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

Eleonora Aruffo et al.

eleonora.aruffo@aquila.infn.it

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We thank Referee 2 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.

This paper uses TD-LIF measurements of total peroxy nitrates (ΣPNs) during the BORTAS campaign to identify biomass burning plumes. Two methods – a threshold defined by the 99th percentile of total PN concentration on the background flight B625, and one based on the six sigma deviation from the mean of background periods in each flight – are used to identify biomass burning plumes and are compared to other

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methods that have been used in the literature. A couple high CO, high CH3CN, but low total PN periods in flight B623 are further analyzed using HYSPLIT back-trajectories, which show that these periods generally include air masses near the surface (pressure greater than 750 hPa) and are not consistent with the fire locations during the period. The paper then uses a neural network approach to try to simulate the HCN and total PN concentrations in two flights, and shows that adding the pressure significantly improves the model fit.

Major Comments: The use of the TD-LIF total PN measurement to identify biomass burning plumes is unique, and could be useful for campaigns and locations where other species are not available. However, I have some serious concerns about this paper. First, PNs are not long-lived tracer species, nor are they unique to biomass burning. PNs are formed in the atmosphere due to the chemistry of reactive organic species and NOx, which can come from not only by biomass burning but from a variety of anthropogenic pollution sources and the interaction of anthropogenic NOx with biogenic VOCs. So it is unclear if this method would work to identify biomass burning plumes outside of the BORTAS dataset, where it is more likely that the measured PNs are due to biomass burning than to anthropogenic pollution.
Response: We agree with the Reviewer. However, also other methods usually employed for the BB identification can present similar limitations: for example, CO is not produced exclusively by BB, but is widely used as BB marker. Some selective species, such as the furfural, have short lifetime and could not be useful in case of aged air masses. In the revised version of the manuscript we added the limitations and benefit of the use of the PNs as BB tracers showing the photochemical ages of the air masses and the PAN thermal lifetime during the B623 flight and we suggest to employ the PNs to have a more complete analysis of the plumes. In detail, the introduction of the PNs can allow to better classify the air masses giving information about for example the age (pag. 15-17 and Figure 4). This point will be further clarified in the other responses below.

Second, while pressure might be a useful discriminant of different air masses in this study, it is unclear why this would be generally true. In this dataset, the different pressures line up with different origins as demonstrated by the HYSPLIT back-trajectories, but that argues more for using back-trajectory models to identify different air masses than the use of pressure itself. In addition, if the high-pressure air masses in flight B623 are not from biomass burning, why is CH3CN elevated during these periods in Figure 1, and why is CH3CN almost perfectly correlated with CO? What is the source of this CH3CN if not biomass burning? Isn't it more likely that near the surface, the PNs thermally decompose, but the air mass is still influenced by biomass burning as indicated by the CH3CN?

Response:

We thank the Reviewer for this comment. The Review 1 raises similar comments and we furnish here the same answer. 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. 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

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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).

Third, the methods in this paper are generally unclear. The detection limits, known biases, etc. for the measurements made in BORTAS are not included here. The method used to identify “background” portions of each flight for the 6-sigma method is not described. The meteorology used to drive the HYSPLIT back-trajectories is not described. The neural network model is not described.

Response: The instrument is briefly described here, since it is extensively described in one of our recent paper (Di Carlo et al., 2013) that we cited in this manuscript for more information about the LOD of the instruments employed during BORTAS, since the configuration and the performance are unchanged. Regarding the background, we selected it for each flight as the mean of the concentrations measured to the exterior of ΣPNs enhancement of the plumes. We added this information in the revised manuscript (pag 7; lines 10-11). The meteorology used to drive the Hysplit back-trajectories has been downloaded from the NCAR/NCEP 2.5 deg global reanalysis archive (ARL server). We added this information in the revised manuscript (pag. 17, lines 15-16). The ANN model has not been detailed described to avoid verbose description available in one of our recent paper (Biancofiore et al., 2015). However, we added further detailed description about these points raised by the Reviewer in the revised version of the manuscript (pag.20; lines 10-24).

Fourth, the comparison with other plume identification criteria is off, as it uses techniques even when the required data is not available. For example, in Table 3 Alvarado et al. is reported to result it 1.3

Response: We agree with the Reviewer. In the new description of the benefit/limitations we highlighted the fact that the availability of the measurements of some species could be a limitation of the methods (pag. 19, lines 10-13). In Table 3 we added the last column (comments) exactly in order to add information about the availability of the data in order to highlight that some methods can not be used in the analysis of all the flights. These comments highlight also that the results given by some methods and for some flights, are not completely reliable because not all the required parameters are available.

Fifth, the paper is not really about an atmospheric measurement technique. TD-LIF is used, but not described, here, and using the total PN measurements to identify smoke plumes is not by itself a measurement technique. Furthermore, there is little science in the paper other than the comparison of this new method with previous methods that have been used to identify smoke plumes, but in those previous studies identifying the smoke plumes was the first part of a larger scientific study rather than an end in itself.

Response: We disagree with the Reviewer, because the aims and scope of AMT are: “the development, intercomparison, and validation of measurement instruments, the techniques of data processing and information retrieval for gases, aerosols, and clouds”. Therefore, we believe that this paper fits the topic of “techniques of data processing”, since introduces a new technique to process data to identify BB plumes, compares different methods and technique, using different species, for the identification of BB plumes and furnish suggestions on how to refine this identification also using the PNs and a neural network.

So based on these I do not feel I can support publication of this paper in AMT. However, major revisions might make it acceptable, so I detail other more minor concerns and typos that could also be fixed in a revision below.

Minor Comments:
P1, L26: “statistical and percentile methods” is not clear – please be more specific about your techniques here.
Response: Done
P3, L14-15: Please describe how these background periods were identified, and make clear if you used the same approach to identify background periods for your PN-based technique.
Response: Done. We added the following sentence: “The background has been selected as the measurements done at low HCN concentrations outside its evident enhancement in the plume.” (pag. 7; lines 10-11)

P4, L22-25: This description of TD-LIF is way too brief given the whole paper is written around it. How selective is it in separating PNs, ANs, and HNO3? What is the accuracy, precision, and detection limit? What are the known biases or problems?
Response: We described in detail the TD-LIF in the BORTAS configuration in our recent paper Di Carlo et al. (2013).
P5, L14-15: The accuracy and detection limit for these instruments should be included in Table 1, not just referenced.

Response: We do not agree: all the informations about the instruments have been referenced and, moreover, Palmer et al. (2012) in Table 2 gives a complete overview of the instruments employed during Bortas. We did not add these informations to make simpler the reading. We added in the manuscript the reference to the Table 2 of Palmer et al. (2013).

P6, L8: Furfural reacts too fast to be considered a "tracer" – you mean these species are known to be emitted by biomass burning.
Response: Done.
P7, Table 2: Make clear that the 6 sigma refers to 6 sigma beyond the mean of the background concentration, not 6 sigma from the mean of the whole dataset.
Response: Done.

P7, L12: Again, how do you identify background to use the 6 sigma method?

Response: Done. We added the sentence reported above (answer to the third comment (pag 7; lines 10-11)).
P14, L18: Please describe the meteorology you used to drive HYSPLIT – that is extremely important to the results.

Response: Done. We added the sentence reported above (answer to the third comment (pag. 17, lines 15-16)).
P16, L8: This is the photochemical age, to be clear, and is not necessarily the same as the chronological age. Please make that clear.

Response: We evaluated the photochemical age using another method and, as suggested by the Review 1, we added a Figure with the age clarifying also this point (figure 4).
P17, L3: I'm not sure why you don't plot flight B623 here, with CO versus CH3CN. I think that would show an extremely strong correlation.

Response: Yes, it does. The CH3CN correlations does not give indication of different air masses as done by the PNs. We detailed the interpretation of the double slopes between PNs and CO as suggested in the second comment.
P17, L7-10: We need a lot more details on the modeling to assess what you have done here.

Response: Done. We added more details about the ANN model (pag. 20; lines 13-26).
P18, L15: A scatter plot of the measured versus simulated total PN mixing ratio for each flight would be useful.
Response: Done (figure 7). P18, L20-L23: Add equations explaining these metrics – the text explanation is not that clear.
Response: Done.
P19, L4: Wouldn't systematic errors show up in the FB as well, so this suggests only an increase in random errors?

Response: We agree with the Reviewer. We corrected the sentence. P20, L4-6 and P21, L4-6: These captions are all messed up, and I'm surprised it wasn't caught earlier before publication in AMTD. They need to be fixed.
Response: Done.
Typos:
P1, L31: Total PNs and HCN were not used as input parameters – this should be NO and CH3CN.

Response: Done.
P2, L29-30: Remove "the" before "40"particles phase"
Response: Done.

P2, L32: "Analysis of the chemistry"
Response: Done.

P3, L5: Instead of levels, use the more specific " volume mixing ratios"
Response: Done.

P4, L9: Cut "of"
Response: Done.

P5, Table 1: Subscript "RONO2"
Response: Done.

P7, L2: I'd suggest "used" instead of "introduced as tracers"
Response: Done.

P13, Figure 2: Use different shapes in addition to different colors, as some readers may be red-green color blind. Also, the use of a green dot in the center of the red circle and vice versa is confusing.
Response: Done.

P15, L5: FLAMBE is an emission dataset that uses satellite data – you might want to refer to the satellite that actually identified the fires instead.
Response: We added information about the MODIS instrument (pag. 18, lines 12-13).

P16, L4-5: This phrasing is very hard to understand.
Response: We modified the sentence.

P18, L1: “impacted”, not “interested”
Response: Done.

P19, L6-8: Lowercase “model”, add period after “indices”
Response: Done.

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