

Response to reviewer #2

The authors thank the reviewer for the useful comments (highlighted in yellow). The point-by-point responses for individual comments are given below.

Reviewer general comment #1

The paper by Chan et al. discusses measurements of light absorption, black carbon mass and nonrefractory aerosol mass in various regions in Canada. It is my opinion that this paper should be rejected for the following reasons: (1) the analysis is fundamentally flawed and premised on extremely poor assumptions (2) the paper is difficult to follow, (3) the figures/tables are poorly conceived and do not always seem to show what the authors purport to show. These will be discussed further below, in both general and specific terms. In order to be publishable, it is my opinion that the manuscript will require a fundamental reworking that is well beyond the scope of a typical revision.

Response to general comment #1

The reviewer's points are well taken. While it appears that some of the concerns from the reviewer are a result of our use of inappropriate notation and errors during the preparation of the ACPD version of the manuscript, which we failed to detect (i.e., the missing bold font and the mismatch in particle coating mass and organic mass fraction in coating mass in table 1), some are a result of our over-interpretation of Figure 4a. We regret taking these data too far given that our original intent for that analysis was only to demonstrate that there is a clear difference in how the response of the PA and LII changes with the removal of non-refractory materials. We concur that adding best fit lines to those figures is inappropriate and the parameters shown on those plots should not be used for that purpose. However, the figures do show that the LII is not affected by removal of non-refractory materials, as hypothesized, and this served as the basis for using the two instruments in combination to explore with high time resolution how light absorption enhancement changes with different types of real world aerosols measured in different locations. Reflecting on the reviewer's comments more closely has encouraged us to look more deeply at our data using more appropriate parameters (e.g., non-refractory to black carbon mass ratio) and we discuss these findings along with more detailed explanations below. These serve to address all of the reviewer's comments.

Reviewer general comment #2a

(1) The analysis is fundamentally flawed: The authors appear to be confusing what should be considered an *intensive* property (the actual absorption enhancement) with what is an extensive property (their $\Delta Babs$). Furthermore, they go on to compare this extensive property, $\Delta Babs$, with another extensive property, ΔM , which is purportedly the "coating mass." The absorption enhancement, when properly defined as an intensive parameter, depends on the *relative* amount of coating material compared to the black carbon mass (see e.g. Bond and Bergstrom, 2006). Furthermore, the authors assume that even their poorly defined $\Delta Babs$ should have a linear relationship with ΔM . Mie theory is, however, an extremely non-linear theory and thus there is no reason whatsoever to think that even properly defined intensive parameters should exhibit a linear relationship.

Response to general comment #2a

The original intention of Figure 4a was to illustrate our observation of the change in the measured signal from the photoacoustic spectrometer between the non-denuded and

denuded samples whereas under the same condition, we observed no such behavior for the laser induced incandescence measurements. In considering the reviewer's comment we realize that we used inappropriate symbols in the axis label and this likely led to confusion. The axis label in Figure 4a and 4c should be labeled as " $B_{\text{abs,non-den}} - B_{\text{abs,den}}$ " and " $SVF_{\text{non-den}} - SVF_{\text{den}}$ " to avoid confusion.

Also, the authors did not intend to refer this difference in measured signal as the "absorption enhancement" that the reviewer is referring to (we agree that this quantity has no unit). The authors acknowledge that the inappropriate term "enhancement" was used in the caption as well as the manuscript when this is merely the change in the PA and LII signal. The wording and associated interpretation should be clarified/changed.

Also note that the authors have agreed to replace the term "particle coating mass" by the "non-refractory mass" or "condensable materials" depending on the content of the sentence to better reflect the measured quantity. More detailed information is given in other responses below.

One important message the authors were trying to point out from the comparison between Figure 4a and 4c is that given the same amount of non-refractory material present on the particle, the soot volume fraction (SVF) measured by the LII is relatively constant. In contrast the black carbon absorption from the Photoacoustic Spectrometer appears to be dependent, to a certain extent, upon the amount of condensable material on the particles. However, as the reviewer has pointed out, to consider the issue of enhancement the change in B_{abs} must be considered relative to the amount of BC present (i.e., this provides some idea of the amount of condensable materials and coating thickness). However, the combined observations shown in the figures may be useful when investigating morphology or amount of condensable materials on the black carbon particle, assuming, of course, the particles are largely internally mixed. We discuss this issue of particle mixing state more below.

The best fit lines in Figure 4a were not an attempt to explain the non-linear nature of the absorption coefficient with a linear function. While, upon further reflection the lines should be removed, the point was to highlight that the slope is not zero, implying that there are changes in the difference in absorption coefficients during non-denuded and denuded cases for various amounts of 'assumed' coating mass present on the particle.

Instead of only making these simple clarifications and figure modifications we have extended the analysis to be more in line with the theory and properties that the reviewer has raised in his/her comments. Therefore, we have now removed some discussion regarding Figure 4 and propose to replace it with more analysis of the time series of the original data in order to reveal some interesting and unique observations from the thermodenuder experiment and how the combination of the two unique in-situ BC measurements may unlock the complexity of ambient measurements and enable us to assess information for distinguishing internally versus externally mixed conditions. This will be briefly mentioned in below.

The following 7 graphs represent the two days of measurements obtained in Toronto during the thermodenuder experiment. For better data presentation, the data gap between the two days is not shown. The first panel shows the time series of the black carbon mass concentration calculated based on the soot volume fraction obtained from the LII. Following this is the non-refractory to BC mass ratio. The non-refractory mass is

obtained from the sum of the mass concentrations of the organics, sulphate, ammonium, and nitrate, all of which were obtained from the AMS. The following panels represent the time series of the SAC, mass concentration of the organics, sulphate, ammonium, and nitrate, respectively. In each panel, we present the denuded and non-denuded measurements separately and the hourly difference between the non-denuded and denuded measurements is shown by the blue line.

A side by side comparison of the two consecutive days of measurements illustrates how complex atmospheric measurements can be and how fast it can change and thus demonstrates how critical the in-situ measurements in this study are in providing unique and valuable information that can not be obtained from traditional integrated base measurements. The first panel shows the BC mass concentration calculated by the LII. The general pattern of the two days shows that the Toronto BC pattern is influenced by the development of the boundary layer height over the course of the day. Starting off with high BC concentration in the early morning due to the presence of the inversion layer containing that days rush hour emissions plus any overnight emissions. BC then gradually decreases over the course of the day because of the rising boundary layer height. This pattern is generally expected in an urban site and when the boundary layer rises there is good potential that the more-recently emitted particles below the boundary layer, which can be expected to be more similar, will mix with a different type of particle residing above the boundary layer. This could lead to a clear externally mixed situation and thus, we explore this.

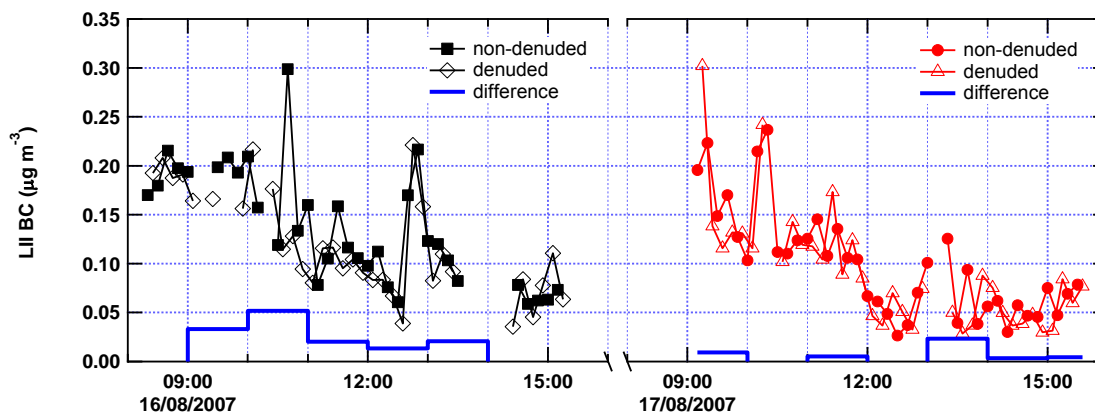
The time series of the non-refractory to BC mass ratio, which is potentially related to coating thickness, shows a slow but gradual increase in value over time on each day. From the AMS mass measurements it can be seen that there was a gradual increase in sulphate mass concentration over time suggesting that photo-oxidation during the course of the day played a role in the increase in non-refractory mass. The two days show different trends for the organics and ammonium mass concentrations. Focusing on the non-denuded SAC measurements (third panel), we can see that SAC on the second day is, despite the fluctuations, increasing slowly over time especially in the early afternoon. This is correlated with the gradual increase in non-refractory to BC mass ratio (second panel) and this is suggesting the non-refractory mass measured by the AMS is, at least partially, non-refractory mass present on the BC particles (i.e., coating). In other words, on the second day, the chemistry of the atmospheric particle is, relatively speaking, simpler and the environment is mostly dominated by an internally mixed condition.

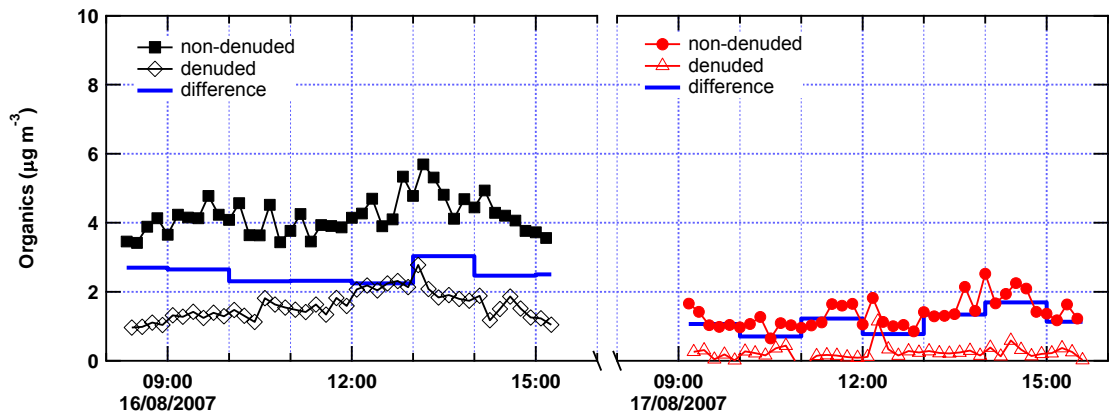
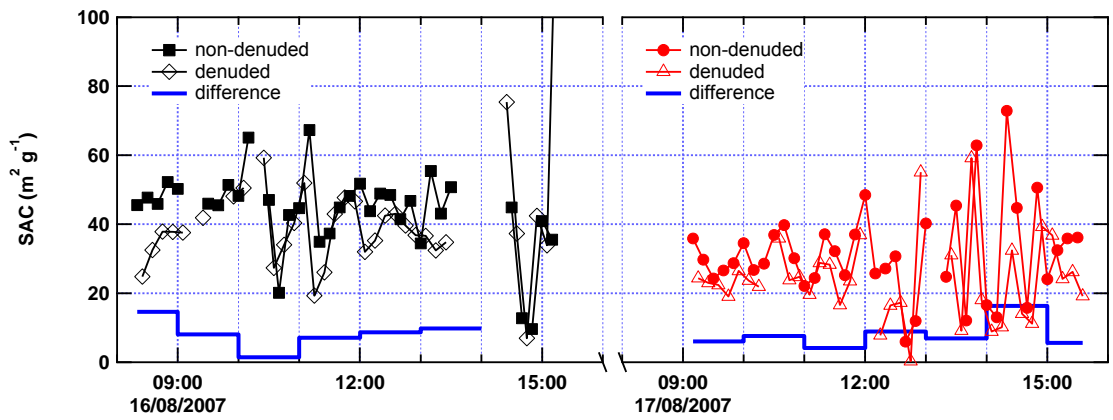
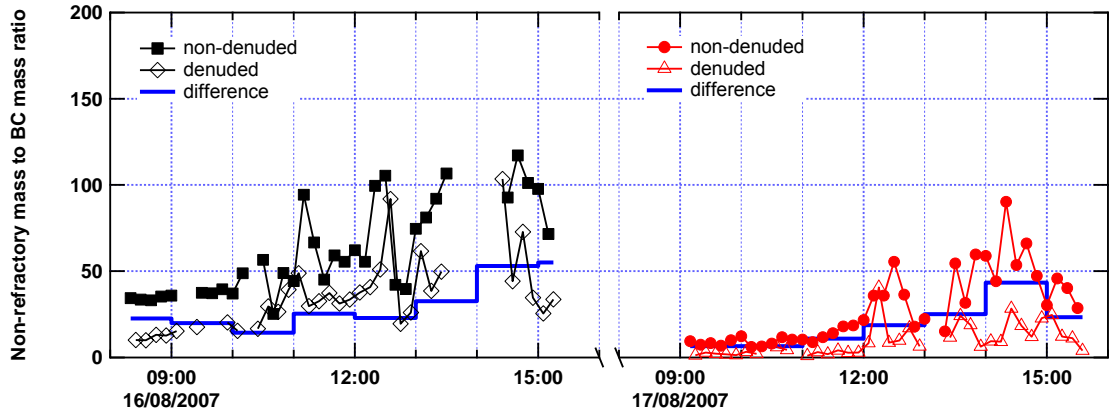
In contrast, the non-denuded SAC data on the first day did not increase with the non-refractory to BC ratio. This could be for a couple reasons. One is that if the situation is truly an internally mixed case and the additional non-refractory mass on the BC particles may have caused some structural changes to the soot aggregate and the light absorption enhancement by the increased coating is offset by the collapse of the aggregate leading to no net change in SAC. Another possibility is that the measured increase in non-refractory mass is related to additional particles mixing into the airmass and thus, there is an externally mixed situation as opposed to the additional non-refractory mass being present on the BC particles. Again, this could result in the observed lack of impact on absorption. If this is the case, the removal of the non-refractory mass should have no net effect on the observed SAC value. Looking more closely on the first day, in the early afternoon, the difference between the non-denuded and denuded SAC values (i.e., the blue line) is increasing very slowly. This implies that

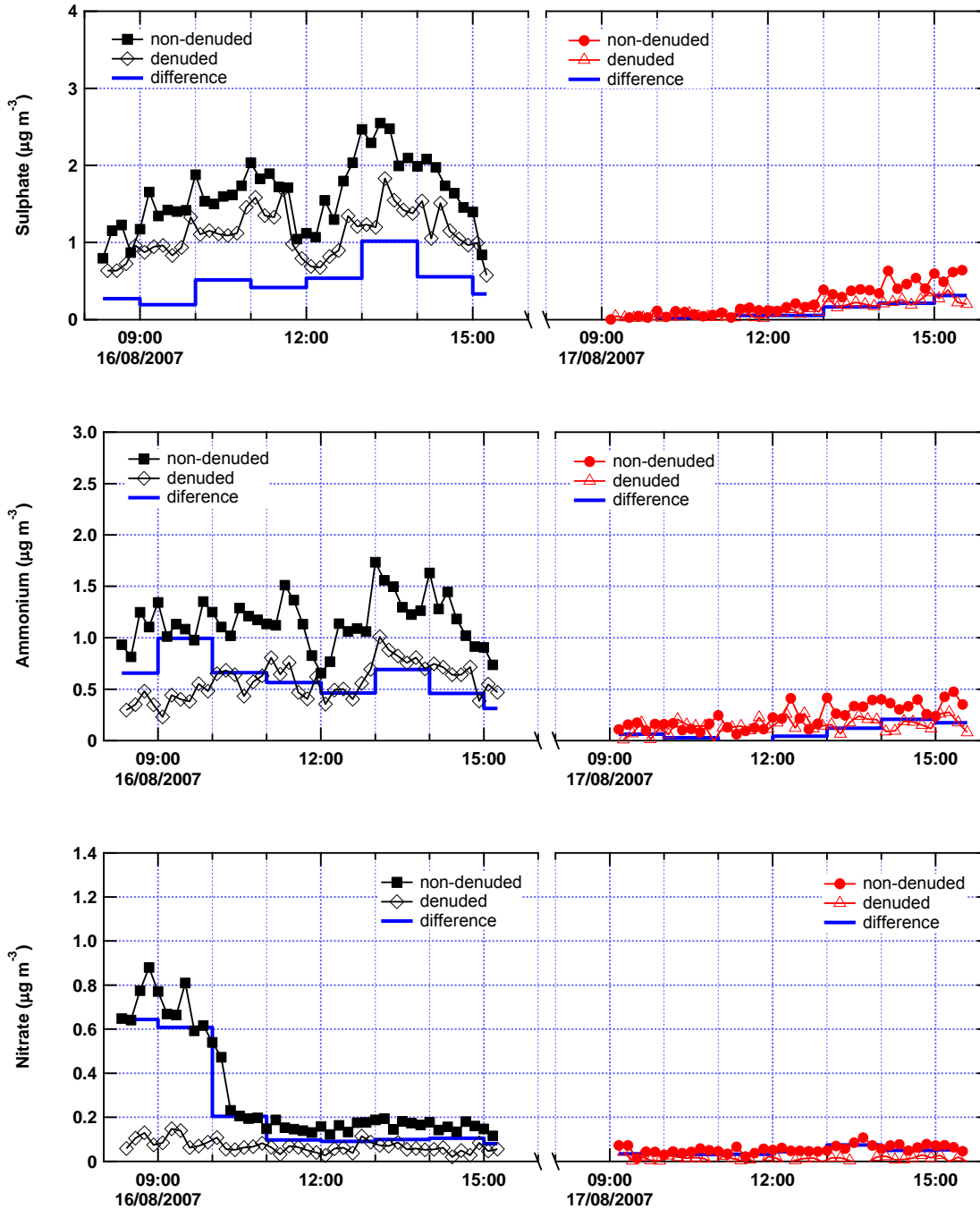
some of the non-refractory mass is depositing on the BC particles, however the SAC rise is small and thus there is likely still a considerable amount of the new non-refractory mass that is not present on the BC particles. Without the thermodenuder setup, if one were to only focus on the non-denuded measurements (black square) over the time period from about 11am to 3pm, it is also possible to see a gradual and observable increase in SAC.

In comparison, the chemistry of the atmospheric particles for the first day is certainly more complicated. For example, in the morning of the first day, a significant amount of organics, sulphate, ammonium, and particularly nitrate, is present at the early morning. These suggest that a considerable amount of chemistry could have occurred on the previous day and overnight and in the early morning and, with respect to nitrate, this is more likely the addition of non-refractory materials deposited on the particles, leading to an internally mixed situation. Interestingly, by removing the non-refractory mass measured prior to 9am (i.e., passing through the thermodenuder) on the first day leads to a SAC value with similar magnitudes as those observed during early morning and late afternoon on the second day which was, we hypothesize, dominated by an internally mixed aerosol. This provides good evidence that the additional non-refractory materials were indeed present on the BC particles. The sudden drop in nitrate at about 10am could be a result of switching air mass with that aloft due to rising boundary layer height and/or warming of the air and nitrate evaporation. After that, the overall chemistry has switched from an internally mixed dominant situation towards a mixed or even externally mixed condition throughout the day.

These observations and examples suggest that the combination of the in-situ SAC and non-refractory to BC ratio can provide useful information for inferring the relative importance of externally versus internally mixed situations. These new results, which come from the reviewer's concern over the impact of such situations on our results, will be brought forward in a revised manuscript thus adding an important dimension to the work







Reviewer general comment #2b

To make clear what I mean when I say that ΔBabs and ΔM are poorly defined and used, consider the difference between two particle ensembles wherein ΔM (as they have defined it) is equal to $10 \mu\text{g}/\text{m}^3$ in both cases, but in one case $\text{Babs} = 15 \text{ Mm}^{-1}$ while in the second $\text{Babs} = 1 \text{ Mm}^{-1}$. In the first case, the actual coating thickness would be small because the amount of black carbon is large (and thus the $10 \mu\text{g}/\text{m}^3$ is distributed among many particles) while in the second case the coatings would be quite thick. In general (although certainly not always, given the surprises Mie theory brings), thicker

coatings equal greater enhancements. Let's say that in the first case, the enhancement is 10% of the uncoated particle but in the second case it is 50%. Then, as they have defined it, $\Delta\text{Babs} = 1.5 \text{ Mm}^{-1}$ in the first case and 0.5 Mm^{-1} in the second. The "enhancement" Babs would appear to be larger in the first case, even though the actual enhancement is smaller.

Response to general comment #2b

The authors agree with the point the reviewer is making here. As mentioned in the previous response, the authors had no intention to imply that the difference in the absorption coefficient is the "absorption enhancement". We chose our terminology loosely and over-interpreted the figure. This can be easily remedied, returning the use of those data strictly to their intended purpose. We are also able to extend the analysis so that new insights, consistent with the terminology and physics that the reviewer is clearly very knowledgeable about, are possible. These are described above.

Reviewer general comment #2c

Also, implicit in the analysis is the assumption that the particles are completely internally mixed with respect to BC and coating mass. However, no justification is given for this assumption based on observations. In fact, I would argue that their observations speak against this. For example, the single scatter albedo (SSA) values measured at the various sites are across the board quite low (0.79, 0.42, 0.68 and 0.68 for the sites listed in Table 1 in order). This suggests a preponderance of fresh emissions, perhaps not surprising given the sites of the measurements close to emissions sources (particularly at the Ottawa street canyon site where $\text{SSA} = 0.42$). Thus, very little time for coatings to form will have passed, which suggests that much of the non-refractory mass was in "old" particles while a preponderance of BC was in "new" particles. If true, this suggests a highly non-uniform system, with some heavily coated and some thinly coated particles. Thus, the thermodenuder measurements, in particular, may not provide a correct measure of what the authors suggest they have measured, namely the absorption enhancement. This is an unavoidable aspect of any field study attempting to get at this effect, and thus is not a reason by itself to reject the paper, but it certainly must be dealt with in a much clearer way by the authors.

Response to general comment #2c

Measuring ambient particles to study variations in SAC as a function of possible controlling factors is no doubt full of challenges, one of which is being able to identify externally mixed over internally mixed particles. The authors appreciate that the reviewer has raised this issue, which we did not consider to the extent that it should have and could have been given our dataset. Consequently, and as shown above, we have thought more about this issue.

In ambient measurements, it is rarely, if ever, possible to have a case with all particles consisting of the same amount of coating or condensable materials, as the reviewer suggests regarding the unavoidability of dealing with external mixtures in field studies. This being said, not every particle can be expected to be identical, especially due to the addition of local source particles on top of an existing regional background, but this is a reflection of real atmospheric conditions. This certainly can be a potential issue for our measurements.

As we have clarified above, the purpose of the thermodenuder experiment was to show that the LII measurement was unaffected by the coating, whatever its nature/origin, while the PA measurement changed significantly when the non-refractory material was removed. This result allows us to look at the relative ratios of these two instrument's inferred black carbon measurements (or SAC) as a function of location and infer that the different types of particles and hence differences in the non-refractory material present are influencing the PA B_{abs} readings.

The authors acknowledge that in the first version of the manuscript we implied the assumption of internally mixed aerosol and subsequently did not provide justification. We have now extended our analysis to remedy this fault by attempting to identify situations of internally mixed over externally mixed particles. We feel that the unique instrument combination we used actually allows us to gain some new insight and thus thank the reviewer for pressing us on this issue. As discussed in response #2a, we use the thermodenuder experiment data to verify the possibility of using the non-refractory to BC ratio and SAC, as well as other mass concentrations in a time series manner to distinguish externally vs. internally mixed situations and we believe we are having some success in achieving this. In the revisions to the manuscript, we are now carefully going through all measurements assessing the extent to which the particles would be externally mixed versus periods when internal mixtures would be more dominant. We have a unique dataset for doing this, allowing us to explore the absorption enhancement in relation to the quantity of non-refractory material using ambient aerosol sources.

Reviewer general comment #3

(2) The paper is difficult to follow: Although there are a number of points to be made here, I will limit my discussion to a few. For one, the authors have chosen to use an unconventional relationship, the PAS absorption-to-LII volume ratio, to describe the influence of coatings on the total absorption. The authors should focus their discussion using a term much more common in the atmospheric literature, the mass (or specific) absorption coefficient. The introduction of this term, as to a more commonly used one, makes the discussion unnecessarily complicated.

Response to general comment #3

The initial intention for using the PA:LII ratio was not to introduce new terminology, but to determine if the pattern in specific attenuation coefficient (SAC) can also be revealed from the PA:LII ratio without the assumption of black carbon material density. The result of this comparison was that this ratio does indeed reveal the same pattern, which is now obvious given that there is only a constant factor (soot density) involved in the conversion. The authors will remove all the discussions of the PA:LII ratio and the normalized PA:LII ratio and only focus on the SAC results. The paper essentially loses no critical content and, along with other improvements, will make it much easier to follow.

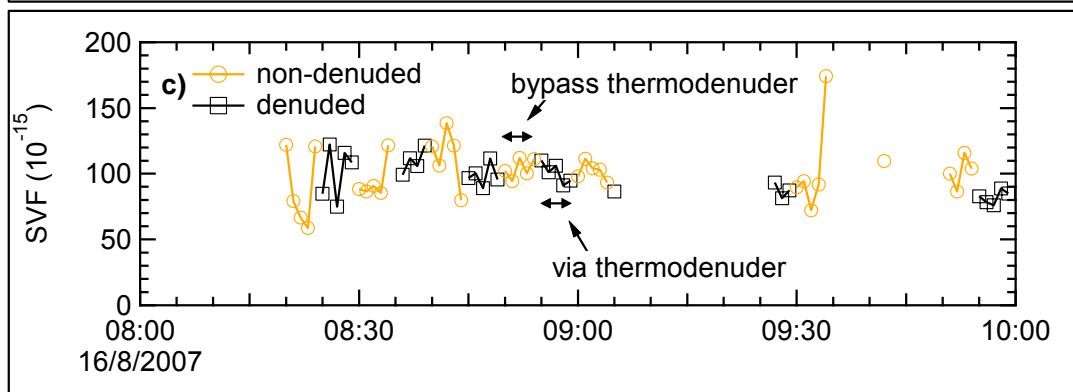
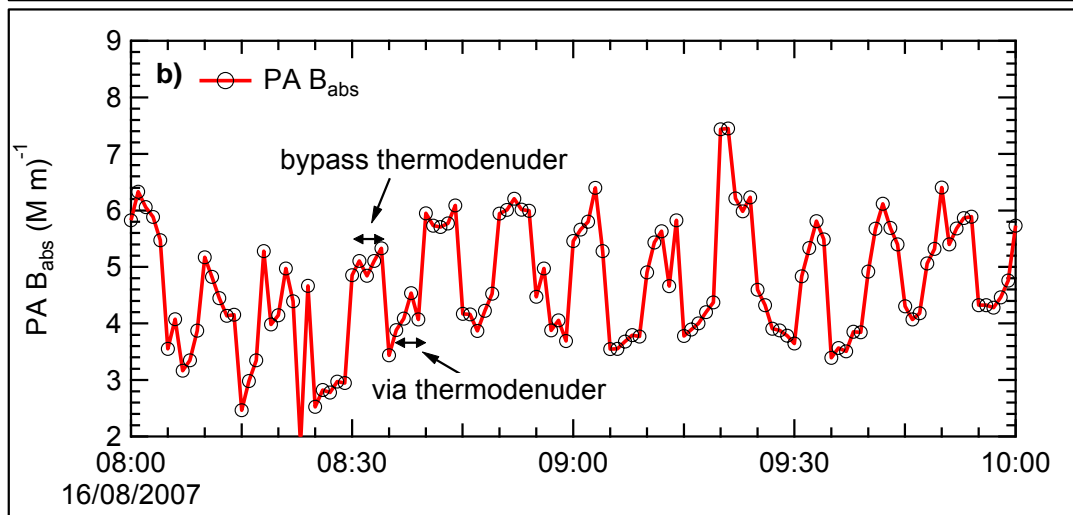
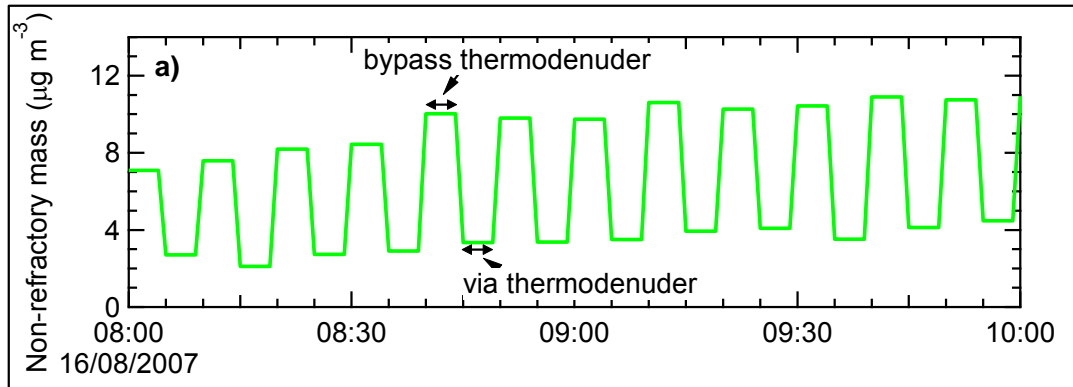
Reviewer general comment #4a

(3) The figures/tables are poorly conceived and do not always seem to show what the authors purport to show: Here are a few examples: (Figure 2) The AMS particle mass measurements are presented in a manner that makes them appear fake. Clear differences in total mass from one on/off cycle to the next are observed (indicating

atmospheric variability) but the values within a given on/off period are shown as perfectly constant. I assume that what is actually being shown is the average value during each on/off period, only that it is shown as multiple points within each period instead of as a single point. However, if my assumption is incorrect and this is the real data, then the authors must address why the particle mass is so constant within a given on/off period, but differs from one period to the next.

Response to general comment #4a

The authors should not have plotted individual 1 minute points for the AMS data in Figure 2a. The AMS was operating with a 5 minute resolution during the thermodenuder experiment, but for ease of data management in merging with the 1 minute PA and LII measurements the 5 minute AMS value was repeated and then we mistakenly plotted this as individual points. Therefore, the measurements were indeed the average value over the denuded or non-denuded period. Examples for the denuded and non-denuded measurements in Figure 2a, 2b, and 2c are now included (see below) to illustrate the different periods in each case.



Reviewer general comment #4b

(Table 1) The values listed for the AMS are confusing. What is meant by "%"? Should these add up to 100%? They don't. Actual mass values would be much more useful than whatever this % value is. Also, there are no values in bold (which are supposedly the mean values).

Response to general comment #4b

After comparing with the original manuscript the authors realize that part of the information in the original table was unexpectedly removed during the conversion to the

ACPD format. The bold font was removed. The authors will make sure these changes appear in the revised version. Below is the revised table. Note that the non-refractory mass is in the unit of $\mu\text{g}/\text{m}^3$. Unfortunately, some information got removed and combined with the next row leading to confusion.

The non-refractory mass was obtained by summing the mass concentrations of organics, sulphate, ammonium, and nitrate. If required, the mass of these four major components can be obtained by multiplying the average percentages for each individual component by the non-refractory mass. In the revised version, we have replaced the percentages of these compositions by their actual mass concentrations. We have also included several new entries such as the BC mass concentration (calculated from the SVF data) and also the non-refractory to BC mass ratio. Note that we have also divided the Toronto data into two subsets as there are distinct differences between them. Quantities that are no longer relevant, such as the scattering data and PA:LII ratio have been removed from the table. All the values below have also been updated to reflect a change in one of the internal parameters set for the photoacoustic instrument. See our response to reviewer #2 on this change.

		Site location				
Inst.	Measure quantity	Toronto 16 Aug (suburban)	Toronto 17 Aug (suburban)	Ottawa (street canyon)	Ottawa (near highway)	Windsor (in/out of city)
PA	B_{abs} (M m^{-1}) ⁻¹	6.0 (SD=2.9, N=42)	3.0 (SD=1.7, N=39)	26 (SD=17, N=27)	5.7 (SD=4.5, N=23)	4.4 (SD=2.9, N=1137)
LII	PPS (nm)	32 (SD=8, N=34)	22 (SD=9, N=38)	51 (SD=4, N=28)	66 (SD=7, N=25)	74 (SD=13, N=1183)
LII	SVF (ppt)	0.073 (SD=0.031, N=34)	0.052 (SD=0.029, N=38)	0.91 (SD=0.45, N=28)	0.33 (SD=0.17, N=25)	0.14 (SD=0.12, N=1183)
LII	BC ($\mu\text{g m}^{-3}$)	0.14 (SD=0.06, N=34)	0.10 (SD=0.06, N=38)	1.7 (SD=0.9, N=28)	0.63 (SD=0.33, N=25)	0.27 (SD=0.23, N=1183)
AMS	Non-ref. mass ($\mu\text{g m}^{-3}$)	7.3 (SD=1.0, N=42)	1.9 (SD=0.6, N=39)	12 (SD=3, N=28)	13 (SD=2, N=28)	9.8 (SD=7.3, N=1187)
AMS	Organics ($\mu\text{g m}^{-3}$)	4.2 (SD=0.5, N=42)	1.4 (SD=0.4, N=39)	10 (SD=3, N=28)	11 (SD=2, N=28)	5.1 (SD=2.3, N=1187)
AMS	Sulphate ($\mu\text{g m}^{-3}$)	1.6 (SD=0.4, N=42)	0.24 (SD=0.2, N=39)	0.88 (SD=0.17, N=28)	1.1 (SD=0.2, N=28)	2.9 (SD=4.0, N=1187)
AMS	Ammonium ($\mu\text{g m}^{-3}$)	1.2 (SD=0.2, N=42)	0.055 (SD=0.018, N=39)	0.49 (SD=0.09, N=28)	0.62 (SD=0.13, N=28)	1.3 (SD=1.6, N=1187)
AMS	Nitrate ($\mu\text{g m}^{-3}$)	0.31 (SD=0.24, N=42)	0.23 (SD=0.12, N=39)	0.38 (SD=0.07, N=28)	0.32 (SD=0.06, N=28)	0.48 (SD=0.51, N=1187)
PA/LII	SAC ($\text{m}^2 \text{g}^{-1}$)	44 (SD=12, N=34)	31 (SD=13, N=38)	16 (SD=10, N=27)	9.3 (SD=5.7, N=23)	19 (SD=6, N=1135)
AMS/LII	Non-ref. to BC ratio	62 (SD=27, N=34)	28 (SD=21, N=38)	8.4 (SD=3.9, N=28)	24 (SD=10, N=25)	53 (SD=55, N=1183)
AMS	Data res. (min)	5	5	5	5	5, 10, 15

Note that the Toronto data presented here are from the measurements obtained when the denuder was bypassed.

Reviewer general comment #4c

(Figure 4) The caption for panel d is very confusing. What do the authors mean “at different stages in a thermodenuder experiment?” This does not appear to be what the panel shows.

Response to general comment #4c

The different stages in panel (d) of Figure 4 refer to the different amounts of coating mass. As we have provided detail composition information for the Toronto data set in the table above, we do not feel the need for this panel any more. This panel will be removed in the revised version.

Reviewer general comment #5

Page 19942-10: A reference to Schnaiter et al., *JGR* (2005) is warranted.

Page 19944-6: A reference to the work by the NOAA group (Schwarz, Gao, Fahey et al.) is clearly warranted.

Response to general comment #5

The corresponding references will be included in the relevant places in the revised manuscript.

Reviewer general comment #6

Methods: The authors need to report the total flow rate and overall residence time through the thermodenuder (and also use consistent spelling throughout the manuscript). Just knowing that this is a Dekati thermodenuder does not help the reader to understand how specifically it was operated, although I will assume that the entire 16.7 lpm were passed through.

Response to general comment #6

The total flow through the cyclone was 16.7 lpm to achieve the size cut of 2.5 μm . This flow was then split for several different instruments with a total flow rate through the thermodenuder of about 11 lpm. The overall residence time in the thermodenuder was experimentally estimated to be about 8 seconds. This information will be included in the revised manuscript as well as the general operating principle of the thermodenuder.

More information regarding particle losses through the thermodenuder is given in response #16. Experimentally, the particle loss through the unheated thermodenuder is generally less than 20% for the particle diameters ranging from about 10 to 40 nm which are mostly encountered at the Toronto site. These results can be included in the revised version of the manuscript if deemed necessary to report in detail.

Reviewer general comment #7

Methods: Detection limits and uncertainties should be reported for all instruments, including (and especially) the DMT PA.

Response to general comment #7

The LII generally has a detection limit of $\sim 8\text{e-}15$ for the soot volume fraction and is given in the instrumentation section. The detection limit for the other instruments will be included in their corresponding sections.

The detection limit for the photoacoustic spectrometer varies slightly due to the sensitivity of the instrument and the signal to noise ratio at various sites. Generally, we believe the PA measurements are good down to about 0.05 (M m)^{-1} . Same goes for the AMS measurements, where we trust the AMS measurements down to about $0.05 \mu\text{g/m}^3$.

We will include all this information in the revised methods section.

Reviewer general comment #8

Methods: The atmospheric community is becoming somewhat familiar with the LII technique for determining BC mass concentrations. However, the method used to estimate the primary particle size (PPS) is not as well known and therefore I suggest much more detail be given regarding this method. For example, how exactly is the heat loss rate determined? What are the uncertainties associated with the PPS method? I feel that this is necessary given that two of the references are to conference proceedings and one is to a thesis.

Response to general comment #8

Detail information regarding the determination of the primary particle size (PPS) has been outlined in the Mewes and Seitzman (1997). The authors have now included a more detail description of the methodology in the determination of the PPS in the revised manuscript which is outlined in the following.

In the low fluence approach of HS-LII used in this study, the dominant cooling mechanism for the black carbon particle is conduction to the surrounding gas. During the conduction phase, the temperature difference between the black carbon particle and the ambient gas decays monotonically in a near-exponential manner (Snelling et al., 2000). By measuring the temperature of the black carbon particle in real time (on a nanosecond time scale) with the two-color pyrometry approach, the rate of temperature decay can be determined. From this the specific surface area and an effective primary particle diameter can be determined. This approach is more fully described in Schulz et al. (2006) and details on the influence of primary particle diameter distributions can be found in Liu et al. (2006).

Liu, F., Stagg, B. J., Snelling, D. R., and Smallwood, G. J.: Effects of primary soot particle size distribution on the temperature of soot particles heated by a nanosecond pulsed laser in an atmospheric laminar diffusion flame, *International Journal of Heat and Mass Transfer*, 49, 777-788, 2006.

Reviewer general comment #9

Methods: To what extent are the authors able to conclude as to the internal vs. external mixing nature of the sampled particles? Neither the PAS or AMS cannot provide this information. Can the LII instrument give some guidance in this regard?

Response to general comment #9

The LII measurements alone can not reveal information about the mixing state of the particles. The LII is only sensitive to particles with a finite amount of black carbon mass. For pure liquid or crystalline particles, which might coexist with particles containing black

carbon (i.e., an external mixture), the light absorption will be insufficient to cause these particles to be hot enough to radiate and therefore they are invisible to LII.

Strictly speaking, in ambient measurements, there is always an external mixture in the sense that there is more than one type of particles present simultaneously in the atmosphere. What is being measured at any given time is a random sample of an atmospheric airmass. If in any situation a certain type of particles, such as freshly emitted combustion generated particles, dominants in the environment, in a relative term this is considered as an internal mixture in a practical sense. As demonstrated in response #2a, we showed we can make some conclusions by carefully comparing the non-refractory to BC mass ratio with the SAC and other supporting information such as the time series of the mass concentration of the sulphate and organics measured by the AMS. In the revised manuscript, we will provide some description regarding the degree of internally mixed conditions based on our best knowledge for each data set.

Reviewer general comment #10

Page 19944-15: I do not see where Murphy (2009) came to the conclusion presented.

Response to general comment #10

In the corresponding section, the authors pointed out that the potential impact on the measured signal in the photoacoustic spectrometer due to evaporation of water is small (based on the given references) and therefore this is assumed not to be a factor in this study. The study of Murphy (2009) however stated that the evaporation of water from ambient particles could reduce the photoacoustic signal but such result is strongly dependent on the mass accommodation coefficient of water on the particle which depends on the composition of the coating materials. Besides, the reference also mentioned that the interference is reduced for particles with a thick organic film because it slows the kinetics of evaporation. Since the non-refractory materials, particularly the organic fraction, observed from this study are quite high the authors believe that the results from Murphy could favour our assumption that the photoacoustic spectrometer measurement is not impacted by water evaporation. Of course, in an externally mixed situation, such impact will be small and irrelevant. We can clarify this in the revised version.

Reviewer general comment #11

P.19953-11: The atmospheric community is much more familiar with mass absorption coefficients than the "PA:LII Ratio." I strongly encourage the authors to reframe their entire discussion in terms of the MAC instead of this ratio (I believe the authors refer to this as the specific attenuation coefficient).

Response to general comment #11

As discussed in the response to comment #3, the discussion of PA:LII ratio has been removed from the manuscript.

Reviewer general comment #12

P. 19953-13: The utility or physical meaning of the “normalized” PA:LII ratio is entirely unclear.

Response to general comment #12

This issue has been addressed previously.

Reviewer general comment #13

Page 19953-25: The authors state that “The light scattering and signal enhancement generally, but not always followed the same site to site pattern as the particle coating mass. The most obvious case is the Bscat values for the Windsor data which are small despite of the largest amount of particle coating mass present on the particles.” If this is true, where is this data in Figure 4b? There should be points at high mass/low scattering, but there are none.

Response to general comment #13

As mentioned in Section 2.1, the thermodenuder experiment was only conducted in Toronto for the purpose of confirming that the LII and PA respond differently to coating material. Thus, all measurements in Figure 4 were measurements taken from Toronto and during the BAQS-Met Windsor study, the thermodenuder was not used (page 19947, line 16).

Figure 4b refers to the change in light scattering between the non-denuded and denuded samples. As a result, data taken with and without the presence of the thermodenuder are essential for generating such a figure. Furthermore, after further consideration, the authors decided to remove the scattering data and any discussion of the scattering data from the manuscript as the scattering data is not the main focus in this study. Another important reason for our consideration comes from the comment pointed out by the first reviewer, which is due to the truncation of the scattering signal for very large particles that are likely to be observed in Windsor. With the help from the manufacturer, it is confirmed that such hypothesis is true and the potential impact can be significant for background particles. Without any particle size measurements it is not possible to estimate the potential impact on the Windsor scattering data and therefore the quality of the data can not be ensured.

Reviewer general comment #14

Figure 2: It would be helpful if the authors presented a denuder on/off time series behind the measurements (particularly in panels b and c) to emphasize which periods are on/off.

Response to general comment #14

This has been addressed in response #4a. Please refer to the figures in response #4a.

Reviewer general comment #15

Figure 2/P. 19950-7: This figure does not really show a time series of the “total particle coating mass”, but actually a time series of the refractory particle mass, both after passing the particles through the thermodenuder and through the bypass line. To state that this is the particle coating mass suggests that the authors have specific knowledge about the mixing state of the particles.

Response to general comment #15

The authors assume the reviewer actually meant non-refractory instead of refractory particle mass.

Figure 2a shows a time series of the sum of the non-refractory mass (i.e., organics, sulphate, ammonium, and nitrate) measured by the Aerosol Mass Spectrometer (AMS) during a period when the sample stream switched between denuded and non-denuded paths. As indicated in various places above, we no longer refer to this as coating mass because we agree with the reviewer's point regarding the assumption this implies. The reviewer is correct, we do not know if the reduction in the mass is actually a reduction in coating on the black carbon we are measuring. There are some parts of our data when we believe this mass is more likely to have been coating the black carbon (e.g., morning nitrate). As discussed earlier in response #2a, we are now considering a range of indicators simultaneously to help us to determine if a given measurement period is likely to be dominated by internally or externally mixed conditions and then make inferences accordingly.

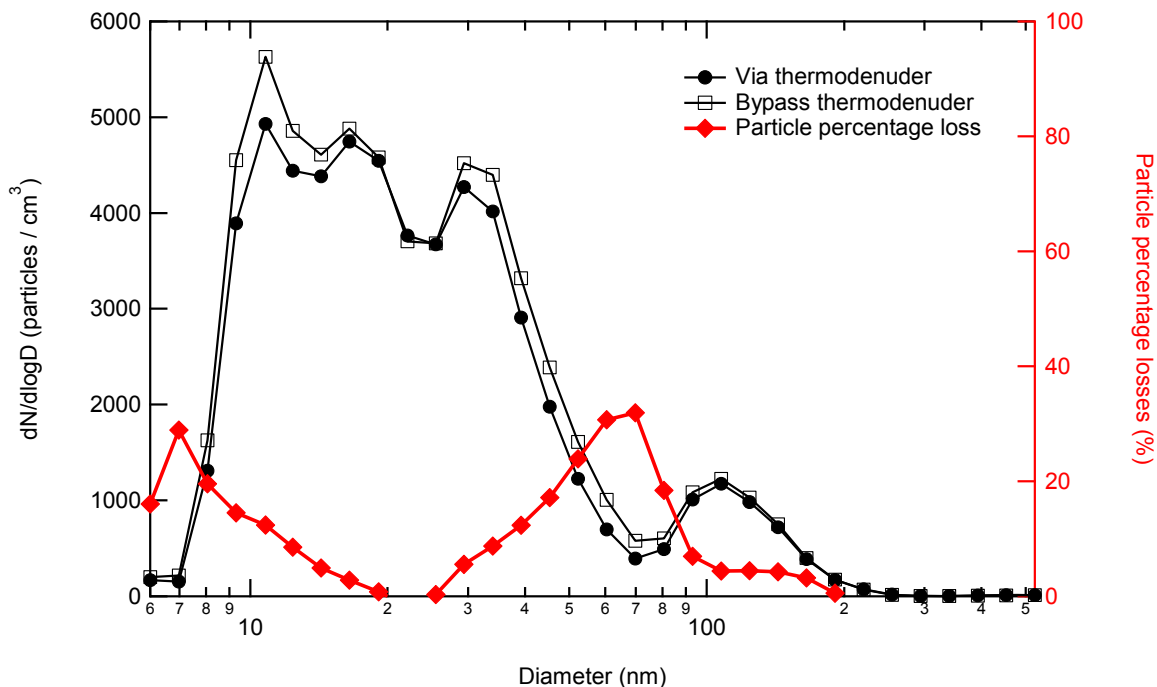
Reviewer general comment #16

Figure 2c: The SVF results presented in this figure is more important than the authors acknowledge. This figure appears to indicate that particle losses through the thermodenuder relative to the bypass are extremely small. This is crucial to the authors interpretation, and should be explicitly mentioned. However, at the same token, I am a bit surprised that there is no particle losses through the thermodenuder. Have the authors validated this in the laboratory?

Response to general comment #16

Given the main intent of the thermodenuder experiment (i.e., to show that the LII is not affected by removal of coating/non-refractory mass while the PA is) the loss of particles was not a large concern. This is because both the PA and LII are compared in a relative sense and they equally affected by losses. Nonetheless, we do have measurements of particle losses in the thermodenuder and a summary figure is given below.

To minimize the effect of short variations in the ambient particles during these measurements continuous measurements of NO and O₃ were used as indicators in identifying periods when the particle counts were more likely stable. Then over the course of a 20 minute period with stable conditions the flow path of the ambient particles alternately passed through the unheated thermodenuder and the bypass path in 5 minute intervals while a Fast Mobility Particle Sizer (FMPS) was used for nearly continuous measurements of the particle size distribution. The figure below shows that for most sizes and a majority of the particles the loss is less than 20% with much of these cases being <10%. A maximum in particle loss of ~30% was observed, however this is related to parts of the distribution where number of particles is small (i.e., 7 nm and 70 nm sizes). As can be inferred from Figure 2c, the particle losses between any consecutive periods was about 10-15% which is consistent with the results in the figure below. This information can be summarized and included in the revised manuscript.



Reviewer general comment #17

P. 19950-21: I see no point or justification in using a cubic spline to estimate values “when the sample was following the alternate flow path.” Since the AMS, PA and LII measurements are all in-phase w.r.t. the thermodenuder on/off cycles, there is no reason to look at these “alternate” values. These points should be removed, and if they are included in any of the other figures they should likewise be removed.

Response to general comment #17

The 1 min PA and LII measurements shown in Figure 2b and c indicate that there were fluctuations in the ambient particle concentrations within the 5 minute cycles of the AMS data and the denuder switching. Clearly, noise from the ambient variability was unavoidable. Therefore, to quantify the differences in the LII and PA measurements between the 5 minute denuded and non-denuded measurements, which were taken sequentially, an approach was needed to account for the fluctuations. Working with 5 minute averages helped smooth out some of the fluctuation, assuming that it was random and not a general decreasing or increasing trend. To account for trends a variety of options were possible. The simplest would have been to ignore this issue and compare a denuded sample to the preceding or the following non-denuded measurement, assuming that the effects of this non-random noise would balance out given sufficient data. However, we felt this was not an acceptable approach. Conceptually then, and given the constraints of our data, the easiest approach would have been to compare the denuded measurements to the average of the non-denuded measurements made before and after. Similar to this and easier to implement was the approach we took. This was to first smooth within the 5 min interval choosing the median PA and LII values. Using the average of the 5 points was also considered but there were some 5 minute periods with single outlier values that we felt would influence some of the results. Then, to account for the trend in the ambient conditions between 5 minute intervals we interpolated the denuded and non-denuded 5 minute time series. A

cubic spline was used but any other polynomial approach could have been used and would not have significantly changed the results. Then with a continuous (interpolated) time series of 5 minute points we computed the differences in LII, PA and AMS at the same time points. However, it should be noted that the overall results are not very sensitive to these decisions for processing the data, but clearly, choosing an approach was necessary, which we then described in the paper.

Reviewer general comment #18

P. 19951-3: I do not see how either assumption 1 or 2 are justified or needed. The measured signal enhancement does not depend on these assumptions. However, the interpretation of the signal enhancement does depend on assumptions.

Response to general comment #18

This section has changed in the manuscript revisions. Clearly, the reviewer is correct that it is the interpretation of the signal enhancement that depends upon certain assumptions. The signal enhancement itself is just a measurement. The revisions take into consideration this point, plus the inclusion of data on particle loss in the thermodenuder (see response #16) and a more direct recognition of the impact that changes in the particle mixing state (externally vs. internally) can have on the results (see response #9, and #15 above).

Reviewer general comment #19

P. 19951-8: I do not understand how the use of the median as opposed to the mean serves to “minimize the impact caused by occasional fluctuations in the time-dependent data,” especially since, at most, 5 points could be included in any of the averages/medians (assuming everything was timed perfectly, which Figure 2 seems to indicate was not the case).

Response to general comment #19

The reason for using the median is discussed above in response #17.

Reviewer general comment #20

P. 19955: The discussion presented here is wrong. The authors are using extensive properties where they should be using intensive properties. The differences between the different “regions” cannot be interpreted in the manner presented here. For example, the decrease in going from “region II” to “region III” is not support for collapse of the BC fractal structure. It could just as easily be a changing balance between fresh and aged (e.g. background) particles. (As an aside, the terminology “regions” is confusing.)

Response to general comment #20

Please see our discussion in response #2.

Reviewer general comment #21

P. 19957-4: The discussion in this paragraph makes no sense. The logic being employed is circular. One can't use SAC values derived here from PA/LII measurements to estimate mass from PA measurements alone. These are not separable.

Response to general comment #21

This information has been removed as mentioned in response #2. We over-interpreted the thermodenuder results given their original intent and have now revised that section to avoid this mistake and also to provide better insight into what those data show, including information on potential changes in mixing state.

Reviewer general comment #22

Section 4.3.1: Only a general discussion is given here. This discussion should be put in the context of the actual observations. Related to this, the observations do not seem to follow from the discussion. Why, for example, are the Toronto PPS values so small? This is supposedly "aged" and should contain collapsed BC, at least relative to e.g. the Ottawa sites.

Response to general comment #22

The original intention of section 4.3.1 was to introduce a new and unique parameter, primary particle size (PPS) that is measured by the LII. This parameter has not been given much attention and we believe there may be some value in this parameter given the in-situ nature of the measurement. The original paragraph was intended to link a possible physical phenomenon to what is captured by the PPS. This section will be moved to the methodology and combined with the description of the PPS determination (see response #8).

Although PPS may be used to infer the degree of particle collapse, after looking the data into more detail it shows that there are more into this parameter. Generally, PPS seems to have positive correlation with the non-refractory to BC mass ratio in all sites, but the relationship changes. After further investigation, we believe the PPS value observed at certain sites could be unique and may be dependent on the particle source (diesel vs. gasoline particles) and the unique local meteorology influences. Therefore, PPS may not necessarily be a universal parameter that allows site to site comparison. In the revised SAC section we will clarify this explicitly.

Reviewer general comment #23

Section 4.3.2: The authors' discussion makes it seem as if they are doing something beyond simply calculating the SAC from their measurements. They are not.

Response to general comment #23

The original motivation for examining the behavior of this ratio was that it is derived directly from the measurements from the two instruments and could be examined in situ if desired. Conversely, an assumption about BC density was needed to put this discussion in the context of SAC. However, in retrospect, we agree with the reviewer that this section on the ratio and the section on SAC becomes repetitive and for presenting our results both are not necessary. Thus, in the revised manuscript we combine those two sections and present results all in terms of the SAC.

Reviewer general comment #24

P. 19960-8: The PA:LII ratio is equivalent to the intensive property the SAC. By “normalizing” to the “particle coating mass”, the authors are taking this intensive property and turning it back into an extensive property, which actually has exactly the opposite effect of what the authors were attempting to do.

Response to general comment #24

As indicated above, the authors have adopted the suggestion of the reviewer to remove the discussion of the PA:LII ratio.

Reviewer general comment #25

P. 19960-25: The statement here is false. See above comment.

Response to general comment #25

This section has been removed so that the focus is on SAC variations. Then as indicated in earlier responses we have improved the discussion to acknowledge the role changes in mixing state can also have on the observations.

Reviewer general comment #26

P. 19963-9: The PA measurements here were made at 781 nm. Absorption by “brown carbon” at this wavelength is very likely to be extremely small (indistinguishable from zero). Thus, this discussion is out of place.

Response to general comment #26

The corresponding sentence in the manuscript has been removed.

Reviewer general comment #27a

P. 19964-20: To the extent that Rayleigh-Debye-Gans theory can be used to accurately describe absorption by fractal BC particles, this discussion does not hold. RDG says that the total absorption by a fractal particle is just the sum of the absorption by the individual spherules. The mass absorption coefficient for an individual BC spherule is relatively constant for spherules smaller than ca. 100 nm. Thus, if we distribute the same total mass per particle amongst some number of different sized spherules comprising that particle, the total per particle absorption (according to RDG) does not differ by much, and certainly is not thought to vary by the extremely large factors observed here. This is because as the size of the primary spherule decreases, the number of spherules per particle increases in an offsetting manner.

Response to general comment #27a

The Rayleigh-Debye-Gans (RDG) theory is commonly used to describe absorption in soot aggregate fractals. However, as the reviewer suspects the theory does not hold perfectly when applied to fractal aggregate particles. Recent work (Liu and Smallwood, 2010) provides such evidence and also estimates that the bias can be as much as 15% from the true absorption characteristics.

In the situation when the atmospheric soot aggregate collapses, as would be expected with more aged soot particles possessing a larger amount of coating material, the diameter of the primary particle is no longer the metric for light absorption. In this case

the particles have assumed a more compact shape than the initial fractal structure and in this form the particles would no longer be expected to follow absorption as predicted by RDG, as the dimensions have become too large.

The authors do not fully agree with the reviewer's point that because the number of primary spherules per particle increases in an offsetting manner as the size of the primary spherule decreases our interpretation is not likely. The scenario the reviewer describes is valuable to consider on a theoretical basis, but with respect to ambient measurements we cannot expect that there would be the same amount of mass per particle or that as the size of the primary spherule decreases the number of spherules per particle would increase in an offsetting manner.

Therefore, all the coating enhancements are based on spherical BC particles and in the real world, BC is likely to be present in aggregate form, especially at sites that are dominant by fresh emissions. Absorption enhancement due to coating and morphology is not simply additive quantities and the coating enhancement can be much more complicated when the coating is present on a BC aggregate rather than spherical particle, which was one aspect we were trying to explore in this study. We can not at this point totally explain why there is such an increase in SAC for the Toronto site although we believe it may have to do with a combination of the coating and morphology factors, related to combustion source and particle age, and possibly the local meteorology. Recent field measurements have been made to look into this aspect more closely and we will acknowledge the limitation of this current dataset in the revised version.

Liu, F., and Smallwood, G. J.: Effect of aggregation on the absorption cross-section of fractal soot aggregates and its impact on LII modelling, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 111, 302-308, 2010.

Reviewer general comment #27b

Furthermore, the authors appear to be implying that the particles observed in Toronto were 'fresher' than those in Ottawa. This does not seem justifiable given the site locations.

Response to general comment #27b

Overall, the particles measured in Toronto are more complicated than the other sites. This site particularly during day time and early evening rush hour encounters many gasoline vehicles on the road and this would normally lead one to suspecting a greater contribution from fresh vehicular emission. At the same time, this site can be engulfed within a large, relatively polluted, regional air mass that contains more aged regional background aerosols. This led to challenges regarding the mixing state, which we have resolved better in our revisions. There are moments when the site is impacted by fresh emission. By which we mean more contribution from tailpipe type of emissions, emitted quite recently, and not literally 'fresher' compared to other places. The Ottawa street canyon site in comparison is a very different situation. This site is mostly dominated by diesel buses, with lots of 'stop and go' running conditions. Also, the air is easily trapped in the local area and is thus very different than the Toronto site. The original intent of the wording 'fresher' has no implication on the relative freshness of specific BC particles

observed among different sites. We were only emphasizing there was a considerable amount of contribution from combustion generated particles from vehicles and we make sure to be clear about this in the revision. With the very nature of the gasoline and diesel particles, it is not possible to draw the line and also not realistic to compare what type of particles can be considered as fresher.

We greatly appreciate the reviewer's comments in encouraging us to explore this issue more closely since as a result we think we have uncovered some additional results of interest from our measurements. In the revised manuscript, we rely on multiple time series and conceptual models to help identify the internally mixed dominant situations and the nature of the external mixtures. Some new analyses will be shown that focus on those sections of the measurements, which will be outlined in detail in the revised manuscript.

Reviewer general comment #28

Figure 3: It would be helpful to color the appropriate axis red to make it more quickly apparent which trace corresponds to which axis.

Response to general comment #28

The changes have been made to the revised figure.

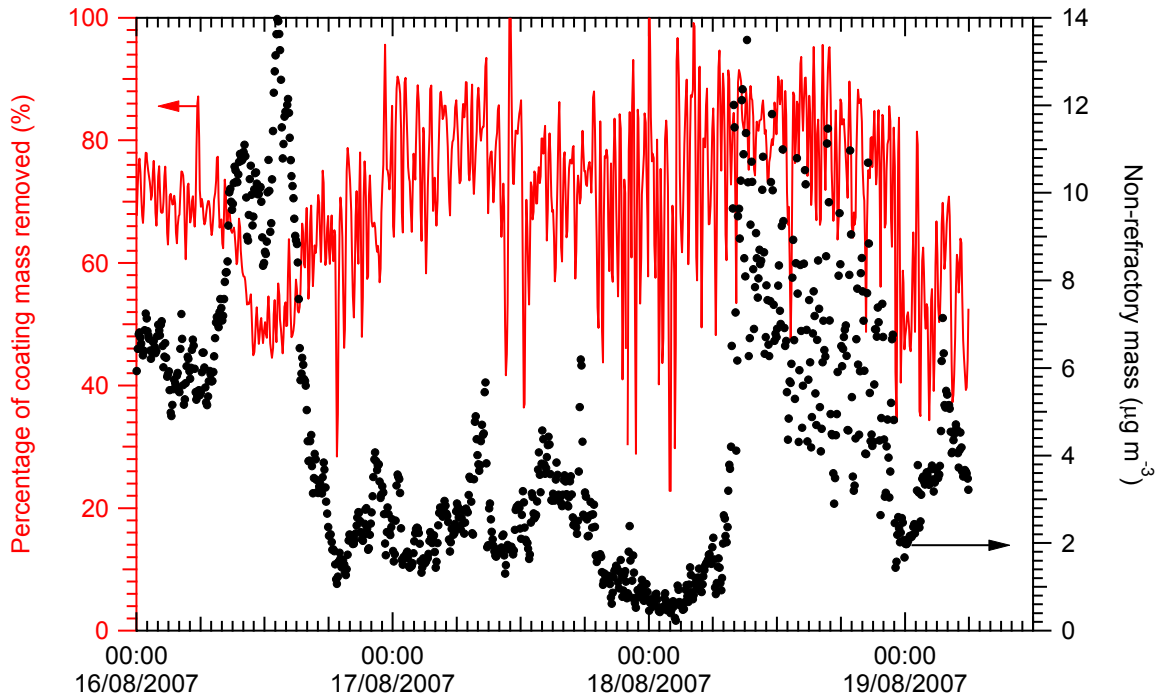
Reviewer general comment #29

Figure 3: The figure caption/figure is confusing. The axis label is "total particle mass loading" but the text refers to this as particle coating mass. Which is correct? And does the total particle mass include the black carbon (e.g. refractory material) mass? Also, I presume the values shown are corrected for particle number losses.

Response to general comment #29

To be consistent, we will use non-refractory mass throughout the manuscript which represents the sum of organic, sulphate, ammonium, and nitrate masses. This does not include the refractory material mass.

These measurements were not corrected for particle losses in the thermodenuder because the real-time particle number size distributions were not available for such a correction. As explained in response #16 the variation in particle number concentration due to changes in ambient conditions appears to be larger than the particle losses in the thermodenuder.



Reviewer general comment #30

Figure 4: The caption for panel d is very confusing. What do the authors mean “at different stages in a thermodenuder experiment?” This does not appear to be what the panel shows.

Response to general comment #30

This has been addressed in the response for comment #4c. The figure and the caption will be revised to avoid confusion.

Reviewer general comment #31

Figures General: I assume that higher quality figures will be included upon revision? Some of the labels/points did not transfer well to pdf.

Response to general comment #31

Yes, high resolution figures will be submitted for the revision.