Chemical Speciation of heavy metals in Cd-polluted soil with different particle-sizes

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Abstract. In this paper, the Cd-contaminated soils in the eastern suburbs of Tianjin were divided into seven grain classes(I-VII). The distribution characteristics of soil grain size were analyzed. The soil content of 40-60 mesh and less than 160 mesh was the highest. The two grain size soils were about 50% in total, and the soil of 140-160 mesh rank had the lowest content, with the maximum content not exceeding 1%. The distribution characteristics of chemical forms of Cd in soils with different grain sizes were analyzed, which were divided into weak acid extractable, reducible, oxidizable and residual forms. The results showed that Cd mainly existed in the weak acid extractable form and the reducible form. The highest Cd concentration was found in 120-140 mesh, followed by 40-60 mesh.

1. Introduction
Dongli District is situated between the central urban area of Tianjin and Tanggu District. The total area was 460 square kilometers. The total population was 68,960 (2013). The land use type is vegetable field, and it is close to the city. It is located in the sewage irrigation area of Beipaihe River. The farmland has been polluted by sewage irrigation and sludge application, and the soil pollution is serious. The parent material of the soil is lake-marsh sediment, the soil texture is sticky. Cadmium, mercury, copper, lead, zinc, chromium, nickel, cobalt, molybdenum and other elements in the soil are obviously enriched in the surface layer. Cadmium is 2.65 times of the national environmental quality standard, and mercury is 4.48 times of the national environmental quality standard. The contents of all elements in the soil below 30 cm decreased rapidly and reached the background range at the depth of 60 cm. According to the regional distribution characteristics of heavy metal elements, the sewage irrigation area of Beipaihe River is polluted by cadmium, mercury, copper, lead, zinc, chromium, nickel, cobalt, molybdenum and other heavy metal elements. Sewage irrigation, sludge application and urban dustfall are the main reasons for the pollution of many heavy metal elements in soil.

The accumulation of Cd in human body may cause irreversible damage to kidney and liver. Since the beginning of the 20th century, Cd poisoning incidents such as "Cd rice" have occurred frequently, and the study of Cd soil pollution has been paid more and more attention. In this paper, the characteristics of Cd content in soils of sewage irrigation area in eastern suburbs of Tianjin were analyzed, and the chemical forms of Cd in different size soil particles were tested and analyzed.[1-5]

1.1 Sample collecting
Samples were collected from the sewage irrigation area in Dongli District Tianjin.

After full mixing of the surface layer (1-20 cm), the samples were packed in plastic bags with good labels in the field, and sundries were picked up indoors for natural air-drying. A total of 12 samples were collected from sewage irrigation area and its surrounding areas. The soil was divided into seven...
grain classes by nylon sieve in the laboratory, which were 40-60 mesh, 60-80 mesh, 80-100 mesh, 100-120 mesh, 120-140 mesh, 140-160 mesh and less than 160 mesh. The corresponding grain size of each grain class was shown in Table 1. The soil of each grain size have been weighed.

Table 1. Table of nylon mesh and aperture size.

|    | I     | II    | III   | IV    | V     | VI    | VII   |
|----|-------|-------|-------|-------|-------|-------|-------|
| mesh | 40-60 | 60-80 | 80-100 | 100-120 | 120-140 | 140-160 | >160 |
| µm  | 420-250 | 250-178 | 178-150 | 150-124 | 124-104 | 104-95 | <95  |

1.2 Materials and methods

The sequential extraction method, namely the European Union BCR three-step method, is used for chemical speciation analysis. It includes weak acid extraction form, reducible form, oxidizable form and residue form. This is also the order in which the difficulty of releasing pollutant elements decreases. The first three forms can affect the environment easily, and the residual pollutant elements can not be released. The determination of Cd in soil was tested by atomic absorption spectrometry (AA-100) based on DZG20.10-1990.

2. Distribution of soil granularity

Table 2. Soil content of different sizes.

|    | #1  | #2  | #3  | #4  | #5  | #6  | #7  | #8  | #9  | #10 | #11 | #12 |
|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| I  | 0.094 | 0.098 | 0.305 | 0.374 | 0.216 | 0.325 | 0.231 | 0.366 | 0.282 | 0.306 | 0.318 | 0.420 |
| II | 0.181 | 0.161 | 0.182 | 0.205 | 0.229 | 0.191 | 0.272 | 0.268 | 0.188 | 0.206 | 0.211 | 0.297 |
| III | 0.015 | 0.030 | 0.015 | 0.013 | 0.010 | 0.022 | 0.010 | 0.009 | 0.017 | 0.021 | 0.012 | 0.008 |
| IV | 0.211 | 0.155 | 0.068 | 0.059 | 0.103 | 0.077 | 0.132 | 0.084 | 0.074 | 0.091 | 0.066 | 0.075 |
| V  | 0.241 | 0.214 | 0.089 | 0.069 | 0.142 | 0.088 | 0.152 | 0.099 | 0.113 | 0.069 | 0.093 | 0.060 |
| VI | 0.006 | 0.003 | 0.002 | 0.001 | 0.001 | 0.009 | 0.001 | 0.001 | 0.001 | 0.008 | 0.004 | 0.001 |
| VII | 0.252 | 0.340 | 0.339 | 0.279 | 0.299 | 0.288 | 0.201 | 0.173 | 0.325 | 0.299 | 0.296 | 0.138 |

Fig. 1. Distribution characteristics of soil size

Fig. 1 shows that the particle size distribution is consistent in different samples. The soil content of 40-60 mesh and less than 160 mesh is high, and the sum of the two grain sizes accounts for about 50% of the total soil content.; the next is 60-80 mesh, which is about 20%; 120-140 mesh, which is about 10%; 100-120 mesh, which is about 8%; 80-100 mesh, which is about 2%; the least is 140-160 mesh, which is not more than 1%. There are some differences in the distribution characteristics of Cd content with soil grain size in different samples. This is related to the degree of soil weathering, the type of soil
utilization and the mineral composition of the soil. Because the content of grade VI soil is too small, it is neglected in the later chemical speciation analysis.

3. Content characteristics of Cd in soils with different grain sizes

The density of Cd in soils with different grain sizes is different. The variation of Cd content with grain size is different in soils of different locations. As shown in Fig. 2, the density of Cd decreases slowly with the decrease of grain size in No. 1, No. 2, No. 4 and No. 5 samples. In No. 8, No. 9 and No. 11 samples, the density of Cd varies serrated with the decrease of grain size. In No. 6 sample, the density of Cd is the lowest in 60-80 mesh size soil, and there is little difference in content among other grain-size soils. In No. 12 sample, the density of Cd decreases obviously with the decrease of particle size. The trend of Cd density in other soil samples was not obvious.

![Fig. 2. The content of Cd in soils with different grain sizes](image-url)
The size of soil particle determines its specific surface, which greatly affects the adsorption of heavy metals by minerals. At the same time, there are some other aspects affect soil adsorbability such as the chemical form etc. As Figure 2 shows, soil adsorbability to Cd is not the smaller the particle size, the better. Therefore, it is necessary to find out the best size range for the adsorption of contaminated elements.

4. Distribution characteristics of chemical forms of Cd in soils with different grain sizes

![Content of four chemical forms of Cd in soils with different grain sizes](image)

Fig.3. Content of four chemical forms of Cd in soils with different grain sizes

The chemical forms distribution of each particle size has a common trend: weak acid extractable state > reducible state > residual state > oxidizable state, and the first two forms have the greatest impact on the environment, which shows that the potential threat of pollution elements to the environment is very serious. How to convert weak acid extractable state and reducible state into residual state is a problem we are facing.

So when using minerals to control pollution, according to the different adsorption properties of different minerals to different metals, the corresponding crushing plan should be formulated to crush the minerals to the appropriate size, so as to achieve the best effect of pollution control[6-12].

5. Conclusions

Firstly, The soil content of grain I and VII was the highest, accounting for about 50% of the total soil weight, and the lowest was the soil of grain VI, which was less than 1%. There were slight differences in soil grain size distribution among different sampling sites. Generally speaking, the order of seven grain size contents was I > VII > II > V > IV > III > VI. Secondly, the distribution of Cd in different samples in different particle sizes was also regular. The samples were divided into four groups according to the distribution Characteristics. The density of Cd in the first group (#1, #2, #4, #5) samples decreased gradually with the decrease of soil particle size; the density of Cd in the second group (#8, #9, #11) samples was the highest in II and IV sizes; The distribution of Cd in the soil of the third group (#6, #7) was contrary to that of the second group, which means the density of Cd in II and IV sizes was the lowest; and the density of Cd in the fourth group (#3, #6, #12) samples had special variation characteristics. Thirdly, different chemical forms of Cd had different contents in soils with different grain sizes. Cd mainly existed as weak acid extractable and reducible states in soil, which had a great impact on the environment. The content of Cd in soil of V size was the highest, followed by the soil of I size.

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