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Usage of Needle and Branches in the Applications of Bioindicator, Source Apportionment and Risk Assessment of PAHs

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Abstract: Biomonitoring studies have enormous benefits providing a fruitful and cost-efficient means of measuring environmental exposure to toxic chemicals. This study collected ambient air and pine tree components, including needles and 1-year-old and 2-year-old branches, for one year. Concentrations, potential sources and temporal variations of atmospheric polycyclic aromatic hydrocarbons (PAHs) were investigated. In general, lower concentration levels were observed in the warmer months. Ambient PAHs pose a serious public health threat and impose a need for calculating cancer risks. It was also intended to define the best tree component reflecting the ambient air PAHs. The consideration of the representative tree component minimizes the unnecessary laboratory processes and expenses in biomonitoring studies. The coefficient of divergence (COD), diagnostic ratio (DR) and principal component analysis (PCA) were employed to specify the PAH sources. As a result of the DR and PCA evaluations, the effect of the industrial area has emerged, besides the dominance of the pollutants originating from traffic and combustion. The results have shown that pine needles and branches were mainly affected by similar sources, which also influenced air concentrations. Inhalation cancer risk values were also calculated and they varied between 1.64×10^{-6} and 3.02×10^{-5}. A potential risk increases in the colder season depending on the ambient air PAH concentrations.

Keywords: PAHs; source apportionment; pine tree; branch; needle; health risk assessment

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are atmospheric pollutants that contain two or more benzene rings, which can have adverse effects on the ecosystem and human health due to their mutagenic and carcinogenic properties [1,2]. PAHs are organic pollutants that can be detected in air, vegetation, soil and water [3–6].

Evaluation of the presence and distribution of these organic pollutants in the ambient air requires analytical methodologies that allow them to be determined quickly and reliably. Air quality monitoring programs for this purpose are conducted through active or passive samplers. Vegetation [7–9] and semipermeable membrane devices (SPMDs) [10] are two common types of passive samplers used for atmospheric PAH sampling. Vegetation sampling for PAHs is a more economical alternative because special sampling equipment is not needed. Plants cover most of the soil surface [11]. The plants can have 6–14 times more surface zones than the corresponding soil surface [8]. Therefore, vegetation has an essential effect on the atmospheric cycle. Biomonitoring studies to assess PAH concentrations in various environments have become the standard tool since the late 1980s [12]. Many plants, lichen and tree species (deciduous and evergreen) have been used as bioindicators to determine urban air quality and pollutant sources [7,9,12–26]. Indeed, in 2004, the European Parliament proposed the use of bioindicators to assess the impact of PAH on ecosystems by Directive 2004/10/EC. Considering the bioaccumulation of PAHs, especially in tree leaves and branches, it is possible to consider vegetation as a prominent hydrocarbon collector.

Tree components are widely used in biomonitoring as reliable and cost-effective in-dicators of environmental pollution because they accumulate a wide range of airborne pollutants and thus, reflect the effects of existing air pollution [2,27,28]. The dynamic exchange of organic chemicals on plant surfaces occurs under the influence of both envi-ronmental conditions and the biological properties of the plant. Plant intake of organic substances is of great importance as it affects the environmental transport and fate of PAHs. The uptake of organic chemicals from plant surfaces was extensively searched in terms of diffusion and penetration. It was stated that plant lipids were the critical chemical component for the assimilation of organic pollutants [29,30]. The lipid-rich cuticle of plant materials is likely to accumulate such persistent pollutants mainly on the leaf surface with an atmospheric deposition [16].

Evergreen plants are preferred as they offer yearly sampling opportunities [21,23,31]. Pine tree components are frequently used in the estimation of PAH components and their distribution in the atmosphere [11,32–34]. The high-lipid wax structure of pine needles is one of the most remarkable plants in the monitoring studies carried out in recent years, as it allows the pollutants to be retained for a long time. However, PAH accumulation in tree components occurs in different amounts due to various environmental conditions such as distance to pollutant source, climatic conditions, terrain conditions, etc. [34]. Therefore, it is important to examine the distribution of PAH in pine tree components in different environments to understand the distribution of PAH in different regions. A quantitative correlation is tried to be established between PAH levels in the air and plants with recent approaches and modeling studies [35].

It is important to determine the main sources of atmospheric PAHs and present the air-tree component relationships for a better understanding of the fate and transport of PAHs in the environment. Identifying the sources of PAHs is also necessary to assess ecological risk and appropriate mitigation measures [36]. For this purpose, there are some generally accepted approaches. The diagnosis rates (DRs) and specific determinants of each selected PAH type, multivariate statistical methods and various emission inventory model approaches (Principal component analysis (PCA), positive matrix fraction (PMF)) are employed to define the sources of PAHs, make their source distributions and reveal their contribution [6,37].

Some PAHs are known as carcinogens and pose a serious threat to human health [38]. The International Cancer Research Agency [39] classifies some PAHs as carcinogens (Group 1, 2A or 2B). Biological monitoring of the exposure to PAHs has been an important topic of interest due to its widespread distribution and toxicological importance. PAHs can be exposed in many ways, such as inhalation of indoor–outdoor air and ingestion, including meals containing PAHs [40]. Exposure to PAHs also causes reproductive disorders and some diseases, including bladder and gastrointestinal cancers, as well as skin and lung cancers [41].

The main objectives of this study can be summarized as (i) to determine the possible sources of PAHs by the DR and PCA methods, (ii) to investigate which tree component better reflects the ambient air and (iii) to reveal the potential health risks of PAHs

2. Material Method

2.1. Sampling

The sampling was performed in Bursa, a densely populated city with developed industry. The samples of branches and needles were collected on a monthly basis for one year from a pine tree in a suburban–industrial area of Bursa. The location of the pine tree sampled is shown in Figure 1. The sampled pine tree was approximately 1.5 km from the Istanbul–Izmir highway. The Bursa Organized Industrial Zone (BOIZ) was located approximately 2.8 km from the tree. There were settlements in the northwest and northeast of the tree.

The samples of ambient air and pine tree components (branch and needle) were wrapped in aluminum foil and brought to the laboratory in airtight bags. Passive air samplers (PASs) containing polyurethane foam (PUF) discs [42,43] were used to deter-mine ambient air concentrations of PAHs. In passive air sampling, increased pollutant

accumulation in the PUF-disc medium (PDM) is explained by the deposition resistance and mass transfer in the PDM-air-section [43]. Mass loads per sampler were converted to concentrations in the air using sample and compound-specific effective air volumes. For passive samplers using PUF disk as an adsorbent, the sampling rate (R) values and site-specific values were estimated from the model and online tool [44,45]. Collected PUF discs were extracted in a Soxhlet extractor with a mixture of acetone/hexane (ACE/HEX) (*v:v*, 1/1) for 24 h, with each cycle for approximately 50 min. Prior to extraction, a recovery surrogate standard was added to each sample to determine the recovery level [20]. Then, fractionation and cleaning procedures were applied. Their details were presented elsewhere [5,20].

Figure 1. The location of the sampled pine tree.

Branch and needle samples were collected from 1.5–2 m heights of the tree. It was paid attention that branch samples were collected as one-year-old and two-year-old.

2.2. Sample Preparation and Experimental Process

The pine needles were wiped with a napkin before extraction to obtain the particulate phase on their surfaces. Needle and branch (1-year-old and 2-year-old) samples were placed separately into dark-colored bottles. The branch and needle samples to be extracted were weighed approximately 5 g each. Fifty mL solvent consisting of dichloromethane and petroleum ether (DCM/PE, 1/1) and 1 mL surrogate standard were added to the bottles and kept in a shaker for approximately 16 h [20]. Then, ultrasonic extraction was applied to these samples for 15 min. Then, another solvent mixture (40 mL) consisting of acetone and hexane (ACE/HEX, 1:1) was added to the remaining samples and ultrasonic extraction was applied for 30 min to them [46]. Subsequently, the sample volume (90 mL) was reduced to 5 mL in a rotary evaporator (Laborota 4001 model, Heidolph, Germany) operating at 30 rpm and 22 °C. Afterward, 15 mL of HEX was added to the sample and its volume was reduced to 2 mL. Samples with decreased volumes were subjected to cleaning and fractionation in a column consisting of 3 g silicic acid, 2 g alumina and 2 g sodium sulfate [5,7,47]. The fractionation

column was cleaned using 20 mL DCM and then 20 mL PE for possible contamination. Then, a 2 mL sample was added to the column and then 20 mL of DCM was poured into the column to collect the PAH compounds [5,43,48]. Then, the solvent volume was reduced to 5 mL in a rotary evaporator and the final volume was reduced to 2 mL after 15 mL of HEX was added. Thus, the process of converting the solvent to HEX was achieved. PAH compounds with a volume of 2 mL were reduced to a volume of 1 mL under pure N_2 gas and taken into vials. The samples were stored in a deep freezer at $-20\ ^\circ$C until the instrumental analysis stage [5]. The samples were analyzed for 14 individual PAH, including Acenaphthene (Ace), Fluorene (Fluo), Phenanthrene (Phe), Anthracene (Anth), Fluoranthene (Flt), Pyrene (Pyr), benz(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (Indeno), Dibenzo(ah)anthracene (DahA), benzo(g,h,i)perylene (BghiP).

2.3. GC Analysis

An analysis of PAHs was performed by an Agilent 7890A model gas chromatograph (GC) and mass spectrophotometer (MS) with an associated Agilent 5975C inert XL triaxial mass detector. The injection volume of each sample is 1 μL and injections were made in a splitless mode. A mass spectrophotometer was run in selected ion monitoring mode (SIM) for high sensitivity. A capillary column (HP 5-MS, 30 m × 250 μm × 0.25 μm) was used in the GC-MS. A modified PAH separation method was applied in the GC reading as follows: wait 1 min at 50 °C, 25 °C/min to 200 °C, 8 °C/min to 300 °C (wait 5.5 min), 5 °C/min to 310 °C, wait 3 min before the end [20].

2.4. Quality and Reliability Measures

One mL of the surrogate standard was added to each sample and blank samples to determine the analysis recovery level. The surrogate standard, including naphthalene-d8, acenaphthene-d10, phenantherened10, chrysene-d12 and perylene-d12, was added to the samples at a concentration of 4 ng/mL. The data with recoveries of 50–120% were included in the calculations.

Blank samples of a minimum of 10% of the total sample numbers were collected for each component to determine possible contamination during transport, sampling and analysis steps. The blank correction was applied by subtracting the mean of the blank from the sample values [5]. Three times the blank standard deviations and mean values were summed to obtain the limit of detection (LOD) values for each PAH compound. LOD has been calculated and the measurement results below this value were not evaluated [49,50]. LOD values ranged from 1.35 ng (DahA) to 37.85 ng (Nap) for PUF samples, from 9,72 ng (DahA) to 75.59 ng (Phe) for leaf samples and from 10.30 (BkF) to 58.20 (Phe) for branch samples.

2.5. Statistical Analysis of Data

Statistical calculations and evaluations were performed using the PASW Statistics 18—SPSS program. In this context, Spearman's or Pearson's correlation test, paired t-test and other relevant tests were applied to the data.

3. Results and Discussion

Monthly samples of pine needles, branches (1- and 2-year-old branches) and ambient air were collected during the one year to determine the distributions and concentrations of PAHs at the sampling point, which could be characterized as a suburban industrial area. Annual average Σ_{14}PAH concentrations for pine needles, 1- and 2-year-old branches and ambient air were 756 ± 232 ng/g DW, 685 ± 350 ng/g DW and 587 ± 361 ng/g DW, respectively. When comparing with the literature data, it is crucial to have a region with similar characteristics, the number of PAH compounds studied and the type of tree species. The data obtained from this study agree with similar literature studies (Table 1). In this context, the values found in this study are similar to the values (Σ_{16}PAH = 626 ± 306 ng/g DW for pine needles) found in a study by Cindoruk et al. [20] in a suburban region in Turkey.

In another study conducted in the industrial area [4], the value found for pine needles was Σ_{16}PAH = 414 ± 265 ng/g DW and Σ_{16}PAH = 995 ± 643 ng/g DW for the branch. In another study conducted in another industrial region [33] (Σ_{16}PAH = 2157 ± 2098 for 2-year-old pine needles 1016 ± 684 for 1-year-old pine needles), much higher results were obtained. The distance from the industrial zone and the type of industrial activities significantly affect these concentrations. In this study, lower values were determined than the values determined by Odabasi et al. [33] due to the distance to the industrial zone. Obtained data from similar studies conducted in Italy [14] in an urban area containing industrial activities (Σ_9PAH = 817.4 ng/g DW) and in Portugal [51] (Σ_{16}PAH = 64–813 ng/g DW) prove that the data obtained in this study are reasonable values.

Table 1. Some PAH biomonitoring data from pine needles and branches.

Site Type	PAH (ng/g DW)	Reference
Urban area (containing industrial activities and heavy-duty traffic)	Σ_9PAH = 817.4 for pine needle	[14]
A metropolitan region, industrial areas	Σ_{16}PAH = 465 (urban areas) for pine needle Σ_{16}PAH = 433 (industrial areas) for pine needle	[52]
Main industrial area	Σ_{16}PAH = 64–813 for pine needle	[51]
Suburban area	Σ_{14}PAH = 626 ± 306 for pine needle Σ_{14}PAH = 548 ± 261 for pine branch	[20]
Industrial site	Σ_{16}PAH = 414 ± 265 for pine needle Σ_{16}PAH = 995 ± 643 for pine branch	[4]
Industrial site	Σ_{16}PAH = 2157 ± 2098 for 2-year-old pine needle Σ_{16}PAH = 1016 ± 684 for 1-year-old pine needle	[33]
Suburban–industrial area	Σ_{14}PAH = 756 ± 232 for pine needle Σ_{14}PAH = 685 ± 350 for 1-year-old pine branch Σ_{14}PAH = 587 ± 361 for 1-year-old pine branch	[53]

3.1. Identification of PAH Sources

Ambient air, pine needle and 1-year-old and 2-year-old pine branches samples were taken to analyze the 14 PAH compounds for a one-year period (December 2015–November 2016). In the literature, pollutants in ambient air have been monitored by using different plants and plant components. The coefficient of divergence (COD), diagnostic ratio (DR) and principal component analysis (PCA) were applied for the source apportionment justification.

3.1.1. Coefficient of Divergence (COD)

The coefficient of divergence (COD) is used to identify similarities or differences between pollutant composition profiles [54–56]. If the COD values are close to zero, the similarity can be mentioned between the two samples, and if it is close to one (>0.2), the difference and absolute heterogeneity can be mentioned [54,55]. There is also another method used to determine the relationship between two samples and it is known as Spearman's correlation coefficient (R_s) [56]. Higher Rs (>0.7) and a lower COD (<0.2) indicate that the two samples have similar influences from the sources [46,55].

It was investigated which tree component was more representative of the ambient air. In this way, it may be appropriate to collect only this component from the tree to represent the atmospheric concentration, and the collection of other components will be prevented. A difference between PAH concentrations determined using the passive air sampler and tree components is expected. This is mainly because the PUFs (polyurethane foams) in the passive air sampler were exposed to atmospheric concentrations for one month in this study. Theoretically, PUFs accumulate all PAHs on them during this one-month sampling period and do not let PAHs leave back into the atmosphere. However, there is an active exchange between air and tree components, although there is an accumulation in the tree

components during the one-month sampling period. As a result, a difference in PAH levels between tree components and PUF discs is likely to be observed. When all data are evaluated in the light of this basic expectation (annual Σ_{14}PAH), the R_s and p values between air and needle, air and 1-year-old branch, and air and 2-year-old branch samples were calculated to be 0.672 and <0.001, 0.652 and <0.001, 0.769 and <0.001, respectively. According to the 'p' results, there is an acceptable relationship between all tree components and ambient air concentrations. Thus, tree components can be used to explain ambient air PAH concentrations. However, Spearman's correlation values (R_s) indicated that the best correlation value was found between air and the 2-year-old branch samples.

The monthly COD and Rs values obtained between ambient air and tree components (air vs. needle, air vs. 1-year-old branch and air vs. 2-year-old branch) are given in Figure 2. The COD values between air-needle, air-1-year-old branch and air-1-year-old branch samples were determined as >0.815, >0.798 and >0.780, respectively. When the COD and Rs values were examined, it was determined that there were lower COD and higher Rs values between the air and 2-year-old branch samples. Generally, a decrease in Rs values was observed in all component pairs in the autumn and winter months (Figure 2). This decrease was observed more clearly in air-needle and air-1-year-old branch component pairs. It was clearly seen that the correlation between air and the 2-year-old branch was better than other components in almost all months. This finding probably indicates that 2-year-old branch samples are more successful in explaining air concentrations.

The similarity of tree components (needle vs. 1-year-old branch, needle vs. 2-year-old branch, 1-year-old vs. 2-year-old branch) is evaluated. COD values were less than 0.437 among all tree component pairs. It can be concluded that the tree components were partially affected by the sources in a similar way. In particular, the lowest COD value (0.345) and the highest R_s value (R_s = 0.876; $p < 0.001$) among the component pairs belonged to the 1-year-old and 2-year-old branches. These two components are affected similarly by PAH sources and may be more successful in explaining each other.

In this study, the seasonal COD and R_s results obtained for needles and branches (needle-1-year-old branch, needle-2-year-old branch and 1- and 2-year-old branches) are given in Figure 3. Higher COD values were observed in the winter and autumn, yet the lowest COD values were detected in the summer. This finding is reasonable because tree components were exposed to more PAH in terms of sources and concentrations in winter and autumn. The result indicated that PAH sources that existed at the site affected tree components to different extents. On the other hand, in the summer months, lower COD values revealed more consistency between each tree component pair. Probably, this was mainly due to lower concentrations and fewer sources of PAHs. In general, there was good consistency between 1- and 2-year-old branch samples with $R_s > 0.86$ in all seasons (Table 2).

The relationships between air and tree components were also investigated by considering the molecular weights of the PAH components. It was found that tree components data were more successful in describing air concentrations in medium molecular weight PAHs (Table 3). The correlation values (R_s and p) between air vs. needle (n = 28), air vs. 1-year-old branch (n = 27) and air vs. 2-year-old branch (n = 28) samples for medium molecular weight (MMW) PAHs were determined as 0.436 and 0.020, 0.524 and 0.005, 0.790 and <0.001, respectively. The correlation values (R_s and p) between air vs. needle, air vs. 1-year-old branch and air vs. 2-year-old branch samples for light molecular weight (LMW) PAHs were determined as 0.228 and 0.363, 0.274 and 0.243, 0.370 and 0.119, respectively. These values for heavy molecular weight PAHs were 0.067 and 0.736, −0.186 and 0.354, −0.381 and 0.089 for air vs. needle (n = 28), air vs. 1-year-old branch (n = 27) and air vs. 2-year-old branch (n = 28), respectively. According to the '*p*' results, there is an acceptable relationship between all tree components and ambient air concentrations. In the evaluation of medium molecular weight PAHs, the best correlation was found between the air vs. 2-year-old branch values (R_s = 0.790; $p < 0.001$).
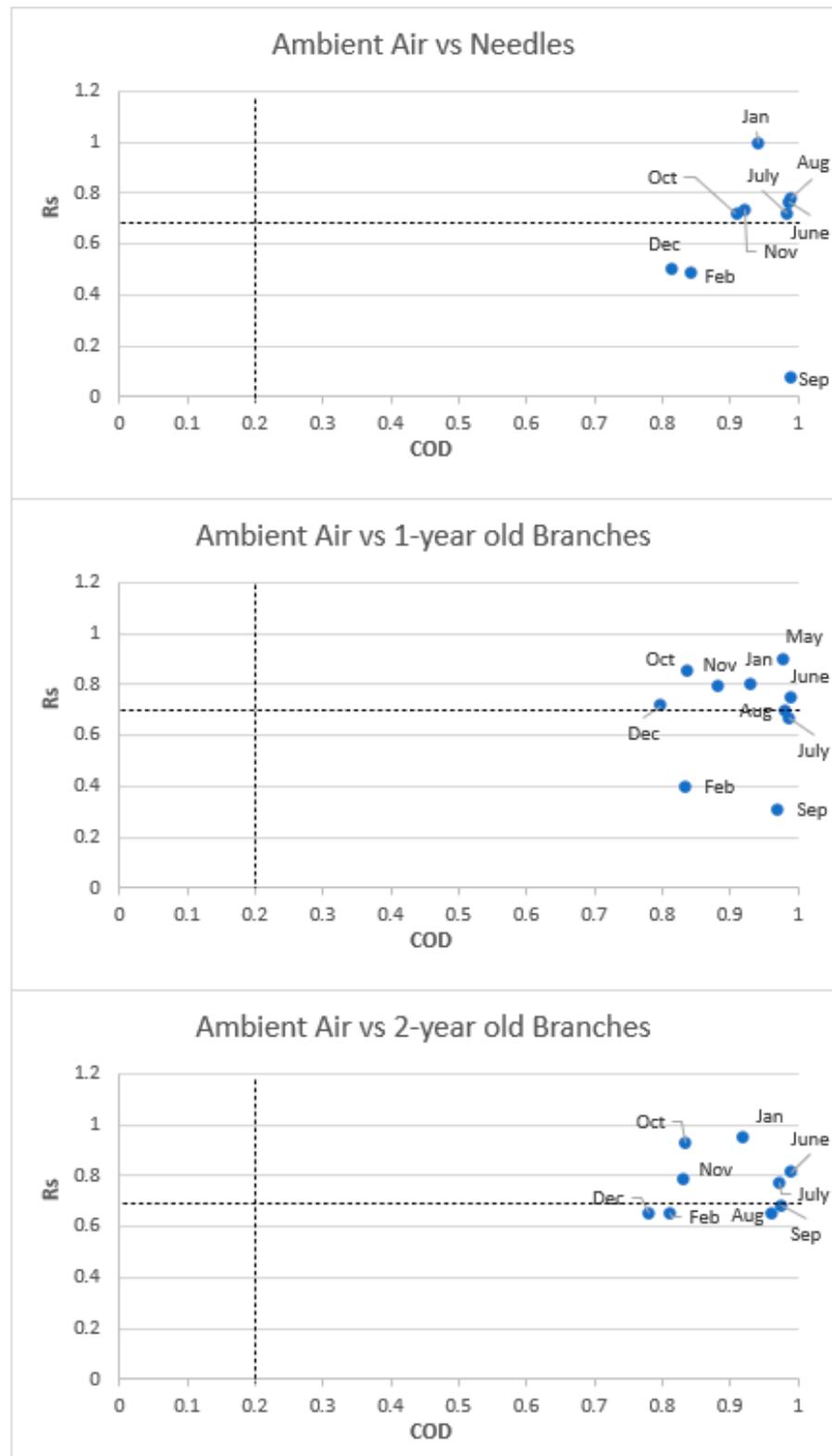
Figure 2. Correlation coefficient (R_s) and coefficient of divergence (COD) values of PAHs for the ambient air vs. tree components.
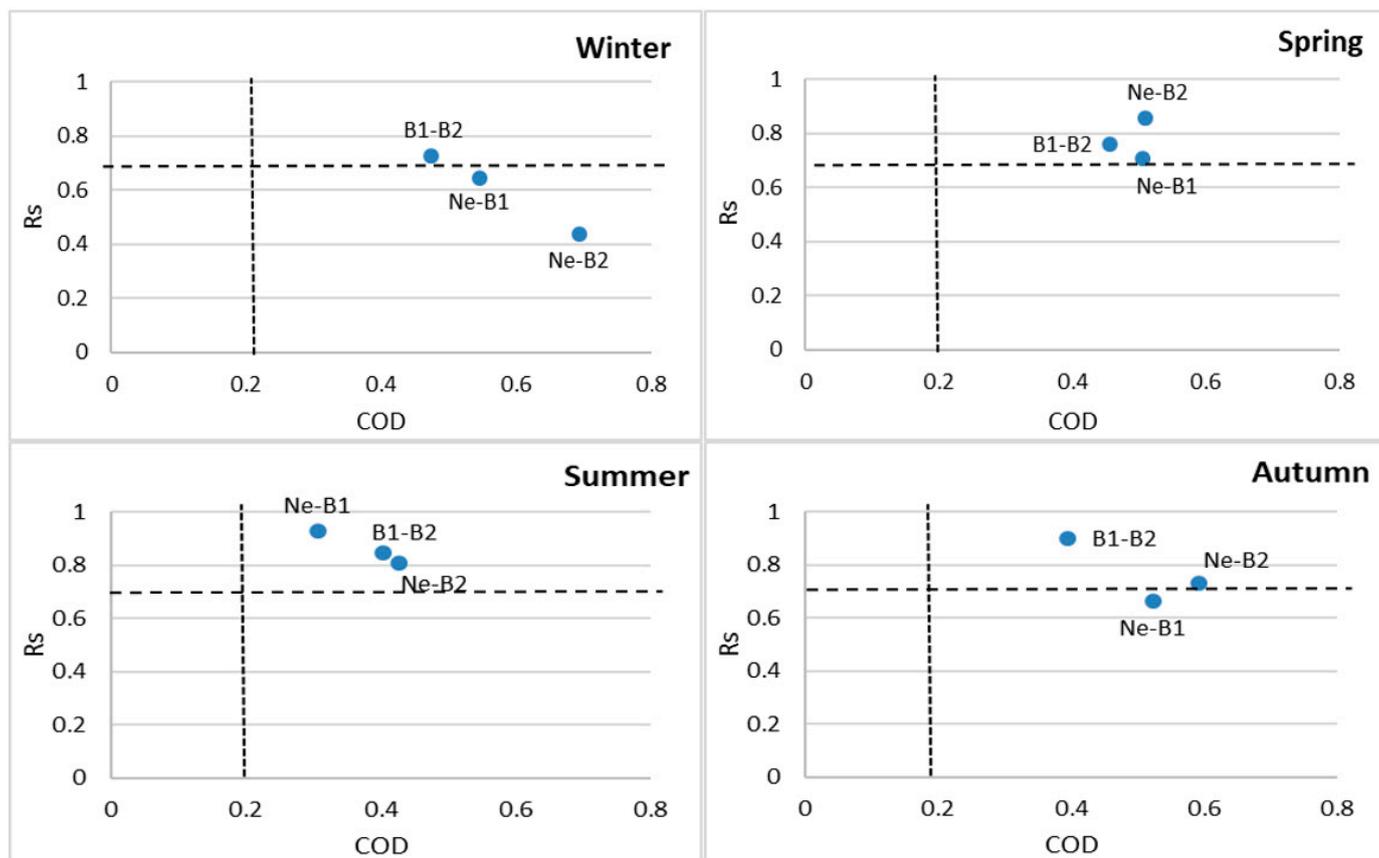
Figure 3. Correlation coefficient (Rs) and coefficient of divergence (COD) values of PAHs for tree components in all seasons. Note: Ne, B1 and B2 refer to the needle, 1-year-old branch and 2-year-old branch, respectively.

Table 2. The correlation coefficient (Rs) values.

Season	Variables	$C_{branch\ (1-year-old)}$	$C_{branch\ (2-year-old)}$
Winter	C_{needle}	0.855 **(0.002)**	0.600 (0.088)
	$C_{branch\ (1-year-old)}$		0.855 **(0.001)**
Spring	C_{needle}	0.790 **(0.002)**	0.776 **(0.003)**
	$C_{branch\ (1-year-old)}$		0.958 **(<0.001)**
Summer	C_{needle}	0.930 **(<0.001)**	0.929 **(<0.001)**
	$C_{branch\ (1-year-old)}$		0.967 **(<0.001)**
Autumn	C_{needle}	0.698 **(0.008)**	0.841 **(<0.001)**
	$C_{branch\ (1-year-old)}$		0.903 **(<0.001)**

Values in parentheses refer to '*p*' values. Bold values indicate that the *p* values are equal to or smaller than 0.05.

Considering the MMW PAH data, the tree components had lower COD values among themselves. For example, the COD values for the needle vs. 1-year-old branch, needle vs.

2-year-old branch and 1-year-old branch vs. 2-year-old branch samples were 0.374, 0.368 and 0.279, respectively. This result indicated that tree components were affected by similar sources and they absorbed the PAHs similarly. Moreover, the COD values between air vs. tree components were also calculated and they were high. These values, for MMW PAH, were 0.950, 0.936 and 0.928 for air vs. needle, air vs. 1-year-old branch and air vs. 2-year-old branch samples, respectively. In terms of correlation values between tree components and air, the highest R_s values were calculated between 1-year-old vs. 2-year-old branch (0.775; <0.001) and air vs. 2-year-old branch (0.790; <0.001) (Table 4).

Table 3. R_s values between air and tree components according to molecular weights of PAHs.

The Molecular Weight of PAHs	Variables	C_{needle}	$C_{branch\ (1-year-old)}$	$C_{branch\ (2-year-old)}$
LMW (light molecular weight)	C_{air}	0.228 (0.363)	0.274 (0.243)	0.370 (0.119)
MMW (medium molecular weight)	C_{air}	0.436 (0.020)	0.524 **(0.005)**	0.790 **(<0.001)**
HMW (heavy molecular weight)	C_{air}	0.067 (0.736)	−0.186 (0.354)	−0.381 (0.089)

Values in parentheses refer to '*p*' values. Bold values indicate that the *p* values are equal to or smaller than 0.05.

Table 4. R_s values among each tree component pair.

The Molecular Weight of PAHs	Variables	$C_{branch\ (1-year-old)}$	$C_{branch\ (2-year-old)}$
LMW (light molecular weight)	C_{needle}	0.813 **(<0.001)**	0.729 **(<0.001)**
	$C_{branch\ (1-year-old)}$		0.857 **(0.001)**
MMW (medium molecular weight)	C_{needle}	0.414 **(0.018)**	0.541 **(0.001)**
	$C_{branch\ (1-year-old)}$		0.775 **(<0.001)**
HMW (heavy molecular weight)	C_{needle}	0.531 **(0.001)**	0.229 **(0.223)**
	$C_{branch\ (1-year-old)}$		0.428 **(0.013)**

Values in parentheses refer to '*p*' values. Bold values indicate that the p values are equal to or smaller than 0.05.

3.1.2. Diagnostic Ratios

Diagnosis ratios among some PAHs are considered to be the "fingerprint" of an emission source, as it presents specific characteristics in the form of molecular patterns versus their mechanism of formation [57,58]. Different PAH ratios are examined to evaluate some of the PAH sources or source groups. The sampling point was exposed to many sources, such as industrial zone, residential areas and highways. Table 5 summarizes the diagnosis rates calculated according to the ambient air values.

The Indeno/(Indeno+BghiP) ratio can be used to distinguish between diesel and gasoline vehicle emissions [6,59–61], as well as to evaluate grass, wood and coal combustion emissions [62]. According to the calculated Indeno/(Indeno+BghiP) ratios, changing between 0.08 and 0.61, the contribution of petrogenic and pyrolytic emissions was observed throughout the year (Table 5). Industrial, domestic and traffic-related sources around the sampling point were detected as important factors based on these findings. When the data for the spring (0.43 ± 0.15) and summer (0.43 ± 0.05) months were evaluated, the gasoline-related sources became dominant as the heating-related sources decreased [62].

Table 5. Diagnostic ratios of atmospheric PAHs.

Diagnostic Ratio	Value	Potential Source	Reference	This Study
Indeno/ (Indeno+BghiP)	<0.2	Petrogenic	[63]	0.08–0.61
	>0.5	Grass, wood and coal combustion	[6]	
	0.2–0.5	Petroleum combustion	[6]	
	0.4	Gasoline	[64]	
	0.3–0.7	Diesel engine	[60]	
	0.56	Coal	[65]	
	0.48	Coal combustion	[62]	
	0.19	Diesel vehicles	[62]	
	0.32	Gasoline vehicles	[62]	
	0.32	Natural gas combustion	[62]	
	0.36	Oil combustion	[62]	
	0.35	Vegetation combustion	[62]	
	0.42	Wood combustion	[62]	
BaA/(BaA+Chr)	0.2–0.35	Coal combustion	[66]	0.55–1.00
	>0.35	Vehicle emission	[67]	
	<0.2	Petrogenic	[63]	
	>0.35	Combustion	[63]	
	0.53	Vehicle emission	[57]	
	0.73	Diesel engine	[68]	
	0.79	Wood burning	[57]	
	0.46	Coal combustion	[62]	
	0.65	Diesel vehicles	[62]	
	0.50	Gasoline vehicles	[62]	
	0.39	Natural gas combustion	[62]	
	0.50	Oil combustion	[62]	
	0.59	Wood combustion	[62]	
Phe/Ant	<10	Pyrogenic	[69]	1.00–48.19
	>15	Petrogenic	[69]	
BaP/BghiP	<0.6	Non-traffic emissions	[66]	0.38–1.36
	>0.6	Traffic emissions	[66]	
Fluo/(Fluo+Py)	<0.5	Petrol emissions	[66]	0.61–0.66
	>0.5	Diesel emissions	[70]	
BaA/Chr	<0.2	Petrogenic,	[63]	1.21–2.97
	>0.35	Combustion	[63]	
	0.20–0.35	Petroleum or combustion	[63]	
	<0.35	Coal combustion	[67]	
	>0.35	Vehicle emission	[67]	
	>0.4	Fresh particles,	[71]	
	<0.4	Ageing (photolysis)	[71]	
LMW/HMW	<1	Pyrolytic	[72]	0.74–2.61
	>1	Petrogenic	[72]	
ΣCOMB/ ΣPAHs	>0.49			0.28–0.57
	0.34	Industrial site	[73]	
	0.7–0.73	Remote site	[73]	
		Combusiton source:	[74]	
		Non-catalyst-equipped vehicles		
	0.19–0.39	Petrogenic	[60]	
		Pyrogenic	[68]	
	>0.7	Non-catalyst-equipped	[68]	
	0.41	Catalyst-equipped	[68]	
	0.51	Heavy duty diesel trucks	[68]	
	0.30	Coal burning	[75]	
	0.8–0.9			

Similarly, BaA/(BaA+Chr) ratios also revealed the contribution of vehicle emissions and combustion in our study [59,67]. Phe/Ant ratio is one of the most frequently used combinations that distinguish pollutant sources from pyrogenic (combustion source) and petrogenic (unburned petroleum product) [76]. In this study, when the seasonal Phe/Ant ratio was evaluated, pyrogenic sources were dominant in winter (5.36 ± 7.55). The diagnostic ratio of BaP/BghiP is used to determine the significance of non-traffic emissions (<0.6) [77]. The values calculated in our study showed that traffic emissions were significant in both summer and autumn (0.71 ± 0.28 and 0.98 ± 0.54), respectively. Fluo/(Fluo+Py) values greater than 0.50 are reported for diesel emissions, while values less than 0.50 are indicative of gasoline emissions [70]. In the sampling region, petroleum emissions (0.20 ± 0.35 in summer, 0.43 ± 0.37 in autumn) dominate according to Fluo/(Fluo+Py) ratios.

Diagnostic ratios of PAH can also provide information about the aging of air masses [6,71,78]. If BaA/Chr ratios are higher than 0.4, it indicates the presence of fresh emissions and relatively little photolysis of the air mass, ratios below 0.4 indicate that the primary sources of PAHs are not local, the air masses are old, that is, convection from other regions [71]. In evaluating this ratio, it has been shown that even transporting PAHs more than a few kilometers could be sufficient to cause a change in source identification interpretation [79]. Differences in travel distances between pairs of PAHs suggest that the use of molecular detection rates for source identification requires careful consideration. BaA/(BaA+Chr) ratios were found to be the most robust diagnostic ratio for air concentrations among molecular diagnostic rates [79]. The results of the present study showed that fresh emissions (2.29 ± 0.70 in winter, 1.23 ± 0.02 in autumn) were released, as expected, from local sources. When the BaA/(BaA+Chr) ratio was evaluated to determine the source of the emissions, it also indicated combustion and traffic emissions (0.69 ± 0.70 in winter, 0.55 ± 0.004 in autumn).

According to the literature, LMW (light molecular weight)/HMW(heavy molecular weight) <1 is an indicator of pyrogenic sources such as fossil fuel or incomplete combustion of wood, while LMW/HMW> 1 becomes an indicator of a petrogenic source, including oil (split oil) or petroleum products [80,81]. In this study, LMW/HMW ratios in the ambient air samples showed a significant dominance of petrogenic sources in winter and autumn with values of 1.92 ± 0.62 and 1.92 ± 0.53, respectively, while a value close to 1 in summer and spring (1.05 ± 0.27 and 1.06 ± 0.44, respectively) revealed the effect of both petrogenic and pyrogenic sources.

Sojinu et al. (2010) [82] conducted studies on 11 plants from the Delta State of Nigeria between April and July 2008 for biomonitoring studies of PAHs. They used Phe/Ant, Flt/Pyr to identify PAH sources and BaA/(BaA+Chr) and Indeno/(Indeno+BghiP) ratios for a more detailed distinction. The most commonly used combination to distinguish between pyrogenic and petrogenic sources is the Phe/Ant ratio to the Flt/Pyr ratio [52,76]. Phe/Ant ratios below 10 and Flt/Pyr ratios above 1 indicate pyrogenic sources [69]. In our study, Phe/Ant ratios varied between 2.23 and 33.23 in pine needles, while this ratio changed from 7.09 to 16.81 and from 4.13 to 25.36 in 1- and 2-year-old pine branches, respectively. High Phe/Ant ratios in pine needles can be attributed to the degradation of Ant in pine needles or the presence of more traveled sources [52,74]. While Flt/Pyr ratios were between 0–9.23 in pine needles and varied between 0.22 and 2.41, and 0.35 and 3.07 in 1- and 2-year-old pine branches, respectively. According to these ratios, pyrolytic and mixed sources were dominant in pine branches and needles as PAH sources while petrogenic and indeterminate sources could be evaluated in some months (Figure 4). When the air samples in the months with uncertain sources were examined, it was revealed that the sources could be defined as pyrolytic and mixed sources in these months.

Indeno/(Indeno+BghiP) ratios (Table 6) in pine needles ranged from 0 to 1.00. This ratio was between 0.31–1.00 and 0–0.56 in 1- and 2-year-old pine branches, respectively. BaA/(BaA+Chr) ratios vary between 0–1.00, 0–0.93 and 0–0.70 in pine needles, 1- and 2-year-old branches, respectively. BaA/(BaA+Chr) and Indeno/(Indeno+BghiP) results indicated that most of the sources can be considered as combustion and mixed while the rest can be considered petroleum-related (Figure 5).
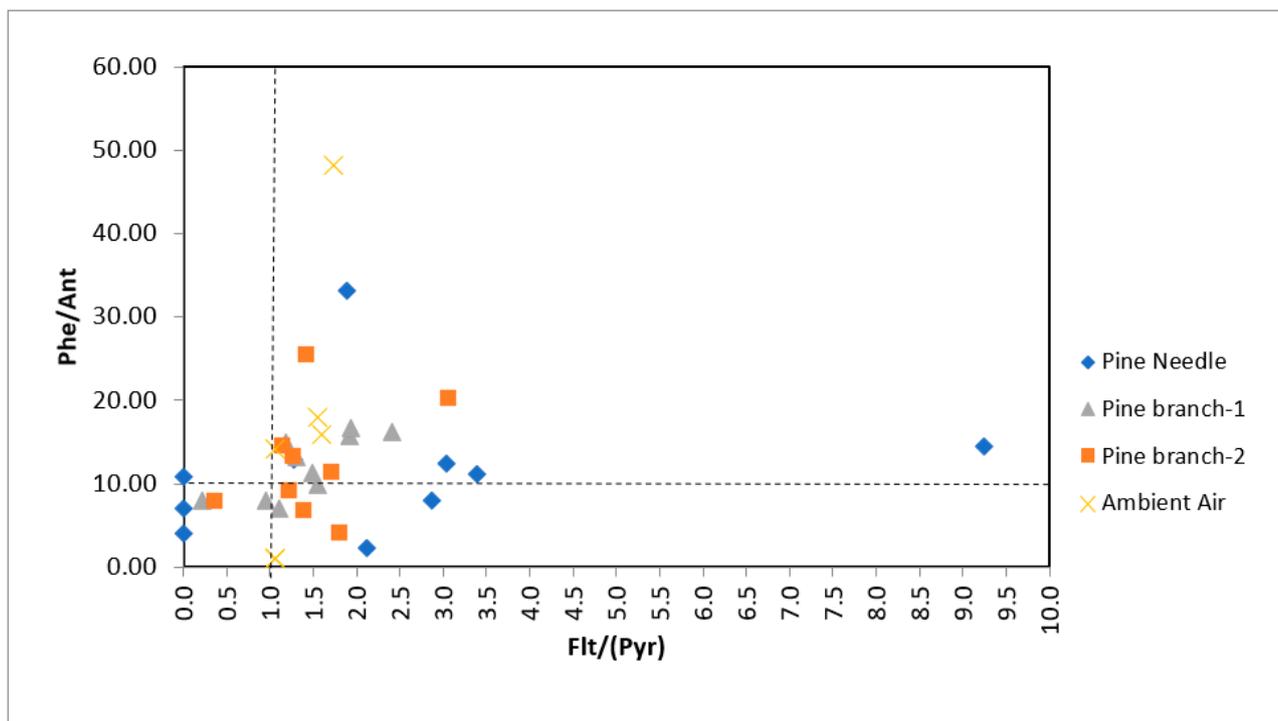
Figure 4. Phe/Ant ratios against Flt/Pyr ratios for the tree components and ambient air. Note: Pine branch-1 and Pine branch-2 refer to 1-year-old and 2-year-old branches.

When the Flt/(Flt+Py) and BaA/(BaA+Chr) ratios are examined (Figure 5), it is clear that the PAH sources in pine needles and pine branches for this study are mainly coming from combustion. In addition to this, it is clear that there is also a petroleum-derived PAH distribution. When examined in terms of ambient air data, it is seen that all data are caused by combustion. A parallel result emerges when the Indeno/(Indeno+BghiP) and BaA/(BaA+Chr) ratios are examined.

The ratio of ΣCOMB (specific main combustion compounds including Flt, Pyr, BaA, Chry, BbF, BkF, BaP, Indeno and BghiP) to the total PAHs (ΣCOMB/ΣPAHs) in pine needles varies between 0.49 and 0.65 in industrial areas, while in remote areas this ratio drops to 0.34 [73]. The high ΣCOMB/ΣPAH ratios in our site (Figure 6) represent PAHs released from combustion [83]. The ΣCOMB/ΣPAHs is also an important ratio used to distinguish petrogenic additives and combustion sources [68,70,74,84–86], and the value of 0.41 represents a non-catalyst equipped vehicle, 0.51 catalyst-equipped vehicle and 0.3 heavy-duty diesel trucks. On the other hand, Cecinato et al. (1999) [75] stated that this value being 0.8–0.9 indicates coal burning. In our study, while the ΣCOMB/ΣPAHs values (Table 6) in pine needles were in the range of 0.09–0.80 with an average of 0.40 ± 0.19, a similar ratio, calculated for the 1- and 2-year-old branches and ambient air (0.47 ± 0.19, 0.41 ± 0.15 and 0.41 ± 0.10, respectively), reveals the contribution of the mixed PAH source distribution, where the industrial region, petrogenic sources and coal burning are also influential (Figure 6).

BFs (BbF, BkF and BjF)/BghiP ratios are utilized to distinguish combustion sources [87]. BFs/BghiP value of 7.11–11.2 shows the effect of industrial furnaces [88]. The values obtained in this study were 9.59 ± 12.67 for needles, 2.57 ± 1.33 and 1.83 ± 2.26 for 1- and 2-year-old pine branches, respectively. These values support industrial activities and traffic contributions. While the Flt/(Flt+Pyr) ratio ranged from 0 to 0.90 and in pine needles, values between 0.18–1.00 and 0.26–1.00 were calculated for 1- and 2-year-old pine branches, respectively. Flt/(Flt+Pyr) ratios above 0.50 are characteristic of grass, wood or coal-burning [23,63,73]. Considering the location of our sampling point, the determined results are reasonable.
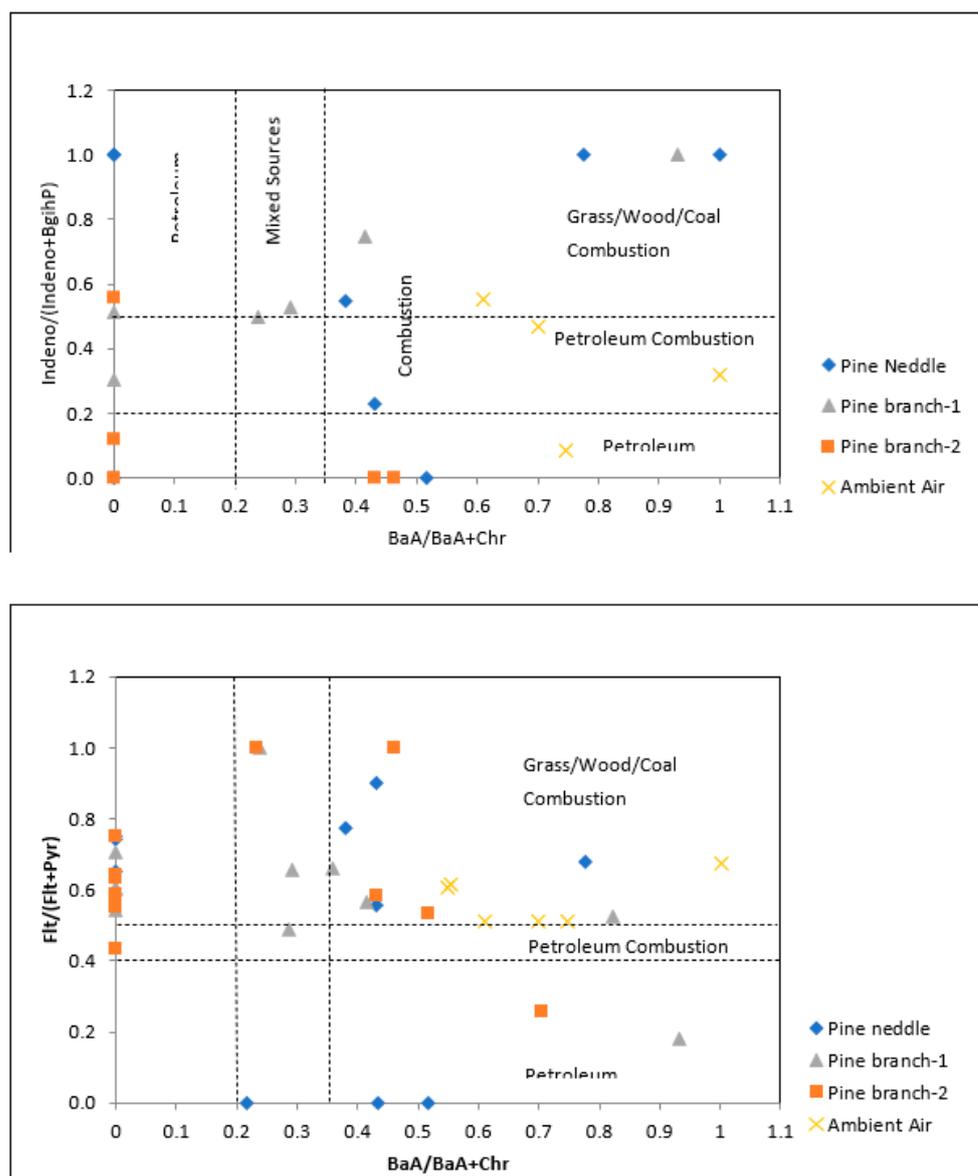
Figure 5. PAH cross-plots for the ratios of Indeno/(Indeno+BghiP) and Flt/(Flt+Py) against BaA/(BaA+Chr) ratios in the studied tree components and ambient air. Note: Pine branch-1 and Pine branch-2 refer to 1-year-old and 2-year-old branches.

3.1.3. Principle Component Analysis (PCA)

In addition to diagnostic ratios, principal component analysis (PCA) is employed to estimate the relative distribution of each source and identify the primary sources of PAH emissions [66]. The standardized distribution of various factors to different concentrations of PAHs is given in Tables S1 and S2. Each principal component is obtained with different factor loadings and determined and evaluated as possible pollution source indicators. In association with PAH, those with component weights ≥0.25 were evaluated as criteria [27]. In this assessment, those with component weights of 1–0.75 were strong; 0.75–0.50 were moderate and 0.5–0.3 indicated weak effects [89,90].

The PCA results for ambient air, pine needles and branches are given in Tables S1 and S2. PCA determined two components for ambient air data. Two factors explained the majority of the variance (91.84%). PC1 was responsible for 63.81% of the variance and mainly had a substantial load for PAH compounds such as Ace, Fluo, Phe, BaA, Chr, BbF, BkF, BaP, Indeno and BghiP, while compounds Flt, Pyr and DahA had a moderate load. A load of Ace, Fluo and Phe compounds characterizes wood, coal and biomass

combustion [91]. The predominance of 5- and 6-ring PAHs is an indicator of gasoline traffic load and incomplete combustion [27]. In previous studies, BaA, BaP and BghiP have been reported to be markers of motor vehicle emissions and oil combustion [66,92–94]. According to the 2016 Bursa Province environmental status report [95], it has been stated that there was illegal construction near the sampling point (Yolçatı district). Illegal structures are not allowed to use natural gas because they have no permission to be connected to the natural gas distribution network. In the same report, it was stated that SO_2 values were high, especially as a result of burning coal for heating purposes. While this contributes to light PAH compounds, the highway was also thought to contribute significantly to heavy PAH compounds. Then, this source could be defined as a mixed source (traffic + heating) indicator of road traffic and combustion for heating purposes.
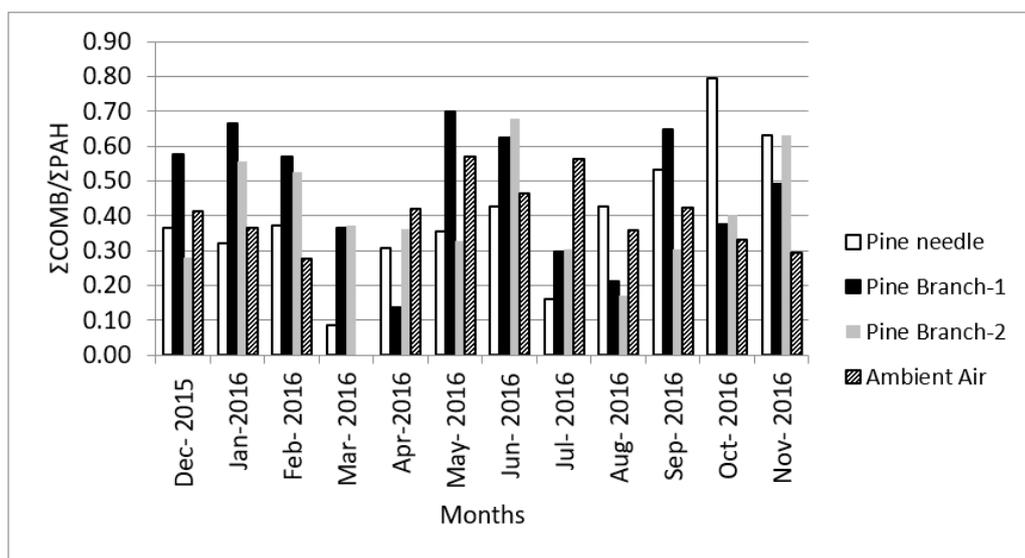

Figure 6. ΣCOMB/ΣPAHs ratios for the tree components and ambient air. Note: Pine branch-1 and Pine branch-2 refer to 1-year-old and 2-year-old branches.

The second component explained with 28.03%, PAH compounds such as BaP and DahA have a moderate load, while Ace, Fluo, Indeno compounds have a light load. BaP, DahA and Indeno compounds originate from vehicle (gasoline and diesel) exhaust emissions [102,103]. Therefore, this component explains the traffic emissions.

As a result of the PCA analysis, the characteristic sources of variances overlap with the sources represented in the diagnosis rates, explained in the above section. It has been revealed that both pyrogenic and petrogenic sources were dominant in diagnosis rates, the dominance of PAHs due to heating increases in cold weather; besides, the contribution of traffic emissions was quite large and there was a variance representing the industrial zone located near the sampling point.

Five components (90.76%) representing the majority of the variance were determined by PCA analysis in pine needles. The high number of components in needles may be due to fluctuations in PAH concentrations in the needle being more affected by biological processes [104] than concentrations in air. The first group component PC1 is responsible for 30.5% of the variance and the main component is BkF (0.805), BaP (0.941), Indeno (0.866) and DahA (0.797) compounds. Syed et al. (2017) [105] stated that a source with a high concentration of BghiP, Indeno and BaP might originate from combustion due to the predominance of heavy PAHs. Many researchers have stated that BaP, Indeno and DhaA are released from vehicle emissions [106–108] and these compounds can be defined as emissions released from gasoline vehicles [109–111] in particular. Therefore, the PC1 component is considered to represent vehicle (gasoline and diesel) emissions.

Table 6. Diagnostic ratios of PAHs in pine needles/branches.

Diagnostic Ratio	Value	Potential Source	Reference	This Study
Indeno/(Indeno+BghiP)	>0.50	Solid fuel (Grass, wood or coal) combustion	[96,97]	0–1 (Needle)
				0.31–1 (1-year-old branches)
	<0.20	Asphalt, tire particles, motor oils and uncombusted fuels, petrogenic	[63,98,99]	0–0.56 (2-year-old branches)
BaA/(BaA+Chr)	0.2–0.35	Petroleum and fuel oil combustion,	[6]	0–1(Needle) 0–0.93 (1-year-old branches)
	>0.35	Solid fuel (Grass, wood or coal) combustion	[6]	0–0.70 (2-year-old branches)
Flt/(Flt+Py)	<0.40	Petroleum	[63]	0–0.90 (Needle)
	>0.50	Solid fuel (Grass, wood or coal) combustion	[23,96,97,100]	0.18-1 (1-year-old branches)
	0.40–0.50	Fossil fuel combustion petroleum and fuel oil combustion	[6]	0.26–1 (2-year-old branches)
ΣCOMB/ΣPHs	>0.49	Industrial site	[101]	
	0.34	Remote site	[101]	0.09–0.80 (Needle)
	0.7–0.73	Combustion source: non-catalyst-equipped vehicles	[74]	
	0.19–0.39	Petrogenic	[60]	0.14–0.70 (1-year-old branches)
	>0.7	Pyrogenic	[68]	
	0.41	non-catalyst-equipped	[68]	
	0.51	catalyst-equipped	[68]	0.17–0.68 (2-year-old branches)
	0.30	heavy duty diesel trucks	[68]	
	0.8–0.9	Coal burning	[75]	

The second component with a high Chr compound and moderate Ant, Pyr and BbF loadings, explaining the total variance at the rate of 24.96%. BaA, Chr and BbF are used as specific indicators of coal combustion in industries [112–115]. Chr has also been stated as the natural gas emission characteristic in previous studies [60,116,117] and the steel industry emission together with BaA [115]. While diesel emissions are rich in Flt, Chr and Pyr, Ant, Phen, BaP, Flt and Pyr are evaluated as markers of wood-burning [115]. In another study, Fla, Pyr, Phe, Ant and BaA were evaluated as coal combustion profiles [102]. BbF compound originates from vehicle (gasoline and diesel) exhaust emissions [103]. This component represents a mixed source as an indicator of industrial and domestic heating (coal, natural gas) combustion and traffic emissions.

PC3 variance (17.31%), with moderate loading of Ace, Fluo, Phe and BaA compounds, characterizes wood and coal combustion [58], as well as being the main compounds emitted from coke ovens (Fluo, Ace, Nap, Phe, Ant ve Flt)[118,119]. This occurrence reveals the industrial zone's influence.

The fourth source with moderate Anth and weak Pyr loading explains 9.95% of the data variance. Ant refers to a petrogenic source (unburned) [107,120] and it is treated more as vehicle emissions in the source allocation [120]. Anth has been evaluated as an indicator of wood burning in some sources [121]. Pyr is an indicator of gasoline vehicle emissions [119]. Therefore, this component is thought to represent vehicle emissions as in PC1. In the PCA analysis evaluation, the fifth source (8.05%) with moderately positive

BghiP loading and weak Fluo, Phe, Anth and Pyr (coal, wood and diesel combustion emissions) [119] loadings can be evaluated as combustion emissions.

On the other hand, four components represent a significant part of the variance (84.56%) in 1-year branches with PCA analysis performed on pine branches. The PC1 component explained 28.43% of the total variance. In the first group of components (PC1), Phe, Ant, Pyr, Chr and Flt compounds have a high load. Phe, Ant, Pyr, Chr and Flt compounds have a high load on PC1. Studies by Ciaparra et al. (2009) [122] and Jang et al. (2013) [123] indicated that a similar profile formed by Ant, BaA and Pyr derivatives partially reflects emissions from the steel industry. BaA, Chr and BbF are used as specific indicators of coal combustion in industries [112–114]. Phe, Ant and Flt compounds are the main components emitted from coke ovens [119]. These compounds are thought to originate from industrial emissions from the industrial area near the sampling point.

The second component has high Ace and Indeno and moderate Fluo, BbF, DahA and BghiP and weak Phe loading, explaining 24.17% of the total variance. Indeno originates from vehicle (gasoline and diesel) exhaust emissions [102]. BbF, BghiP and Indeno come from vehicle emissions [119], Indeno, BghiP and DahA are typical traffic emissions [91,124], Ace, Fluo and Phe compounds load wood, coal and characterize biomass combustion [58,91]. Therefore, this component is a mixed source representing pyrogenic and petrogenic sources.

The third component (21.1%) has a weak load of Flt and BghiP. This composition is typically the source of vehicle emissions (gasoline and diesel) [103]. However, some researchers [125] stated that Flt is an indicator of coal combustion. This variance indicates the vehicle and the source of combustion. The last component (PC4), which explains 10.87% of the variance, has strong BaP (0.828) and weak Anth and Indeno loadings. While BaP is an important indicator of petroleum and diesel emissions [80], Indeno and DahA come from gasoline vehicle emissions [108–111], Anth indicates a petrogenic source [107,120]. Therefore, the PC4 component is considered to represent vehicle emissions.

In 2-year-old pine branches, 88.19% of the variance is represented by five components. When the compound loads were evaluated in the PCA analysis, sources similar to the ones detected with 1-year-old pine branches emerged. PC1 (31.07%) component, which has a high load for Phe (0.895) and Flt (0.91) compounds and moderately loaded for Ace, Anth, Pyr and Chr compounds, is a component of the steel industry and pyrolytic sources [126] can be considered as a mixed source representing together.

The second component, which explains 23.61% of the total variance, has high BkF (0.824) and BbF (0.772) compounds and moderate BaA, Chr and BaP loads. While high loadings of BkF have been associated with coal burning in previous studies [91] and BbF with diesel vehicle emissions [119], BaP and BaA are important indicators for petroleum and diesel emissions [80]. In another study, Anth, BaA, Chr and BaP were evaluated as biomass and coal combustion indicators [124,127]. This component can be considered a mixed source.

The other two components explaining the variance at 15.75% (PC3) and 10.54% (PC4) rates were also associated with moderate Fluo (0.637), BaA (0.535), DahA (0.746) and moderately Indeno (0.63), BghiP (0.543) for PC3 and PC4, respectively. Fluo refers to combustion (coal, wood and diesel) and vehicle emissions [119], DahA [109] and Indeno [11,128] are defined by gasoline emissions. Therefore, these two components are considered to represent vehicle emissions.

The fifth component, explaining 7.23% of the total variance, was associated with moderate Pyr and weakly Ace, Anth, Pyr, BaA, Chr and Indeno compounds. Ace and Anth comes from burning source [91], and the profile of Anth, Pyr and BaA derivatives reflects emissions from the steel industry [122,123]. In this case, this component can indicate the effect of the industrial zone.

Generally, it was determined that ambient air, pine needles and branches reflect the relative distribution of all possible pollutants in the sampling area. Pine needles and branches have been a good tool to reveal the industrial emission source and the traffic effect.

3.2. Carcinogenic Potential

Sixteen PAHs have been listed among priority pollutants by the United States Environmental Protection Agency (US-EPA). Adverse health effects (carcinogens, mutagens and teratogens) from PAH exposure are a major concern [38]. The International Agency for Research on Cancer (IARC) has classified some of the PAH strains in terms of carcinogenic effects. The most important health effect that can be expected if PAHs are inhaled is the risk of lung cancer [41]. The concentrations of PAH species were calculated as BaP equivalent concentrations (BaPeq) using TEF values [129] of each PAH type in order to reveal the carcinogenic potential that may occur as a result of inhalation of atmospheric PAHs. In this study, BaP equivalent concentrations (BaP$_{eq}$) Σ_{14}BaP$_{eq}$ values range from 0.006 to 0.71 ng/m^3 throughout the year (Table S3). These values are below both the international standard value (10 ng/m^3) and the WHO standard value (1 ng/m^3) [130]. Average values of Σ_{14}BaP$_{eq}$ were calculated as 0.33 ± 0.18, 0.02 ± 0.02, 0.05 ± 0.03 and 0.35 ± 0.33 ng/m^3 in winter, spring, summer and autumn samples, respectively. The highest Σ_{14}BaP$_{eq}$ data were reached in winter and autumn.

Lifetime lung cancer risk was calculated using the following formula [131]:

$$Lifetime\ lung\ cancer\ risk = BaPeq\left(\frac{ng^3}{m}\right) \times UR$$

where UR is the respiratory unit risk of exposure to BaP (the theoretical upper limit probability of contracting cancer when exposed to BaP at a concentration of one nanogram per cubic meter over a 70-year lifetime) [132,133]. In this study, UR is equal to 8.7×10^{-5} per ng/m^3 was taken based on an epidemiology study according to the World Health Organization (WHO) [134].

The calculated lung cancer risk values are 2.85×10^{-5}, 1.64×10^{-6}, 4.40×10^{-6} and 3.02×10^{-5} in winter, spring, summer and autumn samples, respectively. These risk values calculated for the study area indicate that US EPA poses cancer risks because it exceeds the guideline safety value of 10^{-6} (a cancer case in a population of one million people for life) [131,135–137]. These values indicate that the risk of epidemiological lung cancer as a result of lifetime exposure to total ambient PAHs is significant and should be considered in maintaining health in the future. In winter and autumn, lung cancer risk values increased by 6.49 and 6.88 times, respectively, compared to the summer season. Risk values increase in parallel with the increase in PAH concentrations caused by heating in the autumn and winter months. Cold seasons pose a higher potential risk to human health.

4. Conclusions

Ambient air, pine needles and branch samples were collected for a one-year period. Diagnosis ratios and PCA analyses applied to all data sets revealed that needles and branches could effectively detect and monitor all contaminant sources in the sampling area. As a result of the PCA analysis, the characteristic sources of variances coincide with the sources represented in the diagnosis ratios. It has been demonstrated that both pyrogenic and petrogenic sources are predominant in diagnosis ratios, PAHs caused by warming in a cold weather increase; besides, the contribution of traffic emission is quite large and there is a variance representing the industrial zone located near the sampling point. The calculated cancer risk values rise with the increase in pollutant concentrations depending on the heating in the autumn and winter months. In winter and autumn, lung cancer risk values increased by 6.49 and 6.88 times, respectively, compared to the summer season. Calculated risk values revealed that epidemiological lung cancer risk is important and should be considered in future health protection.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/atmos13111938/s1, Table S1. PCA analyses results for PAHs in the ambient air and pine needles; Table S2. PCA analyses results for PAHs in the one-year-old and two-year-old branches; Table S3. Total BaP equivalent concentrations (Σ14BaPeq) values in this study.

References

1. Abdallah, M.A.E.; Atia, N.N. Atmospheric concentrations, gaseous-particulate distribution, and carcinogenic potential of polycyclic aromatic hydrocarbons in Assiut, Egypt. *Environ. Sci. Pollut. Res.* **2014**, *21*, 8059–8069. [CrossRef] [PubMed]
2. Fasani, D.; Fermo, P.; Barroso, P.J.; Martín, J.; Santos, J.L.; Aparicio, I.; Alonso, E. Analytical method for biomonitoring of PAH using leaves of bitter orange trees (Citrus Aurantium): A case study in South Spain. *Water Air Soil. Pollut.* **2016**, *227*, 360. [CrossRef]
3. Salihoglu, N.K.; Salihoglu, G.; Tasdemir, Y.; Cindoruk, S.S.; Yolsal, D.; Ruken, O.; Karaca, G. Comparison of polycyclic aromatic hydrocarbons levels in sludges from municipal and industrial wastewater treatment plants. *Arch. Environ. Contam. Toxicol.* **2010**, *58*, 523–534. [CrossRef] [PubMed]
4. Sari, M.F.; Esen, F.; Tasdemir, Y. Biomonitoring and source identification of Polycyclic Aromatic Hydrocarbons (PAHs) using pine tree components from three different sites in Bursa, Turkey. *Arch. Environ. Contam. Toxicol.* **2020**, *78*, 646–657. [CrossRef]
5. Tasdemir, Y.; Esen, F. Urban air PAHs: Concentrations, temporal changes and gas/particle partitioning at a traffic site in Turkey. *Atmos. Res.* **2007**, *84*, 1–12. [CrossRef]
6. Tobiszewski, M.; Namieśnik, J. PAH diagnostic ratios for the identification of pollution emission sources. *Environ. Pollut.* **2012**, *162*, 110–119. [CrossRef] [PubMed]
7. Sanli, G.E.; Tasdemir, Y. Accumulations and temporal trends of Polychlorinated Biphenyls (PCBs) in olive tree components. *Environ. Geochem. Health* **2022**, *44*, 2577–2594. [CrossRef] [PubMed]
8. Simonich, S.L.; Hites, R.A. Importance of vegetation in removing polycyclic aromatic hydrocarbons from the atmosphere. *Nature* **1994**, *370*, 49–51. [CrossRef]
9. Srogi, K. Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: A review. *Environ. Chem. Lett.* **2007**, *5*, 169–195. [CrossRef]
10. Huckins, J.N.; Tubergen, M.W.; Manuweera, G.K. Semipermeable membrane devices containing model lipid: A new approach to monitoring the Bioavaiiability of Lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* **1990**, *20*, 533–552. [CrossRef]
11. Odabasi, M.; Dumanoglu, Y.; Ozgunerge Falay, E.; Tuna, G.; Altiok, H.; Kara, M.; Bayram, A.; Tolunay, D.; Elbir, T. Investigation of spatial distributions and sources of Persistent Organic Pollutants (POPs) in a heavily polluted industrial region using tree components. *Chemosphere* **2016**, *160*, 114–125. [CrossRef]
12. Ratola, N.; Amigo, J.M.; Oliveira, M.S.N.; Araújo, R.; Silva, J.A.; Alves, A. Differences between Pinus Pinea and Pinus Pinaster as bioindicators of polycyclic aromatic hydrocarbons. *Environ. Exp. Bot.* **2011**, *72*, 339–347. [CrossRef]
13. Oishi, Y. Comparison of pine needles and mosses as bio-indicators for polycyclic aromatic hydrocarbons. *J. Environ. Prot.* **2013**, *4*, 106–113. [CrossRef]
14. Piccardo, M.T.; Pala, M.; Bonaccurso, B.; Stella, A.; Redaelli, A.; Paola, G.; Valerio, F. Pinus Nigra and Pinus Pinaster needles as passive samplers of polycyclic aromatic hydrocarbons. *Environ. Pollut.* **2005**, *133*, 293–301. [CrossRef]
15. Ratola, N.; Lacorte, S.; Alves, A.; Barceló, D. Analysis of polycyclic aromatic hydrocarbons in pine needles by gas chromatography-mass spectrometry: Comparison of different extraction and clean-up procedures. *J. Chromatogr. A* **2006**, *1114*, 198–204. [CrossRef] [PubMed]
16. Simonich, S.L.; Hites, R.A. Organic pollutant accumulation in vegetation. *Environ. Sci. Technol.* **1995**, *29*, 2905–2914. [CrossRef]
17. Tomashuk, T.A.; Truong, T.M.; Mantha, M.; McGowin, A.E. Atmospheric polycyclic aromatic hydrocarbon profiles and sources in pine needles and particulate matter in Dayton, Ohio, USA. *Atmos. Environ.* **2012**, *51*, 196–202. [CrossRef]
18. Wang, D.; Tian, F.; Yang, M.; Liu, C.; Li, Y.-F. Application of positive matrix factorization to identify potential sources of PAHs in Soil of Dalian, China. *Environ. Pollut.* **2009**, *157*, 1559–1564. [CrossRef] [PubMed]

19. Zítková, J.; Hegrová, J.; Keken, Z.; Ličbinský, R. Impact of road salting on scots pine (*Pinus Sylvestris*) and Norway Spruce (*Picea Abies*). *Ecol. Eng.* **2021**, *159*, 106129. [CrossRef]

20. Cindoruk, S.S.; Sakin, A.E.; Tasdemir, Y. Levels of persistent organic pollutants in pine tree components and ambient air. *Environ. Pollut.* **2020**, *256*, 113418. [CrossRef]

21. De Nicola, F.; Maisto, G.; Prati, M.V.; Alfani, A. Temporal variations in PAH concentrations in *Quercus Ilex* L. (Holm Oak) leaves in an urban area. *Chemosphere* **2005**, *61*, 432–440. [CrossRef] [PubMed]

22. Hubai, K.; Kováts, N.; Sainnokhoi, T.-A.; Teke, G. Accumulation pattern of polycyclic aromatic hydrocarbons using *Plantago Lanceolata* L. as passive biomonitor. *Environ. Sci. Pollut. Res.* **2022**, *29*, 7300–7311. [CrossRef] [PubMed]

23. Lehndorff, E.; Schwark, L. Biomonitoring of air quality in the cologne conurbation using pine needles as a passive sampler—Part II: Polycyclic Aromatic Hydrocarbons (PAH). *Atmos. Environ.* **2004**, *38*, 3793–3808. [CrossRef]

24. Librando, V.; Perrini, G.; Tomasello, M. Biomonitoring of atmospheric PAHs by evergreen plants: Correlations and applicability. *Polycycl. Aromat. Compd.* **2002**, *22*, 549–559. [CrossRef]

25. Marsili, M.; Stracquadanio, M.; Trombini, C.; Vassura, I. The epicuticular wax of laurus nobilis leaves as a passive sampler of polycyclic aromatic hydrocarbons in ambient air. *Fresenius Environ. Bull.* **2001**, *10*, 26–30.

26. Meharg, A.A.; Wright, J.; Dyke, H.; Osborn, D. Polycyclic Aromatic Hydrocarbon (PAH) dispersion and deposition to vegetation and soil following a large scale chemical fire. *Environ. Pollut.* **1998**, *99*, 29–36. [CrossRef]

27. Kargar, N.; Matin, G.; Matin, A.A.; Buyukisik, H.B. Biomonitoring, status and source risk assessment of Polycyclic Aromatic Hydrocarbons (PAHs) using honeybees, pine tree leaves, and propolis. *Chemosphere* **2017**, *186*, 140–150. [CrossRef] [PubMed]

28. Tarricone, K.; Wagner, G.; Klein, R. Toward standardization of sample collection and preservation for the quality of results in biomonitoring with trees—A critical review. *Ecol. Indic.* **2015**, *57*, 341–359. [CrossRef]

29. Chefetz, B.; Xing, B. Relative role of aliphatic and aromatic moieties as sorption domains for organic compounds: A review. *Environ. Sci. Technol.* **2009**, *43*, 1680–1688. [CrossRef]

30. Zhang, M.; Zhu, L. Sorption of polycyclic aromatic hydrocarbons to carbohydrates and lipids of ryegrass root and implications for a sorption prediction model. *Environ. Sci. Technol.* **2009**, *43*, 2740–2745. [CrossRef] [PubMed]

31. van Drooge, B.L.; Garriga, G.; Grimalt, J.O. Polycyclic aromatic hydrocarbons in pine needles (*Pinus Halepensis*) along a spatial gradient between a traffic intensive urban area (Barcelona) and a nearby natural park. *Atmos. Pollut. Res.* **2014**, *5*, 398–403. [CrossRef]

32. Chrabąszcz, M.; Mróz, L. Tree bark, a valuable source of information on air quality. *Pol. J. Environ. Stud.* **2017**, *26*, 453–466. [CrossRef]

33. Odabasi, M.; Ozgunerge Falay, E.; Tuna, G.; Altiok, H.; Kara, M.; Dumanoglu, Y.; Bayram, A.; Tolunay, D.; Elbir, T. Biomonitoring the spatial and historical variations of Persistent Organic Pollutants (POPs) in an industrial region. *Environ. Sci. Technol.* **2015**, *49*, 2105–2114. [CrossRef]

34. Oishi, Y. Comparison of moss and pine needles as bioindicators of transboundary polycyclic aromatic hydrocarbon pollution in Central Japan. *Environ. Pollut.* **2018**, *234*, 330–338. [CrossRef] [PubMed]

35. Zhu, X.; Fan, Z.T.; Wu, X.; Meng, Q.; Wang, S.W.; Tang, X.; Ohman-Strickland, P.; Georgopoulos, P.; Zhang, J.; Bonanno, L.; et al. Spatial variation of volatile organic compounds in a "hot spot" for air pollution. *Atmos. Environ.* **2008**, *42*, 7329–7338. [CrossRef] [PubMed]

36. Farooq, S.; Ali-Musstjab-Akber-Shah Eqani, S.; Malik, R.N.; Katsoyiannis, A.; Zhang, G.; Zhang, Y.; Li, J.; Xiang, L.; Jones, K.C.; Shinwari, Z.K. Occurrence, finger printing and ecological risk assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in the Chenab River, Pakistan. *J. Environ. Monit.* **2011**, *13*, 3207–3215. [CrossRef] [PubMed]

37. Dvorská, A.; Lammel, G.; Klánová, J. Use of diagnostic ratios for studying source apportionment and reactivity of ambient polycyclic aromatic hydrocarbons over Central Europe. *Atmos. Environ.* **2011**, *45*, 420–427. [CrossRef]

38. 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. Pet.* **2016**, *25*, 107–123. [CrossRef]

39. IARC Working Group. Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. *IARC Monogr. Eval. Carcinog. Risks Hum.* **2010**, *92*, 1–853.

40. ACGIH (American Conference of Governmental Industrial Hygienists). *Polycyclic Aromatic Hydrocarbons (PAHs) Biologic Exposure Indices (BEI) Cincinnati*; American Conference of Governmental Industrial Hygienists: Cincinnati, OH, USA, 2005.

41. Kim, K.H.; Jahan, S.A.; Kabir, E.; Brown, R.J.C. A review of airborne Polycyclic Aromatic Hydrocarbons (PAHs) and their human health effects. *Environ. Int.* **2013**, *60*, 71–80. [CrossRef] [PubMed]

42. Esen, F.; Evci, Y.M.; Tasdemir, Y. Evaluation and application of a passive air sampler for Polycyclic Aromatic Hydrocarbons (PAHs). *J. Environ. Sci. Heal. Part A* **2017**, *52*, 1022–1029. [CrossRef] [PubMed]

43. Evci, Y.M.; Esen, F.; Taşdemir, Y. Monitoring of long-term outdoor concentrations of PAHs with passive air samplers and comparison with meteorological data. *Arch. Environ. Contam. Toxicol.* **2016**, *71*, 246–256. [CrossRef] [PubMed]

44. The University of Iowa. PUF-PAS Sampling Rate Model Interface. Available online: http://s-iihr41.iihr.uiowa.edu/pufpas_model/ (accessed on 28 April 2021).

45. Schuster, J.K.; Harner, T.; Eng, A.; Rauert, C.; Su, K.; Hornbuckle, K.C.; Johnson, C.W. Tracking POPs in global air from the first 10 years of the GAPS network (2005 to 2014). *Environ. Sci. Technol.* **2021**, *55*, 9479–9488. [CrossRef] [PubMed]

46. 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.* **2021**, *194*, 110508. [CrossRef]

47. Esen, F.; Cindoruk, S.S.; Taşdemir, Y. Ambient concentrations and gas/particle partitioning of polycyclic aromatic hydrocarbons in an urban site in Turkey. *Environ. Forensics* **2006**, *7*, 303–312. [CrossRef]

48. Vardar, N.; Tasdemir, Y.; Odabasi, M.; Noll, K.E. Characterization of atmospheric concentrations and partitioning of PAHs in the Chicago atmosphere. *Sci. Total Environ.* **2004**, *327*, 163–174. [CrossRef]

49. Birgul, A.; Tasdemir, Y. Concentrations, gas-particle partitioning, and seasonal variations of polycyclic aromatic hydrocarbons at four sites in Turkey. *Arch. Environ. Contam. Toxicol.* **2015**, *68*, 46–63. [CrossRef]

50. Eker, G. Bursa'nin Zeytinlik Arazilerindeki Topraklarda Poliaromatik Hidrokarbon (Pah) Konsantrasyonlarinin Bölgesel Değişimi. *J. Fac. Eng. Archit. Gazi Univ.* **2017**, *32*, 607–616. [CrossRef]

51. Fernández-Varela, R.; Ratola, N.; Alves, A.; Amigo, J.M. Relationship between levels of polycyclic aromatic hydrocarbons in pine needles and socio-geographic parameters. *J. Environ. Manage* **2015**, *156*, 52–61. [CrossRef]

52. Ratola, N.; Amigo, J.M.; Alves, A. Levels and sources of PAHs in selected sites from portugal: Biomonitoring with Pinus Pinea and Pinus Pinaster needles. *Arch. Environ. Contam. Toxicol.* **2010**, *58*, 631–647. [CrossRef]

53. Çalişkan Eleren, S.; Tasdemir, Y. Levels, distributions, and seasonal variations of Polycyclic Aromatic Hydrocarbons (PAHs) in ambient air and pine components. *Environ. Monit. Assess* **2021**, *193*, 253. [CrossRef] [PubMed]

54. Bano, S.; Pervez, S.; Chow, J.C.; Matawle, J.L.; Watson, J.G.; Sahu, R.K.; Srivastava, A.; Tiwari, S.; Pervez, Y.F.; Deb, M.K. Coarse Particle (PM10–2.5) source profiles for emissions from domestic cooking and industrial process in Central India. *Sci. Total Environ.* **2018**, *627*, 1137–1145. [CrossRef] [PubMed]

55. Liu, Y.; Yan, C.; Ding, X.; Wang, X.; Fu, Q.; Zhao, Q.; Zhang, Y.; Duan, Y.; Qiu, X.; Zheng, M. Sources and spatial distribution of particulate polycyclic aromatic hydrocarbons in Shanghai, China. *Sci. Total Environ.* **2017**, *584–585*, 307–317. [CrossRef] [PubMed]

56. Wu, B.; Guo, S.; Li, X.; Wang, J. Temporal and spatial variations of Polycyclic Aromatic Hydrocarbons (PAHs) in soils from a typical organic sewage irrigation area. *Sci. Total Environ.* **2018**, *613–614*, 513–520. [CrossRef] [PubMed]

57. Dickhut, R.M.; Canuel, E.A.; Gustafson, K.E.; Liu, K.; Arzayus, K.M.; Walker, S.E.; Edgecombe, G.; Gaylor, M.O.; MacDonald, E.H. Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay Region. *Environ. Sci. Technol.* **2000**, *34*, 4635–4640. [CrossRef]

58. Khalili, N.R.; Scheff, P.A.; Holsen, T.M. PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions. *Atmos. Environ.* **1995**, *29*, 533–542. [CrossRef]

59. Kaur, S.; Senthilkumar, K.; Verma, V.K.; Kumar, B.; Kumar, S.; Katnoria, J.K.; Sharma, C.S. Preliminary analysis of polycyclic aromatic hydrocarbons in air particles (PM10) in Amritsar, India: Sources, apportionment, and possible risk implications to humans. *Arch. Environ. Contam. Toxicol.* **2013**, *65*, 382–395. [CrossRef]

60. Kavouras, I.G.; Koutrakis, P.; Tsapakis, M.; Lagoudaki, E.; Stephanou, E.G.; Von Baer, D.; Oyola, P. Source apportionment of urban particulate aliphatic and Polynuclear Aromatic Hydrocarbons (PAHs) using multivariate methods. *Environ. Sci. Technol.* **2001**, *35*, 2288–2294. [CrossRef]

61. Ravindra, K.; Wauters, E.; Tyagi, S.K.; Mor, S.; Van Grieken, R. Assessment of air quality after the implementation of Compressed Natural Gas (CNG) as fuel in public transport in Delhi, India. *Environ. Monit. Assess* **2006**, *115*, 405–417. [CrossRef]

62. Galarneau, E. Source specificity and atmospheric processing of airborne PAHs: Implications for source apportionment. *Atmos. Environ.* **2008**, *42*, 8139–8149. [CrossRef]

63. Yunker, M.B.; Macdonald, R.W.; Vingarzan, R.; Mitchell, R.H.; Goyette, D.; Sylvestre, S. PAHs in the Fraser River Basin: A Critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* **2002**, *33*, 489–515. [CrossRef]

64. Caricchia, A.M.; Chiavarini, S.; Pezza, M. Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the city of Naples (Italy). *Atmos. Environ.* **1999**, *33*, 3731–3738. [CrossRef]

65. Ravindra, K.; Sokhi, R.; Van Grieken, R. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmos. Environ.* **2008**, *42*, 2895–2921. [CrossRef]

66. Shahsavani, S.; Hoseini, M.; Dehghani, M.; Fararouei, M. Characterisation and potential source identification of polycyclic aromatic hydrocarbons in atmospheric particles (PM10) from urban and suburban residential areas in Shiraz, Iran. *Chemosphere* **2017**, *183*, 557–564. [CrossRef]

67. Akyüz, M.; Çabuk, H. Gas–particle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey. *Sci. Total Environ.* **2010**, *408*, 5550–5558. [CrossRef]

68. Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of Fine Organic Aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environ. Sci. Technol.* **1993**, *27*, 636–651. [CrossRef]

69. Baumard, P.; Budzinski, H.; Michon, Q.; Garrigues, P.; Burgeot, T.; Bellocq, J. Origin and bioavailability of PAHs in the mediterranean sea from mussel and sediment records. *Estuar. Coast Shelf Sci.* **1998**, *47*, 77–90. [CrossRef]

70. Hoseini, M.; Yunesian, M.; Nabizadeh, R.; Yaghmaeian, K.; Ahmadkhaniha, R.; Rastkari, N.; Parmy, S.; Faridi, S.; Rafiee, A.; Naddafi, K. Characterization and risk assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in urban atmospheric particulate of Tehran, Iran. *Environ. Sci. Pollut. Res.* **2016**, *23*, 1820–1832. [CrossRef]

71. Lohmann, R.; Northcott, G.L.; Jones, K.C. Assessing the contribution of diffuse domestic burning as a source of PCDD/Fs, PCBs, and PAHs to the U.K. atmosphere. *Environ. Sci. Technol.* **2000**, *34*, 2892–2899. [CrossRef]

72. Wilcke, W. Global patterns of Polycyclic Aromatic Hydrocarbons (PAHs) in soil. *Geoderma* **2007**, *141*, 157–166. [CrossRef]

73. Sun, F.; Wen, D.; Kuang, Y.; Li, J.; Li, J.; Zuo, W. Concentrations of heavy metals and polycyclic aromatic hydrocarbons in needles of Masson Pine (*Pinus Massoniana* L.) growing nearby different industrial sources. *J. Environ. Sci.* **2010**, *22*, 1006–1013. [CrossRef]

74. Hwang, H.M.; Wade, T.L.; Sericano, J.L. Concentrations and source characterization of polycyclic aromatic hydrocarbons in pine needles from Korea, Mexico, and United States. *Atmos. Environ.* **2003**, *37*, 2259–2267. [CrossRef]

75. Cecinato, A.; Marino, F.; Di Filippo, P.; Lepore, L.; Possanzini, M. Distribution of N-Alkanes, polynuclear aromatic hydrocarbons and nitrated polynuclear aromatic hydrocarbons between the fine and coarse fractions of inhalable atmospheric particulates. *J. Chromatogr. A* **1999**, *846*, 255–264. [CrossRef]

76. 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.* **2008**, *107*, 371–379. [CrossRef]

77. Katsoyiannis, A.; Terzi, E.; Cai, Q.Y. On the use of PAH molecular diagnostic ratios in sewage sludge for the understanding of the PAH sources. Is this use appropriate? *Chemosphere* **2007**, *69*, 1337–1339. [CrossRef] [PubMed]

78. Shabbaj, I.I.; Alghamdi, M.A.; Khoder, M.I. Street dust—bound polycyclic aromatic hydrocarbons in a Saudi Coastal City: Status, profile, sources, and human health risk assessment. *Int. J. Environ. Res. Public Health* **2018**, *15*, 2397. [CrossRef] [PubMed]

79. Katsoyiannis, A.; Breivik, K. Model-based evaluation of the use of polycyclic aromatic hydrocarbons molecular diagnostic ratios as a source identification tool. *Environ. Pollut.* **2014**, *184*, 488–494. [CrossRef]

80. Mishra, N.; Ayoko, G.A.; Morawska, L. Atmospheric polycyclic aromatic hydrocarbons in the urban environment: Occurrence, toxicity and source apportionment. *Environ. Pollut.* **2016**, *208*, 110–117. [CrossRef]

81. Soclo, H.H.; Garrigues, P.; Ewald, M. Origin of Polycyclic Aromatic Hydrocarbons (PAHs) in coastal marine sediments: Case Studies in Cotonou (Benin) and Aquitaine (France) areas. *Mar. Pollut. Bull.* **2000**, *40*, 387–396. [CrossRef]

82. Sojinu, O.S.; Sonibare, O.O.; Ekundayo, O.; Zeng, E.Y. Biomonitoring potentials of Polycyclic Aromatic Hydrocarbons (PAHs) by higher plants from an oil exploration site, Nigeria. *J. Hazard Mater.* **2010**, *184*, 759–764. [CrossRef]

83. Yang, H.H.; Lai, S.O.; Hsieh, L.T.; Hsueh, H.J.; Chi, T.W. Profiles of PAH emission from steel and iron industries. *Chemosphere* **2002**, *48*, 1061–1074. [CrossRef]

84. Khedidji, S.; Balducci, C.; Ladji, R.; Cecinato, A.; Perilli, M.; Yassaa, N. Chemical composition of particulate organic matter at industrial, university and forest areas located in Bouira Province, Algeria. *Atmos. Pollut. Res.* **2017**, *8*, 474–482. [CrossRef]

85. Ladji, R.; Yassaa, N.; Balducci, C.; Cecinato, A. Particle size distribution of N-alkanes and Polycyclic Aromatic Hydrocarbons (PAHS) in urban and industrial aerosol of Algiers, Algeria. *Environ. Sci. Pollut. Res.* **2014**, *21*, 1819–1832. [CrossRef] [PubMed]

86. Sienra, M.D.R.; Rosazza, N.G.; Préndez, M. Polycyclic aromatic hydrocarbons and their molecular diagnostic ratios in urban atmospheric respirable particulate matter. *Atmos. Res.* **2005**, *75*, 267–281. [CrossRef]

87. Mantis, J.; Chaloulakou, A.; Samara, C. PM10-bound Polycyclic Aromatic Hydrocarbons (PAHs) in the greater area of Athens, Greece. *Chemosphere* **2005**, *59*, 593–604. [CrossRef]

88. Yang, H.H.; Lee, W.J.; Chen, S.J.; Lai, S.O. PAH Emission from various industrial stacks. *J. Hazard Mater.* **1998**, *60*, 159–174. [CrossRef]

89. Azid, A.; Juahir, H.; Ezani, E.; Toriman, M.E.; Endut, A.; Rahman, M.N.A.; Yunus, K.; Kamarudin, M.K.A.; Hasnam, C.N.C.; Saudi, A.S.M.; et al. Identification source of variation on regional impact of air quality pattern using chemometric. *Aerosol Air Qual. Res.* **2015**, *15*, 1545–1558. [CrossRef]

90. Iqbal, K.; Ahmad, S.; Dutta, V. Pollution mapping in the urban segment of a tropical river: Is Water Quality Index (WQI) enough for a nutrient-polluted river? *Appl. Water Sci.* **2019**, *9*, 197. [CrossRef]

91. Dong, T.T.T.; Lee, B.K. Characteristics, toxicity, and source apportionment of Polycylic Aromatic Hydrocarbons (PAHs) in road dust of Ulsan, Korea. *Chemosphere* **2009**, *74*, 1245–1253. [CrossRef]

92. Ho, K.F.; Lee, S.C.; Chiu, G.M.Y. Characterization of selected volatile organic compounds, polycyclic aromatic hydrocarbons and carbonyl compounds at a roadside monitoring station. *Atmos. Environ.* **2002**, *36*, 57–65. [CrossRef]

93. Li, A.; Jang, J.K.; Scheff, P.A. Application of EPA CMB8.2 model for source apportionment of sediment PAHS in Lake Calumet, Chicago. *Environ. Sci. Technol.* **2003**, *37*, 2958–2965. [CrossRef]

94. Ma, W.L.; Li, Y.F.; Qi, H.; Sun, D.Z.; Liu, L.Y.; Wang, D.G. Seasonal variations of sources of Polycyclic Aromatic Hydrocarbons (PAHs) to a northeastern urban city, China. *Chemosphere* **2010**, *79*, 441–447. [CrossRef] [PubMed]

95. Çed ve Çevre İzinleri Şube Müdürlüğü, Ç.V.Ş.İ. Bursa İli 2016 Yılı Çevre Durum Raporu. 2017. Available online: https://webdosya.csb.gov.tr/db/ced/editordosya/Bursa_icdr2016.pdf (accessed on 28 April 2021).

96. Freeman, D.J.; Cattell, F.C.R. Woodburning as a source of atmospheric polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* **1990**, *24*, 1581–1585. [CrossRef]

97. Jenkins, B.M.; Jones, A.D.; Turn, S.Q.; Williams, R.B. Emission factors for polycyclic aromatic hydrocarbons from biomass burning. *Environ. Sci. Technol.* **1996**, *30*, 2462–2469. [CrossRef]

98. Van Metre, P.C.; Mahler, B.J. Contribution of PAHs from coal-tar pavement sealcoat and other sources to 40 U.S. lakes. *Sci. Total Environ.* **2010**, *409*, 334–344. [CrossRef] [PubMed]

99. De Nicola, F.; Lancellotti, C.; Prati, M.V.; Maisto, G.; Alfani, A. Biomonitoring of PAHs by using Quercus Ilex leaves: Source diagnostic and toxicity assessment. *Atmos. Environ.* **2011**, *45*, 1428–1433. [CrossRef]

100. Budzinski, H.; Jones, I.; Bellocq, J.; Piérard, C.; Garrigues, P. Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Mar. Chem.* **1997**, *58*, 85–97. [CrossRef]

101. Orecchio, S. PAHs Associated with the Leaves of Quercus Ilex L.: Extraction, GC-MS analysis, distribution and sources. Assessment of air quality in the Palermo (Italy) Area. *Atmos. Environ.* **2007**, *41*, 8669–8680. [CrossRef]
102. Ma, J.; Zhang, W.; Chen, Y.; Zhang, S.; Feng, Q.; Hou, H.; Chen, F. Spatial variability of PAHs and microbial community structure in surrounding surficial soil of coal-fired power plants in Xuzhou, China. *Int. J. Environ. Res. Public Health* **2016**, *13*, 878. [CrossRef]
103. Yang, J.; Xu, W.; Cheng, H. Seasonal variations and sources of airborne Polycyclic Aromatic Hydrocarbons (PAHs) in Chengdu, China. *Atmosphere* **2018**, *9*, 63. [CrossRef]
104. Klánová, J.; Čupr, P.; Baráková, D.; Šeda, Z.; Anděl, P.; Holoubek, I. Can pine needles indicate trends in the air pollution levels at remote sites? *Environ. Pollut.* **2009**, *157*, 3248–3254. [CrossRef] [PubMed]
105. Syed, J.H.; Iqbal, M.; Zhong, G.; Katsoyiannis, A.; Yadav, I.C.; Li, J.; Zhang, G. Polycyclic Aromatic Hydrocarbons (PAHs) in Chinese forest soils: Profile composition, spatial variations and source apportionment. *Sci. Rep.* **2017**, *7*, 2692. [CrossRef] [PubMed]
106. Fang, G.C.; Chang, C.N.; Wu, Y.S.; Fu, P.P.C.; Yang, I.L.; Chen, M.H. Characterization, identification of ambient air and road dust polycyclic aromatic hydrocarbons in central Taiwan, Taichung. *Sci. Total Environ.* **2004**, *327*, 135–146. [CrossRef]
107. Motelay-Massei, A.; Ollivon, D.; Garban, B.; Tiphagne-Larcher, K.; Zimmerlin, I.; Chevreuil, M. PAHs in the Bulk Atmospheric deposition of the Seine River Basin: Source identification and apportionment by ratios, multivariate statistical techniques and scanning electron microscopy. *Chemosphere* **2007**, *67*, 312–321. [CrossRef]
108. Sulong, N.A.; Latif, M.T.; Sahani, M.; Khan, M.F.; Fadzil, M.F.; Tahir, N.M.; Mohamad, N.; Sakai, N.; Fujii, Y.; Othman, M.; et al. Distribution, sources and potential health risks of Polycyclic Aromatic Hydrocarbons (PAHs) in PM2.5 Collected during different monsoon seasons and haze episode in Kuala Lumpur. *Chemosphere* **2019**, *219*, 1–14. [CrossRef]
109. 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.* **2003**, *37*, 5307–5317. [CrossRef]
110. Park, S.U.; Kim, J.G.; Jeong, M.J.; Song, B.J. Source identification of atmospheric polycyclic aromatic hydrocarbons in industrial complex using diagnostic ratios and multivariate factor analysis. *Arch. Environ. Contam. Toxicol.* **2011**, *60*, 576–589. [CrossRef]
111. Jamhari, A.A.; Sahani, M.; Latif, M.T.; Chan, K.M.; Tan, H.S.; Khan, M.F.; Mohd Tahir, N. Concentration and source identification of Polycyclic Aromatic Hydrocarbons (PAHs) in PM10 of urban, industrial and semi-urban areas in Malaysia. *Atmos. Environ.* **2014**, *86*, 16–27. [CrossRef]
112. Fang, Y.; Chen, Y.; Tian, C.; Lin, T.; Hu, L.; Li, J.; Zhang, G. Application of PMF receptor model merging with PAHs signatures for source apportionment of black carbon in the continental shelf surface sediments of the Bohai and Yellow Seas, China. *J. Geophys. Res. Ocean* **2016**, *121*, 1346–1359. [CrossRef]
113. Hussain, K.; Hoque, R.R. Seasonal attributes of urban soil PAHs of the Brahmaputra Valley. *Chemosphere* **2015**, *119*, 794–802. [CrossRef] [PubMed]
114. Hussain, K.; Rahman, M.; Prakash, A.; Hoque, R.R. Street dust bound PAHs, carbon and heavy metals in Guwahati City—Seasonality, toxicity and sources. *Sustain. Cities Soc.* **2015**, *19*, 17–25. [CrossRef]
115. Lakhani, A. Source apportionment of particle bound polycyclic aromatic hydrocarbons at an industrial location in Agra, India. *Sci. World J.* **2012**, *2012*, 781291. [CrossRef]
116. Callén, M.S.; Iturmendi, A.; López, J.M. Source apportionment of atmospheric PM2.5-bound polycyclic aromatic hydrocarbons by a PMF receptor model. assessment of potential risk for human health. *Environ. Pollut.* **2014**, *195*, 167–177. [CrossRef]
117. Lee, J.H.; Gigliotti, C.L.; Offenberg, J.H.; Eisenreich, S.J.; Turpin, B.J. Sources of polycyclic aromatic hydrocarbons to the Hudson River Airshed. *Atmos. Environ.* **2004**, *38*, 5971–5981. [CrossRef]
118. Chen, H.-Y.; Teng, Y.-G.; Wang, J.-S. Source apportionment of Polycyclic Aromatic Hydrocarbons (PAHs) in surface sediments of the Rizhao Coastal Area (China) using diagnostic ratios and factor analysis with nonnegative constraints. *Sci. Total Environ.* **2012**, *414*, 293–300. [CrossRef]
119. Jiao, H.; Wang, Q.; Zhao, N.; Jin, B.; Zhuang, X.; Bai, Z. Distributions and sources of Polycyclic Aromatic Hydrocarbons (PAHs) in soils around a chemical plant in Shanxi, China. *Int. J. Environ. Res. Public Health* **2017**, *14*, 1198. [CrossRef] [PubMed]
120. Cao, Q.; Wang, H.; Chen, G. Source apportionment of PAHs using two mathematical models for mangrove sediments in Shantou Coastal Zone, China. *Estuaries Coasts* **2011**, *34*, 950–960. [CrossRef]
121. Zhang, W.; Wei, C.; Chai, X.; He, J.; Cai, Y.; Ren, M.; Yan, B.; Peng, P.; Fu, J. The behaviors and fate of Polycyclic Aromatic Hydrocarbons (PAHs) in a coking wastewater treatment plant. *Chemosphere* **2012**, *88*, 174–182. [CrossRef]
122. Ciaparra, D.; Aries, E.; Booth, M.J.; Anderson, D.R.; Almeida, S.M.; Harrad, S. Characterisation of volatile organic compounds and polycyclic aromatic hydrocarbons in the ambient air of steelworks. *Atmos. Environ.* **2009**, *43*, 2070–2079. [CrossRef]
123. Jang, E.; Alam, M.S.; Harrison, R.M. Source apportionment of polycyclic aromatic hydrocarbons in urban air using positive matrix factorization and spatial distribution analysis. *Atmos. Environ.* **2013**, *79*, 271–285. [CrossRef]
124. Zhao, Z.; Qin, Z.; Cao, J.; Xia, L. Source and ecological risk characteristics of PAHs in sediments from Qinhuai River and Xuanwu Lake, Nanjing, China. *J. Chem.* **2017**, *2017*, 3510796. [CrossRef]
125. Yu, Y.; Yang, Y.; Liu, M.; Zheng, X.; Liu, Y.; Wang, Q.; Liu, W. PAHs in organic film on glass window surfaces from Central Shanghai, China: Distribution, sources and risk assessment. *Environ. Geochem. Health* **2014**, *36*, 665–675. [CrossRef] [PubMed]
126. Kim, L.; Jeon, H.J.; Kim, Y.C.; Yang, S.H.; Choi, H.; Kim, T.O.; Lee, S.E. Monitoring polycyclic aromatic hydrocarbon concentrations and distributions in rice paddy soils from Gyeonggi-Do, Ulsan, and Pohang. *Appl. Biol. Chem.* **2019**, *62*, 18. [CrossRef]

127. Chen, Y.; Sheng, G.; Bi, X.; Feng, Y.; Mai, B.; Fu, J. Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. *Environ. Sci. Technol.* **2005**, *39*, 1861–1867. [CrossRef] [PubMed]

128. Tian, Y.Z.; Li, W.H.; Shi, G.L.; Feng, Y.C.; Wang, Y.Q. Relationships between PAHs and PCBs, and quantitative source apportionment of PAHs toxicity in sediments from Fenhe Reservoir and Watershed. *J. Hazard Mater.* **2013**, *248–249*, 89–96. [CrossRef] [PubMed]

129. Nisbet, I.C.T.; LaGoy, P.K. Toxic Equivalency Factors (TEFs) for Polycyclic Aromatic Hydrocarbons (PAHs). *Regul. Toxicol. Pharmacol.* **1992**, *16*, 290–300. [CrossRef]

130. Hertel, R.F.; Rosner, G.; Kielhorn, J.; Artelt, S.; Boehncke, A.; Creutzenberg, O.; Mangelsdorf, I.; Menichini, E.; Grover, P.L.; Blok, J.; et al. *Selected Non-Heterocyclic Polycyclic Aromatic Hydrocarbons*; World Health Organization: Geneva, Switzerland, 1998; ISBN 9241572027.

131. Callén, M.S.; López, J.M.; Iturmendi, A.; Mastral, A.M. Nature and sources of particle associated Polycyclic Aromatic Hydrocarbons (PAH) in the atmospheric environment of an urban area. *Environ. Pollut.* **2013**, *183*, 166–174. [CrossRef]

132. Cal-EPA. *Air Toxics Hot Spots Program Risk Assessment Guidelines Part II: Technical Support Document for Describing Available Cancer Potency Factors*; Office of Environmental Health Hazards Assessment: Oakland, CA, USA, 2005.

133. OEHHA. *Benzo[a]Pyrene as a Toxic Air Contaminant—California Air Resources Board Office of Environmental Health Hazard-Assessment*; Office of Environmental Health Hazards Assessment: Oakland, CA, USA, 1994.

134. World Health Organization. Air quality guidelines for Europe. *Environ. Sci. Pollut. Res.* **1996**, *3*, 23. [CrossRef]

135. Ramírez, N.; Cuadras, A.; Rovira, E.; Marcé, R.M.; Borrull, F. Risk assessment related to atmospheric polycyclic aromatic hydrocarbons in gas and particle phases near industrial sites. *Environ. Health Perspect.* **2011**, *119*, 1110–1116. [CrossRef]

136. Taghvaee, S.; Sowlat, M.H.; Hassanvand, M.S.; Yunesian, M.; Naddafi, K.; Sioutas, C. Source-specific lung cancer risk assessment of ambient PM2.5-bound Polycyclic Aromatic Hydrocarbons (PAHs) in Central Tehran. *Environ. Int.* **2018**, *120*, 321–332. [CrossRef]

137. U.S. EPA. *Regional Screening Levels for Chemical Contaminants at Superfund Sites*; U.S. Environmental Protection Agency: Washington, DC, USA, 2015.