

Responses to *Reviewer #1*

Specific comments

1. *The correlation between FTIR and AMS is reported in Figure 1. The higher FTIR OM concentration relative to AMS is explained by the presence of OM that is not detected by AMS and associated with dust particles. It would be interesting to additionally report the correlation between the FTIR and AMS OM when the samples characterized by high dust content are removed, in order to support this explanation. This has already been reported. On page 4796, lines 21-23 “Samples with Si concentrations below $0.05 \mu\text{gm}^{-3}$ have a slightly higher correlation of $r = 0.89$ (V-mode) and lie closer to the 1:1 line.”*

It is important to discuss qualitatively and quantitatively the potential interference of dust components (i.e. silica and other metal oxides) in the FTIR OM quantification. Specifically, do metal oxides absorb infrared radiation and if so what is the intensity of this absorption? Which functional group could be affected by the interference? For example, Si-OH groups of silicate may absorb IR radiation at $3400 - 3600 \text{ cm}^{-1}$ and this would lead to an overestimation of OH hydroxyl group concentration and O/C ratio. How could you exclude or quantify dust interference?

The reviewer brings up an important discussion point. The Whistler samples show little presence of absorption peaks from reported Si-OH and silicate groups and we have concluded although other components may absorb in the quantified FTIR region there is negligible interference to reported OM and thus, O/C. For example, Matveen et al., 2005 report two regions of olivine (one of the most common minerals on earth) hydroxyl stretching bands, referred to as Group 1 ($3430\text{-}3590 \text{ cm}^{-1}$) and Group 2 ($3285\text{-}3380 \text{ cm}^{-1}$). We have found only negligible absorption in these regions. The strong absorption around 1800 cm^{-1} as reported in Matveen et al. 2005 is also not observed in the Whistler spectra. Additionally, Allen et al. 1994, Maria et al., 2002 and 2003, report silicate ion absorptions at lower frequencies around 800 cm^{-1} and 1000 cm^{-1} ; all of these peaks are small or absent.

2. *The difference between AMS and XRF sulfur concentration indicates that that 70% of S is apparently not present as sulfate, or if it is sulfate it is not detected by AMS. This discrepancy needs further explanation.*

A comparison of the filters used for FTIR and XRF by ion chromatography (IC) suggest the AMS is not detecting all the sulfate. This may be due to both collection efficiency and transmission efficiency. The following sentence was added to page 4796 line 26: “Comparisons to analysis of FTIR filters by ion chromatography (using the method of Toom-Sauntry and Barrie, 2002) show that most of the XRF S is present as sulfate. This implies that a portion of sulfate is not detected by the AMS and may be the result of the collection efficiency for sulfate and the transmission efficiency of the AMS” In addition, a figure illustrating comparisons between AMS, XRF and IC sulfur is included in Figure R1 below.

3. High concentrations of submicron dust were observed during the entire campaign. Would it be possible to implement the discussion of dust sources, reported at page 4798, comparing the observed dust elemental ratios with those expected for local dust sources? Are there super-micron dust data available for the same site that corroborate a local source for certain wind directions?

The text has been reorganized as suggested. The sentence “The submicron dust elemental concentrations (Fig. 2) were present in ratios similar to those found in Asia and North America (McKendry et al., 2001).” has been moved to 4798, and the figures re-ordered according. The reviewer provides an interesting suggestion that we are unable to address, because supermicron dust composition measurements were not collected during the project.

4. The correlation of PMF factor 4 with fossil fuel combustion sources could be further discussed by investigating the correlation of factor 4 with integrated average BC concentrations.

Filter-averaged BC and the combustion factor are weakly correlated ($r = 0.39$). However, there was no evidence in the AMS OM for the BC spikes that were associated with local trucks. This has been added to the discussion of this factor on page 4800.

5. The correlation between the biogenic factor and Si seems driven by the two high concentration data points. It would be useful to re-evaluate the correlation introducing a normalization function to validate the linear fit.

The reviewer is correct in noting that the correlation is affected by the two high concentration points. With these points excluded the correlation is weak ($0.25 < r < 0.5$) rather than mild ($0.5 < r < 0.75$). We have added that the correlation is strengthened by the two high concentrations points to the text.

Technical corrections

Page 4790, line 8-9

The sum of percentage is larger than 101%. Please verify the values.

These values have been verified. The larger than 100% sum is due to rounding. The values with additional significant figures are as follows. On average, organic hydroxyl, alkane, and carboxylic acid groups represented 33.96%, 32.65%, and 22.52% of OM, respectively. Ketone, amine and organosulfate groups constituted 5.65%, 4.66%, and 0.56% of the average organic aerosol composition.

Page 4792, line 25

The discussion of the oxygen to carbon ratio as measured by AMS is very detailed for the non-AMS user. I would suggest rephrasing the sentence, and explaining the acronyms.

The sentence has been rephrased to clarify OOA-1 and OOA-2 as the more- and less-oxygenated organic aerosol, respectively. “The large concentrations of biogenic SOA

measured at Egbert, Canada, were constrained by a lower limit of the less-oxygenated organic aerosol (OOA-2, O/C ~0.46) and an upper limit of the weighted sum of the more-oxygenated OOA-1 (O/C ~ 0.81) and OOA-2 (Slowik et al., 2009). Slowik and colleagues approximate the O/C ratio from the fraction of m/z 44 (CO_2^+ ion) in the total organic mass spectrum, as presented by Aiken et al. (2008).”

Page 4793, line 14

“Spectroscopy” should be added to *Fourier Transform Infrared (FTIR)*.
“Spectroscopy” has been added.

Page 4793, line 17

“Gas Phase species” instead of “gas phase”
“Gas phase” has been changed to “gas phase compounds” to avoid potential for confusion with biological entities.

Page 4794, line 18

I guess you meant “enabling a distinction between hydrocarbon (C_xH_y) and oxygenated hydrocarbon ($\text{C}_{x-1}\text{H}_{y-4}\text{O}$) fragments”.
Yes, the reviewer is correct in noting that $\text{C}_{x-1}\text{H}_{y-4}\text{O}$ is a likely oxygenated hydrocarbon fragment. This has been changed to “enabling a distinction between hydrocarbon (C_xH_y) and oxygenated hydrocarbon (for example, $\text{C}_{x-1}\text{H}_{y-4}\text{O}$).”

Page 4796, line 21

There are two references called “Hawkins et al. 2010”. Please specify which one you want to cite on this line or verify the publication date in the reference list
We cite Hawkins et al., 2010 and Hawkins and Russell, 2010. The line has been left as is since these references appear distinct due to the number of authors.

Page 4797, line 26

Please verify the percentage values; their sum is 101%.
These values have been verified. The larger than 100% sum is due to rounding. The values with additional significant figures are as follows. On average, organic hydroxyl, alkane, and carboxylic acid groups represented 33.96%, 32.65%, and 22.52% of OM, respectively. Ketone, amine and organosulfate groups constituted 5.65%, 4.66%, and 0.56% of the average organic aerosol composition.

Page 4799, line 20

Figure 5 in the text is commented before figure 4. The figure order should be reversed.
Yes, the reviewer is correct in noting that Fig. 5 is mentioned before Fig. 4 on page 4799. The order of the figures has been corrected to be consistent with this.

Page 4801, line 15

Use *adl* as acronym for above detection limit.
Above detection limit (*adl*) has been added and used.

Page 4819

For consistency, “BDL” should be replaced with “bdl” (lower case).

“BDL” has been changed to “bdl”.

Responses to Reviewer #2

1. Page 4803, lines 22-25: *The suggestion that the correlation between dust and the biogenic factor may be due to adsorption of products of BVOC oxidation onto dust particles can be made stronger by estimating the mass of organics that could adsorb in a monolayer onto the dust surface area. The dust surface probably wouldn't have much impact on adsorption beyond a monolayer.*

For a 0.5 μm particle with 50 $\text{Angstrom}^2/\text{molecule}$ monolayer (with 0.35 organic mass fraction and 176 g/mol molecular weight) then the percentage of monolayer mass to organic mass is only about 2%. At smaller sizes, this fraction increases to an upper bound of approximately 25%. Thus, without size-resolved measurements it is difficult to argue that a significant fraction of the organic mass exists as an adsorbed monolayer.

2. Page 4803, lines 26-29: *I don't think the correlation between the biogenic factor and the product of OM and BVOCs necessarily supports the Odum 2-product model any more than it supports, for example, the Donahue basis set model. The correlation probably supports any kind of SOA absorption model, but since surface area should scale with OM it also could be consistent with an adsorption or absorption/adsorption model [Pankow (1994) *Atm. Env.* 28, 185-188].*

We thank the reviewer for the reference which we have added. Since the Donahue basis set model assume volatility information which we don't have we have decided not to discuss this model.

3. Page 4804, lines 7-10: *Please be more specific about what is meant by "an accumulation effect". Do you mean that as SOA is added the surface area increases so the rate of condensation accelerates?*

The reviewer provides an interesting suggestion. The sentence has been changed to clarify our original meaning of accumulation effect as follows: "In addition to the delay associated with the chemical formation of biogenic SOA, there may also be an accumulation of BVOC contributions as the aerosol passes over multiple forested regions, which would also result in a lag between the peaks in BVOC and biogenic SOA concentrations."

4. Page 4806, lines 1-4: *"Reactive" is probably a better descriptor for aldehydes than "unstable". You might mention that losses could be due to photolysis [Pan et al. (2009) *ACP*, 9, 3851-3865] or oligomerization reactions [Jang and Kamens (2001) *ES&T*, 35, 4758-4766].*

"Too volatile" has been changed to "reactive". We thank the reviewer for the references which have been added.

5. *Is the combustion factor thought to be POA or SOA? There's not much discussion of this factor.*

Although it is likely that the combustion factor has a significant SOA component (as sulfate is a secondary product and we see a sulfate and combustion factor correlation), ambient sampling does not separate POA and SOA. POA and SOA may covary if POA and VOCs are emitted simultaneously from the same sources. The time delay that may initially differentiate them is lost during transport. For combustion sources, an indirect technique for distinguishing POA and SOA uses the expected synchronicity of POA and heavy metal tracers of combustion (for which there is not a biogenic analog) to separate POA temporally from SOA formed several hours later (Russell et al., 2009). However, the combustion source sampled at Whistler was too small and probably too distant to resolve this type of delay between POA and SOA on the 12-hr sampling schedule.

References

Allen, D. T., Palen, E. J., Haimov, M. I., Hering, S. V. and Young, J. R.: Fourier Transform Infrared Spectroscopy of Aerosol Collected in a Low Pressure Impactor (LPI/FTIR): Method Development and Field Calibration, *Aerosol Science and Technology*, 21: 4, 325 – 342, 1994.

Maria, S. F., Russell, L. M., Turpin, B. J., and Porcja, R. J.: FTIR measurements of functional groups and organic mass in aerosol samples over the Caribbean, *Atmos. Environ.*, 36(33), 5185–5196, 2002.

Maria, S. F., Russell, L. M., Turpin, B. J., Porcja, R. J., Campos, T. L., Weber, R. J. and Huebert, B. J.: Source signatures of carbon monoxide and organic functional groups in Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) submicron aerosol types *Journal of Geophysical Research - Atmospheres*, 108, D23, doi:10.1029/2003JD003703, 2003.

Matveev, S., Portnyagin, M., Ballhaus, C., Brooker, R., Geiger, C.A.: FTIR spectrum of phenocryst olivine as an indicator of silica saturation in magmas, *Journal of Petrology*, 46, 603-613, 2005.

Russell, L. M., Takahama, S., Liu, S., Hawkins, L. N., Covert, D. S., Quinn, P. K., and Bates, T. S.: Oxygenated Fraction and Mass of Organic Aerosol from Direct Emission and Atmospheric Processing Collected on the R/V Ronald Brown during TEXAQS/GoMACCS 2006, *Journal of Geophysical Research - Atmospheres*, 114, D00F05, doi:10.1029/2008JD011275, 2009.

Toom-Sauntry, D. and Barrie, L. A.: Chemical composition of snowfall in the high Arctic:1990–1994, *Atmos. Environ.*, 36, 2683–2693, 2002.

Figures

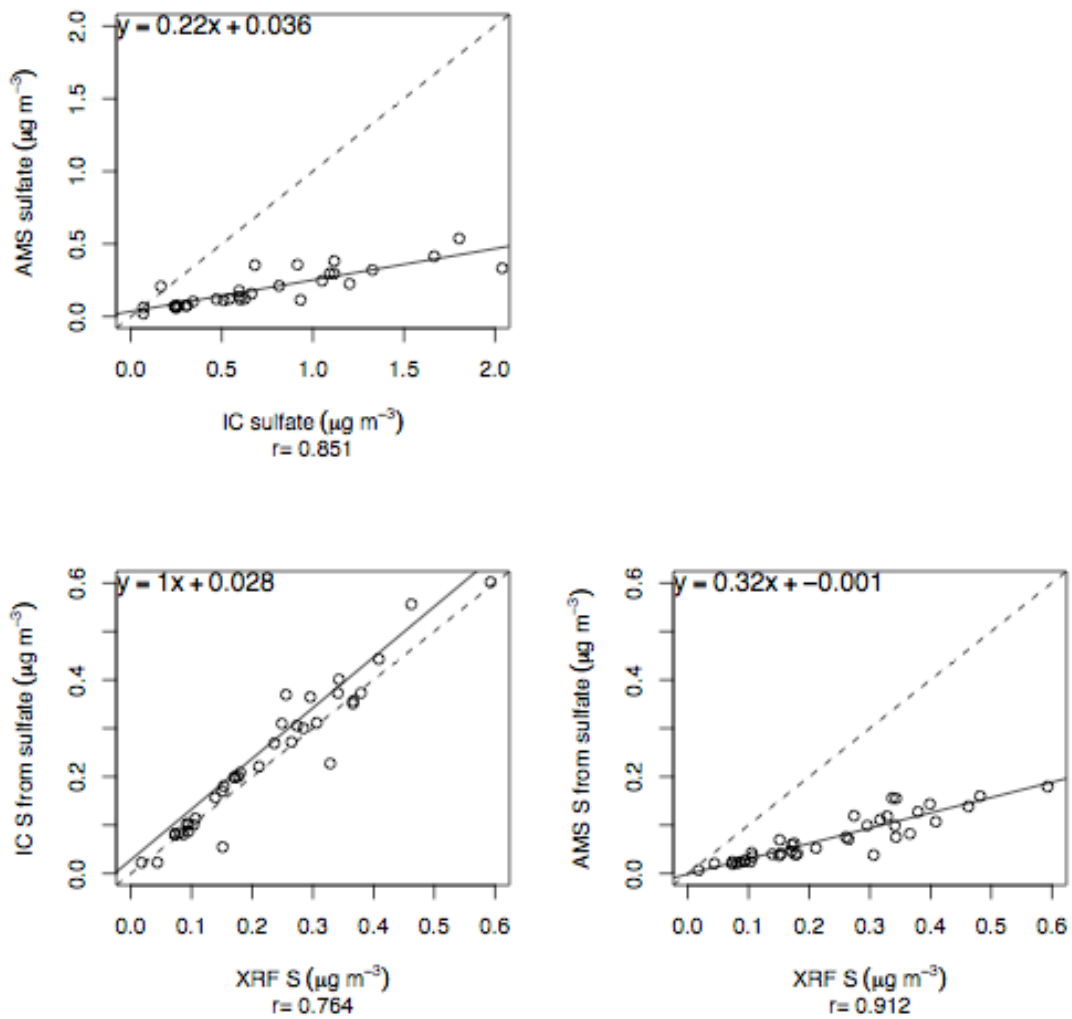


Figure R1. Comparison of a) AMS sulfate to IC sulfate, b) IC S (from sulfate) to XRF S, and c) AMS S (from sulfate) to XRF S.