Study on the Distribution of Heavy Metals in Atmospheric Dustfall in the Area around Linyi University

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Abstract. This paper analyses the atmospheric dust in Linyi City about the content and the form distribution of heavy metals. The main research focuses on the eight kinds of heavy metal elements, including As, Cd, Cr, Cu, Hg, Mn, Pb, Zn. The research results show that the formation distribution of heavy metal element is differ, the morphology of Mn and Cu detection rate of 100%, with five kinds of form exist; Cu, Zn, Mn, Pb, Cd in the exchangeable ions and carbonate combined states accounted for 20% of the proportion of high proportion. Cr, Cd, heavy metal forms with exchangeable ions state, carbonate state, iron, manganese oxide combination state, which accounts for 80% to 95% of the total, unstable state 20% has some impact on the environment and the human body.

1. Introduction

In recent years, with the rapid development of urbanization and industry, serious atmospheric environmental problems have arisen. Dustfall in the atmosphere has a harmful effect on the climatic environment, human body and living things, which has aroused people's great research interest. Atmospheric dust refers to particulate pollutants falling in the dust collecting cylinder with a particle size larger than 10μm in the natural environment. The atmospheric dust can form colloidal pollutants in the air. There are two main sources of atmospheric dustfall: atmospheric dustfall in the natural state is mainly derived from soil particulate matter; and polluted atmospheric dustfall is mainly related to waste discharge in the region. Some heavy metal pollution elements such as Hg, Cd, Cu, As, Pb, Zn, etc., cause serious pollution to urban areas or surrounding biological communities, and harmful substances such as dust and bacteria carried by them have a great influence on the human body and the environment. Atmospheric dust and heavy metal pollutants have a wide range of sources, mainly industrial and agricultural production, transportation and so on. In this paper, the heavy metal content and morphological characteristics of atmospheric dustfall in the surrounding areas of Linyi University were analyzed. Principal component analysis and other analytical methods were used to study the characteristics, sources and forms of atmospheric dustfall.

1.1 Overview of the Study Area

Linyi City, located in the south of Shandong Province, the terrain is complex and is an important part of Luzhong Mountain area. The terrains such as plains, hills, mountains and mountain rivers form the complex terrain of the city. Linyi City center has a flat terrain. Xicheng District mainly includes Linyi University, the trade and logistics area, and the Beng River which passes by. The study on the content and characteristics of atmospheric dust heavy metals will provide important guidance and have significant influence for the future development of Linyi area.
2. Sample Collection and Experimental Research Analysis Methods

Experimental equipment: drying oven; electric heating plate; fume hood; Vista-MPX plasma emission spectrometer, full spectrum direct reading ICP-OES VISTA-MPX (American Wariant); DSHZ-300 multi-purpose water bath thermostat (Taicang, Jiangsu) City Experimental Equipment Factory); TDL-5-A low-speed desktop large-capacity centrifuge (Shanghai Anting Scientific Instrument Factory).

Data Processing Analysis Software: Excel, SPSS, Arcgis.

2.1 Sample Collection and Processing

The sampling was set up around the Spring Festival in 2014, and seven sampling points were set up in Linyi City: 1 university town; 2 logistics city; 3 bus station; 4 residential area; 5 park area; 6 industrial area; Business district. One sample was collected at each sampling point. The sampler used is a plastic drum with a diameter of 40 cm and a height of 50 cm. It is treated with distilled water and dried. It is then taken to the sampling point and fixed on an open roof platform 5 to 10 m away from the ground, away from local obvious pollution sources and tall buildings. 3] to prevent the impact of buildings on natural dustfall. The atmospheric dust is brought back to the laboratory, the dust sample is dried at a low temperature in a dry box, the foreign matter is removed, and the 100 mesh sieve is ground, and the dust sample is thoroughly mixed and then placed in a ziplock bag.

2.2 Experimental Methods

2.2.1 Atmospheric Dust Reduction Heavy Metal Digestion Method. This experiment uses the more common hot plate digestion method. Weigh 0.30 g (accurate to 0.0002 g) of the mixed sample into 50 mL of Teflon, add a small amount of water to wet, add 10 mL of concentrated HCl, and heat the sample on the hot plate in the fume hood to preliminarily decompose the sample. When it is evaporated to about 2 mL, then add 6 mL of HF, 5 mL of HNO₃, and 3 mL of HClO₄. After capping, the heating is continued on the hot plate for digestion. After about one hour, the polytetrafluoroethylene lid was opened and the silicon removal was continued on the hot plate. In order to keep the flying silicon effect good, it should be shaken without interruption. When heated to thick white smoke, cover the lid to decompose the black organic carbide. Due to insufficient digestion, 8 mL of HNO₃, 8 mL of HF, and 3 mL of HClO₄ were added. After the black organic carbide has basically disappeared, open the cover to drive away the white smoke of HClO₄. When the white smoke is exhausted and the contents of the crucible are viscous, remove the crucible with a metal clamp and cool it slightly (note that when clamped with pliers, do not touch the inner wall of the crucible). Rinse the lid and inner wall of the Teflon with water and add 1 mL of HNO₃ solution (1:1) to dissolve the residue in the crucible. Then transfer to a 50 mL volumetric flask to volume and prepare for testing. Due to the different atmospheric dustfall at each sampling point, there is a difference in the organic matter contained. When digesting, observe that the amount of various acids is different. The digested solution should be white or light yellow with no obvious precipitate.

2.2.2 Research Methods for Heavy Metal Forms of Atmospheric Dustfall. For heavy metal speciation analysis, the Tessier five-step method used by most researchers in China is used.

3. Research Results and Discussion

3.1 Study on the Forms of Heavy Metals in Atmospheric Dustfall

3.1.1 Morphological Detection Rate of Each Heavy Metal Element. The five-step continuous extraction method of Tessier used in this experiment can be divided into five forms: exchangeable ionic state (F1), carbonate bound state (F2), and iron-manganese oxide bound state (F3), organic combined state (F4), residual state (F5). The exchangeable ionic state, carbonate bound state and iron-manganese oxide bound state are unstable forms, and they are easily absorbed by the organism, and the organic combined state and the residual state are stable.
Due to the different content characteristics of each sample, some metal elements may not be detected normally or the concentration is low. The detection rate of each metal is shown in Table 1. The detection rate of Cu and Mn is 100% in each form, which is the highest. It shows that they exist in five forms; the forms of Zn and Cd are mainly carbonate-bound, organic-bound and residual, and some are in exchangeable ionic and iron-manganese oxide; Pb and Cr The detection rate of the iron-manganese oxide bound state is 0, indicating that the two elements do not exist in the form of iron-manganese oxide bound state; the detection rates of Cd and Hg vary from one form to another, but all five forms Their existence can be detected; the detection rate of the organic binding state of As element is 0, and the existence form of As does not appear in the organic binding state.

| Table 1. Detection rate of each metal element (%) |
|-----------------------------------------------|
| form                           | Cu   | Zn   | Mn   | Pb   | Cr   | Cd   |
| Exchangeable ionic state       | 100  | 57.14| 100  | 100  | 42.86| 57.14|
| Carbonate bound state          | 100  | 100  | 100  | 100  | 100  | 100  |
| Iron-manganese oxide binding state | 100  | 57.14| 100  | 0    | 0    | 71.43|
| Organic binding state          | 100  | 100  | 100  | 100  | 100  | 100  |
| Residual state                 | 100  | 100  | 100  | 100  | 100  | 100  |

3.1.2 Analysis of Heavy Metals in Cu, Zn, Mn, Pb, Cr and Cd Elements. The main characteristics of heavy metals such as Cu, Zn, Mn, Pb, Cr and Cd were analyzed. The sampling points and the content of each element are shown in Table 2. Heavy metal Cu has the largest amount in the form of residual state, and the content of manganese oxide is the smallest. The content of Cu is much higher than the background value of the soil, and the content ratio of Cu in the bus station reaches 699.70 mg/kg, which exists in five forms. Zn mainly appears in the carbonate-bound state and the residual state. Its total concentration is suburb > bus station > logistics city > university city > residential area > square > yuanbo park, Zn is the indicator element of industry, which also meets the sampling The regional environmental characteristics of the point, many small factories in the industrial area, industrial pollution has increased the pollution degree of Zn. The Mn content is roughly equivalent to the soil background value, which again proves that the source of Mn is essentially soil particles and the contamination is minimal. The concentration of Pb is generally high. The concentration of Pb in logistics city and bus station with large automobile flow rate even reaches 200mg/kg. The pollution of Pb is more serious. The source of Pb in the environment is mainly coal dust and Alkyl lead compounds added to automotive gasoline. Cr and Cd mainly exist in the form of exchangeable ionic state, carbonate bound state, organic combined body and residual state, and the concentration range of the element exceeds 20 times of the background value, which is already polluted.
Table 2. Table of six heavy metal forms (mg/kg)

|     | 1      | 2      | 3      | 4      | 5      | 6      | 7      |
|-----|--------|--------|--------|--------|--------|--------|--------|
| F1  | 3.45   | 0.63   | 0.81   | 1.49   | 1.93   | 0.71   | 0.29   |
| F2  | 6.28   | 15.22  | 5.68   | 6.02   | 14.82  | 0.22   | 10.42  |
| Cu  | F3     | 0.62   | 0.36   | 0.48   | 0.47   | 0.40   | 0.33   | 0.79   |
| F4  | 17.95  | 14.21  | 19.25  | 15.03  | 19.63  | 29.25  | 13.60  |
| F5  | 455.38 | 435.32 | 673.48 | 301.60 | 344.38 | 294.89 | 343.79 |
| Total| 483.68 | 465.74 | 699.70 | 324.61 | 381.16 | 325.4  | 368.89 |
| Zn  | F1     | 0.00   | 0.87   | 0.00   | 0.00   | 0.58   | 853.78 | 1.88   |
| F2  | 87.19  | 73.23  | 39.46  | 52.52  | 57.30  | 950.55 | 71.05  |
| F3  | 0.32   | 0.44   | 0.80   | 0.00   | 0.00   | 16.77  | 0.00   |
| F4  | 27.80  | 20.67  | 19.47  | 19.50  | 18.66  | 240.37 | 14.57  |
| F5  | 900.17 | 1956.72| 1286.16| 899.76 | 501.61 | 316.88 | 791.62 |
| Total| 1015.48| 1151.93| 1327.89| 971.78 | 578.15 | 2378.35| 879.13 |
| Mn  | F1     | 15.04  | 8.64   | 4.16   | 6.02   | 17.59  | 33.97  | 4.87   |
| F2  | 72.99  | 47.71  | 58.99  | 62.67  | 52.86  | 71.77  | 64.26  |
| F3  | 3.77   | 2.64   | 1.58   | 2.56   | 2.11   | 15.31  | 2.00   |
| F4  | 59.32  | 48.17  | 48.67  | 52.92  | 57.64  | 82.61  | 57.64  |
| F5  | 349.52 | 348.33 | 330.39 | 362.20 | 319.75 | 299.37 | 493.68 |
| Total| 500.64 | 455.49 | 443.79 | 486.37 | 452.2  | 503.03 | 622.45 |
| Pb  | F1     | 0.14   | 0.00   | 0.10   | 0.12   | 0.10   | 0.32   | 0.10   |
| F2  | 34.55  | 61.79  | 23.16  | 53.46  | 76.03  | 75.76  | 24.74  |
| F3  | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   |
| F4  | 4.15   | 3.98   | 2.73   | 6.47   | 7.07   | 5.10   | 2.15   |
| F5  | 115.49 | 139.41 | 118.88 | 89.73  | 152.14 | 133.87 | 104.23 |
| Total| 154.33 | 205.18 | 145.57 | 145.57 | 215.10 | 215.05 | 131.22 |
| Cr  | F1     | 0.03   | 0.00   | 0.02   | 0.00   | 0.07   | 0.00   | 0.00   |
| F2  | 1.39   | 1.20   | 0.83   | 1.21   | 1.10   | 1.64   | 1.41   |
| F3  | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   |
| F4  | 8.22   | 11.39  | 9.30   | 8.03   | 15.01  | 9.69   | 9.21   |
| F5  | 31.05  | 67.03  | 46.77  | 55.79  | 60.48  | 50.93  | 125.28 |
| Total| 40.69  | 79.63  | 56.92  | 65.03  | 76.66  | 62.26  | 135.90 |
| Cd  | F1     | 0.03   | 0.47   | 0.00   | 0.00   | 0.21   | 0.14   | 0.00   |
| F2  | 0.47   | 0.50   | 0.29   | 0.44   | 0.46   | 0.40   | 0.55   |
| F3  | 0.01   | 0.01   | 0.00   | 0.005  | 0.006  | 0.027  | 0.00   |
| F4  | 0.41   | 0.24   | 0.23   | 0.31   | 0.33   | 0.65   | 0.18   |
| F5  | 2.92   | 3.18   | 3.15   | 2.97   | 2.40   | 2.00   | 3.34   |
| Total| 3.84   | 4.397  | 3.67   | 3.725  | 3.406  | 3.217  | 4.07   |

The distribution of six heavy metals in atmospheric dust is shown in the histogram of Figure 1-6, which can further lead to the main existence of the elements. The main forms of these six heavy metals in atmospheric dust fall are the residual state and the organic combined state, that is, the steady state. The heavy metals in the residual state and the organic combined state are less biotoxic and are not easily absorbed by organisms. They are not easily released in the natural state, and can exist stably for a long time, and have little impact on the ecosystem. The specific gravity of the exchangeable ionic state and the carbonate bonded state of Cu, Zn, Mn, Pb, and Cd is relatively high, and particularly, the specific gravity of Zn, Pb, and Cd is close to 20%. These two forms are highly mobile and can be directly used by organisms, which has a great impact on the ecosystem. Cr mainly exists in the form of a stable state, but the ionic state, the carbonate-bound state, and the iron-manganese oxide-bound state, which are small in specific gravity, have a great influence on human survival.
Note: F1 Exchangeable ionic state, F2 Carbonate bound state, F3 Iron-manganese oxide binding state, F4 Organic combination, F5 Residual state.

4. Conclusion
In the six heavy metal elements explored, the exchangeable ionic state and carbonate bound state of Cu, Zn, Mn, Pb, and Cd elements are relatively high, and the specific gravity is 10% to 20%. Cr and Cd are mainly in the exchangeable ionic state, carbonate bound state, organic combination, and residual state, the existence of unstable state is harmful to the human body. Through the analysis of this paper, the study of atmospheric dust and heavy metals has important significance, and it has an important guiding role for the development of regional environment and human health, which is conducive to us to understand its hazards and do a good job in pollution control.
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