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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Black carbon measurements in the boundary layer over western and northern Europe" *by* G. R. McMeeking et al.

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We thank both reviewers for their comments on the manuscript. The original reviewers comments are in regular type and our responses are in *italic type*.

Reviewer 1 (M. Shiraiwa)

Major comments:

Throughout the manuscript the authors claim that filter-based methods have a number of artefacts and much less sensitive than SP2. Please specify and discuss more about what artefacts they are and why these artefacts tend to lead overestimation

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of absorption measurements as shown in Figure 6.

The ACPD manuscript refers to filter-based measurement artefacts on page 13799 (line 10) and page 13802 (lines 25-28). We do not wish to go into a lot more detail because we feel they are best described by the cited literature. To address the reviewer's request we will slightly expand and clarify or discussion of filter-based measurement artefacts in the introduction of the revised manuscript.

Please estimate the uncertainty of the derived BC core diameter. This is important as authors discuss the small shift of mass median diameter of BC. In this study Aquadag carbon particles were used as standard to calibrate LII detectors of SP2. The calibration line of LII detectors may change depending on the type of BC, as emissivity and shape of the particle are different (Shiraiwa et al. 2008). If the ambient BC has different characteristic (emissivity, shape) from Aquadag, this will lead to some uncertainties. Please discuss this point in the paper.

We agree and will add a brief discussion of these points in the revised manuscript. Shiraiwa et al. 2008 and Schwarz et al. 2008 both report the uncertainty in the mass determination of a single rBC particle as 30%, which corresponds to an uncertainty in mass equivalent diameter of approximately 10%. We also agree that if the ambient rBc has a different emissivity than Aquadag this will result in a sizing bias, however the shifts jin mean size would still be meaningful assuming the ratio of ambient rBC and Aquadag emissivities remained relatively constant.

The detection limit of BC is reported to be 0.2 fg, which is much better than previous studies. The authors mention that the detection efficiency drops below unity for masses below 0.7 fg. Do authors have any idea of detection efficiency in this mass range? Do LII signals for such small particles, which are close to detection limit, still

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show triangle shapes (which means BC evaporates completely in the laser beam) or are the signals distorted?

We do not have any information regarding the instrument detection efficiency from the manufacturer calibration for the instrument at the time of the measurements. Manual inspection of the individual incandescence signals suggests that the small particle signals have a similar structure to larger signal shapes, however it is difficult to assess without a reference for a distorted signal. We agree that determination of the detection efficiency of the instrument at its detection size limit is important, however the results in this manuscript focus on mass distributions which are largely insensitive to the small particle limit of the instrument, as stated in the text on page 13806, lines 16-18.

Dust can also contribute to the absorption measurement of PSAP, whereas SP2 are insensitive to dust. The large mass absorption efficiency of 18 – 39 m2/g might be due to the contribution of dust. Do authors have any information about dust? At least this should be discussed in the paper. The authors claim that the limited detection range of SP2 (55 - 400 nm) can be one of the reason, but they also say that the scaling factor ranges only 1-1.2, which cannot explain the factor of 2 -3 difference.

We will add this point to the revised manuscript. Though we can not eliminate the possibility that absorption by dust particles was responsible for the increase mass absorption efficiencies, we believe it would have played a minor role for several reasons. First, we are not confident that coarse mode dust particles are sampled efficiently through the Rosemount inlets for the SP2 and PSAP instruments. Haywood et al. (2003) estimate an upper optical diameter cut off of 3 μm for the same inlets used in this study. Second, the aircraft instrument payload included a passive cavity aerosol spectrometer probe (PCASP) which was capable of detecting particles as large as 3 μm and the contribution by mass estimated from particle size distributions

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was minor. Third, we calculated an estimate of the absorption by dust using size distributions measured by the PCASP and a conservative estimate of the dust mass absorption efficiency of 0.05 m^2g^{-1} and found it contributed between 10-20% of the total absorption. Fourth, there was no correlation between the mass absorption efficiency calculated for rBC and the contribution by 1-3 μm particles to total aerosol volume, which we would expect if dust was responsible for a significant fraction of the light absorption. Finally, daily forecasts made during flight planning for the study showed no evidence for long-range transport of dust to the study region.

It is interesting to see the systematic decrease of BC mass mean diameter (D_{gm}) with altitude (Fig. 5c). The authors speculate that the main reason is the BC removal by cloud and precipitation scavenging. In section 3.1, however, authors mention that the ADIENT flights were conducted under conditions with clear skies and little influence from precipitation and loss of BC in precipitation scavenging is minor.

The boundary layer values are due to in situ production in Europe, while the free troposphere (FT) values arise as a result of long range transport; there is no direct link between these aerosol. A lack of convection over Europe does not imply that cloud processing of the FT sampled aerosol did not occur. This could be very aged air which may have precipitation impacts several days prior to sampling.

Minor comments:

- L20, P13799, Please provide a reference for "'... have been shown to be independent on the BC mixing state [reference]".

The revised manuscript will refer to Slowik et al. (2007), who showed that the

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rBC mass measurement was independent of associated coating thickness.

- L25, P13802: Please explain briefly about the approach given by Bond et al. (1999).

The revised manuscript will include an additional sentence summarizing the corrections, which include corrections for the instrument flow rate, sample spot size, and the presence of scattering aerosol co-deposited with the absorbing particles.

- L18, P13804: Please provide a reference for aerosol particle mass analyzer, which is not a common instrument.

The revised manuscript will cite: Ehara, K., C. Hagwood and K. J. Coakley, Novel method to classify aerosol particles according to their mass-to-charge ratio: Aerosol particle mass analyser, Journal of Aerosol Science, 27, 217-234, 1996.

- L14, P13806: Please provide a reference for BC density of 1.8 g cm-3.

The revised manuscript will include a reference to the Bond and Bergstrom (2006) review already cited in the paper and: Cross, E. S., J. G. Slowik, P. Davidovits, J. D. Allan, D. R. Worsnop, J. T. Jayne, D. K. Lewis, M. Canagaratna, and T. B. Onasch, Laboratory and ambient particle density determinations using light scattering in conjunction with aerosol mass spectrometry, Aerosol Science and Technology, 41, 343-359, 2007.

- L16, P13806: Please explain briefly about the recommendations of Schwarz et al. (2010).

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An additional sentence summarizing the recommendations will be added to the revised manuscript.

- L1, P13824: Please add (McMeeking et al., 2010).

Will be done in revised manuscript or removed if the citation is not available in time for publication.

- I would suggest summarizing obtained and reported mass absorption efficiency in table, but this is up to authors.

We prefer to limit the discussion of the MAE values to the text as they are not the focus of the manuscript.

- L1, P13827: Petzold et al. (2008) shows that the diameter of the ship emitted particles is small (D $<$ 0.3 um).

We thank the reviewer for spotting this and have removed the reference to ship emissions in the text.

- Figure 6: Is this PSAP one wavelength PSAP (567 nm)? Did authors compare also with 3-wavelength PSAP measurements?

The PSAP on the FAAM research aircraft was the single wavelength version; that on the DLR Falcon was a 3-wavelength version, but we do not examine the wavelength-dependence of absorption in this work.

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- Figure 6: What are the slopes if y=A*x are used instead of y=A*x+B to fit the data?

Forcing the y-intercept through the origin gives slopes results in only minor changes to the slope.

- Figure 9: Why did authors normalize mass size distribution? I want to rather see non-normalized mass size distribution (dM/dlogD, ug/m3).

The mass distributions were normalized to highlight the changes in mode rather than mass concentration. The revised figure will include text providing the absolute mass concentration for each distribution.

- McMeeking et al. (2010) is missing in the reference list.

This is a paper in preparation so a full reference can not be provided.

Reviewer 2

Introduction: suggest that the word 'refractory carbon' be used in describing what the SP2 measures in order to be adequately specific and to distinguish SP2 from other measurements of absorbing aerosol.

The revised manuscript will adopt the term refractory black carbon (rBC) in keeping with recent SP2 literature.

P13804 ln 12+ There are two points to make clearer here: one is that the manufacturer's calibration was not adequate. The calibration was improved by having

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access to the results from Kondo's laboratory that are based on actual mass rather than inferred mass. Second, a missing point is to state the importance of knowing whether Aquadag represents ambient BC in terms of incandescent response vs BC refractory mass. These authors perhaps already know that Kondo's group has found that this is not the case in Tokyo; fullerene soot better represents ambient aerosol by a large factor. These results are nearing publication. The authors must acknowledge this as an issue and are encouraged to see if the Kondo results are citable.

We agree that these are important concerns and will revise this paragraph to include the Moteki et al. (2010) paper that was published shortly after our manuscript was submitted. We hesitate to modify our reported values based on a single study comparing the calibration material to ambient soot in Tokyo, which may not necessarily represent the rBC sampled in this study. It is also unclear to us if the differences in the laser induced incandescence (LII) signal and particle mass relationships are statistically significant because Moteki et al. (2010) did not provide confidence limits for the linear fits of the LII signal-to-rBC mass data. The relationships for particles in the mass range between 4-10 fg (the peak region of the mass distributions we measured over Europe) rely on three data points (1 for Aquadag and 2 for ambient soot) and appear to become more similar for rBC mass values greater than 10 fg as particle shape becomes a more important factor in determine the LII response. As Moteki et al. (2010) point out, further investigations are needed in this area, which we support and hope to eventually contribute.

P13806 ln 1 The sentence 'The lower mass detection limit for the SP2 was determined by the laser intensity sufficient to heat particles to incandescence." is not correct in principle. Schwarz et al. 2010 as cited here demonstrates that incandescence of a particle alone is an unreliable indicator below a certain threshold that the mass vs incandescence relation is valid. Suggest restructuring this section to reflect

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this result.

We thank the reviewer for pointing this out and will clarify these points in the revised manuscript, highlighting the need for rBC particles to be brought to their vaporisation temperature to ensure accurate mass determination by the SP2.

Supplement p1. The phrase "(due to the power-law relationship between SP2 signal and BC mass)" needs a reference.

We will change the phrase to "due to the apparent power-law relationship between SP2 signal and BC mobility diameter".

P3 Fig. 2. This is very odd behaviour for an SP2 and likely reflects flawed components. Suggest explaining for the benefit of other SP2 users the origin of the strong peak height dependence of the ratio.

We believe the shape of the peak ratio curve depends on two factors. First, the lower ratios at smaller peak heights may be due to the smaller particles not reaching their incandescence temperature, as described by Schwarz et al. (2010). Second, the lower-gain detector response approaches the noise level for smaller particles, limiting the maximum ratio we would expect to be real. To illustrate this, we have also plotted the ratio expected for a low-gain detector signal of 40, which we take to be our minimum detectable signal.

P4/5: Figs. 3 and 4. Is the vertical scale really mass? Ideally it would be.

We agree and believe we have done all that is possible to address this with the available data by converting the mobility-based calibration to mass using the density

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data provided by Moteki et al. (2010).

Smaller points:

P13804 ln 20: It is incorrect and disingenuous to describe NOx as those species that convert on a Mo catalyst. It is well demonstrated that a heated Mo catalyst generally converts more than NOx=NO+NO2 but maybe less than NOy in air masses influenced by urban and regional pollution. See reference below.

Nitrogen oxide measurements at rural sites in Switzerland: Bias of conventional measurement techniques, M. Steinbacher, C. Zellweger, B. Schwarzenbach, S. Bugmann, B. Buchmann, C. Ordóñez, A. S. H. Prevot, and C. Hueglin, J. Geophys. Res., 112, D11307, doi:10.1029/2006JD007971, 2007

Our intention was not to claim that the NO_x instrument measured only NO and NO_2, but rather that we treat what it measured as NO_x, hence our use of the term "operationally defined". We have clarified this in the revised manuscript by explicitly stating the measurement is a surrogate of NO_x and also cite the recommended reference.

P13804 Clean up mixed tenses as A particle sampled by the instrument is illuminated by an intracavity Nd:YAG laser (λ=1064 nm) with a Gaussian profile (TEM00 mode). If it contains sufficient absorbing material, the particle heats and reaches its incandescence temperature and emits thermal radiation, which is measured by two optical detectors. The peak intensity of the detected radiation signal is related to the mass of refractory carbon material and is insensitive to particle morphology or mixing state (Slowik et al., 2007).

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The manuscript will be changed to the text above as recommended by the reviewer.

Use of the general term ‘absorbing material’ here is incorrect.

We will change the text to use the term “absorbing aerosols" in its place.

P13805 ln 11 Change to ‘Gaussian functions’

Will be done in revised manuscript.

P13805 ln 26 State what detector type is being used in this SP2.

The detectors types, identical photomultipliers for the incandescence channels and avalanche photodetectors (APDs) for the scattering channels, are stated in lines 3 and 7 in the original submission. Optical filters are used to select wavelength ranges for each detector.

P13828 ln7 Hendricks et al. aerosol model results could be cited here offering a limit on expected enhancements of BC mass from aviation, which are likely small.

Hendricks, J., B. KaÂ′lrcher, A. DoÂ′lpelheuer, J. Feichter, U. Lohmann, and D. Baumgardner (2004), Simulating the global atmospheric black carbon cycle: A revisit to the contribution of aircraft emissions, Atmos. Chem. Phys., 4, 2521– 2541.

We thank the reviewer for their recommendation and include a reference to the paper in the final paragraph of section 4.5.

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P13847 figure captions Captions do not describe the datasets represented, ie type of average, etc. Specifically Figs. 5, 8, 9, 10 would benefit from this information.

Will be done in revised manuscript.

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