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The Interplay Between Ozone and Urban Vegetation—BVOC Emissions, Ozone Deposition, and Tree Ecophysiology

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Tropospheric ozone (O₃) is one of the most prominent air pollution problems in Europe and other countries worldwide. Human health is affected by O₃ via the respiratory as well as the cardiovascular systems. Even though trees are present in relatively low numbers in urban areas, they can be a dominant factor in the regulation of urban O₃ concentrations. Trees affect the O₃ concentration via emission of biogenic volatile organic compounds (BVOC), which can act as a precursor of O₃, and by O₃ deposition on leaves. The role of urban trees with regard to O₃ will gain further importance as NOₓ concentrations continue declining and climate warming is progressing—rendering especially the urban ozone chemistry more sensitive to BVOC emissions. However, the role of urban vegetation on the local regulation of tropospheric O₃ concentrations is complex and largely influenced by species-specific emission rates of BVOCs and O₃ deposition rates, both highly modified by tree physiological status. In this review, we shed light on processes related to trees that affect tropospheric ozone concentrations in metropolitan areas from rural settings to urban centers, and discuss their importance under present and future conditions. After a brief overview on the mechanisms regulating O₃ concentrations in urban settings, we focus on effects of tree identity and tree physiological status, as affected by multiple stressors, influencing both BVOC emission and O₃ deposition rates. In addition, we highlight differences along the rural-urban gradient affecting tropospheric O₃ concentrations and current knowledge gaps with the potential to improve future models on tropospheric O₃ formation in metropolitan areas.

Keywords: biogenic volatile organic compounds, ozone formation and deposition, roadside trees, rural-urban gradient, stress, urban forest, urban trees
INTRODUCTION

Ground-level ozone (O$_3$, tropospheric ozone) is one of the most prominent air pollution problems in Europe and other countries worldwide. When taken-up by plants, O$_3$ irreversibly damages plant tissue-leading to reduced crop yields and forest growth (Mills et al., 2011). Human health is temporarily or chronically affected by O$_3$ via the respiratory as well the cardiovascular systems (WHO, 2006). The World Health Organization (WHO) has repeatedly released updated recommendations regarding ozone exposure limits. In order to avoid negative impacts on human health, the alert threshold for 8-h average O$_3$ exposure was lowered in 2005 from 120 µg m$^{-3}$ (60 ppb) to 100 µg m$^{-3}$ (50 ppb), and short-time concentrations should not exceed 160 µg m$^{-3}$ (80 ppb, WHO, 2006). However, many (supra-) national legislations incl. the European Unions’ (EU) Air Quality Directive (EU, 2008) are allowing higher O$_3$ exposures (e.g., EU target value 120 µg m$^{-3}$ not to be exceeded on >25 days year$^{-1}$, averaged over 3 years). The set thresholds are frequently reached or exceeded in urban areas, especially during heat waves (Solberg et al., 2008; Holman et al., 2015). Recent data indicates that 95–99% of the EU urban population were exposed to O$_3$ concentrations above WHO air quality guidelines in the period 2006–2016 (EEA, 2018a,b). However, within metropolitan areas large temporal and spatial heterogeneities of tropospheric O$_3$ levels exist (Paoletti et al., 2011; Calafipietra et al., 2016), which are influenced by a distinct rural-urban gradient and a broad range of abiotic and biotic factors (Sicard et al., 2013; Lahr et al., 2015; Hagenbörk et al., 2017).

The recent literature on urban forests and greening (“green urban infrastructure”) largely advocates the environmental services of trees such as air pollution mitigation (e.g., CO$_2$ sequestration, dry deposition), storm water interception, and heat mitigation (Escobedo et al., 2011; Connop et al., 2016; Livesley et al., 2016). In general, the substantial scientific evidence on many positive effects has led to a normative assertion by stakeholders that any increase in urban forests is desirable and will mitigate virtually all kinds of environmental problems (Escobedo et al., 2011). However, the role of urban vegetation on the local regulation of tropospheric O$_3$ concentrations is complex. Among the different urban vegetation forms, trees are key as they can both remove (Hardin and Jensen, 2007) but also contribute significantly to O$_3$ formation (Jenkin et al., 2015). In addition, air chemistry reactions and thus O$_3$ formation are indirectly affected by the cooling and shading properties of vegetation (Yli-Pelkonen et al., 2018). The net effect of a tree on the O$_3$ concentration depends on tree species, its physiological status, environmental drivers of emission, as well as climate and air chemistry such as concentrations of volatile organic compounds (VOCs; see Box 1 for glossary) and nitrogen oxides (NO$_x$). The emission of biogenic VOC (BVOC) by trees as source of tropospheric O$_3$ will gain further importance as climate change progresses (Peñuelas and Staudt, 2010; Trenberth et al., 2014). It is also expected that future urban NO$_x$ concentrations will continue to decline by substituting combustion-powered vehicles, especially Diesel-powered models, with cleaner ones (O’Driscoll et al., 2018). Consequently, urban ozone chemistry might become more sensitive to BVOC emissions. While not all BVOCs will be equally effective and in some cases may actually contribute to a decomposition of O$_3$ (Bonn et al., 2018; Neirynck and Verstraeten, 2018), the combination of higher urban temperatures and lower levels of NO$_x$ is generally thought to increase the importance of BVOCs as precursors of ozone in future urban environments (Chameides et al., 1988).

In this review, we summarize processes related to trees that affect tropospheric ozone concentrations in metropolitan areas from rural settings to urban centers, and discuss their importance under present and future conditions. Urban trees differ in their potential BVOC emission rates and are often exposed to a multiple and high stress environment, that is also particularly prone to climate change impacts; thus, we especially focus on tree species-specific effects and the physiological status as (potential) major factors influencing ground-level O$_3$ formation. In addition, the review will highlight knowledge gaps, e.g., concerning the spatial distribution of species and environmental factors along rural-urban gradients, with the potential to improve future models on tropospheric O$_3$ formation in metropolitan areas.

TROPOSPHERIC OZONE FORMATION AND SINKS

The O$_3$ forming process in the troposphere is generally catalyzed by nitrogen oxides in the presence of radiation, and fueled by methane, carbon monoxide and non-methane volatile organic compounds (NMVOC). The general pathways to tropospheric

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**Box 1** | Glossary of volatile organic compound classes

| VOC | Volatile organic compounds encompass a broad range of gaseous compounds of (hydro-)carbons emitted into the atmosphere—containing alkanes, alkenes, aromatic hydrocarbons, oxygen-containing VOCs (e.g., methane), and nitrogen-containing VOCs. Sources of VOCs are e.g., plants, animals, microbes, and fungi, combustion by traffic, industry, biomass burning, and households. |
| NMVOC | Non-methane volatile organic compounds are VOCs not counting methane, which is mostly emitted by domestic ruminants, natural wetlands, landfills, biomass burning, and fossil-fuel emissions. |
| AVOC | Anthropogenic VOCs such as paraffins, olefins, and aromatics are predominantly emitted by combustion. |
| BVOC | Biogenic VOCs are biologic-originated VOCs. The vegetation emits isoprenoids as isoprene (C$_{10}$), monoterpenes (C$_{10}$), and sesquiterpenes (C$_{15}$), but also OVOCs and GLVs. |
| OVOC | Oxygenated VOCs are a heterogeneous group comprising various alcohols (e.g., methanol, ethanol), aldehydes (acetaldehyde, formaldehyde), ketones and specialized substances such as methyl jasmonates and dimethyl nonatriene. OVOCs are i.a. emitted by (stressed) plants and anthropogenic sources. |
| GLV | Green leaf volatiles are a part of BVOCs combining C$_5$ aldehydes and alcohols emitted by the vegetation during and after biotic and abiotic stress. |
O3 formation are well understood (Brasseur et al., 1999), but the complexity of organic chemistry is still subject to intensive research (Fittschen et al., 2017). Ozone formation is always initiated by the photolysis of NO2. The recycling of NO to NO2 occurs after CO, methane or NMVOC react with OH and generate hydroxyl and peroxy radicals. These readily react with NO, regenerating NO2. Thus, NO3 is recycled in what is referred to as the RO3-NO3 cycle (Figure 1).

At low NO3 concentrations, O3 formation becomes NO3 limited. At medium NO3 concentrations, OH recycling via the RO3-NO3 cycle becomes efficient to sustain the oxidation of high levels of NMVOCs, which finally leads to a regime, where O3 formation becomes VOC-limited (Carter, 1994). The O3 forming potential also depends on the VOCs’ reactivity, which differs among compounds. Isoprene, for example, is the most common BVOC and has a reactivity which is 22 times higher than that of the important anthropogenic VOC (AVOC) benzene (Carter, 1994; Wagner and Kuttler, 2014). The reaction rate constants of CO and methane with respect to OH are about 410 and 14,000 times lower than that of isoprene, which can therefore compete with their reactivity in many environments. For a more detailed description of the chemical reactions involved in tropospheric chemistry we refer to the specialized literature (Atkinson, 2000; Kirchner et al., 2001; Jenkin et al., 2010; Wang et al., 2017).

Recent measurements of OH reactivity (Kim et al., 2011; Kaiser et al., 2016; Nölscher et al., 2016; Williams et al., 2016) have suggested missing emission sources of reactive NMVOCs and missing secondary atmospheric reactions leading to reactive NMVOCs. This uncertainty is largely attributed to the complexity of organic chemistry and precursor emissions. On global and regional scales, BVOCs play a central role in tropospheric chemistry because of their reactivity with respect to OH (Guenther et al., 2012). While plants can release more than 30,000 different BVOCs (Trowbridge and Stoy, 2013), only a few are emitted in relatively large quantities and are highly reactive with atmospheric radicals (Atkinson and Arey, 2003). The most reactive classes of BVOC emitted by plants are isoprene (30%), monoterpenes and higher terpenoids (25%: e.g., sesquiterpenes) whereas oxygenated VOCs (OVOC) are present in lower amounts and less reactive (Atkinson and Arey, 2003; Atkinson, 2007). Based on the maximum incremental reactivity scale (MIR), e.g., isoprene (MIR 10.6) reacts faster with ozone than monoterpenes (MIR 4.0) (Carter, 2000, 2010). Once in the atmosphere, isoprene is undergoing complex chemical cycling initiated by photochemistry, a fate all NMVOC have in common and are leading to a vast network of chemical reactions. Similar, higher molecular weight terpenes (>C15) can also play a significant role in atmospheric chemistry due to their reactivity (Atkinson and Arey, 2003).

Once being produced, O3 has several routes of removal. The most important ones include dry deposition and chemical loss (Monks et al., 2009; IPCC, 2014). On a global scale, the most important chemical loss term is the photolysis of O3 in the atmosphere and subsequent reaction with water vapor (H2O) leading to the production of OH radicals (Brasseur et al., 1999). Globally a gross chemical O3 loss of 4,260 ± 264 Tg year\(^{-1}\) and a net chemical production of 633 ± 275 Tg year\(^{-1}\) was estimated (Lamarque et al., 2013). Under high NO3 emissions (e.g., in an urban context) another chemical conversion of O3 is triggered by the reaction with NO, leading to a temporary production of excess NO2. The reactions between NO, NO2, and O3 are often termed as the triad and represent a null cycle, where no net O3 is produced or removed (Figure 1, NO3 cycle). Yet locally, O3 is chemically converted to NO2 and it can be speculated that O3 deposition can also be facilitated via NO2 uptake by plants. The second largest sink for O3 is deposition on surfaces. Estimates of O3 dry deposition are in the order of 1,094 ± 309 Tg year\(^{-1}\) (Young et al., 2013). Further, another sink of O3 is the ozonolysis of VOCs forming secondary organic aerosols (SOAs), initiated by O3 degrading C-C double bonds in alkenes and leading to the formation of energy-rich Criegee biradicals (Criegee, 1975; Pinto et al., 2010).

Whether the O3 level increases or decreases by VOCs is depending on the chemical species and the relative concentrations of the involved compounds (Sillman and He, 2002). To implement effective mitigation strategies, the
relationship between the different reaction partners as well as their current absolute concentrations has to be considered.

**IMPACT OF TREE SPECIES AND THEIR PHYSIOLOGICAL CONDITION ON THE OZONE DYNAMICS OF URBAN ENVIRONMENTS**

Quantity and quality of BVOC emissions and $O_3$ removal by urban trees depends on community composition, and short- and long-term environmental conditions—affecting tree size and physiological status. In the following, an overview is given on key traits and stressors influencing $O_3$ removal and BVOC emission potential of urban tree vegetation—referring mainly to European examples to keep a manageable length and scope.

**Species-Specific Effects**

**Community Composition**

The sensitivity of plants to specific environmental conditions determines urban species composition, either by affecting mortality of established trees or by suggesting selection preferences to urban planners (Holmes et al., 2013). Three main locations of urban vegetation can be distinguished: street trees ("road-side" trees), parks and private gardens, and urban woodlands. Street trees are exposed to relatively high stress levels and the average lifespan of the trees is short, while trees in parks and private gardens are commonly exposed to less stress. Trees in urban woodland are subjected to relatively low stress levels and may reach a lifespan and size comparable to forests (Sæbø et al., 2005). The environmental conditions and the frequency of these different vegetation types, and thus species community composition, differs largely along rural-urban gradients as discussed below (section The Rural-Urban Gradient in Context of Tree-Ozone Interactions). However, despite an overall high number of species available for planning, only relatively few tree genera and species are highly abundant in streets and parks of northern and central European cities (Grote et al., 2016; Samson et al., 2017b). Common urban species in central to northern Europe are in particular: *Tilia* sp., *Platanus* sp., *Aesculus* sp., *Fraxinus* sp., *Quercus* sp., *Acer* sp., *Picea* abies, and *Pinus* sp. Additionally, *Fagus sylvatica* occurs frequently in parks, private gardens and urban woodlands. In southern Europe, a broader species pool is utilized but likewise dominated by a few tree genera and species: *Platanus × acerifolia, Quercus ilex, Robinia pseudoacacia, Celtis australis, Sophora japonica, Morus sp., Populus sp., Ulmus sp., Pinus sp., and Prunus sp.* (Pauleit et al., 2002; Grote et al., 2016). There is a general trend to introduce more exotic tree species that are supposed to withstand progressing “global warming” and diseases in urbanized areas better than their autochthonous counterparts (Youngstedt et al., 2015). However, whether or not replacing native species with exotic species is still under debate as neophytes may disturb the ecological relationships between co-evolved species (Cornelis and Hermy, 2004; Kühn et al., 2004).

Under standard conditions, the contribution of an individual tree to either $O_3$ removal or BVOC emissions depends primarily on species-specific traits [e.g., high or low BVOC emission rates, (Samson et al., 2017a)], and gaseous exchange is proportional to the size of its canopy, as measured by its leaf mass or surface area (Harrison et al., 2013; Vos et al., 2013). Similar “size-symmetric”-effects of larger tree individuals have been found with regard to air pollution mitigation in particularly when the main removal process is surface deposition rather than stomatal adsorption (Grote et al., 2016). However, large and dense canopies, for example, may allow emitted BVOCs to react on leaf surfaces within the canopy before reacting with gases (Forkel et al., 1999); *vice versa* ozone deposition on leaf surfaces within dense canopies may be reduced due to a non-uniform distribution of ozone sources (Zhu et al., 2009)—attenuating “size-symmetric”-effects.

It should be furthermore considered that canopy size, shape, and density of street trees, despite being highly species/cultivar-specific, can largely be modified by management measures (Janhäll, 2015). Therefore, allometric relationships typically used in the forestry sector (e.g., to determine biomass and crown size from stem diameter and tree height) generally fail to predict tree attributes in the urban context. Surprisingly, closed canopies of trees may contribute to higher pollution in urban canyons by decreasing dispersion (Gromke and Ruck, 2009; Vos et al., 2013). However, this effect is beneficial for pedestrians and bikers when the lanes are located just on the external side of the road (outside the canyon).

**Ozone Deposition Capacity**

Vegetation plays a major role for the dry depositional sink of $O_3$. Dry deposition over lush vegetation is 40 times more efficient than over urban land according to common parameterizations in atmospheric models (Wesely, 1989). Deposition of $O_3$ to vegetation is modulated by a stomatal and a non-stomatal component. In either case, the removal of $O_3$ is ultimately driven by a chemical loss. Stomatal $O_3$ uptake triggers antioxidant reactions in the intercellular space and is largely dependent on stomatal conductance, which is driven by environmental conditions and varies among tree species (as discussed below). If the stomata are open, $O_3$ diffuses into the intercellular space from the atmosphere and is almost immediately deposited by reactions in the apoplast with membrane lipids, moisture and cell organelles; uptake increases with increasing outside concentrations (Wesely and Hicks, 2000). Non-stomatal $O_3$ deposition occurs on leaf surfaces by reactions with waxes, moisture and salts (Barnes et al., 1988; Altimir et al., 2006) and in the boundary layer with emitted BVOCs (see sections Tropospheric Ozone Formation, and Sinks and BVOC Emission Rates). Tree species featuring traits such as a large leaf area index, hairy leaves, leaf waxes and moist surfaces, and keeping their stomata longer open under stressed conditions (see below, section Plant Water Status), are depositing $O_3$ better than species without these traits (Barnes et al., 1988; Altimir et al., 2006; Cape et al., 2009). However, Calfapietra et al. (2016) showed that under standardized conditions, most common tree species in Rome, Italy had rather similar $O_3$ deposition rates per m² leaf area; however, photosynthetically very active trees like *Populus × euramericana* had higher and the gymnosperm *Pinus pinea* had lower $O_3$ deposition rates than the average. As similar plant
traits are likely affecting fine particulate matter (PM2.5) and O₃ deposition rates, available rankings addressing the effectiveness of (deciduous) tree species for PM2.5 deposition (e.g., Yang et al., 2015) can probably be used as a guideline for ozone deposition capacity.

**BVOC Emission Rates**

The production and emission of BVOCs can serve as a protective mechanism of plants against O₃-induced tissue damage, for increasing thermotolerance, communicating with neighboring and interfering individuals and sometimes possibly just to get rid of surplus energy by releasing byproducts of physiological processes (Niinemets et al., 2013). The profiles of emitted BVOCs vary considerably among tree species (Courtois et al., 2009; Niinemets and Monson, 2013) and even genotypes (Blanch et al., 2012). Figure 2 illustrates the available data on standard emission potentials of isoprene, monoterpene, sesquiterpenes and OVOCs of frequent tree species in European cities under non-stress conditions. Isoprene is known as the major BVOC emitted by trees globally (Figure 2) and also one that has the highest potential contributing to tropospheric O₃ formation (Kamens et al., 1982; Loreto and Velikova, 2001; Xie et al., 2008). Among the most common city trees, *Populus nigra*, *P. tremula*, *Quercus robur* and *Q. pubescens* were identified as high isoprene emitters. **Monoterpenes** are emitted by conifers and several broad-leaved trees including *F. sylvatica*, which is dominant in forests of central Europe (Kramer et al., 2010), and thus may be important pre-cursors for particles and O₃ especially in rural-suburban transition zones. Common urban trees such as *Acer platanoides* and *Ulmus minor* are considered low emitters (Singh et al., 2007; Karl et al., 2009) while some as for example *Fraxinus excelsior*, and *Tilia platyphyllos* are generally assumed to be non-monoterpane and -isoprene emitters. **Sesquiterpenes** are mainly emitted in low quantities and have a similar O₃ formation potential than monoterpenes, although less than isoprene, and have thus a minor influence on ozone formation (Holopainen and Blande, 2013). Oxygenated VOCs (OVOCs) have different but generally minor ozone forming potentials. They are typically emitted as signaling compounds or as response to any kind of stressful conditions (Seco et al., 2007). As plant ontogeny can

**FIGURE 2 |** Standard emission potentials (µg g DW⁻¹ h⁻¹; at 30 °C leaf temperature and 1,000 µmol m⁻² s⁻¹ PPFD) of isoprene (ISO), monoterpene (MT), sesquiterpenes (SQT), and oxygenated VOC (OVOC) of frequent tree species in urban areas of northern/central (N/C) and southern (S) Europe. Potential emission rates are grouped in no (white), low (green), medium (yellow), and high (red) emission classes. ISO: low < 10, high > 30; MT and OVOC: low < 2, high > 5; SQT: low < 0.5, high > 1; with medium categories with values in-between. A color gradient indicates emission rates crossing the defined classes; gray indicates: “no data available.” References: a (Fyda et al., 2014), b (Benjamin and Winer, 1998) “high ISO,” c (EMEP/CORINAIR, 1999), d (Curtis et al., 2014), e (Seron et al., 1994), f (Grote et al., 2016), g (Hakola et al., 1998), h (Hakola et al., 2001), i (Hakola et al., 2008), j (Heinrich, 2007), k (Karl et al., 2009), m (König et al., 1995), n (Lamb et al., 1987), o (Meeningen et al., 2016) “low ISO,” p (Owen et al., 1997), q (Paolletti et al., 2011), r (Préndez et al., 2013), s (Singh et al., 2007), t (Steinbrecher et al., 2009), u (Streiling and Matzarakis, 2003), v (Tiwary et al., 2013), w (Veldt, 1989).
influence i.a. foliar defense metabolites (Goodger et al., 2013), it is likely that BVOC emission rates of tree species are changing along ontogenetic trajectories.

Other compounds are also occasionally reported as constitutive emissions from plants. Regarding trees in urban area, alkanes, aldehydes, alkenes, aromatic compounds, esters, and ketones have been determined to originate from Ginkgo biloba (Li et al., 2011). Their impact on air chemistry is generally assumed to be small since anthropogenic emissions are dominating the concentration of these compounds in urban areas by far (e.g., Costa and Baldasano, 1996; Cheng et al., 2010). However, alkanes and alkenes have been found as major emissions over many forests (Kourchchev et al., 2008; Halliday et al., 2015; Rhew et al., 2017); thus, at least the more reactive alkenes are assumed to play a significant role at larger to global levels (Goldstein et al., 1996; Rhew et al., 2017).

Looking at the community level, some general patterns in BVOC emissions can be identified among tree functional types (Dani et al., 2014). For example, trees featuring a high photosynthetic capacity are often also high monoterpane emitters. Deciduous trees are in general higher isoprene emitters and low monoterpane emitters whereas evergreen trees are low isoprene emitters and can be both low and high emitters of monoterpane (Dani et al., 2014). European forest biomes are generally thought to emit higher levels of monoterpenes relative to isoprene, compared to the continental US. For instance, Quercus sp. in the Mediterranean area are often evergreen and primarily monoterpane emitters in contrast to North-American Quercus sp., with relevant changes concerning the interaction of emitted isoprenoids with the atmosphere and air quality (Fares et al., 2015). As under normalized conditions the BVOC contribution of an individual plant is proportional to its BVOC emission rate (Kesselmeier and Staudt, 1999; Niinemets and Monson, 2013) and the size of its canopy (as discussed above), abundant and/or large species with high emission rates tend to dominate the BVOC emission inventory in a given landscape. Furthermore, plant phenology and ontogeny influence emission rates (Goodger et al., 2013; Jardine et al., 2016). However, as “standard conditions” rarely occur in urban settings, ozone removal capacities as well as BVOC emission rates are largely modified by stress as outlined below.

**Stressors Modifying Species-Specific Effects via Tree Physiological Status**

As urban plants are increasingly exposed to numerous stressors (Calfapietra et al., 2015), the vitality of street trees declined drastically over the last 3–4 decades (Bradshaw et al., 1995). While stress levels can vary considerably between urban centers and rural areas (see section The Rural-Urban Gradient in Context of Tree-Ozone Interactions), knowledge of the environmental physiology of trees in urban settings is key in order to understand the responses of trees to different stresses including feedback mechanisms on specific ecosystem services and/or disservices (Calfapietra et al., 2015).

**Meteorological Factors and Air Composition**

Higher temperatures and light intensities are often accompanied by increased formation of secondary air pollutants in the atmosphere including ozone (Chameides et al., 1988). Also, BVOC emissions are strongly positively correlated to temperature (Guenther et al., 1991; Niinemets and Monson, 2013; Guidolotti et al., 2019) as plants can use, for example, isoprene to stabilize the cell membrane during high temperatures (Singsaas et al., 1997). Behnke et al. (2013) showed that *Populus × canescens* leaves in which isoprene production was genetically removed were less heat resistant. However, the temperature sensitivity of BVOC emissions are highly species-specific, related to the emission traits that distinguish trees in isoprene or monoterpenes emitters and, for the latter, in trees without and with isoprenoids pools (Niinemets et al., 2010; Grote et al., 2013). The direct effect of temperature on O₃ deposition is believed to be small; however, as high temperature increases evapotranspiration, and thus potentially drought stress levels, the indirect decrease in O₃ deposition by stomatal closure may be large (Morani et al., 2014). Another relevant but highly variable meteorological factor is wind. Ventilation of canopies increases evapotranspiration and cools down leaves (Drake et al., 1970). Cooler leaf temperatures lead to lower isoprene emissions in *Populus* sp. and *Quercus* sp. (Potosnak et al., 2014a). Further, strong wind gusts can damage trees—leading to the release of BVOCs (Loreto et al., 2006). For example, a burst of monoterpane emission has been measured at high wind speeds in Eucalypts, whose emissions are otherwise extremely low (Guidolotti et al., 2019). In contrast, higher wind speeds may render leaves within closed canopies more available for ozone deposition.

Urban areas are often characterized by higher concentrations of CO₂ and air pollutants (O’Driscoll et al., 2018). Estimating how these conditions will affect BVOC emissions from urban trees is, however, not easy as a number of factors are interrelated, including the chemical composition of the compound(s), the exposure, the concentration and the plant species. However, there is for example a consensus that an increase in CO₂ concentration will induce a reduction of isoprenoid emissions at least at leaf level (Rosenstiel et al., 2003; Calfapietra et al., 2008). On the other hand, an increase of O₃ concentration can have opposite effects depending on the length and level of exposure—with a general stimulation in the cases of acute exposures and a general inhibition under chronic exposures (Calfapietra et al., 2013). For example, Carriero et al. (2016) states an increase of monoterpane emissions under increased ozone concentrations by *B. pendula* whereas Vuorinen et al. (2005) observed no emission changes. Similar, OVOC emissions by *B. pendula* under elevated ozone exposure were found to decrease (Hartikainen et al., 2012) or increase (Carriero et al., 2016), and isoprene emissions under O₃ stress decreased in *P. tremuloides* (Calfapietra et al., 2008) but did not change for *P. tremula* (Hartikainen et al., 2009) and *P. tremula × tremuloides* (Blande et al., 2007). Despite the uncertainties, however, there are numerous publications that indicate a considerable induction of monoterpenes and various OVOCs by O₃ while the effect on isoprene is mostly negative—either because the biosynthesis pathway is very sensitive to ozone damages or more likely because precursors are directed toward protecting agents (Grote, 2019). Ozone deposition is normally negatively influenced by increased CO₂ and O₃ levels as both decrease stomatal conductivity and thereby stomatal O₃
deposition (Medlyn et al., 2001; Wittig et al., 2007). Globally, the increase of O₃ since the industrialization is estimated to have decreased stomatal conductance by 13% (Wittig et al., 2007)—with likely higher values in urban areas.

**Plant Water Status**

Urban vegetation can experience exceptional stresses from water scarcity to flooding, caused by extreme heat, drought, and rainfall events (Wissmar et al., 2004; Colllier, 2006; Livesley et al., 2016).

With increasing drought stress the stomata close and the stomatal depletion of ozone decreases (Wissmar et al., 2004; Livesley et al., 2016), increasing tropospheric ozone levels by up to 10% (Anay et al., 2018). However, trees have evolved different strategies to deal with low water availability. Isohydric species maintain a constant midday leaf water potential by closing their stomata earlier, while anisohydric species keep their stomata open longer and allow the leaf water potential to drop (Sade et al., 2012). By keeping the stomata open during moderate drought, anisohydric tree species such as *Quercus* sp. and *Fagus* sp. can maintain stomatal ozone deposition on hot summer days when ozone levels may become high (Grote et al., 2016). In contrast, isohydric tree species such as *Acer* sp. and *Betula* sp. are more likely to survive severe droughts and remain thus available for O₃ deposition under post-stress conditions (Sade et al., 2012; Klein, 2014). Thus, in selecting tree species for maximizing urban ozone deposition there is a tradeoff between high stomatal deposition during moderate drought and survival during severe drought events.

BVOC emission rates under drought have been found increasing (Funk et al., 2004; Potosnak et al., 2014b), decreasing (Fortunati et al., 2008; Tiwa et al., 2009) or unaffected (Tingey et al., 1981; Pegoraro et al., 2006). Closing the stomata results in increasing leaf temperature as transpirational cooling decreases; this induces isoprene production in the short-term to increase the thermo-tolerance of tissue (Singsaas et al., 1997). Furthermore, when stomata close the supply of CO₂ decreases, whereas the photosynthetic electron transport rate (ETR) remains high. The emission of at least isoprene seems to be positively correlated to the ratio of ETR to net carbon assimilation rate [NAR; (Dani et al., 2015)]. The carbon used for isoprene production is believed to come from stored carbon and isoprene production can thus be maintained even though CO₂ assimilation decreases (de Souza et al., 2018). In contrast, closed stomata can lead also to decreased emissions of at least some BVOCs, which can less easily diffuse into the atmosphere (Saunier et al., 2017). The variable responses reported previously emphasize that BVOC emissions under drought are highly dependent on tree species (sensitivity) as well as the intensity and temporal extend of the stress events (Dani et al., 2015). Different effects are thus explained by species sensitivity as well as drought intensity (Niinemets, 2010; Klein, 2014; Saunier et al., 2018). For example, the same species can possess an increase of isoprene emissions under mild drought while severe drought decreases emissions (Brilli et al., 2007; Genard-Zielinski et al., 2014; Dani et al., 2015). Similar behavior has been observed for monoterpane emissions, with moderate stress suppressing photosynthesis but not BVOC emissions (Funk et al., 2004; Wu et al., 2015). Less is known on the effect of drought on highly volatile BVOC emissions such as methanol, formaldehyde or acetaldehyde (OVOC) or green leaf volatiles [GLV; (Vitale et al., 2007; Saunier et al., 2017)]. On the long term, drought stress is likely to decrease leaf biomass, which has a negative effect on both ozone deposition as well as BVOC emissions.

In snow-prone urban areas, de-icing salt (NaCl) ends up highly concentrated in street tree pits. De-icing salt has been found to have a negative effect on tree health (Czerriawska-Kusza et al., 2004; Munck et al., 2010; Rose and Webber, 2011; Ordoñez-Barona et al., 2018), by inducing water stress (“physiological drought”), with the effects describe above, but also malnutrition and accumulation of excess ions to potentially toxic levels (Ahmad et al., 2012). This is often decreasing leaf biomass & vitality (Shannon et al., 1999) and thereby the ozone deposition capacity. While emissions of isoprene and OVOC were found rather unaffected by mild salt stress (Loreto and Delfíne, 2000; Teuber et al., 2008), it is currently unknown if the same holds true for severe salt stress.

Finally, flooding can also reduce stomatal conductance (Liao and Lin, 2001), and has consequently a negative effect on stomatal ozone deposition as described above (Chaves et al., 2003). Moreover, it has been observed that flooding can also increase methanol as well as GLV, but decrease isoprene emissions (Copolovici and Niinemets, 2010; Bourtsoukidis et al., 2013).

**Nutrition Status**

The urban ecosystem is highly heterogeneous in regard to nutrient availability; for example, some street trees have access only to the limited soil volume underneath the planting pit whereas others access nearby gardens and sewer pipes (Koptinga and Van den Burg, 1995; Day et al., 2010). Nutrients frequently limiting the growth of urban trees are potassium (K) and nitrogen (N), however, deficiencies of magnesium (Mg) and phosphorus (P) as well as micronutrients are common (Koptinga and Van den Burg, 1995; Sieghardt et al., 2005).

Deficient nutrition results in decreased growth and increased sensitivity to pests—leading to relatively reduced leaf area, affecting O₃ deposition negatively (Carriero et al., 2016; Hu et al., 2018). On a single leaf scale, N deficiency has been shown to cause a decrease in BVOC production due to a lower photosynthetic efficiency and thus less available carbon for secondary metabolites (Lerdau et al., 1995; Ormeño et al., 2008). Although direct studies are missing, it can be hypothesized that K and Mg deficiency, key elements of the photosynthetic system, cause similar effects (Lambers et al., 1998). P deficiency could eventually also lead to a decrease in energy-demanding BVOC production due to a shortage of P-rich ATP and NADPH (Ormeño and Fernandez, 2012). In contrast, increased BVOC emissions under warm temperatures, destabilizing the cell membrane and releasing GLVs, may be spurred under P deficiency (Siwko et al., 2007; Ormeño and Fernandez, 2012). Only recently, nutrient deficiency has also found leading to a shift of the emitted BVOC composition; for example, from terpenoids toward GLV in nitrogen-limited *Betula* sp. trees (Carriero et al., 2016). While it thus becomes increasingly clear...
that a shift in BVOC emissions via nutrient deficiency affects the formation and degradation of O$_3$ in the atmosphere, the contradictory results, i.e., either a positive or negative feedback of BVOC emissions due to malnutrition, may relate to reactions triggered on different timescales. Therefore, phenology and long-term allocation processes must be considered, combining the morphoanatomy of leaves with cell biochemistry and physiology (Lerdau et al., 1995, 1997; Ormeño and Fernandez, 2012).

**Herbivores and Pathogens**

Physical injuries by herbivores and pathogens frequently lead to increased GLV and monoterpane emissions (Gatehouse, 2002; Niinemets et al., 2013; Scala et al., 2013). These induced volatiles are emitted rapidly after the stress occurred (Amey et al., 2018) and can account for 9 to 21-fold of the total emissions of damaged tissue (Ghimire et al., 2017). Fungal and pathogen infections of leaves also lead to increased emissions of GLV and monoterpane but often a decrease in isoprene emissions (Kesselmeier and Staudt, 1999; Steindel et al., 2005; Ariamura et al., 2008; Jansen et al., 2009). Thus, even though isoprene decreases, the high monoterpane emission caused by herbivory and pathogens can, under high NO$_3$ levels, contribute to ozone formation (Holopainen and Blande, 2013). The decrease in leaf biomass due to herbivory and pests decreases the ozone deposition on the leaves causing increasing ozone concentrations in the air (Kesselmeier and Staudt, 1999).

**THE RURAL-URBAN GRADIENT IN CONTEXT OF TREE-OZONE INTERACTIONS**

The commonly used terms “urban” and “rural” relate to a range of environmental conditions such as temperature, pollutant and CO$_2$ levels, and land cover types including the extension of sealed surfaces and housing densities, as well as changes in species composition and abundance of vegetation. In general, the availability of growing spaces tends to decrease along the rural-urban gradient (Zipperer et al., 1997). The differences between rural and urban are furthermore fueled by a gradient of human activities, such as emissions from traffic and industries but also vegetation management, that all affect the ozone forming potential and depletion, and thereby the (local) O$_3$ concentration.

Less abundant vegetation does not necessarily mean a low deposition capacity or BVOC emissions since both are strongly related to species, physiological state and stress severity as outlined above. It is therefore interesting that in many urban areas trees are predominantly deciduous (Grote et al., 2016) and in case of Quercus sp., Salix sp., and Populus sp. (and to some lesser degree Platanus sp. and Robinia pseudocacia) belong to the topmost isoprene emitters. These high emitters contribute between 13% [Lancaster, UK; (Wolyniak and Elmendorf, 2011)] and 30% [Hamburg, Germany; (BUE, 2019)] of urban trees in Europe, and seem to have even higher shares in Asia [e.g., 30%, Beijing, China; (Ghirardo et al., 2016)] while US cities seem to have a bit less high emitters [11.4% in Chicago; (Nowak et al., 2010)]. In contrast, suburban and rural forests in northern and temperate regions are commonly formed by evergreen forests (Gallaun et al., 2010), which emit primarily monoterpenes that are far less effective regarding O$_3$ formation. Similar holds true for Mediterranean rural areas that are dominated by Pinus sp. and evergreen Quercus sp. (Sheffer, 2012).

Besides differences in species composition, trees’ physiological status differs in urban compared to rural conditions because of changes in environmental conditions. Most prominently, urban centers are characterized by higher air temperatures as compared to suburbs which is the so called urban heat island (UHI) effect (Ajay et al., 2018; Saaroni et al., 2018). Higher temperatures in urban centers trigger higher BVOC emissions leading to higher ozone concentrations, an effect that is expected to increase with global warming (IPCC, 2014; Li et al., 2015). In contrast, higher CO$_2$ concentrations in urban areas do not only encourage growth but also tend to decrease BVOC emission capacity, particularly regarding isoprene (Gratani and Varone, 2014). The third effect on physiology that is not necessarily stress-related (if considering stress as damage that is not immediately reversible) is related to air humidity and soil moisture availability. Both are commonly lower in urban centers compared to urban woodlands and rural areas (Devakumar et al., 1999; Yang et al., 2017). Restricted water supply will decrease stomatal conductance and thereby stomatal ozone depletion and also modify BVOC emission rates as discussed above. Finally, urban trees, especially roadside trees, are more frequently stressed by drought (Clark and Kjelgren, 1990; Fahey et al., 2013; Bialecki et al., 2018), salt (Equiza et al., 2017), herbivores (Dale and Frank, 2014), and air pollution (Samson et al., 2017a). Stress-induced emissions are different from constitutively driven emissions in both intensity and composition. They are tightly linked to the intensity and duration of stress and thus depend for example on short-time ozone peaks. They also might eventually decrease if plants are substantially damaged although the necessary degree to reach this point is difficult to define. Indeed, considerable amounts of stress-related emission compounds have been found in metropolitan regions (Ghirardo et al., 2016).

In general, large uncertainty exists as to the effects of multiple factors, occurring in urban settings, on BVOC emissions (Holopainen and Gershenzon, 2010). They depend on species abundance and distribution, and furthermore interact with plant ecophysiological responses, such as stomatal regulation, and in particular stress responses, which are largely unknown for many urban species/ecotypes (Sjoman and Busse Nielsen, 2010). Studies show that the quota of ozone produced by BVOCs are up to 12% on average of the daily maximum 1-h O$_3$ concentration in Berlin but up to 60% on very warm days (Churkina et al., 2017), 50–75% during summer in Italy and Spain (Duane et al., 2002), and by a factor of 50 in Las Vegas, NV (Papiez et al., 2009). With increasing temperatures in the future, the heating effect is likely to override the suggested suppressive effect of higher CO$_2$ concentrations (Tingey et al., 1991; Lahr et al., 2015) and increase BVOC emissions in urban areas (Norton et al., 2015). It is therefore reasonable to speculate that combined effects will affect the emission by individual trees much more severely in the highly anthropogenic environment of city centers and suburbs than in rural areas. This assumption is supported by the
fact that high temperatures and the occurrence of drought and ozone stress commonly occur in combination, which not only directly increases emissions but also decreases trees’ resistance to pathogens and herbivores which then can lead to induction of further emissions (Holopainen, 2004; Loreto and Schnitzler, 2010). Indeed, several studies show that higher temperatures in urban areas in combination with drought stress increases insect herbivory (Meineke et al., 2013; Dale and Frank, 2014, 2017).

To calculate the effect of the diverging BVOC emission along the urban-rural gradient on the ozone concentration, it has to be set in relation to the NO$_x$ concentration. In city centers and suburbs, the emissions of NO$_x$ and AVOCs are high compared to rural areas. Toward the rural areas, NO$_x$ and AVOC emissions decrease while BVOC emissions might increase due to an increasing leaf area or decrease depending on conditions discussed above. The emissions of AVOCs in Europe have dropped dramatically in the last 20 years (Stemmler et al., 2005; Dollard et al., 2007). Thus, on warm summer days the emission of BVOCs may be dominant relative to the NO$_x$ formation (Wagner and Kuttler, 2014). In many other urban areas of the world (e.g., China), however, AVOCs are still the major driver of O$_3$ formation (Ran et al., 2011; Wang et al., 2017). With high NO$_x$ concentrations within city boundaries, O$_3$ formation is usually small due to low VOC:NO$_x$ ratios (Atkinson, 2000). With increasing distance from the urban center, however, NO$_x$ concentrations decrease relative to BVOCs—resulting in an increase of the VOC:NO$_x$ ratio and thereby a higher potential of O$_3$ formation in the suburbs and rural areas. An O$_3$ isopleth plot (Figure 3, dashed line) illustrates net O$_3$ production P(O$_3$) as a function of BVOC and NO$_x$ reactivity giving data from Innsbruck, Austria as an example. A hypothetical trajectory from NO$_x$-rich urban conditions to BVOC-rich rural conditions is depicted along the red arrows—as NO$_x$ is diluted, O$_3$ production increases until a ridge after which it decreases due to becoming NO$_x$-limited. This non-linear relationship of tropospheric O$_3$ production has important ramifications for air quality management across urban gradients, because strategies of O$_3$ mitigation will depend on the (local) interplay between NO$_x$ and NMVOC (Sillman and He, 2002).

There is a strong societal demand on improving the air quality and comfort in cities. The focus is put on reducing gaseous and particulate pollution by reducing emissions from traffic, particularly of NO$_x$. In addition, mitigation strategies include measures to increase deposition of pollutants, including NO$_x$ and ozone, which is preferably done by increasing leaf area (Taha et al., 2016; Tong et al., 2016). However, it should be noted that achieving reduction of NO$_x$ by increasing deposition on leaves but simultaneously increasing BVOC emissions by selecting high emitting species can potentially increase the ozone forming potential particularly in the highly populated urban centers (Figure 4).

Considering future climate change scenarios with increasing temperatures, we hypothesize that ozone formation would expand toward the urban centers as with BVOC emissions increase, due to increasing temperatures, being the major driver. This effect would be enhanced if (exotic) species that are more tolerant against heat and drought but also have high BVOC emission potentials would be newly introduced in urban areas (Valkama et al., 2007; Himanen et al., 2009;...

![FIGURE 3](image-url)
Reduced emissions due to higher CO₂ concentrations and more frequent drought stress are not likely to reverse this trend, particularly since trees are often irrigated in arid and semiarid regions or during heat wave events in order to sustain their cooling function. However, estimating the net effect of urban trees on ozone concentrations, deposition would need to be taken into account as well, which would be enhanced by more trees. Ozone concentrations furthermore depend on temporal and spatial variations of biogenic and anthropogenic emissions as well as wind speed, and thus require elaborated air chemistry transport models. Approaches have been made to couple physiological models to such models of air chemistry, but the multitude of direct and indirect effects described here have not been considered (Baumgardner et al., 2012; Cabaraban et al., 2013).

OUTLOOK

Policies are strongly directed toward an improvement of air quality and an increase of resilience against climate change impacts in cities. Decisions need to be based on how these goals can be reached most efficiently while maintaining transport and other energy consuming functions. Obvious solutions are a reduction of emissions by introducing clean energy and transport concepts and providing green infrastructure for cooling and shading. Since a technological reduction of anthropogenic emissions will not immediately take place, an increase of green infrastructure is also supposed to enhance deposition and thus reduce air pollution. This is principally a valid and reasonable approach. However, the efficiency of vegetated urban area to fulfill these ecosystem services depends on various boundary conditions, cannot easily be evaluated, and potential ecosystem disservices, among which is the facilitation of ozone production via BVOC emissions, have to be considered. A general vote for a higher share of green infrastructure is thus difficult to implement and can eventually deliver results that might even be contradictory to expectations. It is thus of utmost importance to consider species properties, stress sensitivity, and physiological responses that can be expected under future environmental conditions. Achieving the goal to abate or at least not to increase ozone concentrations in cities, newly planted tree species would need the following requirements: (i) emit low or no BVOCs under current and future environmental conditions, (ii) have a large resistance to drought and biotic stresses, (iii) maximize biomass in terms of leaf area, and (iv) have a high photosynthetic capacity and therefore high stomatal conductance (and thus being high ozone sinks) (Nowak et al., 2018). This task is, however, complicated by the fact that the new plants will have a distinct effect on future urban environmental conditions.

The necessary efforts to enable such analyses will be substantial since our species-specific knowledge about stomatal responses as well as BVOC emission under various stress conditions is limited. The first requirement is therefore to refine our understanding of urban vegetation responses to local environmental conditions. A key knowledge gap is the response
of BVOCs emissions to stressful conditions, which often lead to large increases that can potentially affect air quality (Grote et al., 2019). However, general responses to extreme heat and dry conditions that may trigger the death of the plant should also be evaluated in particular for urban tree species that might get more important in the future. Secondly, urban air quality needs to be investigated with integrated analyses considering climate, anthropogenic emissions, city structure as well as distribution and responses of vegetation, i.e., street and park trees. Current approaches are still suffering on coarse resolutions and missing climate-vegetation feedbacks but new developments are encouraging (Maronga et al., 2019). Finally, it should be considered that inventories of existing tree distributions are essential to evaluate any spatially explicit modeling approach. This also includes soil conditions and management that affects canopy dimension and physiology (e.g., pruning and irrigation). Only if this information is available, scenario analyses with varying climate, pollutant emissions, as well as vegetation abundance, composition and distribution can successfully be carried out. Thus, integrating ecosystem services and disservices into environmental quality strategies will therefore enable the identification of green infrastructure types, suitable species (combinations), as well as distribution and density of individuals in order to increase people’s overall quality of life in a particular city at reasonable costs.

AUTHOR CONTRIBUTIONS
AF, HS, and BR contributed conception and design of the review. AF and TK composed the figures. AF, HS, TK, AS, CC, SF, and BR wrote the first draft of the manuscript. AF, HS, TK, SF, RG, and BR wrote sections of the manuscript and added to the tables. All authors contributed to manuscript revision, read, and approved the submitted version.

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