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Developing sediment quality criteria for heavy metal pollution in the Le An River with equilibrium partitioning approach

Liu Wen-xin, Tang Hong-xiao

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Abstract—Equilibrium partitioning(EqP) approach was selected to establish the sediment quality criteria(SQC) in the Le An River near Dexing Copper Mine. Both freshwater quality criteria (WQC) for some heavy metals regulated by USEPA and national quality standards of surface water recommended by CNEPA were used as protective levels of aquatic organisms in this study. Meanwhile, the partitioning coefficients were derived directly from measured data. Comparison between SQC in this region and concentrations of contaminants in situ clearly indicated the distribution characteristics of metal contamination along the river. And the results also illustrated that measures of some metals exceeded their SQC levels in different degree, especially Cu.

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

1 Introduction

Acting as repository or source of various contaminants under different conditions, problem sediments may threaten the aquatic organisms immediately or potentially(Chapman, 1995). Proper sediment quality criteria(SQC), therefore, are required to indicate the contamination situation, to assist managers and regulators in making decision on treatment and remediation(Adams, 1992).

To establishment of numerical chemical-by-chemical criteria by equilibrium partitioning approach(EqP), the kernel is partitioning coefficient(K_p)(Shea, 1988). Generally, there are two major ways to obtain K_p: (1) derived directly from measured data from sediments and pore water in situ (Webster, 1994; Van Der Kooij, 1991); (2) simulated by surface complex model and adsorption experiments in laboratory, such as CCM, DLM and TLM, together with graphical extrapolation or computer programs (e. g. FITEQL, MINTEQ, MICROQL; Wen, 1996). Equilibrium partitioning being a fundamental chemical property, EqP-based SQC possess a strong theoretical foundation to explain observed bio-effects based on comprehensive database of water quality criteria(WQC), furthermore, its numerical manner is easy to understand and operated by managers.

Strongly influenced by opencast mining activity nearby, severe pollution of heavy metals in sediments occurs along the Le An River, further impacts the largest freshwater lake in China-Poyang Lake (Tang, 1994). In this paper, we adopt both the final chronic values (FCV) regulated by USEPA and national quality standard of surface water recommended by CNEPA as protective level of aquatic organisms, to establish EqP-based SQC directly from actual detection.

2 Materials and methods

2.1 K_p calculation

All determinations were selected from the comprehensive database (CERP-DBMS; Mao,

1994) and the formula of K_p calculation is as follows:

$$K_p = \frac{C_S}{C_{IW}}; \qquad K_P^* = \frac{C_S}{C_W}, \tag{1}$$

$$SQC = K_P \times WQC + [Me]_{AVS} + [Me]_R. \tag{2}$$

Where, C_S, C_{IW} and C_W represent concentrations of individual metal in sediments, interstitial water and overlay water respectively (K_p^* only being as a rough assistance to K_p when data of pore water are missing). $[Me]_R$ and $[Me]_{AVS}$ in Formula (2) represent the concentrations of metals in residuals of sediments and combined with acid-volatile sulfide(AVS) respectively.

2.2 Water quality criteria(WQC) selection

Freshwater quality criteria of selected heavy metals regulated by USEPA (USEPA, 1990) and recommended by CNEPA (CNEPA, 1989) are listed in Table 1 and Table 2, respectively.

Table 1 Freshwater quality criteria for selected heavy metals currently regulated by USEPA

Selected heavy metals	Freshwater, mg/L, oxidized sediments, chronic values, pH=6.5—9.0
Cu	Exp(0.8545 × (ln($CaCO_3$ hardness) - 1.465))/ 1000
Pb	Exp(1.2730 × (ln($CaCO_3$ hardness) - 4.705))/1000
Zn	0.047(24 h)
Cd	Exp(0.7852 × (ln($CaCO_3$ hardness) - 3.490))/1000
As	0.19
Cr	0.011

Table 2 China national standards of selected heavy metals in surface freshwater(GB 3838-88)

Heavy metals	Grade(Ⅰ), mg/L	Grade(Ⅱ), mg/L	Grade (Ⅲ), mg/L	Grade(Ⅳ), mg/L	Grade(Ⅴ), mg/L
Tot-Cu	0.01	0.01	0.01	1	1
Tot-Pb	0.01	0.05	0.05	0.05	0.1
Tot-Zn	0.05	0.1	0.1	2	2
Tot-Cd	0.001	0.005	0.005	0.005	0.01
Tot-As	0.05	0.05	0.05	0.1	0.1
Cr(VI)	0.01	0.05	0.05	0.05	0.1

2.3 Acid-volatile sulfide(AVS) and sum of simultaneously extracted metals (ΣSEM)

Normalization or correction of metal concentrations with AVS is quite important for its biological effects in sediments, the impacts of metals on aquatic organisms are commonly assessed by the ratio of ΣSEM and AVS(Leonard, 1996; Ankley, 1996). In this study, analytical method of AVS and SEM introduced by Allen *et al*. was adopted (Allen, 1993).

2.4 Speciation of metals in sediments

Speciation of trace metals significantly decided their bioavailability, and consequently their toxicity (Allen, 1993). In our paper, according to chemical stability, the speciation of heavy metals was simply defined as three operational categories: readily bioavailable, moderately bioavailable and inert base on sequential extraction procedure(Mao, 1996).

3 Results and discussion

3.1 Determination of metals in sediments, pore water and overlay water

Results of simplified distribution for metal speciation from CERP-DBMS are listed in Table 3.

As inert fraction (i. e. residuals) only possessing extreme minority in distribution, sum of readily and moderately bio-available fractions is considered in this study, excluding the residual fraction$[Me]_R$ (Mao, 1996). Table 4 represents the concentrations of various metals, also containing the levels of AVS and ∑SEM in sediment samples.

Table 3 Simplified distribution of various fractions for some heavy metals in surface sediments

Site name	Cu(Ⅰ+Ⅱ), %	Cu(Ⅲ), %	Pb(Ⅰ+Ⅱ), %	Pb(Ⅲ), %	Zn(Ⅰ+Ⅱ), %	Zn(Ⅲ), %	Cd(Ⅰ+Ⅱ), %	Cd(Ⅲ), %
HK A01	91(5+86)	9	91(31+60)	9	91(16+75)	9	83(50+33)	17
GK A04	us/ud	us/ud	us/ud	us/ud	us/ud	us/ud	us/ud	us/ud
ZZ A05	96(2+94)	4	88(24+64)	12	87(6+81)	13	83(33+50)	17
DC A07	99(5+94)	1	97(8+89)	3	97(7+90)	3	91(33+58)	9
HS A08	99(2+97)	1	94(19+75)	6	99(6+93)	1	100(50+50)	0
JD A09	us/ud	us/ud	us/ud	us/ud	us/ud	us/ud	us/ud	us/ud
CJW A13	97(1+96)	3	90(20+70)	10	95(5+90)	5	83(33+50)	17
HLM A14	98(2+96)	2	91(24+67)	9	94(6+88)	6	83(50+33)	17
LK A16	us/ud	us/ud	us/ud	us/ud	us/ud	us/ud	us/ud	us/ud

Notes: us/ud is the unsampling or undetecting limited by local conditions; Ⅰ is the readily bioavailability; Ⅱ is the moderately bioavailability; Ⅲ is the inert bioavailability.

Table 4 Concentrations of metals and ∑SEM/AVS in surficial sediments from the Le An River

Sampling sites	Cu, mg/kg	Pb, mg/kg	Zn, mg/kg	Cd, mg/kg	As, mg/kg	Cr, mg/kg	AVS, μmol/g	∑SEM μmol/g	∑SEM/AVS ratio
HK A01	32	58	346	3	15	58	ud	ud	–
GK A04	3500	100	270	3	27	138	0.01	3.82	382.32
ZZ A05	2218	58	203	3	23	100	0.04	7.66	191.41
DC A07	1209	310	1118	6	126	102	0.98	7.87	8.03
HS A08	983	121	617	4	52	111	ud	ud	–
JD A09	442	85	449	3	35	100	0.13	3.86	29.65
CJW A13	910	93	760	4	34	103	0.25	5.13	20.52
HLM A14	350	86	336	3	29	119	ud	ud	–
LK A16	333	83	402	1	29	93	1.46	1.64	1.13

Since AVS remains much lower level and the ratio of ∑SEM/AVS greater than 1 in almost sampling sites, surficial sediments in the Le An River become oxidized, and the correction of AVS on metal bioavailability may be neglected (Wen, 1997). Therefore, calculation of SQC followed such formula: $SQC = K_p \times WQC$ (3). The contents of different metals in pore water and overlay water are tabulated in Table 5 and Table 6, respectively.

3.2 WQC of the Le An River

According to Table 1, the local water quality criteria (WQC) are obtained from water hardness ($CaCO_3$) in the Le An River. The corresponding data are listed in Table 7.

3.3 Discussions

Combined the actual determinations with formulae above mentioned, comparison between initial SQC for each selected metal in this valley and related concentrations in situ along the Le An River is illustrated in Fig.1 individually. For simplicity, only the initial SQC for Cu, Pb, Zn, Cd and Cr derived from WQC regulated by USEPA (marked by legends of SQCA and SQCA* based on K_p and K_p^*) and from Grade(I) in national quality standards of surface water recommended by CNEPA(marked by legends of SQCB and SQCB* based on K_p and K_p^*) are provided.

Table 5 Concentrations of heavy metals in interstitial water from the Le An River(< 0.45 μm)

Site name	Cu, mg/L	Pb, mg/L	Zn, mg/L	Cd, mg/L	As, mg/L	Cr, mg/L
HK A01	0.015	0.009	0.030	0.001	0.007	0.020
GK A04	0.440	0.019	0.080	0.006	0.040	0.015
ZZ A05	0.080	0.008	0.030	0.002	0.010	0.022
DC A07	0.100	0.017	0.200	0.006	0.027	0.022
HS A08	0.020	0.014	0.040	0.002	0.008	0.010
JD A09	0.015	0.003	0.080	0.001	0.005	0.015
CJW A13	0.013	0.002	0.040	0.001	0.007	0.020
HLM A14	0.010	0.001	0.030	0.001	0.010	0.010
LK A16	0.010	0.001	0.045	0.001	0.005	0.018

Table 6 Concentrations of heavy metals in overlay water from the Le An River(< 0.45 μm)

Site name	Cu, mg/L	Pb, mg/L	Zn, mg/L	Cd, mg/L	As, mg/L	Cr, mg/L
HK A01	0.002	0.003	0.022	< 0.001	ud	0.025
GK A04	us	us	us	us	ud	us
ZZ A05	0.050	0.009	0.038	0.002	ud	0.018
DC A07	0.024	0.006	0.020	< 0.001	ud	0.015
HS A08	0.019	0.003	0.009	< 0.001	ud	0.017
JD A09	0.015	0.003	0.040	< 0.001	ud	0.024
CJW A13	0.019	0.003	0.036	< 0.001	ud	0.024
HLM A14	0.011	0.004	0.030	< 0.001	ud	0.032
LK A16	0.010	0.001	0.025	< 0.001	ud	0.021

Table 7 Water quality criteria in the Le An River based on FCV regulated by USEPA

Site name	Total hardness($CaCO_3$, mg/L)	Cu, mg/L	Pb, mg/L	Zn, mg/L	Cd, mg/L	As, mg/L	Cr, mg/L
HK A01	102.3	0.012	0.003	0.047	0.001	0.190	0.011
GK A04	317.3	0.032	0.014	0.047	0.003	0.190	0.011
ZZ A05	189.3	0.020	0.007	0.047	0.002	0.190	0.011
DC A07	143.3	0.016	0.005	0.047	0.002	0.190	0.011
HS A08	179.1	0.019	0.007	0.047	0.002	0.190	0.011
JD A09	163.7	0.018	0.006	0.047	0.002	0.190	0.011
CJW A13	133.0	0.015	0.005	0.047	0.001	0.190	0.011
HLM A14	97.2	0.012	0.003	0.047	0.001	0.190	0.011
LK A16	80.2	0.010	0.002	0.047	0.001	0.190	0.011

Distribution and extent of metal contamination in sediments from the Le An River are clearly illustrated by Fig.1. Apparently, a sectional characteristic of pollution dispersal exist along this river. Less disturbance leads to relative clean sediments in upstream, such as reference site HK A01. Although data of pore water are missing limited by local conditions, intensive toxicity (Wang, 1994) and disappearance of benthic organisms (Zhu, 1994) indirectly demonstrate the substantial overloading of Cu in sediments at GK with respect to relevant SQC. In addition, levels of Zn, Pb, Cd and Cr also surpass individual SQC from GK to ZZ. Undoubtedly, mining activities of Dexing Copper Mine play a decisive role in harmful effects of sediments in this zone. Influence of Cu decreases gradually down to middle stream, i.e. DC to JD, however, other various metals, such as Pb, Zn and Cr, violate the corresponding SQC in different degree. This situation is probably associated with another discharging tributary-Jishui River, which contains amount of waste water originating from some mines of Pb-Zn. In particular, peak laboratory toxicity at DC section infers that it may be caused by synergistic effects of various metals (Wang, 1996), and should merit attention. Close to CJW, changes of hydrological conditions produce deposition of large amount of suspended particles, contents of some metals in sediments rise again relative to neighbor upstream area. From HLM to LK in downstream, grade of pollution reduces with resumption of self-purification capacity in this river, so sedimental quality begins to recover (Zhu, 1994).

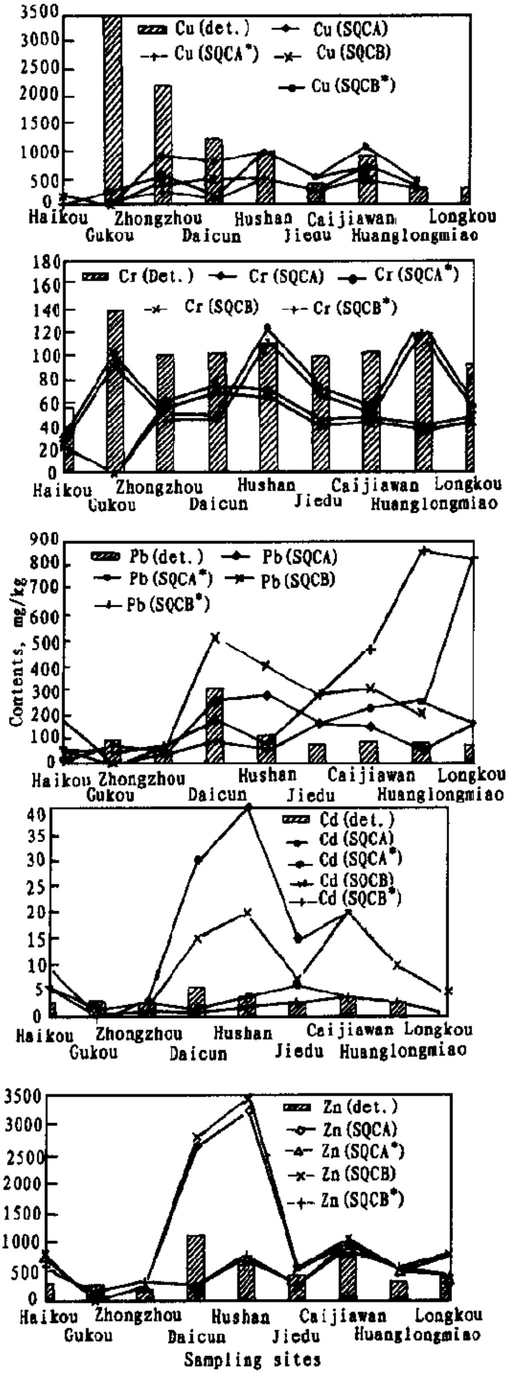

Fig.1 Comparison between EqP-based SQC and measured data in situ for each selected metal

It must be emphasized not to abuse or misuse the EqP-based SQC as clean up criteria during performance of judgement and decision-making because chemical-by-chemical numerical SQC do not consider interactions among existing metals (Landrum, 1995). Therefore, single-metal criteria are best used as "flags" to indicate problem sediments, rather than restrict values to be executed. Meanwhile, not exceeding the SQC for metals does not mean that the sediments are nontoxic, it only ensures that the metals being considered should no have an undesirable biological effects. Similarly, exceeding the criteria for metals does not necessarily indicate that metals will cause toxicity (Ankley, 1996), so we strongly recommend toxicity tests as an integral part of any assessment. At present, EqP-based SQC should combine with response-based SQC organically and orderly, such as Traid (Chapman, 1989). In addition, because AVS varied which depth and season, further research is required to implement the alterations of AVS fully and to supply some missing measures along this valley.

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