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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Model study on the dependence of primary marine aerosol emission on the sea surface temperature" *by* S. Barthel et al.

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We thank the reviewer very much for the critical reading of the manuscript and naming some critical remarks, which led to an improved article. We summarized the review below and our responses to the points are indented and italic.

The authors have chosen to use the PMA source function of Long et al. (2011) as their baseline parameterisation. Not only do the authors justify this decision based upon comparison to only a single station, seemingly ignoring comparison to all the other stations described in the manuscript, they also fail to include any depiction of how

good the agreement between model results and observations was. They must turn what is currently a qualitative justification of their choice based upon a single station into a quantitative assessment based upon all the data at their disposal.

- Cape Verde was not the only station for the justification of the use of the PMA source function of Long et al. 2011. Using a further model domain we compared them also for the European measurement sites, but this comparison was not included in the manuscript. In the corrected version we include also results for the European model domain for June 2006. We compare the four parameterisations mentioned in the manuscript (Fig. 3) with the SST-correction of Sofiev et al. (2011). We added a further section to the manuscript describing the performance of the different parameterizations in addition to showing the results for Cape Verde: "4.2 Validation of the PMA source function As mentioned above, several different parameterizations to compute the PMA emission flux exist. Fig. 2 shows a comparison of measured sodium concentration at EMEP stations and CVAO compared to model results obtained with four different parameterizations. All simulations were conducted with the SST correction function of Sofiev et al. (2011), which resulted in the best agreement to measurements in the Figs. 6-9. To minimize the influence by the SST-correction function the measurement period of June 2006 was used for the model simulations regarding the EMEP-observations. These results are shown in the scatter plots of Fig. 10, where the left panels show only results for air masses, which arrived at the station less than 6h after leaving the coastal region. The modelled and measured sodium concentrations in the PM1 size range are compared in the top panel. In that size range only the data from Virolahti II and Melpitz are available. Since Melpitz is far inland the six-hour-plot shows only data of Virolahti II. The highest model values were derived with the PMA-source function of Sofiev et al. (2011) (purple). The lowest sodium concentrations are modelled using the MMS-combination (blue). The results for all parameterizations are close to the measurements. While the higher model concentrations by Sofiev et al. (2011) and Gong (2003) agree well to the measurements for lower concentrations, the results by MMS and Long et al. (2011) are in better agreement for higher concentrations. At Melpitz

all parameterizations lead to underestimated model concentrations. For PM1 data it cannot be decided which parameterization leads to the best fit. The model results for the different source functions for PM2.5 (middle panel) are similar to the PM1 results, with Sofiev et al. (2011) resulting in the highest, and MMS to lowest concentrations. However, in this size range no qualitative difference between the six-hour and the total data is found. For low sodium concentrations the model results are close to the measurements with a slight overestimation by Sofiev et al. (2011) and Gong (2003) and a slight underestimation by Long et al. (2011) and MMS. For higher measured concentrations the model underestimates the measurements for all source functions. For this size range the model results of monthly averaged sodium concentrations using Sofiev et al. (2011) are closest the measurements. Like PM2.5 the sodium concentration in the PM10-PM2.5 size range shows no clear difference between the six-hour and the all-data results. Here the lowest concentrations are obtained by Long et al. (2011) and the highest by MMS. The results using Sofiev et al. (2011) and Gong (2003) are close together and closer to the MMS-results. While the low values of Long et al. (2011) underestimate the measurements and the overestimation by MMS is small, all three functions (Gong (2003), MMS, Sofiev et al. (2011)) are close to the measurements regarding the monthly averaged value as well as the regression to the 1:1 line. The comparison of the results for Cape Verde in December 2007 are shown in Fig. 11 for all five stages of the Bernerimpactor, with the first and the second stage merged together. For the first/second stage all parameterizations are close together, only Gong (2003) results in slightly lower concentrations. In the third stage Sofiev et al. (2011) and MMS overestimates the measurements while Gong (2003) and Long et al. (2011) are close to the measurements. For the forth stage all model results are in good agreement with the observations. The strongest difference between the source functions exists for the fifth impactor stage, where the modelled concentrations for all parameterizations except Long et al. (2011) overestimate the measurements. The comparison of the results for Cape Verde in December 2007 are shown in Fig. 11 for all five stages of the Bernerimpactor, with the first and the second stage merged together. For the

first/second stage all parameterizations are close together, only Gong (2003) results in slightly lower concentrations. In the third stage Sofiev et al. (2011) and MMS overestimates the measurements while Gong (2003) and Long et al. (2011) are close to the measurements. For the forth stage all model results are in good agreement with the observations. The strongest difference between the source functions exists for the fifth impactor stage, where the modelled concentrations for all parameterizations except Long et al. (2011) overestimate the measurements. The good agreement of Long et al. (2011) to all stages of the Berner-impactor at Cape Verde, while tending to underestimate sodium concentrations at the EMEP-sites may hint at the effect of the SST-correction function. While the EMEP-stations are influenced by seas with water temperatures between 6 and 15°C, the marine aerosols detected at Cape Verde originated at the ocean with a SST between 18 and 24°C. Since the emission rates with the used SST-correction function are equal to the original source function for 25°C, it was decided to use Long et al. (2011) as base source function for this study. However, the choice of source function should be of less importance for the investigation of the SST-effects."

The measurement data used in this work are primarily the concentrations of sodium (Na+) in air obtained during two EMEP intensive measurement periods in June 2006 and January 2007. Here low volume samplers equipped with quartz filters were typically used to collect PM10 and PM2.5 (or PM1). The PM samples are then used for weighing and subsequent chemical analyses. Such samplers employ an aerosol cut-off at ambient relative humidity (RH) which given the high hygroscopicity of sea salt aerosol means that the actual size cut-off of the sampler will be highly dependant on RH. In Figure 1 an example of the hygroscopic growth factor of NaCl is given. At elevated RH (not uncommon at coastal stations in the marine boundary layer (MBL)), the actual size cut of the dry particle diameter (Dp) decreases substantially for very hygroscopic particles like sea salt. Under these conditions, the largest particles able to enter the PM10 sampler will be of significantly smaller Dp (e.g. a PM10 size cut is effectively reduced to a PM5 size cut, etc.). If such data are then compared to the model

results a significant mass underestimation will occur. This will apply to all size fractions of the measurement data (i.e. PM1 and PM2.5 also) and undermines the conclusions of the paper given that they are based upon mass differences between the observed and modelled data. I suggest that the authors apply some cut-off to their data, perhaps remove all days where the ambient RH at the EMEP station exceeds RH=80%. That or they could attempt a similar approach to that adopted by Gryth et al. (2014). This will significantly decrease the uncertainty here.

- Of course it is very important to treat the modelled sea salt as wet aerosol at ambient conditions when comparing the sodium mass to measurements by low-volume-samplers. Therefore we calculated the wet sizes using eq. 15 from the manuscript before the comparison. For this the modelled relative humidity was used. We added a comment on this: "It must be noted that the measurement devices sample at ambient conditions while the model treats the aerosols as dry aerosols. Therefore fit the modelled aerosol size must be corrected with the modelled relative humidity using Eq. 15.

Given the authors apparent lack of attention to the quality of the measurement data, a subsequent question which arises is whether there are any quality issues with the data? No mention of quality assurance is made in the observation section of the methods and discussion of whether any data has been removed for quality purposes is absent. Given that only a few months of data from a few stations are used this is a necessity.

- (See also reply to reviewer 1): The measurements in Europe had already been discussed in Manders et al. 2010 (same stations, earlier data), Tsyro et al. (2011) and several EMEP-reports like Yttri et al. (2008) and been used for sea salt model study by Tsyro et al. (2011), who also focussed on the uncertainties. Therefore a further discussion on measurement uncertainties was considered unnecessary. For the station at Sao Vincente a discussion on the measurements and their quality is included in Müller et al. (2010). Here all data were included from that station as no critical values

were found.

Another issue concerns the authors choice of observation stations. As well as choosing some coastal stations to compare to they choose a number of stations which are at best questionably coastal and some which are distant from any ocean. In these instances are the authors testing a source parameterisation in their model or its transport and deposition dynamics? This obscure approach dilutes the message of the paper which according to the title is the effect of SST on the source of sea spray. These stations should be removed.

- The reviewer criticized the choice of the measurement sites for the comparison to the model data. We are not sure which stations where meant with "coastal" and "best questionable coastal" but try to separate them. Since the station at Sao Vincente (Cape Verde) is 70m off the coast and on an island it can be considered "coastal". At Virolahti II the distance to the sea in the south is less then 10km. Birkenes is less then 20km away from the sea in the southeast. Auchencorth Moss is less then 40km inland from the North Sea in the east and Cabauw is also only 40km to the North Sea in the northwest. So we assume that these four stations were meant with "best questionable coastal" and discuss them in general: Depending on the exact direction of the air mass, it will be a relatively short time over land before it reaches the measurement sites. So the continental influence due to deposition will be low. In these cases the stations are assumed to be "coastal". During westerly winds the air mass remains a little longer over the land before reaching Birkenes (around 200km away) or Auchencorth Moss (around 80km away) with a higher influence of the land. Other real coastal stations were not available for the presented regions and time periods. It would have been preferable to add data from Mace Head, which is currently best station for marine air studies. But measurement data for PM10 and PM2.5 from this station were only available for January 2007 and not for June 2006 (Darius Ceburnis pers. comm.). Therefore the station could not be used in this work to show the difference between summer and winter situation. For this reason we have to use these "best questionable coastal" sta-

tions for the revised manuscript. Due to the reviewers suggestion we included the use of air mass trajectories in the discussion. This is explained in more detail in the next item. Another reason for using the stations is that the model simulations were carried out with a horizontal resolution of 28km. Since all stations are less than 40km away from the coastlines all are within the first or the second grid cell from the sea. In these cases the influence of the deposition within the model is small. If the distance from a station to the sea is less than 20km it could happen it is within the same grid cell as the coast. Due to these reasons we think the error made by using these station is less compared to other sources for possible uncertainties. The results for the inland station Melpitz were included since this is one of the few measurement sites providing PM1 data. Since transport and deposition is identical for the model simulations using different emission parameterizations, the differences in concentrations at this station would still respect the changes in the emissions. However, we agree that due to possible misrepresented deposition and transformation processes the results for this station should not be overrated.

Following on from the previous point I would also like to see some basic trajectory analysis deployed. Just how many days at each station were actually likely to contain significant amounts of sea spray? How does the model compare with measurements on these days compared to those less influenced by sea spray?

- (See also response to reviewer 1) Due to the reviewers concerns about the representability of the measurement stations we followed the suggestion and prepared backward trajectories. These trajectories are not directly shown in the revised manuscript. They are included indirectly within the time series figures 6-8 by different point types. Within the analysis the trajectories have also been included by showing additional plots for data where the air mass came nearly directly from the sea taking less than 6 h. The results are discussed with respect to the trajectories, as example: "Like PM2.5 the sodium concentration in the PM10-PM2.5 size range shows no clear difference between the six-hour and the all-data results. [...] Especially for winter Zb13 leads to

overpredictions. The strongest overprediction exists when the air masses reaches Virolahti II from the northwest. Those air masses were influenced by emissions from the Baltic Sea that was at near-freezing temperatures in January 2007. "

The next issue is whether sea ice is included in their model. I could not find any description of this in the methods section so assume that it is not. This is a flaw given the focus on SST and sea spray emission, especially when the correction factor of Zábori et al. (2012) is applied. This dataset implies that the source of sea spray will increase significantly at low SSTs, thus the difference between an SST of 0°C and a region covered by sea ice will be stark. This problem is illustrated by the Virolahti data. The authors note lower sea spray here in the observational data when compared to their model. The authors reason that this effect is entirely due to the low salinity of the Baltic Sea. However, it is clear that the sea spray source region for this station is likely to be highly influenced by sea ice in the winter. Thus, whilst the authors reasoning on salinity effects may well be important, concrete conclusions cannot be drawn.

- (See also response to reviewer 2): We thank the reviewer very much for mentioning the sea ice problem. We found that while COSMO uses a sea ice parameterisation this was not used by MUSCAT. This resulted in modelled sea salt emissions in sea ice covered regions. We fixed this problem and restarted the model simulations for January 2007. In that month the area in the Baltic Sea covered with ice was small. Larger areas of the sea became frozen not before beginning of February of that year (http://www.ijis.iarc.uaf.edu/cgi-bin/seaice-monitor.cgi?lang=e). Thus we found no significant difference for the results at Virolahti with or without considering sea ice. The other stations are less influenced by sea ice. The inclusion of sea ice in the model is mentioned in the revised manuscript: "Further data needed to compute the emission rates are the SST and the sea ice coverage. Both were taken from the meteorological driver model COSMO. While the sea ice coverage is calculated by the model, the SST data fields are directly taken from reanalysed input data of the GME model."

The manuscript presents some comparison of organic sea spray emissions. However,

given the almost complete lack of discussion of this data (limited to a couple of lines in the discussion) this only seems to dilute the take home message of the manuscript which is the effects of SST on PMA. This should either be expanded upon significantly (thereby changing completely the focus of the manuscript) or be completely removed.

- It is state of knowledge that PMA is enriched with organic material. Therefore it is necessary to include primary organics into model studies on PMA. Since we treated PMA as internal mixture of sea salt and organic material, this organic material influences the modelled sodium concentration and therefore must be described. For this reason we keep it in the section of the model description. Since it is included there a section in the results about the OM concentration needed to be included in the manuscript. Inspite of to the reviewers concerns about the taking home message of the article we kept the discussion of organic the results on organic material within the conclusion, what is necessary due to the strongly contrasting results compared to literature. We tried to increase this part to an additional taking home message: “The variability of the modelled OM-PMA-ratio should be increased when using daily resolved chlorophyll-a concentration instead of the monthly averaged values and including of a wind speed dependence to the parameterization. However it has already been reported by Gantt et al. (2012b) that Long et al. (2011) underpredicts the seasonality at all time scales at Mace Head (53.33°N, 9.90°W) and Amsterdam Island (37.80°S , 77.57°E) and overpredicts OM concentrations. In contrast, here this parameterization underpredicts OM concentrations. These contrasting results are likely due to the different model assumptions. While Gantt et al. (2012b) assumed an external mixture of OM and SS we assume an internal mixture leaving PMA emission rates unchanged leading to much lower modelled OM concentrations in the atmosphere. At the moment it is not clear whether OM replaces SS in the emitted PMA or whether it adds to it, increasing the total emission rate (Gantt and Meskhidze, 2013). Therefore both approaches are currently reasonable, however one need to be aware of these strongly contrasting results.”

Many of the figures are illegible in their current form when printed. I cannot comment

adequately if I cannot read the axis labels. Further to this many of the figures are likely redundant. A single set of nicely presented examples followed by presentation of regression stats in a table (regressions between the observed data and modelled data) would suffice and make it much simpler for the reader to see how well the source functions/correction factors fit the observed data.

- Due to the reviewers concerns about the Figures we changed the boxplots from fig. 15-17 to six scatter plots for PM1, PM2.5, PM10-PM2.5 and January 2007 and June 2006, respectively. We also added tables with some statistical analyses. The time series plots were kept in the manuscript, to give the reader an impression about the temporal variation of the concentrations. The readability of the Figures was improved by using larger labels for example. The plots for PM2.5 and PM10-PM2.5 are intended to cover a whole page.

Please refrain from unreferenced speculation in the introduction and limit it to the discussion. For example on P382 Line 22 “At higher wind speeds the concentration of organics in PMA is lower due to decreased near-surface concentration through stronger oceanic mixing” should either have a reference or be removed.

- Missing reference added

P384 Line 2 The statement “The resulting higher residence time in cold waters leads to an increase in the coalescence of bubbles, thus decreasing the number of smaller bubbles and increasing the number of bigger bubbles (Pounder, 1986)” is controversial. To date no systematic study of the effects of temperature on seawater bubble concentrations has been reported, and there have been conflicting reports from the few investigations on the topic (see P.249 of Lewis and Schwartz (2004)). I suggest either removing this statement completely or a more thorough discussion of the range of conflicting results observed.

- Hole section shortened and kept general: "The SST may influence the physical processes controlling the PMA emission flux through bubble bursting via the viscosity of

the water, the surface tension at the boundary between water and air, the molecular diffusivity and the solubility of gases. These properties impact on the coalescence of the bubbles, the gas exchange between the bubble and the surrounding water and the rising speed, thus the residence time of a bubble (Lewis and Schwartz, 2004, and citations therein)."

Throughout the manuscript when stating particle sizes please remember to state the RH. As a couple of examples P384 Line 24 when you state "for particles with diameter between 0.012μm and 1.8μm" do you mean dry diameter or at some RH? Again on P392 Line 3, please be precise and mention the RH.

- Symbols added to all sizes

A number of sentences need rephrasing to add clarity. For example the sentence on P384 Line 24 makes little sense to me, do you mean it to read "Mårtensson et al. (2003) identified increasing particle production with decreasing SST up to a size of 0.1μm dry diameter. The rate of this production increase with decreasing SST was dependent upon particle sizes with the biggest increases at the smallest particle sizes measured."

- We tried to rephrase some sentences, the named one changed into:" Finally, Mårtensson et al. (2003) also found an increase of the particle production up to a size of 0.1μm in dry diameter with a continuous increase of the factor with decreasing particle size."

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