

Interactive comment on “Multiyear chemical composition of the fine aerosol fraction in Athens, Greece, with emphasis on winter-time residential heating” by Christina Theodosi et al.

Anonymous Referee #1

Received and published: 22 May 2018

The paper by Theodosi et al. reports about the large observational study monitoring particulate matter sources in central Athens emphasizing contribution of biomass burning, especially during winter and in particular during the night. The study presents no new knowledge, nor scientific advancement, although it provides very detail account of sources and is methodologically correct. The paper is often buried in details and often repetitive and better focus on the main idea is necessary. At the moment the paper looks more like a report than scientific paper. Better focus and summary at the end of sections is necessary and perhaps separating results from discussion. The paper ends abruptly with conclusions as an extensive summary. Quite an improvement (including the English) is needed before the paper can be accepted for publication.

We would like to thank the reviewer for his/her comments. We disagree that no new knowledge is provided. Similar works on long-term aerosol chemical characterization are very scarce in Europe. Especially in Greece, this is the first time that daily and 12-h filter samples have been analysed for ions, OC/EC and trace metals to provide a complete chemical characterisation in the largest urban centre for more than two years. Although not easy, as the reviewers have asked for additional details, we tried to decrease the length of the manuscript by removing several sentences and one figure to the supplementary material. Below we list our detailed response to his/her comments (in italics) and the corresponding changes in the manuscript.

Comments:

I guess the authors are overstretching when repeatedly refer to the Greater Athens Area, because a single station in the city centre can hardly described the entire Greater Athens area. Clearly more stations are necessary to monitor greater agglomerate area due to different population/build up density, anthropogenic activities and traffic. Therefore, a better reasoning is required to refer to GAA if possible at all. Very often the authors go into unnecessary simplification and repetition, e.g. regarding temperature inversions and limited mixing. Every specialist is aware of the phenomenon and mentioning it once in detail is enough.

It is clear that several stations are required to obtain a complete picture for a large agglomeration such as GAA but on the other hand it is understandable that it would be very difficult to perform such a chemical analysis in-depth for several stations. As a reminder, in the present work more than 800 filters have been collected and analysed for main ions, OC/EC and metals with emphasis (twice daily) on the winter period. As shown in Gratsea et al. (2017), by comparing Thissio data with several (5) stations of the National Air Pollution Monitoring Network, our station captures quite well the temporal variability of primary pollutants like CO within the GAA. In addition Thissio station is not directly impacted by sources and its position on a hill at the center of Athens allows it to be considered representative of the background in the wider area. For that reason we consider the station as representative as possible for the GAA, at least for its central part. It is also worth noticing that during the sampling period, this was the sole urban background station monitoring PM concentrations in the densely-populated central Athens (gathering 1.03 million people, almost

a third of the GAA population), and its results can be considered relevant for the exposure of a large part of GAA inhabitants.

“The high correlation between the five NAPMN sites and Thissio, as well as the relative difference in absolute levels, support the characterisation of Thissio as an urban background site, non-intensively affected by local traffic; From Gratsea et al., 2017).

However as suggested by the reviewer the term GAA is now not mentioned in the manuscript. Also atmospheric conditions are now mentioned only once in the manuscript.

Minor comments:

Page 2, line 6. through emission reduction measures.

Line 9. : : :toxic and carcinogenic components.

Line 12. Trace metals are also related to chronic and acute...

Line 18. : : :such as traffic and industrial activities.

Line 19. since the winter 2011-2012.

Line 21. the great impact.

Line 25. Linking them to the presence

Line 33. : : :has been undertaken in Southern Europe, offering challenging conditions (what is challenging there by the way?)

Page 3, line 2. the current work was focused on winter period.

Line 4. The aerosol sources during the night are not new. Rephrase to "... highlight the impact of night time PM sources".

Line 10. It is still representative of central Athens, especially during high pollution events during stagnant meteorological conditions. A single site cannot represent the whole GAA as suburban areas were not monitored. It is methodologically wrong to assume that a single site can serve as a reliable average of the entire GAA.

Line 13. why this word of caution when the next sentence explains everything?

Line 17. On a yearly basis, air masses of Northern origin from central and eastern Europe account for almost two thirds of the time.

Line 20. Ventilation is a poor term. You should be stating about stagnant conditions during which most severe pollution events have been occurred persisted for X % of time.

Line 28. Unclear. Were the 447 samples in addition to 848 samples or a fraction of them?

Line 30. Controlled RH=%?? conditions. Please specify.

Page 4, line 17. : : :in detail by Theodosi: : :

Line 26. Not contrast, but patterns, as no one can know in advance if they will contrast.

Line 27. trivial repetitive sentence.

Page 5, line 9. unclear - combined OR night-day?

Line 27. Was it really lower limit at 0.3ug/m³ which is inconceivably low for urban PM_{2.5} concentration. Was it realistic and how did it compare to chemical mass?

Page 6, line 8. zero OC or EC cannot be observed anywhere on Earth (even in Antarctica there is observable BC of 1ng/m³). Refer to below DL of Xug/m³.

Line 10. To be mathematically correct one should only present the arithmetic average if data are normally distributed in which case arithmetic average and median are closely similar number. We don't see that therefore data are lognormally distributed in which case the range and the median should be presented only. It has to be consistently presented either median alone or ALWAYS with the median, rather than selectively presenting median.

All the aforementioned suggestions have been performed.

Line 26. Excellent agreement should not be necessarily expected, "results were in close agreement". Close agreement suggests long-range transport as the main source.

Page 7, line 17. remained within the same order of magnitude between studies with only slight differences in between. Chemical mass closure. Given that all major and minor particulate matter species were measured, the chemical mass closure has been attempted. However, given the large uncertainty in OM/OC ratio and no data for the current study, how useful the chemical closure exercise was?

An OM/OC ratio equal to 1.8 determined from Aerosol Chemical Speciation Monitor (ACSM) measurements at the same location, within the study period (Stavroulas et al., 2018) was used to perform a more accurate mass closure.

Page 8, lin 19. Could further limit dispersion of pollutants.

Line 31. 289 days with smog conditions ...

Page 9, line 29. No statistically significant seasonality can be seen in SO₄ time series considering error bars. Note the lowest concentrations in November-December 2014. Rewrite as the text is not reflecting the Figure.

The text was rewritten as "SO₄²⁻ concentration in the PM_{2.5} fraction presented no statistical significant seasonality with the lowest values in winter"

Page 10, line 4. What is the anthropogenic source of SO₄ during summer if long-range transport is blamed? Is it not biogenic (Mediterranean DMS) instead?

Page 11, line 3. : : :suggesting insignificant influence from wood burning. Is it impossible that fraction of Na increase is due to higher primary in winter?

Yes it could be possible but as both Cl and Mg are decreasing during night and Na is not, this could be an indication of a small contribution from heating and especially biomass burning, as previously reported by Fourtziou et al. (2017).

Page 12. 3.4.4a Crustal elements

Line 26. Present in tailpipe emissions, not included.

Page 14. Lines 31-34. Reword – confusion with mean annual contributions and “such large wintertime contributions” – Corrected.

Page 15, line 13. What is the reason for heavy duty vehicles in central Athens?

Karageorgos and Rapsomanikis (2010) have also mentioned the presence of heavy vehicles in central Athens, as a factor for particle emissions. The main reason is bus circulation, most probably of tourist buses, whose traffic is relatively dense in the area of the site, where various attractions are located.

Line 23. westerly advectons, not flows - Corrected.

Line 28. there is no information whether particles were internally or externally mixed. And even if known there is no sulphate particle in existence - Corrected.

We would like to thank the reviewer for his/her time and all below mentioned technical and minor corrections have been considered.