Nutrient and organic matter dynamics in Lake Glubokoe

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Abstract. In this paper we present the results of field observations carried out at Lake Glubokoe (Moscow Region) in 2017–2019. Basic characteristics of the vertical distribution of main nutrient elements (phosphorus, nitrogen, and silicon) and organic matter (COD and chlorophyll-a) content are shown, along with their seasonal ranges. Due to the lack of surface runoff into the lake, the concentrations of total phosphorus and nitrogen are generally low throughout the year, with almost total depletion of inorganic phosphorus in the epilimnion during the growing season. Sufficient microbial activity allows most of the inorganic nitrogen to be presented in the nitrate form, except for late summer and fall, when plankton death rate exceeds bacterial nitrification capacity. During the period of hypolimnetic anoxia, significant amounts of mineral phosphorus and ammonia nitrogen are released from the bottom sediments. COD value shows a correlation with the intensity of both phyto- and zooplankton growth, which also affect the nutrient content.

1. Introduction

The content and dynamics of nutrients and organic matter in freshwater lakes are the essential parameters affecting their trophic state [1]. Phosphorus and nitrogen are typically considered to be most important among nutrients [2–3]. Many studies have concluded that in marine ecosystems phytoplankton growth is mainly limited by nitrogen, and in freshwater ones – by phosphorus [4], though observational data from various lakes shows that this is not always true for freshwater biomes [5]. This implies the need to observe the dynamics of both these elements when monitoring lakes. At the same time, the distribution of specific nutrients and their suspended and dissolved, mineral and organic forms depends both on the composition of the water inflow into the lake, and the intensity of chemical and biological processes occurring in the lake itself. Therefore, the dynamics of various forms of nutrients can serve as an important indicator of the entire lake’s state.

Another nutrient important for aquatic ecosystems is silicon. Though it generally doesn’t limit the phytoplankton growth, it’s vital for the growth of algae, especially diatoms, so silicon plays a key role in shaping the phytoplankton species composition in the lake. Certain studies show that the inflow of silicon can affect the eutrophication by causing a predominance of certain species in the plankton community [6].

Many recent studies point out that in the near future eutrophication processes in lakes are likely to strengthen due to climate change. And not only lakes exposed to direct anthropogenic impact (in the
form of wastewater discharges etc.) are becoming vulnerable, but also ones located in protected natural areas [7–8]. To diagnose and predict possible changes, it is necessary to have sufficient observations of water physics, chemistry, and biology.

In 2017 our research team began regular observations of physical and chemical characteristics of the Lake Glubokoe in the Moscow Region. Due to its location in a protected natural area, and the vast amount of hydrobiological observations collected by the monitoring station’s staff, Lake Glubokoe can be considered a unique object for comprehensive research in the area. Certain hydrological and water chemistry studies were also conducted [9–10], but their sporadic nature doesn’t allow to make any long-term conclusions.

Creating an extended database of physical and chemical characteristics of the lake would make it possible to use it as a reference object in the framework of international monitoring, to study current trends of the development of lake ecosystems in central Russia and predict their future changes.

2. Materials and methods
Lake Glubokoe (55.75 N, 36.51 E) is located in the western part of the Moscow Region, in the nature reserve of the same name. The area around the lake is covered with forests and is mostly waterlogged. The lake’s surface area is approximately 593,000 m², and the maximum depth is 32 m. The lake is fed mostly by rainfall, which determines low water salinity.

On the basis of long-term data, Lake Glubokoe is usually considered to be mesotrophic, which is also confirmed by our field observations and model estimates, though an α-eutrophic level can be reached during periods of rapid phytoplankton growth [11].

During the summer and fall of 2017, and from March 2018 to the beginning of 2019 we carried out a series of field observations and sampling at a reference station of Lake Glubokoe. The observations were conducted 1–3 times a month, concerning important meteorological events.

Mineral (TIP) and total (TP) phosphorus content in the samples were measured using Murphy-Riley method [12]. Dissolved mineral and total phosphorus content (DIP and TDP, respectively) was measured the same way using samples filtered through 0.45 μm membrane filters. The content of mineral forms of nitrogen, such as nitrates (NO3-N) and ammonium (NH4-N), was measured using ion chromatography technique [13]. Since 2018, total nitrogen (TN) content was measured by ultraviolet photometry after oxidation with potassium persulfate in an alkaline medium. Organic nitrogen content (TON) was measured as the difference between the content of total nitrogen and its two mineral forms. The concentration of silicon (Si) was measured using the molybdosilicate method.

The chemical oxygen consumption (CODc) value was used as an indirect indicator of the organic matter content, measured by bichromate oxidation. The UV-spectrophotometry after acetone extraction was used to measure the concentration of chlorophyll-a (Chl-a) – a photosynthetic pigment which indicates the degree of phytoplankton development.

Data on the total number of crustacean zooplankton in the 1–10 m layer were used to make a rough estimate of the zooplankton’s contribution to the content of organic matter in the lake.

3. Results and discussion

3.1. Phosphorus
The phosphorus content in Lake Glubokoe normally remains low, within the first tens of micrograms per liter; between 50 and 100% of it is presented in dissolved form (table 1). In the surface layer, the total phosphorus (TP) content remains fairly stable over time, typically at 12–25 μg/l. Certain peak values were noted, as high as 36 μg/l, almost entirely in dissolved form, possibly caused by inflow with surface runoff.

Further vertical distribution tends to be relatively uniform (figure 1a), though local phosphorus content highs can be noted in the lower part of the metalimnion during summer (up to 12 μg/l more than in adjacent layers), along with an increased share of suspended organic phosphorus. A possible
explanation is the accumulation of detritus in this layer after periods of intense phytoplankton growth, which is supported by the weather data and the chlorophyll content’s dynamics in the water.

Table 1. Different forms of phosphorus and nitrogen, inorganic silicon, chlorophyll-a and chemical oxygen demand in surface and bottom layers of Lake Glubokoe in different seasons of 2017–2019.

|        | TIP | TP  | DIP  | TDP  | NO₃ | NH₄ | TN  | Si  | Chl-a | COD₉₆ |
|--------|-----|-----|------|------|-----|-----|-----|-----|-------|-------|
|        | mgP/l | mgN/l | mg/l | µg/l | mgO/l |
| summer 2017 | top | 0.004 | 0.016 | 0.003 | 0.009 | -   | -   | -   | 0.42  | 6.4   | 22.0 |
|        | bot | 0.005 | 0.015 | 0.004 | 0.009 | -   | -   | -   | 0.86  | 1.5   | 16.2 |
| fall 2017 | top | 0.006 | 0.021 | 0.003 | 0.010 | -   | -   | -   | 0.51  | 7.0   | 26.0 |
|        | bot | 0.018 | 0.032 | 0.006 | 0.015 | -   | -   | -   | 1.01  | 1.8   | 16.7 |
| spring 2018 | top | 0.005 | 0.021 | 0.004 | 0.017 | 0.23 | 0.04 | 0.63 | 0.73  | 3.4   | 22.2 |
|        | bot | 0.008 | 0.023 | 0.007 | 0.017 | 0.44 | 0.04 | 0.83 | 0.92  | 2.2   | 17.3 |
| summer 2018 | top | 0.005 | 0.022 | 0.004 | 0.017 | 0.04 | 0.04 | 0.58 | 0.72  | 7.5   | 20.1 |
|        | bot | 0.012 | 0.027 | 0.006 | 0.018 | 0.38 | 0.07 | 0.89 | 1.18  | 2.3   | 15.7 |
| fall 2018 | top | 0.005 | 0.022 | 0.004 | 0.018 | 0.05 | 0.08 | 0.66 | 0.86  | 6.6   | 20.6 |
|        | bot | 0.042 | 0.062 | 0.017 | 0.026 | 0.08 | 0.26 | 1.08 | 1.51  | 1.3   | 17.2 |
| winter 2018–2019 | top | 0.006 | 0.027 | 0.007 | 0.022 | -   | -   | -   | 0.95  | 1.0   | -    |
|        | bot | 0.007 | 0.021 | 0.006 | 0.016 | -   | -   | -   | 1.06  | 0.8   | -    |

Dashes indicate the absence of data.

In the bottom layer, more pronounced seasonal dynamics of the phosphorus content was noted: between late fall and mid-summer TP values there remain close to those in the surface layer, but with the development of bottom anoxia during late summer (in 2018 – from early August until the mixing in November) total phosphorus content increased to 40-90 µg/l. As expected, the main contributor was the inorganic phosphorus, since it is the dominant form to be recovered from bottom sediments: while in most cases the TIP/TP ratio is at about 0.25, in the fall the share of mineral phosphorus in the bottom layer reaches 60-80%.

3.2. Nitrogen

The nitrogen content in the surface layer was also quite stable: the total nitrogen concentration varies between 0.5-0.7 mg/l. With depth, nitrogen content smoothly increases (figure 1b), and in the bottom layer these values turn out to be consistently higher, between 0.75 and 1.3 mg/l. According to 2018 data, the overall net nitrogen content in the lake gradually increases during the ice-free period. Since there is no significant inflow into the lake, it is safe to conclude that this occurs due to the intake of atmospheric nitrogen by nitrogen-fixing bacteria (which leads to increased surface TN content), and its recovery from bottom sediments (resulting in increased bottom concentrations).

The seasonal dynamics of the lake's ecosystem leads to a change in the balance of different forms of nitrogen throughout the year. After the spring mixing, their vertical distributions are fairly homogenous: in March 2018, nitrate concentration along almost the entire water column was at about 0.4 mg/l, except for the bottom sample with NO₃ content of 0.58 mg/l; ammonium content did not exceed 0.08 mg/l. When the growing season begins, phytoplankton starts to consume nitrate nitrogen: in 2017 and 2018 the NO₃ concentration in the epilimnion decreased to 0.01-0.04 mg/l by mid-June, and later did not exceed 0.1 mg/l throughout the stratified period. At the same time, the share of organic nitrogen increases from 50% (a typical value for the spring circulation period) to 85-95%.

NH₄ content in the surface layer during the summer period usually remains the same as after the spring mixing. A significant shift towards predominance of ammonium nitrogen is only observed in
fall: in late September – early October 2018 the surface NH$_4$ content exceeded 0.2 mg/l. This was due to the massive dying of phyto- and zooplankton at a rate exceeding the bacterial capacity for oxidation.

**Figure 1.** Vertical distributions throughout 2017–2018 of a) inorganic and total phosphorus; b) total, nitrate, and ammonia nitrogen; c) silicon; d) chlorophyll-a and COD$_{Cr}$.

In the lower part of the metalimnion, nitrogen accumulates during the summer period in the nitrate form: between May and September 2018, NO$_3$ content at 10–12 m grew from 0.32 to 0.43 mg/l, and TN content from 0.7 to 0.9 mg/l. Detritus accumulates there, and the highest activity of nitrifying
bacteria is observed, which transform the ammonium released by the decomposition into nitrate in the presence of oxygen.

During the entire period of stagnation in the summer and fall 2018, total nitrogen content in the hypolimnion (about 0.8 mg/l) and the ratio of its various forms remained almost unchanged. After complete depletion of oxygen in the bottom layer, nitrogen began to escape from the bottom sediments, and by the end of the stratification TN content, there has reached 1.26 mg/l. If at the beginning of anoxia the nitrate content exceeded the ammonium content by order of magnitude, by the end of the stratification period the situation has reversed. This was due to the fact that in the absence of oxygen nitrate nitrogen is reduced by anaerobic denitrifying bacteria, and the bottom sediments mostly release the ammonium form. There are reasons to believe that significant nitrite nitrogen content could also be observed during the bottom anoxia, though we did not measure it in the course of the study. Therefore, the data on mineral nitrogen forms in the hypolimnion remains incomplete.

3.3. Silicon
Total silicon content also increases along with the lake’s depth (figure 1c). In the surface layer its concentration over the observation period varied between 0.33 and 1.07, and in the bottom layer between 0.71 and 1.62 mg/l. During the warm period of the year, the silicon content appears to increase, followed by a moderate decrease slightly.

Silicon content in the surface layer remains practically unchanged during the summer period. In 2017, for almost the entire observation period, the silicon content here remained in the 0.4-0.5 mg/l range, and 2018 between 0.65-0.76 mg/l. The surface silicon concentration increases only at the end of autumn, when microorganisms die (in 2018, Si content in mid-September increased by almost 0.1 mg/l in 10 days), and with the stirring of the water column.

Accumulation of silicon during the growing season occurs in the lower part of the metalimnion: from May to September 2018 its concentration grew from about 0.9 to almost 1.2 mg/l.

The most significant seasonal changes in silicon content, as in the case of other nutrients, were observed in the bottom layer. Over the observation period in 2018, Si concentration grew from 0.9 to 1.6 mg/l, at a consistent rate regardless of the oxygen supply. There are two likely explanations. A number of studies indicate the possibility of silicon being recovered from bottom sediments, both in the presence of oxygen and in anoxic conditions; but most studies do not agree which conditions favor more intensive silicon release from sediments [14]. At the same time, our data show increased salinity in the near-bottom layers of Lake Glubokoe during the stratified period; this may be evidence of groundwater accumulation, which can also serve as a source of additional mineral silicon.

3.4. COD, chlorophyll, and zooplankton
The CODCr value in the lake during the period covered by the study varied between 13 and 38 mgO/l. The ratio of oxygen demand by permanganate (Permanganate index, PI) and bichromate in nearly all samples was at about 0.5, which indicates an approximately equal balance between allochthonous and autochthonous organic matter. Generally, the PI/CODCr ratio varied between 0.25-0.64.

The vertical distribution of CODCr values shows a decrease in the bottom layers (figure 1d), though highest values were not always observed on the surface, but at depths of up to 10 m. This is due to the fact that phyto- and zooplankton growth can be inhibited during excessive heating of the surface horizons, so the highest productivity may shift to cooler layers.

Chlorophyll-a content in Lake Glubokoe water during the periods of highest phytoplankton growth reached 25 µg/l. Like COD, the chlorophyll values tend to decrease with depth, while in the seasonal perspective the maximum is achieved at the end of summer. There’s a sufficiently strong correlation between chlorophyll-a content and CODCr: the concentration of photosynthetic pigments often displays the vertical distribution and yearly variation similar to that of CODCr. The highest chlorophyll content values can also be observed at depths of up to 10 m, but the depth at which maximum values are noted may vary for these two indicators since in different seasons phyto- and zooplankton organisms make different contributions to the CODCr value. Combined graphs of the yearly CODCr
dynamics, chlorophyll-a content, and total number of crustacean zooplankton in the upper 10 m of the water column (Figure 2) show that on different dates the total organic matter content (which is indirectly indicated by the COD$_{Cr}$ value) varies in line with either the phytoplankton, or zooplankton content. E.g., the local maximum in zooplankton growth observed in June and the first half of July 2018 (up to 48.6 ind/l on 28 June) corresponds to a similar extremum in the COD$_{Cr}$ value (with the maximum of about 21 mgO/l on 21-27 June). The local increase in the COD$_{Cr}$ value in the second half of July and the beginning of August, on the contrary, most likely corresponds to an outbreak of increased phytoplankton growth: the highest values of both these characteristics (18.3 mgO/l and 9.9 µg/l) occurred on 22 July.

![Figure 2. COD$_{Cr}$, chlorophyll-a and mean zooplankton density (in the 0–10 m layer) dynamics in March – October 2018.](image)

4. Conclusion

Fairly low concentrations of major nutrients and their mild seasonal dynamics are currently typical for Lake Glubokoe, due to the absence of significant external sources of those elements, either natural or anthropogenic. The relatively low rate of biological production and the presence of nitrifying bacteria allow to maintain a significant predominance of nitrates over other mineral nitrogen forms throughout the year and almost across the entire water column, except the period of massive dying of microorganisms in fall. During the hypolimnetic anoxia in late summer and fall, mineral forms of nitrogen and phosphorus are recovered, so denitrification of nitrates takes place. The highest intensity of biological production is observed at depths between 0 to 10 m, depending on weather conditions.

Regular monitoring of water physics and chemistry of Lake Glubokoe is advisable, among with augmenting the database with observations on the composition of phytoplankton species and microbiological characteristics. That way the lake can become a unique object for further studies of lake ecosystems’ reaction to environmental changes, including climate change, and contribute to the progression of the international limnology.

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