**Environmental analysis of polar and non-polar Polycyclic Aromatic
Compounds in airborne particulate matter, settled dust and soot: Part I:
Sampling and sample preparation**

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Abstract

Interests in Polycyclic Aromatic Hydrocarbons (PAHs) and their derivatives (nitrated PAHs, oxygenated PAHs, Azaarenes and Polycyclic Aromatic Sulfur Heterocycles) have been growing because of their toxicity.

The first part of this review gathers information on sampling of Polycyclic Aromatic Compounds (PACs) in airborne particulate matter (PM), dust and soot, on their extraction thanks to solvent extraction methods, and on sample clean-up for further analysis.

Atmospheric PM is generally sampled on quartz-fiber filters. For settled dust as well as for PM, active samplers are used in most cases.

After sampling, solid/liquid extraction is necessary. At this step, yields can be enhanced depending on the device and solvent used, but also with optimization of solvent volume and extraction time. Most up-to-date extraction devices are Pressurized Liquid Extraction (PLE), Ultrasound Assisted Extraction (UAE) and Microwave Assisted Extraction (MAE).

After the extraction, sample purification (generally by SPE) and concentration is advised.

Keywords

PAHs, Nitrated PAHs, Oxygenated PAHs, Azaarenes, PASHs, Sampling, Extraction

1. Introduction

PAHs have been reported as major hazardous compounds in various environments for decades. From the 1970s, efforts have been made in the United States of America to define a list of priority pollutants, finally resulting in the well-known U.S. EPA's 16 PAH Priority Pollutants list [1].

The toxicity, carcinogenicity and mutagenicity of PAHs have been assessed and reported by the International Agency for Research on Cancer (IARC) since 1983 with regular updates [2–5], but due to the high number of compounds which can be classified as PAHs, it can be tough to assess with certainty the human health risks related to various individual PAHs in environmental samples. Indeed, about 500 PAHs have already been detected in ambient air, and PAHs exposure always happens with complex mixtures [5,6]. Therefore, relying only on individual PAHs or on the sum of the 16 EPA PAHs is not sufficient for a reliable evaluation [7].

Methods have been developed to characterize health and environmental risks based on a single reference compound : Benzo[a]Pyrene (B[a]P), the first PAH to have been thoroughly studied in terms of toxicology [6,8,9]. Toxic Equivalency Factor (TEF) and Potency Equivalency Factor (PEF) approaches with respect to B[a]P have been implemented by various authors to summarize the risks related to PAH occurrence in the environment [8,10–12]. However, even with such kinds of approaches, the PAHs-related carcinogenicity of a sample can be underestimated. Indeed, TEFs and PEFs should be handled with care as they are often approximations. Moreover, for too long, many toxic PAHs with potencies comparable to or higher than B[a]P have been neglected [7,12].

Furthermore, a lot of risk assessment studies are restricted to Polycyclic Aromatic Hydrocarbons in the narrow sense of the term. This can be a major shortcut, since there is growing evidence that polar Polycyclic Aromatic Compounds (PACs) are crucial compounds in terms of toxicity, carcinogenicity and mutagenicity. Indeed, some of them have a more significant toxicology than the non-polar PAHs, because unlike PAHs, they do not require a prior enzymatic activation to exert their toxicity [10,13,14]. Thus, nitrated PAHs for instance have been reported as accounting for over half of the total direct mutagenicity of ambient air [15]. Among polar PACs, nitrated PAHs (NPAHs) and oxygenated PAHs (OPAHs) are the most studied [16–18].

In addition to NPAHs and OPAHs, other polar PACs are of a growing interest: azaarenes (AZAs), sometimes alternatively referred to as Polycyclic Aromatic Nitrogen Heterocycles (PANHs), and Polycyclic Aromatic Sulfur Heterocycles (PASHs). While AZAs are quite similar to the above-mentioned PAHs, NPAHs and OPAHs in terms of sources and

toxicology [10,19,20], PASHs are particularly typical of petrogenic emissions and have been studied sooner in the evolution of environmental analysis of PACs [21,22]. Both categories have also been studied by the IARC and some of their compounds have been classified as possible or probable carcinogens [23].

To illustrate chemical differences between these categories of PACs, Figure 1 gathers the chemical structures of 3-ring oxygenated, nitrated, nitrogen heterocycle and sulfur heterocycle variants of anthracene.

Airborne particulate matter, dusts and soots have been widely described as major sources of exposure to PAHs for human beings in indoor [24–30] as well as in outdoor environments [30–33]. Naturally, these matrices also play an important role in the exposure to polar PACs and their content of polar PACs has been growingly reported in recent years [20,31,33–38]. For PACs occurrence studies, particular focuses have been made on atmospheric particulate matter (PM_{10} , $PM_{2.5}$ and PM_1) because of its well-known negative health effects [18,39]. These effects are especially pronounced for the smallest of these particles, because of their higher surface area per unit mass, in addition to their deeper penetration into lungs [40,41]. According to the IARC, “there is sufficient evidence in humans for the carcinogenicity of particulate matter in outdoor air pollution” [42]. PACs account for an important part of this carcinogenicity.

Other particulate matters such as settled dusts of indoor environments [24,25,27–29], “environmental” third-hand smoke (ETS) [43–46], urban road dust [32,47–49], particulate exhausts and soots from vehicular emissions [32,50–52], are also of a great concern because of their ability to host toxic semi-volatile organic compounds (SVOCs) such as PACs.

The purpose of this paper is to review the different options available to analytical scientists willing to implement methods for the determination of polar and non-polar Polycyclic Aromatic Compounds in airborne particulate matter, dust and soot, especially for environmental evaluation of human exposure pathways to these pollutants.

In a first part, we will focus on the sampling methods applicable to airborne particulate matter and settled dust, and on the preparation of such particulate samples for an optimal extraction of the analytes and a good clean-up of the sample.

2. Sampling

2.1. Atmospheric particulate matter

In terms of sample collection techniques, only a few possibilities are currently implemented in the different studies about PACs analysis in atmospheric PM.

In the vast majority of cases, PM are collected on quartz-fiber filters (QFF) [20,36,53–60].

The main advantages of QFFs over glass-fiber filters (GFF), which can also be used for this kind of sampling [37,61,62], are the higher purity of the material, leading to lower blank levels [63], and its higher thermal stability, enabling the determination of organic and elemental carbon (OC/EC) by calcinating the filter at up to 850°C [36,64,65], a temperature range at which glass filters would be degraded. Therefore, QFF seem to be a better choice than GFF.

An alternative to siliceous materials is the use of organic filters such as PTFE membrane filters [45,66–68]. Generally speaking, these latter are less employed for organic pollutants analysis because of their higher content in organic compounds, increasing the risk of contamination in comparison to their inorganic counterparts. In the other hand, as a drawback, glass and quartz show a much higher physical fragility than PTFE.

Inorganic filters are generally baked out at very high temperatures ($\geq 350^{\circ}\text{C}$) for 6 to 24 hours for their decontamination prior to sampling [36,37,54–56,58,65]. The poor thermal stability of organic filters disables this treatment, which is why washing with organic solvents is preferable [69]. Such solvent washings are also applicable to inorganic filters [20]. Some authors rather proposed a “mild” conditioning of their PTFE filters at stable temperature (20 to 25°C) and humidity (40 to 50%) for 24 to 48 hours [59,66]. This accounts for the absorption of water vapor [70].

For PM collection, sampling heads designed for PM₁₀ or PM_{2.5} are generally adapted on active air samplers [36,45,56,59]. To get more accurate information about the PACs size-fractionation in atmospheric PM, it is possible to use devices differentiating various fractions of PM according to their size.

The most used is the cascade impactor [19,34,57,60,66,71–74]. This device is based on the progressive removal of particles of higher aerodynamic diameter, so that particles of various diameters can be separated into multiple (from 4 to 13) fractions, from the sub-0.1µm range to particles larger than 10µm. The theory of the cascade impactor has been described more precisely by Liaud et al. [61]. The only influence of the use of a cascade impactor instead of “classical” sampling heads on the design of the pumping system is that the selected air flow should meet the requirements prescribed by the impactor manufacturer.

However, a technical issue is likely to arise with cascade impactor: too low mass loadings. Indeed, as the sampled particles are split up, sometimes in a dozen of fractions, the quantities collected on each stage can be insufficient for further analysis. In such cases, either the sampling time should be increased, or multiple fractions should be brought together, but then the information on size fractionation is less precise.

Another possibility to study size distribution is the use of a light-scattering particle counter [68,70]. However, as suggested by the term “counter”, it only gives information about the number and mass concentration for each particle channel. It does not enable to collect the PM fractions for further analyses.

All the PM collection systems introduced above rely on active air samplers. These ones can be divided into three categories: high-volume, medium-volume, and low-volume. A table summarizing various recent works on PACs in airborne particulate matter, with regard to the PM collection system, the active sampler and the main sampling parameters (flow rate, time, total volume) implemented, is presented in the Supplemental Content of this article (Table S.1.).

When discussing the sampling of particulate matter, attention needs to be drawn on possible analytical biases. The first one was highlighted by Albinet et al. for NPAHs, which could be degraded at the sampling stage depending on the temperature inside the sampler [75]. This is a parameter to take into account especially for outdoor sampling campaigns where temperature variations can affect a lot more the results than when sampling is performed in indoor environments.

Conversely, the study of Goriaux et al. highlighted the risk of over-estimation of polar PACs such as NPAHs and under-estimation of PAHs due to on-filter degradation reactions of the parent PAHs [76]. Consistently with the results of Schauer et al. and Tsapakis and Stephanou, they identified O₃ and OH radical as major oxidizing agents responsible for the on-filter degradation of PAHs during sampling, even if the role of NO_x cannot be excluded [77,78]. Ozone levels and sampling time are therefore important parameters to take into account when assessing the risk of sampling artifacts for these compounds.

Similarly, such kinds of reactions can lead to artifact formations of OPAHs. The main solution prescribed to reduce these artifacts is the use of a denuder able to trap or deactivate gas phase oxidants such as ozone. The reduction of the risk of artifact formation of polar PAHs derivatives induced by ozone denuders is a conclusion from the review of Cave et al [79]. On the other hand, results obtained for more volatile PACs could indicate that they are likely to be formed catalytically at the denuder surface, so that sampling biases can still exist with

the use of ozone denuders, as stated by Walgraeve et al. in their review [18]. Moreover, in several of their works, Albinet et al. observed under-estimations of PAHs generally lower than 10% when ozone denuders were not used [80]. Thus, the gain of precision with an ozone denuder seems to be rather minor.

In addition to these artifacts characteristic to PACs, Turpin et al. have reviewed sampling issues related to atmospheric particulate organics, noting risks of volatilization of particulate organics, adsorption of gas phase organics on the filter, and bounce-off of particles, among others [81].

2.2 Settled dust

For what regards settled dust, the easiest and most common sampling method is to collect it in classical vacuum cleaner bags [29,82–84], which can be further fractionated depending on the particles size thanks to sieves [25,48]. Depending on the type of analysis performed afterwards, various other sampling techniques are available, such as simple manual wiping, sweeping or scraping of surfaces [24,85,86] or passive techniques involving dust fall jars or non-electrostatic plates [24]. Active sampling is generally considered as the ideal solution, because it is more time-efficient and offers more control over the sampling procedure.

The most up-to-date and standardized sampling method has been defined by ASTM International and is based on the use of the High Volume Small Surface Sampler (HVS3) [87]. This standardization has had the benefits of reducing the biases between different studies when different sampling devices were used, as well as the biases inside each study due to differences in dust load and carpet type for instance. Some parameters characteristic of each sampling site such as levels of carpet wear and ambient humidity during sampling can still give birth to sampling variations with HVS3 [88].

However, due to the supplemental cost of the HVS3, household vacuum cleaner methods can be preferred, knowing that studies such as the one of Colt et al. have shown an excellent agreement in detection and good correlation coefficients between analyses of typical household pollutants (PAHs, pesticides, PCBs ...) performed with both HVS3 and household vacuum cleaner as samplers [89].

Even if most of the examples quoted in this section concern indoor dust sampling, it is interesting to note that such kinds of sampling techniques (household vacuum cleaners for instance) have also been used for urban road dust collection [48,90,91].

2.3. Sample storage

222 After sampling, it is necessary to store the samples in aluminium foil (or equivalent) to protect
223 them from light, which causes degradation of photosensitive PACs [16]. For the same
224 purpose of avoiding analyte degradation, storage of samples before their extraction should
225 take place either in a refrigerator (3 to 7°C) or in a freezer (-10 to -25°C). In the first case, it is
226 considered that filters can be extracted up to 2 months after sample collection, in the latter,
227 this delay can be extended up to 12 months [80].
228

3. Extraction

The most common extraction methods which have been implemented for PACs in particulate matters belong to the group of solid/liquid extractions. They can be listed as follows: Soxhlet extraction, Pressurized Liquid Extraction (PLE) or Accelerated Solvent Extraction (ASE), Ultrasonic Assisted Extraction (UAE) or sonication, Microwave Assisted Extraction (MAE), and Supercritical Fluid Extraction (SFE).

SFE is an exception to this list. Indeed, after some attempts to implement this technique for PACs in particulate samples in the 90s, some drawbacks have been quickly identified. First and foremost its strong matrix-dependence, precluding a satisfying variability when applied to different kinds of real solid samples, then big differences between various works in terms of ideal parameters and extraction yields, and finally the high expense of the technical investment [92–95]. Despite its well-known advantages such as time-efficiency and a greatly reduced use of organic solvents for instance [94,96,97], in the last decade, very few works have reported its use for particulate matter, a little more for soil matrices [97,98].

The following section will give more details about the choice of the solvent and the solid/liquid extraction methods available for the analysis of polar and non-polar PACs in particulate matter matrices. The need of concentration and purification procedures will also be discussed. We will not differentiate atmospheric PM and settled dusts as extraction methods are the same for both kinds of matrices.

On the other hand, we will not discuss thermal desorption methods, which are relevant but less frequent than solvent extraction. These methods, applied to PAHs and derivatives, are the focus of the review of Liu et al. [99].

We will not discuss miniaturized extraction and micro-extraction techniques either. These are novel and promising for some of them, but to this day they have not been sufficiently implemented to represent an accurate overview of the state of the art. Besides, they have been presented in detail in the review of Manousi and Zachariadis [100].

3.1. Choice of solvent

The solvent selection is one of the most crucial parameters for any extraction method. Its extraction efficiency, its cost, its health and environmental toxicity, and its volatility (for further evaporation, see Section 3.6.) are the main characteristics to take into account when choosing the ideal solvent for a certain application. These criteria are equally applied when implementing Soxhlet, ASE, UAE or MAE methods.

As a general rule, the most frequently used solvents for PACs extractions from particulates are, in increasing order of polarity: n-hexane, cyclohexane, toluene, dichloromethane, acetone, acetonitrile, ethanol and methanol. It is worth noting that benzene has also been used in some works [33,50,86], but because of its huge toxicity, it should be avoided. It may occur that in some cases, other less common solvents give better extraction recoveries and reproducibility, as highlighted by Lintelmann et al. who selected ethyl acetate for the extraction of OPAHs in particulate matter samples [101].

If attempts with different pure solvents do not yield satisfying results, they can be used in mixtures as it is often the case, or sequentially, for instance when several PAC categories are targeted [33,37,49,102,103]. In the case of PM extraction, Jonker and Koelmans hypothesized that the combination of an aromatic solvent (such as toluene) with methanol was particularly interesting because it associates the displacement capacity of the solvent which has the highest chemical similarity to PACs and the swelling capacity of methanol which has the lowest molar volume and therefore increases the accessibility to the sample for the second solvent [104]. This hypothesis was later validated by Masala et al. [105].

In their review, Bandowe and Meusel have reported dichloromethane alone as being a good extraction solvent for NPAHs, dichloromethane / methanol mixtures appropriate for OPAHs, and n-hexane / dichloromethane mixtures more adapted to non-polar PAHs [16]. Nonetheless, it is important to keep in mind that the choice of the “ideal solvent” is not only analyte-dependent, but also matrix-dependent. Anyway, no single solvent can be defined as optimal and comparative studies of solvents should be performed for each application.

3.2. Soxhlet extraction

Soxhlet is the “historical” system for solid samples solvent extraction. It has marked the beginning of environmental analyses of particulate matters, soils, etc. Therefore, it has been widely used in studies of the 90s [93,106,107]. It has especially been implemented by the National Institute of Standards and Technology (NIST) for the certification of air particulate matter and diesel particulate matter Standard Reference Materials (e.g. SRMs 1648, 1649 and 1650) [108,109].

As it earned a status of reliable extraction method, Soxhlet has remained the method of choice for a lot of analytical scientists around the world in more recent times [25,32,55,103,110].

The main drawbacks of Soxhlet are obvious and well-known to all in the environmental field: its time consumption, the high amounts of solvents required and the impossibility of automation. Indeed, Soxhlet extractions are generally from 8 to 48 hours long, in contrast with the other typical extractions whose durations are around 30 minutes. Even if big technical investments, as would require ASE, MAE or SFE, want to be avoided, the Soxhlet drawbacks tend to orient the selection of the extraction method towards sonication for example [18,32,107].

Table 1 regroups the extraction conditions reported by various studies where Soxhlet was used.

Table 1: Typical parameters implemented for solvent extraction with a Soxhlet device

	Authors	Year	Compounds of interest	Solvent	Volume	Time
[108]	Wise et al.	1996	PAHs	Dichloromethane	n.d.	20 h
[106]	Chen and Preston	1997	AZAs	Dichloromethane	n.d.	Overnight / ~ 18 h
[78]	Tsapakis and Stephanou	2003	PAHs	n-Hexane	n.d.	24 h
[111]	Bamford and Baker	2003	NPAHs	Dichloromethane	n.d.	24 h
[32]	Christensen et al.	2005	PAHs	Dichloromethane	170 mL	18 h
[103]	Lalah and Kaigwara	2005	PAHs + PASHs + NPAHs + AZAs	Toluene / Methanol (4:1)	200 mL	8 h
[110]	Delhomme and Millet	2008	AZAs	n-Hexane / Dichloromethane (1:1)	n.d.	20 h
[112]	Lin et al.	2015	PAHs + NPAHs	n-Hexane / Acetone (1:1)	200 mL	22 h
[55]	Gao et al.	2018	NPAHs + OPAHs	Dichloromethane	150 mL	8 h
[25]	Cao et al.	2019	PAHs	n-Hexane / Acetone (1:1)	20 mL	36 h

* n.d.: not disclosed

3.3. Pressurized Liquid Extraction

Starting from the consideration that extractions were favored at higher temperatures, Richter et al. developed the Accelerated Solvent Extraction system around the year 1995 [113]. ASE has become a trademark from the brand Dionex, which is now widely used to characterize Pressurized Liquid Extraction (PLE). It enables to perform solid/liquid extractions based on a principle similar to Soxhlet extractions, but with higher efficiency in terms of time, solvent consumption, and recoveries. The system is designed to flush a solid or semi-solid sample

with extracting solvents under high temperatures (50 to 200°C) and high pressures (500 to 3000 psi, i.e. 35 to 205 bar), during short times (around 10 minutes) [113].

This PLE system also gives the possibility to automate the sample preparation, so that a lot of samples can be extracted sequentially, something which is not possible with Soxhlet. Works focusing on the analysis of Standard Reference Materials (SRM) have studied the efficiency of PLE in comparison with Soxhlet extraction. The results have shown satisfying extraction yields, similar to those of Soxhlet for a majority of compounds, and even higher for high molecular weight (HMW) PAHs, in a far shorter time [95].

After the promising early days of PLE, its extraction efficiency for PACs in particulates has been confirmed [105], which is why the method has been implemented by a lot of labs in the 21st century, and is nowadays the major extraction technique reported in the literature for organic pollutants such as PACs in particulates [36,47,49,58,61,114–116].

Because of the extreme conditions of PLE, there is a possibility of chemical degradation of the analytes during extraction, as showed the example of Lintelmann et al. who observed degradation of PAH quinones (OPAHs) during their PLE protocol [117].

Another risk to take into account with PLE is the possibility of losing analytes during the evaporation steps afterwards, especially if high amounts of solvent are used, as sometimes required with PLE (see Section 3.6.). This analytical bias was reported by Delgado-Saborit et al. who compared various extraction solvents without reaching more than 76% of recovery on the whole extraction procedure, and who finally selected a much simpler method to extract PAHs from their filters, by shaking them in dichloromethane, a strategy that brought higher recoveries [63].

The main parameters to study in the course of a method development with PLE are the solvent, the temperature, the pressure, the heating time, and the number and duration of static cycles (extraction cycle at constant temperature and pressure).

The optimization of these parameters is crucial, as shown by Masala et al. in their study of the enhancement of PAHs extraction from a SRM of Diesel Particulate Matter [105]. In this work, they chose to apply extreme pressures and temperatures during longer static cycles than in the general rule, and they compared carefully different solvents and different proportions of solvent mixtures, to obtain the most efficient extraction possible.

The PLE parameters reported in studies focusing on PACs in dusts and PM are reviewed in Table 2.

Table 2: Typical parameters implemented for solvent extraction with a PLE device

	Authors	Year	Compounds of interest	Solvent	Temp.	Pressure	Heat time	Static time
[95]	Schantz et al.	1997	PAHs	- Dichloromethane - Toluene - Toluene / Methanol (1:1)	100°C	138 bar	5 min	3 x 5 min
[117]	Lintelmann et al.	2005	PAHs + OPAHs	Hexane / Acetone (7:3)	100°C	107 bar	7 min	3 x 5 min
[47]	Albinet et al.	2006	OPAHs + NPAHs	Dichloromethane	120°C	140 bar	6 min	6 min
[118]	Di Filippo et al.	2007	PAHs + NPAHs	Dichloromethane / Acetone (4:1)	100°C	110 bar	5 min	4 x 5 min
[119]	Bandowe and Wilcke	2010	PAHs + OPAHs	1. Dichloromethane 2. Acetone / Dichloromethane / TFA (250:125:1)	120°C	140 bar	6 min	5 min
[58]	Lintelmann et al.	2010	AZAs	Dichloromethane / Methanol (1:1)	100°C	100 bar	5 min	3 x 5 min
[105]	Masala et al.	2011	PAHs	Toluene / Methanol (9:1)	200°C	207 bar	9 min	5 x 30 min
[116]	Nocun and Schantz	2013	OPAHs	Dichloromethane	100°C	100 bar	5 min	4 x 5 min
[61]	Liaud et al.	2015	PAHs	Acetonitrile	120°C	104 bar	6 min	3 x 5 min
[34] [120]	Alves et al. Vicente et al.	2016	PAHs + OPAHs + NPAHs + AZAs	1. Dichloromethane 2. Acetone / Dichloromethane (2:1)	n.d.	n.d.	n.d.	n.d.
[115]	Madruga et al.	2019	PAHs	Dichloromethane	120°C	140 bar	n.d.	n.d.
[49]	Gbeddy et al.	2020	PAHs + OPAHs + NPAHs	1. Dichloromethane 2. Dichloromethane / Methanol / Acetone (1:1:1)	120°C	170 bar	6 min	2 x 5 min

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362 * When several solvents are associated in a cell, the formatting “ / “ designates a mixture of solvents,
363 the list “1. 2. ...” expresses sequential extractions with different solvents, and the list “-“ is used when
364 in a study, various solvents have been tested and compared without a definite choice of a unique ideal
365 solvent.

366 * n.d.: not disclosed

367

368 3.4. Ultrasound Assisted Extraction

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370 Ultrasound Assisted Extraction, frequently called “sonication”, has been widely employed for
371 PACs extraction from particulates, thanks to its low cost, easy implementation in a lot of labs,
372 and time-efficiency. Indeed, the only material requirements are an ultrasound-producing
373 device and adapted vessels.

374 Even if the interesting possibilities offered by PLE, particularly in terms of automation, have
375 increased its use over Soxhlet and sonication in recent years, sonication remains one of the

most frequent extraction methods. With the “classical solvents” cited in Section 3.1, quantitative extractions of PACs from particulate matters are achieved in less than an hour, even sometimes in less than 20 minutes [32,101,121–123]. According to several works, the extraction recoveries obtained with UAE are similar to those obtained with Soxhlet extraction, but in a far shorter time [32,107,124].

García-Alonso et al. compared multiple extraction techniques for PAHs and NPAHs in PM samples. When keeping the same solvent (dichloromethane), PLE and UAE gave comparable extraction yields. Even if they were slightly favorable to PLE, the authors reported the differences between both extractions as insignificant [121]. These results are presented in Figure 2, where the grey bars represent the quantities of analytes extracted by PLE with dichloromethane, and the darkest bars represent the quantities of analytes extracted by UAE with dichloromethane (abbreviated “AG-D”).

Thus, sonication can still be considered as a reliable extraction method for PACs in solid samples.

Nonetheless, it is important to keep in mind that UAE is “less rigorous” than automated methods such as PLE or MAE. Therefore, it can cause higher uncertainties when applied to strongly sorptive matrices such as soots [104].

Moreover, the sonication completely destroys the particulate matter sampling filters, causing the release of a lot of particles, which need to be removed later by appropriate sample filtration and clean-up.

The parameters reported by studies using UAE as extraction method are regrouped in Table 3.

Table 3: Typical parameters implemented for solvent extraction with an UAE device

	Authors	Year	Compounds of interest	Solvent	Volume	Time
[72]	Allen et al.	1997	OPAHs	Dichloromethane	n.d.	30 min
[77]	Schauer et al.	2003	PAHs	Dichloromethane / Methanol / Toluene (1:1:1)	n.d.	30 min
[32]	Christensen et al.	2005	PAHs	Acetone	n.d.	10 min
[101]	Lintelmann et al.	2006	OPAHs	Ethyl acetate	20 mL	15 min
[125]	Delhomme et al.	2008	OPAHs	Dichloromethane	20 mL	20 min

[48]	Dong and Lee	2009	PAHs	n-Hexane / Dichloromethane (1:1)	30 mL	30 min
[126]	Kojima et al.	2010	PAHs + OPAHs + NPAHs	Dichloromethane	n.d.	2 x 20 min
[68]	Wingfors et al.	2011	PAHs + OPAHs	Dichloromethane	5 mL	3 x 10 min
[127]	Barrado et al.	2012	OPAHs	Methanol	10 mL	30 min
[123]	Sangiorgi et al.	2013	PAHs	Acetonitrile	2 mL	20 min
[60]	Wang et al.	2014	PAHs + OPAHs + PASHs	Dichloromethane	n.d.	3 x 10 min
[102]	Große- Brinkhaus et al.	2017	PAHs	1. Dichloromethane 2. Toluene / Methanol (6:1)	1. 7 mL 2. 3 x 7 mL	4 x 20 min
[121]	García-Alonso et al.	2017	PAHs + NPAHs	- Dichloromethane - Dichloromethane / Methanol (2:1)	5 mL	15 min
[122]	Niu et al.	2017	PAHs + OPAHs	Dichloromethane / Methanol (2:1)	n.d.	15 min
[128]	Ali	2019	PAHs	n-Hexane / Acetone (1:1)	n.d.	2 x 20 min

* When several solvents are associated in a cell, the formatting “ / “ designates a mixture of solvents, the list “1. 2. ...” expresses sequential extractions with different solvents, and the list “-“ is used when in a study, various solvents have been tested and compared without a definite choice of a unique ideal solvent.

* n.d.: not disclosed

3.5. Microwave Assisted Extraction

Only a few works have reported the application of MAE to particulate samples up to now. The developments of this technique are relatively recent, so that in the review of Walgraeve et al. published in 2010, only one research group had published data on microwave extraction of OPAHs [18].

Nevertheless, in 1998, Colmsjö already reported the use of MAE as a possibility to extract PAHs from solid environmental samples such as soil, with extraction recoveries comparable to those obtained with Soxhlet. He mentioned acetone or acetone/hexane mixtures as ideal extraction solvents for PAHs in soil matrices with this technique [124].

Recently, more and more groups studying polar and non-polar PACs in particulates have utilized MAE [37,45,59,121,127,129]. Similarly to PFE, this technique enables the heating of an organic solvent above its boiling point to enhance the extraction, thanks to specially adapted vessels placed in a microwave oven. The microwave extraction can be performed

under constant magnetic agitation to ensure homogeneous mixing and uniform temperature [59].

In their study, García-Alonso also compared MAE with UAE and PLE. The results obtained proved to be very heterogeneous. Indeed, as shown in Figure 2, whereas MAE gave the highest extraction recoveries for pyrene and benzo[b]fluoranthene, it was totally ineffective for benzo[a]pyrene and 3-nitrofluoranthene [121]. Barrado et al. reported higher extraction yields of PAHs in dichloromethane with the use of a microwave device than with ultrasound or Soxhlet extractors [127].

Previously published MAE conditions are presented in Table 4.

Table 4: Typical parameters implemented for solvent extraction with a MAE device

	Authors	Year	Compounds of interest	Solvent	Volume	Temp.	Power	Time
[32]	Christensen et al.	2005	PAHs	Acetone / Cyclohexane (1:1)	35 mL	120 °C	n.d.	20 min
[45]	Slezakova et al.	2014	PAHs	Acetonitrile	30 mL	110 °C	n.d.	20 min
[59]	Tutino et al.	2016	PAHs + NPAHs	Acetone / n-Hexane (1:1)	10 mL	110 °C	200 W	25 min
[121]	García-Alonso et al.	2017	PAHs + NPAHs	Dichloromethane	15 mL	120 °C	900 W	40 min
[37]	Du et al.	2018	OPAHs + NPAHs	Acetone / n-Hexane (1:1)	25 mL	110 °C	1 200 W	2 x 10 min

* n.d.: not disclosed

3.6. Extract concentration and purification

Atmospheric particulate matter, dusts and soots are generally very complex matrices. Therefore, a sample clean-up is required before the instrumental analysis. Moreover, when solvent extraction is performed, the extract is often obtained in a relatively large volume (see Sections 3.2. to 3.5.), which should be reduced to optimize the detection limits of the analytical method.

Generally, immediately after the extraction, it can be preferable to filter the extract through syringe filters with Nylon or PTFE membranes (0.45 µm or less) to get rid of the residual particles [32,45,68,116,123].

In some cases, authors also want to ensure the removal of residual water in their extracts, especially to facilitate the solvent removal afterwards. For this purpose, filtration through sodium sulfate can be considered [119].

Then, a major step is the solvent removal. In a lot of works, it is performed by rotary evaporation [19,45,78,86,110,117,119]. This evaporation should take place at a low temperature ($\leq 40^{\circ}\text{C}$) under low pressures in order to avoid analyte degradation. Other techniques have been implemented for solvent removal, in particular the circulation of a nitrogen stream over the extract to shift the liquid/vapor equilibrium towards vaporization of the solvent [47,68,102,114,126,128,130]. This solution has the advantage of being easily automatable and applicable to lots of extracts similarly thanks to specially designed devices. Before the evaporation, it can be interesting to add small quantities of a less volatile solvent which will act as a “keeper”, so that the sample doesn’t reach complete dryness when its solvent is evaporated, and that the more volatile analytes are not evaporated with the solvent. Toluene, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) are good examples of keepers [32,34,36,117,130].

If the kinds of instruments used for solvent removal cited above are not available, it is conceivable to let the solvent evaporate under a lab extractor hood. This process takes a longer time but has the benefit of reducing the risks of analyte losses under such mild conditions, even if light-sensitivity of the compounds should be taken into account. This evaporation procedure is naturally more appropriate if volatile solvents such as dichloromethane, hexane, acetone or methanol are used, in decent quantities.

Finally, the extract should be cleaned up before the analysis to get rid of as many interferences as possible, and to preserve the instrumentation used for the analysis (injector, chromatographic column, mass spectrometer, etc.).

For the particular case of PLE, it is possible to perform “in-cell” clean-up similarly to the extraction. To this purpose, Bandowe et al. used a bulk sorbent containing a modified form of diatomaceous earth to fill in the void in the extraction cells [36]. Gbeddy et al. compared five different materials composed of either activated or deactivated silica gel, pure or mixed with alumina at various proportions, placed on top of the outlet filter. Besides these clean-up materials, they filled the cells with diatomaceous earth and anhydrous Na_2SO_4 to remove potential excess of water [49]. Such clean-up methods enable to get rid of additional off-line purification steps.

In the vast majority of cases, the clean-up step is done by Solid Phase Extraction (SPE). The main SPE supports used are silica and alumina [32,47,57,60,68,126]. Aminopropylsilyl columns have also been proposed for SPE purification of extracts from particulates

[108,131,132]. The choice of the SPE cartridge can have a major influence on the recovery of this purification step, therefore it can be beneficial to compare several commercially available stationary phases [133]. Further details on SPE conditions can be found in the supplemental content of this article (Table S.2.).

SPE experiments in the course of the analytical procedure can also offer the possibility of isolating different fractions of PACs depending on their polarity. Such fractionation steps are useful for assessment of various classes of PACs in the same sample, but using different analytical instruments to enhance the sensitivity for each fraction [52,120].

Apart from SPE, some authors have reported the use of different clean-up methods, more labor-intensive, such as glass column chromatography [25,55,77,119,129] and high performance liquid chromatography (HPLC) [72,114,131]. Sauvain et al. have even described a clean-up procedure composed of successive purification steps through SPE, semi-preparative normal phase liquid chromatography, open column chromatography, liquid-liquid partition and back extraction for diesel particulate, a particularly complex matrix [52]. We would like to highlight that these alternatives are generally found in older works and that nowadays, SPE is by far the most used purification technique.

However, we do not report SPE as a mandatory step for PACs determination. Indeed, important losses of compounds can be expected for PACs with classical SPE phases, especially when the goal is to analyse polar and non-polar simultaneously. Besides, many studies regarding PACs analysis are based on analytical methods without any purification step and still match quality criteria.

After the purification of the extract, important volumes are once more obtained, they can be concentrated as described above.

4. Conclusion

The objective of this first part of our review was to discuss the collection, extraction and purification of particulate samples for the determination of their PAC content.

It is important to note that even before the instrumental analysis of the extract, which will be the topic of the second part of this article, major analytical errors can be made.

The sampling step is crucial. One wants to collect a sufficient amount of sample, which should still be representative of a relatively short period of time if daily or hourly variations are studied, and representative of a relevant sampling place, i.e. not affected by airstream artifacts for instance.

Besides the possible contaminations due to the sampling filter which can easily be avoided, the major issue related to PM sampling is the risk of on-filter reactions causing artificial variations of PACs concentrations such as degradation of PAHs into their oxygenated or nitrated derivatives. To avoid such reactions, the use of ozone denuders has been reported, but gains associated to it can be considered as marginal.

The risk of such biases during the sampling is far lower in the case of settled dust which is less exposed to daylight and atmospheric oxidative conditions. Still, for settled dust as well as for PM, samples need to be completely protected from light and heat between their collection and their extraction, to avoid degradation of PACs.

The most common extraction techniques for PACs in particulates are solvent extractions. Among those, Soxhlet can be considered as obsolete because it is time-consuming, solvent-consuming and offers a poorer reproducibility compared to the others. Issues of reproducibility also arise with UAE. We would rather advise for the use of PLE and MAE, but their high expense should be taken into account.

In future years, as a result of technical evolutions, economic and environmental constraints, we expect non-solvent extraction methods to be increasingly implemented for this application. In this category, thermal desorption (TD) and Solid Phase Micro Extraction (SPME) are the most developed, but other novel sorptive micro-extraction techniques are promising. It is necessary that an extensive assessment of their advantages and drawbacks over solvent extractions be performed, including a comparison of a high amount of methods developed by various labs in various conditions. Depending on these results, they could be applied in routine analysis laboratories, but not before several years. To illustrate this delay between research stage and routine applications of extraction techniques, we can notice that Soxhlet is still applied in some of these quality control labs nowadays.

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553

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557 **Appendix**

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559 Supplementary Material of this article can be found in the online version, at ...

References

- [1] L.H. Keith, The Source of U.S. EPA's Sixteen PAH Priority Pollutants, *Polycyclic Aromatic Compounds*. 35 (2015) 147–160. <https://doi.org/10.1080/10406638.2014.892886>.
- [2] IARC, Diesel and gasoline engine exhausts and some nitroarenes., International Agency for Research on Cancer, Lyon, 2014. <https://www.ncbi.nlm.nih.gov/books/NBK294269/>.
- [3] IARC, Some Non-heterocyclic Polycyclic Aromatic Hydrocarbons and Some Related Exposures, International Agency for Research on Cancer, Lyon, 2010. <https://www.ncbi.nlm.nih.gov/books/NBK321712>.
- [4] IARC, Diesel and gasoline engine exhausts and some nitroarenes, International Agency for Research on Cancer, Lyon, 1989.
- [5] IARC, Polynuclear aromatic compounds, International Agency for Research on Cancer, Lyon, 1983.
- [6] E. Dybing, P.E. Schwarze, P. Nafstad, K. Victorin, T.M. Penning, Polycyclic Aromatic Hydrocarbons in Ambient Air and Cancer, in: *Air Pollution and Cancer*, Straif K, Cohen A, Samet J, 2010: pp. 75–94.
- [7] J.T. Andersson, C. Achten, Time to Say Goodbye to the 16 EPA PAHs? Toward an Up-to-Date Use of PACs for Environmental Purposes, *Polycyclic Aromatic Compounds*. 35 (2015) 330–354. <https://doi.org/10.1080/10406638.2014.991042>.
- [8] I.C.T. Nisbet, P.K. LaGoy, Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs), *Regulatory Toxicology and Pharmacology*. 16 (1992) 290–300. [https://doi.org/10.1016/0273-2300\(92\)90009-X](https://doi.org/10.1016/0273-2300(92)90009-X).
- [9] U.S. Environmental Protection Agency, Health Effects Assessment for Benzo(a)Pyrene, (1984).
- [10] J.F. Collins, J.P. Brown, G.V. Alexeeff, A.G. Salmon, Potency Equivalency Factors for Some Polycyclic Aromatic Hydrocarbons and Polycyclic Aromatic Hydrocarbon Derivatives, *Regulatory Toxicology and Pharmacology*. 28 (1998) 45–54. <https://doi.org/10.1006/rtp.1998.1235>.
- [11] D. Delistraty, Toxic equivalency factor approach for risk assessment of polycyclic aromatic hydrocarbons, *Toxicological & Environmental Chemistry*. 64 (1997) 81–108. <https://doi.org/10.1080/02772249709358542>.
- [12] M. Pufulete, J. Battershill, A. Boobis, R. Fielder, Approaches to carcinogenic risk assessment for polycyclic aromatic hydrocarbons: a UK perspective, *Regulatory Toxicology and Pharmacology*. 40 (2004) 54–66. <https://doi.org/10.1016/j.yrtph.2004.04.007>.
- [13] J.L. Durant, W.F. Busby, A.L. Lafleur, B.W. Penman, C.L. Crespi, Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols, *Mutation Research/Genetic Toxicology*. 371 (1996) 123–157. [https://doi.org/10.1016/S0165-1218\(96\)90103-2](https://doi.org/10.1016/S0165-1218(96)90103-2).
- [14] K. Misaki, T. Takamura-Enya, H. Ogawa, K. Takamori, M. Yanagida, Tumour-promoting activity of polycyclic aromatic hydrocarbons and their oxygenated or nitrated derivatives, *MUTAGE*. 31 (2016) 205–213. <https://doi.org/10.1093/mutage/gev076>.
- [15] C. Schauer, R. Niessner, U. Pöschl, Analysis of nitrated polycyclic aromatic hydrocarbons by liquid chromatography with fluorescence and mass spectrometry detection: air particulate matter, soot, and reaction product studies, *Analytical and Bioanalytical Chemistry*. 378 (2004) 725–736. <https://doi.org/10.1007/s00216-003-2449-1>.
- [16] B.A.M. Bandowe, H. Meusel, Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) in the environment – A review, *Science of The Total Environment*. 581–582 (2017) 237–257. <https://doi.org/10.1016/j.scitotenv.2016.12.115>.
- [17] G. Lammel, Polycyclic Aromatic Compounds in the Atmosphere – A Review Identifying Research Needs, *Polycyclic Aromatic Compounds*. 35 (2015) 316–329. <https://doi.org/10.1080/10406638.2014.931870>.
- [18] C. Walgraeve, K. Demeestere, J. Dewulf, R. Zimmermann, H. Van Langenhove, Oxygenated polycyclic aromatic hydrocarbons in atmospheric particulate matter: Molecular characterization and occurrence, *Atmospheric Environment*. 44 (2010) 1831–1846. <https://doi.org/10.1016/j.atmosenv.2009.12.004>.
- [19] H.-Y. Chen, M.R. Preston, Azaarenes in the Aerosol of an Urban Atmosphere, *Environ. Sci. Technol.* 32 (1998) 577–583. <https://doi.org/10.1021/es970033n>.
- [20] O. Delhomme, M. Millet, Azaarenes in atmospheric particulate matter samples of three different urban sites in east of France, *Atmospheric Environment*. 47 (2012) 541–545. <https://doi.org/10.1016/j.atmosenv.2011.06.044>.

- [21] M.L. Lee, M. Novotny, K.D. Bartle, Gas chromatography/mass spectrometric and nuclear magnetic resonance determination of polynuclear aromatic hydrocarbons in airborne particulates, *Anal. Chem.* 48 (1976) 1566–1572. <https://doi.org/10.1021/ac50005a037>.
- [22] S.G. Mössner, S.A. Wise, Determination of Polycyclic Aromatic Sulfur Heterocycles in Fossil Fuel-Related Samples, *Anal. Chem.* 71 (1999) 58–69. <https://doi.org/10.1021/ac980664f>.
- [23] IARC, Bitumens and bitumen emissions, and some N- and S-heterocyclic polycyclic aromatic hydrocarbons, International Agency for Research on Cancer, Lyon, 2013.
- [24] R.M. Maertens, J. Bailey, P.A. White, The mutagenic hazards of settled house dust: a review, *Mutation Research/Reviews in Mutation Research.* 567 (2004) 401–425. <https://doi.org/10.1016/j.mrrev.2004.08.004>.
- [25] Z. Cao, M. Wang, Q. Chen, C. Zhu, J. Jie, X. Li, X. Dong, Z. Miao, M. Shen, Q. Bu, Spatial, seasonal and particle size dependent variations of PAH contamination in indoor dust and the corresponding human health risk, *Science of The Total Environment.* 653 (2019) 423–430. <https://doi.org/10.1016/j.scitotenv.2018.10.413>.
- [26] H. Choi, F. Perera, A. Pac, L. Wang, E. Flak, E. Mroz, R. Jacek, T. Chai-Onn, W. Jedrychowski, E. Masters, D. Camann, J. Spengler, Estimating Individual-Level Exposure to Airborne Polycyclic Aromatic Hydrocarbons throughout the Gestational Period Based on Personal, Indoor, and Outdoor Monitoring, *Environmental Health Perspectives.* 116 (2008) 1509–1518. <https://doi.org/10.1289/ehp.10972>.
- [27] N.C. Deziel, R.P. Rull, J.S. Colt, P. Reynolds, T.P. Whitehead, R.B. Gunier, S.R. Month, D.R. Taggart, P. Buffler, M.H. Ward, C. Metayer, Polycyclic aromatic hydrocarbons in residential dust and risk of childhood acute lymphoblastic leukemia, *Environmental Research.* 133 (2014) 388–395. <https://doi.org/10.1016/j.envres.2014.04.033>.
- [28] H. Fromme, T. Lahrz, M. Piloty, H. Gebhardt, A. Oddoy, H. Ruden, Polycyclic aromatic hydrocarbons inside and outside of apartments in an urban area, *Science of The Total Environment.* 326 (2004) 143–149. <https://doi.org/10.1016/j.scitotenv.2004.02.002>.
- [29] T.P. Whitehead, C. Metayer, M. Petreas, M. Does, P.A. Buffler, S.M. Rappaport, Polycyclic Aromatic Hydrocarbons in Residential Dust: Sources of Variability, *Environ Health Perspect.* 121 (2013) 543–550. <https://doi.org/10.1289/ehp.1205821>.
- [30] M. Oliveira, K. Slezakova, C. Delerue-Matos, M.C. Pereira, S. Morais, Children environmental exposure to particulate matter and polycyclic aromatic hydrocarbons and biomonitoring in school environments: A review on indoor and outdoor exposure levels, major sources and health impacts, *Environment International.* 124 (2019) 180–204. <https://doi.org/10.1016/j.envint.2018.12.052>.
- [31] C.A. Alves, A.M. Vicente, D. Custódio, M. Cerqueira, T. Nunes, C. Pio, F. Lucarelli, G. Calzolai, S. Nava, E. Diapouli, K. Eleftheriadis, X. Querol, B.A. Musa Bandowe, Polycyclic aromatic hydrocarbons and their derivatives (nitro-PAHs, oxygenated PAHs, and azaarenes) in PM 2.5 from Southern European cities, *Science of The Total Environment.* 595 (2017) 494–504. <https://doi.org/10.1016/j.scitotenv.2017.03.256>.
- [32] A. Christensen, C. Östman, R. Westerholm, Ultrasound-assisted extraction and on-line LC-GC/MS for determination of polycyclic aromatic hydrocarbons (PAH) in urban dust and diesel particulate matter, *Anal Bioanal Chem.* 381 (2005) 1206–1216. <https://doi.org/10.1007/s00216-005-3065-z>.
- [33] N. Tang, T. Hattori, R. Taga, K. Igarashi, X. Yang, K. Tamura, H. Kakimoto, V.F. Mishukov, A. Toriba, R. Kizu, K. Hayakawa, Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their relationship to emission sources in the Pan-Japan Sea countries, *Atmospheric Environment.* 39 (2005) 5817–5826. <https://doi.org/10.1016/j.atmosenv.2005.06.018>.
- [34] C.A. Alves, A.M.P. Vicente, J. Gomes, T. Nunes, M. Duarte, B.A.M. Bandowe, Polycyclic aromatic hydrocarbons (PAHs) and their derivatives (oxygenated-PAHs, nitrated-PAHs and azaarenes) in size-fractionated particles emitted in an urban road tunnel, *Atmospheric Research.* 180 (2016) 128–137. <https://doi.org/10.1016/j.atmosres.2016.05.013>.
- [35] B.A.M. Bandowe, H. Meusel, R. Huang, T. Hoffmann, J. Cao, K. Ho, Azaarenes in fine particulate matter from the atmosphere of a Chinese megacity, *Environ Sci Pollut Res.* 23 (2016) 16025–16036. <https://doi.org/10.1007/s11356-016-6740-z>.
- [36] B.A.M. Bandowe, H. Meusel, R. Huang, K. Ho, J. Cao, T. Hoffmann, W. Wilcke, PM2.5-bound oxygenated PAHs, nitro-PAHs and parent-PAHs from the atmosphere of a Chinese megacity: Seasonal variation, sources and cancer risk assessment, *Science of The Total Environment.* 473–474 (2014) 77–87. <https://doi.org/10.1016/j.scitotenv.2013.11.108>.

- [37] W. Du, Y. Chen, G. Shen, W. Wang, S. Zhuo, Y. Huang, X. Pan, S. Tao, Winter air pollution by and inhalation exposure to nitrated and oxygenated PAHs in rural Shanxi, north China, *Atmospheric Environment*. 187 (2018) 210–217. <https://doi.org/10.1016/j.atmosenv.2018.06.004>.
- [38] S. Tomaz, P. Shahpoury, J.-L. Jaffrezou, G. Lammel, E. Perraudin, E. Villenave, A. Albinet, One-year study of polycyclic aromatic compounds at an urban site in Grenoble (France): Seasonal variations, gas/particle partitioning and cancer risk estimation, *Science of The Total Environment*. 565 (2016) 1071–1083. <https://doi.org/10.1016/j.scitotenv.2016.05.137>.
- [39] R.O. Salonen, A.I. Hälinen, A.S. Pennanen, M.-R. Hirvonen, M. Sillanpää, R. Hillamo, T. Shi, P. Borm, E. Sandell, T. Koskentalo, P. Aarnio, Chemical and in vitro toxicologic characterization of wintertime and springtime urban-air particles with an aerodynamic diameter below 10 µm in Helsinki, *Scandinavian Journal of Work, Environment & Health*. 30 (2004) 80–90.
- [40] E. Fireman Klein, Y. Adir, A. Krencel, R. Peri, B. Vasserman, E. Fireman, A. Kessel, Ultrafine particles in airways: a novel marker of COPD exacerbation risk and inflammatory status, *COPD*. Volume 14 (2019) 557–564. <https://doi.org/10.2147/COPD.S187560>.
- [41] R.P.F. Schins, J.H. Lightbody, P.J.A. Borm, T. Shi, K. Donaldson, V. Stone, Inflammatory effects of coarse and fine particulate matter in relation to chemical and biological constituents, *Toxicology and Applied Pharmacology*. 195 (2004) 1–11. <https://doi.org/10.1016/j.taap.2003.10.002>.
- [42] IARC, Outdoor air pollution, International Agency for Research on Cancer, Lyon, 2016.
- [43] E. Hoh, R.N. Hunt, P.J.E. Quintana, J.M. Zakarian, D.A. Chatfield, B.C. Wittry, E. Rodriguez, G.E. Matt, Environmental Tobacco Smoke as a Source of Polycyclic Aromatic Hydrocarbons in Settled Household Dust, *Environ. Sci. Technol.* 46 (2012) 4174–4183. <https://doi.org/10.1021/es300267g>.
- [44] IARC, Tobacco smoke and involuntary smoking, International Agency for Research on Cancer, Lyon, 2004.
- [45] K. Slezakova, D. Castro, C. Delerue-Matos, S. Morais, M. do C. Pereira, Levels and risks of particulate-bound PAHs in indoor air influenced by tobacco smoke: a field measurement, *Environ Sci Pollut Res*. 21 (2014) 4492–4501. <https://doi.org/10.1007/s11356-013-2391-5>.
- [46] U.S. Department of Health and Human Services, Monograph 13: Risks Associated with Smoking Cigarettes with Low Machine-Measured Yields of Tar and Nicotine, (2001) 251.
- [47] A. Albinet, E. Leoz-Garziandia, H. Budzinski, E. Villenave, Simultaneous analysis of oxygenated and nitrated polycyclic aromatic hydrocarbons on standard reference material 1649a (urban dust) and on natural ambient air samples by gas chromatography–mass spectrometry with negative ion chemical ionisation, *Journal of Chromatography A*. 1121 (2006) 106–113. <https://doi.org/10.1016/j.chroma.2006.04.043>.
- [48] T.T.T. Dong, B.-K. Lee, Characteristics, toxicity, and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in road dust of Ulsan, Korea, *Chemosphere*. 74 (2009) 1245–1253. <https://doi.org/10.1016/j.chemosphere.2008.11.035>.
- [49] G. Gbeddy, P. Egodawatta, A. Goonetilleke, G. Ayoko, L. Chen, Application of quantitative structure-activity relationship (QSAR) model in comprehensive human health risk assessment of PAHs, and alkyl-, nitro-, carbonyl-, and hydroxyl-PAHs laden in urban road dust, *Journal of Hazardous Materials*. 383 (2020) 121–154. <https://doi.org/10.1016/j.jhazmat.2019.121154>.
- [50] C.T. Pham, T. Kameda, A. Toriba, K. Hayakawa, Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in particulates emitted by motorcycles, *Environmental Pollution*. 183 (2013) 175–183. <https://doi.org/10.1016/j.envpol.2013.01.003>.
- [51] I. Sadiqsis, J.H. Koegler, T. Benham, C. Bergvall, R. Westerholm, Particulate associated polycyclic aromatic hydrocarbon exhaust emissions from a portable power generator fueled with three different fuels – A comparison between petroleum diesel and two biodiesels, *Fuel*. 115 (2014) 573–580. <https://doi.org/10.1016/j.fuel.2013.07.062>.
- [52] J.-J. Sauvain, T. Vu-Duc, C.-K. Huynh, Development of an analytical method for the simultaneous determination of 15 carcinogenic polycyclic aromatic hydrocarbons and polycyclic aromatic nitrogen heterocyclic compounds. Application to diesel particulates, *Fresenius' Journal of Analytical Chemistry*. 371 (2001) 966–974. <https://doi.org/10.1007/s002160101047>.
- [53] A. Albinet, F. Nalin, S. Tomaz, J. Beaumont, F. Lestremau, 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, *Anal Bioanal Chem*. 406 (2014) 3131–3148. <https://doi.org/10.1007/s00216-014-7760-5>.
- [54] A.H. El-Mubarak, A.I. Rushdi, K.F. Al-Mutlaq, A.Y. Bazeyad, S.L.M. Simonich, B.R.T. Simoneit, Identification and source apportionment of polycyclic aromatic hydrocarbons in ambient air

- particulate matter of Riyadh, Saudi Arabia, *Environ Sci Pollut Res.* 21 (2014) 558–567.
<https://doi.org/10.1007/s11356-013-1946-9>.
- [55] Y. Gao, L. Yang, J. Chen, Y. Li, P. Jiang, J. Zhang, H. Yu, W. Wang, Nitro and oxy-PAHs bounded in PM_{2.5} and PM_{1.0} under different weather conditions at Mount Tai in Eastern China: Sources, long-distance transport, and cancer risk assessment, *Science of The Total Environment.* 622–623 (2018) 1400–1407. <https://doi.org/10.1016/j.scitotenv.2017.11.200>.
- [56] I.J. Keyte, A. Albinet, R.M. Harrison, On-road traffic emissions of polycyclic aromatic hydrocarbons and their oxy- and nitro- derivative compounds measured in road tunnel environments, *Science of The Total Environment.* 566–567 (2016) 1131–1142.
<https://doi.org/10.1016/j.scitotenv.2016.05.152>.
- [57] Z. Kitanovski, P. Shahpoury, C. Samara, A. Voliotis, G. Lammel, Composition and mass size distribution of nitrated and oxygenated aromatic compounds in ambient particulate matter from southern and central Europe - implications for the origin, *Atmos. Chem. Phys.* 20 (2020) 2471–2487. <https://doi.org/10.5194/acp-20-2471-2020>.
- [58] J. Lintelmann, M.H. França, E. Hübner, G. Matuschek, A liquid chromatography–atmospheric pressure photoionization tandem mass spectrometric method for the determination of azaarenes in atmospheric particulate matter, *Journal of Chromatography A.* 1217 (2010) 1636–1646.
<https://doi.org/10.1016/j.chroma.2010.01.029>.
- [59] M. Tutino, A. Di Gilio, A. Laricchiuta, G. Assennato, G. de Gennaro, An improved method to determine PM-bound nitro-PAHs in ambient air, *Chemosphere.* 161 (2016) 463–469.
<https://doi.org/10.1016/j.chemosphere.2016.07.015>.
- [60] Q. Wang, K. Kobayashi, M. Zhou, S. Lu, S. Dong, D. Nakajima, K. Sekiguchi, M. Terasaki, Study on the size-segregated distribution of 37 species of polycyclic aromatic hydrocarbons in urban atmospheric fine particles of Japan, in: WIT Press, Opatija, Croatia, 2014: pp. 131–143.
<https://doi.org/10.2495/AIR140111>.
- [61] C. Liaud, M. Millet, S. Le Calvé, An analytical method coupling accelerated solvent extraction and HPLC-fluorescence for the quantification of particle-bound PAHs in indoor air sampled with a 3-stages cascade impactor, *Talanta.* 131 (2015) 386–394.
<https://doi.org/10.1016/j.talanta.2014.05.027>.
- [62] S. Masala, H. Lim, C. Bergvall, C. Johansson, R. Westerholm, Determination of semi-volatile and particle-associated polycyclic aromatic hydrocarbons in Stockholm air with emphasis on the highly carcinogenic dibenzopyrene isomers, *Atmospheric Environment.* 140 (2016) 370–380.
<https://doi.org/10.1016/j.atmosenv.2016.06.007>.
- [63] J.M. Delgado-Saborit, N. Aquilina, S. Baker, S. Harrad, C. Meddings, R.M. Harrison, Determination of atmospheric particulate-phase polycyclic aromatic hydrocarbons from low volume air samples, *Anal. Methods.* 2 (2010) 231. <https://doi.org/10.1039/b9ay00157c>.
- [64] D. Hu, Q. Bian, T.W.Y. Li, A.K.H. Lau, J.Z. Yu, Contributions of isoprene, monoterpenes, β -caryophyllene, and toluene to secondary organic aerosols in Hong Kong during the summer of 2006, *J. Geophys. Res.* 113 (2008) D22206. <https://doi.org/10.1029/2008JD010437>.
- [65] Y. Ma, Y. Cheng, X. Qiu, Y. Lin, J. Cao, D. Hu, A quantitative assessment of source contributions to fine particulate matter (PM_{2.5})-bound polycyclic aromatic hydrocarbons (PAHs) and their nitrated and hydroxylated derivatives in Hong Kong, *Environmental Pollution.* 219 (2016) 742–749. <https://doi.org/10.1016/j.envpol.2016.07.034>.
- [66] P. Di Filippo, C. Riccardi, D. Pomata, F. Buiarelli, Concentrations of PAHs, and nitro- and methyl- derivatives associated with a size-segregated urban aerosol, *Atmospheric Environment.* 44 (2010) 2742–2749. <https://doi.org/10.1016/j.atmosenv.2010.04.035>.
- [67] H.-H. Kim, G.-W. Lee, J.-Y. Yang, J.-M. Jeon, W.-S. Lee, J.-Y. Lim, H.-S. Lee, Y.-K. Gwak, D.-C. Shin, Y.-W. Lim, Indoor Exposure and Health Risk of Polycyclic Aromatic Hydrocarbons (PAHs) via Public Facilities PM_{2.5}, Korea (II), *Asian Journal of Atmospheric Environment.* 8 (2014) 35–47. <https://doi.org/10.5572/ajae.2014.8.1.035>.
- [68] H. Wingfors, L. Hägglund, R. Magnusson, Characterization of the size-distribution of aerosols and particle-bound content of oxygenated PAHs, PAHs, and n-alkanes in urban environments in Afghanistan, *Atmospheric Environment.* 45 (2011) 4360–4369.
<https://doi.org/10.1016/j.atmosenv.2011.05.049>.
- [69] M. Morosini, K. Ballschmiter, Methods For The Determination Of Chlorinated Biphenyls In Air, in: *Quality Assurance For Environmental Analysis*, Elsevier, 1995: pp. 526–536.
- [70] D.A. Vallero, Sampling and analysis, in: *Air Pollution Calculations - Quantifying Pollutant Formation, Transport, Transformation, Fate and Risks*, Elsevier, 2019: pp. 263–333.
- [71] A. Albinet, E. Leoz-Garziandia, H. Budzinski, E. Villenave, J.-L. Jaffrezo, Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French

- alpine valleys Part 1: Concentrations, sources and gas/particle partitioning, *Atmospheric Environment*. 42 (2008) 43–54. <https://doi.org/10.1016/j.atmosenv.2007.10.009>.
- [72] J.O. Allen, N.M. Dookeran, K. Taghizadeh, A.L. Lafleur, K.A. Smith, A.F. Sarofim, Measurement of Oxygenated Polycyclic Aromatic Hydrocarbons Associated with a Size-Segregated Urban Aerosol, *Environ. Sci. Technol.* 31 (1997) 2064–2070. <https://doi.org/10.1021/es960894g>.
- [73] J. Ringuet, E. Leoz-Garziandia, H. Budzinski, E. Villenave, A. Albinet, Particle size distribution of nitrated and oxygenated polycyclic aromatic hydrocarbons (NPAHs and OPAHs) on traffic and suburban sites of a European megacity: Paris (France), *Atmos. Chem. Phys.* 12 (2012) 8877–8887. <https://doi.org/10.5194/acp-12-8877-2012>.
- [74] G. Shen, W. Wang, Y. Yang, C. Zhu, Y. Min, M. Xue, J. Ding, W. Li, B. Wang, H. Shen, R. Wang, X. Wang, S. Tao, Emission factors and particulate matter size distribution of polycyclic aromatic hydrocarbons from residential coal combustions in rural Northern China, *Atmospheric Environment*. 44 (2010) 5237–5243. <https://doi.org/10.1016/j.atmosenv.2010.08.042>.
- [75] A. Albinet, E. Leoz-Garziandia, H. Budzinski, E. Villenave, Sampling precautions for the measurement of nitrated polycyclic aromatic hydrocarbons in ambient air, *Atmospheric Environment*. 41 (2007) 4988–4994. <https://doi.org/10.1016/j.atmosenv.2007.01.061>.
- [76] M. Goriaux, B. Jourdain, B. Temime, J.-L. Besombes, N. Marchand, A. Albinet, E. Leoz-Garziandia, H. Wortham, Field Comparison of Particulate PAH Measurements Using a Low-Flow Denuder Device and Conventional Sampling Systems, *Environ. Sci. Technol.* 40 (2006) 6398–6404. <https://doi.org/10.1021/es060544m>.
- [77] C. Schauer, R. Niessner, U. Pöschl, Polycyclic Aromatic Hydrocarbons in Urban Air Particulate Matter: Decadal and Seasonal Trends, Chemical Degradation, and Sampling Artifacts, *Environ. Sci. Technol.* 37 (2003) 2861–2868. <https://doi.org/10.1021/es034059s>.
- [78] M. Tsapakis, E.G. Stephanou, Collection of gas and particle semi-volatile organic compounds: use of an oxidant denuder to minimize polycyclic aromatic hydrocarbons degradation during high-volume air sampling, *Atmospheric Environment*. 37 (2003) 4935–4944. <https://doi.org/10.1016/j.atmosenv.2003.08.026>.
- [79] M.R. Cave, J. Wragg, D.J. Beriro, C. Vane, R. Thomas, M. Riding, C. Taylor, An overview of research and development themes in the measurement and occurrences of polyaromatic hydrocarbons in dusts and particulates, *Journal of Hazardous Materials*. 360 (2018) 373–390. <https://doi.org/10.1016/j.jhazmat.2018.08.038>.
- [80] A. Albinet, E. Leoz-Garziandia, N. Alsac, Guide méthodologique pour la surveillance des hydrocarbures aromatiques polycycliques (HAP) dans l'air ambiant et dans les dépôts, (2015).
- [81] B.J. Turpin, P. Saxena, E. Andrews, Measuring and simulating particulate organics in the atmosphere: problems and prospects, *Atmospheric Environment*. 34 (2000) 2983–3013. [https://doi.org/10.1016/S1352-2310\(99\)00501-4](https://doi.org/10.1016/S1352-2310(99)00501-4).
- [82] M.W. Kadi, N. Ali, H.M.S.A. Albar, Phthalates and polycyclic aromatic hydrocarbons (PAHs) in the indoor settled carpet dust of mosques, health risk assessment for public, *Science of The Total Environment*. 627 (2018) 134–140. <https://doi.org/10.1016/j.scitotenv.2018.01.146>.
- [83] W. Wei, C. Mandin, O. Blanchard, F. Mercier, M. Pelletier, B. Le Bot, P. Glorennec, O. Ramalho, Semi-volatile organic compounds in French dwellings: An estimation of concentrations in the gas phase and particulate phase from settled dust, *Science of The Total Environment*. 650 (2019) 2742–2750. <https://doi.org/10.1016/j.scitotenv.2018.09.398>.
- [84] R. Barro, J. Regueiro, M. Llompert, C. Garcia-Jares, Analysis of industrial contaminants in indoor air: Part 1. Volatile organic compounds, carbonyl compounds, polycyclic aromatic hydrocarbons and polychlorinated biphenyls, *Journal of Chromatography A*. 1216 (2009) 540–566. <https://doi.org/10.1016/j.chroma.2008.10.117>.
- [85] H.Q. Anh, N.M. Tue, L.H. Tuyen, T.B. Minh, P.H. Viet, S. Takahashi, Polycyclic aromatic hydrocarbons and their methylated derivatives in settled dusts from end-of-life vehicle processing, urban, and rural areas, northern Vietnam: Occurrence, source apportionment, and risk assessment, *Science of The Total Environment*. 672 (2019) 468–478. <https://doi.org/10.1016/j.scitotenv.2019.04.018>.
- [86] J. Oda, S. Nomura, A. Yasuhara, T. Shibamoto, Mobile sources of atmospheric polycyclic aromatic hydrocarbons in a roadway tunnel, *Atmospheric Environment*. 35 (2001) 4819–4827. [https://doi.org/10.1016/S1352-2310\(01\)00262-X](https://doi.org/10.1016/S1352-2310(01)00262-X).
- [87] ASTM, Practice for Collection of Settled Dust Samples Using Wipe Sampling Methods for Subsequent Lead Determination, ASTM International, 2002. <https://doi.org/10.1520/E1728-02>.
- [88] E. Svendsen, P. Thorne, P. O'Shaughnessy, D. Zimmerman, S. Reynolds, House Dust Collection Efficiency of the High Volume Small Surface Sampler on Worn Carpets, *Journal of*

- Occupational and Environmental Hygiene. 3 (2006) 334–341.
<https://doi.org/10.1080/15459620600700651>.
- [89] J.S. Colt, R.B. Gunier, C. Metayer, M.G. Nishioka, E.M. Bell, P. Reynolds, P.A. Buffler, M.H. Ward, Household vacuum cleaners vs. the high-volume surface sampler for collection of carpet dust samples in epidemiologic studies of children, *Environ Health*. 7 (2008) 6.
<https://doi.org/10.1186/1476-069X-7-6>.
- [90] G. Gbeddy, A. Jayarathne, A. Goonetilleke, G.A. Ayoko, P. Egodawatta, Variability and uncertainty of particle build-up on urban road surfaces, *Science of The Total Environment*. 640–641 (2018) 1432–1437. <https://doi.org/10.1016/j.scitotenv.2018.05.384>.
- [91] B. Koh, E.-A. Kim, Comparative analysis of urban road dust compositions in relation to their potential human health impacts, *Environmental Pollution*. 255 (2019) 113156.
<https://doi.org/10.1016/j.envpol.2019.113156>.
- [92] B. Zielinska, S. Samy, Analysis of nitrated polycyclic aromatic hydrocarbons, *Anal Bioanal Chem*. 386 (2006) 883–890. <https://doi.org/10.1007/s00216-006-0521-3>.
- [93] O.P. Heemken, N. Theobald, B.W. Wenclawiak, Comparison of ASE and SFE with Soxhlet, Sonication, and Methanolic Saponification Extractions for the Determination of Organic Micropollutants in Marine Particulate Matter, *Anal. Chem*. 69 (1997) 2171–2180.
<https://doi.org/10.1021/ac960695f>.
- [94] S.B. Hawthorne, D.J. Miller, M.D. Burford, J.J. Langenfeld, S. Eckert-Tilotta, P.K. Louie, Factors controlling quantitative supercritical fluid extraction of environmental samples, *Journal of Chromatography A*. 642 (1993) 301–317. [https://doi.org/10.1016/0021-9673\(93\)80095-P](https://doi.org/10.1016/0021-9673(93)80095-P).
- [95] M.M. Schantz, J.J. Nichols, S.A. Wise, Evaluation of Pressurized Fluid Extraction for the Extraction of Environmental Matrix Reference Materials, *Anal. Chem*. 69 (1997) 4210–4219.
<https://doi.org/10.1021/ac970299c>.
- [96] P. Castells, F.J. Santos, M.T. Galceran, Development of a sequential supercritical fluid extraction method for the analysis of nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in urban aerosols, *Journal of Chromatography A*. 1010 (2003) 141–151.
[https://doi.org/10.1016/S0021-9673\(03\)01121-X](https://doi.org/10.1016/S0021-9673(03)01121-X).
- [97] Y. Han, L. Ren, K. Xu, F. Yang, Y. Li, T. Cheng, X. Kang, C. Xu, Q. Shi, Supercritical fluid extraction with carbon nanotubes as a solid collection trap for the analysis of polycyclic aromatic hydrocarbons and their derivatives, *Journal of Chromatography A*. 1395 (2015) 1–6.
<https://doi.org/10.1016/j.chroma.2015.03.038>.
- [98] A.P. Wicker, D.D. Carlton, K. Tanaka, M. Nishimura, V. Chen, T. Ogura, W. Hedgepeth, K.A. Schug, On-line supercritical fluid extraction—supercritical fluid chromatography-mass spectrometry of polycyclic aromatic hydrocarbons in soil, *Journal of Chromatography B*. 1086 (2018) 82–88. <https://doi.org/10.1016/j.jchromb.2018.04.014>.
- [99] H. Liu, S. Ma, X. Zhang, Y. Yu, Application of thermal desorption methods for airborne polycyclic aromatic hydrocarbon measurement: A critical review, *Environmental Pollution*. 254 (2019) 113018. <https://doi.org/10.1016/j.envpol.2019.113018>.
- [100] N. Manousi, G.A. Zachariadis, Recent Advances in the Extraction of Polycyclic Aromatic Hydrocarbons from Environmental Samples, *Molecules*. 25 (2020) 2182.
<https://doi.org/10.3390/molecules25092182>.
- [101] J. Lintelmann, K. Fischer, G. Matuschek, Determination of oxygenated polycyclic aromatic hydrocarbons in particulate matter using high-performance liquid chromatography–tandem mass spectrometry, *Journal of Chromatography A*. 1133 (2006) 241–247.
<https://doi.org/10.1016/j.chroma.2006.08.038>.
- [102] S. Große Brinkhaus, J.B. Thiäner, C. Achten, Ultra-high sensitive PAH analysis of certified reference materials and environmental samples by GC-APLI-MS, *Anal Bioanal Chem*. 409 (2017) 2801–2812. <https://doi.org/10.1007/s00216-017-0224-y>.
- [103] J.O. Lalah, P.N. Kaigwara, Polynuclear aromatic compounds in kerosene, diesel and unmodified sunflower oil and in respective engine exhaust particulate emissions, *Toxicological & Environmental Chemistry*. 87 (2005) 463–479. <https://doi.org/10.1080/02772240500316702>.
- [104] M.T.O. Jonker, A.A. Koelmans, Extraction of Polycyclic Aromatic Hydrocarbons from Soot and Sediment: Solvent Evaluation and Implications for Sorption Mechanism, *Environ. Sci. Technol*. 36 (2002) 4107–4113. <https://doi.org/10.1021/es0103290>.
- [105] S. Masala, T. Ahmed, C. Bergvall, R. Westerholm, Improved efficiency of extraction of polycyclic aromatic hydrocarbons (PAHs) from the National Institute of Standards and Technology (NIST) Standard Reference Material Diesel Particulate Matter (SRM 2975) using accelerated solvent extraction, *Anal Bioanal Chem*. 401 (2011) 3305–3315. <https://doi.org/10.1007/s00216-011-5446-9>.

- [106] H.-Y. Chen, M.R. Preston, Gas/particle partitioning behaviour of azaarenes in an urban atmosphere, *Environmental Pollution*. 97 (1997) 169–174. [https://doi.org/10.1016/S0269-7491\(97\)00059-6](https://doi.org/10.1016/S0269-7491(97)00059-6).
- [107] C.H. Marvin, L. Allan, B.E. McCarry, D.W. Bryant, A Comparison of Ultrasonic Extraction and Soxhlet Extraction of Polycyclic Aromatic Hydrocarbons from Sediments and Air Particulate Material, *International Journal of Environmental Analytical Chemistry*. 49 (1992) 221–230. <https://doi.org/10.1080/03067319208027573>.
- [108] S.A. Wise, M.M. Schantz, M.J. Hays, B.J. Koster, K.E. Sharpless, L.C. Sander, B.A. Benner, S.B. Schiller, Certification of Polycyclic Aromatic Hydrocarbons in Mussel Tissue and Air Particulate Standard Reference Materials (SRMs), *Polycyclic Aromatic Compounds*. 9 (1996) 209–216. <https://doi.org/10.1080/10406639608031220>.
- [109] S.A. Wise, L.R. Hilpert, G.D. Byrd, W.E. May, Comparison of Liquid Chromatography with Fluorescence Detection and Gas Chromatography/Mass Spectrometry for the Determination of Polycyclic Aromatic Hydrocarbons in Environmental Samples, *Polycyclic Aromatic Compounds*. 1 (1990) 81–98. <https://doi.org/10.1080/10406639008034751>.
- [110] O. Delhomme, M. Millet, Comparison of Two Analytical Methods for the Determination of Azaarenes in Atmospheric Particulate Matter, *Polycyclic Aromatic Compounds*. 28 (2008) 518–532. <https://doi.org/10.1080/10406630802375215>.
- [111] H.A. Bamford, J.E. Baker, Nitro-polycyclic aromatic hydrocarbon concentrations and sources in urban and suburban atmospheres of the Mid-Atlantic region, *Atmospheric Environment*. 37 (2003) 2077–2091. [https://doi.org/10.1016/S1352-2310\(03\)00102-X](https://doi.org/10.1016/S1352-2310(03)00102-X).
- [112] Y. Lin, Y. Ma, X. Qiu, R. Li, Y. Fang, J. Wang, Y. Zhu, D. Hu, Sources, transformation, and health implications of PAHs and their nitrated, hydroxylated, and oxygenated derivatives in PM_{2.5} in Beijing, *J. Geophys. Res. Atmos.* 120 (2015) 7219–7228. <https://doi.org/10.1002/2015JD023628>.
- [113] B.E. Richter, B.A. Jones, J.L. Ezzell, N.L. Porter, N. Avdalovic, C. Pohl, Accelerated Solvent Extraction: A Technique for Sample Preparation, *Anal. Chem.* 68 (1996) 1033–1039. <https://doi.org/10.1021/ac9508199>.
- [114] D.Z. Bezabeh, H.A. Bamford, M.M. Schantz, S.A. Wise, Determination of nitrated polycyclic aromatic hydrocarbons in diesel particulate-related standard reference materials by using gas chromatography/mass spectrometry with negative ion chemical ionization, *Anal Bioanal Chem.* 375 (2003) 381–388. <https://doi.org/10.1007/s00216-002-1698-8>.
- [115] D.G. Madruga, R.M. Ubeda, J.M. Terroba, S.G. dos Santos, J.P. García-Camero, Particle-associated polycyclic aromatic hydrocarbons in a representative urban location (indoor-outdoor) from South Europe: Assessment of potential sources and cancer risk to humans, *Indoor Air*. 29 (2019) 817–827. <https://doi.org/10.1111/ina.12581>.
- [116] M.S. Nocun, M.M. Schantz, Determination of selected oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs) in diesel and air particulate matter standard reference materials (SRMs), *Anal Bioanal Chem.* 405 (2013) 5583–5593. <https://doi.org/10.1007/s00216-013-6957-3>.
- [117] J. Lintelmann, K. Fischer, E. Karg, A. Schröppel, Determination of selected polycyclic aromatic hydrocarbons and oxygenated polycyclic aromatic hydrocarbons in aerosol samples by high-performance liquid chromatography and liquid chromatography/tandem mass spectrometry, *Anal Bioanal Chem.* 381 (2005) 508–519. <https://doi.org/10.1007/s00216-004-2883-8>.
- [118] P. Di Filippo, C. Riccardi, C. Gariazzo, F. Incoronato, D. Pomata, S. Spicaglia, A. Cecinato, Air pollutants and the characterization of the organic content of aerosol particles in a mixed industrial/semi-rural area in central Italy, *J. Environ. Monit.* 9 (2007) 275. <https://doi.org/10.1039/b615118c>.
- [119] B.A.M. Bandowe, W. Wilcke, Analysis of Polycyclic Aromatic Hydrocarbons and Their Oxygen-Containing Derivatives and Metabolites in Soils, *J. Environ. Qual.* 39 (2010) 1349–1358. <https://doi.org/10.2134/jeq2009.0298>.
- [120] E.D. Vicente, A.M. Vicente, B.A. Musa Bandowe, C.A. Alves, Particulate phase emission of parent polycyclic aromatic hydrocarbons (PAHs) and their derivatives (alkyl-PAHs, oxygenated-PAHs, azaarenes and nitrated PAHs) from manually and automatically fired combustion appliances, *Air Qual Atmos Health*. 9 (2016) 653–668. <https://doi.org/10.1007/s11869-015-0364-1>.
- [121] S. García-Alonso, R.M. Pérez-Pastor, V. Archilla-Prat, D. Sanz-Rivera, E. Rojas-García, G. Aragón-Urrengoetxea, J.J. Rodríguez-Maroto, Determination of Selected Polycyclic Aromatic Compounds in Particulate Matter Samples with Low Mass Loading: An Approach to Test Method Accuracy, *Journal of Chemistry*. 2017 (2017) 1–12. <https://doi.org/10.1155/2017/3517457>.

- [122] X. Niu, S.S.H. Ho, K.F. Ho, Y. Huang, J. Sun, Q. Wang, Y. Zhou, Z. Zhao, J. Cao, Atmospheric levels and cytotoxicity of polycyclic aromatic hydrocarbons and oxygenated-PAHs in PM_{2.5} in the Beijing-Tianjin-Hebei region, *Environmental Pollution*. 231 (2017) 1075–1084. <https://doi.org/10.1016/j.envpol.2017.08.099>.
- [123] G. Sangiorgi, L. Ferrero, B.S. Ferrini, C. Lo Porto, M.G. Perrone, R. Zangrando, A. Gambaro, Z. Lazzati, E. Bolzacchini, Indoor airborne particle sources and semi-volatile partitioning effect of outdoor fine PM in offices, *Atmospheric Environment*. 65 (2013) 205–214. <https://doi.org/10.1016/j.atmosenv.2012.10.050>.
- [124] A. Colmsjö, Concentration and Extraction of PAHs from Environmental Samples, in: A.H. Neilson (Ed.), *PAHs and Related Compounds*, Springer Berlin Heidelberg, Berlin, Heidelberg, 1998: pp. 55–76. https://doi.org/10.1007/978-3-540-49697-7_2.
- [125] O. Delhomme, M. Millet, P. Herckes, Determination of oxygenated polycyclic aromatic hydrocarbons in atmospheric aerosol samples by liquid chromatography–tandem mass spectrometry, *Talanta*. 74 (2008) 703–710. <https://doi.org/10.1016/j.talanta.2007.06.037>.
- [126] Y. Kojima, K. Inazu, Y. Hisamatsu, H. Okochi, T. Baba, T. Nagoya, Influence of secondary formation on atmospheric occurrences of oxygenated polycyclic aromatic hydrocarbons in airborne particles, *Atmospheric Environment*. 44 (2010) 2873–2880. <https://doi.org/10.1016/j.atmosenv.2010.04.048>.
- [127] A.I. Barrado, S. García, E. Barrado, R.M. Pérez, PM_{2.5}-bound PAHs and hydroxy-PAHs in atmospheric aerosol samples: Correlations with season and with physical and chemical factors, *Atmospheric Environment*. 49 (2012) 224–232. <https://doi.org/10.1016/j.atmosenv.2011.11.056>.
- [128] N. Ali, Polycyclic aromatic hydrocarbons (PAHs) in indoor air and dust samples of different Saudi microenvironments; health and carcinogenic risk assessment for the general population, *Science of The Total Environment*. 696 (2019) 133995. <https://doi.org/10.1016/j.scitotenv.2019.133995>.
- [129] S. Zhuo, W. Du, G. Shen, B. Li, J. Liu, H. Cheng, B. Xing, S. Tao, Estimating relative contributions of primary and secondary sources of ambient nitrated and oxygenated polycyclic aromatic hydrocarbons, *Atmospheric Environment*. 159 (2017) 126–134. <https://doi.org/10.1016/j.atmosenv.2017.04.003>.
- [130] L. Zhu, H. Lu, S. Chen, T. Amagai, Pollution level, phase distribution and source analysis of polycyclic aromatic hydrocarbons in residential air in Hangzhou, China, *Journal of Hazardous Materials*. 162 (2009) 1165–1170. <https://doi.org/10.1016/j.jhazmat.2008.05.150>.
- [131] H.A. Bamford, D.Z. Bezabeh, M.M. Schantz, S.A. Wise, J.E. Baker, Determination and comparison of nitrated-polycyclic aromatic hydrocarbons measured in air and diesel particulate reference materials, *Chemosphere*. 50 (2003) 575–587. [https://doi.org/10.1016/S0045-6535\(02\)00667-7](https://doi.org/10.1016/S0045-6535(02)00667-7).
- [132] R.E. Cochran, N. Dongari, H. Jeong, J. Beránek, S. Haddadi, J. Shipp, A. Kubátová, Determination of polycyclic aromatic hydrocarbons and their oxy-, nitro-, and hydroxy-oxidation products, *Analytica Chimica Acta*. 740 (2012) 93–103. <https://doi.org/10.1016/j.aca.2012.05.050>.
- [133] N. Kishikawa, S. Morita, M. Wada, Y. Ohba, K. Nakashima, N. Kuroda, Determination of Hydroxylated Polycyclic Aromatic Hydrocarbons in Airborne Particulates by High-Performance Liquid Chromatography with Fluorescence Detection, *Anal. Sci.* 20 (2004) 129–132. <https://doi.org/10.2116/analsci.20.129>.