

Interactive comment on “Organic functional groups in aerosol particles from burning and non-burning forest emissions at a high-elevation mountain site” by S. Takahama et al.

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1 Reviewer 1 comments

1.1 General comments

1. The introduction is too broad and leaves little indication as to what the rest of the paper covers exactly. Why OFG measurements are important for assessing radiative impacts of aerosol particles? More generally why OFG characterization is important in aerosol science? Also I would have like to read a short synthesis of previous works

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regarding chemical characterization of wood burning and the influence of aging on this chemical composition in terms of functional groups composition or overall chemical composition(typically AMS results as AMS results are used in this study).

The introduction has been revised to include relevance of high-elevation monitoring sites and functional group analysis. A discussion regarding wood burning has been included in the introduction, and also in the Results and Discussion section where observations of biomass burning aerosols are covered.

Regarding the background information on biomass burning aerosols, the text added to the Introduction is as follows:

“Large mass contributions from sugars and homologous alkane and alkene compounds, have previously been reported by Fine et al. (2002) and Simoneit (2002) (among others) for products of various types of wood or wildfire (plant) burning using gas-chromatograph with mass spectrometry (GC-MS). These methods typically report compounds identified from mass fragments, along with an unrecovered portion comprising an unresolved complex mixture (UCM) thought to be primarily ring-structured compounds, and another set of unidentified compounds (unextractable or unelutable) for which structures are not proposed. Levoglucosan, a thermal breakdown product of cellulose, is often used as a biomass burning marker (Simoneit et al., 1999). Levoglucosan is additionally measured by ion chromatography (Sullivan et al., 2008) or aerosol mass spectrometry (Lee et al., 2010), and has been suggested to contribute from a few to a quarter percent of the organic aerosol mass (Fine et al., 2002; Sullivan et al., 2008). There are also many uncertainties regarding the composition of the organic fraction of BB aerosol, which are dependent on fuel type, burning phase (flaming or smoldering), and also the transformation through aging that occurs. Reid et al. (2005) provides a review on the rapid growth in particle size, recondensation

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of low-volatility products, and condensation of oxidized (presumably more polar and hydrophilic) products, increasing the aerosol hygroscopicity. The oxygenated fraction of BB aerosol is also reported to change with age. Levoglucosan (and presumably other anhydrous sugars) are reported to degrade in BB plumes (Hennigan et al., 2010; Cubison et al., 2011; Hennigan et al., 2011), while mass ratio of organic acid to carbonyl are reported to increase with age of air mass in BB plumes Hawkins and Russell (2010).”

Regarding FTIR and high-altitude measurements in the Introduction:

“Measurements in the free troposphere (FT) can provide information regarding background concentrations (e.g., Nyeki et al., 1998) and detect pollutants transported over long distances (e.g., Leaitch et al., 2009), and yet multi-seasonal records of high-altitude measurements of organic aerosol composition in the FT are sparse. Researchers at one monitoring station, Jungfraujoch, located in the Swiss Alps (~3500 masl), have summarized measurements of inter-annual, seasonal, and diurnal variations of aerosol at the site from long-term measurement program, reporting vertical transport of air masses from the boundary layer between late spring and late summer (Lugauer et al., 1998) and higher aerosol concentrations during these months, with the PM₁ mass primarily composed of organic and sulphate aerosol with smaller contributions from nitrate, ammonium, and black carbon (Cozic et al., 2008).

Functional group analysis by FTIR provides several useful characterizations for organic aerosol measurements. By using the full dimensionality of the feature vector (i.e., the full infrared spectrum that we analyze) in a factor-analytic decomposition of ambient aerosol spectra, component profiles have been shown to retain distinguishing spectral features which have been related to original sources of organic aerosols (Russell et al., 2011). A reduced representation of the FTIR spectrum in molar quantities of functional groups is physically meaningful to the extent that it has been

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linked to predictive models of molecular interactions in the condensed phase within an established thermodynamic framework (i.e., activity coefficients), from which hygroscopic properties and volatilities can be estimated.”

2. The section 2 (Methods) is particularly difficult to read. Please make subsections (ie sampling site and particles collection, Organic functional groups analysis, AMS etc..) and reorganized the text. Some parts can be shortened and simplified (ie sample collection). In this section a lot of analytical approaches or instrumentations are described but their results are barely used in the discussion (ie SMPS, UCPC, XRF). Some of these descriptions can be moved in Supporting Information.

We have demarcated the section by topic to improve readability, but have chosen not to have a Supporting Information document.

3. As OFG is the central point of the results discussed in the paper I would have like to read more information's about this analytical approach: : I am aware that this method has already been described by Russell et al 2009, but in this paper the authors have to describe this method more carefully. How the method is calibrated (one compounds per function, or a mixture, ..) ? What are the detection limits ? What are the uncertainties associated with your OFG concentrations? Is there any shortcomings or biases? Due to this lack of details, I have several issues regarding the significance of the results.

Additional information not covered by Russell et al. (2009) was previously covered by Maria et al. (2003) and Russell (2003), but we have included additional information regarding the analysis in the Methods section. The revision to the text is as follows:

“Using this method, FTIR spectroscopy provides OFG concentrations, including

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alkane, carboxylic acid, organic hydroxyl, primary amine, carbonyl, alkene, and aromatic groups, through chemical bond-based measurements in atmospheric particles collected on a substrate (Russell et al., 2009). Alkene, aromatic, and organonitrate groups were below detection limit for all samples. Our discussion of OM will therefore neglect these compounds; their contribution to the actual OM is estimated to be between 2-5%. Organosulphate groups were above detection limit during only one three day-long sampling period. Ketone group contributions are estimated from a comparison of moles of carboxylic C-OH and total carbonyl quantified; non-acid carbonyl (including aldehydes and ketones) are determined by the moles of carbonyl present in excess of quantified moles of carboxylic C-OH. The moles of carboxylic C-OH and carbonyl for which carbonyl was not determined to be in excess had a correlation coefficient (r) of 0.84 and a regression slope of 1.0. The non-acid carbonyl is determined to be ketonic rather than aldehyde carbonyl, as absorption bands between 2700 cm^{-1} and 2860 cm^{-1} indicative of aldehydic hydrogen were not observed in the Whistler Peaks spectra. The quantified non-acid carbonyl will therefore be referred to as ketones in this manuscript. The uncertainty and detection limit of ketones are therefore estimated through a contribution of the estimated carboxylic C-OH and total carbonyl (Russell et al., 2009). Further details regarding the interpretation of spectra for apportioning absorbance to moles of bond or functional group, with respective detection limits, are provided by Maria et al. (2003) and Russell et al. (2009). Estimation of mass from these quantities is based on the analysis by Russell (2003), where moles of measured bonds are converted to the moles of comprising atoms, and values of OM are calculated from the sum of moles of atoms multiplied by their respective molecular weights. Using this approach, the uncertainty in OM has been calculated to be on the order of 23% (Russell, 2003)."

3.1. All the concentrations are given in $\mu\text{g}/\text{m}^3$. But what does the mass exactly represent? This point is not clear. For hydroxyl groups, does the mass represent the OH or C-OH mass? The same for non acidic carbonyl (O or C=O)? This issue is

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particularly important for alkanes. Does the mass correspond to all the C-H (even C-H associated with primary or secondary alcohols or aromatic compounds) or only C-H from aliphatic compounds? In such conditions, isnt it easier to discuss the results in mole of function/ m^3 ?

We measure moles of bond but convert to mass ($\mu\text{g}/\text{m}^3$) of atoms in aerosol to relate to units commonly used in communities involved in air quality, aerosols, and atmospheric science, and to compare to other OM and OC measurements. The mass calculation is described more explicitly now, as stated above. It is true that molar quantities are probably more useful from a chemistry perspective; molar ratios of O and C atoms are now additionally included in the discussion.

3.2. This issue is directly linked to the previous one. The % of functions given in the results section do not correspond to functionalization rates as calculated by Dron et al, ACP, 2010 (for example). From my point of view, functionalization rates are the most interesting information provided by OFG analysis. Is it possible to assess such functionalization rates with your results? (you need OC concentrations in order to calculate the total molar concentration of Carbon, do you measure OC/EC in your study?)

OC/EC measurements are not reported in our study, but we do measure the organic carbon content as carbon atoms are part of the functional groups we measure. Therefore, we are able to calculate the functionalisation rate as defined by Dron et al. (2010). However, the comparison is not so useful as the size fractions analyzed for comparable classes of aerosols are very different (we measure PM_{10} , while Dron et al., 2010, report PM_{10} for ambient aerosols). Dron et al. (2010) report values of 1.6-2.4 % for acid and 5.8-10.7 % for carbonyls from SOA formed by photooxidation of xylene (a predominantly anthropogenic hydrocarbon) with HONO, and 0.6-3.1 %

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for acid and 0.3-0.5 % for carbonyl for an urban background aerosol measured in Chamonix, France. For a comparable category of aerosol measured at Whistler Peak with predominantly anthropogenic influences [category (a)], the calculated functionalisation rates range between 8 and 17 %, with 0 % for carbonyls (ketones). The size fraction analyzed is a likely reason for the large difference in reported measurements, but additional differences due to aerosol source types, mass recovery, and aging processes are likely to be present.

3.3. Black Carbon (or Elemental Carbon) contains a lot of C-H functions associated with aromatic rings. Is there any biases induced by this specific organic fraction on your results related to OM?

There are no hydrogen atoms (and hence C-H bonds) in graphite, so is not measured by our instrument and does not affect the OM (with no known matrix effects). The C-H groups associated with co-emitted products are indeed measured by the FTIR, and is presumably some fraction of the alkane functional groups present in our "combustion"-derived aerosols.

3.3. I suppose that OM concentrations discussed in the text correspond to the sum of individual functional group concentrations calculated in your samples. Please specify this in the text. Also as aromatics are not measured here, as well as the ether or alkene functions, OM concentrations are potentially under evaluated. Do you have an idea of the magnitude of this bias? And more generally the uncertainties associated with these OM values (at least the sum of all uncertainties associated with each functional group quantified)?

The calculation of OM is now included in our text (Methods section). The relatively high

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detection limit of alkenes and aromatics could bias reported low OM concentrations, but aromatic and alkene groups are expected to account for 2-5% of OM (Russell et al., 2009), as we also now mention in the text. This and other comparisons with AMS measurements suggest biases less than 10%. The revised text is included in a response to an earlier comment.

3.4. Page 2658 line 14 you state that FTIR provides concentrations of aromatic groups. Why aromatic concentrations are not presented in the manuscript? Considering the abundance of aromatic compounds in biomass burning aerosol (methoxy-phenols, PAHs, ...) I am pretty sure that it is not a problem of detection limit.

It is a detection limit issue, but we report that values are below detection limit for two reasons:

1. On a pure mass basis, the molar absorption coefficient (integrated absorption/moles of functional group) is very low (Russell et al., 2009), so the uncertainty is much higher (particularly for lower concentrations).
2. Aromatic and alkene peaks exhibit sharp peaks, and this is confirmed in laboratory standards. In ambient samples, we rarely observe the presence of these peak because they overlap absorbance regions by the more plentiful alkane bonds.

4. You observed a strong biomass burning event between July 28 and August 8. Considering fig 2, there are very little differences of the OFG relative contributions with the other periods. You suggest that this uniformity of the OFG fingerprints along the campaign can be explained by chemical aging of the OM. I globally agree with this assumption, especially for BB aerosol. On the other hand, I believe (maybe I am

C2606

wrong) that OFG of the total OM are mainly driven by HULIS functionalisation. If true these observations suggest that HULIS are reactive.. What is your feeling on this issue?

We propose that the overall uniformity is due to both aging and mixing of aerosols emitted from different sources. As HULIS are thought to be the aged product, it may be that in this case it is an issue of mixing rather than aging, though when examined more closely the “purest” instances of biomass burning aerosol spectra do appear to have composition different from the rest of the periods (Fig. 9).

5. I do not understand very well the complementarity of hierarchical clustering and the PMF analyses. In other words, PMF analysis was not sufficient? (This section is also particularly difficult to read, please try to simplify)

Hierarchical clustering groups spectra into categories (presumably containing spectra from aerosols with similar source and aging histories), while PMF has the potential to directly find a set of common components in all spectra. Given the strengths and weaknesses of each approach for explaining the sources of aerosols to the area, using both methods provides a robust interpretation of the measurements. This is now explained in more detail in the Methods section and Table 1. The revised text in the Methods section is as follows:

“While a successful PMF separation can provide average component profiles comprising the measured set of mixture samples, regression analysis eliminates some uncertainties associated with the bilinear decomposition problem of PMF by fixing the component profile matrix, provided that the profiles are complete and correct. This latter condition is found to be approximately satisfied, as the component profiles

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obtained from PMF are nearly identical to the set of spectra used as regressors (Sect. 3.3.2). Cluster analysis is also used to centre the discussion around a few spectra types, each of which presumably share similar histories (i.e. sources and extent of atmospheric processing). An agglomerative, hierarchical clustering algorithm outlined by (Ward, 1963) is applied to the ambient submicron aerosol spectra after normalizing by their respective dot products (Murphy et al., 2003). In the extreme and idealized case where a single set of components are observed at the site for each FTIR filter sampling period, PMF factors and clusters centres should be approximately identical. However, the more likely scenario is that clusters represent sets of sample mixtures containing relatively similar proportion of components; while PMF factors correspond to the elementary, statistically distinguishable components, with factor strengths indicating their relative contributions to each sample mixture. To address the questions pertaining to effectiveness of separation in and understanding of PMF solutions (Paatero et al., 2002; Ulbrich et al., 2009), a combination of cluster analysis, regression, and PMF approaches is used to provide complementary information and robust interpretations to the analysis of ambient aerosol spectra.”

6. I am very surprised by the OFG fingerprint of BB inferred by PMF (fig 11 and 12). BB OFG exhibits a huge contribution of alkanes (~40%) and a very small contribution of hydroxyl group (~5%) (even smaller than that reported for fossil fuel combustion aerosol !). Biomass burning aerosol particles are however associated with the huge amounts of levoglucosan (C6 compound bearing 3 OH groups) plus other sugars and of methoxy-phenols (guaiacyl and syringyl derivatives), but are not known to contain a lot of alkanes (see for example Fine et al, EST, 2002). Can you discuss this issue?

We thank the reviewer for initiating this discussion. A response has been included in the Results and Discussion section (3.3.2). We believe this observation is due to the degradation of levoglucosan and other anhydrous sugars in an aged biomass burning

C2608

plume, and the fact that the FTIR measures a larger fraction of the OM mass than previously reported (which includes alkane functional groups from alkanolic acids, alkanals, waxes, in addition to those in the remaining sugar compounds).

The revised text is as follows:

“[...] The overall spectral shape and composition is unmistakably attributable to burning sources similar to those observed in many locations (including San Diego, CA, and Mexico City, Mexico; Table 1 and Figure 2D by Russell et al., 2011), and this aerosol type measured by FTIR has been shown to correlate with AMS BB aerosol components (Hawkins and Russell, 2010). The proportion of alcohol, acid, and ketone groups are in general agreement with average compositions for similar measurements of BB aerosol reported previously (Russell et al., 2011). The primary amine fraction is significantly higher than what appears to be a background concentration present during other periods, consistent with other findings of elevated amine concentrations in BB aerosol (e.g., Laskin et al., 2009). Regression analysis also supports this interpretation, with BB contributions explaining 60% of the variation, with 20% contribution from forest components (Fig. 9e). These spectra were observed sometime during the evenings of 17 August to 21 August and 31 August to 3 September, which were periods independently determined to be influenced by fire emissions (Fig. 9f’).

Significant mass contributions from levoglucosan and other anhydrous sugars have been identified in BB aerosol, with levoglucosan mass contributing between 3-16% of OM identified by gas chromatography and mass spectrometry (GC-MS), (Fine et al., 2002); 25% by IC analysis and evolved-gas analysis (EGA) (assuming OM/OC of 1.6, Sullivan et al., 2008). However, levoglucosan or its markers have been reported to degrade in aged BB plumes (Hennigan et al., 2010; Cubison et al., 2011). Degradation of levoglucosan up to 80% have been observed in the laboratory under

C2609

typical atmospheric oxidation conditions (Hennigan et al., 2011). The OM/OC and O/C ratios discussed below indicate an aged BB aerosol, which is consistent with the low hydroxyl organic aerosol fraction reported here. In addition, FTIR resolves most of the OM mass (Turpin et al., 2000; Russell, 2003), possibly providing a more complete picture of relative composition. The FTIR method is sensitive to the organic hydroxyl content of the aerosol (as demonstrated by Russell et al., 2010), but also measures the alkane groups present in levoglucosan and other anhydrous sugars, in addition to hydrocarbon chains including alkanolic acids, alkanals, waxes. There may also be a non-negligible contribution from burning and non-burning leaf-related emissions. For instance, levoglucosan levels in leaves tend to be lower than wood burning (Schmidl et al., 2008; Sullivan et al., 2008), and concentrations of other anhydrosugars formed during pyrolysis of cellulose can vary across fuel type (Schmidl et al., 2008). Lofted plant waxes co-emitted with biomass burning in forests may also provide a partial explanation for this discrepancy, as evidenced by the visible methylene peaks in the spectra.

This pair of sharp peaks has been observed and described by Hawkins and Russell (2010). The authors observed this same spectral feature in a subset of samples collected at the Scripps Pier during summer 2008, and identified it as being associated with the BB PMF factor (Fig. 10E). The sharpness of the peaks, which are located at the sp^3 C-H stretching absorption from methylene groups, is suggested to originate from repeating methylene units in long-chain plant cuticle wax detritus (Hawkins and Russell, 2010). Hawkins and Russell (2010) report several observations in which these compounds were lofted in large wildfires (Simoneit, 1985; Fang et al., 1999; Simoneit et al., 2004; Medeiros et al., 2006).”

7. Amine concentrations are not discussed in the manuscript. Do you think that primary marine aerosol can contribute to the total amine concentrations observed in

C2610

your study?

For the small amount of amines present in most samples, this is a possibility, though from a comparison of spectra to marine-derived FTIR spectra studied previously (Russell et al., 2010), marine aerosol is not a dominant influence at the site. There are no other indicators that were measured then or routinely that suggest the site is significantly influenced by marine sources. This is in part because air from the Pacific with a strong up flow component usually includes significant precipitation that cleans the air before it reaches the site. During periods of long-range transport from across the Pacific, there is often subsidence rather than uplift associated with the flow. In 2006, we saw evidence for sea salt at the Peak but it appeared to have been connected with dry salt lakes in Mongolia rather than the Pacific Ocean. The times when we might see a relatively local marine influence is when flow comes up the valley from the Vancouver area and the aerosol will have a significant anthropogenic component.

8. Why PMF analysis has not been performed with the AMS dataset? It would have been very relevant to combine AMS/PMF and OFG analyses.

The instrument used was the ACSM, which is similar but not identical to the quadrupole AMS. This was the first deployment of a commercial ACSM; algorithms for PMF on ACSM data is currently under development.

1.2 Specific comments

P2656 line 10 : "Ketone".. All along the text non acidic carbonyl function is called

C2611

carbonyl or ketone or non acidic carbonyl. Please choose a denomination, and clearly define it in the method section.

We have made these changes, and have defined it in the methods section (included in a response to a previous comment.)

P2656 line 10 : what do you mean by "forest aerosol"?

The abstract has been revised to reflect our more relevant conclusions (and this phrase has been removed). The revised text is included in response to Reviewer 2 below.

P2659 line 23 : "Sizer" instead of "System".

This has been changed.

P2660 line 21 : What do you mean by 'nearly monodisperse aerosol'?

We meant that the aerosol size distribution has a very narrow distribution but may include (much) smaller modes from multiply charged particles; we have revised the statement to indicate that it is the aerosol which is selected by the DMA at a 10:1 sheath to sample flowrate ratio.

P2661 line 1 : A Single Particle Soot photometer (SP2, Droplet Measurement Technologies, Inc)

C2612

This has been changed.

P2661 line 18 : 120 L m-3 P2664 line 11-12 : Please explain the method used (shortly). What are the implications of the result obtained (slope 1.25). I suppose that you compare your OFG results (OM) obtained in the submicron fraction with the ACMS results. Please specify.

A brief description of the calculation and the significance of this correction has been included:

“The episodic variations in OM concentrations quantified by FTIR are also captured by co-located organic aerosol measurements from the ACSM, with a correlation coefficient of 0.88 and reduced major axis regression slope of 0.57 between the two methods. A time-dependent collection efficiency was estimated for the ACSM, using its ammonium to sulphate ratio (as described by Quinn et al., 2006) with a collection efficiency of 1 for a ratio of zero (sulphuric acid) and 0.45 for a ratio of 1 (ammonium sulphate), with values linearly interpolated in between. This calculated collection efficiency was 0.49 on average; the post-corrected correlation between the ACSM and FTIR OM is 0.88 with a new major axis regression slope of 1.25. The independent correction brings the ACSM-FTIR in agreement within 25% on average, but with a strong correlation, which is more relevant for the analysis in trends considered in this manuscript.”

P2664 line 20, 21, 28, 29 : (r=X, n=??) P2666 line 14-16 and line 28. BB is also a combustion.

We thank the reviewer for bringing this detail to our attention. BB combustion is
C2613

distinguished from fossil-fuel combustion by labeling the latter as anthropogenic combustion in all cases. The number of points for each correlation are also included.

P2667 line 3 : Org/(org+sulfates) ? Not shown in fig 7a.

It is now indicated that the absolute values of concentrations (not the ratios) are shown.

P2668 line 26-27 : Biogenic Part 3, Biogenic Part 1?? Please explain. P2671 : For fig 11, report Fig11A or E instead of fig11a or e

The citation to Schwartz et al. (2010) has been added as these names are factors defined in their work.

P2675 and 2676 : Section 3.4 is useless.

This section has been reduced to highlight the observation of common sources at the site.

2 Reviewer 2

Abstract: As stated above, the abstract does not focus the reader on the key points of the paper.

The abstract has been revised to address key points:

C2614

“Ambient particles collected on teflon filters at the Peak of Whistler Mountain, British Columbia (2182 masl) during spring and summer 2009 were measured by Fourier transform infrared (FTIR) spectroscopy for organic functional groups (OFG). The project mean and standard deviation of organic aerosol mass concentrations (OM) for all samples was 3.2 ± 3.3 ($\mu\text{g m}^{-3}$). Measurements of aerosol mass fragments, size, and number concentrations were used to separate fossil-fuel combustion and burning and non-burning forest sources of the measured organic aerosol. The OM was composed of the same anthropogenic and non-burning forest components observed at Whistler mid-valley in the spring of 2008; during the 2009 campaign, biomass burning aerosol was additionally observed from fire episodes occurring between June and September. On average, organic hydroxyl, alkane, carboxylic acid, ketone, and primary amine groups represented $31\% \pm 11\%$, $34\% \pm 9\%$, $23\% \pm 6\%$, $6\% \pm 7\%$, and $6\% \pm 3\%$ of OM, respectively. Ketones in aerosols were associated with burning and non-burning forest origins, and represented up to 27% of the OM. The organic aerosol fraction resided almost entirely in the submicron fraction without significant diurnal variations. OM/OC mass ratios ranged mostly between 2.0 and 2.2 and O/C atomic ratios between 0.57 and 0.76, indicating that the organic aerosol reaching the site was highly aged and possibly formed through secondary formation processes.”

Introduction: The introduction describes why characterization of high elevation sites is important. It would be helpful to also make the link why functional group analysis is particularly useful and to put the current work in context of similar remote and/or high elevation studies.

The introduction has been modified to put the study in context of high-elevation monitoring stations, and the relevance of functional group analysis.

C2615

Methods: How this work relates to past research and data from this Environment Canada site is not made clear so the first couple of sentences appear irrelevant. Although most of this paper is devoted to FTIR measurements, the description of the FTIR analysis is given the less thorough description than other techniques that are only mentioned once. This should be expanded to give a more complete description of what is being measured and what the sensitivity and MDLs of the method are. In this section, each sampling event is said to last for 3 days but the graphs and later discussion state that it is sometime 5 days. That information should be stated in the methods section. Inclusion of the sampling description in the middle of paragraph about the IR is awkward. The list of what functional groups IR can measure and what is actually able to be measured at this site should be close together in the paragraph. The particle number measurement paragraph is very confusing and should be simplified. There is a repeated sentence in the SP2 paragraph. The description of the analysis of ACSM data is not clear. Explain “to compare similarity.”

The description of the FTIR analysis has been improved. (Revised text is included in response to Reviewer 1 above.)

Results: 3.1 Splitting up the analysis of the data by the unfortunate gap in the data is not atmospherically relevant and should be avoided. Comparisons of the two data sets are misleading in part because there are many more samples in the second time frame than the first. I would suggest seasons or monthly time periods. Paragraph 2: What is the detection limit of ketones. Is the large % of ketones in the samples were it is above the MDL due to masses of ketones way of the MDL or are all the data near the MDL so that the MDL cut-off is driving the 0% for some samples and 27% for other samples on average? Describe why the list of characteristics that correlate with ketones supports your hypothesis that these are biogenic. Are there other functional groups that correlate similarly with these characteristics that you don't

C2616

think are biogenic? Figure 3 could be moved to supplemental material. Although this bit about the NEXAFS is interesting, there is so much going on in the paper that this strikes me as something that could be omitted. I don't know much about tarballs but surely that have more than just a ketone absorption so this does not provide definitive connection between ketones and bb aerosol.

The periods correspond approximately to one spring month (first period) and several months spanning the summer (second period) – we have therefore retained these divisions but refer to them by their season designations.

We have forgone the option of including a supplemental section, so we have retained Fig. 3 in the manuscript – but we have removed Fig. 5 (the comparison of coarse and submicron aerosol for selected periods), which the reviewer had also suggested removing. The connection of ketones and biogenic is not definitive, but the resemblance of entire x-ray spectra with adds further evidence; this is one of the many pieces of evidences we are presenting to make our case.

The non-acid carbonyl detection limit is approximately 0.5 nmoles of bond (Russell et al., 2009); the discussion regarding its absence in some samples is noted below. Regarding the relationship of ketones to biogenic emissions, Schwartz et al. (2010) provides extensive discussion regarding sources of ketones in the region, and is now referenced in Section 3.1.

Results: 3.2 Figure 4, the legend is incorrect. The caption mentions asterisks labels but they do not show up on my copy of the figure. Figure 5 could be moved to supplemental material or excluded. Adding a few soil related elements to figure 6 would be useful for comparison. XRF measurements elements not just metals and not

C2617

all of them are trace so the term trace metals is incorrect here. State what the fact that soil is higher during the day adds to your story or helps explain. In the sentence that starts "The lack of large: : .the word organic is missing just prior to "aerosol originates: : ."

The legend has been corrected. The asterisks have been replaced with ×'s. Figure 5 has been removed. We thank the reviewer for catching the erroneous use of the word metals and omission of the word "organic", which have now been corrected. It is also now stated that the diurnal variations in dust marker concentrations (presumably from more local sources) are meant to provide contrast to organic aerosol concentrations, which appear to be more regional in origin.

Results: 3.3 Comparisons to previous work by your group at this site are confusing. For instance in the first sentence you talk about spring at Whistler. Is that this sampling campaign or the one from earlier? "in perceived chemical characteristics" is unclear It is not clear from Figure 7a that the burning and non-burning are different. Perhaps plotting the relative fraction instead of the absolute data would be helpful. Line 5 on page 2667 regarding figure 7a, you say organic and sulfate but mean nitrate and sulfate. Caption should state that white or no-shading is anthropogenic. This section is too long and without any demarcation to guide the reader. The clustering and PMF of IR spectra both seem to be useful tools for analysis. Are both necessary? Line 16 on page 2669 has a missing reference. Page 2672. Ketones were not observed in the total samples. This is a curious result that would be valuable to provide more insight into. Is the ketone peak hidden when mass is large and if so this could be a bias in our results? Or is the ketone apportioned to CA in the total but not in the more time/size resolved samples? What does this state about limitation of the method? Could you decrease the number of PMF solutions and still provide a complete picture. The discussion on 4 factor results is confusing given that you show 6 factor result that

C2618

is useful.

We do in fact intend to mean organic to sulfate ratio. The absolute values are shown rather than ratios, because of the low concentrations during some periods. But it is indicated that while we talk about ratios, the absolute values are shown for graphical presentation.

We have added demarcations which organize the discussion around a few subtopics. The complementarity of PMF, cluster, and regression analyses are discussed in the Methods section. (Revised text is included in response to Reviewer 1 above.)

The absence of ketones in the total day and night samples is very interesting. The quantified amount of total carbonyl is not below detection limit, but in fact span the range of values in other (submicron and total) samples collected during either day or night. The difference from the submicron samples is that there is as many bonds of carboxylic C-OH quantified as carbonyl, so essentially all of the latter apportioned as acid carbonyl according to our algorithm. However, given the nearly 1:1 correspondence (now added to Methods section), it is unlikely that this is an artifact of our calculations. A possible explanation is perhaps the difference in day-night gas-phase composition and its interaction with particles from the previous day/night – either through changes in gas-particle equilibrium, or heterogeneous reaction and conversion or evaporation.

Conclusions: The first paragraph is summary material that is not necessary to repeat. The second paragraph focuses on the one paragraph analysis immediately preceding the conclusions and which seems excessive. Focus on important points.

C2619

We have combined the first and second paragraphs for brevity, though we did not remove the summary entirely as we mean to provide a synopsis for the casual reader who does not read the entire manuscript.

The last paragraph has been revised as follows to highlight the main points of the work:

“From an analysis of aerosol measurements and air mass backtrajectories, the sampling campaign was divided into periods primarily influenced by anthropogenic combustion, non-burning forest emissions, and biomass burning sources. FTIR aerosol spectra resembling the anthropogenic combustion PMF factor from the Whistler mid-valley campaign (2008) were observed during the anthropogenic combustion periods. These spectra have a characteristic ammonium absorbance (often associated with sulphate) and are dominated by alkane functional groups (39% on average) in the organic aerosol fraction. Spectra of aerosols collected during a few biomass burning periods resembled the biomass burning component from the Scripps Pier campaign (2008) in San Diego, CA. This spectra type contained sharp methylene peaks attributed to plant waxes, and a large contribution of ketones (26% on average) to the organic aerosol mass. Spectra resembling non-burning biogenic forest component from the Whistler mid-valley campaign were also observed during periods determined to be dominated by non-burning biogenic sources. The remaining FTIR spectra appeared to contain a mixture of aerosols from these three sources, which is a plausible outcome due to the remoteness of the sampling location and three to five-day sampling intervals. While PMF decomposition of this spectra set revealed components (anthropogenic combustion, non-burning biogenic, and burning) similar or nearly identical to factors found in previous campaigns, OM/OC ratios and O/C ratios of values often greater than 2.0 and 0.57, respectively, indicating the organic aerosol observed at the site were highly aged and possibly formed through secondary generation mechanisms.”

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