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POLLUTION STATUS AND HEALTH RISK ASSESSMENT OF A SPECIFIC ORGANOPHOSPHATE PESTICIDE-CONTAMINATED SITE

Organophosphate pesticide pollution is a severe global environmental issue, posing significant threats to human health. This study focuses on an organophosphate pesticide production site in North China. Controlled soil and groundwater were sampled using grid sampling and direct-push technology. Analytical methods such as headspace gas chromatography-mass spectrometry (GC-MS), gas chromatography (GC), and purge and trap GC-MS were employed to detect contaminants, including volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), pesticides, and heavy metals. The results indicate that the maximum exceedances in the contaminated soil for benzene, xylene, trichloromethane, Parathion, phosphorodithioic acid, Phorate, and Terbufos were 490.63, 411.22, 3459.09, 507.89, 277.29, 1946.15, and 281.5 times the standard limits, respectively. In groundwater, benzene, dichloromethane, trichloromethane, and Phorate exceeded the standard limits by 220.83, 1374, 1853.33, and 806.67 times, respectively, severely contaminating the local soil and groundwater and damaging the ecosystem. Additionally, the carcinogenic risk values in the contaminated soil for benzene, toluene, phenylethane, xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, Parathion, 1,2,4-trichlorobenzene, trichloromethane, naphthalene, and aniline were $2.75\text{E}-3$, $1.36\text{E}-2$, $1.034\text{E}-2$, $9.72\text{E}-1$, $1.5\text{E}-3$, $8.9\text{E}-3$, $1.85\text{E}-3$, $4\text{E}-3$, $3.48\text{E}-2$, $2.7\text{E}-2$, $1.03\text{E}-3$, respectively. In groundwater, toluene, xylene, dichloromethane, and trichloromethane showed carcinogenic risk values of $8\text{E}-3$, $1.86\text{E}-2$, $1.23\text{E}-2$, $3.07\text{E}-2$, respectively, significantly exceeding the acceptable limits and posing severe threats to the health of nearby residents. Furthermore, the hazard quotient for non-carcinogenic effects of Cypermethrin in soil was 1.15, and 2,6-dichlorophenol in groundwater was 1.22, both slightly above the standard, indicating a mild impact on the health of nearby residents. Overall, this study provides a theoretical basis for subsequent remediation work at the contaminated site through pollutant analysis.

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1. INTRODUCTION

With the acceleration of industrialization and the development of modern agricultural technology, organophosphorus pesticides have been widely used because of their potent inhibitory activity on cholinesterase. However, they have attracted significant attention due to their harmful effects, such as brutal degradation, easy transformation, and strong oxidation [1]. However, due to the abuse of pesticides, improper production and storage, and transportation leakage, organophosphorus pesticides often enter the environment in large quantities, which has caused severe environmental pollution on a global scale. Studies have shown that organophosphorus pesticide synthesis factories have the most severe pollution [2, 3]. For example, the average amount of organophosphorus pesticide residue in the soil at different depths of an abandoned agro pharmaceutical factory in North China, which has stopped production for more than 10 years, reaches 53 ng/g, which seriously affects soil microbial diversity and soil fertility in this region [4]. At the same time, organophosphorus pesticides may enter water bodies through farmland runoff, polluting water quality and producing toxic effects on aquatic organisms, thereby destroying water ecosystems [5]. Even organophosphorus pesticides cause damage to human health through bioaccumulation and amplification, such as inducing diabetes, obesity, endocrine disorders, cancer, and other phenomena [6]. Therefore, understanding the specific pollution status of organophosphorus pesticide-contaminated sites and assessing their impact on the environment and human health has become an urgent problem.

With green development, organophosphorus pesticide pollution needs to be solved urgently. At present, the risk assessment methods of organophosphorus pesticide pollution include environmental monitoring, eco-toxicity testing, residue detection in agricultural products, pesticide analyses in water and soil, mathematical models and GIS technology, etc., to fully understand the potential impact of organophosphorus pesticides on the environment and ecosystem [7–10]. To comprehensively assess the environmental condition of the contaminated site, this study conducted detailed analyses of organophosphate pesticide residues in the soil and groundwater. Sample collection was carried out using grid sampling and direct-push techniques, followed by analytical determinations using headspace gas chromatography-mass spectrometry (GC-MS) and gas chromatography (GC) methods [11, 12]. The research focused on detecting volatile and semi-volatile organic compounds and pesticide residues, including potential pollutants such as heavy metals [13]. This thorough and meticulous analytical approach reveals the types and concentrations of the pollutants and provides a solid data foundation for assessing their impact on human health.

An organophosphorus pesticide factory is located in North China. Founded in 1956, it is China's first enterprise to develop and produce organophosphorus pesticides. It has a production history of more than 60 years, mainly engaged in the production of organophosphorus pesticide crude oil and the mixing and packaging of pesticide products.

Long-term pesticide production and use make local soil and groundwater pollution particularly serious, destroying the local ecological environment and potentially threatening human health [14]. Organophosphorus pesticides can adversely affect crop growth by affecting soil moisture content, soil moisture, and soil pH [15]. Nowadays, environmental pollution is becoming more serious, the study of contaminated sites is not only a scientific problem but also a social one. It is related to the sustainable and healthy development of the ecological environment and the sustainability of human society. Given the environmental pollution and human health hazards of organophosphorus pesticides, this study systematically detected and analyzed the pollutants in polluted areas and evaluated the potential effects of these pollutants on the surrounding environment and residents' health, in particular, the carcinogenic and non-carcinogenic risks of these pollutants, and how they affect human health through environmental pathways [16]. Through this research, we aim to provide scientific basis and constructive suggestions for subsequent remediation and management efforts at the contaminated site and to offer essential insights for formulating related environmental protection policies. Moreover, the findings of this study will serve as a valuable reference and guide for addressing similar environmental pollution issues globally.

2. MATERIALS AND METHODS

Sample collection and processing. Preparation before sampling, on-site positioning, and photography are necessary to ensure the quality of on-site sampling. The first step involves categorizing the contaminated area into three types due to the uneven spatial distribution of soil pollution: areas for verification testing and supplementary remediation, areas for supplementary systematic sampling and testing, and areas where odor and soil pollution do not overlap. In the second step, grids are divided based on the area of contamination. For areas needing remediation less than 100 m², two sampling points are set, for areas between 100 m² and less than 1000 m², three sampling points are set, for areas between 1000 m² and less than 1500 m², four sampling points are set, for areas between 1500 m² and less than 2500 m², five sampling points are set, for areas between 2500 m² and less than 5000 m², six sampling points are set, for areas between 5000 m² and less than 7500 m², seven sampling points are set, for areas between 7500 m² and less than 12 500 m², eight sampling points are set, and for areas larger than 12 500 m², grids do not exceed 40×40 m². The third step involves collecting samples using the professional drilling equipment Geoprobe7822DT (DT22 dual-tube) drilling system. The name of the soil and water samples, sampling location, color and odor of the samples, sampling depth and sampling time of the organophosphorus pesticide contaminated site were recorded by numbering.

Direct-push technology uses a direct-push drill rig that inserts a drill rod, equipped with samplers and sensors, into the stratum by pushing, impacting, or vibrating. This method is

used to rapidly collect representative groundwater samples or acquire related data using equipped detection instruments. The direct-push drilling machine pushes the drill rod into the specified stratum or groundwater layer. Then, the drill bit and inner rod are removed, and an inner tube with a stainless-steel screen at the top is substituted. The outer rod is pulled up, allowing the screen to protrude from the outer rod under gravity and be exposed in the stratum. Groundwater enters the inner tube through the screen, forming a sampler with the connected drill rod to collect representative water samples. Groundwater sampling equipment (such as low-flow sampling systems) is then used to collect groundwater samples at specific depths. This process is repeated to collect groundwater samples from different depth profiles.

Assessment indicators, detection and analysis methods of the status quo of contaminated plots. To comprehensively cover volatile organic compounds, semi-volatile organic compounds, pesticides, and heavy metals in the contaminated site and ensure the accuracy of the assessment, this study referred to several technical guidelines and standards, including the *Technical Guidelines for Environmental Site Assessment* (HJ 25.1-2014), *Technical Guidelines for Environmental Site Monitoring* (HJ 25.2-2014), *Technical Specification for Soil Environmental Monitoring* (HJ/T166-2004), and *Technical Specification for Groundwater Environmental Monitoring* (HJ/T 164-2004). These were combined with the actual conditions of the pesticide factory, resulting in the determination of 36 assessment indicators (Table 1).

Table 1

Soil and groundwater assessment indicators

No.	Compound	No.	Compound
1	benzene	19	Phorate
2	toluene	20	Terbufos
3	phenylethane	21	cypermethrin
4	xylene	22	indene[1,2,3-cd]pyrene
5	1,3,5-trimethylbenzene	23	dibenz[a,h]anthracene
6	1,2,4-trimethylbenzene	24	hexachlorobenzene
7	chlorobenzene	25	aniline
8	1,2,4-trichlorobenzene	26	nickel
9	trichloromethane	27	arsenic
10	naphthalene	28	dichloromethane
11	2-methylnaphthalene	29	1,2-dichloroethane
12	benzoanthracene	30	2-chlorotoluene
13	benz[e]acephenanthrylene	31	4-chlorotoluene
14	benzo[a]pyrene	32	2,6-dichlorophenol
15	benzo[g,h,i]perylene	33	pH
16	1,4-dichlorobenzene	34	anionic surfactant
17	Parathion	35	oxygen consumption
18	phosphorodithioic acid	36	total phosphorus

For the analysis of pollutants in soil, various methods were employed: 1. For 7 substances, including benzene, chlorobenzene, 1,2,4-trichlorobenzene, trichloromethane, naphthalene, dichloromethane, 4-chlorotoluene, purge and trap/gas chromatography-mass spectrometry (GC-MS) was used. 2. For 5 substances, including toluene, phenylethane, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2-dichloroethane, headspace/GC-MS was applied. 3. For 2 substances, including xylene, and 1,4-dichlorobenzene, headspace/gas chromatography (GC) was used. 4. For 16 substances, including 2-methylnaphthalene, benz[e]acephenanthrylene, benzo[a]pyrene, Parathion, phosphorodithioic acid, Phorate, Terbufos, Cypermethrin, dibenz[a,h]anthracene, hexachlorobenzene, aniline, 2,6-dichlorophenol, benzoanthracene, benzo[g,h,i]perylene, indene[1,2,3-cd]pyrene, 2-chlorotoluene, GC-MS was utilized. 5. For 2 substances, including nickel, and arsenic, the self-monitoring technical guideline of the pollutant discharge unit for the non-ferrous metals industry-recycled metals was followed. 6. For 4 parameters, including pH, anionic surfactant, oxygen consumption, total phosphorus, potentiometry was used.

For the analysis of pollutants in groundwater: 1. For 4 substances, including benzene, toluene, phenylethane, and xylene, headspace/gas chromatography (GC) was used, 2. For 6 substances, including 1,2, 4-trimethylbenzene, 1,3,5-trimethylbenzene, naphthalene, 1,2-dichloroethane, 4-chlorotoluene, 2-chlorotoluene, purge and trap-gas chromatography-mass spectrometry (GC-MS) was used. 3. For 6 substances, including chlorobenzene, 1,2,4-trichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, dichloromethane, and 2,6-dichlorophenol, gas chromatography (GC) was applied. 4. For 7 substances, including trichloromethane, 2-methylnaphthalene, Parathion, phosphoro-dithioic acid, Phorate, Terbufos, and Cypermethrin internal laboratory methods were employed. 5. For 6 substances, including benz[e]acephenanthrylene, benzo[a]pyrene, dibenz[a,h]anthracene, benzoanthracene, indene[1,2,3-cd]pyrene, and benzo[g,h,i]perylene, liquid-liquid extraction and solid-phase extraction high-performance liquid chromatography (HPLC) were employed. 6. Aniline was determined using gas chromatography-mass spectrometry (GC-MS). 7. For 2 substances, including nickel and arsenic, the drinking water standard inspection method for metal indices was used. 8. For 4 parameters, including pH, anionic surfactant, oxygen consumption, the total phosphorus, the electrode methods were used.

Methods for health risk assessment of contaminated plots. Based on the current status assessment indicators and analytical methods, pollutants exceeding the standard limits in soil and groundwater were identified as assessment indicators. These exceedance pollutants were further classified into carcinogenic and non-carcinogenic substances. The carcinogenic risk values for the carcinogenic substances and the hazard quotients for the non-carcinogenic substances were calculated using specific formulas and parameters. The obtained data were then compared with national standards to assess the carcinogenic risk and potential harm the contaminated site poses to the surrounding residents.

Due to residential areas near the contaminated site, the risk assessment was conducted using a sensitive land-use approach [17]. Under this approach, for the carcinogenic effects of pollutants, the lifetime exposure of the population is considered, assessing the lifetime carcinogenic risk of pollutants based on exposure during childhood and adulthood. For non-carcinogenic effects, considering that children have lower body weights and higher exposure levels, the assessment of non-carcinogenic effects of pollutants is based on exposure during childhood. The receptor exposure parameters [17] are as shown in Table 2.

Table 2

Receptor exposure parameters

Argument	Children	Adults
Weight (BW), kg	15.9	56.8
Exposure period (ED), a	6	24
Outdoor exposure frequency (EF), d/a	87.5	
Daily air intake ($DARI$), m ³ /d	7.5	14.5
Intake of absorption factors through the air (A), d	0.06	
Mean time to carcinogenic effect (AT_1), d	26 280	
Mean time to non-carcinogenic effect (AT_2)	2190	
Acceptable hazard quotient (HQ)	1	
Exceeding the acceptable carcinogenic risk range of pollutants (CR)	from 1.0E-06 to .01E-04	

A risk value for carcinogenic effects is a probability measure used to quantify the risk of cancer caused by exposure to a specific chemical in the environment, such as 10^{-6} indicating that one person in every million may have an increased risk of cancer due to exposure to a chemical. Non-carcinogenic effect hazard quotient is used to quantify the probability of human exposure to a specific chemical environment, although there is no direct carcinogenic risk it will still lead to human nervous system damage, skin diseases and other health conditions. For example, a value less than or equal to 1 indicates that the current exposure of human exposure to the chemical environment will not have a significant negative impact on human health.

- Calculating the carcinogenic risk of excessive pollutants in soil. The daily exposure can be determined as follows:

$$CDI_1 = \frac{IR EF D_1}{BW_1 AT_1} \quad (1)$$

$$CDI_2 = \frac{IR EF ED_2}{BW_2 AT_1} \quad (2)$$

$$IR = AC_1 \quad (3)$$

$$CDI = CDI_1 + CDI_2 \quad (4)$$

Carcinogenic risk is

$$CR_1 = CDI SF \quad (5)$$

where C_1 , mg/kg, is the excessive pollutant concentration in soil at maximum, IR , mg/kg, the concentration of ingested contaminants, EF , d/a, outdoor exposure frequency, ED_1 , a, childhood exposure period, ED_2 , a, – adult exposure period, BW_1 , kg, – child weight, BW_2 , kg, – adult weight, AT_1 , d, – mean time of carcinogenic effect, CDI_1 , mg/(kg·d), – excessive exposure to pollutants and carcinogens in soil during childhood, CDI_2 , mg/(kg·d), – adult exposure to excessive pollutants and carcinogens in soil, CDI , mg/(kg·d), – total exposure, SF , mg/(kg·d)⁻¹ – respiratory inhalation carcinogenic slope factor, A – intake of absorption factors through the air, CR_1 – carcinogenic risk value of contaminant carcinogen in soil.

- Calculating the hazard quotient of non-carcinogenic substances of excessive pollutants in soil. The daily exposure is

$$CDI_3 = \frac{IR EF ED_1}{BW_1 AT_2} \quad (6)$$

Hazard quotient is

$$HQ_1 = \frac{CDI_3}{RfD} \quad (7)$$

where CDI_3 , mg/(kg·d), excessive exposure to non-carcinogenic pollutants in soil during childhood, AT_2 , d, – mean time of non-carcinogenic effect, HQ_1 – non-carcinogenic excessive pollutants in the soil, RfD , mg/(kg·d) – respiratory inhalation reference dose.

- Calculating the carcinogenic risk of carcinogenic substances of excessive pollutants in groundwater. Daily exposure is

$$IOVER_1 = \frac{A \times C_w DAIR_1 EF ED_1}{BW_1 AT_1} \quad (8)$$

$$IOVER_2 = \frac{A \times C_w DAIR_2 EF ED_2}{BW_2 AT_1} \quad (9)$$

$$IOVER_3 = IOVER_1 + IOVER_2 \quad (10)$$

The carcinogenic risk value is

$$CR_2 = IOVER_3 SF \quad (11)$$

where $IOVER_1$, mg/(kg·d) – excessive exposure to pollutants and carcinogens in groundwater during childhood, A – intake of absorption factors through the air, C_w , mg/dm³, – excessive pollutant concentration in groundwater, $DAIR_1$, m³/d – the daily air intake of children, EF , d/a – outdoor exposure frequency, ED_1 , a – childhood exposure period, BW_1 , kg, child weight, AT_1 , d – mean time to carcinogenic effect, $IOVER_2$, mg/(kg·d) – adult exposure to excessive pollutants and carcinogens in groundwater, $DAIR_2$, m³/d – daily air intake for adults, ED_2 , a – adult exposure period, BW_2 , kg – adult weight, $IOVER_3$, mg/(kg·d) – total exposure, CR_2 – carcinogenic risk value of carcinogenic substances in groundwater, SF , mg/(kg·d)⁻¹ – respiratory inhalation carcinogenic slope factor.

• Calculating the harm quotient of non-carcinogenic substances in groundwater. Daily exposure is

$$IOVER_4 = \frac{AC_w DAIR_1 EF ED_1}{BW_1 AT_2} \quad (12)$$

Hazard quotient is

$$HQ_2 = \frac{IOVER_4}{RfD} \quad (13)$$

where $IOVER_4$, mg/(kg·d) – exposure to excessive pollutants and non-carcinogens in groundwater during childhood, HQ_2 – non-carcinogenic excessive pollutants in groundwater.

Statistical analysis. The Shapiro–Wilk and Levene’s tests were utilized to assess the normality and homogeneity of the data. Natural logarithmic transformation was applied to data that did not follow a normal distribution. Statistical analyses were performed using SPSS software (version 26.0). All values are presented as mean±standard deviation. All statistical tests with p -values less than 0.05 were considered significant. The figures were plotted using Origin 2021 and Adobe Illustrator CC 2019.

3. RESULTS AND ANALYSIS

3.1. RESULTS OF EXCESSIVE POLLUTION IN SOIL AND GROUNDWATER

According to the *Screening value of site soil environmental risk assessment* (DB11/T811-2011), related technical guidelines and specifications such as the Class IV standard in *Groundwater quality standard* (GB/T14848-2017) have established the limit

value of the pollutants exceeding the standard in soil and groundwater and calculated the maximum multiple of exceeding the standard. The relevant values for soil and groundwater pollutants are shown in Figs. 1 and 2, respectively.

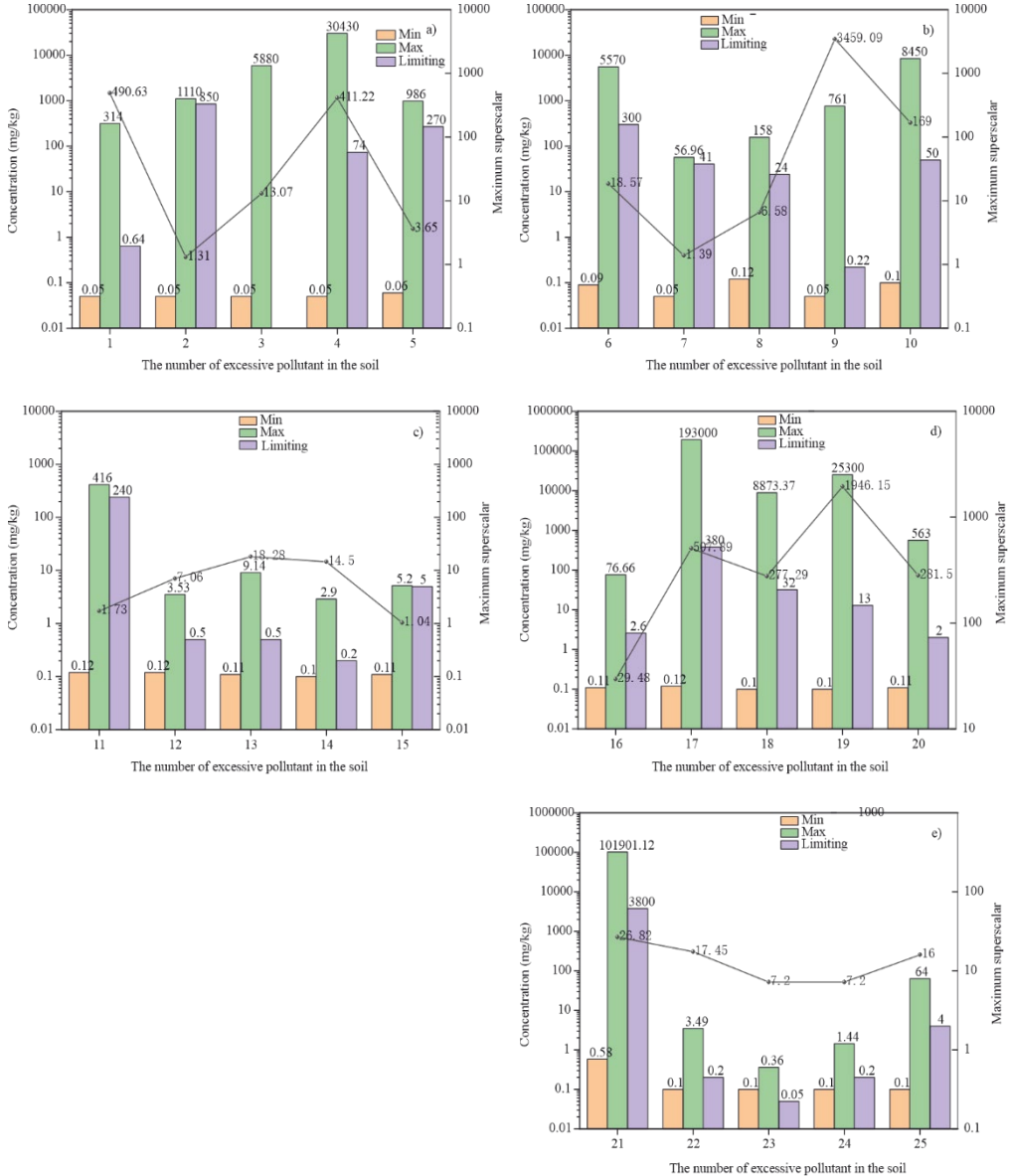


Fig. 1. Correlation values of excessive pollutants in soil: a) 1–5, b) 5–10, c) 11–15, d) 16–20, the numbers on x-axes correspond to assessment indicators presented in Table 1

The levels of soil- and groundwater-related organophosphorus pesticides were measured in this study. The results showed that benzene and xylene in the soil were seriously exceeded by 490.63 and 411.22 times the standard, respectively (Fig. 1a). Trichloromethane, naphthalene, parathion, phosphorodithioic acid, Phorate and Terbufos exceeded the standard by 3459.09, 169, 507.89, 277.29, 1946.15, and 281.5 times, respectively, all exceeding the national standard line (Figs. 1b–d). Other organophosphorus pesticides in the soil exceeded the limit but were not serious. The reason may be that benzene is an essential raw material and organic solvent used in enterprises’ production. Xylene and naphthalene are also organic solvents used in enterprises’ production.

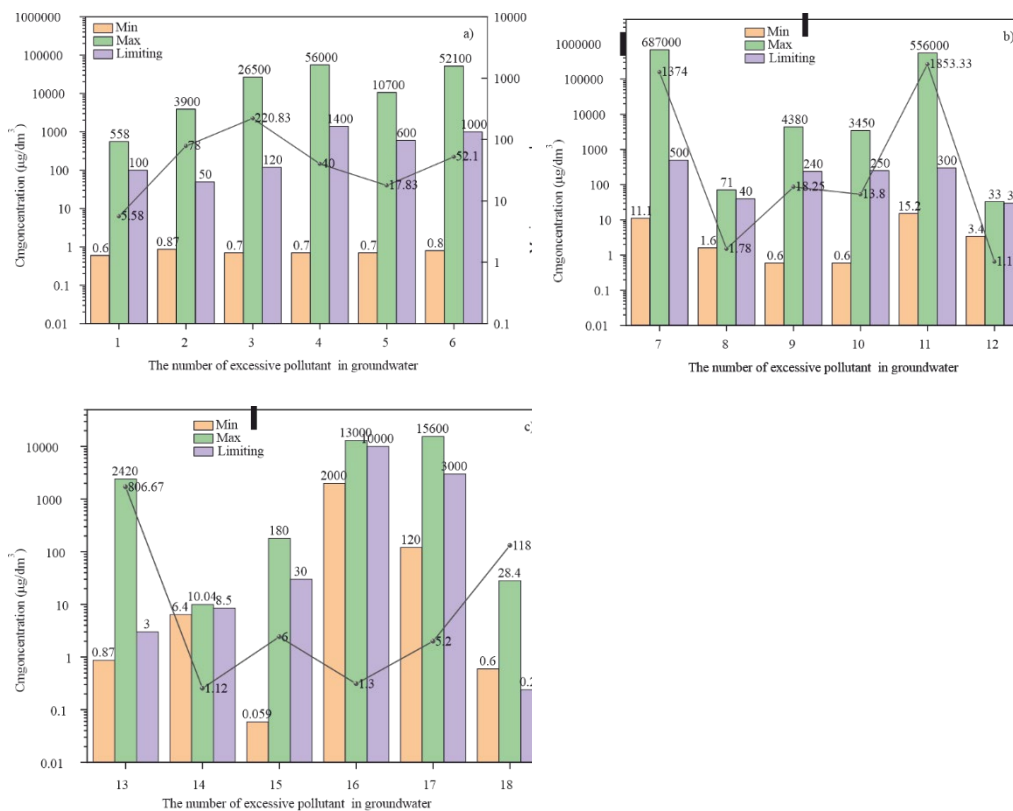


Fig. 2. Correlation values of excessive pollutants in groundwater:

- a) 1 – nickel, 2 – arsenic, 3 – benzene, 4 – toluene, 5 – phenylethane, 6 – xylene,
- b) 7 – dichloromethane, 8 – 1,2-dichloroethane, 9 – 2-chlorotoluene, 10 – 4-chlorotoluene,
- 11 – trichloromethane, 12 – 2,6-dichlorophenol, c) 13 – Phorate, 14 – pH, 15 – anionic surfactant,
- 16 – oxygen consumption, 17 – total phosphorus, 18 – Terbufos

Trichloromethane is not an organic raw material and solvent in the enterprise, but it is produced by the side reaction of trichloroacetaldehyde and liquid base in the production of

Dichlorvos. The main organophosphorus pesticide products produced by enterprises were Parathion, phosphorodithioic acid, Phorate, and Terbufos. They have been used for a long time and have a wide range of uses, so they seriously exceed the standard (Figs. 1d–e).

To comprehensively assess the over-limit of organophosphorus pesticides, a quantitative analysis of groundwater was also performed in this study. The results showed that the benzene compounds were seriously exceeded by 220.83 times (Fig. 2a). In Figure 2b, dichloromethane and trichloromethane exhibit severe exceedances, with maximum excess ratios of 1374 and 1853.33 times, respectively. In Figure 2c, Phorate shows a substantial exceedance, with a maximum excess ratio of 806.67 times. The high exceedances of these substances can be attributed to their prolonged and widespread usage. Benzene is an essential raw material and organic solvent in industrial production. Trichloromethane, although not an intentional raw material or solvent, is formed as a byproduct during the production of DDT through a secondary reaction between trichloroacetaldehyde and liquid alkali. Dichloromethane's severe exceedance may be due to its role as an intermediate product formed during the degradation of trichloromethane in groundwater, with dichloromethane exhibiting a cumulative effect in aquatic environments. Phorate, on the other hand, is a widely used organophosphorus pesticide, leading to its substantial exceedance. This information provides insights into the reasons behind the severe exceedances of these substances in the respective figures.

3.2. CARCINOGENIC RISK VALUE AND NON-CARCINOGENIC HAZARD QUOTIENT OF EXCESSIVE POLLUTANTS IN SOIL AND GROUNDWATER

To further explore the impact of excessive pollutants in soil and groundwater on human health, we refer to the toxicity parameters of excessive pollutants in soil and groundwater [17], as shown in Table 3. Despite 2,6-dichlorophenol, they are all carcinogens.

Table 3

Toxicity parameters of excessive pollutants in soil and groundwater

No.	Pollutant	<i>SF</i> [mg/(kg·d)]	<i>RfD</i> [mg/(kg·d)]
1	benzene	5.50E-02	–
2	toluene	8.0E-02	–
3	phenylethane	1.1E-02	–
4	xylene	2.0E-01	–
5	1,3,5-trimethylbenzene	1.0E-02	–
6	1,2,4-trimethylbenzene	1.0E-02	–
7	chlorobenzene	2.0E-02	–
8	1,2,4-trichlorobenzene	2.9E-02	–
9	trichloromethane	3.1E-02	–
10	naphthalene	2.0E-02	–

Table 3

Toxicity parameters of excessive pollutants in soil and groundwater

11	2-methylnaphthalene	4.0E-03	–
12	benzoanthracene	1.0E-01	–
13	benz[e]acephenanthrylene	1.0E-01	–
14	benzo[a]pyrene	1.0E+00	–
15	benzo[g,h,i]perylene	3.0E-02	–
16	1,4-dichlorobenzene	5.4E-03	–
17	Parathion	6.0E-03	–
18	phosphorodithioic acid	5.0E-04	–
19	Phorate	2.0E-04	–
20	Terbufos	2.5E-05	–
21	cypermethrin (non-carcinogenic substance)	–	8.00E01
22	indene[1,2,3-cd]pyrene	1.0E-01	–
23	dibenz[a,h]anthracene	1.0	–
24	hexachlorobenzene	1.6	–
25	aniline	1.0E-01	–
26	dichloromethane	1.0E-02	–
27	1,2-dichloroethane	3.0E-04	–
28	2-chlorotoluene	7.0E-02	–
29	4-chlorotoluene	1.0E-02	–
30	2,6-dichlorophenol		1.8E-04

The carcinogenic risk values of carcinogenic substances of excessive pollutants in soil are shown in Fig. 3a. The carcinogenic risk values of toluene, phenylethane, trichloromethane, and naphthalene were much higher than the maximum limit, which were $1.36E-2$, $1.034E-2$, $3.48E-2$ and $2.7E-2$, respectively. The reason may be that the respiratory inhalation carcinogenic slope factor and maximum value of these four substances are much higher than the limit. Toluene, phenylethane, trichloromethane, and naphthalene carcinogenic slope factors were $8.00E-02$, $1.10E-02$, $3.10E-02$, and $2.00E-02$ $\text{mg}/(\text{kg}\cdot\text{d})^{-1}$. The maximum values were 1110, 5880, 761, and 8450 mg/kg , respectively. The calculated hazard quotient of Cypermethrin was 1.15, slightly higher than the acceptable hazard quotient.

Nickel, arsenic, pH, anionic surfactant, oxygen consumption, total phosphorus, and 6 kinds of excessive pollutants are not volatile, so they are not evaluated. The carcinogenic risk values of carcinogenic substances of excessive pollutants in groundwater are shown in Fig. 3b. The carcinogenic risk values of xylene, dichloromethane, and trichloromethane were much higher than the maximum limit of $1.86E-2$, $1.23E-2$, and $3.07E-2$, respectively. The respiratory inhalation carcinogenic slope factors of xylene and trichloromethane were $2.00E-01$ and $3.10E-02$ $(\text{mg}/(\text{kg}\cdot\text{d}))^{-1}$, respectively. The maximum values were 52 100 and 556 000 $\mu\text{g}/\text{dm}^3$, respectively. The possible reason for dichloromethane's high carcinogenic risk value is that dichloromethane is an intermediate product of trichloromethane degradation in groundwater, and dichloromethane

has an accumulation effect in a water environment. The carcinogenic slope factor of respiratory inhalation of dichloromethane is $1.00E-02$ (mg/(kg·d))⁻¹. The maximum value is 687 000 µg/dm³. The calculated hazard quotient of 2,6-dichlorophenol is 1.22, slightly higher than the acceptable hazard quotient.

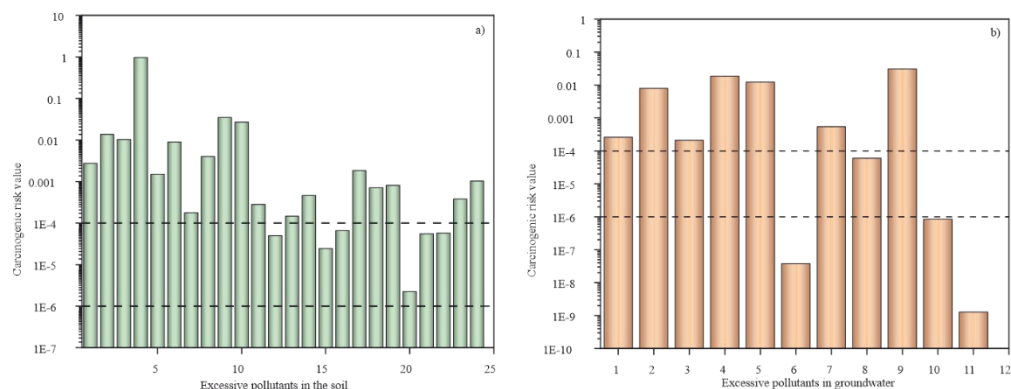


Fig. 3. Carcinogenic risk values for excessive pollutants in soil (a) and groundwater (b):
 a) 1 – benzene: $2.75E-3$, 2 – toluene: $1.36E-2$, 3 – phenylethane: $1.034E-2$, 4 – xylene: $9.72E-1$,
 5 – 1,3,5-trimethylbenzene: $1.5E-3$, 6 – 1,2,4-trimethylbenzene: $8.9E-3$, 7 – chlorobenzene: $1.78E-4$,
 8 – 1,2,4-trichlorobenzene: $4E-3$, 9 – trichloromethane: $3.48E-2$, 10 – naphthalene: $2.7E-2$,
 11 – 2-methylnaphthalene: $2.8E-4$, 12 – benzoanthracene: $0.5E-4$, 13 – benz[e]acephenanthrylene:
 $1.47E-4$, 14 – benzo[a]pyrene: $4.62E-4$, 15 – benzo[g,h,i]perylene: $2.46E-5$, 16 – 1,4-dichlorobenzene:
 $6.59E-5$, 17 – Parathion: $1.85E-3$, 18 – phosphorodithioic acid: $7.1E-4$, 19 – Phorate: $8.08E-4$,
 20 – Terbufos: $2.25E-6$, 21 – indene[1,2,3-cd]pyrene: $5.51E-5$, 22 – dibenz[a,h]anthracene: $5.73E-5$,
 23 – hexachlorobenzene: $3.776E-4$, 24 – aniline: $1.03E-3$, b) 1 – benzene: $2.6E-4$, 2 – toluene: $8E-3$,
 3 – phenylethane: $2.11E-4$, 4 – xylene: $1.86E-2$, 5 – dichloromethane: $1.23E-2$, 6 – 1,2-dichloroethane:
 $3.81E-8$, 7 – 2-chlorotoluene: $5.46E-4$, 8 – 4-chlorotoluene: $6E-5$, 9 – trichloromethane: $3.07E-2$,
 10 – Phorate: $8.4E-7$, 11 – Terbufos: $1.28E-9$

4. DISCUSSION

4.1. EXCESSIVE POLLUTANTS AND CO-EXCESSIVE POLLUTANTS IN SOIL OR GROUNDWATER

Organophosphorus pesticides were detected in soil and groundwater, and it was found that the content of different residual substances seriously exceeded the standard. The results of this study showed that benzene, trichloromethane, and Phorate were the most severely exceeded organophosphorus pesticides in both soil and groundwater, and their exceeding multiples in soil and groundwater were 490.63, 3459.09, 1946.15, 220.83, 1853.33 and 806.67, respectively. The content of residual organophosphorus pesticides in soil is higher than that in groundwater, mainly due to the adsorption on the surface of

soil particles, microbial degradation in soil, and soil structure, which lead to the retention time of organophosphorus pesticides in soil for a long time [18]. The content of trichloromethane was the highest in both soil and groundwater, which may be caused by the discharge or leakage of trichloromethane as a by-product during the production of organophosphorus pesticides [19]. The residual amount of Phorate sulphur substance in soil and groundwater was 1946.15 times and 806.67 times, respectively. Phorate belongs to the thiosulfate subclass organophosphorus pesticide, which is a systemic insecticide against chewing and sucking pests on a variety of plants [20]. Phorate can be oxidized to Phorate oxon, Phorate sulfoxide, Phorate sulfone, etc. through abiotic or biological pathways, producing highly toxic complex organic compounds in the natural environment [21]. However, in this study, the Parathion residue was only seriously exceeded in soil, and the excess was 507.89 times. This phenomenon may be because Parathion is not readily soluble in water, so it can only be enriched in soil [22]. Even the residue of Parathion in soil may lead to soil ecosystem pollution and the destruction of ecological balance [23].

Some organic solvents remained in the soil and groundwater, and their residual amounts were also seriously exceeded, such as benzene, xylene, dichloromethane, etc. Previous studies [19] have shown that benzene is an essential raw material and organic solvent used in enterprise production. Toluene and phenylethane are critical raw materials used in enterprises' production. Xylene is also an organic solvent used in enterprises, Phorate and Terbufos are the main organophosphorus pesticide products produced by enterprises, and they have been widely used for a long time. Trichloromethane was not the enterprise's organic solvent and raw materials but in the production of dichlorvos by chloral and liquid alkali side reaction and generation. The cause of exceeding the standard may be pollution caused by sprinkling in the production process or leakage through sewage pipes into the soil and the expansion of the pollution range due to groundwater migration into the soil.

Parathion had a maximum exceedance factor of 507.89 in the soil, while it did not exceed the limits in groundwater. Phosphorodithioic acid had a maximum exceedance factor of 277.29 in the soil, but it also did not exceed the limits in groundwater. This phenomenon can be attributed to Parathion's solubility in water [23], while Phosphorodithioic acid has limited solubility in water [24]. As a result, Parathion and phosphorodithioic acid tend to accumulate in the soil, with much lower accumulation levels in the water, well below the exceedance values [22]. Furthermore, dichloromethane had a maximum exceedance factor of 1374 in groundwater but did not exceed the limits in soil. Nickel had a maximum exceedance factor of 5.58 in groundwater but did not exceed the limits in soil. Arsenic had a maximum exceedance factor of 78 in groundwater but did not exceed the limits in soil. Dichloromethane is an intermediate product of trichloromethane degradation in groundwater and tends to accumulate in the water environment, posing a significant threat to aquatic ecosystems [25, 26]. Additionally, the pollutants in the site's raw materials, organic solvents, production products, and byproducts do not contain heavy

metals. However, both nickel and arsenic were found to exceed the limits in groundwater. The exceedance of arsenic in groundwater could be influenced by pH, causing arsenic in the soil to undergo desorption, reflecting its easy desorption characteristics under alkaline conditions [27]. The increase in arsenic in groundwater could also be attributed to natural environmental changes, leading to the release of arsenic from arsenic-containing minerals via competitive adsorption and adsorption-desorption processes entering the groundwater. Furthermore, spraying arsenic-containing pesticides and using high-arsenic groundwater for agricultural irrigation can also lead to arsenic infiltration into groundwater [28, 29]. The exceedance of nickel in groundwater may result from natural factors, where rocks and soils with high nickel content receive nutrients and, through sedimentation, enter the groundwater. Additionally, the nickel content in groundwater increases under the influence of natural rainfall and groundwater flow [30]. The exceedance of nickel in groundwater may also be due to the discharge of nickel-containing wastewater and exhaust gases from nearby factories, entering groundwater through rainfall and washout effects [31].

This study also revealed significant exceedances in various compounds. In soil, benzene exhibited the highest exceedance factor of 490.63, while groundwater reached a maximum exceedance factor of 220.83. Toluene had a maximum exceedance factor of 1.31 in soil and 40 in groundwater. Similarly, phenylethane had a maximum exceedance factor of 13.07 in soil and 17.83 in groundwater. Xylene showed a substantial exceedance, with a maximum factor of 411.22 in soil and 52.1 in groundwater. Furthermore, Phorate exhibited a maximum exceedance factor of 1946.15 in soil and 806.67 in groundwater, while Terbufos had a maximum exceedance factor of 281.5 in soil and 118.33 in groundwater. Trichloromethane exceeded significantly, with a maximum factor of 3459.09 in soil and 1853.33 in groundwater. Previous research [25] has indicated that benzene is a crucial raw material and organic solvent used in industrial production. Toluene and phenylethane are essential raw materials in industrial processes, while xylene is an organic solvent. Phorate and Terbufos are major organic phosphorus pesticide products used in industrial production, characterized by extensive use and long duration. Trichloromethane, while not a primary industrial material or solvent, is produced as a byproduct during the production of DDT through a secondary reaction between trichloroacetaldehyde and liquid alkali. The causes of these exceedances may be attributed to contamination resulting from spillage during the production process or leakage through sewage pipelines, leading to soil pollution. Subsequently, these pollutants migrate with groundwater, causing an expansion of the contaminated area.

4.2. HEALTH RISK ASSESSMENT

In soil, the maximum exceedance factor for Terbufos was 281.5 times, while hexachlorobenzene reached a maximum exceedance factor of 7.2 times. Notably, the maxi-

imum exceedance factor for Terbufos was significantly higher than that for hexachlorobenzene. When assessing the carcinogenic risk, it is essential to consider the inhalation carcinogenic slope factor. Terbufos has an inhalation carcinogenic slope factor of $2.50\text{E-}05$, notably lower than the inhalation carcinogenic slope factor of hexachlorobenzene, which is 1.60. The calculated carcinogenic risk value for Terbufos is $2.25\text{E-}06$, placing it within an acceptable range of carcinogenic risk. In contrast, hexachlorobenzene has a calculated carcinogenic risk value of $3.776\text{E-}04$, slightly exceeding the upper limit of the acceptable carcinogenic risk range. This indicates that the differences in carcinogenic risk values primarily stem from variations in inhalation carcinogenic slope factors. In summary, the inhalation carcinogenic slope factor strongly influences the evaluation of carcinogenic risk. Terbufos has a lower factor and a correspondingly lower calculated carcinogenic risk value, which falls within an acceptable range. In contrast, hexachlorobenzene exhibits a higher inhalation carcinogenic slope factor, resulting in a slightly higher calculated carcinogenic risk value, albeit within the acceptable range.

In soil, the maximum exceedance factor for benzene was 490.63 times, while for toluene, it reached a maximum exceedance factor of 1.31 times. Benzene exhibited a significantly higher maximum exceedance factor than toluene. When assessing carcinogenic risk, it is crucial to consider the inhalation carcinogenic slope factor. Benzene has an inhalation *SF* of $5.5\text{E-}02$, while toluene's inhalation *SF* is $8.00\text{E-}02$, placing them within the same order of magnitude. However, it is noteworthy that the maximum concentration of benzene in the soil was 314 mg/kg, which is lower than toluene's maximum concentration, 1110 mg/kg. This difference in maximum concentrations contributes to the variation in carcinogenic risk values. Specifically, the calculated carcinogenic risk value for benzene is $2.75\text{E-}03$, while for toluene, it is $1.36\text{E-}02$, representing a difference of one order of magnitude. Therefore, it becomes evident that the discrepancy in carcinogenic risk values primarily stems from variations in the maximum concentrations of the pollutants. In summary, the assessment of carcinogenic risk is notably influenced by the maximum concentrations of the pollutants, with benzene having a lower maximum concentration and a correspondingly lower calculated carcinogenic risk value compared to toluene, which exhibits a higher maximum concentration and a higher calculated carcinogenic risk value.

In summary, the carcinogenic risk value is mainly related to the respiratory inhalation carcinogenic slope factor and the maximum value of pollutants. However, it has little relationship with the maximum multiple of exceedance.

5. CONCLUSIONS

The pollution at the site has resulted in significant exceedances of several substances in both soil and groundwater. In soil, the maximum exceedance factors for benzene, xylene, trichloromethane, Parathion, phosphorodithioic acid, Phorate, and Terbufos are 490.63,

411.22, 3459.09, 507.89, 277.29, 1946.15, and 281.5 times, respectively. In groundwater, the maximum exceedance factors for benzene, dichloromethane, trichloromethane, and Phorate are 220.83, 1374, 1853.33, and 806.67 times, respectively. These severe exceedances significantly threaten the soil and groundwater at the site, resulting in the degradation of the local ecological environment. Furthermore, some substances in the contaminated soil and groundwater have carcinogenic risk values that exceed acceptable levels. In soil, the carcinogenic risk values for benzene, toluene, phenylethane, xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, Parathion, 1,2,4-trichlorobenzene, trichloromethane, naphthalene, and aniline are $2.75\text{E-}3$, $1.36\text{E-}2$, $1.034\text{E-}2$, $9.72\text{E-}1$, $1.5\text{E-}3$, $8.9\text{E-}3$, $1.85\text{E-}3$, $4\text{E-}3$, $3.48\text{E-}2$, $2.7\text{E-}2$, and $1.03\text{E-}3$, respectively. In groundwater, the carcinogenic risk values for toluene, xylene, dichloromethane, and trichloromethane are $8\text{E-}3$, $1.86\text{E-}2$, $1.23\text{E-}2$, and $3.07\text{E-}2$, respectively, significantly exceeding the upper limits of acceptable carcinogenic risk levels. This poses a severe threat to the health and well-being of the surrounding residents. Additionally, the non-carcinogenic hazard quotient for Cypermethrin in soil and 2,6-dichlorophenol in groundwater is 1.15 and 1.22, respectively, slightly above the standard values. While these values indicate a relatively lighter impact on the health of the surrounding residents, they still warrant attention and remediation efforts. In conclusion, the pollution at the site not only poses significant risks to soil and groundwater but also results in carcinogenic and non-carcinogenic hazards that can impact the health of the environment and the nearby residents.

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