Reply to reviewer #1

We thank the reviewer for the positive feedback and the helpful comments. Below, find our point-to-point response to specific comments.

Detailed response to comments:

We present here our response to each comment (blue font) and we quote the respective part of the revised manuscript (grey font).

1. Line 32-33: not only as CCN but also as IN, and those play a role in the indirect effect as well

The ability of aerosol particles to act as both cloud condensation and ice nuclei has been added in the manuscript.

2. 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

We agree with reviewer that since the Kappa values are dependent on both RH levels and particle size, we should better give a range instead of certain of kappa values. Therefore, the sentence has been revised as follows:

"The kappa values for highly hygroscopic aerosols, such as salts and sulfates, range between 0.5 and 1.4, for organics from 0.01 to 0.5, whereas for non – hygroscopic aerosol such as soot, the kappa values are close to zero (Petters and Kreidenweis 2007)".

3. 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 Sellegrini et al. 2014, don't you mean Holmgren et al. 2014? (https://doi.org/10.5194/acp-14-9537-2014)

The sentence has been rephrased as follows:

"Long-term measurements of aerosol hygroscopicity are useful for the better understanding of the link between particle hygroscopic growth and particle emission sources, formation and transformation processes. A few long-term studies of aerosol hygroscopicity and mixing state by means of the HTDMA technique have been published so far, and some of them are mentioned below (Kammermann et al., 2010, Fors et al., 2011, Holmgren et al. 2014)".

4. 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.

The citation "Bezantakos et al., 2013" was added in Line 94.

5. Line 81-92: please add the different flow values for the HTDMA

The aerosol and sheath flow rates of the HTDMA system were added as suggested by the reviewer in Line 81-92, as follows:

"The DMAs were operated with a sheath flow rate of 3.0 L/min, and a monodisperse sample flow rate of ~0.3 L/min".

6. 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.

We agree with the reviewer that figure2 was incomplete. Therefore, Figure 2 was redesigned with labels describing all parts of the HTDMA system under field operation.

7. 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.

It is necessary to clarify that the HTDMA was operated in parallel with the SMPS at ACTRIS DEM station, which was also mentioned in the manuscript as “Athens station”.

DEM station is the only station in the Athens Metropolitan Area at the suburban location of Ag. Paraskevi and the NCSR Demokritos campus, which submits particle size distribution ACTRIS quality controlled data at the EBAS (nilu.ebas.no), despite the fact that since a few years other ACTRIS stations in Athens have been operating (for aerosol remote and aerosol in-situ data). The following sentence was added, to make it cleared that all the in-situ measurements were performed in parallel at the same site:

“The aerosol number size distributions of ambient aerosol (dry) were measured by means of a Scanning Mobility Particle Sizer system (SMPS) operated at the Athens DEM station.”

8. 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.

DEM station is a member of ACTRIS/GAW network of stations and it operates following ACTRIS/GAW recommendations in terms of sampling configuration and in-situ instrumentation. The RH levels in the sampling lines is kept below the nominal value of 40% by means of a membrane Nafion dryer. The wrong value of 45% was included in the text by mistake.

9. Line 120: “an inversion algorithm applied to” -> “an inversion algorithm is/was applied to”

The typo corrected as “an inversion algorithm was applied to”.

10. 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.

The methodology we follow for inverting the HTDMA data is described in detail in the manuscript by Gysel et al. (2009). This citation added as suggested by the reviewer.

11. Line 125: “x2” is it not usually “Chi” and not x?

It can be either both x or Chi. We use “x^2 “, as described by Gysel et al., (2009).

12. Line 133-134: The two sentences after each other are repetitions with similar meanings, do you really want both to be there

The sentence was rephrased as follows:

“In the present study, the inverted data can be grouped into three cases, representative of the aerosol mixing state (Fig. 3).”

13. Line 135-137: Typo, bit of too many brackets here?

The typo was corrected.

14. 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.

We agree that it should be clearly stated that the broadening can be representative of the degree of mixing of aerosol particles and/or the temporal variability of the GF. Thus, the sentence was rephrased as follows:

“Mean GF-PDFs represent the mean distributions of growth factors and does not necessarily provide a clear picture of the mixing state of these size fractions. More specific, the appearance of a broad mode or two overlapped

modes or two distinct modes does not imply the simultaneously existence of particles of distinctly different hygroscopicity and thus composition but may also result as a matter of temporal GF variation for the long temporal variability data products displayed here. It will be further clarified in the analysis below which factor is prominent at the different cases."

15.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.

We agree that the possibility that BC particles of larger than 30 nm should also be taken into account in most cases, when aging processes quickly move these fresh BC particles to the Aitken mode. This assumption is supported by the fact that during January and February non hygroscopic particles (GF<1.12) are detected inj our suburban aerosol in Athens. We understand your comment is basically in line with this exsplanation and this is now described in more detailed and better clarified is the revised manuscript :

"Non or slightly hygroscopic 30-nm-particles with GF~1.0 are essentially missing, in contrast to particles with D0>30nm indicating that freshly emitted particles, such as bare black carbon, are probably growing faster to sizes larger than 30 nm, and are observed as such largely absent during most of the year with the exception of winter (January & February). Aging processes are not very effective during the dark and colder months, therefore a small fraction of non hygroscopic carbonaceous fresh aerosol is very likely to remain and be detected in these below 30 nm size fraction. It has been found that these aging processes are more efficient for the nuclei mode rather than the higher Aitken modes in modifying their hygroscopicity due to condensation of organics and inorganics onto the pre-existing particles (Vu et al., 2011). Also 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."

16. Figure 4: the vertical black line is not defined.

The vertical black line is now defined in fig.4.

17. 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?

We agree that as presented in Figure 4, the number fraction of the highly hygroscopic particles in the accumulation mode display a minute peak: We went back to the original and inverted data and we found that the number fraction of particles corresponding to this peak is extremely low and close to zero We therefore consider this as a numerical artefact of the inversion code and not a value with physical significance. We propose to make a note in the manuscript as follows:

"The number fraction corresponding to the minute peak appearing at the high hygroscopicity values for the 250 nm fraction is close to zero and does not appear to be physically meaningful. It can only be considered as an artefact of the inversion code."

18. 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

The reference "(fig. 5. Panel A)" belongs to the sentence before and therefore the annual mean growth factors were added as annotation in the figure 5.

19. 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.

We can confirm that this sentence is obviously wrong and was left in the manuscript by mistake due to some copy and paste. Of course there is seasonal variability and we modified the text to describe this finding.

20. 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.

We agree with your suggestion. Therefore, figure 5 was removed from the manuscript. The analysis of seasonal variability of the aerosol hygroscopicity is presented in figure 6, along with the analysis of the kappa values.

21. Line 223-224: monthly average kappa? Are these not the yearly averages?

We confirm that the kappa values presented correspond to the yearly averages. The sentence has been corrected.

22. Line 225: "standard deviation" please change it to GF-PDF standard deviation

Standard deviation was changed to "GF-PDF standard deviation"

23. Line 231-232: sigma for the 250nm particles is as low in September as in August

We agree with the reviewer that sigma for the 250 nm particles is as low in September as in August. The sentence was rephrased.

24.Line 241-242: do you have an idea why February is so much different from January? Why only that month?

February is only markedly different in mixing state. In most size ranges there is a progressive increase in the degree of differences in mixing state from January to February and then a decrease from March onwards. Only in the size range below 30 nm, February strands out as the highest compared to the other months. We have described early that January and February are months when the aging processes are less effective allowing for the different mixing states to appear as such in the suburban aerosol while in all other months and seasons these processes are fast enough to modify aerosol properties like hygroscopicity within the time interval required for the aerosol to spread within the Athens basin from the area of direct emission sources to the background areas.

25. Line 245-246: "Aitken particles and the particles in the accumulation mode (D_0 > 30 nm) and the particles in the accumulation mode" too many accumulation modes

The sentence was rephrased as follows:

"In general, the Aitken particles and the particles in the accumulation mode (D_0 > 30 nm) can be characterized as an external mixture of moderately hygroscopic (i.e. background aged aerosol) and non-hygroscopic aerosol (i.e. fresh local emissions), respectively."

26.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=30nm GF=1.12 means a kappa of approx. 0.075, the same GF for a 250nm is approx. 0.048. I would suggest to define a kappa limit and calculate a GF limit for each dry diameter. Even if that this would not make a big difference in the results.

The hygroscopic parameter κ was calculated as described by Peter and Kreidenweis (2007), by using the mean GF values for each dry size.

$$\kappa = \frac{(GF^3 - 1)(1 - a_w)}{a_w}$$

The mean GF values are the inverted observed values determined by the TDMAinv algorithm by Gysel et al., (2009), before the analysis of the aerosol mixing state and the determination of the non/or slightly and moderately hygroscopic mode.

For the determination of the two hygroscopic modes and the number fraction of each mode, GF = 1.12 was not used as constant value but was the upper limit of the range 0.9 - 1.12 for non-hygroscopic mode. Specifically, two hygroscopic ranges have been selected; a non and/or slightly hygroscopic mode with GF<1.12, and one

moderately hygroscopic mode with GF>1.12. Afterwards, the different integral properties of GF-PDFs (i.e. mean GF and number fraction) were calculated for these GF subranges. The mean GF and the number fraction of non and/or slighlty hygroscopic particles with GF<1.12 is obtained by calculating the mean GF of the subrange of the whole GF-PDF at GF<1.12, according to Eq. (C.9) and Eq. (C.8) in Gysel et al. (2009), respectively. The same procedure was followed and for the moderately hygroscopic mode.

In order to clarify this, the following paragraph was added:

"For the determination of the two hygroscopic modes and the number fraction of each mode, GF = 1.12 is the upper limit of the non-hygroscopic mode. Specifically, two hygroscopic ranges have been selected; a non and/or slightly hygroscopic mode with GF<1.12, and one moderately hygroscopic mode with GF>1.12. Afterwards, the different integral properties of GF-PDFs (i.e. mean GF and number fraction) were calculated for these GF subranges, following the methodology describe by Gysel et al. (2009)."

27. Figure 7, label for f: typo ">/<1.12" should be in subscript as well, not only GF

The label "f" in figure 7 was corrected as: "$f_{GF<1.12}$ / $f_{GF>1.12}$".

28. Line 280-281: "Specifically, for dry particle diameters D_0 > 30 nm, the contribution of the non- and/or slightly hygroscopic mode was maximum in spring and minimum in winter." ??? f_{GF}<1.12 (Fig 7B) shows something completely different: minimum in spring, higher values in winter, maximum in August.

We agree with the reviewer this description was given in the wrong order by mistake and is now corrected in the text.

"The number fraction of each mode also significantly varied from month to month for all dry sizes, with distinct variability in the relative contributions of particles with small or moderate-to-large growth factors. Specifically, for dry particle diameters D_0 > 30 nm, the contribution of the non- or slightly hygroscopic mode was minimum in spring, maximum in August and, in winter"

29. 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.

and

30. Line 285-286: "Specifically, the average number fraction of the slightly hygroscopic particles was 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.

We acknowledge again that the description was wrongly given and we update the text as suggested by the reviewer as follows:

"The number fraction of each mode also significantly varied from month to month for all dry sizes, with distinct variability in the relative contributions of particles with small or moderate-to-large growth factors. Specifically, for dry particle diameters D_0 > 30 nm, the contribution of the non- and/or slightly hygroscopic mode was maximum in spring, maximum in winter and minimum in August. For particles with D_0 = 250 nm, the moderately hygroscopic particles clearly dominate over those with GF<1.12 for all seasons. Specifically, the number fraction of the moderately hygroscopic particles with D_0 = 250 nm, was 0.62, 0.80, 0.67 and 0.70 in winter, spring, summer and autumn, respectively."

31. 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.

Please note that all this information together will make the plot difficult to read. Therefore, a new plot with the mean diurnal growth factors and the standard deviations was added in the supplementary information.

32. Section 3.2.: check again the naming of the GF<1.12 and GF>1.12 fractions! It is mixed up again at a lot of places, naming the fraction with GF<1.2 sometimes non-hygroscopic, sometimes non- or slightly hygroscopic and naming the fraction with GF>1.2 slightly or moderately hygroscopic. Hard to follow this section again.

The modes with GF < 1.12 represent the non/slightly hygroscopic aerosol, whereas the GF > 1.12 represent the moderately hygroscopic aerosol (section 3.2). The naming of the GF<1.12 and GF>1.12 fractions was checked and corrected wherever necessary.

33. Line 324: "whereas the minimum appeared at noon (GF < 1.3) (21:00)" ?? At noon or at 21:00?

Line 324 was corrected as follows:

"whereas the minimum GF (<1.3) appeared at the evening (21:00)".

34. 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?

The time period of the externally or internally mixed fractions was not predefined. We examined our database on a monthly basis. We define three different cases of mixing states the internally mixed ($\sigma \leq 0.07$), continuum of mixing states ($0.07 < \sigma < 0.15$) and externally with distinct modes ($\sigma \geq 0.15$) for the monthly GF-PDFs. The classification of the different months as internally or externally mixed (with the continuum of mixing dates classified within the internally mixed case) was based on this analysis.

This way of classifying the seasonal behaviour of the mixing state was also supported by the number fractions of the two mixing states grouped on a monthly basis. It was found that the number fraction of externally mixed particles was lower than 10% in all cases apart from January and February. This latter phrase we will include it in the text in order to reply to this comment and be more informative for the reader.

35. 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!

And

36. Line 351: "The shape of the diurnal pattern of the larger particles (30, 80 and 250 nm)" only 80 and 250 nm??

And

37. 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.

Comments 35-37 refer to figure 10, and are discussed together, bellow.

As shown in Figure 8 there is very little diurnal variability in the GFs of the non-hygroscopic mode. We also omit the 50 nm as they have the same behaviour as 80 nm. The non or slightly hygroscopic mode is characterized by almost hydrophobic particles, with mean GF close to one. Therefore, we consider suitable to investigate the seasonal diurnal variation of the mean GF of the moderately hygroscopic mode. The results show similar seasonal diurnal variation patterns without significant differences. This is probably indicative of the background aerosol studied in the present work. Since we have a strong indication of the reviewers to reduce the size of the manuscript, and indeed Figure 10 provides similar information as the previous figures, we chose to omit this figure in the revised manuscript. In that way, the length of the manuscript will be reduced without missing important information. The text in the manuscript will be modified accordingly.

38. 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.

DEM station is a station in Athens Metropolitan area (Figure 1). Please see comment 7.

39. Figure 11: why not to include the GF values in this figure instead of having them only in the supplementary?

And

40. 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.

Comments 39 and 40, both refer to figure 11 and will be discussed together below.

The mean GF-PDFs were calculated for each cluster and for the different dry particle sizes (30, 50, 80 and 250nm). The GF-PDFs have been included in Figure 11, in order to provide a more detailed insight into the hygroscopic properties and mixing state characteristics of each cluster. Given that the variation of the number fractions of the non/slightly and moderately hygroscopic modes do not significantly vary between the clusters, we decided to present only the mean GFs of each cluster in Table S2. The mean GFs were higher in the clusters 1 and 3, for all dry sizes. These clusters are related with atmospheric conditions favouring new particle formation or transport of nuclei particles from the city centre to the sampling site. These particles are further mixed with the background aerosol. The less hygroscopic particles are related with cluster 4, which is the most frequent cluster (67%) and represents mainly the contribution of the "regional/urban background aged aerosol", mostly accounting for aged and long-range transported aerosols.

Looking at the GF-PDFs, it can be observed that although the mean growth factors of D_0 > 30 nm do not vary significantly between the clusters. Overall, clusters 2 and 5, which represent 12.1% and 15.3% of the hourly averaged number size distributions, respectively, have similar GF-PDFs patterns and average GFs values for all dry particle sizes. Clusters 1 and 3, which account only for 4.2 % and 1.3 % of the hourly particle number size distributions, are characterized by more hygroscopic particles compared to the other clusters. The particles of cluster 4, which represent 67% of the averaged number size distributions, have the lower GFs values compared to the other clusters.

The following paragraph was added:

"The mean GF-PDFs were calculated for each cluster and for the different dry particle sizes (30, 50, 80 and 250nm). Overall, clusters 2 and 5, which represent 12.1% and 15.3% of the hourly averaged number size distributions, respectively, have similar GF-PDFs patterns and average GFs values for all dry particle sizes. Clusters 1 and 3, which account only for 4.2 % and 1.3 % of the hourly particle number size distributions, are characterized by more hygroscopic particles compared to the other clusters. The particles of cluster 4, which represent 67% of the averaged number size distributions, have the lower average GF values compared to the other clusters"

41. 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.

The mean GF-PDFs were calculated for each dry size and cluster. The mean GF-PDFs are depicted in Figure 11 and the mean GFs are presented in Table S2.

Table S2 Mean GF-PDFs per cluster for different dry particle sizes (30, 50, 80 and 250 nm)

Cluster	$GF_{Ddry=30nm}$	$GF_{Ddry=50nm}$	$GF_{Ddry=80nm}$	$GF_{Ddry=250nm}$
1	1.35	1.16	1.19	1.23
2	1.28	1.11	1.13	1.22
3	1.34	1.17	1.19	1.26
4	1.26	1.10	1.11	1.20
5	1.29	1.11	1.13	1.21

42. Line 458: something went wrong with the formatting of this reference

The format of the reference was corrected.

43. 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.

Language editing was performed prior manuscript publication.

44. 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.

In this study, we investigated the aerosol properties in terms of their hygroscopicity and mixing state by means of an HTDMA system. In that context, detailed analysis of the primary parameter measured with the HTDMA, the GF for selected dry particle sizes, was provided. However, the boxplots for the kappa values have been included in Figure 5 and a more detailed analysis of the kappa values has been provided in the revised manuscript.