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Interactive comment on “Hygroscopic properties of different aerosol types over the Atlantic and Indian Oceans” *by* A. Maßling et al.

Anonymous Referee #2

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General comments:

The paper describes and discusses an interesting dataset of aerosol properties (focusing on aerosol hygroscopicity), measured over the Atlantic and Indian Ocean during two campaigns. The material presented is relevant and contributes to a global picture of aerosol properties in which data from oceanic regions are strongly requested. The analytical measurement and analysis methods are sound, and the merit of the paper is in the first place in the presentation of the dataset. However, I also feel that the authors have not made fully use of the opportunities this dataset offers, e.g. in terms of closure with the chemistry data. Data from this multi-dimensional dataset are presented to much in a "linear" way by first discussing air masses, then chemistry one component after the other, then growth factors, then number fractions, etc. . . without looking carefully at the links between all these parameters. Further, there are some flaws and inconsistencies in the data interpretation. The comments below should first be addressed before the paper can be published.

Specific comments:

Page 142: mention the humidity of the first DMA

Page 145: discussion of the residual ions: apart from mentioning the role of sea salt and biomass burning in the residual ions trends, also the dust episodes should be mentioned as they probably also contribute with extra calcium.

Page 146 line 13-14: It is not as generally true as the authors claim that the ammonium/sulfate ratio is "always" higher for the bigger particles: from DOY 32 to 60 the ratio is rather similar to the smaller particles. Was there any evidence for less cloud processing during that period?

Page 146 line 21: It is not proven that during leg 1-2 sulfuric acid prevails: during these periods the amount of residual ions is rather high, so all cations should be taken into account to calculate the ion balance.

Page 147 line 3-5: also the high sub-μm aerosol mass during period 2 is worth mentioning: it shows that mineral dust is extending into the fine aerosol fraction, which is of relevance for the further interpretation of the hygroscopicity and mixing properties.

Page 147 line 15-16: I don't see the function of this phrase; what is the message here in terms of carbon aerosol? I have difficulties following the reasoning in section 4.3, I think omitting "However" (line 25) and "Furthermore" (page 148 line 4) would make the whole more transparent.

Table 1 shows very consistently high mass together with high EC, high OC and absorption coefficient, with two exceptions: period 1 showing increased OC without any other increased parameter and period 2 showing increased mass without increased EC, OC, or absorption. I would suggest to discuss these grouped features, rather than discuss each of the columns for each of the time periods (i.e. replacing sections 4.2, 4.3, 4.4 with one section). It would reduce the amount of text but make the information available in a more integrated way.

Page 148 line 10 - 14: what the authors consider as a key result seems rather obvious and "as expected" to me: only continental air masses contain EC. EC is known for a long time to be a tracer for anthropogenic influence, hence lines 15-22 seem a bit superfluous.

What is the difference between a "polluted" air mass and " an air mass that had land contact before reaching the ship"? Compared to the oceanic background, also the second can be considered as a polluted air mass. So I don't see why they should be distinguished, as basically the presence of EC and increased mass defines the presence of pollution.

Page 149 line 5: if the detection limit of the PSAP is $0.34\mathrm{Mm}^{-1}$, what does a value of $0.08\ \mathrm{Mm}^{-1}$ in Table 1 mean?

Page 150 line 11: considering the chemical composition during leg 1 and 3, showing high concentration of sea salt in the sub-μm particles, one would expect to find the highest growth factor during those periods. This is inconsistent with what is written here. This needs to be addressed!

Page 150: the periods mentioned in line 24 are inconsistent with the ones mentioned in line 27 (only 3 and 4) and page 151 line 9 (only 9)

Number fractions (page 150 -151): again, I would like to see a more synthesizing discussion: if high EC corresponds to high number fractions of less hygroscopic particles in period 4, why is this not the case in periods 9, 10, 12 and 13? This is a crucial issue: it probably has to do with the aging of the aerosol and the time scales for the transformation of hydrophobic aerosol into hygroscopic.

Page 152 line 5: The reasoning is quite obscure; I don't see what "Although" refers to

Page 152 line 18-19: I don't think it has to be emphasized that growth factors at 75%

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are lower than at 90%, this is very obvious.

Page 152 Line 24: in stead of "distinguished" use rather "separated in 2 modes" (otherwise it could be interpreted as if the modes were not observed).

It is not very clear to me what kind of information the discussion on the 75% RH growth factors adds. What is meant by the phrase (line 152 line 24) "The growth factors of the . . . correspond . . . for this particle fraction."? Also the phrase following this one is unclear. If the 90% growth factors already indicated high amounts of soluble material, obviously the 75% growth factor will confirm that.

Sections 4.5.3. and 4.5.4: how could these observations be explained in terms of chemical composition? What is the relevance of these observations? Results should not only be mentioned but also discussed.

Page 155: from the parameterization it results that larger particles have a higher GF than small particles. The Kelvin effect plays certainly a role here; it is not very difficult to make an estimate and see if this can account for the difference (see e.g. Hameri et al (2000), JGR 105 D17, pp. 22,231 - 22,242) . The authors seem to have completely forgotten about the chemical composition at this point: what does this tell about sea-salt and the difference between 150 nm and 250 nm particles? Initially this period was not indicated as one with significant amounts of sea-salt in the fine particles. In fact Fig. 2 shows that at the end of leg 2 (period 7) there are more residual ions (which?) in the 150 nm particles than in the 250 nm particles.

Page 155 line 6 Replace "considering only one type of air mass" with "for this given air mass".

Is this behavior also observed in other air mass types? How can this in general be related to the chemical properties of the air masses and the chemical properties of the 2 sizes considered?

I would suggest to make a figure presenting the GF(90%) as a function of diameter for different air masses.

Page 155 line 10: Figure 10: there is more difference between marine 6 and marine 8 than between marine 8 and continental 9. How can this be explained? How does period 7 fit in here? Suggest to include this period also in this figure.

Page 155 line 18 - 20 "Differences in . . . increasing RH" If I understand well, this is basically a repetition of the previous phrase (line 14) "At low RH . . . "

Page 155 lines 20 end further are somewhat unclear and ambiguous. Suggest: "A possible reason for this effect of RH could be that at high RH the growth factors for more and less hygroscopic particles are observed as separate modes, whereas at low RH, these modes are no more resolved. This results in a common single mode GF which underestimates the more hygroscopic growth factor, and overestimates the less hygroscopic one."

Using "..these fractions were mixed.." is confusing as it gives the impression of internally mixed aerosol.

Page 155 line 24: What is meant by ". . . but only somewhat explain. . . "?? Does this mean that Tables 5 and 9 are useless for polluted air masses?

Page 156 line 6 - 7: Suggest to add: "As was mentioned before, less and more hygroscopic . . . "

I can not agree with the interpretation of Fig. 11. To me it seems that the sharp increase from 75% to 90% is likely to be a consequence of the overestimated growth factor at 55 and 30%; if these would be replaced with their actual low-hygroscopicity value, the increase would be much more smoothly.

I wonder if it would not be possible to obtain 2 hygroscopicity modes anyhow at these low RH. I presume the merged mode is broader than a single "pure" mode; by assigning a fixed width (eg known from the modes at 75%) to the 2 modes it must be possible to fit two neighboring modes with different GFs. As long as a proper GF estimate for the

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less hygroscopic fraction at low RH can not be made, the discussion and speculations on what might cause the trend is useless. EC and OC probably contribute to the less hygroscopic fraction, but this does not necessarily explain such a trend.

Section 4.6. I think it should be described again how the solubility model is applied. I presume it was as follows: from the chemical composition field data the ratio ammonium/sulfate is obtained; a set of GF corresponding to different ammonium/sulfate ratios is compiled in the lab. The lab GF corresponding to the measured composition is then used as gf$_{empirical}$in equation (2) from which the soluble fraction is obtained. Has the Kelvin effect been taken into account to calculate the soluble fraction for 50 nm particles?

My question: is the GF(90%) strongly dependent on the ammonium/sulfate ratio? I don't think it is, and in that case the soluble fraction trends show exactly the same as the GF: e.g. larger particles have more soluble material (a higher GF, as said before). Strange enough, now the authors use again the argument of longer residence time in the atmosphere, whereas on page 155 the higher GF was attributed to the Kelvin effect and sea-salt. Page 157 lines 12-13-14 are in fact the same as page 151 lines 1-2-3.

Having made the effort of calculating the soluble fraction, one can make an interesting comparison with the impactor data: how does the soluble fraction compare to the ratio (sum of ions)/(mass) for 250 and 150 nm? Is it possible to make a statement on the composition of the internally/externally mixed particles, using the data from soluble fraction, number fractions, and chemistry? Can this support your assumption of EC being present only in the insoluble fraction (page 158 line 4)? It would be really nice to present such a result, rather than producing another time series (soluble fraction).

Finally, in the conclusion it stated that aging processes play a major role in modifying the hygroscopic properties of particles. Knowledge about the time scales of these processes is still lacking, and is strongly requested, e.g. for global modelling. I feel that the dataset presented in this paper holds enough information to obtain some quantitative results on these timescales. It's a pity that the authors have not taken this opportunity, and although it was not within the original scope of the paper, I would strongly encourage them to do so for the final version, while reducing the many wordy descriptions of observed values (I am not requesting it as a condition for publication, I leave it to the authors to decide).

Technical corrections:

Page 136 line 18: add: "of which 3 stages in the sub-μm stage"

Page 137 line 13 - 14: delete "...based on results by taking into account only the hygroscopic characteristics..."

Page 137 line 19: Add: "Although the greenhouse effect caused by greenhouse gases can be ..."

Page 137 line 22 replace "supposedly " with "estimated to be"

Page 138 lines 2-3-4 "For that ...conditions" is basically a repetition of the previous phrase. Knowledge of hygroscopicity does not allow to calculate the size distribution, as it seems from line 4. It allows to calculate the ambient distribution at ambient RH from a distribution measured at a different humidity (mostly dry).

Page 139 line 15: specify briefly why you refer to Bates et al and Quinn et al (for a description of instrumentation? Of the route?...)

Page 139 line 18: "into the region of the Maldives and back to Male" (similar in line 19).

Page 139 line 20: replace "pictured identified" by "shown"

Page 140 line 5-6 is a repetition of the last two lines on page 139.

Page 140 line 11 replace "Sahara Desert" by "(Saharan) mineral dust" (are you sure it was from the Sahara and not from the Sahel?)

Page 142 line 26: "and the sum" should be: "to the sum"

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Page 149 and forward: 50-nm, 150-nm etc. . . : leave out the "-"

Page 156 line 25: delete "because the molar . . . < 308 nm"; is a repetition of the first phrase of the paragraph. Replace (Fig. 2) with (see Fig. 2).

Further: there is often improper use of "However", "Therefore", "Although", "Furthermore", causing confusion. E.g. page 155 line 19: "However, these differences. . . " This phrase enhances the statement made in the previous one (". . . are much more significant for low RH"), hence it should start with "Indeed", rather than with "However" which is used to introduce a contrasting statement.

Other examples of improper use: page 147 line 25 (omit However) , page 148 line 4 (omit Furthermore), page 152 line 5 (not clear what is meant), page 157 line 1 (omit Therefore)

Figures:

Indicate in figure caption 1a and 1b what the numbers near the trajectories mean.

Figure 4: what does "residual ions" here refer to? It causes confusion with the residual ions from figure 2. If it is all ions, then just write "ions".

Figures 5-6-7-8-12 are practically illegible.

Figures 9-10-11: indicate what the error bars mean.

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