

Interactive comment on “Chemical composition and hygroscopic properties of aerosol particles over the Aegean Sea” by S. Bezantakos et al.

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We thank Reviewer 1 for his/her time and effort. Below are our responses to his/her comments.

(1) I find the correction for 30% RH a little superfluous, but of course this can be done, if the authors find a need. It could be interesting to know does it actually matter much to correct from 30 to 0% RH. Perhaps this was tested as well?

Correcting the HTDMA measurements for the fact that the relative humidity in DMA-1 was at 30% leads to a correction of the measured growth factor of the order of 3 to 6% (as indicated in page 5820, line 15 of the manuscript). Indeed, this correction is small, but nevertheless improves the closure between measured (HTDMA) and predicted (us-

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ing the chemical composition cToF-AMS measurements) growth factors.

(2) A more interesting is the choice of TDMAfit routine, which I find is a little dated. For standardization purposes in contrast to other studies of HTDMA datasets, I recommend the authors to consider using the HTDMA inversion methods from M. Gysel et al., 2009, which the authors should have ready access via shared authors (or just asking Dr. Gysel for access to <http://aerosolsoftware.web.psi.ch/>)

Following the suggestion of the reviewer, we employed the TDMAinv algorithm to invert our HTDMA measurements, and then compared the output with that obtained by the TDMAfit algorithm that we used originally. As shown in Figure 1 below, the difference between the estimated growth factors using the two algorithms is within less than $\pm 2.5\%$ (mean difference being less than 1%). Given this good agreement, we decided to stick with using the TDMAfit algorithm to invert our HTDMA data. In the updated version of the manuscript we discuss the comparison between the output of the two algorithms. More specifically, a sentence was added in section 2.2.2, page 5814 after line 14, which reads:

“Measurements inverted also by the TDMAinv algorithm developed by Gysel et al. (2009) gave hygroscopic growth factors that agreed within less than $\pm 2.5\%$ with those calculated by TDMAfit.”

(3) In general the flights were clearly in the boundary layer, but I would like to know if the 2300m flight sets were well above it (most likely)? Partly this could be got from the measurements themselves, but more independent measure could be to use (freely available) re-analysis data sets.

Indeed, some parts of the flights were within the marine atmospheric boundary layer (MABL) and some above it as the reviewer points out. Detailed information about the structure of the atmosphere and the synoptic meteorological conditions during the flights are provided in a publication that will be submitted to ACP very soon (Tombrou

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et al., 2013). In that work, information on the MABL is extracted based on the vertical profiles of water vapor mixing ratio. As shown in the attached Figure 2, the MABL during both flights was below 1 km (indicated by the plateaus). The MABL during the flight of 1 September was between 0.6 and 0.7 km over the South and North Aegean and below 0.5 km over the Central Aegean (Figure 2a). During the flight of 4 September the vertical MABL was confined at very low levels (below 0.4 km) over the eastern and southeastern Aegean Sea due to the very cold sea surface temperature (Figure 2b). Over the western Aegean Sea the MABL was between 0.5 and 0.7 km, increasing towards the south. The less stable conditions over the northern Aegean resulted in a higher MABL (ca. 0.9 km).

To provide an indication of whether the measurements were conducted above or below the boundary layer, we have added the following sentence in page 5810, after line 22, in the manuscript:

“Considering that the marine atmospheric boundary layer (MABL) was always below 1 km during the flights (for more details cf. Tombrou et al., 2013), some parts of the flights were within and some above it.”

(4) I am a little concerned that no view of the size distributions are shown. This is especially important as the location of the Hoppel gap between Aitken and accumulation mode could affect the growth factor detected. This is very much connected to the Figure 4, as the text explains that the GF measurements were done by setting the dry aerosol diameter to match the dominant mode of the distribution. From the data, it seems that most of the time this was the accumulation mode? This is very relevant, as making any kind of conclusions of the hygroscopic parameters of the Aegean sea, it might be that the selection of the dominant mode for analysis (only) will not give a very fair picture of the changes in hygroscopicity of the aerosol on other sizes. Please comment on this, especially considering that the accumulation mode particles (>100nm or so) will most likely have gone through at least a few cycles in the clouds in contrast to Aitken

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mode particles.

We see the point of the reviewer here. In the updated manuscript we have replaced Figure 2, that originally showed the diurnal variation of the particle concentration in the different size modes, with a graph that shows the evolution of 1-h averaged size distributions. Time series of the number concentration of particles in the nucleation, the Aitken and the accumulation mode for the entire period of the campaign (cf. updated Figure attached) are also shown therein. The updated Figure 2 now matches better with the hygroscopicity results shown in Figure 4 of the manuscript. The text corresponding to the description of the size distribution measurements (i.e., page 5817, lines 4-20) has been updated accordingly. The updated text now reads:

“The evolution of the 1-h averaged particle size distributions as measured by the SMPS, together with time series of the number concentration of particles in the nucleation, the Aitken, and the accumulation modes for all the days of the experiment are shown in Fig. 2. The total number concentration of the particles having diameter from 10 to 487 nm varied from ca. 4.4×10^2 to 1.0×10^4 particles cm^{-3} with median value of 1.9×10^3 . Almost 72.1% of the samples exhibited bi-modal distributions, whereas 14.2% and 13.7% of them showed uni-modal and tri-modal distributions, respectively. The total particle number concentration in the nucleation mode varied from 1.7×10^2 to 3.2×10^3 particles cm^{-3} , with a median value of 7.7×10^2 , in the Aitken mode from 1.7×10^2 to 7.1×10^3 particles cm^{-3} , with a median value of 1.0×10^3 , and in the accumulation mode from 1.8×10^2 to 3.4×10^3 particles cm^{-3} , with a median value of 9.0×10^2 . Most often the particles were observed in the Aitken and the accumulation modes during the entire period of the measurements.

During the period from 30 August to 3 September, the majority of the particles resided in the accumulation and the Aitken modes. The rest of the period was characterized by wider size distributions with particles residing also in the nucleation mode (i.e., particles having diameter smaller than 25 nm). This pattern is well correlated with the variability in the origin of the air masses arriving to the station (cf. discussion in Sect. 3 and

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back-trajectory calculations shown in Fig. S1)."

To investigate potential differences in the hygroscopicity of the particles in the different sizes, we also randomly sampled particles from modes other than the dominant one. The measured hygroscopic growth factors had negligible differences: Aitken mode particles had hygroscopic growth factors ranging from 1.00 to 1.56, with an average value of 1.18, while those for the accumulation mode particles ranged between 1.00 and 1.59, with an average value of 1.21. These observations suggest that the aerosols arriving at our station are well-mixed. To highlight this point we have updated the text as follows:

1. lines 15-16 in page 5818 that read:

"(note that in general the dry diameter was selected to be close to the peak of the most dominant mode of the particle size distribution as measured by the SMPS)."

have been replaced with

". Note that although the dry diameter was selected to be close to the peak of the most dominant mode of the particle size distribution as measured by the SMPS, measurements of dry particles in other modes were randomly sampled to investigate potential differences in their hygroscopicity."

2. A new sentence was also added in section 3.1.2, in page 5818 in line 16, which reads:

"For the Aitken (19% of the samples) and accumulation (81% of the samples) mode particles, the average growth factors were 1.18 (ranging from 1.00 to 1.56) and 1.21 (ranging from 1.00 to 1.59), respectively."

(5) Perhaps one could also think that giving an "average GF" on line 18 of page 5818 is misleading. Average of what? Do you think the sampling is fair in the sense of the particle populations? ..and I would change the abstract to have a comment that the "...particles in the dominant mode were internally mixed..."

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We have added a sentence (page 5818, line 16) which gives the mean hygroscopic growth factors and their occurrence both for the Aitken and the accumulation mode particles (see the last addition in the response to comment 4 above). Line 10 in the abstract (page 5807) was also changed from:

"The HTDMA measurements showed that the particles were internally mixed, having hygroscopic growth factors that ranged from 1.00 to 1.59 when exposed to 85% relative humidity."

to

"The HTDMA measurements showed that the particles in the dominant mode were internally mixed and their hygroscopic growth factor ranged from 1.00 to 1.59 when exposed to 85% relative humidity."

(6) Regarding size distributions and kappas in general: The paper would benefit on some more comparison to the long term measurements on the area (from Lemnos site or from the literature). This is because right now it is very hard for the reader to see if the situations observed during the campaign are very common, special for autumn conditions or very specific case. Any relevance on the other papers and studies would make this much easier for the reader.

We fully agree with this comment. However, no long-term hygroscopicity measurements exist for the wider region of the Aegean Sea. Note that the location on Lemnos (North Aegean) was used as a temporary site only for the needs of the Aegean-Game field campaign. Data on the size distribution of the particles are available for the station of Finokalia on Crete (South Aegean). We have added a sentence in section 3.1.1, after line 27 that reads:

"Particle size distribution measurements for the region of the Aegean sea are only available for the station of Finokalia on Crete (Pikridas et al., 2010). According to that study, the average total number concentration of particles having mobility diameters from 10

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to 500 nm is ca. 2.7×10^3 particles cm^{-3} , which is very similar to the concentrations measured in Lemnos."

Regarding kappa values that can be directly obtained by HTDMA or CCNC measurements, only results from a short-term study is available in the literature (Stokes et al., 2011). A comparison of our measurements with the findings of that study is already provided in the manuscript (cf. section 3.1.3; page 5819, lines 5-15).

(7) The section 3.1.3. mentioned that during the comparison periods there was no difference in the particle composition on the size measured. Perhaps it could be good to remind the reader which sizes the AMS on board can measure, and more importantly was such homogeneous composition also the case over the whole aircraft campaign, at all altitudes. The reported kappas could be size dependent, and I could not find any information on the size distribution changes over the flight campaign route, even though i understand that AMS is not really a good SD measuring instrument. The kappas themselves are interesting of course, but removing the size information can lead to somewhat biased idea which particles had which kind of hygroscopicity.

As already mentioned in the manuscript (cf. section 2.1.1), the size range of the particles that the AMS can measure is 50-700 nm (aerodynamic diameter). Indeed the chemical composition (and therefore the predicted kappa values) can be size resolved. However, because of the small particle mass concentrations observed in the region, the size-resolved AMS measurements tend to be noisy (especially in the range of diameters measured by the HTDMA), and thus we avoided using these data in our analysis. Given that, we assumed that the samples are internally mixed in order to predict the hygroscopic parameter using the AMS data (cf. 5824, lines 9-10). To make clear that the aerosol hygroscopic parameters were estimated using the bulk aerosol chemical composition, lines 5-7 in page 5824, were changed. The original sentence was:

"Using the chemical composition measurements discussed above, we calculate the

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aerosol hygroscopic parameter κ_{mix} (Eq. 4) for the entire path of the two flights as shown in Fig. 9."

and now reads:

"Using the bulk chemical composition measurements discussed above, we calculate the aerosol hygroscopic parameter κ_{mix} (Eq. 4) for the entire path of the two flights as shown in Fig. 9."

For more details on this point see also the response to the second comment of reviewer 2.

(8) Table 1 and pg. 5815 Are the values in table 1 from the Duplissy et al or Petters and Kredenweis? In this case, it should be also mentioned in the table caption, not only in text. The text on pg 5815 ln 23-27 are ambiguous as they are reported now. Are you referencing table 1 of this paper or table 1 of the reference?

The references in Table 1 are clarified now: we use Petters and Kredenweis (2007) and Biskos et al., (2009) to obtain the kappa values, and Duplissy et al. (2011) and Hallquist et al. (2009) for the density values of the inorganic and organic species, respectively. Explanatory footnotes in Table 1 and the corresponding text in page 5815 (lines 23-24) have also been updated to clarify the sources we used for the data.

(9) Figure 2: please keep the captions self-explanatory: add information on which dates this plot is relevant for.

Figure 2 has changed as discussed in our response to comment 4 above. Dates are now clearly visible on the x axis of the new figure.

(10) Use of korg of 0 for organics is quite interesting for (presumably) aged organic aerosol. Do you think that this a reasonable suggestion for aged organics? McFiggans et al, 2006, suggest something in the order of 1.07–1.14 for SOA. On your side, a recent paper by Prisle et al, 2011, seems to use similar assumptions. Some discussion could be nice.

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We thank the reviewer for this important comment. We agree that $\kappa_{org} = 0$ may not be very representative for SOAs. As also pointed out in comment 3 of Reviewer 2, best closure between hygroscopic growth factors that are measured with HTDMAs and CC-NCs and estimated from chemical composition measurements in the field is achieved when the hygroscopic parameter of the organic fraction (κ_{org}) is assumed to be in the range 0.0-0.2 (cf. Martin et al., 2011; Shantz et al., 2008). Taking into account the suggestions of both reviewers we have revised our analysis to seek more representative values of the hygroscopic parameter and the density of the organic species of the particles in our measurements. The values we obtained with the new analysis are $\kappa_{org} = 0.03$ and $\rho_{org} = 1300 \text{ kg m}^{-3}$ for the first flight, and $\kappa_{org} = 0.1$ and $\rho_{org} = 1400 \text{ kg m}^{-3}$ for the second. For the details of the new analysis and the respective updates in the manuscript see response to comment 3 of reviewer 2.

(11) Were there any specific measurements of refractory aerosol on the plane or on the site? This is because the closure was done with the AMS measurements, and large (although unlikely) fraction of EC on the samples might tip the modelled kappas somewhat

Refractory aerosol measurements were conducted using a Particle Soot Absorption Photometer on board the aircraft FAAM BAe-146 aircraft (<http://www.faam.ac.uk/index.php/science-instruments/aerosol/220-psap> for more information). BC volume fractions were almost zero and therefore their contribution to the hygroscopic properties of the particles negligible.

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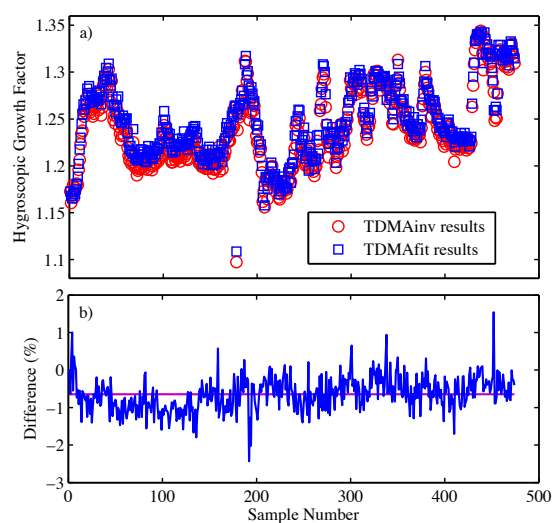


Figure 1: Comparison between the estimated hygroscopic growth factors estimated using the TDMAfit and the TDMAinv algorithms to invert the HTDMA measurements (a), and differences between the hygroscopic growth factors calculated using HTDMAinv and HTDMAfit - the magenta line is the average difference of these two fitting algorithms (b).

Fig. 1.

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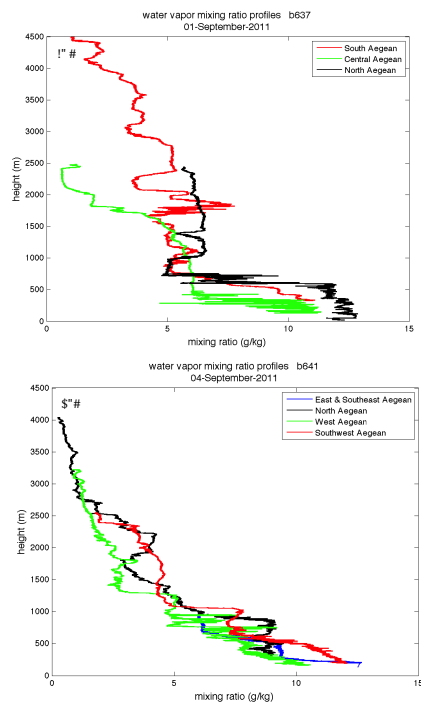
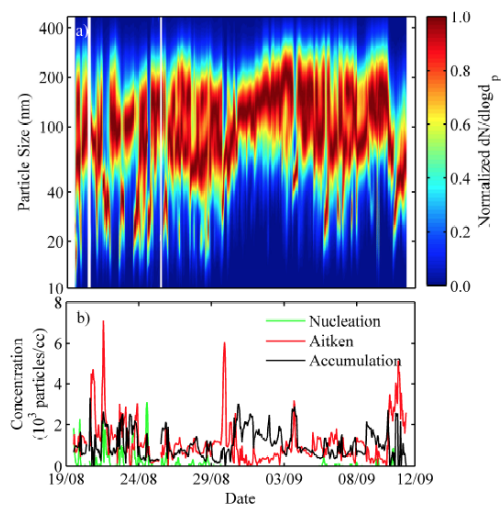


Figure 2. Vertical profiles of the water vapor mixing ratio during the flight on 1 and 4 September 2011.

Fig. 2.

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Updated Figure 2 in the manuscript: Evolution of hourly averaged size distributions of particles having dry mobility diameter from 10 to 487 nm (a), and temporal variation of the hourly averaged number concentration of particles having diameter in the nucleation, Aitken and accumulation modes (b) throughout the whole period of the Aegean-Game field campaign.

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Fig. 3.

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