Distribution of Mercury in Water and Bottom Sediments of the Estuary Area of the Red River (Vietnam)

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Abstract. The paper determined the content of mercury in water-bottom sediments and the feature of its spatial distribution in the estuary area of the Red River (Vietnam). The studies were conducted at 30 stations during the main hydrological seasons of 2014-2016 (during the flood and low water). Samples of bottom sediments were collected on the surface layer with a depth 0…10 cm. The spatial distribution of mercury was carried out using the Kriging interpolation method in ArcGIS 10.2.2. The concentration of mercury in the water of the Red River varied from 0.05 to 0.08 µg/l in low water and 0.07…0.11 µg/l during the flood. Towards the sea, the concentration of dissolved mercury decreased. The spatial distribution of the suspended form and phases of bottom sediments of mercury in the estuary area of the Red River was characterized by an increase in the concentration in the Delta watercourses towards the sea, the presence of a maximum in the marginal filter and a general decreasing gradient at the coast. The Hg content in the suspended form varied from 0.008 to 0.7 µg/l, and in bottom sediments within 0.1…1.25 mg/(kg dry weight). In river waters, the main forms of mercury were dissolved and suspended, and in the marginal filter – in bottom sediments. Bottom sediments of the estuary area of the Red River were characterized by a higher content of Hg compared to unpolluted soils in temperate and northern latitudes, as well as bottom sediments of water bodies of another region of Vietnam.

1. Introduction

Mercury is one of the most toxic metals, which is frequently encountered in the environment. In the aquatic environment, mercury exists in dissolved, suspended forms in water and in bottom sediments. The main dissolved forms of mercury are elemental mercury (Hg^0), complex compounds Hg^{2+} with different inorganic and organic ligands, and organic forms of the metal, mainly methyl and dimethyl mercury [1, 2]. Therefore, the study of mercury pollution should consider the content and distribution of mercury and its compounds in such forms.

The content of mercury in the aquatic environment is determined by a combination of factors, including the route of entrance and the distance from natural and anthropogenic sources. The estuary area of the Red River is an important industrial center in northern Vietnam. The main anthropogenic sources of mercury in this area include fuel combustion, the production of primary metals, especially gold, light sources with mercury content, incineration and waste disposal [3, 4, 5]. Currently, mercury pollution is a serious problem in the estuary area of the Red River. Thus, the study of the content and distribution of different forms of mercury is an important issue and requires special attention.

The purpose of the work is to determine the levels of mercury in water - bottom sediments and its spatial distribution in the estuary area of the Red River (Vietnam).

2. Materials and methods

Studies were conducted at 30 stations on the main watercourses (the Red River and the branches Dai, Ba Lat, Tra Ly, Ninh Co) and the coast (Figure 1) in 2014 - 2016.

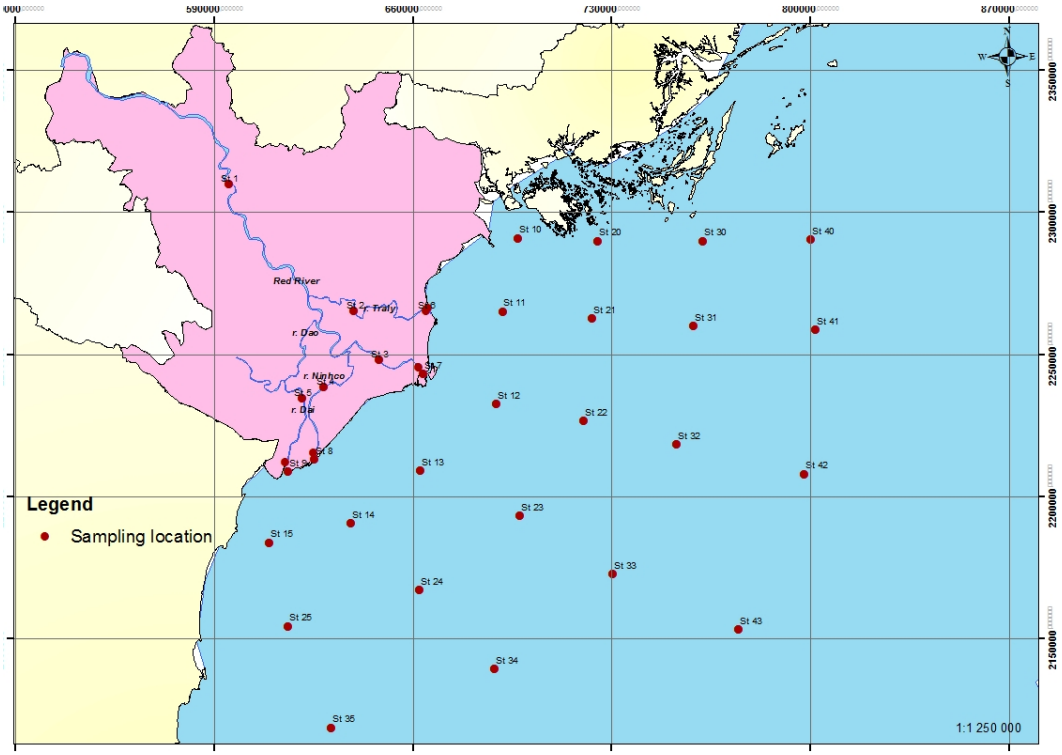


Figure 1. Index map of estuary area of the Red River, – Sampling location.

Water was filtered through a membrane filter with a pore diameter of 0.45 microns. For chemical analysis, the filtrate was fixed with nitric acid. The filter was dried and the mercury content on the suspended matter was determined, with subsequent conversion to the volume of filtered water.

Bottom sediments (BS) were collected by a bottom grab with a depth of 0-10 cm. Each sample was divided into two parts, one was dried at room temperature, after which the Hg content was determined, the second was dried at t +105 °C to determine the hygroscopic humidity with subsequent conversion of the metal concentration on an absolutely dry weight [6].

The determination of the mass concentration of total mercury in water samples was measured by the method of atomic absorption of cold steam. The mercury content in the bottom sediments was determined by the method of pyrolysis without preliminary mineralization on the instrument RA-915+ with the analytical prefix RP-91S (manufacturer - NPF Lumex, St. Petersburg, Russia [7].

The results were statistically processed using the STATGRAPHICS CENTURION software package and presented as mean values and their errors ($x \pm mx$). The significance of differences was assessed using the analysis of variance (ANOVA, LSD–test) at the significance level $p \leq 0.05$.

The spatial distribution of mercury was performed by the Kriging method in the ArcGIS 10.2.2 interpolation toolset, resulting in the construction of maps.

3. Results and discussion

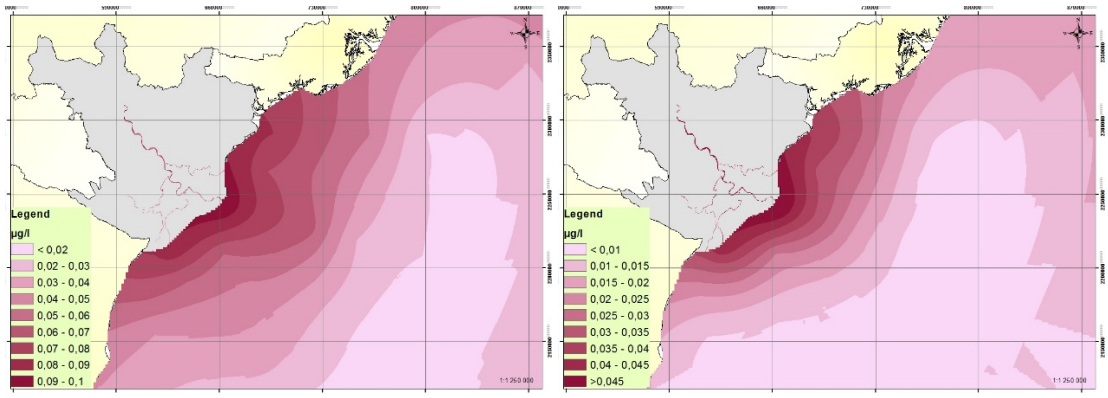
Concentrations of mercury in the dissolved, suspended forms and in bottom sediments in the main watercourses and seashore in the estuary area of the Red River were presented in table 1

Table 1. Content of different forms of mercury in the estuary area of the Red River (a, b, c - the differences were significant at p <0.05)

Stations	Mercury concentration		
	Dissolved form (µg / l)	Suspended form (µg / l)	BS (µg / l)
	The Red River		
St 1	0.08±0.01^{a}	0.07±0.01^{a}	0.1±0.01^{a}
St 3	0.06±0.01^{a}	0.05±0.1^{b}	0.82±0.02^{a}
St 7	0.05±0.01^{ab}	0.6±0.1^{bc}	1.25±0.017^{ab}
	Branches		
Tra Ly	0.035±0.01^{a}	0.2±0.11^{a}	0.16±0.01^{a}
Ninh Co	0.05±0.01^{a}	0.26±0.2^{a}	0.54±0.011^{a}
Dai	0.02±0.01^{a}	0.38±0.1^{a}	0.78±0.01^{a}
	Seashore		
St 12	0.075±0.01^{a}	0.7±0.2^{a}	1.3±0.7^{a}
St 22	0.018±0.01^{a}	0.42±0.1^{a}	0.8±0.1^{a}
St 32	0.008±0.01^{a}	0.25±0.01^{a}	0.7±0.1^{a}
St 42	0.007±0.01^{a}	0.1±0.01^{a}	0.5±0.01^{a}

The dissolved form of mercury

The spatial distribution of dissolved mercury in the dissolved form were presented in Fig. 2.



A B

Figure 2. The spatial distribution of dissolved mercury in water in the mouth area of the Red River for 2014 - 2016: A. during the flood period; B. in low water.

The content of total dissolved mercury in the surface layer of the Red river was not uniform and varied from 0.05 to 0.08 µg/l in the low water and 0.07 – 0.11 µg/l during the flood. The highest concentrations of dissolved forms of Hg were observed at the top of the Delta, where chemical plants and industrial centers were concentrated. The minimum concentration detected at station 7. The mercury content in the surface water of the Tra ly, Ninh Co and Dai Branches was lower than in the water of the Red River and averaged 0.035 µg/l.

At the mouth of the Red River (station 12), the mercury content increased by 1.5 times compared with station 7 and averaged 0.75 µg/l. In the adjacent part of the sea area of the Bac Bo bay towards the sea, the concentration of dissolved mercury decreased.

Unpolluted freshwaters of northern and temperate latitudes, as a rule, contain 0.005 – 0.015 µg/l of total Hg [8]. In the colored waters of lakes and rivers, rich in humic substances, it can reach up to 0.02

µg/l Hg [9].

Data on the concentration of Hg in the waters of a tropical region differed significantly from each other. In the water of South American rivers, which were not subject to local mercury exposure, the metal content in water ranged from 0.003 to 0.01 µg/l [10]. Water of the Bung River (Hue Province, Central Vietnam) contained it from 0.001 to 0.021 µg/l [7]. In the water bodies of South Vietnam, average concentrations in freshwater were observed at 0.013 – 0.04 µg/l [7].

The data obtained reflect the heterogeneity of mercury content in the surface waters of the estuary area of the Red River. In different parts of the Red River metal concentration varied 3 - 4 times, while the levels of its content in the branches. The concentration of mercury in the water of the Red River varied from 0.05 to 0.11 µg/l. These values were slightly higher compared to the values indicated for non-polluted fresh waters of temperate and northern latitudes, as well as non-polluted fresh water bodies of South America, Central and South Vietnam.

In water bodies, the main dissolved metal forms were elemental mercury (Hg^0) and complex Hg^{2+} compounds with different inorganic and organic ligands and organic forms. It was shown that surface waters can be supersaturated with Hg^0 in comparison with the atmosphere and because of its high volatility (elemental mercury evaporates quickly) [2, 11, 12]. The high surface water temperature in the tropics can increase the speed of this process, contributing to reduce the concentration of mercury in the surface layer of standing bodies of water and shallow branches

The suspended form of mercury

In the most of the selected samples of the Red River water, the content of dissolved mercury was several times higher than that in suspended form. Towards the sea, the concentration of suspended mercury in water flow increased and was reached in the estuaries (0.6…0.7 µg/l). High concentrations were also observed up to a distance of 20…30 km (Fig. 3).

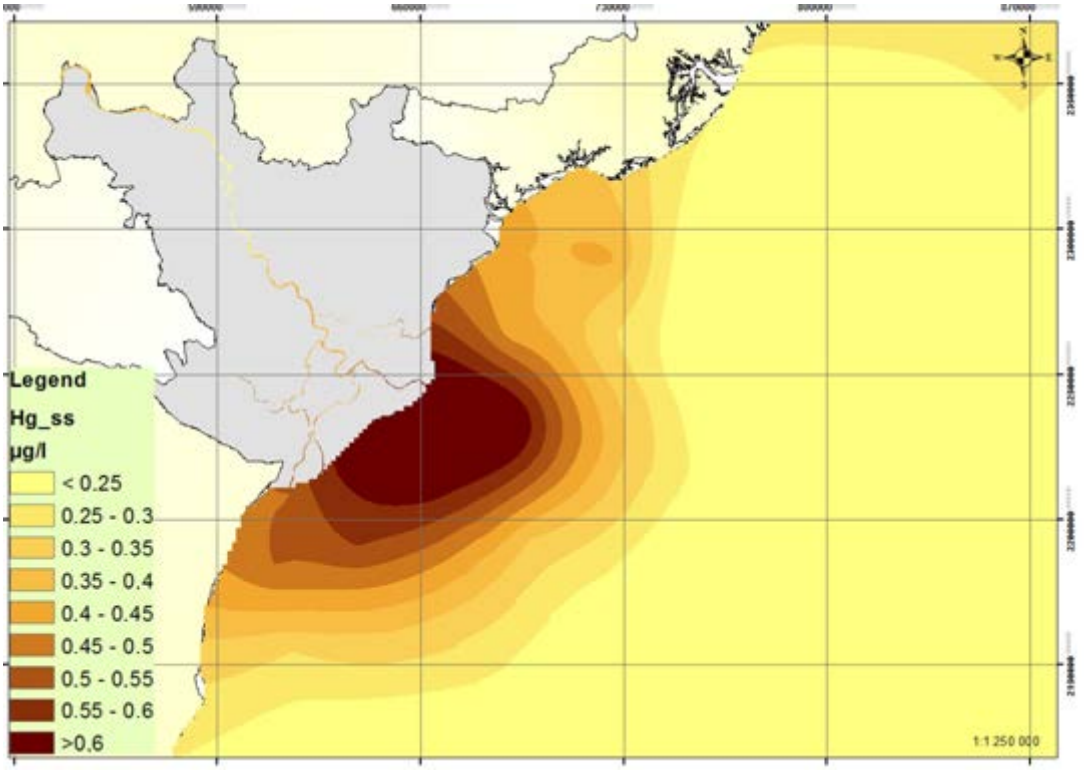


Figure 3. Spatial distribution of mercury suspended form in the estuary area of the Red River for 2014 - 2016

When mixing sea and river waters, migration forms of chemical elements are transformed and the river/sea geochemical barrier is formed. Such a narrow belt (from hundreds of km for large rivers to hundreds of meters for shallow ones), where the mixing of river and sea waters occurs is called a marginal filter [13].

The marginal filter is characterized by flocculation of inorganic and organic dissolved substances with concomitant capture of dissolved forms of metals [14, 15], which can lead to an increase in the proportion of mercury carried on the suspended substance.

In the seaside, concentrations of suspended mercury were reduced to 0.1 µg/l (at station 42). The loss of suspended forms of metal in the seashore was proportional to the loss of the suspended substance itself, and the distribution followed the pattern: as the distance from the mouth decreases, both the total concentration of suspended matter and the proportion of terrigenous particles in its composition [16]. The content of suspended forms of metal was reduced due to the self-purification of the water system from the river material and the transition to marine conditions.

Mercury in bottom sediments

The Hg content in BS of the Red River ranged from 0.1 – 1.25 mg/(kg dry weight). In the upper flow, it varied in a narrow range and has a minimum value (0.09 – 0.19 mg/(kg dry weight)). In the middle flow, it was observed in an average of 0.7 – 0.8 mg/kg due to the intensive flow of discharges from sources. The maximum concentrations of Hg in soils (1.25 mg/kg) was confined in the mouth of the river (station 7) (Fig.4).

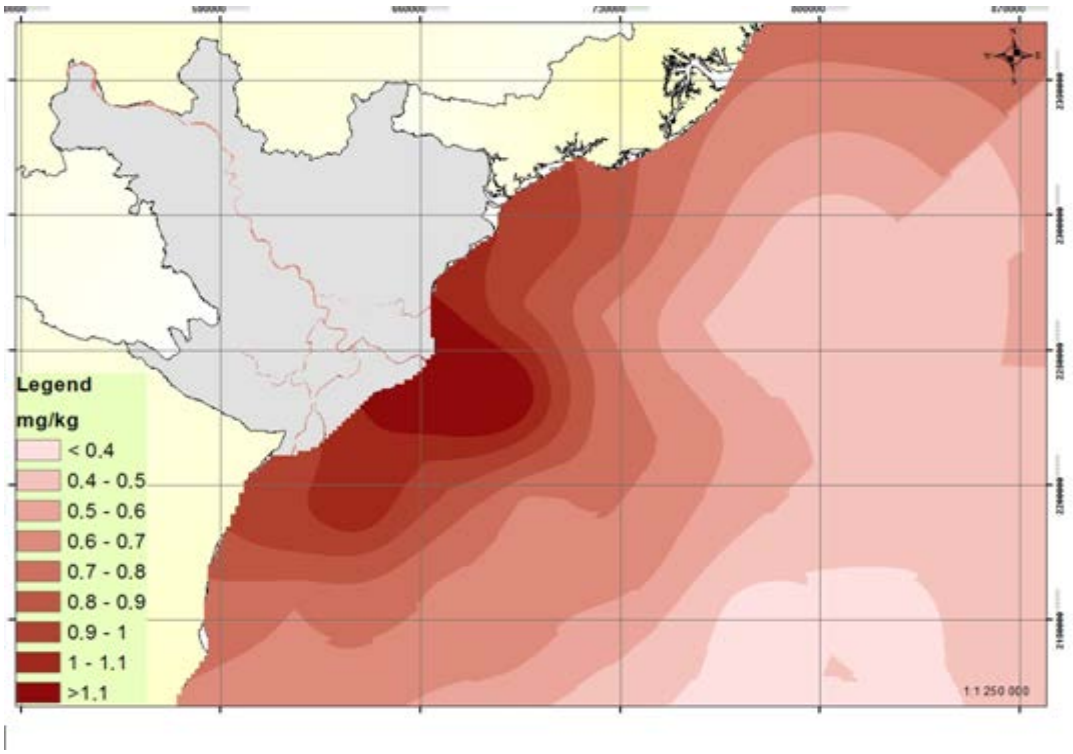


Figure 4. Spatial distribution of mercury in bottom sediments in the estuary area of the Red River for 2014 – 2016.

Low values of the indicator were also revealed for the BS of Tra Ly branch – 0.16 mg/kg, the metal content in the soils of the Ninh Co an Dai branches was on average 0.6 – 0.7 mg/(kg dry weight). In the seashore, peaks of elevated Hg content in bottom sediments were obtained at the mouth of the main branches (station 12), and then decreased to the background value.

The data on background concentrations of Hg in soils was ambiguous. For the northern hemisphere,

this value was determined in the range of 0.01 – 0.07 mg/(kg dry weight) [17, 18]. At the same time, in a number of works indicated the concentration range of 0.02 – 0.4 mg/kg of total Hg for non-polluted BS reservoirs [19, 20]. It was noted that the territory of Amazonia, which was not subject to anthropogenic impact, differed from the regions of the northern hemisphere by the background content of this element; valued from 0.01–0.03 mg/kg were typical for BS freshwater bodies [21].

The data on Hg concentrations in the soils of inland water bodies in South-East Asia were sparse. The Hg concentration in the BS of Dai branch (Ho Chi Minh city, South Vietnam) was 0.007 – 0.014 [7], in the Bung river (Hue province, Central Vietnam) – 0.067 – 0.11 mg/(kg dry weight). The Hg content in the deposits of the Chao Praya river (Thailand) ranged from 0.05 – 0.4 and 0.3 - 5 mg/(kg dry weight) in the dry and wet seasons, respectively [22]. The Hg content in marine sediments was more heterogeneous: in the Nha Trang bay (Khanh Hoa province, South Vietnam) to 0.05 [23, 24], Semarang (Indonesia) – 0.024 – 0.046, Honda bay (Philippines)–0.001-2.4, Thailand bay – 0.07-3.2 mg/(kg dry weight) [25, 26].

The metal concentration in the soils of the estuary area of the Red River ranged from 0.1 – 1.3 mg/(kg dry weight). It can be noted that the bottom sediments in the estuary area of the Red River are characterized by higher concentrations of the element than the northern latitudes of Europe and North America, and also of another region of Vietnam.

In river waters, the main forms of mercury existence are dissolved and suspended. On the river-sea barrier, a radical change in the structure of the metal flow occurs: the main part of the suspended form precipitates in the marginal filter [13]. In the mouths of water flows, mercury is actively sorbed on parts of the suspended matter, especially iron and manganese hydroxides [27, 28]. This phenomenon is accompanied by an increase in the size of the suspended form and the accumulation of mercury in the bottom sediments. In addition, biological processes, such as bioassimilation and bioaccumulation, are also of great importance in the marginal filter. Due to the high biological productivity, such processes of metal deposition by hydrobionts in the mouth area are higher than in other areas of the sea.

4. Conclusions

Thus, the highest concentrations of dissolved forms of Hg were observed at the top of the delta (0.08 μg/l in low water and 0.11 μg/l in high water). Towards the sea, the concentration of dissolved mercury decreased.

The spatial distribution of the suspended form and phases of the bottom sediments in the estuary area of the Red River was characterized by an increase in concentration in the delta water flow towards the sea, the presence of a maximum in the mouths of the sleeves and a general decreasing gradient at the seashore. The bottom sediments at a distance of 20 - 30 km from the coast, being on a marginal filter, marked local barriers within the mouth area. These local barriers were subject to intensive deposition and accumulation of mercury in bottom sediments as a result of successive changes in hydrodynamic and hydrochemical conditions in the estuary area of the Red River.

The bottom sediments of water bodies of the studied region were characterized by a higher Hg content compared to unpolluted soils in the temperate and northern latitudes, as well as bottom sediments of water bodies of another region of Vietnam.

The result of spatial analysis of mercury distribution is the basis for environmental assessment of the risk of heavy metal pollution in the ecosystem, and can also be used in the development of environmental measures and background monitoring systems in the reserve in the estuary area of the Red River (Vietnam).

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