**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Particle characterization at the Cape Verde atmospheric observatory during the 2007 RHaMBLe intensive" *by* K. Müller et al.

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Response to the reviews and the comment by A.A.P. Pszenny and W.C. Keene

General

First of all the author thank both the unknown referees and also A. Pszenny and W.C. Keene for their helpful and constructive remarks for the improvement of the manuscript as a whole by clarified discussions with additions and changes where necessary and a deeper discussion of the analytical observations. The three comments will be addressed one by one in following.

A - Response to the comments of referee 1:

To 1. General comments

The main goal of the manuscript was to describe the findings in the aerosol measurements during the RHaMBLe campaign in May and June 2007. The much longer series of filter measurements and the detailed results will be described in a separate publication. The few long term data discussed and shown here (Figure 6) should help to characterize the aerosol situation during the campaign in a context to these nearly continuous measurements. The campaign took place during a period of low continental influences to the sampling site which is normal for the time of the year but the Saharan dust event immediately before the campaign has influenced the first two days of the campaign considerably.

To 2. Specific comments

2.1.: An explanation of the acronym and the main goals of RHaMBLe will be given in the revised version.

2.2.: In the case of OC/EC analysis the referee was wrong. In the abstract was clearly written that the value of 1.25 μg/m^3 for EC was the maximum influenced from the continental air masses at the very beginning of our measurements. The mean of EC and OC during the campaign was not given but it is found to 0.35 resp. 0.63 μg/m^3 including the first three days. This will be included in the revised manuscript. In the time between 16th May and 14th June the mean of OC and EC was found to 0.24 resp. 0.41 μg/m^3 without major continental influences. The OC/EC analytical method is regularly included in round robin tests in Schmid et al. (2001), INTERCOMP2000 (ten Brink et al., 2004), and EUSAAR (not published). The results in the last 2009 EUSAAR experiments (EUSAAR-2 protocol) have shown that the method used is comparable to the methods with optical corrections, while charring processes cannot be fully excluded but have no significant influences on the results at the temperature of 650 °C used in our method. The impactor samples do not allow a comparison to the optical correction method because the foils are not homogenously covered by aerosol sample.

2.3.: For the Saharan dust iron contents values between 2 and 8 % are available from literature while 3.5 % are typical in most articles. In the most recent publications Lafon et al. (2004) reported from Niger-Harmattan 6.3 % Fe, Guieu et al. (2002) found 4.45 % (2.8 -5.7 %), Bonnet and Guieu (2004) reported 4.5%, Schroth et al. 4.2 %, Moreno et al. (2006) reported values between 1.96 and 4.7 % from different regions in the Sahara. In a modelling study by Hand et al. (2004) 3.5 % for Fe were applied. For estimations 4 % seems to be a suitable value. The impactor design does not allow to analyze the fraction >10 μm. The amount of dust in the fraction above 10 μm depends on the meteorological conditions and the distance to the source region. Major contributions in the coarse mode are expected from mostly local sea spray but not from Saharan dust.

B - Response to the comments of the referee 2:

We do accept the criticism on the introduction in view of the air masses and for the discussion of iron speciation because this is a task for the future and not done during the RHaMBLe experiments where the focus was to characterize the constitution of collected PM for ionic material as well as the traces of OC and EC and metals. Hence, the introduction wille be re-written as will be the interpretation of the back trajectories. For the corrections of the style and language errors the authors thank the referee.

Specific comments: 3.: The explanation of the use of Nuclepore polycarbonate foil pieces and aluminum foils may be a bit confusing. We will rewrite this section to clarify that Nuclepore polycarbonate foil pieces cover between 7 and 10 % of the aluminum foil. Only the polycarbonate foils were used for the metal analysis. This piece was not weighed but the PM spot number was counted. Only the aluminum foils were weighed and the total mass of the impactor stage was calculated by the assumption that every sample spot has the same mass. In earlier experiments we have verified this assumption by multiple OC/EC analyses from on impactor stage. Stage 5 of the impactor has only 15 jets. The problem for the metal analysis is the size of this spot. The spot has a diameter of 6 mm and the irradiated area of the sample in the TXRF has a diameter of 10 mm. To fix the sample at the correct place of the sample holder the sample

must be visible. The sample holder has a diameter of 30 mm and the irradiated area is exactly in the middle. To fix the sample correctly a few mm of tolerance were needed. 4.: Here we made a mistake: not the aluminum foil is meant but the impactor sample. The 7-10 % of the impactor stage area are covered by Nuclepore polycarbonate foil for metal analysis. 10.: Here the same as for reviewer 1 applies: For the Saharan dust iron contents between 2 and 8 % are published. In latest publications Lafon et al. (2004) reported from Niger-Harmattan 6.3 % Fe, Guieu et al. (2002) found 4.45 % (2.8 -5.7 %), Bonnet and Guieu (2004) reported 4.5%, Schroth et al. 4.2 %, Moreno et al. (2006) reported values between 1.96 and 4.7 % from different regions in the Sahara. In a modelling study by Hand et al. (2004) 3.5 % for Fe were applied. For estimation 4 % seems to be a suitable value.

11.: Here we mean the water content of a single particle of this size with its chemical constitution at the atmospheric conditions (temperature and humidity) and not the water content of the collected PM after conditioning under constant temperature and humidity at the weighing room.

13.: The size distribution of the dicarboxylic acids is a finding worth to discuss. Impactor measurements by Hsieh et al. (2007; 2009) from a suburban region in Taiwan were not comparable but in both papers similar observations were reported. The discussion of succinate was coupled to sea spray influences for observed high concentrations in the supermicron modes. No clear indications are given for this observation and the authors do not speculate about origin or processes of formation.

14.: Already explained under 3.

15.: For Figure 1 we used the 500 m back-trajectories which not show that a contact to the African continent took place. The back-trajectories near the surface can be calculated too but with high uncertainties. From these circumstances you have to state that these modeled back trajectories cannot give an exact trace. Uncertainties are possible. In Lee et al. (2009) back trajectories calculated using another model are

given which show a contact to the African continent at 15-May-2007. Our samples of the first two days (14 and 15 May or Julian days 133 and 134) are heavily loaded by Saharan dust which can be shown by the analytical results (cf. Fig. 2-4 and 8-9).

19.: Here we discuss our own measurements during the years 2007 and 2008 which are shown in Fig. 6.

20.: MSA data are published very often but not often connected to DMS and nss-sulfate. Kouvarakis and Mihalopoulos (2004) stated clearly that a point to correlation between MSA and DMS not exist while for MSA and nss-sulfate these correlation are reported by several authors (e.g., Bates et al., 1992, Allen et al., 1997).

21.: The water uptake by the filter itself is an important component and the absence of dust PM measurements are meant here. This has to be clarified in the revised version.

23.: The bromine depletion is probably not fully understood. We do not see really wrong measurements or severe errors in handling for either one of the two groups but we try to discuss possible causes for the analytical results. The concentration of bromide is very low in all samples. Near the detection limit of the IC method uncertainties are high but not that high as reported. Allen et al. (2009) show in their Fig. 11 high depletion of Bromide and Chloride near Cape Verde from ship cruise measurements. The samplers stood side by side on the top of the CVAO tower during the experiment.

28: The Fig. 5 will be corrected and the concentration unit $\mu g/m^3$ will be inserted.

C - Response to comments by Pszenny and Keene:

Reasons for different bromide concentrations The authors see the problem of the comparability of methods and results for the bromine and bromide analysis by NAA and IC in a similar manner. Differences between both methods cannot explain the differences shown in our Figure 10. The discussion in Barrie et al. (1994) is short but seems to result in nearly identical results for both methods. The Sander et al. (2003) review presents results from many previous experiments. Especially, in data from the tropical

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and subtropical oceans high bromide deficits were reported for the PM size fraction above 1 μm whereas for submicron PM often enrichment was observed. Submicron PM contributes in our samples only up to 15$\pm$4 % of mass. Sea salt particles were found mainly in the two supermicron stages of our impactor samples. The methods for Br determination were PIXE, NAA and IC. Results for the enrichment factor for Br are given in a very wide interval between total depletion and enrichment . The cited non-published data of Arimoto et al. (Sander et al., 2003) from the TEN94 experiments (Tenerife), the results of Baboukas et al. (2000), and the results from Keene et al. (2009) are not far from our data found at São Vicente. In the supermicron PM these authors found EFs between 0.025 and 0.99. Minimal enrichment factors were reported for the size fractions between 1 and 8 μm which delivers the highest percentage of PM mass to our samples. In the revised version of the manuscript our data will be discussed in comparison to experimental findings reported by Sander et al. (2003) as well as by results published after this review (see Table 1).

Non-ionic bromine compounds are mainly gas phase compounds and their content in PM will be much lower than the bromide content. We agree with the discussion that the existence of those compounds in PM is not able to explain the difference between both measurements. We will rewrite this part of the manuscript.

Analytical procedures and QA/QC for our measurements The analytical method and the calibration of our ICs were carried out after GLP guidelines. At every analytical run two sets of five point calibration standards were used in the interval between 0.02 and 2 mg/l with r^2 values better than 0.994 at the beginning and the end. In between a control sample was analyzed, too. Twice a year our laboratory takes part in the WHO round robin tests for rain water analysis, until now with success. Unfortunately, in these test samples bromide ions are not analyzed.

The discussion of Bromide was concentrated on the filter samples and the two coarse mode fractions (1.2-3.5 μm and 3.5-10 μm) of the impactor knowing that the determination of Bromide in lower impactor stages at concentrations in the range of the detection

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limit or below is not really possible. The difference between bromide concentrations measured in our samples and those of Pszenny and coworkers is not understood accepting the differences in sampling systems, sample treatment and analytical methods. An analytical error of that size is impossible. The different sampling inlets PM10 and TSP can explain some of the differences and the non-ionic bromine compounds can contribute only insignificantly. The coarse mode PM (dp > 10 μm) can contribute to about 50 % to total Bromide (cf. Fig. 3l in Keene et al., 2009).

Calculation of bromide and chloride depletions The determination of the Br depletion was made according to the Sander review. As the calculation basis for sea water we have used the element ratios given by Sander et al. (2003) after Wilson (1975). In the manuscript sodium was used as the conservative reference element for the Br- and Cl-depletion for the filter samples and the two coarse mode stages of the impactor. The high differences in the chloride depletion to the results of Keene et al. (2009) encouraged the authors to reanalyze the data. A revised discussion of the data set led to the assumption that Na+-data from impactor analyses are biased. All depletion calculations are now performed using Magnesium as the reference element. For Magnesium as the reference element lower bromide depletions and much lower for chloride result for the impactor samples but the depletions for the filter samples do not change much (see Table 2). From this revised calculations the discussion of the chloride depletion will be rewritten but for the discussion of bromide a decrease of the calculated depletion but no significant changes are to be discussed in the revised manuscript.

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Table 1: Selected intervals of Br depletion in supermicron PM samples in tropical and subtropical non-polluted regions from this study and after Sander et al. (2003):

Campaign	Bromide enrichment factor (range)	Bromide enrichment factor (median)
This study filter (PM$_{10}$)	0 - 0.33	0.12
This study, impactor (1.2-10 µm)	0.05 – 0.64	0.17
CGR94, Cape Grim	0.28 (summer) – 0.95 (winter)	0.51
Atl94 and ATL96b, Atlantic oc.	0.07 – 0.99	0.2 (coarse PM)
BEM97, Bermudas	0.025 - 0.722	0.19
SAM81, Samoa	0.18 – 0.81	
Keene et al., 2009	0.13 – 0.55	0.25

Table 2. Revised calculation for the depletion of bromide and Chloride in the PM samples

Ref. Element	Br and Cl depletion [%] PM$_{10}$-Filter		Br and Cl depletion [%] Imp. 1.2-3.5 µm		Br and Cl depletion [%] Imp. 3.5-10 µm	
Na	87.7 (Br)	22.7 (Cl)	89.0 (Br)	33.4 (Cl)	89.3 (Br)	27.9 (Cl)
Mg	**88.0 (Br)**	**20.8 (Cl)**	**82.4 (Br)**	**7.8 (Cl)**	**82.5 (Br)**	**1.0 (Cl)**

Fig. 1. Tables

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