Chemical composition, sources and insights on submicron aerosol atmospheric processing during wintertime outstanding smog episodes

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During and in the aftermath of the previous decade's financial recession in Southern Europe, residential wood burning (RWB) has become a widespread means of domestic heating in cities, leading to severe air quality degradation and changes in atmospheric chemical composition. Previous studies in Ioannina, a mountain city in NW Greece, revealed outstanding PM concentrations during wintertime (Kaskaoutis et al., 2020), associated with intense RWB episodes and favoured by poor ventilation in the city's basin-like setting and shallow nocturnal boundary layer.

In this context, a 1-month intensive field campaign was held during the winter of 2021-22 (6 Dec – 10 Jan) to chemically characterise PM_1 aerosol and gain insight into potential atmospheric processing mechanisms. Near real-time chemical composition of non-refractory submicron particles as well as organic aerosol (OA) mass spectra were monitored using an Aerosol Chemical Speciation Monitor (ACSM) alongside an AE33 aethalometer for black carbon (BC). Source apportionment of OA was conducted by means of positive matrix factorization using the SoFi Pro software package (Canonaco et al., 2021). The aethalometer model was implemented to apportion BC to its fossil fuel combustion (BC_{ff}) and biomass burning (BC_{bb}) components. Concurrent measurements included 12h high volume $PM_{2.5}$ filter samples, a wide range of volatile organic compounds monitored by a Proton Transfer Reaction – Time of Flight - Mass Spectrometer (PTR-ToF-MS), as well as standard pollutants (PM_{10}, NO_x, O_3, CO). The dataset was coupled with wind data and air mass back-trajectories through Non-parametric Wind Regression (NWR) and Potential Source Contributing Function (PSCF) analyses (Petit et al., 2017).

OA was the principal contributor to submicron aerosol (78%), with its concentration levels increasing 2-fold during nighttime compared to the afternoon baseline, and showing a secondary peak during the morning rush hour. BC contributed by ca. 8% to submicron aerosol and was characterized by a bimodal diurnal cycle, which was nevertheless dominated by BC_{bb} throughout the campaign, with nighttime biomass burning (BB%) contributions exceeding 90%. Interestingly, nitrate exhibited an early afternoon peak, while its strong correlation to ammonium (r^2=0.77) points to NH_4NO_3 formation. Chloride was clearly enhanced during the night while sulfate notably exhibited a bimodal cycle. These results point out the need to investigate contributions of organonitrates and organosulfates to nitrate and sulfate, respectively.

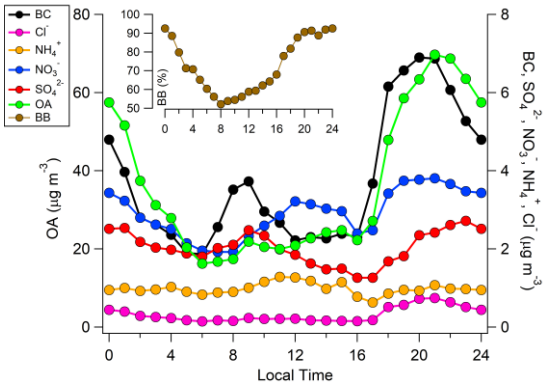

Figure 1. Diurnal variability of major non-refractory PM_1 chemical species, BC and biomass burning contribution (BB%) during the campaign in Ioannina, Greece.

Preliminary PMF results revealed 4 OA factors, namely a mixed hydrocarbon-like OA factor related to traffic and cooking, a biomass burning OA factor contributing the most throughout the campaign and two oxygenated OA factors with different levels of oxidation.

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