This summary has been prepared on the basis of comprehensive reports produced under the Integrated Environmental Monitoring Programme for the Danube-Black Sea Deep Navigation Route Project in 2004-2005.¹

1. Oil Products

November 2004

During the November 2004 survey, oil products were found in all water samples taken from the Danube River. The highest concentrations were recorded in water samples taken downstream of Reni (0.31 mg/l in the surface water layer and 0.97 mg/l in the bottom layer). For the remaining 25 water samples, the average concentration of oil products was 0.058 mg/l, or 1.16 times higher than MAC limit set for fisheries (the dispersion of values was at 0.002 mg/l, and the 0.9-quantile value at 0.13 mg/l).

The concentrations of oil products in bottom sediments sampled near the river shores were significantly higher than in the samples taken along the navigable channel. The average concentration of oil products in bottom sediments sampled within the river channel and delta area was 0.12 mg/g (dry residue), or 7.5 times lower than average concentrations recorded during the field surveys in 1993–1995 (Odessa Branch of the Institute of Marine Biology). The highest concentration of oil products in bottom sediments (0.69 mg/g dry residue) was recorded at the head of the Prirva Branch where it splits off the Ochakiv Branch.

2005

Average concentrations of oil products were below the MAC limit set for fisheries, while maximum concentrations exceeded the MAC limit by 1.6 times. By the TNMN Programme classification, which uses the 0.9-quantile value to classify the waters in terms of oil contamination, the water quality in all sections of the Danube Delta corresponded to Class II meaning that the target water quality level was met.

Higher averages and larger proportion of samples with elevated levels of oil products were characteristic of the summer rainfall flood period (Figure 1). During the summer field survey, oil product concentrations ranged between the 'below detection limit' level to 0.83 mg/l, with average concentration being at about 0.11 mg/l. The highest concentrations were mainly recorded in the bottom-layer samples, taken in the following locations: the Chilia Branch (49 km, bottom layer, navigable channel) – 0.83 mg/l, or 16.6 times higher than the MAC limit set for fisheries; the Chilia Branch (116 km, bottom layer, navigable channel) – 0.23 mg/l, or 4.6 times higher than the fishery MAC limit; the Bystre Branch (0 km, seaward access canal, surface layer) – 0.17 mg/l; the Danube River upstream of Reni (71 mile, bottom layer, navigable channel) – 0.16 mg/l, or 3.4 times higher than the fishery MAC limit.

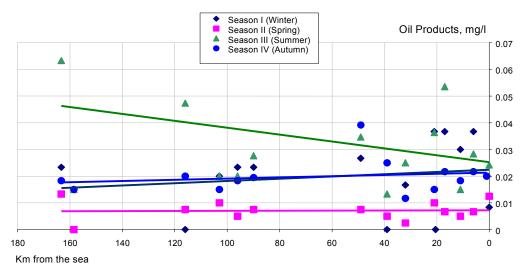


Figure 1. Seasonal and Spatial Dynamics of Oil Product Concentrations in Water

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The available survey data indicate that oil product pollution is generally evenly distributed over the examined river section. More reliable information about the oil product contamination in the Ukrainian part of the Danube River can be derived from the analysis of bottom sediment quality due to the long-term character of the process of oil product accumulation in bottom sediments, which is virtually unaffected by any occasional inputs of pollution. Bottom sediments were sampled and analysed for oil products during three field surveys, with 34 samples taken in total.

Oil product concentrations in samples taken during the spring field survey ranged from <20 to 246 mg/kg, with average concentration being at about 50 mg/kg. During the summer field survey, oil product concentrations in the bottom sediment samples ranged between <20 to 127 mg/kg (average concentration ~ 90 mg/kg). During the autumn field survey, oil products in bottom sediments ranged between <20 to 72 mg/kg (average concentration ~ 32 mg/kg).

Field survey results suggest that the levels of oil products in the bottom sediments generally depend upon the nature and grain-size composition of sediments and vary within a rather narrow margin across the study area.

2. Heavy Metals in Water and Bottom Sediments, and Bioaccumulation

October-November 2004

X-ось: Раст. от устья, km

During the comprehensive field survey, the water was sampled and analysed for heavy metals in soluble and suspended form (Figure 2–5). Field survey data indicate that the bulk concentrations of copper and cadmium tend to increase as one moves downstream. The levels of heavy metals in bottom sediments, sampled in the Chilia Branch and Delta area during the 2004 field survey, are presented in Table 1.

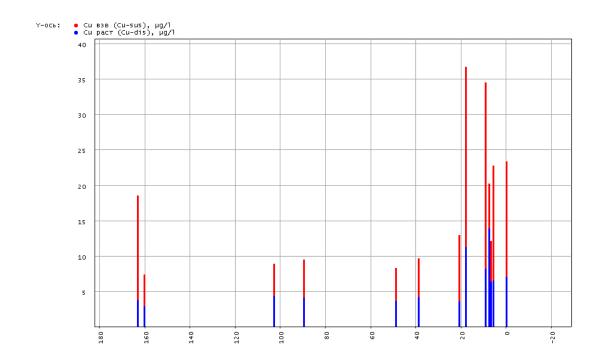
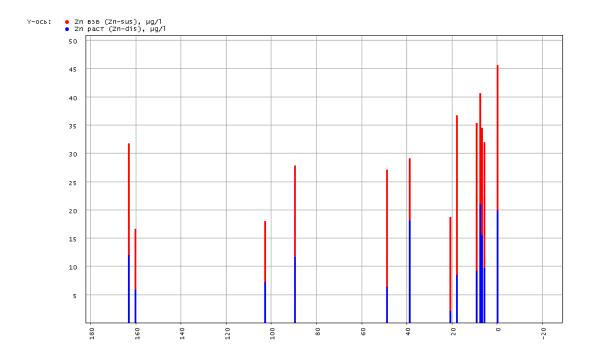
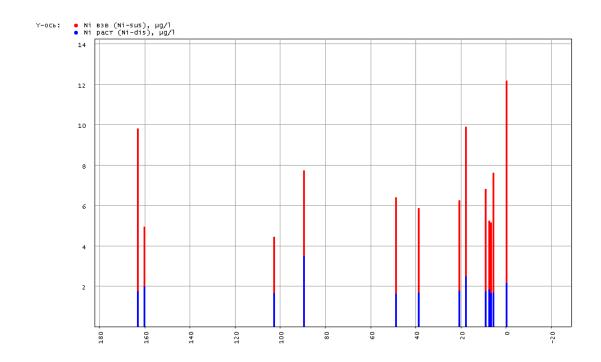


Figure 2. Suspended and Dissolved Copper Levels in Water Samples Taken in October-November 2004



X-ось: Раст. от устья, km

Figure 3. Suspended and Dissolved Zinc Levels in Water Samples Taken in October-November 2004



х-ось: Раст. от устья, km

Figure 4. Suspended and Dissolved Nickel Levels in Water Samples Taken in October-November 2004

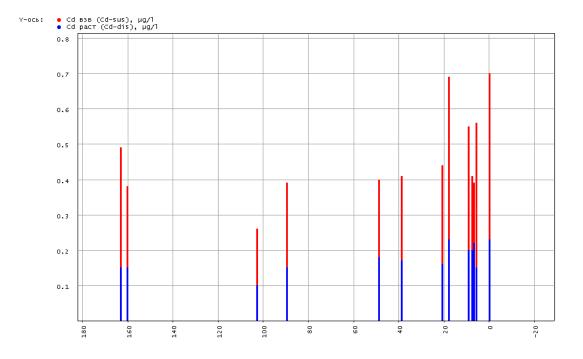


Figure 5. Suspended and Dissolved Cadmium Levels in Water Sampled in October-November 2004

Table 1. Metals in Bottom Sediments

×-ось: Раст. от устья, km

Station		Fe	Mn	Pb	Cu	Zn	Ni	Cd
Code			μg/g of dry weight					
S1	Navigable channel	15800	452	13.0	25.8	63.2	39.1	0,9
S2	Navigable channel	29200	925	19.0	37.6	91.3	63.6	1,9
S3	Navigable channel				17.8	44.4	27.9	1,6
S4	Near the shore	14200	440	14.5	34.0	57.2	27.7	2,0
S5	Navigable channel	21500	720	18.0	33.7	80.9	39.8	2,3
S6	Navigable channel	20400	665	25.0	68.7	110.5	43.0	2,7
S7	Navigable channel	11550	367	9.0	12.2	35.9	20.1	1,9
S9	Near the shore				33.1	76.9	39.5	2,1
	Navigable channel				6.6	22.8	15.6	1,1
S10	Navigable channel				21.4	50.8	32.7	2,0
S11	Navigable channel	6850	170	6.5	7.6	32.0	22.9	0,6
S12	Near the shore				49.9	107.6	51.4	2,2
	Navigable channel				10.4	30.8	22.3	1,1
S13	Near the shore	16050	438	13.0	27.8	65.4	40.3	1,6
S14	Near the shore				39.9	91.2	49.5	2,4
	Navigable channel				7.3	24.9	19.4	0,9
S15	Near the shore	16350	560	11.0	32.9	73.4	50.5	1,8
	Navigable channel				7.8	21.5	19.4	1,1
S16	Navigable channel				7.0	17.3	17.4	1,1
	Target level	-	-	100	60	200	50	1.2
Ba	ckground level	-	-	12.5-50	10-40	50-200	15-60	0.15-0.6

Notes:

- 1) Target level is the value corresponding to Quality Class II ('good quality') according to the Water Quality Classification adopted by the Danube Commission
- 2) Background or baseline level is the one defined in the JDS-2001 report.

There are no regulations in Ukraine with respect to the bottom sediment quality. Table 1 shows the background levels and target values, or sediment quality objectives, set by the Danube Commission. The copper level slightly exceeded the target level at the S06 station (Ochakiv Branch upstream of Prirva Branch), and the nickel levels were above the target level in the mouth section of the Vostochny (Eastern) Branch. The highest number of exceedances was recorded for cadmium.

During the comprehensive field survey, heavy metals were analysed in *Sinanodonta Woodiana* mollusks (collected in the Kurily Shallows area of the Danube Biosphere Reserve on 25.10.2004). Table 2 summarises average concentrations of heavy metals in mollusc tissues. These were compared against the target levels of heavy metals set for molluscs by the Danube Commission (Table 3).

Table 2. Average Concentrations of Heavy Metals in Molluscs

Metal	Measured result, mg/kg	Measuring error, mg/kg
Lead	1.3	0.3
Arsenic	0.7	0.1
Zinc	33.3	2.7
Copper	0.3	0.01
Nickel	<0.2	
Iron	174.5	29.7
Manganese	430.6	86.1
Chromium total	4.1	0.4

Table 3. Target Levels of Heavy Metals in Molluscs Set for the Danube River

Metal	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
Target value, μg/g	20	4	6	20	10	0.4	10	400

2005

Heavy metals were included into the routine monitoring programme and analysed in water samples taken during the field surveys.

Throughout the whole length of the Ukrainian part of the Danube River, concentrations of **iron** were found to be significantly higher than the MAC limit set for fisheries (about 4-6 times higher than MAC limit set for dissolved iron). Iron concentrations appeared to be consistently high throughout the river in spring/summer and tended to decrease in autumn, except for the river section between Reni and Ismail where iron concentrations remained high. Analytical results indicate that the major proportion of iron was present in suspended form (about 85% on the average). In filtered water samples, elevated iron concentrations were only found in spring flood period. Dissolved iron level exceeded the MAC limit on a single occasion in summer, and no such exceedances were recorded in autumn.

Concentrations of **manganese** are also relatively high throughout the Ukrainian part of the Danube River, especially in spring and summer, showing close correlation with iron. In autumn, the levels of manganese were considerably lower, though remained high in the river section between Reni and Ismail. The survey results indicate that a larger proportion of manganese (about 58% on the average) was present in the suspended form. In filtered water samples, the fishery MAC exceedances were recorded only in the period of spring flood.

Throughout the Ukrainian part of the Danube River, the concentrations of zinc were found to exceed the MAC limit for fishery, with the highest and relatively constant zinc levels recorded in the summer period. Significant proportion of zinc was present in the suspended form (about 39% on the average). Survey results indicate that filtered water samples appear to contain zinc at elevated levels throughout a year.

Consistently and sometimes extremely high levels of **copper** were recorded in spring and summer periods. In autumn, 70% of analysed samples showed exceedances of mandatory MAC limits for copper. According to the survey results, significant proportion of copper was present in the suspended form (about 32%). All filtered water samples except of 2 showed exceedances of MAC limits in spring and summer; and 70% of samples analysed in autumn contained copper at concentrations that were up to 9.8 times higher than the MAC limits set for fisheries.

Tables 4-5 show the 2005 concentrations of metals along with the historical data. It appears that the concentrations of dissolved metals (Fe_{dis} and Cu_{dis}) have increased significantly (by 2-fold). Average concentrations of Zn and Mn were fluctuating around or below their historically recorded levels. As regards the bulk values, the historical levels were exceeded for Fe, Zn and Mn. Average bulk levels of Cu were 1.5 times lower than relevant historical values.

Table 4. Comparison of the 2005 Concentrations of Dissolved Fe, Mn, Zn and Cu against the 2000-2004 Levels (data courtesy of the Danube Hydrometeorological Observatory)

		Average	C90	Maximum
F. 1:1 - 1/1	2000-2004	0.105	0.275	0.71
Fe dissolved, mg/l	2005	0.236	0.41	1.26
Cu dissolved., μg/l	2000-2004.	5	8.2	9.6
Cu dissolved., μg/1	2005	7	13	27
7n dissolved ug/l	2000-2004	26	32	467
Zn dissolved μg/l	2005	25	44	304
Mn dissolved ug/l	2000-2004	14	23	141
Mn dissolved, μg/l	2005	10	18	68

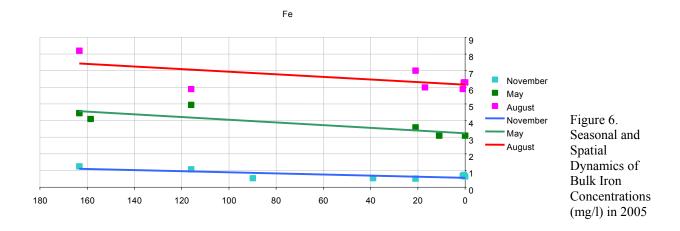
Table 5. Comparison of the 2005 Bulk Concentrations of Fe, Mn, Zn and Cu against the 1997-2001 Levels (data courtesy of the TNMN Programme)

		Danube – Reni	Chilia Branch – Vylkove
Fe bulk, mg/l	1997-2001	0.92	1.01
re bulk, mg/i	2005		3.6
Cu bulk, μg/l	1997-2001	21	21
Cu buik, µg/1	2005		14
Zn bulk, μg/l	1997-2001	27	31
Zii buik, µg/i	2005		95
Ma bulle ug/l	1997-2001	95	84
Mn bulk, μg/l	2005	2	209

The concentrations of **nickel** were consistently high (in all samples except of 2) in the spring and summer period. In autumn, only half of samples showed exceedances of MAC limits set for fisheries, with the most striking exceedance being by 3.4-fold. Significant proportion of nickel was found to be present in the suspended form (about 33%). All filtered water samples except of 1 showed exceedances in the spring period, when the MAC limit set for fisheries was exceeded by about 9-fold. In the summer and autumn period, the exceedances of fishery MAC limit were recorded in 30% of samples.

Cadmium was present in unfiltered and filtered water samples at concentrations that were considerably below the fishery MAC limit. The only exception was a sampling location at the 1st kilometre along the Bystre Branch. The average proportion accounted for by undissolved cadmium was about 29%. Similarly, the levels of **lead** in both unfiltered and filtered water samples were well below the fishery MAC limit, with about 38% of lead present in the suspended form. The concentrations of **arsenic** were consistently lower than the MAC limit set for fisheries in unfiltered and filtered water samples. About 40% of arsenic was present in the suspended form. Throughout the whole length of the Ukrainian part of the Danube River, **mercury** levels in unfiltered and filtered water samples were below our detection limit (0.2 μg/l), except for few unfiltered water samples, which had levels between 0.2 to 0.4 μg/l.

Bulk concentrations of heavy metals in the spring and summer appear to be considerably higher than in the autumn. Figures 6-11 show the spatial distribution of metal concentrations measured in all or nearly all samples.





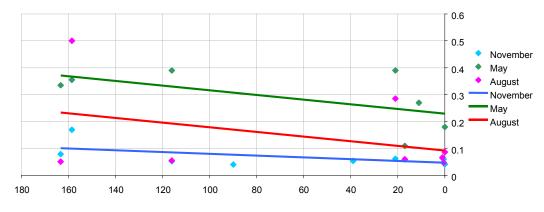


Figure 7. Seasonal and Spatial Dynamics of Dissolved Iron Concentrations (mg/l) in 2005

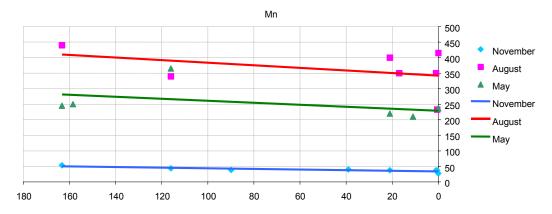


Figure 8. Seasonal and Spatial Dynamics of Bulk Manganese Concentrations (µg/l) in 2005

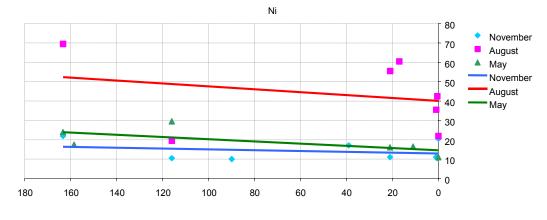


Figure 9. Seasonal and Spatial Dynamics of Bulk Nickel Concentrations (µg/l) in 2005

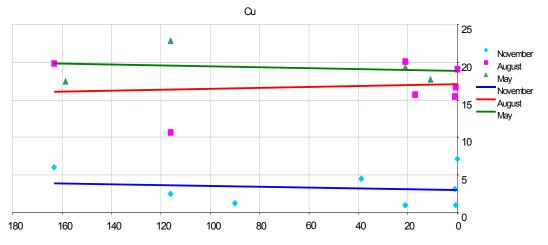


Figure 10. Seasonal and Spatial Dynamics of Bulk Copper Concentrations (µg/l) in 2005



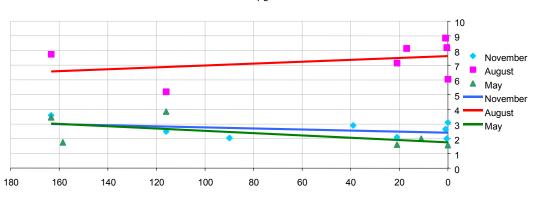


Figure 11. Seasonal and Spatial Dynamics of Bulk Lead Concentrations (µg/l) in 2005

Apart from an obvious seasonal variation, the above figures reflect a prevailing downward trend in bulk metal concentrations as one moves closer to the sea, suggesting the stronger impact of sedimentation and accumulation of metals in bottom sediments.

No significant and systematic change in metal concentrations with depth was established. At the same time, the analysis of spatial pattern showed significant differences among metals in various sampling locations. With iron concentration profiles being quite similar and showing little change with depth in all sampling locations, copper concentrations varied significantly at each sampling location, regardless of average values and hydrological conditions at the time of sampling.

During three field surveys undertaken in 2005 within the freshwater section of the navigation route, 44 **bottom sediment** samples were taken (12 in May; 19 in August; and 13 in November). All sampling locations for bottom sediments were associated with the river delta, its shoreline sections and shallows, where sedimentation rates are highest. The bulk concentrations of the following heavy metals were determined in bottom sediments: zinc, nickel, copper, cadmium, lead, arsenic, and mercury.

Results for these heavy metals in bottom sediment samples taken during three field surveys in 2005 are as follows:

Zn: from 18 to 162 mg/kg, with mean annual value 56 mg/kg;

Ni: from <10 to 125 mg/kg, with mean annual value 21 mg/kg;

Cu: from 0.62 to 60.2 mg/kg, with mean annual value 15.9 mg/kg;

Cd: from <0.1 to 3 mg/kg, with mean annual value 0.58 mg/kg;

Pb: from 5.7 to 96 mg/kg, with mean annual value 21 mg/kg;

As: from ≤ 2 to 3.5 mg/kg;

Hg: from <2 to 2.7 mg/kg.

The strongest correlation between the grain-size composition of sediment and concentration of a certain metal was established for Zn, Fe and Cu, with less evident signs of such correlation in Ni and Cd, and none of them in Pb. There was no possibility to establish any correlation between the grain-size composition and concentration for As and Hg, since the majority of samples had the levels of these metals below our detection limit. Table 6 shows the results of the principal-component analysis and factor loadings for the first four components, which are "responsible" for up to 94% of total dispersion. The first factor (61% dispersion) is associated with the variability of heavy metal concentrations in bottom sediments with various grain-size composition, especially with respect to various combinations of sand+gravelite/shell fraction and aleurite+pelite fraction (Figures 12, 13 and 14-left). The second factor (14%) is associated with the distance to the mouth (Figure 14-right).

As can be seen from the above, the grain-size composition is the major factor. The change in heavy metal concentrations with distance to the mouth appears to be mediated by the grain-size composition of bottom sediments, with the latter showing a continuous increase in fine-sized fraction as one moves towards the sea.

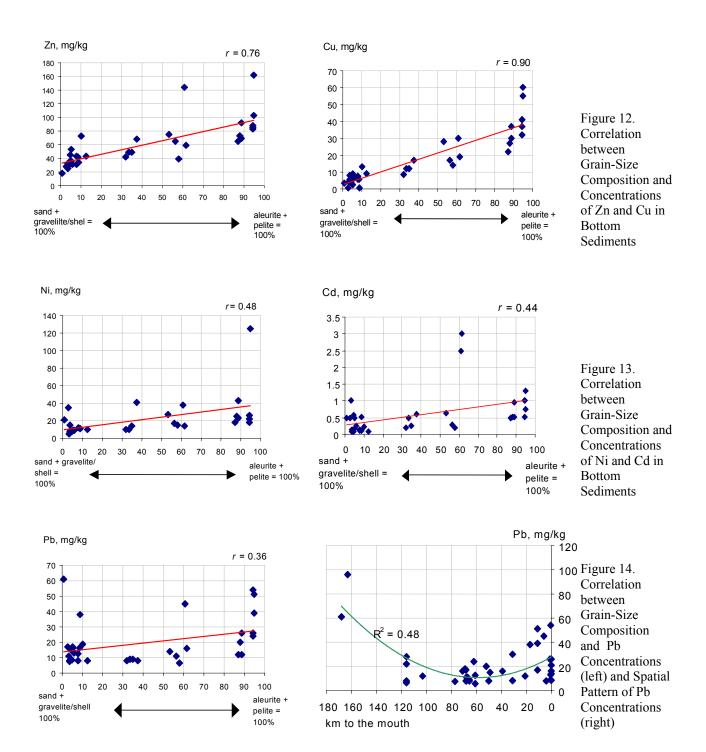


Table 6. Factor Loadings for the First Four Factors, Determined on the Basis of Sediment Quality Monitoring Data

	Factor 1	Factor 2	Factor 3	Factor 4
Aleurite + pelite fraction, %	0.93	0.14	-0.03	-0.26
Distance to the mouth, km	-0.46	0.67	0.29	0.25
Fe, mg/kg	1.00	-0.15	0.31	0.14
Zn, mg/kg	0.89	-0.07	-0.17	-0.03
Ni, mg/kg	0.71	-0.07	-0.10	0.69
Cu, mg/kg	0.95	-0.02	-0.24	0.04
Cd, mg/kg	0.52	0.12	0.80	-0.08
Pb, mg/kg	0.30	0.84	-0.31	-0.02
Proportion in total dispersion (%)	61%	14%	11%	8%

Bioaccumulation of Heavy Metals in Molluscs

During the summer field survey in August 2005, 9 mollusc samples were taken in 6 locations (Figure 15). In three sampling locations (No. 2 – Starostambulske Branch near Limba Island; No. 3 – Anankin Kut within the Canal; and No.8 – Limba Island), parallel chemical analyses were carried out for the *Anodonta sp* and *Unio sp* samples in order to determine the levels of the following heavy metals: zinc, nickel, copper, cadmium, and lead. The results are presented in Table 7. If ranked in terms of actual concentrations measured in mollusc tissues, this list of heavy metals can be presented as follows: Zn>Cu>Ni>Cd>Pb.



Figure 15. Locations of Mollusc Samples during the 2005 Field Survey to Examine the Bioaccumulation of Heavy Metals and Pesticides

Table 7. Heavy Metals in Mollusc Tissues

No.	Sample Description	Sampled Species	Zn,	Ni,	Cu,	Cd,	Pb,
			mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
1	Vylkove, 18.5 km	Unio pictrum	162	3.4	8.5	1.2	0.94
2a	Starostambulske Branch (Limba Island)	Anodonta sp	26	0.60	6.5	0.18	0.092
2б	Starostambulske Branch (Limba Island)	Unio sp	98	4.3	4.4	0.60	0.89
3a	Anankin Kut (within the Canal)	Unio sp	18	0.22	2.6	0.18	0.041
3б	Anankin Kut (within the Canal)	Anodonta sp	156	2.1	3.8	1.8	0.50
4	Kurily Shallows	Anodonta sp	46	0.58	2.5	0.32	0.12
7	Bystre Branch	Anodonta sp	25	0.36	2.0	0.20	0.10
8a	Limba Island	Anodonta sp	29	0.87	3.4	0.24	0.084
8б	Limba Island	Unio sp	58	0.42	4.2	0.40	0.36

For the purposes of comparative analysis, the MAC limits set for non-prey fish consumed as food were used (40 mgZn/kg, 10 mgCu/kg, 0.5 mgNi/kg, 0,2 mgCd/kg, 1 mgPb/kg) along with the target levels of heavy metals in molluscs proposed by the Danube Commission.

The highest concentrations of heavy metals were found in Unio pictrum samples taken near Vylkove (18.5 km): Zn... about 4 times higher than MAC limit; Ni... about 6.8 times higher than MAC limit; Cd... about 6 times higher than MAC limit. The sum of concentrations of five metals (Zn, Ni, Cu, Cd, Pb) accumulated by these species was at 176 mg/kg. Slightly lower concentrations of heavy metals were recorded in *Anodonta sp* samples taken in the Anankin Kut within the Canal: zinc... about 2.5 times higher than MAC limit; nickel... about 8.6 times higher than MAC limit; cadmium... about 3 times higher than MAC limit, with the sum of heavy metal concentrations being at 164 mg/kg. In *Unio sp* samples taken at the Limba Island and Starostambulske Branch (near the Limba Island), the total levels of heavy metals were at 63.38 mg/kg and 108.19 mg/kg, with specific metal concentrations being as follows: Zn... about 3.9 times higher than MAC limit, Ni... about 4.2 times higher than MAC limit, and Cd... about 9 times higher than MAC limit.

The lowest levels of heavy metals, ranging between 21.041 to 49.52 mg/kg, were recorded in one *Unio pictrum* sample (Anankin Kut Canal, sampling location 3a) and four *Anadonta sp* samples (sampling locations 2, 4, 7 (Bystre Branch), and 8a). The lowest level of heavy metals was recorded in one *Unio pictrum* sample from a sampling location 3a (21.0 mg/kg).

Zinc and cadmium showed the highest bioaccumulation rates equal to several thousands, followed by copper with several hundreds.

3. Chlorinated Organic Pesticides in Water, Bottom Sediments and Molluscs

October - November 2004

The picture emerging from the analysis of historical data collected under the TNMN Programme for persistent organic contaminants over 1997-2001 is one of large-scale and long-term contamination of the Danube River by persistent chlorinated organic pesticides (lindane, DDT). The 1997-2001 data collected by the Danube Commission suggest that mean annual concentrations of these pesticides in water were in the range of 0.01-0.13 µg/l (lindane) and 0.05-0.20 µg/l (DDT). These data also suggest that there is a significant statistical dependence between the level of annually available flow and concentrations of organochlorines recorded in the river section between Reni and Vylkove. The progressive decrease in maximum concentrations of chlorinated organic pesticides (COP) in the direction from Reni to Vylkove, along with the previously mentioned relationship between the available flow and concentrations of these compounds (Figures 16-17), suggest that the most likely source of COP inputs to the Ukrainian part of the Danube Delta is transboundary transport. This conclusion is confirmed by the results of field survey carried out in October-November 2004 (Table 8).

Table 8. Concentrations of Chlorinated Organic Pesticides and Atrazine Measured in Water during the 2004 Field Survey

11014 841 (0)		
Parameter	Testing Method Sensitivity	Measured Result
γ-HCCH, mg/kg	0.00008	< 0.00008
4,4'-DDT, mg/kg	0.0002	< 0.0002
4,4'-DDE, mg/kg	0.0002	< 0.0002
4,4'-DDD, mg/kg	0.0002	< 0.0002
Atrazine, mg/kg	0.001	< 0.001

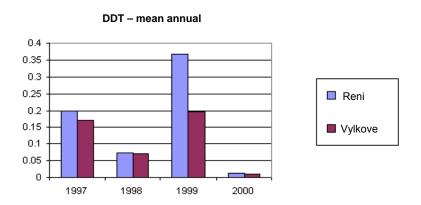


Figure 16. Decrease in COP Concentrations at the Direction from Reni to Vylkove (the TNMN Programme Data for 1997-2001

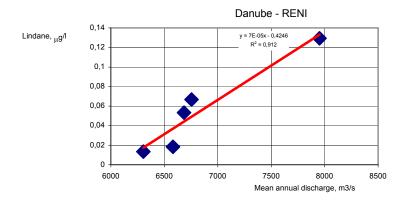


Figure 17. Relationship between Lindane Concentrations and Annual Flow Discharges (TNMN, 1997-2001)

Bottom sediments sampled from the river section between Reni and Vylkove showed a downward trend in COP concentrations at the direction to the Chilia Branch of the Danube River (Table 9). Our field survey results for this section were comparable with the JDS-2001 survey results.

Table 9. Measured Concentrations of Chlorinated Organic Pesticides in Bottom Sediments

Parameter	Measured Result
γ-HCCH, mg/kg	
S05'	0.0005
S04'	0.0009
S07	0.003
S16	0.0018
4,4-DDT, mg/kg	
S05'	0.009
S04'	0.014
S07	0.018
S16	0.022
4,4'-DDE, mg/kg	
S05'	0.005
S04'	0.004
S07	0.006
S16	0.008
4,4 ^I -DDD, mg/kg	
S05'	0.003
S04'	0.004
S07	0.006
S16	0.006

In order to evaluate the bioaccumulation rates of chlorinated organic pesticides in the Bystre Branch, mollusc species (Sin. Anadonta Woodiana) were sampled and analysed for n,n'-DDT and its metabolites, and for γ -HCCH. Results are shown in Table 10. The levels of COP's and their metabolites ranged between 7 to 19 μ g/kg, being comparable with historical data on other sections of the Danube River. According to the Ukrainian standards (SanPiN 42-123-4540-87), the sums of HCCH isomers and DDT metabolites in freshwater fish should not exceed 0.03 mg/kg and 0.3 mg/kg, respectively. The presence of COP's and their metabolites in mollusc muscles suggest that fish (both prey and non-prey) in the Chilia Branch of the Danube River are very likely to have accumulated these compounds, and this issue needs to be further examined during future field surveys.

Table 10. Measured Concentrations of Organochlorines in Molluscs

Measured Compound	Result
γ-HCCH, mg/l	0.0085
4,4'-DDT, mg/l	0.019
4,4'-DDE, mg/l	0.007
4,4'-DDD, mg/l	0.007

Polychlorinated biphenyls (PCBs) and **polycyclic aromatic hydrocarbons (PAHs)** were also analysed in **bottom sediments, aquatic biota** and **water** during the field survey in October-November 2004. The results are shown in Tables 11-13. The levels of toxic compounds appear to be low.

Detection limits for PCBs and PAHs are $0.1-6.0~\mu g/kg$ for soil; $0.01-0.06~\mu g/l$ for water; $0.05-0.6~\mu g/kg$ for molluscs.

Table 11. PCBs and PAHs in Bottom Sediments

			Sample	
No.	Compound	Sample No. 2,	Sample No. 3,	Sample No. 4
		mg/kg	mg/kg	mg/kg
1	Monochlorobiphenyl	< 0.0001	< 0.0001	< 0.0001
2	Dichlorobiphenyl	< 0.0001	< 0.0001	< 0.0001
3	Trichlorobiphenyl	0.010	0.0143	0.0086
4	Tetrachlorobiphenyl	0.0049	0.0027	0.0049
5	Pentachlorobiphenyl	0.0063	0.0083	0.0065
6	Hexachlorobiphenyl	0.0036	0.0025	0.0014
7	Heptachlorobiphenyl	0.006	0.004	0.0042
8	Octochlorobiphenyl	< 0.0001	< 0.0001	< 0.0001
9	∑PCB	0.0308	0.0318	0.0256
10	Fluorene	< 0.0001	< 0.0001	0.0034
11	Fluorantene	0.0257	0.0050	0.0042
12	Benzo(k)fluorantene	0.0161	0.0013	< 0.0001
13	Benzo(a)pirene	< 0.0001	< 0.0001	< 0.0001
14	Antracene	< 0.0001	< 0.0001	< 0.0001
15	Fenantrene	< 0.0001	< 0.0001	< 0.0001
16	Pirene	< 0.0001	< 0.0001	< 0.0001
17	1-phenylnaphtalene	0.0023	< 0.0001	0.0028
18	∑PAH	0.0441	0.0063	0.0104

Table 12. PCBs and PAHs in Molluscs

No.	C	Sa	mple
	Compound	Sample No. 2, mg/kg	Sample No. 3, mg/kg
1	Monochlorobiphenyl	0.0114	0.0065
2	Dichlorobiphenyl	< 0.0001	< 0.0001
3	Trichlorobiphenyl	< 0.0001	< 0.0001
4	Tetrachlorobiphenyl	0.0072	0.0009
5	Pentachlorobiphenyl	0.0017	0.0020
6	Hexachlorobiphenyl	0.0063	0.0066
7	Heptachlorobiphenyl	0.0184	0.0071
8	Octochlorobiphenyl	< 0.0001	< 0.0001
9	∑PCB	0.0450	0.0231
10	Fluorene	0.0008	0.0008
11	Fluorantene	0.0065	0.0079
12	Benzo(k)fluorantene	< 0.0001	< 0.0001
13	Benzo(a)pirene	< 0.0001	< 0.0001
14	Antracene	< 0.0001	0.0185
15	Fenantrene	0.0072	< 0.0001
16	Pirene	< 0.0001	< 0.0001
17	1-phenylnaphtalene	< 0.0001	< 0.0001
18	∑PAH	0.0145	0.0272

Table 13. PCBs and PAHs in Water

		Sample							
No.	Compound	Sample No. 2,	Sample No. 3,	Sample No. 4,					
		mg/l	mg/l	mg/l					
1	Monochlorobiphenyl	< 0.0001	< 0.0001	< 0.0001					
2	Dichlorobiphenyl	< 0.0001	< 0.0001	< 0.0001					
3	Trichlorobiphenyl	0.00040	0.0005	< 0.0001					
4	Tetrachlorobiphenyl	0.0001	< 0.0001	< 0.0001					
5	Pentachlorobiphenyl	0.0003	0.0002	< 0.0001					
6	Hexachlorobiphenyl	0.0003	0.0001	< 0.0001					
7	Heptachlorobiphenyl	0.0001	< 0.0001	< 0.0001					
8	Octochlorobiphenyl	< 0.0001	< 0.0001	< 0.0001					
9	∑PCB	0.0012	0.0008	< 0.0001					
10	Fluorene	< 0.0001	< 0.0001	< 0.0001					
11	Fluorantene	< 0.0001	< 0.0001	< 0.0001					
12	Benzo(k)fluorantene	< 0.0001	< 0.0001	< 0.0001					
13	Benzo(a)pirene	< 0.0001	< 0.0001	< 0.0001					
14	Antracene	0.0012	0.0011	< 0.0001					
45	Fenantrene	< 0.0001	< 0.0001	< 0.0001					
16	Pirene	0.0007	0.0006	< 0.0001					
17	1-phenylnaphtalene	< 0.0001	< 0.0001	< 0.0001					
18	∑PAH	0.0019	0.0017	<0.0001					

2005

As part of routine monitoring programme and integrated field surveys, 80 water samples, 31 bottom sediment samples and 4 mollusc samples were taken and over 680 element determinations carried out.

Pesticides in water. α-HCCH was found to be present in 16% of samples. More specifically, α-HCCH was detected in 7 water samples taken in spring (May), at an average concentration of 0.0174 μg/l (maximum concentration being at 0.025 μg/l); and in 6 water samples taken in August, with an average concentration of 0.0065 μg/l. Consistently higher concentrations were recorded in samples taken from the bottom layer as compared to the surface layer. In autumn, concentrations of α-HCCH were below the specified detection limit (<0.005 μg/l). α-HCCH appears to be present throughout the whole length of the Ukrainian part of the Danube River, from Reni (71 mile) to delta (Bystre Branch, 0 km). The highest concentrations of α-HCCH were recorded in the bottom-layer water samples taken from the Starostambulske Branch (11 km); Chilia Branch (39 km, downstream of the irrigation system effluent discharge outfall); and Chilia Branch (21 km, Vylkove).

 β -HCCH was detected in two spring samples. In summer and autumn samples, concentrations of this HCCH isomer were below our detection limit (<0.010 µg/l). The results of analysis indicate that β -HCCH is present throughout the Ukrainian part of the Danube River, from Reni to delta areas (Starostambulske Branch, 11 km).

Of eight most known HCCH isomers, lindane (γ -HCCH) was the predominate compound, found in three spring samples and one summer sample. In autumn, concentrations of γ -HCCH were below the guideline level ($<0.005 \mu g/l$). The highest concentrations of γ -HCCH were recorded in spring: 0.018 $\mu g/l$ in the Chilia Branch upstream of Vylkove (21 km), and 0.016 $\mu g/l$ in the Danube River near Reni (71 mile, bottom layer).

The DDT compounds were detected only in three samples taken in August 2005. Two water samples taken in the Chilia Branch (49 km, or 4 km upstream of Chilia) from the surface and bottom water layers contained DDT at concentrations of 0.1 μ g/l and 0.054 μ g/l, respectively. One surface-layer sample taken from the Chilia Branch (21 km, or 1 km upstream of Vylkove) had a DDT concentration at 0.1 μ g/l. The n,n'-DDE metabolite was detected in two samples in April: These were surface-layer samples taken from the Chilia Branch (49 km, or 4 km upstream of Chilia) and the Danube River (71 mile, Reni), and they had the measured n,n'-DDE concentrations at 0.003 μ g/l and 0.004 μ g/l, respectively. The levels of n,n'-DDD metabolite in all samples were below the specified guideline levels. The highest concentrations were recorded during spring and summer flooding periods.

As can be seen from the above, a range of chlorinated organic pesticides was present in the water of the Ukrainian part of the Danube Basin in 2005, with the predominate compound being HCCH and its α - and γ -isomers.

Pesticides in bottom sediments. In all bottom sediment samples, HCCH compounds were below our detection limit. The only exception were one bottom sediment sample taken in spring from the Starostambulske Branch (11 km), which had a γ-HCCH concentration of 0.0016 mg/kg, and one sediment sample taken in autumn from the Bystre Branch (0.5 km), in which α -HCCH was detected at a concentration of 0.006 mg/kg. None of the examined bottom sediment samples contained β-HCCH at detectable levels.

Testing results indicate higher inputs of DDT-related compounds. While none of the samples contained n,n'-DDT at a detectable level, n,n'-DDE was found to be present in two samples at concentrations 0.0010 to 0.0028 mg/kg, and n,n'-DDD was detected in 7 of 31 samples at concentrations ranging between 0.0012 to 0.0071 mg/kg. It is notable that all bottom sediment samples that were found to contain chlorinated organic compounds represented delta areas and shallow sections, which had higher sedimentation rates. Moreover, hexachlorobenzene compounds were detected in two bottom sediment samples taken from the Bystre Branch (0 km and -1 km) at concentrations 0.0088 mg/kg and 0.0008 mg/kg, respectively.

Overall, 9 of 31 bottom sediment samples (29%) were found to contain chlorinated organic compounds. All these samples were associated with the following three sections of the Ukrainian part of the Danube River: Bystre Branch, where COPs and their metabolites were detected at the sampling locations '1 km', '0.5 km', '0 km', '-0.5 km' and '-1 km'; and Starostambulske Branch, where organochlorines were found at the sampling location '11 km' and in the shallow section between 68.5 and 71 km (69 km) near the left bank.

<u>Pesticides in molluscs.</u> Organochlorine pesticide compounds were analysed in mollusc muscles of two sampled species (*Unio pictorum* and *Anadonta sp.*) Sampling exercise was carried out in August 2005 at four locations. The results are presented in Table 15, which shows that persistent organochlorine compounds were detected in all mollusc muscle samples.

Table 15. Chlorinated Organic Pesticides in Mollusc Muscles (2005)

Sampling Station	Vylkove, 18.5 km	Tsyhansky Branch	Lebedinka Branch	Bystre Branch
Sampled Species	Unio pictorum	Anadonta sp	Anadonta sp	Anadonta sp
α-НССН	< 0.0004	< 0.0004	< 0.0004	< 0.0004
β-НССН	0.0060	< 0.0020	< 0.0020	< 0.0020
ү-НССН	< 0.0004	0.0016	0.0006	0.0016
DDE, mg/kg	0.0118	< 0.0010	< 0.0010	< 0.0010
DDD, mg/kg	0.0132	0.0040	0.0054	< 0.0010
DDT, mg/kg	0.0060	< 0.0040	0.0078	< 0.0040

 α -HCCH was not detected in the mollusc muscles, while β -HCCH was found in one sample (Vylkove, 18.5 km) at a concentration of 0.0060 mg/kg. Lindane (γ -HCCH) was found to be present in 75% mollusc muscle samples at concentrations ranging between 0.0006 to 0.0016 mg/kg.

n,n'-DDT and its metabolites were found in 75% of samples. n,n'-DDT was detected in two samples taken from the Lebedinka Branch and near Vylkove (18.5 km) at concentrations 0.0078 mg/kg and 0.0060 mg/kg, respectively. DDT metabolites, detected in mollusc muscle samples, were mainly represented by n,n'-DDD (three samples) at concentrations ranging from 0.0040 mg/kg to 0.0132 mg/kg. n,n'-DDE was detected in one sample at a concentration of 0.0118 mg/kg (Vylkove, 18.5 km).

The highest total concentration of chlorinated organic pesticides (0.037 mg/kg) was found in the *Unio pictorum* sample taken near Vylkove (18.5 km). The lowest total COP concentration was recorded in the *Anadonta sp.* sample from the Bystre Branch (0.0016 mg/kg). The bioaccumulation rate, estimated for the Anadonta sp. sample from the Bystre Branch in relation to γ -HCCH, was at 230.

ATTACHMENT A.

Table A.1. The 2005 Water Quality Statistics for the River Section I between 71 Mile (Danube) to 96 km (Chilia

Bran	ch, Ismail)											
	Parameter	Measuring Unit	Water Layer	No. of Determinations	Minimum	060	Maximum	Mean	The TNMN Class	MAC Limit	MAC Limit for Fishery	Average Rate of Exceedance (Fishery MAC Limit)
29	Oil Products (PHC)	mg/l	В	38	n.d.	0.04	0.23	0.02		0.3	0.05	
31	Dissolved Iron (Fe-dis)	mg/l	S B S	51 19 22	n.d. 0.04 0.02	0.04 0.63 0.39	0.1 1.26 0.48	0.02 0.25 0.20		0.3	0.03	2.5 times 2 times
32	Total Iron (Fe total)	mg/l	B S	7 7	1.2 0.95	9.9 6.5	9.9 6.5	4.9 3.6				
33	Dissolved Manganese (Mn-dis)	μg/l	B S	16 18	0.93 0.97 1.6	68 20.8	410 120	38 14		100	10	3.8 times 1.4 times
34	Total Manganese (Mn total)	μg/l	B S	7 7	48 39	550 360	550 360	296 201				
35	Dissolved Zinc (Zn-dis)	μg/l	B S	19 22	2.7 2.3	68.3 40	120 46	30 16	>]]	1000	10	3 times 1.6 times
36	Total Zinc (Zn total)	μg/l	B S	7 7	59 33	160 140	160 140	110 72	III			
37	Dissolved Nickel (Ni-dis)	μg/l	B S	7 7	10 10	32 10	32 10	18 10	>[]	100	10	1.8 times
38	Total Nickel (Ni total)	$\mu g/l$	B S	, 7 7	11 10	83 56	83 56	38 17	III			
39	Dissolved copper (Cu-dis)	μg/l	B S	19 21	2	22	23.5 9.9	9.4 5.3	>[[1000	1	9.4 times 5.3 times
40	Total Copper (Cu total)	μg/l	B S	7 7	2.8	40 16.3	40 16.3	17.8 5.7	III			
41	Dissolved Cadmium (Cd-dis)	μg/l	B S	, 7 7	<0.2 <0.2	2.8 0.3	2.8 0.3	0.7 <0.2 (md) *)	>[]	1	5	
42	Total Cadmium (Cd total)	$\mu g/l$	В	7	0.3	2.9	2.9	1.1	III			
43	Dissolved Lead (Pb-dis)	μg/l	S B	7 7	<0.2	0.4 4.9	0.4 4.9	0.2 (md) *) 2.8	>II	30	10	
44	Total Lead	μg/l	S B	7 7	<1 1.9	2 10	2 10	1.6 5.6	III			
45	(Pb total) Dissolved Arsenic	μg/l	S B	7 7	<1 1	5.5 7.1	5.5 7.1	2.4 <1 (md) *)	>II	50	50	
46	(As-dis) Total Arsenic	μg/l	S B	7 7	<1 1	1 13	1 13	<1 (md) 1.9 (md)	II	30	30	
47	(As total) Dissolved Mercury	μg/l	S B	7 7	<1 <0.2	2.1 <0.2	2.1 0.2	1 (md) <0.2 (md)				
	(Hg-dis)		S	7	< 0.2	< 0.2	< 0.2	<0.2	>II	0.5	none	
48	Total Mercury (Hg total)	μg/l	B S	7 7	<0.2 <0.2	< 0.2	0.3 <0.2	0.2 <0.2	II			
49	α-НССН	μg/l	B S	9 10	n.d. n.d.	0.016 0.007	0.016 0.008	n.d. n.d.				
50	β-НССН	$\mu g/l$	B S	6 6	n.d. n.d.	0.011 n.d.	0.011 n.d.	n.d. n.d.				
51	ү-НССН	$\mu g/l$	В	7	n.d.	0.016	0.016	n.d.	I			
52	DDE	μg/l	S B	7 9	n.d. n.d.	n.d.	n.d.	n.d. n.d.				
53	DDD	μg/l	S B	9 6	n.d. n.d.	0.004 n.d.	0.004 n.d.	n.d. n.d.				
54	DDT	μg/l	S B	6 9	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d. n.d.				
			S	9	n.d.	n.d.	n.d.	n.d.	I			

Notes: 1) Water Layer column: "B" means bottom layer, "S" means surface water layer; 2) C90 column reflects the 0.9-quantile values; 3) "n.d." means 'not detected' (below detection limit); 4) A TNMN Class for parameters, which had the total number of determinations in one water layer below 10, relevant C90 statistics was derived from the whole set of determinations (rather than from a water-layer based set); 5) Cells with values that are higher than a MAC Limit are shadowed in grey.

Table A.2. The 2005 Water Quality Statistics for River Section II (Chilia Branch 89.9 km (1 km downstream of Ismail) to Chilia Branch 21 km (1 km upstream of Vylkove)

to Ch	ilia Branch 21 km (1 km	upstre	am of	f Vylko	ve)	`			`			,
	Parameter	Measuring Unit	Water Layer	No. of Determinations	Minimum	060	Maximum	Mean	The TNMN Class	MAC Limit	MAC Limit for Fishery	Average Rate of Exceedance (Fishery MAC Limit)
29	Oil Products (PHC)	mg/l	В	40	n.d.	0.0435	0.097	0.02		0.3	0.05	
31	Dissolved Iron (Fe-dis)	mg/l	S B S	58 9 9	n.d. 0.033 0.048	0.05 0.45 0.49	0.078 0.45 0.49	0.02 0.18 0.17		0.3	0.03	1.8 times 1.7 times
32	Total Iron (Fe total)	mg/l	В	5	0.59	7.2	7.2	2.6				
33	Dissolved Manganese (Mn-dis)	μg/l	S B S	5 8 8	0.42 2 2.79	6.8 24 10	6.8 24 10			100	10	
34	Total Manganese (Mn total)	μg/l	B S	5 5	43 32	430 370		162				
35	Dissolved Zinc (Zn-dis)	μg/l	B S	9 9	3.3 3.6	120 94	120 94	52 40	>[[1000	10	5.2 times 4 times
36	Total Zinc (Zn total)	μg/l	B S	5 5	48 55	280 360	280 360		IV			
37	Dissolved Nickel (Ni-dis)	μg/l	B S	5 5	10 10	15 11	15 11	12 10	>[[100	10	1.2 times
38	Total Nickel (Ni total)	μg/l	B S	5 5	10 10	77 34	77 34	27 16	II-III			
39	Dissolved copper (Cu-dis)	$\mu g/l$	B S	9 9	1 1	12.5 26.6	12.5 26.6	5.9	>[[1000	1	5.9 times 6.1 times
40	Total Copper (Cu total)	μg/l	B S	5 5	1 1.1	35 18.4	35 18.4		III			
41	Dissolved Cadmium (Cddis)	$\mu g/l$	B S	5	<0.2 <0.2	0.4 0.5	0.4 0.5		>[[1	5	
42	Total Cadmium (Cd total)	$\mu g/l$	B S	5 5	0.2 <0.2	0.5 0.6	0.5 0.6	0.4 0.3	II			
43	Dissolved Lead (Pb-dis)	μg/l	B S	5 5	1.6 <1	3.2	3.2	2.2 <2 (md)	>[]	30	10	
44	Total Lead (Pb total)	$\mu g/l$	B S	5 5	1.8 1.4	8.4 5.9	8.4 5.9		III			
45	Dissolved Arsenic (As-dis)	$\mu g/l$	B S	5	<1 <1	1.3	1.3	1.1 <1 (md)	>[[50	50	
46	Total Arsenic (As total)	$\mu g/l$	B S	5 5	1.1 <1	3.3 1.2	3.3 1.2	2.0	I-II			
47	Dissolved Mercury (Hg-dis)	$\mu g/l$	B S	5 5	<0.2 <0.2	<0.2 <0.2	0.2	<0.2 (md)	II-III	0.5	none	
48	Total Mercury (Hg total)	$\mu g/l$	B S	5	<0.2 <0.2	0.4 <0.2		<0.2 (md)	III			
49	α-НССН	$\mu g/l$	B S	25 25	n.d. n.d.	n.d. n.d.	n.d. 0.023	n.d. n.d.				
50	β-НССН	$\mu g/l$	B S	9 11	n.d. n.d.	0.02 n.d.		n.d.				
51	ү-НССН	$\mu g/l$	B S	17 17	n.d. n.d.	n.d. n.d. n.d.	n.d. 0.018	n.d. n.d.	I			
52	DDE	$\mu g/l$	B S	25 25	n.d. n.d.	n.d.	n.d. 0.003	n.d. n.d.				
53	DDD	$\mu g/l$	B S	9	n.d. n.d. n.d.	n.d. n.d. n.d.	n.d. n.d.	n.d. n.d. n.d.				
54	DDT	μg/l	B S	25 25	n.d. n.d. n.d.	n.d. n.d. n.d.	0.054 0.1		I			

Table A.3. The 2005 Water Quality Statistics for the River Section III (Sampling Locations Downstream of Vylkove and in the Chilia Delta).

												4
		Measuring Unit	er	No. of Determinations					Z	. 1 2	MAC Limit for Fishery	Average Rate of Exceedance Fishery MAC Limit)
		ring	Water Layer	nina	um		unu		The TNMN Class	MAC Limit	Limi	Average Rate e Exceedance (Fishery MAC Limit)
		easn	ater	No. of Determ	Minimum	060	Maximum	Mean	The T Class	AC]	MAC Li Fishery	Averag Exceed (Fisher Limit)
20	Parameter Oil Products (PHC)								11 C	Σ		EX A
29	On Products (PHC)	mg/l	B S	40 58	n.d. n.d.	0.03	0.11 0.17			0.3	0.05	
30	Phenol	mg/l	В	43	n.d.	0.004		0.002		0.001	0.001	2 times
			S	61	n.d.	0.005				0.001	0.001	3 times
31	Dissolved Iron (Fe-dis)	mg/l	B S	14 14	0.016			0.16 0.11		0.3	0.1	1.6 times 1.1 times
32	Total Iron (Fe total)	mg/l	S B	9	0.03							1.1 times
	roun non (re toun)	111.8/1	S	9	0.61							
33	Dissolved Manganese	$\mu g/l$	В	13	2.2					100	10	1.2 times
2.4	(Mn-dis)	,,	S	13	1.93					100	10	1.2 times
34	Total Manganese (Mn total)	μg/l	B S	9 9	20 34							
35	Dissolved Zinc	μg/l	В	14	5.1			35		4000	4.0	3.5 times
	(Zn-dis)	. 0	S	14	6.5				>[]	1000	10	6 times
36	Total Zinc (Zn total)	$\mu g/l$	В	9	36				III			
27	Discolared Wieles	/1	S	9	36 10							1.2 times
37	Dissolved Nickel (Ni-dis)	μg/l	B S	9 9	10		21 19	12 11	>[[100	10	1.2 times 1.1 times
38	Total Nickel	μg/l	В	9	10				TT TTT			1.1 times
	(Ni total)		S	9	10	82		26	II-III			
39	Dissolved copper	$\mu g/l$	В	14	1				>]]	1000	1	5.9 times
40	(Cu-dis) Total Copper (Cu total)	.u.g./1	S B	14 9	1 1							3.1 times
40	Total Copper (Cu total)	μg/l	S	9	1.1				III			
41	Dissolved Cadmium (Cd-	μg/l	В	9	< 0.2				> II	1	_	
	dis)		S	9	< 0.2			\ /	>[]	1	5	
42	Total Cadmium	μg/l	В	9	0.2				II			
43	(Cd total) Dissolved Lead (Pb-dis)	μg/l	S B	9 9	<0.2		3.5	0.4 2.0				
73	Dissolved Lead (1 b-dis)	μg/I	S	9	<1				>[[30	10	
44	Total Lead	$\mu g/l$	В	9	<1		9	5.2	III			
	(Pb total)		S	9	2				111			
45	Dissolved Arsenic (As-dis)	μg/l	В	9	<1	1.7		<1 (md)	>]]-]]	50	50	
46	Total Arsenic	μg/l	S B	9	<1 <1	_	<1 2.7	<1 1.7				
10	(As total)	μ6/1	S	9	<1		2.1	1.2	I-II			
47	Dissolved Mercury	$\mu g/l$	В	9	< 0.2	0.2	0.2	< 0.2	>[]	0.5	none	
40	(Hg-dis)		S	9	<0.2					0.5	110110	
48	Total Mercury (Hg total)	μg/l	B S	9 9	<0.2 <0.2				III-IV			
49	α-НССН	μg/l	B	4	n.d.		0.025					
• /		r-0, *	S	5	n.d.		0.014					
50	β-НССН	$\mu g/l$	В	4	n.d.		0.015					
<i>-</i> 1	HCCH	/1	S	5	n.d.		n.d.					
51	γ-НССН	μg/l	B S	4 5	n.d. n.d.		0.01 0.007		I			
52	DDE	μg/l	S B	3	n.d.		0.007 n.d.					
		ro'	S	4	n.d.		n.d.					
53	DDD	$\mu g/l$	В	3	n.d.		n.d.	n.d.				
C 4	DDT	/1	S	4	n.d.		n.d.					
54	DDT	μg/l	B S	3 4	n.d. n.d.		n.d. n.d.	n.d. n.d.	I			
			b	- +	n.u.		11.U.	11. U .				

Notes: (1) See notes to Table A.1. (2) Highest concentrations of major metal ions were recorded at the Bystre Branch (0 km, sandbar in the area of seaward access channel).