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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Influence of biomass burning on CCN number and hygroscopicity during summertime in the eastern Mediterranean" *by* A. Bougiatioti et al.

Anonymous Referee #2

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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? (2) There are unconsitencies 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. (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? 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? 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?

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

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ammonium sulfate ? to reformulate

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

figure 2c : Caliop shows that the smoke is travelling at higher laitude 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?

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

Figure 3 : need more dates on the x axis

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 reallu substantial increases ? What is the natural vairability 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?

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

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) ?

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

Page 21552, line 1-3 : “The data shown in Fig. 4 indicates that during the majority

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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 coratia 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?

Page 21552, line 8 : two times "that"

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.

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

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them in the 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.

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.” Their 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?

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.

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.

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Page 21556, lines 26-27: “During the focus period. . .” Do you mean outside BB 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?

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?

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!)

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

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.

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

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?

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

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

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”

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