Response to reviews: Airborne measurements of trace gases and aerosols over the London metropolitan region by G. R. McMeeking et al.

We thank Darrel Baumgardner and an anonymous reviewer for their helpful comments on the paper. We have copied the reviewer comments in italics and have colored them blue for D Baumgardner and red for Reviewer #2 and added our responses below in black text. We have combined the reviewer specific comments when appropriate and ordered them by line number in the original submission. We have also re-numbered the specific comments by D Baumgardner to match the discussion paper. In selected cases we show the changes made to the original manuscript in response to the reviewer comments in **bold face**.

General comments

This manuscript is a general summary of mostly airborne measurements with some ground based data to complement them. The data are thoroughly described with one exception noted below. The overall paper is well organized and easy to follow.

The paper by McMeeking et al. is an overview of flight data in terms of VOC emission ratios, aerosol physical properties, and aerosol chemical composition from a series of flights following the M25 road encircling the megacity of London. The measurements are of high quality, and the context of the paper is of interest on a broad scale with data from this developed megacity adding to the literature on megacity emissions on regional concentrations.

We thank both reviewers for their positive comments regarding the manuscript.

In several places, also noted below, a bit more clarification would be helpful, at least for this reviewer.

We have attempted to clarify the paper as requested by the reviewer, focusing on several specific sections highlighted by the reviewer and listed below.

As I note below, I think one of the primary results, the lack of a difference between urban regional aerosol properties, other than the SSA, is not emphasized enough. There is so little difference in the aerosols, whereas there is a large difference in trace gases, should somehow receive more discussion, unless this is to be discussed in greater detail in a complementary paper.

The conclusion that "Our observations indicated that regional aerosol appeared to dominate urban sources" doesn't seem to be well enough supported, or at least I didn't link the similarity in mass concentrations and composition to a dominance of regional sources over urban. Please be sure to clarify this in the conclusions.

How were background concentrations and areas of "background" decided? The only clue to the reader comes on page 30685 line 10, but gives no exact criteria delineating what is a plume, what is background, and what is upwind. This is extremely important to be clear about since the conclusions of the paper regarding the importance of regional aerosol are dependent on how exactly it is defined. Is background aerosol in the air mass upwind of the city and into which London emits (thereby increasing the concentration), or is it aerosol away from the london plume, and may not be indicative of the air mass in which London adds emissions? For example, Figure 9 shows the comparison between background and London plume concentrations. From this figure there is little difference in background concentrations and on 24 June the background concentration is higher than the plume concentration. An extreme *interpretation of this is that the London area actually cleaned the regional plume (which would clearly be at odds with our understanding of urban versus regional emissions). Is it possible that some of the "background" concentration is due to recirculation of London area plumes from previous days? The authors provide synoptic views of the region on flight days, but this does not provide the reader with an understanding of the history of the air masses. The authors MUST give detailed discussion on how plumes were located, how plume vs background was decided, and background concentrations were determined for species such as CO and C2H2 used in ratios and analysis.*

Both reviewer comments refer to the distinction between urban, background, and regional air masses, the associated aerosol properties and the significance of any observed differences. Reviewer #2 is correct to point out the weakness in our original definitions of the air mass types reported in the manuscript and also makes an important distinction between background air that is upwind of London versus background air not upwind of London. D. Baumgardner also notes the lack of emphasis on this major topic of the manuscript as well as to question the conclusions regarding regional versus urban aerosol sources. To address these concerns we have made substantial revisions to the methods used to distinguish different air masses and added to our discussion focusing on the differences in their properties.

New air mass identification scheme:

Our previous system for identifying plume and background periods was subjective and based on wind directions and changes in the concentrations of species expected to be emitted from London. Our new approach is similar, but uses the SP2 BC mass concentrations and model-predicted wind fields to identify the London plume. First, we determined the 75th percentile mass concentrations of BC for each flight for periods when the aircraft was flying the circuits around London. We then classified all portions of each flight that had BC mass concentrations above this values as in the London plume. We used the model-predicted wind fields to identify a few isolated regions where values exceeded the 75th percentile mass concentrations (excluding profiles) but were clearly not emissions from London. We show the locations of the London plume as defined by this method in a revised version of Figure 10.

We also introduced two new air mass classifications based on the reviewer comments. We again used the model predicted wind fields to identify an upwind portion for each flight (other than 22 June flight when we did not fly sufficiently to the north of London to measure an upwind sample). The upwind portions are also indicated in the revised version of Figure10. We also classified all measurements with BC mass concentrations below the 75th percentile as "regional" samples. Note that the new classifications avoid the ambiguous "background" classification used in our previous analysis.

Implications of the new scheme

As might be expected, our new classification schemes have changed our originally reported plume- and background-averaged mass concentrations, so we have made a new version of Figure 9 summarizing the average concentrations for the newly defined air mass types. The differences between plume and upwind samples are now larger compared to the plume versus background comparisons discussed in the originally-submitted manuscript. The regional versus plume differences are similar to our originally reported results, due to the similarity in the subsets of the measurements falling in these regions using our new classification scheme.

We have substantially modified the discussion of the plume versus background results to reflect the new classification scheme and have explicitly stated how we classified the measurements into these categories. The aerosol concentrations in plumes were on approximately 50% higher than the upwind samples on average, but only slightly higher than regional values. The main species responsible for increased aerosol mass in the London plume were nitrate, ammonium and BC, though this last result is partly forced due to our classification scheme. The small differences in aerosol concentrations in the London plume versus the region outside the plume indicates that regional sources are still important, at least during the conditions we sampled. This was most evident for the 24 June flight when pollution from Europe was transported towards the UK by the easterly flow. We stress that the measurements of London emissions were made in much fresher air masses compared to those in the regional samples, and therefore represent a lower limit to the expected secondary production of additional, primarily OA, mass.

Finally, we have emphasized the relatively similar regional versus plume concentrations in our final conclusions in contrast to the changes observed in the trace gases, as recommended by D Baumgardner. The observations are consistent with a number of previous studies suggesting that much of the aerosol burden, at least on regional scales, arises from secondary production of sulfate-, nitrate- and OA-containing aerosol. The perturbation to the regional aerosol from London primary emissions is dominated by small, sub-100 nm particles and by rBC.

As it is written, the paper does a good job of presenting results for London, but falls short of putting these measurements in better context of observations in other locations, e.g. Paris, Los Angeles, Tokyo, and Mexico City. In general, more comparison of these result to other locations will strengthen the paper considerably.

We thank the reviewer for their positive comments and have modified the discussion of the paper to include additional comparisons to observations in other regions. A number of the specific comments suggest places where such comparisons could be added, so we respond to these recommendations below rather than addressing them here.

Emission Ratios calculations (30677-30678): Using the plume and non-plume samples with various ages, and a variety of sources adds significant uncertainty to the measurements. The authors note correlations are stronger "in plume" which suggests that the authors should report those numbers (at least in addition to the other numbers). While the plumes may have fewer points, they likely "better" represent the same general sources, and are younger. The use of plume data, avoids uncertainties in plume age (and photochemical loss) and more importantly reduces the much greater uncertainty associated with mixing of different sources with different emission ratios

We have performed a second set of regressions restricted to the subset of photochemical age < 20 hours and add the new values to Table 3. We have also updated Figure 6 to use the low photochemical age samples, as the reviewer rightly points out that they have less uncertainty associated with different sources and photochemical ages. The text describing emission ratios has been modified to reflect these changes.

Specific/additional comments

In the instrument description I didn't see if the aerosols were dried before entering the PSAP and I would also like Table II to include uncertainty estimates as well as ranges.

The aerosol sampled by the PSAP is not actively dried, but the sample RH is reduced via heating introduced when ambient air is sampled through inlets to the instrument in the aircraft cabin. We have added the following sentence to describe the PSAP sampling:

The PSAP and nephelometer sample air through the same inlet and heating associated with bringing the sample into the warmer aircraft reduces the sample RH. Measurements of RH at the nephelometer inlet indicate the sample RH is typically below 30% (Highwood et al., 2011).

We have also added instrument uncertainty estimates to Table 2 as requested.

30667/9-12 indicate what the VOCs emission ratios were compared to e.g. “Emission ratios of VOCs to C2H2” (and elsewhere in the paper)

We have stated what emission ratios were compared to in this instance and elsewhere in the manuscript (most changes to the original text are in Section 3.2).

30673/Section 2.2: Give more details about the data products from the lidar. I.e. what is it measuring, and what processing is required to give you e.g. bext (Used in Figure13)

We modified Section 2.2 considerably to better describe the lidar data products and associated uncertainties. The revised section is:

We used a mobile Aerosol LIDAR System (ALS) to investigate the aerosol vertical distribution around London. The ALS is a custom-built backscatter lidar emitting in the ultraviolet developed by the Commissariat à l’Energie Atomique (CEA) and the Centre National de la Recherche Scientifique (CNRS) (Chazette et al., 2007). It is now available commercially from the LEOSPHERE Company under the name of EZ Lidar® (www.leosphere.com). It is designed to monitor the aerosol dispersion in the low and middle troposphere and operated with a Nd:YAG laser at the wavelength of 355 nm. The detection system had parallel and cross-polarised detection channels. The resolution along the line of sight was 1.5 m and had an overlap factor close to 1 at ∼ 150 m above the ground level.

The primary ALS measurement is the backscatter coefficient measured at 355 nm, which has both molecular (i.e., gas-phase) and aerosol contributions. It is mounted in a small vehicle allowing it to follow small atmospheric features (Raut and Chazette, 2009; Royer et al., 2011), provide information regarding the vertical distribution of aerosols around London by following a set loop following the M25 ring-road or beltway, and could examine the role of the M25 traffic in the production of anthropogenic aerosols. The lidar signals have been calibrated, corrected from the background sky radiance and range-corrected. We retrieved aerosol extinction coefficients from the measured backscatter coefficients following the procedures described by Raut and Chazette (2007) and Royer et al. (2011), assuming a lidar ratio of 45.5 sr. Uncertainties associated with the retrieval of aerosol extinction coefficient at 355 nm were due to four main sources: a) statistical fluctuations of the measured signal, associated with the random detection process, b) uncertainty in the lidar signal in the altitude range used for the normalization, c) the uncertainty of the a priori knowledge of the vertical profile of the molecular backscatter coefficient as determined from ancillary measurements and d) the uncertainty in the backscatter to extinction ratio (or lidar ratio) and its altitude dependence. Chazette et al. (2010) discuss the different sources of uncertainty and conclude that there is an absolute error of approximately 0.01 km-1 in the retrieved aerosol

extinction coefficient. We assume a lidar ratio of ~45 sr based on similar retrievals of extinction coefficients in a polluted boundary layer in Paris (Chazette et al., 2012).

30678/17-20: Because the VOC / C2H2 ratios were almost systematically a factor of 2 off (except for the alkanes at a kerbside monitoring site which can be easily explained), and C2H2 is the one species across all measurements, is it possible that the C2H2 measurement is either incorrect, and off by a factor of 2 aloft or on the ground or that C2H2 is simply higher in concentration by factor of 2 aloft? That would seem the most reasonable explanation rather than different source regions since all of the measurements are made in and around London.

We have verified the instrument performance during this time and calibration factors did not show any deviations at the time of these measurements, and in general are quite stable. In addition, we suspect any errors in measurement for the concentration for one particular VOC (in this case acetylene) would also affect the other VOCs by the same factor, leading to the same reported ratios. For similar reasons we doubt the ground-based data are in error and in addition these data originate from a monitoring network with a rigorous data quality control and quality assurance program. We agree that the reviewer's final suggestion, that acetylene mixing ratios are simply higher by a factor of two aloft, is a more likely solution than our original hypothesis of the results arising from differences in source regions. Average summertime acetylene mixing ratios at the Eltham ground site were 196 pptv compared to an average of 491 pptv measured by the aircraft during the EM25 campaign. The differences in ratios may arise from the increased influence of mixing with non-urban air away from the surface. We have modified the original text by removing the reference to the influence of different source regions as follows:

"…the ratios measured at the ground sites were approximately twice those measured aloft. **We suspect these differences arise from the larger influence of entrainment on the aircraft measurements and the different lifetimes of the VOCs.** Short-chain alkanes…"

30679/19-25: While VOC emission ratios are within a factor of 2 of those reported in the NE, it does not follow that VOC emissions are generally consistent. Source strength needs to be accounted for in addition to emission ratios which do not give any indication of source strength. It is recommended that the authors rephrase to limit the statement to emission ratios and not "VOC emissions" in general. In addition see previous comment, and potential impact of C2H2 concentration variability on the similarity between NE US and London VOC emission ratios.

We thank the reviewer for pointing out our poor phrasing here, and we have changed the text to refer specifically to emission ratios rather than emissions:

"…indicate VOC **to acetylene** emission **ratios** from cities…are generally consistent…"

The elements that I found missing were size histograms or any information about how the aerosols were number or mass distributed. The PCASP, CAS and AMS all give size resolved information that I think should be presented, if nothing more than averages in the plume, outside the plume and regional, to show if there are obvious shifts in the sizes due to diffusional growth. This is only the addition of one figure.

30681/Section 3.3: Other studies have looked at the evolution of size and number concentrations of particles in a MEGACITY (e.g. Kleinman et al. 2009). The Kleinman study finds little change to the location of the size distribution, but an increase in the number of particles in the accumulation mode, *corresponding to the increase in mass also observed. Could the authors put the results of this work into context of this and other previous studies?*

We agree that size-resolved information would provide additional insight into the aerosol microphysics, however unfortunately the PCASP and CAS instruments as deployed in this campaign lacked sufficient calibration information to provide accurate measurements of relatively small changes in aerosol size. We have used data from these probes only to provide a basic picture of the aerosol size distribution around London. The size-resolved AMS measurements had insufficient signal-to-noise to obtain any meaningful information regarding mass distributions inside or outside the plume. We have added a reference to the Klienman et al. (2009) study that found limited changes in the size distribution but changes in the particle concentrations:

"Kleinman et al. (2009) conducted size distribution measurements over Mexico City and observed minor changes in the size distribution but did observe changes in the number of particles in the accumulation mode that were correlated with changes in particle mass and carbon monoxide."

30682/14-17: Shinozuka et al. (2007) compiles a range of optical properties of aerosols over North America and finds a range of 3.6 +/- 1.3 m^2/g.

We thank the reviewer for bringing the study to our attention. We have included this result in our summary of the mass scattering efficiency as follows:

"The ratio of dry scattering coefficients measured at λ = 550 nm to sub-micron mass yielded a study-average mass scattering efficiency of 3.4 $m^2 g^{-1}$, consistent with values expected for sub-micron dominated mixtures of OA, ammonium sulphate and ammonium nitrate **and similar to the dry mass scattering efficiency of 3.6 ± 1.3 $m^2 g^{-1}$ reported for PM2.5 over the eastern United States (Shinozuka et al., 2007)**."

30682/14-17: The paper [Shinozuka et al., 2007] also examines f(RH) from aircraft, and those results should be compared with results of this study.

30682/24, "The growth factor differed from ~2/3 of the ammonium sulphate dominated aerosol sampled over the Pacific, showing the importance of treating the aerosol as an internal rather than external mixture." Please clarify. How does this show the importance of treating aerosol as internal rather than external?

We have modified the description of the growth factor measurements to be more clear and refer to the previous measurements of Shinozuka et al. (2007). The original text was meant to convey that approximately 2/3 of the aerosol mass observed around London was made up of relatively hydrophilic sulphate and nitrate and 1/3 made up by relatively more hydrophobic organic aerosol. Thus, a simplistic argument might predict that the growth factor would be 2/3 of that observed during the VOCALS campaign when sulfate dominated composition, but observations show it is less due to additional suppression of the growth factor associated with the aerosol mixing state. We have changed the text to simply refer to a previous study showing that OA can suppress hygroscopic growth when internally mixed with other species, which is consistent with our observations:

"The lower humidity-dependence of scattering was consistent with higher mass fractions of relatively hydrophobic OA measured over London compared to the eastern Pacific (Allen et al., 2011)**, which have**

been shown in laboratory studies to suppress hygroscopic growth when internally mixed (e.g., Svenningsson et al., 2006).”

We also compared our results to the f(RH) measurements reported by Shinozuka et al. (2007), who parameterized f(RH) using the parameter γ and report column-averaged values in their Figure 10. We have added the following text to the discussion of the f(RH) measurements to include this comparison:

“Shinozuka et al. (2007) measured f(RH) over North America and parameterized the scattering response at RH1 = 40% and RH2 = 80% using:

f(RH)=((1-(RH_1)/100)/(1-(RH_2)/100))^(-γ) (1)

where γ captures the effects of chemistry, mixing state, size and refractive index. We found that γ ~ 0.3 best fit the average f(RH) observed over London, which is near the lower range of the Shinozuka et al. (2007) column-averaged values.”

Page 30683, Line 6, Might mention that Baumgardner et al. (2007) derived values of 5 m^2 g^{-1} from the SP2 and PSAP in Mexico City but we were very near the sources of rBC.

We have included this observation as suggested:

“When we applied the same correction to our data, we obtained an MAE of 7.8 m^2 g^{-1} for London, almost a factor of two lower than that observed over and downwind of Mexico City. **Baumgardner et al. (2007) reported a lower MAE of 5 m^2 g^{-1} from an SP2 and PSAP in Mexico City than we observed, but their observations were made on the surface and very close to rBC sources.**”

30683/21-30684/1: The authors should state the uncertainty associated with these regressions based on the discussion in the methods section. In addition figures should be included so that the reader has an idea of the scatter of the data, and the range of that the data covers. In the discussion of sub-micron mass to BC ratio, there is no correlation coefficient given, and terms like "roughly" and "as much as" with no quantitative information leaves the reader wanting either a figure so that (s)he can evaluate it or more precision in the language.

The regression coefficients and statistical uncertainties (1 standard deviation) are 0.0013 ± 0.0002 for SSA versus photochemical age and 0.34 ± 0.05 for total mass / rBC mass. Following the reviewer’s suggestion we have added a new figure showing single scattering albedo and non-rBC aerosol mass normalized by rBC mass as functions of photochemical age. We refer to this new figure in our response as Fig. 8.5 to maintain the original figure numbering in our response (though figures will be re-numbered in the revised submission). When revising this section we also noticed a mistake in our original text stating that the increase in SSA from 0.84 to 0.95 occurred by approximately 1 day, but in fact the change occurred over approximately 3 days. We have modified the text to refer to the new figure and describe the uncertainties as follows:

“We investigated the timescales for increases in SSA by comparing its measured values to photochemical age for periods with valid whole air canister samples**, shown in Figure 8.5**. Single scattering albedo increased from approximately 0.84 at t = 0 to approximately 0.95 at t ~**3 days**, consistent with the plume versus non-plume differences and the addition of secondary material including SOA indicated by the increase in the OA/ΔCO and sub-micron mass/ΔCO ratios with photochemical age. The regression of SSA on photochemical age yielded an increase of **0.0013 ± 0.0002 h^{-1}**, but there was considerable variability (r^2 = 0.25). The total sub-micron mass measured by the AMS normalized by rBC increased from roughly 10 μg μg^{-1} BC to as much as 50 μg μg^{-1} BC after 40 h, with an average increase of **0.34 ± 0.05 h^{-1} (r^2 = 0.33)**."

Page 30684, Line 11, "One important distinction between our results and those reported by Moteki et al. (2007) and Subramanian et al. (2010)…was that we considered the entire rBC population but the previous studies restricted their analyses to rBC particles with a specified mass/size range." Clarify. I thought that Subu derived rBC with lognormal fit that should cover the whole range.

We meant to refer specifically to the time-delay-based analysis of the rBC mixing state rather than interpretation of the BC mass concentration or size distributions. Subramanian et al. (2010) states in the first paragraph of Section 4.4 they performed a "similar analysis" to Moteki et al. (2007), in which the mixing state analysis was restricted to particles with a BC content of 5.4 fg/particle. They also investigate the lag times as a function of BC diameter, however we chose to limit our investigation of the BC mixing state in this broader overview paper and do not include a comparison the more detailed lag versus diameter analysis presented in Subramanian et al. (2010). We have changed the text to now read:

"…the previous studies restricted their analyses **of the conversion rate to thickly coated rBC** to particles with**in** a specified mass/size range."

30685/20: Is it valid to assume no sulphate source for an urban area? If sulphate was purely regional, and homogeneous in concentration than the plume and upwind concentrations would be the same. From Fig. 9 it is difficult to tell, but it seems that in many cases the background concentrations of sulphate are higher than the plume concentrations. In that case can the authors justify the sulphate normalization?

Our new classification system shows negligible differences in the sulphate aerosol mass concentrations between the plume and upwind, except in the case of easterly flow when the upwind leg was downwind of two power stations. We have re-phrased the text to state that rather than no urban sulphate source that we expect urban sulfate precursor emissions to be small compared to urban nitrate precursor emissions. According to the London Atmospheric Emissions inventory ~2 kt/year of SO_2 are emitted from region surrounding London compared to 71 kt/year of NO_x. The most important SO_2 sources in the London region are related to road and rail transport and air traffic, which is concentrated near the major airports. The new text reads:

"We normalized by sulphate mass to account for regional contributions to nitrate in the plume, **on the basis that urban sulphate precursor emissions in London are minor compared to nitrate precursor emissions according to the LAEI."**

Page 30686/16, "…only represented a small contribution to sub-micron aerosol mass." Yes, but as previously noted, decreased the SSA from 0.91 to 0.86. Is this consistent with the derived mass scattering and absorption coefficients., i.e., can you get a 5% decrease in SSA with the observed changes in rBC from plume to regional?

On average the BC mass increased from 0.25 μg m^{-3} in regional pollution to 0.6 μg m^{-3} in plumes and sub-micron aerosol increased from 8.2 μg m^{-3} to 8.8 μg m^{-3}. If we assume a mass-absorption efficiency of 8 m^2 g^{-1} and a mass scattering efficiency of 4 m^2 g^{-1} then the predicted absorption increases from 2 to 4.8 Mm^{-1} and scattering increases from 32.8 Mm^{-1} to 35.8 Mm^{-1}, yielding SSA of 0.94 in regional pollution and 0.88 in plumes. While this is a rough calculation, it shows that a 5% decrease in SSA is reasonable for the observed changes in rBC. Even though the rBC mass fraction is relatively low, it doubles in the plumes (from 3 to 6%), which translates to a substantial reduction in SSA.

30687/25-26: Nitrate to CO differences in Mexico City was observed and discussed by DeCarlo et al. 2008, who noted a rapid decrease in NO3/CO with distance from the urban area.

We have expanded our discussion of the nitrate to CO observations in London to include a comparison to the DeCarlo et al. (2008) observations over Mexico City. DeCarlo et al. (2008) attributed the reduction of nitrate relative to CO in the outflow to evaporation upon dilution with regional air and with low concentrations of nitric acid and ammonia or possibly the loss of ammonium to sulfuric acid or ammonium bisulfate. We suspect that stronger regional ammonia sources over NW Europe reduces the dilution effect, though lack the measurement s of ammonia needed to confirm this. Another important difference between our study and DeCarlo et al. (2008) is that they were able to measure emissions at significant downwind of the source they also characterized, whereas we are comparing fresh emissions from London to aged emissions from Europe, which as a whole may have different NO_x/CO and NH_3/CO emission ratios compared to London emissions. Temperature differences may also play role, since the ammonium nitrate-ammonia-nitric acid equilibrium is highly temperature dependent. We have revised the text describing the nitrate-CO ratios as follows:

"This finding contrasts with decreases in nitrate-ΔCO ratios downwind of Mexcio City observed by DeCarlo et al. (2008), which may have resulted from dilution with air with low concentrations of nitric acid and/or ammonia. We lacked the gas-phase measurements of these compounds needed to explore possible reasons for the differences for the differences in nitrate-ΔCO ratios, but suspect stronger regional-contributions to NO_x and ammonia over NW Europe combined with our inability to sample the aged London emissions are responsible."

30687/20 - 30688/26: Is the CO a delta CO above background CO concentration or absolute CO concentration. This is not clear to the reader. From table 4, it appears to be a delta value, but there is no discussion of background values of CO, and what procedure was followed to determine them. If it is absolute CO concentration, then the analysis needs to be done subtracting a background CO value from the measured CO value for comparison to other studies which have done this.

We state that nitrate was correlated with excess CO in line 24, but the reviewer is correct to point out that we should be more clear when referring to these ratios throughout the text and have therefor used "Δ" to indicate when CO is an excess mixing ratio above the background concentration (e.g., ΔCO). We have also added a short section describing the method used to determine the background CO mixing ratios (using the relationship with rBC) and providing the range of estimated CO background mixing ratios (90-98 ppb).

The following section was added to the first paragraph of Section 3.2:

Mixing ratios of CO have a background contribution that we estimated from the intercept of the regression of CO on rBC measured by the SP2. Background CO values were between 90-98 ppb and we subtracted these background values to obtain excess mixing ratios for CO for each flight (ΔCO).

30688/14: The measurements of OA/CO is discussed in Kleinman et al. 2008 for Mexico City and also in DeCarlo et al. (2010) with a comparison to several other field measurements, and it would be interesting to see the London results placed into the context of the other field campaigns discussed in these papers.

We have expanded our discussion of the OA/ΔCO results in this section to include a comparison with the Kleinman et al. (2009) and DeCarlo et al. (2010) studies. We also observe a similar increase in OA/ΔCO with increasing photochemical age. Since we lack the information needed to provide a robust measure of photochemical age we decided to only make the simpler, but rougher distinction between fresh and aged regional pollution in the analysis rather than presenting the OA/ΔCO ratio as a function of time similar to what is shown in Figure 3 in DeCarlo et al. (2010). The contribution of different sources to our measurements further complicates the quantitative interpretation of the OA/ΔCO versus time relationship, since we did not follow a single plume downwind but are comparing measurements with different source regions. The add test is:

The production of secondary OA in urban plumes means that OA/ΔCO ratios increase with age. Several studies showed clear increases in OA/ΔCO from approximately 10 to 80 μg sm^{-3} ppmv^{-1} in aging emissions from Mexico city (DeCarlo et al., 2010; Dzepina et al., 2009; Kleinman et al., 2009). Our observations of higher OA/ΔCO in the regional pollution outside of the London plume are consistent with these observations if we assume that dominant source of OA and CO in the study region originates from urban centres with similar initial OA/ΔCO.

30690/9-12: The increase of nitrate with height in the PBL has also been observed in other studies in LA (Neuman et al. 2003) and Tokyo (Morino et al. 2006). How do their results compare with the results of this study?

We thank the reviewer for identifying these relevant studies and have added references to both, but due to the lack of nitric acid measurements on our sampling platform we have not made a quantitative comparison to either study. We have, however, including a reference to both as they are relevant to the discussion of our results.

“Previous field (Neuman et al., 2003) and modelling studies (Morino et al., 2006) have also observed increases in the fraction of nitrate in the particle phase over urban centres that were associated with decreases in temperature and increases in relative humidity.”

Page 30691/11, “The lidar results also showed a relatively homogenous aerosol concentrations along the loop around London…” Figure 13 seems to contradict this statement since there seems to be a distinctive difference from East to West. Also, Figure 13d is mislabeled as June 16.

We agree and have deleted this statement. The label for Figure 13 d has been fixed.

30692/3: Were the results the dry scattering coefficients or wet scattering coefficient?

Page 30692/6, “This was more than could be reasonable (reasonably) explained by the contribution of the absorption coefficient, which could not be measured…”. But from the previously derived mass absorption coefficient, the SP2 rBC could be converted to an absorption coefficient. Were the scattering coefficients converted to the wavelength of the lidar, i.e. 550 to 355? If not, this explains part of the discrepancy.

The two reviewer comments are relevant to some significant changes we have made regarding the comparison of the aircraft data to the ground-based lidar. The original manuscript reports dry scattering coefficients, however we have updated the calculation to include an f(RH) correction based on the average growth factors measured on the aircraft using the ambient relative humidity. We have modified the text to report the scattering coefficients as being “ambient” and have also modified the methods section to describe how these values were obtained.

Following the reviewer's suggestion we have converted the SP2 measured rBC mass concentrations to estimated light absorption coefficients using the average mass absorption efficiency calculated for each flight day. We use the estimated absorption coefficients and the measured light scattering coefficients to estimate the extinction coefficient at 550 nm. The lidar extinction coefficients were originally converted from 355 to 550 nm by assuming an Angstrom exponent of 1.5, a detail we have now added in the methods section. Including the estimated absorption and adjusting the scattering coefficient to ambient RH provided a better estimate of the ambient extinction coefficient, which was typically 30% higher than the dry scattering coefficients in our original comparison.

Page 30692, Line 11, ""The most likely reasons for the higher lidar results stem from the need to bring aerosol into the aircraft for measurement.". The inlet losses and drying are obvious sources of the uncertainty, but the uncertainty in converting backscattering to extinction is also large and should be mentioned.

Replacing the dry scattering coefficient with the estimated ambient light extinction coefficient, as described above, has improved the agreement between the lidar and aircraft measurements. As a result we have made changes to the text describing the comparison, which also mentions the uncertainties associated with converting from backscattering to extinction as one of several reasons for discrepancies between the aircraft and lidar measurements.

"Lidar- and aircraft-measured extinction coefficients were in relatively good agreement, particularly at higher altitudes and showed similar vertical structure. The discrepancies between aircraft- and lidar-measured values are likely due to modification of the aerosol when it was sampled into the aircraft, such as the loss of coarse mode particles and semi-volatile material, errors in the assumed optical properties needed to convert the lidar backscatter measurements at 355 nm to light extinction coefficients at 550 nm, and deviations from the assumed f(RH) and MAE needed to reconstruct extinction coefficients from the PSAP and nephelometer aircraft measurements."

Page 30692, Line 27, "There was little change in total aerosol mass concentrations between the urban plume and the regional, background aerosol,…". It seems to me that this conclusion is one of the most notable and perhaps should be given more than a single sentence in the conclusions. I understand that the paper is an overview of the data, but perhaps in the summary the key results should be listed as bullets to underscore their importance.

See response to general comments above regarding changes to the conclusions section.

30693/2-3: Check units on ratios, should be "ppmv" not "ppbv".

30705 Table 4: Units are incorrect for OA/deltaCO, should be "ppmv" not "ppbv"

Both fixed. We thank the reviewer for spotting the unit errors.

Figure 3, no PM10

The reference to PM10 in the text refers to an older version of the Figure and was a mistake. We have removed the reference since our focus throughout the analysis is on sub-micron aerosol.

Fig. 4: Flight tracks colored by concentration and shown on top model predictions would be useful for the reader to see general model performance. Also, the color scale legend is very difficult to read.

We have added shaded tracks shaded by aerosol mass concentrations as recommended and increased the size of the color scale legend.

Fig. 5: Please label all axes.

Done

Fig. 6: Seems to be mostly qualitative, and dashed lines are only visible on the G panel, why not on all panels?

We have added dashed lines to each panel as requested.

Figure 6 – Please clarify what is shown in these figures, e.g., how are ratios from aircraft being compared to those on the ground? I was unable to understand the various panels in Figure 6, i.e., are ratios being compared to ratios? How are these data points being selected. This was to me the most confusing section.

We apologize for the confusion regarding the figure. Each panel shows a comparison between selected VOC emission ratios measured for different sites or from different platforms. For example, panel C compares emission ratios measured in the Boston-NYC outflow compared to those measured at a ground-based suburban London monitoring site. Emission ratios for London include those measured by the aircraft and determined for ground-monitoring stations, as described in the text. Other emission ratios were taken from previously reported literature values. Each point represents the emission ratio of a specific measured compound to C_2H_2 and is colored by that compound's class (we have added a list of the compounds in the revised version of the figure). We also replaced the original emission ratios reported for the aircraft with those calculated specifically for the London plume, following the recommendation of the reviewer addressed earlier.

We have also added the following text to the paragraph describing the figure to give a better explanation:

"Each row and column in the figure contains a scatter plot that compares VOC to acetylene ratios measured at a particular site or for a particular study to another site or study. For example Figure 6f compares VOC ratios measured for vehicle exhaust by Harley et al. (1992) to those measured downwind of the north-eastern US by Warneke et al. (2007)."

Fig. 11: Nitrate appears to be a purple trace in the figure but blue in the legend. Please fix.

Fixed

Reviewer References:

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Additional references

We have added several new references in addition to those requested by the reviewers in order to respond to their comments and based on recommendations by a non-reviewer who contacted us, listed here:

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