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Source identification of trace elements in peri-urban soils in eastern China

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Abstract

The source identification of trace elements in peri-urban soils have not been fully explored, especially for the areas in eastern China. Here, 80 soil samples, including 40 from cropland, 11 from orchards and 29 from forests, were collected in a typical peri-urban catchment, Ningbo, eastern China. The concentrations of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn), Pb isotopes and basic soil properties were measured for each soil sample. Multivariate analysis of correlation, regression, principal component analysis (PCA) and isotopic tracers were used. The results showed that the trace elements concentrations significantly differed in land uses, especially for Cd, Cu and Zn. For the 7 trace elements, the Cd, Cu and Zn in crop soils are contaminant elements. In the peri-urban soils, Cr and Ni are dominated by parent material and paedogenic processes. Difference in As and Pb concentrations between land uses maybe attributed to atmospheric deposition induced by fossil fuel combustion. Application of fertilisers, calcium phosphate and calcium superphosphate, livestock manure and compost, are the dominant source of pollutants in peri-urban soils, especially for Cd, Cu and Zn, indicating the key point for pollution control for this area. Calcium and P are effective indicators of Cd, Cu and Zn contamination for the peri-urban catchment.

Key words: trace elements sources; peri-urban soil; land use; multivariate analysis

1 Introduction

Peri-urban ecosystems serve at the transitional zone between urban and rural ecosystems (Chen et al., 2008b; Huang et al., 2009; Simon, 2008; Zhu et al., 2017b). With the rapid urban expansion and industrial development, the peri-urban areas are often the sites responsible both for food, materials and energy supplements and for urban and industrial waste disposal (Chen et al., 2008b; Khai et al., 2007; Xiang et al., 2018; Zheng et al., 2018; Zhu et al., 2017b). The associated fertiliser use, fossil fuel combustion and other related anthropogenic activities may exacerbate the trace element pollution in peri-urban soils (Chen et al., 2008b; Wei and Yang, 2010). Research into the source identification of trace elements will benefit for pollution control (Morton-Bermea et al., 2009; Ungureanu et al., 2017; Wei and Yang, 2010).

Trace elements are introduced naturally into soil through the weathering of parent materials, and can also result from a variety of human activities such as industrial and traffic emission (fossil fuel combustion), mining, smelting, manure and inorganic fertilizers application, road dust and waste disposal (Alloway, 2013; Ravankhah et al., 2017; Teng et al., 2014; Ungureanu et al., 2017; Wong et al., 2002). The soil parent materials and paedogenic processes generally have significant influences on elements of As, Co, Cr, Ni, Zn (Facchinelli et al., 2001; Guagliardi et al., 2013; Sun et al., 2013; Xu et al., 2014). Anthropogenic activities usually contribute the enrichment of As, Cd, Cu, Hg, Pb, Zn (Alloway, 2013; Lu et al., 2012; Manta et al., 2002; Nicholson et al., 2003; Sun et al., 2013; Xu et al., 2014). Anthropogenically derived trace elements have been found to accumulate in topsoil, and can lead to damage animal and human physiological functions via the food chain (Chen et al., 2008b; Fu et al., 2007; Hernandez et al., 2003; Rodriguez Martin et al., 2006; Tóth et al., 2016).

Trace element sources to soil differ by land use, due to differences in management activities, leading to differing contamination profiles (Chen et al., 2005b; Ettler et al., 2014; Liu et al., 2005; Micó et al., 2006; Sheppard et al., 2000; Teng et al., 2014). In ecosystems for which

agricultural practices are intensive, trace elements sources include application of liquid and solid manure (or their derivatives, compost or sludge) or inorganic fertilisers (Alloway, 2013; Gimeno-García et al., 1996; Rodriguez Martin et al., 2006; Xiang et al., 2018). Trace elements in urban soils receive significant loads of contaminants from traffic and industrial activities, and pose a significant challenge to food production in such habitats (Madrid et al., 2002; Meharg, 2016; Teng et al., 2014). In addition, industrial development may contribute significant atmospheric pollutant deposition to soils (Chen et al., 2008a; De Vries et al., 2003; Duan and Tan, 2013; Hernandez et al., 2003; Zheng et al., 2004). However, studies on source identification of trace elements in peri-urban soils usually focused only on the vegetable fields (Chen et al., 2008b; Singh and Kumar, 2006) or mapping spatial distribution of the whole area (de la Cueva et al., 2014; Guagliardi et al., 2013). Therefore, it is essential to identify the differences in concentrations and sources of trace elements for different land uses in peri-urban area.

Soil pollution by trace elements poses severe challenges to soil health and sustainability in China (Chen et al., 2015; Cheng and Hu, 2010; Cheng, 2003; Li et al., 2014; Liu et al., 2010). In China, the peri-urban zone begins beyond the contiguous built-up urban area and can extend as far as 300 km in the case of Chinese coastal cities (Webster and Muller, 2002). For example, the Hangzhou-Ningbo Corridor typifies the long-running and dynamic peri-urbanisation process in the Lower Yangtze Region of eastern China as a whole, arguably the world's largest extended urban region (Webster and Muller, 2002). Importantly, the huge pressure on food supply induced by rapid urbanisation process in the peri-urban area in eastern China has continued for decades (Chen et al., 2008b; Wei and Yang, 2010), we hypothesise that this will lead to distinctive contamination of agricultural soils within this catchment. This current study presents the results of soil trace elements in a peri-urban area in Ningbo city in eastern China. The objectives of this study were (1) to characterise differences in the concentrations of trace

elements for different land uses; and (2) to identify the sources of trace elements in peri-urban areas of eastern China.

2 Materials and methods

2.1 Site description

The Zhangxi catchment (an area of 85 km² and elevation range of 3-763 m), a typical peri-urban area in Ningbo City, was selected as the study area. Ningbo is a coastal city in eastern China that has undergone rapid urbanisation processes in recent decades. The soil layer in the catchment is shallow (ca. 30 cm on average) and is dominated by a silt loam in the 0-20 cm soil layer and sandy loam in the 20-30 cm soil layer. The parental materials/bedrocks are mainly silicate and aluminosilicate rocks, carbonate and aluminosilicate clastic rocks. The region has a moderate subtropical monsoon climate, warm and humid during April to September, and the rainy season is around June. The catchment has an annual mean temperature of 17 °C and mean annual precipitation of 1460 mm. The Zhangxi is a mixed land use catchment, including forest (mainly natural secondary forest) and farmlands (crop, orchard, etc). The cropland is usually treated with manure and inorganic fertilisers in the winter, and the manure are mainly derived from humans and their domestic livestock including pigs and chickens (Xiang et al., 2018; Zheng et al., 2018). Fritillaria, peanut, rice and several types of vegetables are the main crops in study area. The crop rotation patterns include vegetable-vegetable rotation, crop-vegetable rotation and crop-crop rotation.

2.2 Sample preparation and analysis

Eighty representative sites were selected covering the two types of land use (farmlands and forest). Soil samples (0 to 20 cm) were collected in March 2016, including 40 crop, 11 orchard and 29 forest soils (Fig. 1). Each sample comprised a mixture of five sub-samples randomly

obtained in a 2 m² grid. All soil samples were collected with a stainless hand auger and stored in snap-sealed polypropylene bags. Soil samples were dried in a Christ LD freeze dryer, sieved and milled (except for pH and soil texture determination) by hand to a fine powder in a mortar and pestle.

The concentrations of As, Cd, Cr, Cu, Ni, P, Pb, and lead isotope ratios, were determined with the ICP-MS (Thermo Scientific iCAP Q) in direct solution acquisition mode using a Cetac ASX-520 Auto Sampler. The concentrations of Zn, Ca and K were determined with an X-ray fluorescence (Rigaku Nex CG benchtop XRF). For ICP-MS analysis, BDH Prolabo Aristar 69% nitric acid and BDH Prolabo Analar Normapur 30% hydrogen peroxide were used for extraction/digestion. Eight standards were made up including one blank also containing internal standard. Results were calculated from the resulting calibration curve based on the average intensity from 3 replicates of each sample, blank and standard. The XRF analysis was performed in batches of 9 (8 samples and one certified reference material) with analysis lasting approximately 13 minutes per sample. Certified reference materials for ISE-921 (river clay) and blank sample are used for quality control and recovery analysis. The recovery rates for elemental contents were between 79 and 110 % (Table S1).

The soil samples were also analysed for Pb isotopic composition to detect the input of anthropogenic Pb. The nitric acid digestion procedure was used as the sample preparation and using the same ICP-MS for analysis. Five standards were made up including one blank. Certified lead isotope standard VHG-LISPB1-50 in 1% HNO₃ (LGC Standards) was used to make up all standards. Analysis of the samples was carried out using ICP-MS (Thermo Scientific iCap Q) which was connected to the auto-sampler. ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb were acquired at dwell times of 300 ms each. The measured ratios of ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb were calculated from the resultant data based on the average intensity from 10 replicates of each sample, blank and standard, and then Pb ratios of individual sample were corrected using

119 bracketing certified Pb isotopic standards (LGC Standards-VHG-LISPB1-50).

120 Soil samples for pH and soil texture were sieved to pass a 2 mm mesh. The soil pH was
121 measured in water (1:2.5 soil:water ratio, w/v) using a pH-meter (Mettler Toledo Delta 320)
122 (Imperato et al., 2003). The soil texture was determined with a laser diffraction particle size
123 analyser (Malvern Mastersizer 2000) (Sun et al., 2013). The soil organic matter (SOM) was
124 calculated by soil organic carbon which was measured by dichromate oxidation (Yeomans and
125 Bremner, 1988). The C/N ratio was determined with an elemental analyser (Elementar Vario
126 EL III).

128 **2.3 Statistical analysis**

129 The Kolmogorov-Smirnov test was used to determine the normality of the metal
130 concentrations. Differences in trace element concentrations among various types of land use
131 were determined with non-parametric Kruskal-Wallis tests and ANOVA by a Tukey test.
132 Principal component analysis (PCA) was used to cluster trace elements that showed similar
133 behaviour to identify potential sources. Varimax rotation was applied because orthogonal
134 rotation minimises the number of variables with a high loading on each component and
135 facilitates interpretation of results (Sun et al., 2013). Correlation matrix and regression analysis
136 were used to investigate elemental associations amongst the trace elements in the topsoil. For
137 correlation analysis, Pearson's product moment correlation coefficient was used for normal
138 populations, and Spearman's rank correlation coefficient was used for non-normal populations
139 (Micó et al., 2006). Statistical tests were considered to indicate statistical significance at a *p*
140 level of less than 0.05. Outliers are not excluded during all data analysis except for the linear
141 regression of Pb isotopes. All statistical analyses were performed in IBM SPSS Statistics 23.0.

143 **3 Results and discussion**

3.1 Elemental concentrations and soil properties

Descriptive statistics of the concentrations of elements, Pb isotopes and soil properties are summarised in Table 1. Soils could be classified as silt loam based on their clay, silt and sand contents. Only sand and silt had normal distributions, which was basically consistent with the general knowledge that soil properties are normally distributed with small coefficients of variation (Madrid et al., 2002; Sun et al., 2013). The soil pH values ranged from 4.0 to 6.9. Most soils were acidic; 51% had pH values below pH 5.0, and only 13% had pH values above pH 6.0. The acidic pH was partly due to the climate, the parent material and the soil texture (Barton et al., 1994) and partly due to the frequent use of mineral fertilisers (especially N fertiliser) and infrequent addition of fresh organic matter (Sun et al., 2013). For example, it has been reported that soil acidification in China results mainly from high inputs of N fertiliser and the uptake and removal of base cations by plants (Guo et al., 2010). The SOM had a large range, 11 to 172 g kg⁻¹, with a mean value of 47 g kg⁻¹. The high levels of SOM imply an important retention of trace elements by porous carbon with a high adsorption capacity (Micó et al., 2006; Oh and Park, 2002). However, the low clay content may decrease retention, and the acidic pH could also facilitate the mobility, of trace elements (Sun et al., 2013). The K concentration (23.3 g kg⁻¹) was similar with the background value of Ningbo (23.0 g kg⁻¹) (Dong et al., 2007). The mean concentrations of Ca and P for soils were 2.0 and 1.5 times higher than the background values of Ningbo (2.3 g kg⁻¹ and 0.63 g kg⁻¹) (Dong et al., 2007). Calcium and P are commonly used to improve plant growth and yield, and Ca is also commonly applied as lime to raise the pH of acidic soils (Alloway, 2013). Compared with the background values of Ningbo, the significantly high concentrations of Ca and P indicate extensive application of inorganic fertilisers, such as calcium phosphate and calcium superphosphate (Dong et al., 2007).

Data from forests and orchards were combined for further analysis because no significant differences in trace element concentrations were found between them (Fig. 2). In forest and

orchard soils, the coefficients of variation for trace element concentrations varied from 32% for As to 100% for Cr and decreased in the order $Cr > Cu > Ni > Cd > Pb > Zn > As$. In crop soils, the coefficients of variation varied from 23% for Ni to 49% for Cd and decreased in the order $Cd > Cu > Pb > As > Zn > Cr > Ni$. The relatively low coefficients of variation and significantly higher concentrations of trace elements in crop soils than in forest and orchard soils, especially for Cd, Cu and Zn, suggest nonpoint-source agricultural pollution. This pollution may result from extensive use of fertilisers and pesticides (Madrid et al., 2002; Rodriguez Martin et al., 2006; Sun et al., 2010; Ungureanu et al., 2017; Xiang et al., 2018).

The mean concentrations of As, Cr, Ni and Pb in peri-urban soils were lower than background values of Ningbo (Fig. 2), indicating that the anthropogenic inputs of these elements were relatively low. This finding is in agreement with that of Wei and Yang (2010) that Cr and Ni appeared to be relatively less contaminating elements in China (Sun et al., 2013). The mean concentrations of Cu, Cd and Zn in crop soils were 2.9, 1.9 and 1.7 times higher than those concentrations in forest and orchard soils (Fig. 2, Table S2). The significantly ($P < 0.01$) high concentrations of Cu, Cd and Zn indicate an enrichment from agricultural inputs. This finding is in accordance with previous studies (Chen et al., 2008b; Lu et al., 2012; Micó et al., 2006; Wei and Yang, 2010).

For cropland, despite the main agricultural sources for Cd, Cu and Zn, some outliers for them may be partly attributed to the field burning, waste dump or other anthropogenic activities in the peri-urban area in Ningbo (Shi and Ganne, 2009; Zhu et al., 2017a). For forest soils, the top outliers for As, Cd, Cu and Pb shown in Fig. 2 were located mainly in nearby agricultural areas (less 200 m) (Fig. S1), indicate that the outliers may be caused by anthropogenic activities in agricultural areas (Madrid et al., 2002; Rodriguez Martin et al., 2006; Shi and Ganne, 2009; Ungureanu et al., 2017). The outliers of Cr and Ni in forest and orchard soils found in this study (Fig. 2, Fig. S1) may be caused by point pollution by anthropogenic activities, such as the local

field burning, the waste dumping and the nearby road dust (17 m and 50 m away from mountain road) (Sun et al., 2010), because widespread contamination with Cr and Ni has been reported in road dust (Wei and Yang, 2010).

3.2 Inter-relationship and source identification

3.2.1 PCA

PCA loading plot for trace elements, macro elements and basic soil properties in peri-urban soils is shown in Fig. 3. Almost all forest and orchard soils were clustered on the left, indicating that the samples were less contaminated than crop soils. In contrast, almost all crop soils were located on the right, which suggests trace elements enrichment. Two forest soils in the upper left quadrant had high Cr and Ni concentrations, which may attribute to point pollution by anthropogenic activities, such as the local field burning, the waste dumping and the nearby road dust (Sun et al., 2010). Cd, Cu and Zn line angles were sharp and strongly related to the first axis, indicating that they likely had the same above-mentioned agricultural sources. The Cr and Ni distribution differed from those of other trace elements, and the mean Cr and Ni concentrations were low (Fig. 2), indicating that Cr and Ni were predominantly controlled by the parent material and paedogenic processes, which is consistent with the findings of previous studies (Chen et al., 2008b; Křibek et al., 2010; Rodriguez et al., 2008; Sun et al., 2013; Zhao et al., 2014).

PCA for trace element concentrations in crop soils and in forest and orchard soils is shown in Table 2. For crop soils, trace elements could be grouped into a two-component model that accounted for 66% of the total variance. The rotated component matrix showed that As, Cr and Ni were associated with the first principal component (PC), and the PC2 included Cd, Cu, Pb and Zn. For forest and orchard soils, trace elements were grouped into a three-component model that accounted for 73% of the total variance. The rotated component matrix showed that

Cr, Ni and Pb were associated with the PC1, and the PC2 included Cd and Cu, while As and Zn belong to PC3. The results in crop soils and in the forest and orchard soils both imply that Cr and Ni can be defined as natural components. That Pb loading of the PCA differed to Cr and Ni, and concentrations differed in comparison with forest, orchard and crop soils (Table 2), implying Pb pollution in crop soils. Given the low As concentrations and coefficients of variation in forest and orchard soils, the As may derive mainly from atmospheric deposition. In forest and orchard soils, Zn had the similar situation with As. But in crop soils, Zn had a significant enrichment and had similar agricultural sources with Cd and Cu.

3.2.2 Correlations between different elements and soil properties

The correlation matrices between different element concentrations are presented in Fig. 4 and Table S3. Significant correlations between Cr and Ni were found both in forest and orchard soils ($R = 0.91$, $P < 0.01$) and in crop soils ($R = 0.77$, $P < 0.01$) (Fig. 4), these correlations, together with the low mean concentrations, indicated an above-mentioned lithogenic origin (Rodriguez et al., 2008; Sun et al., 2013; Zhao et al., 2014). This finding can also be confirmed by the results of PCA. With the exception of Zn, Pb have significantly positive correlations with other trace elements in crop soils. A similar situation occurred for As. Both As and Pb have significant correlations with Cr and Ni in forest and orchard soils, and significant correlations with Cd in crop soils (see Fig. S2 in supporting information). The results imply atmospheric deposition induced by fossil fuel combustion may cause the enrichment of As and Pb in crop soils. It is reported that atmospheric deposition (such as cement, coal and oil combustion dust, metallurgic dust, vehicle exhaust particles) is the main source of As and Pb (Duan and Tan, 2013; Scudlark and Church, 1988; Shi et al., 2012; Shotyk et al., 1996; Zheng et al., 2004). This finding can be partly confirmed by the correlation ($R = 0.52$, $P < 0.01$) between As with Pb in crop soils (Fig. 4, Table S3), as both them were dominated by fossil fuel

combustion in eastern China (Duan and Tan, 2013; Shi et al., 2012). No correlations between Zn and As, and Pb imply the source is not likely the fertilisers. Close correlations between metal (Cd, Cu and Zn) concentrations in crop soils suggested these elements had the same or similar pollution sources (Hernandez et al., 2003; Sun et al., 2010). This finding was partly in accordance with previous studies in which Cd, Cu and Zn were found to be related to agricultural pollution in agricultural soils (Chen et al., 2008b; Lu et al., 2012; Micó et al., 2006; Wei and Yang, 2010).

The correlation matrix between the concentrations of trace elements and soil properties (including macro elements) in peri-urban soils is shown in Table 3. Significant negative correlations between trace elements and altitude, and C/N indicate the trace element concentrations differed by land use, since forest sites usually located in high altitude (mean altitude, 138 m; range, 19 to 412 m) and rich in carbon concentrations (plant litter) and with lower contaminant burdens in contrast to the crop sites (mean altitude, 25 m; range, -3 to 74 m). Altitude was not correlated with As and Ni concentrations, which confirmed that both of them were derived from origin that is supposed to be independent of altitude. The distribution of the C/N ratio was similar with the altitude due to the significant positive correlation between them ($R = 0.74$, $P < 0.001$) (see Table S4 and Fig. S3 in supporting information). The correlation results for a specific type of land use showed weak correlation between the concentrations of trace elements and soil properties, especially for the forest and orchard land shown in Table 3. This differed from the significant correlated results derived from packaged all data.

Significant positive correlations between metal (Cd and Cu) concentrations and P concentration (Table 3, Fig. 4) in crop soils indicate they have a possible same agricultural origin. Fertiliser application may be the origin, because P, Cu and Cd is closely associated with both inorganic and organic fertilisers, such as application of livestock manure, compost and

phosphate (Alloway, 2013; Eghball and Gilley, 1999; Gimeno-García et al., 1996; Nicholson et al., 2003). Calcium was significantly correlated with Cd, Cu and Zn (Table 3, Fig. 4), especially for Ca and Zn. Close relationship between Ca concentration and P concentration ($R = 0.61$, $P < 0.01$) (Fig. 4) suggests Ca and P are most likely derived from application of inorganic fertilisers, most likely the calcium phosphate and calcium superphosphate mentioned above. Gimeno-García et al. (1996) evaluated the concentrations of Cd, Cu and Zn in different inorganic fertilisers (urea, calcium superphosphate, iron sulphate and copper sulphate) in rice farming areas and found that calcium superphosphate contained the highest concentrations of Cd, Cu and Zn as impurities. Close relationship between Ca and P also implies that both Ca and P are effective indicators and factors explaining the variations of Cd, Cu and Zn in peri-urban soils in Ningbo. Besides, organic fertilisers, such as livestock manure or its derivatives, are usually composted nearby field and used commonly as a soil nutrient source in most of the fields (Xiang et al., 2018; Zheng et al., 2018). This compost (and pesticides) are also in enrichment with trace elements, especially for Cu and Zn and contribute partially to the pollution (Alloway, 2013; Bolan et al., 2003; Gimeno-García et al., 1996; Nicholson et al., 2003).

3.2.3 Pb isotopic composition analysis

Regression analysis (Fig. 5a) showed a significant linear relationship ($R^2 = 0.41$, $P < 0.001$) between Pb concentration and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios. In Fig. 5b, the points of cropland and points of forest and orchard have much overlapping areas. These linear relationship ($R^2 = 0.60$, $P < 0.001$) suggests that the Pb in peri-urban soils was mainly derived from a single, widespread source, or mixed origins with similar isotopic compositions, such as anthropogenic aerosols mostly containing coal and oil combustion dust, metallurgic dust, cement (Duan and Tan, 2013; Wang et al., 2000; Zheng et al., 2004). In Fig. 5b, the $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of

cropland are located mainly at the lower left, whilst the ratios from forest and orchard soils are located mainly at the upper right, especially for orchards. Given the relatively high Pb concentration in crop soils in comparison with forest and orchard soils, the differences in Pb isotope compositions for different land uses suggest the forest and orchard soils is less contaminated than crop soils. This is due to the effect of canopy interception on the atmospheric deposition. Atmospheric deposited elements have been found to be accumulated in the canopy of the forest for several years and can be release to the soil by rainfall and fire (Erel et al., 1997; Ettler et al., 2014; Iverfeldt, 1991; Lindberg, 1989).

The range of Pb isotopic compositions is consistent with the range of Pb isotopic compositions of atmospheric deposition. The range of Pb isotopic composition of crop soils in this study was similar with the range of Pb isotope ratios of PM₁₀ aerosols in Shanghai (ca. 110 km away from this study area) and air in other area (Chen et al., 2005a; Komárek et al., 2008; Mukai et al., 2001; Zheng et al., 2004). However, the range of Pb isotopic composition in our peri-urban soils is similar to the range of deep soil (80-100 cm), while differed from the range of atmospheric deposition reported in Hu et al. (2018)'s study which investigated in peri-urban area of Nanjing City (ca. 330 km away from this study area). These findings indicated that the Pb in peri-urban soils of Ningbo city was likely derived from both natural origin and atmospheric deposition. Given the significant positive correlation between Pb and other (both contaminant and not contaminant) elements in peri-urban soils, the slight enrichment in Pb in crop soils compared with forest and orchard soils may attribute to atmospheric deposition induced by fossil fuel combustion (Cheng and Hu, 2010; Dach and Starmans, 2005; Sun et al., 2013). Besides, atmospheric deposition could contribute to As and Cu enrichments (Al-Khashman, 2004; Hernandez et al., 2003; Rodriguez et al., 2008). The Pb ratios of the two outliers in this study are similar to that of vehicle exhaust (unleaded) (Chen et al., 2005a), but the two locations are far from main roads. These two outliers may be attributed to local field

burning or to fumes from metal smelting due to the similar isotopic compositions (Komárek et al., 2008).

In this peri-urban areas, Cd, Cu and Zn were contaminant elements mainly derived from fertiliser application, and As and Pb were possibly influenced by atmospheric deposition. Hu et al. (2018)'s study suggested that atmospheric deposition along with fertilization were the major sources of heavy metals accumulation, and the relative contribution of atmospheric deposition reaches up to 33.0% compared with fertiliser application (33.8%), industrial emission (25.4%) and soil parent materials (10.8%) in the peri-urban soils of Nanjing city (also belong to the Yangtze River Delta region). While in our study, the influence of atmospheric deposition is relative weak. A possible explanation is that the two study areas are within a subtropical monsoon climate zone. The prevailing wind directions are southeast in summer, and Ningbo city locates in the southeast of the Nanjing city. These resulted in the different influence of atmospheric deposition at the two study areas. Another study in two contrasting peri-urban areas of Yangtze River Delta Region showed that application of large amounts of cow manure to vegetables had caused an accumulation of P, Cu, Zn and available Cd in soil (Huang et al., 2006). The common points for above mentioned studies in peri-urban soils in the Yangtze River Delta region are intensive agricultural production, extensive fertiliser application, many types of crops and related rotation patterns to satisfy the increasing food demands from urban areas. Generally, fertiliser application is an important input for elements contaminant (Cd, Cu and Zn) in crop soils with effectively indicated by Ca and P in this area, but the specific contaminant and indicative elements are depended on the element compose in applied fertilisers.

4 Conclusions

The results showed that the soil trace element concentrations differed according to the type

of land use in peri-urban areas. The mean concentrations of Cd, Cu and Zn in crop soils were significantly higher than their background values of Ningbo and those in forest and orchard soils, i.e., Cd, Cu and Zn are contaminant elements in this peri-urban areas. Despite the contaminant elements, the Cr and Ni are dominant via soil formation. Atmospheric deposition may lead to the difference in As and Pb concentrations between land uses. Application of fertilisers, calcium phosphate and calcium superphosphate, livestock manure and compost, are the dominant source of pollutants in the peri-urban soils in Ningbo, especially for Cd, Cu and Zn. Calcium and P are effective indicators of trace element contaminant (Cd, Cu and Zn) for peri-urban soils in Ningbo city in eastern China. The trace element distribution in peri-urban areas with complex land use patterns require long-term monitoring and continuous study to identify influences on ecological health, especially in areas that are undergoing rapid urbanisation. This study enhances our ability to understand the sources of trace elements in peri-urban soils and is beneficial for pollution control.

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