



Phytoremediation of polycyclic aromatic hydrocarbons (PAHs): air-plant-soil interactions

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Abstract

Polycyclic aromatic Hydrocarbon (PAH) molecules are major concerns in environmental organic pollution. PAHs molecules in the air and their adsorption on soil into plants is a critical issue because they may enter food chain and turn to main source of health problems. Many methods employed for cleanup polluted area but phytoremediation is acceptable more than others in wide area. Several plant species were used for PAHs phytoremediation. PAH molecules transfer in Air-Soil-plant system, directly related to molecule properties and plant morphological characteristics. The entrance strength of PAHs molecular to plant tissue has high relation to hydrophobicity and lipophilic characteristics of molecules. LMW-PAHs may be adsorbed and transferred faster than HMW-PAHs by/in plant cells. Plants morphological particularities such as waxy properties, specific leaf area, cell wall properties, root elongation, number of nodal root and metabolisms are a factor that affects PAHs transfer and degradation in plant tissues. Other environmental properties such as temperature, wind, moisture have indirectly affects PAHs transfer. The antithetical results between traditional data and contemporary investigation must be resolved by implying new methods.

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Intro of PAHs Contamination

Contaminated sites cleanup methods separated to in-situ and ex-situ technologies. The purpose of in-situ method is applying chemical, physical or biological processes to the surface or subsurface to degrade, remove, or immobilize contaminants without removing the bulk soil. Nowadays, several remediation methods such as chemical and physical treatments (soil vapor extraction, Solidification/stabilization, chemical oxidation, soil flushing, Electro-kinetic separation, Electrical resistance heating, steam injection and extraction, conductive heating, radio frequency heating and *in-situ* verification are expensive and may cause secondary contamination. Phytoremediation is the use of plants which represents a favorable, nondestructive, cost-effective, easy access and aesthetic value, in-situ technology for contaminants removal. The phytoremediation mechanisms are using to treat wide areas with shallow contamination in low or moderate level and can conjunct with others. These various mechanisms can treat a wide range of contaminants including metals, radionuclides, volatile organic carbons, petroleum hydrocarbons and Polycyclic Aromatic Hydrocarbons (PAHs).

In recent years many researchers have investigated about PAHs remediation of contaminated soils that phytoremediation gets a special attention among them (Balasubramaniyam, 2015). The PAHs are major concerning environmental pollutants due to their carcinogenicity, mutagenic and tumor-promoting properties (Su and Zhu, 2008; Gao *et al.*, 2010; Abdel-Shafy and Mansour, 2016). PAHs are practically insoluble in water and very slow to degrade except naphthalene and the linear PAH (Crnković *et al.*, 2006; Smith *et al.*, 2006; UNEP, 2016) while several PAHs contaminants can be leach by water in soil media regarded as mobile pollutants (Kanaly and Harayama, 2000). Generally, the hydrophobicity and environmental stability are the major features of pollutant potential of a PAH molecule. The hydrophobicity of a molecule is measured by its octanol-water partition coefficient (log Kow), which is described by its capacity to dissolve into an organic solvent relative to an aqueous solvent.

These features enhance with increasing in size and the number of aromatic rings that molecule possesses (Harvey *et al.*, 2002). Recognition of PAH in Air-Soil-Plant System cycling may be helpful to treat better and choose best plant species for phytoremediation.

Air to leaf transfer of PAHs

Because of incomplete fuel combustion, PAHs emitted to urban and countryside area atmosphere in particulate or vapor phase and finally deposited and precipitated in soils or surface water (Shahsavari *et al.*, 2016; Weerasundara and Vithanage, 2016). PAH particles less than 2.5 µm in aerodynamic diameter are the special concern in terms of environmental health (Srám *et al.*, 1996; Magee *et al.*, 1996). The atmosphere PAHs may enter plants depending on chemical and physical properties of the PAH molecules or the environmental conditions (Simonich and Hites, 1996; Howsam *et al.*, 2000). Overall, the lighter and smaller PAHs tend to deposit into leaves through dry gasses and/or wet deposition. The PAHs molecules properties are influencing the rate and amount of their adsorption to leaves. The larger and heavier PAHs are usually in particulate form and can be deposited in wet and dry formations onto the plant surface (Howsam *et al.*, 2000). PAHs and particulate-bonded PAHs can take up directly via the stomata or be deposited on the leaf surface, while gaseous PAHs may be accumulated in leaves. Few researchers have revealed that the effects of deciduous trees leaves on removing fine particles from the atmosphere is depended on the shapes and sizes of leaves. The amount of PAHs accumulation in vegetation is related to the properties of the particular PAHs and features of the accumulating surface.

Based on the morphological appearance of plant leaves, *Ficus microcarpa*, *Ixora coccinea* and *Baphia nitida*, which have the waxy leaf surface could accumulate more organic pollutant in leaves (Böhme *et al.*, 1999) and influenced by the environmental conditions (Temperature, humidity, UV radiation, and wind) (Franzaring, 1997; Azhari *et al.*, 2011).

Researches indicate that low molecular weight-PAHs (LMW-PAHs) were probably taken up from the atmosphere through the leaves as well as by root (Fismes *et al.*, 2002). Phenanthrene, the most smallest tricyclic aromatic hydrocarbon which commonly has been used as a model substrate for studies on metabolism of carcinogenic PAHs (Zhang *et al.*, 2014) transfer from air to leaves and afterward in xylem was observed, while accumulation of phenanthrene was not shown in cytoplasm of maize (*Zea mays* L.) and spinach (*Spinacia oleracea*) (Wild *et al.*, 2006). Phenanthrene entered the internal mesophyll of both species, and was identified within the mesophyll cell walls, at the surface of the chloroplasts, and within the cellular cytoplasm. It seems that for more knowledge about PAH transferring from air to leaf, traditional data need to be revised to avoid contemporary results like the experiments for measuring PAHs mass transfer (Ahmadi *et al.*, 2016) which can be implied by new methods.

PAHs transfer between shoot and root

In food chain issues and pollutant problems, focusing on PAHs transferred to edible parts of selected vegetables is critical. PAHs transferring to shoot have been reported Samsøe-Petersen *et al.*, 2002. The LMW-PAHs content has stronger linear relation than HMW-PAHs in soil and shoots that has been showed by studies, and also these facts indicated that LMW-PAHs translocation is faster from soil to shoot and implies that root uptake is main pathway of heavy molecular weight-PAHs (HMW-PAHs) accumulation (Khan *et al.*, 2008). An investigation showed that root or shoot accumulations of phenanthrene and pyrene (well-documented carcinogen in mammalian) in contaminated soils were elevated with the increase of their soil concentrations in 12 plant species (Gao and Zhu, 2004). Although, transport of these compounds from roots to shoots usually was the major pathway of shoot accumulation, but translocations of phenanthrene and pyrene from shoots to roots were undetectable till now.

On comparing laboratory and field experiments of PAHs dissipation by *Medicago sativa* L. (Wei *et al.*, 2017), results indicated that between two methods with different soils are great incompatibilities. It has been shown that the concentrations of phenanthrene and pyrene in roots were significantly higher than shoots. Moreover, the concentrations of phenanthrene in plant shoots and roots were significantly higher than pyrene content (Wei *et al.*, 2017). In artificially contaminated soil by PAHs molecules such as pyrene, anthracene (with consisting three benzene rings and has nonmutagenic, noncarcinogenic attributes) and phenanthrene, analyzing of leaflet and root of alfalfa (*Medicago sativa* L.) showed that PAHs enter to the plant and accumulate in different cells and tissues because of different solubility of organic compounds in tissues' water due to hydrophobicity and lipophilic characteristics of PAHs (Alves *et al.*, 2017). A research on salt marsh plant and PAHs interaction showed that vegetated area has low or equivalent level PAHs than non-vegetated and some plants have different fixation promoting mechanisms of PAHs in rhizosediments (Gonçalves *et al.*, 2016).

In heavy metal-PAH contaminated media, for experiments that were performed by using plants such as *Solanum nigrum* L. and *Scirpus triqueter*, researchers suggested that increasing in PAHs degradation may be resulted from any factors that improve plant growth, soil enzymatic activity, bioaccumulation and translocation of heavy metals (by decreasing the effects of heavy metals in plant directly or enhancing microorganisms activity in rhizosphere) (Liu *et al.*, 2013; Ouvrard *et al.*, 2014; Wei *et al.*, 2016; Feng *et al.*, 2017). In *Scirpus triqueter* has been observed that peak of pyrene in shoots reached at 16 hour while phenanthrene peak achieved in 48 hour (Liu *et al.*, 2013). Some investigations about phytodegradation have revealed that the *Festuca arundinacea* (tall fescue grass) and *Panicum virgatum* (switch grass) are capable to degrading the pyrene. Several crops in spiked soils by single or combined cultivation enhanced degradation of phenanthrene and pyrene. Vegetation such as corn

(*Zea mays*), alfalfa (*Medicago sativa* L.), rapeseed (*Brassica napus* L.) and rice (*Oryza sativa*) significantly raised the adsorption amount of PAHs or promoted the efficiency of PAHs phytodegradation in contaminated soils (Cheema *et al.*, 2009; Du *et al.*, 2011). Not only plant species are important in phytoremediation efficiency but also cropping processes affect the average percent of remaining PAHs (Meng *et al.*, 2011). In a research in pot and field experiments with lettuce (*Lactuca sativa* L.), potato (*Solanum tuberosum* L.), and carrot (*Daucus carota* L.) after harvesting, above and below ground biomass were determined and the PAH concentrations in soil were measured and observed that the presence of PAHs in soils had no significant effect on plant growth but in all plants had been grown in contaminated soils, PAHs were detected. However, their concentrations were low compared to the initial soil concentration (Fismes *et al.*, 2002).

Soil to root PAHs Transfer

PAHs contaminants can be absorbed by roots due to plant metabolism or translocation via the transpiration stream (Wenzel *et al.*, 1999; Fismes *et al.*, 2002; Ghanem *et al.*, 2010). Uptake of PAHs by plant roots, have influenced by the soil organic content and the lipid contents of the plant roots. Specific surface area and lipid content of roots are main factors influencing adsorbed PAHs contents. Researches have been shown partially higher PAHs contents in the lateral roots than those in the nodal roots (Jiao *et al.*, 2007). Also, an investigation revealed that artificially addition of root exudates influenced the desorption of phenanthrene and pyrene in soils positively (Gao *et al.*, 2010). Wild *et al.* (2005) showed that some PAHs (anthracene and phenanthrene) radial movement inhibited beyond the cortex root cells of maize and wheat. The results showed that although xenobiotic compounds highly focused within the cortex of plant roots but did not pass beyond the base of roots into stems. Solubility may be one of the important factors that effects PAHs compounds movement from cell walls. The movement of anthracene within maize cell walls was approximately three times slower than of

phenanthrene which reflected differences in solubility due to variation of lipid composition of the cell walls between the plant species. The uptake of both anthracene and phenanthrene were approximately three times faster in maize than in wheat (Harms, 1996; Wild *et al.*, 2005). For some plants that have protective mechanisms in cytoplasm such as sequestration of xenobiotic compounds in cell walls and vacuoles, anthracene was located within the cell walls predominantly (Meagher, 2000). Hence, the passage of PAHs across the root tissues could be predominantly apoplastic. Meanwhile some researchers showed that combinations of plant, arbuscular mycorrhizal and rhizobia have highest PAHs dissipation ability (Andreolli *et al.*, 2013; Ren *et al.*, 2017). The fact of studies mentioned that PAHs molecules transferring from roots to shoot is rare and related to molecule weight and plants morphological properties directly. Attempts to modeling organic chemicals in air-soil-plant system were failed because of the high variability between the experimental studies results and background air concentrations (Collins and Finnegan, 2010). For phytoremediation in a specified area must insist to choose native plants that they will be tolerant to the soil and environmental conditions.

Conclusion

Phytoremediation is recognized as a suitable method to cleanup PAHs contaminated in vast area. The recognition of interactions between PAHs molecules and soil media, atmosphere and plant tissue could solve various problems that encountered by selecting the plant species for phytoremediation technique. Although the studies have been described above indicated clearly the significance of PAHs molecules characteristics from each other and also analyzed certain plant tissue factors that may influence phytoremediation technique. However, reports about the actual selection of a suitable plants, classification of a crop plants or native plants with different remediation capacity are in scarce. Therefore, further studies for selecting suitable, sustainable and adaptable plants to environmental condition to use in phytoremediation can be useful. On the other hand,

improving in understanding of how organic pollutants are taken up by leaves would allow better predictions of these chemicals fate in the environment, develop phytoremediation into a widely accepted technique and distinguish the related risks.

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