Trends in Environmental Analytical Chemistry 50 (2026) e00303

Contents lists available at ScienceDirect

Trends in Environmental Analytical Chemistry

journal homepage: www.elsevier.com/locate/treac

Determination of metal(oid)s and polycyclic aromatic hydrocarbons in size-fractionated airborne particulate matter: methodological approaches, trends, gaps and future needs: a review

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ARTICLE INFO

Keywords:
Particulate matter
Size-fractionated sampling
Urban air quality
Sampling protocols
Analytical methods
Metal(oid)s
Polycyclic aromatic hydrocarbons

ABSTRACT

This review highlights a significant gap in the multi-pollutant characterisation of ultrafine particulate matter (PM <0.1 μm), focusing on metal(oid)s and polycyclic aromatic hydrocarbons (PAHs). Fractionation mechanisms, sampling protocols and analytical methods are examined with an emphasis on integrating quality assurance measures to ensure high-quality data and facilitate cross-study comparability. Based on studies published between 2010 and 2025, research has largely focused on the analysis of pollutants bound to $PM_{2.5}$ or PM_{10}. Only 5% of the studies addressed ultrafine particles (UFPs), which have the greatest toxicological impacts. The measurement of both pollutant groups within a single sampling campaign was rare (14% of the studies). The reliability of analytical data was rarely evaluated. Only 33% of the studies employed certified reference materials for quality control and method validation. Microwave-assisted digestion and ultrasound-assisted extraction were commonly used for sample preparation prior to the determination of metal(oid)s and PAHs, by inductively coupled plasma mass spectrometry and gas chromatography–mass spectrometry, respectively. Both pollutant groups exhibited strong seasonal variability, with elevated concentrations observed during heating periods in cold seasons, as well as associated with fine PM and UFPs, fractions that exhibit high bioaccessibility. Smaller PM fractions were associated with anthropogenic sources, including fossil fuel and biomass combustion, traffic and industrial emissions, while coarse PM reflected naturally-derived crustal material. Overall, these findings highlight the importance of uniform and comprehensive protocols for sampling UFPs and quantifying associated pollutants, which are essential for reliable data and effective urban air quality control strategies aimed at mitigating emissions.

1. Introduction

Particulate matter (PM) is among the most prevalent primary airborne pollutants and represents a significant health and environmental risk, particularly in urban and densely populated areas [1]. The toxicological and environmental implications of PMs are strongly dependent on its size, chemical composition, water affinity and optical properties, such as light scattering and absorption [2]. Both atmospheric and biological behaviour primarily depend on PM chemical composition and particle size [3,4]. Therefore, the systematic classification of particles based on their aerodynamic diameter is considered one of the most important parameters.

Total suspended particles (TSPs with an aerodynamic diameter of 50–100 μm) and coarse particles (PM_{10}, with an aerodynamic diameter <10 μm) tend to deposit in the upper respiratory tract, in the nasopharynx, while fine particles ($PM_{2.5}$, with an aerodynamic diameter <2.5 μm and PM_1, with an aerodynamic diameter <1 μm) and ultrafine particles (UFPs, PM with an aerodynamic diameter <0.1 μm) behave

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https://doi.org/10.1016/j.teac.2026.e00303
Received 2 October 2025; Received in revised form 13 March 2026; Accepted 16 March 2026
Available online 18 March 2026
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similarly to gas molecules, enabling them to reach terminal bronchioles and alveoli, cross the pulmonary blood-air barrier and translocate further into cell tissue and possibly cause damage to the nervous system [5]. The accumulation of PM in the respiratory system is associated with impaired pulmonary and cardiovascular functions, including stroke and lung cancer, neuroinflammation, neuronal apoptosis, induced oxidative stress and dopaminergic neurotoxicity, deterioration of cognitive function and altered brain development [6]. In addition, increased PM concentrations disrupt aquatic and terrestrial ecosystems, leading to soil acidification, nutrient depletion, eutrophication, reduced biodiversity, crop and forest damage, and acid rain formation [5]. Urban outdoor air pollution with PM is classified as a Group 1 carcinogen [7], with bound PM pollutants, such as metal(oid)s and polycyclic aromatic hydrocarbons (PAHs) representing the greatest risk [8].

Metal(oid)s, such as arsenic (As), cadmium (Cd), nickel (Ni) and lead (Pb) are persistent, non-degradable and recognised as genotoxic carcinogens [9]. They accumulate in fatty tissues, have high bioaccumulation potential, can impair organ and endocrine functions and induce DNA mutations [10]. Due to their atmospheric stability, certain elemental ratios serve as reliable tracers of emission sources from combustion, non-exhaust traffic emissions and mineral dust re-suspension [4,7,11,12].

PAHs are semi-volatile organic pollutants that exhibit carcinogenic, mutagenic and immunosuppressive properties [13,14]. They are formed mostly by incomplete combustion of organic matter (e.g. coal, natural gas or oil) or pyrolysis, with main urban sources associated with municipal and domestic emissions [14]. In the atmosphere, PAHs partition based on volatility, with low-molecular-weight (LMW) PAHs (2 −3 rings) occurring predominantly in the gaseous phase, while high-molecular-weight (HMW) PAHs (≥4 benzene rings) exhibiting lower vapour pressures, absorb to PM, with carcinogenicity increasing with molecular weight [14]. More than 95% of HMW PAHs are bound to PM < 3 μm [4]. The United States Environmental Protection Agency (US EPA) has classified 16 unsubstituted PAHs as priority pollutants, of which benzo[*a*]anthracene (BaA), benzo[*a*]pyrene (BaP), benzo[*b*]fluoranthene (BbF), benzo[*g*,*h*,*i*]perylene (BghiP), chrysene (Ch) and indeno[1,2,3-cd]pyrene (IP) are of particular concern [15]. HMW PAHs also serve as characteristic markers of local and regional sources of pollution, as well as the transport distances of pollutants [14,16].

Particulate aerosol samples in urban areas are typically collected by drawing ambient air through filter materials or using inertial impaction with a pump, followed by the subsequent quantification of particle mass and its chemical components by off-site laboratory analysis [17]. Size-selective inlets in cascade sampling setups allow fractionation, with the most common cut-off points of 10, 2.5 and 1 μm [2]. Conventional monitoring relies on high-volume samplers placed at fixed location, adhering to standardised quality protocols (e.g. National Ambient Air Quality Standards) to achieve low limits of detection (LODs) [2]. However, due to easier handling, good collection efficiency and lower costs, portable low-cost and low-volume samplers are increasingly being deployed [17,18].

Published reviews indicate that the majority of atmospheric research has focused on the determination of a single group of pollutants bound to PM (either metals or PAHs), emphasising their sampling protocols, analytical procedures, potential sources and health effects (Table 1).

Table 1
Summary of the existing reviews on the sampling protocols and analytical methods for chemical characterisation of pollutant bound to particulate matter.

Study focus and topic areas covered	Ref.
• Collection methods and analytical procedures to characterise fine particles ($PM_{2.5}$) and ultra-fine particles	[17]
• Characterisation, sampling and analytical methods for organic compounds in air particulate matter samples	[19]
• Sampling, analytical and modelling approaches for health risk evaluation of metals bound to particulate matter	[20]

However, these studies largely addressed PM_{10} and $PM_{2.5}$, leaving knowledge gap regarding UFPs. Moreover, quality assurance and control (QA/QC) were often insufficiently reported, with very few studies routinely reporting the use of certified reference materials (CRMs), raising concerns about data reliability and subsequent cross-study comparability. Therefore, this review provides a comprehensive evaluation of existing sampling protocols and analytical approaches for metal (oid)s and PAHs in size-fractionated PM, with particular emphasis on QA/QC. In addition, it highlights current trends and patterns in their chemical composition, seasonal variations and spatial distribution as well as key metrics for exposure assessment, all of which are essential for evidence-based urban planning for air pollution mitigation.

2. Methodology

The main focus of the review was to provide a comprehensive and critical overview of different sampling protocols, extraction or digestion methods and analytical procedures used for the determination of metal (oid)s and PAHs bound to size-fractionated PM.

An initial search was conducted in the research database and citation indexing platform Web of Science using the keywords ‘urban air’, ‘particulate matter’, ‘metals’ and ‘polycyclic aromatic hydrocarbons’. The search covered studies published from January 2010 onwards and yielded a total of 3948 studies, which were then selected based on various exclusion criteria (Fig. 1).

Papers were initially identified based on their relevance to the topic, publication in peer-reviewed journals and scientific importance. Duplicate records and review articles as well as non-English articles were removed. In the second stage, all retrieved articles were screened based on their titles, keywords and abstracts. The exclusion criteria for further assessment included: studies involving real-time monitoring and receptor modelling were excluded, as well as epidemiological and toxicological studies focusing on *in vitro* effects, oxidative stress and reactions on epithelial cells and DNA changes, studies focusing exclusively on indoor pollution or using low-cost optical sensors for PM determination, studies focusing on phytomonitoring and PM accumulation in various green plants, trees or leaves, as studies where PM monitoring was focused on a one-time event (such as forest fires, fireworks, etc.). Studies conducted in rural environments were also excluded to maintain consistency with the review’s focus on urban atmospheric PM. After applying the exclusion criteria, the abstract and methodology of the remaining articles were evaluated to determine whether they should be included in this review, with particular emphasis on their methodological approaches to ensure scientific relevance and applicability. Only studies that (i) reported the determination of metal(oid)s and/or PAHs in different PM fractions, (ii) employed gravimetric cascade impactor-based sampling techniques, and (iii) were conducted in urban environments, were included in the final analysis. As a result, 80 research articles were identified suitable for the inclusion in this review. The simplified selection process is summarised in Fig. 1, and the key features of the selected studies are systematically presented in Table S1.

3. Results and discussion

3.1. Scope of the study

A total of 80 published studies from 33 countries were included in this review, of which 62% were conducted in Asia, 32% in Europe, 4% in Africa and 2% in North America. The countries represented were Algeria, China, Croatia, the Czech Republic, Denmark, Egypt, France, Germany, Ghana, Greece, India, Iran, Italy, Japan, Lebanon, Malaysia, Mexico, Myanmar, the Netherlands, Norway, Pakistan, Poland, Portugal, Saudi Arabia, Slovakia, Slovenia, Spain, Switzerland, Taiwan, Thailand, Turkey, the United Kingdom and the United States of America (Fig. 2).

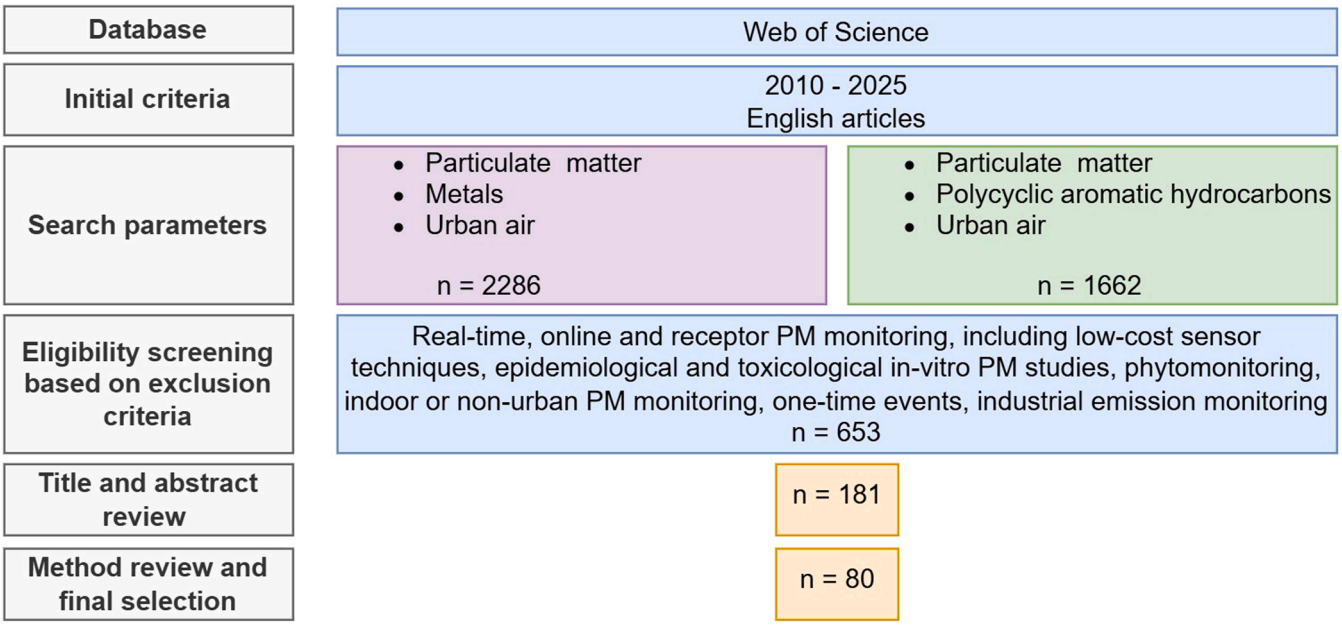

Fig. 1. Flowchart illustrating the simplified study screening and selection process.

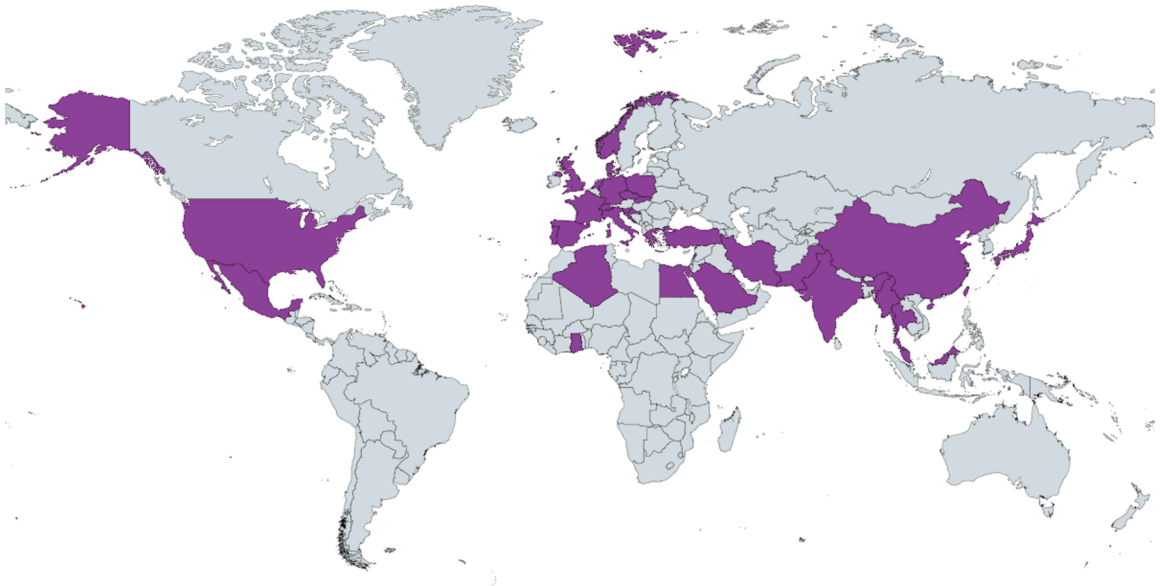

Fig. 2. Map showing the sampling locations of the studies included in this analysis, marked in purple (n = 80). The map was created using Map Chart online software.

Table S1 (Supplementary Information) provides an overview of the studies included in this review. It includes the details on PM sampling approaches and determination of chemical components, with particular emphasis on PM fractions reported across different studies, sampling heights, sampler types and their airflow rates, filters types, extraction and digestion procedures, and the analytical techniques used to determine metal(oid)s and PAHs.

3.2. Sampling methods for PM collection

The majority of the studies reported sampling $PM_{2.5}$ (52%), followed by PM_{10} (30%) and PM_1 (13%). Only 5% of the 80 studies reported sampling PM smaller than 0.1 μm (Fig. 3), despite UFPs representing approximately 90% of the total PM, followed by fine particles (~9%) and coarse particles, which contribute less than 1% [21]. The reason that PM smaller than 0.1 μm has been rarely studied is that the only way to capture the nanosized fraction is by using a water trap. This novel approach was recently reported by Ilenič et al. [18].

The majority of the studies (85%) installed PM samplers at an elevated level (EL; above 2.5 m, e.g. on building roofs). Due to the low mass that accumulates on filters, a constant flow is required for longer periods of time. Therefore, particulate aerosol samplers are categorised as high-volume samplers (HVS; 100 −1000 L min^{-1}), medium-volume samplers (MVS; 20 −100 L min^{-1}) and low-volume samplers (LVS; <20 L min^{-1}). HVS are the most widely used (52%) because they allow adequate sample deposition on the filter media for detecting compounds at lower LODs, but may reduce the adsorption capacity of filters and increase the likelihood of filter clogging. Therefore, LVS are considered more suitable for quantifying personal emission exposures as their flow rates are closer to individuals' inhalation rates (6 L min^{-1}) than those of

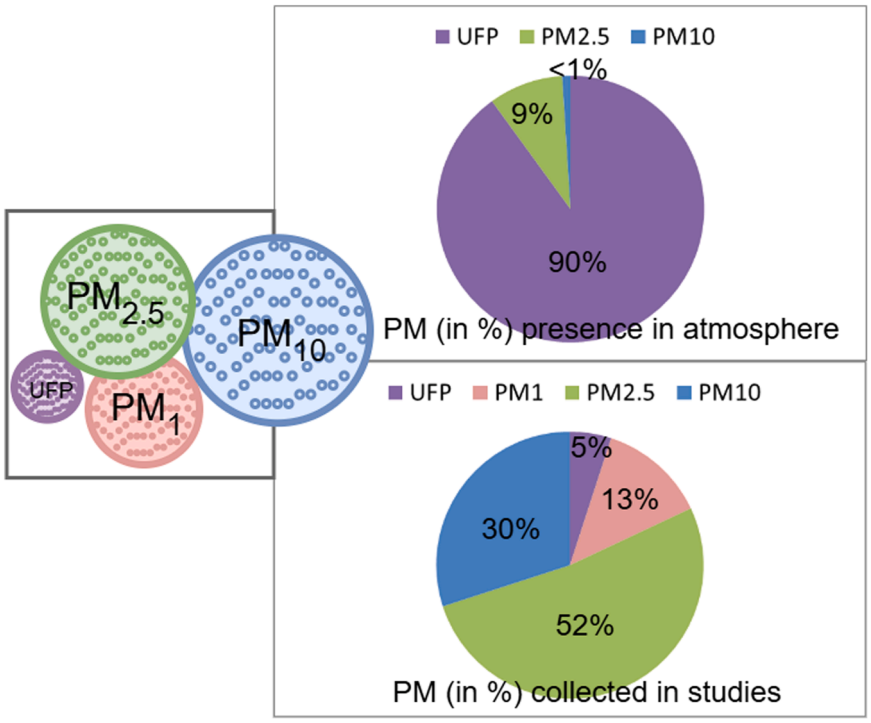

Fig. 3. Comparison of PM size-fractions present in atmosphere [21] with those reported in the studies included in this review.

higher-volume samplers [2]. PAHs were analysed in 55% of the studies and metal(oid)s in 31%, while 14% of the studies measured both pollutants within the same sampling campaign (Table 2), indicating a significant gap in comprehensive PM chemical characterisation.

3.3. Analytical methods for airborne pollutant determination

Prior to PM sample collection, it is essential to identify the nature of the pollutants bound to PM in order to select appropriate analytical procedure, including the types of filter, pollutant extraction methods, solvents used and analytical techniques to obtain reliable data on the chemical composition of size-fractionated PM samples. The main challenges of analytical procedures include the identification and determination of species in the sample, separation of the species, determination of low concentrations with adequate precision and accuracy, and effective elimination of matrix effects [32]. Therefore, it is essential to ensure the accuracy of analytical procedures and results by selecting high-resolution and sensitive techniques along with the use of CRMs [33]. Only 33% of the studies reported their use, namely National Institute of Standards and Technology (NIST) standard reference material (SRM) 1648a (10 studies); NIST SRM 1649b (6 studies), NIST SRM 1649a (3 studies) and NIST SRM 2783, NIST SRM 2786, ERM®-CZ100 PAHs; NIST SRM 2585; NIST SRM 1647c; SRM GSS16; and NIST SRM 981 (one study each). Although, the majority of the studies included in this review were conducted in Asia, CRMs were predominantly applied in European research (62%), particularly the United Kingdom, Greece, Croatia, Spain, Poland, Slovenia, Italy and France. In Asia, CRMs were reported in studies from Iran, China, Taiwan, Turkey and Thailand.

Overall, 82% of the studies included QA/QC in their methods. Several characteristics are important when selecting suitable filter media for compliance measurements, including particle sampling efficiency; mechanical, chemical and temperature stability; blank concentrations; flow resistance; and loading capacity to obtain adequate PM deposits, as well as cost efficiency and availability. Potential positive or negative artefacts due to gas adsorption or particle volatilisation may also affect mass balance and chemical composition [2].

In general, membrane filters have a higher flow resistance and a lower loading capacity than fibre filters [2]. The most common filters used are cellulose filters (CFs; fibrous), glass fibre filters (GFFs; fibrous), mixed cellulose filters (MCEs; membrane), polycarbonate filters (PFs; membrane), polyvinyl chloride (PVCs; membrane) filters, polytetrafluoroethylene (PTFE; membrane) filters and quartz fibre filters (QFF; fibrous) [1].

The choice of filter depends on the nature of the pollutants (organic, inorganic), which in turn determines the subsequent analysis. Overall, QFFs were used most commonly in the included studies (65%), followed by PTFE filters (16%) and GFFs (13%). The use of PFs and fiberglass fabric filters (FGFs) was reported in two studies, while nitrocellulose membrane filters (NCsF) were employed in one study for PM filtration. Several studies reported on the simultaneous use of QFFs and PTFE filters or PTFE filters and GFFs. GFFs are often used with HVS systems due to their high collection efficiency and low airflow resistance. However, due to their poor chemical stability and relatively high content of certain trace element impurities, their use is limited to areas with relatively high levels of air pollution [2,3]. CFs and PFs exhibit the lowest particle sample efficiency, with values below 50%.

Compared with QFFs and PTFE filters, GFFs offer the highest mechanical strength and are the most cost-effective, but they also require pre-treatment (baking at >500 °C) prior to sampling to remove adsorbed organic vapours [2]. PTFE filters are the most chemically inert and exhibit minimal blank values and low hygroscopicity, but they are not suitable for elemental and organic carbon analysis (EC/OC) due to the significant carbon content and subsequently high carbon blank values, potential decomposition during the analysis, which requires high temperatures. EC/OC is best performed on QFFs due to their thermal stability [2]. Based on the overall properties, PTFE filters outperform GFFs and QFFs [2].

3.3.1. Analytical methods for determination of metals bound to PM

Due to its high sensitivity (LODs for toxic metals are typically 0.01–0.1 μg L^{-1}), inductively coupled plasma mass spectrometry (ICP-MS) was used most frequently in the included studies (68%). X-ray analysis, with typical LODs around 1–10 μg g^{-1}, was applied in 20% of the studies, while atomic absorption spectroscopy (AAS), which is less

Table 2
Overview of the included studies assessing metal(od)s and PAHs within the same sampling campaign.

PM	Location	Sampler height	Time (sample number)	Sampler type	Flow rate	Filter type	Pollutant	Analysis	Method	QA/QC	CRM	Calc.	Ref.
PM_{10}	Manlleu, Spain	*nr*	Winter 2013–Dec. 2022 (122)	HVS	30 m^3 h^{-1}	*nr*	Metal, PAHs	ICP-MS, ICP-OES, GC-MS	MAD with HF, HNO_3, $HClO_4$; SOE with DCM, MeOH	Er.: < 10%	*nr*	PMF	[22]
$PM_{10}-PM_{0.25}$	Beirut, Lebanon	GL	Jul. 2012–Aug. 2012 (*nr*)	LVS	9 L min^{-1}	QFF, PTFE	PAHs, metal	*nr*	*nr*	*nr*	*nr*	*nr*	[23]
$PM_{10}-PM_{0.25}$	Delhi, India	EL	Jul. 2014–Jul. 2015 (90)	LVS	30 L min^{-1}, 9 L min^{-1}	QFF, PTFE	Metal, PAH	ED-XRF, GC-MS	UAE with CH_2Cl_2	Er.: < 10% RSD: 75%–86%	*nr*	PCA, DR, LADD, HQ, HI	[24]
$PM_{10}-PM_{<0.1}$	Ljubljana, Dobrova, Maribor, Slovenia	GL	Dec. 2023 (*nr*)	LVS	12 L min^{-1}	PTFE	Metal, PAHs	ICP-MS, GC-MS	MAD with HNO_3, HF, HCl; MSE with Pet Eth and Ace	RSD: 6% for metals, 3% for PAHs, Acc.: 2% for metals, 6% for PAHs; Rec.: 96%–103%	NIST SRM 1648a	*nr*	[18]
$PM_{2.5}$	Zhengzhou, China	EL	Dec. 2012–Jul. 2015 (90)	HVS	1.13 m^3 min^{-1}	QFF	Metal, PAH	ICP-MS, GC-MS	MAD with HNO_3, HCl, UAE with DCM	Rec.: 80%–120% for metals, 79%–104% for PAHs	*nr*	LADD, ILCR, DAD, HQ, HI	[25]
PM_{10}	Volos, Greece	*nr*	Jan. 2014–Dec. 2015 (240)	LVS	2.3 m^3 h^{-1}	QFF	Metals, PAHs	ICP-MS, HPLC-FLD	MAD with HNO_3, H_2O_2; UAE with MeCN	Rec.: 95%–111% for metals, 73%–125% for PAHs	NIST SRM 1648a	ILCR, LADD, BAP_{eq}, HQ, PCA	[26]
$PM_{2.5}$	Beijing, China	EL	Jan. 2014–Feb. 2014 (98)	HVS	1.03 m^3 min^{-1}	QFF	PAH, metal	GC-MS, ICP-MS	UAE with DCM, MeOH, MAD with HCl, HNO_3, HF	Rec.: > 72%	*nr*	BTA, DR, PMF	[27]
$PM_{2.5}$	Gdansk, Diabla Gora, Katowice, Poland	EL	Jan. 2010–Dec. 2010 (1079)	HVS, LVS	*nr*	QFF	Metal, PAH	ETAAS, FAAS, ICP-OES, HPLC	MAD with HNO_3, HF, $HClO_4$, H_2O, HCl; ASE with DCM	Rec.: 91%–101% for metals, 92% for PAHs	NIST SRM 1648a, NIST SRM 1649b	BTA, EF	[28]
$PM_{2.5}$	Lanzhou, China	EL	Dec. 2012–Jul. 2013 (68)	HVS	1.13 m^3 min^{-1}	QFF	Metal, PAH	ICP-MS, ICP-OES; GC-MS	MAD with HCl, HNO_3; UAE with DCM	Rec.: 93%–105%, Prec.: < 5%, RSD: 5%–10% for PAHs	*nr*	PMF, EF, BTA	[29]
$PM_{2.5}$	Thessaloniki, Greece	EL	Jun. 2011–May 2012 (149)	LVS	2.3 m^3 h^{-1}	QFF	Metal, PAH	ETAAS, GC-MS	UAE with DCM; MAD with acids	*nr*	*nr*	BaP_{eq}, DR	[30]
$PM_{2.5}$	Wuhan, China	EL	Oct. 2011–Jul. 2012 (168)	MVS	100 L min^{-1}	QFF	Metal, PAH	ICP-OES, GC-MS	HP and UAE with HNO_3, $HClO_4$; UAE with DCM, MeOH	Rec.: 88%–95%for metals, 80%–112% for PAHs	*nr*	BTA, CMB	[31]

Abbreviations: nr (not reported), EL (sampler at an elevated level), GL (sampler at a ground level), LVS (low-volume sampler), MVS (medium-volume sampler), HVS (high-volume sampler). PTFE (polytetrafluoroethylene filter), QFF (quartz fibre filter), ICP-MS (inductively coupled plasma mass spectrometry), ICP-OES (inductively coupled plasma optical emission spectrometry), ED-XRF (energy dispersive X-ray fluorescence), ETAAS (electrothermal atomic absorption spectrometry), FAAS (flame atomic absorption spectroscopy), GC-MS (gas chromatography mass spectrometry), HPLC (high performance liquid chromatography), HPLC-FLD (high performance liquid chromatography with fluorescence detection), MAD (microwave-assisted digestion), HP (hot plate), UAE (ultrasound-assisted extraction), MSE (mechanical shaking extraction), ASE (accelerated solvent extraction), SOE (soxhlet extraction), HNO_3 (nitric acid), HF (hydrofluoric acid), HCl (hydrochloric acid), $HClO_4$ (perchloric acid), H_2O_2 (hydrogen peroxide), DCM (dichloromethane), MeOH (methanol), Ace (acetone), MeCN (acetonitrile), CH_2Cl_2 (methylene chloride), Pet Eth (petroleum ether), CRM (certified reference material), QA/QC (quality assurance and control), ILCR (incremental lifetime cancer risk), BaP_{eq} (carcinogenic equivalent concentration of benzo[*a*]pyrene), LADD (lifetime daily exposure dose), EF (enrichment factor), HQ (hazard quotient), HI (hazard index), PMF (positive matrix factorisation), DR (diagnostic ratio), PCA (principal component analysis), CMB (chemical mass balance), BTA (backward trajectory analysis), Calc. (calculations), Ref. (reference), RSD (relative standard deviation), Rec. (recovery), Prec. (precision), Acc. (accuracy), Er. (error).

sensitive (LODs are typically 0.1–10 μg L^{-1}) and limited to single-element analysis, was employed in 11% of the studies. These were the most commonly used techniques for measuring metal(oid)s in size-fractionated PM samples.

ICP-MS was used in 19 studies, including two that employed inductively coupled plasma mass spectrometry with magnetic sector (SF-ICP-MS). Inductively coupled plasma optical emission spectrometry (ICP-OES) was reported in 11 studies. Among the X-ray based techniques, total reflection X-ray fluorescence spectroscopy (TXRF), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray fluorescence (ED-XRF) and wave-length X-ray fluorescence were reported in one, one, six and one studies, respectively. In addition, among the AAS techniques, electrothermal atomic absorption spectrometry (ETAAS) and flame atomic absorption spectroscopy (FAAS) were each reported in two studies, while proton induced X-ray emission (PIXE) was reported in one study.

The most common sample digestion technique for metal determination was microwave-assisted digestion (MAD; 83% of the studies). The total metal concentration was also determined in sample digests after hot plate (HP; 21%) digestion, ultrasound-assisted extraction (UAE; 8%) and mechanical shaking extraction (MSE; 4%). For these procedures, nitric acid (HNO_3; 51%), hydrofluoric acid (HF; 18%), hydrochloric acid (HCl; 18%) and perchloric acid ($HClO_4$; 14%) were applied most commonly. Some studies also reported the use of hydrogen peroxide (H_2O_2; 10%), boric acid (H_3BO_3; 2%) and isopropyl alcohol (C_3H_8O; 2%). Table 3 summarises the analytical and extraction techniques.

3.3.2. Analytical methods for determination of PAHs bound to PM

Gas chromatography (GC) was predominately used for the separation of PAHs (85% of the studies). Combined with different detection techniques, PAHs were determined with high sensitivity (with typical LODs of 0.1–5 ng mL^{-1} in solvent extract), speed, selectivity and cost-efficiency. Three studies reported the use of GC coupled to a flame ionisation detector (GC-FID) and 38 studies used MS (GC-MS). In-injection port thermal desorption GC mass spectrometry (TD-GC-MS) was used in three studies, while one study reported the determination of PAHs using GC coupled to a quadrupole time-of flight mass spectrometer (GC-Q-TOF-MS) and GC coupled to a triple quadrupole mass spectrometer (GC-MS/MS).

Other techniques used to separate PAHs were based on high performance liquid chromatography (HPLC; 15% of the studies). Among detection techniques for separated PAHs, the most commonly used was fluorescence detection (HPLC-FLD) (eight studies). Although HPLC-FLD is more sensitive than GC-MS (with typical LODs of 0.01–0.5 μg L^{-1} in the extract), its main limitation is that it can only detect fluorescent PAHs. On the other hand, GC-MS is used more commonly for PAH analysis because it allows for unambiguous identification of both fluorescent and non-fluorescent PAHs and is widely accepted in regulatory methods. Additionally, GC-MS is less affected by matrix interferences, making it more robust for complex environmental samples.

Among the included studies, the most common extraction method for PAHs was UAE (64% of the studies), followed by accelerated solvent extraction (ASE; 23%), Soxhlet extraction (SOE; 21%), MAD (4%) and MSE (4%). The most commonly used solvent was dichloromethane (DCM; 49% of the studies). However, because DCM is a toxic volatile organic compound that can damage the liver and nervous system and is classified as a potential human carcinogen, posing risks through inhalation, ingestion, or skin exposure, safer alternatives such as hexane (Hx) or acetonitrile (MeCN) were often employed. These solvents reduce health and environmental hazards while maintaining efficient solubility and recovery of hydrophobic PAHs. Hx was used in 20% of the studies, methanol (MeOH) in 13%, acetone (Ace) in 12%, toluene (Tl) in 6% and MeCN in 7%. A small number of the studies (<5%) reported the use of diethyl ether (Eth), methylene chloride (CH_2Cl_2), cyclohexane (Chx), sulphuric acid (H_2SO_4) and petroleum ether (Pet Eth) (Table 3).

Table 3
Summary of the analytical and extraction or digestion techniques used in the included studies, with the corresponding study count.

	Metal (oid)s	Polycyclic aromatic hydrocarbons
Analytical technique:		
Inductively coupled plasma mass spectrometry	30	*n/a*
Atomic absorption spectroscopy	4	*n/a*
X-ray analysis	9	*n/a*
Gas chromatography mass spectrometry	*n/a*	46
High performance liquid chromatography	*n/a*	8
Extraction or digestion technique:		
Hot plate	5	*n/a*
Microwave-assisted digestion	20	2
Ultrasound-assisted digestion	2	29
Mechanical shaking extraction	1	2
Accelerated solvent extraction	*n/a*	11
Soxhlet extraction	*n/a*	10

Abbreviations: n/a (not applicable)

3.4. Assessment of health and environmental implications and potential source modelling

Health and environmental risks in the included studies were commonly assessed using the incremental lifetime cancer risk (ILCR; 32% of the studies), the carcinogenic equivalent concentration of BaP (BaP_{eq}; 27%), the lifetime daily exposure dose (LADD; 16%), the enrichment factor (EF; 10%), the hazard quotient (HQ; 8%) and hazard index (HI; 4%). ILCR represents the incremental probability of developing some form of cancer during one's lifetime due to pollutant exposure, while BaP_{eq} quantifies the toxicity of the complex PAH mixtures and their mutagenic and carcinogenic potential. LADD estimates the lifetime exposure dose of a chemical compound, while HQ and HI reflect the probability of experiencing adverse non-cancer effects. For health risk assessment, the studies also reported the use of loss of life expectancy (LLE), the dermal absorption dose (DAD) and the relative abundance ratio of an individual PAH to the carcinogenic marker BaP (RC).

The most commonly applied qualitative method for identifying potential sources of air pollution include the diagnostic ratios (DR; 41%), principal component analysis (PCA; 24%) and the U.S. EPA's positive matrix factorisation (PMF; 22%). PCA is a statistical technique that reduces the dimensionality of complex data sets and identifies hidden patterns and correlations between identified chemical species, while PMF is a receptor model that quantitatively estimates source contributions. Additionally, the characteristic PAH DRs are commonly used to distinguish between pyrogenic and petrogenic origins, such as petroleum, biomass or coal combustion, because these ratios remain relatively constant across emission sources [34].

Source apportionment was addressed using chemical mass balance (CMB), crustal matter contribution (CMC), conditional probability function (CPF), potential source contribution function (PSCF), roadside enrichment (RE), the UNMIX multivariate receptor model from the U.S. EPA, concentration weighted trajectory (CWT), self-organising maps (SOMs) and the weather research and forecast model with chemistry (WRF-Chem).

Backward trajectory analysis (BTA) was also employed to trace aerosol transport pathways and investigate transport mechanisms. The authors of the included studies also reported on the use of additional statistical approaches, including factor analysis (FA), linear regression models (LRMs), absolute principal component score (APCS), multivariate regression analysis (MRA), hierarchical cluster analysis (HCA) and the coefficient of divergence (COD).

3.5. Distribution and sources of metal(oid)s in urban environments

In China, concentrations of metal(oid)s bound to PM_{10} and $PM_{2.5}$ showed pronounced seasonal fluctuations, with winter peaks and $PM_{2.5}$ concentrations consistently higher than PM_{10} concentrations. There was a significant increase during haze events (1.5 −11 times higher than on non-haze days), particularly at high relative humidity (>70%), due to enhanced formation of secondary aerosol species and secondary organic compounds [8]. Among the measured elements, aluminium (Al), barium (Ba), iron (Fe), magnesium (Mg), manganese (Mn), strontium (Sr) and zinc (Zn) were the most abundant, while Cd, chromium (Cr), Ni and Pb posed the greatest cancer risks [8,25]. The trace element concentrations often exceeded World Health Organisation (WHO) limits, with the highest EFs observed for silver (Ag), As, Cd, Pb, selenium (Se), thallium (Tl) and Zn [29]. The total metal(oid)s concentration in PM_{10} decreased in the following order: Zn > As > Pb > Mn > Cu > Cr > Ni > Cd > cobalt (Co), with the highest bioaccessibility observed for Mn, Co and Ni. The concentrations of As, Cr, Co, Cd and Pb surpassed precautionary cancer thresholds. The bioaccessibility of heavy metals depends on the source and is higher for traffic-related metal(oid)s than for coal combustion, because metal(oid)s in vehicles occur in a free state or are adsorbed on the surface and are more soluble in water or other extraction media [35]. Fossil fuel combustion, traffic emissions, industrial emissions and re-suspended dust are considered to be the main sources of PM-bound metal(oid)s in China [35].

In Taiwan, the most abundant elements were Al, Ba, Cr, potassium (K), Mg, Ni and Zn (10 −1000 ng m^{-3}), followed by copper (Cu), Mn, molybdenum (Mo), Pb, antimony (Sb), Se, Sr, titanium (Ti) and vanadium (V) (1 −10 ng m^{-3}). Elements detected at < 1 ng m^{-3} included As, Cd, cerium (Ce), Co, lanthanum (La), neodymium (Nd), praseodymium (Pr), samarium (Sm) and ytterbium (Yb). Five main sources were identified, including traffic, non-ferrous metallurgy, mineral dust and coal [36].

In India, similarly to China, the highest ILCR values were observed on foggy days, with Cr showing the highest carcinogenic risks and the main sources attributed to industrial processes, fossil fuel combustion, biomass and coal combustion, waste incineration and brake wear [37]. The highest HQs were observed for Al, As, Se, silicon (Si) and Zn, all of which were above the limit values [24]. In Iran, the highest PM_{10} bound metal concentrations were observed at traffic intersections near brick kilns, in the following order: Fe > Zn > Cr > Mn > Pb > Ni > Cu > As > Cd. The highest EFs were observed for Co, Cd, As, Pb and Zn [10]. The calculated cancer risks were the highest for Cr, Co, As and Cd [10,38]. Four main sources were identified, including re-suspension of road dust due to vehicular activity (Fe, Co, Ni and Cu), solid waste incineration (Cr, Mn and Cu), coal combustion and automobile exhaust (Cd and As) and smelters/non-ferrous metal plants (Zn and Pb) [10]. In Pakistan, there was high seasonal variability, with the highest metal levels observed in winter and fall. Pb and Cr exhibited the highest potential non-carcinogenic and carcinogenic risks for children through inhalation [39].

In Europe, lower $PM_{2.5}/PM_{10}$ ratios were observed in areas with dry climates or in close proximity to deserts, while higher ratios were reported in urban areas with intense traffic [40]. Crustal elements, such as Al, calcium (Ca), Fe, K, Mg, sodium (Na) and sulphur (S), are predominantly associated with coarse PM, while traffic-related tracers (Ba, Cd, Cr, Cu, Mo, Sb and Zn) indicate tyre and brake wear. Diesel and gasoline emissions are characterised by Cu, Mo, Ni, Pd, Co and Zn, which are typically enriched in fine fractions. Additional source markers include V from marine emissions; La and Ce from mineral dust; and As, Cd, Pb and Sb from coal combustion [36,41,35,40]. In a pan-European study, the dominance of Zn, Ti and Cu indicated diverse pollution sources [42]. In general, smaller PM fractions exhibit a higher affinity for adsorption of toxic substances. Metal(oid)s from high-temperature processes are preferentially bound to fine and UFP PM, while coarse particles are mainly derived from natural sources and mechanical abrasion [17]. In Germany, the highest metal concentrations occurred in winter, particularly for Ca, Fe, K, Pb and Zn and were accompanied by a shift towards smaller particle fractions. Cr and Cu were mainly present in coarse PM fractions, largely attributed to brake wear, while Ni was enriched in the fine PM fraction, reflecting its link to fuel combustion. The highest EFs were observed for Zn, Cu, tin (Sn), Pb, As, Sb and Se, all attributed to traffic sources, with notable Zn emissions associated with tyre tread wear from rubber co-polymers [12]. In Slovakia, the highest concentrations of selected metal(oid)s were found in PM_1, primarily originating from non-exhaust traffic emissions and re-suspended road dust [43]. Combustion processes in domestic heating and traffic have been shown to contribute to submicronic particles and UFPs [3].

In Italy, $PM_{2.5}$-bound Cd and Pb exhibited significant leachability, although most trace elements remained below the threshold levels [44]. The highest concentrations were observed for Cr, Zn and Cd, with Cd, Cr, Cu, Fe, Mn, Mo and Sn predominantly associated with coarse PM and As, Co and Pb enriched in fine PM. Fine particles were mainly emitted from fossil fuel combustion, while coarse particles were dominated by crustal elements from road dust [45]. The highest EFs were observed for V, Ba, Cr, Ni Cu, As, Zn, Sb, Pb, Mo, Cd and mercury (Hg), which were moderately or highly enriched in all locations, arising from vehicles emissions, heating or dye industry. Five main sources were identified, including brake and tyre wear (Ba, Cu, Fe, Mo and Zn), non-exhaust vehicular emissions and road dust re-suspension (Al, Mn, Sb, Ce and La), cement plants (Mg, Ca and Ti), industrial emissions (As and Sb), and fossil fuel combustion and biomass burning (K, Ni and V) [46]. In Slovenia, the analysis revealed that the metal(oid)s in PM_{10} are predominately associated with soil deposition and re-suspension processes, while traffic-related and biomass combustion emissions contributed to significantly elevated concentrations of Ba, Cd, Cu, Ni, Pb, palladium (Pd), platinum (Pt), V and Zn, in the $PM_{<0.1}$ fraction [18].

In Algeria, the coarse PM fraction was prevalent due to the lack of vegetation and soil erosion. Ba and Pb showed the highest concentrations, with greater enrichment in PM_1 and $PM_{2.5}$ in comparison to PM_{10}. The main sources that contributed to elevated metal(oid) concentrations included exhaust emissions, re-suspended road dust and oil combustion. Concentrations were also affected by Saharan dust [47].

In Mexico, metal(oid) contamination was also more dominant in winter, with Fe, Cu, Zn, As, Ni and Cd having the highest observed concentrations [48].

In general, the overview of metal(oid)s bound to PM in different global regions showed great seasonal variations, particularly associated with fine and ultrafine PM fractions. The highest concentrations were observed in winter, especially during haze events. Naturally derived crustal elements such as Al, Ca, Fe and Si are typically found at higher concentrations in coarse PM fractions, whereas As, Cd, Cr, Ni and Pb, primarily originating from anthropogenic sources, are generally enriched in (ultra)fine fractions. These finer particles exhibit high bioaccessibility due to their stronger affinity for adsorption of toxic substances, the occurrence of metals in the free state and high solubility potential.

3.6. Distribution and sources of PAHs in urban environments

In Iran, the highest concentrations of PAHs bound to $PM_{2.5}$ were observed in winter, particularly HMW PAHs [49]. BaP concentrations exceeded the WHO guideline value of 1 ng m^{-3} [9]. The most abundant PAHs in Iran were fluoranthene (Fl), BghiP, acenaphthene (Ace) and IP [50]. There was a similar seasonal pattern in Lebanon, where winter concentrations were 3 −5 times higher than in summer, mainly due to vehicle traffic, diesel generators and nearby power plants [51].

PAHs are typically characterised by strong seasonal variations, primarily due to greater atmospheric stability in winter, enhanced partitioning of HMW PAHs into the particulate phase due to reduced volatility and more efficient volatilisation of LMW PAHs into the gaseous phase combined with intensified photochemical degradation during

summer (23,44,93). PAHs that partition into the gaseou phase generally exhibit lower carcinogenic potential [14]. Elevated temperatures can enhance the evaporation of $PM_{2.5}$-bound PAHs and accelerate their transformation into nitro- and oxy-PAHs, reducing particulate-bound PAHs. Moreover, precipitation washout, a reduced atmospheric boundary layer depth and stronger winds further dilute and disperse pollutants [52-54].

In China, PAH concentrations in $PM_{2.5}$ were highest in winter – 14 times higher than in spring – and often exceeded the WHO annual limit of 5 μg m^{-3} [55-57]. HMW PAHs (with 4 −5 ring) bound to PM_{10} and $PM_{2.5}$ were three times more abundant than LMW PAHs. High loadings of 5- and 6- HMW PAHs are typically indicative of high-temperature combustion sources, such as vehicle emissions, while LMW PAHs are more commonly associated with lower-temperature combustion processes, including biomass and coal burning [58,55,54,56]. Health risks were primarily associated with BaA, BaP, Ch, BbF, benzo[*k*]fluoranthene (BkF), IP, dibenzo[*a*,*h*]anthracene (DahA) and Fl, with BaP concentrations and ILCR values often above safe levels [59,53,25,55,54]. Source apportionment attributed PAHs to vehicle exhaust mixed with soot and coke oven emissions, ship emissions, biomass burning and coal combustion [59,25,60,55,54]. The highest concentrations of PAHs were observed in northern China and the lowest in southern China [61]. In addition, the sources of PAH emissions were more dispersed in the suburban areas and were commonly associated with residential cooking using coal, wood and straw (83).

The distribution of PAHs reflects their sources, with specific tracers of BghiP for gasoline vehicles, BbF and BkF for diesel vehicles, and BaA and Ch for natural gas combustion [62]. In addition, PAHs with 2 −3 rings often originate from wood combustion, PAHs with 3 −4 rings originate from coal and PAHs with 4 −6 rings originate from vehicle and petroleum combustion [14,62]. PAHs with 4 −6 rings contribute to 95% of the total $PM_{2.5}$-bound PAHs [53].

In India, PAH concentrations bound to PM were also highest in winter, with the largest contributions from the combustion of biomass, petroleum and coal. DahA, BaP, BaA, BkF and Ch contributed most to health risks [52,63]. PAHs with 5 −6 rings showed the highest concentrations; they are predominantly associated with fine PM due to their larger surface area and greater absorption capacity [24,63]. HMW PAHs exhibit a greater adsorption capacity than LMW PAHs due to their lower volatility and slower gas–particle partitioning dynamics. Their pronounced hydrophobicity further promotes association with smaller particles, which provide a larger surface area [64].

Similarly to China, PAH levels in India were highest in the morning, attributed to morning traffic, lower temperatures, a lower atmospheric boundary layer height, weaker turbulence and limited photodecomposition, all of which results in lower pollutant dispersion [53]. In Japan, PAHs with four rings peaked in winter, with BaP, BaA, BbF, BkF and IP exhibiting the highest concentrations, originating from traffic, coal and biomass combustion [65]. In Thailand, PAH concentrations were significantly higher during the heating period than during the non-heating period, with BbF, indicative of biomass emissions, showing the highest concentrations. The ratio of total PAHs to PM decreased as PM size increased, a phenomenon that can be attributed to the ageing process, possible photooxidation of PAHs from secondary organic aerosols or adsorption to pre-existing particles through self-nucleation of gaseous phase partitioning [64]. In Taiwan, both $PM_{2.5}$ and PAHs were elevated during winter, revealing potential impacts of long-range transport and indicating the dominance of petroleum and fuel combustion [66]. Similarly, in Malaysia, BbF, BkF, BaP, IP and BghiP were the most abundant, with 80% of the detected PAHs having five or six rings. The DRs indicated mixed sources of incomplete combustion of petroleum fuel and vehicle emissions together with unburnt crude oil and petroleum products such as gasoline, kerosene and diesel [67].

PAH concentrations in Europe showed a north-south gradient, with the highest levels reported in southern regions [68]. In Italy, seasonal differences were limited, with BaP, BkF and BbF dominating, mainly originating from engine emissions [69]. In Spain, the highest PAH levels were observed in winter, with strong seasonal variations, and diesel traffic being the main source of BaP, BbF, DahA, IP, BaA, BkF and Ch [70]. In Greece, IP, BghiP and Ch were the most abundant, with wood burning and traffic as major sources [71,72]. In Poland, BaP bound to PM_1 was 2.5 times higher than in $PM_{2.5}$ [73], while in Croatia, winter concentrations of BghiP, BaP, BbF and IP were highest, with 80% of PAHs bound to $PM_{2.5}$, mostly from domestic heating [13].

In Slovenia, HMW PAHs were distributed between the PM_{10} and $PM_{2.5}$ fractions, with five ring (BaP and BbF) and six ring (BghiP and IP) PAH associated more significantly with smaller PM fractions. Contaminant levels were low, indicating minimal health risks for the population [18]. The concentrations were higher in Portugal than in Italy or Greece, reflecting higher utilisation of fossil fuels and biomass [11]. In the Czech Republic, the highest levels of Fl, Phe, Pyr, BaA and Ch were observed during smog episodes related to coal mining, metallurgy, coke production and residential heating [74]. In the United Kingdom, PAH peaks occurred in the morning and evening, with the evening peaks mainly caused by residential heating [16]. In Turkey, the primary sources of particulate OM were identified as vehicular emissions, coal combustion, and food cooking [75].

In Ghana, there were high concentrations of BghiP, Pyr, Phe, IP and BaP, with Phe and Pyr, serving as markers of emissions from diesel vehicles, and BaP, a marker of gasoline vehicle emissions [62,76]. The BaP values remained below the regulatory limit [76]. Monitoring of PAH concentrations in Egypt revealed the highest levels of IP, BghiP and BaP; they primarily originated from combustion sources [77].

In general, the analysis of PAHs bound to PM showed strong seasonal variations, characterised by high abundance of HMW PAHs in (ultra)fine PM during colder months. The trend is primarily governed by photochemical processes and increased atmospheric stability, and, in certain cases, meant that BaP, DahA, BaA, BbF, and BkF exceeded the regulatory limits. HMW PAHs were more prevalent than LMW PAHs, attributed to their lower volatility corresponding to their higher adsorption capacity of toxic substances. PAH concentrations were also highest in the mornings, likely due to limited photodecomposition rates, lower temperatures, a lower atmospheric boundary layer, weaker turbulence and higher prevalence of sources. Additionally, the studies indicated a global north-south gradient, with the highest concentrations of PAHs found in the southern regions of the Northern Hemisphere. In China, the highest concentrations of PAHs were observed in northern China and the lowest in southern China. Elevated levels of HMW PAHs indicate on a stronger influence of pyrogenic sources, including fossil fuel, biomass and vehicle emissions.

4. Conclusions and future prospects

This review examined 80 studies from 33 countries, published from 2010 to 2025, to evaluate the current sampling and analytical methods for quantifying metal(oid)s and PAHs in size-fractionated PM. Particular attention was given to their chemical characteristics, seasonal variability, spatial distribution and the procedures used to ensure the quality of the data.

Prior to PM sample collection, it is essential to define the target pollutants. This enables the selection of appropriate analytical methods, including adequate filter materials, extraction or digestion procedures and highly selective and sensitive analytical techniques for pollutant quantification. The reliability of the resulting data should be verified through the use of suitable certified reference materials. Despite this need for quality assurance, only 33% of the studies reported the use of certified reference materials, with NIST SRM 1648a being the most commonly employed, certified for both PAHs and metals. Routine evaluation of the accuracy of analytical data and method validation for PM determination is uncommon, largely due to the high cost of certified reference materials.

Among the reviewed studies, 52% focused on the characterisation of

pollutants bound to $PM_{2.5}$, followed by PM_{10} (30% of the studies) and PM_1 (13% of the studies), while only 5% investigated PM smaller than 0.1 μm. This ultrafine fraction is highly prevalent in the atmosphere and has a high pollutant absorption capacity. It can penetrate deep into cell tissues and the circulatory system, exhibiting the most pronounced toxic effects. PM smaller than 0.1 μm has rarely been studied because they are not efficiently retained by conventional filter-based samplers, due to diffusion losses, leading to potential underestimation of PM mass.

In total, 56% of the studies identified the chemical composition of PAHs, 31% focused on metal(oid)s, and only 14% addressed both pollutant groups within the same study.

Inductively coupled plasma mass spectrometry was the most widely employed technique (68% of the studies) for the determination of metal (oid)s in PM size-fractionated samples, followed by X-ray analysis (20% of the studies) and atomic absorption spectroscopy (11% of the studies). Microwave-assisted digestion was mainly used for sample decomposition (83% of the studies), followed by hot plate digestion (21% of the studies), ultrasound-assisted extraction (8% of the studies) and mechanical shaking extraction (4% of the studies). For PAH analysis, gas chromatography mass spectrometry was employed in 84% of the studies, while high performance liquid chromatography was used in 16%. Ultrasound-assisted extraction was the predominant PAH extraction method, used in 64% of the studies. In contrast, other techniques were applied less frequently, including accelerated solvent extraction (23% of the studies), Soxhlet extraction (21% of the studies), microwave-assisted digestion (4% of the studies) and mechanical shaking extraction (4% of the studies).

The most commonly used filters media were quartz fibre filter (65% of the studies), followed by polytetrafluoroethylene filters (16% of the studies) and glass fibre filter (13% of the studies). These filters differ in sampling efficiency; mechanical, chemical and temperature stability; blank values; flow resistance and the formation of artefacts, all of which are important for different analytical applications. The choice of filter media is also influenced by the solubility of filter materials in the extraction solvent, with polytetrafluoroethylene filters outperforming glass fibre filters and quartz fibre filters.

Global PM-bound metal(oid) distribution showed strong seasonal variability, with winter episodes exhibiting the highest concentrations, particularly in (ultra)fine PM. As, Cd, Cr, Ni and Pb – derived from traffic – were the most abundant elements in (ultra)fine PM. They show high bioaccessibility, likely due to their strong affinity for adsorption of toxic substances, their occurrence of the more bioavailable (free) forms, and their high solubility potential. Smaller PM fractions were mainly associated with anthropogenic sources, such as fossil fuel combustion, traffic emissions, industrial processes and waste incineration, while coarse PM primarily reflected naturally-derived crustal material.

Similarly, PM-bound PAHs showed strong seasonal fluctuations, with fine and UFP enriched in HMW PAHs emitted from fossil fuel combustion, biomass burning and traffic. Seasonal and diurnal patterns were influenced by meteorological factors, atmospheric stability and photochemical processes, with BaP, DahA, BaA, BbF and BkF often exceeding health guideline limits, representing high carcinogenic risks. HMW PAHs were more prevalent than LMW PAHs, as their lower volatility allows stronger adsorption onto particulate matter. A north-south gradient was evident in Europe, with the highest concentrations of PAHs found in the southern regions of the Northern Hemisphere. In China, the highest concentrations of PAHs were observed in northern China and the lowest in southern China.

An overview of exceedances of PM_{10} and $PM_{2.5}$ limit values according to the Ambient Air Quality Directive (AQD) and/or WHO guidelines was conducted, together with an assessment of regulatory limit or target values for metals in ambient air (As, Cd, Ni, Pb) and BaP. Approximately 90% of the included studies in this review reported concentrations above the limit values; exceedances were reported in 65% of studies for BaP and in about 35% for metals.

Most of the studies (85%) deployed PM samplers at elevated sites (above 2.5 m, e.g. rooftops), distant from residential and commuter areas, which may limit the representativeness and thereby reduce the accuracy of exposure assessments. Adequate health and environmental risk assessment, typically based on incremental lifetime cancer risk (32% of the studies), carcinogenic equivalent concentration of BaP (27% of the studies) and lifetime daily exposure dose (16% of the studies), is essential for quantifying the potential adverse effects and ensuring public health protection and pollution control. Additionally, the identification of pollutant sources enables more targeted mitigation and more effective regulation, with source apportionment commonly conducted by diagnostic ratios (41% of the studies), principal component analysis (24% of the studies) and the positive matrix factorisation (22% of the studies).

This review highlights a significant gap in the characterisation of the smallest PM fractions, as studies on UFPs remain limited. It also identifies shortcomings in analytical approaches, including the lack of multi-pollutant analyses and the limited use of CRMs to validate analytical procedures and ensure the accuracy and reliability of the data. Future research should focus on the development and implementation of uniform sampling protocols for UFP collection, including reliable analytical approaches to ensure cross-study comparability.

Expanding the availability of CRMs will improve the quality of analytical data. Integrating multi-pollutant analyses into sampling protocols will help better capture the complex composition of UFP and their combined toxicological effects. Together, these improvements will strengthen the scientific basis for environmental policy, regulatory standards, and public health protection.

CRediT authorship contribution statement

Radmila Milačič Ščančar: Writing – review & editing, Supervision, Funding acquisition. **Prashant Kumar:** Writing – review & editing, Supervision, Funding acquisition. **Alenka Mauko Pranjić:** Writing – review & editing, Supervision, Funding acquisition. **Marija Đurić:** Writing – review & editing. **Janez Ščančar:** Writing – review & editing, Supervision, Funding acquisition. **Anja Ilenič:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Funding

Marija Đurić and Alenka Mauko Pranjić acknowledge the support of the Slovenian Research Agency financial support programme group P2–0273, Radmila Milačič Ščančar and Janez Ščančar acknowledge the support of the Slovenian Research Agency financial support programme group P1–0143. Prashant Kumar acknowledges support received through the UKRI-funded GP4Streets (APP44894), RECLAIM Network Plus (EP/W034034/1), GreenCities (NE/X002799/1), GREENIN Micro Network Plus (APP55977) and UGPN-funded (UGPN-NBS and GREENICON) projects.

Declaration of Competing Interest

There is no conflict of interest.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.teac.2026.e00303.

Data availability

Data will be made available on request.

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