Considerations of Atmospheric Behaviors of Polycyclic Aromatic Hydrocarbons, Nitropolycyclic Aromatic Hydrocarbons and Inorganic Pollutants Based on Their Interrelationships

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Airborne particulates were collected during the same periods in downtown Kanazawa, Sapporo and Tokyo and polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) were determined together with several heavy metal elements and water-soluble inorganic ions. The mean concentrations of metal elements and inorganic ions were the highest in Tokyo, followed by Sapporo and the lowest in Kanazawa both in winter and summer, and were strongly dependent on the amount of airborne particulates. These tendencies were different from the cases of PAHs and NPAHs. Correlations between the organic compounds (PAHs and NPAHs) and several inorganic pollutants were strong only in winter samples of Sapporo, but not so strong in Kanazawa and Tokyo. Because PAHs and NPAHs and several combustion-origin inorganic substances are, in general, detected mainly in the fine airborne particulates, it was reasonable that the significant correlations were found only in the winter samples of Sapporo where the generation of the coarse and crustal particulates were suppressed by snow or ice. Though the atmospheric concentrations of PAHs and NPAHs in Kanazawa were much lower than in Sapporo, the correlation among the NPAH compounds and between PAHs and NPAHs were surprisingly similar in these two cities. The strong correlations indicated that the atmospheric behaviors of the PAHs and NPAHs studied were similar in the two cities and that the source of PAHs and NPAHs might be the same. On the contrary, strong correlations were not observed in Tokyo, suggesting the possibility of multiple sources or formations/degradations of PAHs and NPAHs.

Key words —— nitropolycyclic aromatic hydrocarbon, polycyclic aromatic hydrocarbon, urban air, heavy metal element, inorganic ion, correlation coefficient

INTRODUCTION

Some of polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) in the air that are carcinogenic and/or mutagenic[1,2] have been considered to be a cause of the recent increase in lung cancer in urban areas. We have already reported that NPAHs mainly originated from diesel-engine vehicles,[3–5] which explains why atmospheric concentrations of NPAHs were much higher in a downtown area than in a suburban area. Through our simultaneous sampling of airborne particulates in three cities (Kanazawa, Sapporo and Tokyo), we found tendencies of higher concentrations in winter and lower concentrations in summer and of higher concentrations in the daytime and lower concentrations at night in every city.[6] The seasonal changes appeared to be due to the higher atmospheric stability and domestic heating in winter and the diurnal changes appeared to be due to changes in traffic volume, respectively. We also re-

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ported that the atmospheric concentrations of NPAHs, especially 1-nitropyrene (1-NP), were outstandingly high in Sapporo, which had the highest percentage of registered diesel-engine vehicles in the three cities.[6]

On the other hand, the sources and behaviors of several inorganic air pollutants have been determined through many continuous monitoring experiments. In general, once inorganic pollutants are emitted from the sources, they drift in the atmosphere more stably than the organic compounds even if they are influenced, to some extent, by the processes of physical dispersion and dilution. So, it is useful to compare the behaviors of the organic pollutants (PAHs and NPAHs) with those of the inorganic substances to elucidate the complicated mechanisms of urban air pollution.

However, there have been few reports concerning the relationships and differences between these organic and inorganic substances. Therefore, in this study, we focused on the relationships between atmospheric concentrations of PAHs and NPAHs and those of inorganic pollutants, including some heavy metals and water-soluble inorganic ions. Furthermore, we also investigated the relationships between each PAH and NPAH compound to clarify whether they have different sources.

MATERIALS AND METHODS

Sampling —— Airborne particulates were collected in the urban areas of Kanazawa (population; about 450000), Sapporo (about 1200000) and Tokyo (about 8500000). We set MODEL-120 high-volume air samplers (Kimoto Electronics Co., Ltd., Osaka, Japan) by the sides of busy traffic roads near the center of each city. Airborne particulates were collected on 2500QAT-UP quartz fiber filters (20 cm × 25 cm, Pallflex Products). The filters were changed every 12 hours at 6:00 a.m. and 6:00 p.m. for 6-day periods both in winter (January–February, 1995) and in summer (July–August, 1995). Therefore, 12 samples (6 day-samples + 6 night-samples) were obtained at each sampling site in each season. Details of the sampling periods and sampling sites were previously reported.[6] The filters, which adsorbed airborne particulates, were weighed after reaching constant weights and then cut into several pieces for analysis.

Analytical Methods —— The extraction and clean up (silica-gel column chromatography) of the filter samples were done as described previously[7] with some modifications. After these pretreatments, PAHs and NPAHs were determined simultaneously using two HPLC systems.[7] The HPLC system for PAHs consisted of a mobile phase pump (LC-6A; Shimadzu, Kyoto, Japan), a fluorescence detector (820-FP; JASCO, Tokyo, Japan), a column oven (CTO-6A; Shimadzu), an analytical column (201-TP54, 4.6 mm i.d. × 250 mm; Vydac, Hesperia, CA, U.S.A.), and an injector (Model-7125 with a 20 μl loop; Rheodyne, Cotati, CA, U.S.A.). The HPLC system for NPAHs consisted of the same mobile phase pump and the column oven, a chemiluminescence reagent solution pump (DM2M-1006; Sanuki, Tokyo, Japan), a chemiluminescence detector (S-3400; Soma, Tokyo, Japan) and an analytical column (ODS-II, 4.6 mm i.d. × 250 mm; Shimadzu). These two HPLC systems were combined through a switching valve (FCV-12AH; Shimadzu) and a separation column (Cosmosil $5C_{18}$AR, 4.6 mm i.d. × 10 mm; Nacalai Tesque, Inc., Kyoto, Japan). Seven kinds of PAHs (fluoranthene (Fl), pyrene (Py), benz[*a*]anthracene (BaA), chrysene (Ch), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF) and BaP) and four strongly mutagenic NPAHs (1,3-, 1,6- and 1,8-dinitropyrenes (DNPs) and 1-NP) were determined by the internal standard method using 2-fluoro-7-nitrofluorene (FNF) as an internal standard.

Nine kinds of heavy metal elements (Pb, Cd, Cu, Zn, V, Mn, Fe, Ni and Cr), which have been continuously surveyed as indices of air pollution in the urban area,[8] were determined by flame/flameless atomic absorption spectrophotometry (Z-8200; Hitachi, Tokyo, Japan) after the elution of airborne particulates from the filters with HNO_3 and H_2O_2. Eight kinds of water-soluble inorganic ions (NO_3^-, SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, K^+, Na^+ and NH_4^+), which have been monitored as indices of atmospheric acidification, were determined by ion chromatography (IC-5000; Yokogawa, Tokyo, Japan) after ultrasonication with extra pure water purified by E-pure system (Barnstead, Dubuque, IA, U.S.A.).

Chemicals —— 1,3-, 1,6- and 1,8-DNPs, Ch, BbF and FNF were purchased from Aldrich Chemical Co. (Milwaukee, WI, U.S.A.). 1-NP and Py were obtained from Tokyo Kasei (Tokyo, Japan). Fl and BaA were from Nacalai Tesque, Inc. (Kyoto, Japan), and BkF and BaP were from Wako Pure Chemical Industries (Osaka, Japan). All standard solutions of heavy metal elements and water-soluble inorganic ions were purchased from Wako. All other chemi-

cals used in the sample pretreatments were of analytical-reagent grade.

Statistical Calculations —— We calculated the correlation coefficients from all the data by using the general statistical software "ANALYST" (Fujitsu, Tokyo, Japan) installed on a FACOM M-3400 computer (Fujitsu).

RESULTS AND DISCUSSION

Atmospheric Concentrations

Table 1 shows the atmospheric concentrations of PAHs and NPAHs in the three cities. As described in our previous report, concentrations tended to be higher in winter and lower in summer and to be higher in daytime lower at night, except for DNPs and 5-ring PAHs in Tokyo.[6] Only the samples in Sapporo had strong relationships between the concentration of each PAH and NPAH compound and the amount of airborne particulates. In the other two cities, however, the concentrations of these compounds were not always in accordance with the amount of airborne particulates.[6]

Table 2 shows the atmospheric concentrations of metal elements and inorganic ions. The seasonal variations of metal elements were not as great as those of PAHs and NPAHs, although the fact that some metal elements showed higher atmospheric concentrations in summer than in winter has been reported by Mukai *et al*.[9] Only the concentrations of V and SO_4^{2-} were clearly higher in summer in Kanazawa and Tokyo. If only the daytime data are considered, the concentrations of several metal elements, such as Zn, Pb, Mn, Ni and Cr, tended to be higher in summer in Kanazawa and Tokyo. In Sapporo, there were no clear seasonal differences in the concentrations of metal elements between in winter and summer. This lack of difference may be due to an extraordinarily high precipitation (75 mm) during the summer sampling period in Sapporo, which might have suppressed the generation of airborne particulates.

An important finding was the concentrations of both the heavy metal elements and water-soluble inorganic ions were strongly dependent on the amounts of airborne particulates. Figure 1 shows the relationships between airborne particulates and the atmospheric concentrations of Zn and NO_3^- as examples. Most of the other metal elements and inorganic ions showed similar tendencies. The concentrations of the metal elements and the inorganic ions increased with the increase in the amount of airborne particulates in all three cities.

Another interesting result was that the concentration of Fe in Tokyo was considerably high. The atmospheric concentrations of Fe, Mn and Ni are, in general, outstandingly high near steel manufacture plants and the annual concentration of Fe is higher than 3 $\mu g/m^3$ in such areas.[8] Considering that there was not any major steel manufacture plant near the sampling station of Tokyo, the high concentrations of Fe might be due to several large-scale construction works near the station.

Table 1. Atmospheric Concentrations of PAHs and NPAHs Determined in Our Previous Study[6]

Sample			Airborne Particulate $\mu g/m^3$	DNPs pg/m^3	1-NP pg/m^3	4-ring PAHs ng/m^3	5-ring PAHs ng/m^3
Kanazawa	Winter	Day	53.1±28.3	0.91±0.37	59.2± 8.8	3.5 ± 1.2	1.92±0.61
		Night	32.7±18.8	0.62±0.18	38.3± 14.6	2.6 ± 1.4	1.48±1.0
	Summer	Day	85.1±28.7	0.38±0.20	26.7± 13.0	1.6 ± 0.54	0.92±0.38
		Night	52.6±23.1	0.28±0.08	11.3± 4.1	0.49± 0.22	0.42±0.19
Sapporo	Winter	Day	106.2±53.9	5.7 ±3.3	413 ±230	12.6 ±10.2	5.15±4.2
		Night	58.6±40.6	2.6 ±2.2	197 ±151	5.7 ± 4.5	2.23±2.5
	Summer	Day	103.9±19.3	2.4 ±0.83	206 ± 76.5	6.9 ± 3.7	3.87±1.4
		Night	63.7±17.1	2.3 ±0.34	149 ± 64.8	5.2 ± 4.5	2.77±1.6
Tokyo	Winter	Day	177.7±62.2	2.0 ±0.75	163 ± 60.4	9.8 ± 5.2	3.79±1.6
		Night	139.4±48.5	2.2 ±0.73	120 ± 32.0	9.0 ± 4.4	4.36±2.4
	Summer	Day	208.5±21.5	2.3 ±0.58	130 ± 25.8	6.5 ± 1.5	4.97±1.2
		Night	161.4±13.6	2.9 ±0.92	75.3± 21.6	4.3 ± 0.63	4.17±0.88

All data represent mean ± S.D. DNPs =1,6-DNP + 1,8-DNP + 1,3-DNP. 4-ring PAHs = Fl + Py + BaA + Ch. 5-ring PAHs = BbF + BkF + BaP.

Table 2. Atmospheric Concentrations of Metal Elements and Inorganic Ions Analyzed in This Study

Sample			Cu	Zn	Cd	Pb	Fe	Mn	Ni	Cr	V
			ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
Kanazawa	Winter	Day	154± 91	42± 30	0.0±0.0	21±12	244± 233	8.7± 6.7	2.9± 3.6	14±1.0	1.5±0.7
		Night	174± 26	40± 36	0.0±0.0	28±26	250± 307	8.9± 7.1	4.1± 3.0	14±0.4	1.1±0.4
	Summer	Day	103± 27	61± 21	0.1±0.2	25±12	648± 252	15 ± 3.8	7.5± 3.6	16±0.8	2.5±1.0
		Night	163± 40	16± 10	0.0±0.0	18± 2.1	246± 97	6.7± 1.5	3.9± 2.8	14±1.7	1.4±0.4
Sapporo	Winter	Day	399± 67	170±153	0.0±0.0	32±21	1120± 856	23 ±16	10 ± 7.6	21±3.9	2.0±1.6
		Night	183± 29	65± 68	0.0±0.0	12±11	603± 651	11 ±11	6.8± 4.0	18±2.7	1.2±1.2
	Summer	Day	156± 37	129± 60	0.1±0.2	19± 5.1	1470± 713	26 ±11	9.6± 1.3	22±3.3	2.3±1.0
		Night	441±145	132± 72	0.0±0.0	18±12	1060± 496	20 ±11	11 ± 3.9	19±2.3	2.5±1.4
Tokyo	Winter	Day	253±101	479±111	0.6±0.8	91±13	4880±1990	106 ±43	33 ± 8.1	45±6.6	6.8±3.5
		Night	288± 89	603±143	3.9±1.9	151±54	4000±1550	76 ±28	25 ± 4.9	39±5.9	4.9±2.2
	Summer	Day	268± 38	509±136	2.4±1.8	104±22	4430± 637	123 ±21	41 ±10	55±4.2	14.8±3.6
		Night	295± 23	404± 45	5.9±2.4	112±29	3210± 334	82 ±29	36 ± 9.1	36±4.1	13.7±5.8

Sample			SO_4^{2-}	NO_3^-	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	NH_4^+	Total Ions
			μg/m^3	μg/m^3	μg/m^3	μg/m^3	μg/m^3	μg/m^3	μg/m^3	μeq/m^3
Kanazawa	Winter	Day	3.1±1.4	0.89±1.2	1.3 ±2.2	0.35±0.29	0.13±0.13	1.7 ±1.3	0.76±0.52	0.23±0.15
		Night	3.4±1.6	0.74±0.92	2.4 ±3.4	0.34±0.27	0.20±0.19	2.2 ±1.9	0.75±0.74	0.29±0.18
	Summer	Day	5.7±3.3	0.48±0.33	0.08±0.12	0.37±0.16	0.05±0.04	1.0 ±0.57	1.6 ±1.3	0.22±0.10
		Night	2.8±1.2	0.31±0.24	0.00±0.00	0.16±0.03	0.04±0.03	0.90±0.15	0.53±0.53	0.11±0.04
Sapporo	Winter	Day	5.7±3.1	2.6 ±3.3	4.2 ±2.3	2.3 ±1.8	0.38±0.24	1.7 ±1.5	2.1 ±1.6	0.56±0.27
		Night	3.4±1.8	1.3 ±1.5	2.9 ±3.2	1.1 ±1.1	0.26±0.21	1.9 ±1.7	0.87±0.54	0.35±0.17
	Summer	Day	3.3±1.0	0.92±0.50	0.17±0.34	1.2 ±0.51	0.04±0.04	0.35±0.28	0.73±0.36	0.17±0.06
		Night	4.4±3.7	1.1 ±0.83	0.06±0.09	0.94±0.62	0.05±0.06	0.50±0.46	0.91±1.0	0.19±0.14
Tokyo	Winter	Day	3.5±1.3	4.3 ±2.8	2.5 ±0.45	3.8 ±0.95	0.17±0.06	0.68±0.21	1.1 ±0.77	0.47±0.12
		Night	3.7±1.6	2.7 ±1.4	4.1 ±1.3	2.9 ±0.89	0.17±0.07	0.88±0.34	1.2 ±0.75	0.46±0.15
	Summer	Day	22.7±6.0	4.9 ±1.7	0.05±0.08	4.9 ±1.0	0.37±0.10	1.6 ±0.44	5.4 ±1.9	1.0 ±0.20
		Night	18.6±6.8	10.3 ±3.2	0.33±0.41	2.4 ±0.28	0.38±0.12	2.1 ±1.0	6.4 ±1.9	1.0 ±0.13

All data represent mean ± S.D.

Total concentrations of water-soluble inorganic ions were higher in winter and lower in summer in Kanazawa and Sapporo. Especially, the concentrations of Cl^- and Na^+ were much higher in winter in the two cities, suggesting the direct effect of the northwest wind from the Sea of Japan.[10] However, the concentration of Cl^- was also higher in winter in Tokyo, where the influence of the wet seasonal wind in winter might be very small. Considering that Na^+ showed the opposite seasonal variation in Tokyo, the high concentrations of Cl^- in the winter sample might have originated from some artificial emissions.[11]

Relationships between PAHs and NPAHs and Inorganic Pollutants

To clarify how atmospheric behaviors of PAHs and NPAHs were related to those of inorganic substances, the correlation coefficients were calculated from all the data obtained during the present survey (Table 3). Strong correlations were observed between PAHs and NPAHs and inorganic substances except Cl^-, Mg^{2+}, K^+ and Na^+ only in Sapporo, but the correlations were not so significant in Kanazawa and Tokyo. The significant correlations between PAHs and these inorganic substances have been reported by Zheng and Fang.[12] Among the metal elements that had strong correlations with PAHs and NPAHs in Sapporo, Pb, Zn, Cd and V originated from combustion.[13]

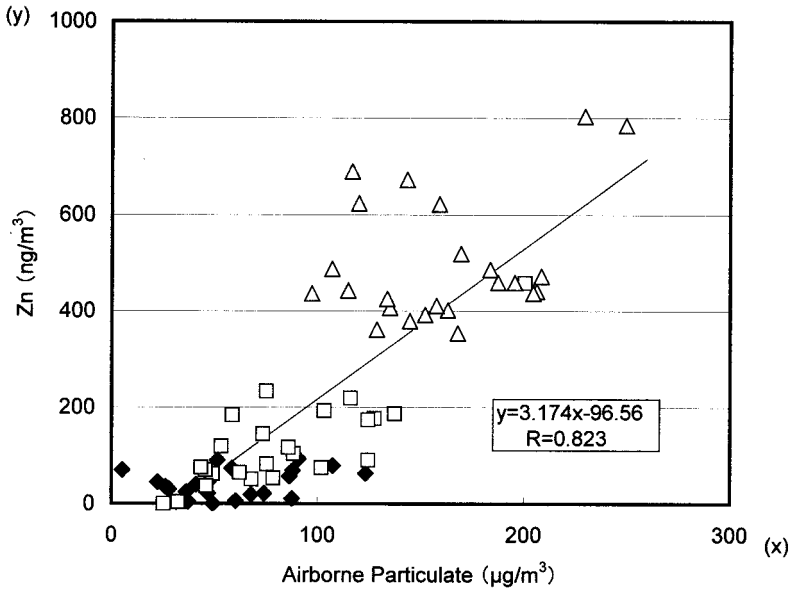

Fig. 1 (a). Plots of Zn *vs*. Airborne Particulates
Symbols: ◆, Kanazawa; □, Sapporo; △, Tokyo.

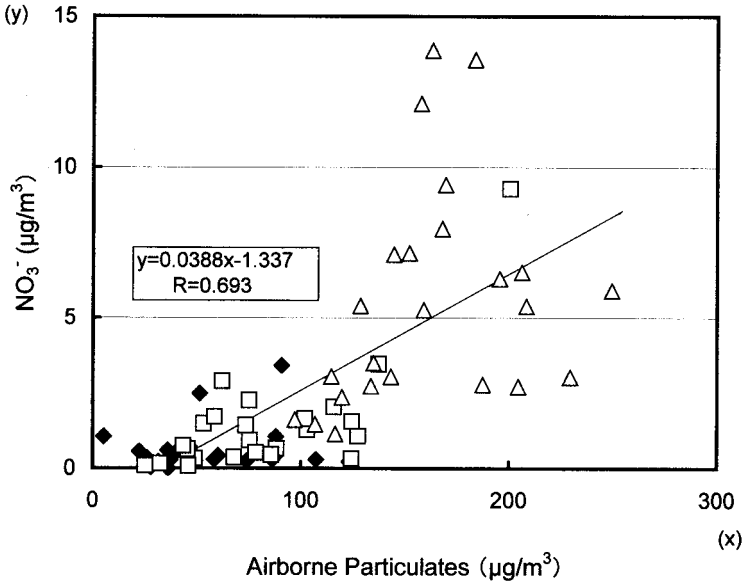

Fig. 1 (b). Plots of NO_3^- *vs*. Airborne Particulates
Symbols: ◆, Kanazawa; □, Sapporo; △, Tokyo.

These strong correlations between the organic compounds and the inorganic substances in Sapporo were mainly due to the winter samples (Table 3). Snow or ice covered the ground and suppressed the generation of coarse and soil-origin particulates. Therefore, the percentage of fine and combustion-derived particulates was relatively high in winter in Sapporo. This tendency was also found through the continuous monitoring on airborne particulates in a high latitude area.[14)]

When airborne particulates were fractionated into five particle sizes at the same sampling site using an Andersen high-volume air sampler, PAHs and NPAHs were mainly observed in the finest fraction (particle size < 1.1 μm).[15,16)] Figure 2 shows the ratios of NPAHs and inorganic substances in the finest fraction expressed as percentages of the total of the five fractions.[16,17)] The metal elements mainly detected in the finest fraction were Cd, Pb, V and Zn. These elements had significant correlations with

Table 3. Correlation Coefficients between Organic Compound (PAHs and NPAHs) and Inorganic Pollutants

Organic compounds	City	Season	A.P.	Cu	Zn	Cd	Pb	Fe	Mn	Ni	Cr	V
5Ring-PAHs = [BbF+BkF +BaP]	Kanazawa	Winter	−0.11	−0.26	0.39	—	0.12	0.25	0.16	−0.06	0.00	0.20
		Summer	0.25	−0.31	0.53	—	0.62	0.43	0.66	0.25	0.44	0.64
	Sapporo	Winter	0.93**	0.71*	0.98**	0.85**	0.79*	0.94**	0.95**	0.72*	0.86**	0.95**
		Summer	0.04	−0.09	−0.24	—	0.15	−0.35	−0.36	−0.46	−0.27	−0.42
	Tokyo	Winter	0.33	0.31	0.14	0.13	0.00	0.40	0.41	0.18	0.48	0.41
		Summer	0.62	0.22	0.70*	0.02	0.08	0.72*	0.23	−0.10	0.37	0.35
1-NP	Kanazawa	Winter	0.04	−0.03	0.04	—	−0.13	−0.03	−0.08	−0.18	0.02	0.22
		Summer	0.25	−0.28	0.62	—	0.88**	0.38	0.69*	0.30	0.44	0.74*
	Sapporo	Winter	0.95**	0.74*	0.91**	0.70*	0.86**	0.95**	0.95**	0.70*	0.85**	0.87**
		Summer	0.06	−0.07	−0.03	—	0.27	−0.15	−0.15	−0.15	−0.12	−0.09
	Tokyo	Winter	0.58	0.40	0.15	−0.20	−0.11	0.59	0.59	0.34	0.84**	0.55
		Summer	0.90**	−0.02	0.75*	−0.35	0.13	0.84**	0.46	0.01	0.73*	0.07
DNPs = [1,3-DNP+1,6-DNP +1,8-DNP]	Kanazawa	Winter	−0.20	−0.44	−0.19	—	−0.39	−0.33	−0.40	−0.48	−0.46	0.18
		Summer	0.15	0.12	0.45	—	0.79*	0.22	0.49	0.20	0.30	0.57
	Sapporo	Winter	0.97**	0.74*	0.90**	0.71*	0.82**	0.95**	0.98**	0.67*	0.84**	0.90**
		Summer	−0.18	0.10	−0.21	—	−0.02	−0.31	−0.32	−0.03	−0.24	−0.23
	Tokyo	Winter	0.30	0.80*	0.59	0.29	0.23	0.75*	0.69*	0.11	0.58	0.68*
		Summer	−0.05	0.60	0.05	0.66	0.30	0.02	−0.16	0.08	−0.12	0.32

Organic compounds	City	Season	SO_4^{2-}	NO_3^-	Cl^-	Ca^{2+}	Mg^{2+}	NH_4^+	K^+	Na^+
5Ring-PAHs = [BbF+BkF +BaP]	Kanazawa	Winter	0.03	0.20	−0.52	0.11	−0.50	0.21	−0.46	−0.49
		Summer	0.55	−0.06	0.03	0.47	−0.26	0.65	−0.05	−0.45
	Sapporo	Winter	0.91**	0.96**	−0.03	0.91**	0.51	0.90**	0.27	−0.38
		Summer	−0.01	0.19	0.04	−0.15	−0.27	0.23	−0.57	−0.31
	Tokyo	Winter	−0.03	0.08	0.53	0.36	0.65	−0.04	0.43	0.72*
		Summer	0.68*	−0.45	−0.27	0.51	0.12	0.34	−0.33	−0.11
1-NP	Kanazawa	Winter	−0.10	0.82	−0.36	−0.12	−0.45	0.02	−0.52	−0.35
		Summer	0.72*	−0.28	−0.15	0.53	−0.48	0.86**	0.03	−0.55
	Sapporo	Winter	0.95**	0.87**	−0.02	0.93**	0.52	0.88**	0.20	−0.39
		Summer	0.17	0.19	−0.19	0.15	−0.22	0.33	−0.55	−0.34
	Tokyo	Winter	0.16	0.62	0.07	0.67*	0.62	0.21	0.24	0.33
		Summer	0.42	−0.60	−0.29	0.74*	−0.09	−0.05	−0.25	−0.32
DNPs = [1,3-DNP+1,6-DNP +1,8-DNP]	Kanazawa	Winter	−0.32	−0.28	0.02	−0.38	−0.09	−0.08	−0.36	−0.02
		Summer	0.57	−0.48	−0.43	0.35	−0.66	0.74*	−0.10	−0.75*
	Sapporo	Winter	0.97**	0.88**	−0.05	0.95**	0.52	0.88**	0.18	−0.42
		Summer	0.06	0.06	−0.40	−0.06	−0.35	0.14	−0.12	−0.12
	Tokyo	Winter	0.37	0.17	0.63	0.62	0.85**	0.22	0.69*	0.64
		Summer	0.12	0.34	0.35	−0.19	0.24	0.28	−0.19	0.33

Level of significance *: $> 1\%$, **: $> 0.1\%$. A.P.: Airborne Particulates. Numbers of the Cd data in Kanazawa and in summer sample of Sapporo were insufficient to calculate the correlation coefficients.

PAHs and NPAHs in the winter samples of Sapporo (Table 3). Fe, Mn, and Cu are, in general, found in the coarse particle fraction and sometimes are regarded as crustal elements. However, they were strongly correlated with PAHs and NPAHs only in the winter samples of Sapporo. A possible source of these elements in winter is tire fragments of vehicles.[18] In addition, spiked tire was widely used in winter season during the time of the study.

Among the inorganic ions that were related to PAHs and NPAHs, SO_4^{2-} and NO_3^- were secondarily formed in the urban air from SO_2 and NO_x, respec-

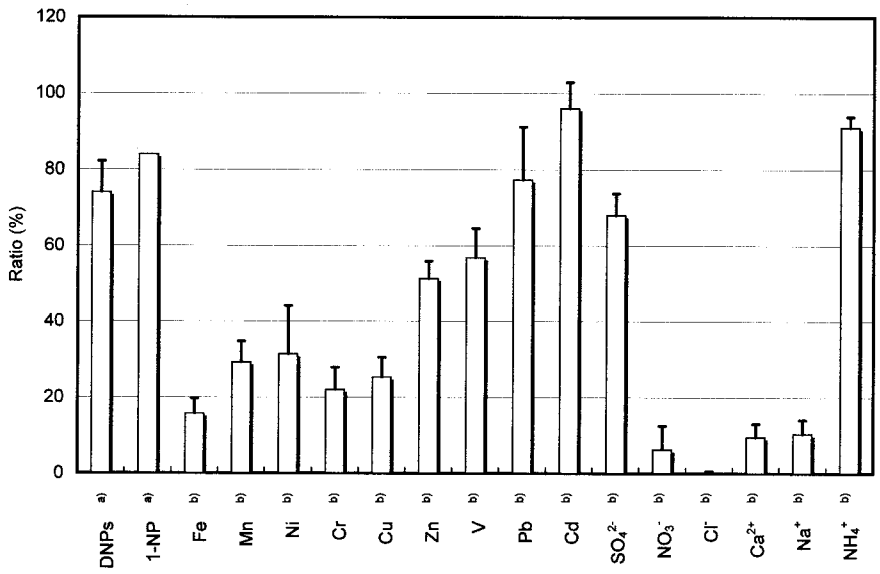

Fig. 2. NPAHs and Inorganic Substances in the Finest Particulate Fraction Expressed as a Percentage of the Total of the Five Fractions

a) Data in Ref. 16) were used for NPAHs. b) Data in Ref. 17) were used for heavy metals and inorganic ions. Each box and vertical bar represent mean and S.D., respectively.

tively, both of which might be directly emitted from vehicle exhausts. On the other hand, NH_4^+ and Ca^{2+} were not directly emitted from the combustion products, such as the exhausts from vehicle engines and domestic heating systems. However, NH_4^+, which was converted from NH_3 gas, might be detected as the inorganic compounds that were neutralized by SO_4^{2-} in the air or on the filters.[19] The behavior of Ca^{2+}, which was mainly observed in the coarse particulates, was not clear in this study.

Relationships between Each PAH and NPAH Compounds

Several researchers have attempted to calculate the correlation coefficients between each PAH compound.[20,21] In those cases, however, the number of PAHs was limited and the samples were collected at only a single site. Moreover, there has been no report concerning NPAHs. In this study, the correlation coefficients were calculated for each city to find the differences in the behaviors of PAHs and NPAHs. The results are shown in Table 4.

Three DNPs were strongly correlated with each other in Sapporo and Kanazawa. 1-NP had also the most significant correlation with each DNP in Sapporo, followed by Kanazawa. However, these strong relationships were not found in Tokyo at all. These results suggested that the emission sources of DNPs and 1-NP were the same in Sapporo and Kanazawa but other sources or the degradation/formation of these compounds should be considered in Tokyo. We previously reported that diesel-engine exhaust was the main source of atmospheric 1-NP commonly in each of the three cities but that the sources of atmospheric DNPs were not necessarily the same as 1-NP in Tokyo.[6] The difference in the correlation coefficients between the three cities in the present study might support our previous results. As another possibility, because the urban area of Tokyo is much wider than those of the other two cities, the air samples of Tokyo might include airborne particulates that had been transported from distant areas after long-time drift. The composition of NPAHs had probably changed during the drift owing to their secondary formation and photolysis.[22,23]

Both 1-NP and DNPs were strongly correlated with PAHs in Sapporo and Kanazawa, but not in Tokyo. The low correlation coefficients in Tokyo might be due to multiple sources and formation/degradation of PAHs and/or DNPs. According to our experiments, the degradation rates of NPAHs, such as 1-NP and 1,3-DNP were significantly larger than those of PAHs, such as Py and BaP both under sunlight and UV light (254 nm).[24] This result indicated that NPAHs were less stable than PAHs in the atmosphere. Because the duration of sunshine was the longest in Tokyo during the present sampling periods, NPAHs, such as DNPs, might be decomposed more rapidly than PAHs in Tokyo.

Though the mean concentrations of NPAHs in Kanazawa were much lower than in Sapporo both

Table 4. Correlation Coefficients between PAH and NPAH Compounds

Compound		1,6-DNP	1,8-DNP	1,3-DNP	DNPs	1-NP	Fl	Py	BaA	Ch	BbF	BkF
	Kanazawa											
1,6-DNP	Sapporo											
	Tokyo											
	Kanazawa	0.98**										
1,8-DNP	Sapporo	0.99**										
	Tokyo	0.42										
	Kanazawa	0.96**	0.96**									
1,3-DNP	Sapporo	0.98**	0.98**									
	Tokyo	0.57*	0.77**									
	Kanazawa	0.99**	0.99**	0.98**								
DNPs	Sapporo	1.00**	1.00**	0.99**								
	Tokyo	0.88**	0.76**	0.87**								
	Kanazawa	0.80**	0.79**	0.86**	0.83**							
1-NP	Sapporo	0.97**	0.97**	0.95**	0.97**							
	Tokyo	−0.05	0.38	0.17	0.12							
	Kanazawa	0.69**	0.70**	0.67**	0.69**	0.76**						
Fl	Sapporo	0.93**	0.92**	0.90**	0.93**	0.94**						
	Tokyo	−0.08	0.55*	0.13	0.14	0.58*						
	Kanazawa	0.71**	0.73**	0.77**	0.75**	0.81**	0.90**					
Py	Sapporo	0.83**	0.81**	0.81**	0.82**	0.85**	0.93**					
	Tokyo	−0.10	0.49	0.05	0.08	0.65**	0.94**					
	Kanazawa	0.85**	0.87**	0.89**	0.88**	0.87**	0.81**	0.93**				
BaA	Sapporo	0.89**	0.87**	0.87**	0.88**	0.91**	0.93**	0.96**				
	Tokyo	0.10	0.35	−0.04	0.13	0.60*	0.73**	0.86**				
	Kanazawa	0.80**	0.82**	0.83**	0.83**	0.88**	0.88**	0.94**	0.96**			
Ch	Sapporo	0.87**	0.85**	0.85**	0.86**	0.89**	0.92**	0.95**	1.00**			
	Tokyo	0.30	0.38	0.06	0.29	0.61*	0.54*	0.71**	0.91**			
	Kanazawa	0.73**	0.75**	0.78**	0.76**	0.81**	0.83**	0.94**	0.93**	0.97**		
BbF	Sapporo	0.84**	0.81**	0.81**	0.82**	0.86**	0.89**	0.91**	0.97**	0.98**		
	Tokyo	0.65**	0.33	0.19	0.53*	0.38	0.30	0.37	0.56*	0.71**		
	Kanazawa	0.69**	0.71**	0.74**	0.72**	0.80**	0.78**	0.89**	0.91**	0.96**	0.99**	
BkF	Sapporo	0.86**	0.83**	0.83**	0.84**	0.87**	0.90**	0.90**	0.98**	0.98**	1.00**	
	Tokyo	0.61*	0.41	0.19	0.53*	0.47	0.40	0.48	0.68**	0.80**	0.98**	
	Kanazawa	0.73**	0.73**	0.78**	0.75**	0.85**	0.78**	0.91**	0.94**	0.96**	0.98**	0.98**
BaP	Sapporo	0.82**	0.78**	0.80**	0.80**	0.83**	0.85**	0.88**	0.96**	0.97**	0.99**	0.99**
	Tokyo	0.54*	0.38	0.18	0.47	0.45	0.40	0.53*	0.80**	0.88**	0.89**	0.94**

Level of significance *: $> 1\%$, **: $> 0.1\%$. DNPs = 1,6-DNP + 1,8-DNP + 1,3-DNP.

in winter and summer, the patterns of the correlation coefficients between NPAH compounds and between PAHs and NPAHs in Kanazawa were surprisingly similar to the patterns of Sapporo. However, the atmospheric behaviors of PAHs and NPAHs in Tokyo were quite different from those in the other two cities.

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