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Technical Information

Measurements of 50 Non-polar Organic Compounds Including Polycyclic Aromatic Hydrocarbons, n-Alkanes and Phthalate Esters in Fine Particulate Matter ($PM_{2.5}$) in an Industrial Area of Chiba Prefecture, Japan

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ABSTRACT Quantitative data of 50 non-polar organic compounds constituting $PM_{2.5}$ were continuously collected and analyzed from June 2016 to October 2017 (approximately 17 months) at Ichihara, one of the largest industrial areas in Japan. Target non-polar organic compounds including 21 species of polycyclic aromatic hydrocarbons (PAHs), 24 species of n-alkanes and 5 species of phthalate esters (PAEs) were simultaneously measured by gas chromatography/mass spectrometry. Basically, the average concentrations of the total PAHs, n-alkanes and PAEs in each season remained nearly level, and seasonal variations were little throughout the study period. These results suggest that the emission sources, which are not influenced by the seasons, are the dominant inputs for the target organic compounds. Diagnostic ratios of PAHs, assessment of n-alkane homologue distributions, carbon preference index, and the contribution of wax n-alkanes from plants were used to estimate source apportionments. These results indicate that anthropogenic sources were the main contributor for most PAHs and n-alkanes throughout the study period. The concentrations of PAEs selected in this study were low because emission amounts of these chemicals were little within the source areas of the sampling site. To our knowledge, this study is the first attempt to simultaneously measure a high number of non-polar organic compounds in $PM_{2.5}$ collected from the ambient air of Japan, and the resultant data will provide valuable data and information for environmental researchers.

KEY WORDS $PM_{2.5}$, Polycyclic aromatic hydrocarbons, n-Alkanes, Phthalate esters, Organic compounds, Japan

1. INTRODUCTION

Particulate matter (PM) is an atmospheric pollutant that has received widespread concern as it causes public health problems and plays important roles in regulating regional and global climate (Fuzzi, *et al.*, 2015; IPCC, 2013; WHO, 2013; Jacob, 1999). Among the PM, particle sizes with aerodynamic diameter less than 2.5 μm ($PM_{2.5}$) are particularly hazardous to public health because of their ability to penetrate into the alveoli of lungs and they are therefore more likely to increase the incidence of respiratory and cardiovascular diseases (Ueda, 2011; Schwartz and Neas, 2000).

According to the information provided by the Ministry of the Environment Japan, 74.5% of stations monitoring general ambient air, and 58.4% of stations monitoring auto-exhaust emissions met environmental quality standards for $PM_{2.5}$ during the 2015 fiscal year (from April to March of the following year), and further countermeasures to reduce the level of $PM_{2.5}$ are required (http://www.env.go.jp/press/103858.html, in Japanese, Accessed on June 1, 2018). For an effective reduction of $PM_{2.5}$ levels, it is important to identify their emission sources and describe their chemical properties in the ambient air. Long time series of quantitative data of the chemical compositions that constitute $PM_{2.5}$ are necessary to provide the required information to achieve $PM_{2.5}$ reduction.

Along with chemical compounds that are utilized for the assessment of $PM_{2.5}$ emission sources (e.g., trace metals), some organic compounds have definitive chemical structures that can be correlated to emission sources and are known as molecular markers. They can originate from many sources, including combustion of fossil fuels, biogenic origin, biomass burning, motor vehicles, waste incineration, steel/plastic manufacturing, cooking, and road dust (Hayakawa *et al.*, 2016; Kawamura and Bikkina, 2016; Wang *et al.*, 2016; Zhang *et al.*, 2013; Alves *et al.*, 2009; Alves, 2008; Brandenberger *et al.*, 2005; He *et al.*, 2004; Simoneit, 2002; Oros *et al.*, 1999; Khalili *et al.*, 1995; Rogge *et al.*, 1993a, 1993b, 1993c; Simoneit *et al.*, 1991).

A wealth of publications have reported that the organic fraction of $PM_{2.5}$ consists of various kinds of organic compounds with different abundances in different areas of the world (Ichikawa *et al.*, 2017; Mikuška *et al.*, 2017; Ahmed *et al.*, 2016; Fang *et al.*, 2016; Li *et al.*, 2016; Alves *et al.*, 2015; Yadav *et al.*, 2013; Park *et al.*, 2006; Simoneit *et al.*, 2004). Moreover, increasing attention has been paid to the study of the organic compounds in $PM_{2.5}$ to improve understanding of the emission sources and source apportionment. However, in Japan, most $PM_{2.5}$ studies have focused on metallic elements, carbonaceous components, and water-soluble inorganic components, and studies into organic compounds remain deficient.

Therefore, we intensively measured 50 different non-polar organic compounds including 21 species of polycyclic aromatic hydrocarbons (PAHs), 24 species of n-alkanes and 5 species of phthalate esters (PAEs) in $PM_{2.5}$ in a long time series at Ichihara, a major industrial area in Japan. Selected non-polar organic compounds were simultaneously measured employing GC/MS. To the best of our knowledge, this paper is the first attempt to simultaneously measure as many non-polar organic compounds in $PM_{2.5}$ collected for a long time series (approximately 17 months) from the ambient atmosphere of Japan. Our results aim to provide useful insights and data for use in improving understanding of the target organic compounds in $PM_{2.5}$ and thereby contribute to better air quality management strategies.

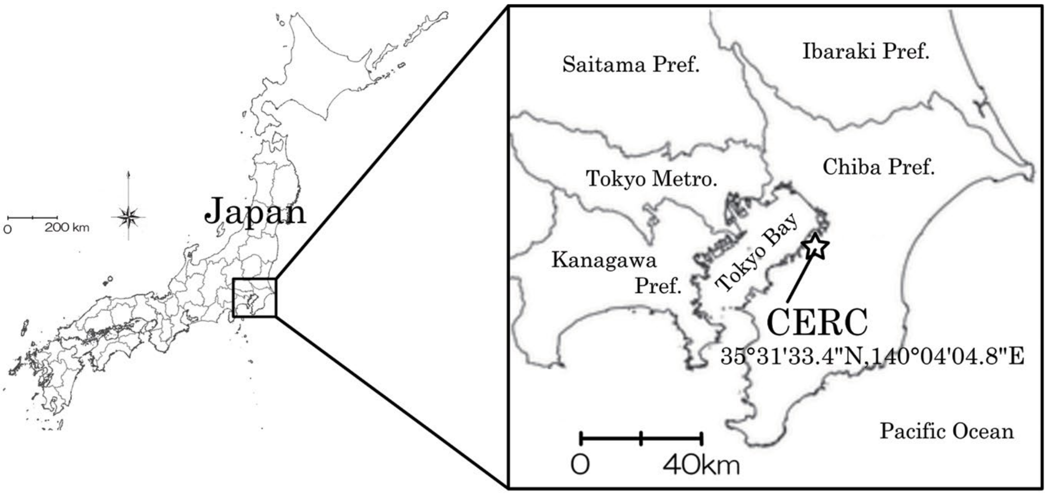

Fig. 1. Map indicating the location of Chiba Prefectural Environmental Research Center (CERC).

2. MATERIALS AND METHODS

2. 1 Sampling Site Description

Sampling was conducted on the roof (12 m height above the ground) of the Chiba Prefectural Environmental Research Center (CERC). The CERC is located between the industrial zone of Tokyo Bay (a large industrial base including gas power plants, heavy petrochemical industries, and many light industries within ca. 2 km radius), and the residential zone of Ichihara, Chiba Prefecture, Japan (Fig. 1). The site is located approximately 200 m southeast of the Japanese National Route 16 (average weekday 24-hour traffic of 42,007 vehicles, of which 29.1% are large-sized vehicles). Ichihara is about 40 km southeast of central Tokyo, and the estimated population is nearly 277,000.

2. 2 Sample Collection

$PM_{2.5}$ samples were collected on 47 mm diameter quartz filter (Pall Corp., 2500QAT-UP, Q-filter) from 13 June 2016 to 25 October 2017. The flow rate of the low volume air sampler (Rupprecht and Patashnick Co., Inc., Partisol-FRM Model 2000 Air Sampler) was 16.7 L/min with a constant sampling rate (accumulating to ca. 24 m^3/d). From our previous study, daily air volumes per sample (24 m^3/d) were too low to quantify some of the organic compounds present in relatively small amounts in the ambient atmosphere, so the samples in this study were sampled on a weekly basis (Ichikawa *et al.*, 2017). Park *et al.* (2006) also pointed out the difficulty of detailed analysis of organic compounds by gas chromatography/mass spectrometry (GC/MS) from daily sampling, supporting the decision to analyze samples on a weekly basis. Some amount of organic compounds may be decomposed or evaporated from the Q-filter during the sampling. However, due to the reason mentioned above those were not taken into consideration in this study.

The sampling periods are described in Table 1. Based on the definition used by the Japanese Meteorological Agency, the four seasons were assigned as follows: March to May for spring, June to August for summer, September to November for autumn and December to February for winter.

Typically, Q-filters are combusted in a furnace with high temperatures to remove the existing organic car-

Table 1. Details of sampling period in each season.

Year	Season*1)	Sampling period			n
2016	Summer	Jun. 13-Jul. 20 Jul. 4-Jul. 11	Jun. 20-Jun. 27 Jul. 11-Jul. 18	Jun. 28-Jul. 4 Aug. 22-Aug. 29	6
	Autumn	Aug. 29-Sep. 5 Sep. 20-Sep. 27 Oct. 17-Oct. 25 Nov. 8-Nov. 15	Sep. 5-Sep. 12 Oct. 3-Oct. 11 Oct. 25-Nov. 1 Nov. 15-Nov. 22	Sep. 12-Sep. 20 Oct. 11-Oct. 17 Nov. 1-Nov. 8 Nov. 29-Dec. 2	12
	Winter	Dec. 2-Dec. 7 Dec. 21-Dec. 28 Jan. 11-Jan. 18 Jan. 31-Feb. 8 Feb. 22-Mar. 1	Dec. 7-Dec. 14 Dec. 28-Jan. 4 Jan. 18-Jan. 25 Feb. 8-Feb. 15	Dec. 14-Dec. 21 Jan. 5-Jan. 10 Jan. 25-Jan. 31 Feb. 15-Feb. 22	13
2017	Spring	Mar. 1-Mar. 8 Mar. 22-Mar. 29 Apr. 12-Apr. 19 May 2-May 10 May 24-May 31	Mar. 8-Mar. 15 Mar. 29-Apr. 5 Apr. 19-Apr. 26 May 10-May 17	Mar. 15-Mar. 22 Apr. 5-Apr. 12 Apr. 26-May 2 May 17-May 24	13
	Summer	May 31-Jun. 7 Jun. 21-Jun. 28 Jul. 12-Jul. 19 Aug. 2-Aug. 8 Aug. 23-Aug. 30	Jun. 7-Jun. 14 Jun. 28-Jul. 5 Jul. 19-Jul. 26 Aug. 8-Aug. 16	Jun. 14-Jun. 21 Jul. 5-Jul. 12 Jul. 26-Aug. 2 Aug. 16-Aug. 23	13
	Autumn	Aug. 30-Sep. 4 Sep. 20-Sep. 27 Oct. 11-Oct. 17	Sep. 4-Sep. 12 Sep. 27-Oct. 4 Oct. 17-Oct. 25	Sep. 12-Sep. 20 Oct. 4-Oct. 11	8

*1)The four seasons were assigned based on the definition used by the Japanese Meteorological Agency.

bon (OC) prior to sampling. However, combustion could activate the Q-filter, resulting in positive artifacts due to the absorption of gas phase organic materials onto the filter. As described in Section 2.3, gravimetric measurements of $PM_{2.5}$ collected in Q-filters were designed in this study and to eliminate the possible positive artifacts during transport, sampling and storage, Q-filters were not combusted.

Travel blank filters were prepared and placed in the same container as the samples and were transported and treated in the same way (e.g., making contact with the sampling devices, and being exposed to the conditions of the sampling site, storage, and all analytical procedures). Sample results reported in this paper were corrected based on the travel blank filters.

Sample filters were placed in petri dishes and enclosed in a sealed bag. All samples were stored in a freezer at -30°C until chemical analysis to prevent evaporation and degradation of components constituting $PM_{2.5}$. A total of 68 effective samples were collected in this study, which included 3 blank samples.

2.3 $PM_{2.5}$ Mass Concentration

Both $PM_{2.5}$ sample filters and travel blank filters were weighed using an electronic microbalance (A&D Company Ltd., BM-20) with a reading precision of 1 μg. Prior to weighing, all Q-filters were kept under equilibrated conditions of constant temperature (21.5 ± 1.5°C) and relative humidity ($35\pm5\%$) for at least 24 hours. An ionizing blower was used to eliminate the effects of static electricity on the weighing process. Obtained $PM_{2.5}$ mass (μg) was calculated by subtracting pre-weight from post-weight of the Q-filters. The $PM_{2.5}$ mass concentrations (μg/m^3) were calculated by $PM_{2.5}$ mass per total volume of suction.

For the accuracy testing of gravimetric measurement, $PM_{2.5}$ mass concentration was measured in parallel using an automatic instrument (Horiba Ltd., APDA-3750A) employing a beta-ray absorption technique. Automatic instrument was installed at the monitoring station of the CERC, at a height of 7 m above the ground. $PM_{2.5}$ mass concentrations observed by two different methodologies showed good positive correlation ($n=64$, $R=0.84$).

2.4 OC Measurement

The OC was measured by the thermal/optical reflectance carbon analysis system (Sunset Laboratory Inc., Lab OC-EC Aerosol Analyzer). The analytical conditions of the IMPROVE method (Chow *et al.*, 1993) were used with the thermal optical reflection protocol (Chow *et al.*, 2001). A total of four fractions (OC1, OC2, OC3, and OC4) and the optical pyrolysis correction of OC (PyC) were determined. The OC was calculated as OC1 + OC2 + OC3 + OC4 + PyC.

2.5 Organic Compounds Measurement

The measured non-polar organic compounds in this study were 21 species of PAHs, 24 species of n-alkanes and 5 species of PAEs, producing a total of 50 species. Details of these compounds, including individual abbreviations, are presented in Tables 2 and 3.

2.5.1 Pretreatment Procedure

A Q-filter was placed in a 10 mL glass flask with stopper and spiked with defined amounts of the internal standard (IS) substances. The IS substances employed in this study were as follows. For PAHs: anthracene-d_{10} (Ant-d_{10}), pyrene-d_{10} (Py-d_{10}), benzo(a)pyrene-d_{12} (BaP-d_{12}), and benzo(g,h,i)perylene-d_{12} (BghiP-d_{12}). For n-alkanes: n-tetracosane-d_{50} (C_{24}-d_{50}). For PAEs: diethyl phthalate-d_4 (DEP-d_4), di-n-butyl phthalate-d_4 (DBP-d_4), bis(2-ethylhexyl)adipate-d_8 (DEHA-d_8), and benzyl butyl phthalate-d_4 (BBP-d_4). Samples were extracted in 5 mL dichloromethane solution twice using an ultrasonic bath for 15 min, followed by filtration through a hydrophilic PTFE syringe filter (ADVANTEC Co. Ltd., DISMIC, pore size of 0.22 μm) to remove insoluble particles and quartz fibers. The extracts were evaporated to dryness under a gentle stream of high purity nitrogen gas and re-dissolved in 100 μL of toluene for GC/MS analysis.

2.5.2 GC/MS Analysis

Analysis of the target organic compounds in the $PM_{2.5}$ samples was carried out by GC/MS (6890 GC/5973 MSD, Agilent Technology) under the following conditions: capillary column DB-5MS (length; 60 m, internal diameter; 0.25 mm, film thickness; 0.25 μm film thickness, Agilent J&W) was used for separation of the compounds; high-purity helium was used as the carrier gas with flow rate of 1.0 mL/min; sample injection amount was 1 μL in splitless mode; the GC oven temperature was initially held at 100°C for 1 min, increasing 20°C/min until 270°C and held for 17 min, increasing 15°C/min until 320°C and then held for 32 min; the injection temperature was set to 280°C and the MS source and

Table 2. Temperature, limit of detection of PAHs (ng/m^3), recovery percentages of PAHs (%), concentrations of $PM_{2.5}$ ($\mu g/m^3$), OC ($\mu g/m^3$), and PAHs (ng/m^3); ratios of PAHs accounting for $PM_{2.5}$ and OC; and diagnostic ratios between PAHs.

Compounds and ratios	Abbreviation	Unit	Recovery (%) (n = 4)	LOD	Range							Average						
					Summer 2016 (n = 6)	Autumn 2016 (n = 12)	Winter 2016 (n = 13)	Spring 2017 (n = 13)	Summer 2017 (n = 13)	Autumn 2017 (n = 8)	Total (n = 65)	Summer 2016	Autumn 2016	Winter 2016	Spring 2017	Summer 2017	Autumn 2017	Total
Temperature		°C			17.5-36.6	−0.4-32.4	−3.5-21.3	−0.8-29.4	14.7-36.4	10.5-32.2	−3.5-36.6	25.4	18.8	7.9	14.4	25.3	20.7	18.5
$PM_{2.5}$		$\mu g/m^3$			4.4-11	5.3-15	7.0-16	9.4-16	6.2-14	4.9-9.4	4.4-16	7.5	10	11	12	9.0	7.4	9.9
OC		$\mu g/m^3$			0.81-1.3	0.80-3.3	1.3-3.7	1.1-2.4	0.66-3.1	1.0-1.9	0.66-3.7	0.96	1.9	2.3	1.8	1.3	1.4	1.7
$OC/PM_{2.5}$		%			9.4-18	12-28	17-26	11-19	11-22	14-22	9.4-28	13	19	20	15	14	19	17
PAHs																		
Fluorene	Fl	ng/m^3	88	0.013	N.D.[*1)]-N.D.	N.D.-N.D.	N.D.-0.070	0.020-0.067	N.D.-0.066	N.D.-0.033	N.D.-0.070	N.D.	N.D.	0.035	0.033	0.020	0.023	0.022
Phenanthrene	Phe	ng/m^3	96	0.0096	N.D.-0.024	N.D.-0.021	0.045-0.30	0.016-0.24	N.D.-0.066	N.D.-0.043	N.D.-0.30	0.0080	0.0069	0.16	0.11	0.021	0.022	0.063
Anthracene	Ant	ng/m^3	97	0.016	N.D.-0.034	N.D.-N.D.	N.D.-0.22	N.D.-0.016	N.D.-0.094	N.D.-N.D.	N.D.-0.22	0.012	N.D.	0.044	0.0084	0.021	N.D.	0.018
Fluoranthene	Fluor	ng/m^3	97	0.0077	0.14-0.56	0.092-0.53	0.22-0.96	0.16-0.69	0.094-0.57	0.11-0.24	0.092-0.96	0.30	0.22	0.50	0.45	0.23	0.17	0.33
Pyrene	Py	ng/m^3	98	0.009	0.12-0.54	0.082-0.43	0.18-0.82	0.14-0.61	0.084-0.55	0.097-0.21	0.082-0.82	0.28	0.19	0.40	0.39	0.21	0.15	0.28
Benzo(c)phenanthrene	BcP	ng/m^3	90	0.063	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Benz(a)anthracene	BaA	ng/m^3	99	0.032	0.067-0.18	0.052-0.16	0.038-0.14	0.037-0.12	N.D.-0.16	N.D.-0.043	N.D.-0.18	0.11	0.083	0.082	0.074	0.057	0.026	0.071
Chrysene	Chry	ng/m^3	88	0.057	N.D.-0.35	N.D.-0.13	N.D.-0.35	0.059-0.27	N.D.-0.34	N.D.-N.D.	N.D.-0.35	0.14	0.066	0.17	0.16	0.098	N.D.	0.11
Benzo(b)fluoranthene	BbF	ng/m^3	95	0.037	0.17-0.84	0.10-0.46	0.14-0.89	0.17-0.47	N.D.-0.75	0.11-0.20	N.D.-0.89	0.37	0.27	0.45	0.33	0.24	0.16	0.31
7,12-Dimethylbenz (a)anthracene	7,12DaA	ng/m^3	90	0.038	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Benzo(j)fluoranthene	BjF	ng/m^3	89	0.051	0.082-0.33	0.065-0.19	0.087-0.38	0.089-0.23	0.054-0.40	0.065-0.15	0.054-0.40	0.16	0.12	0.22	0.16	0.14	0.10	0.15
Benzo(k)fluoranthene	BkF	ng/m^3	90	0.040	0.088-0.35	0.072-0.23	0.08-0.31	0.080-0.21	N.D.-0.32	0.045-0.097	N.D.-0.35	0.17	0.13	0.18	0.15	0.10	0.069	0.13
Benzo(e)pyrene	BeP	ng/m^3	92	0.019	0.13-0.70	0.090-0.35	0.11-0.61	0.12-0.37	0.094-0.75	0.096-0.18	0.09-0.75	0.30	0.21	0.31	0.25	0.24	0.14	0.24
Benzo(a)pyrene	BaP	ng/m^3	96	0.024	0.17-0.81	0.15-0.46	0.12-0.68	0.13-0.45	0.13-0.86	0.13-0.24	0.12-0.86	0.36	0.26	0.30	0.28	0.30	0.18	0.28
3-Methylcholanthrene	3MC	ng/m^3	100	0.046	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Indeno(1,2,3-cd)pyrene	IP	ng/m^3	100	0.026	0.13-0.94	N.D.-0.45	0.13-0.85	0.15-0.46	0.12-1.1	0.12-0.25	N.D.-1.1	0.37	0.29	0.41	0.30	0.33	0.20	0.32
Dibenz(a,h)anthracene	DBahA	ng/m^3	100	0.019	0.054-0.19	0.043-0.14	N.D.-0.13	N.D.-0.072	N.D.-0.15	N.D.-0.040	N.D.-0.19	0.097	0.088	0.06	0.046	0.047	0.030	0.060
Benzo(g,h,i)perylene	BghiP	ng/m^3	96	0.013	0.11-0.82	0.078-0.39	0.14-0.80	0.14-0.41	0.11-0.88	0.12-0.24	0.078-0.88	0.32	0.27	0.40	0.29	0.29	0.19	0.30
Dibenzo(a,l)pyrene	DBalP	ng/m^3	100	0.036	0.049-0.26	0.054-0.17	N.D.-0.21	N.D.-0.098	N.D.-0.24	N.D.-0.046	N.D.-0.26	0.11	0.11	0.098	0.063	0.060	0.032	0.079
Dibenzo(a,i)pyrene	DBaiP	ng/m^3	110	0.056	N.D.-0.19	0.12-0.31	N.D.-N.D.	N.D.-N.D.	N.D.-0.070	N.D.-N.D.	N.D.-0.31	0.13	0.15	N.D.	N.D.	0.031	N.D.	0.061
Dibenzo(a,h)pyrene	DBahP	ng/m^3	100	0.059	N.D.-0.11	N.D.-0.11	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.-N.D.	N.D.-0.11	0.075	0.047	N.D.	N.D.	N.D.	N.D.	0.037
ΣPAHs[*2)]		ng/m^3			1.6-7.3	1.3-4.5	1.7-7.6	1.7-4.7	1.1-7.4	1.1-2.1	1.1-7.6	3.4	2.6	4.0	3.2	2.5	1.6	2.9
$\Sigma PAHs/PM_{2.5}$		%			0.026-0.073	0.018-0.041	0.024-0.057	0.011-0.040	0.013-0.053	0.015-0.032	0.011-0.073	0.043	0.027	0.035	0.027	0.027	0.023	0.030
ΣPAHs/OC		%			0.20-0.55	0.062-0.35	0.097-0.25	0.074-0.33	0.065-0.37	0.089-0.16	0.062-0.55	0.33	0.16	0.18	0.19	0.20	0.12	0.19
Σ3-rings[*3)]		ng/m^3			0.019-0.065	0.019-0.035	0.093-0.43	0.052-0.29	0.019-0.18	0.019-0.074	0.019-0.43	0.027	0.021	0.24	0.15	0.062	0.053	0.10
Σ4-rings[*4)]		ng/m^3			0.41-1.7	0.31-1.3	0.52-2.3	0.45-1.7	0.27-1.7	0.30-0.57	0.27-2.3	0.88	0.62	1.2	1.1	0.65	0.42	0.84
Σ5-rings[*5)]		ng/m^3			0.72-3.2	0.54-1.9	0.57-3.0	0.62-1.8	0.44-3.3	0.48-0.91	0.44-3.3	1.5	1.1	1.5	1.3	1.1	0.70	1.2
Σ6-rings[*6)]		ng/m^3			0.35-2.3	0.38-1.3	0.35-1.9	0.37-1.0	0.32-2.3	0.32-0.57	0.32-2.3	1.0	0.88	0.96	0.71	0.75	0.48	0.80
BeP/(BeP + BaP)					0.42-0.46	0.38-0.54	0.47-0.58	0.44-0.53	0.41-0.47	0.40-0.46	0.38-0.58	0.44	0.46	0.51	0.48	0.44	0.44	0.46
BaA/(BaA + Chr)					0.34-0.70	0.48-0.71	0.29-0.57	0.29-0.41	0.30-0.65	0.36-0.60	0.29-0.71	0.52	0.58	0.35	0.33	0.42	0.46	0.43
IP/(IP + BghiP)					0.52-0.56	0.042-0.56	0.48-0.52	0.49-0.53	0.48-0.56	0.46-0.56	0.042-0.56	0.54	0.49	0.51	0.50	0.52	0.51	0.51
Fluor/(Flour + Py)					0.51-0.55	0.50-0.56	0.52-0.57	0.52-0.57	0.50-0.54	0.53-0.55	0.50-0.57	0.53	0.54	0.55	0.54	0.52	0.54	0.54
BghiP/BaP					0.65-1.0	0.52-1.6	1.2-1.7	0.91-1.5	0.76-1.3	0.92-1.2	0.52-1.7	0.81	1.1	1.3	1.1	0.99	1.1	1.1

Except for the temperature, all of the measured values have been rounded to no more than three significant figures.

[*1)] N.D. : Not detected (below LOD)

[*2)] ΣPAHs = Fl + Phe + Ant + Fluor + Py + BcP + BaA + Chry + BbF + 7,12DaA + BjF + BkF + BeP + BaP + 3MC + IP + DBahA + BghiP + DBalP + DBaiP + DBahP

[*3)] Σ3-rings = Fl + Phe + Ant

[*4)] Σ4-rings = Fluor + Py + BcP + BaA + Chry + 7,12DaA

[*5)] Σ5-rings = BbF + BjF + BkF + BeP + BaP + 3MC + DBahA

[*6)] Σ6-rings = IP + BghiP + DBalP + DBaiP + DBahP

Table 3. LOD of n-alkanes and PAEs (ng/m^3), recovery percentages of n-alkanes and PAEs (%), concentrations of n-alkanes and PAEs (ng/m^3) and ratios of n-alkanes and PAEs accounting for $PM_{2.5}$ and OC.

Compounds, ratios and index	Abbreviation	Unit	Recovery (%) (n = 4)	LOD	Range							Average						
					Summer 2016 (n = 6)	Autumn 2016 (n = 12)	Winter 2016 (n = 13)	Spring 2017 (n = 13)	Summer 2017 (n = 13)	Autumn 2017 (n = 8)	Total (n = 65)	Summer 2016	Autumn 2016	Winter 2016	Spring 2017	Summer 2017	Autumn 2017	Total
n-Alkanes																		
n-Heptadecane	C_{17}	ng/m^3	87	0.0095	0.025-0.076	0.014-0.15	0.052-0.19	0.028-0.15	N.D.[*1)]-0.050	N.D.-0.067	N.D.-0.19	0.044	0.050	0.11	0.065	0.027	0.017	0.056
n-Octadecane	C_{18}	ng/m^3	78	0.0072	0.016-0.071	0.014-0.060	0.027-0.12	0.018-0.094	N.D.-0.27	N.D.-0.058	N.D.-0.27	0.037	0.030	0.066	0.046	0.080	0.023	0.050
n-Nonadecane	C_{19}	ng/m^3	84	0.0042	0.016-0.060	0.014-0.096	0.054-0.16	0.018-0.095	0.0051-0.11	N.D.-0.050	N.D.-0.16	0.035	0.041	0.09	0.047	0.026	0.024	0.046
n-Eicosane	C_{20}	ng/m^3	89	0.0062	0.021-0.085	0.014-0.15	0.067-0.23	0.0071-0.12	N.D.-0.14	0.0080-0.069	N.D.-0.23	0.048	0.061	0.13	0.052	0.027	0.029	0.061
n-Heneicosane	C_{21}	ng/m^3	96	0.0055	0.014-0.13	0.021-0.30	0.10-0.47	0.0096-0.21	0.0089-0.29	0.013-0.063	0.0089-0.47	0.068	0.099	0.21	0.086	0.050	0.034	0.098
n-Docosane	C_{22}	ng/m^3	110	0.0076	0.016-0.24	0.029-0.72	0.22-0.78	N.D.-0.41	N.D.-0.70	0.0098-0.22	N.D.-0.78	0.12	0.20	0.46	0.17	0.088	0.063	0.20
n-Tricosane	C_{23}	ng/m^3	120	0.0059	0.054-0.41	0.094-1.0	0.44-1.9	0.056-0.73	0.041-1.7	0.063-0.25	0.041-1.9	0.25	0.31	0.84	0.32	0.23	0.13	0.37
n-Tetracosane	C_{24}	ng/m^3	130	0.0071	0.085-0.66	0.011-1.7	0.75-2.5	0.042-1.5	N.D.-3.7	0.068-0.62	N.D.-3.7	0.37	0.50	1.5	0.55	0.46	0.33	0.66
n-Pentacosane	C_{25}	ng/m^3	120	0.010	0.35-1.0	0.13-2.1	1.1-3.2	0.46-1.8	0.21-6.2	0.30-1.2	0.13-6.2	0.68	1.0	2.0	1.0	0.96	0.64	1.1
n-Hexacosane	C_{26}	ng/m^3	110	0.0097	0.41-1.2	0.29-2.3	0.9-3.2	0.62-2.0	0.33-6.4	0.61-1.4	0.29-6.4	0.81	1.2	1.8	1.0	1.1	0.92	1.2
n-Heptacosane	C_{27}	ng/m^3	110	0.0061	0.40-2.1	0.37-2.8	0.63-3.7	0.90-1.9	0.70-8.1	0.95-2.1	0.37-8.1	1.2	1.5	1.9	1.3	1.7	1.2	1.5
n-Octacosane	C_{28}	ng/m^3	100	0.015	0.42-3.5	0.40-2.2	0.61-3.0	0.55-1.7	0.44-6.9	0.42-2.5	0.40-6.9	2.3	1.2	1.7	0.91	1.5	1.2	1.4
n-Nonacosane	C_{29}	ng/m^3	100	0.010	0.51-2.4	0.57-4.8	0.73-5.9	1.2-3.2	0.60-6.9	0.83-2.4	0.51-6.9	1.4	2.3	3.0	1.7	2.0	1.6	2.1
n-Triacontane	C_{30}	ng/m^3	100	0.010	0.33-1.4	0.34-2.6	0.40-2.5	0.47-1.2	0.24-4.8	0.47-1.4	0.24-4.8	0.82	1.3	1.3	0.67	1.1	0.85	1.0
n-Hentriacontane	C_{31}	ng/m^3	97	0.013	0.68-1.8	0.74-6.5	0.56-5.5	0.76-1.9	0.57-4.6	0.90-2.5	0.56-6.5	1.1	2.7	2.6	1.2	1.7	1.7	1.9
n-Dotriacontane	C_{32}	ng/m^3	93	0.021	0.29-0.64	0.27-1.8	0.21-1.5	0.21-0.58	0.13-2.2	0.22-0.73	0.13-2.2	0.43	0.80	0.74	0.36	0.53	0.48	0.57
n-Tritriacontane	C_{33}	ng/m^3	92	0.029	0.31-0.62	0.45-3.5	0.24-2.2	0.26-0.85	0.23-2.2	0.36-1.3	0.23-3.5	0.43	1.3	1.0	0.47	0.69	0.83	0.82
n-Tetratriacontane	C_{34}	ng/m^3	92	0.036	0.15-0.23	0.14-0.86	0.084-0.61	0.079-0.26	0.045-1.2	0.11-0.31	0.045-1.2	0.19	0.38	0.33	0.17	0.24	0.21	0.26
n-Pentatriacontane	C_{35}	ng/m^3	92	0.050	0.12-0.22	0.15-1.2	0.081-0.82	0.082-0.24	0.057-1.1	0.13-0.41	0.057-1.2	0.17	0.44	0.40	0.15	0.26	0.26	0.29
n-Hexatriacontane	C_{36}	ng/m^3	97	0.058	0.096-0.19	0.13-0.56	0.080-0.48	0.073-0.19	0.065-0.85	0.086-0.25	0.065-0.85	0.14	0.28	0.24	0.13	0.21	0.18	0.20
n-Heptatriacontane	C_{37}	ng/m^3	96	0.072	0.075-0.15	0.085-0.52	N.D.-0.37	N.D.-0.15	N.D.-0.67	N.D.-0.20	N.D.-0.67	0.11	0.21	0.19	0.093	0.14	0.12	0.15
n-Octatriacontane	C_{38}	ng/m^3	96	0.097	N.D.-0.13	N.D.-0.41	N.D.-0.32	N.D.-0.13	N.D.-0.59	N.D.-0.15	N.D.-0.59	0.062	0.16	0.16	0.063	0.11	0.086	0.11
n-Nonatriacontane	C_{39}	ng/m^3	100	0.096	N.D.-0.12	N.D.-0.37	N.D.-0.29	N.D.-0.096	N.D.-0.52	N.D.-0.12	N.D.-0.52	0.060	0.14	0.14	0.052	0.092	0.065	0.096
n-Tetracontane	C_{40}	ng/m^3	100	0.10	N.D.-0.12	N.D.-0.30	N.D.-0.30	N.D.-0.12	N.D.-0.45	N.D.-0.11	N.D.-0.45	0.063	0.13	0.14	0.062	0.083	0.059	0.096
Σn-Alkanes[*2)]		ng/m^3			4.8-16	5.5-32	8.0-39	7.0-18	4.3-60	8.4-17	4.3-60	11	16	21	11	13	11	14
Σn-Alkanes/$PM_{2.5}$		%			0.084-0.21	0.080-0.29	0.10-0.26	0.064-0.11	0.049-0.43	0.10-0.19	0.049-0.43	0.15	0.15	0.18	0.089	0.14	0.15	0.14
Σn-Alkanes/OC		%			0.59-1.6	0.57-1.2	0.60-1.1	0.37-0.91	0.34-1.9	0.58-1.1	0.34-1.9	1.1	0.83	0.88	0.61	0.93	0.80	0.84
ΣC_{odd}[*3)]		ng/m^3			2.8-8.6	3.2-21	4.1-24	4.6-9.6	2.7-32	4.6-10	2.7-32	5.5	10	12	6.5	7.8	6.6	8.6
ΣC_{even}[*4)]		ng/m^3			2.0-7.3	2.2-11	3.8-15	2.4-8.2	1.6-28	3.4-6.7	1.6-28	5.4	6.2	8.5	4.2	5.5	4.4	5.8
PAEs																		
Di-n-propyl phthalate	DIPP	ng/m^3	91	0.0037	N.D.-0.030	N.D.-0.073	N.D.-0.11	N.D.-0.11	N.D.-0.098	N.D.-0.0048	N.D.-0.11	0.010	0.020	0.034	0.049	0.0098	0.0023	0.024
Diisobutyl phthalate	DIBP	ng/m^3	77	0.0075	0.027-0.21	N.D.-0.32	0.038-0.40	N.D.-0.22	N.D.-0.083	N.D.-0.032	N.D.-0.40	0.12	0.076	0.26	0.068	0.022	0.012	0.097
Di-n-pentyl phthalate	DPP	ng/m^3	85	0.0072	N.D.-0.083	N.D.-0.020	N.D.-0.018	N.D.-0.047	0.0076-0.24	0.0084-0.025	N.D.-0.24	0.017	0.0072	0.0092	0.0076	0.038	0.013	0.015
Di-n-hexyl phthalate	DHP	ng/m^3	79	0.024	N.D.-N.D.	N.D.-N.D.	N.D.-0.082	N.D.-0.058	N.D.-0.26	N.D.-N.D.	N.D.-0.26	N.D.	N.D.	0.039	0.020	0.073	N.D.	0.031
Butyl benzyl phthalate	BBP	ng/m^3	73	0.021	0.059-0.21	0.10-0.91	0.035-0.25	0.035-0.36	0.022-1.5	0.022-0.19	0.022-1.5	0.10	0.30	0.10	0.13	0.37	0.050	0.19
ΣPAEs[*5)]		ng/m^3			0.12-0.36	0.12-0.97	0.23-0.62	0.084-0.52	0.070-1.8	0.049-0.24	0.049-1.8	0.26	0.41	0.44	0.27	0.51	0.090	0.36
ΣPAEs/$PM_{2.5}$		%			0.0016-0.0082	0.0011-0.0088	0.0020-0.0073	0.00065-0.0047	0.00071-0.024	0.00067-0.0041	0.00065-0.024	0.0040	0.0044	0.0043	0.0024	0.0062	0.0013	0.0039
ΣPAEs/OC		%			0.013-0.044	0.0071-0.055	0.0087-0.038	0.0049-0.039	0.0059-0.20	0.0038-0.020	0.0038-0.20	0.028	0.025	0.023	0.016	0.047	0.0068	0.025

All measured values have been rounded to no more than three significant figures.

[*1)] N.D. : Not detected (below LOD)

[*2)] Σn-Alkanes $= C_{17} + C_{18} + C_{19} + C_{20} + C_{21} + C_{22} + C_{23} + C_{24} + C_{25} + C_{26} + C_{27} + C_{28} + C_{29} + C_{30} + C_{31} + C_{32} + C_{33} + C_{34} + C_{35} + C_{36} + C_{37} + C_{38} + C_{39} + C_{40}$

[*3)] $\Sigma Codd = C_{17} + C_{19} + C_{21} + C_{23} + C_{25} + C_{27} + C_{29} + C_{31} + C_{33} + C_{35} + C_{37} + C_{39}$

[*4)] $\Sigma Ceven = C_{18} + C_{20} + C_{22} + C_{24} + C_{26} + C_{28} + C_{30} + C_{32} + C_{34} + C_{36} + C_{38} + C_{40}$

[*5)] ΣPAEs = DIPP + DIBP + DPP + DHP + BBP

Table 4. Monitored target and qualifier ions, and internal standards used in SIM mode of GC/MS analysis.

Compounds	Target ion	Qualifier ion	Internal standard	Compounds	Target ion	Qualifier ion	Internal standard
PAHs				n-Alkanes			
Fl	166	165	Ant-d$_{10}$	C_{17}	57	71	C_{24}-d$_{50}$
Phe	178	176	Ant-d$_{10}$	C_{18}	57	71	C_{24}-d$_{50}$
Ant	178	176	Ant-d$_{10}$	C_{19}	57	71	C_{24}-d$_{50}$
Fluor	202	200	Py-d$_{10}$	C_{20}	57	71	C_{24}-d$_{50}$
Py	202	200	Py-d$_{10}$	C_{21}	57	71	C_{24}-d$_{50}$
BcP	228	227	BaP-d$_{12}$	C_{22}	57	71	C_{24}-d$_{50}$
BaA	228	226	BaP-d$_{12}$	C_{23}	57	71	C_{24}-d$_{50}$
Chry	228	226	BaP-d$_{12}$	C_{24}	57	71	C_{24}-d$_{50}$
BbF	252	250	BaP-d$_{12}$	C_{25}	57	71	C_{24}-d$_{50}$
7,12DaA	256	241	BaP-d$_{12}$	C_{26}	57	71	C_{24}-d$_{50}$
BjF	252	250	BaP-d$_{12}$	C_{27}	57	71	C_{24}-d$_{50}$
BkF	252	250	BaP-d$_{12}$	C_{28}	57	71	C_{24}-d$_{50}$
BeP	252	250	BaP-d$_{12}$	C_{29}	57	71	C_{24}-d$_{50}$
BaP	252	250	BaP-d$_{12}$	C_{30}	57	71	C_{24}-d$_{50}$
3MC	268	267	BaP-d$_{12}$	C_{31}	57	71	C_{24}-d$_{50}$
IP	276	277	BghiP-d$_{12}$	C_{32}	57	71	C_{24}-d$_{50}$
DBahA	278	276	BghiP-d$_{12}$	C_{33}	57	71	C_{24}-d$_{50}$
BghiP	276	277	BghiP-d$_{12}$	C_{34}	71	85	C_{24}-d$_{50}$
DBalP	302	300	BghiP-d$_{12}$	C_{35}	57	71	C_{24}-d$_{50}$
DBaiP	302	303	BghiP-d$_{12}$	C_{36}	57	71	C_{24}-d$_{50}$
DBahP	302	303	BghiP-d$_{12}$	C_{37}	57	71	C_{24}-d$_{50}$
				C_{38}	57	71	C_{24}-d$_{50}$
				C_{39}	57	71	C_{24}-d$_{50}$
				C_{40}	57	71	C_{24}-d$_{50}$
				PAEs			
				DIPP	149	209	DEP-d$_{4}$
				DIBP	149	223	DEP-d$_{4}$
				DPP	149	237	DBP-d$_{4}$
				DHP	149	251	DEHA-d$_{8}$
				BBP	149	206	BBP-d$_{4}$

quadruple temperature to 230°C and 150°C, respectively; and mass spectrum peaks were obtained by electron ionization mode at electron energy of 70 eV with a selected ion monitoring (SIM) mode. Monitored target and qualifier ions, and internal standards used in SIM mode is listed in Table 4.

The individual organic compounds and IS substances were determined by comparing retention times and mass spectrum peaks with those of authentic standards. The five-point calibration curves were plotted based on the IS method for individual compounds and all of the compounds showed good linearity with the Pearson's correlation coefficients of $R > 0.95$.

A recovery test ($n = 4$) was performed to validate the pretreatment method. Known amounts of individual organic compounds were spiked to the blank Q-filter and then prepared and handled by exactly the same procedures as those used for the $PM_{2.5}$ samples. The average recovery for PAHs, n-alkanes and PAEs were 88-110%, 78-130% and 73-91%, respectively (Tables 2 and 3). In addition to the organic compounds described in Tables 2 and 3, we examined naphthalene (NaP), acenaphthene (Ace) and acenaphthylene (Acy) in PAHs, n-dodecane (C_{12}), n-tridecane (C_{13}), n-tetradecane (C_{14}), n-pentadecane (C_{15}), and n-hexadecane (C_{16}) in n-alkanes and diethyl phthalate (DEP), dibutyl phthalate (DBP) and dicyclohexyl phthalate (DCHP) in PAEs; however, the recovery percentages of those compounds were not acceptable. Therefore, these were eliminated from the analyte candidates in this study. The unacceptable recovery percentages for these compounds may have been due to vaporization loss during the evaporation process (NaP, Ace, Acy, and C_{12}-C_{16}) and a high level of background contaminations (DEP,

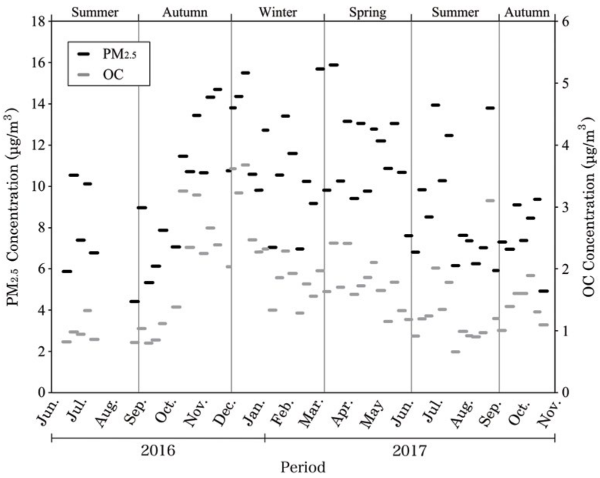

Fig. 2. Temporal variations of $PM_{2.5}$ and OC mass concentrations.

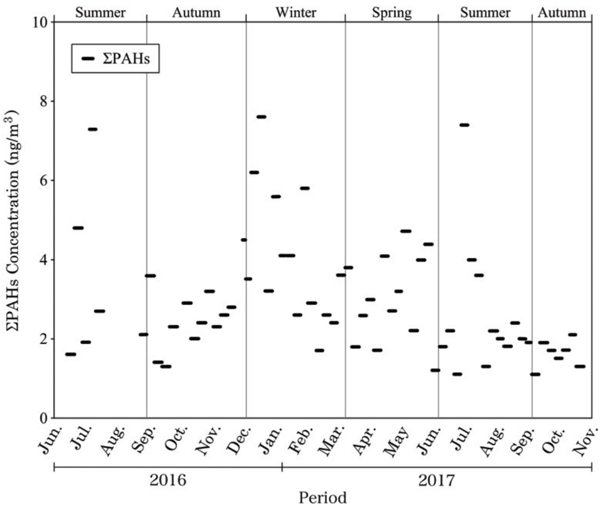

Fig. 3. Temporal variation of ΣPAHs concentration.

DBP, and DCHP).

The limit of detection (LOD) for the individual organic compounds is provided in Tables 2 and 3. It was calculated using the standard deviation of standard solution values ($n=7$) multiplied by 3. Measurement data below the LOD were replaced with the value of LOD/2 for the calculations in this study.

3. RESULTS AND DISCUSSION

3.1 Temporal Variations of $PM_{2.5}$ Mass Concentration and OC

A summary of average concentrations of $PM_{2.5}$, OC and OC/$PM_{2.5}$ and their ranges in each season are shown in Table 2. These observations are also plotted in Fig. 2 to reveal the temporal variation of $PM_{2.5}$ and OC results. During the study period, $PM_{2.5}$ and OC had higher concentrations from October 2016 (autumn) to May 2017 (spring) compared with other periods. This implies that $PM_{2.5}$ and OC vary seasonally. $PM_{2.5}$ and OC showed similar variation patterns over time, and their Pearson's correlation coefficient (R) was 0.80. The overall average value of OC/$PM_{2.5}$ was 17%, which is in good agreement with the value of 19.7% from our previous publication ($n=373$) based on data obtained at the same study site (Ichikawa *et al.*, 2015). These results indicate that OC is one of the major chemical components that contributes to $PM_{2.5}$ mass concentration. Identifying the different proportions of organic compounds could help to identify OC source.

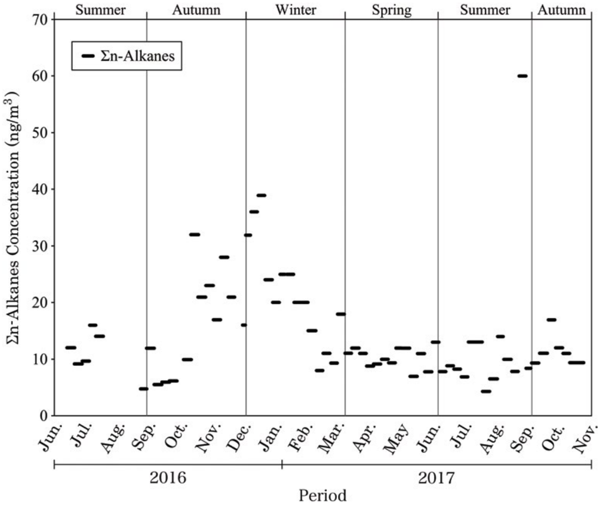

Fig. 4. Temporal variation of $\sum$n-alkanes concentration.

3.2 Temporal Variations of Non-Polar Organic Compounds

3.2.1 PAHs

PAHs are derived exclusively from the incomplete combustion and pyrolysis of organic materials contained in fossil fuels, coal fuels, lubricant oils, biomass, etc., and are ubiquitous environmental contaminants (Alves, 2008; Park *et al.*, 2006; Simoneit, 2002). There are studies indicating or suggesting the linkage between PAH properties and human health problems such as cancer (IARC, 2013, 2010).

Measurement values of individual PAHs in each season are shown in Table 2. The summed concentration of 21 species of PAHs is expressed as $\sum$PAHs. Fig. 3 shows temporal variations of $\sum$PAHs obtained through the long time series analysis. Winter 2016 showed the highest average $\sum$PAH concentration (4.0 ng/m^3) during the study period and other studies conducted in Japan support our results (Suzuki *et al.*, 2015; Kume *et al.*, 2007; Kakimoto *et al.*, 2002). There were a few samples in early summer (July) and early winter (December-January) showing an elevated level of $\sum$PAHs; however, most of the samples were below 4 ng/m^3 during the study period and the seasonal variation was little. Kume *et al.* (2007) have analyzed 21 species of PAHs in $PM_{2.5}$ from February 2001 to January 2002 in Shizuoka, Japan, and their result did not show strong seasonal variations, implying similarity to our result. This result suggests that the emission sources, which are not influenced by the seasons, are the dominant inputs for $\sum$PAHs within the source areas of the sampling site. The overall mean concentration of $\sum$PAHs was 2.9 ng/m^3, which accounts for 0.030% and 0.19% of $PM_{2.5}$ and OC, respectively. Also, $PM_{2.5}$ and OC have positive correlation with $\sum$PAHs with the Pearson correlation coefficient (R) of 0.57 and 0.42, respectively. Our result is approximately one to two orders of magnitude lower than those observed in China (Wang *et al.*, 2016, 2015). Although the individual amounts of organic compounds and their percentages accounting for $PM_{2.5}$ and OC are small, they could be used as molecular markers for source apportionment, which will be discussed later.

As is evident from Table 2, the lighter weight PAHs ($\sum$3-rings = Fl + Phe + Ant) were much lower than that of the heavier weight PAHs ($\sum$4-rings = Fluor + Py + BcP + BaA + Chry + 7,12DaA; $\sum$5-rings = BbF + BjF + BkF + BeP + BaP + 3MC + DBahA; $\sum$6-rings = IP + BghiP + DBalP + DBaiP + DBahP) throughout the year. This is probably because the 3-ring PAHs have relatively higher vapor pressures compared with the higher weight PAHs and tend to partition in the gas phase. The 4-ring PAHs can exist in both gas and particulate phases, whereas the 5-ring and 6-ring PAHs are mainly condensed/adsorbed onto particle phases (Zhang *et al.*, 2016). Among the 4, 5, and 6-ring PAHs, 5-ring PAHs were found to be dominant throughout the year. In summer and autumn, average values of 6-ring PAHs were higher than those of 4-ring PAHs. However, the opposite results were obtained in spring and winter. These results could be attributed to the atmospheric temperature (summer > autumn > spring > winter, Table 2), since 4-ring PAHs have lower vapor pressures than 6-ring PAHs.

The highest average concentrations measured in each season among all the PAHs were as follows; BbF and IP in summer 2016, IP in autumn 2016, Fluor in winter 2016, Fluor in spring 2017, IP in summer 2017, and IP in autumn 2017. Although WHO has not drafted a guideline for BaP, it is classified as carcinogenic to humans (Group 1) by the IARC (2012), and is probably the most studied PAH. BaP concentrations were above the LOD for all the samples, but no BaP values exceeded 1 ng/m^3 which is an annual mean value for the protection of human health as set out in the Directive 2004/107/EC (EU, 2004).

3.2.2 n-Alkanes

In an urban environment, n-alkanes are emitted from a large variety of sources, including the incomplete combustion of fossil fuels, lubricant oils, biomass burning, and biogenic sources such as wind erosion of the vascular plant waxes and direct suspension of pollen microorganisms (Yadav *et al.*, 2013; Alves *et al.*, 2009; Alves, 2008; Simoneit, 2002; Oros *et al.*, 1999; Rogge *et al.*, 1993a, 1993b, 1993c).

Measurement values of n-alkane homologues in each season are shown in Table 3. The sum of C_{17}-C_{40} n-alkane concentrations is expressed as $\sum$n-alkanes. Fig. 4 describes the temporal variation of $\sum$n-alkanes during the study period and the relative abundances of individual n-alkanes normalized by C_{29}, which is one of the most abundant n-alkanes, are presented in Fig. 5 to visually confirm the distribution profile in each season. Winter 2016 showed the higher average $\sum$n-alkanes concentration (21 ng/m^3) than the other seasons. A few samples in late autumn of 2016 (October-November) and early winter of 2016 (December-January) showed relatively elevated $\sum$n-alkanes concentration; however, most of the samples had concentrations below 20 ng/m^3 (overall average of 14 ng/m^3) during the study period and the seasonal variation was little. This result suggests that the emission sources, which are not influenced by the seasons, are the dominant inputs for $\sum$n-alkanes within the source areas of the sampling site. The highest $\sum$n-alkanes concentration was observed in late summer of 2017, when all of the n-alkane homologues appeared at high concentrations. The overall mean concentration of $\sum$n-alkanes accounted for 0.14% and 0.84% of

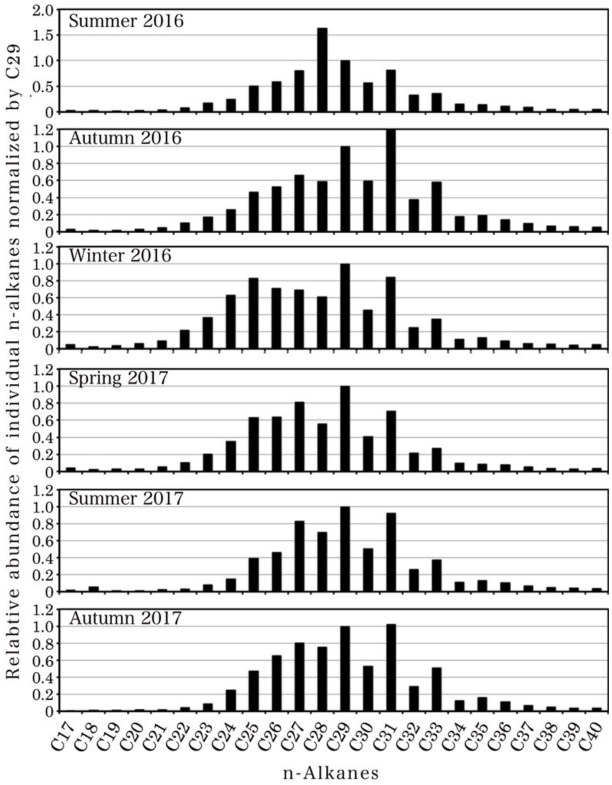

Fig. 5. Relative abundances of individual n-alkanes normalized by C_{29} in each season.

$PM_{2.5}$ and OC, respectively. Also, $PM_{2.5}$ and OC have positive correlation with $\sum$n-alkanes with the Pearson correlation coefficient (R) of 0.57 and 0.80, respectively.

3.2.3 PAEs

PAEs are widely manufactured as plasticizers to make plastic materials flexible, and also in building materials, food, drinking water, soil, medical devices, cosmetics, children's toys, and other products (Wang *et al.*, 2017; Yao *et al.*, 2016; Chou and Wright, 2006). Several epidemiological studies have demonstrated that human exposure to PAEs can induce adverse effects, and PAEs are suspected to be endocrine disruptors, which has stimulated public concern (Okamoto *et al.*, 2011; Chou and Wright, 2006; Duty *et al.*, 2005, 2003). To our knowledge, there is no previous publication involving the measurement of PAEs in $PM_{2.5}$ collected from the ambient atmosphere of Japan.

Measurement values of PAEs in each season are shown in Table 3. The summed concentration of 5 species of PAEs is expressed as $\sum$PAEs. Fig. 6 presents the temporal variation of $\sum$PAEs during the study period.

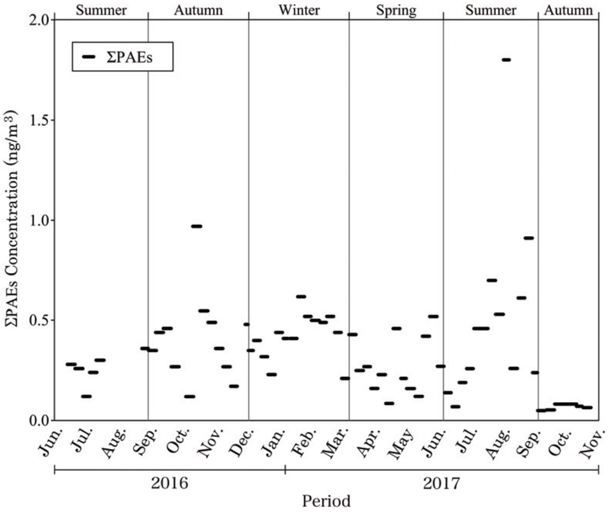

Fig. 6. Temporal variation of ΣPAEs concentration.

Average $\sum$PAEs was found to be higher (0.51 ng/m^3) in summer 2017 than in other seasons; however, average $\sum$PAEs in summer 2016 (0.26 ng/m^3) was about half the summer 2017 value, so there was no clear seasonal pattern. One sample in late summer of 2017 showed a relatively high level of $\sum$PAEs (1.8 ng/m^3); however, most of the obtained data were below 1 ng/m^3 during the study period and thus no clear seasonal variation was observed. The reason is uncertain but the $\sum$PAEs were extremely low in autumn 2017. The overall mean concentration of $\sum$PAEs was 0.36 ng/m^3, which was one and two orders of magnitude lower than $\sum$PAHs and $\sum$n-alkanes, respectively. Also, $PM_{2.5}$ and OC did not indicate correlation with $\sum$PAEs. Therefore, the target PAEs were not substantially emitted within the source area of the sampling site; however, PAEs those were not measured in this study might be contained in high concentrations in $PM_{2.5}$, so further research should target these non-detected compounds.

3.3 Identification of Possible Sources

3.3.1 Diagnostic Ratios of PAHs

The diagnostic ratios of PAHs are a useful tool to identify possible sources and have been developed and applied by many environmental researchers (Wang *et al.*, 2017, 2016; Hayakawa *et al.*, 2016; Zhang *et al.*, 2016; Mikuška *et al.*, 2015; Alves *et al.*, 2009; Alves, 2008; Park *et al.*, 2006; Brandenberger *et al.*, 2005; Yunker *et al.*, 2002; Simcik *et al.*, 1999; Khalili *et al.*,

Table 5. Comparison of PAHs diagnostic ratios from this study with those reported in previous studies.

Emission sources	Diagnostic ratios					References
	BeP/(BeP + BaP)	BaA/ (BaA + Chr)	IP/ (IP + BghiP)	Fluor/ (Flour + Py)	BghiP/ BaP	
Local emission	Index of the aging of particles. Value around 0.5 indicates freshly emitted particles.					Wang *et al.*, 2015; Shen *et al.*, 2013; Alves *et al.*, 2009
Gasoline		0.17-0.38	0.042-0.22	0.37-0.63	0.34-3.3	Rogge *et al.*, 1993a; Simick *et al.*, 1999; Khalili *et al.*, 1995; Li and Kamens, 1993
Diesel		0.45-0.64	0.19-0.70	0.20-0.93	0.36-2.2	Yunker *et al.*, 2002; Simick *et al.*, 1999; Khalili *et al.*, 1995; Rogge *et al.*, 1993a; Li and Kamens, 1993
Coal			0.35-0.62	0.48-0.85	0.15-1.1	Yunker *et al.*, 2002; Simick *et al.*, 1999
Wood burning		0.36-0.43	0.49-0.77	0.41-0.67	0.64	Yunker *et al.*, 2002; Khalili *et al.*, 1995; Li and Kamens, 1993
Coke oven		0.34-0.41	0.61	0.90	0.13-0.20	Hayakawa *et al.*, 2016; Simick *et al.*, 1999; Khalili *et al.*, 1995
Incinerators					1.7-7.1	Simick *et al.*, 1999
Road dust			0.51	0.42	0.91	Yunker *et al.*, 2002; Rogge *et al.*, 1993b
Tire ware				0.17		Rogge *et al.*, 1993b
Brake				0.39	3.5	Rogge *et al.*, 1993b
	Range (Average)					
This study	0.38-0.58 (0.46)	0.29-0.71 (0.43)	0.042-0.56 (0.51)	0.50-0.57 (0.54)	0.52-1.7 (1.1)	

1995; Li and Kamens, 1993; Rogge *et al.*, 1993a, 1993b). The compounds involved in each ratio have the same or similar molecular weight, so it may be assumed that they have similar physicochemical properties. Diagnostic ratios vary during different stages of phase transfer and under environmental degradation. In this study, we calculated diagnostic ratios of BeP/(BeP + BaP), BaA/(BaA + Chr), IP/(IP + BghiP), Fluor/(Fluor + Py), and BghiP/BaP from the measured PAHs shown in Table 2.

Most fresh exhaust emissions typically contain almost the same amount of BeP and BaP. However, BaP more easily degraded than BeP by photochemical reactions in the ambient atmosphere. The atmospheric lifetime of BaP is estimated as ten times shorter than that of BeP (Kalberer *et al.*, 2002). Therefore, the increment of BeP/(BeP + BaP) can be used as in indicator of the degree of photochemical degradation (i.e., aging) of compounds in the atmospheric environment (Wang *et al.*, 2015; Shen *et al.*, 2013; Alves *et al.*, 2009). The seasonal variation of calculated BeP/(BeP + BaP) in this study ranged from 0.38-0.58. Freshly released BeP/(BeP+BaP) should have a ratio close to 0.50 (Mikuška *et al.*, 2015; Park *et al.*, 2006), suggesting that most of the $PM_{2.5}$ containing BaP and BeP was emitted from local or nearby regional sources throughout the study period.

Table 6. CPI and C_{wax} obtained from the measurement results of individual n-alkanes.

Year	Season	n	CPI		C_{wax} (%)	
			Range	Average	Range	Average
2016	Summer	6	0.73-1.4	1.1	4.3-17	9.0
	Autumn	12	1.1-2.0	1.6	12-34	23
	Winter	13	1.1-1.6	1.4	9.7-26	19
2017	Spring	13	0.94-3.2	1.7	8.4-53	25
	Summer	13	1.2-1.9	1.6	8.9-32	24
	Autumn	8	0.95-2.0	1.5	7.7-35	22
	Total	65	0.73-3.2	1.5	4.3-53	22

Table 5 presents five different types of developed diagnostic ratios from previous studies and includes BeP/(BeP + BaP), BaA/(BaA + Chr), IP/(IP + BghiP), Fluor/(Fluor + Py), and BghiP/BaP (Hayakawa *et al.*, 2016; Wang *et al.*, 2015; Shen *et al.*, 2013; Alves *et al.*, 2009; Yunker *et al.*, 2002; Simcik *et al.*, 1999; Khalili *et al.*, 1995; Li and Kamens, 1993; Rogge *et al.*, 1993a, 1993b) and those obtained in this study. From the comparison of the diagnostic ratios shown in Table 5, most of the diagnostic ratios calculated were within the range of gasoline, diesel, coal and wood burning emissions. The emissions from gasoline and diesel emissions from vehicles, and coal emissions from industrial sources are not influenced by the seasons, which supports the assumption mentioned above in Section 3.2.1. Therefore, influences of vehicle and industrial emission sources nearby sampling site could be the possible anthropogenic sources of measured PAHs in this study. Kume *et al.* (2007) have analyzed 21 species of PAHs in suspended particles at urban sites of Shizuoka, Japan, within the area of vehicle and industrial emission sources nearby. Their annual means ratios of IP/(IP + BghiP) and BghiP/BaP were 0.51 and 1.28, respectively, which were in good agreement with those obtained in this study.

Moreover, careful consideration of PAHs usage data should be taken in to account when attempting to identify anthropogenic PAHs sources because PAHs can be emitted from various source types. Therefore, other molecular markers and/or tracers should be gathered for more accurate source apportionment.

3.3.2 Historical Distribution, CPI and C_{wax} of n-Alkanes

Table 3 and Fig. 5 indicate that C_{23}-C_{33} were the main homologues contributing to the $\sum$n-alkanes. Previous research has shown that carbon number with a strong predominance of odd carbon number indicates a significant contribution from biogenic contributors (Rogge *et al.*, 1993c), whose abundances of odd carbon number higher than 24 are approximately one magnitude higher than those of even carbon number. Whereas n-alkanes released from fossil fuel sources do not show such predominant tendency (Alves *et al.*, 2009; Simoneit *et al.*, 1991). Fig. 5 shows that odd-numbered carbon homologues were not dominant during the study period. Therefore, contributions arising from anthropogenic inputs might have been higher than biogenic inputs at the study site.

For the further interpretation of obtained data associated with n-alkanes, we used the carbon preference index (CPI) and contribution of plant wax to n-alkanes (C_{wax}) to assess the variability of sources, and they are listed in Table 6. The CPI can be used to distinguish biogenic and anthropogenic inputs. It is defined as the sum of the concentrations of the odd carbon number n-alkanes ($\sum C_{odd}$) divided by the sum of the concentrations of the even carbon number n-alkanes ($\sum C_{even}$), which was calculated as follows:

$$\mathrm{CPI} = \frac{\sum C_{odd}}{\sum C_{even}} = \frac{\sum (C_{17} \text{ to } C_{39})}{\sum (C_{18} \text{ to } C_{40})} \quad (1)$$

Plant wax n-alkanes exhibit a strong odd carbon number predominance and thus increase the CPI value (Park *et al.*, 2006). Conversely, anthropogenic inputs such as fossil fuels reduce the CPI value. The CPI typical values in the urban environment range from 1.1 to 2.0, while a CPI higher than 2.0 has a stronger biogenic influence (Alves *et al.*, 2009). In the present study, the CPI values during the study period were in the range 0.73-3.2 with an average of 1.5, as shown in Table 6. A CPI value above 2.0 was observed just in one sample in spring 2017 (CPI = 3.2, for 2-10 May), suggesting that most of the measured n-alkanes during the study period were anthropogenic in origin.

Another methodology to analyze the contribution of plant wax sources to n-alkanes can be expressed through C_{wax} (Wang *et al.*, 2015; Yadav *et al.*, 2013; Alves, 2008; Park *et al.*, 2006; Simoneit *et al.*, 1991). C_{wax} gives the percentage concentration input of wax n-alkanes from biogenic sources in sample. The C_{wax} is calculated as follows:

$$C_{wax} = \frac{\sum \left\{ C_n - \frac{(C_{n-1} + C_{n+1})}{2} \right\}}{\sum \mathrm{n \cdot Alkanes}} \times 100 \quad (2)$$

where n is the odd number of analyzed n-alkanes. Measured C_n values below the LOD were replaced with the value of LOD/2, and the negative values of $\{C_n - (C_{n-1} + C_{n+1})/2\}$ were determined as zero. Table 6 shows that the percentages of C_{wax} were in the range of 4.3-53% with an average of 22%. The higher percentage values indicate greater contributions from biogenic sources (Wang *et al.*, 2015). The highest C_{wax} value of 53% was calculated from the same sample as CPI = 3.2, which could possibly mean that the contribution of biogenic sources was larger than sample during the period of 2-10 May 2017. Comprehensive evaluation including the historical distributions of n-alkanes homologues, CPI, and C_{wax}, indicates that the observed n-alkanes may largely originate from anthropogenic sources for most of the samples in this study. Further identification of the emission sources of n-alkanes in $PM_{2.5}$ will be conducted in future research.

4. SUMMARY AND CONCLUSIONS

A long time series (approximately 17 months) of quantitative data of non-polar organic compounds constituting $PM_{2.5}$ was created from samples collected at Ichihara, one of the largest industrial areas in Japan. Sample collection and analysis took place continuously from June 2016 to October 2017. The target non-polar organic compounds were 21 species of PAHs, 24 species of n-alkanes, and 5 species of PAHs, and these were simultaneously measured using GC/MS. The results indicate that anthropogenic sources were the dominant inputs for the most PAHs and n-alkanes throughout the study period. Identification of the emission sources of individual organic compounds in $PM_{2.5}$ will be conducted in future research. To our knowledge, this paper describes the first attempt to measure such a large number of different non-polar organic compounds in $PM_{2.5}$ from the ambient atmosphere of Japan to create a long time series. The findings will provide valuable data and information to environmental researchers. The main findings are as follows:

(1) The average concentrations of $\sum$PAHs, $\sum$n-alkanes, and $\sum$PAEs in each season remained nearly level (except for a few high $\sum$PAHs in early winter and $\sum$n-alkanes in late autumn and early winter), and no strong seasonal variations were observed throughout the study period. These results suggest that the emission sources, which are not influenced by the seasons, are the dominant inputs for the target organic compounds.

(2) The contributions of $\sum$PAHs, $\sum$n-alkanes, and $\sum$PAEs to the $PM_{2.5}$ mass concentration were each less than 1%.

(3) The target PAEs were not substantially emitted within the source area of the sampling site.

(4) All of the calculated BeP/(BeP+BaP) ratios were close to 0.50, which indicates that $PM_{2.5}$ containing BaP and BeP were emitted from local or nearby regional anthropogenic sources throughout the study period.

(5) From the analysis of diagnostic ratios, gasoline, diesel and coal emissions could be possible anthropogenic sources of measured PAHs in this study.

(6) The distributions of n-alkane homologues and calculated results of CPI and C_{wax}, indicate that n-alkanes at the study site may largely originate from anthropogenic sources. Further identification of the emission sources of n-alkanes in $PM_{2.5}$ will be conducted in future research.

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