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Mercury in the Bottom Sediments of the Ship Channel and River Mouths: the Vistula Lagoon

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ABSTRACT: It is studied the distribution of Hg in bottom sediments of estuaries on the banks of the open water area of the Vistula Lagoon and in the Kaliningrad Sea Canal (KSC) isolated from it. Methods for the determination of Hg: inversive voltammetry and highly sensitive flameless atomic absorption spectrometry. It has been established: from spring to autumn the activation of storms and surge events in the lagoon, intensification of the water flushing regime of the channels ensure a significant Hg decrease in river mouths, but in dynamically weakened KSC conditions - an increase in Hg (from 0.05 to 0.85 mg / kg). In KSC bays, the safe level of Hg (0.3 mg / kg) for the period 2000-2015 was not exceeded (0.008 to 0.216 mg / kg), which indicates a favorable ecological and epidemiological situation. Hg determinations by low-sensitivity methods can be used only in qualitative assessments of the variability in concentrations of any dangerous toxicant. Finding a reliable amount of Hg in river mouths requires the use of highly sensitive methods of analysis.

1 INTRODUCTION

The importance of control over such a dangerous toxicant as Hg in the biosphere is difficult to overestimate. Monitoring of water bodies and their depositing component for pollution levels in bottom sediments in river mouths that flow into internal resource-significant water bodies is particularly relevant . Such an object is the Vistula lagoon of the Baltic Sea. The state network for controlling surface land waters in the Kaliningrad region covers only 13points (18 sections). There has been no hydrochemical monitoring of the water area since 1989 (the State Committee on Hydromet had conducted before; only 15 stations had been controlled in the estuary of the Kaliningrad Bay). In recent decades, coastal pollution assessments of Russian lagoon sector have been fragmented (in duration, measurement intervals and survey areas). They have been carried out with different goals by various organizations (2000-2015: AtlantNIRO, GeoHydroBalt (Kaliningrad), Environmental Analytical Center (Moscow), CER-ENERGO (St. Petersburg), etc.). The results of evaluations are not widely available. Among all the methods for the contaminant identification there are often used not expensive, but low-sensitive ones. The variability of pollutant concentrations in the bottom sediments of the water bodies is poorly studied (Bogdanov 2018 a, 2018 b, Bogdanov & Vorontsov, Morozov 2004, Environmental problems of the Kaliningrad region… 1999, 2002, etc.).

The goal is to assess the causes of the variability of content and reliability of methods for determining Hg in the bottom sediments in the Kaliningrad Sea Canal (*KSC*) and in the river mouths flowing into the Vistula Lagoon (Fig. 1).

Table – Sedimentation conditions, long-term and seasonal variability of Hg in bottom sediments in the river mouths of Prokhladnaya, Graevka and KSC

Objects		Sample selection: Station number	year. months	*Hg*, mg / kg	Methods	Sediment composition	Dynamic conditions of sedimentation (Fig. 2)
Prokhladnaya		2	2000.06 2001.06 2010.05 2010.10	0,016 0,010 15,0 2,1	*AAS* *IVA*	Fines and fine-grained sands	The open water area of the bay: the reentering angle of the breakwater at the village Ushakovo, significant surges
KSC sub-latitude area: settlements	Graeyvka villages	4	2000.06 2010.05 2010.10	0,011 0,023 ***0,05*** ***0,85***	*AAS* *IVA*	Fine-grained sands, admixture of medium and fine-grained particles	Minor surges; dynamically weakened zone of circulations in the bays, steamboat wave, disturbance of bottom
Izhevskoye – Vzmorye	Izhevskoye: downward the mouth of the river Grayevka, ship passage, moorings	7	2000.08 2001.06	0,077 0,136 0,133	*AAS*	Fines and fine-grained sands, admixture of black, cheesy oily-clayey slimes of H_2S odor	sediments by turbulence from screw propellers; predominant transfer of matter, energy and pollutants eastward the mouth of the river Pregolya
	village Vzmorye: along the coast, moorings, ship channel	8	2000.08 2015.11 (6 samples)	0,023 0,096 0,008-0,136 0,015-0,216			
Background [4]			2000.06	*0,023*	The upper river courses of Deyma and Pregolya beyond large industrial facilities and residential areas		
Target safe level of concentration				*0,3*	Recommendations and indicative estimates of environmental and hygienic hazard to humans and ecosystems: Dutch lists of pollutants, bottom sediments [1, 8]		
Minimally hazardous concentration with toxicological risks (urgent remediation)				*10*			

AAS – atomic absorption spectrometry using the "cold steam" technique, modified scheme of the Zeeman effect and spectrometers "IMGRE-900" (2000-2001), "SA-915 +" (2015), detection limit (DL) Hg = 0.001 mg / kg; IVA –inversion voltammetry, DL = 0.01 mg / kg

2 OBJECTS AND METHODS

Bottom sediments: layer 0-0.1 m; sands, admixtures of gravel, silt, pelite; dark-colored sludge with H_2S odor; the mouths of the main rivers (Mamonovka, Prokhladnaya, Pregolya, Grayevka, Nelma, Primorskaya); *KSC* sections (stations No. 7, 8); survey time - ice-free periods of 2000, 2001, 2010 and 2015 (Fig. 1, table).

The definitions of Hg are made by accredited laboratories using metrically certified, but different in accuracy methods: highly sensitive non-flame *AAS* (2000-2001 and 2015), IVA (2010). The approximate diagnosis of the ecological and hygienic danger of Hg accumulation is compared with the background content and threshold levels of hazardous concentrations (table) (Bessonov & Yanin 2005, Bogdanov & Vorontsov, Morozov 2004, SP 11-102-97 Engineering … 1997).

3 DISCUSSION OF RESULTS

3.1 *Major sources of mercury and migration factors*

Sources of Hg: solid, liquid, gaseous wastes and spills of Hg-containing substances at industrial, transport, agricultural, residential facilities; emissions from fuel combustion plants; transboundary pollutants transfers and others. Secondary contamination is associated with the resuspension of contaminated bottom sediments by floating craft (table) (Bessonov & Yanin 2005, Bogdanov 2018 a, 2018 b, Bogdanov & Vorontsov, Morozov 2004, Environmental problems… 1999, 2002, Volokh & Yanin 2005).

Conditions and factors of accumulation-scattering Hg. The main ones, besides the existing Hg sources and their functioning characteristics, include hydrometeorological and lithodynamic conditions: wind conditions, surge events, coastal dynamics of water and sediment, size and sorption capacity of bottom sediments and suspensions; seasonal fluctuations in the river water content, etc. (Fig. 2, table).

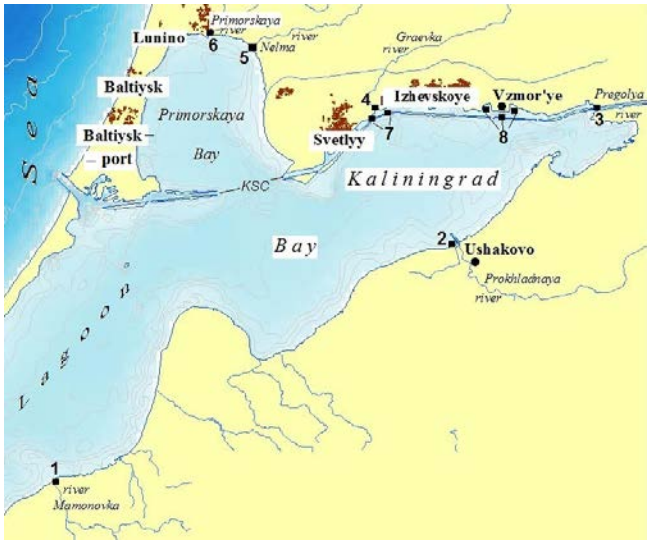

Figure 1. Scheme for sampling sediments: estuaries and KSC (Kaliningrad Sea Canal)

The water content of the rivers increases and the coastal dynamics intensifies in the autumn-winter period. Self-cleaning conditions for studied objects becomes favorable. The maximum marks of water level in the bay fall at September-February (> 80% of occurrence; up to +180 cm 3-4.12. 1999 with W and SW winds and –136 cm 20.10. 1989, E and *NE* winds) [4, 5, 6]. The energy potential of hydro- and litho-dynamic processes off the banks and in the mouths of rivers in the open waters of the lagoon is higher by several orders than in the *KSC*. In its sub latitudinal section dynamically stagnant zones of weak water circulations, sediment and accumulation of pollutants are characteristic (the mouth of the Grayevka river, the bay near the villages of Izhevskoye, Vzmorye and others, Fig. 2).

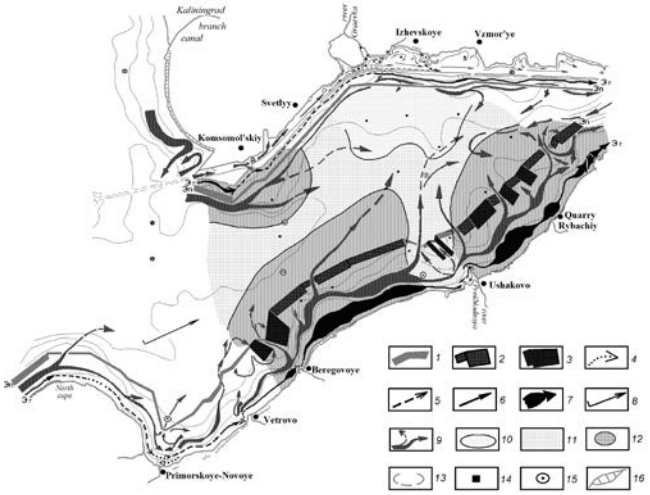

Figure 2. Hydro- and lithodynamics of the estuary of the Kaliningrad Bay [4]. Wave energy fluxes, T / s: ***1, 2*** and ***3*** are transverse to the bay, En = 1-500, 501-1000 and 1001-1496, respectively; ***4, 5, 6*** and ***7*** –paralic zone , Eτ = 0.01-1.1; 1.2-10; 11-50 and 51-104 respectively; ***8*** – the resultant wind value direction of 242° and of 62% frequency during sampling period has corresponded to the average long-term parameters (weather station "Kaliningrad"); ***9*** – the predominant transfer of water, suspensions and pollutants, ***10, 11*** and ***12*** – suspended substances, mg / l: 12-50, 51-100 and 101-231, respectively; ***13*** – bottom features, ***14-15*** – sampling points, ***16*** – ledges of bank erosion.

3.2 *Seasonal dynamics of mercury concentrations in sediments*

These are the seasonal features of coastal dynamics of the receiving reservoir, fluctuations in the water content and washing mode of the watercourses which control the variability of Hg concentrations in the bottom sediments.

During autumn-winter activity of surge events and wind-cut occurrence in the estuaries of rivers that flow into the open water area of the lagoon, alluvium is cleared of pollutants. In our situation - from Hg. *Seasonal self-cleaning*, period from May till October 2010, estuaries, mg / kg: Primorskaya from 53 to 0.53 (100 times), Pregolya from 62 to 5.7 (11 times), Prokhladnaya 15 to 2, 1 (7 times), Nelma from 10.1 to 1.6 (6 times) Mamonovka from 8.1 to 3.9 (2 times). In the estuary of the river Grayevka, open to surge from *S* and *SW* winds, while KSC water area isolated from the sea gulf and dynamically weakened, the amount of Hg from spring to autumn 2010 *increased* ~ 17fold (from 0.05 to 0.85 mg / kg). Episodic increases in Hg emissions are also not excluded, according to the differences in the values of its concentrations in the mouth of the river Grayevka in 2000-2001 and in 2010.

In the alluvium of the river estuaries background and signal *levels of hazardous accumulation* with excess concentrations are recorded everywhere, which is probably due to significant differences in the accuracy and correctness of metal definitions. So, in June 2000 (*AAS* method) and May 2010 (SVM method) at the mouth of the r. Prokhladnaya concentrations differed 1000 times (0.016 and 15 mg / kg, respectively). Obviously, the reason for such variability lies not in the «hurricane» increase in Hg emissions, but in the accuracy of measurement methods (table).

3.3 *Dangerous levels of concentration*

In the bottom sediments of the bays of the sub latitudinal part of the *KSC*, the excess of *hazardous levels of Hg concentration* was not recorded either in 2000–2001 or in 2015 (conditions for an active mode of navigation, tendencies of pollutant accumulation). Moreover, Hg content was comparable among themselves for different years of control that shows the adequacy of the determination methods and the absence of significant long-term changes in the processes of *entry – concentration – scattering* of the metal as well as a fairly favorable ecological and epidemiological situation on Hg.

4 CONCLUSIONS

Regarding the variability of Hg content in the alluvium of the river estuaries in the Vistula Lagoon basin, one can identify the main reasons: openness / isolation of the receiving water area; seasonality of hydrometeorological, wave-energy and surge-surging phenomena; water content and washing mode of river courses. Autumn-winter activation of these natural factors causes self-purification of alluvium in the mouths of rivers on the open shores of Lagoon. The dynamically weakened conditions in the areas isolated from it, with a significant accumulation of

sources of pollutants and fine-grained bottom sediments (<0.1 mm), contribute to Hg accumulation. However, its amount in the sediments of the *KSC* for the period 2000-2015 did not change significantly and was below the dangerous environmental and hygienic levels of Hg concentration.

Hg determinations by low-sensitivity methods can be used only in qualitative assessments of the variability of concentrations of a hazardous toxin.

The final elucidation of the causes of this kind of variability and reliability of Hg amount in bottom sediments requires additional studies of the functioning the sources and conditions of Hg accumulation with the use of highly sensitive methods of analysis.

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