

Interactive comment on “Organic aerosol evolution and transport observed at Mt. Cimone (2165 m a.s.l.), Italy, during the PEGASOS campaign” by M. Rinaldi et al.

M. Rinaldi et al.

m.rinaldi@isac.cnr.it

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The manuscript presents measurements of aerosol chemical composition from a mountain location above the Po Valley, Italy. As a result, the site is influenced by both the local heavily polluted air in the valley below and more aged material from long-range transport within the free troposphere. The aerosol chemical composition is dominated by organic material and the authors focus primarily on this component, which is of great interest within the aerosol community and well within the scope of ACP. My main comment regarding the manuscript is that the authors need to make a more convincing case that some of the stated differences in the organic component

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are statistically significant. This is particularly the case with regards to the elemental ratios. The information presented thus far implies that there is a large degree of variation in the OA component properties and it is not clear that the differences are significant (particularly for the OOAA and OOAB cases). Some additional analysis and perhaps some additional supplementary figures are therefore necessary. Please see the specific notes below.

ANSWER. We thank the reviewer for his comments. Here below we answer to the comment on the difference between OOAA and OOAB. Further on we will comment more in detail the OA elemental analysis. The factors OOAA, OOAB and OOAC were obtained by a standard PMF procedure whose details are extensively discussed in the supporting material (and improved in the new version thanks to the comment of the reviewer). The separation between OOAA and OOAB has a clear physical meaning. This consideration is based mainly on the analysis of the time series: while OOAA is present throughout the campaign, the only period in which OOAB gives an important contribution to OA (being otherwise negligible for the rest of the campaign) corresponds exactly with the period of stagnant conditions due to anti-cyclonic circulation. This demonstrates that PMF was able to capture a different OA source/formation process affecting the site during the stagnation period. The difference with respect to OOAA (reaching the station due to the direct uplift of air masses from the PBL) is supported by the reduced correlation of OOAB with PBL air-masses tracers. We consider the slightly higher oxidation level attributed to PMF to OOAB an indication that OA can reach higher oxidation levels when trapped in stable layers during stagnant conditions (a reasonable assumption). In conclusion, even if OOAA and OOAB have similar elemental ratios, they are still different enough (in time series and diurnal cycles) to represent different OA sources and/or formation processes.

Other than the above, one general comment I have is with regards to the naming of the OA PMF factors: could a more descriptive nomenclature not be used? Adding 'a', 'b' and 'c' to OA does not help in describing or understanding the analysis. It feels

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like every time a new AMS paper comes out with some PMF analysis, we introduce yet another naming method.

ANSWER. We have chosen a more general naming for the factors (accompanied with a detailed description of their properties in the text) because these OA are all fairly oxidized. The lack of "fresh" OA such HOA is due to the fact that these air masses are sampled at least after several hours of transport. Therefore, they do not fit in the usual LV-OOA, SV-OOA and HOA classification, and we did not want to force our solution into it. However, to relate the OOA factors identified in this study with previous results reported in literature, the manuscript reports the correlation coefficients of the OOA mass spectra with LV-OOA and SV-OOA spectra from Mohr et al., 2012 and Crippa et al., 2013.

More specific comments are detailed below. Section 2.2: Regarding changes in particle velocity within the AMS and given the pressure conditions at Mt. Cimone are approximately 800hPa based on Fig. S2, the authors should at least mention that this will result in a systematic change in the particle time-of-flight size distributions reported. Compared to sea-level, a reduction in atmospheric pressure to approximately 800hPa would reduce the particle velocity on the order of 10% in my experience. I would encourage the authors to report the results of any velocity calibrations that they have performed on their AMS (ideally this should have been done around the time of the experiment), so that the potential bias is reported.

ANSWER. Particle velocity calibration was performed at the beginning of the campaign, after transport of the HR-ToF-AMS to Mt. Cimone, therefore at pressure conditions comparable with the measurements. This assures that our pToF measurements are reliable and not biased by deployment at high altitude. This is now specified in the paper (page 5 of revised manuscript). Because the velocity calibration is a well standardized procedure, we do not report the velocity calibration parameters in the paper, but we provide them here in the responses to the reviewer.

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In general, further information regarding calibrations (particularly relating to ionisation efficiency) and filter tests should be reported also. Information on the sampling inlets, drying etc should also be included.

ANSWER. These details have been added as suggested (see page 5).

P14406, L18: 'measurement' should be 'measurements'

ANSWER. Correction done.

P14410, L7: what do the +/- values refer to? Presumably one standard deviation? Please note in text.

ANSWER. Correction done (see page 7, line 16).

P14411, L28: Rephrase sentence here relating to 'being the atmosphere. . .'

ANSWER. Correction done.

P14414, L6: Presuming the +/- values refer to one standard deviation, the variation here is very large at night. Is this driven by a few isolated episodes and/or very low values of NO_x? Some additional figures in the supplementary to describe these trends and ratios would be useful. At present, it isn't clear how significant the differences are between the day and night given the large variability indicated by the standard deviation.

ANSWER. Indeed, the \pm values refer to one standard deviation: this has been added in the text (page 10 Line 30). A standard t-test confirms that the two average CO/NO_x values characterizing night and day samples are statistically significant ($p < 0.01$). However, the referee points out (correctly) that a simple comparison of mean (\pm s. d.) values is not informative enough. Therefore, a new Figure has been added in the supporting material (Figure S4), showing that the CO/NO_x ratio is systematically higher during the night (red dots) than during daytime (green dots), using the same data classification used further on in the text (PBL vs. TR vs. FT). The new plot shows that,

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although night samples are characterized by higher variability, the difference is not due to episodic spikes occurring at night, but to a systematic behavior of the CO/NO_x ratio driven by alternation of air masses of different age at the sampling site through the day. The text has been modified accordingly (see page 11 of revised text).

P14414, L24: replace 'resulted less' with 'resulted in less' or similar alternative.

ANSWER. Done

P14414, L24: Missing 'O' in 'OM:OC'.

ANSWER. Done

P14414, L23-28: Are these differences significant given the quoted variability and uncertainties in the determination of elemental ratios? I have my doubts on this and a more detailed discussion is required here. The answer to this point will impact the rest of the manuscript also, so any changes should be reflected later in the manuscript.

ANSWER. The differences between average O:C and H:C ratios of PBL, TR and FT samples are all statistically significant for $p < 0.01$, according to the standard t-test. Statistic significance is guaranteed by the fact that these numbers derive from averaging of thousands of data. This information has been added in the text. As for the uncertainties in the determination of elemental ratios, Canagaratna et al. (ACP, 2015) estimated a 28% error for O:C and a 13% error for H:C against individual oxidized standards of known chemical composition, but uncertainties are smaller when considering mixtures of numerous compounds. Anyway, it is very unlikely that the measurement uncertainty in the AMS introduced a bias between the averages of the elemental ratios for the three air mass types (if anything, errors will be the same for each air mass type). Moreover, given the large number of data points, it is reasonable to assume that the effect of said uncertainties has been averaged out in the reported mean values. Such averages were calculated over a few hours of measurement time each day for 25 days: the measurement times defining the "PBL" conditions were interposed with the times

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of "transition" and "FT" conditions every day throughout the campaign (new Fig. S6), therefore minimizing the impact of possible biases originating from instrumental errors on the measured mean chemical properties (such errors would instead affect standard deviations). We understand the reviewer's concerns about how the elemental analysis results may affect the interpretation of the Van Krevelen plot (section 3.3) with respect to atmospheric ageing of OA. We believe that the interpretation of our data in the Van Krevelen space is legitimate for the reasons explained above (i.e., statistical significance of the EA ratios), and we also believe that such results would not be invalidated even though the differences between FT and PBL average elemental ratios were statistically not significant. Nevertheless, to prove without any doubt that the slope observed in the Van Krevelen plot is dictated by the different age of the aerosols reaching the station at different times of the day, a new plot has been introduced (Figure S5 in the supporting material), showing the time series of H:C and O:C color coded according to the data classification described in the text (FT vs. TR vs. PBL). The plot shows clearly that, independently on day-by-day variations (that determine the large standard deviations associated to PBL, TR and FT average values), H:C (O:C) is systematically lower (higher) for FT samples with respect to PBL samples, with TR samples having intermediate values. These considerations have been added to the text (see page 11 of revised text).

P14415, L 10-12: The language relating to 'direct sources of low oxidized OA' isn't clear to me here. Usually, direct sources would refer to primary OA i.e. directly emitted material, while oxidized OA is typically assumed to represent secondary OA. Some rephrasing here is necessary to improve the clarity of the explanation. Do the authors mean that the OA at the site has usually undergone significant atmospheric processing and consequently does not resemble recently formed secondary material?

ANSWER. The sentence has been rephrased according to the reviewer comments.

P14415,L24-P14416,L3: This section would be more convincing with a little extra analysis regarding the size distribution peaks. Looking at Fig. 7, it looks like the peaks are

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all very similar and could be determined by e.g. a log-normal fit, rather than giving a fairly wide size range of 300-350nm in the text.

ANSWER. Based on the reviewer's suggestion, we have performed a log normal fit of the size distributions. The fits suggest that ORG peaks at 300 nm while the inorganics (SO₄, NH₄, NO₃) peak between 330 and 340 nm. We therefore modified the statements in the text and specified these differences. We also have added more discussion regarding the size distributions.

P14420, L15-18: This statement regarding heterogeneous reactions would be more convincing if the analysis suggested in the previous comment is undertaken. I don't disagree with the authors interpretation based on Fig. 7 but I'm not convinced that the AMS size distributions have the required sensitivity to rule out organic mass production based on the size distribution analysis as currently described in the text.

ANSWER. We agree with the reviewer that AMS size distribution measurements probably do not have the required sensitivity to investigate SOA ageing via heterogeneous reactions, and therefore we have removed the statement from the conclusions. However, it is pretty clear that the ORG have extra mass below 200 nm dva. It is worth noting that mass below 200 nm is virtually absent in the inorganic species, consistent with previous results. Most likely, the smaller size ORG originate from primary ORG (typically with a dva around 80-100 nm near their emissions point), that eventually grow into larger sizes during transport. Effectively, this could be an indication of processing and ageing of ORG during transport; however, due to the large width of the size distribution and the lack of other information, we have removed any statement that could be misunderstood regarding ageing.

Fig. 5: As mentioned above, I have my doubts as to whether the differences in the averages for each air mass are different. Further discussion and analysis is required in relation to this. Also, I would suggest renaming the 'avrg_***' items in the figure legend.

ANSWER. This comment is addressed above. We have renamed the labels in the

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legend as suggested, and removed "avrg".

Fig. 10: I would suggest using a more colour-blind friendly scale for these plots. Igor has several alternatives to the rainbow palette or see ColorBrewer.org for a wide selection of alternatives.

ANSWER. We have tried different color palettes, but we found that the result is less clear. We prefer to stay with the actual one, that is a pretty standard choice, also considering that the information reported in the plot are also described in the text.

Supplementary material The authors state that there were not significant changes in the mass spectra and time series for different fPeak values in the PMF analysis – it would be useful to illustrate this in the supplement with either some additional figures or tables e.g. the correlations between the various factors and different fPeak solutions could be explored. By definition, changing the fPeak should alter the factor profiles and time series, so some evaluation of these changes would be useful and would give a bound on the use of 'significant'.

ANSWER. This part was extended in the new version of the supporting information, comparing extensively the solutions obtained at varying fpeak values.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 14403, 2015.

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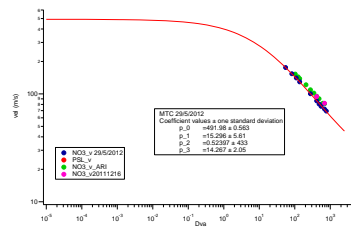


Fig. 1. Velocity calibration plot, comparing the particle velocity vs. vacuum diameter obtained at Mt. Cimone (blue dots) to previous calibrations performed at sea level. Calibration parameters are in the box

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