

# DIURNAL CHARACTERISTICS OF SUSPENDED PARTICULATE MATTER AND PM<sub>2.5</sub> IN THE URBAN ATMOSPHERE OF TOKYO, JAPAN\*

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## ABSTRACT

Suspended particulate matter (SPM) and PM<sub>2.5</sub> in the urban atmosphere of Tokyo, Japan, during the period 22–26 July 2002 were characterized. Samples of SPM and PM<sub>2.5</sub> were collected by low-volume samplers at 6-h sampling intervals, and the concentrations of major ions, elements, and organic and elemental carbon were quantified. Size distributions of particles were simultaneously determined with an Andersen cascade impactor. During the sampling period, vertical profiles of wind were investigated. The major components of SPM and PM<sub>2.5</sub> were organic carbon (OC), elemental carbon (EC), and sulfate. The carbonaceous species (OC + EC = TC) accounted for up to 58% of the SPM or the PM<sub>2.5</sub> mass. On the basis of the ion balance and size distributions of the ionic species, the main chemical form of sulfate was (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The mass concentrations of PM<sub>2.5</sub> made up 70% of SPM on average, which increased to as much as 90% during high-concentration episodes. The OC/TC ratios were larger in the daytime than in the nighttime. The chemical characteristics of the particles indicated that two mechanisms led to high concentrations of SPM and PM<sub>2.5</sub>: (i) an active photochemical process produced high concentrations of OC and sulfate, leading to a high concentration of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in the particles and production of secondary organic aerosols; (ii) stable meteorological conditions resulted in accumulation of primary particles, mainly emitted from vehicle exhaust, resulting in high concentrations of OC and EC.

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\* The views expressed in this article are those of the authors and do not necessarily reflect the policies of the Ministry of Environment Protection of Japan.

## 1. INTRODUCTION

The Kanto Plain, which includes the Tokyo metropolitan area, is one of the most atmospherically polluted areas in Japan. Japan has an air quality standard for suspended particulate matter (SPM: particles with sizes below 10  $\mu\text{m}$  (100% cut point), similar to PM10 (10- $\mu\text{m}$  50% cut point) in US environmental standards), but does not have a standard for PM2.5, so there is little information on the diurnal variation of the components of PM2.5 and the mechanisms leading to high concentrations of PM2.5. Concern about fine particles has been growing because recent epidemiological studies [1, 2] have indicated statistical associations between the effects and the ambient concentrations of fine particles. The US Environmental Protection Agency (US EPA) has promulgated a standard for PM2.5.

In this study, the diurnal characteristics of SPM and PM2.5 in the atmosphere of Tokyo and the mechanisms leading to high concentrations of particles are discussed.

## 2. EXPERIMENTAL

### 2.1 Sampling

Aerosol (SPM and PM2.5) sampling was conducted at the former Suginami Monitoring Station for Air Quality Surveillance in the western area of Tokyo (Fig. 1). The distance between the sampling site and central Tokyo is about 15 km. The sampling site is surrounded by a residential area and is about 300 m from major roads. There are no significant local emission sources near the sampling site.

SPM and PM2.5 samples were collected from 22 July to 26 July 2002 at sampling intervals of 6 h. Two kinds of low-volume samplers were used. For SPM sampling, an S-2 sampler (Shintaku Manufacture, Amagasaki,

Japan) equipped with a cyclone separator (10- $\mu\text{m}$  100% cut point) adjusted to a flow rate of 20 L/min was used. For PM2.5 sampling, an FRM-2000 sampler (Rupprecht & Patashnick, Albany, US) with a WINS impactor (2.5- $\mu\text{m}$  50% cut point) adjusted to a flow rate of 16.7

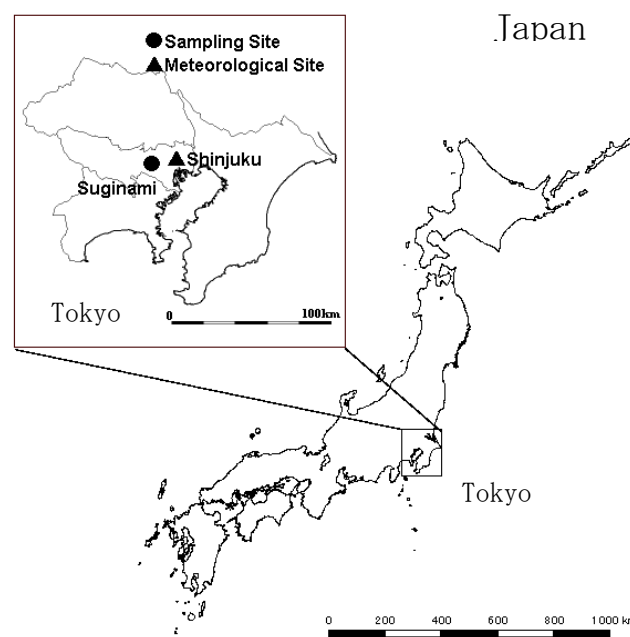


Fig. 1. Locations of sampling and meteorological sites

L/min was used. The SPM and PM<sub>2.5</sub> particles were collected on 47-mm-diameter quartz fiber filters (Pallflex 2500QAT-UP). Prior to sampling, the filters were heated at 800 °C for 2 h to eliminate organic species, and then kept at 20 °C and 50% relative humidity and weighed. After sampling, the filters were stored in a cooler with blue ice to minimize losses due to volatilization and evaporation during transport to the laboratory. In the laboratory, the filters were again kept at 20 °C and 50% relative humidity for 48 h and then reweighed.

The size distribution of particles was determined with an Andersen cascade impactor (AN-200 Tokyo Dylec), which employs nine filters to separate particles with aerodynamic diameters of <0.43, 0.43–0.65, 0.65–1.1, 1.1–2.1, 2.1–3.3, 3.3–4.7, 4.7–7.0, 7.0–11, and >11 µm. The collection time for determining the size distribution was 5 days. During the sampling period, vertical wind profiles were determined by Doppler sodar at Shinjuku (Fig. 1).

## 2.2 Analysis

The samples were analyzed for mass by gravimetry followed by determination of the chemical components. Each sample was divided into four parts for analysis. One quarter, reserved for analysis of Al and Ca, was decomposed with a mixed solution of nitric acid, hydrogen peroxide, and hydrofluoric acid. Another quarter was reserved for analysis of the carbonaceous species. The remaining parts, reserved for analysis of the ionic species, were extracted by ultrasonication with distilled water. The concentrations of NO<sub>3</sub><sup>−</sup>, Cl<sup>−</sup>, SO<sub>4</sub><sup>2−</sup>, and NH<sub>4</sub><sup>+</sup> were determined by ion chromatography, and Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Al, and Ca were analyzed by inductively coupled plasma atomic emission spectroscopy. The concentrations of the carbonaceous species (elemental carbon (EC), organic carbon (OC)) were determined with a thermal–optical carbon analyzer with correction by reflectance [3].

## 3. RESULTS AND DISCUSSION

### 3.1 Diurnal variations of particle concentrations

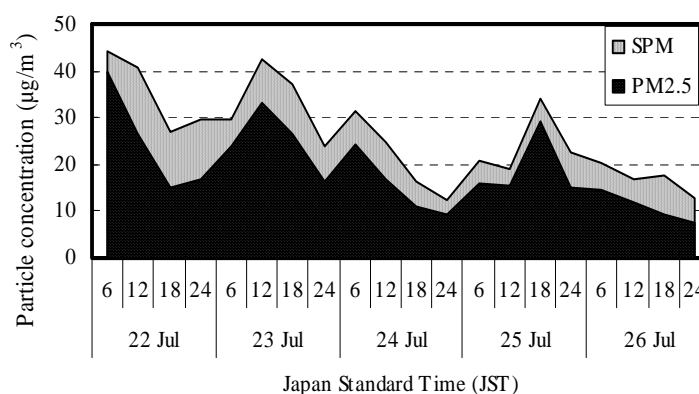
A total of 40 samples were collected during the study period. The diurnal variations of the SPM and PM<sub>2.5</sub> mass concentrations are shown in Fig. 2. SPM mass concentrations ranged from 12 to 44 µg/m<sup>3</sup>, and PM<sub>2.5</sub> mass concentrations ranged from 7 to 40 µg/m<sup>3</sup>. The average mass concentrations of SPM and PM<sub>2.5</sub> were 26 and 19 µg/m<sup>3</sup>, respectively. In Japan, the Air Quality Standard for SPM is 100 µg/m<sup>3</sup> (daily mean), so there were no particularly high concentration episodes during this study. Although the diurnal variation of the particle concentrations exhibited no clear pattern, the particle concentrations varied significantly day to day. The PM<sub>2.5</sub>/SPM ratios ranged from 53 to 90% (72% on average).

The ratios tended to increase for high concentrations of particles. A recent study showing that PM<sub>2.5</sub>/PM<sub>10</sub> was 90% at high particle concentration and 70% at low particle concentration in winter in Tokyo [4] supports these tendencies. These results suggest that fine particles are the major contributor during high-concentration episodes.

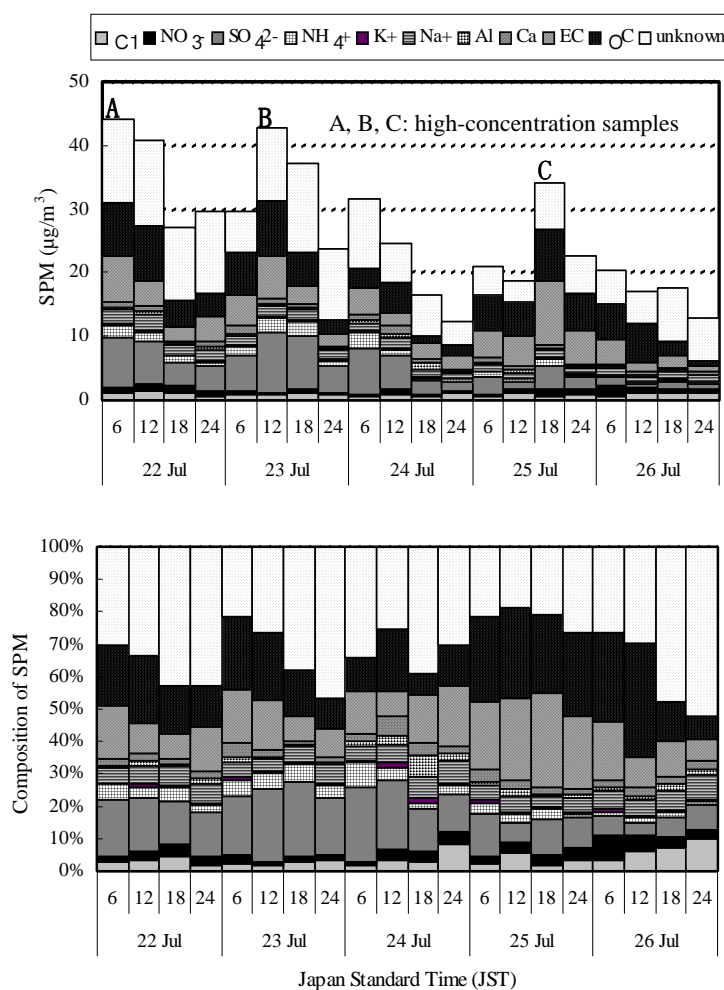
### 3.2 Chemical composition of particles

Figures 3 and 4 show the variations of the particle concentrations and chemical compositions of SPM and PM<sub>2.5</sub>, respectively. “Unknown” is defined as the difference between the particle mass and the sum of the masses of the measured species. Ignoring the unknown species, the major chemical species of both SPM and PM<sub>2.5</sub> were SO<sub>4</sub><sup>2-</sup>, EC, and OC. The variations in the chemical compositions of SPM and those of PM<sub>2.5</sub> were similar; specifically, SO<sub>4</sub><sup>2-</sup> was dominant during 22–24 July, whereas EC and OC were dominant during 25–26 July. The carbonaceous species (OC + EC = TC) accounted for up to 58% of the SPM or the PM<sub>2.5</sub>.

The OC/TC ratios indicated



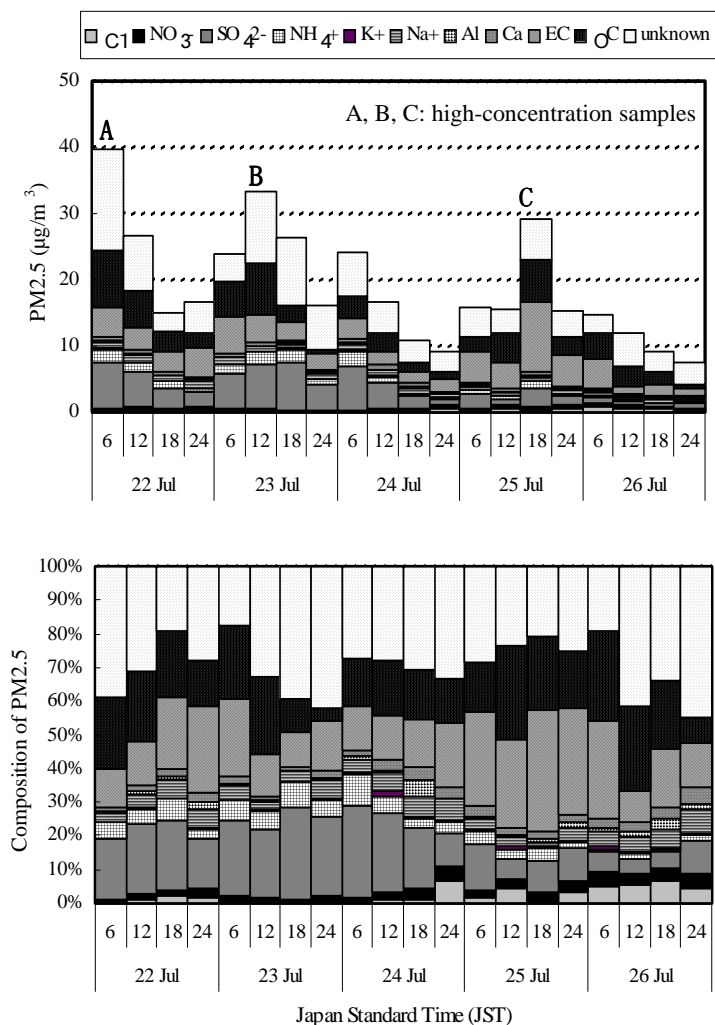
**Fig. 2. Diurnal variations of SPM and PM<sub>2.5</sub>**



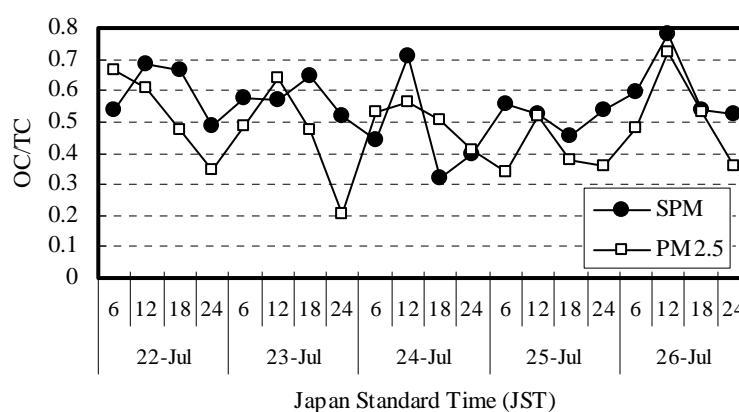
**Fig. 3. Variations of SPM chemical composition**

diurnal pattern which increased in the daytime (0600–1800 JST) and decreased in the nighttime (1800–0600 JST) (Fig. 5). The diurnal patterns of OC/TC for SPM and PM<sub>2.5</sub> were the same; however, the pattern for PM<sub>2.5</sub> was more obvious. These phenomena were probably due to enhanced secondary organic aerosol production because of more favorable conditions for gas–particle conversion of VOCs through photochemical activity [5].

Table 1 compares OC/TC ratios for urban atmospheric aerosols over the past 10 years. The ratio obtained in this study was in agreement with previously reported ratios for Tokyo. Höller et al. [9] suggested that EC/TC ratios in Japan are generally high — and therefore OC/TC ratios relatively low — compared to those reported in the US and Europe. Although this study supported this trend, it is difficult to compare our data for carbonaceous species with those in other studies because the concentrations measured depend on the analytical methods employed [11].



**Fig. 4. Variations of PM<sub>2.5</sub> chemical composition**



**Fig. 5. Variations of OC/TC ratios**

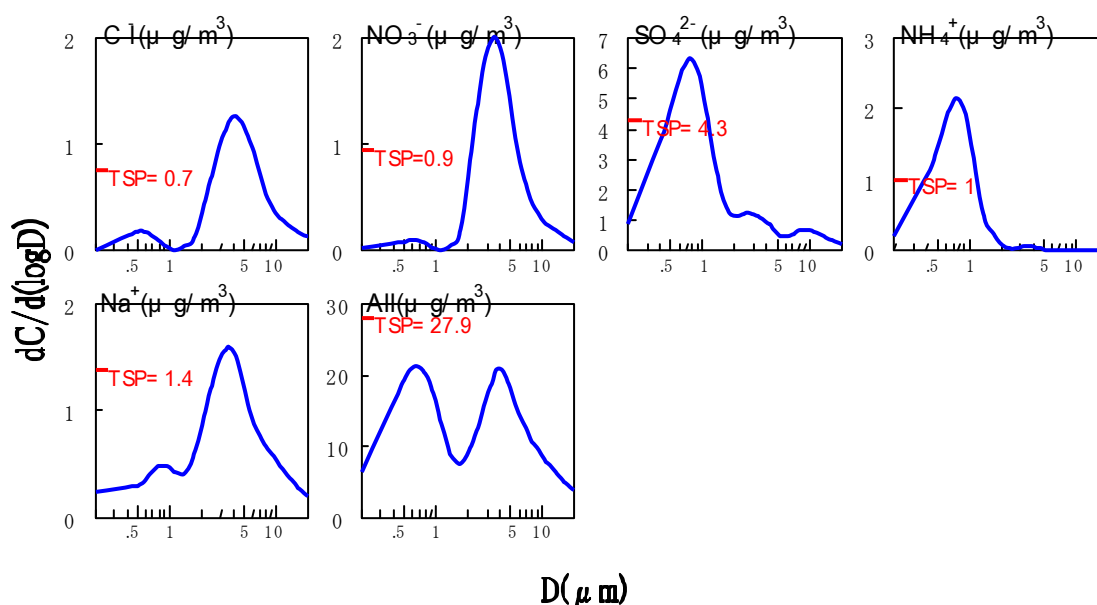
Site	OC( $\mu\text{g}/\text{m}^3$ )	TC( $\mu\text{g}/\text{m}^3$ )	OC/TC	Reference
Chicago, IL, US	2.2	2.6	0.84	Offenberg, Baker (1996) [6]
Washington, DC, US	3.20	5.00	0.64	Malm et al. (1994) [7]
Amsterdam, Netherlands			0.76	Even et al. (2000) [8]
Uji, Japan	2.03	8.50	0.24	Höller et al. (2002) [9]
Tokyo, Japan	7.8	13.2	0.59	Saitoh et al. (2002) [4]
Tokyo, Japan	7.79	13.37	0.58	Miura et al. (2000) [10]
Tokyo, Japan			0.51*	This study

\* Average value of SPM and PM<sub>2.5</sub>

**Table 1. Comparison of OC/TC ratios of urban atmospheric aerosols**

### 3.3 High-concentration episodes

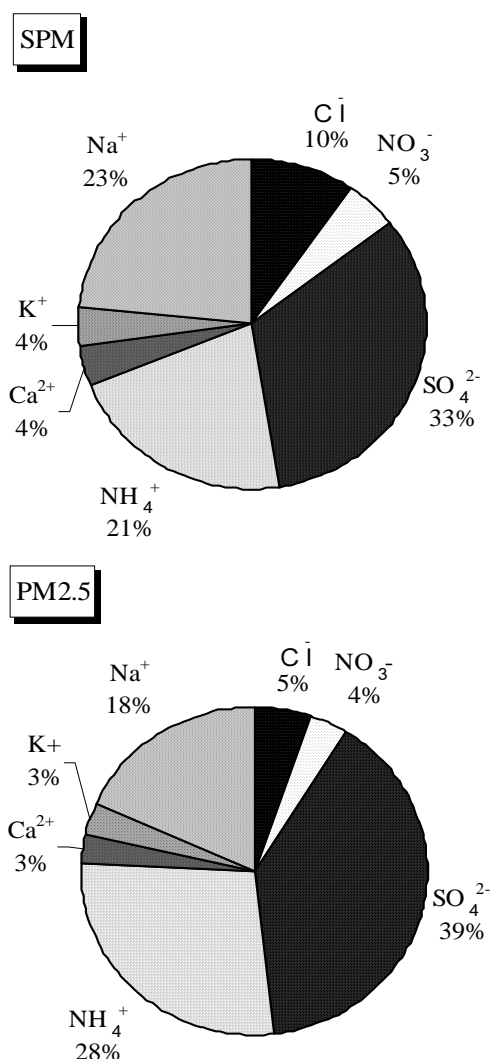
Figures 3 and 4 indicate three high-concentration episodes: episode A, corresponding to the sample collected at 0600–1200 JST on 22 July; episode B, corresponding to the sample collected at 1200–1800 JST on 23 July; and episode C, corresponding to the sample collected at 1800–2400 JST on 25 July. The chemical composition for episode A was similar to that for episode B; however, the chemical composition for episode C was different from those for episodes A and B. For episodes A and B, the greatest contributors to the particle mass were  $\text{SO}_4^{2-}$  and OC. The size distributions of the chemical species estimated with the Andersen cascade impactor, which verified the anion–cation balance, are shown in Fig. 6. This figure



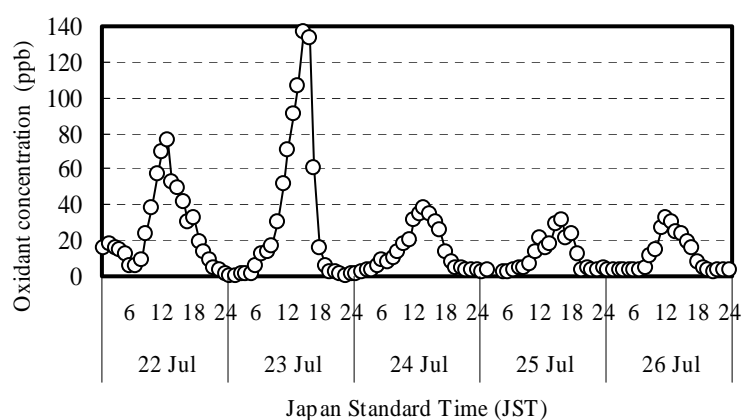
**Fig. 6. Size distributions of chemical species in the atmospheric particles**

suggests that  $\text{SO}_4^{2-}$  was present mainly in the fine particles; we assume that most of the  $\text{SO}_4^{2-}$  was non-sea-salt  $\text{SO}_4^{2-}$ , since most of the  $\text{Na}^+$  was present in the coarse particles. Because most of the  $\text{NH}_4^+$  — the most abundant cation in  $\text{PM}_{2.5}$  (Fig. 7) — was also present in the fine particles, we believe that  $\text{SO}_4^{2-}$  was mostly present as  $(\text{NH}_4)_2\text{SO}_4$  in  $\text{PM}_{2.5}$ . Figure 8 shows time series of oxidant (nearly equivalent to  $\text{O}_3$ ) concentrations at the Sugunami site. High oxidant concentrations were observed on 22–23 July, and, in particular, the oxidant concentration increased to 137 ppb at 1500 JST on 23 July. Hence, it is likely that  $\text{SO}_2$  was photooxidized to sulfate and that high photochemical activity accelerated the production of secondary organic aerosols, resulting in a high concentration of particles.

The notable feature of episode C is that EC was the greatest contributor to the particle mass, particularly for  $\text{PM}_{2.5}$ . EC is abundant in vehicle exhaust and is emitted as fine particles to a large extent [12]. Figure 9 shows the vertical wind profiles at the Shinjuku site at 1800 JST during the sampling period, when traffic was heavy. There are no data for 26 July because of mechanical trouble with the Doppler sodar. On the evening of 25 July, wind was very calm up to a height of 400 m compared to the other days (Fig. 9). Hence, episode C was most likely due to increased



**Fig. 7. Ion balances of particles**



**Fig. 8. Time series of oxidant concentrations at Sugunami**

emissions from vehicle exhaust coupled with meteorological conditions that limited dispersion and caused air stagnation.

#### 4. CONCLUSION

Suspended particulate matter (SPM) and PM<sub>2.5</sub> in the urban atmosphere of Tokyo, Japan, during the period 22–26 July 2002 were characterized. The major components of SPM and PM<sub>2.5</sub> were organic carbon (OC), elemental carbon (EC), and sulfate. The carbonaceous species (OC + EC = TC) accounted for up to 58% of the SPM or the PM<sub>2.5</sub> mass. The chemical characteristics of the particles indicated that two mechanisms led to high concentrations of SPM and PM<sub>2.5</sub>: (i) an active photochemical process produced high concentrations of OC and sulfate, leading to a high concentration of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in the particles and production of secondary organic aerosols; (ii) stable meteorological conditions resulted in accumulation of primary particles, mainly emitted from vehicle exhaust, resulting in high concentrations of OC and EC.

#### ACKNOWLEDGEM

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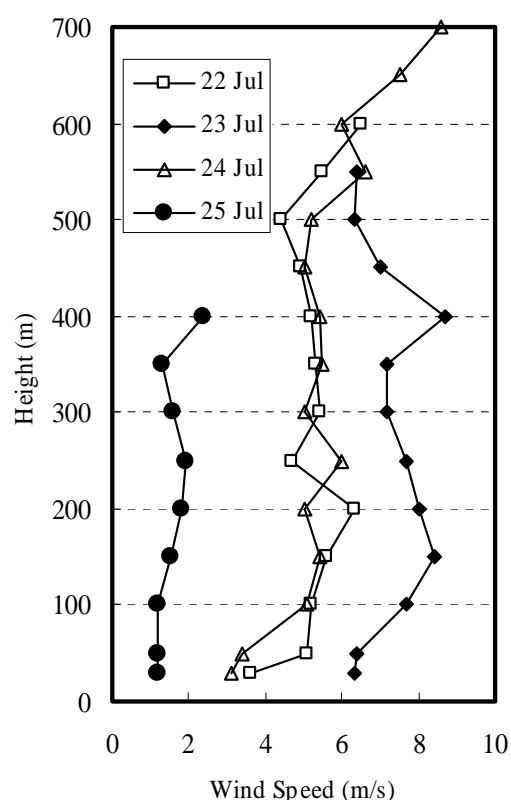


Fig. 9. Vertical wind profiles at 1800(JST).



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