Bull Environ Contam Toxicol (2008) 81:90–94
DOI 10.1007/s00128-008-9386-9

Bioavailability and Toxicity of Heavy Metals in a Heavily Polluted River, in PRD, China

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Received: 30 July 2007 / Accepted: 25 February 2008 / Published online: 20 March 2008

Abstract The research is designed to explore the SEM-AVS concept as a tool to assess bioavailability and toxicity of heavy metals in heavily polluted river sediments. The value of AVS and SEM is in a high level and only a few benthic invertebrate are found. Abundance of benthic invertebrate has significant correlation with SEM/AVS ($r = -0.913$, $p < 0.01$) and SEM-AVS ($r = -0.725$, $p < 0.05$). The analytical results of MDS (Non-matric Multi-dimentional Scaling) analysis indicate the benthic community structures of seven among nine stations where the $\sum SEM_5$-AVS < 0 are similar. The two facts indicate the SEM-AVS concept also is useful to heavily polluted river sediments.

Keywords AVS (acid volatile sulfide) · SEM (simultaneously extracted metals) · Toxicity · Heavily polluted river sediments

The toxicity of heavy metals has long been concerned since it is very important to the health of people and ecology. Most of the researchers have now realized that the toxicity of heavy metals has much to do with the bioavailability not total concentration. AVS is operationally defined as the amount of sulfide that can be volatilized during a cold 1 M HCl extraction. The AVS-bound metals (usually Zn, Cu, Cd, Ni and Pb are considered) are extracted at the same time and are therefore called SEM. AVS has become hot topic of bioavailability of heavy metals in sediments since 1990 when Di Toro D. M. reported AVS has great influence to the bioavailability of Cd. When AVS is present in excess over SEM, theoretically it will bind all reactive trace metals. Hence, the SEM-AVS difference is proposed to be an important indicator of bioavailability and ecological risk of trace metals (DiToro et al. 1990). Based on SEM-AVS differences, reliable predictions of the absence of toxic effects can be made (Ankley et al. 1993; EPA 1995; Hansen et al. 1996). This concept has been widely tested and validated under laboratory conditions (Casas et al. 1994; Berry et al. 1996; EPA 2005; Di Toro et al. 2005; Naylora et al. 2006). Field studies on the validity of relations between SEM-AVS or SEM/AVS and ecological endpoints are relatively scarce but more important in practice (Grethuysen 2006). The research of relationship between AVS, SEM and benthic invertebrate in heavily polluted river has rarely seen so far.

The study area is a heavily polluted river located in Pearl River Delta (PRD), China (Fig. 1). The Pearl River (Zhu Jiang) is China's second large river only to the Yangtse River in terms of annual average flow. It composes of three major branches, the West River (Xi Jiang), the North River (Bei Jiang) and the East River (Dong Jiang), and discharges to the South China Sea via eight outlets. PRD is the network formed by the three distributaries and eight outlets. Since China's reform and opening-up, the economy of PRD has grown rapidly, becoming one of the

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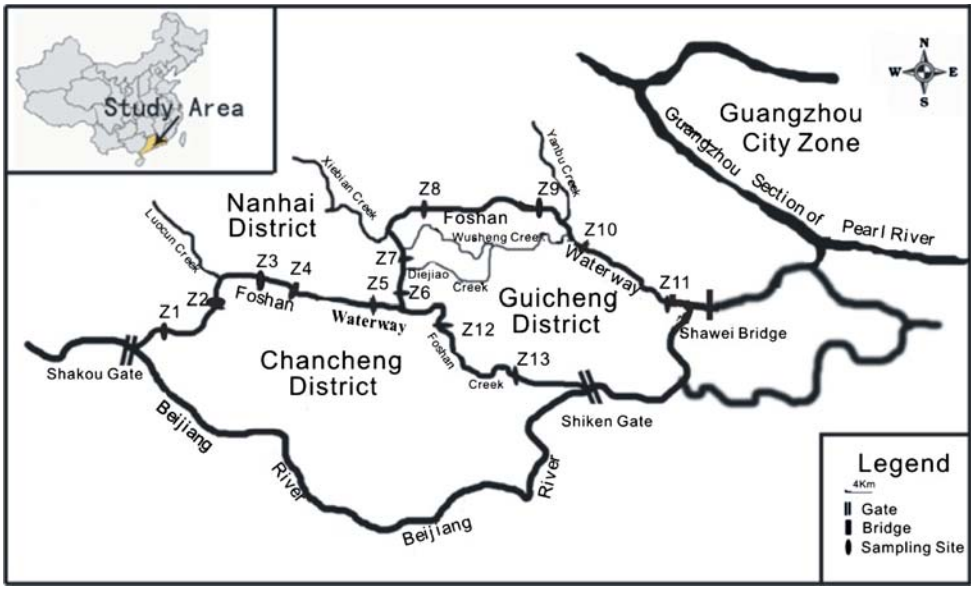

Fig. 1 Map of the study area showing locations of the sampling sites

most important export bases of the world. Foshan is an important industrial city of PRD, and for many years, a large amount of pollutant produced by Foshan City has discharged into Foshan Waterway, causing serious pollution. According to the previous research (Li et al. 2006), sediment Pb, Cd, Hg, Cr, As, Cu, Ni, Zn have reached as high as 382.8, 8.53, 8.27, 1656.1, 66.09, 482.3, 130.7, 1,568.7 mg/kg, respectively.

Materials and Methods

Based on the previous study, 13 sampling stations (Fig. 1), were selected as being representative of the sediments of Foshan Waterway, considering such factors as geometric characteristic of river way, hydrology, distribution of pollution sources and location of wastewater outlets. The details of the sampling stations are given in Table 1. Samples were collected in August 2006 with core samplers. For AVS and SEM content, three replicate core samples were collected by the same procedure and not homogenized. Top 10 cm sediments were sliced and placed in plastic bags filled with N_2 as quickly as possible. Sealed bags then were transfer to a box with ice. The samples were stored at −4°C in laboratory and analyzed in a few days. In the same site, three replicate samples for benthic invertebrate community assessment were collected and sieved in situ through a 0.5 mm mesh size. Cores with overlying

Table 1 Details of the sampling stations

Stations	North latitude	East longitude	Depth[b] (m)	Temp.[b] (°C)	Transparency[a] (cm)	Eh[a,c] (mv)	Eh[b,c] (mv)	DO[b,d] (mg L^{-1})
Z1	23°2.24′	113°1.81′	1.6	29.1	34	−13	46	3.3
Z2	23°3.00′	113°2.86′	1.5	29.3	17	−171	−140	0
Z3	23°3.24′	113°2.99′	2.0	29.1	23	−107	−15	0.2
Z4	23°3.16′	113°4.21′	3.1	30.1	25	−161	−121	0
Z5	23°3.01′	113°5.74′	2.7	29.5	21	−142	−124	0
Z6	23°2.97′	113°6.86′	2.5	29.8	16	−196	−171	0
Z7	23°3.51′	113°6.98′	2.3	29.2	22	−152	−131	0
Z8	23°4.49′	113°7.15′	1.3	29.7	27	−133	−21	0.1
Z9	23°4.50′	113°9.92′	1.6	30.2	24	−155	−117	0
Z10	23°4.03′	113°10.48′	2.1	29.7	25	−149	−129	0
Z11	23°2.73′	113°12.42′	1.4	29.6	26	−103	−20	0.1
Z12	23°2.53′	113°7.06′	1.8	30.1	17	−182	−165	0
Z13	23°1.61′	113°8.11′	1.5	29.9	24	−137	−19	0.1

Note: [a] Refer to sediment; [b] refer to overlying water; [c] refer to sediment oxidation-reduction potential; [d] dissolved oxygen water also were collected at the same time, and placed in a water bath at in situ temperature for 30 min, before overlying water was suck with siphon pipe.

Surface water transparency, water depth, and water temperature was measured before water and sediment sampling. Geographical coordinates were determined with a mobile GPS at each sampling station. Eh was in situ measured by a portable redox device. DO was measured with Iodometric method. AVS concentrations were determined according to the method described by Allen et al. (1993). The extraction concentrations of Cd, Cu, Pb, Zn, Ni, and Fe were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin–Elmer Optima 5300DV) with detection limits of 0.0021, 0.0015, 0.0027, 0.0032, 0.0042, 0.0023 mg/L, respectively. The AVS and SEM concentrations were expressed as μmol/g of dry sediment. Benthic invertebrate were sorted, enumerated and identified to species levels. Data on individuals per species were used to calculate the biological parameters of Abundance, Biomass, and Shannon-Weiner Diversity Index. Data were disposed of by SPSS12.0 and Excel2003.

All glass and plastic ware were cleaned by soaking in 10% HNO_3 (v/v) for more than 24 h, followed by soaking and rinsing with deionized water (Milli-Q). All chemicals used in the experiment were analytical-reagent grade or better. The AVS recovery of the experimental procedure was checked by using sodium sulfide solution with known concentration and appeared to be larger than 92%. At least one duplicate was run for every five samples to verify the precision of the analysis. The recovery rates for heavy metals in the standard reference materials provided by NRCCRM (China National Research Center for CRM's) were around 87%–96% (Pb (86.9%), Zn (93.4%), Cu (87.3%), Cd (96.1%), Ni (88.5%) and Fe (87.7%)).

Results and Discussion

Table 1 shows Eh and DO of sediment and overlying water. Except Z1 station, DO of the other sites is near to zero, and the sediment and overlying water are both in strongly reductive environment. Statistical analysis with SPSS was done and the results were expressed as average ± standard deviation (Table 2), after verifying that the data of 39 samples (3 samples × 13 stations) obey the normal distribution by using the K-S method of non-parameter analysis in SPSS. Table 2 shows that the maximum of AVS is 69.579 μmol/g, the minimum 0.339 μmol/g, and the average is 20.283 μmol/g. Compared with other researches (Mackey et al. 1996; Liu et al. 1999; Lawra et al. 2001), the AVS of Foshan Waterway is the highest. The results also indicate that the area with low AVS corresponds to the lightly polluted area, while the area with high AVS the heavily polluted area. This occurs because of two reasons: one is that surface sediment is always in anaerobic and strongly reductive environment; the other is that sediments in Foshan Waterway are rich in sulfur owing to the long-time effect of pollution sources ashore.

$\sum SEM_5$ (sum of SEM_{Pb}, SEM_{Cd}, SEM_{Cu}, SEM_{Zn} and SEM_{Ni}) is between 1.062 and 23.067 μmol/g, the average is 9.421 μmol/g. Among the five heavy metals, SEM_{Zn} is the highest, which has a maximum of 18.665 μmol/g, and SEM_{Cd} is the lowest (maximum 0.052 μmol/g). Pearson

Table 2 AVS and SEM of sampling stations (n = 3) /μmol g^{-1}

Stations	[a]AVS	[b]SEM_{Pb}	[c]SEM_{Zn}	[d]SEM_{Cu}	[e]SEM_{Cd}	[f]SEM_{Ni}	[g]SEM_{Fe}
Z1	0.723 ± 0.344	0.168 ± 0.031	0.582 ± 0.039	0.207 ± 0.091	0.002 ± 0.001	0.103 ± 0.010	93.457 ± 8.985
Z2	8.967 ± 2.505	0.121 ± 0.041	1.543 ± 0.301	0.201 ± 0.036	0.002 ± 0.001	0.187 ± 0.033	129.401 ± 21.125
Z3	11.276 ± 2.763	0.521 ± 0.043	7.451 ± 0.597	4.321 ± 0.312	0.026 ± 0.008	1.112 ± 0.350	168.037 ± 31.235
Z4	49.579 ± 18.126	0.191 ± 0.040	3.624 ± 0.787	1.837 ± 0.703	0.011 ± 0.003	0.781 ± 0.133	235.554 ± 39.326
Z5	11.139 ± 3.069	0.601 ± 0.244	3.078 ± 0.953	1.394 ± 0.281	0.017 ± 0.005	0.431 ± 0.227	268.309 ± 19.248
Z6	59.013 ± 12.905	0.502 ± 0.108	5.014 ± 0.813	3.812 ± 0.618	0.025 ± 0.006	1.501 ± 0.522	186.347 ± 17.875
Z7	31.274 ± 13.357	1.207 ± 0.313	10.243 ± 2.409	7.875 ± 1.105	0.045 ± 0.006	3.247 ± 0.713	319.792 ± 35.654
Z8	9.261 ± 3.570	0.416 ± 0.119	2.371 ± 0.738	0.582 ± 0.037	0.007 ± 0.002	0.179 ± 0.023	186.181 ± 15.358
Z9	19.327 ± 3.516	0.854 ± 0.174	14.487 ± 4.682	5.992 ± 1.047	0.040 ± 0.007	1.694 ± 0.432	316.021 ± 41.120
Z10	13.285 ± 3.770	0.785 ± 0.316	11.941 ± 2.399	3.012 ± 0.943	0.034 ± 0.004	1.012 ± 0.207	297.856 ± 16.359
Z11	11.213 ± 2.478	0.111 ± 0.018	1.446 ± 0.269	0.191 ± 0.037	0.002 ± 0.001	0.589 ± 0.160	149.210 ± 11.471
Z12	26.406 ± 8.445	0.478 ± 0.191	5.308 ± 1.148	0.999 ± 0.509	0.011 ± 0.002	0.522 ± 0.082	252.354 ± 12.347
Z13	12.219 ± 3.813	0.289 ± 0.104	5.413 ± 1.480	0.968 ± 0.341	0.009 ± 0.002	0.752 ± 0.196	182.890 ± 19.356

Note: [a] Acid volatile sulfide; [b] simultaneously extracted Pb; [c] simultaneously extracted Zn; [d] simultaneously extracted Cu; [e] simultaneously extracted Cd; [f] simultaneously extracted Ni; [g] simultaneously extracted Fe

Table 3 The benthic invertebrate of Foshan Waterway

		Z1	Z3	Z4	Z5	Z7	Z8	Z9	Z10	Z11	Z12	Z13
Annelida	*Tubifex* sp.						903		983	1228		
	Limnodrilus sp.	1474	246	38575	26983	23587	24692	3440	10073	25061	22850	29730
	Branchiura sp.				369			246				246
	Naididae sp.						1563			1228		
Mollusca	*Corbicula fluminea*	246										
	Abundance (ind m^{-2})	1720	246	38575	27352	23587	27158	3686	11056	27517	22850	29976
	Biomass (g m^{-2})	1141.06	0.25	21.72	31.01	19.04	16.12	1.94	5.85	16.56	14.89	34.32
	Diversity Index	0.592	0	0	0	0	0.525	0.354	0.433	0.523	0	0.069

correlation analysis reveals that SEM_{Pb}, SEM_{Zn}, SEM_{Cu}, SEM_{Cd} and SEM_{Ni} are significant correlation ($r = 0.692$–0.950, $p < 0.05$), which means the influences of multiple sources for different metals have similar diagenetic behaviors.

Table 3 shows the monitoring results of benthic invertebrate (No benthic invertebrate is found in station Z2 and Z6, so they are not included in Table 3). Only a few species and small quantity have been found in the study area. The Abundance, Biomass, and Shannon-Weiner Diversity Index representing biological diversity are all low. *Corbicula fluminea* is only found in Z1, while the other species found are pollution bearable ones. *Limnodrilus* sp. appears in high frequency as dominative species. Considering the previous study on Foshan Waterway (Li et al. 2006), the reason for the fewness of benthic invertebrate may be bad living environment caused by heavy pollution of the Waterway. MDS method, which is described by Field et al. (1982) and Warwick et al. (1993) who believe it is a good way to analysis the structure of benthic invertebrate, has been used to analyze the data of benthic invertebrate, following these steps: first, extract the fourth root of original data; then figure out Bray-Curtis incomparability index; finally, analyze the data with MDS module in SPSS (Fig. 2). Figure 2 shows that 7 stations (Z4, Z5, Z7, Z8, Z11, Z12, and Z13) are close to each other, which means the structure of benthic invertebrate of those sites has high comparability.

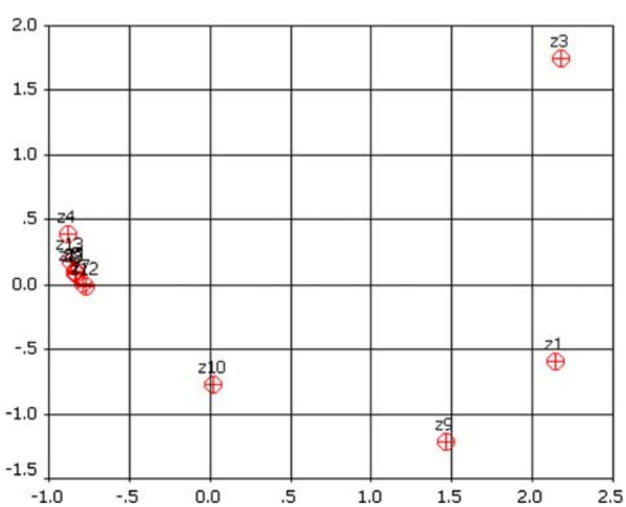

Fig. 2 The MDS analysis results to the structure of benthic invertebrate

To study the relationship between SEM, AVS and benthic invertebrate further, correlation analysis to five variables (Abundance, Biomass, Shannon-Weiner Diversity Index, $\sum SEM_5/AVS$ and $\sum SEM_5$-AVS) has been done: first, normal distributions test to original data (K-S method in SPSS) was done; secondly, Pearson correlation analysis was done to those variables which obey the normal distributions and Spearman analysis to the other variables; lastly, the correlation level of variables was determined according to the correlation coefficient (Table 4). Table 4 shows Abundance has significant correlation with $\sum SEM_5/AVS$ ($r = -0.913$, $p < 0.01$) and $\sum SEM_5$-AVS ($r = -0.725$, $p < 0.05$). But $\sum SEM_5/AVS$, $\sum SEM_5$-AVS, Biomass, and Shannon-Weiner Diversity Index have no correlation at all. Last but not least, according to the results of MDS analysis (Fig. 2), the structures of benthic invertebrate at seven of nine stations where $\sum SEM_5\text{-AVS} < 0$ are similar. From the facts mentioned above, we can get a conclusion that biotoxicity of heavy metals in the heavily polluted river has close relationship with the value of SEM-AVS, so the SEM-AVS concept also is a good tool to assessing bioavailability and toxicity of heavy metals in heavily polluted river sediments.

It is recognized that the extraction Fe by 1 M HCl (SEM_{Fe}) plays an important role in the interrelationship of AVS and SEM. So it has been called “reactive Fe”. Cooper et al. (1998) indicate that when more than 20% of the Fe is bound to AVS, there is enough sulfides to effectively trap trace metals, and temporal variations in AVS and pyrite do not necessarily result in temporal variations in diagenetically-available concentrations of such metals within anoxic sediments. As can be seen in Table 5, only in one sampling station (Z6), the reactive Fe bounded to AVS is more than 20% (25.8%), and the percentage in most of the sites (11 sampling stations) is lower than 10%, which represents low

Table 4 The results of correlation analysis to five variables

	Abundance[a]	Biomass[b]	Diversity index[a]	SEM/AVS[a]	SEM-AVS[a]
Abundance[a]	1	−0.427	−0.321	−0.913**	−0.725*
Biomass[b]	−0.427	1	0.133	−0.118	−0.327
Diversity index[a]	−0.321	0.133	1	0.319	0.424
SEM/AVS[a]	−0.913**	−0.118	0.319	1	0.733
SEM-AVS[a]	−0.725*	−0.327	0.424	0.733	1

Note: ** Means $p < 0.01$; * means $p < 0.05$; [a] Pearson correlation analysis; [b] Spearman correlation analysis

Table 5 $\sum SEM_5$, AVS, and reactive Fe in sediments (μmol g^{-1})

	$\sum SEM_5^a$	$\sum SEM_5$-AVS	$\sum SEM_5$/AVS	NAVS /Fe
Z1	1.062	0.339	1.469	0
Z2	2.054	−6.913	0.229	5.3%
Z3	13.431	2.155	1.192	0
Z4	6.444	−43.135	0.130	18.3%
Z5	5.521	−5.618	0.496	2.1%
Z6	10.854	−48.159	0.184	25.8%
Z7	22.617	−8.657	0.723	2.7%
Z8	3.555	−5.706	0.384	3.1%
Z9	23.067	3.74	1.196	0
Z10	16.784	3.499	1.263	0
Z11	2.339	−8.874	0.209	6.0%
Z12	7.318	−19.088	0.277	7.6%
Z13	7.431	−4.788	0.608	2.6%

Note: The FeS content is assumed to be equal to the excess AVS (NAVS: AVS-SEM molar differences) when the NAVS is positive and is set to zero when NAVS is negative; [a] Sum of the simultaneously extracted Pb, Zn, cu, Cd, and Ni

system stability with respect to sulfide-associated metals in Foshan Waterway.

Acknowledgments Financial support of the National Nature Science Foundation of China [40071074] and Project Management Office of Second Pearl River Delta Urban Environment Project(PRD2)-Foshan Subproject.

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