Response to reviewers' #1 comments

We would like to thank the reviewer for this constructive review. Please find below our response (in bold) to all comments raised and corrections suggested (included here as well).

Anonymous Referee #1

General Comments

This paper describes daily average concentrations of PM2.5 atmospheric aerosol at a suburban measuring station, in the Athens metropolitan area. For comparison and interpretation the authors also use parallel aerosol measurements of a background measuring station (Finokalia). Although the analytical measurements performed in the aerosol (mainly PM2.5 mass, organic carbon (OC), elementary carbon (EC,) water soluble organic carbon (WSOC) and water soluble ions) are not innovative the fact that these measurements were taken almost continuously during 5 years (from May 2008 to April 2013) provides multi-annual trending information that is important to the understanding of atmospheric processes involving particulate carbon. Therefore the data and paper merits to be published. I agree with most of the discussion and conclusions of the manuscript, but I have doubts about the interpretations and conclusions relating with biomass burning originated particulate carbon. The authors interpret the composition and seasonal/annual variability in aerosol/carbon concentrations as an effect of several processes namely the local impact of biomass burning for home heating during winter which they say has been of increasing importance during more recent years as result of the economic crisis that obliged the population to change to biomass fuels. As it is known biomass produces large amounts of carbonaceous particles (principally OC) when burned in less well controlled stoves and heaters. The reasoning of the authors is logical but in my opinion it is not demonstrated, being the winter /summer variability observed also alternatively explained by meteorological specific conditions such as winter more frequent atmospheric inversions and poor dispersion. The utilization of water soluble potassium tracer in Figure 5 did not confirm the predominance of biomass burning during winter periods (may be because there is interference of soil originated potassium, principally during summer). Therefore the subject should be discussed more thoroughly along the manuscript, not treating it as a clear evidence. The presentation of statistics of wood consumption for home heat burning in the Athens area, showing an increase during more recent years, would be a helpful contribution to the demonstration of the biomass burning effect.

We would like to thank the reviewer for his/her comments. We tried to take into consideration his/her remarks but unfortunately there is very limited work on the role of biomass burning on air quality in Greek cities and complete absence of inventories on wood consumption. The only available work comes from Safari et al., 2013 who reported for winter of 2012, the first year of significantly increased

fuel price, a simultaneous increase in wood burning tracers followed by a decrease in fossil fuel tracers. Regarding the use of water soluble potassium, it is worth noting that during winter the interference with soil originated potassium is quite limited as also pointed out by the reviewer. In addition, a specific campaign which took place in winter 2013 revealed significant correlations between water soluble potassium and specific biomass burning tracers, such as levoglucosan and wood burning BC, indicating the accuracy of our conclusions based on the use of this tracer.

Specific comments

Page 17166,

lines 15 and 24- 0.45 μm instead of 0.45 mm

Unit "mm" was replaced by "μm".

Section 2.33 – describe better how TC and IC are analyzed to calculate WSOC.

The following text was added in line 17:

"….Carbon Analyzer. In short, the sample is injected into a combustion cell equipped with oxidation catalyst (Pt) and is heated at 680ºC. TC (Total Carbon) is converted to carbon dioxide, cooled and dehumidified and is transferred through the carrier gas (synthetic air) to the NDIR (Non-Dispersive Infra-Red) gas analyzer. For the IC (Inorganic Carbon) analysis, the sample is injected to the IC reaction vessel where it is acidified, to convert IC to carbon dioxide, and it is volatilized by a sparging process. Then the sample is transferred by the carrier gas to NDIR in order to be detected."

Page 17167

- lines 14 and others (averagestandard deviation (?))

Throughout the article, all average values are provided along with the corresponding standard deviation (AVG ± StdDev)

Page 17168

line 26- (due to emissions from residential heating) – discuss. It can't be said as if it is demonstrated.

From November to March fuel combustion for residential heating constitutes a characteristic source of atmospheric aerosol in Greece. Thus, higher OC and EC values during the coldest period of the year can be mainly attributed to residential

heating, in excess to meteorological factors (lower BL), since the rest of aerosol urban sources (e.g. vehicles) are present all year long.

We have smoothened the phrasing as follows:

"… higher concentrations from November to March. This is mainly attributed to emissions from residential heating and low altitude temperature inversions that trap…"

Page 17169

lines 11 and 12- the number trends for 2008 and 2012 (1.21 and 0.59) given in the text are different from those in Figure 3 (0.99 and 0.43). Should not be equal?

Yes, they should be equal. By mistake we used the median values in the text (1.21 & 0.59) instead of the average values (0.99 and 0.43), provided in Figure 3. This is now corrected.

Page 17170

lines 7-13- The discussion and conclusions here are not very clear and relevant. A R2 of 0.49 is low for taking firm conclusions.

This coefficient is based on 1365 daily samples and also it refers to the square correlation (the respective R is 0.7). The above indicate a statistically significant correlation between OC and EC as also demonstrated by the respective p-value. In all cases, we changed the sentence in line 13 as follows:

"The above suggest that a large fraction of OC and EC is emitted by common primary sources at a regional scale."

Page 17170

- In the text, discussion passes from figure 4 to figure 6. Figure 5 only later in the paper is discussed. Reorder the figures.

Figures were reordered, accordingly.

Page 17170

- section 3.3- there is a discussion here relating OC with WSOC. Being WSOC more than 60% of OC, of course that there is a good correlation between both. More clear information could be taken from the relation between WSOC and WIOC which are independent (?) variables.

OC was measured using a Sunset laboratory analyzer while WSOC was measured through a TOC analyzer, thus both measurements come from independent analytical techniques. As a consequence, the good correlation between the five-year daily values of these two concentrations reflects not only their expected covariance but also the success of the two techniques to capture their common variability. It has to be noted that WIOC is estimated by subtracting the calculated WSOC from OC, so it is not an independent variable.

Page 17171,

lines 20-25- The formation processes of nssSO4 are probably quite different from secondary OC; therefore the conclusion in this part of the text is not clear and relevant.

The sentence was rephrased accordingly:

"WSOC is weakly correlated to nss-SO4 (refs), suggesting that secondary organic products emitted from sources similar to those of sulfate, are not the dominant constituents of WSOC."

Page 17171,

lines 24-25- correlations between nssK+ and WSOC during winter only should probably be more clarifying than for the whole year.

The correlation between WSOC and nssK+ is low regardless the season (in summer R2=0.09 and in winter R2=0.03), indicating that all year round there is limited production of WSOC from biomass burning.

Page 17171,

lines 24-26- Why not use Ca2+ to remove K+ from soil origin, in order to obtain only K+ from biomass burning?

When excluding cases of high Ca2+ (mainly dust events) from the five year dataset, the correlation coefficient between nssK and WSOC or EC does not ameliorate.

Page 17172, **1773**

lines 16-18- To me this is not clear. EC is not very efficiently removed by rainfall; therefore the correlation between EC and nssK+ in winter can result also from higher regional emissions from biomass burning during this period of the year and advection / long range transport to the sampling site.

We suppose that this misunderstanding is due to the fact that in figure 5 the labels (winter & summer) were accidentally misplaced. The upper panel corresponds to

winter and the lower to summer. As a consequence, during winter there is a clear covariance between EC and nss-K, in contradiction to summer when the two variables do not seem to be correlated.

Page 1716, **1776**

lines 9-10- , : : :or more inefficient dispersion of local emissions in Athens during winter.

The suggested addition was made to the text:

"... the increase in OC and EC during the cold season, can be attributed to an additional primary source, most probably heating, or to more inefficient dispersion of local emissions in Athens during winter."

Page 1716, **1776**

lines 13-14- Add a reference demonstrating the maximization of wood burning activities during 2011-2013.

The following reference was added:

(Saffari et al., 2013)

Saffari, A., Daher, N., Samara, C., Voutsa, D., Kouras, A., Manoli, E., Karagkiozidou, O., Vlachokostas, C., Moussiopoulos, N., Shafer, M.M., Schauer, J.J., Sioutas, C., 2013. Increased Biomass Burning Due to the Economic Crisis in Greece and Its Adverse Impact on Wintertime Air Quality in Thessaloniki. Environmental Science & Technology 47, 13313-13320.