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Sediment quality criteria for heavy metal pollution in the Le An River with triad approach

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Abstract—In this study, integrative traid was used to sediment quality in the Le An River, which has been strongly contaminated by large amount of Cu, Pb, Zn, Cd, As and Cr discharging from mining activities. All available data collected from chemical analyses, toxic tests and field survey on benthic macroinvertebrates were transformed into ratio-to-reference(*RTR*) and relevant scales. The responses of receiving environment to mining impacts were illustrated by traid graphs. Traid results indicated that a sectional-distribution pattern existed from upstream to downstream: (a) relative clean upstream; (b) serious contaminated middle stream; (c) gradual recovery downstream. This situation was closely related with local mining activities, which caused obvious degradation of sediment quality in some sections, therefore, remediation was required urgently.

Keywords: triad; sediment quality criteria; heavy metal pollution; Le An River.

1 Introduction

Problem sediments may cause great adverse impacts on aquatic ecosystem, therefore, assessment and remediation of contaminated sediments become the focus by the public and government(Chapman, 1995). Establishment of sediment quality criteria(SQC) are necessary for managers and regulators: (1) to identify the pollution-degraded area; (2) to determine the cause-effect relationships of contaminants; (3) to design monitoring programs and waterload allocations (Power, 1992).

Triad, integrating with measures of three essential components; sediment chemistry, toxicity and benthos in situ, facilitates screening the extent of pollution and interpreting the bio-response data (Chapman, 1990; 1991). Therefore, it may be a preferable choice of SQC establishment to aquatic ecosystem consisting of different virtue of interdependent trophic level(Canfild, 1994; Chapman, 1996).

The Le An River (279 km in length), following into the largest freshwater lake in China, i.e. Poyang Lake, has been seriously contaminated by large amount of waste water discharging from Dexing Copper Mine and other mines nearby (Tang, 1994). As a result, deposition of high concentrations of Cu, Pb, Zn, Cd, Cr and As in sediments caused severe degradation in some sections. The objectives of this study are: (a) to the reveal both geographical distribution and level of heavy metal pollution along this river; (b) to describe the dose-response relationship and its significance in sediment samples from the Le An River.

2 Materials and methods

2.1 Comprehensive database

Several stations were selected from upstream to downstream along the Le An River (Fig. 1)

All original data of triad were collected from the freshwater sediment quality database(CERP-DBMS), available structure of data sets contained the following information for each station:

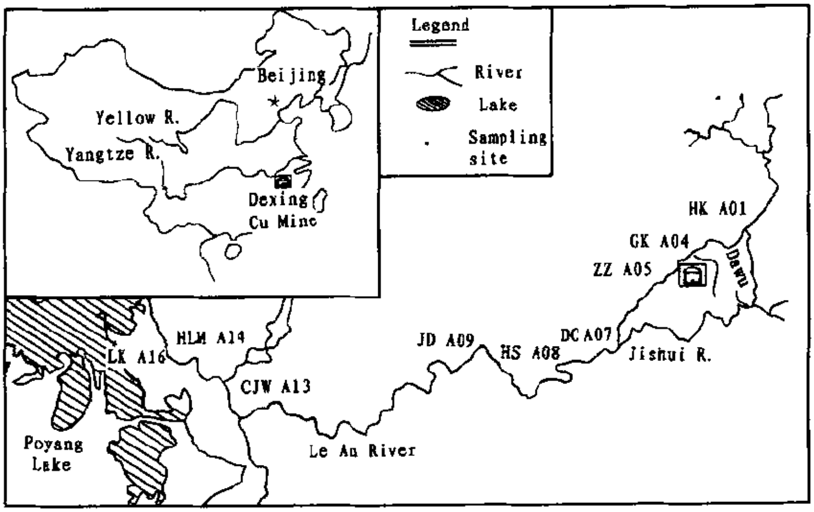

Fig. 1 Diagram of sample stations along the Le An River

location description, sampling date, surficial sediment collection technique and treatment procedure, results of sediment chemistry, benthic infauna alterations and laboratory sediment toxicity tests. Data within CERP-DBMS were maintained in Microsoft EXCEL file format, and databank entries were verified against the primary records(Mao, 1994).

2.2 Chemical analyses(C)

Analytical method of acid-volatile sulfide(AVS) and sum of simultaneously extracted metals ($\sum$SEM) adapted from literature (Allen, 1993). Since the ratio of $\sum$SEM/AVS greater than 1 among almost stations in the Le An River (Wen, 1997), the correction of AVS could be neglected (Hare, 1994). Based on a modified sequential extraction procedure, the speciation of heavy metals in surficial sediments could be simply classified into three levels of bioavailablility according to their stability: readily bioavailable, moderately bioavailable and inert(Mao, 1996). Previous studies demonstrated that summary of readily and moderately bioavailable fractions possessed most part of speciation distribution (Mao, 1996), so inert fraction was no considered in this paper. Cu, Pb, Zn, Cd, As and Cr in less than 63 μm fraction of surficial sediments were detected by AAS and ICP.

2.3 Sediment toxicity testing(*T*)

Exposure toxicity experiments were performed with interstitial water and water extraction of surficial sediments. Species selected for acute and chronic toxic testing included: *Daphnia magna*, *Photobacterium phosphoreum* (Microtox, T3) and a new Photobacterium Q67 (*Vibrio Qinghaiensis Sp. Nov*) which was developed for rapid test in freshwater(Zhu, 1994). The toxicity was quantified by inhibition or lethality percent of individuals. For additional details pertaining to toxicity tests were discussed elsewhere (Wang, 1994; 1996).

2.4 Benthic taxonomic identification (*B*)

Species and abundance of benthic macroinvertebrates were counted and identified to the lowest practical taxonomic level given the condition of the specimen, generally to the species level(Zhu, 1994). Community structure alterations of benthic organisms in the field were indicated by the biodiversity index based on Shannon-Wiener Formula from information theory(Washington, 1984;

Zhu, 1994).

2.5 Ratio-to-reference (*RTR*) calculation and transformation

2.5.1 Sediment chemistry

HK A01 was selected as the reference site in our study. *RTR* (R_{ij}) for concentration of each individual metal in each site(C_{ij}; in HK: C_{rj}) was calculated according to Formula (1). Added up *RTR* values for various metals within different station respectively [Formula (2)], then transformed to numerical scale on the basis of Formula(3)(range from 1 to 100 represented low to high chemical response separately).

$$R_{ij} = \frac{C_{ij}}{C_{rj}}, \quad i = 1,2,\cdots,n; \; j = 1,2,\cdots,m, \tag{1}$$

$$R_i = \sum_{j=1}^{m} R_{ij}, \tag{2}$$

$$R_i^t = 1 + (100 - 1) \times \frac{R_i - R_{\min}}{R_{\max} - R_{\min}}, \quad i = 1,2,\cdots,n. \tag{3}$$

2.5.2 Sediment toxicity

Similar to sediment chemistry, after arc sine transformation (with radian measure), data of inhibition or lethality in toxicity tests were changed into *RTR* values with respect to HK A01, then the summary of *RTR* in each site was converted into corresponding scale individually(range from 1 to 100 represented low to high toxicity respectively).

2.5.3 Benthic infauna

Based on statistical survey of species and abundance of benthic macroinvertebrates, benthic community structure alterations was expressed in form of bio-diversity index derived from the Formula(4) (m representing the number of species in a sample; n_i representing the number of individuals in a species i of a sample from a population, n representing the number of individuals in a sample from a population). Moreover the *RTR* of index in each station was turned into relevant scale like the situation of chemistry and toxicity, then transformed by Formula(5) in agreement with response of other two components(range from 1 to 100 represented low to high bio-response in situ respectively).

$$H = -\sum_{i=1}^{m} [P_i \times \log_2(P_i)]; \; P_i = \frac{n_i}{n}, \quad i = 1,2,\cdots,m, \tag{4}$$

$$R_i^{t'} = 100 - R_i^t + 1, \quad i = 1,2,\cdots,n. \tag{5}$$

2.6 Rank pollution area for possible remediation-decision

Combined scales of various components, differential responses shown as either positive (+) or negative (−) indicated whether or not measurable differences from control/reference conditions(in HK A01) were determined. And some initial advice on treatment in sampling sites are also provided in Table 1.

2.7 Tri-axial graphs

Linking together with scales of three components, effect-based SQC were drawn on corresponding C-T-B tri-axial graphs, representing chemistry, benthos and toxicity respectively (Chapman, 1990).

Table 1 Traid response matrix for initial decision-making and advice (Chapman, 1996)

C-T-B	Possible conclusion	Significance and advice of treatment*
+ + +	Strong evidence for metal-induced degradation	Treatment necessary dependent on degree of degradation and metal(s) responsible(1)
− − −	Strong evidence that there is no metal-induced degradation	Treatment not necessary
+ − −	Heavy metals are not bioavailable	Treatment not necessary
− + −	Unmeasurement metals or conditions exist with the potential to cause degradation**	Further focused studies, as directed by present study result, needed to determine metals or conditions(1)
− − +	Alternation is not due to toxic metals	Treatment not necessary
	Toxic chemicals are bioavailable in the laboratory but not in situ(2)	Treatment probably necessary dependent on degree and source of laboratory effects(1)
− + +	Unmeasured toxic metals are causing degradation(3)	Treatment probably necessary; level dependent on degree
+ − +	Metals are not bioavailable or alternation is not due to toxic metals	Treatment probably not necessary but some additional focused confirmatory studies may be required

*: Treatment includes any or all of: source control, primary, secondary or tertiary treatment; **: Recheck results from chemical analyses(e.g. QA/QC, detection limits) and toxicity studies(e.g. modifying factors such as grain-size and QA/QC) which may indicate retesting. Consideration may need to be given to conducting additional chemical analyses; (1) Ammonia toxicity in sediments may be suspected in some instances; (2) Recheck benthic data (especially statistical analyses to be sure that alternation in not occurring); if not, consideration may be given to source control; (3) Recheck chemical analyses for thoroughness and QA/QC. Consideration may need to be given to conducting additional (e.g. chemical scan) analyses. Further analysis may be required to identify other possible sources/causes of toxicity on benthic alternation.

3 Results

3.1 Bulk sediment chemistry

Concentrations of selected heavy metals in surficial sediments along the Le An River and their *RTR* response values are presented in Table 2.

Table 2 Concentrations of heavy metals in surficial sediments (mg/kg) and relevant *RTR* conversion

Sampling sites	Cu Conc./*RTR*	Pb Conc./*RTR*	Zn Conc./*RTR*	Cd Conc./*RTR*	As Conc./*RTR*	Cr Conc./*RTR*	Σ*RTR*	Scale
HK A01	32/1.0	58/1.0	346/1.0	3/1.0	15/1.0	58/1.0	6.0	1
GK A04	3500/109.4	100/1.7	270/0.8	3/1.0	27/1.8	138/2.4	117.1	100
ZZ A05	2218/69.3	58/1.0	203/0.6	3/1.0	23/1.5	100/1.7	75.2	63
DC A07	1209/37.8	310/5.3	1118/3.2	6/2.0	126/8.4	102/1.8	58.5	48
HS A08	983/30.7	121/2.1	617/1.8	4/1.3	52/3.5	111/1.9	41.3	33
JD A09	442/13.8	85/1.5	449/1.2	3/1.0	35/2.3	100/1.7	21.5	15
CJW A13	910/28.4	93/1.6	760/2.2	4/1.3	34/2.3	103/1.8	37.6	29
HLM A14	350/10.9	86/1.5	336/1.0	3/1.0	29/1.9	119/2.1	18.4	12
LK A16	333/10.4	83/1.4	402/1.2	1/0.3	29/1.9	93/1.6	16.9	11

3.2 Sediment toxic tests

Followed program of toxicity identification evaluation (TIE) and procedure of battery test (BT), arc sine transformation and *RTR* calculation for inhibition or lethality for testing species are listed in Table 3.

Table 3 Arc sine (radian measure) and *RTR* calculation of toxic percents for metal pollution in samples

Site name	T3 inhibition /*RTR*	Q67 inhibition /*RTR*	D. magna exposure lethality/*RTR*	D. magna extraction lethality/*RTR*	*RTR* sum	Scale
HK A01	0.01/1	0.05/1	0.32/1	0.01/1	4	1
GK A04	0.20/20	0.32/6	1.22/4	1.06/106	136	59
ZZ A05	0.13/13	0.12/2	0.52/2	0.64/64	81	35
DC A07	0.78/78	0.89/18	0.28/1	1.33/133	229	100
HS A08	0.33/33	0.42/8	0.56/2	1.06/106	148	65
JD A09	0.49/49	0.36/7	0.59/2	0.88/88	146	63
CJW A13	0.41/41	0.37/7	0.19/1	1.06/106	155	67
HLM A14	0.54/54	0.41/8	0.32/1	0.41/41	104	45
LK A16	0.46/46	0.42/8	1.16/1	0.49/49	103	45

3.3 Field survey of benthos in surficial sediments

Statistical information on benthic community structure in sediment samples as well as *RTR* conversion are summarized in the following table.

Table 4 Statistical investigation on benthic macroinvertebrates and *RTR* conversion along the Le An River

Site name	Species of benthic macroinvertebrates	Abundance of benthic species (ind./m^2)	Benthic infaunal diversity index *H*	*RTR* value	Transformation scale	Correction scale
HK A01	20	5544	2.64	1.00	100	1
GK A04	un(0)	un(0)	0.00	0.00	1	100
ZZ A05	3	84	1.50	0.57	57	44
HS A08	7	252	2.52	0.96	96	5
CJW A13	8	1050	2.22	0.84	84	17
LK A16	5	105	2.32	0.88	88	13

Note: un is the undetected in situ, counted it to be 0

3.4 Sediment quality triad and C-T-B graphs

Proportionally scaling data between 1 and 100 for symmetrical triangle graph are tabulated in Table 5 and illustrated in Fig.2.

Table 5 Summary of *RTR* scale for each component of traid in surficial sediments from the Le An River

Site name	Chemistry(C)	Toxicity (T)	Benthic infaunal alternation(B)	Triad response C/T/B
HK A01	1	1	1	−/−/−
GK A04	100	59	100	+/+/+
ZZ A05	63	35	44	+/+/+
HS A08	33	65	5	+/+/−
CJW A13	29	67	17	+/+/+
LK A16	11	45	13	−/+/−
DC A07	48	100	us/ud	+/+/?
JD A09	15	63	us/ud	+/+/?
HLM A14	12	45	us/ud	−/+/?

notes: us/ud is the unsampling or underacting limited by local conditions; ? is the uncertain by missing benthic community data.

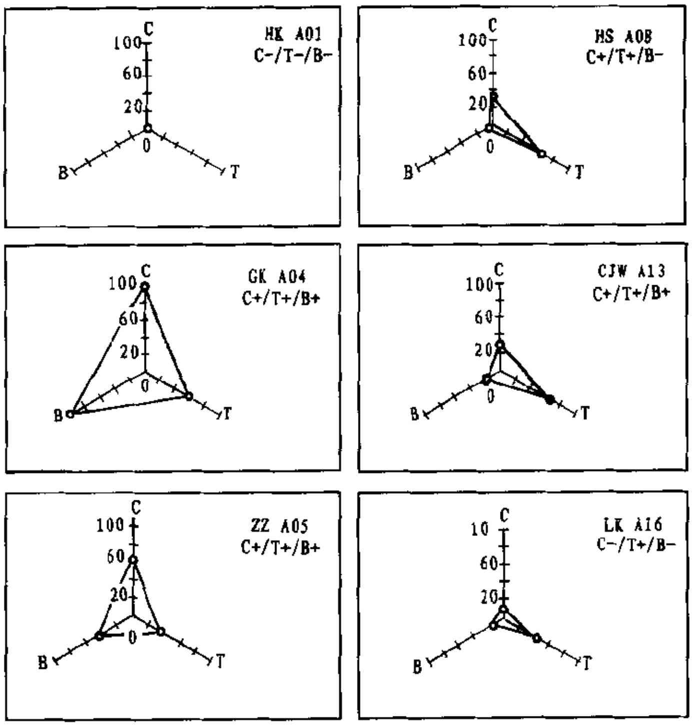

Fig.2 Triad graphs for heavy metal pollution in surficial sediments from the Le An River

4 Discussions

Based on previous tables and Fig.2, relative clean situation exists in upstream zone such as reference site, however, affected by discharging from a factory nearby, higher Zn concentration in HK should be on the alert. Meanwhile, high background level of Cd also needs consideration. Severe contamination copper in sediments from GK to ZZ obviously reflects the adverse impacts from Dexing Copper Mine. Within this district, copper overloading in sediments causes extreme responses to chemistry and benthos consequently, and it could be inferred that the toxicity of sediment mainly originating from copper because of its predominance compared to other metals. From DC to JD, influence of copper gradually decreased, whereas, contents of Zn, Pb and As in sediments increased apparently because another discharging tributary of waste water converged near DC(Fig.1). It is implied that the strongest toxicity of sediment occurring at DC represents the synergistic effects of various metals, such as Cu, Zn, Pb, Cd and so on. Triad can be usable in both reactive and proactive manner, for example, in HS case(C+ /T + /B −), the triad may serve a proactive function by indicating that the receiving environment is being stressed by toxic heavy metals, and additional stresses is unacceptable (Chapman, 1996). Since special hydrological and geological conditions produce reduction of current velocity, and precipitation of large amount of suspended particulates appears in CJW, as a result, levels of various metals in sediments rise again with respect to its upstream section. In downstream area, e. g. HLM and LK, the removal capability of metals subsides with distance extending, so the sediment quality recovers in certain degree, nevertheless, the reason for laboratory toxicity in this region is not clear.

Proper SQC may apply on indication and identification of contaminated area for management and harness, in order to avoid misusing or abusing the SQC, effect-based SQC should combined with numerical SQC, such as EqP-based SQC (Chapman, 1989; 1995). Moreover, further modifications on uncertainty in triad by setting up statistical confidence limits (Alden III, 1992) and necessary amendment in some sites with missing data are also required, as well as seasonal differences of measures for tree components. At last but not least, recommendations on decision-making for remediation on problem sediments along the Le An River must be made after involving other considerations, e. g. local economic and political conditions (Canfield, 1994; Chapman, 1996).

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