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Seasonal trends and retention of polycyclic aromatic compounds (PACs) in a remote sub-Arctic catchment☆

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ABSTRACT

Atmospheric deposition is the most dominant source of polycyclic aromatic hydrocarbons (PAHs) in remote and pristine areas. Despite low bioaccumulation potential, PAHs and their persistent transformation products (PAH-derivatives) are chemicals of concern as they can harm human and animal health through chronic low dose exposure. In this study, atmospheric deposition fluxes of polycyclic aromatic compounds (PACs) were measured on a seasonal basis (3-month periods) from 2012 to 2016 in a remote subarctic forest catchment in northern Europe. The target PACs included 19 PAHs and 15 PAH-derivatives (oxygenated, nitrogenated, and methylated PAHs). The deposition fluxes of ΣPAHs and ΣPAH-derivatives were in the same range and averaged 530 and 500 ng m^2 day^{-1}, respectively. The fluxes were found to be higher with a factor of 2.5 for ΣPAHs and a factor of 3 for ΣPAH-derivatives during cold (<0 °C) in comparison to warm (>10 °C) periods. PAHs and PAH-derivatives showed similar seasonal patterns, which suggests that these two compound classes have similar sources and deposition mechanisms, and that the source strength of the PAH-derivatives in air follows that of the PAHs. The terrestrial export of PACs via the outlet of the catchment stream was estimated to be 1.1% for ΣPAHs and 1.7% for ΣPAH-derivatives in relation to the annual amounts deposited to the catchment, which suggests that boreal forests are sinks for PACs derived from the atmosphere. Some individual PACs showed higher export than others (i.e. chrysene, cyclopenta(*c,d*)pyrene, carbazole, quinoline, and benzo(*f*)quinoline), with high export PACs mostly characterized by low molecular weight and low hydrophobicity (2–3 benzene rings; log K_{ow}<6.0).

1. Introduction

Polycyclic aromatic compounds (PACs) including polycyclic aromatic hydrocarbons (PAHs) and their derivatives, such as oxygenated PAHs (oPAHs), nitrogen heterocyclic PAHs (nPAHs), and methylated PAHs (mPAHs), is a group of persistent organic pollutants (POPs) with toxic properties. PAHs and PAH-derivatives are formed unintentionally during, for example, incomplete combustion of organic materials, such as wood, fossil fuels and domestic waste (Lundstedt et al., 2007; Srogi, 2007) and are ubiquitous in the environment. PAH-derivatives can also be formed via transformation reactions of PAHs, e.g. through atmospheric oxidation mediated by hydroxyl radicals, ozone, nitrite radicals and nitrogen dioxide (Keyte et al., 2013). Despite low bioaccumulation potential, PAHs are chemicals of concern, since they can harm human and animal health through chronic low dose exposure leading to mutagenic and carcinogenic effects (Jung et al., 2012; Rose et al., 2012). The PAH-derivatives have recently received increased attention (Andersson and Achten, 2015; Jin et al., 2023), as they are more polar (less hydrophobic) than their PAH counterparts (Chibwe et al., 2015; Lundstedt et al., 2007), hence more mobile in terrestrial and aquatic environments. Additionally, some PAH-derivatives (e.g., oPAHs and nPAHs) have been reported to be more toxic than their corresponding PAHs (Chibwe et al., 2015; Pašková et al., 2006; Wang et al., 2011; WHO, 2003). PACs, and several other classes of POPs, can be transported over long distances away from their primary sources via vapour phase and particle bound airborne transport (Breivik et al., 2004; Wania and Mackay, 1993). Atmospheric deposition is by far the most dominant source of POPs exposure in remote and pristine areas (Bergknut et al.,

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2011; Newton et al., 2013), and snowfall has been shown to efficiently scavenge POPs from the air (Franz and Eisenreich, 1998; Lei and Wania, 2004). In cold climates, POPs accumulate in the snowpack during the cold season and may become a significant source of contamination to the aquatic environment during spring snow melt (Bergknut et al., 2011; Carrera et al., 2001; Josefsson et al., 2016; Lafreneière et al., 2006; Meyer et al., 2011).

Monitoring programs for PAHs in air and atmospheric deposition have been ongoing since the 1980s in many European countries (e.g., United Kingdom, Norway, Netherlands, Ireland, Iceland, Germany, Sweden) (Shatalov et al., 2004). Also in Arctic and high altitude regions, monitoring of PAHs have been conducted for decades (AMAP, 1998, 2016; Hung et al., 2005) or in long-term campaigns (Arellano et al., 2018). For the PAH-derivatives, monitoring studies have been reported for air, soil, sediment, water and snow (Jin et al., 2023; Drotikova et al., 2020). However, little is known about the atmospheric deposition fluxes of PAH-derivatives and whether these are following the same spatio-temporal trends as the PAHs.

In this study, we investigate fluxes and seasonal changes of PACs in atmospheric deposition sampled at a boreal, subarctic field station in northern Sweden. The PACs included 19 PAHs and 15 PAH-derivatives representing oPAHs, nPAHs and mPAHs. The specific objectives were to (i) investigate seasonal PAC fluxes in atmospheric deposition during a time period of three consecutive years, (ii) characterize the seasonal trends of PAH and PAH-derivatives, and (iii) calculate the input-output budget of PACs via the headwater catchment outlet in relation to the atmospheric deposition affecting the whole catchment area on annual basis.

2. Materials and methods

2.1. Target PACs and chemicals

Target analytes included 19 PAHs and 15 PAH-derivatives. The selected PAHs represent a hydrophobicity range from log octanol/water partition coefficient (log K_{ow}) 3.3 to 6.8 and a molecular size of 2–6 rings (Table S1, Supporting Information), while corresponding data for the PAH-derivatives are log K_{ow} from 2.0 to 5.3 and ring sizes of 2–5 (Table S2, Supporting Information). The PAHs included: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, cyclopenta[*c,d*]pyrene, benz[*a*]anthracene, chrysene, 5-methylchrysene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*c,d*] pyrene, benzo[*g,h,i*]perylene, and dibenzo[*a,h*]anthracene (Table S1, Supporting Information) and the PAH-derivatives included the oPAHs 1-indanone, 9-fluorenone, 4H-cyclopenta[*d,e,f*]phenanthrenone, benzo [*a*]fluorenone, 6H-benzo[*c,d*]pyren-6-one, naphthacene-5,12-dione, benzo[*a*]anthracene-7,12-dione, 7H-benz[*d,e*]anthracen-7-one, and anthracene-9,10-dione; the nPAHs quinoline, benzo[*h*]quinoline, carbazole, acridine, benzo[*f*]quinoline; the oxygenated mPAH 2-methyl-anthracene-9,10-dione (Table S2, Supporting Information). Two internal standard (IS) mixtures were used; IS mixture #1 containing 15 deuterated PAHs: [$^2H_8$]-naphthalene, [$^2H_{10}$]-acenaphthene, [$^2H_{10}$]-fluorene, [$^2H_{10}$]-phenanthrene, [$^2H_{10}$]-anthracene, [$^2H_{10}$]-fluoranthene, [$^2H_{10}$]-pyrene, [$^2H_{12}$]-benz[*a*]anthracene, [$^2H_{12}$]-chrysene, [$^2H_{12}$]-benzo[*b*]fluoranthene, [$^2H_{12}$]-benzo[k]fluoranthene, [$^2H_{12}$]-benzo[*a*] pyrene, [$^2H_{12}$]-indeno[1,2,3-*c,d*]pyrene, [$^2H_{12}$]-benzo[*g,h,i*]perylene, [$^2H_{14}$]-dibenzo[*a,h*]anthracene; and IS mixture #2 containing the PAH-derivatives [$^2H_7$]-quinoline, [$^2H_8$]-9-fluorenone, [$^2H_8$]-carbazole, and [$^2H_8$]-anthracene-9,10-dione. Both IS mixtures had a concentration of 50 pg μL^{-1} per compound. The injection standard (InjS) was (unlabeled) PCB #97 (20 pg μL^{-1}; Cambridge Isotope Laboratory, UK). All reference and internal standards were purchased from Wellington Laboratories, Ontario, Canada, while high-purity solvent grades of dichloromethane (DCM), petroleum ether, toluene, and alumina (active neutral 90) were purchased from Merck (Darmstadt, Germany).

2.2. Sampling

2.2.1. Sampling site

Atmospheric deposition samples were collected at Svartberget field station located within the Krycklan catchment study (KCS) area (64°15′21.9″N 19°46′28.4″). The KCS is a 67 km^2 remote catchment located approximately 60 km west of the Baltic Sea in northern Sweden (Fig. 1). The average annual precipitation and runoff in the catchment was 612 mm and 312 mm, respectively, for the years 1981–2010 (Laudon et al., 2021). The average temperature during the winter season was −9.5 °C with on average 168 days of snow coverage (1981–2010). Precipitation, air temperature and stream runoff are monitored on an hourly basis, and data for our study period (2012–2016) were collected from the KCS database (Laudon et al., 2021). Detailed monthly average data for precipitation, temperature, and snow depth are given in Table S3 in the Supporting Information.

2.2.2. Atmospheric deposition sample collection

An atmospheric deposition bulk sampler was used to passively collect wet and dry deposition (rain, snow and particles) from July 2012 until October 2016. The sampler consisted of a 0.049 m^2 glass funnel with vertical sample sides (collector volume 0.020 m^3) connected to a 25 cm glass cartridge (Ø 2.5 cm, tapered in the bottom end Ø 0.8 cm) filled with 15 g of Amberlite IRA-743® (Sigma Aldrich, diameter 500–700 μm, macroporous styrene-divinylbenzene). A sketch of the sampler is given in Gocht et al. (2007a). The adsorbent (Amberlite IRA-743®) was pre-cleaned using Soxhlet extraction with toluene for 4 h and dried under vacuum for 15 h. This type of sampler has previously been validated and used for monitoring of PAHs and polybrominated diphenyl ethers (PBDEs) (Gocht et al., 2007a; Gocht et al., 2007b), and has also been used for polychlorinated dibenzo-*p*-dioxin and dibenzofurans (PCDD/Fs) and PCBs in atmospheric deposition in Sweden (Bergknut et al., 2011; Gocht et al., 2007a; Gocht et al., 2007b). The sampler has become German standard for collecting PAHs in atmospheric deposition (German Industrial Standard DIN 2 19739–2, 2003). Amberlite IRA-743® is known to efficiently adsorb organic compounds spanning over a broad hydrophobicity range (log K_{ow} of PAHs and PBDEs range from 3.3 to 10; EPI Suite ™ Version 4.11) (Gocht et al., 2007a; Gocht et al., 2007b), and the material is also know to perform well in sampling of organic pollutants in precipitation because of high wettability (i.e. high performance under water-saturated conditions) (Martin et al., 2001). A careful heating of the sampler was applied through thermostat regulated heating pads attached to the sampling device in order to keep the sampler a few degrees above 0 °C (at a minimum) for melting deposited snow, as in Bergknut et al. (2011). No ice build-up was observed during the sampling period. The cartridges were exchanged every third month. After each sampling, 100 mL of acetone was used to rinse the surface of the funnel. The acetone was collected in a pre-cleaned (acetone) glass bottle and kept in the freezer (−20 °C) together with the sampling cartridges until analysis. A few samples were not intact or broken during transport and were not used for analysis due to the risk of contamination (Table S4, Supporting Information). In total, 14 cartridges were analyzed. In parallel, a second type of bulk atmospheric deposition sampler was used consisting of a rectangular 1 m^2 stainless steel funnel with inclined sample sides (collector volume of 0.16 m^3), which was connected to the same type of glass cartridge filled with Amberlite IRA-743®. This sampler has been used for analysis of PCDD/Fs (McLachlan and Sällström, 2009) and was tested as an alternative to the German sampler, but with a higher sampling frequency (monthly exchange of the cartridge). However, the sampler was shown to underestimate fluxes of PACs (Fig. S1, Supporting Information) possibly attributed to breakthrough or other types of losses (e.g., volatilization, degradation, difficulties in washing off the PACs from the sampler surface). Hence, only data from the German sampler were used in calculations and evaluation of data in this study.

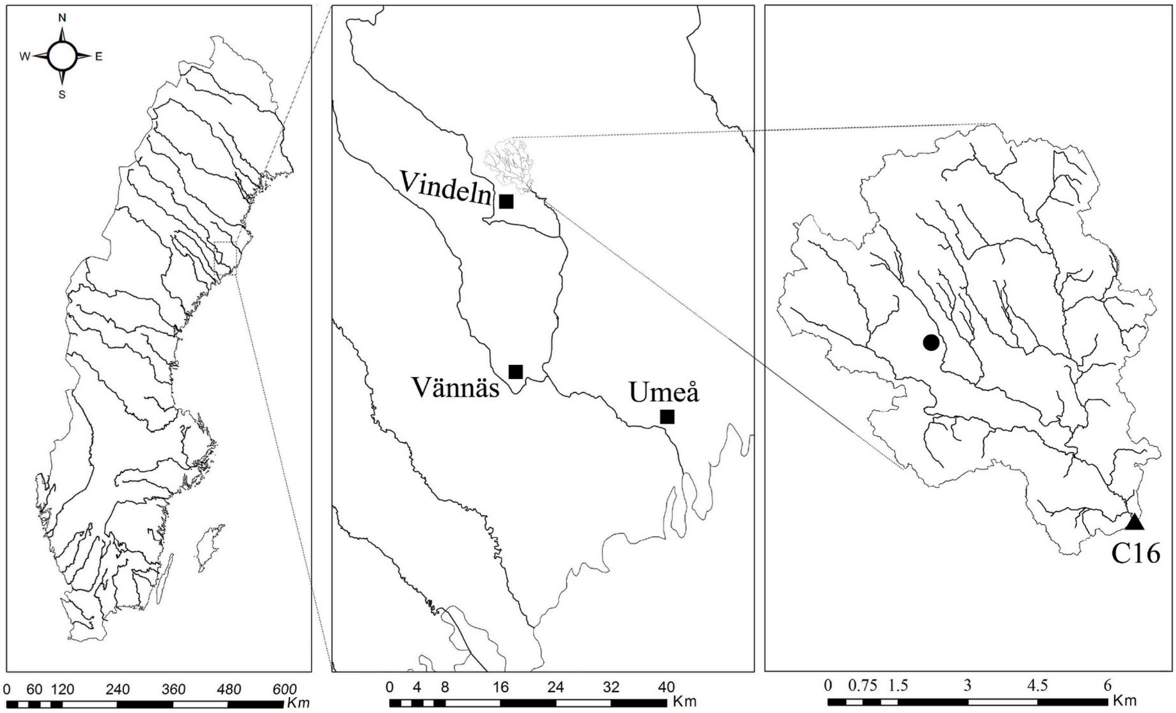

Fig. 1. Map of Sweden and enlargements to show the location of the sampling sites (black dots ● for atmospheric deposition sampling and black triangle ▲ for water sampling) and nearby cities (black squares ■).

2.3. Sample preparation and instrumental analysis

Prior to extraction, the IRA adsorbent was transferred from the glass cartridge to a cellulose thimble placed inside a Soxhlet extraction apparatus and spiked with 50 μL of the IS mixtures (Tables S1 and S2 in the Supporting Information). Soxhlet Dean-Stark extraction was carried out using 400 mL toluene for ~15 h. The acetone used for rinsing the surface of the sampler was filtered through a glass fiber filter (Whatman GF/C, 0.7 μm pore size, diameter 24 mm; pre-heated at 400 °C overnight) and then combined with the Soxhlet extract (toluene). To remove any remaining water, the extract was passed through a Horizon Dry-Disk® (Salem, NH, USA) followed by solvent reduction to 0.5 mL (Biotage TurboVap II system, Uppsala, Sweden). Extracts were cleaned up by using a 1 g alumina column (pre-conditioned with 20 mL 95/5 (v/v) petroleum ether/DCM) which was eluted with 20 mL 95/5 (v/v) petroleum ether/DCM. Subsequently, the extracts were concentrated to 0.5 mL (Biotage TurboVap II) and then further concentrated to 0.2 mL using a gentle nitrogen stream (Organomation N-EVAP Nitrogen Evaporator, Berlin, MA, USA) in 1.5 mL brown glass vials. Finally, the extracts were transferred and evaporated to 150 μL in 300 μL insert brown glass vials using a gentle nitrogen stream (Organomation N-EVAP Nitrogen Evaporator).

Before instrumental analysis, all extracts were spiked with 50 μL of the InjS and then analyzed using gas chromatography coupled to tandem mass spectrometry (GC-MS/MS; Agilent Technologies GC 7890B; 7010 triple quadrupole MS, Palo Alto, CA, USA) equipped with a DB-5 column (60 m, 250 μm i. d., film thickness 0.25 μm; J&W Scientific, Agilent Technologies). Extract aliquots of 2 μL were injected in splitless mode at an injector temperature of 250 °C. PAHs and PAH-derivatives were analyzed in separate runs, but the same GC oven temperature program was used. Briefly, the program started at 70 °C, hold for 2 min, increased by 30 °C min^{-1} to 125 °C followed by increased by 5 °C min^{-1} to 310 °C, and hold for 20 min. More information about quantifier and qualifier for individual PACs is given in Tables S5 and S6 in the Supporting Information. The isotope dilution method was applied for quantification of the target compounds using a 13 points calibration curve ranging from 0.1 ng mL^{-1} to 1000 ng mL^{-1}.

2.4. Quality assurance and quality control

A signal to noise ratio of >3 was required for a positive detection. The method detection limits (MDLs) were calculated (average of blanks plus 3 times standard deviation) from the field blanks ($n = 6$). If no peak was detected in the blank, the lowest level in the calibration curve was used as MDL (Tables S7 and S8, Supporting Information). The MDLs ranged from 3.4 to 3400 ng absolute for PAHs and from 0.5 to 950 ng absolute for PAH-derivatives (Tables S7 and S8, Supporting Information). The overall average recoveries of the ISs for PACs were 72 ± 36% (Tables S9 and S10, Supporting Information).

3. Results and discussion

3.1. Atmospheric deposition fluxes of PACs

Out of the 19 analyzed PAHs and 15 target PAH-derivatives, 14 PAHs and 12 PAH-derivatives were detected in the atmospheric deposition samples. The Σ_{14}PAH fluxes ranged from 86 to 1700 ng m^2 day^{-1} (average 530 ± 490 ng m^2 day^{-1}, median 390 ng m^2 day^{-1}), with fluoranthene (20% of Σ_{14}PAHs), chrysene (19%), and pyrene (15%) as the dominant compounds. The fluxes of the Σ_{12}PAH-derivatives fluxes were in the same range, with values ranging from 91 to 1100 ng m^{-2} day^{-1} (average 500 ± 310 ng m^{-2} day^{-1}, median 370 ng m^{-2} day^{-1}) with 9-fluorenone (51% of Σ_{12}PAH-derivative) and quinoline (17%) as the dominant compounds (Tables S11–S12, Supporting Information).

The average annual Σ_{14}PAHs flux was calculated to 190 ± 180 μg m^{-2} yr^{-1}. This is in good agreement with other long-term studies (at least 1 year) from remote areas in Europe. For example, three different forested landscapes in southern Germany, showed average Σ_{17}PAHs deposition fluxes between 150 and 220 μg m^{-2} yr^{-1} using the same kind of sampler as us (Gocht et al., 2007a), and in four European mountainous sites, Σ_{15}PAHs deposition fluxes ranged from 8.4 to 110 μg m^{-2} yr^{-1} (Arellano et al., 2018; calculated from average monthly values),

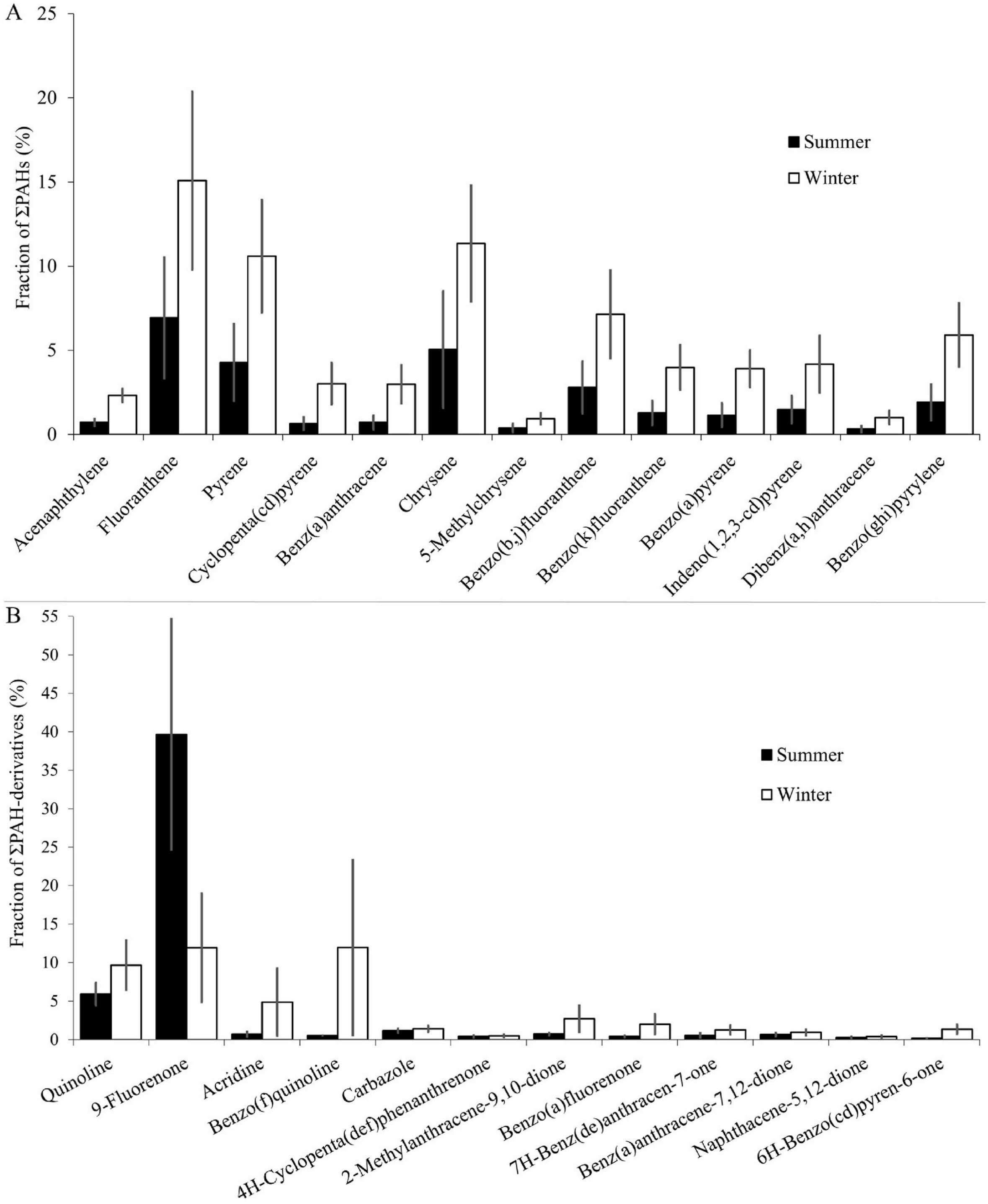

Fig. 2. Fractions of individual PACs in atmospheric deposition over the complete sampling period (2012–2016) separated into cold (<0 °C; $n = 4$) and warm (>10 °C; $n = 4$) periods and plotted as fractions in relation to A) ΣPAHs and B) ΣPAH-derivatives.

while a study from Czech Republic/Austria reported values from 8.3 up to 240 μg m^{-2} yr^{-1} (Nežiková et al., 2019; calculated from daily fluxes) for remote sites. A global EMEP multi-media modelling system (GLEMOS) was used for modelling of atmospheric deposition fluxes of four selected PAHs in air (i.e. benzo(*a*)pyrene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene and indeno(1,2,3-*c,d*)pyrene) (EMEP, 2017). This model prediction estimated lower fluxes in Sweden (<50 μg m^{-2} yr^{-1}) compared to other countries (>100 μg m^{-2} yr^{-1}) including Portugal, Montenegro, Spain, Slovakia, Germany, Poland, Hungary, Czech Republic, and Romania. The average flux of the four selected PAHs (Σ_4PAHs) found in this study during the last measured year (Nov 2015–Oct 2016) was 43 μg m^{-2} yr^{-1} (sum of B[b,j]FA, B[k]FA, B[a]P, and I[1,2,3-cd]P in Table S11in the Supporting Information), while in another study (Hansson et al., 2006), deposition fluxes of the selected Σ_4PAHs were found to be < 10 μg m^{-2} yr^{-1} at two Nordic field stations (Råö located at the Swedish west coast and Pallas located in northern Finland). The modelled and measured deposition fluxes for Sweden and Finland (current study and Hansson et al., 2006) were thus in agreement with the modelled EMEP values (EMEP, 2017).

3.2. Seasonal patterns of PAC fluxes in atmospheric deposition

Average fluxes of ΣPACs were generally lower in summer (average temperature above 10 °C; $n = 4$; Tables S11–12, Supporting Information) than in winter (average air temperature lower than 0 °C; $n = 4$; Tables S11–12, Supporting Information), with only one exception (9-fluorenone) (Fig. 2A–B). The average difference in flux was a factor of 2.5 and 3 higher for ∑PAHs and ∑PAH-derivatives, respectively, and a factor of 3 and 5 higher if the average was calculated on individual PACs. The deviating pattern for 9-fluorenone could potentially be due to formation during atmospheric photodegradation in the summer (Ding et al., 2019). Other studies have likewise found seasonal variations of PAHs in atmospheric deposition at rural and remote sites, with elevated PAH deposition fluxes during cold seasons (Xing et al., 2016; Schifman and Boving, 2015; Nežiková et al., 2019). This has mainly been attributed to transport of air masses impacted by local sources (e.g. residential burning for heating), transport emissions and lower degradation rates due to shorter daylight hours (Keyte et al., 2013). For instance, a long term monitoring study of PAHs in wet deposition (i.e. rain and snow) in Atlantic Canada from 1980 to 2001 showed a correlation between fluxes of 14 PAHs and energy consumption for heating and transport during colder months of the year (December to March) (Brun et al., 1991; Brun et al., 2004). Other potential explanations for higher levels of PAHs in atmospheric deposition during the cold season is the wash-out effect by snowfall, which efficiently scavenges aerosols and POPs bound to these from the atmosphere (Franz and Eisenreich, 1998, Wania et al., 1998; Carrera et al., 2001 ; Arellano et al., 2018) and seasonal differences between long-range air transport patterns to the Arctic (Willis et al., 2018). To the best of our knowledge, no previous seasonal studies of PAH-derivatives in atmospheric deposition have been reported. In the current study, most of the monitored PAH-derivatives showed a similar seasonal trend as the PAHs (Fig. 2A–B), suggesting that PAH-derivatives have similar sources and deposition mechanisms as the PAHs, and that the source strength of the PAH-derivatives in air follows that of the PAHs.

3.3. Terrestrial retention and stream export of PACs

The potential of the terrestrial environment to retain deposited PAHs and PAH-derivatives was estimated on a catchment scale by comparing the total amount of PACs deposited in the catchment with the total amounts of the PACs passing the river outlet (site C16, Fig. 1) on an annual basis. It could be argued that it is not solely the terrestrial retention that is estimated, as losses of deposited atmospheric deposition loads could also be due to revolatilization and environmental transformation reactions. However, revolatilization and soil degradation of PAHs were found to be limited in a full mass balance calculation of PAHs in two rural catchments in Germany (Gocht et al., 2007c), and it was concluded that >90% of the PAHs was retained in the soils. In our case, the study site is located further north with a colder climate and thus assumingly even lower revolatilization and degradation rates. Consequently, although it should be recognized that a smaller fraction can be revolatilized or degraded, claiming soil retention as the dominant loss mechanism in the studied catchment is adequate. The low stream export mainly reflects an efficient terrestrial retention.

For the calculations, we used the same mass balance approach as Bergknut et al. (2011). Similar approaches for PACs in the environment were also used by Schwarz et al. (2011), Motelay-Massei et al. (2007) and Gocht et al. (2007c). In short, the terrestrial retention (R, expressed in %) was defined as the amount of PACs deposited to the catchment area (F_{input}) over a certain time period subtracted by the amounts exported by stream water (F_{output}) during the same time period. Then, this residual was divided with F_{input} and multiplied with 100 to express the fraction in percentage. The F_{output} was calculated by the equation $F_{output} = C_wQ/A$, where C_w denotes the concentration of PACs in the water samples (pg m^{-3}), Q the water discharge (m^3 s^{-1}), and A, the catchment area (m^2). We used the deposition fluxes for the years 2012–2016, and water concentrations and water flow data values from 2015 to 2016. All data used for the calculations of the export of PACs to streams are given in Table S15 in the Supporting Information.

The water PAC concentrations for the calculation of F_{outlet} were taken from sampling site C16 in a previous study (Nguyen et al., 2018) in analogy with Bergknut et al. (2011). They represent bulk levels, thus both the colloids (particle size <0.7 μm) and the dissolved phases. Only compounds detected in both atmospheric deposition and stream water and with a detection frequency >50% were included in the calculations (i.e. 13 PAHs and 12 PAH-derivatives; Tables S13–14, Supporting Information). The amounts of the PACs exported from the catchment were estimated by multiplying the average flux of the PACs during each hydrological season (i.e., snow-free, snow-covered, and spring flood) with the corresponding average water flow during that season (measurements for the years 2015–2016). The amounts of PACs deposited directly onto water surface were considered negligible due to the low percentage of open water in the catchment (~1% of the area).

The estimated average deposition of Σ_{13}PAHs over one year was ~0.19 mg m^{-2} yr^{-1}, which equals an amount of ~13 kg of Σ_{13}PAHs deposited to the whole catchment (67 km^2) over a year, while the estimated average deposition of Σ_{12}PAH-derivatives was ~0.18 mg m^{-2} yr^{-1}, which is equivalent to ~12 kg of Σ_{12}PAH-derivatives deposited over a year. The corresponding Σ_{13}PAHs in stream water exported from the study catchment was ~0.10 kg yr^{-1}, while the annual export of corresponded Σ_{12}PAH-derivatives was estimated to ~0.20 kg yr^{-1} (based on Nguyen et al. (2018)). These amounts correspond to a soil retention of 99% for Σ_{13}PAHs and 98% for Σ_{12}PAH-derivatives, corresponding to 1.1% and 1.7% stream export for Σ_{13}PAHs and Σ_{12}PAH--derivatives, respectively (Table S15, Supporting Information).

The high retention of PACs by the terrestrial environment, efficiently preventing export to stream water, supports the findings of Gocht et al. (2007c), who suggested that remote terrestrial environments are sinks of atmospheric deposited PACs. The efficient retention of ∑PAHs in a rural catchment has also been demonstrated by Schwarz et al. (2011), who found the input to output ratio (the terrestrial retention) to be 93% and 82%, respectively, in two consecutive years for a karst system in Germany. In areas with more anthropogenic activities, not only atmospheric deposition is an important source but also the formation of PACs from local sources. Motelay-Massei et al. (2007) investigated a rural area in France and found the terrestrial export to be 33%. Among the four studies (Sweden (this study), Germany x 2 (Schwarz et al., 2011), and France (Motelay-Massei et al., 2007)), our study site is the coldest, most remote, least populated with hardly no input from local sources and no paved surfaces. It is therefore plausible that our study site has the highest terrestrial retention (and lowest export to stream water).

The terrestrial export was previously investigated for other POPs in the same catchment (Bergknut et al., 2011). The fractions exported of Σ_7PCBs and Σ_{17}PCDD/Fs were in the same magnitude (0.2% and 0.5%, respectively) as those of the PACs found in this study; thus, our results suggest that PAHs and PAH-derivatives are retained in terrestrial environments approximately to the same extent and by similar mechanisms as PCDD/Fs and PCBs. PAHs and PAH-derivatives share the characteristics of having planar chemical structures with the PCDD/Fs and the non-*ortho* and mono-*ortho* PCBs, which have or can assume a planar configuration.

When considering the input-output budget of individual PAHs and PAH-derivatives, a few of the PAHs (2 out of 13) and some of the PAH-derivatives (3 out of 12) showed relatively high export potential compared to other PACs (Fig. 3A–B). For the PAHs chrysene and cyclopenta(*c,d*)pyrene, 2.4% and 1.6% of the deposited amounts were exported, respectively, which is higher than the average of the remaining 11 PAHs (average 0.25%). The PAH-derivatives carbazole, quinoline, and benzo(*f*)quinoline showed even higher values (10%, 3.6%, and 2.0%, respectively). Differences among the individual PACs were also seen when comparing compositional profiles, calculated as the

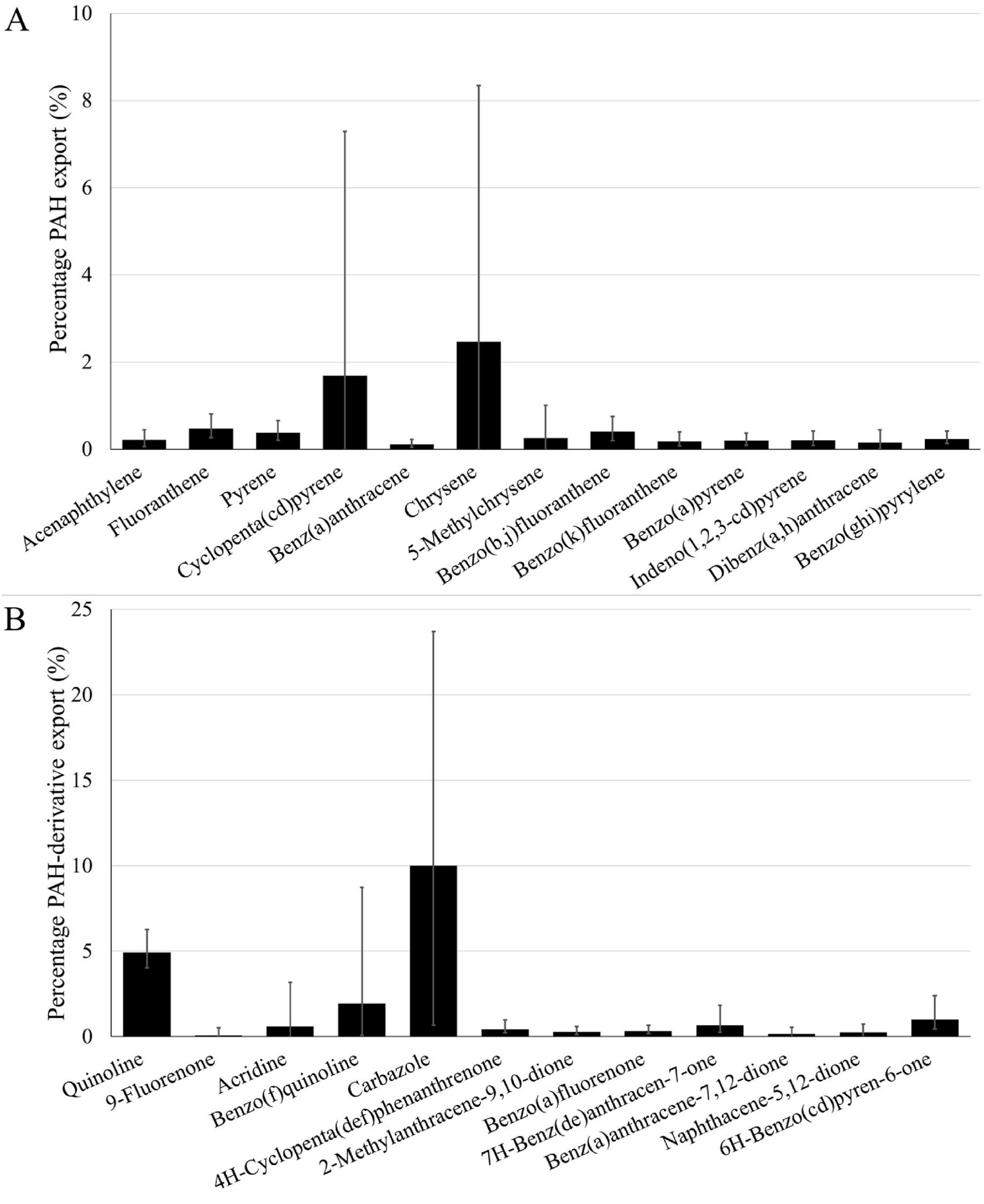

Fig. 3. Percentage (%) export of A) individual PAHs and B) individual PAH-derivatives in comparison to the amount of corresponding PAC deposited to the catchment.

individual PAC in relation to the ΣPAHs and ΣPAH-derivatives in water and atmospheric deposition, respectively (Figs. S2A–B, Supporting Information), with distinctly higher fraction in stream water than in atmospheric deposition for three of the PAHs (chrysene and cyclopenta(*c, d*)pyrene, and acenaphthene) and three of the PAH-derivatives (same as above, i.e. carbazole, quinoline, and benzo(*f*)quinoline).

A potential explanation to the observed higher potential export of some PACs might be higher preferential partitioning to water due to lower hydrophobicity. The composition of PACs in the atmospheric deposition is largely determined by atmospheric conditions (McLachlan and Sellström, 2009) and a change of the substance pattern in the terrestrial environment is expected. For instance, PACs bound to particles in the atmosphere and washed out by rain and snow might redistribute their partitioning towards the water phase in the terrestrial environment. The more highly exported PAHs mostly represent lower molecular mass compounds (2–3 benzene rings; log $K_{ow} < 6.0$), while none of the higher molecular mass compounds (>3 benzene rings; log $K_{ow} > 6.0$) were exported to any higher extent. For PAH-derivatives, higher export potential (>2%) was observed for lower molecular mass compounds with 2–3 benzene rings and log K_{ow} of 2.0–3.4 (i.e. quinoline, benzo(*f*)quinoline, carbazole), while none of the higher molecular mass compounds (>3 benzene rings, log K_{ow} of 3.9–5.3) showed equal or higher export potential.

The differences in compositional profiles between input (deposition) and output (water) samples could also be due to post-depositional formation through transformation reactions. PAH-derivatives are formed via a number of reaction pathways in the environment (Keyte et al., 2013; Manzetti, 2013). Moreover, the primary source of water at the outlet stream is via deeper groundwater with long, decadal time spans, especially during winter (Jutebring Sterte et al., 2021). Thus, post-depositional formation is likely, particularly for the PAH-derivatives.

4. Conclusions

Seasonal changes of the atmospheric deposition of PACs were observed in the studied boreal forest catchment in northern Sweden, with higher fluxes of PACs during cold periods and lower fluxes during warm periods. The PAHs and PAH-derivatives showed similar seasonal trends, which suggests that air source strengths follow each other with higher levels during winter, and that PACs are washed out from the atmosphere by similar deposition mechanisms (e.g., binding to particles in atmosphere, scavenging by snowfall). The fractions of exported PAHs and PAH-derivatives through the headwater outlet were estimated to be $<2\%$ of the total amounts deposited in the catchment for both compound groups, indicating that boreal forest catchments are sinks of deposited PACs from the atmosphere. However, some individual PAHs and PAH-derivatives showed slightly higher fractions of ΣPAHs and ΣPAH-derivatives in the exported water than in atmospheric deposition, suggesting compound specific partitioning of PACs after deposition in the terrestrial environment and a higher export of low-molecular, less hydrophobic PACs.

Credit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2023.121992.

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