Pollution Characteristics of Heavy Metals in Soil of Dawu Water Source Area

Zhizheng Liu^{1,2}, Henghua Zhu^{2,3,*}, Xiaomei Song⁴

¹Institute of Marine Science and Technology, Shandong University, Qingdao, 266237, China;

²Shandong institute of Geological Survey, Jinan, 250013, China;

³School of Environmental Studies, China University of Geosciences, Wuhan, 430074 China;

⁴Shandong Geological Museum, Jinan, 250101, China.

Abstract

In order to understand the environmental quality of the soil in the Dawu water source, 38 sampling points were set up in the Dawu water source of Zibo City to study the content and spatial distribution characteristics of heavy metals Cr, Ni, Cd, Pb, As and Hg in the soil; The single factor and comprehensive pollution indexes were used to determine the soil pollution levels. The research results showed that the overall pollution degree of the water source was relatively light, and the heavy metal content did not exceed the risk screening value of the construction land; the Hg coefficient of variation was large, indicating that there might be point source pollution. Spatially, heavy metals were mainly concentrated in the north-central and eastern regions of water sources, which were consistent with the distribution of cities and towns, and were mainly affected by pollution sources, topography, and human activities. The degree of pollution was Hg>Cd>Pb>As>Ni>Cr, and some areas of the water source had been slightly polluted by Ni, Cd, Hg, and Pb, and Hg severely polluted by Hg. The Nemerow integrated pollution index was 2.41.

Keywords

Dawu Water Source; Soil Heavy Metals; Comprehensive Pollution Index; Spatial Distribution.

1. Introduction

With the continuous development of society, the problem of soil pollution has become more and more prominent. As an important part of the earth's biosphere [1], soil is the foundation or foundation of all terrestrial ecosystems. When the soil environment is polluted, its normal functions will inevitably be affected. It will not only cause changes in the structure in the soil. It will also migrate to other ecosystems, such as groundwater, plants, etc., and be absorbed and enrich by crops, and ultimately affect human health through the food chain [2~3].

Zibo City, Shandong Province is an important industrial park. Many heavy industry companies are located here. During the production process of thrsr companies, certain toxic heavy metals will be produced, which will pollute the soil environment of the water source. The heavy metal pollutants in the groundwater will first accumulate on the surface and enter the groundwater through the vadose zone of the soil under the action of rainfall leaching. The Dawu water source is an important source of drinking water in my country. If it is polluted, it will affect the production and life of human beings.

2. Material and methods

2.1 Overview of the study area

The study area was located in Linzi District, Zibo City (Fig.1). The terrain was high in the south and low in the north, with low hills in the south and sloping plains in the north. There was more precipitation in summer and less precipitation in winter [4]. The northern part of the water source was mainly the Quaternary sedimentary layer, with many layer, and the thickness gradually increase from the front of the mountain to the north. The slope-diluvial layer was formed in the valley between the mountains and the alluvial-diluvial layer was formed along the Zihe River. The exposed soil was mainly clay and sand. It can be seen from the figure that there were a large number of towns and farmlands around the factories, and the Zihe River passes in the east of the Shengli Oil Refinery and Qilu Petrochemical Rubber Factory. Roads and rialways run through the water source and the transportion was convenient. The main crops in Linzi District were wheat and corn, and Qilu Petrochemical Industry was the leading industry in this area.



Fig. 1 Distribution of soil samples

2.2 Sampling and analysis methods

This study selected areas with dense urban distribution of water sources. According to the distribution characteristics of enterprises and rural areas in the area, and taking into account the local topography, dominant wind direction, groudwater flow direction, and relevant requirements for soil pollution investigations, a total of 38 sampling points were set up according to the relevant requirements of soil pollution investigation and sampling. The plum blossom sampling method collected surface soil (0-20cm), removed the surface impurities of the soil sample, passed through a 1mm sieve, put the sample in a brown wide-mouth bottle and stored it under low temperature conditions [5~6], investigated and recorded the surrounding soil information such as pollution characteristics and potential sources of pollution were combined with GPS positioning (Fig.1)

According to the relevant regulations of soil heavy metals, the contents of Cr, Ni, Cd, Pb, As, and Hg in the samples were analyzed and tested. The contents of Pb and Cd were determined by graphite furnace atomic absorption spectrophometry, and the contents of Hg and As were determined by atomic fluorescence method. Flame atomic absorption spectrophotometry was used to analyze the content of Cr and Ni.

2.3 Evaluation method

Multivariate statistics and geostatistical analysis were used to make descriptive statistics such as mean value, median value, range, standard deviation and coefficient of variation [7], and Nemerow Comprehensive Pollution Index was used for pollution assessment.

The calculation formula of Nemerow Comprehensive Pollution Index is as follows:

$$P_i = \frac{c_i}{s_i} \tag{1}$$

$$P_n = \sqrt{\frac{(\bar{P}_i)^2 + (P_{imax})^2}{2}}$$
(2)

Where: P_i is the single factor pollution index of soil pollution i (i=1,2,3...); C_i is the measured value of soil pollutant i (mg/kg); S_i is the background value of soil pollutant i evaluation standard (mg/kg). According to the difference of P_i value, soil pollution is divided into 4 categories: $P_i \le 1$, non- polluting; $1 < P_i \le 2$, slight pollution; $2 < P_i \le 3$, light pollution; $3 < P_i \le 5$, moderate pollution; $P_i > 5$, heavy pollution. P_n is the Nemerow Comprehensive Pollution Index; P_i is the single pollution index of pollutant i (i=1,2,3...); P_{imax} is the maximum single pollution index of pollutant i. According to the Nemerow Pollution level is divided into 5 groups: $P_n \le 0.7$, clean; $0.7 < P_n \le 1$, waring limit value; $1 < P_n \le 2$, slight pollution; $2 < P_n \le 3$, moderate pollution; $P_n > 3$, severe pollution.

2.4 Data processing and analysis

Pearson correlation analysis was used to study the relationship between heavy metals. Microsoft Excel 2019 and SPSS 25 software were used to complete the data statistics and processing. Origin 2019 and MapGIS were used to complete the spatial analysis and mapping.

3. Results and analysis

3.1 Content characteristics of heavy metal elements

The basic parameters of six heavy metal elements in the surface soil of the study area, including Cr, Cd, Pb, and the background values of Zibo were listed in Table 1. The average values of Cd, As, Hg, and Ni in the table were all slightly higher than the soil background values of Zibo. The average value of Cr content was lower than the background value, indicating that human activities had little effect on the content of this heavy metal. The average value of Ni and Pb content was higher than the background value, and the Pb content was 1.107 times of the background value of the surface soil in Zibo, indicating that the content of Pb was mainly affected by human activities. The average content of the six heavy metal elements in the surface soil of the study area was less than the risk screening value of the "Soil environmental quality Risk control standard for soil contamination of development land" GB36600-2018.

The skewness of As, Cr, Ni, Cd, Pb and Hg ranged from 0.01 to 4.074. in which As was left skewed and other 5 were right skewed, indicating that there were more sampling points with As content lower than the average value, and the overall content was lower. There were more sampling points with other five heavy metal elements content higher than the average value. The kurtosis range was 0.02 ~ 18.95. The data distribution of Ni, Cd, Hg was relatively concentrated, and the other elements data distribution was relatively scattered. This might be due to the technological advancement of enterprises, the improvement of production methods, and the continuous improvement of pollutants discharged.

Project	Cr/10 ⁻⁶	Ni/10 ⁻⁶	Cd/10 ⁻⁶	Pb/10 ⁻⁶	As/10 ⁻⁶	Hg/10 ⁻⁶
Min10 ⁻⁶	42.23	12.83	0.08	15.44	2.22	0.02
Max/10 ⁻⁶	88.09	95.38	0.59	61.69	16.19	1.47
Average/10 ⁻⁶	64.87	33.36	0.18	30.89	10.48	0.13
Standard deviation	9.99	14.14	0.12	10.56	2.93	0.26
Coefficient of Variation/%	15	42	64	34	28	200
Skewness	0.01	2.72	2.13	1.34	-0.55	4.074
Kurtosis	0.02	9.80	4.01	1.64	0.22	18.95
Background values	70.8	32.0	0.162	27.9	10	0.045
Construction land screening value		150	20	400	20	8

Table 1. Descriptive analysis of soil heavy metal parameters

Because the content of heavy metals in the regional surface soil was affected by factors such as soil parent material weathering, atmospheric deposition, and external input, the distribution of heavy metals in the regional surface soil was uneven. The larger the coefficient of variation, the greater the variation range of heavy metal content and the more uneven the distribution, which was easily affected by human activities. Existing studies believed that the coefficient of variation was greater than 50% as a strongly differentiated distribution type, the coefficient of variation between 25% and 50% was a differentiated distribution type, and the coefficient of variation was less than 25% as a uniform distribution type [8]. It could be seen from Table 4 that the degree of Hg variation was particularly large, reaching 200%, and the regional distribution was extremely uneven, and there might be point source pollution, which was most likely caused by human factors; Cd was the second, with a coefficient of variation of 64%; the coefficient of variation of Ni, Pb and As were 42%, 34% and 28%, respectively, which belonged to the differentiated distribution type. It could be seen from Figure 1 that the Dawu water source had convenient transportation, which made the spread of heavy metals in the soil further and caused uneven spatial distribution; the coefficient of variation of Cr was the smallest, which was only 15%, indicating that the distribution of Cr was very uniform. Human factors had little influence.

3.2 Spatial distribution characteristics of heavy metal elements

3.2.1 Horizontal distribution characteristics

In order to further observe the distribution and change characteristics of heavy metal elements, the data was processed by CorelDRAW and Excel to further study the pollution of heavy metals in the soil of the water source.

It could be seen from Figure 2 that the spatial distribution characteristics of the contents of Cr, Ni, Pb, Cd and Hg were basically the same, and they were all concentrated on the southeast side of Wangzhu Village, near Qiwangda Group east, and Aihuaishu Village. The surrounding areas were low in content. The areas with high heavy metal content in the northern part of the water source were mainly concentrated in the main traffic line. The possibility of external source input was very high, and heavy industry enterprises such as Qiwangda were concentrated here. The high heavy metal content might be a large-scale production of enterprise. There were many cities and towns in the water source area, so human activities had a certain influence on the content of heavy metals. The points with high pollutant content were not all concentrated around heavy industry enterprises. The pollutant content in water source was not high. It might be related to the topography of the water source in the south and the north. The heavy metal elements in the soil moved northward by wind, and the pollutants on the east side could move through the Zi River, and gradually settle and accumulate where the river's speed slows down [9].

The As content distribution was relatively uniform, and the coefficient of variation was small. The distribution of As content was less affected by human factors. Because people used a large number of pesticides containing As in the past, which caused serious pollution to the environment, now

pesticides containing As were gradually replaced by other pesticides, so the content distribution was relatively uniform.

The study found that the content of heavy metals in the groundwater of the Dawu water source was lower than that in the surrounding soil, and its distribution characteristics were similar to the distribution characteristics of heavy metals in the soil. They were concentrated in Aihuaishu Village, Qiwangda Factory and the southeast side of Wangzhu Village. The type of groundwater in the water source area was mainly karst water, which had poor fluidity and made pollutants more concentrated.



Fig. 2 Spatial distribution of heavy metals in soil

3.2.2 Vertical distribution characteristics

In order to study the variation characteristics of the content of each element in the water source area with depth, the soil heavy metal content at the same depth at the sampling point was average (Table 2). It could be seen from the table that the content of As basically remained unchanged and fluctuates with depth; the content of other elements gradually decreased with the increase of depth, which showed that the five heavy metals of Cr, Ni, Pb, Cd and Hg were mainly concentrated on the surface.

Heary motal alamanta	Sampling depth							
Heavy metal elements	0-0.5m	0.6-1.0m	1.1-1.5m	1.6-2.0m	2.1-2.5m	2.6-3.0m		
Cr/10 ⁻⁶	65.29	68.97	61.25	66.47	66.79	59.02		
Ni/10 ⁻⁶	37.55	36.79	28.09	29.19	34.31	27.59		
Cd/10 ⁻⁶	0.24	0.18	0.11	0.13	0.16	0.13		
Pb/10 ⁻⁶	34.92	35.23	24.06	27.83	27.05	25.10		
As/10 ⁻⁶	10.16	11.22	10.42	11.51	9.86	11.33		
Hg/10 ⁻⁶	0.19	0.22	0.03	0.063	0.04	0.07		

Table 2. Contents of heavy metals in soil at different depths

3.3 Comprehensive Evaluation of Heavy Metal Pollution

The comprehensive pollution index method is a weighted multi-factor environmental quality index that takes into account the average value or the prominent maximum value. It can comprehensively reflect the pollution degree of different pollutants in the soil [10~14]. When grading soil pollution of heavy metal elements, local soil background values are often used as evaluation indicators [15~17].

The evaluation results of the comprehensive pollution index of soil heavy metals (Table 3) showed that the average value of the single pollution index of heavy metal elements was Hg> Cd> Pb> As> Ni>Cr. In terms of individual factors, the average single factor index of Cr was less than 1, indicating that the water source was not polluted by this element. The average value of Hg reaches 2.59, indicating that the area was more polluted by this element. The average value of the remaining four element indexes was greater than 1, indicating that there were already Ni, Cd, Hg and Pb pollution in this area, and the pollution level was relatively light. Cd moderate pollution accounted for 5.3%, indicating that the Cd element content in the soil in some areas of the Dawu water source exceeded the standard. Hg element pollution level reached severe pollution in some areas. Generally speaking, most areas of the study area were mainly non-polluting, with a certain degree of slight pollution, and some areas had moderate to heavy pollution.

Using formulas (1) and (2) to comprehensively evaluate the pollution status of the study area (Table 3), the Nemerow integrated pollution index ranged from 1.03 to 20.85, with an average value of 2.41. Among them, the moderately and lightly polluted points reached 81.58%, the moderately polluted points reached 2.63%, and the severely polluted points reached 15.79%, indicating that the overall pollution of heavy metals in the soil of the water source was moderate to light.

	Single factor index			Number of sample contamination point; Exceeding standard rate/%					
Project –									
	Max M	Min	A	No pollution	Slight	Light	Moderate	Heavy	
		Min	Average		pollution	pollution	pollution	pollution	
Cr	1.24	0.6	0.92	28/73.7	10/26.3	0	0	0	
Ni	2.98	0.4	1.04	24/63.2	13/34.2	1/2.6	0	0	
Cd	3.69	0.5	1.14	26/68.4	7/18.4	3/7.9	2/5.3	0	
Pb	2.21	0.55	1.11	20/52.6	16/42.1	2/5.3	0	0	
As	1.62	0.22	1.05	17/44.7	21/55.3	0	0	0	
Hg	29.46	0.32	2.59	23/60.5	7/18.4	1/2.6	2/5.3	5/13.2	
Nemerow index	20.85	1.03	2.41	0	0	31	1	6	

Table 3. Results of comprehensive pollution assessment of heavy metals

4. Conclusion

(1) The soil heavy metal content of Dawu water source was unevenly distributed, and the six heavy metal elements were all lower than the standard for construction land. Spatially, the polluted areas were concentrated along the Zihe River on the southeast side of Wangzhu Village, near Qiwangda Plant East, and other areas contain less heavy metals.

(2) The evaluation result of Nemerow comprehensive index method showed that the soil was mainly lightly polluted (81.58%), and the main influencing elements were Hg and Cd. The single factor index results showed that the proportions of Cr, Ni, Cd, Pb, As and Hg belonging to minor pollution and below were 100%, 97.4%, 86.8%, 94.7%, 100% and 78.9%, Respectively.

Acknowledgments

This paper has been supported by Construction of 3D visualization information system of Dawu Water source area in Zibo City.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] J.L. Smith, J.J. Halvorson, R.I. Papendick. Using Multiple-Variable Indicator Kriging for Evaluating Soil Quality. Soil Science Society of America Journal, 1993, 57.
- [2] C.F. Li, J.F. Cao, J.S. Lv, et al. Ecological Risk Assessment of Soil Heavy Metals for Different Types of Land Use and Evaluation of Human Health, Environmental Science, vol.39(2018), 5628-5638.
- [3] P. Han, J.H. Wang, X.Y. Feng, et al. Ecological Risk Assessment of Heavy Metals in Soil in Shunyi, Beijing, Journal of Agro-Environment Science, vol.34(2015),103-109.
- [4] X.L. Bao, Y.H. Fei, Y.S. Li. et al. Determination of the key hydrodynamic parameters of the fault zone using colloidal borescope in the Dawu well field and strategies for contamination prevention and control, Hydrogeology & Engineering Geology, vol.47(2020),56-63.
- [5] B.H. Jang, B. Zhang, X.F. Wang, et al. Heavy Metal Pollution and Potential Risk Assessment of Soil in Fushun Western Open-Pit Mining Area, Journal of Northeastern University (Natural Science), vol.41 (2020), 568-574.
- [6] W.J. Wang, T.L. Wu, D.M. Zhou, et al. Advances in soil heavy metal pollution evaluation based on biliometrics analysi, Journal of Agro-Environment Science, vol.36(2017), 2365-2378.
- [7] B. Dai, J.S. Lv, J.C. Zhan, et al. Assessment of Sources, Spatial Distribution and Ecological Risk of Heavy Metals in Soils in a Typical Industry-based City of Shandong Province, Eastern China, Environmental Science, vol.36(2015),507-515.
- [8] J.N. Fan, X.M. He, W. Du, et al. Analysis and comparing environmental baseline values of heavy metals in soil based on standardized method and statistical method, Journal of Huazhong Agricultural University: 1-8 [2021-01-30]. http://kns.cnki.net/kcms/detail/42.1181.S.20201218.1035.004.html.
- [9] F. Liu, Y.M. Guan, G.B. Che, et al. Environmental Monitoring and Ecological risk assessment of Heavy Metals in Soils of Typical Industrial Areas in Siping City, Shandong Chemical Industry, vol.48(2019),236-238.
- [10] C.L. Zhang, W.P. Zhang, H.D. Cheng, et al. Heavy metal contamination and health risk assessment of farmland soil around coal mines in Yuzhou City, Environmental Chemistry, vol.38(2019),805-812.
- [11]C.Y. Li, M.J. Hu, J. Wang, et al. Spatial and temporal pollution characteristics and health risk assessment of heavy metals in surface dust on campus in Lanzhou city, Hubei Agricultural Sciences, vol.38 (2019), 805-812.
- [12] Y. He, J.Y. Li, Y.L. Tian, et al. Pollution level and risk assessment of heavy metals in Municipal Sludge, Environmental Science & Technology, vol.44(2021),131-138.
- [13] T.M. Lu. Organic pollution characteristics and health risk assessment of groundwater in Dawu water source area in Zibo City, Qingdao: Shandong University of Science and Technology, 2020.

- [14]R.Y. You, T.Q. Ao, H. Zhu, et al. Comparative study on water quality evaluation methods of small watersheds, Sichuan Environment, vol.40(2021),73-81.
- [15] C.F. Li, D.L. Liu, P. Zhao, et al. Evaluation of soil heavy metal pollution and ecological risk in a Mining Area, Sichuan Environment, vol.40(2021),141-148.
- [16] J.H. Qi, L.Y. Yang, Y. Zhang, et al. Analysis on Water Quality Change and Influencing Factors of the Sihe River[J/OL]. Journal of University of Jinan(Science and Technology), (2021):1-7[2021-05-15]. https:// doi.org/10.13349/j.cnki.jdxbn.20210323.001.
- [17] T. Jang, W.W. Lin, Y.J. Cao, Pollution and Ecological Risk Assessment and Source Apportionment of Heavy Metals in Sediments of Qingliangshan Reservoir in the Meijiang Basin, Environmental Science, vol.41(2020),5410-5418.