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CHARACTERISTICS OF TRACE METALS SPATIAL DISTRIBUTION IN SEA BED SEDIMENTS OF THE NORTH-WESTERN BLACK SEA SHELF

The present work describes the characteristics of trace metals (TM) content and TM spatial distribution on the north-western Black Sea (NWBS) bottom as identified in the area of investigation (Ukrainian coastal waters); the sources of trace metals and their path-ways into the bottom sediments of the NWBS shelf were studied as well; the level of impact of the different land-based and marine-based sources on the content and distribution of trace metals in the sea-bed sediments of the shelf are described; the spatial distribution of trace metals of natural and anthropogenic origin in the sea-bed sediments of the shelf is presented.

To quantitatively determine the impact of different sources (natural and anthropogenic) on the content and distribution of trace metals on the NWBS shelf bottom, specific statistical analysis of data was carried out. In particular, with the help of cumulative probability curve, the content of trace metals was separated into groups coming from different sources: natural sources – A; technogenic diffuse sources – B, technogenic point sources – C). The method proposed allows separating the share of input of the various sources forming the content and distribution of trace metals in the marine environment, as demonstrated on the example of bottom sediments in the present investigation.

Key words: sea-bed (bottom) sediments, trace metals, separation of sources (natural and anthropogenic), probability density

INTRODUCTION

During the last decades, the superposition of significant anthropogenic impact on the permanent natural geo-chemical distribution of elements has imposed various increases in their background concentrations in the sea-bed sediments of the north-western Black Sea shelf. The negative effect of water and bottom sediments pollution is breaching the ecological equilibrium in the sea which among other impacts leads to damages of internal organs and ultimately to death of marine living organisms or to loss of their capacity to reproduce. Besides, the contamination of biota influences on the quality of sea-food harvested in the Black Sea and hence on human health.

The sea-bed sediments are depositing environment and their chemical composition does best reflect long-term impacts of natural and anthropogenic pressures on the sea. In this relation, the survey of the characteristics of the spatial distribution of trace metals in the sea-bed sediments of the NWBS shelf is a priority issue of a high scientific and practical importance while taking into consideration the increased anthropogenic loading on the investigated area. Worth mentioning is also the regional Black Sea Strategic Action Plan [13] which identifies four most important transboundary environmental problems for the Black Sea: eutrophication/nutrient enrichment, decline in living resources, biodiversity change and chemical pollution. Among the latter, the problems related to chemical pollution cannot be solved without proper understanding of the causal chain pressures-impacts as is the case of any change in Nature related to human activity superimposed over the climate-driven or other factors driven change in the environment.

The *present paper* discusses the level of impact of various sources of trace metals deposited in bottom sediments. The knowledge presented shall assist to identify the priorities in management of the pollution sources.

The sea-bed sediments of the NWBS shelf are the *object* of this study.

The *subject of study* is the trace metals spatial distribution in sea-bed sediments of the NWBS shelf.

MATERIALS AND METHODS

The results from the monitoring of sea-bed sediments of the northwestern part of the Black Sea, carried out in September-October 2007 and published in Kakaranza et al. [4], were used as material for this study. From administrative division viewpoint the investigated region belongs to the Odessa, Nikolaev and Kherson districts of Ukraine. The sea-bed sediments of the investigated area (47 sampling stations, Fig. 1) are represented mainly by mules and Coquina and much less by sands [1, 2, 5, 6, 9, 11]. The deposits investigated are at depths of 15-31 m. According to Mitropolsky et al. [8], in the investigated area metals are basically redistributed with the pellitic fraction (< 0.01 mm) of the sea-bed sediments. The content of metals was measured by the atomic absorption method. The data were statistically processed using *software package STATISTICA 8.0.*

RESULTS AND DISCUSSION

Within the investigated area there are sites with polluted sea-bed sediments due to intensive anthropogenic activity [3, 7, 8, 10, 14]. Those sites include: the sea-bed sediments in port areas (Odessa Oil Harbor, Ports of Ilichevsk and Yujhniy) and in front of them at sections with extensive vessel traffic; areas with regular dredging activities (Ports of Ilichevsk, Odessa and Yujhniy); areas of river discharges (Dniester, Southern Bug, Dnieper) stemming to the Black Sea; damping zones in the Sea; zones of waste water discharges into the Black Sea from municipal and industrial sources; areas of agricultural lands; and sea-bed zones that are locations of drilling platforms.

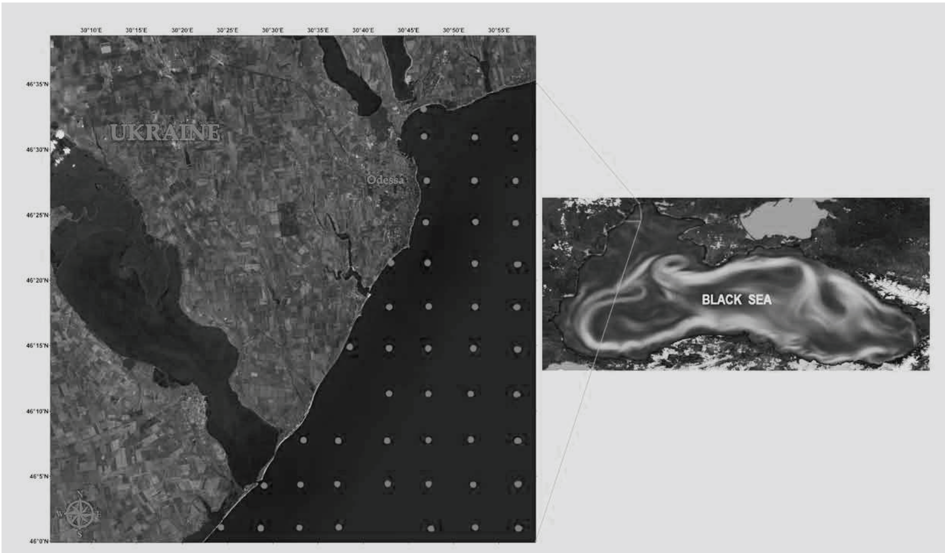

Fig. 1. Maps showing the sampling stations in the north-western part of the Black Sea (left) and the location of the investigated area in the Black Sea (right)

According to their concentration the metals investigated in the area are mainly disposed in the following sequence which may be occasionally in a different order: *Cr > Ni > Cu > Pb > As > Co > Cd > Hg.*

Major objective of the investigation presented here was to determine quantitatively the impact of different anthropogenic (technogenic) sources on the content and distribution of trace metals in the sea-bed deposits of the NWBS shelf. For the purpose the cumulative probability curve was used to separate the metal content into components that were coming from different sources (of natural or of anthropogenic origin).

It is well-known that the distribution of the frequencies of background content of trace metals in Nature (including in the sea-bed deposits) is usually subordinated to the normal (or log-normal) distribution law:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}, \qquad (1)$$

where: *m* – mathematical *expectation*; *s* – standard deviation.

Besides, the probability distribution function (or cumulative distribution function) of a normally distributed random variable is depicted by a straight line in graphs.

We assume, the impact of anthropogenic sources shall lead to change in the frequency distribution features of trace metals content in the natural environment. More particular, this may lead to asymmetrical distribution of frequency of trace metals content in sea-bed deposits, i. e. to deviation of the frequency from the normal law. Herewith, the curve of the density of probability distribution obtains asymmetrical form and on the straight line of the integral probability inflection points appear [12, 15]**.** Frequency histograms offer a direct vision of these varying features of trace metals content (Fig. 2*a*). The analyses of the probability density function and the probability distribution function of the content of trace metals in sea-bed deposits of the NWBS shelf showed that only Co and Pb were distributed according to the log-normal law. The distribution of the content of the remaining metals was subordinated neither to the normal nor to the log-normal law (Fig. 2), certain deviations were well-defined. This was confirmed also by the coefficients of kurtosis and skewness in comparison to their critical values S_k, K_u (Table 1).

Thus, the coefficients of kurtosis and skewness were higher than the critical known for the investigated metals, with the exception of *Co* and *Pb*. The latter two metals were found with an approximately log-normal distribution.

Table 1 also demonstrates that in 2007 the majority of trace metals have been found in the NWBS with maximum concentrations significantly exceeding the background contents referenced for the area [8].

Table 1.

Statistical characteristics of trace metals content in sea-bed sediments of the NWBS shelf in 2007 (μ – average value; σ – standard deviation)

Trace Metals (mg/kg)	**μ, mg/kg**	**σ, mg/kg**	**Min, mg/kg**	**Max, mg/kg**	**Coefficient of variation, C_v**	**Skewness S_k = 0,825 (α = 1 %)**	**Kurtosis K_u = 0,868 (α = 1 %)**
Cr (25-84)	43,74	35,68	5,93	199	0,82	1,978	6,556
Ni (19-67)	22,41	30,39	1,68	204	1,35	4,875	28,539
Cu (8-30)	20,84	15,87	1,38	83,63	0,76	1,682	4,289
Pb (10-25)	11,19	11,52	0,04	39,65	1,00	0,823	-0,030
As (10,6-15,9)	7,50	5,90	0,15	27,70	0,79	1,726	3,281
Co (11-16)	4,3	3,5	0,04	11,38	0,82	0,732	-0,662
Cd (-)	0,36	0,54	0,03	2,99	1,49	3,140	12,443
Hg (-)	0,023	0,013	0,004	0,065	0,57	0,863	1,091

Note: In brackets the range of the background content of trace metals (min – max), in different natural and technogenic types of sediments of the investigated area, is given in [8].

The cumulative curves of section A, in which the trace metal content is lower than in the section B, characterize the distribution of cumulative probability for metals of natural origin. The trace metals of sections B and C (in which the content of trace metals is higher than in section A), have anthropogenic origin. We suggest that the trace metals of section B come from diffuse sources and the metals in section

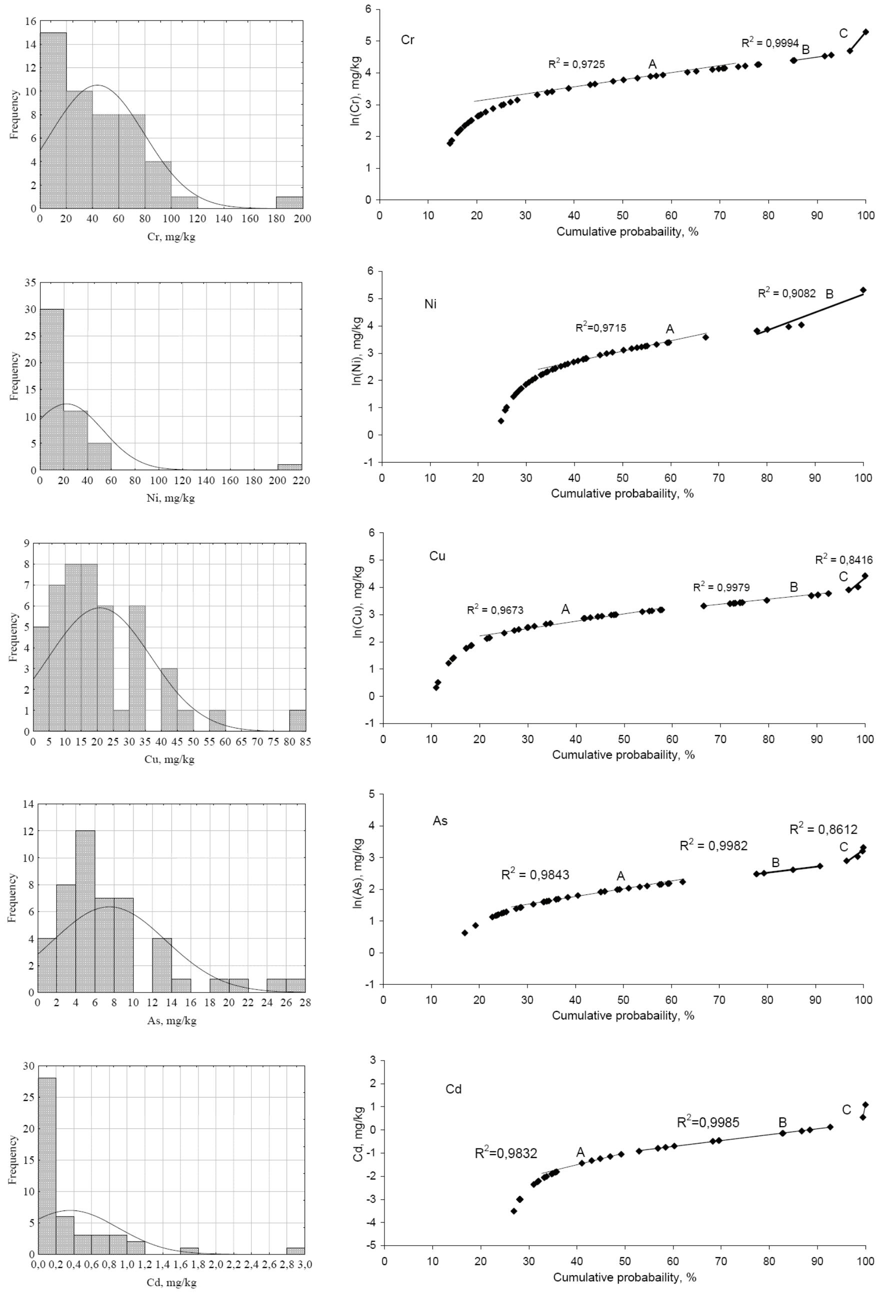

Fig. 2. Frequency distribution (probability density) (a) and cumulative probability curve (b) of the content of Cr, Ni, Cu, As, Cd, Hg, Pb, Co in sea-bed sediments of the NWBS shelf

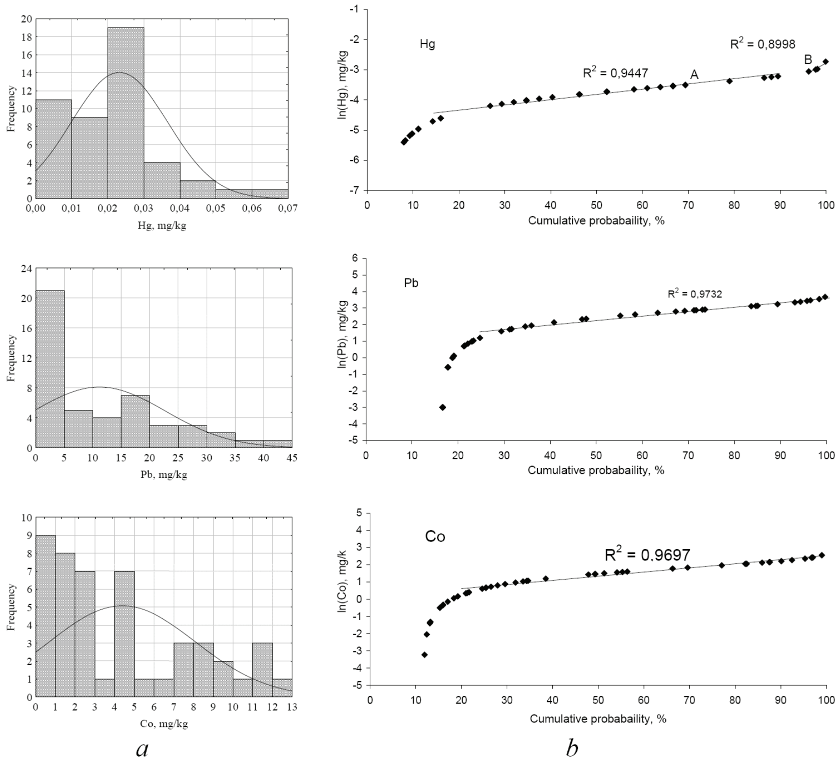

Fig. 2. Frequency distribution (probability density) (a) and cumulative probability curve (b) of the content of Cr, Ni, Cu, As, Cd, Hg, Pb, Co in sea-bed sediments of the NWBS shelf

C – from point sources. Diffuse sources in this paper include both industry and agriculture, which related pollution is brought to the sea via atmosphere, ground waters, coastal erosion and riverine sediments (not riverine water discharges, which are traditionally classified as point sources). Point sources can be both – land-based (e. g. municipal, industrial waste waters) or sea-based (port activitities, illegal ship-borne discharges, dumping, drilling, etc.)

From statistical view-point such distribution of trace metals, as demonstrated in Fig. 2*b* (except for *Co* and *Pb*), means that the elements belong to different sample populations.

The non-parametric Wilcoxon-Mann-Whitney test (Mann – Whitney U-test) was used to determine if the separated samples (natural and anthropogenic) have come from different populations.

The further separation of the trace metals content into components and the drawing of the correspondent contour map of the trace metals distribution were completed for *Cr*, *Ni*, *Cu*, *As*, *Cd*, Hg, which were neither normally nor log-normally distributed.

Table 2 shows the average values (*m*) and standard deviation (*s*) for the investigated trace metals with separation of their content by the origin of sources taking into consideration the natural background. Expectedly, the quantities (*m*) and (*s*) reduced for the metals of natural origin demonstrating the role of the anthropogenic influence for the non-uniform distribution of trace metals in sea-bed sediments of the NWBS shelf.

Table 2.

Parameters (*m* – average value; *s* – standard deviation) of trace metals from different sources located in the NWBS (data 2007)

Trace metals origin	*Cr*, mg/kg		*Ni*, mg/kg		*Cu*, mg/kg		*As*, mg/kg		*Cd*, mg/kg		*Hg*, mg/kg	
	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ
Natural origin	34,061	21,41	14,621	8,8149	13,24	7,003	5,157	2,52	0,111	0,089	0,02	0,01
Anthropogenic origin	109,91	45,001	75,643	63,046	40,71	15,47	17,42	5,837	0,948	0,686	0,053	0,008

The results obtained were compared with data previously presented in [8]. Indeed, for stations approximated by line A, the content of trace metals is lower than the natural background; for stations approximated by lines B and C – they are higher than the natural background.

Fig. 3 shows the contours of the spatial distribution of the total trace metals content (of natural + anthropogenic origin, i. e. before separation) in sea-bed deposits Figs. 4 and 5 show, respectively, the contours of the spatial distribution of the trace metals content of natural and anthropogenic origin (i. e. after separation).

Accordingly, the increase of the metal content in sediments due to anthropogenic sources is well traced in Fig 5. The distribution of the metal content of anthropogenic origin as a whole approximately is identical with the distribution of the trace metals total content, Fig. 3. The similar character of the trace metals total content distribution and of the anthropogenic origin metals means that the technogenic sources have significant influence on the trace metals distribution and to some extent control the processes of this distribution.

The analysis also showed that the investigated trace metals of anthropogenic origin in sea-bed deposits of the NWBS shelf had come mainly from non-point (diffuse) sources, both industrial and agricultural, via the atmosphere and with riverine sediments. Thus, for example (Table 3), in the case of *Cu* at 28 % of the total number of sampling stations, the content was formed by inputs from anthropogenic sources of which 21 % – from diffuse sources and 7 % – from point; for *As* at 19 % of the total number of sampling stations the content was formed by inputs from diffuse sources and 8 % – from point sources, etcetera (see Table 3).

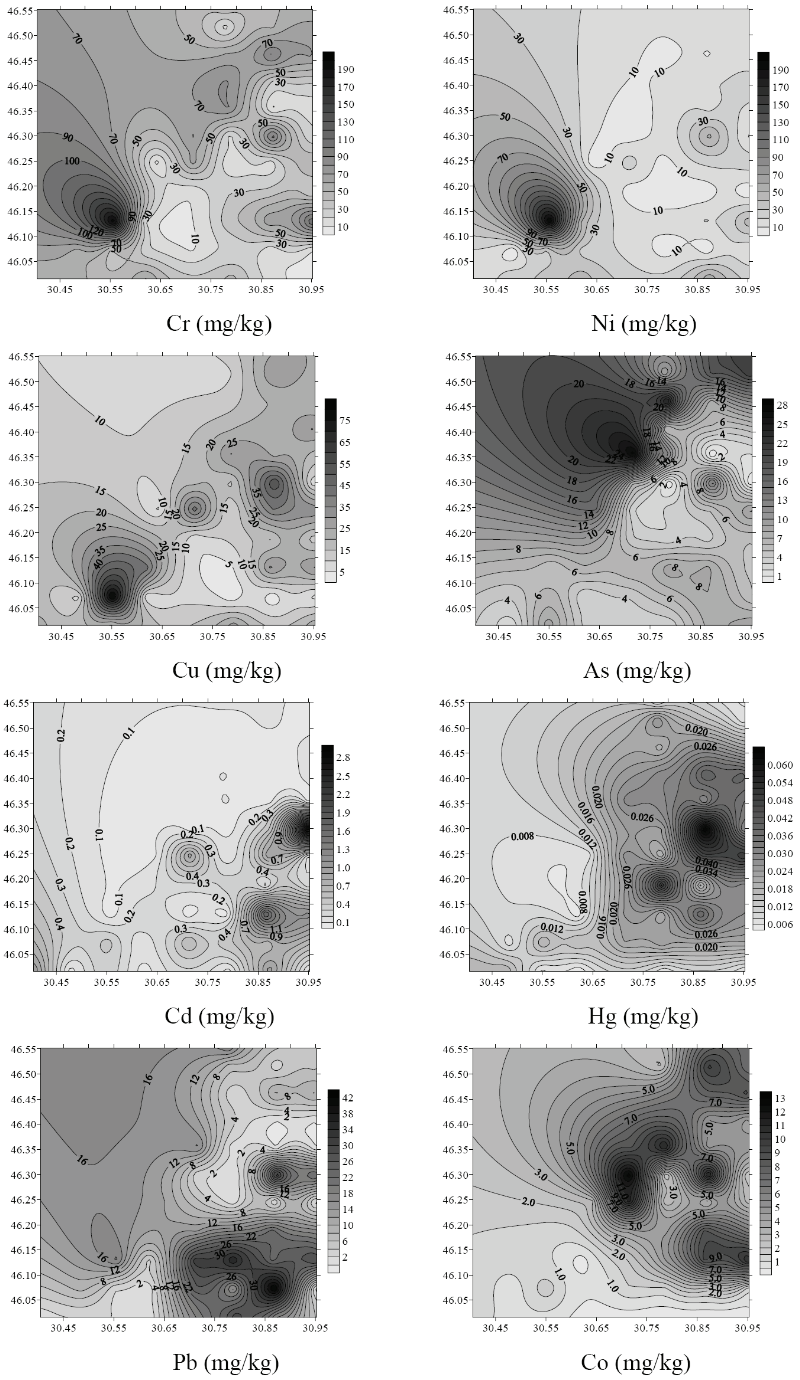

Fig. 3. Distribution of the total content of Cr, Ni, Cu, As, Cd, Hg, Pb, Co in sea-bed sediments of the NWBS shelf in 2007

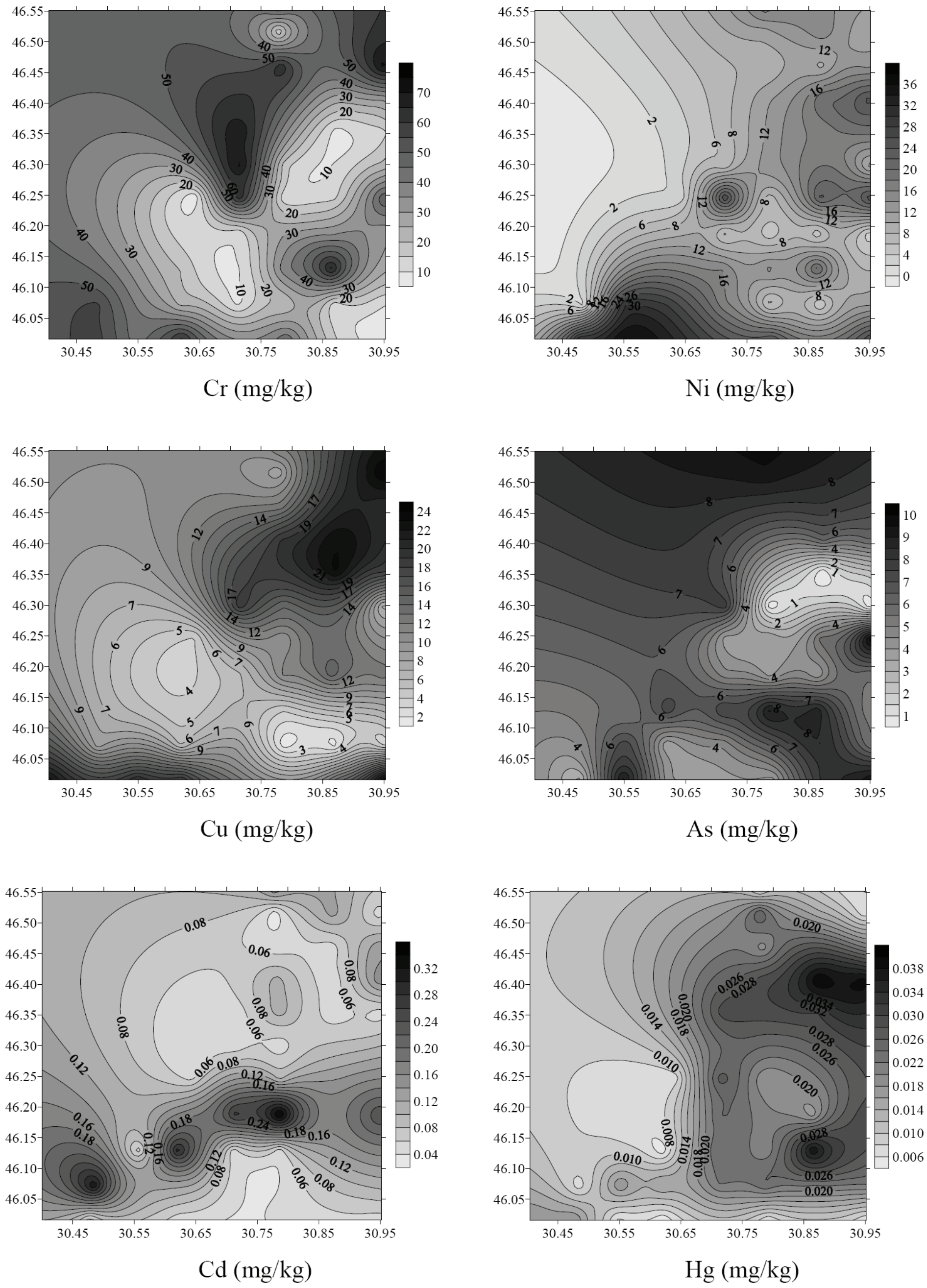

Fig. 4. Distribution of the content of Cr, Ni, Cu, As, Cd, Hg of natural origin in sea-bed sediments of the NWBS shelf in 2007

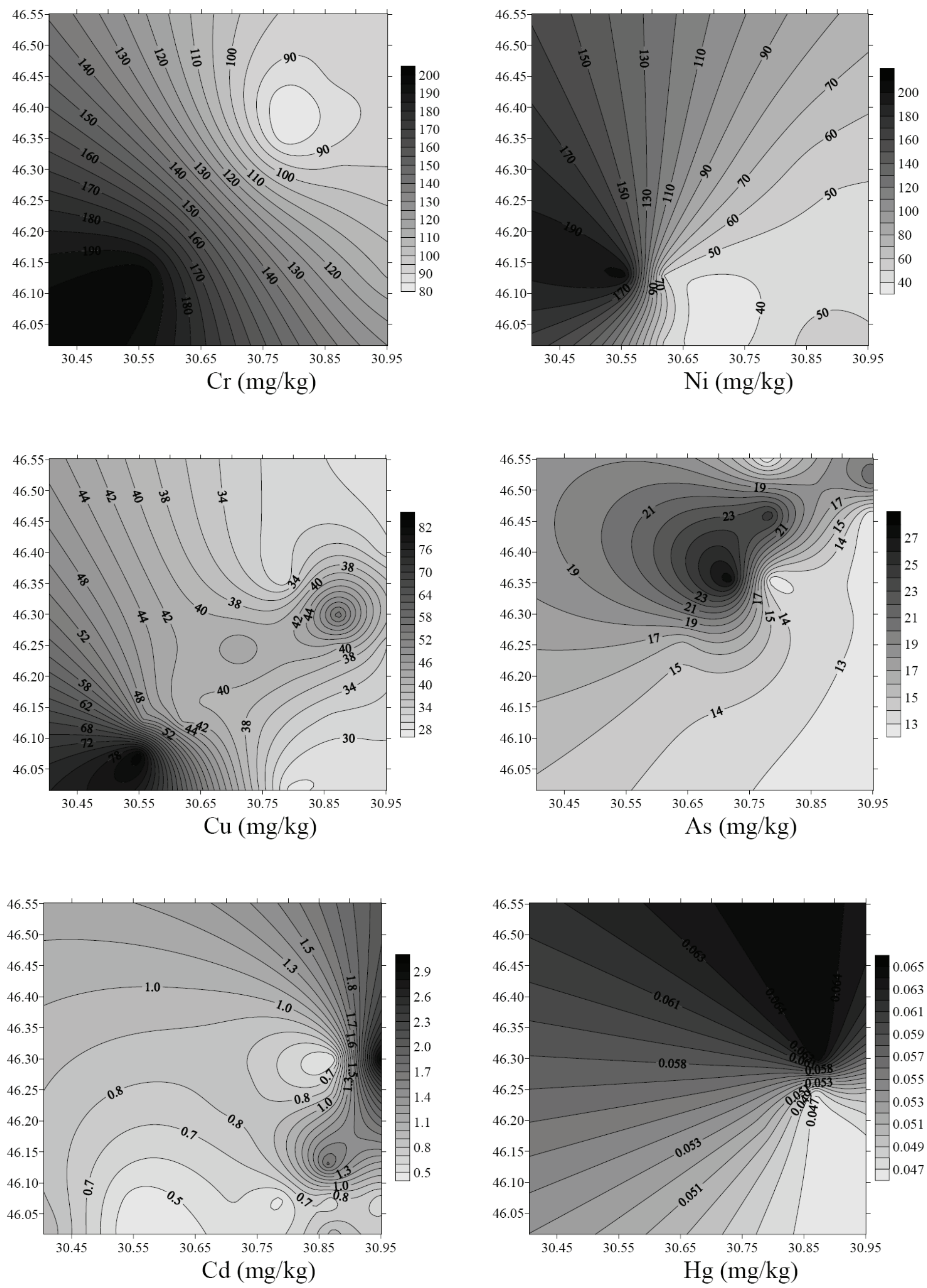

Fig. 5. Distribution of the content of Cr, Ni, Cu, As, Cd, Hg of anthropogenic origin in sea-bed sediments of the NWBS shelf in 2007

Table 3.

Number of sampling stations in the NWBS at which metals arrive from diffuse and/or point sources of pollution (% of the total number of investigated stations (data 2007)

Trace Metals	Number of sampling stations (%)		
	metals from point and diffuse sources	metals from diffuse sources	metals from point sources
Cr	15	9	6
Cu	28	21	7
As	19	11	8
Cd	30	26	4

CONCLUSIONS

The data analysis allows drawing the following conclusions.

The cumulative probability curve can be employed for separation of trace metal content coming from different sources in groups (natural – A; anthropogenic diffuse – B; anthropogenic point – C).

Using the probability distribution function, it is possible to separate quantitatively the level of impact of different anthropogenic sources on the content and distribution of trace metals in sea-bed deposits.

The trace metals *Cr*, *Ni*, *Cu*, *Pb*, *As*, *Co*, *Cd*, *Hg* of anthropogenic origin in the sea-bed deposits of the NWBS shelf come mainly from non-point (diffuse) sources, both industrial and agricultural.

The results obtained and the method applied in this study may be further used to trace the dynamics of anthropogenic influence on the ecosystems of coastal sea waters.

The method proposed in this work might be also used for precision of the natural background of trace metals in sea-bed deposits and in other components of the marine environment.

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ОСОБЛИВОСТІ ПРОСТОРОВОГО РОЗПОДІЛУ ВАЖКИХ МЕТАЛІВ У ДОННИХ ВІДКЛАДАХ ПІВНІЧНО-ЗАХІДНОГО ШЕЛЬФУ ЧОРНОГО МОРЯ

Резюме

У роботі вивчені особливості розподілу вмісту важких металів (ВМ) у донних відкладах північно-західного шельфу Чорного моря та джерела надходження ВМ в донні відклади. Розділено ступінь впливу різних техногенних джерел на вміст і розподіл ВМ у донних відкладах. Виявлено особливості просторового розподілу ВМ природного і техногенного походження у донних відкладах шельфу.

Ключові слова: донні відклади, важкі метали, поділ джерел (природні та техногенні), густина ймовірностей

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ОСОБЕННОСТИ ПРОСТРАНСТВЕННОГО РАСПРЕДЕЛЕНИЯ ТЯЖЕЛЫХ МЕТАЛЛОВ В ДОННЫХ ОТЛОЖЕНИЯХ СЕВЕРО-ЗАПАДНОГО ШЕЛЬФА ЧЕРНОГО МОРЯ

Резюме

В работе изучены особенности распределения содержания тяжелых металлов (ТМ) в донных отложениях северо-западного шельфа Черного моря и источники поступления ТМ в донные отложения. Разделена степень влияния различных техногенных источников на содержание и распределение ТМ в донных отложениях. Выявлены особенности пространственного распределения ТМ природного и техногенного происхождения в донных отложениях шельфа.

Ключевые слова: донные отложения, тяжелые металлы, разделение источников (природные и техногенные), плотность вероятностей.