TITLE

Gaseous polycyclic aromatic hydrocarbon concentrations are higher in urban forests than adjacent open areas during summer but not in winter – exploratory study

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Abstract

While the potential of plants to uptake polycyclic aromatic hydrocarbons (PAHs) is widely acknowledged, empirical evidence of the effects of this process on local atmospheric PAH concentrations and human health is tenuous. We measured gaseous PAH concentrations using passive samplers in urban tree-covered areas and adjacent open, treeless areas in a near-road environment in Finland to gain information on the ability of urban vegetation to improve air quality. The ability of urban, mostly deciduous, vegetation to affect PAHs was season dependent: during summer, concentrations were significantly higher in tree-covered areas, while in the fall, concentrations in open areas exceeded those in tree-covered areas. During winter, concentrations in tree-covered areas were either lower or did not differ from those in open areas. Results of this study imply that the commonly believed notion that trees unequivocally improve air quality does not apply to PAHs studied here.

Capsule: Higher ambient gaseous PAH concentrations were detected within urban tree cover as compared to open areas during summertime

Keywords: PAH, ecosystem service, passive sampler, urban forest, urban vegetation

Highlights:

- Urban tree-cover increases gaseous PAH concentrations during summertime
- Elevated PAH concentrations do not clearly correspond with vegetation properties
- Tree-cover attenuates seasonal PAH concentration fluctuation
1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are formed through the incomplete combustion of carbon-containing fuels and pyrolysis of organic matter, a major source of which is traffic (Marr et al., 1999; Shen et al., 2011). The main concern with PAHs is their slow degradation combined with carcinogenic properties of some of the hydrocarbons – especially those with four or more benzene rings (IARC, 2010; Wang and Busby, 1993). Although about 500 different PAHs have been detected in urban air, only benzo[a]pyrene (BaP), a known carcinogen (IARC, 2010), is typically measured and used as representative of all PAHs. Generally less data are available on ambient air PAH levels than classical criteria air pollutants – such as particles and nitrogen oxides – due to the rather complex and expensive sampling and analytical procedures required for PAHs (Boström et al., 2002). Only recently PAHs were included in official air quality standards, when the European Union set a target value (1 ng m$^{-3}$) for BaP (EEA, 2012).

PAHs display various gas/particle partitioning characteristics, depending on the properties of the specific compound, environmental conditions and the sorbing surface. 2- and 3-ring PAHs are mostly in vapor form, 4-ring PAHs appear in both gas and particle phases, while larger PAHs, such as BaP, are mainly associated with particles (Howsam et al., 2000 and references therein). Gaseous or semi-volatile PAHs that comprise a major fraction of PAHs in urban air are often classified as class 3 carcinogens, implying inadequate data for their classification. While carcinogenicity of many of these substances is still questionable, for example fluoranthene has been considered as a possible important contributor to cancer risk (Boström et al., 2002; Busby et al., 1984; IARC, 2010). According to Ramirez at al. (2011) cancer risk can be underestimated if gaseous phase PAHs are not considered. However, there is no documented evidence suggesting that gaseous PAHs in the urban air relate to human health.

Plants cover over 80% of the earth’s terrestrial surface area and, due to their large surface area and cuticle coating comprised of lipids and waxes, have a great potential to trap atmospheric pollutants, such as PAHs (Simonich and Hites, 1994; Wagrowski and Hites, 1997). The main pathway of this removal is from air to leaf, when PAHs are deposited on vegetation surfaces and diffused into the cuticle and further into the leaf interior (Bakker et al., 2001; Jouraeva et al., 2002; Khun et al., 1998; Wang et al., 2008). Factors affecting the transport of PAHs from air to plant are many, including ambient concentrations of the compound and its atmospheric phase (gaseous/particle associated), compound properties, leaf surface characteristics and air temperature (Howsam et al., 2001 and references therein). Intercepted PAHs in the foliage are eventually transmitted to the soil via litterfall and rain, or are resuspended and revolatilized back into the atmosphere (Howsam et al., 2001).
The phase of a particular PAH determines its deposition mechanism on vegetation: higher molecular weights and thus particle-bound PAHs remain on the surface of a leaf, gaseous PAHs accumulate in the cuticle and the lightest compounds can penetrate further into leaf tissues (Bakker et al., 2001). Seasonality in PAH dynamics (ambient concentrations and gas/particle partitioning) has been observed, being attributed mainly to elevated emissions during winters, and lower temperatures that affect gas/particle partitioning (Harrison et al., 1996; Howsam et al., 2001). For example Lang et al. (2007) observed that gaseous 3- to 6-ring PAHs were more abundant during summer, while particle-bound PAHs were typical during winter, but Ma et al. (2010) reported higher concentrations for both phases during the winter season.

The role of vegetation in absorbing PAHs has raised considerable interest during recent decades. The deposition of PAHs has been observed to be substantially higher into forest soils compared to an adjacent clearing (Horstmann et al., 1997; Matzner, 1984) due to vegetation uptake and subsequent transfer to the soil. Additionally, higher vegetation exerts a greater drag on the air, promoting downward fluxes of atmospheric compounds (Monteith and Unsworth, 1990). Deposition velocity of gaseous PAHs into the forest canopy has been observed to be relatively high, exceeding the deposition velocity of particle-bound PAHs (Horstmann and McLachlan, 1998; Su et al., 2007). Furthermore, the dry deposition of both gaseous and particle-bound PAHs seems to be higher in a deciduous than coniferous forest (Horstmann and McLachlan, 1998). Choi et al. (2008) measured PAH levels along a vertical gradient from below to above the canopy, and found that only the uptake of gaseous PAHs was fast enough to be detected as lowered concentrations at the upper part of the canopy. For particle-bound PAHs, the levels were more uniform at all heights, implying less efficient uptake of these PAHs (Choi et al., 2008).

Although vegetation has been suggested to remove various pollutants and thus improve urban air quality at the city- and local scale (e.g. Alberti, 2008; Nowak, 2006), contrasting views have been reported (e.g. Pataki et al., 2011; Vos et al., 2013). While vegetation on a large scale acts as an important vector of PAHs from the air into terrestrial systems (e.g. Böhme et al., 1999; Wania and McLachlan, 2001), empirical evidence of the significance of this removal capacity for ambient concentrations on a local scale is, to our knowledge, non-existent. A crucial, practical question is whether air quality and thus human well-being would be improved in the proximity of foliage or other adsorbing structures, or would it deteriorate due to, e.g. reduced turbulence and thus reduced pollution dispersion as modeled by Vos et al. (2013). Furthermore, seasonality in the effect of vegetation on PAH concentrations should be apparent, most obviously due to the lack of deciduous leaves in winter resulting in zero uptake by leaves (e.g. Söderström et al., 2005). Despite the substantial amount of literature in which various aspects of
vegetation-PAH interactions have been assessed, to our knowledge there are no studies conducted in urban settings in which aerial concentrations of PAHs have been measured and compared between tree-covered and open locations during different seasons. Consequently, knowledge on the influence of urban vegetation on human health in terms of PAH removal is virtually non-existent.

The objective of this study was to test whether the normative approach according to which vegetation can efficiently improve local urban air quality applies to gaseous PAHs. We hypothesize that (i) ambient air is cleaner, in terms of gaseous PAHs, in tree-covered areas than in adjacent open areas in urban near-road environments and, (ii) that the potential of urban parks/forests to remove PAHs is season dependent, resulting in lower relative concentrations under canopies during leafy period. This study is part of a larger study in which the impact of vegetation on several air pollutants is explored (see Setälä et al., 2013).

2. Materials and methods

Study area

We measured PAH levels using passive sampling devices (PSDs) in urban remnant forest and park areas and in adjacent open (treeless) areas in the cities of Helsinki (60°10′15″N, 24°56′15″E) and Lahti (60°59′00″N, 25°39′20″E) in southern Finland. Ten sites in each city were established close to roads with moderate to heavy traffic flows. Each site included a pair of sampling points: one in an open area and another in a tree-covered area, typically less than 100 meters apart (altogether 40 sampling points in the two cities). The open areas were typically small or medium-sized city squares or other treeless areas close to a road where soil surfaces were either impervious (e.g. asphalt) or pervious with mown lawns. The tree-covered areas were either urban parks of various sizes with scattered, mainly deciduous trees and lawns, or urban forest remnants of mixed forest type (deciduous and coniferous trees) and rich understorey vegetation. Within each site, the samplers were placed at equal distances from the road where possible, but not always on the same side of the road. Distances from the measuring points to the road varied between 8 and 67 m, and average distances for open and tree-covered measuring points were 32.5 m and 36.5 m, respectively. A set of environmental variables were measured from all sites (Table 1). The sampling sites and setup are described in detail in Setälä et al. (2013).

Measurements of PAHs were conducted during two seasons: from 9 August to 10 September 2011 (late summer, referred to as summer) and from 7 March to 11 April 2012 (late winter, i.e. winter). The PSDs were deployed for 30 days during both periods.
Table 1. Environmental variables (vegetation structure and traffic flow) measured at the 20 study sites in Lahti and Helsinki. Traffic flow = number of motor vehicles per day. Traffic flows were obtained from data provided by the City of Helsinki (2011) and the City of Lahti (2012). Values referring to canopy closure, trees and understorey vegetation were estimated from a sector covering 90 degrees from the sampling point towards the road that delineated the area. Trees with a diameter at breast height (DBH) of < 2.54 cm are not included. Large trees = trees with DBH > 32 cm.

<table>
<thead>
<tr>
<th>Site</th>
<th>Canopy closure</th>
<th>Total nr. of trees 100m²</th>
<th>Nr. of large trees 100m²</th>
<th>Understorey vegetation density</th>
<th>Traffic flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lahti</td>
<td>1</td>
<td>87 %</td>
<td>6.8</td>
<td>1.9</td>
<td>dense</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>87 %</td>
<td>0.8</td>
<td>0.4</td>
<td>meager</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>67 %</td>
<td>1.9</td>
<td>0.5</td>
<td>meager</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>60 %</td>
<td>0.8</td>
<td>0.5</td>
<td>intermediate</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>85 %</td>
<td>1.5</td>
<td>0.3</td>
<td>dense</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>74 %</td>
<td>5.7</td>
<td>1.6</td>
<td>intermediate</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>50 %</td>
<td>0.5</td>
<td>0.5</td>
<td>meager</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>62 %</td>
<td>2.6</td>
<td>0.5</td>
<td>dense</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>20 %</td>
<td>1.8</td>
<td>0.8</td>
<td>dense</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>90 %</td>
<td>2.1</td>
<td>0.4</td>
<td>meager</td>
</tr>
<tr>
<td>Helsinki</td>
<td>11</td>
<td>90 %</td>
<td>2.3</td>
<td>0.4</td>
<td>dense</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>90 %</td>
<td>1.1</td>
<td>0.6</td>
<td>intermediate</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>91 %</td>
<td>1.3</td>
<td>0.6</td>
<td>intermediate</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>52 %</td>
<td>1.5</td>
<td>0.7</td>
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<tr>
<td></td>
<td>15</td>
<td>80 %</td>
<td>4.4</td>
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<td>2.8</td>
<td>0.6</td>
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<tr>
<td></td>
<td>17</td>
<td>67 %</td>
<td>2.1</td>
<td>0.1</td>
<td>dense</td>
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<tr>
<td></td>
<td>18</td>
<td>89 %</td>
<td>2.5</td>
<td>0.5</td>
<td>dense</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>88 %</td>
<td>2.6</td>
<td>0.4</td>
<td>meager</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>82 %</td>
<td>155.6</td>
<td>0.0</td>
<td>dense</td>
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</tbody>
</table>
**Time series measuring campaign**

A time series measuring campaign was conducted two years after the main study in 2013, to confirm previous results and to acquire more detailed information on the PAH concentrations during the growing season. Two new study sites were selected, both with an open (meadow, set-aside field) and tree-covered (remnant forest) location at similar distances from the adjacent road. The one site pair was at the outskirts of the city of Lahti, situated 39 m from a road with 20 000 cars per day, and the other pair 45 m from a highway with 20 000 – 40 000 cars per day (City of Lahti, 2012). Gaseous PAHs were sampled during five sampling periods between May and November, each sampling period lasting approximately 30 days. The periods were 28 May - 28 June, 28 June - 5 August, 8 August - 12 September, 13 September - 14 October and 16 October - 11 November.

**Sampling method**

The passive sampler device (PSD) used in this study was similar to semipermeable membrane device (SPMD) (Huckins et al., 1990), consisting of a polyethylene membrane enclosing a triolein lipid. The PSD mimics bioconcentration processes and passively samples bioavailable contaminants from the ambient environment. SPMDs have been successively used for the monitoring of PAHs in water (e.g. Wang et al., 2009) and the air (Piccardo et al., 2010; Söderström et al., 2005).

Customized PSDs consisted of a low-density polyethylene layflat tubing (length 48 cm × width 2.5 cm) enclosing 0.5 mL of > 95% purity triolein (MP Biomedicals, Illkirch, France), weighing 2.3 g in total. A performance reference compound (PRC, Fluoranthene-D10, Dr. Ehrenstorfer GmbH, Augsburg, Germany) was added to the PSDs to observe its dissipation during winter. Both ends were sealed, providing a 45 cm long lipid filled part.

The PSDs were mounted inside (facing downwards) shields made of 2 L zinc buckets to provide shelter from rain, wind and solar radiation. During summer, two PSDs per sampling point were deployed, while during winter only one PSD was used due to only minor variation observed between the two PSDs used per sampling point during summer (120 PSDs altogether). Six field blank PSDs were exposed to ambient air during the deployment and stored at −20°C during exposure.

The shields with the PSDs wired inside were attached to tree trunks or lamp posts using a 40 cm long aluminum rod stretching out of the trunk/post, 2.5-3.5 m above ground. After 30 days of exposure, the PSDs were removed and stored at −20°C until analysis.
Analyses

Once the field studies were completed, surfaces of the PSDs were wiped clean with tissue paper soaked in ethanol, after which they were cut open to insert 400 ng of internal standards acenaphthene-D10, chrysene-D12, naphthalene-D12, perylene-D12 and phenanthrene-D10 (PAH Mix 31 deuterated, Dr. Ehrenstorfer GmbH, Augsburg, Germany). The PSDs were extracted twice for 24 h by dialysis with approximately 50 mL of n-hexane (SupraSolv, Darmstadt, Germany) in a beaker at room temperature. Field blank PSDs and non-exposed PSDs (for detecting contamination in the sampler itself) were treated similarly to exposed PSDs. In addition to that, one reagent blank per each batch was analyzed using the same procedure.

Two extracts were combined and concentrated first by using a rotary evaporator and then under nitrogen stream to 0.5 mL or 50 µL volume. Anthracene-D10 (100 ng, Dr. Ehrenstorfer GmbH, Augsburg, Germany) was added as a recovery standard. The samples were analysed with GC-MS (GCMS-QP2010 Ultra Shimadzu) for 16 EPA priority PAHs. Recoveries of internal standards ranged between 61 and 115 %. The limit of quantification (LOQ) varied between 0.05 and 0.25 ng m\(^{-3}\). Uptake rates (Cranor et al., 2009) were used to determine mean aerial concentrations of the detected PAHs. The field blank samplers contained low concentration of some PAHs, but all reported compounds remained below LOQ. The sampling method used here may under- or overestimate the sampling rate of some PAH constituents. Alvarez (2013) and Piccardo et al. (2010) reported that sampling rates detected under laboratory conditions do not necessarily apply in the field. Systematic differences in temperature (Cicenaite et al., 2007; Piccardo et al., 2010) or wind speed (Söderström et al., 2005) between study areas or photodegradation in open sites (Bartkow et al., 2006) could have affected our results. The average clearance rate constant of PRC (k\(_{PRC}\), Huckins et al., 2002) for tree-covered areas was 18% less than for open areas (results not shown), indicating that uptake rates are slightly lower in the tree-covered areas that result in an underestimation of PAH air concentrations.

The data were analysed with SPSS Statistics, version 22, using Paired Samples t-test to detect statistically significant differences in PAH concentrations between the tree-covered and open study areas. The habitats within site pairs (open and tree-covered, n = 10 in each city) were independent of each other while the habitats within a site were not independent, warranting the use of a paired samples test. P-values < 0.05 were considered to indicate statistically significant differences between treatments. Linear regression was used to detect possible relationships between measured environmental variables and pollution level differences.
3. Results

The following PAHs were identified in the samples: acenaphthene (ACP), fluorene (FL), phenanthrene (PHE), fluoranthene (FLT) and pyrene (PYR). Concentrations for these compounds calculated from the sequestered amounts ranged from 0.09 ng m\(^{-3}\) to 20.8 ng m\(^{-3}\). During the summer period, these PAHs exhibited higher concentrations in tree-covered areas compared to adjacent open areas: the average concentrations for ACP, FL, PHE, FLT and PYR were 51% (\(p = 0.001\)), 41% (\(p < 0.001\)), 62% (\(p < 0.001\)), 18% (\(p = 0.084\)) and 155% (\(p < 0.001\)) higher in tree-covered areas than in open areas, respectively (Fig. 1). The large variation displayed in Fig. 1 C & D is due to varying concentrations between sites, but the pairwise study design and the statistical analysis reveal systematic differences between open and tree-covered measuring points. During the leafy period, concentrations of the PAH constituents were higher in tree-covered measuring points in 89 out of 100 cases (20 sites and 5 compounds totaling 100 comparisons). However, during the leaf-free period in late winter, average concentrations of ACP and FL were 26% (\(p = 0.005\)) and 19% (\(p = 0.031\)) higher in the open areas, respectively, while PHE, FLT and PYR did not show statistically significant differences between the study areas (Fig. 1). Interestingly, levels of most PAHs were substantially lower in Helsinki than in Lahti, despite the generally higher traffic intensity in the former city. Since the relative concentrations of different PAHs as well as the trend between open and tree-covered measuring points were very similar in both cities, results presented in Fig. 1 and Table 2 describe the combined data from the two cities.
Figure 1. The influence (mean ± SD) of tree-cover on PAHs during summer (upper panels: A and C) and winter (lower panels: B and D). Panels A and B denote the relative influence (in percentages) of tree-cover on PAH levels with the zero-line (x-axis) representing PAH levels at the open sites. Panels C and D show the actual PAH concentrations in open (white bars) and tree-covered (dark bars) areas. P-values are presented beneath the PAH constituents (Paired Samples t-test; n = 20, except for winter where n = 17 due to the loss of three samplers). Data from Lahti and Helsinki are pooled. ACP = Acenaphtene, FL = Fluoranthene, PHE = Phenanthrene, FLT = Fluoranthene, PYR = Pyrene.
When a statistically significant difference between tree-covered and open areas in the concentration of a particular PAH compound was detected, we tested whether this difference (concentration at the open site subtracted from that at the tree-covered site) correlates with the measured environmental variables (canopy closure (%), amount of total and large trees per 100m$^2$) i.e. values representing the quantity of vegetation. Concentration difference for ACP and FL correlated weakly but statistically significantly with canopy closure (Table 2): the greater the canopy closure, the smaller the concentration difference, i.e. the lower the concentration in the tree-covered area. For other compounds no such relationships were found (Table 2).

In open sites, distance to the road correlated negatively with PAH-concentrations during summer (Table 2). A similar but statistically non-significant trend was observed in the tree-covered sites during winter. In addition, concentrations of some PAHs in the tree-covered areas correlated positively, to some extent, with number of large trees (trees with DBH > 32 cm) during both seasons (Table 2). Traffic flow did not explain PAH concentrations, neither in open nor tree-covered areas during either season (result not shown).
Table 2. Excerpt of results from linear regression analyses that exhibited a trend (significant differences, $p < 0.05$, in bold) between environmental variables and PAH constituents during summer and winter. The first column describes the difference between open and tree-covered areas and is tested against canopy closure, while in the other columns the actual PAH concentrations measured are tested against number of trees and distance from the road. Canopy closure was not estimated in winter. Data from Lahti and Helsinki are pooled.
<table>
<thead>
<tr>
<th>SUMMER</th>
<th>Concentration differences</th>
<th>Concentrations, Tree-covered areas</th>
<th>Concentrations, Open areas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Canopy closure %</td>
<td>Nr. of trees 100m²</td>
<td>Distance (m) from the road</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>$R^2$ 0.251</td>
<td>0.042</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>$p$ 0.024</td>
<td>0.388</td>
<td>0.611</td>
</tr>
<tr>
<td>Fluorene</td>
<td>$R^2$ 0.258</td>
<td>0.111</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>$p$ 0.022</td>
<td>0.150</td>
<td>0.808</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>$R^2$ 0.022</td>
<td>0.180</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>$p$ 0.532</td>
<td>0.063</td>
<td>0.36</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>$R^2$ 0.000</td>
<td>0.177</td>
<td>0.067</td>
</tr>
<tr>
<td></td>
<td>$p$ 0.968</td>
<td>0.065</td>
<td>0.271</td>
</tr>
<tr>
<td>Pyrene</td>
<td>$R^2$ 0.072</td>
<td>0.279</td>
<td>0.149</td>
</tr>
<tr>
<td></td>
<td>$p$ 0.253</td>
<td>0.017</td>
<td>0.093</td>
</tr>
<tr>
<td>WINTER</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Acenaphthene</td>
<td>$R^2$ 0.030</td>
<td>0.152</td>
<td>0.328</td>
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<td>$p$ 0.464</td>
<td>0.090</td>
<td>0.016</td>
</tr>
<tr>
<td>Fluorene</td>
<td>$R^2$ 0.189</td>
<td>0.159</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>$p$ 0.055</td>
<td>0.082</td>
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<tr>
<td>Phenanthrene</td>
<td>$R^2$ 0.172</td>
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<td></td>
<td>$p$ 0.069</td>
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<tr>
<td>Fluoranthene</td>
<td>$R^2$ 0.151</td>
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<td>Pyrene</td>
<td>$R^2$ 0.028</td>
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<td>0.016</td>
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<td></td>
<td>$p$ 0.484</td>
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Results of the time series study confirmed findings of the main study: concentrations of total gaseous PAHs (ACP, FL, PHE, FLT and PYR) were higher in the tree-covered areas during summer months. However, the situation changed in autumn, as concentrations started to increase in both areas, but were ultimately higher in open areas (Fig. 2).

**Figure 2.** Time series of total gaseous PAH-concentrations (mean ± SD) from late May to November (2013) in open and tree-covered study sites. Values for acenaphthene, fluorene, phenanthrene, fluoranthene and pyrene are combined and results from the two sites are pooled.
4. Discussion

*PAH concentrations in tree-covered and open areas*

To our knowledge this is the first study that has shown that vegetation increases ambient gaseous PAH concentrations. Thus, even though trees are known to uptake PAHs (e.g. Wagrowski and Hites, 1997), it seems that other processes override the effect of uptake and cause increased PAH concentrations under urban tree canopies. The difference between tree-covered and open areas was substantial even though (i) the sampling points at the tree-covered areas were, on average, 4 m further away from the road than open areas, and (ii) uptake rates were slightly lower in tree-covered areas implying an underestimation of concentrations. Given this unexpected result, our first hypothesis that predicted lower gaseous PAHs in tree-covered areas is rejected. However, elevated concentrations in tree-covered areas were only observed during summer, whereas during winter the situation was reversed for two of the five studied compounds, with ACP and FL concentrations being significantly higher in open areas. This partly supports our second hypothesis that the effect of urban vegetation on PAHs is season dependent.

The effect of vegetation was opposite of what we hypothesized. It has been reported that the ability of urban trees to provide cleaner air beneath the canopy can be minor or non-existent (Setälä et al., 2013), but to our knowledge, studies that report increased pollution concentrations under canopies are few. One exception is the study by Harris and Manning (2010) who found that, depending on ambient NO$_2$-levels, the concentration of this pollutant under trees can be higher than just outside the canopy. This was rationalized by NO-production from soils and the subsequent oxidation of NO to NO$_2$. Although NO$_2$ as a compound and its dynamics in the environment are different from those of PAHs, some similarities may exist in the processes causing elevated concentrations under the canopy. For example, according to several modeling studies (Gromke and Ruck, 2007; Vos et al., 2013; Wania et al., 2012) and field monitoring campaigns (Setälä et al., 2013), trees and other vegetation reduce wind speed and thus can have a substantial negative effect on local air quality as the dilution of air pollutants is weakened. According to the modeling study by Vos et al. (2013), the effect of reduced ventilation on urban air quality can be stronger than the pollutant removal capacity of trees. However, concentrations of other gaseous pollutants (NO$_2$ and anthropogenic VOCs) measured during the same campaign as the one described here were not similarly elevated in the forests during the leafy period, nor did they display such seasonal variation in relative concentrations in tree-covered and open areas (see Setälä et al., 2013). This implies that, besides reduced ventilation, other processes were responsible for elevated PAH levels in the
urban parks/forests. Further studies using both passive and active air samplers are required to shed more light on the mechanisms behind the increased summertime PAH concentrations in the vegetated habitats.

Data acquired from the additional measurement campaign conducted during late May to mid-November revealed unequal temporal variation of PAH-concentrations in open and tree-covered areas during the growing season. Despite the lacking data from winter months, our data suggest greater seasonal variation of PAH-concentrations in open areas compared to the tree-covered areas. Tree-cover seems to attenuate the seasonal concentration fluctuation, bringing about higher concentrations in tree-covered areas during summer, while in the fall, concentrations in open areas exceeds those in tree-covered areas. Higher concentrations during leaf-free period in both open and tree-covered areas are associated with elevated emissions from e.g. heating of buildings.

A potential explanation for (i) the enhanced summertime PAH levels in parks, and (ii) the seasonality of these effects may relate to soils. Air-soil gas exchange is a crucial process determining the fate of persistent organic pollutants, such as PAHs (Cousins et al., 1999). Moreover, fugacity models predict that gas exchange between air and soil is the dominant process removing PAHs from the atmosphere and thus is the most important process in polluting soils with these organic contaminants (Lang et al., 2007). As a consequence, soils can serve as a significant repository for airborne PAHs, the amounts of which in the soil are affected by input history and output processes such as volatilization (Sweetman et al., 2005). In essence, the most important parameters leading to seasonality in air-soil gas exchange are temperature and precipitation (Lang et al., 2007, Wang et al., 2011). Consequently, high temperatures and rainfall during summer enable gaseous PAHs to evaporate from the soil, while in winter more gaseous PAHs deposit from air to soil due to low temperatures and high emissions (Wang et al., 2011). The PAHs studied here are all semi-volatile, and as such are more prone to temperature-dependent phase transitions than are lighter and heavier PAHs. It is also known that, as both gaseous and particle-bound PAHs deposit on vegetation surfaces and are later deposited to the soil via interception events and litter fall, tree cover enhances PAH deposition into the soil (Horstmann et al., 1997; Howsam et al., 2001; Matzner, 1984; Peng et al., 2012). Based on the aforementioned literature and our empirical results, we suggest that the vegetation in tree-covered areas promoted PAH trapping into the foliage and accumulation into the soil, which later on enable the development of high summertime beneath-canopy concentrations due to the evaporation of PAHs back into the air. The reduced ventilation in tree-covered areas should further boost the enrichment of PAHs in the air under canopies.
Besides temperature, snow may additionally affect the fate of organic contaminants during winter months. Snow can scavenge organic chemicals effectively from the atmosphere (Lei and Wania, 2004) so that snowpacks close to roads hold higher levels of traffic-derived PAHs than snowpacks further away (Hautala et al., 1995, Kuoppamäki et al., 2014). In the cities of Lahti and Helsinki, snow that accumulated on streets and other open surfaces is mostly removed to snow dump sites. However, snow in parks and other green areas is not removed and these sites are often used as snow depositories in which PAHs can be stored for months (Meyer et al., 2011). This leads to the long-term accumulation of snow-derived PAHs in park soils, from which they will be released to the atmosphere when temperatures rise during the spring and summer.

**Environmental variables**

We are not aware of any previous studies that have attempted to use vegetation properties in explaining ambient PAH concentrations. Although urban parks and forests significantly increased local summertime PAH concentrations, variation in PAH levels were not consistently attributable to the measured vegetation variables for any of the PAH compounds studied. However, the few significant correlations suggest that the impact of some vegetation properties, such as canopy closure and number of trees cannot be ruled out. Yet, while the weak positive trend between the number of large trees (DBH > 32cm) and PAH levels may well be due to reduced ventilation, the correlation between canopy closure and difference in the level of some PAH constituents between tree-covered and open areas remains puzzling: considering our main results and the aforementioned literature, one would expect that higher canopy closure would associate with relatively higher PAH concentrations, but we found the opposite. Taking into account the lack of consistency among the different PAH constituents and the low explanatory power of the regression analyses, these weak and correlative trends should be considered with caution. Overall, the lack of consistent patterns imply that the vegetation-related variables that we expected to be influential, serve as poor indicators explaining local differences in PAH concentrations. Unexpectedly, the amount of traffic did not turn out to correlate with concentrations of any of the studied PAH compounds, which may be due to substantial inputs from sources other than traffic. However, the strongest correlation found in this study, i.e. the inverse relationship between distance from the road and PAH concentrations in the open area, is a clear sign that traffic is the main source for these PAHs. In all, due to the complex dynamics between PAHs and the environment, various confounding factors in the cityscape evidently hamper the identification of influential variables that explain the higher PAH concentrations in tree-covered areas.
5. Conclusions

While our result of increased summertime gaseous PAH levels under the canopy is in contrast with earlier studies (Matzner, 1984; Horstmann et al. 1997), our data confirm earlier findings regarding enhanced pollutant concentrations under the tree canopy due to (i) reduced ventilation (Vos et al. 2013), (ii) enhanced PAH deposition into the soil in tree-covered areas (Matzner, 1984) coupled with seasonal changes in air-soil gas partitioning (Wang et al., 2011), and (iii) pollutant accumulation on the ground via snow (Kuoppamäki et al., 2014). Unlike many other studies in which PAH dynamics have been explored in remote forest ecosystems (e.g. Choi et al., 2008), the current study was conducted in a disturbed, highly heterogeneous urban landscape. In such mosaic landscapes pollutant plumes of high concentrations can enter tree-covered areas not only vertically but also horizontally from, e.g. adjacent roads. This, coupled with reduced wind speeds underneath the canopy, may explain why our results differ from those acquired from rural study sites that receive pollutants more evenly mixed in the air mass.

A better understanding of the sink-source dynamics of organic pollutants such as PAHs is of importance when estimating human exposure risks to, e.g. carcinogenic pollutants. This is of particular interest in tree-covered environments that are commonly used for recreational purposes. To our knowledge no other study has reported increased atmospheric concentrations of gaseous PAHs underneath tree-covered areas – an observation that merits further study to (i) confirm the mechanisms behind the observed phenomena and (ii) to evaluate the role of urban green areas in the provision of ecosystem services.

Acknowledgements

We thank Johan Kotze for checking the English and for many helpful comments. This study was funded by the Maj and Tor Nessling foundation, the Helsinki Metropolitan Region Urban Research Program and the Helsinki University Centre for Environment (HENVI, ENSURE research programme).

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