



Long-term study of nitro- and oxy-PAHs in soil samples at a rural background and a semi-urban site in central Europe

Langzeitstudie zu nitrierten und oxygenierten polyzyklischen aromatischen Kohlenwasserstoffen in Bodenproben zweier unterschiedlicher Standorte

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Abstract

Polycyclische aromatische Kohlenwasserstoffe (PAKs) sowie ihre nitrierten (NPAHs) und oxygenierten (OPAHs) Derivate sind zum Teil langlebig und können in der Atmosphäre über weite Strecken transportiert werden. Trotz ihrer gesundheitsschädlichen Auswirkungen gibt es bisher nur wenige Studien zu den Konzentrationen der PAK-Derivate im Boden an Standorten ohne signifikante direkte Quellen bzw. Kontamination. In dieser Langzeitstudie konnten verschiedene NPAHs und OPAHs im Boden nachgewiesen werden. Durch den Vergleich der Konzentrationen im Boden und der Atmosphäre konnten einige neue Erkenntnisse gewonnen werden. Für das genaue Verständnis von Langzeitschwankungen der Konzentrationen fehlen jedoch noch einige kinetische Parameter.

Introduction

The planetary boundary of chemical pollution is considered to be transgressed (Persson et al., 2022). Polycyclic aromatic compounds (PACs), including polycyclic aromatic hydrocarbons (PAHs) and their nitrated (NPAHs) and oxygenated (OPAHs) derivatives, are an important compound class of chemical pollution. It has already been shown that several PACs are carcinogenic, mutagenic, ecotoxic, endocrine disruptive and cause oxidative stress (Durant et al., 1996; Bolton et al., 2000; Lundstedt et al., 2007; IARC, 2010, 2012; Bandowe and Meusel, 2017). Humans are exposed to these pollutants in several pathways, as the substances can enter the human body by inhalation, oral ingestion and dermal contact (Ruby et al., 2016).

PACs are mainly emitted into the environment by incomplete combustion of fossil fuels and biomass (Baek et al., 1991; Bandowe and Meusel, 2017). In addition, the NPAHs and OPAHs can be formed secondarily in the atmosphere by the reaction of atmospheric oxidants with PAHs (Keyte et al., 2013). After emission, the semivolatile substances can partition between the particulate phase and the gas phase in air. Due to their persistence, PACs can be transported to places far from any primary sources. The chemicals reach the soil mainly by dry deposition adsorbed to particles and by wet deposition (precipitation) (Baek et al., 1991; Bandowe and Meusel, 2017).

In addition, PACs can reach the soil directly from fossil material such as coal and crude oil (Vikelsøe et al., 2002; Bandowe and Meusel, 2017). Because of their volatility, the substances can revolatilize from the soil surface. Thus, the soil can be a storage compartment, which can re-emit these pollutants into the atmosphere (Lammel et al., 2009; Keyte et al., 2013).

Despite the importance of these compounds, there is still a lack of knowledge about the distribution and long-term trends of the PACs in soil. The concentration of a PAC in soil depends on its emission intensity, formation in air and soil, degradation in air, deposition, revolatilization, transport, sequestration, sorption and desorption to soil matrix, degradation in soil (biotic and abiotic), bioaccumulation, plant-uptake, formation of non-extractable residues amongst others (Wilcke, 2000; Semple et al., 2003; Idowu et al., 2019).

The aim of our study was to determine the temporal variations in the concentrations and the composition profiles of OPAHs, O-heterocycles, NPAHs and PAHs in grassland soils of a central European rural background and of a semi-urban site, both in the Czech Republic. By elucidating the difference between soil at semi-urban vs. rural sites and between air and soil concentration, we aim to improve the understanding of the sources, occurrence and fate of PAH derivatives in soil.

Methods and materials

Sampling

We sampled the top 10 cm surface soil at grassland sites in Košetice and Mokrý in the Czech Republic (see Fig. 1). Košetice is a rural background site (85 km from Prague). Košetice location 1 (Kos-1) is next to an observatory measurement station on open area. Location 2 (Kos-2) is close to the confluence of two brooks on an open meadow. The soil samples from Košetice were taken in the summer of each year from 2010 to 2017.

Mokrý is a semi-urban site at the rim of an urban and an industrial area (13 km east-northeast of the city centre of Brno). Location 1 (Mok-1) is near a small forest that is close to the edge of a quarry of a cement works. Location 2 (Mok-2), 3.5 km

south of sampling site 1, is close to the village of Sivice and a cement factory. Samples from seven soils, taken from locations Mok-1 and Mok-2 during all seasons except winter from 2006 to 2015, were analysed. Each location was represented by a mixture of ten sub-samples collected from an area of 25 × 25 m. The samples were air-dried, sieved (2 mm mesh) and stored in a dark room at constant temperature and humidity.



Fig. 1: Grassland soil sampling sites

Determination of PAHs, NPAHs and OPAHs in soils

The soil samples (5 g each) were spiked with deuterated PAHs, OPAHs and NPAHs. Subsequently, the target compounds were extracted from the soil by Soxhlet extraction. After concentration, the extract was cleaned-up by column chromatography using 10%-deactivated silica. The target compounds were eluted with ethyl acetate, followed by dichloromethane. After concentration and addition of an internal standard, the PACs in the soil extracts were analysed by GC-MS. The target compounds in this study were 27 PAHs, 17 NPAHs, 1 NOPAH, 11 OPAHs and 2 O-heterocycles. All targeted compounds, including their physico-chemical properties, are shown in Appendix A.

PAHs were measured on a GC (GC 7890A Agilent Technologies) with a Rxi-5Sil MS column (Restek), coupled to a triple quadrupole mass spectrometer (MS 7000B, Agilent Technologies), using electron ionization (EI) in the positive selected ion monitoring (SIM) mode. All nitrated and oxygenated PAHs were analysed by GC-MS using atmospheric pressure chemical ionization (APCI) in negative mode on a 7890 GC (Agilent Technologies) coupled to a triple quadrupole MS Xevo TQ-S (Waters). A 30 m × 0.25 mm × 0.25 μm Rxi-5Sil MS column (Restek) was used. 1 μL of the samples was injected splitless with helium as carrier gas. The target compounds were measured in the multiple reaction monitoring (MRM) mode. The ratio of the target compound and the internal standard PCB121 was used to determine the target compound concentration.

Results and discussion

Concentration

Out of the targeted 17 nitrated PAHs (NPAHs), 11 oxygenated PAHs (OPAHs), one NOPAH and 2 O-heterocycles, 5 NPAHs, 10 OPAHs and both O-heterocycles were found in soils from Košetice and Mokrá. The average concentration of the Σ_{11+2} OPAHs and O-heterocycles in Košetice ($4.07 \pm 3.08 \text{ ng g}^{-1}$) is

lower than in Mokrá ($5.91 \pm 2.30 \text{ ng g}^{-1}$). Similarly, lower NPAH levels are found in Košetice ($0.31 \pm 0.23 \text{ ng g}^{-1}$) than in Mokrá ($0.54 \pm 0.45 \text{ ng g}^{-1}$). The concentrations normalized to the total organic carbon (TOC) content are even significantly different between the two sites for the OPAHs ($p < 0.05$, Student's t-test) and close to significance for the NPAHs ($p = 0.054$, Student's t-test) (see Fig. 2) showing that the difference is not caused by the influence of the soil TOC content. The higher burden in soil from the semi-urban site Mokrá might be caused by the higher proximity to emission sources showing the importance of primary emitted PAH derivatives, especially the OPAHs, for the soil pollution.

We found a correlation ($r = 0.55$, $p < 0.01$) of the concentrations of the high molecular weight (4-5-ring) OPAHs and O-heterocycles with the TOC content in soil, but no significant correlation for the low molecular weight (2-3-ring) OPAHs and O-heterocycles or for the NPAHs. The lack of significant correlation between the TOC content and the concentrations of NPAHs and the 2-3-ring OPAHs might be due to their higher mobility, degradability and formation in soil (Wilcke et al. 2014; Cai et al., 2017). Compared to the other studies of PAH derivatives in soil, the soil concentration from the background site Košetice is among the lowest ever reported.

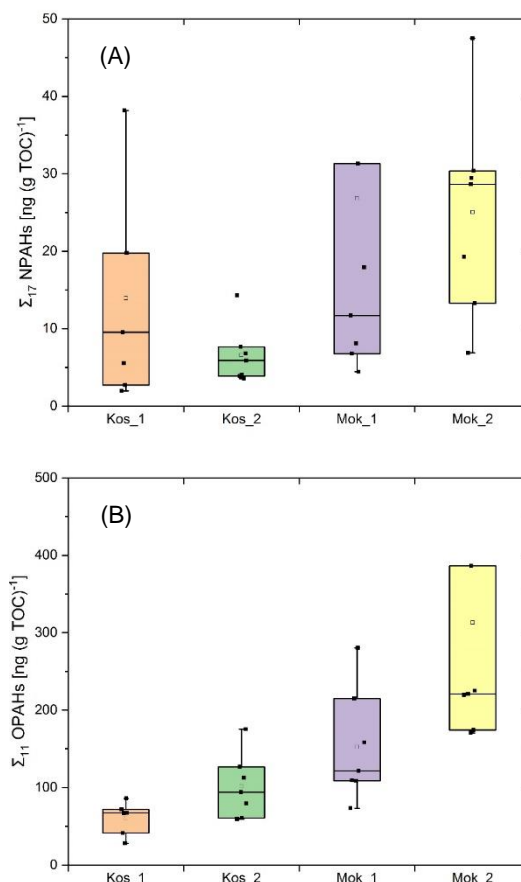


Fig. 2: Concentration of NPAHs (A) and OPAHs (B) in soil normalized to the total organic carbon content (TOC)

Composition patterns

The location average composition patterns of the NPAHs and OPAHs are shown in Fig. 3. 9-fluorenone (9-OFLN), 11-benzo(a)fluorenone (11-OBaFLN) and 11-benzo(b)fluorenone (11-OBbFLN) are the most abundant OPAHs. In air samples at the same location, the relative contribution of 9-OFLN and dibenzofuran (DBF) to the sum of OPAHs and O-heterocycles was significantly higher than in soil samples (Nežiková et al., 2021).

The highest contribution to the Σ NPAHs between 50% and 66% is from 1-nitropyrene (1-NPYR), followed by 6-nitrobenz(a)pyrene (6-NBAP), which differs greatly from the NPAH pattern in air ($\approx 1\%$ and $<1\%$, respectively; Tomaz et al. 2016; Lammel et al. 2020; Nežiková et al. 2021) shown in Fig. 3. It can probably be explained by their susceptibility to photolysis in air (Fan et al., 1996) in combination with slow degradation in soil. The contribution of nitrofluoranthene (NFLT) is between 5–30%. Although the 2-NFLT isomer was not separated from the 3-NFLT, the latter can be neglected in the environment except in immediate vicinity of diesel exhaust (Bamford et al., 2003). In contrast, NFLT has the highest share of all targeted NPAHs in air at Košetice (Nežiková et al., 2021).

In air samples, the ratio of the concentration of 2-NFLT to the concentration of 1-NPYR is often used as a diagnostic ratio for the relative importance of photochemical formation since 1-NPYR is known to be emitted primarily, while 2-NFLT is secondarily formed (Bandowe and Meusel 2017). The ratio of 2-NFLT/1-NPYR in soil in this study, ranging between 0.35 and 0.76 across the four locations, is much lower than in air (23 at Košetice; Nežiková et al. 2021). The indication of the relative importance of primary emissions by this ratio from air is obviously not preserved in soil. However, the ratio is higher at the background site Košetice compared to the semi-urban site Mokra (0.61 ± 0.58 vs 0.36 ± 0.38). More details are given in Wietzoreck et al., 2022.

Temporal variation

The temporal variation of the concentration of PACs in soil at Košetice and Mokra significantly differed between substances. It could be noticed that the concentrations of dibenzofuran, 9-fluorenone, 1-nitropyrene, the 2 ring-NPAHs and some 3-ring PAHs decreased, while it stayed constant or increased for high molecular weight PACs. Nežiková et al. (2021) found a decreasing trend of several NPAHs and OPAHs in air at Košetice between 2015 and 2017 attributable to ongoing emission reductions of PAHs that are also effective for NPAHs and OPAHs. This could be one reason for the decreasing NPAH concentrations. The decrease of the low molecular weight compounds might be explained by higher winter temperatures, leading to a lower share of the compounds in the particulate phase compared to the gas phase. Since deposition of the compounds in the particulate phase is more efficient, lower amounts in this phase could lead to lower concentrations in soil.

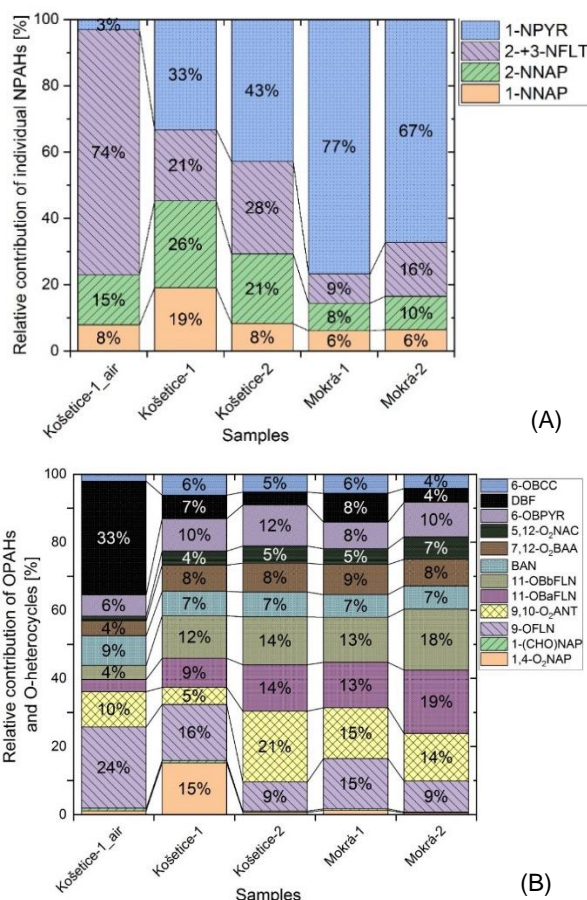


Fig. 3: Composition patterns of NPAHs (A) and OPAHs (B) in soil and air

Summary and conclusion

The concentrations of the PAH derivatives in soil at the central European background site Košetice are among the lowest ever reported. Our results show that several NPAHs and OPAHs are abundant in soil at the background site. 1-NPYR and 6-NBAP, which are identified as highly toxic (IARC, 2012; Abdullahi et al., 2014), were the most abundant NPAHs in soil. The findings suggest that 1-NPYR and 6-NBAP are more stable in soil than in air. Through eventual re-volatilisation, soil may turn into a secondary source of these pollutants. OPAHs were more equally distributed, showing the highest contributions from 9-OFLN, 11-OBaFLN and 11-OBbFLN. We found a correlation of the soil organic carbon content with the high molecular weight OPAHs and PAHs, but not with the low molecular weight OPAHs and PAHs, nor with the NPAHs. In order to study the temporal variation of the air-soil cycling, longer time series and less uncertain biodegradation data in soil are needed.

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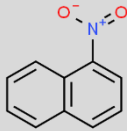
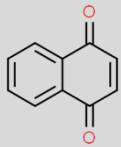
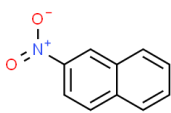
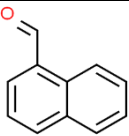
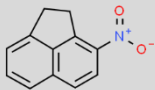
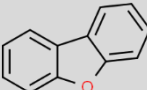
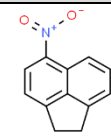
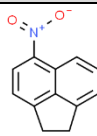
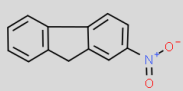
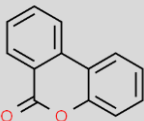
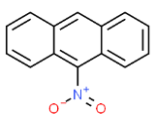
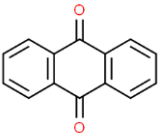
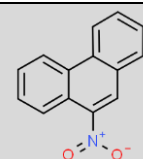
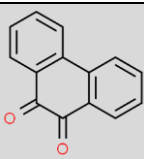
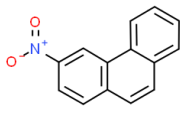
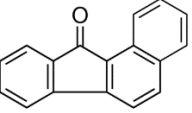
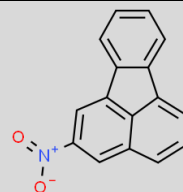
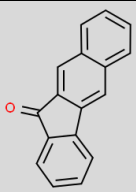
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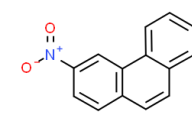
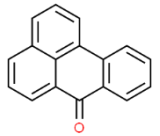
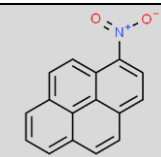
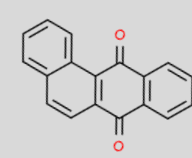
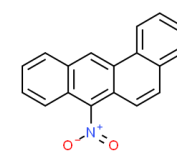
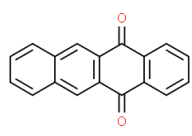
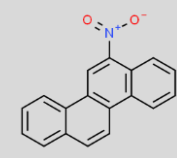
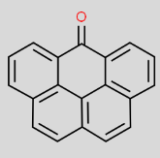
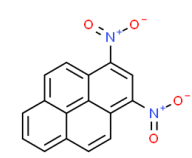
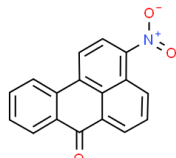
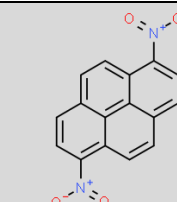
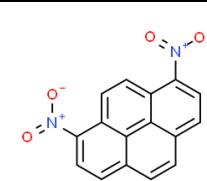
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Appendix A

Table 1: Target compounds including acronyms and structural formulae

Compound	Acronym	Structure	Compound	Acronym	Structure
1-Nitronaphthalene	1-NNAP		1,4-Naphthoquinone	1,4-O ₂ NAP	
2-Nitronaphthalene	2-NNAP		Naphthalene-1-aldehyde	1-(CHO)NAP	
3-Nitroacenaphthene	3-NACE		Dibenzofuran	DBF	
5-Nitroacenaphthene	5-NACE		9-Fluorenone	9-OFLN	
2-Nitrofluorene	2-NFLN		6H-Benzo(c)-chromen-6-one	6-OBCC	
9-Nitroanthracene	9-NANT		9,10-Anthraquinone	9,10-O ₂ ANT	
9-Nitrophenanthrene	9-NPHE		9,10-Phenanthroquinone	9,10-O ₂ PHE	
3-Nitrophenanthrene	3-NPHE		11H-Benzo(a)-fluoren-11-one	11-OBaFLN	
2-Nitrofluoranthene	2-NFLT		11H-Benzo(b)fluoren-11-one	11-OBbFLN	

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Compound	Acronym	Structure	Compound	Acronym	Structure
3-Nitrofluoranthene	3-NFLT		Benzanthrone	BAN	
1-Nitropyrene	1-NPYR		Benz(a)anthracene-7,12-dione	7,12-O ₂ BAA	
7-Nitrobenzo(a)-anthracene	7-NBAA		5,12-Naphthacenequinone	5,12-O ₂ NAC	
6-Nitrochrysene	6-NCHR		6H-Benzo(cd)-pyren-6-one	6-OBPYR	
1,3-Dinitropyrene	1,3-N ₂ PYR		3-Nitrobenzanthrone	3-NBAN	
1,6-Dinitropyrene	1,6-N ₂ PYR				
1,8-Dinitropyrene	1,8-N ₂ PYR				
6-Nitrobenzo(a)-pyrene	6-NBAP	