Abstract

Constant bursting of the city frontiers is taking a massive toll on natural vegetation, deteriorating thereby the purity of the clean air due to the presence of hazardous pollutants in the atmosphere. Rapid industrialization and urbanization have immensely contributed to outdoor air pollution due to vehicular emission, industrial activities, power plant operations, etc., whereas, rural areas face the major problems of indoor air pollution. Among the criteria air pollutants, polycyclic aromatic hydrocarbons (PAHs) are organic compounds having two or more fused aromatic rings, released from natural as well as man-made sources. They are persistent priority pollutants and continue to last for a long time in the environment causing severe damage to human health owing to their genotoxicity, mutagenicity and carcinogenicity. The study of PAHs in the environment has therefore aroused a global concern. Biomonitoring of airborne pollutants through creation of green belts has become the only alternative to provide natural filtering barrier. Thus, plant bioaccumulators can be exploited as biomonitors for indirect assessment of air pollution. In conformity with the above facts, efficacy of specific higher terrestrial plants (generally regarded as foundation species of the ecosystem) with broad foliage-canopy structures in mitigating airborne PAHs pollution (through entrapment into their tissues) has been demonstrated, underscoring prevalent classical and modified isolation techniques (i.e., solvent extraction) coupled with proper analytical procedures for gaining an insight into the assessment of atmospheric PAHs concentrations.

As a basis for passive air pollution biomonitoring, estimation of tolerance characteristics of a terrestrial plant was the primary focus of the study to determine the potentiality of the selected plant against contaminated environment. The study was constructed to evaluate the air pollution tolerance index (APTI) of a commonly found evergreen plant species, *Murraya paniculata*, sampled from polluted places of South Kolkata, West Bengal, India, with dense population and heavy traffic, based on leaf attributes. PAHs accumulating ability of the plant species was also examined so as to establish the species' potential in monitoring of PAHs. *M. paniculata* was found to be tolerant (APTI: 19.78–31.12) towards air pollution with dust capturing potential ranging between 0.85–2.26 mg cm^{-2}. Correlation analysis unveiled the strong relationship of foliar dust with leaf ascorbic acid ($r^2 = 0.931$), leaf extract pH ($r = 0.985$), leaf RWC ($r = -0.822$), total carotenoids ($r = -0.862$) and total chlorophyll ($r = -0.76$). APTI was found to be correlated positively to ascorbic acid

and foliar pH and negatively to total chlorophyll and RWC. Linear variation (r^2 = 0.97) of APTI with PM and other pollution burden was also noticed. Therefore, it can be concluded that APTI not only points out the sustainability of a bioindicator plant under severe pollution load, but also serves as a good indicator of contamination level. Changes in leaf surface micromorphology (such as stomal blockage and guard cell deformation, rough leaf surfaces developed from epidermal undulations, degradation of crystal structures of epicuticular waxes around the stomata and entrapment of dust particles) due to particulate pollution were also endorsed by SEM observation with energy-dispersive X-ray microanalysis. Findings also revealed that *Murraya paniculata* has the tolerance and efficiency of trapping both lighter and heavier PAHs, proving its ability for biomonitoring of atmospheric pollution.

Secondly, attempts have been made for ascertaining the concentrations of atmospheric PAHs using passive biosamplers (i.e., leaves of *M. paniculata*) in preference to classical air sampling methods by virtue of solvent extraction and analytical techniques. For achieving the desired objective, mechanical stirring, sonication, Soxhlet technique and microwave-assisted Soxhlet extraction (MAE) were employed for comparison of the effectiveness of traditional and advanced extraction methods to isolate PAHs from plant leaves. Effects of extraction techniques and operational parameters (solvent and time) on the recovery levels of PAHs were also investigated. Purified extracts, acquired through silica gel column chromatography, were subjected to GC–MS and HPLC–UV analyses for qualitative and quantitative assessment of PAHs. The results displayed that the extraction yields of Soxhlet (272.07 μg g^{-1}) and MAE (280.17 μg g^{-1}) were almost comparable and highest over sonication and mechanical stirring. Keeping the objective of targeting conventional route of extraction primarily, extraction optimization of Soxhlet method revealed toluene as the most favorable solvent for PAHs (because of the strong solute-solvent interactions favoured by intermolecular dispersive forces) and 6 h of extraction time was found to be optimum for obtaining highest recoveries.

The study was then aimed at developing a process intensified route based on solvent extraction for PAHs isolation from the leaf matrix of *M. paniculata* to overcome the limitations of traditional extraction method. In this aspect, MAE was targeted and the influence of MAE parameters on extraction yield of PAHs was evaluated through process optimization by response surface methodology (RSM) incorporating Box-Behnken Design (BBD). A three-level RSM-BBD approach was applied involving three MAE factors, extraction temperature, extraction time and solvent-to-sample ratio, for attainment of the optimal conditions to reach highest yield of PAHs as a desired response. Prior to the optimization study, solvent selection criterion was fulfilled through screening experiments using binary solvent mixtures along with preliminary experimentations on single factor effects. The combination of toluene:acetonitrile exhibited maximum yield (283.77 μg g^{-1}) of PAHs among the other solvent blends. Regarding parameter optimization by RSM, the experimental and predicted response values showed a good linear fit and a quadratic model was also developed correlating the input (independent) variables with the response. Significance of the regression model was confirmed through analysis of variance (ANOVA) (F value: 428.74; $p<0.0001$; R^2: 0.9982). The model represented positive effects of the linear terms and negative effects of the quadratic terms of process parameters on the response. All the interaction terms were again found to be significant with $p<0.05$. On performing model validation, the optimized conditions for maximization of extraction yield are observed to be: extraction temperature: 45.77 ºC, extraction time: 11.67 min and solvent-to-sample ratio: 22.64 mL g^{-1}, thereby achieving 98% accuracy on model prediction. A comparison between conventional Soxhlet method and MAE highlighted that the former method consumes huge amount of extraction solvent (1.8-fold higher) and extraction time (30 times higher) with high energy input and CO_2 emission during the process, suggesting the improved process performance of MAE.

To identify the PAHs occurrence pattern of wide-range dispersal, spatio-temporal distribution of accumulated PAHs across the sampling sites of South Kolkata (Jadavpur (JDV), Rash Behari Connector (RBC), Exide More (EXM) and Tollygunge (TGN)) was monitored over premonsoon, postmonsoon and winter supported by pollutant source characterization using PAHs diagnostic ratios (DRs). In spatio-temporal analysis, total concentrations of PAHs in the foliar samples of *Murraya* sp. ranged from 200.98 to 550.79 μg g^{-1} dry weight, and the highest values being recorded in the samples of 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, and degree of PAHs contamination varied as winter > postmonsoon > premonsoon. 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 as found from source apportionment study.

For prioritizing the role of urban green infrastructures in addressing the issues of Kolkata's air quality, efficiencies of eight indigenous plants of Baishnabghata Patuli Township (BPT), southeast Kolkata, India, were explored as green barrier species and potentials of plant leaves were exploited for biomonitoring of particulate matter (PM) and PAHs. The work focused on studying PM capturing abilities (539.32−2766.27 μg cm^{-2}) of plants (*T. divaricata*, *N. oleander* and *B. acuminata* being the most efficient species in retaining PM) along with the estimation of foliar contents of PM adhered to leaf surfaces (total sPM (large + coarse): 526.59−2731.76 μg cm^{-2}) and embedded within waxes (total wPM (large + coarse): 8.73−34.51 μg cm^{-2}). SEM imaging used to analyze leaf surfaces affirmed the presence of innate corrugated microstructures as main drivers for particle capture. Accumulation capacities of PAHs of vehicular origin (total index, TI > 4) were compared among the species based on measured concentrations (159.92−393.01 μg g^{-1}), which indicated *T. divaricata*, *P. alba* and *N. cadamba* as highest PAHs accumulators. Specific leaf area (SLA) of plants (71.01−376.79 cm^2 g^{-1}), a measure of canopy− atmosphere interface, had great relevance in PAHs diffusion. Relative contribution (>90%) of 4–6 ring PAHs to total carcinogenic equivalent and potential as well as 5−6 ring PAHs to total mutagenic equivalent and potential had also been viewed with respect to benzo[a]pyrene. In−depth analysis of foliar traits (as air pollution biomarkers) and adoption of plant−based ranking strategies (APTI and anticipated performance index (API)) provided a rationale for green belting. Each of the naturally selected plant species showed evidences of adaptations during abiotic stress to maximize survival and filtering effects for reductive elimination of ambient PM and PAHs, allowing holistic management of green spaces.

The interplay between plant-air interaction and cycling of airborne PAHs in terrestrial ecosystem determines their environmental existence and could aid in better employment of plants as biomonitoring tool for ecological restoration. In this context, dynamics of plant (*M. paniculata*) uptake mechanisms were modeled using a mechanistic framework based on material balance. Experimentally determined plant-air (K_{PA}) and particle-gas (K_P) partition coefficients justified the nature of PAHs partitioning into plant and particle phases. Apart from direct exchange between plant and air (manifesting high air-leaf mass transfer coefficient k_{AL} of 85 cm h^{-1} (average) and fugacity capacity of plant foliage: 0.045-1.27×10^4 mol m^{-3} Pa^{-1}), PM adsorption on plant leaf surfaces and uptake and movement of PAHs from foliar PM into leaf layers (cuticle and mesophyll) were observed relating to their overall foliar PM-leaf translocation factor ($TF_{f/L}$) (which is >1). Despite efficient root accumulation (with high root concentration factor (RCF): 0.72-1.12), root to leaf transfer of PAHs was found to be minimal owing to their diminished mass flow and lower values of root-leaf translocation factor ($TF_{R/L}$). After validation of the material balance model, inner tissue absorption and adsorption to the leaf-laden PM are established as the responsible routes of PAHs uptake by a biomonitor plant species from the ambient atmosphere.

Therefore, it can be conclusively opined that the present study offers a broad basis for successful selection and identification of plant biomonitors with proper improved assessment methodology for atmospheric PAHs analysis. The study findings can further assist in strengthening the prediction of bioaccumulation of atmospheric PAHs into a biomonitor plant, providing a robust and indispensable option of advanced biomonitor selection. Also, a proposition for green belting using locally available biomonitor plants has been elaborated as a sustainable foundation for the future management and planning of township, being an unrivalled solution to air pollution.