Regional scale oxidation of organic aerosol observed through HR-ToF-AMS measurements at Mt. Cimone (2165 m asl), Italy

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High resolution time of flight aerosol mass spectrometer (HR-ToF-AMS) measurements have been performed, for the first time, at Mt. Cimone GAW station (44°12' N, 10°42' E, 2165 m asl) from 11 June to 9 July 2012, under the framework of the EU project PEGASOS and the Emilia-Romagna Region project SUPERSITO.

Mt. Cimone (44°12' N, 10°42' E, 2165 m asl) is the highest peak of the Northern Apennines and dominates the highly populated and heavily polluted Po Valley region.

Observed average concentrations (and mass contributions) of the main AMS species during the campaign were 2.8±2.4 μg m^{-3} (63%), 0.92±0.60 μg m^{-3} (20%), 0.33±0.46 μg m^{-3} (7%) and 0.41±0.33 μg m^{-3} (9%) for organics, sulphate, nitrate and ammonium, respectively, assuming a composition dependent collection efficiency (Middlebrook *et al.*, 2012), for an average reconstructed non refractory PM1 mass of 4.5±3.4 μg m^{-3}.

All the main AMS species presented a clear diurnal cycle with higher concentrations during the day and lower during the night, as a result of the planetary boundary layer (PBL) dynamics. During the night the site is well above the shallow residual layer, therefore in the free troposphere, and unconnected to the Po Valley aerosol sources. On the contrary, during the day, the site is inside the PBL and affected by the underlying aerosol sources.

The peculiar character of the site allows the investigation of organic aerosol (OA) ageing occurring at regional scale over the Po Valley. In fact, particles sampled during the day are representative of the early stages of aerosol atmospheric oxidation, comprising processed primary OA and secondary OA formed in the Po Valley basin. During the night, the aerosol sampled at Mt. Cimone is representative of more processed conditions, as the free troposphere contains aerosols with an age from several hours (transported during the day from the underlying valley) to days (transported during previous PBL evolution cycles).

To investigate the OA oxidation, based on the specific humidity (SH) as a tracer of the PBL evolution, we classified as PBL-influenced the samples collected between 12:00 and 18:00 LT, free troposphere (FT) the samples collected between 22:00 and 05:00 LT and transition (TR) all the samples collected in between.

Elemental analysis performed with high resolution mass spectra (Aiken *et al.*, 2007), revealed average H/C ratios of 1.38±0.04, 1.32±0.06 and 1.28±0.06 for PBL, TR and FT samples, respectively, while the O/C ratios were 0.54±0.04, 0.59±0.06 and 0.62±0.06 for PBL, TR and FT samples. Consequently, the OM/OC ratio passed from 1.83±0.05 in PBL, through 1.90±0.08 in TR, to 1.94±0.08 in FT samples.

These results evidence the progressive oxidation of OAs over the Po Valley basin, from few hours after their emission/formation to one or more days of atmospheric processing. On a Van Krevelen space, the data produce a slope of ~ –1, suggesting that the observed regional scale oxidation processes occur mainly through the addition of carboxylic functional groups (Heald *et al.*, 2010).

This is further confirmed by the analysis of the HR mass fragments, showing that, from PBL to FT samples, the average contribution of fragments containing carbon, hydrogen and more than one oxygen atom (CHO>1) passes from 25% to 33%, while both CH and CHO fragments decrease their contribution.

Further analysis of the dataset is currently ongoing to investigate the contribution of organo-sulphates and organo-nitrates as a function of the aerosol ageing.

Concluding, high time resolution online measurements performed at Mt. Cimone GAW station, thanks to the peculiar location of the site, are ideal to investigate and characterize the atmospheric processing of organic aerosols occurring over the Po Valley basin.

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