Responses to reviewer #2

The authors thank reviewer #2 for the helpful comments. Below is the point by point response for the detail comments.

Comment #1

Chan et al. describe an interesting study with surprising results. However, I feel that several of the conclusions drawn are not supported by the data as analyzed and presented in the paper, and cannot recommend publication. In particular, the authors need to provide more evidence to support their conclusion that the spectral attentuation coefficient (SAC) is linearly related to aging, and that at zero-aging, primary soot particles have a given SAC. In the abstract, the authors describe a daunting 50% difference between global models and the Egbert measurements, but a.) the uncertainties in the measurements need to be more carefully considered, and b.) this number and the measurement-model comparison is not explained in the manuscript. The authors further claim that significant differences exist in aerosol composition between the northerly and southerly wind directions, and that these differences are due to different sources. However, for the most part, the statistics presented in the paper do not support this (with notable exceptions in b_asp), and I question whether temperature, which is significantly different between the two wind classifications, is instead the dominant driver of differences in organic aerosol (OA) processing.

Response to comment #1

The "50%" difference mentioned in the abstract is a conservative estimate based on the change in the SAC in Figure 8. Models assume that light absorption by black carbon (i.e. SAC) increases with coating by non-absorbing materials (e.g., Jacobson, 2001; Chung and Seinfeld, 2002; Kim et al., 2008). We find that the SAC for both groups (north and south) deceases with increasing POC (or OM+NO3+SO4, which now replaces POC). We can not say that we measured EC cores coated with inorganics and organics, but certainly condensation on EC cores is a major result of sulphate and nitrate formed by secondary processes and models would likely treat our situation as coated EC particles. If the SAC were assumed constant or increased, the model values would estimate higher light absorption than indicated by our results by 50% or more. Of course, such an estimate depends on the particle lifetime among other things.

As suggested by the reviewer, we have improved our handling and discussion of the uncertainties.

We can not say with certainty why we see a difference between the north and south aerosols, but the important point is that they are different. The fresh particles with a short atmospheric history (1-2 days) from the south reaching Egbert includes a strong influence from anthropogenic sources (e.g. the biggest urban area in Canada and the northeast of US). The fresh emissions tend to dominate the particle composition. On the other hand, except for some specific circumstances such as plumes from the Sudbury region travelling over the site, particles arriving from the north would not have experienced recent dominant contributions from anthropogenic sources. The dominant composition of the north particles may relate to natural sources or to more distant anthropogenic sources. Temperature may indeed be a factor. We have modified the discussion to better address this.

Comment #2

The study divides air masses into two wind direction classifications, north and south. However, these two wind directions are apparently accompanied by very different

meteorology, with southerly winds being much hotter. The authors have not convinced this reviewer that wind direction is the appropriate classification scheme rather than meteorological conditions: the chemical implications of these two approaches on aerosol processing are potentially significant, particularly with respect to aging.

Response to comment #2

Certainly temperature can be a major driving force for the OA processing, particularly via OH production. It must be considered as a possibility here as well as other factors such as the availability of precursor compounds in the atmosphere.

During the biogenic period (Slowik et al., 2009), the winds were out of the north but the temperatures reached 30^{o}C. In that case we suspect that a major role of temperature was in driving the natural emissions at the source. On the other hand, anthropogenic precursor emission are not as related to temperature.

As also discussed in the response to comment #1, at this site aerosols in the southern air masses contain relatively high concentrations of anthropogenic components whereas the situation is different for aerosol particles from the north. Thus, we think a straight temperature separation would be more confusing because the sources and residence times are mostly quite different. The ideal solution will be to first separate the data based on the main source (north and south), and then further divide the data based on temperature, but the limited size of the measurements prohibits that in this case.

We also mention temperature as a potential contribution to our observations in the revised manuscript.

Slowik, J.G., Stroud, C., Bottenheim, J.W., Brickell, P.C., Chang, R.Y.W., Liggio, J., Makar, P.A., Martin, R.V., Moran, M.D., Shantz, N.C., Sjostedt, S.J., van Donkelaar, A., Vlasenko, A., Wiebe, H.A., Xia, A.G., Zhang, J., Leaitch, W.R., and Abbatt, J.P.D.: Characterization of a large biogenic secondary organic aerosol event from eastern Canadian forests, Atmos. Chem. Phys. Discuss., 9, 18113-18158.

Comment #3

The presentation of statistics is misleading in the number of significant figures presented: uncertainties (presumably standard deviations? or standard error of the mean? please specify in table captions) are given to at least two significant figures, which is incorrect: uncertainties are considered valid to one significant figure, and the mean should only be presented to that level of precision. For example, the authors present numbers in the format of 0.51 +/- 0.19. This is properly described as 0.5 +/- 0.2. Further, upon close examination of the numbers, the authors claim that there are significant differences between, for example, the OC_tot/TC ratio between north and south wind directions. However, these two numbers are 74+/-6 and 67 +/- 6, respectively, which are not statistically different (overlapping confidence intervals). The authors need to either perform statistically valid and robust tests on the data, or rewrite the sections of the paper describing supposed differences between OC/EC and OC/TC between the different wind directions.

Response to comment #3

We did indicate in the caption of Table 1 that the “uncertainties” in the parentheses are the standard deviations. The same is true for Table 3. We have revised the significant figures in these Tables as suggested by the reviewer.

We did test the confidence of the OC_tot/TC ratios between the northern (bg) and southern air masses, and we found that based on a 95% C.I. that the northern

OC_tot/TC value ranges from 0.63 to 0.71 while that for the southern air masses it ranges from 0.68 to 0.80. They do overlap slightly, but we do not see where we claimed the difference in the OC_tot/TC ratio between the northern and the southern air masses was significant. If we did, we are more than happy to revise that part. On p.14327, L10-13, we mentioned that the OC_tot/TC ratios were similar among the biogenic and biogenic-excluded periods from the northern air masses. There we did say that those values are different than those from the southern air masses; we will remove the words "In contrast" in that sentence.

Comment #4

The authors use datasets from 2005 and 2007; however, I am unclear as to what the 2005 datasets add to the analysis, and think it unnecessarily complicates the paper.

Response to comment #4

The 2005 data set, which was part of from our long term continuous filter measurements at Egbert, were initially compared with the AMS data which was taken at the same site. The data reveal some interesting findings but due to the lack of measurement points, we added to the analysis the results from the 2007 study. In the 2007 study, several changes were made in order to allow for better comparison between the filter samples and the in-situ AMS measurements. The major changes include the change of cyclone particle size cut from 2.5 micron (for 2005) to 1.0 micron (for 2007) to allow better overlapping particle size range between the AMS measurements and the filter measurements. Another change is to increase the measurement frequency from weekly (for 2005) to daily (for 2007). As the higher time resolution measurements generally provide more insight, attention was devoted to the 2007 data. As similar trends from the 2005 data still exist, they were also included. The attention for the individual data set in the manuscript is not a reflection of their importance. That said, we appreciate the above concern of the reviewer and have removed the 2005 data in the revised manuscript to make the paper clearer.

Comment #5

I am confused as to why the Northerly wind directions are not included in the aerosol aging analysis? The OM/OC ratios appear to be in the same range, and may have larger error bars, but should still fit the trend.

Response to comment #5

The OM/OC ratio is assumed to provide some indication of the relative particle photochemical age based on the assumption that the latter is proportional to the oxygen content in the particle. In Figure 3, we tried to use toluene-benzene ratio for the north, but the concentrations of both the toluene and benzene are too low to be meaningful.

Comment #6

p14431, the authors point out that on the 17 May 2007, the OM and OC are near detection limits - however, the error bars in the figure show very small uncertainties: these uncertainties must be underestimates, and the authors should check their calculations. The authors also carefully describe potential sources of error in the OM/OC ratio, but do not ascribe negative, positive or random biases to these sources of errors, which would be helpful.

Response to comment #6

The measurement uncertainty for the OM/OC ratio is determined based on propagation of error, which in this case is contributed from the uncertainties from the thermal measurements and from the in-situ AMS data. The uncertainties of the in-situ data are just the standard error of the mean for all the data points being averaged for the

corresponding sampling period. The uncertainties from the thermal data come from two sources: one is the instrumental detection limit, which is constant regardless of the data value; the other is based on comparison of the measured concentration of the standard reference material (urban dust) from NIST with the reported concentrations from NIST, which appears related to the magnitude of the concentration. We do not see a clear relationship between large uncertainties and measurements with values close to detection limit. We have re-checked the measurement uncertainties to confirm they are as reported in the manuscript.

The bias direction for the sources of errors for the corresponding measurements will be included in the revised manuscript.

Comment #7
I am concerned that the authors claim that the OM/OC ratios cannot be compared between 2005 and 2007 because different instruments were used: it suggests that not only is there a significant methodological problem, but that the numbers are in and of themselves worthless. If you can't compare the OM/OC numbers for 2005 and 2007, then how can you compare 2005 data to OM/OC ratios in other studies? This suggests that the authors don't trust the 2007 OM/OC numbers, and either they should not be included, or that the numbers are trust-worthy and the differences between 2007 and other studies are process-driven and should be explained. The figure describing the relationship between estimated oxygen mass and POC mass is good, but including the 2005 and 2007 data on the same plot seems inconsistent given that the OM/OC ratios are inconsistent.
Response to comment #7
This statement was a mistake. We did not intend to imply that the 2005 and 2007 instruments do not compare, but there were differences such as the seasons, averaging intervals and filter size cuts that complicate direct comparisons. It is clear from figures 6 and 7 that the 2005 and 2007 data are consistent.

However, the statement has been removed since in response to the reviewer's comment #4 above we have removed the 2005 dataset from the revised manuscript.

Comment #8
I am confused as to why the authors describe the comparisons between the benzenetoluene photochemical clock and the OM/OC ratio (an interesting and relevant comparison), and then use POC as an indicator of aging in the SAC section of the paper. Either OM/OC should be consistently used as an aging indicator, or the case for POC as an indicator could be made. However, I object to the sentence that the relationship between POC and SAC 'appear to be wind direction dependent' (p14334, l21-22). Could this also be a temperature-dependent or sulphate-dependent relationship?
Response to comment #8
OM/OC ratio has been used extensively in the past to refer to the oxidation history of aerosol particles. Instead of simply assuming that this is the case, we try to use what is available to confirm the assumption at the site.

The main objective of this manuscript is to develop a means to estimate or approximate the OM mass with the use of only thermal measurements. In the past, no such attempt has been done, and OC is almost always be converted to OM using a constant factor of 1.4. The factor of 1.4 appears to be a valid ratio to use as an overall average however

since the OM/OC ratio is not always constant as the authors demonstrated in figures 2 and 3 in the revised manuscript as well as other available literatures. As a result, applying a constant factor of 1.4 to all OC.for conversion to OM does not represent a realistic OM and the corresponding photo-oxidation history.

Owing to the small concentration range of the POC, this gives rise to the concern from the reviewer regarding the uncertainty in POC affecting the fit from a least squares regression slope. Although POC is related to oxygenated OC, to avoid potential confusion, we have improved the handling of this issue by replacing the plot of SAC vs. POC by the plot of SAC vs. the amount of particle mass loading in the revised version to assess the impact of processed aerosols on SAC.

The reviewer suggested temperature or sulphate dependent in separating the SAC between the north and the south group. Temperature difference may be a factor (we have included this in the revised manuscript) however it should not be a major factor. During the biogenic period for example, an increase in temperature was observed (Slowik et al., 2009). At Toronto, temperature reached to 30 °C for some days during that period as well.

Comment #9

The use of a linear regression and the scientific interpretation of the derived intercept between SAC and POC assumes a linear relationship between POC and aging, which has not been demonstrated. It should also be noted that the least-squares method of linear regression assumes no uncertainty in the x-axis coordinate, which is clearly not the case between SAC and POC, and another regression approach should be used. The regressions in Figure 8 are questionably significant by eye: if not separated by wind direction, the slope would be near-zero; uncertainty bars around the regression lines would be helpful. It may also be helpful to plot the SAC and POC data against sulphate, which appears correlated with both components.

Response to comment #9

We thank the reviewer for pointing out the POC issue. We realized one problem in the original figure 8 is the small concentration range of POC which makes the assumption of error free independent variable invalid. No doubt this has an affect on the least squares slope of the figure.

In response to all reviewers' comments, we have replaced the last figure (SAC vs. POC) with a figure showing the relationship between SAC with the sum of OM, SO4, and NO3. The sum of OM, $SO4^{2-}$, and $NO3^{-}$ also reflects the degree of atmospheric oxidation and offers some perspective on the potential for the absorbing material to be included. In this figure, it is clearly shown that the trend between the north and south groups is different. Also to mention is that similar observation of decreasing light absorption is also reported from another recent ACPD publication (Lewis et al., 2009).

Another reason for using the new figure is to reduce the uncertainties of the independent variable. To confirm such, we have also computed the geometric mean regression slope using the method from Zobitz et al. (2006); this confirms no significant changes to the slope for both north and south groups when taking into consideration of the uncertainties from the independent variable.

Zobitz, J.M., Keener, J.P., Schnyer, H., and Bowling, D.R. (2006). Sensitivity analysis and quantification of uncertainty for isotopic mixing relationships in carbon cycle research, Agricultural and Forest Meteorology, 136, 56-75.

Lewis, K.A., Arnott, W.P., Moosmüller, H., Chakrabarty, R.K., Carrico, C.M., Kreidenweis, S.M., Day, D.E., Malm, W.C., Laskin, A., Jimenez, J.L., Ulbrick, I.M., Huffman, J.A., Onasch, T.B., Trimborn, A., Liu, L., and Mishchenko, M.I. (2009). Reduction in biomass burning aerosol light absorption upon humidification: roles of inorganically-induced hygroscopicity, particle collapse, and photoacoustic heat and mass transfer, Atmospheric Chemistry and Physics Discussions, 9, 15247-15294.

Comment #10

Technical corrections. The paper needs to be proofread as there are numerous grammatical errors. Examples of problems include l.16 in the abstract (sentence starting with 'whereas' doesn't make grammatical sense) p14322, l 24 should read 'lasted'

Response to comment #10

We have tried to improve the grammar and correct typographical errors.