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Comment on acp-2022-126

Anonymous Referee #1

Referee comment on "Annual Cycle of Hygroscopic Properties and Mixing State of the Suburban Aerosol in Athens, Greece" by Christina Spitieri et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-126-RC1>, 2022

Review

The manuscript present aerosol hygroscopicity measurements performed one year long at the Demokritos station located 8 km to the north east from the city center of Athens. The measurements present important new results, and therefore I suggest the paper for publication in ACP. However, in my opinion still quite a bit of work is to be done on the paper before the publication. Please find my detailed comments below.

Detailed Comments:

- Line 32-33: not only as CCN but also as IN, and those play a role in the indirect effect as well
- Line 48-49: as the kappa theory does not perfectly describe the water activity, you cannot report a certain kappa value for salts either. Kappa is dependent on RH and also particle size, so please say at which RH and D are those kappas are valid or give a range or say that it is an approximation
- Line 59-61: please rephrase the sentence, link between particle hygroscopic growth and what? And you say that there are only a few long-term hygroscopicity studies, there are also quite a few on CCN activity (these also investigate hygroscopicity) please add these as well or say explicitly that you only mean the HTDMA studies here. And are you sure that there are only these long-term HTDMA studies available? Please check again. And by Sellegri et al. 2014, don't you mean Holmgren et al. 2014? (<https://doi.org/10.5194/acp-14-9537-2014>)
- Line 82-84: is there already a paper on this custom-built HTDMA? If yes, please cite it. If there is not please add more details on the instrument regarding performance and

calibration.

- Line 81-92: please add the different flow values for the HTDMA
- Figure 2: please double check the figure that you name and explain all parts of it: the first item with a nafion has a name: Aerosol, I guess it should be Aerosol dryer, the two DMAs could be labelled as well for better understanding. After the first humidifier and before the RH/T measurement no line is drawn. Half of the textbox of the CPC is missing.
- Line 96: "were measured in parallel by the standard SMPS system of the Athens ACTRIS station" was this system moved from the Athens station to the Demokritos station and used there? Or was it operated not exactly where the HTDMA was standing? Not clear from the text.
- Line 100: RH lower than 45%, is that enough? I always have at least lower than 40% in my mind, but even better if lower than 30%. Please comment on it.
- Line 120: "an inversion algorithm applied to" -> "an inversion algorithm is/was applied to"
- Line 122-125: for readers not familiar with the HTDMA inversion, it might be not well understandable. The readers who are familiar with the inversion, it is not necessary. So either explain it better with more details, mentioning at least that when you select a certain size in the first DMA, particles with other sizes go through the DMA as well, that you have multiply charged particles as well and so on... Or leave the whole thing and only refer to the inversion paper, where it is explained in details, and mention that.
- Line 125: "x2" is it not usually "Chi" and not x?
- Line 133-134: The two sentences after each other are repetitions with similar meanings, do you really want both to be there?
- Line 135-137: Typo, bit of too many brackets here?
- Line 182: some boardening? Or the complete boardening? Based on the average you just cannot tell anything about the mixing state. You could have always perfectly internally mixed aerosol and a changing GF with time which would result in a broad GF-PDF as well. You should clearly state this.
- Line 187-189: Or another possibility is that BC is simply bigger than 30nm, and therefore whatever is in the nucleation mode is already little bit hygroscopic, and at the bigger sizes one could have the more hygroscopic material condensed on BC cores or even the pure BC particles as well.
- Figure 4: the vertical black line is not defined.
- Figure 4: D=250nm, there is a small peak at high GF of 1.9 or so. Please comment on it, what that could be, if that is a real peak with something highly hygroscopic or just measurement noise?
- Line 218: "(fig. 5. Panel A)." Where does this reference belong to? If it belongs to the sentence before: the annual mean is not shown in the figure.
- Line 218-219: this sentence is strange: distinct month-to-month variability, but no seasonal variability? What do you mean here? I do see a seasonal variability, For D>30nm higher GFs in spring/late spring, minimum in August then again higher towards the end of the year, and January is again low. 30 looks a bit different with not that pronounced and bit shifted minimum in summer but therefore maybe a higher amplitude of GF change.
- Figure 5 and 6: I do not really see the reason to show both figures. To my opinion figure 6 is better suitable to discuss the seasonal changing of the hygroscopicity. And you could add the average values without any problem to the boxplot as well additionally. And make a third column for the kappa boxplot. Here you even see better that there is a seasonal variability in the hygroscopicity to my opinion.
- Line 223-224: monthly average kappa? Are these not the yearly averages?
- Line 225: "standard deviation" please change it to GF-PDF standard deviation
- Line 231-232: sigma for the 250nm particles is as low in September as in August
- Line 241-242: do you have an idea why February is so much different from January? Why only that month?
- Line 245-246: "Aitken particles and the particles in the accumulation mode (D0 > 30

- nm) and the particles in the accumulation mode" too many accumulation modes
- Line 248-257: about the separation of the non- to slightly hygroscopic fraction from the moderately hygroscopic fraction. Selecting a constant GF of 1.12 as a limit means that for the different dry diameters you define a different hygroscopicity limit: for $D=30\text{nm}$ $\text{GF}=1.12$ means a κ of approx. 0.075, the same GF for a 250nm is approx. 0.048. I would suggest to define a κ limit and calculate a GF limit for each dry diameter. Even if that this would not make a big difference in the results.
 - Figure 7, label for f: typo " $>/<1.12$ " should be in subscript as well, not only GF
 - Line 280-281: "Specifically, for dry particle diameters $D_0 > 30\text{ nm}$, the contribution of the non- and/or slightly hygroscopic mode was maximum in spring and minimum in winter." ??? $\text{fGF}<1.12$ (Fig 7B) shows something completely different: minimum in spring, higher values in winter, maximum in August.
 - Line 282-283: "In the case of Aitken particles, the non-hygroscopic particles almost equal contributed to aerosol hygroscopicity with the slightly hygroscopic particles in all seasons except for spring." sorry, I do not understand this sentence, or as I can interpret it, that is not seen in the graph, please clarify.
 - Line 285-286: "Specifically, the average number fraction of the slightly hygroscopic particles were 0.62, 0.80, 0.67 and 0.70 in winter, spring, summer and autumn, respectively." Do you mean here the fraction of the moderately hygroscopic particles? Please check the naming in the complete discussion on Figure 7, it is very hard to follow this discussion. Maybe it is only coming from the confusion with the names of the different fractions.
 - Section 3.2: you only show average values for the diurnal variations. A box plot would include much more information here as well, e.g. for the mean GF, or at least add the standard deviations to the plots.
 - Section 3.2.: check again the naming of the $\text{GF}<1.12$ and $\text{GF}>1.12$ fractions! It is mixed up again at a lot of places, naming the fraction with $\text{GF}<1.2$ sometimes non-hygroscopic, sometimes non- or slightly hygroscopic and naming the fraction with $\text{GF}>1.2$ slightly or moderately hygroscopic. Hard to follow this section again.
 - Line 324: "whereas the minimum appeared at noon ($\text{GF} < 1.3$) (21:00)" ?? At noon or at 21:00?
 - Figure 9: how was the time period of the particles being externally or internally mixed exactly defined? And is this plot then showing really only the particles that were externally mixed (A) or internally mixed (B)? Or is it showing just the average for the mentioned time period, when you say, that mostly the particles were externally/internally mixed? Please be more specific here! And why do you show different things with the white circles in panel A and B?
 - Figure 10: Is there a reason why you only show the seasonally separated diurnal variation of the moderately hygroscopic fraction? And not for the average GF or for both fractions? If yes, please clarify!
 - Line 351: "The shape of the diurnal pattern of the larger particles (30, 80 and 250 nm)" only 80 and 250nm??
 - Figure 10: is the difference for both 80 and 250nm particles in the different seasons really significant? And also the diurnal variation? For me these curves look quite flat and similar in each season. Showing not only the average but rather a boxplot or standard deviations or doing some statistical test would help to decide on that.
 - Section 3.3: the same question which I have asked in the methods part (comment 7), were the SMPS measurements performed at the same station or in Athens? If they originate from the same place (the SMPS measured there where the HTDMA), then please ignore this comment, only state that clear, if not, then you cannot use the hygroscopicity data to describe the different size distribution peaks from another place, and with that this complete section is not valid to my opinion. But only then.
 - Figure 11: why not to include the GF values in this figure instead of having them only in the supplementary?
 - Figure 11: it looks for me that the different GF values are quite stable for all clusters, and even the number fractions of the two hygroscopic modes does not vary too much.

Is there really a significant difference between the hygroscopicity of the different size distribution clusters? Like GF_50_2 changes between 1.19 and 1.23 if you look at the different clusters. Please provide some analysis, tests there instead of mentioning some selected GF values in the text. An idea would be also to show the average GF-PDFs for the different clusters and compare them. One should see there better if there are differences or not.

- Supplementary tables: some description is missing there. Like what the different abbreviations mean? Like GF_50_1 and GF_50_2. Please add an exact definition to each value.
- Line 458: something went wrong with the formatting of this reference
- Overall, quite a few sentences are a little bit hard to follow in the manuscript, I was not always sure what the authors meant. It would be nice if a language edit could be done prior to publication.
- You present kappa values in the manuscript but do not discuss them a lot. I would suggest to add a more detailed discussion on kappa values, maybe compare it to what other studies found as well.