Reply to reviewer

We thank the reviewer for considering the manuscript worth publishing. Below, we present our point-to-point response to the reviewer's comments in (blue font) and we quote the respective part of the revised manuscript (grey font).

Summary of recommendations for minor revision:

You acknowledge in your review answer to me that "Hindsight, it might have been more ideal to probe at e.g. 30 nm, 60 nm, 120 nm, and 250 nm, at least from a CCN activation perspective". You have to be honest in your paper, and mention this fact in the method section. No one will criticize you for this (knowing you can't change your experiments in hindsight). Instead, the reader will appreciate your honesty, and will understand your choice of selected sizes. Otherwise, it will be impossible to understand your reasoning behind it, and others that follow will not understand and don't know how to plan how they should perform similar measurements in similar environments.

The following paragraph was added:

"One of the limitations of the HTDMA technique for size resolved hygroscopicity measurements arises from selecting several representative size fractions to study but at the same time obtaining data in a relatively high time resolution. In our case, four dry sizes were selected to be studied i.e. 30nm, 50nm, 80nm, and 250nm. Our findings reveal that the 50 nm and 80 nm Aitken particles presented similar hygroscopic properties, whereas larger differences were observed between the Aitken particles and the particles in the accumulation size range i.e. 250 nm. At least from a CCN-prediction perspective, our size selection might not be the optimal one, although the GF-PDFs can be interpolated in time and diameter in between the available measurements to describe the hygroscopic behaviour of the aerosol particles in each size bin of the SMPS, without introducing too much error in CCN predictions as confirmed by previous studies (Kammermann et al., 2010). Alternatively, it might be more ideal the hygroscopic properties of ambient aerosol at the dry diameter, D_0, 60 nm and 120 nm, instead of at 50 nm and 80nm, to be investigated given that the size range between 100 and 150 nm is considered very important for CCN studies".

Line 106: "Both, aerosol and sheath, flows". Should be "Both aerosol and sheath flows".

We revised the sentence as suggested:

"Both aerosol and sheath flows"

Line 203: "two distinct modes does not imply the simultaneously existence of particles". Should be "two distinct modes do not imply the simultaneous existence of particles".

The sentence was rephrased as:

"two distinct modes do not imply the simultaneous existence of particles".

Line 206: "with GFs to be ranged between 1.17 and 1.41". Should be "with GFs ranging between 1.17 and 1.41".

The sentence was rephrased as:

"with GFs ranging between 1.17 and 1.41".

Line 210: “In winter, the existence of two modes indicates that probably both fresh, (non and/or slightly hygroscopic), and aged, (moderately hygroscopic), emissions from traffic and other combustion sources, (biomass burning, residential heating), contribute to the 30 nm size fraction”. What do you mean? Does the traffic contribute to the non and/or slightly hygroscopic, and biomass burning/residential heating to aged-moderately hygroscopic? You have to write this connection between the two sources and the hygroscopicity explicitly in the manuscript.

and

Line 212: “In general, the 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., 2021)”. Again, what do you mean? Which condensation belongs to which particle mode? Write it out explicitly.

In the present study, the measured GFs of the 30 nm particles were in the range of values reported in previous studies in urban environments influenced mainly by traffic and/or other combustion-related sources (e.g. biomass burning). The hygroscopic properties of the 30 nm particles differ between these studies; some report non-hygroscopic particles, while other studies report moderate hygroscopicity at this size. In general, direct emissions from different combustion sources, nucleation and condensational growth play a key role at this size, resulting in particles of different chemical composition (Wang et al., 2018; Enroth et al., 2018; Swietlicki et al., 2008, Kim et al., 2020). The relative contribution of the different emissions sources cannot be quantitatively determined in the present study, although it is evident that fresh combustion-generated aerosols (traffic and wood burning) tend to be less hygroscopic than the aged one (Vu et al., 2021). In general, aerosols emitted from traffic sources increase their hygroscopic growth factor during atmospheric ageing, but this increment is much lower than that of biomass burning aerosols (Vu et al., 2021). Moreover, traffic-related sources emit almost pure black carbon, whereas black carbon from wood burning is to some extent internally mixed with co-emitted organics and thus more hygroscopic (Motos et al., 2019). In the present study, the nuclei particles are characterized as “moderately hygroscopic” in all seasons, except from winter. In winter a complex state of mixing was observed indicating that both primary and photochemically aged emissions contribute to this size range.

Thus, the following paragraph was added:

“In wintertime, a complex state of mixing was observed indicating that both fresh (non and/or slightly hygroscopic) and aged (more hygroscopic) combustion-generated nanoparticles (i.e. biomass burning, traffic) contribute to the nuclei mode, with the time scale and efficiency of the aging process governing the final hygroscopic properties and state of mixing (Wang et al., 2018; Enroth et al., 2018; Swietlicki et al., 2008, Kim et al., 2020, Vu et al., 2021). The externally mixed nature of the nuclei mode reflects the less efficient aging and coating of the fresh combustion-related nanoparticles during the dark and cold months of the year.”

Line 235: “looking at the GF-PDFs of the particles in the accumulation mode a peak appeared in the highly hygroscopic range. However, the number fraction corresponding to at peak is so low that is unimportant to identify the true nature of this negligible small peak”. I understand your reason. But, if this hygroscopic mode is dominating contribution to scattering of solar light for example, then, this statement is not true. Better be a bit careful and write that you have chosen not to focus on this small peak, rather than that it is unimportant.

We understand that the characterization of this small peak as “unimportant” might not be explicitly correct. We went back to the measurement data and we can confirm that this peak whenever presented in the number size distribution spectrum it has a close to zero contribution to the total number concentrations (close to zero number fraction). Therefore, the sentence was revised as follows:

“However, the number fraction corresponding to this peak is extremely low (i.e. close to zero). Thus, we decided not to investigate further the nature of this peak.”

Figure 5. Larger fonts needed for figure.

The fonts have been done larger.

Table 1. What do you mean with cold and warm period? Which measurements are from cold and which are from warm periods?

In the table 1, a number of characteristic GFs is presented for different emission sources and aerosol chemical compositions. The table and the title of the table were updated as follows:

TABLE 1 Mean Growth Factors measured at RH=90% for particles with different chemical composition

Chemical Composition	Growth Factor, (GF)	Source
BC, Mineral Dust	**<1.05**	**Vlasenko et al., 2005**
Biomass Burning	**1.15-1.65**	**Cocker et al., 2001**
Aged wood smoke	**1.3-1.5**	**Kotchenruther and Hobbs, 1998**
Fresh wood smoke	**1.1-1.3**	**Kotchenruther and Hobbs, 1998**
Inorganic Ions	**~1.7**	**Gysel et al., 2002**
Organic Compounds	**1.0-1.7**	**Koehler et al., 2006**
Fresh traffic emission	0.92-1.20	Vu et al., 2021
Aged traffic emission	1.09-1.29	Vu et al., 2021

Line 285: “The number fraction of each mode also significantly varied”. Should read: “The number fraction of each mode was also significantly different”.

The sentence was rephrased as “The number fraction of each mode was also significantly different”.

Figure S3. You never discuss or present the results for this figure in the text (just mention that standard deviations of GFs can be found in Figure S3). So, you should remove this figure.

Figure S3 removed as suggested by the reviewer.

Line 335: “These data provide enough evidence to assume that urban emission are the main source of these nuclei particles, while adequate time for further aging is also ensured. As the particles undergo atmospheric aging their composition changes, in relative terms, due to condensation of secondary aerosol which is most pronounced for the small particles”. Which nucleation particles do you mean? The ones between 00 and 05, or the ones at morning, or the ones between 15 and 20, or the ones between 20 and 00? Sorry, I don’t get it. You have to rewrite the explanation again.

The above paragraph has been revised as follows:

“For the 30 nm particles, it was observed that the GF of the moderately hygroscopic mode was higher (GF > 1.3), between late evening and early morning (00:00 – 05:00 UTC+2), when the relative humidity appeared to have the maximum values (fig. S2) as well as at early afternoon (15:00 – 20:00 UTC+2). At the DEM station, the 30 nm particles are primarily related to traffic emissions and to a lesser extent to new particle formation (Vratolis, et al., 2019). This was also confirmed in the present study by the cluster analysis of the number size distributions. Moreover, in fig.S3, the CPF (conditional probability function) polar plot of 75th percentile of the total number concentration in the size range from 20 to 38 nm is presented (Carslaw and Ropkins, 2012). It is obvious that these particles are predominately originated from the urban area, under moderate wind speeds. Taking into account that the distance between Athens city center and DEM station is around 7 km, the transport time within the Athens value at the indicative wind speeds observed are yielding estimated transport time between ½ hour to a few hours. These data provide enough evidence to assume that the observed nuclei concentrations reflect a synergetic effect between different combustion-related urban emissions (e.g. fresh traffic-related aerosol from the neighbourhood urban area and further growth) especially during daytime, and the development of the local inversion boundary layer during night-time.”

Line 339: “During the photochemical active period of the day, (at noon), secondary formation of condensable organics, which might occur faster than that of inorganics, is probably responsible for the appearance of less hygroscopic Aitken particles than that of 30 nm, which is consistent with the findings presented in previous studies, (Mochida et al., 2008).” Why would the Aitken mode particles be less hygroscopic due to this than the 30 nm particles? Sorry, but I don’t get it again. Please rewrite text again to make it become understandable.

We agree with the reviewer that this paragraph is not easily understandable. If the composition remains the same in the nuclei size range as for accumulation and Aitken mode particles, one would expect lower GFs for smaller particles (Kelvin effect). Here, it is evident that nuclei mode particles are more hygroscopic than the somewhat larger particles at the lower end of the Aitken mode, while hygroscopicity increases with particle size from the Aitken to the accumulation size range. This reflects the differences in the chemical composition between the nuclei mode and the lower end of Aitken particles, with the smaller particles to be a mixture of more hygroscopic compounds. Given that inorganics are more hygroscopic than organics, it is expected higher partitioning of the former to the nuclei size range, while the organics may be more crucial for further growth to larger particles.

In short, the following paragraph was added:

“During the photochemical active period of the day, the secondary formation of condensable organics, which might occur faster than that of inorganics, is probably responsible for the appearance of less hygroscopic Aitken particles (Mochida et al., 2008). Specifically, if the composition remains the same in the nuclei size range as for accumulation and Aitken mode particles, one would expect lower GFs for smaller particles (Kelvin effect). Here, it is evident that nuclei mode particles are more hygroscopic than the somewhat larger Aitken particles. This reflects the differences in the chemical composition between the nuclei mode and the lower end of Aitken particles, with the smaller particles to be a mixture of more hygroscopic compounds. Given that inorganics are

more hygroscopic than organics, it is expected higher partitioning of the former to the nuclei size range, while the organics may be more crucial for further growth to larger particles."

Line 378: "frequency of occurrence during morning and late afternoon traffic rush hours, while an additional peak appeared at noon". Should read: "frequency of occurrence during morning and late afternoon traffic rush hours, with an additional peak that appeared at noon".

The sentence was rephrased as:

"frequency of occurrence during morning and late afternoon traffic rush hours, with an additional peak that appeared at noon".

Cluster 2 seems to be more of a wood burning factor, if it is from the urban area. You claim urban (what do you mean with urban? Car traffic?), but you have to motivate whey the Aitken mode particle number size distribution peaks at 60 nm diameter. If this is car exhaust, the particles would need to grow from around 20 nm diameter to 60 nm diameter within only a few hours transport from Athens to your site, which I think is impossible. If you check that cluster 2 appears more often during wintertime, you will have a strong indication that it comes from wood burning. The high night concentrations already indicate that.

If wood burning was the main contributor, one would expect higher frequency of occurrence in wintertime. But this is not our case. The frequency of occurrence of this cluster shows no significant seasonal variability. Therefore, we consider more appropriate to characterize this cluster as "urban background, nocturnal", which reflects the synergetic effect between particle emissions from different combustion sources (aged traffic, wood burning) and the development of the local inversion-nocturnal boundary layer.

Cluster 4 seems to be totally dominated by long-aged particles (from more distant urban areas than Athens), because there is little diurnal variation and the particles are quite large in size. Could you check the wind directions, that it is not coming from Athens, and it would give some proof of that.

We agree with the reviewer. Cluster 4 was revised as follows:

"Cluster 4 (Mixed urban and regional background) is the most frequent cluster (67%), dominated by aged and long-range transported aerosols."

Cluster 5. Could one claim that the relatively fresh particles likely come from the neighborhood urban area, since the nucleation mode particles between 10 and 20 nm diameter haven't had time to grow to larger sizes?

We agree with the reviewer. Cluster 5 is representative of "Fresh traffic and further growth". The following sentence was added:

“This cluster represents the relatively fresh particles predominately transported in the receptor site from the neighbourhood urban area.”