Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Biogenic and biomass burning organic aerosol in a boreal forest at Hyytiälä, Finland, during HUMPPA-COPEC 2010" by A. L. Corrigan et al.

A. L. Corrigan et al.

alcorrigan@ucsd.edu

Received and published: 31 October 2013

Answer on Referee #1- The authors thank the referee for improving the manuscript by his/her helpful comments. The manuscript will be revised based on the referee's comments as follows:

Comment 1: Introduction, Page 16155, Lines 13-15: The authors say that mass fragments from AMS are not specific to biogenically influenced OOA factors. I don't think this is necessarily true anymore based on several recent studies by Robinson et al. (2010, ACP), Slowik et al. (2010, ACP), and Budisulistiorini et al. (2013, ES&T). These

three recent studies have identified a factor with a distinct fragment ion at m/z 82 that is directly associated with isoprene SOA. Lin et al. (2012, ES&T) showed that this m/z 82 fragment ion was due to the dehydration of isoprene epoxydiol (IEPOX)-derived SOA constituents in the AMS by using authentic standards and generating IEPOX-derived SOA and sending it into a HR-AMS instrument. Interestingly, all 3 studies showed that this isoprene SOA factor (more recently called the IEPOX-OA factor by Budisulistiorini et al. (2013)), increased with increasing sulfate, suggesting a potential anthropogenic influence on isoprene SOA formation.

Reply: The reviewer is correct, for isoprene SOA a unique mass fragment has been identified in AMS measurements and factor analysis. However, for monoterpene SOA, specific mass fragments have not yet been identified in ambient aerosol. The introduction has been updated to include the above-suggested references in regard to isoprene SOA mass fragments.

"Recent work has identified a specific mass fragment associated with isoprene SOA (m/z 82) [Budisulistiorini et al., 2013; Lin et al., 2012]; however, no unique mass fragments have yet been identified for monoterpene SOA in ambient aerosol."

Comment 2: Out of curiosity, were the authors not interested in examining the anthropogenic influences on biogenic SOA formation with their dataset? I'm guessing this might be addressed in a followup study? This study was clearly more focused on the details of how the source apportionment was conducted and what was identified from this source apportionment.

Reply: The dataset provided a unique opportunity to explore the robustness in chemical separation of biogenic and biomass burning organic aerosol for two different methods. However, the dataset is insufficient for the suggested study, as the main periods of anthropogenic pollution occurred during the biomass burning events, which consisted of aged aerosol (by 4-5 days).

Comment 3: Introduction, page 16155, Line 4: Citations are needed for this sentence.

Reply: The following citations have been added: [Finessi et al., 2012; Fu et al., 2010; Schwartz et al., 2010; Szidat et al., 2009].

Comment 4: FTIR analyses and organosulfates: Are the authors familiar with the Claeys et al. work from Hyytiala? They have shown from PM2.5 samples analyzed by LC/ESI-MS techniques that there are numerous organosulfates from monoterpenes and isoprene. This would suggest that FTIR isn't sensitive enough to resolve these compounds. Also, I think there remains some question how other components in the aerosol mixture affect the FTIR's ability to resolve organosulfates well and quantitatively.

Reply: Organosulfate functional groups were above the limit of detection during the enhanced biogenic period and all fire periods. However, the organosulfate group concentrations were very small ($\sim$5 to 25 ng/m3, < 0.5% OM) and below the limit of quantification. Organosulfate groups have been identified by FTIR analysis primarily in regions with high sulfate (relative to nitrate) [Frossard et al., 2011; Hawkins et al., 2010]. Gomez-Gonzalez et al. [2012] reported an average molecular concentration of 20 ng/m3 for summertime PM2.5 aerosol in a Belgian forested site impacted by urban pollution; however some of their samples were below this range, with molecular concentrations of 5 − 50 ng/m3. In Hyytiälä, Yttri et al. [2011] reported an average summertime molecular concentration of 3-4 ng/m3, which is also consistent with the functional group concentration range that we found. The text has been updated with this information as follows:

"Organosulfate groups were detected throughout the campaign, but they were below the limit of quantification. The measured range of organosulfate group was below 5 − 25 ng m-3, consistent with measured ranges of molecular concentrations of organosulfates measured in polluted [Gomez-Gonzalez et al., 2012] and rural [Yttri et al., 2011] forested sites in northern Europe."

Comment 5: Page 16158, Line 24: You didn't define DMPS. Please define this acronym

here. How accurate is the CE determination from AMS vs. DMPS comparison? I think you need to provide more detail here on how exactly this was done. Furthermore, for non-neutralized CE determination, I'm curious as to why the recent Middlebrook et al. (2012, Aerosol Sci. Technol.) composition dependent CE approach wasn't used?

Reply: Further explanation on DMPS comparison and CE determination has been added to section 2.3. "The collection efficiency (CE) of 0.43 was determined from a comparison with a Differential Mobility Particle Sizer (DMPS, [Aalto et al., 2001]) derived mass concentrations in size range 3-600 nm. The DMPS number distributions were converted to volume distributions, and integrated over the size range in question. Black carbon (BC) volume derived from an aethalometer was then subtracted and the remaining volume multiplied by time-dependent particle density, estimated with a weighted average of chemical species densities from the AMS. The neutral-aerosol (base) CE was determined from the average ratio of AMS total mass per DMPS derived mass (minus BC) and was found to be 0.43 with a standard deviation of 0.08. This CE was applied for time periods when the aerosol acidity was neutral, as determined by the ratio of ammonium to sulfate plus nitrate."

The difference between the parameterizations of Quinn et al. [2006] and Middlebrook et al. [2012] are relatively small compared to the uncertainty in determining the base CE. The aerosol in Hyytiälä is largely neutralized and thus not drastically affected by this correction. Reprocessing the AMS data would not have impacted the overall findings presented in this manuscript, which focus more on composition than on magnitude of OM. Moreover, the Middlebrook correction would not change the results in our case either, as stated on p. 16159, the nitrate fraction remained well below the limit where it would have an effect on CE.

Comment 6: Have the authors considered comparing factor 4 from FTIR PMF with biogenic SOA tracers (e.g., Kleindienst et al., 2007)?

Reply: GC-MS SOA tracers were not available. However, monoterpene SOA tracers

from APCI-MS and PTR-MS (see comment 7) were compared to the biogenic factors. Particle-phase cis-pinonic acid (m/z 183) and cis-pinic acid (in addition to isobaric acids from different monoterpenes) (m/z 185) from APCI-MS measurements were correlated with OOA-1a and BIOFTIR. Cis-pinonic acid correlated weakly (r < 0.25) with OOA-1a, while cis-pinic acid correlated moderately (0.5 < r < 0.75) with both OOA-1a and OOA-1. Cis-pinic acid also correlated moderately (r = 0.7) with BIOFTIR, while weak correlation was found with cis-pinonic acid – likely due to its volatile nature. These correlations have been added to the text in sections 3.2.2 and 3.2.3, in addition to updating Figures S4 and S5.

BOA-FTIR factor: "In addition, Factor 4 correlated strongly with monoterpene oxidation products measured by PTR-MS, pinonaldehyde (m/z 99, r = 0.9) [Wisthaler et al., 2001], a monoterpene oxidation fragment (m/z 113, r = 0.8) [Lee et al., 2006], and moderately with APCI-MS particle-phase cis-pinic acid (m/z 185, r = 0.7) [Vogel et al., 2012]."

OOA-1a factor: "The factor correlated strongly with monoterpene oxidation products measured by PTR-MS and APCI-MS, including pinonaldehyde (m/z 99, r = 0.8), monoterpene oxidation fragment (m/z 113, r = 0.8), and cis-pinic acid (m/z 185, r = 0.6).

Comment 7: I'm curious, how did monoterpene oxidation products from the PTR-MS compare to your factor analysis? You don't mention any of these products but mention isoprene products (e.g., MVK + MACR)?

Reply: The correlation between PTR-MS mass fragments and biogenic factors was investigated. Three mass fragments from PTR-MS measurements that are related to monoterpene oxidation products correlated strongly (r>0.75) with AMS factor OOA-1a and the recombined AMS factors OOA-1a and OOA-1b (OOA-1). The mass fragments included: pinonaldehyde fragment (m/z 99) and a monoterpene oxidation product (m/z 113) [Kim et al., 2010; Lee et al., 2006; Wisthaler et al., 2001]. Additionally, m/z 99 and

113 correlated strongly with the biogenic FTIR factor (BIOFTIR). These correlations have been added to the text in sections 3.2.2 and 3.2.3, in addition to updating Figures S4 and S5.

BOA-FTIR factor: "In addition, Factor 4 correlated strongly with monoterpene oxidation products measured by PTR-MS, pinonaldehyde (m/z 99, r = 0.9) [Wisthaler et al., 2001], a monoterpene oxidation fragment (m/z 113, r = 0.8) [Lee et al., 2006], and moderately with APCI-MS particle-phase cis-pinic acid (m/z 185, r = 0.7) [Vogel et al., 2012]."

OOA-1a factor: "The factor correlated strongly with monoterpene oxidation products measured by PTR-MS and APCI-MS, including pinonaldehyde (m/z 99, r = 0.8), monoterpene oxidation fragment (m/z 113, r = 0.8), and cis-pinic acid (m/z 185, r = 0.6).

Comment 8: PMF Factor Designation from AMS: Why is OOA-1a, OOA-1b, and OOA-2 used for factor description? From the Jimenez et al. (2009, Science) paper, I thought the community was now moving to LV-OOA, SV-OOA, and BBOA designations. This makes things a little confusing for readers who are outside of the AMS community. Could the OOA-1a be simply called a biogenic OA factor and the OOA-1b called the biomass burning factor? I realize that the authors had a hard time pulling apart biogenic and biomass burning OA from each other, but this would be an example (I think) were molecular tracers for SOA and POA would help. To be picky, couldn't OOA-1 and OOA-2 be labelled LV-OOA and SV-OOA, respectively?

Reply: Although OOA-1a and OOA-1b correlate strongly with biogenic and biomass burning tracers respectively, the authors believe that these two factors do not have unique chemical signatures to justify naming them as biogenic OA and BBOA. Additionally, the AMS community uses m/z 60 as a characteristic fragment in BBOA factors, which was not present in OOA-1b, due likely to the long transport (4-5 days) of the biomass burning aerosol. Without volatility measurements, the authors cannot justify

labeling them as LV-OOA and SV-OOA and instead adhere to the conventional naming of OOA-1 and OOA-2 [Ulbrich et al., 2009].

Comment 9: It isn't clear how the STXM-NEXAFS data really add to the discussion in this manuscript. Also, since the majority of particles analyzed with this technique are between 1-3 microns, how comparable is this data to the AMS and FTIR data (which are collected as PM1)?

Reply: The authors agree that the STXM-NEXAFS work does not add to the discussion of the manuscript and has therefore been moved to the SI. It is true that the majority of particles analyzed were between 1-3 microns in size, which is likely associated with detritus lofted in the wildfires.

References:

Aalto, P., et al. (2001), Physical characterization of aerosol particles during nucleation events, Tellus B, 36, 344-358.

Budisulistiorini, S. H., et al. (2013), Real-time continuous characterization of secondary organic aerosol derived from isoprene epoxydiols in downtown atlanta, georgia using the aerodyne aerosol chemical speciation monitor, Environmental Science & Technology, 47, 5686-5694.

Finessi, E., et al. (2012), Determination of the biogenic secondary organic aerosol fraction in the boreal forest by nmr spectroscopy, Atmospheric Chemistry and Physics, 12(2), 941-959.

Fu, P. Q., et al. (2010), Contributions of biogenic volatile organic compounds to the formation of secondary organic aerosols over mt tai, central east china, Atmospheric Environment, 44(38), 4817-4826.

Gomez-Gonzalez, Y., et al. (2012), Chemical characterisation of atmospheric aerosols during a 2007 summer field campaign at brasschaat, belgium: Sources and source processes of biogenic secondary organic aerosol, Atmospheric Chemistry and Physics,

C8633

12, 125-138.

Kim, S., et al. (2010), Emissions and ambient distributions of biogenic volatile organic compounds (bvoc) in a ponderosa pine ecosystem: Interpretation of ptr-ms mass spectra, Atmospheric Chemistry and Physics, 10, 1759-1771.

Lee, A., et al. (2006), Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, Journal of Geophysical Research-Atmospheres, 111(D17).

Lin, Y. H., et al. (2012), Isoprene epoxydiols as precursors to secondary organic aerosol formation: Acid-catalyzed reactive uptake studies with authentic compounds, Environmental Science & Technology, 46, 250-258.

Middlebrook, A. M., et al. (2012), Evaluation of composition-dependent collection efficiencies for the aerodyne aerosol mass spectrometer using field data, Aerosol Science and Technology, 46, 258-271.

Quinn, P. K., et al. (2006), Impacts of sources and aging on submicrometer aerosol properties in the marine boundary layer across the gulf of maine, Journal of Geophysical Research-Atmospheres, 111(D23).

Schwartz, R. E., et al. (2010), Biogenic oxidized organic functional groups in aerosol particles from a mountain forest site and their similarities to laboratory chamber products, Atmospheric Chemistry and Physics, 10(11), 5075-5088.

Szidat, S., et al. (2009), Fossil and non-fossil sources of organic carbon (oc) and elemental carbon (ec) in goteborg, sweden, Atmospheric Chemistry and Physics, 9(5), 1521-1535.

Ulbrich, I. M., et al. (2009), Interpretation of organic components from positive matrix factorization of aerosol mass spectrometric data, Atmospheric Chemistry and Physics, 9(9), 2891-2918.

Vogel, A. L., et al. (2013), Online atmospheric pressure chemical ionization ion trap mass spectrometry (apci-it-ms) for measuring organic acids in concentrated bulk aerosol – a laboratory and field study, Atmospheric Measurement Techniques, 6, 431-443.

Wisthaler, A., et al. (2001), Measurements of acetone and other gas phase product yields from the oh-initiated oxidation of terpenes by proton-transfer-reaction mass spectrometry (ptr-ms), Atmospheric Environment, 35(35), 6181-6191.

Yttri, K. E., et al. (2011), Source apportionment of the summer time carbonaceous aerosol at nordic rural background sites, Atmospheric Chemistry and Physics, 11(24), 13339-13357.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 16151, 2013.

C8635