EVALUATION OF THE PHYSICAL-CHEMICAL QUALITY STATE OF THE DANUBE DELTA AQUATIC ECOSYSTEM DURING THE PERIOD 2003-2004

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SUMMARY

The main objective of this paper is to provide data on the Danube Delta aquatic ecosystem quality, based on the long-term analytical investigation of specific indicators, the physical-chemical properties of water and sediment samples collected from Uzlina and Murighiol locations in the period April-October, during two consecutive years (2003 and 2004).

The comparative analysis of the quality characteristics of the Danube Delta aquatic ecosystem in these two years emphasized the dynamic character of the water quality possibly determining an evolution into the unfavorable stages, which lead to worsen life conditions for aquatic organisms.

KEYWORDS: Danube Delta, water, sediment, physical-chemical characterization, parameters.

INTRODUCTION

The territory of the Danube Delta Biosphere Reservation has a total surface of almost 580,000 ha, and includes the Danube Delta, the complex Razim-Sinoe, the seaboard Danube till Cotul Pisicii and the lake Saraturi-Murghiol. From this surface, more than 50% (312,440 ha) is represented by aquatic and terrestrial natural ecosystems included in the universal patrimony.

The major sources of pollution in the Danube Delta Biosphere Reservation are represented by the economical agents from the nearby area, and also by the naval transportation. The release of heavy metals into the aquatic environment causes detrimental effects. Because most heavy metals become associated with particulates, as a result of setting time, they accumulate in the bottom sediments of the receiving water. The knowledge of the fixation mechanisms of heavy metals is an important parameter for the risk assessment concerning the pollution of the ecosystems. Mobility and availability are highly dependent on the way and the strength of the fixation of the heavy metals by the sediment components.

The occurrence of heavy metals in soil and sediments can theoretically include the following fractions [1, 2]:

- free ions or complexes in the pore water;
- adsorptive or exchangeable bound on soil component surface, mainly on iron and manganese oxides and hydroxides, clay minerals and organic matter;
- precipitated as chemical compounds (hydroxides, carbonates and sulfides) ;
- co-precipitates on iron and manganese oxides and hydroxides, phosphate and sulfide minerals;
- organic complexes (on organic solid phases) ;
- residuals, included in detritic minerals, especially silicates.

Because of their accumulation tendency, organics like chlorinated pesticides and polyaromatic hydrocarbons represent another important category of pollutants that have to be controlled periodically.

In order to understand and eliminate the risk factors that might affect this area, many studies have been developed. A vast activity in this field was performed by the Danube Delta Biosphere Reservation Association (DDBRA), whose responsibility is to monitor the quality of the ecosystem and to intervene promptly, when pollution occurs.

The results obtained in a previous study [3] concerning the physical-chemical quality state of the deltaic ecosystems from Uzlina and Murighiol locations, carried out in the period April-October 2003, showed an oxygen deficit and the presence of some chemical parameters (heavy metals, phenolic compounds, mineral oil, o- phosphates, lindane) in concentrations, which exceed the reference values.

Because water quality has a dynamic character, which can determine an evolution to unfavorable stages and to inappropriate life conditions for the aquatic organisms, the investigations started in 2003 were continued in 2004, and the results of both investigations were compared. Relevant information concerning the ecosystem quality was obtained, focusing on the physical-chemical characteristics and an overview of the pollution level evolution in time.

MATERIAL AND METHODS

Water and sediment samples (momentary samples) were taken from two locations - Uzlina and Murighiol (see map of Danube Delta), in the periods April-October 2003 and 2004.

The sampling and preservation of the samples was done in accordance with the recommendations of the specific international guides [4-6].

For the analysis of sediment samples, the fractions of particulates with dimensions <63µm were taken. For the AAS analysis of heavy metals, the samples were digested with aqua regia in a micro-wave apparatus. For the quantitative analysis of the adsorbed organic pollutants, the samples were lyophilized and extracted.

The analyses were carried out with homogenous water and sediment samples. In both types of samples (water and sediment), the contents of heavy metals and organic compounds were analyzed.

In Table 1, the chemical parameters and indicators determined in this study, and the methods of analysis used are summarized.

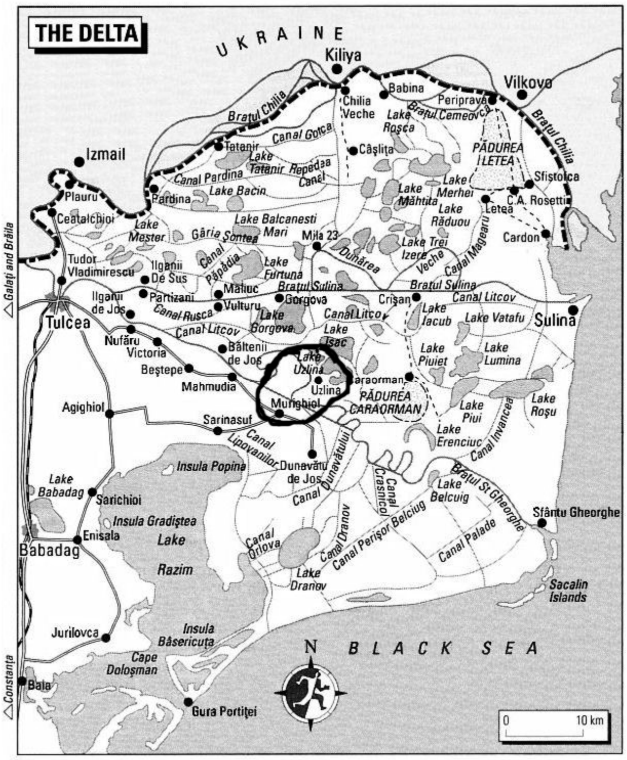

FIGURE 1 - Map of Danube Delta.

TABLE 1 - Uzlina - water sample characteristics from April 2003 until October 2004.

No	Parameters	M.U.	April		May		June		July		August		September		October		ORDER MAPM no. 1 146 Quality class			
			2003	2004	2003	2004	2003	2004	2003	2004	2003	2004	2003	2004	2003	2004	I	II	III	IV
1	pH	pH unit.	7.98	7.32	7.02	8.07	7.32	8.29	7.41	7.49	8.08	7.99	7.69	8.49	7.88	7.88	6.5-8.5			
2	Conductivity	µS/cm	483	381	418	380	397	351	371	386	387	389	414	417	445	430	-	-	-	-
3	Residue filterable	mg/l	273	344	289	184	387	193	241	184	263	281	193	272	173	280	basic	500	1000	1300
4	Dissolved oxygen	mg/lO_2	4.89	4.21	3.92	4.60	1.80	3.79	2.26	4.90	2.41	3.82	4.98	7.95	4.91	6.40	7	6	5	4
5	BOD_5	mg/lO_2	3.60	3.32	3.82	52.32	4.10	18.67	22.41	3.14	7.01	12.77	5.04	3.53	4.68	3.40	3	5	10	25
6	COD-Cr	mg/lO_2	12.0	13.2	13.6	172.8	11.8	54.9	58.8	14.07	19.2	35.60	16.4	11.20	14.8	10.8	10	25	50	125
7	Ammonium N-NH_4^+	mgN/l	0.074	0.15	0.046	0.25	0.036	0.16	<0.01	0.23	0.046	0.49	<0.01	0.10	0.120	0.20	0,2	0.3	0.6	1.5
8	Nitrate N-NO_3^-	mgN/l	1.87	2.28	1.13	1.08	1.92	5.54	0.90	2.77	0.45	1.39	<0.01	1.02	1.71	1.14	1	3	6	15
9	Total Nitrogen	mgN/l	-	13.86	-	25.54	-	30.5	-	27.86	-	8.40	-	2.78	-	5.57	1,5	4	8	20
10	o-phosphate (P-PO_4^{3-})	mgP/l	0.29	0.1	0.27	0.12	0.21	0.05	0.07	0.07	0.13	0.14	0.10	0.09	0.10	0.10	0,05	0.1	0,2	0.5
11	Total phosphorus	mgP/l	-	0.45	-	0.43	-	0.81	-	0.12	-	0.81	-	0.13	-	0.10	0,10	0.2	0.4	1
12	Chloride	mg/l	-	25.12	-	26.79	-	26.79	-	30.14	-	60.28	-	33.49	-	36.84	basic	100	250	300
13	Sulfate	mg/l	-	48.33	-	29.24	-	15.32	-	31.22	-	37.19	-	32.62	-	29.43	80	150	250	300
14	Nickel	mg/l	-	0.008	-	<0.005	-	<0.005	-	<0.005	-	<0.005	-	<0.005	-	<0.005	basic	0.05	0.1	0.25
15	Iron total	mg/l	1.26	0.59	2.16	0.84	0.78	0.61	2.95	1.12	1.58	0.95	0.61	1.47	0.80	1,14	basic	0.1	0.3	1.0
16	Manganese	mg/l	0.055	0.027	0.10	0.03	0.044	0.03	0.11	0.04	0.067	0.04	0.026	0.03	0.026	0.04	basic	0.05	0.1	0.3
17	Zinc	mg/l	0.038	0.005	0.018	0.05	0.027	0.008	0.03	0.01	0.035	0.02	0.01	0.03	0.026	0.02	basic	0.1	0.2	0.5
18	Cadmium	mg/l	0.001	0.001	0.001	0.001	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0,001	<0.001	<0.001	<0.001	basic	0.001	0.002	0.005
19	Chromium total	mg/l	0.01	0.01	0.01	<0.01	<0.01	<0.01	<0,01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	basic	0.05	0.1	0.25
20	Copper	mg/l	0.015	0.014	0.015	<0.005	0.025	<0.005	0.020	0.03	0.019	0.02	0.021	0.02	0.013	0.02	basic	0.02	0.04	0,1
21	Lead	mg/l	-	<0.005	-	<0.005	-	<0.005	-	<0.005	-	<0.005	-	<0.005	-	<0,005	basic	0.005	0.01	0.025
22	Arsenic	mg/l	-	<0.001	-	<0.001	-	<0.001	-	<0.001	-	<0.001	-	<0.001	-	<0,001	basic	0.005	0.01	0.025
23	Anionic surfactants	mg/l	0.127	0.016	0.016	0.099	0.028	0.092	0.307	0.006	0.291	0.092	0.051	0.041	0.038	0,054	basic	0.5	0.75	1
24	Phenol index	mg/l	<0.001	<0.001	0.016	<0.001	<0.001	<0.001	<0.001	<0.001	0.036	<0.001	0.015	<0.001	0.006	<0,001	basic	0.001	0.02	0.05
25	Mineral oil	mg/l	<0,05	<0.05	<0.05	<0.05	<0.05	<0.05	14.80	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0,05	basic	0.1	0.2	0.5
26	Polynuclear Aromatic Hydrocarbons (PAH) -Total -Fluoranthene -Benzo(b) fluoranthene -Benzo (k) fluoranthene -Benzo (a) pyrene -Benzo (ghi) perylene -Indeno(1,2,3-cd)pyrene	µg/l µg/l µg/l µg/l µg/l µg/l µg/l	0.21 <0.02 0.21 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.19 <0.02 0.19 <0.02 <0.02 <0.02 <0.02	0.45 0.09 0.36 <0.02 <0.02 <0.02 <0.02	- - - - - - -	0.17 0.17 <0.02 <0.02 <0.02 <0.02 <0.02	0.13 <0.02 0.13 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.07 0.07 <0.02 <0.02 <0.02 <0.02 <0.02	0.39 0.14 0.12 <0.02 0.13 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	-	-	-	-
27	Pesticides Total -Lindane(γ-HCH) - Atrazine	µg/l µg/l µg/l	0.309 0.309 <0.1	0.12 0.12 <0.1	0.203 0.203 <0.1	0.203 0.203 <0.1	0.34 0.34 <0.1	<0.1 <0.1 <0.1	4.07 4.07 <0.1	<0.1 <0.1 <0.1	<0.1 <0.1 <0.1	<0.1 <0.1 <0.1	<0.1 <0.1 <0.1	<0.1 <0.1 <0.1	0.57 0.57 <0.1	<0.1 <0.1 <0.1	- 0.05 0.02	- 0.1 0.1	- 0.2 0.2	- 0.5 0.5
28	Polychlorobiphenyls (PCB)	µg/l	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	-	-	-

A mobility and availability study was also carried out in the laboratory, using the French standard NF X31–120/ 992 [7].

The analytical technique, to examine the degree of mobility of heavy metals from sediment into the aquatic body, consisted of the following steps: 4 g of pretreated sediment were mixed with 40 ml of buffer solution (1M ammonium acetate and 0.01 M EDTA). The obtained suspension was shaken for 2 h with 40 rpm. The resulting solutions were filtered, and after that analyzed by AAS for metals` determination.

RESULTS AND DISCUSSION

In Tables 2 and 3, the results of the investigation performed in two consecutive years (2003 and 2004) are presented, in order to pursuit the watercourse quality evolution, including the acceptable limits for each parameter.

The evolution of the concentrations found in the water samples during two years, and the comparison of these results with the references values [8], imposed by the *Norm concerning the reference objectives for the surface water quality classification* (ORDER no. 1 146/2003, transposed from Directive 2000/60/EC) are presented in Figures 1-8 for Uzlina, and in Figures 9-17 for Murighiol.

TABLE 2 - Murighiol - water samples characteristics from April-October 2003 and 2004.

No	Parameters	M.U.	April		May		June		July		August		September		October		ORDER MAPM no. 1 146 Quality class			
			2003	2004	2003	2004	2003	2004	2003	2004	2003	2004	2003	2004	2003	2004	I	II	III	IV
1	pH	pH unit.	7.84	8.09	7.87	7.65	7.44	7.15	7.53	7.26	7.78	7.06	7.50	7.63	7.66	7.52	6.5-8.5			
2	Conductivity	µS/cm	635	388	1215	370	1348	439	1489	1050	1376	1174	801	964	505	1070	-	-	-	-
3	Residue filterable	mg/l	319	584	271	248	1060	264	252	480	274	525	198	420	164	495	basic	500	1000	1300
4	Dissolved oxygen	mg/lO_2	5.20	4.82	3.22	4.22	1.10	3.72	1.98	3.30	1.19	4.27	4.96	5.38	4.89	3.85	7	6	5	4
5	BOD_5	mg/lO_2	7.05	3.14	13.82	9.30	21.63	116.05	27.09	14.91	35.52	18.41	7.93	11.25	4.51	11.83	3	5	10	25
6	COD-Cr	mg/lO_2	19.6	10.9	37.8	27.3	57.6	297.6	67.2	70.4	86.4	55.3	29.5	32.0	17.86	33.6	10	25	50	125
7	Ammonium N-NH_4^+	mgN/l	0.046	0.12	0.083	0.20	0.059	0.22	<0.01	0.43	0.01	0.80	<0.01	0.34	1.75	0.31	0.2	0.3	0.6	1.5
8	Nitrate N-NO_3^-	mgN/l	0.46	1.61	0.54	0.29	1.02	1.38	0.34	1.38	1.35	1.39	<0.01	0.55	1.75	0,49	1	3	6	15
9	Total Nitrogen	mgN/l	-	11.08	-	5.54	-	6.93	-	22.3	-	11.14	-	8.3	-	22. 9	1.5	4	8	20
10	o-phosphate (P-PO_4^{3-})	mgP/l	0.29	0.04	0.34	0.12	0.31	0.16	0.06	0.10	0.07	0.50	0.17	0.08	0.08	0.10	0.05	0.1	0.2	0.5
11	Total phosphorus	mgP/l	-	0.51	-	0.45	-	1.06	-	0.18	-	0.68	-	0.10	-	0.10	0.10	0.2	0.4	1
12	Chloride	mg/l	-	30.14	-	23.44	-	40.18	-	231	-	254.53	-	194	-	211	basic	100	250	300
13	Sulfate	mg/l	-	49.72	-	32.62	-	32.22	-	25.06	-	28.04	-	30	-	28.84	80	150	250	300
14	Nickel	mg/l	-	<0.005	-	0.01	-	<0.005	-	<0.005	-	<0.005	-	<0.005	-	<0.005	basic	0.05	0.1	0.25
15	Iron total	mg/l	1.26	0.39	2.49	0.77	8.07	0.99	4.33	0.67	2.56	0.45	1.71	1.95	1.55	2.33	basic	0.1	0.3	1.0
16	Manganese	mg/l	0.053	0.023	0.25	0.04	0.64	0.21	0.32	0.23	0.26	0.08	0.16	0.1	0.05	0.16	basic	0.05	0.1	0.3
17	Zinc	mg/l	0.038	<0.005	0.033	0.02	0.047	0.017	0.04	0.03	0.106	0.03	0.02	0.03	0.02	0.03	basic	0.1	0.2	0.5
18	Cadmium	mg/l	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	basic	0.001	0.002	0.005
19	Chromium total	mg/l	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	basic	0.05	0.1	0.25
20	Copper	mg/l	0.014	0.013	0.014	0.01	0.030	<0.005	0.020	0.02	0.022	0.02	0.026	0.01	0.015	0.01	basic	0.02	0.04	0.1
21	Lead	mg/l	-	<0.005	-	<0.005	-	<0.005	-	<0.005	-	<0.005	-	<0.005	-	<0.005	basic	0. 05	0.01	0.025
22	Arsenic	mg/l	-	<0.001	-	<0.001	-	<0.001	-	<0.001	-	<0.001	-	<0.001	-	<0.001	basic	0.005	0.01	0.025
23	Anionic surfactants	mg/l	0.022	0.249	0.06	0.039	0.035	0.094	0.102	0.019	0.134	0.054	0.025	0.048	0.048	0.089	basic	0,5	0.75	1
24	Phenol index	mg/l	0.002	0.006	0.007	<0.001	0.023	<0.001	0.013	<0.001	0.011	0.011	0.025	0.002	0.008	<0.001	basic	0.001	0.02	0.05
25	Mineral oil	mg/l	<0.05	<0.05	<0.05	<0.05	1.67	<0.05	5.17	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	basic	0.1	0.2	0.5
26	Polynuclear Aromatic Hydrocarbons (PAH) -Total -Fluoranthene -Benzo(b) fluoranthene Benzo (k) fluoranthene -Benzo (a) pyrene -Benzo (ghi) perylene -Indeno(1,2,3-cd)pyrene	µg/l µg/l µg/l µg/l µg/l µg/l µg/l	0.18 <0.02 0.18 <0.02 <0.02 <0.02 <0.02	0.14 0.14 <0.02 <0.02 <0.02 <0.02 <0.02	0.15 <0.02 0.15 <0.02 <0.02 <0.02 <0.02	0.47 0.13 <0.02 0.34 <0.02 <0.02 <0.02		0.23 0.12 0.11 <0.02 <0.02 <0.02 <0.02	0.27 <0.02 0.27 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.12 0.12 <0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	-	-	-	-
27	Pesticides Total -Lindane (γ-HCH) - Atrazine	µg/l µg/l µg/l	0.417 0.417 <0.1	0.1 0.1 <0.1	0.193 0.193 <0.1	<0.1 <0.1 <0.1	0.35 0.35 <0.1	<0.1 <0.1 <0.1	5.06 5.06 <0.1	<0.1 <0.1 <0.1	<0.1 <0.1 <0.1	<0.1 <0.1 <0.1	<0.1 <0.1 <0.1	<0.1 <0.1 <0.1	<0.1 <0.1 <0.1	<0.1 <0.1 <0.1	- 0.05 0.02	- 0.1 0.1	- 0.2 0.2	- 0.5 0.5
28	Polychlorobiphenyls (PCB)	µg/l	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	-	-	-

TABLE 3 - Characterization of the sediments collected in the periods April-October 2003 and 2004 at Uzlina (total concentration).

No.	Component	M.U	April		May		June		July		August		Sept.		Oct.		Adms.lim.values Order MAPM no. 1146/2003
			2003	2004	2003	2004	2003	2004	2003	2004	2003	2004	2003	2004	2003	2004	
1	Copper	mg/kg	-	39.9	36.18	33.2	63.34	23.2	90	39.8	53.11	41	62.76	66.7	56.1	67.7	200
2	Zinc	mg/kg	-	86.8	108.8	109.2	144.57	80.8	164.4	17.4	147.95	138	125.2	136.8	124.1	132.9	300
3	Cadmium	mg/kg	-	<0.5	<0.5	<0.5	0.94	<0.5	0.84	<0.5	0.45	0.96	0.64	<0.5	<0.5	<0.5	3,5
4	Chromium	mg/kg	-	46.4	40.8	39.7	41.1	19.7	42.5	21.4	46.12	37.5	38.5	45.2	42.96	42.1	90
5	Lead	mg/kg	-	14.9	29.8	27.2	40.2	21.7	30.14	20.2	25.73	43.2	28.44	40.1	24.34	37.1	90
6	Mercury	mg/kg	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	90
7	Arsenic	mg/kg	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	17
8	Benzo(a)pyren	mg/kg	-	0.062	-	<0.02	-	0.198	-	0.13	-	0.066	-	0.08	-	<0.02	750
9	Mineral oil	mg/kg	-	<25	35.68	<25	49.62	49.58	124.7	385	55.19	<25	73.6	171	<25	139	-
10	Lindane (γ-HCH)	mg/kg	-	<0.001	<0.001	<0.001	0.036	<0.001	0.21	<0.001	0.025	<0.001	<0.001	<0.001	0.04	<0.001	1.4
11	PCBs	mg/kg	-	<0.01	-	<0.01	-	<0.01	-	<0.01	-	<0.01	-	<0.01	-	<0.01	280
12	Total phosphorus	mgP/kg	-	-	2016	-	1637	-	592	-	983	-	442	-	1407	-	-
13	Nitrat	mgN/kg	-	-	165	-	128	-	200	-	105	-	175	-	154	-	-
14	Manganese	mgP/kg	-	-	567	-	676	-	764	-	623	-	641	-	600	-	-

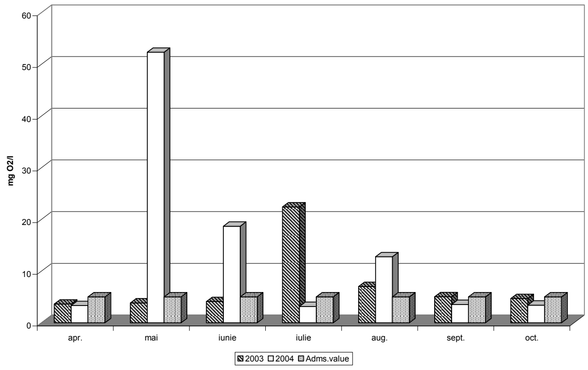

FIGURE 1 – BOD_5

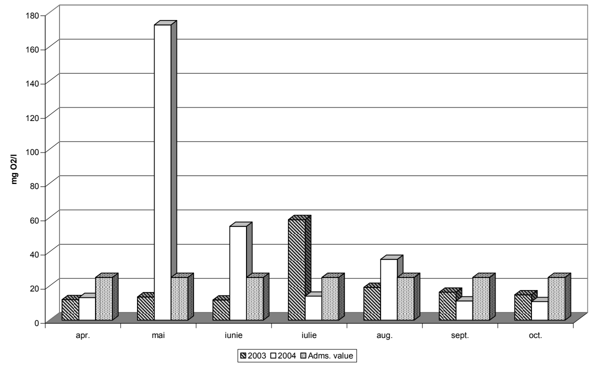

FIGURE 2 - COD – Cr

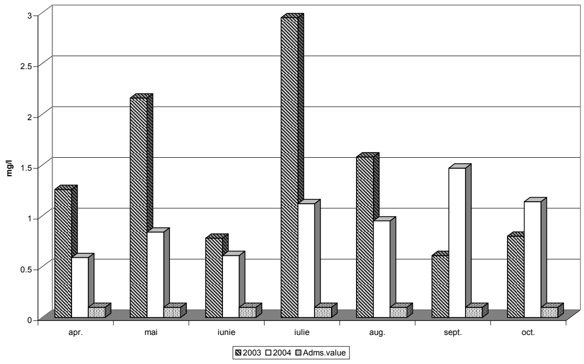

FIGURE 3 – Iron

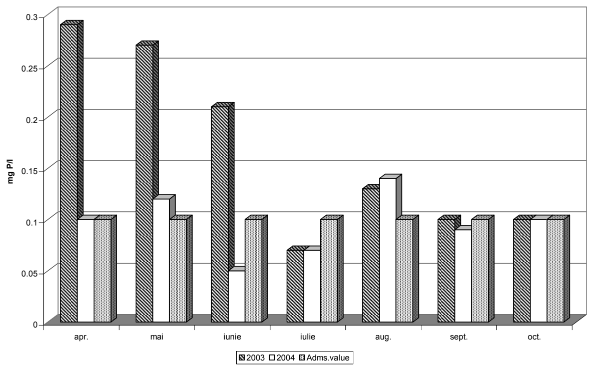

FIGURE 4 – o-Phosphate

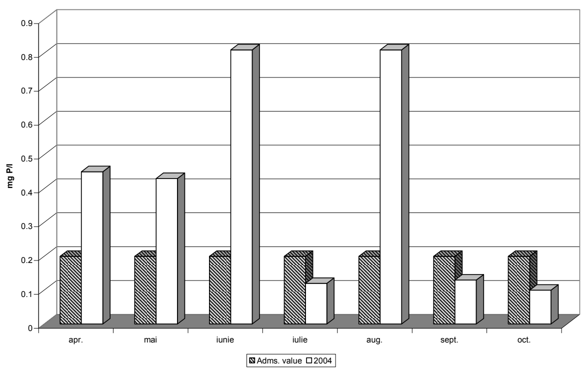

FIGURE 5 – Total Phosphorus

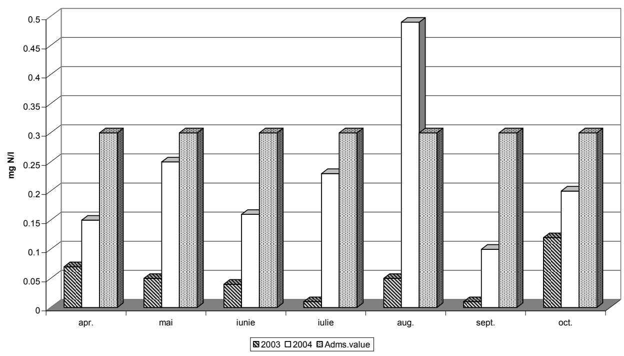

FIGURE 6 – Ammonium

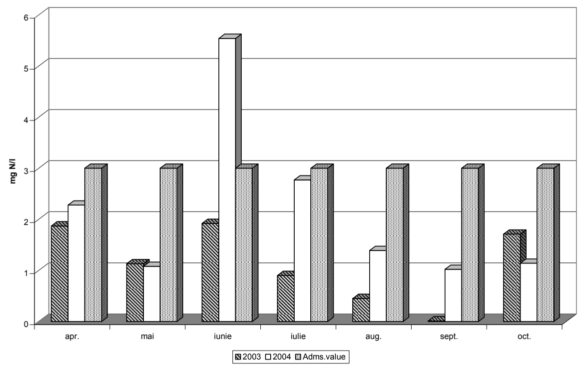

FIGURE 7 – Nitrate

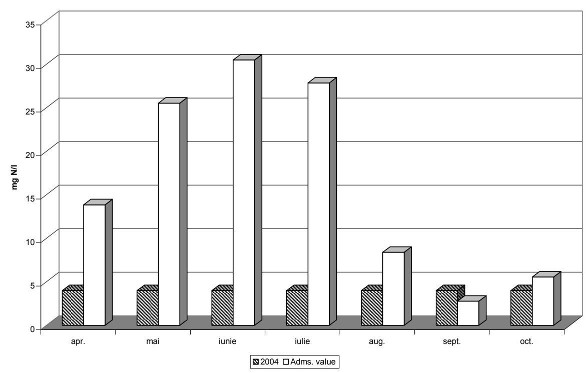

FIGURE 8 – Total Nitrogen

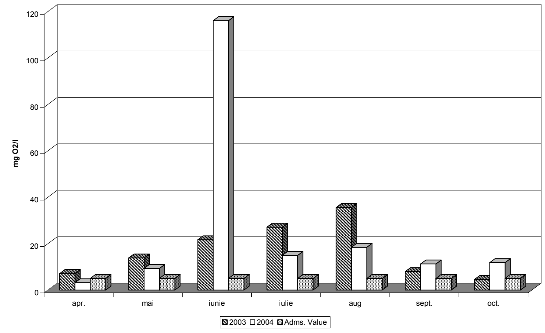

FIGURE 9 – BOD_5

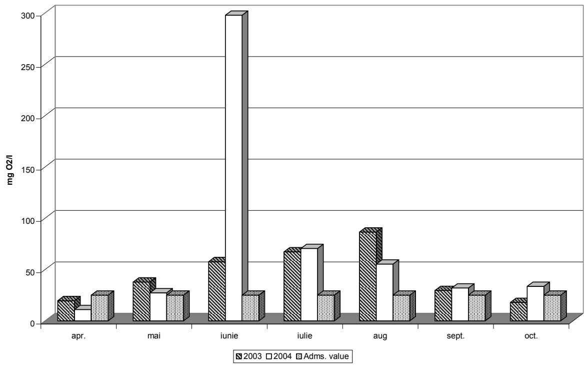

FIGURE 10 – COD – Cr

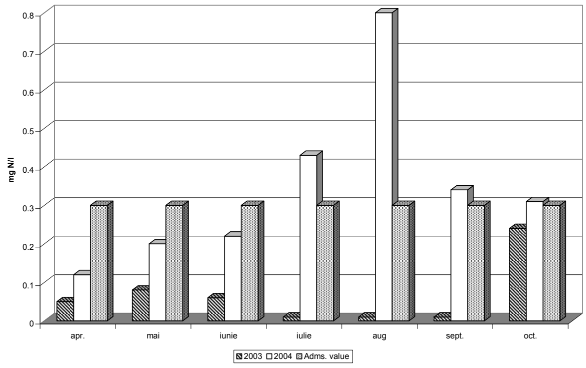

FIGURE 11 – Ammonium

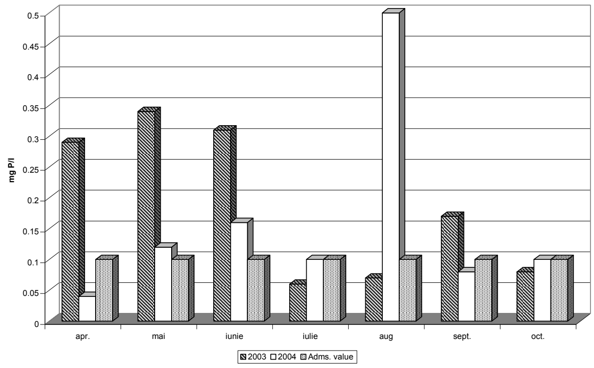

FIGURE 12 – o-Phosphate

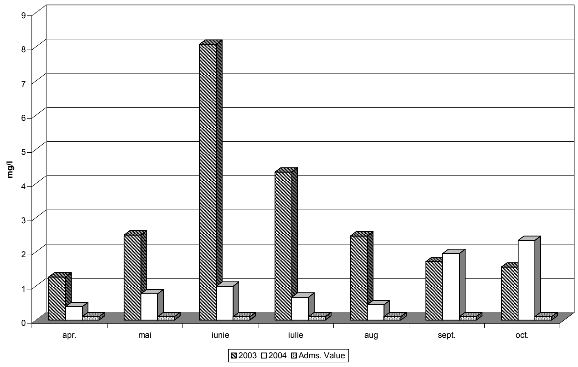

FIGURE 13 – Iron

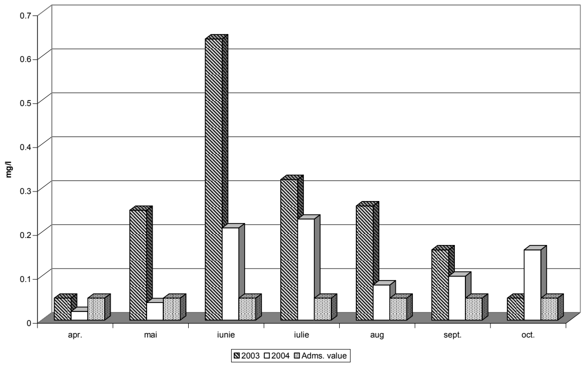

FIGURE 14 – Manganese

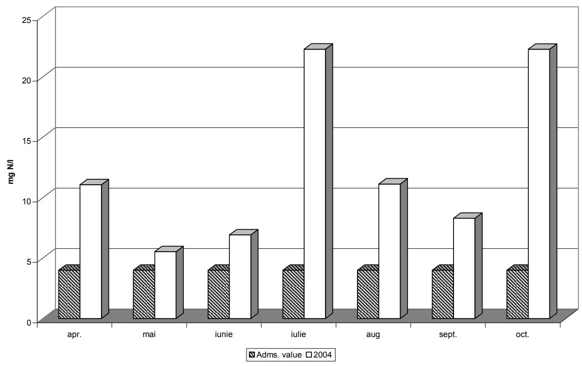

FIGURE 15 – Total Nitrogen

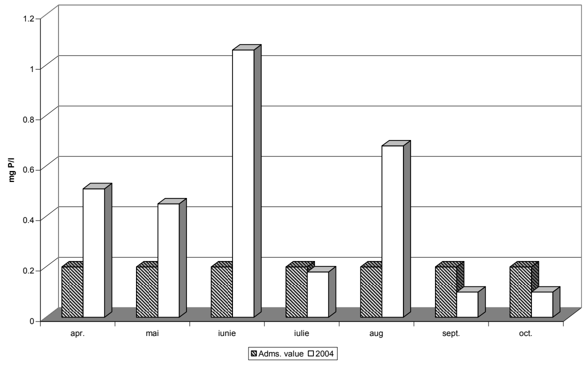

FIGURE 16 – Total Phosphorus

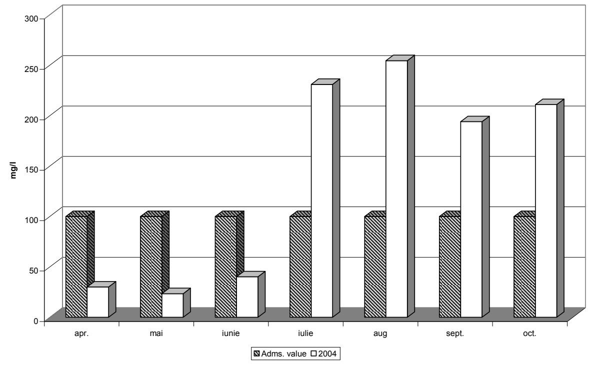

FIGURE 17 – Chloride

The following physical-chemical changes took place in the water samples investigated in 2004, in comparison with 2003:

In Uzlina:

- the watercourse presented a high organic load during summer time;
- ammonium and nitrate concentrations recorded an increase, but only in August, respectively; in June, they did not correspond to the proscribed class according to the national norm; however, the organic nitrogen was present in high concentrations during spring and summer time, reflecting a pollution influence;
- the concentration of the dissolved orthophosphate forms diminished towards the preceding year, when the values recorded in spring and summer time were higher than the admissible limit;
- tied phosphorus content, shown through the total phosphorus value, was high above the critical value, during almost all the investigation periods, tending in autumn to reach the natural reference conditions;
- heavy metal concentrations were below the reference values, with the exception of iron, manganese and copper; iron occurs in high concentration, but in all the periods with a decrease of the values;
- lindane (γ-HCH) was present in higher concentration only in May (0.2 μg/l), when compared with the preceding year 0.3-4 μg/l;
- phenolic compounds were below the detection limit of the method, with regard to 2003, when they exceed the reference value in May, as well as in the period August-October.

In Murighiol:

- organic load was similar in both years of investigation, the highest value being recorded in June 2004;
- increasing of ammonium concentrations with values over the proscribed limit in the period July-September;
- the concentrations of organic nitrogen and phosphorus, analyzed only in 2004, show a specific organic pollution;
- an unexpected increase of the chloride ion concentrations in July (from 40 mg/l found in June to 231 mg/l) and also persisting at this high level in the next months; this increase is also reflected by the higher values of the filterable residue and conductivity in the same period;
- reduction of iron concentration as at Uzlina was recorded in the water-body, but the values lasted also in a surplus domain;
- concentrations of manganese were over the limit proscribed by the national norm, but with values more reduced towards 2003;
- decrease of phenolic compound concentrations was observed in 2003, but not within the tolerable limit for the aquatic life ecological protection.

Results of the sediment sample analyses for the total heavy metals content (Tables 3 and 4) show a relatively uniform distribution during the investigated period in both locations, and are under the reference values that reflect the quality conditions to protect the Danube Delta ecosystem.

The study of the availability of the heavy metals: Cu, Zn, Pb, Mn, Fe, and Cr to migrate from sediment into the aquatic body (Figures 18 and 19) emphasize the following aspects:

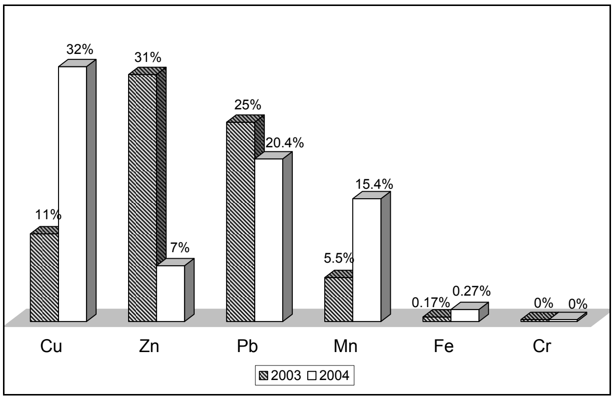

FIGURE 18 – The mobility of heavy metals from Danube sediments in periods April–October 2003 and 2004 at Uzlina.

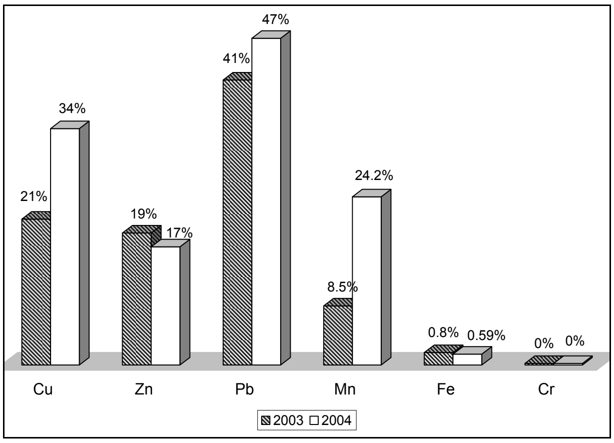

FIGURE 19 – The mobility of heavy metals from Danube sediments in period April–October 2003 and 2004 at Murighiol.

In Uzlina:

- The composition of the sediment has not suffered changes as drastic as those from Murighiol;
- The concentrations of Cu, Zn and Pb in mobile form are lower during this year, that is especially due to the diminution of total concentrations (Cu, Pb) and mobility (Zn);
- manganese has a similar behavior to that from Murighiol, with an about 3-fold increase of the mobile form concentration;
- The mobile form concentration of iron was within the same domain.

In Murighiol:

- The concentrations of Pb and Fe in mobile phase have increased in 2004, and that can be due to their higher total concentration in sediments;
- The increase of about 2.5 times of the manganese concentration may be a consequence of its appearance in an easily exchangeable form;
- There have not been recorded significant changes of Zn and Cu mobile form concentrations.

The sediment texture from Murighiol was significantly altered in 2004, in comparison with the same period of the former year. The exchangeable forms of lead, iron and manganese have increased. The sediment texture from Uzlina has suffered an important alteration only in the case of mobile manganese (3 times higher), whereas the other metals remained to be constant (Fe) or were lower (Cu, Zn, Pb).

In conclusion, the measured values were momentary ones, and show the character of the contamination levels, relating to the periods and locations of the investigation campaign development.

The pollutants found in concentrations that exceeded the limits represent a potential for water quality alteration by negative influences on auto-purification of the river due to the diminution of its biological activity.

Generally, for all investigated periods, we point out that in both locations:

- the watercourses presented a deficit in oxygen, and under saturation, not satisfying the prescribed regulations (6 mg/l), concerning the conditions for aquatic organisms' protection;
- the watercourses presented a high organic load during almost all the investigation periods, reflecting a potential pollution;
- high values for mineral oil were recorded in June 2003 at Murighiol (1.67mg/l) and July 2003 (5.17 mg/l), as well as in July at Uzlina (14.8 mg/l); taking into account that in all the other months of investigation the concentration of this parameter was under the detection limit of the analytical method, this pollutant was accidentally spilled into the river;
- the investigated metal concentrations were in the waterbody within the tolerable limit, with the exception of iron, manganese and copper, which do not correspond to favorable conditions for the water organisms' development;
- the sediment texture alteration that occurred in the last year can be a threat to the water quality by the release of toxic heavy metals into the water bodies.

ACKNOWLEDGEMENT

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