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**A simple QuEChERS-like extraction approach for molecular chemical
characterization of organic aerosols: application to nitrated and
oxygenated PAH derivatives (NPAH and OPAH) quantified by GC-
NICIMS**

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Abstract

An alternative extraction procedure based on Quick Easy Cheap Effective Rugged and Safe (QuEChERS) approach was developed and applied for the analysis of particle-bound PAH derivatives namely, nitrated and oxygenated PAHs (NPAHs and OPAHs). Several analytical parameters such as temperature of GC injection or MS detection settings were optimized. The developed analytical procedure enabled the simultaneous quantification of 32 NPAHs and 32 OPAHs (or oxygenated compounds) using GC-NICI/MS and including typical compounds of secondary organic aerosol (SOA) formed from PAH photooxidation (e.g. 2-formyl-trans-cinnamaldehyde and 6H-dibenzo[b,d]pyran-6-one). QuEChERS-like approach was optimized including the nature of extraction solvent, the sorbent for clean-up, and extraction time. The final extraction procedure was based on a short mechanical agitation (vortex for 1.5 min) using a small amount of acetonitrile (7 ml) as solvent. Since dispersive-solid phase extraction (d-SPE) did not provide satisfactory results, SPE using SiO₂ was selected for sample purification. Identical results were obtained when comparing the QuEChERS-like and the traditional pressurised solvent extraction (PLE) procedures for fortified ambient air particle samples. The validation of the developed protocol was carried out with the analysis of two aerosol standard reference material [NIST SRM 1649a (urban dust) and SRM 2787 (fine particulate matter < 10 µm)]. For numerous NPAHs and OPAHs, this study constitutes the first report of their measurement for both SRMs. Compared to other extractions methods including PLE, the QuEChERS-like protocol enabled an increase of productivity and a decrease of extraction cost. This paper shows that QuEChERS-like extraction procedures are fully adapted to the molecular chemical characterization of aerosol samples and could be extended to other categories of compounds.

Keywords: PAH; Nitro-PAH, Oxy-PAH; QuEChERS; Analysis, Aerosol; SOA

1. Introduction and objectives

Polycyclic aromatic hydrocarbons (PAHs) derivatives (nitrated and oxygenated PAHs, NPAHs and OPAHs) are compounds of major concern due to their toxic properties [1-7]. Some of them are now classified as probably or possibly carcinogenic to humans by the IARC (International agency for research on cancer, groups 2A and 2B) [8,9]. They are formed in the atmosphere from both, direct emission by combustion sources and, secondary formation by homogeneous and heterogeneous photooxidation processes [10]. They are also of scientific interest because they are typically found in the secondary organic aerosol (SOA) formed *via* the photooxidation of PAHs [11,12].

Quantification of particle-bound OPAHs and NPAHs is generally achieved using solvent extraction followed by GC-MS (EI or NICI), LC-MS or LC-MS/MS analysis [13-26]. Other existing analytical techniques used are the following: HPLC-CD, HPLC-FD, UPLC-ToF-MS, GC×GC-ToF-MS, GC-ECD [13,14,27-31].

Extraction of aerosol samples is more commonly achieved using solvent extraction. Use of various methods has been described: soxhlet, ultrasonication, microwave extraction, pressurised liquid extraction (PLE or accelerated solvent extraction, ASE) [13-26] or supercritical fluid extraction (SFE) [32,33]. Different solvents, or mixture of them, were used: methanol, toluene, benzene, ethanol, dichloromethane (DCM), ethyl acetate, hexane and acetone. The analytical procedure usually includes a fractionation or clean-up step of the extracts by solid phase extraction (SPE), open column chromatography or by HPLC. The analysis of OPAHs (ketones and hydroxyl-PAHs) could also require a derivatization procedure (off-line or on-line) [13,16,20,34-37]. The use of solvent-free based extraction techniques was also reported in different papers with thermal-desorption (TD) coupled with GC-ToF-MS or GC×GC-ToF-MS [36,38] and laser desorption/ionization coupled to ToF-MS (LD-LI-ToF-MS) [39].

All these extraction methods are very efficient and allow the chemical characterization of the organic aerosol content including NPAHs and OPAHs. However, they are also time-consuming, labour-intensive, requires the use of a large volume of organic solvent (toxic) and/or a high cost of material investment and maintenance (PLE, TD, LD and SFE). They also can lead to potential degradation of some NPAHs (known to be thermolabile compounds) and OPAHs [40] due to the high temperatures used for extraction (no conservation of the sample integrity).

The QuEChERS extraction procedure (Quick Easy Cheap Effective Rugged and Safe) was initially developed for the analysis of pesticides in fruits and vegetables [41,42]. The main advantages of this technique are to shorten and simplify the sample extraction and purification steps. Considered as a soft extraction method (a lower quantity of interfering compounds are supposedly extracted), it involves an extraction at room temperature (to keep sample integrity) by agitation (or vortex) with, generally, acetonitrile (ACN) as solvent, followed by an optional clean-up procedure by dispersive solid-phase extraction (d-SPE). The total extraction and clean-up time is generally about 10 minutes and the quantity of solvent used is kept at a minimum (5 to 15 ml) [42]. Fewer steps (and time) than traditional extraction procedures are required using the QuEChERS extraction approach minimizing the source of experimental errors. No important cost in material is required (vortex and centrifuge). QuEChERS is now popular in agro alimentary and agrochemical sciences and also, a standard method for foodstuff analysis based on this approach exists [43]. Modified QuEChERS procedures were successfully applied to other food types (fish, shellfish) and environmental matrices (soils, sediments, atmospheric particulate matter) and to other compounds (PBDEs, VOCs, PCBs, pharmaceuticals and PAHs) [42,44-51]. For ambient air and emission aerosol samples, QuEChERS-like extraction procedure was previously applied for the molecular chemical characterization of PAHs [51].

The aims of this study were to evaluate and to report on the applicability of QuEChERS-like extraction procedure for the analysis of nitrated and oxygenated PAHs from aerosol samples. The

extraction protocol was developed with the analysis of fortified ambient air particulate samples using GC-NICI/MS. Results were compared with those obtained with commonly used PLE-SPE approach. The methodology was validated by the analysis of two NIST aerosol standard reference materials (SRM 1649b and 2787). The study included several improvements on the analytical GC-NICI/MS conditions and the quantification of additional compounds (in total, 32 OPAHs /oxygenated compounds and 32 NPAHs quantified) never reported before in both SRMs with some of them typical of SOA formation from PAH photooxidation [11,52-56].

2. Experimental section

2.1. Chemical and solvents

The used chemicals and solvents, their degrees of purity, and the supplier data details are reported in the Supplementary Information (SI). Pure NPAH and OPAH compounds (liquids, powder or solutions) were purchased from various commercial suppliers (Table S1). One oxygenated compound and one OPAH, 2-formyl-trans-cinnamaldehyde and 6H-dibenzo[b,d]pyran-6-one (typical by-products of SOA formation from naphthalene and phenanthrene oxidation, respectively [11,52-54]) were synthesized by Santai Labs (Changzhou, China) and Syntheval (Hérouville-Saint-Clair, France).

2.2. Aerosol samples

Ambient air aerosol samples were collected on quartz fibre filters (Whatman QMA, 20.3 x 25.4 cm; previously heated for 12 h at 500 °C) using a high volume sampler (Graseby Andersen, 70 m³ h⁻¹ equipped with of a PM₁₀ sampling head) at Verneuil-en-Halatte, France (49°16'20"N, 2°30'14"E, suburban location), in February and March 2013. Sampling duration was 24 h. After collection, filters were wrapped in aluminium foil, sealed in polyethylene bags and stored at -18 °C until analysis. Collected filters were cut into 16 or 18 punches (Ø = 47 or 37 mm) in order to perform the development of the QuEChERS-like extraction procedure and the comparison with

PLE extraction method using the same aerosol sample. Homogeneity of the ambient air sampling filters used (Andersen) was evaluated in previous studies for PAHs, NPAHs and OPAHs. No significant disparity between filter punches was observed ($\sigma \approx 5\%$) [57,58]. For the method development of the extraction step, aerosol samples (filter punches) were doped with NPAHs and OPAHs. For this purpose, punches of filters (with aerosols) were spiked with known amounts (5 or 50 ng, depending on the experiments) of NPAH or OPAH standard compounds (5 or 50 μl of a standard solution mixture of 32 NPAHs and 32 OPAHs/oxygenated compounds at about $1\text{ ng }\mu\text{l}^{-1}$ concentration in ACN) (Table 1 and S1).

2.3. Standard reference materials

Two different SRMs, both provided by NIST (Gaithersburg, MD, USA), were analysed to validate the accuracy and the precision of the developed QuEChERS-like extraction method: (1) SRM 1649b (urban dust), and (2) SRM 2787 (fine particulate matter, $< 10\ \mu\text{m}$) [59,60]. For both, PLE and QuEChERS, six samples of SRM 1649b (3 of about 20 mg and 3 of about 50 mg, balance precision = 0.01 mg) and 3 samples of SRM 2787 (about 20 mg) were analysed. Moisture content was determined for SRM 1649b (3.88 %, moisture analyser HR 73, Mettler Toledo; Viroflay, France). NPAH and OPAH concentrations were corrected and reported as dry-mass basis for this SRM. No correction was made for SRM 2787 due to insufficient amount of material available for the determination of moisture content.

2.4. Extraction and purification

For PLE extraction, sample extractions and clean-up were performed following the procedure developed by Albinet et al. (2006) [18] and used latter for the analysis of PAH derivatives [58,61-66]. Extraction protocol with PLE (Dionex, ASE 200) using dichloromethane (DCM) as solvent was as follow: 11 mL cells were used with extraction parameters set at $120\ ^\circ\text{C}$, 140 bars (14 MPa),

3 cycles of 6 minutes for heat and static times, flush 90 % and purge 120 sec. Extracts were then concentrated to near dryness under a nitrogen stream (Zymark, Tubovap II) and dissolved into a small volume of DCM (100 - 200 μ l). Sample extracts were first purified on alumina (neutral) SPE cartridges (500 mg, 3 ml; Macherey Nagel, Hoerd, France). Organic extracts were eluted with 9 ml of DCM. Extracts were concentrated under a nitrogen stream and dissolved in isooctane and then, a second purification was performed on silica SPE cartridges (500 mg, 3 ml; Macherey Nagel, Hoerd, France). Alkanes were eluted with 1 ml of pentane and discarded. NPAHs and OPAHs were then eluted with 9 ml of a DCM/pentane mixture (35/65, v/v). After concentration under a gentle nitrogen stream, residues were dissolved into 100 μ l of acetonitrile (ACN) (or 1 ml for fortified samples with 50 ng of NPAHs and OPAHs) prior to GC/NICI-MS analysis. This purification procedure was reported previously [18,58,61-66].

QuEChERS-like extraction procedure was based on a previous method developed for the analysis of particulate-bound PAHs [51]. Samples were placed in centrifuge glass tubes (\varnothing = 16 mm, L = 100 mm, screw cap with PTFE septum face, Duran, Mainz, Germany) and 7 ml of solvent [different solvents or solvent mixtures tested: ACN, DCM, toluene, ethyl acetate, acetone, acetone/hexane (1/1) and DCM/hexane (9/1)] was added to it and shaken/vortexed using a multi-position vortex for 30 s to 5 min (DVX-2500 Multi-Tube Vortexer, VWR, Fontenay-sous-Bois, France). Unless specified, the agitation (vortex) time was set at 1.5 min. Samples were next centrifuged for 5 min at 4500 rpm (Sigma, 3-16 PK centrifuge). 5.5 ml of supernatant were collected, concentrated to near dryness under a gentle nitrogen stream and dissolved in a small volume of DCM (100 - 200 μ l). For the first experiments (extraction solvent choice), the same clean-up procedure as for PLE extracts was applied ($\text{Al}_2\text{O}_3/\text{SiO}_2$). A single step purification on SiO_2 SPE (phase finally selected after method development; 500 mg, 3 ml; Macherey Nagel, Hoerd, France) with a similar elution protocol as the second purification step for PLE extracts was applied (1 ml of pentane discarded and then elution with 9 ml of DCM/pentane mixture (35/65, v/v)). After

evaporation of solvent, residues were dissolved in 100 μl of ACN (or 1 ml for fortified samples with 50 ng of NPAHs and OPAHs) prior to GC/NICI-MS analysis.

For both PLE and QuEChERS extractions, samples (filter punches or SRMs) were spiked with known amounts of deuterated NPAH and OPAH surrogate standards prior to extraction (Table 1) (5 μl - or 50 μl for fortified samples with 50 ng of NPAHs and OPAHs - of a surrogate standard solution mixture of 5 deuterated NPAHs and 2 deuterated OPAHs at about 1 ng μl^{-1} concentration in ACN).

Prior to analysis, purified samples were spiked with known amounts of 2 labelled internal standards (1-nitropyrene-d9 and 9-fluorenone-d8; 5 or 50 ng added, depending on the experiments) in order to evaluate the recovery rates of labelled NPAH and OPAH surrogates.

2.5. GC/NICI-MS settings

The analysis were performed using an Agilent 7890A GC equipped with a MMI (multimode inlet) and coupled to a 5975C MS working in NICI mode (negative ion chemical ionization) [18] (Table 1). The analyses were carried out with an Optima-5MS Accent column (30 m \times 0.25 mm \times 0.25 μm film thickness; Macherey Nagel, Hoerd, France). Analytes were identified by comparison of retention times of standard compounds and MS fragment pattern. Quantification of NPAHs and OPAHs was based on a daily 8-point calibration curve (gravimetrically diluted standard solutions from 2 to 500 pg μl^{-1} in ACN; $0.9990 > r^2 > 0.8500$ for all compounds except phthalic anhydride, 1,2-naphthalic anhydride, 2,3-naphthalenedicarboxylic anhydride, anthrone, 1,2-naphthoquinone, 5,6-chrysenequinone and 3-nitrobenzo[e]pyrene harder to calibrate; $0.81 > r^2 < 0.60$).

The final selected experimental conditions were 1 μl injection at 140 $^{\circ}\text{C}$ in pulsed splitless mode at 30 psi (for 1.5 min) using a liner SGE 4 mm ID Split / Splitless Tapered FocusLiner W/Wool (splitless time for 1.6 min). Ultra pure He (99.9999 %) was used as carrier gas with a constant flow rate of 1.5 ml min^{-1} . The GC oven program started at 70 $^{\circ}\text{C}$ for 5.1 min, increased at a

rate of 45°C min⁻¹ to 190 °C, following by a gradient of 5 °C min⁻¹ to 320 °C held for 5 min (overall runtime of 38.8 min). Transfer line was set at 320 °C.

The source and quadrupole temperatures were set at 150 °C, methane flow rate of 2.5 ml min⁻¹ (CH₄, 99.9995 % purity + Agilent triple gas clean filter), electron energy of 235 eV and emission value of 50 µA. Autotune Chemstation parameters were adopted for electron multiplier conditions. The MS was run in selected ion monitoring (SIM) mode. Monitored ions and dwell times are shown in Table 1.

3. Results and discussion

3.1. GC/NICI-MS conditions and performances

3.1.1 Optimisation of GC parameters

NPAHs are thermolabile compounds known to decompose at high temperatures. Thus, low temperature injection modes (on-column, cold splitless or solvent vent (= PTV - programmed temperature vaporization)) are preferred for their analysis [14,17,18,22,67,68]. Several authors observed also the thermal degradation of specific OPAHs during the GC injection [23,69,70]. Recently, Cochran et al. (2012) [16] demonstrated the advantages of using pulsed splitless injection mode in comparison to classical splitless for the analysis of NPAHs and OPAHs. The comparison of 3 injection modes (splitless *vs* PTV *vs* pulsed splitless) on the response of the NPAHs and OPAHs was investigated (Fig. S1 in the Supplementary Information, SI). Pulsed splitless injection mode enhanced largely the response of all NPAH and OPAH compounds and notably the heavier ones (e.g. dinitropyrene isomers). On the contrary, the responses using PTV were the lowest, a result in contrast to that reported by Crimmins and Baker (2006) [67]. Finally, pulsed splitless injection mode was selected.

The influence of pulse pressure was further evaluated (Fig. S2). If a higher pulse pressure gave higher NPAH and OPAH responses, multiple peaks were also observed notably for the lighter compounds. A pulse pressure of 30 psi seemed the best compromise and was selected.

Since both NPAHs and OPAHs, are subjected to thermo-degradation, the impact of injection temperature was investigated between 110 to 280 °C (Fig. 1). NPAH responses were significantly lower at injection temperature of 280 °C. NPAH responses reached a maximum at 140 – 200 °C while they were still quite constant for OPAHs. At lower injection temperature of 110 °C, all compounds showed lower responses and standard deviation were highest probably due to poor vaporization reproducibility. Responses of OPAHs and NPAHs were quite similar between 140 °C and 200 °C except for dinitropyrene isomers. Dinitropyrenes are of interest due to their relatively high toxicity [1,2,8,71,72]. They are very difficult to quantify due to their low chromatographic response and because they are present at very low concentrations in the atmosphere ($\approx 10 \text{ pg m}^{-3}$ or lower) [61,63-66]. In order to obtain the highest sensitivity for dinitropyrene isomers and to prevent any thermo-degradation of OPAHs or NPAHs, an injection temperature of 140 °C was finally selected.

The type of liner could also impact the response of the targeted compounds. 3 types of deactivated liners (split/splitless with/without glass wool or frit) were tested (4 mm ID split / splitless tapered focus liner with wool; splitless, 2 mm dimpled; 4mm split liner with glass frit) (Fig. S3). The 4 mm ID split / splitless tapered focus liner with wool provided the best results for all compounds, and notably the high molecular weight ones, and was selected for further analyses. Contrary to O'Connell et al. (2013) [15], no significant influence of the wool package was observed for the OPAH quantification reproducibility in our study.

MS parameters were also optimized. Similar results to those observed by Cochran *et al.* (2012) [16] were obtained for the quantity of reagent gas (CH_4) (Fig. S4). A reagent gas flow of 2.5 ml min^{-1} (50 %) was therefore selected for the analytical procedure. A higher source temperature (300 °C) produced many fragmentations not suitable for a reliable quantification (not shown here). These results were different with the ones showed in the study of Cochran et al. (2012) [16]. A source temperature of 150 °C was overall selected.

The final analytical conditions (section 2.5) enabled the simultaneous quantification of 32 NPAHs and 32 OPAHs. It should be pointed out that the quantification of some compounds of interest, never previously reported, such as 2-formyl-trans-cinnamaldehyde and 6H-dibenzo[b,d]pyran-6-one [11,52-54] were based on specifically synthesised standards. An example of a typical chromatograph is shown on Fig. 2. Peak identification number, retention times and scanned ions are reported in Table 1.

3.1.2 Limits of quantification

Using these conditions, the instrumental limits of quantification (LOQ), defined as the lowest concentration of the compound than can be determined ($S/N = 10$, calculated using the chromatograms of the lowest concentration of the calibration solutions) fall in the range values of 0.02–30.96 pg for OPAHs and of 0.02–8.82 pg for NPAHs (Table 1).

3.2. Extraction solvent

Seven different single or mixtures of solvents [(ACN, DCM, toluene, ethyl acetate, acetone, acetone/hexane (1/1) and DMC/hexane (9/1)] were investigated to determine their suitability as extraction solvent for the QuEChERS-like approach. First tests made using fortified blank filters demonstrated significant lower surrogate recoveries using acetone or acetone/hexane (1/1) (data not shown). These two solvents were therefore not used for the following tests using fortified ambient air filter samples. A comparison of the surrogate recoveries obtained is shown on Fig. S5. Surrogate recoveries were systematically lower using PLE (using DCM) and higher with QuEChERS extraction (using DCM/hexane). No significant differences for the other solvents were observed. Overall, mass of OPAHs and NPAHs extracted using all solvents tested were similar to the results obtained using PLE (Fig. 3 and 4). For NPAHs, the higher quantities determined for 2-nitrobenzothiophene, nitro-phenanthrene and nitro-anthracene isomers using toluene and ethyl

acetate (Fig. 3A) could be linked to with the lower recoveries obtained for their corresponding surrogate, 9-nitroanthracene-d9 (Fig. S5 and Table 1). For both these solvents, significant differences (lower mass extracted) were observed except for 6-nitrobenzo[a]pyrene in comparison to PLE extraction and other solvents tested by QuEChERS-like approach (Fig. 3B). For OPAHs (Figs. 4A and B), no significant differences were observed expect for 5,6-chrysenequinone, phthalic anhydride, 1,2-naphthalic anhydride and 2,3-naphthalenedicarboxylic anhydride with higher quantities determined using ethyl acetate, ACN and DCM. Overall, DCM and ACN QuEChERS based extraction yielded the higher mass extracted for OPAHs.

Finally, ACN seemed to provide the best compromise and was selected for the NPAHs and OPAHs QuEChERS-like extraction protocol. Additionally, this solvent is less toxic than PLE used solvents and fully compatible with the PAH extraction protocol, based on QuEChERS approach, developed previously [51].

3.3. Clean-up SPE phase

Preliminary tests were made using dispersive-SPE (d-SPE) with various sorbents or sorbent mixture including Florisil, SiO₂, Al₂O₃/SiO₂, PSA (primary secondary amine) and C18 (5.5 ml of supernatant put in a tube with about 200 mg of sorbent/sorbent mixture following by vortex agitation for about 1-2 min) . Using d-SPE, resulting chromatograms were not clean (insufficient purification of the sample extracts with high baseline level and numerous and large interfering peaks) and did not allow the quantification of the targeted compounds. Probably, the equilibrium between solid and liquid phases was not reached and/or always broken during the agitation process even using a large amount of sorbent (> 200 mg). Purification of the extracts using d-SPE for the analysis of NPAHs and OPAHs will need further investigations.

Five SPE phases (or combination) [(Al₂O₃, SiO₂, C18, NH₂, GCB (graphitized carbon black)] (500 mg, 3 ml; Macherey Nagel, Hoerdt, France) were investigated to determine the sample extract

purification and NPAH/OPAH recovery efficiencies. On a qualitative point of view, the chromatograms of the Figures S6 and S7 showed that the clean-up efficiencies using C18 and GCB were not as good as the other phases (higher baseline level, numerous large interfering peaks on the chromatograms). Additionally, using GCB, peaks of the target NPAHs and OPAHs cannot be observed on the chromatograms (full adsorption of NPAHs and OPAHs by GCB). Using this sorbent, surrogate recoveries were very low (Fig. S8) and finally, GCB phase was not selected. If surrogate recoveries were similar for NH₂ (except for 1,4-naphtoquinone-d6), Si and Al₂O₃/SiO₂ (always lower using PLE as for previous results, see section 3.2), they were, for anthraquinone-d9, 9-nitroanthracene-d9 and 3-nitrofluoranthene-d9, significantly higher, even over 100% using C18 (150 – 250 %). This was due to the poor extract purification using this phase inducing an overestimation of the surrogates (Figs. S8 and S9). Other phases provided similar qualitative results with clean chromatograms (Fig. S9).

Quantitative results are shown on Figures 5 and 6. Due to the overestimation of surrogates using C18, NPAH and OPAH quantities determined were significantly lower than for the other phases. Additionally, for some compounds (e.g. dinitropyrenes), the standard deviations obtained using this SPE phase were larger (Fig. 5B). Overall, with NH₂, quantities determined were similar than for Al₂O₃/SiO₂ (PLE and QuEChERS) and SiO₂. However, this phase seemed not suitable for the quantification of aldehyde OPAHs with systematically lower quantities found in comparison to other SPE phases. Additionally 1,4-naphtoquinone-d6 recoveries were very low with this phase. According to the qualitative and quantitative results, Al₂O₃/SiO₂ and SiO₂ seemed the most suitable phases and the best compromise for the simultaneous quantification of the 64 target compounds. Between purification efficiency and time, the use of Si phase was the best compromise and was selected for the final NPAH and OPAH analytical procedure.

3.4. Extraction time

Influence of the agitation time (vortex) on the NPAH and OPAH extraction efficiencies was evaluated. Figure 7 displays the results obtained for some compounds. After 30 s of agitation, NPAH and OPAH extraction was almost complete and the extraction efficiency reached a plateau after 1.5 min of agitation. Longer extraction time until 5 min did not improve the extraction efficiency. An extraction time (vortex agitation) of 1.5 min was selected for the QuEChERS-like extraction procedure. A similar agitation time was already selected for the analysis of PAH in a previous work [51].

3.5. Method demonstration and validation on standard reference materials

Two SRMs (NIST 1649b and 2787) were analysed to validate the developed extraction procedure. Experimentally determined concentrations were compared with the available indicative, reference or certified concentrations and the concentrations determined using PLE (Figs. S10 and S11). For SRM 1649b (urban dust), a comparison of the NPAH and OPAH concentrations determined in this study and those available in the literature for SRM 1649, 1649a or 1649b, is also displayed on Tables 2 and 3. It can be emphasised that this study constitutes the first report in the literature of numerous compound concentrations notably for OPAHs and oxygenated compounds (aldehydes and acid anhydrides). For SRM 2787, except some certified NPAH concentrations values, results obtained here were never reported before (Tables 4 and 5).

For both SRMs, the mean experimental concentrations using PLE and QuEChERS-like extraction methods were in good agreement (Tables 2, 3, 4 and 5; Figs S10 and S11). Significant differences were only observed for few compounds namely 3-nitrodibenzofuran, phthalic anhydride (only for SRM 1649b for these both compounds), 2,3-naphthalenedicarboxylic anhydride, 1,2-naphthalic anhydride, 2-nitrofluorene, 9,10-phenanthrenequinone (these last two compounds were

not detected using PLE). Among them, phthalic anhydride, 1,2-naphthalic anhydride, 2,3-naphthalenedicarboxylic anhydride were compounds really difficult to calibrate (see section 2.5).

The results obtained were consistent with the indicative, reference or certified concentrations with the exception of 9-nitroanthracene in SRM 2787 and in a lesser extent, with benzanthrone in SRM 1649b (NIST indicative value). For SRM 1649b, NPAH and OPAH concentrations were also consistent with the values reported previously by various authors for the different versions of SRM 1649 (urban dust) [2,15,18-20,23,28,34,59,73,74]. We only noted a significant difference for 9-nitroanthracene reported recently by Schantz et al. (2012) [74]. In both cases, SRM 1649b and 2787, the high extraction temperatures (200 and 150 °C, respectively in [74] and [60]) used for the extraction could explain the differences observed for this NPAH.

All the results obtained demonstrated the validity of the QuEChERS-like extraction procedure developed in this study for the analysis of atmospheric particulate NPAHs and OPAHs.

3.6. Evaluation of the uncertainties of measurement

Uncertainties of measurement were evaluated by the GUM approach (guide to the expression of uncertainty in measurement) [75]. In both cases, PLE and QuEChERS, 90 % of the total uncertainty (sampling + analysis) is due to the analytical procedure. Details and results of the calculations are reported in the SI. Using PLE, they were in the range 36 - 580 % and for QuEChERS-like extraction procedure; they ranged from 22 to 586 % (Table S2). For both, larger uncertainties were observed for 3-nitrobiphenyl, 5-nitroacenaphthene, 2-nitropyrene, 4-nitropyrene and 6-nitrochrysene due to their low concentration in the SRM 1649b or 2787. By comparison, total uncertainty of the measurement of benzo[a]pyrene (B[a]P) is about 40% [75] (< 50% in agreement with the European standard method NF EN 15549).

4. Conclusions

A QuEChERS-like extraction procedure was developed for the analysis of particle-bound oxygenated and nitrated PAHs. Several improvements were also made on the analytical GC/NICI-MS conditions including the GC injection and the MS parameters. The final analytical procedure enabled the simultaneous quantification of 32 NPAHs and 32 OPAHs (or oxygenated compounds). For fortified ambient air particle samples, identical results were obtained using both, the QuEChERS-like approach and the commonly used extraction method PLE. The validation of the method was achieved with the analysis of two aerosol standard reference materials (NIST SRM 1649b and 2787; urban dust and PM₁₀). Results obtained were in good agreement with both, PLE and concentration values from the NIST and the literature. For numerous OPAHs (or oxygenated compounds) and NPAHs, this work constitutes the first report of their concentrations in both SRMs.

Finally, QuEChERS-like extraction procedure constitutes a simple and efficient method with a minimum of sample handling and steps allowing time saving. A relatively rapid extraction time (only 1.5 min for the simultaneous extraction of up to 60 samples) implies that about 60 “ready to analyse” samples can be processed per working day (sample extraction and purification). The cheap cost per sample extraction can be accounted to the low solvent consumption (7 ml of ACN) and because no costly material investment (< 6 k€) and no maintenance are required. Additionally, one of the main advantages is the QuEChERS-like extraction procedure is a soft extraction technique performed at room temperature preserving the sample integrity. No problem of degradation or formation of by-products is likely to occur unlike PLE as previously demonstrated for OPAHs [40].

Finally, this work showed that QuEChERS-like extraction procedures are fully adapted to the molecular chemical characterization of atmospheric organic aerosol and could be extended to other categories of compounds (e.g. hopanes, steranes, PCBs, PBDEs, pesticides, molecular source tracers, SOA typical compounds...). Further improvements could be achieved by incorporating a d-SPE step as an alternative to SPE used for sample extract clean-up.

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Supplementary information

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/XXXXXXXXXX>

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Figure Captions

Fig. 1. Influence of the injection temperature on the chromatographic response of selected NPAHs and OPAHs. Standard solution at $500 \text{ pg } \mu\text{l}^{-1}$, $1 \text{ } \mu\text{l}$ injected ($n=3$). Pulsed pressure mode at 30 psi. Full scan acquisition mode and determination of the response based on the peak area of quantification ions reported in Table 1.

Fig. 2. Typical reconstituted GC/MS total ion chromatogram obtained for a standard solution of NPAHs and OPAHs ($500 \text{ pg } \mu\text{l}^{-1}$, $1 \text{ } \mu\text{l}$ injected, SIM acquisition mode). For compounds/peak number identification refers to Table 1. Numbers in red refer to surrogate standards and in blue, to internal standards.

Fig. 3. Comparison of the average NPAH quantities extracted according to the extraction solvent used (A: low molecular weight NPAHs, B: high molecular weight NPAHs). Fortified filter punches ($\varnothing=37 \text{ mm}$) (50 ng added, $50 \text{ } \mu\text{l}$ of a $1 \text{ ng } \mu\text{l}^{-1}$ NPAH and OPAH standard solution mixture) originated from the same PM_{10} ambient air filter sample ($n=3$). The error bars show the standard deviation for the triplicate experiments. Extraction solvent for PLE was DCM. QuEChERS extraction time of 1.5 min. For both extractions methods, same clean-up procedure applied using SPE $\text{Al}_2\text{O}_3/\text{SiO}_2$.

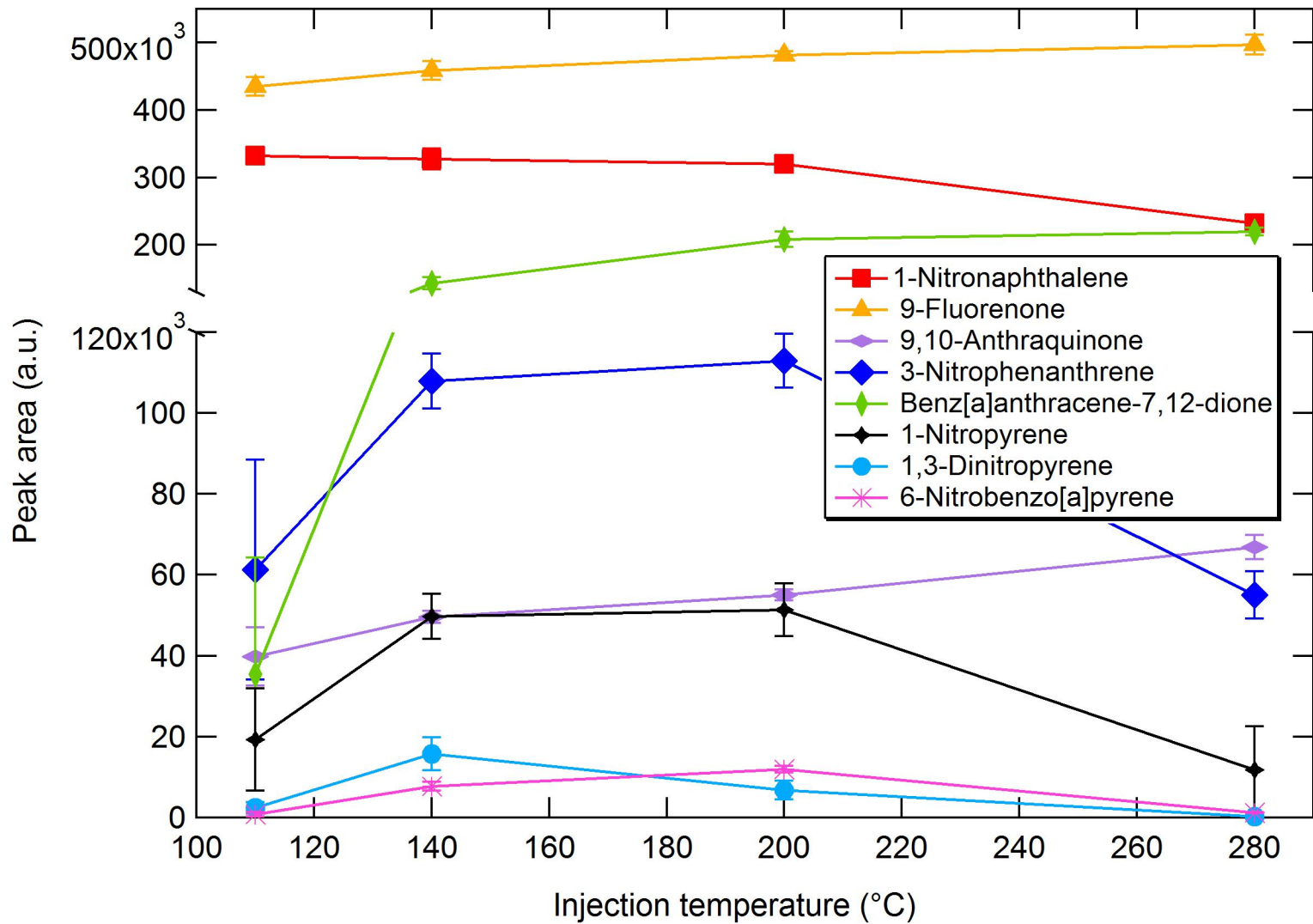
Fig. 4. Comparison of the average OPAH quantities extracted according to the extraction solvent used (A: ketone and quinone OPAHs, B: aldehyde and acid anhydride OPAHs and oxygenated compounds). Fortified filter punches ($\varnothing=37 \text{ mm}$) (50 ng added, $50 \text{ } \mu\text{l}$ of a $1 \text{ ng } \mu\text{l}^{-1}$ NPAH and OPAH standard solution mixture) originated from the same PM_{10} ambient air

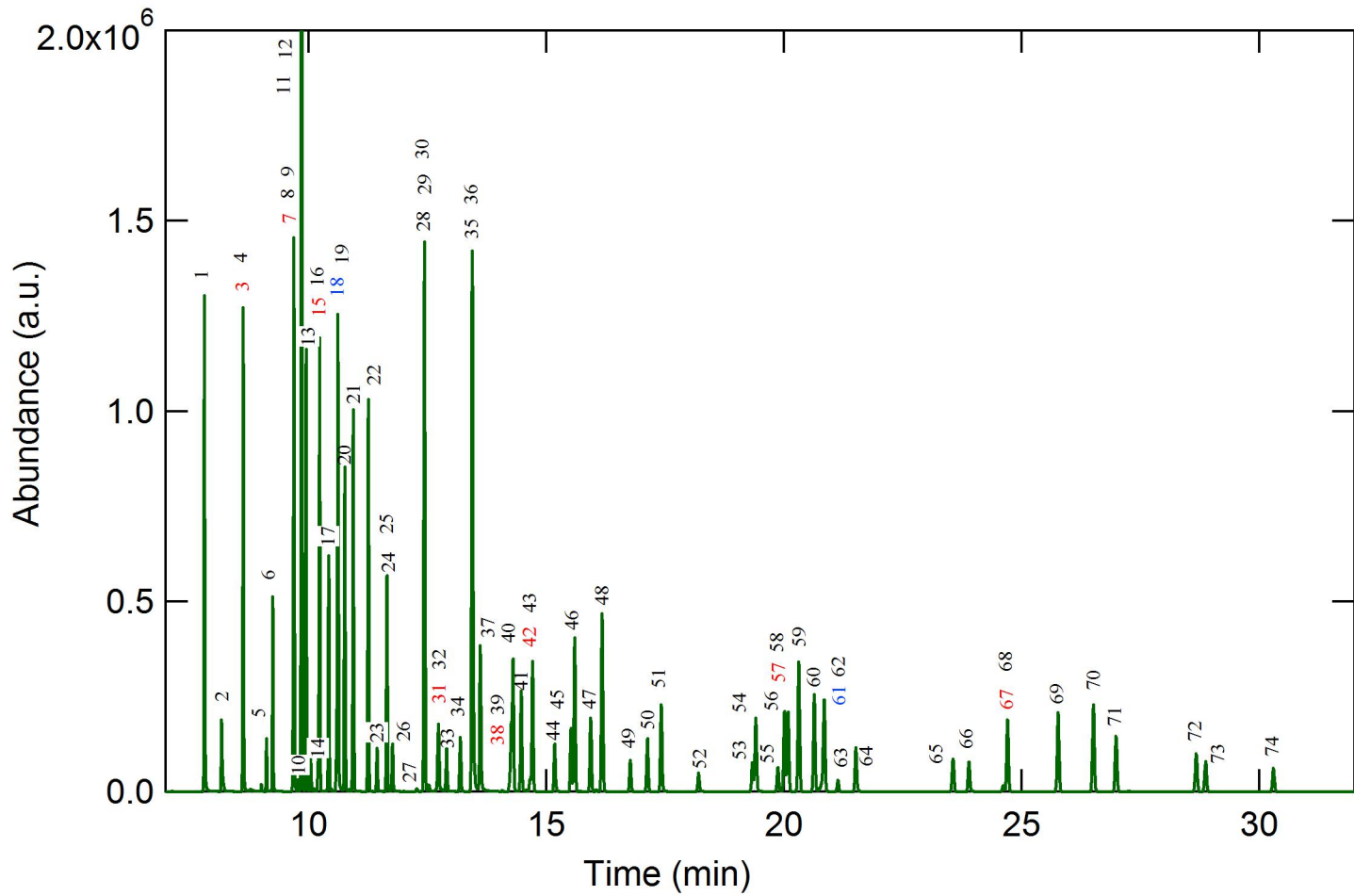
filter sample (n=3). The error bars correspond to the standard deviation for the triplicate experiments. Same analytical conditions as in Fig. 3.

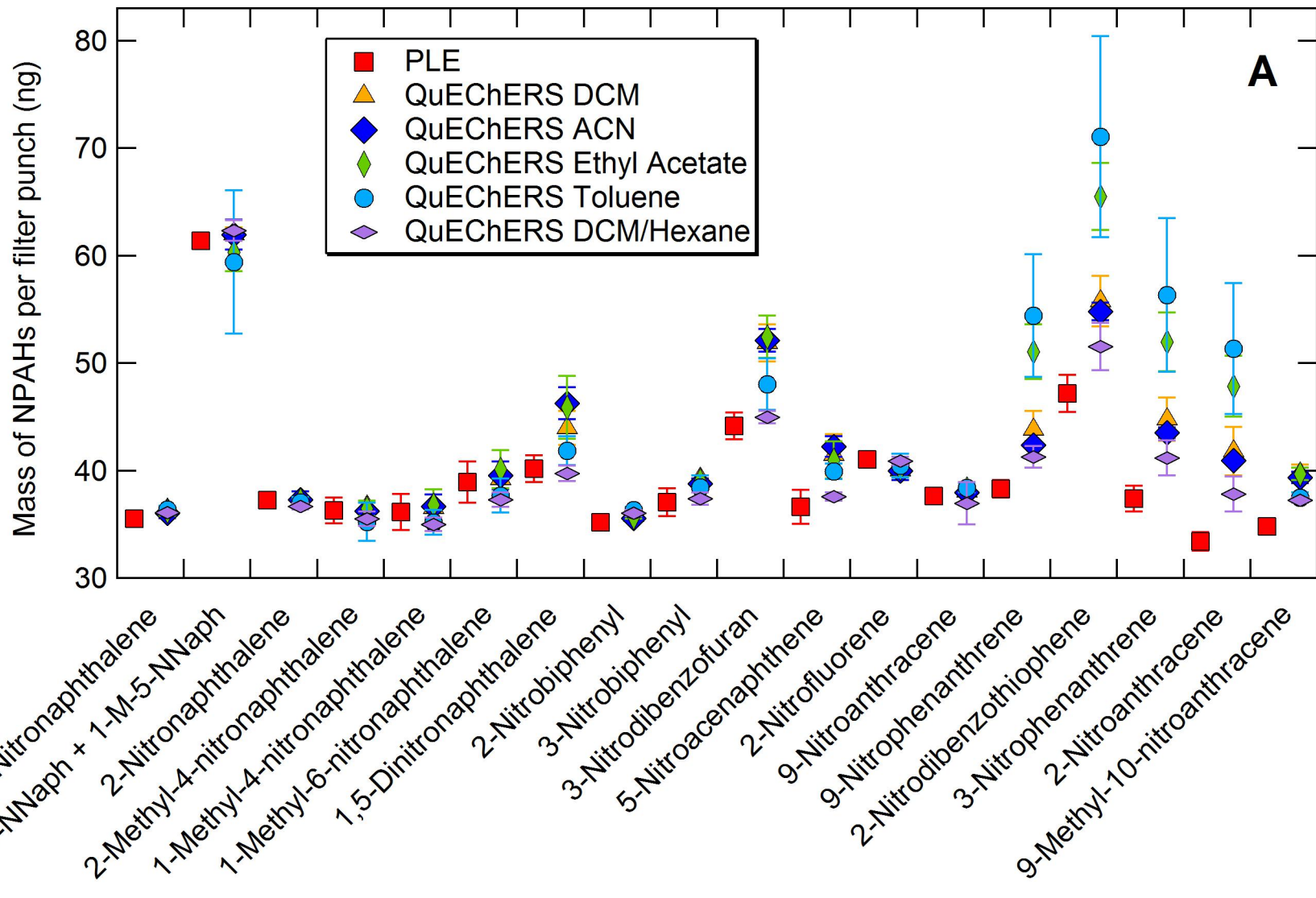
Fig. 5. Comparison of the average NPAH quantities determined according to the phase used for SPE clean-up (A: low molecular weight NPAHs, B: high molecular weight NPAHs). Fortified filter punches ($\varnothing=47$ mm) (5 ng added, 5 μl of a 1 ng μl^{-1} NPAH and OPAH standard solution mixture) originated from the same PM_{10} ambient air filter sample (n=3). The error bars correspond to the standard deviation for the triplicate experiments. Extraction solvent for PLE was DCM and SPE clean-up was performed using Al_2O_3 and SiO_2 cartridges. Same final elution mixture for all SPE phases (9 ml of DCM/pentane, 35/65, v/v). Solvent for QuEChERS-like extraction procedure was ACN and extraction time of 1.5 min.

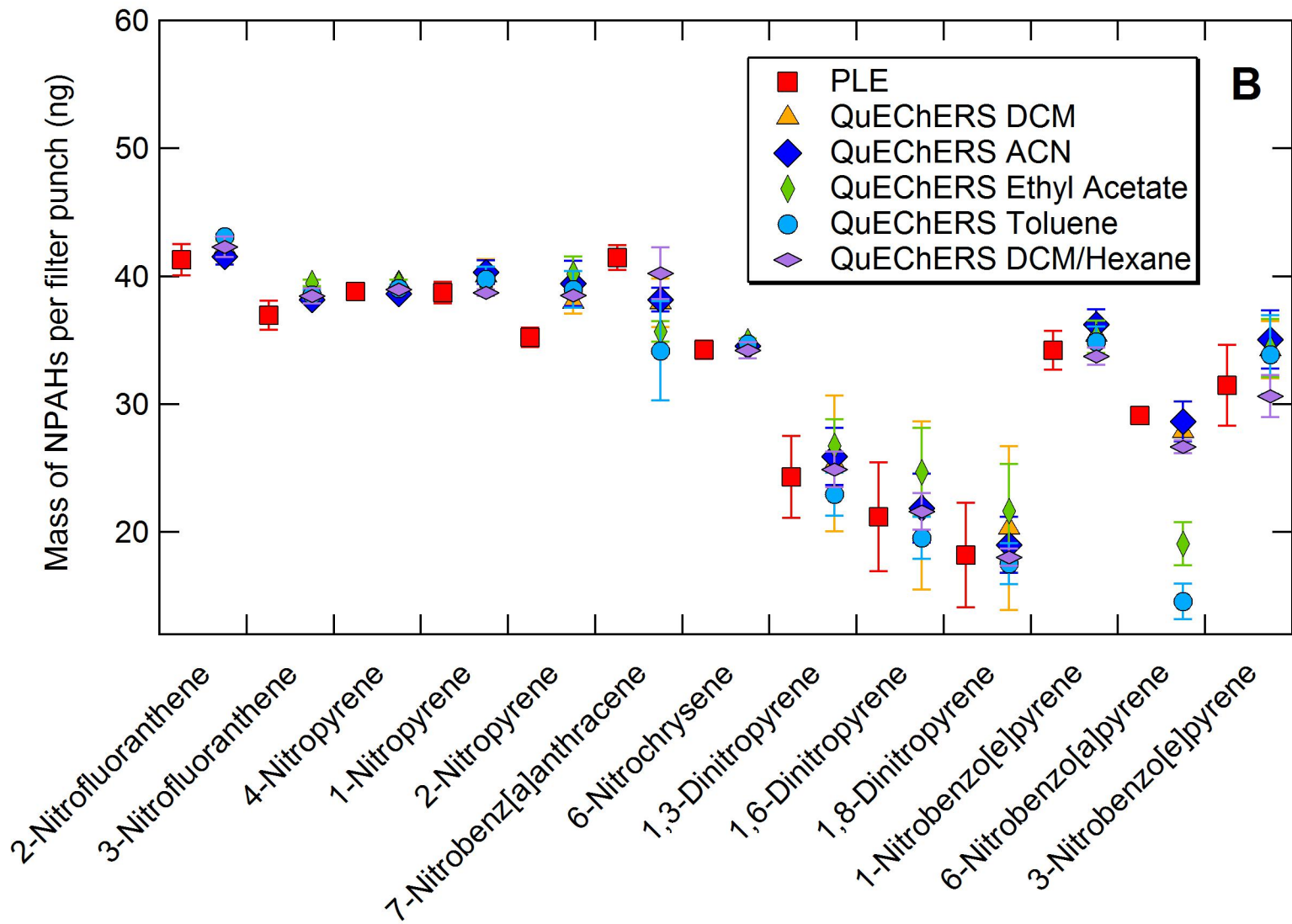
Fig. 6. Comparison of the average OPAH quantities determined according to the phase used for SPE clean-up (A: ketone and quinone OPAHs, B: aldehyde and acid anhydride OPAHs and oxygenated compounds). Fortified filter punches ($\varnothing=47$ mm) (5 ng added, 5 μl of a 1 ng μl^{-1} NPAH and OPAH standard solution mixture) originated from the same PM_{10} ambient air filter sample (n=3). The error bars correspond to the standard deviation for the triplicate experiments. Same analytical conditions as in Fig. 5.

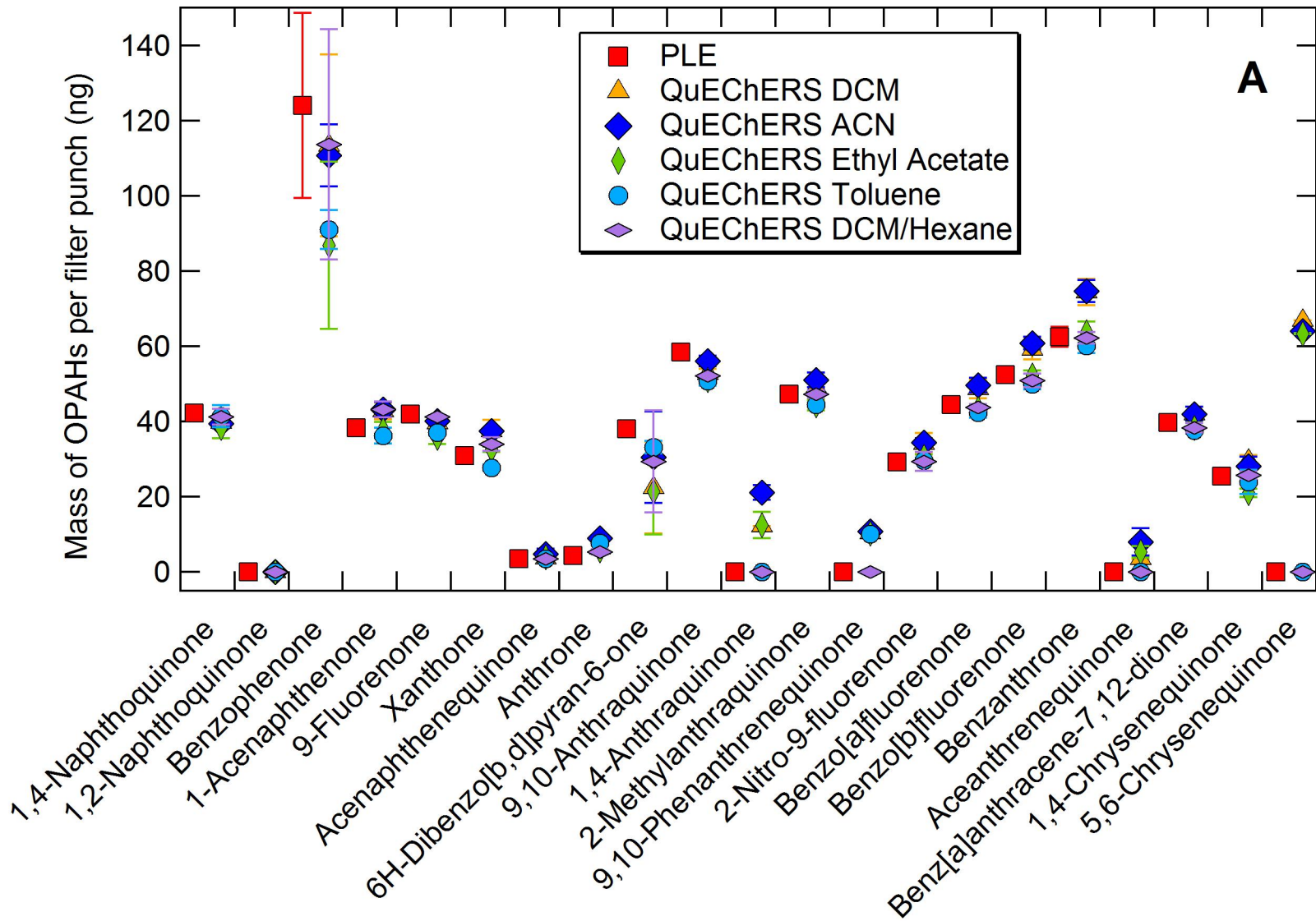
Fig. 7. Comparison of the average quantities extracted for selected NPAHs and OPAHs according to the time of agitation in the QuEChERS-like extraction procedure. Fortified filter punches ($\varnothing=47$ mm) (5 ng added, 5 μl of a 1 ng μl^{-1} NPAH and OPAH standard solution mixture) originated from the same PM_{10} ambient air filter sample (n=3). The error bars correspond to the standard deviation for the triplicate experiments. Extraction solvent was acetonitrile (ACN) and SiO_2 SPE clean-up was used.

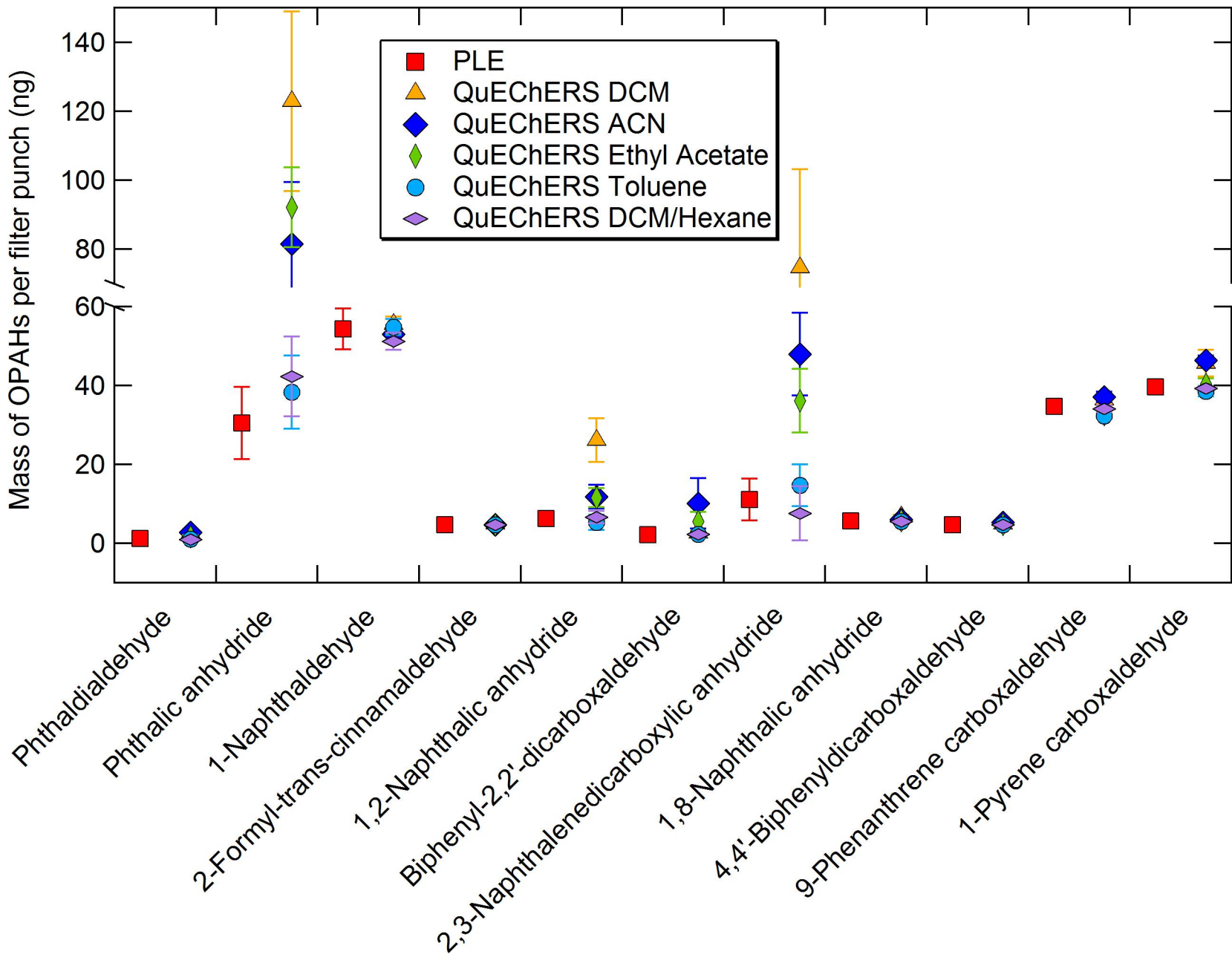


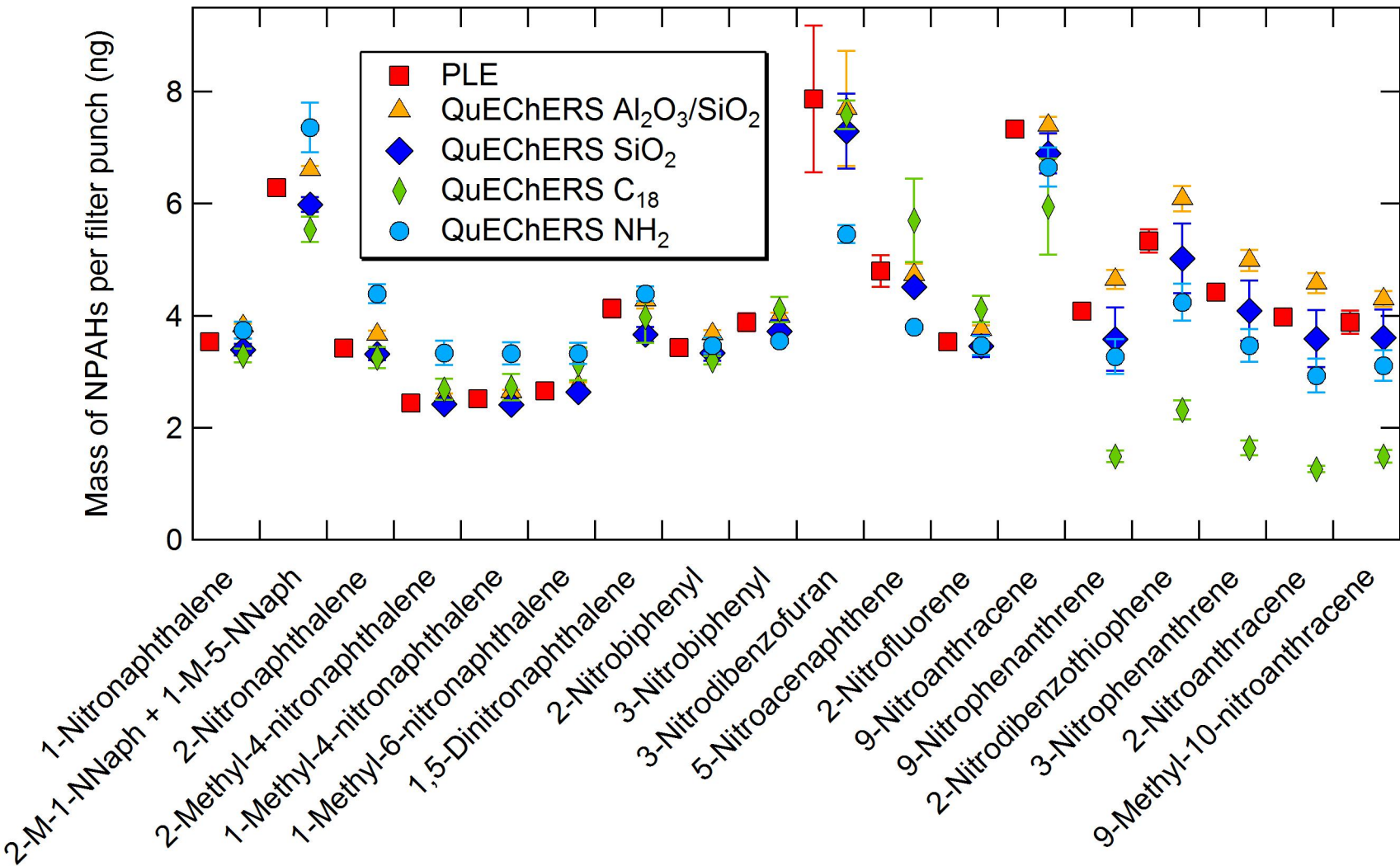


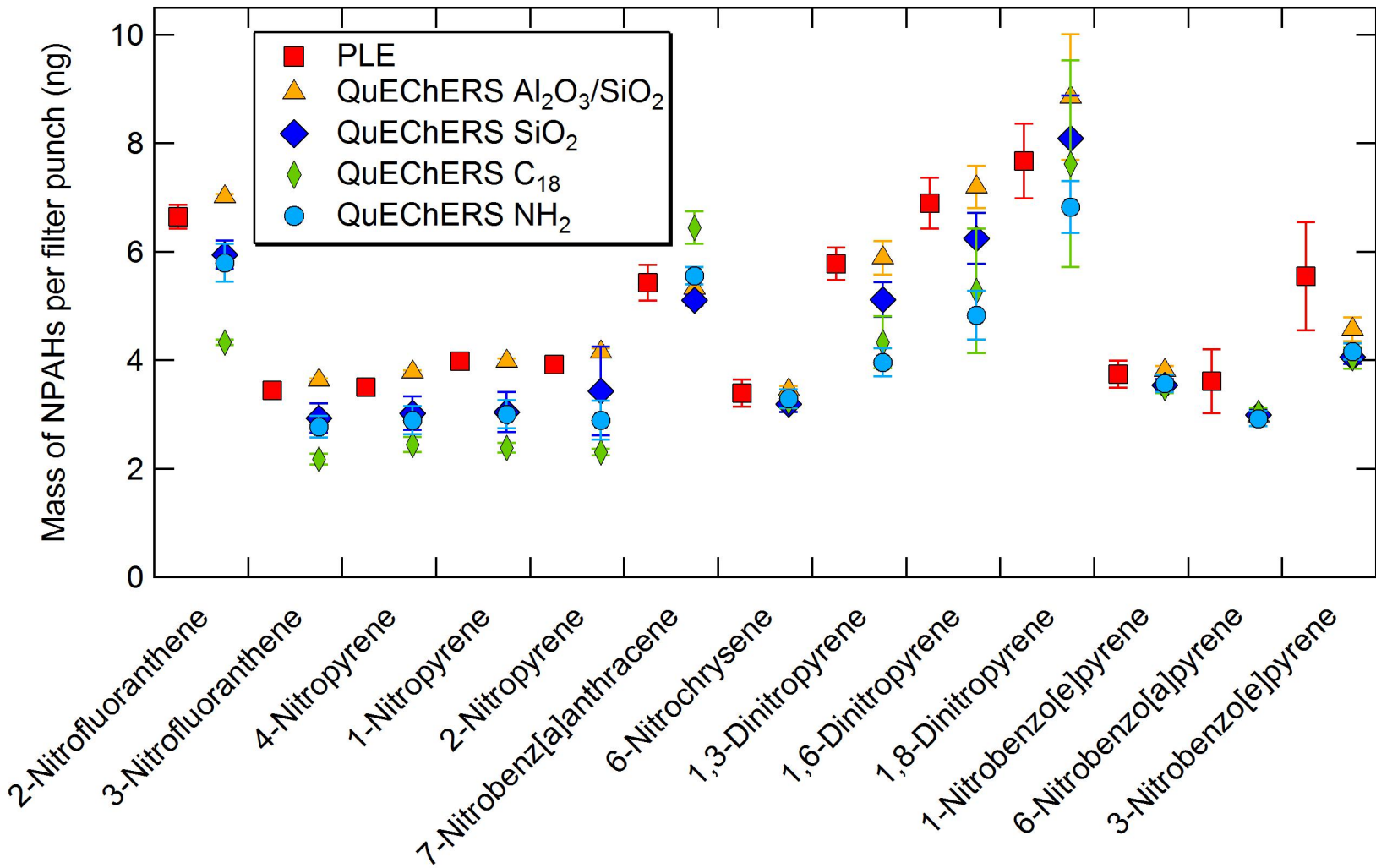


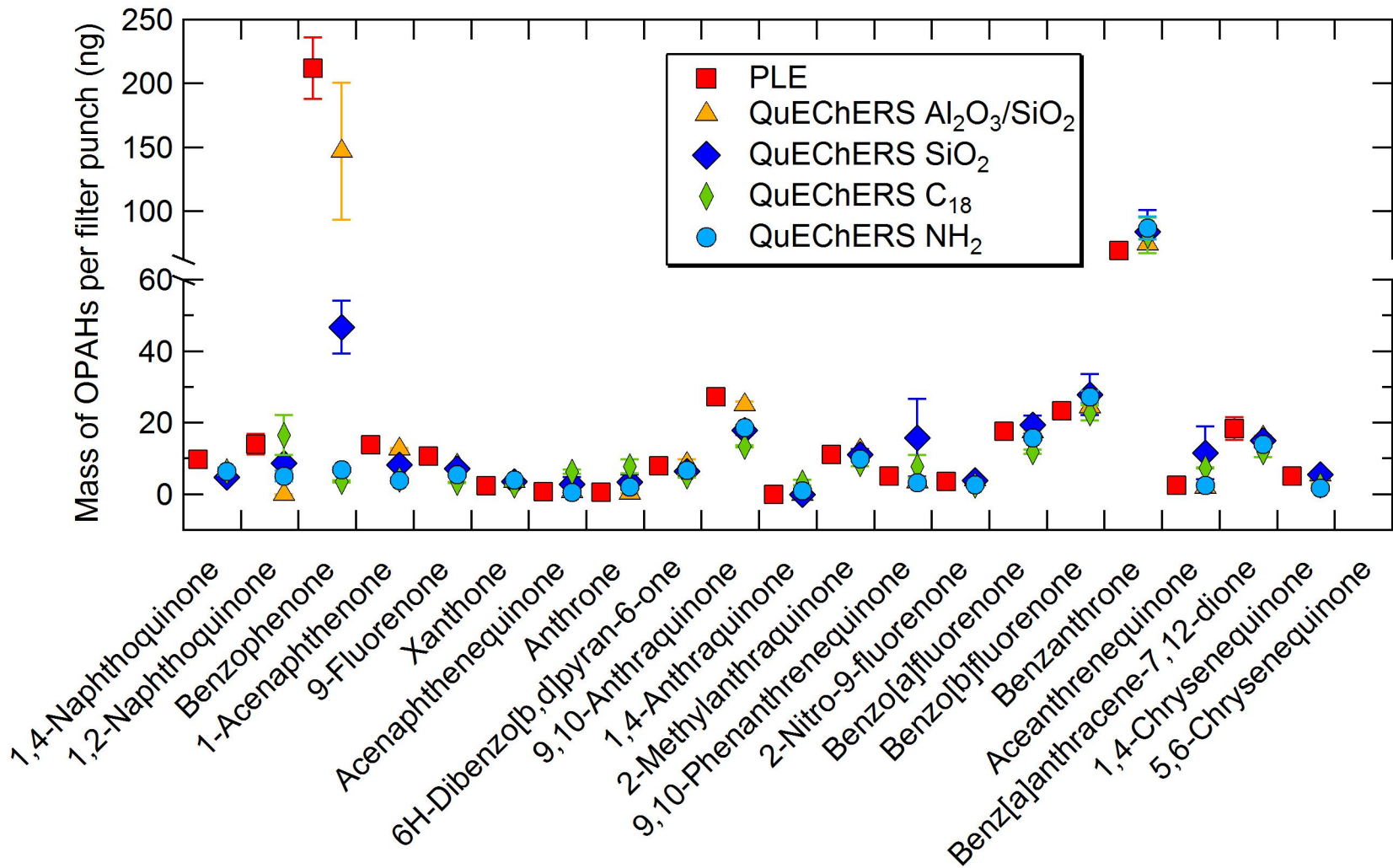


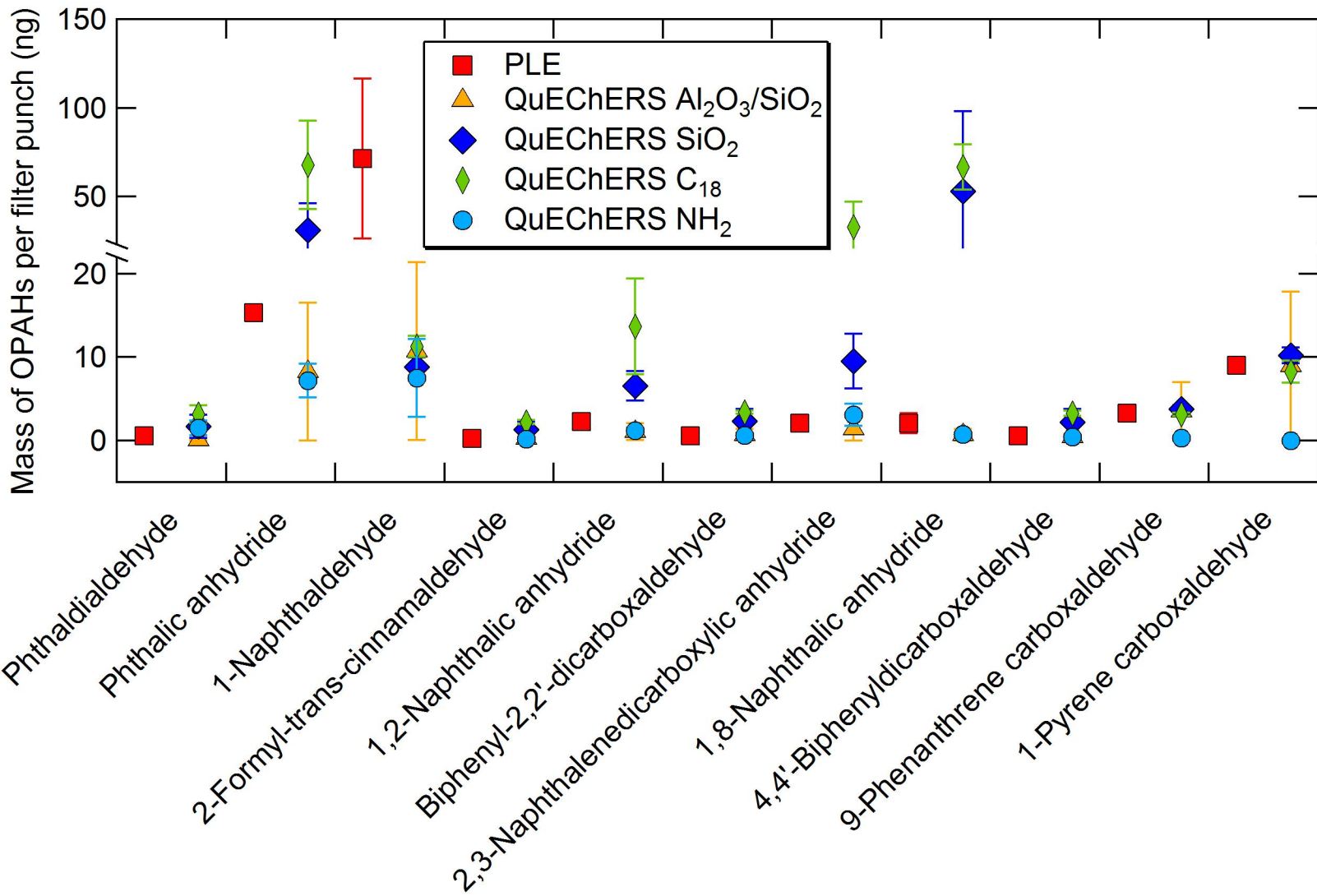












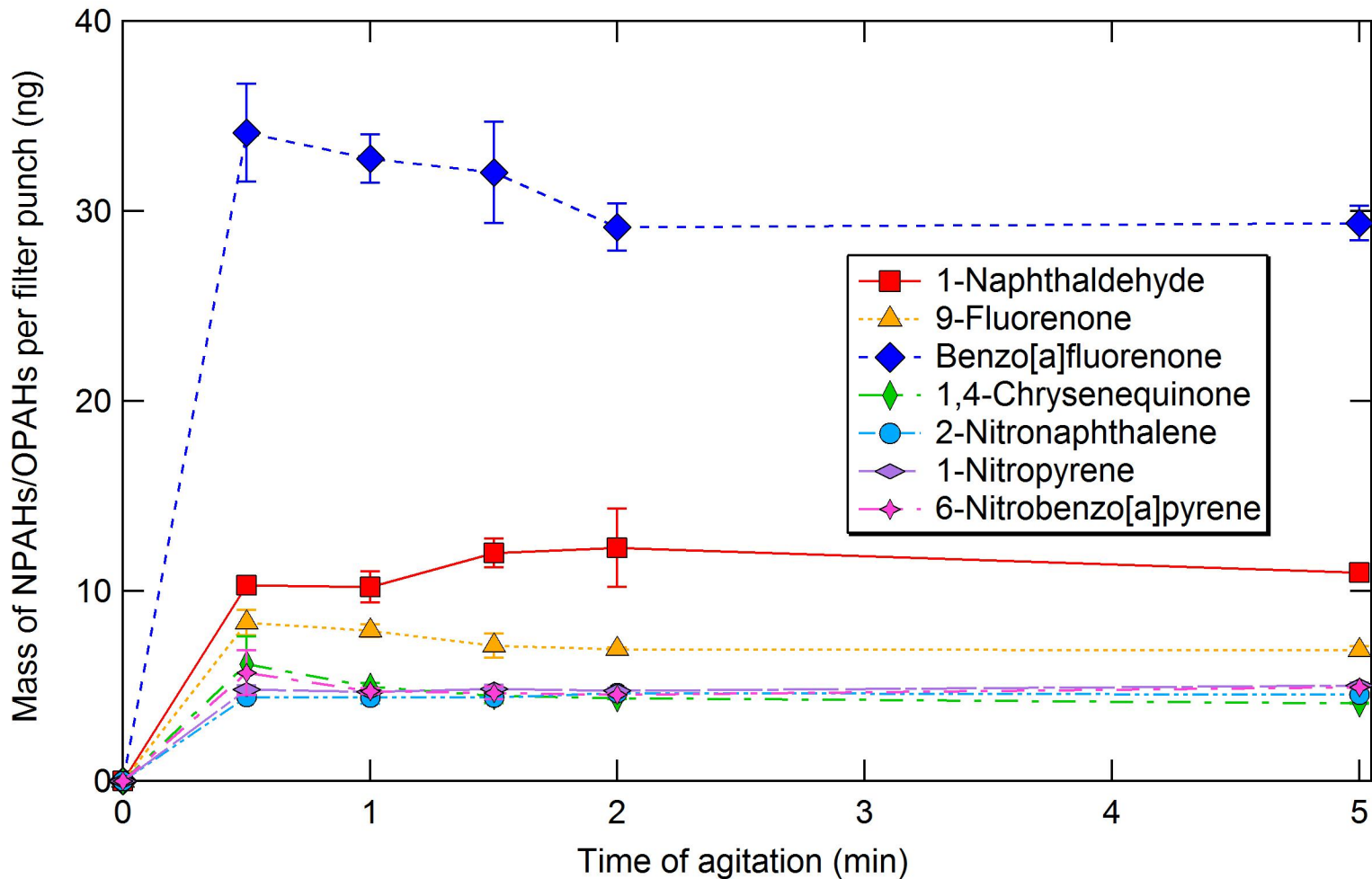


Table 1 GC/MS parameters for OPAH, oxygenated compound and NPAH analysis and chromatogram peak identification number

Compounds	Peak number	Monitored ions (m/z)	Retention time (min)	Dwell time (s)	LOQ ^b (pg)
<i>OPAHs and oxygenated compounds</i>					
<i>1,4-Naphthoquinone-d₆</i>	3	164	8.62	0.06	-
Phthaldialdehyde	1	134	7.81	0.06	0.06
1,4-Naphthoquinone	4	158	8.63	0.06	0.03
1-Naphthaldehyde	5	156	9.12	0.10	0.50
<i>Anthraquinone-d₈</i>	31	216	12.70	0.03	-
Phthalic anhydride	2	148	8.17	0.06	0.08
2-Formyl-trans-cinnamaldehyde	6	160	9.25	0.10	0.71
1,2-Naphthoquinone	9	158	9.70	0.10	30.96
Benzophenone	10	182	9.78	0.10	0.30
1-Acenaphthenone	14	168	10.06	0.10	0.78
<i>9-Fluorenone-d₈</i>	18	188	10.59	0.10	-
9-Fluorenone	19	180	10.62	0.10	0.02
1,2-Naphthalic anhydride	23	198	11.45	0.04	0.36
Biphenyl-2-2'-dicarboxaldehyde	24	210	11.65	0.04	0.22
Xanthone	25	196	11.65	0.04	2.63
Acenaphthenequinone	26	182	11.77	0.04	3.06
2,3-Naphthalenedicarboxylic anhydride	27	198	12.28	0.03	24.63
Anthrone	29	194	12.54	0.03	13.74
6H-Dibenzo[b,d]pyran-6-one	30	196	12.54	0.03	22.73
9,10-Anthraquinone	32	208	12.75	0.03	0.72
1,8-Naphthalic anhydride	35	198	13.45	0.03	0.14
1,4-Anthraquinone	36	208	13.45	0.03	12.82
4,4'-Biphenyldicarboxaldehyde	37	210	13.62	0.03	1.74
2-Methylanthraquinone	39	222	14.27	0.04	0.66
9-Phenanthrene carboxaldehyde	41	206	14.48	0.04	0.77
9,10-Phenanthrenequinone	44	208	15.19	0.06	7.32
2-Nitro-9-fluorenone	45	225	15.53	0.06	2.75
Benzo[a]fluorenone	51	230	17.42	0.10	0.68
Benzo[b]fluorenone	52	230	18.21	0.10	2.38
Benzanthrone	53	230	19.35	0.10	1.96
1-Pyrene carboxaldehyde	54	230	19.42	0.10	2.12
Aceanthrenequinone	55	232	19.88	0.06	4.78
Benz[a]anthracene-7,12-dione	60	258	20.64	0.06	0.46
1,4-Chrysenequinone	64	258	21.52	0.06	2.54
5,6-Chrysenequinone	66	258	23.89	0.08	19.55
<i>NPAHs</i>					
<i>1-Nitronaphthalene-d₇</i>	7	180	9.67	0.10	-
1-Nitronaphthalene	8	173	9.70	0.10	0.04
2-Methyl-1-NN + 1-Methyl-5-NN ^a	11, 12	187	9.86	0.10	0.02
2-Nitronaphthalene	13	173	9.95	0.10	0.18
2-Nitrobiphenyl	16	199	10.24	0.10	0.06
2-Methyl-4-nitronaphthalene	17	187	10.43	0.10	0.19
1-Methyl-4-nitronaphthalene	20	187	10.77	0.10	0.23
1-Methyl-6-nitronaphthalene	21	187	10.95	0.10	0.40
3-Nitrobiphenyl	22	199	11.26	0.04	0.48
1,5-Dinitronaphthalene	28	218	12.44	0.03	0.39
<i>2-Nitrobiphenyl-d₉</i>	15	208	10.20	0.10	-
2-Nitrobiphenyl	16	199	10.24	0.10	0.06
3-Nitrobiphenyl	22	199	11.26	0.04	0.48
3-Nitrodibenzofuran	33	213	12.91	0.03	2.46
5-Nitroacenaphthene	34	199	13.20	0.03	1.24
2-Nitrofluorene	40	211	14.31	0.04	0.40
<i>9-Nitroanthracene-d₉</i>	42	232	14.66	0.04	-
9-Nitroanthracene	43	223	14.72	0.04	0.19
9-Nitrophenanthrene	46	223	15.61	0.06	0.39
2-Nitrodibenzothiophene	47	229	15.95	0.06	2.09
3-Nitrophenanthrene	48	223	16.19	0.06	0.81
2-Nitroanthracene	49	223	16.78	0.06	4.93
9-Methyl-10-nitroanthracene	50	237	17.14	0.10	0.32
<i>3-Nitrofluoranthene-d₉</i>	57	256	20.04	0.06	-
2-Nitrofluoranthene	56	247	20.02	0.06	0.49
3-Nitrofluoranthene	58	247	20.10	0.06	0.57
4-Nitropyrene	59	247	20.32	0.06	0.37
<i>1-Nitropyrene-d₉</i>	61	256	20.80	0.06	-
1-Nitropyrene	62	247	20.86	0.06	0.52
2-Nitropyrene	63	247	21.14	0.06	2.31
<i>6-Nitrochrysene-d₁₁</i>	67	284	24.61	0.08	-
7-Nitrobenz[a]anthracene	65	273	23.56	0.08	1.59
6-Nitrochrysene	68	273	24.71	0.08	0.79
1,3-Dinitropyrene	69	292	25.77	0.25	0.60
1,6-Dinitropyrene	70	292	26.51	0.25	1.75
1,8-Dinitropyrene	71	292	26.99	0.25	8.82
1-Nitrobenzo[e]pyrene	72	297	28.68	0.25	0.96
6-Nitrobenzo[a]pyrene	73	297	28.88	0.25	1.32
3-Nitrobenzo[e]pyrene	74	297	30.30	0.25	2.21

^a 2-Methyl-1-nitronaphthalene + 1-Methyl-5-nitronaphthalene; ^b Instrumental limits of quantification.

In bold and italic: surrogates standards; In italic: internal standards.

Table 2 NPAH concentrations ($\mu\text{g kg}^{-1}$) in SRM 1649b (urban dust).

Compounds	<i>NPAHs</i>						
	This work ^a	This work ^b	NIST ^c	Schantz et al., 2012 ^d	Albinet et al., 2006 ^e	Wise et al., 2006 ^f	Mirivel et al., 2010 ^g
	PLE	QuEChERS	SRM 1649b	SRM1649b	SRM 1649a	SRM 1649a	SRM 1649a
1-Nitronaphthalene	10.6 (2.3) ^h	9.2 (3.4)	7.2 (0.1)	7.8 (0.2)	12.5 (2.6)	6.8 (0.3)	-
2-Methyl-1-NN + 1-Methyl-5-NN ^k	26.0 (11.9)	26.2 (11.6)	-	-	-	-	-
2-Nitronaphthalene	17.7 (5.2)	14.4 (5.1)	11.4 (0.3)	12.3 (1.1)	12.0 (2.4)	10.0 (0.5)	< 816
2-Methyl-4-nitronaphthalene	9.3 (4.1)	9.0 (4.0)	-	-	-	-	-
1-Methyl-4-nitronaphthalene	12.6 (4.3)	12.8 (3.8)	-	-	-	-	-
1-Methyl-6-nitronaphthalene	14.9 (6.3)	14.0 (5.7)	-	-	-	-	-
1,5-Dinitronaphthalene	14.1 (6.9)	15.6 (6.7)	-	-	-	-	246.0 (18.0)
2-Nitrobiphenyl	7.9 (3.1)	7.5 (3.2)	-	-	-	< 5	-
3-Nitrobiphenyl	16.6 (6.6)	15.7 (5.8)	3.5 (0.1)	3.9 (0.2)	-	3.6 (0.5)	-
3-Nitrodibenzofuran	700.9 (124.4)	123.3 (14.2)	-	-	-	-	-
5-Nitroacenaphthene	10.2 (3.8)	12.5 (2.1)	3.1 (0.1)	3.7 (0.2)	-	3.1 (0.3)	-
2-Nitrofluorene	nd ⁱ	53.0 (45.2)	-	-	< 0.4	< 2	< 531
9-Nitroanthracene	36.1 (5.9)	25.7 (3.6)	34.6 (0.7)	255.0 (38.0)	39.1 (4.2)	33.4 (6.1)	< 124
9-Nitrophenanthrene	11.4 (4.6)	15.3	1.8 (0.1)	1.7 (0.1)	1.9 (0.5)	1.7 (0.1)	-
2-Nitrodibenzothiophene	41.3 (18.7)	39.7 (13.1)	-	-	-	-	-
3-Nitrophenanthrene	43.0 (9.5)	29.2 (9.0)	22.1 (0.3)	20.1 (0.4)	34.0 (3.4)	22.0 (0.6)	-
2-Nitroanthracene	33.4 (17.4)	55.7 (23.0)	-	-	-	-	-
9-Methyl-10-nitroanthracene	35.2 (5.2)	61.5 (42.3)	-	-	-	-	-
2-Nitrofluoranthene	322.8 (26.2)	261.9 (29.7)	311.0 (5.0)	307.0 (13.0)	316.1 (47.4)	313.0 (38.0)	-
3-Nitrofluoranthene	ND ^j	ND	4.6 (0.1)	4.1 (0.2)	ND	4.5 (1.8)	< 110
4-Nitropyrene	13.7 (3.0)	27.3 (7.1)	5.5 (0.1)	-	6.0 (0.9)	5.5 (0.6)	-
1-Nitropyrene	104.1 (11.9)	60.9 (9.0)	71.8 (1.3)	73.2 (2.3)	104.5 (6.4)	70.9 (4.3)	123.0 (3.0)
2-Nitropyrene	41.0 (12.0)	42.0 (3.2)	10.8 (0.3)	11.1 (0.5)	190.0 (51.4)	24.4 (4.0)	< 302
7-Nitrobenz[a]anthracene	69.3 (11.4)	35.2 (3.1)	24.2 (0.7)	24.0 (1.8)	11.1 (7.2)	27.8 (6.7)	< 75
6-Nitrochrysene	11.6 (6.3)	18.8 (6.9)	3.8 (0.1)	3.3 (0.1)	1.8 (0.3)	4.01 (0.52)	< 71
1,3-Dinitropyrene	nd	nd	-	-	< 4	< 2	-
1,6-Dinitropyrene	9.8 (2.4)	45.3 (61.8)	-	-	< 3	< 4	-
1,8-Dinitropyrene	29.4 (5.2)	61.8 (33.5)	-	-	< 4	< 2	-
1-Nitrobenzo[e]pyrene	20.1 (4.7)	22.8 (4.7)	-	-	-	< 7	-
6-Nitrobenzo[a]pyrene	79.9 (11.6)	66.6 (14.6)	-	-	25.0 (6.7)	< 40	< 37
3-Nitrobenzo[e]pyrene	58.5 (5.1)	45.3 (14.1)	-	-	-	< 5	-

^a GC/NICI-MS (5% phenyl-methylpolysiloxane column phase), PLE (DCM), n= 6 (3×20 mg; 3×50mg). Concentrations corrected from the moisture content (=3.88 %, moisture analyser HR 73, Mettler Toledo).

^b GC/NICI-MS (5% phenyl-methylpolysiloxane column phase), QuEChERS (ACN), n=6 (3×20 mg; 3×50 mg). Concentrations corrected from the moisture content (=3.88 %, moisture analyser HR 73, Mettler Toledo).

^c [59] GC/NICI-MS (50% phenyl-methylpolysiloxane column phase), PLE (DCM).

^d [74] GC/NICI-MS (50% phenyl-methylpolysiloxane column phase), PLE (Toluene, 200 °C, 13.8 MPa).

^e [18], GC/NICI-MS (5% phenyl-methylpolysiloxane column phase), PLE (DCM).

^f [73], GC/NICI-MS (50% phenyl-methylpolysiloxane column phase), Soxhlet and PLE (DCM).

^g [28], UPLC-APCI-ToFMS, PLE (methanol).

^h Mean concentration (standard deviation).

ⁱ not detected.

^j not determined (2- and 3-nitrofluoranthene separation not achieved using 5% phenyl-methylpolysiloxane column phase).

^k 2-Methyl-1-nitronaphthalene + 1-Methyl-5-nitronaphthalene.

Table 2 NPAH concentrations ($\mu\text{g kg}^{-1}$) in SRM 1649b (urban dust).

Compounds	<i>NPAHs</i>						
	This work ^a	This work ^b	NIST ^c	Schantz et al., 2012 ^d	Albinet et al., 2006 ^e	Wise et al., 2006 ^f	Mirivel et al., 2010 ^g
	PLE	QuEChERS	SRM 1649b	SRM1649b	SRM 1649a	SRM 1649a	SRM 1649a
1-Nitronaphthalene	10.6 (2.3) ^h	9.2 (3.4)	7.2 (0.1)	7.8 (0.2)	12.5 (2.6)	6.8 (0.3)	-
2-Methyl-1-NN + 1-Methyl-5-NN ^k	26.0 (11.9)	26.2 (11.6)	-	-	-	-	-
2-Nitronaphthalene	17.7 (5.2)	14.4 (5.1)	11.4 (0.3)	12.3 (1.1)	12.0 (2.4)	10.0 (0.5)	< 816
2-Methyl-4-nitronaphthalene	9.3 (4.1)	9.0 (4.0)	-	-	-	-	-
1-Methyl-4-nitronaphthalene	12.6 (4.3)	12.8 (3.8)	-	-	-	-	-
1-Methyl-6-nitronaphthalene	14.9 (6.3)	14.0 (5.7)	-	-	-	-	-
1,5-Dinitronaphthalene	14.1 (6.9)	15.6 (6.7)	-	-	-	-	246.0 (18.0)
2-Nitrobiphenyl	7.9 (3.1)	7.5 (3.2)	-	-	-	< 5	-
3-Nitrobiphenyl	16.6 (6.6)	15.7 (5.8)	3.5 (0.1)	3.9 (0.2)	-	3.6 (0.5)	-
3-Nitrodibenzofuran	700.9 (124.4)	123.3 (14.2)	-	-	-	-	-
5-Nitroacenaphthene	10.2 (3.8)	12.5 (2.1)	3.1 (0.1)	3.7 (0.2)	-	3.1 (0.3)	-
2-Nitrofluorene	nd ⁱ	53.0 (45.2)	-	-	< 0.4	< 2	< 531
9-Nitroanthracene	36.1 (5.9)	25.7 (3.6)	34.6 (0.7)	255.0 (38.0)	39.1 (4.2)	33.4 (6.1)	< 124
9-Nitrophenanthrene	11.4 (4.6)	15.3	1.8 (0.1)	1.7 (0.1)	1.9 (0.5)	1.7 (0.1)	-
2-Nitrodibenzothiophene	41.3 (18.7)	39.7 (13.1)	-	-	-	-	-
3-Nitrophenanthrene	43.0 (9.5)	29.2 (9.0)	22.1 (0.3)	20.1 (0.4)	34.0 (3.4)	22.0 (0.6)	-
2-Nitroanthracene	33.4 (17.4)	55.7 (23.0)	-	-	-	-	-
9-Methyl-10-nitroanthracene	35.2 (5.2)	61.5 (42.3)	-	-	-	-	-
2-Nitrofluoranthene	322.8 (26.2)	261.9 (29.7)	311.0 (5.0)	307.0 (13.0)	316.1 (47.4)	313.0 (38.0)	-
3-Nitrofluoranthene	ND ^j	ND	4.6 (0.1)	4.1 (0.2)	ND	4.5 (1.8)	< 110
4-Nitropyrene	13.7 (3.0)	27.3 (7.1)	5.5 (0.1)	-	6.0 (0.9)	5.5 (0.6)	-
1-Nitropyrene	104.1 (11.9)	60.9 (9.0)	71.8 (1.3)	73.2 (2.3)	104.5 (6.4)	70.9 (4.3)	123.0 (3.0)
2-Nitropyrene	41.0 (12.0)	42.0 (3.2)	10.8 (0.3)	11.1 (0.5)	190.0 (51.4)	24.4 (4.0)	< 302
7-Nitrobenz[a]anthracene	69.3 (11.4)	35.2 (3.1)	24.2 (0.7)	24.0 (1.8)	11.1 (7.2)	27.8 (6.7)	< 75
6-Nitrochrysene	11.6 (6.3)	18.8 (6.9)	3.8 (0.1)	3.3 (0.1)	1.8 (0.3)	4.01 (0.52)	< 71
1,3-Dinitropyrene	nd	nd	-	-	< 4	< 2	-
1,6-Dinitropyrene	9.8 (2.4)	45.3 (61.8)	-	-	< 3	< 4	-
1,8-Dinitropyrene	29.4 (5.2)	61.8 (33.5)	-	-	< 4	< 2	-
1-Nitrobenzo[e]pyrene	20.1 (4.7)	22.8 (4.7)	-	-	-	< 7	-
6-Nitrobenzo[a]pyrene	79.9 (11.6)	66.6 (14.6)	-	-	25.0 (6.7)	< 40	< 37
3-Nitrobenzo[e]pyrene	58.5 (5.1)	45.3 (14.1)	-	-	-	< 5	-

^a GC/NICI-MS (5% phenyl-methylpolysiloxane column phase), PLE (DCM), n= 6 (3×20 mg; 3×50mg). Concentrations corrected from the moisture content (=3.88 %, moisture analyser HR 73, Mettler Toledo).

^b GC/NICI-MS (5% phenyl-methylpolysiloxane column phase), QuEChERS (ACN), n=6 (3×20 mg; 3×50 mg). Concentrations corrected from the moisture content (=3.88 %, moisture analyser HR 73, Mettler Toledo).

^c [59] GC/NICI-MS (50% phenyl-methylpolysiloxane column phase), PLE (DCM).

^d [74] GC/NICI-MS (50% phenyl-methylpolysiloxane column phase), PLE (Toluene, 200 °C, 13.8 MPa).

^e [18], GC/NICI-MS (5% phenyl-methylpolysiloxane column phase), PLE (DCM).

^f [73], GC/NICI-MS (50% phenyl-methylpolysiloxane column phase), Soxhlet and PLE (DCM).

^g [28], UPLC-APCI-ToFMS, PLE (methanol).

^h Mean concentration (standard deviation).

ⁱ not detected.

^j not determined (2- and 3-nitrofluoranthene separation not achieved using 5% phenyl-methylpolysiloxane column phase).

^k 2-Methyl-1-nitronaphthalene + 1-Methyl-5-nitronaphthalene.

Table 3 OPAH and oxygenated compound concentrations ($\mu\text{g kg}^{-1}$) in SRM 1649b (urban dust).

<i>OPAHs and oxygenated compounds</i>											
Compounds	This work ^a	This work ^b	NIST ^c	Durant et al., 1998 ^d	Cho et al., 2004 ^e	Albinet et al., 2006 ^f	Mirivel et al., 2010 ^g	Layshock et al., 2010 ^h	Delgado-Saborit et al., 2013 ⁱ	Nocun et al., 2013 ^j	O'Connell et al., 2013 ^k
	PLE	QuEChERS	SRM 1649b	SRM 1649	SRM 1649a	SRM 1649a	SRM 1649a	SRM 1649b	SRM 1649b	SRM 1649b	SRM 1649b
<i>Ketones and quinones</i>											
1,4-Naphthoquinone	51 (41) ^l	61 (11)	-	-	240 (54)	-	-	-	390 (150)	-	250
1,2-Naphthoquinone	407 (36)	625 (274)	-	-	190 (26)	-	-	-	340 (90)	-	2800
Benzophenone	1257 (180)	698 (92)	-	-	-	-	-	-	-	-	-
1-Acenaphthenone	93.2 (46.6)	68 (11)	-	-	-	-	-	-	-	-	-
9-Fluorenone	1336 (105)	715 (88)	1400	1600 (110)	-	1110 (139)	-	780 (40)	-	1190 (70)	760
Xanthone	229 (80)	204 (22)	-	-	-	-	-	-	-	-	190
Acenaphthenequinone	40 (18)	49 (13)	-	-	-	-	-	-	3010 (140)	-	nd
Anthrone	45 (5)	54 (23)	-	-	-	-	-	-	-	-	-
6H-Dibenzo[b,d]pyran-6-one	772 (124)	702 (40)	-	-	-	-	-	-	-	-	-
9,10-Anthraquinone	2479 (213)	1748 (37)	1800	2700 (120)	2030 (192)	2238 (363)	2357 (183)	1600 (110)	1780 (220)	1390 (160)	2600
1,4-Anthraquinone	215 (17)	213 (71)	-	-	-	nd	-	nd	-	-	nd
2-Methylanthraquinone	841 (71)	846 (146)	-	-	-	-	986 (125)	-	370 (140)	-	-
9,10-Phenanthrenequinone	nd ^m	284 (126)	-	nd	1180 (130)	-	1133 (152)	-	1510 (120)	-	nd
2-Nitro-9-fluorenone	21 (9)	25 (7)	-	-	-	-	-	-	-	-	-
Benzo[a]fluorenone	3181 (355)	2875 (140)	-	1900 (210)	-	3512 (284)	-	1650 (90)	-	1880 (70)	780
Benzo[b]fluorenone	6407 (1054)	6880 (1216)	-	5010 (470)	-	4845 (812)	-	-	-	-	-
Benzanthrone *	7149 (533)	6977 (595)	1600	4500 (340)	-	3715 (872)	4661 (460)	4460 (500)	-	3130 (400)	1180
Aceanthrenequinone	52 (21)	89 (55)	-	-	-	-	-	-	-	-	nd
Benz[a]anthracene-7,12-dione *	5608 (206)	4862 (442)	3600	2400 (250)	-	8459 (797)	3442 (322)	2200 (150)	3370 (200)	3750 (190)	1400
1,4-Chrysenequinone	113 (26)	145 (49)	-	nd	-	-	-	-	-	-	-
5,6-Chrysenequinone	nd	nd	-	-	-	-	< 3734	-	-	-	-
<i>Aldehydes and acid anhydrides</i>											
Phthaldialdehyde	nd	nd	-	-	-	-	-	-	-	-	-
Phthalic anhydride	14135 (4834)	3107 (1247)	-	-	-	-	-	-	-	-	-
1-Naphthaldehyde	284 (98)	282 (46)	-	-	-	199 (59)	-	-	-	-	-
2-Formyl-trans-cinnamaldehyde	nd	2 (2)	-	-	-	-	-	-	-	-	-
1,2-Naphthalic anhydride	8107 (2742)	736 (150)	-	nd	-	-	-	-	-	-	-
Biphenyl-2,2'-dicarboxaldehyde	4 (3)	11 (2)	-	-	-	-	-	-	-	-	-
2,3-Naphthalenedicarboxylic anhydride	5996 (1608)	1563 (429)	-	-	-	-	-	-	-	-	-
1,8-Naphthalic anhydride	165 (345)	13589 (3276)	-	19000 (1500)	-	-	-	-	-	-	-
4,4'-Biphenyldicarboxaldehyde	16 (7)	16 (7)	-	-	-	-	-	-	-	-	-
9-Phenanthrene carboxaldehyde	54 (4)	50 (6)	-	-	-	247 (33)	-	-	-	-	-
1-Pyrene carboxaldehyde	156 (23)	183 (32)	-	-	-	-	-	-	-	-	-

^a GC/NICI-MS (5% phenyl-methylpolysiloxane column phase), PLE (DCM), n=6 (3×20 mg; 3×50 mg). Concentrations corrected from the moisture content (=3.88 %, moisture analyser HR 73, Mettler Toledo); ^b GC/NICI-MS (5% phenyl-methylpolysiloxane column phase), QuEChERS (ACN), n=6 (3×20 mg; 3×50 mg). Concentrations corrected from the moisture content (=3.88 %, moisture analyser HR 73, Mettler Toledo); ^c [59] Values from intercomparison program; ^d [2], GC/EI-MS (5% phenyl-methylpolysiloxane column phase), Soxhlet (DCM); ^e [34] GC/EI-MS (5% phenyl-methylpolysiloxane column phase), Sonication (DCM), derivatization procedure; ^f [18] GC/NICI-MS (5% phenyl-methylpolysiloxane column phase), PLE (DCM); ^g [28] UPLC-APCIToFMS, PLE (methanol); ^h [19] GC/EI-MS (5% phenyl-methylpolysiloxane column phase), PLE (DCM); ⁱ [20] GC/EI-MS (5% phenyl-methylpolysiloxane column phase), Sonication (DCM), derivatization procedure; ^j [23] GC/EI-MS (DB-XLB), PLE (DCM); ^k [15] GC/EI-MS (5% phenyl-methylpolysiloxane column phase), PLE (DCM); ^l Mean concentration (standard deviation); ^m not detected; * n = 3 (20 mg).

Table 4 NPAH concentrations ($\mu\text{g kg}^{-1}$) in SRM 2787 [Fine particulate matter ($<10 \mu\text{m}$)]

Compounds	<i>NPAHs</i>		
	This work ^a PLE	This work ^b QuEChERS	NIST ^c SRM 2787
1-Nitronaphthalene	11.5 (0.1) ^d	10.6 (1.6)	-
2-Methyl-1-NN + 1-Methyl-5-NN ^g	35.8 (0.1)	35.6 (0.0)	-
2-Nitronaphthalene	18.9 (0.1)	17.9 (0.4)	-
2-Methyl-4-nitronaphthalene	12.6 (0.2)	12.3 (0.1)	-
1-Methyl-4-nitronaphthalene	13.5 (0.2)	13.8 (0.4)	-
1-Methyl-6-nitronaphthalene	17.5 (0.2)	18.1 (0.4)	-
1,5-Dinitronaphthalene	20.9 (0.0)	21.6 (0.2)	-
2-Nitrobiphenyl	10.1 (0.1)	10.0 (0.0)	-
3-Nitrobiphenyl	26.2 (0.1)	27.2 (1.1)	-
3-Nitrodibenzofuran	95.5 (33.8)	76.9 (25.6)	-
5-Nitroacenaphthene	14.1 (2.2)	17.1 (2.0)	-
2-Nitrofluorene	nd ^e	36.4 (8.4)	-
9-Nitroanthracene	454.1 (2.4)	355.6 (22.0)	942.0 (55.0)
9-Nitrophenanthrene	18.4 (0.6)	16.1 (0.5)	12.5 (0.4)
2-Nitrodibenzothiophene	42.1 (1.1)	48.3 (2.9)	-
3-Nitrophenanthrene	51.9 (4.0)	42.4 (3.4)	26.2 (8.3)
2-Nitroanthracene	nd	nd	-
9-Methyl-10-nitroanthracene	33.6 (2.5)	33.8 (2.4)	-
2-Nitrofluoranthene	313.6 (20.6)	271.4 (14.3)	280.0 (34.0)
3-Nitrofluoranthene	ND ^f	ND	7.2 (0.7)
4-Nitropyrene	12.7 (1.3)	34.0 (3.6)	-
1-Nitropyrene	179.2 (21.3)	66.4 (1.6)	69.5 (3.0)
2-Nitropyrene	75.9 (19.7)	49.3 (3.2)	-
7-Nitrobenz[a]anthracene	105.5 (3.6)	70.8 (5.1)	98.9 (3.5)
6-Nitrochrysene	9.9 (1.2)	13.7 (2.1)	-
1,3-Dinitropyrene	nd	nd	-
1,6-Dinitropyrene	43.8 (1.7)	45.9 (1.3)	-
1,8-Dinitropyrene	53.7 (6.5)	76.1 (0.7)	-
1-Nitrobenzo[e]pyrene	nd	nd	-
6-Nitrobenzo[a]pyrene	113.1 (11.4)	72.3 (9.9)	-
3-Nitrobenzo[e]pyrene	141.6 (11.2)	52.7 (1.3)	-

^a GC/NICI-MS (5% phenyl-methylpolysiloxane column phase), PLE (DCM), n=3 (20 mg). Concentrations not corrected from the moisture content.

^b GC/NICI-MS (5% phenyl-methylpolysiloxane column phase), QuEChERS (ACN), n=3 (20 mg). Concentrations not corrected from the moisture content.

^c [60] GC/EI-MS (50% phenyl-methylpolysiloxane and dimethyl [50% liquid crystal] polysiloxane column phases), PLE (toluene).

^d Mean concentration (standard deviation).

^e not detected.

^f not determined (2- and 3-nitrofluoranthene separation not achieved using 5% phenyl-methylpolysiloxane column phase).

^g 2-Methyl-1-nitronaphthalene + 1-Methyl-5-nitronaphthalene.

Table 5 OPAH and oxygenated compound concentrations ($\mu\text{g kg}^{-1}$) in SRM 2787 [Fine particulate matter ($<10 \mu\text{m}$)]

<i>OPAHs and oxygenated compounds</i>		
Compounds	This work ^a PLE	This work ^b QuEChERS
<i>Ketones and quinones</i>		
1,4-Naphthoquinone	87 (3) ^c	144 (83)
1,2-Naphthoquinone	nd ^d	793 (20)
Benzophenone	4283 (989)	2034 (370)
1-Acenaphthenone	149 (28)	180 (31)
9-Fluorenone	2026 (150)	1021 (47)
Xanthone	164 (16)	315 (12)
Acenaphthenequinone	30 (2)	95 (28)
Anthrone	nd	297 (63)
6H-Dibenzo[b,d]pyran-6-one	2747 (164)	3312 (224)
9,10-Anthraquinone	6848 (447)	4489 (168)
1,4-Anthraquinone	nd	nd
2-Methylanthraquinone	1899 (132)	1671 (88)
9,10-Phenanthrenequinone	nd	nd
2-Nitro-9-fluorenone	22 (1)	27 (0)
Benzo[a]fluorenone	5864 (562)	5773 (262)
Benzo[b]fluorenone	5911 (837)	7350 (553)
Benzanthrone	3738 (554)	8194 (712)
Aceanthrenequinone	70 (6)	93 (8)
Benz[a]anthracene-7,12-dione	2592 (452)	2378 (209)
1,4-Chrysenoquinone	177 (1)	209 (7)
5,6-Chrysenoquinone	nd	nd
<i>Aldehydes and acid anhydrides</i>		
Phthalaldehyde	nd	nd -
Phthalic anhydride	2016 (164)	2038 (694)
1-Naphthaldehyde	2177 (609)	409 (25)
2-Formyl-trans-cinnamaldehyde	nd	1 (1)
1,2-Naphthalic anhydride	946 (421)	147 (84)
Biphenyl-2,2'-dicarboxaldehyde	8 (1)	14 (2)
2,3-Naphthalenedicarboxylic anhydride	146 (174)	575 (358)
1,8-Naphthalic anhydride	33 (2)	19473 (6033)
4,4'-Biphenyldicarboxaldehyde	23 (1)	23 (1)
9-Phenanthrene carboxaldehyde	156 (12)	149 (17)
1-Pyrene carboxaldehyde	340 (28)	367 (71)

^a GC/NICI-MS (5% phenyl-methylpolysiloxane column phase), PLE (DCM), n=3 (20 mg). Concentrations not corrected from the moisture content.

^b GC/NICI-MS (5% phenyl-methylpolysiloxane column phase), QuEChERS (ACN), n=3 (20 mg). Concentrations not corrected from the moisture content.

^c Mean concentration (standard deviation).

^d not detected.

**A simple QuEChERS-like extraction approach for molecular
chemical characterization of organic aerosols: application to
nitrated and oxygenated PAH derivatives (NPAH and OPAH)
quantified by GC-NICIMS**

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Table S1 List and characteristics of the chemicals and solvents used.

Compounds	Supplier	Purity
<i>OPAH and oxygenated compounds</i>		
1,2-Naphthalic anhydride	ABCR	98 %
1,2-Naphthoquinone	Sigma-Aldrich	97 %
1,4-Anthraquinone	Chiron	97.8 %
1,4-Chrysenequinone	Chiron	99 %
1,4-Naphthoquinone	Sigma-Aldrich	97 %
1,8-Naphthalic anhydride	Sigma-Aldrich	98 %
1-Acenaphthenone	ABCR	98 %
1-Naphthaldehyde	Sigma-Aldrich	95 %
1-Pyrene carboxaldehyde	Sigma-Aldrich	99 %
2,3-Naphthalenedicarboxylic anhydride	ABCR	95 %
2-Formyl-trans-cinnamaldehyde	Santai Labs	99 %
2-Methylanthraquinone	Sigma-Aldrich	> 95 %
2-Nitro-9-fluorenone	Sigma-Aldrich	99 %
4,4'-Biphenyldicarboxaldehyde	ABCR	97 %
5,6-Chrysenequinone	Chiron	99.8 %
6H-Dibenzo[b,d]pyran-6-one	Syntheval	97 %
9,10-Anthraquinone	Acros Organics	98 %
9,10-Phenanthrenequinone	Sigma-Aldrich	> 99 %
9-Fluorenone	Acros Organics	> 99 %
9-Phenanthrene carboxaldehyde	Sigma-Aldrich	97 %
Aceanthrenequinone	Sigma-Aldrich	96 %
Acenaphthenequinone	Sigma-Aldrich	> 90 %
Anthrone	Acros Organics	98 %
Benz[a]anthracene-7,12-dione	Acros Organics	99 %
Benzanthrone	Acros Organics	99 %
Benzo[a]fluorenone	Chiron	99.9 %
Benzo[b]fluorenone	Chiron	99.8 %
Benzophenone	Sigma-Aldrich	99 %
Biphenyl-2-2'-dicarboxaldehyde	ABCR	97 %
Phthaldialdehyde	Sigma-Aldrich	> 99 %
Phthalic anhydride	Sigma-Aldrich	> 99 %
Xanthone	Sigma-Aldrich	97 %

Table S1 (continued)

Compounds	Supplier	Purity
<i>NPAH</i>		
1,3-Dinitropyrene	Chiron	95.6 %
1,5-Dinitronaphthalene	Chiron	99.7 %
1,6-Dinitropyrene	Chiron	96.3 %
1,8-Dinitropyrene	Chiron	99.9 %
1-Methyl-4-nitronaphthalene	Chiron	> 99 %
1-Methyl-5-nitronaphthalene	Chiron	> 99.5 %
1-Methyl-6-nitronaphthalene	Chiron	> 99 %
1-Nitrobenzo[e]pyrene	Chiron	99.6 %
1-Nitronaphthalene	Chiron	99.9 %
1-Nitropyrene	Chiron	99 %
2-Methyl-1-nitronaphthalene	Chiron	> 99.5 %
2-Methyl-4-nitronaphthalene	Chiron	> 99 %
2-Nitroanthracene	Chiron	99.8 %
2-Nitrobiphenyl	Chiron	> 99 %
2-Nitrodibenzothiophene	Sigma-Aldrich	99 %
2-Nitrofluoranthene	Chiron	> 99 %
2-Nitrofluorene	Acros Organics	99 %
2-Nitronaphthalene	Chiron	99 %
2-Nitropyrene	Chiron	99.9 %
3-Nitrobenzo[e]pyrene	Chiron	95 %
3-Nitrobiphenyl	Sigma-Aldrich	99 %
3-Nitrodibenzofuran	Sigma-Aldrich	99 %
3-Nitrofluoranthene	Acros Organics	99 %
3-Nitrophenanthrene	Dr. Ehrenstorfer	99.7 %
4-Nitropyrene	Chiron	99.8 %
5-Nitroacenaphthene	Dr. Ehrenstorfer	90 %
6-Nitrobenzo[a]pyrene	Chiron	95 %
6-Nitrochrysene	Acros Organics	99 %
7-Nitrobenz[a]anthracene	AccuStandard	99 %
9-Methyl-10-nitroanthracene	Chiron	99 %
9-Nitroanthracene	Chiron	97.0 %
9-Nitrophenanthrene	Dr. Ehrenstorfer	99.5 %
<i>Deuterated NPAH and OPAH</i>		
1,4-Naphthoquinone-d6	C/D/N isotopes	> 99 %
1-Nitronaphthalene-d7	C/D/N isotopes	> 99 %
1-Nitropyrene-d9	C/D/N isotopes	> 99 %
2-Nitrobiphenyl-d9	C/D/N isotopes	> 99 %
2-Nitrofluorene-d9	C/D/N isotopes	> 99 %
3-Nitrofluoranthene-d9	C/D/N isotopes	> 99 %
6-Nitrochrysene-d11	C/D/N isotopes	> 99 %
9-Fluorenone-d8	C/D/N isotopes	> 99 %
9-Nitroanthracene-d9	C/D/N isotopes	> 99 %
Anthraquinone-d8	C/D/N isotopes	> 99 %
<i>Solvents</i>		
Acetone	Sigma-Aldrich	> 99.9 %
Acetonitrile	VWR	> 99.9 %
Dichloromethane	VWR	> 99.8 %
Ethyl Acetate	Sigma-Aldrich	> 99.7 %
Isooctane	Sigma-Aldrich	> 99 %
Hexane	Sigma-Aldrich	> 98.5 %
Pentane	Sigma-Aldrich	> 99 %
Toluene	Sigma-Aldrich	> 99.9 %
<i>Gases</i>		
Helium	Air Liquide	99.9999%
Nitrogen	Air Liquide	99.9999%
Methane	Air Liquide	99.9995 %

Calculation of uncertainties of measurement

Uncertainties of measurement of NPAH and OPAH concentrations were evaluated by the GUM approach (guide to the expression of uncertainty in measurement) [1]. Uncertainties due to the analytical procedure and to the sampling procedure were evaluated separately:

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

Analysis
Sampling

With:

- C : NPAH or OPAH mass concentration in the airborne sample
- \bar{f} : average response factor of the NPAH or OPAH
- A_E : compound peak area on the chromatogram
- A_{ISE} : surrogate peak area on the chromatogram
- m_{ISE} : mass of surrogate in the calibration solution
- m_{SSF} : mass of surrogate deposited directly on the filter sample
- R : recovery rate determined using a certified reference material (SRM)
- φ_{sam} : air sampling flow rate
- t : sampling duration

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

With:

- k : enlargement factor (equal to 2)

Table S2 Expanded measurement uncertainties of NPAH and OPAH atmospheric particulate concentrations evaluated by the GUM approach for PLE and QuEChERS-like extraction procedures and based on the analysis of NIST SRMs 1649b and 2787.

Compounds	U _{rel} (C)	U _{rel} (C)
	PLE (%) (SRM 1649b)	QuEChERS (%) (SRM 1649b)
1-Nitronaphthalene	90	102
2-Nitronaphthalene	123	107
3-Nitrobiphenyl	580	527
5-Nitroacenaphthene	364	378
3-Nitrophenanthrene	166	127
9-Nitroanthracene	43	44
2-Nitrofluoranthene	33	38
1-Nitropyrene	65	37
2-Nitropyrene	422	373
4-Nitropyrene	205	526
7-Nitrobenz[a]anthracene	344	107
6-Nitrochrysene	575	586
9-Fluorenone	41	69
9,10-Anthraquinone	69	48
Benanthrone	410	399
Benz[a]anthracene-7,12-dione	142	134

Compounds	U _{rel} (C)	U _{rel} (C)
	PLE (%) (SRM 2787)	QuEChERS (%) (SRM 2787)
9-Nitrophenanthrene	152	123
3-Nitrophenanthrene	76	62
9-Nitroanthracene	65	77
2-Nitrofluoranthene	36	32
1-Nitropyrene	193	22
7-Nitrobenz[a]anthracene	91	96

Calculations of uncertainties of measurement are based on samplings performed using high volume samplers DA-80 (Digitel Elektronik AG) ($30 \text{ m}^3 \text{ h}^{-1}$, 24 h, quartz fibre filters $\varnothing=150$ mm, Pallflex). We assumed that error made on filter punches ($\varnothing=47$ mm) is the same for both, PLE and QuEChERS-like extraction procedures, and could be considered as negligible (negligible losses of particles). Note that, about 90 % of the global uncertainty is due to the analytical procedure. Calculations were only made for the compounds for which indicative, reference or certified concentrations values are reported in the certificates of analysis of the NIST SRMs 1649b or 2787. Note that, the fact that certified concentration values do not exist for all the studied compounds increases artificially the global uncertainty. By neglecting this parameter, the uncertainties fall in the range 20 to 156 % for both, PLE and QuEChERS-like extraction procedures.

Additional figures

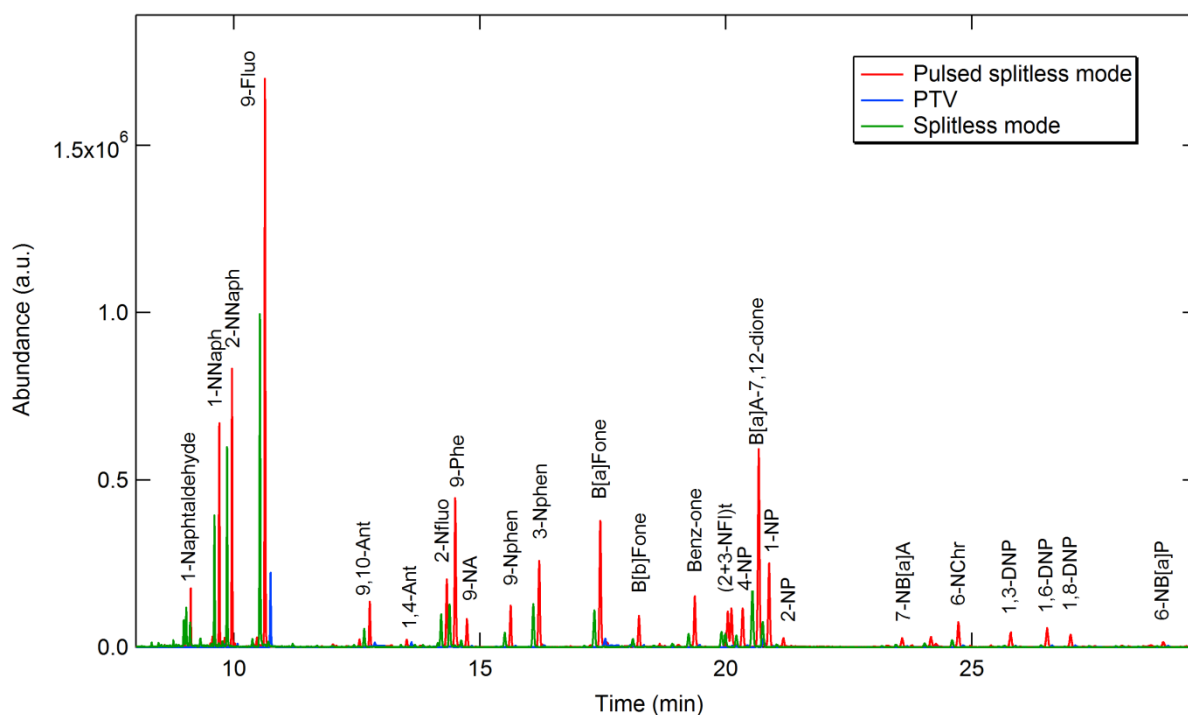


Fig. S1 Influence of the injection mode on the chromatographic response of NPAH and OPAH. Standard solution at $500 \text{ pg } \mu\text{L}^{-1}$, $1 \text{ } \mu\text{L}$ injected. Injection temperature at $280 \text{ }^\circ\text{C}$ for pulsed splitless (45 psi) and splitless mode. For PTV, initial injection temperature at $70 \text{ }^\circ\text{C}$ (1.7 min) then ramp ($900 \text{ }^\circ\text{C}/\text{min}$) until $320 \text{ }^\circ\text{C}$ (hold). Full scan acquisition mode (150 - 300 amu). Note that, the chromatographs were artificially shifted (+ 0.1 min offset) to observe the differences between them.

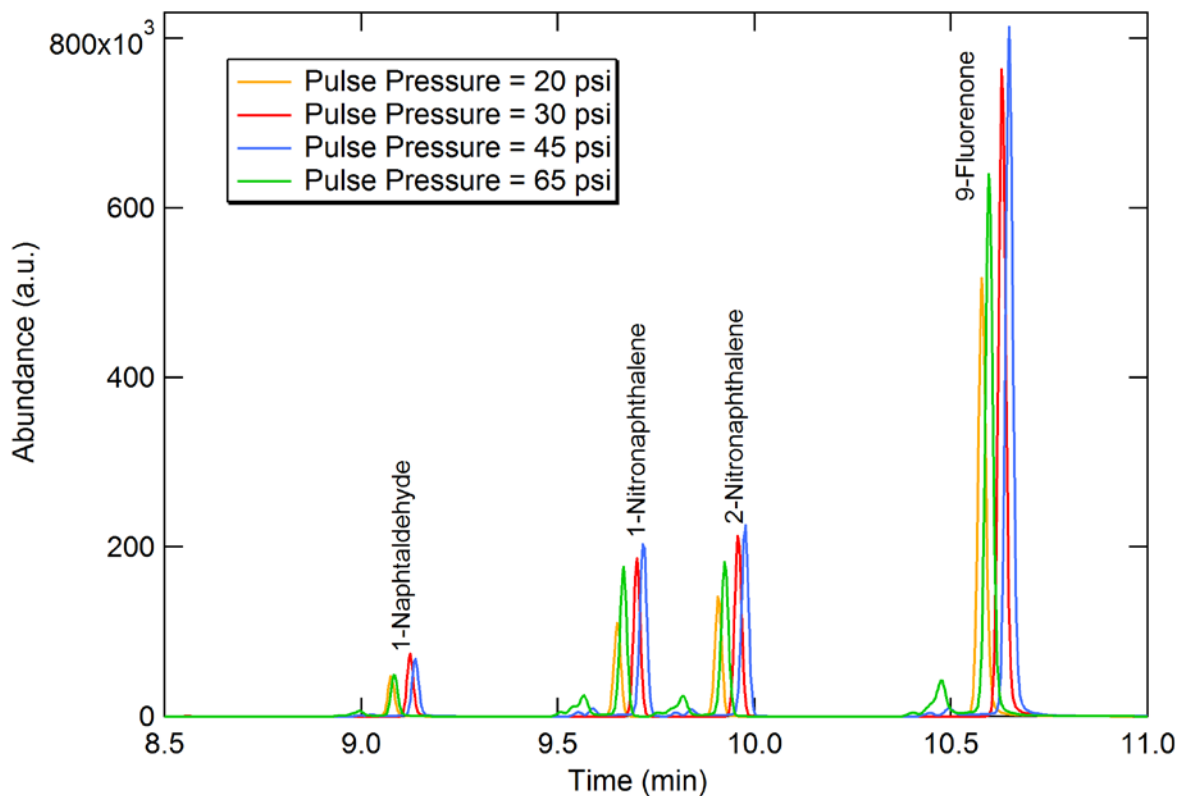


Fig. S2 Influence of the pulse pressure on the chromatographic response of lighter NPAH and OPAH. Standard solution at $50 \text{ pg } \mu\text{l}^{-1}$, $1 \text{ } \mu\text{l}$ injected. Injection temperature of $280 \text{ } ^\circ\text{C}$. SIM acquisition mode. Note that, the chromatographs were artificially shifted (+ 0.1 min offset) to observe the differences between them.

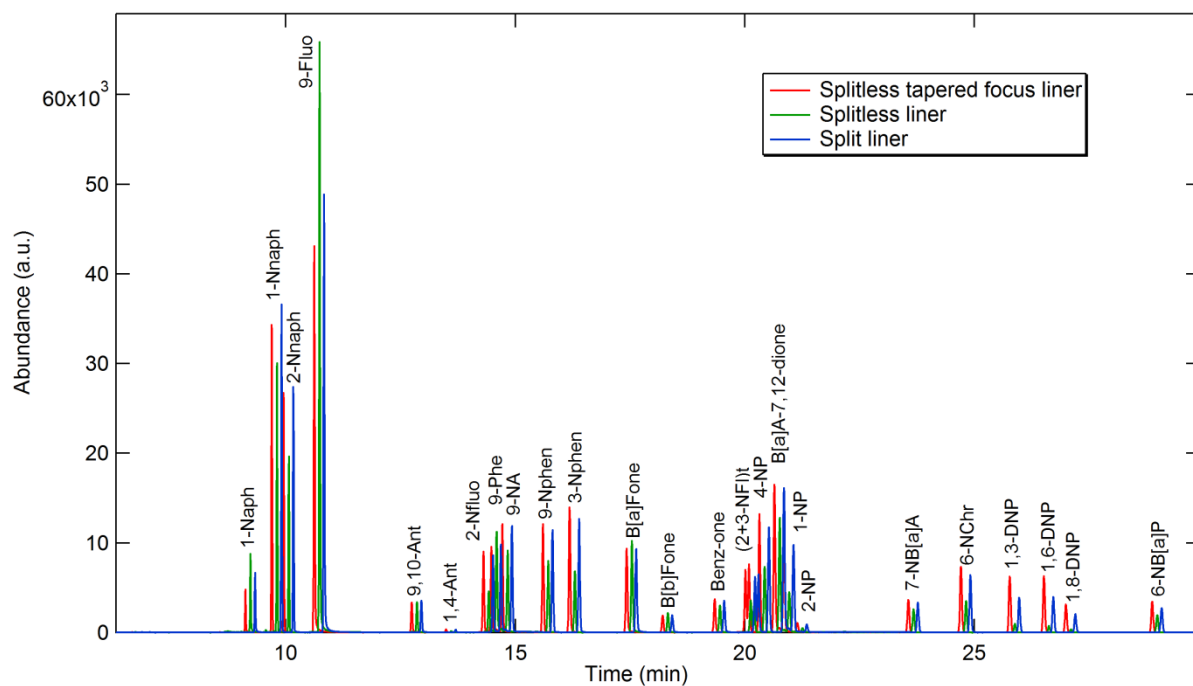


Fig. S3 Influence of the type of liner on the chromatographic response of NPAH and OPAH. Standard solution at $50 \text{ pg } \mu\text{L}^{-1}$, $1 \text{ } \mu\text{L}$ injected. Pulsed pressure mode at 30 psi. Injection temperature of $140 \text{ } ^\circ\text{C}$. SIM acquisition mode. Note that, the chromatographs were artificially shifted (+ 0.1 min offset) to observe the differences between them.

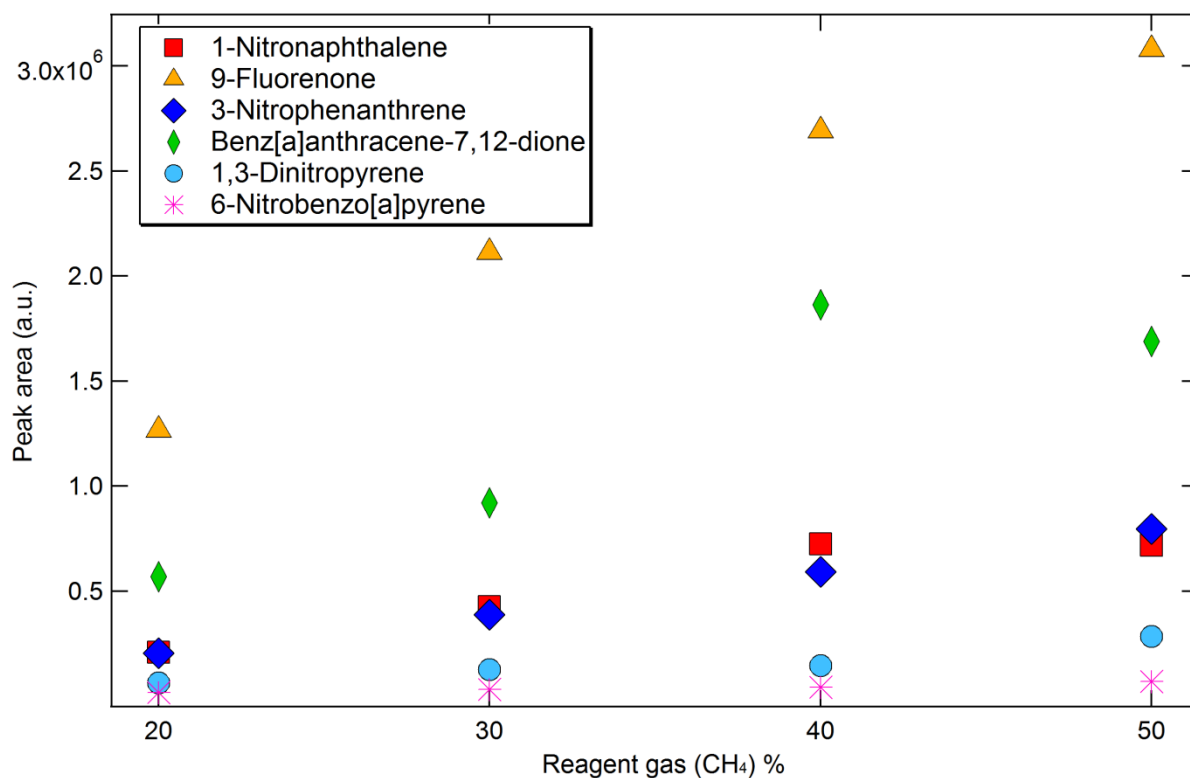


Fig. S4 Influence of the methane flow (NICI reagent gas) on the detector response of selected NPAH and OPAH. Standard solution at 500 pg μL^{-1} , 1 μL injected. Pulsed pressure mode at 45 psi. Injection temperature of 280 °C. Full scan acquisition mode and determination of the response based on the peak area of quantification ions reported in Table 1.

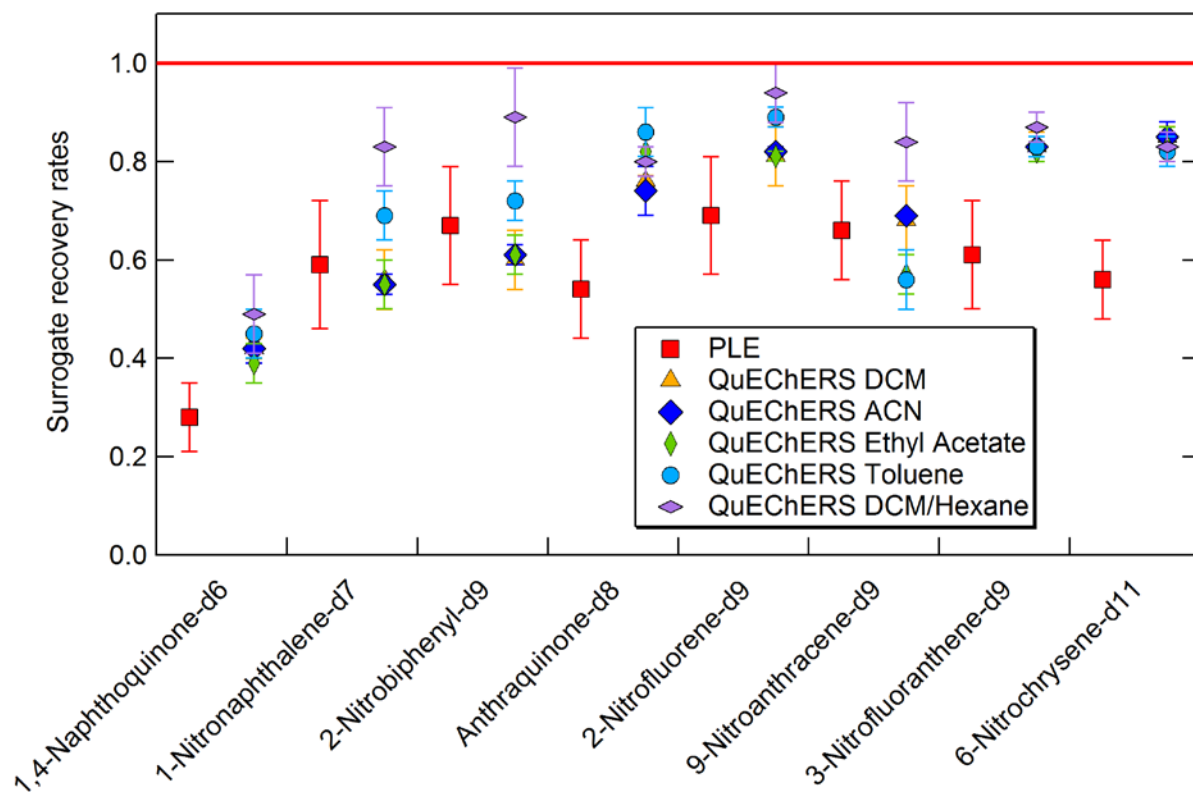


Fig. S5 Surrogate recovery rates obtained for the experiments of comparison of NPAH and OPAH quantities extracted according to the extraction solvent used. Fortified filter punches ($\varnothing=37$ mm) (50 ng added, 50 μL of a 1 $\text{ng } \mu\text{L}^{-1}$ NPAH and OPAH standard solution mixture) originated from the same PM_{10} ambient air filter sample ($n=3$). The quantity of surrogate standards used was similar (50 ng). The error bars correspond to the standard deviation for the triplicate experiments. Extraction solvent for PLE was DCM. QuEChERS extraction time of 1.5 min. For both extractions methods, same clean-up procedure applied using SPE $\text{Al}_2\text{O}_3/\text{SiO}_2$.

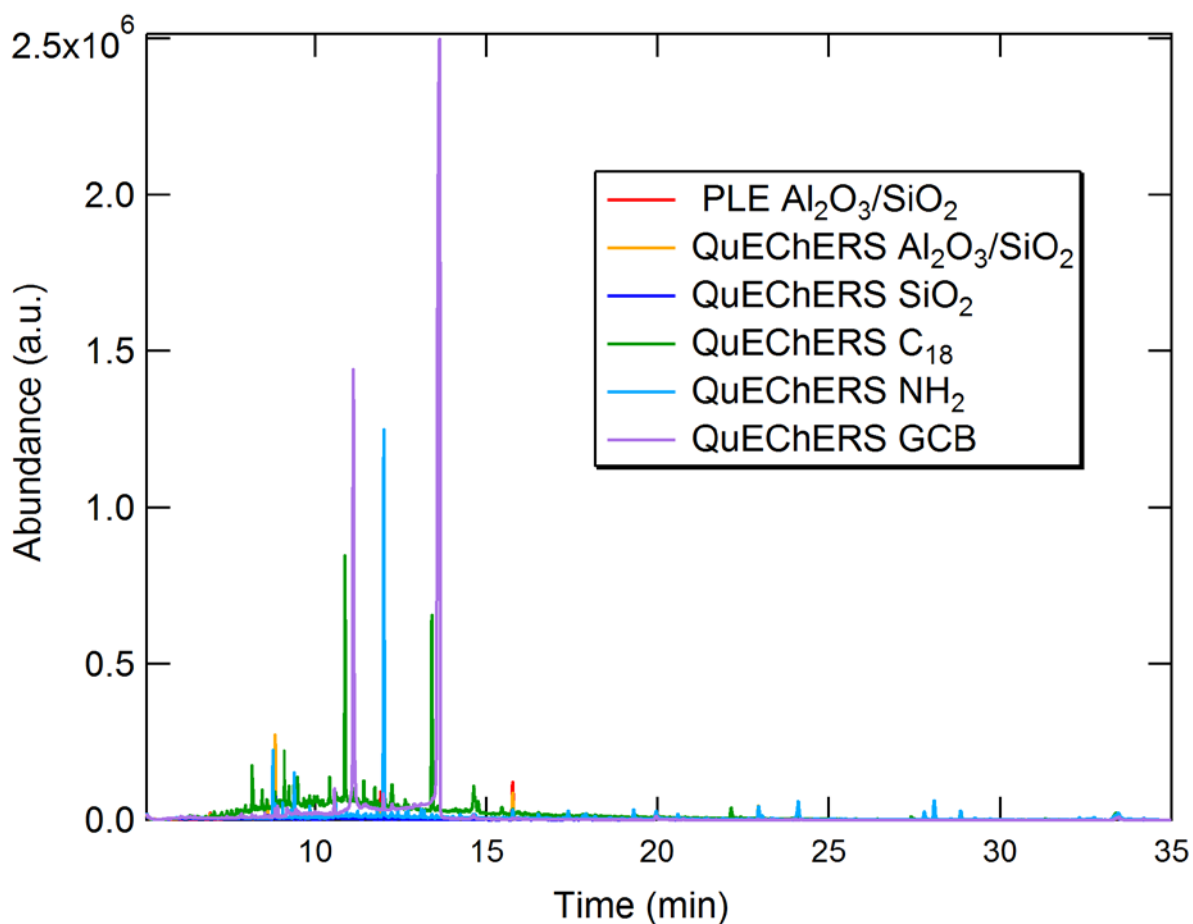


Fig. S6 Qualitative evaluation of the SPE phase purification efficiencies. Examples of chromatograms obtained for the experiments of comparison of NPAH and OPAH quantities determined according to the phase used for SPE clean-up (full scan acquisition mode, entire chromatogram and zoom). Fortified filter punches ($\varnothing=47$ mm) (5 ng added, 5 μL of a 1 ng μL^{-1} NPAH and OPAH standard solution mixture) originated from the same PM_{10} ambient air filter sample ($n=3$). Extraction solvent for PLE was DCM and SPE clean-up was performed using Al_2O_3 and SiO_2 cartridges. Same final elution mixture for all SPE phases (9 mL of DCM/pentane, 35/65, v/v). Solvent for QuEChERS-like extraction procedure was ACN and extraction time of 1.5 min.

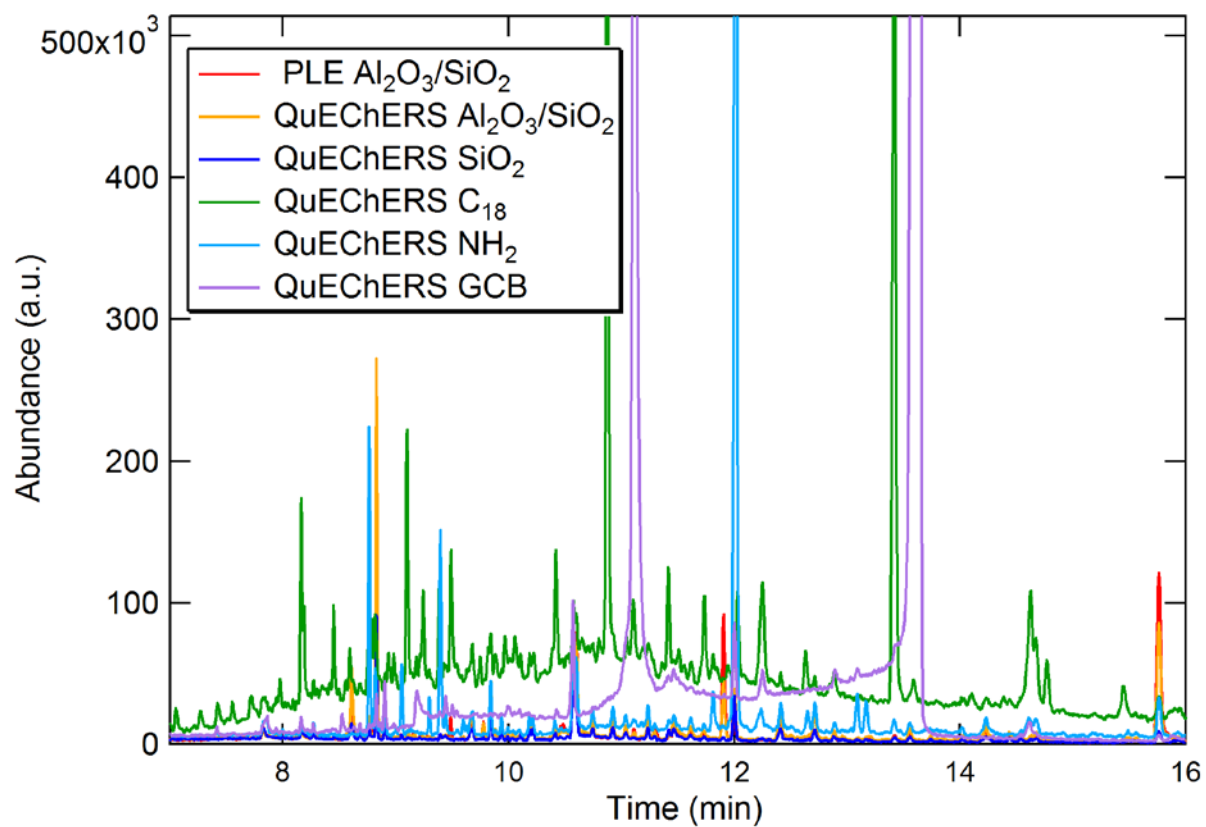


Fig. S7 Qualitative evaluation of the SPE phase purification efficiencies. Zoom, from 0 to 16 min runtime, of the chromatograms in Fig S6.

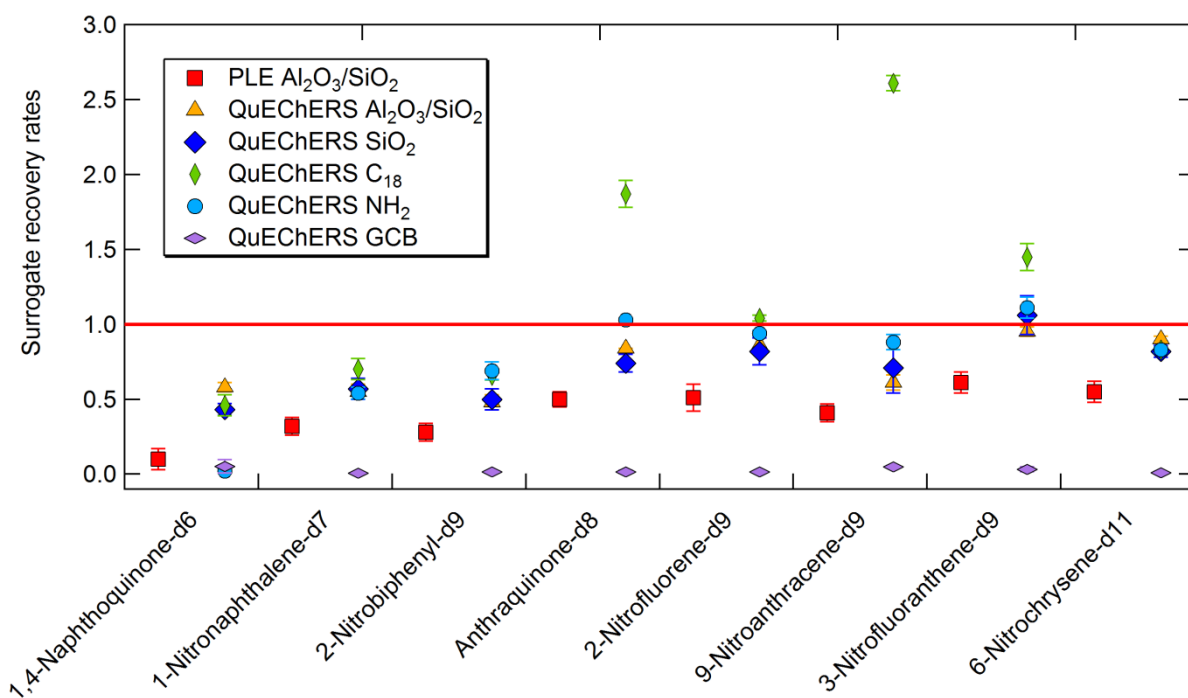


Fig. S8 Surrogate recovery rates obtained for the experiments of comparison of NPAH and OPAH quantities determined according to the phase used for SPE clean-up. Fortified filter punches ($\varnothing=47$ mm) (5 ng added, 5 μL of a 1 ng μL^{-1} NPAH and OPAH standard solution mixture) originated from the same PM_{10} ambient air filter sample ($n=3$). The quantity of surrogate standards used was similar (5 ng). The error bars correspond to the standard deviation for the triplicate experiments. Same analytical conditions as in Fig. S6.

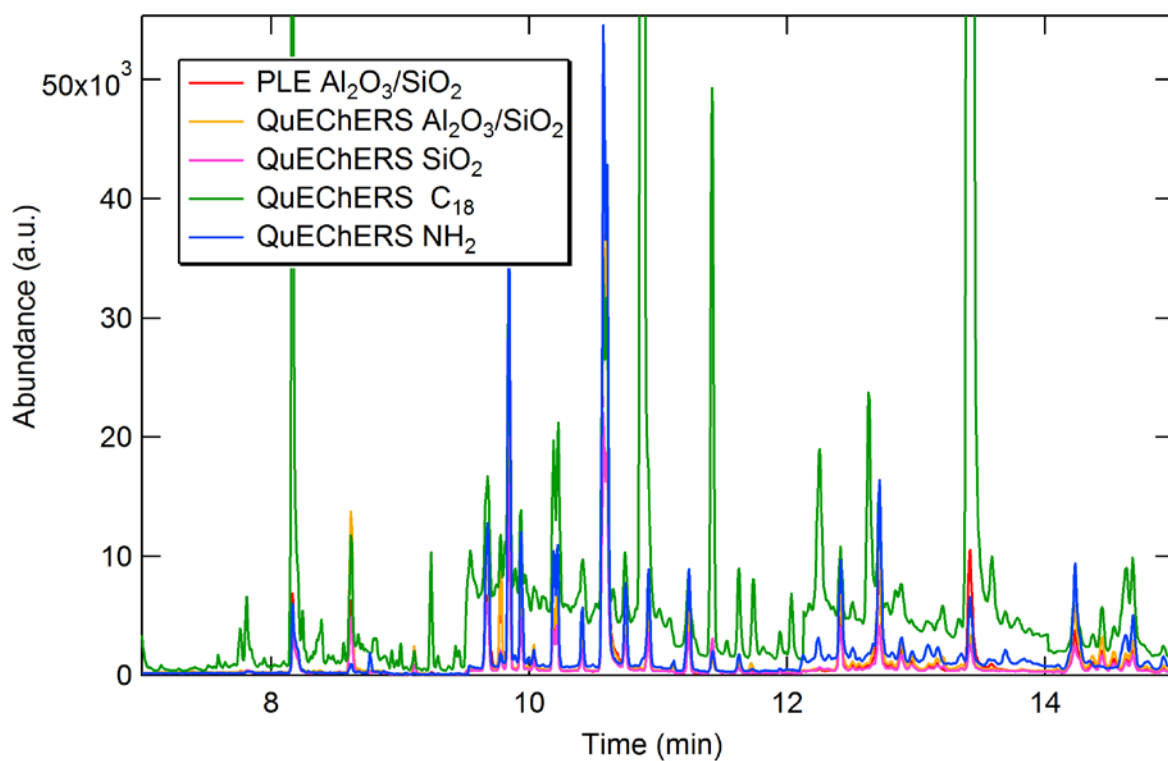


Fig. S9 Qualitative evaluation of the SPE phase purification efficiencies. Examples of chromatograms obtained for the experiments of comparison of NPAH and OPAH quantities determined according to the phase used for SPE clean-up (SIM acquisition mode, zoom). Fortified filter punches ($\varnothing=47$ mm) (5 ng added, 5 μL of a 1 $\text{ng } \mu\text{L}^{-1}$ NPAH and OPAH standard solution mixture) originated from the same PM_{10} ambient air filter sample ($n=3$). Same analytical conditions as in Fig. S7.

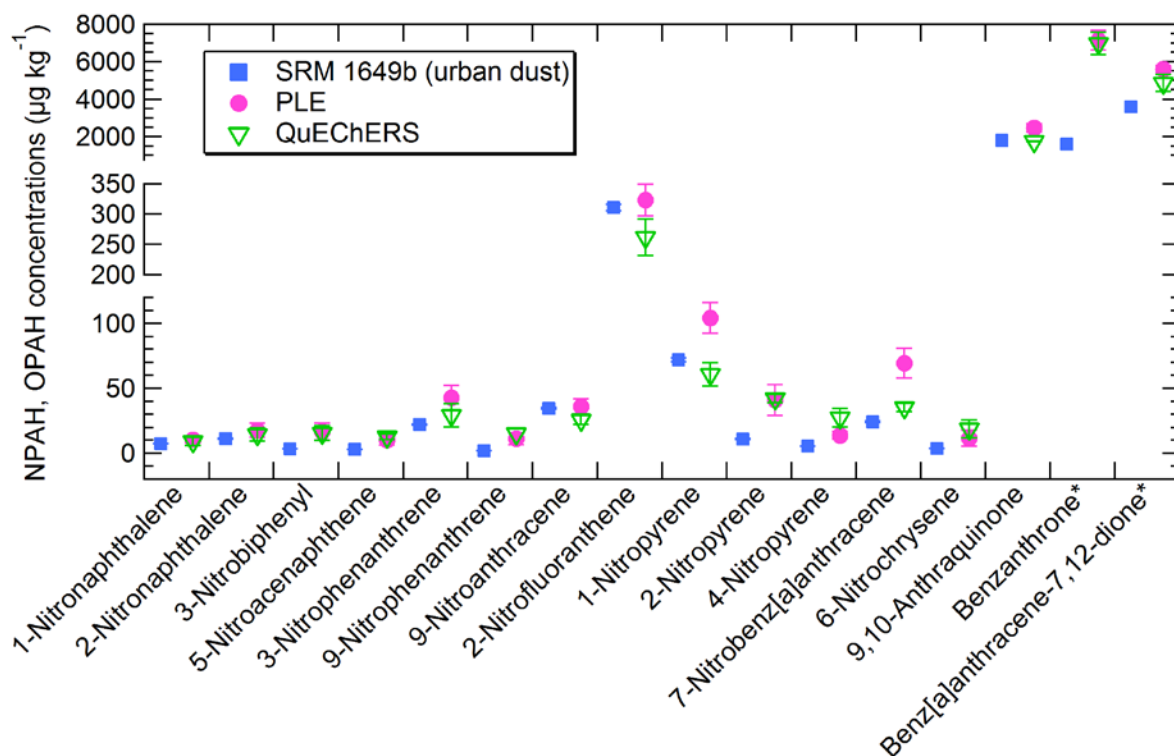


Fig. S10. Comparison of the average NPAH and OPAH concentrations ($\mu\text{g kg}^{-1}$) (dry-mass basis) in the SRM 1649b (urban dust) determined using PLE and QuEChERS-like extraction procedures ($n=6$, 3×50 mg and 3×20 mg) and the NIST reference or indicative concentration values (dry-mass basis) from the SRM certificate of analysis. The error bars correspond to the standard deviation for the 6 analyses. Compounds with an asterisk: $n=3$ (20 mg).

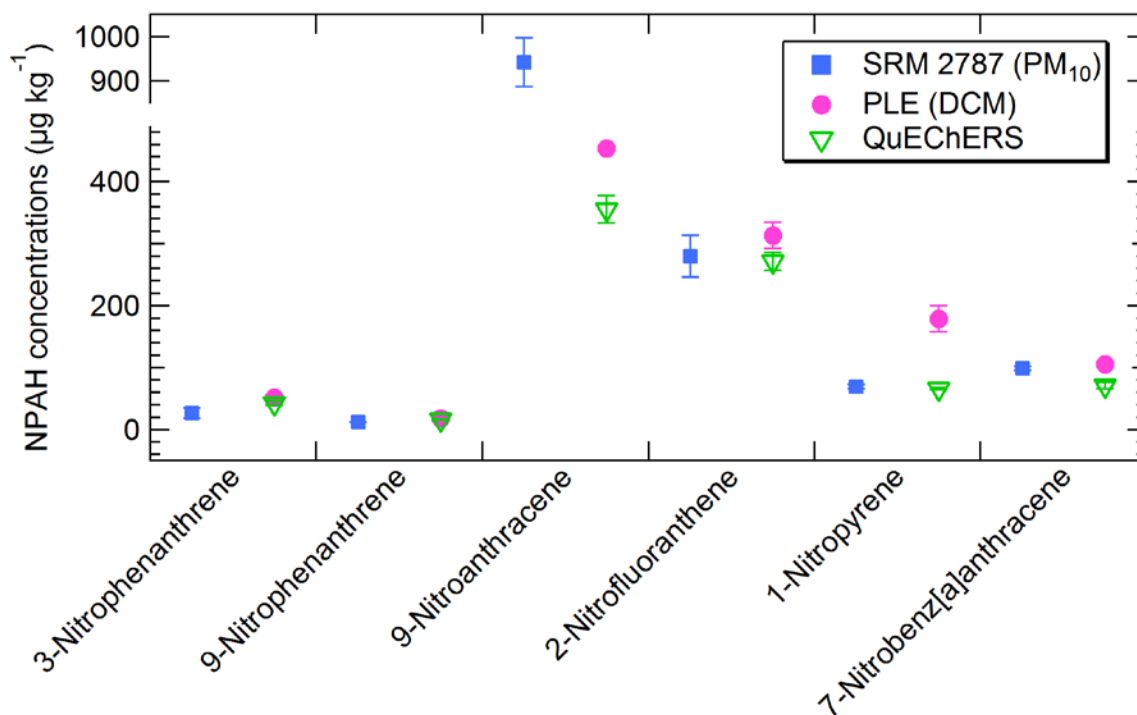


Fig. S11. Comparison of the average NPAH and OPAH concentrations ($\mu\text{g kg}^{-1}$) in the SRM 2787 (fine particulate matter, $<10\ \mu\text{m}$) determined using PLE and QuEChERS-like extraction procedures ($n=3$, 20 mg) and the NIST certified or reference concentration values (dry-mass basis) from the SRM certificate of analysis. The error bars correspond to the standard deviation for the triplicate analyses.

1. Macé T, Lalere B, Labarraque G, Ravantos C, Leoz-Garziandia E, Alleman L, Mathé F (2010) 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 PM_{10} (3/5) (French language). LCSQA / INERIS / LNE / EMD. http://www.lcsqa.org/system/files/guides_incertainitude_partie3_lne_nov2010_v2.pdf