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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Size-resolved CCN distributions and activation kinetics of aged continental and marine aerosol" *by* A. Bougiatioti et al.

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The authors would like to thank the reviewer for the valuable comments that have improved the manuscript. Please find below a point by point answer to the comments. The answers are displayed in italics.

Specific Comments:

Abstract: From the abstract alone, it is unclear what is different from Bougiatioti et al. 2009 (ACP); the goal of this new manuscript should be made clear. What is the suggested origin of the ∼30 nm particles and ∼100 nm particles? The CCN activities should be tied more directly to suggested aging processes; while photochemical

aging and volatilization of less hygroscopic material from aerosol are noted in the abstract, evidence supporting these hypotheses do not appear to be presented in the manuscript.

The difference between the current study and Bougiatioti et al. 2009 (ACP) is very clear: the study of the size-resolved CCN activity, hygroscopicity and activation kinetics and the conclusions thereof drawn from the measurements. The fact that the current study is consistent with hypotheses put forth in Bougiatioti et al. 2009 is a testament of the measurement/analysis methodology (Scanning Mobility CCN Analysis combined with activation curve and Threshold Droplet Growth Analysis) used to infer chemical mixing state, activation kinetics and hygroscopicity.

Linking the properties of small and large particles to their origin is a good point and we have expanded upon this in the manuscript.

Introduction: The introduction is very long and cumbersome; it should be shortened and revised to emphasize only what the reader needs to know to understand the main points of the manuscript. If the goal of the manuscript is to examine the impact of aging on CCN properties, then this should be discussed.

The authors feel that the introduction is a comprehensive overview of studies using size-resolved CCN measurements to infer information on hygroscopicity and activation kinetics, and provides the necessary background for this study. Following reviewer's suggestion we tried however to shorten it where possible. The goals were explicitly stated in the end of the introduction and are further elaborated in the revision.

Page 12610: This paragraph starts with the sentence "Size-resolved CCN activity measurements can quantify the role of composition on CCN activity". However, this is not investigated in detail in this manuscript. In addition, nucleation and biomass burning events are discussed; however, these events are not discussed in terms of the FAME07 data.

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Following reviewer's suggestions these sentences have been now removed. Nucleation and biomass burning events are discussed in the introduction for completeness, even if not observed during the study.

Page 12613, Lines 9-11: It is noted that at the field site anthropogenic pollution can mix with strong dust events; however, this phenomenon is not discussed in the manuscript with respect to the FAME07 data.

The stated features are also broad characteristics of the sampling area and the Eastern Mediterranean. During the campaign however, such events were not observed (as they occur mainly during spring and autumn). Following reviewer's suggestion, this sentence has been now removed.

Section 2.3: This section is awkwardly placed between two CCN methods sections, and it also contains non-aerosol information, despite the label "Aerosol chemical composition and size distribution". Consider reorganizing. Also, for example, lines 15-21 would seem to belong in Section 2.2. Further, the gas-phase and aerosol chemistry measurements are mostly not used in the manuscript and should be utilized to further understand the sources and aging processes of the aerosol.

Section 2.2 refers to sampling relevant for the CCN measurements and Section 2.3 refers to sampling for chemical composition of the aerosol, therefore placed after the CCN sampling section. Section 2.4 elaborates data analysis and therefore is placed after the sampling section. Also, the SMPS determines the aerosol size distribution and is placed in the "aerosol" section rather than the "CCN" section. Concerning the chemical measurements, a table presenting the chemical composition is now introduced in the manuscript. Nevertheless, the first paragraph of 2.3 is now moved to a new section (2.6) entitled "Ancillary measurements"

Page 12619, Lines 22-25: What are the standard deviations (or confidence intervals) associated with these averages? Are they significantly different?

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This is a good point. Standard deviations are now added to the averages, and discussed in the revised text. Using a two-sample t-test for unequal variances, for the 3 pairs of supersaturations (0.51-0.66%, 0.66-0.73%, 0.51-0.73%), we conclude that measurements for 0.51-0.66% and 0.51-0.73% are statistically different at the 95% level, but the values between 0.66 and 0.73% are not. The text has been amended accordingly.

Page 12620, Lines 2-4: Was the aerosol chemistry observed to be nearly the same in both studies? This is not, and should be, discussed.

In Bougiatioti et al. 2009 (Sept.-Oct. 2007), ammonium sulfate represented 62.4±12% of the total inorganic mass, with 80±10% being in the fine mode. Organic carbon was found mainly in the fine mode (74.8±12.3%). Similar values are also found in the current study (Jul.-Aug.2007), with ammonium sulfate representing 56.1±9.9% of the total inorganic mass and 81±4.7% being in the fine mode. For the organic carbon, it is also mainly found in the fine mode (72.3±17.7%). Given this, the aerosol chemical composition (in terms of CCN concentration impact) is arguably similar.

Page 12621, Line 6: State the diameter associated with this maxima here for clarity; this information should be integrated into the discussion of the CCN properties.

This is a good point. The diameter associated with this maxima is now added in the manuscript.

Section 3.2, Paragraph 1: General aspects of aerosol chemistry are noted; however, this information should be integrated into the discussion of the CCN properties.

We follow reviewer's suggestion and corrected accordingly.

Section 3.2, Paragraph 2: How was K derived from the filter analysis? This did not appear to be discussed in the methods section. Did the previously reported FAME07 study experience influences from similar air masses? The statement that "the particles exhibit a small (but detectable) chemical heterogeneity" is vague and confusing;

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specifics should be discussed with respect to the chemical data.

From the filter analysis, κ is calculated from the soluble fractions of the organics and the sulfate ($\kappa = \kappa_s \varepsilon_s + \kappa_{org}\ \varepsilon_{org}$), with κ_s=0.6 and κ_{org}=0.16. This is further clarified in the manuscript.

Page 12623, Lines 12-17: Lower concentrations do not necessarily mean less variability in aerosol chemistry or properties.

Excellent point. The sentence was changed accordingly.

Page 12623, Lines 25-26: Evidence should be provided for the suggested photochemical oxidation. Perhaps comparisons with the O3 and NOx data would be useful.

This is a good point. A graph depicting the variability of the hygroscopicity parameter kappa in relation to ozone concentrations is now introduced in the manuscript and the text has been amended accordingly.

Page 12624, Lines 19-21: Why was the WSOC data from the summer FAME07 study not used?

We did not say the WSOC data were not used, but rather that campaign-average values were. The time-dependant WSOC data were not used as it was found in the Bougiatioti et al. 2009 (ACP) study that they do not considerably affect the closure (varying CCN concentrations by $\sim$1%). This is clarified in the manuscript.

Page 12624, Lines 22-24 & Page 12625, Lines 12-14: Why wasn't a variable K utilized?

We would like to apologize for the error and thank the reviewers for noticing. Indeed, all closure calculations were made with variable κ, resulting from the filter analysis data.

Page 12626, Lines 18-19: Was the variability in average droplet diameter correlated with air masses?

Since the droplet diameters did not differ statistically from the NaCl calibration, they do

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not differ between airmasses.

Page 12628, Lines 10-11: It is stated that 'analysis of the droplet sizes using asymptotic and threshold droplet growth analysis suggests that the activation kinetics of ambient CCN does not vary..''; however, this finding may only apply to aged aerosol air masses and should be noted as such. It should not be generalized, as it likely depends on the extent of aerosol aging.

We did state that this applies to aged aerosol, such as the one sampled at Finokalia. Nevertheless we will emphasize this further.

Page 12628, Lines 13-17: This result is important and should be discussed further. Has this been observed previously? What in particular is unique about this study?

As stated, the measurement site is not influenced by local sources, chemical composition is more or less uniform throughout the year and particles are mainly internally mixed.

Fig.1: Very high altitudes were utilized for the HYSPLIT air masses backward trajectories for this ground-based study. Are these representative of the boundary layer air? Do 100, 300 and 500 m backward trajectories appear similarly?

100, 300 and 500m trajectories suffer from uncertainties due to orography and for that reason 850hPa (i.e 1000m) are used as reference for boundary layer. Note that BL measurements performed at the station showed mean BL values above 1000m (1200-1400).

Technical Comments:

Page 12609, Line 4: Fix spelling

Amended.

Page 12610: For clarity, define size ranges of Aitken and accumulation mode particles.

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Size ranges are now incorporated in the text.

Page 12610, Line 12: Where was FACE-2005

Clarification is added to the text.

Page 12610, Lines 17-20: Please clarify sentence

Done

Page 12611, Line 5: “ammoniated” should be “ammonium”

Amended.

Page 12613, Line 15: Should this state “aerosol source region” rather than implying an exact “aerosol source”?

“Source region” is incorporated in the text.

Section 2.2 Label: Consider renaming “CN and& CCN instrumentation” or similar, as there is “Instrumentation” described in other sections as well, making this label misleading.

Done

Page 12615, Lines 27-28: This sentence is too vague; for example, what was the frequency of CCN calibrations?

We carried out one comprehensive calibration in the beginning and one at the end of the campaign. There was very little variability between them, as can be seen in Bougiatioti et al., (2009)

Page 12618, Line 11: Fix typo

Amended.

Page 12619, Line 4: Briefly describe TDGA

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TDGA is briefly mentioned in the text. The reader is also referred to other publications using the method for a more thorough description.

Page 12620, Line 7: “An example” should be “Examples”

Amended.

Page 12620, Line 10: “diameter” should be “diameters”

Amended.

Page 12620, Line 19: Fix typo

Amended.

Page 12621, Lines 3-5: Clarify this sentence

A possible explanation for the lower activation fractions observed for air masses originating from Central and Eastern Europe is the external mixing with particles of anthropogenic origin that are not “good CCN”, e.g. soot. A clarification statement is now added to the manuscript.

Page 12624, Lines 4-5: What study does this statement correspond to?

As cited, this corresponds to Hildebrandt et al., 2010.

Page 12624, Line 6: Fig 7 does not show CCN activity as implied

We would like to apologize for the error and thank the reviewers for noticing. Figure 9 should have been cited and is now corrected.

Page 12624, Line 7: Is this decrease statistically significant?

A two-sample t-test for unequal variances has been performed for the two sets of values, before, and after 14h local time. It was shown that the 8% decrease observed is statistically significant and the text has been amended accordingly.

Page 12626, Line 24: Fix grammar

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Amended.

Page 12627, Line 7: The extent of organic aerosol oxidation is not presented in this manuscript as implied here.

The extent of the organic aerosol oxidation is expressed by the high WSOC/OC ratio which is, indeed, presented (and not just implied) in the manuscript. This is further validated by the study of Hildebrandt et al., 2010, as cited in the manuscript.

Page 12627, Line 23: Are these averages statistically different?

With the use of a two-sample t-test for unequal variances using the different kappa values it was shown that indeed the two average values are significantly different and the text has been amended accordingly.

Page 12628, Line 3: Why is this value different that that reported on page 12625?

We would like to thank the reviewers for noticing the inconsistency. Values on p. 12628 are now consistent with the ones on p. 12625.

Fig 5 caption: “Example” should be “Examples”

Amended.

Fig 8 caption: Please clarify what is meant by “chemical and mixing state parameters” as this is confusing.

The activation fraction (E), hygroscopicity parameter (κ) and chemical dispersion (σ), presented in Fig.8 are parameters that provide information about the mixing state (homogeneity) (also noted in p.12618 of the manuscript) and the chemical composition of the aerosol (as the hygroscopicity highly depends on this). A clarification is now added in the figure caption.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 12607, 2011.