

This work provides estimates of black and total organic carbon aerosol collected with TSP samplers from 4 regions in the marine boundary layer of the Atlantic. The datasets are novel and the study is potentially suitable for ACP(D) after major revisions.

## **Major comments**

### **Introduction**

#### *Focus of the work*

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 inter-comparisons 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.

To make the manuscript suitable for ACP(D), I suggest re-focusing 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 (P29787L10-19) 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. P29787L16-20. I find it very unusual to mention the project-specific sample names (e.g. QFF9-10) 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 high-fire 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?

The results and discussion section should also be re-arranged 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 CTO-375 or TOT are highly correlated, but lower for the CTO-375. What does this imply for e.g. the potential recalcitrance, heat absorption or chemical reactance of BC or the combustion conditions?

#### *Inadequate use of terminology and interpretation of results*

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 statements 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.

The definition of EC ('EC is a highly reduced, graphitic-like form of BC... P29788L5-8') 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.

- P29791L2-3 Statement 'The CTO-375 BC fraction is also called 'soot-like' BC' seems out of place. I would move it to the introduction or discussion.
- P29792 What does EBC stand for?
- P29792L19 The authors mention that 'risotto char' was used as a standard. I assume they used the international 'rice straw char' standard material?

#### *Lack of control of filter material and blank*

P29791124-26. 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 pre-baking at 450°C. This might have affected the loading during the sampling.

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

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 pre-baked filter that never left the lab and is analyzed after pre-baking. 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.

*Some of the citations are incomplete*

- P29788L24+ The authors describe the CTO-375 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), 495-498  
Zencak, Z., Elmquist, M., & Gustafsson, Ö. (2007). *Quantification and radiocarbon source apportionment of black carbon in atmospheric aerosols using the CTO-375 method*. *Atmospheric Environment*, 41(36), 7895-7906.
- P29787L8-10. 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), 65-102. (this work is cited later in the manuscript)
- 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, L16601.

## **Methods**

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.
- It would be good to add a table indicating the range of space and time covered by each sample.
- How many samples were collected in each region?
- P29790L26+ Please add abbreviation for TOC

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?

OT-21

- P29792L8 'C' missing in unit

## **Results and Discussion**

On P29794L13-14, the authors argue that  $\delta^{13}\text{C}$  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  $^{13}\text{C}$  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 solely marine plankton'.

On P29796L7-9, the authors argue that C4 grass combustion from African grasslands was not likely a contributor to soot-like BC in the South American region. What about C4 grasses in South America?

African plume.

- 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?!
- P29797L8. The authors state that the BC concentrations in the African plume measured with the CTO-375 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 CTO-375 method.

## Figure and Tables

### 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 it 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<sup>a</sup>), 4 & 5 refer to the CTO-375 method. I suggest switching column 2 & 3, and indicating the method and putting the units inside the table.

### 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 OT-21.

Remove 'the' in front of chemothermal oxidation.

### Figure 1

In the caption, I do not understand the abbreviation 'IRMS' referring to

**Writing style**

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.]

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

P29789L10 Instead of 'there is also little information available', I recommend changing this statement to 'There is, however, little information available...'