Atmos. Chem. Phys. Discuss., 11, C8878–C8888, 2011
www.atmos-chem-phys-discuss.net/11/C8878/2011/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Contrasting organic aerosol particles from boreal and tropical forests during HUMPPA-COPEC-2010 and AMAZE-08 using coherent vibrational spectroscopy" *by* C. J. Ebben et al.

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Received and published: 12 September 2011

Referee #1: Comments: This paper describes novel measurements of optical properties of secondary organic aerosol (SOA) from laboratory-generated aerosol and two regions in which biogenic VOC reactivity dominates and infers chemical information mainly from comparison of the laboratory studies with the field samples. The method used in this work represents a very interesting way to analyze ambient aerosol without extraction etc. or use of vacuum and should be of interest to the community. The paper is well written and I think this method and the results represent an exciting new

analytical tool for aerosol. I believe this method has great potential and I look forward to seeing more results employing it! However, before the manuscript is suitable to ACP, the authors should address the following issues in a revised submission for publication in ACP. My main comment is that the authors state that the method used is a way to characterize the chemical composition, which is vague and could be interpreted very broadly that the overall (i.e. all aspects) chemical composition can be deduced from this method. I believe it has to be very carefully phrased what is meant by this claim and certainly their method needs to be compared/contrasted with existing methods for characterization of chemical composition such as AMS measurements of O/C ratios, FTIR analysis or filter extraction methods. As the results are from two major field campaign such results must exist, particularly AMS data.

We very much appreciate the reviewer's comments and are taking them seriously. As outlined below, we have made the changes suggested by the reviewer and hope that the manuscript is stronger as a result.

I) The method description is excellent. However, a statement that simply and clearly states whether this method is a surface or bulk aerosol measurement, or under which conditions, which type of measurement dominates is necessary. I believe this aspect otherwise is hard to understand for non-experts and I highly recommend such a statement early on in the manuscript otherwise readers might get confused. For the implications and for comparison with other data this aspect is also very important. If the measurements are pure surface measurements the question of coatings or contaminations becomes important and should be addressed (see also a later comment).

We thank the reviewer for this comment. We have clarified language in the "SFG Theory" section of the manuscript, as suggested by the reviewer. We have added the following sentence to the first paragraph of the section I: "SFG is forbidden in centrosymmetric media, which means that it is a surface-specific technique for achiral systems."

II) The isoprene/a-pinene ratio is a large and compelling difference between AMAZE and HUMPPA. However an equally important difference is the O3/OH ratio and potentially the NO concentrations. From the manuscript as it stands it is not clear to me how the authors can clearly argue that the differences observed cannot be from the change in chemical regime from O3 to OH and/or medium to low NO and/or relative humidity. I don't disagree with the authors' conclusions but it would be very helpful if their argument could be strengthened, as it is a very important conclusion of the paper. Specifically, by stating (p. 16397 lines 25-end) that AMAZE is an important contrast because of low anthropogenic impact they clearly imply that HUMPPA had high anthropogenic impact and hence a difference in NO regime is important.

These are two interesting remarks by the reviewer. Regarding anthropogenic input during HUMPPA-COPEC 2010, we refer the reviewer to Table 2 of the HUMPPA-COPEC Overview paper that is in review at ACPD (ACPD, 11, 15921-73). The days of filter collection relevant for this current manuscript (17, 21, and 23 July 2010) show no comment regarding anthropogenic events except for the sawmill event on 17 July. We added the following sentence to line 1 of page 16939 of the original manuscript: "We note that noteworthy anthropogenic events did not occur (Williams et al., 2011) on the days of filter collection relevant for this current manuscript (17, 21, and 23 July 2010) except for the sawmill event on 17 July." We do not attempt to argue that the differences we observe in the SFG spectra of boreal vs. tropical forest environments are not attributable to the O3/OH ratio, relative humidity differences, and potentially NO concentrations. For reference, the average NO concentration for HUMPPA-COPEC 2010 is 0.1 ppb, whereas it is 1 ppb for AMAZE-08. We have added the following penultimate sentence to the conclusions: "The differences we observe in the SSP-polarized SFG spectra obtained from particles collected in the boreal vs. tropical forest environments are due to differences in the chemical composition of the particles' surfaces. These differences are likely to be due to a combination of differences in the chemical identity of the hydrocarbon precursors, the O3/OH ratio, the relative humidity, and potentially differences in NO concentrations in the two forest environments, among others."

III) P. 16498 26-27 "...dominated by a-pinene derived SOA particles": I think it can only be said that it is consistent with the lab samples. I recommend making the existing statement weaker or finding additional proof. Have the authors studied laboratory generated b-pinene or limonene SOA, especially as they make such a statement. In particular in figure 1 a-pinene and b-pinene look very similar to each other hence the SOA could look similar unless the authors have information not available to the reader or the reasoning has to be stated more clearly. The authors should add results (if possible) on lab-synthesized b-pinene and limonene SOA to the manuscript - it could (potentially) greatly strengthen the implications.

We certainly appreciate this point and thank the reviewer for making it. We have not yet prepared SOA particles from precursors other than α-pinene and isoprene and are happy to qualify the statement in question. The suggested experiments are subject of a future manuscript, which will include synthesized putative SOA intermediates as reference compounds. We have now changed the following sentence "While it cannot be ruled out that β-pinene and limonene, which were present in the gas phase during the time of the HUMPPA-COPEC-2010 campaign (Table I), are present in the Finnish aerosol particle filter samples, the top three SFG spectra shown in Fig. 3 suggest that the hydrocarbon component of the material collected in the submicron size range on the filters is dominated by α-pinene-derived secondary organic aerosol particles." to "While the SFG spectra of the α-pinene-derived secondary organic material agrees very well with the vibrational SFG spectrum of PM1 filter samples collected in Southern Finland, we cannot conclude at this time that the hydrocarbon component of the material collected in the submicron size range on the filters is dominated by α-pinene-derived secondary organic aerosol particles, mainly because β-pinene was also present in the gas phase during the time of the HUMPPA-COPEC-2010 campaign (Table I)."

IV) Table 1) The paper centrally hinges on comparison between lab and ambient samples. Conditions can substantially influence oxidative chemistry and potentially the resulting SOA composition/properties. Thus, a more explicit list of conditions needs to be listed in Table 1. The chamber samples/conditions should be added or a separate table added for these. The tables for both lab and field should include: representative O/C ratio of aerosol (from AMS) mixing ratios of OH, O3, NO, and the VOCs already listed in the table T, relative humidity, organic and total aerosol load (e.g., PM1). This value should be for the specific days the filters were sampled if possible.

The reviewer raises a very interesting idea, which the authors considered during earlier drafts of the manuscript. We concluded that listing the gas phase data for the relevant days of particle collection gives the impression that those are the relevant conditions for particle formation. Given that the time constants connecting gas phase with particle phase composition are not known, we decided not to provide this information in this manuscript. Instead, we decided to provide the reader with a range of concentrations/conditions, and those are listed in Table 1 of the original manuscript. We also list the relevant information at the relevant sections of the manuscript, and we thank the reviewer for pointing out a nice way to make the data more accessible. The manuscript is part of two Special Issues on AMAZE-08 and HUMPPA-COPEC, respectively, and we respectfully suggest that the readers of the manuscript obtain the gas phase data from the companion papers published in these two Special Issues. Nevertheless, for convenience, we do list the mass loadings in the text on line 18 on page 16938 for HUMPPA-COPEC and on lines 24-25 on page 16939 for AMAZE-08. The temperature ranges are listed on line 9 on page 16937 for HUMPPA-COPEC. The temperature range for AMAZE-08 was not noted in this manuscript, and we now added the following sentence to page 16937 on line 20, where we also list the O/C ratio from AMS: "The temperature at the top of the research tower ranged from 22-32 °C, while the relative humidity ranged from as low as 60% at night time to 100% during the day. The NO concentrations during AMAZE-08 were in the 0.1 ppb range, (see Fig S6 in the SI of the Overview) and the O/C ratio, as determined by the Harvard AMS, was 0.4+/-0.1 for the entire campaign." Conversely, on line 10, page 16937, we added the RH, NO, and O/C information for HUMPPA-COPEC: "The relative humidity ranged from 30-60% during

the night and from 80% to 100% during daytime, while NO concentrations were in the 0.1 ppb range .The O/C ratio, as determined by FTIR and aerosol mass spectrometry (AMS), ranged between 0.5 and 0.7 for the duration of the campaign."

V) Related to the above point. The table would allow better evaluation of a comparison of laboratory ozone/a-pinene SOA and isoprene+OH SOA between the chamber and the field. I could imagine that NO (and HO2/RO2) levels were quite different between the chamber studies and the field studies. This could change the product distribution of isoprene substantially. This aspect of chemical regime and in how far the field and lab samples can be compared should be discussed. For example, how different do the authors expect a-pinene SOA would be under the AMAZE oxidant conditions compared to ozone/a-pinene lab-aerosol.

The reviewer is exactly correct. We paid close attention to maintaining a chamber environment in which the NOx concentration, as determined by a Teledyne NOx analyzer, was below detection limit, which is 1 ppb for this instrument. In fact, recent measurement with Ecophysics instrument (MDL of 25 pptv) show that NOx concentrations in HEC appear to be 200 to 400 pptv. We point out to the reviewer that the NO concentrations during HUMPPA-COPEC 2010 and AMAZE-08 were around 0.1 ppb. At this time, we do not know how different the SFG response would be of α-pinene-derived SOA prepared under conditions that differ from those studied in this work. Future work will certainly address this point but at this time we respectfully submit that the topic is beyond the scope of our present manuscript.

VI) The SOA community has become accustomed to often think about SOA in terms of O/C ratios. The authors should add a short section briefly presenting what is known about the SOA from the field studies in particular O/C ratio, FTIR and filter extraction analysis and how these compares with the lab samples used in this analysis. For example if the O/C ratios are different the chemical composition has to be different and a broad claim that this method can identify chemical composition is not valid. I think adding this is critical in order to have the SOA community fully appreciate this paper and be able to put it in context.

This is a great point raised by the reviewer, and we now list the O/C ratios in the introductory section of the manuscript that described met conditions and the like at the two sites and in Table I.

VII) Have the authors reinvestigated the lab samples after storage time, in case aging of aerosol samples occurred in storage, e.g. via ammonia (Bones et al. 2010 and references therein). I don't expect that this is a big effect, BUT if the method used is surface sensitive it could substantially impact it as the aging/modification will be largest on the surface. This affect could also be different for different types of aerosol.

A statement has been added to address this important point: "SFG spectra of Teflon filters containing synthetic α-pinene-derived aerosol particles, prepared as described in the experimental section, are invariant in the frequency positions of the vibrational resonances but show a 10 to 25% reduction in signal strength in the CH stretching region. We conclude from this result that the chemical composition of the samples, as determined by SFG, is qualitatively the same after several months of storage under these conditions."

Specific comments: 1. P. 16935 line 9: "similar in chemical composition" This statement should be modified. I would say something along the lines of that it is "consistent with respect to property X" to synthetic material. The spectroscopic information retrieved clearly cannot be equated with a full chemical compositional analysis. Also the abstract should make clear whether this statement is derived from bulk-aerosol or aerosol-surface measurements.

This is an important point and we appreciate that the reviewer brought it up. We therefore changed the section in question to "…we show that submicron aerosol particles sampled in Southern Finland during HUMPPA-COPEC-2010 are composed to a large degree of material whose hydrocarbon content, as identified in the CH stretching region, is consistent with that of synthetic α-pinene-derived material."

2. P.16935 line 11-21. The phrasing in this section also should be modified to be more specific about what the results state given the comments above with respect to what is being compared as it cannot be stated with certainty that the ambient conditions and lab conditions are comparable (NO mixing ratio and RO2/HO2/NO ratio).

We appreciate this point - please see our answer to point # 2.

3. P. 16937 line 10-11. The statement on future climate seems out of place. Unless this is addressed later it should be eliminated.

We do agree with the reviewer. This statement has been removed.

4. P. 16937 line 18. How big was the total sampled air volume so one can deduce the inferred aerosol loads.

This is indeed important and we did list the MOUDI loadings on page 16939 of the original manuscript (lines 23-24). See our answer to the following comment as well.

5. P. 16939 line 24-end. Can these mass loadings be compared with those of HUMPPA

This section has been updated as follows: "The MOUDI samples contained 1.016, 0.257, and 0.150 mg of material for the 3.2, 1.0, and 0.3 μm size ranges. The mass loadings of the MOUDI samples from AMAZE-08 are more than an order of magnitude larger than those of the filters collected during HUMPPA-COPEC-2010 (vide supra). The fraction of elemental carbon, a marker for biomass burning, is 63.0, 3.2, and 16.0% of the collected mass on each MOUDI stage for those size ranges, respectively."

6. P. 16940 line 4: Did the authors prepare "model compounds", which sounds like specific chemicals, or "model SOA," which is a mixture?

We appreciate this question regarding clarity of language. We have therefore changed "model compounds" to "model SOA material"

7. P. 16943 end of first paragraph. Here it would also be useful to state clearly and simply whether aerosol surface or aerosol bulk properties are measured.

This section has been updated as follows: "SFG responses obtained from such molecules therefore originate from the aerosol particle surface. Chiral molecules do not possess a center of inversion, and their SFG responses can originate from the surface and the bulk of the aerosol particle, depending on symmetry. Details regarding the role of chirality in SOA particles are discussed in our recently published work. We emphasize that the present work is carried out using the SSP-polarization combination, which is insensitive to molecular chirality and yields SFG signals from the CH oscillators that are located at the surface of the aerosol particles as opposed to those that are located in the bulk."

8. P16946 line 7-8. Please add a statement whether the spectra of -a-pinene, -bpinene or +limonene look different from their enantiomers.

This section has been updated as follows: "...(+)-α-pinene, (+)-β-pinene, (+)-limonene, isoprene, 2-cis-pentene, n-hexene, n-pentene, cyclohexene, and cyclopentene maintained at room temperature, respectively. Using this polarization combination, which does not probe for chirality, there is a negligible difference between the spectra obtained from the enantiomers of neat α-pinene, β-pinene, and limonene."

9. P. 16947 line 20. "The ... spectra ... shows" should be "show"

We apologize for this oversight and have corrected this mistake.

10. P. 16948 line 24. "absent" do the authors mean "present". Otherwise the statement is confusing...

We thank the reviewer for pointing out our oversight, which has now been corrected. "While it cannot be ruled out that _-pinene and limonene, which were present in the gas phase during the time of the HUMPPA-COPEC-2010 campaign (Table I), are present in the Finnish aerosol particle filter samples, the top three SFG spectra shown in Fig. 3 suggest that the hydrocarbon component of the material collected in the submicron size range on the filters is dominated by _-pinene-derived secondary organic aerosol

particles."

11. P.16498 line 21. The lack of variability between clean and more polluted air (supposedly) for July 17 and July 21 is very interesting and it would be interesting to see more discussion. Also, can NO and NOx be compared for the two days. Surely there are measurements.

The reviewer raises the future prospects for our research plan and will understand that this particular question exceeds the scope of the current manuscript. We are currently carrying out a large set of experiments that address the differences in the various conditions, including diurnal cycle, wind conditions, etc, for the entire sequence of the finish campaign and the findings from that work will be communicated in due course.

12. P.16950 lines 3-7 confused me. I think the contrast between the filter samples needs to be made clearer (which one was sampled how long and when...)

We appreciate the reviewers comment and have clarified it as outlined below: "Due to low mass loading, the Teflon filter collected on 23 July, during the probable nucleation event, resulted in infrared absorbances, as determined by FTIR, below detection limit (<1x10-4) in the CH stretching region. However, during the six hours of particle collection, which sampled 2.85m3 of air, enough particles were deposited on the filter that SFG spectra could be recorded in the CH stretching region. In fact, Figure 4b shows that the SSP-polarized vibrational SFG spectrum obtained from the filter collected during the first six hours of the nucleation event, while less intense as expected from the smaller number density of aerosol particles sampled, is spectrally similar to that of the particles collected between roughly 06:00 a.m. 21 July 2010 and 06:00 a.m. 22 July 2010, for which transmission FTIR spectra show absorbances around 10-2. "

References: Bones, DL ; Henricksen, DK ; Mang, SA ; Gonsior, M ; Bateman, AP; Nguyen, TB ; Cooper, WJ; Nizkorodov, SA Appearance of strong absorbers and fluorophores in limonene-O(3) secondary organic aerosol due to NH(4)(+)-mediated chemical aging over long time scales, Journal of Geophysical Research 115, D05203, 10.1029/2009JD012864 (2010).

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 16933, 2011.