

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

Kazuichi Hayakawa <sup>1,\*</sup>, Ning Tang <sup>2,3</sup>, Wanli Xing <sup>3</sup>, Pham Kim Oanh <sup>4</sup>, Akinori Hara <sup>4</sup> and Hiroyuki Nakamura <sup>4</sup>

<sup>1</sup> Low Level Radioactivity Laboratory, Institute of Nature and Environmental Technology, Kanazawa University, O-24 Wake-machi, Nomi, Ishikawa 923-1224, Japan

<sup>2</sup> Institute of Nature and Environmental Technology, Kanazawa University, Kakuma-machi, Kanazawa, Ishikawa 920-1192, Japan; n\_tang@staff.kanazawa-u.ac.jp

<sup>3</sup> Pharmaceutical and Health Sciences, Graduate School of Medical Sciences, Kanazawa University, Kakuma-machi, Kanazawa, Ishikawa 920-1192, Japan; xingwanli@stu.kanazawa-u.ac.jp

<sup>4</sup> Medical Sciences, Graduate School of Medical Sciences, Kanazawa University, 13-1, Takara-machi, Kanazawa 920-8640, Japan; kimoanhpham129@gmail.com; ahara@m-kanazawa.jp; hnakamu@staff.kanazawa-u.ac.jp

\* Correspondence: hayakawa@p.kanazawa-u.ac.jp

## Text S1 Sample Treatments and Analytical Procedures

An area (2 × 5 cm) of each quartz filter containing atmospheric TSP or PM from typical sources was cut into small pieces in a glass flask and an internal standard solution including Pyr-*d*<sub>10</sub> and 1-NP-*d*<sub>9</sub> was added. PAHs, NPAHs and internal standards were extracted twice through ultrasonication with benzene/ethanol (3:1, v/v). The solution was then washed successively with diluted solutions of sodium hydroxide and sulfuric acid, and twice with ultrapure water. After 100 μL of dimethyl sulfoxide (DMSO) was added to the organic solution, the mixture was concentrated using a rotary evaporator, and the residual solution was dissolved in ethanol. After filtering the solution with a membrane disk (HLC-DISK3, pore size 0.45 μm, Kanto Chemical Co., Tokyo, Japan), an aliquot of the solution was injected into the two high-performance liquid chromatographic (HPLC) systems (LC-10A series, Shimadzu Inc., Kyoto, Japan) for the separate detection of PAHs and NPAHs.

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), indeno[1,2,3-*cd*]pyrene (IDP), were identified using HPLC equipped with a fluorescence detector according to the USEPA methods (Wise et al., 2016). The analytical column was a reversed-phase column (Inertsil ODS-P, 4.6 i.d. × 250 mm, GL Sciences Inc., Tokyo, Japan). The mobile phase was a mixture of acetonitrile/water with a flow rate of 1 mL/min and was operated under a gradient concentration. The excitation (Ex) and emission (Em) wavelengths of the fluorescence detector were set at Ex 286 nm and Em 433 nm which are optimum for Pyr and Pyr-*d*<sub>10</sub> [1].

Six NPAHs, 9-nitroanthracene (9-NA), 1-nitropyrene (1-NP), 6-nitrocrysene (6-NC), 7-nitrobenz[*a*]anthracene (7-NBaA), 3-nitroperylene (3-NPer) and 6-nitrobenzo[*a*]pyrene (6-NBaP), were determined using an HPLC equipped with a chemiluminescence detector. The analytical columns were reversed-phase columns (Cosmosil 5C18-MS-II, 4.6 i.d. × (250 + 150) mm, Nacalai Tesque, Kyoto, Japan). The mobile phase was a mixture of an imidazole buffer and acetonitrile. The chemiluminescence reagent solution was an acetonitrile solution containing *bis*(2,4,6-trichlorophenyl)oxalate and hydrogen peroxide. The flow rate of the chemiluminescence reagent solution was 1 mL/min. Pyr and 1-NP were quantified by using Pyr-*d*<sub>10</sub> and 1-NP-*d*<sub>9</sub> with other PAHs and NPAHs. The validity of this method has already been confirmed through our previous published reports showing recoveries that varied between 87 and 104%, with limits of detection (S/N = 3) that varied between 0.25 and 1.5 fmol, and limits of quantification (S/N = 10) that varied between 10<sup>-15</sup> and 10<sup>-12</sup> (over two orders) and showed good linearity ( $r^2 > 0.899$ ) [2–4].

## Text S2 Calculation of source contribution to combustion-derived particulate

Atmospheric particulate ( $P$ ) consists of combustion-derived particulate ( $P_c$ ) and non-combustion derived particulate ( $P_o$ ).  $P_o$  consists of particulate from natural sources such as soils, plants and road surface scraps.  $P_c$  can be divided further into particulate from sources with high combustion temperatures ( $P_h$ ) and particulate from sources with low-combustion temperatures ( $P_l$ ) and is described as follows:

$$P = P_c + P_o \quad (1)$$

$$P_c = P_h + P_l \quad (2)$$

Letting the proportion of  $P_h$  in  $P_c$  be  $x$  ( $0 < x < 1$ ) and the proportion of  $P_c$  in  $P$  be  $y$  ( $0 < y < 1$ ) in Equations (1) and (2), the following equations are obtained for atmospheric concentrations of  $P_h$  ( $[P_h]$ ),  $P_l$  ( $[P_l]$ ),  $P_c$  ( $[P_c]$ ),  $P_o$  ( $[P_o]$ ) and  $P$  ( $[P]$ ):

$$[P_h] = [P_c]x \quad \text{and} \quad [P_l] = [P_c](1 - x) \quad (3)$$

$$[P_c] = [P]y \quad \text{and} \quad [P_o] = [P](1 - y) \quad (4)$$

Therefore,  $x$  is able to provide an estimation on the extent to which high temperature combustion products ( $P_h$ ) are contributing to combustion-derived particulate ( $P_c$ ), and  $y$  is able to provide an estimate on the extent to which  $P_c$  contributes to the total particulate ( $P$ ). From Equations (3) and (4), the concentration ratio of  $P_h$  and  $P_l$  ( $[P_h] : [P_l]$ ) in the atmosphere at the monitoring sites is given by  $x : (1 - x)$  and the concentration ratio of  $P_c$  and  $P_o$  ( $[P_c] : [P_o]$ ) is given by  $y : (1 - y)$ .

Hear  $[1 - NP_h]$ ,  $[1 - NP_l]$  and  $[1 - NP_c]$  are 1-NP concentrations in  $P_h$ ,  $P_l$  and  $P_c$ , respectively, and  $[Pyr_h]$ ,  $[Pyr_l]$  and  $[Pyr_c]$  are Pyr concentrations in  $P_h$ ,  $P_l$  and  $P_c$ , respectively, assuming that both 1-NP and Pyr are not chemically changed in the urban atmosphere during the period between emission to sampling (Figure S1). Atmospheric concentrations of 1 - NP bound to  $P_h$  and  $P_l$  at the monitoring sites are respectively given by  $[1 - NP_h][P_h]x$  and  $[1 - NP_l][P_l](1 - x)$ . The atmospheric concentrations of Pyr bound to  $P_h$  and  $P_l$  at the monitoring sites are also respectively given by  $[Pyr_h][P_h]x$  and  $[Pyr_l][P_l](1 - x)$ , and the following equations are obtained for atmospheric concentrations of 1 - NP ( $[1 - NP]$ ) and Pyr ( $[Pyr]$ ):

$$[1 - NP] = [1 - NP_h][P_c]x + [1 - NP_l][P_c](1 - x) \quad (5)$$

$$[Pyr] = [Pyr_h][P_c]x + [Pyr_l][P_c](1 - x) \quad (6)$$

The atmospheric  $[1 - NP]/[Pyr]$  ratio at the monitoring site can therefore be expressed by the following equation:

$$[1 - NP]/[Pyr] = \{[1 - NP_h]x + [1 - NP_l](1 - x)\} / \{[Pyr_h]x + [Pyr_l](1 - x)\} \quad (8)$$

Replacing  $[P_c]$  in the right side of equation (5) with  $[P]y$  according to equation (6), the atmospheric  $[1 - NP]$  at the monitoring site can be expressed by the following equation.

$$[1 - NP] = \{[1 - NP_h]x + [1 - NP_l](1 - x)\}[P]y \quad (8)$$

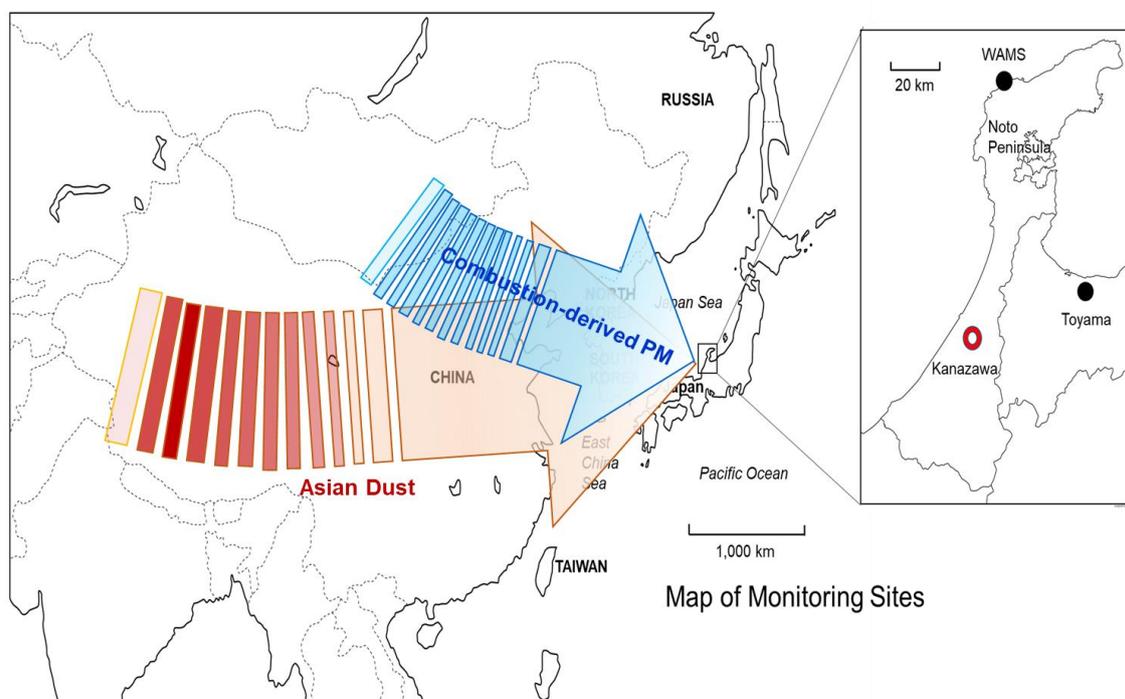
Equation (7) means that the contribution ratio of  $P_h$  to  $P_c$  ( $= x$ ) is a function of  $[1 - NP]/[Pyr]$ .

Here, vehicles and coal combustion are used as standard sources for  $P_h$  and  $P_l$ . By introducing values of  $[1 - NP_h]$  ( $= 65.5 \text{ pmol mg}^{-3}$ ),  $[1 - NP_l]$  ( $= 4.6 \text{ pmol mg}^{-3}$ ),  $[Pyr_h]$  ( $= 180 \text{ pmol mg}^{-3}$ ) and  $[Pyr_l]$  ( $= 3,400 \text{ pmol mg}^{-3}$ ) derived from Table 1 into equations (vii) and (viii), the following equations are obtained.

$$[1 - NP]/[Pyr] = \{65.5x + 4.6(1 - x)\} / \{180x + 3400(1 - x)\} \quad (9)$$

$$[1 - NP] = \{65.5x + 4.6(1 - x)\}[P]y \quad (10)$$

where  $[1 - NP]$  and  $[Pyr]$  are atmospheric concentrations of  $1 - NP$  and  $Pyr$  at the various monitoring sites.  $[1 - NP_h]$ ,  $[Pyr_h]$ ,  $[1 - NP_i]$  and  $[Pyr_i]$  can be obtained by analyzing  $1 - NP$  and  $Pyr$  in  $P_h$  and  $P_i$  [5].



**Figure 1.** Map of sampling sites.

**Table S1.** Correlation coefficients between atmospheric compounds.

	PM <sub>2.5</sub>	PM <sub>&gt;2.5</sub>	P <sub>0</sub>	P <sub>c</sub>	P <sub>h</sub>	P <sub>i</sub>	ΣPAH	ΣNPAH
PM <sub>2.5</sub>								
PM <sub>&gt;2.5</sub>	0.6921							
P <sub>0</sub>	<b>0.9999</b>	0.6934						
P <sub>c</sub>	0.5585	0.4390	0.5456					
P <sub>h</sub>	0.1186	0.0150	0.6518	0.7038				
P <sub>i</sub>	0.6626	0.5732	0.1075	<b>0.9223</b>	0.3800			
ΣPAH	0.6811	0.5954	0.6716	<u>0.8661</u>	0.3116	<b>0.9737</b>		
ΣNPAH	0.3850	0.3268	0.3582	<u>0.8211</u>	0.6689	<u>0.7152</u>	<u>0.7520</u>	

TSP samples were collected in Kanazawa for 7 days in every season from spring, summer, autumn, 2017 to winter, 2018. P<sub>0</sub>, particulate from non-combustion source; P<sub>c</sub>, particulate from combustion source; P<sub>h</sub>, particulate from combustion source with higher temperature (vehicles); P<sub>i</sub>, particulate from combustion source with lower temperature (heating facilities/industries). **Bold** means correlation coefficient  $\geq 0.9$ ; Underline indicates  $0.9 >$  correlation coefficient  $\geq 0.7$ .

**Table 2.** Toxic equivalency factors of PAHs (TEFPAH).

Compound	Relative Potency Factor
BaP	1
BaA	0.1

BbF	0.1
BkF	0.01
Chr	0.001
IDP	0.1

TEF, cited from the reference by USEPA (1993) [6].

**Table 3.** Toxic equivalency factors of NPAHs (TEF<sub>NPAH</sub>).

Compound	Relative Potency Factor
1-NP	1
6-NC	0.2
6-NBaP	0.1
3-NPer	0.08

TEF, calculated from direct-acting mutagenic activities [6].

## References

- 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.
- Hayakawa, K.; Kitamura, R.; Butoh, M.; Imaizumi, 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.
- Hayakawa, K.; Murahashi, T.; Butoh, M.; Miyazaki, M. Determination of 1,3-, 1,6-, and 1,8-dinitropyrenes and 1-nitropyrene in urban air by high-performance liquid chromatography using chemiluminescence detection. *Environ. Sci. Technol.* **1995**, *29*, 928–932, doi:10.1021/es00004a012.
- Tang, N.; Taga, R.; Hattori, T.; Toriba, A.; Kizu, R.; Hayakawa, K. Simultaneous determination of twenty-one mutagenic nitropolycyclic aromatic hydrocarbons by high-performance liquid chromatography with chemiluminescence detection. In *Proceedings of the 13th International Symposium, Bioluminescence and Chemiluminescence Progress and Perspective*; World Science: London, UK, 2005; pp. 441–444.
- 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
- 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).