Chemical composition and sources of ambient aerosol in an urban environment over Athens, Greece: Case study on the role of wintertime biomass burning

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The Greater Athens Area (GAA) is a region where half of the population of Greece is living. Since the advent of economic recession in Greece in 2008, the air quality has been improved due to the limitation of anthropogenic activities emitting gaseous pollutants to the atmosphere (Vrekoussis et al. 2013).

However, during the winter periods of December 2012-January 2013 and December 2013-January 2014, air pollution due to excessive use of residential biomass burning for domestic heating has been reported as a major environmental problem in the area.

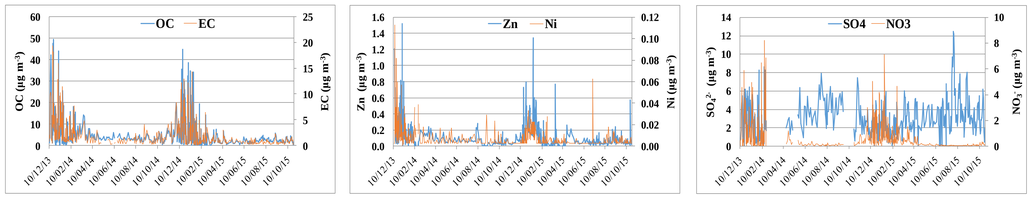
National Observatory of Athens , Thissio (37,97 N., 23,72E.)

View from the sampling site

In this study, a long term comprehensive chemical composition of $PM_{2.5}$ in an urban background site of Athens, Thissio was conducted for the first time to our knowledge. The fine aerosol fraction was chemically characterized for inorganic and organic components.

Seasonal trends of $PM_{2.5}$ masses and its chemical components were quantified, and the contribution of each to fine aerosol mass was estimated, in order to identify the potential sources of atmospheric aerosol in Athens. Overall, the study identified a range of useful tracers for evaluating the contribution of different sources to aerosol over Greece.

Samples were collected during the period 01/2013-10/2015 on quartz fiber filters (Flex Tissuquartz, 2500QAT-UP 47mm, Pall) on a 6h-24h basis resulting to the collection of over 700 samples. Samples have been analyzed for major and trace elements (Al, Fe, Ca, Ti, Zn, Pb, Cu, Ni, P, V, Cr, Mn), water soluble ions (Cl^-, Br^-, NO_3^-, SO_4^{-2}, PO_4^{-3}, $C_2O_4^{-2}$, NH_4^+, K^+, Na^+, Mg^{+2}, Ca^{+2}), organic carbon (OC) and elemental (EC), in order to perform the chemical mass closure exercise. To assess the importance of biomass burning over the GAA three main sugars specific biomass burning tracers (levoglucosan, mannosan and galactosan) were also analyzed during the winter period.



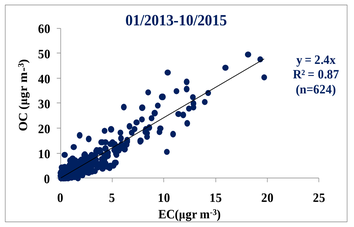
Daily variations in the PM2.5 fraction collected in Thissio from January 2013 to October 2015

OC and EC concentrations during both winter periods are 2-3 times higher

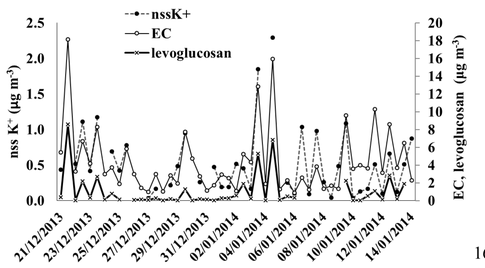
The substantial formation of secondary organic carbon is indicated by OC/EC ratio > 2. Thus, the ratios of 2.4 for the period 01/2013-10/2015 (R^2=0.87; n=624), could be attributed to biomass burning during winter time and to the formation of secondary organic carbon during summer.

Ion concentrations, apart from the distinct winter peak, especially in the case of NO_3^-, due to formation of NH_4NO_3 stabilized at the low temperatures prevailing during the cold period, exhibit a summer maximum, as SO_4^{-2} due to intense photochemistry and absence of precipitation.

Trace metals V, Cr, Cd, Ni, Cu, Cd and Pb exhibited winter peaks, explained by the decrease in the boundary-layer height due to meteorological conditions (low winds, temperature inversion)

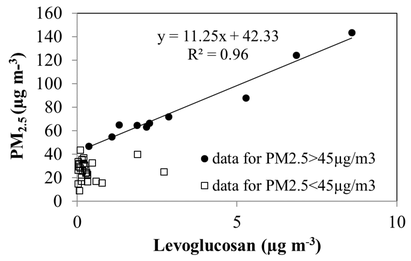


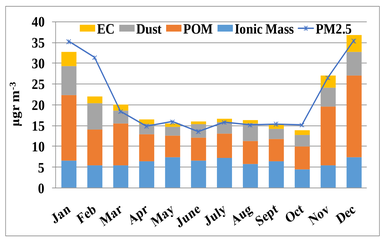
It is noteworthy, that EC, $nssK^+$ and levoglucosan reported as tracers of biomass burning demonstrated similar day-by-day variability, confirming their common origin from wood burning in Athens during wintertime.

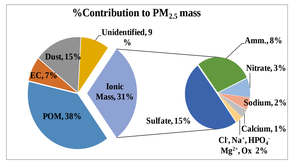


More specifically, the aforementioned species exhibited strong correlation (R^2=0.95-096) with night time $PM_{2.5}$ exceeding 45 μg m^{-3}.

Thus, wood and biomass combustion is almost entirely responsible for the high aerosol loadings ($PM_{2.5}$>45 ug m^{-3}) observed during winter - night time leading to significant exceedances.





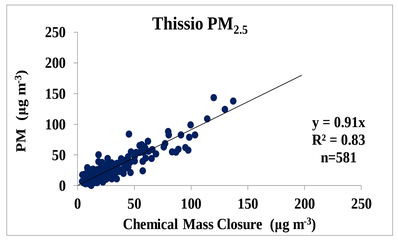


Seasonal chemical mass closure for samples collected at Thissio and annual relative contribution of each aerosol species for the sampling period Jan 13–Oct 15.

Aerosol chemical mass closure calculations indicated that POM constitutes the dominant component contributing about 38% of the $PM_{2.5}$ mass, while EC 7%.

Ionic Mass accounts for a significant part of the $PM_{2.5}$ mass 33±21% (median 31), with SO_4^{2-}, NH_4^+ and NO_3^- as the main ion contributors.

Dust accounts for almost 15%, with higher concentrations observed in spring/summer, while during winter intense anthropogenic activities, such as heating, can account for the observed increase in the fine aerosol masses.



By comparing the aerosol mass and the sum of individual chemical aerosol components a very good correlation was found with a slope equal to 0.91 (R^2=0.83, n=581), indicating a satisfactory mass closure.

Source apportionment analysis has been performed by Principal component analysis (PCA) to identify the sources during winter. Six factors have been identified:

1. OC, EC, K^+: heating
2. Al, Ca, Mn: Sahara Dust
3. V, Pb: heavy oil combustion
4. SO_4^{2-}, $C_2O_4^{2-}$, NH_4^+, : regional transport
5. Na^+, Cl^-: marine aerosol
6. Cu, Ni, Zn : traffic/dust resuspension

These factors underline the key role of atmospheric dynamics and aerosol ageing processes in this Mediterranean environment.

	F 1	F2	F 3	F 4	F5	F6
OC	0.879	0.105	-0.065	0.188	-0.158	0.107
EC	0.891	0.070	-0.040	0.218	-0.107	0.059
Na^+	-0.003	0.207	-0.100	0.056	0.730	0.006
NH_4^+	0.438	-0.181	0.113	0.614	0.053	0.301
K^+	0.739	-0.143	0.066	-0.129	0.315	0.017
Ca^{+2}	0.097	0.774	-0.105	0.060	0.073	-0.016
Cl^-	0.017	0.199	0.060	0.052	0.783	0.138
NO_3^-	0.662	0.030	0.068	0.466	0.092	0.167
SO_4^{-2}	0.275	0.012	0.011	0.783	0.101	0.117
$C_2O_4^{-2}$	0.005	0.088	-0.002	0.756	-0.005	0.001
Al	-0.068	0.892	0.086	0.026	0.162	0.020
Cu	0.185	-0.073	-0.150	0.011	0.181	0.726
V	-0.081	0.133	0.798	-0.039	-0.218	0.122
Zn	0.038	0.054	-0.365	0.356	0.369	0.485
Mn	-0.007	0.879	0.160	-0.041	0.215	-0.079
Ni	0.046	-0.004	0.102	0.149	-0.066	0.822
Pb	0.092	-0.020	0.727	0.109	0.160	-0.184
Expl.Var	2.886	2.354	1.416	2.053	1.627	1.660
Prp.Totl	0.170	0.138	0.083	0.121	0.096	0.098
Source	Heating	Crustal	Oil Combustion	Transport	Sea	Traffic

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