

***Interactive comment on* “Chemical characterisation of atmospheric aerosols during a 2007 summer field campaign at Brasschaat, Belgium: sources and source processes, time series, diel variations, and temperature dependencies” by Y. Gómez-González et al.**

Anonymous Referee #2

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Overall Comments

This manuscript presents detailed chemical measurements made from PM_{2.5} collected from a forested field site that is heavily impacted by urban pollution in Belgium during the summer of 2007. In addition to the detailed chemical measurements obtained for both the gas- (e.g., NO_x, SO₂, O₃) and aerosol-phase (e.g., WSOC, water-soluble inorganics, MSA, etc.) constituents, the authors also collected meteorological data (i.e.,

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T, RH, radiation, precipitation, wind speed, and wind direction). This is a unique data set that is used to try and determine sources, source processes, time series, and diurnal variations of the organic species. Of particular significance is the quantification of novel biogenic organic aerosol (OA) tracers, including several terpenoic acids, such as terpenylic, terebic, homoterpenylic, and MBTCA, as well as several organosulfates and nitrooxy organosulfates. Many of these novel biogenic OA tracers have not been previously quantified in ambient aerosol samples. The authors employ LC/ESI-MS (operated in the negative ion mode) to characterize and quantify these novel species. The use of LC/ESI-MS in this study is excellent and the selection of surrogate standards (when authentic standards were not available) was certainly appropriate since the authors took into account the differences in ionization efficiencies due to changes in the mobile phase conditions. More specifically, the authors selected surrogate standards that eluted around the same time as the novel biogenic OA tracers. The quantification of these novel tracer species certainly provides insights into the formation of biogenic SOA in the atmosphere. Many of the observed trends and correlations correspond to previous laboratory findings. The abundances of many of these tracer compounds appeared highest when temperature was at its highest. However, a few species, including cis-pinic acid, caric acid, limonic acid, and the alpha-pinene-related MW 295 nitrooxy organosulfates peaked at night. Many hypotheses were suggested by the authors as to why this was the case. Due to the lack of laboratory studies on biogenic SOA formation from NO₃ oxidation, the authors can only speculate as to why these species might peak at night. Overall, this manuscript is well organized, concise, well written, and will certainly promote further research by other groups (likely in other locations where biogenic VOC emissions are most important). Due to the fact that many of the biogenic OA tracers examined in this study have remained unquantified in field studies, this study is important to include in the growing body of literature on biogenic SOA formation. The research community cannot assess the importance of some of the previously proposed pathways, such as acid-catalyzed heterogeneous reactions, leading to biogenic SOA formation without this kind of field data. I recommend this study be

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published in Atmospheric Chemistry and Physics once the authors address my specific comments below.

Specific Comments:

1.) Title of Manuscript:

Have the authors considered changing the title to reflect that most of the analyses is focused on biogenic SOA formation? Maybe the following title is more appropriate?

"Chemical characterisation of atmospheric fine aerosols during a 2007 summer field campaign at Brasschaat, Belgium: sources and source processes of biogenic secondary organic aerosol."

2.) Aerosol Acidity and Liquid Water Content:

Since you have IC data throughout this campaign, have you tried estimating aerosol acidity (or some proxy such as nitrate-corrected ammonium-to-sulfate ratio) for your samples? Since you measure and quantify several organosulfate species derived from BVOC oxidation, it seems important to try and correlate this data to some measure (or proxy) of aerosol acidity, especially since previous laboratory work has shown that these only form when acidified sulfate seed aerosols are present (Gomez-Gonzalez et al., 2008; Surratt et al., 2008). There are several studies suggesting that acid-catalyzed particle-phase reactions are important for organosulfate species to form; however, recent studies have also suggested that irradiation of wet aerosols (even neutral ones) might be more important (Noziere et al., 2010, GRL; Perri et al., 2010, Atmos. Environ.) in the atmosphere. Since the mechanism of organosulfate formation in the atmosphere remains uncertain, I think this exercise might be warranted for this study. I refer the authors to recent work by Tanner et al. (2009, Atmos. Environ.). In Tanner et al. (2009), aerosol acidity was estimated from IC data by calculating the nitrate-corrected ammonium-to-sulfate ratios in ambient aerosol collected from the southeastern U.S.

Besides estimating aerosol acidity from the nitrate-corrected ammonium-to-sulfate ra-

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tios, the authors could consider an alternative approach. Recently Xue et al. (2011, Atmos. Environ) used their inorganic composition and meteorological data as inputs into the Aerosol Inorganic Model (AIM-III) (Clegg et al., 1998ab, JPCA) in order to estimate in situ pH through the calculation of H⁺ amount and aerosol liquid water content (LWC). I think this could also be a good approach.

In either case, I encourage the authors to use their IC data to estimate aerosol acidity, especially since biogenic SOA formation has been shown to be enhanced in the presence of acidic aerosols (Offenberg et al., 2009, EST). I would try to correlate this estimate of aerosol acidity to all of the biogenic OA tracers (i.e., don't limit this analysis only to the organosulfates).

Lastly, I should state if you used the AIM-III model, you could estimate aerosol LWC. It would be interesting to see if these novel biogenic OA tracers correlate to aerosol LWC, especially since many groups are now suggesting from laboratory studies the importance of the aqueous phase in forming SOA.

3.) Section 3.2, Lines 4-6:

The authors state that no clear diurnal variations were observed for MSA and low-molecular-weight dicarboxylic acids, suggesting that they are aged products formed over a relatively long time scale.

How do the authors know these are aged products? I'm not sure I agree, especially without some reference to prior work on this. Is it not possible that the LMW DCAs come from the oxidation of anthropogenic VOCs, like that monocyclic aromatics (Fisseha et al., 2004, Anal Chem)? I worry here that it is not solely aging, but some other source like anthropogenic VOC oxidation or aqueous-phase chemistry.

4.) Night-time Peak of Certain OA Tracers:

The authors state that cis-pinic acid, caric acid, limonic acid, and the alpha-pinene-related MW 295 nitrooxy organosulfates peaked at night. The authors can only specu-

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late as to why this is the case. Do the authors have access to NO_y data? If so, have you tried correlating this to these biogenic OA tracers that peak at night? If there was a significant correlation that might indicate the importance of NO₃ radical chemistry. Since monoterpene emissions typically peak later in the day (after isoprene) they likely react with NO₃ at night. Unfortunately, laboratory studies are lacking that examine NO₃ radical chemistry with monoterpenes.

5.) Organosulfates contribution to OC

It might be worth stating specifically in the discussion section the maximum percentage contribution of organosulfates to the OC mass.

6.) Principal Component Analysis (PCA)

This component of the manuscript seems a bit disjointed and not fully described. Do you know what these components mean? Can you attribute these components to types of sources? It isn't clear to me what the authors are trying to do with this analysis.

7.) Temperature

I only want to make a comment here about the temperatures observed during this campaign. It seems your temperature only reaches a maximum of 25 C. This temperature is much lower than what is typically observed in the S.E. USA during the summer (i.e., 30-40 C). Thus, I wonder how much these biogenic OA tracers would contribute in a location like the S.E. USA, especially since there are both high temperatures and large emissions of BVOCs in this region. It likely makes some sense as to why these biogenic OA tracers minorly contribute to the total OC at this location. Thus, are the authors concerned where the remaining unclassified OC fraction is coming from? For example, are anthropogenic VOCs more important? Of course, I recognize the latter question is the "million dollar question" right now in atmospheric aerosol research.

8.) Comparison to other field studies in Europe

Since there are so few studies on quantifying biogenic OA tracers, I think it is worth

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while making some comparisons to a recent study published by Kristensen and Glasius (2011, Atmos. Environ). The authors from this recent study focused on many of the same compounds quantified here. They observed similar diurnal trends and also observed small concentrations (i.e., a few ng m⁻³) of these novel biogenic OA tracers. This is also due to the fact that the temperatures at this forested site in Denmark were quite low (i.e., below 20 C).

Minor Comments:

1.) Figures 3, 4, 5:

The x-axes on these figures are very hard to read. I would highly encourage the authors to increase the size of the font on these axes so that the reader can more easily read the dates.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 23541, 2011.

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