

Interactive comment on “Black carbon concentrations and sources in the marine boundary layer of the tropical Atlantic Ocean using four methodologies” by K. Pohl et al.

## **Response to Referee #2**

First, we would like to express our thanks and appreciation to both referees for their corrections and constructive comments. We believe that the implementation of these suggestions has greatly improved the manuscript. We have termed our responses in the order of which Referee #2 stated. We will restate the referee’s comments as RC-# with the response by the author’s comment as AC-#.

### **Introduction**

*RC-1: The paper reads largely like a method paper or report (P29789L12 ‘we evaluated four methods’) and is not detailed enough in its discussion of BC aerosols in the marine boundary layer in general and over the Atlantic in particular (‘expected BC concentrations are elevated due to intense biomass burning of the grassland biomes and easterly winds’). We already know from a large number of method intercomparisons that every BC method will produce a different amount of BC in a given sample (current hypothesis #2 is trivial). The more interesting questions are what this data tells us about BC’s sources from the land (fuel sectors, regions), transport and degradation and removal pathways in the atmosphere.*

**AC-1:** We have significantly reworked the manuscript so that its primary focus is on the spatial trends and distribution of BC aerosols and the secondary trend is on the method comparisons. The Introduction, Results & Discussion, and Conclusion sections have all been restructured to include a more detailed discussion of BC concentrations in this remote region. We believe that the deviation of the BC concentrations between methods should be helpful in identifying source, transport, degradation, and forms of the aerosols. The reformulated hypotheses are now worded in the following way: (1) black carbon would be elevated in the tropical Atlantic boundary layer compared to other remote environments due to the African emission plume, (2) soot would be the dominant fraction of black carbon, and (3) the use of multiple methods would offer unique insights into assessing the forms of combustion-derived aerosols present.

*RC-2: To make the manuscript suitable for ACP(D), I suggest refocusing the introduction on the science questions rather than the BC methods. For example, it would be helpful to work out more strongly in the introduction (P29787L1019) what we know about the composition of BC aerosols in the atmosphere in general and in marine boundary layer of the tropical Atlantic rather than a discussion of charcoal vs. soot.P29787L1620. I find it*

*very unusual to mention the project specific sample names (e.g. QFF910) in the introduction. This belongs into the method section. Instead, it would be more useful to mention when or for how long the samples were collected to lie out what processes can be evaluated with the dataset. For example, were samples collected during highfire intensity in the N or S grassland biomes in Africa or high fire activity in Brazil? Are samples integrating (for how long) over the region or near sources?*

**AC-2:** We have completely restructured/reworded the Introduction, Results & Discussion, and Conclusion to focus primarily on the scientific findings. Specifically, we have included paragraphs discussing spatial trends and concentrations of BC in marine boundary layer aerosols, as well as expand on the importance of our study region (for example, that it is heavily influenced by the African emission plume and that we sample during a season of high fire activity). We have also restructured the Results & Discussion section to focus primarily on the distribution of BC aerosols in this region and used the multiple methods to assess the form and transport of these aerosols.

We have moved the mention of specific filter numbers into the methods section and kept the Introduction more general and focused on the scientific questions at hand. We have also added sampling intervals into the Methods (48 hour intervals) and included a more detailed table including the locations, dates, volumes, and distance travelled corresponding to each filter sample.

*RC-3: The results and discussion section should also be rearranged to focus on the scientific questions rather than the methods. For example, the authors state that ‘a primary objective of this study was to investigate if the tropical Atlantic could be receiving significant inputs of BC’. I suggest moving this question into the introduction and to discuss the African Plume data first rather than in the middle after the Caribbean and South America. Also, the authors keep on stating that TOC measurements made using CTO375 or TOT are highly correlated, but lower for the CTO375. What does this imply for e.g. the potential recalcitrance, heat absorption or chemical reactance of BC or the combustion.*

**AC-3:** We have completely restructured the Results and Discussion section with the following order: 3.1: Region trends for black carbon with respect to the total organic carbon; 3.1.1 General black carbon concentrations and trends; 3.1.2 Total organic carbon concentrations and trends; 3.1.3 BC/TOC regional patterns; 3.2 Stable carbon isotope analysis for source apportionment; 3.3 Carbonaceous combustion aerosol analysis by sub-region; 3.3.1 African Plume; 3.3.2 Caribbean Sea; 3.3.3 South America; 3.3.4 Subtropical Atlantic. We believe this strengthened the discussion of the observed trends and spatial distribution of BC aerosols, but still allowed for method comparison.

We also emphasized more on what the differences in the methodological difference could mean in terms of BC transport, form and stability. Additionally, we expanded on the

interpretation of the TOC being equivalent for the TOT and CTO-375 methods, but the BC/EC being different between the methods.

*RC-4: Hypothesis #3 ('use of multiple methods off unique insights into the forms of BC present') is interesting, but not worked out well. While BC is being accurately described as a continuum, the main conclusion that 'charcoal is an important fraction of the aerosol BC' is confusing and misleading, as charcoal is not typically considered part of the aerosol pool due to its size. This statement is indicative an inadequate usage of terminology, which is a minefield and used differently in various fields investigating BC in different parts of the Earth system soils, sediments, air etc. I encourage the authors to take another look at what their data tells them about the composition of BC aerosols, with a focus on BC sources and degradation processes during transport*

**AC-4:** We have altered our hypotheses/conclusions so that the presence of charcoal (as determined by the pyrene fluorescence loss method) is more speculative than a solid conclusion. We have deemed the difference of the measured CTO-375 values with the PFL method to be charcoal-like combustion-derived aerosols that include other organics such as carbohydrates, humics, and macromolecular PAHs. We also included previous studies in the deep ocean which have found micro-charcoal fragments, supporting that charcoal-like fragments can be found in the remote region despite the size of the aerosol.

*RC-5: The definition of EC ('EC is a highly reduced, graphitic like form of BC... P29788L58') is inadequate and its use is inconsistent among the four methods. The term BC is more commonly used for samples characterized by optical measurements related to the light absorption of BC; EC is more commonly used for all other methods. I suggest explaining this in the introduction and than using either only BC or EC throughout the manuscript or using BC for optical and EC for non optically measured fractions*

**AC-5:** We have clarified our definition of EC. Additionally, we have also altered our BC terminology so that EC is used for the methods with use high temperature gas evolution, CTO and TOT, and BC for the optical method, optical transmission attenuation. Since the pyrene fluorescence loss method is a novel technique, there has been no suggestions for properly naming the produced values, so we have chosen to call it BC. We have included the method used with each value in subscript: EC<sub>CTO</sub>, EC<sub>TOT</sub>, BC<sub>OT21</sub>, and BC<sub>PFL</sub>. We believe that linking the method to the produced values has made this manuscript easier to follow and more consistent with other current literature terminology regarding BC/EC values. We used the general term of black carbon to discuss the general combustion-derived aerosol patterns in this region.

*RC-6: P29791L23 Statement 'The CTO375 BC fraction is also called 'sootlike' BC' seems out of place. I would move it to the introduction or discussion.*

**AC-6:** We moved the definition that CTO-375 was defined as soot-like BC into the introduction.

*RC-7: P29792 What does EBC stand for?*

**AC-7:** EBC had stood for equivalent black carbon, as suggested by Petzold et al. 2013. We have however removed this terminology.

*RC- 8: P29792L19 The authors mention that 'risotto char' was used as a standard. I assume they used the international 'rice straw char' standard*

**AC-8:** Risotto char is a standard reference material also called grass char (Hammes et al. 2007). We have corrected this in the text.

*RC-9: P29791I2426. The authors mention in the TOT method section that the filter material for some of the samples might have been glass fiber (#1, 22, 23, 24); while they state in the introduction that all filters were quartz fiber, and refer to 'QFF's' throughout the manuscript. I am wondering how the filter material affects the sample total carbon, organic and black carbon backgrounds. It seems that the authors did not run blank filters for each method that were quartz and glass. Can this be added? One problem is that glass fiber filter blanks cannot be assessed for BC using TOT, as they will shrink. Also, it is possible that the glass fiber filters underwent a change in pore size during the prebaking at 450°C. This might have affected the loading during the sampling.*

**AC-9:** The use of a glass versus a quartz fiber filter should have minimal effects on our other measurements with the exception of the TOT method. Both QFF and GFFs have been used in the pyrene fluorescence loss, as blanks, with no carbon being detected on either one. Likewise, we have analyzed GFF and QFF via the CTO method and the similar residual carbon blank is observed for both. We included this analysis into the Supplementary Materials. The OT-21 method used for the optical transmission attenuation is suitable for both quartz and glass fiber filters. To our knowledge, there has not been a direct comparison, however we expect minimal effects.

We have added to the text that the particle retention of these four glass filters could have been different than the samples collected with quartz filters. The particle retention of the quartz fiber filters used (Whatman Product Code 1851-865) is 2.2µm and the glass fiber filters (Whatman Product Code 1822-866) is 1.2µm. The precombustion at 450°C could have affected the pore size of these filters differently, also affecting particle retention. Based on the results, it does not appear that the greater GFF particle retention measured significantly more BC/EC than the quartz filters. However, we have added into the text that sample 1 and 22-24 had the potential to measure different (greater or lower) BC/EC concentrations.

*RC-10: It would be helpful if the authors included an overview table with all the filters, incl. all blank sand standards, and associated results from each method, so the readers can judge if those four samples should be included in the analysis.*

**AC-10:** We have included a table in the SI which shows the %C (determined by chemothermal oxidation) of the field blanks, laboratory blanks, and a GFF. The average SRM values have been included in the Quality Control and Quality Assurance section in the Methods section.

*RC-11: The authors argue in the 2.6 Quality control section that the blank C was constant regardless of the air volume that went through each filter. There are actually two different blanks that should have been analyzed. First, a prebaked filter that never left the lab and is analyzed after prebaking. This represents the C trapped in the filter material. Second, blank filters should have been exposed to the air on the cruise, but not have any air sucked through them. This experimental blank is likely very low for the BC fraction, but might be substantial for organic and thus total organic carbon*

**AC-11:** We did analyze two field blanks and 4 lab blanks. This was not written well or explicitly in the text and has now been textually improved and a table of this information has been added to the Supplementary Materials. The blank used to correct the data was an average of these lab and field blanks. There was no significant difference between the field and lab blanks. Thus we assumed that any carbon associated with a blank would also be associated with a sample and corrected for it.

*RC-12: P29788L24+ The authors describe the CTO375 method in the context of BC in sediments and soil, but fail to mention recent work by this group on aerosols: Gustafsson, Ö., Kruså, M., Zencak, Z., Sheesley, R. J., Granat, L., Engström, E., ... & Rodhe, H. (2009). Brown clouds over South Asia: biomass or fossil fuel combustion?. *Science*, 323(5913), 495498. Zencak, Z., Elmquist, M., & Gustafsson, Ö. (2007). Quantification and radiocarbon source apportionment of black carbon in atmospheric aerosols using the CTO375 method. *Atmospheric Environment*, 41(36), 78957906.*

**AC-12:** We have included these references.

*RC-13: P29787L810. Method comparisons regarding aerosols are missing. Consider citing: Watson, J. G., Chow, J. C., & Chen, L. W. A. (2005). Summary of organic and elemental carbon/black carbon analysis methods and intercomparisons. Aerosol Air Qual. Res, 5(1), 65102.(this work is cited later in the manuscript)*

**AC-13:** We have included this reference in the proper location.

*RC-14: P29786 L26: consider adding recent work:  
Ziolkowski, L. A., and E. R. M. Druffel(2010), Aged black carbon identified in marine dissolved organic carbon, Geophys. Res. Lett., 37, L1660*

**AC-14:** We have decided not to include any dissolve black carbon literature to keep the focus of particulates; however this is a valuable manuscript and will use it as a reference in future works.

*RC-15: The Methods section lacks detail. The Sample collection section is very weak.  
•A brief summary of the cruise tracks should be included.  
•Since samples were collected in both the northern and southern hemisphere, 'summer 2010' is not a clear description of when samples were collected. Please state exactly during which time period filters were collected.*

**AC-15:** We have strengthened the sample collection section to include a detailed table including the dates, air volume, start/end location, and total distance travelled for each filter.

*RC-16: It would be good to add a table indicating the range of space and time covered by each sample.*

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*How many samples were collected in each region?*

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*P29790L26+ Please add abbreviation for TOC*

**AC-16:** We have included a table to include more sample specific information, including the spatial range, air volume, and dates of sampling. We have also defined the abbreviated TOC (total organic carbon).

*RC-17: The Pyrene fluorescence loss section does not contain enough background information to understand the experiment.*

*•Please state at which temperature samples were stored for 30 days and in what type of (open or closed) container and in how much liquid, and what is the ratio of pyrene spiked MQ:sodium azide?*

**AC-17:** We have included the temperature and container type of the pyrene fluorescence loss experiment into the manuscript. More detailed information regarding this experiment can be found in the Supplementary Materials, which we have now cited in this methods section.

*RC-18: OT21• P29792L8 'C' missing in unit*

**AC-18:** This has been corrected.

*RC-19: On P29794L1314, the authors argue that  $\delta^{13}C$  values of 22 per mill of the organic carbon fraction are indicative of marine plankton. Can the authors really exclude land plant derived volatile organics as a source of organic C, since the isotope ratio of tropical land plants (C3 and C4!) cover a wide range (30 to 10 per mill)? And, the following discussion is focused on comparing marine plankton vs. trees (C3). First, yes, trees are burning, but so are crop residues, and most crops are C3 (rice, soy). Second, I am puzzled by the lack of discussion of volatile organic as sources of organic and total C. On P29795L27, the author state that 'the average  $^{13}C$  value of total organic carbon was 27 per mill, which indicated that C3 plant burning most likely had a large input [...] and is too depleted to be*

**AC-19:** We cannot definitively state that 22‰ is a marine stable carbon signature. We have included in the text that it could be a specific mixing of C<sub>3</sub> and C<sub>4</sub> materials. We have included a previous study (Keene et al., 2007) that found significant levels of marine-derived primary organic aerosols in oligotrophic environments, such as our study region to support our hypothesis that the TOC is mostly marine.

*RC-20: On P29796L79, the authors argue that C4 grass combustion from African grasslands was not likely a contributor to sootlike BC in the South American region. What about C4 grasses in South America?*

**AC-20:** We have amended this argument to include that C<sub>4</sub> material could be from South America as well. We have also added the argument that the backward wind trajectories support that aerosols originating from South America are minimal, so Africa was most likely the largest C<sub>4</sub> contributor. Our stable carbon values support this and we expanded upon source apportionment in the Results and Discussion section (3.2 Stable carbon analysis for source apportionment).

*RC-21: The authors state that 'We sampled this plume during the SH dry season when large scale Savanna fires are frequent' This is confusing, because I thought that African savannas burn 'twice'; each hemisphere in its dry season.*

**AC-21:** We specified the Austral winter dry season (of the Southern Hemisphere).

*RC-22: P29797L8. The authors state that the BC concentrations in the African plume measured with the CTO375 method were as low as in the Canadian Arctic. This is a poor comparison of 'apples and oranges', since the arctic BC was not measured using the CTO375 method.*

**AC-22:** We removed this comparison.

*RC-23: Table 1 Please indicate the time period of data collection, grid coordinates of regions, and number of samples analyzed. E.g. it is unclear if 'South America' refers to the continent or the Atlantic region or the continent. Please indicate what type of errors are reported (SD or SE). Why are no errors reported for the  $^{13}\text{C}$  data? Is  $n=1$ ? Also, it is unusual to express  $^{13}\text{C}$  data in 1 per mill resolution, since the measurement uncertainty should be better than 0.1 per mill. Columns 2 (TOC<sub>a</sub>), 4 & 5 refer to the CTO375 method. I suggest switching column 2 & 3, and indicating the method and putting the units inside the table.*

**AC-23:** We specified that standard deviation was used and included error in the  $\delta^{13}\text{C}$  measurements. We expressed the  $\delta^{13}\text{C}$  in per mil since 0.1 per mil would not have changed any of the source assessments; this makes it easier to read in the text. We have also switched the location of the CTO derived TOC (TOC<sup>a</sup>) to the (TOC<sup>b</sup>) column so that the CTO-375 method items are all next to each other. The time periods and grid coordinates as a table have also been included.

*RC-24: Table 2 Please indicate the time period of data collection, grid coordinates of regions, and number of samples analyzed. Please indicate what types of errors are reported, and why no errors are reported for OT21. Remove 'the' in front of chemothermal oxidation.*

AC-24: We reported the instrumental error associated with OT21 measurements and well and the regional standard deviation for this method. “The” was removed from chemothermal oxidation.

RC-25: *Figure 1 In the caption, I do not understand the abbreviation ‘IRMS’*

AC-25: We have defined IR-MS as isotope ratio mass spectrometry.

RC-26: *Throughout the manuscript and tables and figures, please remove all spaces between numbers and degree C (375°C rather than 375 ° C), % or per mill (4% rather than 4 %) and also between ‘<’ or ‘>’ and numbers (<4 rather than < 4). [While numbers and units are commonly separated by spaces, this does not apply to degree, percent and per mill.*

AC-26: We have implemented these unit changes/edits.

RC-27: *Throughout the manuscript (e.g. P29787L10) spell out abbreviations at the beginning of a sentence (Black carbon is ... rather than BC is...)*

AC-27: We changed all abbreviations to be spelled out if they began a sentence.

RC-28: *P29789L10 Instead of ‘there is also little information available’, I recommend changing this statement to ‘There is, however, little information available.’*

AC-28: We have implemented this statement change.