Chapter

Chlorophyll and Its Role in Freshwater Ecosystem on the Example of the Volga River Reservoirs

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Abstract

The present chapter has the aim to considerate the most significant aspects of chlorophyll (Chl) applications in the ecological study of fresh waters on the example of the Volga River reservoirs. Throughout the cascade of seven large reservoirs, Chl varied in wide range from 2.5–9 to over 100 μg/L with mean values of 16.5–41.2, 6.7–44.0, and 3.6–10.6 μg/L in the Upper, Middle, and Lower Volga, respectively. Mean Chl values that constantly decrease from the Upper Volga to Lower Volga, characterize Ivankovo, Uglich, and Cheboksary reservoirs as eutrophic, Saratov and Volgograd reservoirs as mesotrophic, while Gorky and Kuibyshev reservoirs in some years are mesotrophic or eutrophic. Chl seasonal dynamics in the Rybinsk reservoir that is dynamics of phytoplankton biomass, is characterized by spring, summer, and, in some years, autumn maxima. Water temperature and water regime of the reservoir are the main factors in Chl dynamics. Years with low-water conditions are favorable for the high Chl concentrations and intensive development of algae. Seasonally average Chl that make from 5 to 22 μg/L during 1969–2019, show variations in trophic state of reservoir from mesotrophic (Chl < 10 μg/L), to moderately eutrophic (10–15 μg/L), and eutrophic (15–22 μg/L).

Keywords: chlorophyll, phytoplankton, spatial and temporal dynamics, long-term trends, environmental factors, freshwater ecosystem, Volga River reservoirs

1. Introduction

The problem of fresh water and the assessment of the ecological state of rivers, lakes, and reservoirs are acute for humanity in the era of anthropogenic stress and global climate change. At the beginning of the twenty-first century, global climate changes continue [1]. There is an increase in surface air temperature, as well as the temperature of water bodies, which have a significant impact on the structure and dynamics of biological communities in aquatic ecosystems [2–4]. Climate is an important driver of the distributional patterns of individual hydrobionts that may cause changes in community composition [5]. An increase in temperature is considered as eutrophication factor that changes the availability of nutrients, promotes an increase in the internal phosphorus load, and also stimulates abundant and prolonged vegetation of cyanoprokaryotes (blue-green algae) that are the causative agents of water bloom [6–8].

Algae are the basis of the trophic pyramid in the freshwater ecosystem. The main ecological role of algae is oxygen generation and photosynthetic production of autochthonous organic matter, which forms the energy basis for organisms of higher trophic levels and for all subsequent stages of the production process in large lakes and reservoirs [9, 10]. Cells of algae contain photosynthetic pigments that are among the most common indicators used in the study of algocenoses. The main pigment of green plants, chlorophyll-a (Chl), is considered to be a universal ecological and physiological marker of algae. Chlorophyll is an optically active component of the aquatic environment due to its ability to absorb light in a narrow wavelength range. In particular, this unique property of Chl has found application in remote sensing of large water areas [11, 12].

The amount of chlorophyll is closely related to the biomass of algae which makes it possible to express biomass in units of this important component of the plant cell and use Chl as an indicator of the temporal and spatial dynamics of phytoplankton [13–17]. A detailed review of studies of the relationship between Chl and algae biomass is given in [18, 19].

The chlorophyll molecule absorbs light quanta and triggers a complex mechanism of photophysical and photochemical reactions, and therefore, it is not surprising that a close relationship is found between Chl concentration and algae photosynthesis [20, 21]. The rate of photosynthesis calculated per unit of Chl, the assimilation number, is used in studies on primary production [22–24]. The changes in assimilation number under various conditions are considered depending on environmental factors, development and composition of algae [25–30]. From the assimilation number and chlorophyll concentration, primary production can be calculated [31].

Planktonic algae serve as indicator organisms of the ecological state in water bodies. In this aspect, Chl plays not only a functional, but also an indicator role in aquatic ecosystems. The content of Chl is the basis for the scales developed to assess the trophic status and water quality of marine and fresh waters [9, 10, 32, 33]. An analysis of these scales made it possible to identify the boundary concentrations of Chl for oligotrophic, mesotrophic, moderately eutrophic, eutrophic, hypertrophic, and polytrophic waters that are <1–3, 3–10, 10–15, 15–30, 30–60, and > 60 μg/L, respectively [34].

The present chapter has the aim to considerate the most significant aspects of chlorophyll applications in the ecological study of fresh waters on the example of the Volga River reservoirs.

2. Materials and methods

Our data includes two large blocks that are (1) the route surveys carried out at 70–80 stations of seven run-of-river reservoirs in the summer of 2015–2020, and (2) seasonal observations during 2009–2019 carried out once or twice a month from May to October at six standard stations in the lake-like Rybinsk reservoir. Throughout the period, we used integral samples obtained by mixing equal volumes of water taken from each meter of the water column with a 1 m Elgmork bathometer. Chl was determined by the standard spectrophotometric method in seven reservoirs of the Volga

River and by the fluorescent method in the Rybinsk reservoir. We have shown good convergence of the results obtained by these methods with coefficient of determination $R^2 = 0.94$ [35].

The spectrophotometric method [36, 37] due to its simplicity and accessibility, is widely used in the study of algae. Phytoplankton was concentrated on membrane filters with a pore diameter of 3–5 μm. The filters were dried in the dark at room temperature and stored in a refrigerator until analysis. Pigments were determined in 90% acetone extract on a Lambda25 PerkinElmer spectrophotometer; Chl concentrations were calculated using the Jeffrey & Humphrey equation [38].

Currently, the attention of researchers is attracted by the determination of Chl using fluorimeters of various designs. Measurements of chlorophyll fluorescence are taken directly in natural water that makes it possible to evaluate a number of parameters without affecting the integrity of phytoplankton and promptly measure a large number of samples. We used a modification of the method based on the specificity of light-harvesting pigment-protein complexes of the main taxonomic groups of freshwater phytoplankton that are diatoms, blue-green (cyanoprokaryotes), and green algae [39]. The fluorescence intensity was measured in the red region of the spectrum ($\lambda \sim 680$ nm) upon excitation with wavelengths of 410, 490, 540 nm before and after the inhibitor of electron transport chain (ETC) was added to the cuvette and the fluorescence yield increases to the maximum level. Chl concentrations were calculated using equations from [40].

We used the available published data including our own papers [20, 41–47] to discuss the results. Standard software packages for a personal computer Statistic10 and MS Excel 2010 were applied for statistical data processing. Spearman's rank correlation coefficient (r_S) was calculated for small number of observations with $n < 30$.

3. Chlorophyll in the Volga River reservoirs

3.1 Short preface

The Volga River, at 3690 km, is the longest river in Europe and 16th in the world historically has attracted the attention of many scientists from different fields. Much of the principal information has been summarized in the monographs [48, 49]. The river network of the Volga looks like a branching tree in the north that evolves into a single trunk rooting as a delta in the Caspian Sea in the south. The Volga catchment area is located on the Russian Plain, covering various latitudinal and climatic zones from the southern taiga to semi-desert. The most of the Volga River from the town of Tver' to Volgograd that is over 2500 km long, is affected by an uninterrupted cascade of eight large shallow reservoirs, considerably slowing the flow velocity of the river. The reservoirs differ in terms of morphometry, optical regime, chemistry, lateral inflow, water exchange, and trophic status [49]. A schematic map of the reservoirs is shown in **Figure 1** and their basic characteristics are given in **Table 1**.

In accordance with the geographical zonality, three sections are distinguished in the cascade that are Upper Volga (56°51′N, 35°55′ E–57°29′ N, 38°17′ E), Middle Volga (58°03′ N, 38°50′ E–53°31′ N, 49°25′ E), and Lower Volga (53°28′ N, 49°42′ E–46°23′ N, 48°02′ E). With a change of conditions in the drainage basin, the total amount of ions (conductivity) increases and the color of the water decreases from the Upper Volga to the Lower Volga. Water transparency increases with the depth in lower

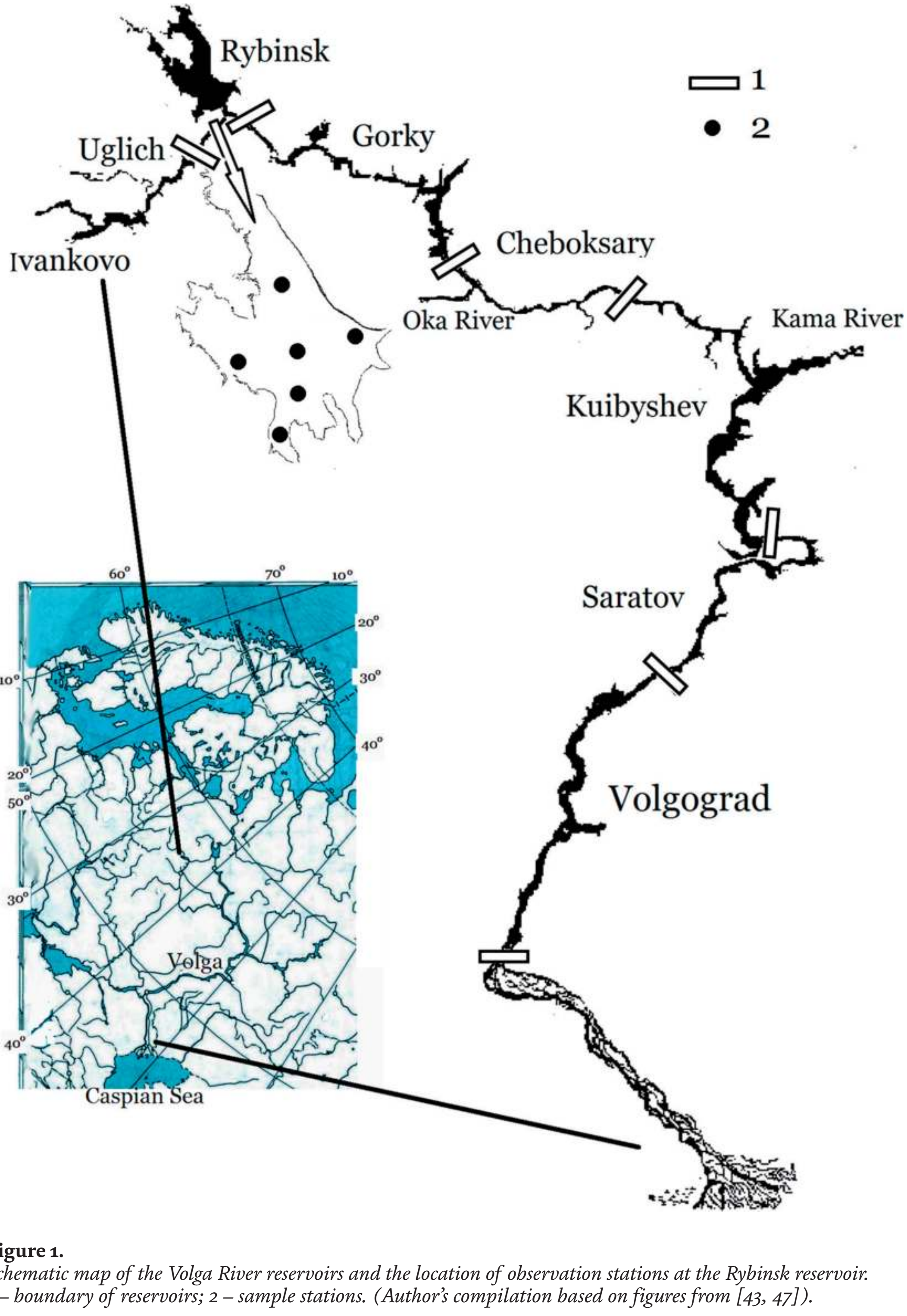

Figure 1.
Schematic map of the Volga River reservoirs and the location of observation stations at the Rybinsk reservoir. 1 – boundary of reservoirs; 2 – sample stations. (Author's compilation based on figures from [43, 47]).

reservoirs. The content of nitrogen and phosphorus compounds in the entire cascade is high enough and do not limit the development of algae [49].

Studies of phytoplankton pigments in the Volga River were started in the middle of the twentyth century, but most of them were carried out at separate reservoirs [41, 50–52]. Our data [43–46] cover the entire cascade and are of interest for a

Parameters	**Upper Volga**		**Middle Volga**			**Lower Volga**	
	Ivankovo	**Uglich**	**Gorky**	**Cheboksary**	**Kuibyshev**	**Saratov**	**Volgograd**
Total water input, km^3 per year	10.07	11.46	49.53	118.89	244.3	248.3	259.2
Surface area, km^2	327	249	1591	1080	6150	1831	3117
Length, km	120	143	430	321	484	348	546
Mean depth, m	3.4	5.0	6.1	4.2	8.9	7.3	10.1
Total storage, km^3	1.12	1.25	8.82	4.60	57.30	12.87	31.45
Water exchange, $year^{-1}$	10.6	10.1	6.1	20.9	4.2	19.1	8.0
Transparency, m	0.8	0.8	1.2	1.2	1.5	2.2	2.0
Water color, Cr-Co degree	53	51	53	42	38	36	34
Conductivity, µSim/cm	240	250	206	355	315	345	424
Total nitrogen, mg/L	1.34	1.27	1.09	1.14	1.08	0.99	0.98
Total phosphorus, µg/L	90	93	68	124	145	127	134

Table 1.
Basic abiotic characteristics of the Volga River reservoirs according to [48, 49].

comparative assessment of the development and state of planktonic algae in reservoirs located in different geographical zones. These are the data needed for environmental monitoring, as well as analysis and forecasting of changes that occur in the aquatic ecosystem under various external impact.

3.2 Chlorophyll distribution and dynamics

The study of summer plankton is of considerable interest, since at this time the negative trends caused by eutrophication or climate change appear in the water ecosystem. Given the great length of the Volga reservoirs, their complex morphometry, and their differences in a number of parameters, the Chl concentrations vary widely in each of them (**Figure 2**). Chl concentrations were typical of summer phytoplankton and generally fell within the same limits as 30 years ago (1989–1991) [43]. The minimum Chl values in all reservoirs were close and amounted to 2.5–9 μg/L, while the maximum values differed to a greater extent. Three groups of reservoirs can be distinguished according to the upper limit of Chl. These are Gorky, Saratov, and Volgograd reservoir with the lowest upper limit of 25–36 μg/L; Uglich and Kuibyshev reservoir with intermediate values of 52–59 μg/L; Ivankovo and Cheboksary reservoir with maximum concentrations over 100 μg/L. In all reservoirs of the Volga, interannual differences in Chl were revealed. Over 6 years of research, Chl concentrations at observation sites differed by 3 and 8 times in the Uglich and Gorky reservoirs, by 50 times in the Cheboksary reservoir, and by 13–16 times in others. The interannual differences in the mean values were much smaller, from 1.6 to 2.6 times only (**Table 2**). The results of ANOVA analysis (**Table 3**) show that the interannual difference in Chl is significant in the Uglich and Gorky reservoirs ($p < 0.01$), is on the verge of significance in the Ivankovo reservoir, and is insignificant in the other four reservoirs.

The distribution of phytoplankton over the water area of the reservoirs was nonuniform. The coefficients of variation of mean Chl concentrations in most cases were 50–70% and exceeded 100% in Cheboksary reservoir (**Table 2**). The heterogeneity of Chl distribution is due to the large extent and complex morphometry of reservoirs, the presence of water masses of different genesis, the inflow of tributary waters, changes in the flow regime in different areas, and surge phenomena. The features of Chl distribution over the water area of the reservoirs are generally preserved and repeated over a long period [43–46]. Higher Chl concentrations are usually noted in areas isolated from the Volga channel; in estuarine sections of tributaries; in coastal shallow waters and bays; in the waters of the tributaries themselves. The amount of Chl in these areas is 1.5–3 times higher than at deep channel section. In all years, the largest tributary of the Volga, the Oka River, stands out with a very high Chl concentration [43–46]. When it flows into the Cheboksary reservoir, Chl increases by an order of magnitude up to 100 μg/L and more. The waters of the Oka River, which differ from the Volga in high mineralization, can be traced in the reservoir for a long distance, creating significant chlorophyll gradients [51].

Throughout the Volga cascade, there is a steady decrease in Chl from the reservoirs of the Upper Volga to the reservoirs of the Lower Volga (**Figure 3**). The same trend was noted in 1989–1991 [43] and has not changed over a quarter of a century. A similar distribution is also observed for the phytoplankton biomass [8]. The explanation is the increase in flow velocity and volume of runoff downstream the Volga, as well as a decrease in the volume of lateral tributaries. It is the water conditions that limit the development of phytoplankton in the Volga to the greatest extent. This is evidenced

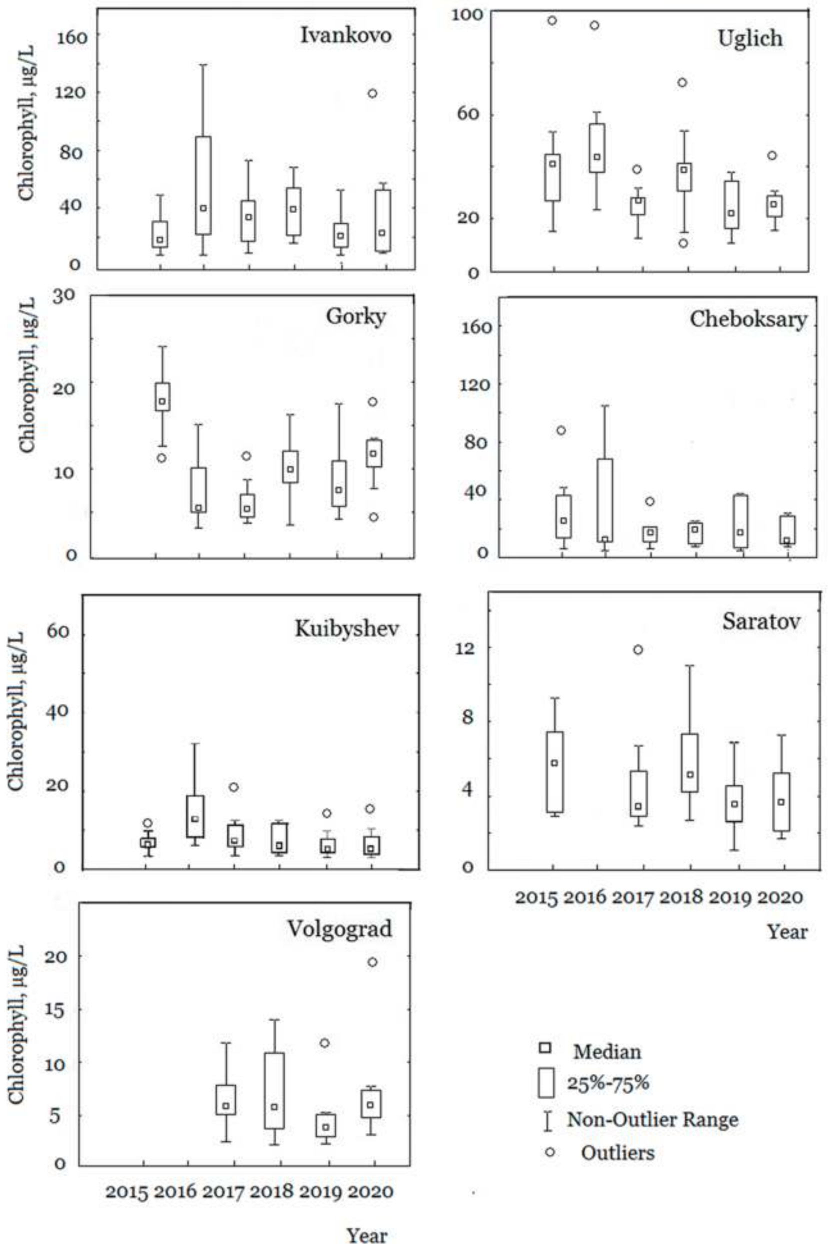

Figure 2.
Box plots of chlorophyll concentrations in the Volga River reservoirs in 2015–2020. Unpublished data.

by the negative relationship between average Chl concentrations in the reservoirs and the total volume of inflow for May–October (**Figure 4**). Similarly, in unregulated conditions in the river Thames, algae abundance decreased in years of high water flow [53], and high chlorophyll concentrations in the Lower Mississippi were noted during periods of low flow [54].

In all reservoirs, interannual changes in Chl are observed, which are determined by the weather conditions of the years and the conditions of water content. However, the average concentrations of Chl over the past 6 years characterize the Ivankovo, Uglich, and Cheboksary reservoirs as eutrophic (Chl is over 15 mg/L), while the Saratov and Volgograd reservoirs are mesotrophic with Chl up to 10 mg/L. The

Reservoir	2015	2016	2017	2018	2019	2020
Ivankovo	24.0 ± 4.0 (54)	20.7 ± 3.7 (56)	22.5 ± 3.6 (47)	41.2 ± 7.3 (58)	38.3 ± 5.9 (55)	23.8 ± 2.0 (60)
Uglich	25.5 ± 2.8 (32)	17.7 ± 3.0 (47)	16.5 ± 1.9 (29)	26.1 ± 4.6 (45)	20.4 ± 2.8 (49)	17.4 ± 4.1 (57)
Gorky	18.4 ± 1.1 (21)	7.5 ± 1.3 (56)	6.7 ± 0.8 (40)	13.1 ± 1.4 (41)	10.1 ± 1.5 (51)	12.1 ± 1.8 (63)
Cheboksary	29.6 ± 8.1 (81)	16.9 ± 6.7 (102)	17.8 ± 6.1 (90)	25.0 ± 0.8 (107)	44.0 ± 15.8 (117)	25.3 ± 10.1 (143)
Kuibyshev	6.1 ± 0.8 (42)	14.8 ± 2.8 (57)	8.3 ± 2.0 (48)	9.8 ± 2.6 (117)	6.1 ± 0.9 (61)	11.9 ± 2.5 (64)
Saratov	5.7 ± 1.0 (41)	—	4.9 ± 1.5 (72)	10.6 ± 2.8 (78)	3.6 ± 0.6 (51)	8.5 ± 2.4 (48)
Volgograd	—	—	6.7 ± 1.0 (44)	9.6 ± 2.2 (86)	4.3 ± 0.7 (56)	10.1 ± 2.7 (25)

Table 2.
Chlorophyll content in the Volga River reservoirs in the years of study according to [46] with additions (mean values with standard error, μg/L; in brackets coefficient of variation, %; dash is missing data).

Reservoir	SS	df	MS	F	p
Ivankovo	11,002	5	2200	2.25	0.06
Uglich	4517	5	903	3.40	0.01
Gorky	1235	5	247	13.5	0.00
Cheboksary	2777	5	555	0.59	0.71
Kuibyshev	594	5	119	1.41	0.23
Saratov	60	4	15	0.83	0.52
Volgograd	208	3	69	2.12	0.11

Table 3.
Comparison of the mean chlorophyll concentrations in the Volga River reservoirs in the years of study using one-way analysis of variance (ANOVA) (SS – sum of squared deviations, df – number of degrees of freedom, MS – mean square, F – Fisher's test, p – significance level). $F_{tabl} > 2.30$. Unpublished data.

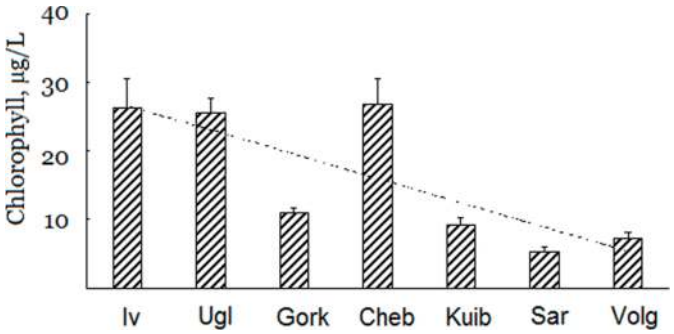

Figure 3.
The course of chlorophyll in cascade of the Volga River reservoirs. Average values for 2015–2020 with standard error. Dotted line is a trend line. Unpublished data. Iv – Inankovo reservoir, Ugl – Uglich reservoir, Gork – Gorky reservoir, Cheb – Cheboksary reservoir, Kuib – Kuibyshev reservoir; Sar – Saratov reservoir, Volg – Volgograd reservoir.

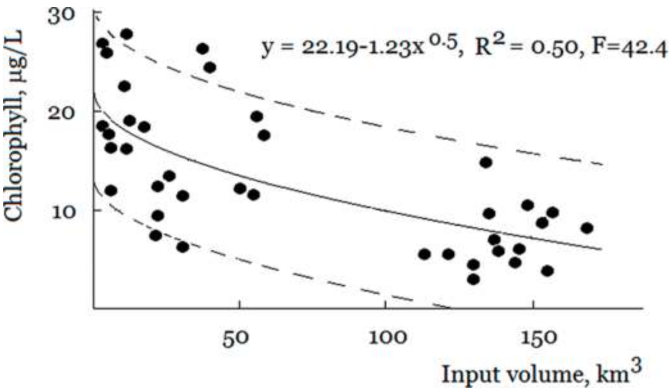

Figure 4.
Correlation between chlorophyll content in the Volga River reservoirs and the total volume of inflow for May–October in 2015–2020 according to [46]. The dotted line is the 95% confidence interval. The volume of inflow is calculated according to the data of the open website of RusHydro http://www. rushydro.ru/hydrology/informer/?date.

trophic status of the Gorky and Kuibyshev reservoirs varies from mesotrophic to moderately eutrophic and eutrophic (**Table 2**).

The assessment of the current trophic status of reservoirs in some cases differs from the assessment in 1989–1991 [43]. At the end of the twentieth century, the Uglich, Saratov, and Volgograd reservoirs were mesotrophic, the Kuibyshev reservoir was moderately eutrophic, and the Ivankovo, Gorky, and Cheboksary reservoirs were eutrophic. Chl concentrations now correspond to the eutrophic type (i.e., higher trophy category) for the Uglich reservoir and moderately eutrophic (lower trophy) for the Gorky reservoir. The values obtained for the Ivankovo, Uglich, and Cheboksary reservoirs during 2015–2020, related to the same trophic gradation, while for the Gorky and Kuibyshev reservoirs, they were different. These variations testify to the high dynamism of the development of the ecosystems of the Volga reservoirs.

4. Chlorophyll in the Rybinsk reservoirs

4.1 Short preface

Rybinsk reservoir, the third stage of the Volga River cascade, located in the southern taiga subzone (58°00′–59°05′ N, 37°28′–39°00′ E) (**Figure 1**). It is a large relatively shallow lake-like water body of slow water exchange of 1.4 year^{-1} [42]. The ratio of the surface area (4500 km^2) and the average depth (5.6 m) is very high and equal to ~800. It indicates a high degree of openness of the reservoir [55] that is subject to frequent wind mixing. As a result, there is a decrease in water transparency and also resuspension of nutrients from bottom sediments.

The Rybinsk reservoir is one of the few large reservoirs in the world where systematic regular observations of the chlorophyll content have been carried out. The research began in 1969 continued for more than 50 years under the guidance of my colleague, teacher, and mentor Dr. Inna Pyrina. The results of long-term study of the seasonal and interannual Chl dynamics and its relationship with regional and global environmental factors were published in a series of original papers and summarized in monographs [20, 41, 42].

4.2 Seasonal dynamics of chlorophyll

The seasonal development of plankton is an annual recurring process influenced by external factors and internal biotic interactions [56]. The development of phytoplankton in the Rybinsk reservoir during the open water period corresponds to the classical PEG model [57]. A short spring maximum with Chl concentration in different years from 15 to 50 μg/L is constantly formed in May–early June at water temperatures from 6–9°C to 11–15°C. In late May–early June, the Chl content becomes below 10 μg/L and remains low for 2–4 weeks. During this period there is a seasonal change of phytoplankton communities [8]. The summer maximum, at which Chl can exceed 100 μg/L in some parts of the water area, covers a long period in July–September. Warming up of the water mass to the maximum and its subsequent cooling occurs during this period. In autumn, the Chl content is usually below 10 μg/L, but in some years, it increased to 20–30 μg/L. The timing of the onset of Chl maxima, their duration, quantity, and the ratio of values vary in different years (**Figure 5**). This is explained by features of development conditions for the algae in a large shallow reservoir, which is an active dynamic environment. The course of seasonal succession of phytoplankton in such an environment is subject to frequent disturbing external influences [57–59], which include wind mixing [60, 61], and in the reservoirs also the operation of hydraulic structures. Diatom algae dominate the phytoplankton of the reservoir in spring and autumn [8]. The diatom maximum during these periods is usually observed in water bodies of the temperate zone [56, 57]. Active wind mixing of the water column promotes water circulation and maintenance of cells in suspension, and also provides an influx of nutrients [59]. The summer phytoplankton community is formed by blue-green algae (cyanoprokaryotes) and diatoms [8]. Cyanoprokaryotes develop abundantly at stable anticyclonic weather with a predominance of calm conditions; active hydrodynamics which is provided by wind mixing of the water column is favorable for diatoms.

In a generalized form, according to the data of long-term observations, five periods are distinguished in the seasonal cycle of phytoplankton in the Rybinsk reservoir [47]. The main parameters of these periods are given in **Table 4**. Each period is characterized by uniform temperature and transparency, which is an indicator of underwater light conditions. Variation coefficient of Chl is minimal at early summer during the seasonal change of communities and is significantly higher during the period of spring and summer phytoplankton maxima, indicating a change in the stability of algocenoses during the growing season.

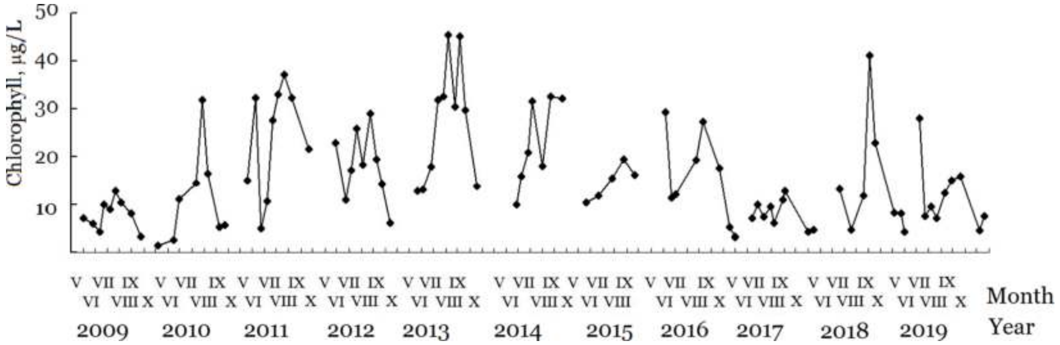

Figure 5.
Seasonal dynamics of chlorophyll in the Rybinsk reservoir during 2009–2019 according to [47].

4.3 Long-term dynamics of chlorophyll

To analyze and predict the changes that occur in biological communities under anthropogenic pressure and climate change, long-term observations are required. Such observations are carried out in water bodies of the world [62–68]. According to published data including our own [20, 35, 42, 43], over the entire period of observations since 1969, the Chl content in the Rybinsk reservoir varied by two orders of magnitude, from 1 to 3 to more than 100 µg/L. This range is observed even during one growing season and causes outliers in the scatterplots (**Figure 6**).

Seasonal average values vary within smaller limits from 5 to 22 µg/L. The long-term dynamics of Chl looks like a broken line with ups and downs (**Figure 7**). This shows the reaction of the community to changing external conditions, which have a multicomponent and complex effect on the development of phytoplankton. An

Parameter	Spring	Early summer	Mid summer	Late summer	Autumn
n	54	92	218	86	89
Chl, µg/L	15.9 ± 1.9 (90)	8.9 ± 0.6 (58)	20.4 ± 1.0 (73)	21.2 ± 1.6 (72)	6.3 ± 0.5 (73)
Temperature, °C	9.9 ± 0.5 (38)	15.7 ± 0.3 (19)	20.4 ± 0.2 (11)	15.0 ± 0.2 (12)	7.2 ± 0.3 (36)
Transparency, m	1.20 ± 0.03 (24)	1.11 ± 0.03 (25)	1.13 ± 0.02 (23)	1.06 ± 0.04 (32)	1.12 ± 0.04 (37)
N_{min}, mg/L*	0.45	0.31	0.19	0.14	0.14
P_{min}, µg/L*	21	18	21	26	65
TN, mg/L*	0.99	1.02	0.91	1.02	0.93
TP, µg/L*	48	48	64	67	140

*Note. * – data obtained in 2001–2012 according to [42]; N_{min} – nitrates, P_{min} – phosphates, TN – total nitrogen, TP – total phosphorus.*

Table 4.
Characteristics of the environmental conditions during five periods of phytoplankton seasonal succession in the Rybinsk reservoir in 2009–2019 according to [47] (mean values with standard error, in brackets coefficient of variation, %; n – observation number).

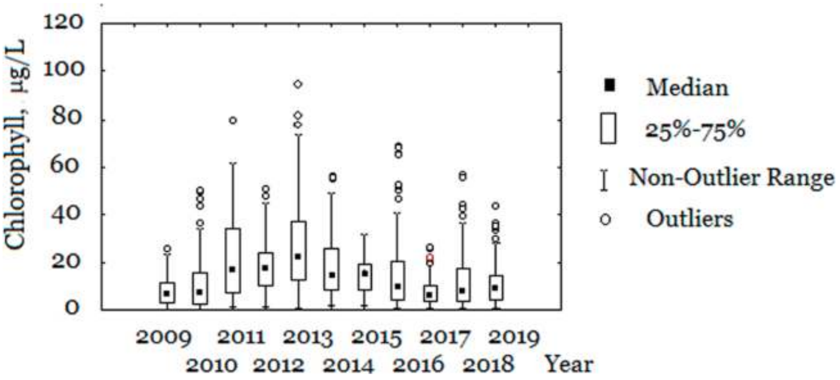

Figure 6.
Box plots of chlorophyll concentrations in the Rybinsk reservoir in 2009–2019 according to [47].

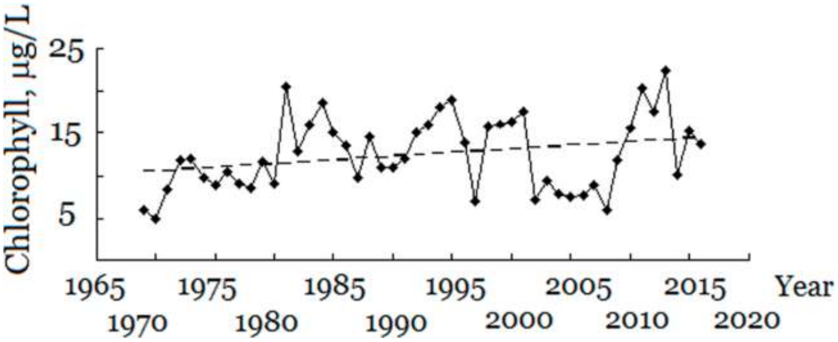

Figure 7.
Long-term dynamics of average annual chlorophyll concentrations in the Rybinsk reservoir according to [42] with additions. Dotted line is trend line.

analysis of long-term data reveals two key effects on interannual Chl variations in the Rybinsk reservoir. Temperature that belongs to the universal and irremovable factors of the environment is the first of them. Temperature is the main factor in the development, seasonal dynamics and spatial distribution of algae, as well as the factor of their geographical distribution and formation of the primary production of water bodies [69–71].

Under global warming, a steady increase in the average water temperature for May–October at a rate of 0.8°C per 10 years has been revealed in the Rybinsk reservoir since 1976 [42]. Against this background, there is a reliable trend towards an increase in average annual Chl value over a 50-year observation period at a rate of 0.4 ± 0.03 µg/L per year ($R^2 = 0.75$, $p < 0.05$) (**Figure 7**). The Spearman correlation coefficient between seasonal average Chl and temperature is not high ($r_S = 0.53$, $p < 0.05$) but it confirms this effect.

The recurrence in Chl dynamics is associated with the second key factor which is the water regime of the reservoir in the years of observation. Negative Spearmen correlation coefficients were obtained between Chl and parameters of water regime: $r_S = -0.65$ for inflow volume and $r_S = -0.85$ for water level. The water regime, in turn, is associated with the cycles of general moisture. High-water periods with cyclonic weather are characterized by increased surface inflow, high water level, high wind activity, and lower temperatures. In low-water years, the anticyclonic type of weather prevails with little precipitation, low reservoir level, increased heating, and a predominance of calm. It is dry years that conditions are favorable for the intensive development of algae and especially the summer species [8, 43, 72, 73]. For the reservoir region, this situation was repeated once every few years over a 50-year period, namely in 1972–1973, 1981, 1984, 1994–1995, 1999–2001, 2010–2013. The conditions of these years served as a trigger for the subsequent increase in Chl, which gradually decreased after the rise, but generally remained at a higher level than in the previous years (**Figure 7**).

The annual increase in Chl over the entire period of research varied and amounted to 1.2 ± 0.1 µg/L in 1969–1984, 2.2 ± 0.3 µg/L in 1987–1996, and 2.4 ± 0.4 µg/L in 2008–2019. In recent years, under the global warming, this increase has become higher, indicating intensification of the eutrophication process. A particularly strong rise in Chl values was noted after 2010, when sunny weather at an anomalously high air temperature persisted for 40 days on the territory of European Russia [74]. Periodicity in rises and falls of Chl is close to the 11-year cycle of solar activity estimated by Wolf numbers ($r_S = 0.83$). The same was noted earlier for a shorter

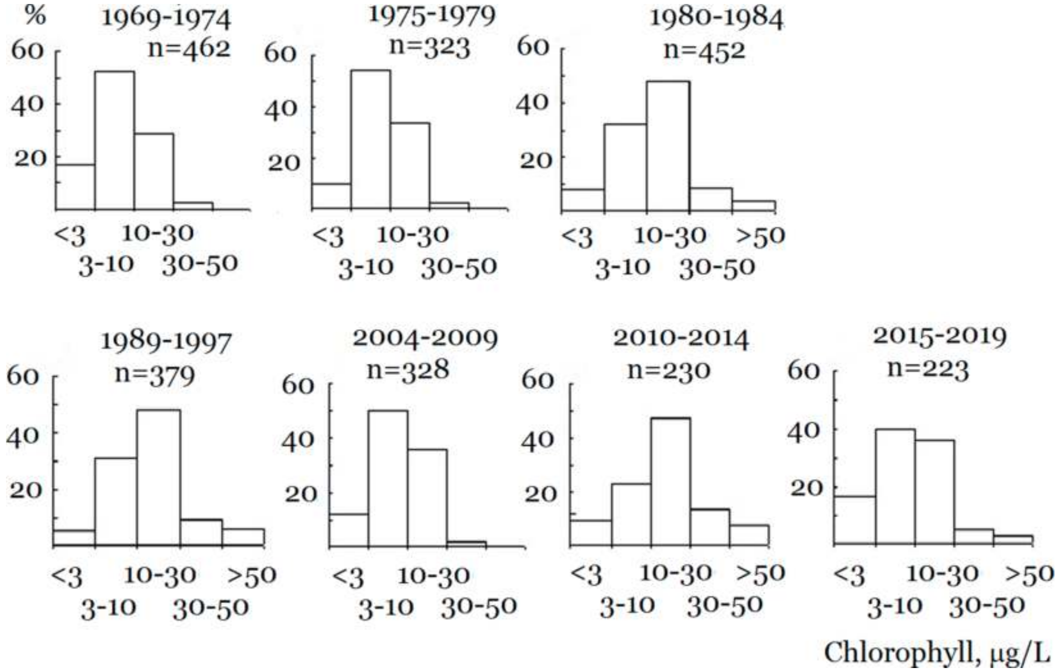

Figure 8.
Occurrence rate of chlorophyll in the Rybinsk reservoir in different periods of 1969–2019 according to [42] with additions (% of the total observation number n).

observation period at the Rybinsk reservoir, as well as for the long-term dynamics of phytoplankton productivity in other water bodies [72, 73, 75, 76].

Seasonally average Chl concentrations serve as the basis for the trophic classification of water bodies [9, 32, 33]. The data in **Figure 7** show that during the 51 years of observation, the reservoir was characterized as mesotrophic 18 times (mean Chl less than 10 μg/L), as moderately eutrophic 15 times (10–15 μg/L), and as eutrophic 18 times (15–22 μg/L).

General level of phytoplankton development and the trends in its long-term variations are well illustrated by the occurrence rate of Chl concentrations (**Figure 8**). In the first 10 years of observations (1969–1979), mesotrophic waters with a pigment concentrations of less than 10 μg/L prevailed in the reservoir. In the 80s and 90s twentieth century the share of eutrophic waters with Chl content equal to 10–30 μg/L, increased significantly. At the same time, the upper limit of Chl values increased, reaching 100 μg/L and above. In the early 2000s there has been a trend towards a decrease in the level of trophy, and the histogram of Chl frequency distribution repeated that of the late 1970s. Data of 2010–2014 showed a sharp rise in values with an absolute (about 70% of the total number of observations) predominance of eutrophic and highly eutrophic waters. In recent years, with high water content and a decrease in temperature, mesotrophic type waters began to predominate again, and the amount of high Chl concentrations decreased to 40%.

5. Conclusion

Chlorophyll-a, the main pigment of the green plants, serves as a universal ecological and physiological marker of biomass, photosynthetic activity, and production capabilities of algae. The study of the most significant aspects of chlorophyll applications in freshwater ecology on the example of the Volga River reservoirs made it possible to consider the spatial and temporal dynamics of phytoplankton.

Route surveys carried out on seven run-of-river reservoirs of the Volga, revealed a wide range of Chl in each of them with minimum values of 2.5–9 μg/L to maximum values from 25 to 36 to over 100 μg/L. The average Chl values obtained in different years differed to a lesser extent with a significant distinction in case of the Uglich and Gorky reservoirs only. Chl concentrations obtained in 2015–2020 were typical of summer phytoplankton and generally fell within the same limits as 30 years ago (1989–1991). The distribution of phytoplankton over the water area of the reservoirs was non-uniform due to the large extent and complex morphometry of reservoirs, the presence of water masses of different genesis, the inflow of tributary waters, changes in the flow regime in different areas, and surge phenomena. The steady decrease in Chl content from the reservoirs of the Upper Volga to the reservoirs of the Lower Volga is due to an increase in flow velocity and volume of runoff downstream the Volga, as well as a decrease in the volume of lateral tributaries. According to the average concentrations of Chl over the past 6 years, currently the Ivankovo, Uglich, and Cheboksary reservoirs are eutrophic, the Saratov and Volgograd reservoirs are mesotrophic, while the trophic status of the Gorky and Kuibyshev reservoirs varies from mesotrophic to moderately eutrophic and eutrophic.

Regular seasonal observations during 2009–2019 carried out at lake-like Rybinsk reservoir showed that phytoplankton development during the open water period corresponds to the classical PEG model with a short spring Chl maximum, long period summer maximum, and, in some years, a short autumn rise. The timing of the onset of Chl maxima, their duration, quantity, and the ratio of values change depending on the conditions of the year. The long-term dynamics of Chl over a 50-year period since 1969 looks like a broken line with ups and downs, reflecting the community's response to changing external conditions. Two main factors that are temperature and water regime have a significant impact on the long-term development of planktonic algae. Seasonally average Chl concentrations that serve as the basis for the trophic classification of water bodies show that, depending on environmental conditions, the trophic status of the Rybinsk reservoir varies from mesotrophic to eutrophic. In recent years, under the global warming, the rate of eutrophication has been increasing.

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Conflict of interest

The author declares no conflict of interest.

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