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

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**Abstract**

$PM_{2.5}$ 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 determined by HPLC with fluorescence and chemiluminescence detections, respectively. Atmospheric concentrations of both PAHs and NPAHs showed seasonal changes (highest in the winter and lowest in the summer), which were different from the variations of TSP and $PM_{2.5}$ (highest in the spring). Contributions of major sources to combustion-derived particulate ($P_c$) in $PM_{2.5}$ were calculated by the NP-method using pyrene and 1-nitropyrene as 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 automobiles (31%) and coal heating facilities/industries (69%). The source of Pyr was almost entirely coal heating facilities/industries (98%). A backward trajectory analysis showed that automobile-derived $P_c$ was mainly from Kanazawa and its surroundings and that coal heating facilities-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 long-range transported from China in the winter. Even in spring when the coal heating season was over in China, PAHs came over to Japan after Asian dust storms passed through Chinese city areas. The main contributor of NPAHs was automobiles 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 automobiles. Thus, changes of atmospheric concentrations of $P_c$, PAHs and NPAHs in Kanazawa were strongly affected not only by the local emissions but also long-range transport from China.

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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 enhances health risks especially in children (WHO, 2016 and 2018). Among different sizes of PM, $PM_{2.5}$ (PM with diameters not more than 2.5 μm) increases the risk of respiratory and cardiovascular diseases including asthma (Anyenda et al, 2016). $PM_{2.5}$ contains several hazardous chemicals associated with these diseases. Among them, polycyclic aromatic hydrocarbons (PAHs) and its derivatives such as nitropolycyclic aromatic hydrocarbons (NPAHs) are known as carcinogens and/or mutagens. In many countries, automobiles are considered as the major source of those PAHs and NPAHs. On the other hand, $PM_{2.5}$ air pollution caused by coal heating and slash and burn agriculture are serious in China and developing countries, respectively. To reduce the health risk, reduction of $PM_{2.5}$ emission generated from fossil fuels and biomass burning is an important issue worldwide. Recently, air quality standards or guidelines of $PM_{2.5}$ have been set by several countries and international organizations. However, present air quality standards measure the atmospheric concentration of $PM_{2.5}$ based on particle size but not on toxic chemicals. The atmospheric behaviors and sources of PAHs and NPAHs are little known, despite their importance to human health.

Far-Eastern Asia is one of the hot spots of air pollution and Asian dust storm (Yellow sand) often attacks not only China but also Korea and Japan. We started an international monitoring network of more than ten cities in Japan, China, Russia and Korea in the 1990s for the continuous survey of atmospheric concentrations of total suspended particulate matter (TSP)-bound PAHs and NPAHs (Hayakawa et al., 2018a). Among those cities, Chinese and Russian cities, especially in 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. On the other hand, Japanese cities showed a constant decrease in

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concentrations of PAHs and NPAHs, especially a significant decrease in the concentration of NPAHs in the 2000s. This was attributed to effective measures against PM and NOx emissions from automobiles (Hayakawa et al., 2018b; Hayakawa et al., 2020a).

At the Wajima air monitoring station (WAMS) of Kanazawa University on the tip of the Noto peninsula, which is on the west coast of the main Japanese island (Honshu), concentrations of PAHs decreased slowly but steadily from 2009 with a seasonal change, highest in winter and lowest in summer (Tang et al., 2015; Zhang et al., 2021). A backward trajectory analysis showed the transport of air mass came over mega city areas in the central and northern China (Yang et al., 2020). These results suggested that the emission of PAHs and NPAHs in China might also have an impact on Kanazawa, because Kanazawa is only about 100 km south of WAMS (Fig. S1). However, the contribution of automobiles to $PM_{2.5}$ was not known in Kanazawa, although automobiles 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 pollutants in Kanazawa. Moreover, a suitable method is necessary to distinguish major sources, such as automobiles and coal combustion.

Recently, we developed a new method (the NP-method) to calculate contributions of major sources to the atmospheric $PM_{2.5}$ by measuring pyrene (Pyr) and 1-nitropyrene (1-NP) as markers (Hayakawa et al., 2020b). In this report, we calculated contributions of automobiles and coal combustion to atmospheric $PM_{2.5}$ in Kanazawa by the method. Using the results, seasonal changes in contributions of automobiles and coal combustion to combustion-derived particulates in Kanazawa and impact of trans-boundary transport from China were discussed.

## 2. Experimental

### *2.1. Sampling of $PM_{2.5}$ and $PM_{>2.5}$*

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A high-volume air sampler (HR-RW, Shibata, Soka, Japan) equipped with a $PM_{2.5}$ attachment was set beside the main road in a residential area of Kanazawa city (136.40E, 36.33N) (Fig. S1). Kanazawa, whose population is 464,000, is a commercial city. There are no obvious sources of combustion $PM_{2.5}$ near the monitoring station except for traffic. TSP samples were collected daily for one week in every season: spring (from April 24 to 30), summer (from August 21 to 27) and autumn (from November 6 to 12) in 2017, and winter (from February 19 to 25) in 2018, on quartz fiber filters. Collected amounts of $PM_{2.5}$ and $PM_{>2.5}$ were calculated from the difference of the filter weights before and after. Filters were kept in a freezer at – 20°C until determination of PAHs and NPAHs (Xing et al., 2020).

### *2.2. Determination of PAHs and NPAHs*

Sample treatments and analytical methods for PAHs and NPAHs are described in Text 1 in Supporting Information. Briefly, nine PAHs, fluoranthene (FR), Pyr, benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), menzo[*a*]pyrene (BaP), benzo[*ghi*]perylene (BghiPe), indeno[1,2,3-*cd*]pyrene (IDP), were quantified using a high-performance liquid chromatograph (HPLC) equipped with a fluorescence detector according to the United States Environmental Protection Agency methods (Wise et al., 2016). 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 quantification. More detailed conditions were described in the previous reports with limits of quantification (Hayakawa et al., 1991, 1995 and 2006; Tang et al., 2005).

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*2.3 Calculation of source contributions*

The NP method for calculating contributions of automobiles and coal heating facilities/industries to $P_c$ in the atmospheric $PM_{2.5}$ was described in Text S1 (Hayakawa et al., 2020b). Briefly, $PM_{2.5}$ is divided into combustion-derived particulate ($P_c$) and non-combustion-derived particulate ($P_o$), and $P_c$ is further divided into particulate emitted from automobiles ($P_h$), that is the source with high combustion temperature and particulate emitted from coal heating facilities/industries ($P_l$), that is the source with low combustion temperature.

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 $y$.

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

$$[\text{Pyr}]\ [\text{Pyr}_h][P_c]x + [\text{Pyr}_l][P_c](1 - x) \quad \text{(ii)}$$

$$[1\text{-NP}] = \{[1\text{-NP}_h]x + [1\text{-NP}_l](1 - x)\}[P]y \quad \text{(iii)}$$

Using values of $[1\text{-NP}_h]$ (= 65.5 pmol $mg^{-3}$) and $[\text{Pyr}_h]$ (= 180 pmol $mg^{-3}$) in particulates from automobiles, and the atmospheric concentrations of1-NP ($[1\text{-NP}_l]$) (= 4.6 pmol $mg^{-3}$) and Py ($[\text{Pyr}_l]$ (= 3,400 pmol $mg^{-3}$) in particulates from coal combustion, and [Pyr] and [1-NP] at the monitoring site, values of $x$ and $y$ can be calculated from equations (i) - (iii). Then concentrations of $P_c$, $P_o$, $P_h$ and $P_l$ are obtained.

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*2.4. Lidar observation*

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 (137.10E, 36.70N, 28mASL), located 45 km east-north-east of Kanazawa. Attenuated backscatter coefficients (532 nm and 1,064 nm) and volume depolarization ratio (532 nm) have been recorded with time-height resolution of 6 m and 15 minutes (Shimizu et al., 2004).

*2.5. Backward trajectory and weather map*

Three-days backward trajectories every six hours were calculated using Hybrid Single-Particle Lagrangian Integrated Trajectory model developed by National Oceanic and Atmospheric Administration (https://ready.arl.noaa.gov/hypub-bin/trajtype.pl). The starting height was set 500 m. Daily weather maps of the North East Asia were provided by the Japan Meteorological Agency (http://www.data.jma.go.jp/fcd/yoho/hibiten/index.html).

## 3. Results and Discussion

*3.1. Seasonal variations of PM, PAHs and NPAHs concentrations*

Figure 1 shows the daily atmospheric concentration of TSP (= $PM_{2.5}$ + $PM_{>2.5}$) in four successive seasons in Kanazawa. For the four seasons, the average concentration of $PM_{2.5}$ was in the order spring > winter > autumn > summer (Table 1). The same seasonal variation was observed in the past monitoring campaign in Kanazawa from

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1997 to 2014 (Hayakawa et al., 2018b). A similar seasonal variation was observed at WAMS over the last 10 years (Tang et al., 2015). In the present study, the highest TSP concentrations were observed in the period April 28-30. The fraction of $PM_{2.5}$ in TSP ($PM_{2.5}$/ TSP) in the spring (69.6%) was larger than the annual average (64.6%) (Table 1). Lidar detected the increase in the concentration of Asian dust in the three days. The daily weather map showed the typical pattern in which the wind flowed from the Asian Continent into the Japan Islands after the cold front passed over the Japan Sea. These results strongly suggested that the increase of TSP in the three days was caused by the Asian dust event. Moreover, the back trajectory of the air mass of this period came through central and northern China including Beijing and Shenyang.

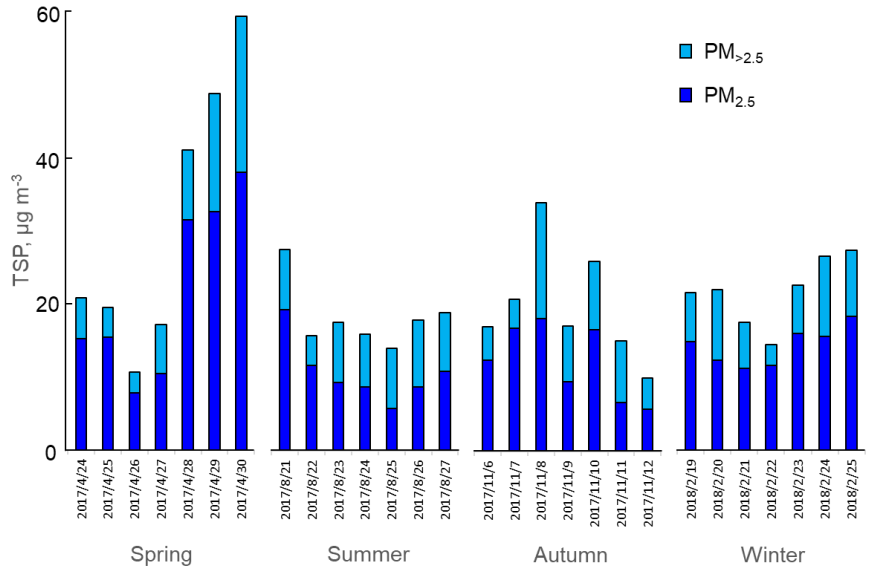


Fig. 1 Daily Atmospheric Concentration of TSP with Fractions of $PM_{2.5}$ and $PM_{>2.5}$ in Four Seasons in Kanazawa

Daily TSP (total suspended particulate matter) samples were collected for seven days in each season from the spring of 2017 to the winter of 2018 at the side of a major road in the suburbs of Kanazawa. Filters were changed daily.

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**Table1**. 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 |

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

b) $TSP = PM_{>2.5} + PM_{2.5}$.

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). A large amount of coal is used for heating in cities of central and northern China in every winter, but not used in Japan. As the result, atmospheric concentrations of PAHs were several ten times higher in Beijing and Shenyang than in Japanese cities (Hayakawa et al., 2018b; Yang et al., 2019; Zhang et al., 2020). These PAHs emitted in China were long-range transported to Japan by the predominant northwest monsoon. This is the reason why the average concentration of ΣPAH in Kanazawa was the highest in the winter (Table 2).

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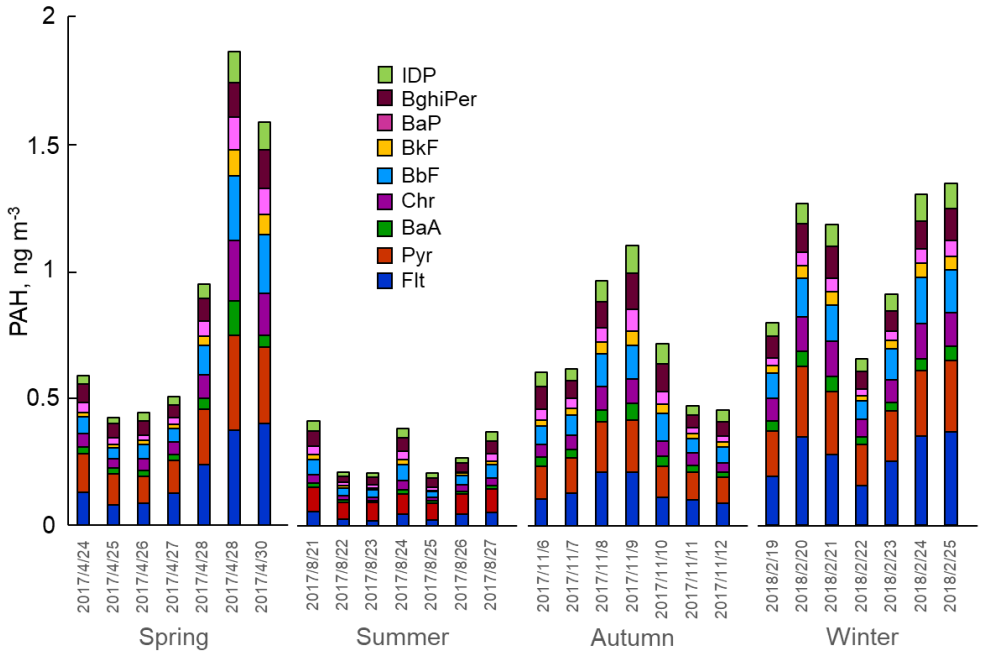


Fig. 2 Daily Atmospheric Concentrations of $PM_{2.5}$-bound PAHs in Four Seasons in Kanazawa

Daily TSP samples were collected for seven days in each season from the spring of 2017 to the spring of 2018 at the side of a major road in the suburbs of Kanazawa. Filters were changed daily.

**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.

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Figure 3 shows the daily atmospheric concentrations of six NPAHs (= ΣNPAH) in the four seasons in Kanazawa. 1-NP and 6-NC showed the highest concentrations among the six NPAHs. The average concentrations of ΣNPAH showed the same order as that of ΣPAH (Table 2). In this study, the air sampler was set on the side of a major road about 2-4 km south of downtown. The winter monsoon brings the polluted air from downtown to the sampling site. Moreover, the emission from automobiles are trapped near the surface of the road by the reversed air bilayer on cold days. This might be the reason for the highest concentration of ΣNPAH in the winter.

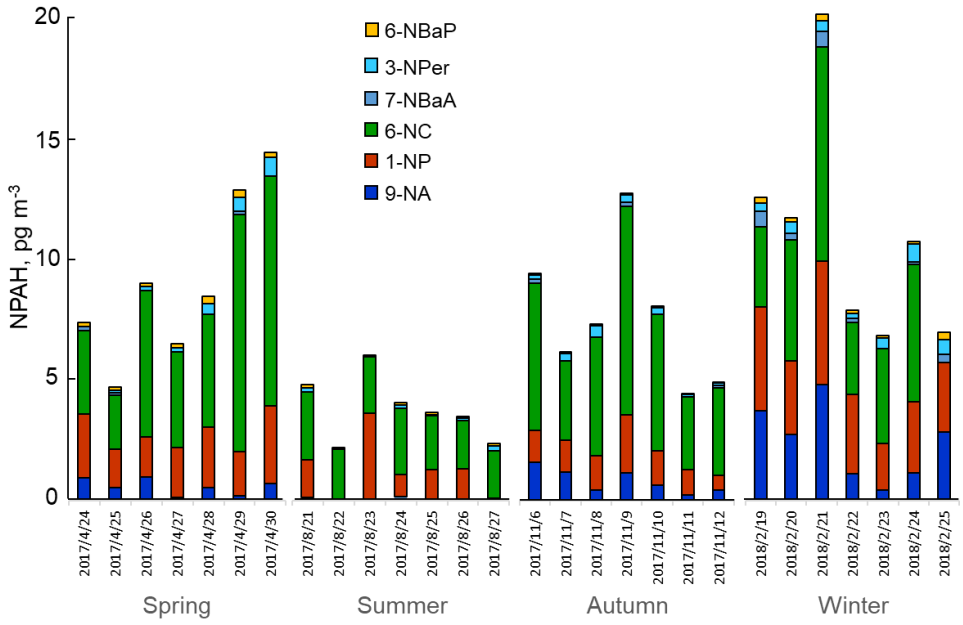


Fig. 3 Daily Atmospheric Concentrations of $PM_{2.5}$-bound NPAHs in The Four Seasons in Kanazawa

Daily TSP samples were collected for seven days in each season from the spring of 2017 to the spring of 2018 at the side of a major road in the suburbs of Kanazawa. Filters were changed daily.

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In the spring of 2017, the concentrations of ΣPAH and ΣNPAH were higher in the last three days (April 28-30) than in the first four days (April 24-27). The concentrations of $PM_{2.5}$, ΣPAH and ΣNPAH were significantly higher ($P < 0.0007$, $< 0.008$ and $< 0.04$, respectively, *t*-test) in the second period, suggesting that the Asian dust event had a strong effect. There were relationships between ΣPAH and ΣNPAH (correlation coefficient 0.7520) and between ΣPAH and $PM_{2.5}$ (correlation coefficient 0.6811), but not between ΣNPAH and $PM_{2.5}$ (Table S1).

### *3.2. Source analysis of $PM_{2.5}$, PAHs and NPAHs*

Both PAHs and NPAHs are formed through combustion of organic matters and are respectively one of the highest concentrated PAHs and NPAHs in $PM_{2.5}$. In addition, since the concentration ratio of NPAH to mother PAH depends greatly on the combustion temperature, the authors recently developed a method (the NP method) for calculating the contributions of automobiles and coal heating facilities/industries. The method uses Pyr and 1-NP as markers of high- and low-combustion temperatures, respectively (Hayakawa et al., 2020b). The strong relationship between Pyr and ΣPAH (correlation coefficient 0.9878) and the relationship between 1-NP and ΣNPAH (correlation coefficient 0.7318) suggest that Pyr and 1-NP are useful representatives of PAHs and NPAHs in this report.

Figure 4 shows the daily atmospheric concentrations of $PM_{2.5}$ in the four seasons. The fractions of $P_c$ and $P_o$ were calculated by the NP-method. The annual average fraction of $P_c$ in $PM_{2.5}$ was very small (2.1%), and the relationship between $P_c$ and $PM_{2.5}$ was not so strong (correlation coefficient 0.5585) (Table S1). But the average concentration of $P_c$ showed a clear seasonal change in the order winter > spring >

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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 (correlation coefficient 0.8661) and ΣNPAH (correlation coefficient 0.8211) (Table S1).

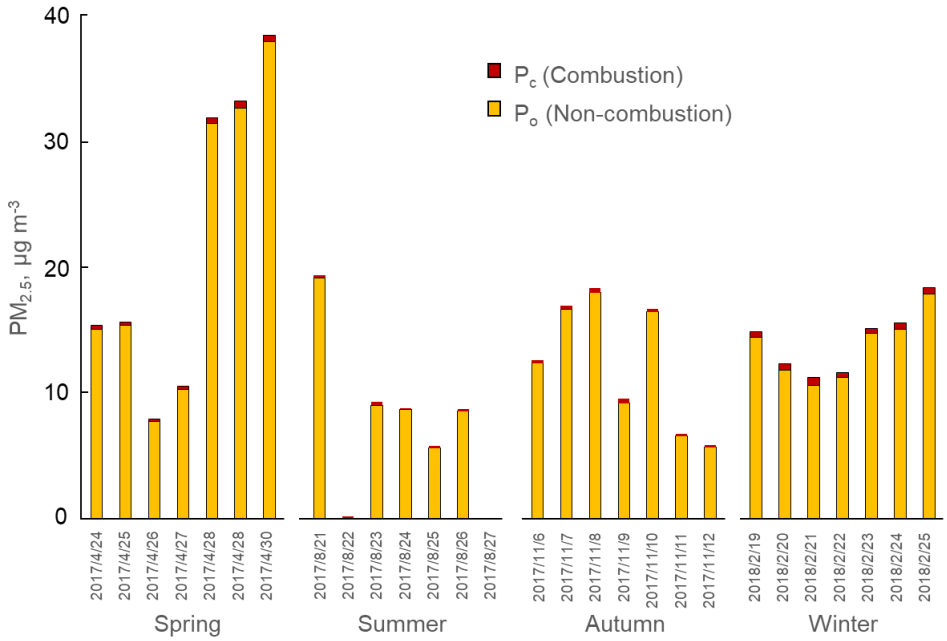


Fig. 4 Daily Atmospheric Concentrations and Compositions of $PM_{2.5}$ in Four Seasons in Kanazawa

Daily TSP samples were collected for seven days in each season from the spring of 2017 to the winter of 2018 at the side of a major road in the suburbs of Kanazawa. Filters were changed daily.

Figure 5 shows the daily atmospheric concentration of $P_c$, in the four seasons, in which the fractions of $P_h$ and $P_l$ were also calculated by the NP-method. The fraction of $P_h$ in $P_c$ was smaller than that of $P_l$ over the year except for August 23, 2017, in which it was 67%. The annual average fraction 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 automobiles (1/3). After the heating season in China, the $P_l$ concentration increased dramatically at the end of April (Fig. 5): it increased from 0.165 ± 0.022 μg $m^{-3}$ (April 24-27) to 0.393

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± 0.103 μg $m^{-3}$ (fApril 28-30), a 238% increase, while the $P_h$ concentration did not increase. Considering the backward trajectory of the air mass came over Chinese mega city areas in the latter period as described above, the increase in the $P_c$ concentration was attributed to the increase of the $P_l$ amount transported from China. The relationship was much strong between $PM_{2.5}$ and $P_o$ (correlation coefficient 0.9999), but not so strong between $PM_{2.5}$ and $P_c$ (correlation coefficient 0.5585) (Table S1). This difference might be caused by the very much small fraction of $P_c$ in $PM_{2.5}$.

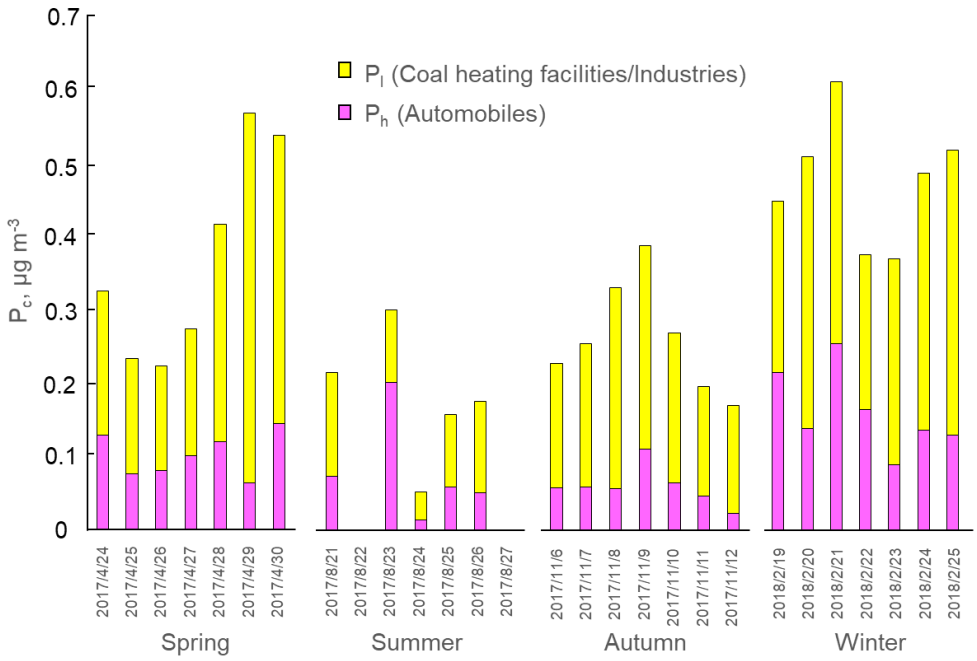


Fig. 5 Daily Atmospheric Concentrations and Sources of $P_C$ in Four Seasons in Kanazawa

Daily TSP samples were collected for seven days in each season from the spring of 2017 to the winter of 2018 at the side of a major road in the suburbs of Kanazawa. Filters were changed daily.

The relationship between ΣPAH and $P_c$ was strong (correlation coefficient 0.8661 in Table S1). This result suggested that the increase in the ΣPAH concentration in the

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winter (Fig. 2) was affected by the emission from coal heating facilities in China. The significant increase of the ΣPAH concentration was observed in the spring (April 28 to 30, 2017). This was also attributed to the long-range transported PAHs from combustion sources such as industries in China.

**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 sum of spring, summer and autumn of 2017 and the winter of 2018.

$P_c$, particulate from combustion source; $P_o$, particulate from non-combustion source; $P_l$, particulate from combustion source with lower temperature (heating

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facilities/industries); $P_h$, particulate from combustion source with higher temperature (automobiles). $PM_{2.5} = P_c + P_o$. $P_c = P_l + P_h$.

We reported that the $P_c$ concentration in the summer of 2017 (0.33 μg $m^{-3}$) was 1/13 of the concentration in the summer of 1999 (2.96 μg $m^{-3}$) (Hayakawa et al., 2020b). Moreover, the $P_c$ concentration in the winter of 2018 (0.71μg $m^{-3}$) was 1/16 of the concentration in the winter of 1999 (11.14 μg $m^{-3}$). The $P_h$ concentration in the summer of 2017 (0.16 μg $m^{-3}$) was 1/17 of the concentration in the summer of 1999 (2.75 μg $m^{-3}$), and the $P_h$ concentration in the winter of 2018 (0.24 μg $m^{-3}$) was 1/44 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 $P_c$ 1999, decreased dramatically in the following 18 years. The major source of PAHs and NPAHs was automobiles in Kanazawa and its surroundings in 1990s, but the atmospheric concentrations of NPAHs were significantly decreased to lesser than 1/40 in 2000s (Hayakawa et al., 2018b). Based on the change in the [1-NP]/[Pyr] ratio, as an automobile emission marker, the authors reported that the above change was attributed to the effect of PM/NOx emission regulations on automobiles (Hayakawa et al., 2018b). The decreases in the amounts of PAHs and NPAHs emitted from automobiles clearly explains why the changes of the $P_c$ concentration were mostly due to decreases of $P_h$ concentrations. Contrary to the significant change of $P_h$, the concentrations of $P_l$ (0.2 1μg $m^{-3}$ in summer and 0.51 μg $m^{-3}$ in the winter of 1999) decreased much more slowly in this period, by factors of 1/1.2 and 1/1.1, respectively. The decrease of atmospheric concentrations of PAHs at the WAMS was also much slower than those in Kanazawa (Tang et al., 2015). This result suggested that there was a slow decrease of the $P_l$ amount transported from China.

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## 4. Conclusions

Atmospheric $PM_{2.5}$ and $PM_{>2.5}$ were separately collected in Kanazawa from the spring (April) of 2017 to the winter (February) of 2018, and nine PAHs and six NPAHs were determined using HPLC with fluorescence and chemiluminescence detections, respectively. The contributions of automobiles and coal combustion to concentrations of $PM_{2.5}$, PAHs and NPAHs in these samples were calculated by the NP-method.

4.1. Atmospheric concentrations of PAHs and NPAHs showed similar seasonal variations: highest in the winter and lowest in the summer.

4.2. The fraction of $P_c$ in $PM_{2.5}$ was much small (2.1%). But the atmospheric concentration of $P_c$ still showed a seasonal variation, which was similar to the variations of PAHs and NPAHs. The annual average contributions of coal heating facilities/industries and automobiles to $P_c$ were 69% and 31%, respectively.

4.3. 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. NPAHs were mainly emitted from automobiles in Kanazawa and its surroundings.

4.4. $P_c$ concentrations in the summer of 2017 and winter of 2018 were respectively 1/13 and 1/16 of the concentrations in 1999. This significant improvement was mostly attributed to the decrease in the $P_c$ amount emitted from automobiles in Kanazawa and its surroundings. But the decrease in the $P_c$ amount transported from China was much less.

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

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**Figure Captions**

**Fig. 1. Daily Atmospheric Concentrations of TSP with Fractions of $PM_{2.5}$ and $PM_{>2.5}$ in Four Seasons in Kanazawa**

Daily TSP (total suspended particulate matter) samples were collected for seven days in each season from the spring of 2017 to the winter of 2018 at the side of a major road in the suburbs of Kanazawa. Filters were changed daily.

**Fig. 2. Daily Atmospheric Concentrations of $PM_{2.5}$-bound PAHs in Four Seasons in Kanazawa**

Daily TSP samples were collected for seven days in each season from the spring of 2017 to the winter of 2018 at the side of a major road in the suburbs of Kanazawa. Filters were changed daily.

**Fig. 3. Daily Atmospheric Concentrations of $PM_{2.5}$-bound NPAHs in Four Seasons in Kanazawa**

Daily TSP samples were collected for seven days in each season from the spring of 2017 to the winter of 2018 at the side of a major road in the suburbs of Kanazawa. Filters were changed daily.

**Fig. 4. Daily Atmospheric Concentrations and Compositions of $PM_{2.5}$ in Four Seasons in Kanazawa**

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Daily TSP samples were collected for seven days in every season from the spring of 2017 to the winter of 2018 at the side of a major road in the suburban Kanazawa. Filters were changed daily.

**Fig. 5. Daily Atmospheric Concentrations and Sources of $P_C$ in Four Seasons in Kanazawa**

Daily TSP samples were collected for seven days in each season from the spring of 2017 to the winter of 2018 at the side of a major road in the suburbs of Kanazawa. Filters were changed daily.

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