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Review

Oxygenated and Nitrated Polycyclic Aromatic Hydrocarbons: Sources, Quantification, Incidence, Toxicity, and Fate in Soil—A Review Study

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Keywords: soil; PAH; OPAH; NPAH; toxicity; fate and behavior



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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic pollutants. Since Blumer [1] first reported PAHs in soil, extensive studies have been conducted to assess PAH toxicity, environmental persistence, and stability. More than 30,000 PAHs have been described, and 16 were listed as priority pollutants by the United States Environmental Protection Agency. PAHs enter the environmental matrix mainly through atmospheric emissions [2], and the global emissions of 16 priority PAHs are estimated to be 499 Gg [3]. PAHs are transported by air currents and have been recorded even in remote areas such as Greenland and Antarctica [4,5].

These persistent organic pollutants have been well studied in the atmosphere, water, and soil and can form related organic pollutants, termed substituted polycyclic aromatic hydrocarbons (SPAHS). PAHs and atmospheric oxides (e.g., O₃, NO₂, OH) can easily form SPAHS, which then migrate to soil and can transform into nitrated PAHs (NPAHs), oxygenated PAHs (OPAHs), and chlorinated PAHs. Polar derivatives of OPAHs and NPAHs have received recent attention [6,7]; in these compounds, the hydrogen on the aromatic ring is replaced by carbonyl and nitro functional groups [7–9]. The formation and release of these polycyclic aromatic compounds (PACs) are mainly caused by the incomplete

combustion of fossil fuels, biofuels, and biomass. Multiple OPAHs and NPAHs have been reported to exert greater toxicity and to be more stable than their parent PAHs [10], although their sources are similar or identical. Therefore, these two types of organic pollutants are often used in comparative studies [11,12].

OPAHs and NPAHs are typical polar derivatives of PAHs and have been studied in various environmental matrices. Apart from the incomplete combustion of fossil fuels and biomass, these compounds can be formed by photochemical reactions in the air [13]. Most research on NPAHs and OPAHs has been conducted in their particulate airborne phase [14–17] and is relatively mature. Since water is a fluid and unstable medium, the incidence of waterborne SPAHs is relatively low. Soil is both a source and a sink of atmospheric pollutants and especially for PACs produced by human activities, through both dry/wet deposition and direct air–soil exchange. A study conducted in the UK estimated that as many as 90% of PACs were stored in soil [18]. In recent years, more and more attention has been paid to soilborne PAH derivatives, both the less-studied polar derivatives and pure OPAHs and NPAHs, and their toxicity [19,20]. Because polar functional groups have the effect of soil minerals and are affected by soil chemistry, the adsorption mechanisms of OPAHs and NPAHs may be more diverse than those of PAHs [21,22]. In short-term incubation experiments of fertile soil, the microbial transformation of parent PAHs was shown to produce OPAHs [23]. The water solubility of OPAHs and NPAHs is higher than the solubility of related PAHs, which generally results in faster vertical leaching in soil [24,25] but differing soil dynamics. In this review, we compare and summarize the research into OPAHs and NPAHs in the soil to provide a systematic theoretical framework for these new organic pollutants (Figure 1).

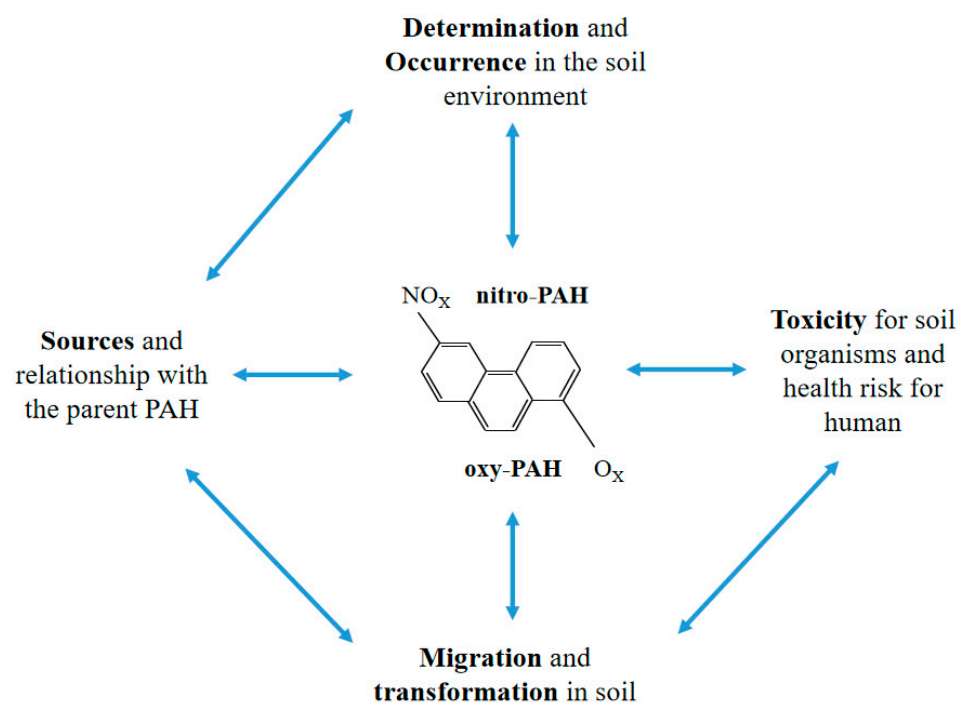


Figure 1. Structure diagram of this review.

This paper is a comprehensive review of journals, books, and related government reports about OPAH and NPAH in the soil environment. It summarizes the sources, detection, occurrence, migration and transformation, toxicity, and health risks. According to the relevant content, representativeness, and the latest methodological progress, the recent studies on OPAHs and NPAHs in soil are included in this review. This can provide a research basis for studying the environmental behavior and fate of polar SPAHs.

2. Sources

Unlike PAHs, which are mainly produced from incomplete combustion sources of coal, biomass, and motor vehicle emissions, OPAHs and NPAHs can be released into the environment simultaneously with PAHs or be formed by the reaction of the parent PAH with free radicals such as OH and NO₃ or through homogeneous or heterogeneous reactions [26,27]. Both NPAHs and OPAHs are mainly formed as direct or indirect products of incomplete combustion, such as of diesel and gasoline engines, or from interactions of gaseous air pollutants. The SPAHs produced by human activities can enter the soil through dry/wet deposition and direct air–soil exchange or as litter from contaminated vegetation [28,29]. The concentrations of PAHs and OPAHs in soil have been shown to be closely related [9,25]; conversion of PAHs to OPAHs in soil involves biological activity driven by climate and soil characteristics such as pH, nutrients, and levels of organic matter [30]. Higher biological activity is expected to result in a higher soil OPAH/PAH ratio [23]. The higher water solubility of OPAHs and NPAHs typically leads to faster vertical leaching in soil [22,24,25], and although the polar functional groups of OPAHs hinder soil transport, they can also bind more easily to soil solids [31].

Soil has great storage capacity for PAHs and their derivatives since soil organic matter is the main adsorbent of PACs [32]. Gas/particle distribution, adsorption-desorption, volatilization, abiotic degradation, biodegradation, leaching, and bioconcentration are important dissipation processes that affect the concentration and spatial distribution of PACs in soil [25,33]. These processes are affected by the physical and chemical properties of PACs, such as the octanol–water partition coefficient, octanol-air partition coefficient, and molecular weight [34]. Soil characteristics such as carbon concentration, moisture content, texture, structure, mineralogy, porosity, and enzyme and microbial properties are also important factors in the fate of OPAHs and NPAHs [23,35]. Climate factors such as temperature, precipitation, monsoon cycle, and hours of sun exposure can also affect the formation, concentrations, and composition of OPAHs and NPAHs in soil. Overall, the soil concentrations and spatial distribution of these compounds cannot be predicted from the degree of human activity.

Measurements of NPAH and OPAH concentrations in the soil must take into account isolation, leaching, volatilization, degradation, and bioconcentration [33]. Once deposited into the soil, these compounds will mainly adsorb to organic matter and remain in the topsoil or be transferred elsewhere through leaching, bioturbation, or colloid-assisted transportation [36]. However, because polar functional groups are affected by soil chemistry, the adsorption mechanisms of OPAHs and NPAHs may be more diverse [22]. Additionally, soil biodegradation of deposited PAHs, photodegradation, thermal degradation, and reactions catalyzed by soil inorganic constituents may all lead to the accumulation of OPAHs and NPAHs [23,37,38]. Microorganism action is another key factor in OPAH and NPAH accumulation. For OPAHs, the situation may be even more special. Because through the bioremediation process, the conversion of parent PAHs to OPAHs may occur, and PAHs containing mainly hydroxyl and carbonyl groups are generated [39]. The concentration of PAHs in the soil can be effectively reduced through the absorption and utilization of microorganisms [9,40], but it is not completely metabolized. The final product may be more toxic, in this regard, has not received sufficient attention. The formation of OPAHs by soil microorganisms has been studied, but the mechanism is still unclear.

3. Quantification

Polar derivatives of PAHs may exert greater toxicity than their parent aromatic compounds and may be enriched in contaminated soil but are rarely included in routine monitoring and risk assessment procedures because of a lack of regulations and standardized analysis methods. However, the more polar SPAHs have garnered research attention over the past few years. Studies in soil have mainly focused on the simultaneous quantification of PAHs and their derivatives [16,41]. Wilcke et al. [42] measured the sum totals of 29 PAHs, 15 OPAHs, and four azaarenes simultaneously in surface soil in Argentina, with an

average recovery rate of 92%. Wei et al. [43] measured the sum totals of 29 PAHs, 15 SPAHs, 4 OPAHs, and 11 NPAHs in surface soil and road dust in China using the methods of Bandowe et al. [44]. Bandowe and colleagues measured PAHs, OPAHs, and NPAHs in urban street dust in Africa, with recovery rates in the range of 53%–152% [45].

There is no standardized method for analyzing polar PAHs in soil, and therefore the methods vary between study groups. Typically, the analysis is based on improved PAHs pre-processing and testing methods or based on airborne particle analysis methods. It is mainly composed of three steps (Figure 2): The first step is to extract the collected soil samples and then to carry out purification and fractionation steps. The third step is to identify and quantify the target compound. Sampling the soil from the surface or deeper depths, freezing or air-drying (freeze-drying) the soil sample before storing it in the refrigerator. If the soil is stored without pre-processing, a desiccant (Na_2SO_4 , diatomaceous earth) can be added to remove the water before or after extracting the chemicals. Soxhlet extraction, accelerated solvent extraction, or ultrasonic extraction are used to remove organic matter from the soil, and solvents differ by the type required for the procedure. The complexity of the soil substrate typically requires additional purification [25,41]; this is because the concentration of SPAHs in the environment is generally lower than that of their parent PAHs and the methods are less sensitive to detecting these compounds. To improve the chromatographic signal quality and signal-to-noise ratio, the interference must be minimized. Solid-phase extraction columns or self-packed purification columns should be used to fractionate the extract to remove impurities and separate the target contaminants. The ratio and order of solvents used for elution will also differ. Internal and external standards are used to quantify targets with improved accuracy [46–48]. Additionally, prior to column fractionation, liquid–liquid extraction can be used to separate SPAHs with basic properties from the extract to improve the analysis of these compounds further.

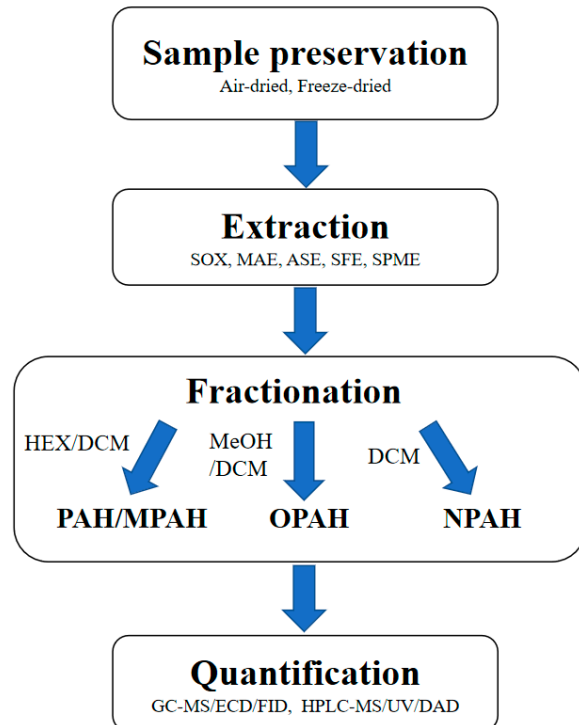


Figure 2. Analysis and detection procedures of polar PAHs.

Finally, the fractions after rotary evaporation and drying by nitrogen, the fractions are typically analyzed by gas or liquid chromatography, often with mass spectrometry. Target quantification is based on the ratio of the analytical peak area to the peak area of the internal standard [49]. Liquid chromatography sometimes harnesses diode arrays or fluorescence;

liquid chromatography with mass spectrometry uses atmospheric pressure chemical ionization or atmospheric pressure photoionization, while gas chromatography-mass spectrometry uses single or triple quadrupole instruments with electron ionization. To analyze OPAHs by gas chromatography, a derivatization step is generally included to increase the volatility and thermal stability of the molecule and reduce its surface interaction. To analyze NPAHs, mass spectrometry is typically operated in negative ion mode to increase the sensitivity of the target. For quality assurance, we recommend using the same analytical method for SPAHs and measuring blank or spiked soil samples in tandem.

4. Incidence

Environmental PAHs typically accumulate in the soil, which may also be the main storage for SPAHs. Research has mainly focused on industrial sites such as power plants, coking plants, and wood mills [9,20,50]. There are also some reports on SPAHs in urban soils. Work on OPAHs and NPAHs in soil has measured surface soil, road dust, and estimated human health risks using computational models. Because PAH derivatives are abundant, SPAHs have garnered research attention. Brorström-Lundén et al. [51] first reported that the background values of OPAHs and NPAHs in soil differed from concentrations in urban areas. After that, more scholars studied OPAHs and NPAHs and found differences in their soil concentrations between land use types (Table 1). Wilcke et al. [42] reported the concentration distribution and correlation between parent compounds and SPAHs in surface soils in Argentina, finding close associations between parent PAHs and their derivatives. Bandowe et al. [44] compared the soil concentrations of 15 OPAHs and 4 NPAHs in Thailand and found relationships with trace metals and that the concentrations and compositions of OPAHs and their parent compounds were similar, but that the ratio of PAHs was higher, perhaps owing to strong local microbial activity and photoactivity. Wei et al. [43] studied road dust and topsoil in Xi'an, China, and reported that PAHs and OPAHs but not NPAHs originated mainly in combustion activities; the enrichment factor in dust and soil was correlated with log octanol–air partition coefficient and log octanol–water partition coefficient. A study in Ghana [45] reported the transformation of PAHs into SPAH derivatives and the higher toxicity of OPAHs and NPAHs. Sun et al. [52] measured the concentrations of 11 NPAHs and 4 OPAHs in agricultural soils of 26 provinces in eastern China and reported that NPAH levels were higher than those of OPAHs, but we believe that this study is not representative. The reason is that the number of the two types of substances studied is quite different. Yadav et al. [53] measured SPAH concentrations in city dust in Nepal and reported that NPAH levels were 2–5 times higher than the levels of parent PAHs. They also concluded that the main exposure route in humans was dermal contact. A study in surface soils in Newcastle, Australia [54] indicated that polar and parent PAHs were widespread. Although it is an industrial city, its overall carcinogenic risk is negligible. According to the research situation of scholars, we mainly compared the occurrence of 14 OPAHs and 11 NPAHs in soil. According to the research situation of scholars, we mainly compared the occurrence of 14 OPAHs and 11 NPAHs in the soil; see Tables 2 and 3 for details.

4.1. OPAHs

For OPAHs, this review also lists a comparison table of different types of single substances around the world (Table 2). Regardless of soil type, the abundance and concentrations of 9-fluorenone are relatively high, which may be closely related to the fate and behavior of its parent PAH. OPAH/PAH (1-INDA/FLUO, 9-FLO/FLUO, 1,2-ACQ/ACENY, and 1,2-ACQ/ACEN) in the topsoil and subsoil in an industrial zone in Uzbekistan ANQ/ANTH) > 1, the OPAHs concentration in the soil is higher than the parent PAHs. The significantly positive correlations between carbonyl-OPAHS and trace metals in industrial waste gas support a common source for PAHs, carbonyl-OPAHS, and trace metals [55]. Higher OPAH concentrations have been associated with human activities, such as low-temperature combustion [42], and the lighter OPAH is detected in the south,

while more OPAHs were detected in the north where human activities are frequent, from north to south 9,10-ANQ/Ant, indicating that it may originate from low-temperature combustion. In addition, the average concentration of Σ OPAHs in street dust in Kumasi, Ghana, is 833 ng g^{-1} . Furthermore, the similar spatial trend of OPAH and alkyl + parent PAHs concentrations is determined by the strong and significantly positive difference between Σ OPAH and Σ alkyl + parent PAHs. The relevance is further confirmed [45]; the composition mode of the OPAH in the street dust of Kumasi mainly consists of 9,10-ANQ, B(A)FLUone, and 9-FLO. The largest amount of 9-FLO was detected in the soil of Newcastle, a famous industrial city in Australia, with a range of $42.8\text{--}1818.1 \text{ ng g}^{-1}$ [54]. Among different land types in the city, the most abundant OPAH is 9-FLO, which, respectively, accounts for 54.5, 44.9, 37.7, and 20.0% of the 7 types of OPAHs in residential, smoking, recreational and industrial areas, followed by 1,4-NQ that accounts for 18.0%, 25.3%, 32.7%, and 46.4% of industrial, smoking, residential and recreational soils accordingly. In industrial soils, BANTone is the most common oxy-PAH, covering 36.6% of 7 oxy-PAHs. However, its contribution to the soil of smoking areas, residential areas, and entertainment venues is relatively small, with 4.1%, 2.2%, and 4.9%, respectively. In soil, OPAH mobility is only slightly higher than that of the low-molecular-weight parent PAHs, which is probably due to complex interactions between OPAHs and PAHs in soil.

4.2. NPAHs

From the perspective of 11 NPAHs that scholars have studied more in recent years, the concentration ranges of substitutes in different land use types do not remain the same (Table 3). Wei et al. [43] investigated the concentrations of 11 NPAHs in the surface soils of Xi'an suburbs. The average concentration was $118 \pm 52 \text{ ng g}^{-1}$, and the higher concentrations were 2 + 3-NFLA and 2,7-DNFLU. Through conducting the analysis with the combustion tracer, it is found that these substances are not derived from combustion activities. The total concentration of 16 NPAHs in road dust in the four cities of Nepal is 2–5 times lower than that of the parent PAHs [56]. 2-NFLUA/1-NPYR represents the secondary contribution from photochemical reactions. Sun et al. [52] analyzed 11 types of NPAHs in the soil of agricultural land in 26 provinces located in Eastern China, and then it was shown that except for 5 types of NPAH, which have a low detection rate. All other substances are logarithmically distributed. Individual NPAH is mostly higher than the soil concentration in other cities. In the meanwhile, from the current study, it was found that higher K_p can make the deposition flux of NPAHs from the air. There are not many studies on polar PAHs in soil, mainly from the above scholars. It can be found that although more scholars have participated in the research of OPAHs and NPAHs, there are still big problems: First of all, there are no unified standards and regulations for the standard samples of the two types of pollutants, which leads to large differences in the research materials of scholars, and there is no way to refer; Secondly, the research on PAC in soil mostly focuses on the occurrence and the associated risk assessment, ignoring formation mechanisms and the dynamics of migration into deeper levels of subsoil. Standardizing the methods and developing techniques for studying both formation mechanisms and migration dynamics should be the next steps in the field.

Table 1. The occurrence of OPAHs and NPAHs in different types of soils.

Region	Land Use	Σ OPAHs (ng g ⁻¹)	# of Oxygen-PAH	Σ NPAHs (ng g ⁻¹)	# of Nitro-PAH	References
Gårdsjön, Sweden	background area	108	8	21	9	[51]
Göteborg, Sweden	urban-diffuse	42–466		11–286		
Patagonian, Argentina	steppe	2.4–38	15	0.05–124	4	[42]
Bangkok, Thailand	urban	12–269	15	0.1–31	4	[44]
Xi'an, China	suburban	854 ± 447	15	118 ± 52	11	[43]
Kumasi, Ghana	urban	833 (57–4202)	10	73 (3–240)	4	[45]
East China	agriculture	9 ± 8	4	50 ± 45	11	[52]
Kathmandu, Nepal	urban	99 (95–384)	3	646 (439–3930)	16	[53]
Pokhara, Nepal		95 (92–433)		568 (409–2030)		
Birgunj, Nepal		115 (93–348)		832 (451–1750)		
Biratnagar, Nepal		606 (227–1150)		2100 (586–24,100)		
Newcastle, Australia	recreation	1515	7	211	3	[54]
	industry	3924		602		
	smoking area	644		239		
	resident	3649		391		

Table 2. Research status of individual OPAH in soil.

Compound	Abbrev	Concentration	References
1-indanone	1-INDA	1.6–35 (industrial area), 0.05–0.54 (steppe), 32.4–59.7 (suburban), 10.5–56.1 (street dust)	[42,43,45,55]
1,4-naphthoquinone	1,4-NQ	0.3–6.7 (industrial area), 2.2–10.7 (suburban), 157.7–1443.1 (industrial heritage)	[43,54,55]
1-naphthaldehyde	1-NLD	1.4–20.6 (industrial area), 0.16 (steppe), 7.9–35 (suburban), 2.6–37.5 (street dust)	[42,43,45,55]
2-biphenylcarboxaldehyde	2-BPCD	0.3–25 (industrial area), 2.15 (steppe), 10.9–22.8 (suburban)	[42,43,55]
9-fluorenone	9-FLO	14–810 (industrial area), 1.02–2.82 (steppe), 371–1243.8 (suburban), 33.2–214.4 (street dust), 0.3–10 (farmland), 42.8–1818.1 (industrial heritage)	[42,43,45,52,54,55]
1,2-acenaphthylene-dione	1,2-ACQ	2.6–14 (industrial area), 1.2 (steppe), 2.4–6.7 (suburban)	[42,43,55]
9,10-anthraquinone	9,10-ANQ	12–959 (industrial area), 0.88–8.9 (steppe), 36.7–92.9 (suburban), 18.1–1241.7 (street dust), 0.9–26 (farmland), 33.2–202.7 (industrial heritage)	[42,43,45,52,54,55]
4H-cyclopenta[d,e,f]phenanthrene-4-one	CPHENone	12.2–48 (suburban), 5.6–131.2 (street dust)	[43,45]
2-methyl-9,10-anthraquinone	2-MANQ	2.3–18 (steppe), 7.9–27.7 (suburban), 7.1–1602.9 (street dust)	[42,43,45]
benzo[a]fluorenone	B(A)FLUone	0.13–5.2 (steppe), 7.1–37 (suburban), 5.7–919.6 (street dust)	[42,43,45]
7H-benz[d,e]anthracene-7-one	BANTone	0.43–16 (steppe), 3.5–19.2 (suburban), 12.7–200.2 (street dust), 25.8–388.3 (industrial heritage)	[42,43,45,54]
benzo[a]anthracene-7,12-dione	7,12-B(A)A	20 (steppe), 12.1–58.1 (suburban), 0.2–8.4 (farmland)	[42,43,52]
5,12-naphthacenequinone	5,12-NACQ	1.5–2.4 (steppe), 2.9–28.6 (suburban)	[42,43]
6H-benzo[c,d]pyrene-6-one	6-BPYRone	1.9–37 (steppe), 2–10.7 (suburban), 6.0–66.0 (street dust)	[42,43,45]

Table 3. Research status of individual NPAH in soil.

Compound	Abbrev	Concentration (ng g ⁻¹)	References
1-Nitronaphthalene	1-NNAPH	0.4–1.8 (suburban), 0.2–267 (farmland), 51.9–77.6 (urban dust), 49.6–205 (industrial heritage)	[43,52–54]
2-Nitrobiphenyl	2-NBP	0.4 (suburban), 0.3–66 (farmland)	[43,52]
5-Nitroacenaphthene	5-NACEN	0.5–3.5 (suburban), 0.7–7.7 (farmland), 35.3–47.8 (urban dust)	[43,52,53]
2-Nitrofluorene	2-NFLU	0.2–0.8 (suburban), 7.5–9.2 (farmland), 21.8–631 (urban dust), 88.7–196 (industrial heritage)	[43,52–54]
9-Nitrophenanthrene	9-NPHEN	0.4–1.9 (suburban), 0.4–17 (farmland), 7.7–84.1 (urban dust)	[43,52,53]
9-nitroanthracene	9-NANT	0.1–0.7 (suburban), 0.2–8.5 (farmland), 0.14–1.24 (urban dust), 21–271(industrial heritage)	[43,52–54]
(2 + 3)-Nitrofluoranthenes	2 + 3-NFLA	5.2–16.3 (suburban), 0.4–29 (farmland)	[43,52]
1-Nitropyrene	1-NPYR	2.3–6.0 (suburban), 8.8 (farmland)	[43,52]
2,7-Dinitrofluorene	2,7-DNFLU	13.0–39.0 (suburban), 2.0–41.0 (farmland), 28.1–44.9 (urban dust)	[43,52,53]
6-Nitrochrysene	6-NCHR	5.7–11.4 (suburban), 26.3–67.2 (urban dust)	[43,53]
6-Nitrobenzo[a]pyrene	6-NBaP	49.9–86.1 (suburban), 50.3–65.9 (urban dust)	[43,53]

5. Toxicity and Human Health Risk

Polar PACs are stable in the environment and can bioaccumulate, and exert toxic and ecotoxicological effects [9,57]. OPAHs and NPAHs are directly mutagenic, and some are estrogenic compounds and generate reactive oxygen species (ROS) responsible for oxidative stress (OS) [58,59]. OPAHs, NPAHs, or the environmental matrix extracts containing OPAHs and NPAHs, have similar or even more obvious toxicity than the related parent PAHs or the PAHs extracts [9,10,58]. The toxicity profile of OPAHs and NPAHs can be seen in Figure 3 outlines the toxic effects of OPAHs and NPAHs in soil.

Polar PAH has received more attention due to its toxicity, persistence, and wide mobility in the soil environment [60]. OPAH is an important class of polar PAHs. Compared with the parent PAH of the same ring, OPAHs have more complex carcinogenic effects due to the existence of negatively charged atoms [61]. Usually, these carcinogenic effects are related to non-enzymatic activation, which will promote the abnormal expression of genes and the mutagenesis of proteins. Similarly, certain NPAHs are also listed as human carcinogens by the International Agency for Research on Cancer (IARC) [62,63]. The substitution of nitrogen atoms in the fused ring structure impacts the physical, chemical, and toxicological properties of NPAHs. In soil, nitrogen may affect the absorption rate of NPAHs and their toxicity to soil organisms. Unlike homocyclic PAHs, the high reactivity of NPAHs and OPAHs may result in volatilization, low adsorption, and high degradation [64]. Relative to their parent PAHs, NPAHs, and OPAHs are weak bases, which can be protonated in soil solution, depending on their basicity and on soil pH [56,65]. In most natural soils, weak bases exist as molecules, and decreases in soil pH may produce the protonated form (cations). These cations can bind with soil cation exchange sites, thereby increasing their half-life and persistence [66].

5.1. Exposure

The exposure pathways are identical for polar PAHs and their parent compounds: water, air, soil, and food through ingestion, inhalation, skin, and eye contact [67–69]. Ingestion of PAHs has been associated more with known morbidities than with other

routes of exposure in humans [70]. NPAHs and OPAHs in the air are produced during the combustion processes of heating, cooking, vehicular traffic, and manufacturing [71–73]. Inhalation is an important exposure route, and levels of NPAH biomarkers are higher in urban populations than in rural ones [74,75]. Inhalation of 1-nitropyrene produced squamous metaplasia and cytoplasmic changes in rats, with a no-observed-adverse-effect level of 0.5 mg/m^3 . NPAHs have been detected in vegetables, fruits, tea, barbecued or baked meat, water, and crop soil [15,76]. Yaffe et al. [70] estimated that the acceptable daily intake of 1-nitropyrene in adults is approximately $9.7 \times 10^{-7} \text{ mg/kg/day}$.

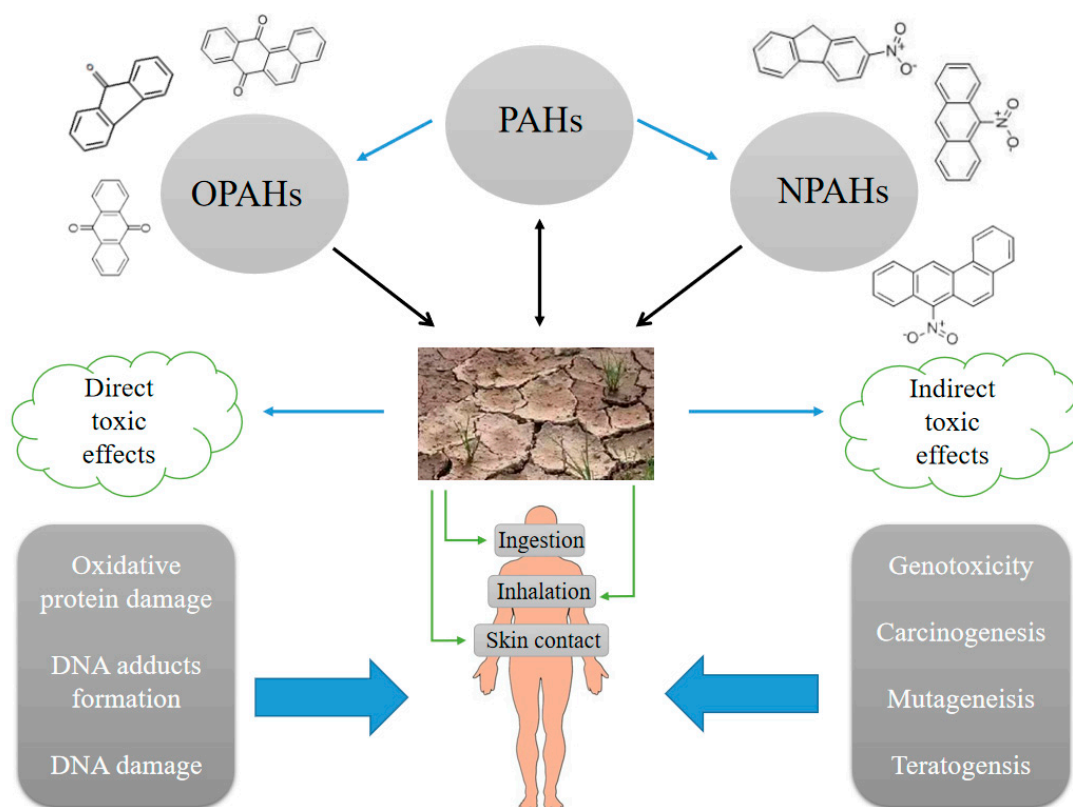


Figure 3. Toxic effects of OPAHs and NPAHs in soil.

5.2. Mutagenicity, Carcinogenicity, and Teratogenicity

There are many PAHs exposed through the soil, which pose a great threat to human health [77–79]. Although PAH does not cause direct DNA damage [80], it can often form highly reactive genetic metabolites through the “activation” effect of organisms in the soil. For example, quinone and anthraquinone, these intermediate products that have the potential to synthesize with DNA [81].

The toxicity of NPAHs in environmental media such as soil, sediments, and air has been studied extensively in multiple test systems. The mutagenicity of several NPAHs and OPAHs was tested in the Salmonella Ames assay [82,83]. For instance, it is shown by the salmonella mutagenicity test (Ames test) that the extracts of soils collected from several Japanese areas ($n = 544$) display mutagenicity. It is suspected that the mutagenicity of these soils is related to others and shown for NPAHs such as 3,6-dinitrobenzene, 1,3,6-trinitropyrene, 3,9-dinitroanthracene, and 3-nitrobenzanthrone [84–88]. These research results verify the mutagenicity, genotoxicity, carcinogenicity, and estrogen activity of the several NPAHs [73,89]. According to the published scientific research results, the human carcinogenic risk assessment workgroup of IARC has classified several SPAHs as the carcinogenic group. Some SPAHs have been assigned a toxic equivalency factor far higher than that of benzo[a]pyrene [90,91].

The mutagenicity of OPAHs and NPAHs in airborne particulates was confirmed *in vitro* [92] and can be double that of the parent PAHs [60]. In the research on human cell mutagenic agents in air-borne inhalable particles in northeast America, OPAH is reported as a highly mutagenic compound *in vitro* [92]. Although *in vitro* and *in vivo* effects of quinones have been described, little is known about the developmental toxicity of OPAHs. Naphthoquinone binds with biological macromolecules, and the alkylation and oxidation/reduction of benzoquinone will produce multiple toxic effects *in vivo*, including oxidative stress, acute cytotoxicity, immunotoxicity, and carcinogenicity [93,94]. Owing to the lack of toxic equivalency factors for NPAHs and OPAHs, it is impossible to correlate the contribution of exposure from the soil with human cancer risks. Instead, the carcinogenicity of polar PAHs is typically compared with that of the parent PAHs [52,56].

5.3. Stress and Genotoxicity

OPAH and NPAH have similar toxicity mechanisms, both of which are related to the ability to activate aromatic hydrocarbon receptors (AhR), and the level of AhR activation can be used as a simple toxicity indicator [83]. The ligand-binding group AhR is an intracellular ligand-activated transcription complex that can activate the transcription of genes related to cytochromes and glutathione S-converting enzymes. The specific action path of AhR is as follows: First, the activated AhR translocates to the nucleus and binds to the AhR nuclear transcription protein (Arnt) in the nucleus to form a heterodimer and then triggers the transcriptional modulation of genes containing heterogeneous response elements [62,95]. The special toxicity of OPAH is reflected in oxidative stress, which is mainly due to the imbalance between reactive oxygen species production and antioxidants [96]. OPAH toxicity may eventually lead to mitochondrial malformations and dysfunction, DNA breakdown, apoptosis, protein and lipid degradation, mutations, and cancer [97]. At the same time, it affects the regulation of gene expression and thus plays a role in tumors [98,99].

The *in vivo* mutagenicity of 2-nitro-fluorinated uranium was also shown in the soil nematode *Caenorhabditis elegans* [100]. The bioluminescent bacterium *Vibrio fischeri* has been used to investigate the short-term toxicity of NPAHs such as 5-nitro-acenaphthene and 5-nitronaphthalene, showing that these compounds were more toxic than related PAHs [101]. In contrast, short-term exposure to 10 NPAHs in algae, Crustacea, or trees of the *Platycladus* genus did not yield evidence of toxicity. A statistically significant increase in genotoxicity was reported in a study that used the DT 40 chicken T lymphocyte bioassay to detect the genotoxicity of soil sample extracts after bioremediation [102]. Using a bioreactor to treat soil contaminated by PAH will increase the genotoxicity of the entire treatment cycle [47,102]. The increase in genotoxicity is attributed to the polar products produced by bioremediation. Due to the production of OPAH and other polar, toxic PAH conversion products, increased mutagenicity was observed after the aerobic bioremediation of soil contaminated by PAH [47]. Using air particle samples, the mutagenicity of OPAH and NPAH components from Beijing is twice that of the parent component [60]. Due to optimization, the bioavailability of soil pollutants may also be improved [103]. Because polar PAHs have high toxicity and potential genetic toxicity to microorganisms, more and more scholars have studied the developmental behavior, fate, and behavior in soil [50,104,105].

6. Transport and Transformation

Soil adsorption of polar PAHs affects their transport, fate, and ecotoxicity. Like other semi-volatile organic pollutants, OPAHs and NPAHs in soil are absorbed into organic matter, and black carbon through nonspecific hydrophobic interactions [28], and the adsorption strength can be described by the compounds' mobility. NPAHs have been shown to have lower mobility than that of their parent PAHs [70,83]. The clay fraction, in particular, is involved in the adsorption of polar PAHs, and the intensity of specific interaction with soil minerals and organic matter is thought to be equal to or higher than the nonspecific hydrophobic interaction [106]. The π - π interactions of the electron-deficient NPAHs and

OPAHs (electron acceptors) with the electron-rich soil organic matter and minerals (electron donors) account for the strong interaction. Other mechanisms include the complexation of a nitril group and cation in clay (e.g., montmorillonite) or of siloxane-containing nitril group and surface oxygen in clay (e.g., kaolinite) [106,107]. Polar PAHs exhibit a high adsorption efficiency to both topsoil and subsoil [19,106], and their concentrations are generally higher in subsoil if the topsoil has been treated with sewage sludge for agricultural purposes; in undisturbed soil. Polar PAHs have low water solubility and are extensively distributed into the solid soil phase, suggesting only negligible vertical through leaching [89]. OPAHs may be transported into the soil through inorganic and organic colloid-assisted transport [19,28,50]. The strong adsorption of NPAHs onto the solid soil phase might be influenced by wind and water erosion.

In addition, many scholars have focused on the biological migration and transformation of PACs in soil. Geng et al. [108] found that the fungi *Neocucurbitaria*, *Penicillium*, *Fusarium*, *Chrysosporium*, *Knufia*, *Filobasidium*, *Wallemia*, and *Rhodotorula* were identified as the keystone taxa, indicating that fungi also had important positions in the interdomain molecular ecological networks of different seasons. Acenaphthylene, benzo[b]fluoranthene, indeno [1,2,3-cd]perylene, benzo[g,h,i]pyrene, and 9-fluorenone were the key environmental factors driving the deterministic assembly processes of the interdomain microbial community in the contaminated soil. The combined bacterial, archaeal, and fungal community structure showed no significant seasonal changes under natural attenuation [11,109]. However, for single microbial communities, bacteria were more sensitive to seasonal variations than fungi and archaea. Similarly, bacteria have been reported to be sensitive to changes in environmental conditions in other studies [110–112]. The differences in sensitivity between bacteria, archaea, and fungi may be due to a large number of contaminant-degrading species in bacteria and the distinctive differences in cellular structure and physiological activity among them [108]. In addition, environmental filtering could govern microbial community assembly [113,114]. These findings extend our knowledge of interdomain microbial community assembly mechanisms and ecological patterns in natural attenuation and provide valuable guidance in associated biotransformation strategies.

As the generation process of PAH derivatives in the soil is relatively irreversible, with the conversion of more parent PAHs to SPAHs, the occurrence of SPAHs in the soil will be greatly accumulated. To our knowledge, no studies have been published on the gas-phase transport of OPAHs or NPAHs in soil, but this transport may be extremely limited because of the compounds' low volatility and strong adsorption to soil. The polar PAHs have low vapor pressure, high octanol-air partition coefficient, and strong adsorption onto soil; therefore, their volatility is estimated to be low. There are still few studies on the fate mechanism of OPAH and NPAH in soil, and further research is needed.

7. Summary and Outlook

This review focused on the state of knowledge in the detection, incidence, toxicity, and fate of OPAHs and NPAHs in soil. SPAHs represented by OPAHs and NPAHs are widespread in the soil environment, and their toxicity and mutagenic properties are more obvious, and their accumulation in organisms is also more complicated. Although their soil concentrations are generally lower than those of their parent compounds, OPAHs and NPAHs are persistent and may pose health risks. Unified testing standards and regulatory control of these compounds are urgently needed, as is research on their exchange between environmental media. The research on related pollutants in the soil also only focuses on the occurrence of surface soil or dust and health risks, and there is a lack of research on the exchange of other media with soil. The adsorption mechanism and vertical distribution in soil and groundwater, as well as the partition between soil solids and pore water, have not been reported. It is also necessary to conduct soil column experiments and infiltration instrument research to simulate its vertical migration in the soil. Due to the lack of relevant research data above, it is necessary to strengthen research to more clearly understand the fate and behavior of OPAHs and NPAHs in the soil environment. According to the

reviewed articles, we can prove that the two types of substances exist and have higher mobility in the soil environment and may cause greater risks to organisms. It could be concluded that PACs should be included in monitoring plans and risk assessment models in the future.

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References

1. Blumer, M. Benzopyrenes in soil. *Science* **1961**, *134*, 474–475. [[CrossRef](#)] [[PubMed](#)]
2. Ravindra, K.; Sokhi, R.; Van Grieken, R. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmos. Environ.* **2008**, *42*, 2895–2921. [[CrossRef](#)]
3. Shen, G.F.; Tao, S.; Wei, S.Y.; Chen, Y.C.; Zhang, Y.Y.; Shen, H.Z.; Huang, Y.; Zhu, D.; Yuan, C.Y.; Wang, H.C.; et al. Field measurement of emission factors of PM, EC, OC, parent; nitro-; and oxy-polycyclic aromatic hydrocarbons for residential briquette, coal cake; and wood in Rural Shanxi; China. *Environ. Sci. Technol.* **2013**, *47*, 2998–3005. [[CrossRef](#)] [[PubMed](#)]
4. Lafamme, R.E.; Hites, R.A. Global distribution of polycyclic aromatic hydrocarbons in recent sediments. *Geochim. Cosmochim. Acta* **1978**, *42*, 289–303. [[CrossRef](#)]
5. Masclat, P.; Hoyau, V.; Jaffrezo, J.L.; Cachier, H. Polycyclic aromatic hydrocarbon deposition on the ice sheet of Greenland. Part I: Superficial snow. *Atmos. Environ.* **2000**, *34*, 3195–3207. [[CrossRef](#)]
6. Cai, C.; Li, J.; Wu, D.; Wang, X.; Tsang, D.C.W.; Li, X.; Sun, J.; Zhu, L.; Shen, H.; Tao, S.; et al. Spatial distribution; emission source and health risk of parent PAHs and derivatives in surface soils from the Yangtze River Delta, eastern China. *Chemosphere* **2017**, *178*, 301–308. [[CrossRef](#)]
7. McCarrick, S.; Cunha, V.; Zapletal, O.; Vondráček, J.; Dreij, K. In vitro and in vivo genotoxicity of oxygenated polycyclic aromatic hydrocarbons. *Environ. Pollut.* **2019**, *246*, 678–687. [[CrossRef](#)]
8. Atkinson, R.; Arey, J. Atmospheric chemistry of gas-phase polycyclic aromatic hydrocarbons: Formation of atmospheric mutagens. *Environ. Health Perspect.* **1994**, *102*, 117–126.
9. Lundstedt, S.; White, P.A.; Lemieux, C.L.; Lynes, K.D.; Lambert, L.B.; Oberg, L.; Haglund, P.; Tysklind, M. Sources; fate; and toxic hazards of oxygenated polycyclic aromatic hydrocarbons (PAHs) at PAH-contaminated sites. *Ambio* **2007**, *36*, 475–485. [[CrossRef](#)]
10. Jung, D.J.K.; Klaus, T.; Fent, K. Cytochrome P450 induction by nitrated polycyclic aromatic hydrocarbons; azaarenes; and binary mixtures in fish hepatoma cell line PLHC-1. *Environ. Toxicol. Chem.* **2001**, *20*, 149–159. [[CrossRef](#)]
11. De Guidi, G.; Falciglia, P.P.; Catalfo, A.; De Guidi, G.; Fagone, S.; Vagliasindi, F.G.A. Soil contaminated with PAHs and nitro-PAHs: Contamination levels in an urban area of Catania (Sicily, southern Italy) and experimental results from simulated decontamination treatment. *Clean Technol. Environ. Policy* **2017**, *19*, 1121–1132. [[CrossRef](#)]
12. Musa Bandowe, B.A.; Wei, C.; Han, Y.; Cao, J.; Zhan, C.; Wilcke, W. Polycyclic aromatic compounds (PAHs, oxygenated PAHs, nitrated PAHs and azaarenes) in soils from China and their relationship with geographic location, land use and soil carbon fractions. *Sci. Total Environ.* **2019**, *690*, 1268–1276. [[CrossRef](#)] [[PubMed](#)]
13. Zhuo, S.; Du, W.; Shen, G.; Li, B.; Liu, J.; Cheng, H.; Xing, B.; Tao, S. Estimating relative contributions of primary and secondary sources of ambient nitrated and oxygenated polycyclic aromatic hydrocarbons. *Atmos. Environ.* **2017**, *159*, 126–134. [[CrossRef](#)]
14. Librando, V.; Fazzino, S. Quantification of polycyclic aromatic hydrocarbons and their nitro derivatives in atmospheric particulate matter of Augusta City. *Chemosphere* **1993**, *27*, 1649–1656. [[CrossRef](#)]
15. Hayakawa, K.; Tang, N.; Akutsu, K.; Murahashi, T.; Kakimoto, H.; Kizu, R. Comparison of polycyclic aromatic hydrocarbons and nitro polycyclic aromatic hydrocarbons in airborne particulates collected in downtown and suburban Kanazawa, Japan. *Atmos. Environ.* **2002**, *36*, 5535–5541. [[CrossRef](#)]
16. Albinet, A.; Leoz-Garziandia, E.; Budzinski, H.; Villenave, E. Polycyclic aromatic hydrocarbons (PAHs); nitrated PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): Concentrations and sources. *Sci. Total Environ.* **2007**, *384*, 280–292. [[CrossRef](#)]
17. De Castro Vasconcellos, P.; Sanchez-Ccoyllo, O.; Balducci, C.; Mabilia, R.; Cecinato, A. Occurrence and concentration levels of nitro-PAH in the air of three Brazilian cities experiencing different emission impacts. *Water Air Soil Pollut.* **2008**, *190*, 87–94. [[CrossRef](#)]
18. Wild, S.R.; Jones, K.C. Polynuclear aromatic-hydrocarbons in the United-Kingdom environment—A preliminary source inventory and budget. *Environ. Pollut.* **1995**, *88*, 91–108. [[CrossRef](#)]
19. Bandowe, B.A.; Meusel, H. Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) in the environment—A review. *Sci. Total Environ.* **2017**, *581–582*, 237–257. [[CrossRef](#)]

20. Hoffmann, T.; Oelmann, Y.; Wilcke, W. Plant diversity enhances the natural attenuation of polycyclic aromatic compounds (PAHs and oxygenated PAHs) in grassland soils. *Soil Biol. Biochem.* **2019**, *129*, 60–70.
21. Burgos, W.D.; Pisutpaisal, N.; Mazzaresse, M.C.; Chorover, J. Adsorption of quinolone to kaolinite and montmorillonite. *Environ. Eng. Sci.* **2002**, *19*, 59–64. [[CrossRef](#)]
22. Weigand, H.; Totsche, K.U.; Kögel-Knabner, I.; Annweiler, E.; Richnow, H.H.; Michaelis, W. Fate of anthracene in contaminated soil: Transport and biochemical transformation under unsaturated flow conditions. *Eur. J. Soil Sci.* **2002**, *53*, 71–81. [[CrossRef](#)]
23. Wilcke, W.; Kiesewetter, M.; Bandowe, B.A.M. Microbial formation and degradation of oxygen-containing polycyclic aromatic hydrocarbons (OPAHs) in soil during short-term incubation. *Environ. Pollut.* **2014**, *184*, 385–390. [[CrossRef](#)] [[PubMed](#)]
24. Schlanges, I.; Meyer, D.; Palm, W.U.; Ruck, W. Identification; quantification and distribution of PAC-metabolites, heterocyclic PAC and substituted PAC in groundwater samples of tar-contaminated sites from Germany. *Polycycl. Arom. Compd.* **2008**, *28*, 320–328. [[CrossRef](#)]
25. Bandowe, B.A.M.; Sobocka, J.; Wilcke, W. Oxygen-containing polycyclic aromatic hydrocarbons (OPAHs) in urban soils of Bratislava; Slovakia: Patterns; relation to PAHs and vertical distribution. *Environ. Pollut.* **2011**, *159*, 539–549. [[CrossRef](#)]
26. Atkinson, R.; Arey, J.; Zielinska, B.; Aschmann, S.M. Kinetics and nitro-products of the gas-phase OH and NO₃ radical-initiated reactions of naphthalene-d₈; fluoranthene-d₁₀, and pyrene. *Int. J. Chem. Kinet.* **1990**, *22*, 999–1014. [[CrossRef](#)]
27. Keyte, I.J.; Harrison, R.M.; Lammel, G. Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons—A review. *Chem. Soc. Rev.* **2013**, *42*, 9333–9391. [[CrossRef](#)]
28. Wilcke, W.; Amelung, W.; Martius, C.; Garcia, M.V.B.; Zech, W. Biological sources of polycyclic aromatic hydrocarbons (PAHs) in the Amazonian rain forest. *J. Plant Nutr. Soil Sci.* **2000**, *163*, 27–30. [[CrossRef](#)]
29. Moeckel, C.; Nizzetto, L.; Di Guardo, A.; Steinnes, E.; Freppaz, M.; Filippa, G.; Camporini, P.; Benner, J.; Jones, K.C. Persistent organic pollutants in boreal and montane soil profiles: Distribution; evidence of processes and implications for global cycling. *Environ. Sci. Technol.* **2008**, *42*, 8374–8380. [[CrossRef](#)]
30. Okere, U.V.; Semple, K.T. Biodegradation of PAHs in ‘Pristine’ Soils from different climatic regions. *J. Bioremed. Biodegrad.* **2012**, *51*, 6. [[CrossRef](#)]
31. Huang, Q.; Weber, W.J. Interactions of soil-derived dissolved organic matter with phenol in peroxidase-catalyzed oxidative coupling reactions. *Environ. Sci. Technol.* **2004**, *38*, 338–344. [[CrossRef](#)] [[PubMed](#)]
32. Nam, J.J.; Thomas, G.O.; Jaward, F.M.; Steinnes, E.; Gustafsson, O.; Jones, K.C. PAHs in background soils from western Europe: Influence of atmospheric deposition and soil organic matter. *Chemosphere* **2008**, *70*, 1596–1602. [[CrossRef](#)] [[PubMed](#)]
33. Semple, K.T.; Morriss, A.W.J.; Paton, G.I. Bioavailability of hydrophobic organic contaminants in soils, fundamental concepts and techniques for analysis. *Eur. J. Soil Sci.* **2003**, *54*, 809–818. [[CrossRef](#)]
34. Wei, C.; Han, Y.; Bandowe, B.A.M.; Cao, J.; Huang, R.-J.; Ni, H.; Tian, J.; Wilcke, W. Occurrence, gas/particle partitioning and carcinogenic risk of polycyclic aromatic hydrocarbons and their oxygen- and nitrogen- containing derivatives in Xi’an, central China. *Sci. Total Environ.* **2015**, *505*, 814–822. [[CrossRef](#)] [[PubMed](#)]
35. Titaley, I.A.; Chlebowski, A.; Truong, L.; Tanguay, R.L.; Massey Simonich, S.L. Identification and toxicological evaluation of unsubstituted PAHs and novel PAH derivatives in pavement sealcoat products. *Environ. Sci. Technol. Lett.* **2016**, *3*, 234–242. [[CrossRef](#)]
36. Krauss, M.; Wilcke, W.; Zech, W. Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in forest soils, depth distribution as indicator of different fate. *Environ. Pollut.* **2000**, *110*, 79–88. [[CrossRef](#)]
37. Arroyo, L.J.; Li, H.; Teppen, B.J.; Johnston, C.T.; Boyd, S.A. Oxidation of 1- naphthol coupled to reduction of structural Fe³⁺ in smectite. *Clays Clay Miner.* **2005**, *53*, 587–596. [[CrossRef](#)]
38. Bamforth, S.M.; Singleton, I. Bioremediation of polycyclic aromatic hydrocarbons, current knowledge and future directions. *J. Chem. Technol. Biotechnol.* **2005**, *80*, 723–736. [[CrossRef](#)]
39. Lemieux, C.L.; Lambert, I.B.; Lundstedt, S.; Tysklind, M.; White, P.A. Mutagenic hazards of complex polycyclic aromatic hydrocarbon mixtures in contaminated soil. *Environ. Toxicol. Chem.* **2008**, *27*, 978–990. [[CrossRef](#)]
40. Murakami, M.; Yamada, J.; Kumata, H.; Takada, H. Sorptive behavior of nitro-PAHs in street runoff and their potential as indicators of diesel vehicle exhaust particles. *Environ. Sci. Technol.* **2008**, *42*, 1144–1150. [[CrossRef](#)]
41. Qiao, M.; Bai, Y.H.; Cao, W.; Huo, Y.; Zhao, X.; Liu, D.; Li, Z. Impact of secondary effluent from wastewater treatment plants on urban rivers, polycyclic aromatic hydrocarbons and derivatives. *Chemosphere* **2018**, *211*, 185–191. [[CrossRef](#)] [[PubMed](#)]
42. Wilcke, W.; Bandowe, B.A.M.; Lueso, M.G.; Ruppenthal, M.; del Valle, H.; Oelmann, Y. Polycyclic aromatic hydrocarbons (PAHs) and their polar derivatives (oxygenated PAHs; azaarenes) in soils along a climosequence in Argentina. *Sci. Total Environ.* **2014**, *473*, 317–325. [[CrossRef](#)] [[PubMed](#)]
43. Wei, C.; Bandowe, B.A.M.; Han, Y.; Cao, J.; Zhan, C.; Wilcke, W. Polycyclic aromatic hydrocarbons (PAHs) and their derivatives (alkyl-PAHs; oxygenated-PAHs; nitrated-PAHs and azaarenes) in urban road dusts from Xi’an; Central China. *Chemosphere* **2015**, *134*, 512–520. [[CrossRef](#)] [[PubMed](#)]
44. Bandowe, B.A.M.; Lueso, M.G.; Wilcke, W. Oxygenated polycyclic aromatic hydrocarbons and azaarenes in urban soils, a comparison of a tropical city (Bangkok) with two temperate cities (Bratislava and Gothenburg). *Chemosphere* **2014**, *107*, 407–414. [[CrossRef](#)] [[PubMed](#)]
45. Bandowe, B.A.M.; Nkansah, M.A. Occurrence; distribution and health risk from polycyclic aromatic compounds (PAHs; oxygenated-PAHs and azaarenes) in street dust from a major West African Metropolis. *Sci. Total Environ.* **2016**, *553*, 439–449. [[CrossRef](#)]

46. Brinkmann, M.; Maletz, S.; Krauss, M.; Bluhm, K.; Schiwy, S.; Kuckelkorn, J.; Tiehm, A.; Brack, W.; Hollert, H. Heterocyclic aromatic hydrocarbons show estrogenic activity upon metabolization in a recombinant transactivation assay. *Environ. Sci. Technol.* **2014**, *48*, 5892–5901. [[CrossRef](#)]
47. Chibwe, L.; Geier, M.C.; Nakamura, J.; Tanguay, R.L.; Aitken, M.D.; Simonich, S.L. Aerobic bioremediation of PAH contaminated soil results in increased genotoxicity and developmental toxicity. *Environ. Sci. Technol.* **2015**, *49*, 13889–13898. [[CrossRef](#)]
48. Zhang, B.-T.; Liu, H.; Liu, Y.; Teng, Y. Application Trends of Nanofibers in Analytical Chemistry. *TrAC Trends Anal. Chem. (Regul. Ed.)* **2020**, *131*, 115992. [[CrossRef](#)]
49. Qiao, M.; Fu, L.J.; Cao, W.; Bai, Y.H.; Huang, Q.X.; Zhao, X. Occurrence and removal of polycyclic aromatic hydrocarbons and their derivatives in an ecological wastewater treatment plant in South China and effluent impact to the receiving river. *Environ. Sci. Pollut. Res.* **2019**, *26*, 5638–5644. [[CrossRef](#)]
50. Han, Y.M.; Bandowe, B.A.M.; Wei, C.; Cao, J.J.; Wilcke, W.; Wang, G.H.; Ni, H.Y.; Jin, Z.D.; An, Z.S.; Yan, B.Z. Stronger association of polycyclic aromatic hydrocarbons with soot than with char in soils and sediments. *Chemosphere* **2015**, *119*, 1335–1345. [[CrossRef](#)]
51. Brorström-Lundén, E.; Remberger, M.; Kaj, L.; Hansson, K.; Palm-Cousins, A.; Andersson, H. *Results from the Swedish National Screening Programme 2008, Screening of Unintentionally Produced Organic Contaminants*; Report B1944; Swedish Environmental Research Institute (IVL): Göteborg, Sweden, 2010.
52. Sun, Z.; Zhu, Y.; Zhuo, S.; Liu, W.; Zeng, E.Y.; Wang, X.; Tao, S. Occurrence of nitro- and oxy-PAHs in agricultural soils in eastern China and excess lifetime cancer risks from human exposure through soil ingestion. *Environ. Int.* **2017**, *108*, 261–270. [[CrossRef](#)] [[PubMed](#)]
53. Yadav, I.C.; Devi, N.L.; Singh, V.K.; Li, J.; Zhang, G. Concentrations, sources and health risk of nitrated- and oxygenated-polycyclic aromatic hydrocarbon in urban indoor air and dust from four cities of Nepal. *Sci. Total Environ.* **2018**, *643*, 1013–1023. [[CrossRef](#)] [[PubMed](#)]
54. Idowu, O.; Semple, K.T.; Ramadass, K.; O'Connor, W.; Hansbro, P.; Thavaman, P. Analysis of polycyclic aromatic hydrocarbons (PAHs) and their polar derivatives in soils of an industrial heritage city of Australia. *Sci. Total Environ.* **2020**, *699*, 134303. [[CrossRef](#)] [[PubMed](#)]
55. Musa Bandowe, B.A.; Shukurov, N.; Kersten, M.; Wilcke, W. Polycyclic aromatic hydrocarbons (PAHs) and their oxygen-containing derivatives (OPAHs) in soils from the Angren industrial area, Uzbekistan. *Environ. Pollut.* **2010**, *158*, 2888–2899. [[CrossRef](#)] [[PubMed](#)]
56. Yadav, I.C.; Devi, N.L.; Li, J.; Zhang, G. Polycyclic aromatic hydrocarbons in house dust and surface soil in major urban regions of Nepal, implication on source apportionment and toxicological effect. *Sci. Total Environ.* **2018**, *616–617*, 223–235. [[CrossRef](#)] [[PubMed](#)]
57. Bleeker, E.; Wiegman, S.; de Voogt, P.; Kraak, M.; Leslie, H.A.; de Haas, E.; Admiraal, W. Toxicity of azaarenes. *Rev. Environ. Contam. Toxicol.* **2002**, *173*, 39–83.
58. Machala, M.; Ciganek, M.; Blaha, L.; Minksova, K.; Vondrak, J. Aryl hydrocarbon receptor-mediated and estrogenic activities of oxygenated polycyclic aromatic hydrocarbons and azaarenes originally identified in extracts of river sediments. *Environ. Toxicol. Chem.* **2001**, *20*, 2736–2743.
59. Xue, W.L.; Warshawsky, D. Metabolic activation of polycyclic and heterocyclic aromatic hydrocarbons and DNA damage, a review. *Toxicol. Appl. Pharmacol.* **2005**, *206*, 73–93. [[CrossRef](#)]
60. Wang, W.; Jariyasopit, N.; Schrlau, J.; Jia, Y.; Tao, S.; Yu, T.W.; Dashwood, R.H.; Zhang, W.; Wang, X.; Simonich, S.L. Concentration and photochemistry of PAHs; NPAHs; and OPAHs and toxicity of PM_{2.5} during the Beijing Olympic games. *Environ. Sci. Technol.* **2011**, *45*, 6887–6895. [[CrossRef](#)]
61. Andersson, J.T.; Achten, C. Time to say goodbye to the 16 EPA PAHs? Toward an up-to-date use of PACs for environmental purposes. *Polycycl. Arom. Compd.* **2015**, *35*, 330–354. [[CrossRef](#)]
62. Chlebowski, A.C.; Garcia, G.R.; La Du, J.K.; Bisson, W.H.; Truong, L.; Massey Simonich, S.L.; Tanguay, R.L. Mechanistic investigations into the developmental toxicity of nitrated and heterocyclic PAHs. *Toxicol. Sci.* **2017**, *157*, 246–259. [[CrossRef](#)] [[PubMed](#)]
63. Trine, L.S.D.; Davis, E.L.; Roper, C.; Truong, L.; Tanguay, R.L.; Simonich, S.L.M. Formation of PAH derivatives and increased developmental toxicity during steam enhanced extraction remediation of creosote contaminated superfund soil. *Environ. Sci. Technol.* **2019**, *53*, 4460–4469. [[CrossRef](#)] [[PubMed](#)]
64. WHO. *Selected Nitro-; and Nitro-Oxy-Polycyclic Aromatic Hydrocarbons: Environmental Health Criteria*; WHO: Geneva, Switzerland, 2003; Volume 229.
65. The Most Neglected Threat to Public Health in China is Toxic Soil. *Economist*, 13 June 2017.
66. Doucette, W.; Dettenmaier, E.K.; Bugbee, B.; Mackay, D. Mass transfer from soils to plants. In *Handbook of Chemical Mass Transport in the Environment*; Thobodeaux, L.J., Mackay, D., Eds.; CRS Press: Boca Raton, FL, USA, 2011; pp. 389–411.
67. Rengarajan, T.; Rajendran, P.; Nandakumar, N.; Lokeshkumar, B.; Rajendran, P.; Nishigaki, I. Exposure to polycyclic aromatic hydrocarbons with special focus on cancer. *Asian Pac. J. Trop. Biomed.* **2015**, *5*, 182–189. [[CrossRef](#)]
68. Yang, J.; Zhang, H.; Zhang, H.; Wang, W.; Liu, Y.; Fan, Y. Smoking modify the effects of polycyclic aromatic hydrocarbons exposure on oxidative damage to DNA in coke oven workers. *Int. Arch. Occup. Environ. Health* **2017**, *90*, 423–431. [[CrossRef](#)]

69. Mortamais, M.; Pujol, J.; van Drooge, B.L.; Macia, D.; Martinez-Vilavella, G.; Reynes, C.; Sabatier, R.; Rivas, I.; Grimalt, J.; Forn, J.; et al. Effect of exposure to polycyclic aromatic hydrocarbons on basal ganglia and attention-deficit hyperactivity disorder symptoms in primary school children. *Environ. Int.* **2017**, *105*, 12–19. [[CrossRef](#)]
70. Yaffe, D.; Cohen, Y.; Arey, J.; Grosovsky, A.J. Multimedia analysis of PAHs and nitro-PAH daughter products in the Los Angeles Basin. *Risk Anal.* **2001**, *21*, 275–294. [[CrossRef](#)]
71. Ciganek, M.; Raszyk, J.; Kohoutek, J.; Ansorgová, A.; Salava, J.; Palac, J. Polycyclic aromatic hydrocarbons (PAHs; nitro-PAHs; oxy-PAHs) polychlorinated biphenyls (PCBs) and organic chlorinated pesticides (OCPs) in the indoor and outdoor air of pig and cattle houses. *Vet. Med.* **2000**, *43*, 217–226.
72. Miller-Schulze, J.P.; Paulsen, M.; Toriba, A.; Tang, N.; Hayakawa, K.; Tamura, K.; Dong, L.; Zhang, X.; Simpson, C.D. Exposures to particulate air pollution and nitro-polycyclic aromatic hydrocarbons among taxi drivers in Shenyang; China. *Environ. Sci. Technol.* **2010**, *44*, 216–221. [[CrossRef](#)]
73. IARC. Diesel and gasoline engine exhausts and some nitroarenes. In *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*; IARC: Lyon, France, 2012; Volume 105, pp. 1–703.
74. Zwirner-Baier, I.; Neumann, H.G. Polycyclic nitroarenes (nitro-PAHs) as biomarkers of exposure to diesel exhaust. *Mutat. Res. Genet. Toxicol. Environ. Mutagen.* **1999**, *141*, 135–144. [[CrossRef](#)]
75. Seidel, A.; Dahmann, D.; Krekeler, H.; Jacob, J. Biomonitoring of polycyclic aromatic compounds in the urine of mining workers occupationally exposed to diesel exhaust. *Int. J. Hyg. Environ. Health* **2002**, *204*, 333–338. [[CrossRef](#)]
76. Alves, C.A.; Vicente, A.M.P.; Gomes, J.; Nunes, T.; Duarte, M.; Bandowe, B.A.M. Polycyclic aromatic hydrocarbons (PAHs) and their derivatives (oxygenated-PAHs, nitrated-PAHs and azaarenes) in size-fractionated particles emitted in an urban road tunnel. *Atmos. Res.* **2016**, *180*, 128–137. [[CrossRef](#)]
77. Baird, W.M.; Hooven, L.A.; Mahadevan, B. Carcinogenic polycyclic aromatic hydrocarbon-DNA adducts and mechanism of action. *Environ. Mol. Mutagen.* **2005**, *45*, 106–114. [[CrossRef](#)] [[PubMed](#)]
78. Chen, S.-C.; Liao, C.-M. Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources. *Sci. Total Environ.* **2006**, *366*, 112–123. [[CrossRef](#)] [[PubMed](#)]
79. Lemieux, C.L.; Long, A.S.; Lambert, I.B.; Lundstedt, S.; Tysklind, M.; White, P.A. Cancer risk assessment of polycyclic aromatic hydrocarbon contaminated soils determined using bioassay-derived levels of benzo[a]pyrene equivalents. *Environ. Sci. Technol.* **2015**, *49*, 1797–1805. [[CrossRef](#)]
80. Martins, M.; Costa, P.M.; Ferreira, A.M.; Costa, M.H. Comparative DNA damage and oxidative effects of carcinogenic and non-carcinogenic sediment-bound PAHs in the gills of a bivalve. *Aquat. Toxicol.* **2013**, *142–143*, 85–95. [[CrossRef](#)]
81. Moorthy, B.; Chu, C.; Carlin, D.J. Polycyclic aromatic hydrocarbons, from metabolism to lung cancer. *Toxicol. Sci.* **2015**, *145*, 5–15. [[CrossRef](#)]
82. Rosenkranz, H.; Mermelstein, R. The mutagenic and carcinogenic properties of nitrated polycyclic aromatic hydrocarbons. In *Nitrated Polycyclic Aromatic Hydrocarbons*; White, C.M., Ed.; Huethig: Heidelberg, Germany, 1985; pp. 267–297.
83. Idowu, O.; Semple, K.T.; Ramadass, K.; O'Connor, W.; Hansbro, P.; Thavamani, P. Beyond the obvious, environmental health implications of polar polycyclic aromatic hydrocarbons. *Environ. Int.* **2019**, *123*, 543–557. [[CrossRef](#)]
84. Takahashi, K.; Asanoma, M.; Yoshida, S.; Ning, G.; Mori, H.; Horibe, Y.; Watanabe, T.; Hirayama, T.; Nukaya, H.; Mizutani, T. Identification of 1;3;6-trinitropyrene as a major mutagen in organic extracts of surface soil from Nagoya city; Japan. *Genes Environ.* **2006**, *28*, 160–166. [[CrossRef](#)]
85. Watanabe, T.; Takahashi, K.; Konishi, E.; Hoshino, Y.; Hasei, T.; Asanoma, M.; Hirayama, T.; Wakabayashi, K. Mutagenicity of surface soil from residential areas in Kyoto city; Japan; and identification of major mutagens. *Mutat. Res.* **2008**, *649*, 201–212. [[CrossRef](#)]
86. Hasei, T.; Watanabe, T.; Endo, O.; Sugita, K.; Asanoma, M.; Goto, S.; Hirayama, T. Determination of 3;6-dinitrobenzo[e]pyrene in surface soil and airborne particles; and its possible sources; diesel particles and incinerator dusts. *J. Health Sci.* **2009**, *55*, 567–577. [[CrossRef](#)]
87. Kawanishi, M.; Watanabe, T.; Hagio, S.; Ogo, S.; Shimohara, C.; Jouchi, R.; Takayama, S.; Hasei, T.; Hirayama, T.; Oda, Y.; et al. Genotoxicity of 3;6-dinitrobenzo[e]pyrene; a novel mutagen in ambient air and surface soil; in mammalian cells in vitro and in vivo. *Mutagenesis* **2009**, *24*, 279–284. [[CrossRef](#)] [[PubMed](#)]
88. Kato, T.; Totsuka, Y.; Hasei, T.; Watanabe, T.; Wakabayashi, K.; Kinae, N.; Masuda, S. In vivo examination of the genotoxicity of the urban air and surface soil pollutant, 3;6-dinitrobenzo[e]pyrene; with intraperitoneal and intratracheal administration. *Environ. Toxicol.* **2013**, *28*, 588–594. [[CrossRef](#)] [[PubMed](#)]
89. IPCS. Selected Nitro- and Nitro-oxy-polycyclic Aromatic Hydrocarbons. Environ Health Criteria No. 229. In *International Programme on Chemical Safety*; IPCS: Geneva, Switzerland, 2003; pp. 1–400.
90. Collins, J.; Brown, J.; Alexeeff, G.; Salmon, A. Potency equivalency factors for some polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbon derivatives. *Regul. Toxicol. Pharmacol.* **1998**, *28*, 45–54. [[CrossRef](#)]
91. Davie-Martin, C.L.; Stratton, K.G.; Teeguarden, J.G.; Waters, K.M.; Simonich, S.L.M. Implications of bioremediation of polycyclic aromatic hydrocarbon contaminated soils for human health and cancer risk. *Environ. Sci. Technol.* **2017**, *51*, 9458–9468. [[CrossRef](#)]
92. Pedersen, D.U.; Durant, J.L.; Penman, B.W.; Crespi, C.L.; Hemond, H.F.; Lafleur, A.L. Human-cell mutagens in respirable airborne particles in the northeastern United States. 1. Mutagenicity of fractionated samples. *Environ. Sci. Technol.* **2004**, *38*, 682–689. [[CrossRef](#)]

93. Bolton, J.L.; Trush, M.A.; Penning, T.M.; Dryhurst, G.; Monks, T.J. Role of quinones in toxicology. *Chem. Res. Toxicol.* **2000**, *13*, 135–160. [[CrossRef](#)] [[PubMed](#)]
94. Ghosal, D.; Ghosh, S.; Dutta, T.K.; Ahn, Y. Current state of knowledge in microbial degradation of polycyclic aromatic hydrocarbons (PAHs), a review. *Front. Microbiol.* **2016**, *7*, 1369.
95. Benigni, R.; Bossa, C. Mechanisms of chemical carcinogenicity and mutagenicity, a review with implications for predictive toxicology. *Chem. Rev.* **2011**, *111*, 2507–2536. [[CrossRef](#)] [[PubMed](#)]
96. Geier, M.C.; Chlebowski, A.C.; Truong, L.; Massey Simonich, S.L.; Anderson, K.A.; Tanguay, R.L. Comparative developmental toxicity of a comprehensive suite of polycyclic aromatic hydrocarbons. *Arch. Toxicol.* **2018**, *92*, 571–586. [[CrossRef](#)]
97. Wincent, E.; Jönsson, M.E.; Bottai, M.; Lundstedt, S.; Dreij, K. Aryl hydrocarbon receptor activation and developmental toxicity in zebrafish in response to soil extracts containing unsubstituted and oxygenated PAHs. *Environ. Sci. Technol.* **2015**, *49*, 3869–3877. [[CrossRef](#)]
98. Dranka, B.P.; Benavides, G.A.; Diers, A.R.; Giordano, S.; Zelickson, B.R.; Reily, C.; Zou, L.; Chatham, J.C.; Hill, B.G.; Zhang, J.; et al. Assessing bioenergetic function in response to oxidative stress by metabolic profiling. *Free Radic. Biol. Med.* **2011**, *51*, 1621–1635. [[CrossRef](#)] [[PubMed](#)]
99. Knecht, A.L.; Goodale, B.C.; Truong, L.; Simonich, M.T.; Swanson, A.J.; Matzke, M.M.; Anderson, K.A.; Waters, K.M.; Tanguay, R.L. Comparative developmental toxicity of environmentally relevant oxygenated PAHs. *Toxicol. Appl. Pharmacol.* **2013**, *271*, 266–275. [[CrossRef](#)] [[PubMed](#)]
100. Beije, B.; Moller, L. 2-Nitrofluorene and related compounds, prevalence and biological effects. *Mutat. Res.* **1988**, *196*, 177–209. [[CrossRef](#)] [[PubMed](#)]
101. El-Alawi, Y.S.; McConkey, B.J.; Dixon, D.G.; Greenberg, B.M. Measurement of short- and long-term toxicity of polycyclic aromatic hydrocarbons using luminescent bacteria. *Ecotoxicol. Environ. Saf.* **2002**, *51*, 12–21. [[CrossRef](#)]
102. Hu, J.; Nakamura, J.; Richardson, S.D.; Aitken, M.D. Evaluating the effects of bioremediation on genotoxicity of polycyclic aromatic hydrocarbon contaminated soil using genetically engineered; higher eukaryotic cell lines. *Environ. Sci. Technol.* **2012**, *46*, 4607–4613. [[CrossRef](#)]
103. Musa Bandowe, B.A.; Bigalke, M.; Kobza, J.; Wilcke, W. Sources and fate of polycyclic aromatic compounds (PAHs; oxygenated PAHs and azaarenes) in forest soil profiles opposite of an aluminium plant. *Sci. Total Environ.* **2018**, *630*, 83–95. [[CrossRef](#)]
104. Aranda, E.; Godoy, P.; Reina, R.; Badia-Fabregat, M.; Rosell, M.; Marco-Urrea, E.; García-Romera, I. Isolation of Ascomycota fungi with capability to transform PAHs, insights into the biodegradation mechanisms of *Penicillium oxalicum*. *Int. Biodeterior. Biodegrad.* **2017**, *122*, 141–150. [[CrossRef](#)]
105. Behera, B.K.; Das, A.; Sarkar, D.J.; Weerathunge, P.; Parida, P.K.; Das, B.K.; Thavamani, P.; Ramanathan, R.; Bansal, V. Polycyclic Aromatic Hydrocarbons (PAHs) in inland aquatic ecosystems, perils and remedies through biosensors and bioremediation. *Environ. Pollut.* **2018**, *241*, 212–233. [[CrossRef](#)]
106. Li, Y.; Liao, X.; Huling, S.G.; Xue, T.; Liu, Q.; Cao, H.; Lin, Q. The combined effects of surfactant solubilization and chemical oxidation on the removal of polycyclic aromatic hydrocarbon from soil. *Sci. Total Environ.* **2019**, *647*, 1106–1112. [[CrossRef](#)]
107. Keiluweit, M.; Kleber, M. Molecular-level interactions in soils and sediments: The role of aromatic π -systems. *Environ. Sci. Technol.* **2009**, *43*, 3421–3429. [[CrossRef](#)]
108. Geng, S.Y.; Xu, G.M.; Cao, W.; You, Y.; Zhu, Y.; Ding, A.Z.; Fan, F.Q.; Dou, J.F. Occurrence of polycyclic aromatic compounds and potentially toxic elements contamination and corresponding interdomain microbial community assembly in soil of an abandoned gas station. *Environ. Res.* **2022**, *212*, 113618. [[CrossRef](#)] [[PubMed](#)]
109. Bourhane, Z.; Lanzén, A.; Cagnon, C.; Said, O.B.; Mahmoudi, E.; Coulon, F.; Atai, E.; Borja, A.; Cravo-Laureau, C.; Duran, R. Microbial diversity alteration reveals biomarkers of contamination in soil-river-lake continuum. *J. Hazard Mater.* **2022**, *421*, 126789. [[CrossRef](#)] [[PubMed](#)]
110. Wang, B.B.; Teng, Y.; Yao, H.Y.; Christie, P. Detection of functional microorganisms in benzene [a] pyrene-contaminated soils using DNA-SIP technology. *J. Hazard Mater.* **2021**, *407*, 124788. [[CrossRef](#)] [[PubMed](#)]
111. Lu, C.; Hong, Y.; Odinga, E.S.; Liu, J.; Tsang, D.C.W.; Gao, Y.Z. Bacterial community and PAH-degrading genes in paddy soil and rice grain from PAH-contaminated area. *Appl. Soil Ecol.* **2021**, *158*, 103789. [[CrossRef](#)]
112. Chen, Z.S.; Hu, H.Y.; Xu, P.; Tang, H.Z. Soil bioremediation by *Pseudomonas brassicacearum* MPDS and its enzyme involved in degrading PAHs. *Sci. Total Environ.* **2022**, *813*, 152522. [[CrossRef](#)] [[PubMed](#)]
113. Liu, Y.L.; Hu, H.Y.; Zanolli, G.; Xu, P.; Tang, H.Z. A *Pseudomonas* sp. strain uniquely degrades PAHs and heterocyclic derivatives via lateral dioxygenation pathways. *J. Hazard Mater.* **2021**, *403*, 123956. [[CrossRef](#)] [[PubMed](#)]
114. Brzeszcz, J.; Kaszycki, P. Aerobic bacteria degrading both n-alkanes and aromatic hydrocarbons: An undervalued strategy for metabolic diversity and flexibility. *Biodegradation* **2018**, *29*, 359–407. [[CrossRef](#)]

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