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

Benjamin A. Musa Bandowe[1,2,3*], Moritz Bigalke[3], Jozef Kobza[4], Wolfgang Wilcke[1]

[1] Institute of Geography and Geoecology, Karlsruhe Institute of Technology (KIT), Reinhard-Baumeister-Platz 1, 76131 Karlsruhe, Germany

[2] Organic Geochemistry Unit (OGU), School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, United Kingdom

[3] Institute of Geography, University of Bern, Hallerstrasse 12, 3012 Bern, Switzerland.

[4] National Agricultural and Food Centre - Soil Science and Conservation Research Institute (SSCRI) Bratislava, Regional working place Banská Bystrica, Mládežnícka 36, 97404 Banská Bystrica, Slovakia

* Corresponding author: Benjamin A. Musa Bandowe
(Email: benjamin.bandowe@giub.unibe.ch, benjamin.bandowe@kit.edu)

# 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 ∑29PAHs concentrations were highest in the Oa and lowest in the Oi horizon, while the ∑14OPAHs and ∑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 ∑29PAHs (2400 – 17000 ng $g^{-1}$), ∑14OPAHs (430 – 2100 ng $g^{-1}$) and ∑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 concentration of ∑29PAH were correlated with those of ∑14OPAH ($r = 0.95$, $p = 0.02$) and ∑4AZA ($r = 0.93$, $p = 0.02$) 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 $K_{OW}$s, pointing at colloid-assisted transport and bioturbation. At some sites, the enrichment factors of OPAHs were negatively correlated with $K_{OW}$ indicating that these compounds were leached in dissolved form. Compared to a study, 13 years before, the concentrations of 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 allows for more diverse mechanisms of partition, sorption and transport in air and soil.

Soil is the major final 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, 1999; 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., 1996a; 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., 1996a; Yang et al., 1991). The spatial distribution of OPAHs and AZAs in forest soil with distance from point emissions 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-PAHs ratios, it is expected that the AZA/related PAHs 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 PAH 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 emission formation of OPAHs? We will test the hypothesis that the concentrations of OPAHs and the OPAH/related-PAH concentration ratios will increase in the order Oi < Oe < Oa because of the increasing formation (and accumulation) of OPAHs from the transformation of PAHs which accompany the decomposition of organic matter.
3. What does the change in concentration and spatial distribution of PAHs from 1994 to 2007 reveal about the long-term behaviour of PAHs in soils?

# 2. Materials and methods

## 2.1 Sampling and soil characterization

In September 2007, we sampled all horizons of the soils at five sites with increasing distances (ca. 500, 1000, 1500, 2000, 2500 m) from an aluminium plant in Žiar nad Hronom (Central Slovakia, Figure 1). The Al plant has been in operation since 1953 and was reconstructed in 1986, when the emissions were substantially lowered (Jamnická et al., 2007; Maňkovská and Steinnes, 1995). The operation of the smelter caused a severe contamination of its surroundings with PAHs, heavy metals and fluoride (Maňkovská and Steinness, 1995; Wilcke et al., 1998, 1996).

**Figure 1**

At each location, we collected samples from all horizons of Typic Dystrudepts or Dystric Cambisols (sites 1, 2, 4 and 5) and Aquic Dystrudepts or Stagnic Dystric Cambisols (site 3, IUSS Working Group WRB, 2014; Soil Survey Staff, 2014), that were accessible by hand digging (Oi, Oe, Oa, A, B and in some soils C horizons) from a soil pit. All samples were collected on the same day. Samples were kept in closed aluminium containers and stored fresh at -18 °C in a freezer until analysis. Several physical and chemical properties (texture, soil pH, effective cation-exchange capacity (ECEC), total organic carbon (TOC) and inorganic carbon (IC) were determined on sub-samples that were dried in an oven at 40 °C, then gently crushed and homogenized (organic layers) or sieved (< 2 mm, mineral soil). The procedures for the determination of the physico-chemical properties are described in detail in previous papers (Bandowe et al., 2010; Bandowe and Wilcke, 2010; Wilcke et al., 2014a, b). Properties of the soil are reported in Table S1 (supplementary information).

## 2.2 Analysis of PAHs, OPAHs and AZAs

About 2-5 g (ground organic horizons) and 13-16 g (mineral soil horizons) from each sampling site were weighed, mixed with inert bulk sorbent (Isolute HM-N, Uppsala, Sweden) and transferred into 33-mL extraction cells (accelerated solvent extractor, ASE 200, Dionex, Sunnyvale, CA). Samples were spiked with 11 perdeuterated PAHs (naphthalene-$D_8$, acenaphthene-$D_{10}$, phenanthrene-$D_{10}$, pyrene-$D_{10}$, benzo[a]anthracene-$D_{12}$, benzo[k]fluoranthene-$D_{12}$, benzo[a]pyrene-$D_{12}$, chrysene-$D_{12}$, perylene-$D_{12}$, dibenzo[a,h]anthracene-D14, and benzo[ghi]perylene-$D_{12}$: 150 µL of a 10 µg mL$^{-1}$ solution of each of the compounds in toluene) as internal standard for PAHs and benzophenone-$D_5$ (150 µL of a 10 µg mL$^{-1}$ solution of the compound in toluene) as internal standard for OPAHs and AZAs. Each sample was extracted twice by pressurized liquid extraction with the ASE 200. The first extraction was with dichloromethane (DCM), while the second extraction was with acetone/DCM/1% trifluoroacetic acid (250:125:1 v/v/v). The ASE was operated with the same settings as reported previously (Bandowe and Wilcke, 2010). The two extracts from each sample were combined and passed through a $Na_2SO_4$ column to remove water. Hexane (1 mL) was added to each extract, rotary evaporated and again 10 mL hexane was added and rotary evaporated to < 1 mL. The extracts of organic horizons were then cleaned up by gel permeation chromatography (GPC). The GPC system consisted of a PrepLinc GPC, equipped with a UV detector (254 nm), an autosampler and glass column (750 mm x 25 mm ID glass column) filled with swelled Bio-beads S-X3 (J2-Scientific, PA, USA). The GPC was run with hexane:dichloromethane (1:1 v/v) as the mobile phase at a flow rate of 5 mL min$^{-1}$.

Extracts of mineral and organic horizons (cleaned on GPC) were transferred onto a column made of 3 g silica gel (10% deactivated). PAHs were eluted with 15 mL hexane:dichloromethane followed by the elution of OPAHs and AZAs with 8 mL dichloromethane and 5 mL acetone. The PAHs fractions and OPAHs+AZAs fractions were collected in separate flasks, spiked with toluene, rotary evaporated, spiked with fluoranthene-

$D_{10}$ (50 µL of 22 a µg $mL^{-1}$ solution) before being transferred into vials for measurements of their PACs concentrations with a gas chromatograph coupled to a mass spectrometer (GC-MS, GC 7890A with a 5975 MSD, Agilent technologies, Palo Alto, CA). Target compounds were quantified with a set of calibration standards that were measured together with samples in the same GC-MS sequence. The internal standard calibration functions were used to quantify masses of all PAC target compounds in our extracts. GC-MS signals, their processing, calibration and quantification were realized with the Agilent ChemStation Software. Further details of the GC-MS parameters and the limits of determinations of our analytical method can be found in previous papers (Bandowe et al., 2014; 2011; 2010; Bandowe and Wilcke, 2010; Lundstedt et al., 2014; Wei et al., 2015).

We determined the concentrations of the following compounds:

- 29 PAHs: 1,2,3,4-tetrahydronaphthalene (THNAPH), naphthalene (NAPH), 2-methylnaphthalene (2-MNAPH), 1-methylnaphthalene (1-MNAPH), biphenyl (BP), 1,3-dimethylnaphthalene (1,3-DMNAP), acenaphthylene (ACENY), acenaphthene (ACEN), fluorene (FLUO), phenanthrene (PHEN), anthracene (ANTH), 1-methylphenanthrene (1-MPHEN), 3,6-dimethylphenanthrene (3,6-DMPHEN), fluoranthene (FLUA), pyrene (PYR), 1-methyl-7-isopropylphenanthrene (RET), benz[a]anthracene (B(A)A), chrysene+triphenylene (CHRY), benzo[b+j+k]fluoranthenes (B(BJK)), benzo[e]pyrene (B(E)P), benzo[a]pyrene (B(A)P), perylene (PERY), indeno[1,2,3-cd]pyrene (IND), dibenz[a,h]anthracene (DIBE), benzo[ghi]perylene (B(GHI)) and coronene (COR);
- 14 OPAHs: 1-indanone (1-INDA), 1,4-naphthoquinone (1,4-NQ), 1-naphthaldehyde (1-NLD), 2-biphenylcarboxaldehyde (2-BPCD), 9-fluorenone (9-FLO), 1,2-acenaphthylenedione (1,2-ACQ), 9,10-anthraquinone (9,10-ANQ), 4H-cyclopenta[d,e,f]phenanthrene-4-one (CPHENone), 2-methyl-9,10-anthraquinone (2-

MANQ), benzo[a]fluorenone (B(A)FLUone), 7H-benz[d,e]anthracene-7-one (BANTone), benzo[a]anthracene-7,12-dione (7,12-B(A)A), 5,12-naphthacenequinone (5,12-NACQ) and 6H-benzo[c,d]pyrene-6-one (BPYRone)

- 4 AZAs: quinoline (QUI), benzo[h]quinoline (BQI), acridine (ACR) and carbazole (CBZ)

## 2.3 Quality assurance and control

All used organic solvents were of high purity for pesticide residue analysis or HPLC grade, purchased from Carlo Erba (Milan, Italy). All labware were machine-washed with soap, rinsed, and dried in a clean oven. All the non-volumetric glassware and metallic labware were also baked at 250 °C for 24 h to remove contaminants. Three procedural blanks made of bulk inert sorbent (Isolute, HM-N) were extracted and their PACs concentrations measured. Most of the target compounds were not detected in the blanks or their amounts in the blanks were insignificant compared to their amounts in the real samples. The mean amounts of PACs the three blanks (where detected) was then subtracted from those measured in the samples to correct for laboratory contamination. We also extracted and analysed replicates ($n = 2$) of the certified reference material ERM-CC013a-PAHs in soils (Federal Institute for Materials Research Testing [BAM], Berlin, Germany). The relative standard deviation (RSD) of ∑29PAH, ∑14OPAHs and ∑4AZAs concentrations in the replicates ($n = 2$) of ERM-CC013a determined with our procedures were 8%, 9% and 12%, respectively. The recoveries of the sum of PAH concentrations for which indicator and certified values were provided was 135±12% (average ± standard deviation). For the OPAHs and AZAs, there are no certified reference materials. We therefore compared our OPAHs and AZAs concentrations to the grand means determined for this same reference material in a recent intercomparison exercise (Lundstedt et al., 2014). The recoveries compared to the grand means in the intercomparison exercise were 101 ± 9%, 83 ± 10% for the OPAHs and AZAs respectively. At the location 2500 m from the Al plant, the A-horizon soil was analyzed in replicates (n = 2). The RSD of the ∑29PAHs, ∑14OPAHs and ∑4AZAs were 24%, 7.4% and 7.1%, respectively. At location 500 m from the Al plant the Oe and A-horizons were analyzed in replicates (n = 2). The RSD of the replicates analysis of Oe horizon were 53%, 5% and 20%, respectively for ∑29PAHs, ∑14OPAHs and ∑4AZAs. For the A horizon at this location the RSD for the replicate analysis were 31%, 16% and 24% respectively for ∑29PAHs, ∑14OPAHs and ∑4AZAs, respectively.

### 2.4 Calculations and statistical analyses

The sum of the concentrations of all analyzed PAHs, OPAHs and AZAs are called ∑29PAHs, ∑14OPAHs and ∑4AZAs, respectively. The sum of the concentrations of all non-alkylated PAHs, the sum of the 16 US-EPA PAHs, the sum of all non-alkylated PAHs with 2-3 rings, and 4-7 rings are called ∑21PAHs, ∑EPA-PAHs, ∑LMW-PAHs and ∑HMW-PAHs, respectively. We calculated the enrichment factors $e$ for each compound as the concentration of a compound in a soil horizon, divided by the concentration of that same compound in the horizon above it within the same soil profile. Concentration data were log (x+1) (where x is concentration) transformed to improve normal distribution of the data sets. Statistical analysis was performed with STATISTICA 7.0 software (Statsoft, Hamburg, Germany). Statistical tests were set to be significant at a $p < 0.05$. Octanol-water partition coefficients ($K_{OW}$) for PAHs were taken from the literature (Mackay et al., 2006; Neff et al., 2005), while those of OPAHs and AZAs were estimates with $K_{OW}$WIN version 1.67 EPI Suite$^{TM}$ (US EPA: http://www.epa.gov/opptintr/exposure/pubs/episuitedl.htm).

## 3. Results

The concentration of ∑29PAHs in the Oi horizon was lowest at the location farthest from the Al plant, but the ∑29PAHs concentrations at the other locations were similar (Table 1, Figure

2). The PAHs mixtures in the Oi horizons were dominated by PHEN (25%), PYR (10%), NAPH (8%) and ANTH (8%) (Figure 3, Table S2). The 2+3-ring PAHs dominated the non-alkylated PAHs mixtures in the Oi horizon, with a mean contribution of 57% to the ∑21PAHs concentrations (Figure S1).

**Table 1**

**Figure 2**

**Figure 3**

At most locations, the Oe horizons showed higher concentrations of ∑29PAHs than the Oi horizons. The highest concentrations of ∑29PAHs in the Oe horizons occurred at the location farthest from the Al plant, with clearly elevated concentrations at the other locations (Table 1, Figure 2). Moreover, PAHs mixtures were dominated by PHEN (13%), B(BJK) (12%), PYR (10%) and FLUA (10%), showing a higher contribution of HMW-PAHs to the PAHs mixtures than in the Oi horizons (Figure 3, Table S2). The 4-ring PAHs (41%) contributed a higher proportion to the ∑21PAHs compared to that of ∑2+3-ring PAHs (25%) (Figure S1). The ∑HMW-PAHs/∑LMW-PAHs concentration ratios in the Oe horizons averaged 3.4 (range: 1.5-6.8) with the highest and lowest values at locations closest and farthest from the Al plant, respectively.

The concentrations of ∑29PAHs in the Oa horizons were much higher than in the two other O horizons. The highest concentration of ∑29PAHs in the Oa horizons was at the location closest to and the lowest farthest away from the Al plant (Table 1, Figure 2). The PAHs mixtures were dominated by 2-MPHEN (14%), B(BJK) (12 %), PHEN (12%) and RET (11 %). The contribution of the ∑2+3ring PAHs, ∑4-ring PAHs, ∑5-ring PAHs and ∑6+7-ring PAHs to the ∑21PAH were 38%, 33%, 21% and 8%, respectively (Figure 3 & S1, Table S2). The ∑HMW-

PAHs/∑LMW-PAHs concentration ratios were 3.8 and 2.4, at the locations closest and farthest from the Al plant, respectively.

In the mineral A horizon, the concentrations of ∑29PAHs were highest closest to and lowest farthest away from the Al plant (Table 1, Figure 2). The relationship between the concentration of ∑29PAHs and distance from the emission source was exponential ($R^2$ = 0.95) (Figure 4). The PAHs mixtures in the A horizons were dominated by B(BJK) (18%), PHEN (15%), IND (10%) and CHRY (9%) (Figure 3, Table S2). The ∑HMW-PAHs/∑LMW-PAHs concentration ratio in the A horizon averaged 2.9 (range: 2.6 – 3.3) and was independent of the distance from the Al plant and higher than in the O horizons.

The concentrations of ∑29PAHs in the deeper mineral horizons (B, Bg and C) did not show consistent decreases with increasing distance from the Al plant. The concentrations of ∑29PAHs were consistently lower with increasing depth of the mineral horizon (i.e. A > B > C) (Table 1).

**Figure 4**

The concentrations of the ∑14OPAHs in the Oi, Oe and Oa horizons were generally higher at locations closest to the plant but did not show consistent changes with distance from the Al plant (Table 1, Figure 2). At the location closest (500 m from Al plant) to the Al plant, the ∑14OPAHs concentrations in the Oi horizon were higher than in the Oe horizon, while at location 2000 m from the Al plant, the reverse was true (Table 1). The concentrations of ∑14OPAHs in the three O horizons at location 2500 m from the Al plant decreased in the order, Oi > Oe > Oa. The composition of the OPAHs mixtures in the Oi horizon was dominated by 9-FLO (28%), B(A)FLUone (21%) and BPYRone (13%). The OPAHs mixtures in the Oe horizon were dominated by 9,10-ANQ (26 %), 9-FLO (14%) and BANTone (11%) and those in the Oa horizon by BPYRone (39%), 1,2-ACQ (19%) and 9,10-ANQ (17%) (Figure 3B, Table S3).

The ∑14OPAHs concentrations in the mineral A horizon (Table 1, Figure 2) were highest closest to and lowest farthest away from the Al plant. Similar to those of the ∑29PAHs, the concentrations of ∑15OPAHs in the A horizon decreased exponentially with distance from the Al plant ($R^2$ = 0.90; Figure 4). The OPAHs mixtures in the A horizons were on average dominated by 9,10-ANQ (29%), 7, 12-B(A)A (25%), B(A)FLUone (17%) and 9-FLO (8%) (Figure 3B, Table S3). Interestingly, the ∑14OPAH/∑29PAH ratio was highest in the one horizon, showing clear visible indications of redox changes (location 3, Bg horizon; Table 2). Here the ratio was higher than in all other horizons, except the Oi horizons closest to the smelter.

Similar to those of the ∑14OPAHs, the concentrations of ∑4AZAs in the Oi horizons were higher than in the Oe horizons at location 1 (500 m from the Al plant) and 5 (2500 m from the Al plant), while the reverse was true at location 4 (2000 m from the the Al plant) (Table 1, Figure 2). The AZAs mixtures in the Oi horizons were dominated by BQI (43%) and ACR (41%), in the Oe horizons by BQI (47%) and CBZ (21%), and in the Oa horizons by BQI (47%) and ACR (44%; Figure 3B, Table S3).

The concentrations of ∑4AZAs in the A horizon were the highest at locations close to and the lowest farthest away from the Al plant (Table 1, Figure 2). The concentrations of ∑4AZAs decreased exponentially with distance ($R^2$ = 0.93; Figure 4). The composition of the AZAs mixtures in the A horizons were dominated by CBZ (40%) and BQI (37%; Figure 3B, Table S3).

The ∑29PAHs, ∑14OPAHs and ∑4AZAs concentrations in the B horizons were highest at the sampling location farthest from the smelter and decreased with decreasing distance. At the location farthest from the Al plant the ∑29PAHs and ∑14OPAHs concentrations were only slightly lower in the B compared to the A horizons, while ∑4AZAs concentrations were identical (Table 1).

To identify the drivers of the vertical distribution, we correlated the enrichment factors *e* at each site with the octanol-water partition coefficients [log $K_{OW}$]. For the PAHs, significant correlations occurred between enrichment factors and their $K_{OW}$ values at site 2 $e_{Oe/Oi}$ ($r = 0.57$, $p < 0.001$), site 3 $e_{Oe/Oi}$ ($r = 0.64$, $p < 0.001$), site 3 $e_{A/Oe}$ ( $r = 0.42$, $p = 0.01$), site 4 $e_{A/Oe}$ ($r = 0.44$, $p = 0.03$) and site 5 $e_{Oe/Oi}$ ($r = 0.60$, $p = 0.01$) (Figs. S2 & S3). For the OPAHs, significant correlations between enrichment factors (Fig S4) and $K_{OW}$ occurred at site 1 $e_{Oe/Oi}$ ($r = 0.76$, $p = 0.007$), site 2 $e_{B/A}$ ($r = -0.71$, $p = 0.020$) and site 5$e_{Oa/Oe}$ ($r = 0.59$, $p = 0.01$). For the AZAs the low number of compounds ($n = 4$) was not suitable for a correlation analysis between enrichment factors and $K_{OW}$ values.

# 4. Discussion

## 4.1. Concentrations and distribution of PACs with distance from the Al plant

The concentrations of ∑29PAHs in the O horizons of the soils were in the range of those of ∑US-EPA PAHs (105 – 14889 ng $g^{-1}$) reported in an extensive ($n = 447$) nationwide survey of German forest soils covering both background and contaminated sites (Aichner et al., 2013; 2015). The concentrations of PAHs in the A horizons of the forest soils near Žiar nad Hronom were elevated compared to mineral horizons of forest soils from background and rural areas of the USA (Obrist et al., 2015). The extensive survey of Aichner et al. (2015) in Germany found a concentration range of 20-9038 ng $g^{-1}$ in the 0-5 cm layer of mineral soils under forest (Aichner et al., 2015), while in mineral horizons of forest soils from northern Czech Mountains the concentration of ∑20PAHs was 238 – 7476 ng $g^{-1}$ (Wilcke and Zech, 1997; Wilcke et al., 1996). The mean and median concentrations of PAHs in mineral forest soils in the review of Wilcke (2000) were 904 and 410 ng g$^{-1}$, respectively. Thus, the concentrations of the ∑29PAHs in the O horizons at the sites nearest (500 – 1000 m) to the Al plant were at the upper end or even above the range reported for forest soils and thus can be considered as strongly contaminated. Even the three sites further away from the Al plant still show concentrations above background. Interestingly, the A horizon was dominated by higher proportions of the HMW-PAHs compared to the O horizons suggesting that the PAHs did not reach the A-horizon by leaching (which would have favoured the LMW-PAHs). Instead, we suggest that the main mechanism of transfer of PAHs from the Oa to the A-horizon was biological mixing.

The concentrations of ∑14OPAHs in our study were much higher than those of ∑9OPAHs measured in organic layers of remote forest soils of USA, the only other study of OPAHs concentration in organic layers of forest soils, we are aware of (i.e. 6±6 to 39±25 ng g$^{-1}$) (Obrist et al., 2015) indicating the substantial enrichment of OPAHs in the forest soils near Žiar nad Hronom, because of the emissions from the Al plant. The OPAHs could have been directly emitted together with PAHs from the Al plant, with additional OPAHs formed by post-emission transformation of PAHs (Lundstedt et al., 2007; Wilcke et al., 2014b).

The dominance of 9-FLO and 9,10-ANQ is similar to findings from organic horizons and mineral forest soils in the USA (Obrist et al., 2015). 9-FLO and 9,10-ANQ were also found to be the most abundant compounds in mineral soils at other locations and in combustion emissions (Bandowe et al., 2014; 2011;2010; Layshock et al., 2010; Vicente et al., 2016).

We are not aware of any measurements of AZAs concentrations in forest soils near an Al plant. However, AZAs were detected in ambient air samples near an Al smelter in Canada, so that the presence of AZAs in our study soils can be expected (Roussel et al., 1992). The concentrations of the ∑4AZAs in surface soils from the cities of Bangkok (Thailand) and Xi’an

(China) were 0.1-31 ng $g^{-1}$ and 784 ng $g^{-1}$, respectively (Bandowe et al., 2014; Wei et al., 2015a). The concentrations of ∑9AZAs in the mineral topsoil (0-10 cm) of an industrial site in the Czech Republic were 640-694 ng $g^{-1}$, while the concentration in a reference rural site was 6.9 ng $g^{-1}$ (Švábenský et al., 2009). The concentrations in the A horizons at our study site were higher than in soils from background and remote locations (e.g., Argentina ∑4AZA: n.d – 0.97 ng $g^{-1}$, Wilcke et al., 2014a) but comparable to those from industrial sites as summarized in Bandowe et al. (2014). The dominance of CBZ is similar to that observed in a study of urban soils in Bangkok (Bandowe et al., 2014). Carbazole was also measured at concentration of 8-268 ng $g^{-1}$, not detected (n.d.) – 37 ng $g^{-1}$ and n.d. – 10 ng $g^{-1}$ in the organic horizon, 0-5 cm and 5-10 cm of mineral horizons, respectively of German forest soils (Mumbo et al., 2016). The study of Mumbo et al. (2016) also showed the trend organic horizon > 0-5 cm > 5-10 cm in the concentrations of carbazole, which is contrary to the trend we observe in the vertical distribution of the ∑4AZA. In our study the ∑4AZAs concentration in the A-horizon was higher than in the O-horizons at most locations.

The distribution of PAHs, OPAHs and AZAs in the organic horizons demonstrate that the Al plant was the main point source for the PACs in O horizons of soils. Although the location 2500 m away from the emission source was clearly least affected, there was no systematic increases in PACs concentrations in each of the organic horizons with decreasing distance to the Al plant. Several factors could explain the lack of distance-concentration relationships including differences in adsorbing surface area among the sampled organic layers, age differences between similar layers at different locations, soil properties (Table S1), composition of tree species, topography, turnover times and vertical transport into deeper horizons.

In the A horizons, the concentrations of ∑29PAHs correlated significantly with those of ∑14OPAHs ($r = 0.95$, $p = 0.016$) and ∑4AZAs ($r = 0.93$, $p = 0.02$), which is in contrast to the

O horizons. The concentrations of several individual PAHs, OPAHs and AZAs were also significantly correlated with each other in A horizons. Such correlations have been observed in other studies in soils and are interpreted as indication of the common origin (emissions from combustion processes taking place in the Al plant) and similar post-emission fates of these three groups of PACs (Bandowe et al., 2014; Obrist et al., 2015; Wilcke et al., 2014). In the study soils, the close correlation of many PACs concentrations with each other can likely be attributed to biological mixing from the organic layer into the mineral A horizon. The higher pH at the two sites nearest to the Al plant could be indicative of a higher biological activity and thus faster biological mixing of the organic layer into the mineral soil. However, these sites were at the same time more strongly contaminated with a number of organic and inorganic pollutants and the higher pH is attributable to the deposition of alkaline dusts associated with the pollutant emissions (Maňkovská et al., 1995; Wilcke et al., 1998; 1996). Because the stronger contamination of these sites likely reduces biological activity in spite of the higher pH, we do not expect marked differences in biological mixing or O with A horizons.

The concentrations of each of the PAC groups in the A-horizons showed a close correlation with distance from the Al plant, indicating that emissions from the Al plant were the major source of most of the studied PACs. Similar exponential relationships between distance from emission source and concentrations of PAHs were also observed in previous studies in forest soils at the same and other locations (Van Brummelen et al., 1996a; Wilcke et al., 1996). In the B horizon, the concentration of PACs did not consistently decrease with increasing distance from Al plant (or indeed even tended to show an opposite trend to what was observed for the A horizons, Table 1). This points to the importance of soil properties for the transport of PACs in the mineral soil, which is overprinting the higher deposition close to the smelter. With increasing distance from the Al plant, the organic matter content as well as the ECEC decreases (Table S1), offering less sorption sites, particularly for the more polar PACs and thus favour greater translocation of PACs into deeper horizons of the mineral soils. Another reason for the stronger depth transport at the farther distances might be the higher sand concentrations allowing for a faster percolation of water and solutes, particularly at site 5.

The ∑HMW-PAHs/∑LMW-PAHs concentration ratios in the Oi horizons averaged 0.85, with the highest value at the location closest to the smelter and lowest at the location farthest away probably indicating a distillation effect, i.e. faster deposition of HMW-PAHs into soils, and longer-range atmospheric transport of LMW-PAHs because of the higher proportion of HMW-PAHs that is partitioned to the particle phase of air (Wei et al., 2015b: Wilcke et al., 1996; Yang et al., 1991).

The ratios of individual OPAHs or AZAs to their related PAHs (and presumed precursors of the OPAHs) are used to indicate whether transformation and transport processes taking place with increasing soil depth lead to the accumulation of OPAHs or AZAs. Several of the OPAHs/related PAH ratios were > 1, indicating the higher abundance of the OPAHs relative to their related and often monitored PAHs (Table 2). Similar observations have been consistently reported in soils, air and combustion emissions (Bandowe et al., 2014, 2011, 2010; Vicente et al., 2016; Walgraeve et al., 2010; Wei et al., 2015a,b; Wilcke et al., 2014; Layshock et al., 2010) and can result from primary emission sources or from post-emission transformation of the PAHs to OPAHs.

**Table 2**

## 4.2 The depth distribution as indicator for sources and transport of PACs.

In general, the concentration of ∑29PAHs in the O horizons increased in the order Oi < Oe < Oa (Figure 2, Table 1). The concentrations of ∑29PAHs in the Oa horizons were higher or similar to the concentration of the underlying A horizons (Figure 2). The vertical trends are in line with previous studies (Krauss et al., 2000; Pichler et al., 1996). The mineral horizon showed consistent decreases of ∑29PAH concentration with increasing depth largely consistent with previous studies (Guggenberger et al., 1996; Krauss et al., 2000). The organic matter concentrations in the mineral horizons, which followed similar trends, can partly explain the decreasing PAH concentrations, because organic matter is the main sorbent of PAHs in soils (Table S1, Wilcke, 2000).

In the O horizons, the enrichment factors of PAHs were at several study sites significantly positively correlated ($p < 0.05$) with the $K_{OW}$ values (Figure S2) reflecting the accumulation of the more hydrophobic PAHs with increasing organic matter transformation (Pichler et al., 1996; Wilcke and Zech, 1997). The HMW-PAHs are less bioavailable, less degraded (more persistent) compared to the more hydrophilic, more bioavailable LMW- PAHs, which are increasingly degraded with increasing organic matter transformation (Guggenberger et al., 1996; Krauss et al., 2000; Pichler et al., 1996). We did not find significant correlations of the enrichment factors with $K_{OW}$ values in the mineral horizons suggesting that the translocation of PAHs from the organic layer into the mineral soil horizons and between the mineral horizons were partly controlled by DOM- and colloid-assisted transport (Guggenberger et al., 1996; Krauss et al., 2000; Wilcke et al., 1996). We interpret the fact that none of the PAH enrichment factors at the location closest to the Al plant correlated with $K_{OW}$ as strong indication that the higher impact of fresh emissions from the Al plant might be influencing the vertical distribution.

In contrast to the ∑29PAHs concentrations, we could not identify a consistent pattern of increasing concentrations of ∑14OPAHs and ∑4AZAs from the Oi to the Oa horizons (Table 2, Figure 2). We attribute this finding to the fact that OPAHs can both be degraded and formed during advancing decomposition of organic matter (Wilcke et al., 2014b), both processes compensating each other.

In few cases the enrichment factors of the OPAHs in the O horizons were significantly positively correlated with the $K_{OW}$ values (Figure S4). In these soils at sites 1 and 5, the preferential degradation of the OPAHs with advancing organic matter decomposition seems to overwhelm the formation of new OPAHs from parent PAHs. Similarly, there were weak but significant correlations of the enrichment factors of OPAHs between the A and Oa horizons and the $K_{OW}$ values (Fig. S4) at site 2 suggesting that at this site leaching of OPAHs from the organic layer into the mineral soils played a role, in spite of the dominating transfer of PACs from the O into the A horizons by biological mixing. This underlines the higher water solubility and resulting leaching of OPAHs than of PAHs in soil. In the mineral horizons, the enrichment factors of OPAHs were significantly negatively correlated with the $K_{OW}$ values at the location 1000 m from the Al plant (Figure S4), suggesting that the vertical translocation of OPAHs at this site was mainly driven by leaching as truly dissolved compound.

At locations 1 (500 m from the Al plant) and 5 (2500 m from the Al plant), the only two sites in which we detected OPAHs in two to three O horizons, the ∑14OPAHs/∑29PAHs concentration ratios and the individual OPAHs/related-PAHs decreased from the Oi via the Oe to the Oa horizons (Table 2). The OPAH/PAH ratio in the Oi horizon reflects the ratios in the primary emission (or transformation in the atmosphere/on plant surfaces) (Weiss, 2000). This suggests that the degradation of organic matter (Oi to Oa) mainly reduces the concentrations of OPAHs relative to PAHs, which may indicate faster degradation of OPAHs (as a result of higher bioavailability) compared to PAHs or faster leaching of OPAHs out of the organic horizon (as a result of higher water solubility) relative to the PAHs. In the mineral horizons, we found increases in the ∑14OPAHs/∑29PAHs concentration ratios with increasing depth. However, this trend was only clear in the profiles in which a Bg or C horizon was present (500 m and 1500 m from the Al plant). In the other profiles and generally from the A to the B horizon the ∑14OPAH/∑29PAH concentration ratios only showed minor changes. The 1,2-

ACQ/(ACENY+ACEN) concentration ratios increased consistently in all study soils. This was occasionally also true for some other individual OPAH/related PAH concentration ratios (Table 2). Such vertical concentration trends suggest faster translocation of the OPAHs, particularly of 1,2-ACQ into deeper mineral horizons by leaching as truly dissolved solute. We attribute the lack of consistent results for other OPAHs or AZAs than 1,2-ACQ to the fact that a multitude of site-specific soil properties interact with OPAHs and AZAs in a way that either inhibits or enhances the transport independent of their water solubility (Bi et al., 2006; Weigand et al., 2002). The increased ∑14OPAHs/∑29PAHs ratios and some individual OPAHs or AZAs/related PAHs ratios in the B and C horizons, might point at a higher risk of ground water resources to be contaminated with PAC mixtures that contain high fractions of OPAHs and AZAs (Schlangers et al., 2008; Weigand et al., 2002), which could have possible (eco)toxicological consequences, considering the higher toxicity of some of these OPAHs and AZAs than of their related PAHs (Anyanwu and Semple, 2016; Bleeker et al., 2002; Lundstedt et al., 2007).

Another explanation for the high ∑14OPAHs/∑29PAHs, particularly in the Bg horizon at site 3 might be the fact, that this soil horizon showed visible influence of redox changes (mottled pattern of bleached and red zones). These redox changes might also influence the formation of OPAHs, relative to PAHs. Redox conditions are known to influence decomposition of PAHs (Leduc et al., 1988) and the alternating redox conditions, affect and change the microbial community (Hanke et al. 2013). The alternating redox conditions in soils might affect formation of OPAHs, when the soil is reoxidized. However, as we have only one sample with an indication for redox changes, these hypotheses needs further testing.

## 4.3 What does the change of PAH distribution from 1994 to 2007 tell us about the transport of PAH in soils.

In the previous study from 1994, when three soils were sampled along the same deposition gradient (distance 1320 to 2180 m), the concentrations of ∑20PAHs were 38596 – 72523, 57273 – 93785 and 35409 – 73003 ng $g^{-1}$ in the Oi, Oe and Oa horizons (Figure 5; Wilcke et al., 1996), respectively indicating marked decreases in the concentrations of PAHs in samples taken in 2007 compared to those taken in 1994 (Wilcke et al., 1996). In the previous study, the concentrations of ∑20PAHs in the A horizons ranged from 1172 to 2485 ng $g^{-1}$ and in the B horizon from 151 to 376 ng $g^{-1}$ (Figure 5) and thus were higher in 2007 than in 1994. These results illustrate that the organic layers recovered from their high PACs load in 1994, because of their limited residence time and the emission control measures established from 1986 on (Jamnická et al., 2007; Maňkovská and Steinness, 1995). The PAHs in the highly contaminated organic layers, however, were not fully degraded but incorporated into the mineral horizons by biological mixing leading to higher concentrations in the A and B horizons in 2007 than in 1994. Our results illustrate that the disappearance of a contaminant load from soil organic layers in forests does not necessarily mean that the compounds were degraded. The reductions we see are also consistent with the emission of PAHs from the Žiar nad Hronom Al smelter which has decreased from 68 t $a^{-1}$ (in 1990), to 12 t $yr^{-1}$ (in 1995) and 0.8 t $yr^{-1}$ (in 2001) (Jamnická et al., 2007).

**Figure 5**

## 5. Conclusions

- This study showed significant inputs of OPAHs, AZAs and PAHs originating from an Al plant into forest soils. The spatial distribution of PAHs, OPAHs and AZAs in the A and some organic horizons identified the Al plant as common source. The lack of a systematic relationship between the distance from the Al plant and the concentrations of PACs in the B underlined the importance of soil properties for vertical PACs redistribution in soils, because the study soils varied particularly with respect to their pH values and sand concentrations.

- The vertical distribution of PAHs and OPAHs in the organic horizons could be explained by the relative accumulation of the more hydrophobic PACs with increasing organic matter transformation. The concentrations of PAHs in the A horizons were significantly correlated with those of OPAHs and AZAs, which is attributable to their common primary source and mixing from the organic layer into the mineral soil by biological activity. The vertical distribution of PAHs in the mineral soil was not significantly correlated with their octanol-water partition coefficients, because of DOM- and colloid-assisted leaching. At several locations, the vertical distribution of OPAHs in the soils was related with the octanol-water partition coefficient demonstrating that leaching in truly dissolved form played a more important role for OPAHs than for PAHs. This was further backed by increases in the ratios of individual OPAHs to PAH ratios with increasing depth of the mineral soil at several locations.
- The PAHs concentrations in the O horizons have significantly decreased between 1994 and 2007, because of improved emission control, turnover of the O horizons at a decadal scale and mixing into the mineral soil. Despite decreasing emissions in recent times, the concentrations of PAHs in the A and B horizons have increased from 1994 to 2007 as a result vertical transport.

## Acknowledgements

We gratefully acknowledge financial support from the Swiss National Science Foundation (SNF 200021_131938/1). Benjamin A. Musa Bandowe acknowledges the P.R.I.M.E. fellowship from the German Academic Exchange Service (DAAD). We also thank Mr.

Alexander Hermann (Institute of Geography, University of Bern, Switzerland) for drawing Fig. 1, Sylvia Bondzio (Institute of Geography, Johannes Gutenberg University Mainz, Germany) and Dr. Daniela Fischer (Institute of Geography, University of Bern, Switzerland) for physico-chemical characterization of the soils.

Table 1. Sum of the concentrations of the three studied PACs groups.

| Sampling point # | Distance from the Al plant [m] | Horizon designation | ∑29PAHs | ∑14OPAHs | ∑4AZAs |
|---|---|---|---|---|---|
| | | | --------------------ng $g^{-1}$-------------------- | | |
| 1 | 500 | Oi | 1100 | 1800 | 110 |
| 1 | 500 | Oe | 6200 | 710 | 43 |
| 1 | 500 | Oa | 21000 | na | na |
| 1 | 500 | A | 17000 | 2873 | 280 |
| 1 | 500 | B | 670 | 130 | 8.3 |
| 1 | 500 | C | 61 | 33 | 0.10 |
| 2 | 1000 | Oi | 1500 | na | na |
| 2 | 1000 | Oe | 6500 | 950 | 45 |
| 2 | 1000 | Oa | 17000 | na | na |
| 2 | 1000 | A | 8400 | 2000 | 200 |
| 2 | 1000 | B | 520 | 90 | 5.2 |
| 3 | 1500 | Oi | 1900 | na | na |
| 3 | 1500 | Oe | 2200 | 840 | 28 |
| 3 | 1500 | A | 4800 | 740 | 58 |
| 3 | 1500 | B | 1000 | 210 | 17 |
| 3 | 1500 | Bg | 47 | 61 | 1.9 |
| 4 | 2000 | Oi | na | 300 | 4.7 |
| 4 | 2000 | Oe+Oa | 1900 | 620 | 32 |
| 4 | 2000 | A | 2600 | 740 | 60 |
| 4 | 2000 | B | 980 | 320 | 14 |
| 5 | 2500 | Oi | 800 | 350 | 54 |
| 5 | 2500 | Oe | 680 | 150 | 14 |
| 5 | 2500 | Oa | 1800 | 120 | 17 |
| 5 | 2500 | A | 2400 | 430 | 27 |
| 5 | 2500 | B | 1900 | 320 | 27 |

[a] na is not available.

Table 2: Ratios of the concentration of OPAHs or AZAs to related PAHs.

| Location/ Horizon | ∑14OPAH/∑29PAH | 1,4-NQ/NAPH | 1-NLD/1-MNAPH | 9-FLO/FLUO | 1,2-ACQ/(ACENY+ACEN) | 9,10-ANQ/ANTH | 7,12-B(A)A/B(A)A | QUI/NAPH | BQI/PHEN | ACR/ANTH | CBZ/FLUO |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-Oi | 1.6 | 0.04 | 1.3 | 36 | 6.2 | 1.2 |  | 0.3 | 0.40 | 0.41 | 0.20 |
| 1-Oe | 0.12 |  | 0.01 | 1.5 | 0.36 | 1.1 |  | 0.03 | 0.02 | 0.05 | 0.09 |
| 1-Oa |  |  |  |  |  |  |  |  |  |  |  |
| 1-A | 0.17 | 0.01 | 0.35 | 6.3 | 0.04 | 1.6 | 1.1 | 0.01 | 0.04 | 0.11 | 3.1 |
| 1-B | 0.19 |  |  | 3.7 |  | 1.5 | 1.7 |  | 0.03 | 0.09 | 0.95 |
| 1-C | 0.53 |  |  |  |  | 0.90 | 0.81 |  |  | 0.01 |  |
| 2-Oi |  |  |  |  |  |  |  |  |  |  |  |
| 2-Oe | 0.15 |  | 0.06 | 4.1 | 0.65 | 1.1 | 0.38 | 0.05 | 0.05 | 0.05 | 0.39 |
| 2-Oa |  |  |  |  |  |  |  |  |  |  |  |
| 2-A | 0.24 |  | 0.47 | 9.7 | 0.42 | 2.1 | 2.1 | 0.07 | 0.04 | 0.17 | 4.3 |
| 2-B | 0.17 |  |  | 5.7 | 0.80 | 0.78 | 0.16 |  | 0.02 |  | 2.0 |
| 3-Oi |  |  |  |  |  |  |  |  |  |  |  |
| 3-Oe | 0.39 | 0.01 | 0.12 | 4.6 | 4.5 | 1.1 | 0.65 | 0.14 | 0.01 | 0.03 | 0.26 |
| 3-A | 0.15 | 0.01 | 0.12 | 5.0 | 0.14 | 0.92 | 1.3 | 0.01 | 0.05 | 0.02 | 2.1 |
| 3-B | 0.21 |  |  | 10 | 0.83 | 0.76 | 2.3 | 0.02 | 0.03 | 0.06 | 2.5 |
| 3-Bg | 1.3 |  | 0.14 | 10 | 7.6 | 1.0 | 7.4 | 0.02 | 0.01 | 0.03 | 5.1 |
| 4-Oi |  |  |  |  |  |  |  |  |  |  |  |
| 4-Oe | 0.33 | 0.01 |  | 3.1 | 1.6 | 1.6 | 3.0 | 0.02 | 0.14 | 0.01 | 0.29 |
| 4-A | 0.29 |  | 0.20 | 9.5 | 0.06 | 1.5 | 3.7 |  | 0.07 | 0.12 | 2.4 |
| 4-B | 0.33 |  |  | 8.9 | 0.20 | 1.5 | 4.3 |  | 0.04 |  | 2.4 |
| 5-Oi | 0.43 |  |  | 2.2 | 13 | 0.96 |  | 0.04 | 0.15 | 0.52 |  |
| 5-Oe | 0.22 |  |  | 1.0 | 5.2 | 0.95 |  | 0.07 | 0.08 | 0.02 |  |
| 5-Oa | 0.07 |  | 0.02 | 1.1 | 2.7 | 0.31 |  | 0.02 | 0.05 | 0.11 |  |
| 5-A | 0.18 |  | 0.42 | 3.6 | 0.16 | 0.82 | 1.9 | 0.01 | 0.02 | 0.01 | 1.6 |
| 5-B | 0.17 |  | 0.16 | 7.8 | 0.18 | 1.8 | 2.1 | 0.01 | 0.04 | 0.15 | 2.7 |

# Figure Legends

Figure 1: Study sites with sampling locations.

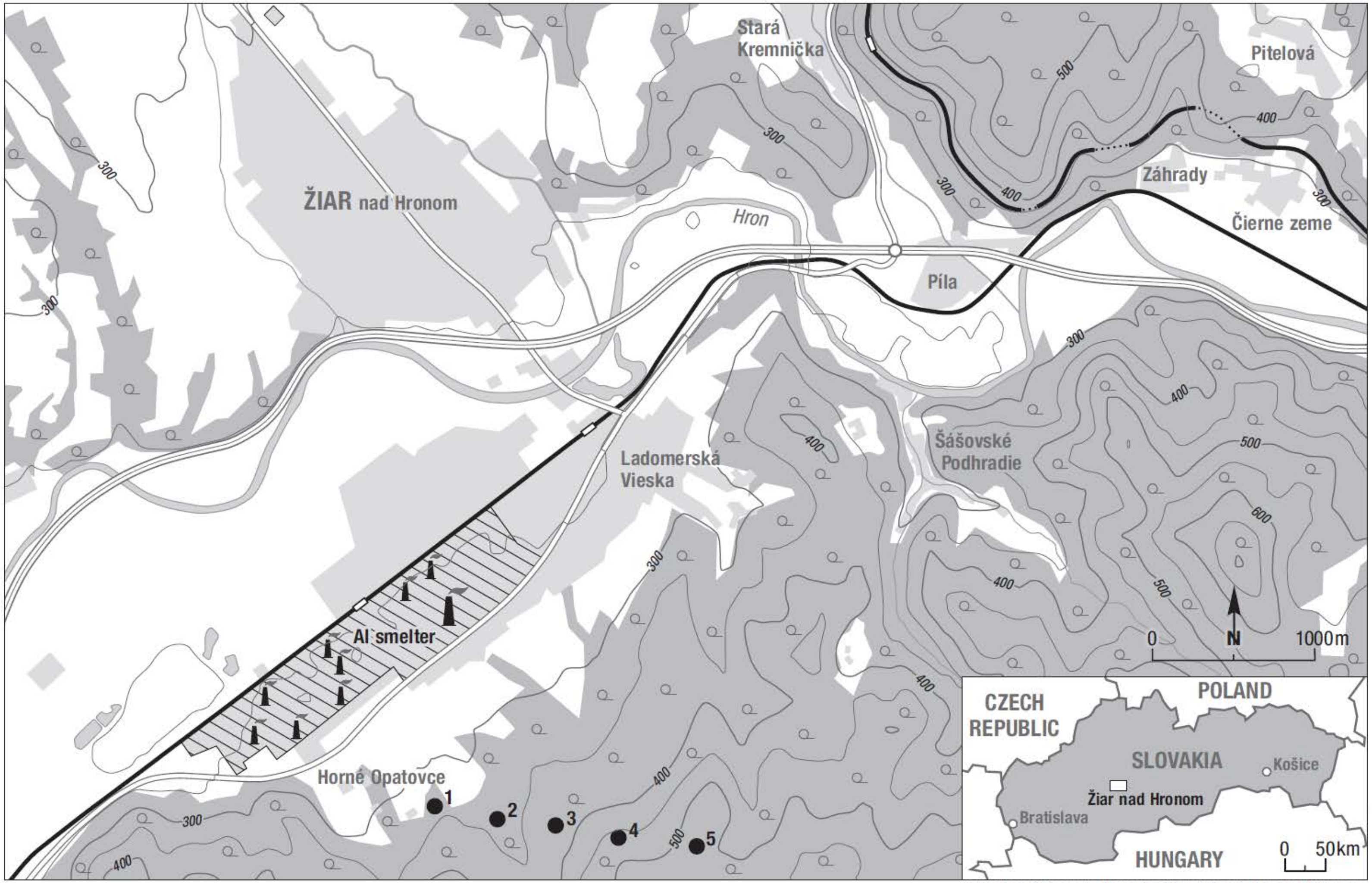
Figure 2: Concentrations of PACs in five soil profiles at sites [a] 500 m [b] 1000 m [c] 1500 m [d] 2000 m and [e] 2500 m from the Al plant.

Figure 3: Average composition pattern of the mixtures of [a] PAHs and [b] OPAHs and AZAs.

Figure 4: Relationships between the concentration of PACs in the A horizon and distance from the Al plant. The continuous line is the best fit for PAHs, the interrupted one for OPAHs and the dotted one for AZAs.

Figure 5: Comparisons of the mean concentrations of PAHs in [a] Oi [b] Oe [c] Oa, [d] A and [e] B horizons between the sampling campaigns in the years 2007 and 1994. The boxes show the range, whisker show 5th and 95th percentile, the central line is the median and the squares dots is the mean of the data set

Figure 1



© Institute of Geography, University of Bern, 2013. Cartography: A. Hermann

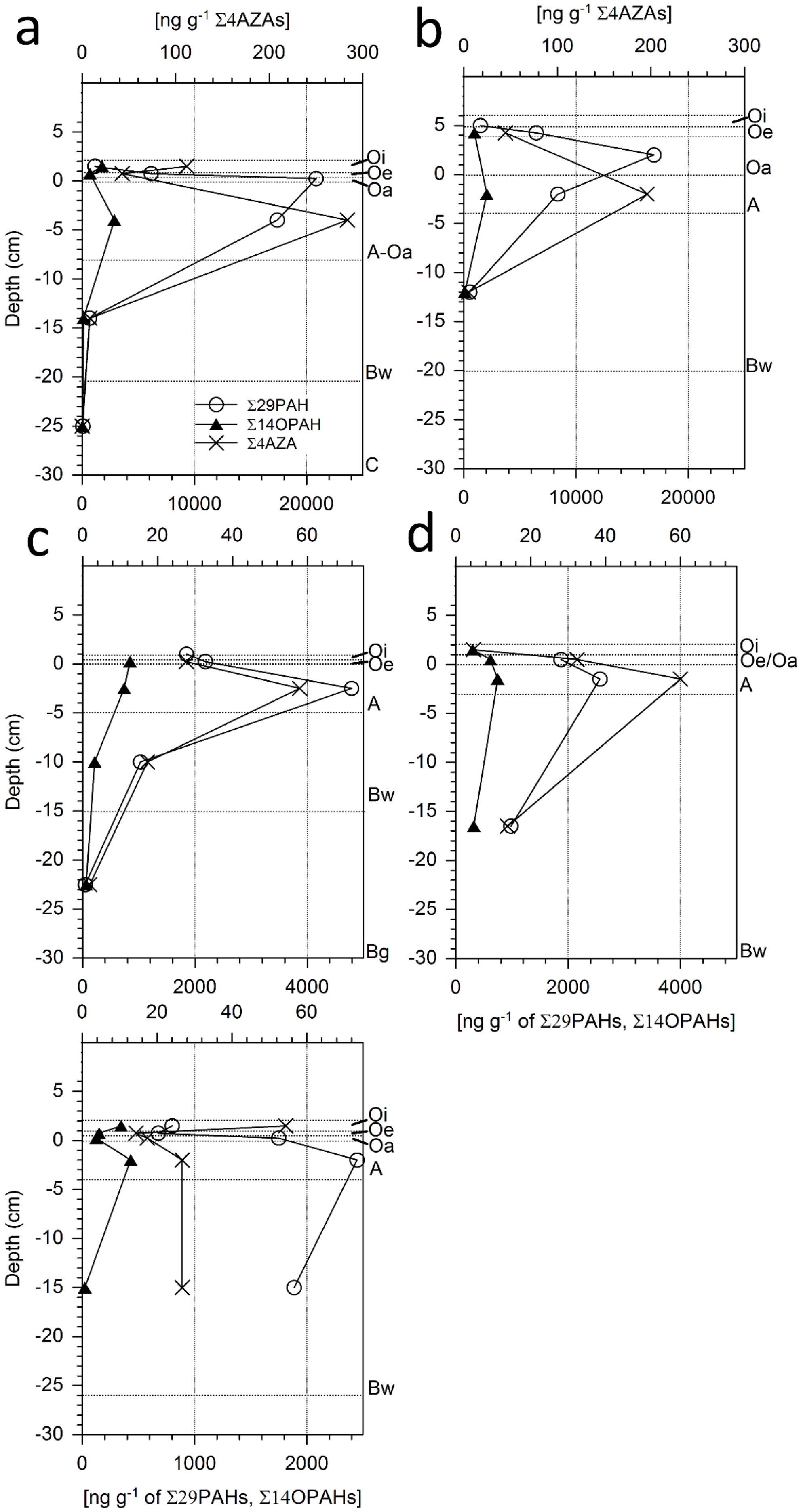
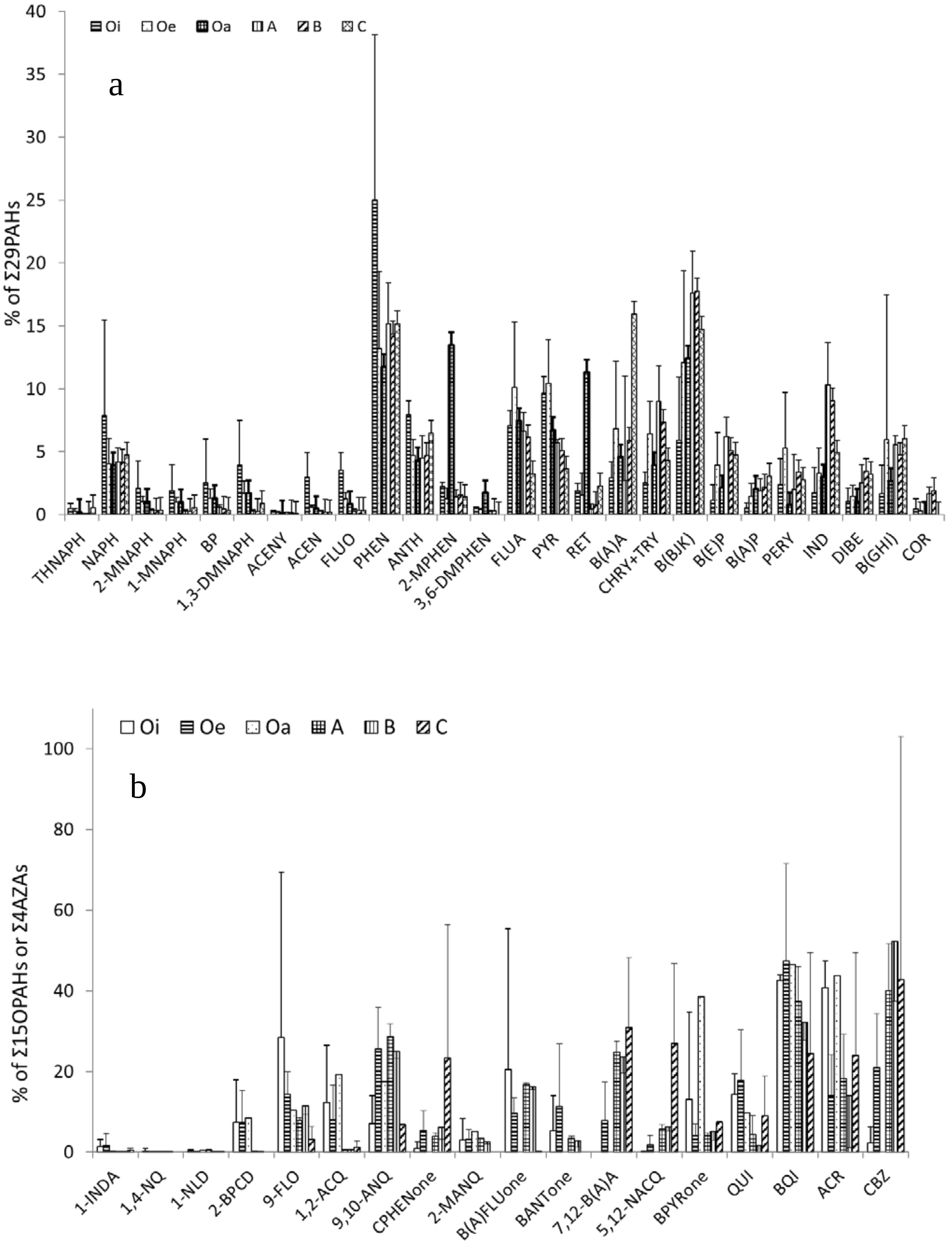

a
[ng g-1 Σ4AZAs]
0
100
200
300
5
0
-5
-10
-15
-20
-25
-30
Depth (cm)
Oi
Oe
Oa
A-Oa
Bw
C
Σ29PAH
Σ14OPAH
Σ4AZA
0
10000
20000
b
[ng g-1 Σ4AZAs]
0
100
200
300
Oi
Oe
Oa
A
Bw
0
10000
20000
c
0
20
40
60
Depth (cm)
Oi
Oe
A
Bw
Bg
0
2000
4000
d
0
20
40
60
Oi
Oe/Oa
A
Bw
0
2000
4000
[ng g-1 of Σ29PAHs, Σ14OPAHs]
0
20
40
60
Depth (cm)
Oi
Oe
Oa
A
Bw
0
1000
2000
[ng g-1 of Σ29PAHs, Σ14OPAHs]

Figure 2

Figure 3



Oi
Oe
Oa
A
B
C
a
% of Σ29PAHs
0
5
10
15
20
25
30
35
40
THNAPH
NAPH
2-MNAPH
1-MNAPH
BP
1,3-DMNAPH
ACENY
ACEN
FLUO
PHEN
ANTH
2-MPHEN
3,6-DMPHEN
FLUA
PYR
RET
B(A)A
CHRY+TRY
B(BJK)
B(E)P
B(A)P
PERY
IND
DIBE
B(GHI)
COR
Oi
Oe
Oa
A
B
C
b
% of Σ15OPAHs or Σ4AZAs
0
20
40
60
80
100
1-INDA
1,4-NQ
1-NLD
2-BPCD
9-FLO
1,2-ACQ
9,10-ANQ
CPHENone
2-MANQ
B(A)FLUone
BANTone
7,12-B(A)A
5,12-NACQ
BPYRone
QUI
BQI
ACR
CBZ

Figure 4

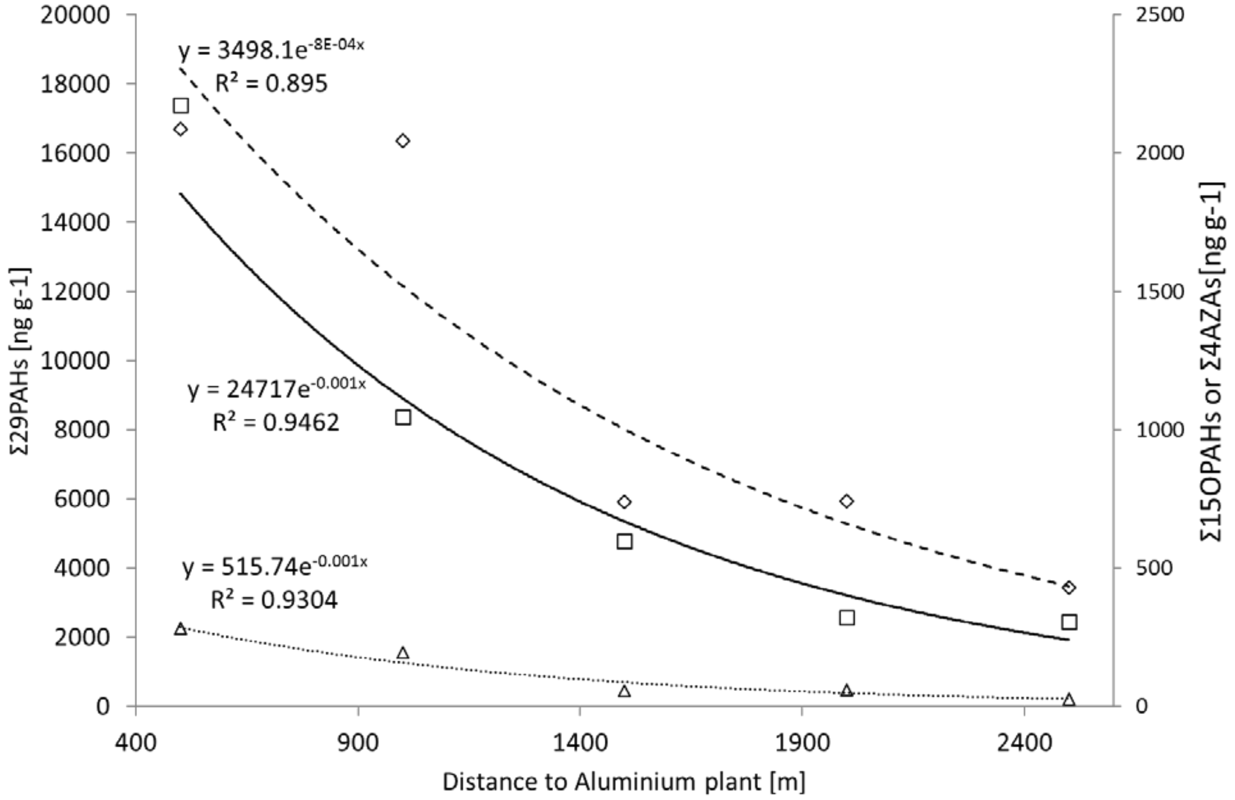
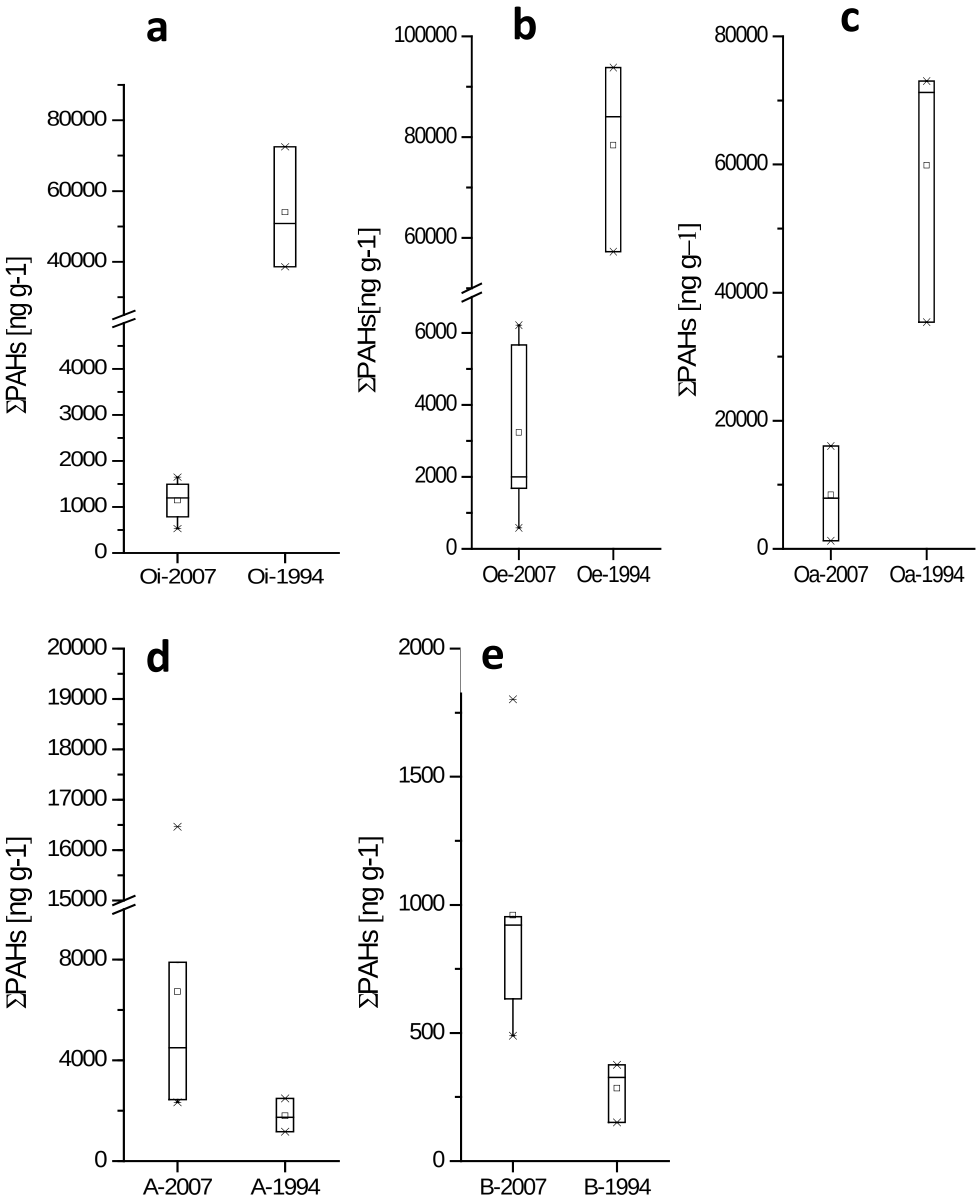

y = 3498.1e-8E-04x
R² = 0.895
y = 24717e-0.001x
R² = 0.9462
y = 515.74e-0.001x
R² = 0.9304
Σ29PAHs [ng g-1]
Σ15OPAHs or Σ4AZAs[ng g-1]
Distance to Aluminium plant [m]
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
2500
2000
1500
1000
500
0
400
900
1400
1900
2400

Figure 5


a
ΣPAHs [ng g-1]
80000
60000
40000
4000
3000
2000
1000
0
Oi-2007
Oi-1994
b
ΣPAHs[ng g-1]
100000
80000
60000
6000
4000
2000
0
Oe-2007
Oe-1994
c
ΣPAHs [ng g−1]
80000
60000
40000
20000
0
Oa-2007
Oa-1994
d
ΣPAHs [ng g-1]
20000
19000
18000
17000
16000
15000
8000
4000
0
A-2007
A-1994
e
ΣPAHs [ng g-1]
2000
1500
1000
500
0
B-2007
B-1994

# References

Aichner, B., Bussian, B., Lehnik-Habrink, P., Hein, S., 2013. Levels and spatial distribution of persistent organic pollutants in the environment: a case study of German forest soils. Environmental Science & Technology 47, 12703-12714.

Aichner, B., Bussian, B.M., Lehnik-Habrink, P., Hein, S., 2015. Regionalized concentrations and fingerprints of polycyclic aromatic hydrocarbons (PAHs) in German forest soils. Environmental Pollution 203, 31-39.

Anyanwu, I.N., Semple, K.T., 2016. Effects of phenanthrene and its nitrogen-heterocyclic analogues aged in soil on the earthworm *Eisenia fetida*. Applied Soil Ecology 105, 151-159

Anyanwu, I.N., Semple, K.T., 2015. Biodegradation of phenanthrene-nitrogen containing analogues in soil. Water, Air and Soil Pollution 226, 252-262

Arp, H.P.H., Lundstedt, S., Josefsson, S., Cornelissen, G., Enell, A., Allard, A-S., Kleja, D.B., 2014. Native oxy-PAHs, N-PACs, and PAHs in historically contaminated soils from Sweden, Belgium, and France: their soil-porewater partitioning behaviour, bioaccumulation in *Enchytraeus crypticus*, and bioavailability. Environmental Science & Technology 48, 11187-11195

Bi, E., Schmidt, T.C., Haderlein, S.F., 2006. Sorption of heterocyclic organic compounds to reference soils: column studies for process identification. Environmental Science & Technology 40, 5962-5970

Bandowe, B.A.M., Lueso, M.G., Wilcke, W., 2014. Oxygenated polycyclic aromatic hydrocarbons and azaarenes in urban soils: A comparison of a tropical city (Bangkok) with two temperate cities (Bratislava and Gothenburg). Chemosphere 107, 407-414.

Bandowe, B., A, M., Shukurov, N., Kersten, M., Wilcke, W., 2010. Polycyclic aromatic hydrocarbons (PAHs) and their oxygen-containing derivatives (OPAHs) in soils from the Angren inidustrial area, Uzbekistan. Environment Pollution 158, 2888-2899

Bandowe, B.A.M., Sobocka, J., Wilcke, W., 2011. Oxygen-containing polycyclic aromatic hydrocarbons (OPAHs) in urban soils of Bratislava, Slovakia: patterns, relation to PAHs and vertical distribution. Environmental Pollution 159, 539-549.

Bandowe, B.A.M., Wilcke, W., 2011. Sauerstoffehaltige Polyzyklische Aromatische Kohlenwasserstoffe (OPAK). In Litz, N., Wilcke, W., Wilke, W (EDS.), bodengefardende Stoffe-12, Erg. Lfg. 12/11, Wilet-VCH, Weinheim, pp. 1-44. ISBN 978-3-527-32802-4

Bandowe, B.A.M., Wilcke, W., 2010. Analysis of polycyclic aromatic hydrocarbons and their oxygen-containing derivatives and metabolites in soils. Journal of Environmental Quality 39, 1349-1358.

Bleeker, E., Wiegman, S., de Voogt, P., Kraak, M., Leslie, H.A., de Haas, E., Admiraal, W., 2002. Toxicity of azaarenes. Reviews of environmental contamination and toxicology 173, 39.

Booth, P., Gribben, K., 2005. A review of the formation, environmental fate, and forensic methods for PAHs from aluminum smelting processes. Environmental Forensics 6, 133-142.

Brinkmann, M., Maletz, S., Krauss, M., Bluhm, K., Schiwy, S., Kuckelkorn, J., Tiehm, A., Brack, W., Hollert, H., 2014. Heterocyclic aromatic hydrocarbons show estrogenic activity upon metabolization in a recombinant transactivation assay. Environmental Science & Technology 48, 5892-5901

Cousins, I.T., Beck, A.J., Jones, K.C., 1999. A review of the processes involved in the exchange of semi-volatile organic compounds (SVOC) across the air-soil interface. Science of the Total Environment 228, 5-24.

Guggenberger, G., Pichler, M., Hartmann, R., Zech, W., 1996. Polycyclic aromatic hydrocarbons in different forest soils: mineral horizons. Zeitschrift fur Pflanzenernahrung und Bodenkunde 159, 565-573.

Hanke, A., Cerli, C., Muhr, J., Borken, W., Kalbitz, K., 2013. Redox control on carbon mineralization and dissolved organic matter along a chronosequence of paddy soils. European Journal of Soil Science64, 476-487.

Horstmann, M., McLachlan, M.S., 1998. Atmospheric deposition of semivolatile organic compounds to two forest canopies. Atmospheric Environment 32, 1799-1809.

IUSS Working Group WRB, 2014. World Reference Base for Soil Resources 2014. International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Rome.

Jamnická, G., Bučinová, K., Havranová, I., Urban, A., 2007. Current state of mineral nutrition and risk elements in a beech ecosystem situated near the aluminium smelter in Žiar nad Hronom, Central Slovakia. Forest Ecology and management 248, 26-35.

Krauss, M., Wilcke, W., Zech, W., 2000. Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in forest soils: depth distribution as indicator of different fate. Environmental Pollution 110, 79-88.

Layshock, J.A., Wilson, G., Anderson, K.A., 2010. Ketone and quinone-substituted polycyclic aromatic hydrocarbons in mussel tissue, sediment, urban dust, and diesel particulate matrices. Environmental Toxicology and Chemistry 29, 2450-2460.

Leduc, R., Samson, R., Albashir, B., Alhawari, J., Cseh, T., 1992. Biotic and Abiotic Disappearance of 4 Pah Compounds from Flooded Soil under Various Redox Conditions. Water Science and Technology, 26(1-2): 51-60.

Lima, A.L.C., Farrington, J.W., Reddy, C.M., 2005. Combustion-derived polycyclic aromatic hydrocarbons in the environment - A review. Environmental Forensics 6, 109-131.

Lundstedt, S., Bandowe, B.A.M., Wilcke, W., Boll, E., Christensen, J.H., Vila, J., Grifoll, M., Faure, P., Biache, C., Lorgeoux, C., Larsson, M., Frech Irgum, K., Ivarsson, P., Ricci, M., 2014. First intercomparison study on the analysis of oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs) and nitrogen heterocyclic polycyclic aromatic compounds (N-PACs) in contaminated soil. Trends in Analytical Chemistry 57, 83-92.

Lundstedt, S., White, P.A., Lemieux, C.L., Lynes, K.D., Lambert, L.B., Oberg, L., Haglund, P., Tysklind, M., 2007. Sources, fate, and toxic hazards of oxygenated polycyclic aromatic hydrocarbons (PAHs) at PAH-contaminated sites. Ambio 36, 475-485.

Mackay, D., Shiu, W.Y., Ma, K.-C., Lee, S.C., 2006. Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Introduction and Hydrocarbons, 2nd Ed. CRC Press, Taylor & Francis Group, Boca Baton, FL, USA.

Maňkovská, B., Steinnes, E., 1995, Effects of pollutants from an aluminium reduction plant on forest ecosystems. Science of the Total Environment 163, 11-23.

Matzner, E., 1984. Annual rates of deposition of polycyclic aromatic hydrocarbons in different forest ecosystems. Water Air Soil Pollution 21, 425-434

Misaki, K., Takamura-Enya, T., Ogawa, H., Takamori, K., Yanagida, M., 2016. Tumor-promoting activity of polycyclic aromatic hydrocarbons and their oxygenated or nitrated derivatives. Mutagenesis 31, 205-213

Moeckel, C., Nizzetto, L., Di Guardo, A., Steinnes, E., Freppaz, M., Filippa, G., Camporini, P., Benner, J., Jones, K.C., 2008. Persistent Organic Pollutants in Boreal and Montane Soil Profiles: Distribution, Evidence of Processes and Implications for Global Cycling. Environmental Science & Technology 42, 8374-8380.

Mumbo, J., Pandelova, M., Mertes, F., Henkelmann, B., Bussian, B.M., Schramm, K-W., 2016. The fingerprints of dioxin-like bromocarbazoles and chlorocarbazoles in selected forest soils in Germany. Chemosphere 162, 64-72.

Neff, J.M., Stout, S.A., Gunstert, D.G., 2005. Ecological risk assessment of polycyclic aromatic hydrocarbons in sediments: identifying sources and ecological hazard. Integrated Environmental Assessment and Management 1, 22-33

Obrist, D., Zielinska, B., Perlinger, J.A., 2015. Accumulation of polycyclic aromatic hydrocarbons (PAHs) and oxygenated PAHs (OPAHs) in organic and mineral soil horizons from four US remote forests. Chemosphere 134, 98-105.

Pichler, M., Guggenberger, G., Hartmann, R., Zech, W., 1996. Polycyclic aromatic hydrocarbons (PAH) in different forest humus types. Environmental Science and Pollution Research 3, 24-31.

Roussel, R., Allaire, M., Friar, R.S., 1992. Atmospheric polycyclic aromatic hydrocarbons at a point source of emissions. part A: Identification and determination of polycyclic aromatic compounds in airborne particulate matter near a Horizontal Stud Soderberg Plant. Journal of the Air & Waste Management Association 42, 1609-1613.

Schlanges, I., Meyer, D., Palm, W.U., Ruck, W., 2008. Identification, quantification and distribution of PAC-metabolites, heterocyclic PAC and substituted PAC in groundwater samples of tar-contaminated sites from Germany. Polycyclic Aromatic Compounds 28, 320-328.

Semple, K.T., Morriss, A.W.J., Paton, G.I., 2003. Bioavailability of hydrophobic organic contaminants in soils: fundamental concepts and techniques for analysis. European Journal of Soil Science 54, 809-818.

Švábenský, R., Oravec, M., Šimek, Z., 2009. Determination of polycyclic aromatic nitrogen heterocycles in soil using liquid chromatography/tandem mass spectrometry. International Journal of Environmental and Analytical Chemistry 89, 167-181.

Soil Survey Staff, 2014. Keys to Soil Taxonomy. 12th ed. United States Department of Agriculture, Natural Resources Conservation Service, Washington D.C., U.S.A.

Totsche, K.U., Danzer, J., Kögel-Knabner, I., 1997. Dissolved organic matter-enhanced retention of polycyclic aromatic hydrocarbons in soil miscible displacement experiments. Journal of Environmental Quality 26, 1090-1100

Van Brummelen, T.C., Verweij, R.A., Wedzinga, S.A., Van Gestel, C.A.M., 1996. Enrichment of polycyclic aromatic hydrocarbons in forest soils near a blast furnace plant. Chemosphere 32, 293-314.

Van Brummelen, T.C., Verweij, R.A., Wedzinga, S.A., Van Gestel, C.A.M., 1996. Polycyclic aromatic hydrocarbons in earthworms and isopods from contaminated forest soils. Chemosphere 32, 315-341.

Vicente, E.D., Vicente, A.M., Bandowe, B.A.M., Alves, C.A., 2016. Particulate phase emission of parent polycyclic aromatic hydrocarbons (PAHs) and their derivatives (alkyl-PAHs, oxygenated-PAHs, azaarenes and nitrated PAHs) from manually and automatically fired combustion appliances. Air Quality, Atmosphere & Health 9, 653-668.

Walgraeve, C., Demeestere, K., Dewulf, J., Zimmermann, R., van Langenhove, H., 2010. Oxygenated polycyclic aromatic hydrocarbons in atmospheric particulate matter: Molecular characterization and occurrence. Atmospheric Environment 44, 1831-1846.

Wei, C., Bandowe, B.A.M., Han, Y.M., Cao, J.J., Zhang, C., Wilcke, W., 2015a. Polycyclic aromatic hydrocarbons (PAHs) and their derivatives (alkyl-PAHs, oxygenated-PAHs; nitrated-PAHs and azaarenes) in urban road dusts from Xian, Central China. Chemosphere 134, 512-520.

Wei, C., Han, Y.M., Bandowe, B.A.M., Cao, J.J., Huang, R.J., Ni, H., Tian, J., Wilcke, W., 2015b. Occurrence, gas/particle partitioning and carcinogenic risk of polycyclic aromatic hydrocarbons and their oxygen and nitrogen containing derivatives in Xian, central China. Science of the Total Environment 505, 814-822

Weigand, H., Totsche, K.U., Kogel-Knabner, I., Annweiler, E., Richnow, H.H., Michaelis, W., 2002. Fate of anthracene in contaminated soil: transport and biochemical transformation under unsaturated flow conditions. European Journal of Soil Science 53, 71-81.

Weiss, P., 2000. Vegetation/soil distribution of semivolatile organic compounds in relation to their physicochemical properties. Environmental Science & Technology 34, 1707-1714.

Wilcke, W., 2000. Synopsis polycyclic aromatic hydrocarbons (PAHs) in soil—a review. Journal of Plant Nutrition and Soil Science 163, 229-248.

Wilcke, W., 2007. Global patterns of polycyclic aromatic hydrocarbons (PAHs) in soil. Geoderma 141, 157-166.

Wilcke, W., Bandowe, B.A.M., Lueso, M.G., Ruppenthal, M., del Valle, H., Oelmann, Y., 2014a. Polycyclic aromatic hydrocarbons (PAHs) and their polar derivatives (oxygenated PAHs, azaarenes) in soils along a climosequence in Argentina. Science of the Total Environment 473, 317-325.

Wilcke, W., Kiesewetter, M., Bandowe, B.A.M., 2014b. Microbial formation and degradation of oxygen-containing polycyclic aromatic hydrocarbons (OPAHs) in soil during short-term incubation. Environmental Pollution 184, 385-390.

Wilcke, W., Mosbach, J., Kobza, J., Zech, W., 1998. Distribution of Al and heavy metals in bulk soil and aggregates at three sites contaminated by the emissions of a Central Slovak Al smelter. Water, Air and Soil Pollution106, 389-402.

Wilcke, W., Zech, W., 1997. Polycyclic aromatic hydrocarbons (PAHs) in forest floors of the Northern Czech Mountains. Zeitschrift Fur Pflanzenernahrung Und Bodenkunde 160, 573-579.

Wilcke, W., Zech, W., Kobza, J., 1996. PAH-pools in soils along a PAH-deposition gradient. Environmental Pollution 92, 307-313.

Wincent, E., Jönsson, M.E., Bottai, M., Lundstedt, S., Dreij, K., 2015. Aryl hydrocarbon receptor activation and developmental toxicity in Zebrafish in response to soil extracts containing unsubstituted and oxygenated PAHs. Environmental Science & Technology 49, 3869-3877

Wincent, E., Le Bihanic, F., Dreij, K., 2016. Induction and inhibition of human cytochrome P4501 by oxygenated polycyclic aromatic hydrocarbons. Toxicology Research 5, 788-799

Wild, S.R., Jones, K.C., 1995. Polynuclear aromatic-hydrocarbons in the United-Kingdom environment - a preliminary source inventory and budget. Environmental Pollution 88, 91-108.

Yang, S.Y.N., Connell, D.W., Hawker, D.W., Kayal, S.I., 1991. Polycyclic aromatic-hydrocarbons in air, soil and vegetation in the vicinity of an urban roadway. Science of the Total Environment 102, 229-240.