

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

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31 **Abstract**

32 Little is known about oxygenated polycyclic aromatic hydrocarbons (OPAHs) and azaarenes  
33 (AZAs) in forest soils. We sampled all horizons of forest soils from five locations at increasing  
34 distances from an Al plant in Slovakia, and determined their polycyclic aromatic compound  
35 (PACs) concentrations. The  $\sum 29$ PAHs concentrations were highest in the Oa and lowest in the  
36 Oi horizon, while the  $\sum 14$ OPAHs and  $\sum 4$ AZAs concentrations did not show a consistent  
37 vertical distribution among the organic horizons. The concentration ratios of PAHs and OPAHs  
38 between deeper O horizons and their overlying horizon (enrichment factors) were positively  
39 correlated with the octanol-water partition coefficients ( $K_{ow}$ ) at several locations. This is  
40 attributed to the slower degradation of the more hydrophobic PACs during organic matter  
41 decomposition. PACs concentrations decreased from the organic layer to the mineral horizons.  
42 The concentrations of  $\sum 29$ PAHs (2400 – 17000 ng g<sup>-1</sup>),  $\sum 14$ OPAHs (430 – 2100 ng g<sup>-1</sup>) and  
43  $\sum 4$ AZAs (27 – 280 ng g<sup>-1</sup>) in the mineral A-horizon generally decreased with increasing  
44 distance from the Al plant. In the A horizons, the concentration of  $\sum 29$ PAH were correlated  
45 with those of  $\sum 14$ OPAH ( $r = 0.95$ ,  $p = 0.02$ ) and  $\sum 4$ AZA ( $r = 0.93$ ,  $p = 0.02$ ) suggesting that  
46 bioturbation was the main transport process of PACs from the organic layer into the mineral  
47 soil. At each location, the concentrations of PACs generally decreased with increasing depth  
48 of the mineral soil. Enrichment factors of PAHs in the mineral horizons were not correlated  
49 with  $K_{ows}$ , pointing at colloid-assisted transport and bioturbation. At some sites, the  
50 enrichment factors of OPAHs were negatively correlated with  $K_{ow}$  indicating that these  
51 compounds were leached in dissolved form. Compared to a study, 13 years before, the  
52 concentrations of PAHs had decreased in the O horizons but increased in the A and B horizons  
53 because of soil-internal redistribution after emissions had been reduced.

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## 59 **1. Introduction**

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

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

79 Soil is the major final sink of PACs in the environment, with some estimates indicating that up  
80 to 90% of PAHs in the United Kingdom environment are stored in soils (Wild and Jones, 1995).  
81 Such estimates are however, to date not available for the polar PACs such as OPAHs and  
82 AZAs. PACs emitted by anthropogenic activities can be deposited to soils by dry/wet  
83 deposition and direct air-soil exchange from contaminated air. PACs can also be scavenged by

84 vegetation and reach the soil via litterfall (Cousins et al., 1999; Moeckel et al., 2008). Forest  
85 soils are a major sink for atmospheric organic micropollutants because of the scavenging effect  
86 of the tree canopy with its large surface area (Horstmann and McLachlan, 1999; Matzner,  
87 1984). PACs in forest soils undergo sorption-desorption, transformation, degradation, transport  
88 (leaching, dissolved organic matter (DOM) and colloid-assisted transport),  
89 volatilization/condensation and bioaccumulation that eventually determine their spatial  
90 distribution (Krauss et al., 2000; Moeckel et al., 2008; Semple et al., 2003). Concentrations of  
91 PAHs in soils generally decrease exponentially with distance from a point source (Van  
92 Brummelen et al., 1996a; Wilcke et al., 1996). The contributions of higher molecular weight  
93 PAHs (HMW-PAHs, > 4 benzene rings) to the total PAHs concentrations usually progressively  
94 decrease with distance from point sources because of their stronger association with particles  
95 and rapid deposition to the soil (Van Brummelen et al., 1996a; Yang et al., 1991). The spatial  
96 distribution of OPAHs and AZAs in forest soil with distance from point emissions sources has  
97 not yet been investigated. It was, however, shown in grassland soils near a power and industrial  
98 plants of the Angren region, Uzbekistan, that the spatial distribution of OPAHs was similar to  
99 those of PAHs (Bandowe et al., 2010).

100 The processes that influence the concentrations, composition patterns and vertical distribution  
101 of PAHs in the three organic (O) horizons of the organic layer on top of mineral soils are  
102 different from those that influence the vertical distribution in the mineral soil (Krauss et al.,  
103 2000; Pichler et al., 1996; Wilcke, 2000). The organic layer of forest soils consists of up to  
104 three distinct horizons (Oi, Oe and Oa) of increasing depth and degree of decomposition. Oi,  
105 Oe and Oa horizons are defined as fresh undecomposed litter, partially decomposed and  
106 completely decomposed organic matter, respectively (Krauss et al., 2000). Depending on soil  
107 properties and climate, these horizons show different states of development and might even be  
108 absent. The concentrations of total PAHs in the organic horizons of forest soils generally

109 increase in the order  $O_i < O_e < O_a$  (Krauss et al., 2000; Pichler et al., 1996; Wilcke, 2000).  
110 The proportion of HMW-PAHs in organic horizons of forest soils also increase in the order  $O_i$   
111  $< O_e < O_a$ . This is because of the higher persistence of HMW-PAHs (than the LMW-PAHs)  
112 and hence higher proportions of the LMW-PAHs than of HMW-PAHs being biodegraded  
113 during the decomposition of organic matter (Krauss et al., 2000; Pichler et al., 1996; Wilcke et  
114 al., 1996).

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

129 To study the distribution and transport of OPAHs and AZAs, we selected a beech forest (*Fagus*  
130 *sylvatica* L.) near an aluminium plant in Žiar nad Hronom (Central Slovakia). Aluminium  
131 smelting on industrial scale releases significant amounts of PAHs (and possibly OPAHs and  
132 AZAs), trace metals and other pollutants from both combustion of fossil fuels used to produce  
133 energy that powers the smelting process and from the carbonaceous electrode material used in

134 aluminium smelting itself (Booth and Gribben, 2005; Maňková and Steinnes, 1995; Wilcke  
135 et al., 1996). This site offers an ideal location to study the distribution of PACs (OPAHs, AZAs  
136 and PAHs) originating from a point source as well as the depth distribution and the underlying  
137 processes that drive these distributions. The distribution and composition of PAHs in soils  
138 sampled from these sites in 1994 was reported earlier (Wilcke et al., 1996). Shortly before the  
139 study of Wilcke et al. (1996), the Al smelter company had undergone restructuring and installed  
140 new technologies for both production and emission control (Jamnická et al., 2007; Maňková  
141 and Steinnes, 1995; Wilcke et al., 1996). This study will therefore also provide useful data  
142 about the effect of the introduction of modern technology in aluminium production and  
143 emission control as well as about the long-term behaviour of PAH in soils. The overall goal of  
144 this study is to gather knowledge about the sources (direct emission vs. post-depositional  
145 formation), spatial distribution, cycling and transport of PACs (PAHs, OPAHs and AZAs) in  
146 forest soils. Our work is guided by the following research questions:

- 147 1. What does the distribution of PAHs, OPAHs and AZAs with increasing distance to the  
148 smelter tell us about its sources and mechanism of transport?
- 149 2. What does the (depth) distribution of PACs tell us about the mobility, transport  
150 mechanism of the different PAC groups, and the post emission formation of OPAHs?  
151 We will test the hypothesis that the concentrations of OPAHs and the OPAH/related-  
152 PAH concentration ratios will increase in the order  $O_i < O_e < O_a$  because of the  
153 increasing formation (and accumulation) of OPAHs from the transformation of PAHs  
154 which accompany the decomposition of organic matter.
- 155 3. What does the change in concentration and spatial distribution of PAHs from 1994 to  
156 2007 reveal about the long-term behaviour of PAHs in soils?

## 157 **2. Materials and methods**

158 2.1 Sampling and soil characterization

159 In September 2007, we sampled all horizons of the soils at five sites with increasing distances  
160 (ca. 500, 1000, 1500, 2000, 2500 m) from an aluminium plant in Žiar nad Hronom (Central  
161 Slovakia, Figure 1). The Al plant has been in operation since 1953 and was reconstructed in  
162 1986, when the emissions were substantially lowered (Jamnická et al., 2007; Maňková and  
163 Steinnes, 1995). The operation of the smelter caused a severe contamination of its surroundings  
164 with PAHs, heavy metals and fluoride (Maňková and Steinnes, 1995; Wilcke et al., 1998,  
165 1996).

166 **Figure 1**

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

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180 2.2 Analysis of PAHs, OPAHs and AZAs

181 About 2-5 g (ground organic horizons) and 13-16 g (mineral soil horizons) from each sampling  
182 site were weighed, mixed with inert bulk sorbent (Isolute HM-N, Uppsala, Sweden) and  
183 transferred into 33-mL extraction cells (accelerated solvent extractor, ASE 200, Dionex,  
184 Sunnyvale, CA). Samples were spiked with 11 perdeuterated PAHs (naphthalene-D<sub>8</sub>,  
185 acenaphthene-D<sub>10</sub>, phenanthrene-D<sub>10</sub>, pyrene-D<sub>10</sub>, benzo[a]anthracene-D<sub>12</sub>,  
186 benzo[k]fluoranthene-D<sub>12</sub>, benzo[a]pyrene-D<sub>12</sub>, chrysene-D<sub>12</sub>, perylene-D<sub>12</sub>,  
187 dibenzo[a,h]anthracene-D<sub>14</sub>, and benzo[ghi]perylene-D<sub>12</sub>: 150 µL of a 10 µg mL<sup>-1</sup> solution of  
188 each of the compounds in toluene) as internal standard for PAHs and benzophenone-D<sub>5</sub> (150  
189 µL of a 10 µg mL<sup>-1</sup> solution of the compound in toluene) as internal standard for OPAHs and  
190 AZAs. Each sample was extracted twice by pressurized liquid extraction with the ASE 200.  
191 The first extraction was with dichloromethane (DCM), while the second extraction was with  
192 acetone/DCM/1% trifluoroacetic acid (250:125:1 v/v/v). The ASE was operated with the same  
193 settings as reported previously (Bandowe and Wilcke, 2010). The two extracts from each  
194 sample were combined and passed through a Na<sub>2</sub>SO<sub>4</sub> column to remove water. Hexane (1 mL)  
195 was added to each extract, rotary evaporated and again 10 mL hexane was added and rotary  
196 evaporated to < 1 mL. The extracts of organic horizons were then cleaned up by gel permeation  
197 chromatography (GPC). The GPC system consisted of a PrepLinc GPC, equipped with a UV  
198 detector (254 nm), an autosampler and glass column (750 mm x 25 mm ID glass column) filled  
199 with swelled Bio-beads S-X3 (J2-Scientific, PA, USA). The GPC was run with  
200 hexane:dichloromethane (1:1 v/v) as the mobile phase at a flow rate of 5 mL min<sup>-1</sup>.

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



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

216 We determined the concentrations of the following compounds:

- 217 • 29 PAHs: 1,2,3,4-tetrahydronaphthalene (THNAPH), naphthalene (NAPH), 2-  
218 methylnaphthalene (2-MNAPH), 1-methylnaphthalene (1-MNAPH), biphenyl (BP),  
219 1,3-dimethylnaphthalene (1,3-DMNAP), acenaphthylene (ACENY), acenaphthene  
220 (ACEN), fluorene (FLUO), phenanthrene (PHEN), anthracene (ANTH), 1-  
221 methylphenanthrene (1-MPHEN), 3,6-dimethylphenanthrene (3,6-DMPHEN),  
222 fluoranthene (FLUA), pyrene (PYR), 1-methyl-7-isopropylphenanthrene (RET),  
223 benz[a]anthracene (B(A)A), chrysene+triphenylene (CHRY),  
224 benzo[b+j+k]fluoranthenes (B(BJK)), benzo[e]pyrene (B(E)P), benzo[a]pyrene  
225 (B(A)P), perylene (PERY), indeno[1,2,3-cd]pyrene (IND), dibenz[a,h]anthracene  
226 (DIBE), benzo[ghi]perylene (B(GHI)) and coronene (COR);
- 227 • 14 OPAHs: 1-indanone (1-INDA), 1,4-naphthoquinone (1,4-NQ), 1-naphthaldehyde  
228 (1-NLD), 2-biphenylcarboxaldehyde (2-BPCD), 9-fluorenone (9-FLO), 1,2-  
229 acenaphthylenedione (1,2-ACQ), 9,10-anthraquinone (9,10-ANQ), 4H-  
230 cyclopenta[d,e,f]phenanthrene-4-one (CPHENone), 2-methyl-9,10-anthraquinone (2-

231 MANQ), benzo[a]fluorenone (B(A)FLUone), 7H-benz[d,e]anthracene-7-one  
232 (BANTone), benzo[a]anthracene-7,12-dione (7,12-B(A)A), 5,12-naphthacenequinone  
233 (5,12-NACQ) and 6H-benzo[c,d]pyrene-6-one (BPYRone)  
234 • 4 AZAs: quinoline (QUI), benzo[h]quinoline (BQI), acridine (ACR) and carbazole  
235 (CBZ)

### 236 2.3 Quality assurance and control

237 All used organic solvents were of high purity for pesticide residue analysis or HPLC grade,  
238 purchased from Carlo Erba (Milan, Italy). All labware were machine-washed with soap, rinsed,  
239 and dried in a clean oven. All the non-volumetric glassware and metallic labware were also  
240 baked at 250 °C for 24 h to remove contaminants. Three procedural blanks made of bulk inert  
241 sorbent (Isolute, HM-N) were extracted and their PACs concentrations measured. Most of the  
242 target compounds were not detected in the blanks or their amounts in the blanks were  
243 insignificant compared to their amounts in the real samples. The mean amounts of PACs the  
244 three blanks (where detected) was then subtracted from those measured in the samples to  
245 correct for laboratory contamination. We also extracted and analysed replicates (n = 2) of the  
246 certified reference material ERM-CC013a-PAHs in soils (Federal Institute for Materials  
247 Research Testing [BAM], Berlin, Germany). The relative standard deviation (RSD) of  
248  $\Sigma 29\text{PAH}$ ,  $\Sigma 14\text{OPAHs}$  and  $\Sigma 4\text{AZAs}$  concentrations in the replicates (n = 2) of ERM-CC013a  
249 determined with our procedures were 8%, 9% and 12%, respectively. The recoveries of the  
250 sum of PAH concentrations for which indicator and certified values were provided was  
251  $135 \pm 12\%$  (average  $\pm$  standard deviation). For the OPAHs and AZAs, there are no certified  
252 reference materials. We therefore compared our OPAHs and AZAs concentrations to the grand  
253 means determined for this same reference material in a recent intercomparison exercise  
254 (Lundstedt et al., 2014). The recoveries compared to the grand means in the intercomparison

255 exercise were  $101 \pm 9\%$ ,  $83 \pm 10\%$  for the OPAHs and AZAs respectively. At the location  
256 2500 m from the Al plant, the A-horizon soil was analyzed in replicates ( $n = 2$ ). The RSD of  
257 the  $\sum 29$ PAHs,  $\sum 14$ OPAHs and  $\sum 4$ AZAs were 24%, 7.4% and 7.1%, respectively. At location  
258 500 m from the Al plant the Oe and A-horizons were analyzed in replicates ( $n = 2$ ). The RSD  
259 of the replicates analysis of Oe horizon were 53%, 5% and 20%, respectively for  $\sum 29$ PAHs,  
260  $\sum 14$ OPAHs and  $\sum 4$ AZAs. For the A horizon at this location the RSD for the replicate analysis  
261 were 31%, 16% and 24% respectively for  $\sum 29$ PAHs,  $\sum 14$ OPAHs and  $\sum 4$ AZAs, respectively.

## 262 2.4 Calculations and statistical analyses

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

## 276 3. Results

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

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

283 **Table 1**

284 **Figure 2**

285 **Figure 3**

286 At most locations, the Oe horizons showed higher concentrations of  $\sum 29$ PAHs than the Oi  
287 horizons. The highest concentrations of  $\sum 29$ PAHs in the Oe horizons occurred at the location  
288 farthest from the Al plant, with clearly elevated concentrations at the other locations (Table 1,  
289 Figure 2). Moreover, PAHs mixtures were dominated by PHEN (13%), B(BJK) (12%), PYR  
290 (10%) and FLUA (10%), showing a higher contribution of HMW-PAHs to the PAHs mixtures  
291 than in the Oi horizons (Figure 3, Table S2). The 4-ring PAHs (41%) contributed a higher  
292 proportion to the  $\sum 21$ PAHs compared to that of  $\sum 2+3$ -ring PAHs (25%) (Figure S1). The  
293  $\sum$ HMW-PAHs/ $\sum$ LMW-PAHs concentration ratios in the Oe horizons averaged 3.4 (range: 1.5-  
294 6.8) with the highest and lowest values at locations closest and farthest from the Al plant,  
295 respectively.

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

302 PAHs/ $\Sigma$ LMW-PAHs concentration ratios were 3.8 and 2.4, at the locations closest and farthest  
303 from the Al plant, respectively.

304 In the mineral A horizon, the concentrations of  $\Sigma$ 29PAHs were highest closest to and lowest  
305 farthest away from the Al plant (Table 1, Figure 2). The relationship between the concentration  
306 of  $\Sigma$ 29PAHs and distance from the emission source was exponential ( $R^2 = 0.95$ ) (Figure 4).  
307 The PAHs mixtures in the A horizons were dominated by B(BJK) (18%), PHEN (15%), IND  
308 (10%) and CHRY (9%) (Figure 3, Table S2). The  $\Sigma$ HMW-PAHs/ $\Sigma$ LMW-PAHs concentration  
309 ratio in the A horizon averaged 2.9 (range: 2.6 – 3.3) and was independent of the distance from  
310 the Al plant and higher than in the O horizons.

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

#### 315 **Figure 4**

316 The concentrations of the  $\Sigma$ 14OPAHs in the Oi, Oe and Oa horizons were generally higher at  
317 locations closest to the plant but did not show consistent changes with distance from the Al  
318 plant (Table 1, Figure 2). At the location closest (500 m from Al plant) to the Al plant, the  
319  $\Sigma$ 14OPAHs concentrations in the Oi horizon were higher than in the Oe horizon, while at  
320 location 2000 m from the Al plant, the reverse was true (Table 1). The concentrations of  
321  $\Sigma$ 14OPAHs in the three O horizons at location 2500 m from the Al plant decreased in the order,  
322 Oi > Oe > Oa. The composition of the OPAHs mixtures in the Oi horizon was dominated by  
323 9-FLO (28%), B(A)FLUone (21%) and BPYRone (13%). The OPAHs mixtures in the Oe  
324 horizon were dominated by 9,10-ANQ (26 %), 9-FLO (14%) and BANTone (11%) and those

325 in the Oa horizon by BPYRone (39%), 1,2-ACQ (19%) and 9,10-ANQ (17%) (Figure 3B,  
326 Table S3).

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

336 Similar to those of the  $\sum 14$ OPAHs, the concentrations of  $\sum 4$ AZAs in the Oi horizons were  
337 higher than in the Oe horizons at location 1 (500 m from the Al plant) and 5 (2500 m from the  
338 Al plant), while the reverse was true at location 4 (2000 m from the the Al plant) (Table 1,  
339 Figure 2). The AZAs mixtures in the Oi horizons were dominated by BQI (43%) and ACR  
340 (41%), in the Oe horizons by BQI (47%) and CBZ (21%), and in the Oa horizons by BQI (47%)  
341 and ACR (44%; Figure 3B, Table S3).

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

347 The  $\sum 29$ PAHs,  $\sum 14$ OPAHs and  $\sum 4$ AZAs concentrations in the B horizons were highest at the  
348 sampling location farthest from the smelter and decreased with decreasing distance. At the

349 location farthest from the Al plant the  $\sum 29$ PAHs and  $\sum 14$ OPAHs concentrations were only  
350 slightly lower in the B compared to the A horizons, while  $\sum 4$ AZAs concentrations were  
351 identical (Table 1).

352 To identify the drivers of the vertical distribution, we correlated the enrichment factors  $e$  at  
353 each site with the octanol-water partition coefficients [ $\log K_{OW}$ ]. For the PAHs, significant  
354 correlations occurred between enrichment factors and their  $K_{OW}$  values at site 2  $e_{Oe/Oi}$  ( $r = 0.57$ ,  
355  $p < 0.001$ ), site 3  $e_{Oe/Oi}$  ( $r = 0.64$ ,  $p < 0.001$ ), site 3  $e_{A/Oe}$  ( $r = 0.42$ ,  $p = 0.01$ ), site 4  $e_{A/Oe}$  ( $r =$   
356  $0.44$ ,  $p = 0.03$ ) and site 5  $e_{Oe/Oi}$  ( $r = 0.60$ ,  $p = 0.01$ ) (Figs. S2 & S3). For the OPAHs, significant  
357 correlations between enrichment factors (Fig S4) and  $K_{OW}$  occurred at site 1  $e_{Oe/Oi}$  ( $r = 0.76$ ,  $p$   
358  $= 0.007$ ), 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  
359 the low number of compounds ( $n = 4$ ) was not suitable for a correlation analysis between  
360 enrichment factors and  $K_{OW}$  values.

361

## 362 **4. Discussion**

### 363 4.1. Concentrations and distribution of PACs with distance from the Al plant

364 The concentrations of  $\sum 29$ PAHs in the O horizons of the soils were in the range of those of  
365  $\sum$ US-EPA PAHs ( $105 - 14889 \text{ ng g}^{-1}$ ) reported in an extensive ( $n = 447$ ) nationwide survey of  
366 German forest soils covering both background and contaminated sites (Aichner et al., 2013;  
367 2015). The concentrations of PAHs in the A horizons of the forest soils near Žiar nad Hronom  
368 were elevated compared to mineral horizons of forest soils from background and rural areas of  
369 the USA (Obrist et al., 2015). The extensive survey of Aichner et al. (2015) in Germany found  
370 a concentration range of  $20-9038 \text{ ng g}^{-1}$  in the 0-5 cm layer of mineral soils under forest  
371 (Aichner et al., 2015), while in mineral horizons of forest soils from northern Czech Mountains  
372 the concentration of  $\sum 20$ PAHs was  $238 - 7476 \text{ ng g}^{-1}$  (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<sup>-1</sup>, respectively. Thus, the concentrations of the  $\Sigma$ 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  $\Sigma$ 14OPAHs in our study were much higher than those of  $\Sigma$ 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<sup>-1</sup>) (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  $\Sigma$ 4AZAs in surface soils from the cities of Bangkok (Thailand) and Xi'an



397 (China) were 0.1-31 ng g<sup>-1</sup> and 784 ng g<sup>-1</sup>, respectively (Bandowe et al., 2014; Wei et al.,  
398 2015a). The concentrations of  $\Sigma$ 9AZAs in the mineral topsoil (0-10 cm) of an industrial site in  
399 the Czech Republic were 640-694 ng g<sup>-1</sup>, while the concentration in a reference rural site was  
400 6.9 ng g<sup>-1</sup> (Švábenský et al., 2009). The concentrations in the A horizons at our study site were  
401 higher than in soils from background and remote locations (e.g., Argentina  $\Sigma$ 4AZA: n.d – 0.97  
402 ng g<sup>-1</sup>, Wilcke et al., 2014a) but comparable to those from industrial sites as summarized in  
403 Bandowe et al. (2014). The dominance of CBZ is similar to that observed in a study of urban  
404 soils in Bangkok (Bandowe et al., 2014). Carbazole was also measured at concentration of 8-  
405 268 ng g<sup>-1</sup>, not detected (n.d.) – 37 ng g<sup>-1</sup> and n.d. – 10 ng g<sup>-1</sup> in the organic horizon, 0-5 cm  
406 and 5-10 cm of mineral horizons, respectively of German forest soils (Mumbo et al., 2016).  
407 The study of Mumbo et al. (2016) also showed the trend organic horizon > 0-5 cm > 5-10 cm  
408 in the concentrations of carbazole, which is contrary to the trend we observe in the vertical  
409 distribution of the  $\Sigma$ 4AZA. In our study the  $\Sigma$ 4AZAs concentration in the A-horizon was  
410 higher than in the O-horizons at most locations.

411 The distribution of PAHs, OPAHs and AZAs in the organic horizons demonstrate that the Al  
412 plant was the main point source for the PACs in O horizons of soils. Although the location  
413 2500 m away from the emission source was clearly least affected, there was no systematic  
414 increases in PACs concentrations in each of the organic horizons with decreasing distance to  
415 the Al plant. Several factors could explain the lack of distance-concentration relationships  
416 including differences in adsorbing surface area among the sampled organic layers, age  
417 differences between similar layers at different locations, soil properties (Table S1),  
418 composition of tree species, topography, turnover times and vertical transport into deeper  
419 horizons.

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

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

436 The concentrations of each of the PAC groups in the A-horizons showed a close correlation  
437 with distance from the Al plant, indicating that emissions from the Al plant were the major  
438 source of most of the studied PACs. Similar exponential relationships between distance from  
439 emission source and concentrations of PAHs were also observed in previous studies in forest  
440 soils at the same and other locations (Van Brummelen et al., 1996a; Wilcke et al., 1996). In the  
441 B horizon, the concentration of PACs did not consistently decrease with increasing distance  
442 from Al plant (or indeed even tended to show an opposite trend to what was observed for the  
443 A horizons, Table 1). This points to the importance of soil properties for the transport of PACs  
444 in the mineral soil, which is overprinting the higher deposition close to the smelter. With  
445 increasing distance from the Al plant, the organic matter content as well as the ECEC decreases  
446 (Table S1), offering less sorption sites, particularly for the more polar PACs and thus favour

447 greater translocation of PACs into deeper horizons of the mineral soils. Another reason for the  
448 stronger depth transport at the farther distances might be the higher sand concentrations  
449 allowing for a faster percolation of water and solutes, particularly at site 5.

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

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

## 465 **Table 2**

### 466 4.2 The depth distribution as indicator for sources and transport of PACs.

467 In general, the concentration of  $\sum$ 29PAHs in the O horizons increased in the order Oi  $<$  Oe  $<$   
468 Oa (Figure 2, Table 1). The concentrations of  $\sum$ 29PAHs in the Oa horizons were higher or  
469 similar to the concentration of the underlying A horizons (Figure 2). The vertical trends are in  
470 line with previous studies (Krauss et al., 2000; Pichler et al., 1996). The mineral horizon

471 showed consistent decreases of  $\sum 29\text{PAH}$  concentration with increasing depth largely  
472 consistent with previous studies (Guggenberger et al., 1996; Krauss et al., 2000). The organic  
473 matter concentrations in the mineral horizons, which followed similar trends, can partly explain  
474 the decreasing PAH concentrations, because organic matter is the main sorbent of PAHs in  
475 soils (Table S1, Wilcke, 2000).

476 In the O horizons, the enrichment factors of PAHs were at several study sites significantly  
477 positively correlated ( $p < 0.05$ ) with the  $K_{OW}$  values (Figure S2) reflecting the accumulation of  
478 the more hydrophobic PAHs with increasing organic matter transformation (Pichler et al.,  
479 1996; Wilcke and Zech, 1997). The HMW-PAHs are less bioavailable, less degraded (more  
480 persistent) compared to the more hydrophilic, more bioavailable LMW- PAHs, which are  
481 increasingly degraded with increasing organic matter transformation (Guggenberger et al.,  
482 1996; Krauss et al., 2000; Pichler et al., 1996). We did not find significant correlations of the  
483 enrichment factors with  $K_{OW}$  values in the mineral horizons suggesting that the translocation  
484 of PAHs from the organic layer into the mineral soil horizons and between the mineral horizons  
485 were partly controlled by DOM- and colloid-assisted transport (Guggenberger et al., 1996;  
486 Krauss et al., 2000; Wilcke et al., 1996). We interpret the fact that none of the PAH enrichment  
487 factors at the location closest to the Al plant correlated with  $K_{OW}$  as strong indication that the  
488 higher impact of fresh emissions from the Al plant might be influencing the vertical  
489 distribution.

490 In contrast to the  $\sum 29\text{PAHs}$  concentrations, we could not identify a consistent pattern of  
491 increasing concentrations of  $\sum 14\text{OPAHs}$  and  $\sum 4\text{AZAs}$  from the Oi to the Oa horizons (Table  
492 2, Figure 2). We attribute this finding to the fact that OPAHs can both be degraded and formed  
493 during advancing decomposition of organic matter (Wilcke et al., 2014b), both processes  
494 compensating each other.

495 In few cases the enrichment factors of the OPAHs in the O horizons were significantly  
496 positively correlated with the  $K_{ow}$  values (Figure S4). In these soils at sites 1 and 5, the  
497 preferential degradation of the OPAHs with advancing organic matter decomposition seems to  
498 overwhelm the formation of new OPAHs from parent PAHs. Similarly, there were weak but  
499 significant correlations of the enrichment factors of OPAHs between the A and Oa horizons  
500 and the  $K_{ow}$  values (Fig. S4) at site 2 suggesting that at this site leaching of OPAHs from the  
501 organic layer into the mineral soils played a role, in spite of the dominating transfer of PACs  
502 from the O into the A horizons by biological mixing. This underlines the higher water solubility  
503 and resulting leaching of OPAHs than of PAHs in soil. In the mineral horizons, the enrichment  
504 factors of OPAHs were significantly negatively correlated with the  $K_{ow}$  values at the location  
505 1000 m from the Al plant (Figure S4), suggesting that the vertical translocation of OPAHs at  
506 this site was mainly driven by leaching as truly dissolved compound.

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

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

534 Another explanation for the high  $\sum 14\text{OPAHs}/\sum 29\text{PAHs}$ , particularly in the Bg horizon at site  
535 3 might be the fact, that this soil horizon showed visible influence of redox changes (mottled  
536 pattern of bleached and red zones). These redox changes might also influence the formation of  
537 OPAHs, relative to PAHs. Redox conditions are known to influence decomposition of PAHs  
538 (Leduc et al., 1988) and the alternating redox conditions, affect and change the microbial  
539 community (Hanke et al. 2013). The alternating redox conditions in soils might affect  
540 formation of OPAHs, when the soil is reoxidized. However, as we have only one sample with  
541 an indication for redox changes, these hypotheses needs further testing.

542 4.3 What does the change of PAH distribution from 1994 to 2007 tell us about the  
543 transport of PAH in soils.

544 In the previous study from 1994, when three soils were sampled along the same deposition  
545 gradient (distance 1320 to 2180 m), the concentrations of  $\Sigma 20\text{PAHs}$  were 38596 – 72523,  
546 57273 – 93785 and 35409 – 73003 ng g<sup>-1</sup> in the Oi, Oe and Oa horizons (Figure 5; Wilcke et  
547 al., 1996), respectively indicating marked decreases in the concentrations of PAHs in samples  
548 taken in 2007 compared to those taken in 1994 (Wilcke et al., 1996). In the previous study, the  
549 concentrations of  $\Sigma 20\text{PAHs}$  in the A horizons ranged from 1172 to 2485 ng g<sup>-1</sup> and in the B  
550 horizon from 151 to 376 ng g<sup>-1</sup> (Figure 5) and thus were higher in 2007 than in 1994. These  
551 results illustrate that the organic layers recovered from their high PACs load in 1994, because  
552 of their limited residence time and the emission control measures established from 1986 on  
553 (Jamnická et al., 2007; Maňkovská and Steinness, 1995). The PAHs in the highly contaminated  
554 organic layers, however, were not fully degraded but incorporated into the mineral horizons by  
555 biological mixing leading to higher concentrations in the A and B horizons in 2007 than in  
556 1994. Our results illustrate that the disappearance of a contaminant load from soil organic  
557 layers in forests does not necessarily mean that the compounds were degraded. The reductions  
558 we see are also consistent with the emission of PAHs from the Žiar nad Hronom Al smelter  
559 which has decreased from 68 t a<sup>-1</sup> (in 1990), to 12 t yr<sup>-1</sup> (in 1995) and 0.8 t yr<sup>-1</sup> (in 2001)  
560 (Jamnická et al., 2007).

561

## Figure 5

## 562 5. Conclusions

- 563
- 564 • This study showed significant inputs of OPAHs, AZAs and PAHs originating from  
565 an Al plant into forest soils. The spatial distribution of PAHs, OPAHs and AZAs in  
566 the A and some organic horizons identified the Al plant as common source. The lack  
567 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

568 vertical PACs redistribution in soils, because the study soils varied particularly with  
569 respect to their pH values and sand concentrations.

570 • The vertical distribution of PAHs and OPAHs in the organic horizons could be  
571 explained by the relative accumulation of the more hydrophobic PACs with  
572 increasing organic matter transformation. The concentrations of PAHs in the A  
573 horizons were significantly correlated with those of OPAHs and AZAs, which is  
574 attributable to their common primary source and mixing from the organic layer into  
575 the mineral soil by biological activity. The vertical distribution of PAHs in the  
576 mineral soil was not significantly correlated with their octanol-water partition  
577 coefficients, because of DOM- and colloid-assisted leaching. At several locations,  
578 the vertical distribution of OPAHs in the soils was related with the octanol-water  
579 partition coefficient demonstrating that leaching in truly dissolved form played a  
580 more important role for OPAHs than for PAHs. This was further backed by increases  
581 in the ratios of individual OPAHs to PAH ratios with increasing depth of the mineral  
582 soil at several locations.

583 • The PAHs concentrations in the O horizons have significantly decreased between  
584 1994 and 2007, because of improved emission control, turnover of the O horizons at  
585 a decadal scale and mixing into the mineral soil. Despite decreasing emissions in  
586 recent times, the concentrations of PAHs in the A and B horizons have increased  
587 from 1994 to 2007 as a result vertical transport.

588

## 589 **Acknowledgements**

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



593 Alexander Hermann (Institute of Geography, University of Bern, Switzerland) for drawing Fig.  
594 1, Sylvia Bondzio (Institute of Geography, Johannes Gutenberg University Mainz, Germany)  
595 and Dr. Daniela Fischer (Institute of Geography, University of Bern, Switzerland) for physico-  
596 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	$\Sigma 29$ PAHs	$\Sigma 14$ OPAHs	$\Sigma 4$ AZAs
			-----ng g <sup>-1</sup> -----		
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

<sup>a</sup>na is not available.

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

Location/ Horizon	$\sum 14\text{OPAH}/\sum 29\text{PAH}$	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.

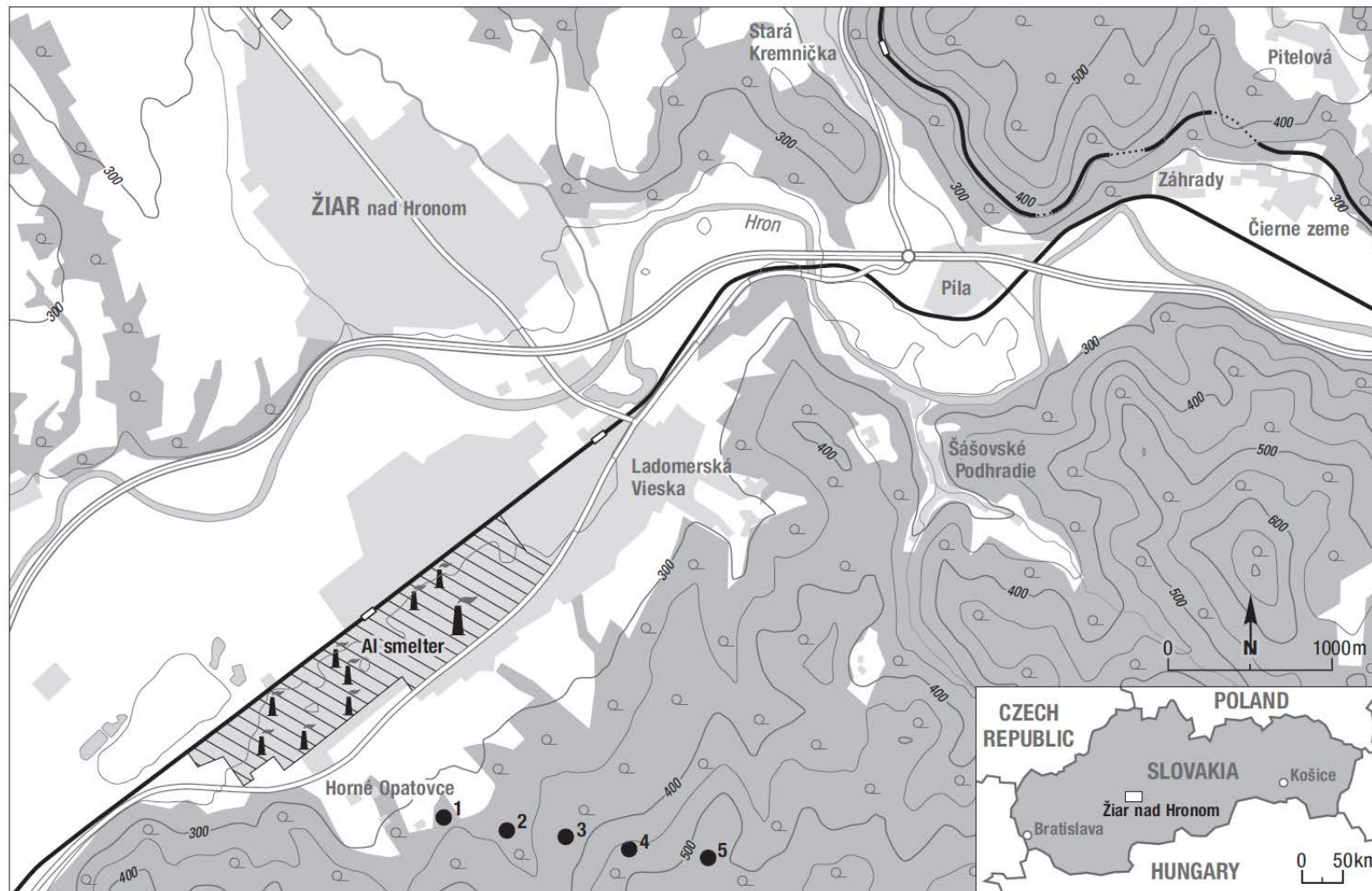
Figure 2: Concentrations of PACs in five soil profiles at sites [a] 500 m [b] 1000 m [c] 1500 m [d] 2000 m and [e] 2500 m from the Al plant.

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 5<sup>th</sup> and 95<sup>th</sup> percentile, the central line is the median and the squares dots is the mean of the data set

Figure 1



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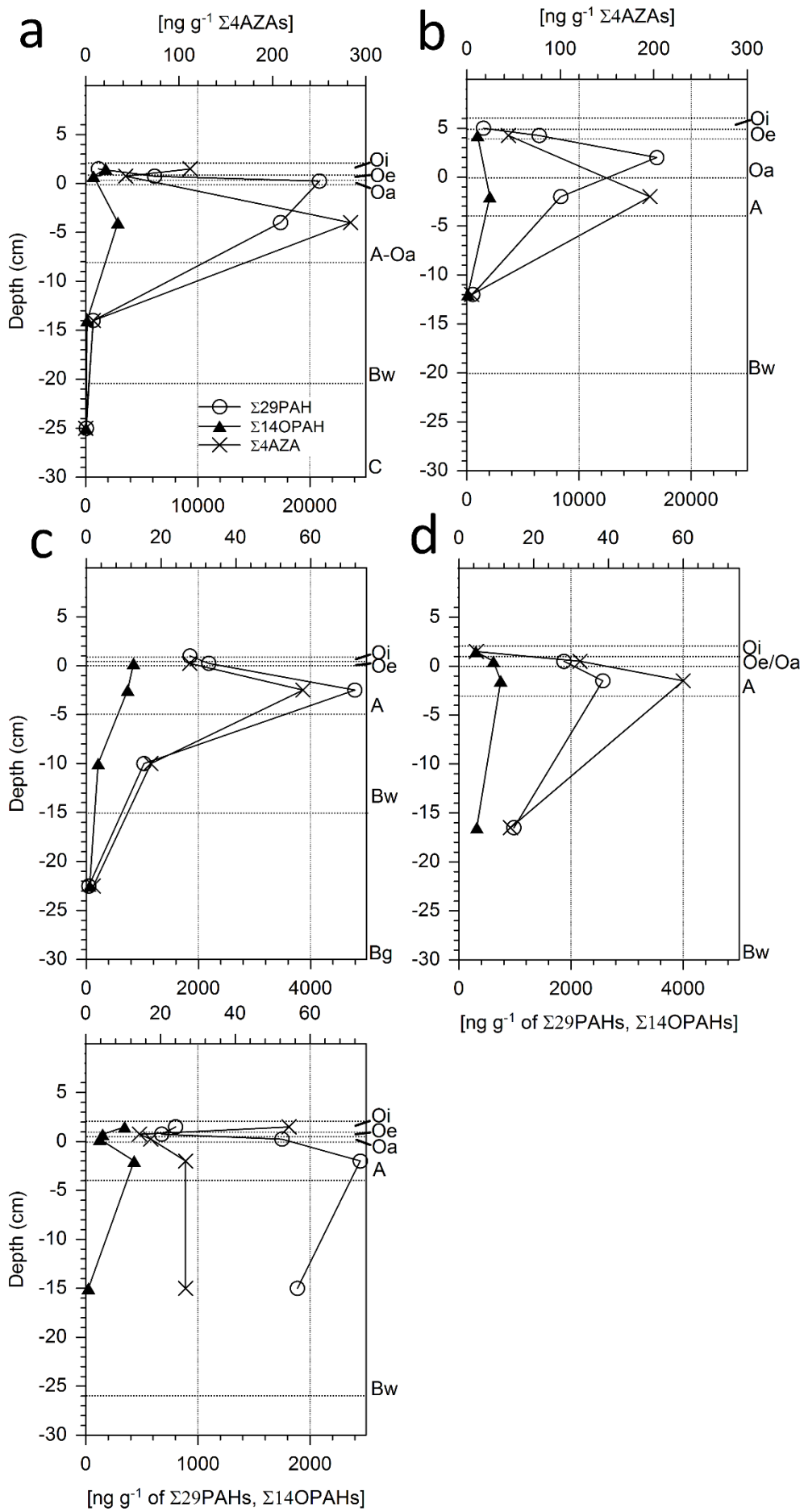


Figure 2

Figure 3

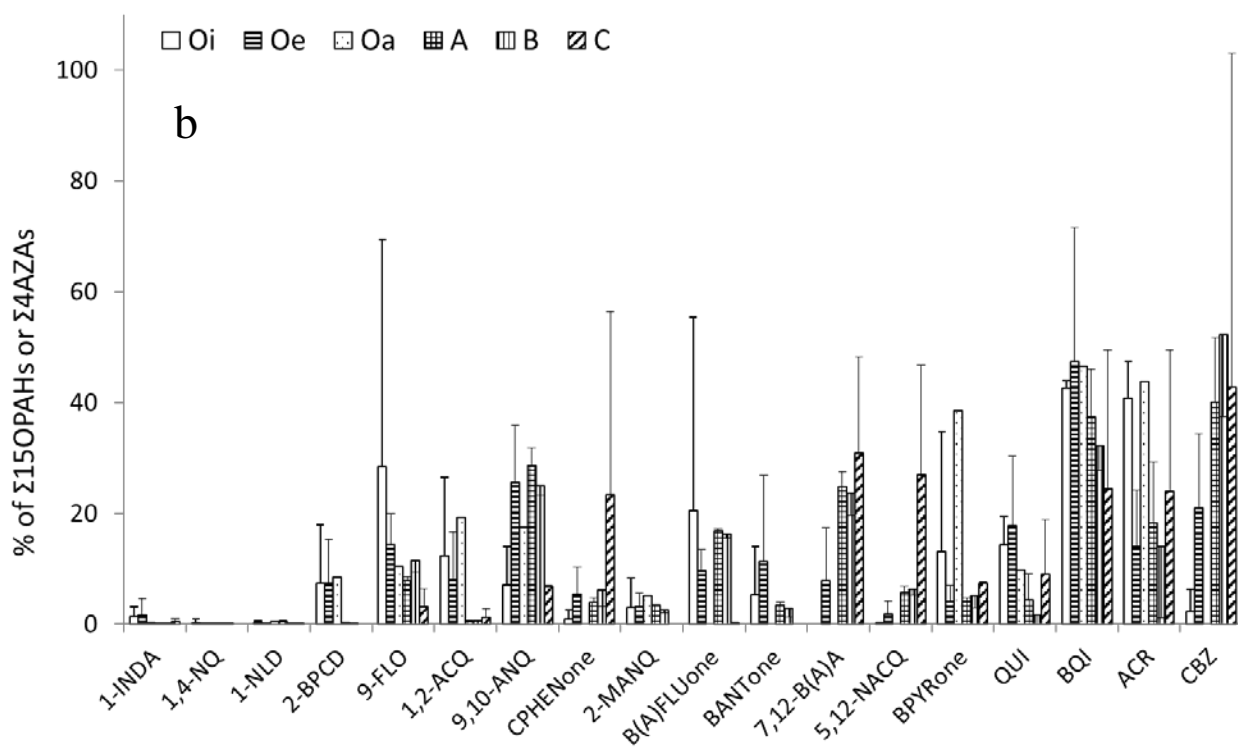
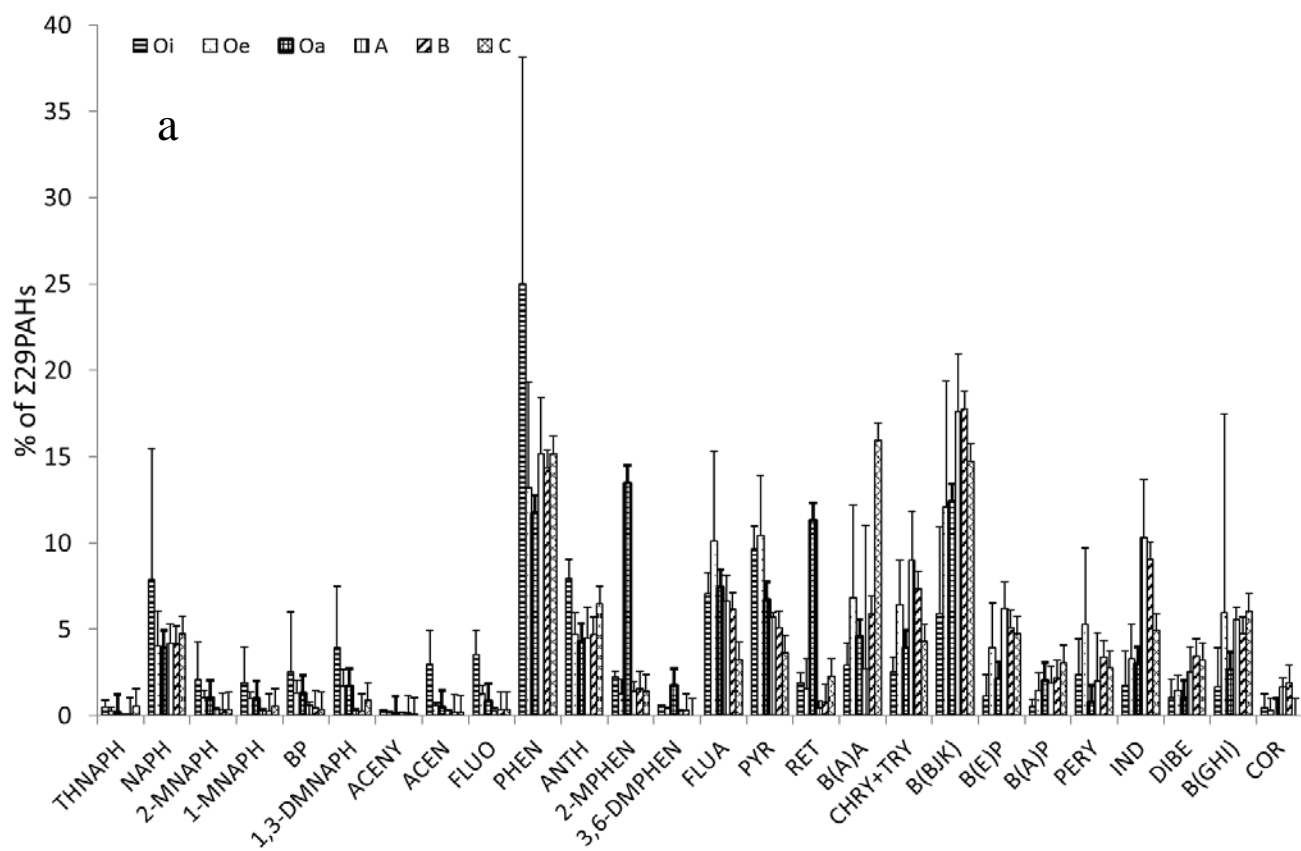


Figure 4

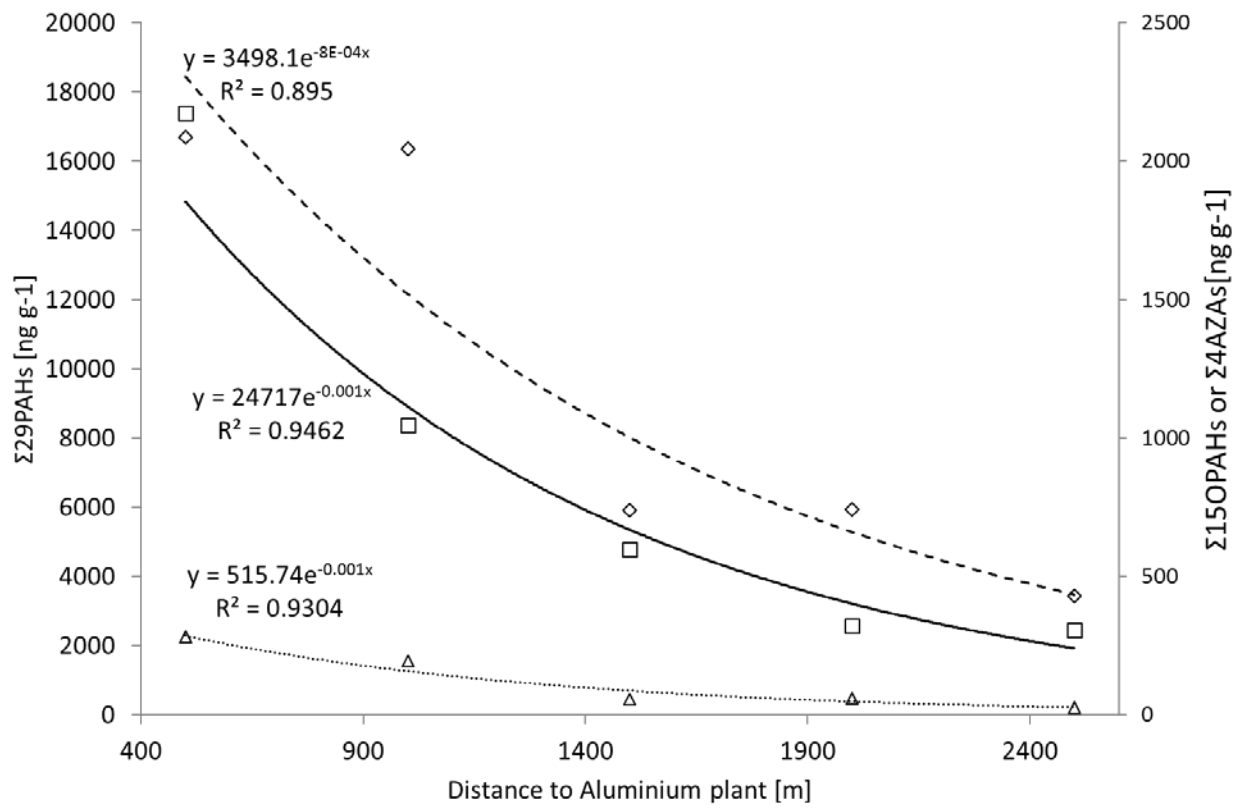
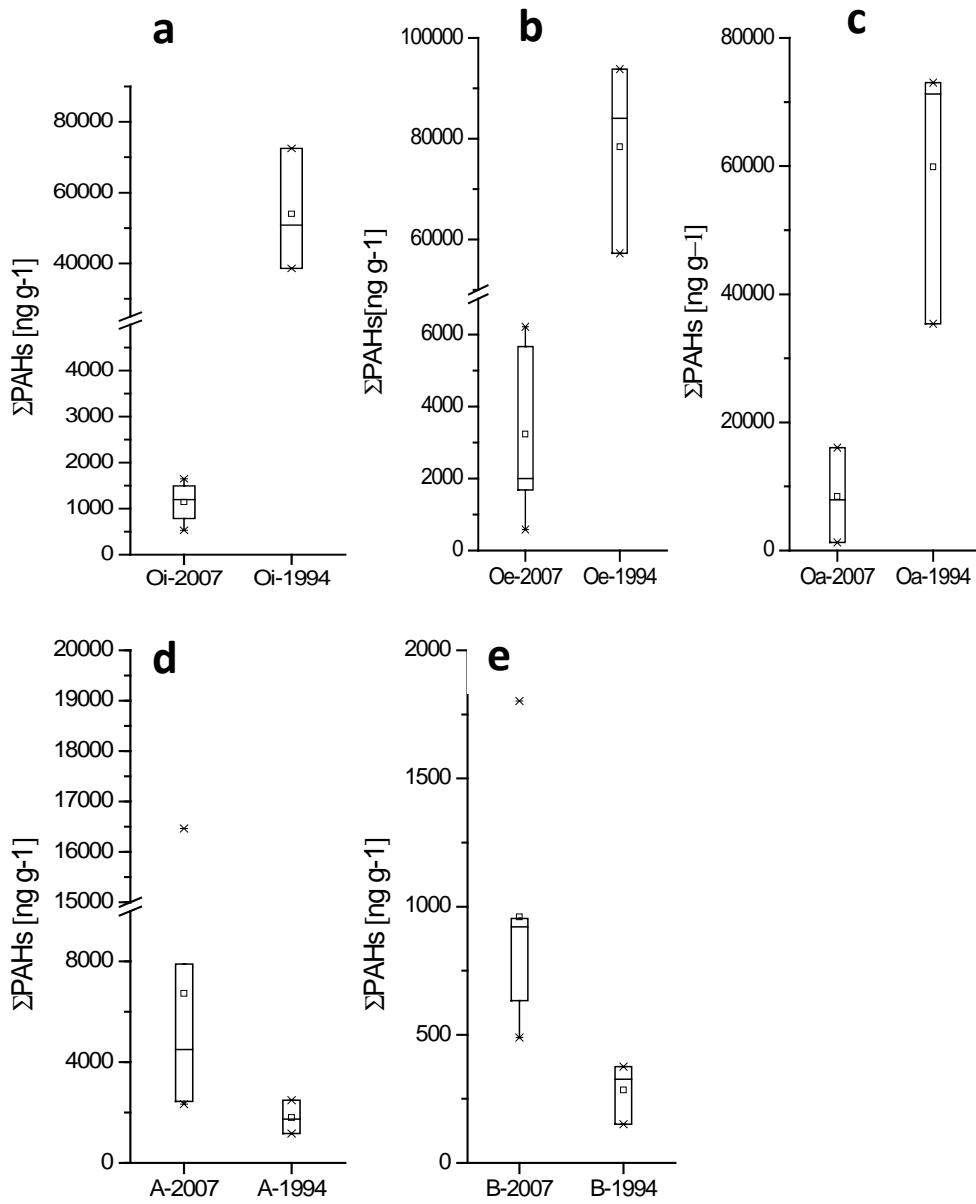




Figure 5



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