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Atmospheric
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Discussions

Interactive comment on "Hygroscopic properties of atmospheric aerosol particles over the Eastern Mediterranean: implications for regional direct radiative forcing under clean and polluted conditions" *by* M. Stock et al.

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Your statement: The solubility model in Eq. 3 contains the theoretical growth factor that is calculated using the growth of inorganics. (...) In the last 10 years there have been numerous publications on the hygroscopicity of organics (make a small literature survey and add a few references). Their growth factors are around 1.1-1.2 at 80-90 % RH and it has been shown that they are soluble in water, although weakly. (...)

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Therefore claiming for instance that about 50 % of aerosol in the 30 nm size range (see Fig. 9) is insoluble, is definitely misleading even though it naturally comes out of your equation, I believe that. So, organics and their growth should be taken into account. How would that change your results?

Our response: It is true that the treatment of organic compounds as a single, completely insoluble class of substances is a strong simplification. Organic compounds are, in fact, ubiquitous in the ambient aerosol at Finokalia, with their relative mass fraction moving towards 50 % in the lowest particle size ranges (Fig. 3).

Follow-up measurements to the ARIADNE campaign showed that fine mode organic aerosol is highly soluble, more precisely 75 % of POM (Hildebrand et al., 2010). However, soluble does not mean hygroscopic. Measurements at Finokalia during EUCAARI (Bougiatioti et al., 2009; Engelhart et al., 2011) showed that the water uptake by aged organic aerosol is relatively modest (a few percent of the total water for the conditions during FAME-08) and largely consistent with what has been observed in laboratory experiments. Thus, the water uptake by organics is expected to represent a minor fraction of the total water uptake only. Second, our solubility model is calibrated against the experimental H-TDMA data. Therefore, the effects of organics, as long as they show a similar RH-dependence as inorganics, are already included in our solubility model and, consequently, the radiative transfer simulations. In conclusion, a separate treatment of organics is not expected to alter our results significantly. We will mention this now in the text.

In addition, we added the following text to the Introduction:

“The major portion of hygroscopic particle growth is usually related to inorganic species, such as ammonium nitrate, ammonium sulphate, and sodium chloride, whose hygroscopic growth behaviour is known relatively accurately (Tang and Munkelwitz, 1994; Brechtel and Kreidenweis, 2000). In contrast, the understanding of the growth behaviour of particulate organic matter (POM) has been more patchy, due to the myr-

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iad of individual species involved (Saxena and Hildemann, 1996). This lack of understanding has also hampered a better understanding of the role of POM on climate (Kanakidou et al., 2005). Considerable improvements have, however, been made in the characterisation of individual organic species as well as lump fractions with regard to their physicochemical properties, based on both, laboratory and field measurements (Fuzzi et al., 2006).”

Furthermore, Section 3.1. was rephrased to eliminate disambiguities:

“Gaussian distributions were fitted to the particle number size distribution recorded by the H-TDMA downstream of the humidification step. On the basis of their modal mean diameters, wet particle growth factors gf_{ve} were calculated for sub-micrometer sizes (30–350 nm) from the ratio between wet and dry particle diameters: $gf_{ve} = \frac{D_{p,wet(ve)}}{D_{p,dry(ve)}}$. Using the particle number integrals, number fractions nf for each of the three hygroscopicity modes were determined, with the sum of these number fractions equalling one. Sodium chloride calibration scans performed at 90 % RH were used to retrieve the real RH inside the second (humidified) DMA. The two-component solubility model introduced below was subsequently used to adjust the hygroscopic growth factors to a standard RH of 90 %. This ensures a maximum comparability of the data collected in this work. In a second step, the information on the three hygroscopicity modes in the sub-μm range was merged into an “overall” hygroscopic growth factor gf_{v-mean} representative for the entire particle population at a given $D_{p,dry}$. This was achieved by a volume-weighted averaging of the growth factors using the modal number fractions nf: $gf_{v-mean} = \sqrt[3]{\sum_{i=1}^{3} gf_{i,ve}^{3} \cdot nf_i}$.”

Also, Section 3.2. (solubility model) was completely rephrased. We withdraw the claim to generally derive true “soluble fractions” from the data:

“A simplistic two-component solubility model was employed to predict the hygroscopic growth factors of the Finokalia aerosol for a wider range of ambient relative humidities (30-95 %). This allows to generalise the hygroscopicity measurements, which were always performed at 90 % RH (H-TDMA) and 85 % RH (H-DMA-APS). For simplicity, the model assumes all particles to be internally mixed, each particle containing an insoluble core as well as a soluble shell. The model was calibrated in the sub-μm range using experimental H-TDMA data, and in the super-μm range using H-DMA-APS data. The key parameter of the hygroscopic growth model is a soluble volume fraction ε, derived from the following equation: $\varepsilon = \frac{gf^3_{measured(RH)}{}^{-1}}{gf^3_{soluble(RH)}{}^{-1}}$. ε changes along with the measured hygroscopic growth factors and is therefore a time-dependent "image" of the hygroscopicity measurement. Here, $gf_{soluble}$ is the hygroscopic growth factor of a hypothetical particle consisting only of soluble material and having the same wet diameter as the measured ambient particle. Calculations were performed for all three hygroscopicity groups identified in the H-TDMA and H-DMA-APS spectra. The total soluble volume fraction ε_{tot} was subsequently determined by weighing their individual soluble fractions with their corresponding number fractions: $\varepsilon_{tot} = \sum_{i=1}^{3} nf_i \cdot \varepsilon_i$. An average hygroscopic growth factor (i.e. representative for an entire particle population at $D_{p,dry}$) can then be calculated for any RH by dissolving the Equation after $gf_{measured}$, and inserting $gf_{soluble}$ for the given relative humidity. In the calculations we always assume a particle state above the deliquescence point."

Here we added the section on POM:

"An important question remains the identification of the soluble fraction. Besides inorganic compounds, a significant part of the POM is expected to be soluble (Fuzzi et al., 2006). For the sake of a simplistic description, we restricted the model description to ammonium sulphate as the soluble species in the sub-μm range and sodium chloride in the super-μm range. These two inorganic species are the most prevalent species in the fine and coarse particle mass modes, respectively, and are expected to dominate the overall hygroscopic growth due to their high water affinity. Therefore $gf_{soluble}$ was associated with ammonium sulphate in the sub-μm range and sodium chloride in the super-μm range using the hygroscopic growth factors of Tang and Munkelwitz (1994).

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We are aware of limitations of our model imposed by the neglection of POM species. As evident from Fig. 3, POM is visibly present in the Finokalia aerosol, with mass fractions approaching 50 % especially at diameters around 1 μm and below 200 nm. Due to the diverse observations related to POM-based hygroscopic behaviour, however, it is not straightforward to opt for a generally valid growth mechanism. Laboratory-based work by Varutbangkul et al. (2006), for instance, determined growth factors of atmospherically relevant secondary organic aerosol (SOA) species across a relatively narrow range of 1.1–1.2 at 90 % RH. Massoli et al. (2010) identified, again in the laboratory, a strong and positive relationship between the oxidation state of SOA and their hygroscopic growth factors across a range 1.0–1.4 at 90% RH. For marine and continental environmental aerosols, Gysel et al. (2007) obtained an adequate agreement between measured and simulated hygroscopic growth factors when assuming an organic ensemble growth factor around 1.2 at 90 % RH. Another question is whether POM will mix ideally with the inorganic species, or alternatively partition to the insoluble core, or even a less hygroscopic shell. To make things even more complicated, the presence of a POM fraction can influence the relative partitioning of semi-volatile compounds like nitrate into the particulate and gas phases (Anasari and Pandis, 2000). Nevertheless, several laboratory studies suggest that the ZSR mixing relationship might be a valid assumption for a range of atmospherically relevant organic/inorganic mixtures (Svenningson et al., 2005; Meyer et al., 2009). It also seems that the presence of POM in an internally mixed aerosol prevents the usual recrystallisation of the inorganic compounds. An essential limitation of the ARIADNE study with this respect remains that no detailed organic speciation could be performed. We therefore do not know even the relative contributions of relatively broad POM fractions such as primary or secondary particles. Therefore we preferred to keep the simplistic two-component solubility model. It needs to be kept in mind that the solubility model is calibrated to the experimental H-TDMA data, i.e. information on all soluble species, wether inorganic or organic, is carried into the calculated soluble volume fraction ε. The model therefore preserves the experimental data. Predictions for RH other than 90 % are expected to be accurate as long as the real POM fraction accumulates water along with increasing RH in a similar fashion as the inorganic fraction, and as long as the POM mixes well with the inorganic fraction during humidification. Since the POM growth factors are expected to be much lower than the inorganic growth factors, we believe that the neglection of POM as an individual soluble fraction will have a limited effect on the light scattering calculations conducted later in this paper."

Also several Figure captions and Table captions will be rephrased. We withdraw the claim to generally derive true "soluble fractions" from the data, and refer to an "equivalent soluble fraction" referring to the simplistic two-component model.

Your statement: P26000, Eq (2) Is there some typing error here? If nfi is the number fraction of the group i then isn't the denominator SUM(nfi) equal to one? Should the equation be: nfi = ni/SUM(ni)?

Our response: You are right, our equation contained a mistake. In the reworked version of the manuscript we actually omitted this formula and described it by words, since it is rather intuitive.

Your statement: P25997 L25. In the H-DMA-APS system you determined the growth of two different sizes: 1.0 and 1.2 μm. Why did you select these dry sizes so close to each other? (...)

Our response: The nominal setting of the instrument was 1.0 μm. The diameter of 1.2 μm was additionally selected because it was stretching the measurement to the upper sizing capability of the H-DMA-APS instrument.

Your statements: P25999, L10. You have used the SDI with $Q = 20$ LPM?

Our response: We would like to thank the reviewer for this hint and apologize, since this was a typo. Indeed, the flow of the SDI is 11 lpm and not 20 lpm. We confirmed all calculations are correct as they have been conducted for 11 lpm.

Your statement: P26000 L13-16: "Larger particles with multiple charges were observed

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as a small mode right of the main peak in the particle number size distribution measured with the dry APS. Therefore this mode was not used for the determination of hygroscopic growth." When you observe a mode after the humidification, how do you know know that this new mode does not contain particles from the multiply charged mode that was observed in the dry APS? Isn't there a possibility that these particles might be of some hygrophobic material that wouldn't grow so much and then appear in the same mode as the smaller particles that have grown by humidity. How much would this affect the results?

Our response: In principle the situation described by the referee cannot be avoided. (A similar situation is, by the way, usually found in H-TDMA measurements). Doubly charged particles with different growth behavior than singly charged particles cannot be identified and affect the hygroscopic growth distribution in an unpleasant way. Our observation was, however, that the peak areas of such potentially doubly charged particles were significantly lower (around 20 % and lower) than that of singly charged particles. This is consistent with the larger, multiply charged particles being much less abundant than the smaller singly charged ones, so that their overall implication on the determined growth factors was minor.

Your statement: P26000 L16-18. "Small hydrophobic particles with higher shape factors and the same electrical mobility as the particles of the main peak appeared in the dry particle number size distribution left to the main peak". You write at this point about dry aerosol. How do you know from the dry size distribution that the particles on the left of the main peak were hygrophobic?

Our response: The the mode to the left ('hydrophobic') of main peak in dry APS curve is also seen in the wet APS curve, which indicates that they were hydrophobic. (there was no additional mode even smaller/further to the left of the 'hydrophobic' mode in the dry APS, that might have grown and be mistaken as the 'hydrophobic' mode in the wet APS). We therefore offer to include one or two additional sentences in the manuscript: "In addition, the calculation of hygroscopic growth factors was also based on a general comparison of dry and humidified particle number size distributions. As e.g. number fractions of dry and wet particles in certain size regimes were compared, it was found that particles with higher shape factors identified in the dry particle number size distributions appeared as hydrophobic particles in the humidified particle number size distributions."

Your statement: Section 3.3.2 the refractive index calculation. Have I understood right: you first calculate an effective refractive index for the whole size distribution. (...) So, is this is kind of a mixture of effective refractive index for the whole size distribution and size-dependent refractive index? Fine, just tell this.

Yes, you're right. When retrieving the refractive index under the dry conditions, it was assumed that it was size independent. And at each time step, only one refractive index has been retrieved by the numerical method. Afterwards, since we have the size dependent information about particle growth factors, we applied those on to the size-independent refractive index at dry conditions to get the a series of "size-dependent" refractive indices under ambient conditions and different relative humidifies.

Your statement: Another question: why would the refractive index not be wavelength dependent?

We are afraid there might have been some misunderstandings. In the manuscript we state "However, we admit that uncertainties introduced by the assumptions in the model - including the spherical shape and homogeneously internally mixed assumptions for the particles as well as the non-size dependent assumptions for the retrieved me$_{dry}$, were not taken into account in the uncertainty analysis." Here, we did not mean that the refractive index is NOT wavelength dependent. On the contract, we actually admit that the refractive indices of aerosol chemical compositions ARE wavelength dependent. But when we did the retrieving it was assumed to be wavelength-independent in the wavelength range between 450 to 700 nm, and the uncertainty introduced into the optical calculations by this assumption was NOT been taken into account when we did

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the uncertainty analyses.

It is worth to notice that for the chemical compounds, such as ammonium sulfate and nitrate, their refractive indices do not vary much in the mid-visible wavelength range from 450 to 700 nm. And this assumption has been used in many previous optical simulations (Sloane, 1986; Sloane, 1984; Sloane, 1983; Hand Book of Chemistry and Physics, 1963; Dalzell and Sarofim, 1969; Hasan and Dzubay, 1983; Tang and Munkelwitz, 1993; Tang and Munkelwitz, 1994; Mallet et al., 2006; Redemann et al., 2001). Bond and Bergstrom (2006) did a nice overview about wavelength dependency of the black carbon's refractive indices. Lee and Tien (1981) and Dalzell and Sarofim (1969) provided parameters which can be used to wavelength-dependent imaginary refractive indices of black carbon by dispersion model. It can be found that from 450 nm to 700 nm, the refractive indices of black carbon can vary from 0.35 to 0.45 or 0.4 $\pm$ 13 %. In another study conducted by Bergstrom et al. (2002), their data show an similar variation between 0.40 and 1.0 μm. They explored the theoretical basis of the wavelength variation of the absorption of solar radiation by elemental carbon (or black carbon), and found that for a wavelength independent refractive index the small particle absorption limit simplifies to a variation in relatively good agreement with the data. Their result implies that the refractive indices of BC were relatively constant in this wavelength region, in agreement with much of the data on refractive indices of BC.

Your statement: Table 5. The refractive indices must be wrong, columns have been changed to rows, obviously just a typing error. It is now there that the real refractive index for marine air is 1.48 and for polluted air 0.01 and that the imaginary refractive index is 1.50 for marine air and 0.02 for polluted air.

Our response: Thank you, this was corrected.

Wolfram Birmili, on behalf of all co-authors.

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