Evaluation of heavy metal contamination and implication of multiple sources from Hunchun basin, northeastern China

J.-W. Moon · H.-S. Moon · N.-C. Woo · J.-S. Hahn · J.-S. Won · Y. Song · X. Lin, Y. Zhao

Abstract Present concentrations and distributions of heavy metals through profiles, surface soil, and stream sediment samples in the Hunchun area, north-eastern China, were investigated to determine the elemental background values. This study also aims to characterize potentially toxic materials such as pulverized fly ash (PFA) from power stations or ash and slag from coal used domestically in urban areas, agrochemicals applied inappropriately, and urban sewage sludges from Hunchun City, as well as to ascertain the possibility of natural enrichment through site characterization by mineralogical and geochemical investigation. The distribution of contaminants in the alluvial soils (fluvisol) of this area has been influenced by several interacting factors. The parent alluvial materials from weathered products of amphiboles have made coatings such as ferrihydrite, goethite, and hematite. This natural inheritance factor is supported by the fact that the concentrations of weak acid-extractable (plant-available) heavy metals are very low, except for Fe and Mn. However, in agricultural soils and adjacent stream sediments, an anthropogenic input of Cd, Pb, Ni and Cr by agrochemicals is strongly suggested. Also, F contamination by coal combustion and the dissolution of F-bearing minerals could cause some future problems. Wide distribution and significantly high concentrations of Cd, Fe, Mn, and F in soils throughout the combination of pollutants originating from lithogenic and the anthropogenic sources pose potential problems in utilizing water resources.

Key words Agrochemical · Heavy metal contamination · Natural enrichment · PFA

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Introduction

The Hunchun area is a central part of the Tumen (Dooman) River basin located in north-eastern China, and directly bordered by North Korea and Russia (Fig. 1). China designated Hunchun as a class A city for foreign investment and industrial activities. Therefore, it was necessary for the Chinese government to construct infrastructures and to assure the water resources and quality. However, several hydrogeologic problems have been identified (TEC 1998): (1) heavy metal contamination of surface water, (2) extreme seasonal variation of a sustainable water supply throughout the year and (3) a shallow water table (~7–10 m below ground surface), which means that groundwater can be easily contaminated. Heavy metal concentration in the soil–water–plant ecological system is of great concern because of possible influences on the food chain (Ma and others 1997). According to a previous study on surface and shallow groundwater contamination, the chemical oxygen demand (COD), biochemical oxygen demand (BOD), and the concentration levels of some heavy metals in surface water have already exceeded Chinese Drinking Water Standards (CDWS).

The authors have already investigated the contamination of surface and groundwater (Woo and others 2000). Based on CDWS, elements, such as Cd, Fe, Mn, and F, were detected in groundwater at contamination level. Therefore, hypotheses established for the main sources of contamination in Hunchun basin are as follows:

1) Leaching from coals and ashes and dispersion from the chimney by dry fall-out and precipitation. Most coal refuse and ash piles for domestic use in the Hunchun basin are scattered throughout the whole area

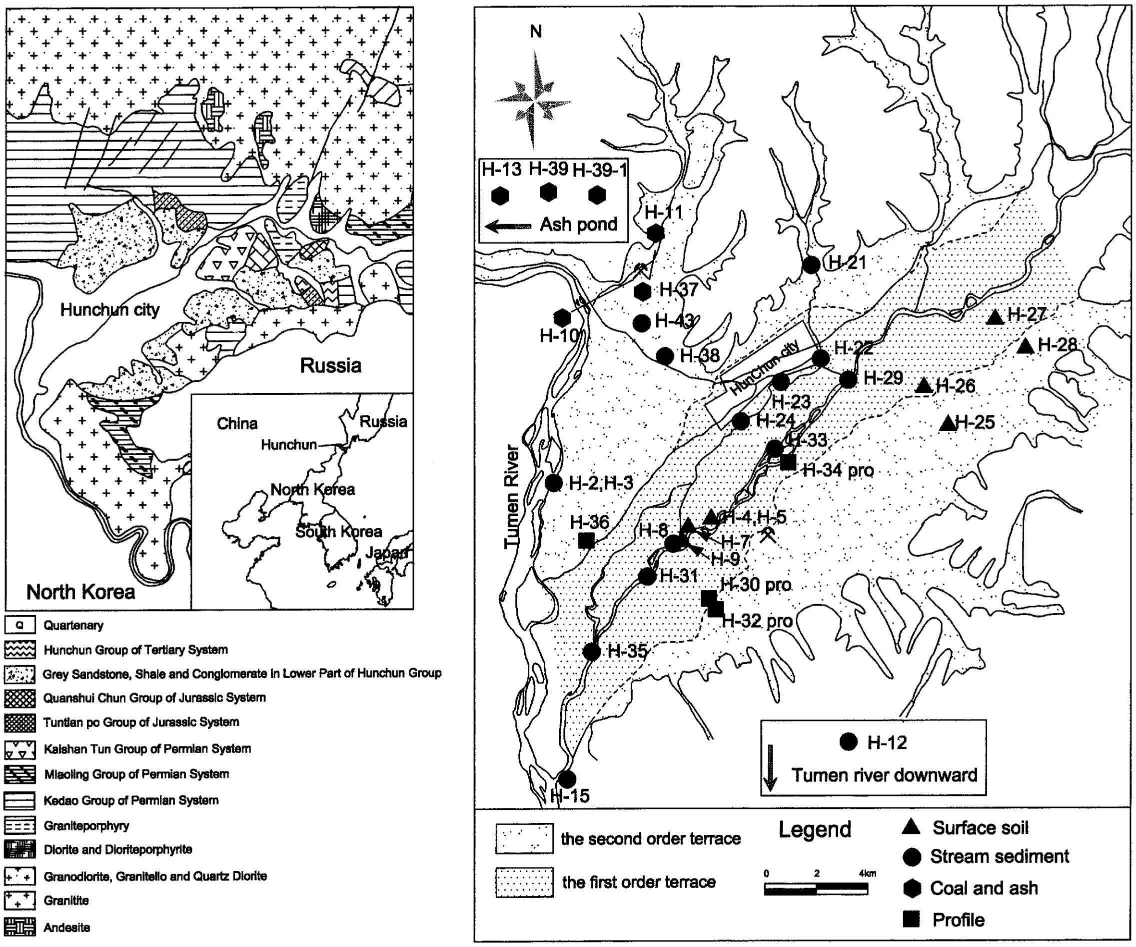

Fig. 1
Geologic map (*left*) and sampling site map (*right*) of the study area

and can be significant sources of groundwater contamination because of the shallow water table;
2) Sludge sewage from urban areas, especially Hunchun City;
3) Inappropriate application of agrochemicals such as fertilizers and pesticides; and
4) Natural enrichment by geological materials.

Based on the above, the concentration and distribution of heavy metals in stream sediments, profiles and surface soils were investigated in the Hunchun area to reveal chemical background values. This study also focused on the characterization and identification of the contaminants' behavior and their possible sources.

Materials and methods

Site description and sample selection

Stream sediments

Stream sediment samples were collected from 15 sites along the Hunchun River and tributaries (Fig. 1). Three subsamples from 0 ~ 10 cm depth of stream-bottom sediment were taken using a stainless steel shovel from an area of about 10 m^2 , then composite samples were taken after mixing three subsamples and were stored in polyethylene bags.

Profile soils

Profiles 1 (the H-30 series) and 2 (the H-32 series) were taken from the second terrace and profile 3 (the H-34 series) from the first terrace.

Profile 1 shows undisturbed horizontal layers under a landslide mass that originated from nearby corn fields. A unit of a narrow reddish-brown layer (1–3 cm) and a wide yellowish-brown band (~ 10 cm) occurred seven times within 1 m depth. In order to investigate possible variations in geological events, seven sections were sampled from only undisturbed layers (Table 1). Because it was obvious that this profile had not been disturbed by any human activities, samples could provide background concentration levels of heavy metals.

Profile 2 samples were taken around the corn field, which showed four layers from the surface:

1) 2-1 layer: top soil affected slightly by cultivation.
2) 2-2 layer: a fine-sized layer with red coating material on the soil grains and vertical channels for water flow. These channels may play a role in the fast drainage of water during precipitation events.
3) 2-3 layer: a sand layer that has a trace of possible paleo-current or groundwater flow structure.
4) 2-4 layer: a lense-shaped dark area within the 2-3 layer.

Profile 3 samples were taken at an alluvial gold mine near Changringzu Bridge, and the samples were collected from three different layers: (1) 3-1 layer: dry, browny, mica-rich sand, (2) 3-2 layer: wet, brownish-gray sandy loam, and (3) 3-3 layer: gravel layer. Soil from a Tertiary oil-rich gravel layer was also sampled to determine the contamination source, although this profile existed outside the study area. This Tertiary gravel layer is connected to the study area as a basement, and it supplies a large amount of groundwater.

Surface soils

In order to investigate the distribution of heavy metals in the surface soil, alluvial soil samples in the southern part of the Hunchun River, which is being used for intense agriculture, were taken from rice and corn fields located on the first and second terraces. Two sets of samples were taken, one during the summer and the other during the winter, to examine any possible seasonal variation of heavy metal concentrations. Soil sampling was carried out as composite (bulk) samples from plough layers (0–25 cm).

Coal and ashes

In the Hunchun basin, there are two large coal mines, many small mines scattered throughout the area, and a power station. Coals, ash, and incompletely combusted coals are piled up in open spaces and dumped into swamps as part of solid waste fill-in around Hunchun City.

PFA and bottom ash are mixed with water and dumped into the ash pond near the Hunchun power station. Coal for domestic and industrial use and fresh ash were sampled to ascertain the leachability of fluorine. Gangues, leached sediment, stream sediments from mine drainage around two large coal mines (Ying-an and Xin-ming) and from an ash pond were also taken.

Sample preparation and metal analysis

In the laboratory, samples were air-dried (25 °C, 2 weeks), sieved at 2 mm, and ground to 80-mesh size. Pebbles, plant debris and other miscellaneous items were removed prior to sampling.

To identify the mineral assemblages and the possible natural sources of heavy metal contamination, X-ray diffraction (XRD) traces were obtained from ground bulk samples. Clay mineral assemblages, which can affect the sorption processes, were identified using a filter transfer method (Moore and Reynolds 1989). An XRD system (MXP-3, MAC Inc.) was used with Ni-filtered Cu-kα radiation, 40 kV/30 mA, divergent and scattering slits of 1 mm, a receiving slit of 0.15 mm, 0.02° 2θ steps, and counting times of 1 s per step.

Total concentration of each heavy metal in the sample was determined using inductively coupled plasma–atomic emission spectrometry (ICP–AES) (Jobin Yvon 138 Ultrace) at the Seoul branch of the Korea Basic Science Institute (KBSI). Approximately 0.1 g of the ground sample was weighed and put in a Teflon bomb. A hot-plate acid reflux digestion method was used with a mixed acid ($HF:HNO_3:HClO_4=4:4:1$). The digested solutions were diluted to 30 ml and stored in presoaked polyethylene bottles in a refrigerator before ICP-AES analysis. Each sample was analyzed three times and the average value was taken. The detection limit of the ICP-AES analysis is 5 ppb to a few hundred ppb, depending on the type of metal. To determine concentrations of partial acid extraction, 5 g of sample (< 2 mm) was equilibrated with 50 ml 0.1 N HNO_3 solution for 2 h in an end-over-end shaker. Sample solutions were then filtered using a 0.45-μm membrane filter and analyzed for elemental concentration using ICP-AES. The blank correction (digested mixed acid solution in total digestion and 0.1 N HNO_3 extractants in partial extraction) were made before each measurement.

Quantitative analyses for fluorine were conducted using X-ray fluorescence spectroscopy (XRF, PW 1480 X-ray fluorescence sequential spectrometer, Philips) with a pellet sample mount. Total carbon content was measured using a wide-range carbon determinator (WR-112 788-600 model, Leco Ltd.). Maximum relative error is ± 0.75 %. Sulfur content in bulk samples was measured using a sulfur analyzer (SC-132 model, Leco Ltd.) with a measuring time of 120 s, and a temperature range of 399–850 °C. Based on the three time measurements of the standard coal sample, the relative error is ± 1 %. Major anionic species in the soil (soil : deionized water = 1 : 1) after shaking for 2 h and partially extracted solution using 0.1 N HNO_3 were analyzed using high-powered liquid chromatography (HPLC) (Universal Ion Chromatography System, Alltech) with a Durasep A-1 Anion column (100 × 4.5 mm) and a Suppressed Conductivity Detector.

Results

Basic soil properties

The alluvisol can be divided into two terraces. The first terrace was close to the Hunchun River and the second terrace was overlain to the first terrace and elevated geomorphologically. The light soil was formed from lag deposition after floods. Although there is a geological time gap, they have the same mineralogical assemblages (Ta-

Table 1
Total concentration of elements for the samples from the Hunchun area (mg/kg). *MSD* Maximum standard deviation; *ND* not detected; *TC* total carbon; *TS* total sulfur

	Sample description	pH	Soil texture	Fe	Al	Cr	Zn	Cd	Pb	Ni	Mn	Cu	F	TC	TS
Stream sediment															
H-1	Tumen River, 2 terrace			19,210	77,940	85.77	57.48	5.600	12.97	32.72	610.4	14.15			
H-2				37,030	36,260	99.72	85.26	2.410	13.86	31.93	701.9	< 1			
H-3				31,800	82,790	64.52	51.07	< 1	4.587	11.31	611.9	< 1			
H-12				43,960	71,120	113.8	146.7	48.33	7.719	52.69	1,094	51.68			
H-8	Hunchun River, 1st terrace	4.90	Sand	22,580	74,680	78.71	45.23	< 1	< 1	24.12	630.6	< 1			
H-15		6.33	Loamy sand	18,540	71,490	17.02	21.54	< 1	< 1	< 1	284.8	< 1			
H-22	Hunchun Creek, 1st terrace	7.69	Sandy loam	18,270	59,230	74.91	37.76	< 1	< 1	11.91	916.8	< 1		0.29	
H-23		6.23	Sandy loam	23,390	75,540	109.8	62.46	< 1	< 1	26.46	701.8	< 1		0.29	
H-24		7.44	Loamy sand	15,160	62,309	52.82	44.46	< 1	< 1	5.073	328.5	< 1		0.63	
H-29	Hunchun River, 1st terrace	6.89	Sand	18,490	70,580	97.95	74.05	29.50	< 1	33.93	575.6	38.36		0.11	
H-31		6.49	Sand	16,890	75,140	85.31	82.24	24.69	< 1	35.24	489.8	31.61		0.19	
H-33		6.45	Silty loam	42,280	95,580	142.2	118.9	3.253	23.74	13.90	776.2	< 1			
H-35		6.17	Silty loam	38,000	88,820	149.0	118.2	40.95	< 1	62.45	914.4	29.28		0.89	
H-21	Hunchun Creek, 2nd terrace	6.64	Loamy sand	11,820	62,340	87.23	39.82	< 1	12.01	27.18	398.5	7.585			
H-38		6.43	Sandy loam	20,110	56,350	29.66	37.02	< 1	< 1	< 1	521.3	4.533			
Profile soil															
H-30	Pro 1-1 (83–101 cm)	6.23	Loamy sand	19,570	57,700	85.17	90.13	33.24	< 1	43.45	616.1	29.78			
(2nd terrace)	Pro1-2 (101–110 cm)	6.58	Sandy loam	22,120	56,640	39.29	42.59	< 1	< 1	17.70	471.2	< 1			
	Pro 1-2-1 (110–124 cm)	6.54	Loamy sand	21,750	83,280	36.49	41.42	< 1	< 1	11.59	429.0	< 1			
	Pro 1-3 (124–136 cm)	6.70	Loamy sand	16,600	71,550	32.37	40.40	< 1	< 1	7.449	321.2	< 1			
	Pro 1-4 (136–150 cm)	6.68	Loamy sand	17,590	50,280	35.45	41.41	< 1	< 1	5.647	376.8	< 1			
	Pro 1-5 (150–161 cm)	6.97	Sandy loam	22,370	83,300	32.47	36.08	< 1	< 1	1.640	374.3	< 1			
	Pro 1-6 (161–180 cm)	7.25	Loamy sand	17,630	36,990	47.39	41.09	< 1	1.200	11.70	525.2	< 1			
H-32	Pro 2-1 (0–30 cm)	5.93	Loam	24,570	76,540	99.86	72.65	< 1	13.89	36.76	961.2	19.10		2.53	
(2nd terrace)	Pro 2-2 (30–70 cm)	6.35	Loam	30,130	62,760	84.44	62.16	< 1	< 1	17.59	721.6	< 1		0.31	
	Pro 2-3 (<70 cm)	6.11	Loamy sand	19,230	91,640	28.80	43.35	< 1	< 1	3.716	629.0	< 1		0.10	
	Pro 2-4 (in Pro 2-3)	6.63	Loamy sand	20,000	30,800	84.70	94.91	39.56	13.82	48.36	562.0	41.75		0.08	
H-34	Pro 3-1 (0–180 cm)	6.63	Loamy sand	32,000	82,160	129.9	99.97	28.83	< 1	54.22	822.8	42.05		0.32	
(1st terrace)	Pro 3-2 (180–250 cm)	5.65	Sandy loam	37,740	89,980	153.1	118.4	35.32	< 1	63.70	900.0	51.02		0.55	
	Pro 3-3 (<250 cm)	6.03	Loamy sand	27,060	82,620	110.6	65.71	5.500	< 1	39.66	880.2	17.08		0.36	
H-36	Oil-rich layer	6.35	Loamy sand	18,610	71,630	16.91	39.98	< 1	< 1	16.91	13,300	< 1			
Surface soil (rice and corn field)															
	Summer														
H-7	1 terrace, corn field	4.77	Silty loam	34,700	84,300	75.84	55.27	< 1	< 1	17.35	729.8	< 1		0.77	
H-9	1 terrace, corn field	5.45	Silty loam	47,220	90,160	120.4	86.25	< 1	< 1	32.14	1,046	23.28		1.06	
	Winter														
H-25	2 terrace, rice field	5.52	Silty clay loam	36,780	77,860	128.4	111.3	37.73	22.51	49.78	1,155	55.81		2.25	
H-26	1 terrace, rice field	6.00	Silty clay loam	37,250	103,400	141.0	110.6	5.158	24.07	57.02	948.8	22.06		2.96	
H-27	1 terrace, corn field	6.00	Silty loam	33,910	86,660	134.2	95.26	2.654	9.733	51.91	814.3	30.38		1.61	
H-28	2 terrace, corn field	5.75	Silty loam	39,450	93,310	65.47	71.20	< 1	< 1	10.71	1,022	10.33		1.78	

Table 1
(Continued)

	Sample description	pH	Soil texture	Fe	Al	Cr	Zn	Cd	Pb	Ni	Mn	Cu	F	TC	TS
Coal and ash samples															
H-4	Xin-ming, gangue	6.57	Silty loam	27,970	81,380	57.74	98.94	< 1	68.58	24.12	455.6	27.92	159	4.20	0.093
H-5	Xin-ming, stream	6.95	Silty loam	30,500	81,940	107.3	117.4	< 1	4.139	35.77	712.8	30.45	222	4.68	0.019
H-10	Ying-an, gangue	7.28	Silty loam	33,060	97,650	100.6	163.4	< 1	24.16	35.94	610.3	41.37	211	4.83	ND
H-11	Ying-an, leachate	7.64	Silt	34,220	88,810	81.88	147.4	< 1	< 1	30.21	680.1	32.63	203	1.99	ND
H-37	Ying-an, gangue	6.93	Silty loam	31,030	98,350	94.61	132.8	< 1	< 1	21.49	674.8	39.69			
H-13	Ash pond	6.69	Silty loam	30,900	134,200	133.5	90.63	< 1	< 1	51.62	477.4	78.02	160	0.464	ND
H-39	Ash pond, stream	6.36	Silt	30,290	134,600	134.3	215.8	< 1	8.391	54.84	647.6	81.52	266	0.375	ND
H-39-1	Ash pond, stream	6.58	Silty loam	32,710	130,100	149.1	207.2	< 1	< 1	59.57	955.2	72.14	390	0.207	ND
H-40	Domestic coal			7,145	27,140	29.70	32.71	< 1	< 1	15.30	47.71	19.50	81	44.4	0.261
H-41	Industrial coal			9,280	47,330	41.07	35.68	< 1	< 1	16.79	89.34	26.98	91	42.3	0.151
H-42	Industrial ash			29,410	106,900	119.6	76.42	< 1	< 1	47.65	306.0	88.41	153	15.4	0.138
MSD				30.4	51.4	2.20	1.11	0.71	0.80	3.34	17.5	0.84	18.0		
Ref 1[a]						47	45	0.37	22	13	270	13			
Ref 2[b]				40,000	71,000										

[a] US soils, typical levels (Sposito and Page 1984)

[b] World soils, sandy soil (Kabata-Pendias and Pendias 1992)

Table 2
Relative contents of mineral composition resulting from the semi-quantitative analysis using XRD. ***, Major; **, minor; *, trace component. Abbreviations: *Qz* quartz; *Ab* albite; *An* anorthite; *Mc* microcline; *Amp* amphibole; *Mi* mica; *Kao* kaolinite; *Sm* smectite; *Chl* chlorite; *Mg* magnesite; *Mt* magnetite; *Ht* hematite; *Py* pyrite; *Gp* graphite; *Fmo* Fe-Mn oxides

Sample description	Qz	Ab	An	Mc	Amp	Mi	Kao	Sm	Chl	Mg	Mt	Ht	Py	Mul	Gp	Fmo
Stream sediments	***	***	*	***	**	**	*	*								
Profile soils	***	***	*	***	**	*	*	*		*						
Surface soils	***	***	*	**	**	**	*	*								
Coal and ash samples																
Coal gangue and mine stream sediment	***	***	*	*	*	*	*		*							
Ash pond and downward stream sediment	***										*	*		***	*	
Domestic coal	***	**							**				**		***	
Industrial coal	***	*							**						***	*
Industrial ash	***	**									*	*		***		*

ble 2). In the entire area (~ 185 km^2), quartz, albite, and microcline constitute the major fraction and anorthite, amphibole, mica, kaolinite, smectite, and magnesite the minor fraction, although the composition of the minor constituents, such as clay minerals, amphibole, and magnesite, varies slightly. In contrast, tailings around Ying-an and Xin-ming coal mines, including gangue mineral and bedrock debris, show very similar mineral composition (Table 2), including quartz, albite, anorthite, chlorite, muscovite, and amphibole, except magnesite in H-5 sample. Coal samples consisted of mainly coals with appreciable or small amounts of quartz, chlorite, muscovite, pyrite, and Fe-Mn oxides (jacobsite and/or iwakaiite). Ash samples contain mullite, quartz, and minor albite, unburnt coal, graphite, hematite, and spinel minerals, including ulvospinel, and/or magnetite.

The basic soil properties of the alluvial soils of the Hunchun basin are somewhat variable (Table 1). Soil pH range was slightly acidic to neutral (5.52–6.39). Organic matter contents were quite different depending on the sampling locations: stream sediment, 0.11–0.89 %; profile soil, 0.08–0.55 %, except profile 2-1 sample; surface soil, 0.77–2.96 %. They showed a relatively high standard deviation except for data from stream sediments.

Representative profiles and surface soils were selected to determine soil texture (Table 1), except for stream sediments and coal-ash samples. The analytical results illustrate that the soil textures varied according to land use. In general, soil profiles showed a characteristic of typical fluvisol, which has good sorting, little organic content, and is a light soil (loam, loamy sand, and sandy loam). On the other hand, surface soils could be divided into two types: the soil texture of rice fields was silty clay loam, and that of corn fields was silty loam.

Distribution of heavy metals based on total concentration

The concentrations of metals were: Fe (11,820–47,220 mg/kg), Cr (16.91–153.1 mg/kg), Pb (< 1–24.07 mg/kg), Cu (< 1–55.81 mg/kg), and Zn (21.54–146.7 mg/kg) in all soil samples except for coal and ash, which were in the reference range (Table 1). However, the concentrations of Mn (284.8–13.300 mg/kg), Cd (< 1–48.33 mg/kg), and Ni (< 1–63.70 mg/kg) (Fig. 2) were found to significantly exceed the critical soil total concentration (Kabata-Pendias and Pendias 1992; Sposito and Page 1984). Fe can apparently be seen as a non-contaminative element, but this will be discussed in the partial extraction results section.

Stream sediments

Metal distribution of total concentration is illustrated in Fig. 2. Based on the reference concentration of Sposito and Page (1984) and Kabata-Pendias and Pendias (1992), the concentration levels of Fe, Zn, and Cr are similar to the reference level. However, Mn, Cu, Cd, Ni, and Pb show relatively high concentration levels, in particular sampling sites such as the main Hunchun River. The sediments of a tributary below coal mines (Cd, < 1 mg/kg; Pb, < 1 mg/kg; Cu, 4.53–7.59 mg/kg; Ni, < 1–27.2 mg/kg) and the creek, which is located between Hunchun City and the main Hunchun River (Cd, < 1 mg/kg; Pb, < 1 mg/kg; Cu, < 1 mg/kg; Ni, 5.07–26.5 mg/kg) show low levels of heavy metal concentrations. In contrast, the levels in samples taken at the Hunchun River close to intensive agricultural land are high (Cd, 3.25–41.0 mg/kg; Pb, < 1–23.74 mg/kg; Cu, < 1–38.36 mg/kg; Ni, 13.9–62.5 mg/kg).

Soil profile

The analytical results of samples from profile 1 show two trends of variation in their concentration of elements (Fig. 3). One that might be expected is a slightly irregular variation of major elements (Al, Ca, Mg, Fe, and Mn) according to the sequentially depositional events and relative variation in mineral assemblages. The other is that Cd, Cu, and Pb were detected at an extremely low level (< 1 mg/kg). Moreover, it was also found that the concentrations of Ni, Zn, and Cr were more regular than those of major elements, except in the first sample (profile 1-1), which was the interfacial sample between upper land mass and lower undisturbed profile samples. It had an enrichment of Cr, Zn, Cd, Ni, Mn, and Cu, which had almost the same contaminated level of other profiles. In the case of Pb, the lowest sample (profile 1-6) showed 1.2 mg/kg (Table 1); however, this value is close to the detection limit (1 mg/kg) of the analysis method employed.

Because of the reddish coating materials, such as ferrihydrite, goethite, and hematite of profile 2-2, Fe content is highest in this layer (Fig. 3). However, the deeper the layer, the less the content of most heavy metals (Pb, Cu, Ni, Zn, Cr, and Mn). This indicates that the leaching process occurred after an influx of heavy metals into the top soil. Especially as there is little Cd in the top layer of this profile. This indicates that Cd had already leached to the groundwater by precipitation. However, although the profile 2-4 (lense-shaped dark mottle in profile 2-3 layer) sample was found to contain relatively high concentrations of heavy metals, this sample was not considered to be a representative layer.

Profile 3 samples were taken at the alluvial gold mine around Changringzu Bridge. The concentrations of heavy metals were correlated with Al and Fe content (Fig. 3); therefore, the profile 3-2 layer plays a role as an accumulative layer. This implies that high Al and Fe concentrations may have a relationship with clay minerals and Fe-Mn oxides. In contrast, the profile 3-3 Tertiary gravel layer contained low levels of heavy metals.

Paddy and corn field surface soils

Most samples have similar mineral assemblages (Table 2) except for small portions of clay minerals and nesquehonite. However, the concentration levels of heavy metals such as Cd (< 1–37.7 mg/kg), Pb (< 1–24.1 mg/kg), Ni (10.7–57.0 mg/kg), and Cu (10.3–55.8 mg/kg) are higher than other soil and stream sediment samples. Cd and Pb are detected in half of the samples taken from farmland.

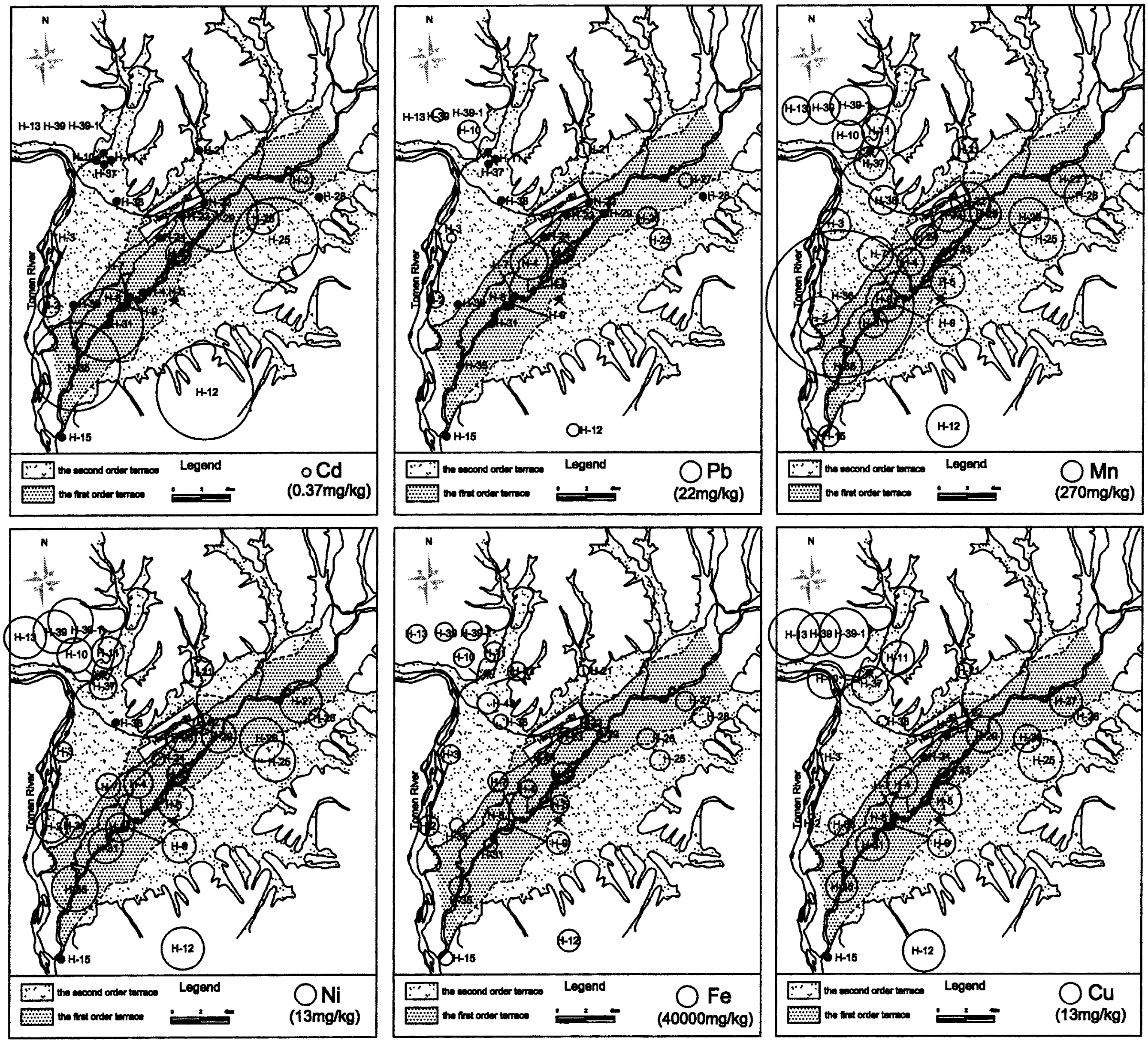

Fig. 2
Concentration distribution of Fe, Mn, Cu, Cd, Ni, and Pb in soil samples. Diameter of each unit circle in the legend is based on the typical levels of US soil (Sposito and Page 1984) and world soils (Kabata-Pendias and Pendias 1992). *Black circles* denote that the concentration of sample does not exceed that of standard unit

Also, the distribution of Cu, Zn, Cr, and Ni in samples from farmland was similar to that in samples from coal mine areas (Fig. 2).

Coal and ash

Heavy metal concentrations were higher in the ash samples and stream sediment of ash ponds than in coals. A geochemical study of trace elements in low-sulfur coals (0.151–0.261 %) showed (Table 3) little Cd and Pb, with trace contents of Cr, Cu, Ni, and Zn. In the case of ash, the trace element contents were within the global coal ash range (Kronberg and others 1987). Total concentration levels of F were 81–91 mg/kg in coal, 153 mg/kg in ash, and 159–220 mg/kg in gangue; and the concentration levels of weak-acid-extractable F was almost two-thirds of the levels.

Partial extraction with 0.1 N nitric acid

This weak acid extraction method is used as an approximation of the potential availability of heavy metals to plants. The results show that there is wide variation in heavy metal extractability by dilute acids (Table 4). The least extractable elements were Cd and Cr, with only 0.08 and 0.21 % of their total concentrations, respectively. In spite of the low percentage of extracted Fe (mean = 0.75 %), the range of absolute extracted concen-

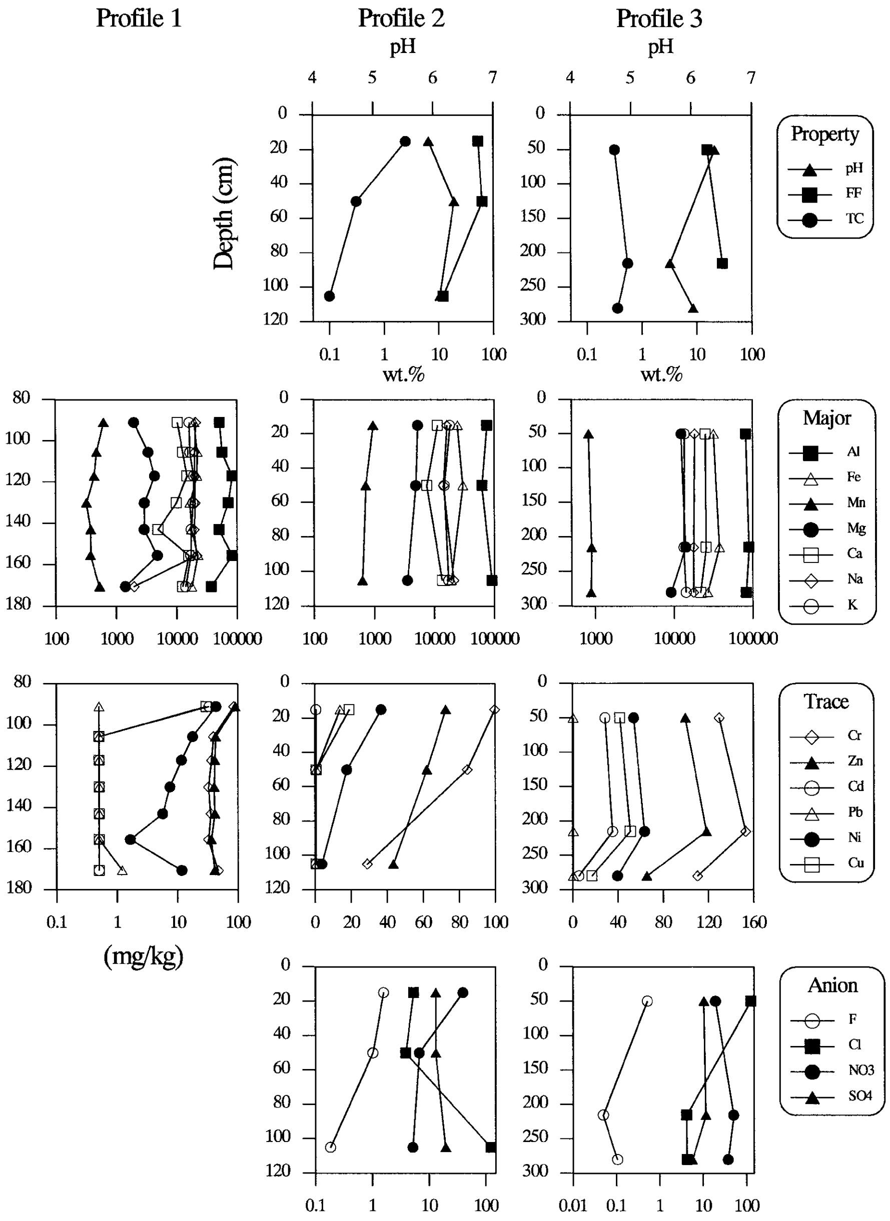

Fig. 3
Variations of elemental concentrations (mg/kg) and physical characteristics in profile 1 (H-30), profile 2 (H-32), and profile 3 (H-34). *FF* Fine fraction (clay+silt); *TC* total carbon content

Table 3
Trace elements (mg/kg) in the coals and ashes from Hunchun basin

	Domestic coal	Industrial coal	Industrial ash	Ash pond	Typical concentration in coal[a]	Range[a]	Global coal[b] ash range	Western Canada[c]
Cd	< 1	< 1	< 1	< 1	0.5	0.1–3	< 0.1–700	
Cr	29.70	41.07	119.6	133.5	20	0.5–60	0.3–150	
Cu	19.50	26.98	88.41	78.02	15	0.5–50	18–270	
Pb	< 1	< 1	< 1	< 1	40	2–80	<2–1500	
Ni	15.30	16.79	47.65	51.62	20	0.5–60	5–450	
Zn	32.71	35.68	76.42	90.63	50	5–300	3–6.2 %	
F	81	91	153	160				174

[a] Clarke and Sloss (1992)
[b] Kronberg and others (1987)
[c] Godbeer and others (1994)

Table 4
Concentrations of in soil samples treated 0.1 N nitric acid (mg/kg) and ratios of heavy metallic contents between partial extraction and total digestion (wt %). *MSD* Maximum of standard deviation; *AO* extraction acid overlapped; *NP* not detected in partial extraction; *NT* not detected at total digestion; *AC* absolute concentration (mg/kg); *RC* ratio of partial-extracted concentration over total-digested concentration (%); *KSA(W)L* Korean standards for action (warning) level of soil by 0.1 N HCl extraction

Elements	Fe		Cr		Zn		Cd		Pb		Ni		Mn		Cu		F	SO_4
	AC	RC	AC	RC	AC	RC	AC	RC	AC	RC	AC	RC	AC	RC	AC	RC	AC	AC
Stream sediment																		
H-1	56.3	0.29	0.07	0.08	0.73	1.27	< 0.05	NP	0.25	1.93	0.61	1.86	7.72	1.26	0.50	3.53		
H-2	121	0.33	0.10	0.10	2.09	2.45	< 0.05	NP	0.60	4.33	0.72	2.25	32.4	4.62	1.46	NT		
H-12	395	0.90	0.31	0.27	6.70	4.57	0.08	0.17	2.54	32.91	0.87	1.65	177	16.17	5.10	9.87		
H-23	509	2.18	0.19	0.17	2.77	4.44	< 0.05	NP,NT	2.38	NT	0.58	2.19	67.2	9.58	2.25	NT		
H-29	84.0	0.45	< 0.05	NP	0.46	0.62	< 0.05	NP	0.29	NT	0.12	0.35	13.8	2.40	0.47	1.12		
H-31	128	0.76	0.46	0.54	0.52	0.63	< 0.05	NP	1.90	NT	< 0.05	np	22.1	4.51	0.45	1.42		
H-33	522	1.24	0.25	0.18	3.69	3.10	0.07	2.15	3.30	13.90	0.64	4.61	164	21.13	8.08	NT		
H-35	335	0.88	0.57	0.38	1.64	1.39	< 0.05	NP	2.46	NT	0.32	0.51	74.6	8.16	2.83	9.67		
Profile soil																		
Pro 2-1	46.7	0.19	< 0.05	NP	3.12	4.29	< 0.05	NP,NT	0.96	6.91	0.97	2.64	48.7	5.07	0.79	4.14	83.0	51.0
Pro 2-2	128	0.43	0.12	0.14	1.49	2.40	< 0.05	NP,NT	0.55	NT	0.66	3.75	5.28	0.73	1.21	NT	106	AO
Pro 2-3	107	0.56	0.06	0.21	1.37	3.16	< 0.05	NP,NT	0.44	NT	0.32	8.61	3.94	0.63	0.48	NT	83.2	30.4
Pro 2-4	88.4	0.44	< 0.05	NP	1.45	1.53	< 0.05	NP	0.31	2.24	0.35	0.72	3.72	0.66	0.42	1.01	105	65.6
Pro 3-1	140	0.44	0.12	0.09	0.88	0.88	< 0.05	NP	0.31	NT	0.33	0.61	9.85	1.20	0.76	1.81	102	AO
Pro 3-2	242	0.64	0.16	0.10	1.59	1.34	< 0.05	NP	0.54	NT	1.06	1.66	16.2	1.80	1.60	3.14	114	AO
Pro 3-3	148	0.55	0.10	0.09	0.80	1.22	< 0.05	NP	0.31	NT	0.36	0.91	14.1	1.60	0.68	3.98	106	AO
H-36	71.8	0.39	0.06	0.35	0.97	2.43	< 0.05	NP,NT	0.07	NT	0.44	2.60	56.8	0.43	0.32	NT		
Surface soil (rice and corn field)																		
H-7	124	0.36	0.12	0.16	1.35	2.44	< 0.05	NP,NT	0.42	NT	0.56	3.23	12.9	1.77	0.85	NT	106	18.4
H-9	191	0.41	0.15	0.12	1.83	2.12	< 0.05	NP,NT	0.55	NT	0.82	2.55	43.7	4.18	3.83	16.45	120	26.4
H-25	516	1.40	0.15	0.12	2.59	2.33	< 0.05	NP	2.85	12.66	1.78	3.58	216	18.71	2.63	4.71	82.4	AO
H-26	263	0.71	0.34	0.24	4.06	3.67	< 0.05	NP	0.88	3.66	2.17	3.81	125	13.18	3.89	17.63	127	AO
H-27	331	0.98	0.29	0.22	3.15	3.13	< 0.05	NP	0.70	7.19	1.68	3.24	54.8	6.73	2.13	7.01	100	2.16
H-28	92.3	0.23	0.06	0.09	1.53	2.15	< 0.05	NP,NT	1.18	NT	1.80	16.81	53.3	5.52	1.96	18.97	86.4	8.80
Coal and ash samples																		
H-4	84	0.30	< 0.05	NP	0.46	0.46	< 0.05	NP,NT	0.29	0.42	0.12	0.50	13.8	3.03	0.47	1.68	109	1003
H-10	278	0.84	0.10	0.10	11.9	7.30	0.10	NT	3.23	13.37	1.82	5.06	21.2	3.47	5.34	12.91	55.2	317
H-13	406	0.82	0.28	0.10	9.69	6.14	0.08	NT	2.53	NT	1.62	6.70	27.5	2.45	5.72	13.28	53.1	194
H-37	254	1.32	0.09	0.21	8.16	10.69	0.10	NT	2.89	NT	1.44	3.14	16.5	5.76	5.27	7.33	54.0	256
H-41	125	1.35	0.41	1.00	2.14	6.00	< 0.05	NP,NT	4.21	NT	0.14	0.83	2.55	2.85	2.02	7.49	58.8	4.20
H-42	506	1.72	0.85	0.71	3.37	4.41	< 0.05	NP,NT	0.75	NT	1.01	2.12	13.9	4.54	5.66	6.40	74.4	2865
KSAL			30				30		1000						500			
KSWL			12				12		400						200			
Max	522	2.18	0.85	1.00	11.9	10.7	0.10	2.15	4.21	32.9	2.17	16.8	216	21.1	8.08	19.0	127	2865
Min	46.7	0.19	0.06	0.08	0.46	0.46	0.07	0.17	0.07	0.42	0.12	0.35	2.55	0.43	0.32	1.01	53.1	420
MSD	0.391		0.001		0.007		0.000		0.007		0.003		0.109		0.066			

tration is 46.7–522 mg/kg. The extractability of Mn is 5.42 % and the range of absolute extracted concentration is also high (2.55–216 mg/kg). Analysis indicates that Fe, which is supersaturated in most of the groundwater (Woo and others 2000), is the main contaminant. However, the concentrations of weak-acid-extractable heavy metals, such as Pb (0.1–4.2 mg/kg), Zn (0.5–11.9 mg/kg), Cu (0.3–8.1 mg/kg), and Cd (< 0.1 mg/kg), were relatively low.

Discussion

Possible dispersion pathways and their sources of heavy metals

A previous study (Woo and others 2000) showed that the ionic composition of the groundwater from the first terrace was of Ca-HCO_3 type and that from the second terrace was of (Ca+Mg)-(SO_4+Cl) type. However, most surface waters were clustered at the edge of carbonates in the anion triangle on the Piper diagram. This is supported by the fact that the pH values of the surface water in the studied area were relatively high (pH 5.67–7.42), and had very similar mineral assemblages. Because mineral assemblages of whole samples are almost analogous throughout the stream sediments, profiles and surface soils, except for a few sites near the coal mines (Table 2), it can be safely assumed that these were formed from identical source materials and processes. The chemical and physical properties of soil from the area are reasonably homogeneous, and this made it difficult to speculate on the natural causes of metal contamination for sites with particularly high levels of metals.

No obvious relationship was found between the heavy metal concentration of stream sediments and the depositional or structural characteristics of soils. However, the metal concentrations varied depending on the sampling locations (Table 1). At site H-38, a downgradient tributary to the Ying-an coal mine, the heavy metal levels were not particularly high (Cd, Ni, Pb < 1 mg/kg). This means that high concentration levels of heavy metals in the sediments of the main Hunchun River were not directly affected by coal mines. Cd and Pb concentrations of tributary stream sediments are < 1 mg/kg for the samples from the first and second terraces, except for the H-21 sample from second terrace. Three samples of Che-Daren Creek between Hunchun City and the main Hunchun River also contained little Cd and Pb (Table 1, Fig. 2). This means that urban wastewater and sewage sludge are not likely sources of contamination.

Therefore, the Cd, Pb, and Ni contamination of stream sediment was considered to result from anthropogenic sources. High levels of Cd and Pb in the main Hunchun River sediments indicate the possibility of inappropriate application of agrochemicals in the agricultural area around the southern part of the Hunchun River, and this is supported by the distribution of concentration levels in the profile samples. Undisturbed layers of profile 1, which have little Cd, Pb, and Cu, show that there was no influx of anthropogenic contaminants during deposition (Fig. 3), except for profile 1-1. This implies that this first soil layer sample might have been mixed with soil from nearby corn fields by soil creeping. Profiles 2 and 3 (Fig. 3) show some heavy metal distributions, but there is little Cd in the top layer of profile 2. This indicates that Cd had already leached to the groundwater by precipitation. Woo and others (2000) previously reported that Cd is one of the main contaminants in surface and shallow groundwater in this area. Also, the prominent leaching capacity of Cd is supported by the fact that the affinity of metal ions to form a water-insoluble complex of Cd with Mn is lower than that of other heavy metals (Kabata-Pendias and Pendias 1992). For the profile 3 samples taken from the first terrace, where the leaching process had progressed, heavy metals were significantly enriched in the second layer, as shown in Fig. 3. The profile 3-3 Tertiary gravel layer contained low levels of heavy metals: this indicates that there was a low influx from the above layer, or that a desorption processes might have taken place by groundwater flow with high hydraulic conductivity (TEC 1998).

Based on the distribution of heavy metals (Fig. 2), such as Mn, Cu, Cd, Ni, and Pb, from the surface soil samples taken in the south-eastern part of Hunchun (an intensely agricultural area), it appears they may be induced from agrochemicals.

Several research sources (Alloway 1990; Fergusson 1990; Herrero and Martin 1993; Mermut and others 1996) have reported that primary sources of Cd, Pb, and Ni in soils are phosphate fertilizers. Copper is also a component of fertilizer and pig fodder. Distinctly higher concentrations of Cu, Zn, Cd, Pb and other metals in clay soils is a result of adsorption by organic matter and inorganic clay minerals such as Fe-Al oxyhydroxides (Norrish 1975).

Soil samples taken at the rice fields (Fig. 4) and profiles (Fig. 3) show higher levels of heavy metal concentrations, total carbon content, and fine fraction (clay and silt size fraction) in the winter. Considering the gradual removal of Cd by crops, the significantly higher Cd of the surface soil, as with Zn and Pb, may be attributed to fertilizer application. This result shows a good correlation with heavy metal concentration and organic carbon content and fine fraction.

The heavy metal contamination in groundwater around the disposal sites of coal wastes is of serious concern regarding proper disposal of these by-products (Bilski and Alva 1995). According to Querol and others (1995), the concentration of trace elements in the fly ash and slag shows preferential segregation; Cd, Pb (fly ash); Cu, Fe, Mn (slag); Cr, Ni, Zn (no segregation). Therefore, the possibility of dry fall-out of fly ash containing Cd and Pb is very low because of the extremely low content in coal and ash (Table 1).

The maximum concentrations of 0.1 N nitric-acid-extractable metals, such as Cd, Cr, Cu, and Pb, are 0.10, 0.85, 8.08, and 4.21 mg/kg, respectively. Based on the KSWLs (Korean Standard of Warning Levels) using 0.1 M HCl, the maximum concentrations of samples in

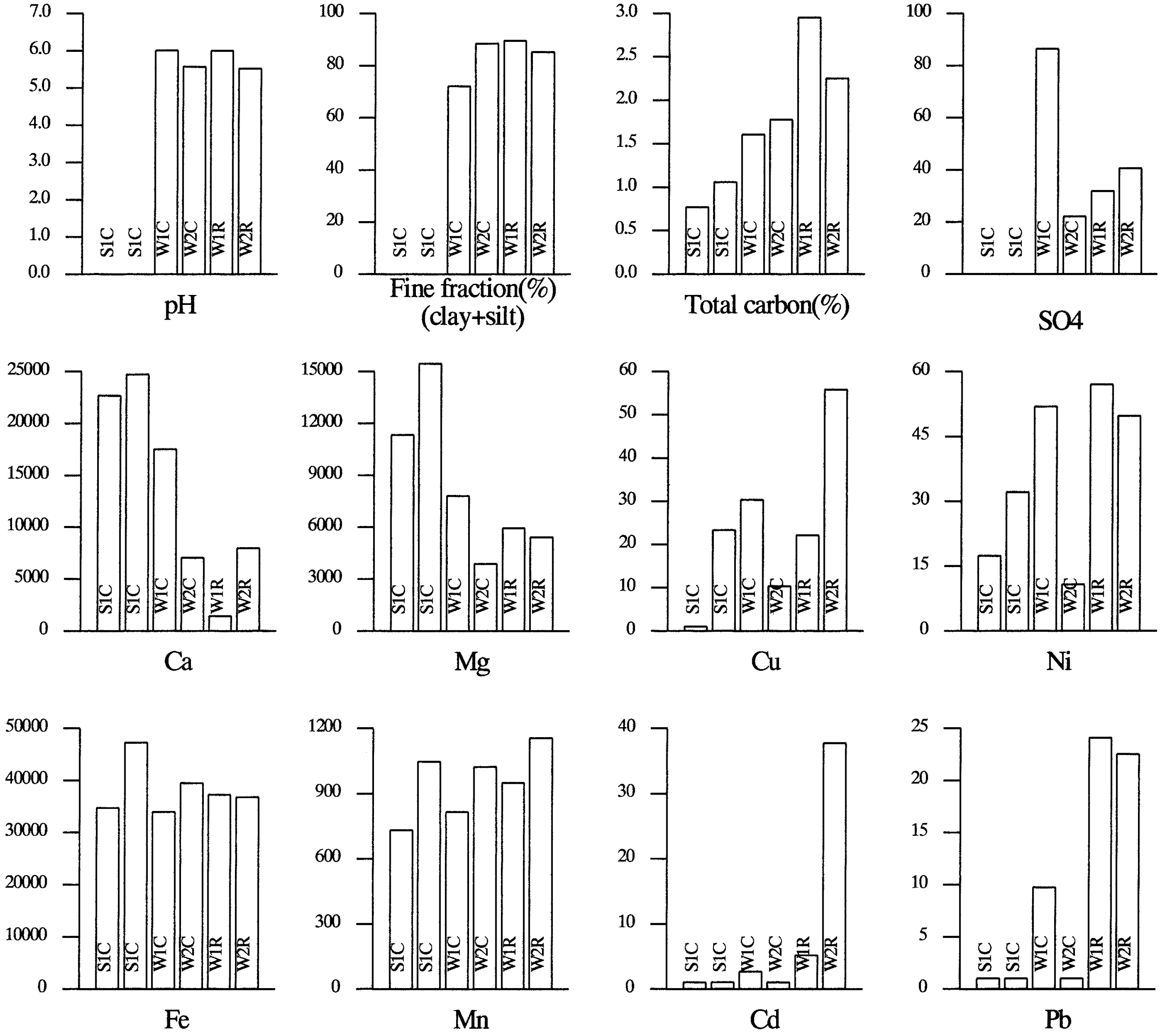

Fig. 4
Variations of elemental concentrations (mg/kg) and physical characteristics of surface (farmland) soil samples. *S* Summer (August); *W* Winter (November); *1* the first terrace; *2* the second terrace; *C* corn field; *R* rice field

the Hunchun basin do not exceed these concentrations (Table 4). Therefore, it can be thought that anthropogenic factors might not cause significant heavy metal contamination of soils in this area, even though there is slight contamination by agrochemicals. Weak acid-extractable Ni and Co are thought to have mostly a natural origin and that they accumulated from the weathering of mafic and ultra-mafic rocks (Voutsinou-Taliadouri 1995). Mitchell (1964) reported that Ni, Co, Mn, Zn, and Cu are the trace constituents of weathering products of hornblende. In this area, enrichment of Fe and Mn can be explained by the weathering of amphiboles, which are major components of igneous rocks. Biotite granite of regional scale, and diorites of small scale, along the Hunchun River (Fig. 1), would be expected to strongly influence the trace metal distribution of the sediment carried and deposited by the river.

Cadmium, nickel, and lead

From a background value of < 1 mg/kg in profile 1 (H-30) and the low content of stream sediment around Hunchun City and coal mines (Fig. 2), it can be easily assumed that Cd, Ni, and Pb were influxed from anthropogenic sources from agrochemicals such as phosphate fertilizers and pesticides. Recently, the Chinese government has limited the use of fertilizers that contain organic P (Zhao, personal communication). The maximum value of Cd is 37.73 mg/kg and the main stream of Hunchun River, which is directly connected to these farmland areas, also has high Cd concentration levels. This means that excessive use of fertilizer and pesticide runoff passes through the surface soil because of the intense precipitation that usually occurs in the rainy season.

Be, Cd, F, and Ni are not found at elevated levels in ash-amended soils (Adriano and others 1980), and Ba, B, Ca, Mo, Pb, S, Se, and Sr generally increase in concentration in the soil to which fly ash is applied (National Research Council 1980). Even though Cd and F are assumed to be influxed with natural dry fall-out or precipitation, Cd will not enrich easily. Coals mined in Hunchun basin also have rare Cd, Ni, and Pb. Therefore, high levels of cadmium that remain in farmlands and adjacent stream sediment indicate that the main source of Cd is anthropogenic fertilizer or pesticide.

The concentration level of Ni was found to be slightly higher than in typical soil (Sposito and Page 1984), and farmland soils show higher partial extracted concentration levels in four categories (Table 4). This implies that the Ni concentration level is affected by both natural and anthropogenic sources. From the analysis of selective dissolution using sodium pyrophosphate, a dissolving reagent of organic metals, only Ni was detectable, and the concentration levels of other heavy metals, such as Cr, Zn, Cd, Pb, and Cu, were below the detection limit (Moon and others, unpublished data). This result indicates that the Ni concentration level over the background value originated from organic phosphate fertilizer.

Iron and manganese

Based on the total concentration of Fe in most soil samples, concentration levels were within the normal range (40,000 mg/kg; Kabata-Pendias and Pendias 1992), except for three samples. However, Woo and others (2000) reported that Fe was found to be supersaturated in most water samples, with mineral phases of hematite and goethite and undersaturated with an amorphous form, $Fe(OH)_3$. The available Fe content (mean value) of the coal and ash samples is the highest among the four categories (Table 4).

The stream sediments have a higher average value than the total mean value, and this implies that stream sediments have been playing a role as a sink for heavy metals. A natural influx, caused by weathering of ferromagnesian silicates to ferruginous products, may have affected extractable iron content. According to Velbel (1989), hornblende dissolves stoichiometrically, and the ferruginous and aluminous weathering products (goethite, gibbsite, and kaolinite) precipitate from solution (neoformation). He showed that only Al and Fe were conserved over microscopic distances; alkali and alkali-earth elements were stoichiometrically removed from the microenvironment during the weathering process. Moon and others (unpublished data) verified the dominant existence of organic Fe and Fe oxide using the sequentially selective dissolution method (Paterson and others 1993), and this extractable phase of Fe could cause regional Fe contamination.

Manganese dominantly exists in the fraction as an amorphous phase and an organic Mn compound. The H-36 soil sample, taken from the oil-rich horizon in the Tertiary gravel layer, shows the highest concentration level of the amorphous fraction, although the total concentration level in the soil sample was not high. Therefore, the easily extractable amorphous phase of Mn is also the main source of groundwater contamination. In addition, the high hydraulic conductivity of the Tertiary gravel layer could stimulate dispersion of Mn.

Harzardous elements, which could have leached from igneous rock bodies and weathered soils, might be adsorbed to colloid phases such as clay minerals, amorphous Fe hydroxide, and Fe-Mn oxides (Hem 1992). Both in pore water and sediment, the adsorption on and desorption from Fe and Mn oxyhydroxides are important processes that control the distribution of these elements (Donahoe and Liu 1998).

Fluorine

Fluorine is difficult to enrich in soil by dry fall-out or precipitation of ash. Woo and others (2000) reported that five wells were supersaturated in F. Considering the lack of other sources, such as fluorite, it can be predicted that a large fraction of F in coals and ashes is leaching continuously.

The solubility of fly ash in water is an important factor in determining the extent of water pollution from fly ash (Rohrman 1971). The greatest movement and loss of leachable solutes occur during a period of rapid flux of soil water, both during and immediately following rainfall (Quisenberry and Phillips 1978). However, water percolating through the soil may bypass much of the total soil mass, leaving isolated volumes of soil solution nearly stagnant (Ritchie and others 1972). Therefore, the fact that a high quantity of F can be detected is supported by previous studies. The results of Ritchie and others (1972) indicate that relatively large connected soil pores were responsible for water moving through distinct isolated areas of soil that had little interaction with water inside the structural unit.

Based on the weak acid-extractable F concentration levels (Table 4), profile and surface soil samples show moderately higher concentration levels (82.4–127 mg/kg) than those of coal and ash samples (53.1–109 mg/kg). There can be two possible explanations: one is the natural enrichment throughout the dissolution of F-bearing mineral phases, and the other is the continuous leaching of F from coal and ash dumps, as well as from fall-out of fly ash.

Conclusion

The distribution of heavy metals in the alluvial soils of the Hunchun basin has been influenced by several interacting factors. The parent alluvial materials were carried by the river and tributaries from the weathered products of several igneous rock bodies in the upstream area and deposited in the Hunchun basin. Weathering of amphiboles, a major mineral in the sediments and soils, have made coating materials that are composed of goethite, ferryhydrite, and Fe-Mn oxides. Therefore, heavy metal concentration levels of the soils were likely to be strongly influenced by the primary mineral weathering. This natural inheritance factor is supported by the fact that concentrations of weak-acid-extractable heavy metals are very low except for Fe and Mn. However, in agricultural soils and adjacent stream sediments, an anthropogenic input of Cd, Pb, Ni, and Cr, in terms of phosphate fertilizer, is strongly suggested. The low fraction of weak acid-extractable (plant available) heavy metals, except Fe and Mn, indicates that this basin has not encountered severe heavy metal contamination, even though the total concentration is high. The enrichment of mobile elements, such as Fe and Mn, may well have both lithogenic and anthropogenic sources.

Coal combustion in power stations and houses is one of the most important factors in the anthropogenic dispersion of heavy metals. Moreover, in the case of developing countries with an anticipated future increase in coal consumption, it is inevitable that ecological and environmental problems related to these emissions will increase substantially. Presently, there is no prominent evidence of heavy metal contamination, except for F by fly and bottom ash from power stations, but, in the future, some problems related to the drinking water will probably occur.

The result of this investigation is expected to provide the Chinese regulatory agencies with a site-specific guideline for future contaminant monitoring programs in this area. In the Hunchun basin, because of the wide distribution of heavy metals and their significantly higher concentrations than allowed by the CDWS, Cd, Fe, Mn, and F can pose potential problems in utilizing water resources. Considering the contamination of soil, which acts as a sink and/or a redistributor, in the development of Hunchun City, detailed studies are recommended, particularly to determine the stability of the Fe-Mn mineral phase, the status and weathering rate of amphiboles in this area, and the characterization of soil properties throughout the whole Hunchun basin.

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