Reply to Alexandre Albinet comments
Author’s response in Blue

Reference added

Reference added

Line 53-54:
Two references added (Nalin et al., 2016; Rogge et al., 1993)

Reference added

Line 62:
Please explain which limitations. Sampling artifacts, etc...
Have a look there and references included:
References added and text corrected. More details added to “error evaluation” please see below author’s comments on Line 156.

Author’s changes in manuscript (L.62).
"However, a long sampling and averaging period creates some limitations such as sampling artefacts, notably where changing atmospheric photolysis conditions (air humidity, temperature, wind direction, ozone or other oxidant concentrations) may have a significant influence on PAHs concentrations and oxidation rates (Albinet et al., 2007b; Albinet et al., 2009, Goriaux et al., 2006, Tsapakis and Stephanou., 2003; Tsapakis and Stephanou., 2007, Ringuet et al., 2012b)."


Reference added

**Line 67-69:** and other ones such as:

Three references added (Albinet et al., 2008; Reisen and Arey., 2004; Srivastava et al., 2018.) text modified.

Author’s changes in manuscript (L.67).
A few studies have used twice daily (12 h) sampling (Albinet et al., 2008; Zhang et al., 2018; Farren et al., 2015; Ringuet et al., 2012b), obtaining limited information on variability in concentrations during the daytime and night-time (Tsapakis and Stephanou., 2007). Shorter time periods for sampling (3 h and 4 h) are still very limited (Reisen and Arey., 2004; Srivastava et al., 2018).

**Line 99:** clean I guess
and that's not only the purpose, see:

Author’s changes in manuscript (L.99).
All samples and blanks were purified on a SPE silica normal phase cartridge (1g/6ml; SIGMA ALDRICH) to reduce the impacts of interfering compounds in the matrix and to help maintain a clean GC injection inlet liner.

**Line 126:** You can say that it’s a modified version of previous published methods:

References added and text corrected
Author’s changes in manuscript (L.126).

The method development for OPAHs and NPAHs was based on previous studies (Albinet et al., 2006; Albinet et al., 2014; Bezabeh et al., 2003; Kawanaka et al., 2007) and conducted using Negative Chemical Ionisation

**Line 126:** 155 eV, really?
Yes 155 ev (autotune settings), According to Agilent manual the maximum can be used in NCI is 240 ev.

**Line 156-157:**
Clearly I doubt about it. If you really want to consider all the possible errors, you should applied a GUM approach. [https://sisu.ut.ee/measurement/9-iso-gum-modeling-approach-bottom-approach](https://sisu.ut.ee/measurement/9-iso-gum-modeling-approach-bottom-approach)
In addition, to estimate the uncertainties, one of the main factor is linked to the extraction efficiency and you don't mention anything about that. Standard reference materials are useful for that (for both PAHs and PAH derivatives). There are many paper about that:
The estimated error (L.157) is due to available information on laboratory test performance. The word ‘‘uncertainty’’ (L.157) was replaced by ‘‘error’’.

Based on our type of data we chose the ‘‘top-down’’ approach where the bias determination can be based on recovery efficiency. Using the step-by-step approach (bottom up) will increase the uncertainty on individual compound and mostly used for ISO accreditation. It is shown in the text that the average recovery efficiencies have ranged from 85% to 96% (L.102). The %RSD average for deuterium labelled compounds was about 3.6% (L.149). In this study we spiked 10 filters covering the different sampling time (3h, 9h, 15h). We agree that SRM are widely used for a better assessment of the analytical method and their use is probably required for publishing in analytical technique Journals. SRM do not provide certified values for most of the derivatives compounds we have used.

Therefore, the overall estimated error, combining the precision and the systematic effects, is less than 20%.

Another source of error can be attributed to sampling artefacts and this has been discussed in previous studies (Schauer, C. et al., 2003, Goriaux, M. et al., 2006, Tsapakis and Stephanou, 2003). The absence of an ozone denuder to trap the gas phase oxidants may lead to an underestimation of the true values of PAHs due to chemical decomposition. Therefore, data from long sampling times and under high ozone ambient concentrations may be biased by sampling artefacts by more than 100 % (Schauer et al., 2003, Goriaux et al., 2006). However, at low ozone levels, negative artefacts were considered not significant (Tsapakis and Stephanou 2003), whilst, at medium ozone levels (30-50 ppb), PAHs values were underestimated by 30 % (Schauer et al., 2003). In addition, heterogeneous reactions during particles sampling may occur on the monolayer surface coverage only with limited diffusion of oxidants to the bulk particles (Keyte et al., 2013 and references therein). Previous studies reported that the formation of NPAHs during high-volume sampling is not significant and calculated to be < 3 % (Arey et al., 1988) and < 0.1 % (Dimashki et al., 2000). Considering the predominant role of ozone levels (below 30 ppb in this study, mean: 8.4 ppb), sampling time and temperature on the magnitude of PAHs concentrations, the estimation of the negative sampling artefacts on our data range between 10 and 20 %, with the highest error estimation attributable to longer sampling time (15h).

**Line 159:** lab or field blanks? How many blanks?
**Line 160:** if they are detected they are not <LOD
**Line 161:** how much?

Text corrected

Author’s changes in manuscript (L.159,160,161).

To determine any sources of contamination during sample preparation and the analytical procedure, the solvent (acetonitrile) and field blanks (n=2) were analysed following the same procedure as for the samples (Extraction, SPE, Evaporation). Most target compounds were found to be below LOD (S/N=3) or orders of magnitude (up to $10^3$-$10^4$) lower than was found in the samples. A small number of compounds found in field blanks (1,8-Napthalic anhydride, Benzo[a]fluorone, 1-Nitronaphthalene, 9-Nitroanthracene) have a higher contribution (4-30 %) to very few filters (2 to 5 samples) collected.
over a 3 h time period, if this was co-incident with low particulate loading conditions. The contribution to each compound from field blanks has been corrected in the final data.

**Line 218:** All this part should be moderated or removed. There are clearly evidences that the validity of this kind of ratios is limited

Limitations for source apportionment using Diagnostic Ratios (DR) increase when the receptor site is far from evident emission sources, e.g. long-time sampling (24h) or by using volatile and reactive compounds such as the ratio ANT/(ANT+PHE) which indicate petrogenic sources. This ratio has not been used in this study and the sampling time scale was short (3h during daytime) which reduce limitations. In addition, the site location (Fig S1) was at urban area and surrounded by busy traffic road, residential buildings, underground, restaurants and thermal power stations.

A recent study (Feng et al., 2019) has used PMF models and DR and showed consistent results from both methods.

Accordingly, we consider the obtained results from diagnostic ratios are representative and may be important for future studies and method comparison.

**Reference:**

**Line 246** please cite actual references which showed that, e.g.

Two references added (Keyte et al., 2016, Magzamen et al., 2015)


Reference added
OK but ANT is mainly in the gas phase and you have data only about the PM phase. As it was shown in the text (L. 299-300) the dominant formation pathway of NPAHs is secondary formation in the gas phase. Heterogeneous reactions may play a role and contribute to the formation of NPAHs. 9-nitroanthracene was reported to be one of the major products for the heterogeneous reaction of adsorbed anthracene on different types of particles (NaCl, SiO₂, MgO) in presence of NO₂ (Jinzu et al., 2011; Wenyuan and Tong., 2014).

Zhang et al. (2013) have reported that ANT in the gas phase can be adsorbed on particles and they showed a high production of 9-NANT during the heterogeneous reaction of adsorbed ANT in presence of O₃-NO, suggesting that NO₃ radicals were formed and reacted with anthracene. In our study the positive strong correlation between ANT and 9-NANT in particle phase does not prove but it supports the heterogeneous formation pathway of 9-NANT. On the other hand, previous studies reported that the formation of NPAHs during high-volume sampling is not significant and calculated to be < 3% (Arey et al., 1988) and < 0.1 % (Dimashki et al., 2000). The mechanisms and levels of formation are still far from being fully understood, especially that the reaction of PAHs with oxidants is highly influenced by surface coverage and PAHs loading (Keyte, I.J., 2013 and references therein) i.e. particles were shown to exhibit a potential inhibiting factor on the reactivity of PAHs due to slow diffusion of oxidants and inaccessibility of PAHs in the bulk particle.

The gas phase reaction of ANT with NO₃ radicals and the formation of 9-NANT either in the gas phase or adsorbed on particles still unclear. Future studies might help us to better understand the chemical transformation of anthracene in the atmosphere, this suggest that probably both pathways contribute to the formation of 9-NANT on particles. Accordingly, this explain why 9-NANT is the most abundant NPAH in this study and in parallel makes ANT one the lowest concentrations in particle phase.

References:

For all this part you should cite the previous articles where this approach has been described and used:
Two references added (Albinet et al., 2008; Tomaz et al., 2016), Bandowe et al. 2014 already cited.
That are not the references showing that References moved beside "commonly used"

For PAHs, Benzo[a]pyrene was chosen as the reference chemical because it is known as the most carcinogenic PAH (OEHHA., 1994, 2002) and is commonly used (Albinet et al., 2008; Tomaz et al., 2016; Alves et al., 2017; Bandowe et al., 2014; Ramírez et al., 2011) as an indicator of carcinogenicity of total PAHs.

Please specify in a Table which TEF values have been used and the references.

The toxicity Equivalency Factor (TEFs) and references used for individual PAHs, OPAHs and Nitro-PAHs are shown in supporting information on Table S3.


Tomaz et al., 2016 cited. Text modified.

Our results were considerably higher than those estimated for western European cities during the winter, such as Grenoble: 1.4 ng m⁻³ (Tomaz et al., 2016), Oporto: 3.56 ng m⁻³, Florence: 1.39 ng m⁻³ and Athens: 0.43 ng m⁻³ (Alves et al., 2017). ECR values estimated for each city were 31 (Grenoble), 6.6 (Oporto), 17 (Florence) and 54 (Athens) times lower than our ECR estimation.

Figure 2 Really difficult to read
Slightly modified and re-arranged. Please see below
% of TP AHS, ∑OP AHS and ∑NPAHs in 3h, 9h and 15h samples

Night-time (15h)

Day-time (3h & 9h)