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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Particle size distributions in the Eastern Mediterranean troposphere" *by* N. Kalivitis et al.

N. Kalivitis et al.

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Response to Reviewer: We would like to thank the reviewer for his/her comments that have helped us to prepare this final version. Most of the suggestions have been taken into account and all raised issues are answered one by one. Minor comments have been also taken into account. Below is a point by point answer (ANS) to the reviewer comments (by Italics).

Reviewer #1 1) In my opinion the systematic disappearance of the Aitken particles is the single most interesting part of this paper and should be explored in more detail, whether here or in a follow-up paper. The dataset definitely seems promising. Since the disappearance occurred every other day, similarities and differences between the days should be discussed more thoroughly. This could be explored with the aid of coagulation sink and condensation sinks (Kulmala et al. 2001). These parameters could

help to pinpoint the processes relevant in the disappearance of the Aitken mode particles and whether they differ between a gradual disappearance and a sudden decrease in Aitken mode particles. If the coagulation sink was large, this could also explain the fact that new particle formation was not observed on a regular basis during this field study as pointed out by the authors. Is there a threshold value of coagulation sink after which Aitken mode particles are lost? Changes from summer to fall in the disappearance is only mentioned but not discussed the article.

ANS: To examine the possible role of the coagulation sink (CoagS) on the population of nucleation mode particles, CoagS was calculated from our measured particle size distribution data. In a first step, the measured dry particle size distributions were adjusted to ambient relative humidity — these are the conditions relevant for the atmospheric aerosol dynamical processes. The necessary hygroscopic growth model was developed as a hybrid from both, experimental hygroscopicity data and chemical particle analysis from impactor samples collected during the same ARIADNE experiment at Finokalia. Below 700 nm particle size, hygroscopic growth factors derived from H-TDMA measurements at 90 % RH were used. These data are still unpublished but were collected for the dry particle diameters 30, 50, 80, 150, 250, and 350 nm using the H-TDMA instrument described in Massling et al. (2003). Chemical particle analysis of impactor samples suggested that ammonium sulfate constitutes the overwhelming fraction of the soluble particle matter in sub-μm particles in the Eastern Mediterranean aerosol. Thus, a simplistic hygroscopic growth model was devised, describing the particles $<$ 700 nm as consisting of an insoluble core and a soluble shell, the latter being represented by ammonium sulfate. Using the experimentally determined growth of ammonium sulfate (Tang and Munkelwitz, 1994) with RH, the simple two-component model allows to estimate the fraction (epsilon) of soluble material in the particle at each of the given dry diameters 30-350 nm. The H-TDMA data suggested that between 50 and 350 nm epsilon varied between 66 and 74 %. Using these soluble fractions, the model was applied to calculate the particle equilibrium diameter of particles between 20 and 700 nm at the corresponding ambient RH. For particles above 1300 nm, a

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hygroscopic growth model based only on average chemical composition was used. A number of three impactor samples collected during ARIADNE suggested a composition of super-μm particles dominated by fresh and processed sea-salt: sodium chloride, 45 %; sodium nitrate, 55 %; insoluble or poorly soluble, 10 %. From this information, a three-component model using an insoluble core, and a soluble shell of sodium nitrate and sodium chloride was devised. The growth of soluble species was, again, based on experimental data (Tang and Munkelwitz, 1994) with both acting like in an ideal mixed solution (Zdanovskii, 1948; Stokes and Robinson, 1966). The described model was, again, used to calculate the particle equilibrium diameters of particles between 1300 and 10000 nm at the prevailing ambient RH. Between 700 and 1300 nm, both models described above were interpolated to provide a smooth transition between the fine and coarse particle modes. Having constructed wet particle size distributions at ambient RH (30 to 95 %, average: 71 %), the coagulation sink rate CoagS was calculated in agreement with Kulmala et al. (2001). Specifically, CoagS indicates the flux of particles of a given diameter onto the population of existing bigger particles due to Brownian coagulation. For the bigger, pre-existing particles a gravimetric density of 1.7 g cm-3 was assumed in consistency with the measured chemical composition, and for the nucleation mode particles 1.4 g cm-3. On a basis of daily values, only a very weak anti-correlation between the coagulation sink and the number of nucleation mode particles is observed, although we would theoretically expect such an anti-correlation (Fig. 1, see document describing the changes performed in the manuscript). The diurnal average patterns also show only minor diurnal cycles in most parameters, although in the early afternoon we can see an increase in the total particle volume after 12:00, which indicates the arrival of particles that represent an increasing coagulation sink (figure not shown). However, RH is increasing again later in the afternoon, which balances out the net effect on CoagS of 20 nm particles (Fig. 2; see document describing the changes performed in the manuscript). This means that the disappearance of the nucleation/Aitken mode particles cannot be explained in a straightforward manner by coagulation losses. However, longer dataset is available for the years 2004 and 2005

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and in a follow up paper the potential effect of coagulation losses on the size distributions will be explored in more detail both on a seasonal and diurnal basis.

Figure 1: N[18-40nm] vs. CoagS (20 nm particles) during ARIADNE – all data.

Figure 2: Diurnal mean patterns (all ARIADNE) for RH, CoagS, dry volume and N(18-40 nm)

References: Kulmala, M., Dal Maso, M., Mäkelä, J.M., Pirjola, L., Väkevä, M., et al.: On the formation, growth and composition of nucleation mode particles, Tellus 53B, 479–490. Massling, A., Wiedensohler, A., Busch, B., Neus, C., Quinn, P., Bates, T., and Covert, D.: Hygroscopic properties of different aerosol types over the Atlantic and Indian Ocean, Atmos. Chem. Phys., 3, 1377–1397, 2003. Stokes, R. H. and Robinson, R. A.: Interactions in aqueous nonelectrolyte solutions. I. Solute-solvent equilibria. J. Phys. Chem. 70, 2126–2130, 1966. Zdanovskii A.: New methods for calculating solubilities of electrolytes in multicomponent systems. Zhur. Fiz. Khim 22: 1475–1485, 1948.

Specific comments: 2) Details on how the formation rates were calculated need to be explained as the results depend on assumed growth rates and assumed initial below the detection limit of the instrument as well as various loss rates.

ANS: The calculations were performed according to Kulmala et al. 2004, Atmospheric Environment, 35, 143 -176.We used Equation 3, which is a simplification of Equation 2. At Finokalia all criteria for this assumption are met. Following the discussion by Kulmala et al. it should be noted though that the formation rates referred here are formation rates for particles with diameters greater than18 nm and not true atmospheric formation rates and thus in the text they should be referred as J18. The above issues have been appropriately included in the manuscript and the Kulmala et al. reference has been added.

3) The data is divided into four time periods A to D. I would like to see characteristic

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trajectories for periods C and D (Figure 2) and typical size distribution for the period D (Figure 5) or the authors should give reason for omitting these in the Figures and in the discussion. According to Figure 3 the period D seems to contain a large contribution from Aitken mode sized particles. The differences in periods B and D could shed some additional light into the disappearance of Aitken mode particles during period B.

ANS: As the reviewers suggested we have added characteristic back trajectories for periods C and D in Figure 2 and rearranged the manuscript accordingly. Concerning the typical size distribution for period D, we have not included it in Figure 5 because they are identical in pattern with Period B, the only difference is the lower loading, both characterizing polluted conditions as shown in Table 1.

4) I recommend showing modeled and measured total number concentrations in Figures9 and 10 in separate panels. The two days seem to differ in terms of total number concentrations and also in terms ratios of Aitken to accumulation mode particles. Currently the comparison between modeled and measured size distributions is quite qualitative. The authors should clarify the processes included in their analysis. In the conclusions the authors state that only coagulation into larger particles and condensation of sulfuric acid are included. How about self coagulation? Section 4.1 mentions self coagulation, but erroneously in a context of coagulation with larger particle sizes. This should be clarified.

ANS: We strongly believe that showing modeled and measured number size distributions in parallel is essential for a direct comparison between model and observations. The two days indeed differ as the reviewer mentions but the criteria for choosing them is the fact that they are representative of the two main patterns of Aitken mode particles depletion. Apart from the qualitative agreement between model and observations we have provided information for the good agreement for the total number concentration. The reviewer is correct that in the conclusion and section 4.1 we have erroneously referred to self coagulation. This has now been clarified.

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Interactive Comment

5) pp. 6583, line 23. Is the temperature difference of the reaction rate taken into account?

ANS: It is not clear which temperature difference the reviewer is referring to.

pp. 6584, line 27. Growth factor of 1.15 is assumed. Reference and/or justification should be given.

ANS: The value for growth factor was taken from parallel HTDMA measurements during ARIADNE campaign. The manuscript is now in preparation (see also answer to the first question).

References: Kulmala, M. et al. (2001). On the formation, growth and composition of nucleation mode particles. Tellus B, 53:479-490.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 6571, 2008.