

## ***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.***

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We thank reviewer #2 for a careful examination of our manuscript and for many thoughtful suggestions to improve its quality.

Reviewer comments (RC): 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 atmo-

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

Author response (AR): The suggestion of the reviewer to modify the title has been followed.

RC: 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 ratios, 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<sup>+</sup> 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

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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.

AR: The suggestion of the reviewer to use the IC data to estimate aerosol acidity and to use these data to better interpret the SOA tracer data is well taken. It turns out that we have a recent article in which IC data from the 2007 Brasschaat campaign have been used to estimate the aerosol acidity (Maenhaut et al., 2011). The aerosol acidity results pertaining to the 2007 Brasschaat campaign have been added to the revised manuscript in a separate paragraph at the end of Section 3.2 (Concentrations and time series of LMW DCAs and selected ionic species) as follows: "In a recent study, the IC data were used to estimate the aerosol acidity of the PM<sub>2.5</sub> samples collected during the 2007 Brasschaat campaign (Maenhaut et al., 2011). The results showed that the acidic species were fairly well neutralised. It was therefore thought that MSA and the LMW DCAs, which were measured in addition to sulfate, nitrate, and chloride by Maenhaut et al. (2011), were mainly present in the salt form and not so much as free acids. NH<sub>4</sub><sup>+</sup> played a very important role in the neutralisation of the acidic species, as it accounted, on average, for 85% of the summed cation equivalents in the sample set." Further, these data were used to provide a possible explanation for the fairly low concentrations of terpenic acids and the organosulfates, which each contribute with only 0.6% to the OC. In the middle of Section 3.3 (Concentrations and time series of terpenic acids and organosulfates) the following paragraph has been included: "A possible reason for the rather low concentrations of the terpenic acids and the organosulfates, which each contributed, on average, with only 0.6% to the OC, is that the PM<sub>2.5</sub> aerosol at Brasschaat was fairly well neutralised, as was evident from the aerosol acidity that was estimated on the basis of IC data (Maenhaut et al., 2011). In this context, laboratory studies suggests that biogenic SOA formation is enhanced

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in the presence of acidic aerosols (Surratt et al., 2007b; Offenberg et al., 2009) and acid-catalysed particle-phase reactions are important for organosulfate species to form (e.g., Gómez-González et al., 2008; Surratt et al., 2008, 2010)."

Ref.:

Offenberg, J. H., Lewandowski, M., Edney, E. O., Kleindienst, T. E., and Jaoui, M.: Influence of aerosol acidity on the formation of secondary organic aerosol from biogenic precursor hydrocarbons, *Environ. Sci. Technol.*, 43, 7742–7747, 2009.

Surratt, J. D., Lewandowski, M., Offenberg, J. H., Jaoui, M., Kleindienst, T. E., Edney, E. O., and Seinfeld, J. H.: Effect of acidity on secondary organic aerosol formation from isoprene, *Environ. Sci. Technol.*, 41, 5363–5369, 2007b.

RC: 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.

AR: We agree that anthropogenic VOCs have to be taken into account as a source for LMW DCAs. The following modifications were made: Introduction: sentence added: "LMW DCAs are among the most abundant constituents of atmospheric aerosols, originate from a multitude of anthropogenic and natural sources, and result from both primary emissions and gas-to-particle conversion processes (e.g., Rogge et al., 1993; Chebbi and Carlier, 1996; Fisseha et al., 2004; Legrand et al., 2005)." Section 3.2: modification made: "No clear diel variations were observed for MSA and the LMW DCAs. This behaviour could be expected for MSA which is believed to originate from long-range transport of maritime air (Maenhaut et al., 2011). The lack of clear diel

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variations for the LMW DCAs may be due to the contribution from anthropogenic precursors, such as monocyclic aromatics (e.g., Fisseha et al., 2004) and/or to aqueous phase chemistry (e.g., Legrand et al., 2005)."

RC: 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 speculate as to why this is the case. Do the authors have access to NO<sub>y</sub> 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 NO<sub>3</sub> radical chemistry. Since monoterpene emissions typically peak later in the day (after isoprene) they likely react with NO<sub>3</sub> at night. Unfortunately, laboratory studies are lacking that examine NO<sub>3</sub> radical chemistry with monoterpenes.

AR: We have no access to NO<sub>y</sub> data; hence, a correlation with the importance of NO<sub>3</sub> radical chemistry cannot be made. As far as we are aware, only the study of Surratt et al. (2008) reports that the MW 295  $\alpha$ -pinane-related nitrooxy organosulfates are formed in the presence of NO<sub>3</sub> radicals. In response, we have made the following modification in Section 3.3 to account for the possibility that the night-time species possibly originate from monoterpene emissions that occur later during day-time or at night: "Furthermore, it is also possible that the portion of the MW 295 nitrooxy organosulfates, cis-pinic, caric, and limonic acid, which is formed in the morning, is not stable during day-time and is converted to higher-generation oxidation products through OH radical-initiated reactions, while the portion that is formed at night results from oxidation of monoterpene emissions that occur later during day-time or at night; additional research to test this hypothesis is warranted."

RC: 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.

AR: This has been specified in the revised version: "The sum of the 7 organosulfates

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and nitrooxy organosulfates analysed ranged from 2 ng m<sup>-3</sup> to 290 ng m<sup>-3</sup> and represented, on average, 0.6% of the OC, with a maximum of 1.8%."

RC: 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.

AR: To motivate the use of PCA, the following sentence has been included in the revised version: "The purpose of performing PCA on a multivariate data set is to transform the many intercorrelated variables into a more limited set of independent, uncorrelated variables (Harman, 1976), which are called components. When doing a PCA on a data set of atmospheric aerosol characteristics and associated meteorological parameters, the resulting components may represent sources or source processes, and often enable one to identify the main sources of the atmospheric aerosol." In the discussion of the first component, we added: "This first component represents organic aerosol and specific organic compounds, whose formation is driven by the temperature". In the discussion of the fourth component we included: "The fourth component seems thus to indicate night-time formation processes." Furthermore, we included the following for components 5 and 6: "Component 5, which is very highly or highly loaded with Cl, Na, Mg, and MSA, is clearly a marine component, whereas component 6, with its loadings for EC, NO, and NO<sub>2</sub>, represents fossil fuel combustion sources, including diesel traffic".

Ref.:

Harman, H. H.: Modern Factor Analysis, 3rd ed., rev., University of Chicago Press, Chicago, Ill., 1976.

RC: 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.

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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.

AR: We were indeed not very fortunate with our Belgian weather during the campaign because we only had temperatures above 22 °C during the first 10 days. It is logical to assume that the concentrations of the measured species can be expected to be much higher in a location like the S.E. USA, where temperatures and biogenic emissions are much higher during summer. Of course, we are puzzled about the remaining unclassified OC at our location and can only speculate that anthropogenic VOCs are likely very important at our site.

RC: 8.) Comparison to other field studies in Europe Since there are so few studies on quantifying biogenic OA tracers, I think it is worthwhile 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<sup>-3</sup>) 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).

AR: The recent article by Kristensen and Glasius (2011) has been referred to in the revised version: it has been mentioned in the Introduction and has been discussed in Results and Discussion where appropriate. 1. Introduction (3rd sentence): "Organic chemical characterisation of fine ambient aerosols has mainly been performed for forest sites, which are little perturbed by urban emissions, such as Hyytiälä, Finland (e.g., Kourtchev et al., 2005, 2008a; Parshintsev et al., 2010), K-pusztá, Hungary (e.g., Ion

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et al., 2005; Kourtchev et al., 2009), and Silkeborg, Denmark (Kristensen and Glasius, 2011), but studies for vegetated areas in Europe that are affected by urban pollution are rather limited (e.g., Kourtchev et al., 2008b, 2011; Zhang et al., 2010)." 3.1 Measurement of terpenoic acids and organosulfates (2nd sentence): "Several field studies have been performed where terpenoic acids have been measured (for a review, see Hallquist et al., 2009); however, the number of field studies where organosulfates and nitrooxy organosulfates have been measured is rather limited (Iinuma et al., 2007b; Worton et al., 2011; Kristensen and Glasius, 2011)." 3.3 Concentrations and time series of terpenoic acids and organosulfates (end of 1st paragraph): "It is worth pointing out that the organosulfates and the terpenoic acids showed the same average contribution of 0.6% to the OC; it has to be realised, however, that due to methodological shortcomings not all of the organosulfates could be measured (see Table S1) so that the true % contribution of the organosulfates to the OC may be higher. Furthermore, surrogate standards were used for their quantitation, which as discussed in a recent article by Kristensen and Glasius (2011), could also lead to an underestimation of their concentrations."

RC: 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.

AR: We will make sure that these figures are printed with sufficient resolution and occupy the whole width of the page.

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

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