Health Risk Assessment of Inhalation Exposure to Airborne Particle-Bound Nitrated Polycyclic Aromatic Hydrocarbons in Urban and Suburban Areas of South China

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Abstract: Airborne particulates (PM$_{2.5}$ and TSP) were collected from outdoor and indoor areas at urban (Haizhu District) and suburban (Huadu District) sites from 2019 to 2020 in Guangzhou. Three nitro-polycyclic aromatic hydrocarbons (nitro-PAHs) in the airborne particulates were identified by a gas chromatograph equipped with a triple-quadrupole mass spectrometer. In the Haizhu District and Huadu District, the nitro-PAH concentrations in PM$_{2.5}$ and TSP did not show a significant decrease from winter to summer. From 2019 to 2020, the difference in the average concentration of nitro-PAHs in PM$_{2.5}$ and TSP in Guangzhou was relatively low and had no statistical significance. The diagnostic ratios of 2-nitrofluorene (2-NF)/1-nitropyrene (1-NP) in TSP are less than five, while for 2-NF/1-NP in outdoor PM$_{2.5}$ in the summer of 2019 and 2020 are more than five, which indicates that nitro-PAHs in the atmospheric PM$_{2.5}$ in Guangzhou during summer mainly originated from the secondary formation of atmospheric photochemical reactions between parent PAHs and oxidants (OH, NO$_3$, and O$_3$). 9-Nitroanthracene (9-NT) made the most significant contribution to the total nitro-PAH concentration. The incremental lifetime cancer risks (ILCRs) of nitro-PAHs in PM$_{2.5}$ and TSP by inhalation exposure indicated low potential health risks in the urban-suburban of Guangzhou.

Keywords: PM$_{2.5}$; TSP; nitro-PAH; inhalation exposure; health risk

1. Introduction

Industrialization and urbanization have resulted in an increasing level of fine particulate matter, or particulates, with a diameter of less than 2.5 µm (PM$_{2.5}$) [1–3]. Numerous studies have found that PM$_{2.5}$-bound chemical components, such as polycyclic aromatic hydrocarbons (PAHs) and their derivatives, can cause harm to humans [4–6]. Polycyclic aromatic hydrocarbons (PAHs) are regularly monitored and have been widely studied in the literature due to their carcinogenic and mutagenic potential, while PAH derivatives such as nitrated PAHs (nitro-PAHs) are not included in existing air monitoring programs and have only recently attracted attention in the context of urban air quality [4–7].

Nitro-PAHs exist in both the gas and particle phases in the atmosphere; their gas/particle partition depends on factors such as the vapor pressure, temperature, and the concentration and properties of the particle. Nitro-PAHs are ubiquitous environmental pollutants that mainly originate from imperfect combustion and the pyrolysis of organic matter [6,7]. Several studies have reported another formation pattern of nitro-PAHs, which was through gas phase reactions between parent-PAHs and oxidant radicals, such as OH, NO$_3^-$, and O$_3$ [8–10]. In the atmosphere, it is widely assumed that OH or NO$_3$ radicals attack the C atoms on the aromatic rings in the PAH molecules, followed by an addition of NO$_2$ to form...
the OH-PAH or NO$_3$-PAH adducts at the ortho position, and a loss of water or nitric acid to nitro-PAHs. The OH-PAH-NO$_2$ loses H$_2$O via a four-membered transition state to form nitro-PAH, and the NO$_3$-PAH-NO$_2$ adduct loses HNO$_3$ via a six-membered transition state to form nitro-PAH [9–12].

Over the last few years, nitro-PAHs have become a source of special concern, since they are more hazardous than PAHs due to their mutagenic, genotoxic, and carcinogenic characteristics. 1-nitropyrene (1-NP) is categorized in Group 2A (probably carcinogenic to humans) [9]. The mutagenicity and carcinogenicity of nitro-PAHs are high compared to those of their parent PAHs because they promote the formation of reactive oxygen species (ROS), some of which are strong mutagens and carcinogens [13]. Mutagenicity has been documented for fluoranthene, pyrene, chrysene, benzanthrone, and their nitrated derivatives; developmental toxicity has been documented for phenanthrene, anthracene, pyrene, benzanthrone, and their nitrated derivatives [14,15]. The environmental sources of nitro-PAHs include diesel emissions, coal-fired emissions, gas fuels, liquefied petroleum gas, etc., especially the combustion process of fossil fuels [16–18] and the reaction of PAHs with hydroxyl radicals, ozone, and nitrogen oxides in the atmosphere [19,20]. Zhao et al. reported that vehicle emissions were one of the primary sources of nitro-PAHs. After the traffic policy was implemented, the nitro-PAH concentration was reduced to 22.49 pg/m$^3$ in Langfang, Hebei Province [21]. Karavalakis et al. pointed out that the usage of biodiesel led to a decrease but also an increase in several nitro-PAHs concentrations in the emissions [22]. Albinet et al. pointed out that incomplete combustion of coal/biomass would release nitro-PAHs as well [23]. According to the previous literature [17,18,24], the concentrations of nitro-PAHs in emissions from combustion units (simulated, diesel, or gasoline vehicles and power plants) were usually 1–2 orders of magnitude lower than those of their related PAHs. Some studies reported that the concentrations of nitro-PAHs emitted from diesel engines are much higher than those from gasoline engines [25,26].

In urban areas, the concentrations of total nitro-PAHs are typically in the range of several pg/m$^3$ to a few ng/m$^3$, although the number of compounds included in each study differs, leading to additional variance [25–32]. Only a limited amount of information on the nitro-PAH baseline concentration can be obtained in urban cities because of local emissions. Therefore, further studies should be conducted at background sites with less anthropogenic pollution and fewer local pollution sources to evaluate the distribution and biological effects of these particles in less urbanized areas compared to urban areas. The aim of this study is to determine the spatial and temporal variation in nitro-PAH concentrations in fine particles in indoor and outdoor areas of Guangzhou, ranging from urban to suburban areas. The long-range transport potential of these pollutants is addressed by determining the particulate mass fraction and the mass size distribution.

2. Materials and Methods

2.1. Sample Collection

The indoor and outdoor environments of Haizhu District (urban area) and Huadu District (suburban area) were chosen as sampling points for PM$_{2.5}$ and TSP in this study. A total of 208 samples and 16 field blanks in sampling points were simultaneously collected during winter (December 2019 and 2020) and summer (July to August 2019 and 2020). PM$_{2.5}$ and TSP samples were, respectively, collected continuously using high-volume samplers (1000 L/min, Wuhan Tianhong Company, Wuhan, China) in outdoor areas and using medium-volume samplers (100 L/min, Qingdao Laoying Environment Technology Company, Qingdao, China) in outdoor areas for 24 h. Ambient meteorological parameters (including temperature, relative humidity, and wind speed) and pollution parameters (NO$_2$, SO$_2$, and O$_3$) were monitored in the sampling site of the Haizhu District. Before sampling, the quartz fiber filters were prebaked in a muffle furnace for 6 h at 600 °C to eliminate organic interference and then equilibrated under constant temperature (25 °C) and humidity (55 °C) for 24 h. The filters were put into a refrigerator, sealed with aluminum foil, and
preserved at $-20^\circ C$. After sample collection, the quartz filters were usually wrapped in aluminum foil and stored at $-20^\circ C$ until analysis.

2.2. Sample Extraction and Analysis

Three nitro-PAHs were examined in this study: [9-nitroanthracene (9-NT), 2-nitrofluorene (2-NF), and 1-nitropyrene (1-NP)]. The pretreatment of filters was similar to that in previous studies [32-34]. Briefly, the quartz fiber filters (PM$_{2.5}$ and TSP) were cut into several pieces. Naphthalene-$d^8$ and phenanthrene-$d^{10}$ were added to the samples as internal standards before extraction. Each filter was extracted twice using pressurized liquid extraction with hexane and acetone (1:1, v/v). For chemical analysis, the extracts were purified and eluted into vials. The analysis procedure for the 3 nitro-PAHs from the PM$_{2.5}$/TSP filter samples is described in the Supplementary Information.

2.3. Quality Control and Assurance

All glassware used during the sample extraction procedure was rinsed with ultra-pure water and then baked at 100 $^\circ C$ to dryness. During the sampling period, blanks were collected to evaluate any background contamination and the results showed that PAH derivatives were not detected in these blanks. The detection limits of the method were 0.0192–0.513 pg/m$^3$ for nitro-PAHs. The recoveries were 87–118% for nitro-PAHs. The recoveries of nitro-PAH surrogates were determined. Before sample extraction and analysis, substitutes were added to the extraction cells to monitor the whole analysis process. The recoveries of 2 spiked perdeuterated surrogates were 87–98% for naphthalene-$d^8$ and 94–123% for phenanthrene-$d^{10}$. The process blank, laboratory blank, and field blank were analyzed, and the measured values of nitro-PAHs could be ignored.

2.4. Exposure Assessment

The respiratory pathway is the main method by which nitro-PAHs enter the human body. The various components of nitro-PAHs have different toxicities, with differing risks of harm to the human respiratory system. Benzo[a]pyrene (BaP) has been identified as a strong carcinogen. Previous studies measured a more reasonable and accurate ratio of the carcinogenic toxicity of nitro-PAHs to BaP through toxicological tests and proposed the concept of toxic equivalence factors (TEFs) [35,36]. This study referred to the relative study results of TEFs of nitro-PAHs and calculated the total equivalent carcinogenic concentration (BaP equivalent concentration, BaP$_{eq}$) of 3 kinds of nitro-PAHs with BaP as the reference. This aimed to assess the health risk of nitro-PAH pollution in PM$_{2.5}$ and TSP. The calculation method is shown in Formula (1).

$$\text{BaP}_{eq} = \sum C_i \times \text{TEF}_i$$

BaP$_{eq}$ is the total equivalent carcinogenic concentration with BaP as the reference, ng/m$^3$; $C_i$ is the concentration of the $i$-th nitro-PAHs, ng/m$^3$; TEF is the carcinogenic equivalent factor of the $i$-th nitro-PAHs. Carcinogenic and mutagenic equivalent factors of nitro-PAHs are shown in Table S1.

The average daily dose (ADD) refers to the daily intake of nitro-PAHs via the respiratory pathway. This study mainly considers the exposure dose of nitro-PAHs through respiratory exposure and the lifetime cancer risk of the population due to nitro-PAHs. Due to differences in ages, sexes, physiological characteristics, and lifestyle habits, the population was divided into children, adult males, and adult females for this study. The ADD of respiratory exposure pathways by different people can be calculated by Formula (2):

$$\text{ADD} = \frac{(C \times \text{IR} \times \text{F} \times \text{EF} \times \text{ED})}{(\text{BW} \times \text{AT})}$$

ADD is the average daily exposure of toxic substances in PM$_{2.5}$ and TSP mg/(kg·d); $C$ is the concentration of toxic substances (e.g., nitro-PAHs) in PM$_{2.5}$ and TSP. This study is based on the BaP total equivalent carcinogenic concentration of the bioavailable concentration...
released by toxic substances in simulated human lung fluid (ng/m$^3$); IR is respiratory volume m$^3$/d; EF is the exposure frequency (days/years); ED is exposure duration (years); F is the indoor and outdoor stay time; BW is body weight (kg); AT is the average exposure time (days). The exposure parameter is the key factor in determining the accuracy of the environmental health risk assessment. The closer the selected exposure parameter is to the actual situation of the target population, the more authentic the results of the environmental health risk assessment will be. According to the manual of the Chinese population exposure parameters issued by the Ministry of Environmental Protection of China at the end of 2013 combined with the actual situation of Guangzhou, the population exposure evaluation parameters are determined. The specific parameters are shown in Table S2.

2.5. Health Risk Assessment

According to the US EPA’s health risk assessment model for respiratory exposure to carcinogenic and toxic substances, the incremental life cancer risk (ILCR) of nitro-PAHs in PM$_{2.5}$ and TSP $^{[20,37]}$ is as follows:

$$
ILCR = q \times ADD
$$

(3)

$q$ is the human carcinogenic intensity coefficient calculated according to animal experimental data, kg·d/mg; ADD is the average daily dose, mg/(kg·d). According to the US EPA IRIS, the carcinogenic intensity coefficient ($q$) of BaP through respiratory exposure is 3.14 kg·d/mg. The US EPA proposes that the level of incremental lifetime cancer risk (ILCR) of pollutants is acceptable between $10^{-4}$–$10^{-6}$; that is, the exposure level is acceptable when the number of health hazards or deaths caused by exposure to pollutants is not more than 1 per 10,000 to 1 million people. An ILCR lower than $10^{-6}$ indicates that the risk degree is not significant, and generally, the necessity of risk management is not great; an ILCR of $10^{-6}$–$10^{-5}$ indicates that a risk is higher than the risk of daily activities and deserves attention; an ILCR of $10^{-5}$–$10^{-4}$ indicates that close attention needs to be paid and a solution should be adopted; an ILCR higher than $10^{-4}$ indicates that the risk degree is significant, which requires the adoption risk management to treat.

2.6. Statistical Analysis

The PM$_{2.5}$- and TSP-bound nitro-PAH concentrations and profiles were compared using IBM SPSS Statistics 20.0 software, with a statistical significance of $p < 0.05$.

3. Results and Discussion

3.1. Nitro-PAHs in PM$_{2.5}$ and TSP

In the summer and winter seasons of 2019, the average concentration of PM$_{2.5}$ outdoors in the Haizhu district of Guangzhou was 24.7 ± 9.12 and 66.5 ± 18.8 µg/m$^3$, respectively, and in Huadu District was 28.6 ± 6.60 and 69.6 ± 12.0 µg/m$^3$; Figure 1 shows that the 35.0 µg/m$^3$ objective PM$_{2.5}$ concentration (GB 3095–2012) was exceeded in both locations in winter. TSP refers to particulate matter suspended in the air with an aerodynamic diameter less than or equal to 100 µm. In summer and winter, the average concentration of outdoor TSP in the Haizhu District of Guangzhou was 41.5 ± 13.8 and 117 ± 41.1 µg/m$^3$, respectively, and was 48.8 ± 12.2 and 132 ± 29.2 µg/m$^3$ in Huadu District. The average concentration of TSP in both locations was under the 300 µg/m$^3$ limit set by the state air quality standard (GB 3095–2012) (Figure 1).
The temporal and spatial variations in nitro-PAH concentrations in PM$_{2.5}$ and TSP in Guangzhou are shown in Tables 1 and 2. In the summer of 2019, the average nitro-PAH concentrations outdoors and indoors in PM$_{2.5}$ in Haizhu District were 0.116 ± 0.0125 and 0.0855 ± 0.0321 ng/m$^3$, respectively, and nitro-PAHs in TSP were 1.11 ± 0.242 and 0.797 ± 0.173 ng/m$^3$. In the winter of 2019, the average nitro-PAH concentrations in PM$_{2.5}$ in Haizhu District were 0.195 ± 0.0176 (outdoors) and 0.152 ± 0.0230 (indoors) ng/m$^3$, and nitro-PAHs in TSP were 1.34 ± 0.202 and 0.996 ± 0.0643 ng/m$^3$, respectively. In the summer of 2019, the average nitro-PAH concentrations outdoors and indoors in PM$_{2.5}$ in Huadu District were 0.447 ± 0.267 and 0.169 ± 0.0290 ng/m$^3$, respectively, and nitro-PAHs in TSP were 0.892 ± 0.130 and 0.642 ± 0.225 ng/m$^3$. In winter 2019, the average nitro-PAH concentrations in PM$_{2.5}$ in Huadu District were 0.235 ± 0.0245 and 0.177 ± 0.0341 ng/m$^3$, respectively, and the nitro-PAHs in TSP were 0.712 ± 0.192 and 0.462 ± 0.0837 ng/m$^3$. There were differences between the average concentrations of nitro-PAHs in PM$_{2.5}$ and TSP from different districts of Guangzhou but the differences were not statistically significant ($p > 0.05$). Owing to the low latitude, the surface of Guangzhou receives more solar radiation. Meanwhile, it is affected by the monsoons, the climate features high temperatures, high humidity, and much rain in summer, while in winter, the climate features low temperatures, dryness, and little rain. In the Haizhu District and Huadu District, there was no decrease in the average nitro-PAH concentrations in PM$_{2.5}$ and TSP from dry winter to wet summer. The small direct emission of nitro-PAHs in summer and photochemical reactions may be important causes of this pattern. The urban air pollution in Guangzhou in summer is mainly O$_3$ and NOx pollution [37,38], which leads to the secondary formation of various nitro-PAHs when exposed to free radicals. In nitro-PAHs, the formation of 1-NP is most significant when exposed to NO$_3$/N$_2$O$_5$ and ·OH radicals, while 9-NT can be formed when exposed to NO$_3$/N$_2$O$_5$ radicals. Therefore, the concentration levels of nitro-PAHs in PM$_{2.5}$ and TSP do not significantly decrease in the wet summer, which may be related to the formation of photochemical reactions with exposure to free radicals.
Table 1. Mean nitro-PAH concentrations (ng/m$^3$) and standard deviations of 9-NT, 2-NF, and 1-NP in PM$_{2.5}$ and TSP in 2019.

| Nitro-PAHs | Summer | | | Winter | | |
|---|---|---|---|---|---|---|
| | Indoor | Mean | SD | Outdoor | Mean | SD | Indoor | Mean | SD | Outdoor | Mean | SD |
| Haizhu District | PM$_{2.5}$ | | | TSP | | |
| 9-NT$^a$ | 0.0612 | 0.0303 | 0.0918 | 0.0198 | 0.0683 | 0.0209 | 0.125 | 0.0203 |
| 2-NF$^b$ | 0.0144 | 0.00670 | 0.0189 | 0.0084 | 0.0388 | 0.0090 | 0.0402 | 0.0162 |
| 1-NP$^c$ | 0.0094 | 0.00410 | 0.00470 | 0.00320 | 0.0444 | 0.0104 | 0.0302 | 0.00650 |
| | | | | | | | | | | | | |
| TSP | | | | | | | | | | | | |
| 9-NT$^a$ | 0.734 | 0.144 | 1.09 | 0.243 | 0.548 | 0.105 | 0.645 | 0.191 |
| 2-NF$^b$ | 0.0151 | 0.00410 | 0.00870 | 0.00450 | 0.047 | 0.013 | 0.0564 | 0.0140 |
| 1-NP$^c$ | 0.0291 | 0.0101 | 0.0141 | 0.00170 | 0.400 | 0.109 | 0.640 | 0.252 |
| Huadu District | PM$_{2.5}$ | | | TSP | | |
| 9-NT$^a$ | 0.0894 | 0.0503 | 0.349 | 0.244 | 0.140 | 0.0293 | 0.192 | 0.0317 |
| 2-NF$^b$ | 0.0166 | 0.00680 | 0.046 | 0.0171 | 0.0130 | 0.00540 | 0.0236 | 0.0155 |
| 1-NP$^c$ | 0.0226 | 0.00670 | 0.0510 | 0.0178 | 0.0241 | 0.00990 | 0.0188 | 0.00410 |
| | | | | | | | | | | | | |
| TSP | | | | | | | | | | | | |
| 9-NT$^a$ | 0.518 | 0.223 | 0.795 | 0.139 | 0.384 | 0.0889 | 0.618 | 0.186 |
| 2-NF$^b$ | 0.0789 | 0.0223 | 0.0463 | 0.0171 | 0.0116 | 0.0109 | 0.0106 | 0.00290 |
| 1-NP$^c$ | 0.0451 | 0.0133 | 0.0510 | 0.0178 | 0.0667 | 0.0289 | 0.0837 | 0.0495 |

$a$, 9-NT: 9-nitroanthracene; $b$, 2-NF: 2-nitrofluorene; $c$, 1-NP: 1-nitropyrene.

Table 2. Mean nitro-PAH concentrations (ng/m$^3$) and standard deviations of 9-NT, 2-NF, and 1-NP in PM$_{2.5}$ and TSP in 2020.

| Nitro-PAHs | Summer | | | Winter | | |
|---|---|---|---|---|---|---|
| | Indoor | Mean | SD | Outdoor | Mean | SD | Indoor | Mean | SD | Outdoor | Mean | SD |
| Haizhu District | PM$_{2.5}$ | | | TSP | | |
| 9-NT$^a$ | 0.0845 | 0.0514 | 0.0928 | 0.0544 | 0.0861 | 0.0484 | 0.0933 | 0.0624 |
| 2-NF$^b$ | 0.0151 | 0.0092 | 0.0305 | 0.0156 | 0.0431 | 0.0232 | 0.0400 | 0.0316 |
| 1-NP$^c$ | 0.0122 | 0.0078 | 0.0056 | 0.0032 | 0.0497 | 0.0238 | 0.0239 | 0.0072 |
| | | | | | | | | | | | | |
| TSP | | | | | | | | | | | | |
| 9-NT$^a$ | 0.8462 | 0.3703 | 1.1768 | 0.7458 | 0.3720 | 0.2283 | 0.7865 | 0.5098 |
| 2-NF$^b$ | 0.0164 | 0.0023 | 0.0083 | 0.0042 | 0.0480 | 0.0357 | 0.0548 | 0.0197 |
| 1-NP$^c$ | 0.0351 | 0.0154 | 0.0132 | 0.0065 | 0.5713 | 0.6148 | 0.4495 | 0.1500 |
| Huadu District | PM$_{2.5}$ | | | TSP | | |
| 9-NT$^a$ | 0.0442 | 0.0290 | 0.1709 | 0.1684 | 0.0638 | 0.0301 | 0.0374 | 0.0194 |
| 2-NF$^b$ | 0.0842 | 0.0225 | 0.0274 | 0.0295 | 0.0170 | 0.00995 | 0.0289 | 0.0291 |
| 1-NP$^c$ | 0.0527 | 0.0161 | 0.0050 | 0.0016 | 0.0049 | 0.0031 | 0.0222 | 0.0187 |
| | | | | | | | | | | | | |
| TSP | | | | | | | | | | | | |
| 9-NT$^a$ | 0.6600 | 0.4440 | 0.8938 | 0.3440 | 0.5141 | 0.1653 | 0.9334 | 0.1686 |
| 2-NF$^b$ | 0.0819 | 0.02744 | 0.0432 | 0.0320 | 0.0141 | 0.0152 | 0.0145 | 0.0115 |
| 1-NP$^c$ | 0.0428 | 0.01211 | 0.0451 | 0.0233 | 0.0676 | 0.0259 | 0.0883 | 0.0578 |

$a$, 9-NT: 9-nitroanthracene; $b$, 2-NF: 2-nitrofluorene; $c$, 1-NP: 1-nitropyrene.

The source of nitro-PAHs can be identified by using the marker method, such as that using 1-NP as a “marker” of nitro-PAHs derived from diesel emissions and using its existence in the surrounding air samples as a sign of traffic pollution from diesel vehicles. Other compounds directly emitted from the combustion chamber of the diesel engine are 9-NT and 2-NF. This study investigated the spatial-temporal contribution of pollution sources of nitro-PAHs in Guangzhou by analyzing the ratio of 2-NF and 1-NP (2-NF/1-
NP). A ratio of 2-NF/1-NP less than five indicates that the primary emission source is
dominant, and a ratio greater than five indicates that the nitro-PAHs are produced by
secondary pollutants [39,40]. The ratio of 2-NF/1-NP in indoor and outdoor PM$_{2.5}$ and
TSP in the Haizhu and Huadu districts of Guangzhou from 2019 to 2020 is shown in
Figure 2. 2-NF/1-NP in TSP was less than five, while 2-NF/1-NP in outdoor PM$_{2.5}$ in the
summer of 2019 and 2020 was more than five (Figure 2), which indicates that nitro-PAHs
in the atmospheric PM$_{2.5}$ in the summer in Guangzhou mainly come from the secondary
formation of atmospheric photochemical reactions between parent PAHs and oxidants such as
·OH, NO$_3$, and O$_3$.

![Figure 2](image-url)

**Figure 2.** The diagnostic ratios of 2-NF/1-NP in PM$_{2.5}$ and TSP during the sampling period.

The spatial-temporal changes in the monomer ratios of the three nitro-PAHs in this
study are displayed in Figure 3, which shows that 9-NT accounts for the highest proportion
of nitro-PAHs. In the summer of 2019, the average proportions of nitro-PAHs in outdoor
environments in Haizhu District were 98.0% (PM$_{2.5}$) and 79.5% (TSP) and the average
proportions in indoor environments were 94.3% and 72.2%. In Haizhu District, for PM$_{2.5}$
and TSP, it was 78.21% and 89.09% (outdoor environment) and 69.51% and 80.68% (indoor
environment), respectively (Figure 3). In contrast, 2-NF and 9-NT are the most abundant
nitro-PAHs in urban and suburban atmospheres of the Mid-Atlantic region, accounting
for approximately half of the total nitro-PAH concentration [41]. 9-Nitroanthracene is
produced from direct sources such as diesel and gasoline exhausts and by the gas-phase
reactions of PAHs with oxides of nitrogen [42]. 1-NP can be formed from the direct emission
diesel vehicles [31]. In addition, 9-NT can also be formed by the heterogeneous reaction
of Ant produced in the combustion process (biomass combustion or vehicle emission) and
a nitrating agent [42]. As a megacity in South China, Guangzhou has a large number of
cars that can contribute large quantities of 9-NT. The high proportion of 9-NT during the
study may come from the heterogeneous reaction of Ant and diesel vehicle emissions.

The previous studies reported that meteorological conditions also can influence the
generation, accumulation, diffusion, removal, and phase partitioning of air pollutants in
addition to emission sources from human activities (local and/or external) [43–45]. Table S3
summarizes the correlations between the meteorological conditions and the total mass
concentration of nitro-PAHs in PM$_{2.5}$ and TSP in the Haizhu District in the sampling
periods. There are correlations between the total mass concentration of nitro-PAHs in
PM$_{2.5}$ and TSP in winter and temperature ($R^2 = 0.431–0.503$, $p < 0.05$), solar radiation
(R² = 0.524–0.561, p < 0.05), and wind speed (R² = 0.470–0.511, p < 0.05). Total nitro-PAH concentrations were significantly different with NO₂ and O₃ concentrations (p < 0.05) during both sampling periods, indicating that the heterogeneous photo-oxidation reactions of parent PAHs with atmospheric oxidants might be an important source. The low-latitude surface of Guangzhou receives high quantities of solar radiation, while the monsoon brings warm ocean air flow in summer. This forms a rainy climate with high temperatures and high humidity; in winter, the cold wind in the northern continent creates a dry and less rainy low-temperature climate. Comparing the correlation between nitro-PAHs and meteorological factors in summer and winter, nitro-PAHs in summer are more affected by the transfer and diffusion of PM₂.₅ and TSP. There may be a secondary generation reaction of nitro-PAHs in winter when the temperature and solar radiation are relatively high, which indicates that nitro-PAHs are correlated with meteorological parameters, unlike in summer. In addition, the secondary-generated nitro-PAHs in the atmosphere of the surrounding areas of Guangzhou (such as Dongguan, Shenzhen, Foshan, etc.) can also affect the concentration of nitro-PAHs in PM₂.₅ and TSP in the urban and suburban areas of Guangzhou through regional transfer.

Figure 3. The composition of 9-NT, 2-NF, and 1-NP in PM₂.₅ and TSP in 2019 ((A): Haizhu District; (B): Huadu District).
3.2. Health Risk Assessment

3.2.1. Exposure Assessment

The ADD of three nitro-PAHs in different general populations (children and adults) in Guangzhou exposed to PM$_{2.5}$ and TSP through the respiratory pathway was estimated according to Formula (3) and the calculation results of BaP$_{eq}$ (Table 3). The ADDs of adult males, adult females, and children calculated based on the nitro-PAH concentrations in PM$_{2.5}$ and TSP in Haizhu District of Guangzhou in the summer of 2019 were $5.81 \times 10^{-11} \pm 6.08 \times 10^{-12}$ (PM$_{2.5}$) and $3.65 \times 10^{-10} \pm 5.70 \times 10^{-11}$ (TSP), $5.04 \times 10^{-11}$ $5.27 \times 10^{-12}$ and $3.17 \times 10^{-10} \pm 4.95 \times 10^{-11}$, and $2.16 \times 10^{-11} \pm 2.26 \times 10^{-12}$ and $1.35 \times 10^{-10}$ $1.62 \times 10^{-10} \pm 2.26 \times 10^{-11}$ (PM$_{2.5}$) and $1.94 \times 10^{-9} \pm 5.72 \times 10^{-10}$ (TSP), $1.40 \times 10^{-10}$ $1.96 \times 10^{-11}$ and $1.69 \times 10^{-9} \pm 4.96 \times 10^{-10}$, and $5.99 \times 10^{-11} \pm 8.38 \times 10^{-12}$ and $7.21 \times 10^{-10} \pm 2.12 \times 10^{-11}$. According to the statistics, adult males receive the highest doses, followed by adult females, and children have the lowest doses. In the same period of study, the exposure doses of nitro-PAHs in PM$_{2.5}$ and TSP in Huadu District were higher in summer than those in Haizhu District, while in winter the exposure doses of nitro-PAHs in PM$_{2.5}$ were higher than those in Haizhu District (Table 3).

| District | Mean PM$_{2.5}$ | SD | Mean TSP | SD |
|----------|----------------|----|----------|----|
| 2019 Summer |
| Males |
| Haizhu | 0.581 | 0.0608 | 3.65 | 0.570 |
| Huadu | 2.80 | 1.10 | 4.14 | 0.513 |
| Females |
| Haizhu | 0.504 | 0.0527 | 3.17 | 0.495 |
| Huadu | 2.43 | 0.950 | 3.59 | 0.445 |
| Children |
| Haizhu | 0.216 | 0.0226 | 1.35 | 0.212 |
| Huadu | 1.04 | 0.406 | 1.53 | 0.190 |
| Winter |
| Males |
| Haizhu | 1.62 | 0.226 | 19.4 | 5.72 |
| Huadu | 1.30 | 0.162 | 4.13 | 1.36 |
| Females |
| Haizhu | 1.40 | 0.196 | 16.9 | 4.96 |
| Huadu | 1.13 | 0.140 | 3.58 | 1.18 |
| Children |
| Haizhu | 0.599 | 0.0838 | 7.21 | 2.12 |
| Huadu | 0.484 | 0.0600 | 1.53 | 0.504 |
| 2020 Summer |
| Males |
| Haizhu | 0.663 | 0.273 | 3.91 | 2.07 |
| Huadu | 1.09 | 0.598 | 4.28 | 1.57 |
| Females |
| Haizhu | 0.575 | 0.236 | 3.39 | 1.79 |
| Huadu | 0.944 | 0.519 | 3.71 | 1.36 |
| Children |
| Haizhu | 0.246 | 0.101 | 1.45 | 0.767 |
| Huadu | 0.404 | 0.222 | 1.59 | 0.581 |
| Winter |
| Males |
| Haizhu | 1.41 | 0.518 | 15.7 | 5.30 |
| Huadu | 0.938 | 0.652 | 5.15 | 1.74 |
| Females |
| Haizhu | 1.22 | 0.449 | 13.6 | 4.59 |
| Huadu | 0.813 | 0.566 | 4.47 | 1.50 |
| Children |
| Haizhu | 0.522 | 0.192 | 5.81 | 1.97 |
| Huadu | 0.348 | 0.242 | 1.91 | 0.644 |

3.2.2. Cancer Risk

The population is exposed to PM$_{2.5}$- and TSP-containing nitro-PAHs through inhalation and the temporal and spatial changes in ILCR caused by respiratory exposure are shown in Table 4. The ILCRs of adult males, adult females, and children that were calculated based on the nitro-PAH concentrations in PM$_{2.5}$ and TSP in Haizhu District of Guangzhou in
the summer of 2019 were $1.83 \times 10^{-9} \pm 1.91 \times 10^{-11}$ (PM$_{2.5}$) and $1.15 \times 10^{-9} \pm 1.79 \times 10^{-10}$ (TSP), $1.58 \times 10^{-10} \pm 1.66 \times 10^{-11}$ and $9.95 \times 10^{-10} \pm 1.55 \times 10^{-10}$, and $6.77 \times 10^{-11} \pm 7.08 \times 10^{-12}$ and $4.25 \times 10^{-10} \pm 6.64 \times 10^{-11}$, respectively, while the ILCRs in winter were $5.07 \times 10^{-10} \pm 7.09 \times 10^{-11}$ (PM$_{2.5}$) and $6.10 \times 10^{-9} \pm 1.80 \times 10^{-9}$ (TSP), $4.40 \times 10^{-10} \pm 6.15 \times 10^{-11}$ and $5.29 \times 10^{-9} \pm 1.56 \times 10^{-9}$, and $1.88 \times 10^{-10} \pm 2.63 \times 10^{-11}$ and $2.26 \times 10^{-9} \pm 6.66 \times 10^{-9}$. According to the statistics, adult males have the highest ILCR, followed by adult females, and children have the lowest ILCR. In the same period of study, the ILCR induced by respiratory exposure to nitro-PAHs in PM$_{2.5}$ and TSP in Huadu District was one order of magnitude higher than that in Haizhu District (Table 4).

### Table 4. Incremental life cancer risk (ILCR) of three nitro-PAHs ($10^{-10}$) in Guangzhou from 2019 to 2020.

| District | PM$_{2.5}$ | TSP |
|----------|------------|-----|
|          | Mean       | SD  | Mean       | SD  |
| 2019     |            |     |            |     |
| Summer   |            |     |            |     |
| Males    | Haizhu     | 1.83| 0.191      | 11.5| 1.79  |
|          | Huadu      | 8.79| 3.44       | 13.0| 1.61  |
|          | Haizhu     | 1.58| 0.166      | 9.95| 1.55  |
|          | Huadu      | 7.62| 2.98       | 11.3| 1.40  |
|          | Huizhu     | 0.677| 0.0708| 4.25| 0.664 |
| Children | Huadu      | 3.26| 1.26       | 4.82| 0.598 |
| Winter   |            |     |            |     |
| Males    | Haizhu     | 5.07| 0.709      | 61.0| 18.0  |
|          | Huadu      | 4.09| 0.508      | 13.0| 4.27  |
|          | Haizhu     | 4.40| 0.615      | 52.9| 15.6  |
|          | Huadu      | 3.55| 0.440      | 11.2| 3.70  |
|          | Huizhu     | 1.88| 0.263      | 22.6| 6.66  |
| Children | Huadu      | 1.52| 0.188      | 4.81| 1.58  |
| 2020     |            |     |            |     |
| Summer   |            |     |            |     |
| Males    | Haizhu     | 2.08| 0.856      | 12.3| 6.49  |
|          | Huadu      | 3.42| 1.88       | 13.4| 4.92  |
|          | Haizhu     | 1.80| 0.742      | 10.7| 5.63  |
|          | Huadu      | 2.96| 1.630      | 11.7| 4.27  |
|          | Haizhu     | 0.772| 0.317| 4.56| 2.41  |
| Children | Huadu      | 1.27| 0.697      | 4.99| 1.83  |
| Winter   |            |     |            |     |
| Males    | Haizhu     | 4.42| 1.63       | 49.2| 16.6  |
|          | Huadu      | 2.94| 2.05       | 16.2| 5.45  |
|          | Haizhu     | 3.83| 1.41       | 42.7| 14.4  |
|          | Huadu      | 2.55| 1.78       | 14.0| 4.73  |
|          | Haizhu     | 1.64| 0.604      | 18.2| 6.17  |
| Children | Huadu      | 1.09| 0.760      | 6.00| 2.02  |

### 4. Conclusions

Airborne particle phase concentrations of three nitro-PAHs were quantified in ambient air collected in the Haizhu District, an urban region, and Huadu District, a suburban area 33 km southeast of Haizhu District, from December 2019 to August 2020. The seasonal pattern of PM$_{2.5}$- and TSP-bound nitro-PAHs in Guangzhou were predominantly ascribed to the changing of meteorological conditions. Nitro-PAHs showed no significant positive correlations with temporal variation from 2019 to 2020, indicating the influence of non-point source pollution. Concentrations at Huadu District were on average two to three times higher than those measured at the Haizhu District site. Concentrations for most nitro-PAHs were higher in summer than in winter, suggesting an increase in the secondary formation of various nitro-PAHs, which, when exposed to free radicals during summer, promoted the accumulation of nitro-PAHs. The relative contribution of gas-phase reactions and primary
emission sources of nitro-PAHs were evaluated using source-specific concentration ratios of 2-NF/1-NP. The ratio of 2-NF/1-NP in TSP was less than five, while 2-NF/1-NP in outdoor PM$_{2.5}$ in the summer of 2019 and 2020 was more than five, indicating that the secondary formation of atmospheric photochemical reactions between parent PAHs and oxidants were an important source of the three nitro-PAHs. 9-nitroanthracene was the most abundant of the nitro-PAHs quantitatively analyzed in the airborne particles at both sites, accounting for approximately 70–90% of the total nitro-PAH concentrations during summer and winter. The incremental lifetime cancer risks (ILCRs) of inhalation exposure to the three nitro-PAHs also indicated that the degree of health risk was still within the controllable range.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ijerph192315536/s1, Table S1: TEF data of the objective nitro-PAH; Table S2: Parameters used in the average daily exposure assessment; Table S3: Correlation coefficients and $p$-values between total nitro-PAHs and meteorological parameters with different airborne particle in Haizhu District in 2019. References [34,46] are cited in the supplementary materials.

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