

Comparison of Atmospheric Polycyclic Aromatic Hydrocarbons and Nitropolycyclic Aromatic Hydrocarbons in Kanazawa, Sapporo and Tokyo

Hitoshi Kakimoto,^{*,a} Moritsugu Kitamura,^a Yutaka Matsumoto,^b Shigekatsu Sakai,^b Fumio Kanoh,^c Tsuyoshi Murahashi,^d Kazuhiko Akutsu,^d Ryoichi Kizu,^d and Kazuichi Hayakawa^d

^aIshikawa Prefectural Institute of Public Health and Environmental Science, Taiyogaoka 1–11, Kanazawa 920–1154, Japan, ^bHokkaido Institute of Environmental Science, Kita-19jo Nishi 12, Kita-ku, Sapporo 060–0819, Japan, ^cTokyo Metropolitan Research Laboratory of Public Health, Hyakunin-cho 3–24–1, Shinjuku-ku, Tokyo 169–0073, Japan, and ^dFaculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi 13–1, Kanazawa 920–0934, Japan

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Air samples were collected at the sides of busy traffic roads in downtown Kanazawa, Sapporo and Tokyo during the same periods both in the daytime and in the night, in winter and summer. We determined the levels of polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs), which are known to be carcinogenic and/or mutagenic. PAHs and NPAHs were analyzed simultaneously with an HPLC system with fluorescence detection for PAHs and another HPLC system with chemiluminescence detection for NPAHs, respectively. The amounts of airborne particulates were larger in the daytime than in the night in all three cities. This result was thought to reflect the diurnal change of such urban activities as traffic volume. Many of the PAH and NPAH compounds showed higher concentrations in the daytime than in the night, and also showed higher concentrations in winter than in summer in the three cities. This result coincided with the trends observed in our continuous surveys in downtown Kanazawa for several years. However, 5-ring PAHs, such as benzo[*a*]pyrene, and dinitropyrenes in Tokyo did not show such diurnal or seasonal differences. The composition ratio of NPAHs and the contribution of diesel-engine vehicles to the atmospheric concentrations of NPAHs were calculated from all the data of this survey. The concentration ratio of dinitropyrenes to 1-nitropyrene became larger with an increase in the ratio of diesel-engine vehicles to the total vehicles registered, suggesting a large contribution of diesel-engine vehicles to the concentrations of these NPAHs in urban air.

Key words — airborne particulate, nitropolycyclic aromatic hydrocarbon, 1-nitropyrene, dinitropyrene, polycyclic aromatic hydrocarbon

INTRODUCTION

It has been known that carcinogenic and/or mutagenic polycyclic aromatic hydrocarbons (PAHs), including benzo[*a*]pyrene (BaP), exist in the air, especially in populated areas. Recently, some nitropolycyclic aromatic hydrocarbons (NPAHs), which are more carcinogenic and/or mutagenic than PAHs, have been found in extracts from airborne particulates.¹⁾ For example, the mutagenicities of 1-nitropyrene (1-NP) and 1,

3-, 1,6- and 1,8-dinitropyrenes (DNPs) are several to 2000 times as strong as that of BaP.²⁾ Diesel-engine vehicles have been considered the main contributor to PAHs and NPAHs in urban air. We have found the following dynamic tendencies of NPAHs through continuous surveys of airborne particulates collected in the urban area of Kanazawa:

(1) Atmospheric concentrations of NPAHs are higher in the daytime than at night in accordance with changes in traffic volume.³⁾

(2) Atmospheric concentrations of NPAHs are higher in winter than in other seasons because of the high stability of air in winter.^{3,4)}

(3) The mean concentration of 1-NP, which was the highest among NPAHs, was one order of

*To whom correspondence should be addressed: Ishikawa Prefectural Institute of Public Health and Environmental Science, Taiyogaoka 1–11, Kanazawa 920–1154, Japan. Tel.: +81-76-229-2011; Fax: +81-76-229-2441; E-mail: hokan-07@pref.ishikawa.jp

magnitude lower than that of BaP, and the concentrations of 1,3-, 1,6-, and 1,8-DNPs were almost two orders of magnitude lower than the concentration of 1-NP.^{4,5)}

In view of the recent increase in lung cancer in urban areas,⁶⁾ it would seem worthwhile to better understand the presence of PAHs and NPAHs in airborne particulates in these areas. However, there has been no report on a comparison of PAHs and NPAHs in airborne particulates collected at the same time in different cities.

This study is a joint survey in Kanazawa, Sapporo and Tokyo, which have different populations, different areas and different meteorological conditions. Airborne particulates were collected both in the daytime and in the night, and in winter and summer in the three cities to compare the atmospheric concentrations of PAHs and NPAHs.

MATERIALS AND METHODS

Sampling — Airborne particulates were collected with a MODEL-120 high-volume air sampler (Kimoto Electronics Co., Ltd., Osaka, Japan) set by the roadside in a downtown area of each city. Samplings were made over two 12-hour periods (in daytime from 6:00 a.m. to 6:00 p.m. and at night from 6:00 p.m. to 6:00 the next morning) for three days in a row. The experiment was done twice, in both the winter (January and February, 1995) and summer (July and August, 1995). The sampling flow rate was approximately 1500 l/min (2160 m³/d). Quartz filters (Pallflex products, 2500QAT-UP, 200 mm × 250 mm) which adsorbed airborne particulates were weighed and cut after reaching a constant weight.

Table 1 shows the distance from the carriageway

to the sampling points, the traffic volume at the sampling points and the number of registered gasoline- and diesel-engine vehicles in each city. "Traffic volume" means the average number of vehicles driven through the carriageways per hour. The sampling stations were located by the side of straight carriageways, having two lanes in both directions except in Kanazawa, where the sampling station was located at a T-junction of two roads, in which both of the roads have two lanes in both directions. This was thought to be one reason the traffic volume in Kanazawa was slightly larger than that in the other two cities.

Methods of Analysis — NPAHs and PAHs were simultaneously analyzed with a chemiluminescence detection HPLC and a fluorescence detection HPLC, respectively.⁷⁾ The former consisted of a mobile phase pump (Shimadzu LC-6A), a chemiluminescence reagent solution pump (Sanuki DM2M-1006), a chemiluminescence detector (Soma S-3400), a column oven (Shimadzu CTO-6A), and an analytical column for NPAHs (Shimadzu ODS-II, 4.6 mm i.d. × 250 mm). The latter consisted of the same mobile phase pump and column oven, a fluorescence detector (JASCO 820-FP), an injector (Rheodyne Model-7125) with a 20 μl loop, and an analytical column for PAHs (Vydac 201-TP54, 4.6 mm i.d. × 250 mm). The former and latter were combined through a switching valve (Shimadzu FCV-12AH) and a separation column (Nacalai Tesque, Inc. Cosmosil 5C₁₈AR, 4.6 mm i.d. × 10 mm).

Seven kinds of PAHs (fluoranthene (Fl), pyrene (Py), benz[*a*]anthracene (BaA), chrysene (Ch), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF) and BaP) were surveyed according to the preferential list of pollutants most in need of monitoring, as determined by the Environmental Protection Agency (EPA). Four strong mutagenic NPAHs, 1,3-, 1,6- and 1,8-DNPs and 1-NP, were also determined.

Table 1. Characteristics of the Three Cities and the Sampling Stations

City	Population, 1997	Number of registered vehicles, 1995		Address	Sampling point		
		Diesel-engine (%)	Gasoline-engine (%)		Location	Traffic volumes (vehicles/h) at sampling point	
					Distance from the carriageway, Distance above ground	Day time	Night time
Kanazawa	434865	142,155 ^{a)} (27.4)	376,132 ^{a)} (72.6)	Katamachi	Korinbo junction (11.0m, 4.0m)	2840	1250
Sapporo	1750627	493,791 (40.8)	716,323 (59.2)	Chuo-ku	Route-12 (4.6m, 1.0m)	2260	680
Tokyo	7817332	724,429 ^{b)} (19.9)	2,913,911 ^{b)} (80.1)	Shinjuku-ku	Yamanote Str. (2.0m, 1.0m)	2040	1250

a) Ishikawa Pref. b) 23 wards, Tokyo metropolitan district.

Chemicals — 1,3-, 1,6- and 1,8-DNPs were purchased from Aldrich Chemical (Milwaukee, WI, U.S.A.). 1-NP was from Tokyo Kasei (Tokyo, Japan). Fl and BaA were obtained from Nacalai Tesque, Inc. (Kyoto, Japan), Ch and BbF were from Aldrich Chemical, Py was from Tokyo Kasei and BaP and BkF were from Wako Pure Chemical Industries (Osaka, Japan). All other chemicals used in the sample pretreatments, for the mobile phase of HPLC and for the chemiluminescence reagent solution, were of analytical-reagent grade.

RESULTS AND DISCUSSION

Concentration of Airborne Particulates

Figure 1 shows the concentration of airborne particulates in the air in the three cities both day and night and in both winter and summer. Among

the three cities, Tokyo showed the largest mean values, followed by Sapporo and Kanazawa. The mean values were larger in the daytime than at night in all three cities without exception. This result likely reflects the larger traffic volume in daytime than that at night, as shown in Table 1, and agrees with the general tendency that the amount of airborne particulates strongly depends on traffic volume.⁸⁾

Concentrations were higher in summer than in winter in Kanazawa, but not in Sapporo and Tokyo. This might be due to varying weather conditions; in winter there is much precipitation in Kanazawa, and in summer there was unusually high precipitation in Sapporo (Table 2).

The average amount of particulates in Tokyo exceeded that in Kawasaki ($148 \mu\text{g}/\text{m}^3$ in July and $105 \mu\text{g}/\text{m}^3$ in February),⁹⁾ which was named the highest among all the survey sites of

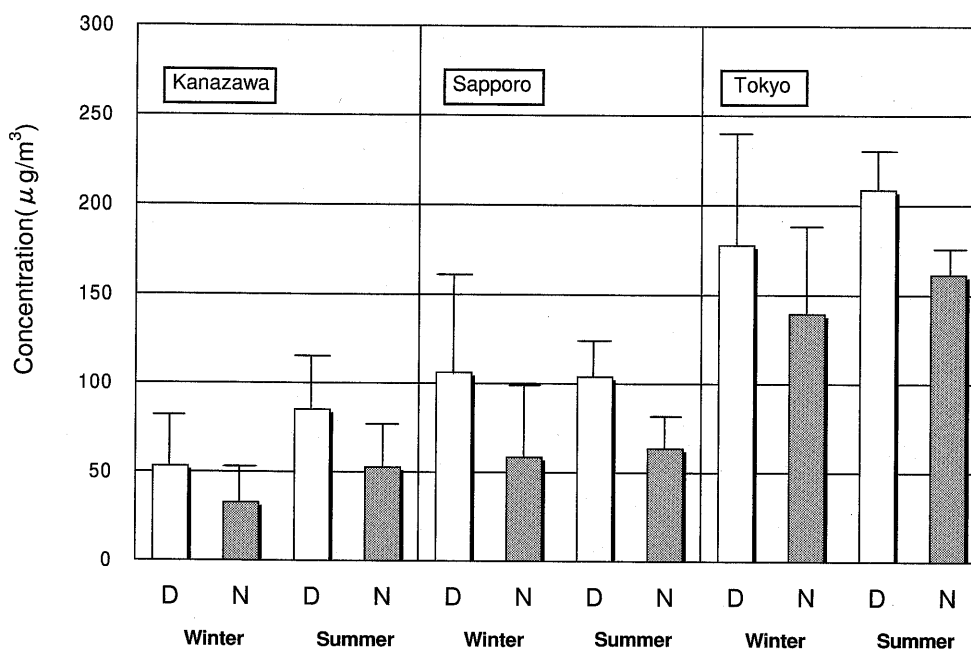


Fig. 1. Amount of Airborne Particulates in Kanazawa, Sapporo and Tokyo
D, day; N, night. Each box and vertical bar represent mean and S.D., respectively.

Table 2. Meteorological Conditions during Sampling Experiments

City	Season	Duration of sunshine (h/d)	Average wind speed (m/sec)	Total precipitation during sampling period (mm)
Kanazawa	Winter ^{a)}	1.9 ± 1.8^c	5.0	42.0
	Summer ^{b)}	8.2 ± 3.3^c	4.6	7.0
Sapporo	Winter ^{a)}	4.7 ± 2.1^c	3.2	8.5
	Summer ^{b)}	0.9 ± 2.0^c	1.9	75.0
Tokyo	Winter ^{a)}	8.8 ± 0.8^c	3.2	0.0
	Summer ^{b)}	7.7 ± 2.0^c	1.7	8.0

a) Winter: 30 Jan.—8 Feb., 1995. b) Summer: 31 July—9 Aug., 1995. c) Mean \pm S.D.

the National Air Survey Network, Japan (NASN) in 1996, both in winter and summer. This result suggests that Tokyo is one of the most polluted areas by airborne particulates in Japan. Downtown Kanazawa ranks in the middle of the nation with respect to airborne particulates.

Concentrations of PAHs and NPAHs

Table 3 shows the concentrations of PAHs and NPAHs in the three cities. Among the 4-ring PAHs surveyed, Py showed the highest concentration, followed by Fl, Ch and BaA in all the cities, while among the 5-ring PAHs, the concentrations of BbF and BaP were higher than the concentration of BkF. The mean concentrations of BaP both day and night in both winter and summer in Tokyo were almost the same as in Sapporo. These concentrations ranged from 0.9 ng/m³ to 2.0 ng/m³ and they were five to ten

times higher than the concentrations in Kanazawa. These values were almost the same as that in Kitakyushu (1.3 ng/m³), where the concentration of BaP was the highest in the NASN in 1996.⁹⁾

The concentrations of NPAHs, especially that of 1-NP, were significantly higher in Sapporo than in the other two cities. The mean concentration of 1-NP, which was higher than the concentrations of the other NPAHs, was one order of magnitude lower than that of BaP in the three cities. The concentration of each DNP in the three cities ranged from 0.1 pg/m³ to 2.1 pg/m³. These values were almost two orders of magnitude lower than the concentration of 1-NP, and three orders of magnitude lower than that of BaP. These facts coincided with our previous study of the air in downtown Kanazawa.⁴⁾ The mean values of 1-NP and DNPs determined in the

Table 3. Concentrations of PAHs and NPAHs Analyzed in This Study

Sample			1,6-DNP pg/m ³	1,8-DNP pg/m ³	1,3-DNP pg/m ³	1-NP pg/m ³	Fl ng/m ³	Py ng/m ³
Kanazawa	Winter	Day	0.28±0.11	0.35±0.16	0.28±0.11	59.2± 8.8	0.85±0.28	1.14±0.44
		Night	0.20±0.05	0.24±0.08	0.18±0.05	38.3± 14.6	0.71±0.40	0.88±0.45
	Summer	Day	0.13±0.06	0.12±0.06	0.14±0.08	26.7± 13.0	0.37±0.12	0.71±0.22
		Night	0.11±0.03	0.09±0.02	0.09±0.03	11.3± 4.1	0.12±0.05	0.20±0.10
Sapporo	Winter	Day	1.88±1.09	2.18±1.37	1.63±0.87	413 ±230	3.16±2.37	5.00±4.12
		Night	0.87±0.74	0.94±0.79	0.82±0.70	197 ±151	1.53±1.02	2.14±1.58
	Summer	Day	0.86±0.29	0.80±0.32	0.74±0.22	206 ± 76.5	1.31±0.46	2.66±1.85
		Night	0.82±0.15	0.75±0.13	0.76±0.06	149 ± 64.8	1.17±0.98	2.09±2.24
Tokyo	Winter	Day	0.62±0.26	0.68±0.26	0.72±0.24	163 ± 60.4	2.99±1.98	3.73±1.99
		Night	0.97±0.36	0.60±0.18	0.65±0.18	120 ± 32.0	2.32±1.27	3.17±1.31
	Summer	Day	1.14±0.39	0.53±0.08	0.66±0.11	130 ± 25.8	1.44±0.28	2.34±0.44
		Night	1.30±0.42	0.69±0.16	0.92±0.34	75.3± 21.6	0.98±0.18	1.43±0.16

Samples			BaA ng/m ³	Ch ng/m ³	BbF ng/m ³	BkF ng/m ³	BaP ng/m ³
Kanazawa	Winter	Day	0.58±0.23	0.93±0.29	0.87±0.31	0.38±0.12	0.67±0.19
		Night	0.32±0.19	0.69±0.37	0.71±0.43	0.32±0.22	0.45±0.35
	Summer	Day	0.21±0.07	0.32±0.13	0.42±0.18	0.18±0.07	0.32±0.13
		Night	0.07±0.02	0.11±0.04	0.20±0.09	0.09±0.04	0.13±0.06
Sapporo	Winter	Day	1.90±1.62	2.56±2.08	2.04±1.65	1.07±0.90	2.04±1.70
		Night	0.88±0.84	1.18±1.06	0.87±0.84	0.46±0.48	0.91±1.15
	Summer	Day	1.21±0.56	1.72±0.83	1.53±0.58	0.74±0.26	1.60±0.56
		Night	0.81±0.51	1.15±0.74	1.10±0.63	0.54±0.29	1.14±0.66
Tokyo	Winter	Day	1.29±0.59	1.79±0.66	1.64±0.68	0.76±0.29	1.39±0.63
		Night	1.47±0.76	2.00±1.09	1.75±1.03	0.85±0.45	1.77±0.93
	Summer	Day	1.00±0.17	1.69±0.61	2.36±0.60	0.96±0.24	1.65±0.38
		Night	0.67±0.09	1.24±0.20	1.90±0.38	0.79±0.18	1.48±0.32

All data represent mean±S.D.

present study were almost the same as the concentrations reported by Tanabe *et al.*¹⁾

Many of the PAH and NPAH compounds showed higher concentrations in the daytime than at night in the three cities (Figs. 2–5). However, 5-ring PAHs and some DNPs in Tokyo did not show such diurnal variation (Fig. 3 and Fig. 5). This might be due to the huge urban activities of Tokyo, with a larger downtown area

and smaller diurnal changes in traffic volume (Table 1). The air samples collected at the sampling site of Tokyo were considered to include airborne particulates that had been transported from other areas. In other words, large amount of particulates from automobile exhaust might be collected after a longer time drift in Tokyo than in the other two cities. Moreover, the effect of the secondary formation of NPAHs from PAHs,

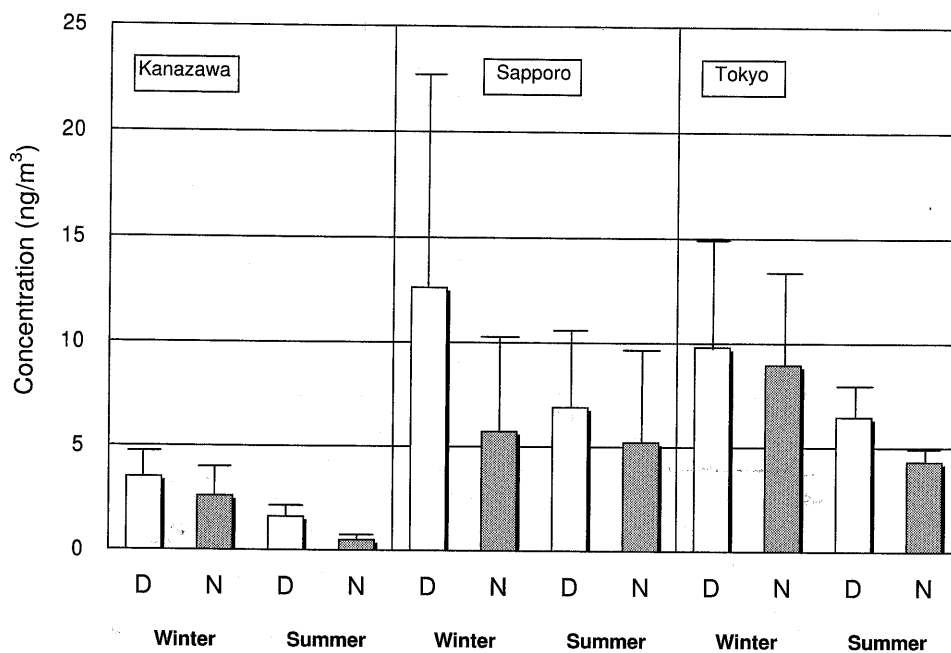


Fig. 2. Atmospheric Concentrations of 4-Ring PAHs (Fl+Py+BaA+Ch) in Kanazawa, Sapporo and Tokyo D, day; N, night. Each box and vertical bar represent mean and S.D., respectively.

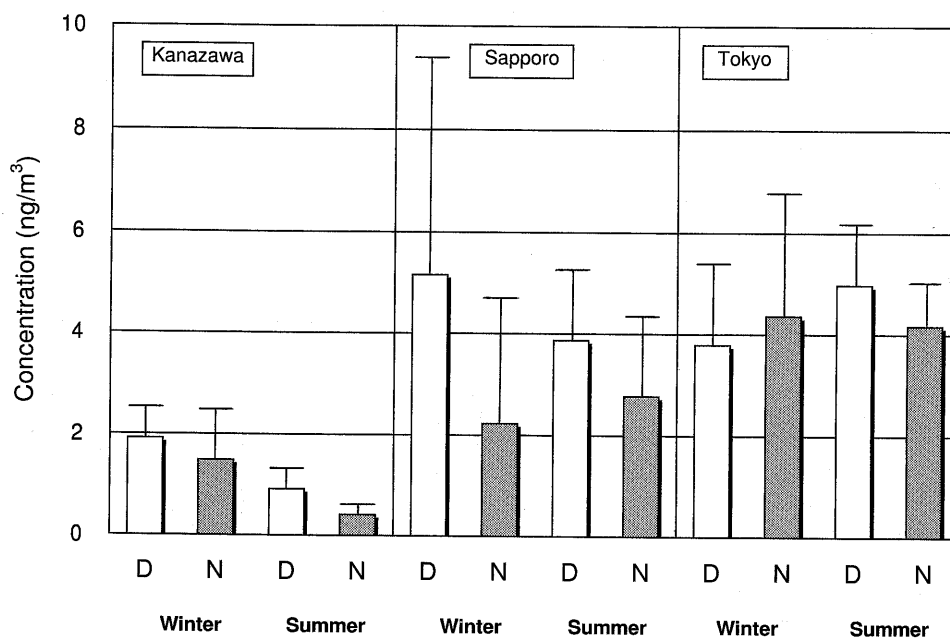


Fig. 3. Atmospheric Concentrations of 5-Ring PAHs (BbF+BkF+BaP) in Kanazawa, Sapporo and Tokyo D, day; N, night. Each box and vertical bar represent mean and S.D., respectively.

which, in general, occurs more easily at night when the ozone concentration is higher than in the daytime, were also considered.¹⁰⁾

Clear seasonal differences were observed for PAHs and NPAHs surveyed in this study, *i.e.*, the concentrations were higher in winter and lower in summer in the three cities (Figs. 2–5). This result might be due to the more stable atmospheric conditions in winter, under which vehicle

exhaust would tend to stagnate in the air for a long time along the roads. The seasonal differences in concentrations of 4-ring PAHs (Fig. 2) were more pronounced than were those of 5-ring PAHs (Fig. 3). This seemed to be due to the tendency of the 4-ring PAHs to have higher vapor pressures than 5-ring PAHs, which would make them more volatile in summer because of the high temperature.

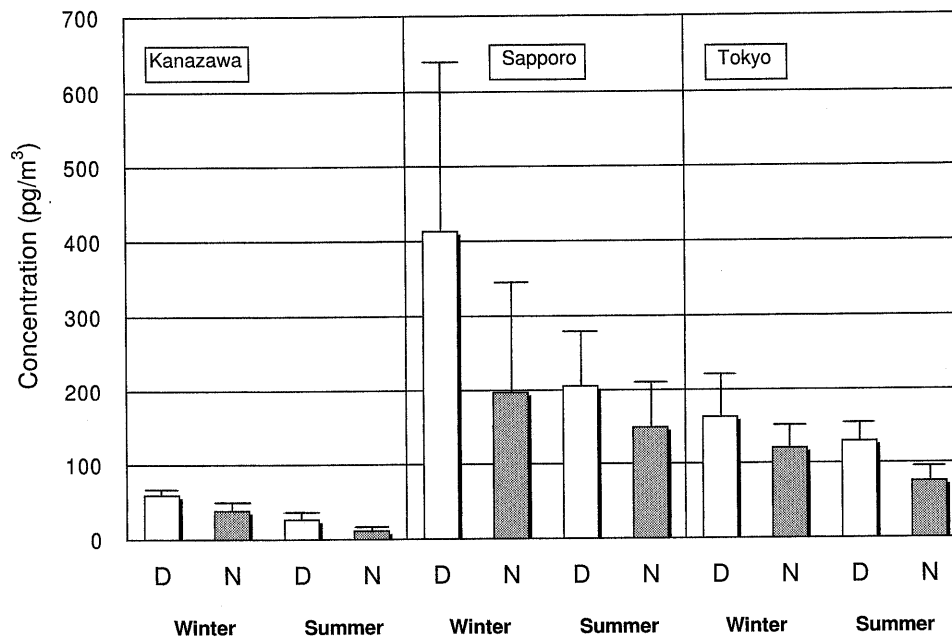


Fig. 4. Atmospheric Concentrations of 1-NP in Kanazawa, Sapporo and Tokyo
D, day; N, night. Each box and vertical bar represent mean and S.D., respectively.

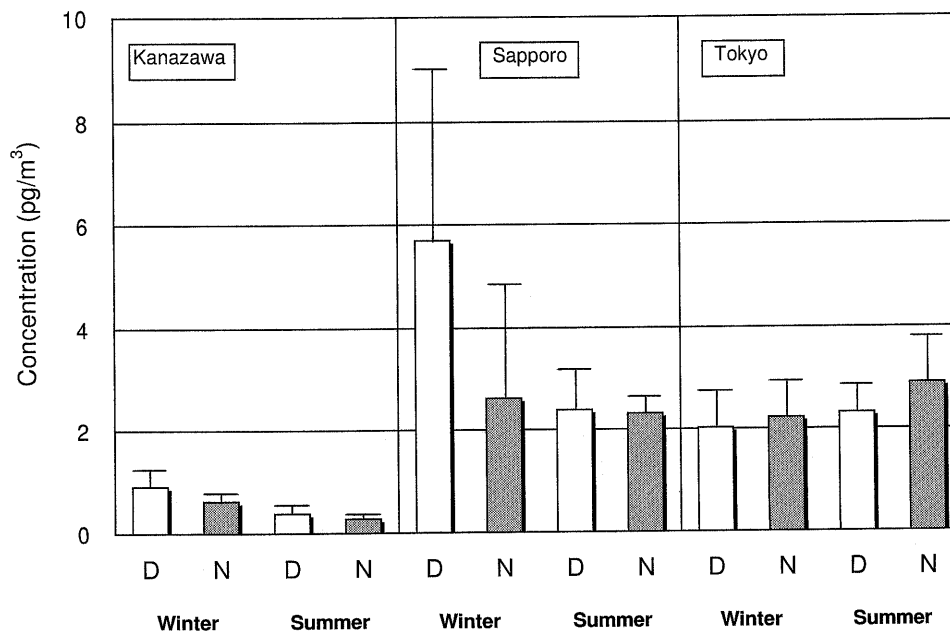


Fig. 5. Atmospheric Concentrations of DNPs (1,3-DNP+1,6-DNP+1,8-DNP) in Kanazawa, Sapporo and Tokyo
D, day; N, night. Each box and vertical bar represent mean and S.D., respectively.

However, there were no clear seasonal differences in the concentrations of 5-ring PAHs in Tokyo in spite of the seasonal difference in atmospheric stability (Fig. 3). This was due to the appearance of relatively high concentrations of less volatile 5-ring PAHs in summer samples in Tokyo, which, in turn, were considered to be due

to very weak winds in summer (Table 2) and probably to a high frequency of winds that transport the pollutants from the central metropolitan area. In the case of NPAHs, no seasonal differences were observed only in the concentrations of DNPs in Tokyo (Fig. 5), where there was not a very large difference in the duration of sunshine

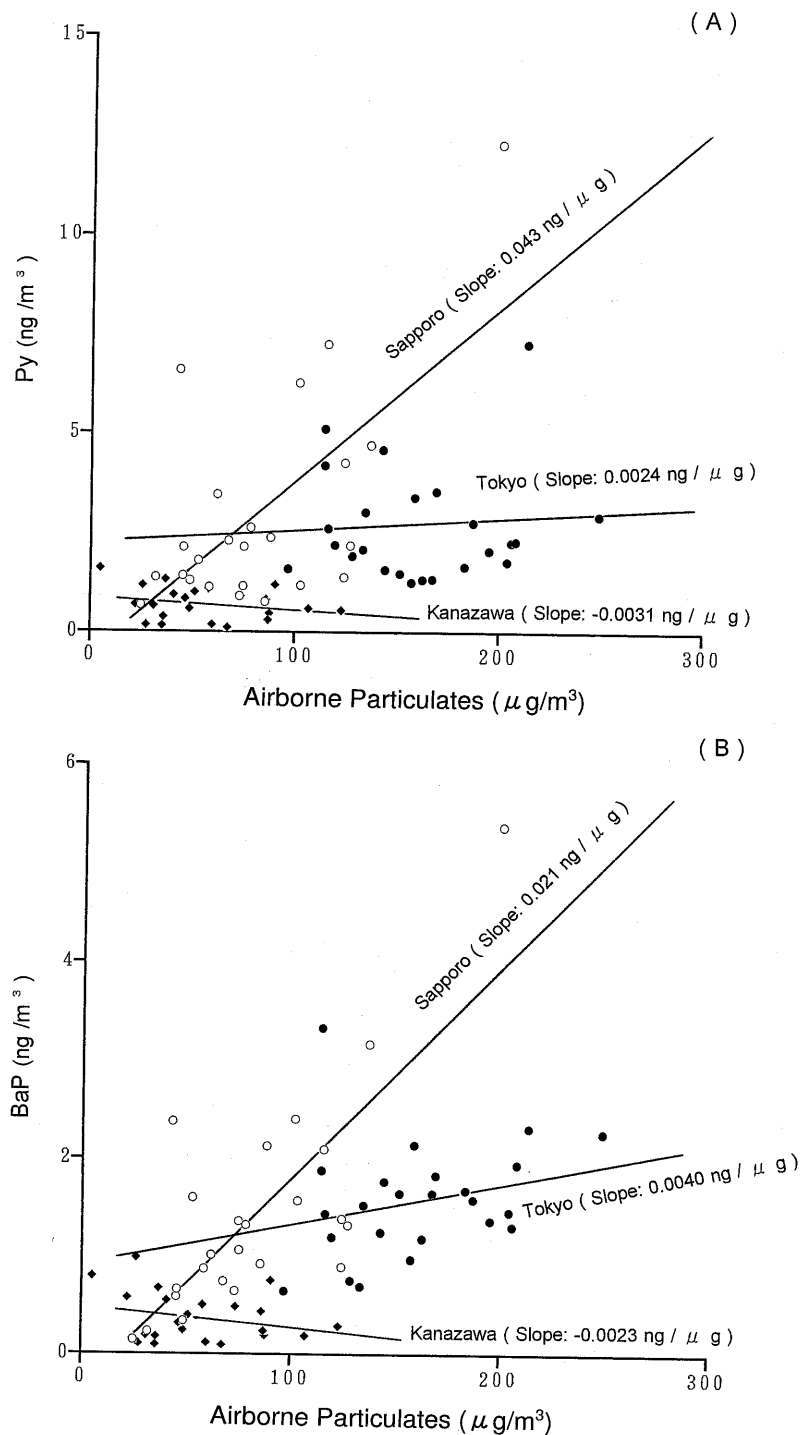


Fig. 6. Plots of PAHs and NPAHs vs. Airborne Particulates
 (A) Py, (B) BaP, (C) 1-NP, (D) DNPs ($=1,3\text{-DNP}+1,6\text{-DNP}+1,8\text{-DNP}$)
 Symbols: \blacklozenge , Kanazawa; \circ , Sapporo; \bullet , Tokyo.

between winter and summer (Table 2). This raises the possibility that the photolysis of NPAHs occurs in the air.

Figure 6 shows the relationships between airborne particulates and PAHs (Py and BaP) and NPAHs (1-NP and DNPs=1,3-DNP + 1,6-DNP + 1,8-DNP). Although the concentrations of

PAHs in Sapporo were almost the same as those in Tokyo and the amount of airborne particulates was significantly larger in Tokyo, the concentrations of NPAHs in Sapporo were clearly higher than those in Tokyo. Because NPAHs (1-NP and DNPs) mainly originate from diesel-engine vehicles,^{3,4)} the higher concentrations of

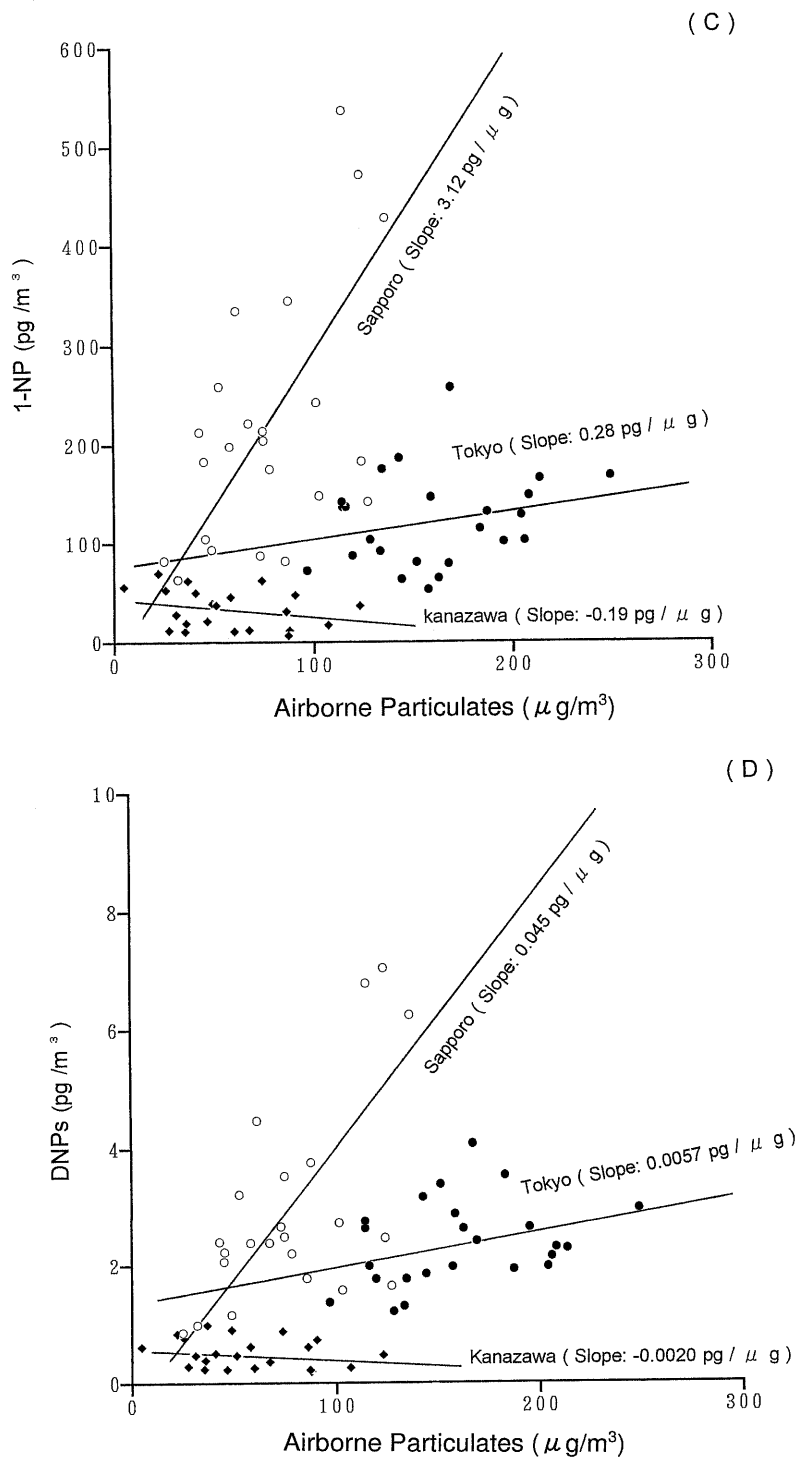


Fig. 6. Plots of PAHs and NPAHs vs. Airborne Particulates

(A) Py, (B) BaP, (C) 1-NP, (D) DNPs (=1,3-DNP+1,6-DNP+1,8-DNP)

Symbols: \blacklozenge , Kanazawa; \circ , Sapporo; \bullet , Tokyo.

NPAHs in Sapporo might be due to its higher percentage of diesel-engine vehicles (40.8% in Sapporo, 27.4% in Kanazawa and 19.9% in Tokyo), as shown in Table 1.

The regression line slopes in Fig. 6 show the ratios of increases in the atmospheric concentrations of each compound to increases in the amount of airborne particulates, and these ratios are, in general, approximately equal to the mean concentrations of each compound per unit weight of airborne particulates. The slopes of PAHs and NPAHs were the largest in Sapporo, followed by Tokyo and Kanazawa. This means that the amount of these compounds per unit weight of airborne particulates was largest in Sapporo. While, the slopes of these compounds in Kanazawa were nearly equal to zero. This means that the amount of PAH and NPAH compounds has no relation to the amount of airborne particulates in the air of Kanazawa.

In addition, the Sapporo/Tokyo ratio of the slopes was larger for 1-NP ($3.12/0.28=11.1$) than for DNPs ($0.045/0.0057=7.9$). These facts suggest that the contribution of diesel-engine vehicles to airborne particulates is larger in Sapporo than in Tokyo. The contribution of diesel-engine vehicles to atmospheric concentrations of NPAHs is discussed below.

Composition Ratio of NPAHs

To obtain an index of the influence of diesel-engine vehicles on NPAHs in the air, the $[DNPs]/[1-NP]$ composition ratio was calculated from the data in Table 3. Since diesel-engine vehicles are the main contributor of 1-NP, smaller values of this ratio indicate increasing contributions of diesel-engine exhaust, while larger values indicate increasing contributions of gasoline-engine exhaust. The ratios were $0.011 \pm$

0.003 in Sapporo, 0.019 ± 0.004 in Tokyo and 0.016 ± 0.005 in Kanazawa, as shown in Table 4. According to our previous report,¹¹⁾ the $[DNPs]/[1-NP]$ ratios of particulates emitted from idling diesel-engine vehicles was 0.013 and the ratio for gasoline-engine vehicles was 0.56. The value of airborne particulates in each city was close to that of the particulates from the diesel-engine vehicles in this study. In addition, the lowest value in Sapporo coincided with the fact that this city has the largest percentage of registered diesel-engine vehicles (about 40%), as described in Table 1.

The $[DNPs]/[1-NP]$ ratio was larger at night than in the daytime, except for the winter samples of Sapporo. The higher ratio at night might be due to a decrease in the traffic volume of large-sized diesel-engine vehicles such as busses between midnight and early morning in the downtown area. The concentration of 1-NP, which is mostly produced by diesel-engine vehicles, decreased in the night more remarkably than did the concentrations of DNPs. On the other hand, the photolysis of DNPs has been reported.^{12,13)} Therefore, the decomposition of DNPs is more likely to occur in the daytime in summer. This might explain why the difference in the composition ratio between the daytime and night was larger in summer than in winter in all cities except Sapporo. As shown in Table 2, the duration of sunshine in Sapporo during the sampling period in summer was very short. So, the photolysis of DNPs in Sapporo in the daytime might be much smaller than in the other two cities.

The (%) contributions of diesel-engine vehicles to atmospheric concentrations of 1-NP and DNPs were calculated from the composition difference of NPAHs, as described previously,⁴⁾

Table 4. Composition Ratio of NPAHs ($[DNPs]/[1-NP]$) and Calculated Contribution (%) of Diesel-engine Vehicles to Atmospheric NPAHs

City	Season	$[DNPs]/[1-NP]$			Calculated contribution (%) of diesel-engine vehicles to atmospheric NPAHs	
		Day	Night	Mean \pm S.D.	DNPs	1-NP
Kanazawa	Winter	0.013	0.014	0.016 ± 0.005	94.1	99.9
	Summer	0.012	0.021			
Sapporo	Winter	0.012	0.011	0.011 ± 0.003	100.0	100.0
	Summer	0.010	0.013			
Tokyo	Winter	0.011	0.016	0.019 ± 0.004	78.2	99.4
	Summer	0.015	0.033			

and the results are also shown in Table 4. In this report, we assumed that there was no emission source of 1-NP and DNPs other than vehicles. Our results showed that 100% of 1-NP and DNPs in Sapporo were due to diesel-engine vehicles. Diesel-engine vehicles contributed almost 100% to the concentration of 1-NP in Tokyo and Kanazawa, while their contributions to DNPs were slightly smaller in Tokyo (78.2%) and Kanazawa (94.1%) than in Sapporo. The contribution of diesel-engine vehicles to 1-NP and DNPs in Kanazawa obtained in this report were almost the same as those in our previous study (99.8% for 1-NP and 94.3% for DNPs).⁴⁾

Recently, we observed that 2-nitrofluoranthene and 2-nitropyrene were not emitted from diesel-engine vehicles but were secondarily formed in the air, and that the concentration ratios of these two compounds to 1-NP were higher in suburban areas than in the downtown area.¹⁴⁾ Considering the high mutagenicities of these compounds, the comparison of the secondarily formed NPAHs in different cities also seems to be important.

CONCLUSIONS

Airborne particulates were collected in the same periods in Kanazawa, Sapporo and Tokyo, and PAHs and NPAHs were analyzed. The findings were as follows:

- (1) The amount of airborne particulates was the largest in Tokyo, followed by Sapporo and Kanazawa. The amount was larger in the daytime than at night in all cities, depending on the activity of the cities, such as traffic volume.
- (2) The concentrations of PAHs in Sapporo and Tokyo were similar and higher than the concentrations in Kanazawa. The concentrations were higher in the daytime than at night and higher in winter than in summer, except for the case of 5-ring PAHs in Tokyo. The seasonal difference in concentrations of 4-ring PAHs was more pronounced than that of 5-ring PAHs because the vapor pressures of the former are higher than those of the latter.
- (3) The concentrations of NPAHs were the highest in Sapporo, followed by Tokyo and Kanazawa. Among the NPAHs, the concentration of 1-NP was outstandingly high in Sapporo. This might be due to the fact that Sapporo has

the highest percentage of registered diesel-engine vehicles.

- (4) The concentrations of NPAHs were higher in the daytime than at night and higher in winter than in summer except for the case of DNPs in Tokyo. The lack of difference in Tokyo might be due to the huge downtown area, a smaller difference in diurnal activity such as traffic volume, and some meteorological conditions.
- (5) The composition ratios of NPAHs ([DNPs]/[1-NP]) of airborne particulates were in the order Tokyo > Kanazawa > Sapporo. This order might be related to the percentage of the total registered vehicles that are diesel-engine vehicles in the three cities.

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