Comparative assessment of the ecological state of sediments in the Ukrainian part of the Danube Delta and Dnipro and Boh Estuary

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1 Introduction

As a result of their unique physical, hydrological and biological conditions, deltas and estuaries are among the most diverse, productive, and ecologically important ecosystems. Conversely, estuaries often serve as a sink for many types of anthropogenic contaminants, including organic pollutants and heavy metals. In this investigation, the sedimentary environments of a large Ukrainian delta and estuary were compared by using chemical analysis, sediment toxicity testing, and bio-indicators based on benthic community indices[4].

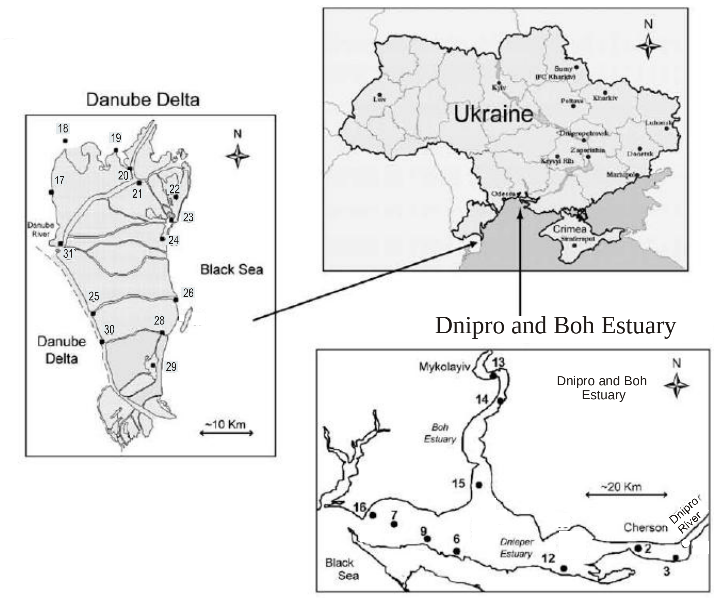

Figure 1. *Sampling sites*

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2 Methods

Sediments were collected in September–October 2006, 2007 and 2008 in the Dnipro and Boh Estuary and in the Ukrainian part of the Danube Delta (24 stations with three replicates at each station, Figure 1).

Methods of sediment sampling, chemical analysis, sediment toxicity testing, and procedures for benthic community analysis have been reported previously (Ho *et al*., 2000; Romanenko 2006; Romanenko *et al*., 2008; Burgess *et al*., 2009). To evaluate the risk of adverse effects on biota the measured contaminant concentrations in sediments were compared with consensus-based sediment quality guidelines (MacDonald *et al*., 2000). The mean overall probable effects concentration-quotient (PEC-Q) attempts to predict the adverse effects of contaminated sediments by combining the expected effects of all measured contaminants for which PECs are available (Long *et al.* 2006).

3 Results

3.1 Contaminant concentrations

The three-year investigation demonstrated that the sediments in the Ukrainian Danube Delta and the Dnipro and Boh Estuary are less polluted compared to the most contaminated marine and estuarine sediments of the world (Ho *et al*., 2002, Burgess *et al*. 2009). For example, even the most polluted Ukrainian stations were considerably less contaminated than sites in North America and Asia. Our sediments were moderately contaminated, with most Danube Delta stations showing higher concentrations than in the Dnipro and Boh Estuary (Table 1). However, Station 2 (at the mouth of the Veriovchiha River) which receives industrial and municipal waste waters from the City of Cherson is characterized by very high concentrations of Zn, Cu, Cr, Cd and Ag, with levels up to ten times greater than at other stations.

Table 1. *Concentration ranges for contaminants in sediments collected in 2006, 2007 and 2008.*

Station	Concentration (mg/Kg)										
	Zn	Cu	Ni	Pb	Cr	Cd	Ag	Mn	∑ PAHs	∑PCB	∑pesticides
The Dnipro and Boh Estuary											
2	650.0-1481.0	137.5-228.0	24.0-50.0	4.8-100.0	369.0-384.0	4.70-10.00	2.00-7.60	368-531	80-33303	186.4-25.0	39.4-209.0
3	35.0-61.7	38.8-65.0	4.2-7.5	23.0-71.0	8.4-95.0	0.10-2.70	0.03-0.06	111-194	803-1488	1.3-36.0	6.8-27.7
6	2.5-129.0	0.7-28.0	2.2-16.8	1.5-70.0	0.8-15.1	0.01-0.10	0.01-0.14	5-138	146-5775	0.7-25.9	4.1-30.8
7	55.2-74.0	14.2-25.5	12.8-32.0	10.0-61.0	31.5-165.0	0.10-0.50	0.07-0.11	276-415	1378-5205	2.3-27.2	12.0-23.4
9	4.5-13.1	0.9-4.2	<0.8-3.8	1.2-2.5	1.3-7.5	0.02-0.03	0.02-0.03	19-20	83-8298	1.2-31.3	4.5-27.1
12	7.5-21.6	2.4-80.0	1.4-7.3	2.0-22.3	3.8-20.0	0.02-0.23	0.03-0.13	58-130	303-1227	0.6-8.7	6.3-21.8
13	7.3-9.8	1.7-6.5	1.0-9.8	1.8-11.8	3.6-25.0	0.01-0.11	<0.01-0.05	34-52	73-227	0.5-31.0	7.2-17.1
14	18.0-190.0	6.0-82.5	3.5-40.7	0.8-52.3	7.5-185.0	0.03-0.70	0.02-0.45	108-100	215-1460	1.1-65.1	14.0-59.4
15	10.5-15.5	3.0-9.0	1.5-9.5	0.7-27.3	5.6-25.0	0.02-0.20	0.01-0.23	74-75	655-1258	0.6-7.3	6.5-15.0
16	1.5-23.5	1.5-6.2	0.8-11.0	1.3-25.8	3.0-16.2	0.01-0.04	<0.01-0.25	21-302	96-397	0.3-41.2	2.0-19.0

The Ukrainian part of the Danube Delta											
17	90.8-98.5	32.2-55.0	21.9-42.0	10.3-56.6	34.3-130.0	0.33-0.55	0.06-0.10	316-356	251-2238	4.4-17.5	20.7-45.2
18	28.8-97.0	3.7-35.6	11.3-46.0	6.3-56.0	17.2-87.5	0.15-0.34	0.03-0.25	166-454	279-1400	6.2-15.5	4.7-19.6
19	35.0-50.6	11.3-29.0	13.8-46.0	4.8-45.8	20.7-40.0	0.05-0.16	0.03-0.05	180-390	73-700	3.1-75.3	11.5-36.2
20	47.5-142.0	10.0-46.0	18.5-59.0	5.3-70.0	52.2-60.0	0.10-1.42	0.07-0.17	484-700	278-4423	0.7-43.2	7.4-178.0
21	94.0-112.0	32.0-45.0	23.5-44.0	8.8-55.1	34.0-140.0	0.22-0.50	0.05-0.16	342-416	377-2337	12.2-81.3	0.6-65.9
22	99.0-104.0	37.0-40.2	21.3-45.0	9.5-66.7	34.4-137.5	0.25-0.50	0.05-0.15	342-458	504-3317	15.3-32.8	0.6-33.1
23	29.4-108.0	3.3-35.0	12.7-52.0	2.5-47.2	15.5-60.0	0.05-0.22	0.03-0.17	110-556	73-816	4.2-68.8	10.4-48.3
24	23.8-139.0	9.8-59.0	4.0-51.0	71.4-1.3	39.4-57.5	0.08-0.61	0.15-0.22	353-516	1850-4991	5.7-73.4	49.5-82.2
25	22.3-118.0	5.0-40.0	16.0-59.0	1.8-68.0	42.5-56.4	0.05-0.44	0.05-0.16	375-722	234-1718	0.4-12.1	1.2-80.1
26	28.8-85.0	7.3-30.0	11.3-39.0	3.0-43.6	20.4-115.0	0.11-0.58	0.03-0.18	119-386	320-1107	1.0-10.2	5.2-69.8
28	88.2-108.5	27.0-34.3	21.0-42.5	10.0-59.2	37.8-105.8	0.19-0.30	0.11-8.00	339-472	266-4495	1.3-20.8	17.2-51.0
29	57.5-74.0	16.0-25.1	22.4-33.8	6.5-34.8	31.7-100.0	0.13-0.33	0.06-0.18	296-379	415-1512	1.1-64.0	12.1-209.4
30	67.7-90.0	0.8-26.0	19.5-42.0	7.5-65.0	34.6-36.2	0.17-0.20	0.05-0.11	304-391	215-825	2.9-6.5	18.2-46.6
31	87.5-118.0	31.8-51.0	26.5-55.0	12.0-69.2	46.2-130.0	0.25-0.42	0.08-0.21	368-741	279-1805	3.3-24.8	0.4-99.7

3.2 Sediment Toxicity Testing

Toxicity tests in sediments showed consistently low survival of midges and Daphnia at only two stations (i.e., Station 2 and 29, Table 2). On average for both estuaries, the survival rate of midges (*Camptochironomus pallidivittatus*) and water fleas (*Daphnia magna*) exceeded 75%, which suggests relatively low sediment toxicity.

4 Benthic Community Analyses

Species richness and Shannon diversity indices for benthic assemblages at all stations varied significantly (Table 2). Minimum values for zoobenthos were registered at Station 2 and maximum values at Station 3; for phytobenthos, minimum indices were registered at Stations 23 and 24, while maximum values were recorded at Station 6. The Dnipro and Boh Estuary was mainly characterized by β-α-mesosaprobity (except Station 2 which was polysaprobic); the Danube Delta prevailingly by α-mesosaprobity and polysaprobity (Stations 18, 19, 22, 24, 26, 29). The maximum Woodiwiss index for the Dnipro and Boh Estuary equalled 4–7 and for the Danube Delta 2–6. The Mayer index was 3–16 and 2–10 for the Dnipro and Boh Estuary and Danube Delta, respectively.

***Table 2**. Results of sediment toxicity testing and benthic community analysis (three-year ranges are shown). zb – macrozoobenthos, phb – phytobenthos, R – species richness richness, H' – Shannon diversity index, P&B – Pantle and Buck index, TBI – Woodiwiss index.*

Sta-tion	Toxicity Testing Results		Benthic Community Indices							
	Midges survival, %	Daphnia survival, %l	R, zb	R, phb	H', zb	H', phb	P&B, zb	P&B, phb	TBI	Mayer index
The Dnipro and Boh Estuary										
2	43.3-80.0	46.7-86.7	2-11	36-52	0.00-2.97	1.69-4.03	2.98-3.60	1.72-2.35	1-5	1-11
3	46.7-96.7	75.0-100.0	22-32	24-44	3.79-4.70	1.65-2.32	2.22-2.56	0.38-2.04	5	4-11
6	83.3-90.0	80.0-95.0	7-10	26-55	2.66-3.03	2.99-4.45	1.68-3.23	1.76-2.02	1-4	1-9
7	73.3-93.3	46.7-73.3	6-8	26-29	0.97-2.81	2.07-2.70	2.18-1.42	1.81-1.82	3-4	3
9	80.0-90.8	75.0-93.3	4-12	33-45	1.35-3.35	2.78-3.91	2.15-2.34	1.74-1.88	2-4	2-5
12	23.3-90.0	70.0-86.7	15-23	23-45	2.73-3.99	2.35-3.48	2.34-2.79	1.89-2.57	4-5	2-10
13	52.5-90.0	80.0-100.0	17-18	24-42	3.17-3.52	2.41-4.12	2.32-2.99	1.87-1.96	4-5	3-10
14	55.0-97.5	80.0-100.0	18-31	23-45	2.43-3.95	1.76-2.83	2.60-3.06	1.32-2.12	2-5	2-4
15	80.0-97.5	90.0-100.0	8-21	19-36	1.38-2.82	0.74-2.79	2.76-2.91	1.56-2.16	4-7	3-12
16	63.3-93.3	70.0-100.0	14-26	25-43	2.68-3.28	2.09-4.19	1.87-2.96	1.60-2.08	4-6	6-16
The Ukrainian part of Danube Delta										
17	52.5-85.0	70.0-95.0	5-7	13-22	1.91-2.59	2.47-3.07	2.87-3.23	1.99-2.05	2	4-3
18	83.3-96.7	80.0-93.8	4-7	8-25	0.47-2.08	1.83-3.45	2.80-3.57	1.31-2.27	2-3	1-2
19	80.0-90.0	80.0-93.8	4-17	8-32	0.90-1.82	1.74-3.17	3.09-3.71	1.85-2.38	1-2	2-6
20	35.0-83.3	80.0-93.3	6-11	11-20	2.10-2.88	2.74-3.13	2.86-3.07	1.96-2.99	2-4	5-7
21	60.0-83.3	80.0-93.3	5-9	10-33	1.76-2.87	1.68-4.30	2.51-2.95	1.91-2.48	2-4	4-5
22	50.0-86.7	90.0-100.0	6-9	24-54	1.74-2.11	2.37-4.77	3.63-3.72	1.71-2.38	2	3-4
23	50.0-83.3	80.0-93.3	2-21	5-34	0.70-3.85	1.49-4.06	2.87-3.22	2.16-2.31	4	3-9
24	70.0-80.0	61.1-93.3	3-13	22-29	1.32-2.99	1.62-3.44	3.00-3.67	1.84-1.94	2-6	3-9
25	80.0-90.0	86.7-100.0	5-8	8-20	1.96-2.55	1.01-3.01	2.40-3.43	1.68-2.09	2	3-5
26	66.7-76.7	73.3-93.3	5-6	9-18	1.30-2.52	2.41-3.03	2.44-3.53	1.79-2.25	2-4	5-6

28	73.3-86.7	60.0-80.0	5-12	4-24	2.13-3.31	1.75-2.81	2.51-3.35	1.91-2.41	3-5	3-10
29	56.7-92.5	40.0-85.0	4-7	33-46	1.89-2.58	3.23-3.94	3.11-3.69	1.75-1.96	2	2-3
30	76.7-92.0	66.7-93.3	5-13	5-16	1.87-2.06	1.29-2.26	2.53-3.08	1.88-2.45	2-6	5-10
31	70.0-93.3	73.3-100.0	8-10	9-15	2.08-2.83	2.62-3.14	2.50-2.69	1.61-2.23	2-3	4-7

5 Discussion

Calculation of expected toxicity (PEC-Q) for the total estuary area was performed without data from Station 2 (Figure 2), since the local source of pollution did not greatly influence the whole estuary. PEC-Q values >1 in the Dnipro and Boh estuaries were exceeded only for concentrations of Cr. In the Danube Delta, PEC-Q values were exceeded for Ni, Cr, Ag, and Mn. So the amount of all PEC_Q >1 for the Dnipro and Boh Estuary (3.18) was 5 times less than for the Danube Delta (17.28), and mean PEC_Q was only 0.1 compared to 0.23 in the Danube Delta (Figure 2). Analysis of mean PEC_Q values at each station separately confirms the expected higher toxicity of the sediments of the Danube Delta, although in general the confidence intervals overlap (Figure 3).

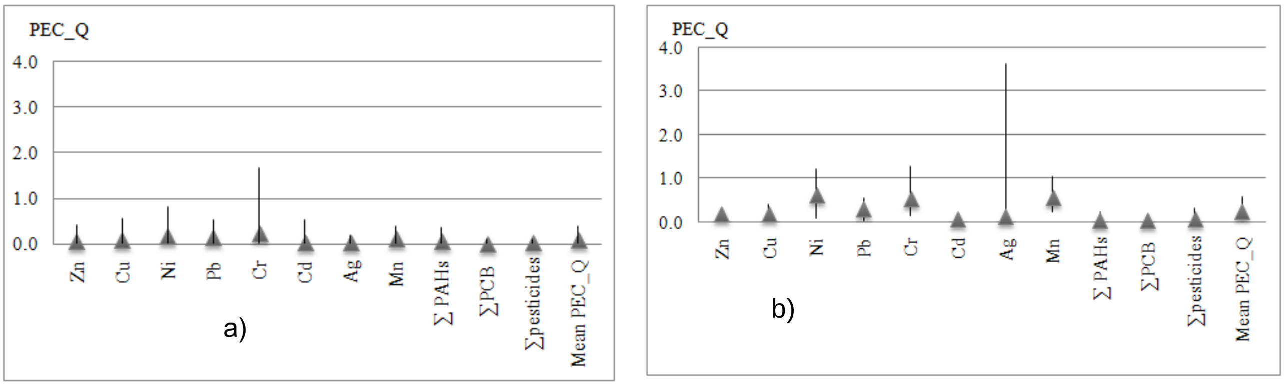

Figure 2. *Expected toxicity for several different chemicals across a) the Dnipro and Boh Estuary (without Station 2) and b) the Ukrainian part of the Danube Delta*

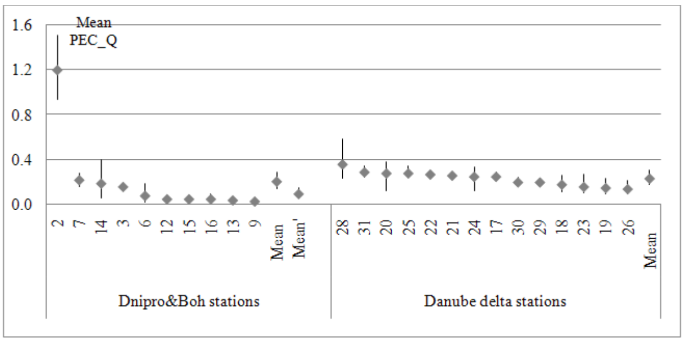

Figure 3. *Expected toxicity based on the PEC-Q at several stations (without Station 2).*

Toxicity testing did not reveal substantial differences between estuaries (Figure 4). Survival for *Daphnia magna* exposed to sediments from both estuaries averaged 83%. Midge (*Camptochironomus pallidivittatus)* mean survival was 77% for the Dnipro and Boh Estuary and 76% for the Danube Delta. However, in both estuaries, stations with reduced survival were detected; for example, Stations 2, 7 and 12 in the Dnipro and Boh Estuary and stations 20, 22, 23 and 24 in the Danube Delta.

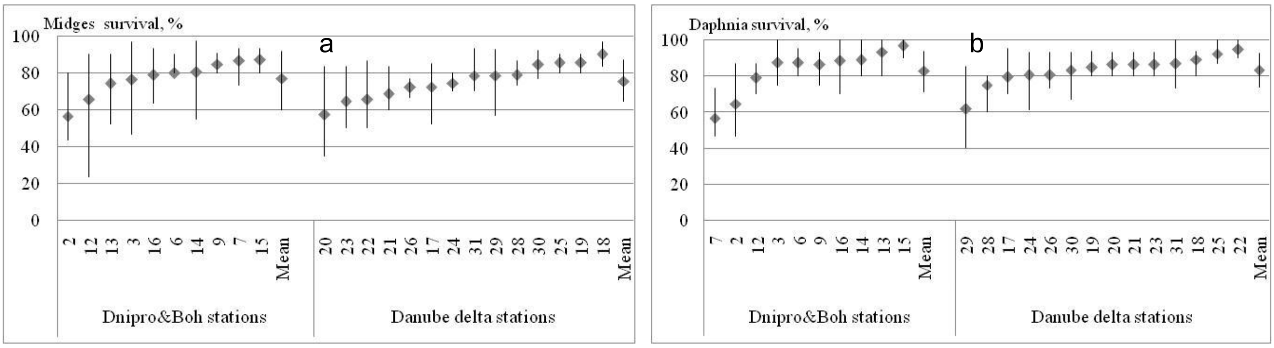

Figure 4. *Mean midge (a) and water flea (b) survival (%) in whole sediment toxicity tests.*

Benthic community analyses based on the state integral index of the assemblages (Lyashenko & Zorina-Sakharova, 2008), which combine all characteristics presented in Table 2, showed that the benthos of the Danube Delta had generally lower values than in the Dnipro and Boh Estuary (Fig. 5). The ranking procedure allows categorization of stations from 'the worst' to 'the best'. However, this index disagreed with the results of the PEC-Qs and sediment toxicity testing. This may suggest sediment contamination did not affect the benthic assemblages, except for Station 2, where all three approaches for assessing benthic condition showed concordance: (1) the highest content of chemicals, (2) maximum mortality in sediment toxicity testing, and (3) minimum values of the state integral index.

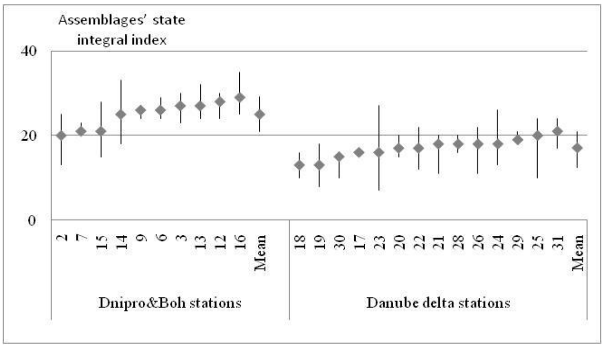

Figure 5. *Benthic community analysis based on the state of the benthic assemblages.*

The search for the relationships between the biotic characteristics, contaminant concentrations and expected sediment toxicity from the set of more than 2000 variables revealed only a few correlations which indicated the negative impact of some pollutants on benthic assemblages. In the Dnipro and Boh Estuary, increasing ∑PCBs, ∑pesticides and ∑*PEC_Q* caused a decrease in species diversity for phytobenthos and the TBI for zoobenthos. In the Danube Delta, the increase in ∑PCBs caused a decrease in TBI, in some years of investigations (fig. 6). Also, it was concluded that the increase in contaminants caused a decrease in the saprobiological indices that was possibly due to the loss of the indicator species.

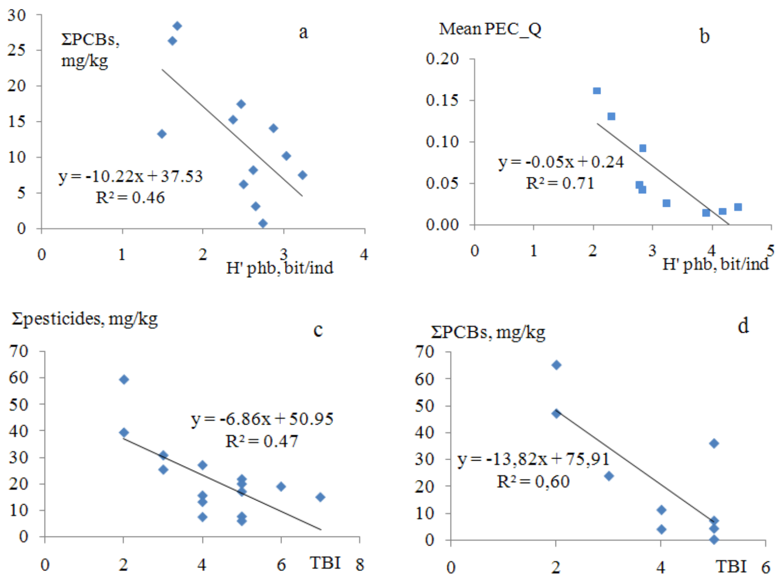

Figure 6. *The relationships between some biotic indices and the content of pollutants in the Dnipro and Boh Estuary and the Danube Delta (a – the Danube Delta, 2006; b – the Dnipro and Boh Estuary, 2007; c – the Dnipro and Boh Estuary, 2006 and 2008; d – the Dnipro and Boh Estuary, 2006)*

6 Conclusion

The Danube Delta showed slightly higher sediment contamination than the Dnipro and Boh Estuary; however, the non-correlation of the three variables PEC_Q, toxicity and benthos showed no risk to the biota.

Only at Station (2), the most contaminated site, did all three approaches show similar results: Mean PEC-Q = 1.2, the highest mortality, and the worst benthic community condition. The lack of agreement between the measures of benthic condition may reflect inaccuracies in the PEC approach or mis-application in these ecosystems (Burgess, R. *et al*., 2009), as well as the absence of a bio-indication assessment scale. On the other hand, under conditions of low toxicity, development of the benthic community is influenced by factors other than contamination, so it is not unexpected that results of the biological indicators and toxicity testing would disagree, although a few correlations suggest the influence of chemical contaminants on the biotic indices. In our opinion, the triad approach will work better under conditions of increasing toxicity. The current study demonstrates that several questions still exist and require further research.

References

Burgess, R. et al. (2009): Concentration and distribution of hydrophobic organic contaminants and metals in the estuaries of Ukraine. Mar Pollut Bull 58: 1103–1115.

Ho K., Kuhn A., Pelletier M., McGee F., Burgess R., Serbst J. (2000): Sediment toxicity assessment: comparison of standard and new testing designs. Arch Environ Contam Toxicol 39: 462–468.

Long E., Ingersoll C., MacDonald D. (2006): Calculation and uses of mean sediment quality guideline quotients: a critical review. Environ Sci Technol 40:1726-1736.

MacDonald, D., Ingersoll G., Berger T. (2000): Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch. Environ. Contam. Toxicol. 39: 20–31.

Romanenko, V.D., Ed. (2006): Methods of hydroecological investigation of surface waters – NAS of Ukraine. Institute of Hydrobiology. – Kyiv.: LOGOS: 408 pp. (In Ukrainian)

Romanenko V., Afanasyev S., Burgess R., Ho K., Lyashenko A., Kipnis L., Konovets I., Terletskaya A., Milyukin M. (2008): Assessment of sediment contamination, toxicity and benthic community composition in Ukrainian part of Danube delta. Proceedings 37th International IAD Conference: 269–276.

Lyashenko A. & Zorina-Sakharova K. (2008): Ecological characteristic of Danube delta water body objects. Proceedings 37th International IAD Conference: 163–167.