



OPEN

Potential of *Pinus eldarica* Medw. tree bark for biomonitoring polycyclic aromatic hydrocarbons in ambient air

Sohrab Hasheminejad, Hossein Moradi[✉] & Mohsen Soleimani

Urban trees' biomonitoring of pollutants such as polycyclic aromatic hydrocarbons (PAHs) yields pertinent and useful data for air pollution management. The aim of this study was to biomonitor PAHs in pine (*Pinus eldarica* Medw.) trees in the city of Isfahan and identify their sources. In total, 34 samples of outer bark of the trees were collected and their contents of 16 EPA PAHs were analyzed. With a median value of 136.3 ng/g, the total PAH contents in tree barks varied from 53.4 to 705.2 ng/g. The average values of the diagnostic ratios for Ant/(Ant + Phe), Flu/(Flu + Py), BaA/(BaA + Chr) and IP/(IP + BP) were 0.19, 0.49, 0.45 and 0.49, respectively, revealing the PAHs majority source of pyrogenic. Meanwhile, principal component analysis showed two major types of PAHs sources including pyrogenic (fossil fuel combustion and industrial activities) and petrogenic (uncombusted) sources. The average ratio An/(An + Phe) and Flu/(Flu + Py) in bark samples was close to their relevant ratios in ambient air which demonstrated the potential use of this approach for biomonitoring of PAHs.

Keywords Air pollution, Bioindicator, PAHs, PCA, Diagnostic ratio

Air pollution is a worldwide concern since it has a negative impact on human health. Growing industrialization has exacerbated air pollution in recent years. Among the air pollutants, organic pollutants (e.g. polycyclic aromatic hydrocarbons (PAHs)) have been more considered due to their properties such as toxicity, bioaccumulation, long-distance transport, and persistence. Increasing population growth, the use of fossil fuels, and the use of fertilizer or pesticides all contribute to an increase in organic pollutants in various environments¹.

PAHs are an important class of organic pollutants that are emitted into the environment from a variety of sources, including pyrogenic, petrogenic, and biogenic sources. PAHs can be found in both gaseous and particulate forms. Because of their carcinogenic and mutagenic properties, they are classified as hazardous pollutants². Because of potential health risks, the United States Environmental Protection Agency (EPA) designated 16 PAHs as priority pollutants (Table S1). For researchers, the proliferation of PAHs into the atmosphere is a human health concern. Monitoring and source identification of PAHs in the environment, on the other hand, is a critical issue for proper management by decision-makers and scientists. There are numerous monitoring strategies, but biomonitoring could be one of the best due to its economic efficiency and ease of use³. Biomonitoring is the process of taking samples of organisms or parts of organisms and providing relevant information on the quality of the environment⁴. Trees are employed as biomonitors to gather vital information such as the spatial or temporal distribution of pollution in a city^{5–8}. The tree's components (stem, branches, leaves, and bark) can be easily utilized to monitor pollution levels in general⁹. Tree bark, on the other hand, is exposed to air pollution and accumulates pollutants in the outer layer of bark^{10–13}. Tree bark is divided into two sections: inner bark and outer bark. The inner bark of older stems contains living tissue, but the outer bark contains dead tissue¹⁴. Since outer pine tree bark has a broad area of layered, porosity, and waxy dead cells, scientists consider it as a good accumulation biomonitor of PAHs to geographical distribution, source identification, and health evaluation^{10,12,13,15–18}. Pollutants are absorbed by tree bark in a variety of methods, including air deposition, which is taken up by roots and leaves^{9,19}. Because PAHs are somewhat soluble in water (Table S1) due to the high log K_{ow} index, uptake of PAHs by roots is unlikely²⁰. *Pinus eldarica* Medw. is a common evergreen species in many cities such as Isfahan. Based on their qualities, pine trees are classified as tolerant in APTI, which indicates *P. eldarica* is not vulnerable to pollution²¹. The PAHs associated with particulate matters (PMs) are prevalent due to the bark structure of pine trees^{22–24}. Diagnostic ratios (DRs) and principal component analysis (PCA) are common tools used in various

Department of Natural Resources, Isfahan University of Technology, Isfahan 8415683111, Iran. ✉ email: hossein.moradi@iut.ac.ir

studies^{2,6,8,13,18,25–27}. The DRs technique is straightforward and effective for identifying pyrogenic or petrogenic sources. However, by integrating DRs data with PAH emission source ratios, it is possible to identify the relevant sources. PCA is a multivariate method that can be used to identify possible PAH sources. Understanding the markers of the various processes is essential in this method of source identification¹⁸.

Isfahan metropolitan is one the industrialized region in Iran having various environmental challenges such as water scarcity and air pollution together with their relevant pollutants and health risks. Soleimani et al. (2022) has found that PMs (particularly PM_{2.5}) are a substantial pollutant in Isfahan city²⁸. They found the concentration of 19 PAHs associated with PM_{2.5} in the range of 0.3–61.4 ng/m³. Furthermore, the highest and lowest PAHs concentrations were associated with summer and winter, respectively²⁸. Accordingly, three sources (transportation, industrial activities, and natural gas combustion) were identified to be the main sources of PAHs associated with PM_{2.5} in Isfahan city. However, there are numerous activities from major industrial activities including power plants (which uses Mazot or natural gas), iron and steel plants (which uses coke and natural gas), oil refinery, petrochemical plant, brick manufacturers, as well as diesel and gasoline vehicles, which may be as source of PAHs emissions²⁸.

In general, biomonitoring of the PAHs has some limitations such as high costs, methodological problems, and needs extensive samplings⁴. As a result, employing tree tissues as a biological indicator is one of the biomonitoring approaches that offers an advantage over the conventional methods. The main aims of this study were (i) to quantify the content of PAHs on outer *Pinus eldarica* Medw. (pine) bark, and (ii) to identify the potential sources of PAHs in Isfahan city using diagnostic ratios (DRs) and PCA methods, and (iii) comparison the result of source identification of the current study with those related to PAHs associated with ambient PM_{2.5}. Providing this pertinent information might reveal the potential of outer pine barks as a reliable method for biomonitoring and PAHs source identification in ambient air which could be beneficial for superior air pollution management.

Materials and methods

Study area

Isfahan city is an industrialized city in central Iran (51° 39' 40" E, 32° 38'30" N), with a proximate elevation of 1600 m and a land area of 480 km². The climate is semi-arid, with maximum and lowest temperatures of 42 and – 12 degrees Celsius, respectively. The total amount of green space in Isfahan city is roughly 37 million m², which is dispersed evenly throughout the city, and *P. eldarica* is a popular tree species in the city's green spaces²⁹. In terms of air pollution sources, the city is surrounded by major industries such as cement and brick factories, iron and steel industries, power plants, oil refineries, and petrochemical facilities. The transportation system in Isfahan city uses gasoline and diesel on a regular basis²⁸. Natural gas combustion is typically used as a source of energy for residential heating and cooking. Pollution is generally at its peak during the cold season due to inversion.

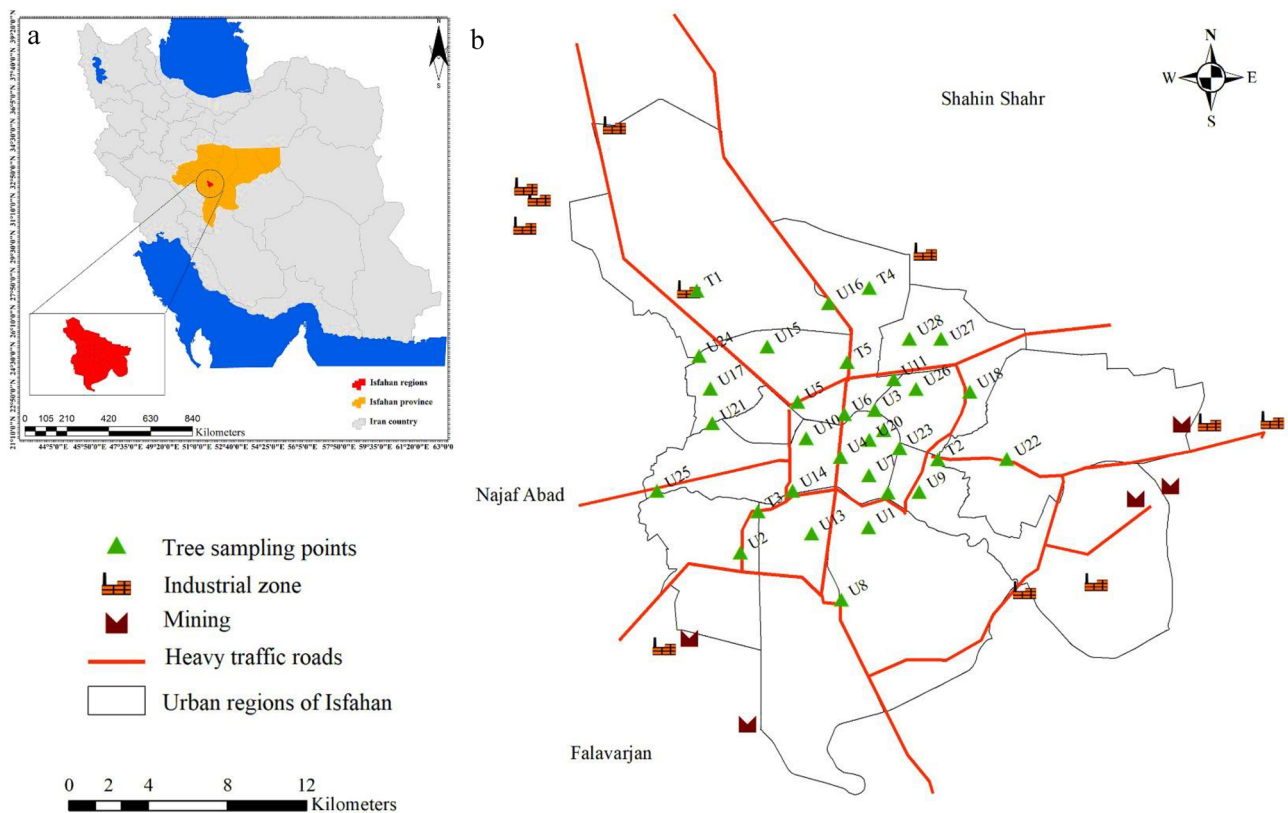
Sampling design

In December 2020, 33 mature pine barks were collected in Isfahan city (Fig. 1). The *Pinus eldarica* Medw. tree, the synonym of *Pinus brutia* var. *eldarica* (Medw.) Silba, is a tall evergreen that can grow up to 12–15 m in height. It has an average growth rate of more than 1 m height per year and usually has six growth flushes and whorls annually. Additionally, its bole diameter at breast height increases at a rate of over 2 cm per year³⁰. It features thick, brownish-gray bark that is layered. Although it is commonly used for its wood and paper as well as an important tree and an excellent choice for urban green spaces due to its ability to withstand tough climate and soil conditions³¹. However, *P. eldarica* is one of the most common trees worldwide which serves as a suitable bio-indicator in urban and industrial areas³². The researchers of the study with help of Mahnaz Bayat, a botanical expert, using voucher specimen number 11226, at the Herbarium of the Department of Natural Resources at Isfahan University of Technology, identified the tree species. A Voucher specimen from each sample has been deposited at the Herbarium under the number 11226. The choice was based on preliminary research and the findings of earlier studies on PM_{2.5} and associated with PM_{2.5} in Isfahan ambient air^{28,33}. As a result, our judicial sampling strategy took into account population density, distance to industrial zones, and roadways. Bark samples with an area of 80 cm² and a height of 1.5 m were taken from the street-side of the trees. All the bark samples were collected with official authorization from Isfahan Municipality under permission number 121.64825. After taking each sample, all bark samples were chopped with an adz and saw. The adz and saw were then cleaned with acetone to remove any organic impurities. The Anti-fungus was then used to fill the damaged area on the tree where the sample was taken. Finally, the samples were stored in polyethylene bags at a freezing temperature (about – 10 °C) and in the dark. An increment borer was used to collect core samples from the same trees. The age of the trees was calculated by counting the annual rings, which ranged from 14 to 57 years old. The ages and a brief description of the trees sampled are shown in Table S2.

Preparation and extraction of samples

To prevent PAH loss, tree barks were freeze-dried in a freeze-dryer machine at – 40 °C for 24 h. A mixer device (Polymix PX-MFC90D) was used to finely grind the dry samples³⁴. Following homogenization, the ground samples were stored in polyethylene bags in a dry, dark, and cool location⁵. Finally, 5 g of each sample was extracted for PAH analysis.

PAHs were extracted from bark samples using a sonication technique. In this method, 150 mL of acetone/dichloromethane 90:10 was extracted for 20 min, and 4 mL of PAH surrogate internal standard (Naphthalene-d₈, Anthracene-d₁₀, Chrysene-d₁₂, Perylene-d₁₂, and Acenaphthene-d₁₀) mixture was added to all samples for QA/QC analyses (Table S3), and all sample volume was reduced to 2 mL by N₂ stream^{23,35}. All samples were cleaned using a silica gel column that had been deactivated with 5% deionized water. 40 mL dichloromethane was used to prewash the column. The extracted sample was then loaded into the column, and the PAHs were eluted



The maps were created using QGIS 3.34. (<https://qgis.org/downloads/QGIS-OSGeo4W-3.34.3-1.msi>)

Figure 1. Study area. Location of Isfahan Province in the center of Iran (a). The sampling sites of pine tree barks distributed in Isfahan city (b).

with 40 mL dichloromethane. Finally, all samples were concentrated to 2 mL using a N_2 stream and transferred to a GC vial⁵. The 16 EPA analyzed PAHs were naphthalene (Nap), acenaphthene (Acy), acenaphthylene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), benzo(a)anthracene (B[a]A), chrycene (Chr), benzo(b)fluoranthene (B[b]F), benzo(k) fluoranthene (B[k]F), benzo(a)pyrene (B[a]P), indeno[1,2,3-cd]pyrene (I[c]P), dibenzo[a,h] anthracene (D[ah]A), and benzo [g,h,i]perylene (B[ghi]P).

PAHs analyses

An Agilent 6890N gas chromatograph with a mass selective detector (Agilent 6890, inert MSD 5973) was used to test the samples for 16 EPA PAHs. The compounds were ionized by electron impact ionization. The capillary column was HP5-MS (30 m, 0.25 m, 0.25 mm), and the carrier gas was Helium at a flow rate of 1.2 mL/min. The data was collected using a specific ion monitoring approach. The limits of detection (LOD) are the lowest PAH concentrations that can be consistently detected. The lowest standard calibration curve and the area of a peak were used to compute LOD. Table S4 reveals PAH LODs, which ranged from 0.3 to 1.2 ng/g for all PAHs except naphthalene. Because of its high volatility and ease of evaporation, the LOD of this analyte was 2 ng/g.

Source identification of PAHs

PAHs with 178 and 202 mass molecular weights are good for masking differences between combustion and petroleum sources, whereas PAHs with 228 and 276 mass molecular weights are less commonly utilized as PAH markers. Higher mass PAHs are usually derived from a variety of petroleum products such as crude oil, creosote, asphalt, and so on³⁵. Therefore, to determine PAHs sources the ratio values of, 178 and 202 mass molecular PAHs such as An/(An + Phe), (anthracene to anthracene plus phenanthrene), Flu/(Flu + Pyr), (fluoranthene to fluoranthene plus pyrene), 228 and 276 mass molecular PAHs including BaA/(BaA + Chr), (benzo[a]anthracene to Benzo[a]anthracene plus chrycene), IP/(IP + BP), (Indeno[1,2,3-cd]pyrene to Indeno[1,2,3cd]pyrene plus Benzo[ghi]perylene), were used in different studies^{27,36,37}. The standard values used to compare with estimated values in this investigation are shown in Table S3. Principal component analysis (PCA) is another method to identify PAHs sources. The PCA results demonstrate different component which show PAHs sources⁸. Package “factoextra” in R was implied for PCA.

Ethical approval

The plant collection and use was in accordance with all the relevant guidelines.

Results and discussion

PAHs concentration in pine tree barks

The concentration of 16 PAHs in pine barks in Isfahan city ranged from 53.4 to 705.2 ng/g dw, with a mean value of 157 ng/g (Table 1). The highest PAHs concentration was found at site U28 (705.2 ng/g dw), which is influenced by a high traffic road as well as dozens of brick-making complexes. The second highest concentration was found in point U27 (290.7 ng/g dw), which is near a road with high traffic volume (Fig. 2). The results of PCA analysis showed the U22 sampling site is located beside a highway and is separated from other sampling sites. Similarly, U6 and U20 sampling sites located in the city center showed a similar pattern (Fig. 3). U6 is located in a residential area and it may also be influenced by heavy traffic during the day. U22 is located in a crowded square nearby a traditional Bazaar as well as a bus terminal. Therefore, these results revealed that the sources of the PAHs in the city might vary depending on the location. Soleimani et al. (2022) found that the sources of PAHs in this metropolis do not change much over seasons because they are mostly sourced by transportation, industrial activities and combustion of fossil fuels²⁸. However, during the cold season, PAH concentrations may change due to climate conditions such as temperature inversion. In addition to the source type, other factors such as distance, meteorological parameters, and photolytic or biological degradation can influence the PAH concentration³⁸. The atmosphere of an urban area may be confined by buildings, trees, and other impediments, allowing PAHs to be deposited on various surfaces such as barks. A comparison between our findings with others presented in Table 2. The PAHs concentrations were stated higher in those studies than in the current study. Based on the average concentrations of individual PAHs, we found that naphthalene, acenaphthylene, fluorene, phenanthrene, and anthracene, which are 2–3 rings components, are predominate (Fig. 4). Then, the four-rings components including fluoranthene and pyrene take the lead. Other individual PAHs had an average concentration of less than 10 ng/g, which is comparable to the previous studies^{5,18,34}. Several studies revealed that the concentration of low molecular weight PAHs measured in various plant tissues might be higher than the high molecular weight PAHs, due to the varied K_{ow} of the individual PAHs which affect PAHs sorption by plants^{5,9,12,18}.

Sources of PAHs in pine tree bark

Cross plots of diagnostic ratios (DRs) of PAHs in pine barks from Isfahan city presented in Fig. 5. The threshold of 0.1 is as a reference value of the An/(An + Phe) ratio. Based on the threshold, values less and more than 0.1 indicate petrogenic and pyrogenic sources, respectively³⁶. Our results showed the ratios were ranged from 0.06 to 0.79, with mean values of 0.19. It demonstrates that the majority of the sites in Isfahan city are exposed by pyrogenic sources. Flu/(Flu + Py) is another ratio used for diagnosis. In relation to this ratio, petroleum is represented by values < 0.4, liquid fossil fuel combustion is represented by values < 0.5, and biomass or coal combustion is indicated by values > 0.5³⁴. The calculated ratio of PAHs in pine bark has a mean value of 0.49 and a range of 0.37–0.62. This ratio illustrates the role of vehicles powered by liquid fossil fuel. According the ratio (BaA/BaA + Chr), the values < 0.2 indicate the petrogenic sources, 0.2 < values < 0.35 indicate the mixed sources of petrogenic and pyrogenic, and values > 0.35 indicate the combustion sources³⁴. According to our findings, the ratio ranged from 0.13 to 0.82, with an average of 0.45, suggesting that one of the main sources of PAHs in the city of Isfahan is pyrogenic. The fact that additional studies found that the values for this ratio can range from 0.22 to 0.55 for gasoline combustion and 0.38–0.64 for diesel combustion further highlights the significance of fossil fuels combustion in Isfahan city³⁹. Values less than 0.2 indicate petrogenic sources, values between 0.2 and

PAHs	Mean	Std deviation	Total	Minimum	Q1	Median	Q3	Maximum	Range
Nap	19.77	39.57	652.28	1.22	5.52	10.73	16.91	223	221.78
Acy	11.39	8.21	375.98	0.3	5.89	8.24	15.7	34.84	34.54
Ace	1.887	1.32	62.281	0.3	1.21	1.454	1.815	5.806	5.506
Fl	10.76	7.84	355.2	4.41	6.42	9.14	12.29	48	43.59
Phe	33.9	24.79	1118.6	7.2	17.79	30.43	38.21	125	117.8
Ant	8.79	12.44	290.13	1.06	2.33	3.58	8.41	60	58.94
Flu	23.63	20.18	779.81	3.77	12.71	16.82	25.11	89.36	85.59
Py	23.81	22.11	785.71	2.76	12.09	16.72	27.59	98	95.24
BaA	3.416	2.589	112.719	0.2	1.697	3.144	4.427	13	12.8
Chr	4.24	3.767	139.914	0.4	1.832	3.202	4.952	14	13.6
BbF	2.281	2.088	75.261	0.4	0.572	1.852	3.079	10	9.6
BkF	3.05	8.5	100.49	0.4	0.58	1.36	2.36	50	49.6
BaP	2.596	2.46	85.66	0.6	0.6	2.143	3.627	13	12.4
IP	2.743	3.257	90.519	1.2	1.2	1.2	2.459	15.805	14.605
DaA	3.48	6.61	114.98	1.2	1.2	1.2	1.2	34.24	34.24
BP	2.192	2.216	72.345	1.2	1.2	1.2	1.2	9.04	7.84

Table 1. The statistical summary of PAHs in pine tree barks in Isfahan city (ng/g dw).

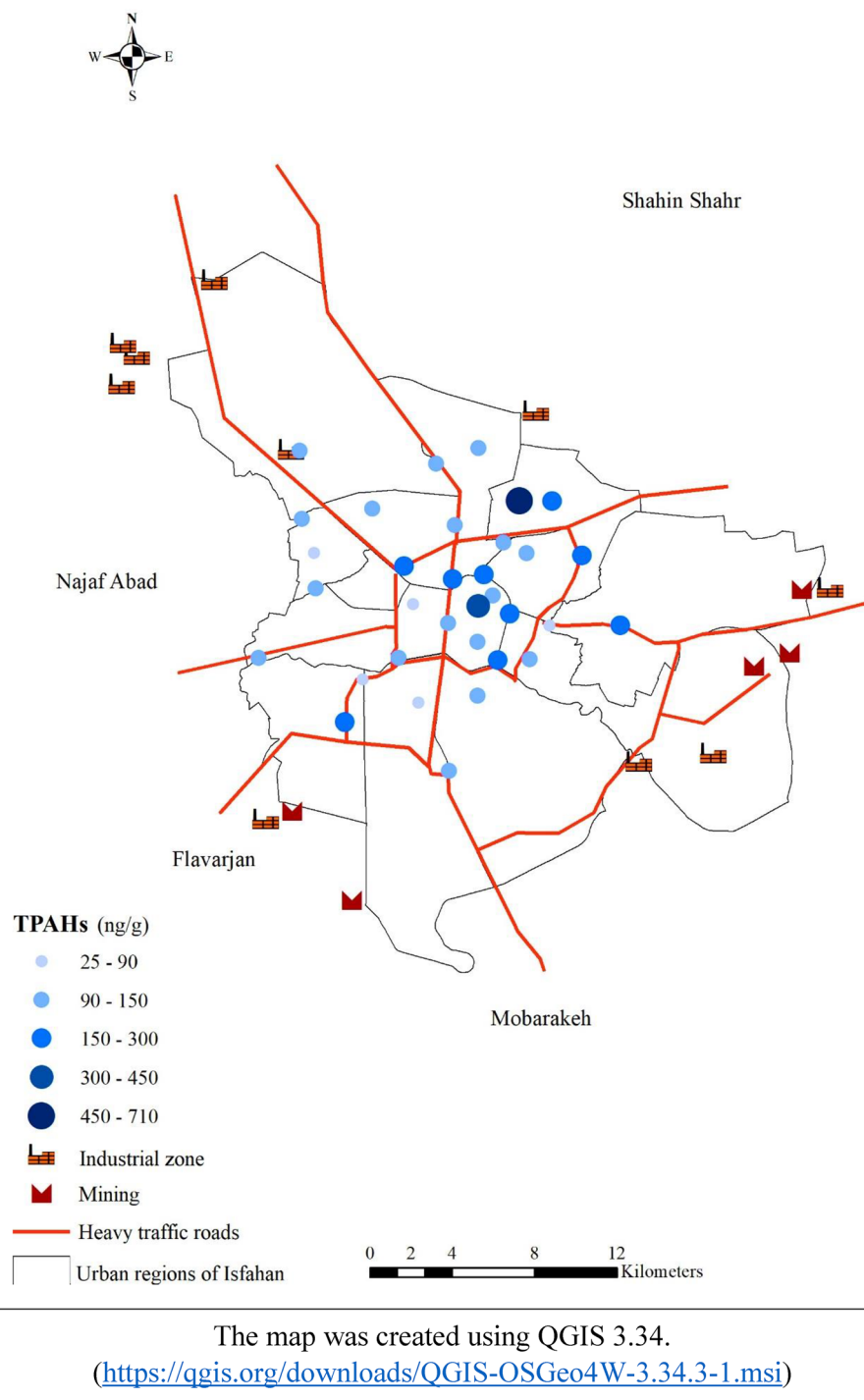


Figure 2. The spatial variation of $\Sigma 16$ PAHs concentrations (ng/g) in pine tree barks of Isfahan city.

0.5 indicate liquid fossil fuel combustion, and values more than 0.5 indicate grass, wood, or coal combustion³⁶. The estimated ratio of this study ranged from 0.46 to 0.53, with a mean value of 0.49. This ratio also indicates that pyrogenic sources are the most prevalent (Table S5). The pattern of PAH dispersion may be influenced by a number of factors, including temperature and photolysis, therefore the results of DRs may not pinpoint precise sources.

In Table 3, a comparison of the diagnostic ratios of PAHs in the pine bark and those measured in $PM_{2.5}$ samples from the same region²⁸ is presented. The ratios of 178 and 202 mass molecular PAHs in pine tree bark were nearly identical to earlier ratios of $PM_{2.5}$ samples. In bark samples, the average An/(An + Phe) and Flu/(Flu + Py) were 0.19 and 0.49, respectively. However, the mean values of these ratios in ambient $PM_{2.5}$ samples was 0.18 and 0.43, respectively, indicating that the results of these investigations likely demonstrated that pyrogenic sources

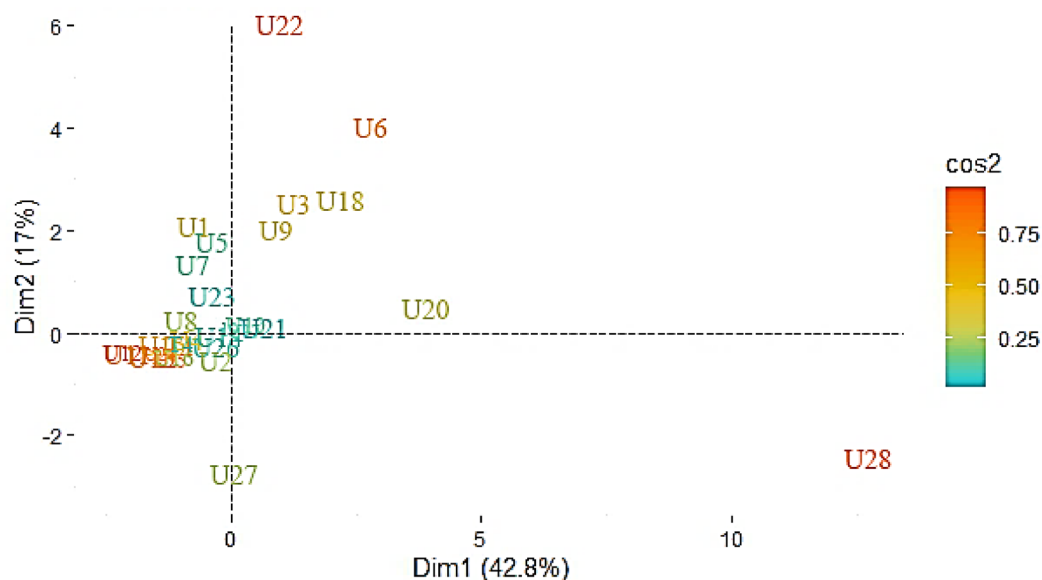


Figure 3. The PCA analysis of PAHs concentrations for sampling sites in pine tree barks in Isfahan city.

Site, country	Numbers of congeners	PAHs concentration (ng/g)	References
Jiangsu province, China	15	1560–6.18	Zhou et al. (2014)
Yangtze plain, China	15	1300–27	Wu et al. (2019)
Rural area, China	16	3803–6.3	Niu et al. (2019)
Sicily, Italy	19	1015–33	Orecchio et al. (2008)
Bursa, Turkey	14	593–81	Sari et al. (2021)
Pohang, South Korea	16	124–26	Choi et al. (2014)
Sao Paulo, Brazil	16	1640–242	Pereira et al. (2007)
Current study	16	705.2–53.4	

Table 2. Comparison of Σ PAHs in tree bark of different geographical regions to the results of the current study (ng/g dw).

are predominated across the city. As a result, employing *Pinus eldarica* Medw barks for PAHs biomonitoring using the mentioned diagnostic ratios may have a high potential to identify PAHs sources.

The PCA results showed four components of relevant PAHs in pine barks of Isfahan city (Fig. 6), where the first, second, third, and fourth components were explaining 42.7%, 17.08%, 10.83%, and 9.4% of total variance, respectively (Table S6). The first component is mostly loaded by PAHs such as BkF, BbF, Py, BaP, Nap, Flu, Phe, Fl, BaA, and Chr, which are mainly markers of industrial activities, diesel, and natural gas combustion^{37,40}. Moreover, Fluorene, Py, Chr, BaA, BeP, and BaP were identified as markers of industrial activities^{35,37}. Around Isfahan city, there are several major industrial zones with a high capacity of producing PAHs, such as power plants, iron and steel plants, brick and cement factories^{28,40}. The first component contains Phe, Fl, BaA, Chr, and Py which are known as indicators of natural gas combustion³⁵. Natural gas is not only utilized for residential heating and cooking in Isfahan city, but it is also used as a fuel in major factories such as power plants and steel plants. Another source of PAHs is diesel combustion, and the markers are BkF, BbF, and BaP^{35,37}. In Isfahan city, diesel fuel is widely used in public transportation and trucks as well as industrial plants²⁸.

The second component related to the combustion of gasoline. indeno[1,2,3-cd]pyrene (I[c]P), BP, and DaA were identified as gasoline combustion markers^{35,41}. Three PAHs were considered as petrogenic markers such as Acy, Ace, and Ant which are found in the third and fourth components⁴². Overall, the findings suggested that the main sources of PAHs in Isfahan City were likely natural gas, as well as diesel and gasoline combustions.

According to the PAHs sources identification, Isfahan is mostly affected fuel combustion in various sources including transportation and industrial activities and their related transportation to move the raw materials, products, and the personnel, as well as power plants and residential heating systems. The Isfahan city witnesses more than a million private gasoline cars and 2500 public diesel vehicles passing through it every day²⁸. Being a highly industrialized city in Iran, Isfahan is surrounded by major industries, including brick factories, iron and steel plants, power plants, oil refineries, and petrochemical facilities. Therefore, industrial activities and transportation as two anthropogenic sources could be the most significant sources of PAHs in ambient air²⁸.

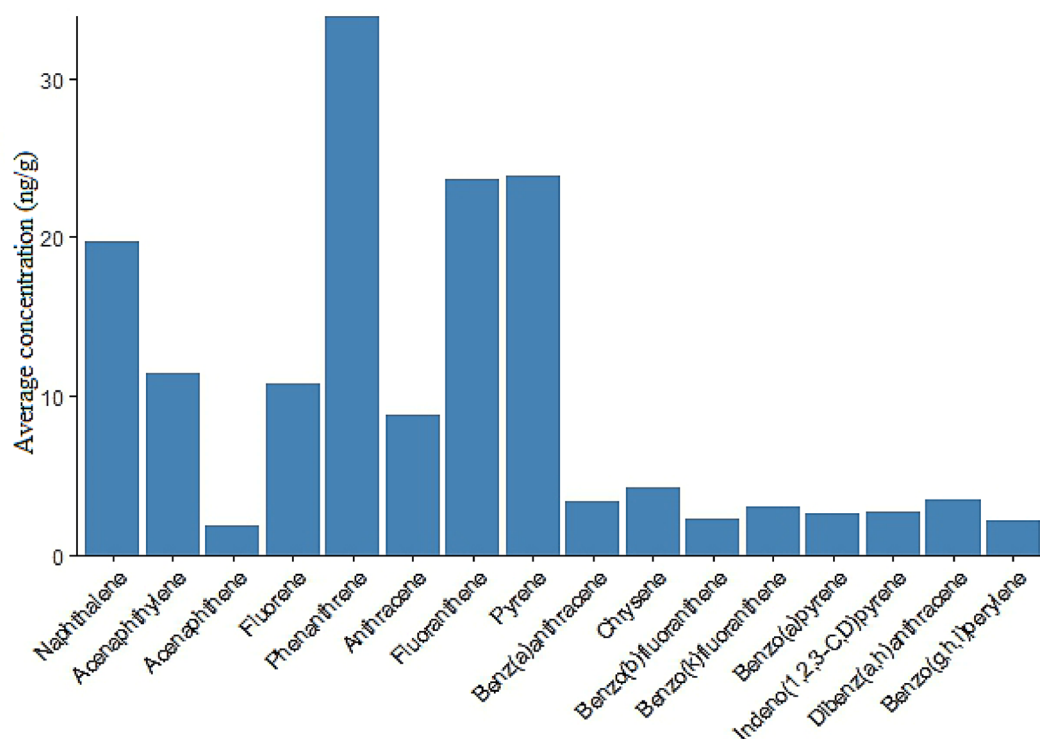


Figure 4. Average concentrations (ng/g) of individual PAHs in pine tree barks in Isfahan city.

PC1 values were high in both U28 and U20 (Fig. 3). U28 is near brick manufacturing zones and the roads with heavy traffic. The point U20 is located in a crowded square surrounded by commercial activity, and car traffic which has expanded dramatically during the last decade. This point may be significantly influenced by the pyrogenic sources such as natural gas, gasoline and diesel combustion. Points U5, U1, and U22 all exhibited high PC2 values, indicating significant gasoline combustion at these sites. U5 and U22 were assigned to the highway side, whilst U1 was assigned to the street side. Samples from the three green spaces (U3, U9, and U18) had high PC1 or PC2 scores. Green spaces have an important role in capturing PAHs⁴³. Ant, Phe, Flu, and Py concentrations of the tree barks were higher at these sampling sites than those from the others. Thus, the trees could sorb PAHs from the environment, demonstrating their potential in purifying the urban air from those compounds.

Conclusion

The concentration of 16 PAHs in pine barks in Isfahan city ranged from 53.4 to 705.2 ng/g dw, with a mean value of 157 ng/g, where three and four-ring PAHs were predominated at all sites. The source identification of PAHs in pine barks and recent research yielded nearly identical results, indicating that vehicle emissions, natural gas combustion, and industrial activities were the major PAHs sources in Isfahan city during the cold season. The diagnostic ratios of PAHs from tree barks and ambient PM_{2.5} in Isfahan city (particularly for An/(An + Phe) and Flu/(Flu + Py) ratios) showed the same possible sources of the compounds. Biomonitoring of PAHs using bark of *Pinus eldarica* Medw. could be a cost-effective, more reasonable, and applicable approach than conventional monitoring. The diagnostic ratios and PCA analysis revealed the pyrogenic source of PAHs in the pine tree barks. Although pyrogenic sources are the main source of PAHs emissions in the city, petrogenic sources (i.e. non-combustion sources) should be considered in air pollution management.

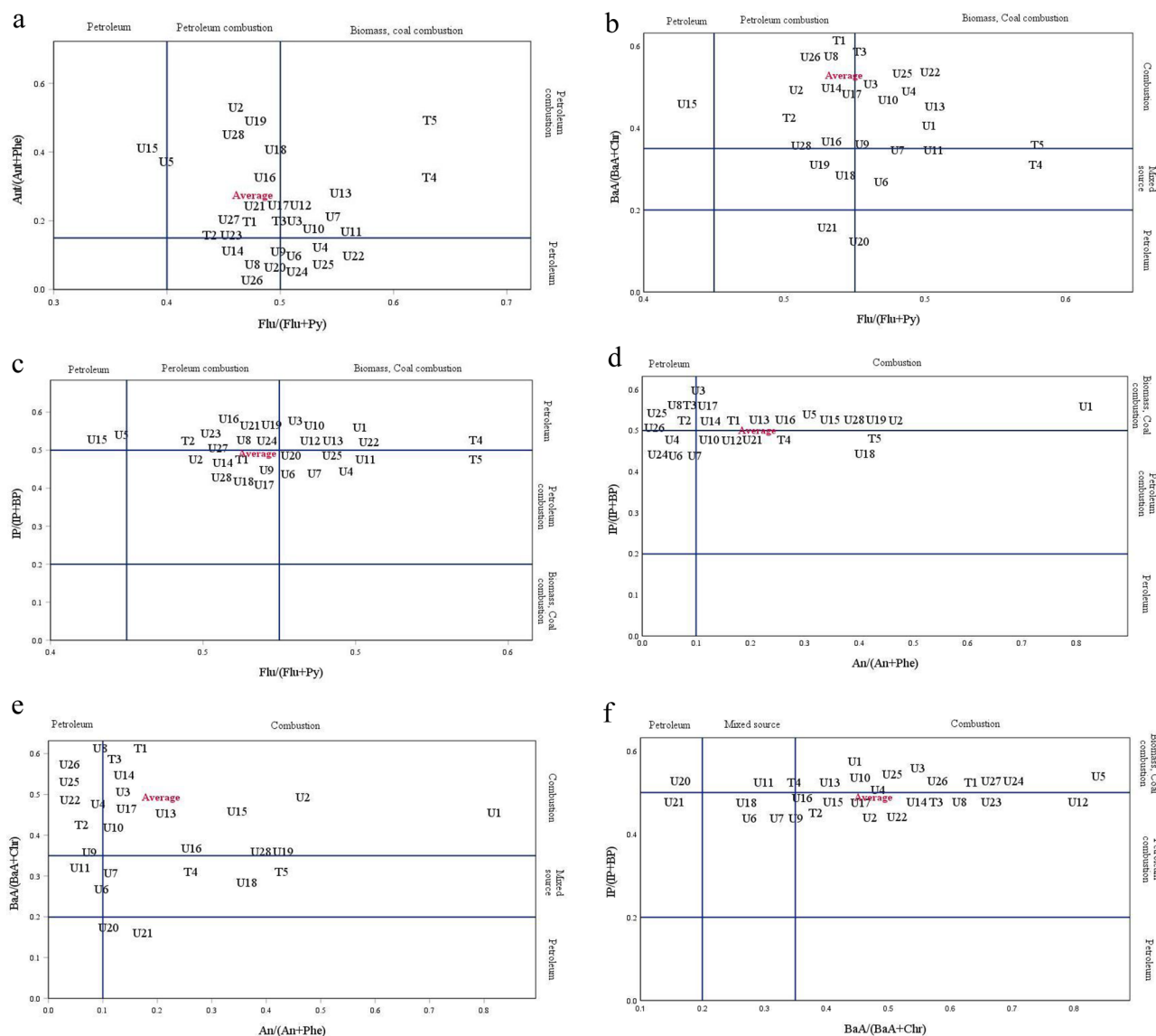


Figure 5. Cross plots of diagnostic ratios (DRs) of PAHs in pine tree barks in Isfahan city.

Ratios	PAHs in PM _{2.5}		PAHs pine bark	
	Mean	Min–Max	Mean	Min–Max
An/(An + Phe)	0.18	0.34–0.09	0.19	0.79–0.06
Flu/(Flu + Py)	0.43	0.58–0.32	0.49	0.62–0.37
BaA/(BaA + Chr)	0.34	0.43–0.17	0.45	0.82–0.13
IP/(IP + BP)	0.31	0.41–0.22	0.49	0.53–0.46

Table 3. The comparison of diagnostic ratios (DRs) in tree bark samples and ambient PM_{2.5} in Isfahan city²⁸.

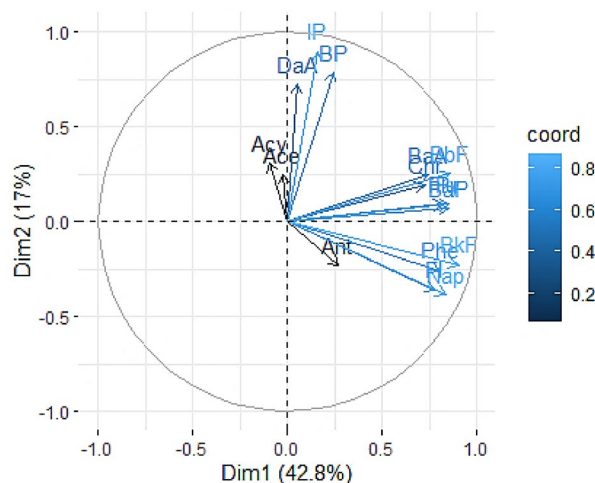


Figure 6. PCA analysis for PAHs concentrations in pine tree barks in Isfahan city.

Data availability

The datasets generated analyzed during the current study are available from the corresponding author on reasonable request.

Received: 16 September 2023; Accepted: 3 March 2024

Published online: 15 March 2024

References

- Li, T. *et al.* Source apportionment of PM_{2.5} in Guangzhou based on an approach of combining positive matrix factorization with the Bayesian mixing model and radiocarbon. *Atmosphere* **11**(5), 512 (2020).
- Ravindra, K., Sokhi, R. & Van Grieken, R. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmos. Environ.* **42**(13), 2895–2921 (2008).
- Costa, C. & Teixeira, J. P. Biomonitoring. In *Encyclopedia of Toxicology* 3rd edn (ed. Wexler, P.) 483–484 (Academic Press, 2014).
- Conti, M. E. *Biological Monitoring: Theory & Applications: Bioindicators and Biomarkers for Environmental Quality and Human Exposure Assessment* Vol. 17 (WIT Press, 2008).
- Rauert, C. & Harner, T. A preliminary investigation into the use of Red Pine (*Pinus Resinosa*) tree cores as historic passive samplers of POPs in outdoor air. *Atmos. Environ.* **140**, 514–518 (2016).
- Yin, S. *et al.* Sources and sinks evaluation of PAHs in leaves of *Cinnamomum camphora* in megacity: From the perspective of land-use types. *J. Clean. Prod.* **279**, 123444 (2021).
- Sari, M. F., Esen, F. & Tasdemir, Y. Characterization, source apportionment, air/plant partitioning and cancer risk assessment of atmospheric PAHs measured with tree components and passive air sampler. *Environ. Res.* **194**, 110508 (2021).
- Choi, S. D. Time trends in the levels and patterns of polycyclic aromatic hydrocarbons (PAHs) in pine bark, litter, and soil after a forest fire. *Sci. Total Environ.* **470**, 1441–1449 (2014).
- Odabasi, M. *et al.* Biomonitoring the spatial and historical variations of persistent organic pollutants (POPs) in an industrial region. *Environ. Sci. Technol.* **49**(4), 2105–2114 (2015).
- Ratola, N. *et al.* Differences between *Pinus pinea* and *Pinus pinaster* as bioindicators of polycyclic aromatic hydrocarbons. *Environ. Exp. Bot.* **72**(2), 339–347 (2011).
- Kuang, Y. W., Zhou, G. Y., Wen, D. Z., Li, J. & Sun, F. F. Analysis of polycyclic aromatic hydrocarbons in tree-rings of Masson pine (*Pinus massoniana* L.) from two industrial sites in the Pearl River Delta, south China. *J. Environ. Monit.* **13**(9), 2630–2637 (2011).
- Niu, L., Xu, C., Zhou, Y. & Liu, W. Tree bark as a biomonitor for assessing the atmospheric pollution and associated human inhalation exposure risks of polycyclic aromatic hydrocarbons in rural China. *Environ. Pollut.* **246**, 398–407 (2019).
- Pereira, G. M., da SilvaCaumo, S. E., do Nascimento, E. Q. M., Parra, Y. J. & de CastroVasconcellos, P. Polycyclic aromatic hydrocarbons in tree barks, gaseous and particulate phase samples collected near an industrial complex in São Paulo (Brazil). *Chemosphere* **237**, 124499 (2019).
- Birke, M., Rauch, U. & Hofmann, F. Tree bark as a bioindicator of air pollution in the city of Stassfurt, Saxony-Anhalt, Germany. *J. Geochem. Explor.* **187**, 97–117 (2018).
- Salamova, A. & Hites, R. A. Evaluation of tree bark as a passive atmospheric sampler for flame retardants, PCBs, and organochlorine pesticides. *Environ. Sci. Technol.* **44**(16), 6196–6201 (2010).
- Chaparro, M. A. E. *et al.* Fine air pollution particles trapped by street tree barks: In situ magnetic biomonitoring. *Environ. Pollut.* **266**, 115229 (2020).
- Wu, X. *et al.* Concentration, exchange and source identification of polycyclic aromatic hydrocarbons in soil, air and tree bark from the Middle-Lower Yangtze Plain, China. *Atmos. Pollut. Res.* **10**(4), 1276–1283 (2019).
- Zhou, L. *et al.* Spatial distribution and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in Camphor (*Cinnamomum camphora*) tree bark from Southern Jiangsu, China. *Chemosphere* **107**, 297–303 (2014).
- Wang, Q. *et al.* Historical records of airborne polycyclic aromatic hydrocarbons by analyzing dated corks of the bark pocket in a Longpetiole Beech tree. *Environ. Sci. Technol.* **38**(18), 4739–4744 (2004).
- Abdel-Shafy, H. I. & Mansour, M. S. M. A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egypt. J. Petrol.* **25**(1), 107–123 (2016).
- Sadeghian, M. M. & Mortazaienezhad, F. Selection and identification of air pollution-tolerant plants by air pollution tolerance index (APTI) in urban parks of Isfahan, Iran. *Afr. J. Biotechnol.* **11**(55), 11826–11829 (2012).

22. Ratola, N., Amigo, J. M. & Alves, A. Comprehensive assessment of pine needles as bioindicators of PAHs using multivariate analysis. The importance of temporal trends. *Chemosphere* **81**(11), 1517–1525 (2010).
23. Ratola, N., Lacorte, S., Barceló, D. & Alves, A. 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 (2009).
24. Chupin, L. *et al.* Microwave assisted extraction of maritime pine (*Pinus pinaster*) bark: Impact of particle size and characterization. *Ind. Crops Prod.* **65**, 142–149 (2015).
25. Bandowe, B. A. M., Bigalke, M., Kobza, J. & Wilcke, W. Sources and fate of polycyclic aromatic compounds (PAHs, oxygenated PAHs and azaarenes) in forest soil profiles opposite of an aluminium plant. *Sci. Total Environ.* **630**, 83–95 (2018).
26. Shukla, S., Khan, R., Bhattacharya, P., Devanesan, S. & AlSalhi, M. S. Concentration, source apportionment and potential carcinogenic risks of polycyclic aromatic hydrocarbons (PAHs) in roadside soils. *Chemosphere* **292**, 133413 (2022).
27. Tobiszewski, M. & Namieśnik, J. PAH diagnostic ratios for the identification of pollution emission sources. *Environ. Pollut.* **162**, 110–119 (2012).
28. Soleimani, M., Ebrahimi, Z., Mirghaffari, N., Moradi, H., Amini, N., Poulsen, K. G., & Christensen, J. H. Seasonal trend and source identification of polycyclic aromatic hydrocarbons associated with fine particulate matters (PM_{2.5}) in Isfahan City, Iran, using diagnostic ratio and PMF model. *Environ. Sci. Pollut. Res.* 1–16 (2022).
29. Soltani, N. *et al.* Ecological and human health hazards of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in road dust of Isfahan metropolis, Iran. *Sci. Total Environ.* **505**, 712–723 (2015).
30. Phillips, G. C. & Gladfelter, H. J. Eldarica Pine, Afghan Pine (*Pinus eldarica* Medw.). In *Trees III. Biotechnology in Agriculture and Forestry* Vol. 16 (ed. Bajaj, Y. P. S.) (Springer, 1991). https://doi.org/10.1007/978-3-662-13231-9_17.
31. Soleimani, M., Amini, N., Sadeghian, B., Wang, D. & Fang, L. Heavy metals and their source identification in particulate matter (PM_{2.5}) in Isfahan City. *Iran J. Environ. Sci.* **72**, 166–175 (2018).
32. Irvani, S. & Zolfaghari, B. Phytochemical analysis of *Pinus eldarica* bark. *Res. Pharm. Sci.* **9**(4), 243 (2014).
33. Santamaría, J. M. & Martín, A. Tree bark as a bioindicator of air pollution in Navarra, Spain. *Water Air Soil Pollut.* **98**, 381–387 (1997).
34. Orecchio, S., Gianguzza, A. & Culotta, L. Absorption of polycyclic aromatic hydrocarbons by Pinus bark: Analytical method and use for environmental pollution monitoring in the Palermo area (Sicily, Italy). *Environ. Res.* **107**(3), 371–379 (2008).
35. Yin, H., Tan, Q., Chen, Y., Lv, G. & Hou, X. Polycyclic aromatic hydrocarbons (PAHs) pollution recorded in annual rings of ginkgo (*Ginkgo biloba* L.): Determination of PAHs by GC/MS after accelerated solvent extraction. *Microchem. J.* **97**(2), 138–143 (2011).
36. Yunker, M. B. *et al.* PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* **33**, 489–515 (2002).
37. Khan, M. F. *et al.* Seasonal effect and source apportionment of polycyclic aromatic hydrocarbons in PM_{2.5}. *Atmos. Environ.* **106**, 178–190 (2015).
38. Netto, A. D. P., Barreto, R. P., Moreira, J. C. & Arbilla, G. Spatial distribution of polycyclic aromatic hydrocarbons in *Terminalia catappa* L. (Combretaceae) bark from a selected heavy road traffic area of Rio de Janeiro City, Brazil. *J. Hazard. Mater.* **142**(1–2), 389–396 (2007).
39. Simcik, M. F., Zhang, H., Eisenreich, S. J. & Franz, T. P. Urban contamination of the Chicago/Coastal Lake Michigan atmosphere by PCBs and PAHs during AEOLOS. *Environ. Sci. Technol.* **31**(7), 2141–2147 (1997).
40. Lin, T. *et al.* Sources of polycyclic aromatic hydrocarbons to sediments of the Bohai and Yellow Seas in East Asia. *J. Geophys. Res.* **116**, D23 (2011).
41. Guo, H., Lee, S. C., Ho, K. F., Wang, X. M. & Zou, S. C. Particle associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. *Atmos. Environ.* **37**, 5307–5317 (2003).
42. Pampanin, D. M. & Sydnes, M. O. *Petrogenic Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Analysis, Synthesis, Toxicity and Environmental Impact* Vol. 1 (Bentham Science Publishers, 2017).
43. Peng, C., Ouyang, Z., Wang, M., Chen, W. & Jiao, W. Vegetative cover and PAHs accumulation in soils of urban green space. *Environ. Pollut.* **161**, 36–42 (2012).

Acknowledgements

The authors would like appreciate the Department of Planning and Human Capital Development, Isfahan Municipality, for providing raw data of PM_{2.5} through the research project Contract No. 96/3439. We also thank Mahnaz Bayat at the Herbarium of Department of Natural Resources, Isfahan University of Technology for her support.

Author contributions

S.H. and H.M. conceived of the presented idea. H.M. identified the species. H.M. and M.S. developed the research. S.H. performed the analyses and computations. H.M. and M.S. verified the analytical methods. M.S. supervised the findings of this work. All authors discussed the results and contributed to the final manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1038/s41598-024-56182-3>.

Correspondence and requests for materials should be addressed to H.M.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2024