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ECOLOGICAL AND GEOCHEMICAL ASSESEMENT OF KUYALNIK ESTUARY

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The long-term investigations of Kuyalnik liman bottom sediments during the period of 2002-2012 years showed that the pollution levels in this estuary by heavy metals (Pb, Cd, Cu, Zn, Cr, V, Mn) and their spatial distribution depend on the location of the local anthropogenic contamination sources and the mechanical composition and types of sediments. The small depth, the limited water exchange and silt structure contribute to the accumulation of heavy metals in bottom sediments of Kuyalnik estuary. This research yields the data on the spatial distribution of heavy metals in the surface (0-20 cm) layer of bottom sediments of Kuyalnik estuary and made it possible to estimate the current level of pollution. All the sediment samples are shown to contain heavy metals (V, Zn, Pb, Cd, Mn, Cu). In particular, the high concentrations of metals that belong to the first class of hazard (Cd, Zn, Pb) are registered. The average concentration for all studied metals except cadmium and zinc do not exceed the geochemical background. The maximum concentration of Pb, Zn, Cd, V exceed the limit values for soil. The level of technogenic pollution was established to be quite equal with the natural clarkes of lithosphere levels.
Keywords: Kuyalnik estuary, sediments, heavy metals, pollution levels, spatial distribution of heavy metals.

Екологічна та геохімічна оцінка Куяльницького лиману. Шихалєєва Г.М., Еннан А.А., Чурсіна О.Д., Шихалєєв І.І., Юрченко Ю.Ю. – Представлені результати багаторічних (2000-2012 р.р.) досліджень рівня забруднення поверхневого шару донних відкладів Куяльницького лиману важкими металами (Pb, Cd, Cu, Zn, Cr, V, Mn). Показано, що просторове розподілення металів залежить як від розташування локальних джерел антропогенного забруднення так і від механічного складу та типів донних відкладів. Встановлено, що рівень техногенного забруднення достатньо близький до натуральних літосферних кларків.
Ключові слова: Куяльницький лиман, донні відклади, важкі метали, рівень забруднення, просторовий розподіл металів.

INTRODUCTION

Relevance of the studies of the heavy metals pollution of Kuyalnik etstuary is important due to the uniqueness and richness of its natural resources and the necessity of involvement and development of recreation and tourism industry of Odessa region.

The most dangerous pollutants that affect all components of aquatic ecosystem are the heavy metals. The period of the self-utilization depends on the type of metals and varies from 13 (Cd) to 5900 (Pb) years [1]. Because of the increasing anthropogenic pressure and global climate changes the complex physical, chemical and biochemical processes occur in the aquatic ecosystem. Thus, the heavy metals migration chains are not studied enough. The accumulation of these metals is not studied deeply, and it is possible that these metals create a threat of the secondary contamination of the aquatic environment. The content and behavior of the heavy metals in the bottom sediments of Kuyalnik estuary currently studied unsufficiently. The reference literature contains only some fragmentary investigations [2-4].

This paper presented the results of the regulary seasonal observations during 2003-2012 years that had been received during the monitoring program of the Kuyalnik estuary natural ecosystem that have been conducted by our institution since 2000.

MATERIALS AND METHODS

According to the regular field, researches covered different seasons (2000-2012), and were carried out in the basin of Kuyalnik estuary, that provided the analyses of the surface sediments heavy metals pollution by the current metals (Pb, Cd, Cu, Zn, Cr, Al, V, Mn). The bottom sediments samples were taken from the the layer of 0-20 cm according to the network of 14 regular sampling monitoring points in the basin of Kuyalnik estuary across the shoreline at a distance of 100-150 m from the water line (Fig. 1).

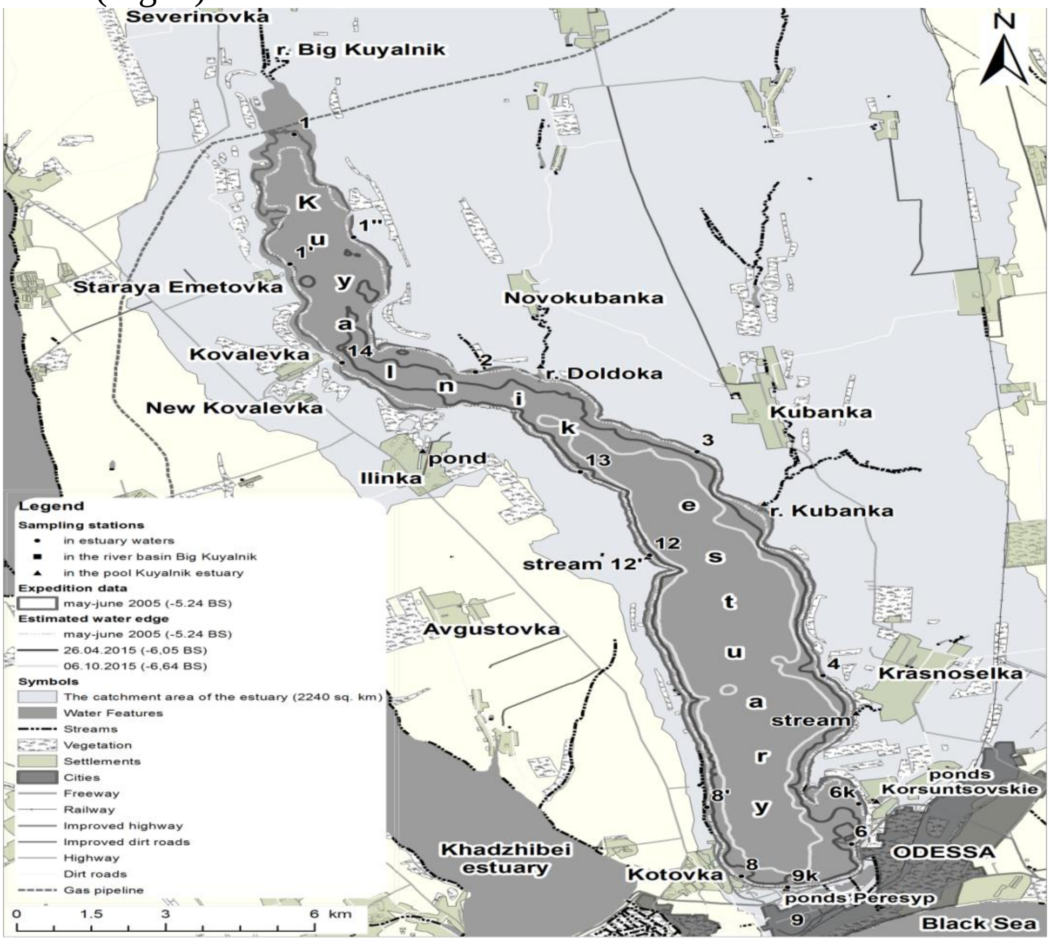

Fig. 1. The scheme of the sampling points

Totally 255 samples had been collected and analyzed. The determination of interchangeable heavy-metal factions had been conducted by atomic absorption spectrometry with electrothermal atomization on the spectrometer "Saturn 3" with the accordance of attachment, named "Graphite-2" according to RD 52.30.556-95 instructions [11]. The samples were dried at the temperature 105 °C till the stable weight. The heavy metals content was calculated in the dry matter.

RESULTS AND THEIR DISCUSSION

The bottom sediments in Kuyalnik estuary generally were represented by gray and black silt. Mechanical composition and a brief description of bottom sediments sampling points presented in table 1.

Table 1

Characteristics of Kuyalnik estuary bottom sediments

The monitoring points number	The type of sediments	Sediments color	Description of monitoring point (Fig.1)
1	2	3	4
1’	Silt	Black	The beam to the north of Old Emetovka village, the western side of Kuyalnik estuary
1”	Silt	Black	The beam opposide Old Emetovka village located on the eastern side of Kuyalnik estuary
2	Silt	Black	The beam nearest to Novokubanka village on the eastern side of Kuyalnik estuary
3 and 3k points	Silty sand with inclusions	Dark gray	Kubanka village, eastern side of Kuyalnik estuary
4	Silty sand with inclusions	Dark gray	Krasnoselka village, eastern side of Kuyalnik estuary

5	Silt Fine sand Small-and medium-grained sand, detrital material	Black Dark gray	The southern part of the dam, left bank
6k	Silty sand	Dark gray	Korsuntsy village, left bank
8'	Clayey silt	Light gray	Right bank of estuary, southern part to the north of Resort
8	Silt Fine sand, Silty sand	Light gray Dark gray	On the territory of balneological resort named after Pirogov, the western side of estuary
9k	Small-and medium-grained sand, detrital material	Gray Dark gray	Southern tip of the estuary, near the confluence of the watercourse system of Peresyp ponds
12	Silty sand	Dark gray	Western side of estuary
13	Silt Silty sand	Dark gray	Western side of estuary
14	Silt	Black	Western side of estuary

Mechanical composition of Kuyalnik estuary bottom sediments surface layer (0-20 cm) in the northern (points 1, 1', and 1") and central parts (points 2, 14, 12, 13, 4, 3, 3-k) were represented mainly by silt factions. In the southern part (points 5, 6-k, 8, 9-k) there was identification of considerable inclusions of sand factions. Generally, the distribution of the bottom sediment followed the rule: from the central axis of the estuary to its peripheral areas, there was consecutive change from finer sediments to sediments of silt and sand direction.

The active reaction of aqueous extracts of sediments during the period of observations varied from slightly acid to slightly alkaline (5,63 – 8,51) with the mean annual – 7,63, redox potential varied from minus 48 to minus 133 mV (mean annual – minus 80,2 mV), humidity varied from 16,5 to 39,7 % (mean annual – 28,9%), organic matter content – from 1.2 to 35.6% (mean annual – 10%). The lower organic matter content was typical for the bottom sediments in the southern part of estuary.

The data about total forms of heavy metals content in the bottom sediments surface layer presented in table 2.

Table 2

The mean values and limits of gross (total) heavy metals content variation in the bottom sediments of Kuyalnik estuary during the observation period of 2000-2012 years

Metal	X (lim)*	σ_x	S_x
Cu	18,6 (1,3-79,5)	7,65	0,41
Pb	15,1(1,3-60,4)	10,89	0,72
Cd	0,85 (0,096 - 3,070)	0,48	0,032
Cr	3,59(0,34-15,76)	2,88	0,192
V	56,6(2,1-236,0)	40,5	2,70
Zn	56,1(2,7-304,8)	41,4	2,76
Mn	7,2(2,1-19,2)	4,63	0,31

* X (lim)*- the average for the period of 2000-2012 years. (limits of variation), σ_x -the standard deviation, S_x – the error of the meanvalue.

The spatial distribution of metals in the water of estuary (Figs. 2, 3) can be characterized as quite heterogeneous. The average and extreme concentrations were shown in Table 1. The maximum concentrations of Zn and V were observed in the bottom sediments of the northern part of estuary, the maximum concentration of Cu - in the northern and central parts, Pb and Cd – in the northern and southern parts of estuary (Fig. 1, 3). As it can be concluded from Figures 2 and 3, the heavy metals in order of decreasing concentrations in bottom sediments of Kuyalnik estuary follow the rules: in the northern part – V> Zn> Cu > Pb> Mn > Cr> Cd, in the central part – Zn> V> Cu > Pb> Mn > Cr> Cd, in southern part – V > Zn> Pb > Cu> Mn > Cr> Cd.

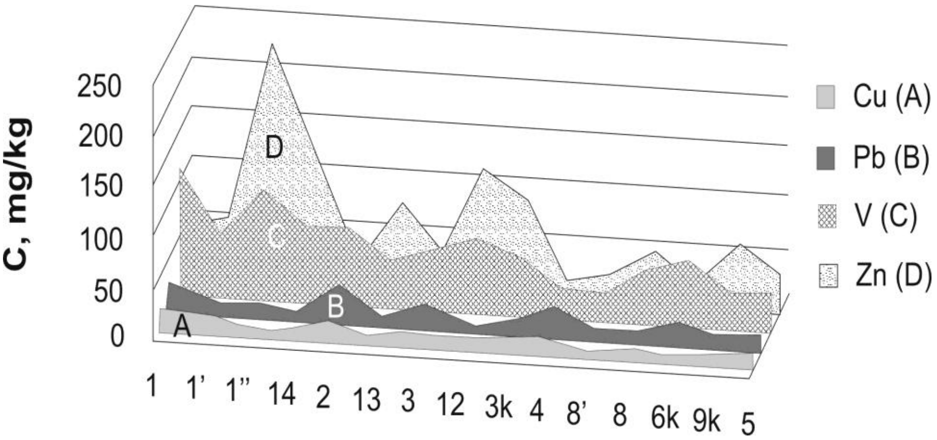

Fig. 2. Distribution of gross forms of Cu, Pb, V, Zn in the sediments of estuary at the observation terriotory (the mean annual data 2000-2012)

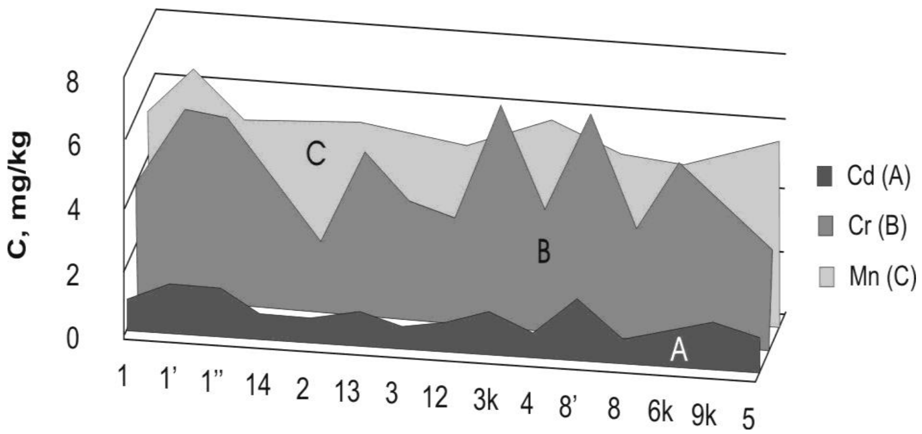

Fig. 3. Distribution of the gross (total) forms of Cd, Cr, Mn in the sediments of the estuary at the observation points (at a mean annual data 2000-2012)

The observed irregularities in the distribution of the investigated heavy metals in the bottom sediments of estuary were determined mainly by the location of the local sources of anthropogenic pollution (sand quarries in the upper reaches of the estuary, farmlands, gas stations and bypass road along the southern tip of the Kuyalnik estuary, the parking of vehicles in recreational areas on the shores of the estuary etc.), the texture and type of bottom sediments (shown in Table 1).

Analysis of the data of the last decade of researches showed that at present time the bottom sediments were polluted by Cu, Pb, V, Zn Cd, Cr, Mn. Even the southern part of the surface layer, which consisted mainly from sand factions and had lower storage capacity enriched by heavy metals.

For the estimation of the bottom sediments quality (including therapeutic muds) most often the sanitary standards for contaminants in soils [5] were used, till the date when the bottom sediments researchers had developed generally accepted own standards. Taking into account this fact, we proposed to conduct the assessment of the level of bottom sediments contamination by metals with the estimation of concentration factor Kc (corresponding to the natural “clarks in litosphere”), the rate of excess of clarks in lithosphere and the hazard ratio Co (corresponding to the rate of excess of sanitary standards for soils).

The results of calculations of the coefficients of concentration and hazard ratio and the value of natural clark and the MAC of the relevant elements of the soils are presented in table 3.

Table 3

Ratio of the average for the study period 2000-2012 concentrations of metals to their natural clark and the MAC

Metal	Xmean. for 2000-2012 mg/kg	Xmean. for 2012 mg/kg	clark mg/kg [6]	MAC for soil, mg/kg [7]	$^*K_k$		$^{**}K_o$	
					2000-2012	2012	2000-2012	2012
Cu	18,6	6,8	47	55	0,39	0,14	0,34	0,12
Pb	15,1	3,7	16	32	0,94	0,23	0,47	0,12
Cd	0,85	0,27	0.13	2	6,54	2,08	0,43	0,14
Cr	3,6	1,4	83	100	0,043	0,017	0,036	0,014
V	56,6	8,9	83	150	0,66	0,11	0,38	0,06
Zn	56,1	82,5	70	100	0,80	1,18	0,56	0,83
Mn	7,2	4,4	1000	1500	0,0072	0,0044	0,0048	0,0029

Calculations showed that the long-term average concentrations of metals (2000-2012) exceeded their clark on Cd. By average for 2012 clark concentrations exceeded the values for Cd and Zn. Hazard ratio, calculated on the average long-term and annual average concentrations for 2000-2012 years for the all studied metals did not exceed 1. According to the maximum concentrations, excess of sanitary standards were detected for substances of the first class of danger (Pb in 12% of cases, Zn 10% of cases, Cd in 7%).

CONCLUSIONS

The small depth, the limited water exchange and silt structure contribute to the accumulation of heavy metals in bottom sediments of Kuyalnik estuary.

This research yields the data on the spatial distribution of heavy metals in the surface (0-20 cm) layer of bottom sediments of Kuyalnik estuary and made it possible to estimate the current level of pollution.

All the sediment samples are shown to contain heavy metals (V, Zn, Pb, Cd, Mn, Cu). In particular, the high concentrations of metals that belong to the first class of hazard (Cd, Zn, Pb) are registered.

The average concentration for all studied metals except cadmium and zinc do not exceed the geochemical background. The maximum concentration of Pb, Zn, Cd, V exceed the limit values for soil. The results of the spatial distribution of metals in the estuary area define territories of high technogenic content of some metals (V, Zn, Pb, Cd).

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Экологическая и геохимическая оценка Куяльницкого лимана. Шихалеева Г.М., Эннан А.А., Чурсина О.Д., Шихалеев И.И., Юрченко Ю.Ю. – Представлены результаты многолетних (2000-2012 гг.) исследований уровня загрязнения поверхностного слоя донных отложений Куяльницкого лимана тяжёлыми металлами (Pb, Cd, Cu, Zn, Cr, V, Mn) . Показано, что пространственное распределение металлов зависит как от расположения локальных источников антропогенного загрязнения, так и механического состава и типов донных отложений. Установлено, что уровень техногенного загрязнения достаточно близок к натуральным литосферным кларкам.

Ключевые слова: Куяльницкий лиман, донные отложения, тяжёлые металлы, уровень загрязнения, пространственное распределение металлов.