Polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and chlorinated pesticides in background air in central Europe - investigating parameters affecting wet scavenging of polycyclic aromatic hydrocarbons

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Abstract

Concentrations of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and chlorinated pesticides (CPs) were measured in air and precipitation at a background site in central Europe. $\sum$ PAH concentrations in air and rainwater ranged from 0.7 to 327.9 ng m^{-3} and below analytical method detection limit (<MDL) to 2.1×10^3 ng L^{-1}. The concentrations of PCBs and CPs in rainwater were <MDL. $\sum$ PCB and $\sum$ CP concentrations in air ranged from <MDL to 44.6 and <MDL to 351.7 pg m^{-3}, respectively. The potential relationships between PAH wet scavenging and particulate matter and rainwater properties were investigated. The concentrations of ionic species in particulate matter and rainwater were significantly correlated, highlighting the importance of particle scavenging process. Overall, higher scavenging efficiencies were found for relatively less volatile PAHs, underlining the effect of analyte gas-particle partitioning on scavenging process. The PAH wet scavenging was more effective when the concentrations of

27 ionic species were high. In addition, the elemental and organic carbon contents of the particulate

28 matter were found to influence the PAH scavenging.

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1 Introduction

31 Semi-volatile organic compounds (SOCs), such as polycyclic aromatic hydrocarbons (PAHs),

32 polychlorinated biphenyls (PCBs), and chlorinated pesticides (CPs), can reach remote and

33 background regions through atmospheric transport and deposition processes (Blais, 2005;

34 Hageman et al., 2006; Grimalt et al., 2001). Wet scavenging is an important mechanism through

35 which atmospheric SOCs enter terrestrial and aquatic ecosystems (van Ry et al., 2002). Non-

36 reactive gaseous SOCs are removed from the atmosphere by gas scavenging process, which is

37 controlled by the SOC equilibrium partitioning with falling raindrops, as described by Henry's

38 law. In contrast, particle-associated species are removed from the atmosphere mainly through

39 particle scavenging (Ligocki et al., 1985), a process controlled by physical parameters including

40 particulate matter (PM) characteristics, cloud microphysics, and meteorological conditions

41 (Poster and Baker, 1996). Therefore, factors that affect SOC gas-particle partitioning, such as

42 ambient temperature, relative humidity, PM chemical composition and surface characteristics,

43 and SOC vapor pressure (Lohmann and Lammel, 2004), may play an important role in

44 determining the relative contributions of gas and particle scavenging processes. It was suggested

45 that SOC scavenging efficiencies would be between one to three orders of magnitude higher in

46 case of in-cloud scavenging compared to that of below-cloud scavenging (Ligocki et al., 1985).

47 Potential variability in scavenging efficiencies has also been suggested between rain events

48 originated from warm and cold clouds (Bidleman, 1988). A number of studies observed

49   variations in scavenging efficiencies of SOCs between different precipitation events (Offenberg

50   and Baker, 2002; Agrell et al., 2002; Liu et al., 2013; Kaupp and McLachlan, 2000; McLachlan

51   and Sellström, 2009; Atlas and Giam, 1988). To this date, studies have mainly focused on

52   determining the relative importance of SOC gas and particle scavenging processes. However, to

53   the best of our knowledge, no comprehensive study has been conducted to understand the causes

54   behind the variability in scavenging efficiencies. Therefore, in this study we aimed at filling this

55   gap by investigating the relationships between a set of aerosol and rainwater properties and SOC

56   scavenging. The present study was conducted at a background site in central Europe, as a follow

57   up with a previously published research (Škrdlíková et al., 2011) in which PAH scavenging

58   efficiencies were determined at that site. The specific objectives of the present study were to (1)

59   measure the concentrations of PAHs, PCBs, and CPs in air and rainwater samples, (2) estimate

60   wet depositional fluxes of target compounds in the study area, (3) determine wet scavenging

61   efficiencies and scavenged mass fractions of the analytes, and (4) investigate the potential

62   relationships between analyte scavenging and meteorological parameters as well as aerosol and

63   rain characteristics. PAHs, PCBs, and CPs were selected because they are widespread

64   atmospheric contaminants and have been found in air at background locations across Europe

65   (Dvorská et al., 2009; Gioia et al., 2007; Roots et al., 2010; Halse et al., 2011). In addition, these

66   chemicals can persist in the environment due to their resistance to photolytic, chemical, and

67   biological degradation (Yolsal et al., 2014).

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2 Experimental

2.1 Sampling site

The sampling was conducted at Košetice observatory located in an open land about 70 km southeast of Prague in the Czech Republic (Fig. S1 in the Supporting Information (SI)). The observatory is classified as a European background site (Dvorská et al., 2008). It is managed by the Czech Hydrometeorological Institute (CHMI) and is part of the European Monitoring and Evaluation Program. The area is covered with snow two to three months per year with the mean annual temperature and precipitation of 7.1 °C and 625 mm. The potential source of pollution in the region is the nearby highway (~ 7 km west of the observatory) connecting Prague to Brno. In addition, due to having dominant westerly winds, atmospherically transported contaminants from the industrial and urban areas of the Czech Republic, notably Prague, may contribute to the pollution in the area.

2.2 Sampling procedure

Rainwater and air samples were collected during the period of December 2011 to January 2014 (Table S1 in the SI). A total of 231 rain samples were collected using an automatic precipitation sampler (Baghira, Czech Republic) equipped with a 1-m^2 stainless steel collection funnel, a lid, and a 5-L glass collection bottle. The opening and closing of the lid is triggered by a precipitation sensor mounted on the sampler. During sampling, rain drains from the funnel and accumulates in the collection bottle. The collected sample volumes were between 0.5 and 1 L, depending on the amount of rainfall for each event. Larger or smaller volumes were discarded - the latter was not deemed to provide enough analyte mass for trace analysis.

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93   Air samples were collected on quartz fiber filters (QFF) (Grade QM-A, 10.1 cm ID, Whatman,

94   UK) and in polyurethane foam (PUF) plugs (55 cm ID, 50 cm height, Organika, Poland) using a

95   Graseby Andersen PS-1 high-volume sampler (GA, USA) with a flow rate of 17 $m^3 h^{-1}$. For each

96   sampling period, two consecutive PUF plugs and one filter paper were deployed. A total of 162

97   gaseous and particulate air samples were collected during the period of study. Nevertheless, only

98   samples from 54 events were considered for determining scavenging ratios because only these

99   were followed by rain events. The collection of these samples started between 6 to 35hrs prior to

100   the onset of rain (predicted by CHMI) and stopped when rainfall started (Table S2 in the SI).

101   This sampling approach was chosen in order to sample rainwater from the same air mass as that

102   of PM. In addition, PM has been suggested to be removed from a travelling air parcel by up to 8

103   and 23% in the first 24 and 72hrs after the onset of rain, respectively (Wiman et al., 1990;

104   Škrdlíková et al., 2011). This means that prolonging the air sampling beyond the onset of rain

105   would potentially lead to underestimating contaminant concentrations in air and, therefore,

106   overestimating scavenging ratios and washed-out mass fractions. In addition, relative humidity

107   substantially increases during rainfall and this would potentially affect gas-particle partitioning

108   of SOCs in the air leading to underestimation or overestimation of gaseous and particulate

109   fraction of contaminants.

110   Field blanks for air samples were prepared at the site following the standard protocol for

111   mounting QFF and PUF plugs onto the sampler without turning on the sampler. No field blanks

112   were generated for rain samples.

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2.3 Meteorological and other supporting data

Cloud top heights were estimated from radiosonde measurements over Prague (Station ID. 11520) (IGRA, 2014) (Table S2 in the SI). Meteorological parameters - i.e. near-ground temperature, precipitation type and intensity, cloud base heights (determined through on-site ceilometer measurements), concentrations of $PM_{2.5}$ and PM_{10}, and their ionic species (i.e. SO_4^{2-}, NO_3^-, NH_4^+), elemental carbon (EC), and organic carbon (OC) contents - were obtained from CHMI (Table S3 in the SI). Aerosol number size distribution data, used for calculating the aerosol surface area, was obtained from the Academy of Sciences of the Czech Republic. Analyte physico-chemical properties were obtained from Estimation Programs Interface Suite 4.11 (USEPA, 2012). The weather charts used to determine the occurrence of frontal passage over the study site were obtained from *Berliner Wetterkarte* (BWK, 2013).

2.4 Chemical analysis and quality control

QFF and PUF samples were extracted with dichloromethane using an automatic extraction system (Büchi B-811, Switzerland). PUF plugs ($n = 2$) related to each sampling period were extracted together. Field blanks were extracted along with each set of 10 samples. The extracts were concentrated under a gentle stream of nitrogen in ambient temperature and fractionated using a silica column for PAHs and a sulfuric acid modified silica column for PCBs and CPs. The method performance was tested prior to sample analysis and no degradation of target analytes due to acid treatment was detected. Analytes in rainwater were extracted using solid-phase extraction (C18 Speedisks, Bakerbond, the Netherlands). The analytes were later eluted using 40 ml of (1:1) dichloromethane: *n*-hexane, concentrated under a gentle stream of nitrogen,

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137 and passed through a glass column packed with anhydrous sodium sulfate (1cm ID, 3 cm height)

138 to remove residual water. Prior to extraction, all air and rainwater samples and blanks were

139 spiked with a solution containing d_8-naphthalene, d_{10}-phenanthrene, d_{12}-perylene, PCB 30, and

140 PCB 185, which were used as recovery standards.

141 Samples were analyzed for 26 parent PAHs (i.e. naphthalene (NAP), acenaphthylene (ACY),

142 acenaphthene (ACE), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), fluoranthene

143 (FLT), pyrene (PYR), benzo(*a*)anthracene (BAA), chrysene (CHR), benzo(*b*)fluoranthene

144 (BBF), benzo(*k*)fluoranthene (BKF), benzo(*a*)pyrene (BAP), indeno(123-*cd*)pyrene (IPY),

145 dibenz(*a,h*)anthracene (DHA), benzo(*g,h,i*)perylene (BPE), benzo(*b*)fluorene (BFN),

146 benzo(*g,h,i*)fluoranthene (BGF), cyclopenta(*c,d*)pyrene (CPP), triphenylene (TPH),

147 benzo(*j*)fluoranthene (BJF), benzo(*e*)pyrene (BEP), perylene (PER), dibenz(*a,c*)anthracene

148 (DCA), anthanthrene (ATT), coronene (COR)), one heterocyclic PAH (i.e. benzo-naphtho-

149 thiophene (BNT)), and one alkylated PAH (i.e. retene (RET)) using a Hewlett-Packard gas

150 chromatograph (GC 6890) interfaced to a Hewlett-Packard mass selective detector (MS 5973).

151 Seven PCBs (i.e. PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180) and 13

152 CPs, namely *α*-hexachlorocyclohexane (HCH), *β*-HCH, *γ*-HCH, *δ*-HCH, *ε*-HCH, *o,p´*-

153 dichlorodiphenyldichloroethylene (DDE), *p,p´*-DDE, *o,p´*-dichlorodiphenyldichloroethane

154 (DDD), *p,p´*-DDD, *o,p´*-dichlorodiphenyltrichloroethane (DDT), *p,p´*-DDT, pentachlorobenzene

155 (PeCB), hexachlorobenzene (HCB), were analyzed using an Agilent GC (7890) coupled with an

156 Agilent Triple Quadrupole MS/MS (7000B). All analytes were separated on a J&W Scientific

157 capillary column (HP-5ms, 0.25 mm ID, 0.25μm film thickness). D_{14}-*p*-terphenyl and PCB 121

158 were used as internal standards for PAH and PCB/CP analysis, respectively. The analytical

159 method recoveries for PCBs/CPs and PAHs ranged from 88 to 100% and 72 to 102%,

160 respectively. The measured analyte concentrations were not recovery corrected.

161 Limits of quantification (LOQ) for analytes were calculated based on instrument detection limits,

162 which in turn are determined using three times the chromatogram baseline noise level. The

163 median LOQs for individual PAHs and PCBs/CPs in air samples were 0.006 and 0.0005 ng m^{-3},

164 respectively. The median LOQs in rainwater samples were 0.05 and 0.45 ng L^{-1}, respectively.

165 LOQ values were used in cases where analyte concentrations in field blanks were <LOQ. The

166 mean concentrations of analytes in five field blanks were subtracted from those in the

167 corresponding samples. The concentrations that were lower than mean + 3 standard deviations of

168 those in field blanks were considered below method detection limit (<MDL) and were

169 substituted with LOQ/2 for calculation of averages.

170 Analysis of ionic species in rainwater was done using a Hewlett-Packard capillary

171 electrophoresis system (HP 3D CE). Measurements were performed using an uncoated silica

172 capillary column (75 μm ID, 70 cm length). The applied separation voltage was 10kV with

173 hydrodynamic injection of 50 mbar/20 sec. Analytes were detected indirectly at 254 nm

174 wavelength. The electrolyte was composed of 5 mM sodium chromate and boric acid with pH

175 adjusted to 8.3 by adding 0.5 mM cetyltrimethylammonium bromide. Quantification was

176 performed using individual calibration curves. Each quantification was performed three times

177 and mean values were used.

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179 **2.5 Calculations and data analysis**

180 Analyte particulate mass fractions, Θ (unit-less), were calculated using equation 1,

$\Theta = C_{ip}/(C_{ig} + C_{ip})$ Eq. (1)

181   where, C_{ip} is analyte (i) air concentration (ng m^{-3}) in particulate phase and C_{ig} is that in gas phase.

182   Daily wet deposition fluxes, F_{wet} (ng m^{-2}), were determined using equation 2,

$F_{wet} = C_{ir} \times P$ Eq. (2)

183   where, C_{ir} is analyte concentration in rainwater (ng L^{-1}) and P is the rain volume received per

184   collection area (L m^{-2}) in each sampling day. Seasonal fluxes were calculated by summing the

185   daily fluxes in each season. Total scavenging ratios, W_t (unit-less), were calculated using

186   equation 3,

$$W_t = \frac{C_{ir} \times 10^3}{(C_{ig} + C_{ip})}$$ Eq. (3)

187   where, multiplication by 10^3 accounts for conversion from ng L^{-1} to ng m^{-3}. The mass fraction of

188   the total analyte burden in air washed out by below- and in-cloud scavenging, ϵ_t (unit-less), is

189   calculated according to Škrdlíková et al. (2011) using equation 4,

$$\varepsilon_t = \frac{b_r}{b_a} = \frac{C_{ir} \times P}{(C_{ig} + C_{ip}) \times h}$$ Eq. (4)

190   where, b_r and b_a are analyte burdens (ng m^{-2}) in rainwater and air, respectively, and h (m) is the

191   height of the air column subject to precipitation, which corresponds to the cloud height from

192   which precipitation originates.

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3 Results and Discussion

3.1 Concentrations and distribution of analytes

3.1.1. Concentrations in air

NAP was targeted for analysis but it did not pass our quality control criteria and, therefore, is not discussed hereafter. In addition, only analytes that were detected in >10% of the samples are discussed herein (Table 1 and 2). $\sum$ PAH (i.e. the sum of 27 PAHs) concentrations in gas phase ranged from 0.6 to 138.6 (mean $\pm$ standard deviation (SD): 11.3$\pm$15.7) ng m^{-3} (Table 1). PAHs with molecular mass <228 Da, namely ACY, ACE, FLN, PHE, ANT, FLT, and PYR, were predominant in gas phase and, on average, accounted for 93% of the $\sum$ PAH concentrations. PHE, FLN, and FLT showed the highest mean contributions accounting for 42, 24, and 12% of the $\sum$ PAH gaseous concentrations, respectively. BKF, BAP, IPY, DHA, BPE, BNT, CPP, BJF, BEP, PER, DCA, ATT, and COR were detected in <10% of the gaseous samples (n = 162) (Table 1). The $\sum$ PAH concentrations in the particulate phase ranged from 0.1 to 189.3 (mean $\pm$ SD: 9.3$\pm$21.2) ng m^{-3} (Table 1). In sum, PAHs with molecular mass > 228 Da were predominant in particulate phase and, on average, contributed to 67% of the $\sum$ PAH particulate concentrations. However, FLT and PYR showed the highest individual contributions and, on average, accounted for 13 and 11% of the $\sum$ PAH concentrations, respectively. The sum of the concentrations of gas and particulate phase PAHs ranged from 0.7 to 327.9 ng m^{-3}, with the mean $\pm$ SD being 20.6$\pm$35.9 ng m^{-3}. The PAH concentration ranges in gas and particulate phase are noticeably higher than those measured by Škrdlíková et al. (2011) (i.e. 0.9 to 34.6 and 0.1 to 16.8 ng m^{-3}, respectively) for samples collected from the same site during 2007-2008 period, but

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218   are slightly lower than those reported by Holoubek et al. (2007) for the period between 1996 and

219   2005 (i.e. 0.4 to 208 and 0.1 to 359 ng m^{-3}, respectively).

220   Except for p,p'-DDE, the targeted chlorinated compounds were mainly detected in gas phase (i.e.

221   <10% in particulate phase) (Table 2). The concentrations of p,p'-DDE in particulate phase

222   ranged from <MDL to 6.8 (mean ± SD: 0.4±0.7) pg m^{-3}. In gas phase, β-HCH, δ-HCH, ε-HCH,

223   and o,p'-DDD were detected in <10% of all samples ($n = 162$). The concentrations in gas phase

224   ranged from <MDL to 43.5 (mean ± SD: 8.1±7.2) pg m^{-3} for $\sum$ PCBs (i.e. the sum of the

225   concentrations of PCB 28, 52, 101, 118, 138, 153, 180), <MDL to 73.8 (11.0±11.6) pg m^{-3} for $\sum$

226   HCHs (i.e. the sum of the concentrations of a- and γ-HCH), <MDL to 104.3 (23.2±19.8) pg m^{-3}

227   for $\sum$ DDTs (i.e. the sum of the concentrations of o,p'-DDE, p,p'-DDE, p,p'-DDD, o,p'-DDT, and

228   p,p'-DDT) and <MDL to 332.3 (96.1±42.0) pg m^{-3} for $\sum$ CBs (i.e. the sum of the concentrations

229   of PeCB and HCB) (Table 2). On average, PCB 28 (40%), γ-HCH (56%), p,p'-DDE (83%), and

230   HCB (90%) predominated $\sum$ PCB, $\sum$ HCH, $\sum$ DDT, and $\sum$ CB concentrations, respectively. The

231   sum of the concentrations of gas and particulate phase PCBs and CPs ranged from <MDL to 44.6

232   and <MDL to 351.7 pg m^{-3}, respectively. The measured concentrations in the present study are

233   considerably lower than those reported by Holoubek et al. (2007) for the samples collected from

234   the same location between 1996 and 2005 (i.e. <MDL to 390 pg m^{-3} for $\sum$ PCBs, <MDL to 771

235   pg m^{-3} for $\sum$ HCHs, 1 to 207 pg m^{-3} for $\sum$ DDTs, and <MDL to 831 pg m^{-3} for HCB). As

236   production and use of these compounds are banned in Europe, the relatively low concentrations

237   in the present study could indicate emission due to volatilization from contaminated soil around

238   Košetice (Fig. S1). This argument is supported by significant correlations found between the

239   ambient temperature at the sampling site and the measured concentrations of PCB 28 ($r = 0.70$, P

240   <0.05, $n = 162$), γ-HCH ($r = 0.74$, P <0.05), and p,p'-DDE ($r = 0.71$, P <0.05). Despite having the

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241 highest mean concentration among the other chlorinated analytes, relatively small correlation

242 was found between the concentrations of HCB and ambient temperature changes (r = 0.25). This

243 could be due to the fact that this compound has different source pathways compared to all other

244 chlorinated chemicals investigated in this study. Although banned, HCB could potentially be

245 released to the environment as an unintended byproduct of organic solvent and aluminum

246 manufacturing and waste burning (EPER, 2014). In addition, this compound is present in some

247 pesticide formulations, such as chlorothalonil, which is currently registered for use in Europe.

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249 **3.1.2. Concentrations in rain**

250 $\sum$ PAH concentrations in rainwater ranged from <MDL to 2.1×10^3 (mean ± SD: 173.3±256.1) ng

251 L^{-1} (Table 3), predominated (mean: 69%) by congeners with <228 Da molecular mass. FLT,

252 PHE, and PYR showed the highest individual contributions and, on average, accounted for 35,

253 14, and 10% of the $\sum$ PAH concentrations. The $\sum$ PAH concentration range in the present study

254 was higher than the one reported by Škrdlíková et al. (2011) for Košetice (i.e. 7.1 to 485.9 ng L^-

255 ^{1}) but noticeably lower than that measured by Holoubek et al. (2007) (i.e. 2.4 to 6310 ng L^{-1}).

256 The concentrations of PCBs and CPs, targeted for analysis in rainwater samples, were below

257 LOQs and, therefore, are not discussed hereafter.

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259 **3.2 Wet deposition fluxes**

260 $\sum$ PAH daily wet deposition fluxes ranged from <MDL to 5.5×10^3 (mean ± SD: 632.9±900.1) ng

261 m^{-2} (Table 4). $\sum$ PAH seasonal fluxes were noticeably higher during winter and spring compared

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262 to summer and autumn (Table 5), which is in agreement with previous observations in Europe

263 (Kiss et al., 2001; Škrdlíková et al., 2011). Seasonal changes in SOC fluxes could be due to

264 different factors, such as variations in atmospheric concentration, precipitation amount

265 (providing that atmospheric concentrations do not change drastically between seasons), and SOC

266 gas-particle partitioning behavior. The increase in PAH fluxes during winter and spring cannot

267 be explained by changes in precipitation amounts, as indicated in Table 5. However, atmospheric

268 concentrations of PAHs were noticeably higher in winter than they were in other seasons (Fig.

269 1), in agreement with a previously published study in Europe (Lammel et al., 2011). This may be

270 due to higher emission rate, lower boundary layer mixing height (Birgül et al., 2011), and lower

271 concentrations of OH radicals in winter (Halsall et al., 2001). This may partly explain the higher

272 fluxes seen during winter periods. Finally, lower temperatures in winter could potentially shift

273 partitioning of the more temperature sensitive SOCs towards particulate phase, and particle

274 scavenging, as opposed to gas scavenging, was suggested to be the dominant wet scavenging

275 mechanism for the removal of PAHs from the atmosphere (Bidleman, 1988; Poster and Baker,

276 1996; Offenberg and Baker, 2002). In the present study, significant negative regressions were

277 found between near-ground temperature and Θ for a number of PAHs including PYR ($r^2 = 0.72$,

278 $P < 0.05$, $n = 150$), FLT ($r^2 = 0.69$, $n = 155$), RET ($r^2 = 0.75$, $n = 156$), and TPH ($r^2 = 0.73$, $n = $

279 162) (Table S4 in the SI), which could provide further explanation for higher fluxes during cold

280 seasons.

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3.3 Scavenging ratios

Scavenging ratios were only determined for those events with air and rainwater sampled from the same air mass ($n = 54$). The rejection criterion was that frontal passage did *not* occur over the site prior ($\pm$ 1 hour uncertainty) to the onset of rain. Out of 54 pair samples, only 32 met the abovementioned criterion (Table S2 in the SI) and, hence, W_t ratios were determined for 32 rain events.

The relative importance of gas and particle scavenging can be calculated theoretically using W_t and gas scavenging ratio obtained through dimensionless Henry's law constant (Offenberg and Baker, 2002; Poster and Baker, 1996). However, this approach was avoided in the present study due to the fact that the equilibrium partitioning of SOCs between gas phase and raindrops, and consequently gas scavenging ratios, is greatly affected by temperature, which may change drastically from cloud to ground level. This process is non-linear and a representative temperature is unknown. This means that Henry's law constants, which are corrected using ground temperatures, may not necessarily represent the true gas scavenging ratios related to falling raindrops. One should also note that theoretical gas scavenging ratios for SOCs in gas phase, being the inverse of their Henry's law constants, may not entirely reflect the underlying mechanism of the compound removal from the atmosphere. For instance, PAHs with higher vapor pressure normally show higher Henry's law constants, as can be seen from experimental data (Bamford et al., 1999). This would result in relatively lower gas scavenging ratios for gaseous PAHs with higher vapor pressure and solubility, which contradicts the concept of SOC gas scavenging.

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305   In the present study, the concentrations of ionic species (i.e. the sum of SO_4^{2-}, NO_3^-) in PM and

306   those in adjacent rainwater samples were significantly correlated (r = 0.71, P <0.05, n = 23). This

307   indicates the efficient removal of PM by rainfall and highlights the importance of particle

308   scavenging in the present study. In general, W_t ratios for individual PAHs ranged from 0 (in cases

309   where concentrations in rainwater were <LOQ) to 3.5×10^5, with the exception of FLT for which

310   W_t ranged between 3.7×10^3 and 1.3×10^6 (median: 1.4×10^4) (Table 6). Overall, W_t values for

311   relatively more volatile PAHs (log K_{oa} between 6.27 and 7.57), namely ACY, ACE, FLN, ANT,

312   and PHE, were up to 10^4, whereas the values for the rest of PAHs (log K_{oa} > 8.70) were up to

313   10^6, but mainly dominated by the values close to 10^5 (Table 6). Taking into account that SOCs

314   are more efficiently removed from the atmosphere by particle scavenging, the current results

315   may imply that increase in affinity of individual PAHs towards organic phase would overall lead

316   to higher scavenging efficiencies. This, together with other parameters that affect analyte gas-

317   particle partitioning, namely temperature, aerosol surface area and chemical composition (e.g.

318   EC and OC contents) (Junge, 1977; Pankow, 1987; Bidleman, 1988), and factors that affect

319   particle removal rate including rain intensity, aerosol and raindrop size and collision efficiency

320   (Mircea et al., 2000; Poster and Baker, 1996; Slinn et al., 1978), may contribute to the observed

321   variability in measured scavenging ratios.

322   Since chlorinated compounds in the present study were mainly detected in gas phase in the air

323   (Table 2), it is likely that their removal from the atmosphere was determined by gas scavenging.

324   The fact that concentrations of these analytes in rainwater were below detection limits may

325   provide further evidence for this argument, as the magnitude of gas scavenging is negligible.

326   The upper- and lower-bound scavenged mass fractions of target analytes corresponding to cloud

327   base and top heights were determined for 32 events, except in one case for which cloud top

328 height was not available (Table S2). $\sum$ PAH upper-bound scavenged mass fractions ranged from

329 1.2×10^{-3} to 0.8 (median: 5.3×10^{-2}), whereas lower-bound mass fractions were between 5.2×10^{-4}

330 and 0.1 (median: 9.7×10^{-3}) (Table 7). The median ratios for the analyte lower-bound mass

331 fractions were nearly an order of magnitude different from those reported by Škrdlíková et al.

332 (2011) for the same site, except for FLN and CHR, which were found to be in agreement (Table

333 7). This could potentially be related to the relatively small number of events considered in that

334 study ($n = 10$). It should be noted that scavenged mass fractions were calculated assuming that

335 analyte concentrations near ground represented those within the air column up to cloud top - i.e.

336 assuming perfect mixing throughout the column. The true scavenged mass fractions could

337 potentially be higher due to a negative vertical concentration gradient (Škrdlíková et al., 2011).

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339 3.4 Factors affecting the scavenging ratios

340 As can be seen from Tables 6 and S3, W_t ratios for $\sum$ PAHs in the present study ranged from

341 2.4×10^3 to 2.3×10^5, with noticeable variability between the events (mean $\pm$ SD:

342 $1.7\times10^4\pm3.8\times10^4$). As discussed earlier, different parameters could contribute to the variability

343 seen in scavenging ratios. In this section, we investigate potential relationships between PAH

344 scavenging efficiencies and precipitation intensity, near-ground temperature, the concentrations

345 of $PM_{2.5}$ and PM_{10}, PM ionic species (i.e. the sum of the concentrations of SO_4^{2-}, NO_3^-, and

346 NH_4^+), EC and OC contents, PM surface area, and rainwater ionic species (i.e. the sum of SO_4^{2-},

347 NO_3^-, and Cl^-). As can be seen from Table S3, the highest $\sum$ PAH W_t was found for the samples

348 collected on 14 April 2012. The ratio was nearly two orders of magnitude higher compared to

349 that obtained for another event with similar precipitation type and ambient temperature (i.e. 11 –

350   12 October 2012). Apart from the concentrations of PM_{10} and ionic species in PM and rainwater,

351   the rest of the parameters were somewhat similar for these two events (Table S3). The

352   concentrations of PM_{10} as well as those for ionic species in PM and rainwater for the former

353   event were 1.4, 1.8, and 11 times the values found for the latter event. This observation suggests

354   that PM removal by rain, and consequently wet scavenging of PAHs that are sorbed to PM, is

355   enhanced in conditions where PM contains high quantities of soluble species. This argument is

356   supported by considerably higher scavenging ratios found for particulate PAHs (a factor of 50 on

357   average) in the former event. This difference was much smaller for gaseous species (a factor of

358   five on average).

> **Comment [P4]:** Response to comment No.6 from Reviewer 1

359   In order to explore the relative importance of the abovementioned parameters in relation to

360   scavenging ratios, correlation analysis was performed between these variables. Among all

361   parameters, aerosol surface area was only available for 2012. In addition, aerosol EC and OC

362   contents could only be obtained for 15 rain events out of 32, as they were recorded once every

363   six days (Table S3). Owing to the fact that EC and OC have high importance in SOC gas-particle

364   partitioning (Lohmann and Lammel, 2004), and in order to enhance the comparability of results,

365   for all other parameters, correlation analysis was only performed for the corresponding rain

366   events. The results showed that the concentrations of rainwater ionic species were significantly

367   correlated with $\sum$ PAH scavenging ratios (r = 0.70, P <0.05, n = 15), whereas weak correlations

368   were found for all other parameters, except the ratio of PM ionic species/PM_{10}, for which a

369   moderate correlation was found (r = 0.34, P >0.05). However, when the data related to 14 April

370   2012 (with exceptionally high W_t ratio) was excluded from the analysis, the suggested

371   importance of rainwater and PM ionic species decreased (r = 0.14 and 0.07, respectively, P

372   >0.05, n = 14). This indicates that the initial analysis may have been overpowered by

373   significantly high values of ionic species related to a single event. Without the data point related

374   to 14 April 2012, moderate correlations were obtained between $\sum$ PAH W_t ratios and EC/PM$_{10}$ (r

375   = 0.34, P >0.05) and OC/PM$_{10}$ (r = 0.37, P >0.05). Although not statistically significant, the

376   current results suggest that the aerosol EC and OC contents are important parameters in

377   determining PAH scavenging efficiencies. This may reflect the affinity of PAHs towards EC and

378   OC, representing adsorption and absorption processes (Lohmann and Lammel, 2004). However,

379   the magnitude of these effects could be different when considering individual PAHs. For

380   instance, the coefficients of correlation between W_t and EC/PM$_{10}$ ratios for PAHs with moderate

381   to high particulate mass fractions, namely PYR (mean $\Theta = 0.40$), CHR (mean $\Theta = 0.74$), and

382   BBF (mean $\Theta = 0.97$), were 0.38, 0.20, and 0.33 ($n = 10$), whereas the coefficients for

383   correlation with OC/PM$_{10}$ ratios were 0.51, 0.53, and 0.03, respectively. Despite not having

384   statistical significance, the results may indicate that the aerosol OC content was more effective

385   than EC for wet scavenging of PYR and CHR. It should be noted that precipitation type (i.e.

386   snow vs. rain) was only available for eight events out of 15. These were mainly identified as

387   rainfall (Table S3), which ruled out the potential impact of precipitation type on scavenging

388   efficiencies. The lack of significant linear relationships between scavenging ratios and aerosol

389   and rainwater properties indicates that the process is not controlled by a single factor but rather

390   by a combination of parameters. The findings of the present study highlight the need for

391   incorporating other PM components, such as EC and OC, in air pollution models for more

392   accurate estimation of particulate PAH scavenging.

393

394

4 Conclusions

The results suggest that volatilization from contaminated soil was the main source of chlorinated compounds in the air over Košetice. Higher $\sum$ PAH fluxes in winter were possibly related to higher PAH atmospheric concentrations and particulate mass fractions in that season. Particle scavenging was found to be significant in the present study, as indicated by the strong correlation between rainwater and PM ionic species. In sum, greater scavenging ratios were found for less volatile PAHs, highlighting the importance of SOC gas-particle partitioning in determining their scavenging efficiencies. The results indicated that PAH wet scavenging could be more efficient in cases where the concentrations of ionic species in PM and rainwater are high. In addition, the high affinity of PAHs towards EC and OC were found to be reflected in the scavenging efficiency. In most model applications which study PAHs, particulates are scavenged either as in conventional air pollution modeling - i.e. accounting for PM ionic composition, but no other PM components (parameterization based on Köhler theory or empirical approaches based on cloud droplet number) (Abdul-Razzak and Ghan, 2000; Gong et al., 2003) - or with insoluble aerosols or aerosol modes (Sehili and Lammel, 2007; Friedman and Selin, 2012). Future studies would need to focus on in-depth analysis of PM chemical composition with the aim to include OC and EC in the parameterizations of particulate PAH wet deposition.

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Table 1. PAH concentrations and detection frequencies in air.

	Gaseous Cons.(ng m^{-3})				*Particulate Cons.*(ng m^{-3})			
	Min.	**Max.**	**Mean ± SD**	**DF %**	**Min.**	**Max.**	**Mean ± SD**	**DF %**
ACY	<MDL	34.5	1.0±3.0	87	<MDL	1.9	$7.8\times10^{-2}\pm2.4\times10^{-1}$	53
ACE	<MDL	3.2	0.3±0.5	90	<MDL	0.2	$1.1\times10^{-2}\pm3.1\times10^{-2}$	22
FLN	<MDL	26.3	2.7±4.0	98	<MDL	2.5	$1.1\times10^{-1}\pm3.4\times10^{-1}$	49
PHE	<MDL	45.0	4.7±5.9	98	<MDL	14.6	0.8±2.2	72
ANT	<MDL	4.7	$1.3\times10^{-1}\pm4.0\times10^{-1}$	81	<MDL	1.5	$6.3\times10^{-2}\pm1.9\times10^{-1}$	53
FLT	7.0×10^{-2}	13.8	1.3±1.6	100	3.0×10^{-3}	26.1	1.3±3.3	99
PYR	3.9×10^{-3}	7.7	0.6±0.8	93	3.5×10^{-3}	20.7	1.1±2.5	99
BAA	<MDL	0.3	$1.4\times10^{-2}\pm3.7\times10^{-2}$	38	<MDL	11.1	0.5±1.2	87
CHR	<MDL	0.4	$6.0\times10^{-2}\pm6.8\times10^{-2}$	95	<MDL	15.8	0.7±1.7	97
BBF	<MDL	0.9	$1.3\times10^{-2}\pm8.2\times10^{-2}$	14	<MDL	13.6	0.7±1.5	96
BKF	<MDL	0.3	$6.2\times10^{-3}\pm2.6\times10^{-2}$	4	<MDL	5.0	0.3±0.6	88
BAP	<MDL	0.5	$8.7\times10^{-3}\pm4.2\times10^{-2}$	3	<MDL	9.1	0.4±0.9	83
IPY	<MDL	0.5	$7.2\times10^{-3}\pm4.6\times10^{-2}$	3	<MDL	10.4	0.5±1.0	81
DHA				2	<MDL	1.2	$4.1\times10^{-2}\pm1.1\times10^{-1}$	56
BPE	<MDL	0.5	$7.4\times10^{-3}\pm4.2\times10^{-2}$	3	<MDL	6.6	0.4±0.7	90
RET	6.5×10^{-3}	5.0	0.2±0.4	100	<MDL	4.0	0.2±0.5	73
BFN	<MDL	0.8	$5.2\times10^{-2}\pm8.2\times10^{-2}$	80	<MDL	4.7	0.2±0.5	72
BNT	<MDL	2.1×10^{-2}	$2.4\times10^{-3}\pm2.2\times10^{-3}$	6	<MDL	0.5	$2.3\times10^{-2}\pm6.2\times10^{-2}$	46
BGF	<MDL	0.4	$5.1\times10^{-2}\pm5.4\times10^{-2}$	93	<MDL	7.7	0.3±0.8	92
CPP	<MDL	0.2	$5.0\times10^{-3}\pm2.2\times10^{-2}$	3	<MDL	10.3	0.3±0.9	73
TPH	<MDL	0.1	$1.5\times10^{-2}\pm1.5\times10^{-2}$	87	<MDL	2.8	$1.4\times10^{-1}\pm3.2\times10^{-1}$	86
BJF	<MDL	0.4	$8.4\times10^{-3}\pm3.9\times10^{-2}$	6	<MDL	7.5	0.4±0.9	91
BEP	<MDL	0.5	$1.0\times10^{-2}\pm4.6\times10^{-2}$	5	<MDL	7.2	0.4±0.8	87
PER				2	<MDL	1.5	$6.9\times10^{-2}\pm1.5\times10^{-1}$	61
DCA				2	<MDL	0.6	$2.9\times10^{-2}\pm6.7\times10^{-2}$	55
ATT				2	<MDL	1.7	$4.7\times10^{-2}\pm1.5\times10^{-1}$	48
COR				2	<MDL	3.3	$1.3\times10^{-1}\pm3.2\times10^{-1}$	64
∑ PAHs	0.6	138.6	11.3±15.7		0.1	189.3	9.3±21.2	

SD: standard deviation; DF: detection frequency (*n* = 162); <MDL: below method detection limit; ∑ PAHs: the sum of the concentrations of individual PAHs with DF >10% in either gas or particulate phase. Concentration ranges and means are only reported for analytes with DF >2%.

Table 2. PCB and CP concentrations and detection frequencies in air.

	Gaseous Cons. (pg m^{-3})				*Particulate Cons.* (pg m^{-3})			
	Min.	**Max.**	**Mean ± SD**	**DF %**	**Min.**	**Max.**	**Mean ± SD**	**DF %**
PCB 28	<MDL	14.3	3.2±2.4	88				1
PCB 52	<MDL	8.4	1.5±1.4	68				1
PCB 101	<MDL	13.9	1.2±1.8	60				1
PCB 118	<MDL	4.0	0.3±0.5	10				<MDL
PCB 138	<MDL	3.9	0.5±0.5	24				2
PCB 153	<MDL	8.0	1.0±1.2	62	<MDL	3.1	0.3±0.3	4
PCB 180	<MDL	2.1	0.3±0.2	14	<MDL	3.3	0.2±0.3	6
α-HCH	<MDL	44.5	4.4±6.0	57				1
β-HCH				2				<MDL
γ-HCH	<MDL	31.4	6.6±6.5	75				1
δ-HCH	<MDL	2.0	0.4±0.3	5				1
ε-HCH				1				<MDL
o,p'-DDE	<MDL	1.9	0.4±0.3	27				<MDL
p,p'-DDE	<MDL	87.3	19.5±15.9	98	<MDL	6.8	0.4±0.7	31
o,p'-DDD	<MDL	2.2	0.3±0.2	6				<MDL
p,p'-DDD	<MDL	2.4	0.4±0.4	17				1
o,p'-DDT	<MDL	8.9	1.5±1.9	45				<MDL
p,p'-DDT	<MDL	11.2	1.6±2.3	36				1
PeCB	<MDL	52.8	9.6±7.3	99				2
HCB	<MDL	279.5	86.5±40.4	99	<MDL	62.7	0.9±6.2	7
∑ PCBs	<MDL	43.5	8.1±7.2					
∑ HCHs	<MDL	73.8	11.0±11.6					
∑ DDTs	<MDL	104.3	23.2±19.8					
∑ CBs	<MDL	332.3	96.1±42.0					

SD: standard deviation; DF: detection frequency (n = 162); <MDL: below method detection limit; ∑ PCBs : the sum of the concentrations of PCB 28, 52, 101, 118, 138, 153, and 180; ∑ HCHs: the sum of the concentrations of α- and γ-HCH; ∑ DDTs: the sum of the concentrations of o,p'-DDE, p,p'-DDE, p,p'-DDD, o,p'-DDT, and p,p'-DDT; ∑ CBs: the sum of the concentrations of PeCB and HCB. Note that only analytes with DF>10% in either gas or particulate phase were considered for calculating the sums. Concentration ranges and means are only reported for analytes with DF >2%.

Table 3. PAH concentrations and detection frequencies in rainwater.

	Concentrations (ng L^{-1})			
	Min.	Max.	Mean ± SD	DF %
ACY	<MDL	23.7	2.1±2.8	67
ACE	<MDL	7.0	1.0±1.2	54
FLN	<MDL	41.6	6.0±5.8	99
PHE	<MDL	268.0	23.5±29.2	99
ANT	<MDL	41.2	1.1±3.2	56
FLT	<MDL	1.1×10^3	61.4±144.6	99
PYR	<MDL	282.5	17.7±27.0	91
BAA	<MDL	76.9	3.1±6.7	63
CHR	<MDL	141.8	9.1±14.9	75
BBF	<MDL	85.2	6.5±13.0	69
BKF	<MDL	42.3	2.8±4.8	63
BAP	<MDL	50.0	2.3±4.9	55
IPY	<MDL	58.2	3.6±7.1	60
DHA	<MDL	3.9	0.3±0.4	25
BPE	<MDL	50.9	3.6±6.5	59
RET	<MDL	44.0	3.1±4.6	73
BFN	<MDL	67.2	3.1±6.0	62
BNT	<MDL	6.7	0.5±0.7	43
BGF	<MDL	70.8	4.9±7.7	70
CPP	<MDL	17.4	1.1±2.2	48
TPH	<MDL	44.2	3.5±5.4	67
BJF	<MDL	63.0	5.6±9.7	64
BEP	<MDL	60.0	4.8±7.6	73
PER	<MDL	7.8	0.5±0.9	39
DCA	<MDL	7.7	0.4±0.7	27
ATT	<MDL	8.0	0.3±0.7	18
COR	<MDL	22.1	1.5±2.9	52
∑ PAHs	<MDL	2.1×10^3	173.3±256.1	

SD: standard deviation; DF: detection frequency (n = 231); <MDL: below method detection limit; ∑ PAHs: the sum of the concentrations of 27 individual PAHs listed on the table.

Table 4. PAH daily wet deposition fluxes (F_{wet}).

	F_{wet} (ng m^{-2})		
	Min.	Max.	Mean ± SD
ACY	<MDL	94.8	8.4±14.0
ACE	<MDL	76.1	4.3±8.8
FLN	<MDL	305.3	29.8±43.7
PHE	<MDL	816.8	102.1±133.1
ANT	<MDL	332.4	4.4±22.6
FLT	<MDL	4.0×10^3	204.1±413.0
PYR	<MDL	753.7	66.6±106.0
BAA	<MDL	182.7	10.6±23.1
CHR	<MDL	407.5	34.0±60.6
BBF	<MDL	569.9	21.5±51.4
BKF	<MDL	165.7	9.8±19.0
BAP	<MDL	180.5	7.1±17.9
IPY	<MDL	178.3	12.2±25.9
DHA	<MDL	13.5	0.6±1.8
BPE	<MDL	161.2	12.1±24.5
RET	<MDL	234.3	12.7±24.3
BFN	<MDL	163.5	11.6±23.0
BNT	<MDL	18.1	1.3±2.7
BGF	<MDL	240.6	18.4±31.7
CPP	<MDL	94.5	3.4±9.8
TPH	<MDL	104.1	12.4±20.0
BJF	<MDL	374.2	20.6±43.4
BEP	<MDL	249.1	16.8±29.8
PER	<MDL	34.7	1.4±3.6
DCA	<MDL	16.7	0.8±2.3
ATT	<MDL	21.3	0.7±2.5
COR	<MDL	66.5	5.0±10.5
∑ PAHs	<MDL	5.5×10^3	632.9±900.1

SD: standard deviation; <MDL: below method detection limit.

Table 5. $\sum$ PAH seasonal wet deposition fluxes (F_{wet}) and precipitation amounts.

2012				2013			
Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
$\sum$ **PAH F_{wet} (ng m^{-2})**							
3.0×10^4	2.3×10^4	6.3×10^3	7.3×10^3	4.0×10^4	1.6×10^4	9.4×10^3	1.1×10^4
Precipitation (mm)							
147.8	76.9	272.4	107.2	169.8	131.6	315.0	82.3

Table 6. PAH scavenging ratios (W_t).

	W_t			Log K_{oa}	Log K_{aw}
	Min.	**Max.**	**Median**		
ACY	NA	6.9×10^4	4.7×10^3	6.27	-2.33
ACE	NA	3.0×10^4	4.5×10^3	6.31	-2.12
FLN	863.9	5.0×10^4	4.8×10^3	6.79	-2.41
ANT	NA	8.4×10^4	2.4×10^3	7.55	-2.64
PHE	2.2×10^3	2.5×10^4	5.4×10^3	7.57	-2.76
RET	NA	3.2×10^4	6.2×10^3	8.70	-2.35
PYR	NA	1.1×10^5	1.2×10^4	8.80	-3.31
FLT	3.7×10^3	1.3×10^6	1.4×10^4	8.88	-3.44
BAA	NA	1.5×10^5	4.7×10^3	9.07	-3.31
CHR	NA	1.6×10^5	1.3×10^4	9.48	-3.67
BFN	NA	1.6×10^5	8.6×10^3	9.57	-3.80
BGF	NA	1.4×10^5	1.4×10^4	9.78	-4.26
PER	NA	1.5×10^5	1.8×10^3	10.08	-3.83
CPP	NA	1.8×10^5	563	10.15	-4.45
BBF	NA	1.4×10^5	7.5×10^3	10.35	-4.57
BJF	NA	1.4×10^5	9.2×10^3	10.59	-4.48
TPH	NA	2.0×10^5	1.9×10^4	10.69	-5.20
BKF	NA	1.4×10^5	5.6×10^3	10.73	-4.62
BAP	NA	9.1×10^4	1.6×10^3	10.86	-4.73
DCA	NA	1.4×10^5	NA	11.11	-4.70
BEP	NA	1.4×10^5	1.3×10^4	11.35	-4.91
IPY	NA	1.5×10^5	7.4×10^3	11.55	-4.85
DHA	NA	1.6×10^5	NA	11.78	-5.24
BPE	NA	1.4×10^5	6.5×10^3	11.97	-5.27
COR	NA	1.8×10^5	4.3×10^3	13.70	-6.06
BNT	NA	3.5×10^5	6.8×10^3	NA	-4.36
ATT	NA	2.3×10^5	NA	NA	NA
∑ PAHs	2.4×10^3	2.3×10^5	8.8×10^3		

K_{oa}: analyte octanol-air partitioning coefficient; K_{aw}: analyte air-water partitioning coefficient. For ease of interpretation, analytes are sorted based on their log K_{oa} values. Log K_{oa} and log K_{ow} values were obtained from Estimation Programs Interface Suite 4.11(USEPA, 2012); NA: indicates an event in which analyte concentration in rainwater was <LOQ.

Table 7. PAH scavenged mass fractions (ε).

	[a] *Upper-bound* ε			[b] *Lower-bound* ε			
	Min.	**Max.**	**Median**	**Min.**	**Max.**	**Median**	[c] **Median**
ACY	NA	2.2	1.4×10^{-2}	NA	1.7	2.3×10^{-3}	5.3×10^{-4}
ACE	NA	0.3	8.9×10^{-3}	NA	8.1×10^{-2}	1.8×10^{-3}	5.2×10^{-4}
FLN	5.4×10^{-4}	1.5	1.5×10^{-2}	4.3×10^{-4}	0.3	3.6×10^{-3}	3.7×10^{-3}
ANT	NA	0.4	1.3×10^{-2}	NA	0.1	2.4×10^{-3}	9.4×10^{-3}
PHE	1.3×10^{-3}	0.3	2.6×10^{-2}	5.4×10^{-4}	5.1×10^{-2}	5.5×10^{-3}	1.5×10^{-2}
RET	NA	0.4	1.2×10^{-2}	NA	0.1	2.8×10^{-3}	NA
PYR	NA	1.1	5.2×10^{-2}	NA	0.2	1.0×10^{-2}	7.5×10^{-3}
FLT	2.8×10^{-3}	0.9	8.1×10^{-2}	1.1×10^{-3}	0.2	1.3×10^{-2}	9.9×10^{-3}
BAA	NA	0.9	1.2×10^{-2}	NA	5.7×10^{-2}	1.9×10^{-3}	4.8×10^{-2}
CHR	NA	1.8	5.2×10^{-2}	NA	0.1	1.2×10^{-2}	1.0×10^{-2}
BFN	NA	1.2	3.0×10^{-2}	NA	0.2	4.1×10^{-3}	NA
BGF	NA	2.4	6.1×10^{-2}	NA	0.1	9.1×10^{-3}	NA
PER	NA	1.9	NA	NA	2.7×10^{-2}	NA	NA
CPP	NA	0.5	3.6×10^{-3}	NA	6.8×10^{-2}	4.6×10^{-4}	NA
BBF	NA	3.0	2.4×10^{-2}	NA	5.0×10^{-2}	3.6×10^{-3}	NA
BJF	NA	3.6	2.7×10^{-2}	NA	0.2	1.6×10^{-3}	NA
TPH	NA	3.2	7.4×10^{-2}	NA	0.3	1.4×10^{-2}	NA
BKF	NA	2.0	2.9×10^{-2}	NA	6.8×10^{-2}	1.9×10^{-3}	NA
BAP	NA	1.5	4.1×10^{-3}	NA	3.9×10^{-2}	5.2×10^{-4}	NA
DCA	NA	2.9	NA	NA	0.1	NA	NA
BEP	NA	2.9	4.0×10^{-2}	NA	7.5×10^{-2}	6.5×10^{-3}	NA
IPY	NA	3.5	1.7×10^{-2}	NA	0.3	1.8×10^{-3}	NA
DHA	NA	3.1	NA	NA	3.8×10^{-2}	NA	NA
BPE	NA	3.6	2.3×10^{-2}	NA	0.2	2.5×10^{-3}	NA
COR	NA	4.8	2.2×10^{-3}	NA	0.2	7.2×10^{-4}	NA
BNT	NA	2.8	NA	NA	0.2	NA	NA
ATT	NA	3.8	NA	NA	4.7×10^{-2}	NA	NA
$\sum$ PAHs 27	1.2×10^{-3}	0.8	5.3×10^{-2}	5.2×10^{-4}	0.1	9.7×10^{-3}	NA

[a] Upper- and [b] lower-bound ε correspond to cloud base and top height, respectively; [c] median ε values reported by Skrdlíková et al., (2011) for could top heights ($n = 10$); NA: indicates an event in which analyte concentration in rainwater was <LOQ. Analytes are sorted based on their log K_{oa} values.

Figure 1 caption

Fig. 1. ∑ PAH median air concentrations in winter (D.J.F.), spring (M.A.M.), summer (J.J.A.), and autumn (S.O.N.) at Košetice.