

Geochemical characteristics of heavy metals in the Xiangjiang River, China

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Abstract

The concentration of the heavy metals Cu, Cd, Pb and Zn in surface water and sediment samples taken from the length of the Xiangjiang River in China, revealed significant pollution in the vicinity of two industrial centres (Shuikoushan & Zhuzhou). Additional insight into the potential adverse effects of these elevated concentrations was obtained from studies of the physiochemical forms (speciation) of these metals in the water column and in sediments.

Introduction

In combination with other research institutions concerned with environmental protection, we have carried out a joint investigation of pollution in the Xiangjiang River. The Xiangjiang River rises in the Haiyang mountains of Kwangsi Chuang Autonomous Region, and flows through several industrial and urban areas (e.g. Shuikoushan, Hengyang, Zhuzhou & Changsha) of Hunan province on its way to Dongting Lake. The river has a length of about 856 km (with 670 km in Hunan province) and the area of the drainage basin is 94 660 km² (Fig. 1).

The region is classified as subtropical. The annual rainfall in the river basin ranges from 1200 to 1700 mm, with about 40–50% of this rainfall occurring between April and June. The annual average runoff amounts to 713×10^8 m³.

The Xiangjiang River basin contains a number

of large deposits of nonferrous metals which has led to the establishment of an extensive metallurgical and chemical industry in the region. The catchment is also intensively farmed. Most of the cities and industries are located in the middle and lower reaches (from Zhuzhou to Changsha) of the river. Past discharges of wastes by industries, especially the Zhuzhou metallurgical plant, has led to extensive metal pollution of the lower reaches of the river.

This paper reports the results of research undertaken to evaluate the extent of heavy metal pollution of the Xiangjiang River and to provide useful information for their control. In general, the species, content distribution, transportation and transformation of heavy metals in the water and the sediments have been studied with a view to understanding the extent of water pollution and geochemical characteristics of pollutants, as well as the pollution history.

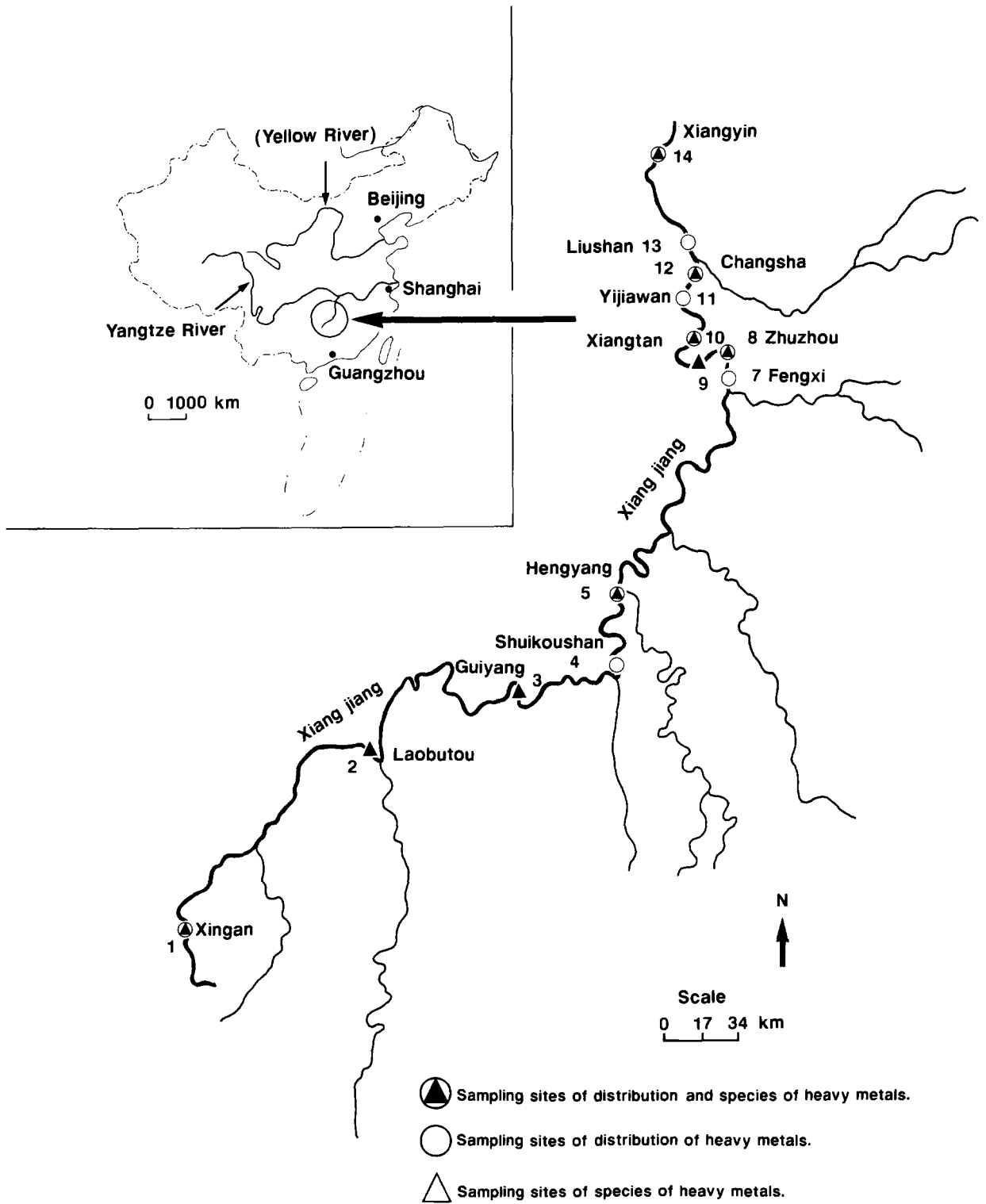


Fig. 1. Sampling station location.

Experimental details

Heavy metal distribution

Sampling

Sediment and water samples for heavy metal analysis were collected during an extensive environmental and aquatic pollution survey of the Xiangjiang River. Samples were taken on three occasions; mean flow (July-August 1979), low flow (November 1979) and high flow (May 1980) at the locations shown in Fig. 1.

Water samples were collected from both sides of the river, from the bow of a shallow-draft boat, in acid-washed polythene bottles which were immersed by hand to approximately 40 cm below the surface, or by an acid-washed polythene bottle which was weighted with a lead sinker. All containers were cleaned by soaking in 14% HNO₃ overnight, followed by rinsing with distilled water, then with five rinses of sample before collection. These samples were immediately adjusted to approximately pH 2 with pure distilled concentrated HNO₃. Sediment samples (approximately 10–20 cm depth) were taken from the river bottom using a sediment sampler (Type: mussel). A subsample was taken from the centre to avoid contamination by the metallic part of the sampler and stored in acid-washed, wide mouthed, polythene bottles.

Analytical methods

An appropriate volume (> 20 ml) of each water sample was pipetted into 100 ml silica beaker, and then evaporated to approximately 1 ml on an electric hot plate. After cooling, the solution was transferred to a silica colorimeter tube and made up to the mark with 1% (v/v) HNO₃. The solution was then analysed for copper, zinc, lead and cadmium using a Shimadzu atomic absorption spectrophotometer (AAS) (model AA-640-13) with graphite furnace atomizer (model GFA-2). A blank was run for each batch.

Sediment samples were air dried, ground to pass an 18 mesh silk sieve to remove rubble and then finely ground in an agate mortar with agate pestle to less than 100 mesh.

To determine the total copper, lead, zinc and cadmium concentrations, approximately 0.5 g of the dry sample was weighted into a teflon beaker, wetted with a few drops of deionized distilled water, then 10 ml of aqua regia added and the mixture heated at low heat (120 °C) for one hour. The temperature was then increased to produce dense white fumes and the mixture evaporated to approximately 0.5 ml. After cooling, the mixture was further digested with 5 ml of HF and then evaporated to dryness. Finally, 1 ml of HClO₄ was added and evaporated to dryness. The residue was dissolved with 1% (v/v) HNO₃, transferred to 50 ml volumetric flask, and made up to the mark with dilute HNO₃ (1% v/v). The heavy metal concentrations in the digest were determined by either flame AAS (Model WFD-Y2, made in China) or atomic absorption spectrophotometer using a Shimadzu AA-640-13 spectrometer with deuterium background correction and GFA-2 graphite furnace atomizer. For low concentrations of Cd and Pb, a chelation-solvent extraction concentration step was employed. Metals were chelated by potassium iodide and ascorbic acid and the metal chelates were extracted into 4-methyl-2-pentanone (MIBK). Concentrations were determined by comparison with standards made up in 1% v/v HNO₃ solution and extracted with KI and ascorbic acid into 4-methyl-2-pentanone. A reagent blank determination was carried out for each batch.

The method developed by Tessier *et. al.* (1979) was used to determine the physico-chemical form of each metal in the sediment samples.

Heavy metal speciation

Sampling

Water samples for the study of Cu, Pb, Zn and Cd speciation were taken at nine locations (Fig. 1) using a shallow-draft wooden boat, in acid-washed polythene bottles, which were immersed by hand to approximately 10 cm below the water surface. With the exception of sites 8 & 9, subsamples were taken close to each bank as well as at the middle of the river and then mixed to pro-

duce a composite sample. All containers were cleaned by soaking in 2N nitric acid overnight, followed by rinsing with distilled water and then with three rinses of sample before collection. Samples were filtered through 0.45 μm membrane filters (cellulose acetate; Tenth Pharmaceutical Factory, Shangshai) using a perspex pressure filtration apparatus as soon as possible after collection. Nuclepore 0.45 μm membrane filters were cleaned with 5% v/v nitric acid, washed in deionized distilled water and soaked in deionized distilled water before use. Samples for total metal determination were acidified using 3 ml 'Suprapur' HNO_3 per 1 litre of sample. The filtrates were collected in precleaned polythene bottles. All of the samples were taken back to the laboratory and stored at 4 °C until analysis.

Analytical methods

Determination of total Cu, Cd, Pb and Zn in filtered (soluble) and unfiltered (total) samples was as follows: an appropriate volume of sample was digested with $\text{HNO}_3/\text{HClO}_4$ in a silica beaker, and then evaporated almost to dryness. After cooling, the residue was dissolved in 10 ml of 0.1 M acetate buffer (pH 4) containing 1×10^{-4} M Hg^{2+} .

The metals Cu, Cd and Pb were determined by anodic stripping voltammetry (Model JA-IA polarography) using a home-made glassy carbon electrode. Total zinc was determined using a PAR Model 384 polarographic analyzer connected to an M303 static mercury drop electrode. A Ag/AgCl reference electrode and electronic magnetic stirrer were used in all measurement. The cell assembly was cleaned before use by soaking in dilute nitric acid followed by tap water then distilled, demineralized water. The standard addition technique was used to quantify the results.

ASV labile Cu, Cd, Pb and Zn were determined by adding 0.5 ml of 1 M acetate buffer (pH 4.7) and 0.1 ml of 10^{-2} M Hg^{2+} to 9.5 ml of filtered sample. The sample was deaerated in the cell with nitrogen for 10 minutes. The metals (except for zinc) were deposited at -0.90 V on the glass carbon electrode, and stripped by using 200 mV s^{-1} ramp to 0.1 V. Depositing time was adjusted

depending upon the metal concentration. Zinc was deposited at the static mercury drop electrode at -1.20 V and stripped by using 4 mV s^{-1} ramp to -0.90 V.

Selected filtered samples (not acidified) were fractionated using the scheme reported by Florence & Batley (1980). Ultraviolet irradiation of 100 ml of sample, containing 0.05 ml of 30% w/w H_2O_2 was carried out in silica tubes for six hours by using 500 W u.v. lamp.

Chelex-100 (50-100 mesh; Bio-Rad) was used in ammonium form, in a glass column (0.8 cm \times 10 cm) with a flow rate of 1.0-1.5 ml min^{-1} . Sodium acetate (analytical grade) was purified three times by crystallization. Nitric acid and perchloric acid were G.R. grade.

On each sampling occasion pH, temperature, dissolved oxygen (DO) and redox potential (Eh) were measured at 40 cm depth using sensors (made in Yi Yang Factory of Scientific Instruments in China) housed in a rugged waterproof assembly.

Additional water samples were taken at each station and analyses for chemical oxygen demand (COD) using the potassium permanganate oxidation method (Institute of Hygiene, 1973).

Results and discussion

Extent of heavy metal pollution in the Xiangjiang River

To evaluate the extent of pollution in the river, a knowledge of the total concentration of heavy metals in river water and sediments was needed. The results shown in Table 1 indicate that on the basis of pH, DO and COD, the quality of Xiangjiang River water is acceptable. However, this is not so for heavy metals, where the concentrations found in the water and sediments (Tables 2 & 3) are generally within the range expected for contaminated water bodies. For example, the total heavy metal concentration in the Xiangjiang River were: Cd 0.1-20 $\mu\text{g l}^{-1}$; Pb 1.6-490 $\mu\text{g l}^{-1}$; Cu 6.5-100 $\mu\text{g l}^{-1}$; Zn 3.3-620 $\mu\text{g l}^{-1}$ (Table 2). Also, the mean concentration of Cu,

Table 1. General water quality in the Xiangjiang River.

Parameter	Units	Time of sampling (1979)	Sample number	Minimum	Maximum	Mean
Temperature	°C	July-August	42	28.5	34.0	31.3
		November	28	9.8	14.7	11.5
pH		July-August	46	6.6	8.3	7.5
		November	28	7.6	8.4	8.1
Eh	mV	July-August	39	282	442	358
		November	28	342	422	375
DO*	mg l ⁻¹	July-August	41	4.0	7.6	
		November	28	9.2	11.1	
COD*	mg l ⁻¹	July-August	34	1.2	27.3	
		November	26	1.1	17.5	

* Water quality standards: DO \leq 4 mg l⁻¹ [National quality criteria for surface water in China]
 COD < 10 mg l⁻¹ [Quality criteria for supply water, WHO]

Table 2. Concentration ($\mu\text{g l}^{-1}$) of total heavy metals in the Xiangjiang River water.

Element	Range	Mean	Sample number	Site of highest concentration	Unpolluted freshwater*
Cd	0.1– 20	1.9	50	4 Shuikoushan	0.15
Pb	1.6–490	29	56	8 Zhuzhou	0.20
Cu	6.5–100	31	59	8 Zhuzhou	0.4
Zn	3.3–620	49	58	8 Zhuzhou	1.8

* Data from Florence & Batley (1980)

Table 3. Concentrations (mg kg⁻¹) of heavy metals in sediments from the Xiangjiang River.

Element	Range	Mean	Sample number	Site of highest concentration	Unpolluted freshwater bodies*	World lake**
Cd	0.17– 78	7.8	52	8 Zhuzhou	0.3	0.4
Pb	11 –2400	290	55	8 Zhuzhou	50	28
Cu	9.2 –1500	100	55	8 Zhuzhou	25	43
Zn	7.9 –7500	660	55	5 Hengyang	75	110

* Data from Vernet *et al.* (1977) for background values in the <80 μm fraction of sediments.

** Data from Förstner (1977) for median values of metal concentrations in the <2 μm fraction of lake sediments.

Cd, Pb and Zn in more than 50 bottom samples show that the Xiangjiang River is significantly polluted (Table 3).

However, use of ranges and mean concentrations of these heavy metals in the water and sediments as a measure of extent and type of pollution in the Xiangjiang River is too simplistic. The con-

centrations of heavy metals in water and sediments taken from different reaches of river may vary considerably depending upon the location of discharged wastes and the hydrological conditions of the river. Therefore, a knowledge of the distribution of heavy metals in the water column and the sediments over the whole river, from up-

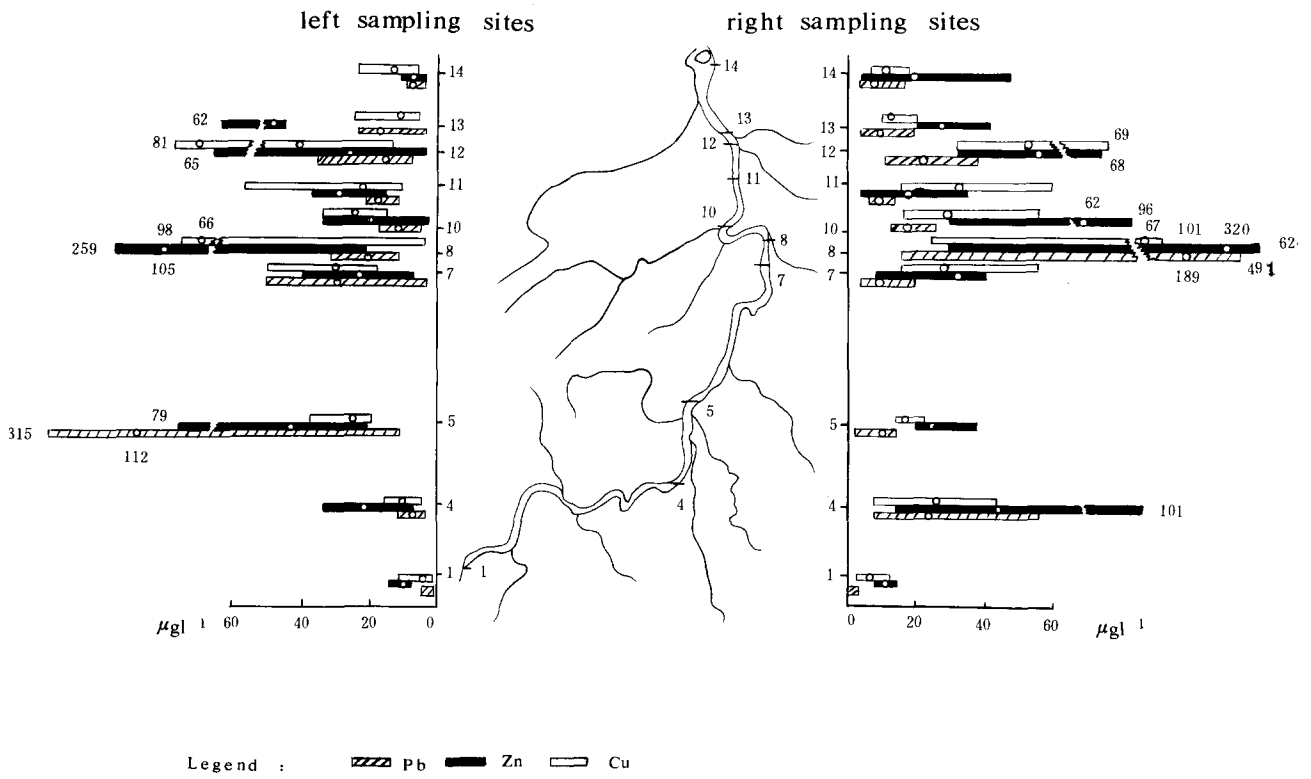


Fig. 2a. Distribution of Pb, Zn and Cu content in the Xiangjiang River water.

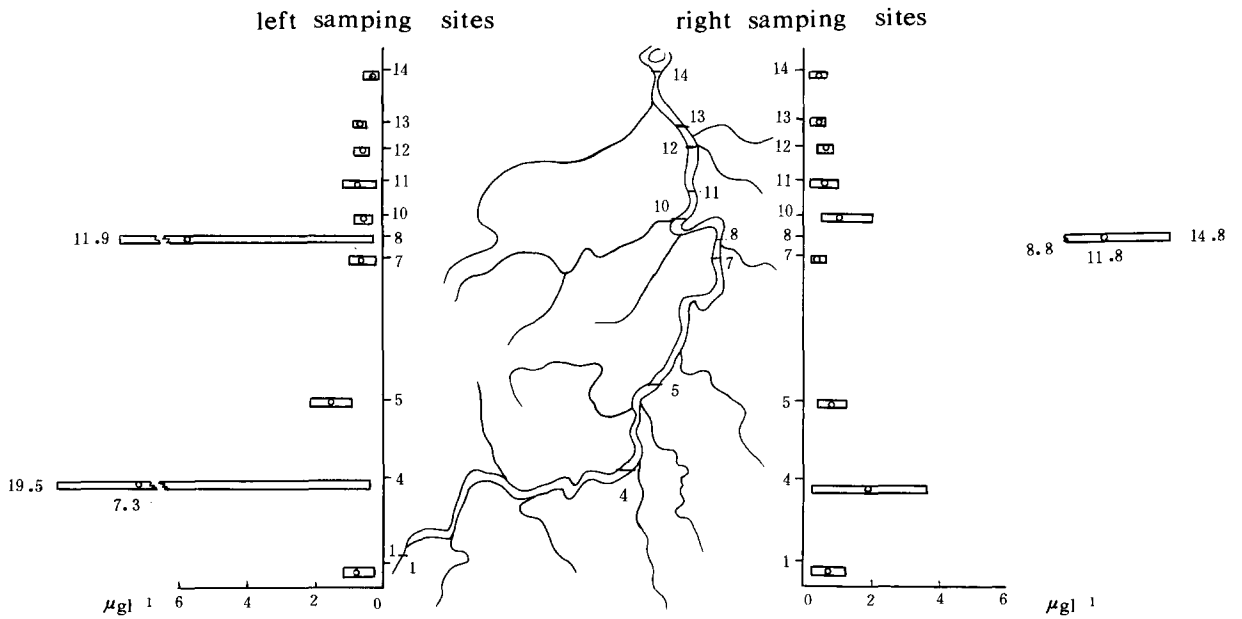


Fig. 2b. Distribution of Cd content in the Xiangjiang River water.

stream reaches to the estuary, is important. The data reported in Figs. 2 & 3 show that the Cu, Cd, Pb and Zn concentrations are higher in the middle and lower reaches of the Xiangjiang River. Water samples collected near waste discharges from a metal mine located in Shuikoushan and from a metallurgical plant located in Zhuzhou, had parti-

cularly high concentrations of Cu, Cd, Pb and Zn (respectively 100, 15, 490 and 620 $\mu\text{g l}^{-1}$).

There appears to be two peaks in the distribution of heavy metals in the river water (Fig. 2). Also the concentration of heavy metals in water samples taken from the majority of the sites on the left side of the river were considerably lower than

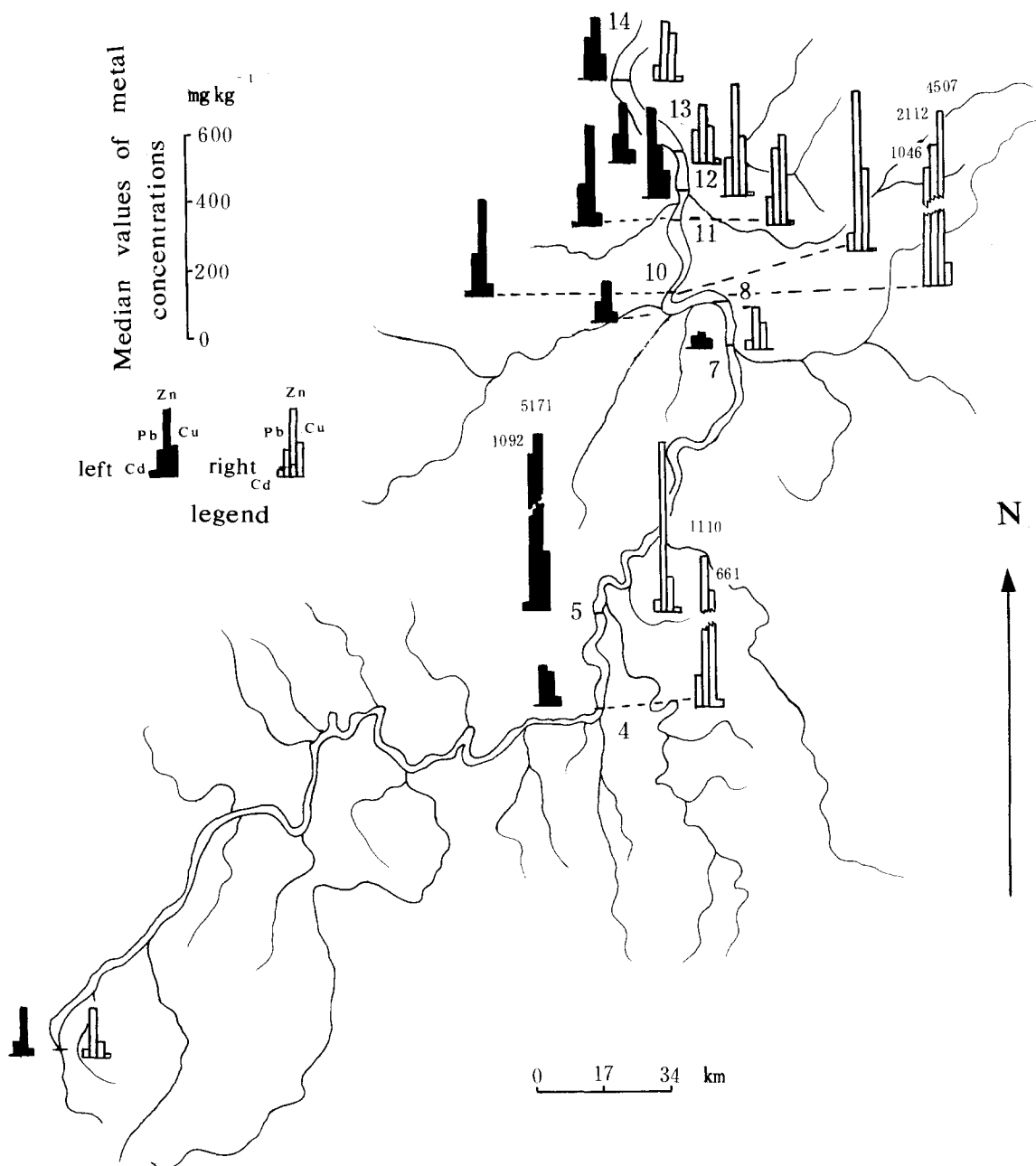


Fig. 3. Distribution of Cu, Zn, Pb and Cd content in the Xiangjiang River sediments.

from the right side of the river. Upstream of the major industrial impacts, the Xiangjiang River is, on the whole, uncontaminated.

The distribution of Cu, Cd, Pb and Zn in the sediments parallels that in water (Fig. 3). The highest heavy metal concentrations were found in bottom sediments collected from the industrial cities of Shuikoushan and Zhuzhou (sites 4, 5 & 8). This observation was also true from heavy metal concentrations in the water column.

It is clear that the distribution of heavy metals in the water and sediments of the Xiangjiang River depends directly on the character of the discharged wastes, which determines the concentration of pollutants in river.

Chemical forms of heavy metals in waters and sediments

The bioavailability and toxicity of heavy metals are not solely dependant on their total concentration, but depend on the physico-chemical forms present (Hart, 1982; Zhang, 1978). The higher the proportion of the biologically active forms, the more serious the pollution. The speciation of heavy metals in water and sediment

samples collected from the Xiangjiang River was undertaken to provide this information.

Firstly, in water samples collected during November 1984, it was found that the dissolved fraction ($< 0.45 \mu\text{m}$) contained rather low concentrations of Cu, Cd, Pb and Zn (Table 4, Fig. 5); the exception was the water sample taken from the right side of the river at Zhuzhou (site 8).

The concentration of heavy metals in the particulate fraction was much higher than in the dissolved fraction for water samples taken from the middle and lower reaches of the river. In the less polluted upstream reaches, the greatest proportion of the heavy metals was generally associated with the dissolved fraction (Table 4).

The speciation of these four heavy metals in the dissolved fraction was further studied using the fractionation scheme reported by Florence & Batley (1980). The results are presented in Table 5. A large fraction of the dissolved Cd was present as free metal ions and labile inorganic and organic complexes ($M + MA_1 + ML_1$). In contrast, approximately 70% of the dissolved Cu was found in the non-labile fraction. When the concentration of organic matter in water increases, it is expected that more Cu would be associated as organic complexes (ML_4 as well as ML_3). The predomi-

Table 4. Total concentration ($\mu\text{g l}^{-1}$) of heavy metals and ratio (%) of dissolved and particulate metal concentrations in Xiangjiang River.

Metal	Fraction (a)	Sampling site									
		1 15 Nov.84	2 14 Nov.84	3 13 Nov.84	5 22 Nov.84	8 28 Nov.84	9 28 Nov.84	10 26 Nov.84	12 11 Nov.84	14 27 Nov.84	
Cd	Mt	0.03	0.04	0.07	1.05	16.3	0.29	0.34	0.57	0.45	
	Md	67	50	71	62	4	76	52	30	44	
	Mp	33	50	29	38	96	24	47	70	56	
Pb	Mt	0.68	0.87	0.96	3.90	129	2.20	3.02	4.90	4.92	
	Md	59	54	53	28	1	32	27	16	19	
	Mp	41	46	47	72	99	68	73	84	81	
Cu	Mt	0.56	0.98	1.11	1.92	39.2	2.46	2.61	5.00	2.80	
	Md	54	55	55	64	31	68	66	40	46	
	Mp	46	45	45	36	69	32	34	60	54	
Zn	Mt	6.1	7.8	7.8	36.3	1140	11.8	29.0	48.0	18.7	
	Md	84	74	68	59	17	66	66	46	33	
	Mp	16	26	32	41	83	34	34	54	67	

(a) Mt = total metal concentration, Md = dissolved metal concentration, Mp = particulate metal concentration, Mp = Mt-Md.

Table 5. Speciation of Cd, Pb, Cu, Zn in Xiangjiang River water* [total concentration in ($\mu\text{g l}^{-1}$), fractions in percent of total].

Element	Fraction	Sampling site								
		1	2	3	5	8	9	10	12	14
Cd	Total	0.02	0.02	0.05	0.65	0.66	0.22	0.18	0.17	0.20
	M + MA ₁ + ML ₁	100	100	80	80	62	60	44	53	50
	MA ₂	0	0	20	2	0	5	0	0	0
	ML ₂	0	0	0	2	2	5	11	6	5
	MA ₃	0	0	0	8	15	20	17	18	25
	ML ₃	0	0	0	5	12	10	17	12	10
	MA ₄	0	0	0	2	0	0	0	6	0
	ML ₄	0	0	0	3	9	0	11	6	10
Pb	Total	0.40	0.47	0.51	1.1	1.1	0.70	0.82	0.80	0.92
	M + MA ₁ + ML ₁	0	6	12	18	26	7	12	25	5
	MA ₂	35	30	26	14	17	29	22	10	16
	ML ₂	0	0	2	20	12	23	18	15	16
	MA ₃	15	21	14	8	9	4	9	6	8
	ML ₃	10	2	0	7	6	7	9	11	5
	MA ₄	40	40	47	15	9	14	10	8	12
	ML ₄	0	0	0	18	22	16	21	25	37
Cu	Total	0.30	0.54	0.61	1.2	12	1.6	1.7	2.0	1.3
	M + MA ₁ + ML ₁	0	0	0	0	48	12	11	15	4
	MA ₂	0	0	0	8	2	12	0	10	8
	ML ₂	0	0	0	8	16	0	15	8	16
	MA ₃	23	26	33	3	2	13	11	13	10
	ML ₃	14	19	13	30	7	21	14	18	14
	MA ₄	43	37	41	23	5	15	19	15	12
	ML ₄	20	19	13	28	20	27	31	23	36
Zn	Total	5.1	5.8	5.3	21	196	7.8	19	22	6.2
	M + MA ₁ + ML ₁	26	28	30	65	62	18	56	58	11
	MA ₂	65	60	59	20	6	51	21	16	60
	ML ₂	0	0	2	2	4	6	3	2	2
	MA ₃	6	3	4	2	9	5	4	8	5
	ML ₃	0	0	2	6	5	6	5	7	7
	MA ₄	4	5	4	1	2	5	6	5	8
	ML ₄	0	3	0	3	12	8	5	4	8
pH		8.3	8.0	8.0	8.0	7.8	7.9	7.8	7.9	7.9

* M-Free metal ions; ML₁ – labile organic complexes; MA₁ – labile inorganic complexes; ML₂ – labile metal adsorbed on organics; MA₂ – labile metal adsorbed on inorganics; ML₃ – non-labile organic complexes; MA₃ – non-labile inorganic complexes; ML₄ – non-labile metal adsorbed on organics; MA₄ – non-labile metal adsorbed on inorganics.

nant forms of Pb in the upstream reaches were non-labile and labile metals adsorbed to inorganic colloidal particles (MA₄ and MA₂); in middle and lower reaches the proportion of nonlabile metal adsorbed on organics and inorganics of Pb increased (ML₄). A large fraction of dissolved Zn

was present in the species MA₂ and M + MA₁ + ML₁.

The forms of each heavy metal in sediment samples taken at four locations in the Xiangjiang River are reported in Fig. 4. The proportion of exchangeable Cd, Cu, Pb and Zn in these sedi-

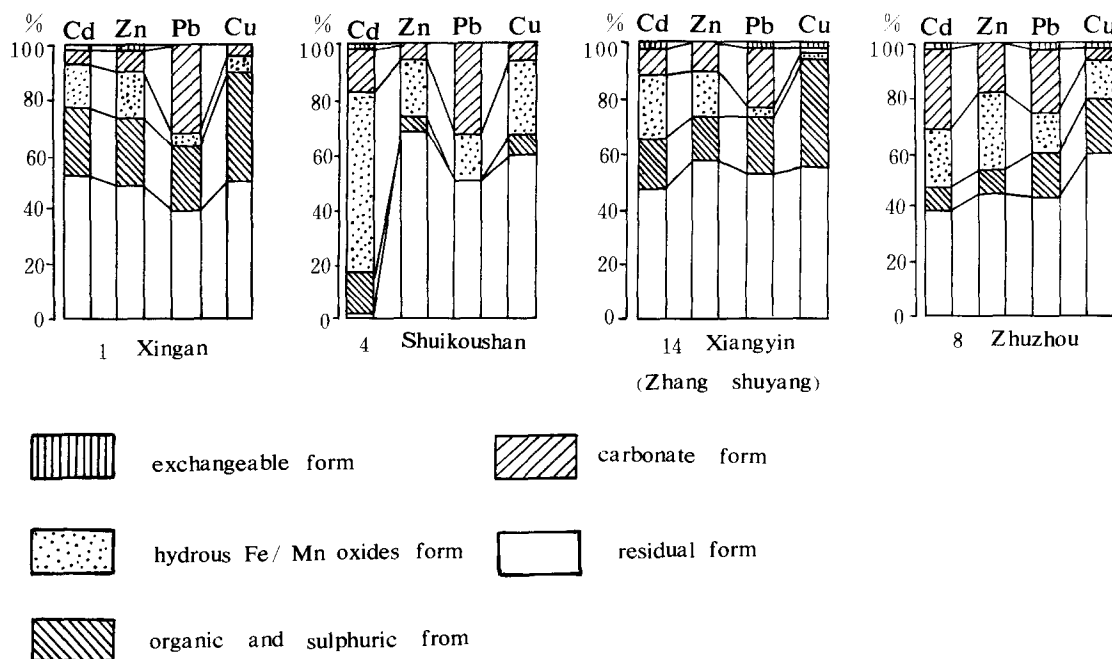


Fig. 4. Proportions of content of heavy metals in the Xiangjiang River sediments.

ments was low, generally not more than 2% of the total. The proportion of carbonate forms was higher than exchangeable forms (Cd 9–33%; Cu 0.8–6%; Pb 23–33%; Zn 6–18%), but is still considerably less than that in the residual fraction. These sediments contained a high proportion of calcium carbonate, with the Ca concentration in the carbonate fraction being 290–1600 mg kg⁻¹, which represents 35–70% of its total content. With the exception of Cu, the amount associated with hydrous Fe/Mn oxides was approximately equal to that in the carbonate fraction. There was some trend for elevated amounts of Cu to be associated in the organic/sulphide fraction.

In summary, we have shown that the concentrations of Cd, Cu, Pb and Zn are high in river water and bottom sediment samples in Zhuzhou and Shuikoushan segments, but are not significantly elevated in the upstream reaches of the Xiangjiang River.

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