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Biogenic Elements and Organic Matter in the Sheksna Reach of the Rybinsk Reservoir

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Abstract—Published and our own data on the concentrations of phosphorus and nitrogen compounds and organic matter in the Sheksna reach of the Rybinsk reservoir have been analyzed, and the state of different areas of the reach has been assesses. Over the past three decades, no substantial variations in the concentrations of biogenic elements have been observed, while the organic matter content (organic carbon) has increased considerably.

Keywords: nitrogen, phosphorus, organic matter, Rybinsk reservoir

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INTRODUCTION

The Sheksna reach is one of the four reaches of the Rybinsk reservoir, which are distinguished by the depth distribution and floor morphology [1]. It is located along the Sheksna valley and is characterized by a basin area of 10600 km^2, watershed area of 38600 km^2, water surface area of 560 km^2, volume of 1.9 km^3, average depth of 3.3 m, and a water replacement rate of 0.3. The Sheksna river watershed occupies two subareas of the forest zone, middle taiga and southern taiga. Waters of the Sheksna basin display high colority and oxidizability due to high population (80%) and swampiness (10%), as well as due to a large amount of peat moors (8%).

Cherepovets industrial hub is one of the largest sources of pollution of the Sheksna reach of the Rybinsk reservoir. It includes metallurgic (Cherepovets Metal Works) and chemical enterprises (industrial associations *Azot* and *Ammofos*). As a result, the Sheksna reach is polluted annually with up to 200 million m^3 of wastewaters containing highly toxic pollutants, such as polycyclic hydrocarbons, polychlorinated biphenyls, heavy metals, nitrogen compounds, petrochemicals, etc., which adversely affect biota. The goal of the present work was to assess the environmental state of different areas of the Sheksna reach with respect to biogenic elements and organic matter at present time.

EXPERIMENTAL

Monitoring of the Sheksna reach was carried out in 2006–2010. Inorganic nitrogen and phosphorus and the main parameters of organic matter [biochemical oxygen demand (BOD$_5$), chemical oxygen demand (COD), colority] were determined by standard procedures [2] aboard a expedition ship and at the certified

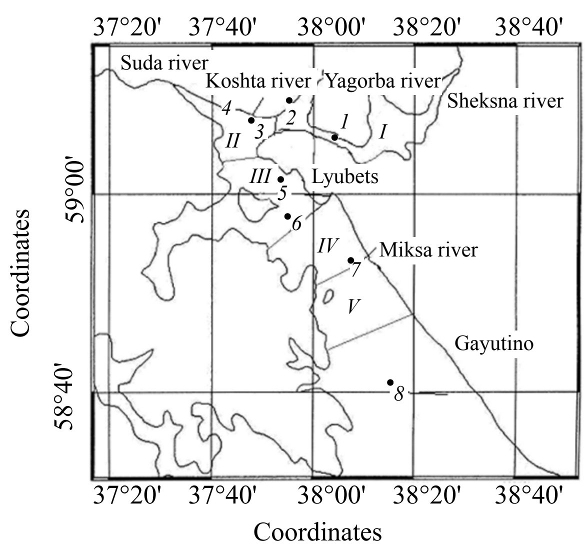

Fig. 1. Sampling map of the Sheksna reach of the Rybinsk reservoir: stations: (*1*) Kabachino, (*2*) Yagorba river, (*3*) Koshta river estuary, (*4*) Suda river estuary, (*5*) Vaganikha, (*6*) Lyubets, (*7*) Myaksa, (*8*) Gayutino; areas: *I*–*V*.

Table 1. Concentrations of biogenic elements in the Sheksna reach of the Rybinsk reservoir

Station	Concentration, mg of N or P per Liter				
	NO_2^-	NO_3^-	N_{total}	PO_4^{3-}	P_{total}
May 2006					
Suda estuary	0.000	0.079	1.08	0.054	0.080
Lyubets	0.000	0.157	0.96	0.038	0.081
Myaksa	0.000	0.118	1.04	0.042	0.072
August 2006					
Suda estuary	0.000	0.028	0.61	0.014	0.083
Lyubets	0.000	0.032	0.93	0.014	0.151
Myaksa	0.000	0.010	0.76	0.007	0.081
July 2007					
Suda estuary	0.004	0.036	1.23	0.021	0.066
Lyubets	0.004	0.038	1.28	0.036	0.086
Myaksa	0.000	0.022	0.86	0.022	0.058
Kabachino	0.000	0.055	4.92	0.031	0.078
Yagorba river	0.000	0.023	–	0.014	–
Industrial wastewater stream	0.015	0.515	7.73	0.316	0.800
Koshta estuary	0.015	0.151	3.25	0.139	0.472
Koshta (bottom)	0.138	0.379	7.63	0.147	0.409
Koshta (surface)	0.027	0.222	3.40	0.034	0.118
Vaganikha	0.012	0.135	4.98	0.059	0.177
Gayutino	0.023	0.057	4.92	0.292	0.420
October 2007					
Suda estuary	0.000	0.070	1.22	0.041	0.084
Lyubets	0.001	0.049	1.06	0.044	0.118
Myaksa	0.000	0.014	1.08	0.021	0.112
Kabachino	0.003	0.031	1.92	0.066	0.129
Yagorba river	0.002	0.014	1.18	0.020	0.082
Industrial wastewater stream	0.015	0.780	4.68	0.700	1.43
Koshta estuary	0.002	0.062	1.69	0.049	0.097
Koshta (bottom)	0.067	0.470	4.18	0.095	0.236
Vaganikha	0.002	0.080	2.09	0.029	0.096
Gayutino	0.012	0.040	1.42	0.049	0.094
June 2008					
Gayutino	0.004	0.15	1.14	0.008	0.058
Myaksa	0.004	0.14	1.03	0.028	0.070
Lyubets	0.003	0.15	1.13	0.026	0.044
Suda estuary	0.000	0.02	0.90	0.016	0.032
Koshta (bottom)	0.029	0.50	3.24	0.067	0.093
Koshta (surface)	0.063	0.41	2.58	0.095	0.137
Yagorba river	0.002	0.02	0.52	0.090	0.127

Table 1. (Contd.)

Station	Concentration, mg of N or P per Liter				
	NO_2^-	NO_3^-	N_{total}	PO_4^{3-}	P_{total}
June 2008					
Koshta estuary	0.002	0.20	3.02	0.066	0.108
Vaganikha	0.002	0.22	3.20	0.068	0.089
Kabachino	0.000	0.04	0.07	0.016	0.056
July 3–August 2					
Gayutino	0.004	0.028	1.02	0.038	0.042
Myaksa	0.000	0.02	0.75	0.043	0.053
Lyubets	0.001	0.029	0.74	0.056	0.061
Suda estuary	0.008	0.09	–	0.020	0.066
Koshta (bottom)	0.246	1.269	3.85	0.058	0.046
Koshta (surface)	0.184	0.905	3.81	0.062	0.115
Industrial wastewater stream (surface)	0.051	0.565	3.23	0.214	0.500
Industrial wastewater stream (bottom)	0.015	0.262	1.89	0.220	0.519
Yagorba river	0.002	0.049	0.85	0.056	0.103
Koshta estuary	0.022	0.163	1.44	0.056	0.100
Vaganikha	0.011	0.11	1.01	0.057	0.096
July 10, 2009					
Gayutino	0.005	0.034	0.73	0.036	0.064
Myaksa	0.003	0.046	0.76	0.017	0.090
Lyubets	0.003	0.034	0.73	0.036	0.089
August 2009					
Suda estuary	0.000	0.033	0.60	0.035	0.060
Koshta estuary	0.014	0.128	0.83	0.050	0.075
Koshta (surface)	0.180	0.430	1.80	0.072	0.115
Industrial wastewater stream	0.009	1.040	1.70	0.220	0.245
Yagorba river	0.003	0.033	0.94	0.038	0.045
Kabachino	0.000	0.011	0.63	0.021	0.052
Vaganikha	0.005	0.070	–	0.048	–
Lyubets	0.000	0.018	0.70	0.018	0.064
Myaksa	0.000	0.024	0.69	0.017	0.050
Gayutino	0.005	0.030	0.90	0.010	0.045
September 2009					
Suda estuary	0.000	0.060	0.61	0.015	0.077
Koshta estuary	0.014	0.120	0.86	0.056	0.100
Gayutino	0.000	0.006	0.62	0.019	0.065
Kabachino	0.002	0.018	0.65	0.024	0.055
Vaganikha	0.006	0.170	0.48	0.021	0.080
Lyubets	0.002	0.052	0.42	0.031	0.089
Myaksa	0.002	0.006	0.36	0.013	0.066

Table 1. (Contd.)

Station	Concentration, mg of N or P per Liter				
	NO_2^-	NO_3^-	N_{total}	PO_4^{3-}	P_{total}
October 2009					
Lyubets	0.044	0.90	0.90	0.038	0.050
Myaksa	0.077	0.53	0.53	0.035	0.051
May 2010					
Gayutino	0.001	0.07	0.83	0.018	0.047
Myaksa	0.003	0.16	1.11	0.016	0.046
Lyubets	0.026	0.06	0.96	0.017	0.047
July 2010					
Gayutino	0.000	0.02	1.07	0.013	0.062
Myaksa	0.000	0.02	1.52	0.024	0.061
Lyubets	0.000	0.03	0.64	0.027	0.070
Yagorba river	0.001	0.02	0.77	0.024	0.088
Suda estuary	0.003	0.04	1.27	0.025	0.081
Industrial wastewater stream	0.003	0.04	1.05	0.030	0.104
Vaganikha	0.003	0.03	1.13	0.017	0.082
Koshta estuary	0.006	0.04	0.88	0.019	0.084
Koshta (bottom)	0.180	0.43	4.83	0.038	0.146
Koshta (surface)	0.017	0.20	1.25	0.027	0.088
Kabachino	0.003	0.04	0.99	0.025	0.058
August 2010					
Suda estuary	0.000	0.00	0.64	0.018	0.073
Koshta estuary	0.003	0.09	1.04	0.070	0.170
Lyubets	0.000	0.03	1.10	0.029	0.104
Myaksa	0.000	0.01	1.39	0.010	0.100
Gayutino	0.000	0.03	0.77	0.010	0.073
October 2010					
Gayutino	0.000	0.03	1.05	0.015	0.062
Myaksa	0.000	0.04	1.12	0.033	0.060
Lyubets	0.000	0.06	0.93	0.032	0.058

Analytical Center (Papanin Institute for Biology of Inland Waters, Russian Academy of Sciences). Organic phosphorus and nitrogen compounds were mineralized by treatment with potassium persulfat and were determined as orthophosphate and nitrate, respectively [3, 4].

Figure 1 shows the location of the monitoring stations.

RESULTS AND DISCUSSION

Biogenic elements. During the examined period, pollution with inorganic phosphorus and nitrogen compounds of areas *1* and *2* (the areas were defined according to [5]) of the upper reach was observed, which is directly related to industrial and municipal wastes of Cherepovets city. Increased concentrations of biogenic elements were found in Koshta and Yagorba rivers; the total nitrogen and total phosphorus contents exceeded several times the corresponding values for not only the Rybinsk reservoir on the whole but also the Sheksna reach where those rivers flow into. Organic compounds (probably polyphosphates) constitute the main part of the total phosphorus and nitrogen contents, and a considerable part of biogenic elements is represented by inorganic forms. The

Table 2. Organic matter parameters of the Sheksna reach in 1964–1966

Date	Colority, deg	C_{org}, mg/L	COD, mg O/L
February 1964	50–65	8.9–11.4	32.9–34.1
May 1964	45–85	8.2–15.2	18.7–31.8
August 1964	36–45	10.0–12.6	25.4–33.6
November 1964	35	9.0–10.2	25.6–28.1
November 1965	35–37	10.8–14.4	29.3–31.7
May 1966	60–100	9.8–11.8	–

Table 3. Organic matter parameters of the Sheksna reach in 1981 and 1982

Date	Colority, deg	BOD_5, mg O/L	COD, mg O/L	C_{org}, mg/L	BOD/COD ratio
February1981[a]	40	–	19.8	8.8	–
March 1981[a]	45	0.3	15.7	8.5	2.0
April 1981[a]	45	0.6	24.3	9.7	3.0
May 1981[a]	65	2.2	26.3	12.2	8.0
June 1981	55	1.4	22.3	10.6	6.9
July 1981	50–90	1.8–1.9	19.6–21.2	11.7–12.2	8.8–9.3
August 1981	55–65	1.7–2.4	22.7–23.0	10.6–12.2	7.5–10.4
September 1981	50–60	1.6–2.3	32.1–39.3	6.3–12.9	4.1–6.7
October 1981	55	0.85–1.3	23.1–41.3	11.0–13.0	3.0–3.7
November 1981	50–60	0.8–1.3	–	–	–
May 1982	–	0.9–1.5	27.7–30.8	12.7–15.4	–
June 1982	40–60	0.7–1.3	26.9–29.6	9.0–11.6	2.6–4.4
July 1982	55–60	–	21.8–22.2	8.2–8.3	–
August 1982	45–60	1.6–1.9	25.6–26.4	8.2–10.3	6.1–7.4
September 1982	40–55	1.2	20.6–26.0	9.0–11.1	5.8–7.0
October 1982	45–70	–	–	8.2–12.9	–

[a] Kabachino station.

maximal concentrations of nitrates and phosphates were determined in industrial wastes directly discharged into Koshta river. The concentration of nitrites in the benthic layer of Koshta river exceeded several times the maximum allowable concentration, which undoubtedly indicates extensive nitrification process and (indirectly) high concentration of ammonia nitrogen. Such conditions are unfavorable for the vital activity of plankton and fishes. The concentration levels of all items in the downstream Sheksna reach (areas *4* and *5*) were similar to those in the Central reach. High nutrient content of water in the region of Cherepovets city is responsible for their concentration over the entire reach. Since 2006 till 2010, the average N/P ratio was 16.0, which suggests that phytoplankton production is generally not limited by both elements. The concentrations of all nutrient forms in 2006–2010 show that there were no considerable changes in both spatial and seasonal distributions of nitrogen and phosphorus compounds in the Sheksna reach as compared to previous decades [6] despite substantial variations of the water regime.

Organic matter. The influx of organic matter (OM) with particular flows is determined by not only their flow rates but also concentration C_{org} therein. It was shown previously that the Volga and Mologa rivers supply approximately equal amounts of organic matter to the Rybinsk reservoir [7]. Next follows the Suda river, and the Sheksna river occupies the forth place. These four rivers provide 87% of the total organic matter intake per annum. Therefore, less than 15% of OM is supplied by small rivers. Obviously, this distribution reflects both discharge rate of each river

Table 4. Organic matter parameters of the Sheksna reach in 2006–2010

Station	Colority, deg	BOD_5, mg O/L	COD, mg O/L	C_{org}, mg/L	BOD/COD ratio
May 2006					
Suda estuary	100	2.1	51.2	23.7	4.1
Lyubets	70	3.3	41.3	22.5	7.9
Myaksa	70	2.6	38.5	16.1	6.8
August 2006					
Suda estuary	65	1.5	–	12.0	–
Lyubets	70	1.0	–	18.0	–
Myaksa	65	2.2	–	18.0	–
July 2007					
Suda estuary	120	0.57	28.7	11.1	2.0
Lyubets	45	0.57	29.1	10.9	2.0
Myaksa	45	0.80	36.9	12.6	2.2
Kabachino	45	2.75	38.1	15.5	7.2
Yagorba river	120	4.47	70.0	26.3	6.4
Industrial wastewater stream	65	3.84	44.4	16.7	8.6
Koshta estuary	50	1.49	39.6	14.8	3.8
Koshta (bottom)	45	3.27	47.0	17.6	7.0
Koshta (surface)	40	3.38	41.1	15.4	8.2
Vaganikha	50	2.24	–	–	–
Gayutino	45	1.49	–	–	–
October 2007					
Suda estuary	100	0.80	35.8	13.4	2.2
Lyubets	60	0.27	44.5	16.7	0.6
Myaksa	55	0.53	50.8	19.1	1.0
Kabachino	55	3.03	34.6	13.0	8.8
Yagorba river	55	0.37	40.9	15.3	0.9
Industrial wastewater stream	45	4.36	46.1	17.3	25.2
Koshta estuary	50	1.43	32.7	12.3	4.4
Koshta (bottom)	50	3.56	43.3	16.2	8.2
Vaganikha	55	0.53	35.4	13.3	1.5
Gayutino	50	0.69	35.8	13.4	1.9
June 2008					
Gayutino	60	0.9	36.3	13.6	2.3
Myaksa	65	1.3	39.4	14.8	3.3
Lyubets	70	1.0	30.9	11.6	3.2
Suda estuary	65	0.8	34.0	12.8	2.4
Koshta (bottom)	60	4.9	47.1	17.6	10.4
Koshta (surface)	60	6.3	47.5	17.8	13.3
Yagorba river	60	2.3	30.1	11.3	7.6
Koshta estuary	60	2.2	41.7	15.6	5.3
Vaganikha	60	2.3	39.0	14.6	5.9
Kabachino	60	1.3	37.8	14.2	3.4

Table 4. (Contd.)

Station	Colority, deg	BOD_5, mg O/L	COD, mg O/L	C_{org}, mg/L	BOD/COD ratio
August 2008					
Gayutino	55	1.3	36.2	13.6	3.6
Myaksa	60	1.3	41.3	15.5	3.1
Lyubets	60	1.1	44.0	16.5	2.5
Suda estuary	130	2.9	51.4	19.3	5.6
Koshta (bottom)	55	5.6	44.4	16.6	12.6
Koshta (surface)	60	5.3	42.8	16.1	12.4
Industrial wastewater stream (surface)	65	8.9	51.8	19.4	17.2
Industrial wastewater stream (bottom)	65	5.5	38.5	14.4	14.3
Yagorba river	60	1.5	38.9	14.6	3.9
Koshta estuary	55	2.4	38.9	14.6	6.2
Vaganikha	60	1.9	38.5	14.4	4.9
July 2009					
Gayutino	60	0.6	39.8	14.9	1.5
Myaksa	80	4.1	38.6	14.8	10.6
Lyubets	80	1.2	43.0	16.1	2.8
August 2009					
Suda estuary	120	2.5	56.2	21.1	4.4
Koshta estuary	90	2.2	48.7	18.3	4.5
Koshta (surface)	90	1.7	46.8	17.6	3.6
Industrial wastewater stream	60	2.9	43.8	16.4	6.6
Yagorba river	60	1.7	43.1	16.2	3.9
Kabachino	60	1.9	43.8	16.4	4.3
Lyubets	80	0.3	49.0	18.4	0.6
Myaksa	70	2.1	47.5	17.8	4.4
September 2009					
Suda estuary	120	1.6	50.0	18.8	3.2
Koshta estuary	60	1.3	40.3	15.1	3.2
Gayutino	65	-	44.5	16.7	–
Kabachino	60	1.3	42.0	15.8	3.1
Vaganikha	60	1.5	44.9	16.8	3.3
Lyubets	60	1.1	42.8	16.1	2.6
Myaksa	65	–	43.3	16.2	–
October 2009					
Lyubets	60	0.8	42.2	15.8	1.9
Myaksa	75	0.2	42.2	15.8	0.4
May 2010					
Gayutino	80	1.2	43.0	16.1	2.8
Myaksa	75	2.1	48.8	18.3	4.3
Lyubets	100	1.3	50.8	19.1	2.6
July 2010					
Gayutino	80	4.4	39.7	14.9	11.1
Myaksa	80	3.6	47.0	17.6	7.6

Table 4. (Contd.)

Station	Colority, deg	BOD_5, mg O/L	COD, mg O/L	C_{org}, mg/L	BOD/COD ratio
July 2010					
Lyubets	80	3.7	51.1	19.2	7.2
Yagorba river	75	2.8	43.2	16.2	6.5
Suda estuary	110	2.9	53.0	19.9	5.5
Industrial wastewater stream	70	2.8	40.5	15.2	6.9
Vaganikha	90	2.9	50.3	18.9	5.8
Koshta estuary	80	2.8	45.0	16.9	6.2
Koshta (bottom)	80	5.2	51.1	19.2	10.1
Koshta(surface)	80	5.3	51.5	19.3	10.3
Kabachino	60	1.5	41.7	15.6	3.6
August 2010					
Suda estuary	40	1.5	28.2	10.6	5.3
Koshta estuary	55	2.1	39.2	14.7	5.4
Lyubets	60	2.2	46.3	17.4	4.8
Myaksa	60	3.7	49.0	18.4	7.6
Gayutino	40	2.4	38.4	14.4	6.3
October 2010					
Gayutino	40	1.9	42.5	15.9	4.5
Myaksa	60	1.1	36.2	13.6	3.0
Lyubets	45	1.2	32.1	12.0	3.7

and different weighted average concentrations C_{org} in the riverwater. The organic carbon content of the Rybinsk reservoir was determined for the first time in 1964 (Table 2) [8, 9]. Previously Organic Matter was characterized only by colority and permanganate index. In 1964–1965, the amount of organic carbon in the Sheksna reach varied from 8.9 to 15.2 mg/L (Table 2). In 1981–1982, the C_{org} values varied within natural seasonal and year-to-year limits and were 6.3–15.7 mg/L (Table 3).

Lower concentrations were typical of the tail water of the Sheksna water power plant, where variations of C_{org} were determined mainly by variations of C_{org} in the Sheksna reservoir. In the second area, the concentration of organic matter was affected by the Suda river containing a large amount of humic substances (Table 4).

Among total organic matter, the labile fraction (BOD_5/COD ratio) amounted to no more than 8% in spring. The minimum value was observed in winter, and the maximum, in the period corresponding to vigorous phytoplankton production (Fig. 2). The BOD_5/COD ratios indicate a moderate self-purification capacity of the examined water reservoirs with respect to natural organic matter. In 2006–2010, the organic carbon content of the Sheksna reach increased relative to its level in 1960s and 1980s and varied from 10.9 to 26.3 mg/L. Taking into account that organic matter input is mostly related to photosynthetic activity of phytoplankton, the observed increase of C_{org} may be regarded as the result of enhanced primary production.

CONCLUSIONS

The state of the upstream Sheksna reach affected by wastewater from the Cherepovets industrial hub can be identified as eutrophic. The Koshta and Yagorba rivers suffer from especially strong anthropogenic load,

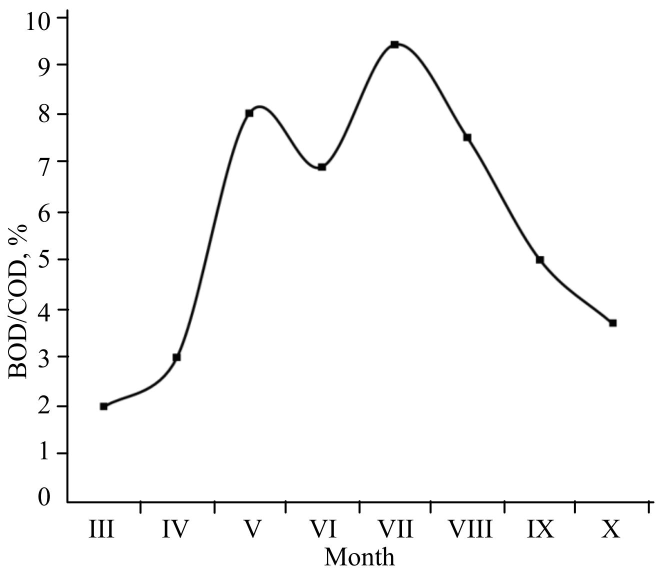

Fig. 2. Seasonal dynamics of BOD_5/COD ratio at the Kabachino station in 1982.

primarily biogenic. Considerably increased concentrations of inorganic nitrogen and phosphorus favor enhanced photosynthesis which directly leads to increased level of organic substances, including labile ones and chlorophyll *a*, in these rivers and adjacent areas. These data indicate that the Koshta river contains insignificant amounts or lacks pollutants suppressing the formation of organic matter to an appreciable extent. It should also be noted that enhancement of photosynthetic processes does not make the pH value higher than 8.5, which could be presumed on the basis of high phytoplankton biomass. Obviously, the concentration of protons is maintained at a relatively normal level due to the buffer capacity of the carbonate–calcium system. The current biogenic element concentrations in the Sheksna reach indicate no appreciable variations in the nitrogen and phosphorus regimes relative to the previous decades in both spatial and seasonal aspects despite substantial variations of the water regime. Increased organic carbon content at the present time reflects growth of the total concentration of organic matter in the Sheksna reach. This growth is related to enhanced primary production since the main contribution of organic matter to the reservoir is provided by photosynthetic activity of phytoplankton.

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