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Atmospheric Measurement Techniques Discussions

Interactive comment on "Impact of Biomass Burning emission on total peroxy nitrates: fire plume identification during the BORTAS campaign" *by* Eleonora Aruffo et al.

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We thank Referee 1 for the careful attention to this manuscript providing us appreciated comments. Below we have included the review comments followed by our responses. In the revision of this manuscript, we will highlight those changes accordingly.

Aruffo et al. reports the use of total peroxy nitrates (ΣPNs) measured by thermal-dissociation laser-induced fluorescence along with other trace gases typically associated with biomass burning (CO, HCN, and CH3CN) to identify biomass burning plumes during the BORTAS campaign. The authors compare their biomass burning

thresholds they determined from their ΣPNs measurements with thresholds published in prior studies. Finally, they utilize an artificial recurrent neural network (ANN) to indicate their measurements correctly identify biomass burning plumes. While the use of ΣPNs or the different speciated acyl peroxy nitrates (e.g., PAN) to identify biomass is not novel (e.g., Alvarado et al., 2010; Fischer et al., 2011; Tereszchuk et al., 2013), the introduction of the thresholds needed for the ΣPNs measurements to indicate biomass burning plumes is an important aspect of this paper to assist the community in better classifying different plumes. Similarly, the use of ANN to identify air mass classification and chemical history is beneficial for the community. However, for this paper to be published in AMT, further discussion, description, and limitations of their techniques need to be addressed-see general and specific comments. Currently, many of the sections fall short in providing the community the details necessary to apply these techniques to the community's own research in identification of air mass history to better understand the emissions and chemistry that impacted the air mass.

General Comments

1) A large fraction of the paper addresses prior methods to identify biomass burning plumes, and the authors compare their method (using ΣPNs) with the prior methods. However, the authors do not address which method, or methods, is best in identifying biomass burning plumes. For example, in Table 3, some methods that agree well with the ΣPNs method also produce potentially false positive identification of biomass burning plumes during other research flights. What are the limitations of these various methods? Which of these methods (or combination of methods) are the most robust in identifying biomass burning plumes in a variety of conditions (for different ages of plume, for different altitudes of plume, for different intensities of fire, and et cetera)?

Response: We thank the Reviewer for this comment. In our manuscript, we would describe different methods employed for the identification of the BB plumes highlighting that the use of only one of these methods can not be always optimal. In same case, in fact, the trace specie utilized could not be available (such as the HCN measured only for 5 flight of the total 16 flights or the furfural/furan); moreover, the use of a fixed threshold for all the flights of a single specie shows evident discrepancy respect to other methods. Our main conclusion is that all the methods have limitations, therefore use only one of them sometimes produce false positive in BB identification. Our suggestion, as tested and reported in the manuscript is to use a combination of methods (more than one compound and other parameters) to improve the BB plume identification. In this contest, as detailed in our response to the comment number 2, we also suggest that ΣPNs observation is another method that permits to discriminate BB plume taking into account also of the age and of the altitude of the plume, and its observation can be used to further reduce the uncertainty in BB identification. We further clarified our purpose in the revised version of the manuscript (pag. 15-20).

2) A discussion of the limitations of the ΣPNs would be extremely beneficial. The authors noted that the results are most robust for pressures less than 750 hPa; however, that leaves the reader to wonder how much of that is due to the thermal decomposition lifetime of ΣPNs and the chemical age of the plumes intercepted during the BORTAS campaign. A figure that shows approximate chemical age (or other form of ages) in the main text or part of supplement, especially versus pressure (or temperature), would improve the discussions throughout the paper. Also, how much does the thermal lifetime of ΣPNs impact your interpretation of Figure 3? For example, in Figure 1, at low altitudes (pressure less than 800 hPa), the measurements of CO and CH3CN show high correlation with each other whereas ΣPNs shows no correlation.

At these high pressures, the lifetime of ΣPNs is less than 1 hour. Is this due to aged biomass burning plume that have stayed in the boundary layer whereΣPNs have thermally decomposed? Or is this due to aged biomass burning plumes that have been transported into the planetary boundary layer, causing the ΣPNs to decompose? Also, a large fraction of biomass burning plumes stay in the planetary boundary layer (e.g., Gonzi et al., 2015), where the ΣPNs lifetime is extremely short (less than 1 hour). With that in mind, at what point does the use of ΣPNs as a marker of biomass burning plume not work? How much of the air higher than 2000 m a.s.l versus lower than 2000 m a.s.l. was impacted by biomass burning (Page 15, line 12)? Finally, there are other types of air masses that maybe classified as biomass burning plumes while using ΣPNs measurements whereas these air masses originate from a different source or combination of sources. For example, Apel et al. (2015) observed and modeled production of PAN downwind of an air mass influenced by both biomass burning and lightning NOx emissions. Similarly, Alvarado et al. (2010) noted that many of the biomass burning plumes observed during ARCTAS were influenced by thunderstorms. How well can your thresholds disentangle these influences?

Response: We thank the Reviewer for this comment. In our paper we compare the ΣPNs and the CO as function of the pressure for the flight B623 and for the B622 and we compare HCN and CO for the flight B622, to highlight the different behaviour existing between them. We derived from these analyses the presence of different layers of air masses above or below 2000 m a.s.l. (about 750 hPa). The fact that also the HCN, a long-lived specie, shows different trends as function of the CO suggested to us that at P > 750 hPa we sampled air masses influenced also by other source in addition to the BB emissions. We explained better this point in the revised manuscript (pag. 17 lines 2-6). In order to better describe the contribution and the limitations of the PNs as BB tracer, we evaluated the chemical age using the parent-daughter method (isoprene-MVK) and the thermal lifetime (as $1/k_{PAN}$) and we added a Figure (see

figure.4 in the revised manuscript) with age and $1/k_{PAN}$ time series as suggested by the Reviewer. The thermal decomposition of PAN as the altitude decreases becomes significant; this is an important indication of the different dynamic processes interesting air masses, suggesting that the air masses at higher altitude with high ΣPNs level have been interested by pyroconvection and rapidly transported at high altitude. On the contrary, the air masses at lower altitude have spent more time in the boundary layer and the PNs have been thermally decomposed into NO2 because of the higher temperature in these layer. This allows a different chemical regimes in the NOx-OHx cycles: in fact, the NO2 at high altitude is not significant (as demonstrated by Alvarado et al. the NO2 is rapidly converted into PNs in BB plumes) but it increases at lower altitude as the PNs decreases: this suggests that the NO2 at lower altitude is the result of the thermal decomposition of the PNs. This is very interesting in the O3 investigation downwind a BB plumes. In this contest, the use of the ΣPNs as BB tracer could help to classify the BB plumes taking into account of different ages of the plumes and of the dynamic of the air masses. The big limitations of ΣPNs as BB marker is that, as other species, can be affected by other sources not only BB emission, and the dependence of its lifetime by physical parameters (i.e. temperature). Therefore, we suggest, for a better BB identification and description, to use a set of chemical species (CO, HCN, CH3CN, furfural/furan and ΣPNs) to select the BB plume. After the identification, we suggest to use the ΣPNs (and furfural) coupled with a physical parameter (especially in aircraft campaign) to describe the ages of the plumes and the dynamic of the air masses (the presence of the PNs is an indication of lower ages of the air masses and of their permanence at higher altitude after the emission). Finally, Apel et al. (2015) analysed the impact on PAN in two cases: 1) isoprene convection and storm (low NOx): in this case, they did not observe impact on PAN; 2) isoprene convection and storm with high NOx produced by lighting: in this case, they observed an enhancement in the PNs production. This should be a limitation of the PNs as BB tracer; however, the fact that in the 6σ method the background is selected as the mean of the concentrations measured to the exterior of ΣPNs enhancement of the plumes

should take into account the contribution due to lighting.

3) What happens if 99th percentile above the background of each flight is used instead of using the value from one flight? As another way to consider it, what would happen if the 6σ above background for B625 is used? Just wondering why you did not use these two methods the same way (either for all research flights or for the background research flight)?

Response: We did not use these two methods, because we choose to apply methods used in other BORTAS papers, in order to compare our work with previous results. In fact, Palmer et al. used the 99th percentile of the B625 background flight and Le Breton et al. used the 6σ above background for each flight, so we applied the same methods.

4) In Figure 4, you show the back trajectories for the air masses sampled. However, between 120° and 90°W, it is hard to tell which trajectories are most important for your analysis since the high and low pressure back trajectories overlap. Also, it appears that there are numerous biomass burning events in that region between 120° and 90°W. How did these biomass burning events impact this study?

Response: We thank the Reviewer for this comment. We modified figure 4 (figure 6 in the revised manuscript) highlighting, in the region suggested, the fires to the east of the Winnipeg Lake (Manitoba) occurred between the 18th and the 20th of July

according with the age of the air masses. These fires should be the source of the air masses sampled during the flight B623. The Figure 4 has been changed, accordingly, in the revised manuscript (figure 6 in the revised manuscript) and commented deeper.

5) The authors barely describe the ANN and the results. Without a more in-depth description of how the authors initialized and ran the model, the section provides minimal benefit to the community. Also, what is the benefit of using ANN if a researcher has access to measurements? Are there other parameters that could be used to improve the performance of ANN (e.g., chemical or transport age of plume)? How well does the chemistry, biomass burning intensity, and/or meteorology need to be known to calculate meaningful results? The authors noted that ANN is ideal since it is capable of simulating non-linear relationships, which causes me to wonder this. It was unclear why the addition of pressure led to instances of causing further disagreement between modeled results and measurements.

Response: We described the ANN initialization at pag.20 (lines 29-31) and we ran the model using a recurrent architecture that provides a multi step memory (pag. 20, lines 23-25). Obviously, since the main focus of the paper is not the development of the ANN, we made a concise description in this manuscript, for more in-depth description of the model we suggest to read one of our previous paper (Biancofiore et al., 2015) where are reported all the details of the ANN. However, we added further detailed description about these points raised by the Reviewer in the revised version of the manuscript (pag.20; lines 11-25).Our main goal, in including the ANN analysis, is to demonstrate that the PNs and HCN are better modelled introducing also the pressure, and especially that the different slopes are well reproduced introducing the pressure. This suggests and confirms that, at least for aircraft campaign in which the altitude can

change significantly, the identification of the BB plumes using only one method (and, even more, if it is used only one specie) not allow to discriminate possible difference in the air masses due to different ages or influence from other sources than fires. The ANN model allows to highlight which are the parameters (or the chemical specie) more significant in modelling a determinate specie, with results in simplified analysis. We tested the ANN model running with or without the pressure because our purpose was to underline if the PNs and HCN level depends significantly by the pressure (that is the altitude in which we sampled the air masses). We agree that, at least for the ΣPNs during the B623 flight, the photochemical age could improve the simulation done using only the O3, CO, NO, CH3CN as input (case A); anyway, in the case B, in which we added the pressure as input, the photochemical age becomes redundant being correlated with pressure. Further analysis can help to understand if the age could further improve the BB plume identification. Regarding the accuracy in the knowledge of the chemistry, biomass burning intensity, and/or meteorology, it is clear that the errors in these parameters influences the performance of the model, fortunately in the campaigns where this method can be used, usually these parameters are measured at the same site or same aircraft and simultaneously with the other compounds, so this is not an issue. Regarding the capability of the ANN of simulating non-linear relationships, our meaning is that these models are able to reproduce the evolution of compounds that have complex chemistry and sometimes non-linear relationship with others. We will make clear this point in the revised manuscript. Finally it is not clear why the Reviewer mentioned that “the addition of pressure led to instances of causing further disagreement between modelled results and measurements”, from our results it is exactly the contrary: we show that the inclusion of pressure as input parameter in the model improves the prediction performance of the model.

Specific comments

1) In general, please double check your grammar. For example, Page 7, line 18 – 19, you are missing a noun in front of are summarized. What is summarized? There are other instances where grammar needs to be corrected throughout the paper.

Response: Done.

2) Be consistent when the names and chemical formulas are introduced. Page 3, line 19, acetonitrile is the first time it is defined, however, the chemical formula is used in numerous lines prior to that (Page 3, line 8; Page 3, line 12, et cetera).

Response: Done.

3) Page 4, line 19 – 20: was HNO3 measured by your instrument as well?

Response: We did not HNO3 measurements during the BORTAS campaign, but our instrument allows to measure this specie in its fourth cell.

4) Page 4, line 23 – 25: Please better explain how the ΣPNs and ΣANs are determined.

Response: In this manuscript we briefly described the thermal dissociation technique to determine ΣPNs and ΣANs, the complete description is available in one of our recent paper (Di Carlo et al., 2013) that we cited here.

5) Page 6, line 6: Convert seconds to either UTC hours and/or local time. Same with Figure 1 on Page 6 and Page 14, line 4 – 5.

Response: Done.

6) Page 7, line 18: I wondered what mixing ratio ΣPNs corresponded to for the 6σ threshold.

Response: The ΣPNs mixing ratio corresponding to 6σ threshold is about 0.134 ppb. Anyway, we did not use this method in order to apply the same method adopted by Palmer et al. (2013).

7) Page 8, Table 3: Please define what the grey areas are in the table in the table caption. Also, what are the units for ΣPN > 0.418? Approximate values for the 6σ would be nice. Finally, please be consistent about the Lewis et al. definition. There are instances where the definition is flipped from < 200 to > 200.

Response: Done. We indicated > or < 200 in the notes column in Table 3 to give some information: the Lewis method requires CO > 200 ppb and the presence of furfural (or furan). In some flight, we had CO > 200 ppb but not furfural (or furan) measurements: this means that the Lewis method is not applicable in these flights. On the contrary, in some cases, we do not have furfural (or furan) measurements, but we have CO < 200 ppb (in this case, the Lewis method indicates 0 percentage of flight impacted by BB and this result is acceptable even if we do not have furfural measurements).

8) Page 14, line 18: Please capitalize Lagrangian.

Response: Done.

9) Page 15, Figure 4: Do you have any measurements of the intensity and emission heights for all these biomass burning events?

Response: No, we did not.

10) Page 16, line 11 – 13: How does deposition (dry or wet) impact the analysis of NOy chemical ages for air sampled in boundary layer?

Response: We evaluated the air masses age using another approach and giving more details about the photochemical age estimated, as suggested by the Reviewer. For this calculation, we did not take into account of the deposition sampling air masses at altitude greater than 1.5 Km a s.l..

11) Page 22, line 17 – 18: Line reads that air masses located at lower pressures are clean of biomass burning and originated from northern Canada. However, I thought that Figure 4 indicated that the air masses at lower pressures were impacted by biomass burning and originated from northwestern United States/southwestern Canada. Please clarify.

Response: We clarified the impact of these fires, as suggested by the Reviewer also in the comment 4) (pag. 18; lines 23-30 and figure 6).

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