

The chemical stability of heavy metals in a natural water system

Tang Hongxiao,¹ Xue Hanbin¹, Mao Meizhou¹, Luan Zhaokun¹

(Received December 6, 1988)

Abstract—A comprehensive investigation of heavy metal pollutants in Xiangjiang river was accomplished to evaluate their chemical stability through three different ways: (1) Chemical speciation by direct measurements; (2) Chemical equilibrium model simulation; (3) Sediment extraction experiments. All the results demonstrated that the directly bioavailable fraction was in a very limited amount. The metal bound to organic ligands, adsorbed particles and precipitated species presented a buffer for solution species. The majority of metals occurred in the residues as solid particulates. It was inferred that the heavy metal pollutants in this aquatic system exhibited a high chemical stability. The critical limits of discharging load and pH values were suggested.

Keywords: chemical speciation; chemical equilibrium model; heavy metal.

INTRODUCTION

It is generally recognized that the bioavailability and ecotoxicity of heavy metal pollutants would be in accordance with their chemical form of species but not with their total quantity. The heavy metals discharged into natural aquatic systems will be submitted to a whole complex of physical, chemical and biological processes. The chemical species distribution and their transformation are largely dependent on the environmental conditions. To identify the bioavailable fraction of the total amount under various conditions and to evaluate the chemical stability of pollutants would give a new basis for drawing up the loading capacity and discharging limit of heavy metals in a water body according to their chemical speciation.

Xiangjiang is a big tributary stream of Yangtze River. It stretches for more than 800 km in Hunan province of middle-southern China. In this valley, the mineral resources of heavy metals are quite abundant. Therefore, the pollution of Pb, Cd, Cu from mines and smelters on several sections of the river became noticeable problems to aquatic environment since a huge amount of polluted bottom sediments accumulated there. For about 6 years, more than 10 institutions have worked on the river to investigate the status and dangers, to fix the pollution control measures and to draft a suitable water quality management plan. Many results have been obtained, the content of this paper is just one of them.

We studied the chemical speciation and chemical stability of the metals through three different ways, i.e., direct measurements, computer simulation and extraction experiments. This part of investigation was aimed at a river section named Xiawan near a large smelter of Zhushou which has discharged waste water excessively and polluted the area heavily.

SAMPLING AND MEASUREMENTS

From 1982 to 1984, many batches of samples including water, suspended solids and bottom sediments were collected near the drainage along the discharging course in the river. The sampling sites were located as described in Fig. 1. S0 is an unpolluted reference point, S2 is a

¹Research Center for Eco-Environmental Sciences, Academia Sinica, P.O.Box 934, Beijing 100083, China

less polluted upstream point. S1 is at the drainage exit. S3-S5 are in the main polluted section. S6 and S7 are in the restoring section with a distance of more than 5 km from S1.

Besides Cd, Cu, Pb, Zn, Hg and other metals, the measured items included ion composition, TOC and organics etc. Except chemical methods, the equipments used were ICP, AAS, ASV, UVS, IC, TOC and Coulter Counter, etc. The results of major ions composition were contrasted with the hydrochemical data during 1954-1980 from a hydrological station nearby.

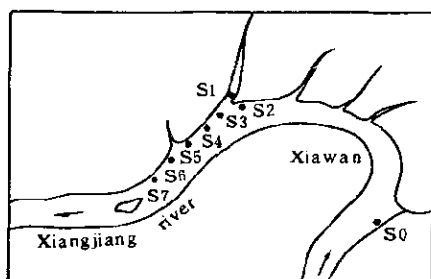


Fig.1 Sampling locations

Chemical speciation of sediments

The total contents of heavy metals in sediments decreased progressively from S1 to S7, such as Cd (75 to 20 ppm), Cu (800 to 280 ppm) and Pb (2800 to 430 ppm). Speciation was carried out by a modified sequential chemical extraction procedure. The fractionated species are: 1. water soluble; 2. cation exchangeable; 3. carbonate bound; 4. easy reducible; 5. moderate reducible; 6. organic-sulfide bound and 7. residues (soluble in aqua regia).

Table 1 Chemical speciation

Metal	Species 1-7 distribution, %						
	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Cu	0.1-0.5	0.1-1.5	0.2-0.8	-	18-31.1	28.4-11.3	52.9-68.2
Cd	0.1-0.3	9.1-20.9	7.5-10.3	9.8-13.5	7.6-10.8	13.0-3.5	53-74.1
Pb	0.1-0.1	0.2-1.0	0.2-0.9	0.6-1.2	0.6-1.7	13.5-1.6	84-93

The statistical figures in table 1 show that the contents of species 1 and 2, which we called it direct bioavailable fraction, is in a range of 1-1.5% (Cu and Pb) and 10-20% (Cd), species 3-6, the so called buffer fraction, in 10-30%, species 7, i.e. inert residues, in 50-90%.

Accordingly, the above measurements show that most parts of heavy metals in the sediments occurred in the residue and heavy fraction, which took the form of solid particulates with crystal structure. This part may be originated from the ore and slag pieces which would exhibit a high chemical stability.

CHEMICAL EQUILIBRIUM MODEL SIMULATION

Natural water body is a multiphase and multicomponent system. In order to predict the species distribution of components at the equilibrium condition, for the simulation of Xiangjiang aquatic system, we selected and modified a widespread REDEQL-2 program. The calculation was performed on a UNIVAC 1100/10 computer.

The model of Xiangjiang river aquatic system includes 12 metals and 12 ligands together with H^+ and OH^- . The principal constitution is listed in Table 2. Their basic concentrations were determined by directly measured data referred to the hydrochemical data over the years.

Where, HA represents the organic ligand mainly of the humic substances, and AD represents the solid suspended adsorbents mainly of the clay minerals. The numeration of components remained in database of program REDEQL-2. This model system involves 134 coordination, 49 precipitation and 5 redox reactions. Except the conditional complexation stability constants of HA and AD, all the other reaction constants were cited from the REDEQL-2 data base.

Table 2 Basic constitution of the model

No.	metals	mmol	-log (mol)	No.	ligands	mmol	-log (mol)
1	Ca	0.68	3.17	1	CO ₃	1.75	2.76
2	Mg	0.16	3.81	2	SO ₄	0.08	4.10
4	K	0.04	4.40	3	Cl	0.05	4.30
5	Na	0.27	3.59	4	F	0.01	5.00
6	Fe(III)	1.00	3.00	7	NH ₃	0.10	4.00
7	Fe(II)	1.00	3.00	8	S	0.10	4.00
8	Mn	1.00	3.00	9	PO ₄	0.01	5.00
9	Cu	10 ⁻³	6.00	14	CN	10 ⁻⁶	9.00
11	Cd	10 ⁻⁴	7.00	15	HA	10 ⁻³	6.00
12	Zn	0.01	5.00	16	AD	0.25g/L	0.60
14	Hg	10 ⁻⁵	8.00	54	AsOH ₄	10 ⁻⁴	7.00
15	Pb	10 ⁻³	6.00	57	NO ₃	0.10	4.00
50	H	10 ^{-4.5}	7.50	99	OH	10 ^{-3.5}	6.50
pH=7.50				pE=6.00			

Complexation constants

The organic complexation agents in natural water are difficult to be identified by species. They are often characterized by the complexation capacity and stability constant, which are usually determined with voltammetry technology. In Xiangjiang water, the contents of organic ligands, mainly the humic substances, are low (10⁻⁷-10⁻⁸ mol/L). Their parameters were determined by anodic stripping voltammetry method. The equation used is:

$$\frac{[M]}{CM - [M]} = \frac{1}{K \cdot CL} + \frac{1}{CL} [M]$$

where, $[M]$ is free metal ion concentration, CM is total metal concentration, CL is total concentration of organic ligands representing the maximum complexation capacity, K is conditional stability constant. CL and K can be estimated respectively from the slope and intercept of the linear plot of $[M]$ vs $[M]/CM - [M]$. The results are listed in Table 3.

Table 3 Complexation capacities and constants

Metal	Complexation capacity, μ mol/L			log K		
	dry season	ordinary	average	dry season	ordinary	average
Cu	0.12	0.16	0.15	7.43	8.07	7.90
Cd	0.042	0.037	0.034	8.47	8.55	8.50
Pb	0.19	0.14	0.16	8.08	7.95	8.00

Adsorption constants

In this model, the adsorption process was taken as complex reaction and the suspended solid was simplified as a ligand similar to anion. Thus surface complexation constants were taken as conditional partition coefficients, which vary with the pH value. From the mass balance expression of adsorption, we have:

$$K_{ad} = \frac{[SM][H^+]^m}{ST[M]} = G \frac{[H^+]^m}{[M]}$$

where $[M]$ is the equilibrium concentration of metals in solution, $[SM]$ is the amount of the metal bound to solid phase (mol/L) and ST is the solids concentration (g/L). The conditional constant $K = G/[M]$ with pH correction will be:

$$\log K = \log K_{ad} + mpH$$

The adsorption isotherms of Cd are shown in Figure 2 as an example. The expressions of $\log K$ vs. pH are drawn as the following:

Cu : pH < 6.0 $\log K = 0.53$ pH - 2.15, pH > 6.0 $\log K = 0.83$ pH - 3.95;

Cd : pH < 6.6 $\log K = 0.29$ pH - 1.56, pH > 6.6 $\log K = 1.12$ pH - 7.07;

Pb : pH < 5.8 $\log K = 0.48$ pH - 1.63, pH > 5.8 $\log K = 0.89$ pH - 4.01;

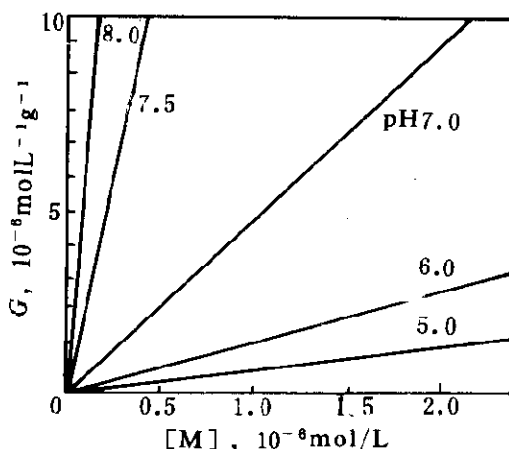


Fig.2 The isotherms for adsorption of Cd onto suspended sediments

MODEL SIMULATION FOR DISCHARGING CASES

Basic conditions

The data listed in Table 2 represent the basic conditions of the aquatic system of Xiangjiang river upon the bed. The total concentrations of components were taken as input of the program to evaluate the distribution of species. Some results for concentrations of Cu, Cd, Pb species higher than 10^{-12} mol/L and the amount of metals bound to HA and AD are listed in Table 4.

The results show that all the free ion concentrations are below 10^{-8} mol/L i.e. about 0.5–1.0 ppb. If the sum of free ions and inorganic complexation species are considered as direct bioavailable fraction, then, this content for Cu, Cd, Pb would be 1.56, 0.65, 21.57 ppb respectively. The organic and solid surface complex species make up the most part (90–97%) of the total metals. Cu and Zn species are dominant respectively in the organic complexes and the solid surface complexes. All three metals are not precipitated under current conditions.

The pH effects

In the range of pH 4–10, the pM–pH diagrams of Cu, Cd and Pb species ($> 10^{-12}$ mol/L) were calculated and presented in Fig. 3. The pH effects were tremendous, but became moderate

at pH range of the natural water (pH value 6–8). We classified the metal species further into five kinds: (1) free ions (MeFR), (2) sum of the inorganic complexes (MeIN), which is illustrated in Fig.3 with dotted curves, (3) organic complexes (MeHA), (4) adsorbed species (MeAD) and (5) precipitates (MePP). Besides, there were (6) residue species (MeRS) which, generally, consist of crystalloid solids.

Table 4 Results of model simulation under basic conditions

species	pM	%	species	pM	%	species	pM	%	species	pM	%	species	pM	%
Cu ²⁺	8.15	0.71	Cd ²⁺	8.26	5.46	Pb ²⁺	8.16	0.69	CuHA	7.09	8.10	CuAD	6.55	7.16
CuCO ₃ ⁰	7.78	1.66	CdCO ₃ ⁰	11.4	.004	PbO ₃ ⁰	7.09	8.13	MgHA	9.57	0.03	CdAD	7.56	0.70
CuSO ₄ ⁰	9.87	0.01	CdSO ₄ ⁰	9.99	.10	PbSO ₄ ⁰	9.48	.03	MnHA	7.78	1.70	ZnAD	5.56	60.9
CuCl ⁺	11.9		CdCl ⁺	10.1	.009	PbCl ⁺	10.8	.001	CuHA	6.16	69.2	PbAD	6.06	22.1
CuF ⁺	11.9	-	CdOH ⁺	9.79	.016	PbOH ⁺	7.79	1.62	CdHA	7.17	6.70			
CuPO ₄ ⁻	11.6	-	CdHA	7.17	66.9	Pb(OH) ₂ ⁰	9.70	.019	ZnHA	7.17	6.80	ΣM	5.40	98.9
Cu(CO ₃) ₂ ¹²⁻	10.8	.002	CdAD	7.65	27.8	PbHA	7.57	2.69	HgHA	8.02	0.90			
CuOH ⁺	8.58	0.26				PbAD	6.06	86.9	PbHA	7.57	2.70			
Cu(OH) ₂ ⁰	11.6	-							ΣHA	7.41	3.90			
CuHA	6.16	69.2												
CuAD	6.55	28.2												

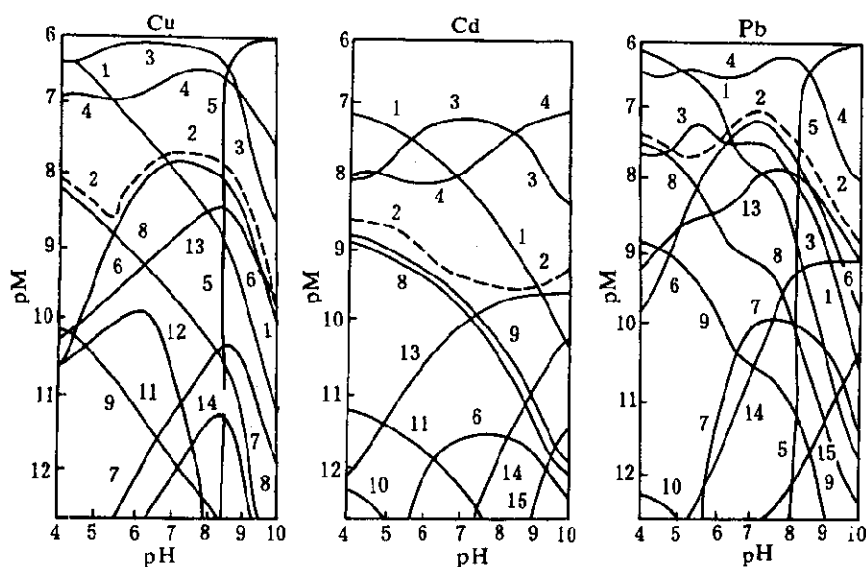


Fig.3 pH-pM diagrams of Cu, Cd and Pb species.

1.MeFR, 2.MeIN, 3.MeHA, 4.MeAD, 5.MePP[Me(OH)₂(S)], 6.MeCO₃⁰, 7.Me(CO₃)₂²⁻, 8.MeSO₄⁰, 9.MeCl⁺, 10.MeCl₂⁰, 11.MeF⁺, 12. MePO₄⁻, 13. MeOH⁺, 14. Me(OH)₂⁰, 15. Me(OH)₃⁻

As shown in Fig.3, the MeFR contents decreased as the pH increased. Above pH 7 they remained only 10⁻⁸ mol/L or less. The MeIN contents were often lower than 5% of the total metal contents except PbIN at medium pH range. The MeHA contents were dominant for Cu and Cd at medium pH range but for Pb it was lower than 10% at all pH values. On the other hand, the MeAD contents for Cu and Cd could be compared to MeHA, MeAD content for Pb was dominant before the existence of MePP. As for MePP in this system, the hydroxides of Cu and Pb precipitated above pH 8.

Concentration effects

The change of total concentrations of metals will effect the distribution of their species. Under the basic conditions with varying total metal concentrations the computation for species distribution has been performed. The ratio and concentrations of metals are $[Cu] = 10[Cd] = [Pb] = 10^{-4} - 10^{-7} \text{ mol/L}$. Their diagrams of $C(\%)$ vs. pM are shown in Fig. 4.

The diagrams showed that for Cu and Cd, the MeHA species were dominant at low concentrations, the MeAD species became to be dominant as the concentration increased and the carbonate precipitates (MePP) became to be dominant as the concentration continued to increase. For Pb, the MeAD species were dominant until carbonate precipitation occurred. Therefore, at $pH=7.5$, if the concentrations were high enough, all three metals tended to precipitate as carbonates.

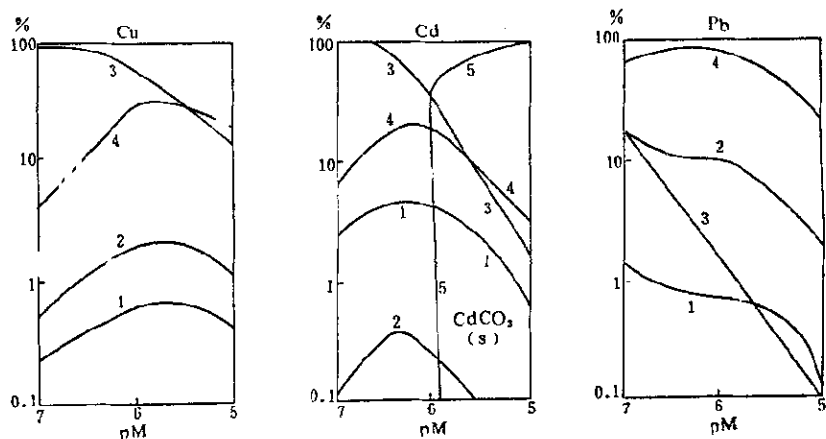


Fig.4 Distribution of metal species in various concentrations, $[Cu]=10[Cd]=[Pb]$

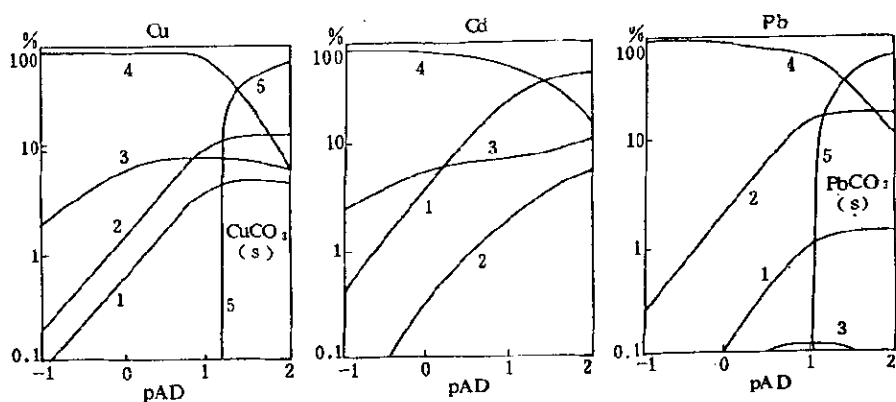


Fig.5 Distribution of metal species in various contents of suspended sediments, $(HA=10^{-6}M)$

Computation under various conditions

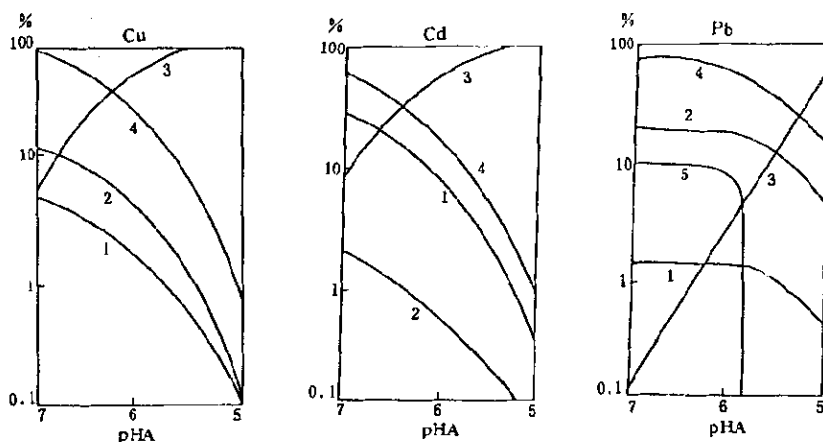


Fig.6 Distribution of metal species in various contents of humic substances ($pAd=0.6$)

In addition, the chemical species distribution of metals under other conditions has been also calculated (Fig. 5 and Fig. 6). It included the responses of a variety of HA or AD contents, redox potentials etc..

EXTRACTION EXPERIMENTS FOR METAL RELEASE FROM SEDIMENTS

In order to observe the release of metals from polluted sediments some static and dynamic model experiments were carried out in laboratory under different conditions.

Static experiments

The static release experiments were performed with the sediment samples collected at S1-S5 sites in Xiangjiang river. These samples were contacted with unpolluted river water and the evolution of metal concentrations in water was monitored from time to time. An example of the results is shown as Fig. 7. At first period of contact, the concentrations of metals in water increased, mostly, owing to the release from concentrated pore water in sediments. 2-3 days later, the concentrations began to decrease, perhaps, because of the transformation reactions of complexation, adsorption or precipitation in new system. After 30-40 days, it reached to an equilibrium state and remained to be constant within 150 days or more. This equilibrium concentration may be regarded as a resulted value by the distribution between the sediment and water under static condition.

Dynamic experiments

Under the flowing water condition a series of dynamic model experiments have been performed. Three different environmental states i.e. strong oxidizing ($E_H = 140-180\text{mV}$), weak oxidizing ($E_H = 50-70\text{mV}$) and reducing ($E_H = \pm 20\text{mV}$) cases were created by aeration with air or nitrogen. A typical example of the results is shown as Fig. 8.

The evolution of released metal concentrations in effluent were similar to that under static conditions. In the first day, the effluent concentrations increased to maximum, at about tenth day or later, it began to decrease and an equilibrium state was established after 40 days. It was inferred that the increase of concentrations was due to the change of environmental conditions and after the transformation the release decreased to a stable level.

All the experimental results demonstrated that the release level is higher under oxidizing conditions than that under reducing conditions, but when the equilibrium state was attained the difference among three conditions was not very large. The inductive data showed that the release metal concentrations in reducing environment were: $\text{Cu}=6-15\text{ppb}$, $\text{Cd}=0.96-1.5\text{ppb}$,

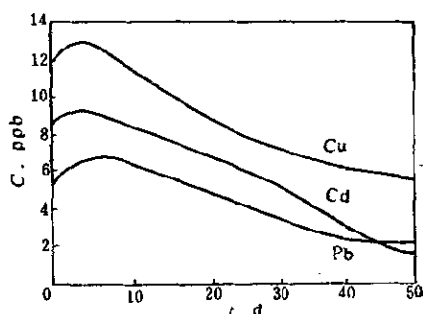


Fig.7 Release of metals in static environment

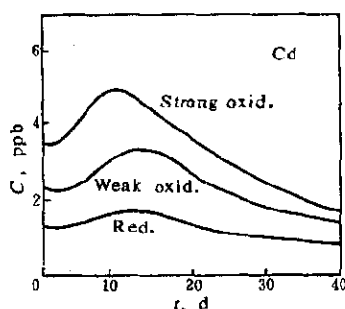


Fig.8 Release of cadmium in dynamic environment

Pb=1.2-6 ppb, and in oxidizing environment were: Cu=18-30 ppb, Cd=1.6-3.2 ppb, Pb=3.4-8 ppb.

In addition, the release experiments under various pH values were also performed. At pH=5, only the release concentration of Cu became to be over 10 ppb. At pH=7-8, the normal condition in the river, all the equilibrium concentrations were below 4 ppb.

DISCUSSIONS

Classification of metal species

In this paper, we classify the metal species into six kinds belonging to three categories as shown in Table 5:

Table 5 Class of metal species in aquation system

Categories	Kinds	Abbrev.
1. Direct bioavailable fraction	(1) Free ions,	MeFR
Soluble species	(2) Inorganic complex	MeIN
2. Buffer fraction	(3) Organic complex	MeHA
Bound species	(4) Adsorbate	MeAD
	(5) Precipitate	MePP
3. Inert fraction	(6) Residue	MeRS
crystalline species		

The first category including the metal species of MeFR and MeIN may be regarded as soluble or direct bioavailable fraction which would exert substantial effects on aquatic biota. Of course, including in this category all the inorganic complex species is a simplified practical approach. In fact, part of them cannot be uptaken even under digestive conditions. However,

such a classification would be rather more reliable in toxicity assessment, although some organic complexes may also be absorbed even readily.

The second category, buffer fraction, includes the bound species such as MeHA, MeAD and MePP. They are in equilibrium with free ions in solution and possess similar features like a buffer. They can give out ions to the solution under certain conditions, but draw them back from the solution under other circumstances. They may be bioavailable indirectly and possess potential effects on biota.

The third category is the analytical residue species (MeRS), inert fraction. They generally consist of crystalloid solids and tend to be chemical stable and inert to biota in natural aquatic system.

This classification can be related to some methods of measurements roughly. The first category of soluble species approximately corresponds to the contents in the filtrate passed through the 0.45μ or 0.2μ membrane, which is commonly used to determine the soluble components as the parameters in water quality standards.

In addition, this fraction could be determined approximately by the voltammetry methods in medium pH range (existing in natural water). The second fraction as bound species could also be determined with this method but in low pH ($< \text{pH } 3$) and deducted the quantity of the first fraction.

Indeed, take the voltammetrically determined species as the soluble and even direct bioavailable portion may be an over-simplified approach, but many inorganic complexes with such ligands as Cl^- , OH^- , CO_3^{2-} and SO_4^{2-} are electrochemically labile as well and there are no other alternative simple methods for the determination of the bioavailability. It would be convenient to set a conventional procedure by this method for the determination of the species distribution of metals in natural water system to divide them into three categories as direct bioavailable, buffer and inert fractions.

Direct bioavailable fraction

The sum of MeFR and MeIN may be regarded as direct bioavailable fraction of metals. Their contents under various conditions were calculated. The results are illustrated by diagrams of C(ppb) vs. pM and C(ppb) vs. pH as shown in Fig. 9. The concentrations of this fraction for three heavy metals possess a positive interrelation with the total concentrations and a negative interrelation with the pH value. The contents of these species for Cu, Cd and Pb, even in the case of $\text{pH}=7.5$ and $[\text{Cu}]=10$ $[\text{Cd}]=[\text{Pb}]=10^{-6}\text{mol/L}$, will be only 19.07, 7.08 and 45.57 ppb and in the case of $\text{pH}=5$, $[\text{Cu}]=10$ $[\text{Cd}]=[\text{Pb}]=10^{-6}\text{mol/L}$, will be 10.10, 6.40 and 73.77 ppb respectively.

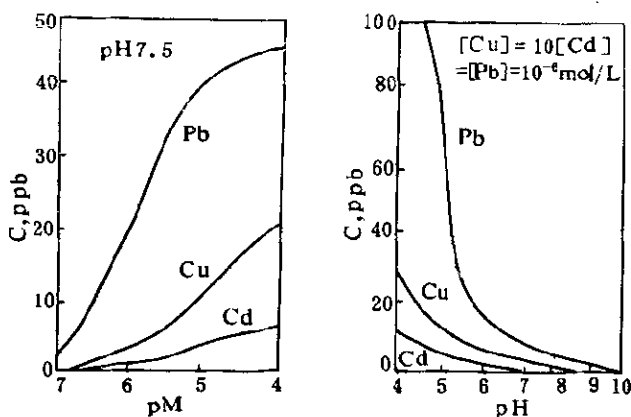


Fig.9 The concentrations of direct bioavailable species under various conditions

Permissible concentration limit

The results obtained by chemical equilibrium model simulation were consistent well with those by chemical speciation measurements and model release experiments.

According to the existing standard in China for permissible concentration limits in water body of the third class, the highest permissible for Cu, Cd and Pb are 30, 10 and 100 ppb respectively. If these parameters were determined after filtration through 0.45μ membrane, they could be compared with the direct bioavailable fraction in this paper. Consequently, by the model computation data, the permissible concentration limits for total metal contents in water body i.e. discharging load in Xiangjiang river at its normal pH=7.5 could be loosened to a level of $[Cu]=10^{-4}$ mol/L (6.5 mg/L), $[Cd]=10^{-5}$ mol/L (1.2 mg/L), and $[Pb]=10^{-4}$ mol/L (20 mg/L).

Even if the permissible limit could be set as the sum of direct and buffer fractions, which made up around 10–50% of total metal content, it would be much more beneficial to save the investment water pollution control facilities.

The chemical stability

On the basis of comprehensive investigation through the three approaches described above, it can be inferred that the heavy metal pollutants in the Xiangjiang river aquatic system tends to be chemically stable. Under normal aquatic conditions and the usual discharging load to this river, the concentrations of soluble species for Cu, Cd and Pb are about 10, 5 and 20 ppb respectively. The bottom sediments, though contained a large quantity of metal pollutants, are in principle chemical stable, because the inert residues have made up about 50–90% of the total metal content. Thus, there is no need to dredge out the accumulated sediments.

For the control of discharging load to this river, it was suggested that the chemical stable area may be: at pH=7.5, the critical limits of total metal concentrations in water should be $[Cu]=10[Cd]=[Pb]=10^{-4}$ mol/L to $[Cu]=10[Cd]=[Pb]=10^{-6}$ mol/L, the critical pH value in water should be 5.0.

The chemical stability and its critical pM–pH diagrams may be more useful and suitable for evaluation the potential effects of heavy metal pollutants in an aquatic system.

Acknowledgements—In addition to the authors, the participants to this work are also Li Jing, Bai Naibin, Cui Chunguo, Liu Zihui, Tian Baoshen, Dong Huiru, Cao Fucang, Fu Yan, Lei Pengju, Wei Jinxi. Authors are grateful for the discussion on this paper with Professor W. Stumm of Institute EAWAG at Zürich.

REFERENCES

- Lu Zongpeng, Mao Meizhou, Wei Jinxi, *Environmental inorganic chemistry*, Verlag Chemie Intern. Co., 1984 pp 373–391
- Mao Meizhou, Liu Zihui et al., *Environmental Chemistry*, 1982, 1(2): 168–175
- MuDuff, R.E., Morgan, J.J., *Tech. Report EQ-75-01*, Keck Lab. Calif. Inst. Tech., 1976
- Stumm, W., Morgan, J.J., *Aquatic Chemistry*, 2nd ed., John Wiley & Sons, 1981
- Stumm, W., Brauner, P.A., *Chemical Oceanography*, Vol.1, p173, 2nd ed., Academic, New York, 1975
- Tang Hongxiao, *Environmental Sciences in China*, 1985, 5(5):38–43
- Tang Hongxiao, Xue Hanbin et al., *Acta Scientiae Circumstantiae*, 1982, 2(4):279–292
- Tang Hongxiao, Xue Hanbin, *Proc. Intern. Conf. Heavy Metals in the Environment*, Heidelberg, 1983, 2
- Xue Hanbin, Tang Hongxiao, *Pollution in the Urban Environment*, Hong Kong, 1985
- Xue Hanbin, Fu Yan, Tang Hongxiao, *Acta Scientiae Circumstantiae*, 1986, 6(1):50–57