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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 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

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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 NO_x 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 P_c 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 (P_c) and non-combustion-derived particulates (P_o), and P_c is further divided into particulates emitted from combustion with high-temperature (P_h) and particulates from combustion with low-combustion temperature (P_l).

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

$$[1 - NP] = [1 - NP_h][P_c]x + [1 - NP_l][P_c](1 - x) \text{ (i)} \quad (1)$$

$$[Pyr] = [Pyr_h][P_c]x + [Pyr_l][P_c](1 - x) \text{ (ii)} \quad (2)$$

$$[1 - NP] = \{[1 - NP_h]x + [1 - NP_l](1 - x)\}[P]y \text{ (iii)} \quad (3)$$

Using the values of $[1 - NP_h]$ (=65.5 pmol mg^{-3}) and $[Pyr_h]$ (=180 pmol mg^{-3}) in particulates from vehicles, and the atmospheric concentrations of 1-NP ($[1\text{-}NP_l]$) (=4.6 pmol mg^{-3}) and Py ($[Pyr_l]$ (=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_c, P_o, P_h and P_l 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) (accessed on 6 January 2021). 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 (TEF_{PAH}) 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 (TEF_{NPAH}) of four NPAHs—1-NP, 6-NC, 6-NBaP and 3-Nper—with regard to that of 1-NP were calculated (Table S3). The TEF_{NPAH} 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 (=$PM_{2.5}$ + $PM_{>2.5}$) in four successive seasons in Kanazawa. Cumulatively, the highest average concentration of $PM_{2.5}$ 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 $PM_{2.5}$ in the TSP ($PM_{2.5}$/ 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.

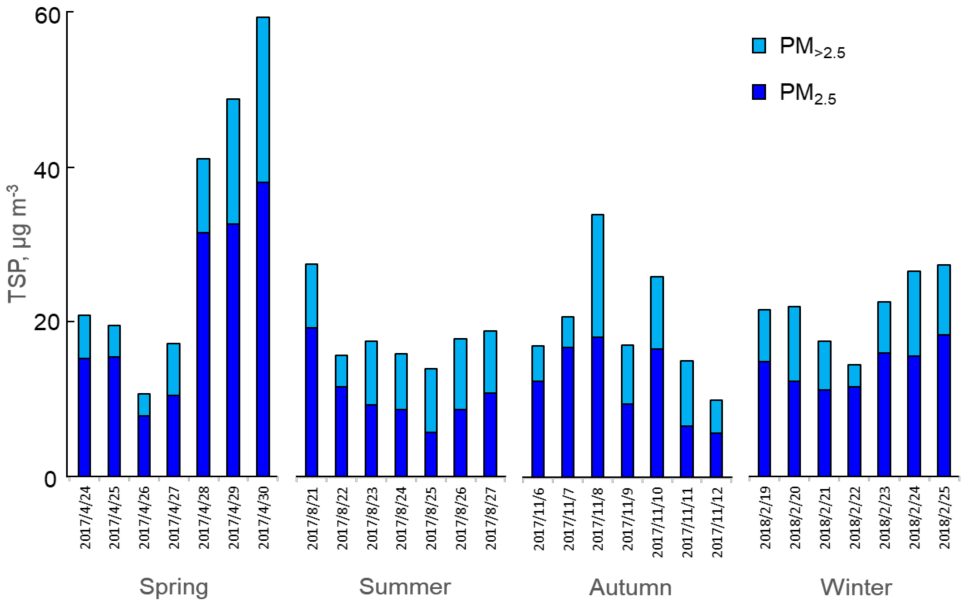

Figure 1. Daily atmospheric concentration of $PM_{2.5}$ and $PM_{>2.5}$ fractions in April, August and November 2017, and February 2018 in Kanazawa.

Table 1. Seasonal Atmospheric Concentrations (Average ± S.D.) of $PM_{>2.5}$ and $PM_{2.5}$ 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
$PM_{2.5}$, μg m^{-3}	21.7 ± 12.1	10.6 ± 4.3	12.3 ± 5.1	14.2 ± 2.6	14.7 ± 7.9
$PM_{2.5}$/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 = $PM_{>2.5}$ + $PM_{2.5}$.

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 form 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 the 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).

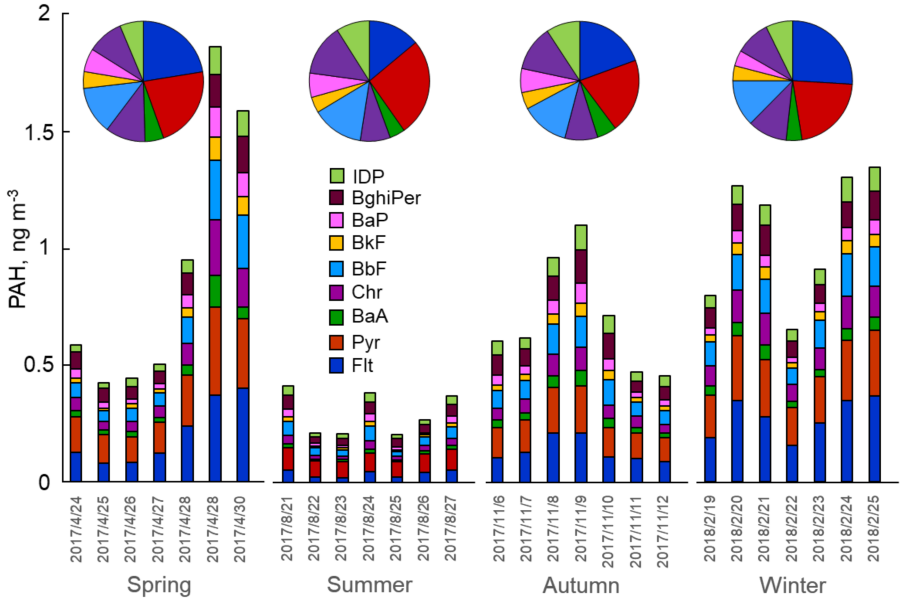

Figure 2. Daily atmospheric concentrations of $PM_{2.5}$-bound PAHs in April, August and November 2017, and February 2018 in Kanazawa. The pie charts show the fractions of the average concentrations of PAHs.

Table 2. Seasonal Atmospheric Concentrations of ΣPAH and ΣNPAH in Kanazawa.

	Spring, 2017	Summer, 2017	Autumn, 2017	Winter, 2018	Annual [a]
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

[a] Annual average ± SD of sum of spring, summer and autumn of 2017 and the winter of 2018. [b] ΣPAH = FR + Pyr + BaA + Chr + BbF + BkF + BaP + BghiPe + DP. [c] 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.

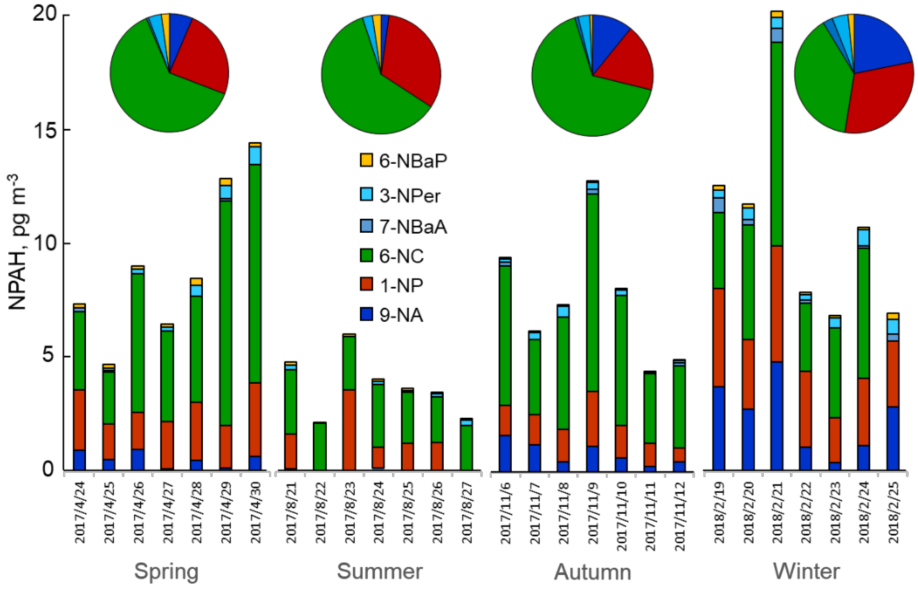

Figure 3. Daily atmospheric concentrations of $PM_{2.5}$-bound NPAHs in April, August and November 2017, and February 2018 in Kanazawa. The pie charts show the fractions of the average concentrations of PAHs.

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 $PM_{2.5}$ was higher in the second period ($p < 0.0007$). These coinciding results suggest the effect of the Asian dust event. There were relationships between ΣPAH and ΣNPAH (correlation coefficient $R = 0.7520$), and between ΣPAH and $PM_{2.5}$ ($R = 0.6811$), but not between ΣNPAH 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 ΣPAH and ΣNPAH. The P_c concentration had relationships with those of ΣPAH (R = 0.8661) and ΣNPAH (R = 0.8211) (Table S1).

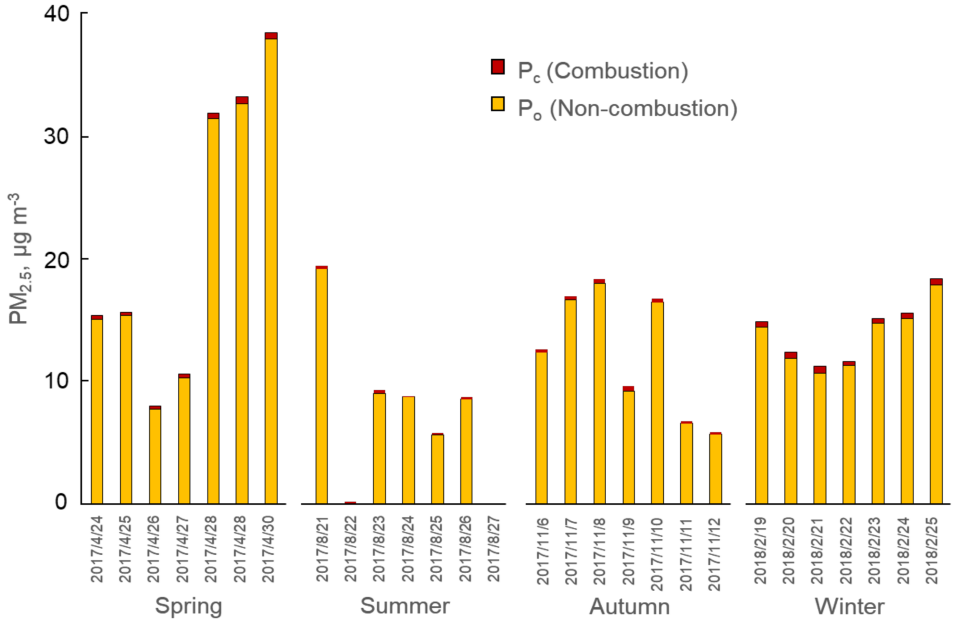

Figure 4. Daily atmospheric concentrations and compositions of $PM_{2.5}$ in April, August and November 2017, and February 2018 in Kanazawa.

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 ± 0.022 μg m^{-3} (24–27 April) to 0.393 ± 0.103 μg 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 $PM_{2.5}$ and P_c (R = 0.5585) (Table S1). This difference might depend on the very small percentage of P_c in $PM_{2.5}$.

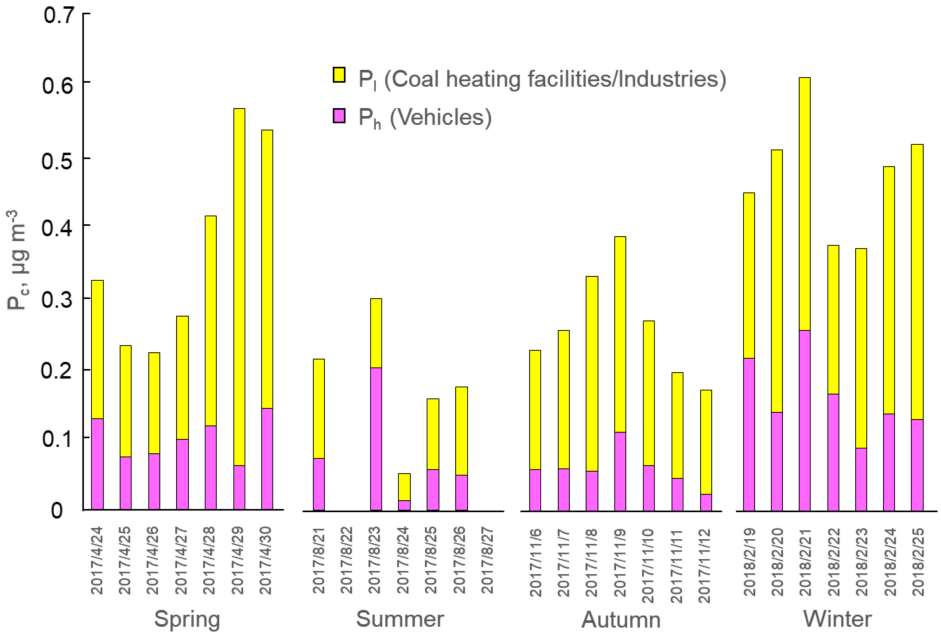

Figure 5. Daily atmospheric concentrations and sources of P_c in April, August and November 2017, and February 2018 in Kanazawa.

Table 3. Seasonal atmospheric concentrations (average ± S.D.) of P_c, P_o, P_l and P_h in Kanazawa.

	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

[a] 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_o 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 μg m^{-3} in Table 3) was 1/13 of the concentration in the summer of 1999 (2.96 μg m^{-3}) [10]. Moreover, the P_c concentration in the winter of 2018 (0.47 μg m^{-3}) was 1/24 of the concentration in the winter of 1999 (11.14 μg m^{-3}). The P_h concentration in the summer of 2017 (0.07 μg m^{-3}) was 1/39 of the concentration in the summer of 1999 (2.75 μg m^{-3}), and the P_h concentration in the winter of 2018 (0.16 μg m^{-3}) was 1/66 of the concentration in the winter of 1999 (10.63 μg m^{-3}). It is surprising that the P_h 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_h. Unlike P_h, P_l (0.21μg m^{-3} in the summer and 0.51 μg 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_l 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 https://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 (TEFPAH), Table S3: Toxic equivalency factors of NPAHs (TEFNPAH).

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