Author responses for the reviewer comment on Chan et al. (acp-2010-598)

General Response
We appreciate the constructive comments from the reviewer, and in response are willing to make modifications to the manuscript to improve it. However, we disagree with the reviewer on some of the issues that were raised. A key issue is some of the values we derived for the SAC from our measurements. Reasons why we believe that these are feasible are summarized below and discussed in further detail in subsequent sections.

Measured or inferred SAC values are dependent upon the method applied to measure EC and most if not all of the results reported to date have relied on integrated filter samples followed by analysis conducted in the laboratory to determine EC. The techniques used have been thermal or thermal-optical approaches and for these EC is defined by the approach (e.g., IMPROVE vs. NIOSH vs. Cachier two-step, etc.) and results vary considerably, thus leading to different SAC values for the same measured B_{abs}. There is not a single accepted approach to measure EC, which means that uncertainty remains among all the measured SAC values, generally leaving comparison to theory to judge whether they are reasonable.

Our data add to the suite of estimates possible, but also challenge current thinking because of their unprecedented time resolution. Theoretical analysis, however, cannot deal with complex morphology that is very often present with black carbon (nano) particles, as it is largely based upon the assumption of spherical particles. Fresh particles, which are more likely in some of the settings where we undertook measurements and which are more likely to be captured with high time resolution, typically exhibit complex morphology. Thus, our measurements clearly have the potential to capture a greater range of SAC values, which is demonstrated by the results in our manuscript.

Given the points above and observing that our lower SAC results are fully consistent with theory for uncoated BC, and that our higher SAC values have also been reported by others (example data from the literature are discussed below) we believe that our results are defensible. Furthermore, our high time resolution observations are revealing phenomena not previously shown and thus should be reported to the scientific community. While one could argue that our 1 minute data are too noisy and uncertain, when one considers our point by point values in the Windsor case studies (in the revised manuscript) one can see that the variations in SAC, PPS, etc., line up in time with other indicators that features of the airmass are changing. Thus our method is giving real 1-5 min information on BC, EC and the SAC, a valuable new contribution. These points and other remarks raised by the reviewer are addressed in more detail below.

Detailed Responses

Detailed response #1 – Range of SAC Values
The authors understand the concern from the reviewer regarding some of the large SAC values reported in this manuscript for the portion of the data acquired in Toronto, but this

should be considered in the context that it only covers a short period of time and represents a fraction of the total data being reported upon in the manuscript. Similarly, only a portion of the SAC data in the literature show such high values, whereas the majority of the literature is in line with the rest of our data (see summary table below). The authors do not agree that the reported SAC values from this work are impossible to attain; in fact, a number of other authors have already reported such values. With our high time resolution we are beginning to shed new light on when and why they occur.

The literature SAC value of 5-6 m^2/g at 781 nm referred to by the reviewer is calculated from Mie theory based on spherical black carbon (BC) particles with very small diameters and with an assumed density that varies from about 1.8 to 2 g/cm^3. This SAC value is a function of particle diameter and is also largely impacted by a number of factors. The structure and composition of particles in the atmosphere are rarely the idealized spherical particle that was modeled. At best they are collapsed aggregates with the coating material leading to an overall spherical shape for the aerosol, while the BC portion is still likely more complex morphologically. It is not uncommon, particularly for freshly emitted BC, to be much more complex, as numerous images from microscopy have shown (e.g., Tumolva et al., 2010).

We hypothesize that there are number of factors that can contribute to the high SAC values. The two major factors that could contribute to the observed SAC in this study are the time resolution and our EC definition (i.e., LII). These factors are discussed in detail below. If permitted, the authors will include a paragraph to discuss the importance and significance of these factors in the manuscript. Other factors that also have an impact on the SAC value which are already mentioned in the manuscript or are obvious will not be included in the following discussion.

Factors that contribute to the variation in measured/inferred SAC:
i.   Time resolution of measurements
ii.   EC definition
iii.   EC morphology
iv.   Locations of measurement
v.   Season / time of day
vi.   Method of absorption measurement / wavelength of absorption measurement
vii.   Types and amount of atmospheric processing

i.   Time resolution of measurements
The most significant difference between the measurements reported in this manuscript and others in the literature is the time resolution. The historical SAC references are all based on a much longer time integration of measurements. e.g., filter based measurements were often daily or even longer in time resolution in order to accumulate sufficient PM mass for EC analysis. In this study, the reported SAC values have significantly higher time resolution, with periods of as little as 1-5 minutes for acquisition. This fundamental difference can have a significant impact on the observed SAC values. Firstly, atmospheric property changes are very dynamic and the shorter the time resolution, the greater the likelihood of measuring such variations. This is particularly

important in the dynamic urban atmosphere. Most often, the observed fluctuations in the data were determined not to be noise as the responses were observed with both the PA and LII instruments.

Producing data with a much shorter time interval will certainly have the potential to yield higher SAC values, which are smoothed out during the traditional integrated sampling. The integrated, filter-based approaches are also known to have the potential to alter particle characteristics as particles remain on the filter for extended periods during and after sampling. This also leads to artifacts in the B_{abs} measurement due to filter effects and layering of the particles. Our *in situ* measurements are much different and are hypothesized to reduce these problems and to reflect conditions when BC particles are suspended in the atmosphere (i.e., more realistic).

Another explanation indicating that high time resolution measurement can reveal greater variability and greater SAC values is that some of the coating materials on the soot particles are quite volatile (SVOC or IVOC) and so evaporate over time. A more volatile coating in a fresher airmass, especially close to some sources, would be much less likely to be captured by integrated sampling methods, but would be captured with our high time resolution in situ technique. In situations such as this – fresh BC particles with complex morphology and a large, but volatile coating – large 1-5 min SAC values can be expected to be quite feasible. The existence and importance of these 'loosely held' coatings are just now becoming appreciated (e.g., Robinson et al., 2007; Lipsky et al., 2006) and this is leading to changes in how transportation emissions, for example, are being modeled (Shrivastava et al., 2006; Greishop et al., 2009)

The fluctuations we've observed and that the reviewer is questioning, which we hypothesize is influenced by coating relative to the amount and shape of the BC, were predominantly in the positive direction (i.e., increases in the SAC values) and were most significant in Toronto, near fresh emissions (gasoline dominated) with low BC levels. On the other hand, measurements over a longer period of time tend to smooth out these observations and render them less visible. The longer the measurement period, the less important these dynamic periods can be expected to be to the overall SAC value.

ii. EC mass definition
In the Mie theory calculation, the BC mass is calculated based on an assumption of a spherical particle and a certain value for the BC material density. In ambient measurements, the EC mass is often measured by thermal analysis. Commonly used thermal analysis methods include the two step thermal method from Cachier et al. (1989), NIOSH 5040 (Birch and Cary 1996), and IMPROVE (Chow et al., 1993). These different methods result in significantly different values for EC mass because of the different operational conditions.

Analysis of over 40 samples of SRM 8785 urban dust standard reference materials by our colleagues (Huang et al., 2011) showed that the EC mass concentration determined by the IMPROVE method is consistently higher by about 60-70% compared to the NIOSH method. To illustrate how this difference can impact SAC, consider the following

example. The BC concentration measured by our LII instrument compares well with the NIOSH 5040 defined EC (McEwen et al. 2011a; 2011b; Smallwood 2009) and exhibits a highly linear relationship. Our resulting SAC ranges from 10-50 m^2/g. If the IMPROVE defined EC was substituted as the reference, the calculated SAC values would reduce to 6-30 m^2/g based on the above information. We anticipate the latter range would be more in line with what the reviewer expects. Thus, the EC method applied in determining SAC has a significant impact.

As thermal EC is operationally defined (Chow et al. 1993; 2001), the EC mass concentration obtained from one method is not said to be more or less accurate than another method but simply defined differently. At this moment there is no universal definition of how atmospheric BC particles should be defined thermally. As a result, with all other factors being equal, the observed SAC value for ambient particles can still vary (up to 60-70% as illustrated above) depending on which thermal method one may choose to use to define EC.

The table in Appendix 1 summarizes some reported ambient SAC values from various studies. The information is grouped according to the EC definition. As mentioned, previous LII work indicated that LII BC mass concentration agrees well with the NIOSH 5040 defined EC mass concentration and therefore it is grouped together with the NIOSH 5040 method data.

This summary (Appendix 1) not only indicates that a large range of SAC values has been observed, even if the same thermal EC definition is used, but also shows that enhancement as high as reported in our work has been observed and published in the past. Further, as illustrated in the above example, when we adjust the SAC values from our work to be consistent with the IMPROVE EC definition, the resulting SAC (6-30 m^2/g) also compares well with the literature values within that group.

 iii.   EC morphology
Combustion generated BC particles have been long observed, through TEM images, not to be spherical, particularly for relatively fresh emissions (e.g., Tumolva et al., 2010). These particles are often in an aggregate form with various shapes, typically described as a chain-like structure with different degrees of branching or as being 'fluffy'. Direct comparison of the results from BC particles with the idealized spherical particle model is not a straightforward matter. For instance, the "mobility diameter" as measured by a technique such as Scanning Mobility Particle Sizer (SMPS) does not equal the volume equivalent diameter (which is what is usually used to express the absorption and particle diameter relationship from Mie theory due to the spherical particle assumption) for BC aggregates. Such a relationship deviates further when BC particles have a fractal dimension much smaller than 3 (i.e., further away from being spherical). Therefore applying an "aggregate enhancement correction factor" to the spherical BC model calculation is likely to be inaccurate (as such an enhancement is likely to be size dependent), as it will contain significant uncertainties due to the variability in the morphology of the BC particles, which may result from different operational conditions and fuel used.

Detailed response #2 – "Sweep Period" Data

One of the comments from the reviewer is that there is no theoretical justification for fitting a straight line in Figure 5 (SAC vs. non-refractory to BC ratio) for the "sweep period" data. In the manuscript, we showed a detailed comparison of different time series in Sect. 3.2.2 leading to the hypothesis that the particles observed during the "sweep period", which come from either the mill (one major BC source in that area) or from aged urban particles existing above the nocturnal boundary-layer, had a good potential for being internally mixed. When compared to other measurements during that particular day and during BAQS-Met, this "sweep period" did indeed appear to capture largely internally mixed particles with a range of coating amounts, relative to BC mass, thus supporting our hypothesis. The line fit to these data further shows that there is considerable similarity in these particles and the line helps identify these conditions for comparison with periods 1, 2, and 3 and ultimately to other observations during BAQS-Met. The point is that many other observations fall to the right of this line and, based upon air mass history and supporting data, are more likely associated with externally-mixed particles (which was mentioned in the revised manuscript as we describe the measurements). Conversely, few, if any, observations fall to the left of this line, suggesting we have identified some form of a limit for the SAC vs. ratio (non-refractory coating mass to BC mass) for measurements with our level of time resolution. The fact that the y-intercept (no coating) gives an SAC for pure BC (theoretical) lends support to this line having meaning (see discussions below).

However, the objective here is not so much to derive an universal relationship between SAC and non-refractory to BC ratio (because this ratio is likely to change for a variety of reasons – see list above), but to illustrate that measurements obtained at the right moment and condition can provide a useful reference given the type of justification we have provided. Depending on the magnitude of the deviation from this reference BAQS-Met relationship and the support of time series data from other tracers, one can infer the degree of mixing of the source particles with background pollutants. On this point, measurements that we inferred were associated with externally-mixed conditions do have other information (e.g., concentration of sulfate, airmass history - discussed in the manuscript) supporting this interpretation. Further, we have also shown measurements from period 3, which were also from the mill. They were also close to the reference line obtained from the "sweep period" and therefore our approach was consistent and reproducible.

As mentioned just above (and also in the revised manuscript), the y-intercept obtained from the fit to the data in the "sweep period", which has a theoretical physical meaning of the SAC value for BC particles with no non-refractory material (i.e., with the non-refractory to BC ratio of zero), has a value of 6.7 m^2/g, similar in magnitude to other values predicted by models for pure BC particles, which is referred to by the reviewer as "undisputed" (see specific response #1). Although the relationship (slope) given by the line may not be the same for air masses away from this region or observed at different times, this relationship does provide useful information for analyzing measurements

conducted during BAQS-Met. The authors are willing to include additional sentences in the manuscript to clarify this. At this stage, we have no intention of deriving a theoretical universal relationship in Figure 5, while we do find it interesting that for that period it was not only steel mill particles that fell on a line, but also the aged particles from above the boundary-layer. Nonetheless more data are needed to explore this relationship and its ultimate meaning. However, we do believe, as stated above, that the line serves a valuable purpose and its intercept (see specific comments #1) and small scatter (R^2) are certainly intriguing.

Detailed response #3 – Questions on PPS

Regarding the reviewer's comments about the PPS, this is a complicated issue and at the moment we cannot provide answers for all the questions. However, this is the first report of applying LII to distinguish between the sources of the BC particles, and is significant in that aspect alone. While further research may lead to improved certainty regarding this measurement, we observed consistently smaller PPS from gasoline port injection soot particles compared to diesel particles and according to our knowledge this is the first time this parameter has been investigated in atmospheric measurements.

In order to fully study PPS, other factors should also be looked at. For example, the composition of the particulate matter generated from the two types of engine exhaust emissions is generally different. One significant aspect is that there is a large difference in organic component in the particles emitted from port fuel injection (PFI) gasoline engines and diesel engines. A study from Cheung et al. (2009) reported OC and EC emissions from a Corolla being 0.95 mg/km and 0.05 mg/km, respectively, leading to the particles being 95% OC for the corresponding operational conditions used in that study. In comparison, OC and EC from a Golf diesel were 24.2 mg/km and 39.1 mg/km, leading to an OC fraction of 38.2%. Further, the OC fraction in diesel particles is also dependent on engine load. Also, the two types of vehicles usually have different aftertreatment emission control devices, which may or may not have an impact on the resulting particles. As a result, more carefully designed experiments will be conducted in the near future in order to investigate the differences between diesel and gasoline engine emissions with a wide range of operational configurations. This should firmly establish the PPS and light absorption relationship, but is beyond the scope of the current study.

Detailed response #4 – OC/EC ratio

Regarding the reviewer's comment about the high EC/OC ratio for gasoline vehicles, his/her statement is incorrect. Indeed it is the opposite (e.g., Cheung et al., 2009). Diesel vehicles usually operate in a globally lean condition but with highly stratified nonpremixed reactants with a locally rich mixture in the fuel jets. In this case, the near-complete combustion results in little OC due to the globally lean conditions, but significant quantities of BC due to soot formation in the locally rich combustion regions. On the other hand, for gasoline vehicles, the mode of operation is homogeneous and close to stoichiometric, resulting in much lower levels of soot formation and thus less BC,

while quenching of the flame at the walls results in more unburned hydrocarbons and thus there is a relatively greater OC fraction.

Detailed response #5 – Inconsistency of SAC and non-refractory to BC ratio
Finally, regarding reviewer's comment about the inconsistency of the reported SAC and non-refractory to BC ratio parameters, the authors have confirmed the correctness of the reported values by reviewing the data and the analysis procedures. The different value reported by the reviewer is due to the reviewer's method of calculation. More specifically, the reported SAC values in the table represent the average of all individual ratios of the absorption coefficient and the soot volume fraction measurements. The value calculated by the reviewer is the ratio of the average absorption coefficient to the average soot volume fraction. Both sets of average SAC values are mathematically correct and have been confirmed by the authors. Taking into consideration the short time resolution of our measurements, consistency with SAC values computed from integrated samples and the possibility of some outliers in the high time resolution data due to measurement uncertainty, the authors agree with the reviewer that the ratio of the averages may be a more appropriate way of reporting these parameters as an overall average. The authors agree to make the changes in the table and add the description in the corresponding text to clarify them, should this be required. However, as we indicated above, the large observed fluctuations in SAC that we explored in more detail during BAQS-Met and somewhat for the Toronto thermodenuder experiments, appear to be consistent with real variations in the atmospheric conditions.

In summary, the authors believe the measurements reported in the revised manuscript provide interesting and reasonable insights that have not been revealed in the prior literature. This is due to the high time resolution of our measurements and thus our data are unique. The high time resolution (1-5 min) of our measurements coupled with the method used to define the EC mass (equivalent to NIOSH 5040) are the main contributors to the reported SAC values in this work. Our work is being followed up with more manuscripts, currently under preparation. As example, we have compared our LII with the more widely known DMT SP2 and observe very good agreement with explainable differences, which suggest that our LII is able to detect ~50 nm and smaller BC particles (important in fresh airmasses, particularly when gasoline engine emissions are important), while the SP2 is not (Liggio, 2011; paper to be submitted soon). The authors agree to include additional information, being the relationship between the thermal EC and the LII BC, to provide a linkage to other SAC values in the literature.

Specific responses
Reviewer's comment #1:
Literature results tell us that the specific absorption coefficient (SAC) for uncoated black carbon at 781 nm is around 5-6 m2/g. This, I think, is undisputed.

Authors' response #1:

In the revised manuscript line 965-972, the authors suggested that the y-intercept of a linear best fit line in Figure 5 (SAC vs. non-refractory to BC ratio) could represent a theoretical value of SAC for BC particles with the absence of non-refractory materials, i.e., 6.7 m^2/g. This value is independent of the EC definition because EC mass concentration appears in the denominator of both SAC and non-refractory to BC ratio. Also, this y-intercept has value very close to the theoretical value that the reviewer referred to as "undisputed". Taking into consideration that this value is obtained from atmospheric measurements and not from idealized spherical BC particles, we believe there is a scientific value behind this y-intercept rather than just a y-intercept of a fitted line. Since atmospheric BC particles rarely exist as uncoated BC particles, this also explains why most of the observed SACs in this work were above this theoretical limit.

Reviewer's comment #2:
This means that a measured SAC of 12 m2/g corresponds to an "absorption enhancement" of 2, 18 m2/g to 3 and 48 m2/g to 8, etc.. The average values observed in this study are typically above 18 m2/g, usually larger, which means that the average absorption enhancement factor is 3+. To me, this seems completely implausible.

Authors' response #2:

The authors disagree with the reviewer that the reported SACs here are implausible. In fact, similar observations were observed from a highly polluted city in China. In the work from Cheng et al. (2009), they said

"Rapid soot aging was observed, which led to large variations in the fractional contributions to σ$_{ap}$ by externally mixed and coated soot. On average, about 37% of the σ$_{ap}$ (~10–60%) arose by the coated soot. The coating enhancement in σ$_{ap}$ (absorption) and σ$_{sp}$(scattering) of the coated soot can reach up to a factor of 8–10 within several hours owing to the secondary processing during daytime."

Therefore, although we agree that the observed SAC observed from Toronto area are high, we believe they are not implausible and are contributed by a number of reasons mentioned earlier in the detailed response #1.

Furthermore, as mentioned earlier, the Toronto measurements reported in this work represent a very small fraction of the total measurements, i.e., a total of 72 (of 5 min) data points vs. over 1135 (of 5, 10, and 15 min) data points in the Windsor data set. Averaging all SAC values (weighted by number of data points rather than by site) yields a grand SAC average of 19.8 m^2/g (based on NIOSH defined EC) or 11.9 m^2/g (based on IMPROVE defined EC). This latter value agrees very well with many long term SAC measurements given in Appendix 1.

Reviewer's comment #3:
This is especially so when one considers the relatively small single scatter albedo values observed during much of the campaign (reported in the original manuscript, not the revised manuscript

Authors' response #3:

In the previous response to Referee #1, we have acknowledged that there are limitations in the nephelometer that is present in the DMT photoacoustic spectrometer for measuring scattering coefficient which is not able to capture forward and backward scattering light. This is potentially a serious issue for particles that are in sub-micron sizes because the forward and backward scattering for these particles are large. In those cases, a significant amount of scattering could be truncated and our scattering coefficients will thus be biased low. Because of the lack of real time particle size distribution measurements it is not possible to accurately correct for the scattering data and the actual scattering measurements can potentially be much larger than what was initially reported in the first version (ACPD). Therefore the single scattering albedo calculated based on these under-estimated scattering coefficient can be biased low. This information was therefore removed in the revised manuscript.

Reviewer's comment #4:
The authors are measuring ensemble properties, and thus we can consider what the average particle must look like to reproduce their observations. As shown in Bond et al. (2006), the theoretical absorption enhancement is largest for small BC cores with relatively "thick" coatings. Such conditions must correspond to particles with a large non-refractory/BC ratio...

Authors' response #4:

The authors hypothesize that large coating with small BC mass is ***one contribution*** to the large SAC for at least some Toronto measurements and we suggested in the revised manuscript that the gasoline emissions dominance could potentially be one contributing factor. However, as mentioned in the detailed response, there are also other factors that contribute to the large SAC that were not considered by the reviewer, namely the time resolution of the measurements and EC definition.

The high time resolution enables us to capture the coating effect in situations when the coating could be semi volatile and thus short lived. One hypothesis from the authors (needing verification with more experiments and measurements) is that if some of the coating on the gasoline soot particles is from the unburned gasoline, there is a possibility that these materials will evaporate over time and leave the particles. On the other hand, the organic material on the diesel may likely be contributed by lube oil (or much less volatile unburned diesel fuel) and relatively speaking is less likely to leave the particle within the time frame when secondary organics begin to condense or partition onto the particles.

As the reviewer hypothesized, the size of the particle solely based on SAC suggested that the EC definition, which has a direct impact to the SAC value, becomes significantly important (see more detail discussion in the next response). Additionally, these exhaust particles are likely to have complex morphology that may further enhance the absorption and the enhancement (Fuller et al., 1995; Iskander et al., 1991). All these factors can potentially lead to the large SAC described by the reviewer.

Authors' response #5:
The reviewer questioned the highest SAC values that were observed in Toronto and inferred that they corresponded to measurements with only moderate value of non-refractory to BC ratio. Then the reviewer performed a calculation to show that the enhancement factor seen in this study (e.g., 30 m^2/g) cannot be predicted by the core-shell model based on the non-refractory to BC ratio, which is ***exactly*** our point throughout this response.

The authors do not believe the simple core-shell model can fully explain the absorption from complicated soot aggregates and especially those with coatings co-existing on the particles. There are numbers of references, including from Bond (Fuller et al., 1999; Bond et al., 2006; Iskander et al., 1991) who acknowledged that the aggregate nature of soot can lead to an increase in light absorption. Due to the large variation of soot structure (due to different sources, emission states, engine condition and fuel used, etc.), we find it difficult to conceive of a single aggregate correction factor that will be sufficient to correct absorption based on a sphere. Furthermore, once soot particles are emitted, many aspects of atmospheric processing can lead to the rapid change of soot structure and collapse of the aggregates (Ramachandran and Reist, 1995; Huang et al., 1994; Hallett et al., 1989; Pagels et al., 2009; Johnson et al., 2005). A number of studies have indeed reported changes on particle light absorption due to the change of soot structure (Lewis et al., 2009; Liousse et al., 1993; Bond and Bergstrom, 2006; Fuller et al., 1995; Iskander et al., 1991). Therefore, if long term integrated measurements already suffered from such variations, it is difficult to believe that such a simple correction will work effectively on measurements with 1-5 minute time resolution.

As a result, our observations show that there are other unaccountable factors that appear to be important for contributing to high SAC at the urban site and are worth investigating. One suggested factor as pointed out in the revised manuscript is that gasoline vs. diesel could be one contributing factor. Another factor is that morphology may play a more important role with ***high time resolution measurements*** than previously expected.

Also, the authors would like to note that the assumption the reviewer used is not completely valid for our data (i.e., our non-refractory mass does not always equal coating mass) as we pointed out in response #4 above. One important factor one should take into

consideration is the externally vs. internally mixed aerosol which we have clearly demonstrated in the thermodenuder experiment section. Therefore, this highlights again our last point that there must be other factors beyond just the coating thickness that high time resolution measurements have the sensitivity to detect and which contributes to high SAC values. However, we would also like to point out that for the Toronto measurements the BC concentrations tended to be very low and indeed this short thermodenuder experiment turned out to be conducted during a rather 'clean' time period. However, with this BC being dominated by gasoline engine emissions and their high OC/EC ratio and with the levels of OC observed we do hypothesize that it was likely that our measurements captured conditions with a large amount of coating relative to BC. Furthermore, this BC was fresh (i.e., more complex morphologically) and quite small in size. All-in-all these are the types of conditions when large enhancements would be possible.

Following on the discussion regarding the incorrect assumption, when we use a more conservative non-refractory to BC ratio of 3 or 5 (with the same assumptions of soot and non-refractory mass density) this leads to final particle diameter of 57 nm and 67 nm, respectively. This has an impact on what the expected enhancement factor should be that is used for comparison.

Finally, we have emphasized in many places of this response that the observed SAC is based on NIOSH EC definition. If we were to use IMPROVE EC definition, the value of 30 m^2/g would change to 18 m^2/g. Therefore, the method employed to define EC obviously plays a significant role and perhaps not enough attention was being devoted to this critical issue in the past.

Reviewer's comment #6:
If the core size is larger, it is impossible to achieve such large absorption enhancements. I think that this is apparent, even given the constraints and limitations of using core-shell Mie theory to describe BC absorption.

Authors' response #6:
The authors understand the reviewer's point such that the same amount of coating on a larger core becomes thinner and leads to lower enhancement. However, as pointed out in the previous response, there are numbers of factors that are equally important in affecting SAC while some are only applicable to high time resolution measurements.

Reviewer's comment #7:
In other words, what is lacking is any sort of justification of the observations via reference to theoretical calculations and/or discussion of what is/is not reasonable.

Authors' response #7:
We will add the necessary justification and include some of the above discussion points should we be able to make more revisions to the manuscript. We also want admit here that some of the observations from this study could be considered to be surprising. Therefore, it is worth presenting to the community what we have observed and to discuss

reasons and potential limitations, as real time measurement will become more and more important in the future. This work may not provide ultimate answers to all our observations but it does identify limitations between theory and ambient measurements and provides a new view for looking at BC light absorption. It also provides some novel means for studying the potential coating impact on light absorption that have not been possible in the past. As a follow-up, a large scale (over 1 month duration) field study was conducted in the summer of 2010 and more focused information will be made available. Experience learned from this work will be useful in investigated those measurements in detail to provide additional answers for explaining atmospheric observations.

Reviewer's comment #8:
For example, the authors fit a line to the "sweep" period SAC vs non-refractory to BC mass ratio (Figure 5). There is absolutely no theoretical justification for fitting a straight line to this data, certainly not one with the steepness indicated by the observations. As such, when they make statements such as "In these cases, there is an apparent lack of the expected relationship..." they should certainly discuss more thoroughly what the expected relationship is (and it is not what was observed during the "sweep" period.)

Authors' response #8:
We have discussed above (detailed response #2, specific response#1) the physical meaning behind the y-intercept in Figure 5. We have also explained the reason for fitting the "sweep period" and why we are comparing this to other periods. In short, the y-intercept appears to contain scientific value and provides a theoretical lower limit of SAC for BC particles with the absence of any coating enhancement. We discussed this value in the revised manuscript.

Reviewer's comment #9:
The authors do present some very interesting information on the PPS for diesel vs. gasoline vehicles in a test facility, observing a clear difference between the two. Is there any chance that they made measurements with the PAS during that same study? If so, what values for the SAC were observed and did they differ between the diesel and gas vehicles?

Authors' response #9:
This is addressed above in detailed response #3.

Reviewer's comment #10:
Gas vehicles are known to have very high EC/OC, and thus should show minimal enhancement, corresponding to observed SAC values near 5-6 m2/g. If they do find the expected low values for the SAC, this would help to provide confidence in their measurement technique.

Authors' response #10:
This is addressed above in detailed response #3 and #4.

Reviewer's comment #11:
Perhaps one or the other of the measurements (PAS or LII) is biased high or low, meaning that the presented values simply need to be scaled by some multiplicative factor to be brought into a "realistic" range…

Authors' response #11:
We have addressed this in the detailed response #1. We have confirmed (through examination of various method development datasets at our disposal, but not all reported here) the validity of the measurements from both the LII and PA, including at the lower BC concentrations. We believe the instruments were operating properly during the study. Above we suggested that other possible factors affecting the magnitude of the SAC, such as how EC is defined and the short time resolution of our measurements.

Reviewer's comment #12:
.. Perhaps there is a physical reason for this (e.g. periods corresponding to low [BC] equate with periods of high coating), but perhaps this is an indication that either the PAS or LII is having trouble at lower [BC]…

Authors' response #12:
The authors have confirmed that sensitivity was not an issue for both PA and LII at the lowest BC concentration. Signals from both instruments, particularly the LII (which was used to estimate BC mass concentration) were much above the detection limits of the instruments even during low BC situations. The authors believe the time resolution is one large factor in contributing to large SAC. Further, as we have demonstrated, the EC definition has a direct impact on the SAC value.

Reviewer's comment #13:
A further issue of note is that some of the numbers reported in Table 1 are inconsistent, in particular the [BC], [NR-mass] and NR-mass to BC ratio. For example, on Toronto 16 Aug, the reported [BC] = 0.14, [NR-mass] = 7.3, corresponding to [NR-mass]/[BC] = 52.1. However, the reported [NR-mass]/[BC] = 62. Same goes for every site location and the various calculated SAC values.

Authors' response #13:
This has been addressed above in detailed response #5.

Appendix 1: Historical observed SAC ranges for atmospheric particles.

SAC range (m²/g)	Reference	Absorption method	EC definition	Notes
7-40	Sharma et al. 2004	Aethalometer (880 nm)	Cachier et al. 1989	
5-20	Liousse et al. 1993	Aethalometer (880 nm)	Cachier et al. 1989	
5-19	Martins et al. 1998	Various	Cachier et al. 1989	
9.3	Lavanchy et al. 1999	Aethalometer (820 nm)	Cachier et al. 1989	
7	Kuhlbusch 1995		Cachier et al. 1989	
6-28	Sharma et al. 2002	Aethalometer (880 nm)	Cachier / IMPROVE	
3-12	Sharma et al. 2002	PSAP (565 nm)	Cachier / IMPROVE	
9-13	Chou et al. 2005	Laser transmission method	IMPROVE	
2-6	Chan et al. 2010	PSAP (567 nm)	Huang et al.	Analysis of SRM urban dust samples show similar EC compared to IMPROVE
17-35	Snyder & Schauer 2007	18.5 at 880 nm; SAC=35 at 370 nm to 17 at 950 nm	NIOSH 5040	
6-55	Jeong et al. 2004	Aethalometer (820 nm)	NIOSH 5040	
5-37	Cheng et al. 2009	Photoacoustic Spectrometer (532 nm)	NIOSH 5040	
5-25	Quinn et al. 2004	PSAP (550 nm)	NIOSH 5040	
9-10	Knox et al. 2009	Photoacoustic Spectrometer (760 nm)		
19-20	Knox et al. 2009	Aethalometer (880 nm)	NIOSH 5040	
50-53	Knox et al. 2009	Aethalometer (370 nm)	NIOSH 5040	
3-9	Huebert et al. 2003		NIOSH 5040	
10-50	This work	Photoacoustic Spectrometer (781 nm)	Other (LII; comparable to NIOSH 5040)	LII BC compares close to 1:1 with NIOSH EC
8-10	Jennings and Pinnick 1980	550 nm	Calculated based on density of 2 g/cm³	
11-12	Japar et al. 1986	Transmission method (650 nm)	Huntzicker et al. 1982	
8-19	Petzold et al. 1997	Laser transmission method (760 nm)	Other (Petzold & Niessner 1995)	

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Original response from the reviewer:

Certainly this manuscript has significantly changed. I find the overall analysis to be much improved. By breaking the data down into case studies, the authors are able to explore more fully some of the variability in their data in potentially interesting ways. However, upon re-reading I've come to realize that, unfortunately, I don't really believe the measurements. Or perhaps a more appropriate way to put this is that I don't think the measurements are particularly accurate, which calls into question the conclusions reached. My reasoning on this is the following:

Literature results tell us that the specific absorption coefficient (SAC) for uncoated black carbon at 781 nm is around 5-6 m2/g. This, I think, is undisputed. This means that a

measured SAC of 12 m2/g corresponds to an "absorption enhancement" of 2, 18 m2/g to 3 and 48 m2/g to 8, etc.. The average values observed in this study are typically above 18 m2/g, usually larger, which means that the average absorption enhancement factor is 3+. To me, this seems completely implausible. This is especially so when one considers the relatively small single scatter albedo values observed during much of the campaign (reported in the original manuscript, not the revised manuscript). The authors are measuring ensemble properties, and thus we can consider what the average particle must look like to reproduce their observations. As shown in Bond et al. (2006), the theoretical absorption enhancement is largest for small BC cores with relatively "thick" coatings. Such conditions must correspond to particles with a large non-refractory/BC ratio.

Yet the largest SAC values (in Toronto) were observed for moderate non-refractory/BC ratios, with values of SAC = 30 m2/g observed even for non-refractory/BC ratios of 10. Using very conservative assumptions, for a core diameter of 30 nm, the corresponding coated particle diameter for a non-refractory/BC mass ratio of 10 is 82 nm (I've assumed a density of the coating material of 1 g/cm3...for larger values the coated particle diameter only decreases). From Mie theory (which is, admittedly, only an approximation), one calculates an absorption enhancement of only 1.4. If one assumes a larger core diameter (say 80 nm), the calculated absorption enhancement increases only to 1.9 for a mass ratio of 10. This translates to an expected SAC of <12 m2/g, which is around the lowest values observed in the study. For a core diameter of 30 nm, the minimum non-refractory/BC ratio that will give SAC > 30 m2/g (enhancement of a factor of 5) is around 6400, which corresponds to a particle diameter of 680 nm and, importantly, a single scatter albedo of 0.9996. If the core size is larger, it is impossible to achieve such large absorption enhancements. I think that this is apparent, even given the constraints and limitations of using core-shell Mie theory to describe BC absorption.

In other words, what is lacking is any sort of justification of the observations via reference to theoretical calculations and/or discussion of what is/is not reasonable. For example, the authors fit a line to the "sweep" period SAC vs non-refractory to BC mass ratio (Figure 5). There is absolutely no theoretical justification for fitting a straight line to this data, certainly not one with the steepness indicated by the observations. As such, when they make statements such as "In these cases, there is an apparent lack of the expected relationship..." they should certainly discuss more thoroughly what the expected relationship is (and it is not what was observed during the "sweep" period.)

The authors do present some very interesting information on the PPS for diesel vs. gasoline vehicles in a test facility, observing a clear difference between the two. Is there any chance that they made measurements with the PAS during that same study? If so, what values for the SAC were observed and did they differ between the diesel and gas vehicles?

Gas vehicles are known to have very high EC/OC, and thus should show minimal enhancement, corresponding to observed SAC values near 5-6 m2/g. If they do find the expected low values for the SAC, this would help to provide confidence in their measurement technique.

But as it stands, I simply do not believe their reported values, finding the SAC values to be implausibly large. Perhaps one or the other of the measurements (PAS or LII) is biased high or low, meaning that the presented values simply need to be scaled by some multiplicative factor to be brought into a "realistic" range. But this would have to be demonstrated. I'll note that I find it intriguing that there seems to be an approximate inverse relationship between the reported SAC and the measured [BC] (i.e. higher [BC] tends to equate with lower SAC). Perhaps there is a physical reason for this (e.g. periods corresponding to low [BC] equate with periods of high coating), but perhaps this is an indication that either the PAS or LII is having trouble at lower [BC]. A further issue of note is that some of the numbers reported in Table 1 are inconsistent, in particular the [BC], [NR-mass] and NR-mass to BC ratio. For example, on Toronto 16 Aug, the reported [BC] = 0.14, [NR-mass] = 7.3, corresponding to [NR-mass]/[BC] = 52.1. However, the reported [NR-mass]/[BC] = 62. Same goes for every site location and the various calculated SAC values.

As it stands, until the authors can provide supporting information to demonstrate clearly that their measurements of SAC are correct (in particular, the exceptionally high SAC values) I think this manuscript is not suitable for publication.