Study on the factors affecting the spatial distribution of heavy metal elements

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Abstract: The contents of As, Cr, Cu, Zn and Pb in soils of the central urban area of Nanjing Jiangbei New area are analyzed by interpolation analysis. The effects of pH value, soil texture and heavy metal species on the contents of heavy metals are studied. The results show that the contents of heavy metals in the study area are more than 1.5 to 6.3 times of the soil background value in Jiangsu Province. The content of heavy metal Cr is 31.92~95.38 mg/kg, and some areas have already exceeded the control value of the second type of construction land in China, 78 mg/kg. The pH value is inversely proportional to the total heavy metal content, which indicates that it is more difficult to enrich heavy metal ions in alkaline environment. The soil texture in this area is dominated by sand grains, and the spatial distribution of sand grain content decreases from southwest to northeast. The clay content is positively correlated with the heavy metal content except Zn. The main forms of the five kinds of heavy metals in soil are residues, reaching 73.86%~88.15%, and with the increase of heavy metals content in soil, the proportion of residual decreases.

1. Introduction
The heavy metals entering the soil form different forms of heavy metals through the reactions of dissolution, adsorption, complexation, precipitation and coagulation[1~3]. The activities[4], migration characteristics[5], biotoxicity[6] and environmental effects[7] of these heavy metals are different. Schramel et al.[8] find that the residual copper content in unpolluted soil is 65%~85% and organic copper is 30%. However, under the condition of pollution, the residual copper content decreases to 40% ~ 50%. Xian et al.[9] study the response of kidney bean to concentration and chemical speciation. The results show that the residual content decreases and the exchangeable content increase when the soil is transformed from neutral to acidic state. At the same time, it is found that the absorption ability of kidney bean plants to heavy metals is positively correlated with the proportion of carbonate and exchangeable. Ni et al.[10] study the adsorption capacity of copper in three soils with different texture. The results show that the adsorption capacity of copper on heavy loam is the strongest, following with middle loam, and the weakest is light loam. The order of strength is exactly the same as the order of their physical clay size.

In this paper, the research area is selected in the central urban area of Nanjing Jiangbei New area. Soil samples from 23 sampling sites (0~20cm) are collected and studied systematically. The pH value, soil texture, heavy metal (As, Cr, Cu, Zn, Pb) content and speciation distribution in soil samples are determined in order to explore the factors affecting the distribution of heavy metals.
2. Materials and methods

2.1 Sampling point setting
The central area of Jiangbei New area (118 °36′12" E to 118 °44′29" E, 32 °1′19" N to 32 °8′15" N) is located in Pukou District, Nanjing City. It belongs to subtropical monsoon climate with four distinct seasons and abundant Rain Water. The location is from the Nanjing Yangtze River Bridge in the west to the Nanjing Yangtze River Bridge in the east, form Laoshan in the north to the Yangtze River in the south. It is the cultural, commercial and economic center of Nanjing Jiangbei New area in the future with a good geographical location and a unique natural environment. Because of the large longitudinal span of the area, three lines are set up horizontally from the left to the right. There are 23 sampling points, including 8 sampling points along the river line, 5 sampling points at the left line of Laoshan to Yangtze river, 6 sampling points at the middle line (encrypted arrangement in the industrial park), and 4 sampling points at the right line.

2.2 Collection and processing of samples
According to pre-determined sampling point positions, sample the soils and record actual longitude and latitude coordinates with a hand-held GPS locator. Because of the large distance between the two sampling points, subsamples are collected at random for 3~5 locations in the range of 100m×100m around the middle position of the sampling cell to improve the representativeness of soil samples in each sampling unit. Use calibration soil sampler to sample the surface 0~20cm surface soil vertically. During the sampling process, try to avoid the external soil and the newly disturbed soil layer, remove the surface debris and gravel in the soil, seal it with a clean polyethylene bag, label both inside and outside the bag, and transport it back to the laboratory as soon as possible. After 15 days of natural air drying in a clean and clean indoor ventilated place, all subsamples of the sampling unit are mixed evenly and then sampled in a quaternary method. About 1kg soil samples are retained and dried and crushed through the 2mm pore sieve in an oven at 105 °C.

2.3 Sample detection
According to Soil Testing Standard (NY/T 1121/2006) published by ministry of agriculture, sampling point soil pH are measured with 1/2.5 ultra-pure water suspension. The ratios of clay (d < 0.002mm), silt (0.002mm<d < 0.02mm) and sand (0.02mm <d < 2mm) in soil are measured by densitometer. Two parallel samples are arranged for each sample. According to the principle of BCR extraction, the acid -soluble, reducible, oxidizable and residue state are extracted from heavy metals, and their contents are determined.

The contents of As, Cr, Cu, Zn and Pb and the speciation of heavy metals are determined by electrocoupled plasma emission spectrometry (ICP-5000). Set blank sample and standard sample to control the accuracy of test. The correlation coefficient of standard curve is more than 0.999. The
detection limits of each heavy metal are 0.035 mg/L, 0.019 mg/L, 0.009 mg/L, 0.02 mg/L and 0.020 mg/L. There are two parallel samples in each sample. The error of determination is less than 10% and the recovery rate of sample is 92% ~ 105%.

3. Results and analysis

3.1 Soil properties and total heavy metal concentrations
According to Table 1, the distribution of heavy metals in the topsoil of the study area is also very uneven due to the large difference in the urban functional regions through the transverse sampling lines. The coefficient of variation of the contents of As, Cu, Zn and Pb of heavy metals is more than 36%, which is highly variable. The order of the average heavy metal content is Zn > Cr > Pb > Cu > As, which is consistent with the conclusions obtained by Wang et al.[13] in the health risk assessment study of heavy metals along the Yangtze River coast of Nanjing. Among them, the content of Zn is 46.62~183.60 mg/kg, and the content of Cr is followed by 31.92~95.38 mg/kg, Pb is 19.24~155.96 mg/kg, Cu is 12.86~56.86 mg/kg, As is 4.02~39.14 mg/kg. Compared with the soil background value in Jiangsu Province (As=9.1, Cr=15.1, Cu=22.8, Zn=64.1, Pb=21.6) [14], except that the Cu content in the soil around the Laoshan Mountain didn’t exceed the background value, the heavy metal contents in other places are more than 1.5 to 6.3 times of the soil background value. The pollution of Cr is the most serious, and some areas have already exceeded the control value of the second type of construction land in China[15].

The range of pH value in the study area is 7.82 ~ 8.86, and the average value is 8.38. The topsoil in the central urban area of Jiangbei New area belongs to alkaline soil.

Table 1. Descriptive statistical analysis of soil physical and chemical properties and total heavy metals (mg/kg)

|       | As    | Cr    | Cu    | Zn    | Pb    | pH    | Sand(%) | Silt(%) | Clay(%) |
|-------|-------|-------|-------|-------|-------|-------|---------|---------|---------|
| Min   | 4.02  | 31.92 | 12.86 | 46.62 | 19.24 | 7.82  | 40.97   | 8.9     | 4       |
| Max   | 39.14 | 95.38 | 56.26 | 183.6 | 155.96| 8.86  | 84.23   | 40      | 19.5    |
| AVG   | 19.94 | 61.83 | 33.23 | 110.22| 60.29 | 8.38  | 64.27   | 22.04   | 9.98    |
| SD    | 9.81  | 18.28 | 14.18 | 42.26 | 32.11 | 0.29  | 11.28   | 7.14    | 4.01    |

Soil texture, which is composed of sand, silt and clay, is a stable characteristic which can reflect the characteristics of soil parent material composition, and has an important effect on the adsorption, migration and transformation of soil matter[11]. The soil texture of the studied area is obtained by the spatial interpolation method of sand, powder and clay content measured at 23 sampling sites by ArcGIS, as shown in Fig.2. The content of sand grains in the soil of the central area of Nanjing Jiangbei New area is the largest, with the variation range of 40.97% and 84.23%. The ratio of silt and clay content is 22.04% and 9.98%, and the variation among regions is quite different. The coefficient of variation of clay content is 40.18%, belonging to a high degree of variation. According to the international soil texture classification standard, the main soil types in the study area are sandy loam, sandy clay loam and clay loam. The spatial distribution of soil texture show that the content of sand grain decrease from southwest to northeast. Due to the accumulation of the Yangtze River current[12], a large amount of sediment is brought from the upper reaches of the river and deposited in the lower reaches of the basin. As a result, the soil along the river line and the left line of Laoshan to the Yangtze river contains a large amount of sand, and the texture of the soil is dominated by sandy clay. The content of clay and silt in the middle line and right line of Laoshan to the Yangtze river are increased, and the texture of the soil begin to incline to sandy clay loam and clay loam.
3.2 Factors affecting the distribution of heavy metals

According to Table 2, pH value is inversely proportional to the total distribution of 5 kinds of heavy metals. There is a significant negative correlation between As, Cu and pH at the level of 0.05, and a significant negative correlation between heavy metal Zn and pH at the level of 0.01. That is to say, when the pH value of the soil is in the acidic state, heavy metals are easier to migrate and diffuse after entering the soil, and when the pH value is increased in the alkaline environment, the heavy metal ions are more likely to precipitate due to reduced activity. With the exception of heavy metal As, the contents of Cr, Cu, Zn and Pb are positively correlated with the content of sand grain, but negatively correlated with the content of silt grain. The clay content is positively correlated with the content of heavy metals except Zn, that is, the heavy metals are more easily adsorbed in soil particles with the increase of clay particles, which is similar to the results of Liu et al. [16].

By cluster analysis of heavy metal content in 23 sampling sites, the sample sites with similar pollutant content can be obtained, as shown in figure 3. According to the average value of heavy metal content, the sampling sites can be divided into T1 < T2 < T3. Figure 4 shows the proportion of the five heavy metals under different total heavy metals.

Table 2. Correlation analysis of heavy metal influencing factors

|       | As   | Cr   | Cu     | Zn     | Pb     | pH    | Sand  | Silt  | Clay  |
|-------|------|------|--------|--------|--------|-------|-------|-------|-------|
| As    | 1    |      |        |        |        |       |       |       |       |
| Cr    | 0.217| 1    |        |        |        |       |       |       |       |
| Cu    | 0.430*| 0.584**| 1    |        |        |       |       |       |       |
| Zn    | 0.284| 0.707**| 0.884**| 1    |        |       |       |       |       |
| Pb    | 0.481*| 0.534**| 0.505*| 0.548**| 1    |       |       |       |       |
| pH    | -0.469*| -0.291| -0.483*| -0.541**| -0.412| 1    |       |       |       |
| Sand  | -0.083| 0.040| 0.031  | 0.229  | 0.146  | -0.624**| 1    |       |       |
| Silt  | 0.005| -0.066| -0.065| -0.190| -0.156| 0.556***| -0.923**| 1    |       |
| Clay  | 0.272| 0.012| 0.114  | -0.107 | 0.014  | 0.420* | -0.932**| 0.871**| 1    |

*indicates a significant correlation at 0.05 level (both sides) and ** indicates a significant correlation at 0.01 level (both sides).
As can be seen from fig. 4, the major forms of heavy metals in the soil in the study area are residual, reaching 73.86%~88.15%, and the proportion of residual forms decreases with the increase of the total amount of heavy metals. The proportion of acid-soluble, reducible and oxidizable of As increase with the increase of total heavy metal content, and the range of acid-soluble is the largest, from 1.94% to 7.76%. According to the study of Zhang et al. [17], acid-soluble arsenic is a part of the environment that is easy to be bioavailable and can cause secondary pollution with the change of environmental conditions, while the residual mainly occurs in the mineral lattice and is relatively stable. The percentage of reducible of Cr is the smallest in all forms, and the ratio varies from 3.52% to 6.34%, but the proportion of reducible increases with the increase of the total amount. The ratio of acid-soluble and reducible of Cu increases with the increase of total heavy metal content, the range is 0%~1.43% and 3.67~8.38%, respectively. Under the condition of different total amount of heavy metal Zn, the ratio of residual is the smallest, ranging from 80.43% to 81.90%. The ratio of acid-soluble is the lowest, 2.96%~7.03%, which increases with the increase of total heavy metal content. The results of Pb speciation analysis of heavy metals in the study area are similar to those of Yang et al. [18]. The acid-soluble of Pb increases with the increase of the total amount of heavy metals, and the ratio varies from 0.43% to 8.41%.

Figure 4. Proportion of various forms of heavy metals in different total quantities

4. Conclusion
(1) The content of heavy metals in soil is Zn > Cr > Pb > Cu > As, which are higher than the background values of Jiangsu Province in local areas, indicating that there is heavy metal pollution in
the soil of the study area.

(2) The pH value of the sampling sites in the study area shows that the soils in the central urban area of Jiangbei New area belong to alkaline soils. The pH value is inversely proportional to the total amount of heavy metals, indicating that it is more difficult to enrich heavy metal ions in alkaline environment. The correlation analysis between soil texture and total heavy metals show that clay is an important factor affecting the distribution of heavy metals. The higher the clay content, the easier it is to adsorb in soil.

(3) The main forms of heavy metals in soil are residues, and with the increase of the total amount of heavy metals in soil, the proportion of residual forms decreases and the contents of other forms increase accordingly.

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