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Major environmental and ecotoxicological processes of heavy metals in Lean River polluted by discharges from mining activities

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Abstract—This paper summarizes the major environmental and ecotoxicological processes of heavy metals pollution from Dexing Copper Mine in Jiangxi Province based on various findings in the Cooperative Ecological Research Project (CERP; Tang, 1994). It shows the knowledge necessary to elucidate metal pollution and its ecological implications. Processes devoted to the ecological implication include generation of acid mine drainage, formation of secondary minerals from precipitation, temporal and spatial distribution of metal pollutants in sediments and relevant toxicity, as well as ecosystem alternation which may relate to chemical pollution.

From the results, it was stated that the major emphasis should be placed on the environmental processes associated with sediment pollution by heavy metals. It shows that ad/desorption on the inorganic minerals, such as Fe/Al oxyhydroxides, play an important role in the immobilization of heavy metals in this river. There were clear indications that metal pollution has resulted in the toxicological and ecological consequences and there would be the risk of secondary pollution in the way of mobilization of bound metals to the overlying water when environmental conditions are varied.

Keywords: heavy metal pollution, mobility, toxicity, ecotoxicology.

1 Introduction

China is undergoing substantial and rapid changes in its society and its economic policies. Among various environmental problems, water pollution is one of the most critical issues facing China today. These pollutants poison aquatic organisms and accumulate in fish and other edible organisms, having serious impacts on human health. Metal mining and smelting in China have been a major concern for the environment protection.

To assess ecological impacts of heavy metal pollution in the aquatic ecosystem, chemical, biological and ecological assessment (He, 1998a) and integration of the disciplinary knowledge (He, 1998b) are needed. To anticipate the consequences of pollution, not only above information but also major environmental and ecotoxicological processes are needed to identify the connection between pollution and its ecological implications. The research area and sampling sites is shown in Fig. 1.

2 Generation of metal pollution and acidity by weathering

Major pollution sources associated with mining activities include the weathering of waste stone piles which produces huge quantity of acid drainage of pH$<$3, the discharge from the ore flotation plant which disposes great amount of alkaline effluent with high content of fine ore tailing's particles of pH$>$12, the non-point sources of pollution in mine area and seepage from the tailings impoundment, as well as discharges from the smelting processes in nearby smelters. Amongst, the acid drainage and industrial discharges are the major threatens to the nearby aquatic ecosystem.

Generation of acidity and metal pollution can be estimated by models (Dai, 1992a; 1992b). In this case, it showed that amount of elements released from weathering of waste stone increases with contacting time and surface area of pyretic waste stone. Main factors affecting the rate of the

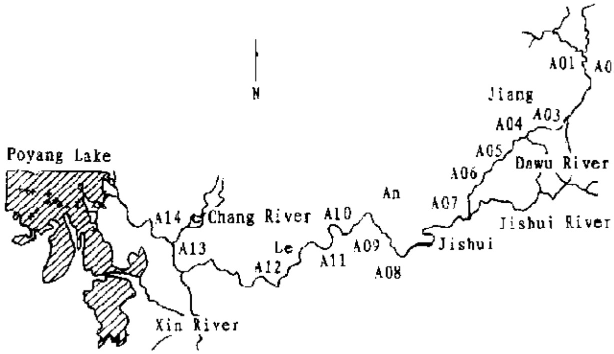

Fig. 1 Research location and sampling site

chemical weathering of the waste stone include rainfall volume, surface area, sulfide and pyrite contents in waste stone, as well as temperature. A simplified weathering model with three factors could be obtained from combination of individual simulations (Dai, 1992b).

Based on in-situ measurements and model calculations, concentrations of metals in polluted waters generated from weathering of pyretic waste stone was found to increase with time during piling and decrease very slowly after disuse of the pile dump. The pH value of the water in the dump would decrease to a minimum of 2.2 during piling and increase to 2.4 in year 2025 when disused in 1991 (Fig. 2). The data obtained by model computation was quite comparable to those obtained in-situ measurements before 1991. The result indicates the potentiality of long term impacts of mining to aquatic ecosystem and the necessity of rehabilitation on the open-cut fields and waste stone piles.

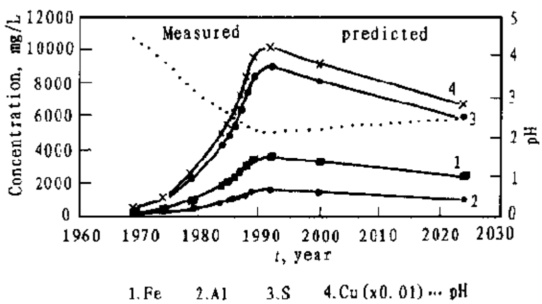

Fig. 2 Prediction of metals concentrations and acidity from waters of waste stone pile (Dai, 1992)

3 Precipitation of metals when mixing

Fortunately, metal concentration in acid drainage decreased significantly after mixing with receiving river water. High concentration of dissolved metals observed in Dawu River in mine area can hardly be observed in downstream of Lean River due to the precipitation of metal oxyhydroxides after mixing. For example, the background concentration of copper in upstream of Dawu River is 15 mg/L and reaches the highest (82.9 mg/L) when receiving acid mine drainage. It decreases continuously after precipitation, receive of alkaline waste water and dilution by inflow river water to concentration as low as 0.03 mg/L at 1000m downstream of the converge of Dawu River and Lean River.

The composition of sediments along Dawu River and in the converge with Lean River showed strong contamination by metals from acid mine drainage and closely related to the formation of abundant amorphous Fe/Al oxyhydroxides (Luan, 1992). Immediately converging with Lean River (A04—A05), the concentration of dissolved Cu should also controlled by co-precipitation of freshly formed Fe/Al oxyhydroxides which occurs at pH > 4.5 (Chen, 1992). However further downstream of the river, it appears that Cu concentration should be mainly controlled by the adsorption of metals on surface of particles (Luan, 1994).

4 Sedimentation and migration of suspended matters and sediments in Lean River

As an example, Fig.3 shows the spatial distribution of copper in the sediments of the Lean River in 1990. The concentration of Cu in the upstream from the mine area is comparable with the content found in average earth's shale and in the sediments of the unpolluted recent lakes. The influences of the Dexing Copper Mine was evident at Dawu River. The Cu concentration reaches as high as 4000 mg/kg and maintains similar level up to 40 km downstream (Ramezani, 1994).

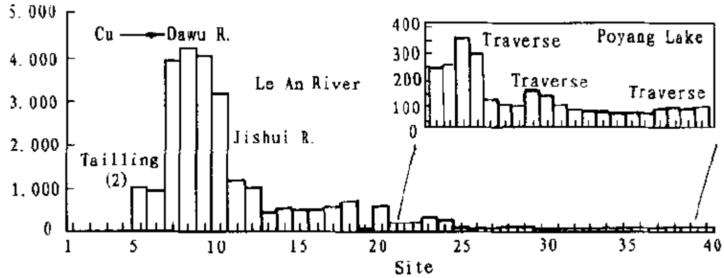

Fig.3 Spatial distribution of copper in the sediments of the Lean River in 1990 (Ramezani, 1994)

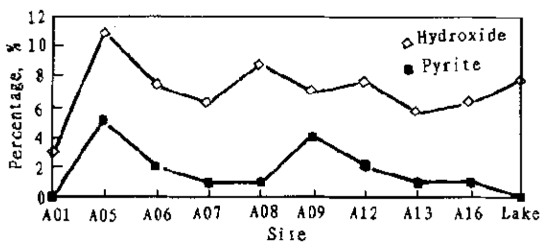

Fig.4 Variation of hydroxides and pyrite in sediments of Lean River (Dai, 1994)

Sediments with high copper concentration are due to aquatic processes such as neutralization, precipitation, flocculation as well as adsorption occurred in the receiving water. Neutralization leads to the precipitation of Fe/Al oxyhydroxides, which in turn flocculates to form flocs and co-precipitates with other metals in both acid and alkaline wastewater. The amorphous Fe/Al oxyhydroxides behavior quite differently from ore tailings. Generally, sedimentation velocities of suspended particles increased with the increment of the composition of ore tailings in river water. Consequently, fine particles may migrate longer distances in the form of suspended matters. The composition of sediments in Lean River was obviously changed due to mining activities. For example (Stark, 1994), hydromicas were found besides illites, which are weathering products of feldspars and other silicate minerals. The former is connected with the formation of the ore deposit. Main mineral and compound related with the sediment may be pyrite and hydroxide (Fig.4). Their content at background site (A01) was lower, but it was high from A05 to A16, especially pyrite in sediment. Pyrite in sediment is due to tailings discharged and hydroxide is formed by precipitation, as evidenced by microscopic examination for presence of the co-existence of other minerals (Dai, 1994). More than 90% of particle with size distributions were in the range of 0.83—3.40 μm and about 50%—60% was less than 1μm.

5 Mobility of sediment-bound metals

It is widely accepted that heavy metals bound to river sediment have potential ecological impacts depending on their mobility and bioavailability. Variations of the environmental conditions would cause changes of mobility and bioavailability or cause metals reenter to the overlying water. Among these environmental conditions, pH, *Eh* and enrichments in organic matters should be the greatest concerns.

The potency of metal release could be defined as the percentage of dissolved metal in the total and it is pH-dependent. Under aerobic condition, the potency of release for different metals in Lean River is following Zn > Cu > Cd and Pb. Release of Zn and Cu were easier and begin at pH 2.5 while Pb is more persistent towards pH variations. The potencies of metals release decrease with distances as shown in Fig.5 due to formation of more stable minerals during migration (Wen, 1996).

Release of sediment-bound metals is obviously pH-dependent. It shows the critical pH values at which the potency of metal release reaches the lowest (Table 1; Wen, 1996). In other words, it indicates the pH thresholds for different metals. Accordingly, sediment-bound Cu, Zn and Cd are sensible to pH variation in Lean River, especially in mine area (A04—05) and in river delta area (A13—16).

Under anaerobic condition such as in the profile of sediment, the mobility and bioavailability of sediment-bound metals depend on the potencies of forming insoluble metals sulfides. It has been suggested that when the ratio of simultaneously extracted metals (SEM) to acid volatile sulfide (AVS) is less than one (the molecular ratio of formed sulfides with divalent metals), metals in sediment should be immobilized and there would not be metal toxicity to aquatic life (Ankly, 1991; Di Toro, 1990). For sediments of Lean River, it could be stated that AVS concentrations were relatively lower than SEM and that the SEM/AVS ratios are much larger than unit (Table 2; Wen, 1997). Formation of metals sulfides should not be the major process to stabilize metals in sediments of Lean River. Only when close to the lake, metals become stable due to the formation of metals sulfides.

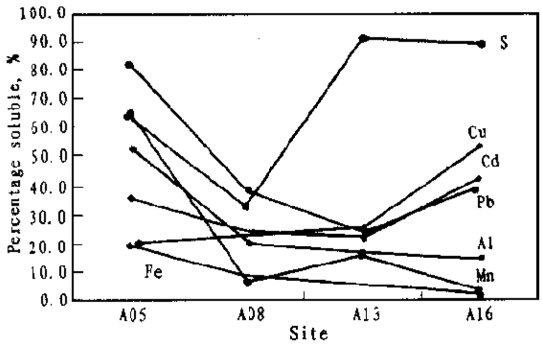

Fig.5 Percentage of dissolved metal concentrations in the total

Table 1 pH thresholds for metal release in Lean River*

Sites	Cu	Pb	Zn	Cd
A04	6.93	4.70	6.68	6.41
A05	6.90	4.97	6.54	6.54
JR	7.22	6.17	7.81	7.22
A07	7.52	6.83	7.52	7.52
A13	6.66	4.83	6.66	6.52
A16	6.57	4.48	6.57	6.571

* pH values below which metal begin to release significantly (Wen, 1996)

Table 2 Mobility of sediment-bound metals as indicated by SEM/AVS*

Sites	AVS, μmol/g	SEM, μmol/g	SEM/AVS
A04	0.01	3.82	382.32
A05	0.04	7.66	191.41
A07	0.98	7.87	8.03
A09	0.13	3.86	29.65
A13	0.25	5.13	20.52
A16	1.46	1.64	1.13

* Adopted from Wen *et al.*, 1997

It is most likely that iron and magnesium oxides are the important metal binding components in sediments of Lean River. Therefore surface complexation model could better describe the ad/

desorption behavior of metals in sediments of Lean River. By analysis of pore water profiles of heavy metals, it was found that these metals are not being leached from the sediments to the overlying water but are rather diffusing to the sediments. The reduction of SO_4^{2-} to HS^- results in the formation of highly insoluble metal-sulfides. This can explain in part the low concentrations of heavy metals in deeper pore waters. Higher concentration of Cu and Cd at the sediment-water interface can be interpreted as a release of the decomposition of biological materials (Yahya, 1994). Significant release of some metals due to oxidation of metal-sulfide occurs below pH 4.5 (Calmano, 1992). On the pH conditions in the pore water (7.15—8.67) of the Lean River sediments, such a release of heavy metals can not be expected.

6 Bioavailability, toxicity and ecological alternation

The biomonitoring of waters and sediments gives evidences on the potential biological effects of pollution. Among varies of indicators, assay on bioaccumulation could elucidate the bioavailability of pollutants in aquatic ecosystem. For example, bioaccumulation of Cu both in phytoplankton and zooplankton in Lean River were obvious (Table 3), indicating the potency of metal transferring from sediments, via overlaying waters, to aquatic organisms.

Table 3 Bioaccumulation of copper in phytoplankton and zooplankton in Lean River (mg/kg)

	Phytoplankton	Zooplankton
A01	321	92
A04	237	677
A05	878	243
A08	407	338
A13	374	631
A16	308	146

Another indicator is the toxicity of waters and sediments. The toxicity of sediments can be assayed either for the interstitial waters or sediment elutriates. As shown in Table 4, while chemical data indicated the most serious sediment pollution occurred at A04, most toxic location was at A07 (Wang, 1994; He, 1998). It is a clear indication that the toxicants causing the biological effects should come from discharges along Jishui River and that the high concentration of sediment-bound copper at A04 was mostly not bioavailable at neutral pH(>4.5).

Table 4 Classified toxicity of waters and sediments in Lean River*

		A01	A04	A05	A07	A08	A13	A16
Overlaying water	1993	2	1	1	5	2	2	2
	1994	2	3	2	5	3	3	–
Sediments	1993	3	2	3	4	3	3	2
	1994	1	2	–	5	2	2	–

* Toxicity was classified into 5 categories, according to the percentage inhibition or lethality (He, 1998)

In ecological survey, no species was observed at A04. In all samples, the midgefly larvae occupied greater part with a wide distribution. Oligochaeta was another important taxonomic group. Aquatic insect larvae (except *Diptera*), as the relatively clean bioindicators, mainly appeared in the upper stream and gradually reappeared in the lower reaches along with the increase of distance. The distribution of species richness, individual abundance and community structure for aquatic organisms changed significantly at A04 and recovered gradually downstream (Zhu, 1994; Xu, 1996). Comparing the toxic and ecological data at A04, the sharp decrease of biodiversity could be due mainly to the strong acidity from Dexing Copper Mine. As for the whole river, variation of these ecological indicators can be predicted by sediment pollution index and acidity (He, 1998c). An example shown in Fig.6, the relative biological indexes with respect to that at A01 can be predicted according to the sediment pollution index. Another indication of influences of metal pollution on ecosystem was that species of relatively clean waters as important bioindicators disappeared in the taxonomic groups of sampling sites until A13.

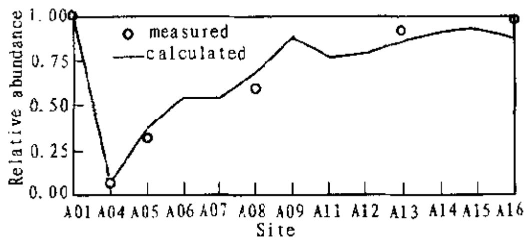

Fig.6 Relative abundance of aquatic organisms in Lean River (He, 1998)

7 Outlining the environmental behavior and ecological impacts

Based on the above information, one can conclude that:

Generation of acid mine drainage and weathering of waste stone piles is the main pollution source and will be a long-term process. Therefore bioremediation soon after open-cut and piles up is necessary.

Influences of mining activities on aquatic environments in Lean River can hardly be evaluated only by monitoring water chemistry, because most of pollutants transferred into sediments in a very short distance after mixing with river water. Therefore it is necessary to set up sediment criteria for metals in Lean River.

The sediment-bound metals in Lean River is not stable and their mobility depends on the environmental conditions, mostly pH and REDOX variations. Discharges of organic pollutants (COD or BOD) may induce dissolution of metals from sediments.

Special attention should be paid to the potential toxicity of metals in delta area of Lean River, where has been the major breeding habitats of fish in Poyang Lake.

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