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Bioaccumulation of HMW PAHs in the roots of wild blackberry from the Bor region (Serbia): Phytoremediation and biomonitoring aspects

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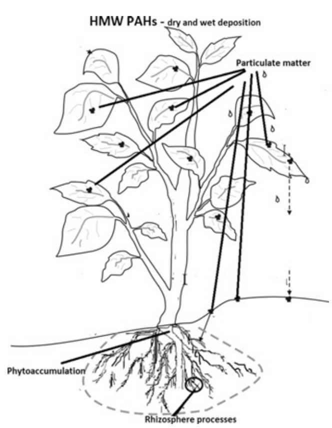
HIGHLIGHTS

- HMW PAHs were analyzed by GC/MS, BCFs, Pearson's correlation study and HCA.
- The accumulation of individual PAH compounds in plant roots was at different level.
- Wild blackberry may be very useful for soil PAH removal or stabilization.
- Roots can be useful in soil monitoring but only in combination with soil data.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the samples of roots and soils from the rooting zone of wild blackberry were collected from the urban-industrial and rural locations near "The Copper Mining and Smelting Complex Bor" (Serbia); they were analyzed by gas chromatographic-mass spectrometric method to determine the content of high-molecular weight polycyclic aromatic hydrocarbons (HMW PAHs). The obtained results were further processed using bioconcentration factor, Pearson's correlation study and hierarchical cluster analysis with the aim of investigating if they may be in favor of wild blackberry as a suitable plant for biomonitoring or phytoremediation purposes. In spite of the fact that numerous complex factors can affect the assimilation and accumulation of PAHs in plants, the obtained data expressed clearly many interesting specifics related to HMW PAH accumulation in roots of wild blackberry that naturally grows in an area, which is heavily polluted by heavy metals. The accumulation of individual PAH compounds in plant roots was at different level. The most abundant compound in all plant samples was benzo[*a*]pyrene and based on the results obtained for this environmental indicator of carcinogenic PAHs, it was possible to make several central conclusions: wild blackberry showed an excellent potential for its extraction from the soil and further accumulation in root tissues which indicate that this plant species may be applied in phytoremediation procedures based on mechanisms such as phytoextraction/phytoaccumulation in roots; phytostabilization and rhizodegradation are also possible as remediation mechanisms; utilization of plant

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roots in soil monitoring is possible but in this case, only the combination with soil data can provide correct information.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic pollutants that may originate from anthropogenic and natural (vegetation fires and volcanoes eruptions) sources. The contribution of anthropogenic activities to their presence in the environment increased in rates that correspond to the industrial and technological civilization development (Banach-Szott et al., 2015; Wilcke, 2000). Incomplete combustion of fossil fuels (gas, oil, coal, wood) and other organic materials (waste materials, tobacco, grilled meat), that may result from the industry, traffic, residential heating and many other anthropogenic sources is recognized as the main cause of PAHs releasing into the atmosphere and other environmental compartments (Alagić et al., 2015a; Maliszewska-Kordybach and Smreczak, 2003; Tao et al., 2006). The main sink for PAHs accumulation is surface soil (Banach-Szott et al., 2015; Bandowe et al., 2010; Cvetkovic et al., 2016; Maliszewska-Kordybach, 2005). In soils from temperate climate regions that are not exposed to direct anthropogenic influence, the concentrations for individual PAH compounds are estimated to be 1–10 μg/kg. However, at present, this range is rarely found and even the lowest measured PAH concentrations are about 10 times higher than preindustrial concentration levels (Wilcke, 2000). According to Gąsecka et al. (2015), several recent studies reported that the concentrations of individual PAHs in soils can vary from the limit of detection up to several hundred μg per kg of soil, whereas in the neighborhood of gas manufacture sites the concentration of PAHs can reach up to 30 g/kg.

Based on the complexity of molecular structure and molecular weights, PAHs are divided into: low-, medium-, and high-molecular weight PAHs (LMW, MMW and HMW PAHs) (Alagić et al., 2015a; Boström et al., 2002; Gan et al., 2009; Simon and Sobieraj, 2006). The compounds with the most complex structure, containing five or more benzene rings in their molecules, i.e. HMW PAHs are considered as most toxic, mutagenic and carcinogenic (Boström et al., 2002; Gao et al., 2011). These toxicants usually attack lung area in humans, by being present in polluted atmosphere, or tobacco smoke, but when they are present in contaminated food of food prepared under pyrolysis conditions (barbecuing food), they can cause carcinogenic changes in digestive organs (Boström et al., 2002). For the sake of protecting human health, 16 PAH compounds have been included in the list of pollutants of highest priority by the United States Environmental Protection Agency (USEPA): naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flr), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a*,*h*]anthracene (DhA), benzo[*g*,*h*,*i*]perylene (BgP), and indeno[1,2,3-*cd*]pyrene (IcP). Except BgP, all HMW PAHs (BbF, BkF, BaP, DhA and IcP) are treated by US EPA as probable carcinogenic (Alagić et al., 2015a; Simon and Sobieraj, 2006; Wang et al., 2012).

In plants, PAHs may cause oxidative stress that produces tissue damages and disturbances in metabolism (Reichenauer and Germida, 2008), which can finally result in morphological symptoms such as: reduction of root and shoot growth, chlorosis, late flowering, and formation of white spots that may develop into necrotic lesions (Alkio et al., 2005). However, it was shown in many studies that plants may evolve some very specific mechanisms for PAH degradation in terms of their transformation into less toxic metabolites. Plants can perform these actions inside their cells using mechanisms very similar to mammals (the "green liver" concept), or by excreting compounds that may change PAH molecules (Alagić et al., 2015a; Abhilash et al., 2009; Gao et al., 2013; Gąsecka et al., 2015; Reichenauer and Germida, 2008). Excretion of various compounds helps plants to accomplish not only a detoxification but also an immobilization of pollutants in soil forming their reactive radicals. The formed radicals can be precipitated, polymerized, or covalently bound to the humic acids. At the same time, the excretion of exudates can adjust geochemical environment in the area of rhizosphere in a way that provides optimal conditions for bacterial and fungal growth, so that plants may further cooperate with their associated microbes which may result in a significant PAH degradation in the soil near plant roots (Alagić et al., 2015a; Gan et al., 2009; Gąsecka et al., 2015; Haritash and Kaushik, 2009; Reichenauer and Germida, 2008). It should be pointed here that actions performed by soil microorganisms usually degrade PAHs more effectively than any plant, because microbial decomposition of PAHs can lead to their total mineralization (Haritash and Kaushik, 2009), whereas plant management refers only to limited transformations of PAHs molecules (mostly LMW PAHs), or to PAH accumulation in the tissues (Alagić et al., 2015a). The accumulation of PAHs in plants is generally at the very low level and their accumulation rates, expressed as bio-concentration factors, BCFs (the ratio of compound concentration in plant part relative to its concentration in the soil), usually range from 0.001–0.4; only in the cases of severe soil pollution, the values of root BCFs could reach up to 2 (Reichenauer and Germida, 2008; Tao et al. 2006; Wilcke, 2000). This is not unexpected because hydrophobic PAHs are typically tightly bounded to the soil particles, i.e. organic matter fraction, where can stay for a long period of time (Banach-Szott et al., 2015; Bandowe et al., 2010; Wilcke, 2000). HMW PAHs, characterized by low water solubility and vapor pressures but with high values of organic carbon partitioning coefficient, Koc, are especially susceptible to this, so called "ageing" process (Simon and Sobieraj, 2006). The final result of the ageing process is the transfer of compounds from accessible compartments of soil to less accessible ones, which consecutively cause their lower availability to plant roots (Reid et al., 2000; Wilcke, 2000). However, in the cases when the root lipid content is high, HMW PAHs as lipophilic compounds with high values of octanol–water partition coefficient, Kow, may enter plant roots relatively easily and the results of many studies proved that the accumulation of PAHs increases as the root lipid content increases (Kang et al., 2010; Reichenauer and Germida, 2008; Sojinu et al., 2010).

For a long period of time, a general opinion was that PAHs usually partition to the epidermis of the root and are not drawn into the inner root or xylem, because this branch of translocation system is water based (Tao et al., 2004). However, Kipopoulou et al. (1999) removed the endodermis from the carrot roots and analyzed the inner plant tissue in their experiment that was conducted in a highly polluted industrial area of Thessaloniki (Greece). Carrot roots, although peeled, were found to have higher PAH content than directly exposed cabbage aboveground parts from the same experiment which was explained by high lipid content and oil channels in the carrot roots. Kang et al. (2010) showed that initially, PAHs adsorb to cell walls, and then gradually diffuse into subcellular fractions of ryegrass root tissues. Once HMW PAHs are accumulated in the root, they usually stay there bounded to the cell wall components or stored in vacuoles (Kang et al., 2010). Only the translocation of some low- or medium-molecular weight PAHs such as Pyr, Phe, and Ant has been proven in plants (Gao and Zhu, 2004; Gao et al., 2013; Kipopoulou et al., 1999; Reichenauer and Germida, 2008; Tao et al., 2006).

Unfortunately, all mentioned findings point to the fact that, in the case of PAHs, the application of higher plants in a classically designed phytoremediation procedure such as: phytoextraction of pollutant from the soil, its further translocation and accumulation into the