

RELATIONSHIPS BETWEEN FRACTIONATIONS OF Pb, Cd, Cu, Zn AND Ni AND SOIL PROPERTIES IN URBAN SOILS OF CHANGCHUN, CHINA

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ABSTRACT: An extensive soil investigation was conducted in different domains of Changchun to disclose the fractionations of Pb, Cu, Cd, Zn and Ni in urban soils. Meanwhile correlation analysis and multiple stepwise regressions were used to define relationships between soil properties and metal fractions and the chief factors influencing the fractionation of heavy metals in the soils. The results showed that Pb, Ni and Cu were mainly associated with the residual and organic forms; most of Cd was concentrated in the residual and exchangeable fractions. Zn in residual and carbonate fraction was the highest. The activities of the heavy metals probably declined in the following order: Cd, Zn, Pb, Cu and Ni. The chemical fractions of heavy metals in different domains in Changchun City were of significantly spatial heterogeneity. Soil properties had different influences on the chemical fractions of heavy metals to some extent and the main factors influencing Cd, Zn, Pb, Cu and Ni fractionation and transformation were apparently different.

KEY WORDS: urban soils; heavy metal; fractionation; soil properties

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1 INTRODUCTION

With the rapid development of urbanization, urban land was exploited and utilized to form different domains being subject to many potential pollution sources such as vehicle emission, industrial activities and household garbage. Particularly, urban soils are seriously polluted by heavy metals, which do damage not only to urban environment but also to public health either as suspended dust breathed by residents via respiratory tracts and ingested by human body via the hand-mouth path (WATT *et al.*, 1993; DE MIGUEL *et al.*, 1997; MIELKE *et al.*, 1999) or by directly drinking ground water polluted by heavy metals. Several authors have indicated that there is the significant exponential relationship between the blood Pb level and the content of Pb in urban soils (WU *et al.*, 2003), and there is sufficient evidence that a high blood Pb level causes decrease in children's IQ scores, retardation of physical growth, hearing problems and impaired learning (BELLINGER *et al.*, 1990; DIETRICH *et al.*, 1990).

The harmfulness of heavy metals principally depends on the proportion of their mobile forms (MA and RAO, 1997; IMPERATO *et al.*, 2003). The forms of a metal, which determines its mobility, toxicity and behavior in the environment (MUSTAFA, 2003), can be examined by the sequential extraction method proposed by TESSIER *et al.* (1979). The method provides the information on the differentiation of bonding strength of metals on various solid phases and their potential reactivity (WILCKE *et al.*, 1999; LU *et al.*, 2003). The soluble and exchangeable fractions are considered readily mobile, while the residual fraction is relatively inactive (LI, 2001). The binding mechanism of heavy metals depends on the properties of soils, which play an important role for the rate of chemical transformation of an element in a solid phase (SPOSITO, 1989). Up to now, the chemical fractions of heavy metals, particularly their relations to soil properties in urban soils have seldom been studied. The objective of the present work is to investigate the distribution of Pb, Cd, Cu, Zn and Ni fractions and the relationships with soil properties in the

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urban soils of Changchun.

2 MATERIAL AND METHODS

2.1 Study Area

Changchun City is located in the middle part of North-east China (43°05′–45°15′N, 124°18′–127°02′E) and at the center part of the Northeast Plain and temperate zone. The urban area of the city occupies an area of 3583km², with approximately 2.98×10⁶ inhabitants. The climate is semi-humid and monsoon one with 4.6℃ of average annual temperature and 567mm of average annual precipitation.

2.2 Sampling

A total of 39 sampling sites (Fig. 1) were chosen to reflect different land use types, which were named development areas (A), roadsides (B), industrial areas (C), residential areas (D), urban parks (E), squares (F), and plant gardens (G), respectively. The soil samples were sieved to pass through a 2-mm sieve for determining soil properties and heavy metal fractionations. A part of each sample was ground further to pass through a nylon sieve with 0.15-mm openings for the total content analysis of heavy metals.

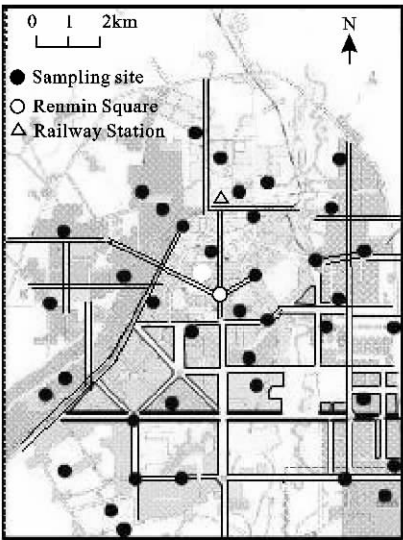


Fig. 1 Sampling sites in different domains of Changchun

2.3 Determination of Soil Properties and Fractionations of Heavy Metals

Particle size distribution was determined by pipette method (GEE and BAUDER, 1986). Soil chemical properties were determined as follows: pH and organic matter (OM) (AVERY and BASCOMB, 1974); cation ex-

changeable capacity (CEC) (CHAPMAN, 1965); electrical conductivity (EC) (LUIS *et al.*, 2002); redox potential (Eh) (FAULKNER *et al.*, 1989). Total Fe, Mn, Pb, Cd, Cu, Zn and Ni were determined by treating soil with *aqua regia* in microwave oven (KINGSTON and HASWELL, 1997). Some properties of soils and the total contents of heavy metals used in the study are given in Table 1.

Table 1 Physico-chemical properties of the urban soils

| Index | Mean | Standard deviation | Range |
|-------------------------|--------|--------------------|---------------|
| pH (H ₂ O) | 7.68 | 0.75 | 5.41–8.59 |
| OM (%) | 5.10 | 2.92 | 1.50–12.78 |
| CEC (cmol/kg) | 35.40 | 4.18 | 26.30–45.22 |
| Eh (mv) | 381 | 46 | 300–524 |
| EC (mS/cm) | 0.38 | 0.28 | 0.16–1.32 |
| Sand (1–0.05mm) (%) | 62.54 | 8.86 | 48.29–78.72 |
| Silt (0.05–0.005mm) (%) | 14.44 | 5.25 | 5.70–30.29 |
| Clay (<0.005mm) (%) | 13.61 | 4.48 | 5.70–21.82 |
| Total Fe (%) | 2.61 | 0.49 | 1.38–4.80 |
| Total Mn (mg/kg) | 531.54 | 91.63 | 428.30–838.40 |
| Total Pb (mg/kg) | 54.81 | 25.94 | 18.93–133.50 |
| Total Cd (mg/kg) | 2.92 | 0.24 | 1.85–11.10 |
| Total Cu (mg/kg) | 41.85 | 18.65 | 9.82–116.60 |
| Total Zn (mg/kg) | 109.69 | 44.22 | 41.98–232.50 |
| Total Ni (mg/kg) | 73.50 | 17.30 | 39.79–139.40 |

The sequential extraction procedure of TESSIER *et al.* (1979) and BRUDER-HUBSCHER *et al.* (2002), selected for this study, was designed to separate the heavy metals into exchangeable (F₁), bound to carbonate (F₂), bound to Fe-Mn oxides (F₃), bound to organic matter (F₄) and residual phase (F₅). All metals were determined with FAAS.

Multiple stepwise regressions were used to determine the principal factors influencing fraction distribution of heavy metals in the urban soils.

3 RESULTS AND DISCUSSION

3.1 Fractionations of Heavy Metals

Pb, Cd, Cu, Zn and Ni fractions expressed as percentages of total contents were listed in Table 2. The results showed that the fractionations of heavy metals appeared great variability among soils. Pb was primarily associated with the residual and organic matter. The percentage of Pb fraction followed the order of the residual>organic>carbonate>Fe-Mn oxide>exchangeable.

Similar to Pb, the residual and organic fractions were also the primary fractions for Cu, while the lowest percentage was the carbonate. The very high percentage of Cu in the organic matter showed that Cu had high affinity with organic matter (IMPERATO *et al.*, 2003).

Table 2 Pb, Cd, Cu, Zn and Ni fractions expressed as percentage of sum of fractions (%)

| | | F ₁ | F ₂ | F ₃ | F ₄ | F ₅ |
|----|-----------|----------------|----------------|----------------|----------------|----------------|
| Pb | Mean±S.D. | 0.67±0.83 | 14.69±10.15 | 10.52±5.03 | 27.83±10.14 | 46.28±18.79 |
| | Range | ND-4.37 | 1.75-63.52 | 1.92-20.24 | 7.61-55.66 | 10.00-88.34 |
| Cd | Mean±S.D. | 18.99±11.67 | 12.99±7.76 | 6.45±3.02 | 6.24±2.45 | 55.32±15.57 |
| | Range | 0.44-59.23 | ND-29.18 | 1.86-15.78 | 0.72-11.62 | 10.01-79.36 |
| Cu | Mean±S.D. | 6.81±4.12 | 1.42±0.86 | 4.99±2.69 | 18.80±11.61 | 67.98±15.26 |
| | Range | 0.26-27.69 | 0.35-5.72 | 2.22-19.06 | 1.72-58.86 | 6.46-89.30 |
| Zn | Mean±S.D. | 2.47±2.41 | 19.90±11.74 | 14.65±5.80 | 13.15±4.48 | 49.94±19.13 |
| | Range | 0.26-9.54 | 5.45-58.66 | 1.88-26.73 | 3.30-24.92 | 6.21-88.08 |
| Ni | Mean±S.D. | 4.53±4.78 | 1.04±0.84 | 6.30±2.37 | 7.84±2.83 | 80.40±5.55 |
| | Range | 0.00-15.85 | 0.00-2.94 | 0.99-10.87 | 1.31-15.08 | 66.91-92.72 |

Note: ND: not determined

The amount of Cu in each fraction followed the order: the residual>organic>exchangeable>Fe-Mn oxide>carbonate.

Most of Cd was concentrated in the residual and exchangeable fractions. The very high percentage of exchangeable Cd in the urban soils indicated that there might be very significant effect on environments. The amount of Cd in each fraction followed the order: residual>exchangeable>carbonate>Fe-Mn oxide>organic matter. The result was in agreement with the observations of MA and RAO (1997). The percentage of Zn fractions followed the order of the residual>carbonate>Fe-Mn oxide>organic matter>exchangeable. Ni was strongly associated with the residual phase with lowest amount in the carbonate fractions. The percentage of the other three fractions was rather low.

It has been suggested that the activities of metals decrease approximately in the order of the extraction sequence from readily available to unavailable because the strength of extraction reagents used increases in this order (TESSIER *et al.*, 1979). The exchangeable metals are most active in the environment among these fractions. The carbonate can become easily migrated and transformed under conditions of lower soil pH. Generally, the exchangeable and carbonate metals are considered to be active fractions in the environments (WU *et al.*, 2003). According to the above results of distribution of heavy metal fractions in the urban soils, the percentage of Pb, Cd, Cu, Zn and Ni in active fractions accounted for 15.36%, 31.98%, 8.23%, 22.36% and 5.57%, respectively, which showed that mobility of the five metals probably declined in the following order: Cd, Zn, Pb, Cu and Ni.

The chemical fractions of heavy metals in different domains in Changchun City were of significantly spatial heterogeneity (Fig. 2). For the percentage of the exchangeable fraction, Cd was relatively high and Pb was rather low in all domains; Cu was the highest in industrial areas,

while the lowest in roadsides; Ni was the highest in urban parks and the lowest in industrial areas, and Zn was highest in urban parks and lowest in residential areas.

The amounts of the carbonate Cd, Pb and Zn were higher than that of Cu and Ni in all domains. The percentage of the carbonate Pb was the highest in residential areas, while that was the lowest in urban parks. It showed that the health of inhabitants lived in the residential areas may be seriously damaged by Pb. The percentage of Cd in carbonate fraction was the highest in industrial areas, while the lowest in urban parks. The carbonate Zn was highest in industrial areas and lowest in the development areas. The carbonate Cu and Ni were rather low and almost equal in all domains.

The percentages of metals bound on Fe-Mn oxides in all domains followed the order Zn>Pb>Cd>Ni>Cu. The Cd, Pb and Cu bound on Fe-Mn oxides was the highest in industrial areas, while those of Cd, Pb and Cu were lowest in gardens and parks. The Zn bound on Fe-Mn oxides was almost equal in development areas, industrial areas and public squares, averaged 17.48%. The Ni bound on Fe-Mn oxides was highest in roadsides and lowest in parks.

The Pb organic fraction was higher than those of other metals in all domains, and the organic fractions of Cu and Zn were higher than those of the Cd and Ni in all domains. The amounts of the residual Cu and Ni were higher than those of Pb, Cd and Ni in all domains. The residual Pb was the highest in the plant gardens, while the lowest in the residential areas. The residual Cd was the highest in development areas and lowest in residential areas. The percentage of the residual Cu was also highest in the development areas, while lowest the industrial areas. The residual Ni in all the domains was rather high. The amount of the residual Zn was the highest in the development areas, while the lowest in the industrial areas.

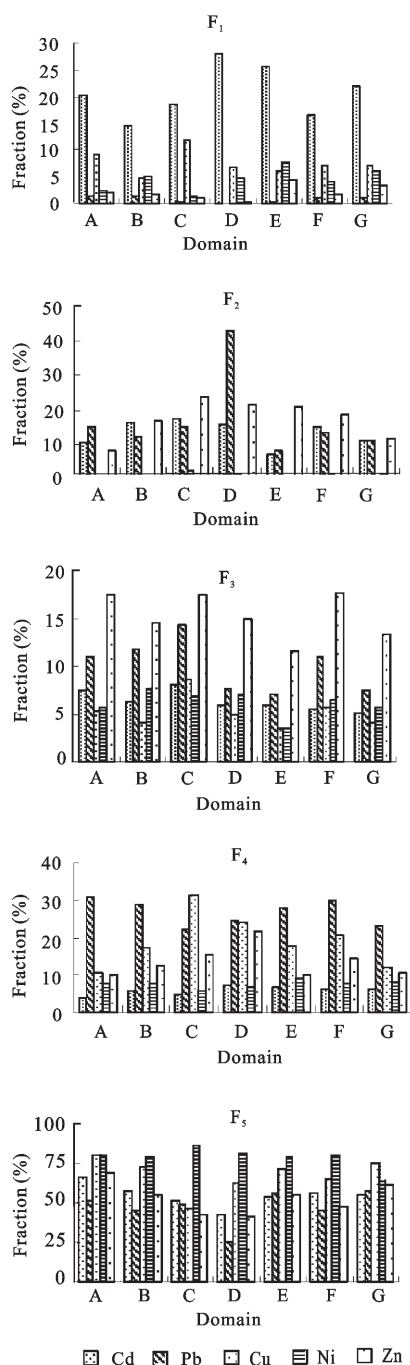


Fig. 2 Mean fractions of Pb, Cd, Cu, Ni and Zn in different domains of the urban soils

The active Pb in all the domains averaged 16.70%, 13.85%, 15.36%, 42.48%, 8.84%, 14.75%, and 12.12%, respectively, and hence the mobility of Pb followed the order of residential areas > development areas > industrial areas > public squares > roadsides > plant gardens > parks. The active amount of Cd in the residential areas was the highest, accounting for 43.88%. Therefore the high active amount of Pb and Cd in the residential areas sug-

gested that Pb and Cd might seriously hazard the health of inhabitants. The amounts of the active Zn in all the domains were rather high. The active amount of Cu in the industrial areas was highest, and the lowest in the roadsides. The amount of the active Ni was lower than 10% in all domains.

3.2 Relationships between Pb, Cd, Cu, Zn and Ni Fractions and Soil Properties

The soil properties play an important role for the fractionation and transformation of heavy metals in soils. As shown in Table 3, urban soil properties had different influences on the fractionations of the metals. The contents of Cd and Zn in exchangeable fractions were significantly and negatively correlated with the soil pH, and significantly and positively correlated with CEC, respectively. This may be related to the fact that pH is the main soil characteristic to influence CEC of soils and the dominant ionic forms in solution (ULRICH, 1983). The pH and CEC were also reported as soil characteristics to respect to soil adsorption of elements such as Cd and Zn (CHRISTENSEN, 1984). When the soil was in oxidation state, the portion of the exchangeable Zn increased with Eh. The amount of the exchangeable Ni was significantly and negatively correlated with the soil EC, and significantly and positively correlated with clay content.

There were the significantly positive correlations between the amounts of Cd and Cu in carbonate phases and pH probably due to deposition of Cd and Cu in the high pH. The CEC had significantly negative influences on the amount of the carbonate metals. The positive correlations between the contents of carbonate Cd, Pb and Zn and sand content in urban soils showed that carbonate metals might be contained in sand grains of the soils.

The Eh was significantly and negatively correlated with the Fe-Mn oxide metals. The amounts of Pb and Cu in Fe-Mn oxide fractions were significantly influenced by the soil pH and CEC. The amount of Ni bound on Fe-Mn oxides was significantly influenced by pH and sand content. The organic Cu was better correlated with EC, OM, silt and clay contents, and that of the organic Zn was significantly correlated with CEC and soil texture. The content of the organic Ni was significantly and negatively correlated with pH and significantly and positively correlated with CEC, Eh, OM and total Fe.

The amount of Cu in residual fractions was better correlated with CEC, total Fe and Eh, and the amount of Zn correlated with Eh and total Fe. The content of Ni in residual fractions was significantly and positively correlated with total Fe and Mn. The content of the residual Cd was significantly influenced by Eh, total Fe and soil

Table 3 Correlation coefficients between percentage of metal fractions and urban surface soil properties ($n=39$)

| Form | Metal | pH | EC | CEC | OM | Eh | Sand | Silt | Clay | Fe | Mn |
|----------------|-------|----------|---------|----------|---------|----------|---------|---------|----------|---------|---------|
| F ₁ | Cd | -0.388 * | -0.007 | 0.363* | 0.223 | 0.111 | -0.167 | -0.033 | -0.007 | -0.009 | -0.183 |
| | Pb | 0.154 | -0.122 | 0.007 | 0.018 | -0.027 | -0.032 | 0.021 | 0.147 | 0.058 | -0.091 |
| | Cu | -0.235 | -0.087 | 0.076 | 0.051 | 0.155 | 0.036 | -0.123 | -0.190 | -0.131 | -0.114 |
| | Zn | -0.484** | -0.127 | 0.349* | 0.173 | 0.318* | -0.254 | -0.02 | 0.055 | -0.293 | -0.197 |
| | Ni | -0.246 | -0.330* | 0.252 | 0.283 | 0.265 | -0.288 | 0.116 | 0.313* | -0.090 | 0.016 |
| F ₂ | Cd | 0.508** | 0.254 | -0.460** | 0.139 | -0.294 | 0.620** | -0.362* | -0.480** | -0.075 | -0.042 |
| | Pb | 0.263 | 0.139 | -0.411** | -0.094 | -0.240 | 0.460** | -0.324* | -0.300 | -0.197 | -0.143 |
| | Cu | 0.362* | 0.217 | -0.398** | -0.18 | -0.368* | 0.284 | -0.164 | -0.170 | -0.158 | -0.158 |
| | Zn | 0.124 | -0.011 | -0.381* | 0.052 | -0.119 | 0.305* | -0.362* | -0.320* | -0.283 | -0.200 |
| | Ni | -0.003 | -0.105 | -0.089 | 0.203 | -0.209 | 0.154 | -0.092 | -0.188 | -0.085 | -0.278 |
| F ₃ | Cd | 0.094 | 0.172 | -0.028 | 0.033 | -0.358* | 0.093 | -0.144 | -0.127 | -0.021 | -0.114 |
| | Pb | 0.441** | -0.057 | -0.437** | -0.287 | -0.340* | 0.328* | -0.195 | -0.065 | -0.294 | 0.000 |
| | Cu | 0.400** | 0.136 | -0.424** | -0.277 | -0.340* | 0.290 | -0.230 | -0.208 | -0.075 | -0.096 |
| | Zn | 0.152 | -0.035 | -0.231 | 0.079 | -0.398** | 0.242 | -0.165 | -0.174 | -0.176 | -0.239 |
| | Ni | 0.515** | 0.225 | -0.200 | -0.026 | -0.149 | 0.318* | 0.005 | -0.101 | 0.036 | 0.286 |
| F ₄ | Cd | -0.008 | 0.164 | -0.002 | -0.16 | -0.174 | 0.104 | -0.327* | -0.163 | 0.064 | -0.107 |
| | Pb | -0.14 | -0.153 | 0.014 | 0.116 | 0.002 | 0.078 | -0.113 | -0.091 | -0.108 | -0.259 |
| | Cu | 0.029 | 0.352* | -0.231 | 0.336* | 0.064 | 0.300 | -0.306* | -0.468** | -0.078 | -0.218 |
| | Zn | 0.282 | 0.244 | -0.538** | 0.211 | -0.291 | 0.624** | -0.96** | -0.545** | -0.231 | -0.317 |
| | Ni | -0.377* | 0.009 | 0.424** | 0.416** | 0.365* | -0.187 | 0.217 | -0.007 | 0.431** | -0.027 |
| F ₅ | Cd | -0.120 | -0.130 | 0.273 | -0.020 | 0.396** | -0.337* | 0.372* | 0.321* | 0.490** | 0.242 |
| | Pb | -0.104 | 0.116 | 0.144 | 0.228 | 0.275 | -0.089 | 0.055 | -0.023 | 0.330* | 0.142 |
| | Cu | -0.274 | -0.151 | 0.379* | 0.049 | 0.386* | -0.277 | 0.119 | 0.211 | 0.435** | 0.055 |
| | Zn | -0.143 | 0.157 | 0.286 | 0.091 | 0.310* | -0.127 | 0.076 | 0.006 | 0.427** | 0.234 |
| | Ni | -0.148 | 0.055 | 0.172 | -0.202 | 0.196 | -0.224 | 0.227 | 0.167 | 0.624** | 0.510** |
| Active | Cd | -0.245 | 0.061 | 0.267 | 0.265 | 0.041 | -0.037 | -0.076 | -0.098 | -0.035 | -0.145 |
| | Pb | 0.180 | 0.244 | -0.342* | 0.067 | -0.090 | 0.449** | -0.344* | -0.369* | -0.195 | -0.147 |
| | Cu | -0.136 | 0.176 | 0.079 | 0.104 | 0.102 | 0.047 | -0.089 | -0.156 | -0.164 | -0.150 |
| | Zn | -0.138 | 0.033 | -0.128 | 0.245 | 0.104 | 0.199 | -0.368* | -0.362* | -0.249 | -0.216 |
| | Ni | -0.232 | -0.328* | 0.222 | 0.300 | 0.213 | -0.245 | 0.094 | 0.262 | -0.099 | -0.322* |

Notes: *Significant at 5% level, **Significant at 1% level

texture, and the residual Pb was correlated with total Fe.

The content of active Pb was significantly and positively correlated with sand content, and significantly and negatively correlated with CEC, silt and clay contents. The amounts of active Pb and Zn were concerned with particle composition. The content of active Zn was influenced by the soil texture. The content of active Ni was significantly and negatively correlated with EC and total Mn, respectively.

It is complex for the influences of the soil properties on the fraction of heavy metals in the urban soil, furthermore among of the soil properties are of different influences one another. Therefore stepwise regression analysis was necessarily used to establish dependent equations so as to disclose influences of the principal soil factors on the fractionation of heavy metals (Table 4). According to variance analysis of dependent equation, it was apparently different for influences of the main soil factors on the fractionation of Cd, Zn, Pb, Cu and Ni. The soil pH and texture was major factors influencing the exchangeable Cd, Cu, Pb and Ni. The exchangeable Cd and

Cu were chiefly correlated with CEC and total Fe, exchangeable Ni was also correlated with EC, OM and total Fe, and exchangeable Zn principally influenced by pH and total Mn. The amounts of Cd, Cu and Ni associated with carbonate fractions were mainly influenced by pH and soil texture, while the carbonate Pb was mainly correlated with total Mn and sand content. The amount of Cd bound to Fe-Mn oxide was influenced by CEC, OM, Eh, total Fe, that of Cu influenced by soil pH, OM and total Fe, that of Pb influenced by pH, EC, OM and total Fe, that of Zn influenced by EC, OM, Eh and total Fe, and that of Ni correlated with pH, EC, Eh and total Mn. The contents of the organic Cd and Ni were influenced by CEC, Eh and soil texture, that of Pb influenced by total Mn, that of Cu influenced by EC, OM, total Fe, clay and silt contents, that of Zn influenced by CEC, OM, sand content and total Mn. The residual fractions of Pb, Cu and Zn were all chiefly correlated with Eh and soil texture. The residual fractions of Cd and Ni were all correlated with OM and soil texture. It was principal influence of the CEC, pH, sand and silt contents on the

Table 4 Dependent equations for the chemical fractions of heavy metals correlated to principal factors in urban soils

| Fraction | Metal | Equation | <i>R</i> | <i>F</i> | <i>P</i> |
|----------------|-------|--|----------|----------|----------|
| F ₁ | Cd | $Y = -4.687 - 0.398X_{\text{pH}} + 0.399X_{\text{EC}} + 0.169X_{\text{CEC}} + 0.055X_{\text{Sand}} - 0.466X_{\text{Fe}}$ | 0.638 | 4.331 | <0.01 |
| | Pb | $Y = -0.431 + 0.080X_{\text{pH}} - 0.020X_{\text{Silt}} + 0.032X_{\text{Clay}}$ | 0.305 | 1.153 | <0.5 |
| | Cu | $Y = 2.855 - 0.128X_{\text{pH}} + 0.0525X_{\text{CEC}} - 0.049X_{\text{Clay}} - 0.250X_{\text{Fe}}$ | 0.428 | 1.725 | <0.5 |
| | Zn | $Y = 23.685 - 2.286X_{\text{pH}} - 0.006X_{\text{Mn}}$ | 0.497 | 6.410 | <0.01 |
| | Ni | $Y = 10.437 - 0.812X_{\text{pH}} - 2.281X_{\text{EC}} + 0.450X_{\text{OM}} - 0.235X_{\text{Silt}} + 0.500X_{\text{Clay}} - 2.263X_{\text{Fe}}$ | 0.662 | 4.133 | <0.01 |
| F ₂ | Cd | $Y = -35.703 + 2.660X_{\text{pH}} + 0.494X_{\text{OM}} + 0.412X_{\text{Sand}}$ | 0.685 | 9.636 | <0.001 |
| | Pb | $Y = -7.840 + 0.512X_{\text{Sand}} - 0.018X_{\text{Mn}}$ | 0.475 | 5.694 | <0.01 |
| | Cu | $Y = 3.817 + 0.114X_{\text{pH}} - 0.0513X_{\text{CEC}} + 0.051X_{\text{Silt}} - 0.832X_{\text{Fe}}$ | 0.950 | 6.068 | <0.01 |
| | Zn | $Y = 47.068 - 10.333X_{\text{Fe}}$ | 0.459 | 9.909 | <0.01 |
| | Ni | $Y = 4.343 - 0.145X_{\text{pH}} - 0.637X_{\text{EC}} + 0.070X_{\text{OM}} - 0.006X_{\text{Eh}} - 0.026X_{\text{Clay}}$ | 0.516 | 2.319 | <0.5 |
| F ₃ | Cd | $Y = 13.054 + 0.220X_{\text{CEC}} + 0.144X_{\text{OM}} - 0.028X_{\text{Eh}} - 1.776X_{\text{Fe}}$ | 0.493 | 2.459 | <0.05 |
| | Pb | $Y = 4.968 + 2.277X_{\text{pH}} - 3.621X_{\text{EC}} - 0.278X_{\text{OM}} - 3.473X_{\text{Fe}}$ | 0.628 | 4.882 | <0.01 |
| | Cu | $Y = 4.580 + 0.855X_{\text{pH}} - 0.165X_{\text{OM}} - 2.022X_{\text{Fe}}$ | 0.595 | 6.068 | <0.01 |
| | Zn | $Y = 43.156 - 5.254X_{\text{EC}} + 0.593X_{\text{OM}} - 0.061X_{\text{Eh}} - 2.762X_{\text{Fe}}$ | 0.554 | 3.371 | <0.01 |
| | Ni | $Y = -13.430 + 1.419X_{\text{pH}} + 0.847X_{\text{EC}} + 0.012X_{\text{Eh}} + 0.004X_{\text{Mn}}$ | 0.655 | 5.609 | <0.01 |
| F ₄ | Cd | $Y = 3.650 + 2.374X_{\text{EC}} + 0.222X_{\text{CEC}} - 0.016X_{\text{Eh}} - 0.461X_{\text{Silt}} + 0.265X_{\text{Clay}} + 1.081X_{\text{Fe}}$ | 0.569 | 2.548 | <0.05 |
| | Pb | $Y = 45.013 - 0.0323X_{\text{Mn}}$ | 0.295 | 3.561 | <0.05 |
| | Cu | $Y = 6.910 + 9.700X_{\text{EC}} + 1.337X_{\text{OM}} - 0.713X_{\text{Silt}} - 0.882X_{\text{Clay}} + 9.470X_{\text{Fe}}$ | 0.676 | 5.289 | <0.01 |
| | Zn | $Y = 30.829 - 0.450X_{\text{CEC}} + 0.295X_{\text{OM}} + 0.119X_{\text{Sand}} - 0.020X_{\text{Mn}}$ | 0.800 | 12.508 | <0.001 |
| | Ni | $Y = -20.908 + 0.464X_{\text{CEC}} + 0.015X_{\text{Eh}} + 0.105X_{\text{Sand}} + 0.276X_{\text{Silt}} - 0.462X_{\text{Clay}}$ | 0.775 | 9.210 | <0.001 |
| F ₅ | Cd | $Y = -3.208 + 0.195X_{\text{pH}} - 0.0381X_{\text{OM}} + 0.006X_{\text{Eh}} + 0.513X_{\text{Fe}}$ | 0.621 | 4.705 | <0.01 |
| | Pb | $Y = -49.215 + 14.014X_{\text{EC}} + 0.114X_{\text{Eh}} - 0.983X_{\text{Clay}} + 15.751X_{\text{Fe}}$ | 0.483 | 2.332 | <0.5 |
| | Cu | $Y = -35.582 + 0.835X_{\text{CEC}} + 0.049X_{\text{Eh}} - 0.867X_{\text{Silt}} + 10.826X_{\text{Fe}}$ | 0.581 | 3.848 | <0.01 |
| | Zn | $Y = -75.565 + 30.663X_{\text{EC}} + 0.147X_{\text{Eh}} - 1.448X_{\text{Silt}} + 32.305X_{\text{Mn}}$ | 0.552 | 4.524 | <0.01 |
| | Ni | $Y = -8.682 + 9.372X_{\text{EC}} - 1.095X_{\text{OM}} - 0.607X_{\text{Silt}} + 0.040X_{\text{Mn}} + 21.597X_{\text{Fe}}$ | 0.808 | 9.617 | <0.001 |
| Active | Cd | $Y = -62.683 + 4.349X_{\text{pH}} + 0.946X_{\text{CEC}} + 0.418X_{\text{Sand}} - 0.758X_{\text{Clay}}$ | 0.644 | 5.292 | <0.01 |
| | Pb | $Y = 22.155 - 1.031X_{\text{CEC}} - 0.726X_{\text{OM}} + 0.230X_{\text{Sand}} + 1.163X_{\text{Clay}} - 0.034X_{\text{Mn}}$ | 0.640 | 4.377 | <0.01 |
| | Cu | $Y = 10.886 + 0.865X_{\text{pH}} - 0.183X_{\text{OM}} - 2.953X_{\text{Fe}}$ | 0.572 | 5.393 | <0.01 |
| | Zn | $Y = 77.117 - 10.654X_{\text{EC}} + 1.119X_{\text{OM}} - 16.164X_{\text{Fe}}$ | 0.511 | 3.943 | <0.1 |
| | Ni | $Y = 9.747 - 2.529X_{\text{EC}} + 0.423X_{\text{OM}} + 0.221X_{\text{Clay}} - 2.156X_{\text{Fe}}$ | 0.566 | 3.567 | <0.01 |

Notes: *R*: correlation coefficients; *F*: Fisher *F*-test; *P*: significant level

amount of the active Cd. It was important influence of CEC, OM, total Mn and soil texture on the active Pb. Moreover, pH, OM and total Fe were the important factors influencing the active Cu and OM, and total Fe were main factors influencing active Zn and Ni.

4 CONCLUSIONS

There was a significant difference in the fractionation of the heavy metals of the urban soils in Changchun City. Pb, Ni and Cu were mainly associated with the residual and organic matter; most of Cd was concentrated in the residual and exchangeable fractions. Zn content in residual and carbonate fraction was the highest. The active of the heavy metals probably declined in the following order: Cd, Zn, Pb, Cu and Ni.

The chemical fractions of heavy metals in soil in different domains in Changchun City were of significantly heterogeneity in space. The percentage of Cd in exchangeable fraction was the highest in residential areas,

while that lowest in development areas. The percentage of Pb bound on Fe-Mn oxide was the highest in industrial areas, while the lowest in urban parks. The percentage of Cu in exchangeable and Fe-Mn oxide fractions was the highest in industrial areas, while the lowest in urban parks. For Zn, the industrial areas were dominated by the carbonate, the residential areas was dominated by the organic, while the organic fraction was the lowest in public squares.

The pH and soil texture had important influence on the exchangeable fractions of Cd, Cu, Pb and Ni, and that of Zn was influenced by pH and total Mn, only. The amounts of Cd, Cu and Ni associated with carbonate fractions were chiefly influenced by pH and soil texture, while the carbonate Pb was chiefly influenced by total Mn and sand content and the carbonate Zn was chiefly influenced by total Fe. The amounts of Cd, Cu, Pb and Zn bound on Fe-Mn oxide were all influenced by OM and total Fe, and that of Ni was correlated with pH, EC, Eh and total Mn. The contents of the organic Cd, Ni, Cu

and Zn were all influenced by soil texture, and the content of Pb was influenced by total Mn. The residual fractions of Pb, Cu and Zn were all chiefly correlated with Eh and soil texture. The residual fractions of Cd and Ni were all chiefly correlated with OM and soil texture. It was principal influence of the CEC and soil texture on the amount of the active Cd and Pb, and was important influence of pH, OM and total Fe on the active Cu, and organic matters and total Fe were common factors influencing the active Zn and Ni.

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