

## ***Interactive comment on* “Chemical composition of boundary layer aerosol over the Atlantic Ocean and at an Antarctic site” by A. Virkkula et al.**

**A. Virkkula et al.**

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REVIEWER #1: The paper reports the finds from chemical filters collected by three samplers high volume air sampler (HV), a virtual impactor (VI) and a small deposit-area low pressure impactor (SDI), during a cruise from Germany to the Antarctic to supply the Aboa a Finnish Antarctic research station. The paper is well written and analysis and interpretation of the data appears to have been done with care. There are a couple of interesting findings which warrant publication such as the use of Pb210 as a marker for biomass burning. Many of the findings from the cruise have been previous published in several other papers which are frequently referred to. This splitting research into fine segments to maximise publications limits the worth of the individual components an where they must be continually accessed for results makes the reading of a manuscript tiresome.

REPLY: It may indeed seem that the reason for splitting the paper is to maximize the number of publications. This is not true but a discussion for the reasons for the split is out of the scope of the journal.

REVIEWER #1: Inclusion of a map showing the actual route of the cruise and indicating the differing air mass regimes mentioned in the text would have been a useful additional figure.

REPLY: We have included the route and trajectory picture as Figure 1 and changed all figure numbers accordingly.

REVIEWER #1: Sampling from the ship was through an inlet. Nothing is said of possible losses through this large diameter sample line. Although only one result is shown from the Aboa Antarctic base we do not know how the samplers were installed there, with or without the same sampling line.

REPLY: We have now described both loss calculations and the sampling at Aboa in more detail.

REVIEWER #1: On page 17 the authors suggest that Pb210 may be attaching to the surface area of aerosols. This is extremely likely. Indeed the epiphaniometer developed at the Paul Scherrer Institute, Switzerland for measuring aerosol surface area relies on the Pb211 isotopes attaching to aerosol surface area and is generally found to be more efficient for accumulation mode particles. If Pb211 successfully attaches to aerosol surfaces then it is a reasonable assumption that Pb210 will also do so.

REPLY: This was a very useful comment and it and a reference to the epiphaniometer has been added to the manuscript.

REVIEWER #1: Figure 1 shows the concentration for a number of ions from the 3 different samplers. Nitrate and ammonium concentrations are generally found to be lower from the high volume sampler compared to the other two. This is presumably due to the cut off size which was 3  $\mu\text{m}$  for the HV and 10  $\mu\text{m}$  for the other

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two instruments. As the SDI had 12 stages and the latter two collected particles  $>4 \mu\text{m}$  would it not have been of value to compare the first 10 stages of the SDI which would should give a closer comparison of aerosol collected on the HV sampler. These findings should also be included in Figure 1.

REPLY: We have now included the sum of SDI stages 1-9 to the figure, corresponding to sizes  $D_p < 2.7 \mu\text{m}$  which is close to the estimated cutoff diameter of the HV sampler.

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REVIEWER #2: The manuscript relates aerosol measurements performed onboard an oceanographic vessel during a cruise over the Atlantic Ocean to the Antarctic Coast. Additional measurements performed at the Antactic station of Aboa are also presented. Authors are provided results on bulk and size segregated chemical composition of particles and their variations according to latitude. The subject is therefore appropriate to ACP. The data set provided in this paper is undoubtedly of interest since very few opportunities exists to perform continuous sampling of aerosols over such a North-South transect. However, at this point, my feeling is that the paper remains very descriptive and superficial (in substance, I feel that an aerosol chemistry paper needs more than just an assessment of sea-salt in the coarse mode and OC and sulphate in the submicron range) and does not provide a sufficiently detailed discussion on the results and their implications. More specifically, the use of impactor data is very limited in this paper although it could clearly bring some additional information on the origin of the aerosols and their deposition velocity. Also, a combination of impactor data and aerosol size distribution is a useful way to understand chemical processes involved with the evolution of aerosol properties upon transport. In both cases, the data exists but only a very little fraction of it is being used within this manuscript. One of the reasons may be that results from the campaign are split into different papers in particular for the impactor data (Virkkula et al., submitted to JGR). That certainly leaves less space to the present paper. Unless the discussion goes into more details possibly including the impactor information (not just  $D_p > 1 \mu\text{m}$  and  $D_p > 1 \mu\text{m}$ ), I do not feel it deserves

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publication. Thus, I am very interested to see the more comprehensive analysis of the campaign data.

REPLY: The paper that the reviewer refers to was published earlier this year (Virkkula et al., J. Geophys. Res.. 111, D05306, doi:10.1029/2004JD004958, 2006). As replied to Reviewer 1, a discussion for the reasons for splitting the paper is out of the scope of the journal. In the JGR paper we presented the modal structure of impactor samples so that we cannot replicate but there is another way of using the impactor data. We have now included a short analysis of concentration decrease as a function of particle size as the the ship's distance from African coast increased.

REVIEWER #2: More specific comments are the following: \* One of the interesting features is the very low level of OC throughout the cruise. I would have expected more discussion on the implication of such results considering the O'Dowd et al paper recently published in Science with opposite results.

REPLY: O'Dowd et al. (2004) and Cavalli et al (2004) presented size-fractionated organic aerosol concentrations measured at Mace Head in 2002. Cavalli et al. (2004) presented the average concentrations of water soluble and water insoluble organic carbon for submicron and supermicron size ranges. The sum of the averages of both size ranges was 1343 ng m<sup>-3</sup> in all data. O'Dowd et al. (2004) split the data into the period with low biological activity (LBA) and high biological activity (HBA). The organic carbon concentrations had a very large seasonal variation: in the LBA period, winter, the average total organic carbon concentration was 70 ng m<sup>-3</sup> in accumulation mode particles ( $0.125 \mu\text{m} < D_p < 0.5 \mu\text{m}$ ) and 619 ng m<sup>-3</sup> in the HBA period. During our cruise the samples from North Atlantic were taken in autumn so the marine biogenic contribution to aerosol was probably low. These samples were taken from air that came from the continents so the organic particles were due to pollution. In regions 1 and 2 the average concentrations of POM (i.e., POM<sub>2-4</sub>=1.4EOC<sub>2-4</sub>) were 814 and 723 ng m<sup>-3</sup>, respectively. These numbers are in good agreement with the average POM concentrations, 670 ± 70 ng m<sup>-3</sup>, observed during ACE-2 at Tenerife during pollution

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outbreaks from Europe (Putaud et al., 2000). In region 4, south of Africa, the average POM2-4 was  $123 \pm 64 \text{ ng m}^{-3}$ . This is in agreement with the average concentration,  $70 \text{ ng m}^{-3}$  in the accumulation mode measured at Mace Head during the period of LBA but it is clearly lower than the  $619 \text{ ng m}^{-3}$  measured during the period of HBA in North Atlantic (O'Dowd et al., 2004). Our cruise south of Africa took place in early December which is spring in the Southern Ocean. The difference may be due to differences in the biological activity in the oceans at symmetric times of the year. On the other hand, our POM2-4 concentrations in region 4 were close to the average POM concentrations  $110 \pm 170 \text{ ng m}^{-3}$  observed at Tenerife during ACE-2 in air masses classified as Arctic (Putaud et al. 2000). The ACE-2 measurements were conducted in summer so there is a clear difference in the concentrations measured at MH and PdH as well.

(References: Cavalli et al.: J.Geophys.Res. 109, D24215, doi: 10.1029/2004JD005137, 2004. O'Dowd et al.: Nature 431, 676-680, 2004. Putaud et al.: Tellus, 52, 141-168, 2000.)

REVIEWER #2: I am not convinced by the discussion on the dilution over the Ocean without more information from the evolution of the size spectrum (from SMPS or impactor data) with distance from the Coast. Also the exponential fit may be questioned for some of the graphs in Fig. 7. ( $k$  is not defined in the text, by the way. It is intuitive but should be defined). Again, O'Dowd et al., in their Science paper have identified a marine source of POM. The original hypothesis for deriving half-value distance contradicts this paper.

REPLY: We have now added a discussion using also the impactor data, added also a simple model where the  $k$  factor is defined, and discussed also the marine sources of POM.

REVIEWER #2: Shouldn't the half-value distance be modified according to the average wind speed during transport? Considering this information, what would be the average life-time and how does it compare to literature data?

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REPLY: This comment is true. Actually the life-time calculation would not require just wind speed but instead the time spent by the air parcel over the ocean. The decrease rate was indeed analyzed first using backtrajectories to calculate the time between the last time an air parcel was over the continent and the sampling location. However, there was no clear relationship between the concentrations and the residence time over the ocean. Instead, there was a very clear inverse exponential relationship between the continental aerosols and the distance of the ship from the African continent as presented in the paper now. This suggests that the calculated backtrajectories in that region did not show the true route of the air masses because the origin of several of the analyzed compounds is clearly continental. The exponential fits yielded transport distances expressed as half-value distances. We have omitted the discussion of the trajectories because it gave no reasonable results.

REVIEWER #2: I really believe that the half-value distance should be discussed in consideration with the size distribution from the impactor data.

REPLY: This is true, but our OC, EC, and Pb-210 data are from the HV samples only. We wanted to compare the results with those for the ions and this is best done by using the same HV samples for this purpose.

REVIEWER #2: I don't recall LONGTERM as a subproject of ACE-2

REPLY: See <http://ies.jrc.cec.eu.int/ace2/longterm.html> for details. Some of the results were presented in the PhD thesis: Nuñez M.J.M. Establishment of chemical properties of the aerosol in the North East Atlantic Ocean. Ph.D. Thesis, University of Lisbon, 2002, 426 pp.

REVIEWER #2: The discussion relating the relationship between BC and EC is not very informative (p.11). Both the mass absorption and mineral dust effects are well known. The question is how the present data set contributes to better understanding of the BC/EC relationship.

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REPLY: The EC and BC data were compared mainly for a quality check of the data because EC was used for mass apportionment of the Hi Vol samples. For this purpose the comparison is good. We agree that the data do not contribute to a better understanding of the BC/EC relationship.

REVIEWER #2: I disagree with the use of "chemical mass balance" when the mass is not measured. Apportionment would be more appropriate.

REPLY: The expression chemical mass apportionment has now been used instead of chemical mass balance.

REVIEWER #2: How was the POM measurements performed during Aerosol99? This information is needed if a measurement artefact is used to explain discrepancies between the 2 campaigns. Also, artefacts with OC measurements go both ways. A fraction of POM could have been lost. Were the aerosol99 measurements performed with denuders? Again, a better investigation discussing the 2 measurement techniques would help.

REPLY: We have now also included two additional campaigns for comparison of organic aerosols and described the OC measurements in these a bit more detailed. However, in none of the papers it was explicitly described whether they have or have not used denuders.

REVIEWER #2: Wouldn't it be more logical to use the same conversion factor to compare the 2 sets of OC data from this campaign and Aerosol99?

REPLY: We have now also calculated the POM concentrations with the same conversion factor as in Aerosols99. However, in all the three comparison campaigns: ACE-2, Aerosols99, and at Mace Head in 2002, different conversion factors were used. The one used here was obtained by Russel (2003) using FTIR spectroscopy for marine air samples. In our opinion, of the factors used in the campaigns referred here it is probably the best-founded one.

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REVIEWER #2: Can you provide a reference for the fact that oxalate is exclusively from biomass burning. I expect a fraction to be of secondary origin.

REPLY: Biomass burning is not the only source of oxalate but it is clearly the dominating one. In biomass burning aerosols concentrations may be in the order of several  $\mu\text{g m}^{-3}$  (e.g., Reid et al, 1998) whereas in clean marine aerosols concentrations are some  $\text{ng m}^{-3}$ . It is not clear whether they oxalate is emitted directly or produced photochemically in the atmosphere from gaseous precursors (Neusüss et al., 2002). The analyses of Falkovich et al. (2005) suggested that the dominating source of oxalate is vegetation combustion and not secondary photochemical processes.

(References: Falkovich et al., Atmos.Chem.Phys., 5, 781-797, 2005. Neusüss et al., J.Geophys.Res., 107, D19, 8031, doi:10.1029/2001JD000327, 2002. Reid et al., J.Geophys.Res., 103, 32 059-32 080, 1998.)

REVIEWER #2: I question the validity of acetate and formate measurements using HV samplers. Most is in the gas phase and simply can condense onto the filter.

REPLY: This is true. We have omitted the use of acetate and formate of the HV samples in the discussions. Only the impactor samples' results are presented.

REVIEWER #2: The last paragraph (3.6) is not really informative. Clearly, the human influence is lower in the Southern Hemisphere. No doubt. As for variations of the degree of neutralization. This is all well known. Again, without the use of the complete data set available onboard, the information reported here does not contribute to any new information on aerosol processing over the ocean.

REPLY: The very clear and quantitative relationships presented in Figures 10 and 11 are rarely presented from a cruise between Northern and Southern Hemisphere and we consider them to be worth publishing.

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Interactive comment on Atmos. Chem. Phys. Discuss., 6, 455, 2006.