

Original Research

Analysis of Heavy Metal Pollution and Potential Ecological Risk at The Relocation Site of a Chemical Plant

Yulu Wei^{1, 2, 3, 4*}, Xin Huang⁴, Siqi Liu^{1, 2, 3, 4}

¹Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd.

²Shaanxi Provincial Land Consolidation Engineering Technology Research Center

³Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natural Resources of China

⁴Shaanxi Provincial Land Engineering Construction Group Co., Ltd.

Received: 30 November 2020

Accepted: 25 January 2021

Abstract

In recent years, the relocation sites of heavy industrial enterprises have caused great harm to human health, environmental and ecological safety, society and economy. Taking a relocation site of the chemical plant as research object, 18 soil samples of 0~20 cm were collected, and the contents of seven heavy metal elements, including Ni, Cu, Cd, Pb, Hg, As and Zn, were tested. The quality ratio statistical analysis, pollution characteristics analysis and potential ecological risk were used to determine the heavy metal pollution. Results show that mean concentration of Ni, Cu, Cd, Pb, Hg, As and Zn were 30.16 mg/kg, 35.10 mg/kg, 0.28 mg/kg, 31.74 mg/kg, 0.92 mg/kg, 18.99 mg/kg and 72.63 mg/kg, respectively. Compared with the background value of Guanzhong area, Shaanxi, China, the heavy metal exceeding rate of sample points was 83.3%. Hg and As were the main pollution source, and they had exceeded the risk screening values in (Soil environmental quality Risk control standard for soil contamination of development land) (GB36600-2018). Geo-accumulation index and potential ecological risks showed that the mercury of Hg was polluted heavily. All these showed that the potential ecological risk in the chemical plant was extremely strong which was mainly determined by industrial production and human activity at the same time.

Keywords: heavy metals, comprehensive pollution index, Geo-accumulation index (I_{geo}), ecological hazard coefficient

Introduction

Chemical industry is closely related to human survival and development. With the rapid development

of industrialization, urbanization and urban civilization in China, chemical enterprises located near cities are incompatible with the concept of urban green development. The cities then require serious pollution enterprises in and around the city to switch production or shut down, and at the same time eliminate the chemical enterprises with serious environmental

*e-mail: 453876296@qq.com

pollution problems in the city. Due to the lack of management in the long-term production process of the polluting enterprises, the field has accumulated heavy metals, volatile organic compounds, persistence and other hazardous and toxic pollutants, making it a contaminated site with high risk and high pollution areas [1], causing great harm to the ecological environment and human survival. These have been worldwide environmental problems. Heavy metal pollution is a very common soil pollution type, especially in chemical industry area or around it. The sources of heavy metal pollution are various, and the situation of multi heavy metal pollution is widespread and quiet serious [2]. Heavy metal pollution including Cu, Cd, Pb, Zn, Ni, As were mainly located surrounding historical high-pollution chemical plants through geographical information system (GIS) technology [3]. Heavy metals in the soil have concealment, hysteresis, accumulation and irreversibility, and are extremely difficult to be treated [4-8], with obvious agglomeration effect in a certain area, such as abandoned industrial site (brownfield). They are directly or indirectly harmful to human health by contaminating surface water and groundwater [9, 10]. Particularly, heavy metals in soils can be directly ingested through three main exposure pathways such as ingestion, dermal contact (skin contact) and breathing into the human body [11, 12]. Consequently, long-term exposure to elevated levels of heavy metals leads to various health risks. In China, 34.9% of the soil sample points in abandoned industrial sites are contaminated. Among them, more than a third of the points are seriously contaminated [13].

Some scholars [14-16] studied the spatial distribution of heavy metals in topsoil from the perspective of functional areas and found that the heavy metals (Zn, Cu, Cd, Pb, etc.) in domestic topsoil were seriously

polluted. Some scholars have carried out studies on heavy metal pollution and potential ecological harm in cities [17-19], proposed the evaluation method of potential ecological harm index, which linked the risk of heavy metal ecological environment with toxicology, and visually demonstrated the degree of stress of heavy metals on the ecological environment [20, 21]. Therefore, it is necessary to carry out investigation, analysis, statistics and evaluation on the pollution of heavy metals in such polluted sites, so as to provide theoretical and technical support for the feasibility of site remediation and reuse.

This paper chooses the site after the relocation of a chemical plant in Weinan City, Shaanxi Province, China as the research object, which belongs to Guanzhong area. The types and concentrations of heavy metal pollutants in the site were determined by soil collection and testing. The harm degree of heavy metals in soil was analyzed by single pollution index (SPI), comprehensive pollution index (CPI), geo-accumulation index (I_{geo}) and potential ecological risk index. Possible sources of heavy metals in and around chemical plants were analyzed by using correlation and principal component analysis. All these provide reference basis and guidance for repair management.

Materials and Methods

Study Area, Soil Sampling and Analysis

The site of the chemical plant is located in the east of Weinan City, Guanzhong area, Shaanxi Province, China, east of G310 National Road, south of Diding Road. This region belongs to semi-humid and semi-arid monsoon climate in warm temperate, which has four

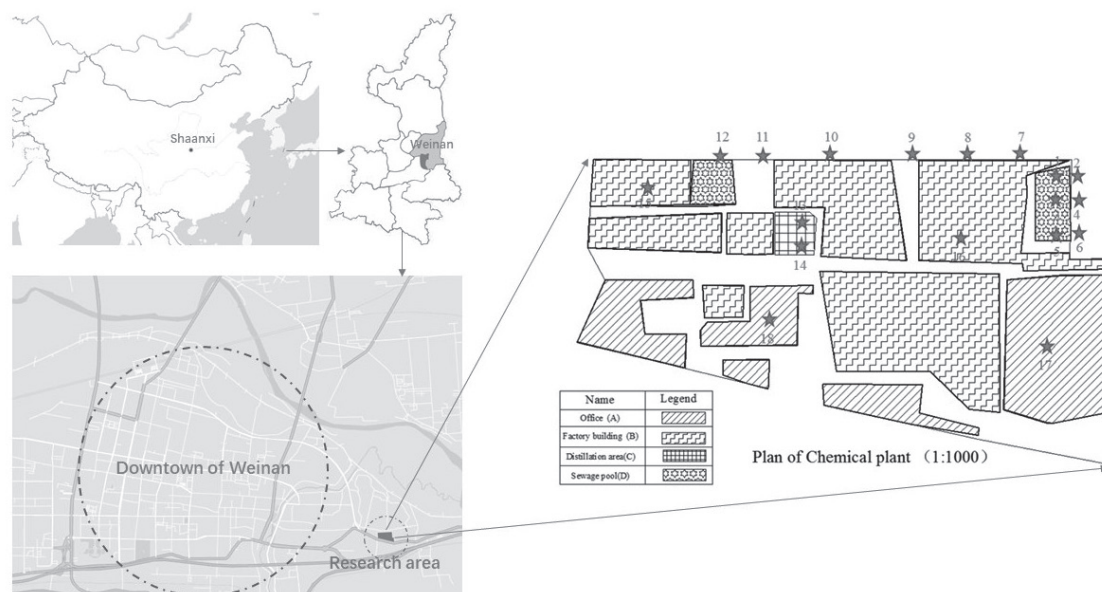


Fig. 1. Plan of chemical plant.

distinct seasons, adequate lighting and the amount of rainfall. The frost-free period is 199-255d. The average annual temperature is 12-14°C. The annual sunshine is 2200-2500 h and the annual rainfall was about 600mm. The main soil type is leached brown soil. The chemical plant was established in June 2003 and mainly produced food grade fumaric acid, cold water soluble food grade fumaric acid, ultrafine fumaric acid, cationic etherifying agent and other products, which predecessor was mainly used to produce pesticides. The plant is mainly divided into four areas: Office (A), Factory Building (B), Distillation area (C), and Pool (D) (Fig. 1), and the key polluted area is Distillation area and Sewage pool. According to its predecessor and current fumaric acid production process, the main pollutants are pesticides, heavy metals and volatile-semi-volatile organic pollutants.

The soil sampling points were arranged in the way of partition distribution [22]. In order to assess soil heavy metal pollution, 113 sampling sites were set up and nearly 300 soil samples were collected, with the deepest sampling depth reaching 3 m, mainly from the non-hardened ground in and around the chemical plant area. Each sampling site was recorded by using a global positioning system. To avoid contamination, the wooden shovel was used to collect the soil samples and each sample was stored in clean self-lock polyethylene bags, labeled and sealed. Moreover, at each sampling site, three subsamples were taken to augment the sample representativeness and mixed to obtain a bulk sample. The soil samples were air-dried at ambient temperature and crushed and sieved through 100 mesh size with mortar and pestle. In order to highlight the problems and facilitate analysis, 18 typical soil samples of 0-20 cm were selected for analysis in this paper.

The contents of Ni, Cu, Cd, Pb, Hg, As and Zn in the soil samples were determined by EHD-24 atomic absorption spectrometer (ICP-MS) after the soil samples were digested by hydrofluoric acid, nitric acid and perchloric acid (the microwave digestion system was CEM Mars6 microwave digestion instrument). To ensure the reliability of the results, internal and external quality control was adopted to monitor the results. The internal quality control of the laboratory mainly adopts the national first-class material analysis standard for precision and accuracy control. 5% samples are randomly selected according to the total number of samples sent, and the codes are compiled to conduct repeatability test and abnormal value repeat check. External quality control of the laboratory is mainly controlled by standard control samples (the standard substance prepared).

Soil Heavy Metal Pollution Evaluation Method

In this paper, the single pollution index method and comprehensive pollution index method were used to

evaluate the pollution degree of heavy metals in soil [23].

1) The evaluation formula of single pollution index (SPI) method is computed as follows:

$$P_i = C_i / S_i \quad (1)$$

C_i is the measured concentration of heavy metals in the soil. S_i is the evaluation standard or reference value of heavy metals in the soil. P_i is the SPI. In this paper, (Soil environmental quality risk control standard for soil contamination of development land) (GB36600-2018) [24, 25] and (Background value of soil heavy metal content in Guanzhong area) are used as evaluation criteria, which are national standard and local standard respectively. $P_i \leq 1$ means the soil is not polluted; $P_i > 1$ means the soil is polluted, and the bigger P_i is, the more serious the pollution is.

2) Comprehensive pollution index (CPI) method takes into account the average value and the highest value of single pollution index and highlights the impact of heavily pollutants on environmental quality. Its evaluation formula is shown as follows:

$$I = \sqrt{\frac{\max_i^2 + \text{ave}_i^2}{2}} \quad (2)$$

\max_i is the maximum value of environmental quality index of each factor. ave_i is the average value of environmental quality index of each factor. $I > 1$ means that the environmental quality does not meet the standard requirements; $I = 1$ means that the environmental mass is in the critical state; $I < 1$ means that the environmental quality is better than the requirements of the evaluation standard.

Geo-Accumulation Index (I_{geo})

The geo-accumulation index (I_{geo}) was initially proposed in the year 1969 by Muller (1969). Since 1969, it has been widely used to comprehend the pollution levels of heavy metals in the soils and also sediments in the worldwide. I_{geo} takes into account the background value impact caused by natural geological processes and the impact of human activities on the environment. It is an important parameter that reflects the natural variation characteristics of heavy metal distribution and identifies the impact of human activities on the environment. The I_{geo} is computed as follows:

$$I_{\text{geo}} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \quad (3)$$

...where C_n is the measured concentration of the heavy metal "n" in the soil sample, and B_n is the average geochemical background value of the measured heavy metal "n". In this paper, B_n is background value of soil heavy metal content in Guanzhong area (shown in

Table 4). Muller classified seven levels based on I_{geo} values namely [26]: $I_{geo} < 0$, not polluted; $0 < I_{geo} \leq 1$, not polluted to moderately polluted; $1 < I_{geo} \leq 2$, moderately polluted; $2 < I_{geo} \leq 3$, moderately polluted to heavily polluted; $3 < I_{geo} \leq 4$, heavily polluted; $4 < I_{geo} \leq 5$, heavily polluted to extremely polluted; and $I_{geo} > 5$, extremely polluted.

Potential Ecological Risk Analysis

The potential ecological risk index is a quantitative index based on the response of element abundance and the synergistic effect of pollutants proposed by Swedish scientist Hakanson in 1980. It is one of the most commonly used methods to evaluate pollution degree of heavy metals in soil and sediments, atmospheric particle size and potential ecological risk. This method not only reflects the potential ecological damage of a single heavy metal in a specific sediment, but also considers the comprehensive ecological effects of various heavy metals, and quantitatively classifies the potential ecological risk grade of heavy metals, which is a comprehensive index to characterize the degree of heavy metals' impact on the ecological environment. Its evaluation formula shown as follows:

$$E_r^i = T_r^i * P^i, \quad RI = \sum_i^m E_r^i \quad (4)$$

...where E_r^i is the potential ecological risk index of the heavy metal "i". T_r^i is the toxicity coefficient of the heavy metal "i". P^i is single pollution index of the heavy metal "i". [27, 28]

Results and Discussion

Descriptive Statistic of Soil Heavy Metals

Descriptive statistical results of the heavy metal in the surface soil samples from the study region are listed in Table 1, including minimum, maximum, median, mean, standard deviation (SD), coefficient of variation (CV) and percentage of sampling points beyond the BGV (PSPBB). The mean contents of Ni, Cu, Cd, Pb, Hg, As and Zn in the soil were 30.16 mg/kg, 35.10 mg/kg, 0.28 mg/kg, 31.74 mg/kg, 0.92 mg/kg, 18.99 mg/kg, 72.63 mg/kg. The mean contents of Cu, Cd, Pb, Hg, As were all bigger than the BGV and the content of Hg and As shown extreme outliers. The maximum contents of Hg was 8.74 mg/kg, which had exceeded the screening value (8 mg/kg) in (Soil environmental quality Risk control standard for soil contamination of development land). This means that Hg shows a significant enrichment state and may pose risks to human health. Further detailed investigation and risk assessment should be carried out to determine the detailed pollution scope and risk level. The maximum contents of As was 123.30 mg/kg, 5 times of the screened value (20 mg/kg), slightly exceeding the

control value of 120 mg/kg. This means As poses an unacceptable risk to human health, and risk control or repair measures should be taken. Although the mean content of Ni and Zn were lower than the background value (BGV), the content of Ni at 5 points and Zn at 6 points were higher than the background value (BGV), and the exceeding rate were 28% and 36%. These results show that the soil heavy metal content in this area has been greatly affected by chemical plant activities.

From the distribution of the minimum and maximum, the content of each element varies greatly. The coefficients of variation (CV) can reflect the average variation degree of each sampling point, and the coefficients of variation (CV) of seven heavy metals followed a descending order as $Hg > As > Cd > Cu > Pb > Ni > Zn$, which can be divided into three levels (Table 1) [29, 30]. The coefficients of variation (CV) of Hg and As was greater than 1, indicating that the content of Hg and As in different locations are significantly different. The coefficients of variation (CV) of Cd and Cu ranged from 0.5~1, indicating that the content of Cd and Cu also have great difference. The coefficients of variation (CV) of Pb, Ni and Zn ranged from 0.2~0.5, indicating that the distribution of Pb, Ni and Zn is relatively concentrated. These high coefficients of variation and high accumulation mean that the study region soils seriously influenced by discrete inputs related to anthropogenic activities, natural or external factors, especially the production process of chemical plants.

Analysis of Single Factor and Comprehensive Pollution Index

Based on the background value (BGV) of soil heavy metal content in Guanzhong area, descriptive statistics on single factor pollution index of heavy metals in surface soils are listed in Table 2. Among the 18 surface soil samples (0~20 cm), the content of heavy metals in 15 samples exceeded the background value, and the exceeding rate was 83%. Among them, there were 3 samples with content of 5 metals exceeding the background value, 2 samples with content of 4 metals exceeding the background value, 3 samples with content of 3 metals exceeding the background value, 7 samples with content of 2 metals exceeding the background value, and the remaining 3 samples without metal content exceeding the background value. Soil samples were mainly polluted by Hg and As. The contamination rate of Hg was as high as 56.3%, with the highest content of Hg and As at point 12, both of which exceeded the screening value (SV). The content of Hg was 104 times higher than the background value (0.084 mg/kg), and the content of As was 8 times higher than the background value (13.1mg/kg). Secondly, the exceeding rate of Cd, Cu and Pb content were relatively high, which were 61.1%, 38.9% and 38.9% respectively. Finally, the exceeding rate of Ni and Zn content were relatively low, which was 27.8% and 18.8%. Although

Table 1. Descriptive statistics of heavy metals in the soils of the study region ($\text{mg}\cdot\text{kg}^{-1}$).

	Ni	Cu	Cd	Pb	Hg	As	Zn
Minimum	12	16.94	0.07	12.3	0.02	8.97	50.27
Maximum	56.7	71.83	0.84	72.89	8.74	123.3	107.3
Median	29.73	24.05	0.21	24.4	0.14	10.34	67.79
Mean	30.16	35.1	0.28	31.74	0.92	18.99	72.63
Standard deviation (SD)	8.87	19.74	0.19	15.56	2.34	30.08	17.54
Screening values (SV)	150	2000	20	400	8	20	—
Background values (BGV)	33.13	26.7	0.184	24.8	0.084	13.1	73.5
Coefficient of variation (CV)	0.29	0.56	0.68	0.49	2.55	1.58	0.24
Percentage of sampling points beyond the BGV (PSPBB)	27.8%	38.9%	61.1%	38.9%	56.3%	18.8%	36.0%

Table 2. Descriptive statistics on single factor pollution index of heavy metals in surface soils.

	Ni	Cu	Cd	Pb	Hg	As	Zn
Mean	0.96	1.26	1.42	1.21	10.46	1.37	0.97
Standard deviation (SD)	0.31	0.72	1.15	0.82	26.15	2.15	0.23
Coefficient of variation (CV)	0.33	0.57	0.81	0.68	2.50	1.57	0.24
Over standard number	5	7	11	7	10	3	4
Over standard rate (%)	27.8	38.9	61.1	38.9	62.5	18.8	36.4

the content of Cd, Cu, Pb, Ni and Zn did not exceed the screening value (SV), the content in some samples was still higher than the background value (BGV). These shows that chemical plants have great influence on the heavy metal content in the study area, so the relevant departments should pay attention to it and monitor the adjacent areas.

The comprehensive pollution results of soil heavy metal pollution are shown in Fig. 2. The higher the comprehensive soil pollution index is, the greater harm to the soil environmental quality will be. It is classified five levels namely: $I \leq 0.7$, safety; $0.7 < I \leq 1$, warning level; $1 < I \leq 2$, mildly polluted; $2 < I \leq 3$, moderately polluted; $I > 3$, heavily polluted. The comprehensive pollution index in Fig. 2b) were calculated based on the screening value (SV) in (Soil environmental quality risk control standard for soil contamination of development land) (GB36600-2018) as the standard. The pollution index of sample point 12 is 4.45, which is the largest. It is judged to be a heavily polluted area, which has great harm to the soil environmental quality, and there is the possibility of chemical plant pollutant leakage. All the other 17 soil samples had a pollution index of less than 0.7, which were considered safe. The comprehensive pollution index in Fig. 2a) were calculated based on the background values (BGV) of Guanzhong area as the standard. Among the 18 soil samples, 1 sample was in the safe level, 2 samples were in the warning level, and the remaining 15 samples were polluted to

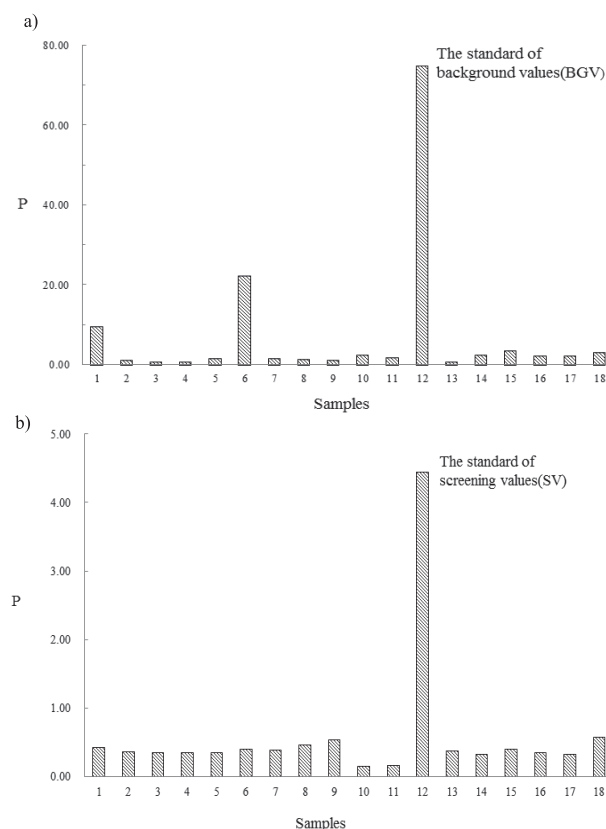


Fig. 2. Comprehensive pollution index of heavy metals in surface soils.

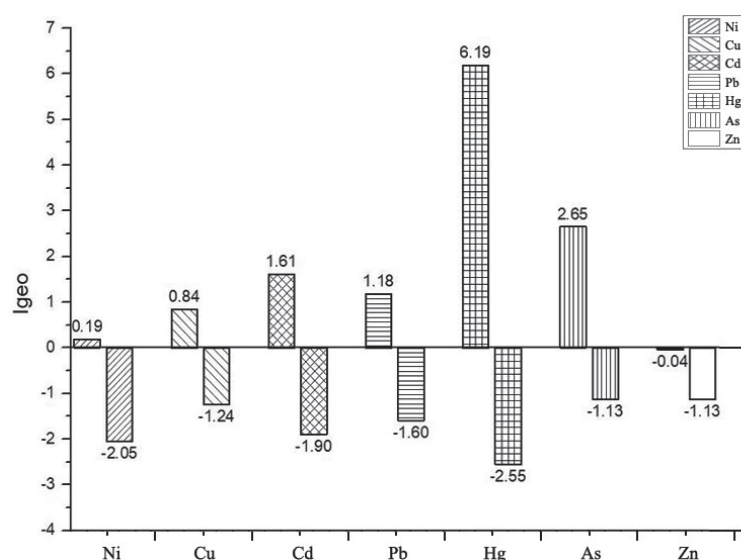


Fig. 3. Minimum and maximum values of (a) geo-accumulation index.

varying degrees, accounting for 83.3% of the total samples. Among the polluted samples, 22.2% were heavily polluted, 27.8% were moderately polluted and 33.3% were mildly polluted. The reason of soil pollution in different degree and higher than background value, may be related to the distance of sampling site from production workshop and waste water discharge place. The sampling points close to the workshop are directly affected by the addition and handling of materials, as well as the omission problem in the residue treatment process and the pipe leakage problem of waste water discharge, and the pollution and affected degree are higher than the sampling points far away. On the other hand, the migration of different metals from chemical plant to surrounding area is different, and the background content of each metal in the soil is also different. All these lead to the different pollution degrees and affected degrees of each sampling site.

Evaluation of Geo-Accumulation Index (I_{geo})

The results of the I_{geo} values were shown in Fig. 3 and Table 3. As can be seen from Table. 3, the mean I_{geo}

values of soil heavy metals were increased in the order of Ni (-0.71) < Zn (-0.66) < As (-0.65) < Pb (-0.56) < Cd (-0.45) < Cu (-0.44) < Hg (0.41). Overall, the mean of I_{geo} for all seven heavy metals, obviously indicates that soil of the study region was not polluted by Ni, Zn, As, Pb, Cd and Cu (Fig. 3). Specifically, Hg had a highest index of I_{geo} (Fig. 3 and Table 3), ranged from -2.55 to 6.19 , in which about 6% and 13% of soil sampling sites were in extremely polluted and moderately polluted to heavily polluted, whereas not polluted to moderately polluted at 25% of sampling sites in the study region (Table 3). However, 6% of monitoring points of the soils were in heavily polluted by As, 11% and 5% of soil sampling sites were in moderately polluted to heavily polluted by Cd and Pb, respectively, in the study region. For Zn, the index of I_{geo} values were smaller than zero at all sampling sites in the study region, which were characteristically classified as not polluted or uncontaminated. The geo-accumulation index (I_{geo}) of heavy metals in different functional areas is shown in Table 4. The distribution of heavy metals in different functional areas is different, so the coefficients of variation (CV) of different heavy metal were different.

Table 3. Classification of Geo-accumulation index (I_{geo}).

	Ni	Cu	Cd	Pb	Hg	As	Zn
Not polluted ($I_{geo} < 0$)	89%	72%	72%	78%	44%	94%	100%
Not polluted to moderately polluted ($0 < I_{geo} \leq 1$)	11%	28%	17%	17%	25%	/	/
Moderately polluted ($1 < I_{geo} \leq 2$)	/	/	/	/	/	/	/
Moderately polluted to heavily polluted ($2 < I_{geo} \leq 3$)	/	/	11%	5%	13%	/	/
Heavily polluted ($3 < I_{geo} \leq 4$)	/	/	/	/	/	6 %	/
Heavily polluted to extremely polluted ($4 < I_{geo} \leq 5$)	/	/	/	/	/	/	/
Extremely polluted ($I_{geo} > 5$)	/	/	/	/	6%	/	/

Table 4. Geo-accumulation index of heavy metals in topsoil of different functional areas.

Heavy metals	Office (A)			Factory building (B)		
	I_{geo}	Pollution Level		I_{geo}	Pollution Level	
Ni	-0.56	0	Not polluted	-0.75	0	Not polluted
Cu	0.44	1	Not polluted to moderately polluted	-0.74	0	Not polluted
Cd	0.59	1	Not polluted to moderately polluted	-0.07	0	Not polluted
Pb	0.74	1	Not polluted to moderately polluted	-0.21	0	Not polluted
Hg	-0.78	0	Not polluted	-0.06	0	Not polluted
As	-0.73	0	Not polluted	-0.46	0	Not polluted
Zn	-	-	-	-0.27	0	Not polluted
Heavy metals	Distillation area (C)			Sewage pool (D)		
	I_{geo}	Pollution Level		I_{geo}	Pollution Level	
Ni	-0.60	0	Not polluted	-0.71	0	Not polluted
Cu	0.65	1	Not polluted	-0.64	0	Not polluted
Cd	-0.50	0	Not polluted	-0.71	0	Not polluted
Pb	-0.61	0	Not polluted	-1.03	0	Not polluted
Hg	1.09	2	Moderately polluted	1.28	2	Moderately polluted
As	-1.12	0	Not polluted	-0.44	0	Not polluted
Zn	-0.30	0	Not polluted	-0.91	0	Not polluted

The order of pollution degree from heavy to light was: Distillation area > Sewage pool > Office > Factory building. This indicates that the pollution is mainly concentrated in the chemical reaction area, and there may be leakage in the production process. The distillation area and sewage pool were moderately polluted by Hg, which was most serious than other heavy metals, and other areas were not polluted by Hg, so the pollution in distillation area and sewage pool was more serious than others. Although the office area was polluted by 3 kinds heavy metals (Cu, Cd and Pb), but the degree of pollution is not polluted to moderately polluted, so the pollution in office area was not serious. Only office area was not polluted to moderately polluted by Cd and Pb, others were not polluted. The office and distillation area was not polluted to moderately polluted by Cu, others were not polluted. There was no heavy metal pollution in the workshop area, which was affected by the harden ground, so the pollutants cannot enter the subsoil.

Potential Ecological Risk Analysis

In order to reflect regional differences, the background value (BGV) of heavy metal in Guanzhong area was selected as the reference value. The toxicity coefficient [31, 32] of Hg, Cd, As, Cu, Pb, Ni and Zn were 40, 30, 10, 5, 5, 5 and 1, respectively. The results were shown in Table 5 and Fig. 4. The mean E_r^i of heavy metal followed a descending order as Hg (418.40) > Cd (42.53) > As (13.70) > Cu (6.30) > Pb (6.04) > Ni (4.81) > Zn (0.97). The degree of potential ecological hazard risk of Hg was the most serious, with the maximum index of potential ecological hazard: 4161.90, which is the most important ecological risk factor. The potential ecological hazard of Cd was moderately ecological hazard, with the index (42.53) slightly exceeded the mild standard (40). The other potential ecological hazards were mildly ecological hazard. As the Fig. 4 shown, the potential ecological hazard of No. 12 and

Table 5. Potential ecological hazard index of heavy metal.

Metal elements		Ni	Cu	Cd	Pb	Hg	As	Zn	RI
E_r^i	Max	8.56	13.45	136.96	16.95	4161.90	94.12	1.46	4414.60
	Min	1.81	3.17	12.06	2.48	9.76	6.85	0.68	43.39
	Mean	4.81	6.30	42.53	6.04	418.40	13.70	0.97	444.36
	Level	Mild	Mild	Moderate	Mild	Extremely heavy	Mild	Mild	Extremely heavy

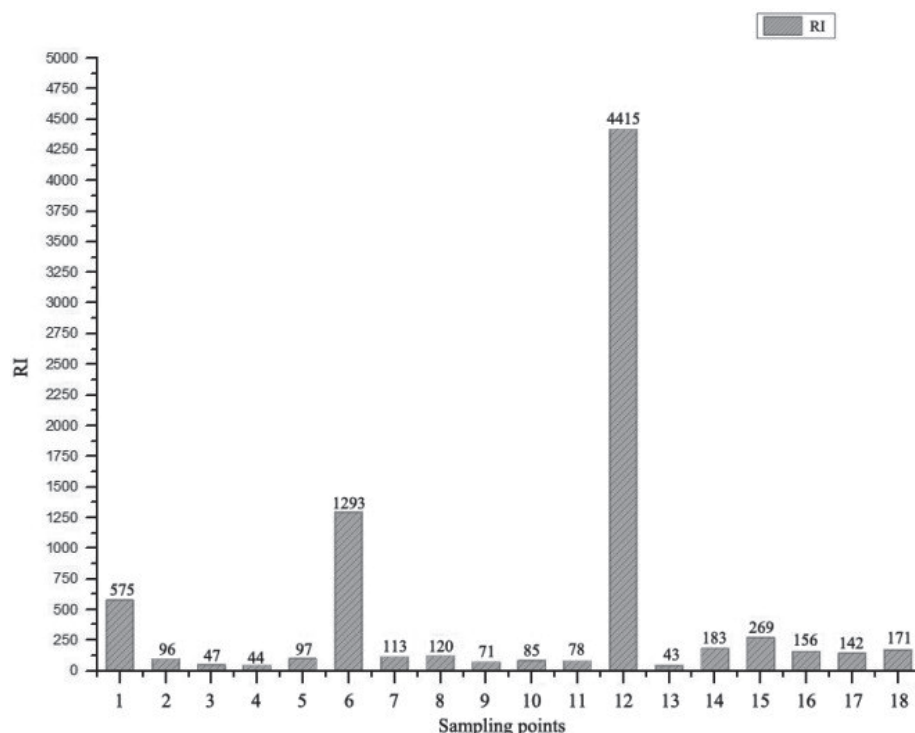


Fig. 4. Potential ecological hazard index of soil samples.

No. 6 soil samples were extremely heavy, which were all affected by heavy metal Hg. The potential ecological hazard of No. 5 soil samples were heavy, others were moderate or mild. The potential ecological hazard index (RI) of heavy metals in chemical plants was 444.36, ranged from 43.39 to 4414.60, with extremely ecological hazard. These caused by the content of Hg exceeding the standard. After Hg was removed, the potential ecological hazard in chemical plants is reduced to mild ecological hazard.

Frequency distribution of potential ecological hazard coefficient of heavy metal was shown in Fig. 5. The

potential ecological hazard of Ni, Cu, Pb, Zn in all samples were mildly ecological hazard. The potential ecological hazards of As were mildly ecological hazard, among them 94% of samples were mildly and 6% of samples were heavily. The potential ecological hazards of Hg were extremely ecological hazard, among them 31% of samples were mildly, 31% of samples were moderately, 19% of samples were Significantly, 19% of samples were extremely heavy. Considering the above factors comprehensively, the potential ecological hazard (RI) in the chemical plant was extremely heavy ecological hazard, which seriously affected

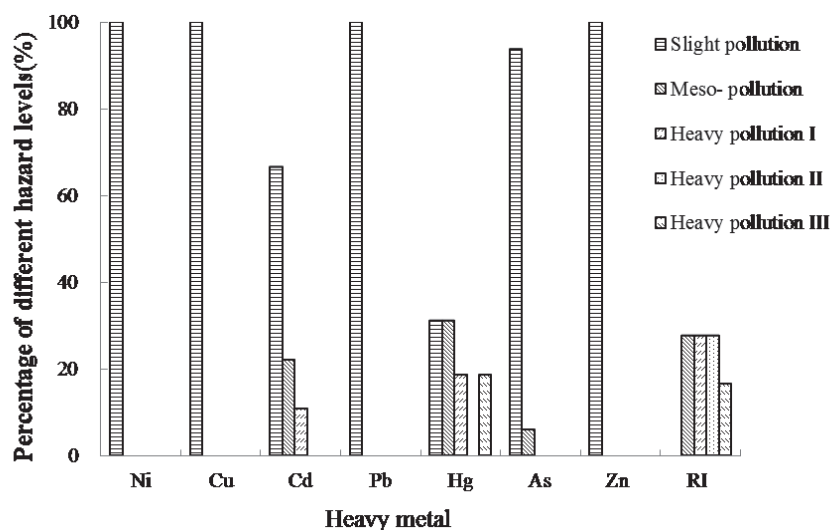


Fig. 5. Frequency distribution of potential ecological hazard coefficient of heavy metal.

Table 6. Pearson correlation analysis between seven heavy metals in the soils.

	Ni	Cu	Cd	Pb	Hg	As	Zn
Ni	1						
Cu	0.085	1					
Cd	-0.146	0.036	1				
Pb	-0.132	0.269	0.938**	1			
Hg	0.893**	0.152	0.090	0.152	1		
As	0.121	-0.312	0.317	0.297	0.031	1	
Zn	0.105	0.301	0.875**	0.846**	0.291	0.176	1

“**” indicates a significant correlation at the 0.01 level (bilateral)

environmental safety and public health. All these need to be paid close attention by government departments.

Correlation Analysis

The sources of heavy metals in soil are mostly influenced by human activities and the parent material of soil, such as chemical plant production, pesticide spraying, traffic emissions and so on. The similarity of the sources will lead to certain characteristics of some heavy metal elements in soil [33, 34]. Therefore, correlation analysis is an important basis to predict the source of heavy metals, and the correlation between heavy metals in soil can provide important information such as the source and route of heavy metal pollution in soil. If the correlation between elements is significant or extremely significant, it indicates that elements generally have homologous relationship or compound pollution.

The raw materials required by chemical plants and the waste water and residue discharged during the production process usually contained one or more of the same heavy metals. The good correlation between heavy metals indicated that these elements have similar sources, consistent with chemical plant production processes and the heavy metals contained in the waste discharge. Pearson correlation analysis between seven heavy metals in the soils was shown in Table 6. Cd, Pb and Zn were significantly correlated with each other at the level of 0.01, while Ni and Hg were significantly correlated at the level of 0.01, and the correlation coefficients were all greater than 60%. Therefore, it can be inferred that the elements of Cd, Pb and Zn have great homology and complex pollution hazards, while the elements of Ni and Hg have great homology and complex pollution hazards respectively too. Cu and As had no significant correlation with other elements, so it is inferred that the sources of Cu and As may be different from others. Therefore, there is no homologous relationship between Hg and As, and they come from different pathways. Based on chemical plant processes, Hg may come from waste water discharge, leakage, or waste residue accumulation during pesticide production.

As may come from fertilizers and pesticides used on surrounding agricultural land. This further proved that leakage of chemical plant emissions was an important source of soil heavy metal pollution in this area.

Comprehensive Analysis

From the above analysis, it can be seen that chemical plants have caused extremely serious heavy metal pollution to the soil. Soil is the basic environmental element that constitutes the ecosystem and the material basis for human survival and development. Heavy metals in the soil can be absorbed by crops and eventually harm human health, resulting in life-threatening conditions. In addition, the waste gas, waste water and waste residue discharged from chemical plants will also cause air pollution, water pollution and solid waste pollution, seriously damage the ecological environment, affect human life and endanger life safety. Therefore, it is necessary to carry out detailed pollution investigations on the remaining sites after the relocation of chemical plants and similar enterprises to assess the health of the land.

At the same time, pollution treatment requires a large amount of investment and manpower, and the repair process is long and difficult, thus hindering economic development. Such preliminary surveys provides accurate data for the later governance, development and utilization. Only by confirming the soil pollution, the types and nature of pollutants accurately and truly, effective measures can be taken to control soil pollution, shorten the time of remediation, save the cost of remediation, and ensure that the land is reused scientifically and reasonably in the later stage.

Conclusions

(1) Compared with the background value of heavy metal content in Guanzhong area, Hg, As, Cd, Cu, Pb, Ni and Zn in the surface soil (0~20 cm) of this chemical plant area showed different degrees of enrichment. The heavy metals content of 83% samples exceeded

the background value. According to the comprehensive pollution index (CPI) method, 83.3% of the soil samples were affected by heavy metals, of which 22.2% were heavily polluted. Hg and As were the most serious pollutants. These mean that the chemical plant had great influence on the heavy metal content in this area, so it should cause the attention of relevant departments, and monitor and control the adjacent area.

(2) The results of the potential ecological hazard analysis and the geo-accumulation index showed that the potential hazard degree of heavy metal in the chemical plant was different, among which Hg reached extremely heavy of ecological hazard and had certain potential ecological hazard. After comprehensive consideration, the potential ecological hazard (RI) in the chemical plant was extremely heavy ecological hazard, and the area with heavy pollution was in distillation area. These seriously affected environmental safety and public health. Therefore, it is urgent to carry out detailed investigation and rehabilitation to restore the ecological environment.

(3) According to the correlation analysis of heavy metals, the sources of most heavy metals are similar, consistent with the production process of chemical plants and the heavy metals contained in the waste discharge, indicating that the leakage of chemical plants' emissions was an important source of soil heavy metal pollution in this region.

Acknowledgements

This research was financially supported by Innovation Capability Support Program of Shaanxi (Program No. 2021KRM079), Natural Science Basic Research Program of Shaanxi (Program No. 2021JQ-959), the Fundamental Research Funds for the Central Universities, CHD (Program No. 300102270505) and The project of Shaanxi Province Land Engineering Construction Group (Program No. DJNY2020-26).

Conflict of Interest

The authors declare no conflict of interest.

Reference

- SHENG L.W., FENG Y.Z., YU H.B., ZHANG X.Q., SUN R.J., ZHANG H. Discussion on Environmental risk assessment of contaminated sites reuse. *Sichuan Environment*, **33** (6), 156, **2014**.
- GASIOREK M., KOWALSKA J., MAZUREK R., PAJAK M. Comprehensive assessment of heavy metal pollution in topsoil of historical urban park on an example of the Planty Park in Krakow (Poland). *Chemosphere*, **179**, 148, **2017**.
- REN W.X., XUE B., GENG Y., SUN L.N., MA Z.X., ZHANG Y.S., MITCHELL B., ZHANG L.M. Inventorying heavy metal pollution in redeveloped brownfield and its policy contribution: Case study from Tiexi District, Shenyang, China. *Land Use Policy*, **38**, 138, **2014**.
- ZOU J.M., SUN J., DAI W., YAO Z.B., YANG T., LIU N.L. Evaluation and analysis of heavy metals in cultivated soils in the suburbs of Beijing. *Journal of Beijing Forestry University*, **35** (1), 132, **2013**.
- ZHANG L.K., LI H.P., HUANG X.M., LI Y.M., JIAO K.L., SUN P., WANG W.D. Soil heavy metal spatial distribution and source analysis around an aluminum plant in Baotou. *Environmental Science*, **37** (3), 1139, **2016**.
- FAN S.X., WANG X.D., LEI J., RAN Q.Q., REN Y.X., ZHOU J.H. Spatial distribution and source identification of heavy metals in a typical Pb/Zn smelter in an arid area of northwest China. *Human and Ecological Risk Assessment* an *International Journal*, **25** (7), 1, **2019**.
- LI K.J., GU Y.S., LI M.Z., ZHAO L., DING J.J., LUN Z.J., TIAN W. Spatial analysis, source identification and risk assessment of heavy metals in a coal mining area in Henan, Central China. *International Biodeterioration & Biodegradation*, 128, **2017**.
- ZHOU M., LIAO B., SHU W.S., YANG B., LAN C.Y. Pollution Assessment and Potential Sources of Heavy Metals in Agricultural Soils around Four Pb/Zn Mines of Shaoguan City, China. *Journal of Soil Contamination*, **24** (1), 76, **2015**.
- FAN X.G., MI W.B., MA Z.N., WANG T.Y. Spatial and temporal characteristics of heavy metal concentration of surface Soil in Hebin industrial park in Shizuishan northwest China. *Environmental Science*, **34** (5), 1887, **2013**.
- REN C.H., LU X.W., CHEN C.C., YANG L.N., YANG G. Contamination assessment and spatial distribution of heavy metals in dust surrounding the Changqing town lead-zinc smelting plant in Baoji. *Acta Scientiae Circumstantiae*, **32** (03), 706, **2012**.
- JIANG H.H., CAI L. M., WEN H.H., HU G.C., LUO J. An integrated approach to quantifying ecological and human health risks from different sources of soil heavy metals. *Total Environment*, 701, **2019**.
- VERMA A., KUMAR R., YADAVE S. Distribution, pollution levels, toxicity, and health risk assessment of metals in surface dust from Bhiwadi industrial area in North India. *Hum. Ecol. Risk Assess*, **26** (8), 2091, **2019**.
- Ministry of Ecology and Environmental of P.R. China, Ministry of Natural Resources of P.R. China. The Communique for Soil Contamination Status Survey in China, **2014**.
- LIU D.H., WANG F.Y., ZHOU W.L., YANG Y.J. Heavy metal pollution in street dusts from different functional zones of Luoyang city and its potential ecological risk. *Environmental Science*, **33** (1), 253, **2012**.
- LI X.Y. Influence of season change on the level of heavy metals in outdoor settled dusts in different functional areas of Guiyang city. *Environmental Science*, **34** (6), 2407, **2013**.
- CASTILLO S., ROSA J.D.D.L., CAMPA A.M.S.D. L., GONZALEZ-CASTANEDO Y., FERNANDEZ-CAMACHO R. Heavy metal deposition fluxes affecting an atlantic coastal area in the southwest of Spain. *Atmospheric Environment*, **77**, 509, **2013**.
- DAI J.R., HU X.P., WANG Z.H. Characteristics of heavy metals pollution in soil and potential ecological risk assessment – a case study of Blue Economic Zone of Shandong Peninsula. *Journal of safety and environment*, **13** (1), 134, **2013**.

18. GU Y.G., GAO Y.P., QIN L. Contamination, bioaccessibility and human health risk of heavy metals in exposed-lawn soils from 28 urban parks in southern China's largest city, Guangzhou. *Applied Geochemistry*, **67**, 52, **2016**.
19. CHEN H.Y., TENG Y.G., LU S.J., WANG Y.Y., WU J., WANG J.S. Source apportionment and health risk assessment of trace metals in surface soils of Beijing metropolitan, China. *Chemosphere*, **144**, 1002, **2016**.
20. ZHANG C.T., YANG Y., LI W.D., ZHANG C.R., ZHANG R.X., MEI Y., LIAO X.S., LIU Y.Y. Spatial distribution and ecological risk assessment of trace metals in urban soils in Wuhan, central China. *Environmental Monitoring and Assessment*, **187** (9), 1, **2015**.
21. LI Y.W., WANG J., JU T.Z., WANG L., LING N., ZHANG S.N., ZHA X.H. Heavy metal pollution characteristics and human health risk assessment in soils from different functional areas of Baiyin, Gansu, China. *Chinese Journal of Ecology*, **36** (5), 1408, **2017**.
22. QIAN J.Y. Back a service chemical engineering business enterprise latent pollution place the 1, 2 th stage environment investigate. *Energy Environmental Protection*, **29** (06), 44, **2015**.
23. ZHANG Z., WANG C.L., LIU N., CHEN H., TIAN J. Environmental investigation of soil and groundwater at the relocation site of a chemical plant. *Sichuan Environment*, **37** (04), 111, **2018**.
24. ZHANG J.L., DING J.F., LU G.N., DANG Z., YI X.Y. Heavy metal contamination in farmland soils at an e-waste disassembling site in Qingyuan, Guangdong, South China. *Environmental Science*, **36** (7), 2633, **2015**.
25. State administration for market regulation. Soil environmental quality risk control standard for soil contamination of development land (GB36600-2018). China Environmental Science Press, **2018**.
26. ZHU D., WEI Y., ZHAO Y., WANG Q., HAN J. Heavy Metal Pollution and Ecological Risk Assessment of the Agriculture Soil in Xunyang Mining Area, Shaanxi Province. Northwestern China, *Bulletin of Environmental Contamination and Toxicology*, 101, **2018**.
27. BLANCHARD D., LOUIS N., ABDOURAHIMI, DANIEL B., SAÏDOU, NDJANA NKOULO II J., BONIFACE K., GODFROY K. Environmental Pollution by Heavy Metals in the Gold Mining Region of East Cameroon. *American journal of environmental sciences*, **14**, **2018**.
28. LIANG Y.H., LIU Q.C., LI Y.K., LIU F. Speciation analysis and ecological risk assessment of antimony in Xikuangshan, Hunan Province. *Polish journal of environmental*, **30** (2), **2021**.
29. ZHENG N., WANG Q.C., LIU J.S., WANG Y., ZHANG Z.S. Spatial variation of heavy metals contamination in the soil and vegetables of Huludao City. *Environmental Science*, **30** (7), 2071, **2009**.
30. LIU Y.L., ZHANG L.J., HAN X.F., ZHUANG T.F., SHI Z.X., LU X.Z. Spatial variability and evaluation of soil heavy metal contamination in the urban-transect of Shanghai. *Environmental Science*, **33** (2), 599, **2012**.
31. SU T., DONG S.W. Mathematical model of comprehensive weighted factors based on analytic hierarchy process for evaluation soil heavy metal pollution. *Journal of Tangshan Teachers College*, **36** (5), 7, **2014**.
32. FANG H.D., CHEN J.F., DUAN J.M., CHEN J.S., LIN Q.J., CHEN S.H. Speciation characteristics and bioavailability of heavy metal elements in PM_{2.5} and PM₁₀ in the suburbs of Xiamen. *Ecology and Environmental Sciences*, **24** (11), 1872, **2015**.
33. JI D.Q., WEN Y., WEI J.B., WU Z.F., LIU Q., CHENG J. Relationships between landscape spatial characteristics and surface water quality in the Liu Xi River watershed. *Acta ecologica sinica*, **35** (2), 246, **2015**.
34. LI G., LU N., HAN J.C., WANG N., WEI Y., SUN Y.Y. Distribution and potential ecological risk assessment of heavy metals in the Yellow River beach region, Shaanxi, China. *Applied ecology and environmental research*, **18** (1), 1253, **2020**.

