The new BIOLA

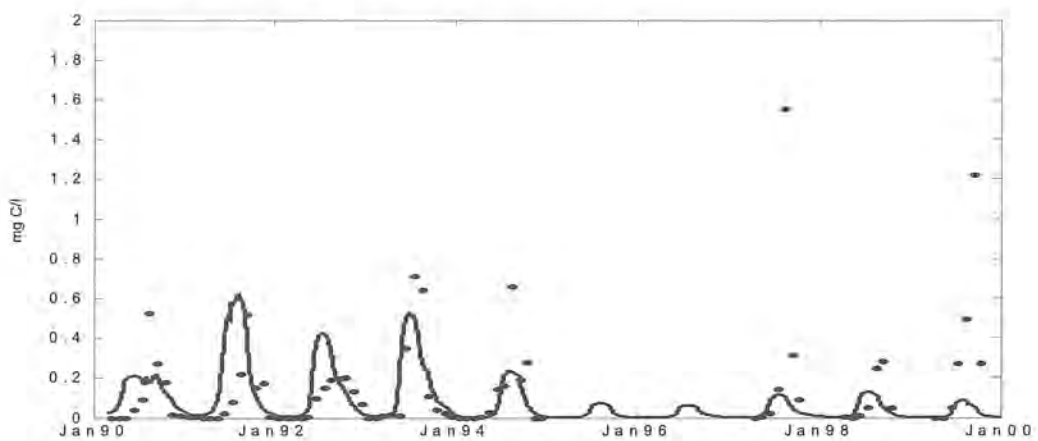
Figure 14 a-c. Phytoplankton except blue-green algae in simulations with the original and the new BIOLA model. Years 1990-1999. Observations were not available for 1995-1996. The dots represent observations and the line the modelled concentrations.



a. Lake Östra Ringsjön. The original BIOLA



b. Lake Östra Ringsjön. The new BIOLA



c. Lake Sätöftasjön. The new BIOLA

Figure 15 a-c. Blue-green algae in simulations with the original and the new BIOLA model. Years 1990-1999. Observations were not available for 1995-1996. The dots represent observations and the line the modelled concentrations.

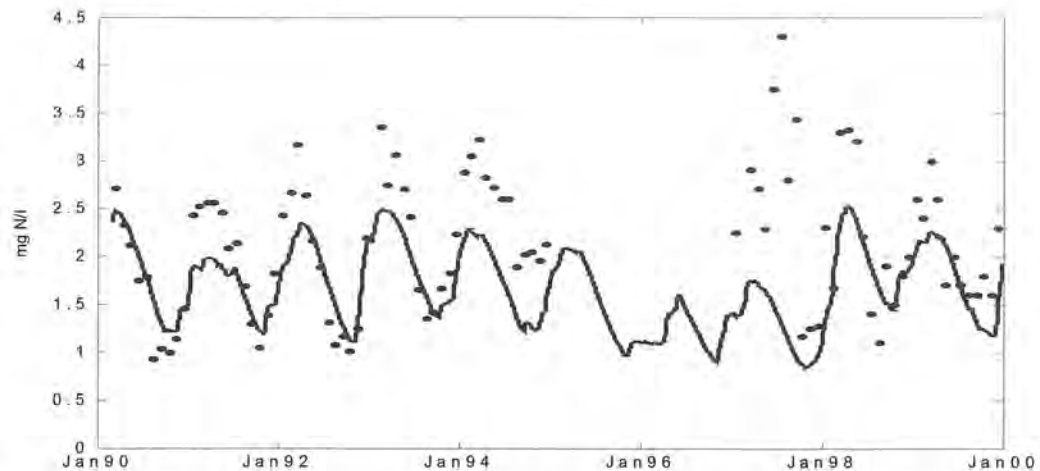


Figure 16. Total nitrogen in Lake Östra Ringsjön. The new BIOLA model. Years 1990-1999. The dots represent observations and the line the modelled concentrations. Observations were not available for 1995-1996.

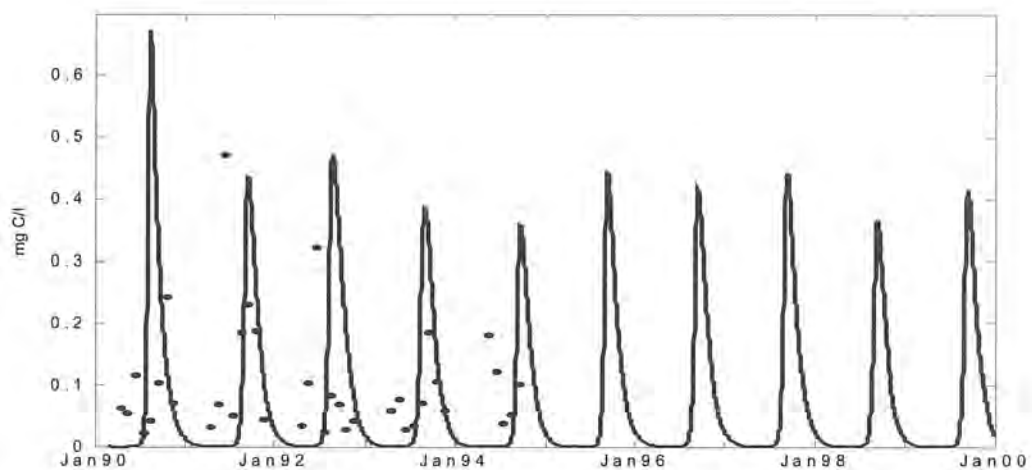


Figure 17. Zooplankton in Lake Östra Ringsjön. The new BIOLA model. Years 1990-1999. The dots represent observations and the line the modelled concentrations. Observations were not available after 1994.

3.1.2 Resuspension from erosion and transportation bottoms

The introduction of resuspension from erosion and transportation bottoms did not affect the total phosphorus modelling much. The change in sediment organic material was negligible. This could be because the amounts of organic material was low in the shallower parts of the lake compared to the deep parts. For Lake Östra Ringsjön, 25 % of the lake bottom was erosion and transportation bottoms (Table 6).

Table 6. Mean depth, area and proportion erosion and transportation bottoms. Mean depth and area from Ringsjökommittén (1991). ET-areas calculated as described in chapter "Model development" above

	Mean depth (m)	Area (km ²)	ET-areas (%)
Lake Sätöftasjön	3.0	4.2	24
Lake Östra Ringsjön	6.1	20.5	25
Lake Västra Ringsjön	3.1	14.8	38

3.1.3 Phosphorus budget

The difference between phosphorus flows out and in of Lake Östra Ringsjön and the whole Lake Ringsjön were calculated for each year (Figure 18). The differences between outflow and inflow for Lake Ringsjön and Lake Östra Ringsjön follow the same pattern; an increasing net outflow of phosphorus until 1995, thereafter a decrease with even a net retention during two years for Lake Östra Ringsjön, and last a high net outflow again during years 1998-1999. Granéli (1999) found from calculations that Lake Ringsjön acted as a phosphorus sink during the period 1990-1995, which contradicts with the model results. Calculations for 1999 (Ekologgruppen, 2000) showed that Lake Ringsjön was a net source during that year, exporting 4 tons phosphorus more to Rönne å than it achieved through tributaries. That is half of the modelled surplus export of 8 tons.

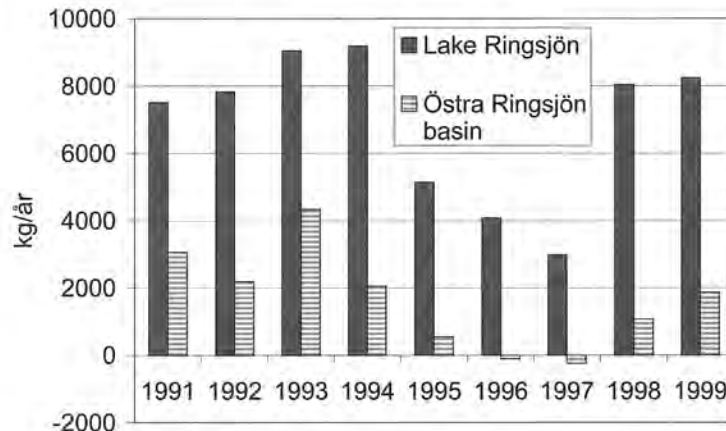


Figure 18. Difference between outflow and inflow of total phosphorus for Lake Ringsjön and Lake Östra Ringsjön. A positive value indicates that the water acts as a source of phosphorus, and a negative that it acts as a sink.

The phosphorus fluxes between the sediment layers, the free water and in- and outflows were calculated for Lake Östra Ringsjön during year 1994. The larger fluxes in are shown in Figure 19 and all the flows in Table 7. The exchange with the sediments was of the same magnitude as the in- and outflows. There was a net accumulation of phosphorus in the lower anaerobic sediment and a large artificial source of phosphorus from the denitrification in the aerobic sediment. The release through diffusion during 1994

corresponded to $1.0 \text{ mg m}^{-2} \text{ d}^{-1}$ on a yearly average, but in the summer the release reached peak values of $2.5 \text{ mg m}^{-2} \text{ d}^{-1}$ (Figure 20). The phosphorus release through diffusion from the aerobic sediment of Lake Östra Ringsjön was at its peak around July each year. This release rate is less than average for eutrophic lakes; hypereutrophic lakes can have release rates up to $50 \text{ mg m}^{-2} \text{ d}^{-1}$ (Nürnberg, 1988).

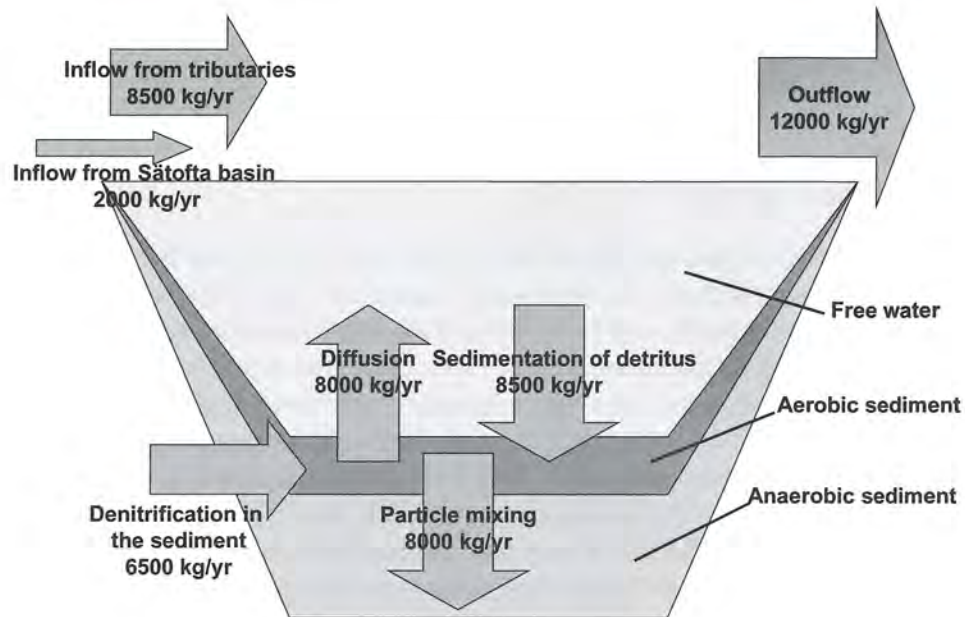


Figure 19. Budget of total phosphorus for the free water and sediment layers of Lake Östra Ringsjön in 1994. The width of the arrows corresponds to the magnitude of the flux. Only fluxes larger than 1000 kg/year are shown.

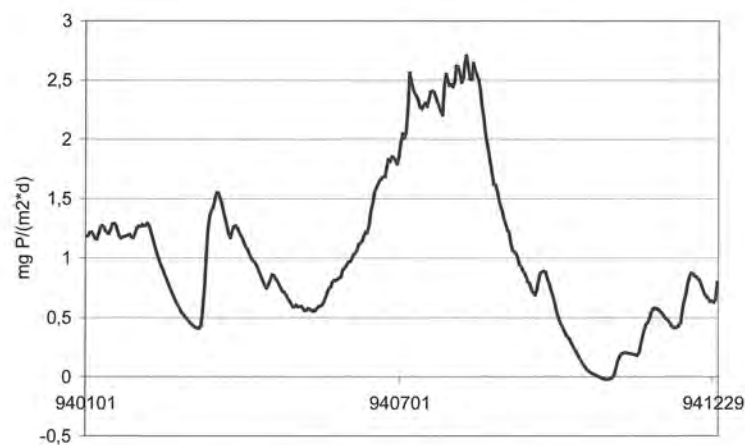


Figure 20. Release of phosphorus through diffusion from the aerobic sediment layer to the free water. Lake Östra Ringsjön during 1994.

Table 7. Fluxes of total phosphorus in and out of the free water and the sediment layers for Lake Östra Ringsjön during the year 1994

Free water			Aerobic sediment			Anaerobic sediment		
Process	Source (kg)	Sink (kg)	Process	Source (kg)	Sink (kg)	Process	Source (kg)	Sink (kg)
Inflow from Lake Sätöfåsjön	2146							
Inflow from tributaries	8647							
Outflow		11767	Particle mixing to anaerobic sediment		7906	Particle mixing from aerobic sediment	7906	
Atmospheric deposition	13		Diffusion from the anaerobic sediment	7		Diffusion to the aerobic sediment		7
Diffusion from aerobic sediment	7854		Diffusion to the free water		7854			
Macrophyte uptake from anaerobic sediment	367					Macrophyte uptake		367
Material advected by erosion	709		Material advected by erosion		709	Sequestering		0
Sedimentation of phytoplankton except blue-greens		12	Sedimentation of phytoplankton except blue-greens	12				
Sedimentation of detritus		8483	Sedimentation of detritus	8483				
Sedimentation of blue-greens		0	Sedimentation of blue-greens	0				
Macrophyte mortality		367	Macrophyte mortality	367				
Denitrification in the water	0		Denitrification in the sediment	6632				
Sum	19737	20629		15501	16470		7906	374
Net	-892			-968			+7532	

The amounts of phosphorus of the different state variables in Lake Östra Ringsjön on one summer and one winter day in 1994 are shown in Figure 21. The largest phosphorus pools were organic and inorganic phosphorus in the anaerobic layer. Sediment organic matter was accumulated in the winter. Dissolved phosphate in the free water was the third largest pool.

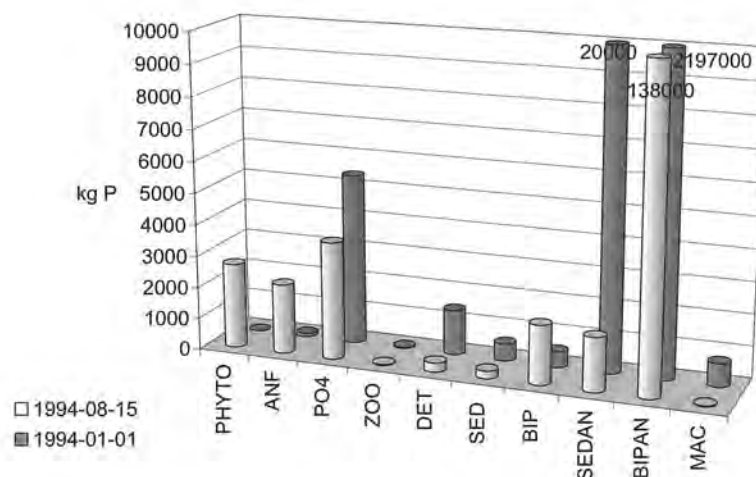


Figure 21. Modelled pools of phosphorus in Lake Östra Ringsjön 1994-01-01 and 1994-08-15. Note that the three largest pools are beyond the scale.

3.1.4 Oxygen concentration in bottom waters

Oxygen concentrations never reached below 6 mg l⁻¹ in Lake Östra Ringsjön (Figure 22). In Lake Sätöftasjön the concentrations were never below 5 mg l⁻¹, but in Västra Ringsjön, the oxygen levels reached below 1 mg l⁻¹ in July 1991 and July 1990. When compared to observations of oxygen concentrations during summer 1999, the simulations did not reproduce the real conditions very well (Figure 23). The high concentrations in the summer 1991 come from oxygen production by a very high macrophyte photosynthesis rate. In August, the oxycline was too deep and too weak compared to observed data.

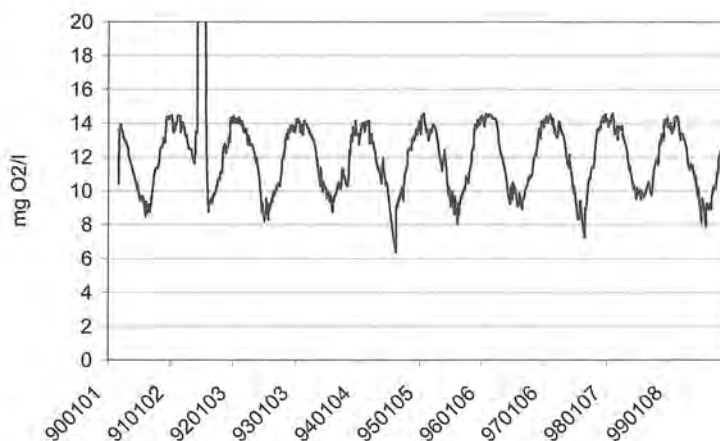


Figure 22. Oxygen concentrations in the deepest water in Lake Östra Ringsjön. The peak out of the scale reached 56 mg l⁻¹.

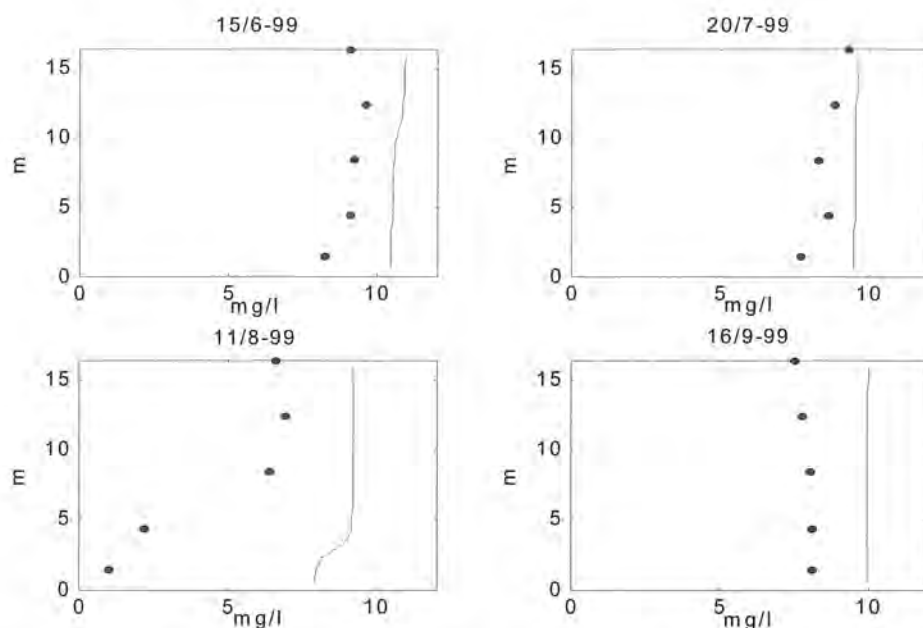


Figure 23. Oxygen concentration profiles on four days during the summer 1999 in Lake Östra Ringsjön. On the ordinate the height from the bottom and on the abscissa the oxygen concentration. The dots represent the observed concentrations and the line the simulated concentrations.

3.1.5 20 years simulation with increased or decreased nutrient load

The model was run for 20-year period; the meteorological and flow data was simply copied, so that the model went twice through the same meteorological and hydrological conditions of years 1990-1999. The concentration data was changed though, so that the first 10 years period was as normal, but then the concentrations were either doubled or halved, to mimic a sudden increase or decrease in nutrient load. Both nitrogen and phosphorus inflow concentrations were changed (Figure 24-25). The effect of changed external load was mainly on the phosphate and thus total phosphorus, and on total nitrogen. Phytoplankton were less affected. The model responded quickly; after about four years a new equilibrium was reached.

3.1.6 Decreased particle mixing velocity

Late during the work, it was found that a decrease in the particle mixing velocity resulted in all state variables being stable, i. e. no drifting. The particle mixing velocity was decreased by a factor 100 to $0.000012 \text{ m d}^{-1}$. The sinking velocity of detritus was increased by a factor 10 to 1.2 m d^{-1} to compensate for too high total phosphorus levels. The total phosphorus got sharper peaks, which is an improvement. The phytoplankton were hardly affected (Figure 26). In future use of the sediment module, it is recommended to run it with the lower particle mixing velocity, w .

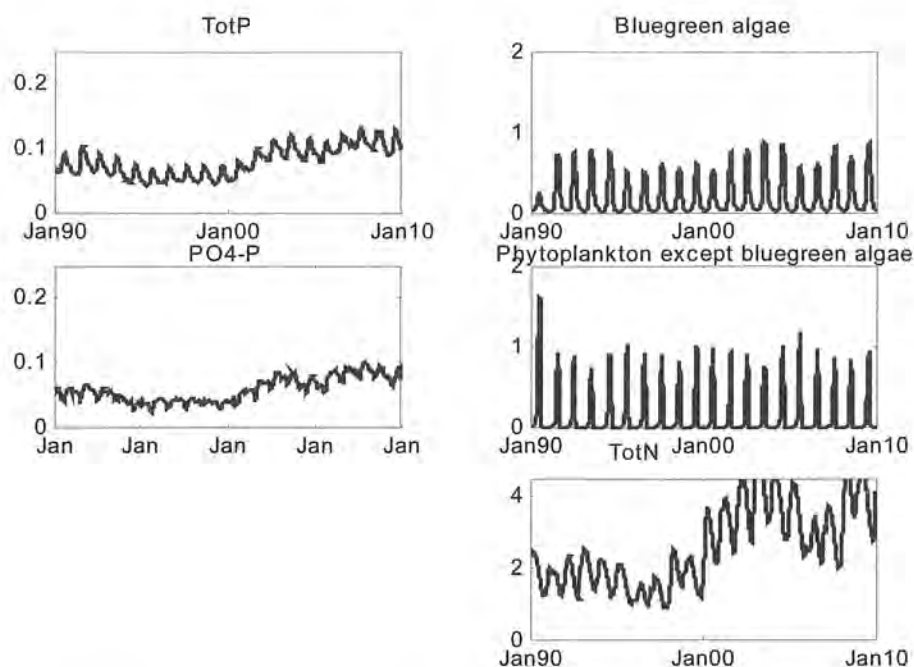


Figure 24. Simulated values of some state variables in a 20 years model run, where the inflow concentrations were doubled after 10 years. Total phosphorus and phosphate are in units mg P l^{-1} , total nitrogen in mg N l^{-1} , and phytoplankton and zooplankton in mg C l^{-1} .

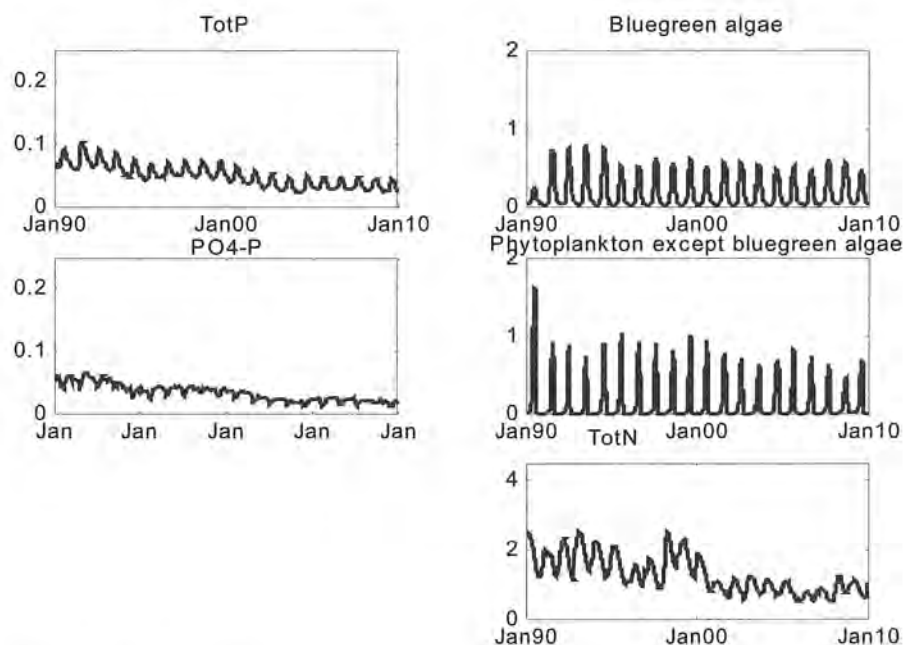
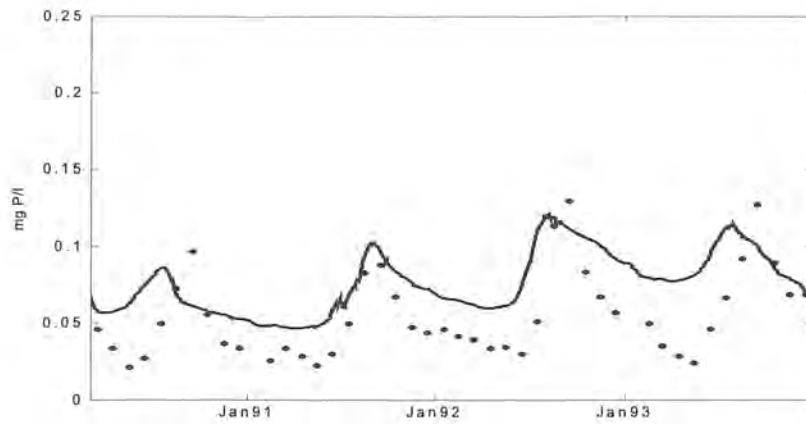
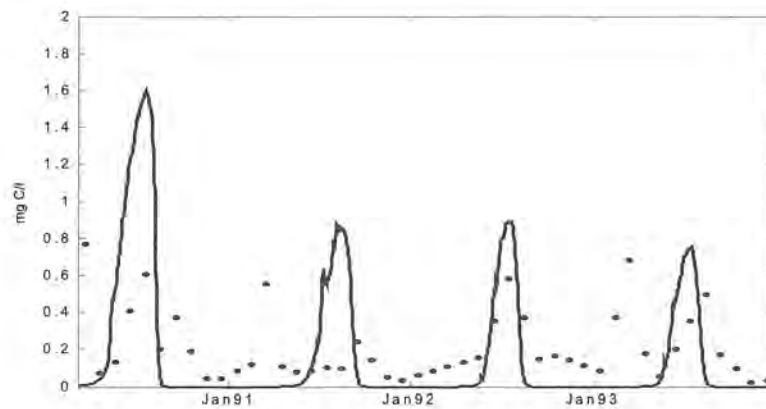


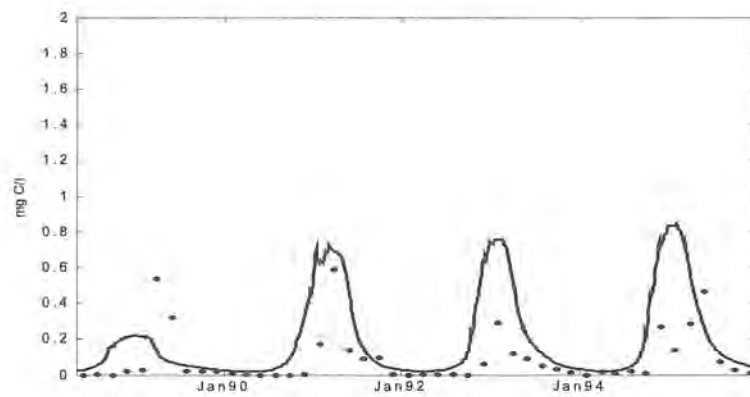
Figure 25. Simulated values of some state variables in a 20 years model run, where the inflow concentrations were halved after 10 years. Total phosphorus and phosphate are in units mg P l^{-1} , total nitrogen in mg N l^{-1} , and phytoplankton and zooplankton in mg C l^{-1} .



a. Total phosphorus



b. Phytoplankton except blue-green algae



c. Blue-green algae

Figure 26 a-c. Calibration results with decreased particle mixing velocity. Lake Östra Ringsjön, years 1990-1993. The dots represent observations and the line the modelled concentrations.

3.2 Miscellaneous tests of the BIOLA model

The model was run with the timestep 5 minutes instead of 10 minutes. The changes in state variables were less than 1 %, so the timestep does not need to be shorter.

The model was run with and without resuspension from erosion and transport bottoms, but the change in sediment organic material was negligible. This could be because the amount of organic material in the sediments was low, except in the deepest parts of the lake.

During the model development, different parameters were varied and the effects studied. One effect worth mentioning here is decreased total phosphorus in the free water when the diffusion coefficient for phosphorus between the upper sediment and the free water was increased.

To see the impact of errors in timing of concentrations, the total phosphorus transport out of Lake Östra Ringsjön was calculated. Average inflow through tributary Hörbyån and tributary Rönne å for period 1990-1999 were used, together with observed concentrations of Östra Ringsjön in 1999. If the total phosphorus was shifted to come one month too early, the transport was 6-20 % smaller than with the correct timing. With a three months too early phosphorus pattern, the transport was up to 28 % wrong.

The r^2 -values of correlation between simulated and observed total phosphorus concentrations in the upper two meters of Lake Östra Ringsjön were calculated for the period March 1990-December 1993. As the timing was wrong, the r^2 -value from monthly values was negative ($r^2 = -0.08$). Yearly mean total phosphorus concentrations of generated much higher r^2 -values ($r^2 = 0.91$). Yearly means do however not give any information about the dynamics.

3.3 Fe:P quotients in Lake Ringsjön sediments

The method of Fe:P quotients was applied on data from Enell's (1983) investigation of Lake Ringsjön sediments in 1981-1982. If the quotient by weight is over 15, the sediments probably has a good phosphorus retention capacity (see chapter "Phosphorus sorption capacity" above). Data on the 2 upper sediment cm as well as averages for the upper 100 cm were available. Lake Sätöftasjön had a quotient close to critical. But Lake Östra Ringsjön and Lake Västra Ringsjön had a quotient below critical in the upper 2 cm, but above critical averaged over the upper 100 cm (Table 8). The two low quotients indicate that the phosphorus retention capacity of the upper 2 cm sediments in Lake Östra Östra Ringsjön and Lake Västra Ringsjön was decreased compared to the underlying layer.

Table 8. Fe:P quotient by weight. Data from Enell (1983)

Lake	Sample thickness	Fe:P-quotient mg Fe (mg P) ⁻¹
Lake Sätöftasjön	2 cm	12
Lake Sätöftasjön	100 cm	13
Lake Östra Ringsjön	2 cm	6
Lake Östra Ringsjön	100 cm	22
Lake Västra Ringsjön	2 cm	7
Lake Västra Ringsjön	100 cm	25

4. Discussion

Model simulation of total phosphorus and blue-green algae improved with the new sediment approach. Probably this was the result of the more equilibrium-driven formulation with less emphasis on redox regulation of sediment dissolved inorganic phosphorus. In fact, as the oxygen levels never reached below the critical oxygen concentration in Sätöftasjön or Lake Östra Ringsjön, there was no redox regulation in the simulations carried out in these basins. In Sätöftasjön and Lake Östra Ringsjön, no clear evidence of redox-regulated phosphorus release was observed, but it would be interesting to see what effect oxygen levels would have in the model. As the modelled amounts of dissolved phosphorus in the sediment at the most increases with a factor 2.5 when the water turns anaerobic, there could be an effect. However, during calibration the diffusion coefficient was often changed by a factor 10 or more, with only minor effects on phosphorus release.

The rather good simulation results can be seen as an indication of that it is possible to model total phosphorus and phytoplankton without a oxygen variable, only with simple diffusion between sediments and water. The bad simulation of water phosphate concentrations affected the total phosphorus concentration. If the phosphate simulation would have followed the observations well, the modelling of total phosphorus concentration might have been much improved. Maybe an improved oxygen simulation could help. There are also some constituents of the total phosphorus concentrations in lakes, which were not considered. Dissolved organic phosphorus and inorganic mineral phosphorus or phosphate sorbed on particles was not calculated. Dissolved organic phosphorus made up 10 % of the total phosphorus of Lake Ringsjön in 1999 (Ekologgruppen, 2000).

Phytoplankton except blue-green algae are supposed to have a concentration up to 0.2 mg l^{-1} during the winter in Lake Östra Ringsjön and Lake Sätöftasjön. Instead, in the modelling, they decreased to their minimum values. As this state variable was highly aggregated, supposed to represent all non-blue-green algae groups, the formulation might need to be changed to consider the properties of different algae groups at different times of the year. In winter and spring, many lakes have blooms of diatoms (phytoplankton with a silica shell) and in late summer of blue-greens, diatoms and dinoflagellates (Horne and Goldman, 1994). In Lake Ringsjön, the dominant algae group in years 1997-1999 was diatoms until July, when blue-greens also became important. But there were also phytoplankton of the groups *Chrysophyceae*, *Cryptophyceae*, *Dinophyceae* (dinoflagellates) and monads at various concentrations. The different groups have different nutrient requirements and other properties, which might call for a more detailed descriptions of processes concerning the phytoplankton state variables. Alternatively the phytoplankton could be split into a larger number of state variables, for example diatoms, blue-greens and other phytoplankton groups. As Savchuk and Wulff (1996) write, "*with highly aggregated parameters more heavy parameterizations of interactions between them are needed, and vice versa*".

When the inflow concentrations were changed in the step-response test, a new equilibrium was reached after roughly four years. Neither phytoplankton nor zooplankton were affected much compared to total phosphorus and nitrogen. This may indicate that they in the model are limited not so much by nutrients, but more by light and/or temperature. Granéli (1999) found that Lake Ringsjön did not respond with decreased algal production following a big

reduction in the nutrient load in the 1980's. For long-term runs, a simpler and more conceptual model could be more useful.

The model results were satisfactory from a qualitative point of view. But if one wants to calculate transports of total phosphorus from the lakes, the error becomes too large. The timing is critical in transport calculations. Low r^2 -values for monthly total phosphorus concentrations also suggest that the quantitative simulation still needs improvement. However, differences in average concentrations between different scenarios might give a good idea of the results of changes in inflow nutrient concentrations.

The steady state requirement was not totally fulfilled because of the accumulation of ammonium and phosphate in the anaerobic sediment layer. However, the accumulation was slow relative to the total amount of ammonium and phosphorus in the anaerobic sediment layer. This seemed to be of less importance for the model performance. In a biogeochemical model of the Baltic, Savchuk and Wulff (1996) had a similar slow accumulation of benthic nitrogen and phosphorus.

From a budget point of view, the concentrations of the state variables in the aerobic sediment layer were balanced by the internal phosphorus source resulting from the denitrification. The denitrification was assumed to use carbon from a never-ending carbon source, and through the mineralisation that comes with denitrification acted as an internal source of nitrogen and phosphorus. The formulation was introduced to give realistic denitrification rates at an earlier time during model development. This internal source, which did not correspond to a natural process, violated the mass conservation of the lake system. According to Soetart *et al.* (2000), "*Mass conservation is perhaps the most stringent principle in mathematical modelling because it assures that the results, even if not realistic, are at least consistent*".

How reliable are the results from the present BIOLA model? There was no time to carry out an uncertainty or sensitivity study during this Master Thesis work. As we do not have any uncertainty analysis, we do not know the reliability of the simulations. The model gives stable and reasonable results for the validation periods, which is an indication that the model is to some extent reliable. Many of the input parameters are not well known or have been tuned so that they are out of the empirically found range. A proper sensitivity analysis would be needed in the future, to know which parameters are critical for a good model performance.

Probably some of the introduced processes and parameters contribute more to the model uncertainty than to model simulations. The anaerobic sediment layer could probably be removed, and the organic matter be split into one slowly and one quickly degradable pool, as mentioned above. The purpose of introducing the second, anaerobic, layer was to capture slow responses of the sediments. For short-time modelling, it may be enough with just one pool of sediment organic matter. The resuspension of organic material from erosion and transportation bottoms had a very small effect on the total phosphorus simulation and could probably also be removed. For lakes shallower or more wind-exposed than Lake Östra Ringsjön, it could still be useful though. What remains, as the factor that probably improved the total phosphorus simulations, is the new diffusive transport between the sediments and the water, where phosphorus can diffuse out from the sediment at both aerobic and anaerobic conditions.

In a complex model like BIOLA, processes can compensate each other and an erroneous flow introduced by one process can be balanced by another process. The more thoroughly the different processes and state variables are checked and found to agree with

observations, the more unlikely such internal error-compensation becomes. For example are the phytoplankton regulated by temperature, light and access to nutrients in BIOLA, and though the coefficients are equal or close to empirically found coefficients, one process could still balance the other in an erroneous way.

The introduction of a second sediment layer can be questioned. It introduced many new model parameters, which are also hard to verify. Information on sediment layer depth and sediment profiles is scarce for Lake Ringsjön as for most lakes. Modelling and understanding of Lake Ringsjön would be improved if it would be possible to perform a sediment study including measurements of release rates. The depth of the aerobic sediment layer can be estimated, but how deep should the anaerobic sediment layer be? The particle mixing velocity has, as far as the author knows, not been extensively studied. However, the concept of an aerobic and an anaerobic sediment layer resembles the natural conditions. They could maybe be replaced by two pools of organic material – one quickly and one slowly degradable. According to Soetart *et al.* (2000) and Lijklema (1993), mineralisation rates are crucial for sediment modelling. The slowly degradable pool could then help to model storage and release of phosphorus over long time periods with changed trophic state.

The model did, however, give quite good simulations over a ten-year period for two different lake basins. So, despite its shortcomings, it probably gives a reasonable estimate of some of the internal processes in lakes.

4.1 Suggested Further Improvements

The further improvements, which seem likely to bear good fruit, are

- Conservation of mass
- Improved oxygen modelling
- Improved phosphate modelling
- Not let the denitrification produce phosphorus or nitrogen from the never-ending carbon source
- A decrease in the particle mixing velocity

It could also be interesting to

- Include pH-dependency of phosphorus sorption
- Include nitrate-dependency of phosphorus sorption
- Have only one sediment layer, but have two organic material state variables, one easily and one slowly degradable
- Introduce one or more additional phytoplankton groups, alternatively a more detailed description of the processes concerning phytoplankton.

4.2 Conclusions

The following general conclusions can be drawn:

- Total phosphorus modelling was improved through introduction of a new formulation of nutrient exchange with the sediment. The new formulation made phosphorus release from the sediments possible also at aerobic conditions. Modelling of blue-green algae also improved, while phosphate and dissolved oxygen were still not modelled satisfactory.
- Anaerobic conditions were never reached in modelling of Lake Östra Ringsjön and Lake Sätöftasjön. Thus the redox regulation was never used and still reasonable dynamics of total phosphorus was achieved. This suggests that total phosphorus can be modelled with reasonable results without redox regulation in these lakes.
- The model responded within about four years to step-response tests of instantly decreased or increased external load.

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Appendix A. The effect of wind speed changes on the temperature profile in Lake Östra Ringsjön

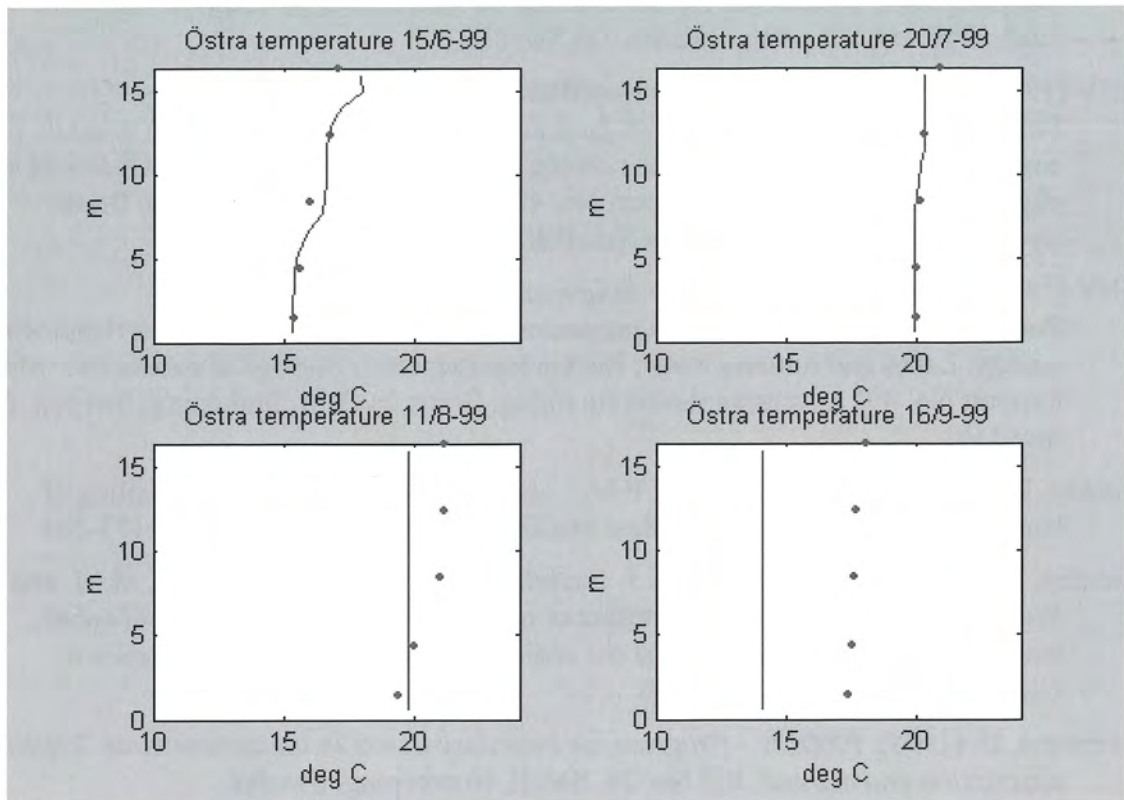


Figure 1. Unchanged wind speed.

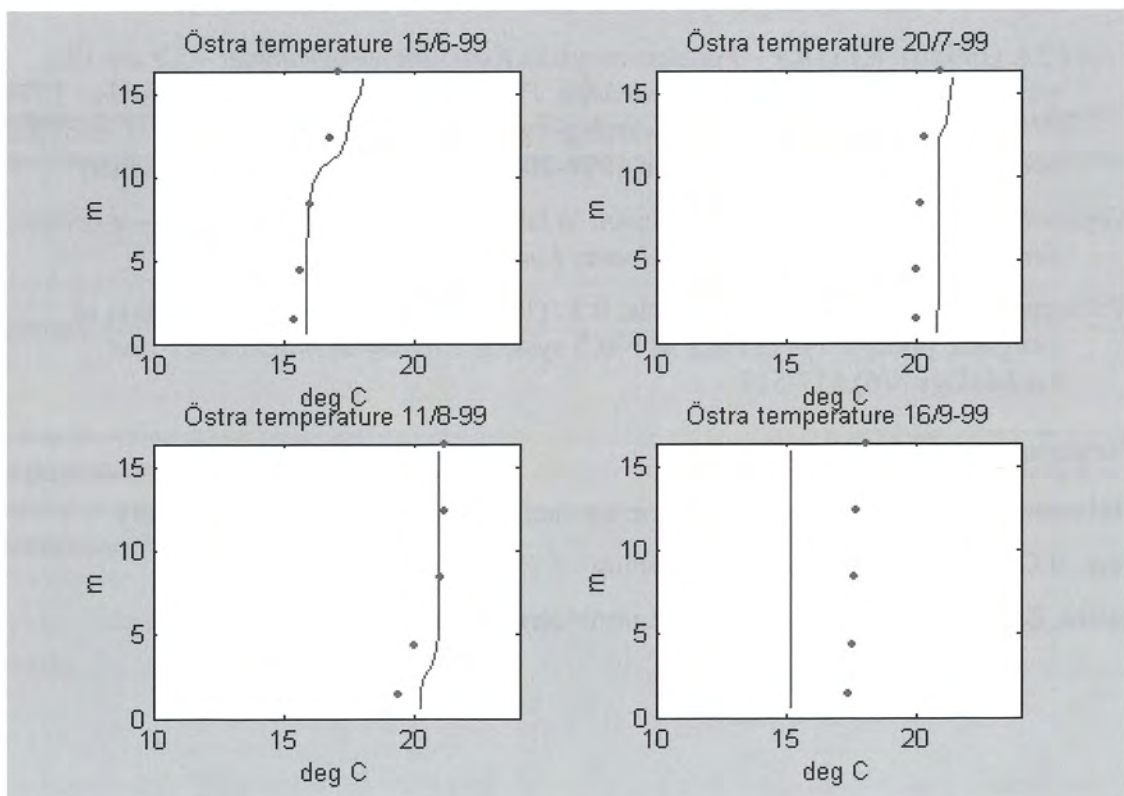


Figure 2. Wind speed multiplied by 0.84.

Appendix B. Values of new parameters, parameters changed relative the old BIOLA version and some other parameters

Symbol	Notation in BIOLA	Parameter	Value used in model	Value from references if different from the value used in the model.	Reference
A_{bottom}	AREA(I)- AREA(I-1)	Sediment area of the specific cell	Varying with depth		Determined by model setup
A_{cell}	AREA	Area of the specific cell	Varying with depth		Determined by model setup
$BIPAN_{\text{min}}$	BIPANMIN	Minimum value of inorganic phosphorus in the lower sediment	$1 \cdot 10^{-10} \text{ g m}^{-2}$		Assumed
$BNHAN_{\text{min}}$	BNHANMIN	Minimum value of ammonium in the lower sediment	$1 \cdot 10^{-10} \text{ g m}^{-2}$		Assumed
C_{NC}	CNC	Ratio between nitrogen and carbon in organic matter	$0.176 \text{ mg N (mg C)}^{-1}$		Calculated from common C:N ratios in organic material (Pers, 2002)
C_{OC}	COC	Ratio between oxygen consumption and carbon released in mineralisation of organic matter	$2.667 \text{ mg O}_2 \text{ (mg C)}^{-1}$		Calculated from common oxygen demand (Pers, 2002)
C_{PC}	CPC	Ratio between phosphorus and carbon in organic matter	$2.44 \cdot 10^{-2} \text{ mg P (mg C)}^{-1}$		Calculated from common C:P ratios in organic material (Pers, 2002)
	DANS	First guess of amount of dissolved phosphate for iteration	4.0 g P m^{-2}		Estimated from Jacobsen (1977)
Φ	-	Source term			-
ϕ	-	Sink term			-
h_{AN}	HAN	Height of the anaerobic sediment layer	0.17 m		Enell (1983) Rosenberg (1999)
h_{AR}	HAR	Height of the aerobic sediment layer	0.03 m		Enell (1983) Rosenberg (1999)

K_A	ANAKOEFF	Ratio between the aerobic and anaerobic PSC	2.5	Jacobsen, 1977
k_{diff}	KDIFF	Diffusion coefficient for transport between aerobic sediment and water	$1 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$	Tuned (Pers, 2002)
$k_{diffANA}$	KDIFFANA	Diffusion coefficient for transport between anaerobic sediment and aerobic sediment	$1 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$ Range: $(2 \cdot 10^{-4} - 2.5 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1})^a$	Tuned (Pers, 2002)
k_{diffP}	KDIFFP	Diffusion coefficient for transport of phosphorus between aerobic sediment and water	$1 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$	Tuned (Pers, 2002)
$k_{diffPAN}$	KDIFFPANA	Diffusion coefficient for transport of phosphorus between anaerobic sediment and aerobic sediment	$1 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$ Range: $(2 \cdot 10^{-4} - 2.5 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1})^a$	Tuned (Pers, 2002)
k_L	KAD	Half-saturation constant for Langmuir isotherm	0.65 g P m^{-3}	Jacobsen, 1977, Furumai and Ohgaki, 1989
k_P	KPKONST	Shading coefficient for phytoplankton and blue-green algae	$5.0 \text{ m}^2 \text{ g}^{-1}$ Range: $0.0004 - 2.26 \text{ m}^2 \text{ g}^{-1}$	Pers, 2002
k_S	SEQCON	Sequestering rate	0.0 d^{-1}	Pers, 2002
k_{sm}	MINMAX	Mineralisation rate in the aerobic sediments	0.02 d^{-1}	Pers, 2002
k_{sm}	MINMAXAN	Mineralisation rate in the anaerobic sediments	0.01 d^{-1}	^d Assumed
k_W	KW	Light extinction coefficient of the water	$1.5 \text{ m}^2 \text{ g}^{-1}$ Range: $0.0 - 1.1 \text{ m}^2 \text{ g}^{-1}$	Tuned (Pers, 2002)
O_{2crit}	OXYLIMIT	Critical oxygen concentration limit	1.0 mg l^{-1}	^b 0.1 mgL^{-1} (Boström et al 1982) and (Håkanson and Jansson, 1983)
$PSC_{aerobic}$	ADSCAP	Phosphate sorption capacity for the aerobic layer	130 g m^{-3}	Jacobsen (1977) Furumai and Ohgaki (1989)
$PSC_{anaerobic}$	ADSCAPAN	Phosphate sorption capacity for the anaerobic layer	52 g m^{-3}	Jacobsen (1977) Furumai and Ohgaki (1989)
$SEDAN_{min}$	SEDANMIN	Minimum value of organic material in the lower sediments	$1 \cdot 10^{-10} \text{ g C m}^{-2}$	Assumed

T_{ref}	TSMIN	General reference temperature	20.0 °C	Pers, 2002
T_{ref}	TSMINAN	General reference temperature	20.0 °C	Pers, 2002
θ	TETASMIN	Temperature coefficient for mineralisation in the aerobic sediments	1.5	1.07 ^c Tuned (Pers, 2002)
θ	TETASMINAN	Temperature coefficient for mineralisation in the anaerobic sediments	1.1	1.07 ^c Tuned (Pers, 2002)
w	W12	Particle mixing velocity between aerobic and anaerobic sediment layer	0.0012 m d ⁻¹	DiToro 2001
v_D	SINKD	Sinking velocity of detritus	0.12 m d ⁻¹	1.2 m d ⁻¹ ^c Tuned (Pers, 2002)
	ZMRT	Mortality coefficient for zooplankton	0.03 d ⁻¹	0.005 d ⁻¹ Tuned (Pers, 2002)
	XMRT	Mortality coefficient for blue-green algae	0.004 d ⁻¹	Tuned

- A larger diffusion than experimentally observed can be motivated because in the model diffusion is a lumped process, describing not only pure diffusion but also transport mediated by bottom organisms activities and bottom currents and turbulence
- The larger oxygen limit is here motivated because the model gives the oxygen concentration in the middle of the cell closest to the sediment, which means roughly 0.5 m above the bottom, but the concentrations close to the sediment surface can be lower than that
- Tuning in the calibration process showed better results with a different value than the reference value
- Assumed to be half the rate of the aerobic sediment layer, because the lower sediments was assumed to contain organic material that is older and less easily broken down. Anaerobic and aerobic degradation rates can be similar in marine sediments (Hulthe *et al.*, 1997), so the oxygen conditions were not considered

Appendix C. Explanations of some scientific terms

aerobic	with oxygen present as dissolved gas in the water
anaerobic	no oxygen present as dissolved gas in the water
benthic	bottom (adj)
calcareous	calcium-rich
cyprinid fish	fish belonging to the family <i>Cyprinidae</i> , carp fish
DW	dry weight
detritus	dead, particulate organic matter in the water
epilimnion	the water above the thermocline
eutrophic	high trophic state
eutrophication	the over-enrichment of receiving waters with mineral nutrients (Correll, 1998).
herbivorous	plant-eating
hypolimnion	the water below the thermocline
hypsograph	area-depth profile which shows the area at each depth
isotherm	here: relationship between sorbed and dissolved amounts of an analysed substance in a sorption-dissorption experiment
macrophyte	higher plants growing in the water
oligotrophic	low trophic state
periphyton	attached algae
phytoplankton	free-floating algae
plankton	free-floating organisms
PSC	maximum phosphorus sorption capacity; a parameter of Langmuir isotherms
resuspension	bringing settled particles back to suspension
sequestering	here used as permanent immobilisation in the sediment
sorption	the sum of adsorption and chemosorption (Boström <i>et al.</i> , 1982)
thermocline	the region of largest (vertical) change in temperature
trophic state	nutrient and productivity status, see further Horne and Goldman (1994)
WW	wet weight (fresh material)
zooplankton	free-floating animals

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