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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.

Anonymous Referee #3

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GENERAL COMMENTS. The paper reports size segregated OPAH and NPAH concentrations in two sites in France. Two measurement campaigns were performed: in July 2009 in the first site, and in September 2010 in the second site. Fine and ultrafine particles induce adverse effects on human health, causing an inflammatory response deep in the lungs, which occurs in the presence of genotoxins in the organic fraction. So it is important to characterize the organic fraction associated to those fractions of particulate matter. Nevertheless it is a difficult task to provide reliable measurements, because of the technical difficulties in the determination of very low concentrations. So

that, we must be very careful in presenting interpretation of results if the quality of data is not treated as a key parameter and if the amount of data is too small.

SPECIFIC COMMENTS. Paragraph 2.3 reports that the only internal standard added was 1-nitropyrene-d. The best way to ensure similar recovery and a good quantization is to use an internal standard that is physically and chemically identical to the analyte. 1-nitropyrene is not suitable for all the nine OPAHs and 18 NPAHs so that their quantization is unconvincing.

Paragraph 2.4

Page 4 Line 24. "Recovery …. in the range 5% -.." is reported. This value is really too low for a recovery. How many analytes are recovered at this low percentage? Nevertheless in 2006 Albinet (Albinet et al. in Journal of Chromatography A, 1121 106–113) writes that recoveries for the most volatile compounds relatively poor were considered as preliminary. Walgraeve et al. in Atmospheric Environment 44 (2010) 1831-1846 write: "Albinet et al. (2006) used PLE for extracting a set of 9 oxygenated and 17 nitro-PAHs by using dichloromethane as the extraction solvent at 120 °C and 14 MPa. Recoveries between 5% (napthalene-1-carboxaldehyde) and 83% (benzo[b]fluorenone) were obtained. Although PLE has promising potential, Lintelmann et al. (2005) reported chemical degradation or rearrangement of PAH-quinones during PLE at temperatures and pressures less than 100 °C and 10.7 MPa, respectively. Different solvents were used including methanol, toluene, and a mixture of hexane and acetone, but irreproducible results from spiked quartz fiber filters were obtained and recoveries were below 80%. Further work is needed in order to determine more precisely the application potential of PLE for oxygenated PAHs extraction".

Line 25. Was repeatability of the entire analytical procedure calculated on spiked filters or on a sampled filter split into two parts? In the first case, using internal standards, the repeatability seems to be low.

Line 28. "filter blanks were done every other day". What does this exactly mean?

Lines 29-30. The authors write “OPAH and NPAH concentrations were corrected from the highest blank value obtained in the analytical process”. What order of magnitude are the blank values? The standard addition method could instead be used to prevent possible artifacts.

Paragraph 3.1 reports a comparison between pollutant concentrations from two different sampling devices. Page5 Lines 8-9. The authors write “Overall, concentrations obtained with both samplers were of the same order of magnitude and could be considered as equivalent, in regard to the uncertainties of measurement evaluated for the DA80, using the GUM approach (global uncertainty of measurement) (Table 1)” Looking at table 1, on the contrary, it seems that a very serious analytical problem has not yet been solved and both the uncertainties of measurements and some differences are too high. In fact, although the uncertainty of measurement takes into account each step of procedure, 23 of the 27 uncertainties listed are even over 70%. Hereupon the explanations are inappropriate:

Lines 16-17. The authors write “First, the reduce pressure on the lower impactor stages could induce the desorption of the more volatiles compounds, especially in summer season”. Why then have 1-nitropyrene 2-Nitronaphthalene 1-Naphthaldehyde so comparable concentrations?

Lines 18-24. The authors write “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 back up filter of the MOUDI sampler than for the impactor stages. In this last case, airflow during sampling runs over the surface of the particle sampling supports (aluminium foils). The formation of secondary compounds is then potentially higher using filtration sampling systems”. The sentence is not clear. However 2-Nitropyrene, 1,4-Anthaquinone and Benzo[a]fluorenone concentrations are higher in the sampling performed by MOUDI.

Lines 27-29. The authors write “NPAH and OPAH particle size distributions obtained during both sampling campaigns could be compared and discussed with a high level of confidence” and Par. 3.2 reports some notes about a comparison between suburban and urban sites. The samplings were carried out in two different months and in two different years. Why should they be comparable? Both sources and meteorological condition could be deeply different.

Par. 3.3 Page 6 Lines 16-17 The authors write: “NPAH and OPAH repartition in the different fraction size classes is presented on Fig. 1 for both sites”. and in Fig. 1 on y-axis the “fraction in size class” is reported. Is it the percentage of ultrafine, fine and coarse OPAH and NPAH based on the total OPAH and NPAH? If so, due to analytical problem is it possible some overestimation in the ultrafine particles of OPAH and NPAH concentrations determining a major distribution in this size? Considering that usually the ultrafine fraction is 1-30% of PM10, is it reliable to obtain OPAH three times more concentrated in this fraction? Albinet [Albinet et al. in Atmospheric Environment 42 (2008) 55–64] reported the fractions of OPAHs equal to ~56% and NPAHs equal to ~63%, associated with the finest particles (Dp<0.39 mm) and this last fraction is even larger than PM0.14.

4. Discussion Page 9 Lines 17-27. This part is an introduction and it is not a discussion. All the following discussion should be supported by more than one measurement campaign in the same site. It is possible that benzo[a]fluorenone is unimodal in a period and bimodal in the immediately following period. NPAH particle size distribution is monomodal or bimodal depending on the meteorological period. Di Filippo et al. in Atmospheric Environment 44(2010) 2742-2749 report that at temperatures between 13 and 18 °C nitro-PAHs showed a bimodal distribution with a peak in the submicron and a peak in the supermicron size range. In summer (9-23 July) at a temperature of 26 °C, the monomodal distribution showed a peak at 0.1 μm fraction.

Holly Bamford and Joel Baker in 2003 [Atmospheric Environment 37 (2003) 2077–2091] write “The relative contribution of gas-phase reactions and primary emission sources of nitro-PAHs were evaluated using source specific concentration ratios of 2-nitrofluoranthene and 1-nitropyrene (2-NF/1-NP)". In the present paper the ratio 2+3-NFlt/1-NP is reported. Maybe the reason is that in lines 25 – 26 of page 10 the authors write: "2-nitrofluoranthene (largely predominant against 3-nitrofluoranthene in ambient air". In any case this ratio becomes imprecise, because 2+3-NFlt is the sum of a primary and a secondary NPAH. Again, any comparison between the two sampling sites should be supported by campaigns carried out in the same period.

Finally size-resolved NPAH and OPAH concentrations and the size-resolved mass distributions are never shown in the paper; only figure 2 reports organic compound percentages, but it is poorly explained in the text.

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