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Heavy metal pollution from copper smelting during the Shang Dynasty at the Laoniupo site in the Bahe River valley, Guanzhong Basin, China

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Abstract: Heavy metal pollution is hazardous for the environment and human health. However, there are few studies of heavy metal pollution caused by historic metallurgical activity. The Laoniupo site in the Bahe River valley, Guanzhong Basin, China, was an important settlement of the Shang Culture (1600–1046 BCE). We studied two stratigraphic profiles at the Laoniupo site, which were used for measurements of magnetic susceptibility, heavy metal concentrations, and AMS ^{14}C ages to provide evidence of copper smelting activity at the site during the Shang Dynasty. The Nemerow Pollution Index and Geoaccumulation Index were calculated to assess the heavy metals record (Cu, Zn, Ni, Pb, Cr, and As) in the topsoil on the loess tableland. According to the Single Pollution Index, the topsoil was slightly polluted by As and unpolluted by Cu, Zn, Ni, Pb and Cr; according to the Nemerow Composite Pollution Index the topsoil was mildly polluted; and according to the Geoaccumulation Index, the topsoil was moderately polluted by As, slightly polluted by Cu, and unpolluted by Zn, Ni, Pb and Cr. The main cause of the heavy metal pollution in the topsoil is the presence of copper slag in the cultural layers that was disturbed by modern farming activity.

Keywords: heavy metal pollution; copper smelting; Laoniupo site; Bahe River; Guanzhong Basin

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1 Introduction

Records of past human activities can be used to trace the development of human civilization. Anthropogenic activities during the Holocene have had a profound influence on the environment, especially the releases of atmospheric greenhouse gases, alteration of the land cover, and soil contamination (Pongratz *et al*., 2008; Ruddiman *et al*., 2008; Ruddiman and Ellis, 2009; Wei *et al*., 2009; Fuller *et al*., 2011; Steffen *et al*., 2011; Zhuang and Kidder, 2014). Metallurgical technology has promoted the development of industry and human civilization, and is regarded as a necessary condition for the emergence of complex societies (Dodson *et al*., 2009; Radivojevic *et al*., 2010). However, smelting was a major cause of early environmental pollution (Zhang *et al*., 2017), and it has had detrimental effects on the environment and human health (Asami, 1988; Alloway, 1995; Duruibe *et al*., 2007; Fu and Wang, 2011; Wuana and Okieimen, 2011; Kwon *et al*., 2017; Longman *et al*., 2018). The combustion of solid fuels results in the release of highly toxic elements (e.g., As, Cd and Pb) at levels exceeding their natural ones, causing an environmental hazard (Liu *et al*., 2016; Kicińska and Mamak, 2017; Kicińska, 2019a). For example, high levels of As, Cd and Ti pollution were detected in the vicinity of a metallurgical plant, based on long-term observations (Kicińska, 2019b).

Copper was the first metal to be smelted. Humans began to use natural copper in the Near East at least 10,000 years ago (Wertime, 1973; Killick and Fenn, 2012), and copper smelting technology was developed in Southeast Asia at ~7950 yr BP (Roberts *et al*., 2009). The earliest copper smelting activity in Europe was at ~6950 yr BP (Radivojevic *et al*., 2010), and became commonplace at ~5950 yr BP (De Ryck *et al*., 2005). Copper smelting emerged in China at ~4000 yr BP, as demonstrated by excavations of archaeological sites (Li, 1985; Sun and Han, 1997; Mei and Shell, 1999; Li and Shui, 2000; Li, 2005; Dodson *et al*., 2009; Yu *et al*., 2015; Wang *et al*., 2016). The damage caused by modern copper smelting to the environment and to human health has been demonstrated in many studies (Conroy *et al*., 1976; Rebele *et al*., 1993; Helmisaari *et al*., 1995; Kozlov *et al*., 1995; Pope *et al*., 2007; Nikolic *et al*., 2010). The influence of historic copper smelting on the environment can be revealed by studies of heavy metals in the sedimentary records of archaeological sites (Grattan *et al*., 2007; Breitenlechner *et al*., 2010). In addition, geochemical analyses of ice cores, peat deposits, pollen, charcoal and paleontological fossil have been used to provide records of the pollution caused by pre-historic and historic smelting worldwide (Hong *et al*., 1996; Pyatt *et al*., 2002; Nocete *et al*., 2005; Mighall *et al*., 2009; Breitenlechner *et al*., 2013). The hazard of historical heavy metal pollution to modern humans and the ecological environment has been widely studied (e.g., Urrutia-Goyes *et al*., 2017; Rouhani and Shahivand, 2020). In addition, many studies of heavy metal pollution in sedimentary strata or at archaeological sites have been conducted in China: e.g., at Kaifeng City, Nanjing City, the Hexi Corridor, Liangwangcheng site, Yuchisi site, Tang Daming Palace site and chariot pit (Yang *et al*., 2004; Zhang *et al*., 2005, 2007; Xu *et al*., 2010; Tian *et al*., 2013a, 2013b; Chen *et al*., 2017a; Zhang *et al*., 2017; Zhao *et al*., 2017; Qiu *et al*., 2019). However, these studies were limited to the assessment of heavy metals pollution during different dynasties and the heavy metals contamination of cultural relics.

The Laoniupo site, an important settlement of the Shang Culture (1600–1046 BCE), is located on the second river terrace (T_2) on the right bank of the Bahe River in the Guanzhong

Basin of Shaanxi Province, China (Figure 1). The area was the core of the western territory of the Shang Dynasty (Liu, 2004). The unearthed bronzes represent the unification of the Bronze culture of the Shang Dynasty which has distinct local characteristics (Song, 1992). From 1985 to 1989, six archaeological excavations were conducted at the Laoniupo site. The accumulation of copper slag and fragments of casting molds indicate the presence of bronze production sites (Liu and Yue, 1991). Chen *et al*. (2017b) analyzed the smelting technology and the age and properties of the bronzes discovered at the site; they found that arsenical copper was produced by smelting arsenic-rich polymetallic ores together with raw copper or high purity copper ores.

However, there are few studies of the heavy metals pollution of the Shang Dynasty sites, which limited our understanding of the potential ecological risk caused by historic human activities. Based on a field investigation and laboratory measurements, we conducted a comprehensive analysis of the influence of Shang Dynasty copper smelting activity on the modern soil environment at the Laoniupo site. The Nemerow Pollution Index and Geoaccumulation Index (I_{geo}), calculated from measurements of heavy metals (Cu, Zn, Ni, Pb, Cr, and As), were used to assess the degree of pollution in the topsoil on the loess tableland. The results are significant for understanding historical human-environmental interactions in China and elsewhere.

2 Study area

The Guanzhong Basin, with an area of ~3.91×10^4 km^2, is located in the southern Chinese Loess Plateau region (Zhao, 2020). It is a Cenozoic faulted basin containing an alluvial plain and loess tableland. The Bahe River is a major tributary of the Weihe River, which flows through the Guanzhong Basin and eventually joins the Yellow River (Figure 1a). Originating in Jiudaogou in the northern piedmont of the Qinling Mountains, it is 104.1 km in length with a drainage area of 2,581 km^2 (Hu *et al*., 2017). It is situated in the semi-humid climatic zone with a warm temperate continental monsoon climate. The annual mean precipitation is 800 mm and evaporation is 776 mm (Hu *et al*., 2017). The precipitation in the region is highly seasonal and nearly 60% of the annual total occurs between July and October (Mo *et al*., 2018), reflecting the strong influence of the East Asian summer monsoon (Liu, 1985; Liu and Ding, 1998).

3 Materials and methods

A field investigation was carried out at the Laoniupo site along the Bahe River valley in the Guanzhong Basin in 2019 and 2020. Two profiles, LNP-1 (109°8'25.68"E, 34°15′26.34"N, 435 m a.s.l.) and LNP-2 (109°8'28.26"E, 34°15′24.34"N, 435 m a.s.l.) in the southern Laoniupo site I area were chosen for detailed study (Figure 1b) (Liu, 2002). The topsoil on the loess tableland, which was cultivated for wheat or maize, was used for the analysis of heavy metals pollution (Figure 2a). After detailed observations and the establishment of pedostratigraphic subdivisions (Figure 2b and Table 1), a total of 15 samples of the Malan loess (L_1) and cultural layers of the Shang Culture were taken from the two profiles for analysis. One copper slag sample and two burnt earth samples were also collected from the cultural layers of the Shang Culture and the topsoil at the Laoniupo site for a comparative study. Three charcoal samples for AMS ^{14}C dating were taken from the cultural layers of the Shang Culture. In addition, 38 topsoil samples at the Laoniupo site were obtained using the 5-point sampling method for assessment of heavy metals pollution (Figure 1c).

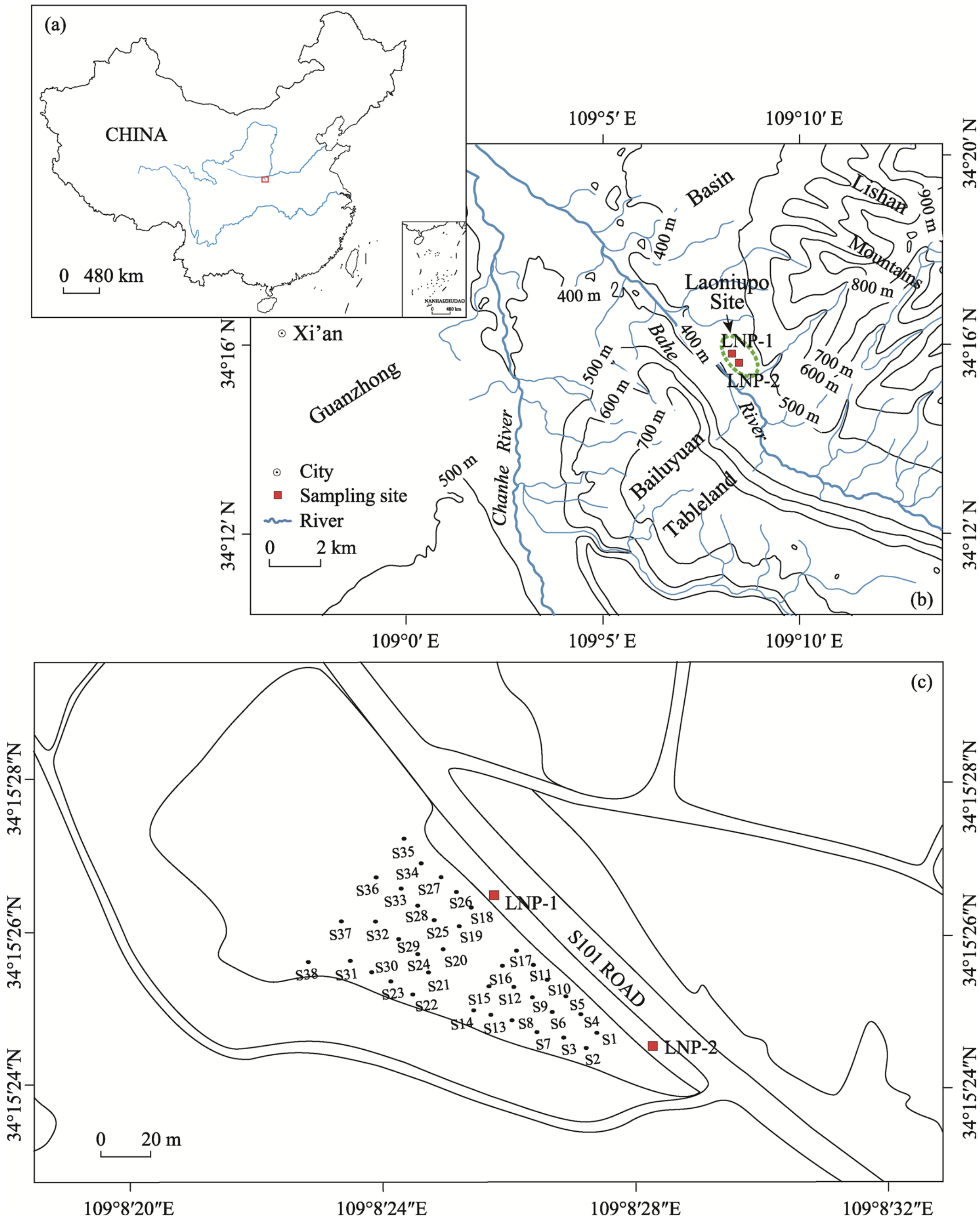

Figure 1 Maps showing (a) location of the Bahe River valley (square) in the Guanzhong Basin; (b) the LNP-1 and LNP-2 profiles at the Laoniupo site in the Bahe River valley marked with squares; (c) the relationship between the LNP-1/LNP-2 profiles and 38 topsoil samples at the Laoniupo site

All samples were air-dried in the laboratory, homogenized using a mortar and pestle, and placed in clean plastic containers until analysis. Magnetic susceptibility was measured on 10 g of sediment with a Bartington MS2 magnetic susceptibility meter (0.47/4.7 kHz) in the Shaanxi Key Laboratory of Earth Surface System and Environmental Carrying Capacity. The pH measurements were made using the NY/T 1377-2007 method with a pH meter (NY/T 1377, 2007). Soil samples were digested following EPA Method 3052 (US EPA, 1996) prior to analysis for heavy metals concentrations. The concentrations of Cu, Zn, Ni, Pb, Cr and As in the digested samples were measured using an Agilent 720 inductively coupled plasma-atomic spectrometer (ICP-AES) system following EPA Method 6010D (US EPA, 2014), in the Beijing Branch of the ALS Laboratory Group (Shanghai). The detection limits were as follows: Cu (0.5 mg/kg), Zn (0.5 mg/kg), Ni (0.5 mg/kg), Pb (0.5 mg/kg), Cr (0.5 mg/kg) and As (1.0 mg/kg). Blank samples were used in the analysis for quality assurance (Table S1). The relative deviations (RD) of duplicate samples were all less than 10%, which confirmed the accuracy of the analytical results (Table S1). Reference materials (VHG-SM75B-100) from VHG Labs, Manchester, USA, were used for quality control (Table S2). The accuracies (AO) obtained were between 97.5 and 106.2%. Charcoal samples were dated using the AMS ^{14}C technique in the Beta Analytic Radiocarbon Laboratory, USA. The AMS ^{14}C ages were calibrated using the IntCal13 calibration curve (Reimer *et al*., 2013) with the BetaCal3.21 procedure.

Table 1 Pedosedimentary descriptions of the LNP-1 and LNP-2 profiles in the Bahe River valley, Guanzhong Basin

Profile	Depth (cm)	Pedostratigraphic subdivisions	Pedosedimentary descriptions
LNP-1	0–5	Topsoil	Dull brown, silt, granular structure, some bio-pores, some earthworm burrows and excrement, abundant well-rounded spherical pellets (1.0–2.0 mm), some plant roots.
	5–180	Cultural layer	Taupe fill, very loose, some burnt earths, charcoals, copper slags and pottery shards retrieved and identified as the artifacts of the Shang Dynasty.
	>180	Malan loess	Dull yellow-orange, silt, blocky structure, loose and porous.
LNP-2	0–5	Topsoil	Dull brown, silt, granular structure, some bio-pores, some earthworm burrows and excrement, abundant well-rounded spherical pellets (1.0–2.0 mm), some plant roots.
	5–130	Cultural layer	Taupe fill, very loose, some burnt earths, charcoals, copper slags and pottery shards retrieved and identified as the artifacts of the Shang Dynasty.
	>130	Malan loess	Dull yellow-orange, silt, blocky structure, loose and porous.

The Nemerow Pollution Index and Geoaccumulation Index (I_{geo}) were used to assess the concentrations of heavy metals at the Laoniupo site. The Nemerow Pollution Index can be used to reflect the Single Pollution Index (P_i) and the Nemerow Composite Pollution Index (NCPI) caused by multiple heavy metals in the soil environment (Nemerow, 1974). P_i was calculated as:

$$P_i = \frac{C_i}{B_i} \tag{1}$$

where C_i is the measured concentration of heavy metal "*i*", and B_i is the evaluation criterion (GB 15618–2018) of heavy metal "*i*" (CNEPA, 2018). The classification of heavy metals evaluated with P_i is shown in Table 2. NCPI was calculated as:

$$NCPI = \sqrt{\frac{(P_{i\max})^2 + (P_{i\text{ave}})^2}{2}} \quad (2)$$

where $P_{i\max}$ is the maximum P_i value of each heavy metal, and $P_{i\text{ave}}$ is the average P_i value of each heavy metal. The classification of heavy metals evaluated with NCPI is shown in Table 2.

Müller (1969) proposed the Geoaccumulation Index (I_{geo}) to assess heavy metals pollution in sediments. It is calculated as:

$$I_{geo} = log_2\left(\frac{C_i}{1.5B_i}\right) \quad (3)$$

where C_i is the content of heavy metal "i" and B_i is the background value of geochemical element "i", allowing for an analysis of the variability of heavy metals as a result of natural processes. Reference geochemical background values in Shaanxi Province were used for comparison (CNEMC, 1990). The classification of heavy metals evaluated with I_{geo} is shown in Table 2.

Table 2 Classification of heavy metals evaluated with Single Pollution Index (P_i), Nemerow Composite Pollution Index (NCPI) and Geoaccumulation Index (I_{geo}) (Müller, 1969; Nemerow, 1974)

P_i		NCPI		I_{geo}	
$P_i \leqslant 1$	Unpolluted	NCPI≤0.7	Unpolluted	$I_{geo} \leqslant 0$	Unpolluted
$1<P_i \leqslant 2$	Slightly polluted	0.7<NCPI≤1.0	Slightly polluted	$0<I_{geo} \leqslant 1$	Slightly polluted
				$1<I_{geo} \leqslant 2$	Moderately polluted
$2<P_i \leqslant 3$	Mild polluted	1.0<NCPI≤2.0	Mild polluted	$2<I_{geo} \leqslant 3$	Moderate to strongly polluted
$3<P_i \leqslant 5$	Moderately polluted	2.0<NCPI≤3.0	Moderately polluted	$3<I_{geo} \leqslant 4$	Strongly polluted
				$4<I_{geo} \leqslant 5$	Strongly to extremely polluted
$P_i>5$	Extremely polluted	NCPI>3.0	Extremely polluted	$I_{geo}>5$	Extremely polluted

4 Results

4.1 Stratigraphy and chronology

Profiles LNP-1 and LNP-2 are situated on the aeolian loess-blanketed terrace (T_2) at the Laoniupo site, which is ~20–25 m above the normal water level of the Bahe River (Figure 1b). The Malan loess in both profiles was distinguished below 180 cm and 130 cm, respectively. Large quantities of anthropogenic materials, including copper slag, burnt earth, pottery shards and bones, were discovered in the cultural layers and in the topsoil at the Laoniupo site (Figures 2c-2f). The topsoil, 0–20 cm in thickness below ground level, was used for the cultivation of wheat or maize (Figure 2a).

The chronology of the cultural layers in the LNP-1 and LNP-2 profiles was established from the AMS ^{14}C ages (Table 3). The cultural layer in the LNP-1 profile (~100 cm in depth) was dated to be 3381–3232 cal yr BP. Two AMS ^{14}C ages from the cultural layer in the LNP-2 profile were obtained at depths of 110 cm and 70 cm, with ages of 3695–3565 cal yr BP and 3722–3576 cal yr BP, respectively. This evidence indicates that the cultural layers accumulated during the Shang Dynasty.

Figure 2 Photos showing (a) the landscape of wheat farmed on the loess terrace at the Laoniupo site in the Bahe River valley, Guanzhong Basin; (b) the pedostratigraphy of the LNP-1 profile; (c) copper slag; (d-e) pottery shards; (f) burnt earth at the Laoniupo site

Table 3 Calibrated radiocarbon dates of the LNP-1 and LNP-2 profiles in the Bahe River valley, Guanzhong Basin

Lab number	Profile name	Depth (cm)	Dating material	Radiocarbon date (yr BP)	Calibrated age (cal yr BP, 2σ)
Beta-559344	LNP-1	100	Charcoals	3100 ± 30	3381–3232
Beta-561180	LNP-2	70	Charcoals	3410 ± 30	3722–3576
Beta-559345	LNP-2	110	Charcoals	3380 ± 30	3695–3565

4.2 Magnetic susceptibility

In loess, the magnetic susceptibility (MS) is determined by the content of ferromagnetic minerals which can reflect the intensity of weathering and pedogenic modification of Chinese loess-soil profiles (Liu, 1985; An *et al*., 1991; Maher and Thompson, 1995; Maher, 1998). The ranges of the MS values are (88.9–181.3) × 10^{-8} m^3/kg in the LNP-1 profile and (104.0–173.1) × 10^{-8} m^3/kg in the LNP-2 profile (Figures 3 and 4, and Table 4). The MS curves are roughly parallel in the two profiles. In both cases, lower MS values occur in the

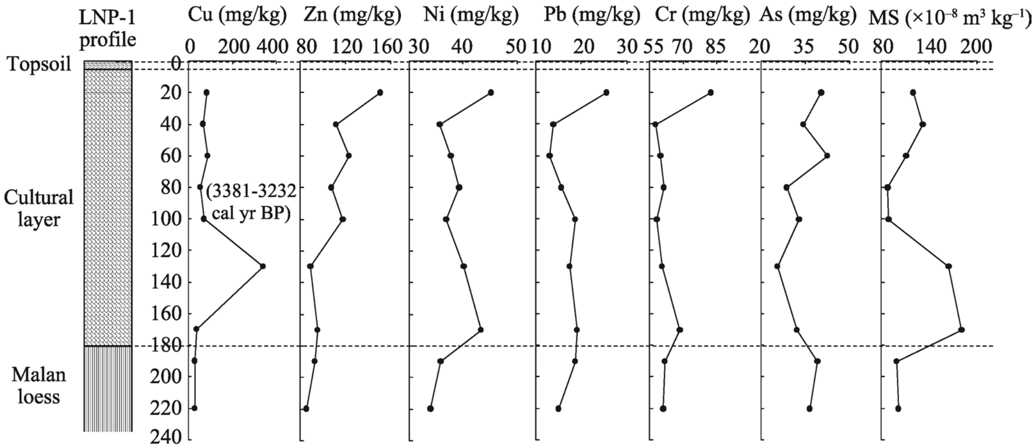

Figure 3 Pedostratigraphy, concentrations of heavy metals Cu, Zn, Ni, Pb, Cr, As and magnetic susceptibility (MS) in the LNP-1 profile in the Bahe River valley, Guanzhong Basin

Table 4 Concentrations of heavy metals Cu, Zn, Ni, Pb, Cr, and As and magnetic susceptibility (MS) in the LNP-1 and LNP-2 profiles in the Bahe River valley, Guanzhong Basin

Profile	Samples	Depth (cm)	Cu (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Cr (mg/kg)	As (mg/kg)	MS ($\times10^{-8} m^3$/kg)
LNP-1	Cultural layer	20	82.0	151.0	45.2	25.4	82.5	40.6	120.7
	Cultural layer	40	64.6	112.0	35.7	13.8	58.0	34.5	132.8
	Cultural layer	60	86.8	123.0	37.8	13.0	60.1	42.7	111.7
	Cultural layer	80	53.4	108.0	39.3	15.6	61.5	28.8	88.9
	Cultural layer	100	70.6	118.0	36.9	18.5	58.5	33.1	89.8
	Cultural layer	130	339.0	89.4	40.2	17.3	60.8	25.8	165.0
	Cultural layer	170	35.0	95.5	43.4	19.0	68.8	32.2	181.3
	Malan loess	190	28.0	93.0	35.9	18.5	62.0	39.3	99.8
	Malan loess	220	28.5	86.0	34.0	14.9	61.4	36.6	101.9
LNP-2	Cultural layer	10	99.7	105.0	35.5	25.8	62.2	46.2	135.3
	Cultural layer	30	70.6	90.9	35.4	19.3	58.6	49.7	140.65
	Cultural layer	50	42.8	104.0	36.7	20.5	69.5	40.5	146.0
	Cultural layer	70	39.6	101.0	33.5	19.9	64.8	42.9	146.3
	Cultural layer	90	43.8	90.0	37.5	22.8	61.5	42.1	173.1
	Malan loess	150	30.2	87.6	33.4	8.6	60.0	41.6	104.0
	Burnt earth	–	47.2	108.0	39.2	19.5	70.1	37.8	–
LNP-S15	Copper slag	–	436.0	158.0	36.6	24.7	61.6	867.0	–

Malan loess, indicating strong dust accumulation with weak weathering and pedogenesis during the last glacial period. Higher MS values occur in the cultural layers in both cases, but the taupe fill, soft texture and loose structure are quite different to the paleosol in the Loess Plateau (Huang *et al*., 2009). The difference can be attributed to the influence of human activities leading to a higher content of ferromagnetic minerals.

4.3 Concentrations of heavy metals

Profiles of the concentrations of heavy metals Cu, Zn, Ni, Pb, Cr, and As in the LNP-1 and LNP-2 profiles are shown in Figures 3 and 4, respectively, and the data are listed in Table 4. Lower concentrations of Cu, Zn, Ni, Pb, Cr, and As occur in the Malan loess, which can be used as a background for comparison with the concentrations of heavy metals in the cultural layers (Mao *et al*., 2017). Higher concentrations of Cu, Zn, Ni, Pb, Cr, and As occur in the cultural layers of the Shang Culture in the two profiles. It is likely that the increased concentrations of heavy metals were caused by the dumping of copper slag at the Laoniupo site during the copper smelting period of the Shang Dynasty (Liu, 2002).

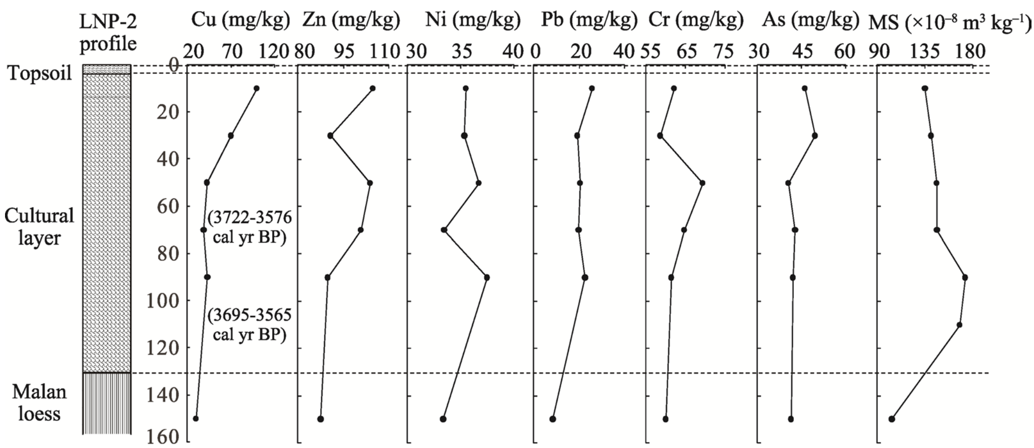

Figure 4 Pedostratigraphy, concentrations of heavy metals Cu, Zn, Ni, Pb, Cr, As and magnetic susceptibility (MS) in the LNP-2 profile in the Bahe River valley, Guanzhong Basin

Thirty-eight topsoil samples were collected from loess tableland at the Laoniupo site (Figure 1c). The concentrations of Cu, Zn, Ni, Pb, Cr, and As in these samples are shown in Figure 5 and listed in Table 5. High concentrations of Cu are recorded at sites S15 and S12, with values of 137.0 and 101.0 mg/kg, respectively. In addition, the Zn concentration is high at sites S14 and S10, with values of 17.0 and 121.0 mg/kg, respectively. A high concentration of Ni occurred at sites S14 (41.8 mg/kg) and S27 (41.4 mg/kg), and high concentrations of Pb and Cr occurred at sites S18 and S27 (33.9 and 31.9 mg/kg, respectively). Additionally, there was a high As concentration at site S15 (51.7 mg/kg). It should be noted that the distribution of heavy metals is irregular, which may be the result of disturbance of the cultural layers in the LNP-1 and LNP-2 profiles by modern farming activity, resulting in the random scattering of copper slag in the topsoil.

The heavy metal concentrations have wide ranges of variation in the topsoil at the Laoniupo site: Cu (31.3–137.0 mg/kg), Zn (80.8–127.0 mg/kg), Ni (32.0–41.8 mg/kg), Pb

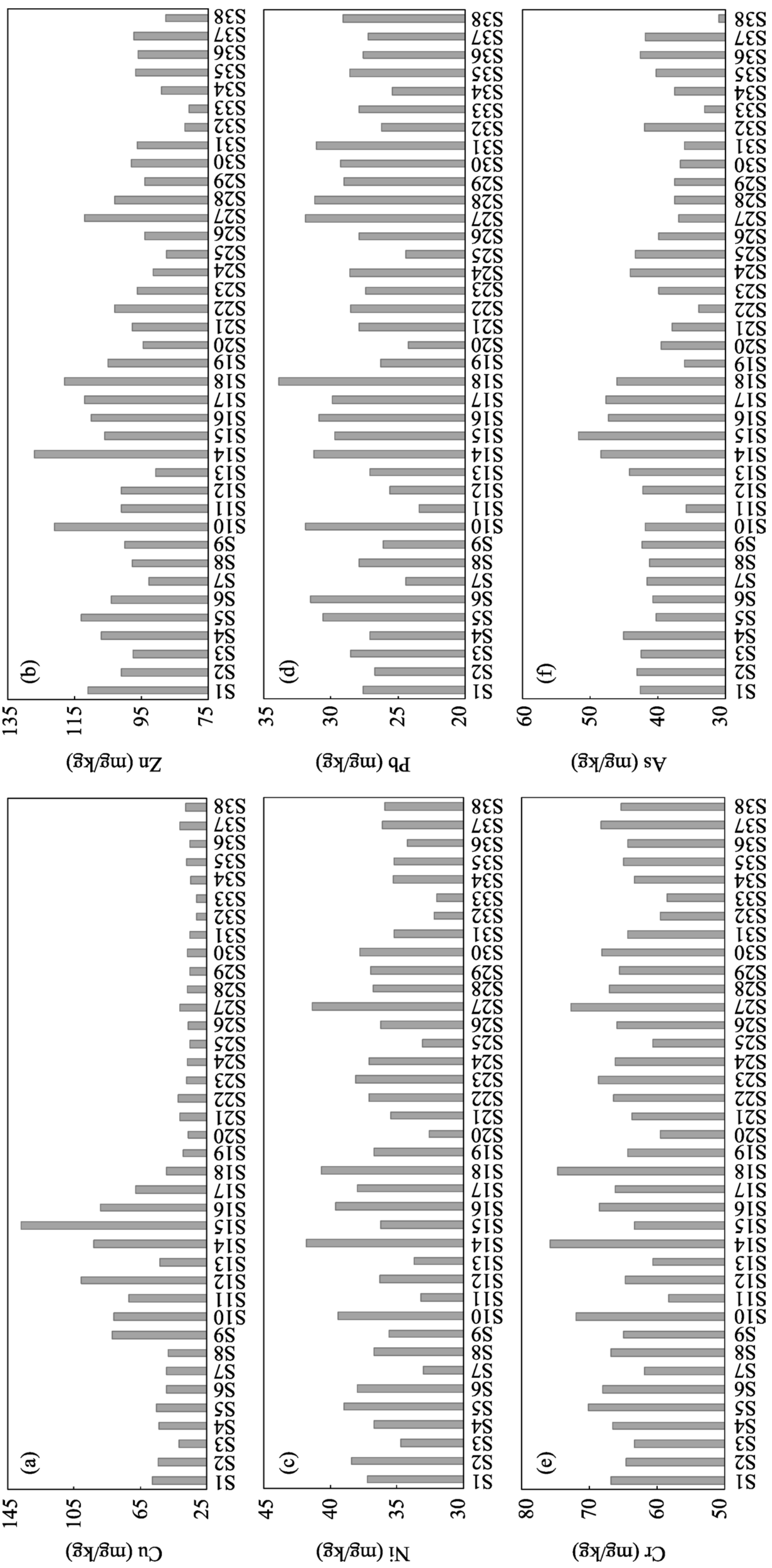

Figure 5 Variations of the concentration of heavy metals Cu, Zn, Ni, Pb, Cr, and As in the topsoil at the Laoniupo site in the Bahe River valley, Guanzhong Basin

(23.4–33.9 mg/kg), Cr (58.3–75.8 mg/kg) and As (31.0–51.7 mg/kg). The background values of Cu, Zn, Ni, Pb, Cr, and As in the topsoil in Shaanxi Province are given in Table 5 (CNEMC, 1990). As shown in Table 5, the mean concentrations of Cu, Zn and As in the topsoil at the Laoniupo site are significantly higher than the background values in the topsoil in Shaanxi Province. The mean concentration of Cu is 2.4 times higher than the background value, and for Zn it is 1.4 times higher, and for As it is 3.7 times higher. The mean concentrations of Ni, Pb and Cr in the topsoil at the site are slightly higher than the background values of topsoil in Shaanxi Province. The highest coefficient of variation (*CV*) is shown for Cu (0.44), indicating that the Cu content of the soil has a high variability and is likely influenced by anthropogenic activities. The skewness (*Sk*) and kurtosis (*Kg*) values for Cu are both greater than 1, which suggests a right-tailed *Sk* and a leptokurtic *Kg* (Beaver *et al.*, 2012). These values also confirm the randomness of the distribution of copper slag in the topsoil at the Laoniupo site.

Table 5 Concentrations of heavy metals Cu, Zn, Ni, Pb, Cr, and As in the topsoil at the Laoniupo site of the Bahe River valley, Guanzhong Basin, the evaluation criterion (GB 15618–2018) and the geochemical background values in Shaanxi Province (CNEMC, 1990; CNEPA, 2018)

Heavy metals	Min (mg/kg)	Max (mg/kg)	Mean (mg/kg)	*SD*	*CV*	*Sk*	*Kg*	GB 15618–2018 (mg/kg)	Background vales (mg/kg)
Cu	31.3	137	52.05	22.94	0.44	1.90	3.88	100	21.4
Zn	80.8	127	100.40	10.01	0.10	0.51	0.40	300	69.4
Ni	32.0	41.8	36.41	2.41	0.07	0.18	–0.18	190	28.8
Pb	23.4	33.9	28.26	2.41	0.09	0.11	–0.36	170	21.4
Cr	58.3	75.8	65.67	4.01	0.06	0.42	0.46	250	62.5
As	31.0	51.7	40.85	4.31	0.11	0.09	0.20	25	11.1

Min = Minimum; Max = Maximum; *SD* = Standard deviation; *CV* = Coefficient of variation; *Sk* = Skewness; *Kg* = Kurtosis

4.4 Assessment of heavy metal pollution

The pH values in the topsoil range from 8 to 8.3, indicating a slightly alkaline soil environment. The evaluation criteria (GB 15618–2018) for Cu, Zn, Ni, Pb, Cr, and As in agricultural land are listed in Table 5 (CNEPA, 2018). The values of the Single Pollution Index (P_i) and Nemerow Composite Pollution Index (NCPI) for the heavy metals in the topsoil at the Laoniupo site are shown in Figure 6a and listed in Table 6. Based on the classification evaluation criteria of the P_i values, the calculated mean value of As (1.63) is considered as slightly polluted, and the values for Cu (0.52), Zn (0.33), Ni (0.19), Pb (0.17) and Cr (0.26) are defined as unpolluted. Additionally, the NCPI value (1.51) indicates that the topsoil is mildly polluted.

The Geoaccumulation Index (I_{geo}) values of the heavy metals in the topsoil at the Laoniupo site are shown in Figure 6b and listed in Table 6. According to the classification evaluation criteria of the I_{geo} values, the mean value of As (1.29) is greater than 1 and less than 2, indicating that the topsoil is moderately polluted by As. The I_{geo} values of Cu range from –0.04 to 2.09, and the mean I_{geo} (0.59) is greater than 0 and less than 1, suggesting that the topsoil is slightly polluted by Cu. The mean I_{geo} values of Zn (–0.06), Ni (–0.25), Pb (–0.19) and Cr (–0.52) are classified as unpolluted. Overall, the major pollutants in the topsoil at the Laoniupo site are As and Cu.

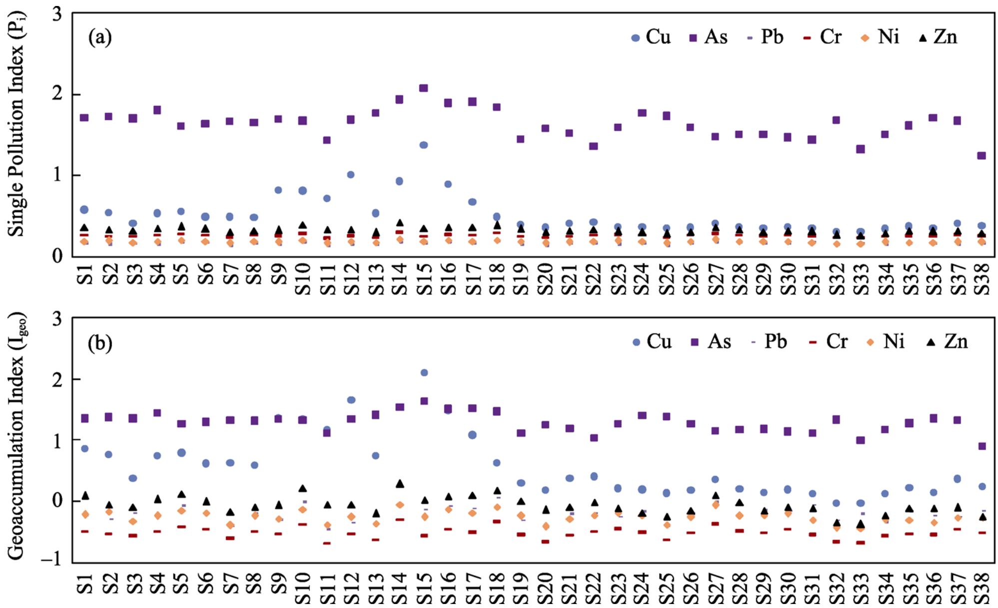

Figure 6 Variations of the Single Pollution Index (P_i) and Geoaccumulation Index (I_{geo}) in the topsoil at the Laoniupo site in the Bahe River valley, Guanzhong Basin

Table 6 Heavy metal pollution evaluated with Single Pollution Index (P_i), Nemerow Composite Pollution Index (NCPI) and Geoaccumulation Index (I_{geo}) in the topsoil at the Laoniupo site in the Bahe River valley, Guanzhong Basin

Heavy metals	Pi			NCPI	I_{geo}		
	Min	Max	Mean		Min	Max	Mean
Cu	0.31	1.37	0.52	1.51	–0.04	2.09	0.59
Zn	0.27	0.42	0.33		–0.37	0.29	–0.06
Ni	0.17	0.22	0.19		–0.43	–0.05	–0.25
Pb	0.14	0.20	0.17		–0.01	–0.46	–0.19
Cr	0.23	0.30	0.26		–0.69	–0.31	–0.52
As	1.24	2.07	1.63		0.90	1.63	1.29

Min = Minimum; Max = Maximum

5 Discussion

5.1 Role of historic smelting activity in heavy metals pollution

A detailed study of the Laoniupo site has revealed the occurrence of copper slag, burnt earth, pottery shards and bones in the cultural layers of the LNP-1 and LNP-2 profiles, as well as in the topsoil. Higher MS values and heavy metals concentrations also occur in the cultural layers. Moreover, it has been inferred that copper smelting slag was deposited at the sites of the two profiles during the Shang Dynasty (Liu, 2002). Additionally, the reason for the heavy metals pollution of the topsoil is the effect of modern farming activity in disturbing the cultural layers in the LNP-1 and LNP-2 profiles, resulting in the random scattering of copper slag in the topsoil on the loess tableland. Based on the heavy metals assessment classification of the Nemerow Pollution Index and Geoaccumulation Index (I_{geo}), the major heavy metal pollutants in the topsoil at the Laoniupo site are As and Cu. These results are consistent with the copper smelting technology practiced at the Laoniupo site. Chen *et al*. (2017b) found in a study of the metal production remains at the Laoniupo site that arsenical copper was produced by smelting arsenic-rich polymetallic ores with raw copper or high-purity copper ores.

Heavy metal pollution caused by historical smelting activity has also been documented in cultural layers elsewhere. The cultural layers and ash pits of late Neolithic–Bronze Age sites in the Hexi Corridor in North China are polluted with heavy metals, which was inferred to be associated with smelting activity (Zhang *et al*., 2017), and the intensity was also related to the density of human settlements (Yang *et al*., 2016). A significant increase in heavy metals concentrations was observed in the cultural layers in urban soils in Nanjing during the Southern Dynasty and the early and late Ming Dynasty, which may reflect the intensification of primitive smelting and metal processing activities (Zhang *et al*., 2005). Ore smelting and the manufacture of artifacts using Pb-containing materials also led to heavy metals pollution during several periods in the history of Nanjing (Zhang, 2007). Levels of Cu pollution near moderate occurred during the Warring States, Northern Dynasty and Song Dynasty period, and Zn was slightly polluted in the cultural layers of the Liangwangcheng site during the Northern Dynasty, in both cases related to metal smelting (Tian *et al*., 2013a). The accumulation of Pb in the cultural layers of the Yuchisi site in Mengcheng was found to increase gradually between 5050 and 4000 cal yr BP due to metallurgical activity (Xu *et al*., 2010). Sedimentary and paleontological materials also provide archives for recording smelting activity and heavy metal pollution. The record of fossil charcoal and chemical elements at Huoshiliang provided evidence for the environmental impact of early smelting activity (Dodson *et al*., 2009; Li *et al*., 2011). The Cu concentration in Erhai Lake in Yunnan Province was 6–12 times higher than background values, due to copper smelting at 3450 yr BP (Hillman *et al*., 2015). Smelting pollution was also recorded by elemental records from Holocene sediments of Daihai Lake in North China (Jin *et al*., 2013). A similar pattern of changes in the concentrations of Cu, Zn and Pb was observed at Liangzhi Lake in Central China, which demonstrated the occurrence of smelting since 5000 yr BP (Lee *et al*., 2008). An 8000-year record of copper smelting and mining at a site on the desert-mountain border in southern Jordan also demonstrated a relatively high level of environmental pollution caused by local copper production in the early Bronze Age (Grattan *et al*., 2007). Additionally, mining activity occurred during 6500–5400 yr BP in the Lake Superior region in North America (Pompeani *et al*., 2014).

During the historical period, pollution has posed an increasing threat to human activity and the ecological environment. There is a long history of environmental risk in the vicinity of metallurgical plants in Europe as a result of metal processing (Kicińska, 2019b). Assessment of Pb, Ni, and Zn pollution in topsoil from an historic shooting range in Kesariani Park (Athens, Greece) has provided a reference for human health risks associated with its restoration for use as public park (Urrutia-Goyes *et al*., 2017). Potential ecological risk assessment of heavy metals at the Rivi site in Iran revealed that historical pollution may have endangered the health of archaeologists (Rouhani and Shahivand, 2020). These studies clearly show that heavy metal pollution is a significant threat to modern humans and the environment worldwide.

5.2 Historic copper smelting technology

Copper was one of the earliest metals discovered and widely used by humans. Bronze ware in China has been produced since the Xia Dynasty. A bronze knife unearthed at the Majiayao Cultural site in Gansu Province was the earliest bronze artifact found so far, and is evidence that China had entered the Bronze Age (Sun and Han, 1997; Li, 2005). Arsenical copper was the first copper alloy produced in human history (Zhang, 2016). It spread widely and gradually replaced red copper in many locations from 5950 yr BP (Liu, 2012). With regard to metallurgical remains, Li *et al.* (2015) defined arsenical copper production at the Xichengyi site as representing two separate metallurgical processes or two different stages of the same process. It is likely that pure copper was smelted first, which was then alloyed with arsenic-rich ore in a separate cementation/co-smelting process. Large quantities of arsenical copper have been discovered in Northwest China (e.g., in Gansu, Qinghai, Xinjiang and Inner Mongolia) (Zhang, 2016).

The Shang Dynasty was a prosperous period in the development of bronzes. Multitudinous bronzes were produced in Central China. Traces of copper smelting, copper fragments, slag and furnace walls of the early Shang Dynasty (16th–14th centuries BCE), and the earliest quenching bronze scraper in China were discovered at the Yuanqu site in Shanxi Province (Cui *et al.*, 2009). Copper slag, pottery models and crucible fragments of the early Shang Dynasty were discovered at the Erlitou site, in Yanshi city (Yang and Sun, 1994). The discovery of a copper casting site of the Erligang Culture demonstrates an advanced copper smelting technology in the middle Shang Dynasty (Yang and Sun, 1994). The culture at a Yin Dynasty site in Anyang represents a peak in the development of Chinese bronzes in the late Shang Dynasty. There were many sites of copper casting workshops, in which unique alloy ratios and pottery models were used in various types of utensil, indicating that the late Shang Dynasty (13th–11th centuries BCE) had a very high level of copper casting technology (Gao, 2006; Liu, 2018). Hanzhong was a frontier area in the Shang Dynasty, and the discovery of more than 700 bronzes indicates the existence of local manufacturing and metal-processing industries at that time (Chen *et al.*, 2009; Mei *et al.*, 2009, 2015). The Tongling mining and smelting site of the Wucheng Culture was the earliest and most important ancient copper smelting site discovered so far, where abundant raw materials were available for smelting copper in the Shang Dynasty (Peng, 2005). Numerous regional bronzes have been discovered in Southern China (e.g., at the Dayangzhou site, Sanxingdui site and Jinsha site) (Jin, *et al.*, 1994, 2004; Peng, 2005; Shi, 2017; Du, 2019). This evidence clearly demonstrates the existence of an advanced copper smelting technology in the Shang Dynasty, confirming its importance for copper smelting activity.

6 Conclusions

The pollution generated by metals smelting is an important hazard for both the environment and human health. Two profiles were chosen at the Laoniupo site, in the Bahe River valley of the Guanzhong Basin, for a detailed investigation of heavy metals pollution. The results show that smelting activity at the site during the Shang Dynasty was a source of heavy metals pollution. The Nemerow Pollution Index and Geoaccumulation Index (I_{geo}) were applied to assess the degree of heavy metals pollution (Cu, Zn, Ni, Pb, Cr, and As) in the topsoil at the site. According to the Single Pollution Index (P_i) for classification, there is slight As pollution, while the levels of Cu, Zn, Ni, Pb and Cr are unpolluted. The Nemerow Composite Pollution Index (NCPI) indicates that the topsoil is mildly polluted. Based on the classification by the Geoaccumulation Index (I_{geo}), there is moderate pollution by As; slight pollution by Cu; and no pollution by Zn, Ni, Pb and Cr. The heavy metals pollution in the topsoil was caused mainly by the disturbance of historic copper slag in the cultural layers by modern farming activity. Overall, the results show that historic smelting pollution should be regarded as an important factor to be considered in the development of modern agriculture, and they are also important for understanding past human-environmental interactions.

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