Ecological Indicators 145 (2022) 109681

Contents lists available at ScienceDirect

Ecological Indicators

journal homepage: www.elsevier.com/locate/ecolind

Original Articles

Differences in accumulation of polycyclic aromatic compounds (PACs) among eleven broadleaved and conifer tree species

H. Pleijel [a,*], J. Klingberg [b,c], B. Strandberg [d,e], H. Sjöman [b,c,f], L. Tarvainen [a], G. Wallin [a,g]

[a] University of Gothenburg, Biological and Environmental Sciences, P.O. Box 461, SE-40530 Gothenburg, Sweden
[b] Gothenburg Botanical Garden, Carl Skottsbergs gata 22A, SE-41319 Gothenburg, Sweden
[c] Gothenburg Global Biodiversity Centre, Carl Skottsbergs gata 22B, 41319 Gothenburg, Sweden
[d] Division of Occupational and Environmental Medicine, Lund University, Lund SE-22100, Sweden
[e] Department of Occupational and Environmental Medicine, Region Skåne, Lund SE-22381, Sweden
[f] Swedish University of Agricultural Science, Department of Landscape Architecture, Planning and Management, SE-23053 Alnarp, Sweden
[g] Environmental Change Institute, School of Geography and the Environment, University of Oxford, Oxford, England

ARTICLE INFO

Keywords:
DBTs
Deciduous tree
Dibenzothiophenes
Evergreen tree
Gaseous
PAHs
Particle bound
Polycyclic aromatic hydrocarbons
SLA
Specific leaf area

ABSTRACT

PACs (polycylic aromatic compounds) are air pollutants formed in incomplete combustion, e.g., in vehicle engines. Vegetation can potentially remove substantial amounts and act as bioindicators of these pollutants. Increased knowledge of the pollutant removal efficiencies of different tree species is essential for understanding the potential benefits trees can provide urban residents. We investigated the leaf/needle content of the two PAC groups, polycyclic aromatic hydrocarbons (PAHs, 32 compounds) and dibenzothiophenes (DBTs, 6 compounds) in seven broadleaved and four conifer tree species in an arboretum of South-West Sweden. PAHs were grouped into low-molecular (L-PAHs, largely gaseous), medium-molecular (M-PAHs, both gaseous and particle-bound) and high-molecular mass (H-PAHs, largely particle-bound) PAHs. DBTs are organosulphur compounds with two benzene rings. In general, conifer needles were stronger accumulators of PACs than leaves of broadleaved trees. Comparing three-year-old and one-year-old needles showed that evergreen conifers accumulated L-PAHs, M-PAHs, H-PAHs and DBTs over several years. In deciduous trees, L-PAHs and DBTs declined from June to September, M-PAHs had no significant net change, but for H-PAHs, there was a significant net accumulation. Conifers had a similar or lower net average annual accumulation of H-PAHs than broadleaved trees, except the deciduous conifer *Larix*, which had the highest uptake rate of this toxicologically important PAH category. Our results suggest that L-PAH accumulation depends on leaf/needle mass or volume, while for H-PAHs leaf/needle area is more important. This explains why conifers represented a stronger sink for L-PAHs and M-PAHs. DBT accumulation in leaves/needles was similar to that of L-PAHs. An important conclusion is that tree leaves/needles accumulate substantial amounts of PAC with strong and complex contrasts between tree species and PAC groups. Another implication of our data is that conifer needles are useful as bioindicators for PAC pollution since they accumulate all PAC categories over several years.

1. Introduction

Due to ongoing urbanization and associated call for densification of cities there has been an intensifying discussion of the role of urban trees and the ecosystem services that they contribute, including air pollution removal (Grote et al., 2016; Barwise and Kumar, 2020). Both modelling studies (Nowak et al., 2006; Dadvand et al., 2015) and empirical observations (Al-Dabbous and Kumar, 2014; Grundström and Pleijel, 2014; Klingberg et al., 2017) show that urban vegetation has the potential for mitigation of air quality, although contrasting statements have been made about the quantitative significance of this process. While Nowak et al. (2006) emphasized the significance of air pollution removal by urban trees, Pataki et al. (2011) argued that the effect of urban vegetation on air pollution has not been well quantified and questioned the significance of such an effect. Yli-Pelkonen et al. (2017), studying air pollutant concentration of urban areas in Finland, concluded that the effect of urban forests on air quality is likely to be small, possibly with the exception of particulate matter. Yin et al. (2011), on the other hand,

* Corresponding author.
E-mail address: hakan.pleijel@bioenv.gu.se (H. Pleijel).

https://doi.org/10.1016/j.ecolind.2022.109681
Received 23 May 2022; Received in revised form 21 October 2022; Accepted 11 November 2022
Available online 15 November 2022

showed the existence of a significant park effect on air pollution levels, which differed between pollutant types, by comparing vegetated and non-vegetated areas in Shanghai, China. City size and topography, tree species, level of air pollution and climate may influence the significance of city trees in air quality improvement.

Polycyclic aromatic hydrocarbons (PAHs) are air pollutants formed under incomplete combustion of organic compounds, such as oil production, combustion of fossil fuels and biomass burning (Gong et al., 2018) as well as wildfires (Wentworth et al., 2018). In urban areas, traffic is typically the dominating source (Wingfors et al., 2001; Harrison et al., 2003; Gong et al., 2018). PAHs belong to the wider group of polycyclic aromatic compounds (PAC). Some of the PAHs, including benzo(a)pyrene, are known to be highly toxic and have adverse effects on human health and ecosystems (Boström et al., 2002; Famiyeh et al., 2021). 16 PAHs, including benzo(a)pyrene and phenanthrene, have been pointed out to be priority pollutants of particular toxicological concern (EPA, 2008). Atmospheric concentrations of PAHs are often strongly elevated in urban environments (Wagrowski and Hites, 1997), contrasts between areas with heavy traffic pollution and *peri*-urban environments being stronger than for other important urban air pollutants such as nitrogen dioxide NO_2 (Klingberg et al., 2017, Klingberg et al., 2022).

PAHs include a range of compounds, which have different molecular mass and chemical-physical properties. Some are comparatively low molecular mass, (L-PAHs, 2–3 benzene rings), and mostly occur in the gaseous phase at temperatures typical of the lower atmosphere, while others, high molecular-mass or H-PAHs (4–6 benzene rings), are to a large extent bound to particles (Yang et al., 2007). It is customary to define an intermediate category of M-PAHs (3–4 benzene rings), which are partly gaseous and partly particle-bound. It can be expected that the interaction with and absorption by leaves differ between these three PAH categories. For example, De Nicola et al. (2017) compared PAH accumulation in the leaves of a deciduous oak species *Quercus robur* with that of needles of the evergreen conifer *Pinus pinaster*. They found that leaves and needles contained comparable levels of total PAHs, but particle-bound PAHs were higher in the oak (attributed by the authors to higher specific leaf area, SLA), while the pine tree (which had higher stomatal conductance than oak in that investigation), contained higher levels of L-PAHs. Wang et al. (2008) investigated six tree species and found, using sequential extraction, that gaseous and particle bound PAHs were primarily present in the inner leaf tissues and in the cuticle, respectively. The relationship between PAH accumulation and SLA has also been investigated by Howsam et al. (2001), Domingos et al. (2015) and Wang et al. (2020). Wang et al. (2020) found the accumulation of five PAHs in wheat leaves to be associated with the wax content, which was in turn significantly correlated with SLA.

L-PAHs in particular, and to a certain extent also M-PAHs, may undergo re-volatilization after they have been deposited to leaves (Wang et al., 2005; St-Amand et al., 2009). Gaseous deposition can reach an equilibrium where reemission and uptake are of the same magnitude (McLachlan, 1999). To reach the equilibrium will take longer time in environments with low atmospheric concentrations of PAHs and for plant tissues with a large potential sink, i.e., capacity to hold PAHs. Different PAHs will also differ in their volatility. Since volatility is temperature-dependent, it may occur that a leaf/needle that reached equilibrium at a lower temperature will become a net emitter if the temperature rises. This can explain why some studies showed uptake of PAHs by leaves was larger in winter than in summer (Huang et al., 2018) as well as the inverse relationship between leaf PAH concentration and air temperature observed for *Ginkgo biloba* by Murakami et al. (2012). A similar pattern of temperature dependence of PAH concentrations was found for *Salix matsudana* by Zhao et al. (2018) and for kale (*Brassica oleracea*) by Franzaring (1997).

Another group of PACs, having chemical properties similar to those of PAHs, are the dibenzothiophenes, DBTs (Cheng et al., 2018). DBTs are organosulphur compounds containing two benzene rings fused to a central thiophene ring. Chemically and physically, when it comes to volatility and hydrophobicity, they are related to the L-PAH anthracene and have been shown to correlate with PAHs in the atmosphere (Jariyasopit et al., 2019). They have not been monitored to the same extent as PAHs. Information about their accumulation in leaves/needles is to the best of our knowledge lacking.

Accumulation of PACs in or on leaves and needles of trees offers an opportunity to obtain an ecosystem service from urban vegetation in terms of removal of air pollutants (Simonich and Hites, 1994; Terzaghi et al., 2013). Testing the pollutant removal efficiencies of a range of tree species, covering different functional types and leaf traits, which are of potential interest as city trees, is essential for improving the understanding of this ecosystem service and the potential benefits it can provide (Corada et al., 2021). Earlier studies have observed considerable differences between species (e.g., Howsam et al., 2000; Wang et al., 2008; Murakami et al., 2012), although most of them covered only a small number of species. Previous studies have suggested that properties like SLA, leaf surface roughness and hairiness, stomatal conductance/ density and leaf wax content are of importance for PAH and particle uptake by leaves (Sæbø et al., 2012; De Nicola et al., 2017). Which leaf characteristics are of largest importance may depend on pollutant type (Grote et al., 2016), where hairiness and ridges on leaves may be more important for super-micrometre particles and stomatal characteristics are of larger significance for sub-micrometre particles and gases (Barwise & Kumar, 2020). In their extensive review, Barwise and Kumar (2020) also highlighted that macromorphological traits promoting pollutant removal include small leaf size. However, there are examples where tree species with similar leaf characteristics in terms of leaf size and hairiness show substantial differences in accumulation of PAHs, as exemplified by the comparison of *Tilia* × *euchlora* and *Pyrus calleryana* by Jouraeva et al. (2002).

Evergreen species, such as most conifers, may in principle continue to accumulate semivolatile organic compounds over several years as shown for DDT and hexachlorocyclohexanes in Scots pine (*Pinus sylvestris*) needles (Kylin and Sjödin, 2003). The fact that conifer needle age may be up to ten years, and PAC accumulation thus may go on for several years, has not always been considered, but for example Lehndorff and Schwank (2004), Piccardo et al. (2005) and Terzaghi et al. (2013) found a continued accumulation of PAHs over several needle age classes in different *Pinus* species.

The content of compounds and elements in leaves/needles can be expressed in different ways. Most common is to use a dry leaf mass basis. However, from a physiological or ecosystem perspective, it can be more relevant to express the concentrations on a leaf area basis, since leaf area index (LAI), the amount of leaf area per unit ground area, is a key property on the ecosystem level. Leaf area is the basis for canopy light interception and thus for its photosynthesis and was promoted as a basis for expression of PAH leaf content by Simonich & Hites (1995).

The accumulation of PAHs, DBTs and other potentially toxic compounds in leaves and needles also represents an opportunity for biomonitoring (Eriksson et al., 1989; Murakami et al., 2012; Odabasi et al., 2015; Zhao et al., 2018; Yang et al., 2019). Species with a higher rate of accumulation of these compounds are preferable for this purpose and it is thus important to compare a range of species with respect to this property. Murakami et al. (2012) pointed out the conifer *Ginkgo biloba* as a suitable biomonitoring plant for PAH because of its high accumulation of PAHs compared to other species. However, a single species is not suitable in all climatic conditions, and it is consequently of value to have information about the PAH and DBT accumulation for a range of species for potential use as PAC biomonitors or to improve local air quality.

We investigated the leaf PAH (32 compounds) and DBT (6 compounds) contents of seven broadleaved and four conifer tree species in the Arboretum of the Gothenburg Botanical Garden to study the changes in the leaf contents over time and their variation among species. Our research questions were:

- Do evergreen conifers differ from deciduous trees with respect to accumulation of L-PAHs, M-PAHs, H-PAHs and DBTs?
- How large is the variation in accumulation of these compounds within and between the groups of evergreen conifers and deciduous trees?
- How strong is the relationship of leaf/needle accumulation of L-PAHs, M-PAHs, H-PAHs and DBTs with SLA?

2. Materials and methods

2.1. Study area

The City of Gothenburg (57°42′N, 11°58′E) is located on the west coast of Sweden. It has a maritime temperate climate with, for the latitude, moderately cool summers, and mild winters. Gothenburg is situated in the nemoral vegetation zone, characterised by temperate deciduous forests (Gundersen et al., 2005). Deciduous trees normally become foliated in late April or early May and defoliate in October.

The Arboretum (collection of living trees from Europe, Asia, North America, and North Africa) of the Gothenburg Botanical Garden enabled comparison of a range of tree species with similar growth conditions in a limited area. The distance to the closest main traffic route was approximately 800 m. Within this distance there are no other important air pollution sources. Eleven tree species representing contrasting leaf/needle characteristics were selected for comparison: seven deciduous broadleaved species (*Betula pendula, Quercus robur, Populus tremula, Sorbus commixta, Prunus sargentii, Fagus orientalis* and *Juglans ailanthifolia*), three evergreen conifers (*Abies sachalinensis, Picea jezoensis* and *Pinus nigra*) and one deciduous conifer (*Larix decidua*). Leaf characteristics of these species are presented in Table S1 of the supplementary information (SI).

2.2. Collection of leaf and needle samples and determination of SLA

Three trees of each species were sampled. A pruning pole was used to cut branches from the upper part of the crown (10–16 m). Branches with leaves/needles in the outer, exposed part of the crown were selected. At least three branches from each tree were sampled. The sampling was designed to study the net accumulation over the leaf/needle life span by comparing the concentrations on two occasions during the leaf/needle life span. The life span is different for deciduous and evergreen species. Leaves from the deciduous trees (broadleaved and *Larix*) were collected 25–26 June and 17–18 September 2018. The September sampling of deciduous trees took place short before then onset of autumn senescence. Shoots from conifers of the age classes current year + 1 (C + 1, one year-old) and current year + 3 (C + 3, three years-old) were collected on 25–26 June in the same year. Like in many evergreen species (e.g., olive trees, Sari et al., 2021) it is straightforward to distinguish different shoot ages in the conifers included in the study; how this is made is illustrated in Figure S1 of the SI. C + 1 and C + 3 needles were sampled to allow investigation of the extent to which a net accumulation of PACs took place as the needle age increased by 24 months. C + 3 was selected since it was the oldest needle age class that was complete in all three investigated evergreen conifer species.

Samples were packed in polyethylene plastic bags and transported to the nearby laboratory in a cool bag. The samples to be analysed for PACs were immediately wrapped in aluminum foil and stored in <−18 °C until analysis. Six leaves from each sampled broadleaved tree and three shoots of each age class and conifer tree species from harvested branches were used for determination of specific leaf area (SLA, i.e., projected leaf area per unit dry mass). Twelve or more leaf discs of a known area (13 or 8 mm in diameter, depending on leaf size) were collected per SLA leaf sample using a puncher. The discs were oven-dried in 70 °C for at least 48 h and then weighed (laboratory balance with 0.1 mg resolution) for SLA determination. For conifers, 20 needles (40 from *Larix* due to small needle mass) from at least three different shoots per tree were removed using tweezers and scanned to determine total projected area using WinSEEDLE (plant image analysis scanner and software from Regent Instruments Inc, Canada; version Pro 5.1a). Needles were dried and weighed using the same procedure as for broadleaved species. Leaf area-based concentrations of PACs were calculated by dividing the dry mass-based concentrations from the chemical analysis by SLA.

2.3. NO_2 and PAC air concentration measurements and PAC air and plant tissues analysis

To characterise the air pollution level, atmospheric concentrations of NO_2 (considered to be a priority air pollutant, along with particles, in relation to existing air quality standards in the City of Gothenburg) and PACs were measured at 2.5 m above ground using passive sampling techniques. The samplers were placed in the Arboretum during four approximately-one-month long measurement periods (Table 1).

NO_2 was measured using passive diffusion samplers of the IVL type (Ferm, 2001; Sjöberg et al., 2001). The samplers have been used in past measurement campaigns in Gothenburg and shown reliable results (Klingberg et al., 2017). Sample analysis was made by the IVL accredited laboratory (https://www.ivl.se).

The PUF (polyurethane foam) disk samplers (14 cm diameter, 1.2 cm thickness, surface area 360 cm^2, density 0.035 g cm^{-3}, Klaus Ziemer GmbH, Germany), used for air PAC sampling, were housed in two stainless steel domes (Tisch Environmental, Inc., OH, USA). This sampler design has been calibrated for a number of PACs, both gaseous and particulate-associated compounds (Harner et al., 2013; Bohlin et al., 2014). The handling of the PUF sampler before and after sampling as well as the PAC analytical procedure and quality assurance results for the PAC analysis are described in detail in the SI text file. 38 PAC compounds were included in the study, 17 parent PAHs and among them 15 US EPA priority PAHs and 15 alkylated species, and 6 dibenzothiophenes (DBTs). In brief, before extraction the PUF and leave/needle samples, an internal standard mixture containing the 16 US EPA priority PAHs were added to the samples. The samples were extracted using a Dionex ASE 350 Accelerated Solvent Extractor (Thermo Fisher Scientific, Inc. MA, USA) equipment using dichloromethane as solvent. The samples were purified and finally the PACs were separated and detected by high-resolution gas chromatography/low-resolution mass spectrometry (HRGC/LRMS). The MS instrument was an Agilent 5975C connected to a 7890A GC (Agilent Technologies, Inc., Santa Clara, CA, USA). Two-ring PAHs, such as naphthalene, may after a 28-day sampling period be in the curvilinear phase of uptake or have reached saturation in the sampling material (Bohlin et al., 2014). Thus, accurate quantification of this compound could not be made, which is therefore excluded from further discussions.

The different PAHs and the category to which they were assorted (L-PAHs, M-PAHs or H-PAHs), as well as the DBT compounds, are presented in Table S2 of the SI.

One of the three replicates from the June sampling for *Populus* was excluded from the analysis since it was an outlier having much higher PAH concentrations than the other two replicates, e.g., 3.8 times higher H-PAH concentration. No such deviation among replicates was obtained for any other species. Values below the analytical LOD (limit of detection) were handled as follows: if all three replicate values for a certain species, age class or sampling period were < LOD the value was set to zero; if at least one value was > LOD, values < LOD were set to 0.5 × LOD. Leaf/needle PAC data, as well as SLA data, presented in the paper are provided in Table S3 of the SI, concentrations of all individual PACs are given in Table S4.

2.4. Calculation of the net average annual accumulation of PACs by leaves and needles

For broadleaved trees and *Larix*, September concentration values were considered to represent the net PAC accumulation during one

Table 1
Overview of start, stop and duration of the four air pollution measurement periods in the Arboretum. Total PAHs (sum of 32 compounds) and DBTs (sum of 6 compounds) as average ± standard deviation of two replicates. Temperature (°C), precipitation (mm) and wind speed (m/s, mean and hourly maximum) data were retrieved from the City of Gothenburg, Environment Administration rooftop measurement station Femman, situated in the centre of the city. Precipitation is provided for 5 days prior to sampling of leaves and needles which took place at the end of period 1 and 4.

Period	Start	Stop	Days	PAHs (ng m^{-3})	DBTs	Temp. (°C)	Precipitation (mm)		Wind speed (m s^{-1})
					(ng m^{-3})		Total	5 days prior to sampling	Mean (max)
1	24 May 2018	26 June 2018	33	1.9 ± 0.04	0.092 ± 0.001	19.0	49	4	3.2 (8.2)
2	26 June 2018	23 July 2018	27	3.4 ± 0.03	1.2 ± 0.002	20.6	16	–	3.0 (7.7)
3	23 July 2018	19 Aug 2018	27	2.2 ± 0.1	0.093 ± 0.007	21.0	46	–	3.1 (11.2)
4	19 Aug 2018	18 Sept 2018	30	3.2 ± 0.4	0.068 ± 0.001	16.5	134	24	3.4 (8.0)

growing season, since the sampling was made shortly before senescence and shedding of leaves and *Larix* needles. Thus, it represents the net annual flux of PAC from the tree canopy as litterfall to the soil. To estimate the net average annual PAC accumulation by perennial needles, C + 3 concentration values were divided by three. C + 3 needles collected by the end of June are marginally older than three years.

2.5. Statistical analysis

Differences between species and leaf/needle age were investigated using a mixed design analysis of variance (ANOVA). For broadleaved trees and *Larix* needles (September vs June) and evergreen needles (C + 3 vs C + 1), age was set as the within-subjects variable (repeated measures) with two levels. The complete results from ANOVA (Figs. 1, 2, 4

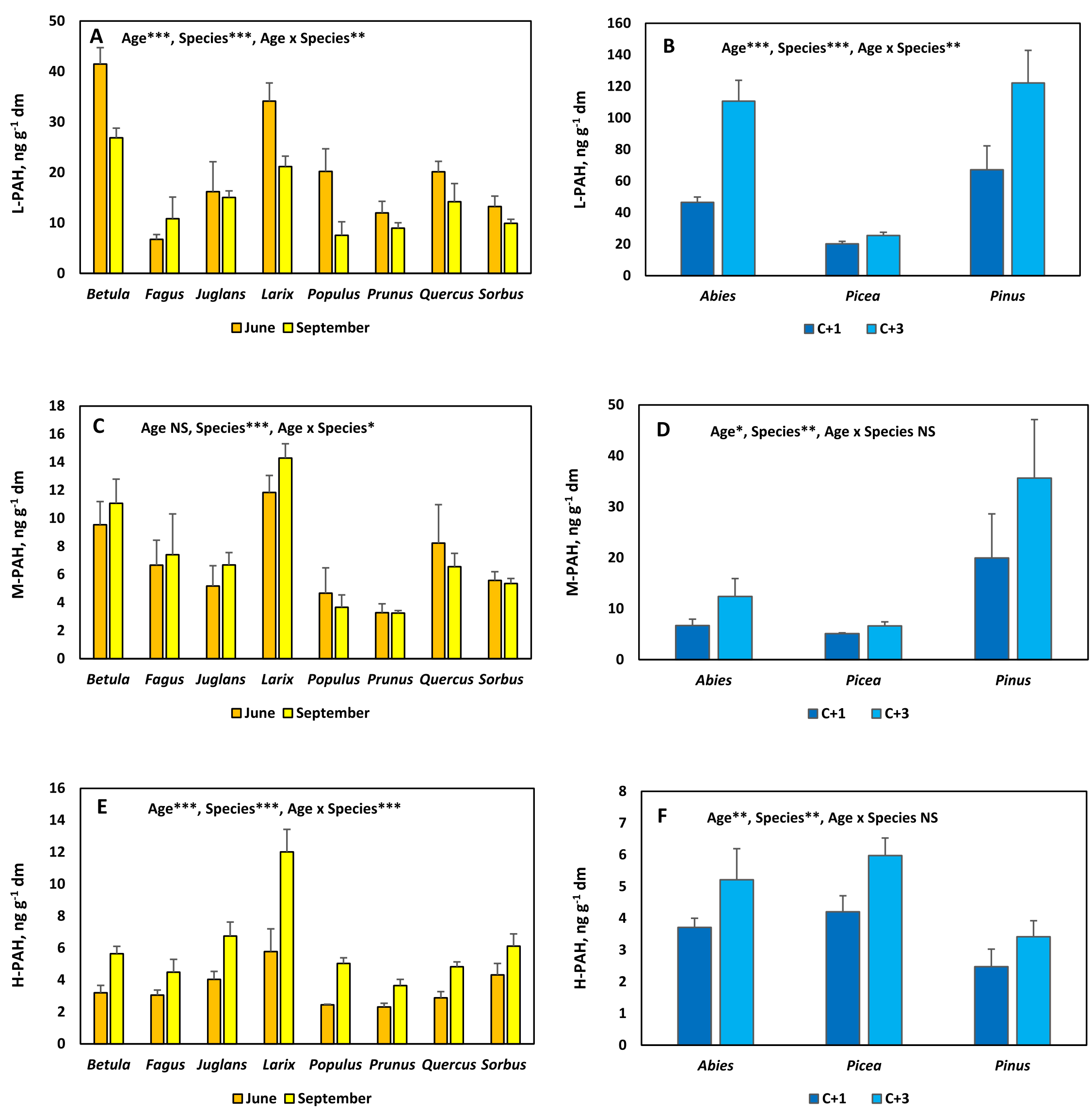

Fig. 1. Average concentration of L-PAHs (A-B), M-PAHs (C-D) and H-PAHs (E-F) in deciduous trees (A, C, E; sampled in June and September) and evergreen conifers (B, D, F; one-year old (C + 1) and three-year old (C + 3) needles sampled in June). Concentrations are given on a dry mass (dm) basis. Error bars show standard deviation for the three replicates of each tree species. The genus to which the trees belong is provided below the x-axis (full species names given in the Materials and methods section). *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$; NS, non-significant. F and p values of the ANOVA are presented in Table S5 of the SI.

and 5) are presented in Table S5 of the SI. Linear regression was used to assess the relationship between September and June levels of L-PAHs, M-PAHs, H-PAHs and DBTs based on data for individual trees. Here, the confidence limits of the slope were used to assess if the regression slope coefficient was significantly different from a hypothetical 1:1 relationship representing no change over time. One-way ANOVA was used to analyse differences in the rate of uptake of L-PAHs, M-PAHs, H-PAHs and DBTs, using both mass-based and leaf area-based concentrations, with Tukeýs honestly significant difference (HSD) as a post-hoc test. IBM SPSS Statistics (version 25) was used for the statistical analyses.

3. Results

3.1. Meteorological conditions and atmospheric concentrations of PAHs, DBTs and NO_2

Table 1 displays the dates, atmospheric total PAHs (sum of all 32 compounds), DBTs (sum of all 6 compounds) and meteorological conditions during the four ~1-month periods during the growing season of 2018 when observations/sampling took place. The total PAH concentrations varied between 1.9 ng m^{-3} (June) and 3.4 ng m^{-3} (July) with August and September falling between these values. There was no clear temporal trend in the atmospheric PAH concentrations over the observation period and variation between months was modest. Total DBT concentrations varied between 0.068 ng m^{-3} (September) and 1.2 ng m^{-3} (July). In Table S6 of the SI, the atmospheric concentrations of L-PAHs, M-PAHs, H-PAHs, DBTs, benzo(a)pyrene, phenanthrene and NO_2 are presented for the four periods. Monthly average NO_2 concentrations during the four periods of Table 1 varied between 5.1 and 5.7 μg m^{-3} (averages of two replicates), showing a small variability during the growing season when the samplings were made, and a modest elevation in relation to rural background concentrations. The summer of 2018 was unusually warm and dry in northern Europe (Bastos et al., 2020), including the Gothenburg region (Johansson et al., 2020). Rainfall was less than average during May, June, and July, but higher than average in August and September. In Gothenburg, the average elevation in temperature compared to 30-year long mean for the period May-September was 3.4°C according to data available at www.smhi.se.

3.2. Leaf and needle concentrations of L-PAHs, M-PAHs, H-PAHs and DBTs

Fig. 1 shows concentrations of L-PAHs, M-PAHs and H-PAHs in leaves and needles of the studied species. F and p values of the ANOVA are presented in Table S5 of the SI. There was a considerable and statistically significant variation among species for all three PAH categories, both for deciduous and evergreen species. With respect to the accumulation over time, there were notable differences both between the three PAH categories and between deciduous trees and evergreen species. A statistically significant loss of L-PAHs, but a significant net accumulation of H-PAHs from June to September in leaves and *Larix* needles of deciduous trees was observed. M-PAHs were intermediate in this respect with no statistically significant difference between June and September concentrations. For the evergreen conifers, there was a statistically significant accumulation from C + 1 to C + 3 needles for all three PAH categories. Significant species-by-age interaction effects were obtained for all the subsets of data presented in Fig. 1, resulting from contrasting development of PAH accumulation with age of leaves/needles among species, except M-PAHs and H-PAHs for evergreen conifers.

Like L-PAHs (Fig. 1A) concentrations of DBTs declined significantly from June to September in leaves of deciduous trees and *Larix* needles (Fig. 2A, $p < 0.001$), except *Fagus*, while there was a concentration increase over time of DBTs and L-PAHs in needles of evergreen conifers (Fig. 2B, $p < 0.001$). The latter, however, varied from large in *Abies* over modest in *Pinus* to almost absent in *Picea*, resulting in a strongly significant ($p < 0.001$) species-by-age interaction effect. F and p values of the ANOVA are presented in Table S5 of the SI.

In Fig. 3, the September concentrations are plotted vs the June concentrations showing data for the individual sampled deciduous trees for L-PAHs, M-PAHs, H-PAHs and DBTs. Again, it is obvious that the deciduous trees experienced a loss of L-PAHs and an accumulation of H-PAHs between the two sampling occasions. From Fig. 3 it also becomes evident that the pattern among the different species is highly consistent with strong ($p < 0.001$) significant regressions. For both L-PAHs and H-PAHs the slope coefficient of the regression line was significantly different ($p < 0.001$) from one (the hypothetical 1:1 relationship representing no change over time), however in different directions. M-PAHs differed little and non-significantly from the 1:1 line. A tendency for heteroscedasticity for L-PAHs was observed, but not for the other PAC categories. Our general conclusions about L-PAHs are not influenced by this. In agreement with the pattern observed for L-PAHs, DBTs exhibited a reduced concentration from June to September with the slope coefficient significantly ($p < 0.001$) smaller than that of the hypothetical 1:1 relationship. This analysis was not made for the evergreen conifers due to the restricted number of species.

In Fig. 4, the leaf/needle concentration of the most abundant PAH, phenanthrene (an L-PAH), which consisted 33 % of total PAH and 49 % of L-PAHs on average for all species, and the highly toxic benzo(a)pyrene (an H-PAH) are presented. F and p values of the ANOVA are presented in Table S5 of the SI. Both phenanthrene and benzo(a)pyrene are on the list of the 16 priority PAHs by US-EPA (EPA, 2008). There was a substantial and statistically significant ($p < 0.001$) variation among the different deciduous trees in phenanthrene concentration (Fig. 4A). Like L-PAHs in general, phenanthrene declined from June to September in deciduous trees but increased significantly ($p < 0.001$) from C + 1 to C + 3 needles.

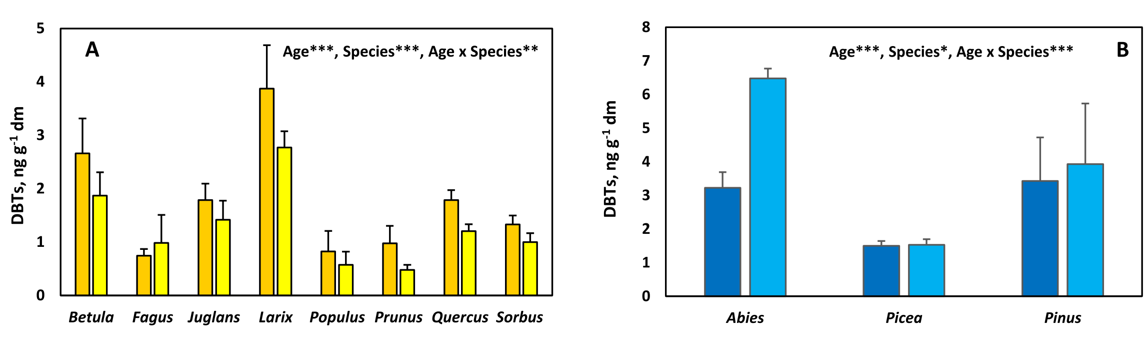

Fig. 2. Average concentration of DBTs in deciduous trees (A; sampled in June and September) and evergreen conifers (B; sampled in June). Data for one-year old (C + 1) and three-year old (C + 3) needles are presented for the evergreen conifers. Concentrations are given on a dry mass (dm) basis. Error bars show standard deviation for the three replicates of each tree species. The genus to which the trees belong is provided below the x-axis (full species names given in the Materials and methods section). *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$; NS, non-significant. F and p values of the ANOVA are presented in Table S5 of the SI.

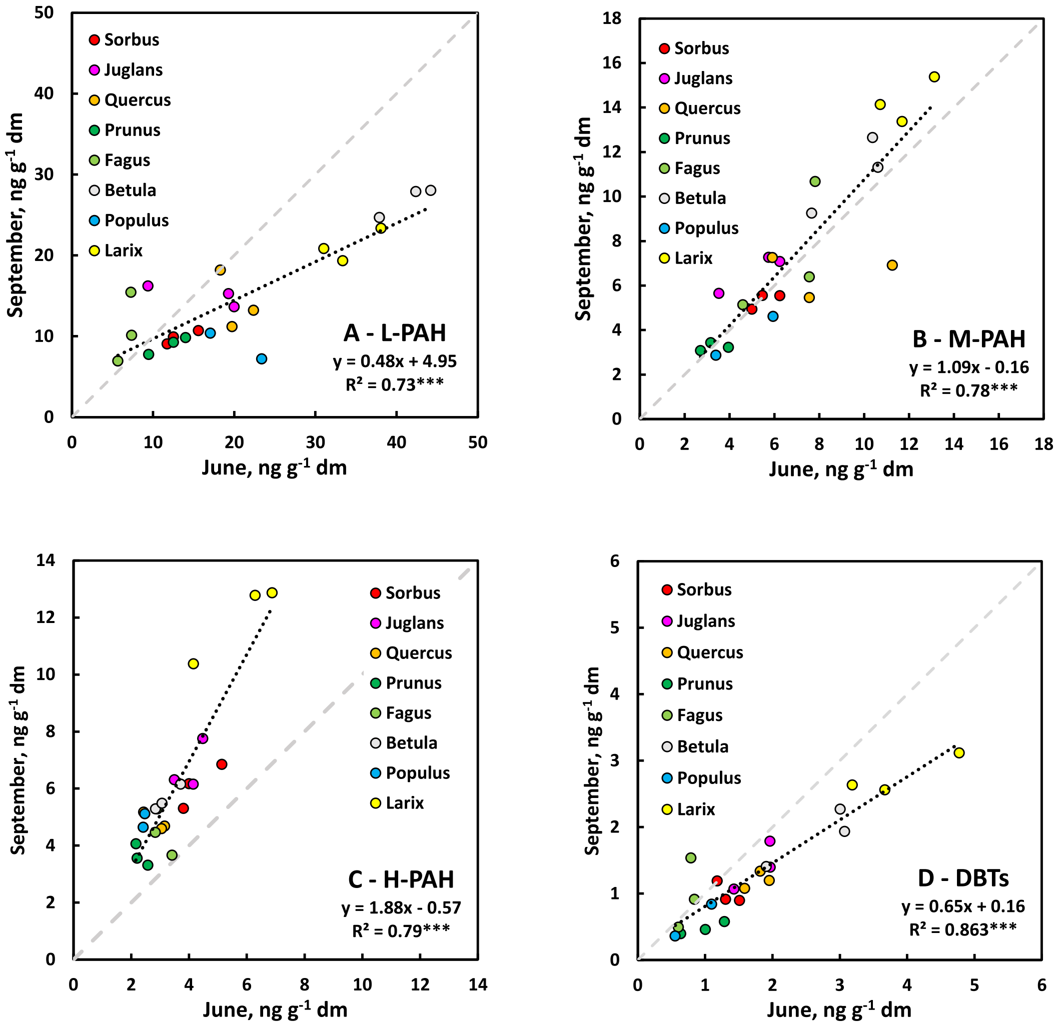

Fig. 3. Leaf and needle (*Larix*) concentrations of deciduous species in September vs June of (A) L-PAHs (B), M-PAHs (C), H-PAHs and (D) DBTs. Each data point represents an individual tree. Concentrations are given on a dry mass (dm) basis. The genus to which the trees belong is provided in each panel (full species names given in the Materials and methods section). ***, $p < 0.001$.

Benzo(a)pyrene, on the other hand, increased significantly ($p < 0.001$) from June to September in the deciduous trees (Fig. 4C). Needle age did, however, not significantly affect the benzo(a)pyrene concentration in the studied evergreens (Fig. 4D). *Pinus* had a comparatively low absolute concentration of benzo(a)pyrene in relation to the other evergreen conifers with respect to H-PAHs (Fig. 1F).

There was a substantial and statistically significant ($p < 0.001$) variation among the different deciduous trees in benzo(a)pyrene concentration, with *Sorbus* being the strongest accumulator (Fig. 4C). A significant interaction ($p < 0.001$) was observed for the deciduous species associated with large variation among species in the absolute levels of phenanthrene as well as in the net loss of this compound from June to September (Fig. 4A).

3.3. Accumulation of PACs in relation to SLA

In Fig. 5 the results of the SLA measurements are presented. F and p values of the ANOVA are presented in Table S5 of the SI. In general SLA was considerably higher in the deciduous species (Fig. 5A) than in the evergreen conifers (Fig. 5B, please note different scale on y-axis). There were statistically significant differences between species among the deciduous trees. In the evergreen conifers species did not differ significantly. SLA neither differed significantly between June and September for deciduous trees, nor between C + 1 and C + 3 needles in evergreen conifers.

It was investigated if there was a relationship between SLA and the net average annual accumulation of the four PAC categories. Such a relationship was obtained only for L-PAHs (Fig. 6A, results for the other PAC categories not shown). This relationship suggests that tree species with lower SLA have a larger per unit leaf mass capacity to accumulate L-PAHs. *Picea*, however, deviated from the general trend by having a comparatively low L-PAH accumulation in relation to its SLA. In Fig. 6B, the corresponding relation between leaf area-based accumulation of L-PAHs and SLA is displayed with a very strong contrast in accumulation between species with high vs low SLA. It should be kept in mind that the calculation of the leaf area-based concentration involves SLA, and the x and y data are thus not completely independent. Thus, no statistical significance was estimated for the relationship in Fig. 6B.

3.4. Ranking of species with respect to net average annual uptake of L-PAHs, M-PAHs, H-PAHs and DBTs

For the ranking of tree species, both mass-based (Fig. 7) and leaf area-based (Fig. 8) net average annual PAC uptake were analysed. As can be inferred from Figs. 7 and 8, there were strong contrasts among the species and among the four PAC categories in terms of the net average annual accumulation rate. Also, the units used to express concentration, mass-based or leaf area-based, strongly influenced the ranking. In

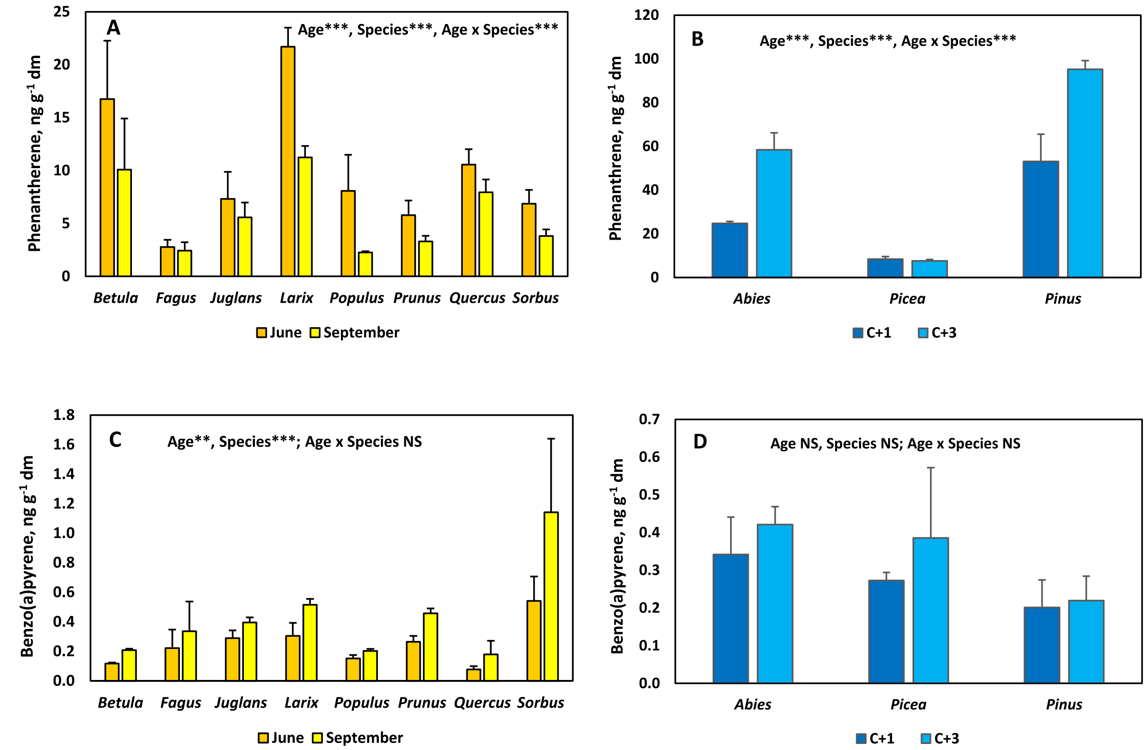

Fig. 4. Average concentrations of phenanthrene (A-B) and benzo(a)pyrene (C-D) in deciduous trees (A, C; sampled in June and September) and evergreen conifers (B, D; sampled in June). Data for one-year old (C + 1) and three-year old (C + 3) needles are presented for evergreen conifers. Concentrations are given on a dry mass (dm) basis. Error bars show standard deviation for the three replicates of each tree species. The genus to which the trees belong is provided below the x-axis (full species names given in the Materials and methods section). **, $p < 0.01$; ***, $p < 0.001$; NS, non-significant. F and p values of the ANOVA are presented in Table S5 of the SI.

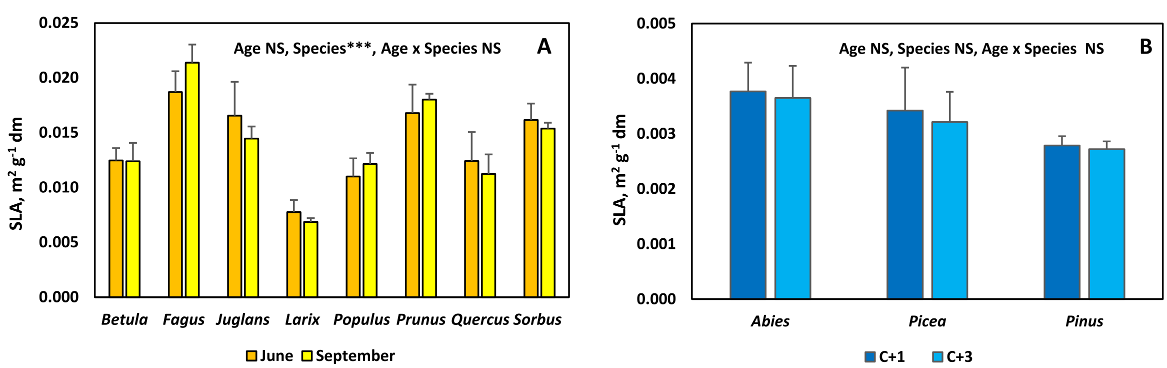

Fig. 5. Specific leaf area using a dry mass (dm) basis of (A) deciduous species sampled in June and September and (B) evergreen conifers sampled in June. Data for one-year old (C + 1) and three-year old (C + 3) needles are presented for the evergreen conifers. Error bars show standard deviation for the three replicates of each tree species. The genus to which the trees belong is provided below the x-axis (full species names given in the Materials and methods section). F and p values of the ANOVA are presented in Table S5 of the SI.

general, the deciduous conifer *Larix* had a high net average annual uptake rate, especially for H-PAHs and M-PAHs, both using a mass-based and leaf area-based concentrations. Conifers with perennial needles exhibited high leaf area-based accumulation, in particular for L-PAHs, M-PAHs and DBTs. *Abies* was a strong accumulator of L-PAHs and DBTs both when using mass-based and leaf area-based units. Among the broadleaved species, *Betula* ranked highest for L-PAHs, M-PAHs and DBTs, while *Juglans* and *Sorbus* had the largest accumulation of H-PAHs.

The ratio between the highest and lowest species-specific mass-based uptake rates among all species of L-PAHs, M-PAHs, H-PAHs and DBTs were 5.4, 6.5, 10 and 5.8, respectively. Corresponding values using leaf area-based units were larger except for H-PAHs: 30, 24, 8.7 and 22 for L-PAHs, M-PAHs, H-PAHs and DBTs, respectively.

4. Discussion

Our study showed that leaf and needle accumulation differed pronouncedly between the four PAC categories. This variation will be obscured if only the sum of PAHs is considered, where e.g., the opposite trends in L-PAHs and H-PAHs, respectively, of deciduous trees between June and September will tend to cancel each other. The semi-volatility of the L-PAHs and DBTs, and to some extent the M-PAHs, means that fluxes can go from the atmosphere to vegetation and in the opposite direction. This has been observed also in earlier studies such as in Yanji, Eastern China, for the broadleaved deciduous species *Salix matsudana* by Zhao et al. (2018). That investigation emphasized the need to consider temperature effects on PAH partitioning in sampling schemes, which is

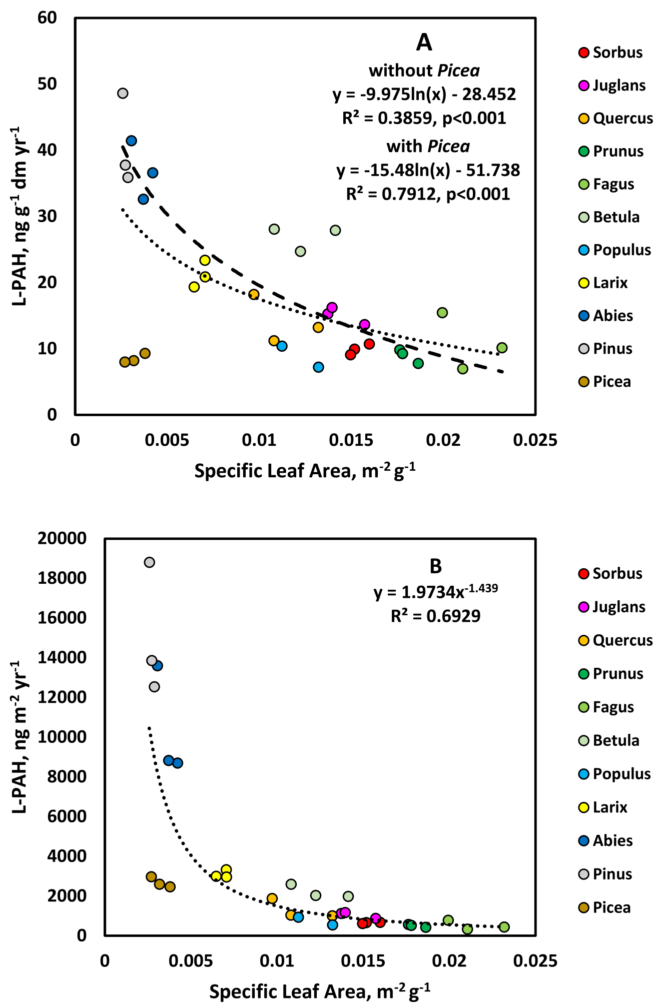

Fig. 6. Relationships of net average annual uptake of L-PAHs (A) expressed on a dry leaf mass (dm) basis and (B) on a leaf area basis with specific leaf area (SLA). Each point represents an individual sampled tree. The genus to which the trees belong is provided to the right of each panel (full species names given in the Materials and methods section).

consistent with our observation. Murakami et al. (2012) also observed a seasonal, likely temperature-dependent effect in the deciduous conifer *Ginkgo biloba* in Tokyo, Japan. In the present study it cannot be excluded that the significant loss of L-PAHs and DBTs from June to September in deciduous trees was promoted by the unusually warm summer of 2018, which also affected the Gothenburg region (Bastos et al., 2020; Johansson et al., 2020).

The decline of L-PAHs and DBTs from June to September in deciduous species was, however, not completely general. Both these compound groups showed a net increase in concentration from June to September in *Fagus*, but not in other deciduous species as evident form Fig. 1A, 2A, 3A and 3D. Although *Fagus* had a high SLA and in general a comparatively low accumulation rate of all studied PAC categories, our data offer no clear explanation of why it differed in the direction of concentration change of L-PAHs and DBTs from June to September compared to other deciduous trees. This observation highlights the complexity in the accumulation of PAC compounds in leaves of different tree species.

The evergreen conifers of our study exhibited a continued net accumulation of L-PAHs and DBTs over three years. This agrees with the observations of Piccardo et al. (2005). They observed a largely continued accumulation of four volatile PAHs in needles of *Pinus nigra* and *Pinus pinaster* over a range of needle ages up to 30 months in the region of Genoa, Italy. Our study shows that a pattern like that of L-PAHs also is characteristic to the much less studied DBTs (Cheng et al., 2013), although the ranking of species with respect to accumulation rate differed to some extent between these two PAC categories. A further example was presented by Odabasi et al. (2015), who found e.g., a doubling in the concentration of the sum of 16 PAHs from C needles to C + 1 needles of *Pinus* trees in western Turkey in an industrial area.

Klingberg et al. (2022) studied PAH accumulation in *Quercus palustris* and *Pinus nigra* in a range of sites with contrasting pollution levels of the urban landscape of Gothenburg, Sweden during the summer of 2018. They found a pattern similar to that of the present study, e.g., that there was a net accumulation of H-PAHs both in a deciduous and an evergreen species, while L-PAHs were lost in the later part of the growing season in deciduous *Quercus palustris*, but a net accumulation from C + 1 to C + 3 in evergreen *Pinus nigra*.

The PAHs that have been analysed in plant tissue in different investigations vary considerably both in terms of the number of compounds included and with respect to chemical identity. This makes comparisons of the concentrations of total PAHs or categories of PAHs difficult. However, like in our study, phenanthrene and benzo(a)pyrene have been included and reported separately in several studies allowing for comparisons of the observed concentrations. Needle phenanthrene varied in the range ~20–80 ng g^{-1} in evergreen conifers at four urban/industrial sites in Germany, Poland and the United States (Lehndorff and Schwark, 2004), largely in agreement with the concentrations (~5–100 ng g^{-1}, Fig. 4B) in needles of evergreen conifers in our study. Çalişcan Eleren and Tasdemir (2021) found average phenanthrene concentrations in *Pinus* needles around 300 ng g^{-1} in a suburban/industrial area of western Turkey. Huang et al. (2018) summarized results from four different studies regarding PAH concentrations in two different *Pinus* species and reported phenanthrene concentrations in the range ~20–250 ng g^{-1}. Furthermore, phenanthrene concentrations of needles of two *Pinus* species in the range 7–410 ng g^{-1} were observed by Piccardo et al. (2005) at seven sites in and around the City of Genua (Italy); like in our study they obtained a pronounced trend for higher concentrations in older needles. De Nicola et al (2017) observed somewhat lower phenanthrene concentrations in *Quercus robur* (33 ng g^{-1}) compared to *Pinus pinaster* (38 ng g^{-1}). De Nicola et al (2017) measured six months old *Pinus pinaster* needles; in our study it was primarily the older (C + 3) needles that had higher phenanthrene concentrations than broadleaved trees (except for *Picea*). In the case of benzo(a)pyrene, we observed concentrations in the range of ~0.1–1 ng g^{-1} in all species. This is comparable with values in the range 0.9–1.1 ng g^{-1} in De Nicola et al (2017), 0.1–3 ng g^{-1} in Piccardo et al (2005) and around 1 ng g^{-1} in Lehndorff and Schwank (2004). The study by Çalişcan Eleren and Tasdemir (2021), however, reported much higher needle benzo(a)pyrene concentrations (average 26 ng g^{-1}).

It made a large difference, e.g., for the ranking of PAC categories with respect to rate of accumulation, if the concentration was expressed on a leaf mass or a leaf area basis. In general, the evergreen conifers ranked higher when using leaf area-based concentrations depending on their generally lower SLA. Leaf uptake of pollutants is primarily regulated by the resistances at the leaf surface, i.e., boundary-layer, cuticle and stomata (Winner and Atkinson 1986). Since the maximum leaf area of a mature tree stand is limited by self-shading (Larcher 2003), leaf area-based assessments of pollutant uptake may therefore be more ecologically relevant for dense stands. Assuming that the trees have the same leaf area, the conifers would then be superior to remove PAC pollutants, but this did not apply to H-PAHs, a category which contains the highly toxic benzo(a)pyrene. Also, *Picea* was mostly not a very strong accumulator. Thus, the pattern of accumulation among the different species is obviously complex and cannot be fully explained by sorting species into general groups like conifers and broadleaves. This is in line with earlier observations like those by Jouraeva et al. (2002) in Syracuse, USA, where the PAH accumulation of *Tilia* × *euchlora* was significantly higher than in *Pyrus calleryana*, two broadleaved species

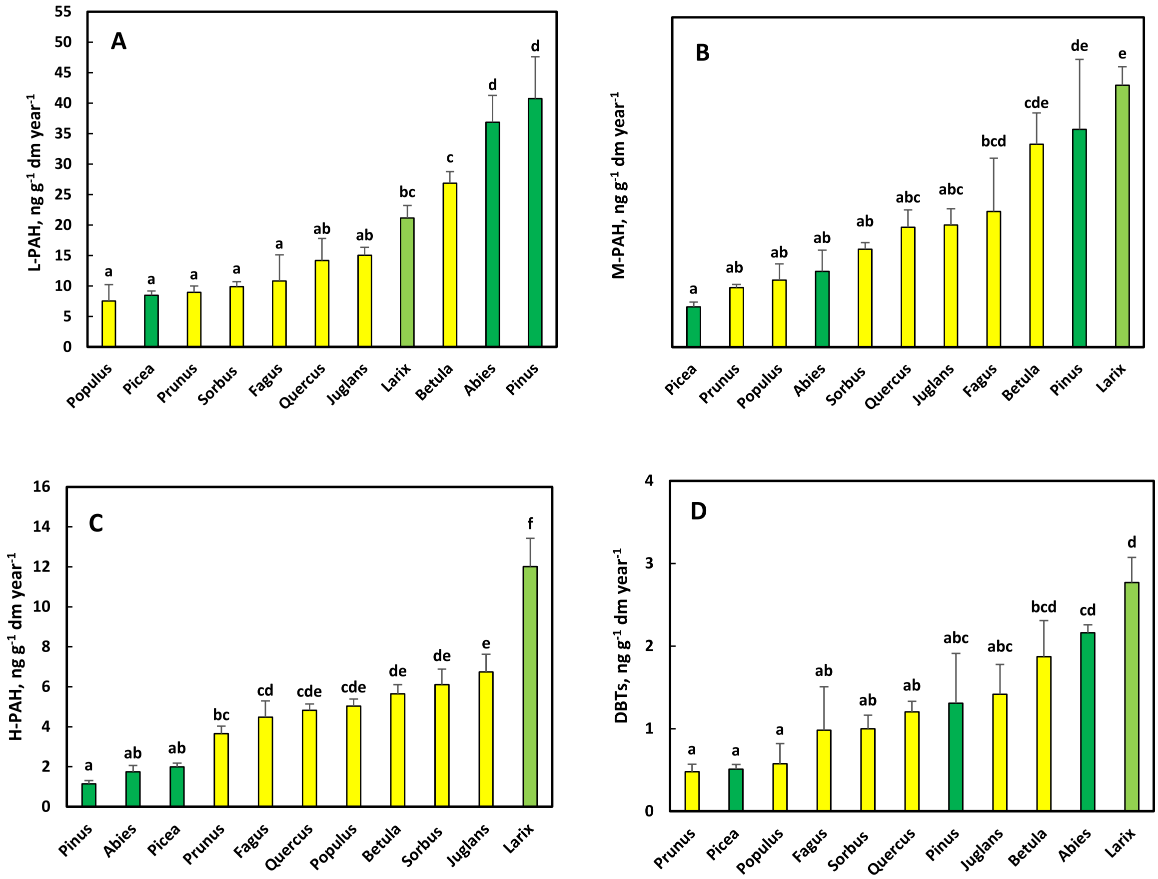

Fig. 7. Ranking of the tree species included in the study with respect to net average annual uptake of (A) L-PAHs, (B) M-PAHs, (C) H-PAHs, and (D) DBTs using mass (dm) based concentration units. In each panel, species are significantly different according to the post-hoc test if letters above the bars are entirely different. Yellow bars, deciduous broadleaved trees; light green bar, deciduous conifer; dark green, evergreen conifers. The genus to which the trees belong is provided below the x-axis (full species names given in the Materials and methods section). Concentrations are given on a dry mass (dm) basis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with similar leaf characteristics. Piccardo et al. (2005) observed *Pinus nigra* to accumulate much larger amounts of volatile PAHs than *Pinus pinaster* at most of the investigated sites in the Genoa region, although both species are evergreen conifers. The larger number of species in our study, and the comparison of four different pollutant categories, further highlights the contrasts and complexity in PAC accumulation in leaves and needles.

Indeed, there was a very large variation in accumulation of the four different PAC categories among the included species, which is hard to generalize with respect to leaf traits. This agrees with the conclusion of the review by Desalme et al. (2013) that PAH concentrations are highly variable between plant species. However, a certain degree of generalization was possible from our data set. SLA was an important leaf trait for the accumulation of L-PAHs. It seems that the larger relative leaf mass in relation to leaf area represents a sink for L-PAHs in trees with lower SLA. This may explain why there was a continued net accumulation of L-PAHs in the evergreen conifers over several years, while this was not the case in the deciduous species. As species with a low SLA also will have larger leaf mass at a given leaf area their total sink for L-PAHs will be much larger than for species with high SLA at the same leaf area.

The pattern of accumulation of different PAC categories in our study are consistent with the view of Wang et al. (2008) that gaseous PAHs deposit, to the inner tissues (partly through stomata, Barber et al., 2004), which explains the role of SLA, while particle-bound PAHs attach to the exterior leaf cuticle. It is then logical that M-PAHs are intermediate, since they exist partly as gases, partly as bound to particles in the atmosphere. Already Simonich and Hites (1995) suggested this pattern of two different compartments, the leaf interior reservoir and the leaf surface, respectively, dominating gaseous and particle-bound PAHs deposition. The same conclusion was drawn by Piccardo et al. (2005) when comparing the deposition pattern of volatile and non-volatile PAHs in two *Pinus* species. Although current knowledge does not allow for a complete mechanistic explanation of the variation in PAC accumulation among different tree species, the present study, along with literature, suggests that stomatal conductance is of importance for PACs in the gaseous phase. Stomatal conductance depends both on intrinsic, genetically controlled factors characterizing different plant groups, but also on meteorological conditions affecting the stomatal aperture based on short-term physiological responses to factors such as solar radiation, temperature and air humidity (Lin et al., 2015). Like particles in general, deposition of particle bound PACs will be sensitive to other leaf traits like leaf surface roughness, waxiness and hairiness (Corada et al., 2021). It should also be noted that temperature will influence the extent to which different PAC compounds exist in the gaseous phase or attached to particles, and thus the extent to which they are subject to different deposition mechanisms. In the study by Klingberg et al. (2022), M-PAHs had higher leaf concentrations in relation to air concentrations than L-PAHs and H-PAHs, which can potentially be explained by the fact that M-PAHs can be subject both to the mechanisms associated with gaseous and particle deposition.

The generally lower SLA of the evergreen conifers can likely explain the fact that accumulation of L-PAHs continued over several years in this plant group, while a loss from summer to autumn was observed for the deciduous species. As explained by Barber et al. (2004), plant leaves with otherwise similar permeability to PAC uptake will take longer to reach equilibrium if SLA is low, i.e., the PAC sink, based on the per unit

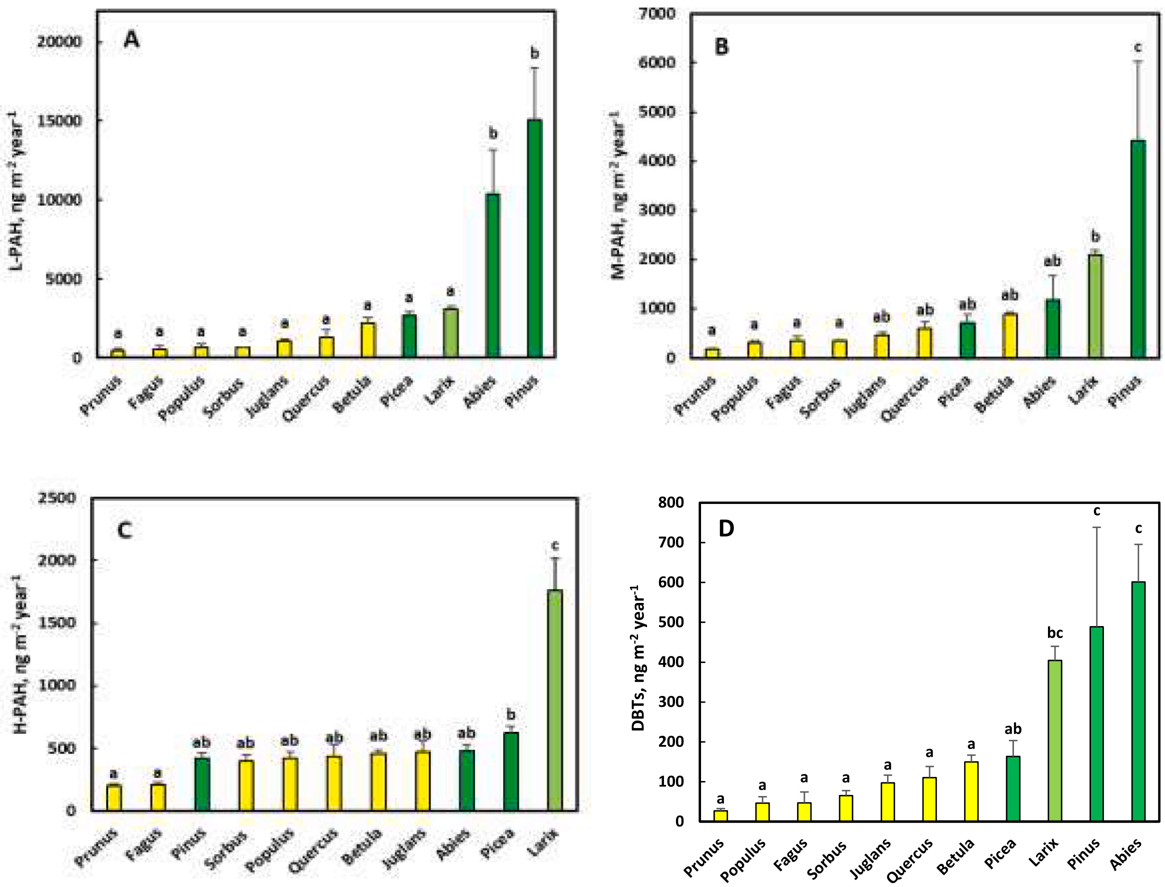

Fig. 8. Ranking of the tree species included in the study with respect to net average annual uptake of (A) L-PAHs, (B) M-PAHs, (C) H-PAHs, and (D) DBTs using leaf area-based concentration units. In each panel, species are significantly different according to the post-hoc test if letters above the bars are entirely different. Yellow bars, deciduous broadleaved trees; light green bar, deciduous conifer; dark green, evergreen conifers. The genus to which the trees belong is provided below the x-axis (full species names given in the Materials and methods section). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

leaf area available mass, is larger. The pattern observed for deciduous trees (Fig. 3) is in line with the framework for the interpretation of measurements of e.g., PACs in plants by McLachlan (1999). For the more volatile L-PAHs and DBTs, the temperature dependent equilibrium between plant and air seems to have been reached, which leads to loss of these PAC categories during the warm summer. In the evergreen conifers, having a larger sink, the equilibrium was not reached, which allowed a continued accumulation of L-PAHs and DBTs over several years. Viippola et al. (2016) observed higher levels of atmospheric L-PAHs in forested compared to open *peri*-urban sites in southern Finland during the summer, but the opposite in the autumn and winter. This pattern can be explained by the re-volatilization from leaves and soil of these compounds under the higher temperatures of the summer while net deposition takes place in the colder seasons and conforms with our observation of net loss of L-PAHs during the summer. In addition to re-volatilization, there may be other mechanisms that reduce the concentration of PACs in leaves and needles, such as destruction by photolysis and degradation by metabolic processes if the PACs penetrate the cuticle and reach the physiologically active plant tissues (Barber et al., 2004; Wang et al., 2005; Wild et al., 2005). This means that the net accumulation observed from leaf concentrations may represent an underestimation of deposition or destruction of PACs associated with leaves. These decomposition processes have not been well quantified under ecologically realistic conditions. However, the continued accumulation over several years in conifers shows that these processes are not very fast. Otherwise, net accumulation would not occur (Barber et al., 2004).

Larix decidua is standing out as a strong PAC accumulator in most respects, regarding both mass based and leaf area-based concentration (Figs. 7 and 8). Especially for H-PAHs it was a very efficient accumulator in comparison with all other species. Murakami et al. (2012) suggested *Ginkgo biloba*, which like *Larix decidua* in our study is a deciduous conifer, as a suitable species for PAH biomonitoring based on its higher rate of PAH accumulation compared to four other species.

For the use of different tree species as biomonitors and/or for the purpose of air pollution removal there are different aspects to consider. Firstly, the total amount of PACs accumulated is important. For L-PAHs, evergreen conifers were superior as accumulators both using mass based and leaf-area based concentrations, while this was not the case for H-PAHs. De Nicola et al. (2017) compared PAH uptake in deciduous *Quercus robur* with that of the evergreen conifer *Pinus pinaster* in Galicia, North-West Spain, and found that the two species accumulated about equal total amounts of PAH, but with *Quercus* absorbing relatively more particle-bound PAHs and *Pinus* taking up a larger fraction of volatile PAHs. In the present study we did not rinse the leaves and needles before analysis. Rinsing and analysis of both the leaves after rinsing and the content of PACs in the fraction rinsed off could be useful for the understanding of deposition mechanisms and to add further information in biomonitoring. Further, in the analysis of the atmospheric content of PACs, the study of particle size fractions and their content of the different PAC categories, would be of interest to highlight sources and deposition mechanisms.

A second consideration is the distribution of PAC uptake over the seasons (Barwise & Kumar, 2020). While the deciduous trees may have relatively large uptake during several months in late spring and early summer, they tended to lose L-PAHs and DBTs at higher temperatures, which can be explained by equilibrium processes (see above). As already mentioned, the evergreen conifers exhibited a net uptake of all PAC categories studied over several years. Since air pollution is often worse in the winter season in temperate regions, air pollution removal would be of larger significance in evergreens (Barwise & Kumar, 2020). The possibility to sample several needle-age classes offers opportunities for biomonitoring to follow pollutant accumulation over a range of years, as was pointed out by Kylin & Sjödin (2003) for DDT and hexachlorocyclohexanes (HCH). Since many evergreen conifers retain their needles 4–10 years, or in some species longer, it would be of great interest to study the extent of PAC accumulation in needles older than C + 3.

One further aspect to consider is the suitability of different species to grow and be cultivated in urban environments. Among broadleaved trees, *Betula* was a strong accumulator of PACs. A limitation in using this species as a city tree is that it is relatively sensitive to drought, which often occurs in urban local climates (Hannus et al., 2021), except in cool climates at high latitudes (Bengtsson, 2000). In addition, *Betula* trees provide an ecosystem disservice, since it produces large amounts of allergenic pollen (Grote et al., 2016). It has been suggested that *Larix* species, a very strong accumulator of M-PAHs, H-PAHs and DBTs in our study, is sensitive to the generally polluted atmosphere of the urban and industrial environment (e.g., Bialobok & Fabijanowski, 1984; Sindelar, 1987), and is sensitive in the morphology and anatomical structure of female generative organs to air pollution (Seta-Koselska et al., 2014). Further investigation is required to understand how important these limitations are for the air pollution removal efficiency of *Larix* in cities. *Pinus nigra*, which is known to be robust with respect to the urban climate (Stoecklein, 2001), was a strong accumulator of L-PAHs and M-PAHs, relatively strong also for DBTs, but not for H-PAHs. With its multiple needle age classes, it would be an example of a tree species of interest both when it comes to biomonitoring and removal of local pollution of volatile PACs. Our study shows the very strong variation among tree species in the rate of accumulation of PACs, which has also been seen by e.g., Wang et al. (2008), Murakami et al. (2012) and Dias et al. (2016), although these studies covered a smaller number of species. Sæbø et al. (2012), reviewing extensive literature, similarly found strong contrasts between different species when rating species with respect to per unit leaf area particle deposition, with conifers quite generally being strong accumulators. This variation should be taken into consideration in urban planning where trees are selected for situations with high local air pollution. In this choice one should be mindful of the fact that different species are among the strongest accumulators of the different PAC categories, although the pattern was similar between L-PAHs and the so far little studied DBT pollutants. To assess the overall effect of vegetation on urban air quality modelling is required, making use of detailed empirical information like that of the present and other studies. The eco-environmental processes (biological and chemical-physical) involved are in many cases non-linear and will have to be represented with respect to both temporal and spatial variation (Li and Convertino, 2021). Important non-linearities in this context can be exemplified by the complex pattern of concentration change over time, which differed substantially between the PAC categories, and the non-linear relationship between air pollution concentrations and distance from local emission sources (Klingberg et al., 2017). Tools such as convergent cross mapping and optimal information flow ecosystem models (Li and Convertino, 2021) can be used to assess causal interaction in complex systems. While the observed within-species variation in leaf/needle PAC content during a given sampling occasion generally was small in the present study, uncertainty analysis (Pianosi et al., 2016) should be undertaken in any numerical environmental modelling, making use of the kind of empirical data presented in this paper. This is essential to understand how the variation in the output of such models can be attributed to variation in its input factors.

Finally, air pollution removal potential only represents one aspect to consider in the choice of species for urban greening to provide ecosystem services in the urban landscape. It is important to keep in mind that in certain situations trees may limit air circulation to an extent which more than offsets the beneficial effects on air pollution by deposition to leaves and needles on a local scale.

5. Conclusions

The main conclusions of this investigation were:

- Leaf accumulation of the four PAC categories L-PAHs, M-PAHs, H-PAHs and DBTs varied strongly among species, and between evergreen conifers and deciduous trees, with a complex pattern.
- SLA was an important trait for accumulation in leaves and needles of L-PAHs.
- Evergreen conifers generally accumulated larger amounts of L-PAHs, M-PAHs and DBTs than broadleaved trees, both using leaf mass- and leaf area-based concentrations units. For H-PAH accumulation rate, evergreens were inferior to (using mass-based concentrations) or of the same magnitude (using leaf-area based concentrations) as deciduous species.
- The accumulation in leaves and needles of DBTs, for which bioaccumulation data for vegetation seems to be missing, was similar, but not identical, to that of L-PAHs.
- The comparatively volatile L-PAHs and DBTs declined in concentration from June to September in deciduous species but increased in evergreens from one-year-old to three-year-old needles. This can be explained by a combination of a larger sink in the conifers and the temperature-sensitive equilibrium governing the relationship between leaf and air concentrations.

CRediT authorship contribution statement

H. Pleijel: Funding acquisition, Conceptualization, Investigation, Writing – original draft. **J. Klingberg:** Conceptualization, Investigation, Formal analysis, Writing – review & editing. **B. Strandberg:** Conceptualization, Investigation, Methodology, Writing – review & editing. **H. Sjöman:** Conceptualization, Investigation, Writing – review & editing. **L. Tarvainen:** Investigation, Writing – review & editing. **G. Wallin:** Conceptualization, Resources, Writing – review & editing.

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

All data used are included in a supplementary file and is thus made available.

Acknowledgements

This work was supported by the Swedish research council FORMAS [grant number 2017-00696]. Håkan Pleijeĺs work with this manuscript was also supported by another FORMAS grant [2018-00174]. Karen Christensen is gratefully acknowledged for technical assistance with PAHs analysis. Håkan Sundberg is gratefully acknowledged for assistance with the collection of samples.

Appendix A. Supplementary data

In the supplementary information (SI) files ("Supplementary – data and information" and "Supplementary – PAC analysis and QA"), properties of the eleven investigated tree species, the investigated PAC and SLA property information, the original PAC data, the detailed ANOVA results, details of PACs air sampling and analytical procedures as well as quality assurance of results are presented. Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecolind.2022.109681.

References

Al-Dabbous, A.N., Kumar, P., 2014. The influence of roadside vegetation barriers on airborne nanoparticle and pedestrian exposure under varying wind condition. Atmos. Environ. 90, 113–124. https://doi.org/10.1016/j.atmosenv.2014.03.040.

Barber, J.L., Tomas, G.O., Kerstiens, G., Jones, K.C., 2004. Current issues and uncertainties in the measurment and modelling of air-vegetation exchange and within plant processing of POPs. Environ. Pollut. 128, 99–138. https://doi.org/10.1016/j.envpol.2003.08.024.

Barwise, Y., Kumar, P., 2020. Designing vegetation barriers for urban air pollution abatement: a practical review for appropriate plant species selection. Npj Climate and Atmos. Sci. 3 (1) https://doi.org/10.1038/s41612-020-0115-3.

Bastos, A., Ciais, P., Friedlingstein, P., Sitch, S., Pongratz, J., Fan, L., Wigneron, J.P., Weber, U., Reichstein, M., Fu, Z., Anthoni, P., Arneth, A., Haverd, V., Jain, A.K., Joetzjer, E., Knauer, J., Lienert, S., Loughran, T., McGuire, P.C., Tian, H., Viovy, N., Zaehle, S., 2020. Direct and seasonal legacy effects of the 2018 heat wave and drought on European ecosystem productivity. Sci. Adv. 6 (24) https://doi.org/10.1126/sciadv.aba2724.

Bengtsson, R., 2000. Urban Trees from A to Z (Stadsträd från A till Z). Swedish. AB Svensk Byggtjänst, Stockholm.

Bialobok, S., Fabijanowski, J. (Eds.) 1984. Concepts of forest management in industrial regions. Contributors: Adamczyk, B., Bialobok, S., Fabijanowski, J., Greszta, J., Lesinski, J.A., Oleksyn, J. & Rachwal, L. 8.1. Forest functions in industrial regions. Ecological Studies No. 49, pp. 231–267.

Bohlin, P., Audy, O., Skrdlikova, L., Kukucka, P., Pribylova, P., Prokes, R., Vojta, S., Klanova, J., 2014. Outdoor passive air monitoring of semi volatile organic compounds (SVOCs): a critical evaluation of performance and limitations of polyurethane foam (PUF) disks. Environ. Sci.-Process Impacts 16 (3), 433–444. https://doi.org/10.1039/c3em00644a.

Boström, C.E., Gerde, P., Hanberg, A., Jernstrom, B., Johansson, C., Kyrklund, T., Rannug, A., Tornqvist, M., Victorin, K., Westerholm, P., 2002. Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. Environ. Health Persp. 110, 451–488. https://doi.org/10.1289/ehp.02110s3451.

Çalişcan Eleren, S., Tasdemir, Y., 2021. Levels, distributions, and seasonal variations of polycyclic aromatic hydrocarbons (PAHs) in ambient air and pine components. Environ. Monit. Assess. 193, 253. https://doi.org/10.1007/s10661-021-09028-8.

Cheng, I., Wen, D., Zhang, L., Wu, Z., Qiu, X., Yang, F., Harner, T., 2018. Deposition mapping of polycyclic aromatic compound in the oil sands region of Alberta, Canada and links to ecosystem impacts. Environ. Sci. Technol. 52, 12456–12464. https://doi.org/10.1021/acs.est.8b02486.

Corada, K., Woodward, H., Alaraj, H., Colling, M.C., de Nazelle, A., 2021. A systematic review of the leaf traits considered to contribute to removal of airborne particulate matter pollution in urban areas. Environ. Pollut. 269, 116104 https://doi.org/10.1016/j.envpol.2020.116104.

Dadvand, P., Nieuwenhuisen, M.J., Esnaola, M., Forna, J., Basagaña, X., Alvarez-Pedrerol, M., Rivas, I., Lopez-Vicente, M., De Castro Pacual, M., Su, J., Jerrett, M., Querol, X., Sunyer, J., 2015. Green spaces and cognitive development in primary schoolchildren. PNAS 112, 7937–7942. https://doi.org/10.1073/pnas.1503402112.

De Nicola, F., Grana, E.C., Mahia, P.L., Lorenzo, S.M., Rodriguez, D.P., Retuerto, R., Carballeira, A., Aboal, J.R., Fernandez, J.A., 2017. Evergreen or deciduous trees for capturing PAHs from ambient air? a case study. Environ. Pollut. 221, 276–284. https://doi.org/10.1016/j.envpol.2016.11.074.

Desalme, D., Binet, P., Chiapusio, G., 2013. Challenges in tracing the fate and effects of atmospheric polycyclic aromatic hydrocarbon deposition in vascular plants. Environ. Sci. Technol. 47, 3967–3981. https://doi.org/10.1021/es304964b.

Dias, A.P.L., Rinaldi, M.C.S., Domingos, M., 2016. Foliar accumulation of polycyclic aromatic hydrocarbons in native tree species from the Atlantic Forest (SE-Brazil). Sci. Tot. Environ. 544, 175–184. https://doi.org/10.1016/j.scitotenv.2015.11.092.

Domingos, M., Bulbovas, P., Camargo, C.Z.S., Aguiar-Silva, C., Brandao, S.E., Dafré-Martinelli, M., Dias, A.P.L., Engela, M.R.G.S., Gagliano, J., Moura, B.B., Alves, E.S., Rinaldi, M.C.S., Gomes, E.P.C., Furlan, C.M., Figueiredo, A.M.G., 2015. Searching for native tree species and respective potential biomarkers for future assessment of pollution effects on the highly diverse Atlantic Forest in SE-Brazil. Environ. Pollut. 202, 85–95. https://doi.org/10.1016/j.envpol.2015.03.018.

EPA, 2008. https://archive.epa.gov/epawaste/hazard/wastemin/web/pdf/pahs.pdf.

Eriksson, G., Jensen, S., Kylin, H., Strachan, W., 1989. The pine needle as a monitor of atmospheric pollution. Nature 341, 42–44. https://doi.org/10.1038/341042a0.

Famiyeh, L., Chen, K., Xu, J., Sun, Y., Guo, Q., Wang, C., Lv, J., Tang, Y.T., Yu, H., Snape, C., He, J., 2021. A review on analysis methods, Source identification, and cancer risk evaluation of atmospheric polycyclic aromatic hydrocarbons. Sci. Total Environ. 789, 147741 https://doi.org/10.1016/j.scitotenv.2021.147741.

Ferm, M., 2001. Validation of a diffusive sampler for ozone in workplace atmospheres according to EN838. International Conference on Measuring Air Pollutants by Diffusive Sampling. Montpellier, France, 26–28 September, pp. 298–303.

Franzaring, J., 1997. Temperature and concentration effects in biomonitoring of organic pollutants. Environ. Monit. Assess. 46, 209–220. https://doi.org/10.1023/A:1005719901961.

Gong, P., Wang, X., Sheng, J., Wang, H., Yuan, X., He, Y., Qian, Y., Yao, T., 2018. Seasonal variations and sources of atmospheric aromatic hydrocarbons and organochlorine compounds in a high-altitude city: Evidence from four-year observations. Environ. Pollut. 233, 1188–1197. https://doi.org/10.1016/j.envpol.2017.10.064.

Grote, R., Samson, R., Alonso, R., Amorim, J.H., Cariñanos, P., Churkina, G., Fares, S., Thiec, D.L., Niinemets, Ü., Mikkelsen, T.N., Paoletti, E., Tiwary, A., Calfapietra, C., 2016. Functional traits of urban trees: air pollution mitigation potential. Front. Ecol. Environ 14 (10), 543–550.

Grundström, M., Pleijel, H., 2014. Limited effect of urban tree vegetation on NO_2 and O_3 concentrations near a traffic route. Environ. Pollut. 189, 73–76. https://doi.org/10.1016/j.envpol.2014.02.026.

Gundersen, V., Frivold, L.H., Löfström, I., Jørgensen, B.B., Falck, J., Øyen, B.-H., 2005. Urban woodland management – The case of 13 major Nordic cities. Urban For. Urban Greening 3, 189–202. https://doi.org/10.1016/j.ufug.2005.03.001.

Hannus, S., Hirons, A., Baxter, T., McAllister, H.A., Wiström, B., Sjöman, H., 2021. Intraspecific drought tolerance of Betula pendula genotypes: an evaluation using leaf turgor loss in a botanical collection. Trees 35, 569–581. https://doi.org/10.1007/s00468-020-02059-7.

Harner, T., Su, K., Genualdi, S., Karpowicz, J., Ahrens, L., Mihele, C., Schuster, J., Charland, J.-P., Narayan, J., 2013. Calibration and application of PUF disk passive air samplers for tracking polycyclic aromatic compounds (PACs). Atmos. Environ. 75, 123–128. https://doi.org/10.1016/j.atmosenv.2013.04.012.

Harrison, R.M., Tilling, R., Callén Romero, M.S., Harrad, S., Jarvis, K., 2003. A study of trace metals and polycyclic aromatic hydrocarbons in the roadside environment. Atmos. Environ. 37, 2391–2402. https://doi.org/10.1016/S1352-2310(03)00122-5.

Howsam, M., Jones, K.C., Ineson, P., 2000. PAHs associated with the leaves of three deciduous tree species. I - Concentrations and profiles. Environ. Pollut. 108, 413–424. https://doi.org/10.1016/S0269-7491(99)00195-5.

Howsam, M., Jones, K.C., Ineson, P., 2001. PAHs associated with the leaves of three deciduous tree species. II: uptake during a growing season. Chemosphere 44, 155–164. https://doi.org/10.1016/S0045-6535(00)00268-X.

Huang, S., Dai, C., Zhou, C., Peng, H., Yi, K., Qin, P., Luo, S., Zhang, X., 2018. Comparison of three plant species in accumulating polycyclic aromatic hydrocarbons (PAHs) from the atmosphere: a review. Environ. Sci. Pollut. Res. 25, 16548–16556. https://doi.org/10.1007/s11356-018-2167-z.

Jariyasopit, N., Tung, P., Su, K., Halappanavar, S., Evans, G.J., Su, Y., Khoomrung, S., Harner, T., 2019. Polycyclic aromatic compounds in urban air and associated inhalation cancer risks: a case study targeting distinct source sectors. Environ. Pollut. 252, 1882–1891. https://doi.org/10.1016/j.envpol.2019.06.015.

Johansson, J., Watne, Å.K., Karlsson, P.E., Pihl Karlsson, G., Danielsson, H., Andersson, C., Pleijel, H., 2020. The European heat wave of 2018 and its promotion of the ozone climate penalty in southwest Sweden. Boreal Environ Res. 25, 39–50.

Jouraeva, V.A., Johnson, D.L., Hassett, J.P., Nowak, D.J., 2002. Differences in accumulation of PAHs and metals on the leaves of Tilia x euchlora and Pyrus calleryana. Environ. Pollut. 120, 331–338.

Klingberg, J., Broberg, M., Strandberg, B., Thorsson, P., Pleijel, H., 2017. Influence of urban vegetation on air pollution and noise exposure - A case study in Gothenburg, Sweden. Sci. Total Environ. 599, 1728–1739. https://doi.org/10.1016/j.scitotenv.2017.05.051.

Klingberg, J., Strandberg, B., Sjöman, H., Taube, M., Wallin, G., Pleijel, H., 2022. Polycyclic aromatic hydrocarbon (PAH) accumulation in Quercus palustris and Pinus nigra in the urban landscape of Gothenburg, Sweden. Sci. Total Environ. 805, 150–163. https://doi.org/10.1016/j.scitotenv.2021.150163.

Kylin, H., Sjödin, A., 2003. Accumulation of airborne hexachlorohexanes and DDT in pine needles. Environ. Sci. Technol. 37, 2350–2355. https://doi.org/10.1021/es0201395.

Larcher, W., 2003. Physiological Plant Ecology. Ecophysiology and Stress Physiology of Functional Groups, Springer, Berlin, Heidelberg, New York.

Li, J., Convertino, M., 2021. Inferring ecosystem networks as information flows. Sci. Rep. 11, 7094. https://doi.org/10.1038/s41598-021-86476-9.

Lin, Y. S., Medlyn, B. E., Duursma, R. A., Prentice, I. C., Wang, H., Baig, S., Eamus, D., de Dios, V. R., Mitchell, P., Ellsworth, D. S., Op de Beeck, M., Wallin, G., Uddling, J., Tarvainen, L., Linderson, M. L., Cernusak, L. A., Nippert, J. B:, Ocheltree, T. W., Tissue, D. T., Martin-St Paul, N. K., Rogers, A., Warren, J. M., De Angelis, P., Hikosaka, K., Han, Q., Onoda, Y., Gimeno, T. E., Barton, C. V. M., Bennie, J., Bonal, D., Bosc, A., Löw, M., Macinins-Ng, C., Rey, A., Rowland, L., Setterfield, S. A., Tausz-Posch, S., Zaragoza-Castells, J., Broadmeadow, M. S. J., Drake, J. E., Freeman, M., Ghannoum, O., Hutley, L. B., Kelly, J. W., Kikuzawa, K., Kolari, P., Koyama, K., Limousin, J. M., Meir, P., Lola da Costa, A. C., Mikkelsen, T. N., Salinas, N., Sun, W. and Wingate, L.: Optimal stomatal behaviour around the world, Nature Clim. Change, 5, 459-464, http://www.nature.com/doifinder/10.1038/nclimate2550, 2015.

McLachlan, M.S., 1999. Framework for the interpretation of measurements of SOCs in plants. Environ. Sci. Technol 33, 1799–1804. https://doi.org/10.1021/es980831t.

Murakami, M., Abe, M., Kakumoto, Y., Kawano, H., Fukasawa, H., Saha, M., Takada, H., 2012. Evaluation of ginkgo as a biomonitor of airborne of airborne polycyclic aromatic hydrocarbons. Atmos. Environ. 54, 9–17. https://doi.org/10.1016/j.atmosenv.2012.02.014.

Nowak, D.J., Crane, D.E., Stevens, J.C., 2006. Air pollution removal by urban trees and shrubs in the United States. Urban For. Urban Green. 4, 115–123. https://doi.org/10.1016/j.ufug.2006.01.007.

Odabasi, M., Ozgurenge Falay, E., Tuna, G., Altiok, H., Kara, N., Dumanoglu, Y., Bayram, D., Tolunay, D., Elbir, T., 2015. Biomonitoring the spatial and historical variations of persistent organic pollutants (POPs) in an industrial region. Environ. Sci. Techno. 49, 2105–2114. https://doi.org/10.1021/es506316t.

Pataki, D.E., Carreiro, M.M., Cherrier, J., Grulke, N.E., Jennings, V., Pincetl, S., Pouyat, R.V., Witlow, T.H., Zipperer, W.C., 2011. Coupling biogeochemical cycles in urban environments: ecosystem services, green solutions, and misconceptions. Front. Ecol. Environ. 9, 27–36. https://doi.org/10.1890/090220.

Pianosi, F., Beven, K., Freer, J., Hall, J.W., Rougier, J., Stephenson, D.B., Wagener, T., 2016. Sensitivity analusis of environmental models: a systematic review with practical workflow. Environ. Modell. Software 79, 214–232. https://doi.org/10.1016/j.envsoft.2016.02.008.

Piccardo, M.T., Pala, M., Bonnacurso, B., Stella, A., Redaelli, A., Paola, G., Valerio, F., 2005. Pinus nigra and Pinus pinaster needles as passive samplers of polycyclic aromatic hydrocarbons. Environ. Pollut. 133, 293–301. https://doi.org/10.1016/j.envpol.2004.05.034.

Sæbø, A., Popek, R., Nawrot, B., Hanslin, H.M., Gawronska, H., Gawronski, S.W., 2012. Plant species differences in particulate matter accumulation on leaf surfaces. Sci. Total Environ. 427–428, 347–354. https://doi.org/10.1016/j.scitotenv.2012.03.084.

Seta-Koselska, A., Szczuka, E., Skórzyńska-Polit, E., Domaciuk, M., Giełwanowska, I., 2014. Roadside Larch Trees (Larix Mill.) and Its Female Generative Organs as a Biomonitor of Air Pollution. Polish J. Environ. Stud. 23.

Simonich, S., Hites, R.A., 1994. Vegetation-Atmosphere partitioning of polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 28, 939–943.

Simonich, S.L., Hites, R.A., 1995. Organic pollutant accumulation in vegetation. Environ. Sci. Technol. 29 (12), 2905–2914.

Sindelar, J., 1987. Health and growth of larch (Larix spp.) progeny from open pollination and controlled cross breeding in the Krusne hory Mountains. Prace Vyzkumneho Ustavu Lesniho Hospodarstvi a Myslivosti 70, 68–69. In Czech with English summary.

Sjöberg, K., Lövblad, G., Ferm,M., Ulrich, E., Cecchini, S., Dalstein, L., 2001. Ozone measurements at forest plots using diffusive samplers. International Conference Measuring Air Pollutants by Diffusive Sampling. Montpellier, France, 26–28 September, pp. 116–123.

St-Amand, A.D., Mayer, P.M., Blais, J.M., 2009. Modelling PAH uptake by vegetation from the air using field measurements. Atmos. Environ. 43, 4283–4288. https://doi.org/10.1016/j.atmosenv.2009.06.011.

Stoecklein, M.C., 2001. The Complete Plant Selection Guide for Landscape Design. Purdue University Press, Lafayette, IN.

Terzaghi, E., Wild, E., Zacchello, G., Cerabolini, B.E.L., Jones, K.C., Di Guardo, A., 2013. Forest filer effect: role of leaves in capturing/releasing air particulate matter and its associated PAHs. Atmos. Environ. 74, 378–384. https://doi.org/10.1016/j.atmosenv.2013.04.013.

Viippola, V., Rantalainen, A.L., Yli-Pelkonen, V., Tervo, P., Setälä, H., 2016. Gaseous polycyclic aromatic hydrocarbon concentrations are higher in urban forests than adjacent open areas during summer but not in winter – Exploratory study. Environ. Pollut. 208, 233–240. https://doi.org/10.1016/j.envpol.2015.09.009.

Wagrowski, D.M., Hites, R.A., 1997. Polycyclic aromatic hydrocarbon accumulation in urban, suburban, and urban rural vegetation. Environ. Sci. Technol. 31, 279–282. https://doi.org/10.1021/es960419i.

Wang, J., Bao, H., Zhang, H., Li, J., Hong, H., Wu, F., 2020. Effects of cuticular wax content and specific leaf area on accumulation and partition of PAHs in different tissues of wheat leaf. Environ. Sci. Pollut. Res. 27, 18793–18802. https://doi.org/10.1007/s11356-020-08409-9.

Wang, D., Chen, J., Xu, Z., Qiao, X., Huang, L., 2005. Disappearance of polycyclic hydrocarbons sorbed on surfaces of pine [Pinua thunbergii] needles under irradiation of sunlight: Volatilization and photolysis. Atmos. Environ. 39, 4583–4591. https://doi.org/10.1016/j.atmosenv.2005.04.008.

Wang, Y.Q., Tao, S., Jiao, X.C., Coveney, R.M., Wu, S.P., Xing, B.S., 2008. Polycyclic aromatic hydrocarbons in leaf cuticles and inner tissues of six species of trees in urban Beijing. Environ. Pollut. 151, 158–164. https://doi.org/10.1016/j.envpol.2007.02.005.

Wentworth, G.R., Akliu, Y., Landis, M.S., Hsu, Y.M., 2018. Impacts of a large boreal wildfire on ground level atmospheric concentrations of PAHs, VOCs and ozone. Atm. Env. 178, 19–30. https://doi.org/10.1016/j.atmosenv.2018.01.013.

Wild, E., Dent, J., Thomas, G.O., Jones, K.C., 2005. Real-time visualization and quantification of PAH photodegradation on and within plant leaves. Environ. Sci. Technol. 39, 268–273. https://doi.org/10.1021/es0494196.

Wingfors, H., Sjödin, Å., Haglund, P., Brorström-Lundén, E., 2001. Characterisation and determination of profiles of polycyclic aromatic hydrocarbons in a traffic tunnel in Gothenburg. Sweden. Atmos. Environ. 35, 6361–6369. https://doi.org/10.1016/S1352-2310(01)00389-2.

Winner, W.E., Atkinson, C.J., 1986. Absorption of air pollution by plants, and consequences for growth. Tree 1 (1), 15–18.

Yang, P., Chen, J., Wang, Z., Qiao, X., Cai, X., Tian, F., Ge, L., 2007. Contributions of deposited particles to pine needle polycyclic aromatic hydrocarbons. J. Environ. Monit. 9, 1248–1253. https://doi.org/10.1039/b708508g.

Yang, Q., Luo, T., Yang, J., Chen, H., 2019. PAH accumulation in plant leaves around coal-fired power plants and identification of their potential use as bioindicators. Arch. Environ. Contam. Toxicol. 76, 346–355. https://doi.org/10.1007/s00244-018-0574-2.

Yin, S., Shen, Z., Zhou, P., Zou, X., Che, S., Wang, W., 2011. Qunatifying air pollution attenuation within urban parks: An experimental approach in Shanghai, China. Environ. Pollut. 159, 2155–2163. https://doi.org/10.1016/j.envpol.2011.03.009.

Yli-Pelkonen, V., Setälä, H., Viippola, V., 2017. Urban forests near roads do not reduce gaseous air pollutants concentration but have an impact on particle levels. Landsc. Urban Plan. 158, 39–47. https://doi.org/10.1016/j.landurbplan.2016.09.014.

Zhao, X., He, M., Shang, H., Yu, H., Wang, H., Li, H., Piao, J., Quinto, M., Li, D., 2018. Biomonitoring polycyclic aromatic hydrocarbons by Salix matsudana leaves: A comparison with the relevant air content and evaluation of environmental parameter effects. Atmos. Environ. 181, 47–53. https://doi.org/10.1016/j.atmosenv.2018.03.004.