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Response to Anonymous Referee #2 comments

The paper by A. Bougiatioti is presenting a study on the hygroscopicity and CCN properties changes of aerosols when biomass burning (BB) events are transported to the Finokalia site. The study is focused on a two or three months period (which is not very clear) when four BB events occurred. Although the retrieval of the hygroscopic properties of BB aerosols would be interesting to the scientific community, there are many (major) points that have to be clarified before the manuscript is considered for publication: (1) there is a need to better describe the statistical analyses used. A careful statistical analysis of the aerosol properties when they are not affected by BB (including their variability over the period chosen) compared to the change in these properties when the plume is sampled at the site (the choice of the boundary of the plume is important: how is this performed? Is it based on the BBOA derived from the PMF, or BC? Is there a threshold used and on which parameter?) is needed. Then, within the plume, the methodology for separating the fraction of aerosols, which are originating from the BB event and their properties from ambient aerosols that have mixed along the transport path is not very clear. Can the external mixing information from the HTDMA data and the PMF analysis be combined to compute an increase of CN and CCN number concentrations due to the contribution of BB aerosols? Can this be compared to the increase of CCN number computed with the first approach (comparison of outside vs inside the plume)? Which multivariable regression analysis is used to retrieve the different organic fraction hygroscopicity parameter? What are the uncertainties?

***Response**: We thank the anonymous referee for the thoughtful review. Most of the issues raised were also concerns of the other anonymous referees therefore we have further elaborated on these points in the revision manuscript. Nevertheless, all the details concerning the identification and source apportionment of the organic aerosol are provided in the separate publication of Bougiatioti et al. (2014). On the other hand, more details concerning the multivariable regression analysis to retrieve the hygroscopicity parameter of each fraction will be provided in the revised version of the manuscript.*

(2) There are inconsistencies in the data set. Even though average kappa's derived from HTDMA and CCN measurements agree within 30% over the whole period (Table 2), a simple reading of Fig6 and Fig7 shows that the discrepancy can be much higher over smaller periods. This needs to be better commented.

***Response**: Indeed overall kappas derived from the HTDMA and CCN agree within 30%. Differences larger than 30% in kappa values derived by the CCNC or the HTDMA are probably caused by the following reasons:*

1) HTDMA detects all sampled particles including the hydrophobic ones (i.e. GF=1; κ=0). On the other hand CCNC will detect only activated particles. In cases of coexisting hygroscopic and hydrophobic, externally mixed, populations $\overline{\kappa_{HTDMA}}$ *(i.e., the average kappa value which is representative of the hygrsocopic properties of the entire sampled particle population) accounts for both (c.f. equation 6 in the manuscript), while only activated particles are accounted in the determination of κCCN.*

2) The hygroscopic parameter of the organic fraction may differ in sub- and super-saturated conditions (e.g. Henning et al., 2012; Chan, M. N., & Chan, C. K, 2007; Wex et al., 2009; Dusek et al, 2011).

Another possibility is that the particles originated from biomass burning may, among others, include surfactants, which influence the discrepancies between the κ-HTDMA and κ-CFSTGC values. Furthermore,water adsorption on nealry hydrophobic particles will be more pronounced at super-than in *sub- saturated conditions. In the case of the larger sampled particles, this may lead to their activation and detection by the CCNC, thus increasing the difference between* κ*CCN and* $\overline{\kappa_{HTDMA}}$ *deruved values.*

(3) The global impact of the results is not very clear:
a. the impact on atmospheric chemistry of the water contained in the organic fraction of the aerosol should be better evaluated: what is the increase of LWC due to organic BB aerosols compared to the LWC that the whole aerosol population would contain (actually, only the contribution of BB organic aerosols relative to the total organic content is evaluated)? Would this increase in LWC really favour chemical reactions that would not have taken place?

Response*: The role and impact of LWC is the focus of a different publication on its own (Nikolaou et al., 2015, ACPD) but the contribution of biomass burning aerosol to the total organic water of the aerosol is mentioned due to the possible atmospheric implications.*

b. The same is true for the direct impact: what is the contribution of BB aerosol liquid content compared to the rest of the population?

Response*: In order to strengthen the aspect of the direct impact of biomass burning, we have included a section on calculations of potential droplet number in marine boundary layer clouds formed over Finokalia. The focus of the analysis is on the relative impact of BBOA CCN on CDNC, supersaturation and the contributions of aerosol number and hygroscopicity on the resulting CDNC. Overall, it seems that there are differences in the droplet number concentrations, impacted by both the distance and from the intensity of the events. The higher the proximity, the lowest the contribution of the chemistry (kappa) to the droplet formation. As the distance grows higher, the concentrations get lower due to dilution, and the influence of the chemical composition gets higher.*

c. The impact on the total number of CCN is not clear neither, as the paper is showing changes in CCN number at variable sursaturations. What is the increase of CCN number due to BB at a given sursaturation?

Response*: For all the fire events, CCN concentrations are provided at the point of critical flow, corresponding to a critical supersaturation, as explained in detail in the Methodology section. Within each fire event, critical supersaturation for e.g. 120 nm particles was 0.14±.0.03 for the Euboea event, or for the 100 nm particles was 0.19±0.03 for the same event. Therefore it is expected that the differences in CCN concentration number are caused by the presence of the BB plume, rather than the different supersaturation.*

Detailed comments are given below:

Page 21542, lines 23-25 : "Laboratory and field studies suggest that the water-soluble component of biomass burning aerosol is highly hygroscopic, about half of ammonium sulfate". Not clear what half of ammonium sulfate is related to. Is half of BB aerosol ammonium sulfate ? to reformulate

Response*: Indeed, the "about half of ammonium sulfate" refers to the hygroscopicity parameter kappa, the text now reads "…is highly hygroscopic, with a hygroscopicity parameter about half of that of ammonium sulfate".*

Page 21549, line 23, I suppose the authors mean 18 august 2012 and not 1992

Response*: Indeed. Amended.*

figure 2c : Caliop shows that the smoke is travelling at higher latitude than the finokalia station right ? does this imply that the contribution of BB aerosol to the global mass loading is underestimated from the ground-based in situ measurements?

***Response**: The Caliop overpass over Crete, on 19 August 2012 between 00:27–00:40 and 11:34–11:47 UTC, is NW of the Finokalia station (Fig. 2a). For the 00:27–00:40 UTC time slot, based on the Caliop data (Fig. 2c), we can clearly see the presence of smoke aerosols mixed with the prevailing polluted dust and marine aerosols in the first 3 km height of the lower troposphere. This implies that for this time slot, the BB aerosols sampled by the ground-based in situ measurements at Finokalia would contribute less (due to dilution) to the global aerosol mass loading than, if measured, over the Western Crete. The text has been rephrased to "According to this classification, over Western Crete the presence of polluted dust (mixed with smoke and marine aerosols) prevails within the marine boundary layer, which for Finokalia is extending up to 0.8–1.2 km height, close to the mean value of 1 km reported by Kalivitis et al. (2007). This implies that for the 00:27–00:40 UTC time slot, the BB aerosols sampled by the ground-based in situ measurements at Finokalia would contribute less (due to dilution) to the global aerosol mass loading than, if measured, over the Western Crete."*

Page 21550, line 23 could you recall what is "the whole measurement period"? it is not clear.

***Response**: Amended.*

Figure 3 : need more dates on the x axis

***Response**: Amended.*

Page 21551, lines 1-2 : "the contribution of organics and BC increased substantially (from 34.9 to 46.5% for organics and from 6.1 to 9.5% for BC) with a simultaneous reduction of that of sulfate" To which period is the increase of BC and organics relative to ? Are those really substantial increases? What is the natural variability in organic and BC concentrations outside the BB events? Are percentages really relevant ? (BC contribution would increase if other components decrease, even if it stays constant.. ?) maybe absolute concentrations would be useful as well here?

***Response**: This increase refers to the observed average concentrations during all fire events, compared to the rest of the timeseries. The percentages express the relative contribution of each component to the total mass during these fire events. These increases are verified to be caused by the presence of BB plumes as described in detail in Bougiatioti et al. (2014), both as far as organics but also as BC is concerned, via source apportionment analysis. Especially for BC, during all BB events there is a clear increase from the contribution of wood burning, compared to that of fossil fuel.*

Page 21551, line 12 can you precise which size range is considered as "larger particles"?

***Response**: Amended. It refers to particles with diameter larger than 100 nm.*

Page 21551, line 13-14 "concentrations exhibited an increase that for the case of the Chios fire was around 65 %, for the Croatia fire around 50 %, the Euboea fire 88% and the Andros fire around 150 %." How was this determined? An increase relative to what ? to the mean concentration over the larger period of measurement (from April to September) ? average concentration during all BB events compared to the average concentration shown figure 3 (20 august to 18 sept) ?

***Response**: The text refers to CCN concentrations higher than the ones before the arrival of the smoke plume (average of around 6 hours). This will be clarified in the text.*

Figure 4 : not easy to read : small and all lines are surimposed

***Response**: The complexity of this figure with all the information that is included limits somewhat the resolution of this figure. Nevertheless the readability is improved once the four figures are placed in one column instead of two.*

Page 21552, line 1-3 : "The data shown in Fig. 4 indicates that during the majority of the identified biomass burning events, CCN concentrations for the larger particles sizes increase, tracking the BBOA trend." this is not really the case for the Croatia fire event.
I am not sure that you can really compare CCN number concentration for different sizes, since they are given for different sursaturations? Larger particles CCN concentrations might increase but if you need higher sursaturations for activating them, they might not contribute to the relevant CCN number concentration if the needed supersaturations needed to activate them are not realistic. In my opinion, increases in CCN numbers should be evaluated at a given supersaturation. If the goal of this discussion is to show that 100 nm particles concentrations are increased in the smoke plume, than it is easier to simply evaluate the increase of this size range from the SMPS size distribution?

***Response**: As mentioned in p.25551, lines 18-20, CCN concentrations are given at the point of critical activation flow* Q_{50}*, corresponding to the instantaneous supersaturation for each particle size. During the separate events, the derived critical supersaturations for a given particle size did not vary by more than 13.6%, being less for the smaller particle sizes. This information can be included in the revised text. The goal of the discussion is to show that smoke plumes contain larger more CCN-active particles, not just more particles.*

Page 21552, line 8 : two times "that"

***Response**: Done.*

Page 21552, lines 12_16 : "It appears that when the BB event is combined with a NPF event within a few hours, 60nm particles are strongly influenced and their CCN concentrations increase considerably. A detailed discussion on these events and their contribution to CCN concentrations is provided by Kalivitis et al. (2015)." Could you shortly give the conclusions from the Kalivitis paper ? Is NPF unambiguously associated to BB event (favoured by BB events) ? If NPF is occurring anyway (independatly of the presence of a BB plume), it should be mentioned otherwise the reader is mislead into the idea that the 60 nm CCN concentration increase is due to the presence of the BB plume.

***Response**: This is a good point. The goal was not to suggest that the 60 nm CCN concentration occurs from the BB plume, rather than to explain that the increase coincides with a NPF event. The exact mechanism for NPF is not known, therefore it is not unambiguously favored by BB events. If that were true, all events would be followed by NPF, which is not the case. It is merely the combination of the two we wanted to point out.*

Page 21552, lines 25-28 : "First of all, it can be seen that apart from the 60nm particles, the remaining sizes appear to be unaffected by the presence of smoke, as their activation fractions at supersaturation levels as low as 0.4% remain, more or less, stable and very close to unity throughout the events." Are the CCN concentrations again a function of supersaturation or are they given for a given supersaturation? there are no indication of the supersaturation on figure 5, to relate to the comments mentioning them in the text.

Response*: The activation fractions are derived from the asymptote of the fitting to a sigmoidal function of the CCN/CN ratio during each supersaturation cycle and is therefore representative for high supersaturations (ss>0.6%). This is the case for all data, for all particle sizes. This will be clarified in the revised text.*

Page 21554, lines 10-12 : "Most of the accumulation mode particles result from condensation of secondary sulfates, nitrates and organics from the gas phase and coagulation of smaller particles (Seinfeld and Pandis, 2006)" Accumulation mode particles can also originate from primary emission processes (combustion, but also marine aerosols have a large contribution (by number) in the accumulation mode) those can contribute to the particles hygroscopicity while not being measured by the ACSM.

Response*: Good point. In order to examine contribution by constituents not measured by the ACSM to the accumulation mode particles we compared the mass derived from the ACSM+BC and the integrated volume distribution from the SMPS converted to mass. During the examined fire events, the ACSM-BC was on average 68.6±19.3% of the SMPS-derived mass. Therefore this is an indication that indeed, part of the accumulation mode particles that may contribute to the particles' hygroscopicity during these events, are not being measured by the ACSM. The text will be changed accordingly to include this difference in mass and the different origin of accumulation mode particles that may contribute to the particles' hygroscopicity.*

Page 21555, lines 21-25 : "It is immediately apparent that the chemical dispersion is reduced with increasing particle size. 60nm particles exhibit the highest dispersion and especially the ones from the Chios fire, suggesting that the smaller particles retain their characteristics for a longer period and their aging takes longer that for the larger particles." There is no indication earlier in the manuscript that 60 nm particles are actually originating from BB emissions. There is no size segregated chemical analysis to show this. Would there be other indication that they are?

Response*: Based on the derived kappa values for each particle size and the chemical composition from the ACSM, the volume fractions for organics and inorganics (mainly ammonium sulfate) were estimated for each particle size. It occurs that 60 nm particles are, on average, 89% composed of organics (the respective values for 80, 100 and 120 nm particles are 70, 50 and 41%). As the main constituent during those events is the biomass burning (both BBOA and OOA_BB) then most probably the 60 nm particles are indeed originating from BB emissions. This information will be added in the revised manuscript.*

Page 21555, lines 14-27 : isn't it possible that the dispersion on kappa value also reflects the mixing with other aerosol types than the BB ones and not only processing of the BB aerosol ? The BB plume does not contain only processed (or fresh) BB but other pollution/natural aerosol. The history of the air mass before arrival to the sampling site is mainly determining how the BB is diluted into other aerosol types.

Response*: Based on the aforementioned comment, the chemical dispersion of kappa values within the 60 and 80 nm particles, which are mostly composed of organics, is mostly due to the processing of the BB aerosol. For the larger particles, indeed, chemical dispersion may be also due to mixing with other types of aerosol. It all depends on which type of aerosol prevails in the volume fractions and interacts, thus, with the other types of aerosol. This will be added along with the estimate of the composition of each particle size.*

Page 21556, lines 1-4 : "This behaviour of the small particles… coagulation mostly occurs for smaller particles and increases the external mixing of those particles by bringing together particles of different nature." I don't see the link between this sentence and the previous one. Which behavior of the small particles are the authors referring to? Coagulation creates internal mixing, external mixing is when the different chemical components are on different particles of the same size. The whole paragraph (until line 25) is confusing, and based on speculation on coagulation/condensation that ignore mixing with other particle type during transport.

***Response**: "This behavior" is referring to the increased chemical dispersion that the 60 nm particles exhibit. The sentence will be changed accordingly for clarification in the revised text. Nevertheless, all reviewers have raised the same issue on the interpretation of the results based on coagulation/condensation. We do agree, that the most probable process that justifies the obtained results is the formation of the smaller particles during the transit by secondary aerosol formation from condensation of mostly organic components (which is seen by the large mass fraction of organics in the smaller particles sizes, as already mentioned). We would like to thank all the reviewers for the scientific quality amelioration of our study. The whole discussion we be changed accordingly in the revised text.*

Page 21556, lines 26-27: "During the focus period…" Do you mean outside BB events?

***Response**: The sentence corresponds to the time periods of the BB events as well as few days before and after the events.*

Page 21557, lines 9-11 : "Given that the solution of the resulting droplets may be non-ideal, the constituents may be partially soluble and the phases may not be completely separated, it is not surprising that the HTDMA-derived kappa_HTDMA values are somewhat lower" which droplets ? Non ideality would account for more than 30% discrepancy?

***Response**: For ambient particles, a difference of 30% between kappa-CFSTGC and kappa-HTDMA are common. In the study of Wu et al. (2013) κ derived from CCN measurements was around 30% (varying with particle diameter) higher than that determined from hygroscopic growth measurements. This is attributed to the fact that both, substance individual and mixture κ values at 86% RH are often significantly lower than those for higher RHs and under supersaturated conditions (Petters and Kreidenweis, 2007). Apart from non ideality of the solution, the presence of surfactants produced during biomass burning events may also increase the discrepancies between κ-HTDMA and κ-CCN. This will also be added in the revised text. Overall, differences between κ values obtained from CCNc and HTDMA measurements are still under investigation in laboratory experiments. Pinpointing the exact reason of these discrepancies, in the current study, is rather difficult as we lack the exact chemical composition of the studied particles.*

Page 21557, lines 16-18 "During the two most intense fire events where the smoke plume had the least transit and atmospheric processing time (i.e. during the Chios and Euboea fire) all sizes exhibited two different hygroscopic modes (Tables 3 and 4; Fig. S3 in the Supplement)." This feature clearly indicates that BB particles were externally mixed with particles of other origins, and that a direct link between the dispersion of kappa and ageing can not be drawn, right?

***Response**: As mentioned further on in the text, these two different hygroscopic modes can be due to the presence of freshly emitted particles and more processed ones, rather than particles of other origin. Positive Matrix Factorization analysis does not recognize any other possible factors e.g. traffic and air masses have not traveled over Greek mainland to be influenced by other major sources. Therefore there is a direct link between the ageing of particles which is reflected in the changes in kappa.*

Figure 7 (compared to figure 6) : the hygroscopicity parameters derived from the HTDMA decrease with increasing particle size (fig 7), while it was the opposite for CCN-derived kappas (fig 6). Can you comment on this ? For the 120 nm particles kappa derived from both techniques disagree by far more than the 30 % mentioned in the text and calculated as an average Table 2 (could be a factor 4 between the two differently derived kappa's!)

Response*: This is a good point. The kappas derived from the CFSTGC are derived from the particles that are activated in the instrument. On the other hand, the HTDMA measures under sub-saturated conditions particles that are not "seen" by the CCN chamber; if some particles do not grow they are directly assigned with a growth factor equal to one (i.e.* $\kappa=0$*), subsequently reducing considerably the derived kappa value. 60 nm particles will activate (if they actually do activate) at higher supersaturations and be detected by the CFSTGC. On the other hand they are all counted by the HTDMA. 120 nm particles activate at lower supersaturations but as they are, in most of the cases, internal mixtures of more and less hygroscopic matter, their κ-HTDMA will be significantly lower.*

Page 21557, line 21: "These distinct modes were not observed during the rest of the events" Were not observed during the other two events?

Response*: Amended. The text now reads "These distinct modes were not observed during the other two events, probably due to …".*

Page 21557, line 29: "Adler et al. had also observed…" This does not necessarily mean that the second larger mode that you observe is entirely due to BBOA.

Response*: We never said that the second larger mode is entirely due to BBOA, this is why we say that it is "probably freshly emitted…in combination with larger, more processed ones". For clarification we will rephrase to "which can be partially due to the presence of freshly emitted….".*

Page 21560, line 26: the multivariable regression analysis should be described

Response*: The multivariable regression analysis is performed within the excel environment. The overall observed hygroscopicity parameter is assumed to be the linear combination of the different components:*

$$\kappa_{CCN} = \varepsilon_{inorg}\kappa_{inorg} + \varepsilon_{BBOA}\kappa_{BBOA} + \varepsilon_{OOA\_BB}\kappa_{OOA\_BB} + \varepsilon_{OOA}\kappa_{OOA}$$

where κ_i *are the hygroscopicity parameters of the main aerosol constituents and* ε_i *the respective mass fractions. At each data point during the fire events one equation is obtained thus a set of 228 equations is obtained for all the dataset. More details concerning the confidence level, the standard error for each variable and p-value will be provided in the text.*

Page 21561, line 13-14: Finally, it seems that the biomass burning organic aerosol becomes more hygroscopic, by almost a factor 2, with atmospheric processing" Is this conclusion derived from the comparison of the kappa_BBOA with the kappa_OOA-BB?

Response*: This is correct. Based on our analysis* $\kappa_{BBOA}=0.057$ *and* $\kappa_{ooa\_BB}=0.138$*.*

Page 21561, line 15: "Using average diurnal profiles..." Were these average performed over the 4 BB events? The figure should show the standard variation.

Response*: Good point. The average diurnal profiles are derived for the whole measurement period. Standard deviation in the form of error bars is added to Figure 8.*

Page 21562, lines 7-9 : two times "for the most intense event"

Response*: Amended.*

Page 21563, line 14-15: "…larger particles appear not to be affected as far as their CCN-activity is concerned". This contradicts p21562 line 21: "hygroscopicity decreases for all sizes"

***Response**: The first part for larger particles' CCN activity refers to the activation fractions and not to the hygroscopicity. This will be clarified in the text.*

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