Response to the comments of Referee # 1

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General comment

This manuscript presents a database focused on polycyclic aromatic hydrocarbons (PAHs) from a year-long sampling campaign in Athens, Greece. This dataset, together with other chemical markers, was combined with receptor modeling to obtain some insights into sources and contributions to the health risks. Although there are hundreds (or even thousands) of papers published on PAHs, this combined strategy is new and has made it possible to estimate the astonishing contribution of residential biomass burning to the measured levels and estimated risks. Therefore, this study can serve as a basis for forcing policy makers to implement measures. Due to its interest for the scientific community and for stakeholders, this article deserves to be published in ACP, after review.

We thank the referee for the assessment of our work and the constructive comments. We have revised our manuscript according to the suggestions. Please find below our responses to every point raised (in italics).

Specific comments:

The writing of a scientific article must be impersonal. Example: "It was found that biomass burning" instead of "We find that biomass burning". Check the entire manuscript.

This point is well taken, but it is a matter of style. That said, we will follow the suggestion and modify the manuscript accordingly.

There are many typos throughout the manuscript. A careful review is required.

We apologize for these oversights, the manuscript has been now carefully reviewed.

Abstract. "responsible for annual mean PAH concentrations (31%) comparable to those from diesel/oil (33%) and gasoline (29%) sources." The sentence speaks of concentrations, but in parentheses percentages are mentioned that, I suppose, represent contributions from sources. Rephrase the sentence to make it clearer.

Thank you for noticing this inconsistency. It is now corrected.

Section 2.2. How was the sampling schedule? Every 3 days? One day each week?

During the non-winter months, we analyzed two samples each week, on alternating days between weeks. We also tried to achieve a fairly representative distribution between weekday and weekend samples (69% - 31%), since it is known that this is an important temporal scale that induces variability in urban PAH levels (Dutton et al., 2010; Lough et al., 2006). The same approach was followed for the winter period, trying at the same time to analyze as many daytime-nighttime pairs as possible, to allow for the characterization of the diurnal patterns. Our intention was to fulfill and go beyond the minimum requirement of the 2004/107/EC directive for indicative measurement of PAHs (14% annual coverage, roughly 1 measurement per week, equally distributed around the year) to be able to compare with the BaP target value. These clarifications are now provided in the revised manuscript.

Four-day air mass back trajectories, arriving at Thissio at 1000 m, were calculated. Why 1000 m?

An altitude of 1000m was chosen to capture the regional transport of pollutants that has a high probability of affecting pollutants in the boundary layer (hence air quality and population exposure to PAHs). This altitude

is supported by numerous studies for the region studied (Grivas et al., 2018; Kalkavouras et al., 2020; Stavroulas et al., 2019). In addition according to estimates using lidar data, the planetary boundary layer over Athens extends, on average, from 892 ± 130 m at 00:00 UTC to 1617 ± 324 m at 12:00UTC (Kokkalis et al., 2020) which also supports our choice of 1000m. This discussion is included in the text.

At what altitude is the sampling site located?

The sampling site is located at an altitude of 146m above sea level and the inlet was at a height of 2 m above the ground. These details are now specified in the revised manuscript.

Section 3.1. Apply statistical tests to compare means between seasons and to assess if there are significant differences and to define confidence levels.

We applied t-tests to search for statistically significant seasonal differences (winter/ non-winter; we follow this scheme since transitional seasons in Athens are of short duration). Mean concentrations were higher during the winter period for the vast majority of PAH members, which is consistent with the strongly enhanced emissions from wintertime sources (i.e. biomass burning) and the increased volatilization and photochemical degradation of PAHs during summer. The results of the statistical analysis are now summarized in a new supplementary Table and discussed in the revised text.

How do you explain the difference in concentrations between Dec2017/Jan2018 and Dec2016/Jan2017?

The difference in PAHs levels between Dec2017/Jan2018 and Dec2016/Jan2017 could be explained by changes in meteorology and emission sources. For instance, BB-related primary pollutants recorded increased concentrations during the second winter, as indicated by black carbon (factor of 2.6 higher). The increased biomass burning contributions to PAH concentrations during the second winter was also verified by the results of the PMF analysis that showed higher BB contributions to Σ-PAHs by a factor of 3.8, during the second winter. Furthermore, a larger number of IPEs were observed during the second period (24 vs. 17). A modeling study (CAMx or WRF) could help identify the relative contribution of sources vs meteorology to the differences between the two winters, but this approach is out of the scope of this article.

Partitioning of PAHs between gas and particle phases was not discussed. Concentrations of many PAHs, especially LMW species, are in reality much higher than those measured in the present study, which only include the condensed form.

Excellent point. Previous works conducted in Athens (Mandalakis et al., 2002; Sitaras and Siskos, 2001, 2008; Vasilakos et al., 2007), that performed both gas- and particle-phase measurements, reported that LMW PAHs were found predominantly in the gas phase (gas-phase fractions: 88-97%), MMW PAHs in both gas and particulate phase (gas phase: 46-90%) and HMW PAHs mainly in the particle phase (particle phase: 71-100%).

By applying the methodology developed by Pankow (1994) we found that the largest fractions of LMW PAHs are partitioned in the gas phase (71% - 100%). Most MMW and all HMW PAHs are partitioned preferentially in the particle phase, at rates ranging between 90%-100%, with the exception of the lighter Flt and Pyr. The results support the decision not to include the LMW PAH members in the source apportionment analysis, since their temperature-dependent partitioning could induce large uncertainties in the source-receptor relationships. It also appears that it was indeed useful to downweight the involvement of Flt and Pyr (15%, 25% in the particle phase) in the PMF model. Moreover, it becomes obvious that caution is needed in the interpretation of results for LMW members in PAH studies that measure only the particle phase, especially using diagnostic ratios, since their temperature-dependent concentrations aren't sufficiently representative of the relationships between PAH members as emitted from sources.

The methodology and outcomes are presented as supplementary material and the main outcomes are discussed in the revised text.

It should also be borne in mind that PAHs suffer photochemical reactions leading to the formation of nitro- and oxy-derivatives.

We would like to thank the reviewer for this suggestion. Note that we are currently working on the analysis of nitro and oxy-derivatives of parent PAHs at the same site, and we will soon be able to verify and provide also a quantitative assessment of secondary photochemical processes (this is now indicated in the conclusions sections as a proposed research direction).

Authors should look for correlations with ozone and NOx concentrations provided by the air quality measurement network to better interpret the results obtained.

This is a good point. In-situ measurements of O_3, NO_x and CO were available at the measurement site, using reference-grade instruments. We also obtained NO_x from a nearby, traffic-impacted, official station (Athinas Str.) of the AQ monitoring network, to see whether there are traffic-background contrasts in the correlations. We performed the correlation analysis separately for winter and non-winter months. The results are presented in a new supplementary table and discussed in the text.

End of page 12. Non-local contributions were associated with trajectories from the Black Sea area, where "extensive summer agricultural burning has been identified". Legislation within the EU has largely outlawed the practice of field burning agricultural wastes, especially in summer. Authors must make sure that it is agricultural burning or wildfires. For this purpose, fire maps and emission inventories by EMEP/EEA (which include emissions from agricultural burning) should be consulted.

We would like to thank the reviewer for his/her comment. Although the (EU) 1306/2013 regulation has forbidden the practice of field burning of agricultural wastes, large scale agricultural biomass burning is still being observed in countries of the Black Sea region, that are not directly bound by EU legislation like Ukraine, Russia (southwestern oblasts) and countries in the Caucasus area (Hall et al., 2021; McCarty et al., 2017). This phenomenon is specifically intensified the period from July to September (Sciare et al., 2008). We have examined GWIS (Global Wildfire Information System) emission inventories and also satellite fire maps (TERRA and AQUA MODIS, VIIRS-NOOA), that verify the identified source area as a major hotspot of fire-related emissions. We provide indicative supplementary figures and data in the Supplement. Discerning between wildfires and agricultural burning can be difficult. However, we examined land use/cover maps in the region, superimposed over the fire maps and it appears that the majority of identified fires occurred in the extensive croplands of Ukraine and Southern Russia. Indicative figures are also included in the Supplement.

Conclusions. I'm not sure about the promotion of electromobility. While exhaust emissions would decrease, non-exhaust emissions would, on the contrary, increase. Heavier battery electric vehicles may result in more tyre/brake wear and resuspension emissions than the current vehicle fleet. Several recent studies have shown that non-exhaust emissions are at least as toxic as those from exhaust emissions. One thing is for sure ... The use of public transport instead of individual transport should be promoted.

Thank you for bringing up this point. EU seems bound to the direction of electromobility, having recently proposed a ban on fossil-fuel powered cars from 2035, a decision that will lead to large cutbacks of vehicular exhaust emissions. However, in the next decades, the majority of PM from the road transport sector is expected to derive from non-exhaust emissions, even without the enforcement of electromobility (Daellenbach et al., 2020). This complex tradeoff between exhaust and non-exhaust emissions is now described in the conclusions, along with the necessity to adopt measures and practices for the reduction of non-exhaust vehicular emissions as that suggested by the reviewer. We also note, that the use of heavier private vehicles could leaded to increased traffic-induced resuspension of particles containing PAHs (Alves et al., 2018; Oliveira et al., 2011).

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