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 #1

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 for general comments (GC), specific comments (SC), and technical corrections (TC) by the order in which they were made by Referee #1 (labeled GC-#N, SC-#N, and TC-#N). We will restate the referee's comments as RC with the response by the author's comment as AC.

RC GC-1: I found the terminology used within the paper a little hard to get used to, as not all of it was consistent with what is generally used within the atmospheric science community. Furthermore, there is a general move in the community to consign the term 'BC' to that which is measured using only the optical methods; most people would refer to that measured by evolved gas analysis as 'EC'. For these reasons, I would strongly urge the authors to modify their terminology to make as consistent as possible with the recommendations presented by Petzold et al. (2013, doi:10.5194/acp-13-8365-2013). I would certainly be in favour of denoting each measured quantity with a subscript to indicate which technique produced it.

AC GC-1: We have changed our terminology to be more consistent with current recommendations by the atmospheric community, namely Petzold et al. 2013, as well as each technique utilized in this study. Analyses using evolved gases are referred to as elemental carbon (EC); this includes the chemothermal oxidation (CTO) and thermal optical transmission (TOT). The method using an optical approach, optical transmission attenuation (OT21), has remained black carbon (BC). Our fourth technique, the pyrene fluorescence loss (PFL), is a novel technique with uses adsorption and does not have a recommended terminology. We have decided to term this as BC. Additionally, we have added the specific method as a subscript to each method. Thus, the following have been now inserted into the manuscript: EC_{CTO}, EC_{TOT}, BC_{OT21}, and BC_{PFL}. We believe that linking the method to the produced values has made this manuscript easier to follow and more consistent with other current literature. When we discussed the patterns of combustion-derived aerosols between all four methods, we used the general term of black carbon.

RC GC-2: As it currently stands, the abstract and conclusions seem to focus mainly on the technical aspects of the paper, i.e. the comparison of the four analysis methods. For the sake of making the paper more relevant to ACP, it would be useful to focus more on the atmospheric implications, specifically the spatial variabilities and the trends in the

disagreements between measurements that may indicate a change in the physical nature of the BC.

AC GC-2: Our manuscript has two main objectives: to discuss BC/EC concentrations in a remote region and to compare four techniques. In response to the reviewer's comment, we have strengthened the discussion of the spatial variability and trends of BC/EC concentrations in the manuscript. We have reworded and organized the Introduction, Results & Discussion, and Conclusion sections to be focused on spatial trends and distribution rather than on the method comparison.

RC GC-3: While I do not dispute that the trends in the measured data are probably a reflection of a change in the physical properties, I do not think that the explanation relating to what the authors term 'charcoal' is adequately supported. Firstly, as the authors admit, large particles of incompletely-combusted fuel are not expected to participate in long range transport, owing to their faster settling velocity. But perhaps more importantly to the paper, other potential explanations for the deviations between the measurements are not explored. These could include (but it probably not limited to) changes in the degree of graphitisation, the presence of metals (e.g. potassium) interfering with the analysis, surface functionalization of the soot and the presence of macromolecular organics (e.g. PAHs, humic-like substances). In addition, the optical transmittance measurement could be further confounded by variations in the mass attenuation cross section, the presence of 'brown' carbon and scattering artefacts on the filter. While the presence of charcoal could be an explanation, this should be presented as a speculative hypothesis rather than a supported conclusion if the other explanations cannot be discounted. The discussion should also seek to include other potential explanations, again if only in a speculative manner. In particular, I would like to see the possibility of the humic-like substances generally present in biomass burning aerosols being responsible to be discounted.

AC GC-3: We have reworded the manuscript to make our use of the word charcoal a more general term rather than an absolute definition. Within the text, we are now using the phrase charcoal-like which could include humics, PAH's, and other organic combustion-derivatives. We have also inserted references which detected charcoal in marine sediments, supporting our claim that it can be found in a remote environment. We agree that charcoal is also an operational definition and we do not have the data to definitively support that the pyrene fluorescence loss technique quantified charcoal. In the text, we now describe that the pyrene fluorescence loss method detects carbonaceous byproducts including, but not limited to, the presence of humic acids or large polycyclic aromatic hydrocarbon structures, changes in the degree of graphitization, or non-thermally refractory incomplete combustion byproducts.

RC GC-4: There are a number of instances within this paper where the authors do not demonstrate a good knowledge of the literature from the recent decade or so, in particular with regards global aerosol modelling. I have pointed out a few of these in the specific comments, but given the considerable advances in the field over the previous 10-15 years, I suggest the authors strive generally to provide more up-to-date references.

AC GC-4: We have addressed this in the specific comments section; we have included more recent literature regarding organic carbon and black carbon-like aerosols via direct measurements in remote marine regions in addition to including some recent model studies from currently used models, such as NCAR CCM3 IMPACT and GISS ModelE. More recent references inserted include, but are not limited to: Koch et al. 2007, Liu et al. 2009, Spracklen et al. 2008, and Hodzic et al. 2010, Bond et al. 2013, Wang et al. 2013.

RC SC-1: Page 29787, line 10: A more recent review of atmospheric black carbon instrumentation should ideally be cited, as there have been major advances in some fields in recent years, in particular laser induced incandescence (LII).

AC SC-1: We have adapted lines 8-10 to be in accordance with Petzold et al. 2013, including newer approaches including LII. We have updated this list to include that the current technical approaches for BC/EC analysis include: light absorption, thermal radiation, thermal carbon evolution, Raman spectroscopy, and microscopy.

RC SC-2: Page 29791, line 25: The authors should clarify this. Are they saying glass fibre filters were used in error? Could this have affected any of the other measurements? Do the authors not have some other way of verifying what material was used for the filter?

AC SC-2: 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. Likewise, we have also analyzed GFF and QFF via the CTO method and the same inherited blank is output for both (this will be expanded in a later specific comment). 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. The TOT method used here saw that samples 1 and 22-24 shrunk after analysis which is best explained if a glass filter rather than quartz filter was used. We had collected filters using both quartz and glass on two co-located high-volume air samplers. We suggest that glass filters were accidently used in place of quartz for the above listed samples. The particle retention of the quartz fiber filters used (Whatman Product Code 1851-865, QM/A quartz air filters) is 2.2µm and the glass fiber filters (Whatman Product Code 1822-866; binder-free glass microfiber filters) is 1.2µm. Based on the results, it does not appear that the greater GFF particle retention measured significantly more BC/EC than the quartz filters.

RC SC-3: Page 29793, line 1: According to this, a precombusted sand blank produced no signal using the CTO-375 method, but earlier in the section, it is stated that this technique had nonzero blanks. Does this mean that the other blanks referred to were not precombusted? If so, this is a problem because the filters used during sampling were precombusted, so the blanks should have been subjected to the same treatment. Or is it that the sand blank produced no signal over the normal blank? Whichever way, this should be clarified.

AC SC-3: We apologize for the confusion regarding the blanks. We have changed the manuscript so that it is explained more clearly in the text. Pre-combusted sand has been used as a methodological blank; no carbon was detected on the sand, thus we propose that there was no BC/EC associated with handling and instrumental analysis. For additional quality control, we also measured blank filters. These blank filters were treated identically to sample filters (pre-combusted, storage, handling, etc), however they did produce a residual carbon value for the CTO-375 technique of 1.7 μgC cm^{-2} and 0.04 μgC cm^{-2} for the TOT method. We interpreted this as an inherent blank value associated with each filter that was only detected in techniques which utilized high temperature gas evolution. Since we treated the filters all the same, we assumed that the non-blank was present for all values produced via CTO-375 and TOT. We used the average blank filter value produced by replicates of the laboratory and field blank filters to correct the CTO-375 and TOT data.

RC SC-4: Page 29793, line 9 (and elsewhere): Using a reference from 1996 for modelled organic concentrations does not seem appropriate, as in-use models of secondary organic aerosols have changed beyond all recognition in the intervening time. The authors should obtain a more up-to-date estimate.

AC SC-4: We have expanded our literature and included more recent studies. We supplemented the use of outdated model estimations in place of actual field estimates of both secondary organic carbon aerosols and BC/EC aerosol concentrations in addition to recent model studies. We believe that using other field studies provided a stronger comparison for the purpose of this study. We also have added more recent, and still widely used, model studies from no earlier than 2007 (up to 2013).

RC SC- 5: Page 29793, line 8: Rather than use a qualitative description of the colour, what was the quantitative Angstrom exponent by the optical transmission method?

AC SC-5: We have removed the qualitative color observation from the text. For this specific analysis, the absorption coefficient had been fixed at 16.6 $m^2 g^{-1}$.

RC SC-6: Page 29795, line 21: There is a wealth of material in the literature on BC in South America, in particular looking at biomass burning in Brazil (c.f. the work of P. Artaxo and coworkers). This is unless they are referring to the region of the Atlantic, in which case they should specifically refer to this.

AC SC-7: We had meant the Atlantic Ocean, specifically the region close to the South American continent, but still in the remote marine boundary layer. We have reworded this sentence to be clearer, as we did not intend to look at BC/EC concentration on land/close to the point sources. We also have added in a sentence more clearly defining what "South America" means for our study (i.e. remote ocean closest to South America in this study.).

RC SC-8 Page 29795, line 24: Again, the use of out-of-date modelling studies does not seem relevant, as model representations of BC have greatly improved in recent years. The authors should strive to use a more up-to-date estimate.

AC SC-8: We have replaced or enhanced the literature comparisons to our results with more recent studies. Similar to the SOA, we chose to use field measurements since it is a better comparison for our study. We also included more recent modeling studies (Koch et al. 2007, Allen et al. 2012, Bond et al. 2013; Liu et al. 2009).

RC SC-9: Figure 1: This would be clearer if the four groupings could be labelled. It would also be useful if the sample locations could be labelled with the sample numbers. If necessary, a second figure should be used.

AC SC-9: We have added text to label each region. This suggestion is much appreciated since we believe the regions we defined in the text are easier to visualize if they are depicted in Figure 1.

RC TC-1: Page 29788: The description of the thermal-optical technique is not correct. The initial heating to 800_C is performed in an oxygen-free atmosphere to remove any organic carbon. The sample is then cooled and then a second temperature ramp is performed in the presence of oxygen to burn off the EC. The EC is typically oxidised at much lower temperatures. The authors should refer to Birch and Cary (1996) for details and revise accordingly.

AC TC-1: We have edited our description to be more accurate in the Introduction portion according to Birch and Cary (1996). We do note that the actual analysis was an adaptation of Birch and Cary (1996); the EC analysis occurred in an oxidizing environment with varying temperature time steps up to 870°C. Thermal optical transmittance (TOT) is another "thermal" method. Here the sample is first heated under an oxygen free atmosphere to evolve off all organic carbon. After cooling a second temperature ramp is performed in the presence of oxygen, evolving the elemental carbon. Pyrogenic carbon formation (charring of organic carbon) is corrected for by using laser transmission (Birch and Cary 1996).

RC TC-2: Page 29790, line 21: Please clarify what is meant by 'inorganic carbon'. I'm guessing the authors mean carbonate, but many would consider 'inorganic' to include the elemental carbon in soot with this definition.

AC TC-2: We have changed inorganic carbon to carbonate carbon.

RC TC-3: Page 29797, line 23: For the sake of consistency, the supplementary material should be referred to as such, rather than 'aux information'.

AC TC-3: We have changed the in-text citation from aux information to Supplementary Material.

RC TC-4: Figure 1: Given that there is very little useful information in the higher latitudes, this figure would be more efficiently presented in a rectilinear projection (the current one appears to be a Mercator).

AC TC-4: We acknowledge that a Mercator projection is poor for higher latitudes, but we felt that the majority of the back trajectories originated from the subtropical region (better represented in data). The rectilinear projection does not appear as clear, especially when we include the aerosol make-up and regional titles. We believe it is best to stay with this current projection. However, we have included a rectilinear project in the Supplementary Materials for comparison. We have made a note in the text that this image is a Mercator projection and that samples 22-24 may have less accurate backward trajectories due to the poorer data amount in the high latitude region.

RC TC-5: Figure 2: Please label the axes and denote the sub-figures with a, b, etc.

AC TC-5: We have added the measurement units into each graph and specified in the caption that the x-axis is the individual filter number.