Biomonitoring of polyaromatic hydrocarbons (PAHs) by Murraya paniculata (L.) Jack in South Kolkata, West Bengal, India: Spatial and temporal variations

Shritama Mukhopadhyay
Jadavpur University
Ratna Dutta (ratna.dutta@chemical.jdvu.ac.in)
Jadavpur University
Aparna Dhara
Jadavpur University
Papita Das
Jadavpur University

Research Article

Keywords: Extraction optimization, PAHs, Evergreen plant species, Spatial and temporal variability, Diagnostic ratios, Field study

Posted Date: September 22nd, 2022

DOI: https://doi.org/10.21203/rs.3.rs-2060280/v1

Abstract

Attempts have been made in the present study for ascertaining the content of atmospheric polycyclic aromatic hydrocarbons (PAHs) using passive biosamplers in preference to conventional air sampling methods. Mechanical stirring, sonication, Soxhlet technique and microwave-assisted Soxhlet extraction (MASE) were employed to extract PAHs from an evergreen plant (*Murraya paniculata*) leaves (having long life-span) sampled from polluted places of South Kolkata, India, with dense population. Effects of extraction methods and operational parameters on the recovery levels of PAHs were also investigated. Purified extracts, acquired through adsorption chromatography, were subjected to GC-MS and HPLC-UV analyses for qualitative and quantitative assessment of PAHs. Spatio-temporal distribution of accumulated PAHs across the sampling sites was monitored over premonsoon, postmonsoon and winter supported by pollutant source characterization. The results displayed that the extraction yields of Soxhlet and MASE were highest among the four techniques. Conditions of extraction with toluene for 6 h were found to be most favourable for PAHs. Total concentrations of PAHs in the foliar samples varied from 200.98 ± 2.72–550.79 ± 10.11 μg g^{-1} dry weight, highest values being recorded in the samples of Exide More (EXM) because of daylong inexorable traffic flow/crowding increasing the burden of ambient PAHs. Widespread changes in meteorology exerted influence on seasonal concentrations of PAHs in plant leaves. Foliar accretion of PAHs differed in the study sites with diverse sources of emission from motor vehicles, fossil fuel and biomass burning along with other human interferences.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are lipophilic environmental carcinogens having pernicious impact on public health owing to their long presence and resistance to biodegradation (Bostrom et al., 2002; IARC, 1983). Anthropogenic pollution has been the key contributor of airborne PAHs emissions and is a menace to ecosystem sustainability. Biomonitoring strategies as eco-based solution are thus broadly adopted for improving air quality on account of process economy, simple sampling procedures and wide scope of experimental manoeuvring (Capozzi et al., 2016; Jiang et al., 2018). Identification and quantification of PAHs after extraction or isolation are the major requirements of biomonitoring for understanding the degree of pollution and state of changes occurring in the environment (Mukhopadhyay et al., 2020). Complex structural characteristics and diversity of plant matrices make the process of target analyte extraction difficult (as there are possible chances of co-extraction of plant pigments and other organic compounds) and hence, in quality analysis, sample preparation is a vital step towards recovery (Domeno et al., 2012; Steiner et al., 2020). Traditional Soxhlet and process intensified extraction approaches (assisted with ultrasonication, supramolecular solvents, supercritical and subcritical fluids, microwave heating, high pressure and temperature, etc.) with gas or liquid chromatographic analysis proved to be indispensable for true detection of PAHs in sample materials (Barreca et al., 2014; Szulejko et al., 2014). Maximum usage of organic solvents (e.g. acetone, hexane, dichloromethane, petroleum ether, toluene, etc.) has also been noticed in numerous extraction applications (Birke et al., 2018; Kargar et al., 2017; Klingberg et al., 2022; Niu et al., 2019; Oishi et al., 2018; Sari et al., 2021; Yang et al., 2017). There is a pressing need for detailed examination of performance characteristics of analytical techniques for advancement of laboratory-based standardization protocols and quality assurance/control checks when dealing with desired matrices of heterogeneous composition (Steiner et al., 2020). It is very common that the extracted solutions would always contain some impurities and interferents, tampering with the analytical outcome and inducing experimental bias which generates false positive results (leading to faulty interpretation or erroneous data due to overlapping peaks of matrix components masking the analyte of interest) during PAHs quantitation. Therefore, the impure extracts often require effective purification and concentration stages to increase the sensitivity and accuracy of the analysis with reduction in the source of experimental bias (Gerssen et al., 2009). Extract clean-up procedures involving adsorbents or solid-phase extraction cartridges are generally used for complex matrices (Blasco et al., 2007; De Nicola et al., 2016; Hussain and Hoque, 2015; Ray et al., 2021; Tian et al., 2019; Yang et al., 2017). Critical evaluation of extraction process parameters through optimization studies is of utmost importance to maximize the extraction yield and deduce the interactive influences of the operating variables. Single factor and multivariate optimization (using Box-Behnken, Taguchi, Plackett-Burman, full factorial, central composite or combined designs) are well-recognized techniques for improvement of the efficacy of sample preparation methodologies (Fazeli et al., 2020; Foan and Simon, 2012; Frempong et al., 2021; Scaramboni et al., 2021).

The plant cover and green spaces are the universal attenuators of air pollution, which absorb the deadly atmospheric pollutants and protect the human population from high risks of vulnerability. PAHs may penetrate the plant leaves either by diffusion through stomatal pores (gaseous uptake) or by atmospheric deposition (in particulate phase) on leaf cuticles and their partitioning from air to outer leaf surfaces and to inner tissues is driven by environmental factors, pollutant properties and plant behaviour (Lin et al., 2006). A multitude of studies has focussed on PAHs determination using leaves of both deciduous and evergreen trees (*Quercus robur*, *Quercus palustris*, pine species (*Pinus pinaster*, *Pinus nigra*), Olive, *Salix matsudana* and *Murraya paniculata*) as good pollution indicators of terrestrial environment and come up with multiple outcomes (De Nicola et al., 2016; Kargar et al., 2017; Karnchanasest and Satayavibul, 2005; Klingberg et al., 2022; Mukhopadhyay et al., 2021; Ray et al., 2021; Sari et al., 2021; Zhao et al., 2018). The levels of foliar PAHs undergo changes in response to spatial and temporal variations in wind flow, diurnal temperature, ambient moisture content, stability class (i.e. presence of clouds during day and night –time), concentrations of tropospheric oxidants, rate of photodegradation and pollution load from mobile or point sources of emission (Bidleman and Leone, 2004; Ohura et al., 2013; Totten et al., 2002; Wang et al., 2015). Diagnostic ratios (DRs), positive matrix factorization (PMF) and principal component analysis with multiple linear regression (PCA-MLR) are commonly employed for source apportionment studies to reveal the origin of PAHs contamination in plants and quantify the percent contribution of the components of emission (De Nicola et al., 2008; Kargar et al., 2017; Yang et al., 2017; Zhou et al., 2014).

As far as air quality is concerned, better assimilation of knowledge about the interactions between the pollutants and vegetative barriers is imperative to effectively implement the biomonitoring scheme for pollution control. Paucity of related field works in and around Kolkata, India, has driven us to undertake such studies as an endeavour towards bridging the gap between scanty information and biomonitoring prospect. In this aspect, the specific objectives of the study were framed to: (i) provide a comprehensive comparative analysis of different extraction methods (viz. mechanical stirring, sonication, Soxhlet and microwave-assisted Soxhlet extraction (MASE)) for performance validation in PAHs recovery from the leaves of *Murraya paniculata* (L.) Jack, (ii) optimize the

suitability of extracting solvents and extraction time, (iii) establish the spatio-temporal patterns of PAHs concentrations in plant samples of selected contaminated zones of South Kolkata and (iv) apply DRs for determination of the primary sources of PAHs along with seasonal effects.

Materials And Methods

Field sampling and sample pretreatment

A field work was executed in the urban areas of South Kolkata, India, during three different seasons (premonsoon (May and June, 2019), postmonsoon (October to mid of November, 2019) and winter (January and February, 2020)), which comprised collection of waxy leaf samples of a dominant tree species, *Murraya paniculata* (L.) Jack, applying proper methodological approaches (Mukhopadhyay et al., 2021) from the roadsides of selected study sites: Jadavpur (JDV), Rash Behari Connector (RBC), Exide More (EXM) and Tollygunge (TGN), with their subsequent storage in plastic zip lock pouch bags for direct shipment to the testing laboratory. The choice of the above sites was mainly based on the following factors: (a) overcrowding of the areas and intense human activities, (b) huge increase in the use of motor vehicles, (c) small-scale polluting units and (d) proximity to the Central/State Pollution Control Board operated regular air quality monitoring networks. Field replicates were also taken from each zone for robust analytical measurements. The overall considerations and representation of sampling locations are clearly delineated in our previous research (Mukhopadhyay et al., 2021).

Pretreatment of the plant leaves involved prewashing, drying and grinding for acquiring desired performance of the process. After washing off the dry mud and other residues from plant foliage, samples were lyophilized (Lyophilizer, Eyela FDU-1100) and dry leaf powder was produced thereafter with a porcelain mortar and pestle for long-term preservation.

Optimization of extraction factors for isolation of PAHs from plant leaves

Extraction methods

Mechanical stirring

Freeze-dried samples of leaves (10 g on dry weight (d.w.) basis) were extracted with 120 mL of high purity n-hexane (primary solvent generally employed for all analyte groups) in an Erlenmeyer flask for 6 h at room temperature using a magnetic stirrer (Remi 2MLH) at moderate speed. The extracts were then passed through Whatman Grade 1 filter papers for filtration. The entire process was repeated thrice to ensure complete extraction of target PAHs and the filtered extracts were combined together for further purification and analysis.

Sonication

About five grams of samples (leaf dry mass) were sonicated with a probe (or sonotrode MS7 of tip diameter 7 mm) sonicator (Ultrasonic Processor UP50H (50 W, 30 kHz), Hielscher Ultrasonics, Germany) at 70% amplitude for 30 min utilizing n-hexane as solvent. Pulsed mode of sonication was applied for extraction to minimize heat generation (Delacour et al., 2019). Six cycles of 5 min sonication with subsequent 5 min of rest period were carried out, 30 mL of fresh solvent being added to the system in each cycle. Temperature as recorded during the operation was in the range of 25–35 C. The processing conditions given by Benson et al. (2018) and Herrera-Pool et al. (2021) were followed with some amendments. After consecutive extractions, all the sample extracts were recovered, integrated and centrifuged (Remi R-8M Plus laboratory centrifuge) at 2800 rpm for 15 min. The supernatant was collected afterwards and stored in a borosilicate glass reagent bottle with screw cap at 4 C for future investigation.

Soxhlet extraction

Ten grams (d.w.) of samples were Soxhlet extracted for 6 h in 120 mL of n-hexane. A filter paper thimble containing the solid plant matrix was loaded in the main extractor chamber of the apparatus for continuous extraction by solvent reflux; the exhaustive extraction cycles being repeated several times throughout the duration at boiling point temperature of the solvent. The final extract was then refrigerated for further separation and clean-up to get active PAHs fraction.

MASE

A microwave extractor (Microwave synthesis/extraction system, Model: NuWav-Uno (11–19/Uno-112), NutechAnalytical Technologies, Pvt. Ltd., Kolkata) was deployed for the said purpose, which involved the usage of a Soxhlet apparatus (i.e. reflux system) for sample extraction aided by microwave heating with appropriate temperature and pressure control. The methodology adopted in the study was slightly modified from the procedures recommended by Herbert et al. (2006) and Ratola et al. (2009). In microwave treatment, lyophilized samples (~ 3 g) were added to 90 mL of n-hexane: acetone mixture (9:1 v/v) in a 250 mL round bottom (RB) borosilicate glass flask and extracted for 30 min at 500 W power and 50 C temperature under a stirring speed of 500 rpm. Pure non-polar solvents are not compatible to MASE because of their low dielectric constants. Therefore, in the proposed work, a mixture of polar (acetone) and non-polar (n-hexane) solvents was used to facilitate the interaction between microwaves and extractant and also to improve the rate of heating. The RB flask holding the sample and extractant was placed inside the oven and connected to an extractor which, in turn, was externally fitted with a condenser attached to a continuous flow of water for cooling. The obtained extract was subjected to filtration upon completion and preserved to avoid loss of target analytes.

Selection of extracting solvent for maximum recovery of PAHs

After validation of the favourable method, efficiencies of various solvents with different polarities (from polar to non-polar range) were analysed in respect of their interactions with the plant matrix and PAHs extraction ability. Extraction experiments were conducted for 6 h with five separate solvent systems: acetone (relative polarity, RP: 0.355), dichloromethane (DCM) (RP: 0.309), n-hexane (RP: 0.009), toluene (RP: 0.099) (Reichardt and Welton, 2010) and acetone: n-

hexane (1:1 v/v) (Merck, Darmstadt, Germany), for the purpose of identifying the best extraction solvent for highest analyte recoveries. In case of binary mixture, solvent composition in volume % has a bearing on the measurement of polarity (Zalewski et al., 1991).

Optimization of extraction time

The extraction time was optimized with the best-suited solvent to ascertain the equilibrium time for maximization of PAHs yield. Extractions were designed for 5 h, 6 h, 7 h and 8 h duration and recoveries of all the analytes were compared among the designed experiments.

Extract purification and concentration

Extract clean-up was achieved through silica gel column chromatography to fractionate PAHs from matrix interferences. The extracts were loaded on a chromatographic column fitted to a retort stand and filled with anhydrous sodium sulphate (2 g; assay ≥99.0%) and preheated silica gel (10 g; 100–200 mesh, chromatographic quality). However, before packing of the column, silica gel slurry was prepared each time in the same organic solvent as used for sample extraction. Cotton plugging was also done at the bottom of the column to maintain a uniform level of silica gel throughout the process. Once the silica bed was in form, excess solvent was drained out taking precaution to avoid development of cracks in the bed. The column was conditioned with 25 mL of n-hexane before purification. In every case, sample extract of volume 8 mL was passed through the silica column and PAHs were eluted with 25 mL of n-hexane in polypropylene vials with screw cap. The eluates were concentrated within a rotary evaporator (Buchi R-3 Rotavapor) under reduced pressure, resuspended in methanol (HPLC grade, assay ≥99.9%) to make up the final volume to 4 mL and stored in a refrigerator till analysis.

Instrumental analysis of PAHs

PAHs were analytically detected by gas chromatography-mass spectrometry in a Thermo Scientific Trace 1300 gas chromatograph (GC) connected with a single quadrupole mass spectrometer (MS) (Thermo Scientific, United States) operated in electron impact ionization mode. The column used was a TG-5MS capillary column having dimensions: 30 m · 0.25 mm · 0.25 µm (Thermo Scientific, United States). Identification of the selected contaminants (qualitative analysis) was carried through proper standardization of the GC-MS system with a certified reference material (Sigma-Aldrich, United States), ensuring measurement reproducibility. The complete analytical procedure was extensively reported in Mukhopadhyay et al. (2021).

PAHs were also eventually quantified using a high performance liquid chromatograph (HPLC, Waters, USA) coupled to UV detection at 254 nm (Waters 2489 UV/Visible detector) and associated with a reversed phase Waters PAH C18 Column, S-5µm (4.6 mm i.d. · 250 mm length) for separation of PAHs and a binary pump (Waters 1525) for drawing two solvents together under high pressure (maximum limit: 5000 psi) creating a gradient. Injector port of the HPLC system was fitted to a 20 µL loop with a sample injection volume of 20 µL. Acetonitrile (ACN) and water of HPLC grades were used as mobile phases and the gradient elution was programmed at a flow rate of 1.5 mL min^{-1} as per the following protocol: 50% ACN for initial 5 min, then increased to 100% in 20 min and maintained for 28 min, again reduced to 50% within 32 min and held for 37 min (Waters Corporation, 2008). Column temperature was set at 30 C with a total run time of 37 min. The method as described above was based on the guidelines of EPA Method 550.1. Breeze^2 software was employed for data acquisition and processing. Retention times of the sample peaks were compared to that of the injected reference standards for recognizing the analytes of interest. A processing method was further developed for determination of concentrations of PAHs in test samples with respect to the certified standard mix (with 10 µg each mL^{-1} of 16 EPA-PAHs, such as naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DB[ah]A), indeno[1,2,3-cd]pyrene (IP) and benzo[g,h,i]perylene (B[ghi]P)).

Quality of the analytical results had been verified by assessing calibration standards, method blanks and spiked samples periodically during the study under similar experimental conditions. Absence of analytes in the blank samples was confirmed and replicate samples were also tested for method accuracy and validation. The mean recoveries of PAHs in spiked sample blanks varied between 78–99% and the minimum limits of detection and quantification for the analytical method ranged from 0.003–0.009 µg g^{-1} and 0.02–0.06 µg g^{-1} respectively.

Spatio-temporal variations of ambient PAHs: Quantitative estimation and diagnostic ratios (DRs) for characterization of sources

The spatial and temporal trends of PAHs uptake and accumulation were examined in plant leaves of various sampling locations in urban environment under distinct climatic conditions of premonsoon, postmonsoon and winter, depending on their concentrations, to assess the integrated exposure with time along with overall status of air quality.

Polluting sources of emitted PAHs in the ambient air of the urban sites were also differentiated by applying DRs (Ray et al., 2017; Tobiszewski and Namiesnik, 2012). DRs, such as Σ(low molecular weight PAHs)/Σ(high molecular weight PAHs) (i.e. ΣLMW/ΣHMW), ANT/(ANT + PHE), FLA/(FLA + PYR), BaA/(BaA + CHR), BbF/BkF, FLU/(FLU + PYR), BaP/BghiP and IP/(IP + BghiP) were evaluated in the present study as major emission source markers on the basis of their concentrations to investigate the origin of PAHs accumulated in the plant leaves. A complete experimental design is depicted in Fig. 1.

Results And Discussion

Comparison of extraction methods

Four distinct extraction methods were compared relating to ease of application, selectivity and extraction efficiency. The results of PAHs extraction acquired with different methods are indicated in Table 1. Both Soxhlet and MASE techniques outperformed sonication and mechanical stirring through the extraction of greater number of LMW and HMW PAHs based upon specific macroscopic and microscopic reasons. Mass transfer of PAHs from the solid plant matrix to the

extraction solvent is regulated by the mechanisms of convection and diffusion. Moreover, PAHs concentration difference between the leaf matrix and solvent is the driving force which controls the rate of extraction (Pinelo et al., 2006).

Soxhlet technique is a semi-batch process involving temperature acceleration (de Castro and Ayuso, 2000). Elevated temperature in Soxhlet extraction expedites the kinetics of mass transfer by increasing the solubility of solute in the solvent and hence improves the extraction efficiency. Besides, high temperature (a) reduces solvent density, viscosity and surface tension which assists in better solvent selectivity, wettability, diffusivity and penetrability for maintaining contact with the solid surface, (b) drastically alters the surface equilibrium by denaturing the analyte-analyte (cohesive) and analyte-matrix (adhesive) interactions owing to the reduction in activation energy of desorption, (c) enhances the solvation power of solvent and (d) allows analyte diffusion into the surface of the matrix along with the mass transfer of targeted solutes into the extracting solvent (Malik and Mandal, 2022). Thus, in Soxhlet method, complete extraction of desired PAHs was possible by virtue of multiple siphoning as the solvent could reach the active sites of the matrix more easily at high temperature and the rapid rate of diffusion promoted mass transfer of PAHs which, in turn, increased the extraction rate. Furthermore, a favourable PAHs concentration gradient (almost constant) was maintained via continuous recycling of fresh solvent through the matrix (with the aid of boiling and condensation) which prevented PAHs saturation in the extractant making the extraction process exhaustive in nature, enhanced the transfer equilibrium and eventually the mass transfer rate in Soxhlet technique (Malik and Mandal, 2022).

In MASE, application of electromagnetic energy (microwaves) to the sample matrix caused damage to the structure of cell membrane, thereby increasing the maximum release of PAHs into the solvent as in the case of Soxhlet. Homogeneous heating by ionic conduction and thermal agitation due to dipole rotation improved the diffusion of solvent into the sample and stimulated the partitioning of PAHs from the matrix to the extractant (Veggi et al., 2013). Induced heat in MASE caused evaporation of residual moisture present in the sample, creating appreciable intracellular pressure which ruptured the cell walls of the leaf matrix and enhanced the leaching of PAHs (Ngamkhae et al., 2022). Increased solubility of PAHs, solvent dispersion and selectivity because of high temperature also raised the extraction efficiency without degradation of analytes. Additionally, the unidirectional flow of heat and mass transfer to the outer side of the cells was responsible for high extraction yield along with reduction in process time and energy loss (Veggi et al., 2013).

Sonication technique transmits the sound energy of ultrasonic waves while propagating through the fluid mix, promoting high solvent inflow into plant matrix, intimate contact between them and rate of mass transfer of analytes. Wave propagation also causes frequent changes in the fluid density (compression and rarefaction) resulting in creation and rupture of vapour bubbles in quick succession (cavitation action) throughout the solvent. Bursting of such bubbles facilitated cell wall breakdown and simultaneous release of PAHs into the extraction solvent. Smith et al. (2006) reported that the ultrasonic-assisted extraction (UAE) is not very much effective for LMW PAHs as compared to Soxhlet and microwave-assisted extraction (MAE) owing to low recovery rates varying between 44–76%. In the present study also, recovery of LMW PAHs (NAP, ACY, ACE, FLU, PHE and ANT) through sonication was not satisfactory (only ACY and ACE could be detected (ref. Table 1)) due to, probably, the lower temperature range (25–35 C) of the process (Ngamkhae et al., 2022).

Mechanical stirring or agitation at room temperature (in a simple shake flask placed on a magnetic stirrer) is an easy extraction technique with low requirements for glassware. However, the stirring method could not efficiently extract the HMW PAHs and the extraction efficiency was appreciably lower than the other methods because of poor selectivity for PAHs, giving inappropriate results (Berset et al., 1999; Graham et al., 2006). Normally, faster extraction occurred initially when the difference in PAHs concentration was maximum. But, gradually, the extraction rate decelerated with the decrease in concentration difference, thereby causing a sharp decline in the rate of mass transfer. The extended extraction time did not further increase the yield once the saturation point was reached (Kalbe et al., 2008). Considerably higher rate of solvent evaporation was also witnessed in agitation extraction, leading to PAHs losses during evaporation.

The above-cited benefits rendered Soxhlet and MASE more effective over other techniques. Cicero et al. (2000) also obtained comparable recoveries in both the cases for the extraction of polychlorinated biphenyl (PCB) congeners from marine sediments. Highest extraction yield of bioactive compounds was again recorded by Ngamkhae et al. (2022) with MAE in contrast to UAE. A comparative study between MAE and UAE by Ratola et al. (2009) for PAHs extraction from pine needles and bark showed relatively same recovery results for the two methods. Hence, sonication might give better results with high extraction efficiency in some other species under optimized extraction conditions. Many studies have suggested high recoveries of PAHs from leaf matrices of various plant species (*Pinus sylvestris*, *Acer campestre*, *Pinus koraiensis*, *Cinnamomum camphora*

and *Phyllostachys edulis*) using Soxhlet extraction (Bi et al., 2018; Chun, 2011; Hubert et al., 2003; Yang et al., 2017). Therefore, in this study, all the other experiments were carried out with the Soxhlet technique.

But, considering the aforesaid advantages of MASE, design and optimization of its parameters is the future aim of the proposed work.

Table 1
GC-MS detection of PAHs in the plant samples: Comparison between extraction methods

	Retention time (min)/Quantification ion (m/z) of PAHs in the analytical standard mix*	Retention time (min)/Quantification ion (m/z) of identified PAHs in the leaf extracts**			
EPA-PAHs		Mechanical stirring	Sonication	Soxhlet extraction	MASE
NAP	6.23, 6.74/128	6.64/128.07	nd	6.89/128.60	nd
ACY	10.23/152	10.26/152.20	10.40/152.69	10.39/152.02	10.35/152.24
ACE	10.60/154	nd	10.80/154.51	10.76/154.07	10.66/154.43
FLU	12.89/166	12.77/166.40	nd	nd	nd
PHE	15.37/178	15.80/178.03	nd	15.17/178.44	15.52/178.61
ANT	15.37/178	15.80/178.03	nd	15.17/178.44	15.52/178.61
FLA	19.30/202	19.43/202.11	19.64/202.52	19.99/202.20	19.50/202.90
PYR	20.59/202	nd	20.45/202.85	20.65/202.52	20.71/202.43
BaA	24.96/228	nd	24.67/228.37	24.94/228.17	24.64/228.44
CHR	24.96/228	nd	24.67/228.37	24.94/228.17	24.64/228.44
BbF	28.37/252	28.89/252.12	28.38/252.54	28.30/252.65	28.51/252.41
BkF	28.37/252	28.89/252.12	28.38/252.54	28.30/252.65	28.51/252.41
BaP	29.69/252	29.86/252.41	29.48/252.38	nd	29.74/252.59
DB[ah]A	36.75/278	nd	36.82/278.52	36.74/278.39	36.43/278.65
IP	36.75/276	nd	36.82/276.29	36.74/276.37	36.43/276.57
B[ghi]P	38.89/276	nd	38.93/276.45	38.89/276.80	38.96/276.62
Total no. of extracted PAHs	16	9	12	14	14

* Reproduced from Mukhopadhyay et al. (2021) for the ease of comparison.

** Optimization studies done using the plant samples of JDV site only. For other experimental runs, optimized parameters were used.

'nd': Not detected.

Choice of best-suited solvent for PAHs extraction

Separation by solid-liquid extraction is greatly influenced by solvent selection, considering solubility, concentration and nature of analytes, capacity of solvents to penetrate and interact with the sample matrix, net polarities of solvents (correlated to their dipole moments, dielectric constant, viscosity, surface tension and cohesive energy density) and kinetic processes of mass transfer (Baskar et al., 2019). High solute distribution coefficient with minimized solvent losses plays a crucial role in solvent selection and solubility of solute is also mediated by the physicochemical properties and chemical structures of both the solute and solvent (Bonventre, 2014). Table 2 portrays the Soxhlet-based PAHs yields against the studied solvents and the observed trend was: total no. of PAHs extracted $_{\text{with acetone}}$ < total no. of PAHs extracted $_{\text{with acetone: n–hexane}}$ < total no. of PAHs extracted $_{\text{with DCM}}$ < total no. of PAHs extracted $_{\text{with n–hexane}}$ < total no. of PAHs extracted $_{\text{with toluene}}$.

Inefficiency of acetone to extract HMW PAHs is evident from Table 2. Similarly, analysis of the extracts obtained with DCM and acetone: n-hexane mixture specified the presence of mainly LMW PAHs and very few HMW PAHs (only BaP, DB[ah]A and IP). But, toluene and n-hexane showed higher selectivity by extracting maximum number of LMW and HMW PAHs from leaf samples. It can be clearly seen that the non-polar solvents were more suitable for the extraction of PAHs. For acetone: n-hexane mixture, although good PAHs recoveries have been reported in case of other solid matrices (Haleyur et al., 2016; Janska et al., 2004), yet, in the current study, lower extraction output was attained when compared with toluene and n-hexane separately. This could have resulted from the complexity of plant cell membrane composed of non-polar lipid tails restricting the transmembrane permeation of polar acetone molecules to a certain degree and hindering, thereby, the diffusion path of n-hexane through the plasma membrane for extraction of PAHs (Orsi et al., 2009; Shinoda, 2016). So, the above phenomenon had affected the extraction efficiency to a great extent. Least extraction capacity of acetone for non-polar PAHs can be ascribed to its high polarity as solvent extraction works on the basic principle of 'like dissolves like' (law of similarity and miscibility which states that a solute better dissolves in a solvent having close relative value of polarity) (Kamarudin et al., 2021) and impermeability of biological membrane with lipid bilayer limiting the free entry of highly polar molecules. DCM is a moderately polar solvent and thus, exhibited lower extraction recovery of hydrophobic PAHs. In addition, it is not recommended to be used as an extraction solvent on account of its volatility (boiling point: 39.6 C) which caused huge solvent loss in Soxhlet method. In contrast, toluene and n-hexane being most non-polar in nature (having low dipole moments), diffusion across the hydrophobic core of lipid bilayer enhanced the extraction performance. According to the results obtained (Table 2), toluene has been proved to be an ideal solvent which solvated almost all the lipophilic PAHs molecules of the matrix completely by means of dispersion interactions. Good relative yields of PAHs from the samples of tree

bark, pine needles and moss species with the application of toluene in Soxhlet technique were also documented by Birke et al. (2018) and Oishi et al. (2018). Alternatively, during dynamic sonication-assisted extraction of PAHs from lichen samples, toluene did not show adequate method efficiency implying the significances of the process and matrix properties on extraction yield (Domeno et al., 2006).

Table 2
Variation in PAHs recovery from plant leaves using different solvents in Soxhlet extraction based on GC-MS analysis

	Retention time (min)/Quantification ion (m/z) of identified PAHs extracted from leaf matrix with various solvents				
EPA-PAHs	Acetone	DCM*	n-Hexane	Toluene	Acetone: n-Hexane (1:1)
NAP	6.89/128.07	6.57/128.06	6.93/128.70	6.24/128.48	6.86/128.24
ACY	10.38/152.09	10.36/152.41	10.32/152.11	nd	nd
ACE	nd	10.54/154.11	10.62/154.49	10.63/154.36	nd
FLU	nd	12.82/166.56	nd	12.53/166.79	12.30/166.05
PHE	15.28/178.03	15.80/178.38	15.22/178.42	15.46/178.20	15.70/178.26
ANT	15.28/178.03	15.80/178.38	15.22/178.42	15.46/178.20	15.70/178.26
FLA	nd	19.43/202.33	19.81/202.72	19.85/202.34	19.40/202.06
PYR	20.64/202.06	nd	20.69/202.57	20.68/202.19	nd
BaA	24.87/228.25	nd	24.89/228.33	24.10/228.53	nd
CHR	24.87/228.25	nd	24.89/228.33	24.10/228.53	nd
BbF	nd	nd	28.53/252.68	28.28/252.89	nd
BkF	nd	nd	28.53/252.68	28.28/252.89	nd
BaP	nd	29.89/252.15	nd	29.35/252.92	29.41/252.12
DB[ah]A	nd	36.65/278.61	36.83/278.49	36.40/278.66	36.49/278.30
IP	nd	36.65/276.39	36.83/276.16	36.40/276.59	36.49/276.62
B[ghi]P	nd	nd	38.90/276.64	38.72/276.43	nd
Total no. of extracted PAHs	7	10	14	15	8
* DCM: Dichloromethane					

Effect of extraction time on PAHs yield

It is necessary to optimize the extraction period in order to protect the analytes, reduce energy consumption and cost of the process. So, duration of extraction demonstrated a strong impact on the effective recovery of PAHs from *Murraya* leaves. The performance of the extraction experiments at different time intervals employing toluene has been depicted in Table 3. The results revealed that the efficient extraction time (i.e. when equilibrium condition achieved between inside and outside of the solid matrix following convective mass transfer) for obtaining highest number of extracted PAHs was up to 6 h, beyond, which, the extraction efficacy reduced (ref. Table 3). Majority of LMW PAHs were not detected in 5 h of experimental run, probably due to the reason that the extraction equilibrium had not reached (i.e. persistence of a non-equilibrium state between the matrix and the solvent) at that time for all the analytes. Typically, exposure to longer extraction time disrupts plant cell membrane, enhancing the release as well as diffusion of PAHs into the solvent (Christou et al., 2021). However, extraction time exceeding the optimum value can lead to break down or conversion of target analytes owing to heat accumulation. Hence, temperature overshoot with the increase in time might have induced PAHs vapourization or thermal decomposition in the course of 7 h and 8 h of extractions and consequently lowered the recovery. Thus, 6 h of extraction was chosen as the optimum time for further considerations. Prolonged extraction periods were not examined as increase in time may not further affect the extraction process or may degrade or transform the analytes. Comparable extraction period has also been studied by Domeno et al. (2006) and Ray et al. (2021) using lower (*Xanthoria parietina*) and higher plant species (evergreen trees and shrubs) for PAHs determination via Soxhlet method respectively.

Table 3
GC-MS profiles of foliar PAHs obtained during varying time periods of extraction using Soxhlet technique

	Retention time (min)/Quantification ion (m/z) of identified PAHs in time course of extraction			
EPA-PAHs	5 h	6 h	7 h	8 h
NAP	6.65/128.05	6.59/128.21	6.62/128.08	6.61/128.08
ACY	10.46/152.13	nd	10.34/152.38	nd
ACE	nd	10.63/154.36	nd	nd
FLU	nd	12.53/166.79	nd	nd
PHE	nd	15.41/178.23	nd	nd
ANT	nd	15.41/178.23	nd	nd
FLA	nd	19.87/202.39	nd	nd
PYR	20.64/202.52	nd	20.90/202.16	20.75/202.24
BaA	nd	24.10/228.53	nd	nd
CHR	nd	24.10/228.53	nd	nd
BbF	28.82/252.14	28.16/252.77	28.22/252.96	28.21/252.57
BkF	28.82/252.14	28.16/252.77	28.22/252.96	28.21/252.57
BaP	29.69/252.28	29.52/252.81	29.69/252.98	29.67/252.99
DB[ah]A	36.53/278.30	36.40/278.66	36.72/278.30	36.60/278.53
IP	36.53/276.04	36.40/276.59	36.72/276.81	36.60/276.56
B[ghi]P	nd	38.77/276.46	nd	nd
Total no. of extracted PAHs	8	14	8	7

PAHs diffusion in plant leaves: Spatio-temporal variability in pollutant concentrations and their emission sources

Identification of air pollution hotspots by assessing spatial and temporal variations of pollutant concentrations is obligatory for enforcing control actions to reduce elevated risks of negative health impacts. Atmospheric concentration, transport and dispersion of PAHs, weather events, air/plant partitioning and uptake dynamics of PAHs in the plant leaves influence their content in tree foliage (De Nicola et al., 2005). Plant leaves can very well be considered as passive air samplers (or biomonitors) having keen propensity for differentiating even small-scale heterogeneity in the levels of urban air pollution (De Nicola et al., 2011). Table 4 illustrates the site- and season-specific leaf PAHs concentrations in the urban locations. The temporal variabilities observed in the total concentration of foliar PAHs (TPAHs in μg g^{-1} d.w.) among the four study points can be described in the order of: $TPAHs_{winter}$ (278.42 ± 3.02–550.79 ± 10.11) > $TPAHs_{postmonsoon}$ (210.52 ± 12.78–401.83 ± 13.61) > $TPAHs_{premonsoon}$ (200.98 ± 2.72–329.17 ± 4.03). Air quality downfall as evidenced in winter months (having highest values of TPAHs) is mostly associated with air stagnation leading to clean, stable and tranquil atmosphere, restricted circulation of air masses (i.e. poor vertical mixing and horizontal dispersion) due to low velocity of the prevailing winds and night-time temperature inversion (Grundstrom et al., 2015). Non-detection of some of the HMW PAHs during winter in some sites (viz. BaP, DB[ah]A and IP at JDV; BaP at RBC and FLA at TGN) might be due to their reaction with the atmospheric oxidants under stable atmospheric stratification, generating secondary pollutants or polar PAHs derivatives (nitrated/oxygenated congeners: NPAHs/OPAHs) (Bandowe and Meusel, 2017). Percentage composition (varying between 59.01–87.44%) of 2-, 3- and 4- ring PAHs, namely NAP, ACY, ACE, FLU, PHE, ANT, FLA, PYR, BaA and CHR, revealed their dominance during premonsoon study of the selected sites. This can be attributed to the conversion of above-stated PAHs into gaseous phases from particulate state in presence of high temperature, enabling their easy permeation into the leaf tissues (internal diffusion by gas-phase transfer), whereas, lower levels of accumulated 5- and 6-ring PAHs may be credited to their photochemical degradation under the same condition (Ambade et al., 2022) which led to an overall decline in TPAHs with respect to other seasons. Contrary to premonsoon, moderate temperature, relatively stable, dry and clear weather in postmonsoon period may be accountable for greater accumulation of PAHs (4.75–23.45% higher TPAHs) in *Murraya* leaves. The current findings are in line with the conclusions drawn by De Nicola et al. (2005), Prajapati and Tripathi (2008), Ray et al. (2021) and Yang et al. (2017).

The spatial differences in the levels of PAHs were significantly affected by the type and intensity of local human impacts, commercial operations and traffic emissions. Therefore, the source profiles were classified in the current study through the use of distinctive characteristic ratios of PAHs (or molecular DRs: concentration ratios of particular PAHs of same molar masses and inherent properties) for minimizing uncertainties. The estimated values of DRs analysed for discerning the heterogeneous sources of PAHs pollution in the sampling sites on seasonal basis are presented in Table 5. It may be inferred that the seasonal variability of emission sources at the sampling areas of South Kolkata had not been found to be very much prominent. ΣLMW/ΣHMW and ANT/(ANT + PHE) ratios are usually employed to distinguish between the pyrogenic and petrogenic sources of PAHs (Pies et al., 2008; Zhang et al., 2008). As shown in Table 5, ΣLMW/ΣHMW < 1 and ANT/(ANT + PHE) > 0.1 are indicative of coal, wood and biomass combustion as well as automobile exhausts (pyrogenic origin) emitting PAHs into the atmosphere for all the sites. Moreover, FLA, PYR, BaA, CHR, BbF, BkF, BaP, IP and B[ghi]P are categorized as combustion-derived PAHs (Bucheli et al., 2004; Hwang et al., 2003). Foliar concentrations (Table 4) of ACY, FLU, PHE, ANT, FLA, PYR, CHR and BkF in the sites again pointed to the release of PAHs from fly ash of open biomass and coal burning (Kakareka and Kukharchyk, 2003; Larsen and Baker, 2003; Lee et al.,

2005), while, in case of TGN site, ΣLMW/ΣHMW > 1 during premonsoon suggested the predominance of petrogenic origin of emission. It is noteworthy that the presence of 4-, 5- and 6- ring PAHs including BaA, CHR, BbF, BkF, BaP, IP and B[ghi]P is a strong indicator of emission from petrol combustion (Dzepina et al., 2007; Ho et al., 2009; Larsen and Baker, 2003; Yunker et al., 2002). The measured DR values for FLA/(FLA + PYR), BaA/(BaA + CHR), BbF/BkF, FLU/(FLU + PYR) and BaP/BghiP had also demonstrated majorly transport-related emissions (from petrol/diesel) and presumed to be the sources for PAHs absorption by the leaves at the study sites. Highest accumulation of TPAHs (μg g^{-1} d.w.) at EXM (329.17 ± 4.03–550.79 ± 10.11) than RBC (296.46 ± 15.52–406.14 ± 9.38), JDV (299.03 ± 15.18–388.64 ± 3.94) and TGN (200.98 ± 2.72–278.42 ± 3.02) (ref. Table 4) in all the seasons may be primarily accredited to the huge vehicular emissions at the point of traffic intersection due to movement/idling of vehicles on the congested roadways. However, at RBC, effects of non-exhaust traffic emissions in premonsoon (BaP/BghiP < 0.6) (such as resuspension of dust particulates from road pavements, construction activities, tyres and brakes, burning of solid fuels and street cafes or restaurants) and contribution from fossil fuel combustion in both pre- and post- monsoon (FLA/(FLA + PYR)≈0.4–0.5) were recognized as well (De La Torre-Roche, et al., 2009; Katsoyiannis et al., 2007). FLA/(FLA + PYR) > 0.5 at TGN signified PAHs outflow from biomass burning during premonsoon together with vehicular activities (De La Torre-Roche, et al., 2009). IP/(IP + BghiP) > 0.5 at JDV and TGN reflected mixed origin of PAHs liberated from coal or biomass burning and cooking fume emissions from chimneys of roadside restaurants (Chen et al., 2015). The maximum variation of seasonal concentrations (μg g^{-1} d.w.) (ref. Table 4) of BaP (29.47 ± 1.99–30.92 ± 0.69) and DB[ah]A (59.64 ± 2.88–62.81 ± 1.54) at JDV confirmed the sources of oil-based cooking (grilling, smoking, frying, barbecuing, roasting, etc.) in several wayside food stalls or commercial kitchens, corroborating the above inference. Observed concentrations of DB[ah]A at EXM and TGN (Table 4) also represented the influences of cooking processes on the outdoor environment. Mainly at RBC and EXM with IP/(IP + BghiP) lying between 0.2–0.5, petroleum-related PAHs pollution was observed to be widespread. Prevalence of lighter and heavier PAHs (NAP, ACY, FLU, PHE, PYR, BaA, CHR and BghiP) in high and low levels in every site is a pointer towards combustion of petroleum products and exposure to cooking oil smoke (Masih et al., 2012). Occurrence of ACE in the leaf samples due to coal combustion and diesel exhausts was recorded, but in low concentration (6.77 ± 0.21–25.32 ± 2.29 μg g^{-1} d.w.) owing to its short half-life and high susceptibility for biodegradation (Chanda and Mehendale, 2005).

Table 4

Locational and seasonal variations in total and individual concentrations (μg g^{-1} d.w.) of PAHs measured in *Murraya paniculata*

	Foliar PAHs concentrations									
	JDV			RBC			EXM			TGN
EPA-PAHs	Premonsoon	Postmonsoon	Winter	Premonsoon	Postmonsoon	Winter	Premonsoon	Postmonsoon	Winter	Premo
NAP	15.24 ± 2.38	*19.75 ± 0.59*	27.08 ± 0.49	20.42 ± 2.31	21.55 ± 1.64	24.16 ± 1.70	43.61 ± 3.45	45.66 ± 1.35	39.22 ± 1.27	9.97 ±
ACY	nd	9.56 ± 0.67	11.28 ± 1.56	nd	14.17 ± 1.33	12.30 ± 1.79	nd	53.29 ± 1.79	55.62 ± 2.47	5.63 ±
ACE	25.32 ± 2.29	nd	7.29 ± 0.28	9.72 ± 1.37	nd	11.86 ± 0.37	nd	6.77 ± 0.21	8.11 ± 1.87	8.98 ±
FLU	7.74 ± 1.76	nd	7.78 ± 0.52	9.80 ± 3.47	10.49 ± 1.43	5.82 ± 0.11	13.80 ± 2.73	11.32 ± 0.66	7.67 ± 1.72	10.56
PHE	23.40 ± 4.33	18.89 ± 0.71	18.44 ± 0.30	13.63 ± 2.07	15.85 ± 1.79	17.27 ± 0.66	12.91 ± 1.63	nd	21.32 ± 1.57	28.62
ANT	16.44 ± 2.94	43.70 ± 1.62	69.11 ± 3.10	39.02 ± 1.45	41.58 ± 1.46	42.83 ± 1.35	26.29 ± 2.46	nd	34.56 ± 2.99	37.84
FLA	nd	39.88 ± 1.37	23.10 ± 0.34	40.73 ± 2.27	46.91 ± 2.33	59.52 ± 2.50	nd	57.88 ± 2.49	70.26 ± 3.78	44.52
PYR	7.93 ± 2.26	32.20 ± 0.89	51.25 ± 2.79	41.52 ± 3.14	55.27 ± 2.69	63.09 ± 2.19	59.66 ± 2.67	nd	75.01 ± 3.89	11.92
BaA	48.50 ± 3.76	nd	81.20 ± 2.96	33.54 ± 1.75	37.67 ± 1.87	50.22 ± 1.81	65.39 ± 3.51	78.17 ± 2.61	86.95 ± 2.81	nd
CHR	31.90 ± 1.68	nd	48.61 ± 1.65	50.83 ± 2.17	50.97 ± 2.41	52.19 ± 2.07	29.59 ± 3.45	58.30 ± 0.88	64.61 ± 3.13	nd
BbF	nd	14.57 ± 1.25	11.60 ± 1.34	nd	24.30 ± 1.32	25.70 ± 1.05	21.96 ± 1.48	22.84 ± 0.51	33.42 ± 4.49	nd
BkF	10.76 ± 2.63	22.37 ± 0.69	25.76 ± 0.94	nd	23.81 ± 1.82	16.46 ± 1.35	19.12 ± 1.97	15.48 ± 0.68	18.36 ± 2.23	nd
BaP	29.47 ± 1.99	30.92 ± 0.69	nd	2.52 ± 0.35	13.22 ± 0.83	nd	2.82 ± 0.53	4.65 ± 0.28	9.73 ± 0.75	3.64 ±
DB[ah]A	59.64 ± 2.88	62.81 ± 1.54	nd	16.32 ± 1.44	8.26 ± 0.65	9.42 ± 0.44	31.08 ± 2.21	36.71 ± 1.72	13.59 ± 1.95	23.16
IP	22.69 ± 3.66	17.53 ± 0.52	nd	nd	1.93 ± 0.10	5.18 ± 0.15	2.94 ± 0.29	3.31 ± 0.52	4.37 ± 0.58	13.43
B[ghi]P	nd	3.49 ± 0.24	6.14 ± 0.82	18.41 ± 1.92	nd	10.12 ± 1.01	nd	7.45 ± 0.47	7.99 ± 2.04	2.71 ±
Total PAHs concentration	299.03 ± 15.18	315.67 ± 10.33	388.64 ± 3.94	296.46 ± 15.52	365.98 ± 17.46	406.14 ± 9.38	329.17 ± 4.03	401.83 ± 13.61	550.79 ± 10.11	200.9 2.72

Concentration values expressed as (mean ± S.D.)

Table 5
Molecular DRs with their obtained values (as mean ± S.D.) for identification of foliar PAHs origin in the sampling sites

	DRs for the plant leaves of urban areas												
PAHs ratio	Seasons	JDV			RBC			EXM			TGN		
		Value	Range	Source	Value	Range	Source	Value	Range	Source	Value	Range	Sc
ΣLMW/ ΣHMW	Premonsoon	0.42 ± 0.03	< 1	Pyrogenic	0.45 ± 0.01	< 1	Pyrogenic	0.42 ± 0.01	< 1	Pyrogenic	1.02 ± 0.26	> 1	Pe
	Postmonsoon	0.41 ± 0.01	< 1	Pyrogenic	0.40 ± 0.01	< 1	Pyrogenic	0.41 ± 0.00	< 1	Pyrogenic	0.55 ± 0.00	< 1	Py
	Winter	0.57 ± 0.02	< 1	Pyrogenic	0.39 ± 0.01	< 1	Pyrogenic	0.43 ± 0.01	< 1	Pyrogenic	0.63 ± 0.01	< 1	Py
ANT/(ANT + PHE)	Premonsoon	0.41 ± 0.01	> 0.1	Pyrogenic	0.74 ± 0.02	> 0.1	Pyrogenic	0.67 ± 0.01	> 0.1	Pyrogenic	0.57 ± 0.01	> 0.1	Py
	Postmonsoon	0.70 ± 0.00	> 0.1	Pyrogenic	0.72 ± 0.03	> 0.1	Pyrogenic				0.43 ± 0.01	> 0.1	Py
	Winter	0.79 ± 0.01	> 0.1	Pyrogenic	0.71 ± 0.01	> 0.1	Pyrogenic	0.62 ± 0.01	> 0.1	Pyrogenic	0.43 ± 0.05	> 0.1	Py
FLA/(FLA + PYR)	Premonsoon				0.50 ± 0.01	0.4–0.5	Fossil fuel combustion				0.79 ± 0.06	> 0.5	Gr wo bu ar en
	Postmonsoon	0.55 ± 0.01	> 0.5	Diesel emission	0.50 ± 0.03	0.4–0.5	Fossil fuel combustion				0.72 ± 0.00	> 0.5	
	Winter	0.31 ± 0.01	< 0.5	Petrol emission	0.49 ± 0.01	< 0.5	Petrol emission	0.48 ± 0.03	< 0.5	Petrol emission			
BaA/(BaA + CHR)	Premonsoon	0.60 ± 0.01	> 0.35	Vehicular emission or combustion	0.40 ± 0.00	> 0.35	Vehicular emission or combustion	0.69 ± 0.04	> 0.35	Vehicular emission or combustion			
	Postmonsoon				0.43 ± 0.01	> 0.35		0.57 ± 0.01	> 0.35				
	Winter	0.63 ± 0.02	> 0.35	Vehicular emission or combustion	0.49 ± 0.02	> 0.35		0.57 ± 0.02	> 0.35		0.41 ± 0.01	> 0.35	Ve en co
BbF/BkF	Premonsoon							1.15 ± 0.17	> 0.5	Diesel emission			
	Postmonsoon	0.65 ± 0.04	> 0.5	Diesel emission	1.02 ± 0.02	> 0.5	Diesel emission	1.48 ± 0.04	> 0.5	Diesel emission	1.65 ± 0.02	> 0.5	Di en
	Winter	0.45 ± 0.04	na	na	1.56 ± 0.17	> 0.5	Diesel emission	1.82 ± 0.03	> 0.5	Diesel emission	2.61 ± 0.06	> 0.5	Di en
FLU/(FLU + PYR)	Premonsoon	0.49 ± 0.01	< 0.5	Petrol emission	0.19 ± 0.04	< 0.5	Petrol emission	0.19 ± 0.02	< 0.5	Petrol emission	0.47 ± 0.18	< 0.5	Pe en
	Postmonsoon				0.16 ± 0.01	< 0.5	Petrol emission						
	Winter	0.13 ± 0.01	< 0.5	Petrol emission	0.08 ± 0.00	< 0.5	Petrol emission	0.09 ± 0.02	< 0.5	Petrol emission	0.35 ± 0.08	< 0.5	Pe en

Range and sources referred from: Akyuz and Cabuk, 2010; Katsoyiannis et al., 2007; Park et al., 2002; Pies et al., 2008; Ravindra et al., 2008$_a$; Ravindra et al., 2
Shukla et al., 2022; Yunker et al., 2002; Zhang et al., 2008.

Note: ‘ ’ stands for paucity of data due to non-detection of specific PAHs of the binary ratios during concentration analysis.

‘na’: Not available

	DRs for the plant leaves of urban areas												
BaP/BghiP	Premonsoon				0.14 ± 0.03	< 0.6	Non-traffic emission				1.34 ± 0.54	> 0.6	Ro en
	Postmonsoon	8.86 ± 0.88	> 0.6	Road traffic emission				0.62 ± 0.07	> 0.6	Road traffic emission			
	Winter							1.22 ± 0.63	> 0.6	Road traffic emission	4.35 ± 0.05	> 0.6	Ro en
IP/(IP + BghiP)	Premonsoon										0.83 ± 0.01	> 0.5	Bi bu co co ar ea
	Postmonsoon	0.83 ± 0.01	> 0.5	Biomass burning, coal combustion and eateries				0.31 ± 0.01	0.2–0.5	Combustion of petroleum fuel			
	Winter				0.34 ± 0.01	0.2–0.5	Combustion of petroleum fuel	0.35 ± 0.11	0.2–0.5		0.79 ± 0.04	> 0.5	Bi bu co co ar ea
Range and sources referred from: Akyuz and Cabuk, 2010; Katsoyiannis et al., 2007; Park et al., 2002; Pies et al., 2008; Ravindra et al., 2008$_a$; Ravindra et al., 2 Shukla et al., 2022; Yunker et al., 2002; Zhang et al., 2008.													
Note: ‘ ’ stands for paucity of data due to non-detection of specific PAHs of the binary ratios during concentration analysis.													
‘na’: Not available													

Conclusion

Accurate determination of PAHs in bio-matrices for air pollution monitoring using comprehensive extraction and analytical approaches is of great relevance. Among the methods considered, Soxhlet and MASE exhibited high efficiencies of PAHs extraction from the leaves of an evergreen species *Murraya paniculata* exposed to traffic hotspots. Soxhlet extraction with toluene ensured high selectivity and yielded maximum number of non-polar parent PAHs. The optimized extraction time of 6 h can certainly be claimed as the equilibration time for PAHs.

Plant uptake of pollutants primarily depends on the fluctuations in environmental, ecological and meteorological factors. Leaf PAHs concentrations (200.98 ± 2.72–550.79 ± 10.11 μg g^{-1} d.w.) and spatial/temporal distribution pattern noticed in different sites seemed to be directly dependent on site-specific characteristics or sources. Based on seasonality, extent of leaf contamination by PAHs was extreme in winter followed by postmonsoon and then premonsoon, the fate of pollutants being controlled by air movement, temperature, partition coefficient and boundary layer or mixing height. The isomer pair ratios (DRs) exemplified the substantial effects of pyrogenic sources of PAHs in all the sites (e.g. ΣLMW/ΣHMW < 1 and ANT/(ANT + PHE) > 0.1) and vehicular pollution and cooking exhausts were found to be the leading causes of deteriorating air quality apart from combustion of solid/liquid fuels and biomass. Atmospheric condition-mediated degradation of PAHs affects proper identification/analysis of polluting sources; hence, multiple DRs have been worked upon to decipher the type of emission. Thus, green belting in the vicinity of severely polluted areas using biomonitor plants such as *M. paniculata* is strongly advised for curbing the hazardous effects of air pollution and reinforcing sustainable practices for ecosystem vitality, human health and well-being. In this context, development of process intensified routes for destructive extraction of PAHs, biomarker (morphological/biochemical/chemical) assessment for screening of plant species for biomonitoring purposes in order to conserve, restore and govern the functions of ecosystem and evaluation of factors effecting bioaccumulation of PAHs would be the future scope of our research.

Declarations

The authors declare no competing interests.

Acknowledgement

The authors gratefully recognize the assistance received from the Department of Chemical Engineering of Jadavpur University, Kolkata, India, for conducting the research work successfully.

Author Contribution Details

Ratna Dutta (Corresponding author); Email:*paul.ratna@gmail.com,*

Assistant professor

Department of Chemical Engineering,

Jadavpur University, Jadavpur, Kolkata-700032, India.

Contribution: She has guided and reviewed (& checked) the manuscript.

Shritama Mukhopadhyay (First author); Email: *mukhopadhyayshritama@gmail.com*

Research Scholar

Department of Chemical Engineering,

Jadavpur University, Jadavpur, Kolkata-700032, India.

Contribution: She has done the major part of the work andhas written the main manuscript.

Aparna Dhara (Second author); Email:*dharaannuju@gmail.com*

M.Tech. Student

Department of Chemical Engineering,

Jadavpur University, Jadavpur, Kolkata-700032, India.

Contribution: She has done a part of work and has written some part of the manuscript and references.

Papita Das (Third author) *papitasaha@gmail.com*

Professor

Department of Chemical Engineering,

Jadavpur University, Jadavpur, Kolkata-700032, India.

Contribution: She has checked the whole manuscript.

Funding declaration

The work presented in the article is not supported by any funding agency which needs to be acknowledged. I declare that the authors have no competing interests as defined by Springer, or other interests that might be perceived to influence the results and/or discussion reported in this paper.

Data availability statement

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request. All of the material is owned by the authors and/or no permissions are required

References

1. Akyuz, M., & Çabuk, H. (2010). Gaseparticle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey. Science of The Total Environment, *408*(22), 5550–5558. https://doi.org/10.1016/j.scitotenv.2010.07.063
2. Ambade, B., Kumar, A., Kumar, A., & Sahu, L. K. (2022). Temporal variability of atmospheric particulate–bound polycyclic aromatic hydrocarbons (PAHs) over central east India: sources and carcinogenic risk assessment. Air Quality, Atmosphere & Health, *15*, 115–130. https://doi.org/10.1007/s11869-021-01089-5
3. Bandowe, B. A. M., & Meusel, H. (2017). Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) in the environment – A review, Science of The Total Environment, *581–582*, 237–257. https://doi.org/10.1016/j.scitotenv.2016.12.115
4. Barreca, S., Mazzola, A., Orecchio, S., & Tuzzolino, N. (2014). Polychlorinated biphenyls in sediments from Sicilian coastal area (Scoglitti) using automated soxhlet, GCMS, and principal component analysis. Polycyclic Aromatic Compounds, *34*(3), 237–262. https://doi.org/10.1080/10406638.2014.886078
5. Baskar, G., Kalavathy, G., Aiswarya, R., & Selvakumari, I. A. (2019). Advances in bio-oil extraction from nonedible oil seeds and algal biomass. In: Azad, K. (Ed.), Advances in Eco-Fuels for a Sustainable Environment, Woodhead Publishing, pp. 187–210.
6. Benson, N. U., Fred-Ahmadu, O. H., Olugbuyiro, J. A. O., Anake, W. U., Adedapo, A. E., & Olajire, A. A. (2018). Concentrations, sources and risk characterisation of polycyclic aromatic hydrocarbons (PAHs) in green, herbal and black tea products in Nigeria. Journal of Food Composition and Analysis, *66*, 13–22. https://doi.org/10.1016/j.jfca.2017.11.003
7. Berset, J. D., Ejem, M., Holzer, R., & Lischer, P. (1999). Comparison of different drying, extraction and detection techniques for the determination of priority polycyclic aromatic hydrocarbons in background contaminated soil samples. Analytica Chimica Acta, *383*(3), 263–275. https://doi.org/10.1016/S0003-

2670(98)00817-4

8. Bidleman, T. E., & Leone, A. (2004). Soil-air relationships for toxaphene in the southern United States. Environmetal Toxicology and Chemistry, *23*(10), 2337–2342. https://doi.org/10.1897/03-405
9. Birke, M., Rauch, U., & Hofmann, F. (2018). Tree bark as a bioindicator of air pollution in the city of Stassfurt, Saxony-Anhalt, Germany. Journal of Geochemical Exploration, *187*, 97–117. https://doi.org/10.1016/j.gexplo.2017.09.007
10. Bi, Y. F., Guo, F. Y., Yang, L., Zhong, H., Wang, A. K., Wang, Y. K., Wu, Z. Z., & Du, X. H. (2018). *Phyllostachys edulis* forest reduces atmospheric $PM_{2.5}$ and PAHs on hazy days at suburban area. Scientific Reports, *8*(12591), 1–11. https://doi.org/10.1038/s41598-018-30298-9
11. Blasco, M., Domeno, C., Bentayeb, K., & Nerin, C. (2007). Solid-phase extraction clean-up procedure for the analysis of PAHs in lichens. International Journal of Environmental Analytical Chemistry, *87*(12), 833–846. https://doi.org/10.1080/03067310701381615
12. Bonventre, J. A. (2014). Solvents. In: Wexler, P. (Ed.), Encyclopedia of Toxicology (Third Edition), Academic Press, pp. 356–357.
13. Bostrom, C. E., Gerde, P., Hanberg, A., Jernstrom, B., Johansson, C., Kyrklund, T., Rannug, A., Tornqvist, M., Victorin, K., & Westerholm, R. (2002). Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. Environmental Health Perspectives, *110*(Suppl 3), 451–88. https://doi.org/10.1289/ehp.110-1241197
14. Bucheli, T. D., Blum, F., Desaules, A., & Gustafsson, O. (2004). Polycyclic aromatic hydrocarbons, black carbon, and molecular markers in soils of Switzerland. Chemosphere, *56*(11), 1061–1076. https://doi.org/10.1016/j.chemosphere.2004.06.002
15. Capozzi, F., Giordano, S., Aboal, J. R., Adamo, P., Bargagli, R., Boquete, T., Di Palma, A., Real, C., Reski, R., Spagnuolo, V., Steinbauer, K., Tretiach, M., Varela, Z., Zechmeister, H., & Fernandez, J. A. (2016). Best options for the exposure of traditional and innovative moss bags: a systematic evaluation in three European countries. Environmental Pollution, *214*, 362–373. https://doi.org/10.1016/j.envpol.2016.04.043
16. Chanda, S., & Mehendale, H. M. (2005). Acenaphthene. In: Wexler, P. (Ed.), Encyclopedia of Toxicology, Academic Press, pp. 11–13.
17. Chen, P., Kang, S., Li, C., Rupakheti, M., Yan, F., Li, Q., Ji, Z., Zhang, Q., Luo, W., & Sillanpaa, M. (2015). Characteristics and sources of polycyclic aromatic hydrocarbons in atmospheric aerosols in the Kathmandu Valley, Nepal. Science of The Total Environment, *538*, 86–92. https://doi.org/10.1016/j.scitotenv.2015.08.006
18. Christou, A., Stavrou, I. J., & Kapnissi-Christodoulou, C. P. (2021). Continuous and pulsed ultrasound-assisted extraction of carob's antioxidants: Processing parameters optimization and identification of polyphenolic composition. Ultrasonics Sonochemistry, *76*, 105630. https://doi.org/10.1016/j.ultsonch.2021.105630
19. Chun, M. Y. (2011). Relationship between PAHs concentrations in ambient air and deposited on Pine needles. Environmental Health and Toxicology, *26*(e2011004), 1–6. https://doi.org/10.5620/eht.2011.26.e2011004
20. Cicero, A. M., Pietrantonio, E., Romanelli, G., & Di Muccio, A. (2000). Comparison of Soxhlet, shaking, and microwave assisted extraction techniques for determination of PCB congeners in a marine sediment. Bulletin of Environmental Contamination and Toxicology, *65*(3), 307–313. https://doi.org/10.1007/s0012800129
21. de Castro, M. D. L., & Ayuso, L. E. G. (2000). Environmental Applications | Soxhlet Extraction. In: Wilson, I.D. (Ed.), Encyclopedia of Separation Science, Academic Press, pp. 2701–2709.
22. Delacour, C., Lutz, C., & Kuhn, S. (2019). Pulsed ultrasound for temperature control and clogging prevention in micro-reactors. Ultrasonics Sonochemistry, *55*, 67–74. https://doi.org/10.1016/j.ultsonch.2019.03.012
23. De La Torre-Roche, R. J., Lee, W. -Y., & Campos-Diaz, S. I. (2009). Soil-borne polycyclic aromatic hydrocarbons in El Paso, Texas: analysis of a potential problem in the United States/Mexico border region. Journal of Hazardous Materials, *163*(2–3), 946–958. https://doi.org/10.1016/j.jhazmat.2008.07.089
24. De Nicola, F., Claudia, L., MariaVittoria, P., Giulia, M., & Anna, A. (2011). Biomonitoring of PAHs by using Quercus ilex leaves: source diagnostic and toxicity assessment. Atmospheric Environment, *45*(7), 1428–1433. https://doi.org/10.1016/j.atmosenv.2010.12.022
25. De Nicola, F., Grana, E. C., Aboal, J. R., Carballeira, A., Fernandez, J. A., Mahia, P. L., Rodriguez, D. P., & Lorenzo, S. M. (2016). PAH detection in *Quercus robur* leaves and *Pinus pinaster* needles: a fast method for biomonitoring purpose. Talanta, *153*, 130–137. https://doi.org/10.1016/j.talanta.2016.01.067
26. De Nicola, F., Maisto, G., Prati, M. V., & Alfani, A. (2008). Leaf accumulation of trace elements and polycyclic aromatic hydrocarbons (PAHs) in *Quercus ilex* L. *Environmental Pollution*, *153*(2), 376–383. https://doi.org/10.1016/j.envpol.2007.08.008
27. De Nicola, F., Maisto, G., Prati, M. V., & Alfani, A. (2005). Temporal variations in PAH concentrations in *Quercus ilex* L. (holm oak) leaves in an urban area. Chemosphere, *61*(3), 432–440. https://doi.org/10.1016/j.chemosphere.2005.01.082
28. Domeno, C., Blasco, M., Sanchez, C., & Nerin, C. (2006). A fast extraction technique for extracting polycyclic aromatic hydrocarbons (PAHs) from lichens samples used as biomonitors of air pollution: dynamic sonication versus other methods. Analytica Chimica Acta, *569*(1–2), 103–112. https://doi.org/10.1016/j.aca.2006.03.053
29. Domeno, C., Canellas, E., Alfaro, P., Rodriguez-Lafuente, A., & Nerin, C. (2012). Atmospheric pressure gas chromatography with quadrupole time of flight mass spectrometry for simultaneous detection and quantification of polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons in mosses. Journal of Chromatography A, *1252*, 146–154. https://doi.org/10.1016/j.chroma.2012.06.061
30. Dzepina, K., Arey, J., Marr, L. C., Worsnop, D. R., Salcedo, D., Zhang, Q., Onasch, T. B., Molina, L. T., Molina, M. J., & Jimenez, J. L. (2007). Detection of particle-phase polycyclic aromatic hydrocarbons in Mexico City using an aerosol mass spectrometer. International Journal of Mass Spectrometry, *263*(2–3), 152–170. https://doi.org/10.1016/j.ijms.2007.01.010
31. Fazeli, F., Ardabili, S. M. S., Piravivanak, Z., Honarvar, M., & Mooraki, N. (2020). Optimization of extraction conditions for polycyclic aromatic hydrocarbons determination in smoked rice using the high performance liquid chromatography-fluorescence detection. Journal of Food Measurement and Characterization, *14*, 1236–1248. https://doi.org/10.1007/s11694-020-00372-w

32. Foan, L., & Simon, V. (2012). Optimization of pressurized liquid extraction using a multivariate chemometric approach and comparison of solid-phase extraction cleanup steps for the determination of polycyclic aromatic hydrocarbons in mosses. Journal of Chromatography A, *1256*, 22–31. https://doi.org/10.1016/j.chroma.2012.07.065
33. Frempong, T. F., Boadi, N. O., & Badu, M. (2021). Optimization of extraction conditions for polyphenols from the stem bark of *Funtumia elastica* (Funtum) utilizing response surface methodology. AAS Open Research, *4*(46), 1–23. https://doi.org/10.12688/aasopenres.13284.2
34. Gerssen, A., McElhinney, M. A., Mulder, P. P. J., Bire, R., Hess, P., & de Boer, J. (2009). Solid phase extraction for removal of matrix effects in lipophilic marine toxin analysis by liquid chromatography-tandem mass spectrometry. Analytical and Bioanalytical Chemistry, *394*, 1213–1226. https://doi.org/10.1007/s00216-009-2790-0
35. Graham, M. C., Allan, R., Fallick, A. E., & Farmer, J. G. (2006). Investigation of extraction and clean-up procedures used in the quantification and stable isotopic characterisation of PAHs in contaminated urban soils. Science of The Total Environment, *360*(1–3), 81–89. https://doi.org/10.1016/j.scitotenv.2005.08.026
36. Grundstrom, M., Tang, L., Hallquist, M., Nguyen, H., Chen, D., & Pleijel, H. (2015). Influence of atmospheric circulation patterns on urban air quality during the winter. Atmospheric Pollution Research, *6*(2), 278–285. https://doi.org/10.5094/APR.2015.032
37. Haleyur, N., Shahsavari, E., Mansur, A. A., Koshlaf, E., Morrison, P. D., Osborn, A. M., & Ball, A. S. (2016). Comparison of rapid solvent extraction systems for the GC–MS/MS characterization of polycyclic aromatic hydrocarbons in aged, contaminated soil. MethodsX, *3*, 364–370. https://doi.org/10.1016/j.mex.2016.04.007
38. Herbert, P., Silva, A. L., Joao, M. J., Santos, L., & Alves, A. (2006). Determination of semi-volatile priority pollutants in landfill leachates and sediments using microwave-assisted headspace solid-phase microextraction. Analytical and Bioanalytical Chemistry, *386*, 324–331. https://doi.org/10.1007/s00216-006-0632-x
39. Herrera-Pool, E., Ramos-Diaz, A. L., Lizardi-Jimenez, M. A., Pech-Cohuo, S., Ayora-Talavera, T., Cuevas-Bernardino, J. C., Garcia-Cruz, U., & Pacheco, N. (2021). Effect of solvent polarity on the Ultrasound Assisted extraction and antioxidant activity of phenolic compounds from habanero pepper leaves (*Capsicum chinense*) and its identification by UPLC-PDA-ESI-MS/MS. Ultrasonics Sonochemistry, *76*, 105658. https://doi.org/10.1016/j.ultsonch.2021.105658
40. Ho, K. F., Ho, S. S. H., Lee, S. C., Cheng, Y., Chow, J. C., Watson, J. G., Louie, P. K. K., & Tian, L. (2009). Emissions of gas- and particle-phase polycyclic aromatic hydrocarbons (PAHs) in the Shing Mun tunnel, Hong Kong. Atmospheric Environment, *43*(40), 6343–6351. https://doi.org/10.1016/j.atmosenv.2009.09.025
41. Hubert, A., Popp, P., Wenzel, K. -D., Engewald, W., & Schuurmann, G. (2003). One-step cleanup for PAH residue analysis in plant matrices using size-exclusion chromatography. Analytical and Bioanalytical Chemistry, *376*, 53–60. https://doi.org/10.1007/s00216-003-1858-5
42. Hussain, K., & Hoque, R. R. (2015). Seasonal attributes of urban soil PAHs of the Brahmaputra Valley. Chemosphere, *119*, 794–802. https://doi.org/10.1016/j.chemosphere.2014.08.021
43. Hwang, H. -M., Wade, T. L., & Sericano, J. L. (2003). Concentrations and source characterization of polycyclic aromatic hydrocarbons in pine needles from Korea, Mexico, and United States. Atmospheric Environment, *37*(16), 2259–2267. https://doi.org/10.1016/S1352-2310(03)00090-6
44. IARC (International Agency for Research on Cancer). (1983). Polynuclear aromatic compounds, Part 1: Chemical, environmental and experimental data. IARC monographs on evaluation of the carcinogenic risk of chemicals to humans, World Health Organization, IARC, Lyon, France, Vol. 32, pp. 1–453. https://monographs.iarc.fr/wp-content/uploads/2018/06/mono32.pdf
45. Janska, M., Tomaniova, M., Hajslova, J., & Kocourek, V. (2004). Appraisal of “classic” and “novel” extraction procedure efficiencies for the isolation of polycyclic aromatic hydrocarbons and their derivatives from biotic matrices. Analytica Chimica Acta, *520*(1–2), 93–103. https://doi.org/10.1016/j.aca.2004.05.073
46. Jiang, Y., Fan, M., Hu, R., Zhao, J., & Wu, Y. (2018). Mosses are better than leaves of vascular plants in monitoring atmospheric heavy metal pollution in urban areas. International Journal of Environmental Research and Public Health, *15*(6), 1–13. https://doi.org/10.3390/ijerph15061105
47. Kakareka, S. V., & Kukharchyk, T. I. (2003). PAH emission from the open burning of agricultural debris. Science of The Total Environment, *308*(1–3), 257–261. https://doi.org/10.1016/S0048-9697(02)00650-2
48. Kalbe, U., Berger, W., Eckardt, J., & Simon, F. G. (2008). Evaluation of leaching and extraction procedures for soil and waste. Waste Management, *28*(6), 1027–1038. https://doi.org/10.1016/j.wasman.2007.03.008
49. Kamarudin, N. A., Muhamad, N., Salleh, N. N. H. N., & Tan, S. C. (2021). Impact of solvent selection on phytochemical content, recovery of tannin and antioxidant activity of *Quercus infectoria* Galls. Pharmacognosy Journal, *13*(5), 1195–1204. http://www.phcogj.com/v13/i5
50. Kargar, N., Matin, G., Matin, A. A., & Buyukisik, H. B. (2017). Biomonitoring, status and source risk assessment of polycyclic aromatic hydrocarbons (PAHs) using honeybees, pine tree leaves, and propolis. Chemosphere, *186*, 140–150. https://doi.org/10.1016/j.chemosphere.2017.07.127
51. Karnchanasest, B., & Satayavibul, A. (2005). Orange jasmine leaves as an indicator of atmospheric polycyclic aromatic hydrocarbons. Songklanakarin Journal of Science and Technology, *27*(4), 877–888.
52. Katsoyiannis, A., Terzi, E., & Cai, Q. -Y. (2007). On the use of PAH molecular diagnostic ratios in sewage sludge for the understanding of the PAH sources. Is this use appropriate? Chemosphere, *69*(8), 1337–1339. https://doi.org/10.1016/j.chemosphere.2007.05.084
53. Klingberg, J., Strandberg, B., Sjoman, H., Taube, M., Wallin, G., & Pleijel, H. (2022). Polycyclic aromatic hydrocarbon (PAH) accumulation in *Quercus palustris* and *Pinus nigra* in the urban landscape of Gothenburg, Sweden. Science of The Total Environment, *805*, 150163. https://doi.org/10.1016/j.scitotenv.2021.150163

54. Larsen, R. K., & Baker, J. E. (2003). Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. Environmental Science & Technology, *37*(9), 1873–1881. https://doi.org/10.1021/es0206184
55. Lee, B. C., Shimizu, Y., Matsuda, T., & Matsui, S. (2005). Characterization of polycyclic aromatic hydrocarbons (PAHs) in different size fractions in deposited road particles (DRPs) from Lake Biwa Area, Japan. Environmental Science & Technology, *39*(19), 7402–7409. https://doi.org/10.1021/es050103n
56. Lin, D., Zhu, L., He, W., & Tu, Y. (2006). Tea plant uptake and translocation of polycyclic aromatic hydrocarbons from water and around air. Journal of Agricultural and Food Chemistry, *54*(10), 3658–3662. https://doi.org/10.1021/jf052909c
57. Malik, J., & Mandal, S. C. (2022). Extraction of herbal biomolecules. In: Mandal, S. C., Nayak, A. K., Dhara, A. K. (Eds.), Herbal Biomolecules in Healthcare Applications, Academic Press, pp. 21–46.
58. Masih, J., Singhvi, R., Kumar, K., Jain, V. K., & Taneja, A. (2012). Seasonal variation and sources of polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air in a semi arid tract of northern India. Aerosol and Air Quality Research, *12*(4), 515–525. https://doi.org/10.4209/aaqr.2011.11.0192
59. Mukhopadhyay, S., Dutta, R., & Das, P. (2020). A critical review on plant biomonitors for determination of polycyclic aromatic hydrocarbons (PAHs) in air through solvent extraction techniques. Chemosphere, *251*, 1–21. https://doi.org/10.1016/j.chemosphere.2020.126441
60. Mukhopadhyay, S., Dutta, R., & Dhara, A. (2021). Assessment of air pollution tolerance index of *Murraya paniculata* (L.) Jack in Kolkata metro city, West Bengal, India. Urban Climate, *39*, 100977. https://doi.org/10.1016/j.uclim.2021.100977
61. Ngamkhae, N., Monthakantirat, O., Chulikhit, Y., Boonyarat, C., Boonyarat, C., Maneenet, J., Khamphukdee, C., Kwankhao, P., Pitiporn, S., & Daodee, S. (2022). Optimization of extraction method for Kleeb Bua Daeng formula and comparison between ultrasound-assisted and microwave-assisted extraction. Journal of Applied Research on Medicinal and Aromatic Plants, *28*, 100369. https://doi.org/10.1016/j.jarmap.2022.100369
62. Niu, L., Xu, C., Zhou, Y., & Liu, W. (2019). Tree bark as a biomonitor for assessing the atmospheric pollution and associated human inhalation exposure risks of polycyclic aromatic hydrocarbons in rural China. Environmental Pollution, *246*, 398–407. https://doi.org/10.1016/j.envpol.2018.12.019
63. Ohura, T., Horii, Y., Kojima, M., & Kamiya, Y. (2013). Diurnal variability of chlorinatedpolycyclic aromatic hydrocarbons in urban air, Japan. Atmospheric Environment, *81*, 84–91. https://doi.org/10.1016/j.atmosenv.2013.08.044
64. Oishi, Y. (2018). Comparison of moss and pine needles as bioindicators of transboundary polycyclic aromatic hydrocarbon pollution in central Japan. Environmental Pollution, *234*, 330–338. https://doi.org/10.1016/j.envpol.2017.11.035
65. Orsi, M., Sanderson, W. E., & Essex, J. W. (2009). Permeability of small molecules through a lipid bilayer: A multiscale simulation study. Journal of Physical Chemistry B, *113*(35), 12019–12029. https://doi.org/10.1021/jp903248s
66. Park, S. S., Kim, Y. J., & Kang, C. H. (2002). Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea. Atmospheric Environment, *36*(17), 2917–2924. https://doi.org/10.1016/S1352-2310(02)00206-6
67. Pies, C., Hoffmann, B., Petrowsky, J., Yang, Y., Ternes, T. A., & Hofmann, T. (2008). Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils. Chemosphere, *72*(10), 1594–1601. https://doi.org/10.1016/j.chemosphere.2008.04.021
68. Pinelo, M., Sineiro, J., & Nunez, M. J. (2006). Mass transfer during continuous solid–liquid extraction of antioxidants from grape byproducts. Journal of Food Engineering, *77*(1), 57–63. https://doi.org/10.1016/j.jfoodeng.2005.06.021
69. Prajapati, S. K., & Tripathi, B. D. (2008). Biomonitoring seasonal variation of urban air polycyclic aromatic hydrocarbons (PAHs) using *Ficus benghalensis* leaves. Environmental Pollution, *151*(3), 543–548. https://doi.org/10.1016/j.envpol.2007.04.013
70. Ratola, N., Lacorte, S., Barcelo, D., & Alves, A. (2009). Microwave-assisted extraction and ultrasonic extraction to determine polycyclic aromatic hydrocarbons in needles and bark of *Pinus pinaster* Ait. and *Pinus pinea* L. by GC-MS. *Talanta*, *77*(3), 1120–1128. https://doi.org/10.1016/j.talanta.2008.08.010
71. Ravindra, K., Sokhi, R., & Van Grieken, R. (2008_a). Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmospheric Environment, *42*(13), 2895–2921. https://doi.org/10.1016/j.atmosenv.2007.12.010
72. Ravindra, K., Wauters, E., & Van Grieken, R. (2008_b). Variation in particulate PAHs levels and their relation with the transboundary movement of the air masses. Science of The Total Environment, *396*(2–3), 100–110. https://doi.org/10.1016/j.scitotenv.2008.02.018
73. Ray, D., Chatterjee, A., Majumdar, D., Ghosh, S. K., & Raha, S. (2017). Polycyclic aromatic hydrocarbons over a tropical urban and a high altitude Himalayan Station in India: temporal variation and source apportionment. Atmospheric Research, *197*, 331–341. https://doi.org/10.1016/j.atmosres.2017.07.010
74. Ray, D., Ghosh, S. K., & Raha, S. (2021). Seasonal foliar uptake of atmospheric polycyclic aromatic hydrocarbons by some local plants in a tropical metropolis in India. Atmospheric Pollution Research, *12*(2), 104–112. https://doi.org/10.1016/j.apr.2020.10.013
75. Reichardt, C., & Welton, T. (2010). Solvents and Solvent Effects in Organic Chemistry, Fourth Edition, Wiley-VCH Verlag GmbH & Co. KGaA, pp. 718.
76. Sari, M. F., Esen, F., & Tasdemir, Y. (2021). Characterization, source apportionment, air/plant partitioning and cancer risk assessment of atmospheric PAHs measured with tree components and passive air sampler. Environmental Research, *194*, 110508. https://doi.org/10.1016/j.envres.2020.110508
77. Scaramboni, C., Neris, J. B., do Nascimento R. d. K. S., Chiaranda da Rosa N. L., Carvalho, J. S., Grosseli, G. M., Campos, M. L. A. M., Fadini, P. S., & Urban, R. C. (2021). Optimization of a low volume extraction method to determine polycyclic aromatic hydrocarbons in aerosol samples. *Frontiers in Environmental Science*, *9*(742251), 1–11. https://doi.org/10.3389/fenvs.2021.742251
78. Shinoda, W. (2016). Permeability across lipid membranes. Biochimica et Biophysica Acta (BBA) – Biomembranes, *1858*(10), 2254–2265. https://doi.org/10.1016/j.bbamem.2016.03.032
79. Shukla, S., Khan, R., Bhattacharya, P., Devanesan, S., & AlSalhi, M. S. (2022). Concentration, source apportionment and potential carcinogenic risks of polycyclic aromatic hydrocarbons (PAHs) in roadside soils. Chemosphere, *292*, 133413. https://doi.org/10.1016/j.chemosphere.2021.133413

80. Smith, K. E. C., Northcott, G. L., & Jones, K. C. (2006). Influence of the extraction methodology on the analysis of polycyclic aromatic hydrocarbons in pasture vegetation. Journal of Chromatography A, *1116*(1–2), 20–30. https://doi.org/10.1016/j.chroma.2006.03.040
81. Steiner, D., Krska, R., Malachova, A., Taschl, I., & Sulyok, M. (2020). Evaluation of matrix effects and extraction efficiencies of LC – MS/MS methods as the essential part for proper validation of multiclass contaminants in complex feed. Journal of Agricultural and Food Chemistry, *68*(12), 3868–3880. https://doi.org/10.1021/acs.jafc.9b07706
82. Szulejko, J. E., Kim, K. H., Brown, R. J. C., & Bae, M. S. (2014). Review of progress in solvent extraction techniques for the determination of polyaromatic hydrocarbons as airborne pollutants. TrAC Trends in Analytical Chemistry, *61*, 40–48. https://doi.org/10.1016/j.trac.2014.07.001
83. Tian, L., Yin, S., Ma, Y., Kang, H., Zhang, X., Tan, H., Meng, H., & Liu, C. (2019). Impact factor assessment of the uptake and accumulation of polycyclic aromatic hydrocarbons by plant leaves: morphological characteristics have the greatest impact. Science of The Total Environment, *652*, 1149–1155. https://doi.org/10.1016/j.scitotenv.2018.10.357
84. Tobiszewski, M., & Namiesnik, J. (2012). PAH diagnostic ratios for the identification of pollution emission sources. Environmental Pollution, *162*, 110–119. https://doi.org/10.1016/j.envpol.2011.10.025
85. Totten, L. A., Eisenreich, S. J., & Brunciak, P. A. (2002). Evidence for destruction of PCBs by the OH radical in urban atmospheres. Chemosphere, *47*(7), 735–746. https://doi.org/10.1016/S0045-6535(01)00326-5
86. Veggi, P. C., Martinez, J., & Meireles, M. A. A. (2013). Fundamentals of Microwave Extraction. In: Chemat, F., Cravotto, G. (Eds.), Microwave-assisted Extraction for Bioactive Compounds. Food Engineering Series. Springer, Boston, MA, pp. 15–52. https://doi.org/10.1007/978-1-4614-4830-3_2
87. Wang, Y., Li, Q., Wang, S., Wang, Y., Luo, C., Li, J., & Zhang, G. (2015). Seasonal and diurnal variations of atmospheric PAHs and OCPs in a suburban paddy field, South China: Impacts of meteorological parameters and sources. Atmospheric Environment, *112*, 208–215. https://doi.org/10.1016/j.atmosenv.2015.04.047
88. Waters Corporation. (2008). EPA Method 550.1 Determination of Polycyclic Aromatic Hydrocarbons in Drinking Water by Liquid-Solid Extraction and High Performance Liquid Chromatography with Ultraviolet Detection. Application Note, pp. 14–15.
89. Yang, B., Liu, S., Liu, Y., Li, X., Lin, X., Liu, M., & Liu, X. (2017). PAHs uptake and translocation in *Cinnamomum camphora* leaves from Shanghai, China. Science of The Total Environment, *574*, 358–368. https://doi.org/10.1016/j.scitotenv.2016.09.058
90. Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., & Sylvestre, S. (2002). PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry, *33*(4), 489–515. https://doi.org/10.1016/S0146-6380(02)00002-5
91. Zalewski, R. I., Krygowski, T. M., & Shorter, J. (Eds.). (1991). Similarity Models in Organic Chemistry, Biochemistry and Related Fields. Studies in Organic Chemistry, Vol. 42, Elsevier Science Publishers B.V., Amsterdam, pp. 342.
92. Zhang, W., Zhang, S., Wan, C., Yue, D., Ye, Y., & Wang, X. (2008). Source diagnostics of polycyclic aromatic hydrocarbons in urban road runoff, dust, rain and canopy throughfall. Environmental Pollution, *153*(3), 594–601. https://doi.org/10.1016/j.envpol.2007.09.004
93. Zhao, X., He, M., Shang, H., Yu, H., Wang, H., Li, H., Piao, J., Quinto, M., & Li, D. (2018). Biomonitoring polycyclic aromatic hydrocarbons by *Salix matsudana* leaves: a comparison with the relevant air content and evaluation of environmental parameter effects. Atmospheric Environment, *181*, 47–53. https://doi.org/10.1016/j.atmosenv.2018.03.004
94. Zhou, L., Dong, L., Huang, Y., Shi, S., Zhang, L., Zhang, X., Yang, W., & Li, L. (2014). Spatial distribution and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in Camphor (*Cinnamomum camphora*) tree bark from Southern Jiangsu, China. Chemosphere, *107*, 297–303. https://doi.org/10.1016/j.chemosphere.2013.12.070

Figures

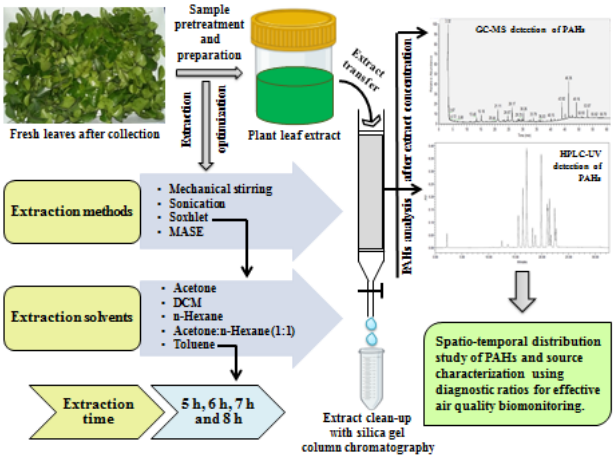

Figure 1

Schematic diagram of the experimental setup