Polycyclic aromatic hydrocarbon (PAH) accumulation in *Quercus palustris* and *Pinus nigra* in the urban landscape of Gothenburg, Sweden

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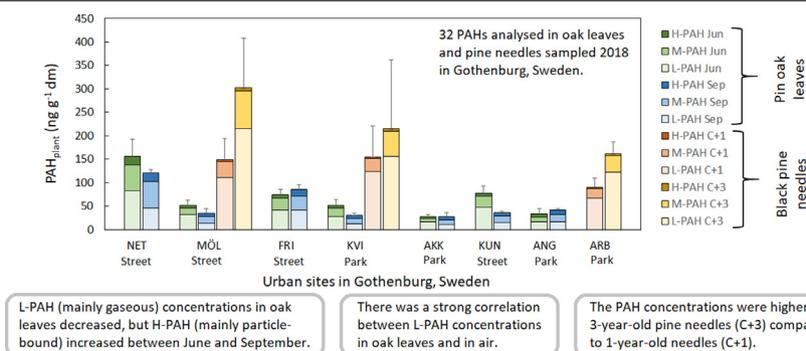[c] Lund University, Division of Occupational and Environmental Medicine, Lund, Sweden
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HIGHLIGHTS

- Gaseous PAH concentration decreased in pin oak leaves between June and September.
- Particulate PAH concentration increased in oak leaves between June and September.
- There was a strong correlation between gaseous PAH concentration in leaves and air.
- PAH concentration increased in 3-year-old black pine needles compared to 1-year-old.
- The choice between mass-based and area-based measuring unit is important.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Trees have the potential to improve urban air quality as leaves and needles capture air pollutants from the air, but further empirical data has been requested to quantify these effects. We measured the concentration of 32 poly-cyclic aromatic hydrocarbons (PAHs) in leaves of pin oak (*Quercus palustris*) and needles of black pine (*Pinus nigra*) in the City of Gothenburg, Sweden, during the summer of 2018. Oak leaves were collected twice (June, September), while one-year-old (C + 1) and three-year-old (C + 3) pine needles were sampled in June to study the temporal development of leaf/needle PAH concentrations. Specific leaf area (SLA) was estimated, which permitted calculation of leaf/needle area-based PAH content that were compared with the mass-based concentration. In addition, the air concentration of PAHs and NO_2 was measured using passive samplers. There was a strong correlation between air concentrations of PAH and NO_2, indicating that the pollutants to a large degree originate from the same sources. In the oak leaves there was a significant decrease in low molecular mass PAHs (L-PAH, mainly gaseous) between June and September, but a significant increase in high molecular mass PAHs (H-PAH, mainly particle-bound). There was a strong correlation between L-PAH concentration in leaves and in air indicating an influence of equilibrium processes between ambient air and leaf. In the pine needles, there was a significant increase of both L-PAH and H-PAH in three-year-old needles compared to one-year-old needles. Pine was superior to oak in accumulating PAHs from the air, especially for L-PAHs when comparing area-based content. However, H-PAH concentrations were higher in oak leaves compared to pine needles on a leaf mass basis, emphasizing the importance of how concentrations are expressed. The results from this study can contribute to the development of urban planning strategies regarding the effect of vegetation on air quality.

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1. Introduction

Although the levels of many air pollutants have declined in Europe in recent decades, air pollution continues to have significant impacts on the health of the European population, especially in urban areas (EEA, 2019). Globally the situation is often worse than in Europe and WHO (2016) has identified air pollution as one of the biggest environmental risks to health.

Outdoor air pollution contributes to the global burden of cancer, especially lung cancer, since the lung receives the largest part of the inhaled doses (IARC, 2013). It is not known what substances contribute most to the cancer risk, but combustion products and their content of polycyclic aromatic hydrocarbons (PAHs) are suspected to play a significant role (Boström et al., 2002; IARC, 2013). PAHs constitute a diverse class of compounds that consist of two or more fused aromatic rings made up of carbon and hydrogen atoms. PAHs range from semi-volatile molecules to molecules with high boiling points and can therefore be found both in gaseous phase and bound to particles in the ambient air (Boström et al., 2002; IARC, 2013). About 500 PAHs have been detected in air, of which the particle-bound benzo(a)pyrene (BaP) is the most well studied and used as an indicator of carcinogenic PAH exposure in the air (Boström et al., 2002; EEA, 2019). In a review including several European and Asian cities Famiyeh et al. (2021) point out that PAH concentrations vary widely and are often exceeding the acceptable air quality guidelines.

Several studies have suggested that urban vegetation and green infrastructure in the built environment has the potential to improve urban air quality (e.g. Nowak et al., 2013; Abhijith et al., 2017; Barwise and Kumar, 2020). Vegetation accumulates atmospheric lipophilic organic pollutants such as PAHs in leaves (Simonich and Hites, 1994a, 1995; Desalme et al., 2013) and methods have been developed to use plant foliage as passive samplers to monitor organic pollutants (Eriksson et al., 1989; Jones et al., 1992; Kylin et al., 1994; Wagrowski and Hites, 1997). In the past few decades, oak and pine species have been commonly used for biomonitoring of airborne PAHs (e.g. Lehndorff and Schwark, 2004; Orecchio, 2007; Sun et al., 2010; De Nicola et al., 2017; Cindoruk et al., 2020; Sari et al., 2020; Eleren and Tasdemir, 2021).

Accumulation of PAHs in vegetation depends on the properties of the accumulating surface and environmental conditions as well as on the properties of the particular PAH (Franzaring, 1997; McLachlan, 1999; Jouraeva et al., 2002). In a study from north-western Spain, De Nicola et al. (2017) compared PAH content in needles of *P. pinaster* and in leaves of *Q. robur* of the same age. Both the investigated species showed a good capacity for uptake of PAHs from the air, as indicated by similar total amounts of PAHs. However, the concentration of 4-, 5- and 6-ring PAHs was higher in *Q. robur* leaves while the concentration of vapor-phase 2- and 3-ring PAHs was higher in *P. pinaster* needles. Generally, conifers have been found to capture larger amounts of particulate matter than broadleaved trees due to their aerodynamic properties with smaller leaves and more complex shoot structures (Freer-Smith et al., 2005). Also important is the time scale, where most conifers do not shed their needles annually and therefore can accumulate air pollutants during longer time periods.

The plant-air partition coefficient (K_{PA}) is defined as the ratio of the equilibrium concentrations in air (C_A) and in the plant (C_P).

$$K_{PA} = \frac{C_A}{C_P} \qquad (1)$$

K_{PA} has been proposed to be proportional to the octanol-air partition coefficient (K_{OA}), assuming that the lipophilic storage compartment of plants behave like octanol (Kömp and McLachlan, 1997). Both K_{PA} and K_{OA} are strongly dependent on temperature (Zhao et al., 2018). The accumulation of semi-volatile organic compounds, such as PAHs, in plants is primarily determined by one of the following processes:

equilibrium partitioning between the vegetation and the gas phase, kinetically limited gaseous deposition, as well as wet and dry particle-bound deposition. For compounds with log $K_{OA} < \sim9$ the equilibrium process is dominating while for PAHs with higher log K_{OA} particle deposition dominates (McLachlan, 1999).

PAH concentrations in leaves are commonly expressed per leaf dry mass. However, the potential to positively affect air quality can be expected to be linked with the area of leaf surface available for gas exchange and particle interception (Nowak et al., 2008; Burkhard et al., 2012; Robinson and Lundholm, 2012). Therefore, it is relevant to express the PAH content both per leaf area and on a unit dry mass basis.

The potential for plant uptake of PAHs is widely acknowledged, but empirical evidence of the effects of this process on local atmospheric PAH concentrations is tenuous (Viippola et al., 2016). The relationship between vegetation and ambient air quality is complex including the processes of dry deposition and atmospheric dispersion. The collective impacts of these processes are context dependent, e.g. dependent on geographical scale, type of pollutant and vegetation characteristics (Janhäll, 2015; Salmond et al., 2016; Barwise and Kumar, 2020) and a need for further empirical data to assess the importance of urban vegetation in the removal of air pollutants has been recognized.

Rising awareness of the potential toxicity of PAHs to human health promotes an increased understanding of its spatial distribution pattern in cities (Yin et al., 2020). There is an increasing interest in using vegetation and trees to provide ecosystem services including urban air pollution mitigation. A successful use of this strategy requires qualitative and quantitative information regarding the degree of pollutant accumulation in the leaves in relation to the air concentration (e.g. St-Amand et al., 2009; Zhao et al., 2018). Measurements of PAH concentrations in air and leaves in parallel under outdoor urban conditions, as in this study, contributes empirical data needed to quantify the effects of urban greenery on PAH concentrations. In addition, variation of the PAH concentration over the urban landscape is quantified using both passive air samplers and leaves. Such knowledge can contribute to sustainable urban planning strategies, effective biomonitoring and estimations of human exposure risks to carcinogenic pollutants.

The objectives of this study were to 1) quantify the PAH and NO_2 air concentration variation in the urban landscape of a high latitude city, here represented by Gothenburg, Sweden, and compare with PAH concentrations in leaves/needles of trees; 2) compare the accumulation of gaseous and particle-bound PAHs in leaves of pin oak (*Quercus palustris*) and needles of black pine (*Pinus nigra*) including the importance of K_{OA} for PAH accumulation; and 3) assess the significance of mass-based compared to area-based plant tissue concentrations. Our hypotheses were:

1. NO_2 and PAH concentrations in the air co-vary over the urban landscape.
2. There is a net accumulation of both gaseous and particle-bound PAHs in pin oak leaves and black pine needles over time.
3. Pine needles are superior to oak leaves in accumulating PAHs.
4. The accumulation of semi-volatile (gaseous phase) PAHs in leaves depend on the physical properties of the respective PAH, in particular the octanol-air partition coefficient (K_{OA}).

2. Materials and methods

2.1. Sampling strategy and study area

To reach our objectives, we measured PAH concentration in leaves of pin oak (*Quercus palustris*) sampled early and late in the growing season (in June when the leaves were fully developed and in September short before leaf senescence started) 2018 at seven street and park sites in the City of Gothenburg, Sweden. Black pine (*Pinus nigra*) needles of two age classes (one-year-old, C + 1 and three-year old, C + 3, where C denotes current year) were sampled in June at three sites to

investigate the PAH accumulation over a two-year time span. The sites were chosen to attain a wide range of pollution levels, using the City of Gothenburg Environmental Administration's air quality map from 2015 (City of Gothenburg, 2015). In addition, air concentration of PAHs (PAH$_{air}$) and NO$_2$ were measured. See Table 1 for further details of the study sites.

The City of Gothenburg (57°42′N, 11°58′E) is located on the west coast of Sweden. It is the second largest city in Sweden with approximately 600,000 inhabitants (SCB, 2018). 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 May and defoliate in October.

2.2. PAH compounds studied

32 PAH compounds were included in the study, 18 parent PAHs and among them 15 US EPA priority PAHs and 14 alkylated species. All analyzed PAHs are presented in Table S1 in the supplementary material. The concentration of these compounds was determined in both plant and air samples. The following four PAH categories are highlighted in this paper; SUM-PAH refers to the sum of the 32 PAH compounds included, L-PAHs refers to low molecular mass PAHs (>90% in gaseous phase), M-PAHs refers to intermediate (medium) PAHs (fractions in both gaseous and particulate phases) and H-PAHs refers to particle bound, high molecular mass PAHs (>90% on particles). See Table S2 for more details on which PAHs are included in the different categories, their molecular mass and number of benzene rings.

2.3. Collection and preparation of leaf and needle samples

Leaves and needles were sampled from three trees, considered as replicates, at each of the sites during 26-28 June and 19-20 September 2018. A pruning pole was used to cut branches from the outer part of the sun exposed crown at a height of about 5 m, except for the taller

pine trees in the Arboretum where about 15 meter collection height was used. The difference in sampling height was not considered to influence the comparison significantly, due to the large distance to emission sources in the Arboretum in combination with the rough tree canopy, facilitating good vertical mixing and thus small vertical variation in uptake. The oak leaves and pine shoots (C + 1 and C + 3) were cut from the branch with care taken to avoid touching the leaves/needles. The samples were packed in polyethylene plastic bags and transported to lab in a cool bag. Pine needles were removed from the shoot. Leaves and needles were stored in polyethylene plastic bags wrapped in aluminium foil for light protection in a freezer (-18 °C) in wait for PAH analysis.

A sub-sample was used to determine specific leaf area (SLA) for leaves and needles which was later used to convert PAH content in the plant tissue from a mass-based unit (ng g^{-1} dry mass) to an area-based unit (μg m^{-2}). Six leaves from each oak tree were randomly selected to be used for determination of SLA. Two 13 mm in diameter or four 8 mm in diameter leaf discs were collected per leaf depending on leaf size, using a puncher, resulting in 12 or 24 discs from each tree that were put in aluminium foil envelopes. The discs were dried in 70 °C for at least 48 h and weighed (laboratory balance Sartorius type 1872, Germany; resolution 0.0001) to determine SLA for dry mass (dm). For pine, 20 needles were randomly collected from three different shoots from each tree and each age class. The needles were scanned to determine total projected area using WinSEEDLE (plant image analysis scanner and software from Regent Instruments Inc., Canada; version Pro 5.1a). Thereafter the needles were dried and weighed using the same procedure as for oak to determine needle SLA.

2.4. PAH and NO$_2$ air concentration measurements

PAH$_{air}$ and NO$_2$ were measured at 2.5 m above ground using passive sampling techniques. The samplers were placed underneath the tree crowns at each site approximately one month (30-34 days depending

Table 1
Name, location, description of the study sites and where the tree species pin oak (*Quercus palustris*) and black pine (*Pinus nigra*) were sampled, respectively. Average tree height is given within brackets. The sites are ordered from most to least polluted based on the expected relative pollution level in the City of Gothenburg.

Site ID	Location	Expected pollution level	Tree species sampled	Description
NET	57° 42′ 43″ N 11° 58′ 22″ E	Very high	Oak (7 m)	Central station in the center of town: Nils Ericsson terminalen Street trees situated right in the center of the city, at a roundabout entering the central station (train and bus). In the direct vicinity of a building construction area and close to a large road construction area.
MÖL	57° 41′ 21″ N 11° 59′ 42″ E	High	Oak (12 m) and pine (9 m)	Urban street: Mölndalsvägen Street trees directly beside a road with traffic-lights nearby causing acceleration and deceleration. The site is about 2.5 km from the city center.
FRI	57° 43′ 08″ N 11° 57′ 44″ E	High	Oak (10 m)	Urban traffic route: Frihamnen Street trees about 50 m from a large traffic route through the city. Close by passes transports to part of the Gothenburg harbor. Poor soil conditions.
KVI	57° 43′ 33″ N 11° 56′ 58″ E	High	Oak (7 m) and pine (7 m)	Urban park: Kvillebäcksparken A newly built park about 1.5 km north of the city center, with lawns, young trees and a playground beside a residential area with 6- to 10-storey apartment buildings. Close by is a shopping area with large parking lots and a highly trafficked city street.
AKK	57° 45′ 07″ N 11° 59′ 07″ E	Moderate	Oak (11 m)	Suburban residential area: Akkas gata A green yard surrounded by 3-storey apartment buildings. Mainly large lawns with a few trees, paved paths and a tennis-court. No traffic directly nearby.
KUN	57° 41′ 02″ N 11° 55′ 37″ E	Moderate	Oak (11 m)	Urban residential street: Kungsladugårdsgatan Street trees in an urban residential area with 3-storey building about 3.5 km from the city center.
ANG	57° 47′ 43″ N 12° 03′ 27″ E	Low	Oak (6 m)	Peri-urban park: Angereds stadspark A park situated in the outskirts of Gothenburg with large open grass fields with a few trees, playground and paved paths. No traffic directly nearby. The *Quercus palustris* were recently moved to the park and did not establish as fast as expected and were therefore not in the best shape.
ARB	57° 40′ 31″ N 11° 57′ 12″ E	Low	Pine (20 m)	Gothenburg Botanical Garden Arboretum The Arboretum is situated approximately 4 km from the city center. It is surrounded by and partly overlapping with a nature reserve. It is about 800 m to the closest traffic route.

on site) prior to the day of leaf and needle sampling. At two sites (the Botanical Garden Arboretum; ARB and in the center of Gothenburg; NET), PAH_{air} and NO_2 concentrations were measured for the entire summer, i.e. during four approximately one-month long measurement periods, compared to two measurement periods at the other six sites. See Table S3 in the supplementary material for further details of the measurement periods such as start and stop time, average NO_2 concentration and weather conditions.

PAH_{air} was measured using PUF (polyurethane foam) disc samplers (14 cm in diameter, 1.2 cm thickness, surface area 360 cm^2, density 0.035 g cm^{-3}, Klaus Ziemer GmbH, Germany) housed in two stainless steel domes (Tisch Environmental, Inc., OH, USA). This sampler design has been calibrated for both gaseous and particulate associated PAH compounds including alkylated species (Harner et al., 2013; Bohlin et al., 2014). Prior to deployment, the PUF discs were precleaned by Soxhlet extraction for 24 h using dichloromethane (DCM), dried under vacuum and stored in multiple layers of solvent rinsed aluminium foil inside airtight polyethylene zip bags.

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). The technique is based on molecular diffusion of gases. The sample analysis was made by the IVL accredited laboratory (www.ivl.se).

2.5. PAH-analysis of PUFs (air) and plant tissues

The plant samples were taken from the freezer and allowed to condition at room temperature for 2-3 h. Two sub-samples of about 5-7 g wet mass were taken, one part for analysis of PAH and the other for dry mass determination. The dry mass was determined by weighing (a laboratory balance, Mettler Toledo) before and after heating at 100 °C for two days in an oven (Nabertherm GmbH, Germany) (Piccardo et al., 2005).

All samples, PUFs and plant tissue, were extracted and cleaned up following the procedure used earlier for the PUF (Bohlin et al., 2008) with some modifications. Details of sample extraction, clean-up and analysis are presented in the supplementary material. In short, prior to extraction, the samples were spiked with internal standard (IS) containing deuterated US EPA 16 PAHs. Samples were extracted using a Dionex ASE 350 Accelerated Solvent Extractor (Thermo Fisher Scientific, Inc. MA, USA) equipment using dichloromethane as solvent. The plant tissue samples were then cleaned in a dialysis procedure using a semipermeable membrane (SPM) (ExposMeter AB, Umeå, Sweden) with n-hexane as solvent (Strandberg et al., 1998). This SPM method can detach organic contaminants such as PAHs from larger molecules such as lipids/waxes in a sample. The membrane pore size is ca 10 Å and molecules bigger than this size cannot penetrate the film in the dialytic procedure, although it allows smaller molecules through. Finally, all samples were purified with an open adsorption column containing silica (SiO$_2$) and aluminium oxide with a solvent mixture consisting of n-hexane and dichloromethane (Strandberg et al., 1998). All PAH compounds were separated and detected by means of high-resolution gas chromatography/low resolution mass spectrometry Agilent 5975C connected to a 7890A GC (GC/MS) (Agilent Technologies, Inc., Santa Clara, CA, USA). The method is assured with native mixtures of all analyzed substances.

The published uptake rates by Bohlin et al. (2014) were used to quantify air concentrations of 15 US EPA PAHs. 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, and was therefore excluded from the SUM-PAHs. The alkylated PAHs were quantified using published uptake rates by Harner et al. (2013) or using the uptake rates for a corresponding US EPA PAH compound.

2.6. Quality control of PAH analysis

PAH_{air} (PUF) duplicate sampling was performed at two sites, ARB and NET to evaluate the precision of the samplers. For the plant samples, both oak and pine, one of the samples were analyzed in triplicate. Good precision is realized for all replicates, PUF and plant samples, of both the gaseous (precision: <10%) and particle bound (precision: 10-30%) PAHs. More information about the replicate PUF comparisons is shown in Table S4 in the supplementary material.

Blanks, three PUF field blanks and six laboratory blanks were analyzed in parallel with the samples to estimate the residual levels of target compounds. The PUF field blanks were brought to the field sampling sites, but remained unopened during the measurement campaigns. Minor residues of some 2-4 ringed PAHs occurred in the blanks, however the amount occurring was <15% of the amount present in the samples. PUF field blanks were used for correcting PUF results and laboratory blanks were used for correcting plant tissue results. Consistent internal standard recoveries (50-120%) were obtained for all (plant tissue and PUF) samples. We could not observe any difference in recovery between sample types. The limits of detection were calculated as three times the standard deviation of the values for the field and laboratory blanks or the background noise of these blanks. The limit of detections (LODs) obtained from the field blanks were used for the PUF and the laboratory blanks for the plant tissue results, respectively. A certified reference material (SRM 1649a urban dust) was used as quality control (QC). The measured levels of 13 PAHs lie, for most part, within 30% of the certified levels.

2.7. Statistical analysis

A paired t-test was used to detect statistically significant differences in PAH_{air} and NO_2 concentrations between the measurement periods in June and September. Linear regression was used to detect possible relationships between NO_2 and PAH concentrations in air, PAH concentrations in air and leaf as well as between the ratio of PAH concentrations between plant and air and the PAH physical property log K_{OA}, which is the 10-logarithm of the concentration ratio between octanol and air.

Differences between sites and concentration changes over time were investigated using a mixed designed analysis of variance (ANOVA) with IBM SPSS Statistics (version 25). Leaf age (June and September for oak and age class C + 1 and C + 3 for pine, respectively) was set to the within-subjects variable (repeated measures) with two levels. The between-subjects factor was set to site in Gothenburg City. p-values < 0.05 were considered to indicate statistically significant differences.

The number of plant and air samples below PAH detection limit can be seen in Table S2 in the supplementary material. If one or two of the three plant samples per site were above detection limit, the value (s) below detection limit were set to half the detection limit. If the concentration in all three plant samples from a specific site and time period were below detection limit, the values were set to zero. The PAH_{air} measurements were in most cases only one sample per site and time period. If more than half of the total number of samples was below the detection limit for a specific compound the values were set to zero for all sites and time periods. This applied only to two compounds (2-methylnaphthalene and dibenzo(a,h)anthracene). The rest of the values below detection limit were set to half the detection limit.

3. Results

3.1. Air concentrations of NO_2 and PAH

A four-fold difference in the air concentrations of NO_2 (Fig. 1a) and a ten-fold difference in concentrations of PAH_{air} (Fig. 1b) was observed across the urban landscape of Gothenburg. The NO_2 concentrations ranged from 20 μg m^{-3} at the most polluted site (NET) to 5 μg m^{-3} at
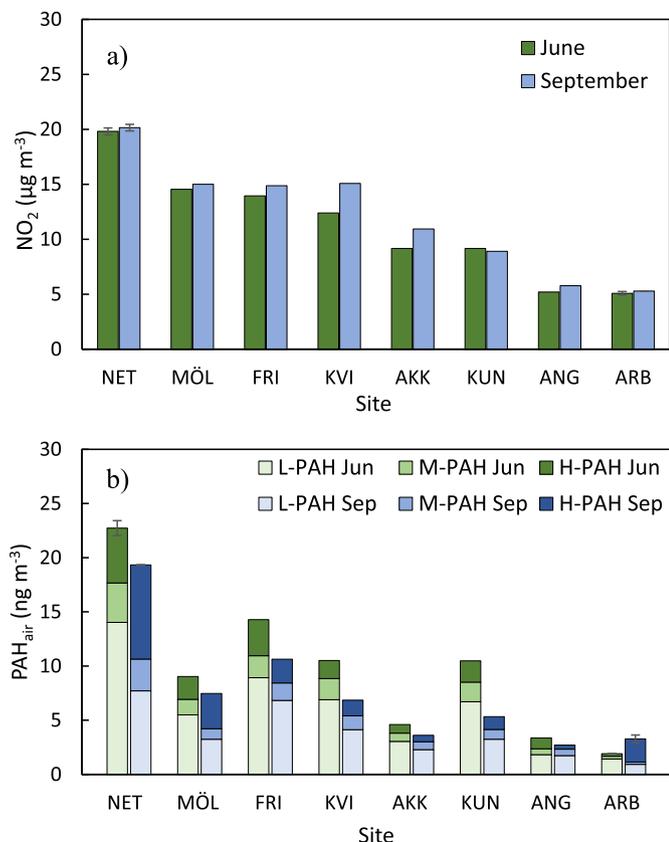
Fig. 1. Air concentrations of NO$_2$ (a) and PAH (b) during the June (green/left bars) and September (blue/right bars) measurement period 2018 at the eight sites in Gothenburg. L-PAH refers to low molecular mass PAHs, M-PAH medium PAHs and H-PAH high molecular mass PAHs. The sites are ordered from the highest (NET) to lowest (ARB) average NO$_2$ concentration. Error bars show standard deviation of NO$_2$ and SUM-PAH$_{air}$ (only applicable to the NET and ARB sites where duplicate measurements were performed), where SUM-PAH refers to the sum of all PAH compounds included. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
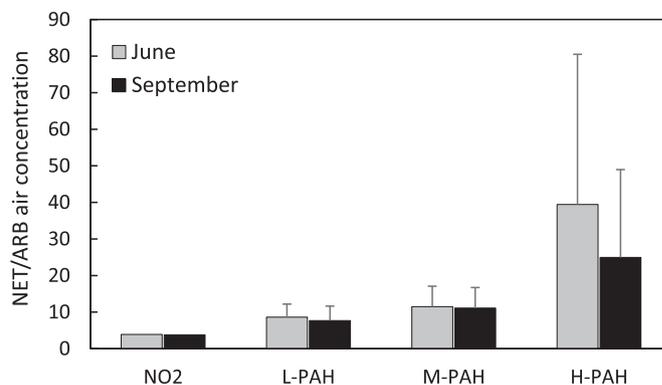

Fig. 2. The ratios of air concentration of the individual 32 PAH compounds included in the study at the most polluted site (NET) and the clean site (ARB), averaged for the PAH categories L-PAH$_{air}$, M-PAH$_{air}$ and H-PAH$_{air}$ for June and September. NO$_2$ is also included for comparison. Error bars show standard deviation. For abbreviations, see Fig. 1.

included in the group. However, for H-PAH$_{air}$ the average ratio was larger in June (39) compared to September (25), when calculated in this way. Also, the standard deviation was much larger for H-PAH$_{air}$ compared to L-PAH$_{air}$ and M-PAH$_{air}$. Small variations in the low concentrations at the clean site ARB have a large influence on the ratio calculations and this was especially apparent for the particle-bound H-PAHs. The sum of H-PAH concentrations was a more robust metric than the concentration of individual H-PAH compounds and therefore used in the presentation of data.

There were strong, positive correlations ($R^2 > 0.59$, $p < 0.001$) for air concentrations of all PAH-groups with NO$_2$ concentrations (Fig. 3). The NO$_2$ concentration explained 73% of the variation in SUM-PAH$_{air}$. The strength of the relationship with NO$_2$ concentration was similar for the different PAH categories. The strong correlation between these pollutants indicates common emission sources.

3.2. PAH concentration in leaves and needles

Fig. 4 shows the PAH concentration in pin oak leaves at the seven different sites during June and September. There was a significant difference in concentration for all PAH categories between sites for the samples of oak leaves. For SUM-PAH, the leaf concentration at the most polluted site was about five times higher compared to the least polluted site. NET was the most polluted site and AKK the least polluted
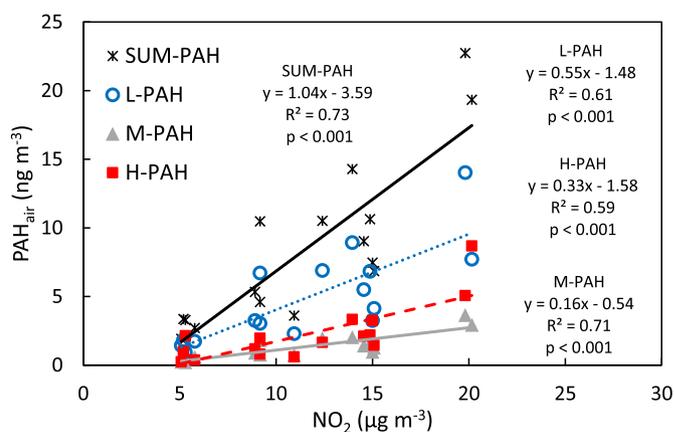
the least polluted site (ARB). The NO$_2$ concentration was significantly higher in September compared to June according to a paired t-test ($p = 0.042$). The SUM-PAH$_{air}$ concentration ranged from 23 ng m^{-3} at the most polluted site (NET) to 2 ng m^{-3} at the least polluted site (ARB) in June. The ratio, based on the sum of all compounds included in the group, between the PAH$_{air}$ concentrations at the most polluted and least polluted site was 9 for L-PAH$_{air}$, 14 for M-PAH$_{air}$, and 22 for H-PAH$_{air}$. In general, the PAH$_{air}$ concentrations decreased from the urban to the suburban sites in a similar way as NO$_2$. The site AKK in a suburban residential area did not have any traffic in the direct vicinity and had lower concentrations compared to the street site KUN. The site MÖL had lower PAH concentrations than expected considering its location directly beside a road (see Table 1). L-PAH constituted the largest part of SUM-PAH, on average 64% in June and 53% in September. Phenanthrene was the most abundant PAH in air (18–38%). SUM-PAH$_{air}$, L-PAH$_{air}$ and M-PAH$_{air}$ were significantly lower in September compared to June ($p = 0.021$, $p = 0.015$ and $p = 0.017$, respectively, based on a paired t-test), but there was no statistically significant difference in H-PAH$_{air}$ between June and September ($p = 0.45$).

The ratio between the most polluted site NET and the clean site ARB was also calculated separately for each of the 32 PAH compounds included in the study and then averaged for the different PAH categories (Fig. 2). For L-PAH$_{air}$ and M-PAH$_{air}$ the ratio was similar in June and September both when calculated as an average of the individual compound ratios and as the ratio based on the sum of all compounds

Fig. 3. Relationships of SUM-PAH$_{air}$ (solid black line), L-PAH$_{air}$ (dotted line), M-PAH$_{air}$ (solid grey line) and H-PAH$_{air}$ (dashed line) with NO$_2$ concentration during the June and September measurement periods for all sites. For abbreviations, see Fig. 1.
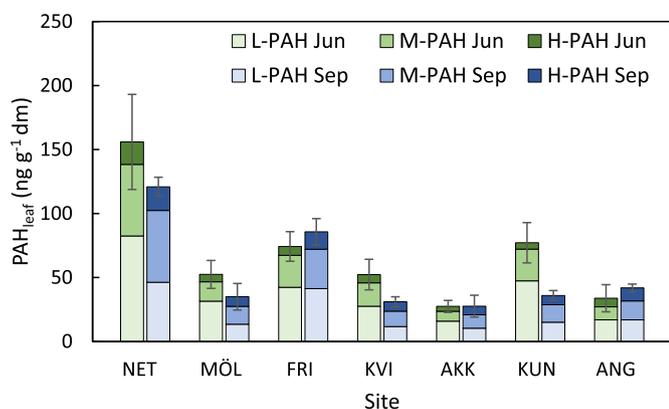
Fig. 4. PAH concentration (ng g^{-1} dry mass) in pin oak leaves at seven sites in Gothenburg in June (green/left bars) and September (blue/right bars) 2018. Error bars show standard deviation of SUM-PAH between the three replicate trees at each site. For abbreviations, see Fig. 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. PAH concentrations (ng g^{-1} dry mass) in one-year-old (C + 1, green/left bars) and three-year-old (C + 3, blue/right bars) pine needles at three different sites in Gothenburg sampled in June 2018. Error bars show standard deviation of SUM-PAH between the three replicate trees at each site. For abbreviations, see Fig. 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

site with respect to PAH concentration in pin oak leaves. On average 56% in June and 40% in September of the SUM-PAH was L-PAH and 12% in June and 21% in September was H-PAH. Phenanthrene was the most abundant PAH in the pin oak leaves (22–42%). For SUM-PAH and L-PAH there was a significant decrease in concentration between June and September (−20% and −41%, respectively), but for H-PAH there was a significant increase (36%). The details of the ANOVA statistics are summarized in Table S5 in the supplementary material.

The L-PAH and M-PAH concentration in oak leaves were strongly and significantly correlated with the air concentration ($R^2 = 0.89$ and $R^2 = 0.85$, respectively; $p < 0.001$) when combining data from the two sampling periods (Fig. 5). The PAH$_{air}$ concentration explained almost 90% of the variation in the PAH$_{leaf}$ concentration for L-PAH and M-PAH indicating a large influence of equilibrium processes between air and leaf, in a similar way as it is for PUF. The correlation was weaker for H-PAH ($p = 0.053$).

Fig. 6 shows the PAH concentration in black pine needles at the three different sites for one-year-old and three-year-old needles (age classes C + 1 and C + 3). Generally, the concentrations in the needles were higher than in the pin oak leaves. However, the needles are older and therefore not directly comparable with respect to accumulation rate. On average 77% in C + 1 needles and 73% in C + 3 needles of the SUM-PAH was L-PAH and 3% in C + 1 needles and 2% in C + 3 needles was H-PAH. Phenanthrene was the most abundant PAH in the black
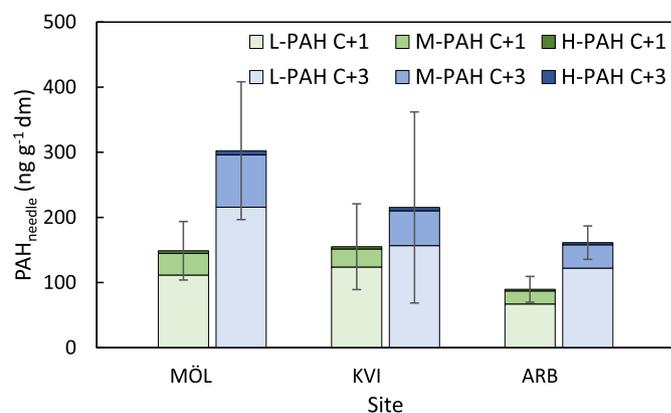
pine needles (53–60%). There was a significant difference only in H-PAH concentration between sites for black pine needles ($p = 0.009$). For SUM-PAH the concentration at the most polluted site was less than two times higher than at the least polluted site. This PAH pattern is consistent with the PAH$_{air}$ (PUF) results for the three sites, although the relative differences in PAH$_{air}$ between sites were larger (Fig. 1). Thus, accumulation in pine needles can accurately reflect differences in PAH levels in the air. Moreover, there was a significant increase in concentration between the needle age classes C + 1 and C + 3 for all PAH groups, 73% increase for SUM-PAH, 63% for L-PAH, 110% for M-PAH and 50% for H-PAH. The details of the ANOVA statistics are summarized in Table S6 in the supplementary material.

3.3. Comparison of PAH accumulation potential between oak leaves and pine needles

The specific leaf area (SLA) for oak and pine was similar between sites. SLA for oak was on average 14.1 ± 0.9 m^2 kg^{-1} (±standard deviation) in June and 13.7 ± 0.6 in September and SLA for pine was 2.5 ± 0.2 m^2 kg^{-1} in one-year-old needles and 2.4 ± 0.2 in three-year-old needles. The SLA values were used to convert PAH concentrations in leaves and needles from a mass-based unit (ng g^{-1} dry mass) to an area-based unit (µg m^{-2}).

At two sites both oak and pine were sampled, and their PAH concentrations were compared (Fig. 7). For oak the September PAH content were considered to represent the uptake during one growing season, since the sampling was made short before senescence and shedding of leaves, and compared to the pine C + 3 PAH content divided by three. The C + 3 needles collected by the end of June are marginally older than three years. As can be noted on the different scales on the x-axis in Fig. 7, the contrast was larger for the gaseous phase L-PAH compared to the particulate phase H-PAH. On average the SUM-PAH content were higher in pine needles than in oak leaves (ratio > 1), regardless if expressed on mass or area basis (ng g^{-1} dry mass or µg m^{-2}). When using the area-based unit pine was even more superior to oak (around 16 times larger accumulation vs 3 times higher for mass-based SUM-PAH concentration). Furthermore, dividing the PAH compounds into L-PAH, M-PAH and H-PAH showed that regarding H-PAHs, which species had the highest PAH content depended on the units used to express concentration. The concentration of H-PAH was higher in oak leaves than in pine needles when expressed per unit mass (ratio < 1).

The SUM-PAH concentrations in oak leaves were strongly and significantly ($p < 0.001$) correlated to the SUM-PAH air concentrations both
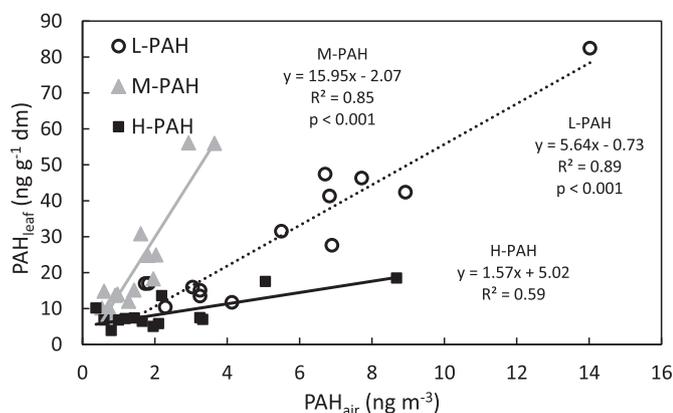

Fig. 5. PAH concentration (ng g^{-1} dry mass) in pin oak leaves in relation to PAH$_{air}$ concentration for the June and September measurement periods. For abbreviations, see Fig. 1.
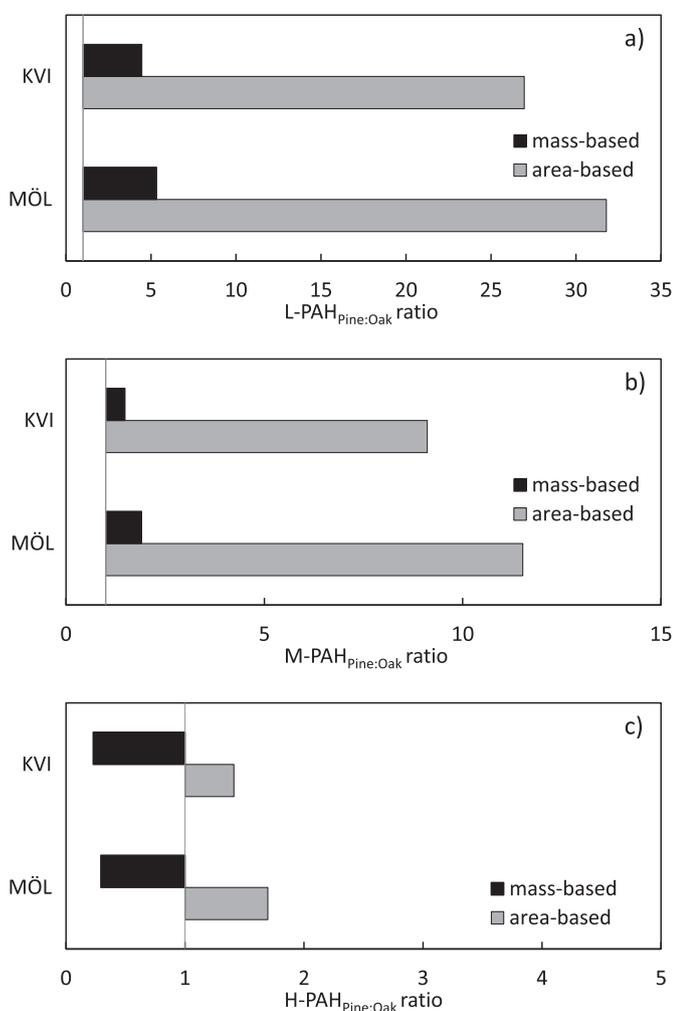
Fig. 7. The mass-based (ng g^{-1} dry mass) and area-based (μg m^{-2}) ratio between pine (C + 3 June)/3 and oak (September) PAH content (i.e. pine/oak) at the sites MÖL and KVI for a) L-PAH, b) M-PAH and c) H-PAH. The grey vertical line shows the ratio 1, representing pine needles and oak leaves having the same PAH accumulation. Note the different scales on the x-axis. For abbreviations, see Fig. 1.

for the mass-based concentration ($R^2 = 0.89$) and area-based concentration ($R^2 = 0.90$).

3.4. Influence of physical properties of PAH on accumulation in leaves/needles

The ratio of PAH concentrations between plant and air was used as a simple way of expressing the accumulation in plant tissue in relation to ambient air and compared to log K_{OA} (Fig. 8). Log K_{OA} values for six PAHs, representing a broad spectrum of physio-chemical properties, were selected covering values from 6.31 to 8.88 (see Table S2). The plant to air concentration ratio was significantly correlated to log K_{OA} ($p < 0.019$). Log K_{OA} explained more than 90% of the variation in the leaf to air ratio for pin oak and more than 70% of the variation for black pine.

4. Discussion

4.1. Air concentrations of PAH and NO_2

We found a clear difference in NO_2 and PAH$_{air}$ (passive PUF air samples) concentration levels between the sites, ranging from the less polluted peri-urban park (ANG) and Arboretum (ARB) to the heavily
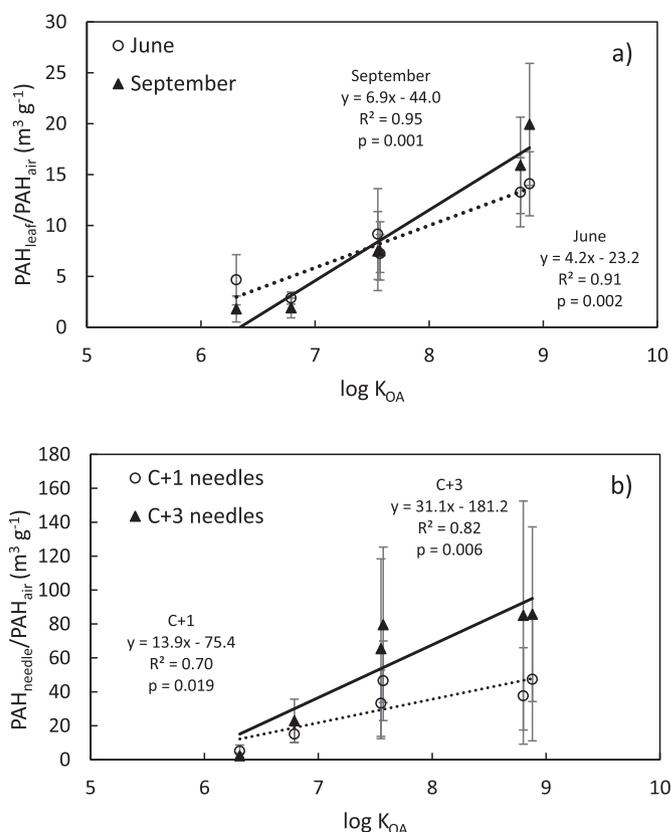

Fig. 8. The relationship between the ratio of PAH in leaf to air (a) and needle to air (b) and log K_{OA} (octanol-air coefficient). Values of PAH content in plant tissue used were in unit per mass (ng g^{-2} dry mass). Error bars show standard deviation (three trees per site and time period). Oak leaves were sampled in June and September, one-year-old (C + 1) and three-year-old (C + 3) pine needles were sampled in June.

polluted site close to the central station (NET) in the center of the City of Gothenburg (for site descriptions, see Table 1). The average NO_2 concentration was comparable to the concentrations received in the two Finnish cities Helsinki and Lahiti (Setälä et al., 2013). The PAH$_{air}$ concentrations were similar to less polluted locations in Europe as measured by Jaward et al. (2004) and Bohlin et al. (2008) using the same type of passive sampler.

The variation among sites was larger for PAH$_{air}$ than NO_2, as also observed by Klingberg et al. (2017). Two processes contribute to this pattern: 1) long range transport of NO_2 contributes significantly to the elevated urban background NO_2 concentrations and 2) NO_2 is to a substantial extent produced as a secondary pollutant from car exhaust emissions of NO that react with O_3 in the atmosphere (Rodes and Holland, 1981), a fast but not instantaneous reaction making the distribution of NO_2 over the urban landscape less tightly connected to sources. This tends to reduce the NO_2 concentration differences between more and less traffic polluted parts of a city. H-PAH showed the largest between site variation. The particle-bound PAHs, especially the larger particles, may have a short life-time in the atmosphere (Janhäll, 2015), which would promote a stronger elevation near major emission sources and therefore also a larger spatial variation, but further investigations are needed to draw a confident conclusion about the cause of the large H-PAH variation.

It is important to point out that the PUF sampler works best for gaseous-phase compounds (Bohlin et al., 2014). The uptake-rates of particulate PAH are dependent on differences in aerosol conditions e.g. amount, size and type of particles and to what particle fraction the PAHs are associated. Particulate PAHs are observed predominantly in fractions of fine particles with a diameter ranging between 0.01 and

0.5 μm (Boström et al., 2002). This fine particle fraction diffuses as gaseous phase substances and is taken up in PUF at a similar rate (Melymuk et al., 2014). If PAH is also present on larger particles, this may affect the accuracy of determining H-PAH. It cannot be ruled out that this has to some extent affected the H-PAH results in this study. Also, differences in aerosol particle content between sampling sites could be a reason for the large standard deviation for H-PAH$_{air}$ shown in Fig. 2.

There was a strong correlation between NO$_2$ and PAH$_{air}$ concentrations (r = 0.85 for NO$_2$ and SUM-PAH), indicating common emission sources, i.e. traffic, and supporting our first hypothesis. Air concentrations of NO$_2$ is routinely monitored and often used as a proxy for other air pollutants. High concentrations of NO$_2$ imply high levels of PAH. However, an important conclusion of our study is that observations of NO$_2$ will underestimate the difference in levels of PAH, especially H-PAH, between less polluted and highly polluted parts of a city. Thus, NO$_2$ should not be used uncritically as an indicator of the air pollution situation as pointed out also by Grundström et al. (2015) comparing NO$_2$ and particle pollution. The difference in pollution level between different sites may be stronger than what NO$_2$ indicates.

4.2. PAH concentration in leaves and needles

As for PAH$_{air}$, there was a pronounced variation in leaf and needle PAH concentration levels between sampling locations, reflecting the local air pollution levels. Remarkably, leaves act like sensitive passive air samplers and can thus reflect small differences in concentration between urban sites, confirming the significant potential for biomonitoring (Jones et al., 1992; Lehndorff and Schwark, 2004; De Nicola et al., 2011).

There was an increase in concentration of H-PAH in the oak leaves from June to September, supporting our second hypothesis for particle-bound PAHs, but a significant decrease in L-PAH, i.e. the opposite of what we hypothesized for gaseous PAHs. Vegetation has been suggested to play a bigger role in removing higher molecular mass PAHs than the lower molecular mass from the atmosphere, due to their higher lipophilicity (Simonich and Hites, 1994a). In addition, the vegetation-atmosphere partitioning of PAHs is temperature dependant. At low ambient temperatures (spring and fall) gaseous phase PAH partition into the waxy surface of vegetation, and at high ambient temperatures (summer) some PAH volatilize and return to the atmosphere (Simonich and Hites, 1994b).

The summer of 2018 was unusually warm and dry in northern Europe, including the Gothenburg region (Bastos et al., 2020). The decrease in L-PAH as observed between June and September, may be due to the equilibrium being shifted, and thus a net outflow has occurred, instead of uptake. The K$_{OA}$ values for H-PAH are so high that they were not affected by the equilibrium shift caused by the high temperatures during the summer months, and thus there was a net uptake. The results from our study provide empirical data that agree with the theoretical consideration based on K$_{OA}$. Similar seasonal variations of the PAH concentrations in leaves, with decreasing concentrations in the warm summer season, have been shown by Franzaring (1997) at an urban site in Germany and by Zhao et al. (2018) at an urban site in China.

The analysis of the pine needles showed that for longer time spans (comparing one-year-old and three-year-old needles) there was a net accumulation of both L-PAH (63% increase) and H-PAH (50% increase). Interestingly, the M-PAH concentrations show the highest increase (110%) in the pine needles. One interpretation could be that since M-PAH can exist both in gas phase and as particle-bound the M-PAHs have two parallel deposition pathways, both uptake via stomata and as deposition on the cuticle with particles. The M-PAHs combination of molecular size (smaller than H-PAH) and lipophilicity (higher than L-PAH) might be optimal for accumulation.

A study by Wild et al. (2005) suggested that PAH photodegradation on vegetation may be an important loss mechanism. To what extent is difficult to estimate due to the highly complex compound fate in vegetation.

The exposure to sunlight varies and once a compound penetrates into the leaf it becomes more protected from photodegradation. Also, particle-bound PAHs may be protected while residing upon the particles.

The leaves and needles were not washed prior to PAH analysis. The results from this study show the total amount of H-PAHs on the leaves, both dissolved and in particulate phase, and could imply a slight overestimation of PAH concentrations compared to studies investigating the dissolved PAH fraction. Rainfall the days before the second measurement period (September) could potentially have washed off particles from the leaves and influenced the H-PAH concentration difference in oak leaves between June and September. However, De Nicola et al. (2008) found no difference in PAH concentrations between unwashed and water-washed *Quercus ilex* L. leaves collected in Naples, Italy, suggesting this process being of limited importance for PAHs. This could be explained by a rapid transfer of particle-bound PAHs from the leaf surface to the inner leaf wax layer, as suggested by Lehndorff and Schwark (2004), where they are physically protected from wash off.

4.3. Comparison of PAH accumulation potential between oak leaves and pine needles

In a study from the UK, Freer-Smith et al. (2005) investigated the effects of particle size on the deposition velocity of particles to five urban tree species (coniferous and broadleaved). They showed that the deposition velocity was greater for ultra-fine particles than for fine and coarse particles and that conifers capture larger amounts of particulate matter than broadleaved trees. It was explained by the aerodynamic properties of conifers with smaller leaves and more complex shoot structures (Beckett et al., 2000). In a review of appropriate plant species selection for urban air pollution abatement Barwise and Kumar (2020) summarize that it is currently unclear which surface feature of different leaf types (broadleaf, needle-like, etc.) are the most influential for the removal of individual pollutants.

In our study the PAH concentration was higher in pine needles compared to oak leaves in most aspects. This could partly be explained by the older age of the needles compared to the leaves. There was however an exception. Concentrations of H-PAH were higher in oak leaves than in pine needles when a mass-based unit was used. If instead the area-based unit was considered, pine appeared clearly superior to oak for all PAH categories with more than 15 times higher SUM-PAH concentrations in pine needles on an annual basis. The low SLA of pine promotes high values of area-based concentrations. Our third hypothesis was thus only partly supported since the relative merit of pine vs oak as PAH accumulators depends both on PAH category and measuring unit. The significance of the area-based PAH content follows from the assumption that PAH is mainly taken up through the leaf surface. The ecosystem uptake may therefore to a large extent be driven by its leaf/needle area available for gas and particle deposition. However, if PAH in the leaves saturates with time, the ecosystem uptake might instead be limited by the total leaf mass. In both cases, duration of the uptake period (i.e. the seasonal variation in stomatal opening and leaf longevity) will have a decisive effect on PAH accumulation.

The L-PAH and M-PAH concentrations in oak leaves were strongly correlated with the air concentrations. One explanation for the weaker correlation between H-PAH$_{air}$ and H-PAH$_{leaf}$ (Fig. 5) may be that the PUF sampler is protected inside the sampling container and therefore mainly samples finer particle fractions while leaves pick up both small and large particles that are deposited on the leaf surface.

The partitioning between plant and air, indicated by the concentration ratio PAH$_{plant}$/PAH$_{air}$ was correlated to log K$_{OA}$ for compounds with log K$_{OA}$ < 9, supporting our fourth hypothesis. Log K$_{OA}$ explained more than 90% of the variation in the leaf to air ratio for oak, implying that the gaseous phase PAHs partitioning between leaf and air was governed by equilibrium processes. The slope coefficient of the regression lines differed strongly in time and between oak and pine, indicating influence of environmental conditions such as temperature

and that the plant specific lipophilicity can differ from that of octanol and between species (Kömp and McLachlan, 1997).

In our observations, net reemission of the particle-bound H-PAHs was not significant, neither in oak, nor in pine. On the other hand, oak showed a substantial loss of L-PAHs from June to September, while pine, having much higher concentrations of these two PAH categories, showed a substantial net accumulation from one-year-old (C + 1) to three-year-old (C + 3) needles. An interpretation of this is that the sink for L-PAHs of oak leaves was rather quickly more or less in equilibrium after which the temperature dependent equilibrium processes became important and lead to reemission in the high temperatures of the summer of 2018. This would explain both the loss in concentration from June to September and the strong and uniform relationship of Fig. 5 covering both sampling periods for L-PAHs. The continued, multiannual accumulation of L-PAHs over time in pine needles suggests that its sink for these compounds is significantly larger than in oak and not in equilibrium after one year. As the sink is not saturated, absorption can continue and since the equilibrium has not been reached, net reemission to the atmosphere is unlikely. Further research is needed to investigate for how many years PAH accumulation can continue in needles.

5. Conclusions

The most important conclusions from this study were:

- There was a larger variation in PAH$_{air}$ concentrations (obtained by passive PUF air samplers) between sites in the Gothenburg conurbation than for NO$_2$. The correlation between NO$_2$ and PAH$_{air}$ was strong, where NO$_2$ explained around 70% of the variation in PAH$_{air}$, emphasizing that the pollutants to a large degree originates from the same sources, essentially road traffic.
- There was a clear difference in PAH concentrations of pin oak leaves and black pine needles between sites in the urban area of Gothenburg. However, the difference between the most and least polluted site was not as large as for the PAH$_{air}$ concentrations.
- In pin oak leaves, there was a significant decrease in gaseous phase L-PAH between June and September, but a significant increase in particulate H-PAH. The correlation between L-PAH in leaves and in air, common for the June and September samplings, was stronger than for H-PAH. This indicates that the L-PAHs were to a larger degree influenced by the temperature sensitive equilibrium processes between the concentrations in ambient air and leaves/needles.
- In black pine needles there was a significant increase of both gaseous and particle-bound PAHs in three-year-old needles (age class C + 3) compared to one-year-old needles (age class C + 1).
- In most aspects black pine needles were superior to pin oak leaves in accumulating PAH from the air. However, H-PAH was higher in pin oak leaves when a mass-based unit was used, but higher in black pine needles when a leaf area-based unit was used.
- A positive linear correlation was found between the log K$_{OA}$ (in the range < 9) and the concentration ratio PAH$_{plant}$/PAH$_{air}$ for both pin oak and black pine, indicating that equilibrium processes govern the partitioning between epicuticular wax and ambient air for L-PAHs.
- This study shows that there is a net accumulation of PAHs in both oak leaves and pine needles, thereby improving air quality. The close correlation between air and plant PAH concentrations emphasize the utility of trees for biomonitoring purposes. Trees can be used in sustainable urban planning to mitigate air pollution although the quantitative significance of this effect was not investigated here. However, it is important to keep in mind that reductions in emissions of PAHs and other air pollutants is the most important measure to improve the air quality.

CRediT authorship contribution statement

Jenny Klingberg: Conceptualization, Investigation, Formal analysis, Writing - Original draft preparation. **Bo Strandberg**: Conceptualization,

Methodology (PAH analysis), Writing - Reviewing and editing. **Henrik Sjöman**: Conceptualization, Investigation, Writing - Reviewing and editing. **Malin Taube**: Formal analysis, Writing - Reviewing and editing. **Göran Wallin**: Resources, Writing - Reviewing and editing. **Håkan Pleijel**: Funding acquisition, Conceptualization, Investigation, Writing - Reviewing and editing.

Declaration of competing interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary tables and details about the PAH analysis

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.150163.

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