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SPATIAL AND TEMPORAL VARIABILITY OF POLLUTANTS IN THE BOTTOM SEDIMENTS IN THE NORTHWEST PART OF THE BLACK SEA

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Abstract. The level of pollution of the bottom sediments in the Northwest shelf of the Black Sea is examined. Modern data are compared with those of the late 20th century and their variability over 30 years. Substantial increase (by two orders) of copper, lead and nickel concentration has been marked.

Key words: Black Sea, Northwest shelf, pollutant, bottom sediments.

1. Introduction

The Northwestern part of the Black sea (NWBS) is a unique marine ecosystem. Characteristic features of the NWBS are fresh water input from the Danube, the Dniper and the Dniester rivers and nutrients that provide one of the biggest productivity levels in the World Ocean. However, since the 1970s, the process of anthropogenic water euthrophication and the near bottom hypoxia linked with it, have caused widespread benthos fauna mortality. A lot of scientific publications were dedicated to the process of the anthropogenic euthrophication of the Black Sea shelf and its consequences (Berlinsky *et al*., 2006; Gomoiu, 2004; Zaitsev, 1977).

In addition to this negative phenomenon a lot of contaminations and pollutants are washed out from the coastal urban agglomerations by the river flow. In the process of sedimentation the suspended matter is accumulated in the bottom sediments. It reinforces negative changes in benthic habitat conditions. For this reason, the attempt is made to examine the matter using the available literature and retrospective data base to analyze the intensity, accumulation and distribution of pollutants including heavy metals and oil in NWBS shelf.

2. Relevance and methodology

The influence of pollutants on the biotic organisms and the environment is widely reflected in scientific literature. Therefore assessment of the level of pollutants accumulated in the bottom sediments in the NWBS shelf should be considered as a rather actual problem.

The average value of the studied parameters were processed by linear interpolation and given to the centers of squares, ranked by hydrological features (Berlinsky *et al*., 2000). The total volume of data base includes 5417 parameters (Hydrological and hydro-chemical status, 1998).

3. Discussion

The aggregate values averaging of pollutants concentration in the bottom sediments of the NWBS was done taking into consideration the spatial and temporal data discreteness which allowed to obtain some interannual dynamics of the investigated parameters, characterized by trends and tendencies (Table 1, 2).

Heavy metals (lead, cadmium, chromium) are present in wastewater of many industrial enterprises and as impurities in a great number of technical reagents used in drilling fluids [8, 10]

The content of heavy metals in the bottom sediments in the NWBS shelf is mainly within the natural geochemical background. For the period of the 1980s the natural geochemical values for mercury, copper, lead, cadmium, nickel and chromium were, 0,06; 3,4; 0,4; 0,17; 5,9 and 2,2 mg/kg accordingly (Geology of the shelf, 1985). The original data base (Hydrological and hydrochemical status, 1998) as well as the data from literature sources (Berlinsky *et al*., 2006; Berlinskyi, 2012) was used for the analyses.

Mercury and its compounds are most dangerous for the living organisms. There is permanent accumulation of mercury in the bottom sediments over the past two decades. The natural geochemical value of mercury concentration was 0,06 mg/kg in the 1980s, but 30 years later it rose up to 0,08 mg/kg which created an additional threat to benthic organisms in the process of desorption, when secondary contamination of the bottom water layer occurred (Table 2).

For the period of the 1980s the natural geochemical value of copper concentration was 3, 4 mg/kg, three decades later it increased by an order

For the same period lead concentration increased by two orders from the values of 0,4 mg/kg in the 1980s up to 22 mg/kg in 2013. This sharp rise in average values is correlated with modern data obtained for the Caucasian coast waters (http://esimo.oceanography). It characterizes the process of the overall growth of the concentration almost in the entire coastal zone located under the huge technogenic press from industrial agglomerations.

Table 1

The average concentration of pollutants in the NWBS shelf in the summer period (1991–2013)

Pollutant, (mg/kg)	Number of the region		
	Danube	Dniester	Open area
Oil	197,5	330,0	152,5
Hg	0,11	0,08	0,12
Cu	26,82	22,10	19,43
Pb	17,1	19,6	11,6
Cd	0,22	0,27	0,13
Ni	32,6	24,6	27,8
Zn	78,95	60,62	41,07
As	8,91	8,47	7,55
Phenols	0,82	0,34	0,50

Table 2

Variability of the natural geochemical background of pollutants in the NWBS

Pollutant, (mg/kg)	1985 [4]	1991–2013 [6]
Oil	200	200
Hg	0.06	0,08
Cu	3,4	25,4
Pb	0,4	19,2
Cd	0,17	0,22
Ni	5,9	33,3
Zn	–	63,98
As	–	9,48
Cr	2,2	–
Phenols	–	0,56

The average meaning of lead concentration in the Caucasian coast is 73,2 mg/kg with fluctuation range from 0,91 up to 1189 mg/g. For the NWBS area the average meaning of lead concentration in the bottom sediments during the period of 1991 – 2013 is 19,75 mg/g with fluctuation range from 15 up to 34 mg/g. The probable reason for this significant increase in the concentration of lead is the intensification of petroleum hydrocarbons mining of Stormy, Arhangelsk and Galitsin deposits located in the NWBS shelf. Thus, the concentration of lead in drilling fluid reaches 505 mg/g [5] (Pankratova, Sebah, 1994). According to Table 1, maximum concentration of lead is marked in the central region near the Crimean Peninsula.

As for cadmium concentration in bottom sediments on the shelf, its max value was 0,39 mg/kg since the 1990s. Since 2013 the concentration decreased to the natural geochemical value for the period of the 1980s, that is 0,17 mg/kg with average value 0,22 mg/kg in the modern period.

The natural geochemical value for nickel was 5,9 mg/g in the 1980s, its concentration in the bottom sediments increased by an order at present. New geochemical value for nickel is more than 40 mg/g .

Thus, it is necessary to mark a significant increase in concentration of such heavy metals as mercury, copper, lead and nickel in the bottom sediments of the NWBS shelf. At the same time the average geochemical values for copper, lead, and nickel have extremely increased. On the other hand cadmium concentration got down to the average geochemical values of the 1980s but the variability was rather high - from 0,35 to 17 mg/g. The reasons for this high variability are not clear and can be linked with local and temporal anthropogenic and technogenic influence.

One of the most important negative ingredients of the aquatic systems is the level of oil concentration in water and bottom sediments. At present there is an intensive process of increasing oil concentration in the bottom sediments in the NWBS shelf.

According to (Pankratova *et al*., 1994; Sebakh and Pankratova, 1995) the average typical value of oil concentration in the uncontaminated areas of the Black and Azov Seas for the 1980s was 200 mg/kg. The cleanest area of the NWBS shelf was its central part. The maximum level of oil concentration was 1,000 mg/kg. In the period from 1992 to 2013 the average value didn’t exceed 200 mg/kg (Table 2), but there is a sustainable tendency to oil accumulation in bottom sediments and in perspective the encrease in the natural geochemical value will be expected. (Rajsintseva *et al*., 1998).

In the modern period the highest values of oil concentration were marked in the Dniester estuary (more than 300 mg/kg). The second is the Danube estuary area with the values a little less than 200 mg/kg. The Dnieper – Bug and Odessa Bay regions have the lowest values – up to 140 mg/kg. The Central part of the NWBS is characterized by the values of 150 – 180 mg/kg (Table 1).

The Danube estuary has a high level of pollutants that is due to their removal with the flow of the Danube, the process of sedimentation of suspended matters and accumulation in bottom sediments. (Rajsintseva *et al*., 1998).

In the shallow water of the Danube estuary the comparison of Ukrainian’s and Romanian’s average pollutants concentration in the bottom sediments has been made (Hydrological and hydrochemical status, 1998; Oaie, *et al*., 1999; Rajsintseva *et al*., 1998; Ungureanu *et al*., 2004). The average data were used for the whole area of the Romanian region of the Denube shown in Oaie, *et al*., 1999, for the separate parts between the Sulina and St. George estuaries. The common results are shown in Table 3.

So, it is possible to mark, that in the Denube estuary the temporal dynamics of oil concentration in the bottom sediments reflects the technogenic presss during the long period (30 years,) at least in the Ukrainian part. So, oil concentration during the period of 1993–1997 was linked with the effect of active navigation and the values were rather high – 1800 mg/kg. Later in the period of 1994–2005 oil concentration decreased sharply to 142,9 mg/kg that was linked with the lack of navigation in this region.

At present oil concentration increased slightly up to 285 mg/kg, probably due to the influence of the active process of navigation via Bystryi arm. Mercury concentration both in Ukrainian and Romanian parts of the Danube region exceeds the natural geochemical condition for the whole NWBS shelf 2 and 7 times respectively (Table 2, 3).

Copper background values in the NWBS at this time make up 25.4 (26.82 mg / kg – for the Danube region over the period of 1991 – 2013), and in estuarine area of the Danube – from 29.52 (Ukrainian part) to 86, 74 mg / kg (Romanian part), i.e. 3 times exceed.

A drastic reduction of cadmium concentration in the Danube region should be marked as a positive factor. In the period of the 1990s its concentration in the Ukrainian part was very high – up to 6,2 mg/kg and at present the values make up from 0,19 mg/kg (Ukrainian part) to 1,71 mg/kg (Romanian part). In the period of 1993–2013 nickel concentration in the Danube region was even less than in the whole NWBS shelf (Table 1, 2). However, in comparison with the period of the 1980s its concentration increased by an order from 5,9 to 33,3 mg/kg. Zink concentration in the period of the 1990s in the Ukrainian part exceeded the concentrations in the Romanian part, but at the beginning of the 2000s this ratio changed in the opposite direction (Table 3). The concentrations of arsenic, phenols, chromium and cobalt are roughly the same in the Romanian and the Ukrainian parts of the Danube.

According to the state of the environment and ecological safety norms, it is recommended to determine 16 priority polycyclic aromatic hydrocarbons (PAHs) as well as six esters of phthalate acid to be included in the list of the controlled chemicals.

PAHs are volatile persistent organic pollutants, characterized by carcinogenic, mutagenic, teratogenic and hepatotoxic effects. They are able to be accumulated in lipid tissues of living organisms and to provoke various serious diseases. PAH is the sum of the 16 determined PAHs indexes – from low molecular weight PAHs (2-3 rings) to high-molecular weight PAHs. Different international agreements included around 60 chemicals in the lists limiting their distribution and requiring the mandatory control of their content in the environment. A group of persistent organic pollutants (POPs) was nicknamed the "dirty dozen", in particular: aldrin, endrin, dieldrin, mirex, DDT, hexachlorobenzene, hep-tachlor, toxaphene, chlordane, polychlorinated biphenyls, dibenzo-p-dioxins and dibenzofuranes.

Table 3

The average concentrations of pollutants in the bottom sediments of the Danube region (mg/kg)

Pollutant, (mg/kg)	1993–1997 (Ukrainian part) [9]	1995–2000 (Ukrainian part) [6]	1995–2000 (Romanian part) [7]	2001–2002 (Romanian part) [11]	2011–2013 (Ukrainian part) [6]
Oil	1800	142,9	–	–	285
Hg	–	0,12	–	0,53	0,15
Cu	48,9	28,31	54,75	86,74	29,52
Pb		24,36	40,95	45,46	21,6
Cd	6,2	0,27	2,16	1,71	0,19
Ni	50,8	–	65,15	71,31	34,86
Zn	138,5	75,64	90,3	161,71	79,74
As	–	10,35	–	13,19	7,6
Phenols	–	0,44	–	–	0,60
Cr	–	74,87	79,76	65,07	79,53
Co	–	–	–	16,77	17,59

The largest percentage of carcinogenic PAHs was in the bottom sediments in the area under the direct influence in the Ukrainian part of the Danube delta and in the Bystryi and Starostambulskyi arms (6.15 and 8.58 correspondently). The reason is a direct impact of anthropogenic pollution on these regions. The minor value of the PAH index (4.72 – 6.28) was recorded for the open area of the sea (Tsymbalyuk *et all*., 2011).

4. Conclusion

A significant increase of copper, lead and nickel concentrations in the bottom sediments in the NWBS shelf by two orders in a period of 1991–2013 compared with the 1980s has been marked.

Concentrations of mercury and zinc in the bottom sediments of the Danube region exceed the corres-ponding values in the NWBS shelf.

The analysis of Ukrainian and Romanian data, obtained in different periods, has been made, that showed their close correlation, common order of values and variability of temporal dynamics reflecting causal regularities of natural fluctuations and anthropogenic impacts on the aquatic ecosystem.

The results of the research can be indicators of anthropogenic impact exerted by industrial and municipal waste emissions and economic activity of the ports and dumping on the shallow waters in the Danube area.

References

[1] Berlinsky N., Yu. Bogatova Yu., Garkavaya G. Estuary of the [in]: The Handbook of Environmental Chemistry. Springer-Verlag: Berlin-Heidelberg 2006, **5**, Part H (Estuaries), 23–264.

[2] Berlinsky N. A., Garkavaya G. P., Bogatova Yu. I. Rayjonirovanie ukrainskogo sektora severo-zapadnoyj chasti Chernogo morya (po gidrofizicheskim i gidrokhimicheskim kharakteristikam) Ehkologicheskaya bezopasnostj pribrezhnoy i sheljfovoy zon i kompleksnoe ispoljzovanie resursov sheljfa. Sevastopol 2000, 9–24.

[3] Berlinsky N. F. Dinamika tekhnogennogo vozdeyjstviya na prirodnye kompleksy ustjevoi oblasti Dunaya. Astroprint, Odessa 2012, 252.

[4] Geologiya sheljfa USSR Litologiya. Naukova dumka, Kyiv 1985, 182.

[5] Gomoiu M-T. New Approaches in the Assessment of the Black Sea Ecosystems Geo-Eco-Marina **9–10**, 2003–2004. National Institute of Marine Geology and Geoecology Modern and Ancient Fluvial, Deltaic and Marine Environments and Processes Proceedings of Euro. EcoGeoCentre, Romania.

[6] Gidrologichni ta gidrokhimichni pokazniki stanu pivnichno-zakhidnogo sheljfu Chornogo morya. ZAT "Vipol", Kyiv 1998, 616.

[7] Oaie Gheorghe, Secrieru Dan, Szobotka Ştefan, Stănică Adrian, Soare Romero. Pollution state of sediments dredged from the Sulina distributary and their influence to the Danube delta front area / Geo-Eco-Marina 1999, **4**, 37–41.

[8] Pankratova T. M., Sebakh L. K., Finkelshtein V. S. Ocenka raspredeleniya i puti migracii tyazhelihkh metallov v ehkosisteme Karkinitskogo zaliva. Trudy YugNIRO 1994, **40**, 150–156.

[9] Rajsintseva N. I, Sarkisova S. A., Savin P. T., Sekundajk L. Yu. Osobennosti raspredelenija zagrjaznjajushhih veshhestv i produkcii organicheskogo veshhestva fitoplanktona v priust'evoj zone reki Dunaj. Jekosistema vzmor'ja ukrainskoj del'ty Dunaja. Astroprint, Odessa 1998, 63–11.

[10] Sebakh L. K., Pankratova N. M. Sebakh L. K., Pankratova T. M. Ocenka zagryaznennosti Chernogo i Azovskogo moreyj v sovremennihkh antropogennihkh usloviyakh. Trudy YugNIRO 1995, **41**, 91–93.

[11] Ungureanu Viorel Gh., Popescu Rodica, Stănică Adrian, Axente Valerica, Milu Consuela. Metals in the Danube river suspended sediments at the mouth of the Sf. Ghreorghe disributary. Geo-Eco-Marina, 2003–2004, **9–10**, 159–166.

[12] Unified state system of information about OS-SETTING in the world's oceans (ESIM) http://esimo.oceanography.ru/esp2/index/index/esp_id/10/section_id/8/menu_id/4065

[13] Zaitzev Yu. P. Severo-zapadnaya chastj Chernogo morya, kak objhekt sovremennih gidrobiologicheskih issledovaniy. Biologiya morya 1977, **43**, 3–6.

[14] Tsymbalyuk K. K. Den'ga Y. M., Berlinsky N. A., Antonovich V. P. Determination of 16 priority polycyclic aromatic hydrocarbons in bottom sediments of the Danube estuarine coast by GC/MS, Geo-Eco-Marina, 2011, **17**, 67–72.