Technical report Comprehensive Assessment Model on Heavy Metal Pollution in Soil

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Received: 7 May 2012 / Accepted: 22 May 2012 / Published: 1 June 2012

Metal pollution in soil poses a serious threat to the human health and safety of agricultural products. Evaluation for distribution and remediation of heavy metal pollution is the most concerned. In this paper, 319 information points of heavy metal distribution in a municipal area of about 100 square kilometers are taken into account. A q-q plot made by SPSS, the single-factor model, and the Neremo index model are employed to study impact factors of heavy metals in soil, such as spatial distribution, pollution index, and degree of pollution. Considering the defect caused by equally treating pollution degrees of different heavy metals in the Neremo comprehensive evaluation model, we propose an improved Neremo evaluation model by introducing the weight factor. A comprehensive assessment model on heavy metal pollution in soil has been established and will play a significant role for government to make decisions on environmental protection and agricultural production.

Keywords: Heavy metal pollution; Assessment; Single factor index; Neremo Index

1. INTRODUCTION

Heavy metal pollution, caused by pollutants such as arsenic and zinc, is tormenting not only Inner Mongolia but other areas, including Hunan Province and Liaoning Province, in China. Pollution is being transferred from air and water to soil, posing a major threat to health and food safety[1]. There are high incidences of occupational diseases and increase of mortality rate. For instance, life spans of such patients are generally less than 45 years[2]. Soil pollution poses the biggest threat to food safety in China. Up to 12 million tones of grains are estimated to be tainted by heavy metals every year, causing more than 20 billion RMB yuan in economic losses[3]. Heavy metals are non-biodegradable and persistent environmental contaminants, which may be deposited on the soil surfaces and then adsorbed into tissues of vegetables. Plants take up heavy metals from the tissue parts exposed to the air in polluted environment as well as from contaminated soil[4]. In 2011, according to a 2-7 years of continuous monitoring data in 118 cities, about 64% of urban groundwater is suffering very heavy metal pollution, about 33% is suffering moderate pollution, and only 3% meets the basic standards of cleanliness[5].

Owing to the severe consequences brought by the heavy metal pollution in soil, it is urgent and necessary to control pollution. To prevent and remedy the contamination,

We must know the migration, transformation behavior and rules of heavy metals insoil, and make an accurate assessment of contamination level and extent at each site. Till now, researchers have made some achievements on the studies of heavy metal pollution. Evaluation methods were proposed in reference 7, which includes the single-factor index evaluation method, Neremo comprehensive pollution index and accumulation index method. But the evaluation methods have not drawn a conclusion on the discipline and the system model. We have sampled 319 sites for five heavy metals (Pb, Hg, Cr, As, and Cd), which are the most harmful to human beings in surface soil of 600 square kilometers. The q-q plot made by SPSS, the single-factor model and the Neremo index model are employed to study the impact factors of heavy metals in soil, such as spatial distribution of pollution, pollution index, and degree of pollution. A novel comprehensive assessment model on heavy metal pollution in soil will be established, which can be useful in environmental protection and agricultural production control.

2. CONSTRUCTION OF SPATIAL DISTRIBUTION GRAPHICS OF HEAVY METALS

In order to show intuitively the spatial distribution of the given five heavy metals, we established a three-dimensional map versus locations and concentrations of metals based on the 319 sampling points. The three-dimensional map shows terrain conditions of the city. Colors of the surface are represented by the concentrations of the different heavy metals.

2.1 Functional regions of the urban

The urban area is divided into five parts, roughly the living, industrial, mountainous, transportation, and park areas, according to functions of the sampling areas. Due to page length limitation, we will discuss the living area only. Fig.1 shows two-dimensional distribution of the functional areas.

It is shown from figure 1 that the industrial areas of the city are located in the northwest coast, the mountain areas are in the northeast to the southeast, and the transportation and the living areas are scattered throughout the city. The distributions are in line with people's living and working needs. However, park areas are not only in small percentage but also relatively scattered. The figure of two-dimensional distribution of the functional areas will be used to analyze the spatial distribution of heavy metals in the whole city.

¹ Fund: National Natural Science and foundation project number:61071025



Figure 1. Two-dimensional distribution of functional areas

2.2 Spatial distribution of heavy metals (As)

The spatial and two-dimensional distributions of extreme concentration points of the heavy metal As have been plotted with Matlab 7 and are shown in fig.2 and fig.3, respectively.



Figure 3. Two-dimensional distribution of As

It can be found from figure2 that the pollution distribution of As is star-shaped (extending equally in all directions from a center point) and as "comet" (extending in a certain direction

from a center point, or broom-like distribution) that the trend of concentration is downward. Fig. 2 indicates that there are two obvious stellar-shaped distributions, i.e. comet-like distributions, and similar stellar-shaped distributions in several regions where the concentration level of As at the center is low. It can be speculated that this phenomenon is caused by the pollution spreading from the near high-pollution points.

Take locations of the sampling points and concentration levels of As, as coordinates and we can obtain the distribution of As shown in Fig.3. As can be seen from Fig.3, there are two peaks with steep slopes. The distribution of the concentrations decreases from the peaks to the surroundings, as was mentioned above in the "stellar distribution". In the left of Fig.3, the terrain seems flat relatively while the color is dark, which indicate that there is relatively high content of As and the pollution spreads in a certain direction. This feature is called comet-like distribution. The spatial distributions of Cd, Cr, Hg, and Pb can be obtained in the same way.

3. STATISTICAL CHARACTERISTICS OF HEAVY METALS

3.1 Distribution analysis with a Q-Q plot

The statistical analysis function of SPSS18 (social science statistical software) is utilized to determine whether the data follow the normal distribution by observing the distribution of data around a straight line in a Q-Q plot. The slope of the line in the Q-Q plot represents the standard deviation, and the intercept indicates average value of data sampled. The rough information about skew and kurtosis of the sample can be also obtained through the Q-Q plot, which can also be used to obtain normal, trend normal, lognormal, and trend lognormal figures of each metal. The normal figure shows whether there are enough placements around the mean value while the decreasing trend figure shows whether the placements are concentrated around the mean value. The trend lognormal figure shows decrease trend of each heavy metal. The concentration distribution of As in living area is used for example to be discussed later.



Figure 4. Normal Q-Q Plot (left) and trend Normal Q-Q Plot (right) of As



Figure 5. Lognormal Q-Q plot (left) and trend lognormal Q-Q plot (right) of As

The corresponding analysis of above four figs shows that As points are very close to the straight line both in the normal Q-Q plot and in the lognormal Q-Q plot, but As points in the decreasing trend lognormal Q-Q plot are closer to the mean values. Therefore we can obtain the lognormal distribution of the element As in the soil of the city.

The same method is also utilized to analyze the remaining four kinds of elements in the five regions. We assume that the distributions of the five elements in the five functional regions most are approximately normal or lognormal. Thus the mean concentration values of each element in each functional region can reflect approximate pollutions of the heavy metals.

3.2 Statistical analysis results

The statistics software SPSS was employed to analyze the distribution of the five heavy metals in the soil of living, industrial, mountain, transportation, and park areas. The results are shown in Table 1. Due to limited space, results for the other four functional areas are not exhaustively listed. The results will help us evaluate the degree of pollution.

| | As $(\mu g/g)$ | Cd (ng/g) | $Cr(\mu g/g)$ | Hg (ng/g) | Pb (µg/g) |
|------------------|----------------|-------------|---------------|-----------|-----------|
| maximum | 11.45 | 1044.5 | 744.4 | 550.0 | 472.4 |
| minimum | 2.34 | 86.8 | 18.46 | 12 | 24.43 |
| average | 6.27 | 289.96 | 69.02 | 93.04 | 69.11 |
| Standard | 2.15 | 183.68 | 107.8 | 102.9 | 72.33 |
| deviation | | | | | |
| Coefficient of | 0.34 | 0.63 | 1.56 | 1.11 | 1.05 |
| variation | | | | | |
| skewness | -0.19 | 6.17 | 37.89 | 8.68 | 23.34 |
| kurtosis | 0.42 | 2.08 | 5.99 | 2.64 | 4.46 |
| K-S probability | 0.70 | 1.02 | 2.29 | 1.50 | 1.78 |
| normal | Appromixate | Appromixate | LgN | LgN | LgN |
| distribution | LgN | LgN | | | |
| Background value | 3.6 | 130 | 31 | 35 | 31 |

Table 1. The statistical characteristics of heavy metals in surface soil of living areas

Notice: sample volume N=44; kurtosis and skew is the value after logarithmic transformation

The characteristics of heavy metals in soils from the five functional areas are analyzed by means of the background value, which is obtained from the nature areas far away from the crowds and industrial areas and considered as the criterion of normal content of the five elements in the soils. Through analysis of the average mean values we find that the contents of Cr, Hg, and Pb in the living areas are 2-4 times of the background value, the contents of As, Cd, and Pb in the industrial areas are 2-4 times of the background value, and the content of Hg even is as high as 9 times and 18 times. The content of each element in the mountains is mostly 1.1-1.3 times of the background value, the content of Cd in the transportation areas are 2-5 times of Cd and Hg in the parks are also 2-3 times of the background value.

The survey shows that the contents of Pb, Hg, and Cr are higher than the other elements in the living areas because of the use of paints and batteries, which contain a lot of Pb, Hg, and Cr. Similarly, the levels of these elements in the industrial areas are higher than the background value because many chemical factories use the elements of As, Cd, and Pb as raw materials. Because Hg has the volatile property, and the Hg element is widely used in smelting salt electrolysis of precious metals, the content of Hg in the industrial areas exceeds as much as 18 times of the background value. There is fewer buildings and factories in the mountains, so the contents of the five kinds of metals at a relatively low level here. Because of the use of pesticides which contain Hg and Cd, the contents of the two elements keep at a relatively high level. According to the difference of the common elements in the functional areas, we can more easily understand the situation of heavy metal pollution in every functional area.

4. EVALUATION OF DEGREE OF POLLUTION

4.1 Single-factor index analysis

Table 2. The evaluation grading standards of the single-factor index method

| Sub-index | $P_{ij} < 1$ | $1 \le P_{ij} < 2$ | $2 \le P_{ij} < 3$ | $3 \le P_{ij}$ |
|---------------|--------------|---------------------|--------------------|-----------------|
| quality grade | clean | Potential pollution | Slight pollution | Heavy pollution |

The pollution indexes of the heavy metals in each region are calculated by equation (1) and shown in Table 3, respectively (due to space limitation, the discussion only lists the living area).

Table 3. The pollution index of each heavy metal in the living area

| Heavy metal element (µg/g) | As | Cd | Cr | Hg | Pb |
|----------------------------|---------------------|------------------|------------------|------------------|------------------|
| C_{1j} | 6.27 | 0.028 | 69.02 | 0.093 | 69.11 |
| S_{j} | 3.60 | 0.013 | 31.00 | 0.035 | 31.00 |
| P_{1j} | 1.7418 | 2.2305 | 2.2264 | 2.6583 | 2.2292 |
| Quality grade | Potential pollution | Slight pollution | Slight pollution | Slight pollution | Slight pollution |

The single factor index evaluation method is employed to get real quantitative information of key pollution elements and excessive multiples, which is one of the most current methods used in evaluation of the degree of heavy pollution in soil. The mathematical expression is written as follows,

$$P_{ij} = \frac{C_{ij}}{S_j}$$
(1)

where p_{ij} is the pollution index of the heavy metal j in the *i*-th functional area soil. C_{ij} is the measured contamination value of heavy metal j in the *i*-th functional area soil, and S_j is the background contamination value of heavy metal j. Heavy metal contaminants As, Cd, Cr, Hg, and Pb are numbered as 1 to 5, respectively.

According to the value of P_{ij} , we can determine which kind of pollutants exceeds and the excessive multiple in every area in the city, and further determine what the most serious pollutants and most serious regions polluted are. According to the related information, the grading standard of single-factor is shown in Table 2.

The above results show that Cd, Pb and Hg are the most serious pollutants in the industrial area, and especially the pollution index of Hg is as 10 times high as the normal value. The phenomenon indicates that there are many factories in the industrial areas taking Hg as raw material. Every heavy metal pollution index in the mountain surface soil is between 2 to 3, showing a state of potential contamination as the pollutants may be transmitted through atmosphere. The most serious pollutant in the transportation area is Hg. Except for Hg, the pollution state is basically the same as in the living area. This phenomenon is mainly caused by the distribution of traffic roads in the living area as Hg is exhausted by automobiles, so the element of Hg is also the most serious contaminant. Compared with that of the mountain area, the content of Cd in the park area is in the state of light pollution because human beings' wastes in the parks are much more than that in the mountains, but compared with those of the living area and the industrial area, the pollution state is very slight.

4.2 Neremo index comprehensive evaluation method

In the above section, the single factor index method was employed to evaluate the pollution of five heavy metals in the five functional areas of the city, but the research shows that the above method cannot express accurately the comprehensive impact caused by each kind of heavy metals.

The Nemero index method takes not only the extreme value but also the environmental quality index based on weighted multi-factors. The method can reflect the degree of soil pollution caused by various pollutants (heavy metals). The expression is written in the following,

$$P_{i} = \sqrt{[(P_{ij\max})^{2} + (P_{ijave})^{2}]/2}$$
(2)

where P_i is the compressive pollution index of the *i*-th functional area, and P_{ijmax} is the corresponding maximum value in the single-factor pollution index, and P_{ijave} is the corresponding

average value in the single-factor pollution index. The soil pollution grading standards on the Neremo pollution index is shown in Table 4.

| Grade | Ι | П | Ш | IV | V |
|--------------------|----------------|-------------------|---------------------|--------------------|--------------------|
| P_i | $P_i \leq 0.7$ | $0.7 < P_i \le 1$ | $1 < P_i \le 2$ | $2 < P_i \leq 3$ | $P_i > 3$ |
| pollution grade | clean | Warning limit | Slight pollution | Moderate pollution | Heavy pollution |

Table 4. Grade standard of the Nemero index method

Based on the analysis of the single-factor method and according to Tables 1 and 2, we can obtain the Neremo index. The results are shown in Table 5 according to equation (2) and Table 4.

| functional area | Living area Industrial area | | Mountain area | Transportation area | Park area |
|-----------------|-----------------------------|-----------|---------------|------------------------|-----------|
| P_{ijave} | 2.4694 | 5.4270 | 1.1915 | 3.8386 | 2.0394 |
| $P_{ij\max}$ | 3.7427 | 18.3530 | 1.3119 | 12.7664 | 3.2855 |
| P_i | 3.1706 | 13.5330 | 1.2531 | 9.4264 | 2.7344 |
| Pollution | Heavy | Heavy | Slight | Heavy | Moderate |
| grade | pollution | pollution | pollution | pollution | pollution |

Table 5. Nemero index of each functional area

The results from Table 5 show that the mountains are slightly polluted, the parks are moderately polluted, and the living areas, transportation areas, and industrial areas are all seriously polluted. The results are consistent with the facts that the relatively slight pollution is due to fewer human activities in the mountain areas and lots of plants in the parks where the pollution is not so high although the soils may have been also polluted by the precipitation and air pollution. Waste water, waste gases and waste residues discharged from the enterprises in the industrial area contain lots of heavy metals which will seep eventually into the soils and cause serious soil pollution. There are a large amount of exhausts containing many heavy metals discharged by motor vehicles running in the transportation areas every day.

4.3 The improved Neremo index

Some discrepancies can be found from Table 5. The average pollution indexes in the industrial and transportation areas are 5.4270 and 3.8586, respectively, while the Nemero comprehensive pollution indexes in the industrial and transportation areas are 13.5330 and 9.4264, respectively, which are almost two times of the average value. The pollution index of Hg in the industrial areas is up to 18.3530, nearly five times of those of the other heavy metals while that in the transportation areas is

12.7664, nearly four times of those of the other heavy metals. It means that the Nemero index formula stresses the maximum value over the final values. Even there is only one index higher while the other indexes are lower, the calculated results of the comprehensive evaluation will be high. This "one-vote veto" type of evaluation model is clearly unreasonable.

Meanwhile, the Nemero index does not consider the weight factor and treats every pollution factor equally. Therefore, any high value of pollution factor will cause the composite value higher. In fact, the different pollution factors have different influences on environmental toxicity, degradation, and removal, so the different pollution factors at the same level should be treated differently, i.e., to increase the weight factor.

To handle the problem existed in the Nemero index, we carried out a correction through analyzing the weight factor. We use P'_{ijmax} instead of original P_{ijmax} , so a revised Nemero index can be expressed as follows,

$$P'_{ij\,\text{max}} = \frac{P_{ij\,\text{max}} + P_{iw}}{2}$$
(3)

where P_{iw} is the top pollution factor of weight in all the pollution factors in the *i*-th functional area $(C_{ii} / S_i)_{\circ}$

Pollution factor weights (ω_j) are calculated according to different pollutants with varying degrees of harm to the environment and human body. According to the background value S_j of each pollution factor, the maximum value is selected to compare with each S_j , and R_j ($R_j = \frac{S_{\text{max}}}{S_j}$) is defined as the relative importance ratio of heavy metal j. Then,

$$\omega_j = \frac{R_j}{\sum_{j=1}^n R_j} \tag{4}$$

The weight values of each metal element are shown in Table 6.

| Type of heavy metal (µg/g) | As | Cd | Cr | Hg | Pb |
|-------------------------------|--------|--------|--------|--------|--------|
| S_{j} | 3.6 | 0.013 | 31 | 0.035 | 31 |
| R_{j} | 19.17 | 5307 | 2.226 | 1971 | 2.226 |
| ω_{j} | 0.0026 | 0.7256 | 0.0003 | 0.2695 | 0.0003 |

Table 6. The weight of each heavy metal

As can be seen from Table 6 that the weight value of Cd is the greatest and that of Hg is the second. The values show that although the contents of Cd and Hg in the uncontaminated soils should be very few, the harm to the human beings is the most serious. This is in good agreement with lots of investigations and studies. So P_{iw} should be chosen as the pollution index of Cd (C_{ij}/S_j) .

On the basis of the single-factor analysis and the available data, the modified Nemero index has been calculated and shown in Table 7.

| Functional | Living area | Industrial | Mountain | Transportation | Park area |
|----------------------|-------------|------------|-----------|-----------------|-----------|
| area | | area | area | area | |
| P _{ijave} | 2.4694 | 5.4270 | 1.1915 | 3.8386 | 2.0394 |
| $P_{ij \max}$ | 3.7427 | 18.3530 | 1.3119 | 12.7664 | 3.2855 |
| P_{iw} | 2.2305 | 3.0239 | 1.1717 | 2.7693 | 2.1580 |
| $P_{ij\mathrm{max}}$ | 2.9866 | 10.6885 | 1.2418 | 7.7679 | 2.7218 |
| P_i | 2.7402 | 8.4763 | 1.2169 | 6.1268 | 2.4049 |
| Pollution | Moderate | Heavy | Slight | Heavy pollution | Moderate |
| grade | pollution | pollution | pollution | | pollution |

Table 7. The modified Nemero index of each functional area

The above table shows that the revised Nemero index is generally reduced, which prevents unrealistically high values caused by a high factor. So the evaluation is more objective and reasonable. The evaluation result shows that the living area becomes moderate pollution from original severe pollution, which is more in line with the fact that people usually discharge the pollutants outside the living area to keep the living environment clean.

5. CONCLUSION

In this paper, Matlab was employed to draw the spatial distribution of five kinds of heavy metals. We took the concentration of every element as vertical axis of in three-dimensional coordinates and drew out the two-dimensional distribution of the concentrations of every element. The figure shows the extreme concentration points of each element intuitively. SPSS18 was employed to calculate and analyze the concentrations of heavy metals in all sampling points, and we got the result that all the elements show normal (or approximately normal) or lognormal distribution (or approximately lognormal). The pollution index of every element in each functional area was obtained through singlefactor index evaluation model. We got the comprehensive evaluation index of the five functional areas by using the Nemero comprehensive evaluation model. The evaluation showed that the living, industrial and transportation areas of the city belonged to heavy pollution areas, the park area was moderately polluted, and the mountain area is slightly polluted. After considering the drawback that the Nemero comprehensive evaluation method takes pollution degrees of all the elements equally, we improved the Nemero comprehensive evaluation model through the introduction of weight. The modified Neremo index is generally decreased, which prevents unrealistically high value caused by a high factor. The modified evaluation is more objective and reasonable. The research can provide an important frame of reference to the government decision-making on environment improvement.

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