Impact of Mn-ore mining on heavy metal accumulation in the soils and vegetables nearby in Hunan Province, China

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Abstract
A stream near a Mn mine is heavily polluted by the discharge of untreated mining wastewater in Hunan province, China, which poses a threat to the agricultural land. In this study, heavy metal concentrations of the stream water and sediments and the soils and vegetables along the stream were determined. The results showed that the stream water and sediments were severely contaminated by heavy metals. The mean values of Cd, Cu, Zn, Pb, Co, Ni, Mn and Cr in the stream water are 0.0009, 0.0004, 0.315, 0.0132, 0.0049, 0.0355, 0.9795 and 0.0212 mg/L, respectively, and those in the soils irrigated by the water are 0.70, 72.7, 1343.2, 60.9, 34.8, 184.8, 21507.7 and 793.3 mg/kg, respectively, which are significantly higher than those in the soils far away from the stream. The concentrations of Cu, Ni, Mn and Cr in the soils irrigated by the stream water are 6.2, 9.7, 40.9 and 17.3 times the local background values. It was also found that the edible parts of vegetables growing on the soils with stream water irrigation contain higher concentrations of heavy metals than those in the soils irrigated by other water. Cd, Zn, Ni and Cr contents in the vegetables exceed the recommended values of the Chinese hygienic standards.

Key Words
Mn mine, heavy metals, soil, vegetables, Hunan province.

Introduction
Hunan province has abundant mineral resources and is a famous location for nonferrous metals in China. However, a large amount of acid mine drainage released from mining activities as well as many poisonous filtrates containing heavy metals from the tailing dump pose a severe threat to water sources and nearby farmlands (Conesa 2007; Lin 2005; Hussein 2005; Granero 2002). Heavy metal concentrations in the soils and vegetables beside a stream polluted by exploiting a Mn mine were determined in this study, aiming to evaluate the hazard risk of mining activities on the local agriculture.

Methods
A stream near a Mn mine in Taojiang county, Hunan province, China, was seriously polluted, with the water being black. There is a large area of agriculture land along the polluted stream (Figure 1).
Three water and sediment samples from the different points of the stream were collected; four soil and vegetable samples in the area irrigated by the stream water, and two soil and vegetable samples far away from the stream and irrigated by other water were collected. In addition, two tailing and three soil samples from undisturbed natural soil profiles were also collected as controls.

The samples of sediments and soils were digested with the mixed acids (HNO_3+HF +$HClO_4$); those of water and vegetables with HNO_3 and $HClO_4$. Cu, Zn, Pb, Ni, Co, Mn and Cr in the solution were determined with the Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES), and Cd with the Graphite Furnace Atomic Absorption Spectrometry (AAS).

Results
Heavy metal accumulation in soil
Heavy metal concentrations of the stream water and sediments and the soils were determined (Table 1). The stream sediments are heavily contaminated with Mn, Zn, Ni and Cr, whose mean values are 77.2, 5.0, 9.5 and 8.2 times the local undisturbed natural soil, respectively. Heavy metal concentrations in the sediments were in the order of Mn>Zn>Cr>Ni>Cu>Pb>Co>Cd. The concentrations of Cu, Zn, Pb, Co, Ni and Cr in the sediments decrease significantly from the upper to the lower reaches of the stream, with the distance from the Mn mine becoming far, which suggests the mining is the main reason for the stream pollution. Cd, Cu, Zn, Pb, Co, Ni, Mn and Cr are heavily accumulated in the tailing from the Mn mining, which are 3.5, 28.8, 9.8, 14.9, 5.4, 46.4, 147.5 and 5.0 times those in the local natural soil, respectively. Moreover, a significantly

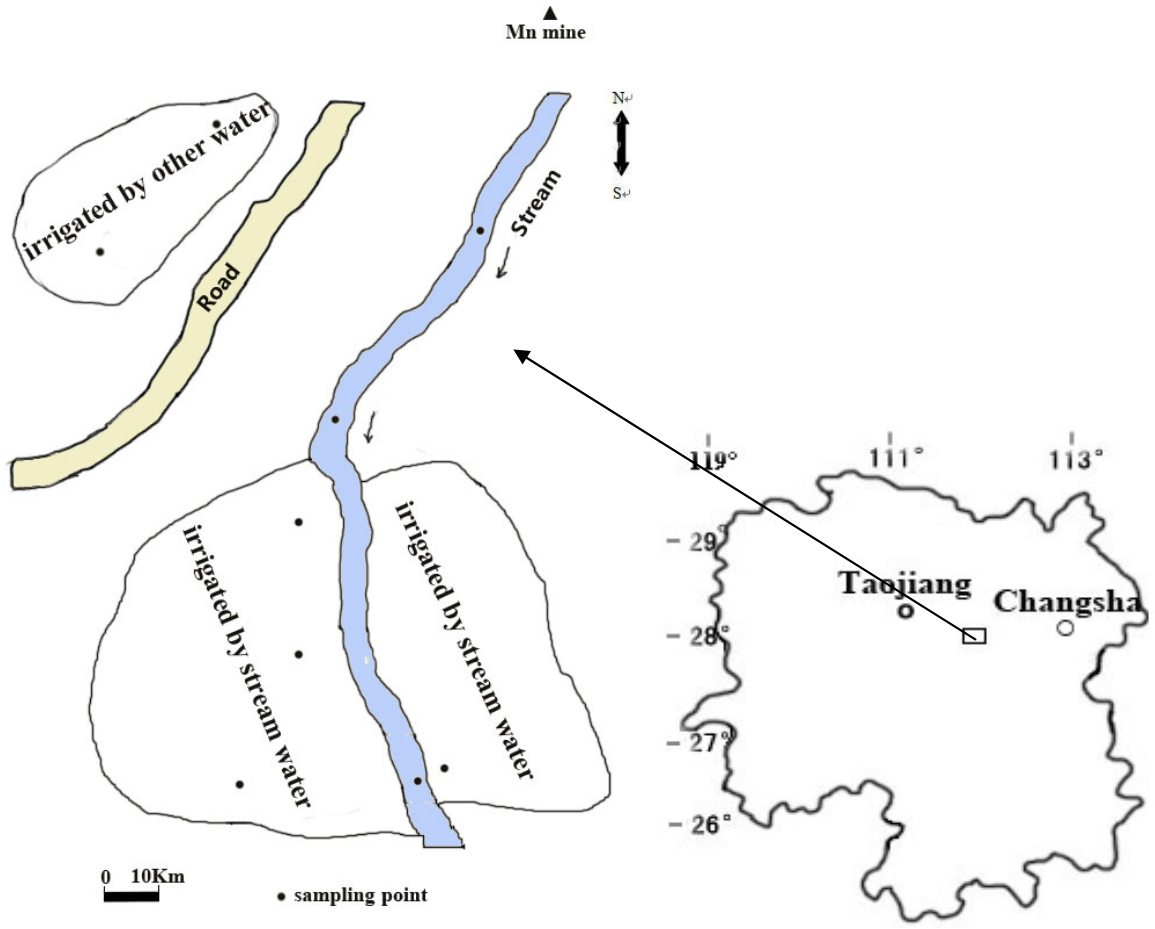

Figure 1. Sketch map showing the sampling points in study area (left) and the study area in Hunan province, China (right).

positive correlation was found between the contents of Cu, Zn, Pb, Co, Ni, Cr, Cd and Mn in the stream sediments and those in the tailings ($r=0.989$, $p<0.01$), which suggests the same source provenance of heavy metals in the stream sediments and the tailings, further proving that the stream was polluted by the mining.

The mean concentrations of Cd, Cu, Zn, Pb, Co, Ni, Mn and Cr in the soils irrigated by the stream water are 0.70,72.7,1343.2,60.9,34.8,184.8,21507.7 and 793.3 mg/kg, respectively, which are 3.5, 6.2, 4.2, 4.1, 2.2, 9.7, 40.9 and 17.3 times those in the local natural soils; while the mean concentrations of Cd, Cu, Zn, Pb, Co, Ni, Mn and Cr in the soils far away from the stream are 0.3, 22.2, 445.1, 17.3,16.5, 31.6, 4299.8 and 247.3 mg/kg, respectively, which are 1.5,1.9, 1.4, 1.2, 1.1, 1.7, 8.2 and 5.4 times those in the natural soil. Apparently, the long-term irrigation with the stream water has severely contaminated the soils nearby.

Heavy metals accumulation in vegetables

Heavy metal concentrations in the edible parts of the vegetables irrigated with the stream water are significantly higher than those irrigated with other water (Table 2). Cd, Zn, Ni and Cr in the vegetables irrigated with the stream water significantly exceed the recommended values. For example, Cd, Zn, Ni and Cr in the edible part of *Allium sativum L.*from the area with the stream irrigation are 22.4, 7.5, 3.6 and 2.8 times higher than the recommended values of the Chinese vegetable hygienic standards, respectively. The edible part of *Lactuca satuva L.*from the area irrigated with the stream water has the highest concentrations of Cd, Cu, Zn and Cr, which are 24.8, 2.7, 16.2 and 10.6 times the recommended values of the Chinese vegetable hygienic standards, respectively. The concentration of Ni is 17.36 mg/kg in *Pisum Sativum Linn* and 5.1 mg/kg in *Bulbus Allii Chinensis* in the area irrigated by the stream water, which exceed the recommended value by 27.9 and 7.5 times, respectively. Cd and Mn concentrations in *Allium sativum L* .in the area irrigated with the stream water are 166.1 and 4.7 times those in the area irrigated with other water. Cd and Zn concentrations in *Lactuca satuva L.* in the area with the stream irrigation are 14.4 and 4.5 times those in the area irrigated with other water. This suggests that the irrigation of the stream water has caused the significant accumulation of heavy metals in the vegetables nearby the stream, which poses severe health risks on the local residents.

Table 1. Concentrations of heavy metals in the stream water, sediments and the soils in the study area, in Hunan province, China

Sampling points		Heavy metals (mg/kg; water, mg/L)							
		Cd	Cu	Zn	Pb	Co	Ni	Mn	Cr
Soils irrigated by stream water		0.70	72.7	1343.2	60.9	34.8	184.8	21507.7	793.3
Soils irrigated by other water		0.30	22.2	445.1	17.3	16.5	31.6	4298.8	247.3
Stream water		0.0009	0.0004	0.315	0.0132	0.0049	0.0355	0.9795	0.0212
Other water		ND[A]	ND[A]	0.101	ND[A]	ND[A]	ND[A]	0.186	ND[A]
Stream sediments	Upper stream	1.3	78.9	1840.3	90.3	32.6	233.6	32056.3	440.1
	Middle stream	0.60	62.3	1607.5	42.5	21.4	184.6	46907.1	352.1
	Lower stream	0.90	32.9	1289.1	29.4	14.2	120.2	42811.7	328.2
	Mean	0.90	58.0	1579.0	54.1	22.7	179.5	40591.7	373.5
Tailing		0.90	349	3447.8	234.3	101.3	899.9	78087.3	271.7
Local non-disturbed natural soil		0.20	11.7	318.0	14.7	15.7	19.0	525.7	45.6
Soil background value in Hunan province [B]		0.10	26.0	94.0	27.0	14.0	32.0	459.0	68.0
Recommended values		0.60[C]	100[C]	300[C]	350[C]	20[D]	60[C]	NA[E]	150[C]

[A] ND means No Detected; [B] China environment monitoring station (1990); [C] Soil Environmental Quality Standard in China (GB 15618, 1995); [D] Tentative Netherlands Soil Quality Criteria (VROM, 1983); [E] NA means no recommended value

Table 2. Heavy metal concentrations in the edible parts of the vegetables growing in study area irrigated with the stream water and other water

	Vegetable species	Heavy metals (mg/kg)					
		Cd	Cu	Zn	Ni	Mn	Cr
Irrigated by stream water	*Allium sativum L.*	1.17	14.47	170.48	2.73	111.95	1.88
	Pisum Sativum Linn	0.008	15.57	133.89	17.36	53.79	0.47
	Bulbus Allii Chinensis	0.008	15.46	47.87	5.10	43.56	2.31
	Lactuca satuva L.	1.24	26.51	324.54	5.13	483.10	5.32
Irrigated by other water	*Allium sativum L.*	0.007	14.24	62.74	0.74	19.58	1.14
	Lactuca satuva L.	0.086	14.75	72.25	1.73	161.69	1.81
Chinese vegetable hygienic standard (Yang 1998)		<0.05	<10	<20	<0.6	NA[A]	<0.5

[A] NA means no recommended value

Conclusion

The exploitation of a Mn mine in Hunan province, China, has made a stream nearby severely polluted, with mean concentrations of Mn, Zn, Ni and Cr in the stream sediment of 40592, 1579, 180 and 373.5 mg/kg, respectively, 77.2, 5.0, 9.5 and 8.2 times those in the local undisturbed natural soil. The significantly positive correlations between heavy metal contents in the stream sediments and those in the tailings prove that the stream pollution is mainly caused by the Mn mining. Cu, Ni, Mn and Cr concentrations of the soils irrigated with the stream water are significantly higher than those irrigated with other water, which are 6.2, 9.7, 40.9 and 17.3 times these in the local natural soil, respectively. Apparently, the irrigation with the stream water has caused the accumulation of heavy metals in the soils nearby. Cd and Mn concentrations in the edible parts of *Allium sativum L.*in the area irrigated with the stream water are 166.1 and 4.7 times those in the area irrigated with other water. Cd and Zn concentrations of *Lactuca satuva L.* in the area irrigated with the stream water are 14.4 and 4.5 times those in the area irrigated with other water. This suggests that the stream water irrigation has caused the heavy metal contamination of vegetables nearby, which poses severe health risks on the local residents.

Acknowledgements

This work was supported by the National Science & Technology Pillar Program of China during the Eleventh Five-year Plan Period (No. 2006BAD20B07) and the National Natural Science Foundation of China (40771093).

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