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Distribution and speciation of heavy metals in sediments at Caijiawan region

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Abstract—Metals in different fractions in samples from surface sediments, cores, riverbank soil, islet soil and agricultural soil at Caijiawan were determined. The effect of particle size, density gradient on metal accumulation in sediments were studied. The chronology of core samples indicated that the pollution history corresponded to the development history of Dexing Copper Mine.

Keywords: heavy metals; sediments; copper mine.

EXPERIMENTAL

Caijiawan is located at the downstream of Le An River, and sediments are rich in this river section. Horizontal and vertical distribution of heavy metals have been studied for understanding the history and status of pollution of heavy metals. Some samples from river water, agricultural field, river bank, and islet were taken at different sites. Soil was taken from the channel side at right river bank. The riverside sediment sample was taken from right islet on river

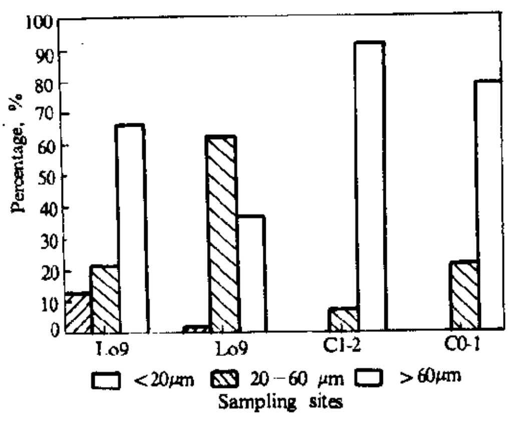

Fig. 1 Distribution of sediment particle size from Caijiawan along Le An River

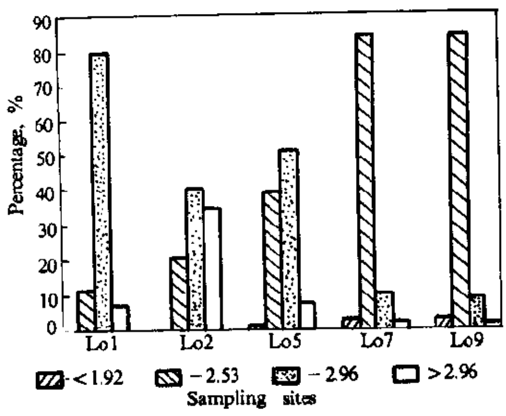

Fig. 2 Distribution of density gradient of sediments from Caijiawan along Le An River

bank, almost 15cm beneath the bank surface. The core 0−1 and core 1−2 represented the first and second surface layer of the core sample respectively. The islet soil was taken at 50 cm beneath the surface soil from the islet.

The particle size distribution of the samples by ultrasonic sieve was shown in Fig. 1. In general, the distribution ratio of metal content in three different particle size were: size range 60 μm is the highest (50−70%); 20−60 μm (20−34%); and < 20μm (3.7−25%).

A heavy-liquid density gradient based on density gradient in tetrabromoethane-acetone system (Mao, 1982) was used to separate the sediments from Caijiawan into district bands. Results showed that the sediments of density less than 2.53 were more than 90%, and the heavy mineral phase was very low (Fig. 2). The sediments deposited in this area were light suspended matters with a density less than 2.53 while those heavy sediments density more than 2.53, especially 2.95, can only be transported for a short distance and may be deposited at the upstream.

The analytical results of Cu, Cd, Pb, and Zn in these samples were listed in Table 1.

Table 1 Concentrations of metal in sediments or soil (< 20 μm) at Caijiawan (ppm)

Soil metal	Agricultural field	Right riverside	Core 0−1	Core 1−2	Soil islet
Cu	158.10	777.14	229.73	297.01	48.65
Cd	6.80	8.40	10.60	10.86	3.64
Pb	36.55	77.12	63.45	62.57	53.89
Zn	174.82	705.22	223.30	313.74	129.86

The data in Table 1 showed that the highest concentrations of all metals appeared in the right bank soil (sediment), as there is a large flowback and sedimentary area in wet seasons, and a dry land in dry seasons. The lowest concentration, closer to the background value appeared in islet soil. The concentration of metals in second surface layer in core samples was higher than that in the first surface layer indicating the sedimentary and transport process of the suspended matters.

The geoaccumulation index (I_{geo}) (Müller, 1979; Schmitz, 1990) of these metals for Cu and Cd, larger than 3, for Zn near 3. Their pollution categories belonged 4 and 3, sub-heavy pollution or moderate pollution respectively; for lead, it was below 1 (clean).

A modified sequential leaching technique (Mao, 1981) was used for the speciation of metals in surface sediments and soils. The results were listed in Table 2. Order of species for copper in sediments was: sulphidic/ organic > residual > reducible > carbonate > exchangeable > water soluble, while in riverside soils it was: Fe/ Mn hydrous oxide > sulphidic / organic > residual phase > carbonate > exchangeable > water soluble fraction. The reason for high sulphidic/ organic phase is due to the increased organic matter in Caijiawan section and high affinity of copper ion for organic matters. As it might be expected, Cd was in the highest

Table 2 Speciation of metals in Caijiawan sediments, % (< 20μm) (Nov. 1989)

Sites	Soluble	Exchange	Carbonate	Reducible	Sul./ Org.	Residue
			Cu			
Surface R. Side	0.47	1.44	2.54	44.33	20.51	30.71
Soil R. Side	0.03	1.99	6.48	52.99	21.60	16.90
Coring 1−2	0.07	7.92	8.33	20.10	31.87	31.71
Coring 0−1	0.12	1.19	8.33	16.98	37.22	36.16
			Cd			
Surface R. Side	0.69	61.33	13.72	7.68	3.28	13.31
Soil R. Side	2.33	50.08	10.54	7.98	2.80	26.27
Coring 1−2	0.75	64.86	13.09	2.57	0.86	17.86
Coring 0−1	0.59	47.37	9.62	2.43	4.19	35.79
			Pb			
Surface R. Side	0.00	0.85	2.52	33.34	13.86	49.43
Soil R. Side	0.72	5.24	2.45	19.52	5.34	66.72
Coring 1−2	2.45	1.88	6.85	6.80	9.32	72.69
Coring 0−1	0.96	0.00	2.67	5.91	6.99	83.47
			Zn			
Surface R. Side	0.21	9.34	6.17	29.99	5.52	48.77
Soil R. Side	0.09	12.83	7.14	33.80	7.00	39.14
Coring 1−2	0.25	13.53	6.93	10.21	12.00	57.07
Coring 0−1	0.22	14.97	7.97	10.98	9.90	55.96

exchangeable fractions and that of Zn lower than that of Cd, and Pb was in the highest residual phase. In general, the residual fractions of metals are higher in sediments.

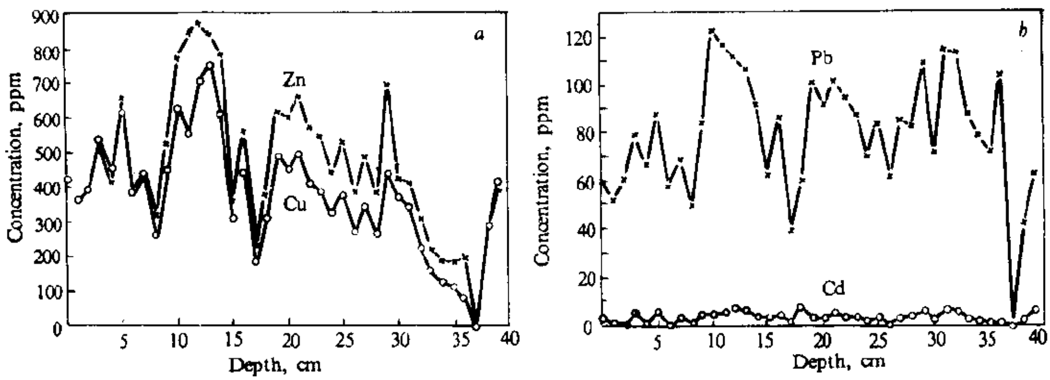

Fig. 3 Profiles of Cu, Cd, Pb, Zn and S at Caijiawan (Nov. 1989)

Sediment cores were taken from the left side curve of the main channel in Le An River at Caijiawan by a plastic tube of 50 mm dia., and 800 mm in length with a rubber cap in November, 1987 and 1989 respectively. The core generally contained finegrained deposit to a depth of 25 cm and 40 cm respectively. Cutting the cores into sections of 1 cm each, and metals were determined. On the basis of the chemical analytical data obtained from the single sections, the longitudinal profiles are shown in Fig. 3.

The distribution of heavy metals and sulphur in two cores indicated that almost all elements enriched up to 33 cm depth. There are four peak concentrations occurred at the 5–6, 13–14, 21–22, 29–30 cm depth, respectively.

Chronological determination of core samples at Caijiawan was carried out with Pb^{210} and Cs^{137}. It was indicated that contamination started in the early sixties, which was incidently at the same time when Dexing Copper Mine started to operate. Similar work was completed by Jiangxi Province (Liu, 1990) with Pb^{210}. The sedimentation rate is 1.4 mm / a. The first period of heavy metal contamination might happen around 1970 corresponding to 20–30 cm depth; the second occurred around 1969, the heaviest was set in 1980, 8 or 9 years before sampling (corresponding to 13–14 cm depth of the cores); the latest one was around 1984 (corresponding to 5–6 cm depth of the profiles). The distributions of metals and peak concentrations coincided well to the history of mining activities of Dexing Copper Mine, the heaviest pollution source in Le An River.

The figures above clearly show that almost all of the elements have the similar profile shape, especially at the peak positions. The elements in sediments have a common source and are interrelated to each other.

BIOAVAILABILITY OF THE METALS IN SEDIMENTS

The bioavailability for metal species in sediments were grouped into three categories: easily, moderate and inert bioavailable (Mao, 1981). The bioavailable fraction distributions of Cu, Cd, Pb and Zn in sediments or soils were shown in Fig. 4. The easily bioavailable copper was low (< 2%), due to its water soluble and exchangeable properties. The moderately bioavailable fractions were relatively high (65–80%), due to the fact that the sum of carbonate bounded, Fe/ Mn hydrous oxide bounded, and sulphidic/ organic bounded copper in sediments was high. The inert bioavailable fractions, which corresponded to the residual fractions, were in a range of 18–35%. The easily bioavailable fractions (48–54%) were found to be very high for Cd. It exists mainly in cation exchangeable form in waters.

Total concentration of lead in sediments was low and it has high inert bioavailable fraction. Zinc is a life essential elements. The easily bioavailable fractions were about 10%, moderately fractions were about 30–40%, inert parts 40–50%.

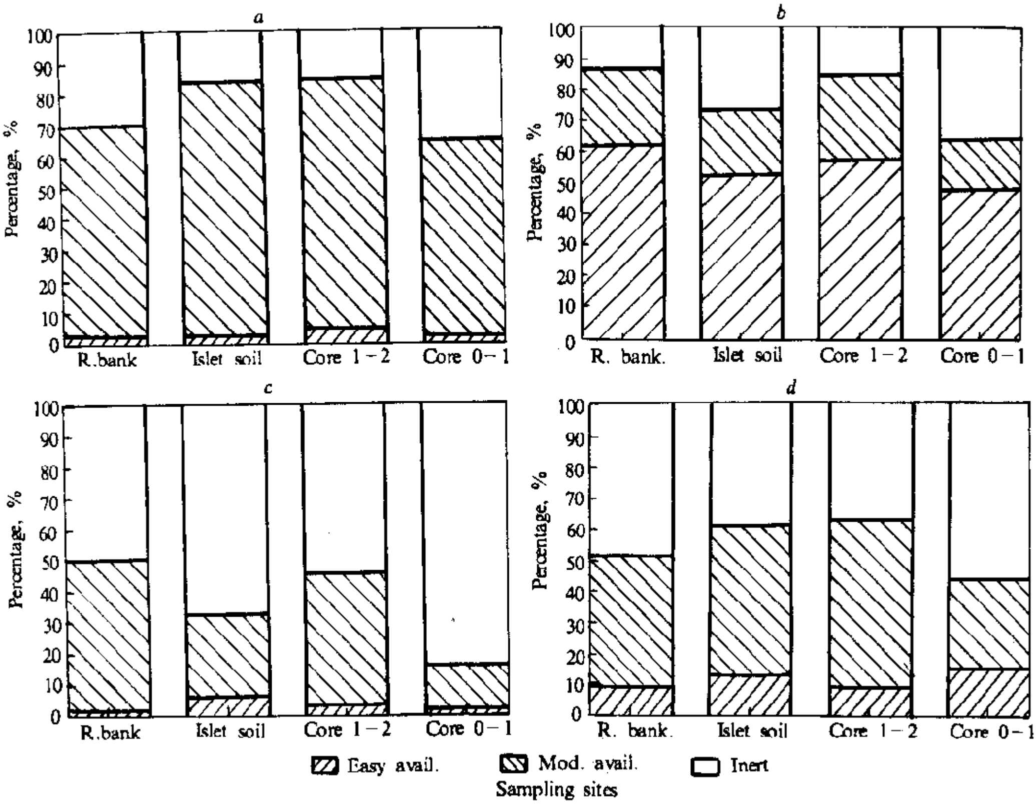

Fig. 4 Bioavailable fractions of Cu, Cd, Pb and Zn in Caijiawan sediments

CONCLUSIONS

Caijiawan is located at the downstream of Le An River and has a wide river cross section in wet seasons, most suspended matters in river water deposit in this area. The concentration of metals in surface sediments were found to be higher than that of Fushan to Shizhengjie section at its upstream. I_{geo} classes reached 4 or 3, belonged to sub-heavy or moderately polluted level. The ration of medium and fine particle size sediment containing high metal concentration are higher than at upstream. Heavy mineral phase in sediments was low. The chronological study indicated that the pollution history can be dated from sixties, corresponding to the development history of Dexing Copper Mine. Bioavailably from speciation of metals in the sediments was preliminarily studied.

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