Biodegradation of PAHs in ‘Pristine’ Soils from Different Climatic Regions

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are an important class of organic contaminants ubiquitously found in soils globally. Their fate in soil varies depending on both soil properties and chemical structure; however, microbial degradation represents the most significant means of loss. It is therefore important to understand the factors that control PAH biodegradation in different soil environments. This review considers PAH biodegradation in “pristine” Antarctic, temperate, tropical and hot desert soils. Pre-exposure of indigenous microbes to PAHs is important for the development of the capacity to degrade PAHs so PAH sources to these soils are discussed. The role of PAH bioavailability in the biodegradation of PAHs in ‘pristine’ soils from different climatic regions is also discussed as well as the factors that control it. Soil organic matter, water content and temperature are seen as the main environmental factors that control PAH bioavailability in these soils. With most studies focussing on temperate soils, there is need for more research on soils from other climatic zones.

Keywords: Bioavailability; Biodegradation; Deserts; Temperate; Tropical; Soils

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important class of hydrophobic organic contaminants (HOCs) widely found in the environment. They have been studied with increasing interest for more than twenty years because of more findings about their toxicity, environmental persistence and prevalence [16,20,57,83,147,149].

PAHs are produced into the environment through natural and anthropogenic sources. Natural sources include their formation as biogenic precursors during early diagenesis [22,76,140] and production by plants and termites [15,75,140]. Production from anthropogenic activities such as petroleum oil refining, combustion, transportation and spillage and the use of domestic heaters are however more significant [51,147]. PAHs are widely distributed in the environment as products of incomplete combustion, and have been detected in various environmental samples including air [51], water [126], sediments [152] and soil [67,68].

The soil environment appears to be the ultimate sink for PAHs as, globally, soils store more than 90% of the total PAHs found in the environment [1,147]. PAHs are delivered into background soils mainly by atmospheric deposition [68,133,144], but the proximity to point sources and soil properties (mainly soil organic matter and total organic carbon) have been found to affect concentrations [21,69]. Moreover, high concentrations of PAHs have been found in urban and roadside soils [69,88], with even higher concentrations found at sites impacted by organic contamination [94,103]. PAHs have been shown to accumulate mainly in the organic layer in soils [126], with a positive correlation between soil PAHs and soil organic matter reported [94,146]. Knowledge of soil PAH concentrations can be used to estimate PAH sources to soil. Since soils may act both as a sink for high molecular weight (HMW) PAHs and as a source of low molecular (LMW) PAHs to the atmosphere, this knowledge is important [37,131,151]. In fact, PAH concentrations in soil have been reported to significantly correspond with levels in air [131], house dust [33] and urban street dust [124]. PAHs differ from other groups of organic compounds because of their unique physical and chemical properties. These properties control their transport and behaviour in the environment.

Physico-Chemical Properties of PAHs

Individual PAHs differ significantly in their physical and chemical properties (Table 1) and can be divided into low molecular weight (e.g., 2 to 3 ring PAHs like naphthalenes, fluorenes, phenanthrenes, and anthracenes) and high molecular weight PAHs (4 to 7 ring PAHs from chrysenes to coronenes). Generally, LMW PAHs are more soluble, and volatile and less hydrophobic [81,153]. As a result, they are more easily lost from the environment. Many HMW PAHs (e.g., benzo[a]pyrene and benzo[b]fluoranthene, benzo(e)pyrene and benzo(j) fluoranthene) are structural isomers with the same molecular weight but different structural formulae. Purified HMW PAHs (five benzene rings and above) are solids and generally do not volatilize because their melting points are greater than 100°C [81]. HMW PAHs also have large resonance energies which make them thermodynamically stable though they can be photo-oxidized at various aromatic positions to form quinones. An example is when benzo[a]pyrene undergoes photoysis. Increase in hydrophobicity endows these chemicals with high octanol: water partition coefficients (kOC) as a result of which they tend to adsorb to soil organic matter, are less bioavailable and therefore are not easily degraded giving rise to greater persistence in soil. High molecular weight PAHs are therefore naturally recalcitrant in the soil environment [25,58].

Fate and Behaviour of PAHs in Soil

When PAHs enter soil, they can be lost or removed by a number of physical, chemical or biological processes. For example, photo-

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<table>
<thead>
<tr>
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<th>Molecular Weight</th>
<th>Structure</th>
<th>Melting Point (°C)</th>
<th>Water Solubility (mg litre(^{-1}))</th>
<th>Log (K_{ow})</th>
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Table 1: Physical and chemical properties of selected PAHs.
oxidation and/or volatilization to the atmosphere, leaching to ground water, irreversible sorption to soil organic matter, uptake by plants and microbial degradation are some of these processes [109,122] (Figure 1). The rate at which these loss processes occur and the extent to which a PAH is affected is dependent on a number of factors including soil type (mineral and organic matter contents), the physico-chemical properties of the individual PAH, soil temperature and moisture, redox potential, nutrients availability, presence and activity of degrading microorganisms and bioavailability of the PAH to degrading microorganisms. [99,108].

Figure 2 shows the possible fate of a PAH in soil [122]. Compounds with low $K_{ow}$ high water solubility and volatility are more mobile and degradable. As a result, they are lost rapidly when they enter the soil (A). Many contaminants however, show a biphasic behaviour where though losses are clearly occurring, the rate and extent of the losses decrease as contact time between the soil and contaminant(s) increase (B). This process has been termed ageing [59,117]. C represents the loss pattern of a recalcitrant PAH in soil [122]. The major biotic means by which PAHs are lost from soils is through degradation by bacteria and bioavailability is crucial to PAH biodegradation in soil [23,30,100,123].

**Bioavailability/Bioaccessibility and Biodegradation of PAHs in Soil**

**Bioavailability/bioaccessibility**

Two steps are involved in the biodegradation of PAHs in soil. The first is the physical uptake of the PAH by the microbial cell and the second is the biological metabolism of the PAH [84]. The second step is a function of the intrinsic biological ability of the microorganism to degrade the PAH but the first is a function of the physical availability of the compound to the cell. Assuming the presence of an adequate metabolic pathway, the degradation of a PAH can only proceed rapidly if the PAH is available to the microorganism in a form (usually in the aqueous phase) that the organism can utilise it [93,115]. Where this is non-existent, the biodegradation of the PAH will be limited by the bioavailability of the PAH to the microorganism. Despite its importance to biodegradation (and by extension to contaminated land assessment), the concept of bioavailability has struggled to progress from a mere research topic to a practical tool for the assessment and management of risks associated with contaminated land. This difficulty is due mainly to confusing and disagreeing definitions (arising from the varied use of the term in different fields) and the absence of a fast and cost effective tool for measuring bioavailability [44,56,107,113]. Semple et al. [113] proposed the use of two definitions, rather than a single term: “bioavailable” and “bioaccessible”. The authors defined the bioavailable compound as “that which is freely available to cross an organism’s cellular membrane from the medium the organism inhabits at a given time” [113]. By contrast, the bioaccessible compound is “that which is available to cross an organism’s cellular membrane from the environment, if the organism has access to the chemical” [113]. The difference between the bioavailable and bioaccessible fractions according to their definition is that whereas the bioavailable compound is available to cross the organisms’ cellular membrane (for degradation, transformation or exertion of a toxic effect) now, the bioaccessible compound can only do so when a restraint in time and/or space has been removed. In other words, the bioaccessible compound comprises that which is actually bioavailable now and that which is potentially bioavailable. Figure 3 conceptualises the bioavailable and bioaccessible fractions of a contaminant in soil [113]. Both of these definitions are important because bioavailability is a descriptor for potential rates of biodegradation; whereas, bioaccessibility describes realistic biodegradation endpoints [107,114]. The significance of defining bioavailability by the terms suggested by the authors lies in the fact that it raises questions about what is actually being measured by current methods that claim to measure the bioavailable fraction.

The concept of ageing (Figure 2) is important to the bioavailability of PAHs in soil [9]. Decreased bioavailability of PAHs to degrading microbes due to sequestration/aging in soil has been reported and two processes have been proposed to be responsible for this. The first is the diffusion of PAHs through dissolution sites present in the rubbery and glassy phases of soil organic matter. Contaminants that diffuse through the glassy phase interact more with soil organic matter because of the presence of more rigid cavities [150]. The second process occurs when surfaces within the nano- and micro-pores in soils adsorb contaminants diffusing through them [102]. Since soils contain many pores with diameters less than 20 nm [9], any PAHs that diffuse into such pores become unreachable by degrading bacteria, resulting in their reduced bioavailability.

**Biodegradation**

Biodegradation of PAHs by microorganisms and the pathways involved have been extensively reviewed elsewhere [13,30,55,70,101,117,155]. Several bacteria capable of degrading PAHs in soils have also been isolated and identified [49,60-62,128]. Biodegradation of PAHs in soil does not depend on the PAH properties alone [40] but also on environmental conditions [86], soil properties [85], bioavailability of the PAH [97] and the degradation potential of the indigenous microorganisms [82].
Temperature, soil moisture content, alkalinity, soil nutrient content and pre exposure to PAHs are some of the environmental and soil properties affecting PAH biodegradation in soil. Generally, bacterial metabolic activity and PAH biodegradation increases with increasing temperature up to an optimum temperature reported to be around 30°C to 40°C [78,156]. Hydrocarbon utilizing bacteria can also adapt to temperature extremes to maintain metabolic activity. Hydrocarbon degradation has therefore been reported at temperatures close to freezing and above 30°C [5,10]. The optimum moisture level for the biodegradation of oil sludge reported in literature is between 30% - 90% of the soil’s water holding capacity [129]. At higher water contents, there is a risk of the onset of anaerobic conditions arising from the slow rate of oxygen diffusion through water. At lower water contents, water availability becomes a limiting factor to microbial activity or PAH bioavailability. PAH degradation has also been shown to be favoured in slightly alkaline soils, as PAH-degrading bacteria become less competitive with increasing acidic conditions [84]. Bacteria require nutrient elements, such as nitrogen and phosphorus for incorporation into biomass and the synthesis of cellular components. The presence of these nutrient elements in soil is therefore critical for the biodegradation of PAHs [14]. The optimisation of the C:N:P ratio is thought to be one of the most important amendments enhancing the rates and extents of PAH biodegradation in soil. It is generally accepted that optimum ratios for PAH biodegradation is approximately 100:10:1 [123].

PAH biodegradation in soil is inducible [79] but the processes through which indigenous soil microbes develop the capacity or “learn” to degrade PAHs are not fully understood [63]. However, the pre-exposure of soils to PAH concentrations higher than background PAH levels [65,121] and a change in the genetic composition of the indigenous soil microbial community are thought to be important factors affecting the process [130]. A change in the genetic composition of the indigenous soil microbial community is necessary where the indigenous microbes have not been exposed to either naturally occurring or anthropogenic compounds similar to the PAH of interest.

In a study to investigate the relationship between pre exposure and metabolism of PAHs in soil, all 14C PAHs, studied except 14C benzo[a]pyrene, were readily mineralized in most of the pre exposed soils, whereas in the uncontaminated soil, less than 5% of each 14C PAH was mineralized [28]. In a similar study to assess the development of pyrene catabolic activity in two similar soils (pasture and woodland), significant decreases in the lag times and significant increases in the maximum rates and extents of 14C-pyrene mineralised were observed with increasing soil-pyrene contact time [83]. The workers also found that the microbial community in the pasture soil (with lower soil organic...
matter) adapted to use pyrene before the community in the woodland soil. This observation was attributed to decreased bioavailability of pyrene in the woodland soil due to a higher soil organic matter content.

Having noted the importance of pre-exposure to the development of PAH degrading capacity and the dependence of PAH bioavailability and biodegradation on soil and environmental factors, this review aims to consider existing knowledge on PAH levels, bioavailability and indigenous biodegradation in background soils from extreme temperature environments, temperate environments and tropical environments.

Biodegradation of PAHs in Soils from Different Climatic Zones

Antarctic soils

Although Antarctic soils are diverse, they have all been generally described as cold, sandy, desert soils, with minimal effective annual precipitation, high pH, low organic matter and nutrient contents and rare occurrences of vegetation, mostly lichens and mosses [5,27]. Mean monthly temperatures in the continental Antarctic region where the most extreme conditions are found are below -15˚C all year round, falling to below -30˚C in winter [135]. Less than 0.35% of the entire terrestrial Antarctic continent is ice free, the remainder is permanently under the cover of ice [45]. Despite this tiny proportion of the continent being ice-free and exposed to weathering processes, there is significant microbial diversity in Antarctic soils. Different PAH degrading microorganisms have been found [29]: up to 13 MPN g-1 [5], 230 MPN g-1 [4] and 7×10⁴ CFU g−1 [112] of hydrocarbon degrading bacteria have been reported to be present in uncontaminated Antarctic soils. Most of these PAH degraders were identified as bacteria rather than fungi [71], e.g. Flavobacterium spp., Corynebacterium spp., Bacillus spp. an isolate from the family of Enterobacteriaceae [71], Pseudomonas spp. or Sphingomonas spp. related to PAH degradative strains from lower latitudes [3,17] and Acinetobacter [80] are some of those isolated from Antarctic soils. These degraders were psychrotolerant, able to tolerate temperatures >20˚C and capable of growing at near 0˚C. They were also able to degrade monoaromatic hydrocarbons, naphthalene as well as its methyl derivatives [3,71].

The presence of PAH-degrading bacteria in background soils is a good indicator that the soils have been exposed to PAHs [26], even at low concentrations. Long range atmospheric transport of low molecular weight PAHs and increased human presence and activity in the Antarctic represent the main sources of PAHs in these soils. Human activities require hydrocarbons for heating, power generation and to power land and air transport vehicles. Elevated levels of PAHs in Antarctic soils have therefore been found mostly in soils with close proximity to current or former scientific bases, fuel stores or automobile or aircraft fuelling stations [8,125]. Accidental discharge of petroleum products during storage and distribution from drums and pipelines is also a significant source [53]. PAHs in uncontaminated Antarctic soils are also either undetectable or detected at background levels [4,5]. For instance, a study was carried out to compare PAH concentrations at fuel spill sites to uncontaminated control sites in three Antarctic locations: Scott Base, Marble Point and Wright Valley. The study found PAH concentrations in the contaminated sites to range from 41 – 8,105 ng g⁻¹ of dry soil. PAHs were, however, undetectable at the control soils [2]. PAH concentrations of up to 27,000 mg kg⁻¹ have also been detected in contaminated soils at McMurdo Station, Antarctica; the highest concentrations were found in soils from unpaved roadbeds and gasoline pumps [89]. Where PAHs have been found in uncontaminated Antarctic soils, low molecular weight PAHs (phenanthrene and fluoranthene) are usually prevalent and are present at levels consistent with pre-industrial times [137]. This is an indication that while local sources are responsible for high levels of PAHs in contaminated soils, long range atmospheric transport from populated areas of Africa, South America, and Australia is the most likely source of PAHs to background Antarctic soils [72].

The fate of PAHs in Antarctic soils includes volatilisation, dispersal, transformation or degradation as a result of physical, chemical and biological processes. Lighter PAHs volatise readily from Antarctic soils and can migrate through soil layers [53]. Less volatile fractions tend not to migrate far from their point of deposition [42]. Lighter molecular weight PAHs are expected to be available for microbial degradation in Antarctic soils [7] because these soils are typically dry and have low organic matter contents. Since the sequestration of organic compounds in dry soils with < 4% moisture is controlled by adsorption onto mineral surfaces and not organic matter [18,134], PAH biodegradation in Antarctic soils should not be limited by sequestration to soil organic matter. PAH bioavailability may however, be limited by poor water activity [78]. Because of the low moisture contents of Antarctic soils, PAHs and microbes may not be able to move around sufficiently enough to come in contact for biodegradation. Microbial degradation of PAHs in Antarctic soils has been measured in microcosms [5] and mesocosms [36]. Low moisture content, alkaline soil pH [5], and low temperature [6,41] have been identified as the limiting factors for PAH biodegradation in Antarctic soils; however, nutrient availability and temperature fluctuations are considered to be the most important [36,132].

When high concentrations of PAHs are introduced into Antarctic soils, they have the potential to further deplete the already low amounts of N and P present in the soils when they are used up by microorganisms during biodegradation [4]. Enhanced biodegradation of PAHs has been achieved in Antarctic soils by the addition of fertilizers containing N and P. For instance ¹⁴C-naphthalene was mineralised to a greater extent when N was added as nitrate or ammonium [5]. The addition of nutrients to the coarse-textured, low-moisture soils prevalent in continental Antarctica has the potential to inhibit PAH biodegradation by decreasing soil water potentials, care must therefore be taken to add the right amount of nutrients and there is no consensus on what that right amount is because of the varying soil and environmental conditions prevalent in Antarctica [6].

Temperature limits the biodegradation of PAHs in Antarctic soils by affecting the physical nature of the PAHs and the metabolic activity of the degrading microbes [36]. At low temperatures, PAHs are more viscous, less volatile and less soluble resulting in reduced bioavailability and subsequent biodegradation [78]. Metabolic activity of PAH-degrading microbes at low temperatures are reduced because they follow the Arrhenius relationship, increasing with increasing temperature [78], usually doubling for each 10°C increase in temperature from 10°C to 40°C [24,36]. As a result, though PAH biodegradation has been reported at low temperatures [46], increasing the temperature has often resulted in increased rates and extents of PAHs degradation [73,136].

Temperate soils

Temperate environments are characterised by their general mildness and four distinct seasons with summer and winter roughly of equal length. 35% - 40% of the global human population live in the hospitable temperate environment comprising roughly 7% of the
Earth's surface area [38]. Temperate and tropical soils share many soil types, making the distinction between them artificial; however, characteristics like soil temperature and soil moisture are often different between the two across all soil types [118]. Temperate soils are different from tropical soils firstly because during a significant portion of the year (winter), they are exposed to sub-optimal or freezing temperatures resulting in reduced biological activity and changes in the physical and chemical properties of the soils. Secondly, agricultural soils in temperate environments are generally younger than soils from the tropics [110]. It is also generally believed that the residence times of organic matter/carbon is longer in temperate soils than in tropical soils due mainly to reduced rates of decomposition arising from lower temperatures and moisture levels in temperate regions [127].

In soils throughout the temperate zone, PAH profiles are similar [137], showing correlations between individual PAH concentrations [143] and a quantitative dominance of higher molecular weight PAHs (e.g. chrysene, pyrene, fluoranthene) produced mainly due to anthropogenic activities [43,94,138]. This similarity in PAH profiles has been explained by the “weathering” of emissions from different sources in the atmosphere, resulting from the transformation of PAHs from different sources during atmospheric transport [66].

Levels of PAHs in background soils from Western Europe have been found to cover a wide range of concentrations from 8.6 to 11,200 μg kg⁻¹ [94]. Land use plays an important role in PAH concentrations in temperate soils. For instance, PAHs in agricultural soils amended with sewage sludge have been reviewed [19], showing the effects of the introduction of sewage sludge can have on PAH concentrations. Sewage sludge may enhance the removal of PAHs from the soil by the introduction of microorganisms adapted to PAH degradation or by increasing the leachability of PAHs through the movement of dissolved organic matter. Conversely, the application of sewage sludge can introduce more organic matter into the soil, resulting in greater sorption of PAHs and subsequent retention in the soils [145]. Long term studies of archived UK agricultural soils amended with sewage sludge revealed PAH levels were three times higher than unamended control soils, particularly with higher molecular weight PAHs [145,148]. The implication may be that the addition of sewage sludge to temperate agricultural soil does more to enhance the retention of PAHs than their losses.

PAH concentrations in temperate soils also differ according to soil type. In most cases, concentrations of persistent organic pollutants are lower in grassland soils than in woodland/forest soils because of the greater ability of the forest canopy to scavenge for persistent organic pollutants [90]. Selected Norwegian grassland soils have been found to have generally lower PAH levels than neighbouring forest systems [94].

Urban temperate soils are often associated with increased human activity resulting in high PAH levels relative to soils from less populated rural areas [69,74]. Distance from point sources, climatic conditions and soil organic matter are other factors that influence levels of PAHs in urban soils. Positive correlations have been drawn between PAH concentrations in temperate soils and soil organic matter [67,94,147].

PAH degraders have been found in pristine soil samples from Norway (up to 2.4 x10⁸ CFU g⁻¹ soil) and Denmark (up to 6.6 x 10⁸ CFU g⁻¹ soil), agricultural soils (up to 9.9 x10⁶ CFU g⁻¹ soil), diffusely polluted (up to 1.1 x 10⁷ CFU g⁻¹ soil) and industrially polluted (up to 1.7 x 10⁷ CFU g⁻¹ soil) soils from Denmark. This shows the ubiquitous presence of PAH degraders following the ubiquitous presence of PAHs in temperate soils. In fact, a correlation has been found between the total PAHs in a temperate soil and the potential for PAH mineralisation in the soil suggesting the dependence of PAH degradation potential on the level of PAH contamination [65]. While studying the total and bioaccessible amounts of PAHs present at a motorway site north of Copenhagen and the prevalence of microbial PAH degraders as well as the potential for PAH degradation, the highest levels of PAH contamination were found in samples closest to the motorway. The highest numbers of bacterial PAH degraders and the greatest potential for PAH biodegradation were also found in the same soils. The fact that the highest levels of PAH contamination was found in the soil with the highest numbers of bacterial PAH degraders appear contradictory and raises questions about PAH persistence. The authors suggested that low bioavailability of PAHs and not a limitation in the bacterial population was responsible for the accumulation of PAHs in the soil with a high number of bacterial PAH degraders. A measurement of the bioaccessible PAH fractions showed that only 1-5 % of the PAHs were actually accessible to the soil microorganisms for degradation. Adsorption of PAHs to soot particles released from diesel engines was given as a possible reason for the reduced bioavailability and consequent reduced biodegradation of the PAHs [64]. Higher soil organic matter content in temperate soils has also been found to result in slower adaptation of indigenous soil microorganisms to PAH degradation [83]. In a study, two similar temperate soils (pasture and woodland) were amended with 100 mg pyrene kg⁻¹ and significant mineralisation of ¹⁴Cpyrene was observed after 8 and 76 weeks soil pyrene contact time respectively. The addition of microbial inocula led to the mineralisation of the previously added ¹⁴C pyrene implying that it was bioavailable but the indigenous microflora had not adapted to its degradation. As the only difference between the two soils was a higher organic matter content in the woodland soil, the authors suggest that the rate of pyrene organic matter content in the woodland soil, the authors suggest that the rate of pyrene transfer from the soil to the microorganisms was slower in the woodland soil due to its higher organic matter content leading to slower adaptation of the microorganisms and subsequent biodegradation. Despite PAH-degrading microorganisms being ubiquitously distributed through temperate soils, the major limiting factor for PAH degradation appears to be bioavailability as controlled by soil type and soil organic matter content.

**Tropical soils**

Geographically, the tropics can be defined as that part of the world located between 23.5 degrees north and south of the equator, representing the land mass between the Tropic of Cancer and the Tropic of Capricorn. Tropical environments are largely warmer than temperate environments with much less temperature variations between seasons. Approximately 87% of the global tropical areas are usually above 25°C. Differences in amounts of precipitation and solar radiation further distinguish between tropical and temperate climates [12,32].

The generalisations that can be drawn from the characteristics of tropical soils have been reviewed as follows: (i) the types and properties of clay minerals are much more varied in the tropics than in glaciated temperate areas; (ii) many tropical soils exhibit significant anion exchange capacity; (iii) organic matter contents in the tropics are similar to those of the temperate region; (v) although the annual addition of organic carbon to the soil is five times greater in tropical udic environments than temperate udic environments, the rate of organic decomposition is also five times greater in the tropics; (v) in udic environments, lack of soil moisture during the dry season decreases organic carbon decomposition just as low temperatures do.
in temperate regions; (vi) the vast majority of the soils of the humid tropics are acidic, and (vii) the vast majority of the cultivated soils of the humid tropics are not acidic [34].

In comparison to temperate soils, published data on the PAH levels of tropical soils is considerably less [35]. Available data show that generally, PAH levels in most tropical soils are lower than in temperate soils. For instance, PAH levels in soils from Lahore, Pakistan were considerably lower than those in soils collected from Birmingham, UK (which were representative of UK PAH levels) even though atmospheric levels were higher [119]. PAH levels of 5 ng g\(^{-1}\) dry weight have been reported for Costa Rican soil [39]. \(\Sigma^{20}\)PAHs in 30 hydromorphic soils of the tropical metropolis of Bangkok was found to range between 12 and 380 \(\mu\)g kg\(^{-1}\) [142]. Higher PAH levels have been found in temperate UK (42 and 11,200 \(\mu\)g kg\(^{-1}\)) and Norway (8.6 and 1,050 \(\mu\)g kg\(^{-1}\)) background soils [69,94]. Shorter PAH accumulation time in tropical soils and enhanced PAH losses through biodegradation, volatilisation, photo-oxidation, and leaching into groundwater have been proposed as the reason why PAHs levels are lower in tropical soils [142]. Although the \(\Sigma^{20}\)PAHs in tropical soils is often less than in temperate soils, low molecular weight PAHs (naphthalene and phenanthrene) are most prevalent and are present at levels comparable to those in temperate soils [39].

Soil-PAH fingerprints are often defined by soil type and PAH sources into the soil. PAHs enter tropical environments mostly through on-going biomass burning and vehicular traffic [137]. By contrast, fossil fuel combustion (known to release higher molecular weight four and five ring PAHs) dominate PAH sources of PAHs into temperate soils [139]. Also, a longer history of industrialisation in the temperate region implies historical PAH sources. This suggest that over time, the more volatile, biodegradable lower molecular weight PAHs would have been removed from temperate soils [68]. Biologically derived PAH sources known to produce low molecular weight PAHs have also been identified as sources of low molecular weight PAHs into tropical soils [139-141].

Microbial diversity in soils is determined by vegetation type, carbon and nutrient availability, soil moisture and soil pH. Soils with similar environmental characteristics will therefore have similar bacterial communities irrespective of geographical location [48]. Studies where indigenous PAH degraders are enumerated in tropical soils are rare but tropical soils with similar properties as temperate soils can be expected to contain similar microbial communities. The presence of microorganisms with the necessary genes for PAH degradation in contaminated tropical soils have been reported [54]. For example, thirty three distinct species of bacteria, fungi and yeast capable of degrading PAHs were collected from petroleum polluted soils and cyanobacteria mats from Indonesia [31]. Also, three \textit{Pseudomonas} species LP1, LP2 and LP3 were isolated from an oil polluted soil in Lagos, Nigeria. They were able to degrade a broad range of PAHs including up to 67.79%, 66.61% and 47.09% of pyrene respectively [95].

Moisture and temperature are the main factors that influence microbial activities in which tropical and temperate soils differ. Tropical soils have higher temperatures all year round [77]. Rates of PAHs degradation in tropical soils are therefore generally expected to be higher than in temperate soils. The higher rates of organic matter turn over observed in tropical soils support this argument [34]. Moisture should therefore be the controlling/limiting factor of microbial activity in tropical soil [98]. PAH biodegradation can be controlled by moisture either directly because microbial activity can be inhibited by poor soil moisture or indirectly by affecting PAH transport and bioavailability [116].

**Hot deserts**

Desert soils can be found globally except in Europe. They are characterised by poor organic matter and water levels, are usually subjected to rather high temperatures (up to 50˚C) and extensive light [104]. There is a paucity of data relating to the sources and levels of PAHs in background hot desert soils because most studies on background soils have been conducted using temperate soils [87]. However, both short and long range atmospheric transport of PAHs and proximity of hot deserts to PAH point sources play significant roles in the background concentration of PAHs in desert soils [52].

Temperature is significant to the fate of PAHs in desert soils. Because of the hydrophobic nature of PAHs and their consequently reduced solubility, PAH volatilisation, solubility and bioavailability are controlled by temperature. At high temperatures, PAHs are less viscous, more easily distributed and can diffuse faster. Bioavailability of some PAHs can therefore be enhanced at elevated temperatures [47]. On the other hand, bioavailability and biodegradation of PAHs can be inhibited by the poor moisture content of the soils. Increased bioavailability and subsequent biodegradation has been achieved by repeated irrigation of polluted desert soils [105,106]. Biodegradation of PAHs in extremely hot desert soils requires the activity of thermophilic bacteria but not much is known about PAH degradation by thermophiles in soil [86,96]. A few microbes capable of degrading PAHs at very hot temperatures have been isolated. For example, \textit{Bacillus thermoleovorans}, which grows at 60˚C, has been isolated from a compost consisting of wooden ties treated with lignite tar and was able to utilise naphthalene as a sole carbon source [11]. \textit{Nocardia otitidiscaviarum} which grows optimally at 50˚C has also been shown to possess PAH degrading capabilities [154]. Other microorganisms able to degrade naphthalene, phenanthrene and anthracene under thermophilic conditions have also been isolated [47,92]. Some of these microbes were found to produce metabolites that were different from those produced during the biodegradation of PAHs by mesophilic bacteria [92]. A new pathway was also identified when \textit{Bacillus thermoleovorans} degraded naphthalene at 60˚C [11]. For some time, it was assumed that at elevated temperatures, reduced oxygen solubility limited effective aerobic degradation of PAHs but more recent discoveries have shown that at elevated temperatures, the oxygen transfer coefficient rises thereby compensating for the reduction in oxygen solubility [86].

**Conclusion**

PAHs are an important class of environmental contaminants produced by both natural and anthropogenic processes. The importance of soil as a reservoir of organic pollutants means that PAHs can now be found in virtually all global soils irrespective of nature or location. When PAHs enter a soil, they interact with the soil in different ways leading to either retention or less depending on the physical, chemical and biological characteristics of the soil. Since global soils differ in their characteristics, the fate of PAHs in soils also differ and it may not always be correct to extrapolate the fate of a PAH in one soil type to another. This makes understanding the interactions between PAHs and soils from different environments important. The weight of available information on these interactions leaves heavily in favour of temperate soils. More research is therefore needed into PAH-soil interactions in tropical and desert soils.
References


