

Article

Distribution Characteristics and Potential Risks of Polycyclic Aromatic Hydrocarbon (PAH) Pollution at a Typical Industrial Legacy Site in Tianjin, North China

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Abstract: Polycyclic aromatic hydrocarbon (PAH) pollution in the soil of industrial legacy sites is a prominent problem when reusing urban land. To estimate the potential risks of PAHs, this study investigated 16 priority PAHs in the soil at different depths in a typical decommissioned industrial site in Tianjin. PAH concentrations were determined via gas chromatography-(tandem) quadrupole mass spectrometry. Incremental lifetime cancer risk (ILCR) assessment was applied to assess the potential risks to the population after land reconstruction. The total concentrations of PAHs in the soil at different depths ranged from 38.3 ng·g⁻¹ to 1782.5 ng·g⁻¹, which were below the risk control standard for soil contamination of development land (GB 36600-2018). Low-ring (two-three ring) PAHs exhibit a dominant component, and the variations in PAH compositions were closely related to the former production units and soil properties. Compared to silty clay layers, PAHs tended to accumulate in the permeable miscellaneous fill layers. Incremental lifetime cancer risk assessment values associated with different exposure pathways for children, adolescents, and adults were calculated. The results showed potential carcinogenic risks for people of varying ages in this area, but they were still acceptable. In general, this legacy site can meet the demands of sustainable land development.

Keywords: PAHs pollution; risk assessment; industrial legacy sites; vertical distribution; land reuse



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1. Introduction

China is currently undergoing an important restructuring of urban industrial structure and optimization of spatial layout [1]. Dramatic changes in land-use patterns have introduced a series of challenges, such as environmental pollution, climate change, and land deterioration, making soil resources increasingly strained [2,3]. With the pursuit of sustainable development, the remediation and reuse of polluted or degraded land have become increasingly important. So far, a large proportion of traditional industries have closed down or moved out of cities so that precious land resources can be reconstituted. However, most industrial legacy sites are polluted to varying degrees, making it impossible to reuse them directly, and polycyclic aromatic hydrocarbon (PAH) contamination is one of the major types of pollution [4,5]. PAHs are a type of semivolatile organic compound (SVOC) with low vapor pressure and hydrophobic property [6]. They are carcinogenic, teratogenic, and mutagenic contaminants, which can be easily bioconcentrated, can be transported over long distances [7–9], and have attracted great attention in terms of the global environment and public health [10,11]. PAHs originate from a wide range of sources, and the dominant contributing sources are the incomplete combustion of fossil fuels and

organic matter diagenesis. Therefore, PAHs are widely present in the environment, especially in areas with coal-combustion activities [12]. Due to their properties, more than 90% of released PAHs finally enter the soil (or sediment) through various pathways, making soil (or sediment) an important reservoir for PAHs [13,14]. After entering the soil, PAHs can be used as the sole carbon source and energy source for biological metabolism via soil microorganisms. If properly performed, the biodegradation of PAHs could represent a remediation strategy for petroleum-contaminated sites [15]. PAHs can combine with other organic matter for co-metabolism [16]. If PAHs are co-metabolized with organic matters and converted into phenols, quinones, and aromatic carboxylic acids via soil microorganisms and photochemical degradation, the conversion products are more toxic than the parent polycyclic aromatic hydrocarbons, resulting in a more severe threat to the environment [17]. Therefore, PAH pollution in the soil has always been a popular research topic.

Lately, there has been increasing research on PAH pollution in industrial legacy sites. Determining the characteristics of PAH in the soil will lay a solid foundation for soil remediation and land utilization [18]. Ma et al. [19] investigated the legacy sites left by relocating 26 chemical enterprises in Beijing and found that more than 30% of the sites were polluted by petroleum hydrocarbons and polycyclic aromatic hydrocarbons. Li et al. [20] studied PAH residues and the carcinogenic risks of dust samples at the surfaces of industrial legacy construction sites and in soil samples and found that the spatial distribution of PAHs in the dust was consistent with $\sum_{16}\text{PAHs}$ in the soil, and carcinogenic PAHs of industrial legacy sites should be regulated for regeneration. Cao et al. [9] investigated the contamination status of PAHs in the top soils of three industrial legacy sites (i.e., steelworks, a coking plant, and a gas station) and showed that the total concentration of 16 PAHs ranged from $371.1 \text{ ng}\cdot\text{g}^{-1}$ to $4073.9 \text{ ng}\cdot\text{g}^{-1}$, and PAH pollution varied greatly among different types of enterprises. Most studies focus on the industrial legacy sites of petrochemical, coking, steel, and chemical industries [21,22], but few have focused on coal-fired power plants. PAHs are an integral part of the coal structure. During combustion processes, organic fragments are released through which cyclization or radical condensation reactions occur, leading to the formation of PAHs [23]. The characteristics and toxicity effects of parent PAHs and halogenated PAHs from active coal-fired power plants have been thoroughly studied [24,25]. However, the residual components of PAHs in the soil of a closed coal-fired power plant years after its abandonment remain unknown. Moreover, many studies have concentrated on PAH contamination in the surface soil of industrial legacy sites, but PAHs that remains in the soil for a long time may further contaminate groundwater [26,27]. Understanding the longitudinal pollution of PAHs from these sites remains an urgent matter.

Due to a high level of industrialization for several decades, several studies have reported a high level of PAH contamination in the sediment, water, and atmosphere of the Haihe River Basin in Tianjin [28,29]. Since coal-fired thermal power plants are a possible contributor to PAH pollution, in the present study, 7 drilling soil cores with a depth of 5 m from a typical former coal-fired thermal plant site, located in the human settlements in Tianjin, downstream of the Haihe River Basin, were collected for investigation. The objectives of this study were (1) to evaluate PAH contamination and longitudinal distribution at a former thermal power plant, (2) to identify the pollution contribution of different production units, and (3) to assess the risks posed by PAH residues at the study site to the environment and human health. The results will provide an environmentally relevant methodology and useful information for managing and remediating PAH contaminated sites. Additionally, this case study can provide data support for further exploration of land reuse and ecosystem response at decommissioned industrial sites.

2. Materials and Methods

2.1. Study Area and Sampling

The legacy site of the former thermal power plant is located in the downtown Hexi district in Tianjin, northeast and adjacent to the Haihe River. The plant was put into

production after its completion in 2005, and after 10 years of production and operation, the unit in the plant was shut down in 2015. Since then, the land has been left vacant, with the original buildings on the site remaining intact until demolition beginning in October 2019. The historical production activities in this site were quite specific, mainly coal-fired power generation. The whole production process included the following steps: the combustion of coal in the boiler to generate heat, the heating of water into steam, the use of steam to drive steam turbine power generation, the power supplied to the power grid after being adjusted by the transformer, and the smoke and dust discharged through the bag filter and desulfurization device after generation.

2.2. Sampling

It has been preliminarily speculated that PAH contamination in soil is closely related to the different production processes, such as ground flushing, ash and slag stacking, and coal conveying [30]. Additionally, the daily maintenance of steam turbines, generators, and other equipment used in coal-fired power plants may also cause potential leakage. Based on the historical production processes at this site and the stationing conditions, a total of seven core sampling sites were set up to investigate the longitudinal characteristics of PAH in this legacy site, as shown in Figure 1. The drilling of the 7 core samples was executed before the demolition of the main structure, in case of disturbance.

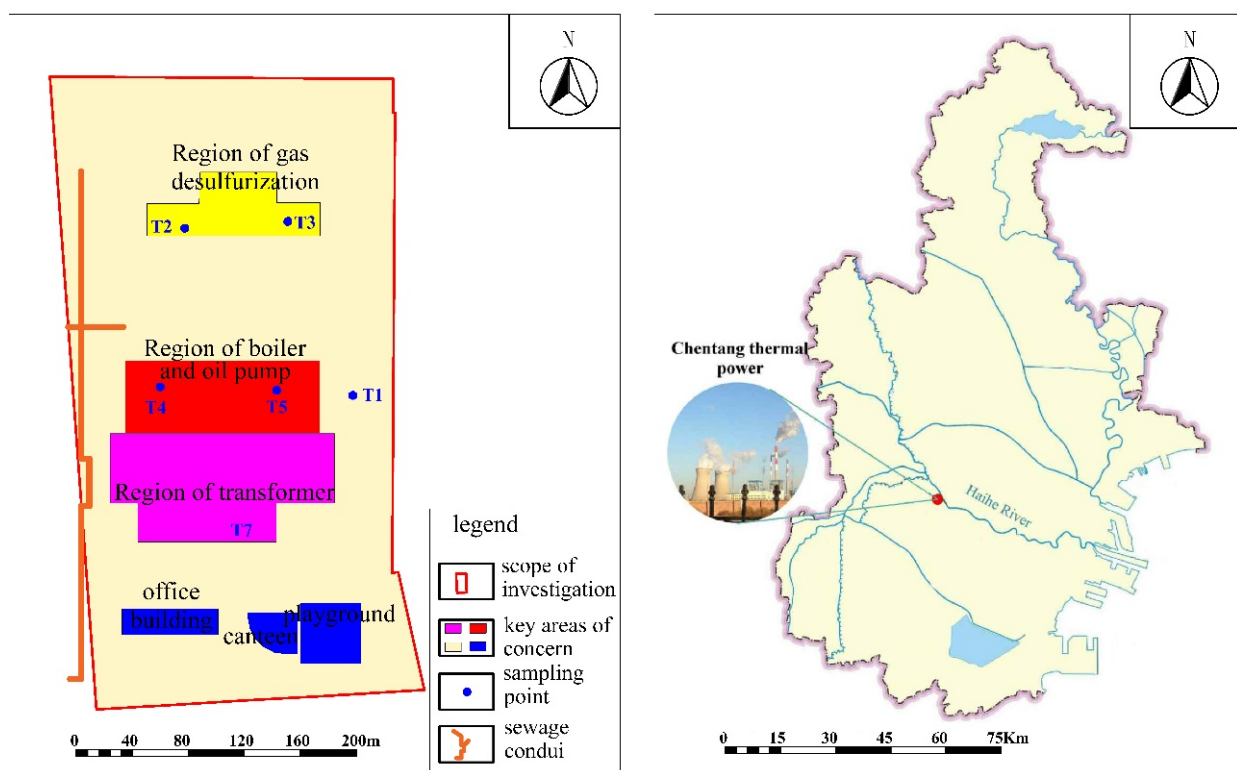


Figure 1. Locations of core sampling sites at the thermal power plant legacy site, Tianjin, China.

The terrain where the site is located is low and flat. The stratigraphic conditions from top to bottom are as follows: (1) the artificial soil filling layer, with a thickness of 2.3–3.7 m; (2) the silty clay layer, with a thickness of 2.3–4.1 m. The buried depth of stable groundwater level ranges from approximately 1.8 to 2.4 m. According to the results of the geological surveys, the soil cores were sampled by Geoprobe (7822DT, USA) at a depth of 6 m with horizon as a base depth in December 2021. Each soil core was sampled at a different depth of 0.3 m, 0.6 m, 0.9 m, 1.2 m, 1.5 m, 2.4 m, 3 m, 4 m, and 5 m. Finally, a total of 70 samples (14 random, duplicated samples excluded) were collected and placed in polyethylene zipper bags and transported on ice to the laboratory. All the samples were

naturally air-dried, ground, passed through 80-mesh sieves to remove non-soil materials such as plant roots and stones, and stored at $-20\text{ }^{\circ}\text{C}$ before analysis. A small amount was taken out from each sample to analyze the physical and chemical properties of the soil, as seen in Table S1 in Supplementary Materials. The lithology and location information of 7 core sites are listed in Table 1.

Table 1. Lithology and location information of 7 core samples sites.

Drilling Sample Cores	Description of Lithology	Processing Units of the Sampling Point
T1	miscellaneous fill layer (0–3.6 m) silty clay layer (3.6–6.0 m)	region of ashery
T2	miscellaneous fill layer (0–3.6 m) silty clay layer (3.6–6.0 m)	region of gas desulfurization
T3	miscellaneous fill layer (0–3.4 m) silty clay layer (3.4–6.0 m)	
T4	miscellaneous fill layer (0–5.1 m) silty clay layer (5.1–6.0 m)	region of boiler and oil pump
T5	miscellaneous fill layer (0–5.4 m) silty clay layer (5.4–6.0 m)	
T6	miscellaneous fill layer (0–3.9 m) silty clay layer (3.9–6.0 m)	region of transformer
T7	depth of miscellaneous fill layer (0–2.7 m) silty clay layer (2.7–6.0 m)	

2.3. Sample Preparation and Analysis

PAH congeners were analyzed following a method described in [31], with some modifications. Approximately 5 g of each soil sample spiked with surrogate standards (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12) was extracted with a mixture solvent of 100 mL acetone/n-hexane (V:V = 1:1) using an automatic Soxhlet extractor. Afterward, the extraction was solvent-exchanged to hexane and concentrated to approximately 1 mL by employing a rotary evaporator. The purification and fractionation processes were performed with a solid-phase extraction column (SPE, florisil, 1 g/6 mL). The column was first washed with 4 mL of n-hexane, and then 1 mL sample extract was transferred to the SPE column. A total of 10 mL of an eluent (a mixture solvent of dichloromethane and n-hexane) was added to the SPE column to achieve the elution of the target PAHs. The clean extract was then evaporated to 1 mL under a gentle stream of high-purity nitrogen and transferred to a 1.5 mL brown bottle before the instrument analysis.

The 16 priority PAHs designated by the United States Environmental Protection Agency (USEPA), naphthalene (Nap), acenaphthene (Acy), acenaphthene (Ace), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (FLu), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno [1,2,3-cd]pyrene (IcdP), dibenz[a, h]anthracene (DBA) and benzo[g, h, i]perylene (BghiP), were analyzed via gas chromatography-(tandem) quadrupole mass spectrometry (TQ8040, Shimadzu, Japan) in the electron-impacting (EI) mode. The chromatographic column was equipped with a DB-5ms fused silica capillary column (30 m $\times$ 0.25 mm $\times$ 0.25 μm , J&W Scientific, Folsom, CA, USA). The oven program for chromatographic column was set as follows: the initial temperature was set at $60\text{ }^{\circ}\text{C}$ (for 1 min), then increased to $200\text{ }^{\circ}\text{C}$ at a rate of $20\text{ }^{\circ}\text{C}/\text{min}$, followed by 1 min retention, and then lifted to $300\text{ }^{\circ}\text{C}$ at a rate of $8\text{ }^{\circ}\text{C}/\text{min}$ followed by 5 min retention, and finally to $310\text{ }^{\circ}\text{C}$ at a rate of $5\text{ }^{\circ}\text{C}/\text{min}$. Helium was assigned as the carrier gas with a flow rate of 1.2 mL/min. The temperatures of ion source, transfer line, and quadrupole trap were maintained at $220\text{ }^{\circ}\text{C}$, $310\text{ }^{\circ}\text{C}$, and $150\text{ }^{\circ}\text{C}$, respectively. Multiple reaction monitoring (MRM) was utilized for quantitative analysis.

2.4. Quality Assurance/Quality Control

Besides the recovery of surrogate standard in every sample, procedure blanks, spiked blanks, spiked matrices, and randomly duplicated samples were also extracted and analyzed in the same way as the real soil samples in every batch of 8 samples. After the injection of each batch of samples, a calibration standard and a solvent blank were injected to check the background and stability of the instrument. The limit of detection (LOD) was quantified as the average of PAHs' concentration determined in blank samples summed with three times standard deviation values of each PAH compound ($\text{LOD} = \text{average} \pm 3 \times \text{SD}$) [32,33], and the limit of quantitation (LOQ), calculated as 3 times LOD, was $0.38\text{--}6.24 \text{ ng}\cdot\text{g}^{-1}$. Only a few PAH congeners with rather low concentrations were detected in the procedure blanks, excluding Nap. Since Nap has great volatility and a high background level, we calculated the other 15 PAHs, excluding naphthalene. The average recoveries obtained from the surrogate standard of d-acenaphthene, d-phenanthrene, d-chrysene, and d-perylene were $70.0 \pm 9.2\%$, $84.4 \pm 12.2\%$, $89.4 \pm 11.3\%$, and $97.5 \pm 14.2\%$, respectively. Recovery rates in the spiked matrices and blanks were $74.3\%\text{--}118.32\%$, with a standard deviation of $8.5\%\text{--}15.3\%$. The quantitation of PAHs was using an external calibration curve method with correlation coefficient (R^2) ≥ 0.99 .

2.5. Lifetime Cancer Risk Assessment

The USEPA standard [34,35] model of Lifetime Cancer Risk Assessment was used to assess the ILCR associated with PAH exposure in the soil of the legacy site. The calculation of ILCR for different population groups in terms of direct ingestion, dermal contact, and inhalation was as follows:

$$\text{ILCRs}_{\text{Ingestion}} = \frac{CS \times \left(CSF_{\text{Ingestion}} \times \sqrt[3]{\left(\frac{BW}{70} \right)} \right) \times IR_{\text{soil}} \times EF \times ED}{BW \times AT \times 10^6} \quad (1)$$

$$\text{ILCRs}_{\text{Dermal}} = \frac{CS \times \left(CSF_{\text{Dermal}} \times \sqrt[3]{\left(\frac{BW}{70} \right)} \right) \times SA \times AF \times ABS \times EF \times ED}{BW \times AT \times 10^6} \quad (2)$$

$$\text{ILCRs}_{\text{Inhalation}} = \frac{CS \times \left(CSF_{\text{Inhalation}} \times \sqrt[3]{\left(\frac{BW}{70} \right)} \right) \times IR_{\text{air}} \times EF \times ED}{BW \times AT \times PEF} \quad (3)$$

where CS is the PAH concentration in soil exposure in the topsoil of the study area ($\mu\text{g}\cdot\text{kg}^{-1}$) (namely PAH concentration in the surface soil), which was obtained by converting the concentrations of PAHs exposure according to toxic equivalents of BaP using the toxic equivalency factor [36]. The other parameters in the formula are listed in Table 2 [37,38].

Table 2. Parameters used in the ILCR calculation formulas.

Parameter	Unit	Child (2–10 Years Old)		Adolescent (11–17 Years Old)		Adult (18–70 Years Old)	
		Male	Female	Male	Female	Male	Female
Body weight (BW)	kg	17.2	16.5	47.1	44.8	60.2	53.1
Exposure frequency (EF)	d·year ^{−1}	350	350	350	350	350	350
Exposure duration (ED)	year	6	6	14	14	30	30
Soil intake rate (IR _{soil})	mg·d ^{−1}	200	200	100	100	100	100
Inhalation rate (IR _{air})	m ³ ·d ^{−1}	10.9	10.9	17.7	17.7	17.5	17.5

Table 2. Cont.

Parameter	Unit	Child (2–10 Years Old)		Adolescent (11–17 Years Old)		Adult (18–70 Years Old)	
		Male	Female	Male	Female	Male	Female
Dermal surface exposure (SA)	$\text{cm}^2 \cdot \text{d}^{-1}$	1800	1800	5000	5000	5000	5000
Solid dust produce factor (PEF)	$\text{m}^3 \cdot \text{kg}$	1.36×10^9	1.36×10^9	1.36×10^9	1.36×10^9	1.36×10^9	1.36×10^9
Dermal adsorption fraction (ABS)	Dimensionless	0.1	0.1	0.1	0.1	0.1	0.1
Dermal adherence factor (AF)	$\text{mg} \cdot \text{cm}^{-2}$	0.2	0.2	0.07	0.07	0.07	0.07
Average life span (AT)	d	25,550	70	70	70	70	70
Carcinogenic slope factor (CSF) ingestion	$(\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1})^{-1}$	7.3	7.3	7.3	7.3	7.3	7.3
Carcinogenic slope factor (CSF) dermal	$(\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1})^{-1}$	25	25	25	25	25	25
Carcinogenic slope factor (CSF) inhalation	$(\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1})^{-1}$	3.85	3.85	3.85	3.85	3.85	3.85

The toxic equivalency quantities (TEQs) of PAHs were calculated first based on the following equation:

$$\text{TEQ} = \sum (C_{\text{PAH}} \times \text{TEF}) \quad (4)$$

where C_{PAH} represents the concentration of individual PAHs.

3. Results and Discussion

3.1. Levels of PAHs in the Legacy Site

In this study, 70 samples from 7 drill holes were obtained from the former thermoelectric plant legacy site. The concentration of PAH compounds ranged from $38.3 \text{ ng} \cdot \text{g}^{-1}$ to $1782.5 \text{ ng} \cdot \text{g}^{-1}$ (dry weight, dw), with an average concentration of $542.2 \text{ ng} \cdot \text{g}^{-1}$ dw (Nap was excluded). Table 3 presents the summary of the detection ranges of the individual PAHs. In total, the detection ratios of high-ring PAHs (5–6 rings) were significantly lower than those of low-and middle-ring PAHs (2–4 rings), which suggested an obvious source of incomplete combustion [8]. This is consistent with the expected characteristics of PAH pollution at this site. The maximum concentration of individual PAHs was anthracene ($818.97 \text{ ng} \cdot \text{g}^{-1}$), followed by phenanthrene ($712.91 \text{ ng} \cdot \text{g}^{-1}$). The standard deviation of all samples for each individual in this area was between 2.41 and 176.84, indicating that there are large differences between different samples at different locations or depths.

The lowest concentration of $\sum_{15}\text{PAHs}$ was detected at a depth of 5 m at site T1, the edge of the former plant, far away from the production area in the upwind direction. The highest concentration was found at 3 m depth ($1782.5 \text{ ng} \cdot \text{g}^{-1}$) at T4, which was influenced by the temporal production process [32] as well as the vertical migration of PAHs [39]. The accumulated concentration of $\sum_{15}\text{PAHs}$ of all sectioned samples from each soil core was also calculated, and the highest cumulative concentration of $\sum_{15}\text{PAHs}$ was also detected at site T4. This again proved the speculation that PAHs originated from local contamination, which was closely related to the production process (boiler and oil pump unit). Seven kinds of carcinogenic PAHs, i.e., BaA, Chr, BbF, BkF, BaP, DBA, and IcdP, were calculated at levels ranging from $4.3 \text{ ng} \cdot \text{g}^{-1}$ to $597.1 \text{ ng} \cdot \text{g}^{-1}$, with an average of $105.8 \text{ ng} \cdot \text{g}^{-1}$, which accounted for 19.5% of the average content of $\sum\text{PAHs}$. Despite the proportion not being particularly high, risks from PAHs at the industrial site still exist for groundwater and human health, even though the site has been abandoned for a long time.

Table 3. Statistical detection ranges of the individual PAHs in all soil samples.

PAH Categories	Ring Number	Detectable Ratio (%)	Range of Concentration (ng·g ⁻¹)	Average Concentration (ng·g ⁻¹)	Standard Deviation	Variable Coefficient	TEFs
Acy	2	98.5%	n.d.–42.3	4.3	5.83	1.37	0.001
Ace	2	78.5%	n.d.–40.2	7.1	9.01	1.26	0.001
Fl	2	7.1%	n.d.–98.9	2.0	12.16	5.96	0.001
Phe	3	100%	1.0–712.9	227.3	176.84	0.78	0.001
Ant	3	100%	2.9–818.9	70.4	139.57	1.98	0.01
FLu	3	100%	2.7–265.1	61.4	63.09	1.03	0.001
Pyr	4	100%	2.8–191.5	49.6	48.52	0.98	0.001
BaA	4	44%	n.d.–149.3	5.5	21.69	3.96	0.1
Chr	4	80%	n.d.–237.3	32.3	43.59	1.35	0.01
BbF	4	21.4%	n.d.–22.5	0.5	2.86	5.50	0.1
BkF	4	100%	0.05–176.6	36.5	36.60	1.00	0.1
BaP	5	42.9%	n.d.–401.2	25.9	56.39	2.18	1
IcdP	5	31.4%	n.d.–24.4	1.1	3.88	3.50	0.1
DBA	5	27.1%	n.d.–13.7	0.8	2.41	2.84	1
BghiP	6	24.3%	n.d.–18.8	0.6	2.92	4.87	0.01
ΣPAHs	/	/	38.3–1782.5	542.2	386.5	0.71	/

The contents of PAHs in this thermal power plant legacy site were lower than those of the eastern coastal developed regions of China, which have a longer industrial history contributing to the pollution of PAHs in soil, such as the Pearl River Delta Region and the Yangtze River Delta Region. It was reported that the highest content of PAHs in soil samples collected from an e-waste recycling site in Guiyu reached 18,600 ng·g⁻¹ [40], and the highest Σ₁₆PAH concentrations in soils from another e-waste recycling site in the Taizhou area reached 361,600 ng·g⁻¹ [41], which were tens to hundreds of times higher than the content of PAHs at this site. PAH contamination here was comparable to the residual levels of other industries in the Beijing–Tianjin–Hebei region, such as a cement factory (536.7 ng·g⁻¹) [42], steel factories (1342 ng·g⁻¹), and coking plants (735.3 ng·g⁻¹) [9,38], which reflects the coordinated development and governance of the Beijing–Tianjin–Hebei region. In addition, the local PAH contamination was also compared with that of other coal-fired power plants in domestic and in the surrounding area. In this study, the PAH concentration in soil was comparable to that in Huainan City, a typical coal resource city in China (528.06 ng·g⁻¹) [43]. However, it was lower than that in the surrounding surficial soil of Xuzhou, China (1089.69 ng·g⁻¹) [25], and it was even lower in fly ash samples and bottom ash samples from an operating power plant in Anhui, China [23]. PAH contents here were also far lower than those in the soils of industrial heritage cities from other countries, such as Indonesia (11,720 ng·g⁻¹) [44], Germany (15,879 ng·g⁻¹) [45], South Africa (28,670 ng·g⁻¹) [21], and France (181,000 ng·g⁻¹) [46]. The relatively low PAH levels in the present study might be related to lower historical input and atmospheric deposition [43]. When compared to the background value around this region (336 ng·g⁻¹ on average) or compared to values from some countries that have always attached importance to cleaner production—for instance, Switzerland (225 ng·g⁻¹) [47] and Japan (320 ng·g⁻¹) [48]—PAH pollution in this legacy site was at a non-negligible level.

3.2. Vertical Profiles of PAHs at the Legacy Site

The vertical distribution of PAHs at different soil depths is illustrated in Figure 2. PAH contents at the surface soil samples (at a depth of 0.3 m) varied within a large range, from 124.4 ng·g⁻¹ to 1258.8 ng·g⁻¹. The grading criteria of PAH contamination stipulate that PAH contamination levels can be divided into four grades: no contamination (ΣPAH concentration < 200 ng·g⁻¹, slight contamination (200 < ΣPAHs concentration < 600 μg/kg), moderate contamination (600 < ΣPAHs concentration < 1000 μg/kg), and severe contamination (ΣPAHs concentration > 1000 μg/kg). PAH concentrations of over half of all the surface

soil samples in this study exceeded moderate and even severe contamination (site T4 and site T6), reflecting severe pollution of the current soil status [25,49].

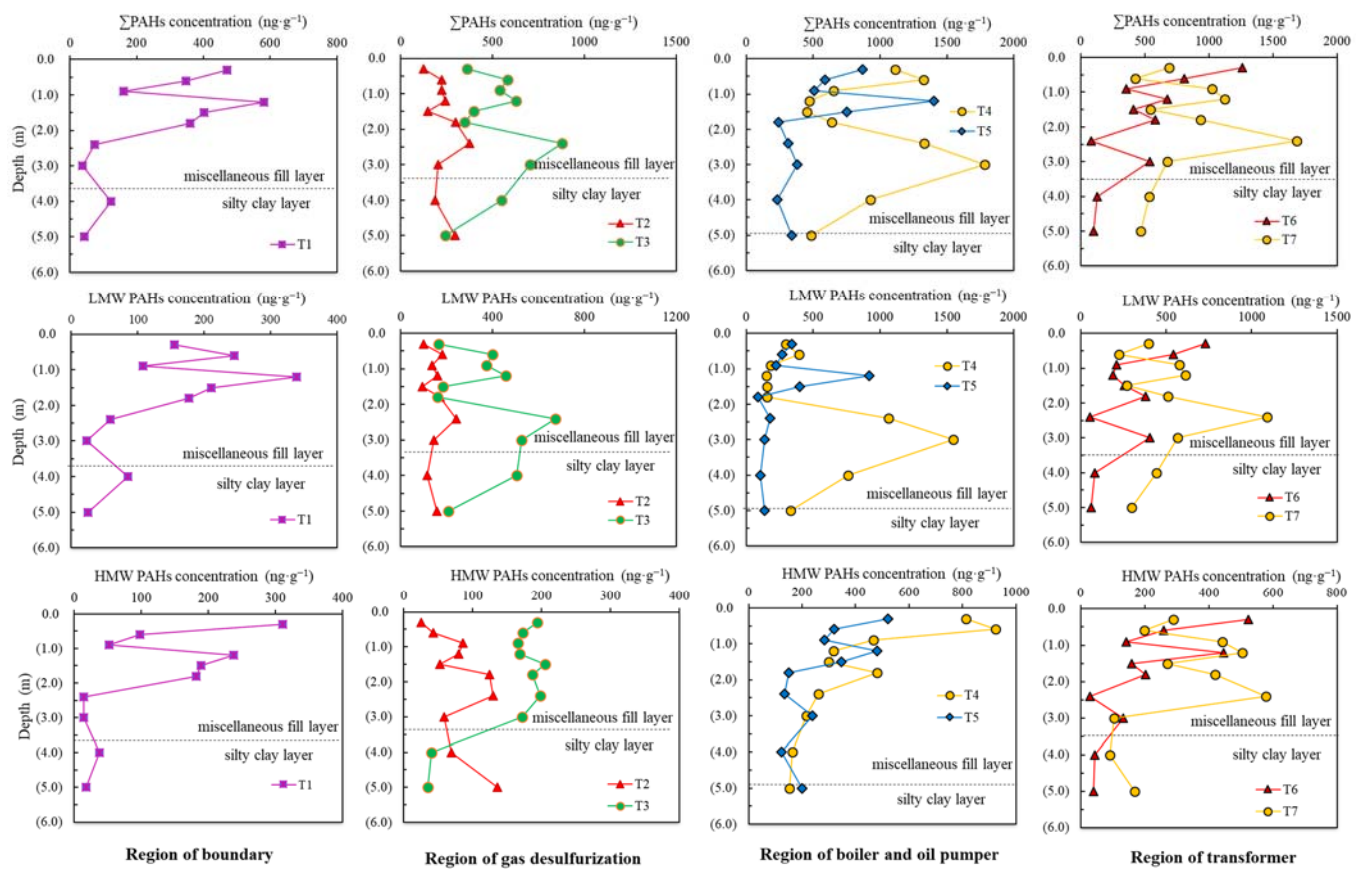


Figure 2. Longitudinal distribution of PAH in each sampling core related to former production unit of the coal-fired power plant; the dividing line indicates the approximate boundary of soil lithology.

Moreover, the longitudinal distribution of Σ_{15} PAHs showed a trend of first increasing, then decreasing, and then continuing to rise to the highest point, then declining, according to Figure 2. The first remarkable rise started at a depth of 0.9–1.2 m. The amounts of LMW PAHs were maintained at a high level, and the concentration of high-molecular-weight PAHs (HMW PAHs) exhibited a prominent increase (especially at T5, T6, and T7), which indicated that PAH accumulation corresponded with the release of the production process at that time; compared to low-molecular-weight PAHs (LMW PAHs), high-molecular-weight PAHs are more likely to seep into the soil nearby [50]. As the soil depth deepened to below 1.8 m, the total concentration of PAHs dropped to the inflection point, then a second increase occurred. Apparently, the amounts of low-molecular-weight PAHs led to a second rise. This was because low-molecular-weight PAHs migrated downward more with groundwater seepage [51] and caused greater accumulation, while high-molecular-weight PAHs were enriched in the upper soil due to their low solubility and strong affinity to organic matter, which severely limited their vertical transport to deep soil [52]. A significant decrease in PAHs appeared in deeper soil at 3.0–5.0 m, which could be attributed to the change in soil lithology, as seen in Figure 3. A remarkable change took place in soil lithology from the miscellaneous fill layer to the silty clay layer at a depth of about 3.5 m. The poor permeability of the silty clay layer with high viscosity and low gravel makes it a barrier to the vertical migration of pollutants [53].

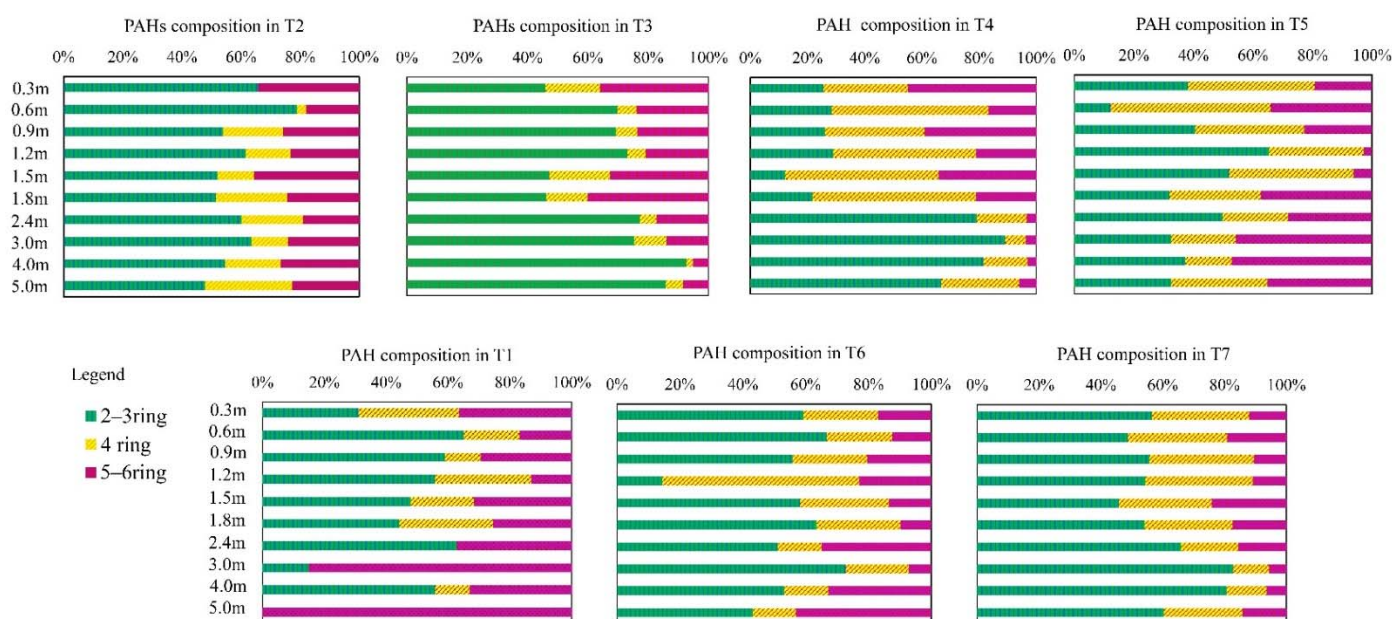


Figure 3. Vertical fractions of PAHs with different ring numbers in the soil of the legacy site.

The composition of PAHs at different depths of soil sampling points involved in this study is shown in Figure 3. In general, the 2-3 ring PAHs were the dominant contaminants out of all 15 PAHs at different soil depths, followed by the 4-ring PAHs. The composition of PAHs in topsoil (above 0.3 m) was not the same as that at other soil depths, with a high proportion of 5-6 ring PAHs (i.e., IcdP, DBA, and BghiP), which should be attributed to sources after shutting down the coal-fired plant, such as vehicular emission [44]. Besides this, PAHs with a low number of rings in the topsoil can also be easily revolatilized into the atmosphere [54]. Therefore, the content of PAHs in topsoil is unstable.

An obvious variation was revealed in the deep soil below the topsoil layer. The composition of PAHs in subsurface soil (at a depth of 0.3–0.9 m) samples mainly included 2-3 ring PAHs, whose proportion could reach more than 50%. Meanwhile, with the increase in depth (until a depth of about 1.8 m), the proportion of medium- and high-ring PAHs increased significantly. Additionally, as the depth of soil samples continued to increase, the proportion of low-ring PAHs increased again, and the proportion exceeded that of low-ring PAHs in surface soil. This regularity of PAH vertical composition manifested in the soil cores was partly due to the physicochemical properties of PAHs. Low-ring PAHs are of greater solubility and permeability than high-ring PAHs, and they are much more mobile to downward migration to deeper soil [51,55]. The composition of PAHs found in the mid-deep soil layers (1.2–3.0 m) was altered greatly compared to deep layers (4.0–5.0 m) and upper soil layers (0–0.9 m). The changes in organic matter in soil properties played a role in the variations, because soil organic matter content reaches its highest value in the soil surface layer and decreases significantly with increasing depth, which affects the adsorption and desorption processes in the soil to a great extent [56]. Accordingly, a better linear correlation between the TOC contents in soil samples and the Σ PAHs concentration—especially the HMW PAHs, as seen in Figure 4—verified the theory that soil organic matter (SOM) is usually responsible for the binding of PAHs in soil [57].

The PAH compositions at sampling sites T4 and T6 were clearly different from the others, with 4-6 ring PAHs dominant in the upper soil layers and the mid-deep soil layers. This may closely relate to the previous production status. These points were located at a downwind area of the boiler and oil pump units and transformer units. A major reason for the impurity of PAH was the impact of wind, and consequently the HMW-PAHs originated from the scattering and spreading of ashes and slags of process units deposited downwind [57,58].

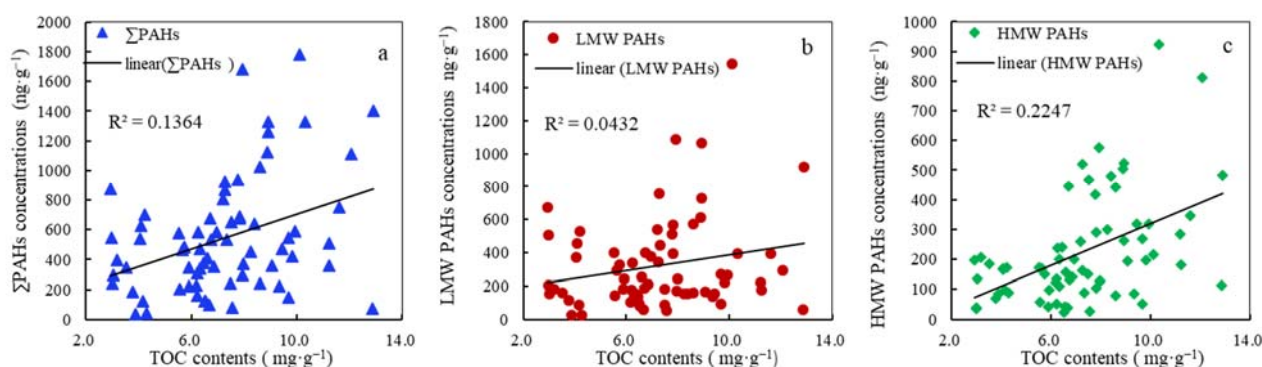


Figure 4. The correlations of TOC contents with Σ PAHs (a), LMW-PAHs (b), and HMW-PAHs (c) and the correlation coefficient (R^2) and significance level (p) are given.

3.3. Influence of Different Process Units on PAH Pollution Status

There was an obvious discrepancy in PAH characteristics in the soil at different sampling sites. The results were concordant with our hypothesis that different process units would lead to different degrees of PAH contamination. In the present study, the Kruskal–Wallis (K–W) nonparametric analysis was applied to investigate the discrepancy of PAH contamination within the regions of the four process units. As seen in Table 4, PAHs in soil samples from different regions of process units exhibit significant differences, because the p values for both Σ PAHs and HMW-PAHs were lower than 0.05 [59]. However, for LMW-PAHs, the data show non-significant differences, because LMW-PAHs are easily volatilized into the atmosphere and settle down over a period of time.

Table 4. Statistical data results of Kruskal–Wallis test, PAHs in soil from different regions of process units.

Statistical Analysis	Σ PAHs	LMW-PAHs	HMW-PAHs
Kruskal–Wallis (χ^2)	13.419	9.709	14.594
p value	0.037 (<0.05)	0.137	0.024 (<0.05)

Figure 5 provides the contamination status of PAHs at key depths of each point, which was collected based on the location of the process unit in the legacy site. The soil at T4 and T5, distributed in the region of the boiler and oil pump, was heavily polluted with PAHs compared to soil in other process regions. According to the distribution of process units in Figure 5, the boiler room was the unit directly related to coal combustion. Due to coal-combustion production activities, the generated PAH first affected the nearby soil, resulting in a high cumulative PAH content in the surrounding soil. This was basically consistent with the results reported by Yang that the highest PAH content in soil was located in the heat-generating area [60]. Besides the area around the boiler and pump, PAH contents in the soils at sites T6 and T7 around the power-generation transformer were slightly higher than in other regions. This result may be related to the consumption or leakage of transformer oil during operation at that time; previous research has mentioned that aromatic hydrocarbons (polycyclic aromatic hydrocarbons and benzene series) make up more than 5% of common naphthenic transformer oil [61].

Due to the long-term operation of the transformer in this site, PAHs entered the surrounding environment with the phenomenon of “running, emitting, dripping, and leaking” and caused different degrees of pollution to the surrounding soil. The pollution content of PAHs at points T2 and T3 in the desulfurization area was lower than that in the soil at the other two regions mentioned above. Although large amounts of PAHs can be found in flue gases from thermal processes that involve incomplete combustion [62], the applied air pollution control devices had a significant effect on the removal of PAH in both particulate and gas phases [63]. The influence of natural factors such as monsoon climate

can also weaken the sedimentation of pollutants in the atmospheric environment [64]. Therefore, the pollution content in the soil around the chimneys, such as T2 and T3, was relatively low.

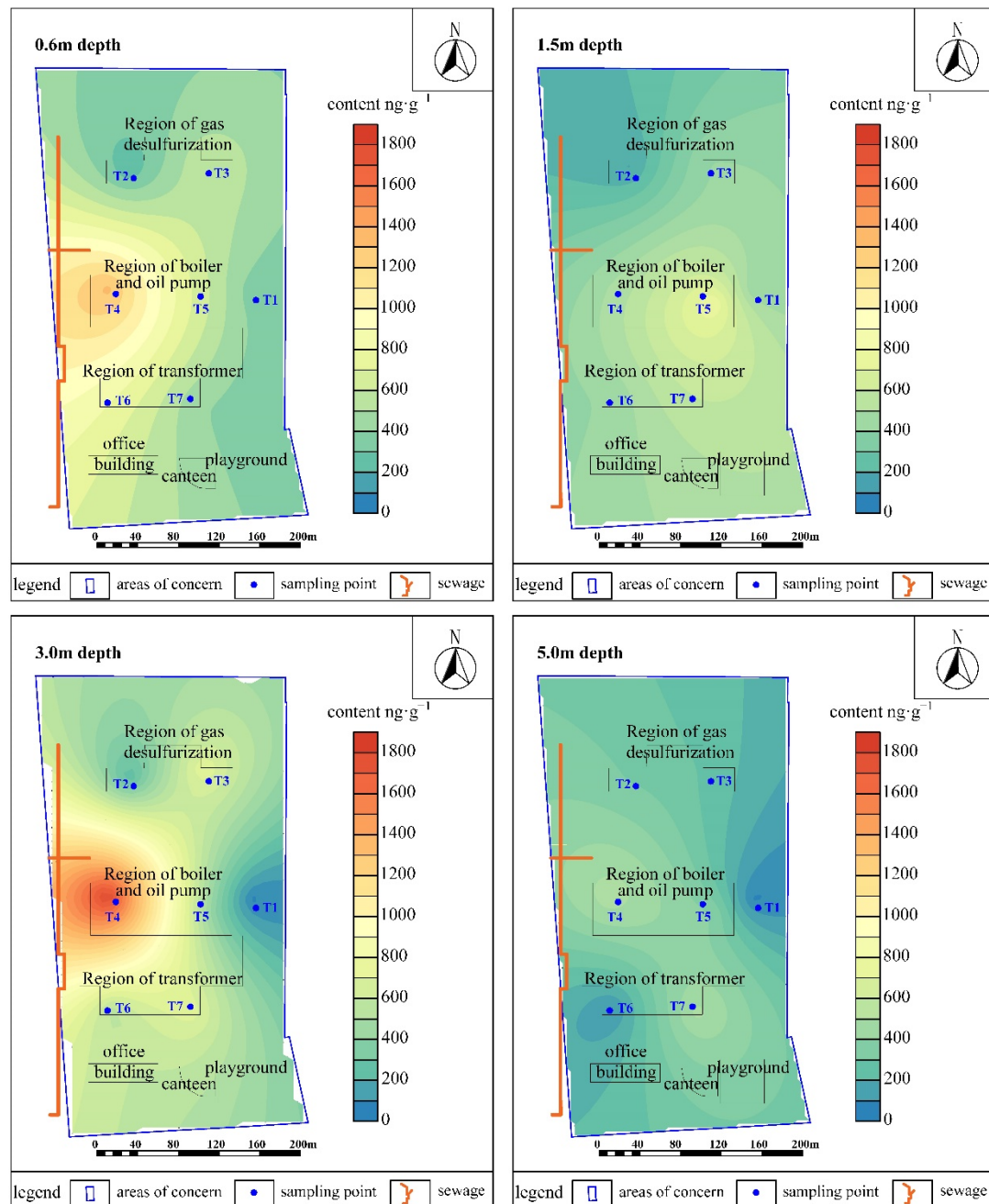


Figure 5. The contamination status of PAHs at key depths of each point collected based on the location of process unit in the legacy site.

Overall, process units contributed differently to PAH pollution in soil within the legacy area. The degree of different production units' PAH pollution ranked in the order of boiler process > power generation and transformation process > flue gas desulfurization process > boundary region (upwind direction).

Regarding the distribution of pollutants, there was no non-point source pollution of PAHs at this legacy site, which suggested that the soil pollution mainly comes from the production activities of the original plant. Additionally, the distribution of PAHs in the soil at different depths also reflected the obvious longitudinal migration of local pollution.

Affected by the change of soil lithology, the migration depth accumulated to about 3.6 m underground at the demarcation of different soil lithologies, and the possibility that PAH continued to migrate slowly downward cannot be ruled out.

3.4. Risk Assessment of Reconstructed Regional Population

The PAH status of this site was compared with the values stipulated in the “Risk control standard for soil contamination of development land (GB 36600-2018)” implemented by China, as seen in Table 5. The controlled individual PAHs cited in the control standard above were all below the specified value, indicating that this legacy land would be classified as non-sensitive. The comparison between total PAHs in this site and the evaluation criteria proposed by Maliszewska [51] showed that 14.3% of all samples were considered heavily polluted ($>1000 \text{ ng}\cdot\text{g}^{-1}$), 21% were considered moderately polluted ($600\text{--}1000 \text{ ng}\cdot\text{g}^{-1}$), and 62% were considered mildly polluted ($200\text{--}600 \text{ ng}\cdot\text{g}^{-1}$). What is particularly noteworthy is that all the samples were from different depths of just seven soil cores; thus, the total amount of PAHs accumulated in the longitudinal direction was a relatively high level, posing important risks to soil–plant system transportation [65] and even groundwater [26].

Table 5. Comparison between PAH in the target site and the “Risk control standard for soil contamination of development land (GB 36600-2018)”.

Stipulated Individuals	Concentration Range (ng/g)	Risk Control Standard for Soil Contamination of Development Land (GB 36600-2018)	Comparison to the Controlled Value
BaA	n.d.–149.33	5500 (mg/kg)	below
BbF	n.d.–22.51	5500 (mg/kg)	below
BaP	n.d.–401.23	550 (mg/kg)	below
IcdP	n.d.–24.38	5500 (mg/kg)	below
BghiP	n.d.–13.69	550 (mg/kg)	below

Since the land met the criteria for reconstruction, it was necessary to evaluate the Incremental Lifetime Cancer Risk Assessment (ILCR) for the reconstruction regional population. The ILCRs of PAHs in the legacy site, classified for children, adolescents, and adults, were further calculated with Equations (1)–(3), and the results can be seen in Table 6. An ILCR of 10^{-6} or less is considered a negligible risk, while ILCRs greater than 10^{-4} indicate potentially high risk; ILCR values between 10^{-6} and 10^{-4} indicate an acceptable potential health risk [38,66]. In general, the carcinogenic risk values of direct ingestion, dermal contact, and inhalation for all populations estimated in this study ranged from 1.2×10^{-8} to 2.1×10^{-6} , 1.2×10^{-8} to 6.2×10^{-6} , and 4.2×10^{-10} to 1.5×10^{-7} , respectively. Although none of the ILCR values exceeded 10^{-4} , 28.6% of the soil samples exceeded the value of 10^{-6} , indicating a potential risk to the local population at this site after reconstruction.

Table 6. Incremental lifetime cancer risks (ILCRs) for people via different exposure pathways.

Exposure Pathways	Range of ILCR for Child		Range of ILCR for Adolescence		Range of ILCR for Adult	
	Male	Female	Male	Female	Male	Female
Ingestion	1.99×10^{-8} to 1.81×10^{-6}	2.08×10^{-8} to 1.88×10^{-6}	1.19×10^{-8} to 1.08×10^{-6}	1.23×10^{-8} to 1.11×10^{-6}	2.17×10^{-8} to 1.96×10^{-6}	2.35×10^{-8} to 2.13×10^{-6}
Dermal contact	1.23×10^{-8} to 1.12×10^{-6}	1.26×10^{-8} to 1.16×10^{-6}	3.41×10^{-8} to 3.14×10^{-6}	3.53×10^{-8} to 3.25×10^{-6}	6.21×10^{-8} to 5.71×10^{-6}	6.75×10^{-8} to 6.21×10^{-6}
Inhalation	4.28×10^{-10} to 3.94×10^{-8}	4.46×10^{-10} to 4.01×10^{-8}	8.29×10^{-10} to 7.63×10^{-8}	8.57×10^{-10} to 7.88×10^{-8}	1.49×10^{-9} to 1.37×10^{-7}	1.62×10^{-9} to 1.49×10^{-7}
Total ILCRs	3.27×10^{-8} to 2.96×10^{-6}	3.38×10^{-8} to 3.08×10^{-6}	4.68×10^{-8} to 4.29×10^{-6}	4.84×10^{-8} to 4.44×10^{-6}	8.52×10^{-8} to 7.81×10^{-6}	9.27×10^{-8} to 8.49×10^{-6}

There was no significant difference in the risks associated with different exposure routes between males and females. However, for different age groups (children, adolescents, and adults), the risks associated with the three exposure routes varied greatly. As shown in Figure 6, the risk of direct ingestion was greater than that of dermal contact and inhalation for children. Meanwhile, for adults and adolescents, the risk of exposure routes decreased in the following order: dermal contact > direct ingestion > inhalation. This is similar to other research in that differences existed in exposure pathways between children and adults [11]. Through all the health risk assessments, the results show potential risks in the legacy site if there is reconstruction, but the integrated lifetime cancer risks associated with exposure to soils with average PAH concentrations for different populations are acceptable.

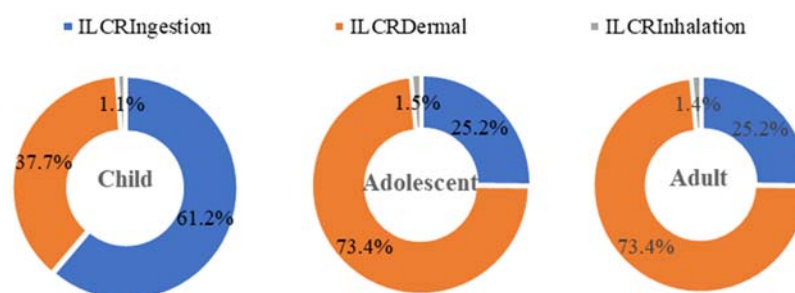


Figure 6. Contributions of different exposure pathways for children, adolescents, and adults calculated by ILCR model.

4. Conclusions

The contaminated soil left after the relocation of industrial factories has attracted great attention. This study focused on the PAH contamination of soil in a typical thermal power plant legacy site in Tianjin, North China, aiming to determine the contamination status and vertical distribution of PAHs at the legacy site, and identify the intimate connection between different process units and the pollutant distribution. This study also provided a preliminary discussion on risk assessment after reconstructing a legacy site. Research on a single industrial site is not universal, but it can provide some methods and ideas for future research. In the thermal power plant legacy site examined, the total concentration of all PAHs ranged from $38.3 \text{ ng}\cdot\text{g}^{-1}$ to $1782.5 \text{ ng}\cdot\text{g}^{-1}$ ($542.2 \text{ ng}\cdot\text{g}^{-1}$ on average), which was at a comparable level to that from heavy industries in the Beijing–Tianjin–Hebei region. The 2–3 ring PAHs were the dominant contaminants among all individual PAHs at different soil depths at this site. PAH contents and constituents at different soil depths showed significant disparity since they were influenced by the physicochemical properties of PAHs as well as the variation of the soil lithology. Additionally, the poor permeability of the silty clay layer with high viscosity and low gravel makes it a barrier to pollutants' vertical migration. The distribution characteristics of PAHs in soil were also closely related to the production processes in the former factory. The degree of different production units in PAH pollution ranked in the order of boiler process > power generation and transformation process > flue gas desulfurization process. Health risks were assessed according to the incremental lifetime cancer risk assessment. In reality, there were potential carcinogenic risks for people of varying ages from this legacy site, but the values of all ILCRs were below 10^{-4} , so the risks were still acceptable.

The present study is a reanalysis of pollution status and risk assessment of PAHs of the industrial legacy site, which has been abandoned and flagged as a residential area. The results of the current study provide an environmentally relevant methodology and useful information for managing and remediating industrial legacy sites. However, the contamination of other chemicals, such as heavy metals, volatile organic compounds, polychlorinated biphenyls and petroleum hydrocarbons, which are always associated with the operation of the coal-fired power plant, remain unexplored. Further studies should be focused on the pollution status of other chemicals, and the complex pollution

mechanism, providing a basis for assessing the possibility of remediating industrial legacy sites for reuse.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/xxx/s1>, Table S1: Basic physicochemical properties and PAH concentration of collected soil samples.

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