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Abstract

A Quick Easy Cheap Effective Rugged and Safe (QuEChERS) like extraction procedure is presented for the measurement of polycyclic aromatic hydrocarbons (PAHs) associated to particulate matter from ambient air or combustion process. The procedure is based on a short mechanical agitation (vortex during 90 s) using a small volume of acetonitrile (7 ml) as extraction solvent. Equivalent extraction efficiencies were obtained when comparing the QuEChERS and the traditional pressurised solvent extraction (ASE) procedures for ambient air and emission (wood combustion) filter samples. The developed QuEChERS extraction protocol was validated with the analysis of a standard reference material (NIST SRM 1649a, urban dust). By comparison to other extractions methods including ASE, the simplicity of the QuEChERS protocol allows to minimize experimental errors, to decrease about a factor 5 the cost per extraction and to increase the productivity per working day by a 10-fold factor. This paper constitutes the first report on the applicability of a QuEChERS-like approach for the quantification of PAHs or other organic compounds in atmospheric particulate matter.

1. Introduction and objectives

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants widely studied due to their known toxicity (carcinogenic and/or mutagenic properties) (IARC, 2010). In the atmosphere, they are released in both gaseous and particulate phases as by-products from the incomplete combustion of organic matter and fossil fuel (Ravindra et al., 2008). In many countries, including Europe and USA, particle-bound PAHs are regulated and monitored in ambient air (ATSDR (Agency for Toxic Substances and Disease Registry), 1995; European Official Journal,

2005; Ravindra et al., 2008). In Europe, a target value for benzo[a]pyrene (B[a]P) in PM_{10} (particulate matter < 10 µm) (B[a]P – as a marker for the suite of PAH compounds) has been set to 1 ng m^{-3} on annual average for every single monitoring station (European Official Journal, 2005).

Particle-bound PAHs are generally sampled by air sampling using different media (e.g. quartz or glass fibre filters). Common methodologies used for the quantification of particle-bound PAHs include solvent extraction and analysis generally achieved using HPLC-Fluorescence detection or by GC-MS (European Committee for Standardization (CEN), 2008; Pandey et al., 2011). Other existing analytical techniques include, for example, HRGC-MS/MS, GC-TOF-MS, GC-FID, GC-ECD (Pandey et al., 2011). Solvent based extraction methods of particulate atmospheric samples are generally carried out using traditional Soxhlet, extraction under reflux, ultrasonication, microwave assisted extraction (MAE), pressurised liquid extraction or accelerated solvent extraction (PLE or ASE). Solvents used are generally toluene, dichloromethane (DCM), hexane, acetone or a mixture of them. Obtained extracts (20 – 200 mL) are then reduced under a nitrogen flow to a final volume lower than 1 mL. The analytical procedure could also include a purification step of the extract by solid phase extraction before analysis. We can also cite in this category the supercritical fluid extraction (SFE) using pure CO_2 (Hawthorne and Miller, 1986; Hawthorne et al., 2000; Pandey et al., 2011). Beside, solvent-free based extraction techniques were developed by different authors using notably thermal-desorption coupled with GC-MS (TD-GC-MS) (Pandey et al., 2011; van Drooge et al., 2009) and, in a lesser extent, laser desorption/ionization coupled to time-of-flight mass spectrometry (LDI-ATOFMS) (Zimmermann et al., 2003).

If all these extraction techniques are really efficient, they are time-consuming, labor-intensive, requires the use of a large volume of organic solvent (toxic), laborious clean up procedures and a high cost of investment and maintenance (ASE, TD-GC-MS, SFE) (Table 1).

The QuEChERS procedure (Quick Easy Cheap Effective Rugged and Safe) was developed with the objective to simplify and shorten the extraction step of organic compounds. This kind of procedure was initially developed for the extraction of pesticides in food matrices (vegetables and fruits) (Anastassiades et al., 2003; Wilkowska and Biziuk, 2011). It is considered as a soft extraction method (less interfering compounds are extracted) which involves extraction with acetonitrile (ACN) followed by an optional clean up procedure by dispersive solid-phase extraction (d-SPE). The total extraction + clean up time is generally about 1 to 5 minutes and the quantity of solvent used (ACN) from 5 to 15 ml (Wilkowska and Biziuk, 2011). The QuEChERS approach requires fewer steps and time than traditional extraction procedures. This is significant, as every additional analytical step complicates the procedure and represents also a potential source of errors. Additionally, no important cost of investment is required (only a vortex and a centrifugation apparatus). Since the development and the publication of the method (Anastassiades et al., 2003), QuEChERS has been gaining significant popularity from academia and industry to quickly being established as a reference method for foodstuff analysis (European Committee for Standardization (CEN), 2009). The QuEChERS procedure was then later successfully applied to other matrices like fish, shellfish, soils and sediments and also to other compounds like PBDEs, VOCs, PCBs, pharmaceuticals, chlorinated compounds and PAHs (e.g; Asensio-Ramos et al., 2010; Bragança et al., 2012; Cai et al., 2012; Forsberg et al., 2011; García Pinto et al., 2011; Gratz et al., 2011; João Ramalhosa et al., 2009; Kalachova et al., 2011; Pule et al., 2012; Smoker et al., 2010; Wilkowska and Biziuk, 2011).

To our knowledge, the QuEChERS extraction procedure was never applied for the analysis of PAHs, or other organic compounds, from atmospheric particulate matter or wood burning emissions. Only one simplified extraction method comparable to the QuEChERS approach is described in the literature (Delgado-Saborit et al., 2010). The major differences of this method, using mechanical shaking, lie in the longer agitation time (15 min) and the purification steps.

Considering the total duration time of the method (estimated > 45 min), this protocol could not be classified as a QuEChERS (quick) extraction procedure.

The objective of this study was to evaluate and to report on the applicability of QuEChERS extraction procedure for the analysis of PAHs in atmospheric particulate matter. The developed QuEChERS approach was applied to the analysis of ambient and emission (wood combustion) air samples using HPLC-Fluorescence detection (HPLC-FLD). Results were compared with those obtained with ASE extraction method (Dionex) according to the European standard reference method EN 15549 (European Committee for Standardization (CEN), 2008). The methodology was validated by the analysis of the NIST standard reference material SRM 1649a (urban dust).

2. Experimental section

2.1. Particulate samples

Ambient particulate samples were collected at INERIS (Verneuil-en-Halatte, France; 49°16'20"N, 2°30'14"E), in February 2012. Sampling site could be classified as suburban. Six PM_{10} samples were collected using a high volume sampler (Graseby Andersen, 70 m^3 h^{-1}) on quartz fibre filter (Whatman QMA, 20.3 x 25.4 cm) previously heated for 12 h at 500 °C. 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 sixteen smaller filter sections (Ø = 47 mm) (filter surface equivalent to a 24 h sampling at 2.3 m^3 h^{-1}) in order to perform the development of the QuEChERS extraction procedure and the comparison with ASE extraction method using the same filter. Homogeneity of the ambient air sampling filters used (Andersen) was evaluated and no significant disparity between filter sections was observed for PAHs (σ = 3 - 8 %) (Leoz-Garziandia et al., 2010).

Emission particulate samples were collected during the research program PEREN²BOIS (Fraboulet, 2012; Fraboulet et al., 2012). Briefly, the measurement procedure consisted of the

sampling in non-isokinetic conditions (sampling velocity > airflow speed in the exhaust pipe), of

the total suspended particulate matter (TSP) emitted by wood combustion in a stove, on a heated

quartz fibre filter (125 ± 10 °C) (Whatman QMA, $\varnothing$ = 74 mm). Sampling duration was 30 min.

Filters were divided in 1.5 cm² sections to perform comparative tests between ASE and QuEChERS

extraction procedures. Note that, the homogeneity of the emission filters was not guaranteed (non

uniform repartition of the particles at the surface of the filter, Fig. A1 in the appendix A.)

2.2. Extraction and purification

DCM and ACN were purchased from Aldrich (HPLC grade). Water used was Milli-Q quality

(Millipore, 18 MΩ). 6-Methylchrysene (10 µL of a solution at 10 ng µL^{-1} in ACN, Supelco, 99 %

purity) was added before extraction as surrogate standard according to EN 15549 (European

Committee for Standardization (CEN), 2008).

Extractions of ambient air and emission particulate samples, and SRM, were performed using

ASE (Dionex, ASE 200) with DCM as solvent. Extraction procedure was the following: 11 mL

cells were used with extraction parameters set at 120 °C, 140 bars, 3 cycles of 6 minutes, flush 90

% and purge 120 sec. Then, extracts ($\approx$ 30 ml) were reduced under a nitrogen stream at a volume of

0.2 ml (Zymark, Tubovap II) and dissolved (adjusted to 1 ml) into ACN for PAH analyses. This is

the traditional extraction procedure used by our group and reported in previous articles (Albinet et

al., 2007a 2007b; Albinet et al., 2008a 2008b; Goriaux et al., 2006; Ringuet et al., 2012a 2012b).

For QuEChERS extraction procedure, samples (filter sections or SRM 1649a) were placed in

centrifuge glass tubes ($\varnothing$ = 16 mm, L = 100 mm, screw cap with PTFE septum face, Duran, VWR)

and totally immersed with 7 mL of solvent (ACN or DCM or ACN/H$_2$O (5/2, v/v)). The influence

of the addition of salts was also investigated (2 g of Na$_2$SO$_4$ or MgSO$_4$) (see section 3.1). Samples

were shaken/vortexed using a multi-position vortex for 30 s to 2 min (IKA, Vortex Genius 3; 8

positions/simultaneous extractions). Next, they were centrifuged for 5 min at 4500 rpm (Sigma, 3-

16 PK centrifuge. 1 ml of supernatant was collected for direct analysis and 3 ml were reduced under a nitrogen stream (0.5 ml) (Zymark, Tubovap II) and adjusted to 1 ml (reduction time was about 10 min for 6 simultaneous samples). In both cases, supernatants were filtered using a 0.20 μm PET syringe filter (Macherey-Nagel, Chromafil Xtra PET 20/25) and collected in an autosampler vial for analysis. The analysis of both, direct and reduced extracts, was performed.

A clean up procedure by (d-SPE) was also applied for emission samples. After extraction and centrifugation, 200 mg of Florisil® was added to 3 mL of collected supernatant and put in a centrifuge tube containing (from SPE cartridges: Aldrich, Supelclean). Samples were vortexed for 1.5 min, centrifuged for 5 min, filtered and analysed.

2.3. Analysis

PAHs were analysed by HPLC-FLD (Dionex P580 / Dionex RF200). The column used was a Supercosil LC-PAH C18 (250 mm × 4.6 mm × 5 μm) (Supelco) thermostated at 30 °C (column oven Croco-Cil). Chromatographic gradient (1.5 mL min^{-1}) was applied as follow: 55/45 (v/v) of a mixture of ACN/water for 14 minutes, followed by a gradient up to 100 % ACN at 67 min. The injection volume was 20 μL for ASE extracts and 60 μL for QuEChERS extracts (except for emission samples, 20 μL for both extraction methods). Injection volumes for both extraction methods were different in order to get similar amounts of compounds injected on the HPLC column (QuEChERS extracts were more diluted). Twelve PAHs were quantified by external calibration (Supelco, PAH mix standard solution, 5 points, from 1 to 20 ng ml^{-1}) (fluorene, phenanthrene, fluoranthene, pyrene;, benz[a]anthracene (B[a]A), chrysene, benzo[b]floranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), dibenzo[a,h]anthracene (D[a,h]A), benzo[g,h,i]perylene (B[g,h,i]P), indeno[1,2,3-cd]pyrene (Ind[1,2,3-cd]P)). The limit of detection and quantification were evaluated at about 6 pg and 20 pg of injected compound, respectively and for all quantified PAHs. Note that, in the case of emission samples, extracts were diluted by a factor

of about 20 and 100 for QuEChERS and ASE extracts, respectively, conducing to similar final dilution factors for both extracts (7 ml × 20 = 140 and 1 ml × 100 = 100 for QuEChERS and ASE, respectively).

3. Results and discussion

The development of the QuEChERS extraction procedure required the evaluation of the influence of different parameters on the PAH extraction efficiency such as, the nature of the solvent of extraction, the shape of the sample, the agitation (extraction) time and the necessity of a clean-up procedure using dispersive-SPE.

3.1. Solvent of extraction

ACN and DCM were investigated to determine their suitability as extraction solvent for the QuEChERS based approach. Results obtained are displayed in Fig. 1. Overall, mass of PAH extracted using both solvents were similar. Minor differences were observed for B[a]A, chrysene, B[b]F, B[k]F and B[g,h,i]P. By taking into account the recovery rate of the surrogate standard (6-methylchrysene), these differences were not significant (Student test applied on every independent PAH, α = 0.05). According to these results, ACN seemed the most appropriate solvent due to its direct compatibility with the analysis by HPLC-FLD (no solvent concentration step and/or solvent exchange).

Other combinations were also tested such as a mixture of ACN/H_2O (5/2, v/v) and the addition of salts like Na_2SO_4 or $MgSO_4$ to ACN, DCM or ACN/H_2O. The addition of water should favour the partitioning of polar compounds between organic and aqueous phases. The joint addition of desiccant (Na_2SO_4 or $MgSO_4$) could have improved the PAH extraction (the hydration of the desiccant is an exothermic process potentially increasing the extraction efficiency) (Anastassiades et al., 2003). However, no significant differences and/or improvements were noticed in these

conditions (Figs. A2 and A3 in the Appendix A). The addition of water to the extraction solvent seemed to decrease the PAH extraction efficiency. PAH losses were more important in this case for the reduced extracts due to the presence of water which required more extensive evaporation conditions.

Finally, ACN (without addition of salts or water) was used in the final PAHs extraction protocol.

3.2. Entire filter vs filter cut in 4 pieces

Extraction procedures using sonication or microwave extraction generally include the preparation of the sample (filter) by cutting it in small pieces in order to increase the surface of exchange with the solvent. The influence of the sample configuration was evaluated (entire filter section *vs* filter section cut in 4 pieces) on the efficiency of the QuEChERS extraction procedure (Fig. 2). No significant differences of PAH extraction efficiency were observed (Student test applied on every independent PAH, $\alpha = 0.05$). To minimize supplementary filter handling and reduce the potential additional source of errors, the extraction of the entire filter sample (filter section $\varnothing = 47$ mm) was chosen for the QuEChERS extraction procedure.

3.3. Extraction time

The results of the influence of the time of agitation (vortex) on the PAH extraction efficiency are presented for phenanthrene, B[a]P and B[g,h,i]P in Fig. 3. After only 30 s of agitation, the PAH extraction was almost complete and the extraction efficiency reached a plateau after 1 min of agitation. Finally, an extraction time (vortex agitation) of 1 min and 30 s was selected for the final QuEChERS extraction procedure to guarantee the robustness of the method while preserving a short extraction time. However, fundamentally, there is no significant difference of extraction efficiency between 1 to 2 min of agitation.

3.4. Application to ambient air PM_{10} samples

The adopted protocol (extraction of the entire filter $\varnothing$ =47 mm with 7 ml of ACN using vortex agitation during 1 min 30s following by 5 min of centrifugation at 4500 rpm and filtration of the extract using syringe filter at 0.2 µm) was then applied to the analysis of PAHs in ambient air PM_{10} samples and compared to the traditional extraction procedure using ASE (Fig. A4). Average PAH concentration ratios obtained using QuEChERS and PLE extraction procedures (concentrations obtained using QuEChERS method divided by concentrations obtained with ASE extraction) (_____ ————————) are presented on Fig. 4.

The results obtained demonstrated that for the heavier PAHs (from fluoranthene to Ind[1,2,3-cd]P) extraction efficiencies using QuEChERS and ASE procedures were equivalent ($R_{(QuEChERS/PLE)}$ equal or close to 1). Significant differences were observed for the lighter PAHs (fluorene, phenanthrene and anthracene) with ratios greater than 1 (from 1.4 to 5.1), indicating larger recoveries for these compounds using the QuEChERS extraction procedure (notably for the direct injection of the extracts). Larger quantities of solvent are used with the ASE procedure, which implies a solvent evaporation step is required increasing the risk of loss for the more volatile PAHs during this step. By avoiding or shortening the solvent evaporation step of the extracts using QuEChERS approach, losses by volatilisation of the lighter (volatile) compounds are minimized. Note that, the larger standard deviations observed for these compounds (fluorene, phenanthrene and anthracene) were due to the larger standard deviations obtained with ASE (not visible on Fig. A4 due to the really low concentration levels of these compounds).

3.5. Validation on standard reference material urban dust (SRM 1649a)

Six samples (about 50 mg, balance precision = 0.01 mg) of the SRM 1649a (urban dust) were analyzed to validate the accuracy and the precision of the investigated QuEChERS method. Experimental concentrations were compared with the certified concentrations and the

concentrations determined using ASE (Table 2). The mean experimental concentrations obtained in this study using ASE and QuEChERS extraction methods were generally consistent with the certified values of concentrations with the exception of fluorene. Using QuEChERS method, recoveries relative to certified values were in the 81 - 111 % range for B[g;h,i]P and fluoranthene / pyrene, respectively. For ASE, they were in the 94 - 119 % range for B[k]F and D[a,h]A, respectively. In both cases, recoveries for fluorene were lower than 80 % (61 and 78 for QuEChERS and ASE, respectively). The really low concentration content of this compound in the SRM 1649a could explain these results. Overall, using the QuEChERS extraction procedure, all the PAH recoveries were in the range 80 - 120 % in agreement with the European reference method EN 15549 (European Committee for Standardization (CEN), 2008). Standard deviations obtained using QuEChERS protocol were 2 to 5 times lower than the ones obtained with ASE. Experimental errors using a simple extraction method, like QuEChERS, are minimized. The results obtained demonstrated the validity of the extraction procedure developed in this study for the analysis of atmospheric particulate PAHs.

3.6. Evaluation of the uncertainties of measurement

The European reference method EN 15549 requires to provide the uncertainty of measurement of B[a]P concentrations associated to the PM_{10} (European Committee for Standardization (CEN), 2008). Uncertainties of measurement were evaluated by the GUM approach (Guide to the expression of Uncertainty in Measurement) (Macé et al., 2010). In both cases, ASE and QuEChERS, 90 % of the global uncertainty (sampling + analysis) is due to the analytical procedure. Details and results of the calculations are reported in the Appendix A. Using ASE, they were in the range 43 - 89 % (59 % in average) and for QuEChERS they ranged from 25 to 84 % (43 % in average) (Table A1). For both, higher uncertainties were observed for fluorene due to its low concentration in the SRM 1649a. Finally, the results obtained showed that global uncertainties of

measurement using QuEChERS extraction procedure are largely lower than the ones obtained using ASE. By reducing the number of steps and sample handling, experimental errors as such the uncertainties of measurement are minimized using the QuEChERS procedure.

3.7. Application to emission samples (wood combustion)

The adopted QuEChERS protocol was then applied to the analysis of PAHs from emission samples of wood combustion (residential heating) to evaluate a potential effect of the sample matrice (mainly soot in this case) on the efficiency of the extraction method. Obtained extracts were opaque and dark. Their purification was proceeded using a d-SPE clean up procedure with Florisil® as solid sorbent. Purified extracts obtained were yellow/green translucent with Florisil® removing polar components that could interfere during the analysis of PAHs by HPLC-FLD.

Average mass of PAHs per filter section quantified using the three different procedures (ASE, QuEChERS and QuEChERS + d-SPE) are presented in Fig.5. It can be emphasized that for the three methods used, the standard deviations obtained were quite large (coefficient of variation – Standard Deviation/Mean - in the range 5 - 67 %) due to inhomogeneous repartition of the particulate matter at the surface of the sampling filter. Most of the compounds did not present statistically significant differences between the three extraction methods (Student test applied on every independent PAH, $\alpha = 0.05$) with the exception of the heavier compounds namely B[g,h,i]P and Ind[1,2,3-cd]P and in a lesser extent B[a]P. For these compounds, higher quantities per filter section were quantified using QuEChERS and QuEChERS + d-SPE procedures. By comparison with ASE, QuEChERS is a soft extraction technique. The extraction is more selective resulting in lower amount of interfering components which induces a noticeable lower noise level in the chromatograms. In combination with the clean up procedure by d-SPE, noise level is even more decreased (Fig. A5). For instance, average signal to noise ratios (S/N) calculated for the B[g,h,i]P, In[1,2,3-cd]P and B[a]P were in the range 14 - 50 for ASE, 33 - 66 for QuEChERS and 135 - 270

for QuEChERS + d-SPE (Table A2). The application of the QuECHERS + d-SPE procedure resulted to obtain "cleaner" chromatograms improving the PAH quantification.

Clean up procedure by d-SPE using Florisil® was also applied to ambient air PM$_{10}$ samples. Results obtained did not show any significant differences (Student test applied on every independent PAH, α = 0.05) of extraction efficiency by comparison with a simple QuEChERS extraction procedure (Fig. A6). Contrary to emission samples, for this type of sample, the purification step using d-SPE does not appear to be necessary.

4. Conclusions

The QuEChERS extraction procedure developed in this work for the analysis of particle-bound PAHs in ambient air and emission samples produced identical results compared to the traditional extraction method using ASE. Comparable or improved PAH extraction efficiencies were obtained for different nature of particulate samples (ambient air PM$_{10}$ and wood combustion emission). The method was also validated with the analysis of a standard reference material (NIST SRM 1649a). The QuEChERS extraction procedure is a really quick, easy and effective method which necessitate a minimum of sample handling and steps allowing time saving. It can be reasonably assume that about 200 to 300 sample extractions can be processed per working day using this protocol (8 simultaneous extractions of about 5 to 15 min in total time in comparison to about 20 extractions using ASE). The developed procedure is equally cheap and safe considering the really low volume of solvent used (7 ml). A cost per sample extraction can be estimated (including the cost in solvent and of the different consumables) about 1.7 € in comparison to about 9 € using ASE and more using other solvent based extraction methods. Additionally, no important cost of investment and no maintenance are required ranking the QuEChERS extraction procedure as a really cheap and rugged alternative technique in comparison to all other extraction methods such as SFE or TD-GC-MS. The

simplicity of the developed method allows also to minimize the experimental errors and thus the uncertainties of measurement. Obtained quantification limits are in agreement with a mandatory monitoring of PAHs in ambient air (Table 3) and could be proposed as an alternative extraction procedure for the reference methods of measurement of PAHs in ambient air or emission samples (e.g. EN 15549, (European Committee for Standardization (CEN), 2008) as for pesticides in foods of plant origin (EN 15662) (European Committee for Standardization (CEN), 2009). Finally, extractions procedures based on a QuEChERS approach could be applied for the chemical characterization of atmospheric organic particulate matter.

Acknowledgements

Appendixes A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://www.journals.elsevier.com/science-of-the-total-environment.

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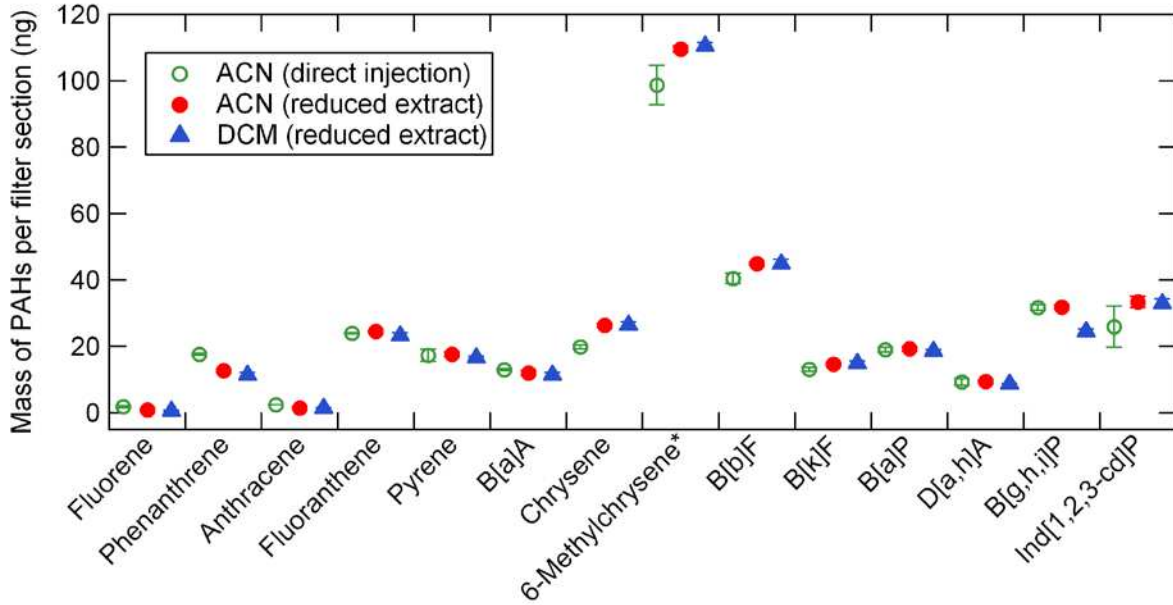
Fig. 1. Comparison of the average PAH quantity extracted according to the extraction solvent used (dichloromethane (DCM) or acetonitrile (ACN) - direct injection and injection of reduced extracts) with the QuEChERS procedure. Filter sections ($\varnothing$ = 47 mm) originated from the same PM_{10} ambient air filter sample (n = 3). The error bars show the standard deviation for the triplicate analysis. *6-Methylchrysene: surrogate standard (100 ng filter^{-1}).
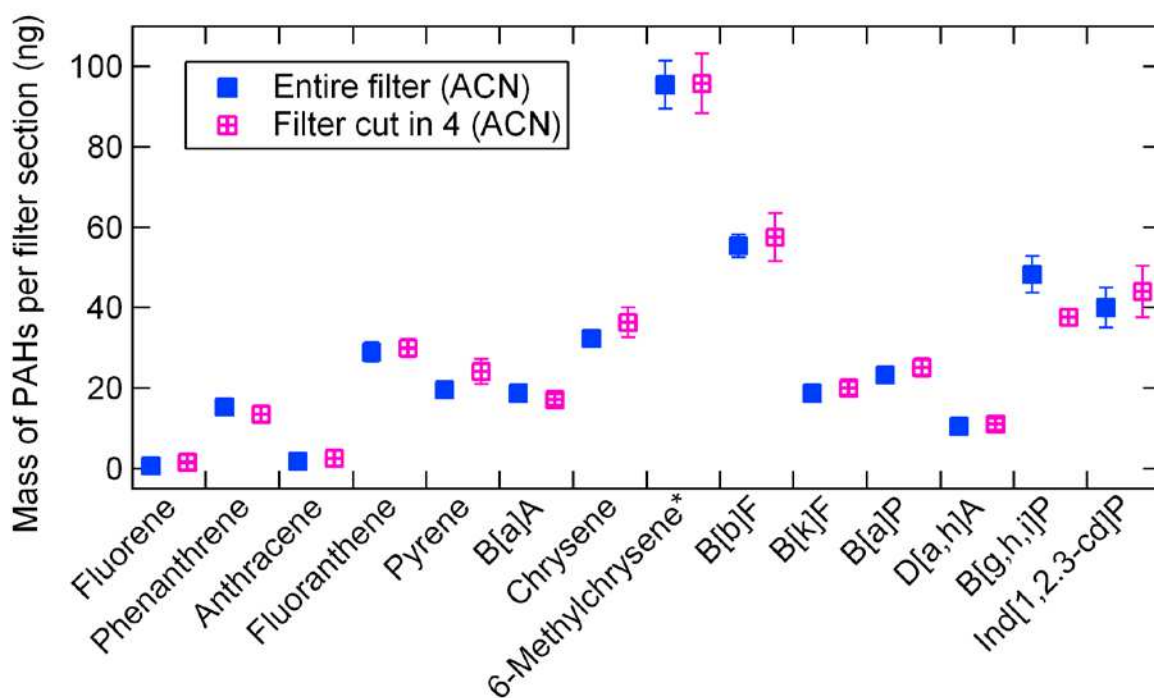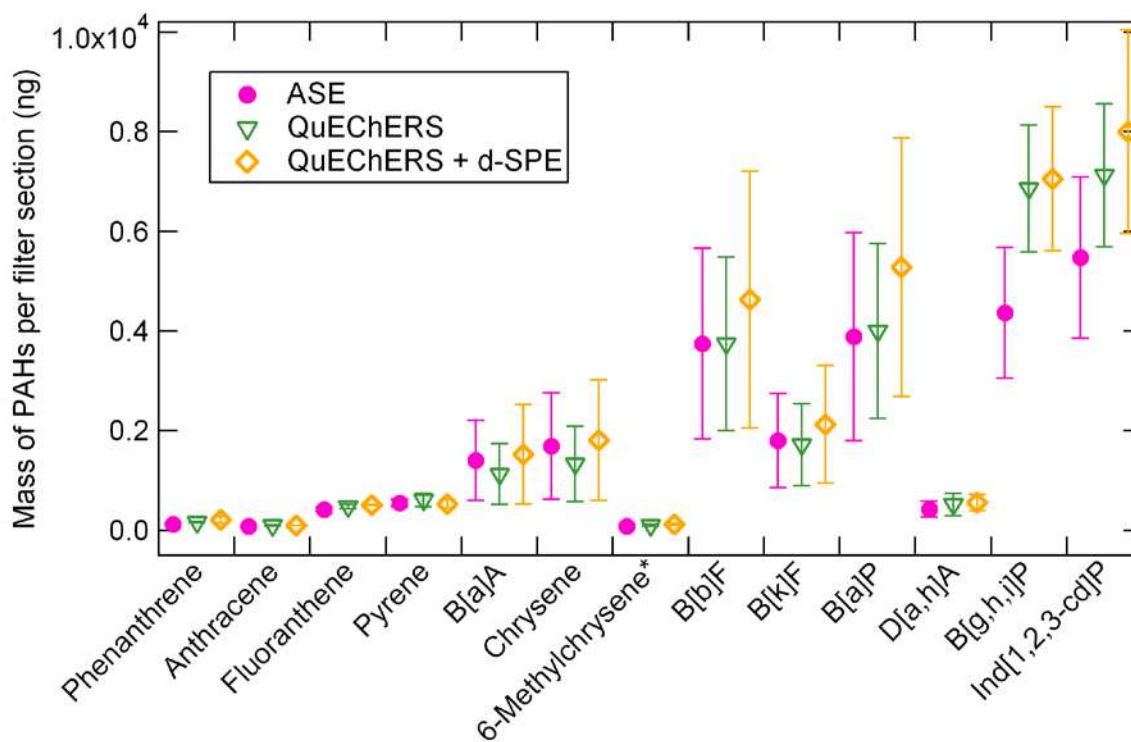
Fig. 2. Comparison of the average PAH quantity extracted using an entire filter section or with a filter cut in 4 pieces in the QuEChERS procedure. Filter sections ($\varnothing$ = 47 mm) originated from the same PM_{10} ambient air filter sample (n = 3). The error bars show the standard deviation for the triplicate analysis. Extraction solvent was acetonitrile (ACN) and the direct injection of the sample extracts was performed. [*]6-Methylchrysene: surrogate standard (100 ng $filter^{-1}$).
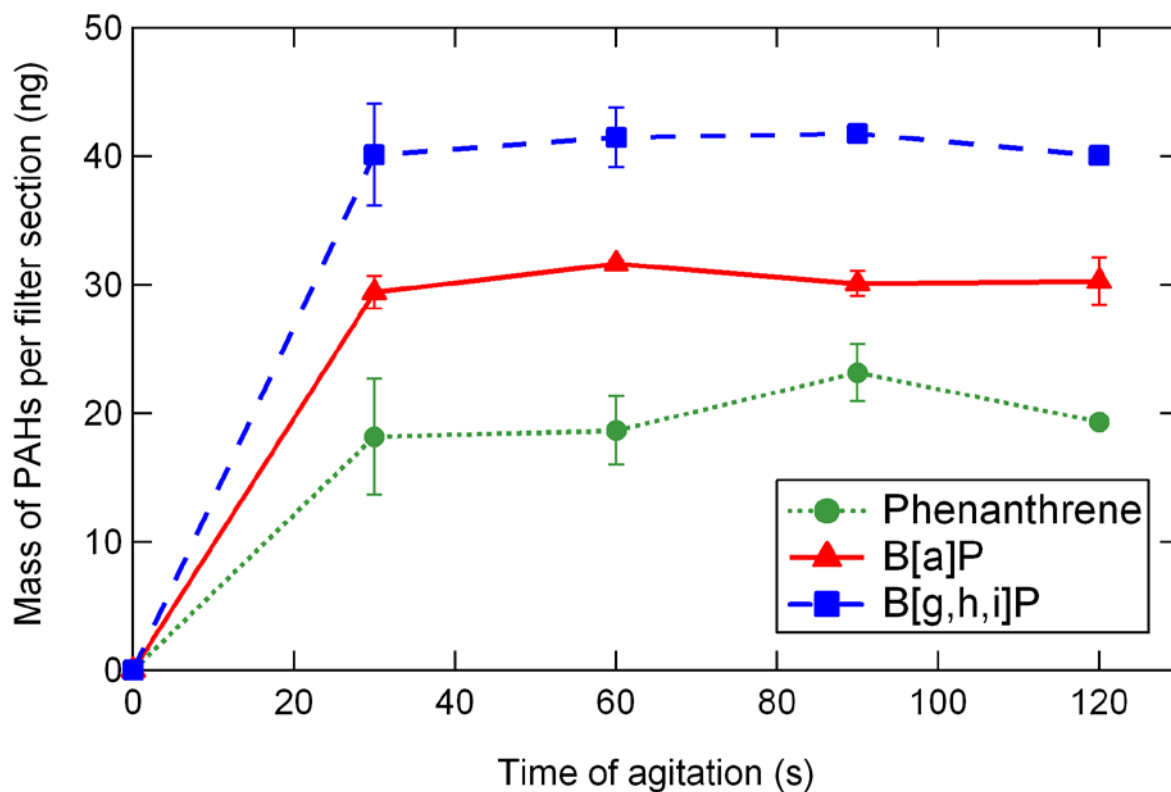
Fig. 3. Comparison of the average PAH quantity extracted for phenanthtrene, B[a]P and B[g,h,i]P according to the time of agitation in the QuEChERS procedure. Filter sections ($\varnothing$ = 47 mm) originated from the same PM_{10} ambient air filter sample (n = 3). The error bars show the standard deviation for the triplicate analysis. Extraction solvent was acetonitrile (ACN) and the direct injection of the sample extracts was performed.
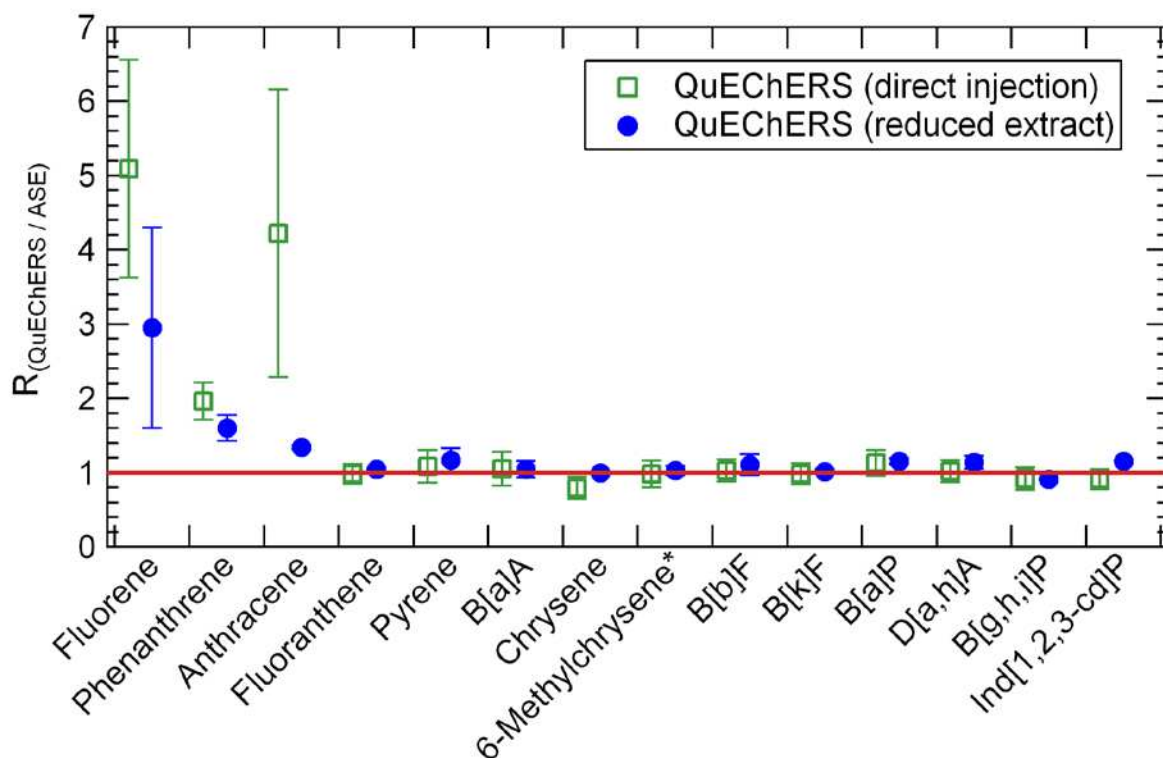
Fig. 4. Average PAH concentration ratios determined using QuEChERS and ASE extraction procedures (R(QuEChERS/PLE)). Extraction solvent was acetonitrile for QuEChERS. For direct injection of the QuEChERS extracts, filter sections ($\varnothing$ = 47 mm) originated from two different PM_{10} ambient air filter samples (n = 10). For the injection of reduced QuEChERS extracts, filter sections were from the same PM_{10} ambient air filter sample (n = 3). The error bars show the standard deviation of the 10 (direct injection) or of the 3 essays (reduced extracts). [*]6-Methylchrysene: surrogate standard (100 ng filter[-1]).

Fig. 5. Comparison of the average quantity of PAH per filter determined according to the used extraction procedure: ASE, QuEChERS and QuEChERS + d-SPE clean-up. Filter sections (1.5 cm²) originated from the same emission filter sample (n = 3). The error bars show the standard deviation of the triplicate analysis. [*]6-Methylchrysene: surrogate standard (100 ng filter[-1]). Same analytical conditions as in Fig 3.

Table 1

Comparison of different particle-bound PAH extraction procedures in terms of time-consumption, solvent volume (per sample) and cost of investment.

Extraction procedure	Solvent (volume)	Extraction time	Reduction time	Optional clean up procedure	Cost of investment
Reflux	Toluene (20 - 60 ml)	30 min - 1 h	15 - 40 min	X	0.2 - 1 k€
Soxhlet	Toluene, DCM, hexane:acetone (100 - 200 ml)	1 - 48 h	> 1 h	X	0.2 - 20 k€
Microwave (MAE)	Hexane:acetone (15 - 30 ml)	20 min - 1 h	15 - 30 min	X	25 - 35 k€
ASE	Toluene, DCM, DCM:hexane (10 ml - 40 ml)	15 - 30 min	15 - 30 min	X	50 - 100 k€
Ultrasonication	DCM, toluene (20 - 80 ml)	30 - 60 min	15 - 40 min	X	0.5 - 2 k€
SFE	CO_2 + DCM, Toluene (5 - 15 ml)	30 - 45 min	10 - 20 min	-	50 - 100 k€
TD-GC-MS	- [a]	- [a]	- [a]	- [a]	50 - 100 k€

[a] Not applicable (solvent-free method)

Table 2

PAH certified and experimental concentrations (mg kg^{-1}) (dry-mass basis) for NIST SRM 1649a (urban dust) and calculated recoveries using ASE and QuEChERS extraction procedures.

Compounds	SRM 1649a Mass fraction (mg kg^{-1})		ASE [a] Mass fraction (mg kg^{-1})		Recovery [c] (%)	QuEChERS [a, b] Mass fraction (mg kg^{-1})		Recovery [c] (%)
Fluorene	0.23	± 0.05	0.179	± 0.024	78	0.139	± 0.012	61
Phenanthrene	4.14	± 0.37	4.547	± 0.677	110	4.294	± 0.146	104
Fluoranthene	6.45	± 0.18	7.118	± 1.162	110	7.167	± 0.233	111
Pyrene	5.29	± 0.25	5.501	± 0.825	104	5.869	± 0.280	111
B[a]A	2.208	± 0.073	2.117	± 0.284	96	2.242	± 0.185	102
Chrysene	3.049	± 0.06	3.116	± 0.529	102	3.074	± 0.144	101
B[b]F	6.45	± 0.64	6.117	± 0.947	95	5.432	± 0.413	84
B[k]F	1.913	± 0.031	1.807	± 0.268	94	1.612	± 0.080	84
B[a]P	2.509	± 0.087	2.401	± 0.430	96	2.077	± 0.123	83
D[a,h]A	0.288	± 0.023	0.343	± 0.057	119	0.264	± 0.022	92
B[g,h,i]P	4.01	± 0.91	4.267	± 0.703	106	3.228	± 0.272	81
Ind[1,2,3-cd]P	3.18	± 0.72	3.520	± 0.590	111	2.612	± 0.107	82

[a] about 50 mg of SRM 1649a extracted, n = 6. Mass fraction were corrected from the moisture content (4.76 %, Moisture analyser HR 73, Mettler Toledo) and from the recovery of the surrogate standard 6-methylchrysene.

[b] Extraction solvent was acetonitrile (ACN) and the direct injection of the sample extracts was realised.

[c] The recoveries are calculated relative to the certified values of the reference material.

Table 3

Typical limits of quantification (LQ) of atmospheric particle-bound PAH concentrations using the QuEChERS method for three types of particulate samplers (filter section of $\varnothing = 47$ mm).

Sampling flow ($m^3\ h^{-1}$)	Sampled volume in 24 h (m^3)	LQ (direct injection / reduced extract) ($ng\ m^{-3}$)
1	24	0.096 / 0.032
2.3	55.2	0.044 / 0.015
30	720	0.032 / 0.011

APPENDIX A

A really Quick Easy Cheap Effective Rugged and Safe (QuEChERS) extraction procedure for the analysis of particle-bound PAHs in ambient air and emission samples

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Calculation of uncertainties of measurement

Uncertainties of measurement of PAH concentrations 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:

$$\frac{u^2(C)}{C^2} = \underbrace{\frac{u^2(mreg)}{mreg^2} + \frac{u^2(Xr)}{Xr^2} + \frac{u^2(mc)}{mc^2} + \frac{u^2(Xd)}{Xd^2} + \frac{u^2(E)}{E^2} + \frac{u^2(R)}{R^2}}_{\text{Analysis}} + \underbrace{\frac{u^2(Q)}{Q^2} + \frac{u^2(t)}{t^2}}_{\text{Sampling}}$$

With:

- C: PAH mass concentration in the airborne sample

- $mreg$: linearity of the external calibration

- Xr: analytical repeatability

- m_c: calibration solutions

- Xd: calibration drift

- E: extraction rate

- 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)

Table A1

Uncertainties of measurement of PAH atmospheric particulate concentrations evaluated by the GUM approach for the ASE and the QuEChERS extraction procedures.

Compounds	$U_{rel}(C)$ ASE	$U_{rel}(C)$ QuEChERS
Fluorene	89 %	84 %
Phenanthrene	54 %	32 %
Fluoranthene	65 %	31 %
Pyrene	49 %	38 %
B[a]A	43 %	30 %
Chrysene	53 %	25 %
B[b]F	49 %	39 %
B[k]F	46 %	35 %
B[a]P	49 %	37 %
D[a,h]A	68 %	39 %
B[g,h,i]P	67 %	55 %
In[1,2,3-cd]P	67 %	51 %

Calculations of uncertainties of measurement are based on samplings realized using high volume samplers DA-80 (Digitel Elektronik AG) (30 m^3 h^{-1}, 24 h, quartz fibre filters $\varnothing$ = 150 mm, Pallflex). We assumed that error made on filter cuts ($\varnothing$ = 47 mm) is the same for both, ASE and QuEChERS extraction procedures, and could be considered as negligible (negligible looses of particles). Note that, about 90 % of the global uncertainty is due to the analytical procedure.
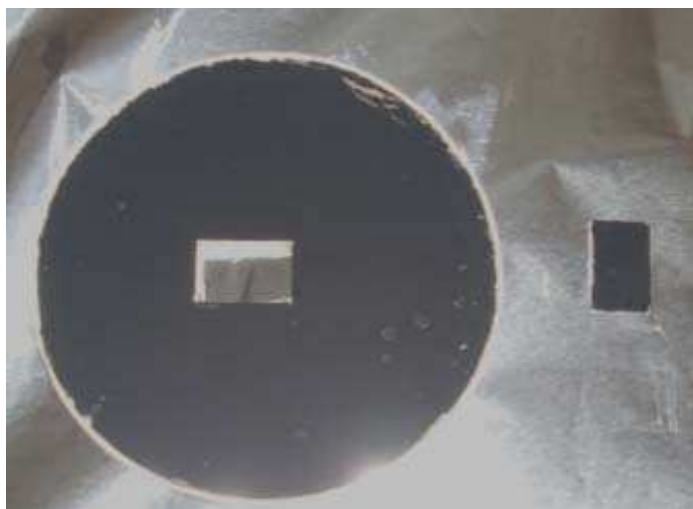
Table A2

Average signal-to-noise ratios (S/N) determined for B[a]P, B[g,h,i]P and Ind[1,2,3-cd]P using ASE, QuEChERS and QuEChERS + d-SPE extraction procedures (emission filter sample, n = 3) (see also Fig. A4).
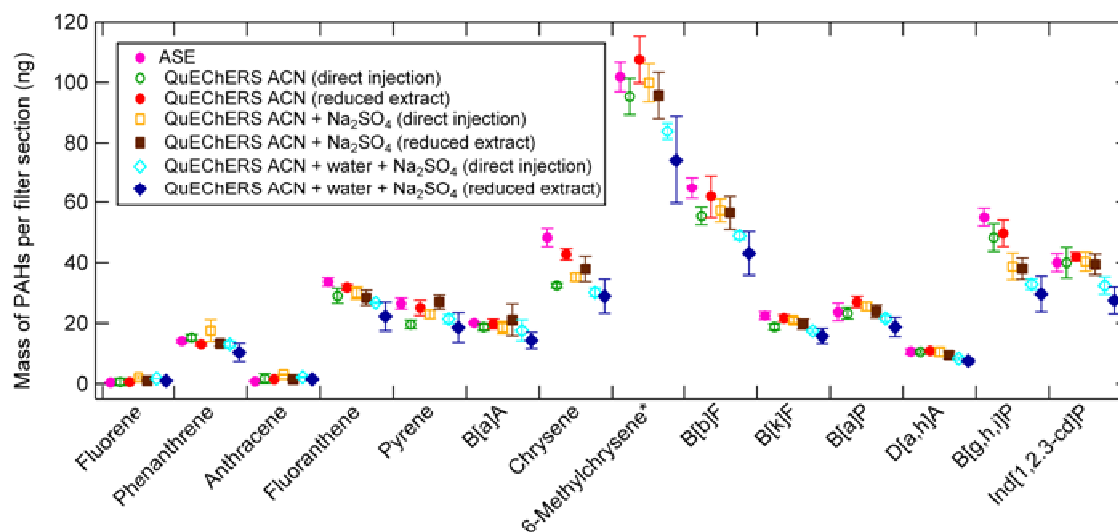
| S/N [a]	B[a]P	B[ghi]P	Ind[1,2,3-cd]P
ASE	50.3	28.9	13.8
QuEChERS	65.5	32.5	47.4
QuEChERS + d-SPE	135.3	270.7	166.0

[a] S/N calculated using Chromeleon software.

**Fig. A1.** Picture of an emission filter sample (wood combustion).

Fig. A2. Comparison of the average PAH quantity extracted according to the extraction solvent used in the QuEChERS procedure (ACN, ACN + Na_2SO_4 or ACN + water + Na_2SO_4) and comparison with the results using ASE (extraction solvent: DCM). Filter sections ($\varnothing = 47$ mm) originated from the same PM_{10} ambient air filter sample (n = 3). The error bars show the standard deviation for the triplicate analysis. [*]6-Methylchrysene: surrogate standard (100 ng filter[-1]).
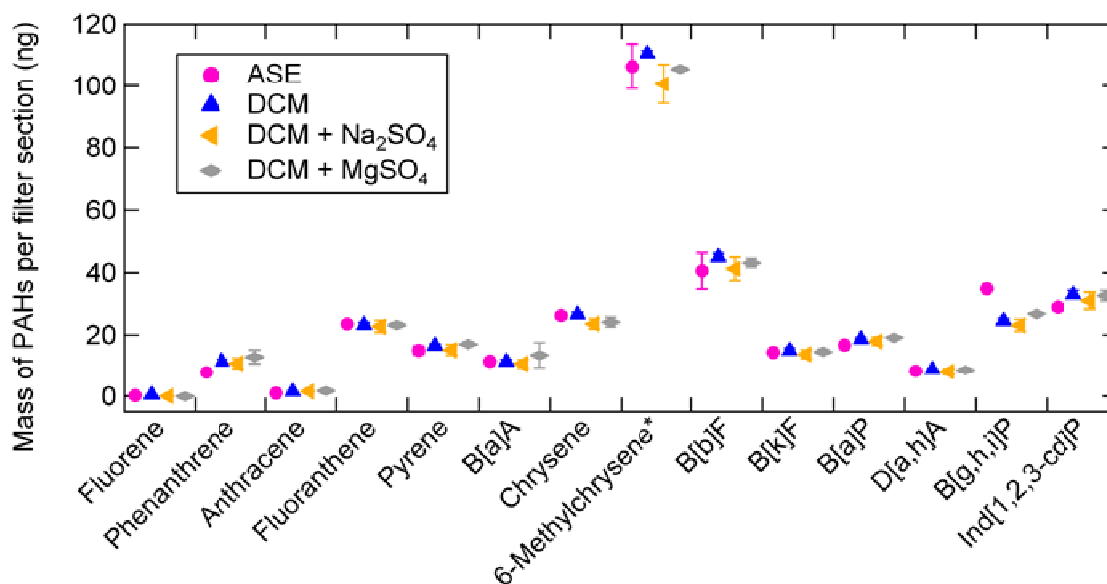
Fig. A3. Comparison of the average PAH quantity extracted according to the extraction solvent used in the QuEChERS procedure (DCN, DCM + Na$_2$SO$_4$ or DCM MgSO$_4$) and comparison with the results using ASE (extraction solvent: DCM). Filter sections ($\varnothing$ = 47 mm) originated from the same PM$_{10}$ ambient air filter sample (n = 3). The error bars show the standard deviation for the triplicate analysis. [*]6-Methylchrysene: surrogate standard (100 ng filter^{-1}).
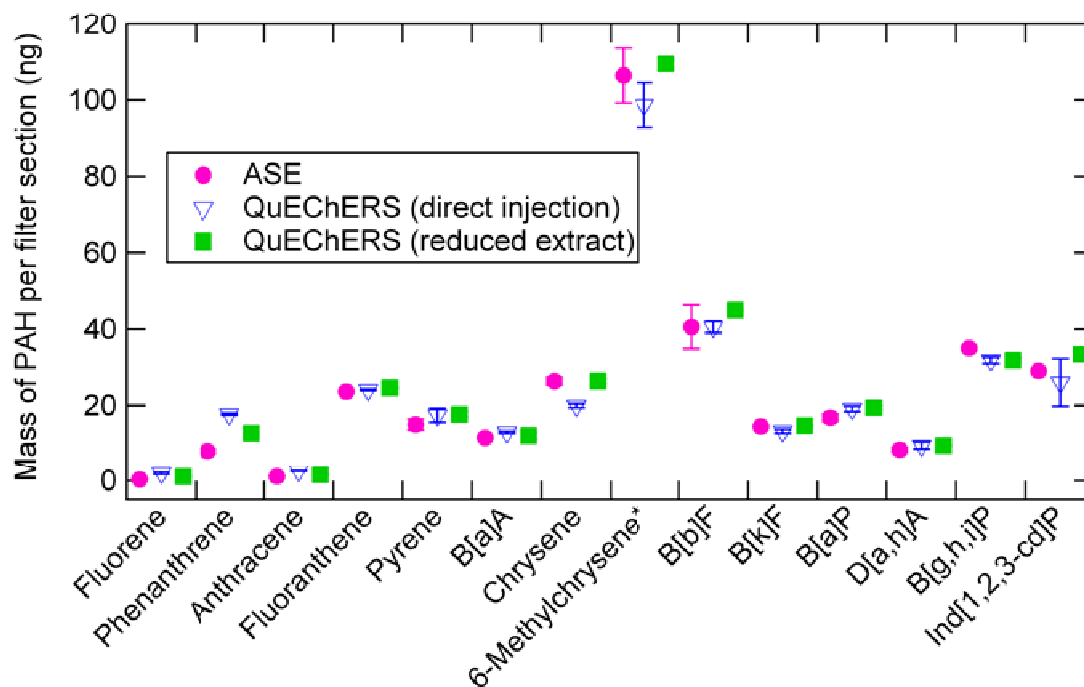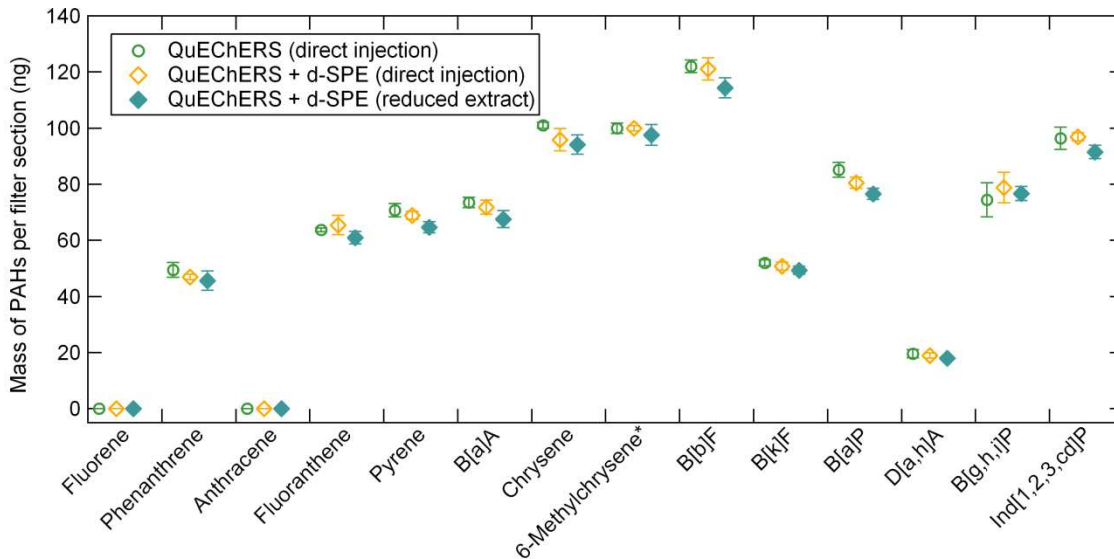
Fig. A4. Comparison of the average quantity of PAH per filter determined according to the used extraction procedure: ASE and QuEChERS. For QuEChERS, extraction solvent was acetonitrile (ACN). Filter sections originated from the same PM_{10} ambient air filter sample (n = 3). The error bars show the standard deviation of the 10 (direct injection) or of the 3 (reduced extracts) essays. [*]6-Methylchrysene: surrogate standard (100 ng filter[-1]).
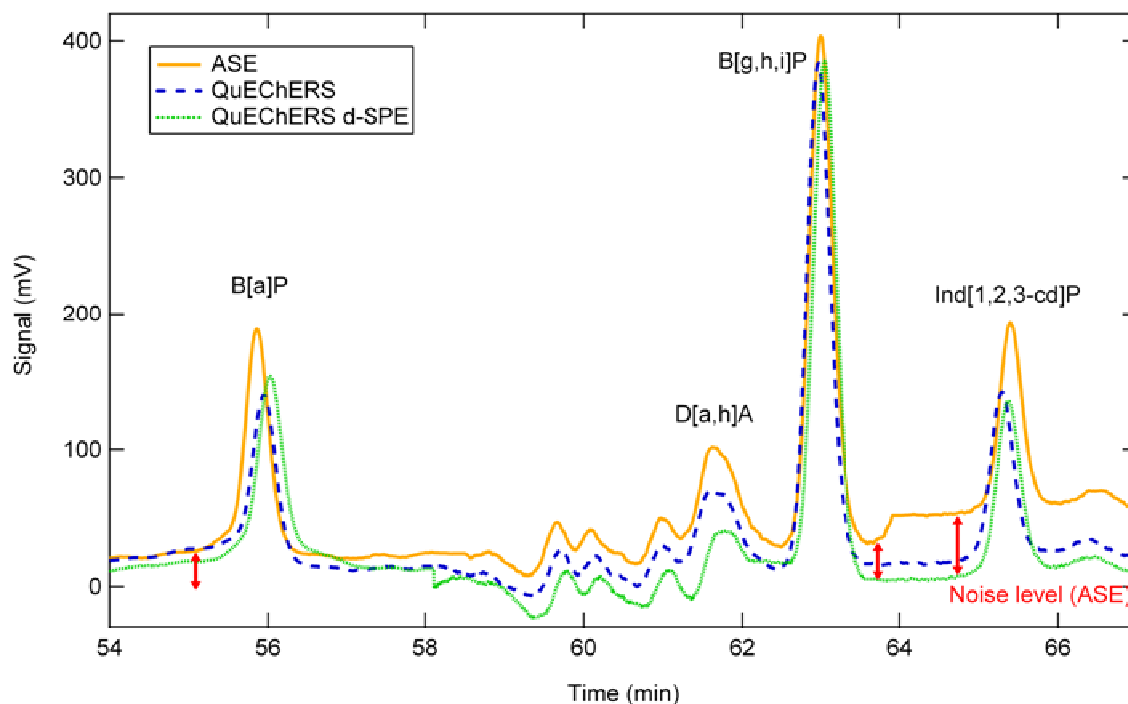
Fig. A5. Examples of chromatograms obtained for the analysis of particulate emission samples (wood combustion) according to the used extraction procedure: ASE, QuEChERS and QuEChERS + d-SPE clean-up. Zoom from B[a]P to Ind[1,2,3-cd]P. Filter sections (1.5 cm²) arise from the same emission filter sample (n = 3). For QuEChERS, extraction solvent was acetonitrile (ACN) and the direct injection of the diluted sample extracts (by a factor 20) was performed. For ASE, extracts were diluted by a factor 100. <u>Warning</u>: a direct comparison of the peak areas is not possible because the total dilution factors were different (about 140 for QuEChERS and 100 for ASE).

Fig. A6. Comparison of the average quantity of PAH per filter quantified according to the used extraction procedure: QuEChERS and QuEChERS + d-SPE clean up. Filter sections ($\varnothing$ = 47 mm) originated from the same PM_{10} ambient air filter sample (n = 3). The error bars show the standard deviation for the triplicate analysis. Extraction solvent was acetonitrile (ACN). [*]6-Methylchrysene: surrogate standard (100 ng filter^{-1}).

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