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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

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Abstract: In this study, the levels of fine particulate matter ($PM_{2.5}$), polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs (NPAHs) in $PM_{2.5}$ samples were determined from 2020 to 2021 in Singapore. For analysis convenience, the sampling period was classified according to two monsoon periods and the inter-monsoon period. Considering Singapore's typically tropical monsoon climate, the four seasons were divided into the northeast monsoon season (NE), southwest monsoon season (SW), presouthwest monsoon season (PSW) and prenortheast monsoon season (PNE)). The $PM_{2.5}$ concentration reached 17.1 ± 8.38 μg/m^3, which was slightly higher than that in 2015, and the average PAH concentration continuously declined during the sampling period compared to that reported in previous studies in 2006 and 2015. This is the first report of NPAHs in Singapore indicating a concentration of 13.1 ± 10.7 pg/m^3. The seasonal variation in the PAH and NPAH concentrations in $PM_{2.5}$ did not obviously differ owing to the unique geographical location and almost uniform climate changes in Singapore. Diagnostic ratios revealed that PAHs and NPAHs mainly originated from local vehicle emissions during all seasons. 2-Nitropyrene (2-NP) and 2-nitrofluoranthene (2-NFR) in Singapore were mainly formed under the daytime OH-initiated reaction pathway. Combined with airmass backward trajectory analysis, the Indonesia air mass could have influenced Singapore's air pollution levels in PSW. However, these survey results showed that no effect was found on the concentrations of PAHs and NPAHs in $PM_{2.5}$ in Indonesia during SW because of Indonesia's efforts in the environment. It is worth noting that air masses from southern China could impact the PAH and NPAH concentrations according to long-range transportation during the NE. The results of the total incremental lifetime cancer risk (ILCR) via three exposure routes (ingestion, inhalation and dermal absorption) for males and females during the four seasons indicated a low long-term potential carcinogenic risk, with values ranging from 10^{-10} to 10^{-7}. This study systematically explains the latest pollution conditions, sources, and potential health risks in Singapore, and comprehensively analyses the impact of the tropical monsoon system on air pollution in Singapore, providing a new perspective on the transmission mechanism of global air pollution.

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1. Introduction

Among air pollutants, fine particulate matter ($PM_{2.5}$: diameter < 2.5 μm) negatively affects human health and is closely related to human respiratory diseases [1]. In recent years, a network for continuous $PM_{2.5}$ monitoring has been established worldwide, and policies have been continuously formulated to improve $PM_{2.5}$ pollution reduction [2]. Following this growing recognition, $PM_{2.5}$, which contains a large number of toxic substances, is easily transported by wind and can persist in the atmosphere for extended periods due to its small size [3,4]. Polycyclic aromatic hydrocarbons (PAHs) have received much attention as the most carcinogenic and mutagenic substances in $PM_{2.5}$ [5–7]. PAHs represent a group of aromatic hydrocarbons with two or more fused benzene rings and are considered ubiquitous atmospheric contaminants [8,9]. Most PAHs are persistent organic pollutants (POPs) in the environment due to their hydrophobicity and chemical inertness [10–12]. However, PAHs can react with ozone and hydroxyl radicals to form a series of PAH derivatives [13,14]. Among these PAH derivatives, nitro-PAHs (NPAHs) have received global attention due to their higher mutagenicity and genotoxicity [15–17].

Southeast Asia remains among the most air polluted regions globally according to the annual update of the Air Quality Life Index in 2022 [18]. This is the result of the reliance on coal for power generation and vegetation fires to support "slash-and-burn" farming methods across Southeast Asia [19,20]. Moreover, South Asia monsoons can transport haze throughout most of the Association of Southeast Asian Nations (ASEAN) countries, including Singapore, Indonesia, Malaysia, Brunei, Thailand, and the Philippines [21]. In addition, the unique climatic conditions in recent years have further exacerbated the haze severity in affected countries, such as the dry weather conditions attributable to the El Niño-Southern Oscillation and positive Indian Ocean dipole during the southwest monsoon season (SW) [22,23]. Therefore, the near-catastrophic extent of seasonal haze episodes prompted the ASEAN Agreement on Transboundary Haze Pollution (AATHP) in 2002 [24,25]. Unfortunately, during the repeated severe air pollution events in Southeast Asia in 2013 and 2019, the pollutant level exceeded 200 $\mu g/m^3$, especially $PM_{2.5}$ [26,27]. Several studies have found that these seasonal haze episodes in an acute setting contribute to worsening asthma problems and other respiratory-related symptoms [28–31]. In addition, studies have consistently reported increased short-term respiratory morbidity and mortality levels due to seasonal exposure to smoke originating from episodic wildfires [32]. Among ASEAN countries, Singapore has experienced smoke haze episodes almost every dry season since the late 1990s due to its geographical location. Singapore is a typical industrial country with a small land area and high population density bordering Malaysia to the north and is adjacent to Indonesia to the south. Several studies have been conducted encompassing short-term measurements of PAHs in Singapore, but the seasonal and yearly variations in PAHs remain poorly understood in this region [33–36].

In the present research, $PM_{2.5}$ samples were collected in the urban environment of Singapore for more than one year. The objective of this study was to (1) better understand the pollution status of $PM_{2.5}$, PAHs and NPAHs in a subtropical urban atmosphere, (2) analyze the seasonal variation and influencing factors of atmospheric transport, (3) explore the potential sources of PAHs and NAPHs in $PM_{2.5}$, and (4) evaluate the potential health risks of PAHs and NPAHs in $PM_{2.5}$. This study represents the first evaluation of the distribution of airborne PAHs and NPAHs during different seasons and an assessment of the potential health risks of PAHs and NPAHs in Singapore.

2. Materials and Methods

2.1. Sample Collection

Seventy-seven $PM_{2.5}$ samples were collected from January 2020 to August 2021 on the National University of Singapore (NUS) campus which is located at a latitude of 1.29° N and longitude of 103.77° E, as shown in Figure 1. The island of Singapore is situated north of the equator, near Malaysia, Indonesia and southern China linking the Indian Ocean to the South China Sea. The northeast and southwest monsoons determine Singapore's climate characteristics [37,38]. Due to the geographical location and typically tropical climate of Singapore, the four seasons were divided into: the northeast monsoon season (NE), SW, presouthwest monsoon season (PSW) and prenortheast monsoon season (PNE). In general, the NE lasts from December to March while the SW ranges from June to September. The PSW extends from April to May and the PNE occurs between October and November. Details the sampling period are provided in Table S1.

Figure 1. The location of the sampling site (the original image comes from the open-source website: https://d-maps.com/index.php?lang=en, accessed on 17 July 2022).

$PM_{2.5}$ samples were collected using a high-volume air sampler (Sibata Sci. Tech. Ltd., Saitama, Japan) equipped with a quartz fiber filter (2500QAT-UP, Pallflex Products, Putnam, CT, USA) at an intake flow rate of 1000 L/min. $PM_{2.5}$ samples were collected for a week at a month, and the filters were changed every 24 h. After sampling, the samples were stored in a desiccator for 48 h and then weighed. These samples were wrapped in aluminum foil and refrigerated at −20 °C until the samples were analyzed.

2.2. Materials and Sample Analysis

The pretreatment process, analytical procedure and quality control process were the same as those in our previous study [39,40]. In each $PM_{2.5}$ sample, ten PAHs—fluoranthene (FR), pyrene (Pyr), benzo[*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 four NPAHs—2-NFR, 1-NPs, 2-NPs, and 6-nitrobenzo[*a*]pyrene (6-NBaP) (Chiron, Trondheim, Norway)—were analyzed with a high-performance liquid chromatography (HPLC) system with fluorescence detection (Shimadzu Inc., Kyoto, Japan). Two internal standards (Pyr-d_{10}

and BaP-d_{12}) were purchased from Wako Pure Chemicals (Osaka, Japan). All reagents were of analytical grade. Blank and standard samples were analyzed every seven samples to avoid cross-contamination and confirm the stability of the HPLC system.

2.3. Airmass Backwards Trajectory Analysis

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (HYSPLIT-4, Windows-based version, NOAA Air Resources Laboratory) developed by the National Oceanic and Atmospheric Administration (NOAA), was used to calculate backwards trajectories and obtain air mass routes during the sampling period [41,42]. Backwards trajectories were generated at 500 m above ground level to ensure that all trajectory started in the atmospheric boundary layer. Each backwards trajectory was calculated at hourly intervals and tracked for 96 h. In this study, cluster analysis of all backward trajectories was conducted based on the monsoon season and premonsoon season characteristics. The meteorological data used in the backwards trajectory calculation were retrieved from the National Centers for Environmental Prediction (NCEP) Global Data Assimilation System (GDAS, global, 2005-present). In addition, meteorological conditions (daily rainfall, mean temperature and mean wind speed) were obtained from the Changi Automatic Weather Observatory, Singapore (http://www.weather.gov.sg accessed on 25 July 2022).

2.4. Health Risk Assessment

The human health risk assessment process in this study considered various exposure pathways in the different environments where humans may be exposed to pollutants and may experience adverse effects. The exposure pathways included ingestion, dermal absorption and inhalation [43,44]. The populations considered included males and females exposed to pollutants in the atmospheric environment. The incremental lifetime cancer risk (ILCR) was assessed combined with the toxic equivalency factor (TEF) model [45,46].

The ILCR values for the ingestion, dermal absorption, and inhalation exposure routes and summation of the three risk forms (the total ILCR) were estimated as follows [47,48]:

$$R_{ing} = \frac{C \times CSF_{ing} \times \sqrt[3]{\frac{BW}{70}} \times IR_{ing} \times EF \times ED}{BW \times AT \times 10^6} \quad (1)$$

$$R_{inh} = \frac{C \times CSF_{inh} \times \sqrt[3]{\frac{BW}{70}} \times IR_{inh} \times EF \times ED}{BW \times AT \times PEF} \quad (2)$$

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

$$\text{Total ILCR} = ILCR_{ing} + ILCR_{inh} + ILCR_{dem} \quad (4)$$

where C is the sum of the toxic equivalent concentrations of the 16 individual PAHs in ng/m^3 (C = TEQ_{PAH}), which can be calculated as follows [49]:

$$TEQ_i = C_i \times TEF_i \quad (5)$$

$$TEQ_{total} = \sum TEQ_i \quad (6)$$

where TEF_i is the toxic equivalent of the individual PAHs as listed in Table S2 [50,51].

R_{ing}, R_{inh}, and R_{dem} denote the risk values considering the ingestion, inhalation, and dermal absorption exposure routes, respectively. The carcinogenic slope factors (CSFs) of BaP were parameterized as 7.3, 25, and 3.85 (1/(mg/kg/day)) for ingestion (CSF_{ing}), inhalation (CSF_{inh}), and dermal adsorption (CSF_{dem}), respectively. Moreover, BW is the average body weight in kg. IR_{ing} is the intake rate under the ingestion exposure route in mg/day, EF is the annual exposure frequency in days/year, ED is the exposure duration in years, AT is the average life span in days, IR_{inh} is the intake rate under the inhalation exposure route in mg/day, PEF is the particle emission factor in mg/kg, SA is the exposed

area of skin in cm^2, AF is the skin adherence factor in mg/cm^2, and ABS is the skin absorption factor in day^{-1}. Details of the parameters used are provided in Table S3 [52,53].

2.5. Statistical Analysis

In this study, the difference of PAH and NPAH concentrations in the $PM_{2.5}$ samples during the different seasons was explored according to one-way ANOVA. The test results were expressed considering a 95% confidence interval. SPSS version 24.0 (IBM Corp., Armonk, NK, USA) was used for statistical analysis.

3. Results

3.1. Distribution of $PM_{2.5}$, PAHs and NPAHs

The $PM_{2.5}$ concentration during the sampling period was 17.1 ± 8.38 $\mu g/m^3$, which was higher than that at the same sampling location in 2015 (13.0 ± 2.73 $\mu g/m^3$) [54]. Moreover, the average $PM_{2.5}$ concentration in Singapore was slightly lower than that of Kuala Lumpur (19.3 $\mu g/m^3$) in Malaysia [55], just half that of Jakarta (33.0 $\mu g/m^3$) in Indonesia [56], and much lower than that of Hanoi (73.6 $\mu g/m^3$) in Vietnam [57]. The PAH concentration was 0.62 ± 0.31 ng/m^3, and the NAPHs concentration reached 13.2 ± 10.7 pg/m^3, which is the first report on NPAHs in Singapore. It has been reported that the concentrations of 1-NP, 2-NP and 2-NFR in Singapore are slightly higher than those at background observatories (Noto Peninsula) but much lower than those in Beijing, Shenyang, and Vladivostok [58,59]. BgPe was the most abundant PAH (PSW: 26%, PNE: 24%, NE: 28%, SW: 23%), while 2-NFR was the most abundant NPAH (PSW: 62%, PNE: 36%, NE: 56%, SW: 40%). As shown in Figure 2, the six analyzed PAHs in $PM_{2.5}$ in previous studies were compared, and the average concentration was 0.72 ng/m^3 in 2006 [50], 0.68 ng/m^3 in 2015 [60], and 0.40 ng/m^3 in 2020 (this study). Due to repeated seasonal haze over the past 20 years, especially after the 2015 Southeast Asian haze caused economic loss (SGD 1.46 billion) in Singapore [61], Singapore has introduced an environmental law on transboundary haze pollution, and imposed fines and penalties for foreign companies to create toxic smog that spread across Singapore, effectively curbing Indonesia's forest fires [62]. Meanwhile, the PAH concentration had a sharp drop in 2020, which might explain why the introduction of Euro VI standards for vehicles in Singapore began on 1 September 2017 [63].

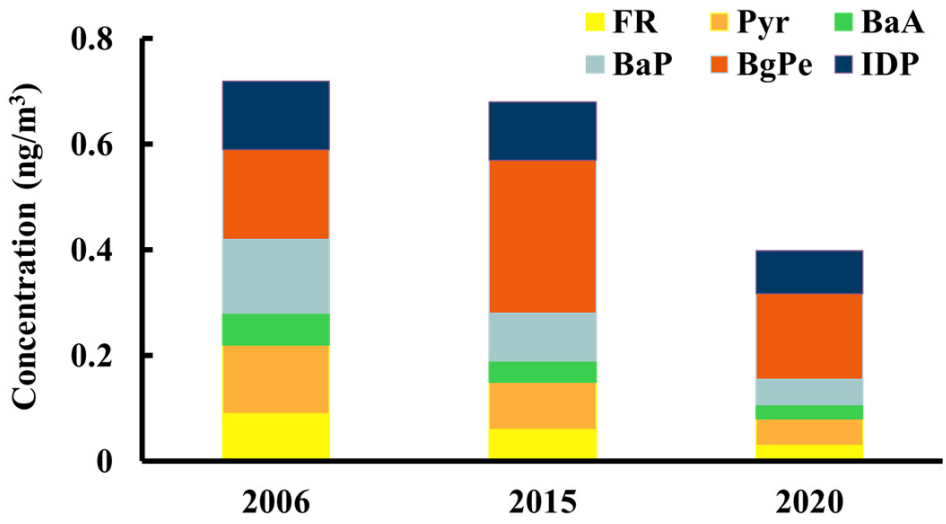

Figure 2. Concentration and composition changes of six PAHs in $PM_{2.5}$ in Singapore in 2006, 2015 and 2020.

The seasonal concentrations of $PM_{2.5}$, PAHs and NPAHs in $PM_{2.5}$ are summarized in Table 1. The $PM_{2.5}$ concentrations during the PNE and SW were 32.8 ± 7.34 $\mu g/m^3$ and 19.8 ± 6.52 $\mu g/m^3$, respectively, which are slightly higher than the air quality target

of Singapore (12 μg/m^3) and 3-fold higher than the World Health Organization (WHO) guideline value (5 μg/m^3). The highest PAH concentration was observed during the PNE, and the lowest was observed during the PSW, where the PAH concentrations reached 0.77 ± 0.12 and 0.47 ± 0.12 ng/m^3, respectively. In regard to NPAHs, the highest concentration was observed during the SW, and the lowest concentrations were observed during the PSW, at 15.5 ± 9.27 pg/m^3 and 10.3 ± 10.0 pg/m^3, respectively. However, according to one-way ANOVA results, the concentration values of PAHs (p = 0.22) and NAPHs (p = 0.64) in $PM_{2.5}$ during the four seasons were not significant difference. This means that no significant change in the emission sources of PAHs and NPAHs during the survey period [35]. Meanwhile, almost uniform weather conditions throughout the sampling period, such as temperature, rainfall, and wind speed, were suggested to be another factor [64–66] (Table S4).

Table 1. The mean concentration and standard deviation of $PM_{2.5}$, ten PAHs and four NPAHs in $PM_{2.5}$ in Singapore from 2020 to 2021.

Compound	PNE	NE	PSW	SW
$PM_{2.5}$ (μg/m^3)	32.8 ± 7.34	11.4 ± 5.16	8.49 ± 3.21	19.8 ± 6.52
FR	0.04 ± 0.01	0.03 ± 0.01	0.02 ± 0.01	0.03 ± 0.01
Pyr	0.06 ± 0.02	0.04 ± 0.02	0.04 ± 0.01	0.06 ± 0.03
BaA	0.04 ± 0.01	0.02 ± 0.02	0.02 ± 0.01	0.04 ± 0.02
Chr	0.08 ± 0.03	0.05 ± 0.04	0.04 ± 0.01	0.07 ± 0.03
BbF	0.08 ± 0.02	0.07 ± 0.04	0.05 ± 0.02	0.07 ± 0.03
BkF	0.04 ± 0.01	0.03 ± 0.02	0.02 ± 0.01	0.03 ± 0.01
BaP	0.06 ± 0.01	0.04 ± 0.03	0.04 ± 0.01	0.06 ± 0.02
BeP	0.09 ± 0.02	0.06 ± 0.04	0.05 ± 0.01	0.08 ± 0.03
BgPe	0.18 ± 0.04	0.17 ± 0.11	0.12 ± 0.03	0.15 ± 0.06
IDP	0.10 ± 0.03	0.09 ± 0.06	0.06 ± 0.02	0.07 ± 0.03
ΣPAHs (ng/m^3)	0.77 ± 0.12	0.61 ± 0.37	0.47 ± 0.12	0.65 ± 0.25
2-NFR	4.22 ± 2.56	7.03 ± 6.36	6.43 ± 8.94	6.19 ± 4.59
1-NP	3.34 ± 1.36	2.00 ± 2.36	1.86 ± 0.85	3.44 ± 2.63
2-NP	0.11 ± 0.07	1.32 ± 1.68	0.60 ± 0.44	0.95 ± 0.66
6-NBaP	4.27 ± 1.74	2.17 ± 2.66	1.41 ± 0.54	4.93 ± 2.66
ΣNPAHs (pg/m^3)	11.9 ± 4.06	12.5 ± 12.5	10.3 ± 10.0	15.5 ± 9.27

3.2. Main Sources of PAHs and NPAHs

3.2.1. Diagnostic Ratios

Several source identification diagnostic ratios were applied in this research. The combination of the [BbF]/([BbF] + [BkF]) and [IDP]/([BgPe] + [IDP]) ratios was used to distinguish traffic or other sources of PAHs and NPAHs in $PM_{2.5}$. Our previous research confirmed that these two diagnostic ratios can effectively discriminate the source of PAHs in the particle phase with high accuracy and independent of spatial and temporal distributions [39,67].

As shown in Figure 3a, most values of [BbF]/([BbF] + [BkF]) and [IDP]/([BgPe] + [IDP]) ranged from 0.66 to 0.81 and 0.26 to 0.49, respectively. These results indicated that traffic emissions were the main contributors to PAHs and NPAHs in $PM_{2.5}$ in Singapore.

On the other hand, [BeP] and [BaP] are structural isomers but are known to significantly differ in terms of the photooxidation rate [68]. The atmospheric degradation of BaP is much faster than that of BeP during transportation due to its higher reactivity [69,70]. Regarding NPAHs, the [2-NFR]/[1-NP] ratio was also used to clarify local sources, in which 1-NP is usually considered to indicate direct emissions, while 2-NFR formed secondarily in the atmosphere via photochemical reactions of parent PAH (FR) [58,71,72]. [2-NFR]/[1-NP] ratio values less than 5 were typically observed at sites near primary emission sources according to a previous study [13,73,74]. Therefore, the values of [BaP]/([BaP] + [BeP]) and [2-NFR]/[1-NP] can generally suitably indicate aerosol ageing to speculate about local emissions and long-range transportation. The results for the [BaP]/([BaP] + [BeP]) and

[2-NFR]/[1-NP] ratios are shown Figure 3b. Most of the [BeP]/([BaP] + [BeP]) values were close to 0.5, while most of the [2-NFR]/[1-NP] values were below 5. Local emissions were the main source of PAHs and NPAHs in $PM_{2.5}$ in Singapore during the four monsoon seasons. However, as shown in Figure 3b, the values of several [2-NFR]/[1-NP] ratios were larger than 5, although their [BaP]/([BaP] + [BeP]) ratios were close to 0.5 (15 February 2020, 14 January 2021 and 14–15 May 2020). This suggested that aged aerosols coming from other areas may also influence atmospheric PAHs and NPAHs in Singapore depending on the day (for details, see Section 3.2.2).

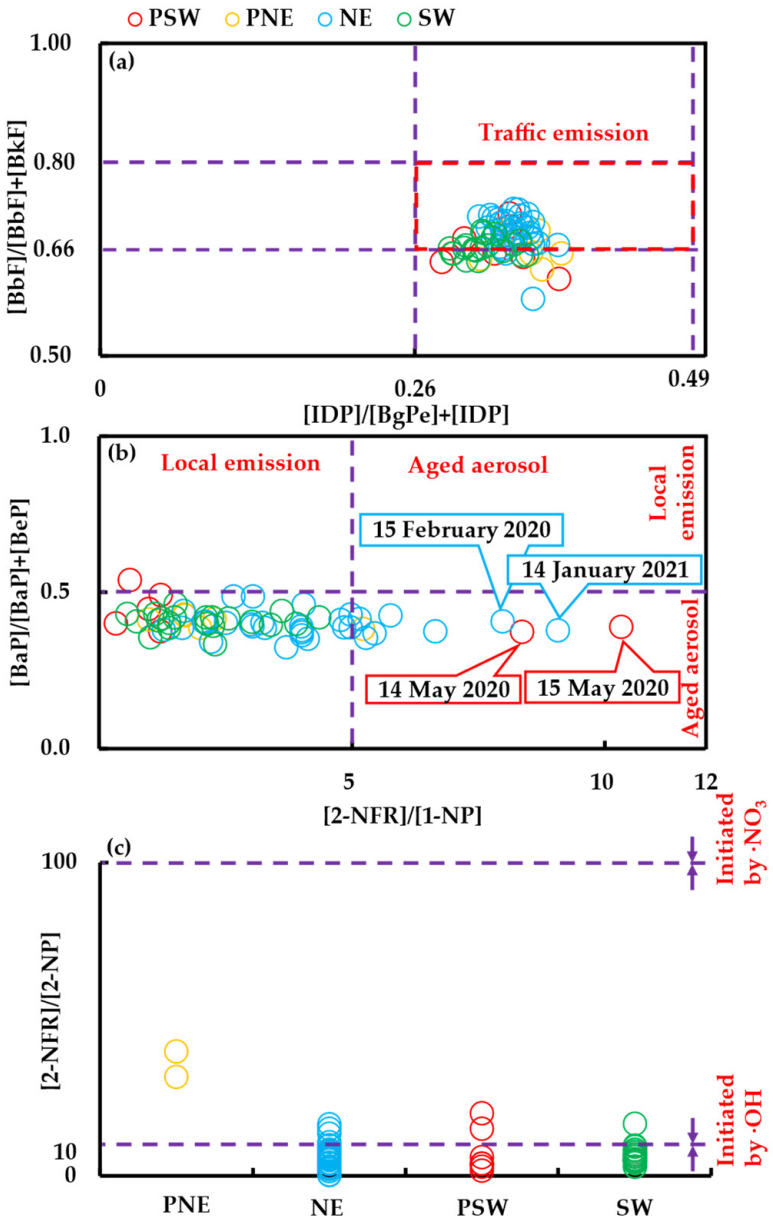

Figure 3. The distribution of diagnostic ratios of PAHs and NPAHs in four monsoon seasons in Singapore: (**a**) The values of the [BbF]/([BbF] + [BkF]) and [IDP]/([BgPe] + [IDP]) ratios; (**b**) The values of [BaP]/([BaP] + [BeP]) and [2-NFR]/[1-NP] ratios; (**c**) the values of several [2-NFR]/[1-NP] ratio.

The [2-NFR]/[2-NP] ratio is used to clarify the advantages of atmospheric reactions initiated by ·OH (close to 10) and NO_3· (close to 100) radicals because 2-NP and 2-NFR are formed in the atmosphere mainly by the ·OH radical and NO_3· radical pathways [58]. As shown in Figure 3c, the average [2-NFR]/[2-NP] ratios ranged from 0.27 to 39.8, which

means that particle-phase 2-NP and 2-NFR in Singapore were mainly formed by the OH radical pathway, in agreement with previous studies [14,39,49].

3.2.2. Airmass Backwards Trajectory Analysis

To explore possible emission sources for long-range transportation during the sampling period, 96 h backwards trajectories of the air masses arriving in Singapore during the different monsoon seasons are shown in Figure 4. During the PNE (Figure 4a) the air masses did not follow a dominant pathway and were partly terrestrial and oceanic in origin, originating from various directions. Thirty-four percent of the air masses originated from the northwest coast of Indonesia across Southern Sumatra province, Lampung province, Banten province, 31% of the air masses originated from Laut Sawu, part of the Pacific Ocean, and 28% of the air masses exhibited a loop trajectory with a low altitude. During PSW (Figure 4b), all air masses originated from the Java Sea and passed through the islands of Bangka Belitung Islands and Billiton Island. Most of the NE air masses were of continental origin; more than half of the air masses stemmed from southern China, such as Fujian Province, Guangdong Province or Taiwan Island/strait (82%); and 16% of the air masses originated from the Philippines (Figure 4c). Sixty-eight percent of the air masses received at the sampling site exhibited obvious Indonesian origin characteristics and thirty-one percent of the air masses originated from the local area during the SW (Figure 4d).

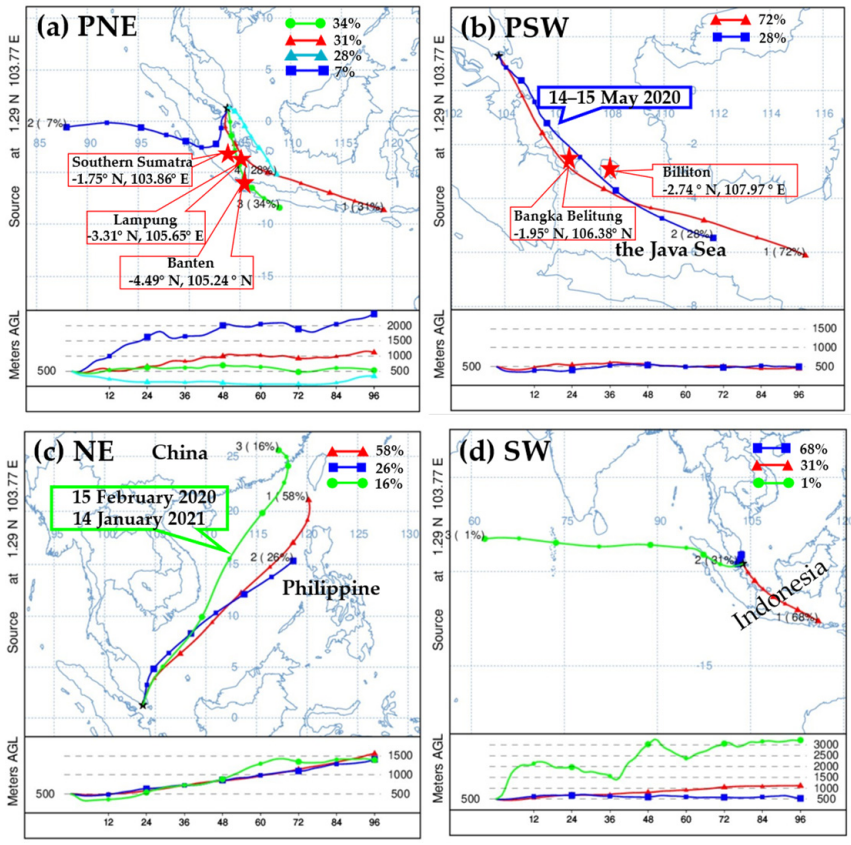

Figure 4. The cluster analysis of 96 h airmass backwards trajectories in four different seasons: (**a**) backwards trajectories air masses in PNE; (**b**) backwards trajectories air masses in PSW; (**c**) backwards trajectories air masses in NE; (**d**) backwards trajectories air masses in SW.

According to previous reports [33,35,75,76], haze usually occurs in Singapore during PNE, PSW and SW since land clearing activities in South Sumatra and Kalimantan in Indonesia. As we mentioned before, a series of active measures taken by the Singapore government to target cross-border pollution has led to a significant decrease in the number of forest fires in

Indonesia. In this study, a few hotspots were observed in Indonesia during the PNE and SW as shown in satellite images (https://www.globalforestwatch.org/, accessed on 20 June 2022). This may be the reason why $PM_{2.5}$, PAH and NPAH concentrations were slightly higher during PNE and SW than during PSW and NE.

Moreover, as mentioned earlier, the ratio of [2-NFR]/[1-NP] during the periods of 14–15 May 2020 (PSW) and 15 February 2020, and 14 January 2021 (NE) was above 5. Meanwhile, the PAH and NPAH concentrations were 0.68 and 29.08 pg/m^3 (14 May 2020), 0.52 and 19.63 pg/m^3 (15 May 2020), 0.36 and 9.6 pg/m^3 (15 February 2020), and 0.57 and 5.87 pg/m^3 (14 January 2021), respectively. These values were higher than most PAH and NPAH concentrations during the period, showing that transboundary pollution has an impact on Singapore's airborne PAHs and NPAHs. As shown in Figure 4b,c, the air masses on 14–15 May 2020 originated from the Java Sea near Indonesia, while the air masses on 15 February 2020 and 14 January 2021 originated from southern China. Although this study could not prove that the air mass passed through the areas mentioned above during high pollution periods in these areas, it can be speculated that long-range transport has the potential to exacerbate air pollution in Singapore during PSW and NE periods.

3.3. Health Effects of PAHs and NPAHs

3.3.1. Toxic Equivalent Concentration Relative to BaP (TEQ)

In general, global-scale modelling and air quality monitoring rely on BaP as an indicator for risk assessment considering the total PAHs and derivatives of PAHs mixtures since BaP was proven to be the major contributor to the cancer risk of PAHs (40–80%) [77]. Some studies have proven that BaP to represent far less than 50% of the cancer risk [78], and the potential exposure risks of other PAHs and derivatives, for example, Dibenz[a,h]anthracene (DBA) [79] and dinitropyrenes (DNPs) [80] which TEFs are equal or higher than that of BaP cannot be ignored. However, these compounds have not been covered in this study. In this study, the ten PAHs and two NPAHs were evaluated, except 6-NBaP and 2-NP, due to the lack of corresponding TEF data. The obtained TEQ results for the total and individual PAHs and NPAHs during the four seasons are listed in Table 2. The total TEQ values of BaP varied between 0.01 and 0.26 pg/m^3 during the four seasons. During the sampling period, the total TEQ concentration was much lower than the European Union standard (1 ng/m^3), and the highest ILCR values were obtained for BaP, BbF, IDP, BkF and BaA in $PM_{2.5}$, which can pose a high carcinogenic risk to human health [33,81,82]. In the future, regular monitoring of atmospheric PAHs is needed to detect changes, especially considering 4- to 6-ring PAHs.

Table 2. The concentration range of ten PAHs and two NPAHs (except 6-NBaP and 2-NP) with respect to the toxic equivalent factor.

		NE	PNE	PSW	SW
PAHs (pg/m^3)	FR	0.01–0.06	0.03–0.05	0.02–0.03	0.01–0.07
	Pyr	0.02–0.12	0.04–0.08	0.03–0.05	0.03–0.12
	BaA	0.48–10.0	2.14–5.66	1.06–3.01	1.07–7.60
	Chr	0.11–1.88	0.43–1.09	0.25–0.54	0.20–1.34
	BbF	1.05–19.0	5.11–10.4	3.27–9.11	3.18–13.6
	BkF	0.73–8.86	2.58–5.09	1.48–3.77	1.65–5.83
	BaP	8.53–196	48.1–75.3	20.6–57.4	27.1–105
	BeP	0.03–0.41	0.13–0.21	0.07–0.13	0.07–0.29
	BgPe	0.41–4.75	1.13–2.26	0.76–1.85	0.71–3.04
	IDP	2.25–25.1	4.64–13.4	3.25–9.47	3.68–14.3
	ΣPAHs	15.1–263	71.1–108	30.8–78.2	38.5–148
NPAHs (pg/m^3)	2-NFR	0.02–0.27	0.02–0.07	0.01–0.22	0.01–0.17
	1-NP	0.02–1.03	0.15–0.53	0.11–0.34	0.07–0.94
	ΣNPAHs	0.02–1.31	0.17–0.53	0.12–0.49	0.08–0.99
Total	(ng/m^3)	0.01–0.26	0.07–0.11	0.03–0.08	0.04–0.15

3.3.2. ILCR Assessment

In the atmospheric environment, humans are exposed to PAH vapor or PAHs contained in particulate matter and dust, which pose a potential carcinogenic risk even at low doses. Many studies have reported that sources of human exposure to PAHs mainly include the inhalation of air (traffic, biomass burning and residential heating-related emissions), consumption of food and skin contact [83]. Laboratory studies suggest that NPAHs are highly toxic and can be up to 1000-fold more toxic than their respective parent compounds, which cannot be ignored [84]. In this study, the accumulated exposure risk for PAHs and NPAHs in $PM_{2.5}$ through direct ingestion, dermal contact, and respiratory exposure could be quantitatively assessed with the ILCR model. An ILCR value below 10^{-6} is considered acceptable, while a value exceeding 10^{-4} indicates the need for risk reduction [77].

Table 3 reveals that the total ILCR values of PAHs and NPAHs under the three exposure routes exhibited the following seasonal characteristics: PNE (males: 7.44×10^{-7}, females: 8.52×10^{-7}) > SW (males: 3.52×10^{-7}, females: 4.03×10^{-7}) > NE (males: 2.92×10^{-7}, females: 3.34×10^{-7}) > PSW (males: 1.76×10^{-7}, females: 2.01×10^{-7}). The ILCR values obtained in this study ranged from 10^{-7} to 10^{-10}, revealing a potentially low cancer risk concern among Singapore residents in regard to incremental lifetime exposure.

Table 3. ILCRs for three exposure routes in four seasons from 2020 to 2021 in Singapore.

	PSW		PNE		NE		SW	
	Male	**Female**	**Male**	**Female**	**Male**	**Female**	**Male**	**Female**
Ingestion	1.44×10^{-7}	1.65×10^{-7}	6.92×10^{-7}	7.92×10^{-7}	2.55×10^{-7}	2.91×10^{-7}	3.07×10^{-7}	3.51×10^{-7}
Inhalation	1.05×10^{-10}	1.01×10^{-10}	1.72×10^{-10}	1.65×10^{-10}	1.24×10^{-10}	1.19×10^{-10}	1.50×10^{-10}	1.44×10^{-10}
Dermal	3.18×10^{-8}	3.64×10^{-8}	5.19×10^{-8}	5.94×10^{-8}	3.75×10^{-8}	4.29×10^{-8}	4.52×10^{-8}	5.17×10^{-8}
SUM	1.76×10^{-7}	2.01×10^{-7}	7.44×10^{-7}	8.52×10^{-7}	2.92×10^{-7}	3.34×10^{-7}	3.52×10^{-7}	4.03×10^{-7}

4. Conclusions

In this study, the abundance of $PM_{2.5}$, PAHs and NPAHs in $PM_{2.5}$ from 2020 to 2021 in Singapore was evaluated. To the best of our knowledge, this is the first report on atmospheric NPAHs in Singapore. Atmospheric yearly average concentrations of $PM_{2.5}$ and PAHs were compared to historical data. The results indicated that the $PM_{2.5}$ concentration in this area was not lower than that according to previous data over the past decade, while there was a significant decline in PAHs in the atmosphere. Singapore adopted Euro VI emission standards for petrol vehicles on 1 September 2017, which could reduce vehicular PAH emissions. $PM_{2.5}$, PAHs and NPAHs exhibited no obvious seasonal characteristics based on comparison of the $PM_{2.5}$, PAH and NPAH concentrations among the 4 seasons. In particular, the pollution level of $PM_{2.5}$ during the four seasons was higher than the target value defined in WHO guidelines. By combining diagnostic ratios and airmass backwards trajectories, the results demonstrated that local traffic emissions constituted a major source of PAHs and NPAHs in Singapore. The [2-NFR]/[2-NP] ratios indicated that the daytime OH-initiated reaction was the dominant formation pathway for 2-NFR and 2-NP in Singapore. This study found that air masses from Indonesia might affect the PAH and NPAH concentrations in $PM_{2.5}$ during PSW. In addition, the air masses from South China during NE might also have an impact on the PAH and NPAH concentrations in $PM_{2.5}$ in Singapore. In addition, the ILCR values during the survey period remained well below the safe limit, indicating that the air quality in Singapore is suitable and that the long-term exposure hazard to residents is minimal. However, continued monitoring of transboundary haze is recommended.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/atmos13091420/s1, Table S1. Sampling periods and sample numbers; Table S2. Toxic equivalent factor (TEF) of PAHs and NPAHs; Table S3. Parameters used for the estimation of the incremental lifetime cancer risks (ILCRs); Table S4. Daily weather conditions in each sample in Singapore from 2020 to 2021.

Author Contributions: N.T. designed the sampling work and performed the PAH analyses for particulate matter; S.J.H., S.B.P., L.Z., H.Z., X.Z., Y.W. and P.B. collected samples and conducted monitoring work; Y.W. analyzed the PAHs; Y.W. and P.B. performed statistical analysis; A.T., B.C. and S.N. reviewed and commented during the creation process of this paper; Y.W. and N.T. wrote this paper. All authors have read and agreed to the published version of the manuscript.

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