Pollution Characteristics and Comprehensive Evaluation of Soil Organic Compounds at a Chemical Contaminated Site

Yulu Wei¹, 2, 3, 4, *, Luyao Wang¹, 2, 3, 4, a

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

*Corresponding author e-mail: 453876296@qq.com, a502295012@qq.com

Abstract. Urban soil is one of the main components of urban ecosystem. Taking organic pollution in a chemical plant after relocation as the research object, which is left behind by a chemical plant after relocation, 13 deep soil samples were collected. According to the requirements of “Soil environmental quality Risk control standard for soil contamination of development land” (GB36600-2018), 43 organic contents were tested and analyzed. Mass ratio statistical analysis, single pollution index method and Nemerow synthetic evaluation index were used to analyze the organic pollution in the site. Results show that chloroform, benzene, trichloroethylene (TCE), 1,2-dichloropropane and 1,2,3-trichloropropane were significantly enriched in the reactor and the sewage pool, and the pollution depth was up to 10m. This shows that the chemical plant has a great impact on the site, and there may be leakage or stolen discharge, which is also an important source of soil organic pollution in this area, so detailed monitoring and remediation work should be carried out in the later stage.

1. Introduction
As one of the main components of urban ecosystem, urban soil has important ecological, environmental and economic functions and is of great significance to the sustainable development of cities. With the rapid development of human society, the process of urbanization is also accelerating, and more and more industrial enterprises have left behind a large number of sites with potential environmental risks in the process of closure and relocation. Specific areas of space with actual hazards and potential threats are called contaminated plots. China has a large demand for chemical products, the use of toxic and harmful raw and auxiliary materials in the production process of chemical products, and the fugitive discharge of chemical waste are likely to cause soil and groundwater pollution. Therefore, chemical pollution sites are one of the more common pollution sites, mainly organic and inorganic waste pollution. These substances can pollute the atmosphere through equipment leaks and spread around the wind. They can also pollute rivers and groundwater through sewage discharge. If it cannot be purified for a long time, it will be absorbed by flora and fauna or
directly referenced by people, which will directly harm the human body and endanger health. They also can infiltrate the soil for a long time by osmosis, causing the soil to adsorb toxic substances, and to diffuse and spread under the action of precipitation and plant growth. Chemical pollutants are very complex. Different types of chemical plants have different characteristic pollutants and different hazards. Typical pollutants mainly include benzene series (BTEX), polycyclic aromatic hydrocarbons (PAHs), and chlorinated hydrocarbons (CHCs) [1].

In the 1970s, highly industrialized western countries began to pay attention to the investigation of soil and water pollution. The first investigation and research was on organic pollution, mainly including the distribution characteristics of organic pollutants in groundwater and soil and the source of pollution. With years of continuous exploration, a certain system of investigation and research methods has been formed. The investigation of organics in western countries and regions mainly focuses on high-concentration monocyclic aromatic hydrocarbons and halogenated hydrocarbons. Based on the valuable experience in the study of organic pollutants in soil and groundwater, it revealed the pollution characteristics and mechanism of organic pollutants. Provide technical support for the next step of governance and repair [2-4].

In the early 1980s, China began to investigate and research the organic pollutants in petrochemical, pesticide, landfill and other sites. The main research objects are volatile organic compounds, petroleum hydrocarbons, polycyclic aromatic hydrocarbons, and organochlorine pesticides. Although domestic experts and scholars have done a lot of basic work in the investigation and research of contaminated sites, and have obtained certain research results, there are few studies on the pollution characteristics and source analysis of chemical-contaminated sites [5-6]. This article analyzes the characteristics of organic matter pollution in the soil of a chemically polluted plot, and provides basic parameters and theoretical basis for the evaluation of this type of polluted plot and further pollution control.

2. Regional overview
The site is a remnant site of a closed chemical plant, which was founded in June 2003. It is located in the eastern part of the Guanzhong Plain. It was formerly a pesticide chemical plant and covers an area of 168 acres. It mainly produces food-grade fumaric acid, cis-butenedioic acid, cationic etherifying agent and so on. The preparation process is: in the presence of a catalyst (V₂O₅-Mn₃O₃, etc.), benzene (or butene) is oxidized to form maleic acid (maleic anhydride), and then isomerized. Benzene and excess air are oxidized in a fluidized bed or fixed bed reactor to generate maleic anhydride, which is absorbed into the maleic acid by the circulating acid solution, and then decolorized and filtered. After texturing, fumaric acid is obtained by filtering, washing and drying.

The site is located in the cutting erosion area, and the terrain is generally flat. The site belongs to a warm temperate semi-humid and semi-arid monsoon climate, with four distinct seasons, sufficient light, and suitable rainfall. The annual average temperature is 12-14 °C, the annual sunshine is 2200-2500h, and the annual rainfall is about 600mm.

The main key pollution areas of the site are concentrated in the distillation zone, reactor, and sewage tank. According to its predecessor and the current fumaric acid production process, it is preliminarily determined that the main pollutants are pesticides, heavy metals, vanadium, and volatile-semi-volatile organic compounds Pollutants.

3. Materials and Methods

3.1. Sample Collection
As the demolition in the site has not been completed, and affected by factors such as hardened ground and non-demolished factory buildings, sampling in most places is temporarily unavailable. This time, only the three areas of "office area", "reactor" and "distillation area" were investigated for organic pollution.
The grid method and the semi-random method are used to set the points, and the sampling is performed in the key areas. 10 sampling points were set up in the sampleable area to collect 0 ~ 2m soil bodies, and a total of 40 soil samples were collected. In the "Reactor (S1)" and "Distillation Zone (S2)", samples were taken to 4m and 10m respectively, for a total of 13 soil samples. Soil samples were sealed in brown (light-proof) glass bottles and sealed with a sealing film. The sample fills the entire space of the container, is transported and stored in an incubator below 4 °C, and is pretreated within 7 days, and the analysis is completed within 40 days.

3.2. Methods
The detection indicators and evaluation standards were determined in accordance with the “Soil environmental quality Risk control standard for soil contamination of development land” (GB36600-2018). Investigations use both rapid detection and laboratory analysis methods. First use a portable gas chromatograph mass spectrometer Mars-400Plus for rapid on-site measurement, select typical points based on the results of the quick test, then perform deep sampling and send to the inspection and testing center for soil organic pollutant detection and analysis. For the analysis and testing of key pollutants in soil samples, refer to the methods specified in the “Technical Specifications for Soil Environmental Monitoring” (HJ / T 166).

3.3. Evaluation method
The single pollution index method and Nemerow synthetic evaluation index were used for evaluation [7].

\[
I = \sqrt{(P_i - C_i)^2 + \frac{\text{max} - C_i}{2}}
\]

Among them \(P_i\) is a single pollution index. \(C_i\) is the measured value. \(S_i\) is an evaluation index, which reference to the screening values in the “Soil environmental quality Risk control standard for soil contamination of development land” (GB3600-2018). \(\text{Max}\) is the maximum value of a single pollution index, and \(\text{avg}\) is the average value of a single pollution index. Table 1 is the classification standard of the comprehensive soil pollution index.

| Pollution index | Degree          |
|-----------------|-----------------|
| P≤0.7           | 1 Non-pollution  |
| 0.7<P<1         | 2 Warning line   |
| 1<P≤2           | 3 Lower pollution|
| 2<P≤3           | 4 Middle pollution|
| P>3             | 5 Serious pollution|

4. Analysis of pollution characteristics
The Mars-400 Plus was used to quickly determine the volatile / semi-volatile organic content of 40 shallow soil samples. The results showed that volatile / semi-volatile organic pollution is mainly concentrated at S1 and S2. Immediately, a deep sampling point was set to 4m (0.5 to 4m) at S1, and a deep sampling point was set to 10m (3.5 to 10m) at S2, and a total of 13 samples were collected.

4.1. Analysis of major pollutants
Descriptive statistical analysis [8] of the organic pollutant detection results of 13 deep soil samples at
S1 and S2 is shown in Table 2. Most of the pollutants were not detected or the detection value did not exceed the standard, and only 5 pollutants had detection values exceeding the standard, which were chloroform, benzene, trichloroethylene, 1,2-dichloropropane, and 1, 2,3-trichlorobenzene. Among them, the maximum content of 1,2,3-trichloropropane was 359.21 mg · kg$^{-1}$, which exceeded the screening value by 0.05 mg · kg$^{-1}$ more than 7,000 times, and the average value of 98.24 mg · kg$^{-1}$ also exceeded the screening value by nearly 2000 times. Showed a clear state of enrichment. Further detailed investigations and risk assessments should be carried out. The average values of chloroform and benzene exceeded the screening values by 2.1 and 1.9 times. Although the average values of trichloroethylene and 1,2-dichloropropane were lower than the screening values, the maximum values of 1.83 mg · kg$^{-1}$ and 1.28 mg · kg$^{-1}$ exceeded the screening values by 2.6 and 1.28 times, respectively. The above results indicate that the organic matter pollution problem in this area is prominent, and detailed investigation and repair work are needed.

From the distribution of the maximum and minimum values, the content of each element is very different. The coefficient of variation reflects the average degree of variation at each sampling point in the sample. The magnitude of the coefficient of variation in this region is: trichloroethylene> 1,2,3-trichloropropane> benzene> 1,2-dichloropropane> chloroform. Some studies have suggested that a coefficient of variation of less than 15% is a weak variation, and a coefficient of variation greater than 36% is a strong variation [9]. Except for chloroform, which is a weak mutation, the coefficients of variation of the other four organics all exceed 0.36, which is a strong mutation. In particular, the coefficients of variation of trichloroethylene and 1,2,3-trichloropropane are as high as 148% and 143%, respectively, indicating that the element is unevenly distributed in two regions and in the depth direction, and the variation is relatively large. This is related to the effects of human factors, soil adsorption, and microbial degradation.

### Table 2. Statistical analysis of organic pollutant content

| Organic pollutants | average | standard deviation | minimum | maximum | Variation coefficient | screening values |
|--------------------|---------|---------------------|---------|---------|-----------------------|-----------------|
| Chloroform         | 0.63    | 0.02                | 0.58    | 0.65    | 0.04                  | 0.30            |
| Benzene            | 1.92    | 2.17                | 0.13    | 5.65    | 1.13                  | 1.00            |
| Trichloroethylene  | 0.46    | 0.67                | 0.01    | 1.83    | 1.48                  | 0.70            |
| 1,2-dichloropropane| 0.49    | 0.47                | 0.02    | 1.28    | 0.97                  | 1.00            |
| 1,2,3-trichlorobenzene | 98.24  | 140.42              | 0.04    | 359.21  | 1.43                  | 0.05            |

### 4.2. Spatial distribution characteristics of soil organic pollutants

In order to understand the vertical migration and transformation of organic matter in soil and the pollution degree at different depths, single-factor pollution index analysis and Nemerow comprehensive factor index analysis were performed for organic matter at different depths in soil [10]. Six typical soil samples were selected for analysis at 0.5 ~ 1.0m(S1), 1.0 ~ 1.5m(S1), 3.0 ~ 4.0m(S1), 3.5 ~ 4.0m(S2), 4.0 ~ 5.0m(S2), 9.0 ~ 10m(S2). It can be known from Table 2 that the 6 layered soil samples are all polluted by organic matter, and there are mixed pollution phenomena of various organic matter. Among them, benzene (S2), trichloroethylene, 1,2 dichloropropane, and 1,2,3-trichloropropane decreased with the increase of soil depth, and the changes were large. The results are the same as the analysis results of the above coefficient of variation. Soil microorganisms are partially degraded. The content of chloroform in each layer of soil is basically the same, and there is no statistical difference, indicating that it is extremely difficult to be degraded. The undegraded
chloroform gradually penetrates into the lower layer of soil through the erosion of surface water, resulting in an increase in the content of the bottom layer of soil. At the same time, the different distribution characteristics of organic pollutants are also related to the characteristics of the pollutants, the physical and chemical properties of the soil, and the leaching rate [11]. It is worth noting that the chloroform content at S1 to 4m is still beyond the standard, and the chloroform, benzene, 1,2,3-trichloropropane content at S2 to 10m is still beyond the standard. This shows that long-term production and sewage activities in chemical plants not only cause shallow soil pollution, but vertical migration of organic pollutants also poses serious harm to deep soil. According to the pollution classification standard of comprehensive pollution index (Table 3). Except that there is only one organic pollutant exceeding 3.0-4.0m at S1, and the pollution index is 1.62 light pollution, the rest are all heavily polluted and multiple pollutants are mixed at the same time. Pollution. The pollution index is the largest at the depth of S2 3.5-4.0m, and the pollution is the most serious, and all five indicators exceed the screening value. The occurrence of such serious organic pollution may be related to the particularity of the sampling point selection, that is, the distance from the production workshop and the waste water discharge port. The closer sampling point is directly affected by the raw material addition, handling, and waste water discharge near the production workshop. There may be the effects of pipeline leakage problems, and the pollution degree is higher than the sampling point at a long distance. On the other hand, it may indicate that the chemical plant may have the phenomenon of stealing drainage, which leads to large-scale organic pollution, and detailed site investigation is needed.

### Table 3. Single factor assessment and comprehensive assessment of organic pollution

| Organic pollutants | 0.5-1.0m | S1 1.0-1.5m | 3.0-4.0m | 3.5-4.0m | 4.0-5.0m | 9.0-10m |
|-------------------|---------|-----------|---------|---------|---------|---------|
| Chloroform        | 1.93    | 2.17      | 2.13    | 2.10    | 2.07    | 2.17    |
| Benzene           | 0.13    | 0.16      | 0.38    | 5.65    | 4.14    | 1.07    |
| Trichloroethylene | 0.07    | 0.06      | 0.03    | 2.61    | 1.13    | 0.01    |
| 1,2-dichloropropane| 0.19    | 0.18      | ND      | 1.28    | 0.77    | 0.02    |
| 1, 2,3-trichlorobenzene | 87.20 | 109.40    | 0.80    | 7184.20 | 4341.40 | 65.80    |
| Comprehensive index-polluted | 62.95 | 78.96     | 1.62    | 5180.92 | 3130.85 | 47.54    |

5. Conclusions and recommendations

(1) Compared with the screening values in the “Soil environmental quality Risk control standard for soil contamination of development land” (GB36600-2018), the site has detected excessive levels of organic pollutants in the S1 and S2 areas, mainly as follows: Chloroform, benzene, trichloroethylene, 1,2-dichloropropane and 1,2,3-trichloropropane. The content of other pollutants except chloroform decreased with the increase of soil depth, and the changes were large; the content of chloroform in each layer of soil was basically the same, and there was no statistical difference.

(2) The pollution depth at S1 is 4m, and S2 is 10m. According to the pollution classification standard, only one chloroform pollutant exists at 3.0 ~ 4.0m at S1, and the pollution index is 1.62, which belongs to the light pollution level, and the rest are mixed severe pollution levels. Among them, the comprehensive pollution index at the depth of S2 from 3.5 to 4.0m is the largest and the pollution is the most serious, and the content of the five pollutants exceeds the screening value. Relevant departments should pay attention and monitor and manage neighboring areas.

Acknowledgements

This work was financially supported by internal research project of Shaanxi Provincial Land Engineering Construction Group Co., Ltd.: “Research on Application of Construction Waste (Clay Bricks) in Slope Land Improvement in Southern Shaanxi” (DJNY2020-26).
References

[1] Li Xiong, Xu Dimin, Zhao Youcai, et al. Application Study on Closed Municipal Solid Waste Landfill Mining [J]. Journal of Tongji university (natural science), 2006, 34(10):1365-1368.

[2] E, Kret, A, et al. Identification of TCE and PCE sorption and biodegradation parameters in a sandy aquifer for fate and transport modelling: batch and column studies[J]. Environmental Science & Pollution Research, 2015.

[3] Iturbe R, Flores C , Claudia Chávez, et al. In Situ flushing of contaminated soils from a refinery: Organic compounds and metal removals[J]. Remediation Journal, 2004, 14(2).

[4] Bojes H K, Pope P G . Characterization of EPA’s 16 priority pollutant polycyclic aromatic hydrocarbons (PAHs) in tank bottom solids and associated contaminated soils at oil exploration and production sites in Texas[J]. Regul Toxicol Pharmacol, 2007, 47(3):288-295.

[5] Li Binghua, Chen Honghan, He Jiangtao, et al. Characteristics and cause of monocyclic aromatic hydrocarbon contamination in shallow groundwater in an area of the Yangtze River delta[J]. Geology China, 2006, 033 (005): 1124-1130.

[6] Liu Xuesong, Cai Wutian, Li Shengtao. Survey of soil and groundwater contamination in oil pollution site [J]. Hydrogeology & Engineering Geology, 2010, 37 (04): 121-125.

[7] Wei Yulu, Li Yan, Wang Zhao. Evaluation of soil heavy metal pollution in a chemical plant after relocation [J]. Land development and engineering research, 2019, 4(11): 63-68.

[8] He Tianhui, Cai Jiannan, He Guanxing, et al. The soil organic matter pollution and comprehensive evaluation in the farmland in Zhongshan city [J]. Sichuan Chemical Industry, 2018, 21(01): 60-62.

[9] Liuianshu, Zhang Zulu, Liu Yang. Sources Identification and Hazardous Risk Delineation of Heavy Metals Contamination in Rizhao City [J]. Acta Geographica Sinicca, 2012, 67(7): 109-122.

[10] Zheng Na, Wang Qichao, Liu Jingshuang, et al. Spatial Variation of Heavy Metals Contamination in the Soil and Vegetables of Huludao City [J]. Environmental Science, 2009, 30 (07): 2071-2076.

[11] Blaha U, Appel E , Stanjek H . Determination of anthropogenic boundary depth in industrially polluted soil and semi-quantification of heavy metal loads using magnetic susceptibility [J]. Environmental Pollution, 2008, 156 (2): 0-289.