

Magnetic evidence for heavy metal pollution of topsoil in Shanghai, China

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Abstract This study presents the results obtained from magnetic susceptibility and heavy metal (Cu, Zn, Pb, and Cr) concentration measurements of soil profiles collected from arable land and urban parks in Baoshan District, an industrial district of Shanghai, China. The study focuses on the investigation of vertical variations in magnetic susceptibilities and heavy metal concentrations and on correlations between magnetic susceptibilities and heavy metal concentrations in soil profiles. The results demonstrate that magnetic enhancement in the surface layer of the soil profile is associated with increased heavy metal pollution. The enrichment factors (EF) and the Tomlinson Pollution Load Index (PLI-EF) are calculated for estimating the level of heavy metal pollution of soil profiles in the study. The significant positive correlations between heavy metal contents, enrichment factors (EF), Tomlinson pollution load index (PLI-CF), modified Tomlinson pollution load index (PLI-EF), and magnetic susceptibility (%) indicate that much of the heavy metal contamination in the study area is linked to combustion derived particulate emissions. The results confirm that the combined magnetic measurement and heavy metal concentration analysis could provide useful information for soil monitoring in urban environments. However, the use of magnetic technique to locate the heavy metal pollution boundary in the soil profile of this studied area should be confirmed by further geochemical analysis.

Keywords soil, pollution, magnetic susceptibility, heavy metals, Shanghai

1 Introduction

With the rapid development of industry and urbanization, heavy metal pollution of soil and the resulting ecosystem degradation have drawn worldwide attention. Screening for polluted areas is critical for subsequent environmental management and pollution control. Recently, the benefits of magnetic technology and the close correlations between magnetic properties and heavy metals (Chan et al., 1998; Petrovský et al., 1998, 2001; Schmidt et al., 2005; Lu et al., 2007; Canbay et al., 2010; Wang, 2013; Xia et al., 2014;) indicate that magnetic measurement is an efficient and inexpensive tool for detecting heavy metal pollution in soils influenced by heavy industry and traffic pollution (Hay et al., 1997; Heller et al., 1998; Hoffmann et al., 1999; Kapička et al., 1999; Hanesch and Scholger, 2002; Lecoanet et al., 2003; Lu and Bai, 2006; Lu et al., 2007; Hu et al., 2007; Blaha et al., 2008; Sharma and Tripathi, 2008; Wang and Sun, 2008; Duan et al., 2009; Canbay et al., 2010; Wang et al., 2013; Xia et al., 2014; Cao et al., 2015). The principle is that anthropogenic magnetic particles (mainly iron oxides such as magnetite) are closely associated with anthropogenic heavy metals during their emission, transportation, and deposition processes in the environment (Jordanova et al., 2004; Blaha et al., 2008; Wang and Sun, 2008) and, in consequence, soil receiving industrial or traffic related dust input often shows magnetic enhancement in the top layer, which can be easily detected by magnetic measurement. Such a magnetic enhancement is characterized by coarse-grained magnetic particles, which is different from the fine grained particles produced by pedogenic process. Among the magnetic parameters, magnetic susceptibility measurements for heavy metal pollution screening are commonly accepted and well used in a number of recent studies (Hoffmann et al., 1999; Boyko et al., 2004; Canbay et al., 2010; Cao et al., 2015).

A number of studies have paid attention to the

relationship between magnetic properties and heavy metal contents of topsoil in order to locate the spatial distribution of pollution (Boyko et al., 2004; Hu et al., 2007; Lu et al., 2007; Canbay et al., 2010; Wang et al., 2013; Xia et al., 2014; Cao et al., 2015). In addition, the vertical variation of magnetic susceptibility has been applied to delineate the boundary between the upper polluted soil layer and the lower unpolluted layer (Wang and Qin, 2005; Lu and Bai, 2006; Blaha et al., 2008). Shanghai is the biggest city and one of the industrial centers in China. In Baoshan District, the northern part of Shanghai, heavy industries such as steel and power plants are present. Previous study demonstrated that total suspended particulates (TSPs) collected in Baoshan District shown higher values of magnetic susceptibility compared to areas elsewhere in Shanghai (Shu et al., 2001). Magnetic signals of the urban topsoil in Baoshan District were extremely enhanced with magnetic susceptibility (Hu et al., 2007). However, such a technique has not been tested on soil profiles in Shanghai. This paper aims to investigate the feasibility of applying the down core variability of magnetic susceptibility as a proxy to monitor the heavy metal pollution boundary in Shanghai.

2 Study area and methods

Located in the northern part of Shanghai, Baoshan District has been the important iron and steel manufacturing base in China. The soils of Baoshan District are mainly formed on the alluvial sediments of the Yangtze River and are

classified as Entisols (Hu et al., 2007). This region has a subtropical monsoon climate with an annual mean temperature of 18.4°C and annual mean precipitation of 1042.6 mm. The wind direction is northeast in winter and southeast in summer. The Baosteel Group was founded in 1978 and was still active during the sampling periods.

In order to study the influences of industrialization on the soil environment of this area, Linjiang Park (built in 1956), Yuepu Park (built in 1985), and a vegetable field have been chosen as sampling sites; all are close to the Baosteel group (Fig. 1). Three soil cores of 40 cm, 40 cm, and 56 cm were collected from Linjiang Park, Yuepu Park, and the vegetable field, respectively. The cores were sectioned at 2 cm intervals and then oven dried at 40°C for further magnetic and geochemical analyses.

Magnetic susceptibility (χ) was measured by a Bartington dual-frequency meter at 0.47 kHz. Heavy metal concentrations for Cu, Zn, Pb, Cr, Fe, and Al were determined by X-ray fluorescence spectrometry (XRF, Philips PW1400 apparatus). Accuracy of determinations was checked by analysis of certified China national reference materials GSD9; precisions were below 10% for all elements.

3 Results

3.1 Magnetic susceptibility (χ)

The depth variations of magnetic susceptibility of the three soil profiles are presented in Fig. 2. All soil profiles show

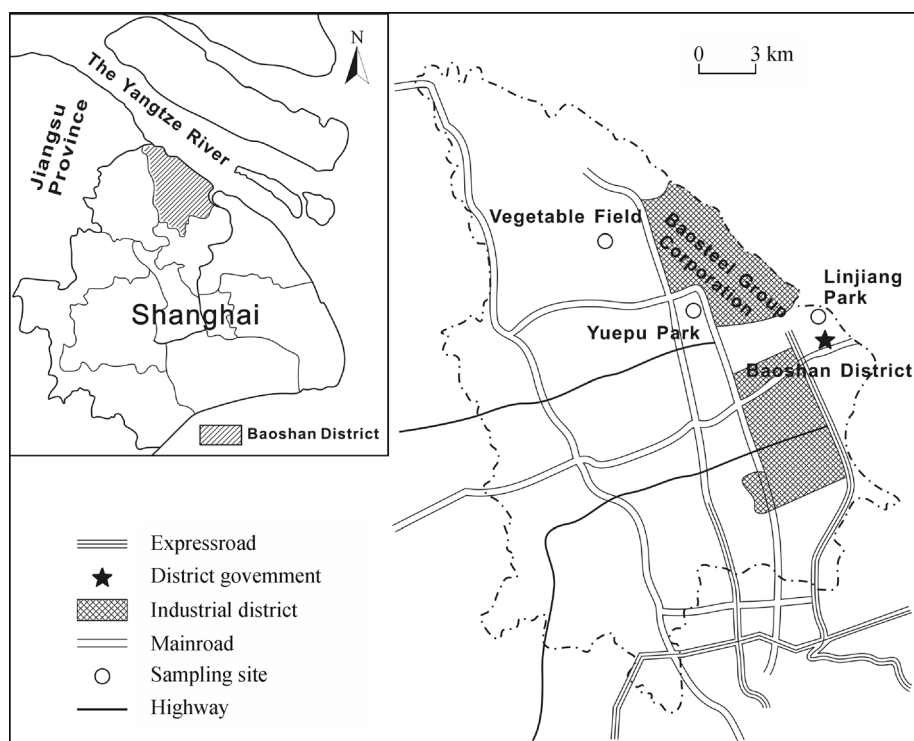


Fig. 1 Map showing Shanghai and the soil sampling sites in Baoshan District.

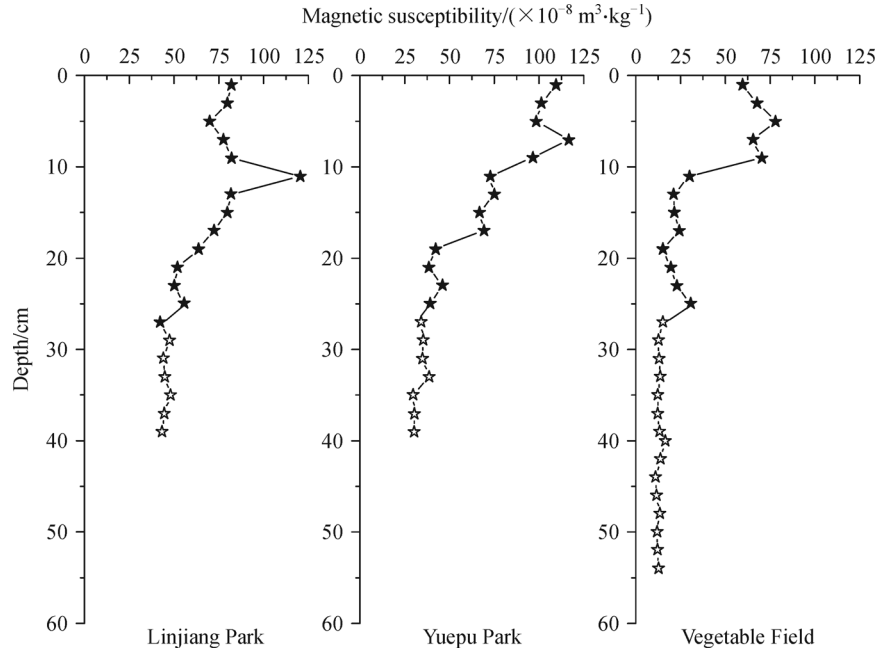


Fig. 2 Vertical distribution of magnetic susceptibility (χ) in soil profiles. The symbols \star and \star represent soil samples from the top 25 cm layer and those below 25 cm, respectively.

Table 1 Magnetic susceptibility ($10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$) of three soil cores

Location	Whole profile		Layer1 (depth < 25 cm)		Layer2 (depth > 25 cm)	
	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD
Linjiang Park	42.4–120.5	64.2 \pm 19.9	50.4–120.5	74.5 \pm 17.4	42.4–48.1	45.0 \pm 2.0
Yuepu Park	29.7–116.5	60.2 \pm 29.3	38.2–116.5	74.7 \pm 26.7	29.7–38.8	33.4 \pm 3.1
Vegetable Field	11.2–78.1	25.9 \pm 20.6	15.1–78.1	40.6 \pm 22.6	11.2–16.5	13.1 \pm 1.3

enhanced magnetic susceptibility in their surface horizons (top 10 cm), and a declining trend of χ values with depth until a depth of around 25 cm, below which χ remains low and stable. Among the three profiles, Linjiang Park shows the highest peak χ value of $120.5 \times 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$. The χ of the layer deeper than 25 cm varies little within each profile, and therefore can be considered as the background level in each profile. A mean value of background χ of $45.0 \times 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$ is observed for Linjiang Park, which is followed by $33.4 \times 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$ for Yuepu Park and $13.1 \times 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$ for the vegetable field (Table 1). In comparison to the background values, the vegetable field shows the maximum magnetic enhancement, with the peak value about six times its background value.

3.2 Heavy metal concentrations and enrichment factors

The down core variations of heavy metal content are illustrated in Fig. 3. Concentration Factor (CF) values of each metal, which are calculated as the ratio between the heavy metal concentration in the sample and the background concentration of the corresponding metal

in soil of Shanghai (Pang, 1995), are presented in Table 2.

As shown in Fig. 3, Cu, Zn, Pb, and Cr in the three profiles are all enhanced in the top layers and decrease with depth. Among the metals, Pb shows a maximum CF value of 2.09, while Cr is most close to the background values in Shanghai, with a maximum CF value of only 1.10 (Table 2). Among the three sites, the maximum values of Cu, Pb, and Cr occur in samples from Linjiang Park. Also the mean CF values of Cu, Pb, Zn, and Cr are the highest in Linjiang Park (Table 2).

The variability in metal concentrations could result from particle size effects and anthropogenic influences (Liang et al., 2008). To minimize particle size effects, enrichment factors (EF) are calculated as (e.g., Sinex and Wright, 1988):

$$EF = \frac{\left(\frac{\text{Me}}{\text{Al}}\right)_{\text{sample}}}{\left(\frac{\text{Me}}{\text{Al}}\right)_{\text{ucc}}}, \quad (1)$$

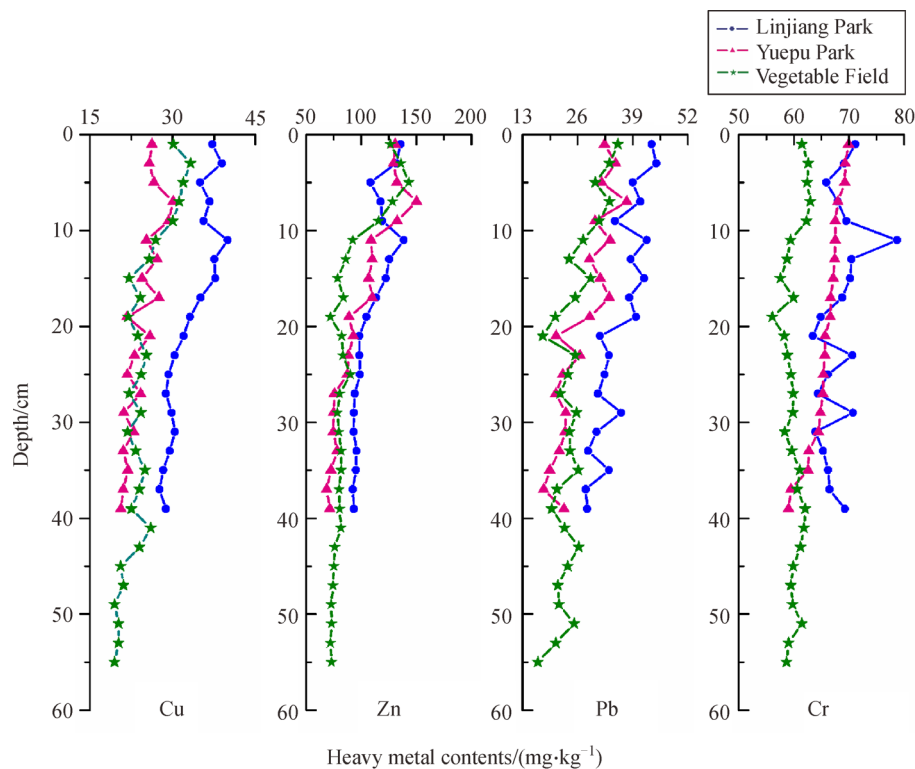


Fig. 3 Down core variations of heavy metal contents in soil profiles.

Table 2 Heavy metal contents (mg/kg) and CF values of three sites soils

Location	Cu		CF-Cu		Zn		CF-Zn	
	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD
Background	23.5				75.8			
Linjiang Park	29.4–42.5	35.1±4.2	1.18–1.70	1.41±0.17	98.9–148.3	116.1±16.4	1.22–1.83	1.43±0.21
Yuepu Park	21.9–32.0	25.9±3.0	0.88–1.28	1.04±0.12	73.6–160.7	106.2±26.3	0.91–1.98	1.31±0.33
Vegetable Field	20.6–35.3	26.0±4.0	0.83–1.41	1.04±0.15	77.1–153.2	94.8±21.7	0.95–1.89	1.17±0.29
Location	Pb		CF-Pb		Cr		CF-Cr	
	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD
Background	21.3				64.6			
Linjiang Park	32.0–58.9	43.7±7.3	1.31–2.09	1.68±0.25	49.1–60.3	52.8±3.0	0.98–1.10	1.06±0.05
Yuepu Park	19.1–50.4	33.9±10.2	0.85–1.76	1.27±0.28	48.1–58.0	52.5±3.0	0.91–1.08	1.02±0.05
Vegetable Field	19.7–47.2	30.4±6.9	0.78–1.67	1.17±0.23	48.1–58.0	52.0±3.3	0.87–0.97	0.93±0.03

where $(Me/Al)_{\text{sample}}$ is the metal to Al ratio in the samples; $(Me/Al)_{\text{ucc}}$ is calculated from the corresponding metal concentration in upper continental crust (UCC), which are in mg/kg: 80,400 for Al, 35.0 for Cr, 25.0 for Cu, 20.0 for Pb, and 71.0 for Zn (Taylor and McLennan, 1995), respectively. Aluminum is used as the reference element for geochemical normalization because Al is one of the most abundant elements on the earth and has been commonly used for normalization purposes (Zhang et al., 2009).

Based on Zhang and Liu (2002), EF values between 0.5 and 1.5 indicate that the metal is entirely from crustal materials or natural weathering processes, whereas EF values higher than 1.5 suggest that the sources are more likely to be anthropogenic. It can be assumed that the increased metal concentrations in the top soils are caused by anthropogenic input (Fig. 4).

Cr has the maximum EF value of 2.7, followed by Pb, Zn, and Cu in decreasing order. Linjiang Park shows the heaviest pollution concentrations of Cu, Pb, and Cr with

peak EF values of 1.84, 2.65, and 2.74, respectively. The heaviest pollution of Zn exists in Yuepu Park with the peak EF value of 2.44. It should be noted that the EF value of Cr has the smallest variation in each profile, although most of the values are well above 1.5. This is possibly due to the lower Cr content in the UCC (35 mg/kg) adopted in this study for the calculation of EF. Different values are reported for Cr in the UCC, such as 85 mg/kg (Rudnick and Gao, 2004). For the Chinese soil background, a value of 61 mg/kg (CEPA, 1990) for Cr was reported. As mentioned above, the background Cr level in soil of Shanghai is 64.6 mg/kg. So the EF here maybe overestimated and Cr is not actually present in high concentrations.

3.3 Correlation between magnetic susceptibility and heavy metals

The trend of the metal concentrations and their EF values show strong similarity to that of the magnetic susceptibility. The relationships between heavy metals and magnetic susceptibility are summarized in Table 3. In addition, to reflect the integrative pollution status, the Tomlinson pollution load index (PLI, Angulo, 1996) was also calculated. PLI is based on the values of concentration factors (CF) of each heavy metal, which is calculated as following:

$$PLI - CF = \sqrt[n]{CF_1 \times CF_2 \times \dots \times CF_n}, \quad (2)$$

where CF_n represents the CF of n^{th} element. Values of $PLI = 1$ indicate heavy metal loads close to the background level, and values above 1 indicate pollution.

Similarly, based on the value of enrichment factors (EF) of each heavy metal, we define another index of the overall pollution status for a sample (PLI-EF), which is defined as following:

$$PLI - EF = \sqrt[n]{EF_1 \times EF_2 \times \dots \times EF_n}, \quad \text{where } EF_n \text{ represents the EF of } n^{\text{th}} \text{ element.}$$

As can be seen from Table 3 and Fig. 5, Zn shows the highest correlation with χ , followed by Cr, Pb, and Cu. In addition, the EF value of each heavy metal presents stronger correlation with χ than its content. The correlation coefficients between χ and heavy metal contents are 0.52 (Cu), 0.86(Zn), 0.63(Pb), and 0.66(Cr), respectively. The overall pollution indexes PLI-CF and PLI-EF also display significant correlations with χ , and the correlations are significant at the 0.01 level.

4 Discussion

4.1 Magnetic enhancement and heavy metal pollution

All soil profiles show enhanced magnetic susceptibility in their surface horizons. According to previous studies (Dearing et al., 1996; Lu, 2003), magnetic enhancement in topsoils can be caused by pedogenic or anthropogenic processes. However, detailed magnetic and electron

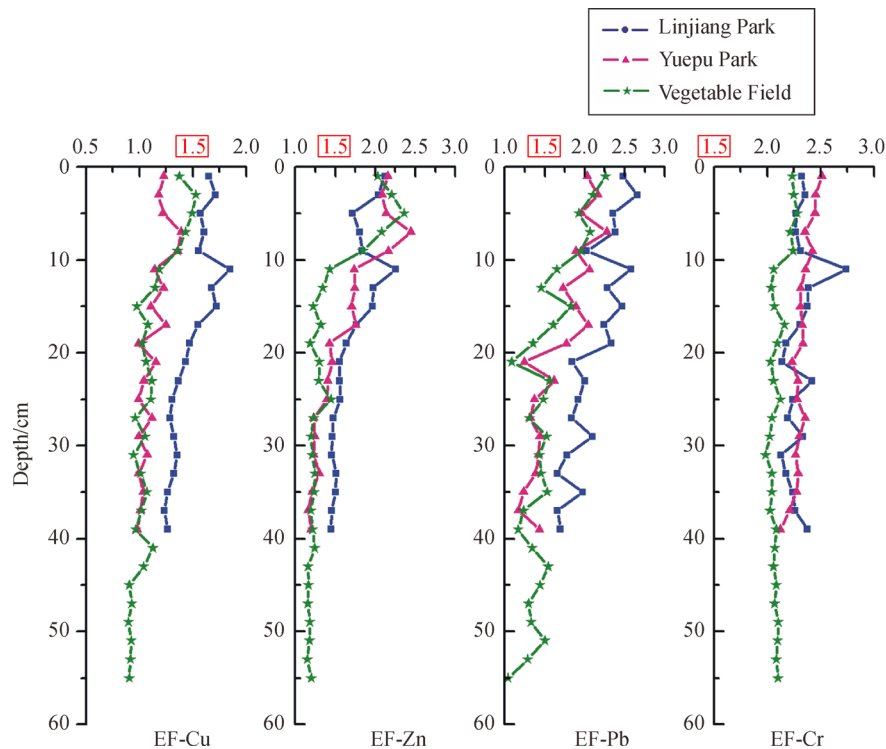


Fig. 4 Down core variations of heavy metal enrichment factor (EF) values in soil profiles. The red EF value of 1.5 marks the pollution criteria.

Table 3 Correlation coefficients between χ and heavy metal contents, EF values, PLI-CF and PLI-EF

	Cu	Zn	Pb	Cr	EF-Cu	EF-Zn	EF-Pb	EF-Cr	PLI-CF	PLI-EF
χ	0.52	0.86	0.63	0.66	0.60	0.88	0.68	0.72	0.78	0.85

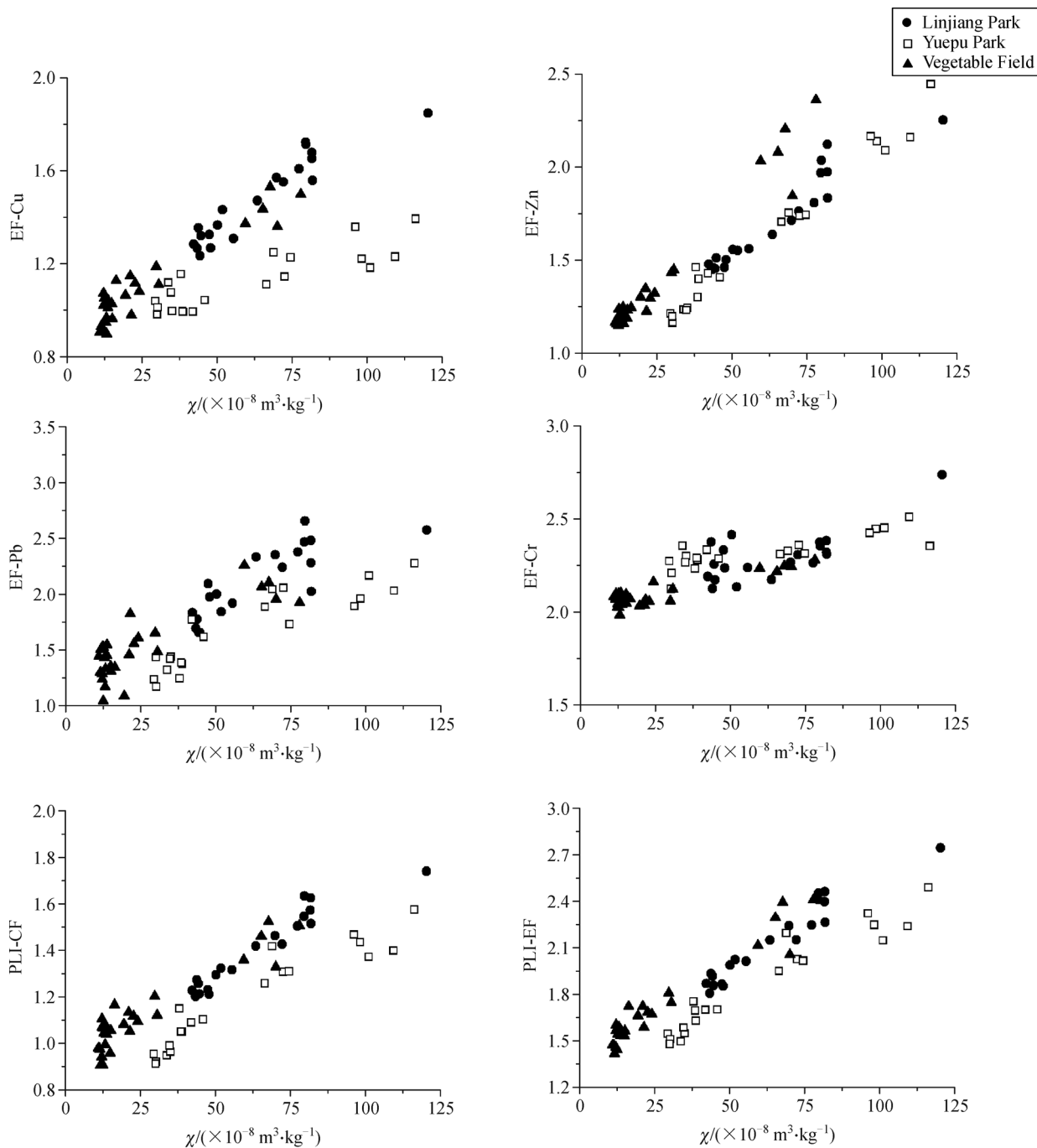


Fig. 5 Scatter plots of χ versus EF value of heavy metals, Tomlinson pollution load index (PLI-CF), and modified Tomlinson pollution load index (PLI-EF).

microscope characterizations of soil samples suggest that magnetic particles in the enhanced surface layers are coarse grained, which is different from the fine SP/SD grains produced by pedogenic processes. The elevated EF values in the magnetic enhancement layer also clearly indicate an anthropogenic input. Therefore, the enhanced magnetic susceptibility can be ascribed to anthropogenic input.

Among the heavy metals, χ has higher correlation coefficients with Zn, Cr, and Pb, but a weaker relationship with Cu. An examination of Fig. 5 indicates that samples from Yuepu Park show a different relationship between χ and the EF value of Cu compared to the other two sampling sites, which suggests that magnetic particles and Cu have a different origin in this location compared to those of the other sites. Although not as obvious as Cu, other elements from Yuepu Park also have slightly different origins from their counterparts in the other sites. Thus, the relationships between χ and heavy metals are both element- and site-dependent. Therefore, to obtain comprehensive information of heavy metal pollution in industrial polluted areas, detailed sampling with a fine spatial resolution is needed to distinguish different sources of pollutants. Nevertheless, the good relationship between PLI-EF and χ suggests that χ can be still used as an overall pollution index in the study area.

In comparison to soils impacted by industry and traffic elsewhere in China, the study area shows a moderate magnetic enhancement. For example, soil in Xuzhou city in northern China has a peak χ value of $775 \times 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$, 16.5 times that of the background value of $47 \times 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$ (Table 4). Similarly, heavy metal concentrations of urban soil in Xuzhou are correspondingly higher than the data of this study (Table 4). Therefore, although different areas may show differences in background χ values, the enhancement of χ relative to background values can still be used in the global qualitative assessment of anthropogenic heavy metal pollution of soil.

4.2 Magnetic detection of the boundary between polluted and unpolluted layers

In general, soils influenced by strong industrial or traffic input show magnetic enhancement in the surface layer, which is normally the top 30 cm, with the maximum values at 5–10 cm (Fig. 6). Such variation in the depth limit

indicates the transportation of atmospherically derived magnetic particles within the soil profile varies with site, which may be related to several factors, such as magnetic particle size, soil density, and rainfall. Based on the relationship between magnetic enhancement and heavy metal pollution, it is natural to use the lower limit of the magnetic enhancement layer as the boundary between the upper ‘polluted’ layer and the lower ‘background’ layer (Blaha et al., 2008). However, it seems that some metals, such as Pb in this study area, show $\text{EF} > 1.5$ at greater depth than this magnetic boundary. This may be caused by the different sources of magnetic particles and heavy metals or, more likely, by different geochemical behaviors of the contaminants. Therefore, magnetic methods can provide preliminary information of pollution depth, but accurate definition of the heavy metal pollution boundary requires further geochemical confirmation.

4.3 Spatial variations of heavy metal pollution

Among the three sampling sites, Linjiang Park is the most polluted, with the highest mean values of EF (except EF-Zn), PLI-CF, and PLI-EF. The vegetable field is the least polluted site. Linjiang Park is located between Baosteel and the Wusong industrial zone, which should have greater influence on the nearby environment. In addition, Linjiang Park is near the downtown area of the Baoshan District, where high transportation density contributes to the relatively serious pollution there. The vegetable field soil is less polluted by heavy metals due to its greater distance from the industrial pollution sources. Nevertheless, elevated heavy metal concentrations and magnetic particles in the surface soil layers suggest that proper pollution control measures should be taken to minimize pollution on arable land.

5 Conclusions

Magnetic enhancement occurs in the surface layer of both agricultural and urban park soils in areas close to industrial bases of Shanghai. Significant relationships between magnetic susceptibility and Cu, Zn, Pb, and Cr concentrations and their enrichment factors indicate that the enhanced magnetic topsoil is subjected to airborne pollutant input. Strong correlations also exist between the

Table 4 Comparison of χ and heavy metal contents of soil profiles in Shanghai with other industrial soils in China

Place	Soil	$\chi/(10^{-8} \text{ m}^3 \cdot \text{kg}^{-1})$	Cu/(mg·kg ⁻¹)	Zn/(mg·kg ⁻¹)	Pb/(mg·kg ⁻¹)	Reference
Baoshan (Shanghai)	Park soil	30–121	21–43	69–161	18–59	This study
	Agriculture soil	11–78	19–35	72–153	17–47	
Xuzhou	Industrial soil	47–775	17–80	53–380	16–120	Wang and Qin, 2005
Hangzhou	Industrial soil	53–914	14–150	47–1250	20–493	Lu and Bai, 2006
Luoyang	Industrial soil	111–1128	47–340	84–570	32–383	Lu et al., 2007

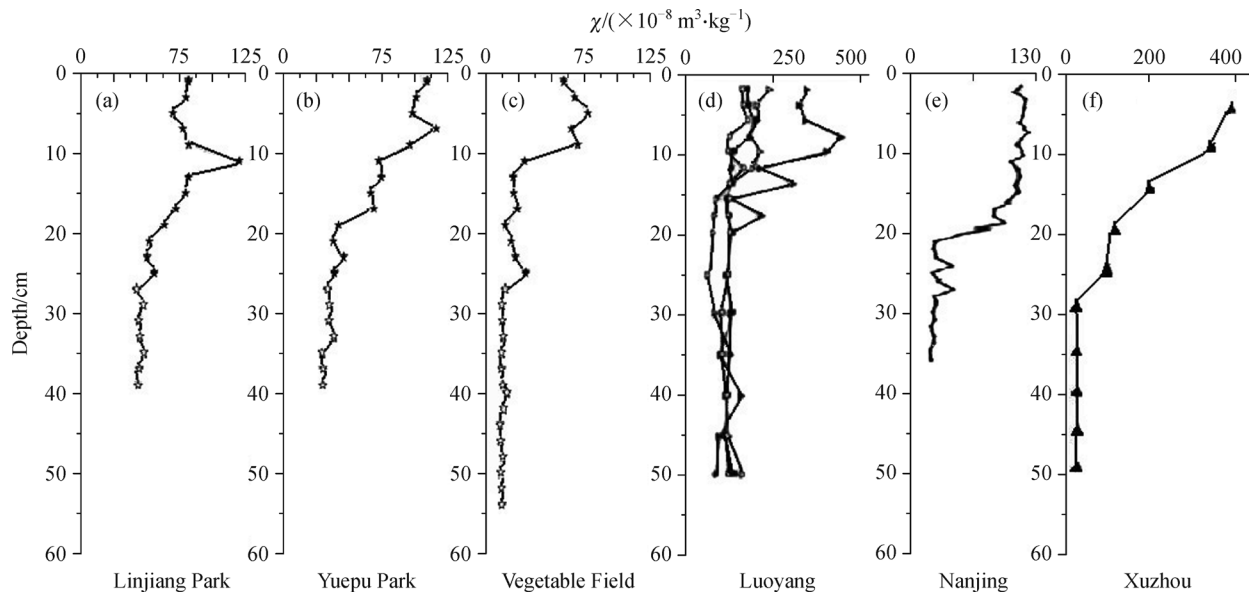


Fig. 6 Comparison of the soil magnetic susceptibility profiles of Shanghai with those from other regions. (a) Soil profile from Linjiang Park; (b) soil profile from Yuepu Park; (c) soil profile from the Vegetable Field; (d) soil profile from Luoyang (Lu et al., 2007); (e) soil profile from Nanjing (Duan et al., 2009); (f) soil profile from Xuzhou (Wang and Sun, 2008).

overall indices of pollution (PLI-CF and PLI-EF) and χ , suggesting that the magnetic technique can provide a simple, rapid, and non-destructive tool for the assessment of soil heavy metal pollution in industrial districts of Shanghai. However, by means of comparing the vertical variations of magnetic susceptibility and EF values of heavy metals in soil profile, the use of the magnetic technique to locate the pollution boundary in the soil profile should be confirmed by geochemical analysis.

Acknowledgements This study was supported by the National Natural Science Foundation of China (Grant No. 41001331), The Programme of Introducing Talents of Discipline to University (111 Project) and the Natural Science Foundation of Shanghai (Grant No. 15ZR1428700). The authors thank Professor Lu Ming and Zhou Limin of East China Normal University for their help with geochemical analysis. Thanks to Cashion for the language modification.

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