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Multi-Year Variability of Organic Matter Content in Water of Rybinsk Reservoir

E. M. Bukbulatova and I. E. Stepanova

Papanin Institute for Biology of Inland Waters, Russian Academy of Sciences, pos. Borok, Nekouzskii region, Yaroslavl oblast, 152742 Russia
e-mail: iris@ibiw.yaroslavl.ru; bem@ibiw.yaroslavl.ru

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Abstract—This study of the Rybisk Reservoir tributaries and stretches investigates the content of organic matter during the years of medium water level (1981–1982) and evaluates the contribution of selected components in its total amount. In 2000–2007, organic matter content has been monitored in the Tsentralnii and the Volzhskii reaches occupying the major of the reservoir area, and annual and seasonal dynamics of organic matter content in the reservoir has been tracked. High correlation between the organic matter indices and the annual flow has been shown. This suggests that the latter plays a predominant role in the formation of the total organic matter content.

Keywords: Rybisk reservoir, organic matter

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INTRODUCTION

Rybinsk Reservoir belonging to three administrative units (Yaroslavl, Vologda, and Tver regions) is the largest basin of the Volga–Kama Cascade, its area and total volume at normal headwater level being of 4550 km^2 and 25.4 km^3, respectively. The reservoir is shallow, average depth at normal headwater level being of 5.6 m. The major (about 2/3) water influx of the reservoir comes from rivers Volga, Mologa, and Sheksna. The rivers valleys are occupied by corresponding stretches, extended relatively narrow areas. The major part of the reservoir water surface is occupied by the Tsentralnii stretch [1].

This worked aimed to analyze own data of long-term monitoring of organic matter content (OMC) in the reservoir water and to elucidate the major factors of the organic matter (OM) formation.

Organic matter (OM) is one of the most important constituents of a water reservoir. From 1941 to early 1960s its content (OMC) in Rybinsk Reservoir was expressed it terms of chromaticity and permanganate demand (permanganate oxidability) as determined in the hydrometeorological service laboratory, the both parameters giving indirect information majorly correlated with the content of colored oxidizable humic compounds, one of a number of organic compounds found in the water. Colorless aqueous humus (produced by aquiprata and incoming with ground water and atmospheric precipitate) remained almost unstudied. The OMC could be better characterized with the chemical oxygen demand (COD) upon the sample oxidation with potassium dichromate. Since 1963 the OMC has been characterized with the most relevant parameter, organic carbon content C_{org} determined via dry combustion of evaporated sample [2]. It was demonstrated that the coefficient to recalculate permanganate oxidability into C_{org} was quite variable (0.6 to 1.3) depending on the Rybinsk Reservoir sampling site [3]. The COD/C_{org} ratio ranged 2.2–4.2 for the involatile (55°C) fraction of Volga reservoirs [4]. Nevertheless, the early indirect data gives remarkable opportunities for comparative analysis. In 1969 we were the first to directly determine the content of organic carbon in water of Volga reservoirs without prior evaporation, taking advantage of the specially designed photochemical and persulfate methods [5]. The C_{org} was determined in the evaporated specimens as well. It was demonstrated that the losses due to evaporation were generally low but

Table 1. Parameters of water flow of uncontrolled tributaries of Rybinsk reservoir [7]

River	Water catchment area, km^2	Amount of forests, %	Amount of bogs, %
Mologa	19700	60–70	–
Chagodosha	9680	72	26
Suda	5255	70–80	25–30
Sit’	1900	35	5
Sogozha	2900	68	0.4
Yagorba	458	61	1.2
Ukhra	1590	56	1.2

Table 2. Extreme and average (in parentheses) of organic matter content (mg C/L) in 1981

Stretch	Winter	Spring	Summer	Autumn	Year overall
Volzhskii	8.7–14.1(11.2)	6.2–9.2(7.7)	8.6–13.8(11.8)	8.0–11.6(9.6)	6.2–14.1(10.1)
Tsentralnii	8.1–15.6(11.3)	8.0–11.1(9.6)	9.8–13.1(11.6)	8.0–11.4(10.2)	8.0–15.6(10.7)
Molozhskii	11.5–15.6(13.6)	12.1	15.3–23.2(18.3)	10.0–11.5(10.8)	10.0–23.2(13.7)
Sheksninskii	8.5–9.4(8.9)	9.7–15.1(13.1)	10.6–12.2(11.4)	9.2–12.9(10.8)	8.5–15.1(11.1)
Reservoir overall	8.1–15.6(11.3)	6.2–15.1(10.6)	8.5–23.2(13.4)	8.0–12.9(10.5)	6.2–23.2(11.4)

Table 3. Extreme and average (in parentheses) of organic matter content (mg C/L) in 1982

Stretch	Winter	Spring	Summer	Autumn	Year overall
Volzhskii	7.2–9.7(9.0)	7.0–9.7(8.9)	10.1–13.7(12.3)	9.2–10.1 (9.9)	7.0–13.7 (10.0)
Tsentralnii	8.4–11.4(9.8)	9.8–13.3(11.0)	8.5–10.6 (9.8)	7.0–13.7 (9.0)	7.0–13.6 (9.9)
Molozhskii	–	13.1– 15.3(14.2)	10.3–11.4(10.9)	11.8	10.3–15.3 (12.3)
Sheksninskii	8.4–11.8(10.1)	12.1–13.0(12.6)	8.2–11.6 (10.1)	9.0–12.1 (10.7)	8.2–13.0 (10.9)
Reservoir overall	7.2–11.8(9.6)	7.0–15.3 (11.7)	8.2–13.7 (10.8)	7.0–13.7 (10.4)	7.0–15.3 (10.8)

could be up to 20% in certain cases [4]. In this work we discuss the OMC data as determined using the persulfate method, and the chromaticity was determined using the chromium-cobalt scale [8].

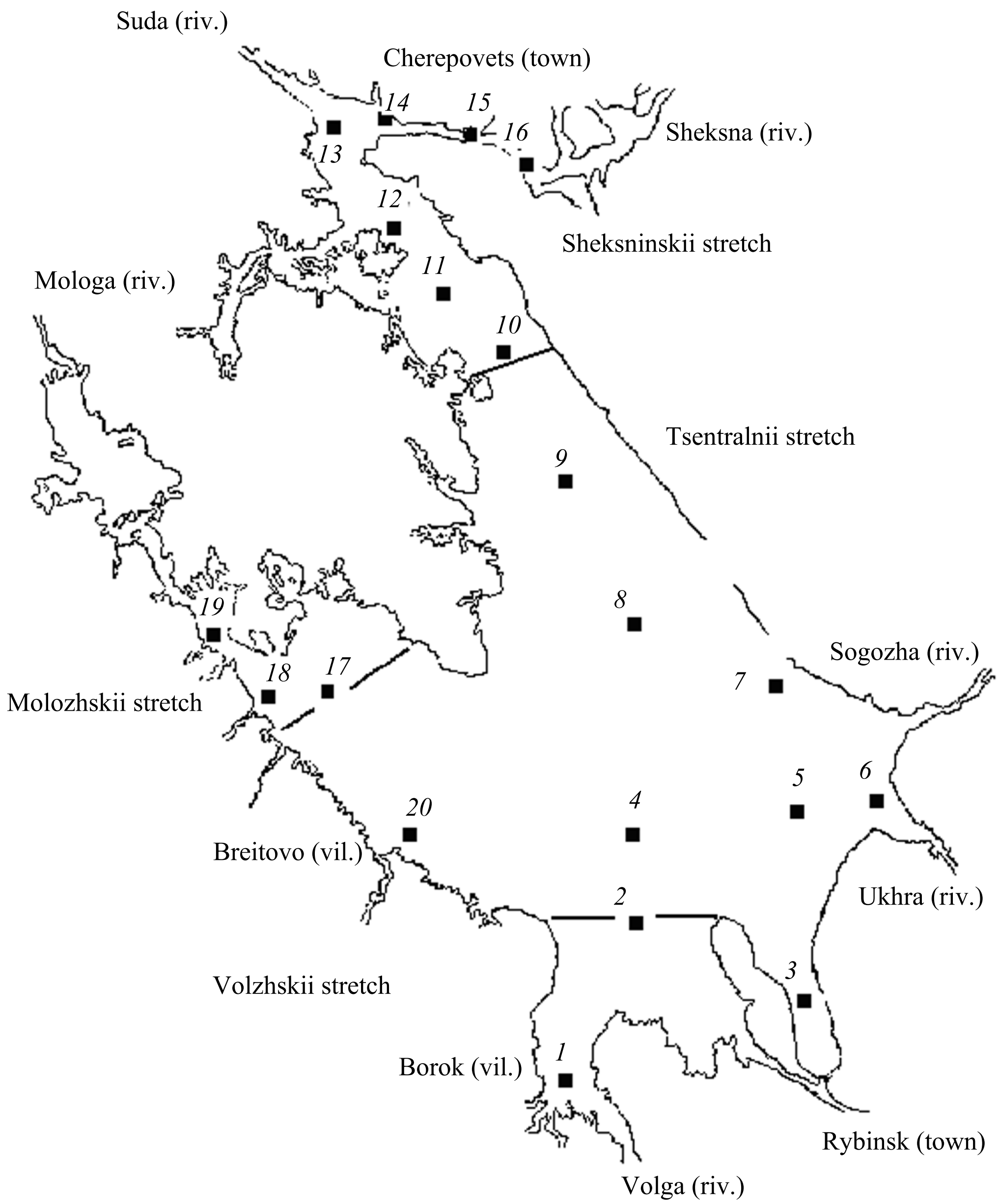
RESULTS AND DISCUSSION

The total OMC in water reservoir is a combined result of the allochthonous compounds income with river flow, atmospheric precipitate, industrial flow, of the autochthonous OM production, of the income from the bed sit, and finally of the opposite processes of physical removal and biochemical decomposition of OM. In 1981–1982 (the conditions close to the medium water level) we thoroughly investigated the Rybinsk Reservoir stretches and tributaries (see figure) to elucidate the above-mentioned components of OMC.

In addition to the monitoring stations marked in the figure, we also sampled water near the site of emission of industrial and domestic wastes of Cherepovets town.

The river flow gave the major contribution to the annual aqueous balance of Rybinsk reservoir. Basins of the rivers entering the reservoir were significantly different in the amount of forests, bogs, ploughed fields as well as in the soil and hydrology conditions (Table 1) [6].

The corresponding draining waters were differently enriched with organic compounds, including the colored humic compounds. During the high water periods



Map of monitoring stations location at Rybinsk Reservoir. (*1*) Koprino, (*2*) Mologa, (*3*) Volkovo, (*4*) Navolok, (*5*) Vsekhsvyatskoe, (*6*) Ukhra, (*7*) Izmailovo, (*8*) Srednii Dvor, (*9*) Gayutino, (*10*) Myaksa, (*11*) Lyubets, (*12*) Vaganikha, (*13*) Ust'e Sudy, (*14*) Ust'e Koshty, (*15*) Yagorba, (*16*) Kabachino, (*17*) Pervomaiskie ostrova, (*18*) Ust'e Sebly, (*19*) Protiv'e, (*20*) Bre'tovo .

water of Chagodosha (tributary of Mologa) and Suda rivers (with amount of bogs ranging from 30 to 80%) was up to 20 mg C/L, and the chromaticity reached 225 degrees of the chromium-cobalt scale. The respective parameters of less bogged and forested tributaries were of 7.0–14.7 mg C/L and 40–165 deg. Our data have revealed that dynamics of allochthonous OM income was correlated with that of the runoff of the major tributaries; in particular, the extremes of OMC corresponded to the mean water and high water seasons. In 1981 the rivers flow gave 428×10^3 t C input to the reservoir OMC, the corresponding value in 1982 was of 393×10^3 t C. The external loading of OM was distributed between the reservoir stretches as follows: Volzhskii 31%, Molozhskii 28%, Sheksninskii 27%, and Tsentralnii 7% [7].

The in-pore solution of grey and grey arenaceous sludges of Rubinsk reservoir contained 19–64 mg C/L whereas the corresponding value for the water stratum

Table 4. Extreme and average (in parentheses) of organic matter content (mg C/L) and chromaticity (deg) of water at reference stations in 2001–2007

Year	Spring	Summer	Autumn	Year overall	Year	Spring	Summer	Autumn	Year overall
C_{org}		Chromaticity			C_{org}		Chromaticity		
2001	–	9.6–14.3 (11.8)	9.3–15.7 (12.3)	9.3–15.7 (12.1)	2001	–	45–65 (54)	50–60 (56)	45 – 65 (55)
2002	–	10.5–3.2 (11.2)	8.0–17.2 (12.5)	8.9–17.2 (11.9)	2002	–	35–50 (43)	40–45 (41)	35 – 50 (42)
2003	–	12.1–4.0 (12.8)	8.9–17.2 (12.5)	8.9–17.2 (12.7)	2003	–	60–65 (63)	55–70 (61)	55 – 70 (62)
2004	12.4–19.3 (15.3)	12.5–18.5 (14.8)	14.5–16.9 (16.0)	12.4–18.5 (15.4)	2004	80–160 (68)	60–105 (72)	50–65 (58)	50 – 105 (65)
2005	–	11.5–26.4 (17.2)	11.9–17.1 (14.9)	11.5–26.4 (16.1)	2005	–	50–100 (68)	50–60 (53)	50 – 100 (61)
2006	10.3–13.8 (11.7)	10.3–14.4 (12.0)	11.3–14.4 (13.0)	10.3–14.4 (12.2)	2006	55–65 (59)	40–50 (44)	35–45 (39)	35 – 50 (42)
2007	10.1–17.4 (14.8)	9.8–17.3 (13.7)	11.3–16.2 (14.4)	9.8–16.2 (14.3)	2007	60–75 (67)	35–70 (54)	45–60 (51)	35 – 70 (53)

was of 10.4–11.4 mg C/L, meaning that there was a constant gradient of OMC favoring the organic compounds flux from the sediments to water (giving about 80×10^3 t C yearly).

The precipitates onto the water surface of the reservoir gave 1.7–2.7 (rain) and 0.8–2.4 mg C/L (snow), the related OM income in 1982–1983 being of 3×10^3 and 3.9×10^3 t C, respectively.

The domestic and industrial wastes of Cherepovets town (Sheksninskii stretch) were rich in organic carbon (20 and 43 mg/L, respectively), but their low volume corresponded to the total input of OM of 1.9 and 2.3×10^3 t C.

Hence, the rivers runoff gave the major contribution to the influx of allochthonous OM.

The content of OM in water of Rybinsk Reservoir is given in Tables 2 and 3.

The Molozhskii stretch is fed with water of Mologa river (and its major tributary Chagodosha river), its basin being forested by 60–70% and significantly bogged. The spring colored water was preserved in the stretch water till August, and then they were diluted and replaced with the low-colored mean water. The chromaticity was changed from 120 to 45 degrees. The extremely high C_{org} value (23.2 mg/L) in August, 1981 was due to strong phytoplankton development.

The C_{org} values at Sheksninskii stretch were of 8.5–15.1 mg/L in 1981 and of 8.2–13.0 mg/L in 1982 (Tables 2 and 3). The upper range was typical of the lower region of the stretch being subject to the influence of Suda river (rich in humic compounds) and of domestic and industrial wastewater of Cherepovets town. The lower values were typical of the upper region (lower pool of Sheksninskaya hydroelectric power station). There, the OMC variation was due to the effect of water coming from the Sheksna Reservoir. The season-averaged values of C_{org} were higher in spring.

Volzhskii stretch contained water with chromaticity of 50°–65° and OMC of 6.2–14.1 mg C/L in 1981–1982. The increased extreme values of OMC were typical of summer phytoplankton development. The lowest values were observed in April due to the influence of transformed winter water of the Uglich reservoir.

Water of Tsentralnii stretch was not homogeneous in organic carbon content in January, 1981. The influence of the Volga water was marked at the Mologa and Navolok stations. The OMC at the

Table 5. Chromaticity (deg) and C_{org} (mg/L) in water of Rybinsk reservoir (averaged over all monitoring stations)

Month	Year						
	2001	2002	2003	2004	2005	2006	2007
				C_{org}			
May	–	–	–	15.6	15.3	11.7	14.8
June	12.1	–	–	16.4	15.5	11.3	13.8
July	10.8	10.7	–	14.7	18.7	12.3	13.5
August	12.1	11.7	12.8	15.2	19.4	–	15.5
September	13.6	10.6	13.5	14.3	16.1	13.0	14.4
October	11.2	–	–	–	13.7	13.0	–
				Chromaticity			
May	–	–	–	108	–	59	67
June	59	–	–	87	79	46	59
July	66	51	–	67	62	43	53
August	55	38	63	76	51	–	42
September	55	41	61	58	55	38	48
October	58	–	–	–	51	40	48

Table 6. Annual variation of chromaticity (deg), C_{org} (mg/L) (averaged over all monitoring stations), and the water flow (V km^3 per year)

May–October	2001	2002	2003	2004	2005	2006	2007
C_{org}	12.0	11.0	13.1	14.8	16.5	12.3	14.4
Chromaticity	55	42	62	78	61	47	57
V[a]	29.1	18.7	26.3	45.2	33.9	29.9	28.4

[a] Data provided by A.S. Litvinov.

Breitovo station was higher due to the effect of the autumn Mologa flood water, as confirmed with the high chromaticity (120 deg). Towards the end of winter, the organic compounds were noticeably transformed, the OMC was down, and its value turned uniform over the stretch.

Winter C_{org} values in 1981 were lower than in 1982. During the ice-free periods water chromaticity at Tsentralnii stretch was almost constant, of 55°–65° (1981) and 45°–50° (1982), except for the Breitovo station where water was more colored in 1981 (75°–100°).

The OMC variation was due to the internal reservoir processes. In particular, in 1982 the lowest value (7.0 mg/L) was observed in November at the Srednii Dvor station, and the highest value (13.3 mg/L) was found at the Mologa station in May. However, such significant variations were not typical, the OMC being in general of 8.6–11.3 mg C/L.

The stretch-averaged OMC was higher in 1981 than in 1982. Summer of 1981 was warm, and organic-producing processes were intense leading to the higher C_{org} values. Analysis of the data for all the stretches (Tables 2–5) showed that Molozhskii stretch was the most rich in OM, the major part of the OM being colored humic substances.

Since 2001, complex monitoring of Rybinsk Reservoir has been carried out at six stationary stations located at Tsentralnii and Volzhskii stretches (see figure, stations *1, 2, 4, 7, 8, 20*). The samples were taken during the open-water season from the 1 m surface level.

The distribution of OM over the monitored region was not uniform in 2001–2007. The peak difference in chromaticity in May was of 15°–20° (up to 40° in 2005). The highest values were usually observed at the Breitovo station. The non-uniform distribution was preserved during summer seasons, but the peak difference was lower. During autumn seasons, the humic compounds content was less varied, the chromaticity difference between the stations being usually within 5°–10°. That could be due to the limited mixing of the tributaries influx water with that of the stretches, even during the summer-autumn hydrodynamically active periods. The station-averaged values of chromaticity were decreasing from spring to autumn.

Seasoned dynamics of the mean total OMC did not show any regularity, except to the data of 2005 revealing a clear maximum in summer (Table 4).

CONCLUSIONS

Analysis of annual and seasoned changes of the organic matter content revealed that they did not exceed natural data scatter, being well correlated with the river flow (Table 6). The river flow gave the majot contribution in the total organic matter income.

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