

Analysis of the Correlation between the Phytoplankton Development Level, Assessed by Chlorophyll *a*, and Nutrient Concentrations in Rybinsk Reservoir

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Abstract—A correlation analysis between chlorophyll *a*, nitrogen, and phosphorus compounds in Rybinsk Reservoir is carried out. During certain periods of the study, a significant correlation between chlorophyll *a* and inorganic nitrogen and phosphorus compounds is shown. The response of phytoplankton to the total nitrogen and phosphorus concentrations is evaluated.

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INTRODUCTION

Physiological indicators of algae growth can serve as criteria for determining the limiting element of their nutrition. The simplest and most common method for determining such an element is to establish the quantitative ratio of nitrogen and phosphorus in water. Limitations can also be revealed when studying the dependence of phytoplankton development on the nitrogen and phosphorus concentrations. For various regions and water bodies, statistically significant estimates of the relationship between the concentrations of nutrients and Chl *a* as an indicator of phytoplankton development, biomass, and productivity of lakes were previously obtained. The chlorophyll–total phosphorus (chl *a*–TP) relationship was discovered by Dillon and Rigler (1974) for 46 lakes of the world:

$$\text{Chl } a = 0.073\text{TP}^{1.45},$$

where the concentration of chlorophyll occurs in mid-summer and that of total phosphorus is mid-spring. A similar equation was also proposed by Jones and Bachman (Jones and Bachman, 1986):

$$\text{Chl } a = 0.08\text{TP}^{1.46},$$

where both indicators are the annual average.

Smith (1982), as a result of summarizing data on 228 lakes, found a multiple regression dependence of the chlorophyll content as a function of the concentrations of total nitrogen (TN) and TP, thereby confirming the influence of the ratio of these elements on the development of phytoplankton:

$$\log \text{Chl } a = 0.653 \log \text{TP} + 0.548 \log \text{TN} - 1.517.$$

It should be noted that the dependences of the indices of phytoplankton development, including those on the content of Chl *a* and nutrients, have been established mainly for small lakes with a stable hydrological regime. For large lakes and reservoirs, due to the complexity of hydrodynamic conditions and the heterogeneity of water masses, these dependences are often insufficiently defined. Some connections were noted for the Volga reservoirs (Mineeva and Razgulin, 1995; Mineeva, 2004; Mineeva et al., 2008) and reservoirs of the Dnieper cascade (Kureyshevich and Zhuravleva, 1997; Kureyshevich and Medved, 2006); however, they are very unstable and depend on a set of many factors, the influence of which is rather difficult to take into account. The study of such dependences in a reservoir is very important.

The aim of this study is to assess and analyze the chlorophyll–nutrient relationships at the present stage of development of the Rybinsk Reservoir ecosystem.

MATERIALS AND METHODS

Nitrites were determined by the colorimetric method after the reaction with sulfanilamide and alfa-naftylamine. Nitrates were noted by the colorimetric method after their reduction to nitrites with copper-bonded cadmium. Ammonium ions were found after microdiffusion distillation and the subsequent reaction with Nessler's reagent. The content of phosphates was found by the colorimetric method with ammonium molybdate (Semenov, 1977). TN was determined after oxidation of the organic fractions with potassium persulfate to nitrates (Gapeeva et al., 1984; Bikbulatov, 1974). Chl *a* was determined by the spec-



Fig. 1. Sampling scheme at the reservoir stations. 1, Koprino; 2, Mologa; 3, Navolok; 4, Izmailovo; 5, Shrednii Dvor; 6, Breitovo.

trophotometric method according to Lorentzen. Samples were taken two times a month from the surface water layer at six standard stations of Rybinsk Reservoir (Koprino, Mologa, Navolok, Izmailovo, Srednii Dvor, and Breitovo) for the entire open water period (May–October), in 2007–2010. The sampling scheme is shown in Fig. 1.

Chlorophyll data were kindly provided by I.L. Pyrina.

RESULTS AND DISCUSSION

In general, Rybinsk Reservoir, in terms of the content of nitrogen and phosphorus elements, is currently classified as a mesotrophic water body; however, in some periods (spring), the Volzhskii reach, to which the stations Koprino and Mologa belong, is eutrophic.

Based on the average chlorophyll concentrations, Rybinsk Reservoir can be classified as moderately eutrophic (Korneva, 2015).

In the years under study, Rybinsk Reservoir was characterized by seasonal patterns of changes in the content of a number of forms of nutrients and some of their ratios, expressed in a decrease in inorganic forms and an increase in the proportion of organic ones in summer. The highest content of all inorganic forms of nitrogen and phosphorus was noted in May due to organic matter decomposed in the process of ammonification and nitrification during the ice period. The nitrogen to phosphorus ratio decreased with the transition from spring to summer. The concentrations of all compounds of nitrogen and phosphorus studied, as well as chl *a*, varied within fairly wide limits, and that of chlorophyll ranged from 0.39 to 55.4 µg/L, which, averaged over the entire studied period, was 12.4 µg/L. The average monthly data are presented in Table 1, and the frequencies of occurrence of various concentrations of chl *a* are shown in Fig. 2a. The most frequently observed concentrations were up to 10 µg/L (116 cases from the entire data set). Phytoplankton development peaks occurred in late summer and early autumn. The TN and TP contents varied from 0.34 to 2.01 and from 0.019 to 0.115 mg/L, respectively. Most often, TP and TN concentrations of 0.04–0.06 and 0.5–1.0 mg/L were observed (Figs. 2b, 2c).

During the study period, for the entire data set, no significant relationship was found between the content of chl *a* and any compound of nitrogen and phosphorus (Table 2) (ammonium ions, nitrites, nitrates, inorganic and organic nitrogen, TN, phosphates, and organic TP). The maximum connection was noted with organic phosphorus (Table 2). A high correlation was noted between the total and organic nitrogen, mineral nitrogen, and nitrates ($r = 0.94$). A less close relationship was found between organic and total phosphorus ($r = 0.71$), and a moderate relationship was also observed between the pairs TP and P_{\min} ($r = 0.57$), N_{org} and N/P ($r = 0.59$), and TN and N/P ($r = 0.63$).

A relationship between nutrients and chlorophyll was established only for some months. The closest

Table 1. Chlorophyll *a* content, µg/L, and nutrients (average for 2007–2010), mg N/L or mg P/L

	Chl <i>a</i>	NH ₄ ⁺	NO ₂ ⁻	NO ₃ ⁻	TN	N _{min}	N _{org}	P _{min}	TP	P _{org}	N/P
May	7.28	0.06	0.005	0.270	0.82	0.360	0.49	0.026	0.042	0.016	22
June	7.95	0.07	0.005	0.220	0.74	0.290	0.47	0.025	0.053	0.027	16
July	12.1	0.07	0.004	0.100	0.93	0.17	0.63	0.017	0.058	0.041	15
August	16.4	0.06	0.002	0.037	0.86	0.100	0.76	0.023	0.062	0.039	15
September	16.8	0.04	0.004	0.044	0.91	0.106	0.68	0.023	0.064	0.040	13
October	8.79	0.03	0.004	0.057	1.00	0.113	0.75	0.027	0.070	0.050	13
Average	12.4	0.05	0.004	0.121	0.88	0.189	0.63	0.023	0.058	0.035	15

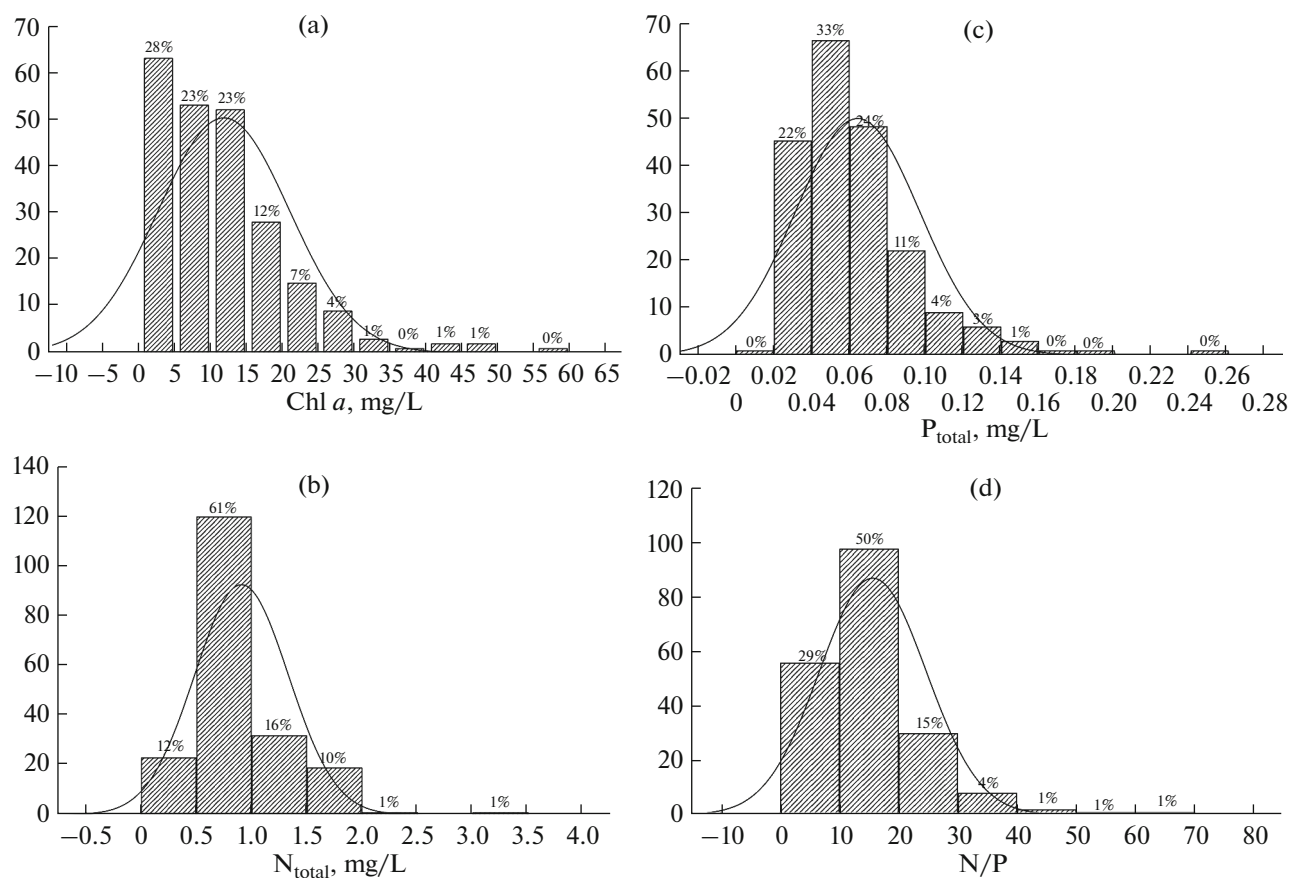


Fig. 2. The frequency of occurrence of various concentrations of chlorophyll *a* (a), total phosphorus (b), and total nitrogen (c); N/P (d); the ordinate axis is the number of cases and the proportion (%) of the total number of observations ($n = 231$).

relationship of nutrients with the Chl *a* content was noted during the open water period. Thus, in May (Table 3) there was a negative correlation between the concentrations of chlorophyll, nitrates, and phos-

phates ($r = -0.56$ and -0.72 , respectively), which indicates their intensive consumption by phytoplankton.

In June, there was also a significant correlation between the concentrations of chl *a* and nitrates

Table 2. Pairwise correlation coefficients between different forms of nutrients and chlorophyll concentration (entire data set)

	Chl <i>a</i>	NH ₄ ⁺	NO ₂ ⁻	NO ₃ ⁻	TN	N _{min}	N _{org}	P _{min}	TP	P _{org}	N/P
Chl <i>a</i>	1.00	-0.08	-0.17	-0.23	0.12	-0.24	0.20	-0.15	0.28	0.47	-0.11
NH ₄ ⁺	-0.08	1.00	0.19	0.13	0.16	0.45	0.00	0.11	0.03	-0.06	0.25
NO ₂ ⁻	-0.17	0.19	1.00	0.45	-0.20	0.50	-0.35	0.28	0.10	-0.12	-0.23
NO ₃ ⁻	-0.23	0.13	0.45	1.00	0.00	0.94	-0.31	0.29	0.05	-0.19	-0.05
TN	0.12	0.16	-0.20	0.00	1.00	0.05	0.94	0.17	0.29	0.20	0.63
N _{min}	-0.24	0.45	0.50	0.94	0.05	1.00	-0.29	0.30	0.06	-0.20	0.04
N _{org}	0.20	0.00	-0.35	-0.31	0.94	-0.29	1.00	0.06	0.26	0.25	0.59
P _{min}	-0.15	0.11	0.28	0.29	0.17	0.30	0.06	1.00	0.57	-0.18	-0.24
TP	0.28	0.03	0.10	0.05	0.29	0.06	0.26	0.57	1.00	0.71	-0.45
P _{org}	0.47	-0.06	-0.12	-0.19	0.20	-0.20	0.25	-0.18	0.71	1.00	-0.33
N/P	-0.11	0.25	-0.23	-0.05	0.63	0.04	0.59	-0.24	-0.45	-0.33	1.00

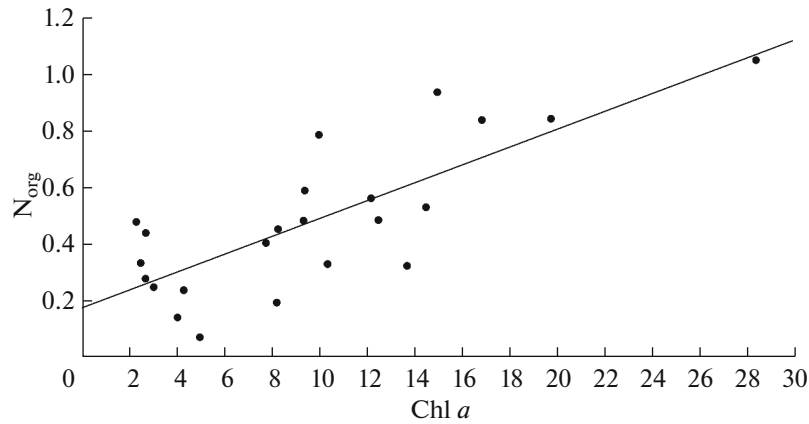


Fig. 3. Graph of the correlation between chlorophyll *a* ($\mu\text{g/L}$) and organic nitrogen (mg/L) in June.

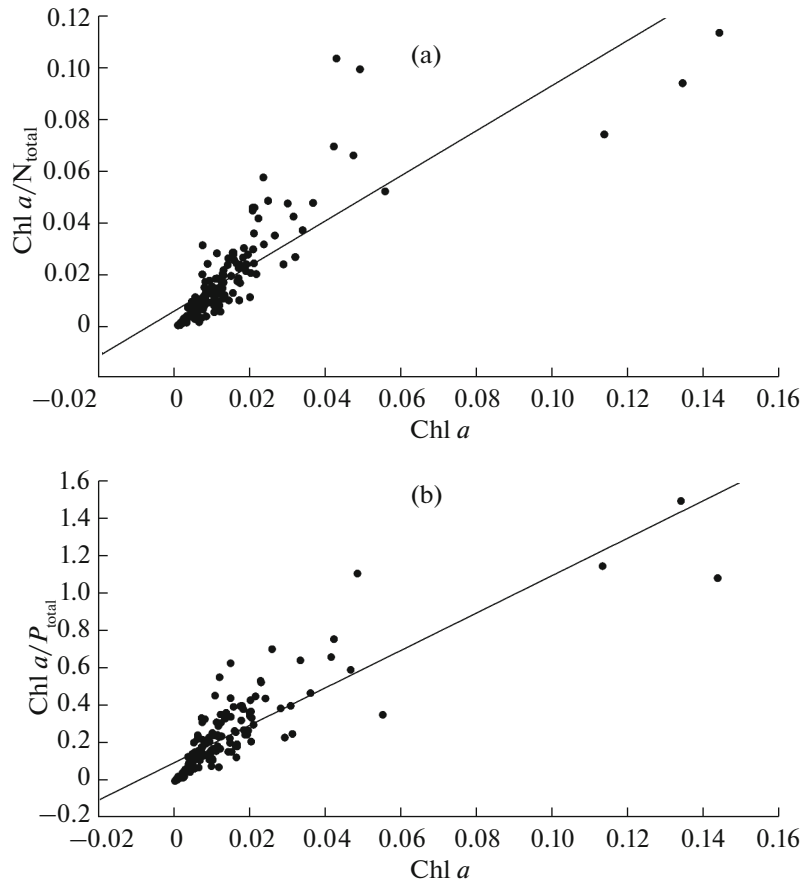


Fig. 4. Relationship between responses and chlorophyll *a* ($\mu\text{g/L}$). (a) Response to TN, (b) response to TP.

($r = -0.66$), as well as N_{min} ($r = -0.63$) and N_{total} and N_{org} ($r = 0.57$ and 0.76). The relationship between these components was expressed by the following formula:

$$N_{\text{org}} = 0.1744 + 0.0316\text{Chl } a \text{ (Fig. 3).}$$

The chlorophyll content correlated positively with N_{total} and N_{org} and P_{total} and P_{org} in September ($r = 0.59, 0.64, 0.49,$ and $0.82,$ respectively) (Table 3). The above coefficients reflect either a moderate (from 0.56 to 0.71) or a significant (0.72–0.84) relationship on the Chaddock scale. In July, August, and October,

Table 3. Pairwise correlation coefficients between different forms of nutrients and chlorophyll concentration during the open water period

Month	NH ₄ ⁺	NO ₂ ⁻	NO ₃ ⁻	TN	N _{min}	N _{org}	P _{min}	TP	P _{org}
May	0.54	0.24	-0.56	-0.09	-0.25	0.12	-0.72	-0.66	-0.23
June	-0.18	-0.41	-0.66	0.59	-0.63	0.78	0.28	0.35	0.11
September	-0.26	-0.41	-0.28	0.59	-0.33	0.64	-0.35	0.49	0.82

correlation analysis did not reveal significant relationships between nutrients and chlorophyll.

When considering the monthly average values of the levels of the elements studied, high values of the correlation coefficients were found in vapors of chl *a*-nitrates ($r = -0.78$), chl *a* and inorganic nitrogen ($r = -0.75$), and chl *a*-N_{org} ($r = 0.65$), while the relationships between the chlorophyll content and the content of the total and organic phosphorus and phosphates were weak.

Such a correlation between the concentrations of chl *a* and nitrogen and phosphorus compounds in reservoirs is noted quite often and cannot be explained unambiguously, since the development of algae does not depend solely on the supply of cells with minerals. The response of phytoplankton to nutrients is mainly determined by the values of the ratios of the concentrations of total nitrogen and phosphorus. It is believed that the development of algae is limited by nitrogen at TN/TP < 10, phosphorus at TN/TP > 15–17, and in the range TN/TP = 10–15, close to the ratio of elements in the cell, there is no biogenic limitation.

During the years of study in Rybinsk Reservoir during the growing season, the TN/TP ratio varied widely (from 4.1 to 66.6), averaging 15.6, which most likely indicates that there is no limitation of phytoplankton development in the reservoir by both elements. This is precisely one of the reasons for the weak pairwise correlations between the elements of nitrogen, phosphorus, and chl *a*. The development of phytoplankton in the reservoir to a large extent depends not only on the supply of cells with minerals, but also on light conditions, the pressure of zooplankton, the dynamics of water masses (especially under the conditions of a well-mixed shallow Rybinsk Reservoir), and differences in the needs of individual groups of algae for nutrients. In the reservoir, the absence of a limitation of phytoplankton development was most often noted (42% of cases) and the limitation in phosphorus and nitrogen was 30 and 28%, respectively.

At TN/TP < 10, the relationship between chl *a* and TP, as well as between chl *a* and TN in the reservoir, can be expressed by the equations

$$\begin{aligned} \text{Chl } a &= -0.007 + 0.2492\text{TP}, \\ \text{Chl } a &= -0.0178 + 0.0584\text{TN}. \end{aligned}$$

At TN/TP = 10–15, there were no connections between these elements, and at TN/TP > 15, the connections were weak.

Since the overall direct relationship between the content of nutrients and the concentration of chl *a* is rather weak, it is possible to determine their influence by indirectly assessing this relationship using the so-called phytoplankton response (“response” or “efficiency”) to nitrogen and phosphorus, which is expressed through the ratio of chl *a*/TP or chl *a*/TN (Kalff and Knoechel, 1978; Hern et al., 1981). Hyun et al., after studying 757 lakes in the United States, concluded that more than a third of the lakes do not obey the Jones–Bachmann equation and introduced the concept of the “response coefficient.” These ratios are the slope coefficients in the equations for the dependence of the chlorophyll content on TN and TP, which reflect the supply of phytoplankton with nitrogen and phosphorus elements, as well as the efficiency of their consumption. In Rybinsk Reservoir, during the period under study, both responses varied in rather wide ranges:

$$\begin{aligned} \text{Chl } a/\text{TP} &\text{ from } 0.003 \text{ to } 1.49 \text{ (average } 0.24), \\ \text{Chl } a/\text{TN} &\text{ from } 0.001 \text{ to } 0.114 \text{ (average } 0.019). \end{aligned}$$

The mean values of the responses obtained were currently similar to those for Rybinsk Reservoir in 1981 and 1982 (Mineeva, 1995) and for lake reservoirs of the Dnieper cascade (Kureishevich and Medved, 2006), in which only responses to phosphorus were studied in the 1980s–1990s. When comparing the average values of chlorophyll responses to TP in the reservoirs of the Dnieper and Volga rivers, it can be noted that they are rather close, despite the fact that the content of TP in the waters of the Dnieper reservoirs is almost two times higher than in the Volga reservoirs, and the water exchange coefficients do not differ significantly. The reason for this may be the lower efficiency of the use of phosphorus compounds by phytoplankton and the large anthropogenic load on the reservoirs of the Dnieper cascade. Seasonal changes are traced for both indicators, with maximums in June and October.

Phytoplankton responses to nutrients are closely related to the chlorophyll content:

$$\begin{aligned} \text{Chl } a/\text{TN} &= 0.0066 + 0.8678\text{Chl } a \\ &\text{(} n = 148, r = 0.86 \text{) (Fig. 4a),} \end{aligned}$$

$$\text{Chl } a/\text{TP} = 0.0985 + 9.9541\text{Chl } a$$

$$(n = 148, r = 0.84) \text{ (Fig. 4b).}$$

Mean values of responses at different TN/P:

$$\text{TN}/\text{TP} < 10; \text{Chl } a/\text{TN} = 0.029,$$

$$\text{Chl } a/\text{TP} = 0.24,$$

$$\text{TN}/\text{TP} = 10\text{--}15; \text{Chl } a/\text{TN} = 0.018,$$

$$\text{Chl } a/\text{TP} = 0.23,$$

$$\text{TN}/\text{TP} > 15; \text{Chl } a/\text{N} = 0.013,$$

$$\text{Chl } a/\text{TP} = 0.27.$$

The Chl *a*/TN responses decreased with an increasing TN/TP ratio:

$$\text{Chl } a/\text{TN} = 0.0285 - 0.006 \text{ TN}/\text{TP}.$$

For the responses to phosphorus, no such regularities were observed.

The responses considered did not depend on the TN/TP ratio; however, for both, high coefficients of multiple correlation with Chl *a*, TN, and TP were obtained. This dependence is quantitatively expressed by the equations

$$\text{Chl } a/\text{TN} = 0.920301\text{Chl } a - 0.014276\text{TN}$$

$$- 0.043191\text{TP} + 0.020501 \text{ (} R = 0.94 \text{),}$$

$$\text{Chl } a/\text{TP} = 11.25791\text{Chl } a - 0.02970\text{TN}$$

$$- 3.15679\text{TP} + 0.30221 \text{ (} R = 0.89 \text{).}$$

CONCLUSIONS

When analyzing pairwise correlations between all studied forms of nitrogen and phosphorus and chl *a* in Rybinsk Reservoir, no significant relationships were revealed for the entire data set. An average degree of connection was noted only between chlorophyll and organic phosphorus ($r = 0.47$). It is shown that there is a significant correlation between chlorophyll *a* and inorganic compounds of nitrogen and phosphorus in certain periods of the study. The phytoplankton responses to TN and TP have been calculated, and a quantitative relationship has been established between the responses, chlorophyll, TN, and TP.

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COMPLIANCE WITH ETHICAL STANDARDS

The author declares that she has no conflict of interest. This article does not contain any studies involving animals or human participants performed by the author.

REFERENCES

- Bikbulatov, E.S., On the method of determination of total phosphorus in natural waters, *Gidrokhim. Mater.*, 1974, vol. 60, pp. 167–173.
- Dillon, P.J. and Rigler, P.H., The phosphorous–chlorophyll relationship in lakes, *Limnol. Oceanogr.*, 1974, vol. 19, no. 5, pp. 767–770.
- Gapeeva, M.V., Razgulin, S.M., and Skopintsev, B.A., Ampoule persulfate method for the determination of total nitrogen in natural waters, *Gidrokhim. Mater.*, 1984, vol. 87, pp. 67–74.
- Hern, S., Lambou, V.W., Williams, L.R., and Tailor, W.D., *Modification of Models Predicting Trophic State of Lakes*, Las Vegas: US EPA, 1981, p. 38.
- Jones, R.A. and Bachman, R.W., Prediction of phosphorous and chlorophyll levels in lakes, *Water Pollut. Cont. Fed-er.*, 1986, vol. 48, no. 9, pp. 2176–2182.
- Kalff, J. and Knoechel, R., Phytoplankton and their dynamics in oligotrophic and eutrophic lakes, *Ann. Rev. Ecol. Syst.*, 1978, vol. 9, pp. 475–495.
- Korneva, L.G., *Fitoplankton vodokhranilishch basseina Volgi* (Phytoplankton of the Volga Basin Reservoirs), Kostroma: Kostromskoi pechatnyi dom, 2015.
- Kureishevich, A.V. and Medved', V.A., Assessment of the ratio between the content of chlorophyll *a* and phosphorus in the water of the Dnieper reservoirs, *Gidrobiol. Zh.*, 2006, vol. 42, no. 1, pp. 35–46.
- Kureishevich, A.V. and Zhuravleva, L.V., Correlation between the chlorophyll *a* content and the concentration of biogenic substances in the water of Dnieper reservoirs, *Gidrobiol. Zh.*, 1997, vol. 33, no. 1, pp. 75–82.
- Mineeva, N.M., *Rastitel'nye pigmenty v vode volzhskikh vodokhranilishch* (Plant Pigments in the Water of the Volga Reservoirs), Moscow: Nauka, 2004.
- Mineeva, N.M. and Razgulin, S.M., On the influence of biogenic elements on the chlorophyll content in the Rybinsk Reservoir, *Vodn. Resur.*, 1995, vol. 22, no. 6, pp. 218–223.
- Mineeva, N.M., Litvinov, A.S., Stepanova, I.E., and Kochetkova, M.Yu., Chlorophyll content and factors affecting its spatial distribution in the Middle Volga reservoirs, *Inland Water Biol.*, 2008, vol. 1, no. 1, pp. 64–72.
- Semenov, A.D., *Prakticheskoe rukovodstvo po khimicheskoy analizu vod sushi* (A Practical Guide to the Chemical Analysis of Land Waters), Leningrad: Gidrometeoizdat, 1977.
- Smith, V.H., The nitrogen and phosphorous dependence of algal biomass in lakes: an empirical and theoretical analysis, *Limnol. Oceanogr.*, 1982, vol. 23, pp. 1248–1255.