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Distribution, Sources, and Health Risk of Polycyclic Aromatic Hydrocarbons in Farmland Soil of Helan, China

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Abstract: With the development of industry and agriculture, polycyclic aromatic hydrocarbons (PAHs) in the agricultural sector have gradually increased to different degrees, leading to an escalation in environmental pollution. In turn, this escalation has presented a significant possibility of endangering agricultural practices on farmland and has had a serious impact on regional sustainable development. Therefore, a total of 117 samples of soil were gathered to research the pollution level, distribution, sources, and health risk of PAHs in Helan farmland soils. A reference was used for the identification and quantification of PAH content using high-performance liquid chromatography (HPLC) with an ultraviolet detector, and their spatial distribution was analyzed utilizing the Arc Geographic Information System (ArcGIS). The source of PAHs was analyzed by absolute principal component scores/multiple linear regression (APCS-MLR). The lifetime cancer risk increment model and Monte Carlo sensitivity analysis were used to assess the potential health hazards to humans associated with PAHs in soil. Within the current study area, PAHs were higher in the northwest. The results showed that the total content of PAHs in Helan farmland soil ranged from 17.82 to 1544.73 $ng \cdot g^{-1}$ with a mean of 408.18 $ng \cdot g^{-1}$, which indicated the middle degree of pollution in farmland soil. The verification results of the APCS-MLR model showed that the correlation coefficient between the measured values and the predicted values ranged from 0.661 to 0.984, which suggested that the APCS-MLR model demonstrated favorable suitability for conducting source analysis of PAHs in the soil within the study region. Based on the contribution of PAHs from each source, the main sources of PAHs in Helan farmland soil were the combustion source (biomass, diesel, and natural gas combustion) and the transportation source (gasoline for vehicles and traffic exhaust emissions). The health risks' estimation showed that PAHs in farmland soil did not have potential health risks for adults but represented a carcinogenic risk for children via the main exposure pathway of ingestion with the mean intake of 1.28×10^{-5}. Meanwhile, the carcinogenic risks (CRs) of dermal contact for the mean value of adults (9.32×10^{-7}) was found to be higher than that for children (3.18×10^{-8}). From the Monte Carlo simulation, the soil particle uptake rate was the most sensitive to the health risks of children and adults with risk probabilities of 26% and 52%, and the risk probabilities from body weight were −11% and −1%, whose negative value indicated that the increase in body weight could reduce the health risks to human. These findings could provide reference for the study of soil organic pollution in Helan farmland soil and contribute significantly to the preservation of the ecological environment, maintaining human health and safety, and promoting the sustainable development of regional farmland.

Keywords: Monte Carlo; PAHs; pollution assessment; soil; source apportionment

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) belong to a group of organic pollutants exhibiting long-lasting characteristics widely present in the environment. PAHs have strong carcinogenicity, teratogenicity, and mutagenicity, so they have the potential to cause significant damage to human and environmental health, ecosystem stability, and sustainable development [1,2]. Seven PAHs have been designated as high-priority organic pollutants and categorized as substances with carcinogenic properties by the United States Environmental Protection Agency (USEPA) [3]. PAHs are easily adsorbed on particulate matter due to their low water solubility, high fat solubility, and difficult degradation [4]. They are also likely to bioaccumulate and be biomagnified through the food chain, which would endanger soil, vegetation, crops, and even the ecosystem, and ultimately lead to human exposure to PAH pollutants directly or indirectly [5,6]. PAHs penetrate the human organism via various exposure pathways such as respiration, skin contact, and dietary intake, thereby increasing the risk of human cancer and greatly threatening human health [7–9].

With the further development of rural life and the social economy, a large number of PAHs, created via agricultural production [10] and living activities, will inevitably enter the environment and eventually enter the soil through the migration process of atmospheric particulate matter and atmospheric dry and wet deposition [11]. Thus, PAHs represent a potential hazard for the quality of farmland soil and the safety of agricultural products, and have a serious impact on regional sustainable development [8,12]. The research scope of PAHs pollution in farmland soil in China has mainly been concentrated in the eastern region, for example, the Yangtze River Delta [13], the Yellow River Delta [14], and Zhejiang province [15]. However, soil PAHs in different environmental systems were influenced by a variety of factors, which could lead to some variability in the contamination and distribution characteristics. Under the momentum of the strong economic development and fragile ecological environment in Helan, more and more organic pollutants have gradually entered the agricultural soil, which could endanger the soil environment [16,17]. However, there was little knowledge about the status, sources, distribution, and health risks of PAHs in the farmland soils of Helan, which was unfavorable for the prevention and control of PAH pollution in Helan farmland soils.

In order to avoid harm to human beings from PAHs in the soil, it has been necessary to understand the source of PAHs more clearly to achieve good risk aversion. PAHs are mainly formed via partially complete combustion of carbon-containing fuels like wood, coal, diesel, and tobacco [17]. Most of the sources of PAHs in soil were anthropogenic, including industrial emissions, solid waste incineration, and vehicle emissions [17]. In recent years, as the problem of soil pollution has become more and more prominent [18], many scholars were concerned to ascertain the source of soil PAHs and to find out whether they were caused by human activities or originate in the soil parent materials. The source component spectrum receptor model, which takes the contaminated area as the research object, can identify source characteristics and evaluate source contributions of the soil pollutant. At present, the receptor models mainly include absolute principal component scores/multiple linear regression (APCS-MLR) [19], the positive definite matrix factor analysis model (PMF) [20], and chemical mass balance (CMB) [21], which have been used by some scholars to quantitatively analyze the pollution sources of soil PAHs [10,22]. Among them, the APCS-MLR model could quantitatively calculate the average contribution of each pollution source to soil PAHs and the individual contribution of each pollution source to each PAH at every sampling point, so some scholars have applied it to the study of PAH source analysis, such as Guan et al. [23] in Lanzhou and Lu et al. [24] in Nanjing. However, few data were obtained from the source of soil PAHs in Helan farmland.

Assessing the potential risks to human health posed by different pollutants is an efficient approach in determining their level of impact, which has found extensive application in detecting the potential health risk from exposure to toxic pollutants in different surroundings [3]. Currently, the majority of research conducted on soil health risk assessment had been founded on the suggested model from the US Environmental Protection Agency (USEPA) [10,25]. However, there were several parameters of health risks with indeterminacy and variability in the human health risk assessment process, such as body weight and soil particle uptake rate [26]. Under the circumstances, the traditional risk assessment model was unavoidably impacted due to the absence of data and the indeterminate nature of the risks [27]. As the uncertainty could be identified and quantified through probabilistic risk [28], it was often used to determine the distribution of risks and figure out the various exposed routes of risk and the risk parameters [29]. The probabilistic health risk model with Monte Carlo stochastic simulation could truly simulate the actual exposure scenario and increase the conformity between the model calculation and the actual situation [30]. As a result, many scholars have carried out studies on health risks using Monte Carlo, such as Chen et al., who provided a health risk assessment of PAHs [31], and Huang et al., who conducted an analysis of the potential health hazards associated with metallic elements [32]. However, the probabilistic health risk model has not been applied to the Helan farmland area.

Thus, the objectives of this study were to: (1) analyze the concentrations and spatial distribution of PAHs in the farmland soil of Helan county, (2) identify the source of PAHs in farmland soils using APCS-MLR, and (3) evaluate health risks due to exposure to PAHs in farmland soils using the Monte Carlo method. The findings of this study could offer a scientific foundation for the restriction and regulation of PAH pollution in soil, the management of health risks, and sustainable development in the farmland soil of western China.

2. Materials and Methods

2.1. Study Area

This research was conducted in Helan county of Yinchuan City located in the autonomous region of Ningxia Hui in China. It covers around 1204.71 km^2. Helan is bounded by the Yellow River to the west [33]. The terrain of Helan is high in the southwest and low in the northeast, open and flat with an incline that runs from the southwest to the northeast. The whole region mainly consists of mountains in the northwest and the eastern plain. Helan has a temperate continental climate, average annual precipitation of 138.8 mm, and strong evaporation of 1666.9 mm [33]. Meanwhile, the annual average wind speed is 4.21 m/s. The wind plays a significant role in facilitating the long-range dispersion of PAHs [34].

2.2. Sample Collection

The sampling sites (38°02′68″ N–39°30′41″ N, 106°02′12″ E–107°53′5″ E) were situated in Helan County. The land use in the study area was all farmland, and the main agricultural crops were corn and soybeans. A total of 117 soil samples in farmland were gathered in November 2022 according to the "Technical Specification for Soil Environmental Monitoring" (HJ/T166-2004 [35]) (Figure 1). Throughout the entire sampling procedure, a GPS system was employed to precisely determine the coordinates of each sampling site, as depicted in Figure 1. The soil samples (0–20 cm depth) were extracted with a shovel made of stainless steel; five samples were gathered across a specified region of 10 m^2, then blended together to create a combined sample [36]. Every individual soil sample was placed inside brown glass bottles, labeled, and subsequently delivered to the laboratory.

2.3. Reagents and Standards

A standard mixture was purchased from TM Standard (Beijing, China), which contained 7 PAHs: chrysene (Chry), benz(a)anthracene (BaA), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-c,d)pyrene (InP), and dibenzo(a,h)anthracene (DahA). The reagents were all HPLC grade. Water used for the analysis was high-purity deionized water taken from the Mili-Q system. All the experimental methods were based on "Soil and sediment—Determination of polycyclic aromatic hydrocarbons—High performance liquid chromatography" (HJ784-2016 [37]).

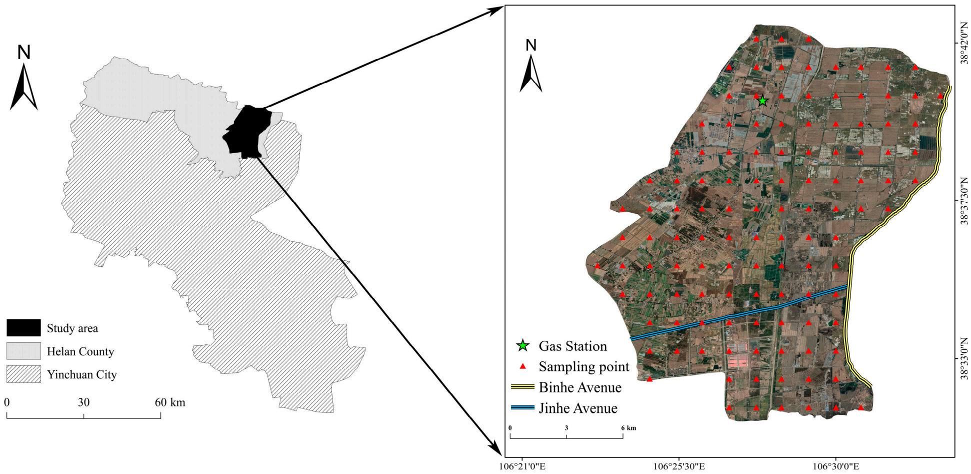

Figure 1. Distribution of sample points in the study area.

2.4. Sample Extraction

In the laboratory, we weighed 5 g of air-dried soil that had been sieved through a 60-mesh sieve. Then, 25 mL of a mixture consisting of n-hexane and acetone in a ratio of 1 to 1 was added. The samples underwent ultrasonic oscillation for a duration of 30 min, followed by ultrasonic extraction for an additional 5 min. Subsequently, the sample was centrifuged at a speed of 3000 revolutions per minute for a period of 15 min. The resulting solution was filtered through an organic filter membrane with a pore size of 0.45 μm and collected in a centrifuge tube.

A C18 solid phase extraction (SPE) column (500 mg, 6 mL, Supelco, Bellefonte, PA, USA) was used as the purification column, and about 5 g anhydrous sodium sulfate was added to the surface layer of the SPE column. The purification column was rinsed with 4 mL dichloromethane, and then the purification column was balanced with 10 mL n-hexane. The entire washing solution was moved to the column and eluted with 10 mL dichloromethane–n-hexane (1 + 1). The eluent was concentrated to about 1 mL using the nitrogen blowing method, and then concentrated to less than 1 mL through adding about 3 mL acetonitrile. The sample solvent was completely converted to acetonitrile, and the volume was determined to be 1.0 mL to be measured.

2.5. Instrumental Analysis

According to the national standard provided for high-performance liquid chromatography (HPLC), a Japanese Shimadzu High-Performance Liquid chromatograph (Essentia LC-15C, Tokyo, Japan) was used, equipped with an ultraviolet detector. Mobile phase A was ultra-pure water, mobile phase B was chromatographic pure acetonitrile, and the temperature of the column chamber was set at 35 °C. The gradient elution procedure was as follows. The volume ratio of mobile phase B remained at 60% from 0 to 8 min. The volume ratio of mobile phase B increased from 60% to 100% during 8–18 min. From 18 to 28 min, the volume ratio of mobile phase B remained 100%. During 28–28.5 min, the volume of mobile phase B decreased from 100% to 60%. From 28.5 to 35 min, the volume ratio of mobile phase B remained at 60%. The flow rate of the pump was set as 1 mL·min^{-1}, and the sample volume was measured as 20 μL with an automatic sampler. The UV absorption wavelength used for peak collection was 254 nm. According to the peak time, 7 types of PAH monomers were quantitatively calculated by external standard method.

2.6. Quality Control

Strict adherence to quality assurance and quality control measures was closely observed throughout the execution of all analytical procedures. Quantitation was performed using an external standard calibration method (five-point calibration: 0.04, 0.10, 0.50, 1.00, and 5.00 μg·mL^{-1}), and the correlation coefficients (R^2) for the calibration curves were all greater than 0.995. The limit of detection (LOD) was calculated as three times the standard deviation of the blank. A calibration curve was established using the concentration of the target component in the standard series of solutions as the vertical coordinate and its corresponding peak area as the horizontal coordinate.

2.7. Absolute Principal Component Scores/Multiple Linear Regression (APCS-MLR)

An APCS-MLR model was used for quantitatively analyzing the pollution sources of PAHs in soil. The factor scores from the factor analysis were first converted to absolute principal component factor scores, and then multiple linear regressions were performed. The regression coefficient was used to calculate the contribution of the pollution source associated with each factor to the substance in the receptor [19,38]. The procedure involved the following calculation steps:

(1) The contents of all PAHs were normalized, and the normalized factor fractions were obtained from the analysis of the principal components as follows:

$$Z_{ij} = \frac{C_{ij} - \overline{C_i}}{\sigma_i} \tag{1}$$

where Z_{ij} was the standardized factor fraction (no dimensional quantity); C_{ij} was the measured content of PAHs in soils; and C_i and σ_i were the average content and standard deviation of element i, respectively.

(2) For all elements, we established an artificial sample with 0 content and calculated the factor scores of the 0-content sample; Z_{0i} was the factor fraction of the sample with 0 content, which was calculated as follows:

$$Z_{0i} = \frac{0 - \overline{C_i}}{\sigma_i} = -\frac{C_i}{\sigma_i} \tag{2}$$

(3) The factor fraction of each sample was subtracted from the factor fraction of the 0-content sample to obtain the APCS of each PAH element.

(4) The multivariate linear regression of APCS with PAH content data could be converted into the contribution of each pollution source to each sample as follows:

$$C_i = b_{0i} + \sum_{p=1}^{n} (APCS_p \cdot b_{pi}) \tag{3}$$

where b_{0i} was the constant term obtained by multiple linear regression of PAH element i; b_{pi} was the regression coefficient of source p to element i; $APCSp$ was the fraction of the adjusted factor p; and $APCS_p{\cdot}b_{pi}$ represented the contribution of source p to C_i. The average $APCSp{\cdot}b_{pi}$ of all samples represented the average absolute contribution of the source.

2.8. Health Risk Assessment

The carcinogenic and non-carcinogenic health risks in adults and children from the average daily intake dose (ADD; mg·kg^{-1}·day^{-1}) were evaluated based on the USEPA recommended health risk assessment model [39]. The ADD was estimated by the exposure of the ingestion, dermal, and inhalation absorption pathways, which could be computed as follows:

$$ADD_{ingest} = \frac{C_i \times R_{ingest} \times EF \times ED}{BW \times AT} \times 10^{-6} \tag{4}$$

$$ADD_{dermal} = \frac{C_i \times SA \times AF \times ABF \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (5)$$

$$ADD_{inhal} = \frac{C_i \times R_{inhal} \times EF \times ED}{PEF \times BW \times AT} \quad (6)$$

where ADD_{ingest}, ADD_{dermal}, and ADD_{inhal} were the daily intake of PAHs in soil by the ingestion, dermal, and inhalation absorption pathways, respectively; C_i was the measured value of *i* of PAHs in soil; R_{ingest} was the soil particle intake rate; *EF* was the exposed frequency; *ED* was the exposure period; *BW* was the body weight; *AT* was the average exposure time; *SA* was the dermal surface area; *AF* was the skin adhesion factor; *ABF* was the skin absorption factor; R_{inhal} was the soil particle inhalation rate; and *PEF* was the soil particulate emission factor. The specific parameters are shown in Table 1.

$$TCR = \sum CR = \sum ADD_i \times SF_i \quad (7)$$

Table 1. Parameter values of the model for probabilistic risk assessment of Helan.

Parameter	Unit	Type of Function Distribution	Value	
			Child	Adult
EF	$d{\cdot}a^{-1}$	Triangular distribution	350 [40]	
R_{ingest}	$mg{\cdot}d^{-1}$	Triangular distribution	66, 103, 161 [41]	4, 30, 52 [41]
AF	$mg{\cdot}cm^{-2}$	Lognormal distribution	0.65, 1.2 [42]	0.49, 0.54 [42]
R_{inhal}	$m^3{\cdot}d^{-1}$	Common practice	8.6 [43]	19 [43]
ED	a	Common practice	6 [32]	24 [32]
PEF	$m^3{\cdot}kg^{-1}$	Common practice	1.36×10^9 [32]	
BW	kg	Lognormal distribution	16.68, 1.48 [43]	57.03, 1.18 [43]
AT	d	Common practice	25,550 (carcinogenic) [32]	
SA	m^2	Common practice	0.23 [43]	0.54 [43]
ABF	-	Common practice	0.01 (carcinogenic) [32]	

The health risk was mainly founded on the health risk assessment method of EPA. The total carcinogenic risk (*TCR*) was determined by adding together the potential risks of all individual carcinogenic elements; therefore, the probability of an individual developing cancer is *CR*. Where ADD_i consisted of ADD_{ingest}, ADD_{dermal}, and ADD_{inhal}, SF_i was the carcinogenicity slope factor, including SF_{ingest}, SF_{dermal}, and SF_{inhal}. SF_{ingest} was the cancer slope factor of the ingestion pathway, SF_{dermal} was the cancer slope factor of the dermal pathway, and SF_{inhal} was the cancer slope factor of the inhalation absorption pathway. The parameters are shown in Table 2 [19].

Table 2. *SFi* data of the 7 prior PAHs.

PAHs	*Sfi* Value of PAHs /($kg{\cdot}d^{-1}{\cdot}mg^{-1}$)		
	SF_{ingest}	SF_{dermal}	SF_{inhal}
Chry	7.30×10^{-3}	3.10×10^{-3}	1.46×10^{-2}
BaA	7.30×10^{-1}	3.10×10^{-1}	1.46
BbF	7.30×10^{-1}	3.10×10^{-1}	1.46
BkF	7.30×10^{-2}	3.10×10^{-2}	1.46×10^{-1}
BaP	7.30	3.10	14.6
DahA	7.30	3.10	14.6
InP	7.30×10^{-1}	3.10×10^{-1}	1.46

In order to better determine the extent of the health risk, it was classified into six levels based on the existing research, and the grading of the evaluation standard is shown in Table 3 [44].

Table 3. Health hazard risk evaluation standard classification.

Risk Level	Degree of Risk	The Range of Risk Score
I	Low risk	1×10^{-6}~1×10^{-5}
II	Low–medium risk	1×10^{-5}~5×10^{-5}
III	Medium risk	5×10^{-5}~1×10^{-4}
IV	Medium–high risk	1×10^{-4}~5×10^{-4}
V	High risk	5×10^{-4}~1×10^{-3}
VI	Extra-high risk	1×10^{-3}~5×10^{-3}

2.9. Monte Carlo Simulation

The Monte Carlo simulation method can accurately simulate the actual exposure scenario and increase the conformity between the model calculation and the actual situation, so it is widely used in the field of fitting prediction. The probability distribution model was established using the parameters of PAHs mass concentration in different environmental media and the type of function distribution in Table 1. Then, the prediction unit was defined founded on the health risk setting. The experimental amount of the Monte Carlo simulation was set to 1000, the confidence interval was 95%, and the other parameters were taken as the software default values. Sensitivity analysis refers to the quantitative study of the influence of one or several sensitive parameters on the risk assessment results and the degree of influence. When the result of the sensitivity analysis was positive, it meant that the factor was positively correlated with the risk probability, and the higher the value, the greater the contribution to the risk. When it was negative, it meant that the factor was negatively correlated with the risk probability, and the impact on the risk value was greater as the absolute value of the value was increasing.

2.10. Methods of Data Analysis

The statistical analysis and principal component analysis of PAH contents in soil were conducted using SPSS 18.0 and Excel 2013. The spatial distribution maps were created utilizing the ArcGIS 10.0 software. The Monte Carlo simulations were conducted utilizing Oracle Crystal Ball 11.1.2.4 in this research study.

3. Results

3.1. Concentration and Distribution of PAHs in Soils

Among the 117 Helan farmland soil samples, the rate of PAHs detected in the soil of the farmland in Helan was elevated, in which the detection rate of Chry, BbF, BaP, and InP reached 100% (Table 4). The total content of seven PAHs (Σ7PAHs) ranged from 17.82 to 2744.1 ng·g^{-1}, and the maximum concentration of Σ7PAHs was more than 150 times higher than the minimum concentration. The distribution of the Σ7PAHs was predominantly skewed towards the lower concentration range, and the concentrations on 50% of the samples were less than the median (255.95 ng·g^{-1}), while the mean concentration was 408 ng·g^{-1}. The average concentration in the seven single components was highest in Chry (344.00 ng·g^{-1}), followed by BaA (305.91 ng·g^{-1}). Among the human carcinogen compounds, BaP was a strong carcinogenic monomer which garnered the most attention due to its potential risk for causing cancer [45]. The findings indicated the level of BaP varied in the range of 0.66~188.61 ng·g^{-1} in Helan farmland; thus, the content was low and did not reach a level that could cause a cancer hazard [46]. No individual PAHs were detected in some soil samples, which showed that the proportion of Σ7PAHs in farmland soil varied greatly.

The spatial distribution of Σ7PAHs in soil samples from the study area is illustrated in Figure 2. It can be seen that there were different degrees of PAHs in the study area. Combined with Figure 1, the locations where samples were obtained near the gas station had higher contents of soil PAHs, which showed higher pollution than the samples obtained at a distance from the gas station. In general, the concentration of the seven PAHs in soils from the western region of the study area was found to be higher compared to that from the eastern region. Simultaneously, the high content of PAHs in the northwestern region was also related to the prevalence of the northwest wind, which indicated that wind direction could have a certain impact on the distribution of PAHs.

Table 4. Descriptive statistics of 7PAHs and Σ7PAHs.

PAH Compounds	Ring of Numbers	Range (ng·g^{-1})	Mean (ng·g^{-1})	Median (ng·g^{-1})	Standard Deviation (ng·g^{-1})	Coefficient of Variation	Detection Rate
Chry	4-ring	1.96~344.00	86.59	25.57	89.96	1.04	1
BaA	4-ring	N.D.~305.91	82.30	66.18	66.27	0.81	0.97
BbF	5-ring	2.34~136.63	33.34	19.37	28.54	0.86	1
BkF	5-ring	N.D.~263.38	66.07	31.75	60.37	0.91	0.98
BaP	5-ring	0.66~188.61	32.19	22.10	34.69	1.08	1
DahA	5-ring	N.D.~267.53	45.26	43.43	35.33	0.78	0.91
InP	6-ring	0.79~214.46	62.42	32.22	56.27	0.90	1
∑7PAHs	/	17.82~1544.73	408.18	255.95	325.65	0.80	1

N.D.—Not Detected.

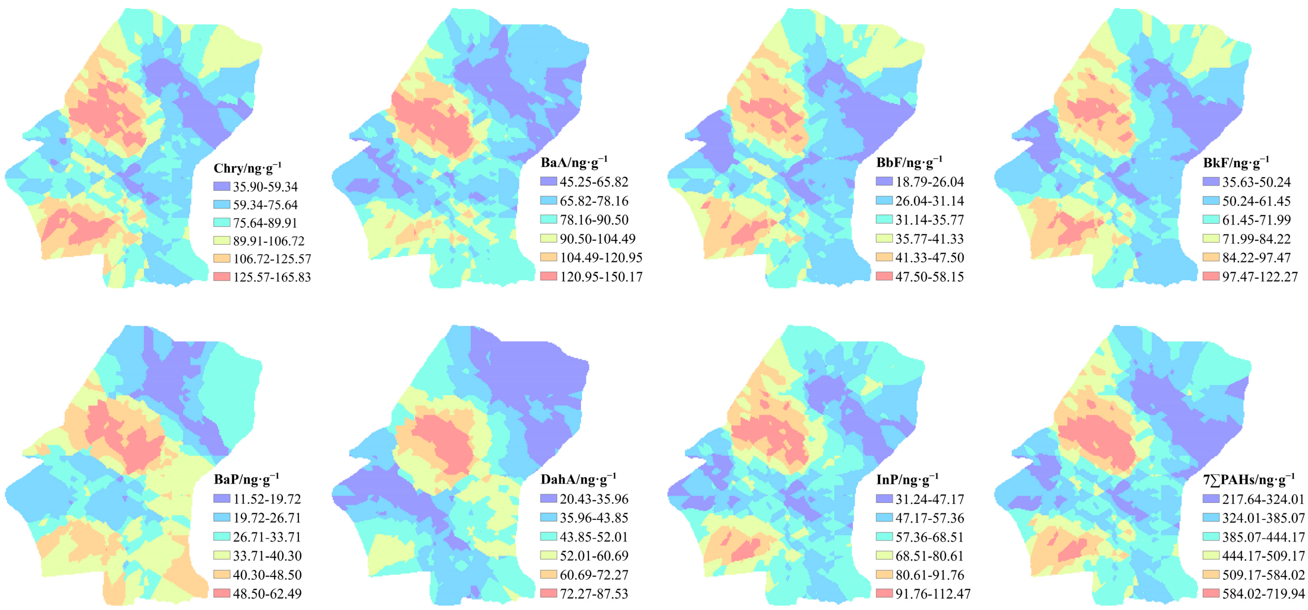

Figure 2. Spatial distribution of 7 single soil PAHs and Σ7PAHs in the soil of the study area.

Due to the absence of established evaluation criteria for soil PAHs in China, a standard suggested by Maliszewska-Kordybach [44] was utilized to assess the level of pollution caused by soil PAHs. According to the concentration of Σ7PAHs, soil pollution can be categorized into four different levels. Concentrations of Σ7PAHs below 200 ng·g^{-1} indicated non-contaminated, while concentrations ranging from 200 to 600 ng·g^{-1} suggested weak contamination. Concentrations between 600 and 1000 ng·g^{-1} were contaminated, whereas concentrations exceeding the threshold of 1000 ng·g^{-1} showed heavy contamination [44]. Based on this categorization, varying levels of PAH contamination were observed in the soil samples collected from the study region, in which 35.9% were non-contaminated, 37.6% were weakly contaminated, 21.4% were considered contaminated, and 5.1% were heavily contaminated. The coefficient of variation (CV) was not only able to reflect the degree of dispersion of variables, but also to intuitively reflect the spatial variation intensity of the samples. In this study, Chry and BaP showed strong variation (CV > 100%), while the other five PAHs showed moderate variation (10% < CV < 100%). It was evident that the PAH contents in the area of study were greatly affected by human activities, for instance cooking food and heating the home through wood burning [3,47].

3.2. Source Identification of PAHs in Soils

Endogenous PAHs in soil mainly came from plant decomposition or natural disasters. In soil, the content of these were usually 1–10 ng·g^{-1} [48]. All ∑ PAH contents in Helan farmland soil were much higher than 10 ng·g^{-1}, indicating that there was exogenous pollution of PAHs in soil. Therefore, in the study area, the sources of PAHs in soil were complicated, being not only endogenous but also exogenous. To further identify PAHs sources, the APC-MLR model was used in this study. The correlation coefficients (R^2) of Chry, BaA, BbF, BkF, BaP, DahA, and InP of the multiple linear regression equation were 0.963, 0.784, 0.945, 0.984, 0.709, 0.661, and 0.661, respectively. The higher R^2 value indicated that the fitting effect of the multiple linear regression equation was better. The seven PAHs in the study area were all high-molecular-weight (HMW) PAHs. The HMW PAHs were relatively more stable and prone to remain in the soil environment around the emission source, which made the model more accurate in predicting the results [49].

Through Table 5, it can be seen that factor 1 had a higher load in the Chry, BaA, BbF, BkF, and InP components. Chry was the specific product of biomass emissions [50]. BbF, BkF, and InP were the indicators of diesel combustion, and BaA was the emission product of natural gas combustion [51], which may be affected by agricultural equipment such as tractors (fuel and fuel leakage). Based on the above analysis, factor 1 represented the combustion source such as products of biomass diesel and natural gas. According to the regression coefficient of the multiple linear regression equation, the contribution rate of each PAH was calculated (Figure 3). The contribution rates of BaA, BaF, and BkF were all above 50%, which were typical products of the combustion of fossil fuels, for instance, diesel and natural gas. With the continuous improvement in the mechanization degree of farmland operations, large agricultural machinery are involved in the harvest and cultivation of crops every year [8]. Though saving extensive human resources, mechanized work has brought a lot of problems such as erratic mechanical operation and oil leakage, which would also lead to PAHs pollution. The burning process on farmland, which included the burning of straw, timber, and crop stalks [52], would also release a large number of harmful substances, for instance, polycyclic aromatic hydrocarbons [17]. Based on the field survey results, some soil samples were collected around the farmers' house and wheat straw was burnt in local farmland during the harvest season. Some rural inhabitants continue to depend on burning straw, firewood, and other biomass to provide heating and to cook [25]. Therefore, factor 1 was indicated to represent the combustion source, including combustion of biomass, diesel, and natural gas.

Table 5. Rotation component matrix of PAHs data in Helan farmland soil.

PAH Compounds	Factor		Common Variables
	1	2	
Chry	**0.924**	0.332	0.963
BaA	**0.819**	0.336	0.784
BbF	**0.962**	0.142	0.945
BkF	**0.962**	0.244	0.984
BaP	0.269	**0.798**	0.709
DahA	0.194	**0.790**	0.661
InP	**0.893**	0.404	0.961
Eigen value	5.115	0.892	
Explain the total variance/%	73.073	12.745	
Cumulative explained total variance/%	73.073	85.818	

The bold emphasizes that this factor was mainly loaded on these PAHs.

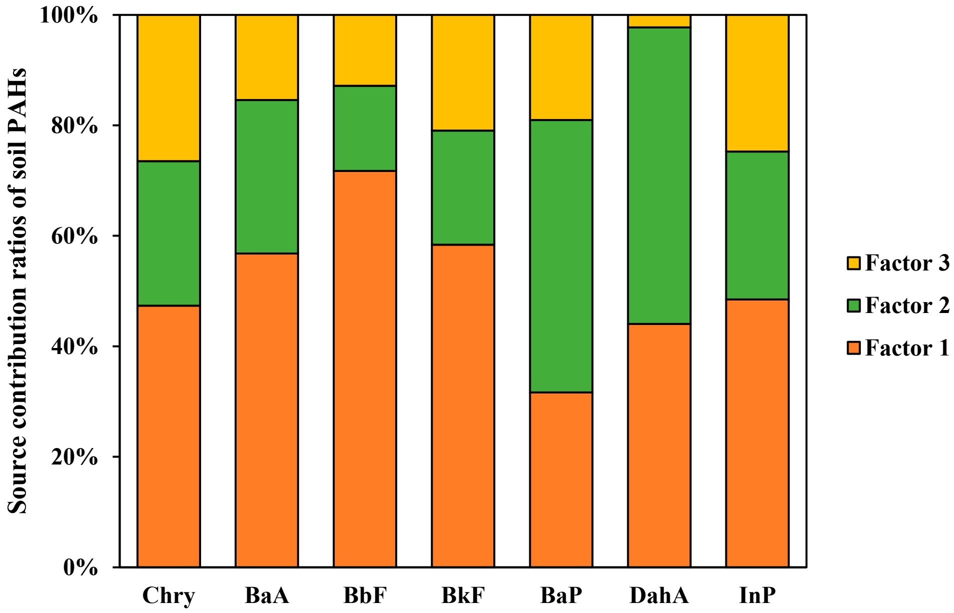

Figure 3. Source contribution ratios of soil PAHs from study area via APCS-MLR model.

The loads of BaP and DahA were higher in factor 2, with contribution rates of 49% and 54%, respectively. BaP was often seen as the main indicator of traffic fuel exhaust emissions [53], and DahA was considered to be a marker of gasoline vehicle emissions [54]. The farmland sampling points were located near the main traffic streets in Helan, which are Binhe Avenue and Jinhe Avenue, which serve as major thoroughfares to other towns. Due to the greater distance from nearby settlements and the reliance on vehicles for human cultivation and crop transportation, continuous emission of PAHs from traffic flow and gasoline exhaust occurred, exerting pressure on both the surrounding atmospheric environment and the soil environment [25,55,56]. Most PAHs are released into the atmosphere directly through exhaust gases emitted by various transportation vehicles as well as tire wear particles [5], subsequently entering water bodies and soils via sedimentation processes [47]. Therefore, factor 2 was indicated as a transportation source (gasoline vehicle and traffic exhaust emission).

Moreover, soil PAHs in the study area also had other sources, such as coking and petroleum pollution [5]. In summary, PAHs in Helan farmland soil mainly come from combustion sources (biomass, diesel, and natural gas combustion), transportation sources (gasoline vehicle and traffic exhaust emission), and other sources.

3.3. Health Risk Assessment

In this study, the PAH health risks of the three exposure pathways for children and adults were calculated based on Equations (4)–(7) provided in Section 2.5. The soil samples exhibited varying levels of cancer risk (10^{-14}~10^{-5}), and the carcinogenic risk to children was higher than to adults through ingestion and inhalation pathways (Table 6).

For the ingestion pathway, the average CR_{ingest} of children and adults were estimated to be 1.28×10^{-5} and 6.03×10^{-12}, suggesting that the contamination of PAHs had the greatest impact on the sensitivity of children (Table 6).

In addition, adults had the higher risk of dermal exposure (mean value: 9.32×10^{-7}) to soil PAHs than children. However, the carcinogenic risk for children from respiratory inhalation exhibited a significantly reduced level compared to oral ingestion and dermal contact, which was linked to the lower volatilization capacity of PAHs [56,57].

According to the recommendation of USEPA, the acceptable range of carcinogenic risk was 10^{-6}~10^{-4}, in which a value between 10^{-6} and 10^{-4} represented a potential risk, and a value higher than 10^{-4} indicated a higher potential health risk [12]. The carcinogenic risk of children and adults was 9.09×10^{-5} and 6.60×10^{-7}, respectively. The results indicated that PAH pollution in Helan farmland soil did not present carcinogenic risk to adults, but it posed a certain carcinogenic risk to children especially via the ingestion pathway.

Table 6. Average daily intake of PAHs for children and adults via different exposure pathways.

Population	Carcinogenic Effect Intake ($mg \cdot kg^{-1} \cdot d^{-1}$)					
		Statistic	CR_{ingest}	CR_{dermal}	CR_{inhal}	
Child	CR	Max	4.24×10^{-5}	9.16×10^{-8}	4.21×10^{-9}	/
		Min	8.11×10^{-8}	9.63×10^{-11}	8.05×10^{-12}	/
		Mean	1.28×10^{-5}	3.18×10^{-8}	1.27×10^{-9}	/
	TCR	Total	8.99×10^{-5}	2.23×10^{-7}	8.92×10^{-9}	9.00×10^{-5}
Adult	CR	Max	1.99×10^{-11}	3.08×10^{-6}	3.6×10^{-9}	/
		Min	3.81×10^{-14}	5.89×10^{-9}	6.90×10^{-12}	/
		Mean	6.03×10^{-12}	9.32×10^{-7}	1.09×10^{-9}	/
	TCR	Total	4.22×10^{-11}	6.53×10^{-7}	7.65×10^{-9}	6.60×10^{-7}

A quantitative sensitivity analysis was performed to assess the variability and uncertainty of parameters in the exposure pathway that contributed most significantly to the estimation of risks. The data in Figure 4 revealed great disparities in the exposure parameters between children and adults. For the total cancer risk, Chry content in soil was the most important factor in both children and adults, with sensitivities of 91% and 80%, respectively. BaA, BbF, BkF, BaP, DahA, and InP also had a certain effect on the total cancer risk, but their sensitivities were all lower than 5%. From the perspective of human exposure parameters, the sensitivity of R_{ingest} to the health risk of children and adults was the maximum, which were 26% and 52%, respectively, indicating that reducing oral intake could reduce health risks to a greater extent, and daily protective measures should be taken. The sensitivity of body weight (BW) was all negative values, which were −11% and −2%, suggesting that an increase in body weight could reduce health risks to some extent, but other exposure parameters such as AF were less sensitive in this study.

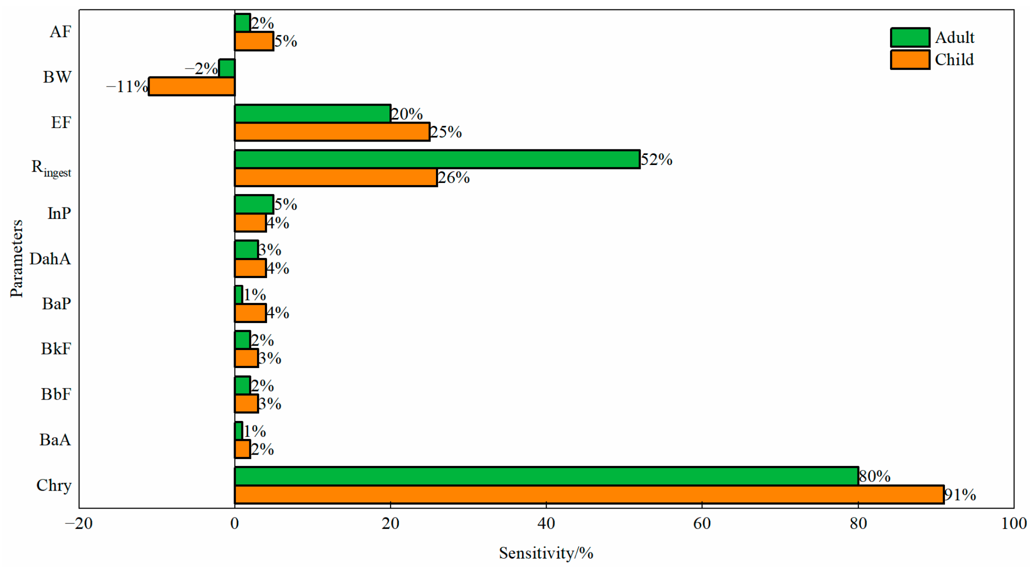

Figure 4. Sensitivity analysis for carcinogenic risk of PAHs.

4. Discussion

The content of PAHs in agricultural soils in Helan county was determined to be 17.82–1544.73 $ng \cdot g^{-1}$, with a mean value of 408.18 $ng \cdot g^{-1}$. Compared with farmland soils in other parts of China (Table 7), Σ7PAHs in farmland soils of Helan were close to Urumqi (10.07~1461.78 $ng \cdot g^{-1}$) [58] and Shandong (11.10~1416.2 $ng \cdot g^{-1}$) [59], lower than

Changchun (328.30~2411.7 ng·g^{-1}) [60] and Guizhou (27.4~2188 ng·g^{-1}) [61], but higher than Nanjing (8.74~141.66 ng·g^{-1}) [62], Zhejiang (8.41~145 ng·g^{-1}) [15], Yinma River Basin (116.71~401.06 ng·g^{-1}) [63], Shanxi (2.08~551 ng·g^{-1}) [64], Fujian (1.42~579.69 ng·g^{-1}) [65], and Huanghuai Plain (12.03~537.95 ng·g^{-1}) [66]. Therefore, in terms of PAHs pollution in farmland soil, Helan farmland soil was at a middle level, which aligned with the findings of Ma et al. [67].

Table 7. Comparison of PAHs in agriculture soils from different regions.

Regions	Land Use	∑7PAHs (ng·g^{-1})	Mean (ng·g^{-1})	Reference
Urumqi	farmland	10.07~1461.78	88.11	[58]
Shandong	farmland	11.10~1416.2	189.7	[59]
Changchun	farmland	328.30~2411.7	1020.6	[60]
Guizhou	farmland	27.4~2188	280.0	[61]
Nanjing	farmland	8.74~141.66	50.90	[62]
Zhejiang	farmland	8.41~145	/	[15]
Yinma River Basin	farmland	116.71~401.06	271.69	[63]
Shanxi	farmland	2.08~55	76.65	[64]
Fujian	farmland	1.42~579.69	65.54	[65]
Huanghuai Plain	farmland	12.03~537.95	51.45	[66]

Under the background of the national strategy of actively promoting the sustainable development of ecological environment protection, Helan county had upgraded, relocated and shut down many high energy-consuming and highly polluting enterprises. These wise measures played a positive role in the protection of farmland soil, which was the reasons for the medium level of PAHs contamination in farmland soil in Helan county in recent years. But a lot of agricultural mechanized equipment was used in harvesting the grain in the farmland, so there were environmentally unfriendly behaviors such as fuel leak [52] and straw burning [63], which would generate and accumulate PAHs in soil.

The main factors in the spatial distribution of PAHs were land use, industrial and transportation layout, climatic conditions, and so on [34,49,56,57,68]. Chen et al. [57] showed that the concentration levels of PAHs were higher in industrial areas and traffic-intensive areas than green space areas. Xia et al. [36] found that the PAHs content was greater in areas close to roads than in areas away from roads. Temperature, monsoon patterns, solar radiation levels, soil physicochemical characteristics, and agricultural practices all significantly influenced the presence and spatial distribution of PAHs in soil [69,70]. The land use in the study area was only farmland, and there were no dense transport and industrial functional areas nearby, so the factors affecting PAHs spatial distribution in this study area could not be related to land use and industrial distribution. Combined with the spatial interpolation map (Figure 2), it could be seen that the contents of the seven PAH monomers in the study area showed a high distribution in the northwest direction, and the reason for this was related to the prevailing northwest wind in the study area, which made PAH gather along the northwest direction. Svetlana Sushkova et al. [34] also concluded that high-molecular-weight concentrations of PAHs and predominance of wind direction in soils contributed a definite weighting to results.

The analysis of soil PAHs sources plays an important role in the prevention and control of soil pollution, the formulation of environmental management policies, the maintenance of regional ecological and environmental security, and sustainable development [40]. Different regions, different soil PAHs input and output pathways, economic and social development, industrial distribution, and other factors could lead to the complexity and diversity of soil PAHs sources [71]. The sources of PAHs were mainly categorized into natural and anthropogenic sources. Natural sources of PAHs were mainly synthesis and decomposition processes of plants and microorganisms, as well as natural fires in forests and grasslands and volcanic eruptions [9]. Most of the PAHs in soil were mainly from anthropogenic sources, including complete combustion of carbon-containing fuels such as wood, coal, diesel, and tobacco, industrial emissions, solid waste incineration, and vehicle emissions [17]. The PAHs in topsoil around oil fields studied by Wang et al. [49] were from petroleum sources and vehicle traffic sources, respectively. In coking contaminated soils, Wang et al. [11] researched that PAHs main source was the coking source. Whereas, in this study of farmland soil in Helan, the main source of PAHs were the combustion source (biomass, diesel, and natural gas combustion) and transportation source (gasoline vehicle and traffic exhaust emission). The results obtained from previous studies had reached similar conclusions, such as those relating to agricultural soils in Shanghai [5], suburban vegetable field soils of Changchun [25], and agricultural soils in eastern China [72]. However, in wetland soils, the main sources of PAHs were petrogenic sources, i.e., biomass burning, diesel emission, and coal combustion [73,74]. The primary sources of PAHs in coking plants were derived from the combustion of coal and biomass [56], and those from oil fields came from petroleum sources and vehicular traffic sources [46]. Based on these findings, it could be considered that some differences in the sources of PAHs in soil mainly depended on land use, which was consistent with the study of Chen et al. [57].

People were exposed to PAHs in the soil mainly through oral ingestion, inhalation absorption, and dermal contact [11]. For children, health risks indicated that the greatest impact was on the risk of ingestion [5]. This was because children had performed frequent hand and mouth activities and contaminated soil was more easily ingested into the body. Therefore, the children living around the farmland were likely to suffer from carcinogenic hazards via ingestion pathways. However, the carcinogenic risk for children from respiratory inhalation exhibited a significantly reduced level compared to oral ingestion and dermal contact, which was linked to the lower volatilization capacity of PAHs [56,75]. Moreover, the dermal absorption also significantly increased cancer risk [76]. For adults, the increased health risk was due to the higher skin absorption, the larger skin area of adults, and the duration of exposure. Furthermore, the increased risk of carcinogenesis in adults could be attributed to the disparity in weight between children and adults [49]. In "Rebuilt Land from a Coking Plant", for children, the risk of direct ingestion was higher than that of dermal contact and inhalation, but for adults, the risks decreased as follows: dermal contact > direct ingestion > inhalation [54]. In Shenzhen city soils, the skin exposure route had the highest carcinogenic risk of PAHs in adults [57]. These findings were consistent with the results of Helan farmland, in which the highest risk was the ingestion pathway in children and the highest risk was the dermal contact pathway in adults. Therefore, it was advised to refrain from ingesting soil orally and to limit dermal contact with soil in order to mitigate potential risks.

Previous studies have shown that children and adults have different sensitivities to soil pollution with PAHs [55]. Particularly, children were considered to be more vulnerable than adults [75]. Similar outcomes were observed in farmland soils in Yinma River Basin [63], urban park soils in Beijing [56], wetland soils in Dajiuhu [77], and urban soils in Shanghai and Xi'an [22,78]. In sensitivity analysis, the soil particle uptake rate was the most sensitive to the health risks of children and adults, and next was body weight. Yang et al. [79] analyzed the health risk of PAHs in the soil of nine coastal wetlands in China and showed that exposure time, the soil particle uptake rate, and PAHs content were the most sensitive to carcinogenic risk. Tong Ruipeng et al. [80] evaluated the health risk of PAHs in soil in Shanghai and pointed out that daily soil intake, exposure time, skin exposure area, and body weight were more sensitive to carcinogenic risk and sensitivity, and there was a negative correlation between body weight and sensitivity. These studies both pointed out that the soil particle uptake rate and body weight were more sensitive parameters for health risk assessment, which is consistent with the conclusions of this study.

From the above, it could be seen that farmland soil in Helan county had been contaminated by PAHs and influenced by human activities and had posed a health risk to children. The monitoring and prevention of soil pollution in the study area should be further strengthened. Meanwhile, the effective measures should be enhanced to better promote the sustainable development of farmland soil, for example, the reasonable use of agricultural machinery, supervision of motor vehicle exhaust pollution, and the control of the combustion of agricultural materials. It was important to note that this study had some limitations. The assessment methodology of this study may result in an overly conservative risk and the bioavailability of PAHs should be considered in future health risk assessments.

5. Conclusions

(1) Σ7PAHs in the study area were higher in farmland soil, with a detection rate of 100% for all PAHs except BaA, BkF, and DahA. The highest average concentration of a single component was observed for Chry (344.00 ng·g^{-1}), followed by BaA (305.91 ng·g^{-1}).

(2) According to the APCS-MLR source apportionment analysis, the primary contributors to soil PAHs in Helan were from combustion sources (biomass, diesel, and natural gas combustion) and transportation sources (gasoline vehicle and traffic exhaust emission). This finding indicated that human activities, such as biomass burning, mechanization, and automobile use, have an obvious impact on the PAHs content in the study area.

(3) The carcinogenic risk showed that PAHs in Helan farmland soil did not present potential health risks to adults, but did present carcinogenic risks for children via ingestion with the mean intake of 1.28×10^{-5}. The sensitivity analysis revealed that the soil particle uptake rate was the most sensitive to the health risks of children and adults with a risk probability of 26% and 52%. The results indicated that reducing oral intake could reduce the health risks of PAHs to human.

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