Reply to comments of William Morgan (Referee)

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 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 OOA PMF factors: could a more descriptive nomenclature not be used? Adding ’a’,’b’ and ’c’ to OOA does not help in describing or understanding the analysis. It feels 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.

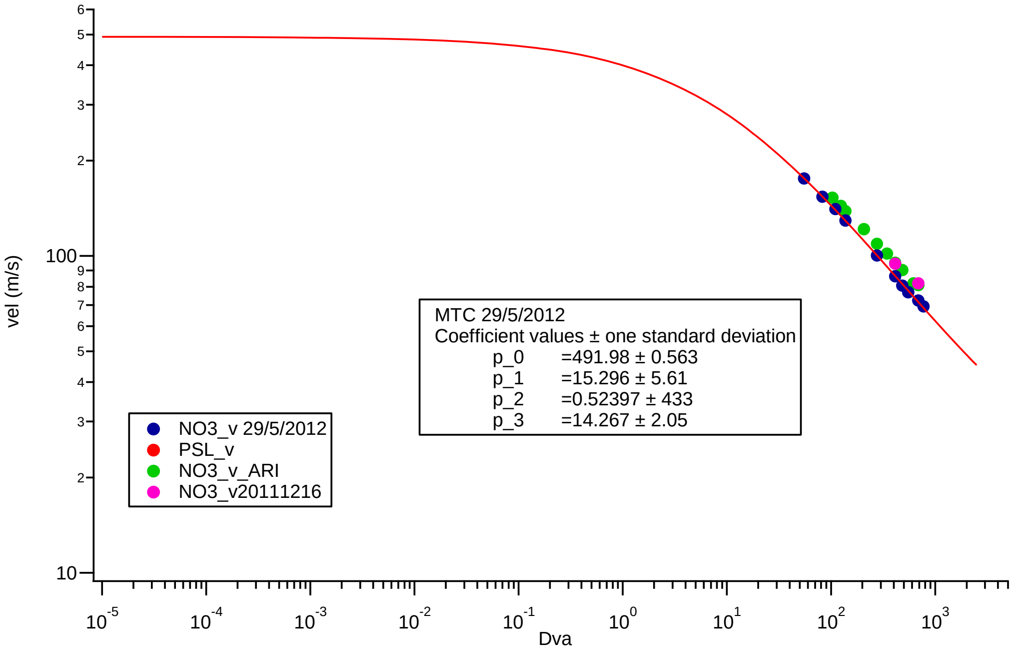

Figure 1. Velocity calibration plot, comparing the particle velocity vs. vacuum diameter obtained at Mt. Cimone (blue dots) to previous calibrations performed at sea level. Calibration parameters obtained at Mt. Cimone are reported in the box.

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 NOx? 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 ± 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/NOx values characterizing night and day samples are statistically significant ($p<0.01$). However, the referee points out (correctly) that a simple comparison of mean (± s. d.) values is not informative enough. Therefore, a new Figure has been added in the supporting material (Figure S4), showing that the CO/NOx 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, 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/NOx 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 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 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 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.

Reply to comments of Anonymous Referee #1

Organic aerosol evolution and transport observed at Mt. Cimone (2165 m a.s.l.), Italy during the PEGASOS campaign

This paper presents results and analysis of aerosol mass spectrometer measurements made at the Mt. Cimone GAW station in June-July 2012. At this high altitude station, organic aerosols (OA) dominated the sub-micron aerosol and were highly oxygenated. Elemental ratio analysis indicates the addition of oxygen atoms during the OA ageing process. Changes in the aerosol loadings and oxidation levels were associated with the influence of boundary layer air versus free tropospheric air at the Mt. Cimone site. Boundary layer was characterized by higher loadings and lower oxidations levels while free tropospheric air exhibited lower loadings and higher oxidation levels. Positive Matrix Factorization (PMF) identified three oxygenated organic aerosol (OOA) components associated with relatively fresh OA from the boundary layer, more aged air at high altitudes during stagnation periods, and very aged OA in the free troposphere.

I have only comments that are minor in nature that are outlined below.

Section 2.2 Were particle velocity and IE calibrations done on site? Did changes in atmospheric pressure not affect the velocity calibrations? How frequently were the IE calibrations done? What is the uncertainty in the AMS measurements?

ANSWER. All the calibrations were done on site, therefore at pressure conditions comparable with the measurements. This assures that pToF measurements presented in the manuscript are reliable and not biased by deployment at high altitude. Details on calibrations and calibrations frequency have been added (page 5 of the revised manuscript). This sentence was also added to the text: "The propagated, overall uncertainty for the total AMS mass concentration is 20–35% (2σ) according to Middlebrook et al. (2012)".

p. 14406, L 18, add 's' to measurement

ANSWER. Done.

p. 14409 L. 7 Please describe the common sampling system. How was it designed for reactive gases? Does this mean just using a Teflon sample line or is there more to it?

ANSWER. Accurate description has been added (see page 6 of revised manuscript).

p. 14410, L. 11-17 – Need to reword sentence to more explicitly indicate that the reporting is for percent contribution to PM1.

ANSWER. Done.

p. 14411, L. 7 – I don't see these ratios listed in Table 1? Why not?

ANSWER. Data for this study have been added in the Table.

p. 14411, L 16 – remove 'anyway', remove 'all'

ANSWER. Done.

p. 14411, L. 17 – is the Cabauw site a mountain site? Why use this location as a comparison? The authors have already indicated agreement with other mountain sites in previous paragraph.

ANSWER. Comparison with Cabauw has been removed.

p. 14411, L. 22 – I would say that the O/C ratio of 0.47 is more than slightly lower than 0.71

ANSWER. We apologize for the confusion. We intended to compare the AA with AI method, therefore the comparison is: 1.49 vs 1.32 (for H:C), 0.47 vs 0.58 (O:C) and 1.77 vs 1.89 (OM:OC).

Figure 3 and 4 – please indicate of the time is local time or something else.

ANSWER. Done.

p. 14415, L. 4 –'synthetically"?

ANSWER. Removed.

p. 14415, L. 10 – deviation from the -1 slope? Is it expected that the slope should be -1? This sentence is confusing? What is meant by analogy with Ng et al.? What can explain the deviation? – that fragmentation of OA molecules is a dominant process at this site?

ANSWER. The sentence has been rephrased as suggested by the reviewer.

p. 14416, L. 5 – PMF does not allow for 'fully' characterizing OA; it merely provides an incremental amount of information.

ANSWER. "fully" was substituted by "further".

Supplementary, Figure S5 – The text in the PMF analysis paragraph is essentially a repeat of the Figure S5 caption. Typo in panel a on the x-axis.

ANSWER. The text is now extended according to the request of the other reviewer. The typo was corrected.

p. 14417, L. 6 'averagely' change to on average

ANSWER. Done.

p. 14417, L. 15-16, don't understand the last part of this sentence.

ANSWER. That part was removed.

Organic aerosol evolution and transport observed at Mt. Cimone (2165 m asl), Italy, during the PEGASOS campaign

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Abstract

High resolution aerosol mass spectrometer measurements have been performed, for the first time, at the Mt. Cimone Global Atmospheric Watch (GAW) station between June and July 2012, within the EU project PEGASOS and the ARPA–Emilia Romagna project SUPERSITO. Sub-micron aerosol was dominated by organics (63%), with sulphate, ammonium and nitrate contributing for the remaining 20%, 9% and 7%, respectively. Organic aerosol (OA) was in general highly oxygenated, consistent with the remote character of the site; our observations suggest that oxidation and secondary organic aerosol (SOA) formation processes occurred during aerosol transport to high altitudes. All of the aerosol component concentrations as well as the OA elemental ratios showed a clear daily trend, driven by the evolution of the planetary boundary layer (PBL) and by the mountain wind regime. Higher loadings and lower OA oxidation levels were observed during the day, when the site was within the PBL, and therefore affected by relatively fresh aerosol transported from lower altitudes. Conversely, lower loadings and higher OA oxidation levels were observed at night, when the top of Mt. Cimone resided in the free troposphere although affected by the transport of residual layers on several days of the campaign. Analysis of the elemental ratios in a Van Krevelen space shows that OA oxidation follows a slope comprised between -0.5 and -1, consistent with addition of carboxylic groups, with or without fragmentation of the parent molecules. The increase of carboxylic groups during OA ageing is confirmed by the increased contribution of organic fragments containing more than one oxygen atom in the free troposphere night-time mass spectra. Finally, positive matrix factorization was able to deconvolve the contributions of relatively fresh OA (OOAa) originating from the PBL, more aged OA (OOAb) present at high altitudes during periods of atmospheric stagnation, and very aged aerosols (OOAc) transported over long distances in the free troposphere.

1 Introduction

Atmospheric aerosols have been intensively studied in the last decades because of their effects on climate, air quality and ecosystems. In many environments, organic aerosol (OA) constitutes a dominant fraction of submicron particles mass (Zhang et al., 2007; Jimenez et al., 2009). OA is made of thousands of individual compounds that can either be emitted directly into the atmosphere (i.e., primary OA or POA) or formed through chemical and physical processes (i.e. secondary OA or SOA). Given the extremely wide range of properties (polarity, vapour pressure, etc.) and number of compounds, typically only 10-20% of the OA mass can be speciated at the molecular level (Seinfeld and Pankow, 2003).

OA is a dynamic component, experiencing both atmospheric oxidation and reversible partitioning. This processing (usually referred as ageing) is generally not completely understood and not well represented in models (Heald et al., 2010). In the last decade, on-line instruments like the Aerodyne Research Inc. Aerosol Mass Spectrometer (AMS) (Jayne et al., 2000; Canagaratna et al., 2007) have provided new insights into OA chemical composition and simplified ways of characterizing atmospheric OA ageing. Ng et al. (2010) showed that OA composition tends to become less variable with photochemical ageing, regardless of their source, with the most oxidized spectra resembling that of fulvic acid. Heald et al. (2010) applied the Van Krevelen diagram (H:C vs. O:C space) to the elemental composition of ambient and laboratory OA, observing that bulk OA elemental ratios follow a line characterized by a slope of −1. This implies that OA ageing involves, on average, the addition of carboxylic acids or equal amounts of hydroxyl and carbonyl functionalities. By contrast, based on a world-wide dataset, Ng et al. (2011) observed a slope of ~-0.5 for the oxidation of SOA which is characteristic of addition of alcohol, carbonyl and carboxyl functionalities during the ageing process, or of the addition of carboxylic groups accompanied by a C-C bond cleavage (molecular fragmentation). Recently, Holzinger et al. (2013) showed that fragmentation gains importance over functionalization as photochemical age of OA increases, as originally proposed by Kroll et al. (2009). Finally, both ambient observations (Jimenez et al., 2009; Morgan et al., 2010) and laboratory studies (Massoli et al., 2010; Lambe et al., 2011) have pointed out that atmospheric ageing lowers OA volatility and enhances their hygroscopicity, evidencing the importance of atmospheric processing in determining the OA climate relevant properties.

In this study, we investigate the atmospheric processing of OA over the Po Valley basin, taking advantage of the unique observatory of Mt. Cimone, part of the Global Atmospheric Watch (GAW) network, by the World Meteorological Organization (WMO), a suitable location to study tropospheric background conditions. As other mountain sites close to anthropogenically-impacted areas, Mt. Cimone provides the opportunity to investigate transport and chemical processing of polluted air masses lifted by convection or by pressure gradients on the mountain slopes (valley breezes) (Marinoni et al., 2008; Gilardoni et al., 2009).

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The first AMS measurements performed at high altitude mountain stations were reported by Hock et al. (2008) and by Lanz et al. (2008). In particular, the latter study highlighted lower concentrations and higher oxygen content in aerosols collected at the Hohenpeissenberg (Germany) and Jungfraujoch (Switzerland) stations compared to measurements performed simultaneously at low altitude sites. Sun et al. (2009) and Freney et al. (2011) confirmed these findings with measurements performed at Whistler Mountain (Canada), and Puy-de-Dome (France), respectively, and provided useful insights of seasonal effects and air mass origin on the physico-chemical properties of regional aerosol particles measured at elevated sites.

The Mt. Cimone GAW/WMO Station is a high altitude research site located in the north Italian Apennines, facing the heavily populated and industrialized Po Valley region. In this study, we present and discuss online sub-micron aerosol chemical composition data collected at Mt. Cimone by high resolution time of flight aerosol mass spectrometer, HR-ToF-AMS (DeCarlo et al., 2006), during summer 2012, within the EU project PEGASOS and of the Agenzia Regionale per la Prevenzione e l'Ambiente (ARPA) – Emilia Romagna SUPERSITO project. The measurements were used to characterize the summer background aerosol transported into the Po Valley basin area, the vertical transport of anthropogenic aerosol from the lower troposphere (typical of summer circulation), and the regional scale oxidation of OA. Prior to this study, aerosol chemical composition data for Mt. Cimone station were reported by Putaud et al. (2004), Marenco et al. (2006), Carbone et al. (2010) and Carbone et al. (2014) using offline aerosol characterization techniques (i.e., filter samples analysed by ion chromatography and organic carbon analysis). All these papers evidenced the importance of the OA fraction in sub-micron aerosol at the site, both in summer and winter conditions. However, this is the first time that online characterization of atmospheric aerosol, particularly of OA, was performed with high resolution on mountain site at the centre of the Mediterranean climate hot-spot region.

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2 Methods

2.1 Sampling site

Mt. Cimone is the highest peak of the North Italian Apennines. The top of Mt. Cimone (44° 11' N, 10° 42' E, 2165m a.s.l.) hosts the Italian Climate Observatory "O. Vittori" that is part of the GAW program of the WMO. The station is situated at the southern border of the Po Valley, which is a highly populated and industrialized area, also characterized by intense agricultural activities. Anticyclonic conditions often favour a reduced ventilation within the basin promoting the build-up of lower troposphere aerosols and pollutants.

Measurements of atmospheric components carried out at this site are generally considered representative for the South European free troposphere (Bonasoni et al., 2000; Fischer et al., 2003). Nevertheless, due to enhanced vertical mixing occurring during summer months, a daytime influence at Mt. Cimone from the PBL has been documented (Fischer et al., 2003; Cristofanelli et al., 2007). For these reasons, this measurement site can represent a suitable location to investigate the influence of both local and long range transport of polluted air masses on the free troposphere composition (Marinoni et al., 2008).

2.2 Online aerosol chemical characterization

The mass loading and the size-resolved chemical composition of submicron aerosol particles was characterized online by the Aerodyne HR-ToF-AMS. The HR-ToF-AMS provides measurements of the non-refractory sulfate, nitrate, ammonium, chloride, and organic mass in submicron particles (NR-PM$_1$). During the whole campaign, the HR-ToF-AMS was operating by alternating between “V” and “W” ion path modes every 5 min. The V-mode is characterized by higher sensitivity and lower mass resolution, while the W-mode provides higher mass resolution, but lower sensitivity. The concentrations reported here correspond to the data collected in V mode. In V-mode, the instrument also acquires information about size distribution of particles, or particle time-of-flight, pToF (Jimenez et al., 2003). The AMS has an effective 50% cut-off for particle sizes below 80 nm and above 600 nm in vacuum aerodynamic diameter (d$_{va}$) as determined by the transmission characteristics of the standard aerodynamic lens (Liu et al., 2007). Changes in ambient pressure may lead to changes in lens transmission efficiencies (Liu et al., 2007; Bahreini et al., 2008), but such effects are not expected to be significant at the pressure conditions typical of Mt. Cimone (Liu et al., 2007; Sun et al., 2009). However, the particle velocity calibration was adjusted to the altitude (and pressure) conditions of the Mt. Cimone site before starting of the measurements. Ionization efficiency (IE) calibrations were performed before and after the campaign and once per week during the campaign. Filter blank acquisitions during the campaign were performed at least a couple of time per day to evaluate the background and correct the gas phase contribution. All data were analysed using standard ToF-AMS Analysis software SQUIRREL v1.51 and PIKA v1.10 (D. Sueper, available at: http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html) within Igor Pro 6.2.1 (WaveMetrics, Lake Oswego, OR). Positive matrix factorization (PMF) analyses on the HR-ToF-AMS data were performed using the PMF2.exe algorithm (v.4.2) in robust mode (Paatero and Tapper, 1994). The

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PMF inputs (mass spectral and error matrices of the OA component) were prepared according to Zhang et al. (2011). The PMF solutions were then evaluated with an Igor Pro-based PMF evaluation tool (PET, v. 2.04) following the method described in Ulbrich et al. (2009) and Zhang et al. (2011). The HR-ToF-AMS collection efficiency (CE) was calculated according to Middlebrook et al. (2012) and evaluated against parallel offline measurements (Fig. S1). The average CE for the campaign was 0.52±0.06. The propagated, overall uncertainty for the total AMS mass concentration is 20–35% (2σ) according to Middlebrook et al. (2012). The aerosol was sampled via a total suspended particle (TSP) aerosol inlet, which is built according to the EUSAAR/ACTRIS protocol to improve the collection performances at high altitude. The aerosol was dried to about 40% by means of a Nafion drier before sampling with the HR-ToF-AMS.

2.3 Additional measurements

Ancillary measurements at Mt. Cimone conducted during the campaign included meteorological parameters and other trace gases (CO, O_3, NO_X). Trace gas measurements were carried out by using a common sampling system designed for reactive gas sampling characterized by an intake line located 2 m above the roof and 7 m above the ground and consisting of a glass tube through which the sampled air is passed at a high flow rate (larger than 20 L s^{-1}). Sample air was supplied to the various analysers via a Teflon manifold pipe (about 1 m long) connected to the glass tube. A particle filter (changed regularly every 15-30 days) prevented dust, rain drops and other unwanted material from entering the inlet.

Surface ozone (O_3) was continuously measured (1-minute time resolution) by a UV-absorbtion analyser Dasibi 1108 W/GEN (Cristofanelli et al., 2015). Carbon dioxide (CO) was measured by a NDIR analyser Thermo Tei 49C. Following Henne et al. (2008), the system and sampling procedures have been modified to carry out observations in remote conditions usually characterized by low mixing ratios. During the PEGASOS campaign, NO_X measurements were carried out by a chemioluminescence analyser (Thermo 42C). This instrument is equipped with a molybdenum converter to determine NO_X, which according to Steinbacher et al (2007), can overestimate the NO_2 up to ~50% due to the

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The measurement of the aerosol absorption coefficient was obtained by a Multi-Angle Absorption Photometer (MAAP 5012, Thermo Electron Corporation), that measures the transmission and the back scattering of a light beam incident on a fiber filter where aerosol particles are deposited by the sampling flow. The equivalent black carbon (eqBC) concentration has been obtained by using a mass absorption efficiency of 6.5 m^2 g^{-1} as recommended by Petzold et al. (2002).

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PM_1 offline aerosol samples were collected on quartz filters as described by Carbone et al. (2014) with a 12 h sampling resolution. Chemical analysis of main inorganic species was performed via ion chromatography and carbon elemental analysis (Carbone et al., 2014).

3 Results

3.1 Online aerosol chemical characterization at Mt. Cimone

Figure 1 shows the time trend of the major non-refractory components of submicron aerosol (NR-PM_1) measured at Mt. Cimone during the campaign, together with the time dependent relative mass contribution of the same aerosol components. NR-PM_1 was clearly dominated by OA through the whole campaign: OA average atmospheric concentration and standard deviation were 2.8±2.4 µg m^{-3}, for an average mass contribution of 63%. Sulphate was the second most abundant species with a concentration of 0.92±0.60 µg m^{-3} (20%), followed by ammonium (0.41±0.33 µg m^{-3}, 9%) and nitrate (0.33±0.46 µg m^{-3}, 7%). Chlorine was usually below the detection limit (80% of the data points) and contributed less than 1 % to the NR-PM_1 (and was therefore excluded from Figure 1b). For comparison, sub-micrometer aerosol chemical characterization measurements performed in spring and summer at high (Jungfraujoch) and rural (Hohenpeissenberg) sites in Europe (Hock et al., 2008; Lanz et al., 2010) report organics ranging from 43% to 50 %, sulphate ranging from 19% to 26 %, ammonium contributing between 13% and 11% and nitrate ranging from 18% to 19% (see Table 1 for a summary of AMS measurements performed at background measurements sites).

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The measured ammonium concentrations were in equivalent concentrations to the sum of sulphate, nitrate and chloride, with a slope of 0.99 and a linear correlation coefficient (R) of 0.99. This means that aerosol particles measured at Mt. Cimone were neutralized. The average NR-PM$_1$ mass during the campaign was 4.5±3.4 µg m^{-3}, in fairly good agreement with PM$_1$ measurements previously performed at the site in the same season, even though with different measurement techniques (Marenco et al., (2006); Carbone et al.(2010); Carbone et al. (2014)). The lowest aerosol mass concentrations were observed during the first days of the campaign up to June 15, when Northern Italy was influenced by a low-pressure system, bringing unstable conditions. Conversely, the highest concentrations were recorded between June 17 and 20 under high pressure conditions characterized by anti-cyclonic circulation (Decesari et al., in preparation), which is known to favour the stagnation of local pollutants produced within the Po Valley basin (See Fig. S2 for further details).

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The results of the elemental analysis (EA) of the organic fraction are presented in Figure 2 as time trends of the H:C, O:C and OM:OC ratios. Average H:C, O:C and OM:OC ratio measured during the campaign are 1.45±0.11, 0.71±0.08 and 2.08±0.10, respectively, corresponding to an average oxidation state (OS$_C$ = 2*O:C - H:C; Kroll et al. (2011)) of -0.02±0.23. These ratios are indicative of a highly oxygenated organic aerosol, in agreement with previous AMS measurements at mountain sites (Freney et al., 2011; Lanz et al., 2010). The values have been calculated using the improved-Ambient (I-A) EA method to derive OA elemental ratios from AMS spectra (Canagaratna et al., 2015).

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The corresponding EA values calculated using the Aiken-Ambient (A-A) method (Aiken et al., 2008), are 1.32±0.08, 0.58±0.07 and 1.89±0.09, respectively, corresponding to an average oxidation state (OS$_C$ = 2*O:C - H:C) of -0.16±0.22. The elemental ratios calculated with the A-A method are reported here just for the purpose of a more direct comparison with papers published before the introduction of the new I-A method (2015). Anyway, through all the paper and in the plots, the more accurate I-A elemental ratios will be reported. Saarikoski et al. (2012) presents results of HR-ToF-AMS measurements in the Po Valley at the site of San Pietro Capofiume (SPC) during April 2008, showing an average H:C ratio slightly higher (1.49) and an average O:C ratio slightly lower (0.47) than those observed at Mt. Cimone, for a resulting average OM:OC ratio of 1.77. Similarly, OM:OC

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higher than 1.7 were observed in the outflow plume over Mexico city and at the mountain site of Altzomoni, above the Mexico city plateau (Gilardoni et al., 2009). The OM:OC ratio observed at SPC in Fall 2011 was 1.6 (Gilardoni et al., 2014). The lower oxidation of the OA collected at SPC during spring and fall with respect to the present measurements can be due to (a) the different season or (b) to oxidation processes involving OA during transport from low altitude sites up to Mt. Cimone. This last aspect will be investigated in Section 3.3.

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3.2 Analysis of the diurnal cycles

The atmospheric concentrations of the major NR-PM_1 components present a clear diurnal cycle with maxima at the early afternoon and minima during the night (Figure 3). The concentration daily trend of the NR-PM_1 components is the result of the PBL dynamics and valley breezes, as during the night the site is well above the shallow nocturnal layer forming over the Po Valley plain and disconnected from the aerosol sources located at the low altitudes. However, Marinoni et al. (2008) showed that in summer, during the night-time, Mt. Cimone station may be affected by polluted air masses present in the residual layer above the Po Valley. Conversely, during the day, with the increase of the PBL height, the site is affected by convective transport from lower altitudes (Schuepbach et al., 2001; Fischer et al., 2003; Freney et al., 2011) and it is directly connected to the pollution sources located in the valley, thus experiencing high aerosol concentrations. During PEGASOS, the time trend of OA (the major contributor to NR-PM_1) correlates with that of specific humidity (SH), which can be used as a tracer of PBL air at high altitudes (Henne et al., 2005) (Figure S3). This good correlation strongly supports the hypothesis that the aerosol transport triggered by the PBL dynamics is the main factor regulating the NR-PM_1 concentrations at Mt. Cimone during the measurement period.

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To further investigate the importance of vertical transport from the PBL to the top of Mt. Cimone during the day, we calculated the daily relative increase (RI) in SH, following the approach introduced by Prevôt et al. (2000) and Henne et al. (2005) for two different sites in the Alps and already applied for Mt. Cimone station by Carbone et al. (2014).

$$RI = \frac{SH_{aft}(CMN) - SH_{mor}(CMN)}{SH_{aft}(SPC) - SH_{mor}(CMN)} \qquad (1)$$

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In Equation 1, SH_{atf}(CMN) is the average specific humidity measured in the afternoon at Mt. Cimone (12:00 to 18:00 LT), SH_{mor}(CMN) is the average specific humidity measured during the night at Mt. Cimone (22:00 to 05:00 LT) and SH_{aft}(SPC) is the average specific humidity measured in the afternoon (12:00 to 18:00 LT) at the rural background station of San Pietro Capofiume (SPC), located in the Po Valley 90 km north-east of Mt. Cimone at 11 m a.s.l. and considered representative of PBL conditions within the Po Valley basin. A RI of 1 corresponds to a complete replacement of the high altitude air by boundary layer air, while no vertical motion yields zero relative increase. RI was calculated for each day of the campaign and the average value was 0.8±0.3, confirming the high influence of vertical convection during the day at the station in summer.

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Similarly to the NR-PM_1 components, OA elemental ratios exhibit diurnal variations (Fig 4). The O:C and OM:OC ratios have lower values in the afternoon and maxima at night, with a minimum O:C hourly average of 0.67±0.10 observed between 14:00 and 15:00, and maximum of 0.75±0.08 between 00:00 and 01:00. An opposite trend is observed for the H:C ratio, with a maximum hourly average of 1.55±0.10 between 14:00 and 15:00, and a minimum of 1.38±0.10 between 00:00 and 01:00. The daily trend of the O:C and OM:OC ratio are almost coincident (correlation coefficient 0.999) confirming the results of Pang et al. (2006) showing that the OM:OC ratio is mainly regulated by the O:C ratio.

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These trends highlight the different age of the aerosols measured at the sampling location in different moments of the day, as a consequence of the PBL dynamics. In fact, the O:C ratio of OA tends to increase and the H:C ratio decreases as a function of its atmospheric residence time, because of the oxidation of reduced species emitted by traffic and combustion and of SOA formation (Aiken et al., 2008; DeCarlo et al., 2008; Heald et al., 2010; Chhabra et al., 2011; Ng et al., 2011; Sun et al., 2011b; Sun et al., 2011a). Particles sampled at Mt. Cimone during the day are representative of an early stage of aerosol atmospheric oxidation, resulting from SOA formed at lower altitudes in the Po Valley and transported upward by turbulence and by thermal winds, typically in few hours. By contrast, at night the aerosol sampled at Mt. Cimone is more processed, as the atmospheric layers affecting the site at night contain aerosols with an age from several hours (residual layers) to days (from long-range transport). This is confirmed by the CO/NOx ratio, often used in the literature as a tracer for air mass photochemical age (Morgan et al., 2010; Freney et al., 2011). CO/NO$_X$ at Mt. Cimone is 159±65 (average ± standard deviation) during the daytime and 287±168 at night, which is a value representative of aged regional emissions. The CO/NO$_X$ ratio is presented in detail in Figure S4, showing clearly that during the night-time the CO/NO$_X$ ratio is systematically higher than during daytime. For these reasons, Mt. Cimone is an ideal site to investigate the processing of organic aerosol over the Po Valley basin. Moreover, according to Marinoni et al. (2008), the footprint of aerosol particles found in the residual layers at night comprises a great part of central Europe, and this corresponds to the region where the full oxidation of organic aerosols that we observed at Mt. Cimone also took place.

3.3 Investigation of regional scale organic aerosol ageing

To investigate the oxidation of OA, data collected at Mt. Cimone during the campaign have been divided based on the position of the station relative to the PBL height, using SH as a tracer of the PBL evolution. Figure S5 shows the average daily evolution of the SH at Mt. Cimone during the campaign that mimics the PBL evolution during the day: the afternoon maximum indicates that the site is within the PBL, under the influence of moist air coming from lower altitudes, while the night minimum indicates that Mt. Cimone station is above the PBL. Following Figure S5, HR-ToF-AMS measurements collected between 12:00 and 18:00 have been considered as PBL samples, those collected between 22:00 and 05:00 have been defined as free troposphere (FT) samples, while all the samples excluded from the previous two groups have been considered as transition samples (TR). As expected, PBL samples were less oxidized (H:C = 1.54±0.06, O:C = 0.69±0.05, OM:OC = 2.05±0.10) than FT samples (H:C = 1.41±0.09, O:C = 0.74±0.07, OM:OC = 2.12±0.10), with TR samples characterized by intermediate values (H:C = 1.45±0.09, O:C = 0.72±0.07, OM:OC = 2.08±0.09), consistent with the average elemental ratios discussed in the Section 3.1. The differences between the average elemental ratios of PBL, TR and FT are statistically significant according to the t-test (p<0.01). The large standard deviations associated to the mean values are due to day-by-day variations, as showed by Figure S6. Figure S6 also

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Formattato: Colore carattere: Automatico shows that, independently on the day-by-day variations, O:C is systematically higher, and H:C systematically lower, in the FT than in PBL air masses, while the TR air masses have intermediate values.

Figures 5 shows the whole campaign data points in a Van Krevelen diagram (Van Krevelen, 1950), together with the average H:C and O:C ratios of PBL, TR and FT samples. The data are lumped within the region delimited by O:C between 0.5 and 1 and H:C between 1.1 and 1.5. The plot illustrates the process of OA atmospheric oxidation in the investigated area characterized by a slope comprised between -0.5 and -1. According to Heald et al. (2010) and Ng et al. (2011), such an intermediate slope can result from a combination of reactions adding carboxylic acids to the OA, occurring both with and without fragmentation of the parent molecules (expected slopes = -0.5 and -1, respectively). Kroll et al. (2011) reported that fragmentation becomes increasingly important for already oxidized material undergoing further processing. This can explain the results at Mt. Cimone, where OA does not resemble recently formed secondary material, in analogy with Ng et al. (2011). An alternative explanation for a slope tending to -0.5 is given by equivalent amounts of addition of carboxylic groups and of hydroxyls or peroxides (Ng et al., 2011).

The addition of carboxylic functionalities during the OA ageing process is confirmed by the analysis of the high resolution mass fragments, showing that, from PBL to FT samples, the average contribution of $C_XH_YO_{Z>1}$, attributed to the fragmentation of carboxylic structures (Aiken et al., 2007; Takegawa et al., 2007; Duplissy et al., 2011), increases from 35% to 43%, while both C_XH_Y and C_XH_YO fragments decrease (Figure 6). The mean elemental compositions calculated for PBL, TR and FT samples fall at distinct positions along the line of average ageing in the Van Krevelen space (Figure 5), suggesting that the observed oxidation of OA is dictated by the different age of the aerosols reaching the station at different times of the day, as also evidenced by Figure S6.

Finally, Figure 7 shows the time-of-flight particle size distributions (pToF) of the main NR-PM_1 components as measured by the HR-ToF-AMS observed during the three regimes (PBL, TR and RL). For each species, there is no appreciable size distribution difference between the three sample sub-sets (PBL, TR and FT). However, the organics pToF peaks

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Formattato: Colore carattere: Automatico at a slightly lower d_{va} (293 nm) compared to sulphate, ammonium and nitrate (which peak between 330 and 340 nm d_{va}), as determined by a lognormal fit of the size distributions. This result indicates that the organic and inorganic components in all the sampled air masses are not entirely internally mixed. Furthermore, organics pToF shows a tail towards smaller particles sizes reaching 90 nm, and appreciable amount of mass below 200 nm d_{va}, which is consistent with previous observations of organics pToF typically having lower d_{va} than e.g., SO_4, due to different sources and formation processes. It is possible that a fraction of the organics observed at $d_{va} < 200$ nm arises from the growth of smaller particles (fresh emission typically peak at d_{va} of 80-100 nm). via condensation processes during transport to high altitude.

3.4 OA source apportionment by PMF

In order to further characterize the OA collected at Mt. Cimone, PMF was applied to the high-resolution OA mass spectra. We screened various solutions with a number of factors from two to ten. A 4-factor solution with rotational forcing parameter fPeak = 0 (Q/Qexp = 2.3) was chosen, yielding four different types of OOA, two of which were recombined into one factor, because of coincident time series and profiles (Fig. S6). The OA components from the PMF analysis were identified by their mass spectra, elemental composition (Fig. 8) and diurnal cycles (Fig. 9), as well as by correlations of their time series with tracers (Tab. 2). A detailed summary of key diagnostic plots of the PMF results and a discussion of the factor solution choices can be found in the supporting information (SI).

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The three resulting factors are all of the oxygenated organic aerosol (OOA) type and have been defined as OOAa, OOAb and OOAc. No "standard" hydrocarbon like (HOA) factor (i.e., with m/z 43 >> m/z 44 and with a significant amount of hydrocarbon-like ions, C_XH_Y) could be extracted by PMF, similarly to other AMS datasets collected at background sites (Hildebrandt et al., 2010; Freney et al., 2011), indicating almost no direct influence of freshly emitted primary aerosols to the observed OA load. This result is consistent with the highly oxidized character of the OA, as described previously. Even though m/z 44 (CO_2^+) dominates the mass spectra of all the three factors, the OOAa factor has a slightly higher

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amount of C_XH_Y ions at m/z 27 ($C_2H_3^+$), 39 ($C_3H_3^+$), 41 ($C_3H_5^+$) compared to the other factors.

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The elemental composition (H:C, O:C) and the OM:OC ratio are also reported in Fig. 8. OOAc is the most oxidized factor, with an OM:OC ratio of 2.48 versus 2.03 and 2.13 of OOAa and OOAb, respectively. Consequently, it has higher O:C (1.02) and lower H:C (1.07) ratio than OOAa (0.67; 1.51) and OOAb (0.75; 1.44). OOAa average concentration was 1.5±1.7 µg m^{-3} during the campaign, which accounts for 55% of the OA. OOAb presented higher concentrations during the period 17-23 June (2.1±1.5 µg m^{-3}) and low concentrations during the rest of the campaign (0.27±0.29 µg m^{-3}), for an average concentration of 0.67±1.1 µg m^{-3} and a contribution of 25%. The concentration of OOAc was 0.54±0.40 µg m^{-3} contributing on average 20% to the OA.

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When looking at the diurnal profiles of the three factors (Fig. 9), we see clear diurnal cycles for OOAa and OOAc (but with opposite trends, having OOAa a maximum at 16:00, and OOAc having a minimum at 14:00) and a less pronounced diurnal profile for OOAb (slightly higher concentration around 12:00-14:00 than during the rest of the day). The fact that OOAa concentration is much higher during the day than at night indicates that this factor derives from sources located within the PBL and is transported at Mt. Cimone by convection and by thermal winds in daytime, as discussed above. Conversely, the trend for OOAc with lower concentrations during the day points to a transport from the free troposphere, or anyway from above the PBL.

The Pearson correlation coefficients (R) between the three PMF factors and several external gas-phase and particle tracers are reported in Table 2. OOAa correlates best with CO, NO_X and BC (0.71, 0.70 and 0.54 respectively), which are attributable to anthropogenic sources located within the PBL, confirming our interpretation of the OOAa source location. OOAb shows lower correlation than OOAa against all the tracers, with higher R values associated with the above enlisted PBL tracers (CO, NO_X and BC), suggesting that this factor too was contributed by PBL sources. Interestingly, OOAb presents the highest correlation with sulphate, which suggests a regional character for this OOA component. The highest correlation for OOAc is with O_3, with a very small correlation with all the PBL tracers. The high correlation of OOAc with O_3 is mainly driven by the coincident daily trends (Figure S11), showing higher concentration at night, a typical feature of O_3 at high-altitude sites (Fischer et al., 2003; Cristofanelli et al., 2007). In fact, during summer, air-masses richer in photochemically produced O_3 are vented to Mt. Cimone in the afternoon, leading to an increase of O_3 along the afternoon until evening, when O_3 observations started to be more representative of the free troposphere.

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The spectral and elemental features of the three OOA factors are in the range of others reported in the literature (Mohr et al., 2012; Holzinger et al., 2013; Sun et al., 2011a). Similar OOA spectra have also been described by Saarikoski et al. (2012) for the Po Valley site of San Pietro Capofiume. Correlation analysis with reference high-resolution spectra (Table 3) suggests that all the OOA components identified can be classified as LV-OOA (low volatile-OOA). However, OOAa and OOAb present qualitatively similar spectral features to the SV-OOA (semi volatile-OOA) reported by Freney et al. (2011), for a similar high altitude station, and by Hayes et al. (2013), for photochemically aged aerosol. The f44 (contribution of organic mass fragments with m/z 44) of OOAa and OOAb is 0.13 and 0.14, respectively, which is across the SV-OOA/LV-OOA border region proposed by Cubison et al. (2011). Therefore, we believe that OOAa and OOAb can be considered either as highly oxidized SV-OOA or LV-OOA with a low oxidation level.

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In summary, OOAa is clearly attributed to sources or formation processes located within the PBL that reach the station when vertical transport (PBL convection and valley/upslope breeze) is maximized. OOAa is the less oxydized factor retrieved by PMF and likely represents a moderately aged local OA. OOAb has a less defined diurnal cycle (still with maximum during daytime) and a slightly higher O:C ratio than OOAa. The period of OOAb maximum contribution coincides with meteorological conditions characterized by reduced horizontal air motion and dominated by breeze regimes (17-23 June, when an anticyclonic high pressure system was present over northern Italy). These conditions favour the accumulation of pollutants within the PBL and in the residual layers above, because of reduced air circulation. Coen et al. (2011) demonstrated that under such meteorological conditions, air masses from residual layers continue to influence the Jungfraujoch high altitude station also during the night, leading to higher minima in the diurnal aerosol concentration than in other conditions. We postulate that the same happens at Mt. Cimone. The entire region influenced by the high pressure system extends beyond the Po Valley

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Finally, OOAc is the product of prolonged atmospheric processing of OA, occurring mainly in the free troposphere, and can be considered as representative of the background FT OA on a spatial scale that comprises all western European areas upwind of Mt. Cimone. These conclusions are confirmed by the plots in Figure 10, showing CO/NO$_X$ vs. SH colour coded by the contribution of each factor. Clearly, OOAa is associated with air masses characterized by reduced photochemical age (low CO/NO$_X$) and strongly influenced by the PBL (high SH), while OOAc contributes more in air masses characterized by high photochemical age (high CO/NO$_X$) and less influenced by the PBL (low SH). OOAb presents intermediate characteristics (mid to low CO/NO$_X$ and intermediate SH), consistent with the hypothesis that OOAb is representative of OA of intermediate age that is accumulated in the residual layers during the period of high pressure, due to the stagnant atmospheric conditions.

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4 Conclusions

The chemical composition of non-refractory sub-micrometric particles was measured for the first time by a HR-ToF-AMS at the Mt. Cimone GAW/WMO high altitude station. Sub-micrometric aerosol was dominated by the organic fraction (on average 63%), with ammonium sulphate as second contributor, for an average NR-PM$_1$ mass of 4.5±3.4 µg m^{-3}. Elemental analysis of the high resolution AMS data showed highly oxygenated OA (the campaign-average H:C, O:C and OM:OC were 1.45±0.11, 0.71±0.08 and 2.08±0.10, respectively), suggesting that strong oxidation and SOA formation processes occur during aerosol transport to high altitudes. Different stages of OA processing could be identified

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when comparing the OA composition during daytime, when the station was affected by the upward transport of PBL air, and the night-time, when the site was in the free troposphere (FT).

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Analysis of the OA elemental ratios in a Van Krevelen space showed that OA oxidation followed a slope comprised between -0.5 and -1, consistent with the addition of carboxylic groups to alkyl structures, occurring both with and without fragmentation of the reagent molecules. The increase of carboxylic groups during OA processing and ageing is confirmed by the increased contribution of $C_XH_YO_{Z>1}$ fragments during night-time measurements.

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Quantitative information on the contributions of more and less aged OA components were achieved by analysing the high resolution AMS data by positive matrix factorization (PMF). OOAa (55%), the least oxidized OOA factor, was related to sources or formation processes located within the PBL, reaching the station mainly during day-time, when vertical transport is maximized. OOAb (25%) was attributed to the accumulation and ageing of OA in the PBL and in the residual layers above the PBL, due to stagnation over the great Alpine region. Finally, OOAc (20%) was interpreted as the product of prolonged atmospheric processing of OA occurring mainly above the PBL, and can be considered as representative of background free tropospheric OA at a continental scale.

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This work highlights the important contribution of organic aerosols to the composition of submicron particles at remote mountain sites. We found that 63% of the NR-PM$_1$ mass that constitutes the background aerosol levels for the Po Valley in the summer is accounted for by highly oxygenated organic matter. No important contribution from primary combustion organic particles (HOA) was measured, indicating that these compounds were likely lost during transport either by evaporation or chemical processing. Most importantly, in spite of the vicinity of strongly emitting pollution sources in the Po Valley, only 55% of the organic matter measured at Mt. Cimone in the summer could be attributed to sources within the PBL, while the remaining fraction (45%) is accounted for by remote upwind sources. This study confirms the importance of regional scale physical and chemical processes and of transboundary transport in determining the background aerosol composition at rural European sites.

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Acknowledgements

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Table 1. Summary of AMS measurements at mountain sites published in the literature.

Reference	Site/ Season	Altitude (m asl)	Organics	Nitrate	Sulphate	Ammonium	Chloride	H:C	O:C	OM:OC
Hock et al. (2008)	Hohenpeissenberg/ spring	985	3.4 (50%)	1.3 (19%)	1.3 (19%)	0.7 (11%)	0.07 (1%)			
Sun et al. (2009)	Whistler Mountain/ spring	2182	1.05±1.03 (55%)	0.05±0.10 (3%)	0.58±0.41 (30%)	0.23±0.16 (12%)	-	1.66±0.06	0.83±0.17	2.28±0.23
Lanz et al. (2010)	Jungfraujoch/ spring	3580	0.7 (43%)	0.3 (18%)	0.4 (26%)	0.2 (13%)	<0.02 (<1%)			
Freney et al. (2011)	puy-de-Dôme/ autumn	1465	2.52 (34%)	1.14 (15%)	2.4(32%)	1.36 (18%)	0.02 (0.3%)	-	-	-
Freney et al. (2011)	puy-de-Dôme/ winter	1465	1.24 (23%)	1.71 (32%)	1.28 (24%)	1.08 (20%)	0.07 (1%)	-	-	-
Freney et al. (2011)	puy-de-Dôme/ summer	1465	15.59 (57%)	2.33 (9%)	5.45 (20%)	3.69 (14%)	0.06 (0.2%)	-	-	-
This study	Mt. Cimone/ summer	2165	2.8±2.4 (63%)	0.33±0.46 (7%))	0.92±0.60 (20%)	0.41±0.33 (9%)	(<1%)	1.45±0.11	0.71±0.08	2.08±0.10

Eliminato: ¶

Table 2. Pearson correlation coefficients (R) between the time series of the three PMF factors and several gas-phase and particle tracers measured at Mt. Cimone.

	BC	CO	T	P	RH	WS	UVB	O_3	NO_X	nitrate	sulphate	Ammonium
OOAa	0.54	0.71	0.48	0.42	0.22	-0.23	0.12	0.45	0.70	0.55	0.48	0.57
OOAb	0.35	0.27	0.36	0.25	-0.01	0.02	0.09	0.28	0.18	0.09	0.64	0.43
OOAc	0.41	0.24	0.16	0.26	-0.12	0.12	-0.10	0.58	0.02	0.12	0.49	0.38

Table 3. Pearson correlation coefficients (R) between the profiles of the three PMF factors and reference high resolution factor profiles found in the literature.

	Saarikoski et al., 2012						Mohhr et al., 2012				Crippa et al., 2013		
	OOAa	OOAb	OOAc	HOA	BBOA	NOA	BBOA	HOA	LVOA	SVOA	SVOOA	LVOOA	HOA
OOAa	0.93	0.92	0.90	0.75	0.38	0.40	0.62	0.19	0.87	0.81	0.86	0.93	0.50
OOAb	0.94	0.92	0.90	0.70	0.30	0.34	0.61	0.17	0.91	0.81	0.81	0.93	0.45
OOAc	0.97	0.94	0.97	0.58	0.21	0.10	0.31	0.07	0.95	0.76	0.59	0.94	0.32

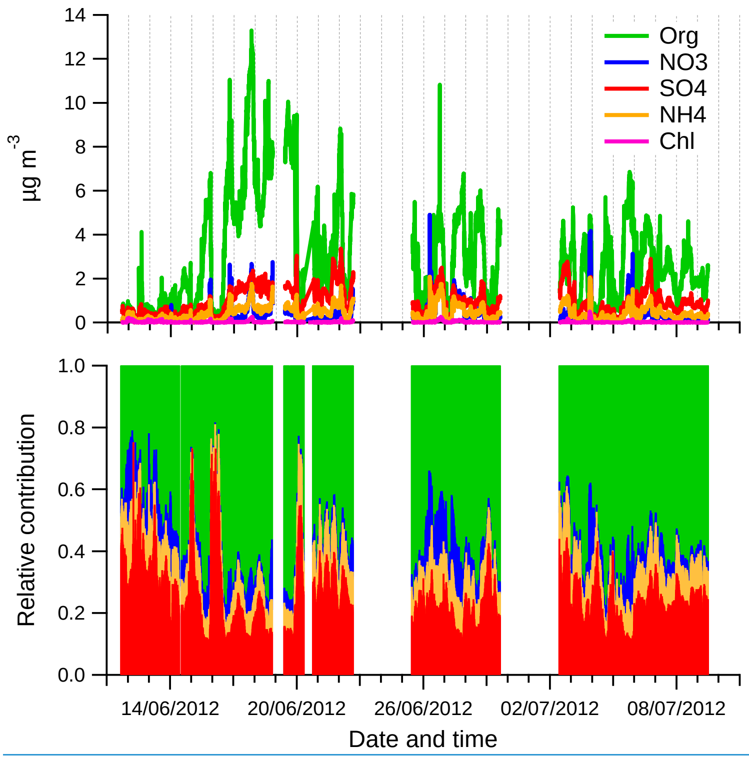

Figure 1. Time series and relative contribution of the main NR-PM$_1$ components. Time is local (UTC+2 hr).

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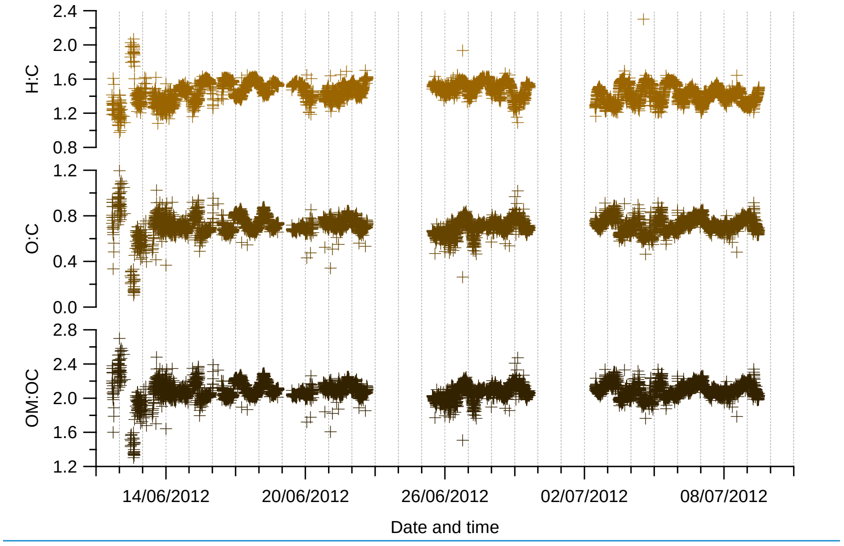

Figure 2. Time series of the H:C, O:C and OM:OC ratios. Time is local (UTC+2 hr).

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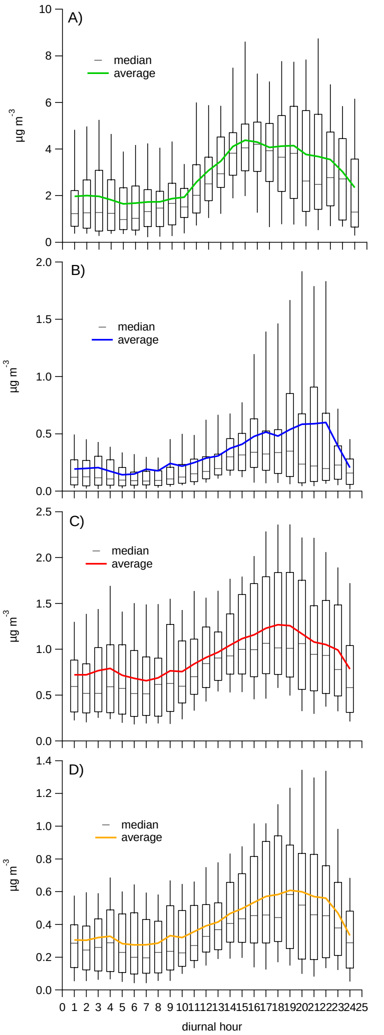

Figure 3. Daily trends of (A) organics, (B) nitrate, (C) sulphate and (D) ammonium. Boxes represent median, 25th and 75th percentile; whiskers indicates 10th and 90th percentile. Time is local (UTC+2 hr).

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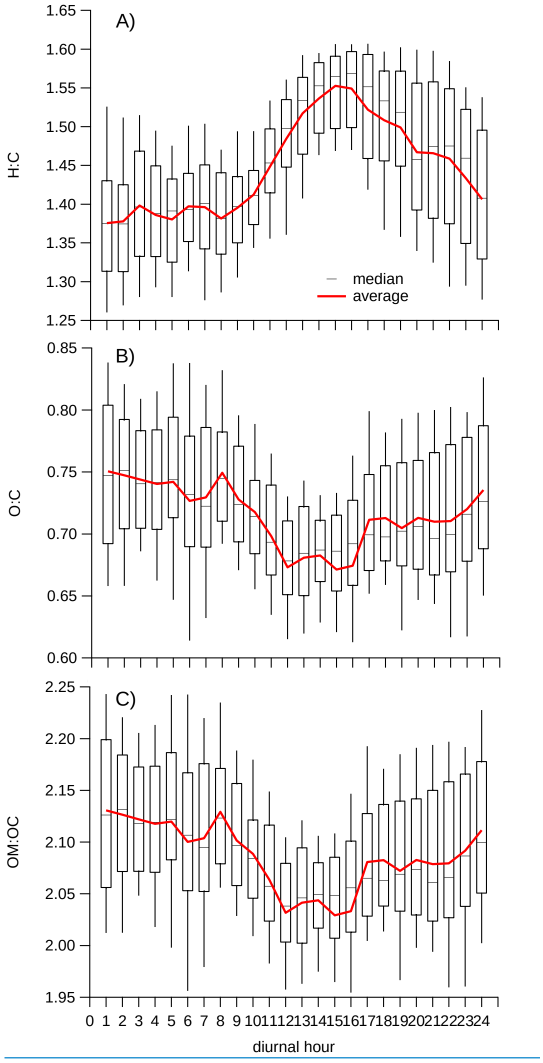

Figure 4. Daily trends of the (A) H:C, (B) O:C and (C) OM:OC ratios. Boxes represent median, 25th and 75th percentile; whiskers indicates 10th and 90th percentile. Time is local (UTC+2 hr).

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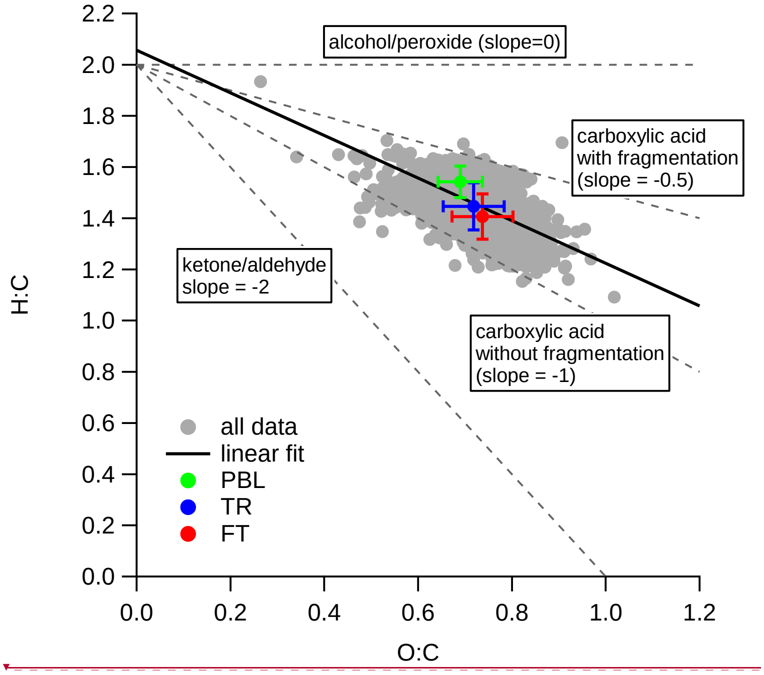

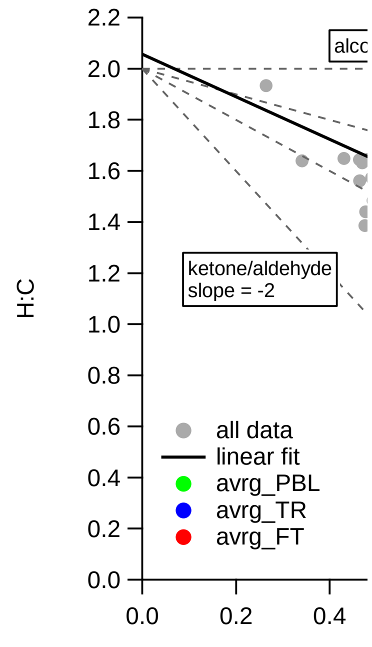

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Figure 5. Van Krevelen diagram presenting the H:C and O:C ratios of all the data points collected during the campaign, superimposed to average values for PBL, TR and FT samples. The solid line represents the fit to the data (not constrained to H:C=2). Dashed lines describes oxidation reactions occurring through addition of carbonyl groups (slope = -2 (Heald et al., 2010)), carboxylic acid without fragmentation (slope = -1 (Heald et al., 2010)), carboxylic acid with fragmentation (slope = -0.5 (Ng et al., 2011)) and alcohol/peroxide (slope = 0 (Heald et al., 2010)).

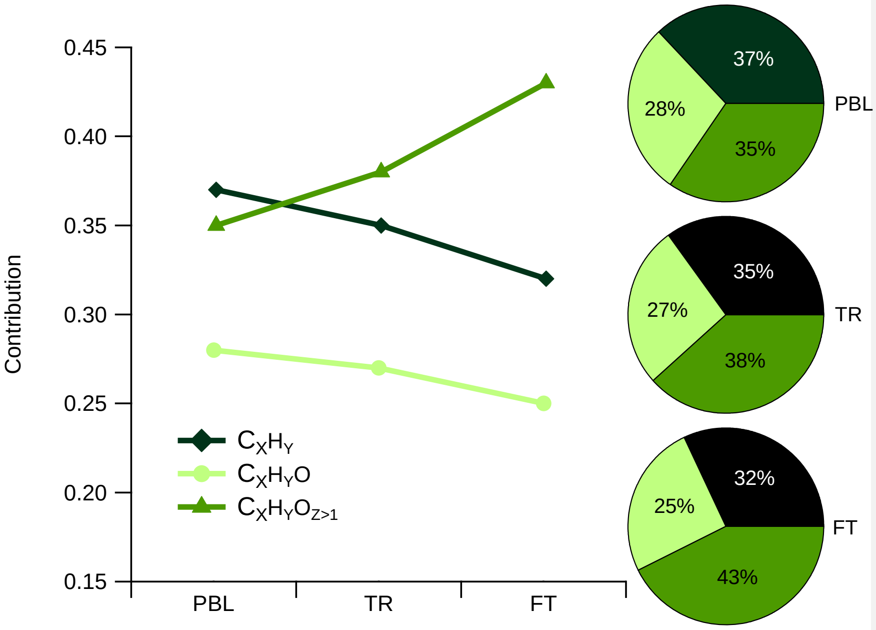

Figure 6. Contribution of organic fragments containing only carbon and hydrogen (C_XH_Y), organic fragments containing carbon, hydrogen and one oxygen atom ($C_XH_YO_1$) and organic fragments containing carbon, hydrogen and more than one oxygen atom ($C_XH_YO_{Z>1}$) in PBL, TR and FT samples.

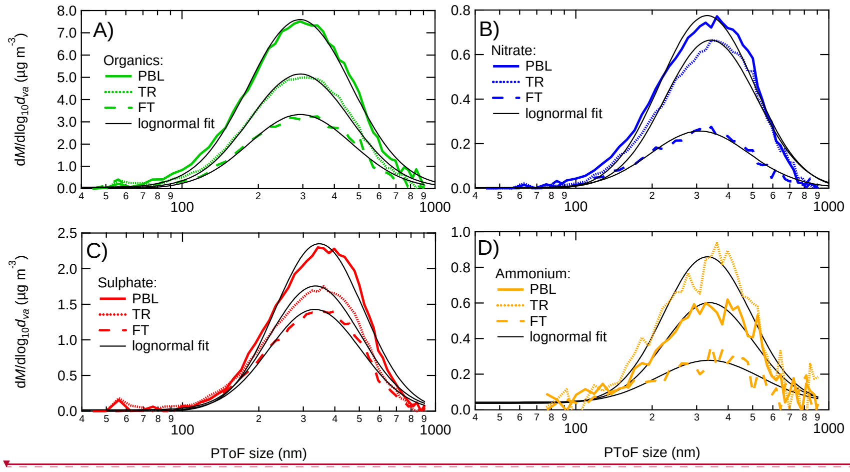

Figure 7. Size distribution of (A) organics, (B) nitrate, (C) sulphate and (D) ammonium in PBL, TR and FT samples. Lognormal fits are reported as black lines.

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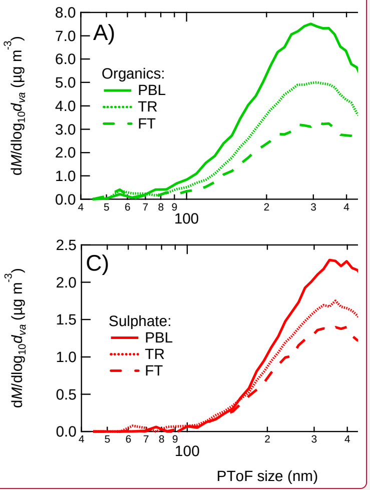

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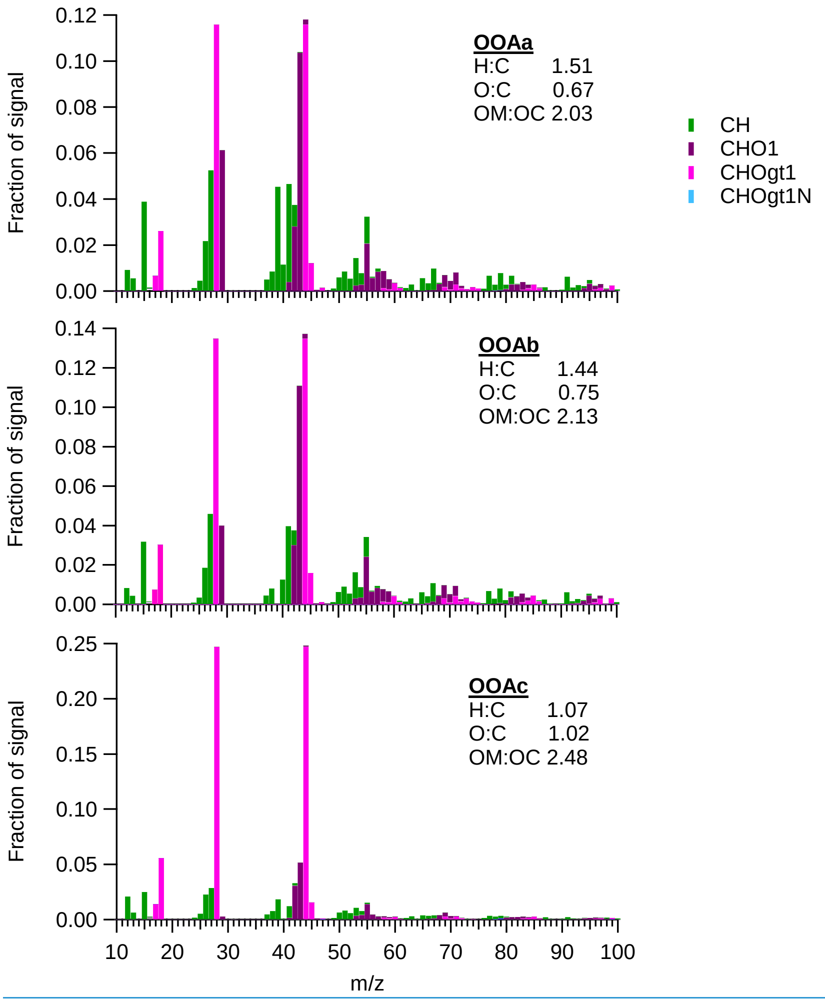

Figure 8. High resolution mass spectra of the three factors extracted by PMF. Insets in each plot reports the results of the elemental analysis (from the I-A method).

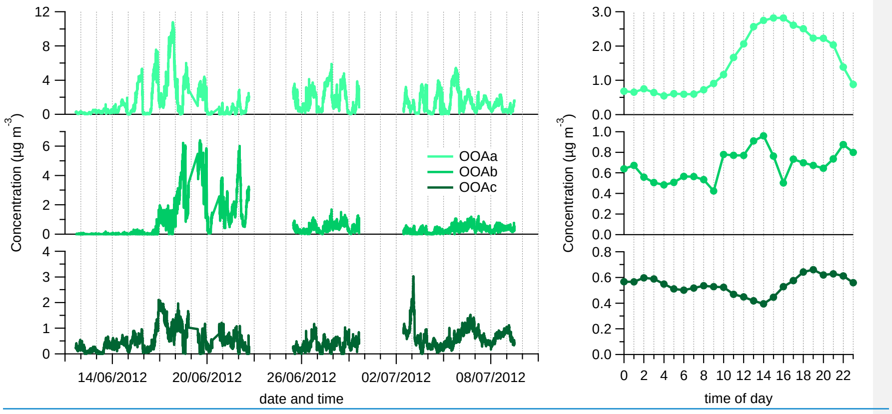

Figure 9. Time series and diurnal trend of the three factors extracted by PMF.

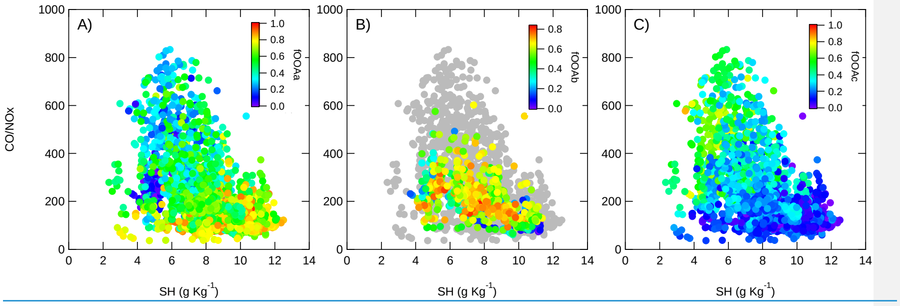

Figure 10. CO/NO$_X$ ratio vs. SH, colour coded by the contribution of factors (A) OOAa, (B) OOAb and (C) OOAc. In (B) only the data points corresponding to OOAb maximum contribution period (17-23 June) have been coloured, to make the plot clearer.