Environmental-Geochemical Characteristics of Cu in the Soil and
Water in Copper-rich Deposit Area of Southeastern Hubei Province,
along the Middle Yangtze River, Central China

Ling Zhang^{a*}, Lu Wang^{b,c}, Kedong Yin^{a,d}, Ying Lv^e, Derong Zhang^a

^a*Key Laboratory of Tropical Marine Environmental Dynamics, South China Sea Institute of
Oceanology, Chinese Academy of Sciences, Guangzhou, 510301, P. R. China*

^b*Department of Marine Geosciences, Ocean University of China, Qingdao, 266100, P. R.
China*

^c*Earth and Atmospheric Sciences Department, Center for Environmental Sciences, Saint Louis
University, MO63108, USA*

^d*Australian Rivers Institute, Griffith University (Nathan Campus), Brisbane, QLD 4111,
Australia*

^e*School of Environment, Beijing Normal University, Beijing, 100875, P. R. China*

***Corresponding author: Ling Zhang**

South China Sea Institute of Oceanology,
Chinese Academy of Sciences,
Guangzhou 510301, People's Republic of China,

Tel: +86 20 89023206

E-mail: yolandezhang@gmail.com

ABSTRACT

In this study, the natural Cu background concentration and Cu natural and anthropogenic contamination in soil, water and crop were investigated systematically in Huangshi area. The results show that regional geology is the dominant factor controlling the natural Cu background concentration in soil and water, and that pH is important to control the vertical distribution of Cu in soil under the same geographical and climatic conditions. The mineralization of rock bodies causes the natural Cu increase in soil and water, whereas, a large number of mining-smelting plants and chemical works are the main sources of Cu anthropogenic contamination. Cu in naturally and anthropogenically polluted soil displays differences in total and available contents, vertical distribution patterns and physico-chemical properties, the same happens in water.

Capsule: Consider the rock-soil-water-crop as a system to study the geochemical activities and environmental pollution of copper.

Key words: natural Cu background; regional geology; natural and anthropogenic contamination; soil; water

1. Introduction

Soil and water are the most important factors for agriculture, and their quality has a tight relationship with the human health. Human activities with rapid industrialization and population growth influence severely the environment including soil, water and atmosphere (Phillips et al., 2001; Marchetti, 2002; Eggermont and Verschuren, 2003; Liao et al., 2005; Perrin et al., 2008). More attention and a wide range of studies have been carried out to study contamination processes of soil and water in most of the impacted world areas (Bryan and Langston, 1992; Cearreta et al., 2000; Santschi et al., 2001; Peng et al., 2005; Borrok et al., 2008; Cecchi et al., 2008).

The natural background concentration of an element is commonly defined as the natural quantity of a given element in a certain material (in absence of external pollution), and reflects the inherent characteristics of that element during existing and developing processes as well as its transformation and transferring. Background concentration is fundamental for the evaluation of soil and water pollution in various environments with different geological and geographically conditions. Therefore, in recent years, many studies have conducted to define geochemical background level to serve as a basis for legislation to assess, prevent and reduce soil contamination (Rieuwerts et al., 2000; Martínez et al., 2007).

Soil metal background concentration is determined by factors such as parent material, soil-type and its physico-chemical properties (Carral et al., 1995; Baize and Sterckeman, 2001; Cobelo-García and Prego, 2003; Fukue et al., 2006), and also by other factors such as hydrodynamic and biogeochemical processes. The difference of parent material is the primary

factor inducing different background concentration; on the other hand, biological and climatic actions may lead to difference of element content in various soils originating from the same parent rock. Physico-chemical properties also affect background concentration, for instance, lower pH in acidic soil leads to desorption of element from soil particles, and makes element more active and easier to be mobile, so that the concentration of element in acidic soil is normally higher than in basic soil. The metal background concentration in natural water can be explained by the reaction of water with rock and sediment, and is related tightly to the regional geology and soil-type. Moreover, it is controlled by other factors such as elemental characteristics, physico-chemical properties (pH, soluble inorganic/organic matter and humic matter etc.), precipitation and runoff.

Human activities have resulted in contamination of water and soil with toxic heavy metals around the world. Especially, metals released from mining-smelting sites or chemical works disturb or severely damage the ecology (Prusty et al., 1994; Ahn et al., 2003; Garcia-Sanchez and Alvarez-Ayuso, 2003; Osher et al., 2006; Kim et al., 2007). The regions along the middle Yangtze River (southeastern Hubei Province) with a developed agriculture and a large population density are important Cu (Fe, Au and other heavy metals) mining and smelting district. The pollution arising from the development of modern industry and agriculture in recent decades has severely damaged the regional ecosystem and consequently, human health. Cu is the main mineralization element in this area and an essential micronutrient for plants and microorganisms catalyzing several key enzymatic processes. However, Cu can also become toxic to microorganisms when presents at elevated concentration (Silver, 1996; Bruins et al., 2000; Borrok et al., 2008). Therefore in this paper,

the rock-soil-water-crop system, considered as a whole, was studied mainly (i) to determine natural Cu background concentration in soil and water; (ii) to estimate the recent Cu contamination in soil, water and crop and (iii) to study the mechanism and conditions of Cu distribution in the system and to assess the natural and anthropogenic impacts on the geochemical activities of Cu.

2. Materials and methods

2.1. Characteristics of the Study area

The study area is centered on Huangshi city (Fig.1) with an area of 1850 km² and a population of 2.5 million, and it is an important agricultural area located in the southeastern part of Hubei Province. Industries developed prosperously in this district and there are many mining and smelting plants, chemical works, electric power plants, cement factories and so on. Most of the factories built in 1950s-1960s had outdated techniques and equipments, and consumed excessive raw energy (mainly coal-burning), even weren't equipped with efficient pollutant-disposal devices. Therefore the atmosphere, soil and water were severely polluted by the large quantities of waste gases, water and residues generated and discharged in the industrial processes. The topography of Huangshi area is composed of low hilly land (consisting of Paleozoic clastic rock and carbonate rock), intermontane basin (consisting of Middle-Cenozoic clastic rock and granite), and the alluvial plain along the Yangtze River, the latter two being main agricultural areas. The water system is well developed in this area with a large number of lakes and reservoirs.

The geology in the area extends from Mid-Upper Cambrian System to Quaternary, and can be separated into geological features: Cambrian dolomite, Ordovician limestone, Silurian microclastic rock, Permian carbonate rock, Tertiary limestone, clayey siltstone, clay rock and carbonaceous shale, Silurian coaly siltstone, Cretaceous-Tertiary siltstone, and Quaternary deposits as alluvium and weathered red-earth distributed across the Yangtze River, lakes, valley and the low hilly area.

Neutral-acidic magma intrusions are dominant as the result of intensive magmatic activity in the Yanshanian and Himalayan periods. The outcrops are mainly Echeng and Tieshan intrusion with some small associated. Echeng intrusion occurred between Mid-Jurassic and Cretaceous-Tertiary and is mainly composed of diorite, orthoclase-diorite, adamellite, granite and granite-porphyry. Tieshan intrusion occurred in Mid-Lower Jurassic and is mainly diorite, quartz-orthoclase-diorite-porphyrite and granodiorite-porphyry.

The study area is a district with a number of large-scale polymetallic ore deposits dominating as Cu and Fe, including seven large-scale Fe-Cu-Au deposits, more than ten middle-scale Cu-Pb-Zn deposits and many small-scale Fe-Cu deposits (Ma and Shan, 1997).

2.2. Sample collection

Twenty soil profiles and eight water samples were collected in autumn 2001 in the localities far from smelting plants and chemical works to study the natural Cu background concentration in terms of regional geology, and contemporarily, nine corresponding rocks were sampled. Four soil profiles derived from neutral-acidic granite area and two water

samples (out flowed from Silurian-Triassic sedimentary rock and from the contact zone between Middle-Cenozoic granodiorite and carbonate, respectively) were collected to determine the natural Cu contamination in soil and water. Seven soil profiles and seven water samples were sampled near smelting plants and chemical works in order to investigate anthropogenic Cu contamination. In addition, seven rice samples were sampled to study the damage made by polluted soil and water. Fig.1 shows the simple geological and geomorphological feature in study area as well as the sampling sites.

2.3. Chemical analysis

25 ml distilled water was added to 5 g soil to make suspension, then pH, electrical conductivity (EC) and potential of soil suspension and water sample (filtered with a 0.45 μ m membrane) were determined within 30 minutes from sampling in the field. The redox potential (Eh) was then calculated (Eh = determined potential pluses that of reference Electrode). The detection limits of the pH Meter (pHS-2) are ± 0.02 pH and ± 2 mV, and the precision of the conductivity meter (DDS-11A) is $< \pm 1.5\%$. The filtered water sample was acidified to be pH <2 and stored in polyethylene bottles for Cu analysis.

Total Cu in soil was determined after treatment with high grade HCl-HNO₃ using an atomic absorption spectrophotometer (SF2-3510) with the precision of $< 3\%$. Available Cu was extracted with DTPA (diethylenetriamine pentaacetic acid)-CaCl₂-TEAC (triethanolamine) and determined using the abovementioned atomic absorption spectrophotometer. Cu content in acidified water and incinerated rice sample was analyzed

using a La-ICPMS with a precision of <10%. Rock sample was ground and sieved through a 63 μ m mesh and the Cu content was determined as for soil. Different solvents were added to the soil sample according to the different existing forms of Cu such as: residual phase, Fe-Mn oxides phase, organic phase, soluble and exchangeable phase (Han et al., 2003), and then Cu content in the various forms was analyzed using the atomic absorption spectrophotometer.

3. Results and discussion

3.1. Natural Cu background concentration in soil

Geochemistry of soil reflects that of parent rock (Reimann and Garrett, 2005), and the geochemical baseline value has a wide range of regional and local variations, which mostly originated from changes of geology. In this paper, Cu background concentration was determined for each geologic unit (with different Cu geochemical pattern) described as intermontane basin soil, alluvial plain soil and low hilly area soil, respectively.

Intermontane basin soil derived mainly from the weathering of Mid-Cenozoic clastic rock and granite, and its Cu content showed great variation. It could be seen from Table 1 (sample S1-S9) that the ranges of total and available Cu were 15-87 mg·kg⁻¹ and 0.75-9.58 mg·kg⁻¹ in surficial soil from clastic rock, 12-200 mg·kg⁻¹ and 1.64-18.1 mg·kg⁻¹ in surficial soil from granite. Cu content of parent rock was the main factor to control Cu in soil, such as S4 profile, Cu content of Mid-Upper Jurassic mottled sand-shale stone was 28 mg·kg⁻¹, and the total Cu content in soil was 28-30 mg·kg⁻¹. And in S8 profile, Cu content of parent rock

(granodiorite-porphyry) was $8 \text{ mg}\cdot\text{kg}^{-1}$, and Cu in soil was only 12-14 $\text{mg}\cdot\text{kg}^{-1}$. Furthermore, there was a positive correlation between total and available Cu contents.

Total and available Cu followed three patterns vertically, (i) Cu content decreased with the depth in S1, S2 and S7; (ii) Cu content was stable in S3, S8 and S9; and (iii) total and available Cu content changed inconsistently, that is to say, total Cu kept stable but available Cu increased at underlayer in S5, and, total Cu increased evidently with the depth but available Cu was almost stable in S6. The above differences were caused by the factors as parent rock, leaching, illuviation and biota. For example, soil in S6 was from the weathering of granodiorite and the soil suspension showed acidic (pH 4.35-5.07) and oxidizing ($E_h > 450 \text{ mV}$) conditions, and Cu ($400\text{-}500 \text{ mg}\cdot\text{kg}^{-1}$) accumulated at the bottom of profile due to acidic leaching during the soil forming.

The alluvial plain sandy soil (with high content of mineral and element) was of Holocene sediment, and six soil profiles (Table 1, S10-S15) showed that the total Cu content was relatively stable (avg. $42 \text{ mg}\cdot\text{kg}^{-1}$) and the vertical distribution was also considerably homogeneous. The physico-chemical properties were quite similar among the profiles. However, there was some diversity in available Cu which generally ranged from 1.02 to $5.54 \text{ mg}\cdot\text{kg}^{-1}$ with extra high value in S13 and S15. The reason caused this abnormality (especially in S13 and S15) might be attributed to the absorption ability (concentration of SO_4^{2-}), organic matter and porosity of different soils, however, further study was needed. The alluvial soil was about 8,000 years old river sediment, which experienced a relatively weak weathering, leaching and illuviation, and hence, the profiles showed few differences in total Cu content and soil properties. However, alluvial plain is located on the first and second terraces of the

Yangtze River with a highly fluctuating underground water table, thus, the impacts of water table on the soil properties should be taken into account.

Low hilly area soil (yellow-brown and red) derived from Paleozoic Era clastic and carbonate rock. S16-S18 (Table 1) showed that the total and available Cu contents in the surficial soil were 59-61 mg·kg⁻¹ and 3.74-6.20 mg·kg⁻¹, respectively. Cu was transferred down in the profile due to the acidic leaching and strong oxidation (for example, S18), and accumulated appreciably relative to the parent rock. Strong Cu accumulation (total Cu of 25-45 mg·kg⁻¹) in red soil (S19, S20) relative to the parent rocks (1-4 mg·kg⁻¹) derived from Permian carbonate rock could be attributed to the neutral-acidic conditions and illuviation.

As soil is a result of weathering rock, the parent rock was the primary factor determining the natural Cu background concentration in soil. For instance, in S4 profile, total Cu ranged between 28 mg·kg⁻¹ and 30 mg·kg⁻¹ relative to 28 mg·kg⁻¹ in corresponding parent rock; and in S8 profile, total Cu ranged between 12 mg·kg⁻¹ and 13.5 mg·kg⁻¹, relative to 8 mg kg⁻¹ in corresponding parent rock.

3.2. Cu natural background concentration in water

Table 2 showed that Cu content in water ranged between 1.71 µg·L⁻¹ and 5.07 µg·L⁻¹ (avg. 3.30 µg·L⁻¹), 5.2 times higher than the background value in the source area (0.63 µg·L⁻¹), suggesting an enrichment of Cu in water due to the mining activity. As seen from the distribution patterns of Cu in water, soil and rock (Fig. 2), the high available Cu content in soil and rock resulted in the high amount of Cu in water (such as the high Cu in the water in

clastic rock area). Cu content in water had a significant correlation with the regional geological background. pH value had a great influence on chemical form and activity of Cu in water. Generally, under neutral-acidic conditions, Cu content in water could be high as the result of dissolution of Cu soluble complexes and ionic compound, such as in W2 and W3 (Cu 4.05-5.07 $\mu\text{g}\cdot\text{L}^{-1}$ and pH 6.95-7.14). However, under alkaline conditions, Cu might be deposited as hydroxide, such as in W5 (Cu 1.71 $\mu\text{g}\cdot\text{L}^{-1}$ and pH 8.29). In addition, the EC value could also indicate the concentration of total dissoluble ions (including Cu) in water. Normally, EC value was high in the water in clastic rock area.

Cu background concentrations in soil and water with different regional geology were plotted in Fig. 2. The intermontane basin was the main cultivated area, and its Cu background concentration was calculated according to the acreage of different parent rocks. The background value in soil was defined as 29 $\text{mg}\cdot\text{kg}^{-1}$ for this area, which was higher than the mean background in average Chinese soil (17.2 $\text{mg}\cdot\text{kg}^{-1}$), and the value 3.30 $\text{mg}\cdot\text{L}^{-1}$ was considered as the Cu background in water.

3.3. Cu natural contamination in soil and water

The mining and metallurgic activities in the area, as well as the local geological (metallogenic) conditions were important sources of Cu in the environment. Moreover, Cu concentration was elevated because the common compositions of local bedrocks were modified due to the hydrothermal processes which increases mineralization (Martínez, 2007). And the major ion chemistry of natural water could be explained by the reaction of water with rock and sediment (Kim et al., 2007).

An increase in Cu natural content often occurred in granodiorite outcrops. SP1-SP4 were from granodiorite localities. As seen in Table 3, SP1, SP2 and SP3 were slightly polluted as Cu contents were 2.1-3.3 times higher than the local background and even 3.5-5.5 times higher than the mean background in Chinese soil. Especially, Cu content in SP4 was 10.3 and 17.4 times higher than the local and Chinese mean background, respectively, indicating a severe Cu contamination in SP4. Cu content changed erratically in the soil profiles (constant in SP3 and SP4, while decreasing downcore in SP1 and SP2). The existing forms of Cu in the naturally contaminated soil were mainly Fe-Mn oxides and residual phase (discussed below), therefore in naturally contaminated soil Cu might not pose a serious threat on the crop in spite of the high total Cu, and it was not readily bio-available as shown by the lower EC values (155-750 μs).

Stream water WP1 and WP2 (WP1 out flowed from Silurian-Triassic sedimentary rock, WP2 seeping from the natural outcrops of the contact zone between Middle-Cenozoic granodiorite and carbonate) were sampled to study the natural contamination. There were abundant metals in Permian Longtan rock-series containing coal, so flowed through which WP1 (lower pH) had higher Cu content, as well as other metals, such as, Ag 0.119, Tl 0.094, Cd 28.0, Co 31.4, Ni 182, Sb 6.38, and Zn 467 $\mu\text{g}\cdot\text{L}^{-1}$. WP2 had very high Cu content (38.1 $\mu\text{g}\cdot\text{L}^{-1}$) due to the mineralization of Tieshan rockmass. The mineralization characteristics of other metals in WP2 were also prominent, such as, Ag 0.427, Tl 0.76, Ni 13.1, As 7.63, Zn 125, and Sr $>2\times 10^4$ $\mu\text{g}\cdot\text{L}^{-1}$. The naturally-increased Cu contents in the two water samples were 2.6-11.5 and 13-60 times higher than the local and the Yangtze River source area background, respectively, showing that the regional geological conditions controlled the element

concentration and the physico-chemical properties (pH 4.70-4.88, EC 1050-7950 μs) in water.

3.4. Cu anthropogenic contamination in soil, water and rice

Using waste water and sewerage to irrigate soil may lead to high level of Cu and subsequent risks for humans. Soil irrigated with the polluted water contains substantially high amounts of heavy metals such as Cu, Zn, Mn and As, and their sources were identifiable waste water from Cu mining-smelting plants and chemical works (Zhang, 2002). Untreated waste water was used to irrigate crop in agricultural areas, and pollutants were transferred to soil and might eventually enter the food chain (Moon et al., 1994; Sponza and Karaoğlu, 2002).

The results showed that Cu contents in water were singularly high (54.1-128 $\mu\text{g}\cdot\text{L}^{-1}$, Table 4, WP3-WP9), and that sewage severely polluted the soil with a total Cu of 4-207 times higher than the local Cu background. The highest available Cu in heavily polluted soil by metals-smelting plants waste reached to 237 $\text{mg}\cdot\text{kg}^{-1}$, which was 8.2 and 13.8 times higher than the local and the Chinese soil mean background, respectively. However, Cu contents in WP4 and WP9 were higher than the available Cu in corresponding polluted soil, which might be attributed to the acidic leaching. High pH and EC values in polluted water suggested that the ion concentration in surficial soil increased greatly, and the sorption and accumulation of heavy metals (Cu et al.) became intensive. Cu decreased dramatically downcore, indicating that surficial soil was polluted heavily in recent years, which caused an abrupt change of physico-chemical characteristics of soil solution, even the proportion of available Cu

increased 25%-30% (Table 5).

The crop could be contaminated due to the heavy pollution of soil and water. Metals in contaminated soil and water could enter agricultural products and cause various physiological changes, lowering their biomass (Sponza and Karaoğlu, 2002), even inducing death. As seen from Fig.3, the rice samples representing background, natural and anthropogenic contamination showed that Cu content in background sample R1 was $0.196 \text{ mg}\cdot\text{kg}^{-1}$. In contrast, the rice (R2-R7) from polluted sites had high Cu and the highest (R6, $22.4 \text{ mg}\cdot\text{kg}^{-1}$) value was 114 times higher than the background. In addition, some other metals were also generally higher in polluted rice samples than in the background, such as the highest values of Pb, Sb, Cr and As in contaminated samples were 39, 3, 11, 34 times higher than in R1, respectively. Cu content in R6 (with low Ni content) was singularly high while there was high Ni content in other samples, which may be attributed to the antagonism between Cu and Ni in S6. Cr content in S6 was 5-11 times higher than that in others, and the cooperative action between Cr and Cu might be the cause. It was noticeable that Cu content wasn't as high as conjectured in R3, R4 and R5 from the sites with anthropogenically heavily polluted soil and water, but Cd content was high in these samples, which might be attributed to the antagonism between Cd and Cu.

3.5. The distribution of existing phases of Cu in soil

Metals can interact with soil components and exist in various solid phase fractions, governing their mobility and bioavailability (Dumat et al., 1997). The potential risk of metals

in soil to man and environment entirely depends on their bioavailability (Van Gestel, 2008), which may be defined as the fraction of metal that is available or can be made available for uptake and, as a consequence, affecting organisms.

The existing phases of Cu in soil representing background, natural and anthropogenic contamination (Table 5) showed that (i) Cu content (except the underlayer of SP4 and the upper of SP5) had the trend of residual phase > Fe-Mn oxides phase > organic phase > soluble and exchangeable phase, and the available Cu (the sum of organic, soluble and exchangeable) in upper soil was higher than in the underlayer; on the contrary, the sum of residual phase and Fe-Mn oxides was reversed (except SP4), indicating that the active and inert Cu were discriminated during long-time farming and accumulated in surficial soil due to topography, climate, precipitation, surface runoff and human activities; (ii) the proportions of active Cu in background and naturally contaminated soil were low (0.4%-7.4%), but the residual Cu accounted for large proportions (70.4%-88.8%), suggesting that Cu might do less harm to crop despite the high total content; and (iii) the proportion of active Cu in heavily polluted soil was high (51.2%), and active Cu was higher in the upper soil than in the underlayer (20 times in SP5), showing that the surficial soil had been severely contaminated in recent years.

4. Conclusions

(i) Natural Cu background concentration in intermontane basin soil and low hilly soil differed greatly. In comparison, it was similar in alluvial plain soil as well as the physico-chemical properties, indicating that parent rock was the key factor controlling the

regional Cu background. The value $29 \text{ mg}\cdot\text{kg}^{-1}$ was defined as the soil background and $3.30 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ represented the water natural background in study area.

(ii) pH was an important factor affecting the vertical distribution of Cu in soil profile, and strong leaching in acidic soil caused the Cu loss from the uppermost part of soil; by contraries, strong illuviation in alkaline soil led to Cu accumulation.

(iii) Granite was the main origin of natural Cu pollution in soil, and natural Cu contamination in water could be attributed to the magnetite and skarn metal sulfide mineralization, and another source was the Permian Longtan group sedimentary rock containing coal.

(iv) The severe Cu anthropogenic contamination in soil and water was resulted from recent mining-smelting and chemical activities and there were clear differences in total and available Cu and vertical distribution patterns, as well as physico-chemical properties (pH and EC) in soil and water. The rice in this area was highly polluted.

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443 Figure 1 The simplified geological and geomorphological map of Huangshi area and the
444 sampling sites

445 Figure 2 Cu concentration in parent rock, background soil and water

446 Figure 3 Metal concentration in rice samples

447 Table 1 Cu background concentration in soils representing intermontane basin, alluvial plain
448 and low hilly area

449 Table 2 Cu background concentration in water

450 Table 3 Cu concentration in naturally contaminated soil and water

451 Table 4 Cu concentration in anthropogenically contaminated soil and water

452 Table 5 Cu concentration in four phases in soil

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Fig.1. The simplified geological and geomorphological map of Huangshi area and the sampling sites

Fig.2. Cu concentration in parent rock, background soil and water.

- 1.gray-black limestone (Cambrian-Ordovician),
- 2.gray-green sand-shale (Mid-Lower Silurian),
- 3.gray-black limestone (Permian),
- 4.mottled sand-shale stone (Mid-Upper Triassic),
- 5.mottled sand-shale stone (Mid-Upper Jurassic),
- 6.granodiorite/magmatic cycle in Mesozoic (Yanshanian),
- 7.purplish-red sandstone (Tertiary),
- 8.alluvial deposit (Quaternary).

Fig.3. Metal concentration in rice samples. R1 represented the background sample, R2 represented the naturally and R3-R7 the anthropogenically contaminated samples. Concentration of As was multiplied by 100, Cu of R6 and Pb of R5 were divided by 10 when the figure was constructed.

Table 1
Cu background concentration in soils representing intermontane basin, alluvial plain and low hilly area

	Depth cm	pH	Eh mV	EC μs	Cu (mg·kg ⁻¹)			Rock/Regional geology
					Rock	Total	Available	
Intermontane basin soil								
S1	2-30	5.95	346	600	50	87	9.58	purplish-red sandstone/Tertiary
	30-60	6.30	326	630		64	4.76	
	60-90	6.50	326	670		65	5.54	
S2	0-20	6.32	516	275	28	71	6.72	purplish-red sandstone/Tertiary
	20-50	5.50	648	200		55	1.92	
S3	0-24	5.58	337	140	13	16	0.75	conglomerate/Tertiary
	24-44	5.90	328	102		19	0.37	
	44-74	5.45	354	131		16	0.50	
S4	0-40	5.39	333	98	200	28	4.70	mottled sand-shale stone/ Mid-Upper Jurassic
	40-110	5.34	338	131		30		
	110-130	5.60	324	135		29	4.60	
S5	0-25	5.47	338	156	8	15	1.40	mottled sand-shale stone/ Mid-Upper Triassic
	25-85	5.70	338	120		15	2.60	
S6	0-25	4.35	464	160	17	200	18.1	granodiorite/magmatic cycle in Mesozoic (Yanshanian)
	25-48	4.47	494	900		250	17.3	
	48-68	4.75	469	945		500	18.9	
	>68	5.07	452	1035		400	18.6	
S7	0-15	6.60	326	74	8	30	4.26	granodiorite/magmatic cycle in Mesozoic (Yanshanian)
	15-30	5.95	334	63		12	1.96	
S8	25-75	7.34	299	76	17	12	4.53	granodiorite/magmatic cycle in Mesozoic (Yanshanian)
	75-175	6.92	305	16		14	4.23	
S9	0-30	5.70	374	70	17	16	1.64	quartz diorite porphyrite/ magmatic cycle in Mesozoic (Yanshanian)
	30-68	5.30	362	80		14	1.20	
Alluvial plain soil								
S10	0-30	9.46	467	500		41	1.02	
	30-60	9.45	392	550		38	1.02	
S11	0-45	9.36	472	1125		41	2.58	
	45-65	9.80	382	1100		35	2.58	
S12	0-25	9.36	394	1215		41	3.60	
	25-50	9.63	452	1200		39	3.22	
S13	0-25	8.52	402	1000		43	7.24	
	25-50	8.92	402	1025		50	16.1	
S14	0-20	8.89	426	1350		47	5.54	
	20-30	9.36	392	500		41	3.60	

S15	0-25	8.82	452	725		44	10.8	
	25-50	9.07	446	1050		41	4.76	
Low hilly area soil								
S16	0-30	6.90	360	900		61	6.20	gray-green sand-shale stone
	30-60	5.68	396	1350		48	4.50	/Silurian
	60-90	5.12	440	1650		44	3.34	
S17	0-14	4.53	430	1095	45	59	3.74	gray-green sand-shale stone
	14-28	4.95	420	975		52	4.50	/Silurian
	28-56	4.06	428	1350		52	6.06	
S18	0-40	5.74	402	220		59	5.28	gray-green sand-shale stone
	40-80	3.97	490	185		71	17.4	/Silurian
	80-120	3.61	532	875		53	4.50	
	120-180	3.80	500	720		76	20.4	
S19	0-30	7.15	280	165	1	25	2.79	gray-black limestone
	30-60	7.64	265	165			2.53	/Permian Qixia Group
S20	non-stratified	6.40	346	825	4	45	8.28	lime dolomites and limestone
/Cambrian-Ordovician								
Cu Background value in intermontane basin soil: 29 mg·kg ⁻¹								

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Table 2

Cu background concentration in water

Sample in bracket represented the corresponding soil

	pH	EC mV	Total Cu $\mu\text{g}\cdot\text{L}^{-1}$	Water/Regional geology
W1 (S5)	7.08	600	2.99	well-water/Mid-Lower Tertiary
W2	7.14	1250	5.07	well-water/Mid-Lower Jurassic
W3 (S4)	6.95	1600	4.05	well-water/Mid-Lower Jurassic
W4 (S3)	6.54	1860	2.62	well-water/Eogene
W5 (S8)	8.29	780	1.71	reservoir-water
W6 (S19)			3.18	trench-water
W7 (S18)			4.11	reservoir-water
W8			2.44	pond-water/Quaternary
Cu Background value in water: $3.30 \mu\text{g}\cdot\text{L}^{-1}$				

Table 3
Cu concentration in naturally contaminated soil and water

	Depth cm	pH	Eh mV	EC μs	Cu	
					Total	Available
Soil ($\text{mg}\cdot\text{kg}^{-1}$)						
SP1	0-25	4.35	564	750	84	12.7
	25-50	5.58	474	720	66	6.46
SP2	0-20	4.05	542	220	95	15.6
	20-30				61	7.5
SP3	0-25	5.13	460	675	61	4.76
	25-45	5.50	468	155	61	7.5
SP4	0-25	6.79	380	675	300	37.9
	25-50	6.35	384	190	300	30.1
Water ($\mu\text{g}\cdot\text{L}^{-1}$)						
WP1		4.88		7950	8.44	
WP2		4.70		1050	38.1	

Table 4

Cu concentration in anthropogenically contaminated soil and water

Sample in bracket was the corresponding water

	Depth cm	pH	EC μs	Cu		Source of pollution
				Total	Available	
Soil (mg·kg ⁻¹)						
SP5(WP3)	0-30	8.49	9600	6000	131	sewage from Cu-mining plant
	30-50	6.40	1950	95	25.9	
SP6(WP4)	0-20	5.22	19500	120	30.1	sewage from chemical works
	20-50	6.60	1700	55	6.84	
SP7(WP5)	0-15			700	245	sewage from chemical works
	15-50			150	15.3	
SP8(WP6)	non-stratified	7.08	1400		204	sewage from metals-smelting plant
SP9(WP7)	non-stratified	6.88	2150		237	sewage from metals-smelting plant
SP10(WP8)	non-stratified	6.44	1000		56.8	sewage from metals-smelting plant
SP11(WP9)	non-stratified	5.08	1575		12.4	sewage from metals-smelting plant
Water (μg·L ⁻¹)						
WP3		8.00	7500	54.1		sewage from Cu-mining plant
WP4		7.51	63000	88.2		sewage from chemical works
WP5		7.18	123000	128		sewage from chemical works
WP6		8.79	12500	72.8		sewage from metals-smelting plant
WP7		7.97	11750	86.2		sewage from metals-smelting plant
WP8		7.83	7000	113		sewage from metals-smelting plant
WP9		7.44	14250	66.1		sewage from metals-smelting plant

Table 5

Cu concentration in four phases in soil

Value in bracket was the proportion to total Cu

	Depth cm	Cu (mg·kg ⁻¹)				Parent material or source of pollution
		Soluble and exchangeable phase	Organic phase	Fe-Mn oxides phase	Residual phase	
S1	2-30	0.30 (1.0)	1.96 (6.4)	3.70 (12.0)	24.75 (80.6)	purplish-red sandstone
	30-60	0	0.34 (1.1)	6.96 (22.5)	23.58 (76.4)	
	60-90	0	0.58 (1.8)	8.14 (24.8)	24.15 (73.4)	
S6	0-25	0.60 (0.6)	6.64 (6.4)	23.64 (22.6)	73.60 (70.4)	mineralized granodiorite porphyry
	25-48	0.60 (0.3)	3.02 (1.5)	22.20 (10.7)	181.25 (87.5)	
	48-68	2.00 (0.6)	2.66 (0.8)	30.90 (9.8)	280.90 (88.8)	
	>68	0.30 (0.1)	0.80 (0.3)	51.84 (17.8)	233.80 (80.4)	
SP4	0-25	2.30 (1.6)	1.86 (1.3)	4.48 (3.2)	131.90 (93.9)	mineralized granodiorite porphyry
	25-50	2.30 (1.6)	21.38 (14.7)	6.50 (4.5)	115.05 (79.2)	
SP5	0-30	244.30 (51.0)	0.80 (0.2)	89.40 (18.7)	144.80 (30.1)	anthropogenic contamination
	30-50	0.85 (1.4)	0.80 (1.3)	26.30 (42.4)	34.15 (54.9)	