Response to Reviewer #1

The authors appreciate the thoughtful and helpful comments from the reviewer for improving the manuscript.

Response to general comment #1

The comparison of the OC and OM as well as the SAC with the POC originated with the 2005 dataset. Because the results seemed unique, we increased the filter sampling frequency during the 2007 campaign. Also, the 2.5 μm size cut used for filter sampling in 2005 was reduced by using a 1.0 μm cyclone in 2007 to allow better particle size coverage between the filter and in-situ measurements. Taking all comments from all three reviewers into consideration, we have removed the 2005 data from the revised manuscript.

Response to general comment #2

The POC defined in this thermal method is the total carbon mass released between 550°C and 870°C under oxygen-free He flow (see page 14323, line14-19), which includes three components i.e., (1) carbonate carbon, (2) charred carbon during 550°C, and (3) the refractory OC (including both oxygenated and non-oxygenated) that possess relatively high bonding energy and could not be released completely at temperatures up to 550°C. i.e., POC is the sum of items (2) and (3). To separate item (1) from the sum of items (2) and (3), the carbon isotope measurements have been used, because of their large difference in $^{13}C/^{12}C$ ratio between carbonate and organic carbon. The isotope measurements (have unpublished yet) shows that POC at the site (Egbert) had minimum impacts from soil dust and sea salt aerosols, which are mainly from carbonate sources.

Based on previous thermal analysis of different standards (Huang et al., 2006), the POC fraction determined from the current thermal method was found to be proportional to the amount of oxygen mass in the standards (i.e., no POC fraction was identified in pure OC compounds). From Fig. 6, it is shown that POC is well correlated with (OM-OC). The term (OM-OC) is the mass of organic matter without carbon. According Fig. 3, the bottom panel indicates that (OM-OC) is well correlated to oxygen mass estimated independently by AMS ($R^2 = 0.89$). Combining Fig.3 with Fig.6, it is indicates that the

higher oxygen mass content, the more POC fraction formed, implying the higher degree of aerosol processing via photochemical reactions though there are some POC/oxygenated OC from the primary sources.

One of the main objectives of this manuscript is trying 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 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, the constant conversion factor (1.4) limits the use of thermal measurements since it is known that OM/OC ratio varies in real situations. In this study, the authors confirmed that the POC obtained from the current thermal method is related to the particle oxygen mass which can be used to infer OM. This extends the use of thermal measurements for other possible usages such as to provide oxidation history of the ambient aerosols or approximate oxygen mass for long term continuous measurements. This is one of the motivations behind this manuscript work. We will state this explicitly in the revised manuscript.

Apart from some of the references cited in the original manuscript regarding the observation of decreasing SAC with aerosol aging, observation of decreasing absorption for biomass burning aerosol upon humidification is also observed from a recent ACPD publication from Lewis et al, (2009)

Lewis, K. A., W. P. Arnott, H. Moosmüller, R. K. Chakrabarty, C. M. Carrico, S. M. Kreidenweis, D. E. Day, W. C. Malm, A. Laskin, J.-L. Jimenez, J. A. Huffman, I. M. Ulbrich, T. B. Onasch, A. Trimborn, L. Lui, and M. I. Mishchenko (2009). Reduction in Biomass Burning Aerosol Light Absorption upon Humidification: Roles of Inorganically-Induced Hygroscopicity, Particle Collapse, and Photoacoustic Heat and Mass Transfer. *Atm. Chem. Phys. Discuss.* **9**, 15247-15294.

<mark>Specific comments</mark>
<mark>**Page 14319, line 9:** Is there a better word than "easier" to use here? Please state the specific characteristic you are describing here, e.g., is it simply that POC evolves in the first EC stage of the analysis?</mark>
Response - we have replaced "easier than EC" with "at relatively lower temperature than EC does".

<mark>**Page 14319-14320:** Might be helpful to have a table summarizing previous OM/OC measurements.</mark>
Response - A summary table is included in the appendix of the revised manuscript to summarize the previous OM/OC values mentioned in the manuscript.

<mark>**Page 14321, lines 1-2:** Slightly confusing. Are the authors referring to light absorption measurements, or light absorption itself? In either case, it would be helpful to have a few sentences discussing how organic mass increases light absorption, either via mixing or addition of light absorbing material.</mark>
Response - We have replaced " thus affecting light absorption also." with "thus affecting both light absorption and its measurements. Particle light absorption can be increased through a lensing effect by non-absorbing OC condensed onto an EC core (Bond et al., 2006) or potentially decreased by collapse of the EC core (Lewis et al., 2009; Liousse et al., 1993; Bond and Bergstrom, 2006; Fuller et al., 1999; Iskander et al., 1991). In addition, filter-based light absorption measurements can have artifacts due the deposition of additional light scattering OC onto the filter (Moosmüller et al., 2009), possibly modified by coating quartz fibers in the filter medium (Subramanian et al., 2007)."

The following have been added to the reference list:

- Subramanian, R., C. A. Roden, P. Boparai, and T. C. Bond (2007). Yellow Beads and Missing Particles: Trouble Ahead for Filter-Based Absorption Measurements. Aerosol Sci. Tech., 41, 630-637.
- Moosmüller, H., R. K. Chakrabarty, and W. P. Arnott (2009). Aerosol Light Absorption and its Measurement: A Review. J. Quant. Spectrosc. Radiat. Transfer, 110, 844-878.

Page 14322, lines 4-6: A map showing the location of the site and major emission sources nearby would be useful.

Response – We have modified the text on page 14322 in the manuscript as follows:

- Lines 5-6, we replaced "CARE is located in an agricultural area, about 70 km north of the city of Toronto." with "CARE is located about 70 km NNW of the city of Toronto. The site is surrounded by crop land with no major local anthropogenic source."
- Lines 9-11, replace "In comparison, air from the north is relatively clean, except when the air passes through Sudbury, Ontario (a significant source of SO_2 from metal refineries)." with "In comparison, air from the north is relatively clean, except when the air passes through Sudbury, Ontario, which is over 310 km NNW of CARE (a significant source of SO_2 from metal refineries). The location of CARE relative to Toronto can be found in Chan and Mozurkewich (2007)."

Page 14325, lines 1-9: I have a minor issue with the assertion that just because CE of 1 was found using the same instrument in the other studies cited by the authors, it is valid to apply a CE of 1 in this study. The manuscript implies that ammonium sulphate mass fractions were < 50% during the 2005 study. Were they the same in 2007? Do the recent Matthew et al. (2008) and Crosier et al. (2007) methods for estimating CE support a CE of one? Finally, it would be useful to have a time series of the CE applied in the 2007 in an appendix or supplementary data somewhere. Why was the CE applied to filter samples?

Response - Since the 2005 data has been removed, based on the suggestions of the reviewers, the CE for the 2005 study is no longer an issue. But we do point out that the AMS used during 2005 was not used during 2007. During the 2007 study, the ammonium sulphate mass fraction varied considerably and occasionally the mass fraction reached over 50%. The AMS CE was estimated based on the AMS correlated light scattering and through comparison with the physical size distribution measurements (SMPS). The details are discussed by Slowik et al. (2009).

To clarify, the AMS CE was never applied to filter samples. The AMS CE was only applied to all the quantities measured by the AMS. After that, the continuous (AMS) measurements were integrated to the same sampling interval as the filter samples for analysis (e.g., determining OM/OC).

- 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, 2009.

Page 14326, line 11: It would be useful to have the wind data shown either in the main manuscript or in the appendix. The authors mention back trajectories, but do not show the results. They may wish to consider examining air mass sources using some kind of backward trajectory statistical analysis approach such as that employed by Ashbaugh

et al., A residence time probability analysis of sulfur concentrations at Grand Canyon National Park, Atmospheric Environment 19, 1263-1270, 1985.

Response - In this study, the focus was trying to study the relationship between chemical compositions (particularly for carbonaceous components) and relevant emission sources. Based on the location and other studies at this site (Slowik et al., 2009; Chan and Mozurkewich, 2007; Rupakheti et al., 2005), the air masses from the northern and the southern are very distinct from each other. The northern aerosol can be dominated by natural sources or by distant anthropogenic sources. Aerosol from the south is frequently dominated by regional anthropogenic sources.

Since the OC, EC, and POC were determined using thermal analysis, the total number of filter samples available for statistic analysis is limited. Due to the size of the dataset, it is not possible to breakdown the data set further into other sectors and to perform the conditional probability function. Thus, we only focus on the north and south directions. A table is given in the Appendix of the revised manuscript to illustrate the breakdown of the wind occurrence. Although attention is put only on two wind directions, the breakdown of the wind occurrence clearly illustrates the predominant wind direction used in the current manuscript is reasonable.

Page 14326, line 22: Was there any reason for the choice of 40% as the selection criteria?

Response - Although the choice of 40% was arbitrary, the value was determined after examination of the breakdown of the wind direction occurrence taking into account of the wind speed. A summary table in the Appendix of the revised manuscript shows how the predominant wind direction for each filter sample is determined. In all cases when it is defined as either north or south, the wind occurrence is almost 80% or higher (one case with 50%). The corresponding section in the revised manuscript is modified to clarify and avoid any possible confusion.

Page 14332, line 7: If direct comparisons between OM/OCtot values measured by different AMS instruments are not meaningful, what does this mean for the applicability of the results on a broader context? How can they make the comparisons to other studies in the following paragraphs if they can't do so for their own measurements? This statement apparently undercuts their entire approach.

Response – What we meant to point out to the reader was that the exact value of OM/OC values depends on factors such as the AMS CE and TE, etc.; although the same thermal method were used for OC measurements, the AMSs used for OM in 2005 and 2007 were different with potentially different CE values. Also, the integration times were much different and the cyclones used in front of the filters had different size cuts between 2005 and 2007. Taking into consideration these factors and suggestions from other reviewers, we have remove the 2005 data from the manuscript and focus only on the 2007 data set in the revised manuscript. We should keep in mind that to make a general comparison on a broader context, some measurement conditions (e.g. size cut and CE and TE in AMS or other advanced instruments) should be consistent.

Page 14332, line 25: It would be more convincing if they compared POC with the independent oxygen mass measurements from the AMS rather than with the OM-OCtot results that depends partly on accurate determination of POC.

Response – We agree. The value of OM-OCtot is partly related to the value of POC. Figure 3 shows the time series plot of the OM-OCtot and the estimated oxygen mass derived from HR-ToF AMS. The correlation coefficient (0.89) shows that the two quantities are highly correlated and therefore the relationship between the POC and the

OM-OCtot is just as good as that with the AMS oxygen mass. Also keep in mind that this AMS oxygen mass is still subject to corrections for AMS CE before one can obtain the "true" oxygen mass in the collected particles (as indicated by the difference in magnitude between oxygen mass and OM-OCtot). These corrections for CE are based on other measurements (e.g. SMPS measurements with assumptions of particle size range, shape and density, etc.). Another potential issue is the sensitivity of the signal. We believe that the relative uncertainties in the OM measurement will be smaller than that for estimating the oxygen mass, which is determined by summing all the measurable peaks which individually has a finite amount of uncertainties. Therefore, all measurements present difficulties in estimating the true OM concentration, but the thermal method offers an independent method for estimating OM/OC and long term and large scale measurements may benefit from this approach.

Page 14333, lines 1-3: I think the authors should add a caveat stating that their parameters may not be valid for POC measured by different OC/EC protocols (e.g., NIOSH 5040, IMPROVE_A) that may have different sensitivities to OM oxygen content. **Response** - This suggestion is followed in the revised version.

Page 14334, line 11: Why not use the toluene-benzene relationship described previously? If POC is determined incorrectly (e.g., the method over- or under-estimates the actual amount of pyrolysis occurring during the analysis), then the EC measurement would be off by the same magnitude, affecting the SAC determination. Samples with high POC may simply represent an underestimate of EC and corresponding overestimate of SAC. If the behavior of SAC really depends on air mass aging, than we should see some kind of relationship with the toluene-benzene ratio if the absorption and EC measurements are truly accurate. This could explain the negative relationship between POC and SAC and is worth including in the discussion that follows. If nothing else the authors could show the relative mass fractions of EC and POC and give an estimate of the sensitivity of the SAC calculation to the accuracy of the POC measurement. If POC is a tiny fraction of EC than I would have a lot more faith in the use of POC as a proxy for aging. Finally, the argument could be better supported by other estimates of the air mass age, such as using the backward trajectory travel time between likely source regions and the measurements or examining the mz43 and mz44 relationships to total organics in the AMS data.
Response - This is not done due to the lack of toluene and benzene sources from the north of this rural site (concentration were very low), therefore, the toluene-benzene ratio (i.e., ratio of two very low values) for northern air masses may not be as meaningful as those for the southern air masses.

It is known that the determinations of OC, POC, EC are procedure and method dependent. As mentioned in the manuscript (p14323, line 2-7), the thermal method used in this study was originally developed for carbon isotope measurements for OC, POC, and EC. Although a thermal optical transmittance (TOT) OC/EC analyzer were used, the OC, POC and EC determination were based on temperature, time and oxidation-reduction environment (Huang, et al., 2006), which is different from IMPROVE and NIOSH 5040 method. For your information, a comparison result between this method and IMPROVE/NIOSH for a NIST urban dust standard is shown in the following slide presented at EGU2009 (we are going to publish these results soon). Therefore, the POC determined by this method (mentioned in the response to the general comments) is not the same as the charring correction in other thermal-optical methods. Thus, we do not expect such an artifact (i.e., higher POC leads to smaller EC) would exist; if it did it would lead to an over estimation of the SAC for the high POC cases. The

data points in the far right hand side in Figure 8 (i.e., with high values of POC) should be adjusted further lower in magnitude and this will further strengthen our observation of decreasing SAC with increasing POC.

OC/EC Measurements of NIST Standard
(SRM8785: urban dust)
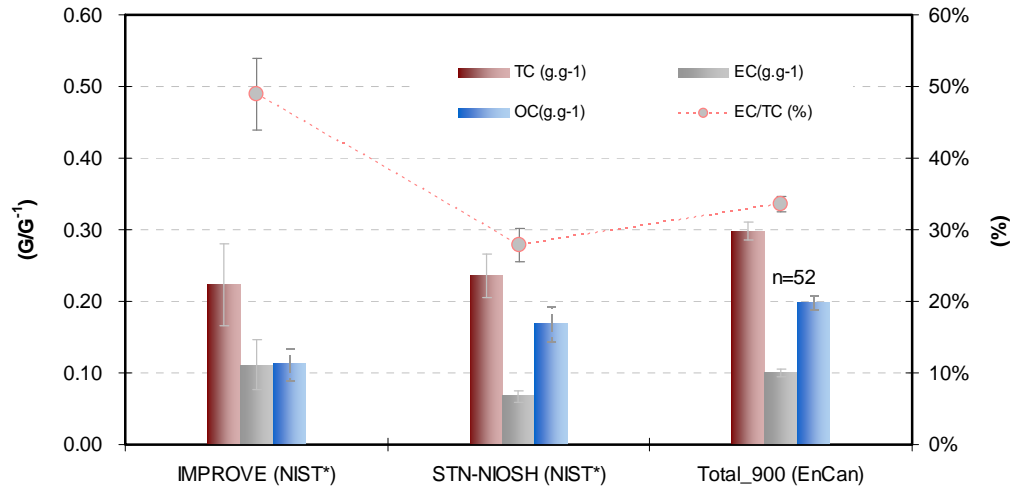
The reviewer raised an interesting question regarding the POC/EC ratio. The authors compute this ratio separately for the north and south groups. For the north group, this ratio has an average value of 0.9 (s.d.=0.4) due to the low concentration of EC from the clean background air. For the south group, due to the contribution of high EC, this ratio drops to 0.6 (s.d.=0.2). However, without another reference to compare to, it is not possible to define/determine whether an artifact does exist.

Due to reviewer's concerns on the POC and its role in aerosol aging, in the revised version, authors have taken the suggestion from the reviewer. The authors have decided to replace the Fig. 8 by the plot of SAC vs. the sum of OM, SO_4^{2-}, and NO_3^- mass (defined as the amount of particle mass loading). Since much of SO4, NO3 and possibly OM are secondary in origin, this provides another qualitative measure of aerosol processing in the atmosphere. Besides, all the three quantities were estimated from the AMS which is completely independent of the SAC. Calculating the slopes of the two groups using both model I and II confirms there are differences between the two groups.
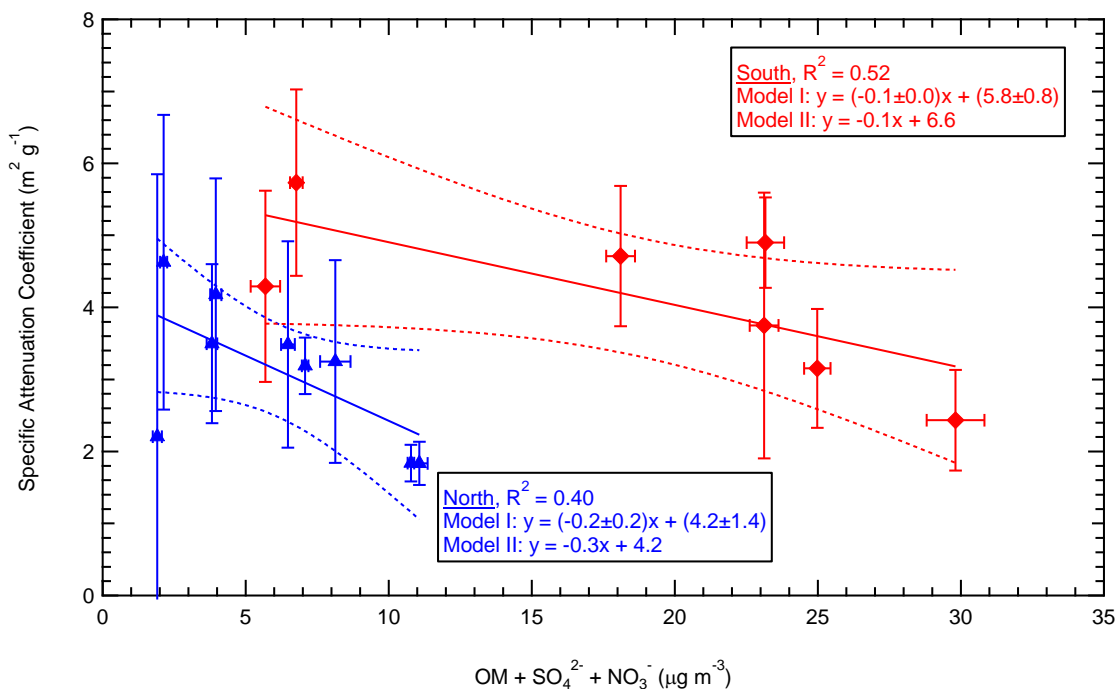
Page 14336, lines 18-21: Agreed, but the results here hinge on POC's ability to serve as a proxy for aerosol aging, which I don't think has been established very well.
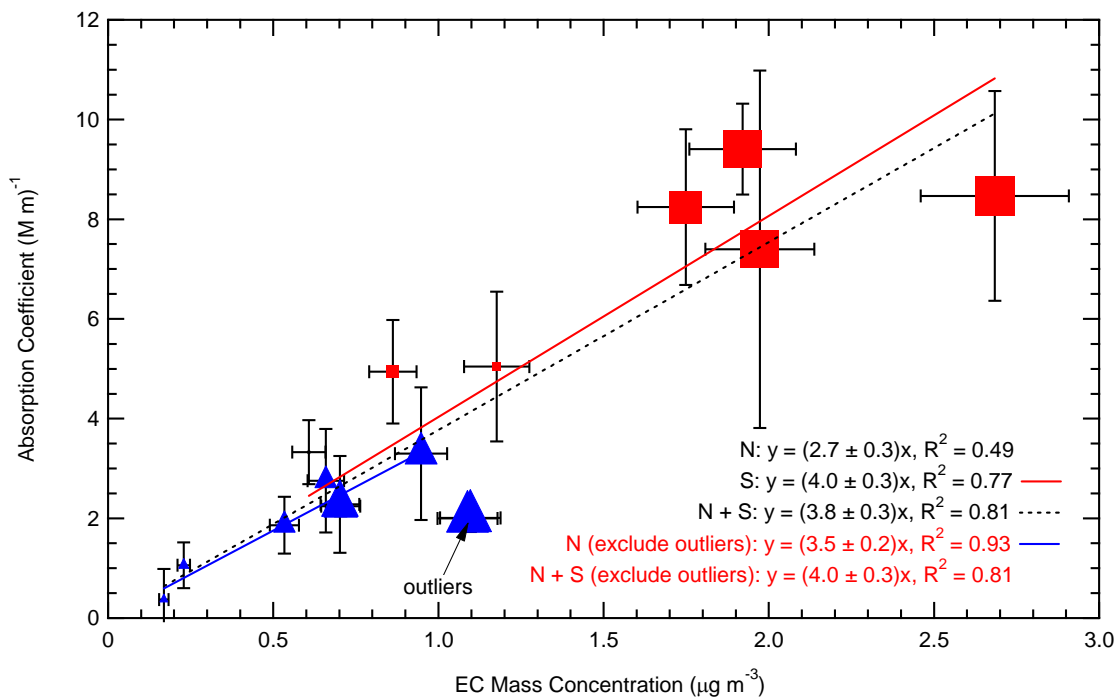**Response** - Using POC to approximate the particle age is based on the assumption that the oxygen content in the particle increases as it ages due to photochemical reactions which is stated in the manuscript. As discussed in the previous point, the plot of SAC vs. the sum of OM, SO_4^{2-}, and NO_3^- mass shows the north and south groups have differences. As a result, we believe the decrease in SAC with increasing the particle mass loading from secondary photochemical processes is not due to artifact and the conclusion should still be valid. Also, we mention that a recent ACPD submission (Lewis et al., 2009) observed a decrease in aerosol light absorption during humidification of biomass burning generated aerosols. They also suggested one possible reason could due to the collapse of soot structure.

Figure 3: Remove arrows.
Response - Arrows have been removed.

Figures 7 and 8: Legend is a little confusing. I assume the points are scaled by concentration, but the legend makes it seem like they are grouped into three concentrations groups. If they are scaled I think it is better to just show two examples of the symbol size at each concentration.
Response - The original marker size in Figure 7 and 8 were scaled by three distinct sizes, representing the range of concentrations indicated by the legend. To reduce the confusion, Figure 7 in the revised manuscript has changed without 2005 data (see attached)   The size of the marker represents the amount of particle mass loading defined as the sum of OM, sulphate, and nitrate mass. Figure 8 is removed and replace by a new figure (see previous response).

Figure axes: Absorption Coefficient (M m)$^{-1}$ vs EC Mass Concentration ($\mu g\ m^{-3}$)

Legend:
N: y = (2.7 ± 0.3)x, R^2 = 0.49
S: y = (4.0 ± 0.3)x, R^2 = 0.77 ——
N + S: y = (3.8 ± 0.3)x, R^2 = 0.81 - - - -
N (exclude outliers): y = (3.5 ± 0.2)x, R^2 = 0.93 ——
N + S (exclude outliers): y = (4.0 ± 0.3)x, R^2 = 0.81

outliers

Technical corrections
Page 14322, line 7: change "regions of the south" to "regions to the south"
Page 14322, lines 12 and 24: change "last" to "lasted"
Page 14323, line 5: delete "as"
Page 14333, line 19: poor wording, "The magnitude of SAC reflects the ability of absorbing
light by EC."
Page 14336, line 6: missing "et al." in the reference
Page 14336, line 12: change "hypothetic" to "hypothetical"
Page 14336, line 17: see above
Page 14337, line 11: a nitpick, but change "[OM-OC]" to "(OM-OC)"
Response – all correction where still appropriate have been made.