PERGAMON

Applied Geochemistry 18 (2003) 749–764

**Applied
Geochemistry**

www.elsevier.com/locate/apgeochem

Environmental quality assessment on a river system polluted by mining activities

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Received 29 January 2002; accepted 29 June 2002
Editorial handling C. Reimann

Abstract

In this study, adverse impacts of heavy metal pollution, originating from mining, smelting and panning activities, on the aquatic ecosystem of the Lean River in south China, were evaluated by integrating the chemical, toxicological and ecological responses of single and multiple metals in overlying water, surface sediment and floodplain topsoil. The assessment results indicated that a highly localized distribution pattern was closely associated with the pollution sources along the river bank. Based on the combined indices, deterioration of local environmental quality was induced mainly by two sources. One was strong acidity and a large amount of Cu in the drainage from the Dexing Cu Mine. Another was high concentrations of Pb and Zn in the effluents released from many smelters and mining/panning activities in the riparian zone. Some possible suggestions on source control may be effective in dealing with these issues.
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1. Introduction

The last two decades have seen considerable progress on derivation of environmental quality values, in terms of guidelines, criteria or objectives (Smith et al., 1996; Long and MacDonald, 1998). Individual jurisdictions have employed different methods involving chemistry, toxicology and ecology, depending on the receptors to be protected. Nevertheless, the individual approach often shows intrinsic deficiencies or limitations, due to complexities and variations in the real world (Chapman et al., 1998; Chapman and Mann, 1999). Some studies have also indicated the examples of misuse or misfit of the concerned approaches (Wang et al., 1999; O'Connor and Paul, 2000). Therefore, most members of the scientific community have recognized that it is more reliable

and reasonable to incorporate appropriate, adequate and sufficient response data from various structural components of an aquatic ecosystem into a framework for environmental quality assessment on the varied temporal and spatial scales (Chapman and Mann, 1999; Krantzberg et al., 2000).

The Lean River is located in Jiangxi Province, South of China. It receives a large amount of acidic mine drainage (pH 2–3) and waste effluents containing Cu, Pb and Zn discharged from the neighboring Dexing Cu Mine (ore production of $\times 10^5$ tons per day) and from many smelters and mining/panning activities along the banks of mainstream and tributaries. Great input of heavy metals and distribution in different bound phases has led to a severe deterioration in the surrounding environments. Some preliminary studies have focused on individual aspects (He et al., 1997, 1998; Liu et al., 1999a, 1999b). However, a comprehensive understanding of environmental quality of heavy metal pollution, dependent on integrative responses from various

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components in the river ecosystem, is still desired. Based on chemical, toxicological and ecological responses from overlying water, surface sediment and floodplain topsoil, the main objectives of this study are: (1) to delineate the distribution and extent of heavy metal pollution; and (2) to evaluate the local environmental quality by integrating the different responses.

2. Material and methods

2.1. Description of studying area

Fig. 1 shows a sketch map of the sampling sites along the Lean River. The river is 279 km long and finally flows into Poyang Lake. The size of the drainage-basin is 9616 km². From the monitoring records at site A08, the average value of the annual runoff volume is 7.1×10^{10} m³, and ranges from 3.4×10^{10} m³ to 12.9×10^{10} m³. During the normal season, the mean current velocity in the upstream of the river is 0.79 m/s, 0.32 m/s in the middle stream, and 0.20 m/s in the downstream. Based on the preceding field investigation, the spatial locations of the main sources of heavy metal pollution along the river were determined as follows. A small activated C manufacture near the upstream site A01 discharges wastewater containing Zn and Pb. A tributary, the Dawu River (14 km long, 0.3–1.5 m/s of current velocity), running through the Dexing Cu Mine, receives a large number of effluents, including ore and tailing seepage, acidic wastewater (pH ~2.4) from weathering of solids and alkaline wastewater (pH ~12)

from ore dressing. Then it flows into the Lean River at site A04. Another confluent, the Jishui River (39 km long, 19.3 m/s of current velocity) is also a metal-polluted river situated beside several sulfide mines, Pb–Zn mines and smelters. It joins the mainstream at site A07. In the middle stream and downstream areas, waste discharges from a thermal power plant at site A09 and from panning activities nearby should be considered. Additionally, a discarded smelter in the adjacent upstream possibly caused some adverse effects on the downstream site A13, due to the release of wastewater carrying heavy metals.

2.2. Sampling and preparation

Overlying water was gathered using precleaned plexiglass bottles, filtered with 0.45 µm filters (Millipore®), then stored in low density polyethylene bottles at 4 °C after acidification (pH ~2). Surface sediment samples were taken by a Van Veen grab sampler, quickly packed and stored at 4 °C. A dialysis device peeper (Mudrich and Azcue, 1995) was filled with deoxygenated distilled water and covered by a 0.2 µm polycarbonate membrane. It was removed from the sediments (the inserting depth was 50 cm) after one week for equilibration. Immediately, interstitial water was extracted from the chambers on the peeper using plastic syringes in a N₂ atmosphere. The topsoils (0–10 cm) in the floodplain (FP) and nonfloodplain (NFP) areas were collected using plastic tools. After air-drying at ambient temperature, the soil samples were ground and sieved to fine particles (<2 µm, i.e. the clay fractions).

Fig. 1. Sketch map of sampling locations along the Lean River.

2.3. Chemical determination

Conventional approaches were employed to determine the physicochemical properties of the samples, such as pH and hardness (Mudrich et al., 1996). Measurements of acid-volatile sulfides (AVS) in the raw sediments and simultaneously extracted metals (SEM) in the remaining acidic solution after AVS extraction, were performed shortly after collection, using the published method (Allen et al., 1993). As to dry-weight normalized total average concentrations of heavy metals, the homogeneous sediment samples were dried at 30 °C and ground, then wet-digested by microwave or heating with concentrated acid mixtures (HNO₃/HClO₄/HF). Similarly, the uppermost soil samples were digested by strong acid solution.

Dissolved organic carbon (DOC) in overlying water was measured by a TOC analyzer (TOC500, Shimadzu) after filtration with 0.45 µm membrane. Determinations of organic matter contents of sediment and topsoil samples were finished using an instrument equipped with infrared radiation detector (LECO, Model CS225). The dry-weight normalized metal concentrations in homogeneous surface sediments were ascertained by flame atomic absorption spectrometry (AAS, Hitachi 170–70) or inductively coupled plasma–atomic emission spectrometry (ICP–AES, JarrellAsh 1155V). Analysis of SEM was implemented with ICP–AES (TJA Environment, ICAP Spectrometer 61E). The metal contents in pore water were determined by graphite furnace AAS (GFAAS, Perkin Elmer 3100). Standard reference sediment sample (CRM 280, COMEUR) and standard reference water sample supplied by the Chinese Academy of Environmental Sciences, were utilized to verify the accuracy of metal analyses in surface sediment and overlying water, respectively. All the recovery rates were around 80–120%. The deviations in the replicates of the standard reference materials and actual samples were generally lower than 10%. The Institute for Sediment Research, University of Heidelberg, Germany, provided the quality assurance/quality control for the soil samples results.

After air-drying and grinding to <30 µm, quantitative mineral analysis of the sediment samples was performed by X-ray diffractometer (XRD, PW1050) with the calibration samples, and with Co radiation, 40 kV/25 mA power. Identification of clay minerals was made by XRD (HZG-4) (Dai et al., 1994).

2.4. Toxicity testing

Examinations on acute and chronic exposure toxicity were carried out with overlying water, interstitial water and water extract of sediments by reconstructing river water based on the measured chemical compositions. Battery tests (BT) were utilized in a variety of toxicity

experiments with different species and end points. The testing species included *Photobacterium phosphoreum* (T3, Microtox), *Photobacterium* Q67 (Ma et al., 1999) as well as *Daphnia magna*. The inhibition or lethality percentage of individuals quantified the results. Bioassays were conducted according to the relevant protocols and procedures developed in the laboratory. The details pertaining to toxicity tests are given elsewhere (Zhou and Zhang, 1989; Ma et al., 1999).

2.5. Ecological response

Plankton species, such as algae, protozoa and zooplankton, were collected by a phytoplankton net with a mesh size of 50 µm. Polyurethane foam cut into identical units (PFU-5×7×8 cm) was used as the artificial matrix for colonization of protozoan communities (Xu et al., 1994). Individual abundance in 1 L of water sample was enumerated by the introduced method (Zhang and Huang, 1991). Benthonic macro-invertebrates were gathered with a 0.05 m² Peterson's grab device, then identified and counted to the practical species level (Zhu and Ren, 1994). Based on a statistical survey of species and individual abundance of aquatic organisms, two bio-diversity indices were employed (Washington, 1984) to quantify the in situ alterations of organism community structure.

$$\text{Margalef index : } D_k = \frac{S_k - 1}{\ln N_k} \quad (1)$$

Here, S_k is the number of species of the k th plankton, N_k the total number of individuals in the k th plankton. Furthermore, the mean diversity index for plankton species at the j th site, DI_j , could be calculated using

$$DI_j = \frac{\sum_{k=1}^u D_k}{u}, \quad j = 1, \dots, n$$

Here, u is the types of plankton studied ($u=3$ in this paper).

Shannon-Wiener index :

$$H_j = -\sum_{i=1}^s [P_i \times \log_2(P_i)], \quad (2)$$

$$P_i = \frac{N_i}{N}, \quad j = 1, \dots, n$$

Here, s is the number of species in a sample, N_i the number of individuals in species i of a sample from a population, and N the number of individuals in a sample from a population.

2.6. Data processing

In Table 1, the hardness-dependent final chronic values (FCVs) of Cu, Pb and Zn in freshwater, i.e. water quality values (WQVs), recommended by United States Environmental Protection Agency (USEPA, 1999), were adopted as the protective levels for aquatic species. The toxic unit (TU) approach was interdisciplinary for evaluating potential additive toxicity, in which each contaminant was assumed to have independent effect, and all endpoints in all toxicity tests were equivalent (Wildhaber and Schmitt, 1996). In this study, criteria toxicity unit of overlying water (OWCTU) and interstitial water (IWCTU) for a single metal and for multiple metals were similarly calculated.

2.6.1. Response indices for single metal at each sampling site

$$\text{Overlying water : OWCTU}_i = \frac{C_{i,OW}}{FCV_i}, \quad i = 1, \dots, m$$

$$\text{Interstitial water : IWCTU}_i = \frac{C_{i,IW}}{FCV_i}, \quad i = 1, \dots, m$$

$$\text{Surface sediment : SEM}_i - \text{AVS} \leq 0, \quad i = 1, \dots, m$$

$$K_{p,i} = \frac{\text{SEM}_i}{C_{i,IW}}, \quad \text{SQV}_i = K_{p,i} \times \text{FCV}_i, \quad i = 1, \dots, m$$

$$\text{Topsoil : TSTU}_i = \frac{C_{i,TS}}{C_{i,TSQV}}, \quad i = 1, \dots, m$$

Here, $C_{i,OW}$ and $C_{i,IW}$ are the concentrations of the i th

metal in overlying water and in interstitial water, respectively. FCV_i represents the final chronic value of the i th metal. $K_{p,i}$ is the partitioning coefficient of the i th metal, in which only the contribution of SEM was considered, while other metal fractions in the solid sediments, for simplicity, were assumed to be inert and not to participate in equilibrium partitioning (EqP). SQV_i represents the preliminary sediment quality value of the i th metal. $C_{i,TS}$ denotes the concentration of the i th metal in topsoil sample. $C_{i,TS}$ is the target value (no biological impact) of the i th metal in the soil quality standards of the Netherlands, namely, Cu: 36 mg/kg, Pb: 85 mg/kg and Zn: 140 mg/kg (Department of Soil Protection in the Netherlands, 1994).

The difference between ΣSEM and AVS , instead of the ratio of ΣSEM to AVS is currently utilized to assess the species distribution and bioavailability of heavy metals (Chen and Mayer, 1999). On the other hand, some authors have indicated that the dry-weight normalized sediment effect concentrations were at least as reliable and accurate as those normalized by the ratio of ΣSEM to AVS (Long et al., 1998; O'Connor et al., 1998). For comparison, the relevant results were provided in this study as well.

2.6.2. Response indices for multiple metals at each sampling site

Overlying water: the Nemeraw Index

$$\text{PI}_{j,OW} = \sqrt{\frac{\left[\frac{C_{i,OW}}{\text{FCV}_i}\right]_{\max}^2 + \left[\frac{C_{i,OW}}{\text{FCV}_i}\right]_{\text{avg}}^2}{2}},$$

$$i = 1, \dots, m, \quad j = 1, \dots, n$$

Table 1
Characteristics of overlying water and water quality values (WQVs, $\mu\text{g/L}$)

Site	Type			Hardness-dependent final chronic values (FCVs) suggested by USEPA ^a		
	Physicochemical properties			Cu	Pb	Zn
	pH	DOC (mg C/L)	Total hardness (CaCO_3 , mg/L)			
A01	6.5	1.0	102.3	9.1	2.6	120.5
A04	3.2	3.0	317.3	24.0	8.6	314.2
A05	6.3	2.0	189.3	15.5	5.0	202.9
A07	6.3	0.0	143.3	12.2	3.7	160.2
A08	6.5	0.0	179.1	14.7	4.7	193.6
A09	6.4	ND ^b	163.7	13.6	4.3	179.4
A13	6.3	1.0	133.0	11.4	3.4	150.5
A14	7.1	2.0	97.2	8.7	2.4	115.4
A16	7.2	ND	80.2	7.4	2.0	98.0

^a Hardness-dependent final chronic values (FCVs) for selected metals: $\text{FCV}_{\text{Cu}} = \exp(0.8545 \times \text{Ln}(\text{CaCO}_3 \text{ hardness}) - 1.702) \times 0.960$; $\text{FCV}_{\text{Pb}} = \exp(1.273 \times \text{Ln}(\text{CaCO}_3 \text{ hardness}) - 4.705) \times (1.46203 - \text{Ln}(\text{CaCO}_3 \text{ hardness}) \times 0.145712)$; $\text{FCV}_{\text{Zn}} = \exp(0.8473 \times \text{Ln}(\text{CaCO}_3 \text{ hardness}) + 0.884) \times 0.986$.

^b ND, not determined.

Here, the subscripts of max and avg denote maximum and average values, respectively. $C_{i,OW}$ is the concentration of the i th metal in overlying water. The water quality status can be classified into 5 ranks: no-, slight-, moderate-, strong- and serious-impact, based on $PI_{j,OW}$ of <1, 1–2, 2–3, 3–5 and 5, respectively.

Surface sediment at the j th site: $\sum SEM_i - AVS \leq 0$

Interstitial water at the j th site:

$$IWCTU_j = \sum_{i=1}^m IWCTU_{i,j}, j = 1, \dots, n$$

Topsoil at the j th site:

$$TSTU_j = \sum_{i=1}^m TSTU_{i,j}, j = 1, \dots, n$$

The scaling data for the various indices could be manipulated with

$$Scale_j = 1 + (100 - 1) \times \frac{V_j - V_{\min}}{V_{\max} - V_{\min}}, j = 1, \dots, n$$

Here, V represents the value of a response index at the j th site. Moreover, the transformation formula for the response value to gain the uniform scale was as followed

$$Scale'_j = 100 - Scale_j + 1, j = 1, \dots, n$$

Since some data in the local dry season (from October to March) were missing, the corresponding results were not included in this study.

3. Results and discussion

In the following, the measured response data of chemical, toxicological and ecological components were respectively given for the selected individual phases in the river ecosystem, namely, overlying water, surface sediment and topsoil. Then, a comprehensive description of the distribution and nature of heavy metal pollution was obtained by integrating the response data of the different components.

3.1. Chemical determinations

Despite recent progress in predicting bioavailability from normalization of bulk sediment chemical concentrations, chemical analysis alone does not provide an indication of biological damage, but is necessary to determine the extent and properties of contamination, and useful in giving a clue to possible pollution sources (Long and Chapman, 1985; Chapman, 1990).

3.1.1. Chemical response from overlying water

Some physicochemical properties of the river water are presented in Table 1. At site A04 near the confluence of mining drainage and the Dawu River, the low pH values of overlying water probably reflected the influence of strong acidic overflow (pH 2–3), originating from the Dexing Cu Mine during the local wet season from April to September.

Table 2 demonstrates the soluble concentrations of Cu, Pb and Zn, and their corresponding toxic units derived from the specific WQVs. The dissolved contents of Cu at most sampling sites were higher than the FCVs suggested by USEPA (1999). In the case of Zn, the contamination primarily occurred at site A07, corresponding to wastewater released from a chemical plant and some Pb–Zn mines along the Jishui River. At site A09, a thermal power plant discharged some effluents containing Zn, and may be the source of the relatively high concentration of Zn in the river water. The exact source of Pb along the river could not be determined. However, an activated C factory nearby may be responsible for contamination at site A01, due to the discharge of wastewater containing Pb and Zn. As to the downstream sites, the impacts, caused by mining and smelting activities along the Dawu River and the Jishui River, should be taken into account. In addition, because the majority of suspended solids was composed of finegrained ore tailings, which included quartz, muscovite, illite, pyrite, and calcite (Rainer et al., 1994), therefore particulate Cu at site A04 and particulate Zn at site A07 were prevalent. Owing to dilution effect and resumption of buffering capacity, the extent of metal contamination gradually diminished in the area downstream from site A07, whereas the transporting of Cu expanded to the site near Poyang Lake.

The Nemeraw Index is often used to indicate the water quality, based on the chemical response from multiple metals. Obviously, the quality status of overlying water in the Lean River exhibits a highly localized pattern (Table 2), closely associated with the distribution of pollution sources and metal species, which is exemplified by the cases at sites A04 and A07. At site A04, the impact of metal contamination only showed a slight grade. This phenomenon suggests that the influence of the dissolved fraction is less significant than that of other bound forms of heavy metals, such as suspended particles. A peak value present at site A07 is not surprising, since it is close to the junction of the tributary carrying large quantities of contaminants (the Jishui River, see Fig. 1). On the whole, the varied trend shown by the Nemeraw Index is consistent with that by $\Sigma OWCTU$.

3.1.2. Chemical response from surface sediment

The concentrations of AVS and SEM in surface sediments are given in Table 3. The dispersal of SEM_{Cu} was

Table 2

Soluble metal concentrations in overlying water ($\mu\text{g/L}$), toxic unit based on the WQVs and water quality rank derived from the Nemeraw Index

Site	Toxic unit (OWCTU_i) of metals based on WQVs and the Nemeraw Index and impact grade					
	$\text{Cu}/\text{OWCTU}_{\text{Cu}}$	$\text{Pb}/\text{OWCTU}_{\text{Pb}}$	$\text{Zn}/\text{OWCTU}_{\text{Zn}}$	ΣOWCTU	$\text{PI}_{\text{j,OW}}/\text{Scale}_j$	Impact grade
A01	29/ 3.2	9/ 3.5	15/0.1	6.8	2.9/40	Moderate
A04	38/ 1.6	19/ 2.2	49/0.2	4.0	1.8/18	Slight
A05	14/0.9	8/ 1.6	7/0.0	2.5	1.3/8	Slight
A07	89/ 7.3	17/ 4.6	313/ 2.0	13.9	6.1/100	Serious
A08	19/ 1.3	1/ 3.0	17/0.1	4.4	2.3/28	Moderate
A09	13/1.0	5/ 1.2	94/0.5	2.7	1.0/3	Slight
A13	13/ 1.1	2/0.6	21/0.1	1.8	0.9/1	No
A14	10/ 1.1	1/0.4	25/0.2	1.7	0.9/1	No
A16	21/ 2.8	1/0.5	40/0.4	3.7	2.2/25	Moderate

The bold data indicate the violation of the corresponding WQVs. Five grades can be classified: no-, slight-, moderate-, strong- and serious-impact, based on $\text{PI}_{\text{j,OW}}$ of <1, 1–2, 2–3, 3–5 and >5, respectively.

correlated with the location effect of pollution sources. For example, sites A04 and A05 corresponded to the acid effluent, carrying large quantity of Cu, from the Dexing Cu Mine into the Dawu River. For SEM_{Zn} , the Jishui River undoubtedly had more direct relationships, as shown by the sharp increase at site A07 relative to the neighboring upstream areas. At site A13 located in a backwater region, sedimentation of suspended solids caused by the change in the hydrological conditions (e.g. the declined flow rate) led to the increase of Cu and Zn contamination with respect to the upstream site. Differing from SEM_{Cu} and SEM_{Zn} , SEM_{Pb} exhibited a stable level throughout the river. In this study, the extent of metal contamination in surface sediments, indicated by the relevant scales respectively using the dry-weight normalized total average concentrations and the difference between ΣSEM and AVS , were roughly equivalent (see Table 3). The exception at site A05 resulted from a relatively high contribution of SEM_{Cu} .

Determinations of heavy metals in pore water and the individual interstitial water criteria toxic units (IWCTU) are listed in Table 4. The results indicated that from the middle stream site A07 down to the confluence with the Xin River at site A13, the release and activity of Cu were enhanced, compared to the upstream sites, which was probably induced by the variation or redistribution of Cu-bound phases in the sediments. Additionally, local anthropogenic disturbances, such as extraction of sand, would be conducive to remobilization of metals. As mentioned above, the main sources of Pb and Zn contamination involved wastewater discharged respectively from: (1) an activated C mill near the upstream site A01; (2) a chemical plant, some small nonferrous metal smelters and Pb–Zn mines along the bank of the Jishui River; (3) a thermal power station and panning activities at site A09; and (4) an abandoned smelter close to site A13.

In addition to several large tributaries, e.g. the Dawu River and the Jishui River (see Fig. 1), many smelters along the mainstream bank often discharged wastewater freely into the river. All these confluences could have a significant influence on the deposition regime, such as hydrodynamic conditions and physiochemical properties of surface water, then resulting in spatial heterogeneity in mechanical composition of sediments along the river. Figs. 2 and 3 exhibit the grain size distribution of solid particles in the wet and homogeneous samples, and relevant mineral constituents in sub-samples sieved to <30 μm , respectively. Clearly, fine silts (2–63 μm fractions), in which quartz was the predominant constituent, while muscovite, illite as well as feldspar were subordinate, held the main part. The presence of pyrite from site A05 to site A16 reflected, to some extent, the influence from the mining activities of the Dexing Cu Mine. These inhomogeneities could affect the partitioning coefficients $K_{p,i}$ of heavy metals, since $K_{p,i}$ values are generally fingerprints of sedimentary properties (Chapman, 1995; Landrum, 1995).

The total average concentrations after dry-weight normalization and preliminary SQVs for single metal calculated using EqP method are depicted in Fig. 4. The results showed that the actual concentrations of Cu and Pb at different sites exceeded the corresponding SQVs, and violation of the SQVs for Zn appeared at sites A01 and A14. Values of single metal presented here, however, should be regarded as working values and groundwork for those of multiple metals (Ankley et al., 1996), because coexistence of various metals commonly occurs in natural sediments. In this study, other chemical forms of heavy metals, except SEM, were referred to as inactive species and excluded in the derivation of $K_{p,i}$ and SQVs. Moreover, abuse or misuse of EqP-based SQVs, in which the quality values are often mechanically regarded as the clean-up regulations or goals

Table 3

Concentrations of AVS ($\mu\text{mol/g}$) and SEM_i ($\mu\text{mol/g}$), difference between SEM_i and AVS, total average concentrations of the different metals (mg/kg, dry weight) and the concerned scales

Site	AVS	$\text{SEM}_{\text{Cu}}/\text{SEM}_{\text{Cu}}-\text{AVS}$	$\text{SEM}_{\text{Pb}}/\text{SEM}_{\text{Pb}}-\text{AVS}$	$\text{SEM}_{\text{Zn}}/\text{SEM}_{\text{Zn}}-\text{AVS}$	$\Sigma\text{SEM}-\text{AVS}$	Scale _j
A01	0.49	0.059/−0.431	0.108/−0.382	0.522/ 0.032	0.20	2
A04	0.01	3.077/ 3.067	0.097/ 0.087	0.509/ 0.499	3.67	49
A05	0.04	6.399/ 6.359	0.125/ 0.085	0.926/ 0.886	7.41	100
A07	0.98	2.842/ 1.862	0.176/−0.804	4.688/ 3.708	6.73	91
A08	ND	ND	ND	ND	—	—
A09	0.13	1.499/ 1.369	0.142/ 0.012	2.104/ 1.974	3.62	49
A13	0.25	1.870/ 1.620	0.144/−0.106	2.925/ 2.675	4.69	63
A14	1.46	0.329/−1.131	0.137/−1.323	1.091/−0.369	0.10	1
A16	ND	ND	ND	ND	—	—
		Total Cu/Scale	Total Pb/Scale	Total Zn/Scale	Sum	Scale _j
A01	—	36/1	44/2	316/18	21	1
A04	—	2878/100	42/1	221/4	105	40
A05	—	2173/75	44/2	201/1	78	28
A07	—	1012/35	208/100	878/100	235	100
A08	—	733/25	94/32	664/69	126	50
A09	—	523/18	68/17	451/38	73	25
A13	—	464/16	75/21	505/45	82	29
A14	—	247/8	67/16	304/16	40	10
A16	—	215/7	81/24	226/5	36	8

ND, Not determined. The bold values indicate a positive difference.

Table 4

Metal concentrations in interstitial water ($\mu\text{g/L}$) and the corresponding toxic unit based on the final chronic values (FCVs)

Site	pH	$\text{Cu}/\text{IWCTU}_{\text{Cu}}$	$\text{Pb}/\text{IWCTU}_{\text{Pb}}$	$\text{Zn}/\text{IWCTU}_{\text{Zn}}$	IWCTU_j	Scale _j
A01	ND	2/0.2	3/ 1.2	22/0.2	1.6	1
A04	NS	NS	NS	NS	—	—
A05	7.2–8.7	10/0.6	9/ 1.8	38/0.2	2.6	48
A07	7.2–8.7	24/ 2.0	6/ 1.6	40/0.2	3.8	100
A08	7.2–8.7	19/ 1.3	3/0.6	20/0.1	2.0	21
A09	7.2–8.7	15/ 1.1	3/0.7	40/0.2	2.0	21
A13	7.2–8.7	19/ 1.7	3/0.9	36/0.2	2.8	54
A14	7.2–8.7	11/ 1.3	4/ 1.6	30/0.3	3.2	70
A16	7.2–8.7	10/ 1.3	1/0.5	25/0.2	2.1	25

ND, not determined. NS, not sampled. The bold data indicate the actual concentrations exceeding the FCVs recommended by USEPA.

(Coates and Delfino, 1993; Landrum, 1995), should be avoided as well.

3.1.3. Chemical response from topsoil

In many cases, elevated concentrations of heavy metals in floodplain soils can exert an influence on the plants and animals living nearby, through the pathways of food consumption and/or direct ingestion. The topsoil samples in the floodplain showed acidic pH values, particularly at site A04 (pH=2.8), which typically reflected the influence of strong acidity in the mining drainage coming from the Dexing Cu Mine via the Dawu River (see Table 5). In comparison with the

background thresholds of soil quality formulated by the Netherlands, Cu was the primary contaminant in this valley, due to its prevailing contribution and widespread occurrence. The topsoil samples in the floodplain from site A04 to site A13 were heavily affected by Cu, and secondly by Zn, while the contents of Pb were rather small. This case is closely related with the geographical distribution of local pollution sources, where the overflows, caused by heavy rainfall during the flooding season, flowed through the mining regions and poured into the main stream at sites A04 and A07 through the Dawu River and the Jishui River, respectively. As a result, strong accumulation of heavy metals in the floodplain

Fig. 2. Distribution of grain size in surface sediments of the Lean River.

topsoil by adsorption and deposition took place and extended further downstream. While the soil samples collected outside of the floodplain contained little heavy metals.

3.2. Toxicological response from water and sediment

Bioassay testing can provide direct evidence of water and sediment toxicity related to contamination, and establish the toxicological significance of chemical data. Thus, determinations of changes in resident biota exposed to or living in the polluted water and sediment are required (Long and Chapman, 1985; Chapman,

1990). However, since most bioassays are usually implemented under laboratory conditions, they may not be directly applicable to actual conditions, in other words, may not accurately imitate the field circumstances.

Table 6 gives the results of toxicity testing for the samples of overlying water and sediments. In this study, the mixed toxicity of various metals is explained by simply assuming additivity. At site A01, both overlying water and surface sediment showed only slight toxicity, possibly because of waste effluents discharged from the activated C mill. Although the river received mining drainage with high concentration of Cu from the Dawu River at site A04, the toxic levels of river water and surface sediment ranged from slight to moderate. Because the heavy metals were mainly bound or adsorbed to suspended particles or to the relatively inert fractions of surface sediments, thereby their bioavailability was restrained to some extent. On the other hand, at site A07, extreme toxicity could be observed in overlying water and surface sediment. There are two possible reasons: one is the additive function of multiple metals, such as Pb and Zn, the other is the change in metal bioavailability produced by redistribution or repartitioning of metal-bound forms. The toxic response at site A09 was attributable to the wastewater released from a neighboring thermal power plant and from the riparian panning activities. It should be noted that sediment toxicity still existed down to site A16, near the discharging point into the largest freshwater lake in China—Poyang Lake. In the case of overlying water,

Fig. 3. Mineral compositions of surface sediments in fractions <30 μm.

Fig. 4. Comparison between actual measurements and SQVs derived from WQVs proposed by USEPA (1999). The solid lines represent the total average concentrations of Cd, Cu, Pb and Zn, and the down-triangles denote preliminary SQVs based on WQVs recommended by USEPA, respectively. (a) Cu, (b) Pb, and (c) Zn.

Table 5

Toxic unit of different metals in topsoil (<2 μm fraction) from the non-floodplain (NFP) and floodplain (FP) areas

Site	pH ^a		TSTU _{Cu}		TSTU _{Pb}		TSTU _{Zn}		TSTU _j		Scale _j	
Type	NFP	FP	NFP	FP	NFP	FP	NFP	FP	NFP	FP	FP	FP
A01	5.0	5.3	0.4	0.4	0.3	0.2	0.6	0.8	1.3	1.4	5	
A04	4.8	2.8	0.6	14.3	0.2	0.4	0.3	1.2	1.1	15.9	100	
A05	4.2	5.2	0.5	8.9	0.3	0.3	0.4	0.6	1.2	9.8	60	
A07	4.4	5.7	0.4	9.6	0.3	0.7	0.4	1.2	1.1	11.5	71	
A08	4.2	4.9	0.6	9.9	0.3	0.6	0.3	1.2	1.2	11.7	72	
A09	NS	NS	NS	NS	NS	NS	NS	NS	–	–	–	
A13	5.2	5.0	0.3	7.4	0.3	0.6	0.2	1.5	0.8	9.5	58	
A14	NS	NS	NS	NS	NS	NS	NS	NS	–	–	–	
A16	NS	NS	NS	NS	NS	NS	NS	NS	–	–	–	

NS, not sampled. The bold values indicate the actual concentrations exceeding the standard levels.

^a The measurements are implemented in CaCl_2 solution.

toxic response could be also found in laboratory tests. However, the precise cause of constant toxic response was not known decisively. Residual heavy metals and unknown/undetected chemicals or conditions are involved.

3.3. Ecological response from water and sediment

In situ alteration, determined via analyses of plankton and infauna species, can provide direct indication of contaminant-related effects in the environment, but only if the non-pollution-related influences can be excluded (Chapman, 1990). In addition, community composition changes alone may provide misleading evidence of in situ toxic chemical effects, since plankton and benthonic communities may be overwhelmingly modified by recruitment cycles, predation, competition, natural events and subtle non-pollution, corresponding variations in the environmental properties of water and sediment (Long and Chapman, 1985).

The field statistical survey on number of species, abundance of plankton and benthos, as well as the bio-diversity

Table 6

Arcsine transformation of inhibition or lethal percentage in toxicity tests for overlying water and surface sediment

Site	Toxicity test in the overlying water			Toxicity test in the surface sediment			
	T3	Q67	Sum/Scale _j	T3	Q67	<i>Daphnia magna</i>	Sum/Scale _j
A01	0.09	0.05	0.14/2	0.01	0.05	0.01	0.07/1
A04	−0.17	0.32	0.15/2	0.20	0.32	1.06	1.58/52
A05	−0.01	0.12	0.11/1	0.13	0.12	0.64	0.89/29
A07	1.00	1.43	2.43/100	0.78	0.89	1.33	3.00/100
A08	0.06	0.42	0.48/17	0.33	0.42	1.06	1.81/60
A09	0.23	0.89	1.12/50	0.49	0.36	0.88	1.73/57
A13	0.09	0.37	0.46/16	0.41	0.37	1.06	1.84/61
A14	0.04	0.41	0.45/16	0.54	0.41	0.41	1.36/45
A16	0.11	ND	—	0.46	0.42	0.49	1.37/45

ND, not determined.

indices are summarized in Table 7. After comparison, the varied trend of species diversity in overlying water was, on the whole, similar to that in surface sediment.

From Table 7, the local biotic community structure at site A01 was still in a steady state. The strongest deterioration in river water appeared at site A04, where only some acid-resistant species survived, as revealed by the distribution of dominant algae species (see Fig. 5), while all benthonic organisms were destroyed thoroughly. Based on the chemical and toxic analyses aforementioned, the adverse effect of strong acidity in the mining wastewater and seepage effluents is another significant reason, in addition to the excess of heavy metals. In the downstream areas, following gradual resumption of dilution effect and self-purification of the river system, the number of plankton and benthonic species and population abundance recovered to different extents. The algae addicted to relatively clean surroundings, such as *Pyrrophyta*, *Xanthophyta* and *Chrysophyta*, reoccurred, as exhibited in Fig. 5. There was strong deposition of heavy metals present at site A13, due to the change of hydrodynamic parameters in the back-water zone (e.g., the declined current velocity), accordingly, aggregation of Cu, Pb and Zn may impair the benthonic multiplicity. In addition, external supplement by biological species migration from Poyang Lake is a possible source for the resumed bio-diversity at site A16.

3.4. Integrative evaluation with various responses

In natural environments, many heavy metals usually coexist, thus quality assessment on multiple metals are more practical and accurate than use of the individual element. The sediment quality triad (SQT), a current approach employed in sediment quality evaluation, is composed of 3 components, i.e. chemistry, toxicity and benthos. The essential assumptions include (1) measured chemicals are appropriate indicators of overall chemical contamination; (2) toxicity tests are appropriate indica-

tors of relevant toxic modes of action; and (3) benthonic community structure is an appropriate indicator of effects in situ. The method allows ecological interpretation of physical, chemical and biological properties and uses a preponderance of evidence approach, rather than relying on single measurements (Chapman, 1990). The response provided by each component is unique and complementary, and the combination of the components is critical, because no single component can offer comprehensive information (Chapman, 1990). Appropriate graphic presentations of triad data (i.e. the triaxial graphs) are useful to describe the geographical trends and magnitude in differences among the sites studied, and to display the relationships between patterns of chemistry, toxicity and biology (Canfield et al., 1994; Chapman et al., 1997). In particular, the SQT can be defined as a conceptual framework for collecting synoptic measurements of the components, and for collectively assessing relative sediment quality (Chapman et al., 1997). Furthermore, the results could offer some preliminary indications on the suitable treatment for each sampling site.

In the present study, this integrative method was further extended to overlying water, surface sediment and topsoil, in which the scaling data were utilized to screen the areas of concern and delineate the response grade of the different components in the river ecosystem, ranged from slight to strong. Table 8 contains the response intensity and descriptions of impacts of heavy metal pollution in overlying water, surface sediment and topsoil in the floodplain. Fig. 6 portrays the varied patterns and relationships of the components in overlying water and surface sediment from upstream to downstream, in which the intermediate responses provide different levels of information. Since many response data on topsoil were lacking, the relevant graphs were omitted.

To the authors' knowledge, only one paper has tested statistically the correspondence among the components using Mantel's Test based on Euclidean distance matrices of the different component data sets, in which a

Fig. 5. Distribution of algae species at different sites from upstream to downstream.

pairwise Spearman rank correlation was used as a measure of similarity (Chapman et al., 1996). The good correspondence among the measures/parameters initially suggested that one of the 3 components in the SQT sufficed to determine pollution status. Nevertheless, this correspondence between measures/parameters was not nearly as consistent on a site-by-site basis (Long and Chapman, 1985). Since some necessary data on the triad components were missing or not determined, Mantel's Test was not adopted in this paper. Alternatively, the burden-of-evidence and professional judgement, as outlined in a priori decision-matrix (see Table 8) can partially reflect the interrelationships between the individual components or parameters, such as consistency or divergence.

The significance and characteristics of various responses to the river system pollution showed a highly localized pattern from upstream to downstream, which was closely associated to the position of pollution sources, according to the preceding analyses. The upstream site A01 only suffered from waste effluents (containing Pb and Zn) from the activated C plant nearby, which caused slight to moderate toxicity in the rainy season. The local environment is, however, relatively stable, as indicated by the negative responses from benthonic and plankton communities and by the normal state of topsoil quality.

In the section from site A04 to site A05, the mainstream received, via the Dawu River, tailing seepage carrying a large amount of Cu, and the acidic overflow generated by large runoff in the wet season or due to interruption of power at the local water treatment plant. This situation accounts for the main negative impacts on water, sediment and topsoil in the floodplain. The lack of maximum toxic effects of heavy metals in overlying water and in surface sediments means that the bioavailability of heavy metals (mainly Cu) is

Table 7
Statistical survey of plankton species in overlying water and benthonic macroinvertebrates in sediments

Site	Overlying water				Surface sediment											
	Algae				Protozoa				Zooplankton				Benthos			
	Species (No.)	Abundance (ind./L × 10 ⁴)	Diversity (DI _j)		Species (No.)	Abundance (ind./m ²)	Diversity (DI _j)		Species (No.)	Abundance (ind./L)	Diversity (DI _j)	Sum (DI _j) / Scale _j ⁱ	Species (No.)	Abundance (ind./m ²)	H _j	Scale _j ⁱ
A01	75	25.9	5.9		37	48	9.3		29	28	8.4	23.6/1	20	5544	2.6	1
A04	11	1.3	1.1		0	0	0.0		3	17	0.7	1.8/100	0	0	0.0 ^a	100
A05	30	23.9	2.3		5	26	1.2		6	24	1.6	5.1/85	3	84	1.5	44
A07	NS	NS	NS		NS	NS	NS		NS	NS	NS	—	NS	NS	—	—
A08	45	35.1	3.5		15	40	3.8		11	18	3.5	10.8/60	7	252	2.5	5
A09	NS	NS	NS		NS	NS	NS		NS	NS	NS	—	NS	NS	—	—
A13	63	41.4	4.8		42	66	9.8		32	40	8.4	23.0/4	8	1050	2.2	17
A14	NS	NS	NS		NS	NS	NS		NS	NS	NS	—	NS	NS	—	—
A16	70	24.7	5.6		41	47	10.4		31	48	7.8	23.8/1	5	105	2.3	13

NS, not sampled. The 'ind.' denotes individuals.

^a This index is counted as 0 in this study due to no detection of benthonic organisms in situ.

Table 8
Integrated description of the impacts invoked by heavy metal contamination

Site	Distance (km) ^a	Overlying water ^b C/T/P	Surface Sediment ^b C/T/B	Topsoil in floodplain ^b C/T/O	Description based on integrated indices
A01	0	40/2/1 +/-/-	2/1/1 -/-/-	5/ND/ND -/?/?	No full evidence of metal-induced degradation. Waste effluent released from the active carbon mill should be controlled due to potential effect on overlying water.
A04	20	182/100 +/-/+	49/52/100 +/+/+	100/ND/ND +/?/?	Severe deterioration was caused by overflow of acidic drainage and ore seepage from Dexing Copper Mine. Direct entry of fine tailing particles via Dawu River also carried a large amount of particulate Cu.
A05	40	8/2/85 -/-/+	100/29/44 +/+/+	60/ND/ND +/?/?	Adverse impact came from the upstream section, and the resumption of the plankton species was retarded.
A07	50	100/100/ND +/?/?	100/100/ND +/?/?	71/ND/ND +/?/?	Extreme deleterious responses were caused by additive effects of multiple metals, originating from the effluents of Pb–Zn mine, chemical plant and nonferrous metal smelter along the Jishui River.
A08	84	28/17/60 +/+/+	50/60/5 +/+/-	72/ND/ND +/?/?	Metals in sediments were bioavailable in laboratory, but not in situ. Metals may stress the system; further pollution should be forbidden. Strong responses from overlying water and topsoil partially resulted from the influence of upstream area.
A09	96	3/44/ND -/+/?	49/57/ND +/+/?	NS/NS/NS ?/?/?	Apparent toxicity was attributed to the waste discharges from the thermal power plant and from riparian panning activities.
A13	159	1/16/4 -/+/-	63/61/17 +/+/+	58/ND/ND +/?/?	The change in hydrodynamic conditions in the backwater zone led to substantial deposition of suspended particles; response intensity of sediment relatively rose again.
A14	166	1/16/ND -/+/?	70/45/ND +/+/?	NS/NS/NS ?/?/?	Toxicity in water and sediment retained. Strong impact in pore water possibly originates from other potentially active binding phases of metals, except AVS.
A16	230	25/ND/1 +/?/-	25/45/13 +/+/-	NS/NS/NS ?/?/?	Regional environmental quality was gradually recovering. Yet residual metals or other unknown, unmeasured chemicals or conditions may induce toxicity. Artificial disturbance should be avoided.

ND, not determined. NS, not sampled. ?, refers to as uncertainty due to lack of relevant data. The “+” and “-” denote positive and negative response intensity (in the form of combined scales) based on the scale of 15, respectively, and indicate whether or not measurable differences occur relative to the control/reference conditions (Liu et al., 1999a, 1999b).

^a The distance is calculated from the local site A01.

^b Symbols C, T, P, B and O represent chemical, toxicological, plankton, benthonic and organism responses, respectively. For the sake of safety, the scales of chemical response from surface sediment adopt the maximum one among IWCTU_j, ΣSEM-AVS and dry-weight normalized total average concentrations.

restrained, due to strong binding to the suspended particles and to the inactive fractions in sediments. Thereby, the low pH appears to be another important factor in mediating serious structural and functional damage of aquatic communities as well as moderate toxicity. The toxicity testing procedures adopted in this paper can partially verify this phenomenon, in which the pH of the medium had been adjusted to neutrality before testing (Zhou and Zhang, 1989; Ma et al., 1999). The weak chemical response from overlying water at site

A05 (C–T–P+) implies that alteration of plankton species is not fully ascribable to the toxic metals.

Located at the confluence of the Jishui River and the Lean River, the main source of pollution at site A07 was the effluent discharged from mining and smelting activities along the tributary bank. High concentration of Zn and Pb as well as enhancement of Cu reactivity, as shown by the positive values of the detected responses, should be paid special attention from site A07 to site A09. Both intensive toxicity and severe community degradation

Overlying water at site A01

Overlying water at site A04

Overlying water at site A05

Overlying water at site A07

Overlying water at site A08

Overlying water at site A09

Overlying water at site A13

Overlying water at site A14

Overlying water at site A16

Surface sediment at site A01

Surface sediment at site A04

Surface sediment at site A05

Surface sediment at site A07

Surface sediment at site A08

Surface sediment at site A09

Surface sediment at site A13

Surface sediment at site A14

Surface sediment at site A16

Fig. 6. Variations in the triad component responses through the Lean River.

were probably caused by the additive effect of multiple metals. The triad can be utilized either in a reactive or in a proactive manner. When degradation has already occurred, responses must be reactive. On the other hand, when contamination and toxicity are high, but benthonic alteration has not been determined, the triad serves a protective function by indicating the receiving environment stressed by toxic chemicals and additional stresses unacceptable (Chapman, 1990). For example, the conflicting response intensities ($C+/T+/B-$) at site A08 in this study, indicated that the benthonic environment is possibly stressed by the toxic metals (Chapman et al., 1996), additional disastrous consequence will occur if the hydrological, e.g. agitation and dredging, and physicochemical conditions, e.g. pH and redox potential (Eh), are disturbed. The occurrence of detrimental responses from overlying water and topsoil in the floodplain was issued from the influence of the upstream site A07. The river ecosystem in downstream section from site A08 slowly revived from the serious deterioration, following resumption of buffered capacity and dilution effect. Owing to the missing data, the response values of water, sediment and topsoil are inconclusive in some areas, so further investigation will be required.

Site A13 was situated in the backwater region joined by the Xin River (see Fig. 1). Spatial variation in geochemical or hydrological conditions (e.g. the decreased flow capacity and velocity) gave rise to considerable deposition of suspended particles. Therefore, the total contents of some metals in surface sediments rose again. Toxicological and benthonic responses were somewhat intensified with respect to the neighboring upstream area.

In the downstream district near Poyang Lake, the selfpurification capacity and dilution effect of the river system have increased. The intensities of chemical response in overlying water and in surface sediment gradually diminished. Communities of benthonic and plankton species began to recover. However, the exact reasons for persistent toxicity present in both phases are not clear. Two possible causes may be involved: one is the residual heavy metal in pore water, the other is some unknown or undetected chemicals or conditions. Thus, additional studies to resolve uncertainties and estimate deviations in the raw data are advisable. Because the application of the (Σ SEM-AVS) model may be complicated by the changes in the vertical sediment profile, the influence of temporal and spatial variations in AVS on sediment quality of heavy metals in the Lean River has to be considered carefully in a future study.

Since the ecological risk generated by metal pollution mostly took place in the midstream area from site A04 to site A13, the priority of remediation should be focused on control of discharging sources, especially two major tributaries (the Dawu River and the Jishui River). As to the Dawu River, it is critical to minimize acidity in drainage created by tailing leakage and acci-

dental overflow, and to reduce the release of waste water containing Cu by constructing a new treatment plant or improving the capacity of available facilities. In the Jishui River, restrictions on the large discharge from mining and smelting activities in the riparian zone as well as on disposal of solid wastes are needed. It should be noted that the relevant remediation methods, such as dredging operations and other engineering, must be considered carefully before being put into practice in order to avoid potential secondary pollution. In addition, consecutive monitoring in the vicinity of the Lean River Delta is necessary to prohibit the expansion of metal contamination into Poyang Lake. The artificial disturbance to bottom sediments has to be avoided as much as possible. To clean the topsoil pollution significantly influenced by overflow in the Lean River, remedial works including physicochemical and biological techniques can be applied to the floodplain with the overload of heavy metals.

Last but not least, the quality values developed in this paper should be regarded as the 'interim' forms or working values, which would be refined over time base on region-specific effects and contaminant information (Chapman et al., 1999a, 1999b). As emphasized by many studies, environmental quality values are scientific tools to screen the pollution situation and to assist in the demonstration of pollutant concentrations. They are neither definitive nor appropriate alone for regulatory use. Regulators or managers must additionally balance the limitations of current scientific knowledge and methods against the actual demands for some degree of uniformity, feasibility and enforceability.

4. Conclusions

The quantitative indices, integrating chemical, toxicological and ecological responses from different components in the Lean River ecosystem, including overlying water, surface sediment and floodplain topsoil, indicated a highly localized distribution pattern closely associated with the pollution sources along the bank. The degeneration of local environmental quality resulted mainly from strong acidity and large quantities of Cu in the drainage from Dexing Cu Mine and from high concentrations of Pb and Zn in the effluents discharged from many smelters and mining/panning activities in the riparian areas. Possible remediation engineering should be considered carefully before being implemented.

Acknowledgements

The authors appreciated the technical assistance of all members in the International Cooperation Ecological Research Project (CERP). The authors are grateful to

the Federal Ministry for Research and Technology (BMFT) in Germany, to the United Nations Education Science and Culture Organization (UNESCO) Office in Paris, and also to the International Man and Biosphere (MAB). This work was also under the auspices of China National Natural Science Fund Committee (No. 20037010). In addition, the helpful suggestions of two referees (Drs. M. Langedal and N. Breward) are acknowledged.

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