Sorption of PAHs in the Soil Environment with Emphasis on the Role of Soil Organic Matter: A Review

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Abstract: Recently sorption of organic pollutants, in particular polycyclic aromatic hydrocarbons (PAHs), has received much attention and researchers agree that organic matter (the amount of organic matter and its nature) is the most important factor affecting the sorption, desorption and fate of organic pollutants in soil and sediments. It is well documented that organic matter of soil and sediments is the main factor to govern the sorption of PAHs and other nonionic compounds in soil and sediments. However, the sorption capacity and affinity of organic matter of different compositions are differs greatly. Therefore; more research is required to understand how the chemical structure of organic matter can control the fate of the pollutants. Many studies have shown that the aliphatic groups of organic matter are responsible for the sorption properties of nonionic organic pollutants such as PAHs On the other hand, several studies have suggested that the key role in the sorption and desorption of PAHs and some nonionic pollutants was played by aromatic domains of organic matter in soil and sediments. Some researchers, do not agree on how the nature of the organic matter affects the sorption properties and sometimes they contradict each other. This article reviews the fate of PAHs in the soil environment. The review emphasizes sorption process especially the role of soil organic matter in sorption behaviors of PAHs.

Key words: Sorption · Pollutants · PAHs · NMR

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are an important class of organic pollutants because of their wide distribution in the environment and their carcinogenic and mutagenic properties [1, 2]. The United States Environmental Protection Agency (USEPA) and The European Union have identified 16 PAHs as priority pollutants because of their wide distribution in the environment and potential human health risks [3]. Soil plays a crucial role in the fate, transport and behavior of PAHs. PAHs are affected by the pore size distribution in soils and the amount and nature of organic matter [4]. The influence of soil clay minerals is less clear. Hundal *et al.* [5] reported that smectites were able to retain as large amount of phenanthrene as soils with high content of organic matter. However, other reports found that the sorption of nonionic PAHs by soil and sediments were independent of clay type and amount [6].

Numerous studies have found that soil organic matter is the most important soil component for PAH sorption. Hence the bioavailability and environmental persistence of PAHs are most affected by organic matter [7-9]. Aspects of the nature of organic matter, such as its origin, composition and maturation (heterogeneity) impact on the sorption of organic pollutants such as PAHs [10]. Soils contain a wide range of physically and chemically different forms of organic matter such as different humic substances, char materials, black carbon and kerogen. Two types of organic matter domains have been classified according to their physical properties: a soft, rubbery, or amorphous domain and a hard, glassy or condensed domain [8, 11]. Some studies have shown that soil organic matter heterogeneity affects the sorption of organic pollutants [8-11]. More information is needed about the structure and composition of organic compounds to illuminate their effect on the sorption capacity and behavior of PAHs and minimize the negative impact of organic pollutants on the environment [10].

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Solid state nuclear magnetic resonance (NMR) spectroscopy has been used to characterize the nature of the soil organic matter and to identify the nature of organic pollutant binding sites. Although the first application of NMR spectroscopy to characterize soil organic matter was reported in 1963 [12] using NMR to identify pollutants binding sites is quite new.

Polycyclic Aromatic Hydrocarbons (PAHs): Hydrocarbons consist only of carbon and hydrogen. There are two types of hydrocarbons: non-aromatic hydrocarbons, which do not contain aromatic ring structures and aromatic hydrocarbons, which contain benzene rings [2]. Polycyclic aromatic hydrocarbons (PAHs) contain two or more aromatic rings. By virtue of the toxic effect of this group on the environment, as well as their widespread occurrence, PAHs are of great concern. According to Zhang *et al.* [13], sixteen PAHs are listed as priority pollutants by USEPA namely: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo [a] anthracene, chrysene, benzo [b] fluoranthene, benzo [k] fluoranthene, benzo [a] pyrene, indeno [1,2,3-cd] pyrene, dibenzo [a,h] anthracene and benzo [g,h,i] perylene.

Toxicity of PAHs: Even though most of the PAHs are toxic, traditionally, concern about PAHs toxicity emphasized on metabolites because of their more toxicity. The induced toxicity of PAHs is caused by their transformation to reactive products by chemical or biochemical processes, in particular the incorporation of oxygen into the PAH ring structure. Therefore photo-oxidation of PAHs to reactive products can increase toxicity [2]. The toxicity of PAHs greatly enhanced when they exposed to simulated solar radiation and natural sunlight, particularly UV-A [8, 14, 15] PAHs are a great concern because of their mutagenic and carcinogenic action. Walker [2] reported that PAHs can cause tumour development in fish. Fish exposed to sediment with PAH pollution at a rate of 250 *mg/kg* can develop hepatic tumours. In pink salmon embryos, mutation occurred after exposure to PAHs; hence there is a strong possibility that some PAHs may lead to mutations. Immunotoxic effects of PAHs have been reported in rodents [2]. PAHs are classified into two groups based on their toxicity. B2 compounds are probable human carcinogens, include benzo [a] anthracene, benzo [a] pyrene, benzo [b]

fluoranthene, benzo [k] fluoranthene, benzo [g,h,i] perylene, chrysene, fluoranthene and indeno [1,2,3-cd] pyrene. Insufficient data are available about the carcinogenic potential of the group D compounds, which include naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene and dibenzo [a,h] anthracene [16].

Sources of PAHs: Some natural processes can produce PAHs, including volcanic eruptions and prairie and forest fires. PAHs may also be produced by microbes and plants via direct biosynthesis [13, 16]. A large proportion of PAHs enter the environment via anthropogenic sources such as coal-fired electricity power plants, open burning, industrial emissions and domestic heating emission from oil, gas, wood and coal, air blowing of asphalt, motor vehicle exhausts and direct release of oil products to the environment. The range of PAHs produced by smoking is significant and includes some PAHs that can cause cancer, such as benzo [a] pyrene, benzo [a] anthracene, benzo [g,h,i] perylene and Fluorene [13, 17].

The Fate of PAHs in Soils: PAHs can undergo a number of processes in soils: they can be bioaccumulated by some organisms, the lowest molecular weight PAHs have a tendency to volatilize and they can adsorb onto the soil mineral and organic matter fraction. They may also be lost by leaching and degradation [4].

Reid *et al.* [18]; Semple *et al.* [4] and Doick *et al.* [19] stated that the fate of PAHs in the soil is affected by factors such as weather and climate, biological diversity and abundance, the amount and the nature of the soil minerals and organic matter and pollutant properties such as solubility, polarity, hydrophobicity, liphilicity and molecular structure.

PAHs with more than three fused rings have a tendency to adsorb onto the soil particles. On the other hand the low water solubility and very low vapor pressures of the larger PAHs make leaching and volatilization unimportant processes. With increasing molecular size and weight, vapor pressure and solubility decrease. Therefore the effect of these factors on PAH fate declines with increase in molecular weight [17, 20].

Degradation: The ability of a soil to degrade PAHs depends on soil fertility and most importantly the catabolic activity of the soil microorganisms. A variety of eukaryotic and prokaryotic organisms are able to

metabolize PAHs. Degradation of PAHs by microorganisms is a major loss pathway in the environment. It is well known that with increases in soil-PAH contact time, the bioavailability of pollutants decreases. It has been found that an increase of the organic carbon content of soil increase sorption of organic pollutants, but adsorption of PAHs leads to a decline in their degradation by microorganisms. Two prerequisites are needed for biodegradation: pollutants must be bioavailable and they must be biodegradable [18, 21]. As mentioned by Semple *et al.* [4], the rate of microbial decomposition is affected by several factors such as:

- The availability of pollutants to microorganisms with the ability to degrade them;
- The population of the degrading microorganisms;
- The activity of the degrading microorganisms; and
- The nature and structure of the pollutants.

Catabolic activity can in enhanced in a number of ways, such as by adding specific enzymes, genetic modification, adding selected microorganisms specific to the target pollutant and using manipulating conditions (e.g. denitrifying or aerobic conditions) [22, 4].

Volatilization: The loss of organic pollutants such as pesticides and PAHs from the surfaces of plants, soil and water in the vapour form, is called volatilization. The physicochemical properties of organic compounds as well as weather conditions can affect the amount of volatilization. Henrys law constant (H) can be used to predict rates of volatilization [23].

$$H = (C_a / C_w)\, RT$$

Where C_a is the concentration of the organic compound in air, C_w is the concentration of the organic compound in water, R is the universal gas constant (8.314 Pa / m³.mol.K) and T is absolute temperature (K). Values of H>10 indicate very high air affinity and value of H<10⁻⁴, very low air affinity [23].

Leaching: The leachability of most PAHs is generally very low because of their high hydrophobicity. Enell *et al.* [24] reported that only 0.3% of total PAHs were leached over a period of 1600 h under saturated conditions. Parameters such as aqueous solubility and partitioning coefficients are very important factors to evaluate risk of pollutant leaching. The interaction between PAHs and dissolved humic material can increase the solubility of the organic pollutants [25].

Kim and Osako [26] showed that leachability of PAHs can be affected by several factors. They used a sandy soil contaminated with phenanthrene and pyrene and found that shaking time and the amount of dissolved humic matter increased the leachability of PAHs. The concentrations of phenanthrene and pyrene in the leachate were 0.121 and 0.027 µ*g/ml* respectively in the absence of dissolved humic matter and increased to 1.211 and 0.313 *g/ml* of phenanthrene and pyrene respectively at a concentration of dissolved humic matter of 126.2 mg/l. At the same time, liquid-to-solid ratio and pH level had no effect on PAH leaching (Kim and Osako, 2003).

Bioaccumulation: The uptake of hydrophobic or lipophilic organic pollutants by organisms is a critical issue because they can bioaccumulate in the food chain. The bioconcentration factor (BCF) can be used as the measure of this phenomenon [23].

Zhang *et al.* [13] suggested that vegetables and in particular leaf vegetables, can act as an indicator of human exposure to PAHs. It has been reported that total PAHs in Chinese vegetables were between 8.6-111µg/g dry wt. It has been reported that PAH concentration in vegetables depends on weather conditions and distance from sources. The PAH concentration in vegetables divided by their concentration in soil (BCF) ranged from 18 to 871 µg/g dry wt for total PAHs [13].

Sequestration: Sorption and diffusion are collectively called sequestration. Two mechanisms of sequestration have been proposed:

Sorption-retarded Diffusion (SRPD): Soils minerals contain many pores with diameters of less than 20 nm. Contaminants diffuse through the water in these soil pores and contaminants in such fine pores are not bioavailable [4, 8]. Pignatello and Xing [27] stated that, according to the SRPD model, there is an inverse dependence between rates of sorption and square of the particle radius, tortuosity, constrictivity and K_d.

Organic Matter Diffusion (OMD): In the presence of enough water and natural organic matter (NOM) partitioning in NOM is the main form of sorption [26].

Organic matter in the soil consists of two physically and chemically different domains: a soft, rubbery, amorphous domain and a hard, glassy, condensed domain. Both domain types contain holes that can interact with organic pollutants [4,8].

Organic Constituents and Their Nature: To better understand the effect of organic matter on the sorption and desorption of organic pollutants, more detailed characterization of the chemistry of organic matter is needed. Samuel *et al.* [28]stated that the sand fractions of the sediments were poor sorbents in comparison to the fines fractions and the capacity for sorption in the fines fraction was strongly related to the amount of organic matter content. The sorption of some PAHs such as pyrene on 14 soil and sediment samples showed a strong correlation between the amount of clay and sediment organic carbon and the adsorption ability. Other soil and sediment properties had no significant impact on the sorption capacity [6]. In contrast, some studies have found clay mineral and some minerals in colloidal fraction in the soil and sediment play a role in the sorption of hydrophobic organic pollutants [5]. Grathwohl [29] emphasized the crucial role of the nature of organic matter in the sorption of nonionic compounds. These results showed that there was a relationship between K_{oc} and the atomic H/O ratio, as sorption decreased with increased proportions of oxygen-containing functional groups in soil organic matter.

When the Freundlich equation was used for naphthalene and phenanthrene sorption, the *Kf* value of the sorption of both pollutants showed a strong correlation with the organic carbon content of the soil [30]. It has been shown that the soil organic carbon content is the main factor controlling the sorption of nonionic hydrophobic pollutants; however the soil carbon content alone is not enough to fully predict sorption and other factors such as the chemical nature of the soil organic matter must be taken into consideration [31-34].

Application of Nuclear-magnetic-resonance (NMR) Spectroscopy: Given the importance of sorption of organic pollutants to organic matter, analytical methods to investigate this interaction have a great importance. Numerous physicochemical methods have been developed to study the nature of organic matter and their effect on the binding to organic pollutants. NMR techniques are important among these methods. NMR methods can provide structural information with the aid of chemical shift and sorption properties of organic matter [35].

Several studies have sought correlation between sorption properties and structural properties of organic matter. Gauthier *et al.* [36] examined the structure and composition of four humic substances using ^{13}C CPMAS NMR and found that the degree of aromacity played a key role in sorption of humic and fulvic acids. Strong correlations were observed between partition coefficient of pyrene and aromacity and molecular weight [37]. A strong relationship between aromacity and binding coefficient for some polycyclic aromatic hydrocarbon was also reported [38]. The chemical composition of organic matter from 18 different sources was examined by solid-state *[13]C* NMR spectroscopy and sorption coefficient and aromaticity showed positive correlations with each other [10]. In twenty-seven soils from different ecological zones, the structure of soil organic matter was investigated by CPMAS *[13]C* NMR. It was shown that there was a positive and strong correlation between aromacity of organic matter and K_{oc} (sorption per unit organic carbon) values of carbaryl and phosalone [31]. It has been concluded that the aromatic constituents of soil organic carbon is a suitable predictor to estimate the capacity of the soil to absorb nonionic pollutants [31-34]. A study of the composition and structure of sedimentary organic matter showed that aromatic carbon content of sediment and the amount of desorption resistant phenanthrene were related to each other, but that not all the aromatic domains had the same affinity for phenanthrene [9].

On the other hand, several studies found a relationship between aliphatic domains of organic matter and sorption affinity. With the use ^{13}C NMR spectra, strong positive relationships have been reported between *Koc* for pyrene and aliphacity, which showed the importance of aliphatic domains in the sorption process. In contrast, the relationship between aromacity and the sorption process for pyrene was very poor. It was suggested that the importance of aliphatic C is at least similar to the importance of aromatic groups with regard to adsorption of pyrene [39].

Salloum *et al.* [41] used cross polarization magic angle spinning carbon-13 (CPMAS- [13]C) NMR to show that natural organic matter with high levels of aliphatic carbon has more affinity to adsorb phenanthrene than highly aromatic compounds such as humic acid and they

suggested that sorption to aliphatic domains resembles that to rubbery type carbon. Moreover, they found that sorption capacity and the shape of sorption isotherms in aliphatic and aromatic domains differed from each other.

A positive and significant correlation was found between the amount of amorphous nonpolar aliphatic poly methylene domains and phenanthrene sorption capacity. Solid-state ^{13}C nuclear-magnetic-resonance (NMR) spectroscopy confirmed that the amorphous aliphatic domains play the key role in the sorption of phenanthrene. Contrary to the finding of other researchers, no strong relationship between K_f and the aromaticity or polarity indices was found and these were not good indicate to predict capacity to retain nonionic hydrophobic organic compounds [41].

Some other researchers tried to find the other characteristics of the soil organic matter that influenced sorption affinity. A negative correlation has been observed between sorption capacity of benzene and carbon tetrachloride and polarity index of these organic compounds [42].

And finally some researchers found no relation between soil organic matter structure and sorption affinity. Kile *et al.* [43] found that the polarity index and individual aromatic and aliphatic groups had a poor correlation with sorption capacity of organic compounds.

CONCLUSION

Recently sorption of organic pollutants has received much attention and researchers agree that organic matter (the amount of organic matter and its nature) and clay minerals in colloidal fractions are the most important factors affecting the sorption, desorption and fate of PAHs in soil and sediments. In recent times, there has been an increasing realization that not only the amount, but also the chemical composition, of organic matter and clay minerals can influence the sorption properties of a soil.

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