Author Response to Referees of Corbin et al. ACPD 2013

J. C. Corbin, B. Sierau, M. Gysel, M. Laborde, A. Keller, J. Kim, A. Petzold, T. B. Onasch, U. Lohmann and A. A. Mensah

General Response to Reviewers

We would like to thank both Anonymous Referees #1 and #2 for their critical consideration of our manuscript and their useful feedback.

In this response, referee comments are formatted in blue sans-serif, responses in black serif, and *"manuscript quotations italicized"*. General comments are addressed first, followed by specific responses to each reviewer.

A general comment by both referees was that the paper may be better suited for AMT rather than ACP. In our opinion, the paper does not use new measurement techniques, but rather presented a characterization of atmospherically-relevant samples. Nevertheless we do agree with the comment that the submitted manuscript lacked sufficient a discussion of atmospheric consequences. This has been addressed in the new version, as detailed below.

As pointed out by Referee #2, three of the six samples are directly relevant to the atmosphere: fuel-lean diffusion-flame soot, fuel-rich diffusion-flame soot, and aircraft-turbine soot. Of the remaining three, all are of direct relevance to the atmospheric-science community: one is commonly used to calibrate the popular SP2 instrument (FS, "Fullerene-Enriched Soot"), another is currently being used to calibrate the SP-AMS itself (RB, "Regal Black"), and the last is frequently used as a laboratory surrogate for diesel soot (GFG, "PALAS GFG").

Addressing the comments of Referees #1 and #2 regarding atmospheric relevance, we have extended the discussion in a number of places and put more emphasis on source apportionment in others. In particular, this extension comprises:

- Extensions to the abstract: *"If atmospherically stable, these species may be useful for distinguishing between different combustion sources. If unstable, they may provide a means to estimate the atmospheric age of an rBC sample. Future studies should attempt to establish which of these scenarios is more realistic."* [lines 26-29]

- New section 3.1.3, "*Atmospheric suitability of* C_1^+/C_3^+", expanding the previous discussion of organic interference of C_1^+/C_3^+ with the paragraph starting with "*Since an organic molecule is more likely to form [...]*" [lines 358–375]

- New section 3.2.3, "*Atmospheric relevance of* rCO_x", starting with the paragraph that begins *"In an atmospheric context,"* and continuing for the next four paragraphs. [lines 457–503]

- Extensions to the conclusions in three places:
    1. *"Two ion ratios were identified for source apportionment, when an air mass contains a mixture of rBC from the two* C_x^{n+} *categories. The first ratio,* C_1^+/C_3^+*, maximizes the rBC detection limit by using the two most intense* C_x^{n+} *peaks in the mass spectrum. In this case, thermodenuding of the rBC sample prior to measurement is recommended due to possible interference by the trace amounts of* C_1^+ *produced during the fragmentation of OM ions. The second ratio,* C_4^+/C_3^+*, aims to avoid this interference by using higher-mass* C_x^{n+} *ions. The sensitivity of* C_4^+/C_3^+ *to an OM coating was tested using a PAH-rich propane-flame sample (CBW). Further tests with thicker coatings and different chemicals should be performed."* [lines 511–518]
    2. *"It is not clear whether these refractory oxygenated moieties play a role in the heterogeneous chemistry of combustion particles. If so, their quantification by SP-AMS could provide a useful measurement of rBC age. If*

not, they may be inert enough to allow their SP-AMS signals to be used in source apportionment, since different sources will produce different amounts of oxygenated moieties following differences in the combustion process." [lines 523–527]

3. *"Future work should aim to quantify these ions for a number of samples, also as a function of atmospheric age, to provide a basis for the interpretation of ambient SP-AMS spectra in which gas-phase interferences are unavoidable. Further studies might also investigate whether the SP-AMS is capable of providing enough information to distinguish between different refractory functional groups, as has been done using well-established offline techniques."* [lines 528–532]

- Extensions to the introduction in two ways:
    1. Reorganization of the first two paragraphs to bring greater emphasis to the motivation for measurements of mixing-state evolution during oxidation. [lines 31–53]
    2. Replacing the last two sentences of the final Introduction paragraph with, *"First, signals from carbon-cluster ions were considered. Two ratios between the most-common such ions were identified, and were directly related to the overall carbon-cluster ion distribution. For an atmospheric aerosol containing a variety of rBC types, this result may be useful in apportioning the SP-AMS carbon-cluster signals between sources. Second, oxygenated-carbon ions originating from the rBC were identified and attributed to refractory oxygenated moieties within the rBC. The potential atmospheric impacts of these ions are discussed."* [lines 99–105]

Responses to Specific Comments by Referee #1

In addition to comments on atmospheric discussion, Referee #1 gave a number of additional comments, which are addressed individually below.

As stated above, the paper could be brought more into ACP's scope if it included more regarding the relevance to atmospheric science. While is some discussion of the atmospheric significance of the functionalization, this is effectively buried within the discussion at the bottom of page 27579. As far as I can tell, the biggest direct link between this work and atmospheric aerosols is the aircraft engine work and to a lesser extent, the CAST source (which while not being identical to atmospheric sources of soot, is at least a combustion source). Minus these, I would have considered recommending this be resubmitted to AMT, or at least qualified as a 'technical note'. But with these included, the paper potentially offers new insights into the composition of atmospheric rBC and can authoritatively comment on the relevance of a number of commonly-used analogues, so I could still consider it in-scope for ACP. All this said, I would still recommend that the atmospheric implications be emphasised more within the paper. Currently, the conclusions are entirely technical, the abstract has a single speculative sentence at the end regarding the atmosphere and the introduction does not really spell out the motivation for this work beyond the ongoing development of the SPAMS as a potential source apportionment tool. I would suggest that the relevance of this work to the atmosphere be more explicitly stated in all three places, detailing the new understanding gained.

Addressed above.

Further to this point, I would consider one of the major atmospheric implications of this work to be the reported observations of functionalization of the particles. The results presented seem to be mainly from the RB particles and a systematic comparison of the CO and CO2 content of the different soot sources relative to the Cx peaks seems to be absent, which I would consider to be a major oversight, even if it could only be considered qualitative at this stage. The authors mention that it is present in the CAST soot without presenting any graphs and speculate that this could be extended to atmospheric soot particles, and yet don't bring the jet engine particles into the discussion. Given the interest in aviation particles from the IN perspective, this seems to be a bit of an omission. For the sake of making the paper more atmospherically relevant (and satisfying my own curiosity), I would strongly recommend that a comparison of the Cx/COx ratios is included in a manner similar to figure 4.

Our curiosity has led to exactly these questions as well, and we do consider this a weakness of the present paper. However, the data in consideration do not allow a meaningful quantitative comparison (as in Figure 4) to be made. For that reason, we elected to present only data from RB. Work is underway to extend this analysis to multiple samples.

Moreover, the jet engine data (the most atmospherically-relevant) suffered from the major problems discussed in the Supplement. In particular, we believe they were too small to be focussed by the SP-AMS lens effectively, and they contained significant amounts of OM. Since it is therefore not possible to correct for CO^+ or CO_2^+ signals produced by OM, the contribution of rCO_x cannot be established.

I do not see where the SP2, APM or DMA2 fit into the results presented in this manuscript. If these instruments were not required to produce the data used in this paper, there is no point even introducing them.

The following sentence has been added:

"These SP2 and APM data were used as a reference for the non-refractory mass contained in the different rBC particle types (Sect.~S5)." [line 123]

Specific comments:

Page 27566: No reference here is made in the introduction to the fullerene signals reported elsewhere in the literature. This should be mentioned here.

We agree that the fullerene signals reported by Onasch et al. (2012) should be mentioned more explicitly in this paper, but have done so in the body of the manuscript as explained below (response to comment on labelled 27572, line 15).

Page 27566, line 25: The authors should expand on what they mean by 'filter system'.

This line was added after "filter system.":

"The filter system split sample between two short parallel sections of tubing, one of which contained both a filter and a valve; the valve was used to control the degree of sample filtration."

Page 27566, line 9: The custom-built DMA had an inadequate description, as the Widensohler reference isn't specific to an individual DMA geometry. I'm left to assume that it is of the Vienna design (on the grounds that most European home builds are), which if it is the case, the authors should cite an appropriate paper (e.g. Winklmayr).

Both statements are correct, Winklmayr et al. (1991) is now cited.

Page 27566, line 15: I note that the flow ratio is 2.5:1, which is very far removed from the nominal 10:1 of both Vienna and TSI DMAs. Given that this is a departure from standard operating conditions, the authors should discuss what effect this has on the data.

This text was added:

The DMA resolution – the ratio of the maximum to the full-width-half-maximum of the predicted transfer function – was therefore 2.5. This is lower than the manufacturer-recommended resolution of 10, and was chosen to maximize the particulate mass loading downstream of the DMA. This setting gives a broad-enough transfer function that a minor overlap likely occurred between different size-selected experiments (Table~1). [line 133–138]

Page 27572, line 15: The authors need to explain what they mean here better. Do they mean that the ions themselves are in the form of fullerenes, or that they originate from fullerenes in the particles, or both? Could graphitic material in the BC also be responsible for making fullerene ions at the point of vaporisation?

We have expanded this discussion to clarify our original meaning and also taken the opportunity to address the first Specific Comment by this reviewer:

"Carbon-cluster ions with x>16 and n>1 were observed for three samples: GFG, CBW, and, especially, FS. Since in general these signals were highest for FS, we believe that they originated from pre-existing fullerene molecules within the rBC particles. However, our data do not rule out the possibility that fullerenes, or simply larger carbon clusters, may form within the instrument during particle vaporization. Previous work by Onasch et~al. (2012) also identified significant signals at $C_{x>16}^{+}$ *originating from a sample of denuded flame soot. They attributed signals above m/z 384 to fullerenes, and smaller ions to linear or ring structures (von Helden et~al., 1993)."* [line 261-267]

As a follow-up, the next paragraph now ends with:

"This is in contrast to Onasch et al. (2012) who did not report multiply-charged ions." [line 280–281]

To our knowledge no other literature on SP-AMS fullerene-ions exists.

Page 27577: I can think of alternative explanations for the tail on the m/z 36 distribution. It could be that some of the particles are not completely vaporising, but enough chemical bonds within the BC are broken such that these clusters can be released after hitting the vaporiser surface, or that some particles that are not being vaporised are bouncing off the surface of the vaporiser and back into the laser beam. These could be tested by comparing with data with the vaporiser removed (I am assuming that there is an abundance of RB data both at ETH and Aerodyne).

These are good and physically plausible hypotheses, however we consider them unlikely.

The first hypothesis (laser preconditioning) requires particles to vapourize incompletely, a scenario we consider unlikely given that our SP-AMS was operated within the plateau of laser power (the current instrument reproduces the data graphed in red by Onasch et al., 2012, Figure 6(b)).

The second hypothesis (bounce) can also be ruled out. Particle bounce is well-established in the AMS (Matthew et al., 2008; Docherty et al., 2013) as a mechanism by which non-refractory particles fail to vapourize on the AMS vapourizer. Therefore, we can assume heat transfer from AMS vaporizer to rBC particle upon bounce to be negligible. Then, the only question is whether the tail of the distribution was due to an artificial increase in Particle Time-of-Flight (PToF) due to bounce. But the distance from AMS (metal) vapourizer to SP-AMS (laser) vapourizer is much smaller than the distance from chopper to laser, so a bounce-related change to PToF should be negligible.

The reviewer comments here were relevant and fair, however we have not changed the manuscript in response since the above hypotheses were not directly raised by our data, and do not affect the relevant statement that "*the peak at m/z 28 appears to decrease faster than at m/z 36*". [line 397-398]

Supplement: The first section of the supplementary material, while possibly useful to those not familiar to the instrument, really just paraphrases what is already in Onasch et al. and the main manuscript. I suggest that this is tightened up.

We agree that this is close to paraphrasing Onasch et al. (2012) but intended the section to lay a foundation for the discussion of rCO_x without any ambiguity. We found that the more general description given in the supplement is about as long as an "rCO_x specific" one, and hope to avoid future repetition by citing this more general description in subsequent work.

Technical corrections:

Line 27564, line 3: I would qualify the statement about combustion particles being the second 'strongest' climate forcing agent as 'in terms of instantaneous radiative forcing' and specify that the statement refers to the BC specifically. The latest IPCC report (amongst other sources) is quick to point out that combustion also produces OM, which can offset or reverse the warming effect of BC and as aerosols are very short-lived, the long-term forcing potential is not significant compared to other agents. I would also question the wording of the point on line 13 identifying combustion as 'ideal candidates for near-term climate mitigation'. Their large radiative forcing makes them ideal candidates for mitigation, but their short lifetime means that the benefit of mitigation will only be felt in the near term if CO2 emissions continue to increase.

This comment combines feedback on [A] the "ranking" of climate-forcing agents and on [B] the usefulness of near-term climate mitigation.

Point [A] is entirely concurred with, and highlights a potential for significant improvement in this paragraph. We agree with the implicit opinion that the light-absorbing component of combustion-generated particles is not separable from the non-absorbing component. This subtlety is addressed in the cited papers but not by our statement. We previously addressed this later (P27564,L15-16) but consider it important enough to change the statement (now in the 1st paragraph of introduction as noted above) to:

> *"Consideration of the short atmospheric lifetime (days to weeks, Cape et al., 2012), human health effects, and damage to crops associated with combustion-generated particles has led to their being highlighted as ideal candidates for near-term climate mitigation (Shindell et al., 2012; Bond et al., 2013)."* [lines 37–40]

To allow for the above paragraph, the original lines 15-19 on the same page have been removed and replaced with "*The need for an improved representation of the mixing of light-absorbing particles with secondary material motivates the atmospheric source apportionment of aged, combustion-generated particles.*" [lines 54–56]

Point [B] is also concurred with, in that near-term climate mitigation alone is a short-sighted solution. However, we also consider it a worthwhile short-term action, as discussed by the cited studies. To address the unintended interpretation discussed by the reviewer, we have rephrased, but retained, this statement (Introduction, 1st paragraph).

Page 27565, line 5 (and elsewhere): The word 'vapourize' and its derivatives should be either spelled 'vaporise' or 'vaporize'.

Done

Page 27566, line 4: The SP2 strictly quantifies according to the amount of incandescent material, which just happens to the refractory, light-absorbing component in the case of rBC. It can also detect the non-BC component in its effect on the scattering cross section but admittedly does not measure the composition.

This comment points out that SP2 incandescence is not calibrated to the mass of light-absorbing material, but to the mass of material that incandesces following light absorption. This is a valid point, and may be meaningful if rBC from different sources contains different degrees of sp^3-hybridization. This may or may not be important for atmospheric rBC (Robertson, 2002). We have removed the unintentional ambiguity from the statement

> *"[SP2-like techniques] quantify rBC mass based only on its most-refractory, light-absorbing component"*

by changing it to

> *"[SP2-like techniques] quantify rBC mass based only on the refractory particulate component that is heated to rBC vaporization temperature"* [lines 93–94]

This statement is consistent with the view of rBC as a material and not a chemical compound that was outlined in the supplemental Section S1.

Page 27568, line 1: The AMS vaporiser cone should be specified to be an inverted Cone

Done

Page 27568, line 12: The laser should also be described as 'active cavity', as this is a key design feature.

Done

Page 27568, line 29: The mass spectrometer mode should be referred to as 'V mode', as this is the commonly used term.

Done

Page 27569: Please provide some references for CAST source, in terms of technical description and characterisation.

The statement *"Manufacturer characterization has been published online at http://www.sootgenerator.com/publ.htm."* has been added. To our knowledge, no peer-reviewed characterization or technical description has been published for the CAST.

Page 27574, line 16: Given that Tim Onasch is a co-author on this paper, it seems inappropriate to cite a personal communication from him. If the measurements were performed at Aerodyne Research, this should be simply stated as such.

Changed to *"measured using a different instrument at Aerodyne Research Inc. but the same RB sample (Onasch et~al., 2012).",* retaining the Onasch label to clarify the discussion.

Page 27577, line 10: I would not agree that the m/z 36 distribution is bimodal. It certainly has a 'tail', but I see no second mode.

"appears bimodal" → *"is broad and possibly bimodal"*

Figure 3: This figure would be clearer in colour.

OK

Figure 6: The symbols and line styles should be included as a legend rather than described in the caption. If the authors are pushed for space, the arrows are surplus to requirements because the respective axes are indicated by the m/z referred to.

A legend was added and the caption simplified.

Specific comments by Referee #2

In addition to the major comments which were addressed in the first section of this Resopnse, Referee #2 made the minor suggestion that the graph symbols were difficult to read. They have been made larger.

References

Docherty, K. S., Jaoui, M., Corse, E., Jimenez, J. L., Offenberg, J. H., Lewandowski, M., and Kleindienst, T. E.: Collection Efficiency of the Aerosol Mass Spectrometer for Chamber-Generated Secondary Organic Aerosols, Aerosol Sci. Technol., 47, 294-309, 2013.

Matthew, B. M., Middlebrook, A. M., and Onasch, T. B.: Collection efficiencies in an Aerodyne Aerosol Mass Spectrometer as a function of particle phase for laboratory generated aerosols, Aerosol Sci. Technol., 42, 884-898, 2008.

Robertson, J.: Diamond-like amorphous carbon, Mat. Sci. Eng., 37, 129-281, 2002.