Study on Soil Heavy Metal Contamination and Risk Estimation in Sixian

Haimin Su\textsuperscript{a} and Aixai He\textsuperscript{b}

School of Environmental and Surveying Engineering, Suzhou University, Suzhou, Anhui, 234000, China
E-mail: \textsuperscript{a}hmsu2004@163.com, \textsuperscript{b}heaxfree2004@163.com

Abstract. At present, heavy metal contamination of soils is a extensive attention on account of the develop rapidly of urbanization and industrialization. In this paper, topsoil samples were gathered and the contents of heavy metals for example: Cd, Cr, Cu, Zn, As and Pb were determined in Sixian City. The contamination degree of heavy metals and potential ecological risk were estimated using uniparted factor contamination index, Nemero integrated contamination method, geo-accumulation index, and potential ecological risk method. The results showed: except As, mean concentrations of Pb, Zn, Cu, Cr and Cd were greater than soil background values in Sixian City. The coefficient of variation of Zn, Pb, Cu and As are greater than 30%, suggesting that they were more probably affected by human disturbance in the soil of Sixian City. The \( P_c \) values ranged between 1.46 and 26.83, displaying almost whole survey region is varying degrees contamination because of heavy metals. The \( I_{geo} \) showed that the average values implied the follow contamination order: Pb > Cd > Cu > Zn > As > Cr. The \( E_i \) values of Cu, Zn, As and Cr were observed in the ranges 5.66 to 21.15, 0.74 to 3.13 and 3.99 to 39.42, 1.54 to 3.57, respectively. The \( RI \) values were less than 150 with 85% light potential ecological risk and 15% moderate risk.

1. Introduction

Soil is a significant component of habitat and one of the important natural resources to maintain human survival and development. As a kind of important pollutants, heavy metals have caught people’s attention to due to their features for easy to accumulate, difficult to degrade, long-term latency and entering the body with food affects human health. The contamination of heavy metal will be a non-returnable procedure in soil, when heavy metals are released into soil, they are hard to transferred or degrade in environment and soil ecosystem structure and function will be destroyed by heavy metals. In the past several decades, heavy metals have been dispersed into environment of soil and affects the environmental quality of the soil. Therefore, studies on geochemical traits and contamination of soil heavy metals are attracted wide publicity [1]. For the past few years, scholars at home and abroad have carried out extensive studies on soil heavy metal contamination and achieved fruitful results. The research content involved the space distribution characteristics of heavy metals in soil, source analysis, geochemical baseline study of heavy metals, morphological feature and biological activity as well as the physico-chemical removal and transformation of soil heavy metals. Common research methods include uniparted factor analysis and integrated analysis method, geoaccumulation index method, enrichment factor method, potential ecological risk evaluation method and principal component analysis (PCA) method [2-5]. The results demonstrated that the pattern of heavy metal contamination varies greatly from region to region. For example, Sun C. et al. reported that meteoric sedimentation dedicated greatly to farmland soil of heavy metals in Chongming Island.
Duan H. et al. declared that heavy metal element such as Mn, Pb, Cu, Ni, Cr is mainly derived from local hardware manufacturing and other industries and transportation of Urban Soils in Yongkang City, Zhejiang Province [7]. These studies mainly focus on large and medium-sized cities, but there are few studies on small cities, such as Sixian City. So, we discuss the contamination of Zn, Cr, Cd, Pb, Cu and As in Sixian City in this paper, so as to provide ecological environment protection and safety of agricultural production for relevant departments.

2. Methods and Materials

2.1. Sample Acquisition and Treatment
The sample collection places are mainly randomly distributed in various functional areas of Sixian City. Five topsoil samples of 0–20cm were collected at each sampling point with 100m×100m grid, after evenly mixing, obtaining 1kg soil samples by quartering method were returned to the laboratory with self-sealing bag. In this research, 40 topsoil samples were gathered. The sample is air-dried at room temperature, eliminating gravel, plant residues and impurities in the laboratory, were crushed and passed 100 mesh sieve for standby. In the process of experiment, first, each sample was weighed with 4 g soil powder to press it into thin slices of 6 mm using the manual tablet press (FY-15), and then We measured the concentration of heavy metals by X-ray fluorescence spectroscopy (X-RF), which the type of the instrument used is Explorer 9000SDD(innov-x System). Because this method can measure many kind of elements so that it is widely in the determination of heavy metals elements [8]. The sample test was calibrated with the national standard sample (GBW07307) making the reference values of the standard sample and the relative standard deviation of the test values less than 10%.

2.2. Method

2.2.1. Uniparted factor and Nemero integrated contamination method
For assessing the soil contamination by heavy metals, the uniparted factor contaminate method is used to evaluate the relative degree of enrichment on heavy metal pollutant in the soil samples [9]. Its calculation formula as follows:

\[ P_i = \frac{C_i}{S_i} \] (1)

Where \( C_i \) is the content of soil heavy metal, \( S_i \) is the geochemical background or baseline value of the same metal, the reference values of non-mining area in Sixian City were regarded as the environmental background values in this study. \( P_i \) is the uniparted factor index. The higher the \( P_i \) value, the higher the heavy metal content and the more serious contamination. contamination exists when \( P_i > 1 \). If \( P_i < 1 \), contamination-free; \( 1 < P_i \leq 2 \), mild contamination; \( 1 < P_i \leq 2 \), middle level contamination; \( 2 < P_i \leq 5 \), serious contamination; \( P_i > 5 \) extremely serious contamination. However, uniparted factor contaminate index cannot fully reveal the contamination condition of the soil environment. Therefore, it is necessary to measure the integrated contamination of different pollutants in soil. the Nemero integrated contamination method is useful to evaluate the integrated contamination level of heavy metals on the basis of uniparted factor method. integrated contamination index were calculated as follows:

\[ P_c = \sqrt{\frac{P_{\text{avg}}^2 + P_{\text{max}}^2}{2}} \] (2)

Where \( P_c \) is integrated contamination index; \( P_{\text{avg}} \) and \( P_{\text{max}} \) are the mean and maximum values of the uniparted factor contamination index of all the elements to be evaluated, respectively. The grading criteria of the Nemero integrated contamination index can be seen from Table one.
### Table 1. The grading standard of Nemero integrated contamination index

| Level | Index range | contamination level |
|-------|-------------|---------------------|
| 1     | $P_c \leq 0.7$ | Clean               |
| 2     | $0.7 < P_c \leq 1.0$ | Basic clean         |
| 3     | $1.0 < P_c \leq 2.0$ | Mild contamination   |
| 4     | $2.0 < P_c \leq 3.0$ | Moderate contamination |
| 5     | $P_c > 3.0$ | High levels of contamination |

#### 2.2.2. The geoaccumulation index ($I_{geo}$)

The geoaccumulation index ($I_{geo}$) put forward by Muller [10] is used to estimate soil metal contamination. The geoaccumulation index thinks about not only the influence of natural geological process on the environment background value, but also the gravity of human productive activity, which can be used as a vital parameter to differentiate the effects of human productive activity. The calculation formula is:

$$I_{geo} = \log_2\left[\left(\frac{C_n}{kB_n}\right)\right]$$  \( (3) \)

Where $I_{geo}$ denotes the geoaccumulation index; $C_n$ represents the estimated value of metal $n$ of sample; $B_n$ represents the chemical nonmetal background value of heavy metal $n$ of the sample or the local soil background value, the reference values of non-mining area in Sixian City were regarded as the environmental background values in this study. And 1.5 is the reference matrix calibration factor on account of source rocks effects. The contamination classification standard of the geoaccumulation index is listed in Table 2.

### Table 2. Contamination grading standard of geoaccumulation index

| Ranks | Range       | contamination degree               |
|-------|-------------|-----------------------------------|
| 0     | $I_{geo} \leq 0$ | Non-contamination                 |
| 1     | $0 < I_{geo} \leq 1$ | Light contamination               |
| 2     | $1 < I_{geo} \leq 2$ | Moderate contamination            |
| 3     | $2 < I_{geo} \leq 3$ | Moderate-serious contamination    |
| 4     | $3 < I_{geo} \leq 4$ | Serious contamination             |
| 5     | $4 < I_{geo} \leq 5$ | Serious-extreme contamination     |
| 6     | $I_{geo} > 5$ | Extreme-contamination             |

#### 2.2.3. The potential ecological risk index

For the purpose of a broader assessment of heavy metal contamination in the soil of Sixian City. The potential ecological risk index ($RI$) [11,12] that synthesizes the mass fraction of heavy metal with their environmental influence and toxicological influence was used for appraising the potential ecological risk of heavy metal to humans and creatures. The $RI$ is introduced by Håkanson to appraise the ecological ecological risk of multi-ply metal pollutants in sediment or soils and is usually used by the majority of environmental workers. The single element potential ecological risk index ($E_i$) is used to obtain the multi-factor composite index($RI$) in samples. The calculation formula is below:

$$C_f^i = \frac{C_i}{S_i}$$  \( (4) \)

$$E_r^i = T_r^i \times C_f^i$$  \( (5) \)

$$RI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i \times C_f^i = \sum_{i=1}^{n} T_r^i \times \frac{C_i}{S_i}$$  \( (6) \)
Where $T_i^r$ expresses the toxicity coefficient (for instance, $Zn = 1$, $Pb = 5$; $Cr = 2$; $Cu = 5$; $As = 10$; and $Cd = 30$). Furthermore, $C_i^f$ is on behalf of the uniparted factor index of some a metal ($i$). $E_i^r$ denotes the environmental risk factor of the $i$th heavy metal, if $E_i^r \leq 80$ makes clear a middle ecological risk, $80 < E_i^r \leq 160$ makes clear a strong ecological risk, $160 < E_i^r \leq 320$ makes clear a very strong ecological risk, $E_i^r > 320$ makes clear a extremely strong ecological risk. And $RI \leq 150$ makes clear a weak ecological risk; $150 < RI \leq 300$ makes clear a middle ecological risk; $300 < RI \leq 600$ makes clear a serious ecological risk, and $RI > 600$ makes clear a very serious ecological risk.

3. Results and Analysis

3.1. Statistical Analysis of Heavy Metals

The statistical characteristics of soil heavy metals are represented in table 3. We can see from table 3, the mass fraction of Cd, Cr, Cu, Zn, As and Pb were found in the scope from 0.32~0.61, 51.42~118.08, 19.36~71.21, 7.00~26.53 and 18.27~88.35 mg/kg, the means of those were 0.42, 67.30, 30.95, 86.27, 13.08 and 33.95mg/kg, respectively. Among them, mass fraction of Cd is greater than II level of State Environmental quality standard for soils (GB 15618-1995), the mean mass fraction of Cr and As were less than the soil environmental background values of Sixian City [13], whereas the mass fraction mean of Cd, Zn, Pb and Cu all were overtop the soil environmental background values of Sixian City with 2.2, 1.4, 3.7 and 1.8 times of their reference elements, respectively. In particular, Cd and Pb are seriously polluted, followed by Cu, Zn and Cr, indicating that they have been enriched at different levels.

The coefficient of variation (CV) is a criterion for the spatial variation of the sample data. In this paper, the CV values of Zn, Pb, Cu and As are 50.79%, 45.37%, 37.27% and 33.40%, which suggested that these elements are more probably impacted due to human interference in soil of Sixian City. While the CV values of Cr and Cd are less than 20%, indicating that they were evenly distributed in space.

### Table 3. Soil heavy metal content statistics of Sixian City unit: mg/kg

| Element | Min | Max | Mean | Variance | Background value | Cv / % |
|---------|-----|-----|------|----------|-----------------|--------|
| Cd      | 0.32| 0.61| 0.42 | 0.08     | 0.19            | 18.67  |
| Cr      | 51.54| 118.08| 67.30| 11.81    | 166             | 17.55  |
| Cu      | 19.36| 71.21| 30.95| 10.34    | 16.78           | 33.40  |
| Zn      | 45.23| 190.42| 86.27| 43.82    | 61.68           | 50.79  |
| As      | 7.00 | 26.53| 13.08| 4.87     | 14.71           | 37.27  |
| Pb      | 18.27| 88.35| 33.95| 15.40    | 9.21            | 45.37  |

3.2. Analysis of contamination Index

The $P_i$ and $P_c$ values of 40 samples soil heavy metals are listed in table 4. $P_i$ for Cd, Cr, Cu, Zn, As and Pb are observed in the scope from 3.44 to 37.52, 0.77 to 1.79, 1.13 to 4.23, 0.74 to 3.13, 0.34 to 3.94 and 1.95 to9.56 respectively. The $P_i$ values of all heavy metals reduced in this order: Cd > Pb > Cu > Zn > Cr > As. The $P_i$ mean of Cd was 5.64, making clear that the research area was extremely polluted by Cd. At some sampling points in the survey region, however, Cd showed higher pollution status ($P_i = 37.52$) that up to 12.5 times of heavy contamination. The next is Pb with 3.69 for high level of contamination. The survey region shows a slight enrichment of Cr, Zn and Cu, the values of $P_c$ 1.02, 1.42 and1.84, respectively. The As $P_i$ value is less than 1.0, displaying no contamination of As in the survey region. The Nemero contamination index ($P_c$) is defined as the composite value of the contamination index. Over the all survey region, the $P_c$ values scope from 1.46 to 26.83, revealing that nearly all of the survey region was light contamination to high levels of contamination by heavy metals. Especially, Cd, Pb and Cu reach 26.83, 7.24 and 3.26 respectively, which are class 4 extremely strong contamination. It is made clear that the survey region is polluted by Cd, Pb and Cu.
Table 4. The evaluation results of contamination index in Sixian City

| Element | Min  | Max  | Mean  | $P_c$ |
|---------|------|------|-------|-------|
| Cd      | 3.44 | 37.52| 5.64  | 26.83 |
| Cr      | 0.77 | 1.79 | 1.02  | 1.46  |
| Cu      | 1.13 | 4.23 | 1.84  | 3.26  |
| Zn      | 0.74 | 3.13 | 1.42  | 2.43  |
| As      | 0.34 | 3.94 | 0.82  | 2.85  |
| Pb      | 1.95 | 9.56 | 3.69  | 7.24  |

3.3. The Geoaccumulation Index Analysis

All of $I_{geo}$ values for selected metals at each sampling site were listed in Fig. 1. The $I_{geo}$ for Cu, Cr, Cd, Pb, As and Zn varied between -0.26 to 1.81, -0.29 to -1.08, -0.58 to 1.58, -1.66 to 0.24, 0.15 to 2.36 and -1.04 to 1.06. The mean of the 6 heavy metals in Sixian City implied the follow contamination order: Pb > Cd > Cu > Zn > As > Cr. At the same time, most of the sampling points could be considered as not contaminated by As and Cr ($I_{geo} < 0$) in the survey region. Cu and Cd also indicated similar pattern of accumulation using mean $I_{geo}$, about 30% for Cu and 22.5% for Cd were defined as unpolluted in survey region, and the remaining 70% for Cu and 77.5% for Cd were lightly polluted and some points for moderate contamination. The most serious element is Pb, for Pb 40% soil samples were classified as lightly polluted, whereas the other soils for Pb qualified for lightly polluted to moderately polluted level and some points for moderate-serious contamination. According to the calculated results, It is apparent that high pollution area of heavy metals was come under observation at the commercial or industrial areas with dense population and heavy traffic. There are researches [14,15] to report that traffic emissions, brakes and tire wear all release Pb and Zn which declare traffic factors is the mail sources of Pb and Zn. The source of Cu may be related to electronics, metallurgy, combustion and mechanical manufacturing in Sixian City.

3.4. The Potential Ecological Risk Analysis

Fig. 2 indicates the $E_i$ values of six different elements in the topsoil samples in this paper. The $E_i$ values of heavy metals were become conscious following order: Cd, Pb, Cu, As, Cr and Zn. The $E_i$ values of Cd, Cr, Cu, Zn and As were observed in the ranges of 33.15 to 116.84, 1.54 to 3.57, 5.66 to 21.15, 0.74 to 3.13 and 3.99 to 29.42, respectively. The $E_i$ mean of Cu, Cr, As, Zn, and Pb were all below 40, suggesting that these elements show weak potential ecological risk in soil of Sixian City. In contrast, the Cd $E_i$ mean was 78.47, displaying that it posed middle ecological risk in more sampling points. The Cd was main polluted element with 11.53% light ecological risk, 76.92% moderate ecological risk and 11.55% strong ecological risk. Only 5.13% of Pb reached moderate risk. In consideration of the disparate virulence of the pollutant for people, the $RI$ was applied to integrated assessment the potential ecological risk caused by multiple elements. About 85% of $RI$ values were below 150 in the survey region, illustrating that most area presented a slight potential ecological risk.
from six elements. About 15% of the survey region were made out to subject to middle risk pollution. Because of the greater $E_i$ values of Cd and Pb, they are usually deemed to make a greater contribution for the risk giving rise to heavy metal contamination.

**Figure 2.** The cumulative percentage of $E_i$ of six elements in Sixian City

4. Conclusions
   (1) The mass fractions of Cr, Cd, Pb, Zn, As and Cu were found in the scope of 51.42–118.08 mg/kg, 0.32–0.61 mg/kg, 18.27–88.35 mg/kg, 7.00 ~26.53 mg/kg and 19.36~71.21mg/kg, respectively. Among them, concentration of Cd is more than second stage of State Environment Quality Standard for Soil(GB 15618-1995), except Cr and As, the mass fractions mean of Cd, Zn, Pb and Cu were greater than the soil environmental background values with 2.2, 1.4, 3.7 and 1.8 times, respectively. The CV values of Zn, Pb, Cu and As are 50.79%, 45.37%, 37.27% and 33.40%, explaining that these elements were in all probability to be disturbed by human productive activities in this survey region.

   (2) The contamination index of all heavy metals reduced in this order: Cd > Pb > Cu > Zn > Cr > As. The $P_i$ mean of Cd was 5.64 declaring that this survey region was extremely polluted by Cd. The next is Pb with 3.69 for high level of contamination. The survey region represented a weak beneficiation of Cr, Zn and Cu. The $P_i$ value of As was below 1.0, explaining non-contamination in this survey region. Throughout survey region, the $P_i$ values scope from 1.46 to 26.83, uncovering that nearly whole survey region was varying degrees contamination by heavy metals, especially, Cd, Pb and Cu reach 26.83, 7.24 and 3.26 are class 4 extremely strong contamination.

   (3) The means of the 6 metals elements in Sixian City implied the follow contamination order: Pb > Cd > Cu > Zn > As > Cr. At the same time, nearly all part of soil samples with Cr and As($I_{geo} < 0$) could be considered as unpolluted in survey region. Cu and Cd also indicated similar pattern of accumulation using mean $I_{geo}$, about 30% for Cu and 22.5% for Cd were be defined as unpolluted in survey region, and 70% for Cu and 77.5% for Cd were lightly polluted and some points for moderate contamination. The most serious element is Pb, for Pb 40% soil samples were classified as lightly polluted, whereas the residual soils for Pb are position as for lightly polluted to medium pollution level and some points for moderate-serious contamination.

   (4) The $E_i$ values six metal elements were found in this sequence: Cd > Pb > Cu > As > Cr > Zn. The $E_i$ mean of As, Cr, Cu, Pb, and Zn were all below 40, accounting for that these elements took shape weak risk pollution status of soil in the Sixian City. In contrast, $E_i$ the mean for Cd was 78.47, explaining that it took shape middle risk pollution in more survey region. Only 5.13% of Pb reached moderate risk. About 85% of $RI$ values ware below 150 in the survey region, illustrating that most area presented a slight risk pollution due to six elements. About 15% of survey region were were made out to subject to middle risk pollution. Cd and Pb are usually deemed to make a greater contribution for the risk giving rise to heavy metal contamination.

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6. Reference

[1] Imperato M, Adamo P. (2003). Space distribution of heavy metals in urban soils of Naples city (Italy). Environmental contamination, 124: 247-256.

[2] Zhang X.W., Wang E.D., An J. (2018). Evaluation of heavy metal contamination of gongchangling iron mining area in Liaoyang city. Chinese Journal of Ecology, 37(6) : 1789-1796.

[3] Huang S.H. (2014). Fractional distribution and risk evaluation of heavy metal contaminated soil in around a lead/zinc mine. Transactions of nonferrous metals society of China, 24: 3324-3331.

[4] Liu W., Yang J.J., Wang J. (2016). Assessment and origin analysis of soil heavy metal contamination of strip mine in Zhundong. Environmental Science, 37(5): 1938-1945.

[5] Lu X.Z., Gu Q.G., Zhang Y.W, (2019). et al. Research on the features of heavy metal accumulation in farmland soil and its potential ecological risk based on environmental geochemical baseline. Acta Pedologica Sinica, 56(2): 408-419.

[6] Sun C., Bi C.J., Chen Z.L.. et al. (2010). Evaluation on environmental quality of heavy metals in farmland soils of Chongming Island, Shanghai City. Journal of Geographical Sciences, 20(1), 135–147.

[7] Duan H.M., Zhu L.D., Li F.Q., et al. (2012). Heavy metals' accumulation and their origins of urban soils in Yongkang. Chinese Journal of Soil Science, 43(4): 956-961.

[8] Li Z.C., Gui H.R., Chen S. (2015). Origin and levels of heavy metal contamination in the moat sediment in Suzhou City, Anhui Province. Journal of Ecology and Rural Environment, 31(4) : 559-565.

[9] Chen S.L., Li J.W., Chen N., et al. (2013). Fujian beaches in different areas of paddy soil heavy metal accumulation features and estimate of environmental quality. Environmental Monitoring in China, 29(2): 34-40.

[10] Muller G. (1969). Index of geo-accumulation in sediments of Rhine River .Geo Journal, 2:108-118.

[11] Tomlinson, D.L., Wilson, J.G., Harris, C.R., et al. (1980). Problems in the estimate of heavy metals status in sturaries and the morphological of a contamination index. Helgoländ Meeresuntersuchungen, 33: 566–575.

[12] Yuan, G.L., Sun, T.H., Han, P., et al. (2014). Origin recognition and ecological risk estimate of heavy metals in topsoil using environmental geochemical mapping: typical urban renewal area in Beijing, China. Geochem. Explor. 136: 40-47.

[13] Su H.M., He A.X., Yuan X.T., et al. (2014). Heavy metal concentrations of agricultural soil and contamination evaluation around coal mine in Suzhou city, Anhui Province. Earth and Environment, 42(3) : 369-374.

[14] Dai B., Lv J.S., Zhan J.c., et al. (2015). Estimate of source, space distribution and ecological risk of heavy metals in soil in a representative industrial mining-based cities of Shandong Province, Eastern China. Environmental Science, 36(2) : 507-515.

[15] Liu D.H., Wang F.Y., Zhou W.L., et al,(2012). Heavy metal contamination in street dusts from different functional zones of Luoyang City and its potential ecological risk. Environmental Science, 33(1): 255-259.