

Analysis of Atmospheric Polycyclic Aromatic Hydrocarbons and Nitropolycyclic Aromatic Hydrocarbons in Gas/Particle Phases Separately Collected by a High-volume Air Sampler Equipped with a Column Packed with XAD-4 Resin

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We developed a sampler for collecting atmospheric polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) by attaching a glass column packed with XAD-4 resin to the gas sampling port of a high-volume air sampler equipped with a filter. When the upper and bottom layers of the column were packed with 64 g and 32 g of XAD-4 resin, respectively, all PAHs and NPAHs in the gas phase were quantitatively collected in the XAD-4 resin column without any break through, while PAHs and NPAHs in the particle phase were collected on the filter. We collected air samples at suburban and downtown Kanazawa by using the proposed sampler. It was found that about 95% of 2–3 ring PAHs and more than 99% of 2-ring NPAHs existed chiefly in the gas phase, that 4-ring PAHs such as fluoranthene (FR) and pyrene (Pyr) and 3-ring NPAHs were in both the gas and particle phases and that the other PAHs and NPAHs having 4-rings or more except for FR and Pyr were almost completely in the particle phase. Our data also indicated that the adsorption of NPAHs to the particle phase in the atmosphere is controlled by the same mechanism as that of PAHs.

Key words — gas/particle partition, XAD-4 resin, polycyclic aromatic hydrocarbon, nitropolycyclic aromatic hydrocarbon

INTRODUCTION

Many polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) are carcinogenic and/or mutagenic. The International Agency of Research of Cancer (IARC), has placed benzo[*a*]pyrene (BaP) in Group 1 (carcinogenic to humans), dibenz[*a,h*]anthracene (DBA) in Group 2A (probably carcinogenic to humans) and benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), indeno[1,2,3-*cd*]pyrene (IDP), 1,6-, 1,8-dinitropyrenes (DNPs), 1-, 4-nitropyrenes (NPs), 5-nitroacenaphthene (NAc) and 2-nitrofluorene (NF) in Group 2B (possibly carcinogenic to humans).^{1,2} Additionally, some hydroxylated PAHs have been

reported to show endocrine-disrupting activity^{3–6} and some quinoid PAHs have been reported to play a role in the biological production of reactive oxygen species.⁷

Because PAHs and NPAHs are formed through the imperfect combustion of fossil fuels such as coal and oil and through the pyrolysis of organic materials, these pollutants are emitted from cars, factories, oil and coal stoves, and cigarettes *etc.* and exist in the atmosphere.^{8–11} Additionally, several NPAHs such as 2-nitrofluoranthene (NFR) and 2-NP are formed in a secondary process through the gas phase reaction of PAHs and OH radical or N₂O₅ in the presence of nitrogen oxides (NO_x) in the atmosphere.^{12,13} The amounts of PAHs and NPAHs in the atmosphere depend on many factors such as the vapor pressure, temperature, atmospheric pressure, and the concentration and properties of dust. Vapor pressures vary widely (10⁻²–10⁻¹⁰ mmHg, at 25°C)¹⁴ so that PAHs and NPAHs exist in both the gas and particle phases in the atmosphere. In gen-

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erally, PAHs having 2 rings exist in the gas phase, PAHs having 5 rings or more exist in the particle phase, and PAHs having 3 and 4 rings are in both phases. Yamazaki *et al.* were able to explain the distribution of PAHs in the two phases by using the sub-cooled liquid vapor pressure of PAHs.¹⁵⁾

On the other hand, the vapor pressures of NPAHs are lower than those of the corresponding PAHs having the same ring number because of the substituent effect of the nitro group. As a result, NPAHs having 4 rings or more such as 1-NP exist in the particle phase even at 40°C, while NPAHs having 2 and 3 rings are in both phases.¹⁶⁾ The concentrations of major PAHs in urban air are in the range from 1 to 100 pmol/m³. However, the concentrations of major NPAHs such as 1-NP are at less than fmol/m³ levels, which are much lower than those of PAHs.¹⁷⁾ Considering that several PAHs are converted to NPAHs through the above described atmospheric reactions and that some of them move from the gas phase to the particle phase, it is important to measure the atmospheric distribution of PAHs and NPAHs in the two phases simultaneously to understand their atmospheric behaviors and effects on human health.

To collect PAHs and NPAHs in the particle phase, a high-volume, middle-volume, low-volume or personal air sampler equipped with a quartz or glass fiber filter has been reported.^{9, 14, 17)} The high-volume air sampler is widely used for the study of atmospheric PAHs and NPAHs because it has the largest flow rate of air. On the other hand, PAHs and NPAHs in the gas phase are collected by introducing a polymer adsorbents such as polyurethane foam (PUF) or styrene-divinyl benzene polymer such as XAD-2 resin. PUF is porous enough not to decrease the flow rate of the air, but the recovery of PAHs having 2–3 rings was low. It is especially poor at collecting Naphthalene (Nap) which has the largest vapor pressure among the PAHs.^{18–21)} XAD-2 resin could collect Nap quantitatively, but it could be used only for low- or middle-volume air samplers at a flow rate of about 30–100 l/min because of the pressure loss attributed to its lower porosity.²²⁾ However, XAD-2 resin can not be used for analyzing NPAHs whose concentrations are 100 times or more lower than those of PAHs.^{17, 23, 24)} On the other hand, XAD-4 resin is made of the same styrene-divinyl benzene polymer as XAD-2 resin but has a larger particle diameter and a larger surface area than XAD-2 resin.²⁵⁾ Furthermore, the average pore size of XAD-4 resin ($D = 48 \text{ \AA}$) is twice

as small as that of XAD-2 resin ($D = 100 \text{ \AA}$), while the molecular size (d) of PAH having 2–4 rings is less than 10 Å. Since the D/d values of XAD-2 and XAD-4 resin are 10 and 5, the adsorption mechanism of them is surface adsorption and pore adsorption, respectively. Therefore, XAD-4 resin which has a pore adsorption effect and large surface area is considered that the adsorption capacity of PAH is larger than XAD-2 resin.^{26, 27)}

In this study, we developed a high-volume air sampler for simultaneous collection of PAHs and NPAHs in the gas and particle phases by introducing a column packed with XAD-4 resin into a high-volume air sampler. By using the proposed sampler, the distribution of PAHs and NPAHs in the atmosphere in downtown Kanazawa was clarified.

MATERIALS AND METHODS

Chemicals—EPA610 PAH Mix [Nap, acenaphthene (Ace), fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (FR), pyrene (Pyr), BaA, Chr, BbF, BkF, BaP, DBA, benzo[ghi]perylene (BgPe) and IDP] were purchased as a PAH standard solution from Supelco (Bellefonte, PA, U.S.A.). Five deuterated PAHs (Nap- d_8 , Ace- d_{10} , Phe- d_{10} , Pyr- d_{10} and BaP- d_{12}) were purchased from Wako Pure Chemical (Osaka, Japan) as internal standards and they were dissolved in acetonitrile (Kanto Chemical, Tokyo, Japan). 1-, 2-Nitronaphthalenes (NNs), 5-NAc, 2-NF, 2-, 9-nitroanthracenes (NAs), 1-, 4-NPs, 1,3-, 1,6-, 1,8-DNPs, 2-nitrotriphenylene (NTP), and 2-fluoro-7-nitrofluorene (FNF) as an internal standard were purchased from Aldrich (St. Louis, MO, U.S.A.). 9-Nitrophenanthrene (NPh), 7-nitrobenzo[*a*]anthracene (NBaA) were purchased from Accustandard Inc. (New Haven, CT, U.S.A.), 1-NFR, 6-nitrochrysene (NC), 1-nitroperylene (NPer) were from Chiron AS (Trondheim, Norway), 3-NFR was from Wako and 6-nitrobenzo[*a*]pyrene (NBaP) was from Chemsyn Science Laboratories (Harrisonville, MO, U.S.A.), respectively. They were all dissolved in acetonitrile. Other reagents were all HPLC analysis grade. Besides, XAD-4 resin (diameter, 250–800 μm; pore size, 48 Å; volume/weight, 0.96 cm³/g; surface area, 725 m²/g) was purchased from Rohm and Haas (Philadelphia, PA, U.S.A.).

Sampler—The glass column (8 cm inner diameter and 12 cm depth) with a glass filter having

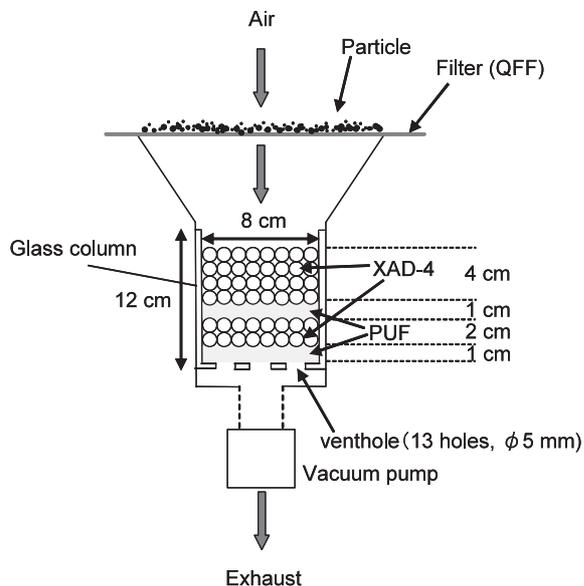


Fig. 1. A Schematic Flow of High-volume Air Sample Equipped with XAD-4 Resin Column

13 ventholes was packed with XAD-4 resin. The amounts of XAD-4 resin in the upper and bottom layers were 64 g (4 cm depth) and 32 g (2 cm depth), respectively. Two PUF sheets (each 8 cm diameter and 1 cm thick) were used: one was set between the above two layers as a separator and the other one was set on the bottom filter as a keeper of the bottom layer (Fig. 1). This column was placed in the shuttle tubing of a high-volume air sampler (HV-1000F, Shibata Science Ltd., Tokyo, Japan) equipped with a quartz fiber filter (QFF, 2500QAT-UP, Pallflex Products, Putnam, CT, U.S.A.).

Air Sampling—The air sampler was set up on a road side in downtown Kanazawa and air samples were collected from November 27 to December 1, 2007 at a flow of 300 l/min. The filters (QFF) and columns (XAD-4 resin and PUF) were replaced every day. After sampling, the filters (QFF) and columns (XAD-4 resin and PUF) were all kept in a refrigerator (-20°C) before analysis.

Sample Treatments—Each filter (QFF) containing particle matters was cut into small peaces (5 mm square) and put in a flask. After adding the internal standards and benzene/ethanol (3:1, v/v), the flask was supersonicated (Iwaki Glass USC-400z 38-s-24 38 Hz, Iwaki Glass, Funabashi, Japan) for 15 min. This procedure was repeated 3 times, using new benzene/ethanol each time. The extracted solution was filtered successively with a paper filter (Toyo No. 6, 125 mm diameter, Toyo Roshi Kaisha, Ltd., Tokyo, Japan) and a membrane filter

(Kanto Chemical HLC-DISK13, diameter 13 mm, pore size $0.45\ \mu\text{m}$). The solution was washed with 5% (w/v) sodium hydroxide solution, 20% (v/v) sulfuric acid solution, and distilled water, successively. After adding $100\ \mu\text{l}$ of dimethylsulfoxide (DMSO), the benzene layer was evaporated and the precipitate was dissolved in ethanol. The sample solution was filtered by a membrane filter (Kanto Chemical HLC-DISK13, diameter 3 mm, pore size $0.45\ \mu\text{m}$).

Internal standards were added to each XAD-4 resin containing gas phase compounds in a beaker. After adding 10 volume of acetone, the mixture was supersonicated for 30 min. This procedure was repeated 3 times, using new acetone each time. After adding $200\ \mu\text{l}$ of DMSO, the acetone solution was evaporated. After the precipitate was dissolved in benzene/ethanol (3:1, v/v), the solution was washed with 5% (w/v) sodium hydroxide solution, 20% (v/v) sulfuric acid solution, and distilled water. After adding $200\ \mu\text{l}$ of DMSO, the benzene layer was evaporated. The precipitate was dissolved in 10 ml of n-hexane, and then applied to a Sep-pak Plus Silica cartridge (Waters, Milford, MA, U.S.A.) which was previously conditioned with n-hexane. The cartridge was treated successively with 10 ml of n-hexane and 10 ml of n-hexane/dichloromethane (1:1, v/v). PAHs and NPAHs were separately eluted in the former and latter effluents, respectively. The recoveries of the analytes by the $3 \times$ solid phase extraction ranged from 86% (1,8-DNP) to 109% (2-NF). After adding $100\ \mu\text{l}$ of DMSO, each solution was evaporated. The precipitate was dissolved in $900\ \mu\text{l}$ of ethanol: pH 5.5 acetic acid buffer (3:1, v/v), and then filtered with a centrifugal filter unit (MILLIPORE, pore size $0.45\ \mu\text{m}$) by centrifuging at 3000 rpm for 5 min.

Analysis of PAHs and NPAHs—Fifteen PAHs were determined by the HPLC/fluorescence detection method according to our previous reports.^{17,28)} Among the NPAHs, 1- and 2-NNs were determined by the GC-MS method reported by Marino, F.²⁹⁾ with several modifications. We used a GC-MS system (Shimadzu, Kyoto, Japan) composed of a GC (GC-17A), an MS (QP-5000), an injector (AOC-17), and a column (30 m \times 0.25 mm, DB-5MS, J & B Scientific, Folsom, CA, U.S.A.). The electron ionizing (EI) mode was operated at an ionizing energy of 70 eV. The sample solution was introduced by the splitless method. The temperatures of vaporizer, interface and column oven were 280, 260 and 60°C , respectively. The samples were analyzed by selective ion monitoring (SIM,

$m/z = 127, 173$). Minimum detection limits ($S/N = 10$) of 1- and 2-NNs by this method were 90 and 134 fmol/injection, respectively, and the calibration curves of 1- and 2-NNs within the range of 0.2–200 μM were linear ($R^2 = 0.9995$, $R^2 = 0.9999$, respectively). The other 13 NPAHs were determined by the HPLC/chemiluminescence detection method according to our previous reports.^{30,31)}

RESULTS AND DISCUSSION

XAD-4 Column Conditions

The glass column packed with XAD-4 resin was able to be installed in a high-volume air sampler equipped with the shuttle tubing for dioxin as described above. To ventilate air, the bottom glass filter had 13 holes of 5 mm inner diameter that corresponds to 1/10 of the area. In general, if the amount of the adsorbent is fixed, the adsorption rate efficiency increases by decreasing the flow rate of gas. However, the flow rate necessary for quantifying NPAHs by a 24 hr-sampling was not less than 300 l/min, when calculating from the background atmospheric concentrations of NPAHs.³²⁾ At the flow rate of 300 l/min, the maximum amount of XAD-4 resin packed in the glass column was 100 g. In this research, the conditions were optimized using PAHs having 2–4 rings since their higher vapor pressures and more existence in the gas phase.

Clean-up of XAD-4 Resin and Recovery Test from Air Samples

As a clean-up method for XAD-2 resin, Soxhlet extraction for 24 hr containing organic solvents such as acetone, methylene chloride, or hexane has been reported.^{33,34)} However, this method requires a large volume of solvents and a long treatment time. On the other hand, supersonic wave extraction could wash materials in a short time with a small volume of solvents. Therefore, supersonic wave extraction was used for cleaning-up XAD-4 resin in this research.

Figure 2 shows the effect of supersonic extraction to remove PAHs having 2–4 rings from XAD-4 resin that abundantly existed in the resin by using 10 volume of acetone. When 30-min supersonic wave treatment was repeated for 5 times, using new acetone each time, more than 99% of the PAHs were removed by the three extractions. Our method required only 1/2 of the solvent and only 1/8 of the treatment time of the Soxhlet extraction method,

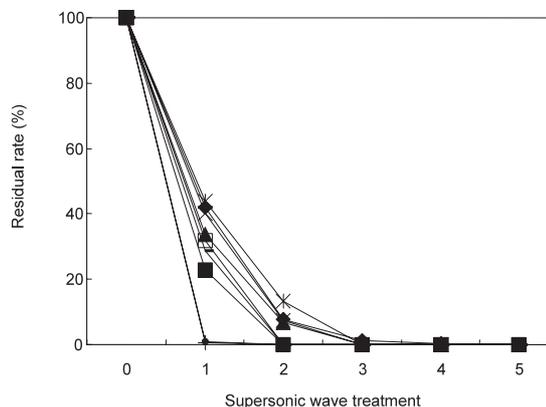


Fig. 2. Effect of Supersonic Wave Treatment to Clean up Contaminated PAHs from XAD-4 Resin Using Acetones as Extraction Solvent

Symbol: (◆) Nap, (■) Ace, (▲) Fle, (×) Phe, (*) Ant, (●) FR, (|) Pyr, (-) BaA, (□) Chr.

Table 1. Standard Addition Recoveries (%) of PAHs from XAD-4

| PAH | Added (nmol) | Extraction time | | | | |
|-----|--------------|-----------------|------|------|------|-----|
| | | 1 | 2 | 3 | 4 | 5 |
| Nap | 270 | 64.7 | 91.1 | 96.5 | 99.1 | 100 |
| Ace | 1.0 | 64.8 | 100 | 100 | 100 | 100 |
| Fle | 4.0 | 69.2 | 98.7 | 100 | 100 | 100 |
| Phe | 10 | 81.5 | 98.8 | 99.8 | 100 | 100 |
| Ant | 0.1 | 82.2 | 100 | 100 | 100 | 100 |
| FR | 0.4 | 92.7 | 99.6 | 100 | 100 | 100 |
| Pyr | 0.1 | 80.8 | 95.3 | 98.8 | 99.7 | 100 |
| BaA | 0.1 | 100 | 100 | 100 | 100 | 100 |
| Chr | 0.1 | 95.6 | 100 | 100 | 100 | 100 |

All data represent the mean values of five experiments.

which suggests that it is applicable for routine analyses.

To the glass column packed with the cleaned-up XAD-4 resin, 100 μl of ethanol solution containing PAHs having 2–4 rings was added. The XAD-4 resin was supersonic wave extracted for 5 times and the PAHs recovered in each solution were determined as shown in Table 1. Recoveries were more than 64% for all the compounds after a single extraction, and more than 96% for Nap, which was the least extracted PAH, after three extractions. Therefore, PAHs collected on the XAD-4 resin column from the atmosphere were extracted with ethanol for three times in the following experiment.

As shown in Fig. 1, the two layers, 64 g (upper) and 32 g (bottom) of XAD-4 resin in the glass column were separated by a PUF sheet (1 cm thick) in order to check the leak of PAHs and NPAHs from the column. Air samples were collected by the pro-

Table 2. Time of Effect of XAD-4 Amount on Recovery (%)^{a)} of PAHs from Air Samples

| PAH | Suburban air ^{b)} | | Urban air ^{c)} |
|-----|----------------------------|-----------------------|-------------------------|
| | (32/32) ^{d)} | (64/32) ^{d)} | (64/32) ^{d)} |
| Nap | 74 ± 22 | 97 ± 2.2 | 99 ± 0.3 |
| Ace | 71 ± 4.9 | 99 ± 1.4 | 99 ± 0.9 |
| Fle | 80 ± 2.7 | 99 ± 0.9 | 99 ± 1.0 |
| Phe | 83 ± 17 | 97 ± 2.6 | 97 ± 2.0 |
| Ant | 100 ± 1.3 | 100 ± 0.0 | 100 ± 0.6 |
| FR | 100 ± 0.4 | 99 ± 0.6 | 100 ± 0.7 |
| Pyr | 91 ± 0.0 | 99 ± 0.3 | 99 ± 0.2 |

a) Recovery (%) = recovered from upper layer (ng)/[recovered from upper (ng) + recovered from lower layer (ng)] × 100. b) The concentrations of gas phase PAHs in suburban air determined are as follows: Nap, 783 ± 83 pmol/m³; Ace, 4.3 ± 1.2 pmol/m³; Fle 16 ± 4.4 pmol/m³; Phe 13 ± 3.2 pmol/m³; Ant, 0.4 ± 0.2 pmol/m³; FR, 3.0 ± 0.8 pmol/m³; Pyr, 3.2 ± 0.9 pmol/m³ (n = 10). c) The concentrations of gas phase PAHs in suburban air determined are described in Table 3. d) Amount (g) of XAD-4 resin packed in upper and bottom layer, respectively. All data represent mean ± S.D. (n = 3). Sampling time, 24 hr. Flow rate, 300 l/min.

posed apparatus in suburban (Kanazawa University Kakuma Campus station) and downtown Kanazawa (National automobile exhaust monitoring station) at a flow rate of 300 l/min for 24 hr, considering that the concentrations of PAHs and NPAHs were different between these stations.^{17,32)} The adsorption efficiency of the upper layer of XAD-4 resin was calculated according to the Eq. (1). Moreover, when the amount of the compound in the bottom layer exceeded 1/2 of the amount in the upper layer, the leak was suspected.

$$\text{Adsorption efficiency (\%)} = \frac{[\text{PAH or NPAH (ng) in the upper layer}]}{[\text{PAH or NPAH (ng) in the upper layer} + \text{PAH or NPAH (ng) in the bottom layer}]} \times 100 \quad (1)$$

Table 2 shows the recovery of PAHs and NPAHs from suburban and urban air in Kanazawa by the proposed column packed with different weight of XAD-4 resin. When the total amount of XAD-4 resin packed in the column was 64 g (32 g for the upper layer and 32 g for the bottom layer, see Fig. 1), recoveries of 2- and 3-ring PAHs such as Nap, Ace, Fle and Phe in the suburban air were more than 71% and almost all of the recoveries were in the upper layer. Even Nap, which was the most volatile PAH tested, did not show any leakage to the bottom layer. When the total amount of XAD-4 resin packed in the column was 96 g (64 g for the upper layer and 32 g for the bottom layer), more than 97% of Nap (783 pmol/m³) and Phe (13 pmol/m³) in the suburban air, and more than 99% of Nap (1763 pmol/m³)

and more than 97% of Phe (79 pmol/m³) in the urban air were recovered in the upper layer. Recoveries of the other PAHs having 4 rings such as FR and Pyr in the gas phase were more than 99% in the upper layer. This result suggested that the proposed method could separately and quantitatively collect PAHs and NPAHs in the gas/particle phases from the atmosphere in Kanazawa.

Distribution of PAHs and NPAHs in Gas/Particle Phases in the Atmosphere

Air samples were collected on the sidewalk of the urban road in Kanazawa by using the proposed sampler from November 27 to December 1, 2007. The average temperature was 9.15–9.65°C. Both filters (QFF) and columns (XAD-4 and PUF) were newly changed every day. Table 3 showed the mean, minimum and maximum concentrations of PAHs and NPAHs of the four days. Each concentration means the sum of the amounts collected in the two layers. The break through from the bottom layer was not observed for every compound. Among PAHs, the total concentration of Nap (1763 pmol/m³) having 2 rings was the highest, followed by Fle (151 pmol/m³) having 3 rings. But the concentration of Fle was more than one order of magnitude lower than that of Nap. Among NPAHs, the total concentration of 1-NN (4426 fmol/m³) having 2 rings was the highest, followed by 2-NN (2838 fmol/m³). Among 3-ring NPAHs, 9-NPh (250 fmol/m³) showed the highest concentration, but the concentration was more than one order of magnitude lower than that of NNs. Among NPAHs in the particle phase, the concentration of 4-ring 2-NTP (413 fmol/m³) was the highest. Although there has not been any report on a direct comparison of Nap and 1-, 2-NNs in the gas phase, the concentration of Nap in suburban Kanazawa was lower than that in the industrial area in Taiwan³⁵⁾ and the concentrations of 1-, 2-NNs in Kanazawa were higher than those around the city of Marseilles in France.³⁶⁾

Table 3 shows that many PAHs and NPAHs existed in not only the gas phase but also the particle phase in the atmosphere because of their wide range of vapor pressures.¹⁴⁾ Two- to three-ring PAHs such as Ace, Fle, Phe and Ant were mainly in the gas phase, 4-ring FR and Pyr were in both the gas and particle phases, and 5–6 ring PAHs such as BbF, BkF, BaP, DBA, BgPe and IDP were in the particle phase. On the other hand, 2-ring NPAHs such as 1-, 2-NNs were mainly in the gas phase, 3-ring

Table 3. Atmospheric Concentrations of PAHs and NPAHs at Road Side in Downtown Kanazawa

| Compound | Gas | | | Particle | | |
|----------------------------------|------------------------------------|------|------|------------------------------------|------|------|
| | Mean \pm S.D. (<i>n</i> = 4) | Min. | Max. | Mean \pm S.D. (<i>n</i> = 4) | Min. | Max. |
| PAH (pmol/m³) | | | | | | |
| Nap | 1762 \pm 561 | 1251 | 2587 | 1.0 \pm 0.3 | 0.7 | 1.4 |
| Ace | 41 \pm 19 | 15 | 61 | 0.1 \pm 0 | 0.1 | 0.1 |
| Fle | 150 \pm 93 | 41 | 244 | 0.5 \pm 0.2 | 0.3 | 0.7 |
| Phe | 79 \pm 20 | 54 | 99 | 2.9 \pm 1.5 | 1.5 | 3.8 |
| Ant | 3.9 \pm 1.9 | 3.4 | 6.5 | 0.1 \pm 0 | 0.1 | 0.2 |
| FR | 11 \pm 4.2 | 7 | 17 | 3.4 \pm 1.8 | 1.8 | 4.8 |
| Pyr | 8.7 \pm 8.7 | 5 | 13 | 2.6 \pm 1.1 | 1.5 | 3.7 |
| BaA | ND | ND | ND | 1.1 \pm 0.4 | 0.6 | 1.7 |
| Chr | ND | ND | ND | 2.5 \pm 0.9 | 1.5 | 3.8 |
| BbF | ND | ND | ND | 2.6 \pm 1.2 | 1.3 | 4.3 |
| BkF | ND | ND | ND | 0.9 \pm 0.5 | 0.5 | 1.7 |
| BaP | ND | ND | ND | 1.3 \pm 0.6 | 0.7 | 2.1 |
| DBA | ND | ND | ND | 1.6 \pm 0.7 | 0.8 | 2.6 |
| BgPe | ND | ND | ND | 2.7 \pm 1 | 1.7 | 4.2 |
| IDP | ND | ND | ND | 1.7 \pm 0.6 | 1.1 | 2.6 |
| Total | 2054 \pm 671 | 1377 | 2995 | 25 \pm 11 | 20 | 40 |
| NPAH (fmol/m³) | | | | | | |
| 1-NN | 4426 \pm 968 | 3616 | 5560 | < 226 | — | — |
| 2-NN | 2838 \pm 558 | 2229 | 3317 | < 336 | — | — |
| 9-NPh | 250 \pm 1.9 | 248 | 251 | 29 \pm 9.4 | 23 | 36 |
| 2-NA | 2.4 \pm 0.1 | 2.3 | 2.4 | 3.9 \pm 1.6 | 2.2 | 4.1 |
| 9-NA | 56 \pm 34 | 22 | 105 | 113 \pm 49 | 85 | 169 |
| 3-NFR | ND | ND | ND | 5.6 \pm 1.4 | 4.4 | 5.3 |
| 1-NP | 7.3 \pm 6.4 | 3.4 | 18 | 76 \pm 30 | 52 | 129 |
| 1,3-DNP | ND | ND | ND | 0.4 \pm 0.2 | 0.3 | 0.6 |
| 1,6-DNP | ND | ND | ND | 0.6 \pm 0.3 | 0.3 | 1.1 |
| 1,8-DNP | ND | ND | ND | 21 \pm 0.6 | 1.3 | 2.9 |
| 7-NBaA | ND | ND | ND | 36 \pm 28 | 13 | 74 |
| 6-NC | ND | ND | ND | 49 \pm 19 | 29 | 80 |
| 2-NTP | ND | ND | ND | 413 \pm 278 | 238 | 756 |
| 6-NBaP | ND | ND | ND | 7.8 \pm 2.3 | 5.9 | 11 |
| 1-Nper | ND | ND | ND | 1.4 \pm 1.4 | 0.6 | 3.1 |
| Total | 7580 \pm 1566 | 6077 | 9058 | 739 \pm 422 | 492 | 1256 |

ND: not detected. Sampling period, 2007/11/27–2007/12/1. Temperature, 9.15–9.65°C. Both filters (QFF) and columns (XAD-4 and PUF) were replaced every day.

NPAHs such as 9-NPh, 2-NA and 9-NA were in both the gas and particle phases, and 4-5 ring PAHs such as 3-NFR, 1,3-, 1,6-, 1,8-DNPs, 7-NBaA, 6-NC, 2-NTP, 6-NBaP and 1-NPer were in the particle phase. The ratio of NPAH in the gas phase to the total NPAH in the atmosphere was smaller than that of the corresponding PAH: Phe > 9-NPh, Ant > 2-, 9-NNAs, FR > 3-NFR and Pyr > 1-NP, because the introduction of a nitro group increases the polarity of the molecule. The boiling points of 1-, 2-NNs (304°C, 314°C), 9-NA (403°C) and 1-NP (446°C) were higher than those of Nap (218°C), Ant (337°C) and Pyr (404°C), respectively.

Figure 3 shows the distribution (%) of each compound in the gas phase calculated from the Eq. (2).

$$\text{Distribution (\%)} \text{ in the gas phase} = \frac{[\text{PAH or NPAH (ng/m}^3\text{) in the gas phase}]}{[\text{PAH or NPAH (ng/m}^3\text{) in the gas phase} + (\text{PAH or NPAH (ng/m}^3\text{) in the particle phase)]} \times 100 \quad (2)$$

Two 4-ring PAHs (FR and Pyr), and two 3-ring NPAHs (2-NA and 9-NA) were in both gas and particle phases. In summer season, the ratios of these compounds in the gas phase were larger. The percentages of FR and Pyr, for examples, increased to

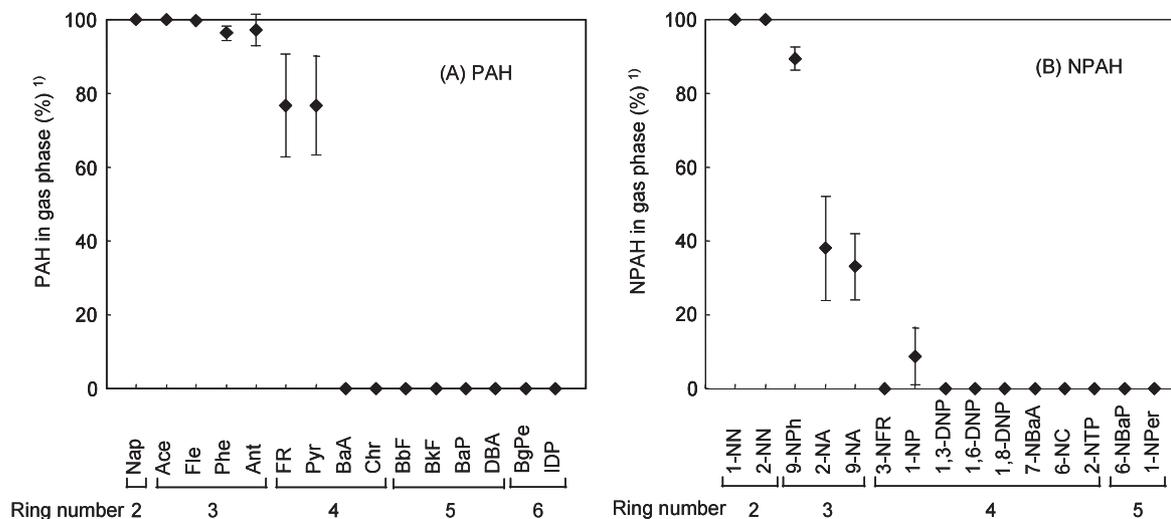


Fig. 3. Distribution of (A) PAHs and (B) NPAHs in Gas Phase in Kanazawa

¹⁾ PAH or NPAH in gas phase (%) = [PAH or NPAH (ng) in gas phase]/[(PAH or NPAH (ng) in gas phase) + (PAH or NPAH (ng) in particle phase)] × 100.

16% and 11%, respectively, at 25.4°C.

On the other hand, from the fact that the gas/particle phase partition of BaP in the atmosphere were not the same at different places even at the same temperature, Yamazaki *et al.* found that the adsorption of the gas phase PAH to the particle phase in the atmosphere followed the Langmuir model, because of much lower concentration of the PAH than the concentration of suspended particle matter in the atmosphere.¹⁴⁾

$$\text{Log} \frac{A(TSP)}{F} = -\frac{a}{T} + b \quad (3)$$

Where, A is the concentration of PAH in the gas phase (ng/m^3), F is the concentration of PAH in the particle phase (ng/m^3), TSP is the total concentration of suspended particle matter ($\mu\text{g}/\text{m}^3$), T is the absolute temperature (K), a and b are constants.

In this report, the determination results of not only PAHs but also NPAHs in Table 3 were introduced in the above Eq. (3). The ratios existing in the gas phase $A(TSP)/F$ at the same temperature were in the order: Ant > 1-NN > 2-NN > Pyr > 9-NA > 1-NP. However, this order is not the same as the reversed order of boiling points of PAHs and NPAHs. The boiling points of PAHs and NPAHs tested in this work were in the following order: Nap (218°C) < 1-NN (304°C) < 2-NN (314°C) < Ant (337°C) < 9-NA (403°C) < Pyr (404°C) < 1-NP (446°C). The difference between them suggests that the steam in the atmosphere increases the hydrophobicity of the surface of the XAD-4 resin which adsorbs polar NPAHs more easily than non-polar PAHs.³⁷⁾

In conclusion, a sampler for PAHs and NPAHs in the gas and particle phases in the atmosphere has been developed by introducing the XAD-4 resin column in the gas sampling port of high-volume air sampler. Using this sampler, we found that about 95% of 2–3 ring PAHs and more than 90% of 2-ring NPAHs existed chiefly in the gas in the atmosphere at an urban road side. Our data also indicated that the adsorption of NPAHs to the particle phase in the atmosphere is controlled by the same mechanism as that of PAHs.

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