

## Characteristic of Size-Classified Airborne Particulates in Kobe, Japan

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Airborne particulate samples were collected and fractionated into five sizes (diameter of < 1.1, 1.1–2.0, 2.0–3.3, 3.3–7.0, > 7.0  $\mu\text{m}$ ) with a high volume cascade impactor. The size distribution of airborne particulates was bimodal, having two peaks, coarse (> 7.0  $\mu\text{m}$ ) and fine (< 1.1  $\mu\text{m}$ ), which accounted for approximately 29% and 42%, respectively. Inhalable particulates accounted for approximately 50% of the total. The mass percentages of these extracts were also similar to airborne particulate concentrations. Eight authentic polycyclic aromatic hydrocarbons (PAHs; fluoranthene, pyrene, benz[*a*]anthracene, benzo[*e*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene) were detected in airborne particulates. The concentration of PAHs was dependent on size, with the following order: airborne particulates larger than 7.0 < 3.3–7.0 < 2.0–3.3 < 1.1–2.0 < smaller than 1.1  $\mu\text{m}$ . Almost all of the PAHs detected existed in fine airborne particulates smaller than 1.1  $\mu\text{m}$ . Ionic species in size-classified airborne particulate were also investigated.  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{K}^+$  existed in the fine particulates, whereas  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  existed in the coarse particulates. It is likely that  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were generated from the combustion of fossil fuel and air, and  $\text{Na}^+$  and  $\text{Cl}^-$  from sea salt. Since  $\text{NO}_3^-$  was generated from atmospheric  $\text{NO}_2$ , these concentrations were related to each other. The sampling site is located near a highway, so the results suggested that the main source of most fine particulates was car exhaust, especially diesel exhaust.

**Key words** — airborne particulates, size distribution, polycyclic aromatic hydrocarbon, ion species

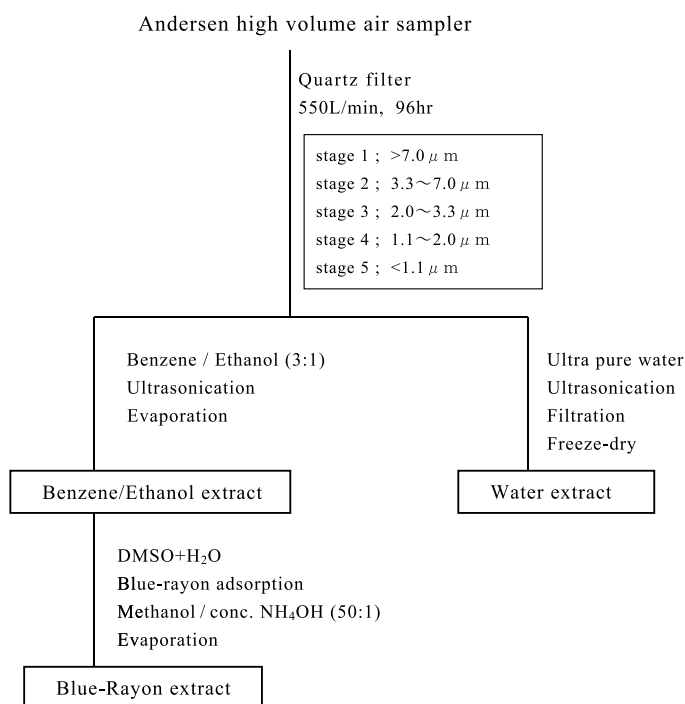
## INTRODUCTION

Interest in the relation between human health and air pollution has grown significantly in recent years. From epidemiological studies, there is evidence of an association between particulate air pollution and adverse health effects.<sup>1–4)</sup> Many organic air pollutants exist on the surface of respirable airborne particulates.<sup>5)</sup> Some components are known, or suspected, to be carcinogens.<sup>6)</sup> Epidemiological studies suggest a relationship between airborne particulates and the incidence of human bronchus cancer.<sup>7–9)</sup> The main carcinogenic compounds in airborne particulates are thought to be PAHs and their derivatives. Airborne particulates are composed of a heterogeneous mixture of particles varying in size and chemical composition. The particulates differ in sources, size ranges, formation mechanisms, and chemical composition. Their physical properties affect their transport and deposition in the human respiratory system, while their chemical composition determines their impact on health. The chemical composition, health impact and rate of deposition of these particles vary significantly with the size of particles. Therefore detailed information on the chemical composition of airborne particulates in different size ranges is essential for health and environmental assessments. In this study, the concentrations and size distributions of airborne particulates, concentrations of PAHs and ionic species as well as their distributions in the particulates were investigated.

## MATERIALS AND METHODS

**Collection of Samples** — Size-classified airborne particulates were collected using a high-volume five-stage cascade impactor air sampler, the AH-600 (Sibata Sci. Technol. Ltd., Tokyo, Japan), equipped with quartz filters (Tokyo Dylec Co. Ltd., Tokyo, Japan). This cascade impactor can fractionate airborne particulates into particles larger than 7.0  $\mu\text{m}$  (stage No. 1), 3.3–7.0  $\mu\text{m}$  (stage No. 2), 2.0–3.3  $\mu\text{m}$  (stage No. 3), 1.1–2.0  $\mu\text{m}$  (stage No. 4), and smaller than 1.1  $\mu\text{m}$  (stage No. 5). Twenty-five sets of samples were collected on the roof of a building of Kobe-Gakuin University (Kobe, Japan) between April 1999 and March 2000 during weekdays for 96 hr, and the average flow rate of air was set at 550 l/min. The sampling site is located near a highway. To analyze the profile of size-classified airborne

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**Fig. 1.** Sampling and Extraction Procedure for Airborne Particulates

particulates, the filters weighed before sampling were allowed to equilibrate at room temperature (20–22°C) under 20–30% humidity for 24 hr, then reweighed to determine the net weight of airborne particulates deposited, and stored at –20°C.

**Extraction of Organic Substances** — The extraction method is shown in Fig. 1. After each filter was divided into two parts, one part of the filter was cut into small pieces and sonicated in benzene/ethanol (3 : 1, v/v), and the solvent was evaporated to dryness under reduced pressure to give the crude organic extracts (benzene/ethanol extract). An aliquot of the benzene/ethanol (B/E) extract dissolved in 1ml of dimethyl sulfoxide was suspended in water then treated with Blue-Rayon (Funakoshi Co. Ltd., Tokyo, Japan), a selective adsorbent for polycyclic compounds,<sup>10</sup> and after the Blue-Rayon had been treated with methanol/ammonia (50 : 1, v/v), the eluent was evaporated to give the Blue-Rayon (BR) extract. Recovery of the PAHs was determined by spiking a standard mixture of corresponded PAHs. In short a standard mixture of the PAHs was spiked in water, and then treated with Blue-Rayon, which extract analyzed by HPLC. The mean recoveries of the PAHs were about 87% (data not shown). Furthermore, the other part of the filter was cut into small pieces and sonicated in ultra pure water, and the solution was freeze-dried as the water (W) extract.

Each extract was weighed and stored at –20°C.

**Analysis of PAHs** — Ten PAHs (anthracene, fluoranthene, pyrene, chrysene, benz[*a*]anthracene, benzo[*e*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene) were analyzed by HPLC with a fluorometric detector. HPLC was performed with a Waters M600 controlled system equipped with a model U6K injector (Waters Co., U.S.A.) coupled to a Shimadzu RF-530 fluorescence spectromonitor (Shimadzu, Japan). The analytical conditions for airborne particulate samples were as described in a previous study.<sup>11</sup> An aliquot of each Blue-Rayon extract was redissolved in tetrahydrofuran, and then subjected to HPLC.

**Analysis of Ionic Species and Determination of Atmospheric Nitrogen Dioxide Concentration**

— To estimate the behavior and source of ionic species in size-classified airborne particulates, the concentrations of cations (Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>) and anions (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>) were determined. To consider the relation of atmospheric nitrogen dioxide to ionic species, the atmospheric concentration of nitrogen dioxide was also determined.

The water extract was subjected to ion chromatography (IC). The IC determination was performed in a Shimadzu PIA-1000 (Shimadzu) equipped with an electric conductivity detector. IC-A3 and IC-C3 (Shimadzu, IC-A3; 2 mm i.d. × 150 mm, IC-C3;

**Table 1.** Size Distribution of Airborne Particulates and Extract Matters

Stage No.	Particle size ( $\mu\text{m}$ )	Concentration ( $\mu\text{g}/\text{m}^3$ )		B/E extract ( $\mu\text{g}/\text{m}^3$ )		W extract ( $\mu\text{g}/\text{m}^3$ )	
		Mean $\pm$ S.D.	%	Mean $\pm$ S.D.	%	Mean $\pm$ S.D.	%
1	> 7.0	14.61 $\pm$ 11.65	29.33	3.14 $\pm$ 1.71	21.21	3.76 $\pm$ 3.14	20.91
2	3.3–7.0	6.84 $\pm$ 6.26	13.74	2.18 $\pm$ 0.97	14.69	2.76 $\pm$ 5.08	15.35
3	2.0–3.3	4.31 $\pm$ 4.38	8.66	1.85 $\pm$ 0.54	12.5	2.17 $\pm$ 6.85	12.07
4	1.1–2.0	3.27 $\pm$ 1.85	6.57	1.94 $\pm$ 0.84	13.1	1.42 $\pm$ 1.82	7.91
5	< 1.1	20.77 $\pm$ 10.05	41.7	5.71 $\pm$ 2.13	38.51	7.86 $\pm$ 5.10	43.76

Each data is the mean of twenty-five sets of samples.

2 mm i.d.  $\times$  100 mm) columns were used and 8 mM *p*-hydroxybenzoic acid/3.2 mM Bis-Tris and 2.5 mM oxalic acid served as the mobile phase, respectively. The flow rate was 0.12 ml/min and 0.1 ml/min, respectively.

ADVANTEC Filter Badge NO<sub>2</sub> (Toyo Roshi Kaisha, Ltd., Japan) was used to measure atmospheric nitrogen dioxide according to the instruction manual. In short, the badge was exposed to air for 96 hr then reacted with a coloring reagent, and the 24 hr average concentration of nitrogen dioxide was determined by measuring the absorbance at 545 nm.

## RESULTS AND DISCUSSION

### Profile of Size-Classified Airborne Particulates

Using the method described, airborne particulates were divided into 5 sizes; larger than 7.0  $\mu\text{m}$ , 3.3–7.0  $\mu\text{m}$ , 2.0–3.3  $\mu\text{m}$ , 1.1–2.0  $\mu\text{m}$  and smaller than 1.1  $\mu\text{m}$ . Average mass concentrations ( $\mu\text{g}/\text{m}^3$ ) of airborne particulates and extracts are shown in Table 1. The amount of airborne particulates were in the range of 7.82–30.5  $\mu\text{g}/\text{m}^3$  (particle size; > 7.0  $\mu\text{m}$ ), 7.66–14.5  $\mu\text{g}/\text{m}^3$  (3.3–7.0  $\mu\text{m}$ ), 1.21–8.3  $\mu\text{g}/\text{m}^3$  (2.0–3.3  $\mu\text{m}$ ), 1.56–6.48  $\mu\text{g}/\text{m}^3$  (1.1–2.0  $\mu\text{m}$ ) and 14.3–33.2  $\mu\text{g}/\text{m}^3$  (< 1.1  $\mu\text{m}$ ), respectively. Seasonal variations of the amounts were evidenced and found to be in other investigations.<sup>12–15</sup> The size distribution was bimodal, having two peaks, coarse (> 7.0  $\mu\text{m}$ ) and fine (< 1.1  $\mu\text{m}$ ), whose mass amounts accounted for approximately 29% and 42%, respectively. Similar results have been reported in other studies.<sup>15–19</sup> Mass percentages of the B/E extract and W extract were similar to airborne particulate concentrations. Fine airborne particulate is a health concern as respiratory morbidity and risks of death increase.<sup>20,21</sup> In the present study, inhalable particulates accounted for approximately 50% of airborne particulates, which showed that fine particu-

lates have a considerable association with respiratory disease.

### Analysis of PAHs in Airborne Particulates

Table 2 presents the results of an analysis of ten PAHs in BR extract from size-classified airborne particulates. Eight of the ten PAHs were detected in airborne particulates. Total PAH concentrations were in the following order: airborne particulates larger than 7.0 < 3.3–7.0 < 2.0–3.3 < 1.1–2.0 < smaller than 1.1  $\mu\text{m}$ . The concentrations were dependent on the size of airborne particulates. Almost all these PAHs existed in fine airborne particulates smaller than 1.1  $\mu\text{m}$ . It is known that particulates emitted from diesel engined vehicles are mainly less than 1.1  $\mu\text{m}$ .<sup>19,22</sup> The sampling site is located near the highway, it is suggested that most of the particulates smaller than 1.1  $\mu\text{m}$  were originated from diesel exhaust particles. The difference of the PAHs detected in this study and our previous study<sup>11</sup> might reflect both the difference of sampling site and period.

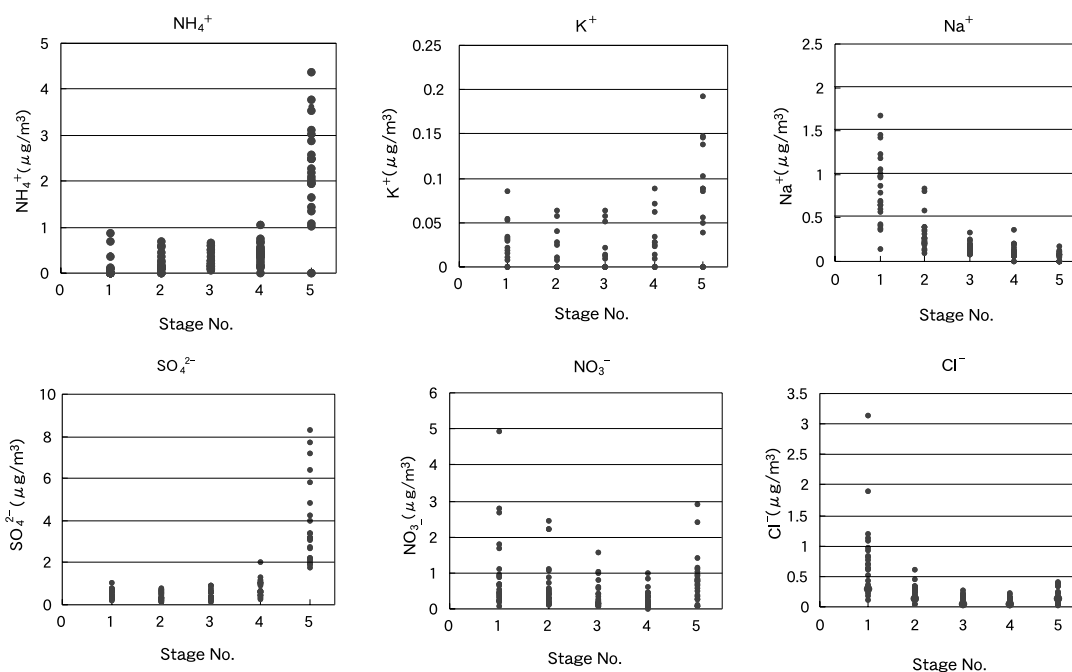
### Analysis of Ionic Species and Determination of the Atmospheric Nitrogen Dioxide Concentration

Airborne particulates are mainly composed of carbon, metallic species and ionic species.<sup>23</sup> Investigating the ionic species in size-classified airborne particulates is important for estimating the source of airborne particulates. The distribution and concentration of cationic and anionic species in size-classified airborne particulates are shown in Fig. 2 and Table 3. NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and K<sup>+</sup> existed in stage 5, whereas NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and Na<sup>+</sup> existed in stage 1. Generally, SO<sub>4</sub><sup>2-</sup> arises from the combustion of fossil fuel, and NO<sub>3</sub><sup>-</sup> from combustion at high temperature. It is suggested that (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> exists in fine particulates since gaseous NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> react with each other quickly. It is likely that fine particulates arise from combustion, whereas coarse particulates come from soil and sea salt. It is thought that the source of Na<sup>+</sup>

**Table 2.** Concentration of PAHs in Blue-Ray Extract from Size-Classified Airborne Particulates

PAHs	ng /m <sup>3</sup> air				
	stage No.				
	1	2	3	4	5
Anthracene	—	—	—	—	—
Fluoranthene	—	—	—	—	0.211
Pyrene	—	—	—	—	0.131
Chrysene	—	—	—	—	—
Benz[ <i>a</i> ]anthracene	—	—	—	—	0.178
Benzo[ <i>e</i> ]pyrene	—	—	—	—	0.136
Benzo[ <i>b</i> ]fluoranthene	—	—	—	—	0.425
Benzo[ <i>k</i> ]fluoranthene	—	—	—	0.063	0.165
Benzo[ <i>a</i> ]pyrene	—	—	—	0.112	0.291
Benzo[ <i>ghi</i> ]pelyrene	0.019	0.019	0.026	0.045	0.148
Total	> 0.019	> 0.019	> 0.026	> 0.22	> 1.69

PAHs in the extracts were analyzed by reversed-phase HPLC with a spectrofluorometric detector. HPLC conditions: apparatus; Waters M600 multisolvent delivery system with U6K injector column; Capcell Pack C<sub>18</sub> (4.6 mm × 250 mm), mobil phase; water/acetonitril gradient, 2.3 ml/min detector; fluorescence spectromonitor (Shimadzu RF-530, Ex. 290 nm, Em. 430 nm). (—), not detected.

**Fig. 2.** Distribution of Cationic and Anionic Species in Size-Classified Airborne Particulates

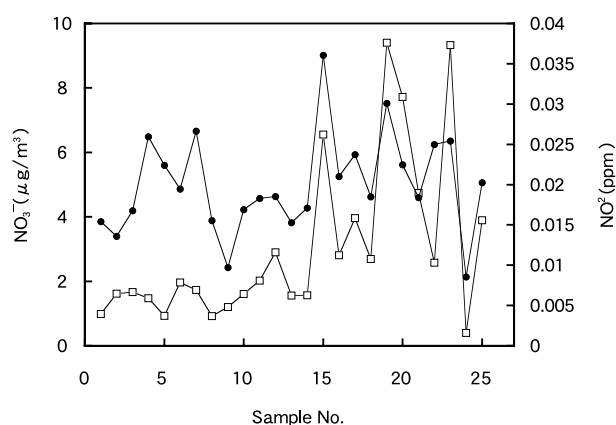
and Cl<sup>-</sup>, which existed in coarse particulates, was sea salt, and NO<sub>3</sub><sup>-</sup> is generated from atmospheric NO<sub>2</sub>. To consider the relation of atmospheric NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>, the atmospheric concentration of NO<sub>2</sub> was determined. The relation of NO<sub>2</sub> in air and NO<sub>3</sub><sup>-</sup> in airborne particulates is shown in Fig. 3. Behavior of both species well agreed with each other. The NO<sub>3</sub><sup>-</sup> concentration is dependent on the atmospheric NO<sub>2</sub>

concentration. The result suggested that airborne particulates and NO<sub>2</sub> are generated from same sources.

As mentioned above, an investigation of the profile of size-classified airborne particulates revealed that inhalable fine particulates accounted for 50 percent of all airborne particulates and about 90 percent of PAHs existed in smaller airborne particu-

**Table 3.** Concentration of Anionic and Cationic Species in Size-Classified Airborne Particulates

Stage No.	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
	$\mu\text{g}/\text{m}^3$ (Mean $\pm$ S.D.)					
1	0.10 $\pm$ 0.23	0.02 $\pm$ 0.02	0.85 $\pm$ 0.41	0.79 $\pm$ 0.62	0.96 $\pm$ 1.10	0.51 $\pm$ 0.21
2	0.20 $\pm$ 0.20	0.01 $\pm$ 0.02	0.34 $\pm$ 0.20	0.25 $\pm$ 0.13	0.65 $\pm$ 0.68	0.41 $\pm$ 0.19
3	0.28 $\pm$ 0.19	0.01 $\pm$ 0.02	0.16 $\pm$ 0.06	0.13 $\pm$ 0.06	0.36 $\pm$ 0.37	0.47 $\pm$ 0.22
4	0.44 $\pm$ 0.26	0.02 $\pm$ 0.03	0.15 $\pm$ 0.20	0.11 $\pm$ 0.05	0.28 $\pm$ 0.25	0.80 $\pm$ 0.39
5	2.19 $\pm$ 1.07	0.05 $\pm$ 0.06	0.35 $\pm$ 1.11	0.16 $\pm$ 0.12	0.80 $\pm$ 0.67	3.71 $\pm$ 1.93

**Fig. 3.** Comparison of Atmospheric NO<sub>2</sub> Concentration and NO<sub>3</sub><sup>-</sup> Concentration in Particulates

□; Total concentration of NO<sub>3</sub><sup>-</sup> ( $\mu\text{g}/\text{m}^3$ ). ●; concentration of atmospheric NO<sub>2</sub> (ppm).

lates less than 1.1  $\mu\text{m}$ . From the result of analysis of ionic species, it is supposed that the sources of these particulates are car exhaust, especially diesel exhaust. Previously we have reported the cytotoxicity of airborne particulates.<sup>24</sup> The results obtained in the present study demonstrated that inhalable fine particulates account for 50 percent of all particulates and these particles contain many compounds. Fine airborne particulates enter respiratory system. We face chronic exposure to these airborne particulates. Therefore, it is necessary to investigate further the risk of size-classified airborne particulates to human health.

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