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WATER QUALITY AND PROTECTION: ENVIRONMENTAL ASPECTS

Long-Term Variations in the Biogenic Matter Runoff of the Dnestr River

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Abstract—Long-term observation data were used to carry out comparative analysis of variations in the biogenic matter runoff of the Dnestr River over a period of fifty years. Based on data of a weekly monitoring in 2002–2004, annual dynamics of biogenic matter runoff was analyzed for the Dnestr River and for Dnestr Liman. It was found out that, in spite of the "buffer" role of the latter, the contribution of biogenic substances, finding their way in the sea with the Dnestr River water, to the eutrophication of the northwestern Black Sea remains appreciable (about 60 thousand ton year^{-1}). Dissolved organic compounds account for 70% of the present-day biogenic matter runoff of the Dnestr River.

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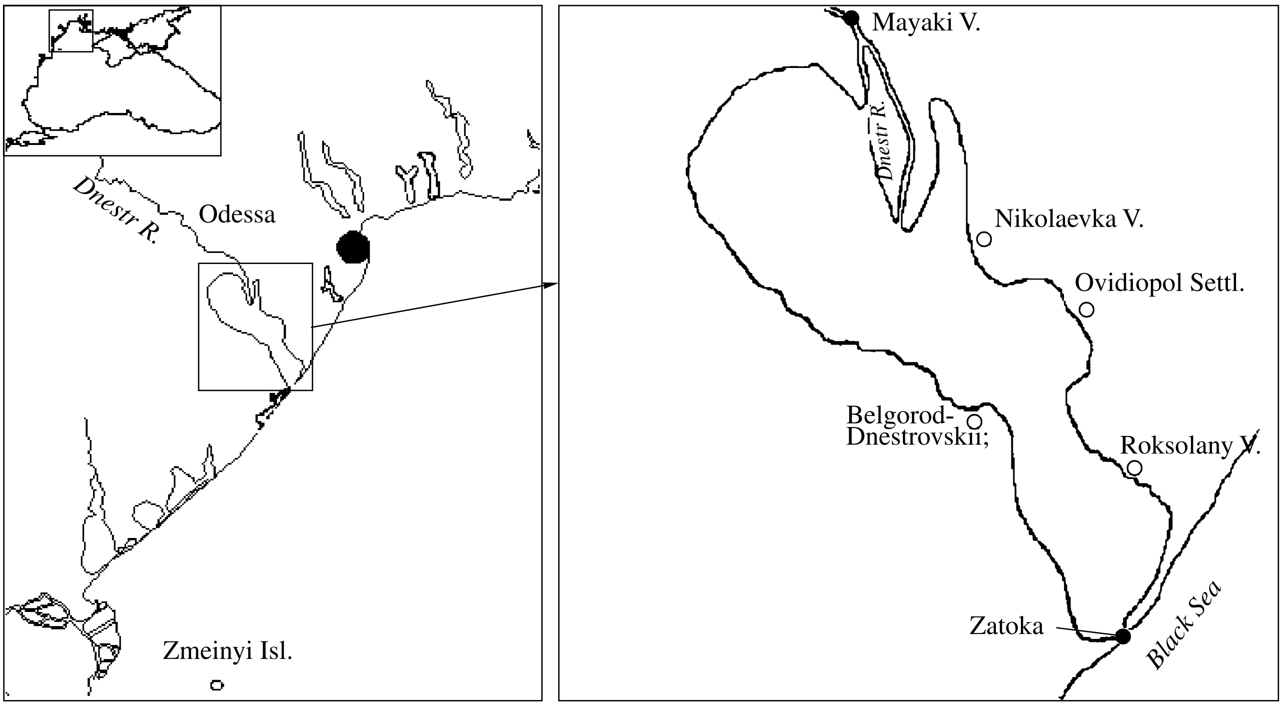
INTRODUCTION

Export of biogenic substances with the waters of rivers flowing into the Black Sea, and its spatial and temporal variations determine the intensity of biohydrochemical processes occurring in the nearshore areas of river mouths, promoting the formation of biogenic matter stock in the marine environment, which, in turn, forms the resources and biopotential of the marine ecosystem. Human-induced enrichment of natural waters in biogenic substances, or eutrophication, disturbs the natural biogeochemical balance in ecosystems and chemical cycles, manifesting itself most clearly in inland and partially enclosed water bodies. The shallow-water northwestern Black Sea, where eutrophication processes has been developing for more than 30 years, can be regarded as an example of such negative human impact. Eutrophication results in the formation of water blooming zones in the surface water layer and hypoxia in the bottom ones—such phenomena are observed in this part of the Black Sea every year. Its catchment area is 1463000 km^2 (exceeding almost 28 times the water surface area, which is 52900 km^2). The northwestern Black Sea is affected by human activity mostly via the Danube, the Dnestr, and the Dnepr (with the Southern Bug) rivers. The total annual runoff of these rivers is about 260 km^3 year^{-1}, which accounts for one-seventh of the total volume of the seawater in the northwestern shelf zone of the Black Sea [12].

The Dnestr is one of the largest rivers of Ukraine and Moldova (currently, its water runoff is about 10 km^3 year^{-1}). It originates on the northern slope of the East Carpathians and flows over Podol'sk Plateau and the steppe zone of Ukraine. Its length is 1352 km. Its catchment area (82000 km^2) is a densely populated and urbanized zone with high industrial potential and developed agriculture. The Dnestr River water flows into the Dnestr Liman, which is one of the largest water bodies in the northern Black Sea coast (its water surface area being 360 km^2), where the transformed waters of the Dnestr, the Dnepr with the Bug, and the Danube rivers merge. Analysis of long-term variations in the biogenic matter runoff of the Dnestr River allowed us to reveal certain regularities in the formation of biogenic matter stock in the coastal waters of the Dnestr Liman, relevant for predicting the biological productivity in this region of the northwestern Black Sea.

BACKGROUND DATA

The analysis of long-term variations in the biogenic matter runoff of the Dnestr River was based on the data published in the literature [1, 6, 7, 10, 13] and materials of our own field studies carried out in 1977–1978 (22 surveys) and in 1987–1988 (11 surveys). The surveys were implemented according to the following scheme: the river (Mayaki village)–the liman (Nikolaevka Village, Ovidiopol Town, and the Roksolany Village)–the liman outlet (the Zatoka Port). From November 2003 to November 2004, the surveys were carried out on a weekly basis according to the following scheme: the river (Mayaki Village)–the liman outlet (the Zatoka Port) (Fig. 1). The following characteristics were determined: water salinity, suspended matter, dissolved and suspended forms of N, (NH_4^+, NO_2^-, NO_3^-, and N_{org}), P (PO_4^{3-}, P_{org}), and Si, dissolved organic matter (OM) by permanganate oxidability. Standard determination methods were used [11].



Schematic map of water sampling sites in the Dnestr River mouth (Mayaki V.) and in the Dnestr Liman (Zatoka Port) in 2003–2004

BRIEF HYDROLOGICAL AND HYDROCHEMICAL CHARACTERISTIC

Three periods can be singled out in the hydroecological state of the Dnestr River and the Dnestr Liman. The first one was prior to river runoff regulation, when the hydrological and hydrochemical regime formed under the effect of natural factors alone. During this period, considerable water runoff fluctuations were related to snow melting and frequent storm floods in the catchment area. The second period was the period of partial river runoff regulation. It began in 1954, when the Dubossary Reservoir and the Dubossary Hydroelectric Power Plant were put in operation, which led to the river current velocity deceleration and a decrease in its water turbidity. The third period began in 1987, when the Dnestr Reservoir and the Dnestr Hydroelectric Power Plant were put in operation. During this period, the hydrological regime of the middle section of the Dnestr River was considered fully regulated [13].

Prior to the water runoff regulation (1951–1953), terrigenous flow was the main source of biogenic substances in the lower reach of the Dnestr River and in the Dnestr Liman. The maximum values of biogenic substance concentrations were recorded during spring and autumn floods [1, 2, 3]. While assessing changes that occurred over the subsequent fifty years in the biogenic matter runoff of the Dnestr River, these values can be adopted as the "norm" (Table 1). In 1952–1954, the total biogenic matter runoff, calculated based on the respective average monthly values, was about 50000 km^3 $year^{-1}$, out of which N accounted for 6.2, P for 0.4, and Si for 42.7 thousand tons. The seasonal distribution of the biogenic matter runoff was as follows: 11% fell on winter, 60% on spring, 17% on summer, and 12% on autumn.

The studies carried out in 1977–1978 showed that, as compared to 1951–1953, the concentration ofNO_3^- in the Dnestr River water grew four times, and that of PO PO_4^{3-}, five times. Accumulation of mineral and organic compounds of N, P, and Si was observed in the liman. In 1985–1988, the water in the lower reach of the Dnestr became even more rich in N and P compounds [7]. In 1987, putting in operation of the Dnestr Reservoir and the HPP smoothed the annual fluctuations in the water runoff of the Dnestr River and decreased the water exchange rate in the liman. Under natural conditions, the liman was flushed by the river water about 19 times a year, but after the filling of the Dnestr Reservoir, this number dropped to 16–17 times. This caused a considerable increase in the biogenic substance concentrations in the liman water. At that time, the maximum concentration of NH_4^+ reached 2.5 mg dm^{-3}; that of NO_2^-, 0.078 mg N dm^{-3}; NO_3^-, 3.70 mg N dm^{-3}; PO_4^{3-}, 0.46 mg P dm^{-3}; Si, 7.1 mg dm^{-3}, and OM (by PO)12.2 mg O dm^{-3}. Water blooming was permanently observed in the liman, resulting in the deterioration of the oxygen regime in the bottom water layer in some areas. These years were the worst in terms of the environmental situation in the region of the Dnestr River

Table 1. Long-term variations in the hydrochemical characteristics in the Dnestr River mouth (Mayaki V.) and in the Dnestr Liman mouth (the Zatoka Port) in 1951–2004 (dash means no data available)

Study area, mouth of	pH	$N\text{-}NH_4^+$	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$	N_{org}	$P\text{-}PO_4^{3-}$	P_{org}	Si, mg dm^{-3}	PO, mg O dm^{-3}
		mg N dm^{-3}				mg P dm^{-3}			
1952–1953 [1]									
Dnestr River	8.20	0.121	0.018	0.33	–	0.019	–	4.30	6.20
Dnestr Liman	8.20	0.015	0.012	0.17	–	0.028	–	2.34	3.38
1977–1979*									
Dnestr River	7.97	–	0.080	1.29	1.38	0.091	0.028	4.00	–
Dnestr Liman	7.97	–	0.026	0.71	0.71	0.048	0.021	2.21	–
1985–1988 [4, 6]*									
Dnestr River	7.75	0.615	0.191	1.30	0.51	0.090	0.041	4.41	4.20
Dnestr Liman	7.75	0.220	0.110	1.34	0.47	0.113	0.190	1.00	5.37
2003–2004*									
Dnestr River	7.44	0.073	0.031	0.86	1.70	0.074	0.028	2.46	2.42
Dnestr Liman	7.44	0.025	0.011	0.32	1.43	0.018	0.017	1.37	2.31

* authors' materials.

and the Dnestr Liman. The annual volume of the sea water discharging from time to time into the liman increased from 3.7 km^3 under natural conditions to 4–4.5 km^3 [6, 13]. The inflow of the liman water, enriched in biogenic substances and OM, from the Dnestr Liman to the northwestern Black Sea resulted in the formation of vast zones of water blooming in the surface water layer and hypoxia in the bottom water layer in the adjacent nearshore area.

In the 1990s, during the period of industrial and agricultural decay in the region under consideration, when Dnestr runoff decreased, there appeared a tendency toward a decrease in the concentration of biogenic substances and an increase in that of dissolved OM delivered from the liman to the nearshore area [4, 5].

RESULTS AND DISCUSSION

The Dnestr River mouth. Hydrological and hydrochemical monitoring, carried out in 2003–2004, revealed appreciable seasonal variations in the investigated characteristics in the lower reaches of the Dnestr (Tables 1, 2), This is indicative of unstable hydrochemical regime affected by various natural and anthropogenic factors.

In spite of the opinion that the Dnestr runoff is completely regulated [9], water level fluctuations near the village of Mayaki are considerable. At the average amplitude of 94 m, the range of diurnal fluctuations in the water level exceeded one meter, varying from 37 cm in September to 139 cm in June of 2004. Judging by the period, close to the natural synoptic one, level variations from day to day are wind-induced. Even when smoothed by moving average with a one-month period, the difference between the spring flood (108 cm) and the autumn low-water period (85 cm) was appreciable. Water level variations in the liman outlet (the Zatoka Port) were somewhat lower. With the average amplitude of 499 cm, the range of diurnal fluctuations in the water level was 67 cm (from 460 to 527 cm). This can be explained by the damping effect on wind-induced surges and the motion of water between the liman and the sea through the Tsaregrad Branch. After smoothing with moving average with a period of one month, water level varied between 488 and 511 cm, i.e., by 23 cm.

The unfavorable environmental state of the Dnestr River ecosystem can be seen from variations in pH in the river mouth from 6.74 to 8.20. All the year round, pH dropped from time to time to <7.00.

The main form of N occurrence in water in the lower reaches of the Dnestr is N_{org}, which accounts for up to 70% of the total N concentration in summer. The main form of mineral nitrogen is NO_3^- (Tables 1, 2). The high concentrations of NO_3^-, recorded in spring during photosynthesis processes development, testify to the human origin of NO_3^-. In summer, the concentration of NO_3^- declined because of both its consumption by phytoplankton and its decreased input from the catchment area because of low precipitation. On the whole, lower NO_3^- concentration was recorded in the Dnestr River water, as compared to the data of 1970–1990, although NO_3^- concentration values were 2.6 times higher than the norm observed in the 1950s (Table 1).

Table 2. Mean values of some hydrochemical characteristics in the Dnestr River water (Mayaki V.) in 2003–2004

Month	Runoff, km^3	Hydrochemical characteristics										PO, mg O dm^{-3}
		TDS, g dm^{-3}	Suspeded matter, mg dm^{-3}	pH	$N\text{-}NH_4^+$	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$	N_{org}	$P\text{-}PO_4^{3-}$	P_{org}	Si, mg dm^{-3}	
					mg N dm^{-3}				mg P dm^{-3}			
November	0.90	0.65	6.09	7.75	0.110	0.042	0.935	3.56	0.062	0.031	2.73	1.91
December	0.85	0.50	10.79	7.16	0.115	0.020	0.922	1.64	0.096	0.037	2.78	2.20
January	0.97	0.48	21.02	7.33	0.157	0.013	1.089	1.95	0.084	0.015	2.12	1.95
February	0.92	0.50	3.84	7.45	0.178	0.010	0.987	1.01	0.082	0.029	2.20	1.94
March	1.03	0.51	8.25	7.52	0.083	0.034	1.047	1.57	0.073	0.023	2.66	2.23
April	1.09	0.45	26.73	7.46	0.050	0.022	0.956	1.5	0.041	0.023	2.01	2.29
May	1.26	0.41	19.52	7.45	0.038	0.050	1.173	1.51	0.054	0.013	2.68	2.13
June	0.95	0.38	16.99	7.22	0.017	0.069	0.699	2.17	0.062	0.025	1.88	2.39
July	0.85	0.43	14.45	7.62	0.016	0.023	0.368	1.46	0.062	0.042	1.74	5.86
August	1.08	0.38	43.50	7.80	0.029	0.028	0.648	0.97	0.082	0.044	2.88	2.27
September	0.83	0.41	19.01	7.68	0.040	0.016	0.694	1.19	0.098	0.026	2.89	1.97
October	0.82	0.41	13.66	6.92	0.051	0.042	0.650	1.85	0.088	0.028	2.76	2.22
Mean	0.96	0.46	17.27	7.44	0.073	0.031	0.855	1.70	0.074	0.028	2.46	2.42

As compared to the data for previous years, the concentration of NH_4^+ significantly decreased (Table 2). The maximum values were observed in autumn and winter, i.e. during the period of accumulation of OM destruction products in the water and a decrease in the intensity of mineralization processes.

All over the observation period, appreciable concentrations of NO_2^- were observed in the lower reaches of the Dnestr. The maximum values were recorded in spring and summer, while the minimum values, in winter. Despite of the fact that, as compared to the period of intense anthropogenic eutrophication of the Dnestr water, the concentration of NO_2^- decreased 3 to 6 times, the observed values testify to the river water contamination with domestic effluents.

The concentration of mineral and organic P compounds in the water varied within a wide range. The maximum values of PO_4^{3-} concentration were observed in autumn and winter, whereas the minimum ones were observed in spring, which can be explained by the Dnestr water dilution during spring floods and byPO_4^{3-} consumption by aquatic plants. The concentration of P decreased as compared to 1970–1990.

In the Dnestr water, dissolved forms of N and P prevailed over suspended ones. In spring and summer, a certain increase in the concentration of suspended forms took place because of phytoplankton vegetation.

The concentration of Si (the most conservative indicator, not subjected to anthropogenic impact) was relatively stable. However, in summer, it was 1.5–2 times lower (Tables 1, 2). Water runoff regulation promoted intense development of diatomic phytoplankton, which resulted in an almost twofold decrease in Si concentration, as compared to the period prior to runoff regulation (Table 1).

Despite the fact that the weekly values of dissolved OM varied within a wide range (from 1.31 to 15.43 mg O dm^{-3}), the mean monthly values remained stable and inconsiderable, varying from 1.46 to 3.58 mg O dm^{-3}. The maximum values of dissolved OM were recorded in summer, and the minimum ones, in spring. The comparison of the data obtained in 2003–2004 with the historical data (Table 1) demonstrates a decrease by a factor of 2 to 3 in PO. It should be noted that the technique of PO determination has remained, actually, unchanged for the last fifty years.

Dissolved OM (represented, mainly, by humic substances delivered from the catchment area, and by products of autochthonous OM destruction, resistant to bacterial decomposition) prevail over suspended OM. Similarly, dissolved forms of N and P prevailed over suspended ones. The percentage of suspended OM increased with the intensification of destruction processes in summer and decreased in autumn (Table 3).

Weekly and monthly observations did not reveal any regularity in the variations in suspended matter concentration. However, in season-averaged values of suspended matter, an increase was recorded from winter to summer, followed by a decrease from summer to autumn. This regularity is phase opposition to the TDS in the Dnestr water and can be explained by higher water turbidity during spring and autumn floods.

Table 3. Ratio (in per cent) of (1) dissolved and (2) suspended forms of N, P, and OM (by PO) in the Dnestr River water (Mayaki V.) in 2003–2004

Season	Hydrochemical characteristics							
	N_{tot}		P_{min}		P_{tot}		OM	
	1	2	1	2	1	2	1	2
Winter	82.4	17.6	87.2	12.8	83.5	16.5	79.1	20.9
Spring	77.4	22.6	77.3	22.7	69.2	30.8	81.1	18.9
Summer	77.5	22.5	76.8	23.2	74.5	25.5	66.0	34.0
Autumn	92.3	7.7	86.1	13.9	90.2	9.8	85.0	15.0

Table 4. Mean monthly values of some hydrochemical characteristics in the Dnestr Liman mouth (Zatoka Port) in 2003–2004

Month	Hydrochemical characteristics										
	Salinity, ‰	Suspended matter, mg dm^{-3}	pH	$N\text{-}NH_4^+$	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$	N_{org}	$P\text{-}PO_4^{3-}$	P_{org}	Si, mg dm^3	PO, mg O dm^{-3}
				mg N dm^{-3}				mg P dm^{-3}			
November	15.8	15.52	8.19	0.031	0.006	0.215	4.23	0.023	0.026	1.388	1.87
December	8.9	23.97	7.64	0.041	0.010	0.547	1.93	0.031	0.019	1.470	2.30
January	11.9	9.20	7.47	0.023	0.006	0.429	1.59	0.055	0.006	1.688	2.54
February	15.0	8.73	7.18	0.022	0.007	0.305	0.76	0.028	0.007	1.595	1.46
March	9.0	12.72	8.51	0.011	0.019	0.476	0.31	0.007	0.009	1.080	1.92
April	5.1	18.95	7.46	0.018	0.009	0.312	1.04	0.007	0.011	0.610	2.12
May	3.1	16.01	7.59	0.014	0.008	0.305	1.58	0.004	0.009	0.818	2.36
June	7.9	18.69	7.76	0.017	0.010	0.203	2.24	0.002	0.028	1.106	2.64
July	6.8	8.85	7.98	0.012	0.010	0.358	0.86	0.006	0.014	1.395	2.92
August	3.6	35.87	8.57	0.021	0.007	0.109	1.16	0.011	0.021	2.380	3.58
September	13.1	10.93	8.18	0.063	0.025	0.129	1.03	0.024	0.025	1.040	2.05
October	7.2	13.35	7.77	0.038	0.016	0.428	0.55	0.027	0.031	1.747	2.19
Mean	8.89	16.52	7.84	0.025	0.011	0.317	1.43	0.018	0.017	1.373	2.31

The Dnestr Liman. Previous studies have shown that the liman plays a very important role in the transformation of biogenic substances flow from the river to the sea. Here, the accumulation and formation of new OM takes place because of processes within the water body (Tables 1, 4). The high intensity of photosynthetic processes in the liman is confirmed by the pH values, which reached 8.20–8.50 in some periods, a decrease in the concentration of mineral forms of N (NH_4^+ and NO_3^-), P (PO_4^{3-}), and Si as compared to the values in the river water. Lower concentrations of dissolved OM (as compared to the previous periods) were also observed.

Water salinity in the liman mouth (the Zatoka Port) varied from 1.0 to 17.8‰; therefore, to obtain actual data on the amount of biogenic substances, OM, and biogenic substances entering from the liman to the sea, hydrochemical information was classified by salinity: <7‰ (45% of the data) was assumed to be the liman water, and >7‰ (55% of the data), sea water. Seasonal variations in hydrochemical characteristics in the liman at the salinity in the mouth <7‰ is close to the variations in the Dnestr mouth (Table 5). The inflow of the seawater in the liman entailed a decrease in the range of the extreme and mean values of biogenic substances and OM because of the dilution of liman water by seawater (Table 6).

The ratio of mineral to organic N forms in the liman differed from that in the river: in the Dnestr mouth, the mean annual share of mineral N was 37%, while in the liman it did not exceed 20%. Such difference in the concentration of mineral and organic nitrogen N is due to its intense consumption by phytoplankton in the liman, where water blooming is recorded the year round.

Seasonal dynamics in the ratio of dissolved and suspended forms of N and P in the liman water also dif-

Table 5. Extreme and mean values of some hydrochemical characteristics in the Dnestr Liman water (Zatoka Port) at water salinity less than 7‰ in 2003–2004

Season	Range	Salinity, ‰	Suspended matter, mg dm^{-3}	pH	N-NH_3^+	N-NO_2^-	N-NO_3^-	N_{org}	P-PO_4^{3-}	P_{org}	Si, mg dm^{-3}	PO, mg O dm^{-3}
					mg N dm^{-3}				mg P dm^{-3}			
Winter	minimum	3.24	7.84	7.21	0.006	0.009	0.333	1.15	0.003	0.002	1.370	2.16
	maximum	6.47	72.71	8.06	0.073	0.014	1.542	3.48	0.057	0.027	1.940	2.47
	mean	5.39	33.76	7.77	0.040	0.012	0.742	2.07	0.032	0.022	1.630	2.32
Spring	minimum	1.00	11.45	6.93	0.002	0.006	0.180	0.54	0.002	0.010	0.400	1.75
	maximum	5.57	27.35	8.68	0.023	0.076	0.712	1.99	0.021	0.010	2.550	2.74
	mean	3.09	17.71	7.76	0.014	0.019	0.341	1.36	0.008	0.009	0.893	2.25
Summer	minimum	2.20	5.10	7.41	0.009	0.001	0.049	0.30	0.000	0.002	1.200	2.02
	maximum	6.90	65.91	8.75	0.036	0.010	0.475	2.67	0.018	0.038	2.550	3.93
	mean	3.91	30.44	8.20	0.020	0.006	0.168	1.56	0.008	0.025	1.972	3.08
Autumn	minimum	2.90	10.50	7.20	0.029	0.006	0.252	0.67	0.033	0.028	1.656	1.86
	maximum	6.90	21.67	8.30	0.035	0.008	0.827	0.41	0.042	0.039	2.245	2.32
	mean	4.43	15.38	7.59	0.033	0.006	0.592	0.27	0.038	0.034	2.002	2.11
Annual mean		3.89	24.48	7.90	0.022	0.011	0.358	1.42	0.022	0.013	1.556	2.54

Table 6. Extreme and mean values of some hydrochemical characteristics in the Dnestr Liman water (Zatoka Port) at water salinity exceeding 7‰ in 2003–2004

Season	Range	Salinity, ‰	Suspended matter, mg dm^{-3}	pH	N-NH_3^+	N-NO_2^-	N-NO_3^-	N_{org}	P-PO_4^{3-}	P_{org}	Si, mg dm^{-3}	PO, mg O dm^{-3}
					mg N dm^{-3}				mg P dm^{-3}			
Winter	minimum	7.87	1.91	6.72	0.000	0.002	0.016	0.23	0.009	0.007	0.77	1.17
	maximum	17.80	21.16	8.38	0.087	0.012	0.700	2.31	0.079	0.008	2.70	4.38
	mean	13.45	9.03	7.33	0.027	0.007	0.345	1.28	0.039	0.018	1.56	2.05
Spring	minimum	8.96	5.03	7.39	0.005	0.000	0.041	0.23	0.001	0.004	0.42	1.55
	maximum	15.45	17.66	8.65	0.023	0.005	0.651	0.69	0.005	0.013	1.00	2.33
	mean	12.47	12.36	8.13	0.014	0.002	0.424	0.65	0.004	0.01	0.79	1.91
Summer	minimum	7.50	4.08	6.94	0.005	0.000	0.019	1.25	0.002	0.009	0.47	2.65
	maximum	14.40	9.37	8.60	0.021	0.033	1.009	1.07	0.008	0.016	2.35	3.59
	mean	9.96	6.85	7.87	0.012	0.013	0.296	1.29	0.004	0.014	1.05	2.92
Autumn	minimum	7.83	1.00	6.75	0.001	0.002	0.035	0.46	0.007	0.01	0.51	1.55
	maximum	17.74	35.60	8.35	0.137	0.088	0.323	6.07	0.04	0.052	2.05	2.32
	mean	14.35	12.61	8.04	0.042	0.018	0.149	2.25	0.021	0.025	1.22	1.97
Annual mean		13.01	10.41	7.80	0.027	0.011	0.285	1.43	0.021	0.021	0.015	2.15

fered from the dynamics of this ratio in the river water. Thus, the concentration of dissolved N forms exceeded that of suspended ones two to three times in winter and spring and five to six times in summer and autumn (Table 7).

Such variations are due to the intense metabolic activity of aquatic organisms during the warm season of the year and the intensification of destruction processes in autumn. Similarly to the 1980s [8], the prevalence of suspended forms of P_{tot} over its dissolved forms was

Table 7. Ratio (in per cent) of (1) dissolved and (2) suspended forms of N, P, and OM (by PO) in the Dnestr Liman water (the Zatoka Port) in 2003–2004

Season	Hydrochemical characteristics							
	N_{tot}		P_{min}		P_{tot}		Organic matter	
	1	2	1	2	1	2	1	2
Winter	73.9	26.1	72.0	28.0	62.9	37.1	49.5	50.5
Spring	72.4	27.6	84.2	15.8	40.9	59.1	67.0	33.0
Summer	86.4	15.2	54.5	45.5	27.8	72.2	80.7	19.3
Autumn	82.6	17.4	80.4	19.6	68.4	31.6	93.2	6.8

Table 8. Export of biogenic substances and OM (thousand ton year^{-1}) by the Dnestr River to the Dnestr Liman and to the Black Sea at the average Dnestr water runoff of 7.36 km^3 year^{-1} for 1985–1988 and 11.55 km^3 year^{-1} for 2003–2004

Recipient water body	Hydrochemical characteristic	1985–1988	2003–2004
Liman	N-NH_4^+, thousand ton year^{-1}	4.53	0.84
Sea		1.62	0.29
Liman	N-NO_2^-, thousand ton year^{-1}	1.41	0.36
Sea		0.81	0.13
Liman	N-NO_3^-, thousand ton year^{-1}	9.57	9.94
Sea		9.84	3.67
Liman	N_{org}, thousand ton year^{-1}	3.75	19.31
Sea		3.48	16.90
Liman	N_{tot}, thousand ton year^{-1}	19.26	30.45
Sea		15.75	20.99
Liman	P-êO_4^{3-}, thousand ton year^{-1}	0.66	0.86
Sea		0.92	0.21
Liman	P_{org}, thousand ton year^{-1}	0.30	0.34
Sea		2.20	0.20
Liman	P_{tot}, thousand ton year^{-1}	0.96	1.20
Sea		3.12	0.41
Liman	Si, thousand ton year^{-1}	32.46	28.44
Sea		11.56	15.93
Liman	Organic matter, thousand ton year^{-1}	30.91	27.98
Sea		62.08	26.88
Liman	Σ, thousand ton year^{-1}	83.59	88.07
Sea	Σ, thousand ton year^{-1}	92.51	64.21

observed in summer and autumn, the fact that can be explained by the accumulation of suspended forms of P_{tot} in newly formed OM.

Hydrochemical monitoring carried out in 2003–2004 revealed significant accumulation of mineral and organic compounds of N and P, resulting from the processes within water body as the river water flows through the liman. Thus, the concentration of NH_4^+, NO_2^-, and NO_3^- in the liman was almost 3 times as low as in the river mouth; that of PO_4^{3-}, almost 4 times; and Si, almost 2 times (Tables 1, 5). The concentrations of suspended matter, N_{org}, and OM in the liman mouth are similar to the values existing in the river water because of the formation of new OM. However, the comparatively high concentration of OM in the water flowing from the liman to the sea continues to promote seawater eutrophication in the nearshore area.

The input of mineral and organic forms of N, P, and Si and dissolved OM from the Dnestr to the liman and then to the Black Sea, was compared for the periods, for which sufficient hydrochemical observation data were available: 1985–1988 and 2003–2004 (Table 8).

The comparison has shown that the runoff of mineral and organic substances of the Dnestr River grew from 83.59 thousand ton year^{-1} in 1985–1988 (the period of a median water runoff) to 88.07 thousand ton year^{-1} in 2003–2004 (the period of high water runoff). This is due to the input of appreciable amount of organic N compounds from the river to the liman. In 2003–2004, the input of organic N compounds from the liman to the sea which decreased to 63.58 thousand ton year^{-1} due to the assimilation of mineral forms of N and P in the liman.

CONCLUSIONS

Analysis of long-term (1952–2004) variations in the concentration of biogenic substances and OM in the water of the lower reaches of the Dnestr has shown that in 2003–2004 the values of NH_4^+, NO_2^-, and PO_4^{3-} decreased to in the level recorded in 1950–1953. The concentration of Si also decreases because of the river runoff regulation and the settling of Si in the reservoirs. An increase in NO_3^- and N_{org} concentrations was also recorded. Similar tendencies were observed for the water flowing from the Dnestr Liman to the northwestern Black Sea.

The comparison of losses of biogenic substances, occurring as the Dnestr River water flows through the liman, proved the intensification of the process of accumulation of N, P, and Si mineral compounds. Thus, in 1952–1953, up to 26% of those compounds were accumulated in the bay; whereas, in 2003–2004, the process under consideration became more intense, and about 50% of such compounds accumulated in the liman.

In spite of the "buffer" role of the Dnestr Liman, the contribution of the biogenic substances delivered into the sea by the Dnestr River water to the eutrophication of the northwestern Black Sea remains appreciable, totaling about 60 thousand ton year^{-1}, out of which mineral compounds of N, P, and Si amount to ~20 thousand ton year^{-1}, whereas dissolved organic substances amount to ~44 thousand ton year^{-1}.

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REFERENCES

1 1. Almazov, A.M., *Gidrokhimiya ust'evykh oblastei rek* (Geochemistry of River Mouth Areas), Kiev: Izd. AN USSR, 1962.

2. Almazov, A.M. and Denisova, A.I., *Gidrokhimiya Dnestrovskogo limana* (Hydrochemistry of Dnestr Liman), Kiev: Izd. AN USSR, 1955.

3. Almazov, O.M., Runoff of Dissolved Salts and Biogenic Substances by Rivers of the UkrSSR into the Black Sea, *Nauk. Zapiski Odes'Ko Biologichno Stantsi*,1961, Iss. 3, pp. 90–107.

4. Garkavaya, G.P., Berlinskii, N.A., Bogatova, Yu.I., and Goncharov, A.Yu., Zoning of the Ukrainian Sector of the Northwestern Black Sea (by Hydrophysical and Hydrochemical Characteristics), in *Ekologicheskaya bezopasnost' pribrezhnoi i shel'fovoi zon i kompleksnoe ispol'zovanie resursov shel'fa* (Environmental Safety of the Coastal and Shelf Zones and Multipurpose Use of Shelf Resources), Sevastopol, 2000, pp. 9–24.

5. Garkavaya, G.P., Berlinskii, N.A., Bogatova, Yu.I., *et al.*, Problems of Anthropogenic Eutrophication of the Dnestr River and the Dnestr Liman and Their Effect on the Northwestern Black Sea, *Naukovi Zapiski Ternopil'Skogo Natsional'Nogo Pedagogichnogo Universitetu, Ser. Biologiya*, , 2005, no. 3(26), pp. 74–76.

6. *Gidrobiologicheskii rezhim Dnestrovskogo limana* (Hydrobiological Regime of the Dnestr Liman) Braginskii, L.P., Ed., Kiev: Nauk. Dumka, 1992.

7. Zhdanova, G.A., Shevtsova, L.V., Kuz'ko, O.A., et al., Ecological Assessment of Water Quality of the Lower Dnestr, *Gidrobiol. Zh.*, 1995, vol. 31, no. 6, pp. 22–34.

8. Zubkova, E. and Shlenk, D., Present-Day State of the Dnestr River Quality, in *Integrirovannoe upravlenie prirodnymi resursami transgranichnogo basseina Dnestra* (Integrated Management of Natural Resources of the Transboundary Basin of the Dnestr), Chisinau: Eco-TIRAS, 2004, pp. 128–132.

9. *Proekt "Morya SSSR"* (Project "Seas of the USSR"), Terziev, F.S., Ed., St. Petersburg: Gidrometeoizdat, 1991, vol. IV, iss. 1.

10. Ropot, V.M., Stratulat, G.V., and Sandu, M.A., *Problemy kachestva, ispol'zovaniya i okhrany vodnykh resursov SSR Moldovy* (Issues of Quality, Use and Protection of Water Resources of the Moldova SSR), Chisinau: Shtiintsa, 1991, pp. 3–112.

11. *Rukovodstvo po metodam khimicheskogo analiza morskikh vod* (Guide on the Methods of Chemical Analysis of Seawater), St. Petersburg: Gidrometeoizdat, 1993.

12. *Severo-zapadnaya chast' Chernogo morya: biologiya i ekologiya* (Northwestern Black Sea: Biology and Ecology), Kiev: Naukova Dumka, 2006.

13. Shevtsova, L.V., Hydrobiological Studies of the Dnestr: Results, Problems, and Ways for Their Solution, *Gidrobiol. Zhurnal*, 1998, vol. 34, no. 6, pp. 35–44.

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