Response to reviewers' #2 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 #2

This MS presents an assessment of OC and EC concentrations in Athens (Greece) over a 5-year period, providing a comparison for a shorter period of time with a background station in Crete. The results from the assessment are interesting for the scientific community, even if the methodologies applied are not especially novel. However, the long and uninterrupted series of data is very valuable and makes up for this. I would recommend publication after a number of issues have been addressed. I am mostly concerned by the interpretation of wood burning as a source, as there seem to be some contradictions in the text (please see below).

-page 17163

*line 5: please add "road traffic" before "wintertime high energy consumption", as this is probably the more relevant source.

Done.

*line 6, please add "traffic but also" before "secondary organic aerosol"

Done.

*line 13: please clarify this sentence, what does "in excess of other significant sources" mean?

The sentence was rephrased as follows:

"Athens is located in Eastern Mediterranean, a well known crossroad of long range transported aerosols from discrete regional sources that are superimposed on other significant local sources of pollution ..."

* line 18: "prevailing emissions" from what kind of sources? Please specify.

As prevailing emissions we mean those coming from sources such as vehicles, fuel combustion and long-range transport of aerosol, as described in the list of references provided. The text was changed accordingly:

"Studies performed in Athens basin demonstrated the prevailing emissions of carbonaceous aerosol all year round, namely from vehicles, fuel combustion and long-range transport"

* line 23: the authors could stress that this is the major contribution of their work, the extremely long and uninterrupted series.

We thank the reviewer for his suggestion. We added the following sentence:

"The long measurement duration and the completeness of the data series allowed the performance of thorough and concise investigation of carbonaceous aerosol properties, sources and variability in the area, as a major contribution of this work."

* line 27: "stalked", should this maybe be "occurring"?

Done.

- page 17164

*line 6: please define ACTRIS

The following definition was added:

ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure Network, http://www.actris.net/)

* line 20: is a website available for the station? If so, please provide

The relative website address was added:

http://finokalia.chemistry.uoc.gr/

* line23: "during most of the period", how long is this? I understand 2 different samplers were used?

The following information was added:

"…(R&P Co) during most of the period (90 % of the sampling time) and Partisol FRM Model 2000 PM2.5 & PM10 air samplers (R&P Co) (10 % of the sampling time)…"

- page 17165

* lines 10-15: please describe briefly the limitations of this sampling approach: it has been pointed out that the back-to-back filter configuration does not allow enough time for equilibration of gases on the second filter, and that therefore this approach may underestimate the positive OC artefact.

The following sentence was added in the relevant paragraph:

"Nevertheless, it has been reported that the back-to-back filter configuration does not allow enough time for equilibration of gases on the second filter, and therefore this approach could underestimate the positive OC artefact."

- page 17166

* line 2: was it a laboratory or a fiels Sunset instrument?

It is a laboratory instrument as already mentioned in line 2.

* line 18: "IC", how was the IC concentration obtained? By decarbonisation with an acid of one sample, running another sample and calculating the difference? Please describe briefly.

Following a similar comment by the first reviewer we added the following description 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 17168

* line 10: please add reference to Querol et al. (2013): Variability of carbonaceous aerosols in remote, rural, urban and industrial environments in Spain: implications for air quality policy; Atmos. Chem. Phys., 13, 6185-6206, 2013 www.atmoschem-phys.net/13/6185/2013/ doi:10.5194/acp-13-6185-2013

The suggested reference was added.

* line 27: "local sources" should be "local emissions", given that it is the emissions and not the sources that are trapped.

Replaced

* line 27: "Particulate OC" should be "particulate "OC and EC", given that this process affects both OC and EC.

Done.

- page 17169

* line 11: "reproduced by OC": why does winter OC not decrease in 2012, as is the case for EC? If the economic recession is indeed the cause for this trend (which is likely), then the behaviour of OC and EC should be more similar during this period.

In winter 2011 lower temperature values were recorded, resulting in more frequent use of residential heating (namely biomass burning). On the other hand, during winter 2012 even if ambient temperature was higher (compared to 2011), biomass burning was more widely used as a choice for residential heating.

Winter 2012 OC does not seem to follow the decreasing trend of EC because the clear daily spikes during winter 2011 & 2012 (Fig. 1), that are attributed to biomass burning, seem to be partly smoothened during the calculation of inter-annual average values for the respective winters (Fig. 3). Furthermore this is the reason for the observed increase of the standard deviations during winter 2011 and 2012.

Since the aforementioned data seem to be confusing, it was attempted to strengthen the conclusions in this work with a combination of presented figures and calculated ratios, rephrasing the text as follows:

"The summer vs. winter contrast is further shown in Fig. 3, on an annual basis. Winter refers to December–February period of the December year, while summer to June–August. The EC summer levels after 2008 appear slightly reduced compared to 2008, coinciding to the economic recession period in Greece, which led to reduction of traffic emissions (Vrekoussis et al., 2013). In winter, there is an increase during the last two years (2011–2012), attributed to the massive turn of Athens residents in wood burning for main domestic heating. The average values of OC do not present a clear inter-annual trend, since the obvious increase of standard deviations during winter 2011 and 2012 seem to have masked the daily spikes that are clearly demonstrated in Figure 1 and are attributed to wood burning. The summer to winter ratio of EC mass concentration presents a significant…"

- page 17170

* line 9: "are proportional" should be "are mostly proportional"; an R2 of 0.49 is not especially high.

Done.

* line 12: "suggest that OC and EC" should be "suggest that a large fraction of OC and EC", not all of OC and EC because the correlation is not too high.

Done.

* line 23: Figure 6 is referenced here but Figure 5 was not discussed before

Figures were reordered accordingly.

- page 17171

* line 19: please describe briefly what the SCiare and Pio methodologies are based on

The following description was added:

"The concentration of non-sea salt sulfate (nss-SO2−4) has been estimated following the equation described in Sciare et al. (2005) and Pio et al. (2007):

[sea salt]=$[Na^+]+[Cl^-]+[Mg^{2+}]+[ss\text{-}K^+]+[ssCa^{2+}]+[ss\text{-}SO_4^{2-}]$

Sea salt sulfate ($ss\text{-}SO_4^{2-}$) was calculated in accordance with the composition of sea water and was then subtracted from the total sulfate concentration, in order to calculate the quantity of non-sea salt sulfate (nss- SO_4^{2-})."

* line 29: "improves during summer": this would suggest that during summer one significant origin of WSOC is long-range transport and aerosol ageing, given that nss-SO42- is a tracer of this kind of processes.

Even if it slightly improves in comparison to winter, it still remains low, thus we cannot talk about a significant origin of WSOC, just that long-range and ageing could be also considered as additional contributors.

- page 17172

* line 2: "in winter", because in winter a significant source of WSOC is biomass burning

Done.

* line 10: please add "water-soluble" before potassium

Done.

* line 21: "calculated" could be "obtained"

Done.

* line 22: "neither do they improve on a seasonal basis": this is unexpected: if biomass burning is a source of winter OC and EC, as described until now in the text, then nss-K+ should correlate at least partly with OC in winter. If this is not the case, how do the authors explain it?

By writing "neither do they improve on a seasonal basis" it was intended to highlight that there are low square correlation coefficients all year round. More specifically, the summer square correlation coefficient between nssK and EC is 0.02 while during winter it is 0.11. Additionally, the summer square correlation coefficient, between nssK and OC is 0.02 while during winter it is 0.04. A slight improve is observed during winter, but biomass burning seems not to be the main source of OC and EC.

On the other hand based on high resolution measurements performed in winter 2013 (Mihalopoulos et al, unpublished data) a clear correlation is observed between nss-K+, OM and EC during intense episodes of biomass burning. The absence of significant correlation between OC and nss-K using the entire data set indicates that the influence of biomass burning during intense wood burning episodes (clearly shown in Figure 1) is masked when calculating the five year summer and winter square correlation coefficients.

* line 24: "mainly fossil fuel combustion", I agree that traffic is the main source, but some correlation should be observed if biomass burning is a (although minor) source. Please explain.

Please see the comment above.

Additionally, the covariance between winter values of nssK and EC is clearly illustrated in Figure 5. (In figure 5 the titles "summer" and "winter" were accidentally reversed and will be reordered.)

- page 17173

* line 11: "influence of wood burning during the last years": here it is suggested that wood burning is a relevant source and therefore it contradicts the results on lines 21-27 on page 17172.

Please see the two previous comments.

* line 11: I think Figure 5 should be Figure 8?

Yes, figures were reordered accordingly.

- page 17175

* line 9: ratio =1: was the OC/ECmin also calculated graphically, to verify that the local OC/ECmin is similar to the literature value proposed? What values were obtained?

The graphical calculation of OC/ECmin from April to October, results in a value of 2.3, which is not reliable for comparative reasons, since the estimation of OC/ECmin through a linear regression requires only periods during which conditions are highly unfavorable for the formation of SOC, in order to lead to secure estimation of OC/ECmin value.

Therefore, in our applied equation (page 17174, lines 6-9) OC/ECpri ratio, derived from literature under traffic conditions (tunnel studies), was used.

* line 16: what was the % of SOC with respect to OC? It would be interesting to see whether the Athens values are similar in relative terms to other Southern European cities, and not only in absolute values.

In line 12 of the same page it is mentioned that SOC constitutes 75 ± 6 % of OC in Athens.

* line 17: figure 9: an additional Figure (or an additional variable in Fig 9) would be useful, showing the variability of the % of SOC in OC throughout the year. This would allow to verify that the relative contribution of POC to OC is higher in winter

Given all available data series, SOC was calculated only from April to October, since there were no reliable data to support the estimation of SOC during winter. During the coldest period of the year, the primary emission sources such as biomass burning, fossil fuel and vehicles (with characteristically different OC/ECpri ratio values) are expected to contribute to OC/EC ratio and thus, the approximation of primary OC/EC ratio (and the subsequent estimation of SOC) in the aerosol samples would be debatable.

- page 17176

* line 5: please review the order of figures

Figures were reordered accordingly.

- page 17177

* line 10: please add "mostly" or "largely" before "proportional"

Done.

* line 11: please add "mainly" before "emitted"

Done.

* line 21: it does, according to Figure 2, with winter maxima and an additional maximum in high summer.

The text was rephrased as follows:

"….On the contrary, EC concentration during winter presents a noticeable increase since 2011, which can be attributed to the selection of wood as the major fuel source for domestic heating. OC concentration does not present a clear inter-annual pattern, probably because the contribution from other sources and the episodic nature of biomass burning, as depicted from the increased calculated standard deviations, may have balanced out the aforementioned trend."