PROCESSES OF BIOGEOCHEMICAL MATTER CYCLE UNDER THE CONDITIONS OF ARTIFICIAL EUTROPHICATION

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Abstract. During the last decades a huge amount of different wastes has accumulated in the lakes in NE Estonia. In order to plan measures for improving the condition of the lakes, it is necessary to understand the mechanisms of processes taking place in the water—sediment boundary.

The experiments conducted under the conditions of artificial eutrophication (fertilizers were added to microcosms) showed the existence of different mechanisms of matter cycle. The nutrients introduced during the phase of accelerating growth become immediately involved in the process of photosynthesis. This brings about a rapid increase in the oxygen content, a decrease in water transparency, coagulation, sorption, and destruction of substances. When nutrients are added during the deceleration phase of phytoplankton growth, the nutrients, that are mainly in an inorganic form, are deposited to the bottom from where they are transported back into the euphotic zone during the stagnation and vernal isothermia.

Key words: artificial eutrophication, lake ecosystems, microcosms, biogeochemical cycle.

INTRODUCTION

Comprehensive ecological studies carried out in the Kurtna Lake District in North-East Estonia showed that the lakes (39) fall into 3 groups according to their ecological state: the lakes where natural hydrochemical conditions prevail and those where the hydrochemical conditions have altered and strongly altered. The main pollutant is SO_4^{2-}, which now exceeds the natural background level 70 times (Ilomets et al., 1991). Comparing the present situation with the data obtained by Riikoja (1940) in 1937 we find that the SO_4^{2-} concentration has since that time increased 1.6—185 times depending on the feeding regime of the lake.

The trophic structure and human impact greatly influence the trophic level of lakes and long-term and seasonal alterations in their oxygen regime. In the near-bottom water layer of several lakes a permanent oxygen deficit has formed with important changes in the biogeochemical cycles. Some of the lakes of the Kurtna Lake District have for many years been used as a natural discharge system for industrial waste waters (especially mining waters) and chemical compounds of different composition have been accumulating there (Punning et al., 1989). For the management of these polluted lakes it is necessary to know the mechanisms that influence the oxygen dynamics and its effects on metabolism at the sediment—water boundary. The microcosm approach (Cooke, 1971; Goldman,

1962; Lund, 1972; Menzel, 1977; Taub, 1976; Бурдин, 1978, 1979; Лиепа et al., 1984) may be appropriate for observing the behaviour of some chemical components (P, SO_4^{2-}, Cl^-, F^-) and the changes in the oxygen regime at different stages of induced eutrophication. The nature of the biogeochemical cycles depends on whether the nutrients are introduced during the phase of accelerating or decelerating phytoplankton growth.

METHODS

The experiments were carried out in Lake Räätsma. The lake is situated in a glacio-karstic depression in the southern part of the Kurtna Kame Field (Fig. 1). The lake is 1100 m long, with a surface of 17.5 ha, and the greatest depth of 10.8 m. Lake Räätsma is a closed lake with a very small through-flow, mainly from springs in the lake and in the littoral zone. According to Mäemets (1977) it represents the siderotrophic type of lakes, which are rare in Estonia. The water is slightly alkaline (pH 7.5—8.5), the content of mineral substances is about 100 mg·l⁻¹, and the content of organic substances is small. The concentrations of major ions are the following (mg·l⁻¹): HCO^- 43.7, SO_4^{2-} 29.1, Cl^- 3.4, Ca^{2+} 8.9, Mg^{2+} 4.5, Na^+ 1.3, K^+ 1.3 (Sagris, 1989).
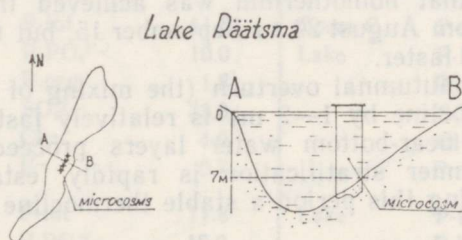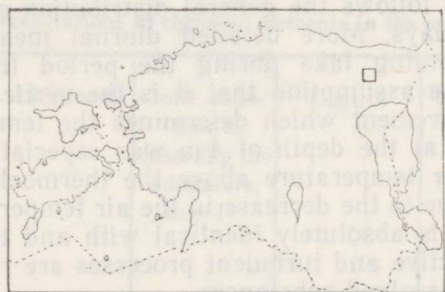

Fig. 1. Location of the Kurtna Kame Field and a scheme of the installation of the microcosms.

In 1990, polyethylene tubes (microcosms) were placed into the lake for different periods so that they would represent the whole vertical profile of the lake. Cylindrical microcosms with a diameter of 76 cm were pressed down to the sediment depth of 40—50 cm with 20 cm above the lake surface. At the experimental sites the water depth was from 7.1 to 7.6 m, so the cosms contained 3.2—3.4 m³ of water.

121

Altogether four identical microcosms were installed into Lake Räätsma during the period from February 29 to June 26, 1990. To three of these an aqueous solution of nitrodiammonium phosphate (a complex fertilizer), which contains 24% N and 32% P, was added; one tube was left as control. The measurements started 3—4 days after the installation. Water samples were analysed for temperature, inorganic and organic P, sulphate, chloride, fluoride, and oxygen at the depths of 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0 m. Sampling was done on the average twice a month, besides from August 17 to September 1 four times diurnally. The phosphate ion was determined by a colorimetric method using ascorbic acid and the solution of ammoniummolybdate, antimonyltartrate, and sulphuric acid. Total phosphorus was determined by boiling with potassium peroxide (Унифицированные методы..., 1971). The concentrations of SO_4^{2-}, Cl^-, and F^- were measured with the help of an ionchromatographic method using a conduction detector; temperature and dissolved oxygen were determined by an apparatus called Termooksümet UT-801 (Punning & Toots, 1987) equipped with a membrane electrode.

EXPERIMENTAL DATA

The basic data on the experiments are given in Table 1.

Temperature regime. The results (Fig. 2) indicate that the water temperature in the cosms follows the general distribution of the temperature in the lake in a few days. More detailed diurnal measurements in the cosms and the surrounding lake during the period from August 18 to September 1 verify the assumption that it is the vertical turbulence and not the horizontal movement which determines the temperature distribution. The thermocline at the depth of 4 m was especially notable during that period. The water temperature above the thermocline dropped from 20—22 °C to 17.5 °C due to the decrease in the air temperature. The annual range of temperature is absolutely identical with and typical of dimictic lakes (Fig. 2). Convective and turbulent processes are responsible for the vertical transport of dissolved substances.

The measurements in the lake in 1989—1991 and in all the cosms in 1990—1991 showed that homothermia was achieved from March 25 to April 7 and again from August 20 to September 15, but the vernal homothermia was achieved faster.

The first stage of autumnal overturn (the mixing of the upper layers and a drop of thermocline by 1—2 m) is relatively fast, but the rise of temperature in the near-bottom water layers proceeds more slowly. Accordingly the summer stratification is rapidly established, lasting 10—20 days and during this period a stable thermocline is formed at the depth of 3—4 m.

The findings of the episodic studies carried out earlier are in accordance with the present data. In 1985 homothermia was completed by April 17 and September 19.

Oxygen regime. The oxygen regime was studied in the lake and in the cosms A and C at 8 different depths during a period of 475 days with the average frequency of once a month and in addition 2—4 times diurnally from August 17 to September 1, 1990. The measurements were carried out at the same hours, during the diurnal sampling at sunrise, at noon, at sunset, and sometimes at midnight. Although there are no differences between the temperature regimes of the lake and the background cosm C, some differences can be noticed in the distribution of oxygen. In the

spring and summer of 1990 the concentration of O_2 was almost the same at all depths, but at the same time the following year the concentration of O_2 was 3—4 $mg \cdot l^{-1}$ higher above the thermocline in cosm C (control). Differences can also be observed in the 7.0-m layer, where the O_2 concentration in cosm C was $<1 mg \cdot l^{-1}$ during practically the whole experimental period, whereas the O_2 concentration in the lake increased to 6.0—8.0 $mg \cdot l^{-1}$ after the vernal homothermia.

The differences between the regimes of cosm C (control), the lake, and cosm A, to which fertilizer was added, were considerable (Fig. 3). During the first 30 days after the fertilizer was added the O_2 concentrations were smaller in the cosm A profile than in cosm C. However, from the end of March 1990 the concentration of O_2 in cosm A started to increase and reached its maximum in the beginning of May which was 4 $mg \cdot l^{-1}$ more than the concentration in cosm C. The difference was even greater in the first half of September. The decrease of O_2 concentration in the epilimnion of cosm A in winter was much faster than in cosm C and with a weaker vertical gradient. The following winter minimum was similar in both cases, the absolute O_2 content in the spring of the following year was also identical in both cosms.

Table 1

Initial concentrations of chemical elements in the microcosms

Cosm	Date of installation	Additional	Conc. at the time of inserting the admixture, $mg \cdot l^{-1}$	Control	Component	Conc. at the time of inserting the admixture to the studied cosm, $mg \cdot l^{-1}$
A	29. 02. 90	P-tot	11.8	Cosm C	P-tot	0.025
		P-PO$_4$$^{3-}$	10.0	Lake	P-PO$_4$$^{3-}$	0.005
		P-org	1.8		P-org	0.020
		SO$_4$$^{2-}$	33.0		SO$_4$$^{2-}$	26.0
		Cl$-$	4.0		Cl$-$	3.6
		F$-$	0.7		F$-$	0.15
D	06. 06. 90	P-tot	11.8	Lake	P-tot	0.01
		P-PO$_4$$^{3-}$	10.0		P-PO$_4$$^{3-}$	0.01
		P-org	1.8		P-org	0.0
		SO$_4$$^{2-}$	28.0		SO$_4$$^{2-}$	25.0
		Cl$-$	3.5		Cl$-$	3.2
		F$-$	0.3		F$-$	0.1
G	26. 06. 90	P-tot	11.8	Lake	P-tot	0.02
		P-PO$_4$$^{3-}$	11.8		P-PO$_4$$^{3-}$	0.02
		P-org	0.05		P-org	0.0
		SO$_4$$^{2-}$	34.2		SO$_4$$^{2-}$	26.0
		Cl$-$	0.8		Cl$-$	0.0
		F$-$	3.7		F$-$	3.2

spring and summer of 1990 the concentration of O_2 was almost the same at all depths but at the same time the following was the concentration of O_2 was 3—4 mg l^{-1} higher above the thermocline even O_2 concentration. Differences can also be observed in the 7.0 m layer where the O_2 concentration in mesh was <1 mg l^{-1} during practically the whole experimental period whereas the O_2 concentration in the lake increased to 60—80 mg l^{-1}. The differences between the regimes of cosm C (control) the lake and cosm A increase. When fertilizer was added (in 3) the first 0.5 m of above the thermocline even considerable (Fig. 3). During smaller quantity of zeolite than in cosm A. However, from the end of March to the beginning of O_2 in cosm A started to increase and reached its maximum in the beginning of May, which was approximately than that of cosm C and cosm C. The difference was even greater in the first half of September, the decrease of its concentration at the optimum of cosm A in which was much quicker than in cosm C and within certain cases the absolute O_2 content in the spring of the following year was also identical in both cosms.

EXPERIMENTAL DATA

The basic data on the experiments are given in Table 1.

Temperature regime. The results (Fig. 2) indicate that the water temperature in the cosms follows the general distribution of the temperature in the lake in a few days. More detailed diurnal measurements in the cosms and the surrounding lake during the period from August to September. Additional convection processes which determine the temperature distribution throughout the whole cosm especially notable during that in summer water temperature the thermocline dropped from 20—25 °C due to the decrease in air temperature. The thermal range of temperature is absolutely identical with and typical of the lakes. Convective and turbulent processes are responsible for the vertical transport of dissolved substances.
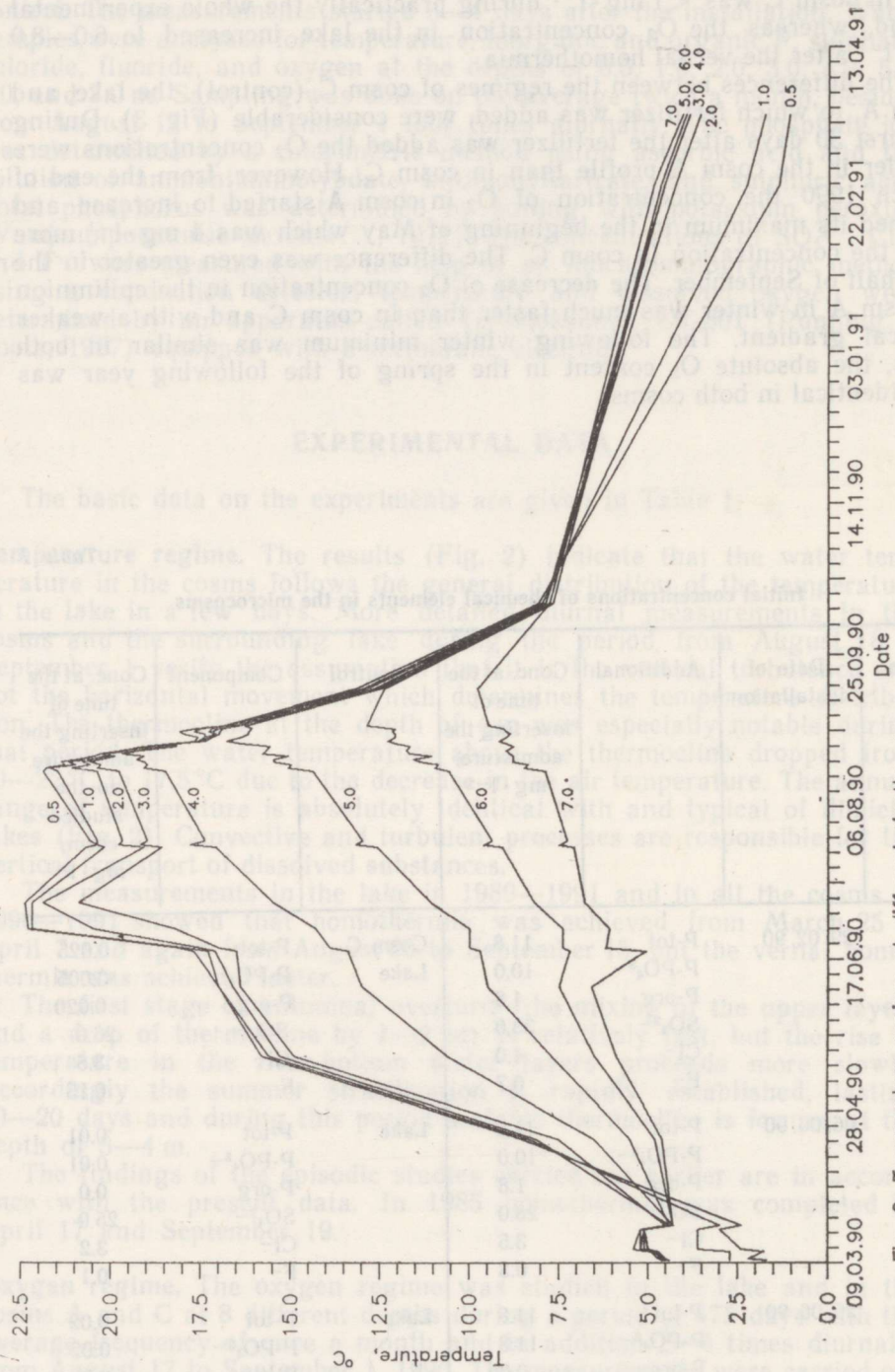

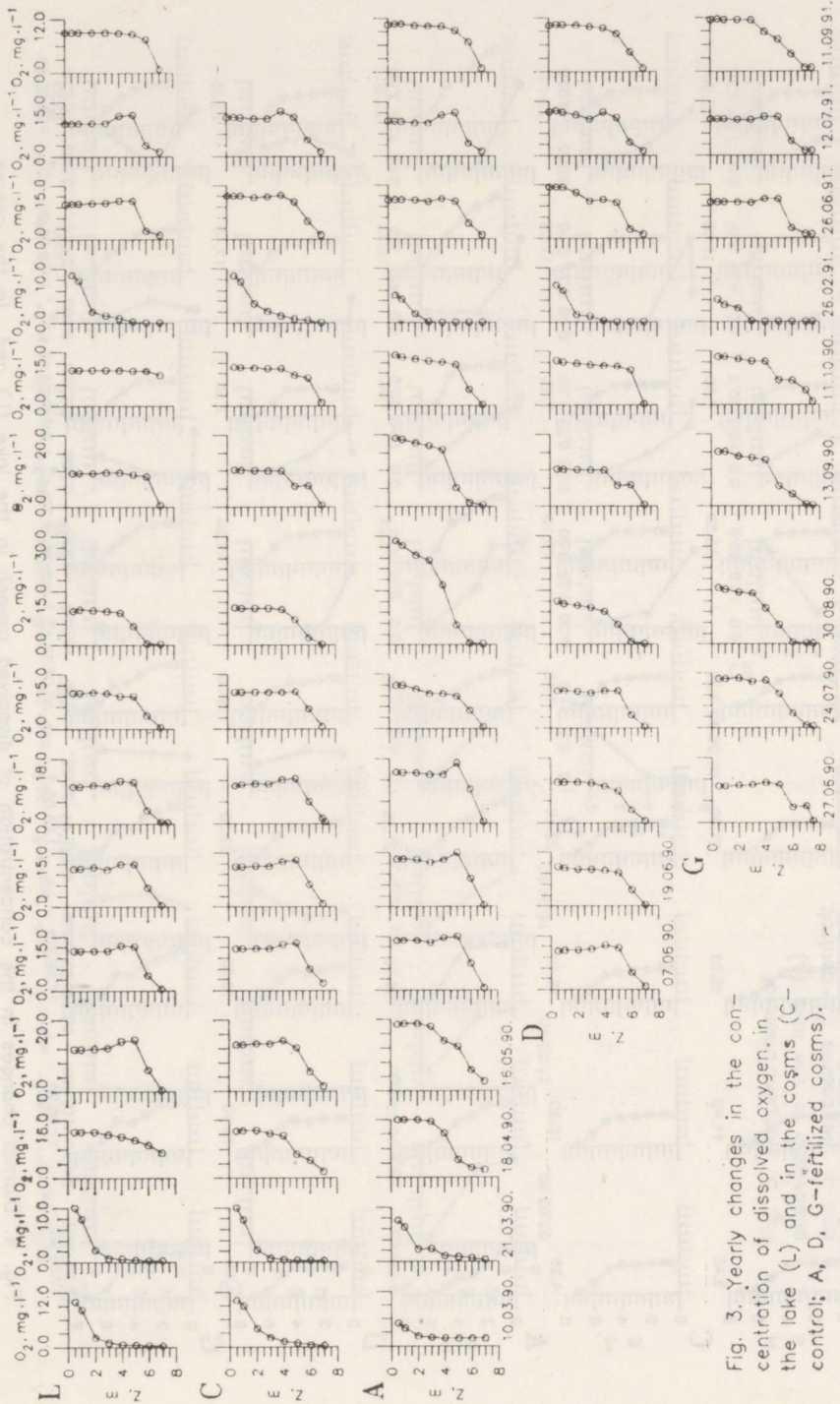Fig. 2. Temperature regime at different depths.

124

Fig. 3. Yearly changes in the concentration of dissolved oxygen, in the lake (L) and in the cosms (C—control; A, D, G—fertilized cosms).
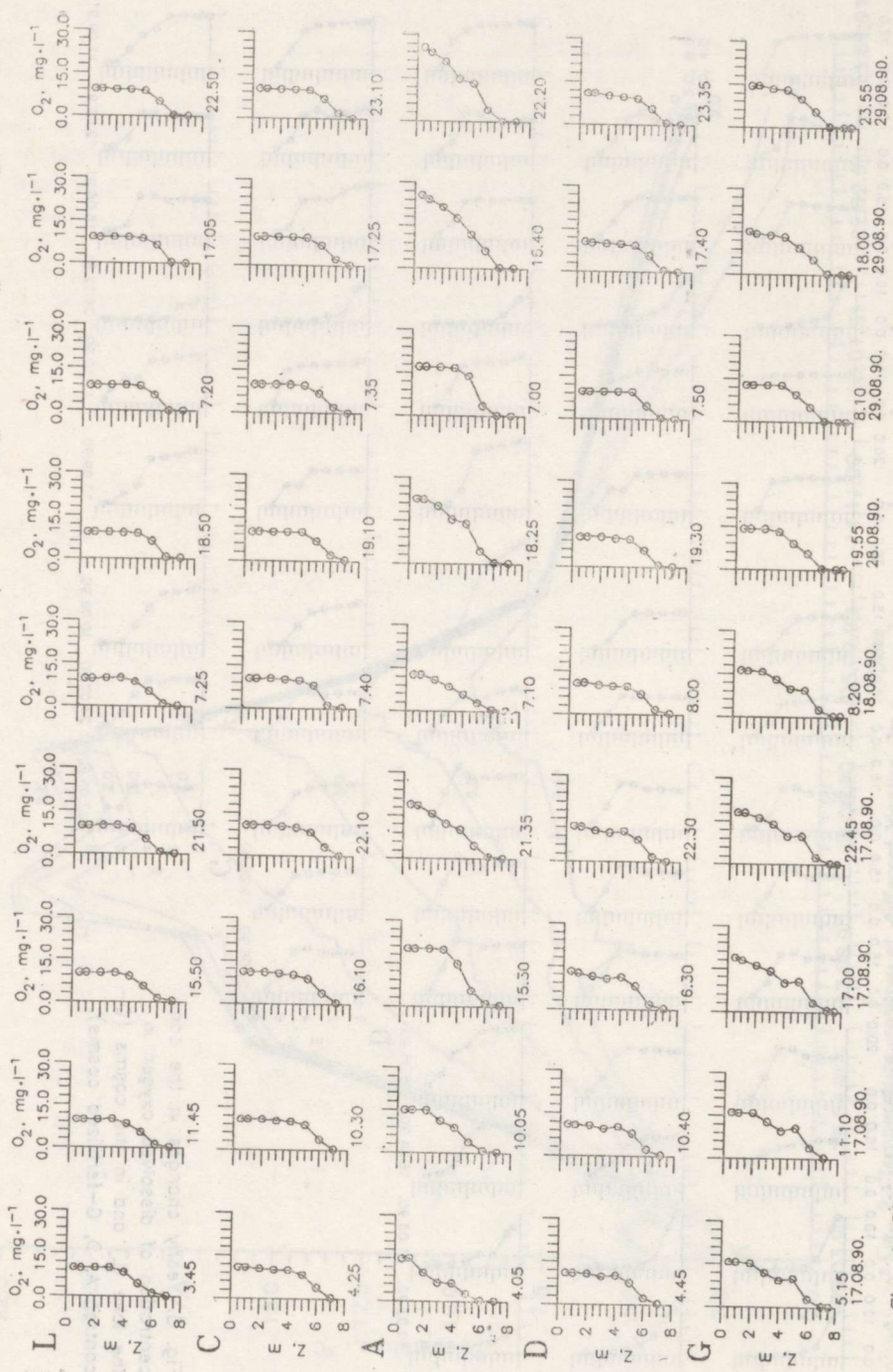
Fig. 4. Diurnal changes in the concentration of dissolved oxygen in the lake (L) and in the cosms (C–control; A, D, G–fertilized cosms)
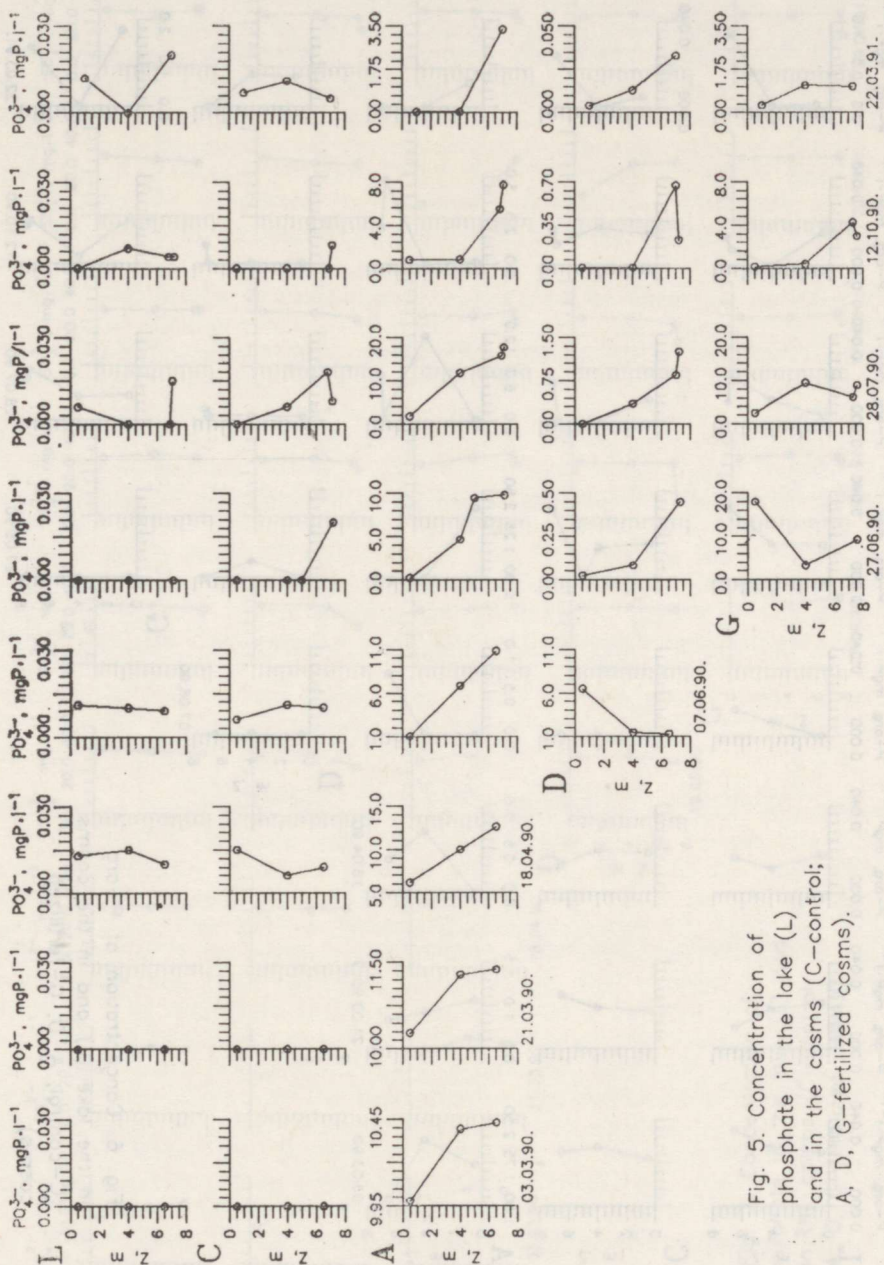
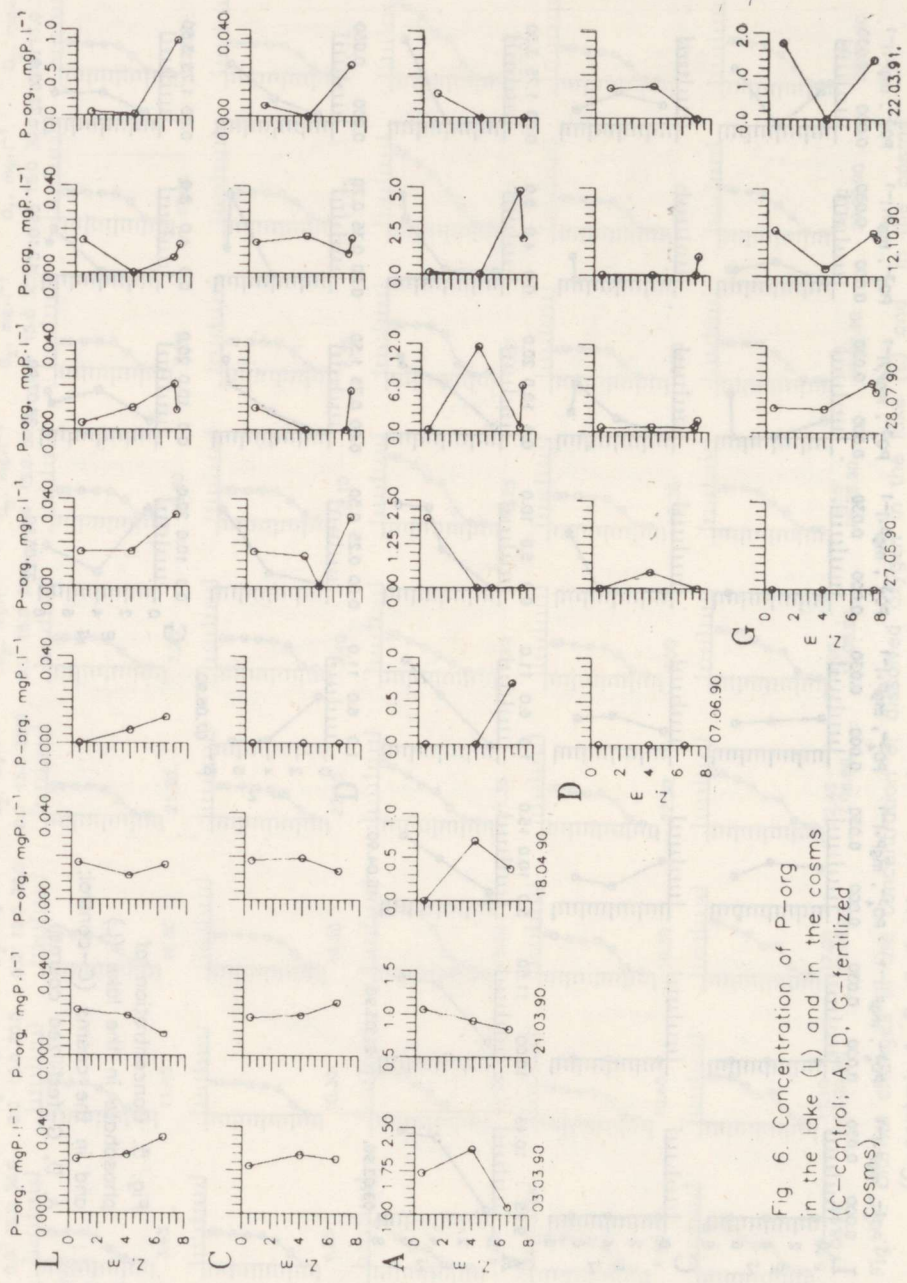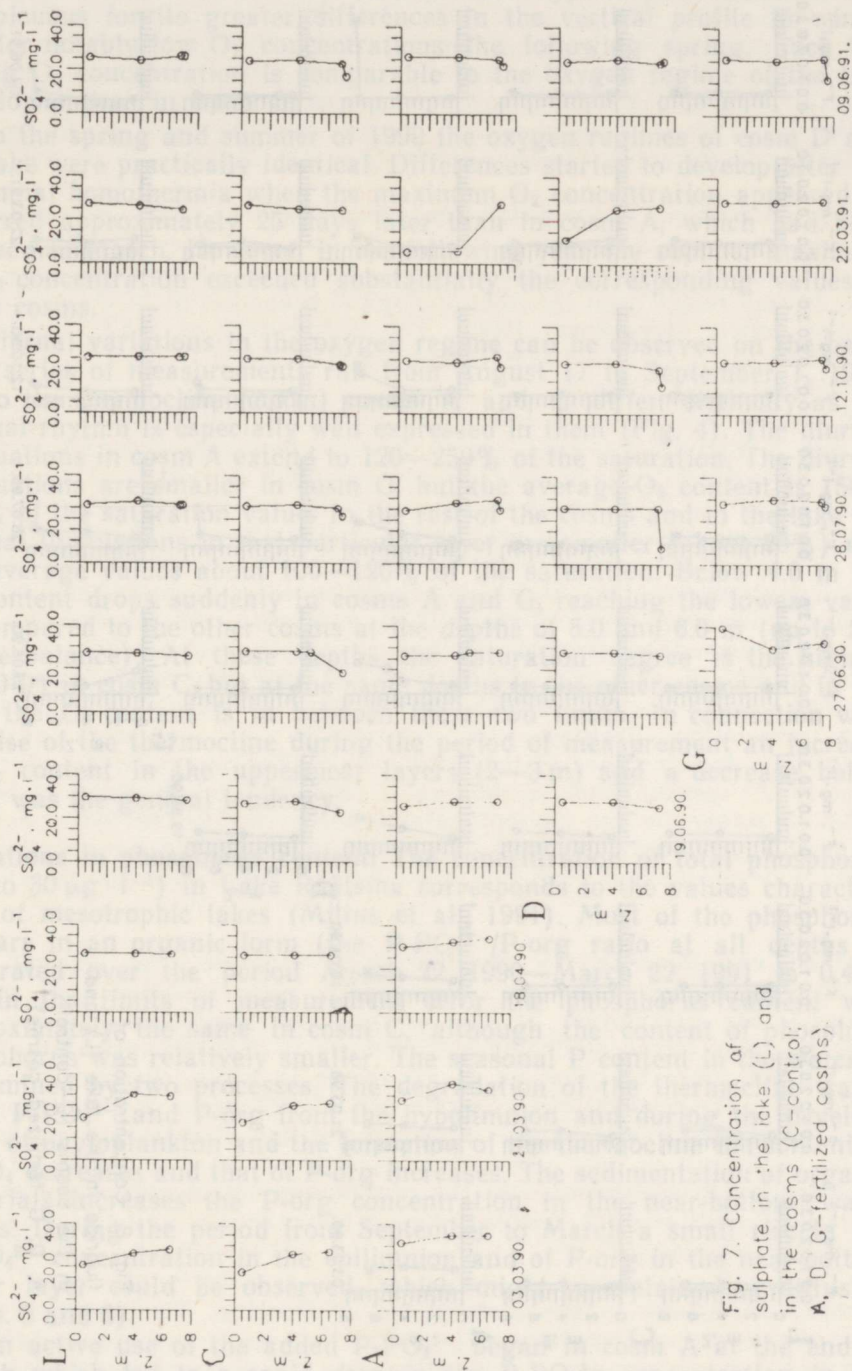Fig. 5. Concentration of phosphate in the lake (L) and in the cosms (C-control; A, D, G-fertilized cosms).

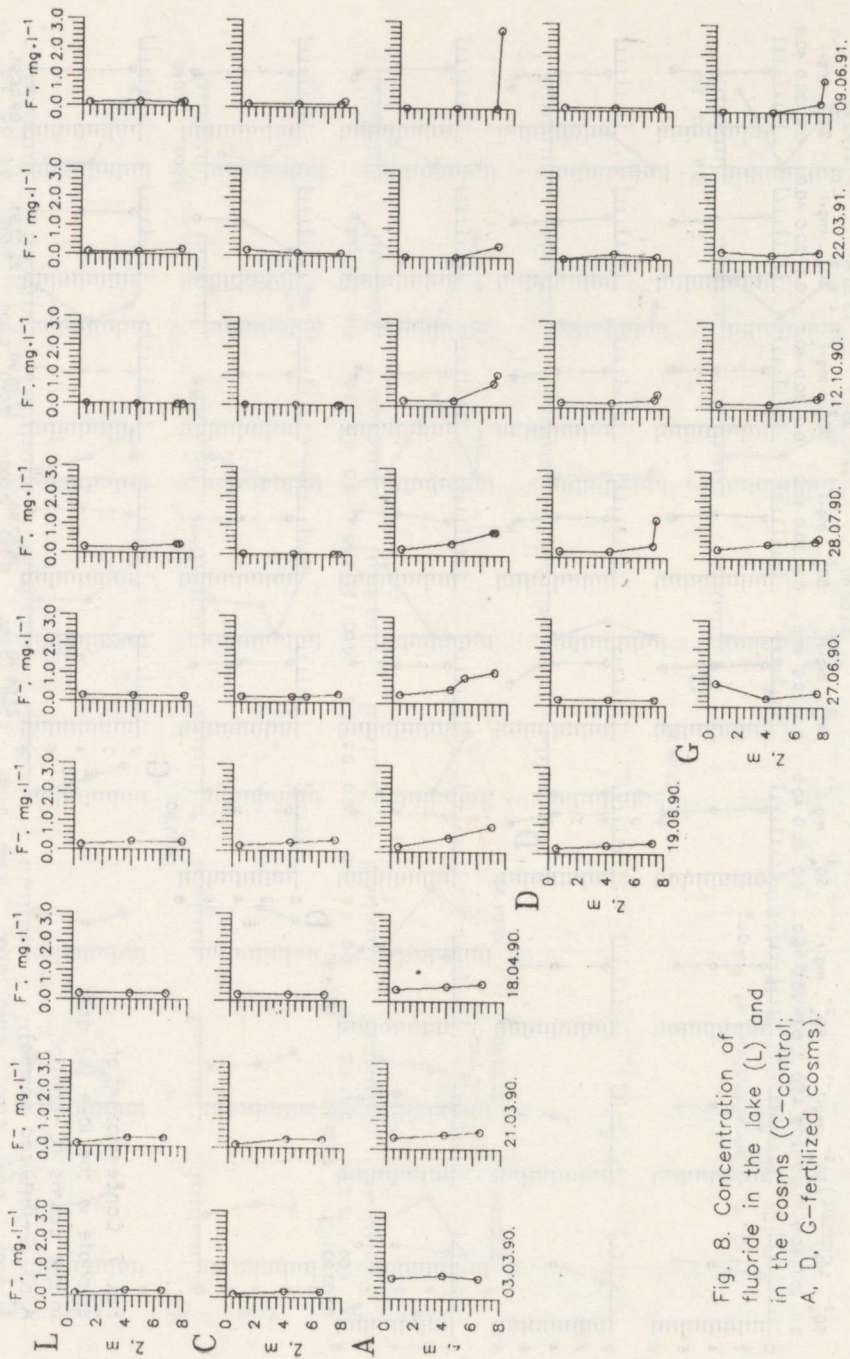Fig 6. Concentration of P—org in the lake (L) and in the cosms (C—control; A, D, G—fertilized cosms)

128

Cosms D and G were exposed respectively in the beginning and end of June (Table 1). The maxima of O_2 in cosm G, to which the same amount of nutrients was added as to cosm A, appeared in July and September. The absolute value of both maxima was approximately 3 mg·l⁻¹ smaller above the thermocline than in the hypolimnion. Cosm G was conspicuous for its angular differences in the vertical profile in under and ...

Fig. 7. Concentration of sulphate in the lake (L) and in the cosms (C-control; A, D, G-fertilized cosms).

129

Fig. 8. Concentration of fluoride in the lake (L) and in the cosms (C-control; A, D, G-fertilized cosms).

Cosms D and G were exposed respectively in the beginning and end of June (Table 1). The maxima of O_2 in cosm G, to which the same amount of nutrients was added as to cosm A, appeared in July and September. The absolute value of both maxima was approximately $3\ mg \cdot l^{-1}$ smaller above the thermocline than in the hypolimnion. Cosm G was conspicuous for its greater differences in the vertical profile in winter and for notably low O_2 concentrations the following spring. Such low spring O_2 concentration is comparable to the oxygen regime of the lake and lower than in cosm C.

In the spring and summer of 1990 the oxygen regimes of cosm D and the lake were practically identical. Differences started to develop after the autumnal homothermia when the maximum O_2 concentration appeared. It occurred approximately 25 days later than in cosm A, which had been exposed in March. However, in the following year the summer maximum of O_2 concentration exceeded substantially the corresponding values in other cosms.

Diurnal variations in the oxygen regime can be observed on the basis of a series of measurements run from August 17 to September 1, 1990. Up to the thermocline (2.0 m) cosms A and G differ distinctly as the diurnal rhythm is especially well expressed in them (Fig. 4). The diurnal fluctuations in cosm A extend to 120—250% of the saturation. The diurnal fluctuations are smaller in cosm G, but the average O_2 content is 150—200% of the saturation value. In the rest of the cosms and in the lake the diurnal fluctuations in that particular layer are smaller (about 20%) and the average values about 100—120% of the saturation. Below 4.0 m the O_2 content drops suddenly in cosms A and G, reaching the lowest value as compared to the other cosms at the depths of 5.0 and 6.0 m (up to 5% of the balance). At these depths the saturation degree is the highest (c. 20%) in cosm C, but at the same depths in the other cosms and in the lake the O_2 content is in between these two limits. In connection with the rise of the thermocline during the period of measurement an increase in O_2 content in the uppermost layers (2—3 m) and a decrease below 6.0 m was the general tendency.

Variations in phosphorus content. The concentration of total phosphorus (up to $30\ \mu g \cdot l^{-1}$) in Lake Räätsma corresponds to the values characteristic of mesotrophic lakes (Milius et al., 1991). Most of the phosphorus appears in an organic form (the $P\text{-}PO_4^{3-}$/P-org ratio at all depths as integrated over the period March 22, 1990—March 22, 1991 is 0.45). Within the limits of measurement error the phosphorus content was approximately the same in cosm C, although the content of phosphate phosphorus was relatively smaller. The seasonal P content in the water is determined by two processes. The degradation of the thermocline transports $P\text{-}PO_4^{3-}$ and P-org from the hypolimnion and during the development of phytoplankton and the formation of the thermocline the content of $P\text{-}PO_4$ decreases and that of P-org increases. The sedimentation of organic materials increases the P-org concentration in the near-bottom water layers. During the period from September to March a small rise in the $P\text{-}PO_4^{3-}$ concentration in the epilimnion and of P-org in the near-bottom water layer could be observed, which might be explained by diffusion (Figs. 5 and 6).

An active use of the added $P\text{-}PO_4^{3-}$ began in cosm A at the end of March which led to a rapid drop in the $P\text{-}PO_4^{3-}$ concentration in the epilimnion (from $12\ mg \cdot l^{-1}$ in March down to $0.01\ mg \cdot l^{-1}$ in June). Below the thermocline the concentration of $P\text{-}PO_4^{3-}$ was relatively stable until July. Thereafter the amount of total P increased rapidly and the role of organic P gained importance in deeper layers. The growth of the

amount of P near the bottom due to sedimentation was synchronous with the increase of O_2. The changes in the concentration of P compounds in cosms D and G were similar. From cosm D, to which nutrients had been added in the early spring, the phosphate was removed within a short period of time (10—20 days) during the phase of the decelerating growth of phytoplankton. There the amount of P-org was quite insignificant so that the concentration in the epilimnion during the total homothermia did not exceed $0.5 \, mg \cdot l^{-1}$ (the corresponding value in cosm A is over $5 \, mg \cdot l^{-1}$, in cosm G $3.5 \, mg \cdot l^{-1}$). The decrease of $P-PO_4^{3-}$ concentration in the upper layer of cosm G was slower, after 20 days the P-org concentration in the whole vertical profile was $3.0—6.0 \, mg \cdot l^{-1}$.

Seasonal variations in the distribution of sulphate. According to our earlier studies (Punning & Punning, 1987) in winter the concentration of the sulphate ion is lower in the near-bottom water layers than near the surface. It may result from the microbiological reduction of SO_4^{2-} caused by oxygen deficit (Jørgensen, 1990). The distribution of SO_4^{2-} was quite similar at all depths in Lake Räätsma and in cosm C during the whole observation period (Fig. 7).

Comparison of cosm C with cosm A revealed substantial differences. In cosm A the high concentration of oxygen was accompanied by a steady decrease in SO_4^{2-} content. In the winter of 1991 the SO_4^{2-} concentration in the upper 4 m layer was 5 times smaller than in cosm C. However, the corresponding values in the near-bottom water did not differ. In cosms D and G, to which the nutrients were added after the most intensive growth of phytoplankton, the SO_4^{2-} concentrations decreased substantially (especially in cosm G) until the autumn overturn. From then on the concentration increased (except in the epilimnion of cosm D), but in the spring of 1991 it was still lower than in the beginning of the experiment. The curves of the vertical distribution of SO_4^{2-} in Fig. 7 show that there is a correlation between the distribution of sulphates and O_2 production: the increase of the latter is simultaneous with the decrease of the SO_4^{2-} concentration in the upper layers which indicates that SO_4^{2-} might be sorbed by the phytoplankton and carried to the lower part of the profile. A sudden drop in SO_4^{2-} concentration in the near-bottom layers was observed during the midsummer stratification period and in winter.

Seasonal variations in the distribution of chlorine. The vertical and temporal variations in the lake and cosm C were identical and rather similar to the distribution of the sulphate ion. Analogically with the sulphate ion a temporal downward decrease in the concentration of the chloride ion could be observed in all cosms to which the fertilizer had been added. The removal of Cl^- was especially intensive during the active blooming of the phytoplankton (in the second half of May in cosm A and in the beginning of July in cosm G). The vertical distribution of Cl^- concentration demonstrates that the compounds bound with Cl^- are not stable—the profiles were smeared during homothermia and the declining phase of phytoplankton.

Seasonal variations in the distribution of fluorine. The temporal and spatial behaviour of fluorides (Fig. 8) is in many ways the same as described above in connection with other ions. The F-concentration became homogeneous in the vertical profile in the lake and cosm C soon after they were exposed. As the concentration was small ($0.15 \, mg \cdot l^{-1}$), the fluctuations during the vegetation period fell within the limits of a measurement error. The removal of practically all F^- from the vertical

column was typical of all cases. The initial distribution was reestablished by the next spring. The distribution of F⁻ in the cosms to which nutrients had been added was significantly different from the control. Analogously to Cl⁻ distribution the redistribution of fluorides occurred in the vertical profile. This process was concurrent with a rise of the concentration in deeper layers during the period of active photosynthesis (cosms A and G) and a decrease in all layers during the following autumn and winter.

The analysis of the curves of the vertical distribution (Fig. 8) demonstrates that F⁻ is removed from the water by the organic material that is being deposited; therefore F⁻ is more bound with the sediments than Cl⁻ is. Probably F⁻ is also transported as a difficult-to-dissolve compound CaF_2 since the concentrations in the near-bottom water layer were also smaller in the end of March 1991 than in the end of 1990 (in case of cosms enriched with fertilizers the addition of an extra 0.3—0.6 $mg \cdot l^{-1}$ of F⁻ should be taken into account (cf. Table 1).

DISCUSSION

The seasonal variations in the distribution of oxygen and anions in the microcosms with different concentrations of nutrients and in the lake enable us to draw the following conclusions about the biogeochemical processes during different seasons.

The diurnal measurements of the O_2 content and water transparency revealed a close correlation between these parameters (Fig. 9). This allows to consider the O_2 content as a satisfactory integral indicator of the state of a lake. Assuming that photosynthesis proceeds basically above the layer where transparency can be measured, some conclusions can be drawn about the production and utilization (respiration and destruction of organic matter) of O_2 during the given period (Table 2).
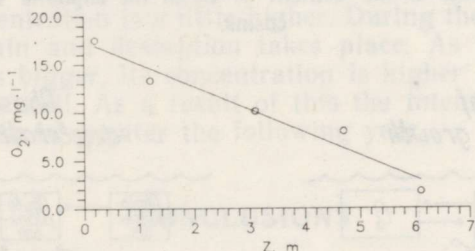

Fig. 9. O_2 content and the transparency of water.

Table 2

Consumption of oxygen in the lake and cosms with different amounts of nutrients
(September 1, 1990)

Object (cf. Table 1)	Transparency of water, m	Consumption of oxygen, $\mu g \cdot l^{-1} \cdot min^{-1}$		BEL / EL
		In the euphotic layer (EL)	Below the EL (BEL)	
Lake	4.7	1.3	0.2	0.15
C	6.1	1.1	0.2	0.18
A	0.2	3.9	22.1	5.67
D	3.1	3.8	0.4	0.11
G	1.2	4.1	1.3	0.32

The curves of the alterations of the O_2 content presented in Fig. 10 indicate that the most clearly expressed periods of active photosynthesis were the second half of April and the autumn of 1990; these were probably due to an influx of nutrients from bottom layers during homothermia.

Now, using all these data on the changes of the O_2 content and the distribution of SO_4^{2-}, F^-, Cl^-, $P-PO_4^{3-}$, and P-org concentrations in the vertical profiles in the different microcosms and Lake Räätsma during the experiment, it is possible to establish a model of the biogeochemical matter cycle. Depending on the period when the fertilizers are added, two situations may occur (Fig. 11).
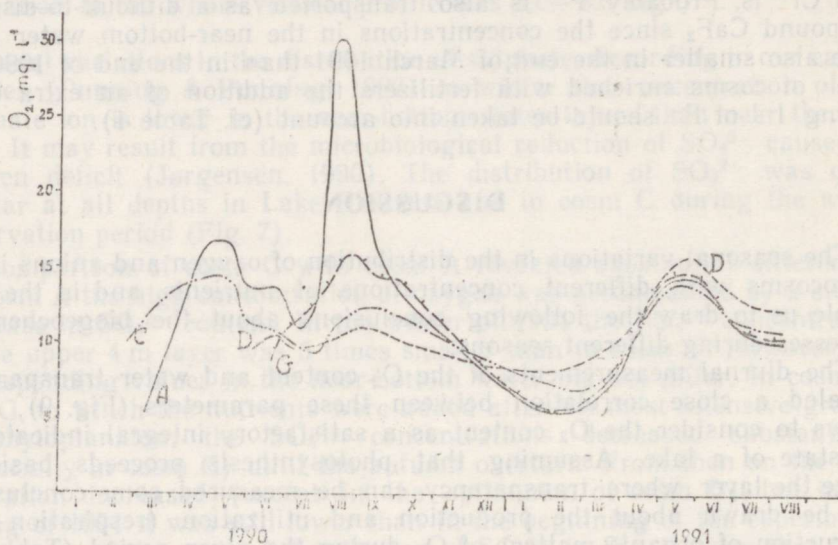

Fig. 10. Integrated values of the content of O_2 in the euphotic layer in the different cosms.
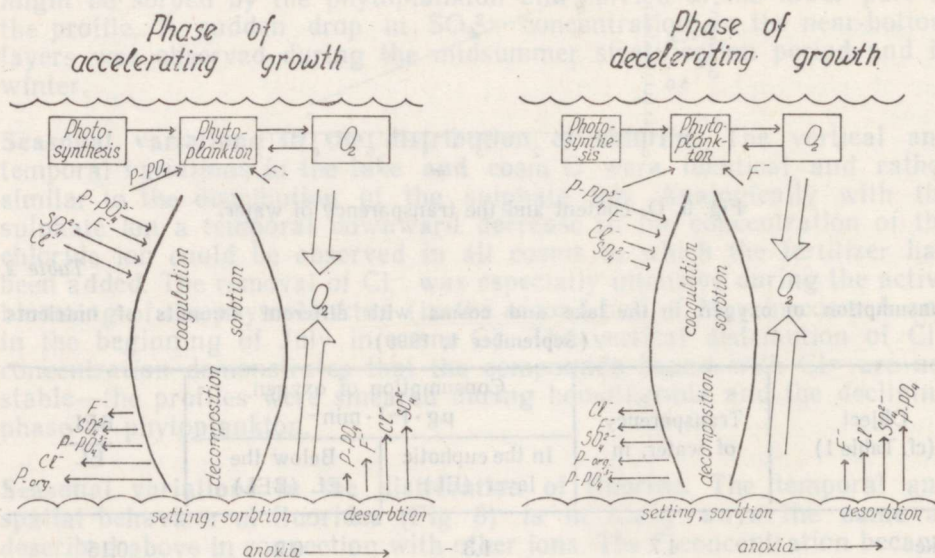

Fig. 11. Scheme of biogeochemical processes in the microcosms depending on the phase of the addition of the nutrients. The length of arrows indicates the intensity of the processes.

134

1. In case of an active process of phytoplankton blooming the $P\text{-}PO_4^{3-}$ is immediately taken up by the primary production and the content of O_2 will increase rapidly. Part of the O_2 will be utilized in the epilimnion in the process of respiration.

Simultaneously, the sinking of particles with sorbed ions and coagulation occur. In this process part of the sulphate, $P\text{-}PO_4^{3-}$, Cl^-, and F^- are transported out of the epilimnion and the concentrations in the upper part of the epilimnion decrease. As the sedimentation rate in the metalimnion decreases, the decomposition of organic matter may start. In this process $P\text{-}org$, $P\text{-}PO_4^{3-}$, SO_4^{2-}, F^-, and Cl^- will be partly released to the hypolimnion. Part of the matter will be deposited on the bottom and continue the sorption of different chemical compounds in the presence of oxygen.

During the winter stagnation the anoxia increases and desorption and reduction start in the bottom—water interface.

As most of $P\text{-}PO_4^{3-}$ was transferred into $P\text{-}org$ during the preceding blooming period and P cannot be directly used in this form in the primary production process, the situation in the ecosystem stabilizes and is comparable with the background. During the spring overturn period all the compounds are released from the bottom and transported to the upper part. The concentration of F^- decreases; probably F^- is partly used as a biophilic compound in the primary production and transformed into an insoluble form. Part of Cl^- is most likely not desorbed and SO_4^{2-} is reduced.

2. If the nutrients are added during the phase of decreasing growth of phytoplankton, $P\text{-}PO_4^{3-}$ forms insoluble Ca^-, Mg^-, and Fe^- phosphates, and they will be rapidly (in 5—10 days) transported in the particulate form out of the active zone. The principal mechanism is similar to the previous one, only the shares of different released compounds are different. The main part of $P\text{-}PO_4^{3-}$ will be deposited at the bottom and $P\text{-}org$ concentration in water will be much lower.

As the mass of organic compounds in the bottom—water interface is lower, the O_2 concentration is a little higher. During the stagnation strong anoxia occurs again and desorption takes place. As the amount of the unused $P\text{-}PO_4^{3-}$ is bigger, its concentration is higher after the following overturn period as well. As a result of this the intensity of the primary production will also be greater the following year.

CONCLUSIONS

The results of the present studies can be generalized as schemes of the matter cycles given in Fig. 11. The nutrients added during the phase of the increasing growth of phytoplankton cause a rapid increase in the O_2 content, decrease in the transparency of water, coagulation, sorption of ions, and degradation of organic matter. The O_2 content in the near-bottom water layers drops, especially during stagnation. This causes a reduction of the environment and favours the desorption of nutrients which will be transported to the upper layers next spring. Despite of their large amount the added nutrients are inactivated in the sediment and the next year the photosynthesis will be comparable with that of the lake. A principally different process is initiated when nutrients are added during the declining phase of phytoplankton growth. In this case the nutrients (mainly in inorganic form) are deposited to the bottom sediments from where they are released to the euphotic zone during the stagnation and the vernal isothermia thus starts a more intensive primary production as compared with the background.

ACKNOWLEDGEMENTS

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