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Main Emission Sources and Health Risks of Polycyclic Aromatic Hydrocarbons and Nitro-Polycyclic Aromatic Hydrocarbons at Three Typical Sites in Hanoi

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Abstract: Particulate matter-bound polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs (NPAHs) were first systematically studied in downtown (XT), suburban (GL) and rural (DA) sites in winter and summer in Hanoi, Vietnam, from 2019 to 2022. The mean concentrations of PAHs and NPAHs ranged from 0.76 ng m^{-3} to 50.2 ng m^{-3} and 6.07 pg m^{-3} to 1.95 ng m^{-3}, respectively. The concentrations of PAHs and NPAHs in winter were higher than in summer, except for NPAHs in XT. We found the benzo[*a*]pyrene (BaP)/benzo[*ghi*]perylene (BgPe) ratio could effectively identify biomass burning in this study, in which a higher [BaP]/[BgPe] value indicates a greater effect of biomass burning on PAHs and NPAHs. The results indicated that atmospheric PAHs and NPAHs were mainly affected by motor vehicles (especially the unique motorcycles in Southeast Asia) in the summer in Hanoi. In winter, all sites were affected by the burning of rice straw to varying degrees, especially DA. The incremental lifetime cancer risk (ILCR) in Hanoi was first determined through ingestion, inhalation and dermal absorption. The results showed that residents in Hanoi faced high health risks, while females experienced higher health risks than males. The ingestion and dermal pathways indicated higher exposure risks than the usually considered inhalation pathway.

Keywords: air pollution; polycyclic aromatic hydrocarbons; nitro-polycyclic aromatic hydrocarbons; biomass; Hanoi

1. Introduction

Among all air pollutants, polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs (NPAHs) are widely noted for their carcinogenicity and mutagenicity, and are associated

with oxidative stress and DNA damage [1–4]. PAHs are formed through the incomplete combustion of organic materials. For example, the incomplete combustion of petroleum, biomass and coal for industry, vehicle (cars and motorcycles) emissions, residential heating and cooking in daily life are the main anthropogenic sources of atmospheric PAHs [5,6]. PAHs can also be formed through natural sources, for example, forest fires, volcanic activity and living vegetation [7]. Most NPAHs, for example, 6-nitrobenzo[*a*]pyrene and 1-nitropyrene, are formed during the incomplete combustion of fossil fuel and atmospheric reactions, but some NPAHs (e.g., 2-nitropyrene) can only be formed through atmospheric reactions [8,9].

The inhalation of urban air and tobacco smoke, ingestion of cooked food and drinking water, and dermal absorption of the particles that adhere to exposed skin are considered the main exposure pathways in humans [10]. The inhalation exposure pathway is utilized for those PAHs and NPAHs inhaled by humans through breathing the exhaust gases emitted by the combustion of fossil fuel/biomass [11]. The ingestion exposure pathway is used for the adsorption and formation of those PAHs and NPAHs created during the production, transportation and storage of the foods [12,13]. Different from the inhalation and ingestion pathways, dermal exposure is the main pathway when skin is exposed directly to the consumer products that have high levels of PAHs and NPAHs. Skin exposure can be at both the internal boundary and external boundary during the health risk assessment [14]. Previous researches have shown the close relationship between cancer, heritable (paternal germ-line) mutations and human reproduction and exposure to PAHs [15,16]. The metabolites of certain PAHs and NPAHs, such as benzo[*a*]pyrene and 6-nitrochrysene, which have been reported by the International Agency for Research on Cancer as Group 1 (carcinogenic to humans) and Group 2A (probably carcinogenic to humans) substances, respectively, might show harmful biological activities to humans [17–19]. Moreover, some NPAHs (with direct-acting mutagenicity) that can cause a higher toxicity than their parent PAHs have been increasingly considered [20]. In addition, the study of Shen et al. showed approximately 1372, 709 and 796 cancer cases might occur among one million residents in Shenyang, Chongqing and Changsha, China, due to exposure to PAHs and NPAHs. The study of Yadav et al. showed approximately 102–788 cancer cases might occur among one million residents in Delhi, India, and Thepnuan et al. reported approximately 100 cancer cases might occur among one million residents in Chiang Mai, Thailand [21–23]. The lack of detection of PAHs and NPAHs can cause severe underestimations of fine particulate matter ($PM_{2.5}$)-related health risks since high health-risk PAHs and NPAHs are mainly in particulate matter [24,25]. Thus, the detection of PAHs and NPAHs in $PM_{2.5}$ is essential, especially in lower- to middle-income countries that are developing rapidly and suffer severe air quality problems [26].

Vietnam is located on the eastern Indochina Peninsula in Southeast Asia and has a population of over 96 million people. In this study, we collected $PM_{2.5}$ samples at downtown, suburban and rural sites in Hanoi, Vietnam, during the summer and winter from 2019 to 2022. The aim of this research was to (1) determine the characteristics of atmospheric PAHs and NPAHs and the influencing factors of the concentration, composition and emission sources at these different typical sites, and (2) comprehensively evaluate the incremental lifetime cancer risks (ILCRs) of PAHs and NPAHs along three exposure pathways. The results of this study will provide valuable, comprehensive and systematic information for atmospheric conservation not only in Hanoi but also in other regions of Vietnam and Southeast Asian countries with a similar environment.

2. Materials and Methods

2.1. Site Depiction Description

Vietnam has exhibited a relatively high constant growth rate of the gross domestic product (GDP) of approximately 6.5% over the past two decades [27]. The high development speed has aggravated air pollution, with severe health risks to the people of Vietnam [28,29]. Biomass combustion and emissions from motor vehicles, especially

motorcycles, are considered to be typical sources of atmospheric PAHs and NPAHs in Vietnam [30–32]. Vietnam is the 5th largest rice exporter in global rice production, and approximately 4×10^7 tons of rice is produced in Vietnam each year [33,34]. Rice is harvested two times a year in Vietnam; after each harvest season, there are large amounts of crop residues (e.g., rice straw and rice stubble) that must be treated/processed [35–37]. To complete field preparation faster during the two planting periods, straw is normally directly burned in the field [38,39]. Moreover, the registered motorcycles in Vietnam account for over 80% of all registered vehicles, and the number of motorcycles reached more than 6 million units in 2018 [40,41].

In Hanoi, the capital of Vietnam, the air pollution and health risks of PAHs and NPAHs caused by the above reasons have caused much concern [42–45]. However, to the best of our knowledge, there have only been two investigations so far other than our groups, and these studies were limited to PAHs only. Relevant research in Hanoi was first started in 2005, and roadside particulate and gaseous PAHs were studied [42]. Saha et al. observed the impact of biomass combustion, even in the non-rice straw burning season, through the investigation in 2009–2010 [43]. Our research group first reported concentration and composition of NPAHs and toxic equivalent assessment results of atmospheric PAHs and NPAHs in residential and roadside sites of Hanoi, and we found that the burning of rice straw after the harvest could result in the emission of high levels of PAHs and NPAHs via laboratory and field experiments, and calculated the unit emissions of PAH and NPAH emitted by burning rice straw [32,46–48]. Moreover, we simply analyzed the inhalation health risks caused by Hanoi traffic and calculated only PAHs [49,50]. However, the above-mentioned past studies on PAHs and NPAHs in Hanoi lacked an overall analysis. For example, different functional sites in Hanoi include downtown, suburban and rural sites, and in different seasons. In addition, previous scholars conducted simple assessments of the health risks but did not consider ingestion and dermal exposure, the results of which are very likely to underestimate the exposure health risks of PAHs and NPAHs in Hanoi. Therefore, three sites, namely, Xuân Thuỷ (XT), Gia Lâm (GL) and Đông Anh (DA), were selected in Hanoi, Vietnam, as shown in Figure 1. Sampling site XT is situated in the inner part of Hanoi city, far away from rice fields, and represents downtown Hanoi. Sampling site GL is located at the junction of downtown and rural sites, and represents the suburban site of Hanoi. Sampling site DA is situated in the residential site of Hanoi, and is close to rice fields, representing rural Hanoi.

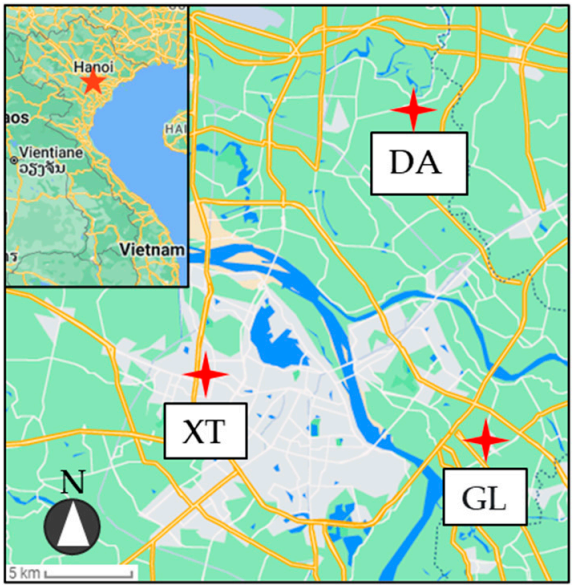

Figure 1. Locations of the three sampling sites in Hanoi, Vietnam (Used by permission. Google maps: https://www.google.com/maps) (accessed on 3 March 2023).

2.2. Sampling

The $PM_{2.5}$ samples were collected on filters (2500QAT-UP, 25 mm φ and 47 mm φ, Pall Life Sciences, Ann Arbor, MI, USA) by a mini sampler with a Sibata pump (MP-Σ500NII) at a flow rate of 3 L minute^{-1}. The samples were gathered in the winter and summer from 2019 to 2022 in Hanoi, Vietnam. The sampling periods in GL ranged from 24–30 December 2019, 9–15 January 2020 and 15–21 February 2020 (n = 21, called GL-Winter) and from 9–21 June 2020, 7–19 July 2020, and 5–17 August 2020 (n = 21, called GL-Summer). The sampling periods in XT ranged from 20–27 January 2022 (n = 8, called XT-Winter) and 30 June 2022–22 July 2022 (n = 15, called XT-Summer). The sampling periods in DA ranged from 26 November 2021–10 December 2021 (n = 15, called DA-Winter) and 27 June 2022–24 August 2022 (n = 15, called DA-Summer). All filters were replaced every two days in summer and one day in winter. It should be noted that the DA-Winter samples were collected during the rice straw burning period, and the rest of the samples were obtained during the non-rice straw burning season. All sampled filters were stored at −20 °C before analysis.

2.3. PAHs and NPAHs Analysis

Ten PAHs, including fluoranthene (FR), pyrene (Pyr), benz[*a*]anthracene (BaA), Chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), benzo[*e*]pyrene (BeP), benzo[*ghi*]perylene (BgPe) and indeno [1,2,3-*cd*]pyrene (IDP) (Supelco Park, Bellefonte, PA, USA), and six NPAHs, including, 2-nitrofluoranthene (2-NFR), 6-nitrochrysene (6-NC), 7-nitrobenz[*a*]anthracene (7-NbaA), and 6-nitrobenzo[*a*]pyrene (6-NbaP) (Chiron AS, Trondheim, Norway), 1-, 2-nitropyrenes (NPs) (Aldrich Chemical, Osaka, Japan) were analyzed in this study. Pyrene-d_{10} (Pyr-d_{10}) and benzo[*a*]pyrene-d_{12} (BaP-d_{12}) were used as the internal standards that supplied by Wako Pure Chemicals (Osaka, Japan). All other analytical reagents used in this study were of analytical grade.

Details of the sample analysis process are provided in our previous research and shown in the Supplementary Materials (Text S1) [51,52]. In summary, the sample filters were cut into small pieces and placed into different flasks. Two internal standards (Pyr-d_{10} and BaP-d_{12}) were then added. Dichloromethane was added to each flask, and the compounds were then ultrasonically extracted, concentrated, diluted and filtered. High-performance liquid chromatography with fluorescence detection (Shimadzu Inc., Kyoto, Japan) was used to analyse the PAHs and NPAHs.

Blank filters were applied in this study to avoid filter contamination during the sampling and transport processes, and the results of the blank filters showed no contamination in the process. The method of recovery was evaluated through the addition of internal standards. The recovery rates were 87% ± 7% for Pyr-d_{10} and 88% ± 6% for BaP-d_{12}. In addition, blank filters were adopted in three sites to avoid filter contamination during the sampling and transport processes. The same procedures with other sample filters were used to treat the blank filters, including weighing, storage and analysis. The analysis of the blank filters showed no detection of target PAHs and NPAHs, indicating that no contamination occurred during the transportation and storage of the sample filters.

2.4. Health Risk Assessment

Previous reports showed that toxicity equivalency (TEQ) and incremental lifetime cancer risk (ILCR) effectively determine the carcinogenic risk of PAHs and NPAHs. The equations of TEQ are expressed as follows:

$$TEQ_i = C_i \times TEF_i \quad (1)$$

$$TEQ_{total} = \sum TEQ_i \quad (2)$$

In Equation (1), the C_i and TEF_i are the concentration and reference toxicity equivalence factors, respectively, of each PAH and NPAH (Table S1).

The U.S. EPA standard model was used to calculate the ILCR under different exposure pathways, the equations of which are shown below [53,54]:

$$ILCR_{ing} = (C \times CSF_{ing} \times \sqrt[3]{(BW/70)} \times IR_{ing} \times EF \times ED)/(BW \times AT \times 10^6) \quad (3)$$

$$ILCR_{inh} = (C \times CSF_{inh} \times \sqrt[3]{(BW/70)} \times IR_{inh} \times EF \times ED)/(BW \times AT \times PEF) \quad (4)$$

$$ILCR_{dem} = (C \times CSF_{dem} \times \sqrt[3]{(BW/70)} \times SA \times AF \times ABS \times EF \times ED)/(BW \times AT \times 10^6) \quad (5)$$

In Equations (3)–(5), $ILCR_{ing}$, $ILCR_{inh}$ and $ILCR_{dem}$ are the risk values for ingestion, inhalation and dermal exposure, respectively, C is the concentration of TEQ_{PAH} (ng m^3), and CSF_{ing}, CSF_{inh} and CSF_{dem} are the carcinogenic slope factors for ingestion, inhalation and dermal exposure ((mg kg^{-1} $day^{-1})^{-1}$), respectively [11,55,56]. The values of CSF_{ing}, CSF_{inh} and CSF_{dem} capture the cancer-causing ability of BaP at 7.3, 25 and 3.85 ((mg kg^{-1} $day^{-1})^{-1}$), respectively. BW is the average body weight (kg), EF is the annual exposure frequency (day), ED is the duration of exposure (years), SA is the exposed area of skin (cm^2), AF is the skin adherence factor (mg cm^{-2}), ABS is the skin absorption factor (day^{-1}), and IR_{ing} and IR_{inh} are the intake rates under the ingestion and inhalation exposure routes (mg day^{-1}), respectively [12,57]. The specific values are shown in Table S2.

The sum of all three ILCRs under the different exposure pathways is the total ILCR, which can be calculated as follows:

$$\text{Total}_{ILCR} = ILCR_{ing} + ILCR_{inh} + ILCR_{dem} \quad (6)$$

3. Results

3.1. Concentrations of PAHs and NPAHs

Figure 2 provides the average concentrations of PAHs and NPAHs at the three sites in Hanoi during the sampling periods, the details of which are listed in Tables S3 and S4. The average total concentrations of PAHs and NPAHs at all sites were higher in the winter than in the summer, except for XT-Summer. The results showed that the concentration tendency of PAHs and NPAHs in Hanoi was similar to that in other Asian countries (e.g., China and Japan), in which the main reasons are the differences in sources and meteorological conditions between winter and summer [3,52,58]. However, unlike other Asian countries, the concentrations of PAHs and NPAHs in the downtown site, XT (2.95 ng m^{-3} and 58.0 pg m^{-3}), were much lower than GL (suburban site, 12.1 ng m^{-3} and 494 pg m^{-3}, $p < 0.01$) and DA (rural site, 22.1 ng m^{-3} and 548 pg m^{-3}, $p < 0.01$) in the winter. A reduction in traffic and factory manufacturing during the COVID-19 pandemic might be one reason for the relatively low concentration at XT, although the sampling periods were not during the lockdown period. In the summer, the concentrations of PAHs and NPAHs in XT (2.55 ng m^{-3} and 115 pg m^{-3}) were higher than those in GL (2.20 ng m^{-3}, $p > 0.05$ and 55.3 pg m^{-3}, $p < 0.01$) but lower than those in DA (4.38 ng m^{-3}, $p < 0.01$ and 137 pg m^{-3}, $p < 0.05$). In addition, the winter–summer ratios of the atmospheric concentrations of PAHs and NPAHs in XT were 1.16 and 0.48, respectively. As shown in Table S3, the increase in PAHs in winter is mainly due to the increase in the particle phase distribution of 4-ring PAHs under the lower temperature condition [24,59]. However, the concentration of NPAHs in the summer was higher than that in the winter, which is due to the increase in the concentration of the secondary formation of NPAHs caused by the strong atmospheric reactivity in the summer and the lack of detection of several NPAH species in the winter (Table S4). This is an important result, and we will identify the phenomenon in our future studies. Nevertheless, compared with XT, the winter–summer ratio of the atmospheric concentrations of PAHs and NPAHs in DA (5.50, 8.93) and GL (5.05, 4.00) were much higher. This result cannot simply be explained by the above reasons. Since the winter sampling of DA was performed in the rice straw combustion period, and the sporadic combustion of RS used as fuel in daily life in the GL site can still emit high concentrations of PAHs and NPAHs [32,47,48], therefore, burning RS in winter may be a reason for the increased concentrations of atmospheric PAHs and NPAHs in DA and GL.

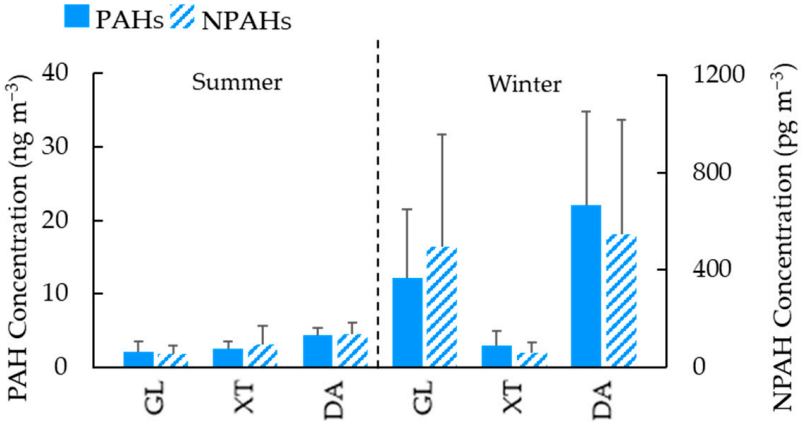

Figure 2. Average concentrations of PAHs (ng m^{-3}) and NPAHs (pg m^{-3}) at three sampling sites in Hanoi.

3.2. Prospective Emission Sources of PAHs and NPAHs

The emission sources of PAHs and primary NPAHs can notably control the corresponding composition characteristics [60]. Therefore, to identify the potential sources, diagnostic ratios of PAHs, and primarily NPAHs, such as the ratios of [FR]/([FR] + [Pyr]), [BaA]/([BaA] + [Chr]), [BbF]/([BbF] + [BkF]) and [IDP]/([BgPe] + [IDP]), have typically been used in many studies [6,61–63].

Figure 3 showed the values of the PAHs diagnostic ratios at all sampling sites and periods. As shown in Figure 3a, the value of [FR]/([FR] + [Pyr]) in Hanoi was mainly higher than 0.5, which indicates emissions resulting from biomass/coal during winter. The [FR]/([FR] + [Pyr]) value in Hanoi was mainly lower than 0.5, which indicates the notable effect of traffic emissions in summer [64–66]. The [BaA]/([BaA] + [Chr]) results showed that the emissions of PAHs and NPAHs resulting from biomass/coal burning cannot be ignored in both summer and winter. The [BbF]/([BbF] + [BkF]) and [IDP]/([IDP] + [BgPe]) results showed that the levels in both summer and winter in Hanoi were affected by traffic emissions (Figure 3b) [6,67,68]. Based on the above results, the atmospheric PAHs and NPAHs of the three different functional sites in Hanoi were comprehensively impacted by biomass combustion and vehicles simultaneously all year. Even in the winter of our selected DA (RS burning period), the proportion of biomass combustion was not fully highlighted. This indicates that these commonly used diagnostic ratios give uncertain results when evaluating the contribution rates of atmospheric PAHs and NPAHs in Hanoi.

Figure 4 shows the ratio of BaP and BgPe in the atmosphere at the three different functional sites in Hanoi in this study and different emission sources in the previous studies. According to ours and other previous studies on the different emission sources of atmospheric PAHs and NPAHs, the [BaP]/[BgPe] ratios are between 0.08 and 0.49 in motorcycle emissions [42,69–73], 0.6 and 1.64 in biomass burning [74–79] and 0.53 and 0.90 in automobile emissions [6,80–85]. In this study, the ranges of [BaP]/[BgPe] in summer were 0.34–0.47 (GL), 0.23–0.34 (XT) and 0.26–0.42 (DA), which are close to the emission characteristics of motorcycles. In winter, the ranges of [BaP]/[BgPe] were 0.24–0.73 (GL), 0.33–0.51 (XT) and 0.51–1.05 (DA), which are close to the other referenced cities with vehicles as the primary source but lower than the ratio of biomass burning. Our previous studies showed that atmospheric PAHs and NPAHs at the urban stations in Hanoi mainly came from motorcycles, and the contribution rate of vehicles was relatively low [31,46,49]. In addition, as mentioned in the previous section, the DA site is very close to the rice fields, and the samples of DA-Winter were collected during the RS burning period in Hanoi. Therefore, due to the [BaP]/[BgPe] value for motorcycles (median ratio = 0.37) being significantly lower ($p < 0.01$) than DA-winter (median ratio = 0.81) and higher than the [BaP]/[BgPe] value for biomass burning (median ratio = 0.70), the high [BaP]/[BgPe] ratio of DA-Winter shows that atmospheric PAHs and NPAHs were mainly affected by RS burning. The [BaP]/[BgPe] median values in GL and XT were 0.55 and 0.41, respectively. The [BaP]/[BgPe] median value in GL was significantly higher ($p < 0.05$) than those for motorcycle exhausts (median ratio = 0.37), and the [BaP]/[BgPe] median value in XT was higher than motorcycle exhausts. This indicated that the other two sites in Hanoi were also impacted by RS burning to varying degrees, although the sampling period was not the main period of RS burning. This may be related to the habit of burning RS as fuel for daily life in some sites of Hanoi in winter [32,47,48,86].

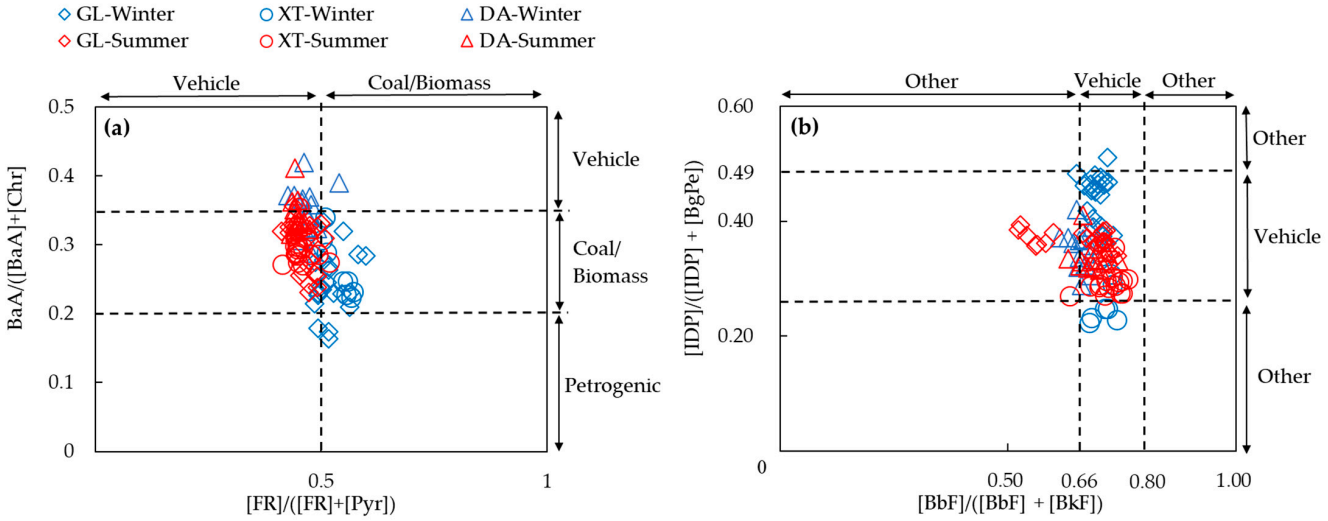

Figure 3. Distribution of PAHs' isomer ratios among different emission sources at three sampling sites in Hanoi: (**a**) [FR]/([FR] + [Pyr]) and [BaA]/([BaA] + [Chr]) [64–66]; (**b**) [BbF]/([BbF] + [BkF]) and [IDP]/([BgPe] + [IDP]) [67,68].

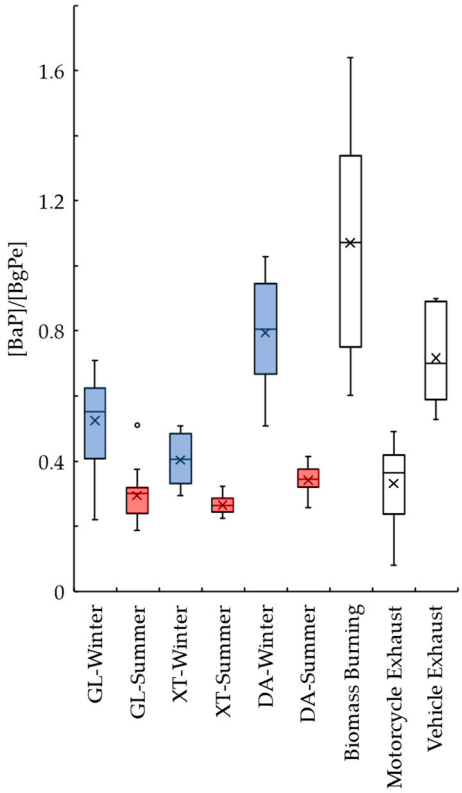

Figure 4. The [BaP]/[BgPe] ratios of three sampling sites in Hanoi in this study with biomass burning [74–79], motorcycle exhausts [42,69–73] and vehicle exhausts [6,80–85].

Figure 5 shows the diagnostic ratio distributions of NPAHs and the corresponding sources. 1-NP is mainly formed during the combustion process, whereas 2-NFR and 2-NP are formed through atmospheric reactions [87]. [2-NFR]/[2-NP] ratios close to 10 and 100 are typically used to determine if the formation pathway of NPAHs is dominated by OH and NO_3 radical-initiated reactions, respectively [88,89]. As shown in Figure 5a, the [2-NFR]/[2-NP] ratio in this study ranged from 1.89 to 20.8, and closer to 10, the results of which are similar to those in our previous studies in Hanoi, Singapore and Xinxiang, China [32,58,63]. This result showed the importance of the OH radical-initiated reaction pathway in Hanoi in both summer and winter. [2-NFR]/[1-NP] ratios

indicate atmospheric NPAHs mainly originate from primary emissions (≤5) or secondary formation (>5) [90]. Although this ratio reflects the aging of aerosols, it is also affected by the atmospheric reaction rate of 1-NP degradation and 2-NFR formation [91]. As shown in Figure 5b, most of the ratios of [2-NFR]/[1-NP] in DA-Winter were close to 5 and were significantly lower ($p < 0.01$) than in other sites and seasons. Higher 1-NP levels and a lower formation rate of 2-NFR during the rice straw burning period were considered (Table S4). Similar [2-NFR]/[1-NP] results were found in other studies in Lanzhou (mean = 4.70) that experienced a biomass burning period [92].

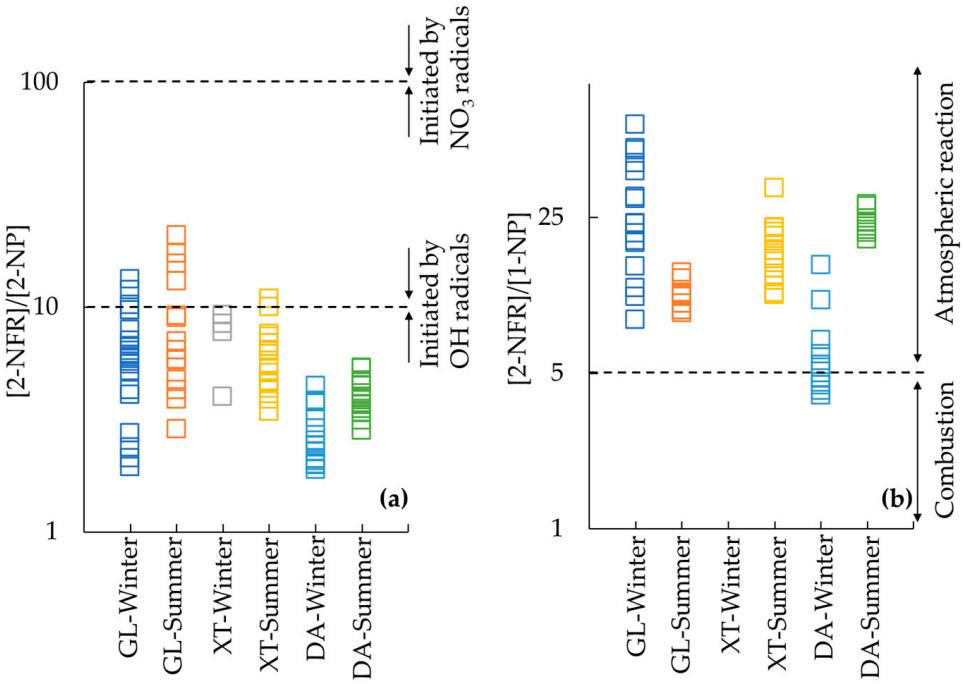

Figure 5. Distribution of NPAHs' isomer ratios among different emission sources at three sampling sites in Hanoi: (**a**) [2-NFR]/[2-NP]; (**b**) [2-NFR]/[1-NP].

3.3. Health Risk Assessment

3.3.1. BaP Equivalent Concentration

Among all PAHs, BaP has been found to be the primary contributor to cancer risk, and the BaP equivalent concentration (TEQ) has been widely used as an indicator for modelling air quality and assessing the health risk [93,94]. Table S5 shows the TEQ of each PAH and NPAH. During winter, the average total TEQs in GL, XT and DA were 1730 ± 1577 pg m^{-3}, 363 ± 319 pg m^{-3} and 3877 ± 2548 pg m^{-3}, respectively, which were higher than those in summer, with corresponding values of 298 ± 218 pg m^{-3}, 335 ± 152 pg m^{-3} and 571 ± 111 pg m^{-3}, respectively. The highest total TEQ appeared in DA, followed by GL, emphasizing the health effect of biomass burning on the rural residents of Hanoi. In both winter and summer, BaA, Chr, BbF and BaP were the major contributors to the total TEQ, accounting for 58.0% to 85.2% of the total TEQ. 6-NC showed the highest contribution among all three NPAHs due to its high atmospheric concentration and high toxic equivalent factor (10 times higher than that of BaP) [95,96]. Compared with other motorcycle-dominated cities in Southeast Asia, the TEQs in winter in GL and DA were higher than the background site in winter in Ho Chi Minh City, Vietnam (0.91 ng m^{-3}), and the Mae Sot District, Thailand (1.57 ng m^{-3}), the samples of which were collected during a biomass burning period [73,97]. The results show the relatively high health risks in Hanoi, Vietnam, compared with other motorcycle-dominated cities.

3.3.2. ILCR Assessment

The ingestion, inhalation and dermal contact pathways have been reported to be the main pathways for human exposure to PAHs and NPAHs [98]. Based on the total TEQ, the mean ILCR values for the three exposure routes in Hanoi were assessed, as shown in Table 1. The mean ILCR values for males and females were all higher than the acceptable threshold of the ILCR recommended by the U.S. EPA, at 1×10^{-6} [99]. The mean ILCR in DA (3.00×10^{-5} and 3.26×10^{-5} for males and females, respectively) was the highest, followed by GL (1.37×10^{-5} and 1.49×10^{-5} for males

and females, respectively), which indicates that approximately 30 and 33 cancer cases might occur among one million males and females, respectively, in rural Hanoi. The results showed relatively high health risks for the residents of Hanoi, especially in the rural site. The risks under the three exposure routes were ranked in the following order: ingestion > dermal > inhalation. In this study, females in Hanoi experienced slightly higher health risks than males, which is different from other studies [51,63]. The reason might be due to the relatively long lifetime of females (80 years) relative to males (75 years) in Vietnam, causing a more extended exposure period. The mean ILCR values in GL and DA in this study were higher than those in our previous study (the mean ILCR values ranged from 7.5×10^{-6} to 2.3×10^{-5}), and the results were calculated by using the TEQ [50]. The comparison revealed that the lack of determination of the ILCR through ingestion and dermal ingestion could cause underestimations of the health risks in Hanoi. However, the mean ILCR value in this study was lower than the ILCR value in our previous study obtained by using the CALUX bioassay (the mean ILCR value ranged from 1.0×10^{-4} to 2.8×10^{-4}) to determine the TEQ, which is based on the ligand-activated aryl hydrocarbon receptor (AhR)-mediated induction of biological responses to PAHs and can more particularly identify the AhR-mediated risk of PAHs [50,100]. Therefore, future studies in Hanoi should consider all three exposure routes for a more precise determination of ILCR and CALUX-based TEQ values.

Table 1. The mean ILCRs for three exposure routes from 2019 to 2022 in Hanoi, Vietnam.

	GL		XT		DA	
	Male	**Female**	**Male**	**Female**	**Male**	**Female**
Ingestion	1.07×10^{-5}	1.17×10^{-5}	3.69×10^{-6}	4.01×10^{-6}	2.36×10^{-5}	2.56×10^{-5}
Inhalation	5.22×10^{-9}	4.76×10^{-9}	1.79×10^{-9}	1.64×10^{-9}	1.14×10^{-8}	1.04×10^{-9}
Dermal	2.94×10^{-6}	3.19×10^{-6}	1.01×10^{-6}	1.10×10^{-6}	6.44×10^{-6}	7.00×10^{-6}
Total	1.37×10^{-5}	1.49×10^{-5}	4.70×10^{-6}	5.11×10^{-6}	3.00×10^{-5}	3.26×10^{-5}

4. Conclusions

This study surveyed the concentration, composition and health risk of PM-bound PAHs and NPAHs from 2019 to 2022 at three specific sites in Hanoi, Vietnam. The concentrations of PAHs and NPAHs were highest in a rural site (DA) in winter and were lowest in a suburban site (GL) in summer. Combining several diagnostic ratios of PAHs and NPAHs, we found that the atmospheric PAHs and NPAHs of all areas in Hanoi were affected by the burning of RS with varying degrees in winter, especially during the large-scale RS burning period, while in the summer, the motorcycle was considered the main contributor. The [2-NFR]/[2-NP] ratios showed that OH-initiated reactions comprised the main formation pathway of 2-NFR and 2-NP in Hanoi. The ILCR values in this study were higher than the safe limit, especially in the RS burning period. We first reported that the three exposure routes for ILCR determination showed that ingestion yielded higher health risks than the dermal and inhalation pathways in Hanoi. The implementation of this study will urge the Vietnamese government to take further measures to control RS combustion.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/atmos14050782/s1, Text S1. Pretreatment and instrumental analysis of PAHs and NPAHs. Table S1: The toxic equivalent factor (TEF) of PAHs and NPAHs; Table S2: Parameters of incremental lifetime cancer risks (ILCRs); Table S3: Average PAHs' concentration (ng m^{-3}) at three sites in Hanoi during the sampling periods; Table S4: Average NPAHs' concentration (pg m^{-3}) at DA and XT in Hanoi during the sampling periods; Table S5: The toxic equivalent concentration range (pg/m^3) of PAHs and NPAHs (except 2-NP, 7-NbaA and 6-NbaP). References [57,101–106] are cited in the supplementary materials.

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References

1. De Oliveira Alves, N.; Martins Pereira, G.; Di Domenico, M.; Costanzo, G.; Benevenuto, S.; De Oliveira Fonoff, A.M.; De Souza Xavier Costa, N.; Ribeiro Júnior, G.; Satoru Kajitani, G.; Cestari Moreno, N.; et al. Inflammation response, oxidative stress and DNA damage caused by urban air pollution exposure increase in the lack of DNA repair XPC protein. *Environ. Int.* **2020**, *145*, 106150. [CrossRef]
2. Yang, L.; Zhang, H.; Zhang, X.; Xing, W.L.; Wang, Y.; Bai, P.C.; Zhang, L.L.; Hayakawa, K.; Toriba, A.; Tang, N. Exposure to atmospheric particulate matter-bound polycyclic aromatic hydrocarbons and their health effects: A Review. *Int. J. Environ. Res. Public Health* **2021**, *18*, 2177. [CrossRef]
3. Zhang, H.; Zhang, L.L.; Yang, L.; Zhou, Q.Y.; Zhang, X.; Xing, W.L.; Hayakawa, K.; Toriba, A.; Tang, N. Impact of COVID-19 outbreak on the long-range transport of common air pollutants in KUWAMS. *Chem. Pharm. Bull.* **2021**, *69*, 237–245. [CrossRef]
4. Zhang, X.; Zhang, H.; Wang, Y.; Bai, P.C.; Zhang, L.L.; Wei, Y.; Tang, N. Personal $PM_{2.5}$-bound PAH exposure and lung function in healthy office workers: A pilot study in Beijing and Baoding, China. *J. Environ. Sci.* **2023**, *133*, 48–59. [CrossRef]
5. Xing, W.L.; Yang, L.; Zhang, H.; Zhang, X.; Wang, Y.; Bai, P.C.; Zhang, L.L.; Hayakawa, K.; Nagao, S.; Tang, N. Variations in traffic-related water-soluble inorganic ions in $PM_{2.5}$ in Kanazawa, Japan, after the implementation of a new vehicle emission regulation. *Atmos. Pollut. Res.* **2021**, *12*, 101233. [CrossRef]
6. Xing, W.L.; Yang, L.; Zhang, H.; Zhang, X.; Wang, Y.; Bai, P.C.; Zhang, L.L.; Hayakawa, K.; Nagao, S.; Tang, N. Variations in traffic-related polycyclic aromatic hydrocarbons in $PM_{2.5}$ in Kanazawa, Japan, after the implementation of a new vehicle emission regulation. *J. Environ. Sci.* **2022**, *121*, 38–47. [CrossRef]
7. Lee, B.K. Sources, distribution and toxicity of polyaromatic hydrocarbons (pahs) in particulate matter. In *Air Pollution*; IntechOpen Limited: London, UK, 2010. [CrossRef]
8. Arey, J.; Zielinska, B.; Atkinson, R.; Winer, A.M.; Ramdahl, T.; Pitts, J.N. The formation of Nitro-PAH from the gas-phase reactions of fluoranthene and pyrene with the OH radical in the presence of Nox. *Atmos. Environ.* **1986**, *20*, 2339–2345. [CrossRef]
9. Marino, F.; Cecinato, A.; Siskos, P.A. Nitro-PAH in ambient particulate matter in the atmosphere of Athens. *Chemosphere* **2000**, *40*, 533–537. [CrossRef]
10. Boffetta, P.; Jourenkova, N.; Gustavsson, P. Cancer risk from occupational and environmental exposure to polycyclic aromatic hydrocarbons. *Cancer Causes Control* **1997**, *8*, 444–472. [CrossRef]
11. Knafla, A.; Phillipps, K.A.; Brecher, R.W.; Petrovic, S.; Richardson, M. Development of a dermal cancer slope factor for benzo[a]pyrene. *Regul. Toxicol. Pharmacol.* **2006**, *45*, 159–168. [CrossRef]
12. Chen, J.W.; Wang, S.L.; Hsieh, D.P.; Yang, H.H.; Lee, H.L. Carcinogenic potencies of polycyclic aromatic hydrocarbons for back-door neighbors of restaurants with cooking emissions. *Sci. Total Environ.* **2012**, *417–418*, 68–75. [CrossRef] [PubMed]
13. Yoon, E.; Park, K.; Lee, H.; Yang, J.-H.; Lee, C. Estimation of excess cancer risk on time-weighted lifetime average daily intake of pahs from food ingestion. *Hum. Ecol. Risk Assess. Int. J.* **2007**, *13*, 669–680. [CrossRef]
14. National Institute of Technology and Evaluation. Basic Manual for Calculation of the Estimated Human Exposure Used in the Risk Assessment of Consumer Products. Available online: https://www.nite.go.jp/en/chem/risk/ghs_risk_consumer_guidance_ap1_e.pdf (accessed on 21 April 2023).
15. Armstrong, B.; Hutchinson, E.; Unwin, J.; Fletcher, T. Lung cancer risk after exposure to polycyclic aromatic hydrocarbons: A review and meta-analysis. *Environ. Health Perspect.* **2004**, *112*, 970–978. [CrossRef] [PubMed]
16. Raymond, C.V. Estimating the lung deposition of particulate polycyclic aromatic hydrocarbons associated with multimodal urban aerosols. *Inhal. Toxicol.* **1998**, *10*, 183–204. [CrossRef]
17. IARC. Bitumens and bitumen emissions, and some n- and s-heterocyclic polycyclic aromatic hydrocarbons. In *Monographs on the Evaluation of Carcinogenic Risks to Humans*; International Agency for Research on Cancer: Lyon, France, 2013; Volume 103.
18. IARC. Diesel and gasoline engine exhausts and some nitroarenes. In *Monographs on the Evaluation of Carcinogenic Risks to Humans*; International Agency for Research on Cancer: Lyon, France, 2013; Volume 105.
19. IARC. *Monographs on the Evaluation of Carcinogenic Risks to Humans*; International Agency for Research on Cancer: Lyon, France, 2015; Volume 109.
20. Taga, R.; Tang, N.; Hattori, T.; Tamura, K.; Sakai, S.; Toriba, A.; Kizu, R.; Hayakawa, K. Direct-acting mutagenicity of extracts of coal burning-derived particulates and contribution of nitropolycyclic aromatic hydrocarbons. *Mutat. Res. Genet. Toxicol. Environ. Mutagen.* **2005**, *581*, 91–95. [CrossRef]

21. Thepnuan, D.; Chantara, S. Characterization of $PM_{2.5}$–bound polycyclic aromatic hydrocarbons in Chiang Mai, Thailand during biomass open burning period of 2016. *Appl. Environ. Res.* **2020**, *42*, 11–24. [CrossRef]
22. Yadav, A.; Behera, S.N.; Nagar, P.K.; Sharma, M. Spatio-seasonal concentrations, source apportionment and assessment of associated human health risks of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons in Delhi, India. *Aerosol Air Qual. Res.* **2020**, *20*, 2805–2825. [CrossRef]
23. Shen, R.; Wang, Y.; Gao, W.; Cong, X.; Cheng, L.; Li, X. Size-segregated particulate matter bound polycyclic aromatic hydrocarbons (pahs) over China: Size distribution, characteristics and health risk assessment. *Sci. Total Environ.* **2019**, *685*, 116–123. [CrossRef] [PubMed]
24. Tang, N.; Araki, Y.; Tamura, K.; Dong, L.; Zhang, X.; Liu, Q.; Ji, R.; Kameda, T.; Toriba, A.; Hayakawa, K. Distribution and source of atmospheric polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in Tieling city, Liaoning province, a typical local city in Northeast China. *Asian J. Atmos. Environ.* **2009**, *3*, 52–58. [CrossRef]
25. Tang, N.; Sato, K.; Tokuda, T.; Tatematsu, M.; Hama, H.; Suematsu, C.; Kameda, T.; Toriba, A.; Hayakawa, K. Factors affecting atmospheric 1-, 2-nitropyrenes and 2-nitrofluoranthene in winter at Noto Peninsula, a remote background site, Japan. *Chemosphere* **2014**, *107*, 324–330. [CrossRef]
26. Gulia, S.; Khanna, I.; Shukla, K.; Khare, M. Ambient air pollutant monitoring and analysis protocol for low and middle income countries: An element of comprehensive urban air quality management framework. *Atmos. Environ.* **2020**, *222*, 117120. [CrossRef]
27. Vo, V.C. Forecast on electricity demand for industry and construction sectors in Vietnam by 2030. In Proceedings of the 2019 International Conference on System Science and Engineering, Dong Hoi, Vietnam, 20–21 July 2019. [CrossRef]
28. Liu, X.; Deng, B.; Fu, J.; Xu, Z.; Liu, J.; Li, M.; Li, Q.; Ma, Z.; Feng, R. The effect of air/fuel composition on the HC emissions for a twin-spark motorcycle gasoline engine: A wide condition range study. *Chem. Eng. J.* **2019**, *355*, 170–180. [CrossRef]
29. Phung, D.; Hien, T.T.; Linh, H.N.; Luong, L.M.T.; Morawska, L.; Chu, C.; Binh, N.D.; Thai, P.K. Air pollution and risk of respiratory and cardiovascular hospitalizations in the most populous city in Vietnam. *Sci. Total Environ.* **2016**, *557–558*, 322–330. [CrossRef] [PubMed]
30. Kitamura, Y.; Hayashi, M.; Yagi, E. Traffic problems in Southeast Asia featuring the case of Cambodia's traffic accidents involving motorcycles. *IATSS Res.* **2018**, *42*, 163–170. [CrossRef]
31. Pham, C.T.; Kameda, T.; Toriba, A.; Hayakawa, K. Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in particulates emitted by motorcycles. *Environ. Pollut.* **2013**, *183*, 175–183. [CrossRef]
32. Pham, C.T.; Boongla, Y.; Nghiem, T.D.; Le, H.T.; Tang, N.; Toriba, A.; Hayakawa, K. Emission characteristics of polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons from open burning of rice straw in the north of Vietnam. *Int. J. Environ. Res. Public Health* **2019**, *16*, 2343. [CrossRef]
33. General Statistical Office Vietnam. *Statistical Yearbook of Vietnam 2021*; Statistical Publishing House: Hanoi, Vietnam, 2021.
34. Le, H.A.; Khoi, N.Q.; Mallick, J. Integrated emission inventory and modelling to assess the distribution of particulate matters from rice straw open burning in Hanoi, Vietnam. *Atmos. Pollut. Res.* **2022**, *13*, 101416. [CrossRef]
35. Công, L.H. Coffee plantations in Ninh Binh Province during the French Colonial Period. *J. Sci. Soc. Sci.* **2015**, *60*, 55–61. [CrossRef]
36. Lasko, K.; Vadrevu, K. Improved rice residue burning emissions estimates: Accounting for practice-specific emission factors in air pollution assessments of Vietnam. *Environ. Pollut.* **2018**, *236*, 795–806. [CrossRef]
37. Stelte, W.; Sanadi, A.R.; Shang, L.; Holm, J.K.; Ahrenfeldt, J.; Henriksen, U.B. Recent developments in biomass pelletization—A review. *BioResources* **2012**, *7*, 4451–4490. [CrossRef]
38. Hong Phuong, P.; Nghiem, T.; Mai Thao, P.; Nguyen, T. Emission factors of selected air pollutants from rice straw open burning in the Mekong Delta of Vietnam. *Atmos. Pollut. Res.* **2022**, *13*, 101353. [CrossRef]
39. Zhang, H.; Zhang, X.; Wang, Y.; Bai, P.C.; Hayakawa, K.; Zhang, L.L.; Tang, N. Characteristics and influencing factors of polycyclic aromatic hydrocarbons emitted from open burning and stove burning of biomass: A brief review. *Int. J. Environ. Res. Public Health* **2022**, *19*, 3944. [CrossRef] [PubMed]
40. Nguyen, D.V.; Vu, A.T.; Polders, E.; Ross, V.; Brijs, T.; Wets, G.; Brijs, K. Modeling the injury severity of small-displacement motorcycle crashes in Hanoi City, Vietnam. *Saf. Sci.* **2021**, *142*, 105371. [CrossRef]
41. Nguyen, Y.T.; Le, A.; Duc, K.N.; Duy, V.N.; Nguyen, C.D. A study on emission and fuel consumption of motorcycles in idle mode and the impacts on air quality in Hanoi, Vietnam. *Int. J. Urban Sci.* **2021**, *25*, 522–541. [CrossRef]
42. Kishida, M.; Imamura, K.; Takenaka, N.; Maeda, Y.; Viet, P.H.; Bandow, H. Concentrations of atmospheric polycyclic aromatic hydrocarbons in particulate matter and the gaseous phase at roadside sites in Hanoi, Vietnam. *Bull. Environ. Contam. Toxicol.* **2008**, *81*, 174–179. [CrossRef]
43. Saha, M.; Maharana, D.; Kurumisawa, R.; Takada, H.; Yeo, B.G.; Rodrigues, A.C.; Bhattacharya, B.; Kumata, H.; Okuda, T.; He, K.; et al. Seasonal trends of atmospheric pahs in five Asian megacities and source detection using suitable biomarkers. *Aerosol Air Qual. Res.* **2017**, *17*, 2247–2262. [CrossRef]
44. Nhung, N.T.; Schindler, C.; Dien, T.M.; Probst-Hensch, N.; Perez, L.; Künzli, N. Acute effects of ambient air pollution on lower respiratory infections in Hanoi children: An eight-year time series study. *Environ. Int.* **2018**, *110*, 139–148. [CrossRef]
45. Trinh, T.T.; Trinh, T.T.; Le, T.T.; Nguyen, T.D.; Tu, B.M. Temperature inversion and air pollution relationship, and its effects on human health in Hanoi City, Vietnam. *Environ. Geochem. Health* **2018**, *41*, 929–937. [CrossRef]

46. Pham, C.T.; Kameda, T.; Toriba, A.; Tang, N.; Hayakawa, K. Characteristics of atmospheric polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in Hanoi-vietnam, as a typical motorbike city. *Polycycl. Aromat. Compd.* **2012**, *32*, 296–312. [CrossRef]
47. Pham, C.T.; Le, H.T. Distribution and toxic equipvalent assessement of polycyclic aromatic hydrocarbons (pahs) in particulate matter emmited from Rice Straw Open field burning in Hanoi. *VNU J. Sci. Nat. Sci. Technol.* **2021**, *37*, 97–106. [CrossRef]
48. Pham, C.T.; Ly, B.T.; Nghiem, T.D.; Pham, T.H.P.; Minh, N.T.; Tang, N.; Hayakawa, K.; Toriba, A. Emission factors of selected air pollutants from rice straw burning in Hanoi, Vietnam. *Air Qual. Atmos. Health* **2021**, *14*, 1757–1771. [CrossRef]
49. Pham, C.T. Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in motorcycle exhaust. *Polycycl. Aromat. Compd.* **2018**, 137–153. [CrossRef]
50. Trung, N.T.; Anh, H.Q.; Tue, N.M.; Suzuki, G.; Takahashi, S.; Tanabe, S.; Khai, N.M.; Hong, T.T.; Dau, P.T.; Thuy, P.C.; et al. Polycyclic aromatic hydrocarbons in airborne particulate matter samples from Hanoi, Vietnam: Particle size distribution, aryl hydrocarbon ligand receptor activity, and implication for cancer risk assessment. *Chemosphere* **2021**, *280*, 130720. [CrossRef] [PubMed]
51. Wang, Y.; Zhang, H.; Zhang, X.; Bai, P.C.; Neroda, A.; Mishukov, V.F.; Zhang, L.L.; Hayakawa, K.; Nagao, S.; Tang, N. PM-bound polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons in the ambient air of Vladivostok: Seasonal variation, sources, health risk assessment and long-term variability. *Int. J. Environ. Res. Public Health* **2022**, *19*, 2878. [CrossRef]
52. Yang, L.; Zhang, L.L.; Zhang, H.; Zhou, Q.Y.; Zhang, X.; Xing, W.; Takami, A.; Sato, K.; Shimizu, A.; Yoshino, A.; et al. Comparative analysis of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons (pahs), nitro-pahs (npahs), and water-soluble inorganic ions (wsiis) at two background sites in Japan. *Int. J. Environ. Res. Public Health* **2020**, *17*, 8224. [CrossRef] [PubMed]
53. Chen, S.C.; Liao, C.M. Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources. *Sci. Total Environ.* **2006**, *366*, 112–123. [CrossRef]
54. De Miguel, E.; Iribarren, I.; Chacón, E.; Ordoñez, A.; Charlesworth, S. Risk-based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). *Chemosphere* **2007**, *66*, 505–513. [CrossRef]
55. U.S. EPA. 1994, Benzo[a]pyrene (BaP) (CASRN 50-32-8). Available online: https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?substance_nmbr=136 (accessed on 9 April 2023).
56. Wang, Z. *Regional Study on Soil Polycyclic Aromatic Hydrocarbons in Liaoning: Patterns, Sources and Cancer Risks*; Dalian University of Technology: Dalian, China, 2007.
57. NCD Risk Factor Collaboration. Height and body-mass index trajectories of school-aged children and adolescents from 1985 to 2019 in 200 countries and territories: A pooled analysis of 2181 population-based studies with 65 million participants. In *Yearbook of Paediatric Endocrinology*; Bioscientifica Ltd.: Bristol, UK, 2021. [CrossRef]
58. Zhang, H.; Yang, L.; Zhang, X.; Xing, W.L.; Wang, Y.; Bai, P.C.; Zhang, L.L.; Li, Y.; Hayakawa, K.; Toriba, A.; et al. Characteristics and health risks of polycyclic aromatic hydrocarbons and nitro-pahs in Xinxiang, China in 2015 and 2017. *Int. J. Environ. Res. Public Health* **2021**, *18*, 3017. [CrossRef]
59. Tang, N.; Hattori, T.; Taga, R.; Igarashi, K.; Yang, X.; Tamura, K.; Kakimoto, H.; Mishukov, V.F.; Toriba, A.; Kizu, R.; et al. Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their relationship to emission sources in the Pan–Japan Sea Countries. *Atmos. Environ.* **2005**, *39*, 5817–5826. [CrossRef]
60. Yang, L.; Suzuki, G.; Zhang, L.L.; Zhou, Q.Y.; Zhang, X.; Xing, W.L.; Shima, M.; Yoda, Y.; Nakatsubo, R.; Hiraki, T.; et al. The characteristics of polycyclic aromatic hydrocarbons in different emission source areas in Shenyang, China. *Int. J. Environ. Res. Public Health* **2019**, *16*, 2817. [CrossRef]
61. Lara, S.; Villanueva, F.; Martín, P.; Salgado, S.; Moreno, A.; Sánchez-Verdú, P. Investigation of pahs, nitrated pahs and oxygenated pahs in PM10 urban aerosols. A comprehensive data analysis. *Chemosphere* **2022**, *294*, 133745. [CrossRef] [PubMed]
62. 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.* **2021**, *29*, 26449–26464. [CrossRef] [PubMed]
63. Wang, Y.; Zhang, H.; Zhang, X.; Bai, P.C.; Zhang, L.L.; Huang, S.J.; Pointing, S.B.; Nagao, S.; Chen, B.; Toriba, A.; et al. Abundance, source apportionment and health risk assessment of polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons in $PM_{2.5}$ in the urban atmosphere of Singapore. *Atmosphere* **2022**, *13*, 1420. [CrossRef]
64. Hu, R.; Liu, G.; Zhang, H.; Xue, H.; Wang, X. Levels and sources of pahs in air-borne $PM_{2.5}$ of Hefei City, China. *Bull. Environ. Contam. Toxicol.* **2017**, *98*, 270–276. [CrossRef]
65. 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]
66. Zhang, F.; Chen, Y.; Cui, M.; Feng, Y.; Yang, X.; Chen, J.; Zhang, Y.; Gao, H.; Tian, C.; Matthias, V.; et al. Emission factors and environmental implication of organic pollutants in PM emitted from various vessels in China. *Atmos. Environ.* **2019**, *200*, 302–311. [CrossRef]
67. Chen, Y.; Li, X.; Zhu, T.; Han, Y.; Lv, D. $PM_{2.5}$-bound pahs in three indoor and one outdoor air in Beijing: Concentration, source and health risk assessment. *Sci. Total Environ.* **2017**, *586*, 255–264. [CrossRef] [PubMed]
68. Xing, W.L.; Zhang, L.L.; Yang, L.; Zhou, Q.Y.; Zhang, X.; Toriba, A.; Hayakawa, K.; Tang, N. Characteristics of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons at a roadside air pollution monitoring station in Kanazawa, Japan. *Int. J. Environ. Res. Public Health* **2020**, *17*, 805. [CrossRef] [PubMed]

69. Hien, T.T.; Nam, P.P.; Yasuhiro, S.; Takayuki, K.; Norimichi, T.; Hiroshi, B. Comparison of particle-phase polycyclic aromatic hydrocarbons and their variability causes in the ambient air in Ho Chi Minh City, Vietnam and in Osaka, Japan, during 2005–2006. *Sci. Total Environ.* **2007**, *382*, 70–81. [CrossRef]
70. Hien, T.T.; Thanh, L.T.; Kameda, T.; Takenaka, N.; Bandow, H. Nitro-polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbons in particulate matter in an urban area of a tropical region: Ho Chi Minh City, Vietnam. *Atmos. Environ.* **2007**, *41*, 7715–7725. [CrossRef]
71. Insian, W.; Yabueng, N.; Wiriya, W.; Chantara, S. Size-fractionated PM-bound pahs in urban and rural atmospheres of northern Thailand for respiratory health risk assessment. *Environ. Pollut.* **2022**, *293*, 118488. [CrossRef] [PubMed]
72. Kishida, M.; Mio, C.; Fujimori, K.; Imamura, K.; Takenaka, N.; Maeda, Y.; Lan, T.T.; Shibutani, Y.; Bandow, H. Seasonal change in the atmospheric concentration of particulate polycyclic aromatic hydrocarbons in Ho Chi Minh City, Vietnam. *Bull. Environ. Contam. Toxicol.* **2009**, *83*, 747–751. [CrossRef]
73. To, T.H.; Nguyen, D.T.; Le, X.V.; Duong, H.H. A comparison of $PM_{2.5}$ and pahs in ambient air between an urban background site and a background site in Ho Chi Minh City. *Vietnam J. Sci. Technol. Engr.* **2019**, *61*, 79–83. [CrossRef]
74. Hosseini, S.; Urbanski, S.P.; Dixit, P.; Qi, L.; Burling, I.R.; Yokelson, R.J.; Johnson, T.J.; Shrivastava, M.; Jung, H.S.; Weise, D.R.; et al. Laboratory characterization of PM emissions from combustion of wildland biomass fuels. *J. Geophys. Res. Atmos.* **2013**, *118*, 9914–9929. [CrossRef]
75. Noblet, C.; Besombes, J.L.; Lemire, M.; Pin, M.; Jaffrezo, J.L.; Favez, O.; Aujay-Plouzeau, R.; Dermigny, A.; Karoski, N.; Van Elsuve, D.; et al. Emission factors and chemical characterization of particulate emissions from Garden Green Waste burning. *Sci. Total Environ.* **2021**, *798*, 149367. [CrossRef]
76. Samburova, V.; Connolly, J.; Gyawali, M.; Yatavelli, R.L.N.; Watts, A.C.; Chakrabarty, R.K.; Zielinska, B.; Moosmüller, H.; Khlystov, A. Polycyclic aromatic hydrocarbons in biomass-burning emissions and their contribution to light absorption and aerosol toxicity. *Sci. Total Environ.* **2016**, *568*, 391–401. [CrossRef]
77. Shen, G.; Tao, S.; Wei, S.; Zhang, Y.; Wang, R.; Wang, B.; Li, W.; Shen, H.; Huang, Y.; Chen, Y.; et al. Reductions in emissions of carbonaceous particulate matter and polycyclic aromatic hydrocarbons from combustion of biomass pellets in comparison with raw fuel burning. *Environ. Sci. Technol.* **2012**, *46*, 6409–6416. [CrossRef] [PubMed]
78. Wang, H.L.; Zhuang, Y.H.; Hao, Z.P.; Cao, M.Q.; Zhong, J.X.; Wang, X.K.; Nguyen, T.K. Polycyclic aromatic hydrocarbons from rural household biomass burning in a typical Chinese village. *Sci. China Earth Sci.* **2008**, *51*, 1013–1020. [CrossRef]
79. Wiriya, W.; Chantara, S.; Sillapapiromsuk, S.; Lin, N.-H. Emission profiles of PM10-bound polycyclic aromatic hydrocarbons from biomass burning determined in chamber for assessment of air pollutants from open burning. *Aerosol Air Qual. Res.* **2016**, *16*, 2716–2727. [CrossRef]
80. Ciganek, M.; Neca, J.; Adamec, V.; Janosek, J.; Machala, M. A combined chemical and bioassay analysis of traffic-emitted polycyclic aromatic hydrocarbons. *Sci. Total Environ.* **2004**, *334–335*, 141–148. [CrossRef]
81. Gao, B.; Guo, H.; Wang, X.M.; Zhao, X.Y.; Ling, Z.H.; Zhang, Z.; Liu, T.-Y. Polycyclic aromatic hydrocarbons in $PM_{2.5}$ in Guangzhou, Southern China: Spatiotemporal patterns and emission sources. *J. Hazard. Mater.* **2012**, *239–240*, 78–87. [CrossRef] [PubMed]
82. Kim, K.H.; Anthwal, A.; Goo Park, C.; Jo, S.J.; Chae, Y.Z.; Park, J.A.; Heub Jung, J.; Ryeul Sohn, J.; Oh, J.M. Monitoring of polyaromatic hydrocarbons and volatile organic compounds in two major traffic tunnels in Seoul, Korea. *Environ. Technol.* **2012**, *33*, 1963–1976. [CrossRef] [PubMed]
83. Manoli, E.; Kouras, A.; Karagkiozidou, O.; Argyropoulos, G.; Voutsa, D.; Samara, C. Polycyclic aromatic hydrocarbons (pahs) at traffic and urban background sites of Northern Greece: Source apportionment of ambient PAH levels and PAH-induced lung cancer risk. *Environ. Sci. Pollut. Res.* **2015**, *23*, 3556–3568. [CrossRef] [PubMed]
84. Sánchez-Piñero, J.; Moreda-Piñeiro, J.; Turnes-Carou, I.; Fernández-Amado, M.; Muniategui-Lorenzo, S.; López-Mahía, P. Polycyclic aromatic hydrocarbons in atmospheric particulate matter (PM10) at a southwestern Europe coastal city: Status, sources and Health Risk Assessment. *Air Qual. Atmos. Health* **2021**, *14*, 1325–1339. [CrossRef]
85. Slezakova, K.; Castro, D.; Pereira, M.C.; Morais, S.; Delerue-Matos, C.; Alvim-Ferraz, M.C. Influence of traffic emissions on the carcinogenic polycyclic aromatic hydrocarbons in outdoor breathable particles. *J. Air Waste Manag. Assoc.* **2010**, *60*, 393–401. [CrossRef]
86. Nguyen, H.T.; Le, T.K.; Nguyen, K.M.; Han, L.T.N. Potential of biochar production from agriculture residues at household scale: A case study in Go Cong Tay District, Tien Giang Province, Vietnam. *Environ. Nat. Resour. J.* **2018**, *16*, 68–78. [CrossRef]
87. Yang, L.; Zhou, Q.Y.; Zhang, H.; Zhang, X.; Xing, W.L.; Wang, Y.; Bai, P.C.; Yamauchi, M.; Chohji, T.; Zhang, L.L.; et al. Atmospheric behaviour of polycyclic and nitro-polycyclic aromatic hydrocarbons and water-soluble inorganic ions in winter in Kirishima, a typical Japanese commercial city. *Int. J. Environ. Res. Public Health* **2021**, *18*, 688. [CrossRef]
88. Arey, J.; Atkinson, R.; Aschmann, S.M.; Schuetzle, D. Experimental investigation of the atmospheric chemistry of 2-methyl-1-nitronaphthalene and a comparison of predicted NITROARENE concentrations with Ambient Air Data. *Polycycl. Aromat. Compd.* **1990**, *1*, 33–50. [CrossRef]
89. Arey, J.; Zielinska, B.; Atkinson, R.; Aschmann, S.A. Nitroarene products from the gas-phase reactions of volatile polycyclic aromatic hydrocarbons with OH radical and N_2O_5. *Int. J. Chem. Kinet.* **1989**, *21*, 775–799. [CrossRef]

90. Ciccioli, P.; Cecinato, A.; Brancaleoni, E.; Frattoni, M.; Zacchei, P.; Miguel, A.H.; De Castro Vasconcellos, P. Formation and transport of 2-nitrofluoranthene and 2-Nitropyrene of photochemical origin in the troposphere. *J. Geophys. Res. Atmos.* **1996**, *101*, 19567–19581. [CrossRef]
91. Yang, L.; Zhang, L.L.; Chen, L.J.; Han, C.; Akutagawa, T.; Endo, O.; Yamauchi, M.; Neroda, A.; Toriba, A.; Tang, N. Polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons in five East Asian cities: Seasonal characteristics, health risks, and yearly variations. *Environ. Pollut.* **2021**, *287*, 117360. [CrossRef]
92. Zhang, L.; Yang, L.; Bi, J.; Liu, Y.; Toriba, A.; Hayakawa, K.; Nagao, S.; Tang, N. Characteristics and unique sources of polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons in $PM_{2.5}$ at a Highland Background Site in northwestern China. *Environ. Pollut.* **2021**, *274*, 116527. [CrossRef]
93. Delistraty, D. Toxic equivalency factor approach for risk assessment of polycyclic aromatic hydrocarbons. *Environ. Toxicol. Chem.* **1997**, *64*, 81–108. [CrossRef]
94. Zhang, L.L.; Morisaki, H.; Wei, Y.J.; Li, Z.; Yang, L.; Zhou, Q.Y.; Zhang, X.; Xing, W.L.; Hu, M.; Shima, M.; et al. $PM_{2.5}$-bound polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons inside and outside a primary school classroom in Beijing: Concentration, composition, and inhalation cancer risk. *Sci. Total Environ.* **2020**, *705*, 135840. [CrossRef] [PubMed]
95. Feng, B.; Li, L.; Xu, H.; Wang, T.; Wu, R.; Chen, J.; Zhang, Y.; Liu, S.; Ho, S.S.; Cao, J.; et al. $PM_{2.5}$-bound polycyclic aromatic hydrocarbons (pahs) in Beijing: Seasonal variations, sources, and risk assessment. *J. Environ. Sci.* **2019**, *77*, 11–19. [CrossRef]
96. Kelly, J.M.; Ivatt, P.D.; Evans, M.J.; Kroll, J.H.; Hrdina, A.I.; Kohale, I.N.; White, F.M.; Engelward, B.P.; Selin, N.E. Global cancer risk from unregulated polycyclic aromatic hydrocarbons. *GeoHealth* **2021**, *5*, e2021GH000401. [CrossRef] [PubMed]
97. Janta, R.; Sekiguchi, K.; Yamaguchi, R.; Sopajaree, K.; Pongpiachan, S.; Chetiyanukornkul, T. Ambient $PM_{2.5}$, polycyclic aromatic hydrocarbons and biomass burning tracer in Mae Sot District, Western Thailand. *Atmos. Pollut. Res.* **2020**, *11*, 27–39. [CrossRef]
98. Han, B.; Liu, Y.; You, Y.; Xu, J.; Zhou, J.; Zhang, J.; Niu, C.; Zhang, N.; He, F.; Ding, X.; et al. Assessing the inhalation cancer risk of particulate matter bound polycyclic aromatic hydrocarbons (pahs) for the elderly in a retirement community of a Mega City in North China. *Environ. Sci. Pollut. Res.* **2016**, *23*, 20194–20204. [CrossRef] [PubMed]
99. U.S. EPA. Exposure Factors Handbook: 2011 Edition (Final Report). U.S. Environmental Protection Agency, Washington, DC EPA/600/R-09/052F. 2011. Available online: https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=236252 (accessed on 9 April 2023).
100. Pieterse, B.; Felzel, E.; Winter, R.; van der Burg, B.; Brouwer, A. Pah-CALUX, an optimized bioassay for ahr-mediated hazard identification of polycyclic aromatic hydrocarbons (pahs) as individual compounds and in complex mixtures. *Environ. Sci. Technol.* **2013**, *47*, 11651–11659. [CrossRef]
101. U.S. EPA. *2010 U.S. Environmental Protection Agency (EPA) Decontamination Research and Development Conference*; EPA/600/R-11/052; U.S. Environmental Protection Agency: Washington, DC, USA, 2011.
102. Collins, J.F.; Brown, J.P.; Alexeeff, G.V.; Salmon, A.G. Potency equivalency factors for some polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbon derivatives. *Regul. Toxicol. Pharmacol.* **1998**, *28*, 45–54. [CrossRef]
103. Panis, L.I.; De Geus, B.; Vandenbulcke, G.; Willems, H.; Degraeuwe, B.; Bleux, N.; Mishra, V.; Thomas, I.; Meeusen, R. Exposure to particulate matter in traffic: A comparison of cyclists and car passengers. *Atmos. Environ.* **2010**, *44*, 2263–2270. [CrossRef]
104. Zhang, Z.H.; Khlystov, A.; Norford, L.K.; Tan, Z.K.; Balasubramanian, R. Characterization of traffic-related ambient fine particulate matter (PM 2.5) in an Asian city: Environmental and health implications. *Atmos. Environ.* **2017**, *161*, 132–143. [CrossRef]
105. The World Bank, Life Expectancy at Birth, Total (Years)—Vietnam. Available online: https://data.worldbank.org/indicator/SP.DYN.LE00.IN?locations=VN (accessed on 9 April 2023).
106. USDOE. The Risk Assessment Information System (RAIS). U.S. Department of Energy's Oak Ridge Operations Office (ORO). 2011. Available online: http://rais.ornl.gov/ (accessed on 9 April 2023).