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# Urban stress-induced biogenic VOC emissions impact secondary aerosol formation in Beijing

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## Abstract

Trees can significantly impact the urban air chemistry by the uptake and emission of reactive biogenic volatile organic compounds (BVOCs), which are involved in ozone and particle formation. Here we present the emission potentials of "constitutive" (cBVOCs) and "stress-induced" BVOCs (sBVOCs) from the dominant broadleaf woody plant species in the megacity of Beijing. Based on an inventory of BVOC emissions and the tree census, we assessed the potential impact of BVOCs on secondary particulate matter formation in 2005 and 2010, i.e., before and after realizing the large tree-planting program for the 2008 Olympic Games. We found that sBVOCs, such as fatty acid derivatives, benzenoids and sesquiterpenes, constituted a significant fraction ($\sim 15\,\%$) of the total annual BVOC emissions, and we estimated that the overall annual BVOC budget may have doubled from $\sim 3.6 \times 10^9\,\mathrm{g\,C\,year^{-1}}$ in 2005 to $\sim 7.1 \times 10^9\,\mathrm{g\,C\,year^{-1}}$ in 2010 due to the increase in urban greens, while at the same time, the emission of anthropogenic VOCs (AVOCs) could be lowered by 24 %. Based on our BVOC emission assessment, we estimated the biological impact on SOA mass formation in Beijing. Compared to AVOCs, the contribution of biogenic precursors (2–5 %) for secondary particulate matter in Beijing was low. However, sBVOCs can significantly contribute ($\sim 40\,\%$) to the formation of total secondary organic aerosol (SOA) from biogenic sources; apparently, their annual emission increased from $1.05\,\mu\mathrm{g\,m^{-3}}$ in 2005 to $2.05\,\mu\mathrm{g\,m^{-3}}$ in 2010. This study demonstrates that biogenic and, in particular, sBVOC emissions contribute to SOA formation in megacities. However, the main problems regarding air quality in Beijing still originate from anthropogenic activities. Nevertheless, the present survey suggests that in urban plantation programs, the selection of plant species with low cBVOC and sBVOC emission potentials have some possible beneficial effects on urban air quality.





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## 1 Introduction

Plants are the dominant source of biogenic volatile organic compounds (BVOCs) (Guenther et al., 2012). On a global scale, the source strengths of BVOC exceed those of anthropogenic VOCs (AVOCs) by an order of magnitude. Due to their high reactivity, BVOCs play important roles in determining atmospheric processes, such as secondary organic aerosol (SOA) and ozone formation, or in the presence of anthropogenic nitrogen oxides ($NO_x$), altering the concentrations of hydroxyl radicals, the main atmospheric oxidants (Claeys et al., 2004; Ehn et al., 2014; Fuentes et al., 2000; Goldstein et al., 2009; Pun et al., 2002). Thus, in changing the oxidative capacity of the troposphere, BVOCs can influence the local and regional air composition with substantial impacts on climate.

Plant BVOC emissions are species-specific, whereby the terpenoids isoprene and monoterpenes normally dominate the overall BVOC profile of woody plants (Harrison et al., 2013; Kesselmeier and Staudt, 1999). Isoprene and monoterpenes are volatiles that are predominantly emitted from plant foliage in a "constitutive" (cBVOC) manner (Niinemets, 2010) as a function of light, temperature, and seasonality. In addition to "constitutive" emissions, significant quantities of "stress-induced" BVOCs (sBVOCs) (Niinemets, 2010) can be emitted into the atmosphere following abiotic (e.g. $O_3$) and/or biotic (e.g. herbivores) stresses (Behnke et al., 2009; Fäldt et al., 2003; Ghirardo et al., 2012; Heiden et al., 1999, 2003; Holopainen and Gershenzon, 2010; Joó et al., 2011; Kleist et al., 2012; Loreto and Schnitzler, 2010; Mentel et al., 2013; Peñuelas and Staudt, 2010; Toome et al., 2010). For instance, the monoterpenes linalool, ocimene and 1,8-cineole; the class of sesquiterpenes (SQT); benzenoids such as methyl salicylate (MeSa), and volatile lipoxygenase products are typically induced and emitted from green foliage after exposure to ozone (Behnke et al., 2009; Bourtsoukidis et al., 2012; Heiden et al., 1999; Kiendler-Scharr et al., 2012; Niinemets, 2010) or herbivores (Amo et al., 2013; Arimura et al., 2005; Holopainen and Gershenzon, 2010). Important with respect to air chemistry, SQT and MeSa can significantly contribute to the SOA forma-





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tion even at relatively low concentrations due to the higher SOA-forming potential compared to isoprene and monoterpenes (Mentel et al., 2013; Sakulyanontvittaya et al., 2008). However, despite their potential to influence ozone and SOA formation, sBVOC fluxes are rarely considered in the context of atmospheric chemistry (Berg et al., 2013; Bergström et al., 2014). Both field and laboratory studies have shown that single stress factors, such as heat, water limitation, salinization, and ozone, can alter sBVOCs formation and change the overall BVOC emission rates (Joó et al., 2011; Kleist et al., 2012; Loreto and Schnitzler, 2010; Pellegrini et al., 2012; Wu et al., 2015). Nevertheless, the net effect of multiple stress factors, which frequently co-occur in nature, on sBVOC emission remains still poorly understood (Holopainen and Gershenzon, 2010). Perennial plants, such as trees growing in largely populated urban habitats, constantly suffer from a chronic multi-stress environment (Calfapietra et al., 2013b). For example, due to the "heat island effect", air temperatures in large cities are oftentimes much higher (up to 10 °C) than those that are recorded in surrounding suburban and rural areas (Chen et al., 2006; Peng et al., 2012). In addition to high temperatures, the heat island effect is also associated with higher radiation, increased air pollution levels, and more frequent drought episodes. These factors together negatively impair plants and enhance sBVOC emissions. Furthermore, because anthropogenic $NO_x$ concentrations in urban environments are high, BVOC emissions can lead to enhanced ozone formation and thus directly contribute to formation of ozone and particle matter (Calfapietra et al., 2013b; Churkina et al., 2015; Hellén et al., 2012; Papiez et al., 2009; Wang et al., 2013). The effect of $NO_x$ on SOA formation is not fully understood and depends on BVOC/$NO_x$ ratio and specific VOC mixture. $NO_x$ effects on SOA formation range from the suppression of new particle formation (Wildt et al., 2014), an enhancement or decrease of SOA yields (e.g. Kim et al., 2012; Kroll et al., 2006; Ng et al., 2007; Pandis et al., 1991; Presto et al., 2005; Zhang et al., 2012) to the formation of $NO_3$, an important night time oxidant of BVOC with considerable SOA yields (Fry et al., 2009, 2011; Rollins et al., 2009).





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Over the past two decades, large tree-planting programs have been initiated to improve the livelihoods of city dwelling residents. Consequently, the urban green space is increasing in America, Europe and Asia but most notably in China (Zhao et al., 2013). Increasing the urban "green lung" by planting trees results in diverse benefits, including decreasing the heat island effect and increasing $CO_2$ uptake and the deposition/detoxification of ozone, $NO_x$ and AVOCs. However, the possible impacts of BVOC emissions on ground-level ozone formation and SOA formation are oftentimes not considered.

In the present work, we investigated whether BVOC emissions from green areas in Beijing contribute to the formation of particulate matter. With a population of more than 21 million (2013) and heavy air pollution (Chan and Yao, 2008), Beijing represents an ideal location for assessing the importance of BVOC emissions from plants growing in a megacity. Before the summer Olympic Games in 2008, the municipality of Beijing aimed to improve the air quality by a large-tree plantation program, more than doubling the number of urban trees and shrubs (Table 1). For planting, strong cBVOC emitters were used, risking high emissions with the consequences outlined above. Despite of all of the progress that has been made, the air quality in Beijing is still poor throughout the year. Additionally, air pollution may negatively affect plant performance and further induce sBVOC emissions, which have a high potential to form organic particulate matter (Mentel et al., 2013; Bergström et al., 2014). We therefore also considered sBVOC emissions for our evaluation, studied whether cBVOC and sBVOC emissions may significantly contribute to air pollution and compared their contribution to that of AVOCs. For this evaluation we conducted an extensive BVOC inventory of the most abundant woody broadleaf plant species of the administrative districts of Beijing. We found some plant species with high sBVOC emission potentials and estimated SOA formation from these emissions. We furthermore constructed a phylogenetic tree based on the taxonomic data that might be of use for future planting programs. "Picking the right tree for urban greening" (Churkina et al., 2015) has potential beneficial effects on air quality.





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## 2 Materials and methods

### 2.1 Plant material

We used 21 different deciduous and one evergreen woody plant species (see Table 1) that are commonly found in the urban area of Beijing. Trees were naturally grown in the park of the Beijing Institute of Landscape Architecture under ambient environmental conditions. Tree age ranged between 8 and 25 years (see Table S6 for age and size details). Only *Populus tomentosa* and *Salix babylonica* (not available in the park) were two-years old, originating from a local plant nursery, and were potted (40 cm × 40 cm) in standard soil and grown under ambient conditions. Two fully developed leaves from three trees were independently measured for each species in the period from August to mid-October in 2011. Each measured leaf originated from a different branch. Approximately 30–60 min prior to analysis, healthy whole plants or branches were cut off from the trees. Immediately, a second cut of 2–4 cm was done under water to remove embolisms and the branches were transferred to the lab for gas-exchange and BVOC measurements (see Sect. 2.4). Cutting branches followed by laboratory measurements allows measurements under more controlled and standard conditions and minimizes foliage perturbation. This procedure is commonly used when accessibility to large and tall natural trees with the cuvette system without branch disturbance is difficult or impossible (e.g. Affek and Yakir, 2002; Geron et al., 2006; Harley et al., 1998; Helmig et al., 1999; Klinger et al., 1998; Monson et al., 2007). On the basis of own experiences, measuring cut brunches do not alter terpene for several hours (e.g., Ghirardo et al., 2011; Welter et al., 2012) and lipoxygenase-derived compound emissions in distant foliage (e.g., Ghirardo et al., 2011). This agrees with Loreto et al. (2006). They show that except a small amount of acetaldehyde, no other VOCs were emitted from broadleaf plant species when the mechanical wounding (cutting) is remotely located. Furthermore, a very recent report showed that mechanical wounding do not affect benzenoid compound emissions neither (Misztal et al., 2015), conversely to insect damaged plants (Ghirardo et al., 2012; Holopainen and Gershenzon, 2010).





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To take into account the high variability in emission rates, which is due to analytical approaches (Ortega and Helmig, 2007; Tholl et al., 2006) and intra-species specific variability in cBVOC and sBVOC emissions (Kesselmeier and Staudt, 1999; Niederbacher et al., 2015), leaves from the same plant were treated as technical replicates and plant averages ($n = 3 \pm \mathrm{SE}$) were used as biological replicates.

### 2.2 Climate, $NO_x$, $O_3$ and $AOT_{40}$ data

Climate (light, temperature, precipitation, relative humidity (RH), wind speed, and pressure), NO, $NO_2$, and $O_3$ data were continuously collected at an 8 m height from the 325 m-tall meteorological tower at the Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing. The data were collected at a 1 h time resolution and averaged into daily means.

The accumulated amount of $O_3$ over the threshold value of 40 ppb ($AOT_{40}$) is an $O_3$ exposure plant index that is set by the US-Environmental Protection Agency and the United Nations Economic Commission for Europe (UNECE). $AOT_{40}$ was calculated using the following equation:

$$\mathrm{AOT}_{40} = \Sigma R_{\max}([\mathrm{O}_3] - 40\,\mathrm{ppb})\Delta t \quad (1)$$

The function $R_{\max}$ is zero for hourly averaged $[O_3] < 40$ ppb and unity for $[O_3] > 40$ ppb, meaning that the sum only includes $O_3$ values exceeding 40 ppb. The sum was determined over time ($\Delta t = 1$ h) from the beginning of July until the end of the sampling period (beginning of October 2011) and for daytime only (6 a.m.–8 p.m.). Values were then converted from ppb · h to ppm · h.

### 2.3 Laboratory study of ozone-induced BVOC emissions

The model plant species *Populus* × *canescens* (Gray poplar), *Gossypium hirsutum* (cotton), *Solanum lycopersicum* (tomato), and *Nicotiana tabacum* (tobacco) were used in the laboratory experiments and exposed to elevated levels of $O_3$ for a short period





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of time. Plants were placed individually in continuously stirred tank reactors (CSTR) at the Institute of Bio- and Geosciences (IBG-2) in Jülich (Mentel et al., 2009; Wildt et al., 1997) and flushed with purified air (15–40 L $min^{-1}$, depending on the size of the plants). Details of the experimental procedures and set-up can be found elsewhere (Behnke et al., 2009).

Prior to $O_3$ fumigation, plants were allowed to reach steady-state photosynthetic activities under constant chamber temperature and 800 µmol $m^{-2}$ $s^{-1}$ PPFD, with a chamber temperature between 20 and 25 °C during the different experiments and an RH between 50 and 80 %, depending on the size of the plants and the air flow. Ozone was then applied at a concentration of 8–900 nmol $mol^{-1}$ for 1–2 h. BVOCs were collected continuously by trapping online at an approx. 76 min time resolution on solid sorbents (Tenax TA/Carbotrap, Grace-Alltech, Rottenburg-Hailfingen, Germany) for 10 and 20 h following $O_3$ exposure and were analyzed using GC-MS as described previously (Behnke et al., 2009; Wildt et al., 1997).

### 2.4 BVOC and gas-exchange analyses

The leaf emission potentials of BVOCs were determined by enclosing fully mature leaves in a cuvette system (standard measuring head 3010-S of a portable gas exchange system GFS-3000, Walz GmbH, Effeltrich, Germany; volume 40 mL, surface 8 $cm^2$) after allowing them to acclimate (30–45 min, until photosynthetic gas exchange became stable) to standard conditions (1000 µmol $m^{-2}$ $s^{-1}$ PPFD, 30 ± 0.1 °C leaf temperature, 40 % RH). Cuvettes were flushed with 1 L $min^{-1}$ VOC-free synthetic air (79 % $N_2$, 21 % $O_2$) that was mixed with pure $CO_2$ to a final $CO_2$ concentration of 380 µmol $mol^{-1}$. The air exiting the cuvette was diverted into a T-piece, from where 3 L of air was sampled with two adsorbents in series containing polydimethylsiloxane foam (Gerstel, Mülheim an der Ruhr, Germany) and 50 mg of CarboPack B (Sigma-Aldrich, Germany) at a flow rate of 100 mL $min^{-1}$. All of the flows were controlled using mass flow controllers (MKS, Andover, USA) and the flow rates were verified using a calibrated





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mass flow meter (ADM-3000, Agilent Technologies, Palo Alto, USA). The remaining air exiting the cuvette was sub-sampled for $CO_2$ and $H_2O$ analysis using an infra-red gas analyzer (IRGA, GFS-3000, Walz GmbH). The sample tubes were then sent to BIOP-EUS (Germany) and stored at −20 °C for approximately two weeks prior to chemical analysis.

The identification and quantification of different BVOCs were achieved by thermo-desorption (Gerstel) and gas chromatography-mass spectrometry (GC-MS; GC type: 7890A; MS type: 5975C; both from Agilent Technologies, Palo Alto, CA, USA), as previously described (Ghirardo et al., 2012). Each day, a control (empty cuvette) was measured for background subtraction. BVOC were identified with the 2011 National Institute of Standards and Technology Mass Spectral Library (NIST, USA), Wiley library (v.275, USA) and by comparing the retention time and spectra with those of authentic liquid standards (Sigma-Aldrich). For the calibration of isoprene, 10 ppm of standard was diluted at final concentration of 10–250 ppb, passed through the whole system, and sampled in GC-MS tubes. The other volatiles were calibrated based on calibration curves that were obtained by injecting pure liquid standards (Sigma-Aldrich) into the GC-MS after being diluted in hexane (HPLC-grade, Sigma-Aldrich) at different concentrations (1–1000 pmol $\mu L^{-1}$; standards solvent$^{-1}$). The calibration procedures are described elsewhere (Kreuzwieser et al., 2014). Volatiles that were not available as standards were calibrated using $\delta$-2-carene resolved in hexane at different concentrations between 1–1000 pmol $\mu L^{-1}$ (standards solvent$^{-1}$) ($R^2$ = 0.9997). In addition, a defined amount of $\delta$-2-carene was added to each sample as an internal standard to take into account the changing MSD sensitivities during each GC-MS run. The emission rates of BVOC were calculated on a leaf-area basis (nmol $m^{-2}$ $s^{-1}$). The net photosynthesis and transpiration rates were calculated by the GFS-3000 system based on the equations of von Caemmerer and Farquhar (1981).





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## 2.5 Classification of BVOCs into "stress-induced" (sBVOCs) and "constitutive" (cBVOCs)

The classification of volatiles as "stress-induced" and/or "constitutive" followed the review of Niinemets (2010) and was based on the generalized findings of an extensive literature search (Beauchamp et al., 2005; Behnke et al., 2010; Bourtsoukidis et al., 2012; Fäldt et al., 2003; Ghirardo et al., 2012; Hakola et al., 2006; Heiden et al., 1999, 2003; Holopainen and Gershenzon, 2010; Joó et al., 2011; Pinto et al., 2010; Toome et al., 2010). Stress-induced BVOCs included the stress-induced monoterpenes (E)-$\beta$-ocimene, linalool and 1,8-cineol (sMT), all sesquiterpenes (SQT), benzenoids (BZ) and green leaves volatiles (GLV) while constitutive BVOCs (cBVOC) included the hemiterpene isoprene (IS) and all constitutively emitted monoterpenes (cMT) that were not included as sMT (Table S1, in the Supplement). This classification fully agreed with the BVOC emission pattern that was obtained in the laboratory study using the four plant models that were exposed to $O_3$ (see Fig. 1). The relative contribution of sMT to the overall MT emission was small; thus the sMT and cMT were combined in Fig. 3 and 4. However, we considered the sMT separately for sBVOC emission scaling, SOA-formation potentials, multivariate analysis and when calculating the overall fraction of sBVOCs vs. total BVOCs (see sections below).

## 2.6 BVOC emission budget

The measured potential emission rates for isoprene were corrected for seasonal changes in enzyme activities in relation to the annual fluctuation of temperature and light, as calculated with the "Seasonal-Isoprenoid-Model" SIM (Lehning et al., 2001). Depending on the calculated activity for the date of measurement and the measured leaf mass per area (LMA), the potential emission factors ($g\,C\,g\,DW^{-1}\,h^{-1}$) for isoprene were derived (Table S5A, in the Supplement). Similarly, the emission factors for light-dependent monoterpene emission (i.e. de novo biosynthesis) were determined, assuming that for deciduous species all and for evergreen species half, of the measured





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non-induced monoterpene emissions fall into this fraction (Ghirardo et al., 2010; Harley et al., 2014). For all stress-induced BVOCs we assumed a constant emission factor during the period of substantial $O_3$ concentration (Mid-April to Mid-October).

Actual emissions were calculated in hourly resolution from daily emission factors for isoprene and light induced monoterpenes emissions. The monoterpene emissions from storage were calculated using a phenomenological model (Guenther et al., 1995). For sBVOC emissions, we applied the temperature-dependent equation that is generally used to describe emissions from storage structures. The parameters of this equation have been modified to reflect the response of SQT emissions to $O_3$ concentrations as described in Bourtsoukidis et al., 2012 in the following way: (i) the emission response was described in response to the measured $O_3$ concentration during 2011, (ii) the determined emission rates were related to the temperature as measured in parallel with the $O_3$ concentrations; and (iii) the parameters of the Guenther/Tingey algorithm describing storage emission as a function of temperature, the scaling parameter beta ($0.12\,K^{-1}$) and a reference temperature (48 °C), had been defined to give the least overall deviation from the values determined with the Bourtsoukidis et al., 2012, method. All of the emissions that were determined per gram of dry weight were scaled to the whole city of Beijing by multiplying with the leaf biomass per tree and the tree number per species, corrected by phenological development. The leaf biomass is derived from measured diameters using the equation from Nowak for urban trees considering a species-specific shading factor (Nowak, 1996). Phenological development is described by an empirical function based on repeated leaf area index measurements of seven dominant tree species (Fig. S2, in the Supplement). For species for which no emission rates were available (another 12 tree and shrub species are listed in Table 1 plus *Robinia pseudoacacia*), literature estimates of emission factors were used (Table S5B, in the Supplement). *Robinia* is the only plant species that was not covered by the current inventory, although it was one of the most abundant tree species in Beijing in 2002 (Yang et al., 2005). We used the given tree number for 2005 and increased it for 2010 by the factor of 2.45 (the average increase of all other species). For





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species with no known emission factors (*Jasminum, Kerria, Sorbaria,* and *Weigela*), we used an average emission factor that was derived from all of the deciduous shrubs (Table S5B, in the Supplement). Because literature values could only be obtained for isoprene and constitutive monoterpene emissions, a ratio was calculated between the measured emissions and those based on literature values (Table 2: "percent measured from total"). All of the induced sBVOC emissions increased by this ratio to estimate the total emissions. However, the percentages of measured emissions over the total were between 84 and 96 %, indicating that the majority of emissions were likely to be covered in this analysis (see also Table 2).

### 2.7 Phylogenetic tree, multivariate data and statistical analyses

The taxonomic data of the 22 woody species analyzed were used to generate a phylogenetic tree using the web tool iTOL (http://itol.embl.de/) (Letunic and Bork, 2006, 2011) (Table S7). The correlation between plant-specific BVOC profiles, assimilation rates (Table S2) and taxonomic data were evaluated using principal component analysis (PCA) statistical methods from the software package "SIMCA-P" (v13.0.0.0, Umetrics, Umeå, Sweden). This analysis conceptually follows the method previously described (Ghirardo et al., 2012; Kreuzwieser et al., 2014), where the emission rates of BVOC groups (i.e., IS, cMT, sMT, SQT, BZ, GLV) and the assimilation rates ($A$) were used as the '$X$' variables, logarithmically transformed ($X = |\log(X)|$), centered and scaled with 1 $SD^{-1}$ as data pre-processing. In addition, the phylogenetic data were numerically converted (Table S8, in the Supplement). The results were validated by "full cross validation" and significant at the 95 % confidence level.

### 2.8 SOA- formation potentials from biogenic and anthropogenic VOC

For estimates of SOA-formation potentials we defined a box with a surface area that was equal to the area of the city of Beijing (1434 $km^2$). The height of the box was fixed to 2 km, as a typical proxy for the height of an inversion layer. The biogenic or





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anthropogenic VOCs entering the volume of the box were multiplied by the mass yield that was determined for the different VOC classes (Mentel et al., 2013). Accounting for the height of the assumed box, the transformation of the flux density from VOC mass to particle mass enabled the estimation of the source strengths ($Q$) for particulate organic mass.

Average flux densities for VOCs were obtained from the data given in Table 2 by dividing the total annual emissions by the surface area of Beijing. Considering a vegetation period of $\sim 1/2$ year, these numbers were multiplied by 2 to obtain the average emissions over a day. The results for the average flux densities over the vegetation period were then multiplied by the particle mass yields (isoprene = 0.02 $\mu g\,\mu g^{-1}$ (Kiendler-Scharr et al., 2012), monoterpenes = 0.06 (Mentel et al., 2009), benzenoids and SQT = 0.22 (Mentel et al., 2013)) to obtain the source strengths for particulate matter.

As postulates for this procedure, we assumed that (i) the load of particulate matter in the air of Beijing is high, and hence, nucleation and new particle formation are not important compared to the addition of organic matter to the existing particles. This allows neglecting the effect of suppression of new particle formation by isoprene (Kiendler-Scharr et al., 2009). (ii) The suppressing effect of GLV on particle mass formation (Mentel et al., 2013) is negligible. GLVs contribute to 6 % of the total BVOC emissions and even less to the total VOC emissions (< 1 %). At such low levels, the suppressing effect is marginal (Mentel et al., 2013). A potential contribution of GLVs to particle mass formation was also neglected because the mass yields are also low ($\sim$ 0.03, Hamilton et al., 2009). (iii) All other VOC contributions to SOA formation were assumed to be independent of each other, i.e., the total SOA mass can be described as linear combination of individual contributions from AVOC and BVOC.

To obtain the mass of organic matter on particles originating from BVOCs, we assumed that the atmospheric lifetime of particles is approx. 4 days. With the relationship between concentration $C$, source strengths $Q$ and lifetime $\tau$ ($C = Q \cdot \tau$), we obtained the data listed in Tables S3–S4.





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To compare the contribution of BVOC to AVOC emissions to the organic particulate matter, we used benzene, toluene and xylenes data as main anthropogenic compounds. The source strengths for benzene, toluene and xylenes were calculated from the ambient summer measurements at an urban background site (Wang et al., 2015) using an average OH concentration of $5\times 10^6$ molecule $cm^{-3}$ (Lu et al., 2013) and the corresponding rate coefficients (Atkinson, 1990). The SOA yields were taken from the recent study by Emanuelsson et al., 2013, corresponding to 0.14 at an organic aerosol concentration of 10 µg C $m^{-3}$.

## 3 Results

### 3.1 Laboratory study of stress-induced BVOC emissions from different plant models

To classify plant BVOC emissions into the categories "constitutive" or "stress-induced" (Table S1, in the Supplement), we analyzed the leaf BVOC emissions from four model plants (poplar, cotton, tomato, and tobacco) following $O_3$ fumigation under controlled conditions in continuously stirred tank reactors (CSTR) inside a climate chamber (Mentel et al., 2009; Wildt et al., 1997). Under unstressed conditions, the emission of sBVOCs such as benzenoids (BZ), sesquiterpenes (SQT), green leaf volatiles (GLVs) and some monoterpenes, was negligible. The sum of all sBVOC emissions from unstressed plants was consistently lower than 0.05 nmol $m^{-2}$ $s^{-1}$ (based on the projected leaf area) in any model plant, and the averages were as low as 0.005 nmol $m^{-2}$ $s^{-1}$ (Fig. 1a). In contrast, sBVOCs were apparent when plants experienced $O_3$ stress, reaching emission rates of up to 50 nmol $m^{-2}$ $s^{-1}$ and average rates of ca. 3.3 nmol $m^{-2}$ $s^{-1}$ 24 h after $O_3$ exposure (Fig. 1b). The emissions of sBVOC appeared directly following pulses of $O_3$ exposure, and their emission strengths were dependent on the $O_3$ flux density into the plant foliage (data not shown), which agrees well with previous studies (Beauchamp et al., 2005; Behnke et al., 2009). Together,





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these data suggest that sBVOCs are virtually absent from the volatile fingerprint of green foliage under unstressed conditions; however, they can be induced in relatively large amounts following acute stress episodes, here simulated by applying $O_3$.

### 3.2 Urban trees in Beijing release large quantities of stress-induced BVOCs

During the measurement campaign in Beijing (August–October 2011), the climate was warm and characterized by relatively high light intensities, air temperatures, $NO_x$ and $O_3$ levels (Fig. 2a–c). The ozone concentrations measured at an 8 m height from the 325 m-tall meteorological tower at the Institute of Atmospheric Physics – Chinese Academy of Sciences (IAP-CAS) were from 10–40 ppb (daily mean), reaching daily maxima of 60–100 ppb. The $O_3$ data indicated that plant leaves may have frequently experienced oxidative stress during summer, but more importantly, the high (from 30–40 ppm · h), relatively constant $AOT_{40}$ values (the accumulated amount of ozone over the threshold value of 40 ppb) suggest that all of the urban plants were exposed to chronic $O_3$ stress for the entire summer period.

We analyzed the BVOC emission potentials ("standard emission factors") of the most abundant woody broadleaf tree species covering the urban area of Beijing (Fig. 3 and Table 1), observing highly plant species-specific BVOC profiles. The highest BVOC emission potentials (20–35 nmol $m^{-2}$ $s^{-1}$) were measured for the cBVOC isoprene originating from the tree species *Salix babylonica* (Sb) and *Populus tomentosa* (Pt), two well-known strong isoprene-emitters. Significant isoprene emission rates (range 3–5 nmol $m^{-2}$ $s^{-1}$) were also observed from the plant species *Sophora japonica* (Sj), *Euonymus japonicus* (Ej), *Platanus* × *acerifolia* (Pa) and *Berberis thunbergii* (Bt). As notable monoterpene-emitting plant species, we detected Ej and Bt, exhibiting a BVOC potential of approx. 3–5 nmol $m^{-2}$ $s^{-1}$; these species are thus classified as both isoprene- and monoterpene-emitting species.

Importantly, we detected a diverse chemical spectrum of sBVOCs from most of the woody broadleaf plant species (Fig. 3a–c), which were also emitted at significantly high rates (0.1–10 nmol $m^{-2}$ $s^{-1}$). BZ, GLV and SQTs were emitted at rates that were





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~ 100–1000 times higher than those that were detected from unstressed plants in laboratory studies (Fig. 1), clearly indicating plant stress. We estimated to what extent sBVOCs were emitted from plants in Beijing compared to each plant's specific cBVOC profile based on the classification from the laboratory survey. The proportion of sBVOCs dominated the overall emission profile for two-thirds of the species (mean value of 83 %; Fig. 4b, see black points). The major contributors to the fraction of sBVOCs were GLV compounds (Fig. 4b), followed by BZ and SQT compounds. Even for strong cBVOC emitters, such as *Populus tomentosa* (Pt) and *Salix babylonica* (Sb), the contribution of sBVOCs to the total BVOC budget was significant, accounting for 7 and 20 % of the total moles of BVOC, respectively. Together, the BVOC profiles suggest that most of the plant species that are found in Beijing grow under stress conditions and that the contribution of sBVOCs is a significant fraction of the total amount of plant volatiles that are emitted in the air of Beijing.

### 3.3 The stress-induced BVOC response is phylogenetically related to plant taxa

We further examined correlations between BVOC emission rates and plant taxa using a principal component analysis (PCA), aiming to analyze the phylogenetic relationships. The most positively correlated plant species to emit sBVOCs was *Berberis thunbergii* (Bt), followed by *Malus spectabilis* (Ms), *Euonymus japonicus* (Ej), *Sophora japonica* (Sj), *Prunus cerasifera* (Pc) and *Salix babylonica* (Sb) (Fig. 5). *Berberis thunbergii* belongs to the family Berberidaceae, evolving from the stem Eudicotyledons. In contrast, Ms, Ej, Sj, Pc and Sb, all members of the Fabids clade, originated from Eudicotyledons throughout Gunneridae/Pentapetalae/Rosids (Fig. 5, depicted in blue). Thus, it appears that the trait to emit sBVOCs is phylogenetically related. Furthermore, Bt, Ej and Sb were also correlated with cBVOC emissions, indicating that both species can be generally classified as overall strong BVOC emitters (cBVOCs + sBVOCs). *Sophora japonica* and Pa showed a much weaker correlation with cBVOC emissions. The PCA further indicated that the plant species that were phylogenetically related to





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the clade Asterids (Fig. 5, depicted in orange) and from the family Magnoliaceae (in green) were low-to-moderate sBVOCs emitters and low-to-moderate cBVOC emitters.

We also observed that the tree species *Ailanthus altissima* (Aa), *Prunus persica* (Pp), *Ginkgo biloba* (Gb), *Platanus* × *acerifolia* (Pa) and *Koelreuteria paniculata* (Kp) were not correlated with sBVOCs, indicating that these species can be classified as non- or low-emitters of sBVOCs. *Ailanthus altissima* and Kp, from the respective families Simaroubaceae and Sapindaceae, belong to the order of Sapindales (Fig. 5, depicted in white). *Ginkgo biloba*, as member of the family Ginkgoaceae is not closely related to any other plant species (yellow). Isoprene emission (and net $CO_2$ assimilation rates Table S2, in the Supplement) was strongly correlated with the species *Populus tomentosa* and *Salix babylonica* (Pt and Sb) from the family Salicaceae (Fig. 5, depicted in cyan).

### 3.4 BVOC emissions in Beijing before and after the 2008 Olympics

To understand how increases in the green area of Beijing in the years before and following the Olympic Games have affected the total BVOC budgets, we based our calculations on the tree inventories of 2005 and 2010 and used in each case the weather data of the year when the measurements were performed (2011), so that the comparison is independent from climate condition (Table 2, Fig. S1 and Table S3, in the Supplement). Overall the total BVOC emissions were always dominated by isoprene (mainly *Populus* and *Salix*) and monoterpenes (dominated by *Euonymus*), accounting for 63–65 % and 21–22 % of the total BVOC, respectively (Table 2). Importantly, the sBVOCs significantly contributed to the overall BVOC budget (15–16 %), originating mainly from *Euonymus* (38 %), *Sophora* (26 %), and *Salix* (13 %). The total annual BVOC emission might have therefore doubled from 2005 to 2010 (from $3.6 \times 10^9$ to $7.1 \times 10^9$ g C year$^{-1}$, see Table 1–2) as a consequence of the increased number of trees, assuming that the impacts of plant stress on the sBVOC emissions in 2005 were similar to the impacts of plant stress in 2010.





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### 3.5 Impacts of stress-induced BVOCs on SOA formation in the air of Beijing

Based on the annual BVOC budget calculation, we analyzed the putative importance of BVOC emissions for secondary aerosol (SOA) formation compared to SOA formation via anthropogenic VOCs (AVOCs). We were particularly interested in quantifying the contribution of sBVOCs to the overall biogenic SOA-formation potential. We estimated the potential contribution of cBVOC, sBVOC and AVOC emissions to the particle mass in the air for 2005 and 2010, i.e. before and after the realized large-tree planting programs (Fig. 6a and Table S3, in the Supplement).

The estimated average SOA mass formation from all of the BVOCs was approx. 1.05 µg in 2005 and 2.05 µg in 2010, respectively. The SOA production rates from sBVOCs constituted a considerable portion of the total biogenic SOA (~ 40 %) (Fig. 6a and Table S3). Therefore, neglecting the sBVOC emissions would lead to a 64 and 62 % lower estimates of organic particulate matter originating from biogenic sources in Beijing, respectively, for 2005 and 2010. The AVOCs were the dominant precursors of organic aerosol production (Fig. 6b and Table S4), where SOA formation via BVOCs accounts for less than 5 % of the total (Fig. 6c and Table S4). Nevertheless, the BVOC emissions increased between 2005 and 2010, while in contrast, the AVOCs decreased. The contribution of VOCs from biogenic sources to SOA formation increased from ~ 2 in 2005 to ~ 4 % in 2010 (Fig. 6c).

## 4 Discussion

### 4.1 Multiple urban stresses cause strong taxa-related stress-induced BVOC emissions

Plants are constantly exposed to a variety of abiotic and biotic stresses in natural environments, including heat, wind, intensive sun light, and herbivorous and microbial attacks. As such, unstressed trees growing under optimal conditions are unlikely





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to exist in nature (reviewed in Niinemets, 2010). Theoretically, stress-induced BVOCs (Table S1, in the Supplement) are elicited after exceeding a stress threshold and, depending on the severity of the stress, are emitted in relatively large amounts. We have validated this concept utilizing different model plant species via $O_3$ fumigation. The use of $O_3$ as an abiotic stressor by generating an oxidative burst is a common procedure in plant science and mimics plant responses following pathogen attack or leaf wounding (Heiden et al., 2003). In accordance with other studies (Beauchamp et al., 2005; Behnke et al., 2009; Heiden et al., 1999, 2003), these data demonstrate that the degree of sBVOC emissions can change dramatically from negligible emissions under unstressed (or plant-optimal) conditions (pmol $m^{-2}$ $s^{-1}$) to significantly elevated emissions (nmol $m^{-2}$ $s^{-1}$) following stress. The emission rates are quite similar between laboratory-grown plants that are grown in the urban environment of Beijing. Overall, it appears that sBVOC emissions dominated the overall emission pattern ($\sim$ 83 %) of two-thirds of the analyzed species, indicating that plants in Beijing are commonly exposed to severe levels of multiple stresses, typically of urban environments (Calfapietra et al., 2013b). Thus, it is imperative that future research also considers sBVOC emissions and their impact on chemical processes in the troposphere.

The sBVOCs are biosynthetically formed in response to stress from different biochemical pathways (Laothawornkitkul et al., 2009) that are commonly found in green plants. Green leaf volatiles originate from the lipoxygenase (LOX) pathway, which produces oxylipins (i.e., jasmonic acid derivatives) as a defense response. Upon leaf damage, fatty acids that are stored in the lipids become available substrate for LOX enzymes and are partially converted into GLV. Benzenoids are produced from the shikimate pathway, and the most common BZ methyl salicylate is required for plant-stress signaling (e.g., Liu et al., 2011). The volatile isoprenoids SQTs and MTs originate, respectively, from the cytosolic mevalonate and the plastidic methylerythritol phosphate (MEP) pathways, and both classes are crucial infochemicals between plants and insects (e.g., Ghirardo et al., 2012). Although the exact mechanisms leading to the induction of sBVOCs require further examination, oxidative stress generally causes dra-





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matic changes in the chemical-physical properties of the plant cell (Arimura et al., 2011; Kanchiswamy et al., 2015) and can therefore activate enzymes that are related to sBVOC emissions (within minutes to hours) following gene activation and the translation of the respective proteins (hours to days). Thus, sBVOCs can be activated in most plant species, but the emission strengths (rarely investigated) are plant-taxa-specific (Fig. 5). Because the sBVOC emission potentials are genus- and species-dependent, some plant families might be more suitable than others for expanding the urban greening area. While comparison with literature is not possible for sBVOCs, the phylogenetic analysis of cBVOCs agrees well with previous studies, indicating that species from the family Salicaceae and Fagaceae are strong cBVOC emitters, in contrast to the plant species within the Oleaceae and Rosaceae families, which are non-emitters of cBVOCs (Benjamin et al., 1996; Karlik et al., 2002). Whether these cBVOCs are needed to maintain plant fitness in the analyzed tree species and to cope with severe urban stress conditions remains to be elucidated.

### 4.2 The importance of measuring stress-induced BVOC emissions

The present study supports the hypothesis that different plant species under stress can emit a large spectrum and high amounts of stress-induced VOCs (Niinemets, 2010), which in turn can potentially influence air quality in urban environments. It has been reported very recently that sBVOCs compose a substantial part of the total BVOCs that are emitted into the atmosphere and that their quantification in dependence on environmental conditions is urgently needed (Bergström et al., 2014; Bouvier-Brown et al., 2009; Guenther, 2013; Mentel et al., 2013). Online above-canopy measurements have shown that significant amounts of benzenoids (e.g., MeSa), SQT products, and GLVs exist in the atmosphere (e.g., Karl et al., 2008). Very recently, global BZ emissions from biogenic sources have been estimated to be in the same range as from anthropogenic sources (Misztal et al., 2015). Moreover, the scientific interest in BZ and SQT compounds has increased as it has been shown that these compounds may play significant roles in SOA formation due to their higher formation potential compared to





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that of cBVOCs (Bergström et al., 2014; Mentel et al., 2013). However, measuring sBVOCs such as SQT in ambient air is challenging due to their high reactivity with $O_3$ and/or other reactive oxygen species (i.e., OH radicals), and sBVOCs might thus already be oxidized before being detected. With respect to this effect, the use of purified synthetic air in combination with an enclosure cuvette measurement was essential for determinating the real plant species-specific sBVOC emission potential. Using this setup, many species that are commonly classified as "non-emitting species" (according to their "constitutive" emission potentials) actually emit several hydrocarbons at significant emission rates. Thus, our traditional view of classifying plants as "emitting" or "non-emitting" BVOC species – based only on isoprene and monoterpene emission potentials – should be revised. The implementation of sBVOCs into BVOC emission models (i.e., MEGAN and BEIS) paves the way for a more realistic representation of overall BVOC emissions.

### 4.3 Modeling BVOCs

A number of constraints and uncertainties should be noted that are related to the modeling and measuring approaches. First, phenological development and seasonal variations in emission factors have been lumped for all deciduous species in this investigation. This grouping was necessary because measuring the BVOC emission potentials of all plant species was not feasible. Second, we neglected any impacts other than instantaneous weather conditions and continuous seasonal development, for instance, emissions occurring during budbreak (Aalto et al., 2014) or flowering (Baghi et al., 2012). Third, we used the conventional calculation methods for emission determination, although the underlying assumptions of these algorithms might be very different for the actual production pathways (Grote et al., 2013). Fourth, the constitutive BVOC emissions of isoprene and monoterpene might also increase under stressed conditions (Behnke et al., 2009; Blande et al., 2007; Niinemets, 2010). Fifth, toluene, benzene and xylenes have been assumed to originate solely from anthropogenic sources, although a very recent study supports biogenic sources (Misztal et al., 2015). Sixth, emission





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potentials of constitutive BVOCs based on cut plants/branches may be somehow lower than those from uncut branches due to disturbance in carbon allocation (Funk et al., 1999; Ghirardo et al., 2011). Consequently to points 4th–6th, the possible underestimation of those stress-related BVOC in the actual analysis may mean that the relative importance of biogenic emissions, compared to anthropogenic, might actually be larger. Seventh, other BVOCs other than terpenes might originate from specific and non-specific storages or be synthetized de novo under stress (Iriti and Faoro, 2009). A specific emission function for sBVOC has not yet been reported because the observed responses (i.e., to $O_3$ stress) cover only a small range of species and are quite different in magnitude (Calfapietra et al., 2013a). Taken together, considerable uncertainties about the absolute BVOC estimates are apparent and may be reduced with increasing knowledge about production pathways and environmental dependencies. This estimate is, however, conservative, making it more likely that the relative importance of the sBVOC over cBVOC and biogenic vs. anthropogenic VOC emissions in Beijing has been underestimated rather than overvalued.

### 4.4 Impacts of the enlargement of urban greening in Beijing

Air pollution is costly to human health and well-being, resulting in premature death, lost work days, health problems and hospital costs, damage to buildings, and reduced agricultural yields. Large-scale greening efforts (e.g., "the million tree-planting") have thus been initiated worldwide in an effort to reduce urban heat island effects, increase carbon sequestration, remove pollutants, increase space for recreation, and increase the aesthetic value of cities (McPherson et al., 2011; Morani et al., 2011). Enlarging the urban green area by planting trees improves air quality by actively removing pollution. However, while the benefits of planting trees are clear, the possible disadvantages (in terms of the contribution of BVOCs) of planting the "wrong trees" are often not taken into account (Churkina et al., 2015).

In the present analysis, we investigated some impacts of a large greening initiative, namely the tree plantation action that occurred before the summer 2008 Olympics, in





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an effort to improve air quality issues. This initiative more than doubled the number of trees between 2005 and 2010 in Beijing species selection and was performed in favor of fast growth and previous experiences on development rather than on BVOC emission potentials. Using the tree coverage before and after this activity in combination with our BVOC emission survey, we quantified the impact of the altered BVOC emissions on the air quality in Beijing. Theoretically, this impact can be characterized as the ozone- and SOA-formation potentials of different biogenic and anthropogenic VOC emissions. However, neither the $O_3$ formation potential of sBVOC such as BZs or some SQT nor the partitioning of their oxidation products in pre-existing matter of high mass or pre-existing particulate matter are well characterized. Due to the present lack in experimental data and in absence of a model that exactly considers all facets of SOA formation, we use the results of recent laboratory experiments (Mentel et al., 2009, 2013) for a rough estimate of SOA formation from BVOC in Beijing. Mentel et al., 2013 measured the SOA formation potentials of constitutive and stress-induced BVOC emissions for masses in the range of 8–40 $\mu g\,m^{-3}$. This is somewhat less than the mass loading in the air over Beijing ($\sim$ 20–200 $\mu g\,m^{-3}$, e.g. Sun et al., 2010) but still in a realistic range for moderately polluted atmospheres. Furthermore, a model study implementing SOA formation from sBVOC emissions demonstrated that these emissions can substantially contribute to the formation of particulate organic matter on a regional scale (Bergström et al., 2014). Our calculations for the megacity Beijing revealed that the SOA-formation potential originating from BVOC sources might have doubled from 2005 to 2010 and that the contribution of sBVOC emission to SOA formation from BVOC is substantial.

The yields used here for the formation of organic SOA mass from the oxidation of BVOC were determined for conditions where the surface of particulate matter is comparable to that of moderately polluted atmospheres but less than that in megacities. As mass formation from the oxidation of volatile organic compounds also depends on the mass of pre-existing matter (Odum Jay et al., 1996; Pankow, 1994), the contribution of BVOC to SOA mass formation in Beijing may be somewhat higher than estimated above.





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The SOA production from the sBVOCs as estimated here agrees with recent estimations using a tracer method in which the contribution of the SQT $\beta$-caryophyllene yielded $0.21 \pm 0.18\,\mu g\,m^{-3}$ (Guo et al., 2012) compared with our estimation of $0.78\,\mu g\,m^{-3}$ for the sum of all SQT and for BZ. Thus, the extent of SOA production rates derived from sBVOC emissions in this work agrees with the observed concentrations of BVOC tracers and could contribute to a considerable portion of approx. 40 % to the BSOA (total $2.05\,\mu g\,m^{-3}$ in 2010).

Nevertheless, in the heavily polluted area of Beijing the relative importance of organic SOA mass from BVOC oxidation is still rather small, at least on an annual basis. Compared to SOA potential from anthropogenic VOC sources, it is estimated to account for less than 10 %. However, it should be noted that our simplified assumptions made for anthropogenic VOCs seem to result in an unrealistically high SOA production (i.e., more than $30\,\mu g\,m^{-3}$ from xylenes). Despite the likely overestimation, the atmospheric concentrations of particulate organic matter from anthropogenic VOC sources are by far larger than those that can be derived from BVOC emission (e.g., 17 times more SOA from toluene than from SQT and BZ). This is further supported by the observation on toluene being a major precursor of Beijing SOA (Guo et al., 2012). However, the relative importance of stress-induced BSOA increased, from 2005 to 2010, because anthropogenic pollution decreased and the vegetated area was increased.

Another way to visualize the relevance of BVOC emissions in urban air chemistry is to compare them with anthropogenic car emissions (Curtis et al., 2014). Supposing that the enlargement of the urban vegetation cover in Beijing from 2005 and 2010 was hypothetically managed using only "non-emitting plants" (e.g., *Ailanthus altissima* and *Prunus persica*), the carbon reduction in terms of BVOCs would have been $3.5 \times 10^9\,g\,C\,year^{-1}$ (Table 2), equivalent to 1.5 million cars (assuming 115 mg AVOC $km^{-1}$ $car^{-1}$ (Ho et al., 2009) and the typical car being driven 20 000 km $year^{-1}$). This comparison is rather conservative because it does not consider the fact that AVOCs are less reactive than BVOCs, i.e., in the same amount, BVOCs can produce more SOA than can AVOC vehicles.





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## 5 Conclusion

Efforts to reduce anthropogenic pollution in the megacity of Beijing were generally successful and led to a reduction of AVOC of 25–30 % from 2005 to 2010. Nevertheless, pollution in this megacity is still dominated by anthropogenic trace compounds, although the vegetated area doubled from 2005 to 2010. Hence, a plantation of large areas in megacities does not lead to an unacceptable increase in pollution. In contrast, considering that vegetation effectively removes pollutants such as $O_3$, $NO_x$, and formaldehyde, from the atmosphere, a plantation of large areas in megacities has many advantages.

While BVOC emissions from plants still contribute only to a minor amount of the VOC load in Beijing, decreasing anthropogenic pollution may increase the importance of BVOCs. The more successful AVOC emissions are reduced, the higher the contribution of BVOCs will be. However, there is an easy and cost-efficient way to optimize effects arising from BVOC emissions. The landscape planning of megacity urban areas should consider the species-specific emission potentials of both "constitutive" and "stress-induced" BVOCs to mitigate the BVOC load in urban areas. In particular, large-scale tree planting operations should choose non-emitting plants of both "constitutive" and "stress-induced" BVOCs. We conclude that "picking the right tree for urban greening" (Churkina et al., 2015) has potentially beneficial consequences on the air quality of megacities.

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**Table 1.** Absolute abundance of woody plant species found in 2005 and 2010 in the urban area of Beijing city. In bold, the 22 broadleaf species studied and the abbreviation (Abr.) used in the text for each species. The number of trees and thus the urban vegetation cover was increased between 2005 and 2010 in order to improve environment air quality for the 2008 Olympic Games. The data were derived from Beijing Municipal Bureau of Landscape and forestry, inventory of the green space in Beijing based on census data from 2005 and 2010.

| Plant type | Species (Chinese) | Abr. | Latin name | English name | 2005 Nr. (× 10 000) | 2010 Nr. (× 10 000) |
|---|---|---|---|---|---|---|
| Evergreen trees | 白皮松 | | *Pinus bungeana* Zucc.ex Endl. | Lacebark Pine | 9.24 | 28.34 |
| | 侧柏 | | *Platycladus orientalis* (L.) Franco | Chinese Arborvitae | 142.324 | 471.26 |
| | 桧柏 | | *Juniperus chinensis* (L.) Antoine | Chinese Juniper | 118.114 | 257.14 |
| | 雪松 | | *Cedrus deodara* (Roxb.) G.Don | Himalayan Cedar | 12.72 | 37.86 |
| | 油松 | | *Pinus tabulaeformis* Carr. | Chinese Pine | 58.14 | 129.28 |
| | 云杉 | | *Picea koraiensis* Nakai | Korean Spruce | 3.76 | 7.51 |
| Deciduous trees | 白蜡 | ***Fv*** | ***Fraxinus velutina*** Torr. | Velvet Ash | 22.84 | 63.88 |
| | 白玉兰 | ***Md*** | ***Magnolia denudata*** Desr. | Yulan Magnolia | 7.89 | 14.05 |
| | 碧桃 | ***Pp*** | ***Prunus persica*** cv. Duplex | Flowering Peach | 20.02 | 47.99 |
| | 臭椿 | ***Aa*** | ***Ailanthus altissima*** (Mill.) Swingle | Tree of Heaven | 15.77 | 22.69 |
| | 垂柳 | ***Sb*** | ***Salix babylonica*** L. | Weeping Willow | 101.24 | 260.20 |
| | 杜仲 | | *Eucommia ulmoides* Oliv. | Hardy Rubber Tree | 4.32 | 9.51 |
| | 国槐 | ***Sj*** | ***Sophora japonica*** L. | Japanese Pagoda Tree | 80.38 | 192.98 |
| | 合欢 | | *Albizia julibrissin* Durazz. | Silk Tree | 4.24 | 6.88 |
| | 海棠 | ***Ms*** | ***Malus spectabilis*** (Ait) Borkh. | Chinese Flowering Crabapple | 9.10 | 40.3076 |
| | 栾树 | ***Kp*** | ***Koelreuteria paniculata*** Laxm. | Golden Rain Tree | 17.64 | 31.10 |
| | 马褂木 | ***Lc*** | ***Liriodendron chinense*** x tulipikera | Chinese Tulip Tree | 0.25 | 0.4 |
| | 毛白杨 | ***Pt*** | ***Populus tomentosa*** Carr. | Chinese White Poplar | 125.75 | 201.96 |
| | 楸树 | ***Cb*** | ***Catalpa bungei*** C.A.Mey. | Manchurian Catalpa | 1.07 | 10.07 |
| | 柿树 | ***Dk*** | ***Diospyros kaki*** L.f. | Japanese Persimmon | 9.59 | 12.63 |
| | 悬铃木 | ***Pa*** | ***Platanus× acerifolia*** (Ait) Willd. | London Plane | 7.62 | 23.43 |
| | 银杏 | ***Gb*** | ***Ginkgo biloba*** L. | Maidenhair Tree | 46.34 | 166.02 |
| | 榆树 | ***Up*** | ***Ulmus pumila*** L. | Siberian Elm | 18.94 | 43.82 |
| | 元宝枫 | | *Acer truncatum* Bunge | Shantung Maple | 15.65 | 26.79 |
| | 紫叶李 | ***Pc*** | ***Prunus cerasifera*** *Ehrh.* cv. "Atropurpurea" | Pissard Plum | 20.01 | 37.92 |
| Evergreen shrubs | 大叶黄杨 | ***Ej*** | ***Euonymus japonicus*** Thunb. | Evergreen Euonymus | 437.61 | 922.96 |
| | 沙地柏 | | *Sabina vulgaris* Ant. | Savin Juniper | 327.93 | 808.80 |
| | 小叶黄杨 | | *Buxus microphylla* Sieb.et Zucc var. *koreana* Nakai | Korean Box | 169.66 | 257.23 |
| Deciduous shrubs | 棣棠 | | *Kerria japonica* (L.) DC. | Corchorus | 58.35 | 140.38 |
| | 丁香 | ***Sp*** | ***Syringa pekinensis*** Rupr. | Broad-leaved Lilac | 32.64 | 76.01 |
| | 红瑞木 | | *Cornus alba* L. | Tatarian Dogwood | 24.51 | 78.16 |
| | 金银木 | ***Lm*** | ***Lonicera maackii*** (Rupr.) Maxim. | Amur Honeysuckle | 21.86 | 62.93 |
| | 锦带花 | | *Weigela* florida (Bunge) A. DC. | Old-fashioned Weigela | 10.67 | 52.73 |
| | 连翘 | ***Fs*** | ***Forsythia suspensa*** (Thunb.) Vahl | Weeping Forsythia | 64.93 | 168.61 |
| | 小叶女贞 | ***Lq*** | ***Ligustrum quihoui*** Carr. | Wax Leaf Privet | 139.71 | 267.26 |
| | 小檗 | ***Bt*** | ***Berberis thunbergii*** DC. | Japanese Barberry | 154.45 | 82.77 |
| | 迎春 | | *Jasminum nudiflorum* lindl . | Winter Jasmine | 97.45 | 194.73 |
| | 榆叶梅 | | *Prunus triloba* Lindl. | Flowering Almond | 20.73 | 46.11 |
| | 珍珠梅 | | *Sorbaria kirilowii* (Regel) Maxim. | False Spirea | 28.54 | 52.07 |
| | 紫薇 | | *Lagerstroemia indica* L. | Crape Myrtle | 35.85 | 57.24 |





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**Table 2.** Annual BVOC emission estimates in Beijing for the year 2005 and 2010, modeled as described in the text in hourly resolution. Abbr. BVOC groups: cMT = constitutive monoterpenes; sMT = stress-induced monoterpenes, SQT = sesquiterpenes; BZ = benzenoids; GLV = green leaves volatiles; BVOC class: c = constitutive; s = stress-induced. Meas.: BVOC estimates based on the 22 plant species measured. Total: BVOC estimates including estimations from plant species not measured (see Table 1) as well as *Robinia pseudoacacia* based on data provided in Yang et al. (2005). The differences of BVOC between pre-Olympic (2005) and post-Olympic (2010) are reported below the estimations of the total BVOC for the years 2010 measured and total, respectively.

| BVOC group | BVOC class | 2005 (Meas.) [$10^6$ g C yr$^{-1}$] | 2010 (Meas.) [$10^6$ g C yr$^{-1}$] | 2005 (Total) [$10^6$ g C yr$^{-1}$] | 2010 (Total) [$10^6$ g C yr$^{-1}$] | 2005 Meas. vs Total [%] | 2010 Meas. vs Total [%] | 2005 BVOC group vs. sum (all) total [%] | 2010 BVOC group vs. sum (all) total [%] |
|---|---|---|---|---|---|---|---|---|---|
| Isoprene | c | 2219 | 4281 | 2302 | 4445 | 96 | 96 | 64.7 | 62.9 |
| cMT | c | 651 | 1312 | 747 | 1568 | 87 | 84 | 21.0 | 22.2 |
| sMT | s | 3 | 6 | 3 | 7 | 87 | 84 | 0.1 | 0.1 |
| SQT | s | 122 | 223 | 140 | 267 | 87 | 84 | 3.9 | 3.8 |
| BZ | s | 119 | 236 | 137 | 282 | 87 | 84 | 3.9 | 4.0 |
| GLV | s | 200 | 412 | 229 | 493 | 87 | 84 | 6.4 | 7.0 |
| Sum | c | 2870 | 5593 | 3049 | 6013 | | | 86 | 85 |
| Sum | s | 444 | 877 | 509 | 1049 | | | 14 | 15 |
| Sum (all) | c + s | 3314 | 6470 | 3558 | 7062 | | | 100 | 100 |
| Difference (2005–2010) | | | 3156 | | 3504 | | | | |





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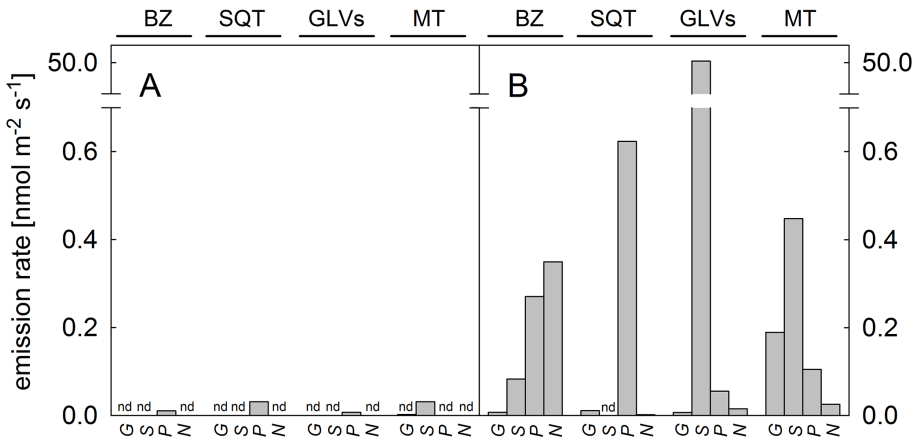


**Figure 1.** Example of stress-induced BVOC emissions **(a)** before and **(b)** one day after $O_3$ exposure in different plant model species from the laboratory study. Measurements were performed continuously throughout the day with a time resolution of approx. 76 min. Bars indicate daily means. Experiments were replicated different times with similar results. The plant species that were used and the number of biological replicates ($n$) were: $G$ = *Gossypium hirsutum* (Cotton, $n = 4$); $S$ = *Solanum lycopersicum* (Tomato, $n = 7$); $P$ = *Populus* × *canescens* (Poplar, $n = 17$); $N$ = *Nicotiana tabacum* (Tobacco, $n = 27$). Abbr. of VOC: BZ = benzenoids; SQT = sesquiterpenes; GLVs = green leaf volatiles; MT = monoterpenes.





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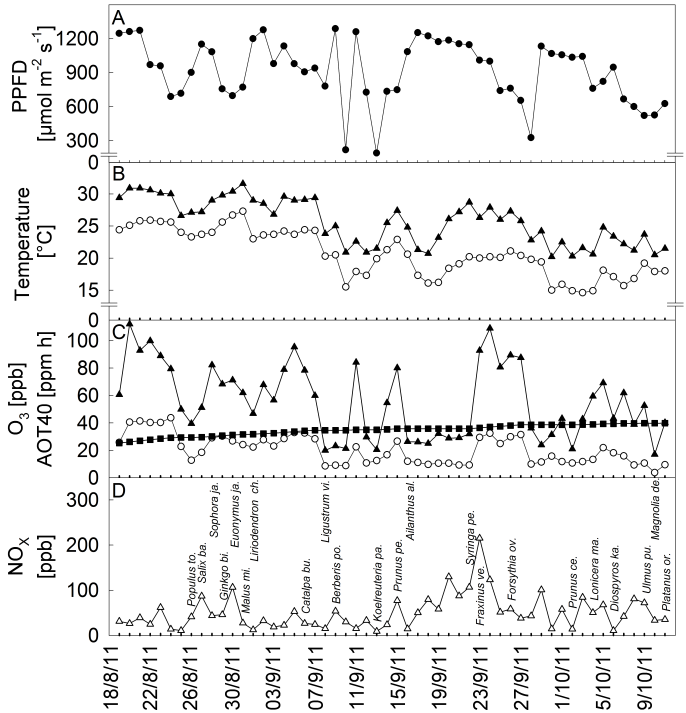


**Figure 2.** Climate data during the BVOC field campaign (August–October 2011) at an 8 m height. **(a)** Light, daily means (black circles); **(b)** air temperature, daily means (white circles), daily maximum (black triangles); **(c)** ozone, daily means (white circles), daily maximum (black triangles) $AOT_{40}$ (calculated from beginning July, black rectangles); **(d)** $NO_x$ ($NO + NO_2$), daily means (white triangles). The sampling time of each plant species is given along the *x* axis.





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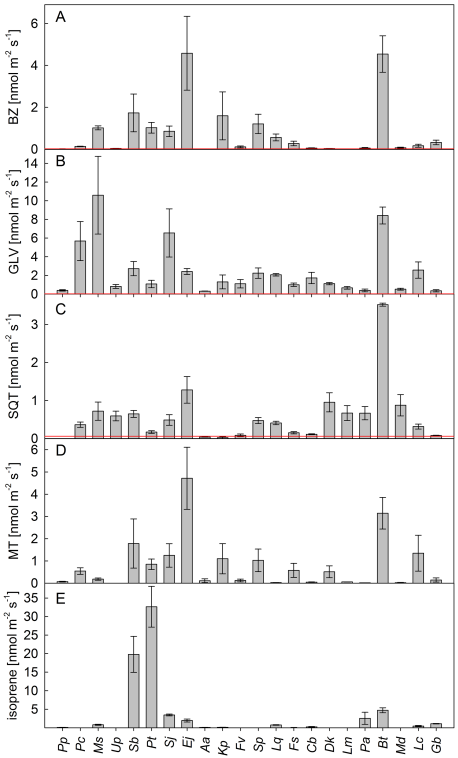


**Figure 3.** BVOC emission rates from 22 broadleaf tree species that are commonly found in the urban area of Beijing. The species were sorted by the phylogenetic tree based on the taxonomic data (Fig. 5). **(a)** BZ = benzenoids; **(b)** GLVs = green leaf volatiles; **(c)** SQT = sesquiterpenes; **(d)** MT = monoterpenes; **(e)** isoprene. For the sBVOC in panels A-C, the red lines indicate the double maximum emission rates between all of the unstressed model plants of Fig. 1a to each sBVOC group. For graph clearness, the MT emissions were not divided into constitutive and stress-induced, the latter being marginal compared to the total MT emissions.





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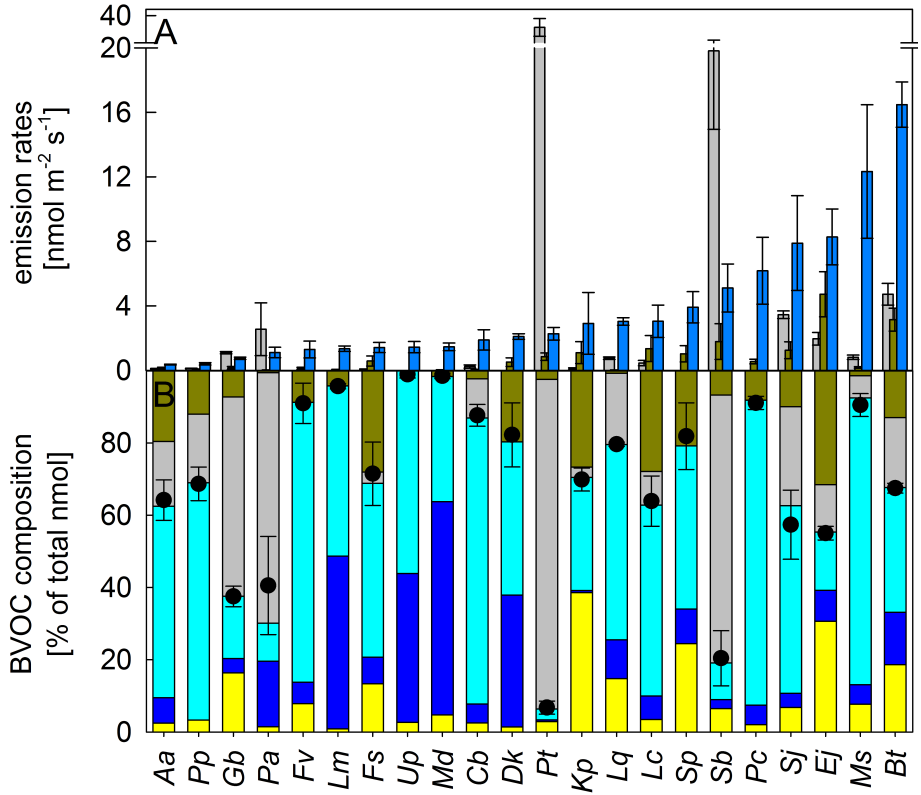


**Figure 4. (a)** BVOC emission rates and **(b)** composition of 22 broadleaf plant species sorted from low (left) to high (right) stress-induced BVOC emitters. Abbreviations are given in Table 1. Color code: gray = isoprene; green = monoterpenes (MT); cyan = green leaf volatiles (GLV); blue = sesquiterpenes (SQT); yellow = benzenoids (BZ); light blue = stress-induced BVOC (sBVOCs = SQT + BZ + GLV). Black point indicates the percentage of sBVOCs over the total BVOCs. The means of 3 plants ± SE.





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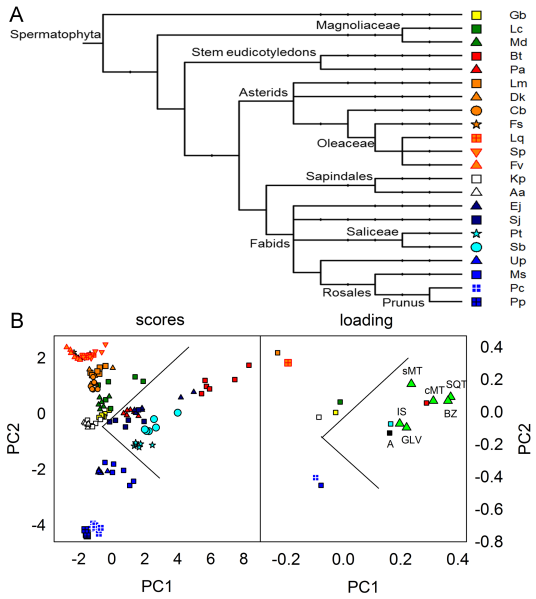


**Figure 5. (a)** Phylogenetic tree based on the taxonomic data of the 22 plant species that were analyzed according to iTOL (http://itol.embl.de/). The taxonomic orders/families/species are given only for the main branching points (the complete phylogenetic tree with all internal notes can be found in Table S7). **(b)** Principal component analysis of BVOC emission rates, net assimilation and numerically converted taxonomic data (Table S8, in the Supplement) (left = score plot; right = loading plot). Abbreviations of plant species are given in Table 1. BZ = benzenoids; SQT = sesquiterpenes; GLVs = green leaf volatiles; sMT = stress-induced monoterpenes, cMT = constitutive monoterpenes; IS = isoprene; A = net assimilation. Color code in score plot of **(b)** reflects **(a)**. To improve visualization, only the most significant parameters are shown in the loading plot: (■) net assimilation, (▲) BVOC, (■) Ginkgoaceae, (■) Magnoliaceae, (■) Stem Eudicotyledons, (■) Asterids, (■) Oleaceae, (□) Sapindales, (■) Saliceae, (■) Rosales, and (■) Prunus. $R^2X$ (Explained $X$ variation): PC1 = 15.1 %, PC2 = 8.6 %; significance at 95 % confidence.





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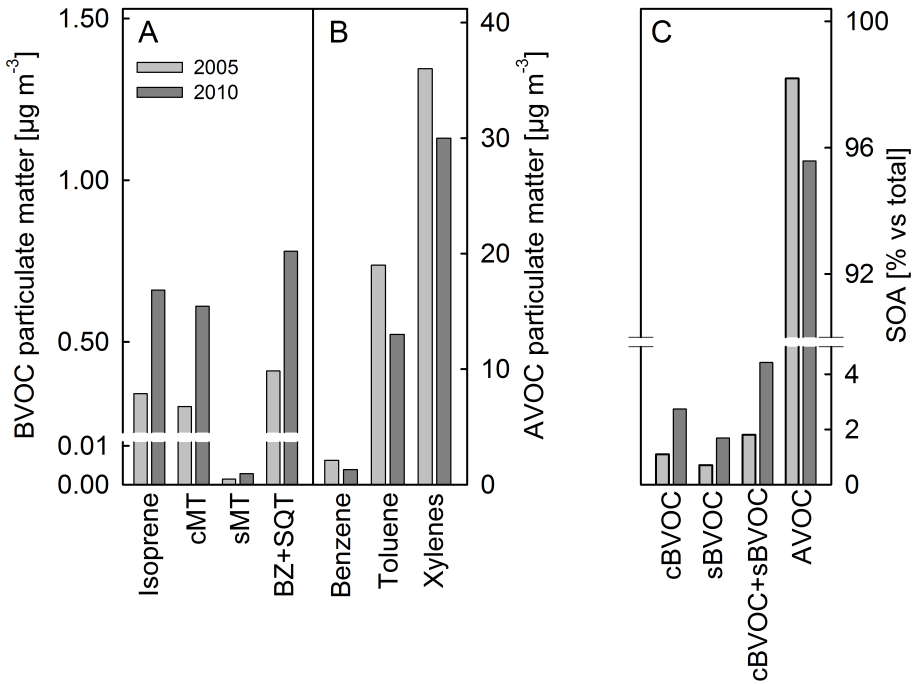


**Figure 6.** Atmospheric concentrations of secondary organic particulate matter (SOA) originating from **(a)** biogenic VOC (BVOC), **(b)** anthropogenic VOC (AVOC) and **(c)** the percentages to total SOA expected at a 2 km height of the planetary boundary layer in Beijing. Bars in gray denote data for 2005 and in dark gray data for 2010. In panels A and C, "c" and "s" denote "constitutive" and "stress-induced" BVOCs, respectively.





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