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Sources and fate of polycyclic aromatic compounds (PAHs, oxygenated PAHs and azaarenes) in forest soil profiles opposite of an aluminium plant

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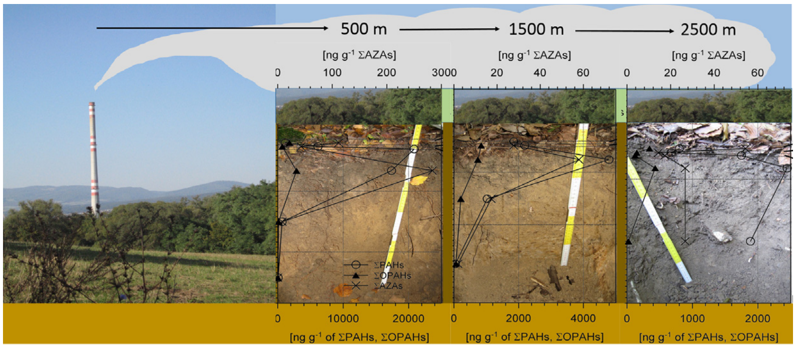
HIGHLIGHTS

- Polycyclic aromatic compounds (PACs) in forest soils were studied.
- Redistribution of PACs from Oi to Oa horizons was driven by organic matter turnover.
- Oxygenated PAHs (OPAHs) did not accumulate in deeper O horizons.
- In mineral soil, OPAHs were leached in dissolved and PAHs in colloidal form.
- PAHs concentrations decreased in O but increased in A & B horizons compared to 1994.

GRAPHICAL ABSTRACT



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ABSTRACT

Little is known about oxygenated polycyclic aromatic hydrocarbons (OPAHs) and azaarenes (AZAs) in forest soils. We sampled all horizons of forest soils from five locations at increasing distances from an Al plant in Slovakia, and determined their polycyclic aromatic compound (PACs) concentrations. The $\sum$29PAHs concentrations were highest in the Oa and lowest in the Oi horizon, while the $\sum$14OPAHs and $\sum$4AZAs concentrations did not show a consistent vertical distribution among the organic horizons. The concentration ratios of PAHs and OPAHs between deeper O horizons and their overlying horizon (enrichment factors) were positively correlated with the octanol-water partition coefficients (K_{OW}) at several locations. This is attributed to the slower degradation of the more hydrophobic PACs during organic matter decomposition. PACs concentrations decreased from the organic layer to the mineral horizons. The concentrations of $\sum$29PAHs (2400–17,000 ng g^{-1}), $\sum$14OPAHs (430–2900 ng g^{-1}) and $\sum$4AZAs (27–280 ng g^{-1}) in the mineral A horizon generally decreased with increasing distance from the Al plant. In the A horizons, the concentrations of $\sum$29PAHs were correlated with those of $\sum$14OPAHs ($r = 0.95$, $p = 0.02$) and $\sum$4AZAs ($r = 0.93$, $p = 0.02$) suggesting that bioturbation was the main transport process of PACs from the organic layer into the mineral soil. At each location, the concentrations of PACs generally decreased with increasing depth of the mineral soil. Enrichment factors of PAHs in the mineral horizons were not correlated with K_{OW}, pointing at colloid-assisted transport and bioturbation. The enrichment factors of OPAHs (in mineral horizons) at a site were negatively correlated with their K_{OW} values indicating that these compounds were leached in dissolved form. Compared to a study 13 years before, the concentrations of

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PAHs had decreased in the O horizons but increased in the A and B horizons because of soil-internal redistribution after emissions had been reduced.

1. Introduction

Environmental contamination with polycyclic aromatic compounds (PACs) such as polycyclic aromatic hydrocarbons (PAHs), oxygenated PAHs (OPAHs) and nitrogen heterocyclic PAHs (azaarenes, AZAs) is a source of concern because of their (eco)toxicological properties, persistence and bioaccumulation. PAHs have been the main focus of previous studies on soils (Wilcke, 2007; 2000). However, recent studies show that fractions of soil extracts that contain the much less studied polar derivatives of PAHs (e.g., OPAHs and AZAs) and pure OPAHs and AZAs can induce (eco)toxicological effects of similar or higher magnitude as the PAH-containing fractions or pure PAHs (Anyanwu and Semple, 2016; Bandowe and Wilcke, 2011; Brinkmann et al., 2014; Lundstedt et al., 2007; Misaki et al., 2016; Wincent et al., 2016, 2015). Some OPAHs and AZAs are also more persistent and bioaccumulative than PAHs (Anyanwu and Semple, 2016, 2015; Arp et al., 2014; Lundstedt et al., 2007).

All PACs are produced and emitted to the environment from incomplete combustion of fossil fuels and biomass (Bleeker et al., 2002; Booth and Gribben, 2005; Lima et al., 2005; Lundstedt et al., 2007). OPAHs are also formed by post-emission transformation of PAHs via photolysis, photooxidation, chemical degradation, thermal degradation and biodegradation (Bandowe and Wilcke, 2011; Lundstedt et al., 2007; Walgraeve et al., 2010). AZAs and OPAHs have higher water solubility and lower vapour pressure than their related PAHs. They have functional groups that allow for more diverse mechanisms of partition, sorption and transport in air and soil.

Soil is the major sink of PACs in the environment, with some estimates indicating that up to 90% of PAHs in the United Kingdom environment are stored in soils (Wild and Jones, 1995). Such estimates are however, to date not available for the polar PACs such as OPAHs and AZAs. PACs emitted by anthropogenic activities can be deposited to soils by dry/wet deposition and direct air-soil exchange from contaminated air. PACs can also be scavenged by vegetation and reach the soil via litterfall (Cousins et al., 1999; Moeckel et al., 2008). Forest soils are a major sink for atmospheric organic micropollutants because of the scavenging effect of the tree canopy with its large surface area (Horstmann and McLachlan, 1998; Matzner, 1984). PACs in forest soils undergo sorption-desorption, transformation, degradation, transport (leaching, dissolved organic matter (DOM) and colloid-assisted transport), volatilization/condensation and bioaccumulation that eventually determine their spatial distribution (Krauss et al., 2000; Moeckel et al., 2008; Semple et al., 2003). Concentrations of PAHs in soils generally decrease exponentially with distance from a point source (Van Brummelen et al., 1996; Wilcke et al., 1996). The contributions of higher molecular weight PAHs (HMW-PAHs, >4 benzene rings) to the total PAHs concentrations usually progressively decrease with distance from point sources because of their stronger association with particles and rapid deposition to the soil (Van Brummelen et al., 1996; Yang et al., 1991). The spatial distribution of OPAHs and AZAs in forest soil with distance from point sources has not yet been investigated. It was, however, shown in grassland soils near a power and industrial plants of the Angren region, Uzbekistan, that the spatial distribution of OPAHs was similar to those of PAHs (Bandowe et al., 2010).

The processes that influence the concentrations, composition patterns and vertical distribution of PAHs in the three organic (O) horizons of the organic layer on top of mineral soils are different from those that influence the vertical distribution in the mineral soil (Krauss et al., 2000; Pichler et al., 1996; Wilcke, 2000). The organic layer of forest soils consists of up to three distinct horizons (Oi, Oe and Oa) of increasing depth and degree of decomposition. Oi, Oe and Oa horizons are defined as fresh undecomposed litter, partially decomposed and completely decomposed organic matter, respectively (Krauss et al., 2000). Depending on soil properties and climate, these horizons show different states of development and might even be absent. The concentrations of total PAHs in the organic horizons of forest soils generally increase in the order Oi < Oe < Oa (Krauss et al., 2000; Pichler et al., 1996; Wilcke, 2000). The proportion of HMW-PAHs in organic horizons of forest soils also increase in the order Oi < Oe < Oa. This is because of the higher persistence of HMW-PAHs (than the LMW-PAHs) and hence higher proportions of the LMW-PAHs than of HMW-PAHs being biodegraded during the decomposition of organic matter (Krauss et al., 2000; Pichler et al., 1996; Wilcke et al., 1996).

In the mineral horizons, total PAHs concentrations and the contribution of HMW-PAHs to total PAHs concentrations generally decrease with increasing depth (Guggenberger et al., 1996; Wilcke, 2000). The vertical distribution in the mineral horizon is driven by the higher concentrations of organic matter in topsoils (A horizons) of forest soils that serve as a strong sorbent for the PAHs. The depth distribution of PAHs can be explained by the vertical transport via leaching as truly dissolved solute (mainly LMW-PAHs) and DOM/colloid-assisted transport and retention (mainly HMW-PAHs, Guggenberger et al., 1996; Totsche et al., 1997). The stronger leaching of truly dissolved LMW-PAHs explains the decreasing contributions of the more hydrophobic HMW-PAHs to total PAHs concentrations with increasing mineral soil depth. The individual OPAH/related-PAH concentration ratios in the mineral horizons were found to increase with increasing depth because of the higher water solubility of the OPAHs than of their related PAHs (Bandowe et al., 2011, 2010). Like the OPAH/related-PAH ratios, it is expected that the AZA/related PAH ratios will increase with increasing depth of the mineral soil.

To study the distribution and transport of OPAHs and AZAs, we selected a beech forest (*Fagus sylvatica* L.) near an aluminium plant in Žiar nad Hronom (Central Slovakia). Aluminium smelting on industrial scale releases significant amounts of PAHs (and possibly OPAHs and AZAs), trace metals and other pollutants from both combustion of fossil fuels used to produce energy that powers the smelting process and from the carbonaceous electrode material used in aluminium smelting itself (Booth and Gribben, 2005; Maňkovská and Steinnes, 1995; Wilcke et al., 1996). This site offers an ideal location to study the distribution of PACs (OPAHs, AZAs and PAHs) originating from a point source as well as the depth distribution and the underlying processes that drive these distributions. The distribution and composition of PAHs in soils sampled from these sites in 1994 was reported earlier (Wilcke et al., 1996). Shortly before the study of Wilcke et al. (1996), the Al smelter company had undergone restructuring and installed new technologies for both production and emission control (Jamnická et al., 2007; Maňkovská and Steinnes, 1995; Wilcke et al., 1996). This study will therefore also provide useful data about the effect of the introduction of modern technology in aluminium production and emission control as well as about the long-term behaviour of PAHs in soils. The overall goal of this study is to gather knowledge about the sources (direct emission vs. post-depositional formation), spatial distribution, cycling and transport of PACs (PAHs, OPAHs and AZAs) in forest soils. Our work is guided by the following research questions:

1. What does the distribution of PAHs, OPAHs and AZAs with increasing distance to the smelter tell us about its sources and mechanism of transport?
2. What does the (depth) distribution of PACs tell us about the mobility, transport mechanism of the different PAC groups, and the post-