Concentrations and Sources of Atmospheric PM, Polycyclic Aromatic Hydrocarbons and Nitropolycyclic Aromatic Hydrocarbons in Kanazawa, Japan

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Abstract: PM$_{2.5}$ (fine particles with diameters 2.5 micrometers and smaller) and PM$_{>2.5}$ were separately collected in Kanazawa, Japan in every season, from the spring of 2017 to the winter of 2018, and nine polycyclic aromatic hydrocarbons (PAHs) and six nitropolycyclic aromatic hydrocarbons (NPAHs) were respectively determined using high-performance liquid chromatography (HPLC) with fluorescence and chemiluminescence detections. The atmospheric concentrations of both the PAHs and NPAHs showed seasonal changes (highest in the winter and lowest in the summer), which differed from the variations in the total suspended particulate matter (TSP) and PM$_{2.5}$ amounts (which were highest in the spring). The contributions of major sources to the combustion-derived particulate (P$_c$) in the PM$_{2.5}$ were calculated using the 1-nitropyrene-pyrene (NP) method, using pyrene and 1-nitropyrene as the representative markers of PAHs and NPAHs, respectively. The annual average concentration of P$_c$ accounted for only 2.1% of PM$_{2.5}$, but showed the same seasonal variation as PAHs. The contributions of major sources to the combustion-derived particulate (P$_c$) in the PM$_{2.5}$ were calculated using the 1-nitropyrene-pyrene (NP) method, using pyrene and 1-nitropyrene as the representative markers of PAHs and NPAHs, respectively. The annual average concentration of P$_c$ accounted for only 2.1% of PM$_{2.5}$, but showed the same seasonal variation as PAHs. The sources of P$_c$ were vehicles (31%) and coal heating facilities/industries (69%). A backward trajectory analysis showed that the vehicle-derived P$_c$ was mainly from Kanazawa and its surroundings, and that coal heating facilities/industry-derived P$_c$ was transported from city areas in central and northern China in the winter, and during the Asian dust event in the spring. These results show that large amounts of PAHs were transported over a long range from China during the winter. Even in the spring, after the coal heating season was over in China, PAHs were still transported to Japan after Asian dust storms passed through Chinese city areas. By contrast, the main contributors of NPAHs were vehicles in Kanazawa and its surroundings. The recent P$_c$ concentrations were much lower than those in 1999. This decrease was mostly attributed to the decrease in the contribution of vehicle emissions. Thus, the changes in the atmospheric concentrations of P$_c$, PAHs and NPAHs in Kanazawa were strongly affected not only by the local emissions but also by long-range transport from China.

Keywords: polycyclic aromatic hydrocarbon; nitropolycyclic aromatic hydrocarbon; automobile; coal combustion; seasonal change; long-range transport

1. Introduction

Air pollution caused by particulate matter (PM) is a growing global concern. The World Health Organization (WHO) reported that air pollution kills seven million people
annually, and that it enhances health risks, especially in children [1,2]. Among the different sizes of PM, PM$_{2.5}$ (PM with diameters of no more than 2.5 µm) is carcinogenic and increases the risk of respiratory and cardiovascular diseases, including asthma [3]. PM$_{2.5}$ contains several hazardous chemicals associated with these diseases. Among them, polycyclic aromatic hydrocarbons (PAHs) and their derivatives—such as nitropolycyclic aromatic hydrocarbons (NPAHs)—are known as carcinogens and/or mutagens. In many countries, vehicles are considered the major source of PAHs and NPAHs. PM$_{2.5}$ air pollution caused by coal heating and slash and burn agriculture are serious in China and developing countries, respectively. Therefore, the reduction of the PM$_{2.5}$ generated from the combustion of fossil fuels and biomass is an important global issue. Recently, air quality standards and guidelines for PM$_{2.5}$ emissions have been set by several countries and international organizations. However, the present air quality standards measure the atmospheric concentration of PM based on particle size, and not on the toxic chemical contained within. The atmospheric behavior and sources of PAHs and NPAHs in particular are poorly understood, despite their human health hazards.

East Asia is a hot spot for air pollution, and Asian dust storms (yellow sand) are frequent events not only in China but also in Korea and Japan. An international monitoring network of more than ten cities in Japan, China, Russia and Korea was started in the 1990s for the continual surveillance of the atmospheric concentrations of total suspended particulate matter (TSP)-bound PAHs and NPAHs [4]. Chinese and Russian cities, especially in the central and northern parts of China, showed extremely high concentrations of PAHs and NPAHs in winter. This was attributed mainly to emissions from coal heating facilities. By contrast, Japanese cities showed a constant decrease in their concentrations of PAHs and NPAHs, and an especially significant decrease in the concentration of NPAHs in the 2000s. This was attributed to effective measures against vehicular PM and NOx emissions [5,6].

The Wajima air monitoring station (WAMS) of Kanazawa University is located on the Noto peninsula on the west coast of the main Japanese island (Honshu). The concentrations of PAHs decreased slowly but steadily from 2009, with a seasonal pattern, peaking highest during the winter and dropping during the summer [7,8]. A backwards trajectory analysis showed that the air masses travelled over mega city areas in central and northern China [9]. This suggests that the emissions of PAHs and NPAHs in China may also have an impact on Kanazawa, because Kanazawa is only about 100 km south of the WAMS (Figure S1). However, the contribution of vehicles to PM$_{2.5}$ was not known in Kanazawa, although vehicles were considered to be the major contributor of PAHs and NPAHs. It was not easy to distinguish the effects of domestic emissions from the trans-boundary transport, because the concentrations of pollutants transported from China might not be high enough relative to those of domestic Japanese emissions. Moreover, a suitable method is necessary in order to distinguish between major sources like vehicles and coal combustion.

Recently, a new method was developed (the NP method) to calculate the contributions of major sources to the atmospheric PM$_{2.5}$, using pyrene (Pyr) and 1-nitropyrene (1-NP) as markers [10]). In this report, this method is applied in order to calculate the contributions of vehicles and coal combustion to atmospheric PM$_{2.5}$ in Kanazawa. Based on this method, the seasonal changes in vehicular and coal combustion contributions to combustion-derived particulates in Kanazawa, and the impact of trans-boundary transport from China are further clarified.

2. Experimental
2.1. Sampling of PM$_{2.5}$ and PM$_{>2.5}$

A high-volume air sampler (HR-RW, Shibata, Soka, Japan) equipped with a PM$_{2.5}$ cut-off quartz fiber filter was installed close to a main road in a residential area of Kanazawa.
city (136.40° E, 36.33° N) (Figure S1). Kanazawa is a commercial city in Japan, with a population of approximately 464,000. There are no obvious sources of combustion PM$_{2.5}$ near the monitoring station except for traffic. TSP samples were collected daily (24 h) for one week each season: spring (from 24 to 30 April), summer (from 21 to 27 August) and autumn (from 6 to 12 November) in 2017, and winter (from 19 to 25 February) in 2018. The PM$_{2.5}$ and PM$_{>2.5}$ concentrations were calculated from the difference of the filter weights before and after use. The filters were kept in a freezer at $-20$ °C until the analysis of the PAHs and NPAHs [11].

2.2. Determination of the PAHs and NPAHs

The sample treatment and analytical methods for PAHs and NPAHs are described in the Supplementary Materials (Text S1). Briefly, nine PAHs, fluoranthene (FR), Pyr, benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[ghi]perylene (BghiPe), and indeno[1,2,3-cd]pyrene (IDP), were quantified using a high-performance liquid chromatograph (HPLC) equipped with a fluorescence detector, which was operated according to the United States Environmental Protection Agency methods [12]. Six NPAHs—9-nitroanthracene (9-NA), 1-NP, 6-nitrocrysene (6-NC), 7-nitrobenz[a]anthracene (7-NBaA), 3-nitroperylene (3-NPer), and 6-nitrobenzo[a]pyrene (6-NBaP)—were quantified using an HPLC equipped with a reducing column packed with platinum/rhodium, and a chemiluminescence detector. Several deuterated PAHs and NPAHs were used as surrogates and internal standards for the quantification. More detailed conditions were described in the previous reports, along with the limits of quantification [13–15].

2.3. Calculation of Source Contributions

The NP method for the calculation of the contributions of vehicles and coal heating facilities/industries to Pc in the atmospheric PM$_{2.5}$ are described in Supplementary Materials (Text S2) [10]. Briefly, PM$_{2.5}$ is described as being comprised of combustion-derived particulates (Pc) and non-combustion-derived particulates (Po), and Pc is further divided into particulates emitted from combustion with high-temperature (Ph) and particulates from combustion with low-combustion temperature (Pl).

When the proportion of Ph in Pc is $x$ ($0 < x < 1$) and the proportion of Pc in P is $y$ ($0 < y < 1$), the following Equations are expressed using $x$ and $y$.

$$[1 - NP] = [1 - NP_{b}][P_{c}]x + [1 - NP_{c}][P_{c}](1 - x) \quad (i)$$

$$[Pyr] = [Pyr_{n}][P_{c}]x + [Pyr][P_{c}](1 - x) \quad (ii)$$

$$[1 - NP] = \{[1 - NP_{b}]x + [1 - NP_{c}](1 - x)\}[P][y] \quad (iii)$$

Using the values of $[1 - NP_{b}]$ (=65.5 pmol mg$^{-3}$) and $[Pyr_{n}]$ (=180 pmol mg$^{-3}$) in particulates from vehicles, and the atmospheric concentrations of 1-NP ([1-NP]) (=4.6 pmol mg$^{-3}$) and Pyr ([Pyr]) (=3400 pmol mg$^{-3}$) in particulates from coal combustion [5], and [Pyr] and [1-NP] at the monitoring site, values of $x$ and $y$ can be calculated from equations (i–iii). Then, the concentrations of P$_{b}$, P$_{n}$, P$_{h}$ and P$_{i}$ are obtained.

2.4. Lidar Observation

The lidar observation data for the vertical and temporal distributions of Asian dust particles were obtained from the Asian dust and aerosol lidar observation network (https://www-lidar.nies.go.jp/AD-Net). The lidar is stationed in Imizu city, Toyama prefecture (137.10° E, 36.70° N, 28 m ASL), located 45 km east-north-east of Kanazawa. The attenuated backscatter coefficients (532 nm and 1064 nm) and volume depolarization ratio (532 nm) were recorded with a time-height resolution of 6 m and 15 min [16].
2.5. Backward Trajectory and Weather Map

Three-day backward trajectories, every six hours, were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory model developed by National Oceanic and Atmospheric Administration, Washington, DC [17]. The starting height was set to 500 m. The daily weather maps of North East Asia were provided by the Japan Meteorological Agency [18].

2.6. Health Risk Assessment

In order to assess the carcinogenic risk posed by atmospheric PAHs, the concentrations of six PAHs—BaP, BaA, BbF, BkF, Chr and IDP—were expressed using the relative potency factors (TEFPAH) shown in Table S2 [19] as BaP equivalent concentrations (BaPeq). The direct-acting mutagenic activities of NPAHs were assayed using the Ames test with the Salmonella typhimurium YG1024 strain without S9mix [20]. The relative potency factors (TEFNPASH) of four NPAHs—1-NP, 6-NC, 6-NBap and 3-Nper—with regard to that of 1-NP were calculated (Table S3). The TEFNPASH values were used for the estimation of 1-NP equivalent concentrations (1-NPeq) in this study.

3. Results and Discussion

3.1. Seasonal Variations of PM, PAH and NPAH Concentrations

Figure 1 shows the daily atmospheric concentration of TSP (=PM2.5 + PM>2.5) in four successive seasons in Kanazawa. Cumulatively, the highest average concentration of PM2.5 was in the order spring > winter > autumn > summer (Table 1). A similar trend was observed in past monitoring campaigns in Kanazawa, from 1997 to 2014 [4], and also at the WAMS over the last 10 years [7]. In the present study, the highest TSP concentrations were observed in the period 28–30 April. The percentage of PM2.5 in the TSP (PM2.5/TSP) of the spring (69.6%) was larger than the annual average (64.6%) (Table 1). The lidar detected an increase in the concentration of Asian dust in the three days. The daily weather map showed a typical pattern in which the wind flowed from the Asian Continent towards the Islands of Japan after a cold front passed over the Sea of Japan. These results strongly suggest that the increase of TSP in the three days was caused by an Asian dust event. Moreover, the back trajectory of the air mass during this period came through central and northern China, including Beijing and Shenyang.

![Figure 1](image_url)
Table 1. Seasonal Atmospheric Concentrations (Average ± S.D.) of PM>2.5 and PM2.5 in Kanazawa.

|                  | Spring, 2017 | Summer, 2017 | Autumn, 2017 | Winter, 2018 | Annual a |
|------------------|--------------|--------------|--------------|--------------|----------|
| PM>2.5, µg m⁻³   | 9.5 ± 9.9    | 7.6 ± 1.7    | 7.7 ± 4.2    | 7.4 ± 2.7    | 8.0 ± 4.2 |
| PM2.5, µg m⁻³    | 21.7 ± 12.1  | 10.6 ± 4.3   | 12.3 ± 5.1   | 14.2 ± 2.6   | 14.7 ± 7.9 |
| PM2.5/TSP b, %   | 69.6         | 58.2         | 61.5         | 65.7         | 64.6     |

Annual average ± SD of the sum of the spring, summer and autumn of 2017, and the winter of 2018. TSP = PM>2.5 + PM2.5.

Figure 2 shows the daily atmospheric concentrations of nine PAHs (=ΣPAH) in the four seasons in Kanazawa. Pyr and Flt showed the highest concentrations among the nine PAHs. The average concentrations of ΣPAH were in the order winter > spring > autumn > summer (Table 2), which was different from the order of the TSP. The seasonal PAH compositions (pie charts) show that the fraction of Flt was the smallest in the summer. The reason for this is that Flt with four rings has the largest vapor pressure among the nine PAHs; thus, the distribution of Flt in the particle phase decreases with the increasing temperature. Other than this, there was no significant difference in the seasonal composition of PAHs, and the composition of the PAHs did not vary significantly over the last twenty years [5]. Thus, both the winter monsoon and spring Asian dust storm increase the concentration of PAHs, but do not have any effects on their composition. Huge amounts of coal are used for heating purposes in central and northern China every winter, but are not used in Japan. As a result, the atmospheric concentrations of PAHs were several tens of times higher in Beijing and Shenyang than in Japanese cities [5,21,22]. These PAHs emitted in China were transported over a long range to Japan by the predominant northwest monsoon. Hence, the concentration of ΣPAH in Kanazawa was the highest in the winter (Table 2).

Figure 2. Daily atmospheric concentrations of PM>2.5-bound PAHs in April, August and November 2017, and February 2018 in Kanazawa. The pie charts show the fractions of the average concentrations of PAHs.
Table 2. Seasonal Atmospheric Concentrations of ΣPAH and ΣNPAH in Kanazawa.

|                  | Spring, 2017 | Summer, 2017 | Autumn, 2017 | Winter, 2018 | Annual * |
|------------------|--------------|--------------|--------------|--------------|----------|
| ΣPAH b, ng m⁻³  | 0.86 ± 0.56  | 0.30 ± 0.09  | 0.66 ± 0.23  | 1.00 ± 0.26  | 0.71 ± 0.41 |
| ΣNPAH c, pg m⁻³ | 7.90 ± 3.02  | 3.32 ± 1.18  | 6.53 ± 2.47  | 9.56 ± 4.06  | 6.83 ± 3.68 |

*Annual average ± SD of sum of spring, summer and autumn of 2017 and the winter of 2018.

ΣPAH = FR + Pyr + BaA + Chr + BbF + BkF + BaP + BghiPe + DP. ΣNPAH = 9-NA + 1-NP + 6-NC + 7-NBaA + 3-NPer + 6-NBaP.

Figure 3 shows the atmospheric concentrations of six NPAHs (ΣNPAH) during the four seasons in Kanazawa. Among the six NPAHs, 1-NP and 6-NC showed the highest concentrations. The average concentrations of ΣNPAH showed the same order as those of ΣPAH (Table 2). The major NPAH was 6-NC, followed by 1-NP, and these two NPAHs attributed more than 70% of the total NPAHs in all of the seasons. The fraction of 9-NA was the smallest in the summer. With three rings, 9-NA has the highest vapor pressure among the six NPAHs. The low distributions of 9-NA in the particulate phase may be due to its volatility, especially so with increasing temperatures. The concentration ratio of 1-NP to 6-NC was the largest in the winter. In this study, the air sampler was close to a major road, 2–4 km south of downtown Kanazawa. The winter monsoon brings polluted air from downtown to the sampling site. Moreover, the emissions from vehicles are trapped near the surface of the road by the first inversion boundary layer over the ground. This might be the reason for the highest concentration of ΣNPAH in the winter.

Figure 3. Daily atmospheric concentrations of PM₂.₅-bound NPAHs in April, August and November 2017, and February 2018 in Kanazawa. The pie charts show the fractions of the average concentrations of PAHs.

In the spring of 2017, the concentrations of both ΣPAH and ΣNPAH were higher in the last three days (28–30 April) than they were in the first four days (24–27 April) (P < 0.008 and < 0.04, respectively, t-test). The concentration of PM₂.₅ was higher in the second period (P < 0.0007). These coinciding results suggest the effect of the Asian dust event.
There were relationships between $\Sigma$PAH and $\Sigma$NPAH (correlation coefficient $R = 0.7520$), and between $\Sigma$PAH and PM$_{2.5}$ ($R = 0.6811$), but not between $\Sigma$NPAH and PM$_{2.5}$ (Table S1).

3.2. Source Analysis of PM$_{2.5}$, PAHs and NPAHs

The NP method differentiates between combustion sources with high- and low-temperatures [10]. We reported that, in Kanazawa, vehicles and coal combustion facilities/industries were major sources of high- and low-combustion temperatures, respectively [5]. The contributions of vehicles and coal combustion facilities/industries to PM$_{2.5}$ and $P_c$ were estimated in this study. Figure 4 shows the daily atmospheric concentrations of PM$_{2.5}$ in the four seasons. The percentages of $P_c$ and $P_o$ were calculated by the NP-method. The annual average percentage of $P_c$ in PM$_{2.5}$ is very small (2.1%), and the relationship between $P_c$ and PM$_{2.5}$ is weak ($R = 0.5585$) (Table S1). However, the average concentration of $P_c$ showed a clear seasonal change in the order winter > spring > autumn > summer. This order was the same as of the orders of $\Sigma$PAH and $\Sigma$NPAH. The $P_c$ concentration had relationships with those of $\Sigma$PAH ($R = 0.8661$) and $\Sigma$NPAH ($R = 0.8211$) (Table S1).

Figure 4. Daily atmospheric concentrations and compositions of PM$_{2.5}$ in April, August and November 2017, and February 2018 in Kanazawa.

$P_o$ is mostly composed of suspended soil particles, road surface/tire-derived particles, sea salt, and plant-derived particles such as pollen. The concentrations of $P_o$ from 28 to 30 April, when Asian dust came to Kanazawa, were about two times higher than those from 24 to 27 April (Figure 4). This suggests that Asian dust storms might increase the concentrations of soil minerals in $P_o$.

Figure 5 shows the daily atmospheric concentration of $P_c$ in the four seasons, in which the percentages of $P_h$ and $P_l$ were also calculated by the NP-method. The percentage of $P_h$ in $P_c$ was smaller than that of $P_l$ over the year, except for 23 August 2017, when it was 67%. The annual percentage of $P_h$ in $P_c$ was 31% (Table 3), suggesting that the source of $P_c$ was a mixture of coal heating facilities/industries (2/3) and vehicles (1/3). After the heating season in China, the $P_l$ concentration increased dramatically at the end of April (Figure 5). It increased from $0.165 \pm 0.022 \mu g m^{-3}$ (24–27 April) to $0.393 \pm 0.103 \mu g m^{-3}$ (28–30 April), a 238% increase, while the $P_h$ concentration did not increase. Considering that the backward trajectory of the air mass came over Chinese mega city areas in the latter period, this event was attributed to the increase in the $P_l$ amount transported from China. The relationship was very strong between PM$_{2.5}$ and $P_o$ ($R = 0.9999$), but not so strong between

Figure 5. Daily atmospheric concentration of $P_c$ in the four seasons.
PM$_{2.5}$ and P$_c$ ($R = 0.5585$) (Table S1). This difference might depend on the very small percentage of P$_c$ in PM$_{2.5}$.

![Graph showing daily atmospheric concentrations and sources of P$_c$ in April, August and November 2017, and February 2018 in Kanazawa.](image)

**Figure 5.** Daily atmospheric concentrations and sources of P$_c$ in April, August and November 2017, and February 2018 in Kanazawa.

**Table 3.** Seasonal atmospheric concentrations (average ± S.D.) of P$_c$, P$_o$, P$_l$ and P$_h$ in Kanazawa.

| Season       | Spring, 2017 | Summer, 2017 | Autumn, 2017 | Winter, 2018 | Annual a |
|--------------|--------------|--------------|--------------|--------------|----------|
| P$_c$, µg m$^{-3}$ | 0.36 ± 0.14  | 0.18 ± 0.10  | 0.26 ± 0.08  | 0.47 ± 0.08  | 0.33 ± 0.15 |
| P$_o$, µg m$^{-3}$ | 21.4 ± 12.1  | 10.2 ± 6.2   | 12.0 ± 5.0   | 13.6 ± 2.6   | 14.6 ± 8.1 |
| P$_c$/PM$_{2.5}$, % | 1.7          | 1.7          | 2.1          | 3.3          | 2.1       |
| P$_l$, µg m$^{-3}$ | 0.26 ± 0.14  | 0.10 ± 0.04  | 0.20 ± 0.05  | 0.31 ± 0.07  | 0.23 ± 0.11 |
| P$_h$, µg m$^{-3}$ | 0.10 ± 0.03  | 0.07 ± 0.07  | 0.06 ± 0.03  | 0.16 ± 0.06  | 0.10 ± 0.06 |
| P$_h$/P$_c$, %     | 27.8         | 41.2         | 23.1         | 34.0         | 31.0      |

*Annual average ± SD of the sum of the spring, summer and autumn of 2017, and the winter of 2018. P$_c$, particulate from a combustion source; P$_o$, particulate from a non-combustion source; P$_l$, particulate from a combustion source with a lower temperature (heating facilities/industries); P$_h$, particulate from a combustion source with a higher temperature (vehicles). PM$_{2.5}$ = P$_c$ + P$_o$. P$_c$ = P$_l$ + P$_h$.

The relationship between ΣPAH and P$_c$ was strong ($R = 0.8661$ in Table S1). This suggests that the increase in the ΣPAH concentration in the winter (Figure 2) is affected by
emissions from coal heating facilities in China. The significant increase of the ΣPAH concentration was observed in the spring (28 to 30 April 2017). This was also attributed to the long-range transport of PAHs from combustion sources in China.

As described in Figure 4, the increased \( P_c \) in the spring may be mainly attributed to Asian dust storm events. It has been reported that natural dust is long-range transported from the Sahara, Africa to Europe, and from central Australia to New Zealand and Antarctica over the seas [23,24], but the long-range transport of soot-bound PAHs has not been proved in these areas. The above result showed that Asian dust, and also \( P_c \), PAHs and NPAHs, were transported long-range from China to Kanazawa, Japan. This report provides evidence for the long-range transport of combustion-derived particles which affect the urban air quality in city areas.

The \( P_c \) concentration in the summer of 2017 (0.33 \( \mu g \) m\(^{-3}\) in Table 3) was 1/13 of the concentration in the summer of 1999 (2.96 \( \mu g \) m\(^{-3}\)) [10]. Moreover, the \( P_c \) concentration in the winter of 2018 (0.47 \( \mu g \) m\(^{-3}\)) was 1/24 of the concentration in the winter of 1999 (11.14 \( \mu g \) m\(^{-3}\)). The \( P_c \) concentration in the summer of 2017 (0.07 \( \mu g \) m\(^{-3}\)) was 1/39 of the concentration in the summer of 1999 (2.75 \( \mu g \) m\(^{-3}\)), and the \( P_c \) concentration in the winter of 2018 (0.16 \( \mu g \) m\(^{-3}\)) was 1/66 of the concentration in the winter of 1999 (10.63 \( \mu g \) m\(^{-3}\)). It is surprising that the \( P_c \) concentration, which was more than 94% of \( P_c \) in 1999, decreased dramatically in the following 18 years. In the 1990s, the major source of PAHs and NPAHs was vehicles in Kanazawa, but the atmospheric concentrations of NPAHs decreased significantly—to less than 1/60—in the 2000s [5].

Based on the change in the [1-NP]/[Pyr] ratio, the authors reported that the above changes were attributable to the regulations on vehicular PM/NO\(_x\) emissions [25]. The decreases in PAH and NPAH emissions from vehicles clearly explain the way in which the changes in the \( P_c \) concentration were mostly due to \( P_c \). Unlike \( P_c \), \( P_c \) (0.21\( \mu g \) m\(^{-3}\) in the summer and 0.51 \( \mu g \) m\(^{-3}\) in the winter of 1999) decreased much more slowly during this period, by factors of 1/1.2 and 1/1.1, respectively. The decrease in the atmospheric concentrations of PAHs at the WAMS was also much slower than those in Kanazawa [7]. This result suggests that there was a slow decrease in the \( P_c \) amount transported from China.

3.3. Health Risk Assessment

Recently, the urban atmospheric concentrations of PAHs and NPAHs were studied in many countries [21,26–33]. The concentrations of PAHs in Kanazawa are as low as those in several cities in the EU and the United States, and much lower than those in central and northern Chinese cities. In order to estimate the cancer risks of PAHs, BaP, which has a relatively strong carcinogenic potential, has often been used as the marker in PAH monitoring. Several countries and organizations have set BaP concentration limits, and the WHO recommends atmospheric BaP concentrations below 0.12 ng m\(^{-3}\) [34]. However, the annual mean concentrations at many monitoring stations in the world were still over this reference level [35]. The annual atmospheric concentration (mean ± SD) of BaP in Kanazawa was 0.040 ± 0.026 ng m\(^{-3}\), with a maximum concentration of 0.12 ng m\(^{-3}\), which is not over the WHO reference level. Moreover, it should be emphasized that the average percentage of \( P_c \) in PM in Kanazawa was not more than 7.5%, which is much smaller than the values of Beijing and Shenyang, where the percentages of \( P_c \) in the TSP were over 40% in the winter [5]. These results suggest that the present air quality of Kanazawa is clean enough with regard to combustion-derived pollution.

The order of the BaPeq concentration of the six PAHs in Kanazawa, calculated using the TEF\(_{PAH}\) in Table S2, was spring (70.5 pg m\(^{-3}\)) > winter (64.5 pg m\(^{-3}\)) > autumn (59.5 pg m\(^{-3}\)) > summer (28.1 pg m\(^{-3}\)), which is similar to the concentration order of the nine PAHs. In addition, BaP was the largest contributor (not less than 62%) in all of the seasons. Moreover, the order of the toxicity of the atmospheric four NPAHs, calculated using the TEF\(_{NPAH}\) in Table S3, was winter (3.72 pg m\(^{-3}\)) > spring (2.96 pg m\(^{-3}\)) > autumn (2.07 pg m\(^{-3}\)) > summer (1.48 pg m\(^{-3}\)), which is also consistent with the concentration order of the four NPAHs. In addition, 1-NP showed the largest mutagenic contribution, which was 57–72%, followed by 6-NC, the contribution of which was 20–42%. This order was constant.
over the year. These results suggest that the winter monsoon and the spring Asian dust storm changed the atmospheric concentrations of the PAHs and NPAHs, but did not change their compositions in Kanazawa.

4. Conclusions

PM$_{2.5}$ and PM$_{>2.5}$ samples were collected seasonally from the spring of 2017 to the winter of 2018, and nine PAHs and six NPAHs were determined using HPLC with fluorescence and chemiluminescence detections, respectively. The contributions of vehicles and coal combustion, and the effects of long-range transport from China on those atmospheric pollutants in Kanazawa were calculated using the NP method.

- The atmospheric concentrations of PAHs and NPAHs showed similar seasonal variations: they were highest in the winter and lowest in the summer.
- The percentage of P$_c$ in the PM$_{2.5}$ was much smaller (2.1%). However, the atmospheric concentration of P$_c$ showed seasonal variation. The annual average contributions of coal heating facilities/industries and vehicles to P$_c$ were 69% and 31%, respectively.
- The high concentrations of P$_c$ and PAHs in the winter and during the Asian dust event in the spring were largely attributed to the long-range transport of emissions from coal heating facilities and industries in China. The NPAHs were mainly emitted from vehicles in Kanazawa.
- The P$_c$ concentrations in the summer of 2017 and the winter of 2018 were respectively 1/13 and 1/16 of those detected in 1999. This significant improvement was mostly attributed to the decrease in the P$_c$ quantities emitted from vehicles in Kanazawa. However, the decrease in the P$_c$ amount transported from China was much lower.

Thus, the seasonal and long-term changes of the air pollution in Kanazawa, caused by P$_c$, PAHs and NPAHs, were characterized by domestic emissions from vehicles and coal combustion emissions transported from China.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4433/12/2/256/s1. Figure S1: Map of monitoring sites, Table S1: Correlation coefficients between atmospheric compounds, Table S2: Toxic equivalency factors of PAHs (TEF$_{PAH}$), Table S3: Toxic equivalency factors of NPAHs (TEF$_{NPAH}$).

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References

1. WHO. Ambient Air Pollution: A Global Assessment of Exposure and Burden of Disease; WHO: Geneva, Switzerland, 2016; pp. 1–131, ISBN 9789241511353.

2. WHO. Air Pollution and Child Health: Prescribing Clean Air; WHO/CED/PHE/18.01; WHO News Releases: Geneva, Switzerland, 2018.

3. Anyenda, E.O.; Higashi, T.; Kambayashi, Y.; Nguyen, T.T.T.; Michigami, Y.; Fujimura, M.; Hara, A.J.; Tsuiguchi, H.; Kitaika, M.; Asakura, H.; et al. Associations of Cough Prevalence with Ambient Polycyclic Aromatic Hydrocarbons, Nitrogen and Sulfur Dioxide: A Longitudinal Study. *Int. J. Environ. Res. Public Health* **2016**, *13*, 800, doi:10.3390/ijerph13080800.

4. Hayakawa, K.; Tang, N.; Nagato, E.G.; Toriba, A.; Sakai, S.; Kano, F.; Goto, S.; Endo, O.; Arashidani, K.; Kakimoto, H. Long Term Trends in Atmospheric Concentrations of Polycyclic Aromatic Hydrocarbons and Nitropolycyclic Aromatic Hydrocarbons: A Study of Japanese Cities from 1997 to 2014. *Environ. Pollut.* **2018**, *233*, 474–482, doi:10.1016/j.envpol.2017.10.038.

5. Hayakawa, K.; Nagao, S.; Inomata, Y.; Inoue, M.; Matsuhi, A. *Trans-Boundary Pollution in North-East Asia*; Nova Science Publishers: New York, NY, USA, 2018; ISBN 978-1-53613-742-2.

6. Hayakawa, K.; Suzuki, N. Special Issue “Recent Advances in Polycyclic Aromatic Hydrocarbons Research: Occurrence, Fate, Analysis and Risk Assessment”. Available online: https://www.mdpi.com/journal/ijerph/special_issues/PAHs (accessed on 31 December 2019).

7. Tang, N.; Hakamata, M.; Sato, K.; Okada, Y.; Yang, X.-Y.; Tatematsu, M.; Toriba, A.; Kameda, T.; Hayakawa, K. Atmospheric behaviors of polycyclic aromatic hydrocarbons at a Japanese remote background site, Noto peninsula, from 2004. *Atmos. Environ.* **2015**, *120*, 144–151, doi:10.1016/j.atmosenv.2015.08.090.

8. Zhang, H.; Zhang, L.; Yang, L.; Zhou, Q.; Zhang, X.; Xing, W.; Hayakawa, K.; Toriba, A.; Tang, N. Impact of COVID-19 Outbreak on the Long-range Transport of Common Air Pollutants in KUWAMS. *Biol. Pharm. Bull.* **2021**, in press.

9. Ye, L.; Zhang, L.; Zhang, H.; Zhou, Q.; Zhang, X.; Xing, W.; Takami, A.; Sato, K.; Shimizu, A.; Yoshino, A.; et al. Comparative analysis of PM₁₅-bound polycyclic aromatic hydrocarbons (PAHs), nitro-PAHs (NPAHs) and water-soluble inorganic ions (WSIs) at two background sites in Japan. *Int. J. Environ. Res. Public Health* **2020**, *17*, 8224, doi:10.3390/ijerph17128224.

10. Hayakawa, K.; Tang, N.; Toriba, A.; Nagato, E.G. Calculating sources of combustion-derived particulates using 1-nitropyrene and pyrene as markers. *Environ. Pollut.* **2020**, *265*, 114730, doi:10.1016/j.envpol.2020.114730.

11. Xing, W.; Zhang, L.; Yang, L.; Zhou, Q.; Zhang, X.; Toriba, A.; Hayakawa, K.; Tang, N. Characteristics of PM₁₅-bound polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons at a roadside air pollution monitoring station in Kanazawa, Japan. *Int. J. Environ. Res. Public Health* **2020**, *17*, 805, doi:10.3390/ijerph17030805.

12. Wise, S.A.; Sander, L.C.; Schantz, M.M. Analytical methods for determination of polycyclic aromatic hydrocarbons (PAHs)—A historical perspective on the U.S. EPA priority pollutant PAHs. *Polycycl. Aromat. Compd.* **2015**, *35*, 187–247, doi:10.1080/10406638.2014.970291.

13. Hayakawa, K.; Kitamura, R.; Butoh, M.; Imaiizumi, N.; Miyazaki, M. Determination of diamino- and aminopyrenes by high-performance liquid chromatography with chemiluminescence detection. *Anal. Sci.* **1991**, *7*, 573–577, doi:10.2116/analsci.7.573.

14. Hayakawa, K.; Murahashi, T.; Butoh, M.; Miyazaki, M. Determination of 1,3-, 1,6-, and 1,8-dinitropyrenes and 1-nitropyrene in exhaust particulates fractionated by silica-gel column chromatography. *Anal. Sci.* **2015**, *31*, 639–644, ISSN-13-978-9812561183.

15. Shimizu, A.; Sugimoto, N.; Matsui, I.; Arai, K.; Uno, I.; Murayama, T.; Kagawa, N.; Aoki, K.; Uchiyama, A.; Hayakawa, K. Continuous observations of Asian dust and other aerosols by polarization lidar in China and Japan during ACE-Asia. *J. Geophys. Res.*, *2020*, *109*, D19S17, doi:10.1029/2004JD005881.

16. National Oceanic and Atmospheric Administration, Lagrangian Integrated Trajectory model. Available on line: https://ready.arl.noaa.gov/hypub-bin/trajtype.pl (accessed on 12 February 2020).

17. Japan Meteorological Agency, Daily Weather Map. Available online: http://www.data.jma.go.jp/jcfd/yoho/hibiten/index.html (accessed on 12 February 2020).

18. USEPA, Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons. EAP/600/R-93/089 (1993). Available online: https://www.epa.gov/risk/relative-potency-factors-carcinogenic-polycyclic-aromatic-hydrocarbons-pahs (accessed on 12 February 2021).

19. Hayakawa, K.; Nakamura, A.; Terai, N.; Kizu, R.; Ando, K. Nitroarene concentrations and direct-acting mutagenicity of diesel exhaust particulates fractionated by silica-gel column chromatograph. *Chem. Pharm. Bull.* **1997**, *45*, 1820–1822, doi:10.1248/cpb.45.1820.

20. Yang, L.; Suzuki, G.; Zhang, L.; Zhou, Q.; Zhang, X.; Xing, W.; Shima, M.; Yoda, Y.; Nakatsu, R.; Hiraki, T.; et al. The characteristics of polycyclic aromatic hydrocarbons in different emission source areas in Shenyang, China. *Int. J. Environ. Public Health* **2019**, *16*, 2817, doi:10.3390/ijerph1612817.
22. Zhang, L.; Morisaki, H.; Wei, Y.; Li, Z.; Yang, L.; Zhou, Q.; Zhang, X.; Xing, W.; Hu, M.; Shima, M.; et al. PM2.5-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, doi:10.1016/j.scitotenv.2019.135840.

23. Ansmann, A.; Bösenberg, J.; Chaikovsky, A.; Comerón, A.; Eckhardt, S.; Eixmann, R.; Freudenthaler, V.; Ginoux, P.; Komguem, L.; Linné, H.; et al. Long-range transport of Sahara dust to northern Europe: The 11–16 October 2001 outbreak observed with EARLINET. J. Geogr. Res. 2003, 108, D24, doi:10.1029/2003JD003757.

24. Nguyen, H.; Riley, M.; Leys, J.; Salter, D. Dust storm event of February 2019 in central and east coast of Australia and evidence of long-range transport to New Zealand and Antarctica. Atmosphere 2019, 12, 256, doi:10.3390/atmos12020256.

25. Hayakawa, K. Polycyclic Aromatic Hydrocarbons: Environmental Behavior and Toxicity in East Asia; Springer: Berlin/Heidelberg, Germany, 2018; ISBN 978-981-10-6774-7.

26. Cetin, B.; Ozturk, F.; Keles, M.; Yurdakul, S. PAHs and PCBs in an eastern Mediterranean megacity, Istanbul: Their spatial and temporal distributions, air–soil exchange and toxicological effects. Environ. Pollut. 2017, 220, 1322–1332, doi:10.1016/j.envpol.2016.11.002.

27. Franco, J.; de Resende, F.; de Almeida Furtado, L.; Brasil, F.; Eberlin, N.; Netto, P. Polycyclic aromatic hydrocarbons (PAHs) in street dust of Rio de Janeiro and Niterói, Brazil: Particle size distribution, sources and cancer risk assessment. Sci. Total Environ. 2017, 599–600, 305–313, doi:10.1016/j.scitotenv.2017.04.060.

28. Hamid, N.; Syed, H.; Junaid, M.; Mahmood, A.; Li, J.; Zhang, G.; NaseemMalik, R. Elucidating the urban levels, sources and health risks of polycyclic aromatic hydrocarbons (PAHs) in Pakistan: Implications for changing energy demand. Sci. Total Environ. 2018, 619–620, 165–175, doi:10.1016/j.scitotenv.2017.11.080.

29. Yang, J.; Xu, W.; Cheng, H. Seasonal variations and sources of airborne polycyclic aromatic hydrocarbons (PAHs) in Chengdu, China. Atmosphere 2018, 9, 63, doi:10.3390/atmos9020063.

30. Byambaa, B.; Yang, L.; Matsuki, A.; Nagato, E.G.; Gankhuyang, K.; Chuluunpurev, B.; Banzragch, L.; Chonokhuu, S.; Tang, N.; Hayakawa, K. Sources and characteristics of polycyclic aromatic hydrocarbons in ambient total suspended particles in Ulaanbaatar city, Mongolia. Int. J. Environ. Res. Public Health 2019, 16, 442, doi:10.3390/ijerph16030442.

31. Hu, H.; Tian, M.; Zhang, L.; Yang, F.; Peng, C.; Chen, Y.; Shi, G.; Yao, X.; Jiang, C.; Wang, J. Sources and gas-particle partitioning of atmospheric parent, oxygenated, and nitrated polycyclic aromatic hydrocarbons in a humidcity in southwest China. Atmos. Environ. 2019, 206, 1–10, doi:10.1016/j.atmosenv.2019.02.041.

32. Emine, A.; Fatma, E. Atmospheric polycyclic aromatic hydrocarbons (PAHs) at two sites, in Bursa, Turkey: Determination of concentrations, gas–particle partitioning, sources, and health risk. Arch. Environ. Contam. Toxicol. 2020, 78, 350–366, doi:10.1007/s00244-019-00698-7.

33. European Environment Agency, Annual Mean BaP Concentrations in 2018, Annual Mean BaP Concentrations in 2018 (2020). Available online: https://www.eea.europa.eu/data-and-maps/figures/annual-mean-baP-concentrations-in-4 (accessed on 12 February 2021).

34. WHO, Review of Evidence on Health Aspects of Air Pollution—REVIHAAP Project: Final Technical Report, WHO Regional Office for Europe (2013). Available online: https://www.euro.who.int/en/health-topics/environment-and-health/air-quality/publications/2013/review-of-evidence-on-health-aspects-of-air-pollution-revihaap-project-final-technical-report (accessed on 12 February 2021).