

Response to reviewers

We thank both anonymous reviewers for their comments. Both raised similar concerns regarding the number of flights we analyzed and questioned why we did not examine additional flights. We agree that it is desirable to have as many case studies as possible when performing this types of analysis and would have preferred to have more examples to investigate. Unfortunately aircraft measurements must be performed within fixed operational time windows, which, combined with changing meteorological conditions, means there are often few opportunities to study any particular process. In addition, the large expense of aircraft campaigns means they often have multiple scientific goals, so not every flight targets the same objective. Finally, air traffic control restrictions often prevent operations in the desired region.

For this study, the flights we examined took place during a loose campaign of three 2-3 week sampling periods spread over a 1.5 year window. During this period meteorological conditions favorable for examining the aging processes of urban plumes in regions where we could perform the required flight operations were rare. There were a total of 14 research flights conducted as part of the ADIENT campaign, but of these only three examined the aging of plumes downwind of UK urban regions, and it is these three that are the focus of our manuscript. Given the rarity of these measurements over Europe we feel that even though the number of flights is small, the data are still of value. The original manuscript provides sufficient meteorological background and information regarding the photochemical environment to describe conditions where the results are representative and applicable to observational and/or modeling studies in similar situations.

To address the reviewers' concerns regarding the representativeness of our results we have added the following sentence (highlighted in **bold**) to the conclusions of the revised manuscript:

“...additional measurements are urgently needed to verify or refute these findings given their implications for radiative forcing calculations. **Observations downwind of UK urban regions during different times of the year (e.g., winter) and different transport patterns (e.g., westerlies) could establish if our limited number of observations represent typical aging behavior or only represent spring/summer conditions under easterly flow.** Even if rBC optical properties are shown to be ...”

We address the reviewers other comments below. The original comments are in presented *italic font* and our responses are in regular roman font. Revisions are given in **bold font**.

Reviewer #1

P 14995 Method. What time of day were flights? How many flights in campaign? Why was the 1 flight on 16 April and 2 flights on 24 June selected for detailed analysis? If not already in text it should be made clear, that June data in Figures is for second flight on 24 June.

The April 2008 flight took place between approximately 1000-1500 UTC and the two June 2009 flights took place between approximately 0900-1200 UTC and 1300-1700 UTC, respectively. There were a total of 14 flights during the campaign, but only three targeting the aging of urban plumes, as discussed above. The June data shown in all figures includes both flights. We have added the following text to the first paragraph of the Methods section:

“We performed ~~several~~ **14** research flights...as part of the APPRAISE-ADIANT and EM25 projects. Our analysis focuses...in the absence of significant cloud processing of the aerosol. **These dates were the only periods when meteorological conditions in regions where the aircraft was allowed to operate were suited our objectives. McMeeking et al. (2010) presents a broader overview of rBC observations during the other flights in the campaign.**”

In discussion of instruments please indicate approximate RH at point of measurement. All that is needed is a determination of whether particles have been dried out. This may be of relevance in this paper for just the nephelometer and PSAP.

We have added to the discussion of instruments as follows:

“... We removed PSAP data from the analysis when the aircraft was changing altitude or flying through clouds. **The aircraft does not have an active drying system, however heating of the sample when it was drawn into the cabin acted to dry the sample. Our best estimate of the sample relative humidity (RH) for the optical instruments was measured at the nephelometer and was < 35% for the April 2008 flight, but higher for the first (~60%) and second (~40%) June 2009 flights.**”

O3/NOx appears to satisfy the authors objectives in picking out plumes and background air. With only a ratio presented on a log scale, it was not possible to gain an appreciation of what gas phase concentrations were in different air masses.

We have also added a new Table giving average ozone and NO_x mixing ratios for the air masses identified in Figure 2 and added references to it in our discussion of the ozone and NO_x mixing ratios.

P 14995 line 21 nominal rBC range of approximately 5-300 fg. Please give mass equivalent diameter, which is 170-650 nm for a density of 2 g cm⁻³.

The reviewer is correct to point this out, however we now realize we introduced a typo. The approximate size range of the SP2 is actually 0.5-300 fg, not 5-300 fg, so the mass equivalent diameter range is approximately 80-650 nm for a density of 2 g cm⁻³. We have added the mass equivalent diameter range, but for our assumed BC density of 1.8 g cm⁻³ for consistency (80-680 nm).

P14996 thickly coated particles from time delay. Please provide literature estimates of shell core ratio (as a function of size if necessary) that qualifies a particle as thickly coated from time delay data.

We have added a reference to Moteki and Kondo (2007), who found an abrupt increase in the time delay at a threshold total particle diameter / BC core diameter ratio of 2 ± 0.5 .

P 14997 line 29 – P14998 line 1 “Correlation coefficients of 0.69 and 0.73 for CO and rBC were determined...” What are these substances being correlated against? I would guess HOA, but it is not stated.”

The reviewer is correct. We have revised the text to make it clear the reported correlations are with respect to HOA.

P 14998 line 13 Light scattering at 550 nm. McMeeking et al. (2010) state that PSAP was at 567 nm. How was difference handled in constructing SSA? It is small. One over lambda or ignored are permissible answers.

The PSAP light absorption corrections convert the 567 nm measurement wavelength to 550 nm because there is a wavelength adjustment implicit in the Bond et al. (1999) corrections. See note of clarification provided by Ogren (2010). The reviewer is correct to note that we did not make this clear in McMeeking et al. (2010), so we have added a note to the revised manuscript to be explicit.

“We calculated SSA from measured light scattering and absorption coefficients, both corrected to STP and for well-known instrument artifacts. **The PSAP correction procedure provided by Bond et al. (1999) also adjusted the absorption coefficient measured at $\lambda = 567$ nm to 550 nm, which was needed to compare with the scattering coefficient measured at $\lambda = 550$ nm. The magnitude of the correction was < 3%; see discussion in Ogren (2010) for details.** We were interested to see how changes...”

P14998, NO_x measurements. Is the temperature of the molybdenum converter (800 C) a misprint? 350 is a normal operating temperature. Above 500 C, NH₃ will get oxidized.

The referee is correct. The manual states 325 C. Text has been revised.

On lines 24-26, it is recognized that the converter is not measuring just NO_x. The measurement is called a “surrogate for nitrogen oxides”. This is inappropriate terminology, especially because the NO_x fraction probably changes from order 10% in rural area to order 100% in a fresh plume. Measurements called NO_x should be referred to as NO_y, with a definition given.

We have used the same terminology as was used in several previously published manuscripts involving the BAe-146 instrument (e.g., McMeeking et al., 2010; Morgan et al. 2009; Hopkins et al. 2009) and feel this is the most appropriate terminology. Many components of NO_y are not measured at this converter temperature and the majority of the nitrogen species detected is NO and NO₂. We have defined NO_x as a surrogate for nitrogen oxides to acknowledge that other oxidized nitrogen species are detected.

P 15001 Background of CO of 150 ppb in April and 90 ppb in June. Background has many possible meanings. This appears to be an operational definition. How is background defined?

The reviewer is correct that this is an operational definition. We determined the background CO from the y-intercept of the regression of CO on rBC mass concentrations and CO on NO_x. The revised text is now:

“**Operational** background CO mixing ratios were determined from relationships between rBC, NO_x and CO, **defined as the average y-intercept of the regression of CO on BC and NO_x**, and were 150...”

Regarding the trend with time of year. A decrease in the summer is consistent with OH chemistry. Is the large change from 150-90 ppb in agreement with OH variation at this latitude or is it due primarily [to] meteorological factors (i.e., winds in relation to emission areas)?

Rather than examine OH measurements, which are rare, we instead have added a reference to Novelli et al. (1998), who examined CO in the troposphere. As part of their study they reported the seasonal cycle of CO at Mace Head, Ireland, which should be representative of our study region in terms of its latitude. The

show that CO mixing ratios drop off rapidly in the spring from approximately 150-170 ppb in March/April to ~80-100 by early July. Novelli et al. (1998) used a box model to simulate the CO seasonal cycle and found that both changes in OH oxidation rates and the CO source from biomass burning emissions were important in driving the seasonal cycle. We have modified the text to include these findings and thank the reviewer for raising the question. The revised text now reads:

..and 90 ± 10 ppb for the June flight. **Novelli et al. (1998) showed that the seasonal cycle of CO at Mace Head, Ireland, a background site at roughly the same latitude as our flight area, decreased from a springtime maximum of approximately 150 ppb to a summertime minimum of 80-90 ppb.** Lower summertime CO background mixing ratios results from increased hydroxyl radical concentrations in the summer that increase the removal rate of CO. **Novelli et al. (1998) also used a box model to simulate the seasonal CO cycle and found that it was driven by changes in hydroxyl concentrations and emissions from biomass burning.**

P 15004 start of section 3.4 It would be clearer to state in first sentence that f is lower in urban plumes. As it currently reads there is a connection to the observed O₃ to NO_x ratio and a connection to predicted transport. With CO and NO_y measurements the urban plume should be identifiable, independent of model predictions.

We have modified the first sentence to:

“We observed a clear ~~difference~~ **decrease in f for rBC measured** in urban plumes compared to rBC measured in other regions around the UK...”

P 1505 line 20-23 PSAP overestimate of light absorption I am familiar with Lack's plot which shows PSAP artifact as a function of organic aerosol. I have not gone back to original papers. Is there any reason to expect that the artifact won't occur for species other than organics? On P15006 line 20 it is states that there is no relation between MAE and OA mass. OA is often a minor fraction of total aerosol. Is there any relation between MAE and aerosol concentration?

Lack et al. (2008) suggest two mechanisms that may be responsible for the artifact. The first is that liquid-like organic particulate matter is redistributed around the filter fiber filaments and modifies the filter surface and related light scattering. The second is that pre-existing absorbing particles, such as rBC, are coated as OA deposition and redistribution occurs, enhancing absorption. Non-organic aerosol species can affect the PSAP measurement through other mechanisms, but their influence is already accounted for through the Bond et al. (1999) correction procedures, which depend on the light scattering coefficient, which in turn scales with total mass. We did check to see if there was a relationship between total mass and MAE, but found no evidence of any effects.

P 15007 line 2-7. I don't understand. What physical shift in the rBC core mass distribution would give you an increase in MAE? What is the mechanism?

There are two ways a shift in BC size could affect the calculated MAE, one from a measurement limitation, the other from a physical change in the average BC absorption properties. We address the former in the original manuscript: “shifts in the rBC core mass distribution that result in a higher fraction of rBC particles being detected by the SP2”. In other words, if the SP2's underestimate of the true rBC mass were to become smaller because more particles were in the instruments detection range (resulting in

a larger rBC mass measurement for the same true mass of BC compared to a population with a small BC mass distribution) there would be an artificial decrease in the calculated MAE, even if the absorption for both cases was identical.

A second, physical change in MAE, can occur if the BC size distribution changes. The mass absorption efficiency (MAE) for BC particles has been examined previously using Mie theory. Just to pick one example, Figure 1 from Bond et al. (2006) shows that MAE increases from $5 \text{ m}^2 \text{ g}^{-1}$ to nearly $7 \text{ m}^2 \text{ g}^{-1}$ for a change in diameter from 10 to 200 nm, and then decreases with increasing diameter. Though the size dependence of MAE is not as strong as for mass scattering efficiency, it still plays a role. The physical mechanism, as described by Bond et al. (2006) is that for small particles the MAE is constant because the entire volume of the particle absorbs light. For large particles the MAE decreases with the inverse in diameter because only the particle surface absorbs light. The peak at intermediate sizes occurs “when the frequency of the incident radiation approaches the characteristic frequency of the system (governed by size), so an engineer might think of this as resonance.” Mie theory only applies to spherical particles, so these processes may be different for non-spherical BC in the atmosphere. Regardless of the exact behavior, the main point we wanted to raise in the manuscript with this section was that size alone can affect the MAE, however our observations of the BC size distribution indicate that the changes in size are not sufficient to offset the expected absorption amplification.

We have revised this paragraph to better explain these processes. We have also added a reference to Bond et al. (2006) when discussing potential physical explanations for the MAE observations. The revised text now reads:

“...Physical increases in MAE coinciding with shifts in the rBC core mass distribution that result in a higher fraction of rBC particles being detected by the SP2 could give a relatively constant MAE (Subramanian et al., 2010). **The SP2 would measure more of the total rBC mass for a larger diameter rBC population compared to a smaller diameter population with identical total mass concentration and absorption coefficient. The resulting calculated MAE would be lower, even if the true MAE were constant. Physically, Mie theory shows that the MAE can change with particle diameter due to interactions between the incident radiation and absorbing region of the particle (Bond et al., 2006).** For ~~this~~ **these effects to offset the expected amplification due to mixing to occur**, changes in mixing state resulting in more thickly coated rBC particles would have to coincide with increases in the rBC mass size distribution...”

P 1507 line 12-14 “Large amounts of small rBC below the detection limit of the SP2 could still play a role in explaining our results...” Which results.

The “results” we refer to is the lack of observed changes in MAE. We have revised the text as follows:

“Large amounts of small rBC below the detection limit of the SP2 could still play a role in explaining ~~our~~ **results the lack of observed changes in MAE.**”

P 15008 “The coating may be partially absorbing, also reducing the absorption enhancement” Is it possible to give a short explanations? Statement seems counter-intuitive.

This phenomenon, recently investigated by Lack and Cappa (2010) using Mie theory, occurs because the “lensing effect” of the absorbing particle coating is less than that for a non-absorbing coating. The

differences arise from “modification of the photon path through the particle due to the absorbing coating, causing fewer (or more) photons to be focused towards the core” and “absorption of photons by the coating material, causing fewer photons to reach the core”. Lack and Cappa (2010) point out that the second process does not affect the total absorption because it does not matter where the photon is absorbed. We realize our statement in the text, while technically correct, implies that we would not measure an increase in MAE for BC particles coated with absorbing material, which is not true. Our intention was to point out that the properties of the coating could be playing a physical role in our MAE measurement, so we have revised the text as follows:

“The coating material may be partially absorbing, also reducing the absorption enhancement **by directing fewer photons to the rBC core** (Lack and Cappa, 2010). **Despite this, the addition of non-rBC light absorbing material would lead to an increase in calculated MAE because its calculation assumes rBC is the only light absorbing material present in the aerosol.** We ~~would~~ expect the effect to be more important in biomass burning impacted regions where brown carbon plays an important role.”

Figures 2-4 and 6. The color scale could be improved. I can only distinguish 3 colors, dark red, red, and yellow in either the html or print friendly version.

The color scale was chosen to make it useful for color-impaired readers, but this does limit the number of colors available, as the reviewer points out.

Reviewer #2

Figures 3, 4 and 6 are not very informative, could the authors consider using some other illustration method like in figures 2 and 5 were done.

We are not sure how Figure 2 differs from Figures 3, 4 and 6. We believe the reviewer would like more quantitative information for the results shown in Figures 3, 4 and 6. We have added a new table to the revised manuscript that gives the mass concentrations (Figure 3), average OOA and HOA mass concentrations and OOA/(OOA+HOA) ratio (Figure 4) and number fraction of thickly coated rBC particles averaged for the box regions identified in Figure 2 and shown in Figure 5. We hope this satisfactorily addresses the reviewer’s concern.

Introduction, line 13, ...McMeeking et al., 2011, there are two papers from McMeeking et al., 2011 in the reference list, which one?

We have changed the text and references to fix this. The reference the reviewer commented on is McMeeking et al. (2011a), which discusses rBC hygroscopicity. McMeeking et al. (2011b) refers to our in progress analysis of a complementary set of flights.

Page 15005, lines 12-14, Would the authors like to explain these possibilities more detailed and maybe give their favorite explanation.

This section of the manuscript lists potential explanations for differences between the observed rBC mixing rates for our study and those reported previously. They include differences in photochemical environment, initial rBC mixing state at source, coagulation rates and potential cloud processing in the other studies. We have added more detail for how these processes could differ for these environments, but

have refrained from picking a “favorite” in the absence of the information needed to make such a decision (e.g., VOC mixing ratios, actinic flux, rBC mixing state for sources). The revised text now reads:

“There a number of potential explanations for these differences. **The photochemical environment over the UK is different from that downwind of Mexico City. Less light is available for photochemical reactions due to the higher latitude and lower elevation and VOC concentrations may be different, though we lack VOC observations to confirm this. The photochemical environment affects the formation of secondary organic aerosol (SOA) and associated condensation onto pre-existing rBC particles. The initial rBC mixing state of the rBC emissions may differ between Japan, the UK, and Mexico City due to different rBC sources, leading to different mixing rates downwind. Coagulation rates and potential cloud processing could also play a role, though we lacked sufficient information to make any detailed comparisons across sites.**

Page 15006, line 4 how well [λ^{-1} dependency suits in this case? Why just this?

The wavelength dependence was chosen by Subramanian et al. (2010) and we do not have sufficient information to comment on its appropriateness nor to use a different value. The original text in our manuscript could be interpreted that we chose the wavelength dependence, so we have added an additional reference to the text to make this clear:

“Converting the Mexico City measurements to $\lambda = 550$ nm assuming a λ^{-1} wavelength dependence (Subramanian et al., 2010), within the range...”

References

Bond, T. C., et al.: Limitations in the enhancement of visible light absorption due to mixing state, Journal of Geophysical Research, 111, D20211, doi:10.1029/2006JD007315, 2006.

Hopkins, J. R., et al.: Direct estimates of emissions from the megacity of Lagos, Atmospheric Chemistry and Physics, 9, 8471-8477, 2009.

Novelli, P. C., et al.: Distributions and recent changes of carbon monoxide in the lower troposphere, Journal of Geophysical Research, 103, 19015-19033, doi:10.1029/98JD01366, 1998.