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Evaluation on Soil Heavy Metal Pollution by Fuzzy Mathematics

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The experiment aims to measure the degree of contamination of heavy metals in soil. This paper takes Dunhua District, Taiyuan City as an example to detect heavy metals in soil of five sampling sites through the fuzzy mathematics and the atomic absorption method. With the consideration of soil pH values, the soil quality of sampling sites is finally evaluated by fuzzy mathematics. The results show that the average pH value of the experimental soil samples is 8.02, which is weakly alkaline soil. The population degree of the west of Dongjiying is the highest, while that of Echi is the lowest.

1. Introduction

The heavy metals in soil will not be decomposed by microbes. Once the heavy metals exceed the limit, it will have a negative impact on the local soil environment, the ecological environment and the health of residents. Therefore, it is of great practical significance to analyze and evaluate the pollution of heavy metals in soil.
This paper takes Dunhua District, Taiyuan City as an example and combines pH values of local soil to analyze the heavy metals in soil of five sampling sites through fuzzy mathematics and atomic absorption method.

2. Literature review

Urban polluted land seriously restricts and harms urban economic development and urban population health. As a material guarantee for promoting urban development, the quality of land determines the speed and scale of urban modernization. In recent years, with the acceleration of urbanization and the expansion of urban scale, the shortage of urban land resources has become increasingly apparent. Because of the extensive economic policy implemented in China in the early years, coupled with the weak concept of soil environmental protection, the risk of urban soil pollution in the process of industrial development is increased. The polluted soil not only affects the quality of the urban ecological environment, but also brings potential harm to the urban residents' human health belt. These soils, which may be "invaded" by toxic and harmful substances in the original production and operation activities, are likely to pose a threat to human health if they do not carry out the necessary measures. Therefore, the risk assessment of human health and environmental damage caused by soil pollution is carried out.
The exchange of pollutants in soil is frequent and complex, and the pollutants, especially heavy metals, are more changeable, which makes it difficult for the understanding of the spatial distribution of heavy metals in the soil, the discrimination of pollution sources and the plan for the prevention and control of soil pollutants the water and the atmosphere. The study of source apportionment of soil pollution is usually divided into diffusion model and receptor model according to different research objects. The diffusion model is concerned with the dynamic behavior of matter in the medium. The diffusion model is used to calculate the impact of each source on the research area according to the pollutant emission and pollutant physical and chemical properties in the study area. However, these values have uncertainty to a certain extent, which makes the prediction results unreliable. The research object of the receptor model is the contaminated area. By analyzing the physicochemical properties of the source and receptor, the contribution of the pollution source to the receptor or the monitoring points is calculated by the qualitative identification of the potentially harmful sources of the

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receptor, and the contributions of the sources to the various components of the receptor or the monitoring points are popularized in many scholars.

In recent years, environmental workers at home and abroad have studied the heavy metal pollution in soil more and more deeply, and have obtained a series of research results. Similar to the study of soil heavy metal pollution in foreign countries, researchers in China have just started to study heavy metal pollution in soil. Due to the limitation of theory and technology, the comprehensive evaluation method of fuzzy mathematics is used to evaluate the pollution of soil heavy metals. With the in-depth study of heavy metal pollution in soil, the toxicity difference between different kinds of heavy metals is also included in the evaluation system, as the different toxicity of heavy metals means that the possible harm to the human body is different. In order to study the toxic effects of different heavy metals in soil, soil risk assessment technology has been widely used. Baveye and Laba carried out soil pollution by the close value method, which reflected the pollution points and pollution factors which needed to be controlled first in soil pollution, but it could not reflect the degree of pollution (Baveye and Laba, 2016). In the study of the impact of soil pollution on human health, Tang and others focused on the content of pollutants in the soil. At the same time, the environmental risk caused by soil pollution was described by the T system. The potential ecological hazard index method was a comprehensive method that could take into account the chemical characteristics of soil, the toxicological characteristics of heavy metals in the soil and the ecological hazards of heavy metals. This method could explain and evaluate the potential hazards of heavy metals in soil, and provide a theoretical basis for the subsequent remediation and treatment of soil (Tang et al., 2017). The total amount and chemical form of heavy metals in the sediments were analyzed by Korneikova, and the mass fraction of heavy metals (Cu, Cd, Pb and Zn) was also far beyond the two-grade standard value of soil environment. Plants growing around them are also polluted by different heavy metals, and the ability of different plants to absorb and accumulate heavy metals is very different (Korneikova, 2018). The total amount and chemical form of heavy metals in the tailings and soil sediments around the mining area were studied by El and other researchers. It showed that the soil pollution around the mining area was a multi metal compound pollution mainly of Cu, Zn, As, Cd and Pb, with high comprehensive pollution index. The water extraction state and EDTA extraction state of Cu, Zn, As and Cd were contained in the mining area, which had higher quantity, higher bioavailability and greater potential harm to the surrounding ecosystem. The environmental pollution of mining area water is similar to soil pollution. It is also a polymetallic compound pollution mainly composed of Cu, Zn, Cd and Pb. Some heavy metal elements in the sediments were mainly in residual state. The exchangeable state of Cd and Pb and the organic state content of Cu and Zn were very high, and there were certain potential threats to the environment (El et al., 2017). Olaya-Abril and so on researchers used multiple linear regression to analyze the source of multi element in surface soil, and pointed out that metallurgical, mining and waste emissions were the main causes of pollution in this area. At the same time, the trend of surface soil pollution was presented from point source pollution to surface pollution (Olaya-Abril et al., 2017). Nwachukwu and others adopted the enrichment factor method to analyze the pollution sources of different soil in the forest or natural pollution. The analysis pointed out that the enrichment factor method considered the human activity interference or the natural variation, so it is necessary to determine whether the soil is subject to the maximum allowable value of the surface element simply considering whether the surface element is more than the maximum value (Nwachukwu et al., 2017). Rajaram et al. carried out the source apportionment of heavy metals in India based on GIS technology and multivariate statistical analysis. It is found that CO, Cr and Ni were mainly controlled by parent rocks, while Cu, Zn and Pb were mainly affected by human activity null values (Rajaram et al., 2017). Vajčnerová and other researchers analyzed the source analysis results of soil heavy metals in the same area by principal component analysis, factor analysis and cluster analysis, and found that the pollution thematic map generated by the combination of GIS and multivariate statistics could better determine the source of pollutants (Vajčnerová et al., 2016).

To sum up, in the above research work, the soil pollution is mainly studied by means of close value method, multiple linear regression, GIS technology analysis, cluster analysis and so on. The total amount of heavy metals and chemical forms in the soil are discussed, but the method of fuzzy mathematics is seldom studied. Therefore, based on the above research situation, the evaluation of soil heavy metal pollution is mainly studied by fuzzy mathematics. The relevant theoretical foundation of fuzzy mathematics and the corresponding formula structure are put forward. This method can well explain the toxic differences between different kinds of heavy metals as well as the possible harm to human body.

3. Experiment

3.1 Sample Collection

According to the results of the second soil survey, the soil of irrigation areas in Dunhua is divided into cinnamon soil, meadow soil and saline soil. The sampling sites are mainly distributed in sewage irrigated areas of five towns in Dunhua District, Taiyuan City, including the south of Wangda, the west of Dongjiying, the east of Xigu, the south of Echi, the north of Mengfeng. 95 samples, which are not less than one kilogram, are collected.

3.2 Sample Analysis

Samples are dried naturally, quartered 0.5 kilogram, separated from plant residues and stones, grinded 100 times, and saved in sample sacks. The soil pH values are determined by the potential method, organic matters (SOM) by the potassium dichromate method, soil grades by the hydrometer method, and the bulk density of soil by the core cutter method. The heavy-metal ions are measured through the HCI-HNO3 digestion which is mixed with acid reagents based on national standards, and 50 ml is kept after filtering. Heavy-metal ions Cu, Ni, Cr, Zn, Pb, Cd and heavy metals Hg, As are measured by the flame atomic absorption spectrometry (AA240FS) and analyzed by the AFS-3100 atomic fluorescence spectrometry (from Beijing Kechuang). Each sample is determined in parallel for three times and its average value is picked out for statistical analysis.

3.3 Evaluation Method

The soil heavy metals in Qingxu County are evaluated through fuzzy mathematics. Firstly, the membership function needs to be determined, the fuzzy relationship matrix is established, as well as u= {Cu, Ni and Hg} is taken as the set of evaluation factors. v= {grade 1, grade 2 and grade 3} is set. The membership degree of soil heavy metal pollution at all levels is obtained by the membership function, forming a fuzzy matrix of 3*3, which is the fuzzy relationship matrix.

Due to the difference in the contribution of individual evaluation indexes to the environmental complex, various weights should be given. There are many methods to calculate the weight. In general, the weight is the ratio of the measured concentration of pollutant factors in soil and the corresponding classification standard. The formula is as follows:

$$w_i = \frac{\frac{c_i}{s_i}}{\sum_{i=1}^{n} \frac{c_i}{s_i}}$$

where C_i is the measured value of each index and S_i is (S1+S2+S3)/3. Three weights of heavy metal factors are calculated according to this formula, forming the matrix W_i= {a, b, c}, which is called the weight fuzzy matrix with the weight value of each evaluation factor.

According to the above methods, the fuzzy relationship matrix and the weight fuzzy matrix of each sampling site are calculated, and evaluated by the single-factor decision model and the weighted average model. The single-factor decision model is to calculate the membership degree at all levels and normalize based on the principle of taking the small one and then the big one. The weighted average model is:

$$b_j = \sum_{i=1}^{n} w_i r_{ig}, \qquad j = 1,2,3$$

where b_j is the membership degree of j for the final evaluation result, W_i is the corresponding weight, r_{ig} is the corresponding element in the fuzzy relationship matrix S, and n is the number of evaluation factors.

3.4 Evaluation Criteria

The soil environmental quality standard values (GB15618-1995) are used for analysis and evaluation. The specific criteria are shown in Table 1.

*Table 1: Soil Environmental Quality Standard Values（mg*kg-1）*

Evaluation standard		As	Hg	Cd	Pb	Cr	Cu	Ni	Zn
Two countries	PH<6.5	40	0.3	0.3	250	150	50	40	200
	6.5<pH<7.5	30	0.5	0.3	300	200	50	50	250
	pH>7.5	25	1.0	0.6	350	250	100	60	300

4. Results and Discussion

4.1 Physical and Chemical Properties of Soil

Table 2: Surface soil basic properties

Sampling point	Meng Feng Village North	Goose pool village south	West Valley Township East	Wang Anshan East	Dongjiaying Village West
Cation exchange capacity	59.35	61.49	85.27	118.95	79.75
pH average	8.02	7.97	8.06	8.38	7.61
Organic matter%	2.18	1.56	1.40	1.40	1.27
Bulk weight ($g\cdot cm^{-3}$)	1.373	1.312	1.249	1.249	1.471
Grit%	50	30	41	41	78
Powder%	43	60	48	48	17
Cosmid%	7	10	11	11	55
Soil texture	Loam	Pink loam	Pink loam	Loam	Sandy loam

The physical and chemical properties of the surface soil in irrigation areas in Dunhua District, Taiyuan City are shown in Table 2. The average cation exchange capacity in irrigation areas is 80.96cmol·kg-1, of which the capacity in the south of Wangda is the highest (118.95cmol·kg-1). The soil pH distribution is concentrated, with the average pH value of 8.01 belonging to the weak alkaline soil and pH values of surface soil of about 8. The highest average value is 8.38 in the south of Wangda, and the lowest is 7.61 in the west of Dongjiaying. The organic matters in the surface soil are between 1.27% and 2.18%, and the average soil organic matters in irrigation areas are 1.69%. Therefore, the soil in irrigation areas is more suitable for agricultural production from the distribution of organic matters. The bulk density of soil refers to the quality of unit volume with unspoiled soil structures and is a measure of soil elastic status. The overall density distribution is between 1.197 and 1.471 g·cm-3, with the average of 1.320 g·cm-3, and the bulk density of different sample sites is shown in Table 2. The soil texture can be divided by the fineness ratio, and the soil texture of these five sampling sites all belongs to loam soil. The soil structure in irrigated areas is mostly broken and granular, and the color is brownish red.

4.2 Average Value of Heavy Metals in Irrigation Areas

Table 3: soil average content of heavy metal elements（mg·kg-1 ）

Sampling point	Cu	Zn	Hg	Ni	Pb	Cr	Cd	As
Wang Anshan East	38.452	103.713	0.186	36.588	35.796	28.691	1.256	6.576
Dongjiaying Village West	42.112	156.763	0.190	41.788	36.046	30.793	1.422	6.638
West Valley Township East	39.516	106.730	0.132	37.549	32.000	28.764	1.215	5.867
Meng Feng Village North	40.606	109.610	0.246	37.973	34.319	28.707	1.234	6.338
Goose pool village south	35.302	96.974	0.119	32.226	49.181	24.291	1.107	5.406
Coefficient of variation	0.241	0.290	0.491	0.226	0.328	0.438	0.142	0.195

The analysis of eight heavy metals in irrigated areas is shown in Table 3. The highest value of Cu in irrigation areas is 106.285 cmol·kg-1, and the average level is 39.198 cmol·kg-1. The over-limit ratio is only 1% in accordance with the national secondary standard, but it is 91.4% based on the background value of Shanxi Province that shows the value of Cu is not higher than that of the secondary standard, conforming to the need of agricultural production, but there is a trend of pollution. The highest value of Zn in the sample sites is up to 573.26539.198 cmol·kg-1, and that of Hg is 0.981 cmol·kg-1. However, both average values of Zn and Hg (114.758 and 0.17mg·kg-1 respectively) are not higher than the secondary standard. The value of Ni exceeds the secondary standard by 4.3 percent and the background value of Shanxi Province by 62.9 percent with less pollution. The values of As and Cr are very low, basically with no pollution. The value of Cd (0.6mg·kg-1) is higher than that of the secondary standard, belonging to the most polluted heavy metals. Thus, there is a large number of Cd in the sewage which is used to irrigation in Dunhua District. The sewage must be dealt with to control the pollution of Cd.

4.3 Correlation between Heavy Metal Content and Soil Physical and Chemical Properties

In order to reveal the relationship between the heavy metal pollution and soil properties, the SPSS software is used to analyze their correlation. The Table 4 shows the correlation coefficient matrix between soil heavy metal content and soil physical and chemical properties. The analysis displays a negative correlation existed between heavy metals in soil with pH values. The negative correlation between Zn and its pH value is the most obvious that shows the pH value is an important property to affect the soil heavy metal content. The correlation between heavy metal content and cation exchange capacity is not obvious, of which Zn, Hg, Pb and cation exchange capacity are negatively correlated, while the other five heavy metals are positively correlated inconspicuously. The bulk density is also an important factor for the heavy metal content. As shown in Table 4, the heavy metal content is positively correlated with the soil bulk density. Hg and As are positively correlated with organic matters and others are negatively correlated.

Table 4: Soil heavy metal elements and soil physical and chemical properties of the correlation coefficient matrix

	Cu	Zn	Hg	Ni	Pb	Cr	Cd	As
CEC	0.061	-0.021	-0.188	0.161	-0.379	0.362	0.275	0.495
pH	-0.446	-0.785	-0.141	-0.489	-0.111	-0.254	-0.054	-0.035
Organic matter	-0.091	-0.506	0.570	-0.222	-0.135	-0.086	-0.273	0.254
Bulk weight	0.265	0.719	0.122	0.323	0.355	0.078	0.417	0.002

5. Analysis of Fuzzy Mathematics Evaluation Results

Samples from five sampling sites are chosen as evaluation objects, As, Cu, As, Ni, Hg, zinc, Cd, Cr and Pb, as individual evaluation factors, are analyzed, membership functions between heavy metals in soil and the corresponding environment quality grade are established, and the fuzzy relationship matrix is calculated according to the establishment method and evaluation criteria. Taken the south of Echi as an example, the fuzzy relationship matrix is shown in Table 5.

Table 5: Goose pool South membership matrix

Heavy metal	Cu	Zn	Hg	Ni	Pb	Cr	Cd	As
A degree of membership	0.862	0.853	0.967	1.000	0.883	1.000	0.000	1.000
Secondary membership	0.138	0.147	0.033	0.000	0.117	0.000	0.000	0.000
Three-degree membership	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000

Comprehensive evaluation is carried out based on the single-factor decision model and the weighted average model. In accordance with the control significance of the soil environmental quality at all levels, the score of first class environmental quality is set at 100, the second at 80, and the third at 60, so as to calculate evaluation scores of each sample site. From the evaluation scores, it can be seen intuitively that the environmental quality of soil heavy metals in each sampling sites can be greatly improved. The calculation formula of scores is as follows:

$$c = \sum_{j=1}^{m} \delta_j c_j, \qquad \delta_j = \frac{b_j^k}{\sum_{j=1}^{m} b_j^k}$$

where k is the selected positive real number, δj is a set of weights, bj is the environmental quality corresponding to the j (j=1, 2, 3... m) of the evaluation vector B, cj is the standard score for the environmental quality of j, and c is the final score. The evaluation results are shown in Table 6.

As you can see in Table 6, the highest score of two evaluation results is in the south of Echi, that is the pollution in the south of Echi is the least. The lowest score is in the west of Dongjiaying, namely the pollution in the west of Dongjiaying is the most serious. Because of the negative correlation between the heavy metal content and the pH value, and the lowest pH value of this sampling site (7.61), the pollution in the west of Dongjiaying is the worst. According to the distribution of the evaluation score and the membership degree, the pollution degree of heavy metals in different sampling sites can be obtained: the west of Dongjiaying > the east of Xigu > the south of Wangda > the north of Mengfeng > the south of Echi. In addition to the soil pH values and the distance from irrigation channels, the usage of pesticide and fertilizer, the road traffic flow on both sides of the farmland and other factors also have a certain influence. The evaluation results of two fuzzy mathematical models reflect that all sampling sites are at the third level of pollution, and the comprehensive pollution of heavy metals is serious.

Table 6: Fuzzy mathematical model evaluation

Evaluation model	Sampling point	Wang Anshan South	Dongjiaying Village West	West Valley Township East	Meng Feng Town North	Goose pond village south
Single factor decision model	Degree of membership 1	0.127	0.092	0.131	0.135	0.147
	Degree of membership2	0.096	0.131	0.054	0.045	0.025
	Degree of membership3	0.777	0.777	0.815	0.820	0.828
	Evaluation score	60.212	60.162	60.172	60.181	60.225
	Grade	Three	Three	Three	Three	Three
Weighted average model	Degree of membership1	0.375	0.333	0.384	0.410	0.445
	Degree of membership2	0.102	0.158	0.077	0.082	0.033
	Degree of membership3	0.523	0.510	0.593	0.509	0.522
	Evaluation score	75.422	74.481	75.323	76.874	77.657
	Grade	Three	Three	Three	Three	Three

6. Conclusion

The average pH value of soil samples in this experiment is 8.02, which is weakly alkaline soil, and the heavy metal content in soil of the experimental areas is basically lower than the national standard. From the experimental process, when the soil heavy metal content increases, the pH value will decrease and the capacity will also rise. From the experimental results, the pollution degree of sampling sites from low to high is the Echi, the north of Mengfeng, the east of Wangda, the east of Xigu, and the west of Dongjiaying

Improving irrigation water and irrigation methods are effective measures to alleviate farmland pollution. The usage of sewage to irrigate farmland in these experiment areas causes higher soil heavy metal content. The local must adjust its irrigation measures and avoid the usage of sewage, so as to effectively improve the farmland pollution situation.

Reference

Baveye P.C., Laba M., 2016, Comment on "Potential of integrated field spectroscopy and spatial analysis for enhanced assessment of soil contamination: A prospective review" by Horta et al. Geoderma, 271(521), 254-255, DOI: 10.1016/j.geoderma.2015.11.025

El A.A., Rhoujjati A., El Hachimi M.L., 2017, Pollution and ecological risk assessment of heavy metals in the soil-plant system and the sediment-water column around a former Pb/Zn-mining area in NE Morocco, Ecotoxicology & Environmental Safety, 144(5), 464-474, DOI: 10.1016/j.ecoenv.2017.06.051

Korneikova M.V., 2018, Comparative Analysis of the Number and Structure of the Complexes of Microscopic Fungi in Tundra and Taiga Soils in the North of the Kola Peninsula. Eurasian Soil Science, 51(1), 89-95, DOI: 10.1134/s1064229318010106

Nwachukwu M., Uwaezu O., Ogbuja O.I., 2017, A Comparative Assessment of Heavy Metal Pollution in Soil using pH Enrichment Factor and Pollution Index, American Journal of Environmental Sciences, 13(2), 191-203, DOI: 10.3844/ajessp.2017.191.203

Olaya-Abril A., Parras-Alcántara L., Lozano-García B., 2017, Soil organic carbon distribution in Mediterranean areas under a climate change scenario via multiple linear regression analysis, Science of the Total Environment, 592, 134-143, DOI: 10.1016/j.scitotenv.2017.03.021

Rajaram R., Ganeshkumar A., Vinothkumar S., 2017, Multivariate statistical and GIS-based approaches for toxic metals in tropical mangrove ecosystem, southeast coast of India. Environmental Monitoring & Assessment, 189(6), 288, DOI: 10.1007/s10661-017-5980-9

Tang P.Z., Liu J.Z., Lu H.W., 2017, Information-based Network Environ Analysis for Ecological Risk Assessment of heavy metals in soils, Ecological Modelling, 344, 17-28, DOI: 10.1016/j.ecolmodel.2016.10.009

Vajčnerová I., Šácha J., Ryglová K., 2016, Using the Cluster Analysis and the Principal Component Analysis in Evaluating the Quality of a Destination, Acta Universitatis Agriculturae Et Silviculturae Mendelianae Brunensis, 64(2), 677-682, DOI: 10.11118/actaun201664020677