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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aging of aerosols emitted from biomass burning in northern Australia" *by* Andelija Milic et al.

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Author response to Referee #1

The authors thank the reviewer for interest in our work and for the helpful comments to improve the manuscript. We have addressed each of comments as outlined below. All page and line numbers refer to the revised manuscript (Revised_manuscript_trackChanges.docx) where all changes (track changes) are available (revised supplementary material is included in the revised manuscript pdf file). The link for the revised manuscript is given at the end of this document. If the text is significantly changed only the number of section is given (e.g. "Biomass burning events", Sect. 3.2.4).

Comment: This manuscript studied the biomass burning organic aerosol in Australia

by using a c-ToF-AMS. The heavy biomass burning causes that 90% of NR-PM1 is organics. Five intense BB events with different burning conditions are analyzed. The enhancement of ozone and SOA in biomass burning plumes in examined. PMF analysis on background OA resolved three factors, BBOA, OOA, and IEPOX-SOA. The IEPOX-SOA is identified for the first time in Australia. The manuscript is well structured and the content is appropriate for ACP. However, most of the work presented here has been done before. The manuscript in its current form does not add significantly to the literature. Thus, I recommend major revisions. More in depth analysis and conclusions are required.

Response: We agree that this kind of work has been done previously, however it is the first time that this has been done within the Australian continent. The Australian continent is globally an important source of BB emissions, particularly the tropical savannah region. However, data related to BB emissions are remarkably lacking for this region. Therefore, we think that the results from this work provide valuable information to enhance the understanding of the loading and composition of fresh and aged organic aerosols from biomass burning in Australia, Southern Hemisphere and in general.

The following has been modified or added to the manuscript: âĂć The title of the manuscript is modified. âĂć Separation on "close BB" and "distant BB" periods is clarified. âĂć More analysis and discussion are added for BB events, including back-trajectories and Sentinel hot spot locations. âĂć The suggestions regarding isoprene-derived OA are incorporated in the manuscript. âĂć Discussion regarding the sea salt-chlorides and f44-resolved size distribution is modified and clarified.

Major comments

Comment 1: Whether this study is suitable/capable to study the aging of biomass burning OA. Previous field studies on this topic usually used aircraft to follow the biomass burning plumes, which ensures investigating the same air mass (Cubison et al., 2011; Yokelson et al., 2009; Forrister et al., 2015; May et al., 2015). However, this is not

the case in this study as the air mass is changing. In fact, many observations in this study can be explained by changes in air mass or physical changes, instead of aging of biomass burning OA. For example, an increase in f44 and a decrease in f60 (Figure 4b) could be simply due to an BBOA-rich air mass mixing with OOA-rich background air or physical changes during dilution (May et al., 2015). This could be potentially revealed in Figure 4a (close BB) if the authors color the data points by OA concentration. The data points with higher f60 and lower f44 would have higher OA concentration.

The authors may use MODIS sensor and backtrajectory analysis (section 2.1.7) to pinpoint fire position and calculate transport time. Then, the oxidation rate of BBOA or its tracers (such as f60) can be calculated, which is highly uncertain now. The aging time may also be estimated by using the photochemical clock, such as NOx/NOy ratio.

The OA in the five biomass burning events (section 3.2.4) is dominantly from fresh biomass burning, which provides a good opportunity to study the properties of fresh BBOA. The study would benefit from expanding related discussions. For example, "different burning conditions" are vaguely mentioned multiple times to explain the difference between the five biomass burning events. However, can the authors be more explicit about the relationship between specific burning conditions/burning materials with OA concentration, f44, f60, ΔO3, etc? It is helpful to bring Table S2 to the main text.

Response 1: The authors are aware that more conclusions about the BB aging can be drawn when tracking the plume is available. However, the limitation of the stationary measurements made it extremely difficult to track any plume with certainty. We agree that process of aging is not covered by this study. However, results for aged BB emissions, including SOA and ozone formation and change in particle size, are presented in this study. Therefore, the title of the manuscript is changed from: "Aging of aerosols emitted from biomass burning in northern Australia" to "Fresh and aged aerosols emitted from biomass burning in northern Australia". The sentence at Page 3, lines 14-16 is also modified: "This publication presents insights into fresh and aged aerosols emit-

ted during the SAFIRED, while a detailed description of the campaign can be found in Mallet et al. (2016)".

Considering the number of fires that occurred across the area during the campaign, ground-based (stationary) measurements and the limitations of satellite detection (once per day) it was difficult to identify the exact source of fires. The backtrajectories analysis was done for all days and all elevated signals, and while the path of trajectories can indicate the sources it is a challenge to apportion the signals to a specific event. In the case of all close fires, according to backtrajectories air masses could reach the ATARS within less than half an hour. The approximate time for air masses to reach the sampling location from the particular fire was included into the "Biomass burning events" section (Sect. 3.2.4) at Page 12.

The "biomass burning events" section (Sect. 3.2.4) is expanded as suggested. The Sentinel hotpots and the backtrajectories for BB events are presented. More discussion about differences in BB events is given. Text was changed through the "Biomass burning events" section (Sect. 3.2.4) at Page 12. Table S2 is now in the main text (Table 1).

Comment 2: IEPOX-SOA related. Firstly, it is not appropriate to label the PMF factor as IEPOX-OA. While the majority of this factor is from the reactive uptake of IEPOX, this factor also likely includes contribution from isoprene OA formed via other pathways. For example, a recent study by Schwantes et al. (2015) showed clearly that SOA formed via the reactive uptake of isoprene nitrooxy hydroxyepoxide could also produce fragment m/z 82. In addition, the mass concentration of this PMF factor cannot be fully explained by the total IEPOX SOA tracers (Hu et al., 2015; Budisulistiorini et al., 2015). Thus, it is more appropriate the name the factor as isoprene-derived OA (Xu et al., 2016; Pye et al., 2016). Secondly, since the isoprene-OA factor is identified for the first time in Australia, more analysis could be done related to this factor. For example, does this factor correlate with sulfate, which has been shown in previous studies (Xu et al., 2015a; Budisulistiorini et al., 2015)? What's the NO concentration at the measurement

site? Is IEPOX formed locally or from transport? What's the particle pH? As shown in Figure 9f, in general, IEPOX-OA correlates well with Org 82. However, some data are scattered (i.e., Org 82 0.004 to 0.008 μg m-3 range). What happens for these data? Is it due to sources other than IEPOX uptake contributing to Org 82?

Response 2: Thank you for the comment. The PMF factor "IEPOX-SOA" is changed for "isoprene-derived OA" throughout the manuscript and supplementary material. Moreover, the following sentence is added to Page 15, lines 24-26: "In order to consider other possible pathways in isoprene-derived OA formation (Schwantes et al., 2015), the PMF factor has been named as isoprene-derived OA (Pye et al.; Xu et al., 2016)".

According to calculations for the composition depended collection efficiency, 22% of the aerosol were acidic. Furthermore, the correlation of IEPOX-SOA and sulfate is found to be weak (R of 0.3) (Fig. S18). However, two periods (period before 5th of June and after 15th of June) could be clearly separated on the plot. While there is no correlation between sulfate and isoprene-derived OA factor for the first period, when plotting only data collected from the 15th of June, correlation is found to be slightly higher (R of 0.4). The following is added to the manuscript at Page 16 line 6-14: "The main path for isoprene-derived OA formation is proposed to be acid catalysed IEPOX uptake (Lambe et al., 2015; Lin et al., 2011). According to calculations for the composition depended collection efficiency, 22% of the aerosol were acidic. In order to estimate whether the acidity of the particles had an influence on isoprene-derived OA generation in ATARS, the correlation between sulfate (taken as proxy of aerosol acidity) and isoprene-derived OA factor was examined. The correlation between the factor and sulfate can be considered as weak (R of 0.3) (Fig S18). However, two periods can be clearly distinguished from the graph: the period before 5th of June and the period after 15th of June. While there is no correlation between sulfate and isoprene-derived OA factor for the first period, when plotting only data collected from 15th of June, correlation is found to be slightly higher than correlation for all background data (R of 0.4)".

The concentration of NO at the measurement site is not available. Unfortunately due to

the issue with instrumentation, NOx data are unreliable and thus not used in analysis.

As isoprene-derived OA was found to be prominent over the night period, one of the suggestions was detection of distant masses as suggested at Page 16, line 27.

After further investigation of the scattered data (i.e., Org 82 0.004 to 0.008 μg m-3 range) we couldn't tell what other source contributed. Further analysis of the biogenic loadings and sources for this region are needed in order to make more detailed conclusions regarding the isoprene-derived OA.

Minor comments

Comment 1: Page 2, line 6: Elemental carbon (EC) is not the same as black carbon (BC). EC is defined by thermal properties and BC is defined by optical properties (Andreae and Gelencsér, 2006).

Response 1: Elemental carbon (EC) is used throughout the manuscript. "Black" is removed from the sentence at Page 2, line 6.

Comment 2: Page 4, line 4. It is stated that sampled air mass had mainly passed over land. However, this seems to contradict with the conclusion in Page 8 Line 18-20, that a significant portion of chlorides could be sea salt.

Response 2: The sampled air masses mainly passed over the land according to a dominant wind direction (southeast) and backtrajectories, as illustrated in the Figure 1 in Mallet et al. (2016). The high chloride concentration was detected (by the AMS, Figure 1c and by the BAM Figure S3a) during the close BB periods when air masses were passing over the land affected by fires (as stated in the manuscript at Page 8 line 27), meaning that they originated from fires. This is especially the case of close fires on the 25th and 26th of June (Fig. 1c). However, oceanic influence cannot be excluded as on some days (e.g. period between 3rd and 6th of June) in the afternoons northeast winds were dominant (Figure 4c in Mallet et al. (2016)). More precisely on the way to the sampling station air masses were passing over the land and then

turning over the ocean before reaching the ATARS. Furthermore, the measurement period between 19th and 22nd of June was characterised by air masses coming mostly along the Australian east coast and passing over some of the land before reaching the station (Mallet et al., 2016). The oceanic influence through high chloride concentration that has a sea salt origin can be clearly seen from the Fig S3a. Chlorides from BAM were detected during the influence of close BBs, but also during the oceanic influenced days. Therefore the Mg2+/Na+ ratio for oceanic-influenced days was close to the see salt ratio (Figure S3b) and the sea salt-related chlorides were collected on filters (BAM) (Figure S3a). The least terrestrial fetch (indicated by low radon concentration) was also observed during the days with the high ocean breeze (Mallet et al., 2016).

To clarify this in the manuscript the following is added at Page 4, lines 4-7: "However, on some days (e.g. between 3rd and 6th of June) in the afternoon hours northeast wind direction was dominant, directing the air masses from land to pass over the ocean before being detected at ATARS. Moreover, an oceanic influence was observed between 19th and 22nd of June (Mallet et al., 2016)".

The following sentences are modified on the Page 9, line 3 – Page 9 line 8: "Mg2+/Na+ ratio values for the filters collected during the high oceanic influence (between 3rd and 6th and 19th and 22nd of June) were close to the sea salt Mg2+/Na+ ratio of 0.12 (Fig. S3b). At the same time low terrestrial fetch (low radon concentration) was observed (Mallet et al., 2016). Moreover, the chlorides collected on filters were prominent during the period of oceanic influence (Fig. S3a). This suggests that a significant portion of chlorides detected on the BAM filters was of a sea salt origin, which is refractory and therefore not well measured by the AMS, thereby explaining the poor chloride correlation" and at Page 8, line 27: "Increased chloride concentration during the close BB periods was also indicated by the BAM data (Fig S3a)".

A new Figure, Fig S3a that shows the BAM chloride time series is added to the supplementary material and Fig. S3 is now Fig. 3b. Figure 3b is also modified: z-axis (date) was added to the graph.

Comment 3: Page 4 Line 19-20. It is not clear if the CE is determined by using the UMR data or the HR data. Or HR data are used in the squirrel panel? Also, sulfate fragments should not have interference from organic fragments in HR data. Thus, HR data should be used throughout the analysis.

Response 3: CE was determined using the HR data in PIKA and these data are used through the analysis as stated now at Page 4, lines 21 and 22: The AMS collection efficiency was determined using the calculations provided within the PIKA Toolkit" and Page 4, lines 25-27: "Significant improvement was made in distinguishing sulfate fragments from organic fragments at the same m/z by performing HR peak fits in PIKA (Sect. S1 in supplementary material). Therefore, HR peak fitting fata (PIKA) were chosen for further analysis".

Comment 4: Page 7, line 31: It is not clear how the "close BB" and "distant BB" periods are separated. The criteria for separation should be clearly stated?

Response 4: The authors agree that more specific definitions should be given for "close" and "distant" BB periods and clear presentation of data separation should be given.

The measurement period was separated into "close BB" and "distant BB" periods based on organics, carbon monoxide and particle number concentration and their correlation, as well based on the distance of known fires (Sentinel hot spots) from the ATARS.

Firstly, we were looking at the time series of organics, carbon monoxide and particle number concentration (Figure 2, Page 25) in order to identify the periods of significant BB influences, e.g. their high signals (e.g. on 9th and 26th of June) gave us a guide on which days intense/close BB took place. The increases in BB markers (levoglucosan, soluble non-sea salt potassium and Org 60) also showed the same trend (Figure 3, Page 26). After identifying these periods, the next step was to relate these signals to the possible BB events. Therefore, we have mapped all fires (Sentinel hot spots) that

have happened during these periods and have confidence level of 50% and more. To make sure that everything is included (e.g. close fires with low intensity) we have gone through every measurement day and mapped all the events that have occurred.

Hot spots detected within 20 km occurred on 30th of May, between 7th and 11th and 25th and 26th of June (Figure 2, Page 25). Taken the distance of 20 km and increased concentrations of organics, carbon monoxide and particle number, these days were taken as “close BB” periods. Knowing that ATARS was constantly affected by the BB air masses the remaining measurement days were taken as “distant BB” periods. In summary, “close BB” periods refer to periods where close fires (within 20 km) have taken the place and correlated increases in carbon monoxide, organics and particle number concentration were observed (Fig. 2), while the rest of the measurement is defined as “distant BB” periods.

In order to clarify the close and distant BB periods the paragraph at Page 8, line 3- Page 8 Line 16 is modified: “The sampling site was constantly impacted by fire emissions with periods of heavy BBs characterized by high aerosol and gas phase concentrations, for instance CO reaching up to $\sim$104 ppb and organics up to 350 μg m-3 (Fig. 2). The most intense BB episodes were on the 30th of May, between the 7th and 11th of June, and on the 25th and 26th of June (Fig. 1c) (Mallet et al., 2016). During intense fire periods, organics, CO and particle number concentration showed correlated increases (Fig. 2). Moreover, looking at Sentinel Hot spots during these periods, hot spots were detected within 20 km from the ATARS. Based on this, the dataset was separated into periods of “close BB” (corresponding to high organics, CO and particle number concentration signals and close events (< 20 km)) and “distant BB” (corresponding to less intense organics, CO and particle number concentration signals and distant events (> 20 km)). It is important to emphasize that all periods during the measurement that have not been included in close BB periods have been assigned to distant BB periods, as ATARS was constantly influenced by BBs. The selection does not mean that emissions from distant fires were not present during the close BB periods but that the

influence of fires near the measurement station during these periods was dominant. Nine intense BB events were identified from close BB periods as single source emissions (Desservettaz et al., 2016). Five of the nine BB events (Fig. 2) were analysed here (Sect. 3.2.4), due to the instrument not sampling during the remaining events. Most of the events occurred in the afternoon/night time (Table 1)”.

In order to indicate distant BB periods the following is added to Fig. 2 caption at Page 25: “The distant BB periods cover all days of the measurement other than days included in close BB periods”.

Comment 5: Page 8, line 14: The authors can use the NO+/NO2+ ratio to infer if the nitrate functionality originates from inorganic or organic nitrate (Xu et al., 2015b; Farmer et al., 2010).

Response 5: According to the NO+/NO2+ ratio in our study, close BB period between 7th and 11th of June is characterised by nitrate that originates from the ammonium nitrate rather than from organic nitrate (NO+/NO2+ ratio is higher for organic nitrates than ammonium nitrate (Farmer et al., 2010)) (see Figure below). Other two close BB periods (on 30th and between 25th and 26th) produced inorganic as well as organic nitrates. Periods influenced with ocean breezes (between 3rd and 5th and 19th and 22nd of June) seem to have higher portion of organic than inorganic nitrates.

Time series of NO+/NO2+ ratio throughout the campaign. Solid lines indicate close BB periods. Dashed line indicates NO+/NO2+ ratio for ammonium nitrate.

Comment 6: Page 10, line 22-23: This sentence is really confusing and should be re-written.

Response 6: The diurnal trends of the f44, ΔO3/ΔCO and ΔOA/ΔCO ratios for close BB periods and diurnal trend of ΔO3/ΔCO ratio for distant BB periods are added to the Fig. 5 and therefore apart from the sentence that was mentioned in the comment, the changes are made throughout the “Secondary organic aerosol (SOA) formation”

section (Sect. 3.2.2 at Page 11).

Comment 7: Page 11, line 22. Is the OA mass loading related to wind speed or wind direction?

Response 7: The wind direction was highly variable influencing detected signals related to the event F. This is incorporated into the manuscript at Page 13, lines 22-26: "However, the f44 value was highly variable during the event F, ranging from 0.07 to 0.18. Other parameters including f60 and organics varied as well. On that time, the wind direction significantly varied between 140° and 80° and likely influenced changes in detected air mass. One of the explanations can be detection of fresh plume and aged masses coming from the distant fires with the change in wind. The low correlation between f60 and f73 might also be an indicator for detection of different BB air masses (Fig. S8)".

Comment 8: Page 12, line 14. The authors may check if the relationship between f60 and f73 changes with burning conditions or burning materials.

Response 8: We have observed changes in f60/f73ratio for different events (varying between 1.2 and 2.5) (Fig. S8), however there was no trend in relationship of f60/f73 ratio and burning conditions/material (using the MCE value). Low correlation between f60 and f73 for the event F (r2=0.16) was likely due to the changes in masses that were detected during this time period (due to high variability in wind direction).

The sentence at Page 12, lines 16 and 17 is modified: "Different factors were considered including f44, time of day, ΔO3/ΔCO, f60, f60/f73, organic concentration and MCE". The following is added to the manuscript at Page 13 lines 25 and 26: "The low correlation between f60 and f73 might also be an indicator for detection of different BB air masses (Fig. S8)" and at Page 14, lines 19-21: "Events were characterised with different f60/f73 ratios (varying between 1.2 and 2.5), but there was no trend in the relationship of f60/f73 ratio and burning material/conditions (MCE values) (Fig. S8)".

Figure illustrating f60/f73 ratio changes for different events and relationship between this ratio and MCE (Fig. S8) is added to supplementary material.

Comment 9: Page 12, line 31. Is there any study to show that fresh emissions from biomass burning contain OOA?

Response 9: Contribution of primary (fresh emissions) from biomass burning to OOA portion of emitted OA cannot be excluded as shown in wood burning studies, Heringa et al. (2012) and Weimer et al. (2008). The references are added at Page 15, lines 12 and 13.

Comment 10: Page 13, line 10. Cite Xu et al. (2015a).

Response 10: The citation is added to the new version of the manuscript at Page 15, line 23.

Comment 11: Page 14, lines 8-11: The low correlation between IEPOX-OA and BBOA could be simply due to that these two factors are from completely different sources and a correlation is not expected. The discussion in this sentence is not supported and should be removed.

Response 11: The sentence was removed from the manuscript (Page 17, lines 11-14) and figure S15 (supplementary material) that corresponds to the statement was removed as well.

Heringa M, DeCarlo P, Chirico R, Lauber A, Doberer A, Good J, et al. Time-resolved characterization of primary emissions from residential wood combustion appliances. Environmental science & technology 2012; 46: 11418-11425. Mallet MD, Desservettaz MJ, Miljevic B, Milic A, Ristovski ZD, Alroe J, et al. Biomass burning emissions in north Australia during the early dry season: an overview of the 2014 SAFIRED campaign. Phys. Discuss., doi:10.5194/acp-2016-866, in review, 2016 2016. Pye HO, Murphy BN, Xu L, Ng NL, Carlton AG, Guo H, et al. On the implications of aerosol liquid water and phase separation for organic aerosol mass. Schwantes RH, Teng AP, Nguyen

TB, Coggon MM, Crounse JD, St. Clair JM, et al. Isoprene NO3 Oxidation Products from the RO2+ HO2 Pathway. The Journal of Physical Chemistry A 2015; 119: 10158-10171. Weimer S, Alfarra M, Schreiber D, Mohr M, Prévôt A, Baltensperger U. Organic aerosol mass spectral signatures from woodâĂŘburning emissions: Influence of burning conditions and wood type. Journal of Geophysical Research: Atmospheres (1984–2012) 2008; 113. Xu L, Middlebrook AM, Liao J, Gouw JA, Guo H, Weber RJ, et al. Enhanced formation of isopreneâĂŘderived organic aerosol in sulfurâĂŘrich power plant plumes during Southeast Nexus. Journal of Geophysical Research: Atmospheres 2016; 121.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/acp-2016-730/acp-2016-730-AC1-supplement.pdf

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