**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Physical and chemical properties of pollution aerosol particles transported from North America to Greenland as measured during the POLARCAT summer campaign" *by* B. Quennehen et al.

B. Quennehen et al.

b.quennehen@opgc.univ-bpclermont.fr

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Interactive comment on "Physical and chemical properties of pollution aerosol particles transported from North America to Greenland as measured during the POLARCAT summer campaign" by B. Quennehen et al. Anonymous Referee #1 Received and published: 19 April 2011

Referee Comment:

This manuscript provides an interesting analysis of a unique airborne dataset collected

near Greenland in summer 2008. This dataset is one of the few collected in summertime in this region of the troposphere, and includes measurements from state-of-the-art sensors such as the AMS. The data are of high quality and the topic, aerosol characteristics relevant to Arctic climate forcing, are important and should be published. However, the manuscript has several significant issues that must be addressed by major revision before publication in Atmos. Chem. Phys. There are four primary issues: 1) There is no evaluation of data quality, and the surprising results of a soot-dominated Aitken mode are dependent upon this quality, 2) The analysis relies upon the absolute accuracy of the long-distance FLEXPART simulations, rather than upon values measured aboard the aircraft, 3) There is over interpretation of highly scattered data of limited or no statistical significance, and 4) The logic behind the conclusion that the Aitken mode is dominated by soot particles is unclear, and perhaps flawed.

General response: We thank referee n°1 for his constructive comments on our manuscript. We have revised the manuscript attempting to take into account all the comments raised. In the following we first respond to the four primary issues. In the end we answer the less critical secondary issues.

Each of these primary issues is addressed in turn below, followed by less significant issues. 1) Evaluation of data quality. There are at least three sets of measurements that must be compared and discussed to demonstrate that the data are of sufficient quality to allow for quantitative analysis: size distributions, chemical composition, and light scattering. Size distributions can be easily integrated over the diameter range of efficient transmittance of the AMS inlet/aerodynamic lens. Assuming a density (or calculating one based upon the AMS composition + PSAP estimates of BC contribution), one can quantitatively compare the calculated and measured aerosol mass using a scatterplot and two-sided (orthogonal distance) linear regression analysis. Agreement within the stated uncertainties would permit further quantitative analysis. Similarly, using Mie theory one can calculate the light scattering of the aerosol and compare it to the nephelometer values. Further, nephelometer-based scattering and AMS con-

centration should be highly correlated. If an independent CPC were available on the aircraft, one could also integrate the size distribution and compare it to the concentration reported by the CPC. Differences in sample RH (especially for the PCASP) should be considered in all of the above calculations. Finally, the heated size distribution and non-heated size distribution should be compared for any cases that may exist when the thermodenuder was not on. Figure 3 suggests that there are serious discrepancies between the aerosol mass calculated from size distributions and the AMS mass. These discrepancies need to be examined more quantitatively and evaluated before proceeding with any further analysis. Because the size distributions (Figs. 7, 8) are so different from earlier measurements in plumes transported long distances from forest fire sources, it is imperative that confidence in these measurements be established at the outset.

Authors response: As proposed by the reviewer an extended study has been carried out to evaluate the data quality of measurements used within this study. An extended paragraph dedicated to the data quality discussion has been added to the revised manuscript. In particular we checked consistency and correlations of three independently measured datasets as there are size distributions from SMPS and PCASP (plus total concentrations from CPC 3010), chemical composition from AMS, and light scattering from the TSI nephelometer. In general we can state that datasets are coherent (covariance) when compared to each other. A section has been added in the manuscript to describe the data quality evaluation. We also present one more figure dedicated to data quality evaluation in the revised manuscript. In more detail:

a) Comparison of number concentrations measured with a CPC 3010 and calculated from the SMPS size spectrum demonstrates that the SMPS integral retrieves 70-100% of the number concentrations found with the CPC-3010.Some runaway values are detected when the CPC fluctuates rapidly and fluctuations are important. In these cases the SMPS cannot follow these fluctuations and may overestimate (higher CPC concentrations at the beginning of the SMPS scan, and lower concentrations at the end)

or underestimate (lower CPC concentrations at the beginning of the SMPS scan, and higher concentrations at the end) CPC concentrations. As an information we have to know that the SMPS is scanning from low to high voltages, thus from small to large diameters. Thus, we should have variations due to non constant CPC number concentration within single scans. However, this should not infer a systematic error, but rather fluctuations around total concentrations. We did not observe very often particles below 20 nm (this means that the spectra did not show significant amounts of particles between 20-30 nm), thus potentially small amounts below 20 nm.

b) Regular comparisons of both SMPS systems and both GRIMM instruments have been performed at ambient temperatures. Comparisons were usually made before take-off (without thermodesorption). In addition, pressure dependent intercomparisons have been performed in the laboratory of corresponding SMPS and GRIMM systems at ambient temperatures. These intercomparisons revealed that size spectra have been identical for both systems. The difference of 7% in counting efficiency of the two CPCs downstream the two DMA columns of SMPS and NVSMPS systems have been taken into account. Both identical DMA columns have been calibrated for their transfer functions. A sentence has been added in the revised manuscript to clarify that point.

c) A very good agreement is found between light scattering coefficients derived from Mie calculations using the SMPS+PCASP size distributions and the directly measured nephelometer data. The Mie calculations have been performed according to the Bond code (Bond et al., 2006; Mätzler 2002) taking into account just the angles seen by the TSI nephelometer. Deviations between measured and calculated scattering coefficients should be primarily due to the use of a constant complex refractive index for the Mie calculations and also due to uncertainties in the SMPS size distributions (in case that aerosol concentration changed during the 2 minute lasting scan). In general, the Mie calculations based on dry aerosol spectra match the nephelometer measurements (also dry), this means that size spectra are pretty good, and despite the bad SMPS time resolution, also the temporal correlation of Mie simulations and nephelometer

measurements is surprisingly good.

d) In general nephelometer measurements of scattering coefficients and AMS mass concentrations should be well correlated. However, we find that AMS fluctuations in mass concentrations are much more important than variations in scattering coefficients. This might be due to the fact that the AMS is measuring close to detection limit. Another finding is that the temporal correlation of AMS derived mass and measured scattering coefficient is not very good. The intercomparison yields much better results when comparing experimental nephelometer data to Mie calculations from size spectra.

e) Likewise, that finding presented in the above paragraph is particularly true for the intercomparison of AMS versus SMPS + PCASP derived mass concentrations. AMS mass concentrations and mass concentrations derived from size distributions are not very well correlated in time. In particular, the AMS mass concentrations are a factor of 2-3 below the mass concentrations derived from size spectra with a reasonable particle density of 1.7 g/cm3. The background concentrations in the instrument's vacuum chamber were high due to the small amount of time available for pumping. This adds noise to the signal and increases the limit of detection (see Schmale et al. 2011). Although the SMPS detects black carbon and other refractory material that the AMS is not sensitive to, a factor of two appears to be rather large. Additional reasons might be underestimation of the correction factors for the AMS inlet system. However, this explanation remains speculative.

2) Over-reliance upon FLEXPART simulations. According to p. 11780, lines 10-15, periods of flight influenced by Canadian boreal fires (BF), Alaskan boreal fires (AK), and anthropogenic pollution from North American sources (AN) were identified solely by qualitative reference to plots of the column-integrated potential emission sensitivity (PES) from FLEXPART. The FLEXPART transport model is an exceptional tool, and one that is capable of providing substantial insight into emission sources and transport pathways. However, it is only as good as the meteorological fields driving it and the

parameterizations for convective transport and boundary layer height within its code. In no case should it be used as the only source of information regarding airmass origins following transport of many days it is simply not consistently accurate enough for such use. In particular for aircraft observations, minor altitude errors can translate into complete mismatches between in situ data and the FLEXPART transport paths. For ex-ample, in Fig. 5 there are periods where FLEXPART identifies that the aircraft should be in emissions from Alaskan fires, yet the CO mixing ratios are near 100 ppbv the hemispheric background CO values. Yet observations from these time periods are analyzed as if the aircraft is in the midst of an Alaskan forest fire plume–which it clearly cannot be! Similar, if less extreme, issues are found for the identification of the BF airmasses in the other flights. It is likely that a plot of FLEXPART-reconstructed CO at the location of the aircraft would show little similarity to the actual measured values. Airmass properties must be evaluated first on the basis of measured values, and then the sources evaluated in part by using the FLEXPART results. On p. 11782, lines 5-11, the measured number concentration enhancements are ra-tioed with FLEXPART-calculated CO emissions to examine the change in particle concentrations with transport time. This analysis presumes that the FLEXPART simulations precisely track the transport of CO directly to the aircraft, including quantitatively determining the dilution of the plume over transport times of 6-13 days. It is unlikely that FLEXPART has this level of skill. It would make much more sense to used measured enhancements of CO over background to calculate this change in aerosol concentration over time. After all, if one can calculate a delta-N from the measurements, why not also calculate a delta-CO from the measurements, and use that internally consistent ratio? I suggest that the authors select time periods of high CO mixing ratios as the foundation of their analysis, and use the FLEXPART simulations to help identify source regions of the layers. They need to reconstruct in-flight concentrations of CO from the FLEXPART simulations to demonstrate that the model can be used ascribe the source regions to specific features in the measurements. Analyses need to be based on measured values whenever possible, with interpretation only supported by–not dependent upon– the simulations of

transport over such.

Authors response: We agree with the reviewer that we should never select episodes based on FLEXPART only, since the model can - of course - be wrong. In that respect, it is of course somewhat problematic that except CO no long-lived gaseous tracers have been measured on the aircraft. In addition, the CO enhancements are relatively small so that plume identification for this campaign is not easy. We understand the reviewer's concern that there may be over-reliance on the model, while facing a limited measurement data set available. In the revised version of the manuscript we added one figure to compare FLEXPART-reconstructed CO along the aircraft trajectory (of used flights with identified air mass origins from NA) with measured ones, in order to help interpreting measured CO excess plumes. Thus, we first and foremost check for CO excess peaks in the measurements and then try to identify the air mass origins through the FLEXPART the simulations. Thus, whenever measured CO did not exceed significantly the CO background value this will not include the data into the analysis. In particular, several AK designed air masses in Fig 5d will are excluded now, since no experimental excess CO has been detected. These periods cannot be taken into account for the analysis. We adopted this protocol, suggested by the referee, for any pollution plume selection. The text in the manuscript has been modified in that sense. It is expected for combustion sources that both gaseous and particulate tracers are present. Whereas CO is considered a relatively inert gaseous tracer, particulate traces are less inert, since during transport, the particle concentrations (number, mass, chemical constituents) may change due to physical processes like precipitation scavenging, coagulation, dry deposition. Therefore, it makes sense to consider the entire dataset of available gas phase and particle parameters, hence giving the priority to rather inert CO. We would like to add that plume filamentation, stronger dilution near the edges of the plume and less dilution within the center may influence the measured quantities. Therefore we have to keep in mind that the aircraft might have crossed plumes near the edges and in the center or even slightly out of the plume during an identified episode. Consequently, we cannot expect a homogeneous concentrations of CO enhancement

within the plume. As response to the reviewer's comment related to p. 11782, lines 5-11, we normalized aerosol number concentrations with CO enhancements calculated from measurements in order to calculate changes in aerosol concentration over time. After all, the proposed ratio based on purely experimental data should be more consistent than merging experimental data with model simulations. These ratios then replace the number concentration enhancements over FLEXPART-calculated CO emissions (Fig. 6a). This procedure limits the errors potentially due to FLEXPART incapability to precisely track the transport of CO directly to the aircraft, including quantitative determination of the dilution of the plume over transport times of 6-13 days. Figure 6b has been deleted entirely. The manuscript has been modified accordingly. In addition, FLEXPART source apportionment have been added in Fig. 3 (Fig. 4 in the revised manuscript).

3) Over interpretation of highly scattered data. In Section 4.2, the ratio of measured delta-N to modeled CO_emi is calculated (see point 2 above). These data are then plotted in Fig. 6, and exponential fits are made to calculate the decay of the dilution corrected number concentration as a function of time, and its increase as a function of CO. It is difficult to believe that there is any statistical significance to these scattered data–particularly the second panel. The legends on the panels indicates "R2" values of 0.42 and 0.23, but R2 values are not applicable to nonlinear regression. Is this a reduced Chi-squared value, perhaps? Are the uncertainties in the values used as inverse weights to the fits, as would be appropriate? In any event, these plots should be redone using values normalized by measured delta-CO, rather than modeled CO_emi, as noted above.

Authors response: As described in response to the second major point highlighted by the reviewer (see above) Figures 6a and 6b have been removed. The text has been adapted accordingly in the revised version of the manuscript. The main interest in showing them was to demonstrate the highly scattering of the data due to wet scavenging. The text has been modified and we added some wording to describe the

scattering of the data.

4) Assessment of soot to Aitken mode. In Sections 4.4 and 4.5, an argument is made that the small amount of absorbing material found, presumably soot, is attributable to < 20 nm particles in the Aitken mode. This is deduced because ". . . large fractions of the SMPS measured Aitken mode are detected in the NVSMPS distribution of refractory particles below the detection limit of 20 nm". This sentence is unclear. How can large fractions be detected if they are smaller than the detection limit? This analysis would be more supportable if number size distributions of the SMPS and the NVSMPS for example conditions were shown, and the particles could be quantitatively mapped from the refractory Aitken mode to the non-refractory Aitken mode. The presence of the soot mass at sizes <20 nm would be quite surprising, and counter to extensive evidence collected in broad regions of the atmosphere in a range of conditions (see Schwarz, et al., Global-scale black carbon profiles observed in the remote atmosphere and compared to models, Geophys. Res. Lett., 37, L18812, doi:10.1029/2010GL044372, 2010.) The claim in Section 4.5 that "the ratio. . . between V_psap and V_aitken gives information about the fraction of BC particles within the Aitken mode" is true only if we accept the premise that the BC is within the Aitken mode–it does not provide independent evidence that this is the case.

Authors response: We think that we cannot maintain our conclusion that BC is principally seen in the Aitken mode. This cannot be proven unambiguously from limited measurements performed on board the ATR aircraft. The relevant paragraphs and statements have been withdrawn. Instead, we added a paragraph (including one figure and one table) that is dedicated to a closer analysis of the SMPS and NVSMPS size distribution measurements at ambient and elevated (280°C) temperatures and in particular on the shift of the accumulation mode modal diameter as we compare ambient to refractory (280°C) size distributions. When classifying air masses (AN, BF) from NA of all identified time periods according to the shift in accumulation mode diameter (shift between ambient temperature and elevated temperature modal diameter), it is demon-

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strated that the anthropogenic NA air mass can be clearly distinguished from BF air masses from NA. The shift in accumulation mode modal diameter is most important for AN air mass, thus illustrating that the corresponding accumulation mode particles are basically volatile at 280°C (94% volatility in volume, in other words 6% of the accumulation mode particle volume is refractory (= BC, refractory organics, etc...)). In contrast, the fraction of refractory accumulation mode particle volume within BF air masses is on average 25-30%. The shift in modal diameter can be interpreted being proportional to the thickness of a coating layer around refractory accumulation mode particles. In order to refine the study and to work out some graduations we distinguished BF air masses yielding modal accumulation mode diameter relative shift smaller than 30 % and between 30-50%.alternatively: "below and above 30%. Furthermore, when comparing number concentrations of the accumulation mode particles at ambient and elevated temperatures, it becomes clear that only a smaller percentage of the ambient temperature accumulation mode particles constitute this mode in the refractory spectra. The other accumulation mode particles are more volatile. When comparing number concentrations of all refractory particles over the respective concentrations at ambient temperature we conclude that most particles are somewhat composed of a refractive fraction which can be BC, but also refractive organic material at 280°C. This finding is true for both categories, namely AN as BF air mass particles.

Minor issues. A) There are several more minor issues that should be corrected in a substantially revised manuscript. Several of the figures are very difficult to read. In particular, in Fig. 1 it is hard to see the blue and yellow portions of the flight, indicating Alaskan forest fire and anthropogenic influence, respectively.

Authors response: Fig. 1 was modified: The original map is now zoomed to allow a closer view of flight tracks.

B) In Fig. 2 it is difficult to see the continental outlines and so gather a geographical reference for the transport pattern. In this figure the authors should keep in mind (and point out to the reader) that the PES is plotted on a logarithmic scale, and that many

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of the features to which the eye may be drawn might be very minor contributors to the budget of the measured airmass. This is why reconstructed, source-apportioned values of CO along the aircraft flight track are so valuable, and more quantitative than these maps (see Fig. 1 of Warneke et al., Biomass burning in Siberia and Kazakhstan as an important source for haze over the Alaskan Arctic in April 2008, Geophys. Res. Lett., 36, L02813, doi:10.129/2008GL036194, 2009).

Authors response: Continental outlines have been broadened, we state explicitly in the figure caption that PES is plotted on the logarithmic scale. The reconstructed, source-apportioned values of CO along the flight tracks for all four respective flights are presented together with measured CO enhancement (Figure 3).The former Figure 3 became Figure 4 in the revised manuscript.

C) In Fig. 3, it would be helpful to remove the cloudy portions from the data (since they are discarded anyway), and to provide a plot of aircraft flight altitude on the right-hand axis.

Authors response: Cloudy portions are presented in a different way (semi-transparent) and the flight altitude has been added. Former figure 3 became Figure 4 in the revised manuscript.

D) The use of yellow for the "AN" category begins in Fig. 3 and continues throughout the figures and tables. The yellow is very hard to see in many of these elements. In Fig. 3D the big plume of organic material at 14:30 and 16:15 is not identified as a haze layer of interest; the same with the 18:30-19:30 time period in Fig. 3C. Also, the AMS and size distribution curves appear to be poorly correlated in these two panels, drawing the reader's concern.

Authors response: The less visible colours have been changed throughout corresponding figures. Big plumes of organic material at 14:30 and 16:15 in Fig. 3D and at the 18:30-19:30 in Fig. 3C are not discussed here due to Asian origin (Asian origin is now mentioned in figures). Comments are added in the manuscript about these plumes to

clarify their origins (other than North-America). In general, the readability of the figure has been improved.

E) In Figure 4 the y-scale changes from panel to panel; it would be helpful to keep these fixed as in Fig. 3.

Authors response: Y-scales are now identical. The entire figure has been changed to better compare AMS mass concentrations (sulphate, organics) with those derived from size spectra (non-refractory and refractory mass), as requested from reviewer 2). In a first step the AMS mass (organics, sulfate) and SMPS+PCASP mass data (refractory, non-refractory) are presented separately, in a second step we then merge both data sets to compare total mass from volatile aerosol size distributions (spectra at ambient temperature minus those at 280°C) with AMS mass (material volatilized/ionized below 600°C). By the way former figure 4 became figure 6 in the revised manuscript.

F) In Figure 7 it is very hard to distinguish the solid line from the curves with symbols. I would also suggest using a linear y-scale rather than logarithmic. If particles of some size range do not show up on a linear plot, then they are not important contributors to the number distribution. If they contribute to mass and you wish to highlight this, then show a volume distribution as well.

Fitted and measured number size distributions (using particularly larger symbols) are plotted in 2 different colours. In addition, the axis has been moved to semi-log instead of log-log as recommended by the reviewer.

G) In Figure 8, the curves between the literature values and the current study are very different, drawing the reader's concern. Perhaps they could be normalized by delta-CO (if available in the literature values) to reduce dilution effects? Also, the reanalysis I suggest using data selected by in situ measurements rather than FLEXPART transport patterns might reduce the differences.

Authors response: Unfortunately, delta CO are available for Petzold et al. but not for

Fiebig et al.. At least we have to keep in mind that delta CO values for the Petzold size spectra on average have been larger by a factor of almost 5 (varying between 3-10) compared to this study. This of course reduces effective differences in former figure 8 by the above factors. Therefore we added figure 8b, to compare size distributions of Petzold et al and of this study, both normalised with their respective delta CO.

The choice of time windows, now basically motivated by in-situ CO enhancement measurements (and partly particulate matter considerations) is not changing a lot the results since differences are mostly due to wet scavenging (as shown in the following part of the paper) and of course emission strength. The normalisation of size spectra by CO enhancements, results in good comparison of size spectra concerning the Aitken mode, however the accumulation mode observed during POLARCAT is less dominant as compared to the Petzold et al. (2007) study. The text has been changed to discuss the added information.

H) Figure 9 is very hard to read because of small symbols and lines.

Authors response: Symbols and lines are now enlarged as requested.

I) Figure 10 needs a legend or caption to explain the color code.

Authors response: The colour code is explained in the figure caption.