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Analysis of Environmental Geochemical Characteristics of Atmospheric Deposition in Yellow River Delta, China

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Abstract. Atmospheric deposition is the main input route of some elements in soil. Heavy metals in the deposition matter have a significant impact on soil environmental quality. Taking Binzhou Economic Development Zone of Shandong Province as the investigation area, this paper studied the effects of heavy metal deposition on soil environmental quality were studied. Through the enrichment factor analysis and principal component analysis, it is found that elements such as Ni, Zn, Cd, Pb, Se, and F were affected by human activities to varying degrees and were significantly enriched. The comprehensive environmental geochemistry grade of dry and wet atmospheric deposition in the survey area is first class. It provides scientific basis for regional environmental health risk assessment and pollution prevention and control.

Keywords. Atmospheric deposition, enrichment factor, principal component analysis, geochemical characteristics

1. Introduction

In recent years, with the rapid development of urbanization and industrialization, air pollution in Chinese cities has become increasingly serious. The atmospheric dust pollution has become an inevitable problem in urban development. Dust fall refers to the airborne particles that fall to the ground naturally under atmospheric conditions. Usually, it is the dust discharged in the process of human production and living and the surface particulate matter (soil dust, road dust, construction dust, etc.) carried by surface wind. It can be divided into dry settlement and wet settlement, and its particle size is mostly between 10 μm and 100 μm [1].

Atmospheric deposition is not only a major source of nutrients needed to maintain primary productivity, but also a major input of additional and extraneous pollutants. The pollutants discharged into the atmosphere will generally be adsorbed on atmospheric particles and enter the water environment such as lakes and oceans and the soil environment such as farmland and vegetable fields in the way of settling with the

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atmospheric particles. The environmental problems such as water eutrophication, soil acidification, heavy metal pollution in water and soil will destroy the balance of water and soil ecosystem.

There are also many researches on atmospheric dry and wet subsidence. Andersen et al. [2] studied the atmospheric deposition characteristics of heavy metals such as Cu, Pb, Cd, Zn, Ni and Cr in Copenhagen area, described the regional differences of heavy metal levels in Copenhagen area, and found that there was an exponential positive correlation between atmospheric deposition and the concentration of heavy metals in the soil. Morselli et al. [3] studied the influence of dry and wet precipitation of atmospheric heavy metals on local pollution in Bologna. Maria et al. [4] collected sediment particles based on the NF X 43007 standard, studied the spatial variability of particulate pollution deposition fluxes, identified areas with high deposition rates, and correlated them with climate variables and surrounding possible emission sources. Yang et al. [5] studied the characteristics of atmospheric dry and wet deposition of heavy metals in the urban area of Changchun, and found that the content of heavy metals in atmospheric deposition of Changchun was significantly higher than that in the surface soil, and discussed the possible sources of heavy metals such as Cu, Hg, Pb and Cd.

Yang et al. [6] showed that the input of dry and wet atmospheric deposition is the main source of heavy metals in the farmland ecosystem by studying Chengdu Economic Zone. Wang et al. [7] investigated the atmospheric dry and wet subsidence in JuYe County, Shandong Province, and discussed the influence of the subsidence of local atmospheric heavy metals and other elements on the soil environmental quality of arable layer in the southwest plain of Shandong Province. Dai et al. [8] collected samples of near-surface atmospheric dust and different pollution end elements in Jining urban area, systematically analyzed the element content characteristics of atmospheric dust and pollution end elements, and studied the spatial distribution of dust fall and pollution sources. The results showed that the element content of different pollution end elements, such as coal-burning automobile exhaust, traffic and buildings, was significantly different. Pan et al. [9] investigated the heavy metal pollution of road dust in the main urban area of Xi'an in detail, and determined the concentration of 8 heavy metals such as CO by X-ray fluorescence method, and determined the source resolution by using principal component analysis and multiple linear regression analysis.

The influence of atmospheric environment on the input of heavy metals in soil can be revealed through the study of atmospheric dry and wet deposition in a region, and then the status and evolution characteristics of soil heavy metals environmental quality can be judged. Taking Binzhou Economic Development Zone of Shandong Province as the investigation area, this paper studied the influence of heavy metal deposition on soil environmental quality in this area, analyzed the environmental geochemical characteristics of dry and wet atmospheric deposition, and provided a scientific basis for regional environmental health risk assessment and pollution prevention and control.

2. Sample Collection and Treatment

2.1. Survey Area Profile

The investigation area is Binzhou Economic and Technological Development Zone of Yellow River Delta, under the jurisdiction of Binzhou City. It is located in the north of Shandong Province, Lubei Plain, the hinterland of the Yellow River Delta and the southwest coast of Bohai Bay. It is adjacent to Lijin County in the east, bordering Huimin and Yangxin County in the west, Bincheng District and Zhanhua County in Binzhou City in the north, and Boxing County and Gaoqing County in the south. It has jurisdiction over 3 sub-district offices, such as Dudian Street, Shahe Street and Lize Street,188 administrative villages, with a population of 200,000. It is located at 37°15’41”-37°25’55” north latitude, 117°47’01”-117°58’13” east longitude, with a total area of 189.20 km^2.

2.2. Sample Collection

The sampling period began on May 11, 2018 and ended on April 3, 2019. The sampling density was 1 point /16 km^2, and 12 collection containers were placed in the whole area (Figure 1). According to the density of sampling points, the project was projected into the 1:25,000 land use status map. Then, according to the location of each sampling point in the village and town, the field survey was conducted to select the location of containers and keep the containers. The container was a cylindrical plastic collection drum with an inner diameter of 27 cm and a height of 70 cm. Before use, the collection bucket should be soaked in 10% (V/V) HCl for 24 h, and then washed with pure water. The reagents were analytical pure reagents and distilled water or water of the same purity. The cleaned dust collecting cylinder shall be covered with the cylinder head, carried to the sampling point, and then removed. The container was placed on the roof platform of residents (Figure 2). The container was placed far away from main roads, garbage, dust piles, villagers’ chimneys and other places that may easily cause dust. The sampling port was about 1.0 m away from the platform to avoid the influence of dust from the platform.

3. Environmental Geochemical Characteristics of Dry and Wet Atmospheric Deposition

3.1. Element Content Characteristics of Dry and Wet Atmospheric Fallout

Table 1 is the statistical table of elements parameters of dry and wet atmospheric fallout. As can be seen from Table 2, the content of Ni, F and other elements varied in a relatively large range, with coefficient of variation of 0.61 and 0.46. This indicated that Ni, F and other elements were not uniformly distributed in the survey area and were affected by human activities. The variation range of other elements was relatively small, and the coefficient of variation was 0.36-0.21, the coefficient of variation was small. Compared with the background value of surface soil in the survey area, the content of As element in atmospheric deposition was relatively low compared with the background value of this element in surface soil. The results indicated that the surface soil As element was less affected by atmospheric dry and wet deposition. The contents of Cr, Cu, Hg and other elements were consistent, indicating that these elements in the surface soil were not affected by atmospheric dry and wet deposition. However, the contents of Ni, Zn, Cd, Pb, Se, F and other elements were relatively high, showing different degrees of enrichment, indicating that these elements in atmospheric dust fall were affected by human activities to different degrees. The content of heavy metal elements in atmospheric dust varied greatly in different regions. The content of heavy metal elements was relatively high near urban areas, while the content of heavy metal elements was relatively low near rural areas.

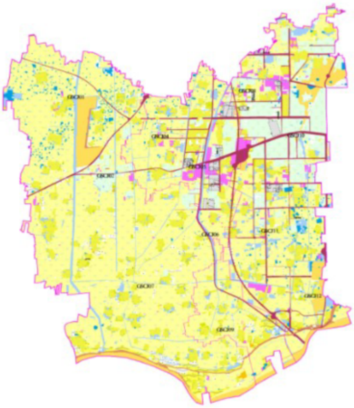

Figure 1. Location of sampling points in the survey area.

Figure 2. Sampling container placement.

Table 1. Statistical table of elements parameters of dry and wet atmospheric deposition (10^{-6}).

Element	Maximum value (μg/g)	Minimum value (μg/g)	Mean value (μg/g)	Standard deviation	CV	Median	Topsoil background values
Cr	60.30	29.90	44.62	9.37	0.21	44.05	59.54
Ni	204.00	31.40	78.55	48.26	0.61	67.20	27.19
Cu	69.90	14.20	39.63	13.81	0.35	38.45	21.49
Zn	458.00	133.00	315.92	94.72	0.30	306.50	64.07
Cd	1.86	0.43	1.25	0.43	0.34	1.17	0.16
Pb	76.00	28.10	54.24	14.16	0.26	50.15	21.86
As	8.26	1.23	5.27	1.89	0.36	4.97	10.26
Hg	0.08	0.03	0.06	0.01	0.21	0.06	0.03
Se	3.39	1.11	2.57	0.62	0.24	2.54	0.20
F	5887.00	741.00	2802.08	1276.34	0.46	2697.50	546.09

3.2. Enrichment Factor Analysis

The element enrichment degree of atmospheric deposition material is usually expressed by the ratio of the element content in the dust fall to the content in the surface soil, namely the enrichment coefficient. In addition, element enrichment factor is an effective means to judge element pollution sources and study the distribution, transportation and enrichment of atmospheric dust elements [10-12]. Enrichment factor (EF) refers to the ratio of the relative concentration of an element in the atmosphere to its relative concentration in the earth's crust. The calculation method of the enrichment factor EF for an element is $\text{EF} = (C_{i,A}/C_{r,A})/(C_{i,s}/C_{r,s})$. Wherein, $C_{i,A}$ and $C_{r,A}$ refer to the concentration of sample elements and reference elements in atmospheric deposition materials respectively. $C_{i,S}$ and $C_{r,S}$ refer to the concentration of an element and reference element in the topsoil, respectively. When EF is less than 2, no enrichment is considered. When EF is greater than or equal to 2 and less than 5, slight enrichment is considered. When EF is greater than or equal to 5 and less than 20, it is considered that there is moderate enrichment, and human activities play an obvious role. When EF is greater than or equal to 20 and less than 40, strong enrichment is considered. EF greater than or equal to 40 is considered to be highly enriched, and this element is mainly derived from human activities [13, 14].

Through the statistical analysis of each element of the atmospheric dry and wet deposition in the investigated area, it was found that Cr element was less affected by the atmospheric dry and wet deposition. Through correlation analysis among various elements (Table 2 and Figure 3), it was found that Cr had a good correlation with other elements. The enrichment coefficient of each element was calculated, and no abnormal enrichment of Cr element was found. Therefore, Cr was finally selected as the reference element to calculate the enrichment factors of other elements [7, 14]. The calculated results are shown in Table 3.

Table 2. Matrix of correlation coefficients.

Element	Cr	Ni	Cu	Zn	Cd	Pb	As	Hg	Se	F
Cr	1.000									
Ni	0.679	1.000								
Cu	0.817	0.586	1.000							
Zn	0.928	0.631	0.810	1.000						
Cd	0.819	0.332	0.716	0.913	1.000					
Pb	0.918	0.596	0.783	0.976	0.919	1.000				
As	0.808	0.725	0.572	0.659	0.476	0.655	1.000			
Hg	0.705	0.478	0.771	0.808	0.822	0.828	0.309	1.000		
Se	0.657	0.243	0.820	0.778	0.838	0.809	0.262	0.827	1.000	
F	0.671	0.950	0.634	0.654	0.363	0.633	0.646	0.570	0.389	1.000

Table 3. Average enrichment coefficient and enrichment factor of elements in atmospheric deposits in the area.

Items	Cr	Ni	Cu	Zn	Cd	Pb	As	Hg	Se	F
Average dry and wet atmospheric fallout	44.62	78.55	39.63	315.92	1.25	54.24	5.27	0.06	2.57	2802.08
Topsoil background values	59.54	27.19	21.49	64.07	0.16	21.86	10.26	0.03	0.20	546.09
Enrichment coefficient	0.75	2.89	1.84	4.93	7.81	2.48	0.51	2.00	12.85	5.13
Enrichment factor	1.00	3.85	2.46	6.58	10.42	3.31	0.69	2.67	17.15	6.85

The enrichment coefficient of As was less than 1, and EF was 0.69, indicating that the enrichment degree of As was not high and close to the natural background, so it can be considered that As was mainly derived from soil dust. The enrichment coefficient of Cu, Ni, Pb and Hg was between 1.5 and 3, and the enrichment factor was between 2 and 4. Slight enrichment exists, which was mainly from the crust and was slightly affected by human activities. The enrichment coefficients of Zn, F, Cd and Se were 4.92, 5.13, 7.81 and 12.85, and the enrichment factors were 6.58, 6.85, 10.42 and 17.15, respectively. It was moderately enriched. The results showed that the sources of these elements were influenced by natural sources and human production activities.

3.3. Principal Component Analysis

In order to study the sources of various elements in the atmospheric dust fall in the investigated area, principal component analysis was conducted for 10 elements in the dust fall, and the principal component rotation variance matrix was shown in Table 4. The results showed that two principal components could be extracted from 10 elements, which reflected the total variance of 72.38%, that was, these two principal components could reflect most of the information of the studied elements.

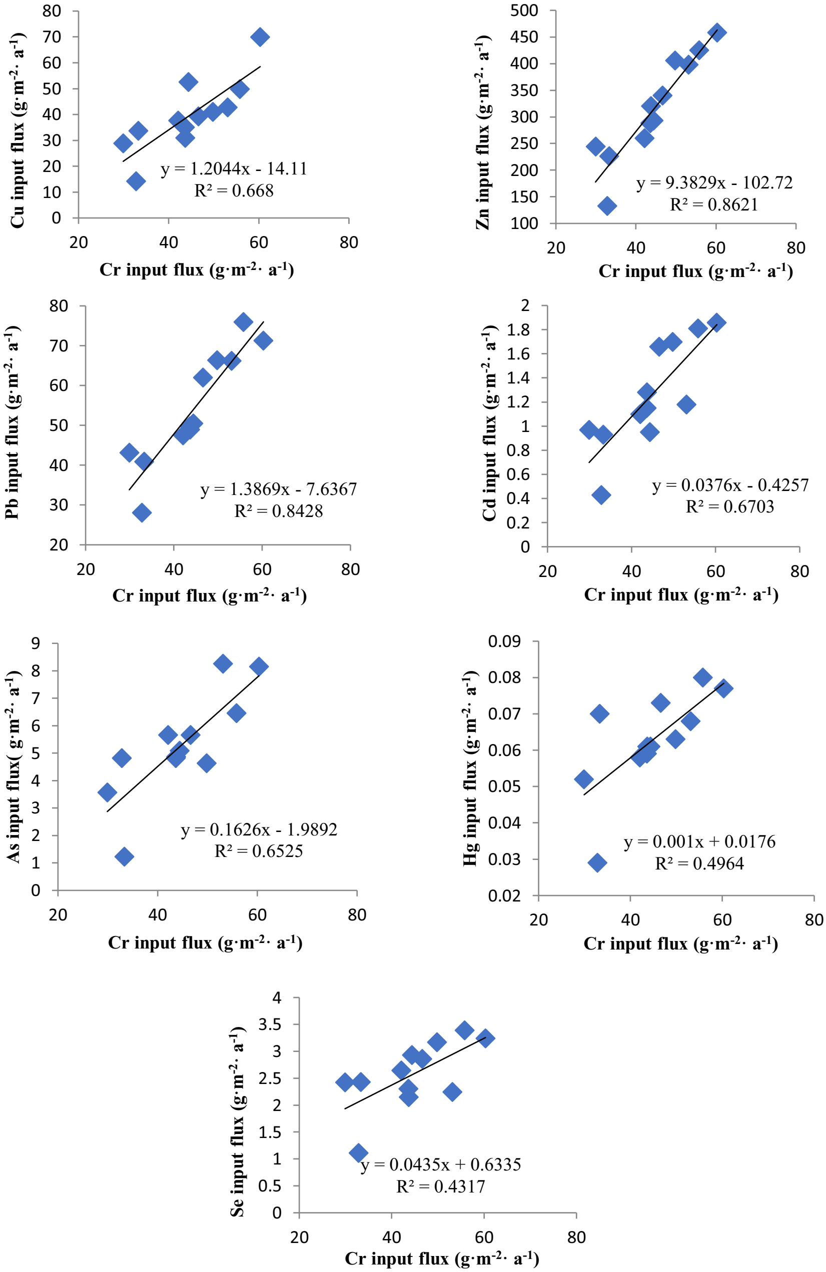

Figure 3. Scatter diagram of correlation between input fluxes of Cr and the other elements in atmospheric sediment.

Table 4. Principal component rotation variance matrix of atmospheric deposition elements.

Element	Principal component	
	F1	F2
Zn	0.969	-0.084
Pb	0.965	-0.124
Cr	0.946	0.090
Cu	0.889	-0.084
Cd	0.865	-0.410
Hg	0.848	-0.314
Se	0.796	-0.521
F	0.751	0.533
Ni	0.716	0.647
As	0.710	0.509
Characteristic value	7.238	1.538
Variance	72.38%	15.378

The principal component F1 accounted for 72.38% of the cumulative total variance, among which, the loads of Zn, Pb, Cr, Cu, Cd, Hg and Se were all higher than or equal to 0.8, indicating that there was a significant correlation between the seven elements, which was consistent with the analysis results of element correlation matrix. The variation coefficients of the seven elements ranged from 0.21 to 0.35, and the enrichment coefficients of Zn, Pb, Cu, Cd, Hg and Se were all greater than 1.5 and the enrichment factors were greater than 2, indicating that the six elements in the atmospheric deposition in the survey area had similar sources and were affected by human activities. The variation coefficient of Cr element was 0.21, and its average value was less than the background value of surface soil. It had a small proportion in the principal component F2. The enrichment coefficient was less than 1, and there was no obvious enrichment.

The principal component F2 accounted for 15.378% of the cumulative total variance, and the heavy metal elements with higher load were F, Ni and As. The correlation coefficient between F element and Ni element was high. There was a significant correlation. This suggests that the two elements are of similar origin. The coefficient of variation of these two elements were 0.46 and 0.61, respectively. The enrichment coefficients were 5.13 and 2.89, respectively. The load in the principal component F1 was also higher than 0.7. These two elements were significantly enriched by the influence of exogenous substances produced by human activities. As element also occupies a high proportion in the two principal components, and its coefficient of variation was 0.36. However, the enrichment coefficient was only 0.51. There was no enrichment of As.

3.4. Geochemical Characteristics and Spatial Distribution of Annual Flux Density of Atmospheric Dry and Wet Deposition

The annual precipitation flux of heavy metals from dry and wet atmospheric deposition is closely related to atmospheric pollution, climatic conditions and local micro-environment. Mining activities such as mineral resources mining and smelting and chemical enterprises such as smelting plants and coking plants are the main sources of heavy metals in atmospheric dust.

Table 5. Statistical table of annual sedimentation flux of dry and wet atmospheric deposition in the survey area ($mg/m^2 \cdot a$).

Element	Cr	Ni	Cu	Zn	Cd	Pb	As	Hg	Se	F
Maximum	40.33	150.51	50.12	300.26	0.11	50.03	0.63	0.01	0.29	4470.60
Minimum	0.90	0.86	0.39	30.63	0.01	0.77	0.08	0.0	0.03	200.22
The minimum annual subsidence flux reaching the limit value of type II soil 10 years later*	5550	305	616	3656	2	6630	464	5	\	\

Note: *Technical Requirements for 1:50000 Geochemical Survey and Evaluation of Land Quality (Trial).

According to the statistical analysis of the element data of atmospheric dry and wet deposition in the investigation area, the annual fluxes of heavy metal deposition in the investigation area are relatively small, which are far lower than the minimum subsidence fluxes that reach the limit value of the second-class soil 10 years later (Table 5). The results indicated that the geochemical quality of atmospheric environment in the survey area was good, and the effect on soil quality of agricultural land was small.

The deposition fluxes of each element of dry and wet atmospheric deposition in the survey area were distributed in Shawayu Village of Shahe Town and Pantoudian Village of Dudian Town near the towns. The main reason is that there are thermal power plants, biological pharmaceutical factories, carpet factories, aluminum companies and other textile and chemical enterprises distributed around these two collection points of atmospheric dry and wet deposition, which provide material sources for heavy metals in atmospheric dust. The larger value of annual deposition flux of each element of atmospheric dust in the survey area is distributed in the surrounding areas of cities and towns, especially the densely distributed areas of factories and enterprises. However, in rural areas, especially in areas far away from factories and enterprises, the annual deposition flux of various elements of atmospheric dust is relatively small.

4. Conclusion

(1) The element content characteristics of atmospheric dry and wet deposition were analyzed. It was found that the surface soil As element was less affected by atmospheric dry and wet deposition. The contents of Ni, Zn, Cd, Pb, Se and F were relatively high and enriched in different degrees, indicating that these elements were affected by human activities in different degrees in atmospheric dust fall.

(2) Through enrichment factor analysis, Zn, F, Cd and Se were moderately enriched, indicating that the sources of these elements were jointly affected by natural sources and human production activities.

(3) The principal component analysis of ten elements in the dust fall showed that two principal components could be extracted from ten elements, which reflected the total variance of 72.38%. Principal component F1 accounted for 72.38 % of the cumulative total variance. The enrichment coefficients of Zn, Pb, Cu, Cd, Hg and Se were all greater than 1.5, and the enrichment factor was greater than 2, indicating that the six elements in the atmospheric deposition in the survey area had similar sources, and the principal component F2 accounts for 15.378% of the cumulative total variance. The correlation coefficient between F element and Ni element was high. There was a

significant correlation. The variation coefficient and enrichment coefficient of the two elements were high. The load in the principal component F1 was also higher than 0.7. It showed that these two elements were affected by the exogenous material produced by human activities.

Acknowledgments

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