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UNESCO MAB Cooperative Ecological Research Project on Heavy Metal Pollution and Its Ecological Effects*

(1987.7–1990.12)

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DESCRIPTION

Background

China is rich in nonferrous metal sulfide resources. Weathering processes of sulfide minerals generate acid mine drainage and cause water pollution. Ore dressing not only gives large amounts of ore tailings in the reservoir, which often leads to leakage and pollutes neighboring aquatic systems, but also discharges large amounts of alkaline wastewater together with concentrated suspension of ore tailings. The acid mine drainage and the alkaline wastewater mix together and enter into the receiving water body and undergo a series of physico-chemical reactions depending on the reacting species and eco-environmental conditions, thus strongly affecting the water quality of relevant aquatic systems and consequently the biological organisms in the ecosystem (Fig. 1).

About Dexing Copper Mine

Dexing is the largest opencast copper mine in China, situated near Le An River, Jiangxi Province. The ore mainly consists of copper sulfides with pyrite and multielement sulfides. More than 50 million tons of waste stone and more than 10 million tons of ore tailings have already been discarded. As the climate in Jiangxi is temperate and rainy, water flow varies considerably in different seasons. Impact of metals on the aquatic systems also varies under different

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eco-environmental conditions.

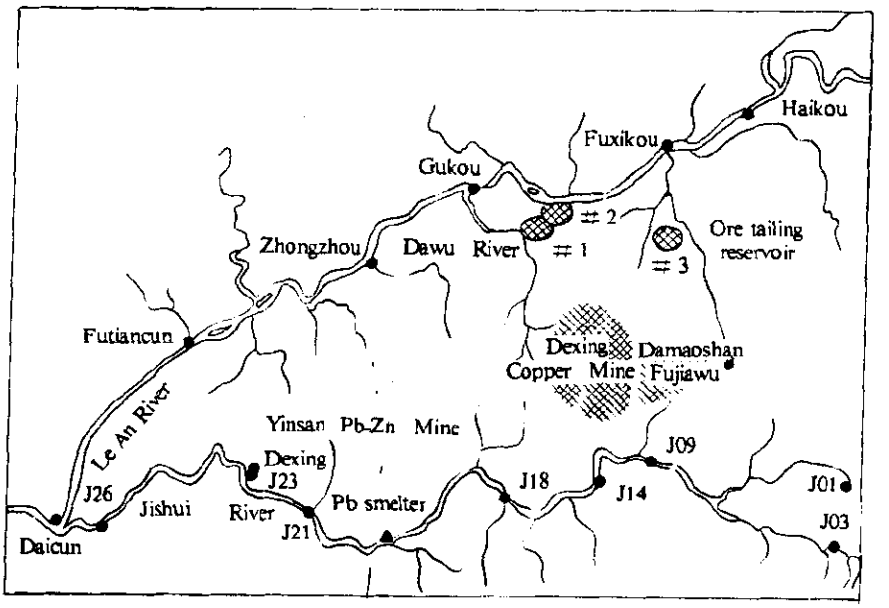

Fig. 1 Sketch on Dexing County, Jiangxi Province

Polluted Dawu River

Dawu River, 14 km long, runs through Dexing Copper Mine, and then flows into Le An River. The pollution sources along the river are seepages from mineral deposits with pH about 2.8, the acid drainage from wastestone dump with pH 2.3 and the alkaline wastewater as the concentrated suspension of ore tailings from ore dressing plant with pH higher than 12. Dawu River has already become the reacting bed of the chemical species of the polluted wastewater and seriously worsened the ecological environment.

Le An River-Poyang Lake area

Le An River, 279 km long, is located in the northeastern region of Jiangxi Province and flows west into Dexing, Leping and Poyang counties.

Jishui River, 30 km long, is another metal-polluted tributary of Le An River. There are small copper sulfide mines, a medium sized Pb-Zn mine and a lead smelter in Dexing County, discharging acidic wastewater into Jishui River which finally runs into Le An River at Daicun, Leping County. At Caijiawan of Poyang County, Le An River joins with Xin River and Chang River, named Rao River, 30 km away from Lake Poyang.

Lake Poyang, is one of the largest lakes in China. It is connected with rivers including Rao River-Le An River ecosystem in Poyang County. So far, there is no systematic study of metal pollution along Dexing Copper Mine-Le An River-Poyang Lake area.

Ecological effects of metal pollution in the aquatic ecosystem

Aquatic biological organisms are sensitive to acid mine drainage. The production of fishes and lotus roots (edible) in the mid-and upstream of Le An River were decreased quite a lot since the mining activities in Dexing County were intensified in the last decade as claimed by surrounding inhabitants of local counties. Decline of fertility of soils near the river banks and decrease of rice production in Poyang County were observed in the past decade and decline of rice and tea production in the mid-and upstream was complained by farmers in Leping and Dexing as they use the river-water for irrigation. So far little scientific data are available in this region.

OBJECTIVES

The CERP C2 in 1987–1990 is mainly the study of the impact assessment of the present and future mining activities in Le An River-Poyang Lake area with the following aims:

(1) To adopt scientific methods in the study of the extent of metal pollution in space and time variation and to study the metals in sediments and biota of relevant aquatic systems.

(2) To carry out the study of the transport and fate of metals in the aquatic system.

(3) To start a prediction model for the future impact of metals in mining activities for controlling metal pollution and protecting the environment.

Specific objectives:

(1) Impacts of acid drainage and metal pollution on the aquatic system at mining area.

(2) Metal flux assessment along Le An River-Poyang Lake area.

(3) Ecological effects of acid mine drainage on algae in Le An River.

(4) Hydrological data collection, and evaluation for Le An River.

(5) Water quality modeling for studying the impacts of metal pollution on Le An River.

METHODOLOGY

General research approach

The general research approach is shown in Fig. 2.

Research design and main tasks

The CERP C2 sub-project was designed to be composed of the following sub-topics:

1. Impacts of acid mine drainage and metal pollution on the aquatic system at mining area (Tang, H.X.):

(1) Weathering of pyritic minerals at wastestone dump (Dai, Z.H. and Wang, Z.H.)

The releasing rate of metals and acid from wastestone dump through weathering process at wastestone dump was studied by field survey along the dump to the dam of the acidic wastewater reservoir in rainy and dry seasons in 1987–1988 (11 sampling sites). Some simulation experiments for the oxidation and leaching processes of waste minerals of different grain size were carried out at different acidities under different oxidizing conditions.

(2) Occurrence, pathways and fate of metals in the aquatic system (Tang, H.X., Luan, Z.K., Cao, F.C. and Chen, M.)

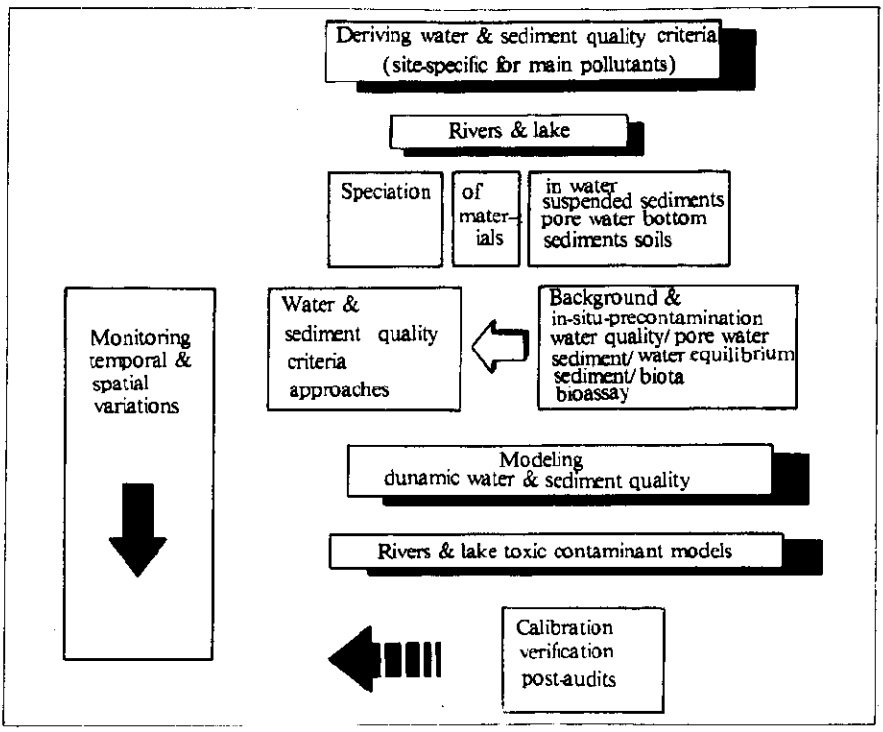

Fig. 2 The research approach

Metal pollution along Dawu River at mining area was assessed by sampling at 20 sites from Dawu River spring to downstream at Gukou, the site which discharges wastewater into Le An River. Main physico-chemical processes undergoing in the aquatic system were studied. Simulation experiments on neutralization, flocculation, precipitation of Fe (Al) in acidic solution and oxidation of Fe(II) in concentrated Fe(III) solution at low pH, adsorption of metals on Al(Fe) oxides, clay minerals and ore tailings and flocculation in systems resulting from acid mine drainage with alkaline tailings were studied.

2. Metal flux in Le An River-Poyang Lake area (Mao, M.Z. and Liu, J.Y.):

(1) Assessment of metal contamination along Le An River (Mao, M.Z., Liu, Z.H. and Dong, H.R.)

Field survey along Le An River was carried out in 1987–1989 in dry and rainy seasons and the distribution of metals in river water and sediments (suspended matter) has been assessed. The sampling sites were selected along the river starting from upstream through Gukou and Daicun downwards to Caijiawan near the lake.

(2) Impact of metals from Jishui River on Le An River (Mao, M.Z., Lin, Y.H., Liu, J.Y., Dong, H.R. and Liu, Z.H.)

River water and sediments in Jishui River were sampled along the upstream downwards to

Daicun. Metal pollution sources along the river were assessed.

(3) Speciation of metals in river sediments (Mao, M.Z., Liu, Z.H. and Dong, H.R.)

Geochemical speciation of river sediments from Le An River and Jishui River was carried out by sequential extraction followed by anodic voltametric determination after Tessier *et al.* (Anal. Chem., 1974, 51(7):844) and Salomons *et al.* (ES&T, 1980, 494).

(4) Assessment of metal contamination in Le An River-Poyang Lake area (Schmitz, W, Mao. M.Z., Wang, Z.H., Ramezani, N., Liu, Z.H. and Dong, H.R.)

To assess the impact of heavy metals from the mining activities on Le An River-Poyang Lake aquatic system, two sediment cores at Caijiawan were taken in November 1988 and 1989.

Three sediment cores were taken in April 1989, one at Caijiawan, one at Longkou (Le An River mouth) and one about 5 km NE from Longkou in Poyang Lake. Again vertical core profiles were taken at 20 stations along Le An River and on three rays in Poyang Lake in April 1990. Sediments were collected at 40 stations along Le An River from Dexing Copper Mine entering Poyang Lake up to 15 km at the same period (Fig. 3)

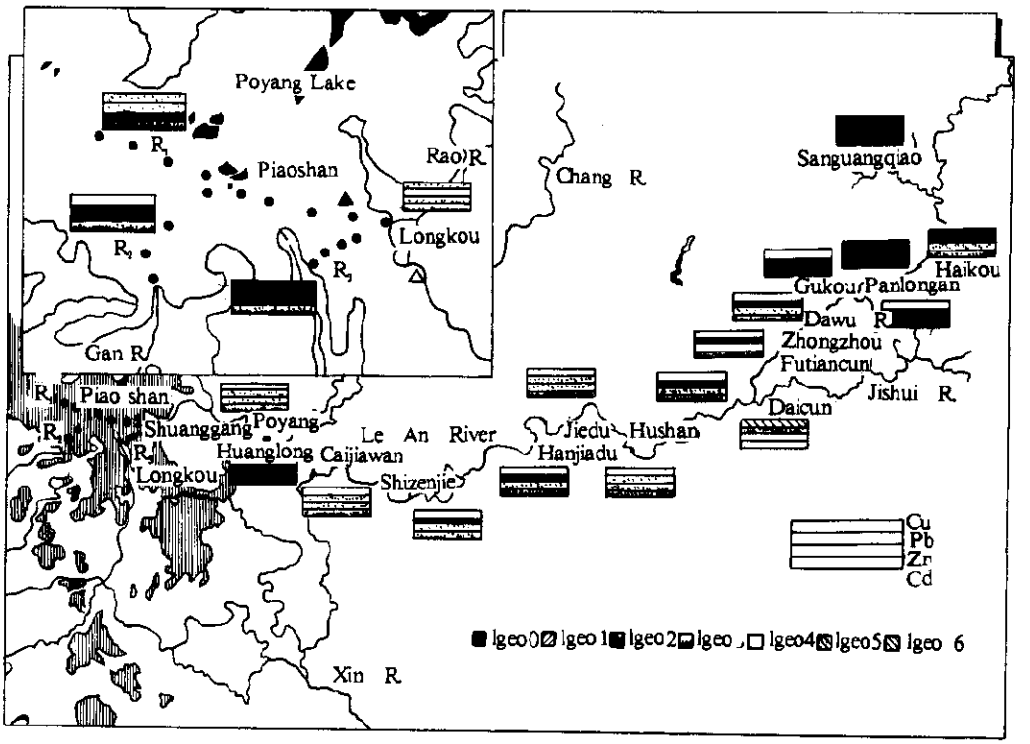

Fig. 3 Sediment quality (April 1990)

3. Ecological effects of acid mine drainage on algae in Le An River (Zhu, N.K., Xia, X.J., from RCEES, and Wang, H.J., Wang, Y.H. from NIAT):

(1) Biological assessment

Sampling, identification and characterization of aquatic phytoplanktons and algae species were undertaken. 14 sampling sites were selected along the river starting from upstream to downstream. Algae samples were collected simultaneously with water and sediment samples for chemical analysis in dry and rainy seasons, 1987–1988 and May 1989, 1990.

(2) Biological productivity of algae and bioaccumulation of metals on algae and some other biological organisms were studied; and interaction of metal-algae-sediment was started on a multichambered device for toxicity in Hamburg-Harburg.

4. Water quality modeling for studying the impacts of metal pollution on Le An River (Lin, Y.H., Chen, M., W. Salomons, Li, Q., Zou, G. G. and Tang, H.X.)

For evaluation and predicting the water quality under various eco-environmental conditions, models have to be established for the aquatic systems:

(1) Chemical equilibrium models for different sections of Dawu River and Le An River indicating distribution of different chemical species after bearing the impacts from acid mine drainage and the alkaline wastewater.

(2) River model (software supplied by Institute of Soil Fertility, Holland) was used to predict water quality in different segments of Le An River.

SCIENTIFIC RESULTS

Impacts of metal pollution on the aquatic systems at mining area

At wastestone dump, it was found that the generated acid mine drainage was highly acidic (pH 2.3–2.7) and contained high concentration of Fe, S and metals. The amount of elements released was correlated with rainfall (as leaching process). The mole ratio of S/ Fe of the weathering products increased in the acid mine drainage as Fe decreased during dry season by precipitation, but S/ Fe decreased with increasing of rainfall by leaching process.

A weathering model for pyritic minerals in wastestone dump was preliminarily formulated by the overall weathering rate and the relationship between the amount of sulfide being weathered in natural conditions and, the relevant environmental factors affecting the pyritic wastestone weathering based on the data collected in situ and obtained by simulation experiments.

Along Dawu River, it was found that Fe, Cu and S contents in the aquatic system increased gradually from upstream, the dissolved Fe and S decreased by oxidation and precipitation, but Cu remained in river water. After receiving the concentrated pollutants from the acid mine drainage, a large amount of Fe, S and metals accumulated in the sediments. Higher the pH, stronger became the precipitation. After receiving the alkaline wastewater, precipitation of Fe(Al) was nearly completed and metals together with ore tailings transported along the river and settled down into the river basin.

In the dry season, the dissolved metal species were lower than the limited levels, while in rainy seasons, river water in lower reaches near Gukou varied in quality. As the acidic and alkaline wastewater could not mix well at increasing flow rate, neutralization and precipitation reactions extended to Le An River.

After the acidic wastewater treatment plant was set up in 1988, it was the alkaline wastewater containing ore tailings with high pH affected Le An River mostly.

Simulation experiments on the main physico-chemical processes occurring in the field, such as neutralization, flocculation, precipitation of Fe, Al in moderate acidic solution and oxidation of Fe (II) in highly concentrated Fe (III) solution at low pH were carried out. Simulations for adsorption of metals on hydroxides of Fe, Al, clays and ore tailings are undertaken as well.

A chemical equilibrium model-MINTEQA2 has been used for simulating calculation of the chemical species in aquatic systems of Dawu River under various conditions.

Metal flux in Le An River-Poyang Lake area

Assessment of metal contamination along Le An River (1987–1989)

It was found that the river water was slightly contaminated and the suspended matters including the ore tailings were transported downwards along the river.

The trend of metal contamination in the sediment (suspended matter) can be observed, and it was found to be slightly higher in dry seasons than in rainy seasons. Variation of Cu and S content was more evidently shown as compared with that of Fe and Al in the whole aquatic system. The river sediments were polluted by Cu, Fe and by Zn and Pb to a lesser extent. Copper in the river sediments amounts to several thousands ppm at Gukou, a few hundreds ppm at Daicun and a few tens ppm at Caijiawan, near the lake in 1987–1989.

The impact of metals from Jishui River on Le An River was such that large amounts of Cu, Zn and Pb were discharged into the river and transported downwards, thus extravasated the metal contamination of Le An River.

Speciation of metals in river sediments

Metal speciation is important in making accurate estimation of aquatic impacts and the toxicity and bioavailability of metals vary with different chemical species. As to the chemical speciation of some river sediments from Jishui and Le An River, it was found that the orders of distribution of chemical species and their stabilities for the two rivers were different. In Le An River sediments, there were more residual specials of Cu, Pb, Zn and Cd found at Gukou and Caijiawan while in Jishui River sediments there were more less-stable carbonate bounded and reducible phases present. Along Le An River there were less-stable phases at Gukou than Caijiawan and the stable residual phases predominated in downstream indicating the transformation, transport and fate of these geochemical species along the river with more stable species near the lake.

Assessment of metal pollution of river sediments in Le An River-Poyang Lake area (1989–1990)

By comparison of the average metal concentrations for unpolluted sediments (fraction < 2μm) from recent lakes (F"o" rstner *et al.*) with those of the surface sediments (fraction < 20μm) from Le An River to Poyang Lake, it was found that upstream Le An River concentrations of Cu, Zn and Pb were found within the range for recent lakes. For Cd, it is noticeable that the sediments are already moderately polluted (I_{geo}-class 2).

Starting at the converging point of Dawu River, which is mostly affected by acid mine drai-

nage and alkaline wastewaters, namely Gukou of Le An River down to Futiancun, Cu reaches the highest grade (6), indicating a very strong pollution. The indices for Zn and Cd increase by one grade compared to the upstream background values. Nearly 30% of Cu is partitioned in the organic/ sulfidic fraction, suggesting again the influence of binding agents as carrier modifiers. In contrast, 40—50% of Zn has been found in the reducible fraction, indicating that oxyhydroxides are the main carrier for Zn. At about 40 km downstream of Dawu River mouth, Jishui River is also strongly polluted by Zn, Cd (both I_{geo}—class 4) and Pb (I_{geo}-class 3) due to a number of small Pb-Zn mines.

Further downstream, the pollution indices for Cu, Zn and Cd remain between I_{geo}-class 3—4, the sediments are strongly polluted.

Entering the Poyang Lake at Longkou the situation becomes less serious. Up to 5 km from Longkou the lake sediments clearly indicate heavy metal contamination caused by the mining operations in the upper reaches. Sites in lake remote from this tributary in a range of 10—15 km are comparable to the background values in the upstream Le An River.

These findings clearly characterize the Rao River-Le An River system as a point source for the southeastern part of Lake Poyang. This is also proved by sediment cores for example from Caijiawan and 2 km northeast of Longkou in Poyang Lake (Fig. 2).

Ecological effects of acid mine drainage on algae in Le An River

As the slope of Le An River is considerable, the up-and mid-stream basin is full of rocks, pebbles and sand, not much river sediments can be obtained. Thus there were very little aquatic vascular plants, benthic invertebrates and fishes in Le An River.

It was found that the algae species were about the same in different seasons, only the number of total species was different, higher in rainy season and upper stream, lowest at Gukou, mouth of Dawu River with highest concentration of Cu and total S, indicating the ecological effects of acidic wastewater from the mining activities. The number of algae increased gradually downwards along Le An River. It was found that algae productivity was in the reverse order of acidity and Cu, S contents in the river water and sediments. *Bacillariphyta* among the algae seemed to be acid resistant as its percentage was found to be increased as acidity of the river water was increased. The trend for algae growth is similar in Le An River and Jishui River.

Metals were found to be bioaccumulated in algae and shell fishes. In Xiangtun (near the mine area) Cu and Zn amounts to several hundreds ppm, Pb in tens ppm, Cd tens ppm in some algae (e.g., *Potamogetom Malainus* and *Hydrilla Varlicillata*). In *Hydrilla Verlicilla*, Cu content was found to be over 2000 ppm (whole stem, dry weight after digestion) in December 1989.

Simulation experiments on the effects of acid wastewater and the metals (Cu for example) on algae growth and interaction of metal-algae-sediment (samples in April 1990) were started in Hamburg-Harburg.

Water quality modeling

Based on the collected hydrological and meteorological data of the main hydrological stations (up-, mid- and downstream), Le An River was divided into 10 segments and total flow (run-off), runout, flow rate, water level and water volume at different segments were calculated

and estimated. These hydrological data were evaluated together with chemical analytical data into the water quality model.

As the river model is simpler and more appropriate than MEXAMS model with our present known scientific and environmental information, river model used as a quasi-chemodynamic model, involves simple chemical speciation, chemically active and inert fractions. Water soluble, exchangeable cations, carbonate bounded and reducible phases obtained by Tessier's procedure were combined as the chemically active species and the sum of the two phases—sulfide (organic) bounded and residual phase as inert fractions. In the model, water fraction is divided into soluble fraction and suspended matter fraction. Either suspended matter or sediments contain chemically active and inert fractions. Using mass balance principle, transport of metals can be calculated. Prediction of Cu, Zn distribution in water and sediments at different seasons along Le An River was studied. Taking flow rate to be 50, 80–100 and 500–1200 m^3/ s respectively in dry, normal and rainy seasons, it was found that Cu, Zn in sediment were largest at Daicun (near copper mine area) in dry seasons, while in rainy seasons, Cu, Zn are largest at Caijiawan near Poyang Lake. Cu content amounts to 300 ppm and Zn 600–700ppm. These results are in agreement with surface metal concentration of the core sample obtained at Caijiawan in April 1989.

SUMMARY

The CERP C2 is an inter-disciplinary eco-environmental study of metal pollution in an aquatic system affected by mining activities. The static environmental problems—the extent of pollution (contamination) in space and in time— has been studied through field survey in 1987–1990. Some simulation experiments were carried out in order to elucidate the better understanding of the environmental processes undergoing from the mining area to the river nearby. The biological assessment and the ecological effects of the acid mine drainage on algae were started, and hydrological data and other relevant environmental parameters collected. Efforts are made to coordinate these data obtained but still need improvement.

The CERP C2 is quite a large project for the study of metal pollution in such an aquatic ecosystem as to encompass the largest copper mine in China, an area rich in nonferrous metal resources (Dexing), and a river more than 200 km long (Le An River). The input of metals from the pollution sources at Dexing mining area to Le An River undergoes a series of physical, chemical and biological transformation processes under varying eco-environmental conditions.

Sediments criteria for metals in aquatic system is important. However, collection of suspended matter and bottom sediments in some cases were quite difficult, thus water quality criteria was emphasized in the first stage.

Some specific topics such as weathering and eco-environmental study of wastestones, oxidation and adsorption of Fe species in river, better strategies for controlling the acid mine drainage and the alkaline wastes, the interaction of algae population with metal polluted sediments and so on, were being started.

The study of metal transport and sedimentation of metal near the lake is important, but

work can only be started on 1990. The formulation of water quality prediction model was started at the present stage. Thus this study can be considered to be a first step to protecting the aquatic eco-environment toward sustainable development of this area where eco-environment as well as mining, fishery and agricultural problems have to be solved urgently.

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