Geochemical processes of mercury transformation in the river-sea system

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Abstract. In this paper, the average concentrations of mercury in river water and suspension in seawater were presented. The authors gave the spatial distribution of mercury in the dissolved and suspended forms and in the bottom sediments. The studies were carried out at 30 stations twice a year (in the period of high water and low water) in the period 2014 – 2016. Samples of the bottom sediments were collected in the surface layer. The spatial distribution of mercury was performed by Kriging interpolation in ArcGIS 10.2.2. It was shown that the river flow is dominated by dissolved forms of mercury at the top and suspended forms in the mouths of watercourses, while the sea is dominated by dissolved forms. The geochemical transformation processes of the river sedimentary substance (dissolved and suspended forms of mercury) in the mixing zone of the river and sea waters (in the area of the so-called marginal ocean filter) have been studied in detail. It has been shown that, the marginal filter is characterized by flocculation of inorganic and organic dissolved substances with concomitant capture of dissolved forms of metals, which can lead to an increase in the proportion of mercury carried on the suspended substance. 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.

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 (Hg0), complex compounds Hg2+ 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 entry route and the distance from natural and anthropogenic sources. The mouth 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 considered as a serious problem in the estuary area of the Red River. Thus, the study of the content and distribution of various forms of mercury and the processes of their transformation is an important issue and requires special attention.

Objective: to determine the average mercury content in river and sea waters, its spatial distribution, as well as the main geochemical relationships between fresh and seawaters in the river-sea transition zone in the estuary area of the Red River in Vietnam.
2. Materials and research methods
The Red River is the largest river in the north of Vietnam. It has 2 main tributaries: the right - the Da River and the left – the Lo river [3]. For the population, the Red River performs important functions. It is an object of recreation, a source of water for agriculture, industry and a receiver for wastewater. The object of the study is the river and seawater of the estuary area of the Red River. The top of the estuary area of the Red River is located 210 km from the sea, slightly below the mouth of the tributaries. Below this peak begins the main branch of the Delta, which has the same name. From the main branch of the delta to the left and to the right leaves a number of branches (branches Dai, Ba Lat, Tra Ly, Ninh Co) (figure 1)

The mouth area of the Red River belongs to the estuary-Delta type [4], and is divided into extensive multi-branches river delta, small estuaries along the lower portions of some branches and open deep tidal wellhead coast. Wellhead coast of the Red River is the coastal area of the Bac Bo bay, East sea.

The studies were conducted at 30 stations on the main delta watercourses (the Red River and the Dai, Ba Lat, Tra Ly, and Ninh Co branches) and on the coast (figure 1).

![Figure 1. Index map of estuary area of the Red River, – Sampling location.](image)

Sampling of water was carried out in low-flow periods and high water periods of 2014 – 2016 years. Water sampling was carried out according to GOST R 51592-2000 [6] and DO - GOST 17.1.5.01-80 [7].

The water was filtered through a membrane filter with a pore diameter of 0.45 µm. The filter was dried and the mercury content of the suspended substances was determined, then converted to the volume of filtered water. Each sample was dried for 11 hours at a temperature of 110 °C, after which the Hg content was determined [8].

The mercury content in each water sample was determined in the biochemistry laboratory of the Department of environmental engineering of Vietnam Maritime University on the mercury analyzer RA-915+ with the prefix PIRO by atomic absorption method of cold steam with a measurement range of 0.001–5 mg/kg [7].

The calculation of the coefficients of adsorption heavy metals (HM) suspended substances was carried out according to the formulas [3]:

\[
\text{Adsorption coefficient of HM: } \kappa_i = \frac{A_i}{R_i} \cdot 100
\]

where \(A_i\) – the amount of suspended heavy metal i in water (tons); \(R_i\) - the total flow of heavy metals (tons).

Statistical analysis. Statistical processing of the results was performed using the program R – 3.5.1...
for Windows. The results were presented in the form of average values and their errors (x±mx). The significance of the differences was assessed by the analysis of variance (ANOVA) at the significance level p≤0.05.

Spatial interpolation. The spatial distribution of mercury was carried out by Kriging interpolation in ArcGIS 10.2.2, which uses a “variogram” to express spatial variation, and minimizes the error of predicted values estimated by the spatial distribution [9]. In the context of geostatistics, kriging is a generalized linear regression method used with a variogram model to interpolate spatial data. In this study, the spatial data are measured concentrations of dissolved and suspended mercury.

3. Results and discussion

Average mercury content in river flow. Mercury, like other chemical elements in river waters, is present in truly dissolved, colloidal and suspended state. In this paper, two main forms of mercury are considered: dissolved and suspended.

Figure 2 shows the spatial distribution of the content of dissolved forms of mercury in the Red River delta.

Figure 2. Spatial distribution of dissolved forms of mercury by seasons in the Red River Delta 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.

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].

Unlike the distribution of dissolved forms, the concentration distribution of the suspended form of mercury in the water of the red river delta was characterized by the presence of a maximum in the mouths of the branches (in figure 3).
Figure 3. The spatial distribution of the suspended form of mercury in the Red River Delta for 2014-2016.

Maximum concentrations of the suspended form of mercury (0.6 – 0.7 mg/kg) were observed in the mouth of the main channel of the river. This may be due to coagulation and flocculation of inorganic and organic solutes with concomitant capture of dissolved forms of metals [10].

It was found that in almost all main watercourse there was a decrease in suspended mercury content relative to its content in the top of the delta.

The ratio of dissolved and suspended forms of mercury in the river flow

The ratio between the suspended and dissolved forms of elements in the river flow expresses, according to N.M. Strakhov [1960], the relative mobility of such elements in modern physicochemical conditions.

To study the characteristics of the mercury distribution processes in the water column, it is necessary to determine the coefficients of their adsorption by suspended solids. The result of the calculation of this coefficient for mercury and other heavy metals is shown in table 1.

Table 1. Coefficients of the adsorption of heavy metals by suspended substance in the Red river and its tributaries for 2014 – 2016.

| Heavy metal | Watercourse          | Total |
|-------------|----------------------|-------|
|             | Duong branch         | Dai branch | Tra Ly branch | Ninh Co branch | Ba Lat branch |     |
| Cu          | 0.03                 | 0.03    | 0.01          | 0.05           | 0.03          | 0.03 |
| Pb          | 0.09                 | 0.10    | 0.09          | 0.10           | 0.09          | 0.09 |
| Zn          | 0.04                 | 0.04    | 0.05          | 0.05           | 0.04          | 0.04 |
| Hg          | 0.25                 | 0.15    | 0.18          | 0.22           | 0.23          | 0.20 |
| Cd          | 0.25                 | 0.28    | 0.32          | 0.23           | 0.30          | 0.27 |
| As          | 0.20                 | 0.21    | 0.15          | 0.15           | 0.19          | 0.20 |
| Cr          | 0.35                 | 0.31    | 0.25          | 0.35           | 0.26          | 0.32 |
| Fe          | 0.56                 | 0.68    | 0.62          | 0.65           | 0.72          | 0.64 |

The HM accumulation took place more intensively in the mouth of the Red river (Ba Lat branch). The highest total adsorption coefficients are for iron (0.64%), chromium (0.32%), cadmium (0.27%), mercury and copper (0.2%).

According to the results obtained in the table, it can be noted that in the branches of Tra Ly, Ninh Co and Ba Lat due to low flow rates during high water and low water, the total adsorption coefficients of
HM were approximately 2 – 2.5 times higher than in the Duong and Dai branches.

Average mercury content in seawater

The spatial distribution of dissolved mercury at the mouth of the Red River is shown in figure 4.

![Figure 4](image)

**Figure 4.** 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.

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.

In water bodies, the main dissolved metal forms were elemental mercury (Hg0) and complex Hg2+ compounds with different inorganic and organic ligands and organic forms. It was shown that surface waters can be supersaturated with Hg0 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.

Towards the sea, the concentration of suspended mercury in watercourses increased and was reached in the estuaries (0.6 - 0.7 µg / l). High concentrations were observed up to a distance of 20–30 km (figure 5).

![Figure 5](image)

**Figure 5.** Spatial distribution of mercury suspended form in the estuary area of the Red River for 2014 – 2016.
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. 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.

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 open seawaters, the prevalence of dissolved forms of mercury over suspended ones is observed, which directly indicates a high geochemical mobility of such a metal in the sea.

Comparison of mercury content in river flow and seawater
It is clearly seen that in river waters the main forms of mercury existence are dissolved and suspended. On the river-sea barrier there is a radical change in the structure of metal flow: the main part of the suspended form precipitates in the marginal filter [13]. At the mouths of watercourses mercury adsorbed on the active parts of the suspended substances, particularly hydroxides of iron and manganese. 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 bio-assimilation 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 estuary area is higher than in other areas of the sea of Vietnam.

4. Conclusion
It was found that the maximum content of dissolved mercury was observed at the apex of the delta (0.08 µg/l in low water and 0.11 µg/l in high water). Towards the sea, its concentrations decreased.

The peculiarity of the mercury distribution in suspended forms in the estuary area of the Red River was an increase in their concentration in the delta streams towards the sea, a maximum in the estuaries of the Red River and a general decreasing gradient at the seashore.

In river water bodies of the mouth area of the Red River, the main forms of mercury existence were dissolved and suspended. In the marginal filter, the main part of the suspended form of mercury fell into the DO. In open sea waters, the prevalence of dissolved forms of mercury over suspended ones was observed, which directly indicated a high geochemical mobility of such a metal in the sea.

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