

***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 #1 for a careful examination of our manuscript and for many thoughtful suggestions to improve its quality.

Reviewer comments (RC): The abstract contains too many technical details that should be left to the main text. Because of this, the impact of the work is lost. I recommend omitting the sentence beginning on line 6, "The objectives. . ." as this work is not an

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overview on the study but rather a focused work on a specific set of analytes. This sentence should appear in the Introduction. For same reason as above, omit the sentence beginning on line 14, "The measurements of MSA. . ." as these details can be left for the Methods section. Since the work is not focused method development, this is not needed in the abstract. For same reason as above, omit the phrase beginning on line 23, ". . . , except the MW 295. . ." and on line 2 (next page) "the exceptions" to the end of the sentences. For the abstract, it is sufficient to say that most of the terpenic acids peaked at day time without listing those that did not. Is also sufficient to say that temperature correlations for some species were observed without listing all exceptions. Regarding the correlations among organic species referenced in the abstract, it would be more impressive to give the implications of high, very high, or substantial correlations rather than simply stating that they were observed. This is especially true since no particular species are listed. One would assume that in any study, some organic components would be correlated. If the authors could draw one or more interesting conclusions from the correlations, they could state that "X and Y were correlated, indicating . . ." which would give readers a better indication of the findings. Otherwise there is no point in drawing attention to the correlations. The final sentence of the abstract is awkward. Consider rephrasing as, "It was found that MBTCA and terebic acid showed an Arrhenius-type relationship with temperature" or something to that effect. Emphasize the finding rather than all that was explored. These changes should tighten the abstract and present a more focused paper.

Author Response (AR): The changes recommended by the reviewer have been accepted. As a result, the abstract is now more concise and focused. The revised abstract reads as follows: "Measurements of organic marker compounds and inorganic species were performed on PM_{2.5} aerosols from a Belgian forest site that is severely impacted by urban pollution ("De Inslag", Brasschaat, Belgium) during a 2007 summer period within the framework of the "Formation mechanisms, marker compounds, and source apportionment for biogenic atmospheric aerosols (BIOSOL)" project. The measured organic species included (i) low-molecular weight (MW) dicarboxylic acids

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(LMW DCAs), (ii) methanesulfonate (MSA), (iii) terpenoic acids originating from the oxidation of α -pinene, β -pinene, d-limonene and Δ^3 -carene, and (iv) organosulfates related to secondary organic aerosol from the oxidation of isoprene and α -pinene. The organic tracers explained, on average, 5.3% of the organic carbon (OC), of which 0.7% was due to MSA, 3.4% to LMW DCAs, 0.6% to organosulfates, and 0.6% to terpenoic acids. The highest atmospheric concentrations of most species were observed during the first five days of the campaign, which were characterised by maximum day-time temperatures > 22 °C. Most of the terpenoic acids and the organosulfates peaked during day-time, consistent with their local photochemical origin. High concentrations of 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) and low concentrations of cis-pinonic acid were noted during the first five days of the campaign, indicative of an aged biogenic aerosol. Several correlations between organic species were very high ($r > 0.85$), high ($0.7 < r < 0.85$), or substantial ($0.5 < r < 0.7$), suggesting that they are generated through similar formation pathways. Substantial correlations with temperature were found for OC, water-soluble OC, MBTCA, and several other organic species. MBTCA and terebic acid were highly correlated with temperature ($r > 0.7$) and showed an Arrhenius-type relationship, consistent with their formation through OH radical chemistry.”

RC: The sentence on line 15 (Introduction) beginning "Comprehensive" is out of place. It belongs at the start of the Introduction. In the current location it cuts between the goals of the current study and the measured species, which belong together. With respect to this statement, have any papers been published from the BEARPEX study in California that might relate to the BIOSOL project? In the description of the BIOSOL project, the objectives listed are fairly generic. Most field studies look at sources, time series and diel variations of aerosol species, gases, and meteorological parameters. The uniqueness of this study certainly merits unique objectives and specific scientific questions. The motivation behind this work could be highlighted here by describing the objectives that drove the authors to measure MSA and the specific terpenoic acids listed. Further, the introduction is lacking a framework of background information on

the species measured or the type of questions being addressed. The authors have not done themselves justice in omitting these details. Omit the sentence on line 25 beginning "The measurements of MSA" as this belongs in the Methods section. The second paragraph of the introduction is very well done. If the first paragraph is expanded and modified as suggested, it would read very well.

AR: The word "Comprehensive" has been omitted from the sentence on line 15. With regard to the statement made, the following recent paper has been added (see comments made by reviewer #2 and our responses):

Kristensen, K. and Glasius, M.: Organosulfates and oxidation products from biogenic hydrocarbons in fine aerosols from a forest in North West Europe during spring, *Atmos. Environ.*, 45, 4546–4556, 2011.

With regard to the studies made for vegetated areas that are affected by urban pollution, we have limited ourselves here to studies in Europe. Papers from the BEARPEX study in California are definitely relevant to the present study, are not included at this stage but will be discussed at a later stage, for example, in the beginning of Section 3.1.

We understand the comments made about the listed objectives being rather generic and the lack of a framework of background information on the species measured. With regard to the listed objectives, we felt that it was rather difficult at this introductory stage to be much more precise. Concerning a framework of background information on the species measured, it has to be realized that the number of species measured is quite high so that we considered it an almost impossible task to deal with this issue in much detail in the introduction. With regard to the comment made about unique objectives and specific scientific questions, we believe these issues were to some extent covered in the second part of the Introduction starting with "Special emphasis was given . . .".

To address the different concerns of the reviewer, the first section has been expanded as follows: "These species were selected for various reasons that relate to their bio-

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genic/anthropogenic origin, formation processes (gas-phase oxidation/heterogeneous chemistry), long-range transport or local production. MSA is a photo-oxidation product of dimethyldisulfide produced by phytoplankton blooms (e.g., Saltzman et al., 1983) and is believed to result from long-range transport of maritime fine aerosol at our study site (Maenhaut et al., 2011). LMW DCAs are among the most abundant organic 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). The terpenoic acids and organosulfates reflect SOA processes involving local biogenic emissions and rapid photochemical reactions (for a review, see Hallquist et al., 2009).” In addition, the second paragraph has been expanded as follows: “On the other hand, terpenylic acid and related lactone-containing compounds were target analytes because they have been proposed as early oxidation products of α -pinene formed by OH radical chemistry (Claeys et al., 2009; Yasmeen et al., 2010, 2011). Hence, it was of interest to compare their time series with those of cis-pinonic acid, an established first-generation oxidation product of α -pinene (e.g., Hoffmann et al., 1998; Glasius et al., 1999; Yu et al., 1999), and of MBTCA and other terpenoic acids.”

Ref.:

Chebbi, A. and Carlier, P.: Carboxylic acids in the troposphere, occurrence, sources, and sinks: a review, *Atmos. Environ.*, 30, 4233–4249, 1996.

Fisseha, R., Dommen, J., Sax, M., Paulsen, D., Kalberer, M., Maurer, R., Hofler, F., Weingartner, E., and Baltensperger, U.: Identification of organic acids in secondary organic aerosol and the corresponding gas phase from chamber experiments, *Anal. Chem.*, 76, 6535–6540, 2004.

Glasius, M., Duane, M., and Larsen, B. R.: Determination of polar terpene oxidation products in aerosols by liquid chromatography–ion trap mass spectrometry, *J. Chrom.*

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A, 833, 121–135, 1999.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155–5236, 2009.

Hoffmann, T., Bandur, R., Marggraf, U., and Linscheid, M.: Molecular composition of organic aerosols formed in the α -pinene/O₃ reaction: Implications for new particle formation processes, *J. Geophys. Res.*, 103, 25569–25578, 1998.

Rogge, W. F., Mazurek, M. A., Hildemann, L. M., and Cass, G. R.: Quantification of urban organic aerosols at a molecular level: identification, abundance and seasonal variation, *Atmos. Environ.*, 27A, 1309–1330, 1993.

Saltzman, E. S., Savoie, D. L., Zika, R. G., and Prospero, J. M.: Methanesulfonic acid in the marine atmosphere, *J. Geophys. Res.*, 88, 897–902, 1983.

Yu, J., Cocker III, D. R., Griffin, R. J., Flagan, R. C., and Seinfeld, J. H.: Gas-phase ozone oxidation of monoterpenes: Gaseous and particulate products, *J. Atmos. Chem.*, 34, 207–258, 1999.

RC: pg. 23547, lines 20-26 - Since the aerosol composition and quantity varied so drastically between the first 10 days and the remaining sampling days, it is important to emphasize whether or not the transport pattern (wind strength and direction) changed. This would help to convince readers that the local temperature change is what drove the observed chemical differences, rather than temperature coinciding with large scale meteorology and therefore being only correlative (not causative) in the observations. The authors state that the direction was "mainly from the southwest" but it is not well

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established that the wind direction remained constant from the first period to the second.

AR: As stated, the wind speed was low during the entire campaign. Further, we verified that the wind direction remained constant from the first period (first 10 days) to the second, so that the local temperature change drove the observed chemical differences. This has been mentioned more clearly in the text as follows: “The wind direction was mainly from the southwest, the direction of the city, and the North Sea, and was not significantly different between the first 10 sampling days characterised by higher temperatures and the remainder of the campaign.”

RC: Section 3.1, Measurement of terpenoic acids and organosulfates. First sentence: add references to other forest studies where the chemical composition has been investigated.

AR: In response, the following sentence has been added after the first 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).”

Ref.:

Worton, D. R., Goldstein, A. H., Farmer, D. K., Docherty, K. S., Jimenez, J. L., Gilman, J. B., Kuster, W. C., de Gouw, J., Williams, B. J., Kreisberg, N. M., Hering, S. V., Bench, G., McKay, M., Kristensen, K., Glasius, M., Surratt, J. D., and Seinfeld, J. H.: Origins and composition of fine atmospheric carbonaceous aerosol in the Sierra Nevada Mountains, California, *Atmos. Chem. Phys.*, 11, 10219–10241, 2011.

RC: pg. 23553, lines 1-5 - Rather than repeating and/or it would be more appropriate to say, "The high value at Brasschaat suggests that one or more of the following are occurring: (1) the source regions of MSA precursors. . . (2) the source strengths . . .

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(3) the conversion to MSA . . . and (4) less removal by wet deposition.

AR: The pertaining sentence has been modified according to the reviewer's suggestions.

RC: pg. 23554, line 2 - insert "can" before "lead to enhanced." Again, it would be relevant here to emphasize that a change in the transport direction (source change) was not the cause of the chemical changes but rather the change in local temperature. This would strengthen the final points of the paper as well, since there is a focus on the Arrhenius relationship.

AR: "can" has been inserted. Further, it has been repeated that the wind direction did not change between the first 10 sampling days and the remainder of the campaign: "Thus, the concentrations of the LMW DCAs, especially succinate, but also oxalate at Brasschaat were strongly affected by the local weather conditions, such as temperature and O3 concentration, and not by the wind speed and direction which were not significantly different between the first 10 sampling days and the remainder of the campaign."

RC: Section 3.3 An additional figure with diurnal trends would be very helpful to distinguish the 3 categories of compounds. One panel for those with trends, one for daytime peaks, and one for nighttime peaks would be very illustrative of the differences observed.

AR: Here, we have not followed the suggestion of the reviewer to include an additional figure with diurnal trends. Three categories of compounds are observed, i.e., compounds which do not show clear diel differences (like LMW DCAs), peak during day-time, or peak during night-time, for the reason that these diel patterns can already be seen in the figures with the time series shown (Figs. 3, 4, and 5). We have preferred to draw more attention to the figures and have emphasised the diel patterns in the legends to Figures 4 and 5. Furthermore, we will ensure that the figures are of sufficient resolution, so that the diel differences are clear.

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The following sentence has been added after the first one: "Figures 4 and 5 show time series for selected terpenic acids and organosulfates that peak during day-time or at night." The legends to the figures have been extended as follows:

Fig. 4: Note that all terpenic acids shown mainly peak during day-time during the first 10 sampling days.

Fig. 5: Note that the α -pinene-related nitrooxy organosulfates (MW 295), limonic acid, and cis-pinic acid mainly peak during night-time, while the MW 216 and 212 organosulfates mainly peak during day-time.

RC: pg. 23555, paragraph 2 It is worth pointing out that the concentration of organosulfates was equal to that of terpenic acids, perhaps even in the abstract. The fact that they contribute equally to OC is notable.

AR: Paragraph 2 has been extended as follows: "It is worth pointing out the organosulfates and the terpenic 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." That the organosulfates and the terpenic acids contributed, on average, with 0.6% to the OC, each, is also included in the revised abstract.

RC: Section 3.5 The activation energies presented here are hard to interpret for anyone not immediately studying Arrhenius behavior. It is worth a sentence or two describing their role in interpretation of data and what one can conclude by comparing them. The list of "this is higher than that" is not useful without interpretation of what these comparisons mean. If the comparisons find significantly new information, that should be presented in the abstract as "activation energies were compared to determine.. and . . . was found".

AR: We very well understand this concern about the meaning of the activation energy. Please, note that in this respect the following statement was made in the Conclusions section: “More research is warranted on the temperature dependence of the terpenoid acid to determine whether Arrhenius parameters such as the activation energy can provide useful information on biogenic SOA ageing.”

Rates of chemical reactions depend not only on substrate concentrations, but also on the activation energy (E_a) required for the reaction to occur. Temperature determines the fraction of molecules present with sufficient energy to react, i.e., above the E_a of that specific reaction. At a given temperature, the higher E_a , the fewer molecules will be present with sufficient energy to react. However, higher E_a 's also imply a larger relative increase in reaction rates, and thus a higher temperature sensitivity (e.g., Box 1 in Davidson and Janssens, 2006). Higher temperatures will thus stimulate the rate of reactions with high E_a more than they will that of reactions with low E_a . However, in the case of intermediate compounds, changes in the concentration with temperature are less easily interpretable. Both the formation and destruction reactions are characterised by an E_a , such that the change in concentration of such a compound with temperature depends on the temperature responses of both the formation and destruction reactions. In any case, the much lower E_a for cis-pinonic acid than for MBTCA should be interpreted as MBTCA concentrations exhibiting a much larger relative increase with temperature compared to concentrations of cis-pinonic acid.

Ref.:

Davidson, E.A. and Janssens, I. A.: Temperature sensitivity of soil carbon decomposition and feedbacks to climate change, *Nature*, 440, 165–173, 2006.

The following sentences have been added to Section 3.5: “A higher E_a value implies a larger relative increase in reaction rates with temperature, and thus a higher temperature sensitivity (e.g., Box 1 in Davidson and Janssens, 2006). The much lower E_a value for cis-pinonic acid than for MBTCA should be interpreted as MBTCA con-

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centrations exhibiting a much larger relative increase with temperature compared to concentrations of cis-pinonic acid. For a more detailed discussion on the meaning of the Arrhenius parameter E_a , see the supplement.” Finally, as mentioned in the revised text, more information has been given about the meaning of E_a in the supplement, essentially repeating most of the reply formulated above.

RC: Conclusions: I am uncomfortable with the authors stating that "temperature was a main driver in biogenic SOA formation at the study site" as less than 5% of the OC was characterized in total, and only a fraction of the characterized OC showed a strong temperature dependence. This is an over-statement and should be scaled back. Despite the overall correlation between OC and temperature, it would be more appropriate to say that for the characterized species, temperature was a main driver, while for OC overall, it was correlated. Without speciation, I don't think the temperature can be proved to be a cause of SOA formation.

AR: The first two sentences of the conclusions: “Based on the results of this study it is clear that temperature was a main driver in biogenic SOA formation at the study site. Substantial to high correlations with temperature were found for OC, WSOC, MBTCA, and several other organic species.” has been replaced by: “Based on the results of this study it is clear that temperature was a driver in the formation of selected biogenic SOA tracers and that it also correlated with the OC as a whole, despite the fact that, on average, only 5.3% of the OC could be assigned on the molecular level. This may suggest that temperature also plays a role in the formation of non-biogenic organic species, which remain uncharacterised and which are possibly derived from anthropogenic volatile organic compound precursors at our highly industrialised urban site.”

RC: Technical Corrections pg. 23543, line 12- omit "and" between "(MSA)" and "(iii)" since there are 4 items in the list, not 3. pg. 23544, line 8- replace "of PM2.5" with "on PM2.5" pg. 23546, line 19- insert "carbon" after "inorganic" pg. 23546, lines 14-21 - this is a run-on sentence and is awkward. Please separate and rewrite. pg. 23550,

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line 22 - omit "of the supplement" since it's redundant with the notation Table S1. pg. 23553, line 12 - start a new paragraph with "When the samples are separated" pg. 23554, line 21 - insert "temperature" after "cooler night time" pg. 23555, line 29 - insert a comma after "campaign"

AR: have all been corrected.

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