



## Research article

# Contributions of long-range transport from the Asian continent and local emissions on atmospheric PM<sub>2.5</sub>, polycyclic aromatic hydrocarbons, and their nitro-derivatives in Kanazawa and Noto Peninsula, Japan

Kazuichi Hayakawa<sup>a,\*</sup>, Pham Kim-Oanh<sup>b</sup>, Akinori Takami<sup>c</sup>, Hiroshi Odajima<sup>d</sup>, Edward G. Nagato<sup>e</sup>, Akinori Hara<sup>f</sup>, Hiroyuki Nakamura<sup>f</sup>

<sup>a</sup> Institute of Nature and Environmental Technology, Kanazawa University, Kanazawa City, 923-1224, Japan

<sup>b</sup> Asia Center for Air Pollution Research, Niigata City, 950-2144, Japan

<sup>c</sup> Regional Environment Conservation Division, National Institute for Environmental Studies, Tsukuba City, 305-8506, Japan

<sup>d</sup> Department of Pediatrics, National Hospital Organization Fukuoka National Hospital, Fukuoka City, 811-1394, Japan

<sup>e</sup> Faculty of Life and Environmental Sciences, Shimane University, 1060, Nishikawatsu-machi, Matsue, 690-8504, Japan

<sup>f</sup> Department of Hygiene and Public Health, Faculty of Medicine, Institute of Medical, Pharmaceutical and Health Sciences, Kanazawa University, Kanazawa City, 920-8640, Japan

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## ABSTRACT

This study collected samples of particulate matter that are 2.5  $\mu\text{m}$  or less in diameter (PM<sub>2.5</sub>) in Kanazawa, Japan, and Noto Peninsula located 100 km north on the windward side of the westerlies from the Asian continent and characterized the extent of polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs (NPAHs) pollution in Kanazawa. Emission areas and specific sources of PM<sub>2.5</sub> and of PAHs and NPAHs were clarified via back-trajectory analysis and the NP-method, respectively. The results indicate that during 2020 and 2021, most PAHs (93%) in Kanazawa were transported from the Asian continent by westerlies and that the main source was coal and biomass combustion. The presence of NPAHs in Kanazawa was caused by a mixture of transport from the Asian continent (53%) and local emissions (47%), with the main source of the latter being from vehicles. Although the content of combustion-derived particulates (P<sub>c</sub>) was <2.4% of PM<sub>2.5</sub> in Kanazawa, this showed a similar seasonal variation (winter > summer) to that of PAHs. The contribution of P<sub>c</sub> transported from the Asian continent exceeded that of locally emitted P<sub>c</sub>. The current situation of Kanazawa is considerably different from that of 1997, when local vehicles were the main source of pollution.

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their nitro-derivatives (NPAHs) are generated from the incomplete combustion of organic matter and are ubiquitous air contaminants. Several of these are carcinogenic and/or mutagenic. The International Agency for Research on Cancer (IARC) has classified over 60 PAHs and related compounds into four groups based on carcinogenicity. Benzo[a]

\* Corresponding author.

E-mail address: [hayakawa@p.kanazawa-u.ac.jp](mailto:hayakawa@p.kanazawa-u.ac.jp) (K. Hayakawa).

pyrene (BaP), a well-known representative PAH, is classified into Group 1 (carcinogenic to humans) and several other PAHs and NPAHs are classified into Group 2A (probably carcinogenic to humans) or Group 2B (possibly carcinogenic to humans) [1]. The United States Environmental Protection Agency has prioritized up to 16 PAHs with two to six rings because of health concerns [2]. Recently, an association between elevated PAH concentrations in the air and asthma progression has been reported [3,4]. Consequently, concern has been growing about the relationship between respiratory exposure to airborne PAHs and NPAHs and potential human disease risk.

World coal and oil consumption has steadily increased since the industrial revolution. The World Health Organization has reported that ambient air pollution was very serious in the Western Pacific [5]. Oil and coal account for >60% of the world's primary energy production, with approximately 30% of which is consumed in this region. The primary energy types differ greatly among countries: coal in China, Mongolia, and Far-Eastern Russia, but oil in Korea and Japan [6]. The combustion of coal, oil and biomass produces many types of pollutants, including carbon dioxide, sulfur oxides, nitrogen oxides, PAHs, NPAHs and PM<sub>2.5</sub>. A large amount of coal consumption used for heating, in the winter in particular increases the atmospheric concentrations of particulate matter of 2.5 μm or less in diameter (PM<sub>2.5</sub>) and this contains large amounts of PAHs. Furthermore, the amount of coal consumed has been gradually increasing in China. In the 1990s, the East Asia international monitoring network that include Japan, China, Russia, and Korea began studying air pollution in this region. Atmospheric concentrations of PAHs and PM<sub>2.5</sub> were significantly higher than those in China and Far-Eastern Russia in the initial years and have remained high thereafter [7–9]. By contrast, in Japan the urban concentrations of PM bound PAHs and NPAHs underwent a large increase with the rapid development of automobile transportation during the 1970s–1990s. Since then, technological innovations such as engine innovations, emission treatments, and fuel reform have progressed to reduce the emissions of PM and nitrogen oxides from vehicles. Consequently, urban atmospheric concentrations of both PAHs and NPAHs dramatically decreased to less than one tenth of the concentrations in the 2000s [10,11].

The Kanazawa University Wajima Atmospheric Monitoring Station (WAMS) at the tip of Noto Peninsula started the continuous monitoring of atmospheric PM, PAHs, NPAHs, metals, and inorganic ions in 2004 [12,13]. WAMS, which is 100 km north of Kanazawa, is located on the windward side of an area that received predominantly westerly winds from the Asian continent. Furthermore, this site, locating in a sparsely populated, lacks PAH sources, such as factories. At this site, the transboundary transport of PAHs from the Asian continent has been observed to change seasonally (high in winter and low in summer) [12]. The decline in the PAH concentrations was much slower than that in Kanazawa, the capital city of Ishikawa Prefecture and a typical local city close to the Japan Sea. In Kanazawa, concentrations of PAHs often increase during Asian dust (yellow sand) events, with an increase in the concentration of PM<sub>2.5</sub>, although the concentration of NPAHs do not increase [14]. Clarifying the differences in generation, transport, and effect of these air pollutants on Kanazawa and the Noto Peninsula and identifying the contrasts between Japan and China may not only help address environmental problems in the Western Pacific but also globally. However, the simultaneous collection of domestic and transboundary emissions of airborne particulates has not yet been done in Kanazawa.

The purpose of this study was to clarify the contributions of air pollutants transported from the Asian continent and from domestic emissions in Kanazawa, with comparison to WAMS as a background site. Atmospheric PM<sub>2.5</sub> was collected simultaneously in Kanazawa and the Noto Peninsula and both PAHs and NPAHs were analyzed. The concentration ratio of NPAH to the parent PAH varies dramatically between biomass combustion, coal combustion, and vehicle emissions because the nitration of PAHs to NPAH is dictated by temperature [15]. Therefore, a source description method for atmospheric PAHs, NPAHs, and PM, using 1-nitropyrene (1-NP) and pyrene (Pyr) as monitoring markers was previously developed (NP-method) [16]. Although several source analysis methods have been reported including the PAH diagnostic ratios method [17], this method has the advantage of not requiring any other source information, analyzing each contribution ratio of the mixed sources, and being applicable to not only PM and PAHs but also for NPAHs [14]. Therefore, the NP-method was used to calculate contributions of mixed sources in this study. This is the first research paper to clarify source contributions and emission areas for PAHs, NPAHs, and PM<sub>2.5</sub> in the Western Pacific region.

## 2. Experimental

### 2.1. Sampling

Kanazawa, the capital of Ishikawa prefecture, is a commercial city with a population of 461,000. It is located on the Japan Sea coast, on the central Honshu Japanese Island. PM<sub>2.5</sub> samples were collected at Site K (36.5° N, 136.7° E): beside a main road in the residential area 4 km south of the downtown area of the city. PM<sub>2.5</sub> samples were also collected at Site N (WAMS, 37.4° N, 136.9° E), which locate at the tip of Noto Peninsula. Both sites are located at 50 m above sea level (Fig. S1). WAMS is the only background site in Japan that continues long-term monitoring of PAHs and NPAHs facing the Japan Sea. Daily PM<sub>2.5</sub> samples were collected simultaneously at both sites using high-volume air samplers equipped with glass fiber filters at a flow rate of 750–1000 L min<sup>-1</sup> for two successive weeks in February, April, August, and November 2021 and in February, March, April, and August 2022. PM<sub>2.5</sub> samples collected at Site N using the same method in every February since 2006 were used in this study. Atmospheric concentrations of PM<sub>2.5</sub> were calculated from filter weights before and after sampling, and filter samples were kept at -20 °C until analysis.

### 2.2. Determination of 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), BaP, benzo[*ghi*]perylene (BghiP), 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 EPA methods [18]. Six NPAHs,

9-nitroanthracene, 1-NP, 6-nitrocrysene, 7-nitrobenz[a]anthracene, 3-nitroperylene, and 6-nitrobenzo[a]pyrene, 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 are described in previous reports along with the limits of quantification [19–22].

### 2.3. Calculation of source contributions

Molecular concentrations of Pyr and 1-NP were used for the NP-method to calculate source contributions [16,23]. Briefly, atmospheric particulates ( $P = PM_{2.5}$ ) are divided into combustion-derived particulates ( $P_c$ ) and non-combustion-derived particulates ( $P_h$ ).  $P_c$  is further divided into particulates emitted from combustion with high-temperature ( $P_h$ ) and particulates from combustion with low-combustion temperature ( $P_l$ ). 1-NP and Pyr are also divided into 1-NP<sub>h</sub> and Pyr<sub>h</sub> (emitted from combustion with high-temperature), respectively, and 1-NP<sub>l</sub> and Pyr<sub>l</sub> (emitted from combustion with low-temperature), respectively. When the proportion of  $P_h$  in  $P_c$  is  $x$  ( $= [P_h]/[P_c]$ ,  $0 < x < 1$ ) and the proportion of  $P_c$  in  $P$  is  $y$  ( $= [P_c]/[P]$ ,  $0 < y < 1$ ), the proportion of 1-NP<sub>h</sub> in 1-NP ( $= 1-NP_h + 1-NP_l$ ) in the air is  $a$  ( $0 < a < 1$ ), and the proportion of Pyr<sub>h</sub> in Pyr ( $= Pyr_h + Pyr_l$ ) in the air is  $b$  ( $0 < b < 1$ ), the following equations are obtained.

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

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

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

$$[1-NP_h]/[Pyr_h] = [1-NP]a/[Pyr]b \quad (iv)$$

$$[1-NP_l]/[Pyr_l] = [1-NP](1 - a)/[Pyr](1 - b) \quad (v)$$

Values for  $[1-NP_h]$  ( $65.5 \text{ pmol mg}^{-3}$ ) and  $[Pyr_h]$  ( $180 \text{ pmol mg}^{-3}$ ) for vehicles, and  $[1-NP_l]$  ( $4.6 \text{ pmol mg}^{-3}$ ) and  $[Pyr_l]$  ( $3400 \text{ pmol mg}^{-3}$ ) for coal/biomass combustion were all cited from our previous study [16]. Introducing  $[Pyr]$  and  $[1-NP]$  at the monitoring site into the above equations enables  $x$ ,  $y$ ,  $a$  and  $b$  to be obtained. Then, the concentrations of  $P_c$ ,  $P_o$ ,  $P_h$ , and  $P_l$  are calculated.

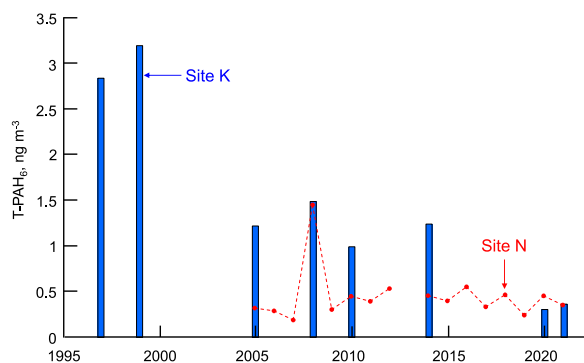
### 2.4. Backward trajectories and weather maps

Three-day backward trajectories, every 6 h, were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory model developed by the National Oceanic and Atmospheric Administration, Washington DC, USA (NOAA, HYSPLIT tutorial May 2022, Version 5.2.1) [24], with initial conditions: Starting locations (Latitude (°), Longitude (°), Hight (m above sea level); 36.55, 136.67, 1000 (for Site K), and 37.23, 136.54, 1000 (for Site N); Initial height; 1000 m; Total run time; 72 h. The daily weather maps of Northeast Asia were provided by the Japan Meteorological Agency [25].

## 3. Results and discussion

### 3.1. Long-term changes in concentrations and sources of atmospheric PAHs and NPAHs

Asian dust can be transported over long distances from the Asian continent to Japan across the Japan Sea by westerlies, typically in the spring. In Kanazawa, during this season, atmospheric PAH and  $PM_{2.5}$  concentrations often increase, whereas the NPAH levels do not [14]. This suggests differences in emission sources between PAHs and NPAHs. However, it is not possible to know how much of this pollution originates from the Asian continent and transported to Kanazawa without stringent atmospheric monitoring at the



**Fig. 1.** Long-term changes in T-PAH<sub>6</sub> concentrations in February at sites K and N  
T-PAH<sub>6</sub> = Pyr + BaA + Chr + BbF + BkF + BaP.

background site.

According to monitoring records of total suspended particulate matter (TSP)-bound PAHs and NPAHs at Sites K (Kanazawa) and N (WAMS N), both sites showed seasonal variations with PAH concentrations being the highest in January or February [7]. The annual mean concentration of six PAHs ( $T\text{-PAH}_6 = \text{Pyr} + \text{BaA} + \text{Chr} + \text{BbF} + \text{BkF} + \text{BaP}$ ) at Site K was  $>3.3 \text{ pg/m}^{-3}$  in February 1997 and 1999 but began to decline rapidly in the 2000s. The recent  $T\text{-PAH}_6$  concentration was  $<1/10$  of the concentrations in the 1990s. On the other hand, the  $T\text{-PAH}_6$  level at Site N peaked in February 2008 when the Beijing Olympic Games were held [12,13] and remained almost constant thereafter, at approximately  $0.4 \text{ pg m}^{-3}$ . As a result, the difference between the two sites has disappeared in 2020 and 2021 (Fig. 1).

The molecular concentration ratio of NPAH to PAH in the PM from vehicle emissions is much larger than those from coal and biomass combustion [7]. Fig. 2 shows comparisons of molecular concentration ratios of TSP-bound 1-NP and Pyr and fractions of nine TSP-bound PAHs in the atmosphere between 1997 and 2021. The atmospheric  $[1\text{-NP}]/[\text{Pyr}]$  ratio in the winter of 1997 was 0.166 in Kanazawa, which was not very different from that in vehicle emissions (0.425) but much larger than that from coal combustion (0.001). This suggests that the main contributor to atmospheric PAHs and NPAHs in the urban area of Kanazawa in the 1990s was vehicles. However, the atmospheric  $[1\text{-NP}]/[\text{Pyr}]$  ratio dropped considerably with the decrease in the concentrations of these pollutants in Kanazawa after the 2000s (Fig. 1) and was as low as 0.0123 in 2021. This change was due to rapid progress in vehicle engine technology development and fuel reform in response to vehicle PM/NOx regulations, which have been repeatedly tightened since the 1990s [7].

It has been reported that the composition of PAHs varies by source. It has been reported that the proportion of high molecular weight PAHs, such as six-ring PAHs, becomes greater than that of low molecular weight PAHs as combustion temperatures increase [26]. Fig. 2 shows that the proportion of six-ring PAHs (BghiP and IDP) in the total PAHs decreased from 25% in 1997 to 21% in 2021, whereas the proportion of four-ring PAHs (Flt, Pyr, BaA, and Chr) increased from 51% to 54%. This result might also suggest that PAH emissions from vehicles considerably decreased between 1997 and 2021.

### 3.2. Recent concentrations and emission sources of atmospheric PAHs and NPHs

Fig. 3 shows seasonal variations in  $\text{PM}_{2.5}$ ,  $T\text{-PAH}_9$  ( $\text{FR} + \text{Pyr} + \text{BaA} + \text{Chr} + \text{BbF} + \text{BkF} + \text{BaP} + \text{BghiP} + \text{IDP}$ ) and 1-NP concentrations at the two sites in the period from November 2020 to August 2021. The  $\text{PM}_{2.5}$  concentration peaked in March at Site N and April at Site K, whereas  $T\text{-PAH}_9$  and 1-NP concentrations peaked in February at both sites. These differences at Site K were the same as those previously reported at Site N [12].

Table 1 shows the maximum and minimum monthly mean concentrations of  $\text{PM}_{2.5}$ ,  $T\text{-PAH}_9$ , and 1-NP at Sites N and K in the monitoring period. The highest concentrations of  $\text{PM}_{2.5}$  ( $16.5 \pm 7.6 \text{ } \mu\text{g m}^{-3}$ ) and  $T\text{-PAH}_9$  ( $0.64 \pm 0.40 \text{ ng m}^{-3}$ ) at Site K were observed respectively in March and February. They were very close to the levels of  $\text{PM}_{2.5}$  ( $15.7 \pm 14.0 \text{ } \mu\text{g m}^{-3}$ ) and  $T\text{-PAH}_9$  ( $0.66 \pm 0.39 \text{ ng m}^{-3}$ ) at Site N for the same months. The lowest concentrations of both pollutants almost occurred in August. From these, the seasonal concentration ratios (highest month's concentration/lowest month's concentration) of  $T\text{-PAH}_9$  were 19.7 and 4.6 at Sites K and N, respectively. There was a tendency that the seasonal ratio of  $T\text{-PAH}_9$  concentration was larger than that of  $\text{PM}_{2.5}$  at both sites, particularly at Site N, although they were in SD values. By contrast, 1-NP showed a seasonal change at Site K, although the seasonal ratio (1.86) was smaller than that of  $T\text{-PAH}_9$  (4.62).

Table 2 shows annual mean concentrations of  $\text{PM}_{2.5}$ ,  $T\text{-PAH}_9$ , and 1-NP at Sites N and K with their site ratios (N/K ratio) and correlation coefficients ( $R$ ) between the sites. There are no major emission sources (e.g., factories) around Site N as well as between Sites N and K. Assuming that there is no loss during transportation between the two sites, the site ratio (N/K) of the pollutant concentration indicates the fraction of long-range transport from the Asian continent at Site K. The site ratios of  $T\text{-PAH}_9$  (0.93) and  $\text{PM}_{2.5}$  (0.89) were close to 1. However, the site ratio of 1-NP (0.57) was much smaller.  $T\text{-PAH}_9$  showed the largest correlation coefficient ( $R = 0.934$ ) between the two sites over the 6 months, followed by that of 1-NP (0.851);  $\text{PM}_{2.5}$  had the lowest  $R$ -value (0.420). These results suggest that PAHs at Site K were almost the same as those at Site N. However, at Site K, 1-NP had additional selective loading.

Both PAHs and NPAHs are contained in  $P_c$ . To obtain monthly atmospheric concentrations of  $P_c$  at both sites, the value of  $y$  ( $= [P_c]/[\text{PM}_{2.5}]$ ) was calculated by the NP method using monthly mean concentrations of Pyr and 1-NP. Values of Site K and N were in the

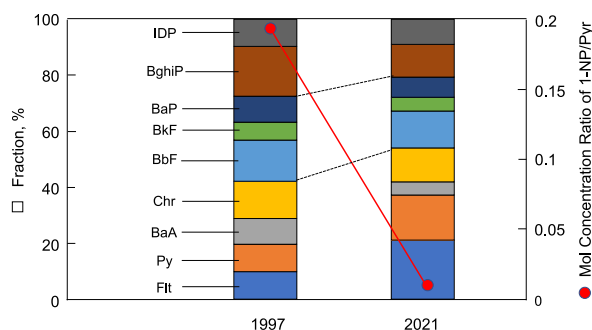
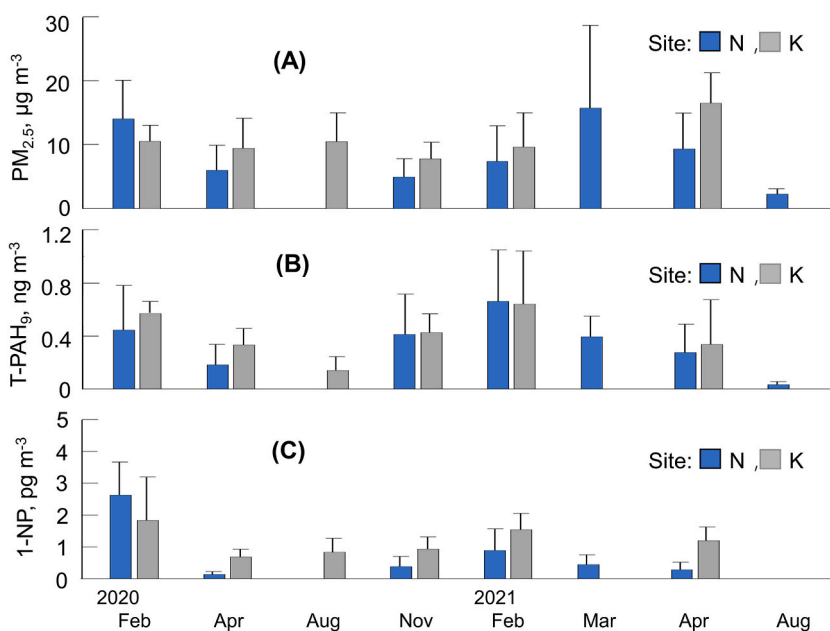


Fig. 2. Change in winter atmospheric PAH composition and Concentration ratio of 1-NP to Pyr in Kanazawa between 1999 and 2021.



**Fig. 3.** Seasonal Changes in (A)  $PM_{2.5}$ , (B) T-PAH<sub>9</sub> and (C) 1-NP Concentrations at Sites N and K Box and bar mean concentration and standard deviation, respectively. T-PAH<sub>9</sub> = FR + Pyr + BaA + Chr + BbF + BkF + BaP + BghiP + IDP.

**Table 1**

Monthly mean concentrations of  $PM_{2.5}$ , T-PAH<sub>9</sub> and 1-NP at sites N and K.

Site	Pollutant, Unit	Max. Conc		Min. Conc. August	Seasonal Ratio High/Low
		Feb.	March or Apr.		
N	$PM_{2.5}$ , $\mu\text{g m}^{-3}$		$15.7 \pm 14.0^*$	$2.3 \pm 1.1^*$	6.83
	T-PAH <sub>9</sub> , $\text{ng m}^{-3}$	$0.66 \pm 0.39^*$		$0.034 \pm 0.031^*$	19.7
	1-NP, $\text{pg m}^{-3}$	$2.64 \pm 1.04^{**}$			
K	$PM_{2.5}$ , $\mu\text{g m}^{-3}$		$16.5 \pm 7.6^*$	$10.5 \pm 5.5^{**}$	1.57
	T-PAH <sub>9</sub> , $\text{ng m}^{-3}$	$0.64 \pm 0.40^*$		$0.14 \pm 0.09^{**}$	4.62
	1-NP, $\text{pg m}^{-3}$	$1.56 \pm 0.51^*$		$0.84 \pm 0.48^{**}$	1.86

Year: \*2021 and \*\*2020. T-PAH<sub>9</sub> = FR + Pyr + BaA + Chr + BbF + BkF + BaP + BghiP + IDP.

**Table 2**

Annual mean concentrations<sup>a</sup> of  $PM_{2.5}$ , T-PAH<sub>9</sub> and 1-NP at sites N and K with Site ratios (N/K) and correlation coefficients (R).

Pollutant, unit	Site N	Site K	N/K	R
$PM_{2.5}$ , $\mu\text{g m}^{-3}$	$9.4 \pm 8.2^a$	$10.6 \pm 6.6^a$	0.89	0.420
T-PAH <sub>9</sub> , $\text{ng m}^{-3}$	$0.39 \pm 0.31^a$	$0.42 \pm 0.30^a$	0.93	0.934
1-NP, $\text{pg m}^{-3}$	$0.63 \pm 0.84^a$	$1.19 \pm 0.77^a$	0.57	0.851

<sup>a</sup> Concentrations are mean  $\pm$  SD of six months (February, April and November 2021 and February, March and April 2022). T-PAH<sub>9</sub> = FR + Pyr + BaA + Chr + BbF + BkF + BaP + BghiP + IDP.

ranges from 0.70% (April 2021) to 2.40% (November 2020) and from 0.63% (April 2021) to 1.85% (November 2020), respectively (Table S1). Although the mass of  $P_c$  was extremely small, its atmospheric concentration showed seasonal variations (highest in February) with a correlation coefficient of  $R = 0.5873$  (Fig. 4). Changes in  $P_c$  concentrations whose peaks were in February correlated with changes of T-PAH<sub>9</sub> ( $R = 0.937$  at Site K and 0.528 at Site N), but different from  $PM_{2.5}$  whose peaks were in March.

### 3.3. Emission regions

The westerly wind plays an important role in long-range transport of pollutants from the Asian continent to the Japanese islands [25]. Fig. 5 shows major clusters of air masses from Sites N and K for four months in 2021. In March and April, the fraction of trajectory clusters passed through northeast China or Mongolia to the east side of the Korean Peninsula (the sum of the proportions of the blue and red lines in Fig. 5) were over 80% at Site N and 100% at Site K. This similarity indicates that pollutants transported by the

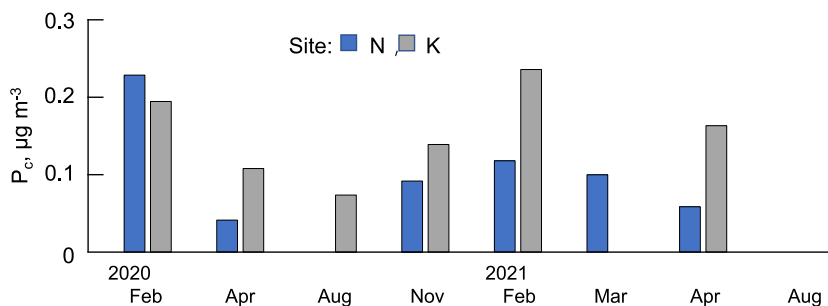
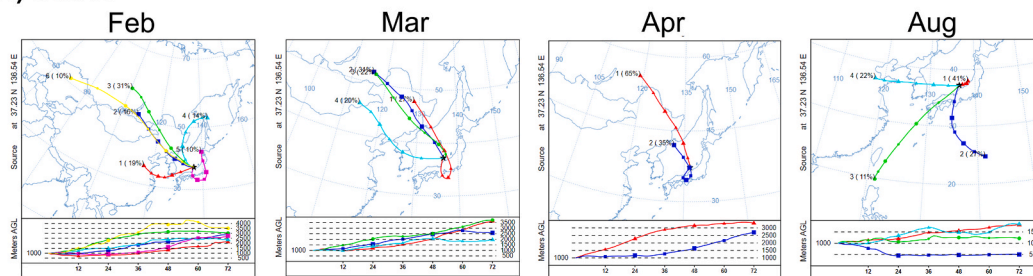


Fig. 4. Seasonal changes in  $P_c$  concentrations at sites N and K.

### (A) Site N



### (B) Site K

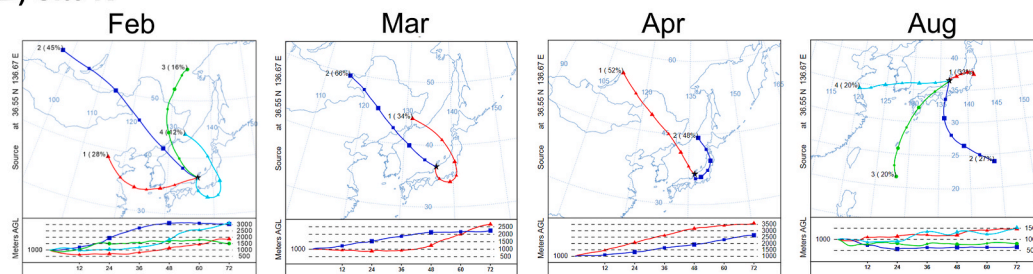


Fig. 5. Back trajectories of air mass at (A) Site N and (B) Site K in February, March, April, and August 2021.

north-easterly winds from the above areas to Site N might have easily reached Site K. In February, in addition to the above-mentioned trajectories, 19% of the total clusters at Site N and 28% at Site K came from central China and passed through the west side of the Korean Peninsula. This wind also brings pollutants emitted from urban areas on the east coast of China to Sites N and K. However, completely different trajectory clusters from the above seasons were present during August. Clusters from the Asian continent were much weaker, and others were from areas within the Japanese islands or from the Pacific Ocean and the South/East China Sea.

The trajectories color-coded into groups were shown on the map for each month along with their fraction %.

The above results indicate that the content of the PAHs transported from the Asian continent to Site N was almost equal to those at Site K. The reasons for these similar PAH concentrations were that two sites were only 100 km apart on the same westerly wind routes and that emission of PAHs was very small in Kanazawa relative to that from the Asian continent. Possible major PAH generation areas were the highly populated cities in China near the Japan Sea and surrounding Bohai Sea and Yellow Sea.

$PM_{2.5}$  showed the second largest site ratio ( $N/K = 0.89$ ; Table 2) but the smallest correlation coefficient ( $R = 0.420$ ), and this may be because  $PM_{2.5}$  had a much longer transport distance than that of PAHs. The westerly wind route can pass over multiple and complex generation areas that are not limited to producing Asian dust. In contrast, 1-NP had a site ratio ( $N/K = 0.57$ ) much smaller than 1, despite a relatively high correlation coefficient ( $R = 0.851$ ). This suggests the addition of NPAHs locally emitted at Site K.

### 3.4. Emission sources

During the combustion process of organic matters, the formation of nitrogen oxides in the flame gas and the subsequent formation of NPAHs from parent PAHs are temperature dependent. Therefore, the concentration ratios of NPAHs to their parent PAHs in PM increase with combustion temperature [7]. Sources of  $PM_{2.5}$ , PAHs, and NPAHs at both sites were identified via the NP-method. First,

the contributions from high- and low-temperatures combustion sources to PAHs were calculated. As mentioned above, coal (combustion temperature 1100–1200 °C) is the largest energy source in China and Mongolia, and is a major source of PAHs and NPAHs in urban areas during the winter heating season. Vegetation fires such as rice straw burning (combustion temperature 400–600 °C) are still common in agricultural fields in the autumn (e.g., after the rice harvest). These sources are low-temperature combustion sources in the NP-method. However, vehicles (combustion temperature 2700°C-3000 °C) are a major source of PAHs and NPAHs in urban areas. Concentrations of PAHs were much higher in PM emitted from coal and biomass combustion than those in PM from vehicles and the concentration ratios of NPAHs to the corresponding PAHs ([NPAH]/[PAH]) were much larger in PM from vehicles. The NP-method depends on this difference to identify the two major sources [7].

Fig. 6A showed a big change in sources of PAHs in Kanazawa. The contribution of high combustion temperature, i.e. vehicles to Pyr accounted for 38.8% in 1997, but decreased significantly to 3.0% in 2021. As mentioned in Fig. 1, the concentration of T-PAH<sub>9</sub> at Site K decreased to less than 1/10 during the same period. This significant decrease in the PAH concentration mainly ascribed to the successive emission controls against vehicles in Japan [7]. Putting the fact that the site ratio (N/K) of T-PAH<sub>9</sub> was almost 1 (Table 2) into consideration, Fig. 6A suggested that the current atmospheric PAHs in Kanazawa were mainly long-range transported from the Asian continent.

Next, the contributions of combustion sources to 1-NP were examined. The contribution of sources with high combustion temperatures, such as vehicle engines, to 1-NP at Site K was 97.0% in 1997 and 89.0% in 2021, which were much larger than that of vehicles (Fig. 6B). Moreover, the seasonal ratio (High/Low) of 1-NP (=1.86) was much smaller than that of T-PAH<sub>9</sub> (4.62), and the N/K ratio of 1-NP was 0.57 (Table 2). These results suggest that, although the emissions of primary NPAHs from vehicles significantly decreased in the 2000s [23], vehicles remained as the main contributor for primary NPAHs in Kanazawa. The 1-NP detected in Kanazawa was the sum of long-range transport and local emissions.

Finally, the  $P_c$  and  $P_n$  fractions of PM<sub>2.5</sub> ( $= P_c + P_n$ ) were calculated by the NP-method. The proportion (%) of  $P_c$  in PM<sub>2.5</sub> was not more than 2.4% over the period and was slightly higher at Site K than at Site N (Table S1). This value is considerably smaller than the 42% in TSP in Beijing city in winter 2010 but close to the 1.4% in Beijing in summer 2010 and 1.0% in Kanazawa in summer 2013 [14]. This is because winter PM<sub>2.5</sub> consists of a much larger fraction of  $P_c$  in the urban atmosphere in central and northern China than in Japan. Fig. 6C shows the contribution of combustion sources to  $P_c$  during the same period. The fraction of  $P_c$  emitted from vehicles at Site K was 94% in February 2021 (Table S1), suggesting that current amount of  $P_c$  was very small in Kanazawa.

The contribution of vehicles accounted for >95% of 1-NP and  $P_c$  and 40% of Pyr in Kanazawa in 1997, when vehicles were the major contributor to urban atmospheric PAHs and NPAHs. However, contributions from vehicles decreased significantly for Pyr and  $P_c$  to 3% and 37%, respectively in Kanazawa in 2021 (Fig. S2). This was ascribed to effective countermeasures against PM/NO<sub>x</sub> emissions from vehicles [27]. Several Clean Air Policies have worked in China to reduce recent urban air pollution. Furthermore, in China, due to city closures due to COVID19, PM<sub>2.5</sub> concentrations in urban air have decreased [28,29]. These facts suggest that amounts of PAHs emitted from fossil fuel combustion in the Asian continent will further decrease, and as a result, it is estimated that the concentration of PAHs and  $P_c$  in Japan's atmosphere will further decrease in the future [19]. This is the first report which determined contributions of vehicles and coal combustion on PAHs, NPAHs and PM<sub>2.5</sub> in urban air in East Asia separately for long-range transport and local emission.

#### 4. Conclusion

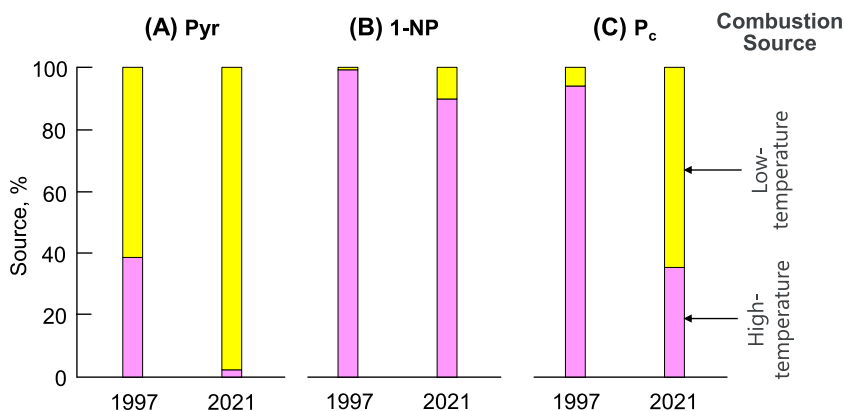
PM<sub>2.5</sub> samples were collected simultaneously at Site K in Kanazawa and Site N in the Noto Peninsula, where Site N was 100 km north of Site K on the windward side of the westerlies from the Asian continent. Atmospheric concentrations of PAHs have decreased at Site K over the last two decades, although PAHs concentrations have not decreased at Site N. The difference between the atmospheric PAHs at these two sites disappeared in 2020 and 2021. Recent contributions of long-range transport and local emissions on atmospheric PAHs, NPAHs and of  $P_c$  in Kanazawa were estimated using the NP-method by comparing both sites in 2020 and 2021. 1) Most PAHs (93%) in Kanazawa were transported from the Asian continent, where the main source was coal and biomass combustion. 2) NPAHs were derived from a mixture of transport from the Asian continent (53%) and local emission (47%), where the main source was vehicles. 3) The  $P_c$  accounted for <2.4% of PM<sub>2.5</sub> and showed a similar seasonal variation to that of PAHs (high in winter and low in summer). The contribution of coal and biomass combustion in  $P_c$  formation was 48%–63%, and most of this was transported from the Asian continent.

#### Data availability statement

All the data associated with this study are available without any restriction.

#### CRediT authorship contribution statement

**Kazuichi Hayakawa:** Supervision, Project administration, Investigation, Formal analysis. **Pham Kim-Oanh:** Investigation. **Akinori Takami:** Investigation. **Hiroshi Odajima:** Investigation. **Edward G. Nagato:** Writing – review & editing. **Akinori Hara:** Investigation. **Hiroyuki Nakamura:** Project administration, Methodology.



**Fig. 6.** Contributions of High- and Low-Temperature Combustion Sources to (A) Pyr, (B) 1-NP and (C) P<sub>c</sub> in Kanazawa in Winters of 1997 and 2021. High-temperature source = vehicles, Low-temperature source = mainly coal/biomass combustions. Source contributions (%) to each compound were calculated by the NP method in section 2.3.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e27320>.

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