Supplementary Material

Particle size distribution of nitrated and oxygenated polycyclic aromatic hydrocarbons (NPAHs and OPAHs) on traffic and suburban sites of a European megacity: Paris (France)

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Table S1. Operating characteristics of the MOUDI.

Stage	50 % cut-off diameter (µm)
Inlet	18
1	10
2	5.6
3	3.2
4	1.8
5	1.0
6	0.56
7	0.32
8	0.18
9	0.10
10	0.056
Total filter	0.01*

* limit of particle size collected on the total filter has been selected arbitrarily

Changes in flow during and between sample collections would introduce variability in the size of particles collected on each impactor stage. The flow measured at the beginning and end of each run differed by less than 10 %. This variation would cause a change of approximately 5 % in the impactor stage cut-off sizes. Because the flow was not recorded during sampling and these sampling errors introduce only minor variations in D_{p50}, for the remainder of this work the air flow is taken to be constant (1.8 m^3 h^{-1}).

Reagents and materials

Chemical reagents and gases used in this study are reported in Table S1, together with the name of suppliers and the purity grades.

Table S2. List and characteristics of the chemicals, solvents and gases used.

Compound	Supplier	Purity (%)
OPAHs		
1-Naphthaldehyde	Acros	95
9-Fluorenone	Acros	99
9-Phenanthrenecarboxaldehyde	Aldrich	97
9,10-Anthaquinone	Acros	98
1,4-Anthaquinone	Chiron	97.8
Benzo[a]fluorenone	Chiron	99.9
Benzo[b]fluorenone	Chiron	99.8
Benzanthrone	Acros	99
Benz[a]anthacen-7,12-dione	Acros	99
NPAHs		
1-Nitronaphthalene	Cluzeau	99
2-Nitronaphthalene	Cluzeau	99
2-Nitrofluorene	Cluzeau	98
9-Nitroanthracene	Chiron	86.6
9-Nitrophenanthrene	Cluzeau	100
3-Nitrophenanthrene	Cluzeau	99.7
3-Nitrofluoranthene	Cluzeau	99.5
1-Nitropyrene	Cluzeau	99
2-Nitropyrene	Cluzeau	99.9
4-Nitropyrene	Chiron	99.8
7-Nitrobenz[a]anthracene	Cluzeau	99
6-Nitrochrysene	Cluzeau	98
1,3-Dinitropyrene	Cluzeau	99.9
1,6-Dinitropyrene	Cluzeau	97.5
1,8-Dinitropyrene	Chiron	99.9
1/3-Nitrobenzo[a]pyrene	Chiron	99.7
6-nitrobenzo[a]pyrene	Cluzeau	99.8
Labelled deuterium NPAHs/OPAHs		
3-Nitrofluoranthene-d9	Cluzeau	99.3
1-Nitronaphtalene-d7	Cluzeau	99.4
2-Nitrofluorene-d9	Cluzeau	98.8
6-Nitrochrysene-d11	Cluzeau	99.7
Anthraquinone-d8	Cluzeau	98.6
1-Nitropyrene-d9	Cluzeau	99.2
Solvent		
Methylene Chloride	Sigma-Aldrich	> 99.8
Pentane	Sigma-Aldrich	> 99.0
Isooctane	Sigma-Aldrich	> 99.5
Acetonitrile	VWR	> 99.9
Gases		
Helium	Air Liquide	99.9999
Nitrogen	Air Liquide	99.999
Methane	Air Liquide	99.995
Argon	Air Liquide	99.9999

Analytical procedures

Extractions

Sample extractions were realised using pressurised solvent extraction (Dionex, ASE 200) with CH_2Cl_2 as the solvent. The extraction procedure was performed as the follows: 33 mL cells at 120 °C, 140 bars, 3 cycles of 6 min, flush 50 % and purge 120 s.

NPAH and OPAH analyses

Prior to analyses, extracts were purified on solid phase extraction (SPE) (alumina and silica (Upti-clean Aln 500 mg/3 mL, interchim and Upti-clean Si-S 500 mg/3 mL, Interchim)) using a protocol described in a previous publication (Albinet et al., 2006). After purification, extracts were evaporated under argon stream near to dryness and dissolved in isooctane.

NPAHs and OPAHs were analysed by GC/MS, using a Perkin-Elmer Clarus 500 coupled with a Perkin-Elmer Turbomass gold in the NICI mode in selective ion monitoring mode (Albinet et al., 2006). The column used was a DB-5MS (30 m × 0.25 mm × 0.25 µm film thickness, Agilent J&W). Program settings were as follow: gas flow at 1.2 mL min-1, cool splitless injection (40 to 320 °C) of 1 µL, and transfer line at 300 °C. The initial oven temperature was 60 °C for 2 min, then increasing at 45°C min^{-1} until 150 °C for 5 min; and 5 °C min^{-1} to 300 °C for 7 min. Total run time was 46 min. MS parameters were as follow: electron energy 45 eV; source temperature 150 °C; methane was used as the reagent gas for NICI. Monitored ions and deuterated standards were listed in Table S2.

Table S3. Selected ion monitoring conditions for OPAHs and NPAHs.

Compounds	Monitored ions (m/z)	Dwell time (s)	Labelled internal standards	Monitored ions (m/z)	Dwell time (s)
			OPAHs		
1-Naphthaldehyde	156	0.08	Anthraquinone-d8	216	0.08
9-Fluorenone	180	0.04	Anthraquinone-d8	216	0.08
9-Phenanthrenecarboxaldehyde	206	0.08	Anthraquinone-d8	216	0.08
9,10-Anthraquinone	208	0.04	Anthraquinone-d8	216	0.08
1,4-Anthraquinone	208	0.04	Anthraquinone-d8	216	0.08
Benzo[a]fluorenone	230	0.04	Anthraquinone-d8	216	0.08
Benzo[b]fluorenone	230	0.04	Anthraquinone-d8	216	0.08
Benzanthrone	230	0.04	Anthraquinone-d8	216	0.08
Benz[a]anthracen-7,12-dione	258	0.08	Anthraquinone-d8	216	0.08
			NPAHs		
1-Nitronaphthalene	173	0.08	1-Nitronaphtalene-d7	180	0.04
2-Nitronaphthalene	173	0.08	1-Nitronaphtalene-d7	180	0.04
2-Nitrofluorene	211	0.08	2-Nitrofluorene-d9	220	0.08
9-Nitroanthracene	223	0.04	2-Nitrofluorene-d9	220	0.08
9-Nitrophenanthrene	223	0.04	2-Nitrofluorene-d9	220	0.08
3-Nitrophenanthrene	223	0.04	2-Nitrofluorene-d9	220	0.08
2+3-Nitrofluoranthene[a]	247	0.08	3-Nitrofluoranthene-d9	256	0.08
1-Nitropyrene	247	0.08	3-Nitrofluoranthene-d9	256	0.08
2-Nitropyrene	247	0.08	3-Nitrofluoranthene-d9	256	0.08
4-Nitropyrene	247	0.08	3-Nitrofluoranthene-d9	256	0.08
1-Nitropyrene-d9	256	0.08	3-Nitrofluoranthene-d9	256	0.08
7-Nitrobenz[a]anthracene	273	0.08	6-Nitrochrysene-d11	284	0.08
6-Nitrochrysene	273	0.08	6-Nitrochrysene-d11	284	0.08
1,3-Dinitropyrene	292	0.04	6-Nitrochrysene-d11	284	0.08
1,6-Dinitropyrene	292	0.04	6-Nitrochrysene-d11	284	0.08
1,8-Dinitropyrene	292	0.04	6-Nitrochrysene-d11	284	0.08
1-Nitrobenzo[a]pyrene	297	0.08	6-Nitrochrysene-d11	284	0.08
3-Nitrobenzo[a]pyrene	297	0.08	6-Nitrochrysene-d11	284	0.08
6-Nitrobenzo[a]pyrene	297	0.08	6-Nitrochrysene-d11	284	0.08

[a] The separation of these two isomers could not be achieved on the DB-5MS column.

Calculation of uncertainties of measurement

Uncertainties of measurement of PAC concentrations (OPAHs and NPAHs) were evaluated by the GUM approach (Guide to the Expression of Uncertainty in Measurement) (Macé et al., 2010). Uncertainties due to the analytical procedure and to the sampling procedure were evaluated separately:

$$\frac{u^2(C)}{C^2} = \frac{u^2(\bar{f})}{\bar{f}^2} + u^2\left(\frac{A_E}{A_{ISE}}\right) + \frac{u^2(m_{ISE})}{m_{ISE}^2} + \frac{u^2(m_{SSF})}{m_{SSF}^2} + \frac{u^2(m_{SSE})}{m_{SSE}^2} + \frac{u^2(R)}{R^2} + \frac{u^2(Q)}{Q^2} + \frac{u^2(t)}{t^2}$$

Analysis Sampling

With:

- C: PAC mass concentration in the airborne sample
- $\bar{f}$: average response factor of the PAC
- A_E: compound peak area on the chromatogram
- A_{ISE}: internal standard peak area on the chromatogram
- m_{ISE}: mass of internal (deuterated) standard in the calibration solution
- m_{SSF}: mass of surrogate added
- m_{SSE}: mass of surrogate quantified in the extract
- R: recovery rate determined using a certified reference material
- Q: air sampling flow rate
- t: sampling duration

$$U_{rel}(C) = \frac{k \times \sqrt{u^2(C)}}{C} \times 100$$

With:

- k : enlargement factor (usually equal to 2)

Additional figures

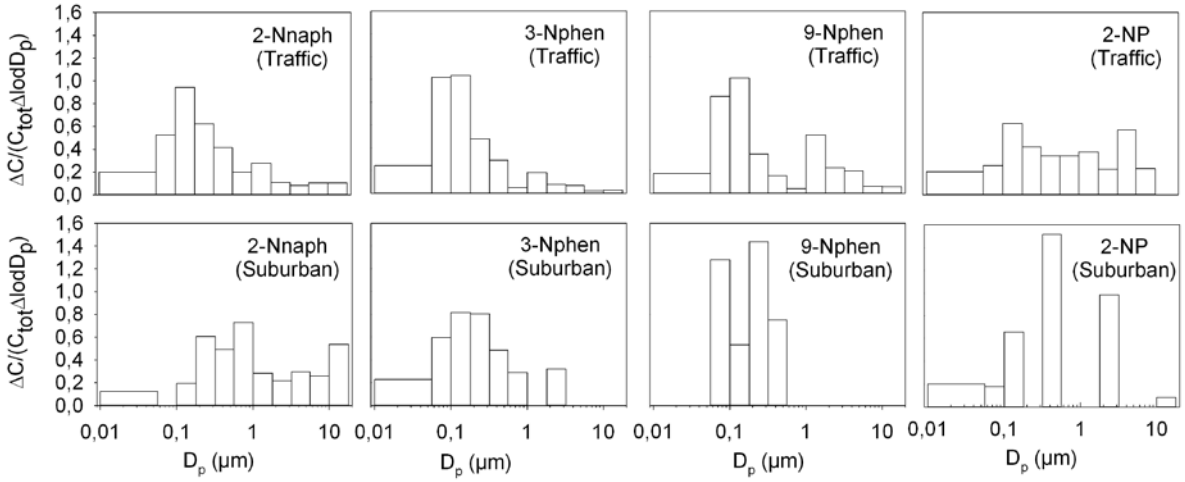

Figure. S1. Particle size distributions of 2-nitronaphthalene (2-Nnaph), 9-nitrophenanthrene (9-Nphen), 3-nitrophenanthrene (3-Nphen) and 2-nitropyrene (2-NP) at the traffic and suburban sites.

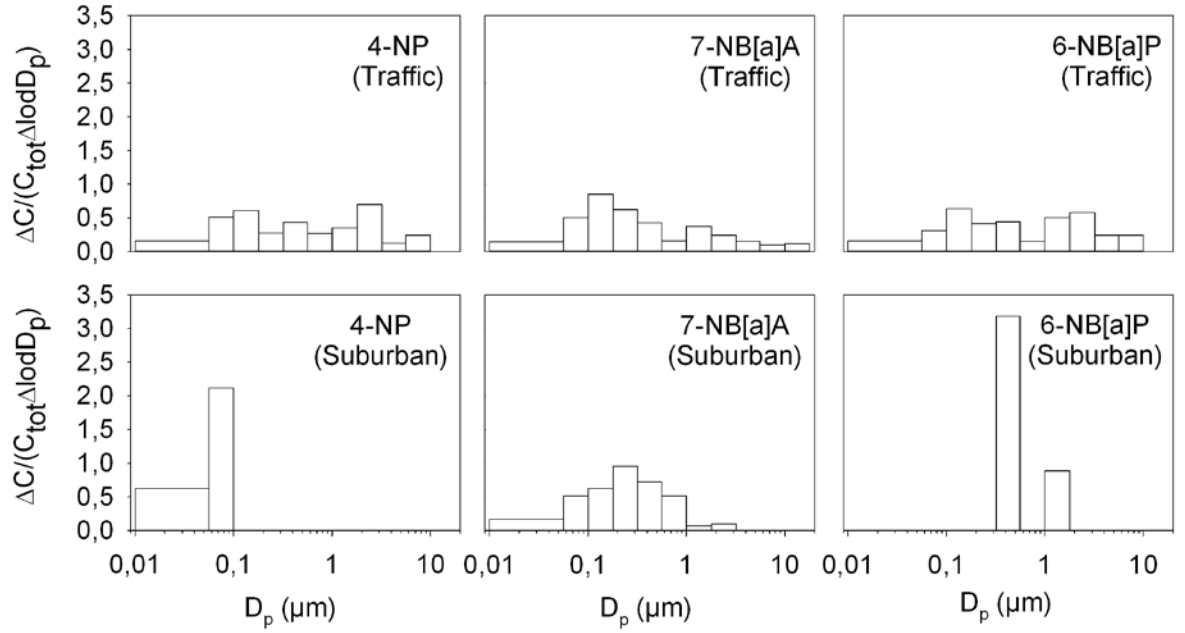

Figure. S2. Particle size distributions of 4-nitropyrene (4-NP), 7-nitrobenz[a]anthracene (7-NB[a]A) and 6-nitrobenzo[a]pyrene (6-NB[a]P) at the traffic and suburban sites.

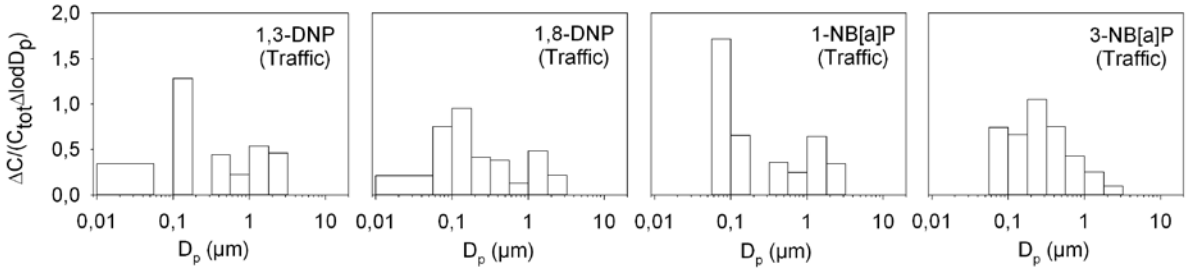

Figure. S3. Particle size distributions of 1,3-dintropyrene (1,3-DNP), 1,8-dintropyrene (1,8-DNP), 1-nitrobenzo[a]pyrene (1-NB[a]P) and 3-nitrobenzo[a]pyrene (3-NB[a]P) at the traffic suburban sites. Missing graphs correspond to the compounds not quantified.

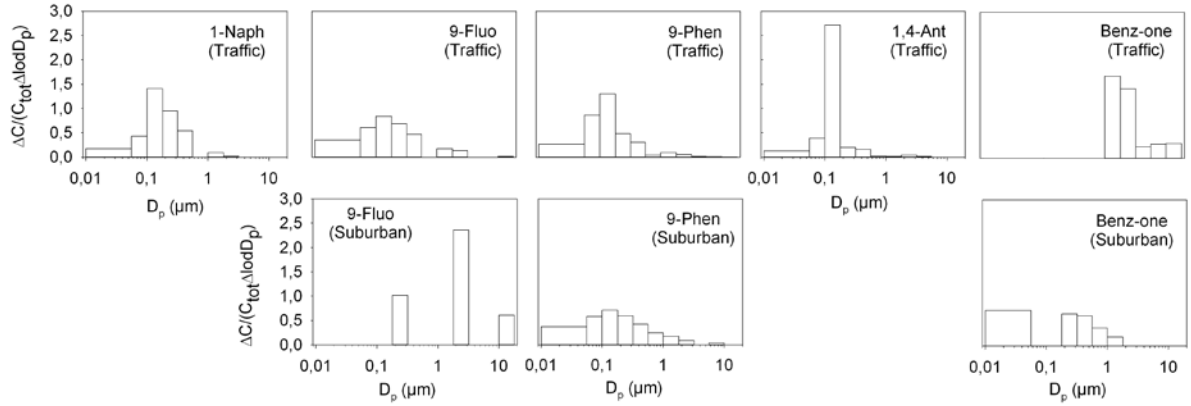

Figure. S4. Particle size distributions of 1-naphthaldehyde (1-Naph), 9-fluorenone (9-Fluo), 9-phenanthrenecarboxaldehyde (9-Phen), 1,4-anthraquinone (1,4-Ant) and benzanthrone (Benz-one) at the traffic and suburban sites. Missing graphs correspond to the compounds not quantified.

References

Albinet, A., Leoz-Garziandia, E., Budzinski, H., and Villlenave, E.: Simultaneous analysis of oxygenated and nitrated polycyclic aromatic hydrocarbons on standard reference material 1649a (urban dust) and on natural ambient air samples by gas chromatography-mass spectrometry with negative ion chemical ionisation, J. Chromatogr., A, 1121, 106-113, 2006.

Macé, T., Lalere, B., Labarraque, G., Ravantos, C., Leoz-Garziandia, E., Alleman, L., and Mathé, F.: Rédaction de guides pratiques de calcul d'incertitudes et formation des AASQA -

Estimation des incertitudes sur les mesurages des B[a]P réalisés sur site dans la fraction PM10 (3/5) (French language), LCSQA / INERIS / LNE / EMD, 2010.