

Comparison of Atmospheric Nitropolycyclic Aromatic Hydrocarbons in Vladivostok, Kanazawa and Toyama

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Airborne particulates were collected simultaneously at Vladivostok, Kanazawa and Toyama. 1,3-, 1,6-, 1,8-Dinitropyrenes (DNPs), 1-, 2-, 4-nitropyrenes (NPs), 2-nitrofluorene and 6-nitrochrysene in the particulates were analyzed by HPLC with chemiluminescence detection. All compounds were detected not only in Kanazawa but also in Vladivostok and Toyama. Moreover, five unknown peaks which might be nitropolycyclic aromatic hydrocarbons were detected only in chromatograms of Vladivostok. The [DNPs]/[1-NP] ratios at all stations were near the value found in diesel-exhaust particulates, suggesting that one of the main contributors of these compounds was diesel-engine vehicles not only in Kanazawa and Toyama but also in Vladivostok. However, the difference in traffic volume at two stations in Vladivostok did not have a significant effect on the concentrations of DNPs and NPs in contrast to two stations in Kanazawa. These results suggested sources other than diesel-engine vehicles also contributing to DNPs and NPs in Vladivostok. Seasonal variations similar to those in Kanazawa were observed in Vladivostok and Toyama. As in Kanazawa, the [2-NP]/[1-NP] ratio in Vladivostok was larger at the lighter traffic station than that at heavier traffic station. This suggested that, as in Kanazawa, 2-NP was formed in the atmosphere in Vladivostok.

Key words — nitropolycyclic aromatic hydrocarbon, dinitropyrene, mutagenicity, carcinogenicity, airborne particulate

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) including benzo[*a*]pyrene (BaP) in the air have been considered as a cause of lung cancer.¹⁾ In recent years, the concentration of BaP showed a downward trend in Japan.²⁾ However, the rate of death of lung cancer has increased annually.³⁾ The Ames test using the *Salmonella typhimurium* (*S. typhimurium*) strains was often used as a mutagenicity assay.⁴⁾ By this test, the direct-acting mutagenic activity of airborne particulates in the absence of metabolic-activating enzymes (-S9 mix) has been increasing year by year in spite of the decrease of the indirect-acting mutagenic activity.²⁾ Some of nitropolycyclic aromatic hydrocarbons (NPAHs) in airborne particulates, especially 1,3-, 1,6- and 1,8-DNPs exhibited direct-

acting mutagenicity.^{5,6)} Therefore, it is essential to clarify the relationship between the increase of lung cancer and atmospheric NPAHs.

NPAHs are formed mainly through imperfect combustion of organic matters. NPAHs were detected in exhaust particulates from diesel- and gasoline-engine vehicles,⁷⁾ and also detected in smoke from factories,⁸⁾ carbon black, photocopier toners,⁹⁾ waste water and sediments.⁷⁾ Additionally, several NPAHs were found to be formed in the atmosphere.^{5,10-12)}

According to our previous studies in Kanazawa, large correlation coefficients between the atmospheric concentrations of DNPs (1,3-DNP + 1,6-DNP + 1,8-DNP) and 1-NP and the traffic volume suggested that automobiles were the major source.¹³⁾ The concentrations of DNPs and 1-NP were higher in winter than in summer because of the highly stable air in winter and of the oil heating.^{14,15)} Moreover, 2-NP was not detected in diesel-particulates but was found in the atmosphere.¹⁵⁾ The same results were

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also observed in Tokyo and Sapporo.¹⁶⁾

However, in countries using large amounts of coal energy, the contributors and behaviors of NPAHs in urban air are not known. Vladivostok, Russia, is a typical city which uses large amounts of coal energy. Therefore, in this study, we collected airborne particulates simultaneously in Vladivostok, Russia, Kanazawa and Toyama, Japan, and determined NPAHs such as DNPs and NP. By comparing the data of the three cities, we hoped to obtain a better understanding of the characteristics of NPAHs in three cities.

MATERIALS AND METHODS

Chemicals — 1,3-, 1,6-, 1,8-DNPs, 1-NP and 2-fluoro-7-nitrofluorene (FNF, internal standard) were purchased from Aldrich Chemical Company (Milwaukee, WI, U.S.A.). 2-, 4-NP and 2-nitrofluorene (NFR) were kindly provided by Dr. Yoshiharu Hisamatsu of the National Institute of Public Health (Tokyo, Japan) and 6-nitrochrysene (NC) was kindly provided by Dr. Nobuyuki Sera of the Fukuoka Institute of Health and Environmental Science (Fukuoka, Japan). All other chemicals used were of analytical-reagent grade.

Sampling and Pretreatment Procedures of Airborne Particulates — High-volume air samplers (Kimoto Electric Company Limited, Osaka, Japan) were set at five stations in Vladivostok, Kanazawa and Toyama: V-1 (Vladivostok, Russia) was on the roof of a three-story building and there were no heavy traffic roads or factories near V-1. V-2 (50, Svetlanskaya street Vladivostok, Russia) was on a veranda which was about 4 m above ground level and over a heavy traffic road. K-1 (Kanazawa, Japan) was on the roof of a three-story building and 6 km southeast of the downtown area. There were no major contributors of NPAHs such as heavy traffic roads or factories near K-1. K-2 (Kanazawa, Japan) was on the sidewalk 1 m away from a heavy traffic road and about 1.5 m from ground level. T-1 (Toyama, Japan) was on the roof of a four-story building and there were not any major contributors near T-1.

Airborne particulates were sampled simultaneously over a week in each season in 1999 (January 26–February 2, April 22–29, July 26–August 2, November 1–8). Filters were changed at 10:00 am every day. Airborne particulates were collected on quartz fiber filters (2500QAT-UP, 8" × 11", Pallflex

Products, Putnam, CT, U.S.A.) at a flow rate of 1–1.5 m³/min. After being dried in a desiccator in the dark, the filters were weighed and then stored in a refrigerator (–20°C) until use.

The filters were treated according to our previous report.¹⁷⁾ A piece of each filter containing less than 10 mg airborne particulates was thoroughly cut into small pieces. The small pieces were placed in a flask. NPAHs were extracted ultrasonically twice with benzene/ethanol (3 : 1, v/v) and then the solution was filtered. The filtrate was cleaned by extraction with sodium hydroxide solution, sulfuric acid solution, water, and then was evaporated to dryness. The residue was dissolved in ethanol and refluxed with sodium hydrosulfide. The reaction solution was extracted with benzene, and the benzene phase was evaporated to dryness. The residue was redissolved into 0.5 ml of acetonitrile containing 10 mM ascorbic acid. This sample solution was injected into the following HPLC system.

HPLC — 1,3-, 1,6-, 1,8-DNPs, 1-, 2-, 4-NPs, 2-NFR and 6-NC were simultaneously analyzed by using a HPLC system with chemiluminescence detection¹⁷⁾ with several modifications. The HPLC system consisted of two mobile phase pumps (LC-10A, Shimadzu, Kyoto, Japan), a chemiluminescence reagent solution pump (DMX-2000, Sanuki, Tokyo, Japan), a chemiluminescence detector (CLD-10A, Shimadzu, Kyoto, Japan), a system controller (SCL-10A, Shimadzu, Kyoto, Japan), a chromatopac integrator (C-R4A, Shimadzu, Kyoto, Japan), a degasser (DGU-14A, Shimadzu, Kyoto, Japan), an auto sample injector (SIL-10A, Shimadzu, Kyoto, Japan), a column oven (CTO-10AC, Shimadzu, Kyoto, Japan), a guard column (Cosmosil 5C18-MS, 4.6 i.d. × 10 mm, Nacalai Tesque, Kyoto, Japan) and two analytical columns (both Cosmosil 5C18-MS, 4.6 i.d. × 250 mm, Nacalai Tesque, Kyoto, Japan) connected in series.

RESULTS AND DISCUSSION

Chromatograms

Figure 1 shows chromatograms of NPAH standards and extracts from airborne particulates collected at V-1, V-2, K-1, K-2 and T-1 on the same day in winter, 1999. Peaks of 1,3-, 1,6-, 1,8-DNPs, 1- and 2-NPs were all detected at every sampling station. Peaks at 18.3 min and 33.5 min were identified as 2-NFR and 4-NP, respectively, by using the standards, although the intensities of these peaks

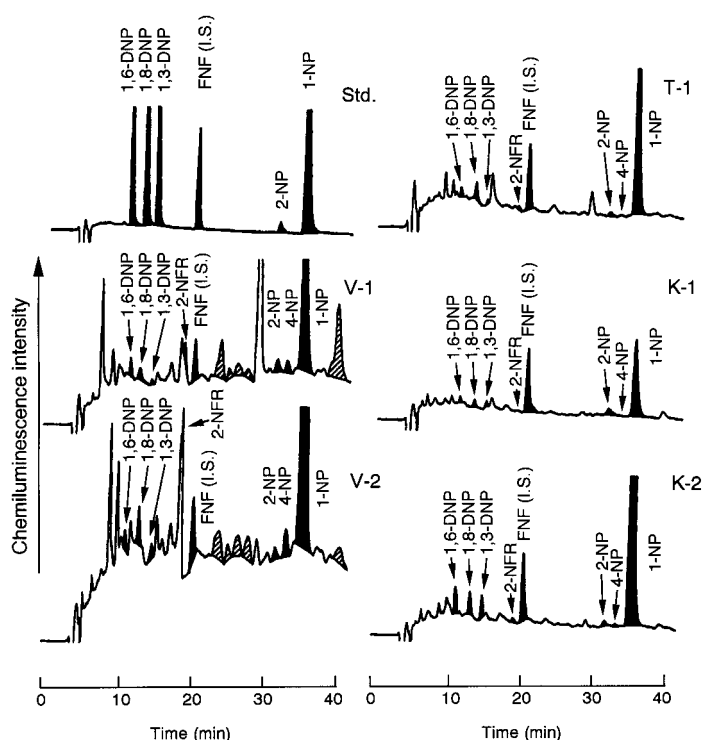


Fig. 1. Chromatograms of Extracts from Airborne Particulates Collected at Five Stations
Sampling period, January 28, 10:00 am – 29, 10:00 am, 1999.

were weak at T-1, K-1 and K-2 and the resolution between 2-NFR and the neighboring peak was incomplete. 6-NC was also identified at 52.5 min at every station (data not shown). In addition, several unknown peaks were observed in the chromatograms. Among these unknown peaks, five large peaks (diagonal; 23.5 min, 25.3 min, 26.5 min, 27.9 min and 41.2 min) were significant only in chromatograms of V-1 and V-2. Although other unknown peaks such as peaks at 15.3 min, 15.9 min, 17.2 min, 29.4 min, 31 min and 37.5 min were also observed, these peaks were detected not only in Vladivostok but also in Kanazawa and Toyama. These results suggested that the five large unknown peaks were characteristic only in Vladivostok. In the present method, NPAHs were reduced into corresponding aminopolycyclic aromatic hydrocarbons (APAHs), and peroxyoxalate-chemiluminescence (PO-CL) detection was highly sensitive and selective to APAHs.¹⁷⁾ Considering the fact that NPAHs were not detected directly by the PO-CL detection method, these peaks might be detected after reductive conversion of NPAHs. We are presently attempting to identify these unknown peaks.

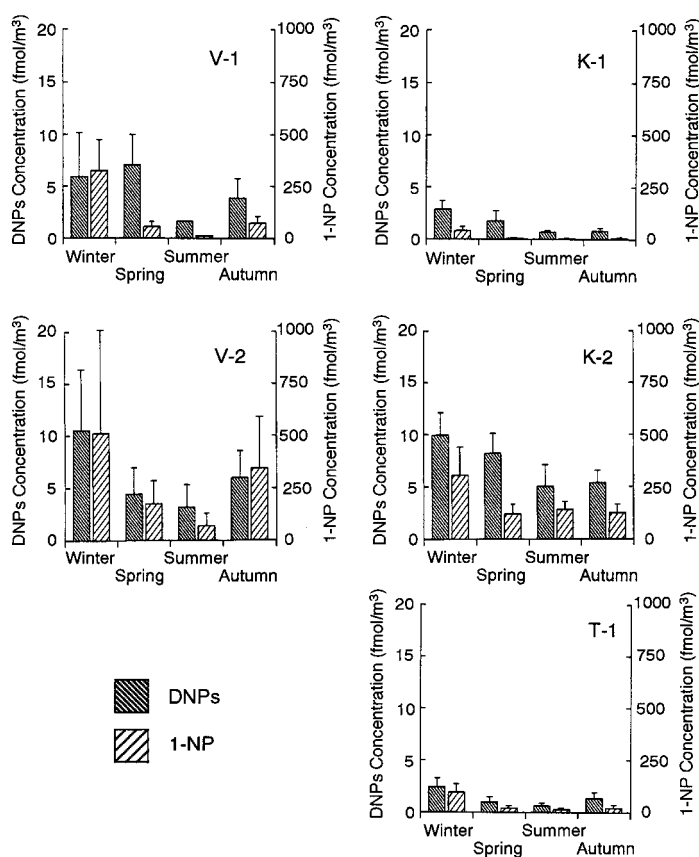
Concentrations of NPAHs

The sum of direct-acting mutagenic contributions of the three DNPs and 1-NP was over 30% of the detect-acting mutagenicity of extracts from diesel-exhaust particulates in the *S. typhimurium* YG 1024 strain.¹⁸⁾ 2-NP was a typical NPAH which was secondary formed in the urban air.¹⁹⁾ Therefore, we compared the atmospheric concentrations of 1,3-, 1,6-, 1,8-DNPs, 1- and 2-NPs at five stations (Table 1). The mean concentrations of the three DNPs and 1-NP at five stations were in the order V-2 \approx K-2 > V-1 \gg K-1 \approx T-1, although there were small exceptions. As observed in our previous study, the main contributor of three DNPs and 1-NP in downtown Kanazawa was diesel-engine vehicles.²⁰⁾ Each concentration level of DNPs and NPs in V-2 similar to that in K-2 suggested the possibility that the automobiles were also one of the main contributors of these NPAHs in Vladivostok. The concentrations of these NPAHs were relatively higher at the station near heavier traffic roads (K-2) than those at the lighter traffic station (K-1). However, at V-1, in spite of the lighter traffic volume, the concentrations of DNPs and 1-NP were almost as high as those at V-2. This result could not be explained by only the contribution of automobiles.

Table 1. Atmospheric Concentrations of 1,3-, 1,6-, 1,8-DNPs, 1- and 2-NPs at Five Stations

| City | Sampling station | concentration (fmol m ⁻³) | | | | |
|-------------|------------------|---------------------------------------|-----------|-----------|-----------|-----------|
| | | 1,3-DNP | 1,6-DNP | 1,8-DNP | 1-NP | 2-NP |
| Vladivostok | V-1 | 2.2 ± 1.9 | 1.5 ± 1.3 | 1.7 ± 1.4 | 213 ± 226 | 521 ± 556 |
| | V-2 | 2.7 ± 2.7 | 1.9 ± 1.8 | 1.9 ± 1.2 | 434 ± 352 | 338 ± 311 |
| Kanazawa | K-1 | 0.5 ± 0.7 | 0.4 ± 0.3 | 0.5 ± 0.4 | 20 ± 32 | 47 ± 33 |
| | K-2 | 2.3 ± 1.6 | 2.5 ± 1.1 | 2.4 ± 1.1 | 241 ± 146 | 117 ± 52 |
| Toyama | T-1 | 0.3 ± 0.2 | 0.3 ± 0.2 | 0.5 ± 0.5 | 36 ± 38 | 162 ± 217 |

Mean ± S.D. (*n* = 28 or 20)

**Fig. 2.** Seasonal Concentrations of DNPs and 1-NP at Five Stations

Each column and vertical bar represent mean value and S.D. (*n* = 7 or 5), respectively. DNPs = 1,3-DNP + 1,6-DNP + 1,8-DNP.

The concentrations of 2-NP at the five stations were in the order V-1 > V-2 > T-1 > K-2 > K-1 (Table 1). This order was different from that of the three DNPs and 1-NP described above. The finding concerning 2-NP are discussed below.

Seasonal Variations of NPAHs

We previously reported that the atmospheric concentrations of DNPs and 1-NP were higher in winter than in summer not only in Kanazawa but also in Tokyo and Sapporo.¹⁶⁾ As possible causes of the seasonal variations in Japanese cities, the tem-

perature inversion in the boundary layer, kerosene heaters in winter, and the degradation of NPAHs in summer have been proposed.^{13,21-24)}

Figure 2 shows the seasonal concentrations of the three DNPs and 1-NP in the atmosphere at five stations. The same seasonal variation as in Kanazawa was observed in Vladivostok and Toyama. As the same cause as in the Japanese cities, diesel-engine vehicles were also considered in downtown Vladivostok. However, the concentrational differences between V-1 and V-2 were significant in summer but not in winter. As a cause of high concentra-

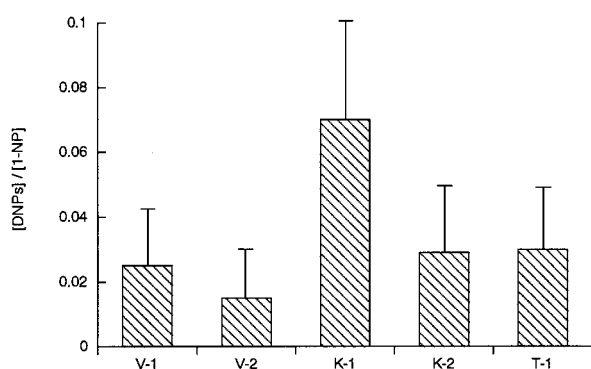


Fig. 3. [DNPs]/[1-NP] Ratio at Five Stations

Each column and vertical bar represent mean value and S.D. ($n = 28$ or 20), respectively. [DNPs] = [1,3-DNP] + [1,6-DNP] + [1,8-DNP].

tions of NPAHs at V-1 in winter, other contributors should be considered.

Composition of NPAHs

We reported the difference of [DNPs]/[1-NP] ratios of particulates from gasoline-engine and diesel-engine vehicles.^{14,20} Under the assumption that neither formation nor degradation had occurred in the atmosphere, the ratios were used to assess the contribution of diesel-engine vehicles.²⁰ Consequently, as the main contributor of the three DNPs and 1-NP in the urban air of Japan, diesel-engine vehicles have been considered. Figure 3 shows the [DNPs]/[1-NP] ratios at the five stations. The values at V-1 (0.025) and V-2 (0.015) were near the value previously found for diesel-exhaust particulates (0.013) and smaller than those at K-1 (0.07), K-2 (0.029) and T-1 (0.03). Although this result suggested a large contribution of diesel-engine vehicles at V-1 and V-2, the numbers of diesel- and gasoline-engine vehicles registered in Vladivostok are not known. Moreover, as other possible reasons for the lower values in Vladivostok, other contributors than automobiles and the difference of diesel- or gasoline-fuel between Russia and Japan might be considered.

2-NP was not detected in particulates from diesel-engine vehicles but was detected in airborne particulates, and the concentration ratio of 2-NP to 1-NP was higher in the suburban air than in urban air in Kanazawa.^{14,19,25} From these results, we concluded that 2-NP was formed in the atmosphere. As a mechanism of the formation of 2-NP in the atmosphere, a daytime reaction in which pyrene reacted with a hydroxyl radical in the presence of sunlight followed by nitration with nitrogen oxides has been pro-

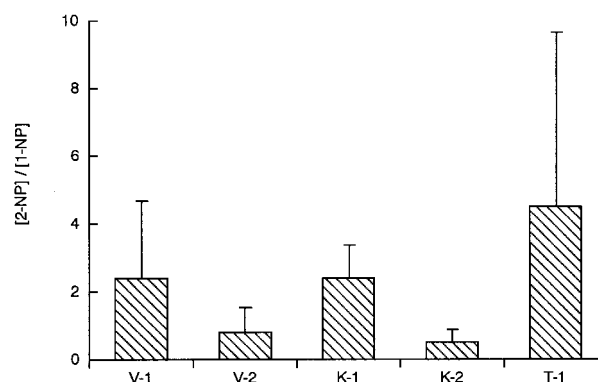


Fig. 4. [2-NP]/[1-NP] Ratio at Five Stations

Each column and vertical bar represent mean value and S.D. ($n = 28$ or 20), respectively.

posed.¹⁰ In this study, we calculated the [2-NP]/[1-NP] ratio in the atmosphere to clarify the atmospheric formation of 2-NP (Fig. 4). The values were in the order T-1 (4.5) > V-1 (2.4) = K-1 (2.4) > V-2 (0.8) > K-2 (0.5). As observed in Kanazawa, the ratios were larger at the lighter traffic station (V-1) than at the heavier traffic station (V-2) in Vladivostok. Considering that the [2-NP]/[1-NP] value depended on the existing time in the atmosphere, this result suggested that 2-NP was formed in the atmosphere also in Vladivostok. In our past surveys in Kanazawa, the concentration of 2-NP was always lower than that of 1-NP. In the present study, however, the concentration of 2-NP was higher than that of 1-NP at three stations (V-1, K-1 and T-1). This result is consistent with reports concerning foreign cities.²⁶

As described above, the differences of chromatograms, concentrations and compositions of NPAHs between Vladivostok and Kanazawa suggested not only diesel-engine vehicles but also other contributors for the atmospheric NPAHs in Vladivostok. For example, several NPAHs were identified in coal fly ash.²⁷ Another important fact is that a large amount of coal has been consumed in power plants, factories and city and domestic heaters in Vladivostok. The formation of NPAHs through the combustion of coal and their release into the air are not known. The identifications of NPAHs and the determination of their concentrations in particulates from the consumption of coal are now being studied. Moreover, the determination of NPAHs in particulates emitted from power plants, factories and heaters which use coal will provide more useful information for clarifying the behaviors of NPAHs including unknown peaks detected in extracts from airborne particulates

in Vladivostok.

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REFERENCES

- Epstein, S. S., Fujii, K. and Asahina, S. (1979) Carcinogenicity of a composite organic extract of urban particulate atmospheric pollutants following subcutaneous injection in infant mice. *Environ. Res.*, **19**, 163–176.
- Matsumoto, Y., Sakai, S., Kato, T., Nakajima, T. and Sato, H. (1998) Long-term trends of particulate mutagenic activity in the atmosphere of Sapporo. 1. Determination of mutagenic activity by the conventional tester strains TA98 and TA100 during an 18-year period (1974–1992). *Environ. Sci. Technol.*, **32**, 2665–2671.
- Ministry of Health, Labour and Welfare, Japan. (1997) The Population Dynamic Statistics.
- Ames, B. N., McCann, J. and Yamasaki, E. (1975) Methods for detecting carcinogens and mutagens with the *Salmonella* mammalian microsome mutagenicity test. *Mutat. Res.*, **31**, 347–364.
- Pitts, Jr., J. N., Cauwenberghe, K. A. V., Grosjean, D., Schmid, J. P., Fitz, D. R., Belser, Jr., W. L., Knudson, G. B. and Hynds, P. B. (1978) Atmospheric reactions of polycyclic aromatic hydrocarbons: facile formation of mutagenic nitro derivatives. *Science*, **202**, 515–519.
- Tokiwa, H., Nakagawa, R. and Ohnishi, Y. (1981) Mutagenic assay of aromatic nitro compounds with *Salmonella typhimurium*. *Mutat. Res.*, **91**, 321–325.
- Tokiwa, H. and Ohnishi, Y. (1986) Mutagenicity and carcinogenicity of nitroarenes and their sources in the environment. *Crit. Rev. Toxicol.*, **17**, 23–60.
- White, C. M. (ed.). (1985) *Nitrated Polycyclic Aromatic Hydrocarbons*, Hüethig, Heidelberg, Germany.
- Cvačka, J., Barek, J., Fogg, A. G., Moreira, J. C. and Zima, J. (1998) High-performance liquid chromatography of nitrated polycyclic aromatic hydrocarbons. *Analyst* (London), **123**, 9–18.
- Nielsen, T., Seiz, B. and Ramdahl, T. (1984) Occurrence of nitro-PAH in the atmosphere in a rural area. *Atmos. Environ.*, **18**, 2159–2165.
- Arey, J., Zielinska, B., Atkinson, R., Winer, A. M., Ramdahl, T. and Pitts, Jr., J. N. (1986) The formation of nitro-PAH from the gas-phase reactions of fluoranthene and pyrene with OH radical in the presence of NO_x. *Atmos. Environ.*, **20**, 2339–2345.
- Marino, F., Cecinato, A. and Siskos, P. A. (2000) Nitro-PAH in ambient particulate matter in the atmosphere of Athens. *Chemosphere*, **40**, 533–537.
- Hayakawa, K., Murahashi, T., Butoh, M. and Miyazaki, M. (1995) 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.*, **29**, 928–932.
- Murahashi, T., Miyazaki, M., Kakizawa, R., Yamagishi, Y., Kitamura, M. and Hayakawa, K. (1995) Diurnal concentrations of 1,3-, 1,6-, 1,8-dinitropyrenes, 1-nitropyrene and benzo[*a*]pyrene in air in downtown Kanazawa and the contribution of diesel-engine vehicles. *Jpn. J. Toxicol. Environ. Health*, **41**, 328–333.
- Hayakawa, K., Murahashi, T., Akutsu, K., Kanda, T., Tang, N., Kakimoto, H., Toriba, A. and Kizu, R. (2000) Comparison of polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in airborne and automobile exhaust particulates. *Polycycl. Aromat. Comp.*, **20**, 179–190.
- Kakimoto, H., Kitamura, M., Matsumoto, Y., Sakai, S., Kanoh, F., Murahashi, T., Akutsu, K., Kizu, R. and Hayakawa, K. (2000) Comparison of atmospheric polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in Kanazawa, Sapporo and Tokyo. *J. Health Sci.*, **46**, 5–15.
- Hayakawa, K., Kitamura, R., Butoh, M., Imaizumi, N. and Miyazaki, M. (1991) Determination of diamino- and aminopyrenes by high performance liquid chromatography with chemiluminescence detection. *Anal. Sci.*, **7**, 573–577.
- Hayakawa, K., Nakamura, A., Terai, N., Kizu, R. and Ando, K. (1997) Nitroarene concentrations and direct-acting mutagenicity of diesel exhaust particulates fractionated by silica-gel column chromatography. *Chem. Pharm. Bull.*, **45**, 1820–1822.
- Murahashi, T. and Hayakawa, K. (1997) A sensitive method for the determination of 6-nitrochrysene, 2-nitrofluoranthene and 1-, 2- and 4-nitropyrenes in airborne particulates using high-performance liquid chromatography with chemiluminescence detection. *Anal. Chim. Acta*, **343**, 251–257.
- Hayakawa, K., Butoh, M., Hirabayashi, Y. and Miyazaki, M. (1994) Determination of 1,3-, 1,6-, 1,8-dinitropyrenes and 1-nitropyrene in vehicle exhaust particulates. *Jpn. J. Toxicol. Environ. Health*,

- 40, 20–25.
- 21) Kamiya, A. and Ose, Y. (1988) Isolation of dinitropyrene in emission gas from a municipal incinerator and its formation by a photochemical reaction. *Sci. Total Environ.*, **72**, 1–9.
- 22) Chapman, O. L., Heckert, D. C., Reasoner, J. W. and Thackaberry, S. P. (1966) Photochemical studies on 9-Nitroanthracene. *J. Am. Chem. Soc.*, **88**, 5550–5554.
- 23) Hisamatsu, Y., Nishimura, T., Tanabe, K. and Matsushita, H. (1986) Mutagenicity of the photochemical reaction products of pyrene with nitrogen dioxide. *Mutat. Res.*, **172**, 19–27.
- 24) Holloway, M. P., Biaglow, M. C., McCoy, E. C., Anders, M., Rosenkranz, H. S. and Howard, P. C. (1987) Photochemical instability of 1-nitropyrene, 3-nitrofluoranthene, 1,8-nitropyrene and their parent polycyclic aromatic hydrocarbons. *Mutat. Res.*, **187**, 199–207.
- 25) Murahashi, T., Kizu, R., Kakimoto, H., Toriba, A. and Hayakawa, K. (1999) 2-nitrofluoranthene, 1-, 2- and 4-nitropyrenes and 6-nitrochrysene in diesel-engine exhaust and airborne particulates. *J. Health Sci.*, **45**, 244–250.
- 26) Ciccioli, P., Cecinato, A., Brancaleoni, E., Frattoni, M. and Zacchei, P. (1996) Formation and transport of 2-nitrofluoranthene and 2-nitropyrene of photochemical origin in the troposphere. *J. Geophys. Res.*, **101**, 19567–19581.
- 27) De Raat, W. K., Boers, J. P., Bakker, G. L., de Meijere, F. A., Hooimeijer, A., Lohman, P. H. M. and Mohn, G. R. (1994) Contribution of PAH and some of their nitrated derivatives to the mutagenicity of ambient airborne particles and coal fly ash. *Sci. Total Environ.*, **153**, 7–28.