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Distribution and speciation of metals in sediments along Le An River

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Abstract— Distribution of metal concentration and metal speciation in sediments along Le An River were studied. A high concentration of copper in sediments was found at Gukou, receiving Dexing Copper Mine effluents. It was decreased from Gukou to Daicun rapidly, but tended to increase from Daicun to Caijiawan. Speciation of Cu, Cd, Zn and Pb were studied by sequential selective chemical extraction. The speciation fractions were classified into three bioavailable categories: easily bioavailable, moderately bioavailable and inert bioavailable. The geoaccumulation index, I_{geo}, was used to illustrated the pollution level of heavy metals in sediments.

Keywords: chemical speciation; sediments; heavy metals.

It is very important to study the distribution of metal concentration and metal speciation in river sediments in order to understand the effect of Dexing Copper Mine exploitation on the eco-environment of Le An River.

A series of sedimentary or suspended matter samples were taken by a plastic tube or plastic ladle at the sampling sites (Fig. 1). Some soil samples were obtained from the riverbank for comparison. The samples were transferred into a polyethylene bag and air squeezed out and brought back to the laboratory and stored at 4℃.

Distribution of metal concentration

Samples of sediment and soil were dried by air and oven at 105℃, passed through 100 mesh nylon sieve, digested by $HClO_4$–HF (pressure bomb) at 180℃, 6 hours. Analytical results by ICP and AAS were shown in Fig. 2.

Metal concentration at Haikou or Fuxikou are the lowest in whole river except Zn. The highest Cu, Co, Cr, Ni, Fe and S concentrations in sediments were found at Gukou causing from the mining activities. The metal concentration in sediment were decreased rapidly from Gukou to Daicun. The highest Pb and Zn concentration were found at Daicun, a convergent point of Le An River and Jishui River. Chemical composition was changed as pollutants transported from Jishui River into Le An River.

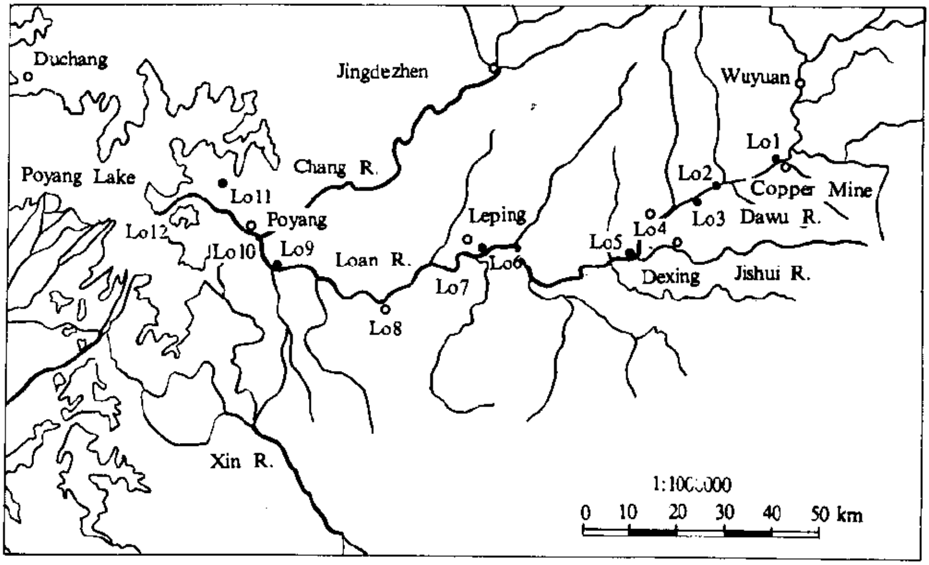

Fig. 1 Sampling sites along Le An River

Sediments were transported by flood at longer distance in rainy season than in dry season and accumulated in winded channel side. The concentrations of some metals were increased from Daicun to Caijiawan, particularly at Jiedu as suspended matter deposited in the large sandbank.

Metal concentrations in agricultural soils were lower than in the sediments, while at Fuxikou and Gukou (in mine area) the metal concentration was higher.

Metal speciation in sediments along Le An River

The samples were separated by a modified sequential extraction procedure for the speciation of heavy metals (Tessier, 1979; Förstner, 1983; Mao, 1981), after dried in air and passed through 100 mesh nylon sieve. A part of samples were passed through an ultrasonic sieve of dia. 20 μm and then treated as mentioned above.

The procedure of sequential extraction for heavy metals in sediments is illustrated in Table 1.

The analyzed results of Cu, Cd, Pb, Zn, Fe and Mn in different fractions of sediments were shown in Fig. 3. A low copper content was found at Haikou.

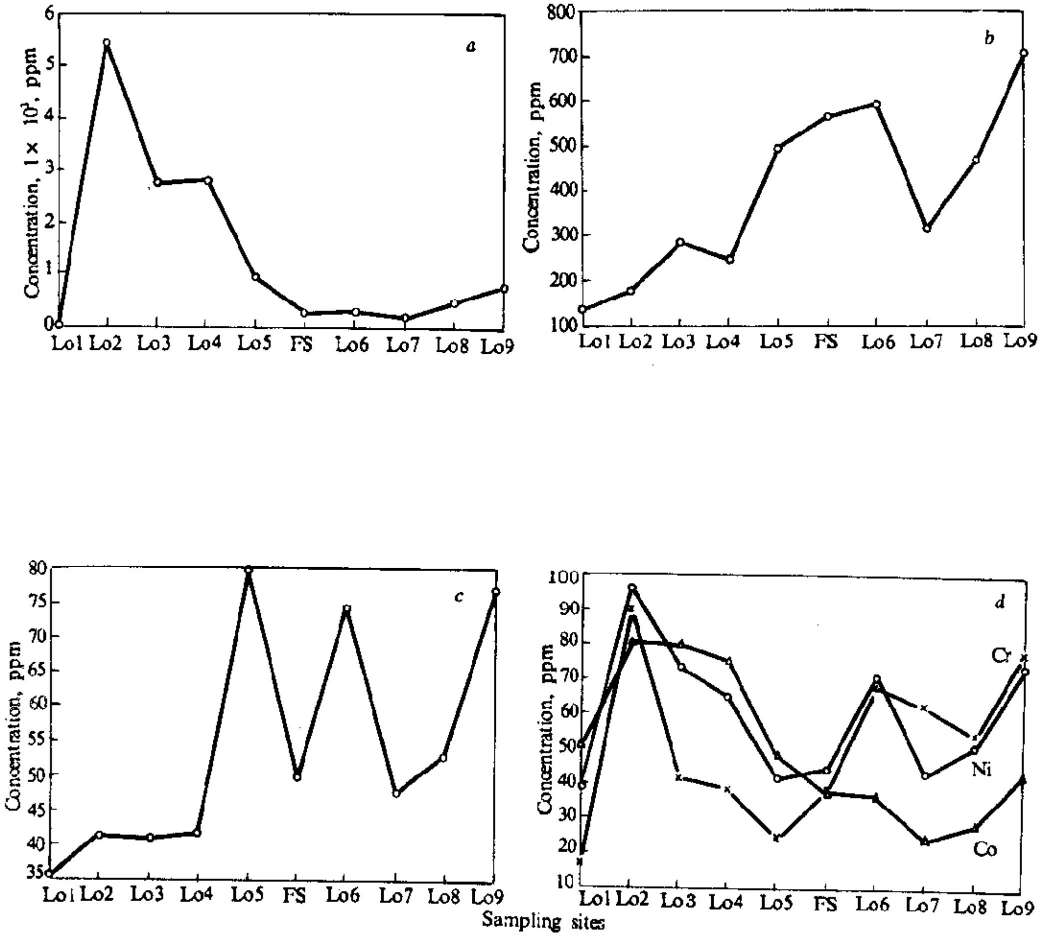

Fig. 2 Distribution of metal concentration in sediments along Le An River

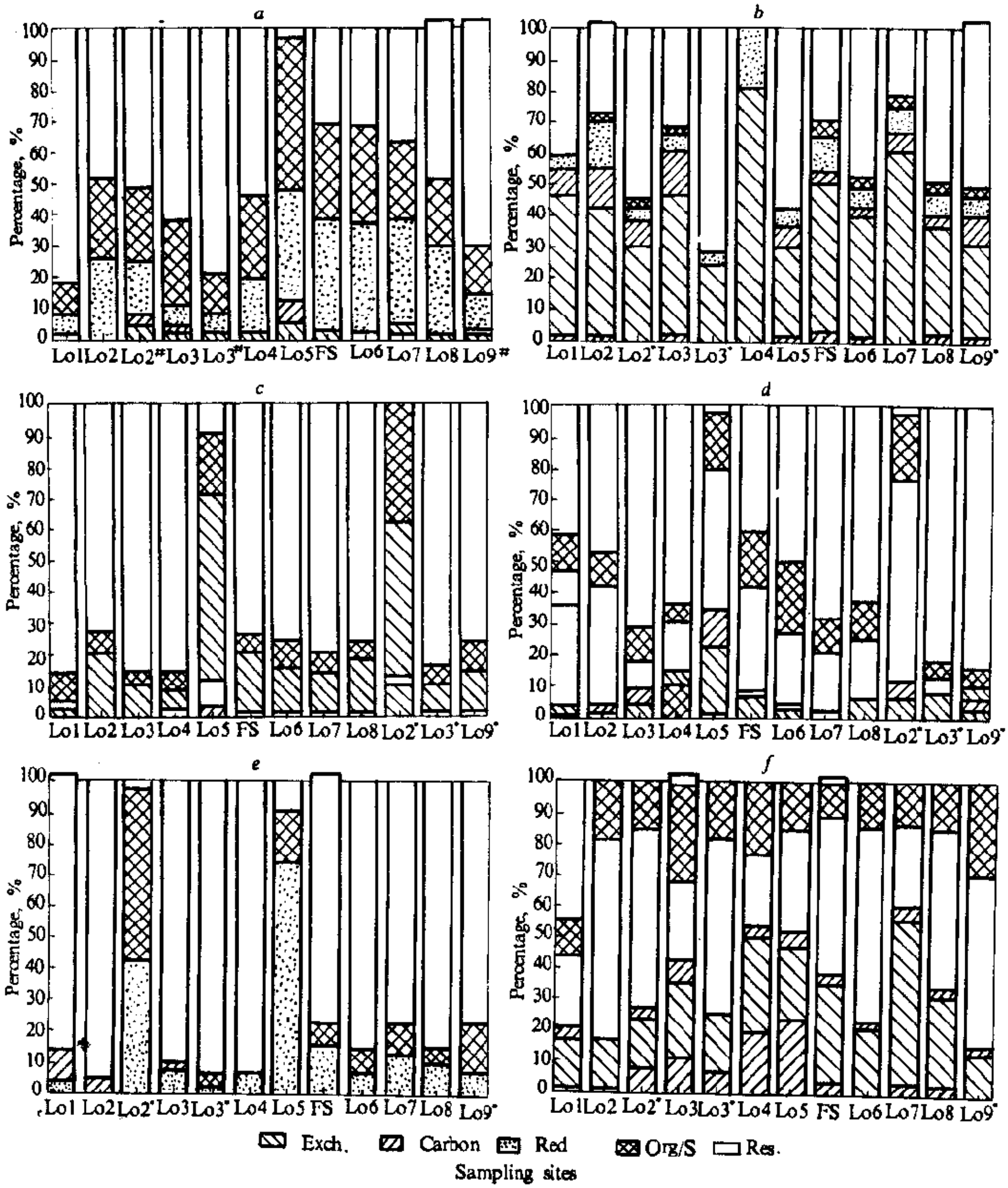

Fig. 3 Distribution of metal speciation in sediments along Le An River

Speciation of Cu in sediments at Haikou has a distribution order: carbonate fraction almost 88.5% (by concentration, the same hereinafter) > Fe/ Mn hydrous oxides (8.4%) >

Table 1 Scheme of procedure for sequential extraction of heavy metals in sediments samples

	Sediment or suspended matter sample				
Water soluble	Distilled water		1 : 20	2h	25℃
Exchangeable	1 mol/ L $MgCl_2$	pH 7	1 : 20	2h	25℃
Carbonatic fraction	1 mol/ L NaOAc, HOAc	pH5	1 : 20	2h	25℃
Moderately reducible	0.4 mol/ L $NH_2OH \cdot HCl$ in 25% HOAc		1 : 20	2h	96℃
Sulphidic/ organic	30% H_2O_2 +0.02 HNO_3 extr. with 1 mol/ L NH_4OAc–6%HNO_3	pH 2	1 : 20	4h	85℃
Residual fraction	HNO_3 – $HClO_4$ – HF (pressure bomb)		1 : 20	6h	180℃

sulphidic/ organic (1.8%), residual fraction (zero). Situation was different in soil sample at Fuxikou near Haikou and Dexing Copper Mine. The dominant fraction of copper was the residual (82%), next sulphidic/ organic (10%) and moderately reducible (6%). This distribution showed an evidence for the soil containing Cu.

Sampling site at Gukou was located at the left bank of Le An River downstream, almost 1 km away from the convergent of two rivers. A sizeable amount of flocculates, from natural flocculation, can be found there. Phases with different density were separated by a heavy liquid method (Mao, 1982), a heavy mineral phase (density more than 2.96) can be amounted to 34%. Sequential extraction fractions of copper were distributed as follows (November 1987): Sulphidic/ organic (64.2%)> moderately reducible (27.6%) > carbonate fraction (7.9%), residual fraction near zero; while in November 1989, residual phase (47.7%) > sulphidic/ organic phase (26.4%) > Fe/ Mn hydrous oxide fraction (25.1%). These data indicated that metal concentration from Dexing Copper Mine were not steady. A high sulphidic metal concentration existed in the sediments but not accumulated over there. The speciation distribution of copper in soil at Gukou riverbank clearly indicated that water soluble, exchangeable, carbonate, and residual fractions in the soil samples were slightly higher than that in sediments respectively. At Zhongzhou (5 km downstream from Gukou) Le An River is divided into two tributaries by a large sandbank, the sampling site at the left bank of the main river and the river bed consisted of coarse sand and shingle. There are large quantity of fine sediment materials in the river bed, especially in the winding river section after flooding, mostly tailings from Dexing Copper Mine. Selective extraction fractions of Cu was in the order: residual fraction (62%) > sulphidic/ organic (27%) > moderately reducible (7.1%) > carbonate fraction (2.1%) > cation exchangeable (1.7%). Results showed that the stable fraction of Cu in sediments, the residual fraction increased. The moderately stable fraction, Fe/ Mn hydrous oxides and sulphidic/ organic, decreased obviously. The metals in particles from effluents of copper mine were transformed by physical or chemical processes. For example, some metal ions adsorbed weakly on the particle and transported by the hydraulic flow. Some metals in sedimentary particles would be released into water as result of disturbance of gold dredging in the river bank from Zhongzhou to Xiangtun. The dredging activities would disturb the setting materials and promote metals releasing into water from sediment and exacerbate water pollution.

At Daicun, the metal concentrations were increased and the residual fractions of Cu, Pb, Zn, Fe and Mn except Cd decreased to the lowest at all sampling sites downwords. Cd in residual fraction was increased up to 56%, as it mainly came from Pb–Zn mine and the nonferrous smelter along Jishui River. In other fractions, particularly cation exchangeable and moderately reducible fractions, the metals were easily released and entered into waters.

Fushan located at the middle of Le An River which winded at the Leping flatlands. The flow rate is lower than that at upstream and there are much more sediments in the river bed,even in deposited sandbank. The sediments consisted of soils from upstream riverbank and suspended matters partly from ore, tailings, and slugs from mine and smelter. The sequential extraction gave three fractions: residual fraction (30.5%), sulphidic/ organic (31%) and Fe/ Mn hydrous oxide phase (35.5%). The sum of the three more stable phases came up to 97%.

A large sandbank, caused by flood and winded river channel, was formed at Jiedu. The result of distribution of metal speciation was similar to that in Fushan. A large amount of coal fly ash emitted from a large coal power plant, slurry, domestic sewage and scrap were discharged from Leping County into the river.

The distribution of selective extraction fractions of Cu was found to be changed at Hanjiadu, 5km downstream from the county. Sulphidic/ organic and moderately reducible fractions were decreased, and water soluble and cation exchangeable increased slightly, residual fraction also increased significantly.

Shizhengjie without industrial pollution is a ferry on Le An River. Coarse sand is the main component in the river bed and bank. The distribution of Cu fractions is just like that at Gukou: residual fraction (50%) > moderately reducible (28%) > sulphidic/ organic (21%), the sum of other fractions only 1%.

Caijiawan of Poyang County is in the downstream of Le An River which was divided into two parts by a large sandbank and pollutants were deposited at the right channel and finally flowed through into Poyang Lake in the rainy seasons, but sandy in the dry seasons. The coring samples were taken from left side near the sandland; one sample beneath the sandbank between the channels. It was found that the soils in the right bank or in the sandbank were not polluted by the river water or the sediments. Cu concentration was found to be high in the right bank and coring samples. Distribution of copper in surface sediments was found to be: residual fraction (61%) high, cation exchangeable (11.8%), water soluble fraction (8.8%) and Fe/ Mn hydrous oxides, carbonate, reducible fraction (5.5%) and sulphidic/ organic (4.2%) lowest in the fractions.

The sediments in Caijiawan were separated into three sized parts by ultrasonic sieve. Size less than 20 μm are higher in metal content than that of 20–60 μm. In fine sample (< 20μm) the major copper fractions were in residual fraction and sulphidic/ organic fraction with almost equal amount of moderately reducible, and the rest was carbonate fraction, exchangeable and water soluble fraction in sequence. It was shown that copper bounded with sulphidic/ organic and Fe/ Mn hydrous oxide fractions were increased but decreased significantly in residual fractions of fine sediments.

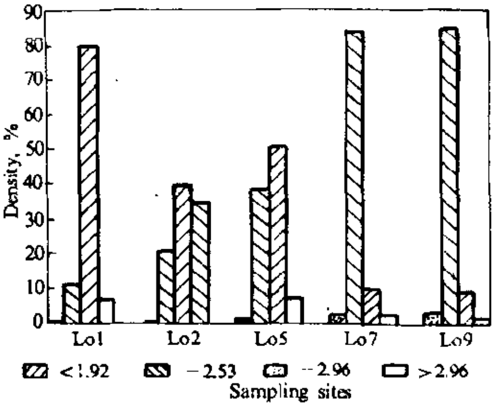

Fig. 4 Density gradient distribution of sediments

A heavy-liquid density gradient in tetrabromoethane- acetone system was used to separate the sediments from Caijiawan into distinct bands (Mao, 1982). Results showed that the sediments of density less than 2.53 were found to be high (> 90%), and the ratio of heavy mineral phase was very low (Fig. 4).

Speciation of Cd, Pb and Zn in river sediments

Speciation of Cd in sediments is quite different from that of Cu. The dominant extraction fractions of Cd were cation exchangeable and residual fractions, and their sum was nearly 80%. Other fractions were low, but moderately reducible and carbonate fractions could reach up higher than 10% in a few sites, and lower in sulphidic/ organic fractions. The data indicated that cadmium in sediments at Haikou came dominately from flyash of mining and smelting activity, partly came from effluent containing Zn from active carbon factory.

The total concentration of lead in sediments of Le An River did not reach beyond the environmental permissible limit. Pb in residual fractions was 73—86% of total Pb, the others were sulphidic/ organic and Fe/ Mn hydrous oxide fractions, except at Daicun. The order of the fractions of Pb at Daicun was moderately reducible fraction (60%) > sulphidic/ organic (20%) > residual fraction (9.3%) > carbonate fraction (8.3%) > water soluble (3%). The effect of metal effluent from Jishui River is evidently observed.

Speciation of Zn in Le An River sediments was not similar to that of lead. Its residual fractions were high but lower than that of lead; the others were higher than that of corresponding lead. Zn in sediments tended to release into water it was actively bounded to hydroxide and carbonate phases in sediments (Schuman, 1981).

Bioavailability of the metals in sediments

The sequential selective chemical extraction fractions of heavy metals in sediments can be classified into three categories (Mao, 1981): easily bioavailable (water soluble plus cation exchangeable fraction), moderately bioavailable (carbonate fraction, Fe/ Mn hydrous oxide fraction, and sulphidic/ organic bounded metals), and inert bioavailable (residual fraction). These categories are interrelated to the stability (or transformation) and the bioassay (toxicity) of metal extraction fraction in sediments. For example, the metal ions of water soluble fraction in the sediments have larger toxicity on algae and fish; the metals in the moderately bioavailable category can be released from fractions at changing environmental conditions and be transformed into metal ion species. Particularly as the river water became acidic. The metals bounded with residual fraction are stable at normal environment and can be classified as an inert category.

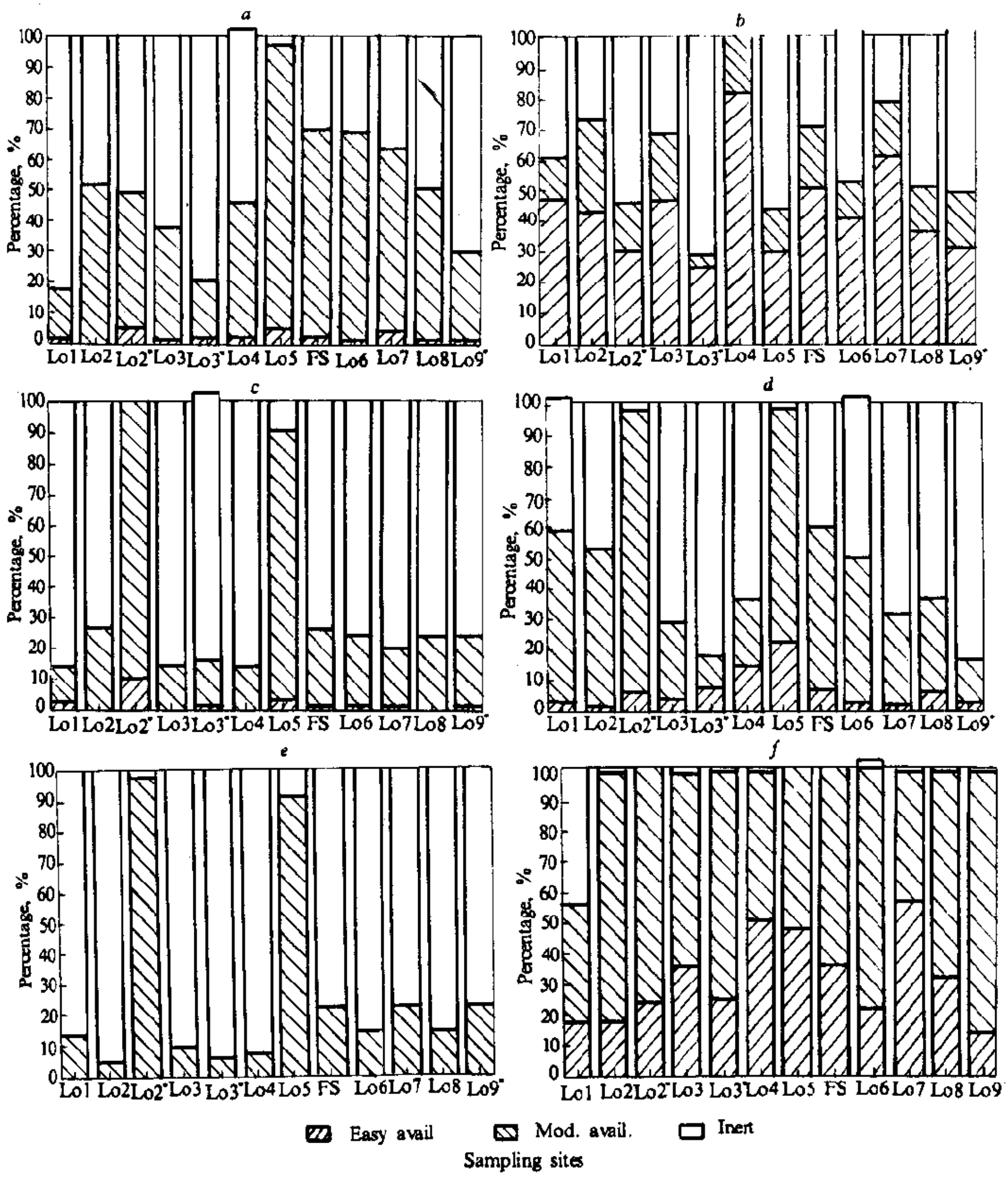

Fig. 5 Distribution of metals in bioavailable categories in Le An River sediments

The three bioavailable categories of the metal speciation in Le An River sediments are illustrated in Fig. 5.

The geoaccmulation index (I_{geo})

The geoaccumulation index, an empirical formula, proposed by Müller (Müller, 1979; Schmitz, 1990), can illustrate the pollution level of sediments caused by heavy metals semiquantitatively. I_{geo} is definited as follows:

$$I_{geo} = log_2 \frac{C_n}{1.5 \times B_n} ,$$

where C_n is the concentration of element n in the isolated fraction < 20 μm; B_n is the average geochemical background values of the elements n; The factor 1.5 is a correction value for variations in the geochemical background concentration.

Table 2 The classes of geoaccumulation index (I_{geo})

I_{geo} index	Class	Pollution degree
> 5	6	Very heavy pollution
4–5	5	Heavy pollution
3–4	4	Sub-heavy pollution
2–3	3	Moderately pollution
1–2	2	Sub-moderately pollution
0–1	1	Lighter pollution
< 0	0	Clean

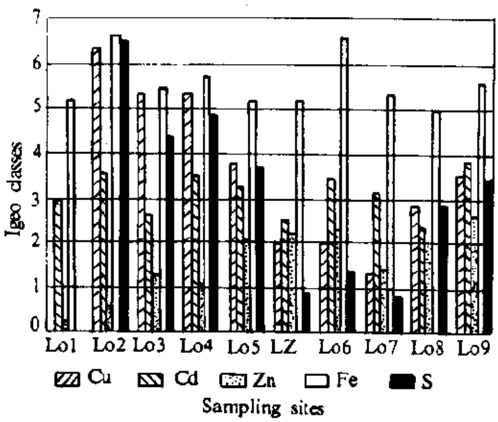

Fig. 6 I_{geo} class of heavy metals in Le An River Sediments

Geoaccumulation index, I_{geo} are divided into seven classes, each class indicates that the concentration of metal is 10 times higher than the previous (low) one (Talbe 2).

In Table 2, the 6th class, heaviest pollution class, indicated that the enriched degree of heavy metals in sediments reaches 100 times ($1.5 \times 2^6 \rightarrow 100$) or above that of background concentration of unpolluted sediment.

Based on the above empirical formula the I_{geo} value of heavy metals in sediments of Le An River (Fig. 6) was calculated.

Fig. 6 shows that heavy pollution degrees of copper appeared at Gukou (> 6), Zhongzhou (> 5), and Xiangtun (> 5) sediments. It is very clear that a large amount of Cu which came from effluent of Dexing Copper Mine was mainly accumulated in this river bed section. High level sulphur only occurred at Gukou (> 6), Zhongzhou (> 4), and Xiangtun (> 4) sediments. Sulphur mainly originated from sulfide minerals and Na_2S in the floatation process of Dexing Copper Mine. The I_{geo} values of iron in sediments are very high along the river. The highest classes (> 6) appeared at Jiedu and Gukou respectively. The effects of dredging activities on disturbing sediments at Jiedu and of discharging tailings on iron accumulation are very significant. A large amount of iron in red soil of the river sides have been transported into water, which constituted an important factor of high Fe. The I_{geo} classes of Mn are between 3 and 5. The disturbance from dredging activities is why I_{geo} classes of Mn reached up to 5 in Fushan and Jiedu sediments.

Although cadmium concentration in the sediments are not high, average background is only 0.4 ppm in the unpolluted sediments of fluvial and marine (Salomons, 1984), its pollution classified in Le An River sediments are about 3, a medium pollution degree. The pollution class of lead in river sediments zero; 1 for Zn in most sites, and 3 at right bank at Caijiawan.

CONCLUSION

The highest metal concentration were found in the river section from Gukou to Daicun. Geoaccumulation index (I_{geo}) showed that the sediments belonged to heavy pollution from Gukou to Daicun, sub-heavy to moderately polluted level at Caijiawan.

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