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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Urban stress-induced biogenic VOC emissions impact secondary aerosol formation in Beijing" *by* A. Ghirardo et al.

Anonymous Referee #2

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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

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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.

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.

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.

General Comments

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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 side-project 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.

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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. 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.

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?

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

Section 2.8: Please make it more clear that the yields used for this calculation were

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"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).

Sensitivity and Quantitative Error Analysis Are Neglected

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?

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

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any literature support for making this assumption in this area?

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.

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.

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

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also include an investigation of their potential impact on oxidant reactivity or ozone concentrationsâĂŤboth 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.

Other Comments

In the abstract authors state that "sBVOCs can significantly contribute ($\sim$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.

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.

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.

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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?

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.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 23005, 2015.