Journal of Environmental Sciences Vol. 8, No. 4, pp. 443–453, 1996 ISSN 1001-0742

Speciation and distribution characteristics of heavy metals in the Changjiang River water

Chen Xibao, Zhang Shen, Dong Wenjiang, Zhang Licheng

Institute of Geography, Chinese Academy of Sciences, Beijing 100101, China

Cheng Yanxun

Institute of Petroleum Processing, Beijing, China

Abstract——In this paper, the forms of Zn, Cd, Pb and Cu in water from the Changjiang source to the estuary area were determined by ASV method. The main results are as follows: (a) The total contents (*Ct*) of Zn, Pb, Cu and Cd in the source were 4.0, 1.88, 1.28 and 0.07 μg/L respectively, while *Ct* were in the order of Zn (20.1μg/L) > Cu (14.9 μg/L) > Pb (6.73 μg/L) > Cd (0.15 μg/L) in mainstream and Zn (93.6 μg/L) > Cu (7.71 μg/L) > Pb (5.65 μg/L) in the estuary area. However most of them were presented as Mp. Their dissolved contents (Cs) were in lower levels of Zn (1.4 μg/L) >Cu (1.3 μg/L) > Pb (0.11 μg/L) > Cd (0.012 μg/L). (b) The distribution of soluble forms is related to the type of metal and to the environmental variables. From source to the mainstream, the major form of Zn from MALi converted into MAb, Cd resembles Zn in forms of distribution, Pb, mainly existed as MAb, Cu, as MLb. But in the estuary area, the major forms of Cd and Pb were all MAb, then MALi varied with salinity of water.

Keywords: heavy metal; speciation; river; water.

1 Introduction

In water environment, a trace heavy metal always occurs in particular physico-chemical forms. The environmental impact of a heavy metal is critically dependent on its various forms present, not total metal concentration. It was reported that labile forms was the active form of the metal (Florence, 1980). So, the study on trace heavy metals forms has been exciting great interest. Since the 1970s many papers or professional works in this respect have been published (Florence, 1980; Hart, 1978; Leppard, 1983; Wu, 1983; Chen, 1986; 1990). But, there has not been any report of studies on speciation of Zn, Cd, Pb and Cu in the Changjiang River water. In this study, the speciation of Zn, Cd, Pb and Cu in water from the Changjiang River source to the estuary area have been studied systematically, which can serve as scientific basis for exploiting water resource and evaluating water quality.

2 A survey of the Changjiang River valley

The Changjiang River rises in the Tanggular Mountains of the Qinghai-Tibet Plateau. The river head has two branches, which are Chumaer River in the north and Muluwusu River in the south. The confluent of both is called Tongtian River which is named Jinshajiang River after flowing through Yushu and Zhimenda and is named the Changjiang River after flowing through Yibin again. Customarily, the river reaches between Yibin and Yichang, and Yichang and Hukou are called the upper and middle reaches respectively, and from Hukou downward is called the lower reaches. It flows into the East China Sea. The total length is 6300 km.

In the source area, there is quite few anthropogenic influence on metal concentrations in water. The natural landscape had been undisturbed. Thus, it's one of the typical background districts on the globe. The region is situated in subfrigid zone of plateau, lack of both oxygen and rainwater, the annual precipitation is only 200—400 mm and gradually reduces from the east to the west, and from the south to the north. The river water is supplied primarily by melted glacier and precipitation. Mineralization rate of river water is low in the south, and high in the north. Type of aquatic quality is $[C]_{II}^{Ca}$ for the south river (Bugu and gaer river) and $[C]_{III}^{Na}$ for the Tuotuo River situated in the north.

The middle and lower Changjiang River has subtropics and monsoons climate and abounds with water and heat resources. Rain water is the main supplement of the river water, whose mineralization rate is lower, ranging between 150—250 mg/L. The type of the water quality is HCO_3^--Ca^{2+}. Along the valley, economics is very well developed, and there are plenty of large cities, factories, mining enterprises and important agricultural zones. As a consequence, a large amount of waste materials are discharged into the river every year. However, owing to quite high discharge of the river, the pollutants have been diluted, and hence the water quality has not been changed on the whole. But, contaminated water belts along river banks close to cities are considerably long, which exert certain influence on species and concentrations of heavy metals in the water.

Shanghai, the major industrial city is located on the south of the river mouth. Wusong River and Huangpu River converge in urban districts of Shanghai, then flows into the Changjiang River at Wusong mouth. In the estuary area, the complicated and specific aquatic chemical and hydrodynamic factors, resulted from mixture of fresh and salt water and different tides occurred, will exert a combined effect on distribution and migration forms of heavy metals in the water.

3 Study methods

3.1 Sampling

It was based on study objective and the environmental feature to locate sampling sites. Only three samples (No. 1, 2, 3) were collected on July 13—14, 1989 in the source area because some of the rivers were almost dried-up during the period.

Chongqing, Wuhan and Nanjing reaches were selected as representatives for the upper, middle and lower Changjiang River respectively. Again, one typical location on each upper, middle and down streams of the representatives was chosen as the contrast (4, 7, 10), control (5, 8, 11) and self-purification sites (6, 9, 12) for sampling. On May 10—12, July 6—8 and Nov. 20—22, 1989 sampling was carried out on Nanjing, Wuhan and Chongqing reaches respectively. The samples (No. 13—26) of the estuary were taken on Jan. 1986 (Wang, 1990; Liu, 1990; Chou, 1990). The locations of sampling sites are shown in Fig. 1.

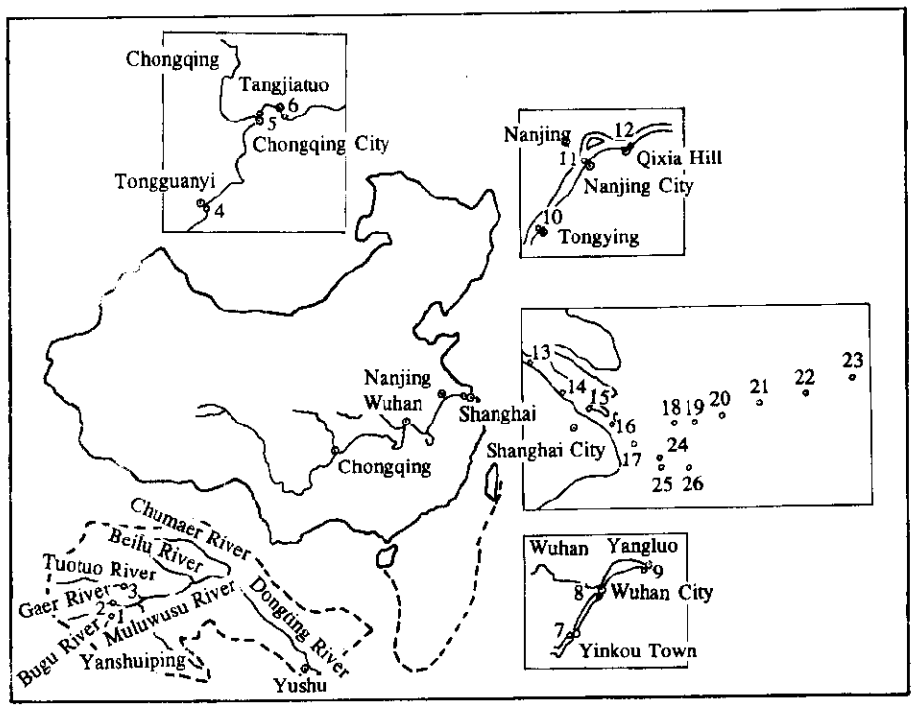

Fig. 1 Map of showing sampling sites from the source to the estuary of the Changjiang River

Polythene bottles for sample collecting and filters were cleaned successively with detergent, diluted nitric acid, deionized distilled water, then rinsed several times with sample water before collection. Membranes were cleaned successively with 5% v/v nitric acid and deionized distilled water, and then stored in the deionized distilled water before use.

Two samples were taken from approximately 10 cm under the water surface. One of them was filtered through 0.45 μm membrane as early as possible to separate suspended particles from soluble metals. Two filtrates were collected, then one of them and the other unfiltered sample were all acidified till pH being 2 with high purity nitric acid with negligible blank concentrations for determination of dissolved (*Cs*) and total metals (*Ct*). The other filtrate was not acidified and was used to determine metal species. All of the samples were taken back to the laboratory and stored under 4℃ until analysis.

3.2 Analytical methods and species classification

The heavy metal forms were measured by ASV technique with three electrode systems

which combined with UV-irradiation and Chelex-100 resin separation (Florence, 1980; Chen, 1986). The standard addition technique were used to quantify the results. Then, the contents of various forms were calculated from the data obtained.

According to the above analytical scheme, the dissolved heavymetals were first divided into two groups (Table 2): ASV labile metal (*MALi*) and bound or nonlabile metal (*MALb*), each of which was subdivided. These operationally defined species are as follows:

MALi: 1. $M+MA_1+ML_1$—— Free metal ions (or aquo ions) (M), simple inorganic (MA_1) and organic complexes (ML_1).

2. MA_2, ML_2—— These species were mainly metal adsorbed on or occluded in, inorganic (MA_2) and organic (ML_2) colloidal particles, and were not dissociated on passage through Chelex-100 resin.

The above metal species are readily dissociated under the ASV measurement conditions.

MALb: 3. MA_3, ML_3——nonlabile inorganic (MA_3) and organic (ML_3) complexes which were dissociated on passage through Chelex-100.

4. MA_4, ML_4——These species were metal adsorbed on or occluded in, inorganic (MA_4) and organic (ML_4), and were stronger inorganic (MA_4) and organic complexes (ML_4) than the corresponding metal-Chelex-100 complexes.

MALb species are hardly or not dissociated under the ASV measurement conditions.

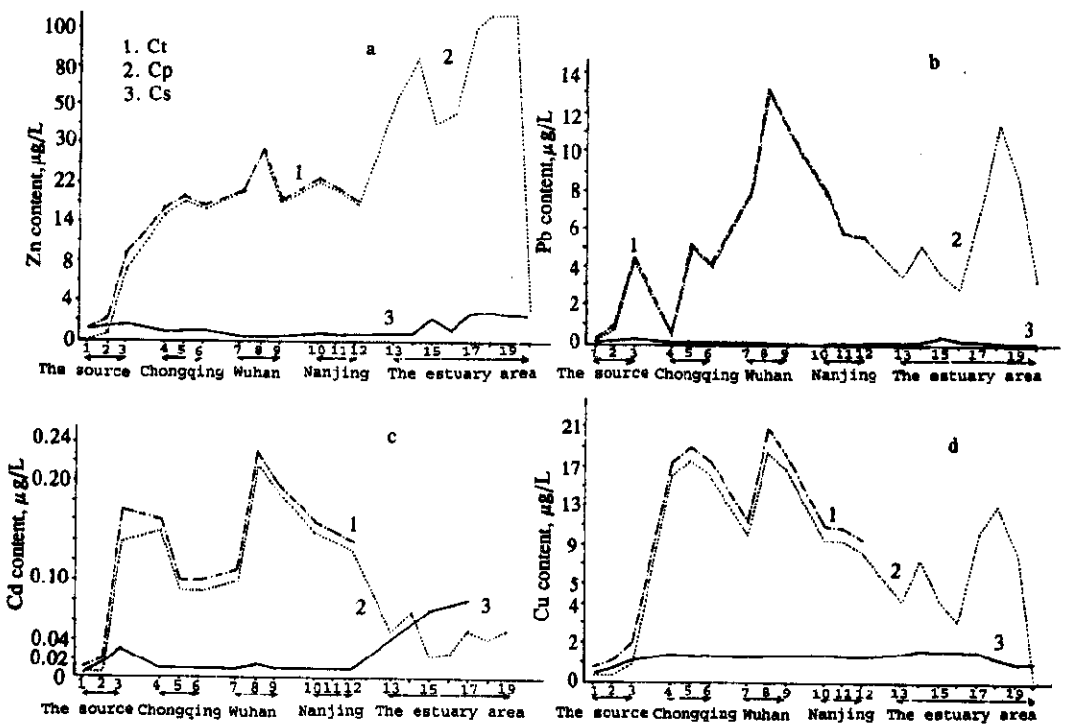

Fig. 2 The contents distribution of total (*Ct*), suspended particulate (*Cp*) and dissolved (*Cs*) Zn, Cd, Pb and Cu in the Changjiang River and the estuary water

4 Results and discussion

4.1 The total content (*Ct*) distribution of heavy metals

The content distribution of total (*Ct*), suspended particulate (*Cp*) and dissolved (*Cs*) heavy metals are shown in Fig. 2

From *Ct* curve it has been seen that in the source, total contents (*Ct*) are gradually increased in the order of sampling sites from south to north, such as total Cd content in Tuotuo River (site No. 3) is 17 times as high as in Buqu River (site No. 1). This distribution feature is mainly related to lower metal contents in limestones and sand rocks occurred predominantly in the south, where as higher contents in volcanic clastic rock of the north as well as hydrological conditions. However, their average ($\overline{C}_t$) is low, and within normal background value range of fresh water (Table 1).

Table 1 Comparison of background values (μg/L) of heavy metals in waters of the Changjiang River source to other freshwater

Waters	Zn		Cd		Pb		Cu	
	Total (*Ct*)	Dissolved (*Cs*)	Total (*Ct*)	Dissolved (*Cs*)	Total (*Ct*)	Dissolved (*Cs*)	Total (*Ct*)	Dissolved (*Cs*)
The source river	4.0	1.4	0.067	0.017	1.88	0.19	1.28	0.76
The upper Xiangjiang Xiang li fen pai... Guiyang	7.2	5.4	0.047	0.03	0.84	0.46	0.88	0.48
Xiangjiang River system	4.1	3.5						
The river water in Beijing-Tianjin area	1.4	1.3	0.016		0.74		1.01	
The second Songhua River	6.9		0.03		2.5		2.6	
The Songhua River	3.88	1.26	0.064	0.053	1.02	0.84	1.4	1.26
Beijiang River system of Zhujiang	1.68	1.60	0.09	0.06	1.42	0.84	1.49	1.30
Unpolluted freshwater in the world	8.0	1.8		0.02	0.6	0.2	1.0	0.40

In the mainstream, *Ct* was obviously higher than that in the source. However, over 90% of total metals existed in suspended particulate forms which were composed of three parts: (a) Abundant silt and sand containing-heavy metals, derived from natural circumstance. (b) Metals-containing pollutants, according to incomplete statistics, there were about 1.0×10^{10} m^3 waste water discharged into the river every year, which contained waste residues, pesticide etc. (c) The existing suspended particles associated with dissolved heavy metals in the water. From these it can be seen that all heavy metals were not drawn anthropogenically into the river water. But, the comparison of total metal contents of the mainstream to the source, and each control site to each contrast site of each reach reveal that contaminated influence on near shore water mass off cities is still marked. Besides, the total content distribution was not uniform, since the amount of metal-contained pollutants dis-

charged and contents of silt and sand of, each river reach vary during sampling period. The highest contents of total Zn, Cd and Pb appeared in Wuhan reach, whereas Cu, in Chongqing. Their average ($\bar{C}t$) were in the order of Zn (20.1 μg/L) > Cu(14.9 μg/L) > Pb (6.73 μg/L) > Cd(0.15 μg/L). In general, the total metals of each self-purification site, as a result of metals to be adsorbed, deposited and migrated, were lower and close to contrast site.

The estuary area, the mean contents (Ct) of total Zn, Cu and Pb(No. 13—17, 24—26) were: 93.6, 7.71 and 5.65 μg per liter respectively (Wang, 1990; Liu,1990).

4.2 The content (Cp) distribution of the suspended particulate heavy metals

In the source area, the content (Cp) distribution was similar to the totals(Ct; Fig. 2). Since the river water in the southern part of the area was rather clear, which contained less suspended particulate matter(SPM), while the Tuotuo River in the north was muddy, in which content(Cp) of particulate metals rose spontaneously. The mean values of ratio of Cp to Ct for three sampling sites were in the order of Pb(79.6%)>Cd(52.5%)>Cu (39.8%) ≥Zn (39.5%). The formation of suspended particulate metals in this region were, in significant extent, due to loose surface structure of the soil, dry hydrological and cold climate conditions.

In the mainstream, the content (Cp) and its proportion (%) was obviously higher than that of the source area. Reasons for this are mainly: (a) the river has abundant SPM (silt and sand) derived from the upper reaches. For example, it is known from hydrological data in 1985 that SPM content was 1.18 kg/m^3 in July and 0.15 kg/m^3 in Jan. at Hankou station; (b) dispersity of these SPM was higher, for instance, at Nanjing station, taking mechanical composition of SPM whose grain diameter < 60 μm as 100%, that of SPM with a diameter <2 μm reached 42%. These extremely small particles possessed large specific surface area, surface energy and developed surface charges which resulted in physico-chemical adsorption readily taking place at the phase interface and stable existence of SPM in the water; (c) although the major composition of clay minerals of SPM in the river is kaolinite with lower adsorbing ability, it is known that SPM consists of clay minerals and silica covered by surface coatings of hydrous iron oxide and organic matter which have a strong association with trace heavy metals. The Changjiang River contained relatively abundant organic matter and Fe, Mn compound. It has been determined that the contents of humic acid in the filtered water, SPM and sediments of the middle and lower reaches were 2, 4 and 4.6 μg/L(Tao, 1988) respectively, and total Fe and Mn in the lower reaches were about 6000 and 120 μg/L respectively. Therefore, the proportions (%) of Cp to Ct of the above heavy metals were quite high and that of Pb, Zn, Cd and Cu were 97.5, 96.6, 92.5 and 90.0%, respectively.

In the estuary, the heavy metals except for Cd were still presented in suspended particulate forms (Wang, 1990; Liu, 1990). The mean contents (Cp) of Zn, Cu, Pb and Cd for seven sampling sites (No, 13 to 17, 24 to 25) were 104.3, 7.2, 5.9 and 0.044 μg/L, respectively. Evidently, the content of Zn was higher than that in both the source and the mainstream, perhaps, which was resulted from contamination in Wusong estuary water.

Contents of Cu and Pb were all higher than the source and lower than the mainstream, but Cd, lower than both. With regard to proportion of *Cp* to *Ct*, Cu was near to 80%, Pb and Zn were all about 95%. This can be comparable with over 90% proportion of *Cp* to *Ct* for Pb, Cu and Zn fluxes when the Mississippi River flowed into the Mexico Gulf (Wu, 1982). But, both the physico-chemical and hydrodynamic variables exerted significant influence on the forms distribution of heavy metals in the river-sea mixing water. Fig. 3 shows that *Cp* (μg/L) of four elements all rise with increase of salinity and reach maximum at sampling sites No. 24 and 25, where salinity is about 25 ‰, it then rapidly drop. The causes for this non-conservative behavior of substances are as follows: (a) the high values occurred at sites No. 24 and 25 may be caused by sewage discharge from land while the sites No. 24 and 25 are on the front area of the plume front of the Changjiang diluted water; (b) gradient of salinity destroyed stability of suspended colloid or fine suspensions carrying heavy metals, and hence caused its flocculating, coagulating, aggregating, and finally settling under gravity onto the bottom sediments. These processes are in consistent with movement rule of substance in estuarine zone reported by Beckett R. (Beckett, 1986).

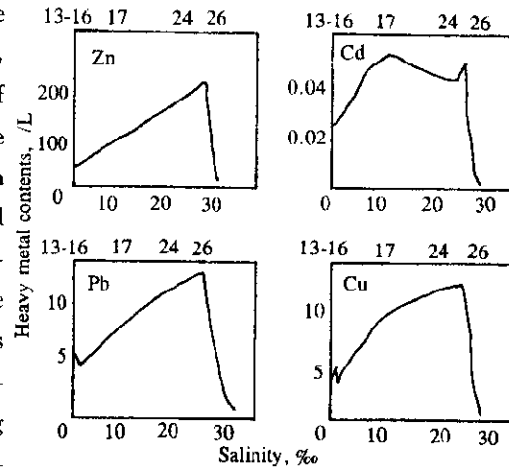

Fig. 3 The content (*Cp*, μg/L) variation of suspended particulate heavy metals with salinity (‰)

4.3 The content (*Cs*) distribution of dissolved heavy metals

In the source, the contents (*Cs*) of dissolved heavy metals were low and uniform in distribution (Fig. 2). This distribution feature was mainly decided by the environmental conditions, such as low metal concentration in most of rocks in this region, dry and cold climate resulted in weak chemical weathering, and the slightly alkaline river water benefitting elements to be deposited, etc. As a consequence, their contents (*Cs*) are within normal background value range of fresh waters in the world (Table 1).

In the mainstream, the contents (*Cs*) of dissolved metals were also low, only within the range of 0.6%—15% of *Ct*, and they were rather uniform in distribution as compared to the case of *Cp*. The mean contents (*Cs*) are in the order of Cu (1.38 μg/L) > Zn (0.65 μg/L) > Pb (0.082 μg/L) > Cd (0.01μg/L), content levels of Cu, Zn and Cd are closed to Cu (1.46 μg/L), Zn (0.2 μg/L), Cd (0.013 μg/L) of the lower Mississippi River (Shiller, 1987), respectively.

In the estuarine area (Wang, 1990), a comparison of the four dissolved metal contents (*Cs*) to the mainstream shows that *Cs* (μg/L) of Cu and Pb were almost equivalent to those of the mainstream, whereas *Cs* (μg/s) of Zn and Cd were elevated and close to three and seven times of the mainstream. Furthermore, *Cs* (μg/L) > *Cp* (μg/L) for Cd. This different distribution status were related to chemical properties of the elements and rather higher

$[Cl^-]$ in the esturarine mixed water. It is well known that complexes and adsorbed behavior increase in the series Cd<Zn<Pb and Cu (in sequence of Irwing-williams series), by contrary, their affinity to Cl^- ion decreases in the series Cd>Zn>Pb>Cu. So, as salinity i.e. $[Cl^-]$ increasing, the desorption and complexation to Cl^- of Cd then Zn prevailed against Pb and Cu, in consequence, Cs of Cd and Zn were heightened to respective level.

The results mentioned above illustrated that: the heavy metals transported mainly in suspended particulate form from the upper to the lower Changjiang River and its estuary. Finally, the majorities were deposited onto the bottom where salinity was about 25 ‰, except that Cd. In the transportation processes from river to sea water, its major existing form was converted from suspended particulate to soluble form. Lastly most of which was maintained in mixed water in the soluble form.

4.4 Various forms distribution of dissolved metals

Forms distribution of dissolved metals, expressed as a percentage of the dissolved metals, are shown in Table 2 along with pH.

Table 2 The contents (*Cs*, μg/L) and speciation (%) of dissolved Zn, Cd, Pb and Cu in the Changjiang River water

Metals	Sampling waters	Sites No.	pH	*Cs*	$M+MA_1+ML_1$	MA_2	ML_2	MA_3	ML_3	MA_4	ML_4
Zn	The source river	1	7.82	1.1	36.4	18.0	27.3	9.1	0	9.1	0
		2	7.86	1.5	30.0	8.0	25.3	26.7	0	10.0	0
		3	8.00	1.6	28.1	6.2	21.9	25.0	0	15.6	3.1
	The upper	4	7.45	0.85	0	0	0	35.3	5.9	47.1	11.8
		5	7.58	0.90	0	0	0	33.3	11.1	44.4	11.1
		6	7.66	1.0	0	0	0	30.0	5.0	45.0	20.0
	The middle	7	6.92	0.4	0	0	0	25.0	0	50.0	25.0
		8	7.46	0.4	0	0	0	25.0	0	50.0	25.0
		9	7.00	0.4	0	0	0	25.0	0	50.0	25.0
	The lower	10	7.45	0.68	0	0	0	36.8	0	44.1	19.1
		11	7.35	0.60	0	0	0	25.0	0	41.7	33.3
		12	7.61	0.66	0	0	0	30.3	0	39.4	30.3
Cd	The source river	1	7.82	0.005	100.0	0	0	0	0	0	0
		2	7.86	0.015	66.7	0	0	33.3	0	0	0
		3	8.00	0.03	33.3	0	33.3	33.3	0	0	0
	The upper	4	7.45	0.01	50.0	0	0	50.0	0	0	0
		5	7.58	0.01	50.0	0	0	50.0	0	0	0
		6	7.66	0.01	50.0	0	0	50.0	0	0	0
	The middle	7	6.92	0.01	50.0	0	0	50.0	0	0	0
		8	7.46	0.015	33.3	0	0	33.3	0	33.3	0
		9	7.00	0.01	50.0	0	0	50.0	0	0	0
	The lower	10	7.45	0.01	50.0	0	0	50.0	0	0	0

Table 2 (continued)

		11	7.35	0.01	50.0	0	0	50.0	0	0	0
		12	7.61	0.01	50.0	0	0	50.0	0	0	0
Pb	The source river	1	7.82	0.10	20.0	10.0	0	30.0	0	30.0	10.0
		2	7.86	0.18	16.7	5.6	0	38.9	5.6	27.8	5.6
		3	8.00	0.28	17.9	3.6	3.6	37.5	3.6	30.4	3.6
	The upper	4	7.45	0.088	11.4	0	0	20.4	0	60.2	8.0
		5	7.58	0.10	10.0	0	0	25.0	0	55.0	10.0
		6	7.66	0.075	13.3	0	0	20.0	6.7	46.7	13.0
	The middle	7	6.92	0.081	12.4	0	0	24.7	0	50.6	12.4
		8	7.46	0.085	11.8	11.8	0	17.6	0	41.2	17.6
		9	7.00	0.067	0	14.9	0	22.4	0	44.8	17.9
	The lower	10	7.45	0.085	11.8	0	0	17.6	0	58.8	11.8
		11	7.35	0.080	12.5	0	0	17.5	0	51.2	18.8
		12	7.61	0.080	12.5	0	0	16.2	0	50.0	21.2
Cu	The source river	1	7.82	0.43	13.9	0	0	0	30.2	25.6	30.3
		2	7.86	0.75	13.0	0	0	6.7	29.3	20.0	31.0
		3	8.00	1.10	22.7	0	13.6	4.6	23.6	11.8	23.7
	The upper	4	7.45	1.40	7.1	0	0	7.1	21.4	21.4	42.91
		5	7.58	1.35	7.4	0	0	2.2	33.3	18.5	38.5
		6	7.66	1.38	7.2	0	0	3.6	32.6	21.7	34.8
	The middle	7	6.92	1.35	7.4	0	7.4	4.4	18.5	20.0	42.2
		8	7.46	1.38	7.2	0	7.2	2.9	20.3	21.7	40.6
		9	7.00	1.38	7.2	0	7.2	2.9	23.9	18.1	40.6
	The lower	10	7.45	1.40	7.1	0	7.1	6.4	25.7	15.0	38.6
		11	7.35	1.38	7.2	0	7.1	5.8	28.3	15.2	36.2
		12	7.61	1.39	7.2	0	7.2	4.3	29.5	14.4	37.4

4.4.1 Zinc

In the source, it mainly existed in labile form (*MALi*), which was similar to present form in background waters of Xiangjiang and Hengjiang Rivers. Based on aquatic chemical properties of Zn and pH, aquatic quality type of the river water etc., it is deduced that major composition of labile forms were $ZnOH^+$ then $ZnHCO_3^+$, Zn^{2+} and $ZnCl^+$. In the mainstream, in contrast to the source, all zinc was present in bound form, in which a high proportion of dissolved Zn(~70%) was associated with inorganics. This reflected variations of the environmental conditions from the source to the mainstream. In the Changjiang River valley, owing to strong chemical weathering and leaching of soil surface matter under the influence of climate and hydrologics, in addition to anthropogenic effects, the main stream had higher concentrations of inorganic and organic adsorbing matter, and complexing agents than

the source, their adsorbing and complexing to Zn suppressed dissolved zinc content (*Cs*).

4.4.2 Cadmium

In the source, was similar to Zn in speciation distribution, its composition, perhaps, was Cd^{2+}, $Cd(H_2O)_6^{2+}$and $CdCl^+$, and next was $CdHCO_3^-$ according to aquatic chemistry of Cd and the environmental conditions of the river water. In the mainstream, Cs of Cd was much lower, it was approximately equally divided between ($M+MA_1+ML_1$) and MA_3 forms.

4.4.3 Lead

Because of strong adsorbed and complexed properties of Pb, especially by inorganic colloidal species at pH of natural water, the predominant form of lead was bound inorganic forms (MA_4+MA_3) in the Changjiang River water, while the proportion of MA_4 form rose to 40%—50% in mainstream. Based on speciation models for Pb in freshwater (Florence, 1980), geochemical phase associated with Fe-Mn in the sediments of the river source, having good correlativily to Fe in SPM of the river estuary (Liu, 1990) and pH>7 of the river water, it is considered that MA_3 form is a basic carbonate, e.g., $Pb_2(OH)_2CO_3$ and MA_4 is Pb adsorbed on inorganic colloidal particles consisted of hydrated ferric oxide, manganese dioxide, silica and soil minerals etc. This speciation distribution results in a low dissolved concentration, being <0.1μg/L.

4.4.4 Copper

In the Changjiang River water, non-labile organic form (ML_3+ML_4) was important dissolved species of Cu, which was also primarily associated with organic matter in the sediments of the source. Owing to the similarity of outer electron configurations of Cu to that of transition metals, Cu becomes a strong complex former. Its stability constant complexes with fulvic acid is higher than the other three metals. It has been determined (Tao, 1988) that the major component of humates, in the mainstream water, was lower-molecular weight, more easily soluble fulvic acid with stronger complexing ability to Cu than humic acid. The fulvic complex Cu to form easily dissolved species, in addition, other organic ligands presented can also complex Cu forming molecular complexes.

Therefore, the proportion of (ML_3+ML_4) form was, as contrast to the source, increased to 60%—70%, Cs (μg/L) of Cu was also elevated, toxic Cu^{2+} ion concentration was reduced.

Dissolved species of Pb and Cd in the estuary area (Chou, 1990).

The mean proportions of various forms contents to total dissolved content (*Cs*) were: *MAb* (bound inorganic forms corresponding to MA_3+MA_4, 41%) > *MALi* (labile forms corresponding to $M+MA_1+ML_1+MA_2+ML_2$, 31%) > *MLb* (bound organic forms corresponding to ML_3+ML_4, 28%) for Cd, and *MAb* (40%) > *MALi* (39%) > *MLb* (21%) for Pb. But, as Pb and Cd were transporting from the river to sea, the contents (μg/L) and the proportion (%) of their labile forms would rise with increase of salinity in the off shore direction, whereas those of the bound organic forms (*MLb*) would decease in the same direction. This phenomenon is mainly attributed to the increase of ionic strength which cause Pb

and Cd disorped from colloids and dissociated of complexes Pb and Cd. In addition, concentrations of organic matter are found to be decreases with the increase of salinity. These species features in distribution are basically in agreement with the results that the proportion of heavy metals complexes with organic ligands decreased with the increase of salinity reported by Mantoura (Mantoura, 1978).

In summary, river water in the source area is clear, whereas, from the mainstream to the estuary, the near-shore water off cities has been contaminated to some extent. In the waters the above discussed heavy metals always presented in their respective major forms with several other forms which varied with change of environmental conditions in the migration processes in which SPM, organic matter and carbonate all played an important role.

References

Beckett R. Water quality management-The role of particulate matter in the transport and fate of pollutants (Ed. by Hart BT). Water Studies Center Chisholm Institute of Technology Melbourne. 1986:129

Chen XB, Zhang S. China Environmental Science, 1986; 6(2):131

Chen XB, Zhang S, Ying WM, Zhao GY, Chen H. Studies on the water environmental background values of chemical elements (Ed. by Zhang Shen). Beijing: Surveying and Mapping Press. 1990:105

Chou FQ, Qian G. Biogeochemical study of the Changjiang Estuary (Ed. by Yu GH). Beijing: China Ocean Press. 1990: 312

Florence TM, Batley GE. CRC Critical Reviews in Analytical Chemistry, 1980; 9(3):219

Gao GS, Chen JS. Environmental Chemistry, 1983; 2(4):28

Hart BT, Davies SHR. A study of the physico-chemical forms of trace metals in natural water and wastewaters. Canberra: Australian Government Publishing Service. 1978

Leppard GG. Trace element speciation in surface waters and its ecological implications. New York: Nato Conference Series, Plenum Press. 1983

Liu DZ, Liu GY, Shao MH. Biogeochemical study of the Changjiang estuary (Ed. by Yu GH). Beijing: China Ocean Press. 1990:347

Mantoura RFC, Andrew Dickson, Riley JP. Science, 1978; 6(4):387

Shiller AM, Boyle EA. Geochim Cosmochim Acta, 1987; 51(12):3273

Tao S, Chen JS, Deng BS, Cao XL, Ren JS. China Environmental Science, 1988; 8(3):286

Wang ZF, Zhang BZ, Zhang J, Lu Y. Biogeochemical study of the Changjiang Estuary (Ed. by Yu GH). Beijing: China Ocean Press. 1990:283

Wu DH, She ZS, Ren SF, Hong F, Qiu JW. China Environmental Science, 1983; 3(2):101

Wu YD. Oceanic environmental chemistry. Beijing: Science Press. 1982:85

(Received May 24, 1995)