Assessment of heavy metal pollution in water and sediments in the red river delta (Vietnam)

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Abstract. The paper studied the features of distribution of main heavy metals in the water-bottom sediments system in the Red River Delta (Vietnam). The tasks were to determine the flow of heavy metals, to study the adsorption processes of heavy metals in suspended matter and burial in bottom sediments. The studies were carried out during the main hydrological seasons of 2014 – 2016 years at 6 stations of main branches of the river for 8 basic heavy metals (Cu, Pb, Zn, Hg, Cd, As, Cr and Fe). Each year, the total flow of heavy metals entering the top of the delta was 98.8 thousand tons. The total flow of all heavy metals differed by hydrological seasons and by watercourses. In general, 1.76% - 16.25% of the flow of heavy metals accumulated throughout the year, the highest accumulation rates are for lead, iron and zinc. In the branches Ba Lat, Tra Ly, Ninh Co, due to the decrease in flow rates, an intensive process of the accumulation of suspended substances and sorbed heavy metals was observed.

1. Introduction

The mouth of the Red River is one of the largest estuary area in Vietnam. Today it consists of the delta (14.6 thousand km²) and the estuary seashore (1300 km²) [1-3]. The top of the estuary area of the Red River, to which tides and storm surges spread, is 210 km from the sea, slightly below the mouth of the tributaries Da (right) and Lo (left) rivers. The top of the modern delta is located 25 km below the top of the estuary area, here the first delta sleeve departs to the right - Day [1]. The main branch, like the entire river, is called the Red (Hong Ha) (Figure 1).

To date, the content of pollutants, especially heavy metals in water bodies in the Red River delta has increased rapidly. Heavy metals (HM) have high toxicity for living organisms in relatively low concentrations, as well as the ability to bioaccumulate and biomagnify [4]. They fall into the Red River delta in two main ways: along with water drains from the top of the delta, as well as discharges of industrial enterprises with irrigated wastewater, fertilizers and pesticides in the delta. In hydraulic systems, heavy metal compounds are found in the water column, in sediments, and in organisms of hydrobionts [4,5]. To study their regime and balance in the Red River delta, it is necessary to consider the distribution of their compounds in the water-bottom sediments-hydrobionts system.

In the framework of this research, the features of the distribution of the main heavy metals in the water-bottom sediment system in the territory of the Red River delta (Vietnam) were studied. The tasks were to determine the flow of heavy metals from the top of the delta, their content in water and...
in bottom sediments, to study the processes of adsorption of heavy metals in suspended matter and their entry into bottom sediments.

2. Materials and methods

Observations were made at 6 stations on the main branches of the river (Figure 1).

The studies were carried out during the main hydrological seasons of 2014 – 2016 years (during flood and low water periods). Sampling of river water was carried out by using a plastic bathometer with the volume of 1 litre. Sampling of sea water was carried out by using a BM-48 marine bathometer (F. Nansen's bathometer) [5-8]. The samples of the surface layer of bottom sediments were taken in synchronization with the sampling of water in accordance with the requirements of Vietnam [2,9].

The determination of HM in suspended substances and in bottom sediments was carried out by atomic absorption spectrometry [10-12].

Calculation of heavy metals through the watercourse was carried out according to the formula [12-14]:

$$R_i = Q_r \frac{\sum Q_i C_i}{\sum Q_i}$$  \hspace{1cm} (1)

where, $C_i$, $Q_i$ – concentration of heavy metal and water flow, referred to at time $i$; $Q_r$ – the total water flow, referred to the time intervals from the beginning to the end of the research; $R_i$ – total flow of heavy metals.

Calculation of the adsorption possibility of heavy metals in suspended forms and their entrance in bottom sediments was given by the formulas [12,15,16]:

In suspended forms:

$$A_i = C_i \times V$$  \hspace{1cm} (2)

where, $A_i$ – the amount of suspended heavy metal i in water (kg); $C_i$ – the concentration of heavy metal i (mg/l); $V$ – water volume (m$^3$)

Entrance in bottom sediments:
where, $M_i$ – the mass of heavy metal $i$, buried in bottom sediments; $A_i$ – the concentration of heavy metal $i$ in the bottom sediments; $S_i$ – the amount of heavy metal $i$ entering the bottom sediments.

Calculation of the adsorption coefficients of HM by suspension and bottom sediments was given by the formulas [12,17,18]:

The adsorption coefficient of HM:

$$k_i = \frac{A_i}{R_i} \times 100$$  \hspace{1cm} (4)

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

Coefficient of entrance in bottom sediments:

$$k_2 = \frac{M_i}{R_i} \times 100$$  \hspace{1cm} (5)

where, $M_i$ – the mass of heavy metal $i$, buried in bottom sediments; $R_i$ – total flow of heavy metals (tons).

The total coefficient of accumulation of HM:

$$k = k_1 + k_2$$  \hspace{1cm} (6)

3. Results and discussion

3.1. Distribution of heavy metals (HM), coming from the Red River basin, along delta watercourses

The concentrations of pollutants, including heavy metals in river water, are represented by the sum of concentrations of suspended and dissolved forms of pollutants [13,19]. To analyze their behavior in the estuary area of the Red River, it is necessary to consider not only the content of their dissolved compounds in water, but also to investigate the distribution of HM in phases: suspended forms, colloid-dispersed forms and bottom sediments.

The entrance in the top of the Red River delta, both dissolved and sorbed on suspended matter, is mainly determined by the processes of accumulation and secondary entrance of HM into the water in the catchment area of the Red River. These processes, taking place in various physical, geographical, hydrochemical and even climatic conditions, are rather complicated. Therefore, in the research the results of the total flow of HM coming from the top of the delta were calculated as both dissolved and suspended forms [20,21].

The total flow of HM entering the top of the delta was carried out in Table 1.

According to the data given in Table 1, it couldn be seen that the entrance of HM in the Red River delta varies according to hydrological seasons:

- Fe in the flood time was more than 2,63 times in the low water period. The total flow of iron in the Red River was 88.2 thousand tons per year.
- Flow Pb, Zn, Hg, Cd, As, Cr during the flood period was also more than in the low water 2.8 – 10 times.
- Flow Cu in the low water period and during the flood time were slightly different.

The calculation of the distribution of TM entering the Red River delta along main streams was carried out as follows. First, a calculation was made of the flow of main HM for the Red River (the main channel) and the Duong and Day branches according to mean annual concentrations, using data on their entrance, received in Hanoi and data on the distribution of flow between these watercourses.
Table 1. The total flow of heavy metals in the top of the Red River delta for the hydrological seasons (Shontai) for 2014 – 2016.

| Heavy metal | Low water | Concentration $C_i$ (mg/l) | Flow HM (t/season) | Flood time | Concentration $C_i$ (mg/l) | Flow HM (t/season) | Total flow HM (t/year) |
|-------------|-----------|-----------------------------|--------------------|-----------|-----------------------------|--------------------|----------------------|
| Cu          | 0,038     | 1357,3                      | 0,02               | 1345,7    | 2703,0                      |                    |                      |
| Pb          | 0,012     | 428,6                       | 0,02               | 1345,7    | 1774,3                      |                    |                      |
| Zn          | 0,015     | 535,8                       | 0,08               | 5382,9    | 5918,6                      |                    |                      |
| Hg          | 0,00008   | 2,9                         | 0,00012            | 8,1       | 10,9                        |                    |                      |
| Cd          | 0,0006    | 21,4                        | 0,0008             | 53,8      | 75,3                        | 75,3               |                      |
| As          | 0,0021    | 7,5                         | 0,00055            | 37,0      | 44,5                        | 54,5               |                      |
| Cr          | 0,00015   | 5,4                         | 0,0004             | 26,9      | 32,3                        | 56,4               |                      |
| Fe          | 0,68      | 24288,1                     | 0,95               | 63921,4   | 88209,5                     |                    |                      |

Then the flow of HM in Hanoi, taken 100%, was assigned to the systems of main watercourses (Tra Ly, Ninh Co and Ba Lat) in accordance with the distribution of annual flow through the systems of main watercourse [2,5]. Due to the fact that HM came into five designated sectors of the shallow coastal zone of the Red River, water flow and HM in the delta was also broken into five private watercourses (Table 2).

Table 2. Annual distribution of heavy metals by seasons in the main watercourses in the Red River delta for 2014 - 2016.

| HM | Hydrological season | Duong | Day | Tra ly | Ninh Co | Ba Lat | Total | Year |
|----|---------------------|-------|-----|--------|---------|--------|-------|------|
| Cu, t | Low water       | 216,1 | 331,4 | 47,3   | 51,7    | 52,8   | 699,3 | 1579,1 |
|       | Flood time       | 201,9 | 312,9 | 125,8  | 90,8    | 148,4  | 879,8 |       |
| Pb, t | Low water       | 108,1 | 135,6 | 23,7   | 17,2    | 19,8   | 304,3 | 808,5 |
|       | Flood time       | 161,5 | 146,0 | 80,1   | 42,4    | 74,2   | 504,2 |       |
| Zn, t | Low water       | 64,8  | 75,3  | 26,0   | 21,5    | 16,5   | 204,2 | 801,9 |
|       | Flood time       | 201,9 | 166,9 | 91,5   | 48,4    | 89,0   | 597,7 |       |
| Hg, t | Low water       | 0,3   | 0,5   | 0,0    | 0,0     | 0,1    | 0,9   | 3,6  |
|       | Flood time       | 1,0   | 1,0   | 0,2    | 0,1     | 0,3    | 2,7   |       |
| Cd, t | Low water       | 2,2   | 3,0   | 0,5    | 0,4     | 0,7    | 6,7   | 35,5 |
|       | Flood time       | 10,1  | 10,4  | 3,4    | 1,8     | 3,0    | 28,7  |       |
| As, t | Low water       | 2,2   | 2,3   | 0,2    | 0,2     | 0,3    | 4,7   | 24,0 |
|       | Flood time       | 8,1   | 8,3   | 1,1    | 0,6     | 1,2    | 19,4  |       |
| Cr, t | Low water       | 8,6   | 12,1  | 2,8    | 2,6     | 4,0    | 30,1  | 158,6 |
|       | Flood time       | 50,5  | 52,1  | 9,2    | 4,8     | 11,9   | 128,5 |       |
| Fe, | Low water       | 5,4   | 6,0   | 1,2    | 1,5     | 2,0    | 16,1  | 52,9 |
| thous. t | Flood time     | 13,1  | 10,4  | 4,6    | 2,7     | 5,9    | 36,8  |       |
Overall 55.7 - 81% of the flow of HM occurred during the flood period, 19 - 44.3% - at the low water period. The largest seasonal variability of the HM entrance was observed for cadmium and chromium, and the smallest variability for copper.

3.2. The processes of HM adsorption by suspended substances and their entrance into bottom sediments

Due to the decrease in flow velocities in the main channels and delta branches, as we approach the sea edge of the delta and in the seashore, the process of accumulation of suspended substances and sorbed pollutants was observed at the sea border of the delta and in the seashore [13,21,22].

Calculation the entrance of the pollutants, sorbed by suspended substances and entering into the bottom sediments was carried out on the basis of observations amount of the pollutant flow according to formulas (2) and (3). The area of the accumulation territory and average depths of the estuary area of the Red River were used from the data of Mai (2006), Cao (2009) and field observations during the research [5, 12]. Data on the content of HM, adsorbed by suspended substances and entering into the bottom sediments were shown in Fig. 2 on the watercourses in the estuary area of the Red River. Concentration of heavy metals in the bottom sediments in the river part increased.

Figure 2. Map-scheme The amount of heavy metals along the watercourses in the estuary of the Red River in 2014 - 2016. A. The amount of heavy metals in suspended forms. B. The amount of heavy metals deposited by bottom sediments.

It was found that practically all main watercourses show a decrease in the content of suspended HM relative to their content at the top of the delta. However, when comparing these results, it was found that, the concentration orders of the suspended and dissolved forms in water coincided.

Compared to the amounts of accumulation of HM by bottom sediments in all delta watercourses, it was noted that the content of TM in the bottom sediments in the Duong, Day and Ba Lat branches were relatively 23%, 26% and 25% of the accumulation amounts of HM.

4. Conclusion

Each year, the total flow of heavy metals entering the top of the delta was 98.8 thousand tons, including 89.3% of the total flow represents iron flow. The flow of HM into the Red River delta changed according to the hydrological seasons: the total flow of the HM during the flood period was 2.6 to 10 times higher than in the low water period.

In all the main delta branches, 55.7 - 81% of the HM flow occurred during the flood period, 19 - 44.3% - at the low water period. The largest seasonal variability of the HM entrance was observed for cadmium and chromium, and the smallest variability for copper.

The total flow of all heavy metals was found in the main delta branches, in the order: Duong > Day > Ba Lat > Tra Ly > Ninh Co.
In comparison with the sum of HM accumulation by suspended substances and bottom sediments, the HM content in the main delta watercourses was observed in the order: Day > Ba Lat > Duong > Tra Ly > Ninh Co. It was found that the possibility of HM accumulation on watercourses differ.

In general, 1.76% - 16.25% of the flow of heavy metals accumulated throughout the year, the highest accumulation rates were for lead, iron and zinc.

In Ba Lat branch, sorption coefficients by bottom sediments for most HM were the highest values in comparison with other branches. However, because of the low flow velocities during the flood and low water periods in the branches of Tra Ly, Ninh Co and Ba Lat, the total coefficients accumulation of HM were approximately 2 to 2.5 times higher than in the branches of Duong and Day. It could be noted that the closer to the sea edge of the delta, the more intensive the accumulation of heavy metals was observed.

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