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Study on the heavy metal speciation modeling in aquatic system of Le An River

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Abstract — This paper aimed at evaluating the river models and calculating by the parameters established. As a result, the prediction of pollution under different loading and hydrological conditions are suggested.

Keywords: heavy metal contaminants; metal speciation; aquatic system.

INTRODUCTION

Toxicity of metal ions is different from one species to another depending on the water quality condition and the species distribution in aquatic system. It will be more reasonable that criterion of water quality for environment management is established on the speciation of metal. The model of heavy metal speciation in surface water of river was studied.

This paper aimed at (1) evaluation of river models and calculation by the parameters established and comparison of data from field survey and simulation calculation; (2) prediction of pollution under the different loading and hydrological conditions.

METHODOLOGY

Sampling of water and sediments

The sampling of water and sediment along river were carried out three times 1989–1990, dry season (Oct. to March next year), rainy season (May to July), and normal season (June to Sept.). The concentration of metals in water and sediment were analyzed by ICP and AAS. The results (Fig. 1 and Fig. 2) show that the Cu concentration in sediment near Dawu river mouth (No. Lo. 2) in dry season is higher than rainy season, but reverse at downstream, the tendency is higher in rainy season due to the increasing of suspended matter.

The metal concentration in water may separate into two parts, the dissolved and the particulate, by filtration (0.45 μ), the particulate part is estimated to be dominant 80 to 90%. This part may also be divided into active and inert parts (Table 1).

The structure of the metal speciation model

The data from field and speciation of metals in sediment were evaluated. The species in sediment are distinguished into six parts, i. e., water soluble, cation exchangeable, carbonate

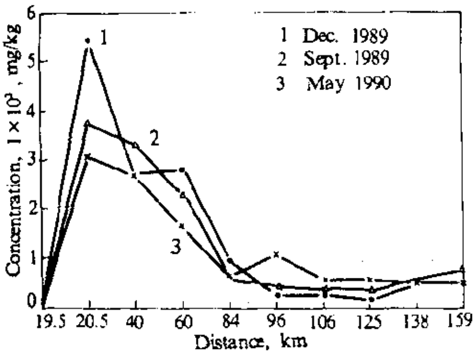

Fig. 1 The concentration of Cu in sediment

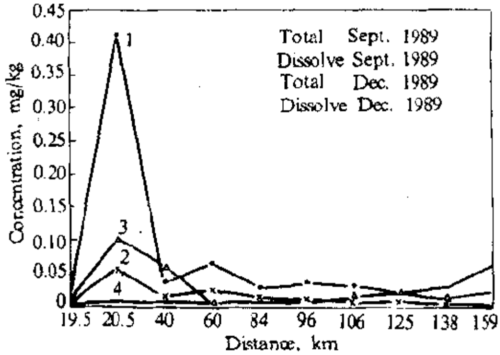

Fig. 2 The concentration of copper in water

Table 1 Active and inert copper in suspension

Species	Lo. 1	2	3	4	5	6	7	8	9	10
Active, %	7.99	25.85	10.97	19.24	47.66	38.34	37.14	38.37	29.70	26.62
Inert, %	92.01	74.15	89.03	80.76	52.34	61.66	62.88	61.63	70.30	73.38

bounded, ferric-manganese bounded, organic-sulfide bounded, and the residue (Tessier, 1979). Based on their chemical properties, the first four part are named active part as these are easy to release into waterbody. The organic-sulfide bounded and residue forms are non-active part, or inert part. It is necessary to model movement and transport of the active and inert part in suspended sediment separately. According to the distribution of metals of various grain size fractions, metals mainly in fractions < 20 μm are transported in suspended sediment. A model of the transport of the particles and dissolved metals is described below (Salomon, 1988).

The velocity of flow in Le An River is mostly greater to 0.2 m / s during flood season, higher than the velocity in which the suspended sediment (< 20 μm) can transport downwards; but in dry season, the velocity of flow in upstream is higher than 0.2 m / s; however, in downstream the velocity is much lower. Dilution and resuspension of sediments will determine the concentration of particulate and the dissolved metals. Considering above processes, the general equation for the transport of metal in the water is:

$$\frac{dC}{dt} = D\frac{\partial^2 C}{\partial x^2} + V\frac{\partial C}{\partial X} - Ks \cdot C + R, \tag{1}$$

where C is the metal concentration in suspended matter, active or inert part (mg / L); V is the average velocity of flow (m / s); D is the dispersion coefficient (m / s); Ks is the sedimentation and resuspension coefficient of metals (L / s); R is the point or nonpoint source load (mg / L).

Similarly, the expression can be used to calculate the chemical active part of elements in suspended particulates as well as the inert part does. In order to calculate the dissolved metals in water, it is necessary to define the partition coefficient to represent the equilibrium relationship of the dissolved species in water and the active part of elements in suspended matter.

The partition coefficient is expressed as follows:

$$Kp = Cse /\ Cdw, \tag{2}$$

where, Kp is the partition coefficient of metal in water and suspended matter (L / kg); C_{se} is the metal concentration of the active part metal in suspended matter (mg / kg); C_{dw} is the concentration of dissolved metal in water (mg / kg).

The total concentration of metal in water is:

$$Ct = Cdw + Cac + Cin, \tag{3}$$

where Cac and Cin are the concentration of the active and inert metal in water (mg / L).

$$Cac = Cse \cdot SS \cdot 10^{-6}, \tag{4}$$

where SS is the concentration of suspended matter in water (mg / L).

In the model, the balance of total suspended matter SSt in water is:

$$SSt = SSi + SSp - SSout - SSd, \tag{5}$$

where SSi and SSp are the flux of suspended matter from upstream and the lateral boundary (g). SSout is the output flux of suspended matter to downstream (g); SSd is the flux of suspended matter sedimentated to the bottom (g).

$$SS = SSt /\ Q \tag{6}$$

where Q is the volume of water at the segment (m^3).

Expression (1) to (6) can be used to represent the physical and chemical processes of metal in the river, they are, dispersion transport, precipitation, dissolution, adsorption, desorption, sedimentation.

Segmentation of river and the hydrological data

In order to simulate the transport and transformation of metal in water of river, it is necessary to separate the river into several segments based on the hydrological data and the situation of river (Lin, this issue). It may be divided into three reaches (Table 2).

There are three hydrological stations located at up-, middle- and downstream. The main hydrological information was collected from 1975—1986. Based on hydrological data, the runoff, level and velocity of water flow were calculated. The results showed at Table 3 that river flow and velocity vary significantly from upstream to downstream. In flood season, the runoff of the river can reach several thousands of m^3/s, but in dry season, only tens to hundreds m^3/s.

Table 2 The reaches of Le An River

Reaches	Length, km	Gradient, %	Width, m	Depth, m
Upstream	61.4	1.0	50–100	1–5
Midstream	83.6	0.34	100–150	2–8
Downstream	72.5	0.065	> 200	5–15

In order to simulate exactly, the river may separate into ten segments (Fig. 3) from the discharging point of waste water to downstream about 159 km long. The flow and velocity, runout and water quality from boundary have been estimated and deduced from meteorological and hydrological data, the results obtained are shown in Table 3.

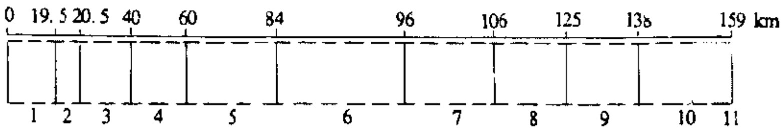

Fig. 3 Scheme of segments on Le An River

Table 3 Flow velocity and runout from boundary in normal season

Segment	1	2	3	4	5	6	7	8	9	10	11
Q, m^3/s	116	129	134	149	184	199	204	219	224	244	
V, m/s	0.92	0.80	0.75	0.69	0.42	0.38	0.32	0.28	0.27	0.26	0.20
Qb, m^3/s	10	3	5	15	35	15	5	15	15	20	

Notes: V — velocity of flow; Q — runoff; Qb — runout from boundary.

Calculation of parameters: partition coefficient, sedimentation coefficient and dispersion coefficient

Kp, partition coefficient, was calculated for each segment based on the concentration of metal dissolution in water and the active part of metal in suspended matter. The results in Table 4 show that the partition coefficient varies from segment to segment. The concentration of active part element in segment No. 2 is so high that the dissolved concentration in water may reach up several hundreds ppb. At downstream, the coefficients are almost the same value.

Table 4 Partition coefficient, Kp of Cu at different segments

Segments	1	2	3	4	5	6	7	8	9	10
Kp, L/kg	5800	5099	1166	2825	500	500	500	500	500	500

The sedimentation coefficient, Kd, was calculated:

$$Kd = dp / St, \tag{7}$$

where dp is the average depth of water for each segment (m); St is the sedimentation velocity of suspended particulates (m / s).

Table 5 Sedimentation coefficient, *K*s of segments

Segments	1	2	3	4	5	6	7	8	9	10
Ks (L / s) $\times 10^{-3}$	0.92	1.98	0.51	0.16	0.16	0.15	0.05	0.05	0.05	0.05

The dispersion coefficient, D_l was calculated based on Fick Law:

$$N = \frac{D_l A}{\Delta X} \cdot \Delta C, \tag{8}$$

where D_l is the dispersion coefficient (m^2/ s); A is the section area of segment (m^2); X is the distance of midpoint between segments (m); C is the differential concentration of segments (g / m^3); N is the mass flux of pollutant element in the cross section (g / s · m^2).

Its value was assumed as 100 m^2/ s in calculation since not much effect on the terminal results.

Input and output file of the programme

The data of input file are the flow and velocity of water in each segment, length of segment, runoff input and sedimentation coefficients, partition coefficients, dispersion coefficient, background water quality and pollution loading, in addition to the concentration and composition of suspension including the species distribution of metals in sediment and particulates.

The results of output file showed that the environmental parameter, the concentration of element in dissolved water, particulate (inert and active part) and in sediment (total, inert and active), the content of suspension and so on.

Table 6 The distribution of Cu species of soil along Le An riverbank

Lo. species	*Ct*, ppm	*Cac*, %	*Cin*, %
Fuxikou	42.15	7.99	92.01
Gukou	232.93	24.79	75.21
Zhongzhou	64.64	7.92	92.08
Caijiawan	42.60	14.51	85.49

Ct: total conc.; *Cac*: active part; *Cin*: inert part

CALCULATION AND DISCUSSION

In order to understand the simulation of the river model on heavy metal transport, the present paper is focused in the concentration distribution of copper in sediment and water.

Total Cu concentration distribution in sediment

The results of calculation showed in Fig. 4 are the tendency of the Cu concentration changing from the discharging mouth (No. Lo. 2) to downstream (No. Lo. 10) at different seasons. It reached 3–4 thousands mg / kg at sediment near Dawu River mouth, then decreased to 7–8 hundreds mg / kg at downstream about 160 km (No. Lo. 10). In normal season, the Cu concentration in segment near the discharging mouth is higher than in the flood season, but the transported distance of copper in normal season is shorter. The Cu concentration in segment near the mouth of Dawu River in dry season is more serious, but the polluted river-section shorter than in other seasons.

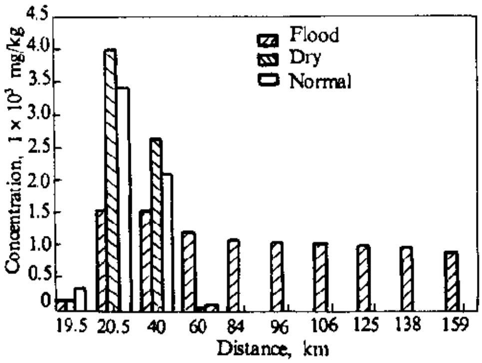

Fig. 4 The calculated Cu concentration in sediments

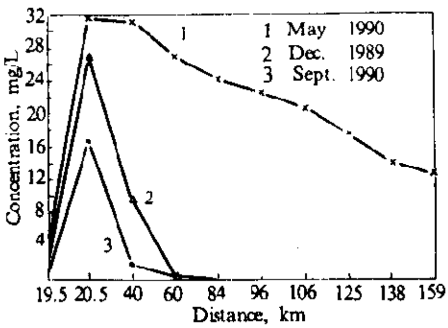

Fig. 5 The calculated Cu concentration in water

The concentration of copper is changing slowly along river, the attenuation of concentration dominate the transport process. Sedimentation of pollutants at bottom diminish, the distance that the pollutant can reach in is longer, even over 200 km to Poyang Lake (No. Lo. 13). The velocity of flow in flood season rises rapidly and is higher than that of the suspended particulates transporting downwards.

Comparison of calculated results and field monitoring data, the tendency of Cu concentration distribution is in accordance with each other. In different seasons, the Cu concentration (in sediment) in segment near the discharging mouth changes dramatically, differed from calculation at different flow. The results indicate that the sedimentation effect is the main process in normal and dry seasons.

The Cu concentration distribution in river water

The Cu distribution in river water from simulating model (Fig. 5) is similar to that in sediment. In dry season, the concentration in segment near discharging mouth is higher than that in flood season, but reversed in dry season, downwards over 50 km, the decreasing gradient in dry season is steeper than that in flood season.

The range of Cu concentration in different seasons at location Lo. 2 to Lo.3 are 4.5–25 ppm depending on the discharging load of pollutants. It drops to 0.5–0.05 ppm in segment downwards over 50 km, 0.01–0.005 ppm at Lo. 10.

The comparison of calculated and field data show that the Cu concentration distribution in water depends on the ratio of runout and drainage water. Higher the flow more drainage will lead to the high concentration in water at downstream segment. Less the drainage and less the flow in dry season will only lead to the high concentration in segment near the discharging mouth.

Speciation distribution of copper in sediment

The results shown in Fig. 6 are the total, inert and active concentration of copper in sediment. The inert part of element bounded in sediment is the residue together with organic-sulfide bounded species that are stable in sediment and the active part of element in sediment can be liberated into water. The speciation partition of copper in sediment from the sequential extraction (Mao, 1989) indicated that the inert part of element is 50–90%. The active part is 10–50% (Table 8). The percentage of the inert part calculated is in accordance with the experimental results. The difference may rise from the loads coming from nonpoint input and the drainage composition estimated from the monitoring data at different period of time.

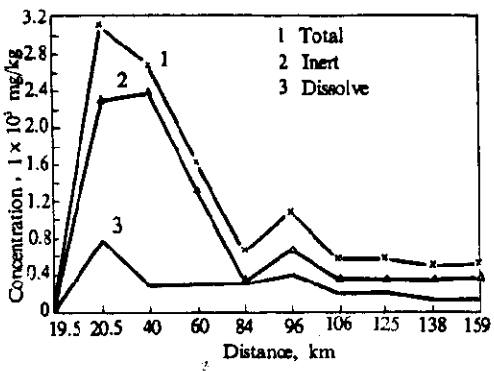

Fig. 6 The speciation of Cu in sediments at normal season (Sept. 1989)

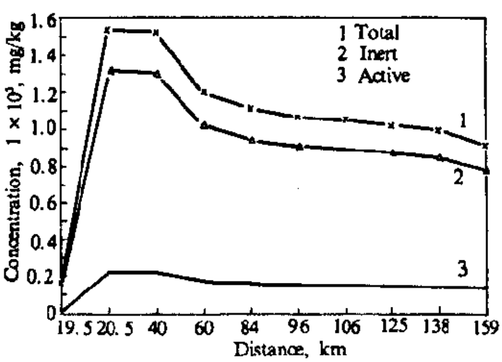

Fig. 7 Speciation of Cu in sediments at flood season (May 1990)

By comparison with the speciation distribution in flood and normal season (Fig. 6 and Fig. 7), it is found that the percentage of inert part in flood season is higher at downstream caused by the transport of suspension containing the ore residue and the tailing. While in normal season, the particulate copper in suspension mostly deposited in segment near the discharging mouth.

The percentage of the active part would be higher than that in flood season at downstream.

Speciation distribution of Cu in water

The results calculated from the model are the total, dissolved and particulate concentration of copper (inert and active part) in water during flood season (Fig. 8). Over 90% of copper existed in suspension, the inert part of copper in suspension is about 80%, the dissolved species is < 10%, 53 to 100 ppb in water. While in normal season, the concentration of dissolved species can rise to 300 ppb (Fig. 9). The ratio of particulate to dissolved species keep constant at different seasons (about 9:1).

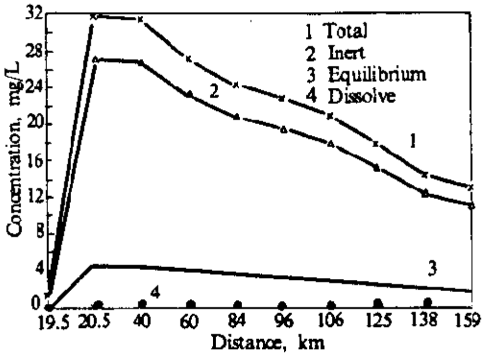

Fig. 8 The total, dissolved Cu in water, active and inert species in suspension at flood season

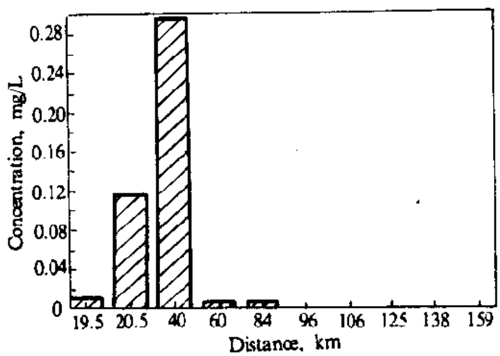

Fig. 9 The dissolved Cu concentration in water at dry season

The comparison of the calculated data with the monitoring data shows that the calculated species of particulate is higher than the monitoring data, 10 to 20% of total concentration while the dissolved species in water is approximately same. Difference may raise from the input assumption that the particulate copper in suspension of drainage dominate 90% of total concentration in water.

Simulation of speciation by a simple model conducted by a set of assumptions, further study will be carried out, enough monitoring data is urgently needed.

CONCLUSION AND SUGGESTION

The option of the heavy metal model has been conducted by a large of information and a set of assumptions. The estimation of pollution has been conducted at different seasons in a set of boundary input and drainage. The comparison of calculated and monitoring data was found to be basically in accordance with. The modeling seems to be reasonable.

The parameter estimation needs a large amount of hydrological data and the monitoring data, the field investigation should be continued in future.

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REFERENCES

Fostner, D. and W. Salomons, Proc. NATO Adv. Res. Workshop Nerri/ Italy, New York: Plenum Press, 1983:245
Klenkel, P. K., Modeling of river (Ed. by Hsien Wen Shen), New York: John Wiley, 1981:17
Louis, J. Thibdeaux, Chemodynamics, New York: John Wiley, 1979:72
Tessier. A., Campell, PGC, Bisson, M., Anal. Chem., 1979, 51:844

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