

Seasonal Variation of PM_{2.5} Components Observed in an Industrial Area of Chiba Prefecture, Japan

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ABSTRACT

In order to survey the seasonal variation of the chemical composition of particulate matter of 2.5 μm or less (PM_{2.5}), PM_{2.5} was sampled from 8 February 2013 to 31 March 2014 in an industrial area of Chiba Prefecture, Japan. Chemical measurements of the sample included: ionic components (Na⁺, NH₄⁺, Ca²⁺, Mg²⁺, K⁺, Cl⁻, NO₃⁻ and SO₄²⁻), carbonaceous components - organic carbon (OC) and elemental carbon (EC), and water-soluble organic carbon (WSOC). Also, secondary organic carbon (SOC) was measured based using the EC tracer method, and char-EC and soot-EC were calculated from the analytical results. The data obtained were interpreted in terms of temporal variation. Of the overall mean value of PM_{2.5} mass concentration obtained during the study period, ionic components, OC and EC accounted for 45.3%, 19.7%, and 8.0%, respectively. NO₃⁻ showed a unique seasonal distribution pattern due to a dependence on temperature and absolute humidity. It was estimated that an approximate temperature of 14°C, and absolute humidity of 7 g/m³ were critical for the reversible reaction of NH₄NO₃ (p) \rightleftharpoons NH₃ (g) + HNO₃ (g). The amount of OC and EC contributing to the monthly PM_{2.5} mass concentration was higher in autumn and winter compared to spring and summer. This result could be attributed to the impact of burning biomass, since WSOC and the ratio of char-EC/soot-EC showed a similar pattern during the corresponding period. From the comparison of monthly WSOC/OC values, a maximum ratio of 83% was obtained in August (summer). The WSOC and estimated SOC levels derived from the EC tracer method correlated (R=0.77) in summer. The high occurrence of WSOC during summer was mainly due to the formation of SOC by photochemical reactions. Through long-term observation of PM_{2.5} chemical components, we established that the degree to which the above-mentioned factors influence PM_{2.5} composition, fluctuates with seasonal changes.

Key words: PM_{2.5}, Japan, Chiba Prefecture, Seasonal variations, Chemical analysis, Carbonaceous components, Ionic components

1. INTRODUCTION

Over the last decade, significant evidence has proven that particulate matter, smaller than 2.5 μm , is particularly hazardous to public health due to its ability to penetrate the thoracic cavity (Takebayashi *et al.*, 2011; EPA, 2009; WHO, 2005). As a result, many countries have established regulatory standards regarding PM_{2.5} mass concentration. In Japan, environmental quality standards were enforced in September 2009. This standard states that the annual PM_{2.5} mass concentration is required to be less than, or equal to 15 $\mu\text{g}/\text{m}^3$ and that the daily PM_{2.5} mass concentration should be less than or equal to 35 $\mu\text{g}/\text{m}^3$. PM_{2.5} contains a multitude of source content. This contributes to the physical and chemical complexity that is still poorly characterised. As a result, drawing a link between PM_{2.5} emission sources, ambient mass concentrations and health effects becomes a complicated process. For a detailed understanding of the health risks associated with PM_{2.5} exposure, characterisation of their physical and chemical properties is required.

Moreover, according to information provided by the Ministry of the Environment Japan (MOEJ), only 27.6% of stations monitoring general ambient air, and 29.4% of stations monitoring auto-exhaust emissions, met environmental quality standards for PM_{2.5} during the 2011 fiscal year. Countermeasures are clearly needed to reduce the level of PM_{2.5}, and acquiring data for physical and chemical characterisation is a priority. However, long-term studies examining the temporal variability of PM_{2.5} chemical components are limited in Japan. In this study, the value and seasonal variation of major PM_{2.5} components were measured. These included ionic components, and carbonaceous compo-

nents (organic carbon (OC) and elemental carbon (EC)) in the ambient atmosphere. These results aim to provide useful insights and information to further our understanding of the chemical profile of PM_{2.5}. This has the potential to aid strategies for air quality improvement and management programs.

2. MATERIALS AND METHODS

2.1 PM_{2.5} Sampling Site

Sampling was conducted on the roof (12 m height above the ground) of Chiba Prefectural Environmental Research Center (CERC). 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), and the residential zone of Ichihara, Chiba (Fig. 1). The site is located approximately 150 m southeast of the Japanese National Route 16. According to a road traffic census conducted by the Ministry of Land, Infrastructure, Transport and Tourism (MLIT, 2009), the 2009 fiscal year, weekday 24-hour traffic volume, was on average 36,742 (small vehicles: 26,854; large vehicles: 9,888). Ichihara is about 40 km southeast of central Tokyo, and the estimated population is nearly 276,000.

2.2 PM_{2.5} Sampling Conditions and Mass Concentration Determinations

Prior to sampling, quartz filter paper (Pall Corp., 2500QAT-UP, Q-filter) with a 47 mm diameter was pre-treated for 1.5–2 hours, at 350°C in a drying furnace to lower the analytical background level. Pre-treated Q-filters were stored in a sealed stainless steel container, in a plastic desiccator at room temperature until use.

Samples for PM_{2.5} chemical analysis were collected daily from 8 February 2013 to 31 March 2014. Sampling was done on pre-treated Q-filters, for 24-hour periods (starting from JST 10 a.m. (UTC+9) every day). The flow rate of the low volume air sampler (Thermo-Scientific Inc., 2025i Sequential Air Sampler) was 16.7 L/min with a constant sampling rate of 24 m³/d.

Exposed Q-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.

PM_{2.5} mass concentration was measured in parallel, using an automatic instrument (Horiba Ltd., APDA-3750A) employing a beta-ray absorption technique. Measurements were done at the monitoring station of the CERC, at a height of 7 m above the ground. These data were collected from the same source as the one used for the continuous monitoring of PM_{2.5} mass concentration for the Air Pollution Control Act. The situation of the monitoring point is fully exposed to the atmosphere without the interference of any obstacles.

Based on the definition used by the Japanese Meteorological Agency, the four seasons were assigned: March to May for spring, June to August for summer, September to November for autumn and December to February for winter.

2.3 Chemical Analysis

Sampled filters (deposition area of 11.95 cm²) were each cut into 4 pieces. Each piece was prepared for sequential chemical analysis to determine the following categories: (1) ionic components (Na⁺, NH₄⁺, Ca²⁺, Mg²⁺, K⁺, Cl⁻, NO₃⁻ and SO₄²⁻), (2) carbonaceous components (organic carbon (OC) and elemental carbon (EC)), (3) water-soluble organic carbon (WSOC)

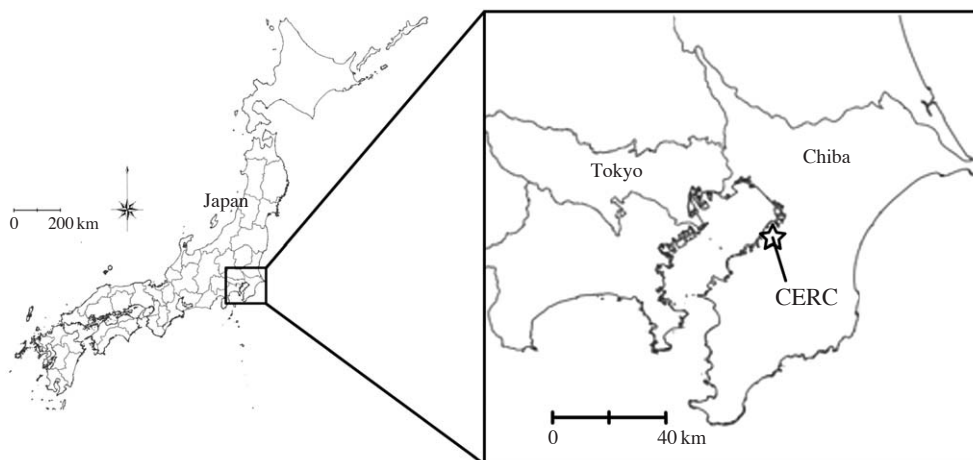


Fig. 1. Map indicating the location of Chiba Prefectural Environmental Research Center (CERC).

and (4) field blanks were prepared and analyzed in the same way as the ambient samples to identify contaminations.

2.3.1 Ionic Components

Ionic components were extracted using a sonicator in 8 mL of ultrapure water ($> 18 \text{ M}\Omega\cdot\text{cm}$ resistance) for 30 min at room temperature. After sonication, the extract was filtered through a hydrophilic polymer syringe filter (GL Science Inc., pore size of $0.45 \mu\text{m}$) before instrumental analysis. The analytical conditions for ion chromatography to quantify cations and anions are listed in Table 1.

2.3.2 Carbonaceous Components

Collected Q-filters were punched into 1 cm^2 pieces to determine organic carbon (OC) and elemental carbon (EC) by the thermal/optical reflectance carbon analysis system (Sunset Laboratory Inc.). The analytical conditions of the IMPROVE method (Chow *et al.*, 1993) were used with the thermal optical reflection protocol (Han *et al.*, 2010; Han *et al.*, 2007; Chow *et al.*, 2001). A total of seven fractions (OC1, OC2, OC3, OC4, EC1, EC2 and EC3) and the optical pyrolysis correction of OC (PyC) were determined. OC was defined as $\text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{PyC}$ and EC was defined as $\text{EC1} + \text{EC2} + \text{EC3} + \text{PyC}$.

2.3.3 Water-Soluble Organic Carbon

An aliquot of the extract used to analyze ionic components described in section 2.3.1 was used to measure WSOC (Kumagai, 2011). WSOC was quantified using the total organic carbon analyzer (Shimadzu Corp., TOC-5000). The amount of sample injected to quantify WSOC was $100 \mu\text{L}$.

3. RESULTS AND DISCUSSION

3.1 Data Validation

Validation techniques were performed on all of the data sets obtained following chemical analyses ($n=$

414) to check for discrepancies. This included validating the ionic balance of ionic components and comparing the sum of the measured chemicals with the measured $\text{PM}_{2.5}$ mass concentrations to check for internal consistency.

The ionic balance was calculated by comparing the total electro charge of positive charged cation species with the total electro charge of the negative charged anion species. We defined the range of “total anions equivalent/total cation equivalent” as 0.8-1.2, in accordance with the provisional $\text{PM}_{2.5}$ analytical procedure manual officially announced by MOEJ (MOEJ, 2007).

Furthermore, the daily $\text{PM}_{2.5}$ mass concentrations measured by the automatic instrument, and the $\text{PM}_{2.5}$ mass concentrations calculated by using a formula (1) were compared (organic carbon (OC); elemental carbon (EC):

$$\text{Cal. Mass} = 1.375[\text{SO}_4^{2-}] + 1.29[\text{NO}_3^-] + 2.5[\text{Na}^+] + 1.4[\text{OC}] + [\text{EC}] \quad (1)$$

Square brackets indicate the mass concentration ($\mu\text{g}/\text{m}^3$) of individual components as determined by chemical analysis. This is a modified version of the chemical mass closure model formula originally published in the $\text{PM}_{2.5}$ analytical procedure manual, officially announced by the MOEJ (2007). The original formula includes metallic elements, such as Al, Fe, Ca, Si and Ti, which were not included in this study, and was adapted without those metallic elements. According to MOEJ (2007), the acceptable range for “calculated $\text{PM}_{2.5}$ mass concentration/measured $\text{PM}_{2.5}$ mass concentration” is 0.8-1.2. This study didn't include metallic elements and our criteria were slightly adapted to accept ratios higher than 1.2 as outliers. Compared to carbonaceous or ionic components, metallic elements account for a small portion of the total $\text{PM}_{2.5}$ mass. Yonemochi *et al.* (2013) quantified 54 metallic elements in $\text{PM}_{2.5}$ collected at Kazo, Saitama Prefecture, Japan, and the level of those metallic elements were in the range of $5.5 \text{ pg}/\text{m}^3$ to $170 \text{ ng}/\text{m}^3$. Data was inter-

Table 1. Analytical conditions of ion chromatography analysis.

	Cation	Anion
Column	TSKgel SuperIC-CR, 4.6 mm I.D. \times 15 cm (Tosoh Corp.)	TSKgel SuperIC-AZ, 4.6 mm I.D. \times 15 cm (Tosoh Corp.)
Mobile phase	220 mM methanesulfonic acid +100 mM 18-crown-6-ether	190 mM NaHCO_3 +320 mM Na_2CO_3
Temperature of column oven	40°C	40°C
Flow rate	0.8 mL/min	0.8 mL/min
Injection volume	30 μL	30 μL
Detector	Conductivity	Conductivity
Chemical suppressor	Equipped	Equipped

preted in 373 out of 414 data sets using the validation techniques described above.

3.2 Dominating Chemical Components

Tables 2 and 3 show the monthly and seasonal mean

concentrations of carbonaceous components and ionic components, respectively. As shown in Fig. 2, the annual mean value of PM_{2.5} mass concentration was accounted for by ionic components (45.3%), OC (19.7%) and EC (8.0%).

Table 2. Monthly and seasonal mean concentrations of PM_{2.5}, individual fractions of OC and EC, Total OC, Total EC and Total carbon.

Year	Month	n	Mean concentration (µg/m ³)											
			PM _{2.5} mass	OC1	OC2	OC3	OC4	EC1	EC2	EC3	PyC	Total OC	Total EC	Total carbon
2013	Feb	12	17.10	0.16	1.27	0.71	0.35	1.60	1.00	0.07	1.14	3.64	1.53	5.16
	Mar	26	19.85	0.14	1.25	0.64	0.29	1.64	0.72	0.06	1.02	3.34	1.40	4.74
	Apr	28	15.75	0.11	1.08	0.56	0.24	1.21	0.66	0.04	0.83	2.81	1.08	3.88
	May	30	13.07	0.09	1.05	0.53	0.22	0.93	0.65	0.05	0.73	2.62	0.90	3.52
	Jun	28	13.21	0.06	0.90	0.39	0.16	0.65	0.77	0.05	0.60	2.11	0.87	2.97
	Jul	31	19.77	0.05	1.10	0.55	0.25	1.13	0.94	0.05	0.96	2.91	1.16	4.07
	Aug	31	20.95	0.06	1.13	0.53	0.23	1.25	0.75	0.04	0.85	2.79	1.19	3.98
	Sep	25	10.64	0.06	0.93	0.56	0.23	0.81	0.60	0.04	0.53	2.30	0.92	3.22
	Oct	31	10.32	0.10	0.96	0.58	0.21	0.95	0.42	0.03	0.45	2.29	0.96	3.25
	Nov	29	17.39	0.26	1.56	0.94	0.37	2.23	0.46	0.04	0.90	4.03	1.83	5.86
	Dec	28	16.98	0.32	1.60	1.00	0.40	2.19	0.48	0.05	0.80	4.12	1.91	6.04
	2014	Jan	27	15.13	0.24	1.56	0.70	0.30	1.81	0.53	0.05	0.77	3.58	1.62
Feb		25	17.51	0.16	1.74	0.62	0.28	1.74	0.51	0.05	0.85	3.65	1.44	5.09
Mar		22	16.53	0.18	2.00	0.59	0.27	1.59	0.47	0.03	0.94	3.98	1.15	5.13
Spring	106	16.30	0.13	1.35	0.58	0.25	1.34	0.63	0.04	0.88	3.19	1.13	4.32	
Summer	90	17.98	0.06	1.04	0.49	0.21	1.01	0.82	0.04	0.80	2.60	1.07	3.67	
Autumn	85	12.78	0.14	1.15	0.69	0.27	1.33	0.49	0.04	0.62	2.87	1.24	4.11	
Winter	92	16.68	0.22	1.54	0.76	0.33	1.83	0.63	0.05	0.89	3.75	1.63	5.37	
Annual mean	373	16.01	0.14	1.30	0.63	0.27	1.41	0.64	0.05	0.81	3.16	1.28	4.44	

Table 3. Monthly and seasonal mean concentrations of PM_{2.5}, cation and anion.

Year	Month	n	Mean concentration (µg/m ³)									
			PM _{2.5} mass	Cation					Anion			
				Na ⁺	NH ₄ ⁺	Mg ²⁺	Ca ²⁺	K ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	
2013	Feb	12	17.10	0.07	1.91	0.02	0.07	0.10	0.50	3.38	3.04	
	Mar	26	19.85	0.21	2.21	0.05	0.18	0.10	0.28	1.96	5.10	
	Apr	28	15.75	0.15	1.66	0.03	0.11	0.10	0.09	0.67	4.61	
	May	30	13.07	0.11	1.33	0.03	0.11	0.08	0.03	0.39	3.74	
	Jun	28	13.21	0.11	1.53	0.03	0.10	0.08	0.04	0.44	4.29	
	Jul	31	19.77	0.16	2.16	0.03	0.10	0.05	0.02	0.20	6.68	
	Aug	31	20.95	0.12	2.26	0.03	0.14	0.07	0.04	0.11	6.64	
	Sep	25	10.64	0.16	0.67	0.01	0.05	0.07	0.04	0.15	2.26	
	Oct	31	10.32	0.12	0.73	0.01	0.03	0.08	0.10	0.49	2.01	
	Nov	29	17.39	0.08	1.48	0.01	0.04	0.09	0.27	1.81	2.93	
	Dec	28	16.98	0.06	1.34	0.01	0.04	0.08	0.46	2.17	2.09	
	2014	Jan	27	15.13	0.08	1.47	0.01	0.05	0.10	0.37	2.11	2.53
Feb		25	17.51	0.10	1.95	0.02	0.06	0.13	0.20	1.75	4.33	
Mar		22	16.53	0.13	1.94	0.02	0.06	0.11	0.19	1.63	4.53	
Spring	106	16.30	0.15	1.78	0.03	0.12	0.10	0.15	1.16	4.50		
Summer	90	17.98	0.13	1.98	0.03	0.12	0.07	0.03	0.25	5.87		
Autumn	85	12.78	0.12	0.96	0.01	0.04	0.08	0.14	0.82	2.40		
Winter	92	16.68	0.08	1.67	0.01	0.06	0.10	0.38	2.35	3.00		
Annual mean	373	16.01	0.12	1.62	0.02	0.08	0.09	0.19	1.23	3.91		

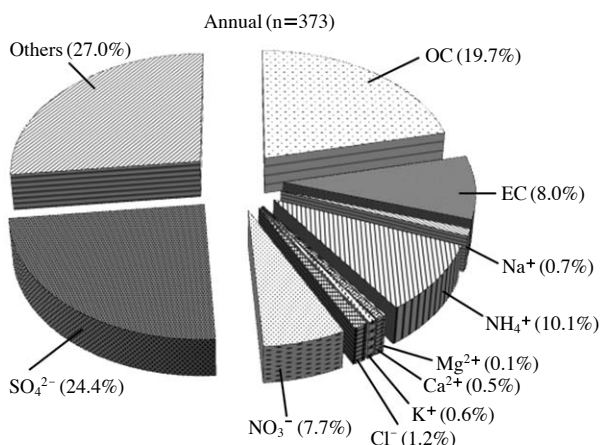


Fig. 2. Annual mean contribution of chemical components in $PM_{2.5}$ mass concentration ($n=373$).

The sum of SO_4^{2-} , NO_3^- and NH_4^+ accounted for 93.2% of the total ionic components, which is in good agreement with results obtained in Maebashi and Akagi, Japan (Kumagai *et al.*, 2009). Moreover, a study performed on the US east coastal areas (Zhao and Gao, 2008), showed that SO_4^{2-} , NO_3^- and NH_4^+ accounted for 91.9% of the total water-soluble ions in $PM_{1.8}$, which is consistent with our result. Other ionic components, Na^+ , Ca^{2+} , Mg^{2+} , K^+ , and Cl^- accounted for 0.7%, 0.5%, 0.1%, 0.6%, and 1.2% of mean value of $PM_{2.5}$ mass concentration, respectively, which can be assigned as minor components.

This result indicates that OC, EC, SO_4^{2-} , NO_3^- and NH_4^+ are the five major chemical components that contribute to $PM_{2.5}$ mass concentration. It also correlates with values reported in Nagoya, Japan, where the sum of SO_4^{2-} , NH_4^+ , NO_3^- , OC and EC accounted for nearly 75% of $PM_{2.5}$ mass concentration (Yamagami *et al.*, 2011). These aerosol species are removed from the troposphere on approximately a weekly basis primarily by wet scavenging and secondarily by dry deposition (Saikawa *et al.*, 2009).

According to a study conducted in Xi'an, China, the ratios of OC and EC to the total $PM_{2.5}$ mass were 20.4% and 4.7%, respectively (Han *et al.*, 2010). Although the $PM_{2.5}$ mass concentrations measured in China are approximately one to two orders of magnitude higher than those observed in Japan (Huang *et al.*, 2014), the contribution of OC and EC to the mean value of $PM_{2.5}$ mass concentration may not be significantly different.

An undetermined fraction (defined as "Others" in Fig. 2) represented 27.0% of the mean value of $PM_{2.5}$ mass concentration. This fraction is assumed to contain metallic elements, moisture content, atoms other than carbon constituting organic matter, and analyti-

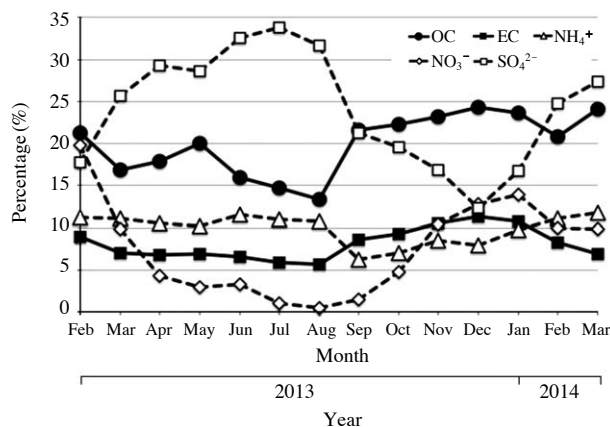


Fig. 3. Seasonal variation of five chemical components accounting for monthly $PM_{2.5}$ mass concentration.

cal uncertainties of the measurement.

3.3 Temporal Variations of the Five Major Components

Since the ionic and carbonaceous components constitute the major fractions of $PM_{2.5}$, it is important to present and discuss their temporal variations. Fig. 3 shows the monthly percentage of OC, EC, SO_4^{2-} , NO_3^- and NH_4^+ to $PM_{2.5}$ mass concentration. Interestingly, OC, SO_4^{2-} and NO_3^- exhibited seasonal fluctuation. OC and NO_3^- were more prevalent in autumn and winter than in spring and summer. In contrast, SO_4^{2-} concentrations were higher in spring and summer and lower in autumn and winter. EC and NH_4^+ did not show variation during the studied period.

As shown in Fig. 3, NO_3^- varied the most notably on the time scale. The percentage of NO_3^- decreased to below 5% in April (middle of spring) and remained relatively consistent until October (middle of autumn). When the percentage of NO_3^- started to increase, the percentage of SO_4^{2-} decreased. SO_4^{2-} and NO_3^- in fine particulate matter are considered to exist as neutralized salts $(NH_4)_2SO_4$ and NH_4NO_3 , respectively.

As shown in Fig. 3, the percentage of NH_4^+ remains a constant value. It is assumed that the alternating ratios of SO_4^{2-} and NO_3^- are due to affinity of NH_4^+ for both of these anions.

Correlation coefficients between NH_4^+ versus SO_4^{2-} and NH_4^+ versus NO_3^- were drawn in Fig. 4 to examine the assumption mentioned above. From October 2013 to January 2014, it was observed that as NO_3^- started to show a stronger correlation with NH_4^+ , SO_4^{2-} and NH_4^+ showed a weaker correlation. Conversely, from March to September, the correlation coefficient of NH_4^+ versus NO_3^- started to decrease as that of NH_4^+ and SO_4^{2-} increased. These data present a sim-

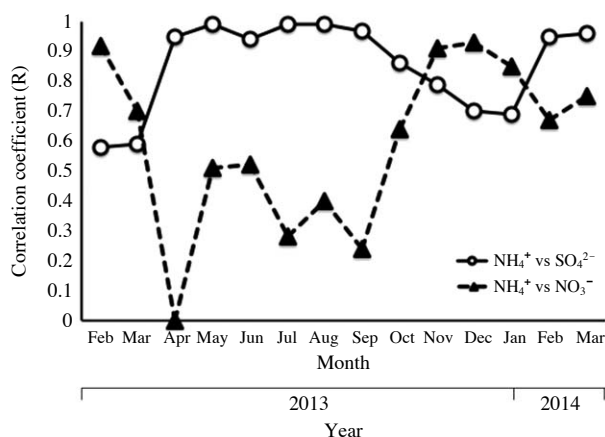


Fig. 4. Comparison of correlation coefficient between NH₄⁺ and SO₄²⁻ set and NH₄⁺ and NO₃⁻ set.

ilar pattern as the data in Fig. 3, which shows the monthly variation in SO₄²⁻ and NO₃⁻ as a total of PM_{2.5} mass concentration. This suggests a preference for the formation of NH₄NO₃ during autumn and winter and (NH₄)₂SO₄ in spring and summer. Recent studies carried out in Japan analyzed the high levels of PM_{2.5} occurring during spring through winter (Hasegawa *et al.*, 2014; Ichikawa *et al.*, Accepted). Studies showed that high concentrations of NH₄NO₃ were measured in accordance with high pollution event. Our results suggest that, by actively reducing the emissions that specifically contain the precursors of NH₄NO₃ is likely to be one of the important factors to constrain high pollution event during spring through winter.

3.4 Correlation between Nitrate and Atmospheric Parameters

For the accumulation of particulate NO₃⁻ in PM_{2.5}, the condensation of gaseous NH₃ and HNO₃ are generally thought to be the main pathways. From the results obtained, concentrations of NO₃⁻ between November and March were relatively higher than those measured between April and October.

Previous studies have shown that NH₄NO₃ is usually found in the accumulation mode of 0.1-0.3 μm in aerodynamic diameter (Wall *et al.*, 1988), however they are volatile under atmospheric conditions and can dissociate to NH₃ (g) and HNO₃ (g) in the reversible process. The balance of this reversible process is said to be dependent on temperature and humidity (Zhao and Gao, 2008). We examined the correlation between NO₃⁻ concentration and atmospheric parameters that are measured at the monitoring station located in CERC. Since relative humidity is a parameter dependent on temperature, absolute humidity was applied for the evaluation of atmospheric humidity

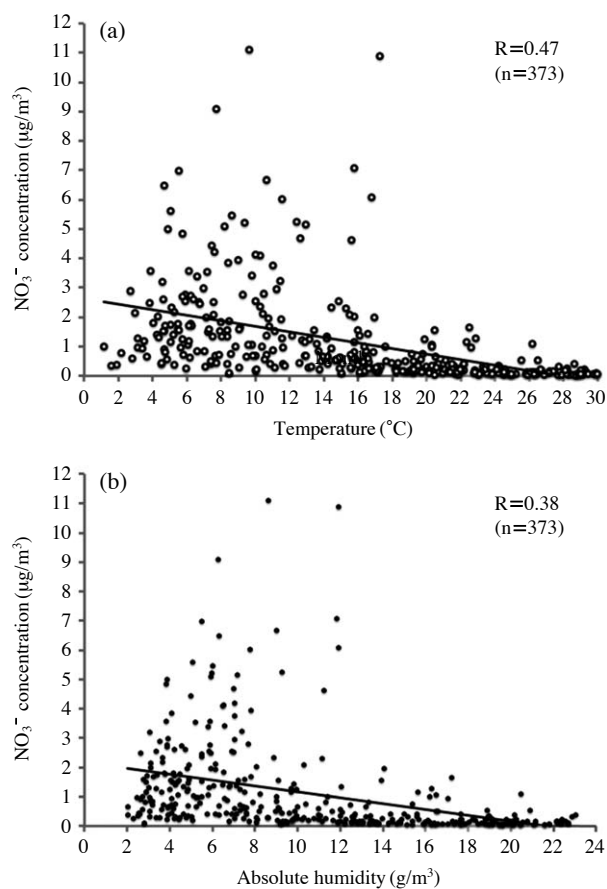


Fig. 5. Relationship between the daily concentration of NO₃⁻ and daily meteorological parameters measured at CERC; (a) temperature, (b) absolute humidity.

and NO₃⁻ concentration. Daily NO₃⁻ concentrations were plotted against daily mean temperatures (a) and absolute humidity (b), as shown in Fig. 5. Both diagrams indicated a moderate correlation (other atmospheric parameters had no correlation with NO₃⁻ concentration). NO₃⁻ concentrations also displayed a stronger dependence on temperature ($R=0.47$, $p < 0.01$) than on absolute humidity ($R=0.39$, $p < 0.01$). These results are similar to those obtained by Hara (Hara *et al.*, 1989), which show that HNO₃ (g) turns into NO₃⁻ (p) in the fine mode range by the reaction with NH₃ (g), which tends to occur at lower temperatures. For further understanding into how the NO₃⁻ concentration is affected by temperature and absolute humidity, multiple regression analysis was employed. The calculated multiple correlation coefficient was 0.52, in addition, temperature and absolute humidity were statistically significant with NO₃⁻ concentration at 1% level, respectively. This result suggests that temperature and absolute humidity are important factors

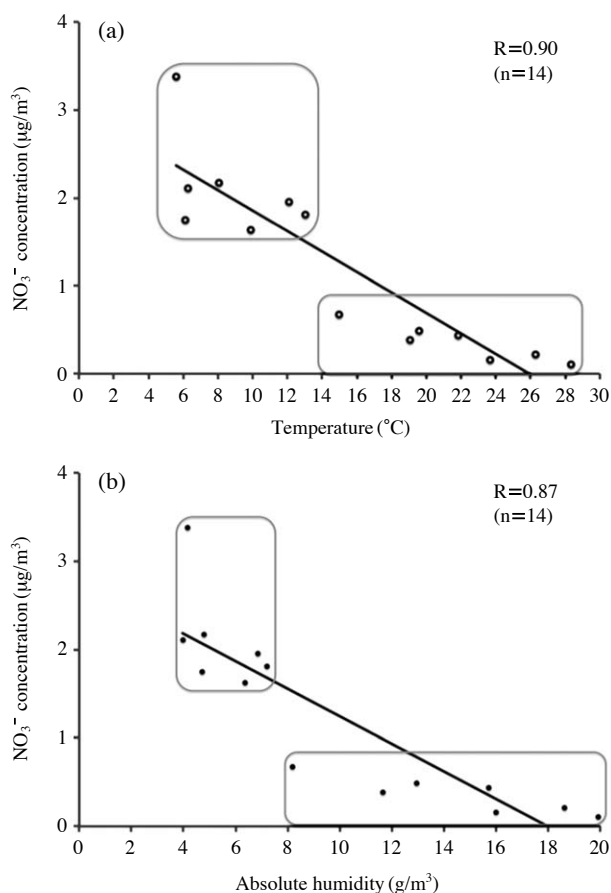


Fig. 6. Relationship between the monthly-based concentration of NO_3^- and meteorological parameters measured at CERC; (a) temperature, (b) absolute humidity.

for the reversible reaction of $\text{NH}_4\text{NO}_3 (\text{p}) \rightleftharpoons \text{NH}_3 (\text{g}) + \text{HNO}_3 (\text{g})$.

Fig. 6 represents the monthly comparison between NO_3^- concentration and temperature (a), and absolute humidity (b). Bimodal distribution patterns (indicated by gray square in Fig. 6) were seen for both scatter diagrams. According to these results, a temperature of around 14°C , and absolute humidity of 7 g/m^3 define the optimal conditions (critical points) for the reversible reaction of $\text{NH}_4\text{NO}_3 (\text{p}) \rightleftharpoons \text{NH}_3 (\text{g}) + \text{HNO}_3 (\text{g})$. The reversible reaction shifted to the left to increase $\text{NH}_4\text{NO}_3 (\text{p})$ when the mean ambient temperature and absolute humidity were lower than the critical points. On the other hand, its major fraction shifted to increase $\text{NH}_3 (\text{g})$ and $\text{HNO}_3 (\text{g})$ when they were above the critical points.

Matsumoto *et al.* (2012) collected size fractionated aerosol samples with diameters of smaller than $2.0 \mu\text{m}$ (fine mode) and $2.0\text{-}10 \mu\text{m}$ (coarse mode) in Yamashi Prefecture, inland area of Japan. They analyzed

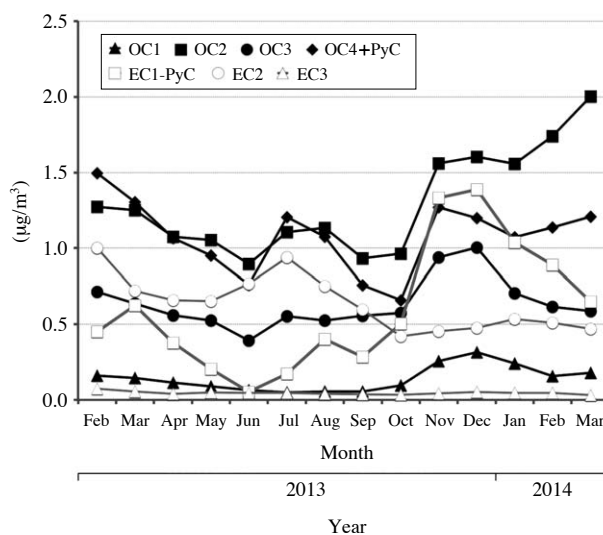


Fig. 7. Temporal variations of individual fractions of OC and EC.

the same ionic species as this study, and highlighted the importance of the amount of coarse sea-salt particles rather than the ambient temperature for the partitioning of NO_3^- into coarse particles as well as the partitioning of HNO_3 into gas phase. Further research is required to evaluate and verify the partitioning of NO_3^- in the atmosphere.

3.5 Temporal Variation of Individual Fractions of OC and EC

OC and EC originate from the combustion of fossil fuel and burning of biomass. OC is composed of the carbonaceous part of organic aerosols that are directly emitted from anthropogenic and biogenic sources, namely primary organic carbon (POC), and secondary organic carbon (SOC). SOC is formed by photochemical reactions of anthropogenic and biogenic volatile organic compounds (VOCs). On the other hand, EC is produced by incomplete combustion and exists exclusively in a primary state.

Fig. 7 illustrates the time series variations of individual fractions of OC, EC measured on a monthly basis. A total of seven fractions: OC1, OC2, OC3, OC4+PyC, EC1-PyC, EC2 and EC3 were separately measured in order to accommodate the definition of OC ($\text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{PyC}$) and EC ($\text{EC1} + \text{EC2} + \text{EC3} + \text{PyC}$). During summer, OC2, OC4+PyC, EC1-PyC and EC2 showed slightly increased levels. All of fractions, except for EC2 and EC3, tended to exhibit higher concentration when the cold season set in (autumn and winter). According to Zhang *et al.* (2012), OC2 and OC3 are associated with SOC and

biomass burning sources. As such, a minor increase in OC₂ during summer could be attributed to SOC creation, and the increase in OC₂ and OC₃ during winter might be due to the influence of biomass burning.

3.6 Evaluation of Estimated SOC

The importance of SOC has long been recognised, however there is no direct way to separate and quantify POC and SOC from the total measured OC, because of the complexity of the SOC reaction pathways and the vast number of products formed by photochemical reactions. A number of indirect methods have been developed to estimate SOC, such as the use of measured water soluble organic carbon (WSOC) and primary emission indicator (Weber *et al.*, 2007), CMB models (Zhang *et al.*, 2006), and the EC tracer method (Zhang *et al.*, 2012; Miyazaki *et al.*, 2006; Turpin and Huntzicker, 1995).

In this paper, we estimated secondary organic carbon (SOC) by means of the EC tracer method, because this method only requires ambient measurements of both OC and EC, which is easy to apply. EC is resistant to chemical reactions in comparison with OC and mainly comes from primary sources. As such, it has been used as an indicator of primary anthropogenic pollutants (Turpin and Huntzicker, 1991). Castro *et al.* (1999) evaluated the production of SOC using the following equation (2):

$$\text{SOC} = \text{OC}(\text{total}) - \text{EC} \times (\text{OC}/\text{EC})_{\text{min}} \quad (2)$$

OC (total) is the total OC, and (OC/EC)_{min} is the minimum ratio of OC to EC obtained from the data of the daily samples of each month. Table 4 lists: measured PM_{2.5} mass concentration, OC, EC, (OC/EC)_{min}, calculated POC and SOC by means of EC tracer method, and the percentages of POC and SOC against PM_{2.5} mass concentration and OC. Each of these components is represented as monthly, seasonal and annual values. The estimated SOC accounted for 8.5%, 7.2%, 7.9% and 6.3% of PM_{2.5} mass concentration and 43.6%, 49.2%, 35.3% and 27.9% of OC in spring, summer, autumn and winter, respectively. One possible explanation for the high SOC ratio in summer is due to active photochemical reactions. Miyazaki *et al.* (2006) conducted semi-continuous measurements (hourly) of OC and EC in Tokyo in 2004, and derived POC and SOC by the EC tracer method. Their derived SOC accounted for 47%, 37% and 34% of OC in summer, autumn and winter, respectively, which correlates with our estimation, despite using an alternative measuring technique. A good correlation (R=0.87) was observed between monthly POC and EC levels, which suggested a high probability that these emissions had similar carbonaceous sector sources.

3.7 Temporal Variation of WSOC

Fig. 8 shows a similar temporal variation patterns for OC and WSOC. The numeric value given above the x-axis represents the ratio (%) of WSOC/OC for

Table 4. Monthly and seasonal mean concentrations of PM_{2.5}, OC, EC, POC, and SOC. Contribution ratio of POC and SOC to total PM_{2.5} and OC.

Year	Month	n	Mean concentration (µg/m ³)					(OC/EC) _{min}	Percentage (%)			
			PM _{2.5} mass	OC	EC	POC	SOC		POC/PM _{2.5} mass	SOC/PM _{2.5} mass	POC/OC	SOC/OC
2013	Feb	12	17.10	3.64	1.53	2.57	1.07	1.68	15.0	6.3	70.6	29.4
	Mar	26	19.85	3.34	1.40	2.01	1.32	1.43	10.1	6.6	60.2	39.5
	Apr	28	15.75	2.81	1.08	1.31	1.50	1.22	8.3	9.5	46.6	53.4
	May	30	13.07	2.62	0.90	1.58	1.04	1.75	12.1	8.0	60.3	39.7
	Jun	28	13.21	2.11	0.87	1.06	1.05	1.22	8.0	7.9	50.2	49.8
	Jul	31	19.77	2.91	1.16	1.49	1.43	1.28	7.5	7.2	51.2	49.1
	Aug	31	20.95	2.76	1.24	1.45	1.34	1.22	6.9	6.4	52.5	48.6
	Sep	25	10.64	2.30	0.92	1.68	0.63	1.83	15.8	5.9	73.0	27.4
	Oct	31	10.32	2.29	0.96	1.28	1.01	1.34	12.4	9.8	55.9	44.1
	Nov	29	17.39	4.03	1.83	2.64	1.39	1.44	15.2	8.0	65.5	34.5
	Dec	28	16.98	4.12	1.91	3.00	1.12	1.57	17.7	6.6	72.8	27.2
	2014	Jan	27	15.13	3.58	1.62	2.45	1.13	1.51	16.2	7.5	68.4
Feb		25	17.51	3.65	1.44	2.80	0.85	1.94	16.0	4.9	76.7	23.3
Mar		22	16.53	3.98	1.15	2.32	1.66	2.02	14.0	10.0	58.3	41.7
	Spring	106	16.30	3.18	1.13	1.81	1.38	1.61	11.1	8.5	56.3	43.6
	Summer	90	17.98	2.59	1.09	1.33	1.27	1.24	7.5	7.2	51.3	49.2
	Autumn	85	12.78	2.88	1.24	1.87	1.01	1.54	14.5	7.9	64.8	35.3
	Winter	92	16.68	3.75	1.63	2.71	1.04	1.68	16.2	6.3	72.1	27.9
	Annual mean	373	16.01	3.15	1.29	1.97	1.18	1.53	12.5	7.5	61.6	38.5

each month. The total mean value of WSOC/OC was 66.2%. Ueno *et al.* (2011) observed WSOC/OC in two sites in Tokyo in the summer of 2008 and the winter of 2009, and these values ranged between 60-70%. Kumagai *et al.* (2009) also conducted an annual cycle study from April 2005 to March 2006 in Maebashi, Gunma Prefecture, Japan. The results showed a WSOC/OC average of 58% ranging from 49-70%.

On a monthly basis, WSOC/OC reached a maximum ratio of 83% in August, which was due to enhanced photochemical reactions. WSOC and SOC formation are closely related because they both have polar functional groups (e.g. hydroxyl, carbonyl and carboxyl) produced by oxidation reactions (Kumagai *et al.*, 2009; Kondo *et al.*, 2007; Miyazaki *et al.*, 2006). Thus, increased OC in July and August could be attributed to the formation of SOC from photochemical reactions. These data indicate that secondary formation is important as a source of WSOC and OC.

In order to evaluate the relationship between WSOC and SOC, a correlation analysis between WSOC and estimated SOC (derived in section 3.6 by means of the EC tracer method) was conducted. Their correlation coefficients (R) based on seasonal values, were 0.53, 0.77, 0.66 and below 0.01 in spring, summer, autumn and winter, respectively. Correlation values were high in summer, which means that WSOC and SOC are interrelated to some extent. Moderate correlation was seen in spring and autumn, however, no correlation was found in winter. This suggests that, in winter, there are other factors contributing to, and influencing the levels of WSOC.

The WSOC/OC levels showed a gradual increase in the period from late autumn to winter. As stated above, WSOC and estimated SOC showed no correlation during winter, suggesting that a different factor/s is contributing to the rise in WSOC during this period. As shown in Fig. 7, all of the OC fractions exhibited similar incremental patterns to WSOC in autumn and winter. There are deals of evidence (Feng *et al.*, 2013; Fu and Kawamura, 2011; Kumagai *et al.*, 2010) that the formation of WSOC is closely related to formation of biomass burning. The linkages of OC fractions and WSOC in this study also suggest that the effects of burning biomass need to be considered during autumn to winter.

Open incineration is now prohibited in Japan, however, the burning of agricultural wastes (e.g. stubble and dry grass) on farmlands based on customary observations or practices are exceptionally accepted. Burning agricultural wastes is frequently practiced in the period during spring to winter. Moreover, there is a biomass power generation plant located in the industrial zone of Ichihara. They predominantly use wood

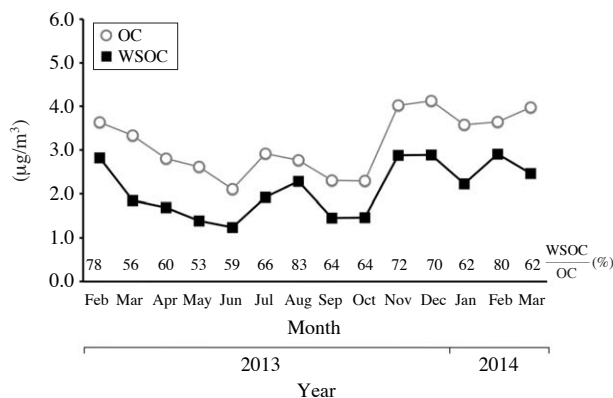


Fig. 8. Temporal variations of OC and WSOC. Numeric value given above the x-axis indicates monthly value of WSOC/OC in percentage.

chips, which could be a partial source of emission. We presume that burning biomass is an important local emission source component of PM_{2.5}, and it should be considered a target for control measures to mitigate PM_{2.5} levels.

3.8 Temporal Variations of Char-EC and Soot-EC

According to previous studies, EC is subdivided into two classes: char-EC and soot-EC (Han *et al.*, 2010; Han *et al.*, 2009; Han *et al.*, 2007). Char-EC and soot-EC are derived from EC1-PyC, and EC2+EC3, respectively. Char-EC is defined as solid graphitic carbon produced by incomplete combustion of organic substances, and it is mainly emitted from biomass and coal combustion. Soot-EC is defined as carbonaceous particles that formed through the high temperature condensation of hot gases emanating from solid and liquid fuels during combustion, and is considered to be present largely in vehicle emissions (Han *et al.*, 2010; Han *et al.*, 2009). Studies on char-EC and soot-EC concentrations are still limited in Japan and it would be valuable to determine and analyze the data of these compounds on a long-term basis.

The temporal variations of char-EC and soot-EC are demonstrated in Fig. 9. Their average concentrations were 0.60 µg/m³ and 0.69 µg/m³, for char-EC and soot-EC, respectively, accounting for 42.7% and 57.3% of the overall mean concentration of EC, respectively. Char- and soot-EC showed different seasonal patterns: the former tended to show higher concentrations from late autumn (November) to winter (February) and relatively lower concentrations through spring (April) and summer (September). The latter exhibited exactly the opposite results.

Using the char-EC/soot-EC ratio as an indicator to

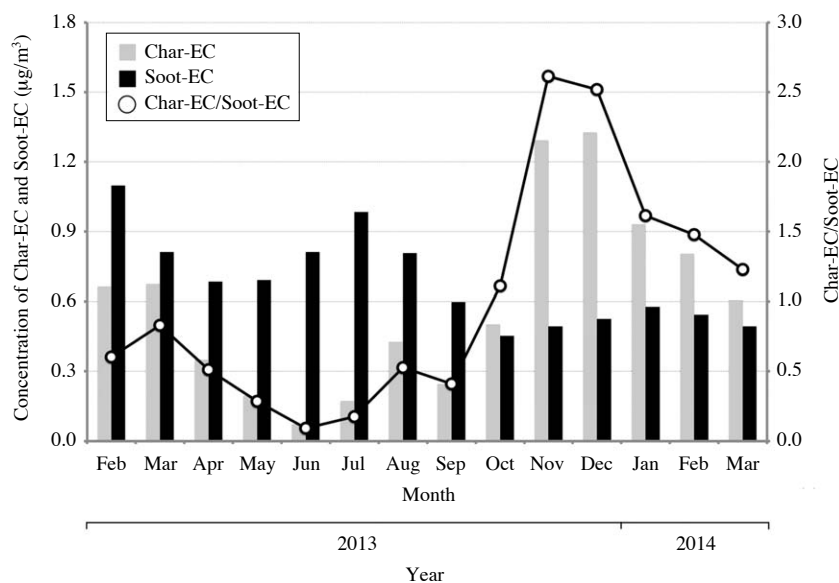


Fig. 9. Temporal variations of char-EC, soot-EC and char-EC/soot-EC

identify source has been suggested elsewhere (Han *et al.*, 2010; Chen *et al.*, 2007). Different monthly values of char-EC/soot-EC are presented in Fig. 9. Clear temporal variation was seen in char-EC/soot-EC, with the highest value of 2.7 in late autumn (November), and lowest value of 0.07 in summer (June). Generally speaking, motor vehicle emissions have a char-EC/soot-EC ratio of lower than 1.0. On the other hand, burning biomass by smouldering at low temperatures results in high char-EC/soot-EC ratios (Han *et al.*, 2010; Chen *et al.*, 2007). Char-EC/soot-EC ratios were lower than 1.0 between February 2013 and September 2013, and considering the index from previous reports, motor vehicles were one of the contributing factors. From October 2013 to March 2014 the value of char-EC/soot-EC exceeded 1.0, indicating the possibility that biomass burning and coal combustion were one of the main contributors to PM_{2.5} during these periods. Furthermore, over time, char-EC/soot-EC and WSOC showed similar patterns, as is evident in Figs. 8 and 9. This led us to the conclusion that burning biomass makes a greater contribution to PM_{2.5} than coal combustion. Consequently, increasing carbon fractions (Fig. 7) in autumn and winter could be attributed to burning biomass.

4. CONCLUSIONS

This study was designed to survey the seasonal variation of PM_{2.5} chemical components emitted mainly from local sources. PM_{2.5} was sampled on quartz fil-

ter for 24-hour periods using a low volume air sampler from 8 February 2013 to 31 March 2014. The sampler was placed on the roof floor of the Chiba Prefectural Environmental Research Center and samples collected daily. A total of 373 valid samples were used in this study. Measurements of ionic components (Na⁺, NH₄⁺, Ca²⁺, Mg²⁺, K⁺, Cl⁻, NO₃⁻ and SO₄²⁻), carbonaceous components; organic carbon (OC) and elemental carbon (EC), and water-soluble organic carbon (WSOC) were carried out. Secondary organic carbon (SOC) based on the EC tracer method, and char-EC and soot-EC were also calculated from the analytical results. Data obtained were interpreted in terms of the properties of temporal variation.

From the analytical determination, ionic components, OC and EC accounted for 45.3%, 19.7%, and 8.0% respectively of the overall mean value of PM_{2.5} mass concentration. Among the ionic components, the sum of the SO₄²⁻, NO₃⁻ and NH₄⁺ concentrations accounted for 93.2% of the total ionic components. The chemical components, SO₄²⁻, NO₃⁻, NH₄⁺, OC and EC constituted approximately 70% of mean PM_{2.5} mass concentration, meaning that these five species were the major chemical components.

NO₃⁻ showed a unique seasonal distribution attributable to temperature- and absolute humidity dependence, separating it from other major chemical components. We estimated that a temperature of ~14°C, and relative humidity of ~7 g/m³ were the critical points for the reversible reaction of NH₄NO₃ (p) = NH₃ (g) + HNO₃ (g).

Seasonal fluctuations of EC and OC were clearly

observed, showing that autumn-winter concentrations were relatively higher than those recorded in spring-summer time. This result could be attributed to the impact of burning biomass, since WSOC and char-EC/soot-EC showed similar patterns during corresponding periods. Based on monthly measurements of WSOC/OC, a maximum ratio of 83% was obtained in August (summer). WSOC and estimated SOC, derived from the EC tracer method, showed good correlation ($R=0.77$) in summer, thus, the high prevalence of WSOC in summer is mainly due to the formation of SOC by photochemical reactions.

Major chemical components of $PM_{2.5}$ obtained in Chiba Prefecture, Japan, were interpreted in terms of monthly and seasonal profiles. Different approaches were taken to identify factors that possibly contribute to $PM_{2.5}$. Interestingly, many of these factors fluctuated depending on different time periods. This type of research could provide insight and further understanding into the chemical profiles of pollutants, which could significantly aid abatement strategies in the process of air quality management.

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