Chemical composition and mass closure of ambient aerosol in an urban environment over Athens, Greece: The role of wintertime biomass burning on air pollution levels

C. Theodosi[1], M. Tsagkaraki[1], P. Zarmpas[1], D. Paraskevopoulou[2], P. Nicolaou[1], E. Liakakou[2], M. Lianou[2], E. Gerasopoulos[2], N. Mihalopoulos[1, 2]

[1] Environmental Chemical Processes Laboratory, University of Crete, Heraklion, Crete, 71003, Greece
[2] Institute for Environmental Research and Sustainable Development, National Observatory of Athens, P. Penteli, Athens, 15236, Greece
Keywords: atmospheric aerosol, Athens, biomass burning; domestic heating; mass closure
Presenting author email: mihalo@chemistry.uoc.gr

The Greater Athens Area (GAA) is a region where half of the population of Greece is living. Since winter 2011-2012 the atmosphere in the GAA and other Greek cities is burdened from extended residential biomass burning for heating purposes. This study examines the chemical composition of $PM_{2.5}$ aerosol samples collected on a daily basis from December 2012 until now, at downtown Athens, in Thissio (National Observatory of Athens, 37.97 N, 23.72 E, 110 m). To assess the importance of biomass burning as a source of air pollution aerosols samples during winterime were further studied with specific emphasis on biomass burning tracers. Positive Matrix Factorization (PMF) was also applied to better constrain the aerosol sources over Athens.

In total, more than 700 daily $PM_{2.5}$ samples were collected and analysed for the for major ions (Cl^-, Br^-, NO_3^-, SO_4^{-2}, PO_4^{-3}, $C_2O_4^{-2}$, NH_4^+, K^+, Na^+, Mg^{+2}, Ca^{+2}), trace elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, V, Zn, Mn, Ni, Pb, P, S, Sb), organic carbon (OC) and elemental carbon (EC), identifying a range of useful tracers for monitoring the contribution of different sources to aerosol over Greece.

Based on filters analyzed from January 2013 to October 2015, chemical mass closure was performed (Figure 1a). The relative contributions of the ionic mass, POM, dust, EC are found to be 31%, 38%, 15% and 7%, respectively (Figure 1b). The chemical mass closure exercise can explain about 91% of the recorded fine aerosol mass, while water can contribute significantly to fine aerosol mass collected on quartz fiber filters (9%).

Ion concentrations, apart from the distinct peak in winter especially for NO_3^-, due to formation of NH_4NO_3 stabilized at the low temperatures prevailing during the cold period, exhibit a summer maximum especially for SO_4^{-2}, due to intense photochemistry and absence of precipitation. The analyzed trace metals V, Cr, Cd, Ni, Cu, Cd and Pb exhibit peak values during winter time. Given the variety of their sources eg. traffic, industrial activities, heavy oil combustion, the decrease in the boundary-layer height due to meteorological conditions (low winds, temperature inversion), could account for their winter maximum values.

During the heating period (Nov. – Dec.), $PM_{2.5}$, POM and EC are increased, due to seasonal activities, highlighting the importance of intensive combustion of wood and biomass for heating purposes, as an additional source of pollution in Athens during winter. Wood and biomass combustion is entirely responsible for high levels of PM during night time leading to significant exceedances.

It is noteworthy, that EC, benzo[a]pyrene and levoglucosan significant key tracers of biomass burning demonstrated similar day by day variability, confirming their common origin from wood burning in Athens during wintertime. The aforementioned species exhibited strong correlation (R^2=0.95-096) with night time $PM_{2.5}$ exceeding 45 μg m^{-3}. Thus, wood and biomass combustion is almost entirely responsible for the high aerosol loadings observed during winter/night time leading to significant exceedances. PMF and PCA statistical analysis confirmed the above findings.

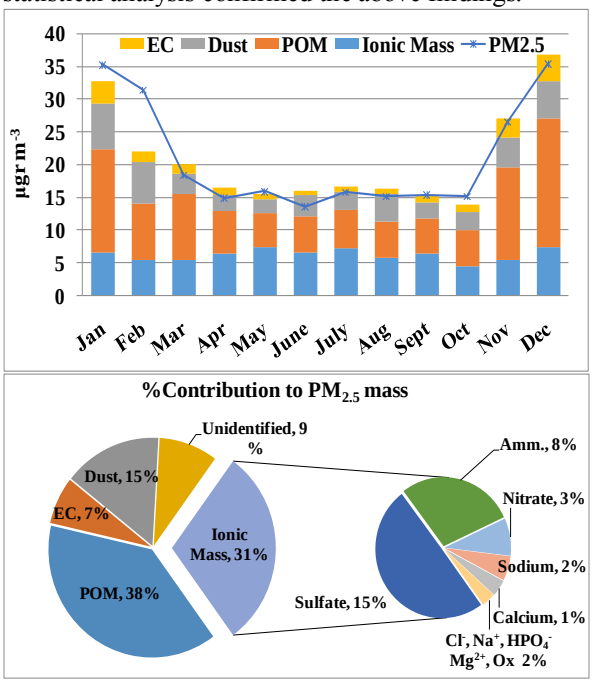

Figure 1. (a) Seasonal chemical mass closure for $PM_{2.5}$ samples collected at Thissio and (b) annual relative contribution of each aerosol species for the sampling period Jan 13–Oct 15.

This work was supported by the State Scholarship Foundation ("IKY Fellowships of Excellence for Postgraduate Studies in Greece – Siemens Programme") in the framework of the Hellenic Republic–Siemens Settlement Agreement.