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Atmospheric
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Interactive comment on "Hygroscopicity and composition of Alaskan Arctic CCN during April 2008" *by* R. H. Moore et al.

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Reviewer #2

We thank the reviewer for the thoughtful and detailed comments that have lead to important improvements for the manuscript. Italicized responses are shown below.

General comments:

Moore et al. provide a detailed characterization of CCN measured in the Alaskan Arctic during the ARCPAC study and examine trends in CCN properties. Given the accelerated rate of climate . . . be quite useful in considering springtime aerosol mixing state.

We have added the additional references suggested by the reviewer and discuss inclusion of the AMS and PALMS data in the specific comments below.

Specific comments:

Page 21790, Lines 13-14: Is a comparison to biogenic oxygenated organic aerosol relevant for this location and time of year?

The hygroscopicity versus O:C parameterizations reported by Jimenez et al. (2009) and others (e.g., Chang et al., 2010; Duplissy et al., 2011) have been developed from ambient and smog chamber measurements of SOA from biogenic sources and from the oxidation of anthropogenic VOCs (e.g., trimethylbenzene). We are not aware of any similar parameterizations in the literature developed specifically for springtime Arctic haze. Consequently, the reference to the existing parameterizations seems relevant to place the measurements in context.

Page 21790, Lines 14-15: Could mixing state, or other factors, be influencing the sensitivity of aerosol hygroscopicity to the O:C ratio?

Excellent point. The disagreement between AMS-derived hygroscopicities and CCN-derived hygroscopicities (as well as the CCN closure analysis results) certainly points to possible size-dependent composition or mixing state influences on kappa, as discussed in the manuscript text. However, extrapolating, e.g., the Jimenez et al. (2009) parameterization to the O:C values observed during ARCPAC would suggest an organic kappa greater than 0.3, which is inconsistent with the observed hygroscopicities at the highest organic volume fractions (see Figure 7 in the manuscript). Thus, we conclude that while the Jimenez et al. correlation holds for O:C ratios over the range of 0.2-0.8 (which is what they reported), at higher O:C ratios kappa likely reaches an asymptotic limit.

Introduction: It may be more useful to only summarize springtime CCN measurements in the Arctic since the sources of CCN vary with time of year. Also, the introduction reads as a comprehensive overview of Arctic CCN measurements; however, several studies are missing, e.g. Zhou et al. 2001 (JGR), Leck et al. 2002 (JGR), Wylie and Hudson 2002 (JGR), Lohmann and Leck 2005 (Tellus), Mauritsen et al. 2011 (ACP).

We have included the additional references suggested by the reviewer, noting that some of them are from late summer-fall and that many are analyses of the same studies already referenced.

Section 2.2, 1st paragraph: What collection efficiencies were utilized to adjust the AMS data, and how were they derived?

Phase dependent collection efficiencies were applied to all species measured by the AMS as described in Middlebrook et al. (2011).

Page 21796, Lines 7-10: If the “unclassified” particles were consistent with the other particle types, why were then not identified and included in the analysis? What fraction of the total particles did the unclassified type comprise?

As stated in the text, “The unclassified compositional type refers to particles that could not be identified by the automated data processor, although subsequent inspection of these spectra showed them to be consistent with the distribution of other particle types”.

We rely on automated methods for analyzing the PALMS data since analyzing each single particle spectra by hand would be computationally prohibitive. While the automated method works well for the vast majority of particles sampled, in a few cases it is unable to resolve the particle type for a number of reasons. A sample of spectra marked as “unclassified” were then inspected by hand and were found to be consistent with the distribution of particle types identified by the automated method. Thus, the unclassified particles were assumed to follow the same proportions as the classified particles and are not included as a separate particle type in the calculations for Figure 5. Brock et al., (2011) did report the unclassified fraction of particles as a separate

type, which was between 4-8% of particle number for all four air mass types.

Section 3.1: It would be useful to the reader to provide sampling altitudes for each of the identified air masses. Also, it should be noted that the particle volume composition reported refers only to non-refractory material measured by the AMS. Was the Arctic boundary layer air mass type defined such that only time periods with depleted ozone were considered?

Sampling altitudes are shown in Figures 1, 3, and 4 for each air mass type. The text in the bulleted points has been modified per the reviewer’s comment to note that only non-refractory material is considered. As discussed in more detail by Brock et al. (2011), the Arctic Boundary Layer air mass type includes time periods when ozone was depleted or photochemically-active bromine was enhanced, or both.

Page 21800, Lines 9-11: It would be useful to compare the observed average geometric mean diameter for the biomass plume to that observed previously in the literature.

We have added a reference here to Brock et al. (2011), who discusses the similarity between the observed mean sizes during ARCPAC and those reported by past studies (e.g., Petzold et al. (2007) and Drentener et al. (2006)) for long-range transport of biomass burning emissions.

Page 21800, 3rd paragraph: At what altitudes was the nucleation mode present? To determine whether these particles were statistically significant, couldn’t the raw data (rather than just averages) be examined further to determine if this phenomenon was real? How did the particle size distributions vary with altitude? Of particular interest would be a comparison between the particle size distributions in the background and Arctic boundary layer air masses at <500 m amsl. This discussion could be improved overall.

The raw NMASS data consist of 5 size bins which are processed using the overlapping portion of UHSAS size distribution and a non-linear inversion algorithm to obtain an *interpolated aerosol size distribution. Consequently, there is increased uncertainty associated with the smallest size bins in the raw data. Our approach in averaging the distributions is to improve the sampling statistics, and thus the confidence in the presence of the small mode, as well as to provide characteristic size distributions to assist in interpreting the CCN activation data. Thus, we include the caveat related to the increased uncertainty which may affect the prominence of the aerosol nucleation mode.*

While we agree that a detailed discussion of the altitude dependence of the particle size distributions in each air mass type would be very interesting, we feel that it is somewhat tangential to the current study, which is focused on the CCN and hygroscopic properties of the aerosol.

Page 21802, Lines 2-4: Could this observation be due to similar source/chemistry influences?

Given the wide variation in non-refractory chemical composition measured by the AMS across different air types (e.g., organics dominate the background and biomass burning air types with smaller organic contributions in the pollution plumes and in the Arctic boundary layer), it seems that size effects explain the similarity of the activation curves. However, as discussed later in Section 3.2, source/chemistry influences may have important secondary effects.

Page 21802, Lines 15-16: Mineral dust appears to be considered to be nonhygroscopic in this study; however, previous work (e.g. Twohy et al. 2009, GRL) has shown that mineral dust particles can act as CCN. Was the mineral dust observed via the PALMS instrument internally mixed with secondary species? What was the composition of the dust? This chemical information about the dust may give insights into its hygroscopicitiy.

The reviewer is correct that fresh and aged dust can act as CCN via either adsorption activation (e.g. Kumar et al., 2011) or from dissolution of soluble coatings. A detailed

analysis of the secondary species measured by the PALMS was not performed; however, it does appear that most particles are somewhat internally mixed with sulfate and organic species present on the dust particles. This was noted in the manuscript text on Page 21812, Lines 10-14. Since the PALMS does not provide quantitative mass fractions, it is not possible to quantify the impact of these species on particle hygroscopicity; however, we have added some additional language to these lines noting that dust can act as CCN in some cases. To the limited extent that PALMS can resolve different types of dust, the mineral content varied throughout the study, including iron-rich, calcium-rich, and aluminosilicates.

Page 21802, Lines 19-22: The connection to the Arctic is unclear here.

Herich et al., 2009 performed measurements in northern Sweden, while Covert and Heintzenberg (1993) and Engvall et al. (2008) both performed measurements in Svalbard. Hegg et al. (1996) performed measurements near Prudhoe Bay, Alaska. We have added the word "Arctic" to "Previous studies" in the text to make the connection clearer.

Page 21803, Line 25: The surface tension of water is assumed in this study. However, it should be noted that previous work by Lohmann and Leck (2005, Tellus) found that the presence of surface-active organics was necessary to model CCN concentrations in that study. If a surface tension sensitivity study is not completed, justification of this assumption should be provided.

It is known that an assumed surface tension of water is likely to introduce bias in the predicted hygroscopicity parameter for carbonaceous aerosol (e.g., Petters and Kreidenweis, 2007; Moore et al., 2008; Padro et al., 2010; Asa-Awuku et al., 2010). Deconvoluting such effects however is far from trivial; recognizing this, Petters and Kreidenweis (2007) suggested the convention of using a surface tension parameter equal to that of water (at the median temperature which the CCN instrument is operated at), and gives rise to the "effective" kappa that convolutes both effects. Given that the com-

munity adopts this convention regularly, we do so as well. This has now been clarified in the text, and the words "for simplicity" have been replaced with "by convention".

Page 21806: Why are O:C ratios not reported? Also, the discussion of Figure 8 should be clarified. The f44 discussion on this page and the following page may deserve its own section in the manuscript to improve clarity. In discussing the relationship between O:C ratio and hygroscopicity, it would be useful to refer the reader to laboratory studies of organic acids, for example.

O:C ratios are calculated from the correlation of Aiken et al. (2008) and are included for comparison in Figure 7; however, since the C-ToF-AMS actually measures f_{44} *and* f_{43} *rather than O:C, we choose to report these values instead. The reader is then free to use any relevant correlation to infer O:C.*

We have adopted the reviewer's suggestion of creating a new section for the f44 discussion.

References to Chang et al. (2010) and Duplissy et al. (2011) have been added to supplement the current reference to Jimenez et al. (2009).

Page 21812, 2nd paragraph: The construction of a CCN closure scenario based on the PALMS data is a very good direction; however, only two particle types are really considered. Could a more realistic scenario be constructed based on a combination of the PALMS and AMS data? For example, treatment of dust and sea salt could be included. This extension be a great addition to the study here.

We thank the reviewer for this excellent suggestion. Our intent in the closure study is to determine the error associated with simplified composition and mixing state assumptions used for computing CCN concentrations in large scale models. This enables modelers to quantitatively assess the uncertainties associated with CCN predictions employing these assumptions. While a more complicated closure scenario would likely improve predictions (assuming the AMS non-refractory mass loadings and

PALMS number fractions could be reconciled in an internally consistent way), it is unlikely that such a complex method will be used in a large model for some time. Thus, as a first step toward increasing complexity, we consider the simple 2-mode, external mixture scenario. The reported size-dependent hygroscopicity parameters (kappa) are available for those who want to capture the overall effect of aerosol composition and mixing state on CCN activity in a more complete way (although, it does not explicitly resolve the influences of each effect).

Technical comments:

Page 21790, Lines 5-7: It is stated that 4 distinct air mass types were observed, but only 3 are listed here.

We have added the fourth type.

Page 21790, Line 10: It does not seem necessary to state in the abstract that m/z 43 and 44 peaks from an aerosol mass spectrometer were used to determine that the organic aerosol was found to be well-oxygenated; the character of the aerosol could simply be stated here.

Done.

Page 21795, Line 26: This sentence should be reworded as the C-ToF-AMS does not volatilize refractory material; therefore, it is an overstatement to say that it "gives relatively little information".

Done.

Page 21796, Line 3: Is this a reflectron time-of-flight mass spectrometer? If so, this should be stated.

Yes. It is stated.

Page 21798, Line 3: Fix spelling of "transfer".

Done.

Page 21798, Line 20 & Page 21799, Line 1: “constitute” should be “constituted”.

Done.

Page 21799, Line 18: Delete extra “the”.

Done.

Page 21799, Last paragraph: It is suggested that this paragraph be moved to the AMS methods section (section 2.2). Also, provide justification for utilizing an organic density of 1400 kg m-3.

Done.

Page 21800, Line 2: “coexist” should be “coexisted”.

Done.

Page 21800, Line 12: Fix significant figures in reported uncertainty.

Significant figures are correct. We have fixed the typo denoting the uncertainty as an arithmetic standard deviation rather than a geometric standard deviation.

Page 21802, Line 1: Should “around” be “above”?

Yes. Fixed.

Page 21802, Lines 26-28: The relevance of this statement to the current project is unclear here.

The summer concentrations are more similar to the ARCPAC concentrations than those from past spring studies, perhaps because of the unusual fire activity during 2008.

Page 21803, Lines 3-4: This statement is confusing, and it’s relevance is unclear.

We have modified the wording to improve clarity.

Page 21804, Lines 22-25: Provide references for these assumptions about the organics.

Done.

Page 21812, Line 20: Is this referring to AMS mass spectra? Please clarify.

Yes. We have explicitly stated “AMS mass spectra”.

Fig. 5: This is a very informative figure! What are the uncertainties in the PALMS number fractions

Thank you. The relative uncertainty of the PALMS number concentrations is estimated to be 15%, as noted on Page 21796, Line 13. We struggled with a way to clearly communicate the number fraction uncertainties in Figure 5, and thus, decided to just report the mean values.

References Cited (and not already referenced in the discussion manuscript):

Asa-Awuku, A., *et al.* (2010) Water-soluble SOA from alkene ozonolysis: Composition and droplet activation kinetics inferences from analysis of CCN activity, *Atmos. Chem. Phys.*, **10**, 1585-1597.

Chang, R. Y.-W., *et al.* (2010) The hygroscopicity parameter (κ) of ambient organic aerosol at a field site subject to biogenic and anthropogenic influences: Relationship to degree of aerosol oxidation, *Atmos. Chem. Phys.*, **10**, 5047-5064.

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Kumar, P., Sokolik, I.N., and Nenes, A. (2011) Measurements of Cloud Condensation Nuclei Activity and Droplet Activation Kinetics of Fresh Unprocessed Regional Dust Samples and Minerals, *Atmos. Chem. Phys.*, **11**, 3527-3541

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Lohmann, U. and C. Leck. (2005) Importance of submicron surface-active organic aerosols for pristine Arctic clouds, *Tellus*, 57B, 261-268.

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Padro, L.T., *et al.* (2010) Investigation of cloud condensation nuclei properties and droplet growth kinetics of the water-soluble aerosol fraction in Mexico City, *J. Geophys. Res.*, **115**, D09204.

Wylie, D.P. and J.G. Hudson (2002) Effects of long-range transport and clouds on cloud concensation nuclei in the springtime Arctic, *J. Geophys. Res.*, **107**, 4318.

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