Trees in urban parks and forests reduce O$_3$, but not NO$_2$ concentrations in Baltimore, MD, USA.

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Abstract

Trees and other vegetation absorb and capture air pollutants, leading to the common perception that they, and trees in particular, can improve air quality in cities and provide an important ecosystem service for urban inhabitants. Yet, there has been a lack of empirical evidence showing this at the local scale with different plant configurations and climatic regions. We studied the impact of urban park and forest vegetation on the levels of nitrogen dioxide (NO₂) and ground-level ozone (O₃) while controlling for temperature during early summer (May) using passive samplers in Baltimore, USA. Concentrations of O₃ were significantly lower in tree-covered habitats than in adjacent open habitats, but concentrations of NO₂ did not differ significantly between tree-covered and open habitats. Higher temperatures resulted in higher pollutant concentrations and NO₂ and O₃ concentration were negatively correlated with each other. Our results suggest that the role of trees in reducing NO₂ concentrations in urban parks and forests in the Mid-Atlantic USA is minor, but that the presence of tree-cover can result in lower O₃ levels compared to similar open areas. Our results further suggest that actions aiming at local air pollution mitigation should consider local variability in vegetation, climate, micro-climate, and traffic conditions.

Keywords: urban trees, air pollution, ecosystem services, urban vegetation, nitrogen dioxide, ozone
1. Introduction

Air pollution is amongst the most recognized environmental problems around the world. Although concentrations of some air pollutants, such as nitrogen dioxide (NO₂) and ground-level ozone (O₃), have generally decreased within the past decades, their levels continue to exceed limits known to affect human health in many urban areas (Duncan et al., 2016; EEA, 2016; Pfister et al., 2014). The principal sources of NO₂ are energy production, industry and road traffic (EEA, 2016), but in cities nitrogen oxides (NOₓ = NO + NO₂) are mostly emitted from traffic-related combustion as NO, which is quickly oxidized by O₃ to NO₂ - or directly as NO₂ (Anttila et al., 2011). The latter has been a growing trend worldwide, including USA, due to increasing proportion of modern diesel engines (Anenberg et al., 2017). Elevated NO₂ concentrations can cause an increase in respiratory symptoms and infections in asthmatic individuals and children (Kampa & Castanas, 2008) and result in increased prevalence of atopic sensitizations, allergic symptoms, and diseases (Krämer et al., 2000). Ground-level O₃ is formed in reactions where volatile organic compounds (VOCs) interact with NOₓ in the presence of sunlight (Calfapietra et al., 2013; Loreto & Schnitzler, 2010). Ozone concentrations are thus dependent on both emissions of NOₓ and VOCs. VOCs include anthropogenic sources such as traffic and manufacturing as well as natural compounds (biogenic VOCs) such as isoprene which are emitted by trees. In regions of high VOCs, ozone concentrations are highly sensitive to NOₓ levels and vice versa. Urban and suburban populations are exposed to higher than ambient concentrations of ground-level O₃ especially during hot summer periods (Churkina et al., 2017) and in case of acute exposure inhabitants may suffer from reduced lung function and lung diseases (Uysal & Schapira, 2003).
A logical way to improve air quality is the reduction of emissions of air pollutants (Duncan et al., 2016; EEA, 2016), but it has been suggested that urban vegetation, especially trees, which can absorb and capture air pollutants with their large leaf area, could be also used to clean polluted urban air (Beckett et al., 2000; Nowak et al., 2006). For example, gases such as NO₂ (Chaparro-Suarez et al., 2011; Hu et al., 2016; Rondón & Granat, 1994; Takahashi et al., 2005) and O₃ (Hu et al., 2016; Manes et al., 2012; Wang et al., 2012) are absorbed from air through the stomata into the leaf interior of a plant. Such uptake of air pollutants by urban plants is often considered to result in effective ambient air quality improvement in city-scale and consequently to provide an important ecosystem service (e.g. Jim & Chen, 2008; Manes et al., 2012; Nowak et al., 2008). This has been emphasized especially in the interpretation of model studies (e.g. Baumgardner et al., 2012; Hirabayashi et al., 2012; Morani et al., 2011; Nowak et al., 2013; Selmi et al., 2016).

Recently, the overall significance of this ecosystem service has been challenged by contradictory results from local-scale studies and related critical comments (Churkina et al., 2017; Gromke & Ruck, 2009; Harris & Manning, 2010; Pataki et al., 2011; Pataki et al., 2013; Vos et al., 2013). Although studies comparing locally measured pollutant concentrations e.g. in urban forests and in adjacent open areas have been scarce, an increasing number of such studies have been published (Brantley et al., 2014; Fantozzi et al., 2015; Harris & Manning, 2010; Setälä et al., 2013; Tong et al., 2015; Viippola et al., 2016; Yin et al., 2011; Yli-Pelkonen et al., 2017). For instance, Setälä et al. (2013) and Yli-Pelkonen et al. (2017) did not find differences in gaseous pollutant concentrations between tree-covered and open near-road environments in hemi-boreal
climatic conditions, while Viippola et al. (2016) observed elevated gaseous PAH concentrations in road-side forests and parks compared to adjacent treeless areas during summer in Finland.

Some recent studies have used a city-wide measurement network of passive or active air collectors and combined this data with environmental variables such as land use, vegetation coverage and traffic. For instance, Rao et al. (2014) used a land-use regression model combined with NO$_2$ measurements at 144 sites in Portland, USA, and estimated a significant modelled NO$_2$ reduction due to tree canopy across the city. Irga et al. (2015) used portable active instruments for monthly air samples at eleven sites in Sydney, Australia, but found no observable trends in NO$_2$ concentrations between the sites with a range of different traffic and greenspace densities. Caballero et al. (2012) used passive samplers to study spatial and temporal variations of NO$_2$ levels at 79 sites in the city of Elche in Spain and observed that the spatial distribution of NO$_2$ depended mainly on the urban structure and traffic configuration, but the role of tree-cover on pollution levels could not be assessed with the study setup. García-Gómez et al. (2016) applied passive samplers and active monitors in studying O$_3$ and NO$_2$ levels in three peri-urban forests and one rural forest dominated by *Quercus ilex* and nearby open areas in Spain and found lower O$_3$ and NO$_2$ concentrations under tree canopies in the rural site and in one peri-urban site for O$_3$ and in two peri-urban sites for NO$_2$. Furthermore, Yin et al. (2011) studied six urban parks in Shanghai, China, and observed lower NO$_2$ concentrations inside parks with tree-cover as compared to a single reference site without tree-cover. Thus, the literature shows that different climatic conditions, plant configurations, degree of urbanization and the scale of a study area yield variable measurement results regarding the potential of urban vegetation to reduce the levels of gaseous air pollutants. This makes the interpretation of the modelling results even more
challenging and indicates the need for more empirical field-study data on the topic, that can also be used in model improvement.

Local temperature differences within a city and between tree-covered and open areas may also have an impact on air pollutant levels, as open areas receive more radiation that could influence photolysis reactions or heat the air locally, thereby affecting chemical reaction rates (Jacob, 1999). Temperature differences within a city can be related to land-use changes caused by urbanization. On an urban-rural scale, this difference is known as the Urban Heat Island (UHI) effect, but variability exists within the urban area as well. As with air quality, this variability can be linked to heterogeneity in urban form and has been linked with the presence or lack of vegetation and impervious surfaces (Scott et al., 2017). Thus, controlling for local variations in temperature is an important consideration.

The objective of our study was to explore the influence of urban tree-cover on the concentrations of gaseous air pollutants NO₂ and O₃ under early summertime conditions in Baltimore, MD, USA and thus provide much needed empirical evidence on the ability of urban vegetation to improve air quality. Based on previous findings from the above-mentioned studies, where the sampling sites were not in the close proximity to busy roads, we hypothesized that (1) air quality regarding the studied gaseous air pollutants in tree-covered urban areas is improved compared to adjacent open areas, and 2) the air quality improvement relates to temperature, amount of canopy cover and traffic volume.

2. Methods
2.1. Sampling

We measured the concentrations of NO₂ and ground-level O₃ using dry deposition passive collectors developed by the Swedish Environmental Research Institute IVL and temperature using 50 Maxim Integrated Products, Inc., “iButton” Model DS1923 Hygrochron thermometer/hygrometers. We installed the air collectors and thermometers either under tree canopies in tree-covered areas or in adjacent open areas in Baltimore, MD (39°17′57″N, 76°36′34″W), eastern USA (Fig. 1). NO₂ collectors and their analysis were provided by Metropolilab, Helsinki, Finland, and O₃ collectors and their analysis by IVL. The sampling of NO₂ and O₃ is based on molecular diffusion. The gas is adsorbed to a filter paper inside the collector and the amount of gas is analyzed by extracting it from the filter to distilled water, after which the amount of gas is determined with a spectrophotometer (Ayers et al., 1998). The NO₂ sampling method has been used successfully in numerous studies with results corroborated by active air monitoring instruments (Ayers et al., 1998; Ferm & Rodhe, 1997; Klingberg et al., 2017; Krupa & Legge, 2000; Caballero et al., 2012; HSY, 2014). The O₃ collectors have proved to be reliable and accurate according to our own tests alongside municipal active O₃ measuring instruments. iButton thermometers have an accuracy of 0.5 degrees C. The iButtons are shielded by a custom radiation shield that is naturally aspirated and made of White98 F-23, a commercial material manufactured by White Optics that is highly reflective for visible light and most often used in industrial lighting applications.

2.2. Sampling sites and dates
We established twenty-five sampling sites in urban parks and forests in Baltimore (Fig. 1). Four of the sites were situated in park-like block courtyards. At each site we installed air collectors and thermometers at the sampling points in two habitats: in a tree-covered area and in an adjacent open area. The tree-covered areas were as largely tree-covered around the sampling point as possible, but often included some non-canopy-covered area within a 50 m radius from the sampling point. Similarly, the open areas were as widely open around the sampling point as possible, but often included some amount of trees within a 50 m radius from the sampling point, usually situated close to the perimeter of this circle. Within each site, we situated the sampling points (open and tree-covered) at the approximately same distance from the nearest major road, but not in close proximity to heavily trafficked roads, as the idea was to study ambient urban air pollutant levels in green areas and not pollution coming from a single source. Some sites were situated within the urban street grid with low traffic streets. At different sites, depending on the availability of suitable mounting structures and the location of habitats, the distance between the sampling point pairs (open and tree-covered) and the nearest major road varied; ranging between 25 and 543 m (mean 136 m). The distance between the two sampling points (open or tree-covered) within each site ranged between 23 and 187 m (mean = 79.4 m). The tree-covered habitats consisted of mainly broadleaved, mature trees. The open habitats were mainly lawns or grasslands. The soil surface at these open habitats was either completely pervious or partly impervious with some asphalt surfaces.
Figure 1. Locations of the twenty-five study sites (marked as dots) in Baltimore, MD, USA. The dot in a small map on the right depicts the location of greater Baltimore in USA. At each of the 25 sites, air quality and temperature was measured in both tree-covered and open habitats.

We mounted the air samplers under rain shields and the thermometers inside radiation shields and attached them to lamp posts or similar structures in the open areas and to tree trunks (directly under the canopy) in the tree-covered areas. We mounted the air samplers and thermometers 3-4
m above ground to prevent samplers being too close to ground surface where O₃ gets depleted (Mills et al., 2010), yet representing the height in which humans are exposed to these pollutants. Measurements were carried out during early summer, from 5 May to 25 May, 2016 (20 days), when plant leaves were practically fully developed.

We determined the percentage of canopy cover at each site from satellite images (using Google Earth Pro, version 7.1.2.2041) by measuring the area covered by tree canopy within 50 m radii from the sampling point in both habitats. The percentage of canopy cover ranged between 25 and 100 % (mean = 63.9 %) in tree-covered habitats and between 0 and 73 % (mean = 23.8 %) in open habitats. Mean daily temperatures ranged between 14.5 and 16.3 °C (mean = 15.5 °C) in tree-covered habitats and between 15.4 and 17.5 °C (mean = 16.3 °C) in open habitats, being significantly lower in the tree-covered habitats than in the open habitats (5.2%, p<0.001, n = 23 due to two lost thermometers). We determined traffic volume at each site by calculating the cumulative traffic volume from the largest streets within 200 m radii from the sampling point in the tree-covered area using traffic flow data (annual average daily traffic), obtained from Baltimore Metropolitan Council (2016) and Maryland Department of Transportation (2016). Traffic volume (motor vehicles day⁻¹) ranged between 0 and 179,066 (mean = 36,138). We did not estimate traffic volume separately for open habitat sampling points as the open and tree-covered habitat circles with 200 m radii would overlap to such extent that traffic volume would practically be the same.

The sampling sites situated in remnant forest patches, parks and park-like block courtyards in residential areas were dominated by broad-leaf deciduous trees, including tree species (Fraxinus
Ulmus americana, Fagus grandifolia, Prunus serotina, Robinia pseudoacacia and Ailanthus altissima) typical to Baltimore City. The sampling sites situated in the outskirts of the city additionally included dominant forest tree species (broad-leaf deciduous) (Quercus montana, Liriodendron tulipifera, Acer negundo, Fraxinus pennsylvanica, Platanus occidentalis and Acer saccharinum) typical to forests outside of the city of Baltimore. A wind rose showing the prevailing wind direction and speed during the measuring period is shown in Fig. 2. The monthly average temperature in Baltimore in May 2016 was 16.0 °C, representing slightly lower temperatures than usually in May in Baltimore.

Figure 2. Wind direction and speed during 5 May – 25 May, 2016 in Baltimore (Johns Hopkins Homewood Campus measuring station).

2.3. Data analysis
We tested changes in NO\textsubscript{2} and O\textsubscript{3} concentrations using linear models, with NO\textsubscript{2} and O\textsubscript{3} modelled following a normal distribution. Two types of analyses were performed. First, we evaluated the concentrations of NO\textsubscript{2} and O\textsubscript{3} across the whole dataset using the following model structure:

\[
\text{NO}_2 \sim \text{habitat type} + \text{O}_3 + \text{mean daily temperature}, \text{ and}
\]

\[
\text{O}_3 \sim \text{habitat type} + \text{NO}_2 + \text{mean daily temperature}.
\]

Here habitat type represents a factor with two levels; tree-covered and open areas. Second, we evaluated the concentrations of NO\textsubscript{2} and O\textsubscript{3} per habitat type. This resulted in four analyses:

\[
\begin{align*}
\text{NO}_2_{\text{tree}} & \sim \text{traffic volume} + \text{canopy cover}_{\text{tree}} + \text{O}_3_{\text{tree}} + \text{mean daily temperature}_{\text{tree}} \\
\text{NO}_2_{\text{open}} & \sim \text{traffic volume} + \text{canopy cover}_{\text{open}} + \text{O}_3_{\text{open}} + \text{mean daily temperature}_{\text{open}} \\
\text{O}_3_{\text{tree}} & \sim \text{traffic volume} + \text{canopy cover}_{\text{tree}} + \text{NO}_2_{\text{tree}} + \text{mean daily temperature}_{\text{tree}} \\
\text{O}_3_{\text{open}} & \sim \text{traffic volume} + \text{canopy cover}_{\text{open}} + \text{NO}_2_{\text{open}} + \text{mean daily temperature}_{\text{open}}
\end{align*}
\]

The subscripts above relate to the measurements in that particular habitat type. Traffic volume was square-root transformed into a normal distributed variable, due to a few very high values. Model selection was performed in all six models by removing predictors, one at a time, if their p-values were greater than 0.1. All data analyses were performed using R statistical software, version 3.4 (R Core Team, 2017).

3. Results
While the mean NO$_2$ concentration appears lower in tree-covered areas than in open areas (Fig. 3), the difference is not statistically significant (Table 1). However, O$_3$ concentrations were significantly lower in tree-covered areas compared to open areas (Table 1, Fig. 3). Across the whole dataset, both NO$_2$ and O$_3$ levels were significantly positively related with mean daily temperature, and NO$_2$ and O$_3$ levels were significantly negatively correlated with each other (Table 1). Traffic volume was retained in all four models dealing with NO$_2$ and O$_3$ per habitat type. NO$_2$ in both the tree-covered and open areas increased significantly with traffic volume, while O$_3$ in both the tree-covered and open areas decreased significantly with traffic volume (Fig. 4, Table 1). Additionally, NO$_2$ concentrations in the tree-covered areas increased significantly with temperature and NO$_2$ concentrations in the open areas decreased significantly with the percentage of canopy cover (Fig. 4, Table 1).

**Table 1.** Linear model results (see Figs. 3 and 4), testing the effects of various variables on NO$_2$ and O$_3$ levels across the whole dataset and per habitat type. The subscripts (tree or open) relate to the measurements in that particular habitat type. Coefficients with standard errors (in brackets) and p-values (below standard errors) are presented. The intercept included open habitat type in the first two models (whole dataset models).

<table>
<thead>
<tr>
<th>Variable</th>
<th>Intercept</th>
<th>Habitat type</th>
<th>NO$_2$ / O$_3$</th>
<th>Mean daily temperature</th>
<th>Canopy cover</th>
<th>Traffic volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$</td>
<td>Coefficient</td>
<td>-33.787 (11.874)</td>
<td>-0.315 (0.123)</td>
<td>4.490 (0.825)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SE</td>
<td>0.007</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>O$_3$</td>
<td>Coefficient</td>
<td>24.363 (18.140)</td>
<td>-3.997 (1.437)</td>
<td>-0.337 (0.156)</td>
<td>2.382 (1.212)</td>
<td></td>
</tr>
<tr>
<td>SE</td>
<td>0.186</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>p</td>
<td>0.008</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.056</td>
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<tr>
<td></td>
<td>Coefficient</td>
<td>SE</td>
<td>p</td>
<td>Coefficient</td>
<td>SE</td>
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<td>--------</td>
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<td>--------</td>
</tr>
<tr>
<td>NO₂ tree</td>
<td>-67.769</td>
<td>16.614</td>
<td>&lt;0.001</td>
<td>5.501</td>
<td>1.080</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>NO₂ open</td>
<td>25.558</td>
<td>1.613</td>
<td>&lt;0.001</td>
<td>-0.002</td>
<td>&lt;0.001</td>
<td>0.030</td>
</tr>
<tr>
<td>O₃ tree</td>
<td>53.364</td>
<td>1.194</td>
<td>&lt;0.001</td>
<td>-0.019</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>O₃ open</td>
<td>57.579</td>
<td>1.134</td>
<td>&lt;0.001</td>
<td>-0.012</td>
<td>0.006</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3.** Concentrations of (a) NO₂, and (b) O₃ in open and tree-covered areas (n = 25). The dashed grey line indicates the mean (labelled), the box indicates the first through third quartiles, and whiskers delineate the wide interquartile range, 1.5 times the first through third quartiles. Data points falling outside this range are shown as dots.
Figure 4. Relations between (a) NO$_2$ concentrations in tree-covered areas and traffic volume (square-root transformed number of motor vehicles day$^{-1}$, annual average of daily traffic, presented within 200 m radius from the sampling point in the tree-covered area); (b) NO$_2$ concentrations in open areas and traffic volume; (c) NO$_2$ concentrations in tree-covered areas...
and mean daily temperatures (°C) in tree-covered areas; (d) NO₂ concentrations in open areas and canopy cover in open areas (m², within the 50 m radius from the sampling point); (e) O₃ concentrations in tree-covered areas and traffic volume, and (f) O₃ concentrations in open areas and traffic volume. See Table 1 for statistical results.

4. Discussion

Our study, performed in early summertime (May) in urban forest/park environments in the Mid-Atlantic USA, suggests that the concentrations of NO₂ are not significantly reduced in tree-covered habitats compared to adjacent open habitats, but that O₃ concentrations are. That NO₂ concentrations did not differ between tree-covered and open habitats is in contrast to our hypothesis and those earlier empirical studies (García-Gómez et al., 2016; Grundström & Pleijel, 2014; Fantozzi et al., 2015; Klingberg et al., 2017; Rao et al., 2014; Yin et al., 2011), where some NO₂ reduction by tree-canopy was detected. However, our finding that NO₂ concentrations in the open habitats decreased with the increasing percentage of canopy cover (within a 50 m radius from the sampling point in the open habitat) may indicate some absorption of NO₂ by the trees. On the contrary, our result that NO₂ levels were not reduced in tree-covered habitats corroborates those empirical findings, where no clear reduction of NO₂ levels by urban tree cover was observed either on city-level (Irge et al., 2015) or on local level in near-road environments (Setälä et al., 2013; Yli-Pelkonen et al., 2017), or where even higher concentrations of NO₂ were reported inside the urban tree canopies than outside (Harris & Manning, 2010). Our findings showing air quality improvement by urban tree-cover in terms of O₃ support our hypothesis and similar earlier empirical findings (García-Gómez et al., 2016;
Harris & Manning, 2010) and a number of city-scale modeling studies (e.g. Baumgardner et al., 2012; Selmi et al., 2016), but are partly in contrast to local-level findings of e.g Grundström & Pleijel (2014), Fantozzi et al. (2015) and Yli-Pelkonen et al. (2017). Although data on O₃ uptake rates by all the tree species in our study area is not available, broad-leaf deciduous trees are generally estimated to be relatively efficient in O₃ removal (Manes et al., 2012).

For instance, Harris & Manning (2010) used passive samplers and temperature loggers in Springfield, Massachusetts, USA, and found higher NO₂ and lower O₃ levels inside urban tree canopies than directly outside (30-45 cm) the canopies, at locations with varying distance from a major highway. They suggested that this is due to NOₓ/O₃ chemistry related to gas interactions between soil and the air, as described by Fowler (2002). However, they did not find differences in temperature between inner and outer canopy locations and suggested that temperature had little or no effect on the pollutant levels. In contrast, our open sites were much farther from tree canopies and shade, and grow hotter during the day. Fantozzi et al. (2015) studied one site in Siena, central Italy, and found lower NO₂ concentrations in a measurement transect under the canopies of Quercus ilex L., extending 1-10 m from a busy road, compared to a nearby open-field transect. They observed reduced O₃ concentrations inside the canopy transect only during post-summer rainfalls. Yli-Pelkonen et al. (2017) measured NO₂ and O₃ concentrations on average 25 m from busy roads at 10 sites in Helsinki, Finland, where NO₂ concentrations were on average similar to and O₃ concentrations clearly lower than in our study in Baltimore, but did not find differences between tree-covered and adjacent open road-side habitats. The variable results from different parts of the world indicate that the impact of vegetation on the concentration of gaseous air pollutants such as NO₂ and O₃ may largely depend on the type and
structure of local vegetation, climatic conditions, proximity to traffic pollution sources and regional and local ambient pollutant levels.

It is well established that formation of O$_3$ needs photolysis and is positively related to temperature (Cardelino & Chameides, 1990; Churkina et al., 2017; Finlayson-Pitts & Pitts, 1997; Paoletti et al., 2014), which was also detected in our study. As it is also likely that increased shade and the observed lower mean daily temperatures within the tree-canopies also reduce solar radiation under the canopies (Shashua-Bar & Hoffman, 2004; Renaud et al., 2011; Lehmann et al., 2014), this may result in decreased concentrations of O$_3$ in tree-covered habitats compared to open habitats (Cardelino & Chameides, 1990). Thus, the observed lower O$_3$ concentrations in the tree-covered habitats may not result solely from the O$_3$ uptake by tree canopy, but also from the reduced solar radiation and temperatures. That NO$_2$ levels in our study decreased with temperature across the whole dataset and in the tree-covered habitats may also indicate a slight NO$_2$ uptake by the tree canopies, which were cooler than open areas. However, as NO$_2$ levels did not differ significantly between tree-covered and open habitats, the reason for the weak relationship between NO$_2$ concentration and temperature remains unsolved.

Traffic volume's positive relation to NO$_2$ levels and negative relation to O$_3$ levels, as well as the negative relation between NO$_2$ and O$_3$ levels, indicate that NO$_2$ in the study area originates mainly from road traffic (see e.g. Clements et al., 2009; Setälä et al., 2013; Yli-Pelkonen et al., 2017) as higher traffic volume produces more NO$_x$. While at low concentrations, NO$_x$ is a precursor to ozone formation, at higher concentrations (all else being equal), NO$_x$ catalyzes ozone destruction, which results in O$_3$ depletion (e.g. Rodes & Holland, 1981). In all, the
interplay between traffic density, NO\textsubscript{2} and O\textsubscript{3} depends on an array of factors in urbanized settings, even at sites situated far from heavily-trafficked roads.

The prevailing wind direction (long-term average) in May in Baltimore is from the south, but during the measuring period north-eastern winds dominated (Fig. 2). However, as our sampling sites were relatively far away from heavily-trafficked roads or neutrally situated within the street network, we did not place the sampling sites according to the prevailing wind direction. Furthermore, our relatively long sampling period is bound to diminish the impacts of short-term wind direction changes and thus the wind direction is unlikely to cause systematic bias in our measurement campaign.

As has been noted in earlier studies, it is possible that reduced air flow within tree-covered areas in near-road environments (Belcher et al., 2012; Gromke & Ruck, 2009; Renaud et al., 2011; Wuyts et al., 2008) can increase pollutant levels within the canopy and thus have negative impacts on local air quality (Setälä et al., 2013; Viippola et al., 2016; Vos et al., 2013), while in open areas the polluted air mass is mixed by wind and diluted more rapidly. However, as in the current study in Baltimore the sampling sites were not in close proximity to heavily-trafficked roads, such “trapping effect” of highly polluted air mass under the canopies is unlikely and the actual uptake of the studied gaseous pollutants by tree canopies should be observable.

Our results suggest that one should not take for granted the notion that urban trees provide overall air quality benefits. For instance, NO\textsubscript{2} concentrations are not necessarily decreased in the tree-covered areas via absorption of NO\textsubscript{2} by trees. However, tree-cover seems to provide air
quality improvement regarding O$_3$, at least in the early summer conditions in Baltimore. This may not be the case during the heat wave periods in mid-summer, when elevated emissions of biogenic volatile organic compounds could, in combination with NO$_x$ emissions from traffic, contribute to increased O$_3$ formation in urban areas (Churkina et al., 2017; Manes et al., 2012). However, as tree species in the study area are not strong emitters of reactive biogenic volatile organic compounds, their ozone forming potential is minor (Benjamin & Winer, 1998).

5. Conclusions

Our results, obtained from the period when gas exchange between foliage and the atmosphere is active in Baltimore, Mid-Atlantic USA, suggest that trees in urban forests and parks can result in reduced O$_3$ levels, but that the impact of trees on NO$_2$ concentrations is negligible. That O$_3$ concentrations were reduced under tree canopies was in line with our hypothesis and likely results from absorption of O$_3$ by tree canopies, or from lowered temperatures and reduced solar radiation under tree canopies - or combination of these. That NO$_2$ concentrations did not differ between tree-covered and open habitats was in contrast to our hypothesis and suggests that urban park and forest vegetation do not necessarily provide significant and uniform air quality improvement regarding NO$_2$, as it is often stated by city-scale model calculations.

Thus, urban inhabitants spending time in tree-covered areas in urban parks and forests may receive lower exposure to O$_3$ concentrations, at least when temperatures are moderate, but the same conclusion does not hold for NO$_2$. We stress that trees and other vegetation provide many other ecosystem services for urban dwellers to enjoy, such as reduced temperatures under tree
canopies. Our results further suggest that actions aiming at local air pollution mitigation should consider local variability in vegetation, climate, micro-climate, and traffic conditions. We conclude that the key measure to reduce human exposure to NO$_2$ and ozone, should be reduction of emissions from traffic, and placing recreational areas far from pollutant sources.

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