Comparison of Atmospheric Polycyclic Aromatic Hydrocarbons and Nitropolycyclic Aromatic Hydrocarbons in an Industrialized City (Kitakyushu) and Two Commercial Cities (Sapporo and Tokyo)

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Airborne particulates were collected at a site near a group of factories in Kitakyushu, one of the most industrialized cities in Japan, and at downtown sites in Sapporo and Tokyo, typical large commercial cities. We determined the levels of polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs), which are known to be carcinogenic and/or mutagenic. The atmospheric concentrations of most PAHs with 4-, 5-, and 6-rings were higher in Kitakyushu and Tokyo than in Sapporo. On the other hand, atmospheric concentrations of the strongly mutagenic NPAHs were the highest in Sapporo, intermediate in Tokyo, and lowest in Kitakyushu. The atmospheric concentrations of 1-nitropyrene (1-NP) in Kitakyushu were one order of magnitude lower than those in the two commercial cities. Therefore the concentration ratios of NPAHs to their nucleus PAHs were significantly smaller in Kitakyushu than in the two commercial cities. This result suggested that the atmospheric levels of NPAHs in Kitakyushu were comparatively low, although the air in Kitakyushu was as heavily polluted with PAHs as the air in Tokyo. The concentration ratio of dinitropyrenes (DNPs) to 1-NP in Kitakyushu was much higher than that in the other two cities. A possible reason for the above two differences between the two types of cities is the contribution of chimney exhaust of steel manufacturing plants in Kitakyushu, which contains high concentrations of PAHs.

Key words —— polycyclic aromatic hydrocarbon, nitropolycyclic aromatic hydrocarbon, urban air, diesel exhaust particulate, steel manufacturing plant, airborne particulate

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INTRODUCTION

In Japan, the mortality rate from lung cancer has increased in recent years. The age-adjusted mortality rate from lung cancer is especially high in urban or populated areas,[1] and degradation of air quality is considered to be one of the reasons. Some polycyclic aromatic hydrocarbons (PAHs) in the atmosphere, including benzo[*a*]pyrene (BaP), are carcinogenic. Estimates of the toxicities of several PAHs indicate that they have high probabilities of inducing cancer or tumors.[2] Moreover, nitropolycyclic aromatic hydrocarbons (NPAHs), which are more carcinogenic and/or mutagenic,[3] have been found in extracts of airborne particulates.[4,5] However, the atmospheric behavior of NPAHs is not well known because of their extremely low concentrations and the low detection sensitivity.

Most NPAHs are generated when PAHs produced by the incomplete combustion of a fossil fuel are combined with nitrogen oxide produced by combustion of N_2 under high-temperature conditions.[4] Therefore most sources of artificial emissions of PAHs and NPAHs are thought to be almost the same. On the other hand, NPAHs are also generated by radical reactions of PAHs and nitrogen oxide in the atmosphere.[6,7]

In previous studies, we continuously monitored airborne particulates in Kanazawa, Sapporo, and Tokyo and measured the atmospheric concentrations of PAHs and NPAHs using HPLC with fluorescence and chemiluminescence detections.[8–13] These studies demonstrated that;

Table 1. Characteristics of the Sampling Sites

City	Population[a)]	Percentage of registered diesel engine vehicles[b)]	Volume of kerosene purchased per home (l)	Total precipitation (mm)	
				Winter[c)]	Summer[d)]
Kitakyushu (industrialized)	1016264	26.3	224	7	188
Sapporo (commercial)	1822300	38.5	1343	27	92
Tokyo (commercial)	7846823	20.5	85	13	62

a) Data were obtained from the latest home page of each city. Population of Tokyo means the population of 23 wards in the Tokyo metropolitan area. *b*) The data of Kitakyushu represents the percentage of registered diesel engine vehicles in Fukuoka Prefecture. *c*) Winter: 27–31 Jan. and 3–7 Feb., 1997. *d*) Summer: 28 July–1 Aug. and 4–8 Aug., 1997.

The main emission source of PAHs and NPAHs is the exhaust of diesel-engine vehicles in urban air.[10)]

The atmospheric concentrations of PAHs and NPAHs strongly depend on traffic volume, which is high in the daytime and low at night.[10,11)]

Atmospheric concentrations of PAHs and NPAHs were higher in winter than in summer because of higher atmospheric stability and larger combustion of heating fuel in winter.[11)]

The concentration ratios of dinitropyrenes (DNPs) to 1-nitropyrene (1-NP) decreased as the percentage of the vehicles using diesel fuel increases.[12)]

Atmospheric concentrations of PAHs and NPAHs were partly correlated with those of inorganic air pollutants such as several heavy metals originating from combustion processes and some inorganic water-soluble ions.[13)]

Although these three cities (Kanazawa, Sapporo and Tokyo) differ considerably in size, they are all commercial cities, that is, they are not strongly affected by emissions from industrialized areas. Thus it is not clear whether the atmospheric PAHs and NPAHs in industrialized areas are the same as those in commercial cities. The purpose of this study was to determine whether the atmospheric behavior and compositions of PAHs and NPAHs in Kitakyushu, an industrialized city, were different from those in commercial cities.

MATERIALS AND METHODS

Sampling —— Airborne particulates were collected in the urban areas of Kitakyushu (northern Kyushu), Sapporo (central Hokkaido), and Tokyo (central Honshu). Single, high-volume air samplers (MODEL 120F, Kimoto Electronics Co., Ltd., Osaka, Japan) were placed on the roof of a three-story building near an industrialized area of Kitakyushu and by the sides of busy traffic roads near the centers of Sapporo and Tokyo. Airborne particulates were collected on 2500QAT-UP quartz fiber filters (20 cm × 25 cm, Pallflex Products) at a flow rate of 1.0–1.5 m^3/min. Air was sampled at each location for 10 24-hr periods (corresponding to weekdays) both in winter (starting on 27–31 Jan. and 3–7 Feb.) and in summer (starting on 28 July–1 Aug. and 4–8 Aug). All sampling periods started and ended at 10:00. Characteristics of the sampling sites and weather conditions (total precipitation) during the sampling periods are shown in Table 1. The filters, which adsorbed airborne particulates, were weighed after reaching constant weights and then cut into several pieces for analysis.

Analytical Methods —— The filter samples were pretreated as described previously[9)] with several modifications. Pretreatment consists of extraction, clean up, and reduction of the nitro groups to amino groups. After pretreatment, PAHs and NPAHs were determined simultaneously using two HPLC systems.[9)] The details of the apparatus of the HPLC systems for PAHs and NPAHs were described previously.[13)]

Compounds were measured using 2-fluoro-7-nitrofluorene (FNF) as an internal standard. The compounds measured included 10 types of PAH (fluoranthene (Fl), pyrene (Py), benz[*a*]anthracene (BaA), chrysene (Ch), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), BaP, dibenz[*a*,*h*]anthracene (DahA), benzo[*ghi*]perylene (BghiP) and Indeno[1,2,3-*cd*]pyrene (IcdP)) and four strongly mutagenic NPAHs (1,3-, 1,6-, and 1,8-DNP and 1-NP).

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, Py, and IcdP were obtained from Tokyo Kasei (Tokyo, Japan). Fl and BaA were from Nacalai Tesque, Inc. (Kyoto, Japan), and BkF, BaP, DahA, and BghiP were from Wako Pure Chemical Industries (Osaka, Japan). All other chemicals used in the sample pretreatments were of analytical reagent grade.

Table 2. Atmospheric Concentrations of PAHs and NPAHs Determined in This Study

Compound		Kitakyushu		Sapporo		Tokyo	
		Winter	Summer	Winter	Summer	Winter	Summer
A. P.	$\mu g/m^3$	64 ± 31	43 ± 25	75 ± 34	75 ± 38	130 ± 30	83 ± 25
Fl	ng/m^3	1.1 ± 0.42	0.49 ± 0.55	1.7 ± 0.79	0.63 ± 0.16	1.3 ± 0.65	0.38 ± 0.13
Py	ng/m^3	0.87 ± 0.32	0.49 ± 0.49	2.2 ± 1.1	0.89 ± 0.26	1.5 ± 0.77	0.63 ± 0.40
BaA	ng/m^3	0.66 ± 0.46	0.30 ± 0.34	0.64 ± 0.25	0.46 ± 0.17	0.87 ± 0.50	0.32 ± 0.16
Ch	ng/m^3	1.1 ± 0.68	0.39 ± 0.46	0.82 ± 0.32	0.59 ± 0.19	1.2 ± 0.71	0.43 ± 0.23
BbF	ng/m^3	1.1 ± 0.86	0.58 ± 0.71	0.58 ± 0.25	0.58 ± 0.21	0.91 ± 0.56	0.61 ± 0.30
BkF	ng/m^3	0.48 ± 0.35	0.30 ± 0.35	0.28 ± 0.13	0.25 ± 0.091	0.40 ± 0.23	0.25 ± 0.12
BaP	ng/m^3	0.76 ± 0.61	0.45 ± 0.53	0.53 ± 0.25	0.50 ± 0.22	0.78 ± 0.45	0.48 ± 0.24
DahA	ng/m^3	0.28 ± 0.20	0.14 ± 0.15	0.17 ± 0.10	0.17 ± 0.081	0.25 ± 0.14	0.16 ± 0.084
BghiP	ng/m^3	0.80 ± 0.58	0.44 ± 0.39	0.66 ± 0.30	0.91 ± 0.41	1.1 ± 0.55	0.88 ± 0.44
IcdP	ng/m^3	0.75 ± 0.55	0.44 ± 0.44	0.53 ± 0.27	0.53 ± 0.25	0.77 ± 0.41	0.50 ± 0.26
1-NP	ng/m^3	0.014 ± 0.0079	0.0057 ± 0.0027	0.27 ± 0.11	0.13 ± 0.057	0.17 ± 0.084	0.045 ± 0.019
1,3-DNP	pg/m^3	0.10 ± 0.082	0.17 ± 0.13	1.2 ± 0.62	0.35 ± 0.11	0.67 ± 0.32	0.35 ± 0.24
1,6-DNP	pg/m^3	0.41 ± 0.32	0.13 ± 0.088	1.1 ± 0.47	0.35 ± 0.12	0.94 ± 0.47	0.22 ± 0.12
1,8-DNP	pg/m^3	0.32 ± 0.12	0.16 ± 0.070	1.6 ± 0.56	0.82 ± 0.29	1.4 ± 0.56	0.44 ± 0.22

A. P., airborne particulate. Data are expressed as mean ± S.D. ($n = 10$).

RESULTS AND DISCUSSION

Concentrations of PAHs and NPAHs

The atmospheric concentrations of PAHs and NPAHs and the amounts of airborne particulates in each city are shown in Table 2. Little precipitation was observed during the winter sampling periods in Kitakyushu and Tokyo (Table 1). This might explain why the amounts of airborne particulates in these two cities were higher in winter than in summer.

The concentrations of PAHs and NPAHs were higher in winter than in summer in each city. This result is similar to our previous ones.[12] The concentrations of Fl and Py were higher in Sapporo than in Tokyo and Kitakyushu in both winter and summer. However, the concentrations of the other PAHs with 4-, 5-, and 6-rings in winter were higher in Kitakyushu and Tokyo than in Sapporo. The differences in the concentrations of these PAH compounds among the three cities were small in summer.

Although the urban air of Kitakyushu was as heavily polluted with PAHs as that of Tokyo, atmospheric concentrations of NPAHs in Kitakyushu were lower than those in Tokyo and Sapporo in both winter and summer. Interestingly, the concentrations of 1-NP in Kitakyushu (0.014 ng/m^3 in winter and 0.0057 ng/m^3 in summer) were at least one order of magnitude lower than the concentrations in the other two cities.

The percentages of registered vehicles with diesel engines and the volume of kerosene purchased per home differ considerably among the three cities (Table 1). Therefore the ratio of particulates carrying adsorbed pollutants to the amount of total airborne particulates may also differ for each city. The concentrations of PAHs and NPAHs should thus be expressed not only as an atmospheric concentration (ng/m^3 air) but also as a fraction of the total mass of particulates (ng/mg particulates). The concentrations of PAHs and NPAHs in airborne particulates are shown in Table 3. The concentrations of PAHs except for Fl and Py in airborne particulates were

Table 3. Concentrations of PAHs and NPAHs in Airborne Particulates

Compound		Kitakyushu	Sapporo	Tokyo
Fl	ng/mg	13 ± 4.9	15 ± 11	7.3 ± 3.2
Py	ng/mg	12 ± 1.8	20 ± 13	13 ± 2.6
BaA	ng/mg	7.8 ± 2.5	7.3 ± 2.7	5.3 ± 1.7
Ch	ng/mg	12 ± 4.8	9.6 ± 3.7	7.3 ± 2.7
BbF	ng/mg	14 ± 1.8	7.8 ± 1.0	7.3 ± 0.38
BkF	ng/mg	6.6 ± 0.2	3.5 ± 0.78	3.0 ± 0.053
BaP	ng/mg	10 ± 0.58	6.8 ± 1.1	6.1 ± 0.16
DahA	ng/mg	3.6 ± 0.75	2.3 ± 0.33	2.0 ± 0.072
BghiP	ng/mg	11 ± 0.47	10 ± 0.69	9.7 ± 2.1
IcdP	ng/mg	9.9 ± 0.61	6.9 ± 1.0	6.1 ± 0.36
1-NP	ng/mg	0.23 ± 0.096	2.7 ± 1.6	0.94 ± 0.49
1,3-DNP	pg/mg	4.1 ± 0.18	11 ± 9.4	4.7 ± 0.85
1,6-DNP	pg/mg	7.9 ± 6.5	10 ± 8.8	5.0 ± 3.2
1,8-DNP	pg/mg	5.9 ± 1.8	16 ± 9.4	8.2 ± 3.2

Data are expressed as mean ± S.D. ($n = 20$).

slightly higher in Kitakyushu than in the other two cities, although the total amount of airborne particulates in Kitakyushu was considerably lower than in the other two cities. Kitakyushu has many steel manufacturing plants, which are possibly the main contributors of atmospheric PAHs. These plants are located only 2 km north of the sampling site. Therefore the ratio of the particulates emitted from these plants to the total amount of airborne particulates may be higher in Kitakyushu. The order of the concentrations of PAHs in airborne particulates differed slightly from the order of the atmospheric concentrations shown in Table 2. For example, the concentrations of BbF, BkF, and BaP in the airborne particulates were higher in Kitakyushu than in Sapporo and Tokyo, although the atmospheric concentrations of these three 5-ring PAHs were similar and higher in Kitakyushu and Tokyo and lower in Sapporo.

However, the concentration of 1-NP in airborne particulates was the highest in Sapporo, intermediate in Tokyo, and lowest in Kitakyushu. This order is in agreement with the order of the atmospheric concentrations. The concentrations of each DNP in airborne particulates were also the highest in Sapporo, and the concentrations in Kitakyushu and Tokyo were similar and slightly lower than the concentrations in Sapporo. This order is different from the order of the atmospheric concentrations of DNPs.

Concentration Ratios of PAHs and NPAHs

The concentration ratios of several PAH compounds have been often used in order to deduce the origins and behavior of environmental PAHs.[14–17] The [BaA]/[Ch] ratio is regarded as an indicator of the aging of air masses with higher values for freshly emitted air masses, and this ratio has a value of about 0.40 at sites distant from PAH sources.[17] In the present study, however, there were no clear differences in the [BaA]/[Ch] ratio among the three cities, which ranged from 0.69 to 0.77, suggesting that the differences in the average ages of the air masses among the three cities were small. The larger ratios observed in this study suggest that the sampling points in the three cities were close to the sources of emission of PAHs, and therefore the PAH composition may have undergone little metamorphosis.

Larger values of [Fl]/[Py] and smaller values of [BghiP]/[IcdP] and [BghiP]/[BaP] have been regarded as indicators of contributions of coal combustion.[14,16] The [Fl]/[Py] ratio was larger in Kitakyushu and the [BghiP]/[IcdP] and [BghiP]/[BaP] ratios were smaller in Kitakyushu than those in the two commercial cities. These results might be due to the effects of coal combustion at steel manufacturing plants in Kitakyushu. The increase in the [BghiP]/[BaP] ratio observed in Kitakyushu during the previous 20 years[14] might be due to a decline in steel manufacturing.

Table 4. Concentration Ratios of PAH and NPAH Compounds

Ratio	Kitakyushu	Sapporo	Tokyo
[Fl]/[Py]	1.2	0.74	0.74
[BaP]/[Py]	0.72	0.32	0.52
[1-NP]/[Py]	0.011	0.11	0.076
[DNPs]/[Py]	0.00066	0.0012	0.0013
[1-NP]/[BaP]	0.016	0.39	0.16
[DNPs]/[BaP]	0.00091	0.0045	0.0026
[DNPs]/[1-NP]	0.060	0.011	0.017
[BaA]/[Ch]	0.69	0.77	0.72
[BkF]/[BaP]	0.65	0.51	0.52
[BghiP]/[IcdP]	1.0	1.5	1.6
[BghiP]/[BaP]	0.93	1.4	1.5

All ratios were calculated from the mean concentration of each compound in every city.

We previously used the [DNPs]/[1-NP] ratio to estimate the contribution of diesel exhaust to the atmospheric NPAHs.[10] This ratio was much smaller in diesel exhaust particulates (DEP; 0.013) than in gasoline exhaust particulates (0.56) and the ratio for airborne particulates was close to the ratio for DEP at urban sites in commercial cities.[12] In the present study, the [DNPs]/[1-NP] ratios in Sapporo (0.011) and Tokyo (0.017) (Table 4) were close to the ratio for DEP. The [DNPs]/[1-NP] ratios in Kitakyushu (0.052 in winter and 0.069 in summer) were several times higher than the ratios in the commercial cities. This suggests that Kitakyushu had another major source of NPAHs other than diesel exhaust.

We also calculated this ratio for Muroran, a large steel manufacturing center in Hokkaido. The value in Muroran was 0.024, which was calculated from the mean atmospheric concentrations of 1-NP (0.068 ng/m^3) and DNPs (1.54 pg/m^3) in winter.[18] The sampling site of Muroran was located near steel and coke manufacturing plants and also faced a busy traffic road. Therefore the air samples collected in Muroran might contain both diesel exhaust and exhaust from the steel and coke manufacturing plants. This can explain why the [DNPs]/[1-NP] ratio in Muroran was slightly larger than the ratios in the above two commercial cities but smaller than that in Kitakyushu.

We previously showed that the ratios [1-NP]/

[Py], [DNPs]/[Py], [1-NP]/[BaP], and [DNPs]/[BaP] were much larger at a downtown site than at a suburban site in Kanazawa.[19] This result suggested that the degradation rate of 1-NP and DNPs in the atmosphere was much faster than the degradation rate of Py and BaP. In the present study, the above four ratios were notably smaller in Kitakyushu than in the commercial cities (Table 4). In particular, the [1-NP]/[Py] and [1-NP]/[BaP] ratios in Kitakyushu were one order of magnitude smaller than those in the commercial cities. The [1-NP]/[BaP] and [DNPs]/[BaP] ratios in Muroran were 0.0056 and 0.00013, respectively.[18] Both of these values were still smaller than those in Kitakyushu. The above results suggest that the emissions of steel manufacturing plants contained abundant PAHs but only small amounts of NPAHs.

In conclusion, clear differences in the composition of atmospheric PAHs and NPAHs were observed between the industrialized city of Kitakyushu and the commercial cities of Sapporo and Tokyo. The air of Kitakyushu was heavily polluted with PAHs that were probably emitted from steel manufacturing plants. However, the concentration of 1-NP in Kitakyushu was not much higher than the concentrations of DNPs. This result might be mainly due to differences in the composition of PAHs and NPAHs between DEP and the exhaust from steel manufacturing plants. Since we have few data on the emission sources other than DEP, it is necessary to determine the exact composition of PAHs and NPAHs of the emission sources, such as exhaust of steel manufacturing plants and other sources originating from coal combustion.

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