Urban stress-induced biogenic VOC emissions and SOA forming potentials 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 the municipal tree census and cuvette BVOC measurements on leaf-level, we build an inventory of BVOC emissions, and assessed the potential impact of BVOCs on secondary particulate matter (SOA) 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 (~40%) of the total annual BVOC emissions, and we estimated that the overall annual BVOC budget may have doubled from ~4.8 10^9 g C $year^{-1}$ in 2005 to ~10.3 10^9 g C $year^{-1}$ in 2010 due to the increase in urban greening, while at the same time the emission of anthropogenic VOCs (AVOCs) was lowered by 24%. Based on the BVOC emission assessment, we estimated the biological impact on SOA mass formation potential in Beijing. Constitutive and stress-induced BVOCs might produce similar secondary aerosol in Beijing. However, the main contributors of SOA-mass formations originated from anthropogenic sources (>90%). This study demonstrates the general importance to include sBVOCs when studying BVOC emissions. Although the main problems regarding air quality in Beijing still originate from anthropogenic activities, the present survey suggests that in urban plantation programs the selection of low emitting plant species has some potential beneficial effects on urban air quality.

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), or when BVOCs are in the presence of anthropogenic nitrogen oxides (NOx), they increase ozone formation and alter 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 through altering the chemical lifetime of reactive gases with substantial impacts on climate.

Plant BVOC emissions are species-specific and 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 (E)-β-ocimene and β-myrcene, and the monoterpenoids (terpenoid-derived compound) linalool and 1,8-cineol (sMT), the classes of sesquiterpenes and sesquiterpenoids (SQT), benzenoids (BZ) such as methyl salicylate (MeSa), and volatile lipoxygenase products (GLV) 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). With respect to air chemistry, SQT and MeSa can significantly contribute to the SOA formation even at relatively low concentrations due to their 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 often much higher (up to 10 °C) than those recorded in surrounding suburban and rural areas (Chen et al., 2006; Peng et al., 2012). In addition to high temperatures, urban trees are exposed to harsh conditions (Calfapietra et al., 2014), including air pollution levels, lack of root space and aeration, nutrient deficiency, and more frequent drought/flood episodes (Calfapietra et al., 2013b). These factors together negatively impair plants and enhance sBVOC emissions. Enhanced sBVOC emissions can affect the local air quality (Calfapietra et al., 2013b; Churkina et al., 2015; Hellén et al., 2012; Papiez et al., 2009; Wang et al., 2013) by their impacts on the chemical processes in the atmosphere.

Over the past two decades, large tree-planting programs have been initiated to improve the livelihoods of city 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, increasing CO_2 uptake, and the deposition/detoxification of ozone, NOx and AVOCs (e.g. Beckett et al., 2000; Nowak et al., 2013). Positive effects have certainly been established; however, tradeoffs by possible impacts of BVOC emissions on ground-level ozone formation and SOA formation are often not considered.

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 sBVOC and cBVOC 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 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 possible consequences outlined above. Despite 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, leading to further increases of SOA (Mentel et al., 2013; Bergström et al., 2014).

In the present work we investigated the importance of sBVOC emissions from the green area of the megacity Beijing, assessed the potential contribution of cBVOC and sBVOC to form SOA formation, and compared it to that of AVOCs. Our aim was to understand whether neglecting sBVOC is legitimate when studying BVOC emissions from stressful environments such as a megacity. We further assessed the impact of BVOCs on the SOA mass forming potentials due to the enlargement of green areas. Lastly, we were interested in comparing the relative potential impacts of biogenic and anthropogenic VOCs in the air of Beijing. For this purpose we conducted an extensive survey of BVOC emissions at leaf-level from the most abundant woody broadleaf plant species of the administrative districts of Beijing. We constructed a phylogenetic tree based on the taxonomic data and BVOC emissions for generalizing the sBVOC emission potentials of related plant species. Further, we built a BVOC emission inventory and calculate the BVOC budgets in the years 2005 and 2010 for the area of Beijing. Finally, we roughly estimated the SOA formation potentials from sBVOCs, cBVOCs and AVOCs.

2 Materials and Methods

2.1 Classification of BVOCs into ‘constitutive’ (cBVOCs) and ‘stress-induced’ (sBVOCs)

The classification of volatiles as ‘constitutive’ and ‘stress-induced’ 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)-β-ocimene and β-myrcene, the stress-induced monoterpenoids linalool and 1,8-cineol (all referred as sMT), all sesquiterpenes (SQT), benzenoids (BZ) and green leaves volatiles (GLV). Constitutive BVOCs (cBVOC) included the hemiterpene isoprene (IS) and all constitutively emitted monoterpenes (cMT) that were not included as sMT (Supplementary Table S1).

To demonstrate this classification, we performed highly controlled laboratory experiments, where we exposed plants to constant levels of O_3 for a short time and in absence of other abiotic and biotic stress factors. We used model plants, i.e., plant species that are widely used as reference organisms in plant physiology. These species were *Populus* × *canescenss* (gray poplar), *Gossypium hirsutum* (cotton), *Solanum lycopersicum* (tomato), and *Nicotiana tabacum* (tobacco). Plants were placed individually in continuously stirred tank reactors (CSTR) at the Research Centre 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 (Beauchamp et al., 2005; Behnke et al., 2009; Heiden et al., 1999, 2003). 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} of photosynthetic photon flux density (PPFD), with a chamber temperature of 20-25 °C and RH of 50-80% during the different experiments, depending on the size of the plants and the air flow. Ozone was then applied as pulse exposure (1-2 h) at a concentration of 800-900 nmol mol^{-1}. Sampling of BVOCs started after the removal of ozone from the chamber to avoid reaction between O_3, BVOC, and adsorbent sampling tubes. Collection was performed continuously for 24 h by trapping for 45 min (sampling time) every 76 min (time of chromatographic run) on solid sorbents (Tenax TA/Carbotrap, Grace-Alltech, Rottenburg-Hailfingen, Germany). The samples were analyzed using gas chromatography-mass spectrometry (GC-MS) as described previously (Behnke et al., 2009; Wildt et al., 1997). Means of the last 10 h measurements are presented.

2.2 The Beijing survey and data analysis

2.2.1 Climate, NOx, O_3, AOT40, and AVOC data in Beijing

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 at the 325 m tall meteorological tower of 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 (AOT40) 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) (Roy et al., 2009). AOT40 was calculated using the following equation:

$$AOT_{40} = \Sigma \; R_{max} ([O_3] - 40 \text{ ppb}) \, \Delta t \qquad (1)$$

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 (Δt = 1h) from the beginning of July until the end of the sampling period (beginning of October 2011) and for daytime only (6-20 h). Values were then converted from ppb·h to ppm·h.

2.2.2 Plant species measured

In Beijing we measured 21 different deciduous and one evergreen woody plant species (see Table 1) that are commonly found in the urban area of this megacity. 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 Supplementary 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, were potted (40x40 cm) in standard soil, and grown under ambient conditions. Measurements were performed in the period from August to mid-October in 2011. For each plant species three trees were measured. For each tree we performed measurements on two fully developed leaves originating from two different branches. Approximately 30-60 minutes prior to analysis, healthy whole plants or branches were cut off the trees. Immediately after a second cut of 2-4 cm was done under water to remove embolisms, and the branches were transferred to the laboratory for gas-exchange and BVOC measurements (see section 2.2.3). 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

our experiences, measuring cut branches does not alter considerably terpene emissions for several hours (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) who showed that except for a small amount of acetaldehyde, no other BVOCs were emitted from broadleaf plant species when the mechanical wounding (cutting) is remotely located. Furthermore, a very recent report showed that mechanical wounding does not affect benzenoid compound emissions either (Misztal et al., 2015) in contrast to insect damaged plants (Ghirardo et al., 2012; Holopainen and Gershenzon, 2010). 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±se) were used as biological replicates.

2.2.3 BVOC and gas-exchange analyses at leaf-level

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 (1,000 μmol m^{-2} s^{-1} PPFD, 30 ± 0.1 °C leaf temperature, 40% RH). This procedure allows collection under steady-state BVOC emissions (Ghirardo et al., 2011, Ghirardo et al., 2014). 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 in glass tubes (Gerstel, Mülheim an der Ruhr, Germany) containing two adsorbents in series made of 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} for 30 min. All of the flows were controlled using mass flow controllers (MKS, Andover, USA), and the flow rates were verified using a calibrated 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 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, 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 μl^{-1}; standards $solvent^{-1}$). The calibration procedures are described elsewhere (Kreuzwieser et al., 2014). Volatiles that were not available as standards were quantified using calculated response factors (Kreuzwieser et al., 2014) based on both molecular mass and the response factor obtained using δ-2-carene at different concentrations between 1-1000 pmol μl^{-1} (standards $hexane^{-1}$) resulting in linear MS signals (R^2=0.9997). In addition, a defined amount of δ-2-carene was added to each sample as an internal standard to take into account the changing of mass selective detector (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 & Farquhar (1981).

2.2.4 Phylogenetic tree and statistical analyses

The taxonomic data of the 22 woody species were used to generate a phylogenetic tree using the web tool iTOL (http://itol.embl.de/) (Letunic and Bork, 2006, 2011) (Supplementary Table S7). The correlation between plant-specific BVOC profiles, net assimilation rates (Supplementary 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 s.d.$^{-1}$ as data pre-processing. In addition, the phylogenetic data were numerically converted (Supplementary Table S8). The results were validated by 'full cross validation' and significant at the 95% confidence level.

2.3 Modeling BVOC emissions and crude estimates of SOA at city-level in Beijing

2.3.1 BVOC emission budget

We calculated the total BVOC emission budgets for Beijing at city-level. Calculations were based on the absolute abundance of woody plant species (obtained from the tree inventory of 2005 (Beijing Municipal Bureau of Landscape and Forestry, 2006) and 2010 (performed in the same way as 2005, unpublished) (Table 1)), cuvette measurements of BVOC emission rates on leaf-level from the Beijing survey, leaf mass per area (LMA, g m^{-2}), plant phenology, additional literature data, and by using hourly temperature and radiation data for the whole year 2011. The results are presented in Table 2. The emissions were differentiated into cBVOC and sBVOC emissions and the total emission budgets in Beijing were calculated in the following steps:

(i) Species-specific (*s*) potential emissions, or emission factors (*EF*, µgC gDW^{-1} h^{-1}), were determined, which were obtained for all measured emission compounds (*c*) by converting measured emissions (*EM*, nmol m^{-2} s^{-1}) as follows:

$$EFc,s = \frac{EMc \times MMc \times 3600}{1000 \times REAc,s \times LMAs} \quad (2)$$

MM is the molar mass of all carbon atoms within a compound and *REA* represents the relative enzyme activity (normalized to the average EA in June and July, a period of about 27^{o}C on average) (Supplementary Figure S2). Enzyme activity (*EA*) depends on ozone concentration and on the previous temperature and radiation conditions, for stress-induced (*ni*) and non-stress induced (*si*) emissions, respectively (Lehning et al., 2001).

$$EA_{si} = \begin{cases} 1 & if \text{ estimated daily peak } [O_3] > 40 \ (= \text{between day 132 and 287}) \\ 0 & else \end{cases} \quad (3)$$

$$EA_{ni} = EA'_{ni} + \alpha \times PPFD \times arrh - \mu \times EA'_{ni} \quad (4)$$

$$arrh = 6601E5 \times e^{\left(-\frac{AE}{8.314 \times tk}\right)} \quad (5)$$

$[O_3]$ is the estimated peak ozone concentration (ppb) using a second order polynomial based on the day of the year that is parameterized with 2011 measurements. PPFD is photon flux density (µmol m^{-2} s^{-1}) and *tk* is the daily average temperature (*K*). The parameters α, μ, and *AE* (activation energy) are taken from Lehning et al., (2001) and are assumed to be valid for all species except *Populus tomentosa* and *Salix babylonica*, where we adjusted *AE* on the basis of the two available measurement events. Ozone concentrations stayed above the threshold from mid-April to mid-October (see also Figure 2). For all species where no emission measurements were carried out (e.g., most of the evergreens), we used literature values for isoprene and constitutive monoterpene emissions. Averages of emission factors derived from all of the deciduous shrubs were used for the four plant species (*Jasminum, Kerria, Sorbaria, Weigela*) with actual unknown factors. All emission factors are given in Supplementary Table S5A, which allowed the estimations of BVOC from all the plant species found in Beijing ('total '; Table 2) beside from those directly measured ('measured'; Table 2). Stress-induced emissions from species not measured where not directly simulated (see below).

(ii) Species- and compound-specific emissions per hour and g dry weight (*Ec*, *s*) were determined from temperature and light conditions according to Guenther et al., (1995) and Guenther (1997, 1999).

$$Ec,s = \begin{cases} EFc,s \times REAc,s \times cl \times cti99 & c = isoprene \\ SF \times EFc,s \times REAc,s \times cl \times cti97 + (1 - SF) \times EFc,s \times ctm & c = MT \\ EFc,s \times REAc,s \times ctsi & c = sBVOC \end{cases} \quad (6)$$

$$ctsi = e^{(\beta \times (tk - TKR))} \quad (7)$$

SF is the 'splitting factor' between *de novo* and pool BVOC emissions that were assumed to be 0.5 for evergreen and 1 for deciduous species, respectively (Ghirardo et al., 2010; Harley et al., 2014). The parameters *cl*, *cti*, and *ctm* are light- and temperature-dependent terms that are

described in Guenther et al. (1993, *cl* and *ctm*), Guenther et al. (1997, *cti*97) and Guenther et al. (1999, *cti*99). Stress-induced BVOC emissions were calculated assuming an exponential dependency on temperature (*ctsi*), which is similar to *ctm* but uses parameters that are derived from the [O_3] dependency presented in Bourtsoukidis et al. (2012). Therefore, the Bourtsoukidis algorithm was first used to simulate relative emission rates in response to [O_3], measured during summer and autumn 2011. Then we applied the *ctsi* algorithm to the temperature values measured in parallel to [O_3] and adjusted the scaling parameter β and the reference temperature *TKR* to match the response of the Bourtsoukidis model (β = 0.24, TKR = 316.5K/43.5°C). Since the assumed reference temperature is different from the temperature during measurements, *EAsi* values need to be corrected for the temperature difference using the *ctsi* equation.

(iii) Calculated emissions were scaled to city level. Therefore, maximum foliage biomass was determined according to equations and parameters provided by Nowak (1996) for shrubs (depending on height and crown diameter) and trees (depending on trunk diameter at breast height). Tree data were available for all species except for *Robinia pseudoacacia*, where we assumed the diameter to be equal to the average diameter calculated from all other trees (Supplementary Table S5C). Maximum foliage biomass was multiplied by relative leaf area development (*RLA*) throughout the year, which was calculated using the following function (Grote et al. 2007):

$$RLA = \begin{cases} 0 & if\ doy \le DF \\ e^{\left(-\frac{(doy-DF+NDF)^2}{(0.5NDF)^2 \ln(2)}\right)} & if\ DF < doy < (DF+NDF) \\ 1 & if\ (DF+NDF) < doy < DS \\ e^{\left(-\frac{(doy-DS)^2}{(0.5NDS)^2 \ln(2)}\right)} & if\ doy \ge DS \end{cases} \quad (8)$$

DF is the day of the year (*doy*) at which daily cumulative temperature first crosses a threshold (0 ^{o}C) and flushing occurs; *DS* is the day at which leaf senescence starts; and *NDF* and *NDS* are the number of days necessary for full leaf development and senescence, respectively (see Fig. S2). Parameters have been estimated from pooled monthly measurements of 9 deciduous tree and shrub species (*NDF* = 140, *NDS* = 260, *DS* = 210). The function was used for all deciduous species while for evergreens RLA is always equal to 1. Hourly emissions are multiplied by foliage biomass per tree at the particular day and tree number. Again, the

number of *Robinia pseudoacacia* trees in the inventory of 2005 was added from an inventory carried out in 2002 (Yang et al., 2005). In the inventory of 2010, the number was increased 2.45 fold, i.e., the average increase of all other species recorded (Table 1).

(**iv**) We estimated the amount of total sBVOC emissions using the fraction of 'measured' to 'total' cBVOCs for 2005 and 2010, respectively. This fraction, which was 94 % in 2005 and 93 % in 2010, was then used to calculate total sBVOC emissions from the measured sBVOCs.

2.3.2 Estimation of SOA-formation potentials from biogenic and anthropogenic VOCs

For a rough estimate on the role of BVOCs for 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 assumed to be 2 km, as a typical proxy for the height of an inversion layer. The flux densities for biogenic VOCs were converted to source strengths for the given volume of the box by dividing the assumed height of the planetary boundary layer (PBL):

$$Q = \Phi_{av} / z \quad (9)$$

Where Q is the source strengths related to the volume of the box and z is the height of the PBL. Average flux densities for VOCs, Φ_{av}, were obtained from the data given in Table 2 by dividing the total annual emissions by the surface area of Beijing. The results for the average flux densities were then multiplied by the incremental mass yields (isoprene = 0.02 µg $µg^{-1}$ (Kiendler-Scharr et al., 2012), monoterpenes = 0.06 (Mentel et al., 2009), benzenoids and SQT = 0.22 (Mentel et al., 2013)), GLV = 0.03 (Hamilton et al., 2009) to obtain the source strengths for particulate matter.

To obtain the mass of organic matter on particles originating from BVOCs, we assumed that the atmospheric lifetime of particles is approximately 4 days. With the relationship between concentration C, source strength Q and lifetime:

$$\tau \, (C = Q * \tau) \quad (10)$$

we obtained the data listed in the Supplementary Tables S3–S4.

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 contributions of individual VOC classes to SOA formation are independent on each other, i.e., the total SOA mass can be described as a linear combination of individual contributions from AVOC and BVOC. This procedure neglects effects of partitioning on SOA formation.

To compare the contribution of BVOC and AVOC emissions to the organic particulate matter, we used benzene, toluene and xylenes data as main anthropogenic compounds. The SOA formation potentials 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 5×10^6 cm^{-3} (Lu et al, 2013) and the corresponding rate coefficients (Atkinson, 1994). Thus, using these typical summer time conditions, a production rate (ug SOA m^{-3} s^{-1}) was calculated, assuming a yield of SOA. Here the SOA yields were taken from the recent study of Emanuelsson et al. (2013), corresponding to 0.14 at an organic aerosol concentration of 10 μg C m^{-3}. One may note that the absolute AVOC emissions are not needed for these estimations since we directly can use the production rate and the assumed lifetime of the organic aerosol (4 days). Although the same assumptions on PBL-height and area as used for BVOC emission can be utilized to derive AVOC flux from measured concentration, the net result on SOA source strength remain identical. For a more detailed evaluation of AVOC emissions and comparison with existing emission inventories we refer to the study by Wang et al. (2015).

The aim of our estimates on the SOA formation potential of BVOC and AVOC emissions was to assess the relative importance of sBVOCs, cBVOCs and AVOCs on SOA formation potentials in the megacity of Beijing. The results do not represent an exact prediction, but only rough numbers as average over a year for the two years under consideration. Our estimate neither considers diurnal cycles of BVOC emissions, nor their temperature dependencies nor other variables that influence particle formation from the BVOCs. Depending on (i) the meteorological conditions, (ii) stress intensity for the plants and (iii) traffic conditions in Beijing, these numbers may vary by an order of magnitude.

3 Results

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

To demonstrate the classification of plant BVOC emissions into the categories 'constitutive' or 'stress-induced' (Supplementary Table S1), 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 ~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 with previous studies (Beauchamp et al., 2005; Behnke et al., 2009). The theoretical classification of cBVOCs and sBVOCs fully agreed with the BVOC emission pattern that was obtained in the present laboratory study when plants were exposed to O_3.

Together, these data demonstrate that BVOCs can be classified into cBVOCs and sBVOCs, and the latter are virtually absent from the volatile fingerprint of green foliage under unstressed conditions, but they can be induced and emitted in relatively large amounts following 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, NOx 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 might have frequently experienced oxidative stress during summer, but, more importantly, the high (from 30-40 ppm·h), relatively constant AOT40

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 (Kesselmeier and Staudt, 1999). 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 monoterpenes-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 ~100-1000 times higher than those 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 8% and 22% of the total carbon emitted as 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 into 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 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 *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, Supplementary Table S2) 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 emission budget 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 of climate condition (Table 2, Supplementary Fig. S1 and Table S3). Overall, the total BVOC emissions were always dominated by isoprene (mainly *Populus* and *Salix*) and GLV (dominated by *Sophora*), accounting for 51-54% and 23-25% of the total BVOC, respectively (Table 2). Importantly, the sBVOCs significantly contributed to the overall BVOC budget (38-41%), originating mainly from *Sophora* (45%) and *Salix* (23%). The total annual BVOC emission

might have doubled from 2005 to 2010 (from 4.8 10^9 g C $year^{-1}$ to 10.3 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.

3.5 Contribution of stress-induced BVOCs on SOA mass formation potentials 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. Additionally, we estimated the potential relative contribution of BVOC 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 Supplementary Table S3).

The estimated average SOA mass formation potentials from all of the BVOCs was approx. 1 µg m^{-3} (range 0.1 – 4 µg m^{-3}) in 2005 and 2 µg m^{-3} (range 0.2 – 8 µg m^{-3}) in 2010. The fraction of biogenic SOA produced from sBVOC was found to be ~70% (Fig. 6A and Supplementary Table S3). Therefore, potentially sBVOCs could produce similar amounts of SOA as cBVOCs. The AVOCs were, however, by far the dominant precursors of organic aerosol production in Beijing (Fig 6B and Supplementary Table S4), where SOA formation via BVOCs accounted for less than 2% in 2005 and 5% in 2010 of the total (Fig 6C and Supplementary Table S4). Taking into accounts the uncertainties of our approaches, the contribution of all BVOCs to SOA formation is unlikely to be higher than 10%. However, the relative SOA forming potentials from biogenic sources more than doubled from 2005 to 2010 (Fig 6C) due to increasing of BVOC and decreasing AVOC emissions.

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 to exist in

nature (reviewed in Niinemets, 2010). Theoretically, stress-induced BVOCs (Supplementary Table S1) are elicited and emitted in relatively large amounts after exceeding a stress threshold. 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 and those that are grown in the urban environment of Beijing. The BVOC emission profiles indicated that plants in Beijing are commonly exposed to severe levels of multiple stresses, typical of urban environments (Calfapietra et al., 2013b). The significant contribution of sBVOCs over the total BVOC emission (14-15%, Table 2) indicates that it is imperative for future research to consider 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 dramatic 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. To the best of our knowledge, there is no information available on the relation of taxonomy and sBVOC emission potentials. 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). Knowing these taxonomic relations can be very useful for generalizing unknown emission potentials of many plant species. For example, six-thousands species are found in the natural and urban landscape in California (Karlik et al., 2002). When the number of plant species is extremely high, performing accurate measurement might be not feasible and methods based on taxonomic relations are useful (e.g., Zhihui et al., 2003). However, whether plant cBVOC and sBVOC emissions 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 contribute to the SOA formation. 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 relative to 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, 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 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 determining the real plant species-specific sBVOC

emission potential. Using this set-up, we found that 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 such as the 'Model of Emissions of Gases and Aerosols from Nature' (MEGAN) (Guenther et al., 2012) and 'Biogenic Emission Inventory System' (BEIS) (Pierce et al., 1998) paves the way for a more realistic representation of overall BVOC emissions.

4.3 Uncertainties of the absolute estimates

Some uncertainties should be noted that are related to the modeling and measuring approaches, i.e., uncertainties related to the upscaling from leaf-level emission rates to the total urban BVOC budgets: First, phenological development and seasonal variations in emission factors have been lumped together for all deciduous species in this investigation except for *Populus* and *Salix*. This grouping was necessary because a repeated measuring of LAI and BVOC emission potentials was not feasible, given the large number of plant species. Second, we neglected any impacts other than instantaneous weather conditions and continuous seasonal development such as 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 cBVOC emissions of isoprene and monoterpene might change depending on temperature and light under stressed conditions (Behnke et al., 2009; Blande et al., 2007; Niinemets, 2010). Fifth, emission potentials of cBVOCs based on cut plants/branches may be somehow lower (e.g., max 1-5%, Ghirardo et al., 2011) than those from uncut branches due to disturbance in carbon allocation (Funk et al., 1999). Sixth, 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). Uncertainty introduced by parameters of the phenological (see *RLA*, equation #8) and enzymatic calculations are estimated to be low. For example, changing the phenological parameters *NDF*, *NDS*, and *DS* by ± 10%, which keeps the LAI within the range of measurements, results in overall emission changes of ± 5%. A test

across a range of activation energy (*AE* in calculation of the Arrhenius term *arrh*), reaching from 30,000 to 150,000 (standard is 51,165), showed a variation of isoprene and monoterpene emissions between 98 and 112 %. The uncertainty of stress-induced emissions has been tested by varying the limit ozone concentration at which the stress-induced emission is triggered from 0 (emission takes place all over the year) to 60 ppbv (limiting the emission period from July to mid-August). Any [O_3] limits up to 40 ppbv were not significantly changing the results.

Regarding estimations of SOA formation potentials, the uncertainties are related to the simplifications used here. Absolute numbers given for SOA formation from AVOC and BVOC depend on (i) the yields used for the estimate, (ii) the meteorological conditions, (iii) the chemical conditions. Due to partitioning, yields of SOA formation also depend on the mass of particulate matter present in an air mass. At high particle mass, yields are higher than at low particle mass (e.g., Pankow, 1994; Odum et al., 1996; Presto and Donahue, 2006). The absolute amount of SOA as estimated here directly scales with the yields. The incremental yields used here for isoprene, MT, SQT, and BZ were measured at mass loads similar to that in moderately polluted areas. Our results therefore do not lead to intolerable underestimation of SOA formation from BVOC. Moreover, the process of partitioning concerns SOA formation from AVOC as well as from BVOC. Hence the ratio of SOA formation from BVOC over that of AVOC contains less uncertainty than the absolute numbers. Similarly, meteorological conditions affect mainly absolute numbers given for SOA formation. As an example, the height of the PBL, z, (equation 10) inversely scales with such absolute numbers because, at constant BVOC emission fluxes, the BVOC source strengths related to the volume is inversely proportional to z: Doubling or halving z halves, or doubles SOA formation in the respective volume. The SOA formation potential of a given BVOC, i.e., the total amount of SOA formed in the total volume from the surface to the PBL stays constant. The uncertainties with respect to chemical conditions mainly concern the role of NOx in the chemical system, unknown reactivity of sBVOCs, and the role of GLV. The effect of NOx on SOA formation is not fully understood. It depends on the BVOC/NOx ratio and specific VOC mixture. NOx effects range from the suppression of new particle formation (Wildt et al., 2014) to 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). Again this adds uncertainties to the absolute number given here. But we assume that the relative contributions of SOA formation from AVOC and BVOC should be less affected. Using a box model as

done here implies that all VOCs have reacted. In the real atmosphere this might be different because in particular VOCs with long atmospheric lifetimes are transported out of the considered volume. Using a box model therefore overestimates the importance of VOCs with long atmospheric lifetimes. Among the AVOCs considered here, benzene has the longest atmospheric lifetime. Its contribution to SOA formation therefore may be overestimated. However, as benzene oxidation contributes less than 3 % to the SOA formation from AVOC, this error is negligible. This is different for the benzenoids emitted from vegetation. Also some of the benzenoids may have long lifetimes, but they significantly contribute to particle formation from BVOC. Hence, SOA formation from some of the sBVOC may be overestimated. Also, our treatment of GLV emissions may have led to an overestimation of SOA formation. Whereas Hamilton et al. (2009) give a yield of about 3% for typical GLV, Mentel et al. (2013) report a suppressing effect. Our treatment of using an additive behavior and applying the yield given by Hamilton et al. (2009) therefore may have led to an overestimation of SOA formation from BVOC. In consideration of all these uncertainties, the numbers given here for the absolute numbers are very crude. We estimate their possible error from -90 % up to 200%. Nevertheless, our estimates agree with recent values obtained using a tracer method: The contribution of the SQT β-caryophyllene yielded 0.21 ± 0.18 μg m^{-3} (Guo et al., 2012), compared to 0.78 μg m^{-3} of our estimation using the sum of all SQT and BZ. The uncertainties for relative data may be lower than those for the absolute data. However, the main conclusion drawn from this estimate is robust: even if the uncertainty limits would be 2 time higher than estimated here, we still can conclude that SOA formation from BVOC in megacities is still negligible compared to SOA formation from AVOC.

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 (Pöschl, 2005), 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 (Beckett et al., 2000; Nowak et al., 2013), the possible

disadvantages (in terms of the contribution of BVOCs) of planting the 'wrong trees' are unknown and 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 an effort to improve air quality issues. This initiative more than doubled the number of plants between 2005 and 2010 in Beijing and was performed based on criteria in favor of fast plant growth and survival in urban environment rather than on BVOC emission potentials. Using the tree coverage before and after this activity in combination with our BVOC emission survey, we assessed the impact of the altered BVOC emissions on SOA-formation in Beijing. Theoretically, this impact can be characterized as the SOA-formation potentials of different biogenic and anthropogenic VOC emissions.

Independent of the uncertainties of our model approaches, the SOA-formation potential originating from BVOC sources have doubled in Beijing from 2005 to 2010 due to doubling of the BVOC sources. The relative contribution of sBVOC emissions is comparable to cBVOC and should not be neglected when studying BVOCs in urban environments. In Beijing, the overall importance, based on annual basis, of biogenic sources compared to the anthropogenic is marginal (<10%) due to the very high AVOC levels.

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*) or other plant species related phylogenetically (Fig. 5), the carbon reduction in terms of BVOCs would have been 5.5 10^9 g C $year^{-1}$ (Table 2), equivalent to 2.3 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 BVOC have a higher SOA formation potential than AVOC, i.e., in the same amount, BVOCs can produce more SOA than can AVOC vehicles.

Conclusion

The present study highlights the importance of including stress-induced BVOCs in future studies. Although air pollution in Beijing remains dominated by anthropogenic VOCs, the

contribution of biogenic VOCs doubled in concert with the vegetated area from 2005 to 2010. The relative importance of sBVOCs on SOA mass formation was similar to the one originating from traditionally measured BVOCs.

Despite the fact that plantations of large areas in polluted megacities does not lead to an unacceptable increase in SOA, 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 BVOCs to mitigate the VOC load in urban air. In particular, large-scale tree planting operations should choose non-emitting plants of both 'constitutive' and 'stress-induced' BVOCs. However, 'picking the right tree for urban greening' (Churkina et al., 2015) has only limited potential beneficial effects on air quality in Beijing.

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Tables

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 the municipal census data (the data of 2005 are available on: Beijing Municipal Bureau of Landscape and Forestry, 2006; data for 2010 were collected in the same way as 2005, unpublished).

Plant type	Species (Chinese)	Abr.	Latin name	English name	2005 Nr. (x 10,000)	2010 Nr. (x 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	40.31
	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

1

Table 2

Annual BVOC emission estimates in Beijing (city-level) for the year 2005 and 2010, modeled in hourly resolution from leaf-level emissions from the 'Beijing survey' as described in the text. 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 estimates 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 estimates of the total BVOC for the years 2010 measured and total, respectively.

BVOC group	BVOC class	2005 (Meas.) [10^6 gC yr^{-1}]	2010 (Meas.) [10^6 gC yr^{-1}]	2005 (Total) [10^6 gC yr^{-1}]	2010 (Total) [10^6 gC yr^{-1}]
Isoprene	c	2506	5003	2618	5258
cMT	c	281	601	356	804
sMT	s	18	42	19	45
SQT	s	374	817	397	879
BZ	s	296	659	315	709
GLV	s	1052	2435	1119	2620
Sum	c	2786	5603	2973	6062
Sum	s	1739	3953	1850	4253
Sum (all)	c + s	4526	9557	4823	10314
Difference (2005-2010)			5031		5491

Figures

Fig.1

Example of stress-induced BVOC emissions (**A**) before and (**B**) 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 as determined by the time resolution of a chromatographic run. Bars indicate daily mean of BVOC fluxes. 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* × *canescensis* (Poplar, n=17); **N =** *Nicotiana tabacum* (Tobacco, n=27). Emissions appeared as pulses lasting several days and also depended on stress intensity (Beauchamp et al., 2005). With respect to the classification into sBVOC and cBVOC the results were always similar: BZ, SQT and GLV were only emitted after stress application. For monoterpenes there were constitutive as well as stress-induced emissions. Data from the laboratory experiments in Jülich were only taken for classification as sBVOC and cBVOC, respectively. Abbr.: BZ = benzenoids; SQT = sesquiterpenes; GLVs = green leaf volatiles; MT = monoterpenes; nd = not detectable.

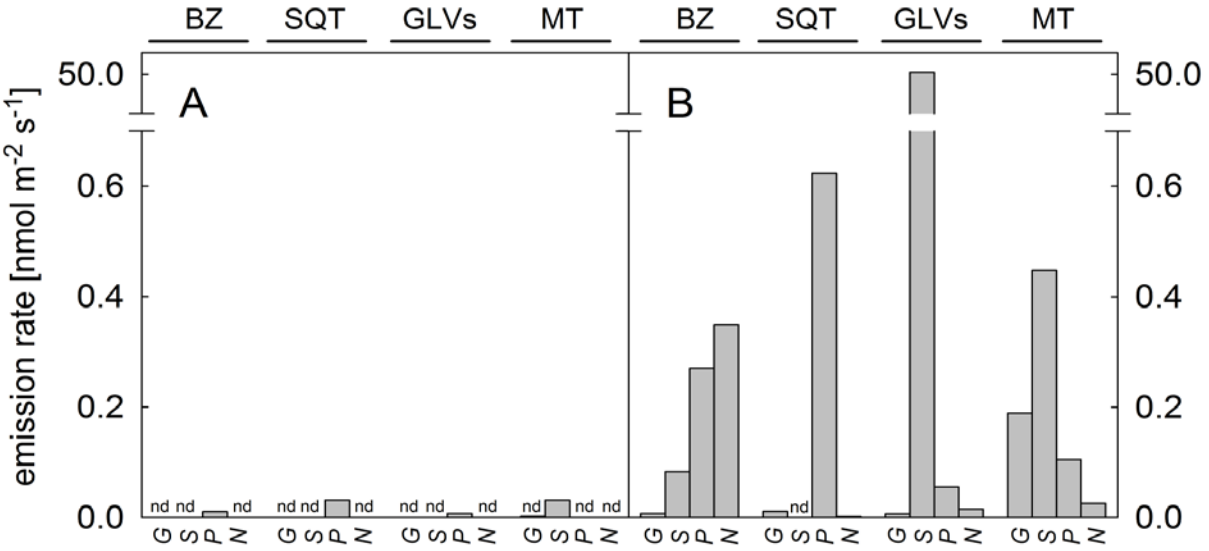

Fig.2

Climate data during the BVOC field campaign (August-October 2011) at an 8 m height. (**A**) Photosynthetic photon flux density (PPFD), 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) AOT40 (calculated from beginning July, black rectangles); (**D**) NOx (NO + NO_2), daily means (white triangles). The sampling time of each plant species is given along the x-axis.

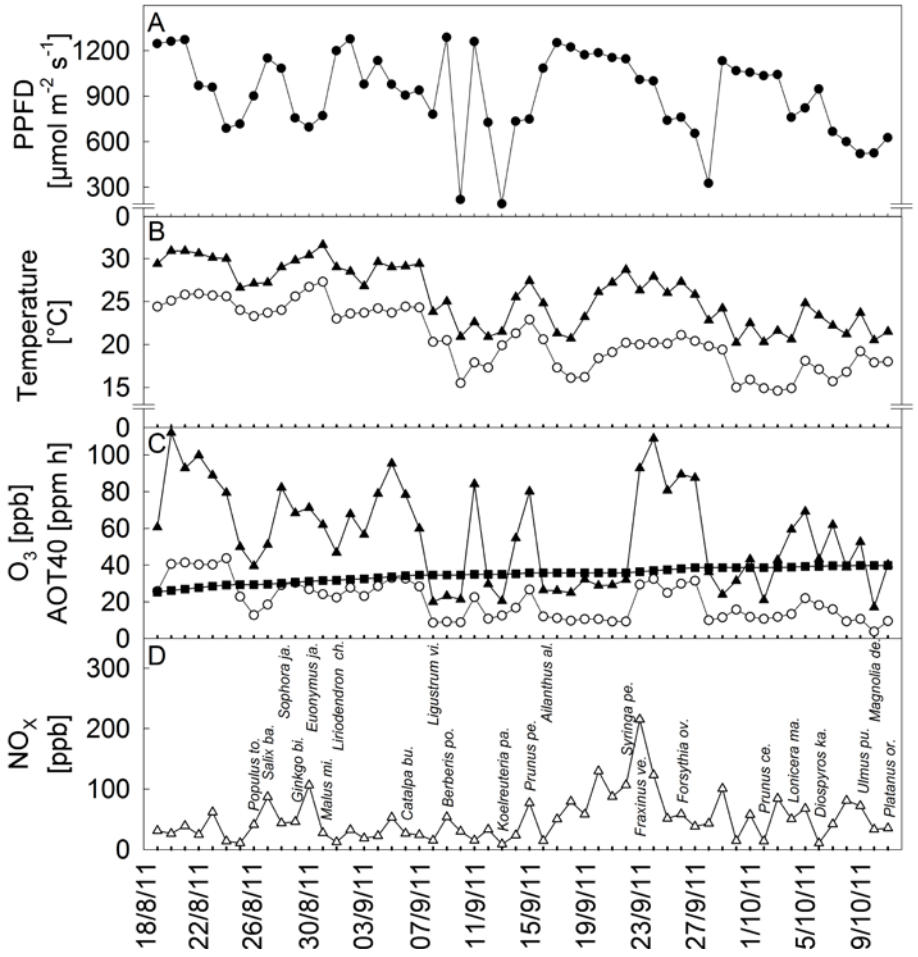

Fig.3

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.

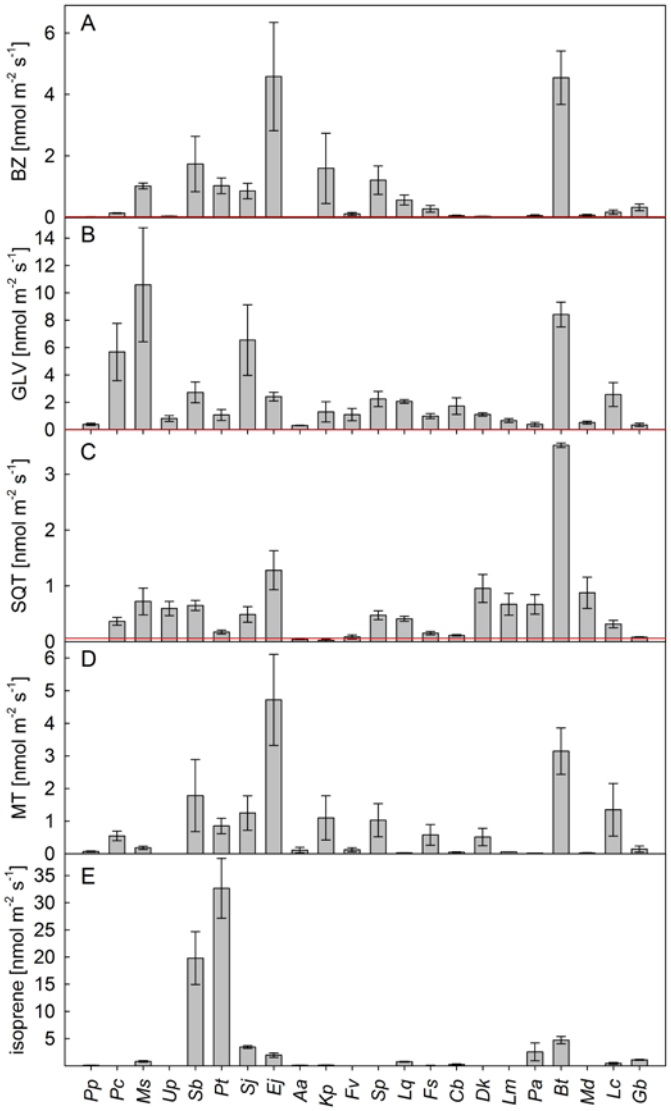

Fig.4

(**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: **A**: white = cBVOCs; black = sBVOCs (sBVOCs = BZ + GLV + SQT); **B**: gray = isoprene; green = monoterpenes (MT); yellow = benzenoids (BZ); cyan = green leaf volatiles (GLV); blue = sesquiterpenes (SQT). Black point indicates the percentage of sBVOCs over the total BVOCs. The means of 3 plants ± s.e.

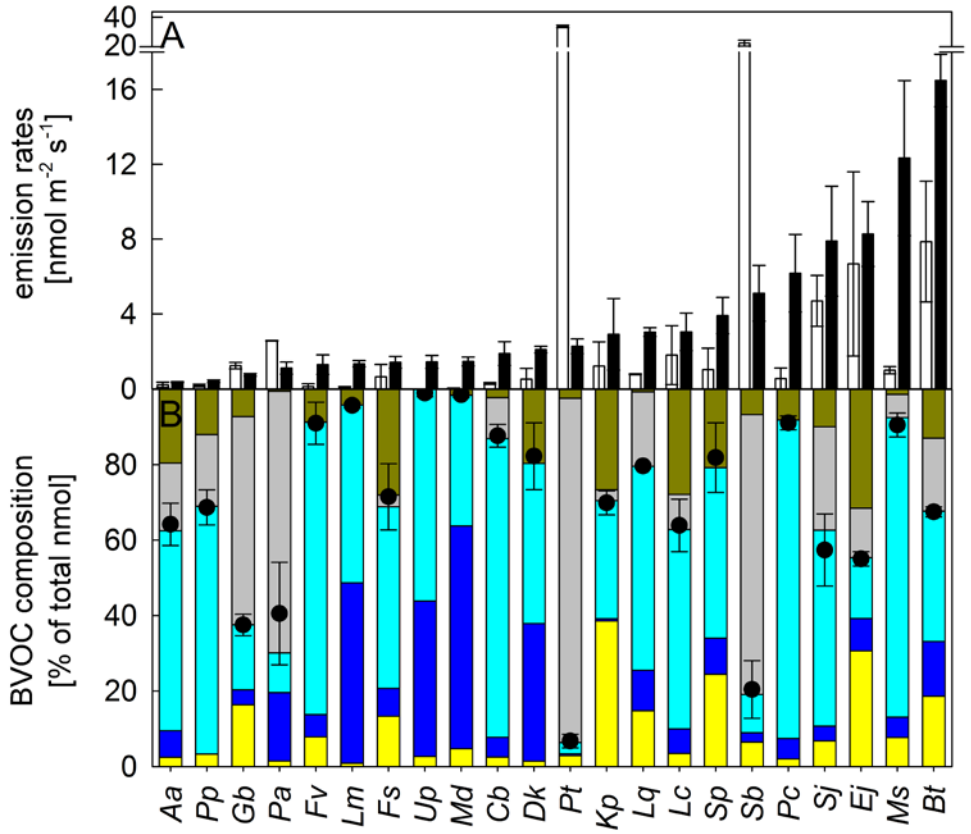

Fig.5

(**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 Supporting Information Table S7). (**B**) Principal component analysis of BVOC emission rates, net assimilation and numerically converted taxonomic data (Table S8, Supporting Information) (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 panel B reflects panel 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).

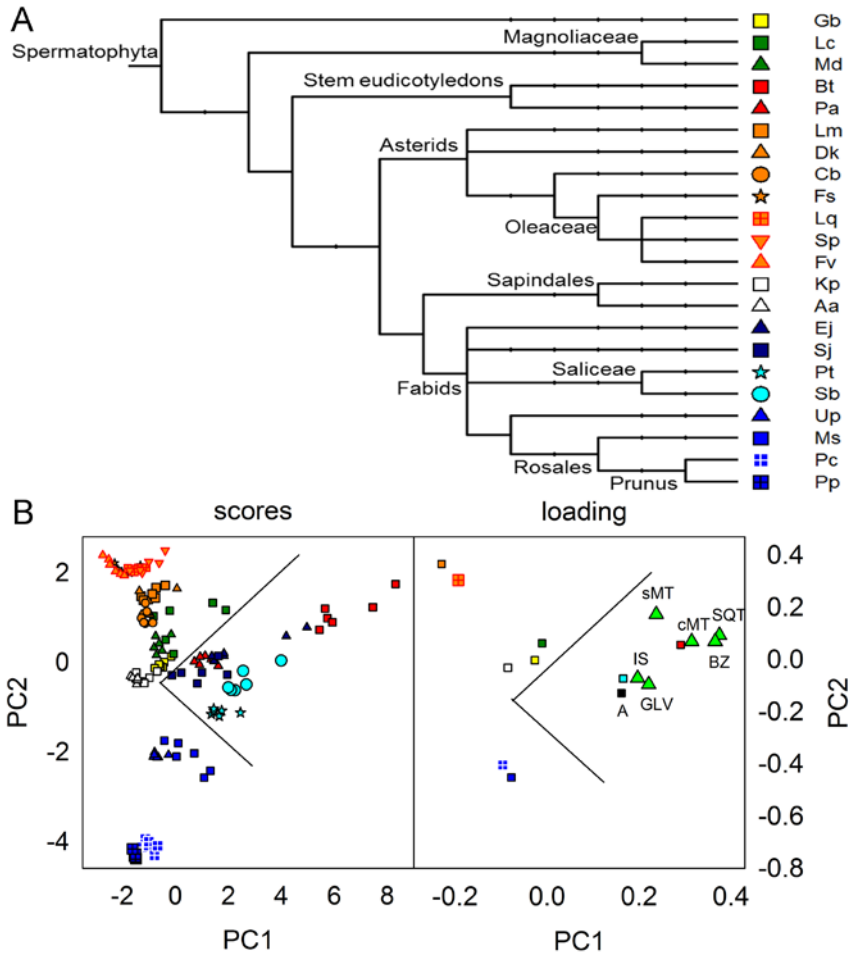

Fig.6

Potential atmospheric concentrations of secondary organic particulate matter (SOA) originating from (**A**) biogenic VOC (BVOCs), (**B**) anthropogenic VOC (AVOCs) and (**C**) the percentages to total SOA estimated 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.