Mathematical modelling for distribution of heavy metals in estuary area of Red River (Vietnam)

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Abstract. In this paper, the authors studied the features of spatial distribution of some heavy metals (Pb, Hg, As) in the system “suspended substance - bottom sediments” in the mouth area of the Red River (Vietnam). A mathematical modelling for diffusion processes of heavy metals in a suspended form, in bottom sediments and the spatial analysis for the results of these models were proposed and implemented. The studies were carried out during main hydrological seasons of 2014 - 2016 (during the flood and inter-natal periods). The propagation of heavy metals was modeled by solving the equation of turbulent diffusion. A spatial analysis of the content of heavy metals in the suspended form and in the bottom sediments was implemented by using the interpolation model in ArcGIS 10.2.2. The distribution of Pb, Hg, As concentration of the suspended form and bottom sediment phases in the estuary area of the Red River was characterized by maximum in the mouths of the branches and general decreasing gradient towards the sea. Maximum concentrations of Pb, Hg in suspended forms were observed in the surface layer of water at the river-sea barrier. The content of Hg and As in the estuary region of the Red River was observed in the following order: SSsurf< SSbott< BS; and content of Pb – SS > BS.

1. Introduction
The mouth of the Red River is known as one of the largest in Vietnam. It consists of a delta (14.6 thousand km²) and a wellhead seashore (1,300 km²) [1,2]. There is a powerful transport and industrial hub on the basis of cities and small industrial towns of North Vietnam on this territory [3]. Main rice fields are also concentrated here. In addition, there are a significant number of discharges from industrial centers of China and mining industry on the top getting to the Red River [4]. Such concentration of production facilities determines the high level of pollution in the estuary area of the Red River.

Delta watercourses are the main ways to get pollutants, including heavy metals in the seaside. Heavy metals falling into the mouth area can be partially accumulated there. Excess of these metals together with water fall into the seashore. They can exist in various forms, for example, suspended, colloidal and truly dissolved particles; free hydrated cations, oxo- and hydroxo- complexes. Complexes with inorganic, especially organic ligands, are sorbed and accumulated by hydrobionts and bottom sediments [5]. However, bottom sediments can serve as a source of secondary pollution of the aquatic ecosystem [6]. As a result, the study of heavy metals migration in the water-bottom sediment system in the estuarine seacoast is of great importance in regard to assessment of ecological state in the estuary region [7].
Processes of diffusion, convection and diffusion-convection are mechanisms for the spread of pollutants, including heavy metals, in the aquatic environment. Research into diffusion mechanism of heavy metals distribution in reservoirs is based on the construction of a mathematical model for heavy metals diffusion in water and in bottom sediments [8].

The authors have set a purpose to study spatial distribution of heavy metals (Pb, Hg, As) in a suspended form and in bottom sediments of the seashore. For this purpose, a mathematical modelling for diffusion processes of heavy metals and spatial analysis for the results of these models were proposed and implemented.

2. Materials and methods

The observations were carried out in the following stations: along the main channel of the Red River on the delta (5 stations St 1 - St 5); stations St 6 - St 9, that refer to the mouth of the Trali, Balat and Ninhko branches respectively; on the seashore (26 stations) (Figure 1).

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

The studies were implemented during the main hydrological seasons of 2014 - 2016 (during flood and inter-natal periods). Samples of bottom sediments were taken from the surface horizon (0-20 cm) in synchronism with sampling of water in accordance with Vietnamese requirements.

Heavy metals (Pb, Hg, As) in suspended solids and in bottom sediments were determined by means of atomic absorption spectrometry [4,9,10].

The heavy metals propagation was simulated by solving numerically the equation of turbulent diffusion of the following type [6,10,11]:

\[ \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = K_x(t) \frac{\partial^2 C}{\partial x^2} + K_y(t) \frac{\partial^2 C}{\partial y^2} + F + B \]

where \( C \) – heavy metals concentration; \( u \) – flow rate; \( K_x, K_y \) – turbulent diffusion coefficients. Axis Ox – along the coast, and axis Oy – along the coastline.

\( F \) – the function of heavy metals sources in the seashore, \( B \) – decrease or increase in the amount of heavy metals due to interfacial transformation processes.

The diffusion coefficients depend on the scale of the phenomenon was modeled by equivalent time dependence [8]:

\[ K_{x,y} = \frac{1}{2} \rho^2 t \]
where, diffusion rate \( p \) was approximately 0.6 cm/s.

The basic equation describing heavy metals propagation in suspended matter in the seaside was the equation of turbulent diffusion [8,11]:

\[
\frac{\partial S}{\partial t} + V \frac{\partial S}{\partial y} = \frac{\partial}{\partial y} \left( K_i \frac{\partial S}{\partial y} \right) - U \frac{\partial S}{\partial y}
\]

where, \( S \) – heavy metals concentration in suspended substances, mg/kg; \( U \) – hydraulic size of the sediment (the rate of their uniform precipitation in calm water), m/s.

An algorithm was developed to calculate the content of heavy metals sorbed by bottom sediments [13]:

\[
C_B S = G \cdot C_t \\
C_t = C_0 \cdot e^{-K \tau S}
\]

The amount of adsorbed heavy metals was calculated:

\[
q = C_0 \cdot V - C_t \cdot V_S
\]

The total amount of heavy metals sorbed by bottom sediments was counted as follows:

\[
q_{total} = q + q_{Fe(OH)_3}
\]

where, \( C_0 \) – initial concentration of heavy metals, mg/dm\(^3\); \( C_t \) – concentration of heavy metals in water at time \( \tau \), mg/dm\(^3\); \( C_B S \) – content of heavy metals in bottom sediments, mg/kg, \( S \) – area with bottom sediments, m\(^2\); \( G \) – distribution coefficient; \( V \) – volume of water delivered to the water body during the estimated period of time, dm\(^3\); \( \tau \) – time, days; \( K \) – constant of heavy metals sorption rate by bottom sediments; \( q \) – the amount of heavy metals sorbed by bottom sediments (silt, sandy ooze, sand); \( q_{Fe(OH)_3} \) – the amount of heavy metals sorbed by iron hydroxide (III).

A mathematical model was derived for migration and transformation processes of heavy metals compounds in the seaside of the Red River estuary. The results of suspended heavy metals concentration obtained in the models were analyzed by using ArcGIS 10.2.2 (Fig. 2) [14].

Figure 2. Interpolation model for spatial analysis of HM distribution in ArcGIS environment 10.2.2.

The interpolation model was used in special tools ArcToolbox to carry out spatial analysis and define the content of heavy metals in either the suspended form or the bottom sediments.
3. Results and discussion

Heavy metals in water and suspended substance

The highest concentrations of dissolved forms of Pb, Hg, As were observed at the top of the delta. In this area, chemical plants, industrial centers and rice fields are concentrated. Maximum concentration of Pb, Hg, As in a suspended form was observed in the mouths of the Red River branches (Fig. 3). Accumulation of suspended solids and sorbed pollutants was observed due to a decrease in flow rates in the main channel and delta arms, as one approaches the sea edge of the delta and in the seashore [10].

![Figure 3](image)

**Figure 3.** Spatial distribution of heavy metals suspended form in the estuary area of the Red River for 2014 - 2016: a – Lead; b – Mercury; c – Arsenic.

Toward the sea, the concentration of the suspended form of lead began to decrease, and then increased with a distance of 30-40 km from the mouth. Maximum concentrations of these elements were observed in the surface layer of water at the river-sea barrier at 40 km. This can be witnessed due to flocculation of inorganic and organic solutes with concomitant capture of metals in dissolved forms. This process is the main mechanism for extracting dissolved trace elements during estuary water mixing. It reaches maximum intensity in the salinity range of 15 - 20 ppt. [11,15].

The contents of Hg and As in the suspended forms were observed at a maximum in the mouth of the main riverbed. Both total suspension concentration and fraction of terrigenous particles in its composition decreased as the distance from the mouth diminishes (Fig. 3). So it can be noted that the river runoff is the preeminent source of supply of elements in the estuary seashore.

**HM Distribution between the suspended phase and the sediment phase**

Figure 4 shows comparative histograms of the studied elements content in the suspended matter of the surface water layer (SSsurf), in the suspended matter of the bottom layer of water (SSbott) and in the surface layer of bottom sediments (BS) at stations St.1, St.7, St.12, St.22, confined to the delta, river, middle and sea areas of the mouth area of the Red River.

![Figure 4](image)

**Figure 4.** Comparative histograms of the studied elements content in the suspended matter of the surface water layer (SSsurf), in the suspended matter of the bottom layer of water (SSbott) and in the bottom sediments (BS) on the main parts of the estuary area of the Red River for the period of 2014 - 2016.

Distribution of Hg, Pb and As differed from the following features: the content of Hg and As in the
mouth region of the Red River was observed in an order: $SS_{surf} < SS_{bott} < BS$. A common feature in distribution was predominance of the suspended phase over the sediment phase.

Maximum content of all the metals studied in suspended matter in the surface water layer and bottom sediments was confined to station St.7 (i.e. the mouth of the Balat river arm).

*Spatial distribution of heavy metals in bottom sediments of the Red River estuary*

Distribution of the heavy metals (Pb, Hg, As) in the bottom sediments in the mouth area (Fig. 5) revealed a pronounced common feature. It was exposed by an increase in heavy metals content in the bottom sediments of the estuary towards the sea. Concentration of heavy metals in the bottom sediments in the river part increased.

Figure 5. Spatial distribution of heavy metals in bottom sediments in the estuary area of the Krasnaya River for 2014 - 2016: a – Lead; b – Mercury; c – Arsenic.

Lead content began to boost from the mouth of watercourses to a distance of 30-40 km in the marine part, with maximum lead content in bottom sediments at the stations 12, 13 (Pb concentration reaches 68.5 to 87 mg/kg), where are 30 km from the shore.

The peaks of enhanced content of Hg and As in bottom sediments at the mouth of the main riverbed were recorded in (St. 7), then it decreased to the background value.

4. Conclusion

Spatial distribution of suspended form and phases of heavy metals of bottom sediments in the Red River estuary was characterized by an increase in concentration in delta waterways towards the sea; presence of a maximum in the mouths of the branches and a general decreasing gradient at the seashore. Distribution of Pb and Hg in the suspended matter was described with considerable heterogeneity. Maximum concentrations of these elements were observed in the surface layer of water on the river-sea barrier.

Distribution of Hg, Pb and As differed from the following features: the content of Hg and As in the mouth region of the Red River was observed in an order: $SS_{surf} < SS_{bott} < BS$.

A common feature in distribution of Pb was predominance of the suspended phase above the bottom sediment phase.

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