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Importance of biological and abiotic factors for geochemical cycling in a freshwater eutrophic lake

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Abstract. Here we report the results of a comprehensive biogeochemical monitoring of Rostherne Mere in 1998, including changes in dissolved oxygen, organic carbon and nitrogen, nitrate/nitrite, ammonia, Al, Na, S, K, Mg, Ca, Si, Fe, Mn, orthophosphate, particulate N & P, suspended solids, temperature, pH, chlorophyll-*a* and zooplankton. The results demonstrated the major influence of primary producers on the overall geochemical cycling of N, P and Si, and suggested that the significance of zooplankton might have been previously underestimated. For major anions and cations, however, the influence of biota on lake water concentrations appeared to be negligible, reflecting the fact that these chemicals were present far in excess of plankton requirements. Thus changes in concentrations of Ca, K, Na, Mg and S were rather limited and must have reflected changes in hydrological and meteorological parameters. K, however, demonstrated a transitional pattern, reflecting some influence of biological uptake. During the stratification period, the slow processes of bacterial decomposition in the hypolimnion gradually released chemicals contained in the materials accumulated in the bottom layer, remarkably increasing the concentrations of dissolved compounds of those elements present in amounts comparable with the pool stored in the sedimenting detritus (e.g. orthophosphate P, ammonia N, Si and DOC). The decomposition also resulted in a drop in the redox potential, followed by partial denitrification and chemical release from the sediments. The hypolimnion of the Mere was confirmed to remain at the stage of Mn release, characterised by accumulation of DOC, orthophosphates, ammonia and initial stages of denitrification. High levels of P released from the sediments during the stratification period suggest that the lake's recovery after sewage diversion might be further delayed.

Introduction

Rostherne Mere, arguably, is the best-studied British freshwater lake (for maps, general description and further references see, e.g., Woof and Wall 1984; Carvalho 1993; Krivtsov et al. 1998, 2001d, 2002b). The previous studies have addressed the lake's water and nutrient budgeting (see Krivtsov et al. 2001b, 2002b and references therein), and there is an impressive long term monitoring record of the lake's planktonic community (*e.g.* Pearsall 1923; Griffiths 1925; Lind 1944; David 1963; Belhcher and Storey 1968; Reynolds and Rogers 1976; Reynolds 1978; Reynolds and Bellinger 1992; Sigee and Holland 1997; Sigee et al. 1998, 1999a, b; Krivtsov et al. 1999c, f, 2000b, 2001c, 2002) and water chemistry (*e.g.* Tatersall and Coward 1914; Gorham 1957; Grimshaw and Hudson 1970; NWWA 1983; Tipping 1984; Clay 1992; Carvalho 1993; Krivtsov 1995; Stephen 1997; Krivtsov et al. 1999a, e, 2003b; Krivtsov 2000). Enhanced by availability of a specially designed simulation mathematical model (Krivtsov et al. 1998), this background information makes the mere a suitable subject for analysis of complex interactions among various ecosystem components (*e.g.* Krivtsov et al. 1999b, d, 2000d, 2001a). These analyses are important not only for the management of Rostherne Mere itself, but may have profound implications for other temperate lakes in general (Krivtsov et al. 2000a, c), including an assessment of their history, current status, and long-term future dynamics.

Despite the wealth of accumulated data, only a few studies provided simultaneous analysis of the overall ecosystem functioning and geochemical cycling in the lake, based on comprehensive data sets including time series of chemical profiles and biota. Whilst these studies variously addressed certain aspects of the lake's biogeochemistry in greater detail, consideration of variables studied in each case was relatively (i.e. compared to the research presented here) limited. Most of these studies (Grimshaw and Hudson 1970; Davison and Woof 1984) were carried out before sewage diversion (for details of sewage diversion see Carvalho 1993) rather a long time ago, whilst the recent research (Krivtsov et al. 2001d), did not include analysis of Fe, Mn, S, Na, DOC and Al. The purpose of this paper is to provide an up to date information on the seasonal dynamics of biota and hydrochemical profiles, to analyse interrelations between the dynamics of biological community and geochemical turnover of C, P, N, Si, Ca, Mg, K, Na, S, Fe, Mn and Al, and to assess implications for long term trophic status of the mere.

Materials and methods

Lake water samples

Water samples were taken at Rostherne Mere from 1 to 3 sampling sites clearly identified by mooring buoys. The sampling interval varied between 2 and 4 weeks and was generally higher during the periods of intensive change in spring and summer. From each sampled site an integrated sample from the epilimnion was collected using a 4.5 m weighted polyethylene hose and from the deepest site samples were also taken using a deep water sampler from the following depths : 0–1, 3, 5, 7, 10, 13, 16, 19, 22, 25 m and the bottom layer (approximately 30 m). Transparency of the lake surface layer, dissolved oxygen, temperature, pH, and conductivity were determined on site using standard field equipment.

Samples for chemical analysis were taken by filling plastic sampling bottles with water from the integrated sample and from a deep water sampler. Samples of the lake surface water were taken by submerging plastic bottles directly into the sampled medium. All sampling bottles were soaked overnight in 10% hydrochloric acid and subsequently double rinsed in distilled water prior to use. On site, immediately prior to sampling, all sampling equipment was rinsed with sampled water. To prevent any possible contamination the latter procedure was carried out downwind from a sampling point.

Determinations of Chlorophyll-*a* (Chl), Suspended Solids(SS), $PO_4^{\cdot}P$, particulate P (PP), Dissolved Organic Carbon (DOC), total dissolved N (TDN), $NO_x^{\cdot}N$, $NH_4^{\cdot}N$, particulate N (PN), K, Mg, Ca, Si, Fe, Mn, Al, S, Na were made in the laboratory using the methods described below. For phytoplankton population counts subsamples of the integrated sample were immediately fixed with Lugol's iodine solution. Zooplankton samples were taken by vertical hauls using a net with a pore size of 250 μm. Zooplankton was washed off the filter into a universal tube with 70% ethanol solution.

Physical measurements

Dissolved oxygen and water temperature were determined in the field by a Phox (Phox instruments) 62TE meter. The instrument was calibrated at 0 and 100% Oxygen saturation before and after usage. pH was measured in the field by a Phox 42E meter calibrated at pH 4 and 7 or 7 and 10 (depending on the range measured) before and after usage. Conductivity (in micro-Siemens) was measured in the field by a Phox 57 meter. A Secchi disc was used in the field to determine the extent of the approximate depth of the euphotic zone. The disc attached to the measure tape was lowered from the sun-facing side of the boat through the water column until no longer seen and pulled back until just visible.

Chemical analysis

Immediately after returning to the laboratory known volumes of lake water were vacuum filtered through GF/C (pore size 1 μm) and cellulose nitrate (pore size 0.2 μm) filters. Filtrates were placed in plastic bottles pre-washed in 10% hydrochloric acid and subsequently double rinsed with distilled water. To the aliquots of filtrates intended for metal analyses using ICP (see below) 100 μl of the aristar nitric acid was added per 30 ml of filtrate. Samples were subsequently stored in a 4 degrees temperature cold room awaiting analysis. As N and P speciation is prone to fast changes in the stored samples, nutrient analyses were normally carried out during the next few days. Metal analyses, for practical reasons, were normally performed within a couple of months after the sampling date.

Digestions of filter papers for N and P were as in Mackereth et al. (1978) and American Public Health Association (1995) respectively. As a result of these digestions all forms of N and P were assumed to have been converted into nitrates and orthophosphates respectively.

Concentrations of C, N and P in the filtered lake water and in the digests of filter papers (N and P only) were measured using a Skalar mass flow autoanalyser (Skalar analytical B.V., 1993). The procedure for the nitrate/nitrite analysis was based upon that of Morris and Riley (1963). NO_3 was reduced to NO_2 in contact with copper-coated cadmium. Subsequently, NO_2 was measured by complexing with sulphanilamide and coupling with *N*-(1-naphtyl)-ethylenediamine to form a red azo-dye measured spectrophotometrically at 540 nm. Phosphate was analysed with acidified molybdate to form reduced phosphomolybdenum blue (DoE 1979–1990) and measured spectrophotometrically at 880 nm. The automated procedure for ammonia determination was based on the Berthelot reaction modified by Skalar. Ammonia was chlorinated to monochloramine which reacts with salicilate to form 5-aminosalicilate. After oxidation and oxidative coupling, the absorption of the formed green complex was measured at 660 nm. For determination of total dissolved nitrogen (TDN) the sample was mixed with a Borax buffer. After that an excess potassium persulfate was added and the mixture, heated to 97 degrees, pumped through a UV digestor. The nitrate was determined by the Griess reaction after reduction to nitrite in Cadmium Copper column. The colour was measured at 540 nm. Concentration of organic N was subsequently calculated by subtracting ammonia and nitrate/nitrite levels from TDN. For DOC determination a sample was first acidified and the inorganic carbon removed by pumping nitrogen. After addition of buffered persulfate the sample was irradiated in an UV digestion process. Then, after addition of hydrohylamine, the sample was passed through a gas permeable dialiser. The generated CO_2 diffused into a recipient stream of a weakly buffered phenolphtalein solution. The colour intensity measured at 550 nm decreases proportionally to the changes in pH caused by the absorbed CO_2.

The Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) technique was used for determinations of K, Mg, Ca, Si, Fe, Mn, Al, S and Na. Elements were detected by the HORIZON spectrometer (manufactured by VG Elemental) equipped with a concentric glass nebuliser. Elemental concentrations were calculated by Evolution software (Microactive Australia PTY LTD 1994) using a PLWater method developed by the Analytical Geochemistry Unit of Manchester University.

Suspended solids

Immediately after returning to the laboratory, known volumes of lake water were vacuum-filtered through individually pre-weighed Whatman GF/C filters. The papers were dried overnight at 105 °C (before and after filtering) to constant weight. The weight of SS per litre was calculated from the difference in filter paper weights before and after filtering.

Chlorophyll-a

Immediately after returning to the laboratory, 500 ml aliquots of the sample were filtered through Whatman GF/C filter paper, which was consequently cut into small pieces and put in a universal tube. Chlorophyll-*a* was extracted with 96% ethanol over 20 h in the dark and then measured using an ultraviolet spectrophotometer (Pye Unicam SP8-100) in supernatant after centrifugation for 10 min at 3000 rpm (Jespersen and Christoffersen 1987).

The equation below was used to calculate the Chlorophyll-*a* concentration (see Holm-Hansen and Riemann 1978):

$$\text{Chlorophyll-}a : (g/l) = (Ve * f * A)/(Vs * L)$$

Where: V_e = total volume of solvent (ml); V_s = total volume of sample (l); L = light path (1 cm); A = absorbance at 665 nm–absorbance at 750 nm; f = 1/specific extraction coefficient*1000. The specific extraction coefficient for chlorophyll_*a* in ethanol is 83.41 g^{-1} sm^{-1} (Jespersen and Christoffersen 1987).

Population counts

Phytoplankton samples

250 ml of the integrated sample fixed with Lugol's Iodine solution mixture was placed in a measuring cylinder and left undisturbed for 48 h to ensure the complete sedimentation of the preserved algae. Then the top liquid was carefully sucked up by a simple device consisting of a pump, a trap and a tube with a nozzle bent upwards (Krivtsov 1995). To make sure that no algae remained in suspension, sucked liquid was collected in a trap and subsequently examined under a light microscope. The sedimentation process was repeated when necessary.

After sucking up of the top clean water, the bottom 25 ml were placed in a 30 ml universal tube and stored in a 4 degrees temperature cold room. Population counts were made under low power light microscopy using a Sedgewick-Rafter slide in which 1 ml of sample was placed. Identification and counting of major phytoplankton species was carried out using an algal identification key (Bellinger 1992).

Zooplankton counts

Samples were stored in a cold room prior to analysis. Animals were identified and counted using Sedgwick-Rafter chamber in which 1 ml of sample was placed using a wide-bore pipette. At times with the high population counts dilutions were performed prior to microscopic examinations. It should be noted that due to a large mesh size the quantitative zooplankton data related specifically to adult crustacea, which are large enough to be caught in the net used for sampling.

Results

Changes in the variables monitored in this study are briefly detailed below. The selected hydrochemical profiles are presented as 3D graphs. The viewing properties (e.g. elevation, rotation, perspective) of the particular graphs were chosen to obtain maximum visibility of the data. This presentation of hydrochemical profiles follows the presentation adopted in our previous work (Krivtsov et al. 2001d). Significant Pearson correlation coefficients for the monitored time series are listed in Table 1.

Changes in physical parameters and stratification of the water column

Water temperature was low both at the beginning and end of the year, and higher during the summer. Stratification started to establish at the end of April and was set by the beginning of summer, with a thermocline typically recorded at about 10 m. Hypolimnion temperatures were progressively increasing, however, throughout the summer reaching 12 degrees at the end of August.

Recorded levels of pH were always alkaline. For the mixed periods pH profiles were uniform, while for the stratified period a characteristic pattern with a clear epilimnion maximum was always recorded. The maximum pH (9.2) was recorded on 30 July and 13 Aug at the 3, and 3 and 5 m depths respectively.

For the colder periods oxygen profiles were more or less uniform, while for the summer a characteristic stratified pattern was revealed. Hypolimnion never was completely anoxic. However, it should be noted that the oxygen content in the deep samples was mostly measured after placing them in a plastic container, and some enrichment of samples with oxygen could have occurred during these transformations.

Biological and chemical changes in the epilimnion (integrated samples)

Changes in orthophosphate P, NO_x˙N and Si are presented in Figure 1. Higher levels of these nutrients were recorded during the colder periods of the year, with P, NO_x˙N and Si concentrations reaching as much as 0.4, 2.2 and 2.2 ppm respectively. During the summer months the epilimnion nutrient stock was depleted to very low levels, with Si concentrations reaching as low as 80 ppb, and orthophosphates and NO_x˙N falling to practically undetectable levels (Figure 1).

Both ammonia nitrogen and Al fluctuated between undetectable levels and 160 ppb, while Fe and Mn in the epilimnion were hardly detectable. Maximum and minimum Al levels were recorded in May and June/July respectively, while both maximum and minimum ammonia levels were recorded in winter samples.

Figure 2 presents changes in epilimnion concentrations of K, Mg, Na, S, Ca and DOC. All these factors, apart from S, remained relatively uniform,

Table 1. Pearson correlations for the time series.

	Al	CA	ChlL	Cyclops	Daphnids	Diaptomus	DO	DOC	Inorganic fraction	K	Mg	Na	NH$_4$.N	No$_x$.N	Organic fraction	pH	PN	PN/PP	PO$_4$.P	PP	PP(> 1 mkm)	PP(0.2–1 mkm)	S	Secchi Depth	Si	SS aver
Al	1.00																									
CA	−0.42	1.00																								
Chl			1.00																							
Cyclops				1.00																						
Daphnids	0.42			0.51	1.00																					
Diaptomus		0.40				1.00																				
DO							1.00																			
DOC			0.74					1.00																		
Inorganic Fraction			0.58					0.55	1.00																	
K	−0.54		−0.45				0.62			1.00																
Mg	−0.54	0.89				0.44					1.00															
Na	−0.54	0.40					0.64			0.67	0.40	1.00														
NH$_4$.N													1.00													
No$_x$.N			−0.79					−0.60	−0.45					1.00												
Organic Fraction			0.95					0.64	0.53	−0.47				−0.86	1.00											
pH			0.65	0.42			−0.51			−0.46				−0.70	0.65	1.00										
PN			0.95			−0.46	0.51	0.66	0.51					−0.86	0.95	0.67	1.00									
PN/PP					−0.48											0.47	0.64	1.00								
PO$_4$.P			−0.82				0.50	−0.53	−0.40	0.45				0.86	−0.82	−0.85	−0.85	−0.48	1.00							
PP			0.95				0.53	0.68	0.60	−0.58				−0.77	0.90	0.72	0.94	0.46	−0.82	1.00						
PP (> 1 mkm)			0.96			−0.47	0.56	0.68	0.58	−0.55				−0.82	0.94	0.72	0.96	0.46	−0.82	0.99	1.00					
PP (0.2–1 mkm)																				0.43		1.00				
S														0.39									1.00			
Secchi Depth		0.41	−0.84					−0.60	−0.64	0.58		0.49		0.75	−0.86	−0.51	−0.81		0.68	−0.79	−0.80			1.00		
Si			−0.89					−0.58	−0.56					0.86	−0.86	−0.67	−0.87		0.88	−0.89	−0.88			0.78	1.00	
SS aver			0.95					0.67	0.68	−0.45				−0.84	0.98	0.63	0.92		−0.79	0.90	0.93			−0.88	−0.87	1.00
T			0.77				−0.53	0.46	0.39	−0.47				−0.74	0.75	0.87	0.72		−0.94	0.72	0.71			−0.58	−0.80	0.73

All correlations shown are significant on at least 95% probability level ($p < = 0.05$)

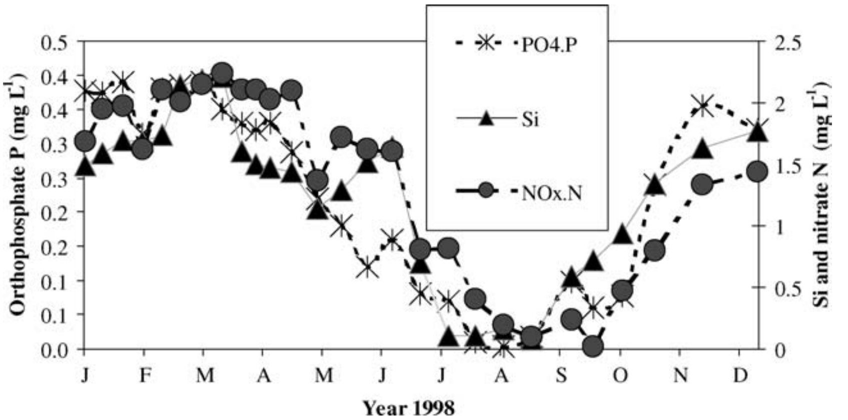

Figure 1. Changes in the epilimnion concentrations (ppm) of Si, NO_x^-N and orthophosphate P.

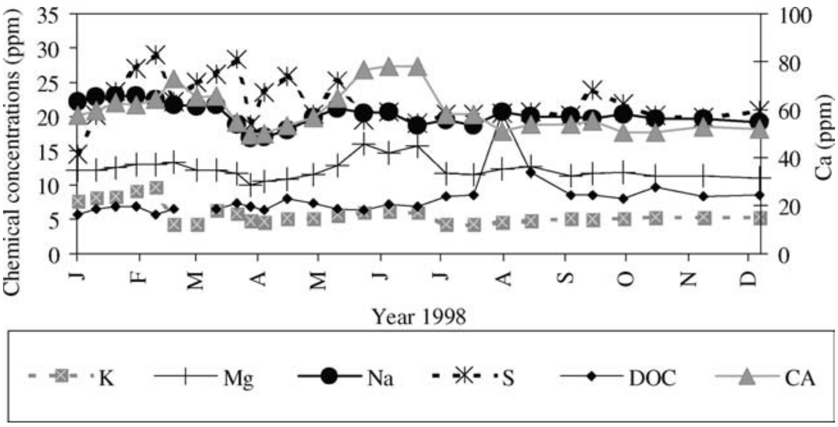

Figure 2. Changes in the epilimnion concentrations (ppm) of K, Mg, Na, S, Ca and DOC.

with K, Mg, Na, DOC and Ca ranging between 4.3 and 9.6, 10 and 15.9, 16.8 and 23, 5.7 and 20.6, 49.6 and 78.1 ppm respectively. S levels were generally slightly higher in spring, and K in January–February. Absolute maximum levels of Ca and Mg were recorded in June/early July and were accompanied by a small increase in K, while the highest value of DOC was registered on 13 Aug.

Changes in epilimnion chlorophyll_*a* concentrations are presented in Figure 3 together with changes in Secchi depth. The former variable ranged between 0.06 and 114 μg/l, and the latter between 77 cm and 3.5 m. It could be seen that these variables negatively correlated, with rises in Chl corresponding to dips in Secchi depth. The maximum values of Chl and minimum values of

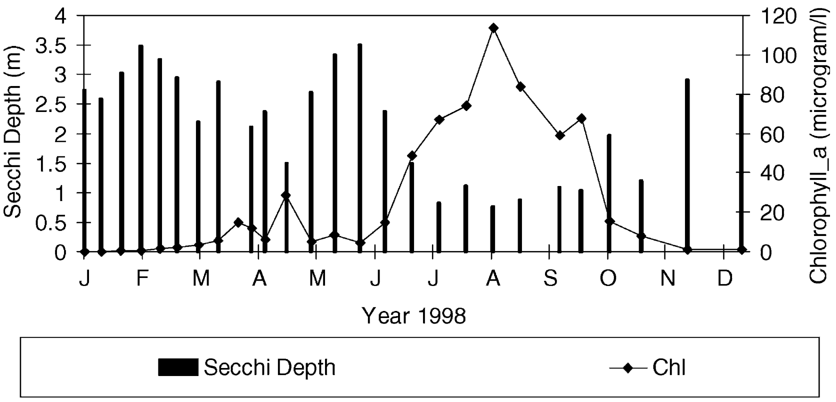

Figure 3. Changes in epilimnion Chlorophyll_*a* concentrations (μg/l) and Secchi depth (m).

transparency were recorded on 13 Aug during the peak of the *Microcystis* bloom.

Zooplankton counts were generally higher in spring. The most prominent peaks of Cladocerans (*Daphnia*) and Copepods (*Cyclopes*) were recorded on 11 May, when they almost reached concentrations of 1500 and 2200 animals/m^3 respectively. There was another prominent peak of Copepods in August and Cladocerans also peaked in November. Diaptomus numbers remained relatively low throughout the year, with the maximum concentration of just below 500 animals/m^3 recorded at the beginning of June.

Suspended solids (SS) concentrations were higher in the summer, and the maximum of 12.8 ppm was recorded on 27 Aug during the bloom of *Microcystis*. Both organic and inorganic fractions appeared to follow changes in total SS. During warmer periods the organic fraction normally considerably exceeded the inorganic one. During colder periods the relationship was not, however, that clear cut and in some cases was even reversed (e.g. January and February samples).

As regards the dynamics of particulate P concentrations in the epilimnion water, the contribution of SS fraction 0.2–1 μm was always small and recorded concentrations were often near or even below the detection limit. P associated with SS fraction >1 μm was always detectable ranging between 15 and 160 μg/l recorded on Nov 21 and Aug 13 respectively.

Changes in the epilimnion concentrations of particulate N and particulate N/ particulate P ratio are presented in Figure 4. Concentrations of particulate N not exceeding 0.1–0.2 ppm were typical for colder periods, while higher concentrations were recorded for warmer periods. The absolute maximum of 1 ppm was recorded on 13 Aug and coincided with the peak of the *Microcystis* bloom. The Particulate N/P ratio for most of the year fluctuated between 4 and 8. Extreme values of 1.6 and 9.6 were recorded on 11 May and 12 Oct respectively.

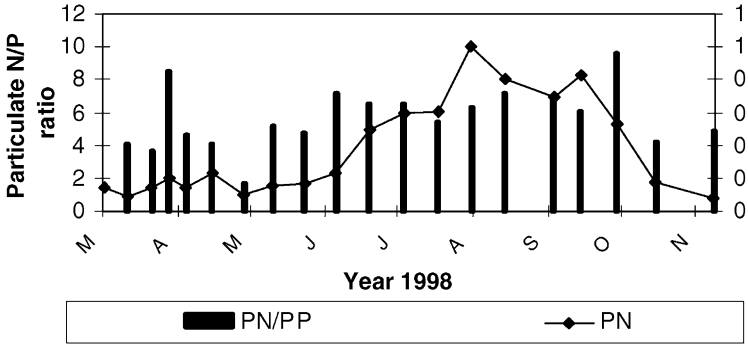

Figure 4. Changes in the epilimnion concentrations of particulate N and particulate N/particulate P ratio (fraction > 1 μm).

Changes in chemical profiles

Orthophosphate P profiles were uniform throughout the water column during the colder periods, but were characterised by a progressive increase in hypolimnion P concentration during the stratified period. The maximum concentration = 0.8 ppm was recorded on 27 Aug at the depth 25 m. Although PO_4 profiles normally showed a characteristic pattern of increase from the surface downwards, the concentrations in the bottom layer were occasionally slightly lower than at the 25 m depth.

Hypolimnion levels of particulate P associated with the suspended solids fractions 0.2–1 μm and >1 μm dramatically increased throughout the stratified period and on 27 Aug reached maximum levels of 114 ppb and 1.2 ppm

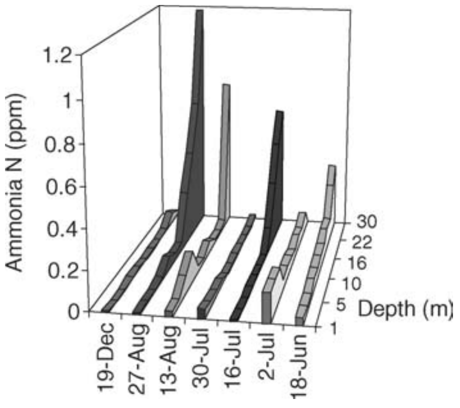

Figure 5. Changes in NH_4N profiles (ppm).

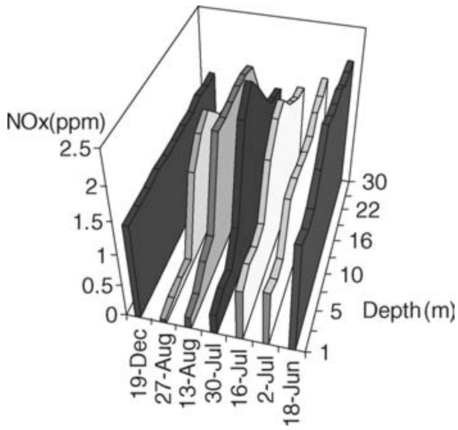

Figure 6. Changes in NO_x·N profiles (ppm).

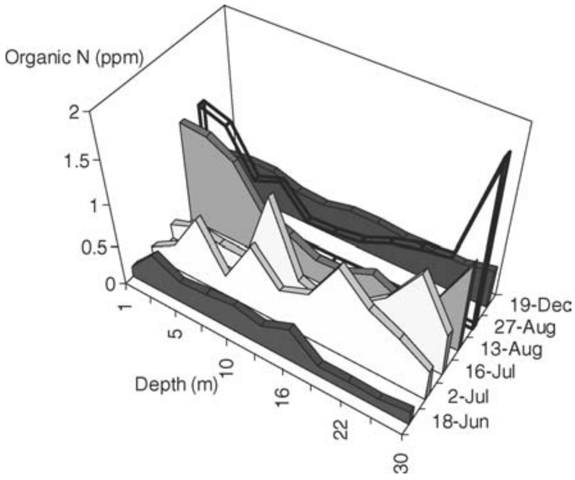

Figure 7. Changes in dissolved organic N profiles (ppm).

respectively. The bigger fraction typically contributed more than 90% of the total particulate P pool.

Ammonia profiles (Figure 5) were also characterised by increased hypolimnion levels during stratification, with the maximum concentration of 1.2 ppm recorded in the bottom layer on 27 Aug. The hypolimnion concentrations recorded on 2 and 30 July were, however, dramatically less than levels recorded in the hypolimnion during the rest of the stratified period. A few samples (e.g. 2 and 30 July, 13 Aug) also showed relatively elevated ammonia levels in the epilimnion (Figure 5).

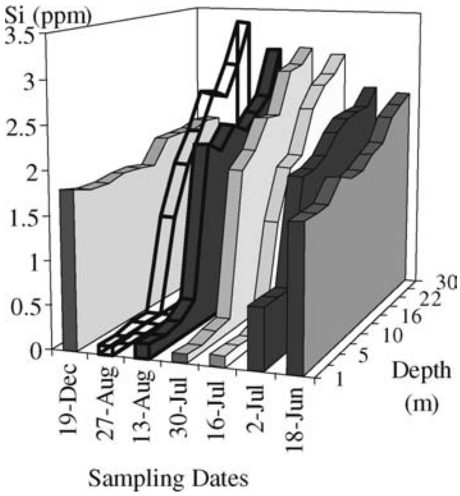

Figure 8. Changes in Si profile.

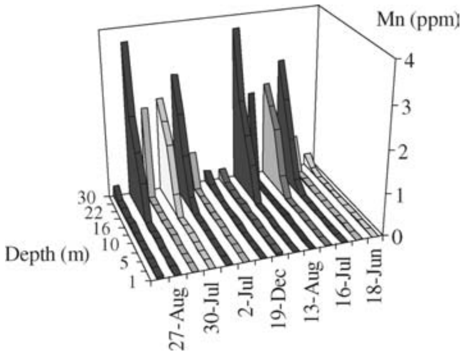

Figure 9. Changes in Mn profile.

Dynamics of the NO_x˙N profiles (Figure 6) were similar to those of orthophosphates, with a characteristic increase from the top downwards during the stratified period. Likewise, the maximum concentrations for most of the sampling dates during the stratified period were not recorded at the very bottom (Figure 6). Unlike the PO_4 and ammonia cases, however, hypolimnion NO_x˙N concentrations never exceeded levels characteristic of the unstratified water column in winter/early spring.

Changes in the profiles of organic N are shown in Figure 7. Hypolimnion levels of organic N demonstrated a progressive increase throughout the stratified period with the depth of an absolute maximum steadily shifting downward, from 16 m on 18 June right to the bottom on 13 Aug. Epilimnion levels were also elevated for most sampling dates during this period. Moreover,

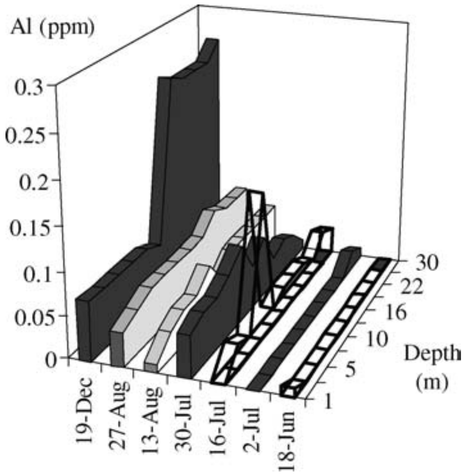

Figure 10. Changes in Al profile.

Table 2. Iron concentrations (ppb) in the hypolimnion.

Date	25 m Depth	Bottom
18-Jun-98	ND	20
02-Jul-98	ND	30
16-Jul-98	ND	ND
30-Jul-98	ND	30
13-Aug-98	ND	50
27-Aug-98	ND	60
19-Dec-98	40	150

ND – undetectable.

samples from 2 and 16 July revealed an additional peak around the thermocline. Maximum concentrations obtained for the epilimnion, hypolimnion and thermocline maxima were 1.2, 2 and 1.2 ppm on 13 and 27 Aug, 27 Aug and 16 July respectively.

Changes in the Si profiles are shown in Figure 8. Distribution of Si within the water column was typically uniform during the mixed periods of the year. During the stratified period, however, concentrations in the epilimnion were considerably lower while hypolimnion levels were remarkably high, with the maximum concentration of 3.3 ppm recorded on 27 Aug.

S and Na profiles did not reveal any major changes. On 19 Dec, however, hypolimnion concentrations of both S and Na were somewhat reduced.

Fe (Table 2) and Mn (Figure 9) in the epilimnion were mostly undetectable. Their hypolimnetic levels, however, showed an increase throughout the stratified period. This was particularly prominent for Mn, whose maximum concentration in the bottom layer reached 3.7 ppm on 27 Aug.

The profiles of Mg and K were relatively uniform throughout the sampling sequence and overall demonstrated a very similar pattern. On 2 July epilimnion concentrations of both chemicals were slightly elevated in comparison with the levels recorded at other depths.

The pattern of changes revealed by Ca profiles was fairly similar to that of Mg and K. Unlike those two elements, however, Ca hypolimnetic concentrations on 19 Dec were considerably elevated.

Changes in the Al profile are presented in Figure 10. At the beginning of summer the concentrations were low throughout the water column and gradually increased thereafter. Compared to the average column levels, hypolimnion concentrations were elevated to a variable degree (not withstanding the 30 July sample). A prominent maximum of 0.26 ppm was recorded on 19 Dec in the bottom layer. Another interesting feature of the Al profiles was a local thermocline maximum around 7–10 m. For example, in the 16 July sample the Al concentration at 7 m depth reached 0.17 ppm.

Changes in DOC profiles were characterised by a major hypolimnetic maximum of 26 ppm recorded on 27 Aug, which was coincident with the epilimnion maximum.

Chlorophyll_*a* profile was characterised by a uniform distribution of measured concentrations during the colder unstratified periods, which was followed by a bimodal distribution during the period of stratification. The increase in hypolimnion chlorophyll levels, however, was delayed compared to the increase in the epilimnion level and the maximum concentration in the bottom layer (206 μg/l) was recorded on 27 Sep when the epilimnion Chl levels already started to decline.

Discussion

Physical parameters and stratification of the water column

As a deep temperate lake, Rostherne Mere usually shows clear and typical stratification during the warmer periods of the year (Davison and Woof 1984; Carvalho 1993; Stephen 1997). This was indeed the case for this study. It is worth mentioning, however, that hypolimnion temperatures recorded by our previous research (i.e. 6–8 degrees – see Krivtsov et al. 2001d) were typically lower than those recorded in this study (i.e. up to 12 degrees). In temperate stratified lakes of similar to the Rostherne Mere's morphometry, hypolimnion temperatures may increase either due to ingress of ground water or to the temporary breakdown of stratification during periods of windy weather. Interestingly, the previous research conducted at Rostherne also indicated the possibility of hypolimnion temperature during the stratified period being either low (i.e. in the range of 5–7 degrees – Stephen 1997) or elevated (i.e. 8–11 degrees – Grimshaw and Hudson 1970). Rostherne and a number of other meres of the Shropshire-Cheshire plain were thought to be effectively sealed at the bottom by an impervious layer of clay sediments (Reynolds 1979), preventing any significant exchange with the ground water. It is possible, however, that the suggested sealing may not be perfect (see e.g. Gorham (1957) for possible explanations of variation in the permeability of the clay and silt layer in Cheshire meres), and that certain combinations of the meteorological and hydrological parameters may at times trigger some limited ingress of the ground water, which is relatively warm in relation to the hypolimnion. Since chemical concentrations in the groundwater are different from those in the hypolimnion, such ingressions could be expected to alter the hypolimnion concentrations first of all in the boundary layer. The magnitude of such changes would depend upon the concentrational gradient and the volumes of the added water. Considering that the ground water in the area was shown to have very low P concentrations (Carvalho 1993), the limited decrease of the bottom P concentrations (compared to the 25 m depth), recorded on a number of sampling dates in 1998, seems to support this point. It is worth noting, however, that during summer 1998 the weather was quite windy at times, and the possibility of the stratification breakdowns from top to bottom cannot be ruled out. The probability of the relevant importance of the two factors discussed above (i.e. mixing by wind and ground water ingress) could be estimated by a special modelling study accounting both for geomorphology and hydrology of the area, and meteorological conditions of the research period. This, however, is far from straightforward, and remains, therefore, the scope of further work.

Epilimnion time series (integrated samples)

In Rostherne, the planktonic community in Spring is normally dominated by diatoms and limited either by light or Si (Reynolds and Bellinger 1992; Krivtsov et al. 1998). A clear water phase usually follows the demise of the diatom population and coincides with the establishment of stratification in May. Thereafter cyanobacteria and *Ceratium* take over until the autumn turnover. Nutrient levels in the epilimnion reflect such a pattern of the phytoplankton development and are normally characterised by a dramatic spring depletion of the dissolved Si, accompanied by a concurrent less dramatic decrease in dissolved N and P species (Krivtsov et al. 1998). Reflecting the summer increase in biological uptake, the latter two chemicals are depleted even further (Carvalho et al. 1995; Krivtsov 1995) with N concentrations sometimes falling to practically undetectable levels (Stephen 1997).

Although this pattern was fully confirmed in our previous research (Krivtsov et al. 2001d), in 1998 some notable differences were obvious. Despite the excessive availability of Si, the diatom peak in spring did not occur and the local peak of Chl recorded on the 3 Apr resulted from the increased concentrations of flagellates (Krivtsov 2000). The diatom increase happened only in June/July and was followed by an immediate increase in *Ceratium* and cyanobacteria, without any clear water phase or a clear separation of the Chl peaks associated with these different types of community (Figure 3). The delayed diatom increase resulted in an unusually delayed major drop in the dissolved Si, which was the first among the major nutrients to reach its threshold level for algal uptake.

Since in spring all other conditions appeared to be suitable for a normal development of the diatom population, a remarkable delay of the diatom bloom could most likely be related to the combined effect of low temperatures and elevated zooplankton numbers. Although zooplankton was previously thought to be relatively unimportant for the functioning of the Rostherne Mere ecosystem (Moss et al. 1994), the possibility of a significant zooplankton contribution to algal limitation was not completely ruled out (Carvalho 1993). Studies conducted elsewhere, e.g. in the Canadian experimental lakes area (see Paterson et al. 2002, and references therein), demonstrated that zooplankton (in particular Daphnia) can considerably affect phytoplankton abundance and influence biogeochemical cycling of nutrients. Both in our previous research (Krivtsov et al. 2001d) and in this study, the correlation analysis of the yearly time series suggested a considerable zooplankton contribution to phytoplankton limitation. The zooplankton spring maximum in 1996 followed, and in 1998 preceded the diatom bloom. Although the magnitudes of the spring zooplankton peaks were similar in both years, the increase in 1998 had already started by middle March, whereas in 1996 it was recorded only at the end of March–early April. Timing of the establishment of the zooplankton population is determined by a number of factors, including food availability and fish recruitment. The tentative link between fish recruitment and the recorded delay of the diatom bloom has been dealt with elsewhere using methods of mathematical modelling (Krivtsov et al. 2001a).

Ammonia N concentrations in the epilimnion were low throughout the year and did not show any clear pattern. The phytoplankton is known to prefer ammonia to other nitrogen sources, and the previous research in Brazil showed that the contribution of ammonia to phytoplankton uptake may be much higher than the contribution of nitrate, whereas the turnover time for ammonia in surface waters is much lower (Mitamura et al. 1995). Erratic patterns of ammonia N fluctuation had also been noted in Rostherne Mere before (Grimshaw and Hudson 1970). Epilimnion increases in ammonia concentrations could happen due to excretions of zooplankton (Horne and Goldman 1994). In well-oxygenated conditions, however, ammonia is prone to a fast oxidation to nitrites and then to nitrates. Considering that zooplankton counts were relatively low, the absence of elevated ammonia levels in the well oxygenated epilimnion comes as no surprise.

Phytoplankton is known to exert a major influence on the dynamics of certain chemicals dissolved in the epilimnion water (Reynolds 1984), and statistical analysis of data from 39 lakes distributed worldwide have previously revealed significant correlations between sedimentation fluxes of particulate matter, C, N and P, with such common trophic variables as Secchi depth, total P, Chl, and primary production (Tartari and Biasci 1997). Phytoplankton influence is most prominent for those chemicals whose supply and dissolved pool are comparable with algal requirements. In the current research this was most clearly shown in the cases of P, N and Si (Figure 1). All three nutrients demonstrated a characteristic drop coinciding with the enhanced phytoplankton development (Figure 3). This development was characterised by a considerable increase in particulate P and N (Figure 4) levels, and was also accompanied by a dramatic decrease in transparency (Figure 3). Considering levels of suspended solids and Chl, it appears that phytoplankton, especially during the bloom periods, was by far the most prominent contributor to the suspended solids pool. Dynamics of the particulate N/P ratio therefore indicates that phytoplankton might at times have been N limiting, which is in line with suggestions of Moss et al. (1997). The lowest ratio, however, was demonstrated in May when Chl in the water was scarce and the contribution of particles of other origin cannot therefore be ruled out. It is also worth mentioning that zooplankton numbers appeared to have a significant negative relationship both with particulate N and the PN/PP ratio (Table 1). The latter, therefore, could have reflected dynamics of the ecosystem components other than phytoplankton.

DOC demonstrated stability of a yearly baseline above 5 ppm. The persistence of these background levels even through the winter may be attributed to the catchment input of humic and fulvic acids (Davison and Woof 1984). The levels during the *Microcystis* bloom, however, were much more elevated, indicating that a significant contribution to the summer levels of DOC comes from the biological community.

The fact that Al levels at the beginning of the sampling period were mostly below the detection limit could be related to the high allochtonous supply of organic substances, capable of binding Al. High allochtonous organic inputs could have happened due to the high precipitation, which would also result in the increased supply of cations derived from the catchment, i.e. Ca, K, Mg, Na. Thus recorded negative correlations of Al with the latter elements seem to support the above suggestion. It should be noted, however, that no significant correlation between Al and DOC (also a possible indicator of high organic inputs) was recorded.

In summer, a decrease in lake water Al coincided with the algal bloom, and could, therefore, have been related to the biological intake. Unfortunately, high detection limits of the technique rendered only limited information on Al changes and no stronger speculation could, therefore, be made.

For major anions and cations the influence of phytoplankton on lake water concentrations appeared to be negligible, reflecting the fact that these chemicals were present far in excess of plankton requirements (Figure 2). Thus changes in concentrations of Ca, K, Na, Mg and S were rather limited and must have reflected changes in hydrological and meteorological parameters. K, however, demonstrated a transitional pattern, reflecting some influence of biological uptake (Table 1). Epilimnion levels of Ca, K and Mg were especially high in June/early July samples, possibly reflecting an increase in evaporation.

In general, the yearly changes in epilimnion chemical concentrations recorded in this study were broadly similar to the ones obtained by the previous research (Gorham 1957; Grimshaw and Hudson 1970; Clay 1992; Carvalho 1993; Stephen 1997). These studies and the present one show similarities in relation to the recorded yearly time series of $NO_x^{\cdot}N$, S, K, Mg, Na, Ca (Grimshaw and Hudson 1970), Si (Carvalho 1993) and P (Stephen 1997). There are, however, some notable differences, especially in the dynamics of P revealed by the present study and the one conducted by Grimshaw and Hudson (1970). In the latter case epilimnion P demonstrated no dramatic changes which could be related to biological uptake. Since the lake at the time was receiving a continuous discharge from a sewage treatment works, inputs from the effluent could have been sufficient to counteract any depletion caused by the planktonic biota (Carvalho 1993). Reynolds and Bellinger (1992) concluded that the operation of the sewage treatment works promoted light limitation of the lake phytoplankton. The effect of sewage input is to reduce the impact of phytoplankton in reducing the concentrations of lake chemicals by uptake needed for their growth. It therefore appears that at the time of the previous research (Grimshaw and Hudson 1970) even the increased biological production could considerably have influenced only the yearly dynamics of $NO_x^{\cdot}N$. Now that official continuous inputs of sewage have ceased since 1991, epilimnion concentrations of P progressively start to reflect the influence of the primary producers. It is also worth noting that Carvalho (1993) questioned the methods used by Grimshaw and Hudson (1970) for P determinations, suggesting that their results might not have shown the true picture of P dynamics in the lake (Carvalho 1993).

Correlation analysis of the epilimnion time series

In line with the discussion presented in the previous section, most of the significant correlations recorded for the lake water constituents (Table 1) could be broadly subdivided into the following categories:

- Positive correlations among direct indices of the particulate (including planktonic abundance (i.e. Chl, SS, PN, PP, DOC) and T.
- Negative correlations between, on the one hand, indices of the particulate (including planktonic) abundance, and, on the other hand, water transparency and the epilimnion levels of certain chemicals (N, Si, P, K, H^+).
- Positive correlations among those elements, whose levels were affected by the biological uptake, and transparency (Secchi depth).
- Correlations determined by similarities/differences in physico-chemical properties of certain elements, manifested in their response to changes in environmental parameters (e.g. positive correlations among Ca, Mg, Na and their negative correlation with Al).

Negative correlations between zooplankton and indices of particulate material abundance in the lake water.

These subdivisions are based not only on the results presented here, but are also in line with literature references (e.g. quoted above) related both to Rostherne Mere and other lakes (located world wide). It should be noted that other types of statistical analysis (in particular, multivariate techniques, e.g., CCA, PCA, factor analysis) may be helpful for describing the patterns of relationships observed in ecosystems (e.g. Krivtsov et al. 1999f, 2002a, 2003a; Krivtsov 2004). However, a large number of variables investigated in the present study would limit the suitability of these techniques here. Therefore, the interpretation of the correlation matrix presented above appears to be the most suitable way to analyse the current data set. In future, we are planning to apply a number of multivariate statistical techniques to a larger data set, incorporating measurements of a lower number of variables over a longer time period, and, perhaps, also including data from other lakes.

Chemical profiles

Studies of eutrophic lakes in Sweden (e.g. Brunberg and Bostrom 1992; Eckerrot and Pettersson 1993; Brunberg 1995) have previously shown that nutrient release from sediments may be greatly enhanced due to the bacterial decomposition of settled phytoplankton, particularly at the declining stage of algal population development. Eckerrot and Pettersson (1993) demonstrated that sedimentary Chl, and bacterial abundances and production rates varied seasonally, with peaks during spring and fall sedimentation.

The results of this study also suggest that the plankton dynamics influenced not only chemical concentrations in the upper layer, but appeared to affect hypolimnion levels as well. Following the removal of easily sedimented detritus from the epilmnion, the concentrations of chemicals associated with the particulate matter dramatically increased in the bottom layer. The spectacular increase in the hypolimnion Chl levels suggests that most of this particulate matter was contributed by algae, cyanobacteria and autotrophic protozoa. The characteristic delay between Chl increases in the epi- and hypolimnion could potentially be used for calculation of the sedimentation and decomposition rates (see Krivtsov et al. (2001d) for modelling methodology). It should be noted, however, that the previous research conducted in Russia and Estonia indicated that elevated levels of Chl may result from the build up of degradation products (Noges et al. 1996).

Decomposition of organic matter could be expected to result in a release of CO_2 leading to a subsequent drop in the hypolimnion pH (Hutchinson 1957). In Rostherne, however, the elevated levels of basic cations (i.e. Ca, Mg) in comparison with C released from decaying biomass buffer the system and prevent developing of the acidic conditions in the bottom layer. As a result, the lower part of the pH profile demonstrates only a very gentle moderate decline and the actual pH levels hardly ever drop below neutral. Changes in the pH profile, therefore, follow a pattern which is usual for an anoxic basin (Hutchinson 1957) and was previously reported for Rostherne (Davison and Woof 1984). This involves an elevation in the epilimnion due to the CO_2 consumption and a slight decrease in the hypolimnion due to the CO_2 production.

The slow processes of bacterial decomposition in the hypolimnion gradually released chemicals contained in the materials accumulated in the bottom layer, remarkably increasing, therefore, the levels of elements present in amounts comparable with the pool stored in the sedimenting detritus. The latter could be illustrated by the case of orthophosphate P, ammonia N (Figure 5), organic N (Figure 7), Si (Figure 8) and DOC.

The organic decomposition, however, appeared to have much more serious consequences for the geochemistry of the hypolimnion than a simple increase in elemental concentrations due to the release from the decaying materials. It resulted in a drop in the redox potential, followed by partial denitrification and chemical release from the sediments. In 1998 approximately 21 mg of orthophosphate P (calculated using the modelling methodology described by Krivtsov et al. 2001d) were released from inorganic compounds and non-diatomal detritus in a hypolimnion column with a square crossection and a side = 10 cm between 2 July and 27 Aug, giving a combined release rate from the two sources of approximately 37.5 $mg/m^2/day$. Unfortunately, owing to the peculiarities of the lake's dynamics in 1998, it would be difficult to assess the exact contribution of the latter sources towards accumulation of hypolimnion P. Nevertheless, it is apparent that the estimates of P release rates for the two studies broadly agree with each other.

Similarly to phosphates, ammonia levels in the hypolimnion also gradually increased throughout the summer. Such accumulation in Rostherne was reported previously (Grimshaw and Hudson 1970). In the present study, the increase in ammonia coincided with a characteristic decline in nitrate/nitrite N concentrations in the deepest (i.e. 30 m) layer. Such a coincidence could be attributed to the process of denitrification, which was also previously reported for Rostherne's hypolimnion (Davison and Woof 1984).

The typical sequence of hypolimnion stagnation consists of four phases first described by Hutchinson (1957). It starts from the initial Mn release followed by the accumulation of Fe and eventual production of sulphide, well documented by Verdouw and Dekkers (1980), Mayer et al. (1982) and Davison et al. (1982). In Rostherne, Fe, Mn and C were to various extents shown to serve as electron acceptors in the process of organic decay (Davison and Woof 1984; Davison et al. 1985). Davison and Woof (1984) carried out sampling of the deep layers using a peristaltic pump and no contamination of the ingressed oxygen was therefore ensured. Based on a yearly data set they concluded that the stagnation of the bottom layer of Rostherne Mere remains on the stage of Mn release (Davison and Woof 1984). In Rostherne, the deoxygenation of water above the active reducing sediment appears to be insufficient to ensure a considerable release of iron or sulphide. To maintain the rapidly oxidised iron in solution, the water column must have a sufficient reduction potential. Rostherne Mere, however, is relatively deep and has a large hypolimnetic reservoir of substances capable of consuming electrons. The lake, therefore, is a finely poised system which does not reach the stage of Fe accumulation, but remains at the phase of Mn and ammonia release accompanied by initial denitrification (Davison and Woof 1984).

The results of this study clearly demonstrated a progressive accumulation of Mn in the bottom layer (Figure 9). Some limited accumulation of Fe also was recorded (Table 2). In the water column, however, the levels of both Mn and especially Fe were often undetectable or near the detection limit of the technique used and no unambiguous Fe profile pattern can therefore be presented. It is worth noting that unlike in the previous studies (Davison and Woof 1984; Carvalho 1993), during the conduct of this research the hypolimnion never appeared completely anoxic. It is worth mentioning, however, that oxygen levels in the bottom layer were measured on the samples pulled up using a deep water sampler. Some gas exchange could have occurred during processing of the sample, and the oxygen presence, therefore, could have been recorded in the potentially anoxic samples.

An interesting feature of the chemical profiles recorded on 19 Dec was increased hypolimnetic levels of Ca and Al, accompanied by decreased levels of S and Na. Both temperature and profiles of certain other chemicals (e.g. nitrates, orthophosphates) were, however, uniform and the column, therefore, must have been well mixed. Deviations from the expected uniformity of chemical profiles in Rostherne winter samples was also noted by Grimshaw and Hudson (1970). Precise interpretation of this phenomenon requires further work.

Concluding remarks

The results of this research have clearly demonstrated the major influence of primary producers on the overall ecosystem dynamics and suggested that the significance of secondary producers might have been previously underestimated. Phytoplankton biomass in lakes correlates with high nutrient inputs, and the prevalence of phytoplankton in the overall primary production is common in eutrophic lakes characterised by high nutrient concentrations (see, e.g., Trifonova 1998; Trifonova et al. 2002, for results from a number of Eastern European lakes).

Phytoplankton is known to exert a major influence on the dynamics of certain chemicals dissolved in the epilimnion water (Reynolds 1984). This is most prominent for those chemicals whose supply and dissolved pool are comparable with algal requirements. In the current research this was most clearly shown in the cases of P, N and Si (Figure 1). All three nutrients demonstrated a characteristic drop coinciding with the enhanced phytoplankton development (Figure 3). This development was characterised by a considerable increase in particulate P and N (Figure 4) levels, and was also accompanied by a dramatic decrease in transparency (Figure 3). Considering levels of suspended solids and Chl, it appears that phytoplankton, especially during the bloom periods, was by far the most prominent contributor to the suspended solids pool. Dynamics of the particulate N/P ratio therefore indicates that phytoplankton might at times have been N limiting, which is in line with suggestions of Moss et al. (1997). The lowest ratio, however, was demonstrated in May when Chl in the water was scarce and the contribution of particles of other origin cannot therefore be ruled out. It is also worth mentioning that zooplankton numbers appeared to have a significant negative relationship both with particulate N and the PN/PP ratio (Table 1). The latter, therefore, could have reflected dynamics of the ecosystem components other than phytoplankton.

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The hypolimnion of the Mere was confirmed to remain at the stage of Mn release, characterised by accumulation of DOC, orthophosphates, ammonia and initial stages of denitrification. High levels of P released from the sediments during the stratification period suggest that the lake's recovery after sewage diversion might be further delayed.

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