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Atmospheric
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Discussions

Interactive comment on "Particle size distribution of nitrated and oxygenated polycyclic aromatic hydrocarbons (NPAHs and OPAHs) on traffic and suburban sites of a European megacity: Paris (France)" *by* J. Ringuet et al.

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First of all, we would like to thank the referee for his constructive review. All the comments have been taken into consideration.

GENERAL COMMENTS: Reviewer 3 is right; it is really difficult to provide results of quality for compounds in such low concentrations in ambient air. Therefore, quality assurance and control procedures have been carefully applied all along this work. For example, field and analytical blanks have been systematically made at each step of the analytical process, we evaluated the global uncertainties link to our measurements (never reported before in any paper), we tried to make and to propose a direct comparison of the particulate atmospheric concentrations determined between two types of particulate samplers put in parallel (never reported in previous similar studies on particle size distribution of OPAHs and NPAHs) and, the results presented herein are the compilation of at least 7 consecutive sampling days.

SPECIFIC COMMENTS

Paragraph 2.3: The reviewer is totally right about the use of only one compound as surrogate standard (1-nitropyrene-d9). In an ideal analytical procedure, it should be used a deuterated compound corresponding to each targeted compound. However, this kind of analytical protocol is not applicable because, it's too expensive, and because, labelled or deuterated compound are not always commercially available When we initiated this study, only one deuterated OPAH was commercially available (9,10-anthraquinone-d8). It was chosen to use it as internal standard (GC/MS-NICI quantification). Only recently (since few months), 9-fluorenone-d8 is commercially available and it is now added in our analytical procedure as surrogate standard for OPAHs as 1-nitropyrene-d9 for NPAHS.

Paragraph 2.4 - Page 4 line 24: The very low recovery rate of 5 % was only obtained for the more volatiles compounds such as 1- and 2-nitronaphthalene and 1-nitronaphthaldehyde. Results for these compounds were no discussed here due to their poor recovery rates and to their poor association to the particulate phase.

We agree that potential degradation of OPAHs could occur during the extraction procedure using PLE. In our case, we tested and proved the reproducibility of the method using urban dust SRM 1649a (Albinet et al., 2006) and SRM 1649b (in order to estimate the global uncertainties of measurement). The analytical procedures, including extraction, were the same for all the samples analysed here. We expect that, the potential degradation of individual OPAH was the same for all the samples and was reproducible, as demonstrated by the analysis of SRM 1649 a and b.

Page 4 line 25: As said above, the repeatability of the entire analytical procedure (reproducibility) was evaluated using a certified reference material, NIST SRM 1649a and b. The sentence will be modified as follow: “Recovery rates were in the range 5 % - 84 %, the repeatability of the entire analytical procedure was about 15 % in average, evaluated using the NIST SRM 1649a and b (urban dust)” (Albinet et al., 2006).

Page 4 line 28: During both field campaigns, a filter blank was done every two days. The sentence will be modified in the text: “every other day” will be substituted by “every two days”.

Page 4 line 29-30: Overall, the blank levels obtained during both field campaigns were in the range < LOD to below 10 % of the average individual OPAH and NPAH concentrations. This will be specified in the final version of the article.

Paragraph 3.1 - Page 5 line 8-9: It is right that the concentrations obtained with both sampling devices are not in total agreement, for all the compounds. Nevertheless, to our knowledge (and we want really to insist on that), this kind of comparison was never reported in previous similar studies on particle size distribution of OPAHs and NPAHs. OK, the results are not perfect but the easy solution would have been to cover up it and to only show the results about the MOUDI measurements. Here, we propose a comparison and we try to find some explanations in the disparities observed. It is not perfect but it has the merit to exist. If anybody has additional explanations about the differences observed (except problems linked to limits of quantification and analytical drift) we are totally opened to listen it. Moreover, we just want to specify that in the case of PAHs, differences of 20 % are commonly obtained using two same samplers put in parallel (e.g. Digitel, DA-80).

Uncertainty values reported in the Table 1 are high but, the major part of the OPAH and NPAH concentrations are in the pg m-3 range. Furthermore, the calculation takes into account the whole protocol (sampling + analytical process). A detailed analysis of the calculation highlights that, the main important parameter in the global uncertainty budget is the extraction efficiency (about 50 %). The high values obtained do not mean that the extraction of the target compounds was not done properly (recovery level of surrogate standard 1-NP-d9 was always > 90%). In fact, this is mainly due to the differences with the concentrations reported in the certified reference material (SRM 1649b). The available concentration values for NPAHs and OPAHs are not certified but are only indicatives. By neglecting this parameter, uncertainties fall in the range 22 to 140 %. As an example, the uncertainty for 1-NP is 83 % and by neglecting the extraction efficiency parameter the uncertainty is about 56 %. By comparison, the total uncertainty for the measurement of benzo[a]pyrene (B[a]P) on PM10 in ambient air is about 40 % (Macé et al., 2010) (< 50 % in agreement with European standardized method NF EN 15549). Just remember that NPAH concentrations are about 2 to 3 orders of magnitude lower than PAH concentrations in ambient air. These details will be specified in the final version of the article.

Page 5 line 16-17: As specified above, we are not able to explain all the differences observed between both samplers. In the case of 1-nitronaphthalene, 2-nitronaphthalene and 1-napthaldehyde the concentrations are very close with both devices due probably to their low abundance in particulate phase. The concentrations showed have to be considered with caution and are not discussed in the article but just showed as supplementary information.

Page 5 line 18-24: The sentence will be modified in the final version of the article. Âń Second, the difference of technology between both samplers could play a role in the disparities observed. The contact between collected particles and ambient air is probably greater in the case of the DA-80 (filtration) and the backup filter of the MOUDI sampler than for the impactor stages. In the case of the MOUDI the airflow just runs over the sampling media (aluminium foils), while for the DA-80, the airflow pass through the filter inducing that sampled particles are more exposed to atmospheric oxidants. The formation of secondary compounds is then potentially higher using filtration sampling systems”.

The higher quantities of 2-nitropyrene, 1,4-anthraquinone and benzo[a]fluorenone obtained with the MOUDI are in disagreement with the explanation proposed here. However, NPAHs and OPAHs could be formed in the presence of atmospheric oxidants but could also be degraded. For example, the formation of 1,4-anthraquinone has never been reported in the presence of atmospheric oxidant. On the contrary its degradation was recently reported (Ringuet et al., 2012).

Page 5 line 27-29: Sampling campaigns were not realized during the same period (month and year) but, observed weather and temperatures were nearly the same and we expect that the comparison of the observations made is relevant. The comparison concerns two sites of really different typologies (suburban vs traffic). We were really focused on this difference with, on one hand, the traffic site, with a poor influence of long-range transport of pollutants (2 meters away from the ring road of Paris) and on the other hand, the suburban site, with a clear influence of long-range transport of pollutants and aerosol ageing.

Paragraph 3.3 - Page 6 line 16-17: It should be read in the text “NPAH and OPAH fraction in the different size classes”. The percentage of NPAHs and OPAHs in each size class is based on the total OPAH and NPAH concentrations. It will be specified in the final version of the article. Results presented here are totally similar than the ones reported by Albinet et al., 2008. For the suburban sites, the fraction in the ultrafine modes are similar to the study of Albinet et al., 2008. Only at the traffic site, the fraction of OPAHs are really higher but, it should take into consideration that in this study, samplings were made at about 2 meters away from the ring road of Paris (10 million inhabitants) explaining that the results could be quite different.

Discussion - Page 9 line 17-27: This part is an introduction in order to understand the following discussion. It is totally true that the results and conclusions made have to be supported by more than one field campaign. Nevertheless, this article constitutes a

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database for the study of OPAH and NPAH particle size distributions. Future studies can compare their results with those presented here. The main objective was to highlight the problematic linked to PAH derivatives in order to perpetuate this kind of study and to realize long term studies on these sites, for example.

Yes, the particle size distribution of OPAHs and NPAHs could change depending on the meteorological conditions. As reported by Di Filippo et al., 2010, the temperature influences strongly the particle size distribution of NPAHs and OPAHs. Nevertheless as mentioned above, both field campaigns were realised in summer and the average temperatures were similar (Table 1) and results are then comparable. Here, we just want showed that, for isomers (benzo[a]fluorenone and benzo[b]fluorenone), the particle size distributions were different for the same sampling period.

Unfortunately, the separation of 2- and 3-NFlt could not be achieved with the chromatographic column used (5 % phenyl-substituted methylpolysiloxane phase (DB5-MS)). Considering the relative low proportion of 3-NFlt reported in other previous studies [< 1% (Bamford and Baker, 2003; Zielinska et al., 1989) and <50% (Feilberg et al., 2001)], it was decided to us to use the 2+3-NF/1-NP ratio but with precaution. Again, we agree that sampling campaigns have to be carried out in on the same sampling sites to confirm or infirm all the results obtained. In this way, this paper could be a base for long term studies.

The concentrations of OPAHs and NPAHs are reported in Table 1. Fig. 1 to 5 and Fig S1 to S4 show their particle size distributions. The representation of the NPAH and OPAH particle size distributions in these figures allow to give a greater importance to the smaller particles. This type of representation is commonly used in the studies dealing with particle size distributions of compounds of interest (e.g. Albinet et al., 2008; Allen et al., 1997; Allen et al., 1998; Kawanaka et al., 2004; Venkataraman and Friedlander, 1994; Venkataraman et al., 1994; Schnelle-Kreis et al., 2001). The size-resolved mass distribution was not determined. Only one cascade impactor was used during this the sampling campaign. In order to properly weigh the sampling me-

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dia (aluminium foils), it is necessary to let them equilibrate at controlled temperature and humidity for at least 24 h (European Committee for Standardization (CEN), 1999). In this case, there is a strong risk to lose semi-volatile compounds like NPAHs and OPAHs.

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