

Interactive comment on “Temporal and spatial variations of aerosol physical and chemical properties over West Africa: AMMA aircraft campaign in summer 2006” by A. Matsuki et al.

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Response to Referee1

The authors wish to thank the referee for thoroughly reading the article and providing highly relevant remarks. We have addressed each of the referee comments below, and the article is revised accordingly.

Questionnaire

- > *Does the paper address relevant scientific questions within the scope of ACP?*
- > *Does the paper present novel concepts, ideas, tools, or data?*
- > *Are substantial conclusions reached?*

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> Are the results sufficient to support the interpretations and conclusions?

Yes, the paper addresses differences in aerosol composition, volatility and CCN activity over Western Africa during off-monsoon, transitional and monsoon conditions. The results of "in-situ" and offline measurements are shown and cross-compared. Interesting conclusions are drawn from the data, though – given the data scattering especially of the volatility/CCN measurements – some conclusions seem a little overstressed.

With regard to the volatility/CCN measurements, please find response to the specific comment below (4475/28-4476/13).

> Are the scientific methods and assumptions valid and clearly outlined?

> Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)?

Methods are described including their inherent assumptions. However, some vital assumptions (see detailed comments) are not explained, also only few info on device calibration and inlet system conditions are given, the latter ones being possibly relevant for volatility representativity. Maybe a little more raw data material (e. g., average "real" and not fitted size distributions would enhance the paper.)

In reply to the reviewer's comment we now show raw data for fitted size distributions presented in Figure 4. Size distributions have been fitted with four lognormal modes. In addition, Table 1 has been enlarged to better describe the measured size distributions with now four modes, to better account for the total size range of the measured particle spectra. We have to emphasize that the presented lognormal description represents a fairly good description between 20 nm and 1.5 μm , but not beyond, due to the lack of measured size distributions (SMPS+OPC instrumental combination) beyond 2 μm . The text has been modified accordingly in the revised manuscript.

> Do the authors give proper credit to related work and clearly indicate their own new/original contribution?

> Are the number and quality of references appropriate?

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Sufficient references are used.

> Does the title clearly reflect the contents of the paper?

The title speaks of "temporal and spatial variations". If the term spatial refers to altitude only, it is fine, otherwise it should be rephrased.

The term spatial refers mainly to altitude. We use the term “vertical” which maybe more appropriate for the study.

> Does the abstract provide a concise and complete summary?

Abstract is fine, see specific comments.

> Is the overall presentation well structured and clear? > Is the language fluent and precise?

Structure and language are fine.

Specific comments

4464/1-9: The reader gets the impression, that the described project is able to make statements valid for all of West Africa. This is certainly not the case, as West Africa is significantly larger than the investigated region. Please clarify appropriately.

We agree that the paragraph should more precisely describe the actual work that is presented in this paper. The paragraph now appears in the revised version as: “While the Sahelian belt in West Africa stretches in the border between the global hot-spots of mineral dust and biomass burning aerosols, the presence of West African Monsoon is expected to create significant vertical and temporal variations in the regional aerosol properties through transport and mixing of particles from various sources (mineral dust, biomass burning, sulfates, sea salt). In order to improve our understanding of the evolution of the aerosol-cloud system over such region across the onset of the summer monsoon,…”

4464/24-4465/1: Too detailed for abstract. Please shorten.

In relation to the comment made later for 4482/15-20, the paragraph is removed from

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the conclusions and replaced the too detailed sentence in the abstract.

4465/1: TEM-EDX – acronym without explanation. Though well-known to a certain community, it should be avoided.

Explanation for the acronym is added.

4465/12-14: If aerosol basics should be addressed here, it should be exact: most sulfate is probably not directly emitted, neither by "anthropogenic" or "natural" sources (wherever the division may be), but formed later from the gas phase.

It is rephrased as: "Aerosols can be either natural or man-made, that are formed directly from the source as primary particles (mineral dust, sea salt, soot, biomass burning smoke, biogenic debris), or as secondary particles following condensation of precursor gases (sulfates, nitrates, organic)."

4468/chapter 2.1: How were the instruments measuring volatile/non-volatile species calibrated? Experience teaches that usually aerosol instruments even of the same type show deviations, unfortunately. How were the OPC and the SMPS joined together to a single size distribution (distributions in Fig. 4 are smooth)? What assumptions have been made to do so? At least, both are measuring different aerosol properties and should not give the same results.

Instruments were cross-checked before the campaign in the laboratory, the SMPS systems of LaMP participated in EUSAAR intercomparison workshops at IfT. Also, we inter-compared the pairs of SMPS and OPC without the thermo-desorption column before each flight, (thus, before starting to heat the column to 285 degrees). We found that the spectra of the both SMPSs overlap fairly well and relative error was less than 10 %. To take into account the OPC sensitivity to aerosol optical properties, OPC data are corrected using complex refractive indices of 1.528 - 0.029i for the monsoon layer, 1.526 - 0.015i for the SAL layer, however, no correction for the top layer has been applied (thus we simply kept the refractive index of the latex calibration beads for the

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GRIMM instrument). The OPC size distribution data have been recalculated (Mie code from Bohren Huffmann) for the above complex refractive indices.

The above indices (for monsoon layer and SAL) have been deduced, using the complex refractive indices of chemical compounds determined by Raut Chazette (2008) + the relationship given by Horvath (1998): $\text{ref index} = \sum_i (\text{fraction}_i * \text{ref index}_i)$, where i is a chemical compound.

After that correction, SMPS and OPC data are plotted together and are then fitted, see attached figures. In addition the measured data have been added. Unfortunately, there is no overlap of SMPS (20-300 nm) and OPC (300-2000nm) measured size ranges. Thus, the smoothness of the entire spectra is due to the fitting. The measured data are simply plotted as they are, taking into account the recalculated OPC size spectra of monsoon and SAL layers. Again the text has been modified accordingly in the revised manuscript.

4469/2-8: While the conditions for the volatility measurements are defined, the conditions for the general size distribution measurements remain undefined, except for the notion "in-situ". However, there are severe doubts that a measurement inside an aircraft can be addressed as in-situ for the outside air. What were the temperature and humidity conditions for the size distributions measurements as function of flight altitude and outside temperature and humidity? How much highly volatile material was lost during the transfer into the OPC/SMPS?

T and RH: We consider the aerosol particles to be sized at relative humidities below the deliquescence points. This is true for the SMPS with dried sheath air and very likely for the OPC measurement within the aircraft cabin. Checking all the ATR-42 profiles of dew point temperature with respect to measurement conditions in the OPC, we can conclude that in the OPC instrument we did not exceed 50% of RH between sea level and 1 km in altitude with decreasing RH as the ATR-42 climbs in altitude (max RH of 25% at 2 km in altitude, and max RH of 20 % at 3 km, etc.). This decreasing trend is due to the almost constant temperature in the aircraft cabin (approximately 35-38°C)

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and thus, “constant” temperature in the OPC instrument at pressure conditions inside the instrument that resemble the respective ambient air pressure conditions outside the aircraft.

Volatile material loss: The mass loss of particular matter is difficult to quantify. Assuming sulfate to be an important dominant submicrometer aerosol component, the volatility temperature of sulfuric acid and of its neutralized products, ammonium sulfate ((NH₄)₂SO₄) and ammonium bisulfate (NH₄HSO₄) are important to take into account. Also Nitrate (i.e., often in the form of NH₄NO₃) is found to be even more volatile than sulfate (Bassett and Seinfeld, 1984; Rood et al., 1985; O’Dowd and Smith, 1993). Within previous studies, particles consisting of sulfuric acid and other volatile compounds (e.g., ammonium nitrate, ammonium chloride), were found to evaporate at temperatures between 70 and 150 °C, typically at 100 - 110 °C for sulfuric acid (Clarke et al., 1987; Pinnick et al., 1987; O’Dowd and Smith, 1993; Smith and O’Dowd, 1996; Cantrell et al., 1997; Kreidenweis et al., 1998). Ammonium sulfate and bisulfate were found to evaporate at temperatures between approximately 150 °C and 220 °C (Clarke et al., 1987; Pinnick et al., 1987; Rood et al., 1987; O’Dowd and Smith, 1993; Hudson and Da, 1996; Smith and O’Dowd, 1996). Around 300 °C, all the above mentioned components have evaporated completely and the remaining, particulate material is termed ‘refractory’. In addition, light (low mass) VOC compounds tend to evaporate at already low temperatures. Unfortunately, we do not have knowledge about VOC component partitioning and total mass fractions. Therefore, the mass loss of VOC particular matter (light components) in SMPS and OPC instruments is difficult to quantify but should not exceed noteworthy mass fractions at instrumental temperatures. The text has been modified accordingly in the revised manuscript.

4469/13: "one spectrum"

Corrected.

4470/23-24: Please explain shortly why C, N, O is excluded. Not everyone may know the problems.

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Following lines are added in the revised version to explain the difficulties related to the quantification of the lighter elements:

“X-ray peaks of lighter elements such as C, N and O were not included in the quantification of the relative atomic ratio, due to the uncertainties caused by the significant absorption of low energy X-rays within the samples, and also by the fact that the collision film substrate itself contains some C and O.”

4471/1-3: *Sentence can be omitted.*

Done.

4474/2-9 and Fig. 5: 1. When the particles up to 1 μm show the same volatility behavior as the shown restricted size range, why the size range was restricted? 2. It is mentioned, that for larger particles, the volatile fraction has other values – but which? 3. Data are extremely scattered. How significant is the trend for SOP2a2, which is pronounced by manual drawing? 4. In the paragraph about the size distributions it was mentioned, that averages showed less variance when it was done over particular trajectories rather the flight altitude. So, why for volatility flight altitude was preferred as discriminator?

As mentioned above the fitting of the size distributions has been extended to 4 log-normal modes. Using these fitted size spectra we present now volatility behavior of the entire range of submicrometer aerosol particles up to 1 μm as proposed by the reviewer. Indeed the SMPS and OPC instruments connected to the thermo desorption column measure the response of the entire size spectra to elevated temperature. The major information of figure 5 is that submicrometer aerosol is much less volatile during dry season (SOP1), as compared to SOP2a1 (monsoon onset) and SOP2a2 (monsoon fully developed). The higher volatility of the aerosol after the onset of the monsoon seems to increase from SOP2a1 to SOP2a2. The volatile aerosol stems particularly from the 100-300nm accumulation mode particles. Nevertheless, also during SOP2a1 and 2a2, a fraction of the particles seems to be as refractory as almost the

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entire submicrometer aerosol population during SOP1. A look at the volatility behavior of aerosol particles in the size range 1-2 μm does not show the same volatility trends as observed for submicrometer aerosol. Indeed, these supermicrometer particles are much more refractory with respect to temperature (and thus, less volatile) and show no clear trends when comparing periods SOP1, 2a1, and 2a2. The latter result is certainly due to the fact that supermicron particles are predominantly composed of non-volatile coarse mode mineral and sea salt particles (Matsuki, 2010). The text has been modified accordingly in the revised manuscript.

4474/10-26: Given the highly scattered data points in Fig. 5 even after averaging (!), this interpretation without the performance of a statistical test on which confidence level the mean values are different is rather pointless.

The overall objective of the presented measurements is to give an idea of what has been the volatility behavior of the aerosol particles observed during the three months of aircraft measurements. The idea is neither to present case studies, nor to generalize about aerosol volatility behavior. In contrast, highly scattered data points in figure 5 show clear trends, not forgetting about the variability of the aerosol particle properties. Thus, there is no interest to average volatility behavior. Therefore each data point is integrating 2 min (duration of SMPS scans) of all the aircraft soundings performed during the three observational periods SOP1, 2a1, and 2a2.

4475/2: ". . . hygroscopicity . . . controlled by particle size" is a little mistakable.

Indeed. We omitted hygroscopy and the line now appears:

"At a first glance, the cloud nucleating properties are controlled by particle size and by the amount of soluble material contained in the particles or coating the particles."

4475/28-4476/13: Those results are interesting. However, what are the values of regression and correlation coefficients for the four populations showed in Figure 7? A value of approximately 1 as stated in 4476/1 might not fit to Figure 7. And was the range of 121-288 nm found to fit best to the CCN/CN ratios? Were tests made for other

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activation diameters? 120 nm might be a threshold set too high.

We agree that a value of approximately 1 is an overstatement given the significant scatter in the plot. We refrain from making any comment on the curves in the revised manuscript. Our intention here is not to formulate or parameterize the relationship between the CCN/CN ratio and the number fraction of aerosols in a certain size range. Rather, we just want to compare the CCN properties of the four populations by looking at how each group gather or scatter over the plot. In this respect, we still think that the figure captures fairly well the characteristics of the different populations. Now we set 100nm as threshold diameter, and the average plots for the four populations with error bars (1 standard deviation) are imposed in addition to actual plots. We also tested other activation diameters (e.g, 80nm, 40nm), but the plots gather too much to the upper-left corner since the $CN_{xxx-288} / CN$ ratios approach close to 1 especially during SOP2a2.

4476/14-16: Hydrophilic, -phobic, hygroscopic seem to be mixed-up in this paragraph (according to the first sentence, Monsoon is more hydrophobic, but according to the second one it is more hydrophilic, the latter fitting the figure).

Thank you for pointing out the mistake. The message we want to convey here is that the particles in the monsoon layer are more “hydrophobic”.

4476/24-27: Is dust per se cloud-inactive (see also comment on 4481/26)? If so, what these particles could be composed of? SEM/TEM should tell.

We did find fine dust particles as cloud residues in our own study, and work by Twohy et al., (2009, GRL) for example, proposed submicron dust particles do not always have to be “aged” to be able to act as CCN. It is not our intention here to give readers the impression that we think dust *per se* is cloud-inactive, so perhaps we better remove the part “with minor contribution from refractory particles (e.g. soot and dust)”. Dust particles were mostly identified as fine flakes of aluminosilicate clay minerals (described more in detail in section 3.5).

4477/3: *replace SEM and TEM by scanning and transmission or explain acronyms. Explain acronym EDX.*

Acronyms are already explained in the “2.2 Sample and analysis” section, so we believe the correction here is not necessary.

4477/8-11: *Reword*

The sentence is replaced as:

“Coarse (thus supermicron) particles collected on the first stage of the impactor were analyzed by SEM-EDX. In general, these coarse particles were dominated by dust particles. Significant number of sea salt particles appeared only during SOP2a2 within the prevailing monsoon flux where the air mass origin can be traced back to the gulf of Guinea (Fig. 3).”

4478/7: *Is it possible to quantify (roughly) or "qualify", how often a residuum was found after evaporating the biomass burning particle? I. e., how often they were internally mixed?*

Yes, it is always better if we can tell what fraction of the biomass burning particles was internally mixed. We carefully looked over the images of all biomass burning particles again, and found 40-50% of them to have soot like residues. This is now mentioned in the revised manuscript.

4478/13: *Electron-transparent?*

Corrected.

4478/13-21 and Fig. 8: *- Cosmetic: Same font size and length for all axes. - Mention, that the C (and perhaps O?) signal also has contribution from the substrate. - Where does the conclusion of acidity for the particles with satellite droplets derive from? Probably they were droplets during impact, but of which chemistry? Bigg 1980 used CaF₂-coated substrates for an acid reaction of the particles.*

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Same font size and length were employed in the original manuscript, but it was modified during the typesetting process. We will make sure that they appear correctly in the revised version. The figure caption is modified accordingly.

Bigg (1980) states in his report that sulfuric acid can nevertheless be correctly identified through its morphology without the fluoride coatings. He found similar particles with satellite droplets (he calls it 'droplet rings') on inert substrate, and confirmed by using CaF₂ coated film that these particles were predominantly sulfuric acid. The numerous droplets are also commonly identified surrounding ammonium bisulfate (NH₄HSO₄) particles, but not around ammonium sulfate particles ((NH₄)₂SO₄). Thus, identification of satellite structure around sulfate particles can be used as a good indicator of their acidic states.

4479/16: It is also interesting to see, that there seems to exist a persisting background mixture of these three components for all samples. Does this indicate locally well mixed air? Or rather aged air passing different source regions beyond the 5-day trajectory limit? Or is it just an effect of averaging and there exist samples without particular particle species?

Unfortunately, the number of particles analyzed in each sample is rather small (about 25) because of the labor intensity and limited TEM operation hours. It is difficult for us to conclude that a certain species was completely missing from a sample due to the limited counts, but we are safe to say that fine mineral dust was quite often scarce in the monsoon layer during the wet period (SOP2a2). Otherwise, we found the three types co-exist in most of our samples (90%) with variable relative abundances. It is difficult to explicitly locate the source of these particles, but trajectories tell us that the descending air mass arriving at high altitudes above 4km (Free troposphere) was possibly more aged and had distant sources. Biomass burning particles in the monsoon layer during the wet season may be more strongly influenced by sources along the monsoon flux. In my opinion, the mixture of the three types occurs possibly through the exchange (e.g. dry tongues and MCS passage) between the SAL (mineral dust rich) and the monsoon

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layer (biomass burning rich) along the African Easterly Jet.

4480/25: Though the term "internal mixture with sulfate" is technically speaking correct for K_2SO_4 , to me that notion implies that K and S are present possibly as different compounds – was that the intention?

Excess S relative to K suggests that not all SO_4^{2-} was in the form of K_2SO_4 . The susceptibility of these particles against electron beam also implies presence of ammonium sulfate. In any case, we prefer to change the phrase as “secondary production of sulfate” to avoid any misunderstanding.

4481/10: "which are assumed"?

Corrected.

4481/26: It is reported that mineral dust is found together with soluble components in different places (e. g. Falkovich et al. 2001, J. Geophys. Res. 106D, 18029-18036; Mori et al. 2003, Atmos. Environ. 37, 4253-4263; Kandler et al. 2007, Atmos. Environ. 41, 8058-8074 and others), so a (large) difference is not necessarily to be expected.

The part in question is removed and the initial paragraph (4481/22-29) now appears in the revised manuscript as:

“Small inclusions of soluble components may potentially induce activation of the supposedly insoluble dust particles (Kelly et al., 2007; Levin et al., 1996). If we compare the detection frequencies of elements between the clear-sky dust particles with that of cloud residues, we saw a slight enrichment of elements such as Na, Mg, S, K, and Ca within clouds. These elements may as well have facilitated their initial activation.”

4482/15-20: This paragraph may be suitable for an abstract, but not here.

This paragraph appears in the abstract of the revised manuscript.

4483/1: cloud active. . . particles being able to act as CCN?

Corrected.

Table 1/Fig. 4: How well are the raw data described by the fitted distributions? Interpreting fitted spectra only by a forced number of modes may hide features of the "real" distribution.

As already mentioned above we present raw data, in addition to fitted size distributions presented in figure 4. To refine fitting we extended the number of lognormal modes to 4 modes, to better account for the total size range of the measured particle spectra. We have to emphasize that the presented lognormal description represents a fairly good description between 20 nm and 1.5 μm , but not beyond, due to the lack of measured size distributions (SMPS+OPC instrumental combination) beyond 2 μm . Correlation coefficients have been added to give an idea of the fitted curves quality.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 4463, 2010.

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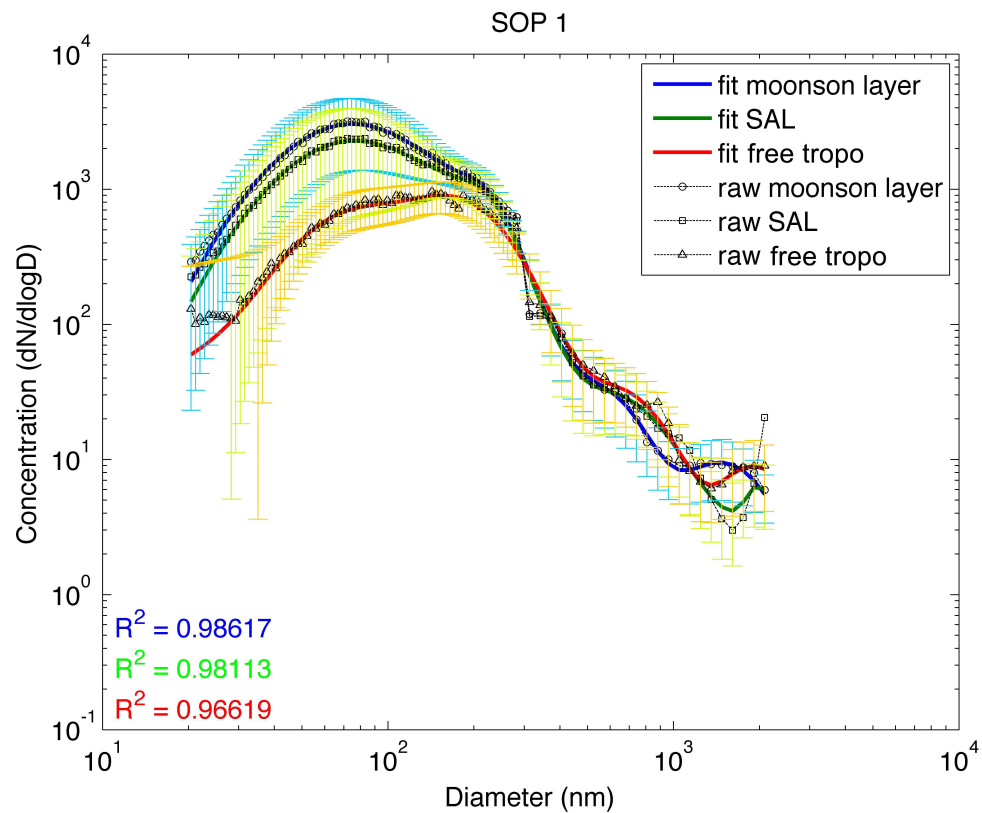


Fig. 1. Fig4_dry

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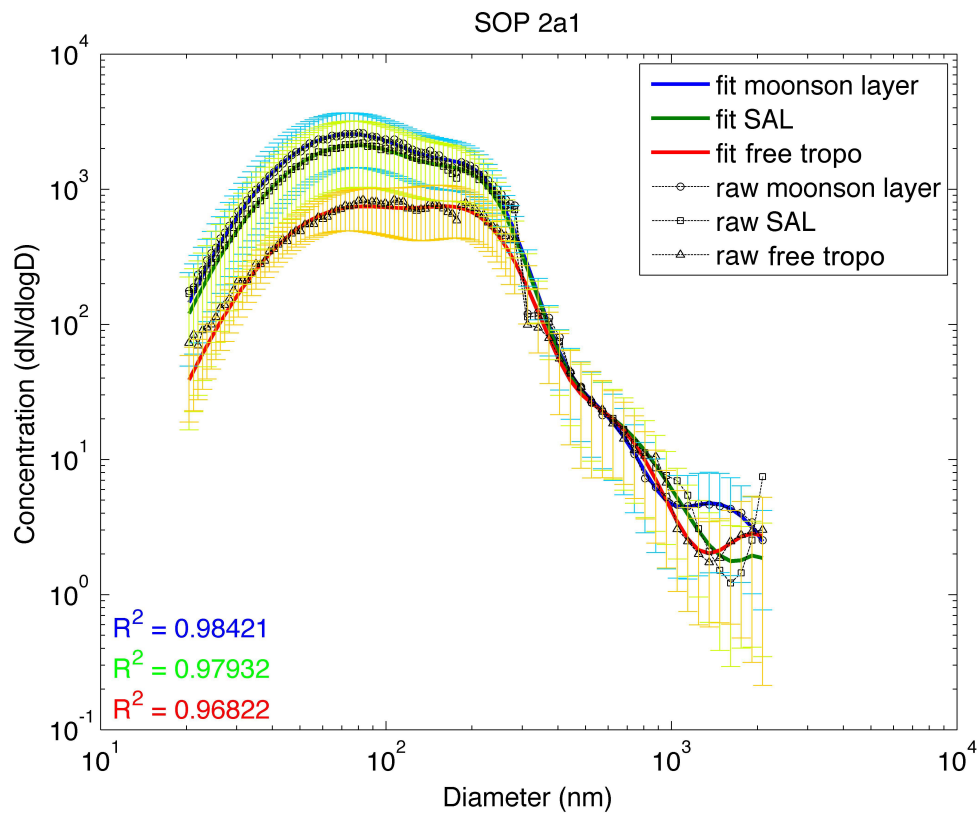


Fig. 2. Fig4_monsoon_onset

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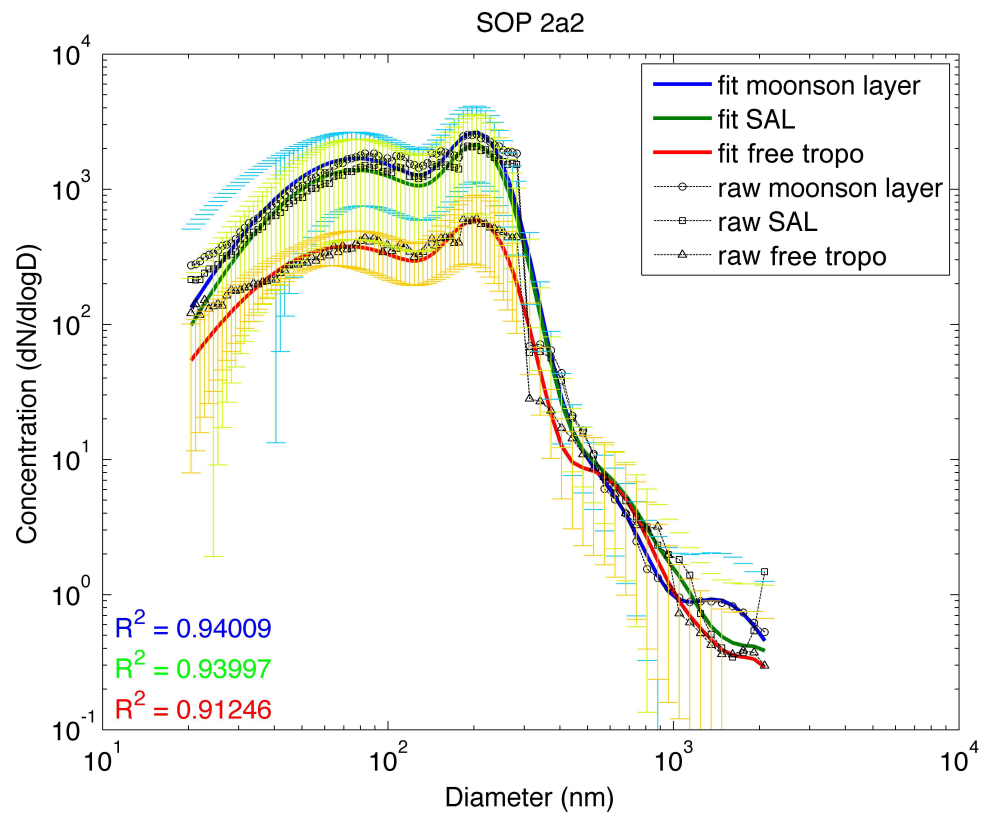


Fig. 3. Fig4_high_monsoon

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