Bull Environ Contam Toxicol (2009) 83:583–590
DOI 10.1007/s00128-009-9802-9

Metal Pollution in Huayuan River in Hunan Province in China by Manganese Sulphate Waste Residue

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Received: 3 September 2008 / Accepted: 21 June 2009 / Published online: 1 July 2009

Abstract The Huayuan River in Hunan Province in China is subject to ongoing mining activity with Mn extraction. In this study, the level and environmental significance of metals (including Mn, Cd, Pb, Cu, Zn, Ni and Fe) concentrations in the surface water and river sediments have been investigated along a 187 km reach of the Huayuan River. Using the X-ray fluorescence (XRF) analysis, we analyzed the characterization of metals in manganese sulphate waste residue (MSWR) deposited along the bank of Huayuan River. The speciation of metals in both sediment and MSWR was established using the BCR-three step sequential extraction procedure. In the water samples, the average concentrations of Mn, Cd and Pb exceeded the acceptable concentrations for drinking water in the WHO Guidelines for drinking water quality, Vol. 1, Recommendations, Geneva (2004) and Chinese (GB 5749-2006) guidelines, respectively. The average concentrations of Mn, Cd, Pb and Zn in the river sediments were found to be considerably higher than the corresponding world average shale values. The percentages of Cd (31.4%), Mn (31.1%), Zn (12.8%) and Pb (8.1%) associated with exchangeable and weak acid fraction in the sediments were higher than other metals. Mn (5.81%), Zn (0.208%), Pb (0.0292%) and Cd (0.0113%) were identified in MSWR by XRF analysis. The percentages of Mn, Cd, Zn and Pb associated with the exchangeable and weak acid soluble fraction in MSWR were 41.9%, 31.1%, 23.8% and 9.8%, respectively. The peak solute and sediment-bound metal concentrations were found at the sites of MSWR deposited along the bank of Huayuan River. The results suggested that MSWR deposited along the bank may have a closely relation with the metal pollution of Huayuan River. The results obtained may be useful to assess both short and long-term environmental impact of the MSWR deposited activities and support decisions for a future remediation of this river.

Keywords Huayuan River · Water pollution · Sediment · Manganese sulphate waste residue · Speciation

The Huayuan River lies in the Huayuan County Xiangxi autonomous prefecture in Hunan Province in China (E109°43′, N28°29′), starting from the Chadong Mountain of Huayuan County, feeding into the You River at the Jiangkou Town of Baojing County, and meeting with the Xiongdi River at the urban center in the Huayuan County. The Huayuan River is 187 km long and covers a catchment area of 2797 km^2. Its annual average flow is 71.46 m^3/s, and the total surface flow is 2.255×10^{10} m^3. There are 12 branches with a length of over 5 km, and some parts can be voyaged. The altitude of river source is 324 m, and the estuary altitude is 25 m. Its annual average water temperature is 24°C. The Huayuan River is the main drinking water source for approximately 3×10^6 of population and also supports the raising and breeding of aquatic products. Its pollution, therefore, will have a serious effect on the security of drinking water, eco-environment, integrated control for pollution, and planned management in this district.

It is estimated that the storage of manganese mine in the Huayuan County may reach as many as approximately

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3.112×10^7 t, which is the biggest in Southern China. And the Huayuan County is known as "the eastern manganese city" (Xie 2004). There are many manganese ore processing enterprises in this area. These enterprises produce electrolysis metal manganese by adding H_2SO_4 to rhodochrosite and the technology of leaching Mn ion out. After 1 t of metal manganese is produced from rhodochrosite, approximately 7 t of manganese sulphate waste residue (MSWR) will be output (Yao et al. 1997). Our previous work indicated that MSWR was identified to contain some potential harmful substances (Hu et al. 2007). Although a harmless disposal method used for processing MSWR has been proposed (Hu et al. 2007), people pay little attention to the method. At present, a large amount of MSWR is still deposited along the bank of Huayuan River. Long-term weathering and eluviations may cause the leak of noxious substances from MSWR into the Huayuan River. Therefore, it is necessary to assess whether MSWR deposited along the bank has caused the metal pollution in the Huayuan River.

This study was conducted to examine the metals concentrations in the water and sediments in the Huayuan River, to analyze the speciation of metals in the sediment and MSWR deposited along the bank, and to investigate the relationship between the metal contamination in the Huayuan River and MSWR deposited along the bank.

Materials and Methods

All chemicals used in the study were analytical grade. BCR-701 (EUR 19775), with the certified extractable contents (mass fraction) of Cd, Pb, Zn, Cu, Ni and Fe in the river sediments and MSWR following the BCR-three step sequential extraction procedure, was used to verify the accuracy of the procedure and determination of the elements. Doubly distilled deionized water was used in this study. All reagent stock solutions: 1,000 mg/L of metals (including Mn, Cd, Pb, Zn, Cu, Ni and Fe) used were of analytical reagent grade supplied by National Environmental Bureau (NEB, China). Reagent blanks were determined for each new batch of reagent.

Ten sampling sites (S0–S9) were chosen along the river (Fig. 1; Table 1). In selecting these sites, the following criteria were considered: the distribution of MSWR deposited sites, slope of the river bank, route of the river, location of industries, and accessibility for sampling. At each sampling site, 36 water samples (3 samples a month, 12 months) were collected using the polyethylene containers during January and December in 2007. The containers were soaked with 5% HNO_3 for 24 h, rinsed with doubly distilled deionized water 8 times, and washed with the river water before sampling. The digestion method employed for the total metal concentration of water

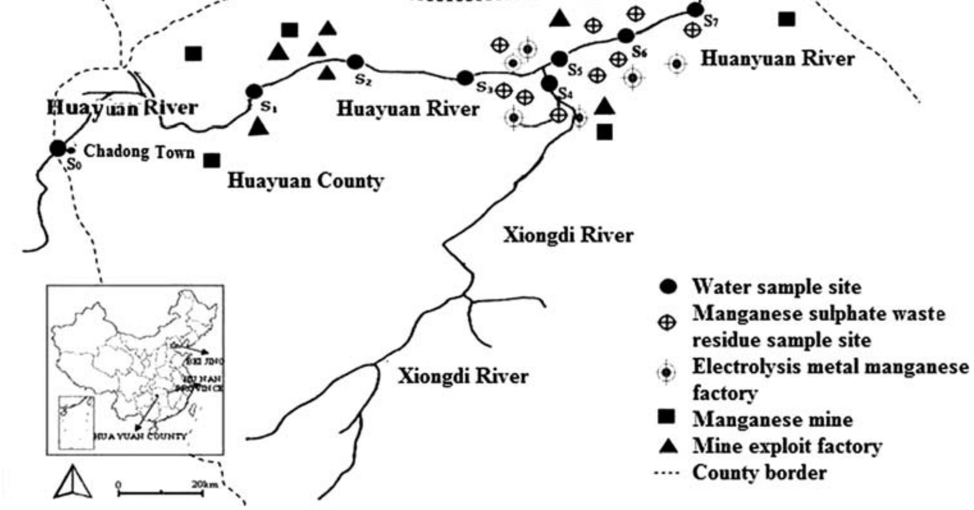

Fig. 1 A map of the Huayuan River system showing the locations of the studied river, sampling sites, manganese mine, mine-exploiting factories and electrolysis metal manganese factories

Table 1 A list of sampling sites

Site number	Name of sampling site	Location
S0	Chadong	Reference site
S1	1,000 m upstream of Maogou Bridge	Mn exploitation industrial area
S2	1,000 m downstream of Maogou Bridge	Rough manganese-processing area
S3	Zhugao Beach	Before electrolysis manganese industrial area
S4	Fu Bridge	Entrance of the Xiongdi River to the Huayuan River
S5	Xiongdi–Huayuan River	Connection point of the Xiongdi River and the Huayuan River
S6	Moyan Slope	Electrolysis manganese industrial area
S7	Shizi Bridge	Shizi power plant
S8	Shuangyan Beach	Shuangyan power plant
S9	Jiangkou	Entrance of the Huayuan River to the You River

samples was the HNO_3–$HClO_4$ method as described by NEB (2002, China). This method involved gently heating 100 mL of water sample and 5.0 mL of 69% HNO_3 on a hot plate. When the solution volume was reduced to 10 mL, the solution was stopped heating. After cooling, 5.0 mL of 69% HNO_3 and 2.0 mL of 70% $HClO_4$ were added into the solution, kept on heating until the liquid nearly dried, and dissolved the residue with 2% HNO_3. Filtering with a 0.45 μm filter membrane, the solution obtained was carefully transferred into a 50 mL volumetric flask and made up to the mark with 2% HNO_3 for analysis. The reference samples were prepared at the same time.

The river sediments were collected at the bottoms of Huayuan River at the corresponding sites of water sampling during January and December in 2007 (Fig. 1; Table 1). At each sampling site, 36 samples (3 samples a month, in 12 months) were collected. The samples were taken with a Kajak gravity corer®. The corer was driven into the sediment by gravity, and the sediment was retained in a PVC tube. The diameter of the PVC tube was 70 mm. In the laboratory, the sediment samples were air-dried, disaggregated using an agate pestle and mortar, and sieved through a 63 μm nylon sieve to isolate the silt and clay fraction. Then, they were sealed in the clean polyethylene containers and stored in a refrigerator for analysis. 12 MSWR samples were collected from each site of 9 MSWR deposited sites along the bank of Huayuan River (Fig. 1). After they were air-dried and disaggregated, the MSWR samples were passed through a 63 μm nylon sieve. To reduce spatial variability at each sampling site, 12 composite samples were prepared by combining and homogenizing 108 individual samples, and then stored in the polyethylene containers. Before taking sample aliquots for analysis, the composite MSWR samples in the containers were homogenized by manual shaking for 5 min. Samples of the sediment and MSWR were analyzed with the BCR-three step sequential extraction procedure (Rauret et al. 1999). The residual fraction was digested with aqua regia, according to the ISO 11466 (ISO 1995). In this case, the residual material was transported into a reaction vessel. 1.0 ml of water was added to obtain a slurry, and 7.0 mL of 12.0 mol/L HCl followed by 2.3 mL of 15.8 mol/L HNO_3, was added drop by drop to reduce foaming. The reaction vessel was allowed to stand for 16 h (overnight) at room temperature for slow oxidation of the organic matter in the sample. Then, the suspension was digested on a hot plate at 130°C for 2 h in an open system. After cooling the reaction vessel to room temperature, the digests were filtered through the filter paper (Whatman 41) into 50 mL volumetric flasks. The insoluble residue on the filter paper was washed with 0.5 mol/L HNO_3, and the volumetric flask was filled with 0.5 mol/L HNO_3 up to the mark. The reagent blanks were negligible and no detectable contamination was found when aliquots of the sequential extraction reagents were processed and analyzed with the samples. The sediment and MSWR samples were respectively analyzed in 4 replicates, for which the relative standard deviations were less than 10% for all metals. The laboratory quality control consisted of analyses of the BCR-701 freshwater sediment certified reference material in 6 replicates for each extraction procedure applied. The result is shown in Table 2.

A Varian Spectra AA-6800 (Shimadzu, Japan) atomic absorption spectrophotometer was used to measure the concentrations of Mn, Cd, Pb, Zn, Cu, Ni, and Fe, respectively. The detection limits for 7 metals were 0.002, 0.0004, 0.001, 0.002, 0.001, 0.02 and 0.001 mg/L for Mn, Cd, Pb, Zn, Cu, Ni, and Fe, respectively. Measurements were carried out in triplicate. The quantitative recoveries of metals were established through 6 replicates analysis of certified reference materials (NEB, China) for selected metals and were within 2% variation. The results of the water and sediment samples at each sampling site were obtained from 12 composite samples (once a month, in 12 months). To determine the composition of MSWR samples, the X-ray fluorescence (XRF) analysis was

Table 2 Certified and determined concentrations (mg/kg) of extractable contents of Mn, Cd, Pb, Zn, Cu, Ni, and Fe in certified reference material of fresh sediment BCR-701

Element	Step 1		Step 2		Step 3	
	Certified value	Determined value	Certified value	Determined value	Certified value	Determined value
Cd	7.34 ± 0.35	7.12 ± 0.28	6.77 ± 0.28	7.72 ± 0.25	0.27 ± 0.06	0.29 ± 0.08
Pb	3.18 ± 0.21	3.09 ± 0.17	126 ± 3.0	123 ± 5.0	9.3 ± 2.0	8.27 ± 1.5
Zn	205 ± 6.0	208 ± 8.0	114 ± 5.0	113 ± 6.0	45.7 ± 4.0	45.6 ± 5.4
Cu	49.3 ± 1.7	48.9 ± 1.2	124 ± 3.0	125 ± 6.0	55.2 ± 4.0	53.5 ± 5.3
Ni	15.4 ± 0.9	14.8 ± 0.7	26.6 ± 1.3	25.9 ± 1.9	15.3 ± 0.9	15.8 ± 1.6
Fe[a]	71 ± 1	67 ± 2	7698 ± 106	8547 ± 265	1079 ± 53	954 ± 65

Data were expressed as Mean ± SEM (n = 6)

[a] For Fe, the value by Kubová et al. (2004) was taken as an indicative value

performed in an X-ray fluorescence spectrometer (Phillips PW with rhodium anticathode controlled by SuperQ/Quantitative software version 1.1, Eindhoven, The Netherlands). Glass discs for the XRF analysis were made from samples using the following instrumentation: muffle furnace (GALLUR, max T 1,300°C with temperature ascent speed regulator, Valencia, Spain), Wolfram Carbide disk mill (Fritsch Pulverisette 9, Idar-Oberstein, Germany), crucible (5% Au/Pt ZGS); glass discs conformator (Pt/Rh 30 mm diameter).

The statistical analysis was performed using the Student's *t*-test in the SPSS 13.0 software. A probability (p) value < 0.05 or less was considered to indicate statistically significant difference between one site and the adjacent upstream site. Data were expressed as Mean ± SEM.

Results and Discussion

The mean metal concentrations in the Huayuan River water are presented in Table 3. In the water samples, the concentrations of Ni was found to be negligible, while other metals were found to be in the ranges of Mn 0.063–2.543 mg/L, Cd 0–0.1226 mg/L, Pb 0–0.592 mg/L, Zn 0.166–7.230 mg/L, Cu 0–0.065 mg/L, and Fe 0.240–2.210 mg/L. The concentrations of Mn, Cd, Pb, Zn, Cu, Ni, and Fe at S0 (reference site) were well within the GB (GB 5749-2006 2006 China) and WHO (2004) guidelines. But, the concentrations of Mn, Cd, Pb, Zn, Cu and Fe at both S1 and S2 were statistically significantly increased when compared to those at S0, which may be affected by several manganese mine exploiting factories nearby (Fig. 1).

Table 3 The mean concentrations (mg/L) of Mn, Cd, Pb, Zn, Cu, Ni and Fe of water samples from 10 sites selected along the Huayuan River compared to GB and WHO guidelines for drinking water respectively

Element	Mn	Cd	Pb	Zn	Cu	Ni	Fe
GB	0.1	0.005	0.01	1.0	1.0	0.02	0.3
WHO	0.4	0.003	0.01	3.0	2.0	0.02	3.0
S0	0.063 ± 0.002	BDL	BDL	0.166 ± 0.012	BDL	BDL	0.240 ± 0.020
S1	0.115 ± 0.023**	0.0015 ± 0.0004*	0.014 ± 0.003*	0.200 ± 0.026*	0.005 ± 0.00*1	BDL	0.520 ± 0.036*
S2	0.281 ± 0.034*	0.0898 ± 0.0020**	0.128 ± 0.021**	1.120 ± 0.130**	0.006 ± 0.002	BDL	0.610 ± 0.053
S3	0.076 ± 0.004**	0.0017 ± 0.0002**	BDL	0.220 ± 0.052**	BDL	BDL	0.400 ± 0.032*
S4	2.543 ± 0.430	0.0252 ± 0.0034	0.195 ± 0.024	0.348 ± 0.063	0.035 ± 0.017	BDL	0.650 ± 0.046
S5	1.356 ± 0. 130*	0.0053 ± 0.0003**	0.043 ± 0.016**	0.324 ± 0.045	0.028 ± 0.006**	BDL	0.588 ± 0.051*
S6	2.382 ± 0.253*	0.1226 ± 0.0262**	0.592 ± 0.023**	7.230 ± 1.004**	0.065 ± 0.024*	BDL	2.210 ± 0.356**
S7	1.112 ± 0.106	0.1180 ± 0.0113	0.083 ± 0.018**	0. 954 ± 0.053**	0.025 ± 0.010*	BDL	0.591 ± 0.030**
S8	1.350 ± 0.125	0.0051 ± 0.0002**	0.055 ± 0.006*	0.296 ± 0.046**	0.012 ± 0.002*	BDL	0.320 ± 0.021*
S9	1.201 ± 0.085	0.0015 ± 0.0002**	BDL	0.260 ± 0.021	BDL	BDL	0.280 ± 0.028
Average	1.047	0.037	0.111	1.016	0.017	BDL	0.6409

Data were expressed as Mean ± SEM of 12 composite samples for each sampling site

BDL Below detection limit. *GB* Standard for drinking water quality (China, 2006). *WHO* World Health Organization guideline for drinking water (2004)

* $p < 0.05$ and ** $p < 0.01$ compared to the adjacent upstream site. S0–S9 are indicated in Fig. 1

Because of the self-purification of the river, the concentrations of other 5 metals at S3 (except the concentration of Fe exceeding the GB guideline) did not exceed the GB and WHO guidelines. The tributary stream (the Xiongdi River) acts as a point source of metal contaminants, because the metal concentrations at S4 were statistically significantly higher than those at the connection point S5. Starting at S6, the Huayuan River enters the electrolysis manganese industrial area. A large amount of MSWR is deposited along the bank of Huayuan River in this area. The concentrations of Mn, Cd, Pb, Zn, Cu, and Fe were statistically significantly increased and reached a maximal value at S6. At S6, the concentrations of Mn, Cd, Pb, Zn and Fe exceeded the GB guidelines by 23.8, 24.4, 59.2, 7.2, and 7.3 times, respectively. When compared to the WHO guidelines, the concentrations of Mn, Cd, Pb and Zn at S6 exceeded the guidelines by 5.9, 40.8, 12.2, and 2.4 times, respectively. From S7 to S9, the metal concentrations were decreased with distance downstream. The mechanism may be natural attenuation processes, such as trace element diffusion to internal sorption sites in solid phases by migration, surface precipitation or changing a solid solution into more crystalline and stable structural sites (Tessier et al. 1996; Gong and Donahoe 1997; Thompson et al. 1999). Though the concentrations of Cd, Pb, Zn, Cu and Fe at S9 were under the WHO and GB guidelines, the concentration of Mn at S9 still exceeded the WHO and GB guidelines. The above comparison is important because the river water is daily used by the locals for domestic purposes without further treatment.

The river sediments play an important role as pollutants and reflect the history of river pollution. They act as both carriers and sinks for contaminants in aquatic environments (Jain 2004). The total concentrations (mg/kg) of Mn, Cd, Pb, Zn, Cu, Ni, and Fe in the sediments of Huayuan River are presented in Table 4. A comparison of metal concentrations in the river sediments with the world shale standard is generally taken as a quick and practical method of tracing metal enrichment. Except in the case of Cu, Ni, and Fe, the total concentrations determined in the sediments of Huayuan River were found to be considerably higher than the corresponding shale values. The high levels of Mn, Cd, Pb and Zn observed in the sediments could be caused by the Mn extraction industry activities because MSWR was directly discharged into the Huayuan River without disposal in several enterprises. To date, we have not given the reason why the largest Mn concentration in the sediments of Huayuan River was observed at S8 while the peak values of other 6 metals were found at S6. Further investigation will be required to solve this problem.

Metal cations in the river sediments may be present in several different physicochemical forms, i.e., as simple or complex ions, as easily exchangeable ions, as organically bound, as occluded by or co-precipitated with metal oxides or carbonates or phosphates and secondary minerals, or as ions in crystal lattices of primary minerals (Lake et al. 1984). It is necessary to identify and quantify the forms in which a metal is present in the river sediments to gain a more precise understanding of the potential and actual impacts of elevated levels of metals in the river sediments and to evaluate processes of downstream transport, deposition and release under the changing environmental conditions. The chemical partitioning of exchangeable and weak acid soluble, reducible, oxidisable and residual

Table 4 The total concentrations (mg/kg) of Mn, Cd, Pb, Zn, Cu, Ni and Fe in the sediment of Huayuan River

Element	Mn	Cd	Pb	Zn	Cu	Ni	Fe
Average shale[a]	850	0.30	20	95	45	68	46700
S0	500.29 ± 20.85	12.63 ± 1.23	143.58 ± 9.65	182.65 ± 8.65	5.11 ± 0.16	31.61 ± 2.65	12244.53 ± 500.36
S1	1401.72 ± 90.65	65.77 ± 2.65	576.25 ± 43.65	2318.37 ± 99.65	25.73 ± 2.65	57.37 ± 4.68	7559.87 ± 236.31
S2	1240.88 ± 98.60	49.1 ± 3.62	270.92 ± 16.32	1274.59 ± 87.65	8.52 ± 0.86	58.87 ± 6.35	5247.10 ± 198.36
S3	465.16 ± 30.56	72.49 ± 4.63	764.93 ± 39.65	2449.45 ± 69.56	9.9 ± 0.64	91.01 ± 5.32	5933.57 ± 164.62
S4	12367.96 ± 500.23	244.19 ± 10.65	946.45 ± 40.31	3404.04 ± 154.35	104.29 ± 5.68	55.56 ± 2.64	26508.95 ± 562.81
S5	2281.79 ± 152.32	120.99 ± 12.32	524.96 ± 26.35	2575.53 ± 45.65	40.65 ± 2.65	51.83 ± 3.68	5954.21 ± 263.31
S6	2411.88 ± 123.65	334.04 ± 25.68	1392.71 ± 80.65	37178.12 ± 850.50	133.72 ± 6.35	81.06 ± 3.97	23170.96 ± 687.21
S7	2509.99 ± 156.35	172.23 ± 18.65	904.46 ± 64.35	3320.12 ± 650.32	70.28 ± 5.62	98.99 ± 7.35	8811.23 ± 237.14
S8	9617.11 ± 400.23	82.75 ± 5.90	474.36 ± 32.24	2487.44 ± 165.34	28.15 ± 1.68	67.43 ± 3.65	9253.08 ± 357.61
S9	5442.02 ± 228.65	26.52 ± 2.31	374.7 ± 27.65	1404.66 ± 54.62	15.42 ± 1.08	31.54 ± 1.46	16217.57 ± 428.87
Average	3843.20	118.07	637.33	5659.49	44.17	62.52	12090.10

Data were expressed as Mean ± SEM of 12 composite samples for each sampling site

Total concentrations: The total metals = step 1 + step 2 + step 3 + residual

[a] Turekian and Wedepohl (1961). S0–S9 are indicated in Fig. 1

phases in the sediments of Huayuan River was determined by the BCR-three step sequential extraction procedure (Rauret et al. 1999). The metal concentrations associated with 4 steps at 10 sampling sites in the Huayuan River are presented in Fig. 2.

Step 1: The fraction of exchangeable and weak acid soluble metals is held by the electrostatic adsorption. The amount of metals in this phase indicated the environmental conditions of the overlying water bodies (Modak et al. 1992). There were higher percentages of Mn 31.1%

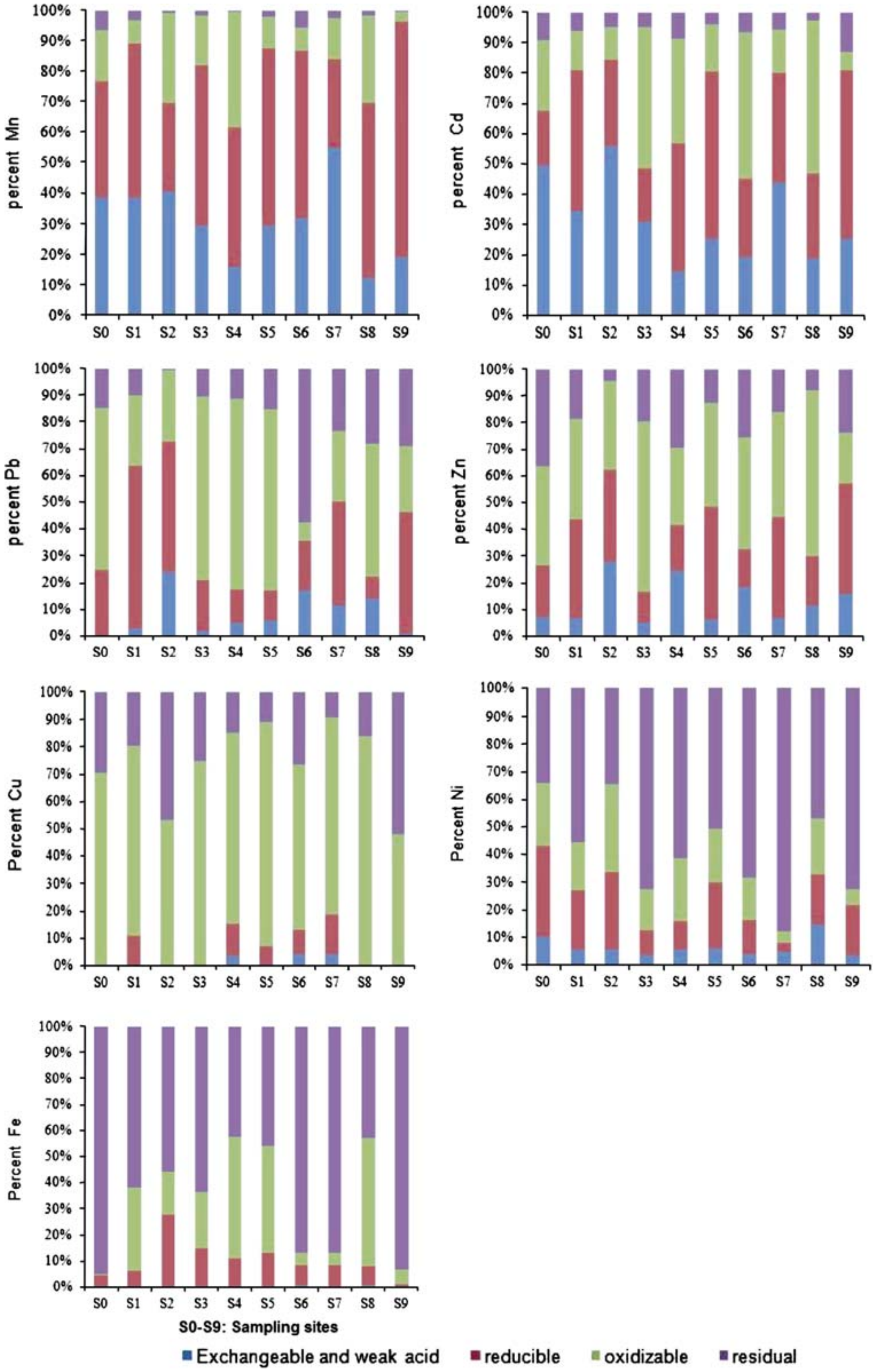

Fig. 2 Speciation of metals in the sediments collected from 10 sampling sites of Huayuan River

(12.5–54.8%) and Cd 31.4% (14.1–55.6%), in comparison with Zn 12.8% (4.9–27.7%), Pb 8.1% (0–23.9%), Ni 6.1% (3.3–14.4%), Cu 1.1% (0–3.9%), and Fe 0.1% (0–0.5%). This fraction is generally considered to constitute the immediate nutrient reservoir for aquatic organism.

Step 2: The metal content in the reducible phase, which has been proved to be sensitive to anthropogenic inputs (Modak et al. 1992), was retained Mn 49.2% (28.8–77.3%) and followed by Cd 35.6% (17.9–55.9%), Pb 28.9% (8.2–48.5%), Zn 27.4% (11.4–42.7%), Ni 17.9% (9.0–33.4%), Fe 10.2% (0.9–27.8%) and Cu 5.4% (0–14.7%). The high percentages of Mn and Cd of the river sediments in this fraction could be caused by the electrolysis manganese industry activities.

Step 3: The percentage of Mn 17.1% (7.6–29.3%) in this fraction was the lowest, while the percentages of other metals were progressively increased from Ni 17.3% (3.9–22.6%), Fe 22.2% (0.3–49.3%), Cd 26.4% (6.2–50.4%), Zn 40.2% (18.7–64.0%), Pb 43.0% (6.6–71.4%), to Cu 68.4% (48.0–84.0%) which showed the highest.

Residual Fraction: This is expected to be chemically stable and biologically inactive (Modak et al. 1992). The high percentages of Fe 67.5% (42.6–95.3%), Ni 58.7% (34.2–88.0%), Cu 25.1% (9.2–51.9%), Pb 20.0% (0.4–57.7%) and Zn 19.4% (4.1–36.4%) were found in the residual fraction, while the low percentages of Cd 6.5% (3.9–12.8%) and Mn 2.5% (0.5–6.4%) were observed in the residual fraction. Metals in this form are considered as a tight bound and a guide to the degree of contamination of the fluvial system. The higher the metal percentage is presented in this category, the smaller the pollution in the zone is.

According to the Risk Assessment Code (RAC), the river sediments having 11–30% exchangeable and weak acid soluble fraction are at medium risk (Jain 2004). Mn (31.1%) and Cd (31.4%) in the river sediment may pose a high risk to the local environment, while Zn (12.8%) may pose a medium risk to the local environment.

To explore the contribution of MSWR deposited along the bank to the metal pollution in the Huayuan River, the main characterization of MSWR samples was performed by XRF analysis. As shown in Table 5, Mn, Cd, Pb, Zn, Cu, Ni and Fe were identified in the MSWR samples. These metal elements were also detected in the water and sediment samples from the Huayuan River. Among them, the content of Cd was the lowest (0.0113%). The contents of other metals were progressively increased from Cu (0.0172%), Ni (0.0181%), Pb (0.0292%), Zn (0.208%), Mn (5.81%), to Fe (8.54%) which shared the highest.

To study the speciation of metals in the MSWR samples, the extractable contents of Mn, Cd, Pb, Zn, Cu, Ni and Fe were analyzed by the BCR-three step sequential extraction procedure. The metal concentrations associated with 4 phases in the MSWR samples are presented in Fig. 3. Most of Mn and Cd were divided into the exchangeable and weak acid soluble fraction (41.9% and 31.1%,respectively) and reducible fraction (46.6% and 38.9%, respectively). The proportions of Mn and Cd in the oxidisable fraction (10.9% and 12.3%, respectively) and residual fraction (0.6% and 17.7%, respectively) were relatively low. On the contrary, Ni and Fe were found exclusively in the residual fraction (Ni 71.9% and 66.3%, respectively) which were bound in the mineral lattice. But, the exchangeable and weak acid soluble (10.6% and 0.1%, respectively), reducible (5.3% and 9.6%, respectively), and oxidisable (12.1% and 24.0%, respectively) forms of Ni and Fe were found. Pb was presented predominantly in the reducible fraction (60.4%). The percentages of exchangeable and weak acid soluble fraction (9.8%) and oxidisable fraction (14.5%) occurred, and 25.0% of total content of Pb was associated with residual fraction. There were 4 operationally defined carrier phases of Zn including the oxidisable fraction (32.3%), residual

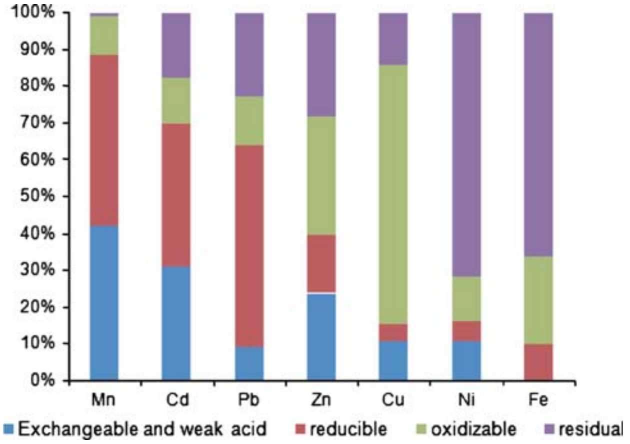

Fig. 3 Speciation of metals in MSWR collected from the bank of Huayuan River

Table 5 The element composition (weight %) of MSWR samples obtained by XRF analysis

Oxide						
SiO_2 (33.5)	Al_2O_3 (10.8)	Fe_2O_3 (8.54)	MnO (5.81)	SO_3 (2.65)	K_2O (1.82)	CaO (1.41)
P_2O_5 (0.712)	MgO (0.690)	Na_2O (0.496)	TiO_2 (0.375)	ZnO (0.208)	BaO (0.114)	I (0.0475)
TeO_2 (0.0438)	V_2O_5 (0.0311)	PbO (0.0292)	Sb_2O_3 (0.0280)	Yb_2O_3 (0.0222)	Cr_2O_3 (0.0224)	ZrO_2 (0.0206)
NiO (0.0181)	CuO (0.0172)	SnO_2 (0.0153)	As_2O_3 (0.0136)	SeO_2 (0.0142)	CdO (0.0113)	Others (0.1305)

fraction (28.1%), exchangeable and weak acid soluble fraction (23.8%), and reducible fraction (15.8%). Cu was preferentially bound in the oxidisable (70.8%) and reducible (14.0%) fractions, while the exchangeable and weak acid soluble fraction and the residual fraction accounted for 10.6% and 4.6% respectively.

From an environmental view, data obtained from the sequential extractions can be helpful to assess the risk associated with the metal burden in MSWR. Since MSWR contained a large amount of exchangeable and weak acid soluble fraction of Mn and Cd, it is possible that the soluble metals were leached out into the surrounding environment under the condition of weathering and eluviations. The metals could flow into the Huayuan River with the rain or infiltrate into the ground water through the underground surface flow. Mn, Cd and Pb were mainly presented in the reducible fraction, and they may be easily released under the acid condition (Zhang et al. 2003). On the other hand, the acid rain always falls in this area (Wu et al. 2000), and the acid rain may enhance the dissolution of soluble weathering products, which was described in other zones with the same effect (Simón et al. 2001).

Conclusion

1) The Huayuan River water is seriously polluted. The average concentrations of Mn, Cd, Pb, Zn and Fe in the water samples were higher than the corresponding values of WHO and GB guidelines for drinking water. The main pollution parameter is Mn in the Huayuan River, and its content is higher than the WHO and GB guidelines even at entrance to the You River.
2) The average concentrations of Mn, Cd, Pb and Zn in the sediment samples are higher than the corresponding values of the world shale standard. Mn and Cd in the sediment samples are mainly associated in the exchangeable and weak acid soluble and reducible fractions, which may pose a high risk to the local environment according to RAC.
3) MSWR contains the main pollution parameters (i.e., Mn, Cd, Zn and Pb) identified in the water and sediment of the Huayuan River. The percentages of Mn, Cd, Zn and Pb associated with the exchangeable and weak acid soluble fraction in the MSWR samples were 41.9%, 31.1%,23.8%, and 9.8%, respectively.
4) Based on the comparison analysis of characterization and speciation of metals from the samples of water, sediments in the Huayuan River, and MSWR deposited along the bank, it was indicated that MSWR deposited along the bank may have a closely relation with the metal pollution of Huayuan River.

Acknowledgments This work was supported by the Scientific Research Foundation for Doctor in University of South China (Grant No. 5-03-XJQ-03-044).

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