# Chemical Composition of PM$_{2.5}$ and PM$_{10}$ and Associated Polycyclic Aromatic Hydrocarbons at a Roadside and an Urban Background Area in Saitama, Japan

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## ABSTRACT

The chemical compositions of PM$_{2.5}$ and PM$_{10}$ and associated high-molecular-weight polycyclic aromatic hydrocarbons (PAHs) were investigated during winter and summer at a roadside and an urban background site in Saitama, Japan. The average concentrations of PM$_{2.5}$ exceeded the United States Environmental Protection Agency standards during both periods. Carbonaceous components were abundant in both the observed and calculated (by means of a mass closure model) chemical composition of PM$_{2.5}$. Traffic-related pollutants (elemental carbon and high-molecular-weight PAHs) were strongly associated with PM$_{2.5}$ rather than with larger particles. The mass concentrations of PM$_{2.5}$, as well as those of EC and PAHs associated with the particles, at the two sites were strongly correlated. Comparison of our data with source profile ratios indicates that diesel-powered vehicles were probably the main source of the measured PAHs. The PAHs concentrations were affected by meteorological conditions during our study. Our results highlight the need for the establishment of standards for PM$_{2.5}$ in Japan.

**Key words:** Diesel exhaust particles, PAHs, Traffic-related pollutants, Source profile ratio, PM$_{2.5}$

## 1. INTRODUCTION

During the last decade, increasing attention has been paid to fine particles in the urban atmosphere, owing to the various harmful effects these particles have on human health. Many studies reported that PM$_{2.5}$ (particles with a 50% cut-off aerodynamic diameter $<2.5\,\mu$m) is more strongly related to daily mortality than are coarse particles (Schwartz *et al*., 2002; Schwartz *et al*., 1996; Dockery *et al*., 1993). PM$_{2.5}$

can penetrate more deeply into the lungs and may reach the alveoli, causing serious respiratory diseases (WHO, 2003). Motor vehicles exhaust is the main source of PM$_{2.5}$ in the urban environment (Harrison *et al*., 1999; Schauer *et al*., 1996). Diesel exhaust contains substantially more particulate matter than gasoline-fueled vehicle exhaust, and the use of diesel-powered vehicles is leading to the deterioration of air quality in urban areas. The mass-weighted size distribution of diesel exhaust particles (DEPs) is mainly distributed between fine (PM$_{2.5}$) and ultrafine ($\sim 0.1$ $\mu$m) particles (Kittelson *et al*., 1988). These particles have the following characteristics:

a) Large surface area, which makes them excellent carriers for adsorbed organic and inorganic compounds.

b) High proportion (50-75%) of elemental carbon (EC, which is commonly used as a tracer for the exhaust of diesel-powered vehicles, and recently found to alter pulmonary endothelial function, which is an important factor in the development of hypertension and heart failure, Shah *et al*., 2008; Fujita *et al*., 1998).

c) High levels of certain polycyclic aromatic hydrocarbons (PAHs) (Zielinska, 2005; USEPA, 2002).

Because of these unique characteristics, more attention should be paid to the contribution of DEPs to particulate matter in urban environments.

Adsorbed PAHs play an important role in the carcinogenicity of DEPs, especially at low exposure levels. In the atmosphere, PAHs are present in both the gaseous phase and the particulate phase (Ligocki and Pankow, 1989). PAHs with 2 rings are found in the gaseous phase, those with 3 or 4 rings can be found in both phases, and PAHs with 5 or more rings tend to exist as solids adsorbed on fine particulate matter (Baek *et al*., 1991; Yang *et al*., 1991). Most high-molecular-weight PAHs are classified as possibly carcinogenic to humans by the International Agency for Research on Cancer (IARC, 2003). Benzo[*a*]pyrene (BaP) is classified as a highly carcinogenic compound. Inves-
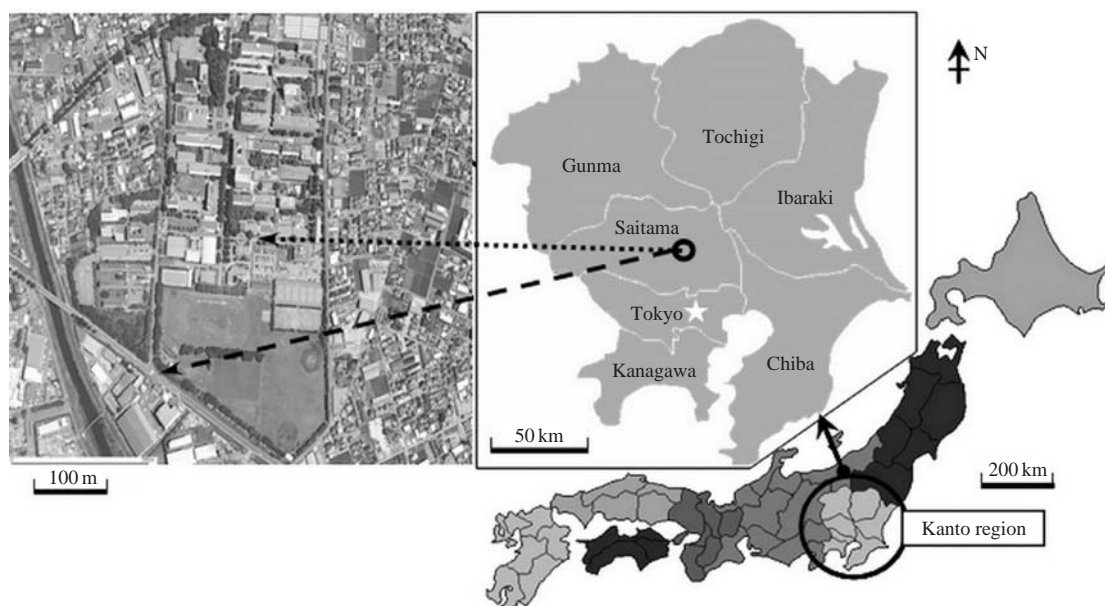
**Fig. 1.** Locations of sampling sites: roadside (dashed arrow) and urban background site (dotted arrow).

tigation of the levels and behaviors of high-molecular-weight PAHs is urgently needed for assessment of the risk associated with these compounds. In Japan, many researchers have investigated PAHs in the urban environment (Hagino *et al*., 2007; Kawanaka *et al*., 2004; Ohura *et al*., 2004; Hayakawa *et al*., 2002; Koyano *et al*., 2002). However, there have been few studies that have investigated both the levels of particulate PAHs and the chemical composition of the particulate matter on which they are adsorbed, particularly near major roads and highways, where potential risk of human exposure is strongly suspected to be high.

In this study, we investigated the chemical composition of PM$_{2.5}$ and PM$_{10}$ (particles with a 50% cut-off aerodynamic diameter $<10\,\mu$m) and their associated high-molecular-weight PAHs at a roadside and an urban background site in Saitama, Japan. The contribution of the chemical components of the DEPs, and their associated toxic agents, to airborne particulate matter is discussed in this paper. We focused on EC and PAHs because they are typical constituents of DEPs.

# 2. MATERIALS AND METHODS

## 2.1 Sampling Sites

Our study was conducted at two sites in the city of Saitama, which is located in the central Kanto region of Japan (Fig. 1); the city is the seat of Saitama Prefecture and has a population of more than 1 million. The

two sites were chosen to represent a roadside and an urban background area. Route 57 (a main prefectural road with high traffic volumes of both diesel- and gasoline-powered vehicles, around 21,000 vehicles per weekday) was chosen as the roadside site. Samples were collected at curbside on a street corner near Saitama University at a height of 1.5 m above the ground. The urban background site was on the campus of Saitama University, about 250 m northeast of the roadside site. At this site, samples were collected at about 15 m above the ground, on the roof of a four-story building (Department of Applied Chemistry, Saitama University).

## 2.2 Sampling Protocols

Airborne particulate matter was sampled during two periods at each site: winter (December 16-28, 2004) and summer (July 20-August 2, 2005). During these periods, samples of PM$_{10}$ and PM$_{2.5}$ were collected using a pair of Federal Reference Method (FRM, Partisol sequential air sampler model 2025, Rupprecht & Patashnick Co., Inc., East Greenbush, NY, USA) air samplers and cyclone separators; the flow rate was maintained at 16.7 L/min for 12 h. Quartz fiber filters (47 mm diameter, Pallflex, 2500 QAST; Shibata Scientific Technology) were used as collecting media. Prior to sampling, the filters were heated at 800°C for 2 h to eliminate organic species, kept at 20°C and 50% relative humidity for 48 h, and then weighed. The filters were shielded from direct sunlight and rain. Background contamination was measured using operational

blanks (unexposed filters), which were processed simultaneously with the field samples. In the laboratory, all filters were kept at 20°C and 50% relative humidity for 48 h, reweighed, and then stored in the refrigerator ($-40 \pm 5$°C) until they were chemically analyzed.

At the roadside, traffic volume was recorded on videotape for later manual counting of the numbers of diesel- and gasoline-powered vehicles. Vehicles were counted for 10 min at each hour, and the total volumes of vehicles in both directions were counted. During the sampling period, meteorological parameters (ambient temperature, relative humidity, wind speed, and wind direction) were monitored at the roadside with an EDO MET-9800 system (Shibata Scientific Technology).

During the winter, the data for nitrogen oxides ($NO_x$) and ozone ($O_3$) were obtained with an ambient air-quality monitoring station at a height of about 20 m above the ground, on the roof of the Saitama Institute of Public Health, which is 450 m away from Saitama University on northeast direction. In the summer, $NO_x$ and $O_3$ were monitored at the roadside using a nitrogen oxides analyzer (DKK Corporation, Tokyo, Japan) and a UVAD-1000 $O_3$ analyzer (Shimadzu Corporation, Kyoto, Japan), respectively. Prior to monitoring, both analyzers were multipoint calibrated with a NO gas cylinder (Japan Fine Products Corporation, Kanagawa, Japan). The obtained calibration curves represent the best fits for all the data points ($R^2 = 1.00$ and $R^2 = 0.998$ for NO, and $O_3$ respectively).

### 2.3 Chemical Analysis

All samples were analyzed for EC and organic carbon (OC) using a thermal optical carbon analyzer (DRI model 2001, Sibata Scientific Technology) with the IMPROVE thermal/optical reflectance protocol reported by Chow et al. (1993). Briefly, a 0.503 cm$^2$ (8 mm diameter) punch aliquot of a sample quartz filter was heated at 120 (OC1), 250 (OC2), 450 (OC3), and 550 (OC4)°C in a helium atmosphere, and at 550 (EC1), 700 (EC2), and 800 (EC3)°C in an oxidizing atmosphere of 2% oxygen and 98% helium. The analysis was repeated three times for each sample for better accuracy. For analysis of ions, an area of 1.90 cm$^2$ aliquot of each filter was extracted with 0.3 M NaHCO$_3$ and deionized water during the analysis of anions ($NO_3^-$, $SO_4^{2-}$, and $Cl^-$) and cations ($K^+$, $Na^+$, $NH_4^+$, and $Ca^{2+}$), respectively. All extracts were analyzed using an ion chromatograph (Dionex-100 IC) equipped with an electric conductivity detector. Mixed standards of five concentrations within the ranges of 0.1-2.5 ppm (w/v) for anions and 0.05-0.8 ppm (w/v) for cations were used to draw standard calibration curves.

**Table 1.** Conditions for HPLC analysis of PAHs.

| | |
|---|---|
| Column | Wakosil-PAHs, 4.6*250 mm (Wako Pure Chemical Industries) |
| Column temperature | 40°C |
| Eluent | CH$_3$CN : H$_2$O (DI[a]) 85 : 15 |
| Detector | Fluorescence detector |
| Flow rate | 1 mL/min. |
| Retention time | 0-20 min. |
| Injection volume | 20 μL |

[a]Deionized water

The residual filter area remaining after the analysis of carbonaceous components and ions was used for extraction of PAHs. The residual area was cut into small pieces, which were ultrasonically extracted twice with 3.0 mL of acetonitrile (HPLC grade, Wako Pure Chemical Industries, Japan) for 1 h. The combined extracts were centrifuged at 2,500 rpm for 10 min and then filtered through a 0.2-μm syringe filter. The volume of the filtrate was reduced to 0.5 mL using a gentle stream of nitrogen gas ($N_2$), and the residue was transferred to 1-mL vials and analyzed by high-performance liquid chromatography (Shimadzu LC-10Avp series, Shimadzu Corporation, Kyoto, Japan). Table 1 summarizes the chromatographic conditions used during the analysis. The chromatographic peaks of the samples were identified by comparison of their retention times to those of standards. Selected PAHs were quantified by comparison of the measured peak areas with those of standards of known concentration. The quantified compounds were pyrene (PYR), benzo[a]anthracene (BaA), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), indeno[1,2,3-cd]pyrene (IndP), and benzo[ghi]perylene (BghiP). PAH concentrations are reportedly lower during summer than during winter (Hayakawa et al., 2002; Smith and Harrison, 1996). For that reason and because of the time required for extraction and analysis, only samples collected during winter were analyzed for selected PAHs as described above. Finally, WRPLOT View software (Lakes Environmental Software Inc., Ontario, Canada) was used for drawing the rose diagrams of wind direction.

## 3. RESULTS AND DISCUSSION

### 3.1 Contribution of PM$_{2.5}$ to PM$_{10}$

During all the sampling periods, the mass concentrations of PM$_{10}$ were below the air quality standards for suspended particulate matter in Japan (SPM, which corresponds to PM$_7$, 100 μg/m$^3$) and in the United States (PM$_{10}$, 150 μg/m$^3$ daily average). In contrast, the average concentrations of PM$_{2.5}$ exceeded the United

**Table 2.** Average mass concentrations (arithmetic mean $\pm$ SD) of PM$_{2.5}$, PM$_{10}$ and carbonaceous components, as well as EC/TC, and PM$_{2.5}$/PM$_{10}$ ratios and correlations between sites.

| | Roadside ($\mu$g/m$^3$) | | | | Urban background ($\mu$g/m$^3$) | | | |
| | PM$_{2.5}$ | | PM$_{10}$ | | PM$_{2.5}$ | | PM$_{10}$ | |
| | Winter | Summer | Winter | Summer | Winter | Summer | Winter | Summer |
|---|---|---|---|---|---|---|---|---|
| Mass | 31$\pm$7 | 34$\pm$6 | 37$\pm$9 | 43$\pm$6 | 23$\pm$7 | 27$\pm$5 | 28$\pm$8 | 33$\pm$5 |
| EC | 5.3$\pm$3.2 | 6.5$\pm$2.4 | 6.4$\pm$4.1 | 7.1$\pm$2.4 | 2.9$\pm$2.0 | 3.3$\pm$0.9 | 3.0$\pm$2.3 | 3.8$\pm$0.9 |
| OC | 9.5$\pm$4.9 | 9.9$\pm$1.8 | 11.0$\pm$6.3 | 11.4$\pm$2.1 | 7.0$\pm$3.3 | 8.5$\pm$1.9 | 7.3$\pm$3.8 | 9.3$\pm$1.7 |
| TC | 14.8$\pm$7.8 | 16.4$\pm$3.9 | 17.4$\pm$9.9 | 18.5$\pm$3.9 | 10.0$\pm$5.4 | 11.8$\pm$2.7 | 11.3$\pm$6.2 | 13.1$\pm$2.4 |
| EC/TC | 0.35$\pm$0.1 | 0.40$\pm$0.1 | 0.36$\pm$0.1 | 0.39$\pm$0.1 | 0.29$\pm$0.1 | 0.28$\pm$0.0 | 0.26$\pm$0.1 | 0.29$\pm$0.0 |
| PM$_{2.5}$/PM$_{10}$ | Winter | | Summer | | Winter | | Summer | |
| | 0.83$\pm$0.0 | | 0.74$\pm$0.1 | | 0.81$\pm$0.0 | | 0.64$\pm$0.1 | |

Pearson correlation coefficients ($r$) between both sites[a]

| | PM$_{2.5}$ | | PM$_{10}$ | |
| | Winter | Summer | Winter | Summer |
|---|---|---|---|---|
| Mass | 0.94 | 0.94 | 0.90 | 0.86 |
| EC | 0.93 | 0.84 | 0.83 | 0.55 |
| OC | 0.88 | 0.87 | 0.87 | 0.70 |
| TC | 0.93 | 0.83 | 0.87 | 0.66 |

[a]$p < 0.01$, $n = 24$ for winter, and $p < 0.01$, $n = 22$ for summer
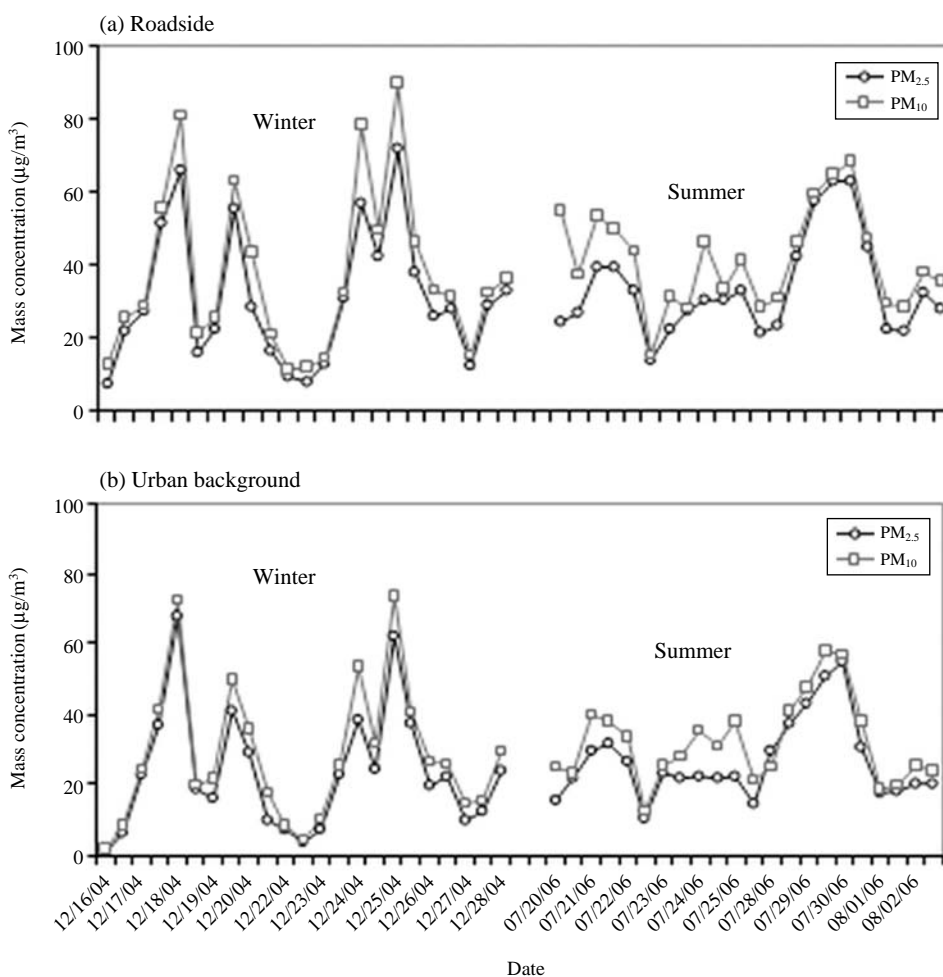


**Fig. 2.** Temporal variation of PM$_{2.5}$ and PM$_{10}$ mass concentrations during winter and summer at the roadside and the urban background site.

(a) Roadside
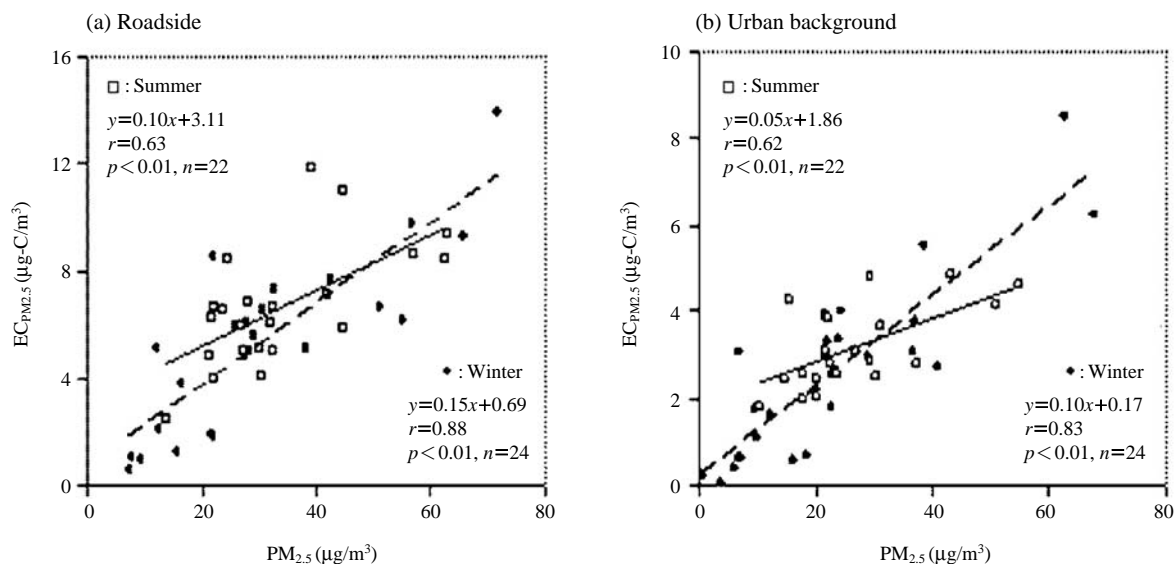


(b) Urban background



**Fig. 3.** Correlation between $PM_{2.5}$ and $EC_{PM2.5}$ mass concentrations at the roadside and the urban background site during winter and summer.

States Environmental Protection Agency (USEPA) standard for $PM_{2.5}$ (15 µg/m³, annual average, Table 2). Moreover, the USEPA daily average standard for $PM_{2.5}$ (35 µg/m³) was exceeded at both sites on a few days (25% and 18% of $PM_{2.5}$ data during winter and summer, respectively). The concentrations of $PM_{2.5}$ and $PM_{10}$ showed identical temporal variations (Fig. 2) and were strongly correlated (Pearson correlation coefficients: $r=0.98$ and 0.94 at the roadside and $r=0.98$ and 0.93 at the urban background site during the winter and summer periods, respectively). The average values of the $PM_{2.5}/PM_{10}$ ratio during winter were 0.83 and 0.81, whereas the values were 0.74 and 0.64 during summer at the roadside and the urban background site respectively. These values agree with those reported by Sasaki and Sakamoto (2006) for $PM_{2.5}/PM_{10}$ at Saitama sampling sites. These results indicate that $PM_{2.5}$ makes up the largest fraction of $PM_{10}$ at various places in Saitama.

Many other urban areas in Japan are affected by high concentrations of $PM_{2.5}$. Saitoh *et al.* (2002) reported an average concentration of 27.9 µg/m³ for $PM_{2.5}$ measurements carried out from December 26, 1998, to January 9, 1999, at Shinjuku, Tokyo; and $PM_{2.5}$ was the major contributing fraction of $PM_{10}$. Ma *et al.* (2004) reported three high-concentration episodes for $PM_{2.5}$ ($>65$ µg/m³) in the Kansai area.

### 3. 2  Carbonaceous Components

Table 2 lists average mass concentrations of EC, OC, and total carbon (TC) observed during winter and summer. As expected, the concentrations of carbona-

ceous components were higher at the roadside than at the urban background site during each sampling period. However, the concentrations at the two sites were strongly correlated, especially for the $PM_{2.5}$ fraction (see Table 2).

The EC/TC ratios for $PM_{2.5}$ and $PM_{10}$ were very similar during the two study periods at both the roadside and the urban background. This observation seems to indicate that EC was associated with $PM_{2.5}$ rather than with larger particles. To confirm that this was the case, we investigated the correlation between the mass of particulate matters ($PM_{2.5}$ & $PM_{10}$) and the EC concentrations in both fractions. At both sites, $PM_{2.5}$ and EC were strongly correlated (Pearson correlation coefficients: $r=0.88$ and $r=0.83$, $p<0.01$, $n=24$ at the roadside and the urban background site, respectively) during winter (Fig. 3). However, they were only moderately correlated during summer. As for the relation between $PM_{10}$ and the EC, the correlation coefficients were: $r=0.73$ and $r=0.72$, $p<0.01$, $n=24$ at the roadside and the urban background site, respectively. These findings indicate that EC, which is mainly emitted from combustion sources (diesel-powered vehicles in the current study area), was associated with $PM_{2.5}$ at both sites.

During winter, the contribution of TC to the mass of $PM_{2.5}$ was 47% (EC: 17%, OC: 30%) at the roadside, whereas it was 43% (EC: 13%, OC: 30%) at the urban background site. Similar percentages were observed during summer. Moreover, at both sites the temporal variations of TC were similar to those of $PM_{2.5}$. The high levels of carbonaceous components

could be attributable to traffic emissions. Particularly, the higher EC concentrations observed at the roadside compared with those observed at the urban background site are attributable to the exhaust of diesel-powered vehicles. This is supported by the observation that EC was significantly correlated ($r=0.50$, $p<0.02$, $n=24$ and $r=0.45$, $p<0.05$, $n=22$ during winter and summer, respectively) with the percentage of diesel-powered vehicles traveling on the road. However, the narrow range of the diesel-powered vehicles percentage (19-32%) as well as the meteorological conditions could explain the moderate correlation coefficients that were obtained. Furthermore, EC was strongly
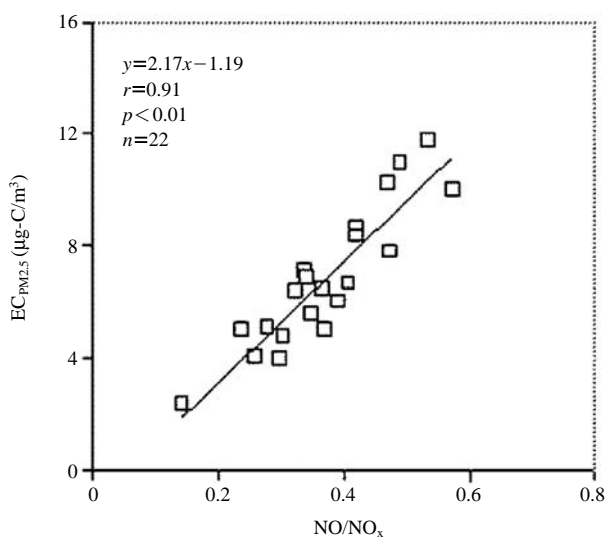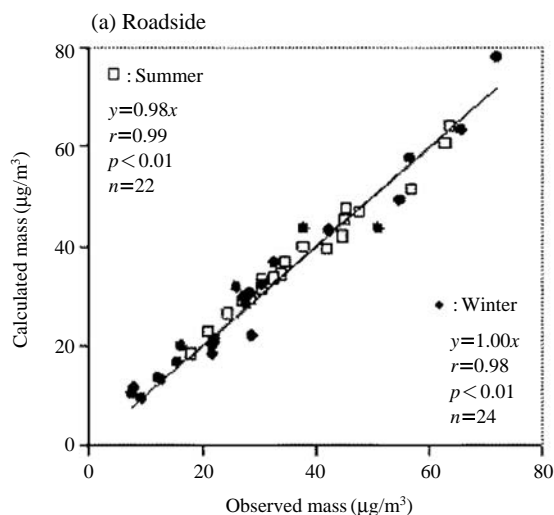


**Fig. 4.** Correlation between NO/NO$_x$ and EC$_{PM2.5}$ at the roadside during summer.

correlated ($r=0.91$, $n=22$, $p<0.01$) with the NO/NO$_x$ ratio measured at the roadside during summer (Fig. 4). The NO/NO$_x$ ratio represents the primary emitted NO$_x$ which are mainly emitted by diesel-powered vehicles. These correlations indicate that diesel-powered vehicles traveling on the road may have been the major source of EC measured during our study.

## 3.3 Chemical Composition of PM$_{2.5}$ Calculated with the Mass Closure Model

Using the analytical data for the chemical components measured, we constructed a mass closure model (Harrison *et al*., 2003) for the chemical composition of the particulate matter measured at the two sites. We focused on the chemical composition of PM$_{2.5}$. The model is described briefly as follows:

**Sulphate** : Sulphate concentrations were increased to the equivalent mass of ammonium sulphate using a factor of 1.38. A further 29% increase was applied to allow for water content.

**Nitrate** : Nitrate concentrations were increased to the equivalent mass of ammonium nitrate using a factor of 1.29. A further 29% increase was applied to allow for water content.

**Chloride** : Chloride concentrations were increased to the equivalent mass of ammonium chloride using a factor of 1.51. A further 32% increase was applied to allow for water content.

**EC** : EC mass was unchanged because EC exists in the form of graphitic carbon.

**OC** : Factors of 1.3 and 1.7 were used to convert carbon masses to organic compound masses at the roadside and the urban background site, respectively.

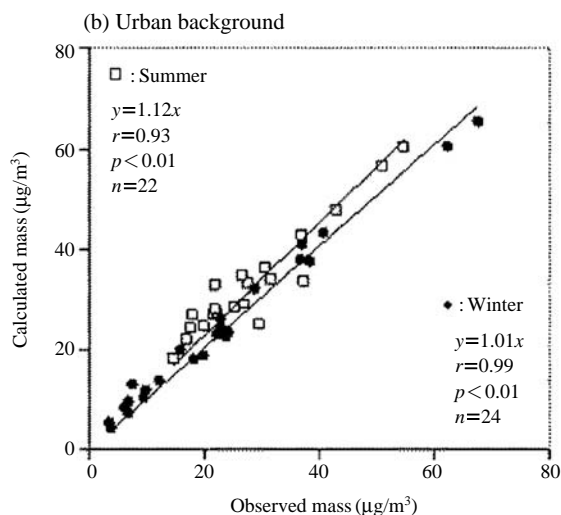Harrison *et al*. (2003) used a factor of 1.4 to convert



**Fig. 5.** Observed mass concentration of PM$_{2.5}$ plotted against calculated mass concentration at the roadside and the urban background site during winter and summer.
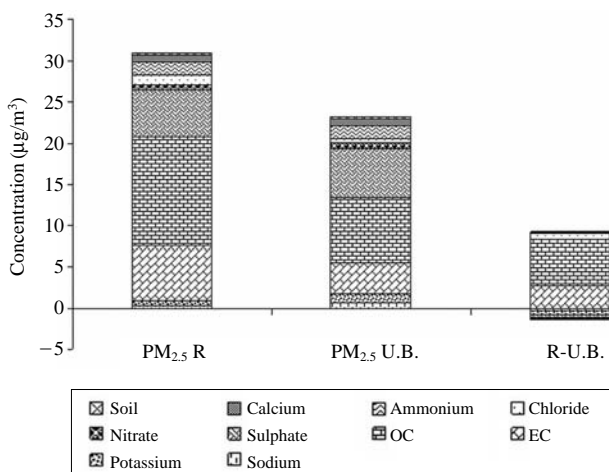
**Fig. 6.** Calculated chemical composition of $PM_{2.5}$ at the roadside (R) and the urban background site (U.B.), along with the difference between the two (R-U.B.) on July 25, 2005.

**Table 3.** Average concentrations (arithmetic mean$\pm$SD) of measured PAHs at the investigated sites in winter.

| | $PM_{2.5}$ (ng/m$^3$) | | $PM_{10}$ (ng/m$^3$) | |
| --- | --- | --- | --- | --- |
| | Roadside | Urban background | Roadside | Urban background |
| PYR | $0.27\pm0.29$ | $0.17\pm0.10$ | $0.20\pm0.14$ | $0.18\pm0.11$ |
| BaA | $0.41\pm0.41$ | $0.22\pm0.21$ | $0.44\pm0.45$ | $0.25\pm0.22$ |
| BaP | $0.52\pm0.47$ | $0.36\pm0.38$ | $0.57\pm0.52$ | $0.45\pm0.46$ |
| BkF | $0.27\pm0.20$ | $0.21\pm0.18$ | $0.29\pm0.22$ | $0.25\pm0.20$ |
| BbF | $0.57\pm0.46$ | $0.43\pm0.39$ | $0.57\pm0.48$ | $0.50\pm0.47$ |
| BghiP | $0.77\pm0.64$ | $0.58\pm0.56$ | $0.80\pm0.68$ | $0.64\pm0.60$ |
| IndP | $0.62\pm0.52$ | $0.48\pm0.36$ | $0.59\pm0.51$ | $0.51\pm0.41$ |
| Total | $3.37\pm2.90$ | $2.33\pm2.08$ | $3.46\pm2.81$ | $2.70\pm2.33$ |

OC to organic compounds for the background site in their study. However, in our study we used a factor of 1.7, which was applied during a similar study in Japan (Takahashi *et al*., 2008). This factor was derived from the observation of a study conducted in Tokyo by Takegawa *et al*. (2005). For soil particles, Harrison *et al*. (2003) assumed the contribution from soil particles and road dust on the basis of Fe analysis. However, in our study we did not analyze Fe. Therefore, we multiplied $PM_{2.5}$ mass concentrations by the factors mentioned by Takahashi *et al*. (2008) to estimate the contribution of soil particles to $PM_{2.5}$ (0.051 and 0.010 during winter and summer, respectively). In Fig. 5, the mass concentrations calculated with the model are plotted against the measured mass concentrations during both winter and summer. The good agreement between the calculated and observed concentrations of $PM_{2.5}$ at the investigated sites indicates the validity of our model. The chemical composition of $PM_{2.5}$ was quite similar at both sites. Fig. 6 shows the chemical composition of $PM_{2.5}$ at both the roadside and the urban backgrounds site. The most abundant components were OC, EC, sulphate, and nitrate. Carbonaceous compounds showed high contributions to the calculated chemical composition of $PM_{2.5}$ (on average 56% at the roadside and 55% at the urban background site). Sulphate and nitrate were associated with carbonaceous components. However, during certain periods (July 29-30, 2005), sulphate was more abundant than the other components. In contrast, nitrate contributions were lower on the same dates. The wind direction on these dates was not stable, but it tended to parallel the road. Usually, high sulphate

concentrations and low nitrate concentrates indicate that an aerosol has traveled long distances (Hagino *et al*., 2007; Baek and Aneja, 2004). Therefore, we suspect that an air mass that included pollutants from other areas passed through the atmosphere at our investigation area on those dates.

The highest contribution of carbonaceous components was observed during days when the wind was coming mainly from the southwest, that is, from the roadside toward the urban background site. Therefore, we strongly believe that at the latter site, the contribution of carbonaceous components can be attributed to motor vehicle emissions. Moreover, at the roadside, the concentrations of several chemical components such as EC and OC were markedly lower on the weekend than during the week. This reduction was associated with the reduction in the number of diesel-powered vehicles on the weekend. The difference between data for the weekday and weekend was marked in the case of the EC concentration, whereas for the OC, the weekend concentrations were closer to the weekday concentrations.

## 3. 4 PAHs

### 3. 4. 1 Association with $PM_{2.5}$

Table 3 lists the average concentrations (arithmetic mean$\pm$SD) and total concentrations of the selected PAHs during winter. At the roadside, the average total PAH concentrations were $3.37\pm2.90$ ng/m$^3$ in $PM_{2.5}$ and $3.46\pm2.81$ ng/m$^3$ in $PM_{10}$. The average $PM_{2.5}/PM_{10}$ ratios for the individual PAHs were 0.95 and 0.81 at the roadside and the urban background site, respectively. For example, the ratio for BaP ranged from 0.83 to 0.98 (average 0.93) at the roadside, whereas the ratio ranged from 0.59 to 0.97 (average 0.82) at the urban background site. The concentrations of individual PAHs (except for PYR) in the $PM_{2.5}$ fraction and their concentrations in the $PM_{10}$ fraction were strongly correlated (Table 4). Thus, we can conclude

**Table 4.** Correlations between sites, between PM$_{2.5}$ and PM$_{10}$, and between individual PAHs in winter.

|  |  | PYR | BaA | BaP | BkF | BbF | BghiP | IndP |
|---|---|---|---|---|---|---|---|---|
| Correlation between sites | PM$_{2.5}$ | 0.657 | 0.901 | 0.964 | 0.974 | 0.967 | 0.950 | 0.952 |
|  | PM$_{10}$ | 0.484 | 0.919 | 0.976 | 0.983 | 0.957 | 0.954 | 0.975 |
| Correlation between PM$_{2.5}$ and PM$_{10}$ | Roadside | 0.469 | 0.999 | 0.998 | 0.995 | 0.970 | 0.999 | 0.986 |
|  | U.B. | 0.635 | 0.994 | 0.992 | 0.984 | 0.942 | 0.992 | 0.992 |
| Correlation between individual PAHs* | IndP | 0.778 | 0.954 | 0.976 | 0.958 | 0.906 | 0.992 | 1 |
|  | BghiP | 0.778 | 0.938 | 0.969 | 0.960 | 0.903 | 1 |  |
|  | BbF | 0.725 | 0.955 | 0.967 | 0.979 | 1 |  |  |
|  | BkF | 0.757 | 0.973 | 0.989 | 1 |  |  |  |
|  | BaP | 0.785 | 0.986 | 1 |  |  |  |  |
|  | BaA | 0.815 | 1 |  |  |  |  |  |
|  | PYR | 1 |  |  |  |  |  |  |

*Measured in PM$_{2.5}$ at the roadside

that most of the measured PAHs were found in the PM$_{2.5}$ fraction. These results are consistent with those of previous studies in some Japanese cities, including Saitama (Kawanaka *et al*., 2004; Ohura *et al*., 2004). The results also showed that the concentrations of individual PAHs in both PM$_{2.5}$ and PM$_{10}$ decreased in the order BghiP > IndP > BbF > BaP > BaA > PYR, at both sites. This order indicates that the concentrations of high-molecular-weight PAHs were higher than those of low-molecular-weight PAHs. The same order was observed by Koyano *et al*. (2002) during a study of two different sites in Tokyo and by Tham *et al*. (2007) in Higashi Hiroshima.

**3.4.2  Variation and Behavior of Selected PAHs**

The concentrations of the individual PAHs (except pyrene) at the two investigated sites were strongly correlated (Table 4). The correlation was stronger for the heavier and more carcinogenic 5- and 6-ring PAHs than for the lighter PAHs. Koyano *et al*. (2002) reported that there were no big differences in the PAH concentrations measured at two different sites (urban and suburban site) in Tokyo during winter. In a study conducted in two cities in Shizuoka Prefecture, Ohura *et al*. (2004) reported that high-molecular-weight PAHs ($\geq$ 5 rings), with the exception of BaP, showed substantially the same profile for both cities in winter and summer. It seems that high-molecular-weight PAHs are distributed widely over large urban areas in Japanese cities. This trend could be explained by strong association of PAHs with PM$_{2.5}$. Using a low-pressure cascade impactor, Kawanaka *et al*. (2004) measured size distributions of nine PAHs and 2-nitrofluoranthene (2-NF) in atmospheric particulate matter collected 20 m above the ground at Saitama University. They reported that 87-95% and 2.9-5.8% of these compounds were found in fine particles (< 2.1 µm) and ultrafine particles (< 0.11 µm), respectively. Particles with a diameter range of 0.1-3.0 µm remain airborne for at
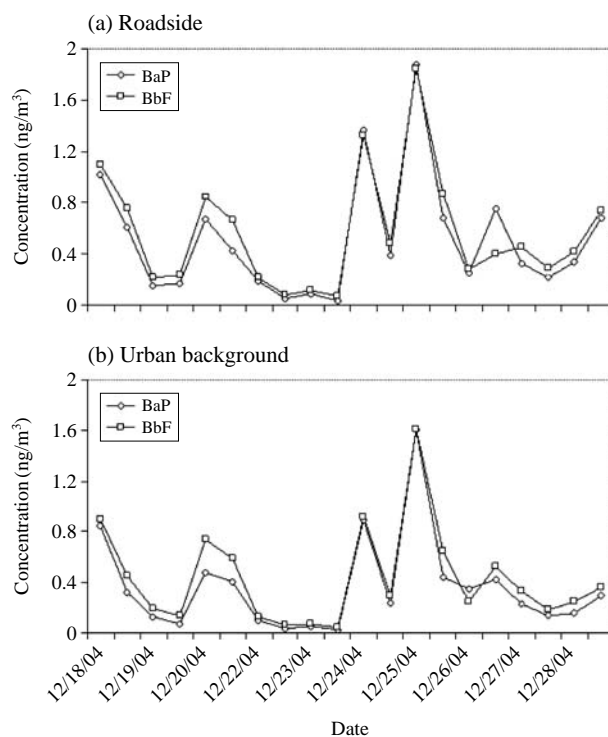


**Fig. 7.** Temporal variation of BaP and BbF measured in PM$_{2.5}$ at the roadside and the urban background site in winter.

least a few days, owing to their slow dry deposition as well as low efficient wet deposition (Baek *et al*., 1991). Thus, PAHs adsorbed on the surface of PM$_{2.5}$ are subjected to long-range transport and can be distributed over long distances; this is particularly true for high-molecular-weight PAHs that resist thermal and photodegradation (Ravindra *et al.*, 2008; Zielinska, 2005).

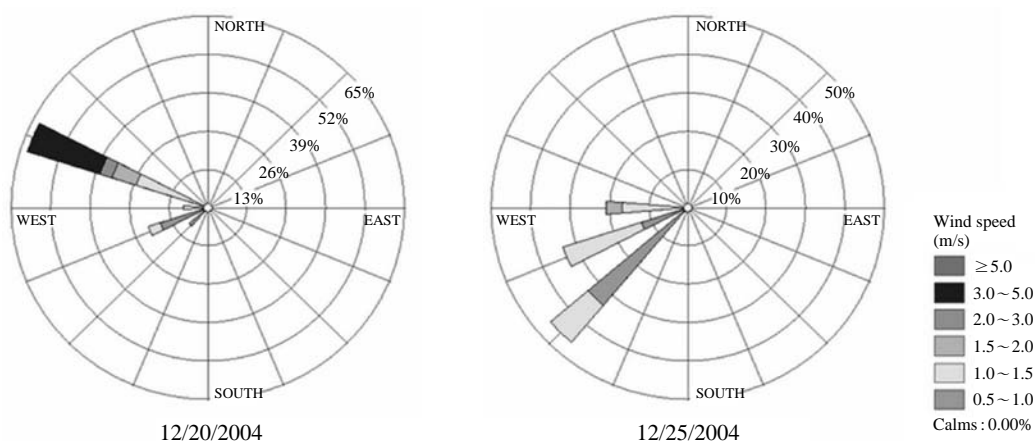Fig. 7 shows the temporal variations of BaP and BbF concentrations at the roadside and the urban back-

**Fig. 8.** Rose diagrams for wind direction on December 20 and 25, 2004. The plots show the directions from which the wind was blowing.

ground site. The PAH concentrations were affected by both wind speed and wind direction. For example, during the first half of the winter sampling period, the speed of the main prevailing wind was 3-5 m/s, whereas during the second half of the winter, the range was 1-2 m/s. High wind speed leads to more dilution of pollutants in the air mass. Thus, the decrease in wind speed could explain the lower concentrations of PAHs during the first half of the winter. Moreover, the main wind direction also varied. Rose diagrams for wind direction on December 20 and 25, 2004, are shown in Fig. 8. Maximum concentrations of the individual PAHs were observed during days when the prevailing wind was from the southwest, that is, coming from the roadside toward the urban background site (e.g., December 25). Low PAH concentrations were observed when either of the sites was in the upwind direction or when the wind direction paralleled the roadside (e.g., December 20). During a study conducted at Saitama University (designated as a suburban site), Hagino *et al.* (2007) carried out high-resolution time measurements of submicron aerosols in winter (from December 14, 2004 to January 9, 2005) using an Aerodyne aerosol mass spectrometer. They reported that concentrations of hydrocarbon-like organics (HOA) were affected by meteorological conditions. HOA concentrations increased at night, owing to stagnation of air masses at night; and the concentrations also increased during periods of low wind speed, owing to particle growth. Our observations appear to agree with these results.

The concentrations of all the PAHs showed the same temporal variation in both $PM_{2.5}$ and $PM_{10}$ fractions, and there was a strong relationship between the concentrations at the two sites (Table 4). This would

**Table 5.** PAH source profile ratios (arithmetic mean±SD) obtained for winter samples.

|  |  | IndP/BghiP | BaP/BghiP | BaA/BaP |
|---|---|---|---|---|
| $PM_{2.5}$ | Roadside | 0.76±0.08 | 0.66±0.12 | 0.78±0.16 |
|  | U.B. | 0.79±0.16 | 0.64±0.10 | 0.64±0.25 |
| $PM_{10}$ | Roadside | 0.72±0.08 | 0.71±0.15 | 0.76±0.17 |
|  | U.B. | 0.75±0.15 | 0.67±0.11 | 0.58±0.19 |
| Reference value | Diesel exhaust | 0.73-0.76[a] | 0.46-0.81[b] | 1.0[a] |
|  | Gasoline exhaust | 0.42-0.47[a] | 0.30-0.40[b] | 0.5[a] |

[a]Li and Kamens, 1993; [b]Simcik *et al.*, 1999

be expected if all of the PAHs were emitted by the same source. We suspect that in our study area, traffic emissions are the main source of PAHs. The maximum PAH concentrations were observed during weekdays, whereas the minimum concentrations were observed on weekends, during which there was usually a clear reduction in the number of diesel-powered vehicles (e.g., December 19 and 26).

### 3. 4. 3 Source Profile Ratio

The contribution of various sources of airborne materials can be evaluated using the concentrations of marker compounds, such as certain PAHs, and their ratios (Alves *et al.*, 2001; Harrison *et al.*, 1996; Li and Kamens, 1993). Table 5 lists the calculated the IND/BghiP, BaP/BghiP, and BaA/BaP ratios during our study and the corresponding reference values. Our ranges of IndP/BghiP and BaP/BghiP ratios were similar to the diesel exhaust ranges reported by Li and Kamens (1993) and Simcik *et al.* (1999), respectively. At the roadside, our calculated BaA/BaP ratio was close to the ratios reported by Li and Kamens (1993) for diesel exhaust, whereas at the urban background

**Table 6.** Pearson's correlation coefficients ($r$) between EC and selected PAHs measured in winter.

|  | Roadside | | Urban background | |
|---|---|---|---|---|
|  | PM$_{2.5}$ | PM$_{10}$ | PM$_{2.5}$ | PM$_{10}$ |
| BaP | 0.600[a] | 0.633[a] | 0.366 | 0.341 |
| BkF | 0.602[a] | 0.636[a] | 0.392[c] | 0.401[c] |
| BbF | 0.661[a] | 0.654[a] | 0.445[b] | 0.409[c] |
| BaA | 0.516[a] | 0.525[a] | 0.170 | 0.164 |
| BghiP | 0.586[a] | 0.615[a] | 0.346 | 0.368 |
| IndP | 0.516[a] | 0.595[a] | 0.242 | 0.251 |
| Total PAH | 0.598[a] | 0.622[a] | 0.477[b] | 0.379[c] |

[a]: $p < 0.01$; [b]: $p < 0.02$; [c]: $p < 0.05$; $n = 20$

site, the ratio was lower than the ratio at the roadside but not as low as the range for gasoline exhaust.

In addition to evaluating source profile ratios, we analyzed the correlations between PAHs and EC (EC can be used as a tracer for diesel exhaust). The results showed that almost all the PAHs were significantly correlated with EC in both fractions (PM$_{2.5}$ and PM$_{10}$) at the roadside, whereas only BkF and BbF were significantly correlated with EC at the urban background site (Table 6). The significant correlation between PAH and EC concentrations, along with the similarities in the profile ratios, strongly suggests that diesel-powered vehicles were the main source of the selected PAHs. These findings are consistent with those of Hagino *et al.* (2008, 2007), who concluded that HOA concentrations measured at 38 m above the ground were influenced mainly by combustion sources like traffic.

# 4. CONCLUSIONS

PM$_{2.5}$ and PM$_{10}$ and their associated traffic-related compounds (EC and PAHs) were investigated during winter and summer at a roadside and an urban background site in Saitama, Japan. At both sites, PM$_{2.5}$ was the main component of PM$_{10}$. EC was strongly associated with PM$_{2.5}$ rather than with larger particles. Furthermore, components related to the exhaust of diesel-powered vehicles were the most abundant chemical components of PM$_{2.5}$. Even though the roadside and the urban background site were separated by 250 m, the PM$_{2.5}$ concentrations, as well as the measured concentrations of PAHs associated with PM$_{2.5}$, were strongly correlated. The correlation was stronger for the heavier and more carcinogenic 5-6-ring PAHs. Despite the new regulations on diesel exhaust gas in October 2002 by the Ministry of Environment (Total Emission Reduction of Nitrogen Oxides and Particulate Matter from Automobile in Specified Areas; Auto-

mobile NO$_x$/PM Law) in some Japanese prefectures in Kanto area, including Saitama, and October 2003 by the Tokyo Metropolis, Chiba, Saitama, and Kanagawa Prefecture (Diesel Vehicle Exhaust Gas Regulations based on the Ordinance on Environmental Preservation to Secure the Health of Citizens), the source profile ratios indicated that diesel-powered vehicles were probably the main source of the measured PAHs.

Our results emphasize the risks associated with human exposure to PM$_{2.5}$ in urban areas. These risks are expected to be particularly high in areas located near traffic roads with high volumes of diesel-powered vehicles. Given the rate of urbanization, which results in more roads and highways in the city, and the fact that PAHs associated with fine particles travel for long distances, the risk posed by these particles can be expected to extend over the entire urban environment. Establishing air quality standards for PM$_{2.5}$ in Japan is an important countermeasure to control such risks. To accomplish this goal, air quality monitoring networks should be established to provide information suitable for assessing exposure and health effects. In particularly, monitoring networks for PM$_{2.5}$, rather than larger particles (SPM or PM$_{10}$), should be established in the urban environment. Evaluation of human exposure to PM$_{2.5}$ and traffic-related air pollutants is strongly recommended, especially in places where sensitive populations (children and elderly people) are living.

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