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► **To cite this version:**

Pascale Henner, Michel Schiavon, Jean-Louis Morel, Eric Lichtfouse. Polycyclic aromatic hydrocarbon (PAH) occurrence and remediation methods. *Analysis*, 1997, 25 (9-10), pp.M56-M59. hal-00193277

HAL Id: hal-00193277

<https://hal.science/hal-00193277>

Submitted on 3 Dec 2007

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Revised version

Analisis Magazine 25, M56-M59, 1997.

Correspondence: Dr. Eric Lichtfouse, INRA-CMSE-PME, 17, rue Sully, 21000 Dijon, France

Eric.Lichtfouse@dijon.inra.fr

Polycyclic aromatic hydrocarbons (PAH) occurrence and remediation methods

Pascale HENNER, Michel SCHIAVON, Jean-Louis MOREL and Eric LICHTFOUSE*

Laboratoire Sols et Environnement, INRA/ENSAIA-INPL, 2, avenue de la Forêt de Haye, BP 172, 54505 Vandoeuvre-Lès-Nancy, France.

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are potentially mutagenic and carcinogenic substances occurring at various concentrations in atmosphere, soils, waters and sediments. PAHs, inherited both from natural and anthropogenic processes, are persistent organic pollutants (POP) due to their chemical stability and biodegradation resistance. The increase of road transportation, and of industrial and agricultural activities has led to a notable build up of PAH amounts in the environmental media. For cases of heavy soil pollution, the main remediation methods are containment, thermal desorption, incineration, and microbial degradation. Phytoremediation, a low-cost process based on microbial activation in the root zone, is a novel method under deep investigation.

Résumé

Les hydrocarbures aromatiques polycycliques (HAP) sont des substances potentiellement mutagènes et cancérigènes présentes à des concentrations variables dans l'atmosphère, les sols, les eaux et les sédiments. Les HAP, issus de processus naturels ou anthropiques, sont des polluants organiques persistants (POP) de part leur inertie chimique et leur résistance à la biodégradation. L'accroissement des transports routiers, des activités industrielles et agricoles a induit une augmentation notable de la quantité d'HAP dans l'environnement moderne. Dans les situations de pollutions massives du sol, les principales techniques de réhabilitation sont l'isolement, la désorption thermique, l'incinération, et la biodégradation microbienne. La phytoremédiation des HAP, un processus bon marché fondé sur l'activation des micro-organismes du sol par les racines, est une nouvelle méthode en plein développement.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), some of which are known precursors of mutagenic derivatives, are widely occurring in natural media such as soil, sediment, water, air and plants as a result of both natural and anthropogenic processes [1 and refs. therein]. The main PAH sources are highlighted in Table 1. Since natural fires and petroleum formation have been occurring all through earth times, PAHs have undoubtedly been circulating through biogeochemical cycles for millions of years. Nonetheless, the increasing use of fossil fuels and their combustion products by human beings during the two past centuries raises several questions about PAHs hazards for living organisms. First, apart from accidental oil spills leading to massive pollutions, the precise origin of trace PAHs, e.g. natural vs. anthropogenic, is rarely clear. Second, the toxicity of PAHs, like other hazardous chemicals, requires their bioavailability. And since most PAHs are highly hydrophobic, their pathways of transfer through geological and biological media are far from being understood. Third, unambiguous correlations between PAH sources and carcinogenic effects have been reported only for intense exposure to PAHs such as for coal-mine workers. Here we report the major aspects about PAHs in the literature with emphasis on molecular structures and properties, origin and distribution, analytical methods, fate in the soil-plant system and remediation techniques.

* Author for correspondance

Table 1

Main sources of polycyclic aromatic hydrocarbons (PAH)	
PETROGENIC SOURCES (fossil fuels)	PYROGENIC SOURCES (combustion products)
PETROLEUM	VEHICLE EXHAUSTS
COAL	ROAD AIRBORNE PARTICLES
ANCIENT SEDIMENTS	INDUSTRIAL FUMES
	VEGETATION FIRES

2. Molecular structure and properties

The molecular structures of the 16 PAHs defined as priority pollutants by the American Environmental Protection Agency (EPA) are drawn on Figure 1. PAHs are relatively neutral and stable molecules, including one or more benzenic rings, substituted or not, on a linear or angular layout. PAHs have low solubilities [2, 3] and low volatilities, except small components like naphthalene. Their lipophilicity is high, as measured by water-octanol partition coefficients (Kow). PAH show long half-lives in geological media. In an aerobic sediment, for example, half lives range from 3 weeks for naphthalene up to 300 weeks for benzo[a]pyrene [4]. PAHs are regarded as persistent organic pollutants (POP) in the environment. This persistence is increasing with ring number and condensation degree [5].

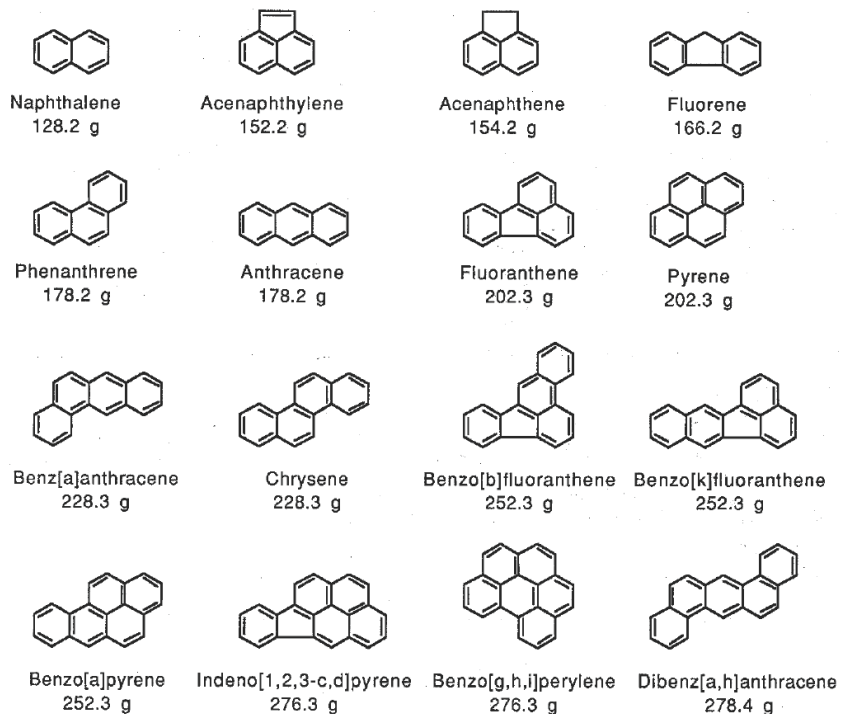


Figure 1. Molecular structure of the 16 polycyclic aromatic hydrocarbons (PAHs) selected as priority pollutants by the American Environmental Protection Agency (EPA). Numbers are molecular weights.

3. Toxicity

The carcinogenicity levels of some PAHs are given in Table 2. Monoaromatic hydrocarbons such as benzene-toluene-xylene mixtures (BTX) are known phytotoxic [6], albeit the mechanisms of growth inhibition are unclear. BTX either disturb exchanges between seeds, soil and atmosphere, or they alter plant tissues. Higher PAHs are less phytotoxic in the short term, but some of them and their metabolites are suspected to be mutagenic and carcinogenic (Table 1). Indeed, their ability to form DNA adducts can induce mutations.

Table 2. Carcinogenicity levels of PAHs [7]. Keys : (-) no effect, (+-) very weakly active, (+) weakly active, (+++) active, (+++++) very active.

PAH	CARCINOGENICITY
Naphthalene	(-)
Anthracene	(-)
Pyrene	(-)
Chrysene	(+-)
Benz[a]anthracene	(+)
Dibenz[a,h]anthracene	(+++)
Benzo[a]pyrene	(+++++)

Some PAHs, like benzo[a]pyrene, are immunodepressive in a dose-response manner, a property correlated with carcinogenicity [7]. PAHs present a risk for the environment, especially if they can enter the food chain through contact, inhalation or ingestion. A link has been disclosed between coal exposure and cancer among coal miners and chimney sweepers [7], but here other carcinogenic substances than PAHs may be responsible. In fact, very few data assessing a correlation between a pure PAH and cancer in humans are available. Effects on human beings are therefore assumed to be the same as the ones observed on mice, guinea-pigs, and other animals.

4. Indigenous sources

PAHs may be indigenous as a result of rapid aromatization of biological compounds during humification processes. They can also reflect contributions from ancient hydrocarbon sources, such as coal residues, provided that the soil has been initially formed by weathering of a petroleum source-rock or coal seam. These sources are regarded as natural or pristine.

5. Exogenous sources

These sources include either natural inputs, e.g. the migration of petroleum from deeper horizons, or anthropogenic inputs such as fossil fuel spills and deposition of airborne particles from car exhausts. Nevertheless, the precise origin of PAHs in airborne particles from pristine areas is difficult to assess. Vegetation fires are both natural and anthropogenic sources of PAHs. It is sometimes possible to distinguish, on structural grounds, petrogenic sources that account for the direct contribution of uncombusted fossil fuel, from pyrolytic or pyrogenic sources formed at relatively high temperatures by the incomplete combustion of fossil fuels and vegetation fires.

6. Distribution

PAHs are found worldwide in soils and sediments, even in the most pristine areas such as the Poles [8-10]. Reported background contents of PAHs in soils of North America and Europe extend from 50 to 500 $\mu\text{g.kg}^{-1}$ [9]. Because vehicles, heating systems and waste incineration exhausts are the main anthropogenic sources, PAHs contents increase in the vicinity of large urban and industrial areas [4,8,10]. PAHs are carried at long distances by air in the troposphere, bound to particulate carbon. Thus, they can form a worldwide deposit by wet or dry deposition [11]. Indeed, the qualitative distribution of PAHs in modern media are often similar, strengthening the influence of the well-mixed airborne source [8]. This source include a major part of PAHs produced by pyrolysis at moderate temperature, e.g. fires and car exhausts. Since the beginning of the industrial revolution, the rate of deposition has exceeded the rate of degradation in the soils [4]. Consequently, PAHs accumulate in the top soil.

7. Fate of PAHs

The main pathways of PAHs are shown on Figure 2. PAHs are hydrophobic compounds whose mobility in the soil-plant system is low [3]. Equilibriums between solid, aqueous and vapour phases are very slow. As for pesticides [12], PAHs and their metabolites are expelled from the aqueous phase to adsorb on the hydrophobic surfaces such as organic matter [13-15]. They are either trapped in the pores, fixed with covalent or hydrogen bonds, or bound during humification processes [16]. PAHs structure and stability stand in the way of their biodegradation [17] by micro-organisms, e.g. fungi and bacteria. Biodegradation is slow and is a function of environmental parameters such as oxygen, water and nutrient contents. Migration of PAHs from the top soil is slow. PAHs seem to migrate bounded to particles [4]. The major ways of entry of PAHs in the plant seems to be through the leaves, from the vapour phase and by contact with contaminated soil particles [18]. Entry through roots and translocation to shoots is still hypothetic because the way to xylem requires PAHs (compounds with very low solubilities) to solubilize in the symplasm. PAHs seem also to adsorb on the root cell walls.

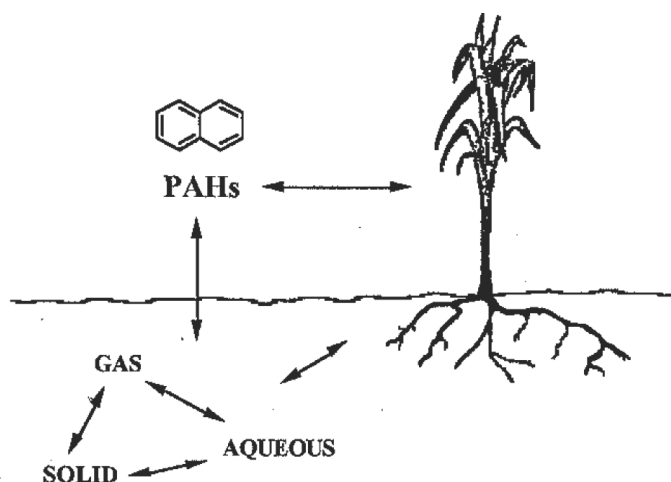


Figure 2. Main possible pathways of PAHs in the soil-plant system.

8. Analysis

Extraction of PAHs in soils is mainly conducted with several methods : shake, humic acid extraction, supercritical fluid, soxhlet and ultrasonic bath. Soxhlet and ultrasonic extractions give similar yields [19]. Yields decrease with increasing soil organic matter and pollutant contents. Bound residues are usually not available with these techniques [20,21]. A part of bound residues may be recovered by humic acid extraction, e.g. with 0.1 M NaOH. Identification and quantification of PAHs is currently achieved by liquid chromatography coupled to UV detector, or by gas chromatography coupled to mass spectrometry (GC-MS).

9. Remediation of PAH contaminated soils

The strategies of PAH remediation depend on the extent of contamination, the horizontal and vertical limits of the pollution as well as its qualitative and quantitative content [22]. While containment withdraws temporarily the pollutants, the other treatments attempt to remove, stabilize or degrade them.

9.1 Containment

Contaminated materials are enclosed in physical, chemical or hydraulic barriers which prevent the pollutants to migrate and contaminate groundwaters [23-25]. In France, monitoring rules for containment are as strong as for rubbish dumps. For example, waters circulating through the site must be continuously collected and analysed. Access to and use of the site are restricted. This technique is usually temporarily used while waiting for an another way of treatment.

9.2 Thermal techniques

Incineration and thermal desorption are the most effective and used techniques, although their cost is relatively high because they involve soil excavation, transport then heat treatment [22-25]. Soil can be used freely after treatment.

9.3 Physical and chemical techniques

Pollutants may be first extracted then transferred in gaz or liquid phases. These fluids are then specifically treated. For instance, volatile and soluble compounds can be extracted with vacuum, air or water. Non volatile or non soluble compounds such as high molecular weight PAHs are extracted with the help of surfactants, acids, heat or physical treatments to enhance their availability [22-25]. Alternatively, when the later methods fail, the application of an electric current may favor the migration of pollutants by electro-osmosis.

9.4 Microbial degradation

Bioremediation uses the natural capacity of soil micro-organisms to degrade PAHs. Degradation conditions are optimized by aeration, agitation, moistening and addition of nutriments. Genetically engineered strains, with multiple degradative abilities, are usually less competitive than well-adapted natural strains. Landfarming is a technique whereby pollutants are incorporated in a top layer of an agricultural soil [5,26]. No culture is conducted on the soil during the treatment. Nutriments are incorporated to stimulate bioactivity. Degradation is performed during the whole year, except in winter when humification process is greater.

Composting is another way of treatment. Composting of petroleum by-products may be performed with high contents of pollutant. Here, the compost structure is optimized by adding

agents like sawdust, wood cuttings, coco fibers, moss, sand or vermiculite. Enhanced degradation is achieved by aeration, humidification and regular mixing of compost piles.

On the other hand, bioreactors are laboratory scale units now effectively used on an industrial scale. Bioreactors are either fixed or rotative. They can be loaded either with soil samples or with slurry phases [20,27-30]. Here, the inoculum is usually either a given volume of soil with its natural microflora or engineered strains. Because the degradative ability depends on plasmids, new plasmid-enriched strains have been designed.

9.5 Phytoremediation

Phytoremediation is the use of plants, their associated microflora and agronomical techniques to lower soil toxicity by extraction, degradation and stabilisation of the pollutants [22]. It fulfills the need of an efficient and low-cost on-site remediation technique. Here, plant roots modify favourably the life habitat of micro-organisms by exudate release [31,32], nutrients supply, e.g. nitrogen and sugars, and aeration and water drainage [22]. Roots also increase the contact surface between micro-organisms, soil and pollutants [33]. Further, the number and diversity of micro-organisms are greatly increased in the rhizosphere, as well as the metabolic capacities and specific associations like mycorrhizae [33]. Therefore, biodegradation of PAHs should be quicker and greater in the presence of plants.

Indeed, several recent studies show that the concentration of organic pollutants such as PAHs can be notably reduced by vegetation [13,31,33-37]. However, since these results are based on the observed decrease of the parent molecule, the molecular mechanisms of dissipation are still unclear. It is not known, for example, whether plants could drain PAHs and their metabolites upward to shoots and leaves. Dissipation may also result from enhanced formation of bound residues which could be released in the long term. Lastly, production, solubilization and transfer of toxic metabolites has to be studied in order to predict a possible migration of the pollution toward other media such as groundwater and plants. Nonetheless, phytoremediation appears as a mild and low cost method to remediate contaminated soils from ancient industries, railways, etc.

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