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

By A. Ghirardo et al.

Text is formatted as follows: **The referees' comments are written in bold.** *Responses to the remarks are written in italic.* Changes in the text of the manuscript are marked with apostrophes (“ ”).
A copy of the revised manuscript including all the track changes is appended.

Final response of the authors to the referees' remarks.

We thank all three reviewers for their helpful comments and we followed their suggestions whenever possible. We feel that these changes have helped substantially to improve the manuscript.

*There were some critics that were common to all three reviewers. Before addressing these remarks in detail we would first like to address these points in general, summarized as **1-4** below, to avoid repetition and explain the major changes of the revised manuscript.*

1. **Uncertainties in the approaches used for the calculation of BVOC budget (city-level) and SOA formation potentials that need to be better acknowledged. Lack of description in the methods.**

Uncertainties due to our modelling approaches are now taken into account and discussed in the new section '4.3'. The methods have been exhaustively described, using equations instead and in addition to text as suggested by the reviewers.

Concerning our estimates of SOA formation potentials from BVOC in Beijing, those are indeed very crude. We are also aware that many environmental variables affect BVOC emissions as well as particle formation from these emissions. However, the aim of our estimates was to assess the relative importance of stress-induced BVOC (sBVOC) compared to constitutive BVOC (cBVOC), and to provide a rough idea on the importance of biogenic VOC compared to anthropogenic VOC (AVOC) in the air of Beijing. We found high emission rates of sBVOC from most of the plant species growing in Beijing and we aim to indicate that those groups of compounds, which are normally not sufficiently studied or even ignored, are not irrelevant when compared to cBVOC. In order to state whether biogenic sources of VOC matter in the polluted city or not, we had to assess their potential impact on SOA and compare them to those originating from anthropogenic sources.
To achieve our last goal, we used a simple model together with yearly BVOC budgets for the rough estimation of SOA forming potentials. Our analysis show that, compared to the anthropogenic emissions, the biogenic emissions in Beijing are of much less importance. This statement can be maintained even if it would be wrong by a factor of 4. Our main conclusion is that in stressful environments, such as vegetation growing in megacities, the sBVOC can potentially contribute to SOA in a similar way as the commonly studied cBVOC. This conclusion is independent of the type of model used to estimate SOA, but is dependent on BVOC measurements and the model used to estimate BVOC budgets.
However, we understand that giving a single number for the contribution of BVOC to SOA may give the wrong impression that this number would be an exact number. This was not our intention and we apologise for that. To avoid such wrong impressions, we will now give our estimations on uncertainty limits. Variability of mass formation due to variability of emissions, meteorology and chemistry is not included in this uncertainty. We would also like to point out that the main results are independent of

the uncertainty of SOA formation and that we have removed SOA values from the abstract. We also followed the general remarks of the referees and focused our paper on the relative importance of stress-induced BVOC compared to constitutive BVOC (also in the abstract). Finally, we have changed the title accordingly.

We again thank all referees for highlighting our unintended flaws.

The title of the manuscript reads now:
"Urban stress-induced biogenic VOC emissions and SOA forming potentials in Beijing"

The text, in the abstract, reads now:

…" 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%)."

2. Changes of BVOC emission budgets and SOA estimates.

Motivated by the reviewers question we checked and refined the calculations. We noted that the emission factors derived from the measurements at 30°C had to be corrected to the reference temperature in the ozone-dependent equation. This has been corrected and added to the methodology description. It has also led to higher sBVOC emissions, which required a re-calculation of further steps until the calculations of SOA forming potentials. Please note that some results in the revised version are different from those in the original version, including BVOC emission budget at city-level and relative contributions of different BVOC classes (i.e., Isoprene, MT, SQT, BZ, GLV), which in turn has an effect on the relative contribution of the plant species. The changes of enzyme activities, due to a different reference temperature period, lead to a more realistic BVOC emission budget This can be seen from the fact that emission factors are now much closer to literature values (see also the new Table S5) and that the current BVOC estimates based on our process-model approach are in the same order of other estimates (Zhihui et al., 2003) found using traditional algorithms (Guenther et al., 1995, 1999). The relationship between the response factors and those found in the literature is consistent for isoprene (r2=0.75) and for monoterpene in half of the plant species (r2=0.9, slope 1.03). Some plant species show contradictive results due to the fact that isoprene and monoterpene emissions from some plant species are simply reported in literature as zero.
Overall, the main outcome of the study did not change. The new modelled BVOC budgets for 2005 and 2010 are still very low compared to AVOC, and the increases of SOA due to the new calculation are neutralized by the correction of the vegetation period, as pointed out later in the response to reviewer #2.

We are thankful for the very constructive comments, which helped us assess and report more realistic BVOC emissions from the urban area of Beijing in the actual revised manuscript.

3. Laboratory experiments on ozone exposures in the Jülich Plant Atmosphere Chamber facility.

Another common critic is that we do not give adequate information for the experiments on ozone exposures. We will therefore give some more information. However, to avoid overlengthening the manuscript and to avoid too much repetition of published method already described in detail (e.g. Beauchamp et al., 2005; Behnke et al., 2009; Heiden et al., 1999, 2003) we kept the extra information

as short as possible. We would like to mention that for those who are interested, more information on the experiments and similar results can be found in previous publications.

We would like to point out that the results of these experiments were used in the present manuscript only for the general classification of cBVOC and sBVOC. Our experiments mainly confirmed what can be found in existing literature and can be concluded from basic biochemistry and plant physiology. Still, these experiments clearly demonstrate how the sBVOC pattern can potentially change from unstressed to stressed conditions. The absolute emission strengths are secondary because they are a function of plant species, time following the stress and stress intensities.

Moreover, our classification is general and based on model plants, which are useful plant species to interpreting and understanding molecular mechanisms in fundamental research. The plant-species used are independent of those measured in Beijing and therefore, those species do not need to be representative of plant species found in Beijing. Please note that none of the data obtained from ozone experiments in Jülich was used for the estimation of BVOC emissions or SOA formation from BVOC in Beijing. For this purpose only the data obtained from the survey in Beijing were used. We have reorganized the methods to better explain this.

4. The unimportance of the phylogenetic study

The only point we disagree on concerns the unimportance of the phylogenetic study. For 'constitutive' BVOC emissions, there is evidence indicating that plant taxonomy can be used for generalising the emission potentials of many (although not all) plant families (Benjamin et al., 1996; Karlik et al., 2002; Zhihui et al., 2003). Until now, there is no information available on the relation between taxonomy and stress-induced BVOC emission potentials. Knowing these taxonomic relations can be very useful when the number of plant species is extremely high. For instance, 6-thousands species are found in the natural and urban landscape in California (Karlik et al., 2002), or even 25 thousand vascular plant flora species are estimated to be growing in the Mediterranean Basis. We believe that this information is valuable and might be of some use when assessing regional or local BVOC budget and SOA-formation potentials in future studies, when emission factors are unknown. We have now put more emphasize on explaining the importance of the phylogenetic study with regard to sBVOC in the revised version of the manuscript. We agree with the reviewer, however, that the phylogenetic study has a secondary relevance compared to the importance of sBVOC and we therefore kept this part short in the revised manuscript.

The new text in the introduction reads:

"We constructed a phylogenetic tree based on the taxonomic data and BVOC emissions for generalizing the sBVOC emission potentials of related plant species"

The new text in the discussion reads:

"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)."

Following our detail responses to the remarks of the referees
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Anonymous Referee #1

Received and published: 2 October 2015
Major comments
The current study presents some important and interesting results. The strengths are a detailed measurement campaign of biogenic emissions from trees planted in Beijing, some laboratory measurements of stress BVOCs and finally modeling efforts to understand their contribution to aerosol formation. While the measurements are solid, there are significant uncertainties in the modeling approach that need to be better acknowledged. Also, the presentation of the research needs to be improved in a number of areas. In my opinion, the important conclusion of the paper is given in Section 4.2, "The importance of measuring stress-induced BVOC emissions." Finally, what is the relevance of phylogenetic modeling? How are these results relevant to this study? This should be removed. They might warrant publication in a separate paper.

We thank reviewer#1 for the useful comments. The revised version of the manuscript now includes uncertainty results of the modelling approaches, which has also been discussed. We have now also improved the presentation of the research by the reorganization the material and method section in accordance with the suggestions provided by reviewer#1. We have also directed the focus of the paper on the importance of measuring the sBVOC rather than giving certain values of biogenic SOA formation in Beijing, and explained the reason for the phylogenetic analysis. Please also see our general response and appended revised manuscript.

The title of the manuscript, "Urban stress-induced biogenic VOC emissions impact secondary aerosol formation in Beijing," highlights a result from a very simple box model that has numerous assumptions. First, all the steps in the model need to be presented more clearly, from the emissions inventory to the secondary aerosol calculations. Much of this is described via words in the text. The methodology could be much clearer if equations were employed instead. Second, there are some critical variables in the model of aerosol formation: the chemical reaction rates, the height of the boundary layer, and the residence time. While there is some detail about the reaction rates, there are no references and little justification for the other two variables. While the simple model will use the same boundary layer height and residence time for anthro aerosols and therefore they do not affect the bio/anthro comparison, that's not true about the rate constants and the anthro emission rates. Overall, there needs to be a detailed analysis of uncertainty. For example, the aerosol mass numbers in the abstract have three significant figures. This is certainly not justified by the large uncertainties in the model results.

We agree. We have changed the title to:

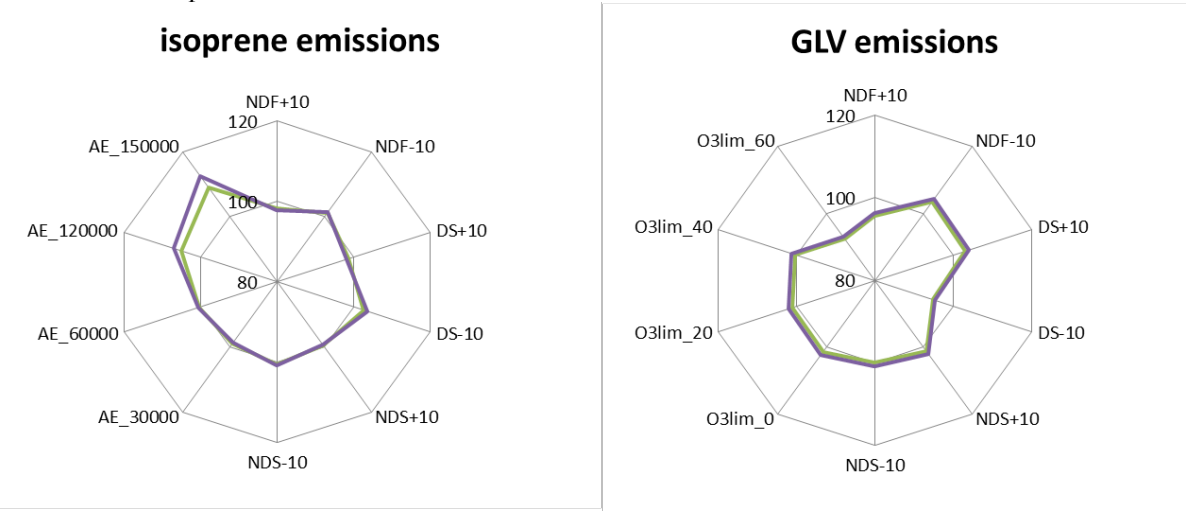
"Urban stress-induced biogenic VOC emissions and SOA forming potentials in Beijing"

The manuscript now focuses on the importance of measuring sBVOC rather than giving the exact number of SOA formations. Please also see our general response. With respect to our estimate of SOA formation potentials we refer to our general response and to the detailed responses below.

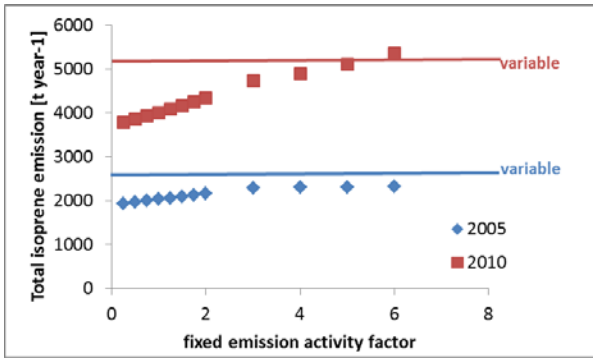
In regards to just the emissions inventory, there should also be an error analysis. For example, what is the effect of the phenology corrections? What uncertainty do they introduce? In addition, there is almost no detail given about the tree inventory data. How was that collected? And again, equations should be used to give the detailed steps in the emissions model.

Encouraged by the reviewers' comments, we tested the uncertainty introduced by parameters of the phenological (see RLA, equation #8) and enzymatic calculations. Changing the phenological

parameters NDF, NDS, and DS by +/- 10 %, which resulted in LAI curves that stayed within the range of measurements, gave overall emission changes of -5 to +5 percent. A test across a range of activation energy (AE in calculation of the Arrhenius term arrh), reaching from 30000 to 150000 (standard is 51165), 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 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 did not significantly change the results. We have now discussed this part in the uncertainty section of our revised manuscript.



Another potential bias of error is the activity correction, which is based on literature values alone. This only concerns the constitutive emissions because stressed emissions are supposed to have an activity factor of 1 (high ozone concentration) almost throughout the vegetation period. However, since a higher activity increases the direct emission but decreases the estimated emission factor, there is an immanent feedback for all species that have been explicitly measured. Overall, emissions are increasing with increasing emission activity factor (see figure). Variable (more reasonable) emission activity generally results in higher emissions despite emission activity mostly below 1, since measurements late in the year result in relatively large emission factors.



In addition, we have now re-written the emission inventory part which should now be clearer and include a number of equations for each developmental step. We also explicitly state that the tree inventory used was the official municipal tree inventory which it is. Following information on how the tree inventory was built: the landscape plant specifications of 44 dominant species were recorded in 630 different plots (20 × 20 m); all trees were identified and the data was used for the estimation of the individual plant biomass; for each plant species, thirty healthy and mature leaves were collected and the leaf area was measured. The final biomass was calculated by relating leaf area to tree height or to tree diameter at breast height (DBH, tree diameter at 1.3 m above ground surface) (Chen et al., 1998). When the regression equations were not available for a specific plant species, the equation of similar species with a similar size and leaf shape was used.

Some detailed questions about the stress experiment: The lab experiments are pulses of ozone, as opposed to the relatively constant ozone exposure in the field. Are there any previous studies that show the same pattern of stress BVOCs are observed in each case? Also, of the model plants, only one was a tree species. Three of the four don't appear to be good analogs to the field plants.

The fumigation lasted for a short time (O_3 pulse) only because BVOC measurements at high ozone concentrations give wrong emission data due to reactions of ozone with BVOC in the gas phase and on cartridges. Therefore, the ozone stress was set as a pulse to allow BVOC measurements after the ozone was removed from the chamber.

The plant material used in Jülich are common plant species used in plant physiology as model plant, i.e. plant species on which genetic/proteomic/metabolomic data is available and useful for the interpretation of the treatment effect. The plant species used in Jülich are not representative for the plants found in Beijing. However, in our opinion this was not necessary because the general response of plant, in term of BVOC pattern, to abiotic stress is very similar, as indicated from the broad literature data (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) and supported by this study. The sBVOC emissions strengths are dependent of the O_3 flux density into the foliage (Beauchamp et al., 2005) but not sBVOC profiles, which are the result of more general leaf damage independently from abiotic or biotic stresses. Although the different abiotic or biotic stresses can cause the release of specific compounds, these compounds still belong to the same class of volatile, which have been grouped as sBVOC. The biological reasons of sBVOC emission upon abiotic and biotic stresses are discussed in section 4.1.

Considering the conclusion that the field plants are emitting stress BVOCs, another possibility is that these BVOCs were emitted because of handling and damage from being inserted into the cuvette, particularly the SQTs. Need to provide some assurance/evidence this was not the case.

In nearly all of the experiments in Jülich sBVOC were not emitted before stress application. They were emitted during and for a short time after applying abiotic stress (ozone). Therefore, particular attention was taken during the handling of the plants without alteration of sBVOC, as indicated by sBVOC emissions before O_3 and from control experiments of the ozone treatment.

The quality of the manuscript needs to be improved. While some typos are in manuscript are inevitable, the list of minor corrections below is extensive. Also, there are lots of references to Supplementary materialâ˘A ˇ Ttoo many for a paper that is already long. Finally, the quality of the manuscript varies. There are some sections with numerous grammatical errors and where the prose is not focused.

The language has been checked by a native English speaker.

Minor comments:
23007, 13: "greening" instead of "greens."

Corrected

23007, 13-14: should state why ABVOCs are decreasing.

The statement "could be lowered" was changed with "lowered". We did not investigate the reason why these emissions reduced, we have only measured them.

23007, 19-20: The units are confusing here. These are correct for aerosol mass, but the statement refers to emissions. Are you saying the emissions increase caused the stated biogenic SOA increase? This should be clearer. After reading the entire paper, I see these numbers are the result of a very simplified modeling approach. As mentioned in the major comments, these results should not be presented this way in the abstract.

We agree with Referee#1. There was a half sentence missing between the VOC emissions and the SOA mass formation. We have replaced the sentence and included the uncertainty of our estimates:

"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%)."

23008, 5-9: The phrase "and ozone formation" should be moved to "altering ozone formation and the concentrations of hydroxyl radicals" since it also depends on NOx.

We agree with Referee#1. We changed the text to:

"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)."

23008: 11: add the mechanism which explains this: through altering the chemical lifetime of radiatively important gases.

We thank Referee#1 for pointing out the need for clarification. We changed the text to:

"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."

23008, 12-13: "whereby" is not a good conjunction here, since the species specificity is not causing isoprene and monoterpenes to be dominant. "And" would be more appropriate.

We have exchanged "whereby" *with* "and".

23008, 22: My preference is to call linalool a monoterpenoid, not a monoterpene and to reserve the term monoterpene for C10H16 compounds. I understand you consistently use this convention, but realize it's confusing to some.

We agree with Referee#1 that it can be confusing calling the tertiary alcohol linalool simply a 'monoterpene'. We agree that linalool and 1,8-cineol are terpenoid-derived compounds from monoterpenes, where the original C10H16 skeleton of the parent monoterpene has been modified by the removal of one or more skeletal atoms. This has been consistently corrected over the whole manuscript. Because both linalool and 1,8-cineol are both stress-induced BVOC, we have now included both monoterpene and monoterpenoid compounds with the abbreviation "sMT":
The text, in the introduction, reads now:

"The monoterpenes (E)-β-ocimene and β-myrcene, and monoterpenoids (terpenoid-derived compound) linalool and 1,8-cineol (sMT)."

The text, in the methods, reads now:
"Stress-induced BVOCs included the stress-induced monoterpenes (E)-β-ocimene and β-myrcene, and the stress-induced monoterpenoids linalool and 1,8-cineol (all referred as sMT)".

23009, 16: What is "higher radiation" referring to? Solar radiation? I don't think the urban heat island effect increases solar radiation. In any case, explain further and provide a citation.

We thank Referee#1 for pointing out that this sentence was unclear. We removed it and reformulated the sentence. We feel that our hypothesis, i.e., factors that contribute to urban tree stress can cause stress-induced BVOC emissions, are now better explained.

This has been changed to read:

"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)."

23009, 18-20: You have already stated the relationship between BVOCs, NOx and ozone formation.
We agree with Referee#1. Our intention was to introduce the potential effects of stress-induced BVOC in urban environments.

This has been changed to read:

"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."

23010, 14: The hyphen in "large-tree" should be removed. Large refers to the plantation program, not the trees. Table 1 says shrubs were also planted.

Referee#1 is correct. We have removed both the hyphen and the "tree" from the sentence.

This has been changed to read:

"..the municipality of Beijing aimed to improve the air quality by a large plantation program.."

23010, 16: "Despite of" should just be "Despite"

"Despite of" was corrected with "Despite".

Overall Materials and Methods section: the order of presentation is confusing, since you jump back and forth between the measurement and the modeling components of your study. You start by describing the trees to be measured, then turn to modeling, and finally return to the measurement of the trees. The order should flow more logically.

We thank reviewer#1 for pointing this out. We have now completely reorganized the Material and Methods with a more logical and clearer structure:

First section:
" 2.1 Classification of BVOCs into 'constitutive' (cBVOCs) and 'stress-induced' (sBVOCs)"
This section explains the theoretical and general classification of BVOC into cBVOC and sBVOC and uses model plants and chamber measurements to demonstrate it.

Second section:
"2.2 The Beijing survey and data analysis"
This section includes data and data analysis from our survey in Beijing which includes (2.2.1) climate data, NOx, O3, (2.2.2) plant species measured, (2.2.3) emissions of BVOC at leaf-level, phylogenetic tree, (2.2.4) multivariate data, and statistical analyses.

Third section:
"2.3 Modelling BVOC emissions and crude estimates of SOA at city-level in Beijing"

This section includes (2.3.1) the upscaling of BVOC from leaf-level to city-level, and (2.3.2) estimation of the SOA-formation potentials from biogenic and anthropogenic VOC.

23011, 21: "does not" not "do not." Also, "terpene emissions" instead of "terpene."
Both mistakes have been corrected.

23011, 24: "except for" instead of just "except"
Corrected.

23011, 26: "does not" instead of "do not"
Corrected.

23011, 27 "either" instead of "neither"
Corrected.

23013, 11: I don't understand what the 76 min time resolution refers to. Is that the collection time for the cartridge? Also, the fumigation lasted 1-2 hours, and then it was back to clean air for the remaining 10 and 20 hours? The timing of these experiments should be stated more clearly. Also, state the rationale for the selected timings, and be explicit about what you were attempting to simulate.

The 76 min time resolution indeed refers to the time for a chromatographic run of the on-line measurements. Samples are continuously collected every 45 min and thermally deadsorbed in real time.

We have now clarified this:

"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)."

The fumigation lasted for a short time only because BVOC measurements at high ozone concentrations give incorrect emission data due to reactions of ozone with BVOC in the gas phase and on cartridges. Hence, the ozone stress was set as a pulse to allow BVOC measurements after the ozone was removed from the chamber. We explained this further in the text. Please see also our general response to this point.

23013, 24: Were these stainless steel or glass absorbent tubes?
All tubes used for trapping BVOC were made of glass. The collection tubes were purchased from Gerstel, which uses glass as standard material for tubing.

We have now added this info in the text:

"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)…"

23015, 15-16: refer to experiments, not figures, since the figures have not yet been introduced.

We agree with referee#1. The whole sentence has been removed because it contains redundant information already present in figure legend 3 and 4.

23015, 20-22: What was the average and maximum correction in percent that was produced by this algorithm?

Due to the fact that measurements were carried out relatively late in the year (August to October), the calculated activity in this period is estimated to be considerably smaller than during the reference period June/July, now mentioned in the description. The average correction due to this factor is slightly above 2-fold while the maximum correction factor is about 8-fold for the latest measurement of trees in mid-October.

23015, 25 – 23016, 2: Is this assumption valid for all evergreen plants? What are the uncertainties associated with this assumption?

The assumption to assign half of the monoterpene emissions from evergreen plants to emissions from pools and the other half to directly produced emissions is relatively uncertain. Literature about such splits is scarce and depends heavily on the selected species, but ratios between 0.58 and 0.33 for evergreen temperate species (Ghirardo et al. 2010) indicate that the assumption is not unreasonable. The overall uncertainty is also limited by the fact that only 6 evergreen species are considered in the inventory. Changing the splitting factor to the extremes 0 and 1, changes the monoterpene emission rate by a moderate ± 14 %.

23016, 10-17: This description is not very clear and needs to be rewritten. In particular, I cannot follow the logic of (i). The methodology you used should be clear without needing to read the entire references. Perhaps some equations would make this section more clear? Step (iii) is somewhat clearer.

We completely rewrote the section in order to increase clarity and improve the structure. In particular, we describe how emission factors are derived, how the emission rates are calculated, and how this is scaled to the city level. Basic functions have been added so that it should not be necessary anymore to look up the references. Please see our general response.

23016, 19: "tree number per species" should be "number of trees per species." Also, some detail should be given about the tree inventory.

The expression has been changed according to the reviewer's suggestion. We used the official tree inventories obtained from the municipality during the 5th (published) and 7th (yet unpublished) census data.

This reference has been added:

1. Beijing Municipal Bureau of Landscape and Forestry, 2006. Inventory of the green space in Beijing based on census-2005. Beijing press, Beijing, China, pp. 110-130.

23016, 19: corrected by phenological development: is this the same SIM correction mentioned on the previous page? Reading further, this is described below. The order here is a bit confusing. Also, there should be more clarity, since phenological development is used to describe both the leaf-level emissions factor and also the leaf area/mass.

We agree that the previous description was confusing. We have now completely rewritten the section. Please refer to our general response and corresponding changes in the methods. Indeed, the SIM model is only used to estimate the emission factor from measured emissions as well as to calculate emissions on a particular day. Leaf area phenology is considered for scaling emissions throughout the year.

23016, 25: It's fine to use literature values for unmeasured trees. How did the measured values compare to literature values? Maybe this is presented in the results?

This is an interesting question. Indeed, for isoprene we found quite a close relationship (r2 = app. 0.8) although our estimated emission factors were somewhat higher than indicated in the literature. For monoterpenes the relationship was poor because monoterpene emission rates are often indicated as 0 or almost 0 in the literature, while in our measurements monoterpenes, which we assume as typically constitutive, are quite abundant (e.g. Berberis, Sophora, Koelreuteria). For Magnolia and Ginkgo the opposite was true: the literature indicates quite high monoterpene emissions while we found only minor amounts. If we exclude the species showing such contradictions (about one half of the sample), the relationships are strong (r2=0.9, slope 1.03). This indicates that literature values are often very uncertain, relying on one or two measurements only. We did not include this part in the results because the comparison between our values and those in the literature is beyond the scope of this paper.

23017, 6: Should be "emissions were increased."
Corrected

23017, 26: This estimate of boundary layer height will have a big impact on the calculation. Also, there are covariances between temperature, pollution and boundary layer height that make using a single value problematic. There should be a reference for this. Overall, this is a very crude estimate of aerosol formation since it does not account for transport, residence times and chemistry.

The remark is correct; there are covariances between these quantities. However, we neither determine the impact of diurnal variations of BVOC emissions on SOA formation nor determine the role of the boundary layer nor the role of other quantities that impact BVOC emissions and subsequent particle formation from these BVOC. We therefore clarified that we roughly estimated the contribution of BVOC to particle formation in Beijing. See also our general response to this point.

23018, 6-12: Equations would make this clearer. This seems to be working backwards. You are starting with leaf-level estimates, and then you scale forward. Why is this necessary?
We added an equation showing how we estimated concentrations of SOA precursors from average emission rates. Please see our general response.

23018, 10-12: Need to acknowledge uncertainty in these estimates.
Uncertainty limits are given now. Please see also our general response.

23018, 25-28: Again, the 4 days is a very important assumption. Isn't the transport time much shorter than this? More information and references should be given to support this assumption.
Please see our general response and our response to the next remark.

23019, 1-8: Need more detail. Was this using the same concentration-lifetime assumption as above? How were concentration measurements converted to source strengths? Need to be more explicit here.

We used a box model where transport in and out of the assumed box is neglected. We therefore entitled the respective section in material and methods SOA-formation potentials and not SOA formation. For many of the emitted BVOC, particularly many sBVOC, the chemical lifetime is very short, neglecting transport. For the anthropogenic VOC this assumption is not justified as their lifetime is longer (2-4 hours for xylenes and up to 2 days for benzene at the OH concentrations assumed in the manuscript). Assuming that most of the anthropogenic emissions are in Beijing itself and not upwind of Beijing, our procedure will cause an overestimation of anthropogenic SOA formation, thus an underestimation of the biogenic fraction. However, there are also sBVOC where reactivity towards OH seems to be low. In particular, the dominant benzenoid methyl salicylate has to be mentioned where the SOA formation potential is high (Mentel et al. 2013) and the reactivity is low (Bergström et al., 2014; and unpublished results from our group). Neglecting transport of unreactive BVOC leads to an overestimation of the biogenic fraction.

For many of the sBVOC emitted from the plants in Beijing there are no data on reactivity and thus on lifetimes. The chemical system is underdetermined, hindering more exact calculations. Considering that even very large uncertainties in our rough estimation do not change the general statements we leave the rough estimation as it is. Please see also our general response.

23020: 9-10: These values are lower than I expected for a heavily polluted city. Would these values have represented a violation of either US or European air quality standards?

Please note that our data show daily means. These values are consistent with the values found in July and September in the period of 2001-2006 from six different urban sites in Beijing (see data in Tang et al., 2009). Air quality standards in Europe are actually set to 120 ug m^{-3} (56ppbv) for O_3 as maximum daily 8 h mean concentration and to 200 ug m-3 (99ppbv,) for NO_2 as maximum concentration of 1 h mean. Comparing O_3 values during the time periods of 01.07.2011-31.10.2011 (123 days), the ozone concentrations in Beijing exceed EU air quality standards 40 times. Please note that this comparison refer to the summer period, although most of the air quality issues in Beijing occur in winter time.

23024, 1-4: Careful: your theoretical models have three components: threshold, dependence on severity, and large amounts. Your experiment has only demonstrated the first and last of these components.
We agree with referee#1 and removed from the sentence "the second component", which was not demonstrated in our study.

23024, 12: Should be "and those that are grown"
Corrected.

23024, 12-14, Yes, but need to temper this statement, since overall stress BVOCs are a much lower percentage (14-15%, Table 2) due to the high cBVOC emission rates of the remaining third.
We agree with referee#1. Our intention was to discuss the BVOC profiles to urban plant stress. We have therefore rephrased the sentence accordingly. We have further clarified the importance of sBVOC by giving percentage values based on overall BVOC emissions (sBVOC + cBVOC). We changed the text to:

"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"

23025, 18 and following: this material would be more appropriate in the Introduction. And again, this phylogenetic perspective adds little to the paper.
We prefer to keep this sentence because it allows us to discuss our observations (high sBVOC emissions) and the current literature, including hypotheses and recent evidence (Bergström et al., 2014; Bouvier-Brown et al.,2009; Guenther, 2013; Mentel et al., 2013; Niinemets, 2010). In regard to the phylogenetic analysis, we have now explained in further details its importance. Please see also our general response.

23026, 12: I agree with this point, but you need to define these acronyms and give some references to the literature that describes these models.
The acronyms have been defined and references describing these models have been added:

"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."

23027, 1-3. I appreciate that you are acknowledging the potential systematic uncertainties in your results. But specific to cut branches, you are here acknowledging a potential bias, where on page 23011, lines 17-28, you have a lengthy defense of this procedure. You should harmonize your two discussions of this source of potential bias.

The reviewer is correct. We have added the possible bias in the methods and discussed the uncertainty in the discussion parts. Therefore, the readers can find the reasons for the cut-branch approach in the methods, i.e., the possibility to perform laboratory-controlled measurement of large and tall natural trees without branch disturbance, based on extensive and valuable literature data.

This procedure is not known to considerably affect sBVOC and cBVOC over a period of several hr (e.g. 16 hr, (Ghirardo et al., 2011). Our procedure is much faster, i.e., max 2 h 15 min (1 h max between cut and start measurement, 45 min photosynthesis adaptation, 30 min BVOC collection). We agree with reviewer #1, acknowledging that the potential systematic uncertainty of the approach is of crucial scientific importance. The uncertainty related to our approach has been therefore quantified and discussed in the discussion section:

"emission potentials of cBVOCs based on cut plants/branches may be somehow lower (eg., max 1-5%, Ghirardo et al., 2011) than those from uncut branches due to disturbance in carbon allocation (Funk et al., 1999). "

23028, 2: remove "species selection"

Done

23028, 3: previous experiences of development of what?
The sentence has been rewritten for clearness:

"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."

23028, 5-6: no, you made no assessment of ozone formation, so this statement is not correct. You only considered SOA formation.
We fully agree. We have corrected the sentence as following:

'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.'

23028, 6-22: First, this section does not belong in the discussion and is repetitious with material included elsewhere in the paper. Second, why bring up air quality and ozone formation now? This section reads as if were written for a purpose not in line with the rest of the paper. The final sentences just reiterate points that were made in the Results and don't provide much synthesis. This entire section is weak and not focused.

We agree. We have now completely removed this section.

23028, 23-29: This is a return to material that is logical and well suited for the Discussion section.

We thank the reviewer to point this out. We have now completely rewritten this part and moved the uncertainty of our estimations to the corresponding section ("4.3 Uncertainties of the absolute estimates"). However, we would like to point out that the main statement of our manuscript is very robust even if the uncertainties of our estimation are higher by a factor of 4.

23029, 3: Note the use of error bars for the literature estimate. Assessing and adding these to the current work will be necessary before publication.
Uncertainty limits are included now.

23029, 13-16: I am getting confused by the logic of this paragraph. First, you point out that the biogenic fraction of SOA is small. Then you say that the anthro estimate is probably too high. Is

the next section just getting back to your original point, or are you saying something new? This paragraph should be condensed and more focused. And then the next two sentences appear to seesaw back and forth. Just be clear: state your point, while acknowledging the small contribution.

We have rewritten the paragraph, by condensing and avoiding any confusion. We focused on the importance of measuring the stress-induced BVOC versus the (traditional) constitutive BVOC, and we clearly state that in Beijing the contribution of SOA mass formation is dominated by anthropogenic sources:

"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 environment. 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. "

23029: 20-29: This is a very nice comparison! Removing some of the weakly focused text in the Discussion will allow this to be highlighted.
We thank reviewer #1 for supporting the comparison, as we believe that this can help visualizing the results.

23030, 2-3: This is not a conclusion of your research. You only briefly mentioned this, and it was from a source that you didn't create. It shouldn't start your Conclusion section.
We agree. The sentence has been removed.

23030, 6: Don't say pollution, since you only assessed particulate matter, and not gas-phase chemistry.
We agree. We changed "pollution" with "SOA".

23030, 6-9: Again, this is not a conclusion from your research.
We agree. The sentence has been removed.

23030, 12: "successfully" not "successful."
Corrected.

23030, 10-20: Overall, a good paragraph for the conclusion, but remove the quotes from constitutive and stress-induced. Also, you should reword the final sentence, because again this is not the conclusion of your research. A more appropriate conclusion would be, 'We conclude that "picking the right tree for urban greening" (Churkina et al., 2015) can potentially reduce the formation of pollution in megacities.' You have not assessed the benefits of trees on air quality in your study.
We thank the review for the suggestion. The text has been corrected, respectively shortened, accordingly.

Table 1: Make "Chinese Flowering Crabapple" have a consistent significant figures.
Corrected.

Table 2: The final four columns do not add anything to the analysis and can be easily calculated if someone was interested. They should be removed.
We agree. The final four columns have been deleted in the actual version of table 2.

Figure 6: Between the interrupted vertical axes used in panels a and c and the mixed vertical axes that are used in panels a and b, the main points of this figure are obscured. Since cBVOC contribute so little, they should either be removed or allowed to have negligible bars. Or, the categories could be reduced to only c- and sBVOCs, to match panel c.

Overall we agree with reviewer #1 and we have therefore modified the figure to improve visualization of the main outcome of the analysis. In the revised figure, the panels A and B are separated and they are scaled differently to match panel C up to the axes breaks. However, we prefer to keep the interrupted axes in order to show (i) the increases (~doubling) of cBVOC and sBVOC (panel A), (ii) decreases of AVOC (panel B), and (iii) much lower impact of BVOC in respect to AVOC on SOA forming potentials. The interrupted axes also allow comparison between the pre-Olympic (2005) and post-Olympic (2010) situations of points i-ii-iii. Comparing the different Y-axis scales, the reader can also visualize the absolute contribution from BVOC and AVOC on SOA forming potential.

Anonymous Referee #2

Ghirardo et al. present results of BVOC emissions from a generous survey of plant samples collected in Beijing. Authors demonstrate that stress emissions (such as benzenoids, sesquiterpenes, and green leaf volatiles) constituted a major fraction of the total BVOC emissions in Beijing. They make this argument, in part, based on the lack of these same stress BVOC emissions measured from 4 model species tested in the Jülich plant facility prior to acute ozone exposure. The authors scale leaf-level constitutive and stress BVOC emissions to the city-level in order to estimate the BVOC contribution to SOA formation in Beijing. The contribution to SOA formation is estimated for BVOC emissions before and after a large tree-planting program was implemented for the 2008 Olympic Games. They conclude that total BVOC emissions contributed to 1.05 µg m-3 and 2.05 µg m-3 SOA in 2005 and 2010 respectively, and that stress BVOC constituted 40% of the biogenic SOA. Overall, biogenic SOA was a minor component of total OA constituting 2% and 4% of total OA in 2005 and 2010 respectively.
The research on plant stress emissions, particularly as it pertains to urban tree planting programs, is an important issue that deserves attention. This research falls well within the scope of ACP. However, prior to publication, I suggest major revisions in three general areas summarized here and described in more detail below.

1) The lack of clarity and illogical organization in the methods section make it very difficult to understand the overall design and objectives of the individual research components presented here.
We agree. The material and methods have now been reorganized and better explained. Please see general responses as well as specific responses to referee#1.

2) The conclusions the authors draw about SOA formation are highly over-stated given the uncertainties associated with these calculations. The authors list some of the uncertainties in Section 4.3, but no attempt is made to perform even simple sensitivity tests to investigate the potential range of reasonable estimates. Related to this, there is no attempt to estimate a quantitative uncertainty associated with the SOA calculation. Given that these results demonstrated that sBVOCs only contributed to 0.08% (2005) and 0.16% (2010) of the total SOA in Beijing, it is likely that the error could actually preclude the confidence of the assertion made in the title of this manuscript.

Uncertainties have been included now. Please also see our general response and comments to referee#1. The title of the manuscript has been revised by removing the impact of BVOC on SOA:

"Urban stress-induced biogenic VOC emissions and SOA forming potentials in Beijing"

3) Perhaps most importantly, results from the comprehensive survey of the plant emissions in Beijing (including a thorough investigation of stress emissions) and the state of-the-art plant stress laboratory experiments performed at Jülich are only given a cursory discussion even though they represent the strengths of the scientific work presented. Those results could be discussed in more detail and the focus on the potential implications for SOA formation could be drastically reduced to increase the overall strength of the manuscript. I also suggest revising the title accordingly to emphasize the stronger components of the manuscript

We agree with the reviewer and we have changed the title of the paper (see previous comment).

Section 2: Materials and Methods is Unclear
The lack of clarity and illogical organization of the methods section severely impedes understanding of the overall experimental design. The authors used many different methods (field samples, laboratory measurements, modeling) and it would be helpful to include an overview paragraph in Section 2 before starting Section 2.1 that provides an overall framework for how all these different pieces fit together. Furthermore, the organization of the different sub-sections within Section 2 does not flow logically (for example, section 2.4 describes how emission rates were measured from samples collected as described back in Section 2.1), and it is difficult to determine how the methods described in each sub-section fit into the overall objective/design of the research (for example, how does the phylogenetic component fit with the rest of the work presented here?). More thoughtful organization could greatly improve the readability to help clearly convey the overall design of the project. For example, I suggest re-organizing this section with 3 main sections defined as follows: 1) field samples Include the survey of Beijing plant emissions here (sample collection, summary of trees represented, and leaf-level emission rate measurement technique) 2) laboratory experiments Include the Jülich experiments here and make it more clear how these experiments fit into the overall design of the project. The way it is written now, these experiments do not fit with the rest of the paper and look like just a sideproject that was added. 3) Modeling/calculations Include how the emission budgets were calculated and the approach used for estimating contribution to SOA mass. This is just one idea for a possible organizational framework that would help clarify the design of the project.

There are others, but I do think it is critical that the authors have some over-arching organization to describe these methods, and that the individual sections clearly state how that component contributes to the overall objectives of the work.
The description in Section 2.6 was particularly confusing. After reading this section I am still unclear exactly how the emissions inventory was obtained and how the sBVOC emissions were scaled up. The authors state on P. 23017, L. 5-7: "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." I don't understand what this means. Could the authors use equations to better communicate exactly how this was done? Additionally, there should be a more clear connection between the main body of the text in Section 2.6 with the information presented in Table 2. For example, it could be stated more clearly in the main body of the text in Section 2.6 that the measured emissions presented in Table 2 have been scaled up to city-level based on the emissions measurements performed from the "Beijing survey". However, there were some tree species not included in the survey that needed to be taken into account.

We agree. We have now completely re-organized the methods and followed the suggestions.
Please see also our general response and response to reviewer#1.

The authors accounted for these emissions via literature values as they describe well on P. 23016, L.23 – P. 23017 L. 9 but they never link this text back to Table 2; nowhere in this part of the text is this description connected to the "Total" emissions columns presented in Table 2. This link needs to be established to help readers understand more clearly. Additionally, I recommend changing the last two column headings in Table 2 from "group vs. sum (all) total [%]" to something like "relative contribution to total emissions [%]" which is clearer language.

We have clarified these points in the methods and reported in the supplementary table 5.
Please see also our general response.
In table2, we have removed the last two columns because they can be easily calculated as suggested by reviewer#2.

P. 23016, L. 10-13: Could the authors briefly describe the SQT response based on the Bourtsoukidis et al., 2012 paper? What does it mean that "the determined emission rates were related to the temperature as measured in parallel with the O3 concentrations"? Can they be more specific about what is meant by the term "related" here?

We have now described how we have modelled the sBVOC emissions, based on the observations found in Bourtsoukidis et al., (2012) describing the (cor-) relation between O_3 and sBVOC.

This has been changed to read:

"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 [O3] dependency presented in Bourtsoukidis et al. (2012). Therefore, the Bourtsoukidis algorithm was first used to simulate relative emission rates in response to [O3], measured during summer and autumn 2011. Then we applied the ctsi algorithm to the temperature values measured in parallel to the [O3] 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."

How were the anthropogenic VOC emissions estimated? This should be described more clearly.

We agree. For the anthropogenic SOA contribution one can directly calculate the production rate from available long term ambient observations of VOC concentrations (due to longer atmospheric lifetime). Thus we did not estimate any anthropogenic emission. We have now extended the description of the calculation of the anthropogenic SOA contribution to organic aerosol to make this clearer. We also refer to a recent study where the most extensive available anthropogenic emission inventories have been evaluated.

The revised part reads as following:

"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 5×106 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)."

Section 2.8: Please make it more clear that the yields used for this calculation were "incremental mass yields" (calculated from the slope of plotting organic aerosol mass vs. reacted hydrocarbon mass) rather than the more traditional SOA mass yield definition (i.e. Odum et al., 1999). Also, authors need to state more clearly in this section that this is a drastic over-simplification of the SOA formation process. Can they provide a more clear rationale for why they deviate from

more common approaches to SOA modeling (such as volatility-basis-set as one example)? They are estimating all anthropogenic SOA from only 3 precursors: benzene, toluene, xylenes. They are ignoring NOx-dependent chemistry, which is not appropriate for an urban, polluted environment like Beijing. They ignore the effect of background organic aerosol on absorption, but also use it as a rationale for ignoring nucleation. Overall, the SOA modeling approach used in this work is unsatisfactory and the focus on the SOA results de-values the strengths of this paper, which should be better highlighted (discussed below).

We changed the phrase "yield" to "incremental mass yield" in the respective chapter and mentioned that we use the data given in Mentel et al. (2013). We are aware that our estimation of the SOA formation potential is based on an over-simplification because we neglect partitioning. However, as noted on p. 23028, lines 13 ff., the measurements to determine incremental yields were made at somewhat lower mass but still within a realistic range for megacities.

As stated in our general response, we do not aim to give exact model results. We just want to show that SOA mass formation from BVOC in Beijing is of minor importance. Considering the under determination of the chemical system and the robustness of our main statement versus uncertainties in our estimation, we refrain from more sophisticated modelling.

This is also the reason for choosing only the three dominant anthropogenic precursors for the estimate, for neglecting nucleation, and for neglecting the NOx dependence. We nevertheless add some words regarding our motivation to neglect, for instance, nucleation and a NOx dependence of SOA mass formation.

We have added text in the discussion section that reads as following:

"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."

Sensitivity and Quantitative Error Analysis Are Neglected

We now give uncertainty limits.

Section 2.8: Extremely low volatile organic compounds generated from BVOC oxidation substantially contribute to SOA formation (Ehn et al., 2014), and these extremely low volatile compounds are easily lost to chamber walls at a rate that will vary depending on the type/size/geometry of the chamber. Can you discuss the implications of these findings on the SOA yield values you used here and can you broaden the scope of your methods to include SOA mass yields that have been presented by others outside of the Jülich group to get a more representative sample of SOA yields presented from the entire SOA research community? For example, an SOA yield of 6% for monoterpenes is quite low. The studies used as a basis for these SOA yields were conducted under low NOx conditions. NOx can drastically effect SOA yields, so are these SOA yields really the most appropriate for application in a polluted, urban environment?

Indeed, the extremely low volatile products of BVOC oxidation (ELVOC) are very efficiently lost on our chamber walls. Thus, mass formation may depend on the geometry and the type of chambers. Results obtained in all chamber experiments might be biased by wall losses. It is an open field of science to quantitatively determine the impact of ELVOC wall losses on SOA mass formation. As we have only experience with our own chamber, we only refer to this chamber: When providing enough particle surface, the impact of wall losses diminishes rapidly in our chamber. We therefore assess the yields used here as lower limits, but we assume that "real" mass yields are not much higher.
However, as requested by the referee, we now also refer to yields measured from other groups to get a more representative idea on the importance of BVOC for SOA formation in Beijing.

Regarding the NOx dependence of SOA mass formation we refer to Wildt et al. (2014). To the best of our knowledge this is the only dataset obtained with a realistic BVOC mix emitted from plants, in a

realistic range for particulate matter in moderately polluted atmosphere, and at quite constant OH concentrations: SOA mass formation is not really strongly affected by NOx as long as NOx does not drastically affect [OH]. Only new particle formation is strongly suppressed by NOx. According to the high burden of particulate matter in a megacity we neglected new particle formation.

On P. 23018, L. 7-9 the authors state that they assumed plants were active for only half the year and thus they multiplied the emission fluxes calculated from the numbers in Table 2 by two. How sensitive are your results to this assumption? Additionally, is there any literature support for making this assumption in this area?

We estimated the contribution of BVOC on the SOA formation in Beijing by looking for yearly emissions. The biogenic emissions increase in concert with active vegetation, which occurs only for a certain period of the year. Increases in biogenic emissions contribute to particle formation during this period. For the rest of the year the biogenic contribution will be zero. On average the assumption of a certain length of the vegetation period does not substantially impact the result.
However, referee 2 correctly points out an inconsistency in our procedure. As we also do not take into account daily variations of BVOC, their temperature- or light-intensity dependence, it is also unnecessary to take into account a certain vegetation period. We therefore will remove this point and we mention that our estimate just gives an average yearly contribution.

The calculations required to scale laboratory emissions measurements up to the urban scale necessitate making highly uncertain assumptions about total emissions and individual SOA mass yields from those emissions. Some of the assumptions that were made are noted in Section 4.3. However, authors neglected to perform even a simple sensitivity analysis to investigate the implications of these assumptions. I suggest at a minimum that the authors investigate how sensitive their final SOA values are to the concerns raised above.

We give numbers for uncertainties now (factor of 2) and we performed a simple sensitivity analysis by using different yields for sesquiterpenes (see second to last comment). We included some words in the discussion section. However, even a much higher uncertainty (e.g., factor of 4) does not change the main statement given in the manuscript.

On page 23028: L. 20-22 authors state, " 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". This line illustrates how the SOA results are misrepresented in this manuscript. The highly uncertain SOA estimates actually showed that sBVOCs contributed 40% of the biogenic SOA, which only contributed 2%-4% of total SOA, so the use of the word "substantial" here could be quite misleading. What if the uncertainty was taken into account? Would these results still be "substantial"? Prior to publication, an effort must be made to better define the uncertainty associated with the SOA estimate to avoid overemphasizing the role of sBVOCs in SOA formation in Beijing.

We apologize for the previous unclear sentences. We have reformulated the phrase in view of the uncertainty tests and made our two points clearer:

(i) sBVOC should not be neglected when studying BVOC, because their SOA forming potential might be comparable to that of cBVOC (~70 %)
(ii) in Beijing the actual main contributors of SOA-mass formation potential originate from anthropogenic sources.

The new text now reads:
"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%)."

Focus More on the Experimental Work

Section 3.5: This section summarizes results that are the major focus of the manuscript title and a large fraction of the discussion in Section 4, but it makes up just a small component of the results (and the weakest scientific component of the results). The most important results presented in this paper are shown in Section 3.2 and discussed in Section 4.2, and I suggest that the manuscript is revised to focus on the significant emissions of measured stress BVOCs. Furthermore, it is unclear why the authors chose to look only at the implications of these results for SOA formation and did not also include an investigation of their potential impact on oxidant reactivity or ozone concentrationsâ˘Aˇ Tboth of these potentially being larger effects of sBVOCs on the urban atmospheric chemistry of Beijing than the SOA mass produced from sBVOCs. Additionally, the results from the laboratory studies performed at Jülich were presented only briefly in Section 3.1. These results could be more thoroughly investigated.

We fully agree with referee #2 and we have revised the manuscript to focus on the significant emissions of measured stress BVOCs. We also agree that it would be very informative to have some ideas on the impact of BVOC on reactivity or ozone formation in the air over Beijing. However, the data availability on OH-reactivity and the ozone formation potential of many BVOC, in particular sBVOC, is sparse. We therefore focussed on SOA formation from BVOC and sBVOC for which we have some data on their importance.

With respect to the data used for classification into sBVOC and cBVOC we refer to our general statement.

Other Comments
In the abstract authors state that "sBVOCs can significantly contribute (_40%) to the formation of total secondary organic aerosol from biogenic sources; apparently, their annual emission increased from 1.05 µg m-3 in 2005 to 2.05 ug m-3 in 2010" (P. 23007, L.17-20).
Firstly, these are units of concentration, not emission, so it isn't clear what the authors mean when they say "apparently, their annual emission increased from [. . .]". Furthermore, in Section 3.5 the authors state that 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" (P. 23023, L.9-10). The units here are just a mass. There is an inconsistency between these units in the abstract and the results section 3.5. Secondly, what is this an "average" of? It is not clear from the text.

We agree. The sentence in the abstract was misleading. We therefore changed the respective text to:

"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%)."

Throughout the paper, the authors could better distinguish between laboratory work conducted on the 4 model species at Jülich and the laboratory work conducted using samples collected in Beijing for the "survey". Often the text just refers to "laboratory studies" (Page 23021, L. 1) or "laboratory survey" (Page 23021, L. 4). The language could be much clearer.
We agree. We have reorganized the methods and followed the reviewer suggestion. Please see also our general response and details to review#1.

On P. 23018, L. 18-19 authors state: "GLVs contribute to 6% of total BVOC emissions and even less to the total VOC emissions (<1%)." I cannot reconcile this statement with the results presented in Figure 4, which clearly demonstrate that GLVs constitute a major fraction of the plant emissions.

The sentence and the values refer to the total BVOC budget calculated for Beijing. Figure 4 depicted standards emission rates of BVOC, measured at 30°C, 1000 PAR. Light and temperature strongly and differentially affect the emission of cBVOC as compared to sBVOC.
However, the new calculations led to a significant higher amount of GLV and those emissions have now been taken into account for SOA forming potentials.

P. 23020, L. 28 – P. 23021 L. 2: Authors conclude that plants in Beijing were clearly stressed because the emissions that they have defined as "stress emissions" were emitted at rates 100-1000 times higher than the emission rates of the plants used in the Jülich experiments. Can the authors comment on how representative the 4 model plant species are of the plants surveyed in Beijing? Couldn't the constitutive emissions of compounds like SQTs just be different between different types of plants? Are these "stress emissions" higher here in Beijing than in other similar plants located in a forest environment?

The plants used in Jülich are not at all representative of the plants in Beijing. But this is not required. Please refer to our general response.
Concerning SQTs, in nearly all of the experiments in Jülich, SQTs were not emitted before stress application, or the emission strengths were negligible. SQTs were emitted during and for a short time after the stress application. SQT emissions are stress-induced emissions not constitutive emissions. Comparison of Beijing forested environments: Unfortunately, sBVOC are not well investigated so far and in our opinion this would be important for future research. However, this does not help at the moment; we have no answer to this question. Please also note that plants normally cope with continuous stressful environment (but different in intensity), and completely "unstressed plants" are more likely to be found only under optimal laboratory conditions.

Figure 1: caption reads, "Experiments were replicated different times with similar results." Can the authors be more quantitative regarding the variation that was observed? Error bars should be included.
Furthermore, the responses of the different plants was quite variable. Can the authors discuss this in more detail, and comment on the implications of this plant variability for the stress emissions expected from plants in Beijing.

The absolute amounts of the GLV emissions as well as of other sBVOC are dependent on ozone concentration and on the time after ozone exposure (Beauchamp et al., 2005). Besides a plant to plant variability, there is also a time dependency of the stress-induced emissions and the dependency on the stress intensity. In such case, error bars are useless.
The exact absolute amount and the biological variabilities are not relevant to the present study as these values are not used in our calculations, but used as an example to show to the readers how the BVOC pattern can dramatically change from unstressed condition to abiotic stress conditions and how the emission rates can potentially increase to significant amount. We used laboratory experiment to avoid any stress condition in pre-stress condition, and to control the stress under abiotic condition. The results are robust because they were repeated several time "(Cotton, n = 4).. (Tomato, n = 7).. (Poplar, n = 17), (Tobacco, n = 27)", giving overall the same change in sBVOC pattern.

The plant to plant variability and the species-specific response of the plant species found in Beijing needed for our study are given in the following figures 3-4 and they are based on our survey in Beijing. Species-specific response is studied in our phylogenetic study shown in Fig.5.

To avoid confusion, the figure caption has been improved. It now reads:

"Example of stress-induced BVOC emissions (A) before and (B) after O3 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. ."

Figure 4: The color scheme in this figure made it very difficult to read. Cyan, blue, and light blue are too similar to one another. Furthermore, it was not immediately clear that the sBVOCs are only shown in panel (a) because the authors simply list the color code in the text together. I suggest revising the color scheme to better distinguish between compound classes and I suggest including a legend rather than simply describing the color code in the text.
We have revised the figure and removed the confusing colour of panel (a). Now the colour are different to distinguish cBVOC, sBVOC and each group of BVOC (isoprene, MT, SQT, BZ, GLV). We could add the colour code in the figure, if the journal allows or the editor deems this to necessary.

Anonymous Referee #3
Received and published: 1 October 2015

In this study, the impact of biogenic volatile organic compounds (BVOC) on secondary aerosol (SOA) formation in megacity Beijing has been investigated. In the Beijing, there was a large tree-planting program for the 2008 Olympic Games and the BVOC emissions from woody plants were estimated before and after the games in 2005 and 2010. The authors determined the abundance of different plant species in the urban area of Beijing and selected 22 woody plant species for detailed VOC emission analysis. Furthermore, four model plant species were exposed to elevated concentrations ozone to measure stress-induced BVOC emissions. The BVOC emissions were classified into two groups: constitutive and stress-induced BVOCs. Finally, the SOA formation potential of biogenic and anthropogenic VOC was estimated based on VOC emission budgets.
The results obtained indicate that annual BVOC budget may have doubled from 2005 to 2010 due to the tree-planting program. The stress-induced BVOCs were estimated to be contributed ca. 40 % to the formation of total biogenic SOA. In addition, an average concentration of biogenic SOA were estimated to be doubled from 2015 to 2010; however it still contributes only ca. 4 % of total SOA formation. Although, biogenic SOA contributes only a few per cent to total SOA, the selection of suitable low-emission plant species could have positive effects on urban air quality.

The study presents new and important results on the biogenic VOC emissions (including stress-induced emissions) and the SOA formation in the urban megacity Beijing. Although the study contains many assumptions and generalizations, the results can be used to estimate the importance of biogenic emissions in urban areas. The manuscript is quite well organized and written, and the scope of is suitable for publication in this journal. The methods and experiments have been well described and conducted as well as the results are well reported and analyzed. Overall, the manuscript is suitable for publication in this journal. However, there are some minor comments and suggestions that should be considered before publication.

General comments

This study shows that a large scale tree-planting could lead to substantial increase in concentrations of particulate matter in urban areas which might have adverse health effects. Please discuss shortly toxicological/adverse health effect of biogenic SOA in the manuscript. Is biogenic SOA as "toxic" as anthropogenic SOA which often contains, e.g., PAH compounds.

We agree with reviewer #3 that health effect is an important consequence of particulate matter in urban areas, but we feel that discussing the toxicological/adverse health effect of biogenic SOA is beyond the scope of this paper. We have therefore included a reference (review) on health effect of atmospheric aerosol but we prefer to avoid increasing the length of the manuscript.

Reference:
Pöschl, U.: Atmospheric aerosols: Composition, transformation, climate and health effects, Angew. Chemie - Int. Ed., 44(46), 7520–7540, doi:10.1002/anie.200501122, 2005.

Obviously, tree-planting have also positive effects. For instance, plants can also remove a considerable amount of particulate matter and harmful gaseous compounds from urban air (see, e.g., Beckett et al, 2000; Nowak et al. 2013). Please add more discussion on the positive effects of plants on urban air quality.

We thank the reviewer #3 for suggesting two useful and important references which we included in the introduction where we indicate briefly the unchallenged positive aspects of urban greens. Since the amount of particulate matter removed from the air was not investigated in this study, we didn't bring it up in the discussion.

Table 1 shows results from woody plant inventory in the urban area of Beijing. The most abundant species are evergreen trees, however, none of them were used in detailed analysis. Why do evergreen trees have been excluded? What could contribution of evergreen trees be on VOC emissions and SOA formation? Please clarify the role of evergreen trees.

The modelled BVOC and consequently the SOA data include estimation budget calculated from both deciduous and evergreen tree species. We have clarified this point in the material and method. Please see our general response.

Among evergreen trees, all the coniferous trees have been excluded from cuvette measurements. Our results strongly indicate that enclosing coniferous twig into cuvettes leads to incorrect assessment of BVOC emission potentials due to the mechanical stress (Ghirardo et al., 2010). Coniferous plant species contain resin duct as storage of monoterpenes. By introducing twigs and needles into cuvettes, resin droplets are disturbed and consequently monoterpenes are released leading to incorrect emission rates. We knew from our experience that to achieve reliable BVOC emission of evergreen, twigs need to be prepared in advance (weeks) by removing all the needles in contact with the cuvette before enclosure The cuvette enclosure needs to be performed at least the day before BVOC measurement and after long acclimatisation (Ghirardo et al., 2010), which is incompatible with the present survey due to the large number of species used and the limited time period available for measurements (summer). Therefore, we tried to avoid artefacts and referred to the literature data. The proportion of measured BVOC compared to all modelled BVOC was found to be 93-94% (Table 2).

VOC compounds have been classified "constitutive" and "stress-induced" classes. For instance, alpha-pinene has been classified as "constitutive" BVOC. To my knowledge, emissions of many "constitutive" monoterpenes can increase significantly after abiotic or biotic stress, especially for conifers. How has this been taken into account in model calculations? Has this any effect on final results and conclusions?

The reviewer is correct. This point was already mentioned in the uncertainty of the BVOC budget:

"..Fourth, the cBVOC emissions of isoprene and monoterpene might also increase under stressed conditions (Behnke et al., 2009; Blande et al., 2007; Niinemets, 2010).".

Consequently, the amounts of sBVOC might be underestimated rather than overestimated. *Overall the final results and conclusion are unlikely to change significantly. Please refer to our general response.*

In the ozone fumigation test, VOC emissions were collected for 20 h after ozone exposure. Please clarify what are long term emissions of stressed plants? What will emissions be after several days/weeks? Please discuss long term effects on VOC emission and SOA formation (Does it have any effect on results and final conclusions?).

The results from the ozone fumigation tests were made to distinguish between sBVOC and cBVOC. They were not used to estimate sBVOC emissions in Beijing and therefore have no impact on the final conclusion (see our general response). We have no data on long term effects and we therefore refrain from discussing long term effects. We refer the interested reader to already published data on these experiments.

There are many assumptions and generalizations in model calculations. How realistic are the results? Please make a rough error analysis to get an estimate of the reliability of the results (e.g. 10 % or 50 %). In addition, compare the modeled results with measured ones in more detail (e.g., VOC and mass concentrations).

We agree. We have assessed our uncertainties. Please see our general response.

Please check language.
Language has been professionally edited by American Journal Experts (AJE), and rechecked by a native English speaker.

Specific comments/ technical corrections:
Materials and methods (page 23011): In this study, several separate experiments and studies have been combined together. At the beginning of this chapter (before Ch. 2.1), a short summary would help reader to understand easier the experiments and model calculations conducted in this study.
We agree. Please see our detail response to reviewer#1.

2.1 Plant material (page 23011): "Two fully developed leaves from three trees were independently measured for each species in the period from August to mid-October in 2011." Please define what has been measured.
We have clarified the sentence with the following:

"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 originated from two different branches."

Page 23011, line 14: lab => laboratory
Corrected

Page 23012, line 13-14: ": set by the US-Environmental Protection Agency and the United Nations Economic Commission for Europe (UNECE)." Please add an appropriate reference.

The following reference has been added:
Roy, S., Beig, G. and Ghude, S.: Exposure-plant response of ambient ozone over the tropical Indian region, Atmos. Chem. Phys., 9(1), 5253–5260, doi:10.5194/acpd-9-4141-2009, 2009.

2.3 Laboratory study of ozone-induced BVOC emissions (page 23012). Why do those model plant species have been selected? Are they representative? Please clarify in the text.

The data were only used for classification of BVOCs into sBVOCs and cBVOCs. The use of model plants, i.e., plant species that are widely used as reference organisms in plant physiology, allows for a comprehensive understanding of the plant response to stress factor (in this case ozone), because genomic, proteomic and metabolomic data are available in the respective database.

Please refer to the general response and response to review 1.

Page 23014, line 23: Please define acronym MSD if not commonly know.
MSD stands for "mass selective detector" and it has been spelled out now.

Page 23016, line 15: " :a reference temperature (48 C)". The reference temperature of 48 C seems to be high, please clarify the background of this high reference temperature.

We adjusted the parameters β and reference temperature from the standard Guenther model for temperature dependency of emissions in order to fit the measured emission response to measured temperature. The standard iterative procedure (Excel solver) gave the values 0.12 and 321K/48°C, describing a relatively flat, exponentially increasing relationship. This has now been refined by first calculating ozone concentrations from temperature and then fit the Guenther model to the emissions that are calculated with the Bourtsoukidis equation based on the calculated concentrations. This way, the whole temperature range could be used, resulting in β and Tref values of 0.24 and 316.5K, respectively. The reference temperature in this case is a purely empirically derived value and is not necessarily of physiological significance.
NOTE: Motivated by the reviewers question we checked and refined the calculations and also noted that the emission factors derived from the measurements at 30°C had to be corrected to the reference temperature in the ozone-dependent equation. This has been corrected and added to the methodology description. It has also led to higher stress-induced emissions, which required a re-calculation of further steps that have been followed. The overall result in the paper is not considerably different from the original version. Please see also our general response.

Page 23017, line 25-: "The height of the box was fixed to 2 km, as a typical proxy for the height of an inversion layer." Please give a suitable reference for 2 km inversion layer used in calculations.

Our response: the height of the box was used as typical proxy. This height can change strongly and thus change SOA formation. However, keeping other meteorological and chemical quantities constant, changes of the PBL height alone do not substantially change the SOA formation potential. Keeping emission rates of AVOC and BVOC at a fixed ratio, changes of the PBL height alone also do not substantially change the contributions of AVCOC and BVOC to SOA formation. See also our general response.

Page 23018, line 25-: " we assumed that the atmospheric lifetime of particles is approx. 4 days." Please give a suitable reference or clarify the use of 4 days particle lifetime.

The lifetime of 4 days was used as a typical proxy. Keeping other meteorological and chemical quantities constant, assuming that the lifetime of SOA formed from the mix of AVOC, BVOC and sBVOC vary by an order of magnitude, it does not substantially change the contribution of AVOC, BVOC, and sBVOC to the SOA formation potentials. Please see also our general response.

Page 23020, line 20: "two well-known strong isoprene-emitters." Please give a suitable reference.
The following reference has been added:

Kesselmeier, J. and Staudt, M.: Biogenic volatile organic compounds (VOC): an overview on emission, physiology and ecology, J. Atmos. Chem., 33, 23–88, doi:10.1023/A:1006127516791, 1999.

Page 23023, line 10: "1.05 _g in 2005 and 2.05 _g in 2010". Please check units (_g/m3?).
Thanks for pointing this out. We have corrected the units to µg m^{-3}

Page 23026, line 1-: "However, measuring sBVOCs such as SQT in ambient air is challenging due to their high reactivity with O3 and/or other reactive oxygen species (i.e., OH radicals), and sBVOCs might thus already be oxidized before being detected." Furthermore, SQT and other low-volatile compounds easily condense (or stick) onto walls of sampling pipes and leaves of plants. Please clarify this point in the text. Is condensation onto sampling lines inhibited during experiments?

The collection of BVOC is performed immediately following the exit of air out of the cuvette (few cm), using a high flow rate (1L min^{-1}) in order to minimise losses of sampling and to quickly reach a steady-state of BVOC emissions. All lines after the cuvette are thermally isolated. Condensation of low-volatile BVOC in lines is therefore not inhibited in our setup, but reduced. For the quantification, this process is negligible, because we are collecting under BVOC steady-state emissions. We are aware of the adsorption/desorption of semi-volatile compounds into/from Teflon tubes from measurements of plant emissions followed by background measurements in our daily experience based on proton transfer reaction mass spectrometer (PTRMS), which allows monitoring BVOC emission online at fast time-resolutions (seconds). We have seen many times the adsorbing/desorbing processes occurring between BVOC and tubing by using pure standards mixtures containing volatile and semi-volatile substances, including for instance MT and SQT.

In our setup, after an initial phase where an adsorption occurs, the equilibrium is reached and BVOC fluxes are under steady-state. Our collections started after 30-45 minutes of enclosing the cuvette when BVOC emissions were on the steady-state. Therefore, the effect of condensation mentioned is unimportant.

We have clarified and cited this into the text:
"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 cm2) after allowing them to acclimate (30-45 min, until photosynthetic gas exchange became stable) to standard conditions (1,000 $\mu mol\ m^{-2}\ s^{-1}$ 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)."

Page 23028, line 13-: "Mentel et al., 2013 measured" => Mentel et al. (2013) measured
Corrected

Page 23028, line 27: "Odum Jay et al." => Odum et al. Please check also the reference (p. 23039, l. 13).
Corrected

Table 1 (page 23042): Please add a reference for the plant coverage data base used in this study.
We have added the missing reference:

Beijing Municipal Bureau of Landscape and Forestry, 2006. Inventory of the green space in Beijing based on census-2005. Beijing press, Beijing, China, pp. 110-130.

Table 2 (page 23043): Explanations of column abbreviations could be first before other in the caption text (easier to read).
The explanation of column abbreviations is logically presented, namely, from left to right and from top to bottom in each column. We retained this order.

Figure 1 (page 23044): What is reason for high value of GLVs? Please add error bars of emission rates (e.g. standard error/deviation). Abbr. "nd" not defined.
The reason for the high GLV emissions is the relative short-time delay between ozone exposure and measurement. All sBVOC are emitted in pulses and, in case of single O3 exposures, GLV emissions start very early and strongly (Beauchamp et al., 2005). Please see our general response and similar remark to Referee # 2.

Abbreviation of 'nd' (not detectable) has been added. We thank the referee for pointing out our omission.

Figure 2 (page 23045): Abbr. PPFD not defined (panel A).
The acronym PPFD (Photosynthetic Photon Flux Density) has been now defined in figure legend 2.

Figure 4 (page 23047): The upper panel (A) is not easy to read. Should only total emission rate be presented because relative concentration of different compounds are presented panel B.

We agree with the reviewer that the old version of panel A was difficult to read. We now show in panel (A) the sum of cBVOC (white bars) and sBVOC (black bars) and hope that the new panel is clearer. By keeping cBVOC and sBVOC separate, we believe that the reasons for the low percentages over the total BVOCs found in Pt and Sb are now evident: the cBVOC emission rates are dominating the overall emission in these two plant species, whereas the stress-induced BVOC response is still significant. We have changed the y-labels to "SOA forming potential [μg m-3]".

References:

Beauchamp, J., Wisthaler, A., Hansel, A., Kleist, E., Miebach, M., Niinemets, Ü., Schurr, U. and Wildt, J.: Ozone induced emissions of biogenic VOC from tobacco: relationships between ozone uptake and emission of LOX products, Plant. Cell Environ., 28, 1334–1343, doi:10.1111/j.1365-3040.2005.01383.x, 2005.

Behnke, K., Kleist, E., Uerlings, R., Wildt, J. J., Rennenberg, H. and Schnitzler, J. P. J.-P.: RNAi-mediated suppression of isoprene biosynthesis in hybrid poplar impacts ozone tolerance., Tree Physiol., 29(5), 725–36, doi:10.1093/treephys/tpp009, 2009.

Behnke, K., Kaiser, A., Zimmer, I., Brüggemann, N., Janz, D., Polle, A., Hampp, R., Hänsch, R., Popko, J., Schmitt-Kopplin, P., Ehlting, B., Rennenberg, H., Barta, C., Loreto, F. and Schnitzler, J.-P.: RNAi-mediated suppression of isoprene emission in poplar transiently impacts phenolic metabolism under high temperature and high light intensities: a transcriptomic and metabolomic analysis., Plant Mol. Biol., 74(1-2), 61–75, doi:10.1007/s11103-010-9654-z, 2010.

Benjamin, M. T., Sudol, M., Bloch, L. and Winer, A. M.: Low-emitting urban forests: A taxonomic methodology for assigning isoprene and monoterpene emission rates, Atmos. Environ., 30(9), 1437–1452, doi:10.1016/1352-2310(95)00439-4, 1996.

Bourtsoukidis, E., Bonn, B., Dittmann, a., Hakola, H., Hellén, H. and Jacobi, S.: Ozone stress as a driving force of sesquiterpene emissions: a suggested parameterisation, Biogeosciences, 9(11), 4337–4352, doi:10.5194/bg-9-4337-2012, 2012.

Chen, Z.X., Su, X.H., Liu, S.Z., Gu, Y.Z., Li, Y.M., 1998. The study on ecological benefit of garden afforestation in Beijing. Chinese Landscape Architecture 14(56), 51-54.

Fäldt, J., Arimura, G., Gershenzon, J., Takabayashi, J. and Bohlmann, J.: Functional identification of *AtTPS03* as (*E*)-beta-ocimene synthase: a monoterpene synthase catalyzing jasmonate- and wound-induced volatile formation in *Arabidopsis thaliana*., Planta, 216(5), 745–751, doi:10.1007/s00425-002-0924-0, 2003.

Funk, J., Jones, C. and Lerdau, M.: Defoliation effects on isoprene emission from Populus deltoides, Oecologia, 333–339, doi:10.1007/s004420050734, 1999.

Ghirardo, A., Koch, K., Taipale, R., Zimmer, I., Schnitzler, J.-P. and Rinne, J.: Determination of de novo and pool emissions of terpenes from four common boreal/alpine trees by 13CO2 labelling and PTR-MS analysis., Plant cell Environ., 33(5), 781–792, doi:10.1111/j.1365-3040.2009.02104.x, 2010.

Ghirardo, A., Gutknecht, J., Zimmer, I., Brüggemann, N. and Schnitzler, J.-P.: Biogenic volatile organic compound and respiratory CO2 emissions after 13C-labeling: online tracing of C translocation dynamics in poplar plants, PLoS One, 6(2), e17393, doi:10.1371/journal.pone.0017393, 2011.

Ghirardo, A., Heller, W., Fladung, M., Schnitzler, J.-P. and Schroeder, H.: Function of defensive volatiles in pedunculate oak (Quercus robur) is tricked by the moth Tortrix viridana, Plant cell Environ., 35(12), 2192–2207, doi:10.1111/j.1365-3040.2012.02545.x, 2012.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J. and Zimmerman, P.: A Global-Model of Natural Volatile Organic-Compound Emissions, J. Geophys. Res., 100(D5), 8873–8892, doi:10.1029/94JD02950, 1995.

Guenther, A., Baugh, B., Brasseur, G., Greenberg, J., Harley, P., Klinger, L., Serça, D. and Vierling, L.: Isoprene emission estimates and uncertainties for the central African EXPRESSO study domain, J. Geophys. Res., 104(D23), 30625, doi:10.1029/1999JD900391, 1999.

Hakola, H., Tarvainen, V., Bäck, J., Ranta, H., Bonn, B., Rinne, J. and Kulmala, M.: Seasonal variation of mono- and sesquiterpene emission rates of Scots pine, Biogeosciences, 3, 93–101,

doi:10.5194/bg-3-93-2006, 2006.

Heiden, A., Hoffmann, T., Kahl, J., Kley, D., Klockow, D., Langebartels, C., Mehlhorn, H., Sandermann, H. J., Schraudner, M., G, S. and Wildt, J.: Emission of volatile organic compounds from ozone-exposed plants, Ecol. Appl., 9(3), 1160–1167, doi:10.2307/2641386, 1999.

Heiden, A., Kobel, K., Langebartels, C., Schuh-Thomas, G. and Wildt, J.: Emissions of oxygenated volatile organic compounds from plants Part I: Emissions from lipoxygenase activity, J. Atmos. Chem., 45, 143–172, doi:10.1023/A:1024069605420, 2003.

Holopainen, J. K. and Gershenzon, J.: Multiple stress factors and the emission of plant VOCs., Trends Plant Sci., 15(3), 176–184, doi:10.1016/j.tplants.2010.01.006 Available, 2010.

Joó, É., Dewulf, J., Amelynck, C., Schoon, N., Pokorska, O., Šimpraga, M., Steppe, K., Aubinet, M. and Van Langenhove, H.: Constitutive versus heat and biotic stress induced BVOC emissions in Pseudotsuga menziesii, Atmos. Environ., 45(22), 3655–3662, doi:10.1016/j.atmosenv.2011.04.048, 2011.

Karlik, J. F., McKay, A. H., Welch, J. M. and Winer, A. M.: A survey of California plant species with a portable VOC analyzer for biogenic emission inventory development, Atmos. Environ., 36(33), 5221–5233, doi:10.1016/S1352-2310(02)00569-1, 2002.

Kiendler-Scharr, A., Andres, S., Bachner, M., Behnke, K., Broch, S., Hofzumahaus, A., Holland, F., Kleist, E., Mentel, T. F., Rubach, F., Springer, M., Steitz, B., Tillmann, R., Wahner, A., Schnitzler, J.-P. and Wildt, J.: Isoprene in poplar emissions: effects on new particle formation and OH concentrations, Atmos. Chem. Phys., 12(2), 1021–1030, doi:10.5194/acp-12-1021-2012, 2012.

Kleist, E., Mentel, T. F., Andres, S., Bohne, A., Folkers, A., Kiendler-Scharr, A., Rudich, Y., Springer, M., Tillmann, R. and Wildt, J.: Irreversible impacts of heat on the emissions of monoterpenes, sesquiterpenes, phenolic BVOC and green leaf volatiles from several tree species, Biogeosciences, 9, 5111–5123, doi:10.5194/bg-9-5111-2012, 2012.

Mentel, T. F., Kleist, E., Andres, S., Dal Maso, M., Hohaus, T., Kiendler-Scharr, A., Rudich, Y., Springer, M., Tillmann, R., Uerlings, R., Wahner, A. and Wildt, J.: Secondary aerosol formation from stress-induced biogenic emissions and possible climate feedbacks, Atmos. Chem. Phys., 13(17), 8755–8770, doi:10.5194/acp-13-8755-2013, 2013.

Pinto, D. M., Blande, J. D., Souza, S. R., Nerg, A.-M. and Holopainen, J. K.: Plant volatile organic compounds (VOCs) in ozone (O3) polluted atmospheres: the ecological effects., J. Chem. Ecol., 36(1), 22–34, doi:10.1007/s10886-009-9732-3, 2010.

Tang, G., Li, X., Wang, Y., Xin, J. and Ren, X.: and Physics Surface ozone trend details and interpretations in Beijing , 2001 – 2006, Atmos. Chem. Phys., 8813–8823, 2009.

Toome, M., Randjärv, P., Copolovici, L., Niinemets, U., Heinsoo, K., Luik, A. and Noe, S. M.: Leaf rust induced volatile organic compounds signalling in willow during the infection, Planta, 232(1), 235–243, doi:10.1007/s00425-010-1169-y, 2010.

Wildt, J., Kley, D., Rockel, A., Rockel, P. and Segschneider, H. J.: Emission of NO from several higher plant species, J. Geophys. Res., 102(D5), 5919–5927, doi:10.1029/96JD02968, 1997.

Zhihui, W., Yuhua, B. and Shuyu, Z.: A biogenic volatile organic compounds emission inventory for Beijing, Atmos. Environ., 37(27), 3771–3782, doi:10.1016/S1352-2310(03)00462-X, 2003.

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.

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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), 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

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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

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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).

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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 70 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

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Economic Commission for Europe (UNECE) (Roy et al., 2009). AOT40 was calculated using the following equation:

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

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 (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

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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

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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).

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2.2.4 Phylogenetic tree and statistical analyses

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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, 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

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(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°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).

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The classification of volatiles as 'stress-induced' and/or 'constitutive' followed t review of Niinemets (2010) and was bas on the generalized findings of an extensi 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 BVO included the stress-induced monoterpene (E)-β-ocimene, linalool and 1,8-cineol (sMT), all sesquiterpenes (SQT), benzenoids (BZ) and green leaves volati (GLV) while constitutive BVOCs (cBVO included the hemiterpene isoprene (IS) a all constitutively emitted monoterpenes (cMT) that were not included as sMT (Table S1, Supplementary material). Thi classification fully agreed with the BVO emission pattern that was obtained in the laboratory study using the four plant mo that were exposed to O_3 (see Fig 1). The relative contribution of sMT to the overa MT emission was small; thus the sMT a 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 overal fraction of sBVOCs versus total BVOCs (see sections below). ¶
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$$EA_{si} = \begin{cases} 1 & if \text{ estimated daily peak } [O_3] > 40 \ (= \text{between day 132 and 287}) \\ 0 & else \end{cases} \quad (3)$$

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

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

$[O_3]$ 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

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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.

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(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):

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

DF is the day of the year (*doy*) at which daily cumulative temperature first crosses a threshold (0 °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

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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

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Deleted: The measured potential emission rates for isoprene were correcte for seasonal changes in enzyme activities relation to the annual fluctuation of temperature and light, as calculated with 'Seasonal-Isoprenoid-Model' SIM (Lehr et al., 2001). Depending on the calculate activity for the date of measurement and measured leaf mass per area (LMA), the potential emission factors (g C g DW^{-1} h for isoprene were derived (Table S5A,
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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.

Moved down [2]: As postulates for t procedure, we assumed that (i) the load o 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 matt to the existing particles. This allows neglecting the effect of suppression of ne 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, th suppressing effect is marginal (Mentel et al., 2013). A potential contribution of GL to particle mass formation was also neglected because the mass yields are als low (~0.03, Hamilton et al., 2009). (iii) A other VOC contributions to SOA formati 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.¶

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Deleted: To obtain the mass of organic matter on particles originating from BVOCs, we assumed that the atmospher lifetime of particles is approx. 4 days. W the relationship between concentration C source strengths Q and lifetime τ ($C = Q$ τ), we obtained the data listed in Supplementary material Table S3-4. ¶ To compare the contribution of BVOC to AVOC emissions to the organic particula 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 si (Wang et al., 2015) using an average OH concentration of 5×10^6 molecule cm^{-3} (L al, 2013) and the corresponding rate coefficients (Atkinson, 1994). The SOA yields were taken from the recent study b Emanuelsson et al., 2013, corresponding 0.14 at an organic aerosol concentration 10 µg C m^{-3}. ¶

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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

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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.

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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 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 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

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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

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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

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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.

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4.2 The importance of measuring stress-induced BVOC emissions

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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

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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

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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.

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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.

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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

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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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References

Aalto, J., Kolari, P., Hari, P., Kerminen, V.-M., Schiestl-Aalto, P., Aaltonen, H., Levula, J., Siivola, E., Kulmala, M. and Bäck, J.: New foliage growth is a significant, unaccounted source for volatiles in boreal evergreen forests, Biogeosciences, 11(5), 1331–1344, doi:10.5194/bg-11-1331-2014, 2014.

Affek, H. P. and Yakir, D.: Protection by isoprene against singlet oxygen in leaves, Plant Physiol., 129(1), 269–277, doi:10.1104/pp.010909, 2002.

Amo, L., Jansen, J. J., van Dam, N. M., Dicke, M. and Visser, M. E.: Birds exploit herbivore-induced plant volatiles to locate herbivorous prey, Ecol. Lett., 16(11), 1348–1355, doi:10.1111/ele.12177, 2013.

Arimura, G., Kost, C. and Boland, W.: Herbivore-induced, indirect plant defences, Biochim. Biophys. Acta, 1734(2), 91–111, doi:10.1016/j.bbalip.2005.03.001, 2005.

Atkinson, R.: Gas-Phase Tropospheric Chemistry of Organic Compounds, J. Phys. Chem. Ref. Data, Monograph(2), doi:10.1016/j.atmosenv.2007.10.068, 1994.

Baghi, R., Helmig, D., Guenther, A., Duhl, T. and Daly, R.: Contribution of flowering trees to urban atmospheric biogenic volatile organic compound emissions, Biogeosciences, 9(10), 3777–3785, doi:10.5194/bg-9-3777-2012, 2012.

Beauchamp, J., Wisthaler, A., Hansel, A., Kleist, E., Miebach, M., Niinemets, Ü., Schurr, U. and Wildt, J.: Ozone induced emissions of biogenic VOC from tobacco: relationships between ozone uptake and emission of LOX products, Plant. Cell Environ., 28, 1334–1343, doi:10.1111/j.1365-3040.2005.01383.x, 2005.

Beckett, K. P., Freer-Smith, P. H. and Taylor, G.: Particulate pollution capture by urban trees: Effect of species and windspeed, Glob. Chang. Biol., 6(8), 995–1003, doi:10.1046/j.1365-2486.2000.00376.x, 2000.

Behnke, K., Kleist, E., Uerlings, R., Wildt, J. J., Rennenberg, H. and Schnitzler, J. P. J.-P.: RNAi-mediated suppression of isoprene biosynthesis in hybrid poplar impacts ozone tolerance, Tree Physiol., 29(5), 725–736, doi:10.1093/treephys/tpp009, 2009.

Behnke, K., Kaiser, A., Zimmer, I., Brüggemann, N., Janz, D., Polle, A., Hampp, R., Hänsch, R., Popko, J., Schmitt-Kopplin, P., Ehlting, B., Rennenberg, H., Barta, C., Loreto, F. and Schnitzler, J.-P.: RNAi-mediated suppression of isoprene emission in poplar transiently impacts phenolic metabolism under high temperature and high light intensities: a transcriptomic and metabolomic analysis, Plant Mol. Biol., 74(1-2), 61–75, doi:10.1007/s11103-010-9654-z, 2010.

Beijing Municipal Bureau of Landscape and Forestry: Inventory of the green space in Beijing based on census-2005, Beijing Press Beijing, China, 110–130, 2006.

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Benjamin, M. T., Sudol, M., Bloch, L. and Winer, A. M.: Low-emitting urban forests: A taxonomic methodology for assigning isoprene and monoterpene emission rates, Atmos. Environ., 30(9), 1437–1452, doi:10.1016/1352-2310(95)00439-4, 1996.

Berg, a. R., Heald, C. L., Huff Hartz, K. E., Hallar, a. G., Meddens, a. J. H., Hicke, J. a., Lamarque, J. F. and Tilmes, S.: The impact of bark beetle infestations on monoterpene emissions and secondary organic aerosol formation in western North America, Atmos. Chem. Phys., 13(6), 3149–3161, doi:10.5194/acp-13-3149-2013, 2013.

Bergström, R., Hallquist, M., Simpson, D., Wildt, J. and Mentel, T. F.: Biotic stress: a significant contributor to organic aerosol in Europe?, Atmos. Chem. Phys., 14(9), 13643–13660, doi:10.5194/acp-14-13643-2014, 2014.

Blande, J. D., Tiiva, P., Oksanen, E. and Holopainen, J. K.: Emission of herbivore-induced volatile terpenoids from two hybrid aspen (Populus tremula × tremuloides) clones under ambient and elevated ozone concentrations in the field, Glob. Chang. Biol., 13(12), 2538–2550, doi:10.1111/j.1365-2486.2007.01453.x, 2007.

Bourtsoukidis, E., Bonn, B., Dittmann, a., Hakola, H., Hellén, H. and Jacobi, S.: Ozone stress as a driving force of sesquiterpene emissions: a suggested parameterisation, Biogeosciences, 9(11), 4337–4352, doi:10.5194/bg-9-4337-2012, 2012.

Bouvier-Brown, N. C., Goldstein, A. H., Gilman, J. B., Kuster, W. C. and de Gouw, J. A.: In-situ ambient quantification of monoterpenes, sesquiterpenes, and related oxygenated compounds during BEARPEX 2007 – implications for gas- and particle-phase chemistry, Atmos. Chem. Phys., 9, 5505–5518, doi:10.5194/acpd-9-10235-2009, 2009.

Von Caemmerer, S. and Farquhar, G. D.: Some relationships between the biochemistry of photosynthesis and the gas exchange of leaves, Planta, 153, 376–387, doi:10.1007/BF00384257, 1981.

Calfapietra, C., Pallozzi, E., Lusini, I. and Velikova, V.: Modification of BVOC Emissions by Changes in Atmospheric [CO2] and Air Pollution., in Biology, Controls and Models of Tree Volatile Organic Compound Emissions, edited by Ü. Niinemets and R. Monson, Springer Netherlands., 2013a.

Calfapietra, C., Fares, S., Manes, F., Morani, A., Sgrigna, G. and Loreto, F.: Role of Biogenic Volatile Organic Compounds (BVOC) emitted by urban trees on ozone concentration in cities: a review, Environ. Pollut., 183, 71–80, doi:10.1016/j.envpol.2013.03.012, 2013b.

Chan, C. K. and Yao, X.: Air pollution in mega cities in China, Atmos. Environ., 42(1), 1–42, doi:10.1016/j.atmosenv.2007.09.003, 2008.

Chen, X.-L., Zhao, H.-M., Li, P.-X. and Yin, Z.-Y.: Remote sensing image-based analysis of the relationship between urban heat island and land use/cover changes, Remote Sens. Environ., 104(2), 133–146, doi:10.1016/j.rse.2005.11.016, 2006.

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Churkina, G., Grote, R., Butler, T. M. and Lawrence, M.: Natural selection? Picking the right trees for urban greening, Environ. Sci. Policy, 47, 12–17, doi:10.1016/j.envsci.2014.10.014, 2015.

Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O., Artaxo, P. and Maenhaut, W.: Formation of secondary organic aerosols through photooxidation of isoprene, Science, 303(5661), 1173–1176, doi:10.1126/science.1092805, 2004.

Curtis, a. J., Helmig, D., Baroch, C., Daly, R. and Davis, S.: Biogenic volatile organic compound emissions from nine tree species used in an urban tree-planting program, Atmos. Environ., 95, 634–643, doi:10.1016/j.atmosenv.2014.06.035, 2014.

Ehn, M., Thornton, J. a, Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petäjä, T., Wahner, A., Kerminen, V.-M., Kulmala, M., Worsnop, D. R., Wildt, J. and Mentel, T. F.: A large source of low-volatility secondary organic aerosol., Nature, 506(7489), 476–9, doi:10.1038/nature13032, 2014.

Emanuelsson, E. U., Hallquist, M., Kristensen, K., Glasius, M., Bohn, B., Fuchs, H., Kammer, B., Kiendler-Scharr, A., Nehr, S., Rubach, F., Tillmann, R., Wahner, A., Wu, H.-C. and Mentel, T. F.: Formation of anthropogenic secondary organic aerosol (SOA) and its influence on biogenic SOA properties, Atmos. Chem. Phys., 13(8), 2837–2855, doi:10.5194/acp-13-2837-2013, 2013.

Fäldt, J., Arimura, G., Gershenzon, J., Takabayashi, J. and Bohlmann, J.: Functional identification of AtTPS03 as (E)-beta-ocimene synthase: a monoterpene synthase catalyzing jasmonate- and wound-induced volatile formation in Arabidopsis thaliana, Planta, 216(5), 745–751, doi:10.1007/s00425-002-0924-0, 2003.

Fry, J. L., Kiendler-Scharr, A., Rollins, a W., Wooldridge, P. J., Brown, S. S., Fuchs, H., Dube, W., Mensah, A., Dal Maso, M., Tillmann, R., Dorn, H.-P., Brauers, T. and Cohen, R. C.: Organic nitrate and secondary organic aerosol yield from NO3 oxidation of β-pinene evaluated using a gas-phase kinetics / aerosol partitioning model, Atmos. Chem. Phys., 9, 1431–1449, 2009.

Fry, J. L., Kiendler-Scharr, a., Rollins, a. W., Brauers, T., Brown, S. S., Dorn, H. P., Dubé, W. P., Fuchs, H., Mensah, a., Rohrer, F., Tillmann, R., Wahner, a., Wooldridge, P. J. and Cohen, R. C.: SOA from limonene: Role of NO3 in its generation and degradation, Atmos. Chem. Phys., 11(8), 3879–3894, doi:10.5194/acp-11-3879-2011, 2011.

Fuentes, J., Lerdau, M., Atkinson, R., Baldocchi, D., Bottenheim, J., Ciccioli, P., Lamb, B., Geron, C., Gu, L., Guenther, A., Sharkey, T. and W, S.: Biogenic hydrocarbons in the atmospheric boundary layer: a review, Bull. Am. Meteorol. Soc., 81, 1537–1575, doi:http://dx.doi.org/10.1175/1520-0477(2000)081<1537:BHITAB>2.3.CO;2, 2000.

Funk, J. L., Jones, C. G., & Lerdau, M. T. Defoliation effects on isoprene emission from Populus deltoides. Oecologia, 118(3), 333–339, doi:10.1007/s004420050734, 1999.

Geron, C., Owen, S., Guenther, a, Greenberg, J., Rasmussen, R., Huibai, J., Li, Q. and Baker, B.: Volatile organic compounds from vegetation in southern Yunnan Province, China: Emission rates and some potential regional implications, Atmos. Environ., 40(10), 1759–1773, doi:10.1016/j.atmosenv.2005.11.022, 2006.

Ghirardo, A., Koch, K., Taipale, R., Zimmer, I., Schnitzler, J.-P. and Rinne, J.: Determination of de novo and pool emissions of terpenes from four common boreal/alpine trees by $^{13}CO_2$ labelling and PTR-MS analysis, Plant cell Environ., 33(5), 781–792, doi:10.1111/j.1365-3040.2009.02104.x, 2010.

Ghirardo, A., Gutknecht, J., Zimmer, I., Brüggemann, N. and Schnitzler, J.-P.: Biogenic volatile organic compound and respiratory CO_2 emissions after ^{13}C-labeling: online tracing of C translocation dynamics in poplar plants, PLoS One, 6(2), e17393, doi:10.1371/journal.pone.0017393, 2011.

Ghirardo, A., Heller, W., Fladung, M., Schnitzler, J.-P. and Schroeder, H.: Function of defensive volatiles in pedunculate oak (*Quercus robur*) is tricked by the moth *Tortrix viridana*, Plant cell Environ., 35(12), 2192–2207, doi:10.1111/j.1365-3040.2012.02545.x, 2012.

Ghirardo, A., Wright, L. P., Bi, Z., Rosenkranz, M., Pulido, P., Rodríguez-Concepción, M., Niinemets, Ü., Brüggemann, N., Gershenzon, J. and Schnitzler, J.-P.: Metabolic flux analysis of plastidic isoprenoid biosynthesis in poplar leaves emitting and nonemitting isoprene., Plant Physiol., 165(1), 37–51, doi:10.1104/pp.114.236018, 2014.

Goldstein, A. H., Koven, C. D., Heald, C. L. and Fung, I. Y.: Biogenic carbon and anthropogenic pollutants combine to form a cooling haze over the southeastern United States., Proc. Natl. Acad. Sci. U.S.A., 106(22), 8835–40, doi:10.1073/pnas.0904128106, 2009.

Grote, R., Monson, R. and Niinemets, Ü.: Leaf-level models of constitutive and stress-driven volatile organic compound emissions, in Biology, Controls and Models of Tree Volatile Organic Compound Emission, edited by Ü. Niinemets and R. Monson, Springer Netherlands., 2013.

Guenther, A.: Biological and Chemical Diversity of Biogenic Volatile Organic Emissions into the Atmosphere, ISRN Atmos. Sci., 2013, 1–27, doi:10.1155/2013/786290, 2013.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J. and Zimmerman, P.: A Global-Model of Natural Volatile Organic-Compound Emissions, J. Geophys. Res., 100(D5), 8873–8892, doi:10.1029/94JD02950, 1995.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K. and Wang, X.: The model of emissions of gases and aerosols from nature version 2.1 (MEGAN2.1): An extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5, 1471–1492, doi:10.5194/gmd-5-1471-2012, 2012.

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Formatted: English (U.S.)

Guo, S., Hu, M., Guo, Q., Zhang, X., Zheng, M., Zheng, J., Chang, C. C., Schauer, J. J. and Zhang, R.: Primary sources and secondary formation of organic aerosols in Beijing, China., Environ. Sci. Technol., 46(18), 9846–53, doi:10.1021/es2042564, 2012.

Hakola, H., Tarvainen, V., Bäck, J., Ranta, H., Bonn, B., Rinne, J. and Kulmala, M.: Seasonal variation of mono- and sesquiterpene emission rates of Scots pine, Biogeosciences, 3, 93–101, doi:10.5194/bg-3-93-2006, 2006.

Hamilton, J. F., Lewis, a. C., Carey, T. J., Wenger, J. C., Borras i Garcia, E. and Muñoz, A.: Reactive oxidation products promote secondary organic aerosol formation from green leaf volatiles, Atmos. Chem. Phys., 9(1995), 3815–3823, doi:10.5194/acpd-9-3921-2009, 2009.

Harley, P., Fridd-Stroud, V., Greenberg, J., Guenther, A. and Vasconcellos, P.: Emission of 2-methyl-3-buten-2-ol by pines: A potentially large natural source of reactive carbon to the atmosphere, J. Geophys. Res., 103(D19), 25479, doi:10.1029/98JD00820, 1998.

Harley, P., Eller, A., Guenther, A. and Monson, R. K.: Observations and models of emissions of volatile terpenoid compounds from needles of ponderosa pine trees growing in situ: control by light, temperature and stomatal conductance, Oecologia, 176, 35–55, doi:10.1007/s00442-014-3008-5, 2014.

Harrison, S. P., Morfopoulos, C., Dani, K. G. S., Prentice, I. C., Arneth, A., Atwell, B. J., Barkley, M. P., Leishman, M. R., Loreto, F., Medlyn, B. E., Niinemets, Ü., Possell, M., Peñuelas, J. and Wright, I. J.: Volatile isoprenoid emissions from plastid to planet, New Phytol., 197(1), 49–57, doi:10.1111/nph.12021, 2013.

Heiden, A., Hoffmann, T., Kahl, J., Kley, D., Klockow, D., Langebartels, C., Mehlhorn, H., Sandermann, H. J., Schraudner, M., G, S. and Wildt, J.: Emission of volatile organic compounds from ozone-exposed plants, Ecol. Appl., 9(3), 1160–1167, doi:10.2307/2641386, 1999.

Heiden, A., Kobel, K., Langebartels, C., Schuh-Thomas, G. and Wildt, J.: Emissions of oxygenated volatile organic compounds from plants Part I: Emissions from lipoxygenase activity, J. Atmos. Chem., 45, 143–172, doi:10.1023/A:1024069605420, 2003.

Hellén, H., Tykkä, T. and Hakola, H.: Importance of monoterpenes and isoprene in urban air in northern Europe, Atmos. Environ., 59, 59–66, doi:10.1016/j.atmosenv.2012.04.049, 2012.

Helmig, D., Klinger, L. F., Guenther, A., Vierling, L., Geron, C. and Zimmerman, P.: Biogenic volatile organic compound emissions (BVOCs). I. Identifications from three continental sites in the U.S., Chemosphere, 38(9), 2163–2187, doi:10.1016/S0045-6535(98)00425-1, 1999.

Ho, K. F., Lee, S. C., Ho, W. K., Blake, D. R., Cheng, Y., Li, Y. S., Fung, K., Louie, P. K. K. and Park, D.: Vehicular emission of volatile organic compounds (VOCs) from a tunnel study in Hong Kong, Atmos. Chem. Phys. Discuss., 9(3), 12645–12674, doi:10.5194/acp-9-7491-2009, 2009.

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Holopainen, J. K. and Gershenzon, J.: Multiple stress factors and the emission of plant VOCs, Trends Plant Sci., 15(3), 176–184, doi:10.1016/j.tplants.2010.01.006 Available, 2010.

Iriti, M. and Faoro, F.: Chemical diversity and defence metabolism: How plants cope with pathogens and ozone pollution, Int. J. Mol. Sci., 10(8), 3371–3399, doi:10.3390/ijms10083371, 2009.

Joó, É., Dewulf, J., Amelynck, C., Schoon, N., Pokorska, O., Šimpraga, M., Steppe, K., Aubinet, M. and Van Langenhove, H.: Constitutive versus heat and biotic stress induced BVOC emissions in Pseudotsuga menziesii, Atmos. Environ., 45(22), 3655–3662, doi:10.1016/j.atmosenv.2011.04.048, 2011.

Kanchiswamy, C. N., Malnoy, M. and Maffei, M. E.: Bioprospecting bacterial and fungal volatiles for sustainable agriculture, Trends Plant Sci., 20(4), 206–211, doi:10.1016/j.tplants.2015.01.004, 2015.

Karl, T., Guenther, A., Turnipseed, A., Patton, E. G. and Jardine, K.: Chemical sensing of plant stress at the ecosystem scale, Biogeosciences, 5, 1287–1294, doi:10.5194/bg-5-1287-2008, 2008.

Karlik, J. F., McKay, A. H., Welch, J. M. and Winer, A. M.: A survey of California plant species with a portable VOC analyzer for biogenic emission inventory development, Atmos. Environ., 36(33), 5221–5233, doi:10.1016/S1352-2310(02)00569-1, 2002.

Kesselmeier, J. and Staudt, M.: Biogenic volatile organic compounds (VOC): an overview on emission, physiology and ecology, J. Atmos. Chem., 33, 23–88, doi:10.1023/A:1006127516791, 1999.

Kiendler-Scharr, A., Wildt, J., Dal Maso, M., Hohaus, T., Kleist, E., Mentel, T. F., Tillmann, R., Uerlings, R., Schurr, U. and Wahner, A.: New particle formation in forests inhibited by isoprene emissions, Nature, 461(7262), 381–4, doi:10.1038/nature08292, 2009.

Kiendler-Scharr, A., Andres, S., Bachner, M., Behnke, K., Broch, S., Hofzumahaus, A., Holland, F., Kleist, E., Mentel, T. F., Rubach, F., Springer, M., Steitz, B., Tillmann, R., Wahner, A., Schnitzler, J.-P. and Wildt, J.: Isoprene in poplar emissions: effects on new particle formation and OH concentrations, Atmos. Chem. Phys., 12(2), 1021–1030, doi:10.5194/acp-12-1021-2012, 2012.

Kim, H., Barkey, B. and Paulson, S. E.: Real refractive indices and formation yields of secondary organic aerosol generated from photooxidation of limonene and α-pinene: The effect of the HC/NOx ratio, J. Phys. Chem. A, 116(24), 6059–6067, doi:10.1021/jp301302z, 2012.

Kleist, E., Mentel, T. F., Andres, S., Bohne, A., Folkers, A., Kiendler-Scharr, A., Rudich, Y., Springer, M., Tillmann, R. and Wildt, J.: Irreversible impacts of heat on the emissions of monoterpenes, sesquiterpenes, phenolic BVOC and green leaf volatiles from several tree species, Biogeosciences, 9, 5111–5123, doi:10.5194/bg-9-5111-2012, 2012.

Klinger, L. F., Greenburg, J., Guenther, A., Tyndall, G., Zimmerman, P., M'Bangui, M., Moutsamboté, J.-M. and Kenfack, D.: Patterns in volatile organic compound emissions along a savanna-rainforest gradient in central Africa, J. Geophys. Res., 103(D1), 1443–1454, doi:10.1029/97JD02928, 1998.

Kreuzwieser, J., Scheerer, U., Kruse, J., Burzlaff, T., Honsel, A., Alfarraj, S., Georgiev, P., Schnitzler, J.-P., Ghirardo, A., Kreuzer, I., Hedrich, R. and Rennenberg, H.: The Venus flytrap attracts insects by the release of volatile organic compounds, J. Exp. Bot., 65(2), 755–766, doi:10.1093/jxb/ert455, 2014.

Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C. and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation, Environ. Sci. Technol., 40(6), 1869–1877, doi:10.1021/es0524301, 2006.

Laothawornkitkul, J., Taylor, J. E., Paul, N. D. and Hewitt, C. N.: Biogenic volatile organic compounds in the Earth system, New Phytol., 183(1), 27–51, doi:10.1111/j.1469-8137.2009.02859.x, 2009.

Lehning, A., Zimmer, W., Zimmer, I. and Schnitzler, J.-P.: Modeling of annual variations of oak (Quercus robur L.) isoprene synthase activity to predict isoprene emission rates, J. Geophys. Res., 106(D3), 3157–3166, doi:10.1029/2000JD900631., 2001.

Letunic, I. and Bork, P.: Interactive Tree Of Life (iTOL): an online tool for phylogenetic tree display and annotation, Bioinformatics, 23(1), 127–8, doi:10.1093/bioinformatics/btl529, 2006.

Letunic, I. and Bork, P.: Interactive Tree Of Life v2: online annotation and display of phylogenetic trees made easy, Nucleic Acids Res., 39, 1–4, doi:10.1093/nar/gkr201, 2011.

Liu, P.-P., von Dahl, C. C. and Klessig, D. F.: The extent to which methyl salicylate is required for signaling systemic acquired resistance is dependent on exposure to light after infection, Plant Physiol., 157(4), 2216–26, doi:10.1104/pp.111.187773, 2011.

Loreto, F. and Schnitzler, J.-P.: Abiotic stresses and induced BVOCs, Trends Plant Sci., 15(3), 154–166, doi:10.1016/j.tplants.2009.12.006, 2010.

Loreto, F., Barta, C., Brilli, F. and Nogues, I.: On the induction of volatile organic compound emissions by plants as consequence of wounding or fluctuations of light and temperature, Plant. Cell Environ., 29(9), 1820–1828, doi:10.1111/j.1365-3040.2006.01561.x, 2006.

McPherson, E. G., Simpson, J. R., Xiao, Q. and Wu, C.: Million trees Los Angeles canopy cover and benefit assessment, Landsc. Urban Plan., 99, 40–50, doi:10.1016/j.landurbplan.2010.08.011, 2011.

Mentel, T. F., Wildt, J., Kiendler-Scharr, A., Kleist, E., Tillmann, R., Dal Maso, M., Fisseha, R., Hohaus, T., Spahn, H., Uerlings, R., Wegener, R., Griffiths, P. T., Dinar, E., Rudich, Y. and Wahner, A.: Photochemical production of aerosols from real plant emissions, Atmos. Chem. Phys., 9, 4387–4406, doi:10.5194/acpd-9-3041-2009, 2009.

Mentel, T. F., Kleist, E., Andres, S., Dal Maso, M., Hohaus, T., Kiendler-Scharr, A., Rudich, Y., Springer, M., Tillmann, R., Uerlings, R., Wahner, A. and Wildt, J.: Secondary aerosol formation from stress-induced biogenic emissions and possible climate feedbacks, Atmos. Chem. Phys., 13(17), 8755–8770, doi:10.5194/acp-13-8755-2013, 2013.

Misztal, P. K., Hewitt, C. N., Wildt, J., Blande, J. D., Eller, a. S. D., Fares, S., Gentner, D. R., Gilman, J. B., Graus, M., Greenberg, J., Guenther, a. B., Hansel, a., Harley, P., Huang, M., Jardine, K., Karl, T., Kaser, L., Keutsch, F. N., Kiendler-Scharr, a., Kleist, E., Lerner, B. M., Li, T., Mak, J., Nölscher, a. C., Schnitzhofer, R., Sinha, V., Thornton, B., Warneke, C., Wegener, F., Werner, C., Williams, J., Worton, D. R., Yassaa, N. and Goldstein, a. H.: Atmospheric benzenoid emissions from plants rival those from fossil fuels, Sci. Rep., 5(February), 12064, doi:10.1038/srep12064, 2015.

Monson, R. K., Trahan, N., Rosenstiel, T. N., Veres, P., Moore, D., Wilkinson, M., Norby, R. J., Volder, A., Tjoelker, M. G., Briske, D. D., Karnosky, D. F. and Fall, R.: Isoprene emission from terrestrial ecosystems in response to global change: minding the gap between models and observations, Philos. Trans. A. Math. Phys. Eng. Sci., 365(1856), 1677–1695, doi:10.1098/rsta.2007.2038, 2007.

Morani, A., Nowak, D. J., Hirabayashi, S. and Calfapietra, C.: How to select the best tree planting locations to enhance air pollution removal in the MillionTreesNYC initiative, Environ. Pollut., 159, 1040–1047, doi:10.1016/j.envpol.2010.11.022, 2011.

Ng, N. L., Chhabra, P. S., Chan, a. W. H., Surratt, J. D., Kroll, J. H., Kwan, a. J., McCabe, D. C., Wennberg, P. O., Sorooshian, A., Murphy, S. M., Dalleska, N. F., Flagan, R. C. and Seinfeld, J. H.: Effect of NOx level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes, Atmos. Chem. Phys., 7(4), 5159–5174, doi:10.5194/acpd-7-10131-2007, 2007.

Niederbacher, B., Winkler, J. B. and Schnitzler, J. P.: Volatile organic compounds as non-invasive markers for plant phenotyping, J. Exp. Bot., doi:10.1093/jxb/erv219, 2015.

Niinemets, U.: Mild versus severe stress and BVOCs: thresholds, priming and consequences, Trends Plant Sci., 15(3), 145–53, doi:10.1016/j.tplants.2009.11.008, 2010.

Nowak, D. J.: Estimating leaf area and leaf biomass of open-grown deciduous urban trees, Forest Sci., 42, 504–507, 1996.

Nowak, D. J., Hirabayashi, S., Bodine, A. and Hoehn, R.: Modeled PM2.5 removal by trees in ten U.S. cities and associated health effects, Environ. Pollut., 178(2013), 395–402, doi:10.1016/j.envpol.2013.03.050, 2013,

Odum J, R., Hoffmann, T., Bowman, F., Collins, D., Flagan Richard, C. and Seinfeld John, H.: Gas particle partitioning and secondary organic aerosol yields, Environ. Sci. Technol., 30(8), 2580–2585, doi:10.1021/es950943+, 1996.

Ortega, J. and Helmig, D.: Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques - Part A, Chemosphere, 72, 343–364, doi:10.1016/j.chemosphere.2007.11.020, 2007.

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Pandis, S. N., Paulson, S. E., Seinfeld, J. H. and Flagan, R. C.: Aerosol formation in the photooxidation of isoprene and β-pinene, Atmos. Environ., 25(5-6), 997–1008, doi:10.1016/0960-1686(91)90141-S, 1991.

Pankow, J. F.: An absorption model of gas/particle partitioning of organic compounds in the atmosphere, Atmos. Environ., 28(2), 185–188, doi:10.1016/1352-2310(94)90093-0, 1994.

Papiez, M. R., Potosnak, M. J., Goliff, W. S., Guenther, A. B., Matsunaga, S. N. and Stockwell, W. R.: The impacts of reactive terpene emissions from plants on air quality in Las Vegas, Nevada, Atmos. Environ., 43, 4109–4123, doi:10.1016/j.atmosenv.2009.05.048, 2009.

Pellegrini, E., Cioni, P. L., Francini, A., Lorenzini, G., Nali, C. and Flamini, G.: Volatiles Emission Patterns in Poplar Clones Varying in Response to Ozone, J. Chem. Ecol., 38, 924–932, doi:10.1007/s10886-012-0162-2, 2012.

Peng, S., Piao, S., Ciais, P., Friedlingstein, P., Ottle, C., Bréon, F.-M., Nan, H., Zhou, L. and Myneni, R. B.: Surface urban heat island across 419 global big cities, Environ. Sci. Technol., 46(2), 696–703, doi:10.1021/es2030438, 2012.

Peñuelas, J. and Staudt, M.: BVOCs and global change, Trends Plant Sci., 15(3), 133–144, doi:10.1016/j.tplants.2009.12.005, 2010.

Pinto, D. M., Blande, J. D., Souza, S. R., Nerg, A.-M. and Holopainen, J. K.: Plant volatile organic compounds (VOCs) in ozone (O3) polluted atmospheres: the ecological effects., J. Chem. Ecol., 36(1), 22–34, doi:10.1007/s10886-009-9732-3, 2010.

Poeschl, U.: Atmospheric aerosols: Composition, transformation, climate and health effects, Angew. Chemie - Int. Ed., 44(46), 7520–7540, doi:10.1002/anie.200501122, 2005.

Presto, A. A. A. and Donahue, N. M.: Investigation of alpha-pinene + ozone secondary organic aerosol formation at low total aerosol mass., Environ. Sci. Technol., 40(11), 3536–3543, doi:10.1021/es052203z, 2006.

Presto, A. A., Huff Hartz, K. E. and Donahue, N. M.: Secondary organic aerosol production from terpene ozonolysis. 2. Effect of NOx concentration, Environ. Sci. Technol., 39(18), 7046–7054, doi:10.1021/es050400s, 2005.

Pun, B. K., Wu, S. Y. and Seigneur, C.: Contribution of biogenic emissions to the formation of ozone and particulate matter in the Eastern United States, Environ. Sci. Technol., 36(16), 3586–3596, doi:10.1021/es015872v, 2002.

Rollins, A. W., Kiendler-Scharr, A., Fry, J., Brauers, T., Brown, S. S., Dorn, H.-P., Dubé, W. P., Fuchs, H., Mensah, A., Mentel, T. F., Rohrer, F., Tillmann, R., Wegener, R., Wooldridge, P. J. and Cohen, R. C.: Isoprene oxidation by nitrate radical: alkyl nitrate and secondary organic aerosol yields, Atmos. Chem. Phys., 9(2), 6685–6703, doi:10.5194/acpd-9-8857-2009, 2009.

Roy, S., Beig, G. and Ghude, S.: Exposure-plant response of ambient ozone over the tropical Indian region, Atmos. Chem. Phys., 9(1), 5253–5260, doi:10.5194/acpd-9-4141-2009, 2009.

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Sakulyanontvittaya, T., Guenther, A., Helmig, D., Milford, J. and Wiedinmyer, C.: Secondary Organic Aerosol from Sesquiterpene and Monoterpene Emissions in the United States, Environ. Sci. Technol., 42(23), 8784–8790, doi:10.1021/es800817r, 2008.

Sun, J., Zhang, Q., Canagaratna, M. R., Zhang, Y., Ng, N. L., Sun, Y., Jayne, J. T., Zhang, X., Zhang, X. and Worsnop, D. R.: Highly time- and size-resolved characterization of submicron aerosol particles in Beijing using an Aerodyne Aerosol Mass Spectrometer, Atmos. Environ., 44(1), 131–140, doi:10.1016/j.atmosenv.2009.03.020, 2010.

Tholl, D., Boland, W., Hansel, A., Loreto, F., Röse, U. S. R. and Schnitzler, J.-P.: Practical approaches to plant volatile analysis, Plant J., 45(4), 540–560, doi:10.1111/j.1365-313X.2005.02612.x, 2006.

Toome, M., Randjärv, P., Copolovici, L., Niinemets, U., Heinsoo, K., Luik, A. and Noe, S. M.: Leaf rust induced volatile organic compounds signalling in willow during the infection, Planta, 232(1), 235–243, doi:10.1007/s00425-010-1169-y, 2010.

Wang, J.-L., Chew, C., Chang, C.-Y., Liao, W.-C., Lung, S.-C. C., Chen, W.-N., Lee, P.-J., Lin, P.-H. and Chang, C.-C.: Biogenic isoprene in subtropical urban settings and implications for air quality, Atmos. Environ., 79, 369–379, doi:10.1016/j.atmosenv.2013.06.055, 2013.

Wang, M., Shao, M., Chen, W., Lu, S., Liu, Y., Yuan, B., Zhang, Q., Chang, C.-C., Wang, B., Zeng, L., Hu, M., Yang, Y. and Li, Y.: Trends of non-methane hydrocarbons (NMHC) emissions in Beijing during 2002–2013, Atmos. Chem. Phys., 15(13), 1489–1502, doi:10.5194/acp-15-1489-2015, 2015.

Welter, S., Bracho-Nuñez, A., Mir, C., Zimmer, I., Kesselmeier, J., Lumaret, R., Schnitzler, J.-P. and Staudt, M.: The diversification of terpene emissions in Mediterranean oaks: lessons from a study of Quercus suber, Quercus canariensis and its hybrid Quercus afares, Tree Physiol., 32(9), 1082–1091, doi:10.1093/treephys/tps069, 2012.

Wildt, J., Kley, D., Rockel, A., Rockel, P. and Segschneider, H. J.: Emission of NO from several higher plant species, J. Geophys. Res., 102(D5), 5919–5927, doi:10.1029/96JD02968, 1997.

Wildt, J., Mentel, T. F., Kiendler-Scharr, A., Hoffmann, T., Andres, S., Ehn, M., Kleist, E., Müsgen, P., Rohrer, F., Rudich, Y., Springer, M., Tillmann, R. and Wahner, A.: Suppression of new particle formation from monoterpene oxidation by NOx, Atmos. Chem. Phys., 14(6), 2789–2804, doi:10.5194/acp-14-2789-2014, 2014.

Wu, C., Pullinen, I., Andres, S., Carriero, G., Fares, S., Goldbach, H., Hacker, L., Kasal, T., Kiendler-Scharr, a., Kleist, E., Paoletti, E., Wahner, a., Wildt, J. and Mentel, T. F.: Impacts of soil moisture on de novo monoterpene emissions from European beech, Holm oak, Scots pine, and Norway spruce, Biogeosciences, 12(1), 177–191, doi:10.5194/bg-12-177-2015, 2015.

Yang, J., McBride, J., Zhou, J. and Sun, Z.: The urban forest in Beijing and its role in air pollution reduction, Urban For. Urban Green., 3, 65–78, doi:10.1016/j.ufug.2004.09.001, 2005.

Zhang, H., Lin, Y. H., Zhang, Z., Zhang, X., Shaw, S. L., Knipping, E. M., Weber, R. J., Gold, A., Kamens, R. M. and Surratt, J. D.: Secondary organic aerosol formation from methacrolein photooxidation: Roles of NOx level, relative humidity and aerosol acidity, Environ. Chem., 9(3), 247–262, doi:10.1071/EN12004, 2012.

Zhao, J., Chen, S., Jiang, B., Ren, Y., Wang, H., Vause, J. and Yu, H.: Temporal trend of green space coverage in China and its relationship with urbanization over the last two decades, Sci. Total Environ., 442(2013), 455–65, doi:10.1016/j.scitotenv.2012.10.014, 2013.

Zhihui, W., Yuhua, B. and Shuyu, Z.: A biogenic volatile organic compounds emission inventory for Beijing, Atmos. Environ., 37(27), 3771–3782, doi:10.1016/S1352-2310(03)00462-X, 2003.

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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

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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

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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.

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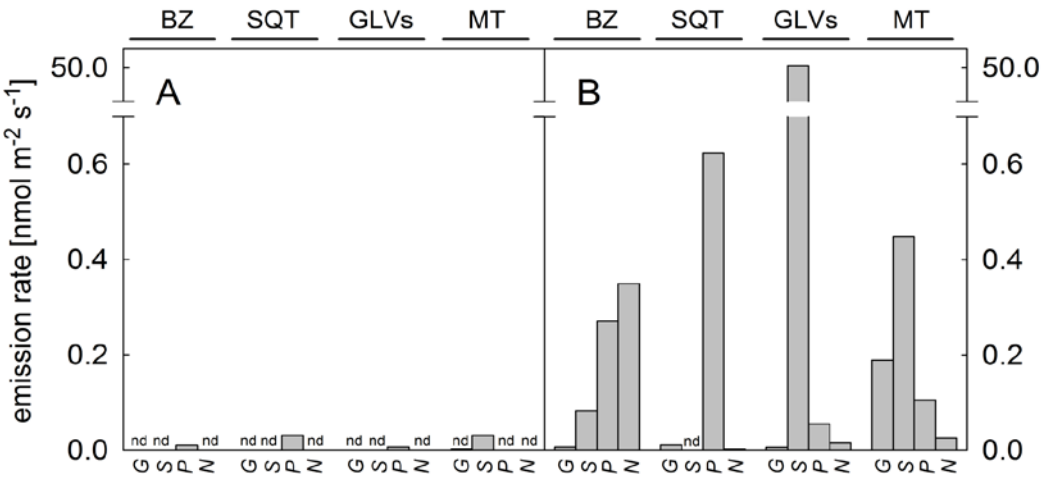


Fig.2

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.

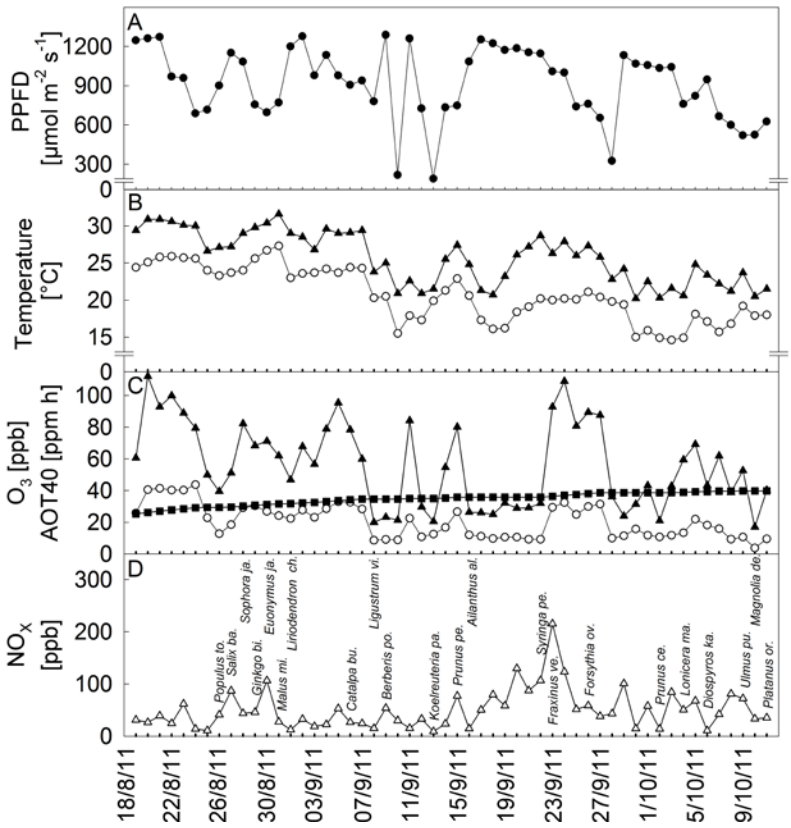


Fig.3

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.

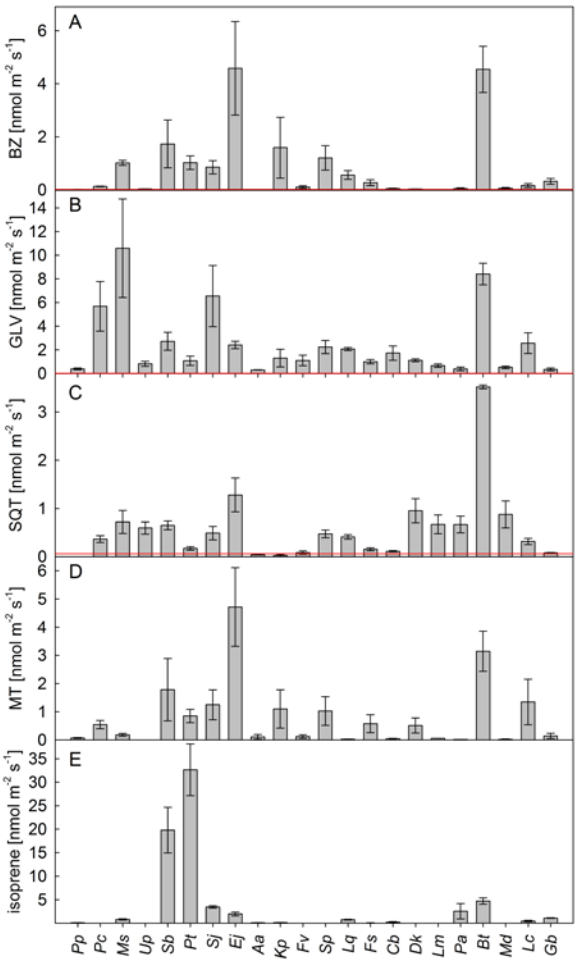
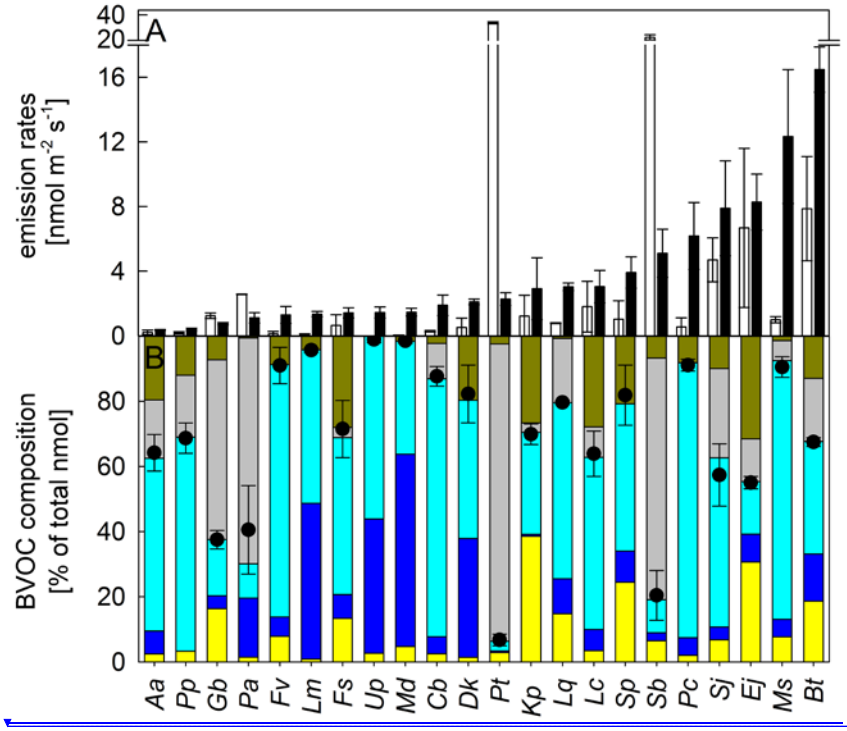


Fig.4

(**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.



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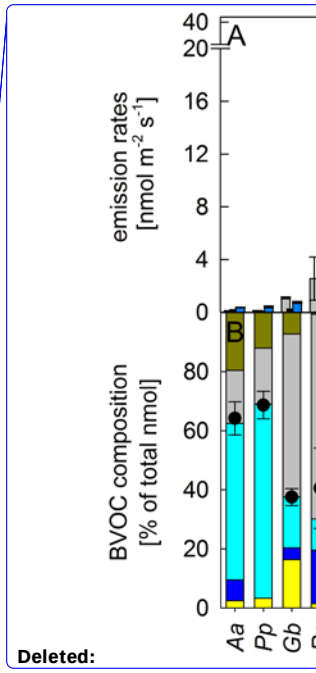

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Fig.5

(**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).

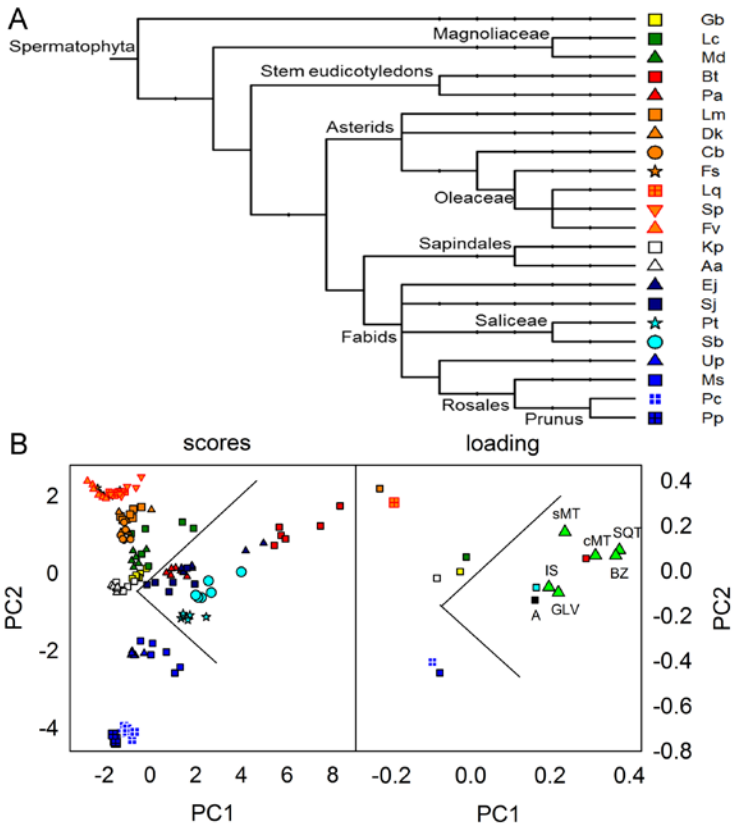
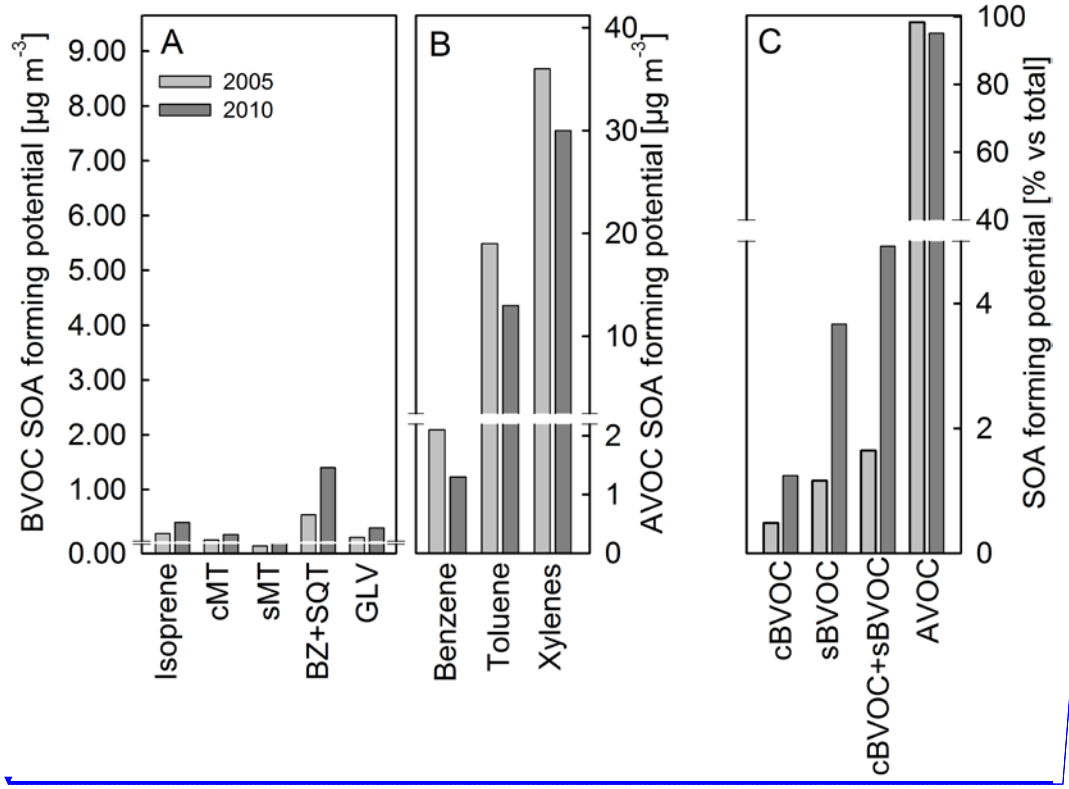
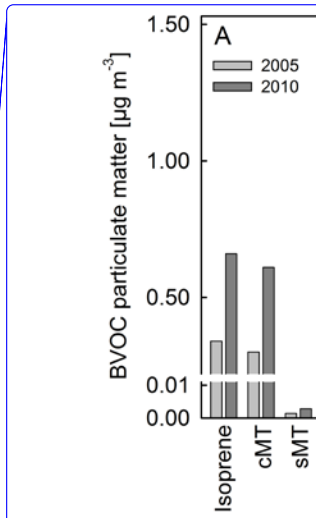


Fig.6

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.





Supplementary Materials

Urban stress-induced biogenic VOC emissions and SOA forming potentials in Beijing

Andrea Ghirardo[1],*, Junfei Xie[2,3,4]*, Xunhua Zheng[2], Yuesi Wang[2], Rüdiger Grote[5], Katja Block[1], Jürgen Wildt[6], Thomas Mentel[7], Astrid Kiendler-Scharr[7], Mattias Hallquist[8], Klaus Butterbach-Bahl[5] and Jörg-Peter Schnitzler[1]

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Figure S1

BVOC emission budget for Beijing before (2005) and after (2010) the 2008 Olympics

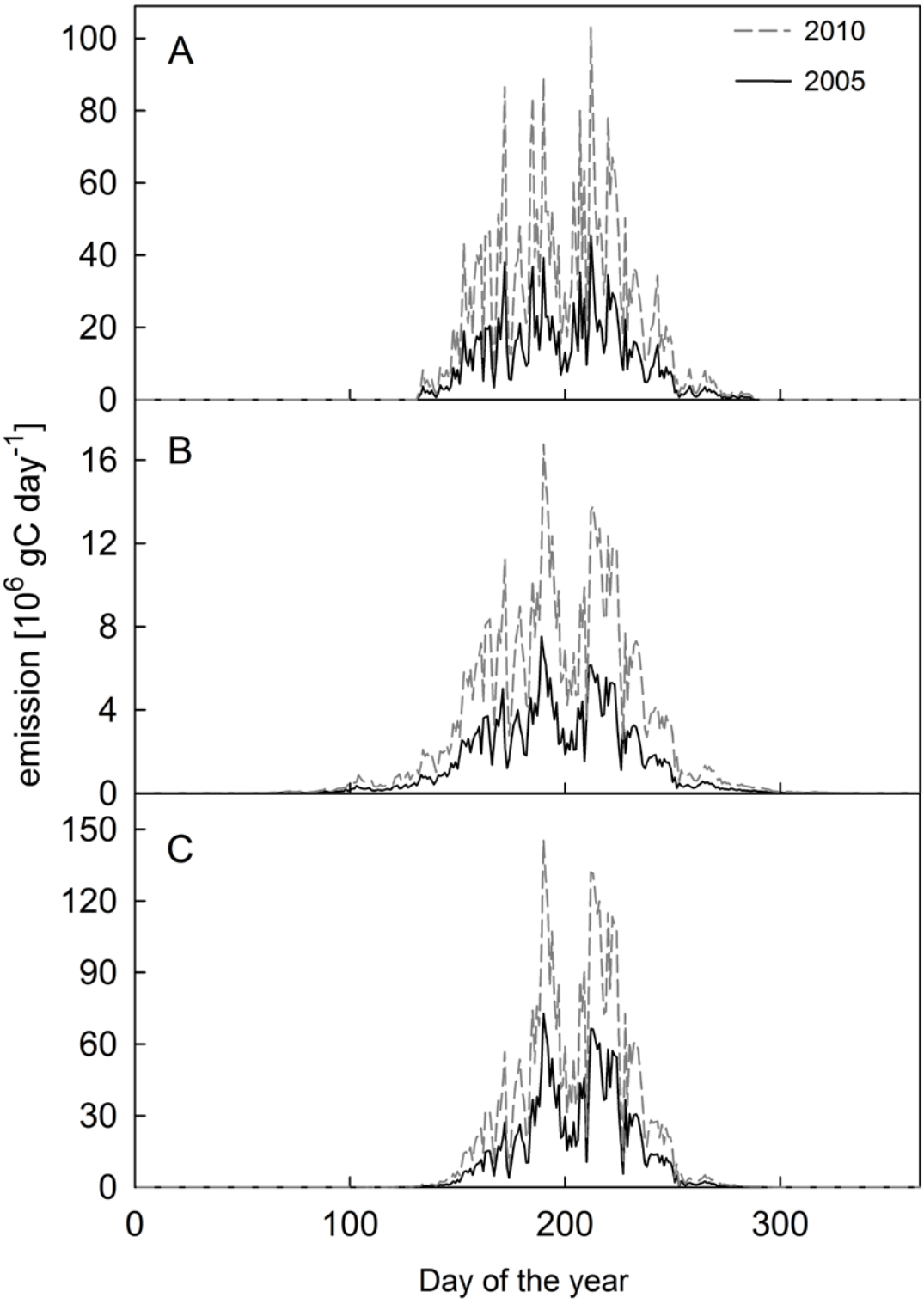

Figure S2

Relative measured (symbols) and simulated (lines) (**A**) leaf area index and (**B**) emission activity.

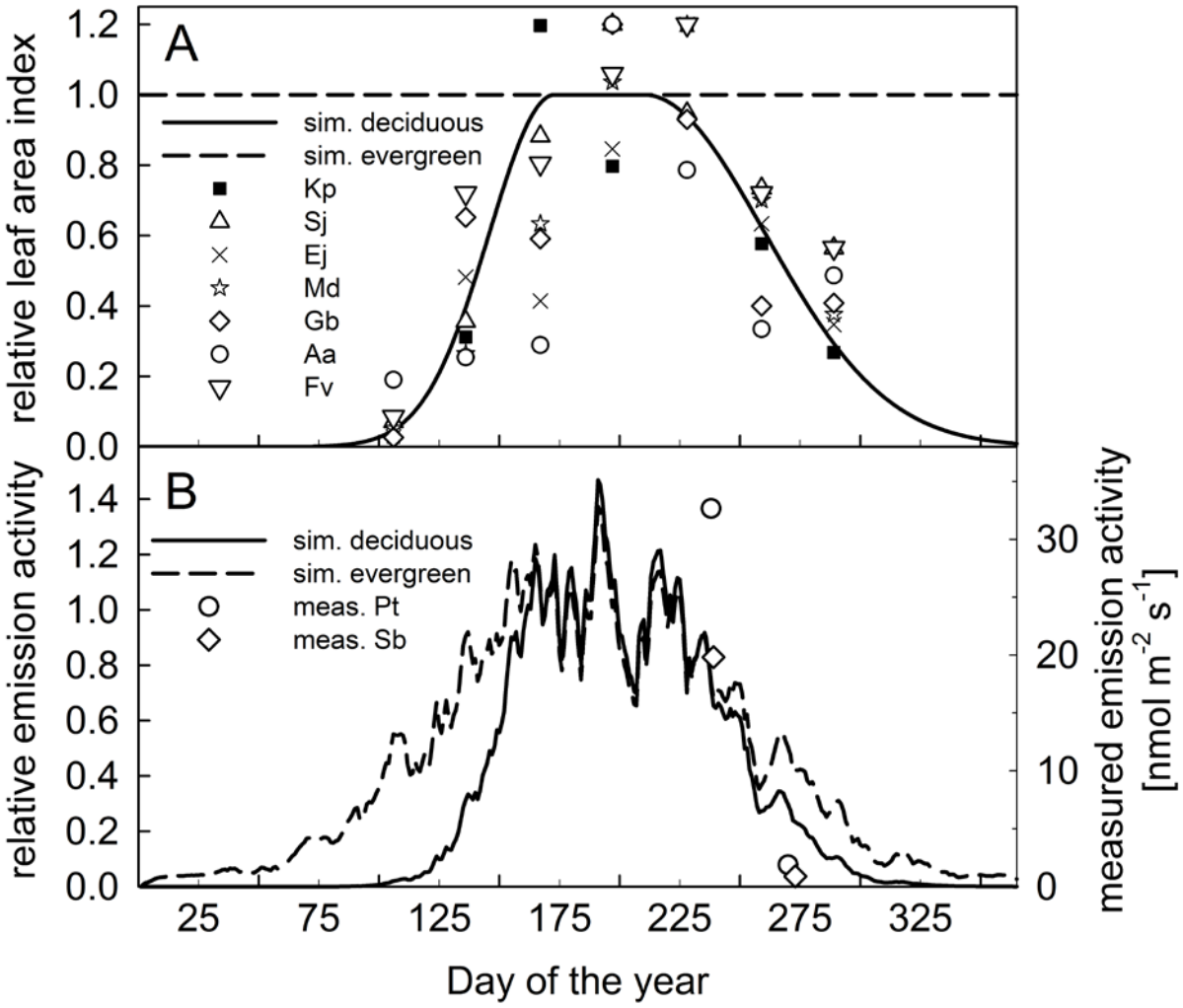

Table S1

Classification of BVOCs into 'constitutive' (c) and 'stress-induced' (s)

BVOC	Group	Class
Isoprene	Isoprene	c
α-pinene	cMT	c
α-thujene	cMT	c
Camphene	cMT	c
Sabinene	cMT	c
β-pinene	cMT	c
δ-3-carene	cMT	c
γ–terpinene	cMT	c
Limonene	cMT	c
Terpinolene	cMT	c
β-ocimene	sMT	s
β-myrcene	sMT	s
Linalool	sMT	s
Eucalyptol	sMT	s
α-cadinol	SQT	s
α-copaene	SQT	s
α-cubebene	SQT	s
α-farnesene	SQT	s
α-ylangene	SQT	s
β-bourbonene	SQT	s
γ-muurolene	SQT	s
α-cedrol	SQT	s
(*E*,*E*)-farnesol	SQT	s
Calarene	SQT	s
Geranyl acetone	SQT	s
β-(*E*)-Caryophyllene	SQT	s
Cis-caryophyllene	SQT	s
Isolongifolene	SQT	s
Junipene	SQT	s
Benzaldehyde	BZ	s
Benzeneacetaldehyde	BZ	s
Benzyl alcohol	BZ	s
Methyl benzoate	BZ	s
Benzyl benzoate	BZ	s
Methyl Salicylate	BZ	s
Phenol, o-methoxy-	BZ	s
Phenol, 2-methoxy-4-(2-propenyl)	BZ	s
(*Z*)-3-hexenol	GLV	s
(*Z*)-3-hexenylacetate	GLV	s

Table S2
Net assimilation rates (A) of the plant species measured during the Beijing survey.

Plant type	Abr.	Latin name	English name	**A** [µmol m^{-2} s^{-1}]
Trees	***Fv***	***Fraxinus velutina*** Torr.	Velvet Ash	3.8±1.8
	Md	***Magnolia denudata*** Desr.	Yulan Magnolia	2.7±0.7
	Pp	***Prunus persica*** cv. Duplex	Flowering Peach	11.0±1.6
	Aa	***Ailanthus altissima*** (Mill.) Swingle	Tree of Heaven	3.3±0.6
	Sb	***Salix babylonica*** L.	Weeping Willow	7.7±0.9
	Sj	***Sophora japonica*** L.	Japanese Pagoda Tree	7.4±0.6
	Ms	***Malus spectabilis*** (Ait) Borkh.	Chinese Flowering Crabapple	5.7±2.5
	Kp	***Koelreuteria paniculata*** Laxm.	Golden Rain Tree	3.6±0.4
	Lc	***Liriodendron chinense*** x tulipikera	Chinese Tulip Tree	4.5±1.8
	Pt	***Populus tomentosa*** Carr.	Chinese White Poplar	9.5±1.6
	Cb	***Catalpa bungei*** C.A.Mey.	Manchurian Catalpa	6.2±1.4
	Dk	***Diospyros kaki*** L.f.	Japanese Persimmon	3.0±0.7
	Pa	***Platanus* × *acerifolia*** (Ait) Willd.	London Plane	8.0±1.8
	Gb	***Ginkgo biloba*** L.	Maidenhair Tree	4.8±0.6
	Up	***Ulmus pumila*** L.	Siberian Elm	9.0±1.3
	Pc	***Prunus cerasifera*** *Ehrh.*	Pissard Plum	3.7±0.3
Shrubs	***Ej***	***Euonymus japonicus*** Thunb.	Evergreen Euonymus	6.0±0.4
	Sp	***Syringa pekinensis*** Rupr.	Broad-leaved Lilac	7.1±2.1
	Lm	***Lonicera maackii*** (Rupr.) Maxim.	Amur Honeysuckle	2.5±0.4
	Fs	***Forsythia suspensa*** (Thunb.) Vahl	Weeping Forsythia	5.9±1.7
	Lq	***Ligustrum quihoui*** Carr.	Wax Leaf Privet	6.8±1.0
	Bt	***Berberis thunbergii*** DC.	Japanese Barberry	9.0±1.0

Table S3

Potential average source strengths (Q) for secondary organic particulate matter originating from biogenic VOC (BVOC) and atmospheric concentrations (C). Estimations for 2 km height of the planetary boundary layer.

BVOC group	BVOC class	Yield	Q (2005) $g\ m^{-3}\ s^{-1}$	C (2005) $\mu g\ m^{-3}$	Q (2010) $g\ m^{-3}\ s^{-1}$	C(2010) $\mu g\ m^{-3}$
Isoprene	c	0.02	$5.8 \cdot 10^{-13}$	0.2	$1.2 \cdot 10^{-12}$	0.4
cMT	c	0.06	$2.4 \cdot 10^{-13}$	0.08	$5.3 \cdot 10^{-13}$	0.18
sMT	s	0.06	$1.3 \cdot 10^{-14}$	0.004	$3.0 \cdot 10^{-14}$	0.01
SQT+BZ	s	0.22	$1.6 \cdot 10^{-12}$	0.54	$3.9 \cdot 10^{-12}$	1.4
GLV	s	0.03	$3.7 \cdot 10^{-13}$	0.13	$8.7 \cdot 10^{-13}$	0.3
Sum	c+s			0.95		2.29

Table S4
Potential average source strengths (Q) for secondary organic particulate matter originating from anthropogenic VOC (AVOC) and atmospheric concentrations (C). Estimations for 2 km height of the planetary boundary layer.

AVOC group	Yield	Q (2005) g m^{-3} s^{-1}	C (2005) µg m^{-3}	Q (2010) g m^{-3} s^{-1}	C(2010) µg m^{-3}
Benzene	0.14	$6.2 \cdot 10^{-12}$	2.1	$3.8 \cdot 10^{-12}$	1.3
Toluene	0.14	$5.6 \cdot 10^{-11}$	19	$4.0 \cdot 10^{-11}$	13
Xylenes	0.14	$1.0 \cdot 10^{-10}$	36	$8.7 \cdot 10^{-11}$	30
Sum		$1.62 \cdot 10^{-10}$	57.1	$1.3 \cdot 10^{-10}$	44.3

Table S5A. Standard emission factors [µgC g(DW)$^{-1}$ h^{-1}] calculated from measurements data: isoprene (**EFiso**); constitutive monoterpenes from de novo production (**EFmono_P**) and storages (**EFmono_S**); stress-induced monoterpenes (**EFmono_I**); sesquiterpenes (**EFsqt**), benzenoids (**EFbz**), and green leaf volatiles (**EFglv**) . Values have been corrected according the relation of simulated maximum enzyme

	day measured	Rseas	LMA	EF_iso	EF_mono_P	EF_mono_S	EF_mono_I	EF_sqt	EF_bz	EF_glv
Ailanthus altissima	259	0.19	50.32	2.4	5.1	0.0	0.0	2.8	0.4	8.4
Berberis poiretii	252	0.34	53.20	56.6	73.6	0.0	1.9	126.7	65.4	121.1
Catalpa bungei	249	0.42	37.21	3.2	0.3	0.0	1.0	4.7	0.9	28.4
Diospyros kaki	279	0.27	58.53	0.0	13.5	0.0	0.5	39.0	0.6	18.1
Euonymus japonicus	242	0.51	43.03	19.2	46.2	23.7	0.0	37.6	53.8	28.3
Forsythia ovata	269	0.21	49.03	1.3	23.1	0.0	0.8	9.3	6.8	24.5
Fraxinus velutina	266	0.23	44.54	0.0	5.1	0.0	0.0	5.2	2.8	27.3
Ginkgo biloba	241	0.45	55.04	9.5	1.9	0.0	0.7	2.1	3.4	3.6
Koelreuteria paniculata	256	0.24	48.29	2.2	41.2	0.0	0.3	1.3	36.1	29.3
Ligustrum vicaryi	251	0.39	58.11	7.1	0.0	0.0	0.5	11.7	6.4	23.5
Liriodendron chinense	245	0.42	45.88	5.1	28.6	0.0	1.9	10.7	2.3	34.8
Lonicera maackii	277	0.14	35.79	0.0	0.0	0.0	4.9	85.5	0.6	33.7
Magnolia denudata	283	0.09	54.67	0.0	1.0	0.0	1.0	114.3	3.7	26.9
Malus micromalus	244	0.41	59.66	7.1	2.9	0.0	0.4	18.9	10.8	111.6
Platanus acerifolia	284	0.08	44.94	152.0	0.0	0.0	2.4	119.5	3.8	27.7
Populus tomentosa	238	0.43	75.92	216.7	11.1	0.0	0.2	3.4	8.2	8.5
Populus tomentosa (in fall)	270	0.10	75.92	52.1	29.0	0.0	0.1	26.6	3.1	28.1
Prunus cerasifera	275	0.15	41.30	0.0	37.6	0.0	0.0	37.6	5.6	234.5
Prunus persica	258	0.18	39.29	3.4	4.1	0.0	0.1	0.0	0.7	14.0
Salix babylonica	239	0.38	54.40	206.9	36.0	0.0	1.2	20.3	21.7	34.1
Salix babylonica (in fall)	273	0.08	54.40	43.4	11.7	0.0	0.0	14.8	3.4	63.9
Sophora japonica	240	0.50	34.57	43.5	30.5	0.0	1.0	18.4	13.0	99.0
Syringa pekinensis	265	0.22	47.85	0.0	40.5	0.0	1.0	28.6	29.3	54.2
Ulmus pumila	282	0.10	54.98	0.0	0.0	0.0	0.0	69.7	1.8	37.9

Table S5B. Standard emission factors [ugC g(DW)$^{-1}$ h^{-1}] for isoprene (**Efiso**) and monoterpenes (**Efmono**) from literature.

	Efiso	**ref**	**Efmono**	**ref**
Acer truncatum	1.0	6, 8, 33,36	1.4	7, 8, 19, 20, 33, 36
Albizia julibrissin	40.9	4, 13, 30	0.2	13, 30
Eucommia ulmoides	19.7	23	0.8	23
Robinia pseudoacacia	49.8	1, 10, 12, 14, 18, 19, 28, 34, 35, 36	3.3	18, 19, 22, 35, 36
Cedrus deodara	0.0	36, 38	3.9	5, 22, 36
Juniperus chinensis	0.3	15, 25, 26, 27, 31, 32, 36	2.1	15, 25, 26, 27, 31, 36
Picea koraiensis	2.6	16, 17, 18, 31	2.5	2, 17, 18, 31
Pinus bungeana	0.1	4, 17, 21, 26, 31, 33, 36	5.3	5, 17, 21, 26, 31, 33, 36
Pinus tabulaeformis	0.1	4, 17, 21, 26, 31, 33, 36	5.3	5, 17, 21, 26, 31, 33, 36
Platycladus orientalis	0.0	35	2.2	35
Cornus alba	0.1	9	1.6	9
Jasminum nudiflorum	0.0	29	1.5	**
Kerria japonica	3.3	**	1.5	**
Lagerstroemia indica	0.2	5, 23, 32, 36	0.0	5, 23, 36
Prunus triloba	1.9	20, 28, 37	0.2	3, 37
Sorbaria kirilowii	3.3	**	1.4	**
Weigela florida	3.3	**	1.4	**
Buxus microphylla	14.2	3, 11, 24, 26	0.1	3, 11, 24
Sabina vulgaris (Juniperus)	0.3	15, 25, 26, 27, 31, 32, 36	0.1	15, 25, 26, 27, 31, 36

** average of all other deciduous trees

ref:

1 Benjamin et al., 1996. Low-emitting urban forests: A taxonomic methodology for assigning isoprene and monoterpene emission rates. Atmos. Environ. 30, 1437-1452.

2 Bourtsoukidis et al., 2014. From emissions to ambient mixing ratios: online seasonal field measurements of VOCs over a Norway spruce-dominated forest in central Germany. ACP. 14: 6495-6510

3 Bracho-Nunez et al., 2013. Leaf level emissions of volatile organic compounds (VOC) from some Amazonian and Mediterranean plants. Biogeosciences, 10: 5855-5873.

4 Chang et al., 2012. An inventory of biogenic volatile organic compounds for a subtropical urban-rural complex. Atmos. Environ. 56: 115-123.

5 Corchnoy et al., 1992. Hydrocarbon emissions from twelve urban shade trees of the Los Angeles, California, Air Basin. Atmospheric Environment. Part B. Urban Atmosphere 26, 339-348

6 Cronn et al., 1982. Analysis of atmospheric hydrocarbons during winter MONEX. Tellus 34, 159-165.

7 Curtis et al., 2014. Biogenic volatile organic compound emissions from nine tree species used in an urban tree-planting program. Atmos. Environ. 95: 634-643.

8 Evans et al., 1982. Estimates of isoprene and monoterpene emission rates in plants. Bot. Gaz. 143, 304-310

9 Geron et al., 1994. An improved model for estimating volatile organic compound emissions from forests in the eastern United States. Journal of Geophysical Research 99(D6): 12773-12791.

10 Geron et al., 2001. Isoprene emission capacity for US tree species. Atmos. Environ. 35, 3341-3352

11 Guenther & Greenberg, 2000. Not published (ENCLOSURE Database)

12 Guenther et al.,1996. Estimates of regional natural volatile organic compound fluxes from enclosure and ambient measurements. J.Geophys.Res. 101, 1345-1359.

13 Guenther et al., 1996. Leaf, branch, stand and landscape scale measurements of volatile organic compound fluxes from U.S. woodlands. Tree Physiology 16: 17-24.

14 Guenther et al., 1994. Natural volatile organic compound emission rate estimates for U.S. woodland landscapes. Atmos. Environ. 28, 1197-1210

15 Hewitt et al., 1992. A qualitative assessment of the emission of non-methane hydrocarbon compounds from the biosphere to the atmosphere in the U.K.: present knowledge and uncertainties. Atmos. Environ. 26: 3069-3077

16 Isebrands et al, 1999. Volatile organic compound emission rates from mixed deciduous and coniferous forests in Northern Wisconsin, USA. Atmos. Environ. 33, 2527-2536

17 Karl et al., 2009. A new European plant-specific emission inventory of biogenic volatile organic compounds for use in atmospheric transport models. Biogeosciences 6, 1059-1087

18 Klinger et al., 2002. Assessment of volatile organic compound emissions from ecosystems of China. J.Geophys.Res. 107(D21): 4603.

19 Lamb et al., 1983. Natural hydrocarbon emission rate measurements from vegetation in Pennsylvania and Washington. PB84-124981. Nat. Tech. Inf. Serv.. Springfield, Virginia, U.S.A., US. Environmental Protection Agency

20 Lamb et al., 1987. A national inventory of biogenic hydrocarbon emissions. Atmos. Environ. 21(8): 1695-1705.

21 Lenz et al., 1997. Scaling up the biogenic emissions from test sites at Castelporziano. Atmos. Environ. 31(SI): 239-250.

22 Noe et al., 2008. Monoterpene emissions from ornamental trees in urban areas: a case study of Barcelona, Spain. Plant Biol 10, 163-169

23 Nowak et al., 2002. Brooklyn's urban forest.In. Newtown Square, PA: U. S. 1-107.

24 Owen et al., 1998 PhD Thesis Lancaster University (from ENCLOSURE Database)

25 Owen et al., 2000. Extrapolating branch enclosure measurements to estimates of regional scale biogenic VOC fluxes in the northwestern Mediterranean basin. Journal of Geophysical Research, 105(D9): 11573-11584

26 Owen et al., 2001. Volatile organic compounds (VOCs) emitted from 40 Mediterranean plant species: VOC speciation and extrapolation to habitat scale. Atmos. Environ. 35(32): 5393-5409.

27 Papiez et al., 2009. The impacts of reactive terpene emissions from plants on air quality in Las Vegas, Nevada. Atmos. Environ. 43(27): 4109-4123.

28 Préndez et al., 2013. Biogenic volatile organic compounds from the urban forest of the Metropolitan Region, Chile. Environmental Pollution 183: 143-150.

29 Rasmussen, 1978. "Isoprene plant species list" Special report of Air Pollut. Res. Section, Washington State University,Pullman.

30 Singh et al., 2014. Ozone forming potential of tropical plant species of the Vidarbha region of Maharashtra state of India. Urban Forestry & Urban Greening 13(4): 814-820.

31 Steinbrecher et al., 1999. A Revised Parameterisation for Emission Modelling of Isoprenoids for Boreal Plants. Biogenic VOC emissions and photochemistry in the boreal regions of Europe – Biphorep: European Commission.

32 Tambunan et al., 2006. Isoprene emission from tropical trees in Okinawa Island, Japan. Chemosphere, 65: 2138-2144.

33 Tiwary et al., 2013. Systems scale assessment of the sustainability implications of emerging green initiatives. Environmental Pollution 183: 213-223.

34 Wang et al., 2002. Study on emission of isoprene from major plants living in Taihu Basin. Chinese Bulletin of Botany (in Chinese). 19(2):224-230; http://wenku.baidu.com/view/ab5bfe2bdd36a32d737581eb.html

35 Wang et al., 2003. A biogenic volatile organic compounds emission inventory for Beijing. Atmos. Environ. 37, 3771-3782

36 Winer et al., 1983. Investigation of the role of natural hydrocarbons in photochemical smog formation in California. Contract No. AO-056-32. 1983. Riverside, California, U.S.A., Statewide Air Pollution Research Center.

37 Winer et al., 1992: Emission rates of organics from vegetation in California's central valley, Atmos. Environ. 26a, 2647–2659.

38 Xiaoshan et al., 2000. Seasonal variations of isoprene emissions from deciduous trees. Atmos. Environ. 34(18): 3027-3032.

Table S5C. Height, diameter at breast height (in case of trees) or crown diameter (in case of shrubs) used for calculating the BVOC emission budget.

Plant species	morphological type	phenological type	height	dbh	crown diam
Berberis poiretii	shrub	deciduous	1.4	-	1.3
Cornus alba	shrub	deciduous	1.2	-	0.5
Forsythia ovata	shrub	deciduous	2.1	-	2.1
Jasminum nudiflorum	shrub	deciduous	0.9	-	1
Kerria japonica	shrub	deciduous	1.4	-	2.1
Lagerstroemia indica	shrub	deciduous	1.8	-	0.9
Ligustrum vicaryi	shrub	deciduous	1.1	-	1.3
Lonicera maackii	shrub	deciduous	3.5	-	3.6
Prunus triloba	shrub	deciduous	2.4	-	3
Sorbaria kirilowii	shrub	deciduous	2.0	-	1.9
Syringa pekinensis	shrub	deciduous	2.9	-	2.8
Weigela florida	shrub	deciduous	1.8	-	0.5
Acer truncatum	tree	deciduous	8.5	17.4	-
Ailanthus altissima	tree	deciduous	9	18.1	-
Albizia julibrissin	tree	deciduous	8.1	16.7	-
Catalpa bungei	tree	deciduous	7.6	16.3	-
Diospyros kaki	tree	deciduous	8	13.9	-
Eucommia ulmoides	tree	deciduous	10.1	25.3	-
Fraxinus velutina	tree	deciduous	10.4	19.9	-
Ginkgo biloba	tree	deciduous	8.9	16.6	-
Koelreuteria paniculata	tree	deciduous	10.2	22.3	-
Liriodendron chinense	tree	deciduous	8.3	15.8	-
Magnolia denudata	tree	deciduous	3.8	5.7	-
Malus micromalus	tree	deciduous	4.7	15	-
Platanus acerifolia	tree	deciduous	10.5	23.2	-
Populus tomentosa	tree	deciduous	14.6	30.1	-
Populus tomentosa (in fall)	tree	deciduous	14.6	30.1	-
Prunus cerasifera	tree	deciduous	4.9	16.6	-
Prunus persica	tree	deciduous	3	13.8	-
Robinia pseudoacacia	tree	deciduous	10.5*	22.0*	-
Salix babylonica	tree	deciduous	11.3	23.6	-
Salix babylonica (in fall)	tree	deciduous	11.3	23.6	-
Sophora japonica	tree	deciduous	10.5	23.5	-
Ulmus pumila	tree	deciduous	11.4	18.7	-
Buxus microphylla	shrub	evergreen	1.3	-	1.5
Euonymus japonicus	shrub	evergreen	1.3	-	0.3
Sabina vulgaris (Juniperus)	shrub	evergreen	0.8	-	0.3
Cedrus deodara	tree	evergreen	8.7	24.1	-
Juniperus chinensis	tree	evergreen	8.0	15.4	-
Picea koraiensis	tree	evergreen	4.2	13.8	-
Pinus bungeana	tree	evergreen	6.2	14.8	-

Pinus tabulaeformis	tree	evergreen	5.0	15.1	-
Platycladus orientalis	tree	evergreen	7.8	18.7	-

* calculated as average of literature values from other deciduous shrub species

Table S6
Age and size details of the plant species measured during the Beijing survey.

Abr.	Age (years）	Height (m)
Sj	25	6
Gb	20	8
Ej	12	1
Ms	13	5
Lc	10	8
Cb	14	9
Lq	12	0.6
Bt	13	1
Kp	20	7
Pp	10	4
Aa	15	12
Sp	10	2
Fv	18	12
Fs	12	2
*Pt**	2	2.4
*Sb**	2	1.1
Pc	9	5
Lm	8	3
Dk	20	6
Up	13	7
Md	15	4
Pa	10	4

Table S7

(**A**) Taxonomic data loaded as input data into iTOL (http://itol.embl.de/) for the generation of the (**B**) phylogenetic tree of the 22 plant species analyzed in the Beijing survey.

A) Input data: Taxonomic data

Populus_tomentosa
Prunus_persica
Catalpa_bungei
Fraxinus_velutina
Diospyros_kaki
Liriodendron_chinense
Prunus_cerasifera
Malus_spectabilis
Platanus_acerifolia
Ailanthus_altissima
Sophora_japonica
Ginkgo_biloba
Forsythia_suspensa
Ligustrum_quihoui
Berberis_thunbergii
Koelreuteria_paniculata
Magnolia_denudata
Lonicera_maackii
Ulmus_pumila
Euonymus_japonicus
Syringa_pekinensis
Salix_babylonica

B) Output data: Phylogenetic tree with internal nodes

((((((((((((((Liriodendron_chinense)Liriodendron,(Magnolia_denudata)Magnolia)Magnoliaceae)Magnoliales)Magnoliidae,((((((Berberis_thunbergii)Berberis)Berberidoideae)Berberidaceae)Ranunculales,(((Platanus_acerifolia)Platanus)Platanaceae)Proteales)stem_eudicotyledons,(((((((Lonicera_maackii)Lonicera)Caprifoliaceae)Dipsacales)campanulids,(((Diospyros_kaki)Diospyros)Ebenaceae)Ericales,(((((Catalpa_bungei)Catalpa)Catalpeae)Bignoniaceae,(((Ligustrum_quihoui)Ligustrum,(Syringa_pekinensis)Syringa,(Fraxinus_velutina)Fraxinus)Oleeae,((Forsythia_suspensa)Forsythia)Forsythieae)Oleaceae)Lamiales)lamiids)asterids,((((((Populus_tomentosa)Populus,(Salix_babylonica)Salix)Saliceae)Salicaceae)Malpighiales,(((Euonymus_japonicus)Euonymus)Celastraceae)Celastrales,(((((Sophora_japonica)Sophora)Sophoreae)Papilionoideae)Fabaceae)Fabales,(((((Malus_spectabilis)Malus)Maleae,((Prunus_cerasifera,Prunus_persica)Prunus)Amygdaleae)Maloideae)Rosaceae,((Ulmus_pumila)Ulmus)Ulmaceae)Rosales)fabids,((((Koelreuteria_paniculata)Koelreuteria)Sapindaceae,((Ailanthus_altissima)Ailanthus)Simaroubaceae)Sapindales)malvids)rosids)Pentapetalae)Gunneridae)eudicotyledons)Mesangiospermae)Magnoliophyta,(((((Ginkgo_biloba)Ginkgo)Ginkgoaceae)Ginkgoales)Ginkgoidae)Acrogymnospermae)Spermatophyta)Euphyllophyta)Tracheophyta)Embryophyta)Streptophytina)Streptophyta)Viridiplantae)Eukaryota)cellular_organisms);