Pollution Source Analysis of Heavy Metal and Ecological Risk Assessment in Urban Fringe

Siqi Liu¹, 2, 3, 4, *
¹Shaanxi Provincial Land Engineering Construction Group Co., Ltd. Xi’an, China
²Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd. Xi’an, China
³Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natural Resources. Xi’an, China
⁴Shaanxi Provincial Land Consolidation Engineering Technology Research Center. Xi’an, China

*Corresponding author e-mail: 4102090209@chd.edu.cn

Abstract. With the rapid development of modern urbanization, the unreasonable industrial structure has impacted urban environment, which greatly restricts the use of land resources safely. Especially in some cities with rapid urbanization, on the one hand, urban development requires a large amount of lands; on the other hand, the urban environment exceeds its bearing capacity, and human settlements environment have been negatively affected. Taking the typical urban fringe of Xi’an as the research area, this study detected Cd, Cr, Cu, Ni, Pb and Zn combined with GIS, RS and GPS technologies. Totally 26 sample points were collected. The pollution index method (single pollution index, Nemerow comprehensive pollution index method), geo-accumulation index method and potential ecological risk index method were used to evaluate the results, and the pollution sources were analysed. According to the analysis results, Cd, Pb and Zn existed obviously ecological risks. The Pb pollution of each sample point was quite different. Sample points 1-13 were located in the east of the research area, mainly distributed on both sides of the traffic road. Pb pollution was relatively serious. The average value of Igeo (Pb) reached 4.20, which belongs to strong pollution - extremely strong pollution. The heavy metal pollution of Zn was universal, however, the toxicity response parameter of Zn is low, T1'=1, so the ecological risk was not significant. The detection rate of Cd was only 11.5%, but the value was much higher than background value, which should be paid attention to. The results showed that there are different degrees of heavy metal pollution and potential ecological risks in the research area, which supported the safe use of land in urban fringe areas.

Keywords: Heavy metal pollution, urban fringe, ecological risk.

1. Introduction
Since the reform and opening up of China, the rapid development of urbanization and industrialization has brought great changes to people's lives, and material life has been greatly satisfied as a result [1-2].
However, at the same time, there have been a series of problems such as environmental pollution, waste of resources and imbalance of industrial structure [3-4]. As an important part of urban ecological environment, urban soil is the natural foundation of different human activities [5]. Along with the urban development, a large number of soil pollution incidents happened around the country, such as arsenic poisoning occurred in Jinchengjiang District of Hechi City in 2008, and toxic soil incident occurred in a campus in Changzhou in 2016. Heavy metal pollution is a very common kind of urban soil pollution. The sources of pollution are diverse, and the composite pollution is more serious. Industrial production, human activities and transportation are the direct ways to lead to soil heavy metal pollution, and the pollution is persistent, latent and irreversible [6-7]. According to Duan's research on Yongkang City, Zhejiang Province, Cr, Ni, Cu and Pb mainly came from the local hardware manufacturing industry and transportation [8]. Zhuang carried out risk assessment on soil heavy metals in the urban fringe of Shanghai that Cr pollution was relatively serious, and the distribution of industries, traffic and human activities were the main factors affecting the distribution of heavy metals in soil [9]. The survey data showed that there were 36.3% of the potentially polluted enterprise land and its surrounding sites exceeding the pollution criteria, while approximately 1/3 of the contaminated sites will be redeveloped and utilized as urban construction land [10].

Urban fringe is the reflection of urban expansion on agricultural land, and is the transition zone between urban and rural areas, which has dual attributes of urban and rural areas. At the same time, it is also a reserve for urban development and expansion, which mainly undertakes the role of industrial land transfer and urban service function supplement. Urban sprawl in northwest China has the characteristics of spontaneity, disorder and low speed, which ignores the construction of ecological environment and the health risk control of human settlements [11-12]. Xi'an is one of the old industrial bases in China. In recent decades, as a result of the optimization of industrial structure and urban land conservation, many industrial factories in Xi'an have been demolished or relocated to the suburbs of the city [13-14]. This study took Xi'an construction land soil safety risk control as the starting point, in order to fully understand the impact of industrial urban fringe on soil quality and ecological environment, samples were collected in typical urban fringe areas in the western suburbs of Xi'an The method of analysis is used to find out the status of soil pollution in the study area, and provide a reference for the next step of soil remediation and urban land comprehensive development.

2. Methods and Materials

2.1. Study Areas and Sample Points
The study area is located in Yanta District, Xi'an City, Shaanxi Province, adjacent to the expressway in the west, West Third Ring Road in the east, Keji West Road in the north and Yudou road in the south. It was a typical urban fringe area including Shuangqizhai Industrial Park and some urban villages. According to the analysis and interpretation of the land use planning of the main urban area in Xi'an urban master plan (2008-2020), the industrial land mainly originated from the industrial transfer and industrial upgrading, as shown in figure 1. In recent years, with the expansion of the city and the adjustment of the industrial structure, the agricultural land has been gradually transformed into the urban construction land. Since 2004, a variety of industrial enterprises such as automobile repair, mechanical processing, automatic equipment manufacturing, building materials, logistics and other industrial enterprises have gradually formed in the villages in the city. The development process had certain spontaneity and disorder, which had caused potential harm to the ecological environment.
The layout of sampling points in this project adopts 3S technology combined with geographic information system (GIS), remote sensing (RS) and global positioning system (GPS). During sampling, the surface debris was stripped off, and the sampling depth was 0-20 cm. A total of 26 soil samples were collected (Figure 2).

**Figure 1.** Study area and land use pattern

**Figure 2.** Sample points location

2.2. *Pollution Index (PI)*

Pollution index (PI) method is a basic approach to assess environmental pollution. In this research, referring to relevant standards and regional background, the ratio relationship between sample and reference value can be clearly figured out. Nemerow pollution index method is calculated based on single pollution index. This method stresses the maximum pollution of individual heavy metal.
P_i = C_i / S_i  \quad (1)

P_e = \left\{ \frac{P_{i_{\text{max}}} + P_{i_{\text{ave}}}}{2} \right\}^{1/2}  \quad (2)

Where C_i stands for the measured results of heavy metals in urban soil, S_i is the evaluation criteria of heavy metals referred to national standards GB36600-2018 and GB15618-2018, and P_i is the single pollution index. P_{i_{\text{max}}} is the maximum value of single pollution index; P_{i_{\text{ave}}} is the mean value of single pollution index; P_c is the Nemerow comprehensive pollution index. According to the pollution degree, P_c was divided into five classifications that P_c≤0.7 was clean, 0.7<P_c≤1 was low pollution, 1<P_c≤2 was moderate pollution, 2<P_c≤3 was high pollution, and P_c>3 was significantly high pollution.

2.3. Geo-accumulation Index (I_{geo})
Geo-accumulation Index (I_{geo}) method takes the influence of background value caused by natural geological process into account, and also pays attention to the influence of human activities on heavy metal pollution. It is a very important way to measure the impact of human activities.

I_{geo} = \log_2 \left\{ \frac{C_n}{K B_n} \right\}  \quad (3)

Where C_n is the concentration of single heavy metal in urban soil; B_n is the background value of the heavy metal in urban soil, K is the coefficient taken into account the variation of background value that may be caused by the difference of rocks in different regions, normally K=1.5. Usually I_{geo} is divided into seven classifications that I_{geo}<0 is clean, 0\leq I_{geo}<1 is clean to moderately polluted, 1\leq I_{geo}<2 is moderately polluted, 2\leq I_{geo}<3 is moderately polluted to heavily polluted, 3\leq I_{geo}<4 is heavily polluted, 4\leq I_{geo}<5 is heavily polluted to extremely polluted, 5\leq I_{geo} is extremely polluted.

2.4. Potential Ecological Risk (PER) Index
The potential ecological risk (PER) index method takes the toxicity difference and ecological sensitivity of various heavy metal elements into consideration, introducing toxicity response parameters, and quantitatively divides the potential pollution degree of heavy metals to the ecological environment [15].

\begin{align*}
C_f^i & = C_f^i / C_m^i \quad (4) \\
E_f^i & = T_f^i \times C_f^i \quad (5) \\
RI & = \sum_{i=1}^{n} E_f^i \quad (6)
\end{align*}

Where C_f^i stands for the pollution coefficient of heavy metals; C_m^i represents the measured concentration of heavy metals in soil. C_m^i was used to calculate the required reference ratio. This assessment combined with the soil background value of Xi’an to determine the reference ratio comprehensively. E_f^i is the potential ecological risk index of single heavy metal. T_f^i is a single heavy metal toxicity response parameter, and the heavy metal toxicity response coefficient formulated by Hakanson was used as the evaluation basis (Table 1). RI is divided into four classifications that RI<150 is low risk, 150\leq RI<300 is moderate risk, 300\leq RI<600 is high risk and 600\leq RI is significantly high potential risk.
Table 1. The value of $C_n^i$ and $T_r^i$

| Heavy metals | Cd       | Cr   | Cu   | Ni   | Pb   | Zn   |
|--------------|---------|------|------|------|------|------|
| $C_n^i$      | 0.2866  | 70.8 | 26.0 | 64.0 | 38.8 | 31.2 |
| $T_r^i$      | 30      | 2    | 5    | 5    | 5    | 1    |

3. Results
Totally of 26 soil samples were tested in this research, and 6 heavy metal indexes of Cd, Cr, Cu, Ni, Pb and Zn were tested. The results are shown in Table 2. Except for the low Cd detection rate of 11.5%, which was not included in the statistics, the average values of Cr, Cu, Ni, Pb and Zn were 94.65 mg·kg$^{-1}$, 80.34 mg·kg$^{-1}$, 39.18 mg·kg$^{-1}$, 573.36 mg·kg$^{-1}$ and 260.57 mg·kg$^{-1}$, respectively. The values of Pb and Zn were significantly higher than the soil background value of Xi’an city (the background value of Pb is 38.8 mg·kg$^{-1}$, and the background value of Zn is 31.2 mg·kg$^{-1}$). It was probably due to human activity. The values of Cr and Cu were slightly higher than the soil background value of Xi’An city (the background value of Cr is 70.8 mg·kg$^{-1}$, and the background value of Cu is 26 mg·kg$^{-1}$). The variation coefficients of Cr, Cu and Pb were all greater than 50%. The element with the largest standard deviation was Pb, which reaches 517.93, reflecting the large difference of Pb content in various points. The element with the smallest standard deviation and coefficient of variation was Ni (11.59 and 29.59%, respectively), reflecting the similarity in the content of Ni in various points and the similarity in the content of each sample.

Table 2. The descriptive statistics of samples

|              | Cd       | Cr   | Cu   | Ni   | Pb   | Zn   |
|--------------|---------|------|------|------|------|------|
| Mean (mg·kg$^{-1}$) | /       | 94.65 | 80.34 | 39.18 | 573.36 | 260.57 |
| Median (mg·kg$^{-1}$) | /       | 49.35 | 49.89 | 39.03 | 571.07 | 225.38 |
| SD           | /       | 103.75 | 97.43 | 11.59 | 517.93 | 113.91 |
| Minimum (mg·kg$^{-1}$) | /       | 17.71 | 27.72 | 22.24 | 23.22 | 101.57 |
| Maximum (mg·kg$^{-1}$) | 5.72    | 375.15 | 532.21 | 69.16 | 1346.77 | 511.55 |
| CV (%)       | /       | 109.61 | 121.27 | 29.59 | 90.33 | 43.71 |

The calculation results of Nemerow pollution index are shown in Table 3. Three samples are heavily polluted (Grade V), accounting for 11.5% of the total. Five samples were moderately contaminated (level IV), accounting for 19.2% of the total; Six samples were mildly contaminated (class III), accounting for 23.1% of the total; Three samples were slightly contaminated (class II), accounting for 11.5% of the total; Nine samples were clean (Grade I), accounting for 34.6% of the total. Among them, the pollution at points 1-13 was generally slightly polluted or above, and the pollution at point 8 was the most serious, with $P_c$ reaching 6.82, mainly due to the large value of $P(Cr)$, which was 4.81, followed by $P(Pb)$ and $P(Zn)$, which were 2.83 and 2.05 respectively.
Table 3. The Nemerow pollution index results

| Sample points | P<sub>c</sub> | Pollution degree | Sample points | P<sub>c</sub> | Pollution degree | Sample points | P<sub>c</sub> | Pollution degree |
|---------------|------------|-----------------|---------------|------------|-----------------|---------------|------------|-----------------|
| 1             | 1.75       | III             | 10            | 1.61       | III             | 19            | 1.91       | I               |
| 2             | 2.24       | IV              | 11            | 2.12       | IV              | 20            | 0.18       | I               |
| 3             | 1.52       | III             | 12            | 1.88       | III             | 21            | 0.49       | I               |
| 4             | 2.25       | IV              | 13            | 1.83       | III             | 22            | 3.20       | V               |
| 5             | 1.40       | III             | 14            | 0.09       | I               | 23            | 0.89       | II              |
| 6             | 2.28       | IV              | 15            | 0.08       | I               | 24            | 0.25       | I               |
| 7             | 2.25       | IV              | 16            | 0.74       | II              | 25            | 0.62       | I               |
| 8             | 6.82       | V               | 17            | 0.10       | I               | 26            | 0.28       | I               |
| 9             | 3.30       | V               | 18            | 0.80       | II              |               |            |                 |

As shown in figure 3, Cd, Cr, Cu, Pb and Zn all existed different degrees of pollution, among which Zn and Pb existed the most significant pollution, whose average value of I<sub>geo</sub> were 2.34 and 2.10 respectively, showing a certain spatial difference. I<sub>geo</sub>(Ni) at all points was less than 0, indicating that the element was clean. The Pb pollution at each point was significantly different, and the Pb pollution at sampling points 1-13 was relatively serious. The average value of I<sub>geo</sub>(Pb) reached 4.20, which was significantly higher than that at other points. Zn pollution was common in the study area. The maximum value of I<sub>geo</sub>(Zn) appears at the sampling point 8 (3.45), which was a strong pollution, while the minimum value appears at the sampling point 5 (1.12), which was a moderate pollution. The average value of I<sub>geo</sub>(Cu) was 0.65, and I<sub>geo</sub>(Cu) at 19 sampling points were less than 1, accounting for 73.1% of the total. Although the detection rate of Cd was very low, with only 3 sample points collecting data, its value was far greater than the background value of this area, and there was a certain risk.
The statistical results of the comprehensive risk index at each point evaluated by the Hakanson potential ecological risk index method are shown in Figure 4. A total of three sampling points RI exceeding 600, namely sampling point 1 (750), sampling point 2 (601) and sampling point 25 (667), are classified as significantly high ecological risk level. The main reason was that $E_i'(Cd)$ had a large value, which posed a great potential threat to the ecology, resulting in numerical mutation. RI of 7 sampling sites was greater than 150 and less than 300, which was mainly influenced by $E_i'(Pb)$ and belonged to the moderate ecological risk level. In general, except for sampling point 25, which had a high risk of pollution, sampling point 14-26 all belong to the low risk level. According to the calculation results of Nemerow comprehensive pollution index and geological accumulation index, although the heavy metal pollution of Zn was obvious, due to the low toxicity response parameter of Zn, $T_i|=1$, the impact on ecological risk was not significant.
4. Discussion and Conclusion
As a backup place for urban development, urban fringe areas have complex social and ecological environment and lack systematic planning for a long time. Their development has strong spontaneity and disorder [16-17]. This research area included centralized industrial parks and scattered industrial enterprises in urban villages, including automobile repair, mechanical processing, building materials, logistics, etc. There is no clear boundary between industrial, residential, commercial, educational land, which influences each other within a narrow space. According to the above calculation results, Cd, Pb and Zn have obvious ecological risks, but they distributed in different ways. Although the Cd detection rate was low, only 11.5%, there was a high ecological risk in a small range due to the large detection value of Cd, which was far higher than the background value of the region, and the large toxicity response parameter of single heavy metal, $T_{IC} = 30$. These areas were mainly used for container processing and parking of large freight vehicles, which was the main reason for the high Cd enrichment level. The Pb pollution at each point varies greatly. The sampling points 1-13 were located in the east of the study area, mainly on both sides of the road, and the Pb pollution was relatively serious. The heavy metal pollution of lead in urban soil mainly comes from the combustion products of fossil fuels, such as automobile exhaust emissions [18]. The traffic flow in this section was large, and motor vehicle related activities such as automobile repair, motor vehicle exhaust pollution detection institutions and driving test venues were distributed along the road, which were the main reasons for the high Pb content in the soil in this area. According to the value of $I_{geo}(Zn)$, it could be seen that Zn pollution was universal in the study area. Industrial activities such as mechanical manufacturing, building materials and automobile tire wear would lead to the enrichment of Zn content, which mainly existed in the form of compounds. Although the toxicity response parameter of Zn was low, $T_{IC} = 1$, it still needed to be paid attention to.

This study focused on the perspective of ecological risk assessment and control, taking western suburbs of Xi’an typical urban fringe area as the research object. According to the Nemerow pollution index, 65.4% of the samples showed mild pollution or above. Based on the calculation results of the potential ecological risk index, 38.5% of the sampling points had moderate or even serious potential ecological risk. Although the parameter ratio set in this study was relatively low, the calculation...
results were generally large. However, combined with the ecological environment problems existing in the field investigation, this study objectively reflected the ecological harm of heavy metals to the region, and provided a scientific basis for the realization of the safe use of land in urban fringe areas.

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