Source analysis of non-fossil carbon in atmospheric aerosols collected at urban sites in Nagoya using carbon isotopes

（名古屋市において採取された都市大気
エアロゾル中非化石燃料起源炭素の
炭素同位体を用いた発生源解析）

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Abstract

Atmospheric aerosols including particular carbonaceous aerosols are paid attention to as one of the air pollutants causing harmful damages on humans such as circulatory, respiratory, infectious and allergic diseases. They have not only optical properties of scattering and absorbing of solar and terrestrial radiations but also play a role as nuclei of ice formation and cloud condensation. Carbonaceous aerosols account for the significant portion of tropospheric aerosols. The concentrations of specific carbonaceous fractions such as organic, elemental, and water-soluble carbon, vary depending on the locations as urban, rural, and mountain areas. The sources and formation mechanism of carbonaceous aerosols are so diverse that the identification of the sources and origins of carbonaceous aerosols are not easy task. To protect our health from those pollutants, it is very important to clarify where highly concentrated carbonaceous aerosols are emitted from and how they are generated.

There are two sources of carbonaceous aerosols: fossil and non-fossil sources. The understanding of relative contributions between them leads to decrease the concentration of carbonaceous aerosols. Radiocarbon (^{14}C) contained in carbonaceous aerosols is a potential tracer to investigate the source of carbonaceous aerosols. The contribution of fossil and non-fossil carbonaceous aerosols should be distinguished with ^{14}C and specific organic component of carbonaceous aerosols

The aim of this study is to reveal and understand the sources of non-fossil carbonaceous aerosols collected at Nagoya, based on the analyses of ^{14}C concentration and chemical components of aerosols. Firstly, the

influence of carbonaceous aerosols emitted by the Siberian forest fire on organic carbon (OC) concentration in $PM_{2.5}$ collected at Nagoya were discussed. In May 2003, higher concentrations of OC in $PM_{2.5}$ were observed in Nagoya. ^{14}C concentrations in total carbon (TC) showed higher values from May to early June (47.0–68.4 pMC, n=3) than those in other periods during April 2003 to March 2004 (28.3–41.9 pMC, n=23). The OC/elemental carbon (EC) ratios were also significantly higher from May to early June (1.3–2.0, n=3) than the ones in other periods (0.79–1.3, n = 23). In addition, OC concentrations from May to early June (5.8–9.4 $\mu g/m^3$, n=3) were typically high, compared to the average of all samples (4.9 $\pm$ 2.4 $\mu g/m^3$). These results suggest that the abundant OC fraction from May to early June in Nagoya consisted predominantly of non-fossil carbon (non-FC). Moreover, backward air mass trajectories from this time frame indicate that the air mass to Nagoya likely passed through East Siberia where fire events were prevalent. In contrast, the backward trajectories show that the air mass after early June did not originate mainly from Siberia, and correspondingly, the ^{14}C and OC concentrations showed lower values than those from May to early June. It is concluded that non-FC originating from the forest fire in East Siberia was transported to Nagoya. The highly concentrated OC and ^{14}C of $PM_{2.5}$ at Nagoya were induced by the East Siberia fire events.

In the second, to investigate seasonal variations and sources of the carbonaceous compounds in aerosols emitted from biomass burning and vegetation in urban site, we measured OC, EC and ^{14}C, and concentration of levoglucosan (proposed as "an unequivocal biomass burning tracer") in total

suspended particulate matter collected at Nagoya. Higher ^{14}C concentrations were observed in the intervals from spring (56.4 pMC) to summer–early fall (57.4 pMC) than during late fall–winter (47.1 pMC). In particular, ^{14}C concentration in April was controlled strongly by the amount of pollens contained in the aerosols, and it showed the highest ^{14}C value of about 70 pMC. Levoglucosan concentrations indicated clear seasonal variations: the contents from late fall–winter were higher than those in other seasons, similar to other observations in Japan (Kumagai *et al*., 2010; Ueno *et al*., 2012). The levoglucosan concentrations showed a strong correlation with the concentration of non-fossil carbon in total carbon (TC_{nf}) estimated from ^{14}C of TC from the early fall–winter. Furthermore, TC_{nf} was roughly divided into two origins: biomass burning (TC_{bb}) and biogenic carbon except for biomass burning (TC_{bio}). The contributions of TC_{bb} to TC_{nf} and TC in the late fall–winter showed the highest value. Meanwhile, TC_{bio} concentration was higher than TC_{bb} concentration in all seasons, and the main sources of TC_{bio} were considered to be dependent on the season: pollens in spring and biogenic secondary organic aerosols in summer. Our results reveal that the relative contributions of TC_{bb} and TC_{bio} to the highly-concentrated TC, were significantly different in each season.

These results clarify the sources of the non-fossil carbonaceous aerosols at Nagoya in the urban site and suggest that the carbonaceous aerosols long-transported from Siberia and emitted from vicinity, influenced on seasonal and eventic variations of concentrations in carbonaceous aerosols at Nagoya.

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List of abbreviations

AERC: Aichi Environmental Research Center

ASHC: Aichi Shinshiro Health Center-Shitara Branch

BSOA: biogenic secondary organic aerosol

BVOC: biogenic volatile organic compound

CC: carbonate carbon

CMB: chemical mass balance

EC: elemental carbon

$EC_{(Source)}$: biomass burning emission data of EC in 96 species from Sullivan *et al.* (2008)

FC: fossil carbon

FIRMS: Fire Information for Resource Management System

FVOC: fossil volatile organic compound

HC: periods of high concentrations of TC

HYSPLIT: Hybrid Single-Particle Lagrangian Integrated Trajectory

IARC: International Agency for Research on Cancer

LC: periods of low concentrations of TC

$Lev_{(Source)}$: biomass burning emission data of levoglucosan in 96 species referred from Sullivan *et al.* (2008)

MODIS: Moderate-Resolution Imaging Spectroradiometer

non-FC: non-Fossil carbon

OA: organic aerosol

OC: organic carbon

$OC(TSP)/OC(PM_{2.5})$: OC in TSP/OC in $PM_{2.5}$

$OC_{(Source)}$: biomass burning emission data of OC in 96 species referred from

Sullivan *et al.* (2008)

OM: organic matter

PM: particulate matter

pMC: percent modern carbon

PMF: positive matrix factorization

PM$_{2.5}$: particulate matter of an aerodynamic diameter smaller than 2.5 μm

POA: primary organic aerosol

PBAP: primary biological aerosol particles

PTFE: polytetrafluoroethylene

SOA: secondary organic aerosol

SPRINTARS: Spectral Radiation–Transport Model for Aerosol Species

TC: total carbon

TC$_f$: fossil carbon in TC

TC$_{nf}$: non-Fossil carbon in TC

TC$_{bb}$: cabon emitted from biomass burning in TC

TC$_{bio}$: non-Fossil carbon subtracted TC$_{bb}$ in TC

TC$_{(Source)}$: biomass burning emission data of TC in 96 species calculated from Sullivan *et al.* (2008)

TOR: thermal/optical reflectance

TSP: total suspended particulate matter

VOC: volatile organic compound

WISOC: water-insoluble organic carbon

WSOC: water-soluble organic carbon

^{14}C: radiocarbon

1. Introduction

1.1. Atmospheric aerosols

Atmospheric aerosols defined as a suspension of liquid or solid particles are paid attention to as one of the air pollutants causing harmful damages on humans such as causing circulatory, respiratory, infectious and allergic diseases (Pöschl, 2005). Recently, the International Agency for Research on Cancer (IARC) concluded that outdoor air pollution and particulate matter (PM) such as $PM_{2.5}$ (an aerodynamic diameter smaller than 2.5 µm) are carcinogenic to humans (IARC, 2013).

They also possess some chemical properties such as both scattering and absorbing of solar and terrestrial radiations (Pöschl, 2005). Further, atmospheric aerosols play a role as ice and cloud condensation nuclei. Atmospheric aerosols can also influence on the global radiation balance both directly and indirectly (Ackerman *et al.*, 2000; Ramanathan *et al.*, 2001).

Atmospheric aerosols are emitted directly and indirectly from natural and anthropogenic sources. Particles are directly emitted by incomplete combustion of both fossil fuel and biomass/biofuel, traffic-related suspension of road, soil, mineral dust, sea spray, and biological materials such as pollens, plant fragments and microorganisms. Those particles emitted directly are defined as primary aerosol particle. Low volatility particles generated from the reactions of the gaseous precursors such as volatile organic compounds (VOC), sulfur oxide (SO_x) and nitrogen oxide (NO_x) in the atmosphere are defined as secondary aerosol particle. Atmospheric aerosols consist of various sized particles and

contain variety of chemical compounds. The concentrations of atmospheric aerosols vary in the range of about $1-100$ µg/m^3 (Van Dingenen *et al.*, 2004; Krejci *et al.*, 2005; Raes *et al.*, 2000; Williams *et al.*, 2002). Atmospheric aerosol is a complex mixture of substances such as sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), metals and carbonaceous components such as organic carbon (OC) and elemental carbon (EC) (e.g. Shi *et al.*, 2011). The concentrations of these chemical components show the different values at the times, regions, meteorological conditions, and particle size fractions (IPCC, 2013). To evaluate the influence of aerosols on human health and climate, the understanding of the components and characterization in those particles and the emission sources are extremely important.

1.2. Carbonaceous aerosols

Carbonaceous aerosols account for the significant portion (20–90%) of tropospheric aerosols (Kanakidou *et al.*, 2005). Total carbon (TC) is traditionally divided to the carbon fractions such as OC and EC using thermal separating methods. Based on the solubility in water, OC is classified as water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WISOC). It was reported that the carbonaceous aerosol in PM$_{2.5}$ has more or less different characteristics in concentration and abundance of each component at the urban, rural, and mountain areas in central Europe (Pöschl, 2005). The EC/TC ratios in PM$_{2.5}$ were different at the different urban sites such as Tokyo (0.35–0.44, Ueno *et al.*, 2012) and Nagoya (0.42, Yamagami *et al.*, 2011), and at rural site in Maebashi (0.28, Kumagai *et al.*, 2009) in Japan, as observed in Europe. Because EC is

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directly emitted from fossil fuels and/or biomass burning, these observations demonstrate that the impact of incomplete combustion such as diesel, other fossil fuel and biomass burning on the concentration and composition of carbonaceous aerosols is larger in urban area than rural area. Organic aerosol (OA) components can be classified as primary OA (POA) or secondary OA (SOA) which is related to their emission sources. POA originates from combustion such as fossil fuel and biomass/biofuel as EC, and from biological materials. SOA components are formed by reactions and condensation of both fossil VOC (FVOC) and biogenic VOC (BVOC) in the atmosphere. The composition of carbonaceous aerosol is governed by local sources, meteorological conditions, location, season, and transport from other regions. Recent studies suggest that SOA appears to be dominated by oxidation of BVOCs on a global scale (Kanakidou *et al*., 2005). Because the sources and formation mechanisms of carbonaceous aerosols are so various that the estimation of the sources of carbonaceous aerosol is quite difficult. Studies of carbonaceous aerosol are still insufficient.

1.3. Study of carbonaceous aerosol sources

To determine the source of carbonaceous aerosols, molecular tracers and inorganic ions indicating primary emissions and secondary aerosol formation have been used (e.g., Fu *et al*., 2010; Haddad *et al*., 2011a; Haddad *et al*., 2011b: Hallquist *et al*., 2009; Miyazaki *et al*., 2012). For example, levoglucosan ($C_6H_{10}O_5$), an organic compound with six carbon

ring structure formed from the pyrolysis of carbohydrates such as starch and cellulose, is a potential tracer to identify the source of aerosols (Puxbaum *et al.*, 2007). Kleindienst *et al.* (2007) measured organic compounds such as pinic acid, 3-hydroxyglutaric acid and 2-methyltetrol formed from BVOCs, and estimated the contribution of SOA generated from BVOC. However, it is argued that the approaches using organic molecular tracers are sometimes restricted due to the short life time of the tracers and the variability of those emission factors in the atmosphere (Hoffmann *et al.*, 2010; May *et al.*, 2012; Xie *et al.*, 2014).

Source apportionments of atmospheric aerosols including organic aerosols have been conducted based on the source-receptor techniques focused on organic molecular tracer as mentioned above. Source-receptor techniques like the chemical mass balance (CMB) and the positive matrix factorization (PMF) have also been used to identify carbonaceous aerosol sources and to quantify the contribution of each source (Bressi *et al.*, 2014, Jaeckels *et al.*, 2007; Miyazaki *et al.*, 2012; Schauer *et al.*, 1996; Stone *et al.*, 2008). Bressi *et al.* (2014) identified seven sources at urban background site in Paris: $PM_{2.5}$ (biomass burning, road traffics, marine aerosols, heavy oil combustion, metal industry, ammonium nitrate and ammonium sulfate). They determined the relative contribution of each source to $PM_{2.5}$. Road traffics and biomass burning were considered as important sources of POA, contributed by 14% and 12% to $PM_{2.5}$, respectively. Miyazaki *et al.* (2012) estimated five sources of WSOC using PMF with organic compounds in deciduous forest in northern Japan. They indicated that biogenic SOAs (BSOAs) accounted for about 40% and were the major source in WSOC.

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The source of BSOA was divided into two sources: α/β-pinene and isoprene. Moreover, it was estimated that primary biological aerosol particles (PBAPs) such as pollens have a contribution of about 57 % to the WSOC in early summer. They demonstrated the seasonal changes of biogenic aerosol sources of WSOC. Recently, aerosol mass spectrometer has been used to observe chemical compositions at a high time resolution. The mass spectra has been used with PMF to study the sources of OA (hydrocarbon-like (HOA), biomass burning (BBOA), cooking (COA), semi-volatile oxygenated (SV-OOA) and low volatile oxygenated (LV-OOA)) and these contributions to OA (Crippa *et al.*, 2014; Lanz *et al.*, 2007). Lately, the comparison among the results from different source receptor methods and chemical transport models has been conducted and used jointly those calculated results to elucidate the compositions and origins of $PM_{2.5}$ (Bove *et al.*, 2014).

1.4. Estimating of carbonaceous aerosols using radiocarbon

Radiocarbon (^{14}C) is a tracer that can be used to obtain source information on carbonaceous components in PM (Glasius *et al.*, 2011; Schichtel *et al.*, 2008; Szidat *et al.*, 2004; 2009a). ^{14}C atoms contained in the carbon originated from fossil fuel sources have been abolished completely according to its radioactive decay (half-life of 5370 years), while carbon in most living organisms has the ^{14}C content similar to that of carbon dioxide in the atmosphere. Therefore, ^{14}C allows distinguishing between modern and fossil sources. Fossil carbon (FC) in atmospheric

aerosols is emitted from fossil fuel combustion and is generated by the reactions of fossil-derived VOCs. Contemporary carbonaceous components originate from biomass burning, cooking, emissions of biological particles such as pollens and fungal spores, and the reactions of BVOCs. They are classified as non-fossil carbon (non-FC).

The ^{14}C analysis of carbonaceous aerosols has been conducted in the world, especially in America, Europe and Asia (Heal, 2014). ^{14}C analysis of aerosols was first applied to investigate the source of the TC content (Bench *et al.*, 2007, Fushimi *et al.*, 2011, Glasius *et al.*, 2011; Schichtel *et al.*, 2008; Shibata *et al.*, 2004; Takahashi *et al.*, 2007; Yang *et al.*, 2005). The contents of non-FC in TC were reported in Arizona (0.49–0.56, Bench *et al.*, 2007), Beijing (0.33–0.48, Yang *et al.*, 2005) and Tokyo (0.3–0.5, Takahashi *et al.*, 2007). These reported that more than 30% in TC originated from non-FC in the urban sites where a large amount of fossil fuels are consumed. The results indicated necessity of evaluating the source of non-FC. More recently, ^{14}C analysis has been applied to various carbonaceous fractions such as OC, EC, and WSOC (Currie *et al.*, 2002; Heal 2014; Pavuluri *et al.*, 2013; Szidat *et al.*, 2004; Wozniak *et al.*, 2012; Zhang *et al.*, 2012; Zotter *et al.*, 2014). Zhang *et al.* (2012) demonstrated that the ^{14}C concentrations in individual carbonaceous fractions such as WSOC, WISOC, and EC have significantly different values from each other.

To clarify the emission sources of carbonaceous aerosols, source identification and apportionment of non-FC and FC have been conducted based on the analysis of ^{14}C and organic molecular tracer, and by aerosol mass spectrometry (Gelencsér *et al.*, 2007; Haddad *et al.*, 2011a; Huang *et*

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al., 2014; Szidat *et al.*, 2006, 2009b; Yttri *et al.*, 2011a, 2011b; Zhang *et al.*, 2015). Szidat *et al.* (2006) quantitatively estimated the contributions of three sources (biomass burning, fossil fuel combustion, and natural biogenic emissions) of carbonaceous aerosols using levoglucosan and the ^{14}C concentrations of OC, WISOC and EC. They indicated that ^{14}C in different carbon fractions helped an estimation of the major sources of carbonaceous aerosols. Szidat *et al.* (2009b) analyzed the ^{14}C concentrations and levoglucosan of carbonaceous aerosols. They demonstrated that EC originated from wood burning was three times higher at the rural site than at the urban site in Sweden. These results also indicated that the carbonaceous aerosols in the urban site were more influenced by the fossil EC emissions than those in the rural site. Huang *et al.* (2014) suggested that the emissions of not only primary aerosol but also secondary aerosol precursors (VOCs in particular) should be controlled. Zhang *et al.* (2015) measured the ^{14}C concentrations of both OC and EC fractions, and indicated that non-FC accounted for a half of both TC and OC at four cities (Xi'an, Beijing, Shanghai and Guangzhou) in China. They also estimated that 40−65% of non-FC was emitted from biomass burning using the data of both levoglucosan concentration and source information of biomass burning. These results suggested that non-FC is prominent in carbonaceous aerosols and the emission from biomass burning makes an important contribution. Further, they reported that a part of non-FC, except for the contribution from biomass burning, increased in the period of higher concentration of $PM_{2.5}$. It is apparent that ^{14}C and organic molecular tracer such as levoglucosan give the detail source information of carbonaceous aerosols.

1.5. Source analysis of carbonaceous aerosols in Japan

The Japanese archipelago is located in the east of China that is emitting huge amounts of aerosols. Air pollutants transported from China have been reported and they are a serious problem in Japan (Hidemori *et al.*, 2014; Kaneyasu *et al.*, 2014; Mukai *et al.*, 1990; Takami *et al.*, 2007). Moreover, smoke originated from the Siberian forest fires affected regional air quality in Japan (Jeong *et al.*, 2008; Kaneyasu *et al.*, 2007; Murayama *et al.*, 2004). Carbonaceous aerosols from China and Siberian forest with a long-range transport have been widely observed in the Japanese archipelago, such as Fukuoka (Kaneyasu *et al.*, 2014), Wajima (Tang *et al.*, 2005), Akita (Kawashima and Haneishi, 2012), and Sapporo (Agarwal *et al.*, 2010), and the top of Mt. Fuji (Kaneyasu *et al.*, 2007). However, the emission sources of carbonaceous aerosols at the central and east urban sites in Japan have not been completely explained yet.

Air pollutants are not only transported from other countries but also emitted from domestic regions. Iijima *et al.* (2008) estimated using PMF that diesel exhaust was the most significant source of air pollutants (70% contribution to PM) in Tokyo. Kumagai *et al.* (2010) estimated that OC emitted from biomass burning was 47% of OC in winter in Maebashi at the suburban site in Japan. Moreover, OC originated from secondary formation was estimated to be 75% of OC in summer in the same site. ^{14}C suggested that fossil sources contributed remarkably to the enhanced concentration of SOA at daytime in Kisai and Maebashi in summer (Fushimi *et al.*, 2011).

Minoura *et al.* (2012) demonstrated using ^{14}C data that the relative contribution of non-FC to TC was higher in winter than in summer, and accounted for 48% of TC in winter even at Kudan of central part in Tokyo. Although the understanding of relative contributions of fossil and non-fossil sources to carbonaceous aerosols is very important to decrease the concentration of PM, the source apportionment is still ambiguous. Especially, both the emission sources and the mechanisms of causing high concentrations of carbonaceous aerosols are poorly understood in Japan.

1.6. Research objectives

The objectives of this study are to understand the sources of urban carbonaceous aerosols at Nagoya based on the analyses of ^{14}C concentration and chemical components in PM. In the first, the influence of carbonaceous aerosols emitted from forest fire in Siberia on OC in $PM_{2.5}$ at Nagoya is discussed. This research assessed the relationship between the highly concentrated TC and non-FC transported from Siberia. In the second, seasonal variations and sources of carbonaceous aerosols collected at Nagoya are discussed. The source of urban carbonaceous aerosols with higher concentration of TC in Nagoya is also discussed on the basis of the analysis of ^{14}C and levoglucosan.

2. Influence of carbonaceous aerosol originating from the 2003 Siberian forest fire on organic carbon in PM$_{2.5}$ in Nagoya

2.1. Introduction

Among emission sources for carbonaceous aerosols, VOC, ozone and CO$_2$, it is known that forest fires comprise a significant of global emissions (Crutzen *et al.*, 1979). The fire-related emission has a significant linkage with the climatic system because of their influence on radiative forcing (Jeong *et al.*, 2008). Moreover, aerosols originating from forest fires have sometimes led to serious declines in the air quality of the East Asian countries and North America (Agarwal *et al*., 2010; Jaffe *et al*., 2004). Siberian forest fires, in particular, are of concern in the northern parts of East Asian countries. In fact, a number of field studies have been conducted in oceanic (Ding *et al.*, 2013), mountainous (Kaneyasu *et al.*, 2007), and remote (Genualdi *et al.*, 2009) environments to clarify the transport and effects of aerosols after release from biomass burning. To interpret the highly-concentrated OC at the monitoring sites where can be affected by Siberian forest fires, Agarwal *et al.* (2010) and Ding *et al.* (2013) used organic molecular tracers of biomass burning, such as levoglucosan and secondary reaction products of VOC (dicarboxylic acids and 2-methylglyceric acid). However, the use of ^{14}C as a tracer of aerosols originated by forest fires, which has been transported over long distances and affects the atmospheric air quality in urban environments, has not been reported in the East Asia region. To investigate the influence of Siberian

forest fires on carbonaceous aerosols transported over long distances to Nagoya, a representative metropolitan area in Japan, ^{14}C concentrations in TC of PM$_{2.5}$ were measured.

In Nagoya, OC concentrations showed extraordinarily high values in May 2003 compared to those in other seasons (Yamagami *et al.*, 2011). This period corresponds to the occurrence of the largest Siberian forest fire in the late 20th century (Nedelec *et al.*, 2005). The smoke from the fires affected regional air quality not only over East Asian countries such as Korea (Lee *et al.*, 2005) and Japan (Jeong *et al.*, 2008; Kaneyasu *et al.*, 2007; Murayama *et al.*, 2004), but also along the west coast of North America (Bertschi and Jaffe, 2005; Jaffe *et al.*, 2004). This section discusses the behavior of the ^{14}C tracer of Nagoya aerosol samples and uses a backward trajectory analysis to confirm the source areas, thus demonstrating that carbonaceous aerosols transported over long distances from Siberian forest fire site can affect urban sites in Japan. Other possible causes for the increase in the non-FC content of PM$_{2.5}$ during this period are also discussed.

2.2. Methods
2.2.1. Sample collection

PM$_{2.5}$ was collected at Nagoya, a major city in the central part of Japan (latitude 35°18′N, longitude 136°91′E; Fig. 2.1). Nagoya has a population of more than 2,200,000. Samplings of PM$_{2.5}$ were conducted for 23.5 h using a low-volume air sampler (FRM-2000, R&P) from April 2003 to March 2004 at an urban site in Nagoya. Two PM$_{2.5}$ samples were collected in parallel, one onto polytetrafluoroethylene (PTFE) filters

(TK15-G3M, Pallflex) and the other onto quartz-fiber filters (2500QAT-UP, Pallflex); these samples were collected at a flow rate of 16.7 L min^{-1}. The quartz-fiber filters were pre-heated at 900°C for 3 h to remove residual carbon prior to sampling. The PTFE filters were conditioned in a constant temperature and humidity room (20 ± 0.5°C, 50 ± 3% relative humidity (RH)) for 24 h prior to weighing. Then, these samples were stored at -25°C in a freezer until further analyses.
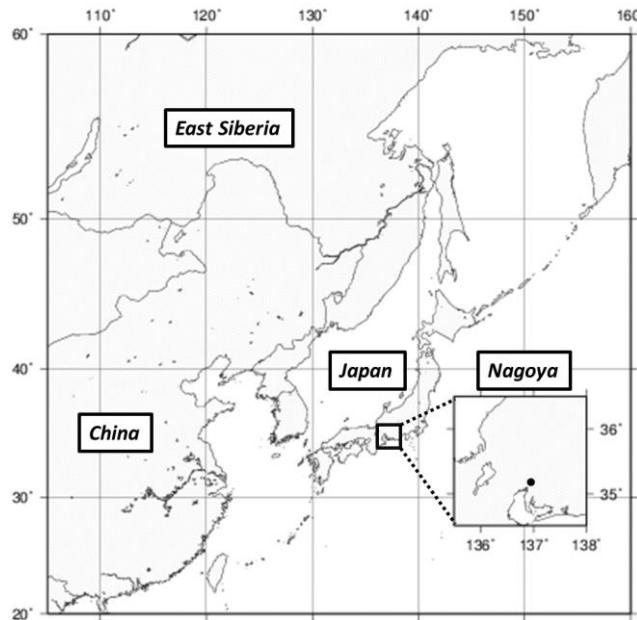
Fig. 2.1. Map showing the location of Nagoya, Japan (latitude 35°18 N, longitude 136°91 E).

2.2.2. Analysis of carbonaceous and ion components

A 1.5 cm^2 aliquot of the quartz filter with aerosol particles was inserted into an oven, and then, OC and EC were analyzed with a Sunset

Lab OC/EC Analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) protocol (Chow *et al.*, 2001). To extract ion species, the PTFE filter with aerosol particles was ultrasonically treated with Milli Q water. After the extraction, filter debris and suspended insoluble particles were removed using a PTFE filter. Anion species such as Cl^-, NO_3^-, and SO_4^{2-} and cation species such as Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} were determined by ion chromatography (Dionex, ICS-2000i and 4000i, respectively).

2.2.3. Radiocarbon analysis

For the analysis of ^{14}C concentrations of TC in $PM_{2.5}$, quartz-fiber filter samples from 3- to 11-day intervals were pooled following the sampling order shown in Table 2.1; at least 1 mg C is required for achieving ^{14}C measurements with a sufficient accuracy. As a result of pooling, 26 samples were prepared for the ^{14}C concentration analysis. An aliquot of the filter was inserted into a pre-heated quartz tube with CuO and Ag wires and then heated at 900°C for 6 h. The CO_2 in the resultant gas was separated and purified in a vacuum line, and then, it was reduced to graphite with H_2 on an iron powder catalyst in a sealed quartz tube at 650°C for 8 h. The ^{14}C concentration of the graphite was measured with a Tandetron accelerator mass spectrometry system (AMS, Model-4130, HVEE) at the Centre for Chronological Research, Nagoya University (Nakamura *et al.*, 2004). In this study, ^{14}C concentration is expressed as percent modern carbon (pMC), which is the fraction of the $^{14}C/^{12}C$ ratio in samples normalized to the ^{14}C

concentration reference from 1950 (Stuiver and Polach, 1977). ^{14}C concentrations for each sample were calculated using the following equation:

$$^{14}\text{C concentration (pMC)} = (^{14}\text{C}/^{12}\text{C})_{\text{sample}} \, / \, [(0.7459 \times (^{14}\text{C}/^{12}\text{C})_{\text{HOxII}}] \times 100$$

$$(2.1)$$

where HOxII is a *National Institute of Standards and Technology* (NIST) standard material (oxalic acid, SRM-4990C), which was used as ^{14}C concentration reference. Mass-fractionation in the carbon isotopes was corrected by the δ^{13}C value, which was measured by the AMS system with an error of less than $\pm$ 1‰; this error includes the effects from both machine instability and graphite production (Nakamura *et al.*, 2004). In addition, the ^{14}C decay of the reference material in the period from 1950 to the sampling date was also corrected (Stuiver and Polach, 1977).

Table 2.1.

Sampling dates, sample names of PM$_{2.5}$ samples collected at an urban site in Nagoya every 23.5 h for ^{14}C measurement (daily from April 2003 to March 2004).

	Date[a]	Sample name[b]
	22, 23, 24, 27, 30, April	Apr
	6, 7, 11, 12, 13 May	May-P1
	18, 20, 21, 22, 25, 27, 28, 29 May	May-P2
	2, 3, 4, 5 June	Jun-P1
	8, 9, 10, 11, 12, 15, 16, 17, 18 June	Jun-P2
	19, 22, 23, 24, 25, 26, 30 June	Jun-P3
	1, 2, 6, 7, 8, 14, 15, 16, 21 July	Jul
	5, 7, 11, 19, 20, 21 August	Aug-P1
	24, 25, 26, 27, 28, 31 August	Aug-P2
2003	1, 2, 3, 4, 7, 8 September	Sep-P1
	9, 10, 11, 15, 16, 17, 18, 21, 28 September	Sep-P2
	14, 15, 16, 19. 20, 21 October	Oct-P1
	22, 23, 27, 28, 29, 30 Octorber	Oct-P2
	3, 4, 5, 6 November	Nov-P1
	9, 10, 11, 12, 13, 16, 17 November	Nov-P2
	19, 20, 21, 25 November	Nov-P3
	26, 27, 28 November	Nov-P4
	1, 2, 3, 4, 7, 8, 9, 10, 11, 14, 15 December	Dec-P1
	16, 17, 18, 21, 23, 24 December	Dec-P2
	4, 5, 6, 7, 8, 11, 13, 19, 20 January	Jan-P1
	21, 22, 25, 26, 27, 28, 29 January	Jan-P2
	1, 2, 3, 4, 5, 8, 9, 12, 15, 16 February	Feb-P1
2004	17, 18, 19, 20, 23, 24, 25 February	Feb-P2
	1, 2, 3, 4, 8, 9, 10 March	Mar-P1
	11, 12, 15, 16, 17, 18 March	Mar-P2
	22, 23, 24, 25, 28, 31 March	Mar-P3

[a]Date indicates the day that sampling started. The start time was 9:30 a.m., and the stop time was 9:00 a.m. on the following day. These times are local.
[b]Sample name indicates the pooled groups for ^{14}C analysis.

2.2.4. Air mass trajectory analysis and SPRINTARS simulations

Five-day back air mass trajectories were calculated using the Hybrid

Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2003). The trajectories were calculated for every 12 h from the start time of each sampling at 1500 m height using the model vertical velocity with data from the National Centers for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR). In addition, it was referred to simulations of diffusion and transport of OM in East Asia that were calculated by the Spectral Radiation−Transport Model for Aerosol Species (SPRINTARS; Takemura *et al.*, 2000, 2002, 2005).

2.3. Results and discussion

2.3.1. Carbonaceous components in PM$_{2.5}$

The monthly averages of PM$_{2.5}$ mass, OC, EC, and SO$_4^{2-}$ concentrations in addition to the OC/EC ratios from April 2003 to March 2004 at Nagoya are shown in Table 2.2. Some data were previously reported by Yamagami *et al.* (2011). During the sampling periods, the most abundant component in PM$_{2.5}$ on average was SO$_4^{2-}$ of 5.7 ± 3.8 µg/m^3, followed by EC of 4.9 ± 2.6 µg/m^3 and OC of 4.9 ± 2.4 µg/m^3. Carbonaceous components comprised 37% of PM$_{2.5}$ in weight.

Table 2.2. Monthly average for PM$_{2.5}$, OC and EC in PM$_{2.5}$ (average $\pm$ S.D.) collected in Nagoya from April to December in 2003 and January to March in 2004.

Month	Sample number	PM$_{2.5}$ (μg/m^3)	OC (μg/m^3)	EC (μg/m^3)	OC/EC	SO$_4^{2-}$ (μg/m^3)
April	5	24.9 $\pm$ 7.8	4.38 $\pm$ 1.49	5.66 $\pm$ 4.27	1.10 $\pm$ 0.66	4.36 $\pm$ 0.97
May	13	34.0 $\pm$ 10.6	6.94 $\pm$ 3.34	4.77 $\pm$ 1.41	1.58 $\pm$ 0.89	8.44 $\pm$ 4.81
June	20	29.0 $\pm$ 9.1	5.36 $\pm$ 2.64	5.57 $\pm$ 1.68	1.05 $\pm$ 0.58	6.76 $\pm$ 3.49
July	9	24.0 $\pm$ 4.5	3.66 $\pm$ 0.47	4.50 $\pm$ 1.04	0.88 $\pm$ 0.31	6.37 $\pm$ 2.44
August	12	26.5 $\pm$ 10.9	4.43 $\pm$ 1.67	4.75 $\pm$ 1.27	0.94 $\pm$ 0.35	8.68 $\pm$ 4.43
September	15	24.0 $\pm$ 11.3	4.16 $\pm$ 1.70	4.52 $\pm$ 2.17	1.07 $\pm$ 0.44	8.16 $\pm$ 5.48
October	12	22.9 $\pm$ 12.8	4.68 $\pm$ 2.53	4.77 $\pm$ 2.86	1.10 $\pm$ 0.36	3.80 $\pm$ 2.14
November	18	29.5 $\pm$ 19.7	5.71 $\pm$ 3.15	6.82 $\pm$ 4.25	0.93 $\pm$ 0.27	4.70 $\pm$ 2.25
December	17	23.1 $\pm$ 16.6	4.88 $\pm$ 3.22	4.79 $\pm$ 3.41	1.09 $\pm$ 0.20	3.31 $\pm$ 2.12
January	16	17.1 $\pm$ 5.8	3.70 $\pm$ 1.05	3.33 $\pm$ 1.44	1.20 $\pm$ 0.25	3.15 $\pm$ 0.97
February	17	27.1 $\pm$ 15.0	4.90 $\pm$ 2.04	4.54 $\pm$ 2.41	1.20 $\pm$ 0.31	5.58 $\pm$ 3.98
March	19	26.0 $\pm$ 14.6	4.69 $\pm$ 1.91	4.50 $\pm$ 2.43	1.14 $\pm$ 0.27	5.31 $\pm$ 3.26
All	173	26.1 $\pm$ 13.3	4.86 $\pm$ 2.44	4.88 $\pm$ 2.62	1.11 $\pm$ 0.45	5.68 $\pm$ 3.78

2.3.2. ^{14}C concentration of TC in PM$_{2.5}$

The analysis of ^{14}C concentrations of TC in PM$_{2.5}$ was conducted with 3- to 11-day pooled samples (Table 2.1). Plots of the ^{14}C concentrations of pooled samples and TC concentrations of daily data from April 2003 to March 2004 are shown in Fig. 2.2(a): ^{14}C values are shown in Table 2.3. The ^{14}C concentrations from May-P1 to Jun-P1 showed as high as 47.0–68.4 pMC (n = 3), whereas the values stayed relatively low at 39.8 pMC in Apr and 28.3–41.9 pMC (n = 22) from Jun-P2 to Mar-P2. Plots of the OC and EC concentrations and OC/EC ratios of the pooled samples from April 2003 to March 2004 are shown in Fig. 2.2(b): the data are shown in Table 2.3. The OC/EC ratios of 1.3–2.0 (n = 3) from May-P1 to Jun-P1 were significantly higher than those in other periods, i.e. from Apr and Jun-P2 to

Mar-P2, the values were 0.79–1.3 (n = 23). In addition, the OC values from May-P1 to Jun-P1, were 5.8–9.4 µg/m^3 (n = 3), which were high values such as those in Nov-P1, P4 and Dec-P2 (7.0, 9.7, 6.7 µg/m^3 , respectively); all samples was 4.9 ± 2.4 µg/m^3 on average. The OC/TC ratios and ^{14}C concentrations from May-P1 to Jun-P1 were higher by 10% and 20 pMC or more, respectively, than the concentrations in Apr and from Jun-P2 to Mar-P3 (Table 2.4). These results indicate that the abundant OC fraction in Nagoya from May-P1 to Jun-P1 in 2003 increased ^{14}C concentration.
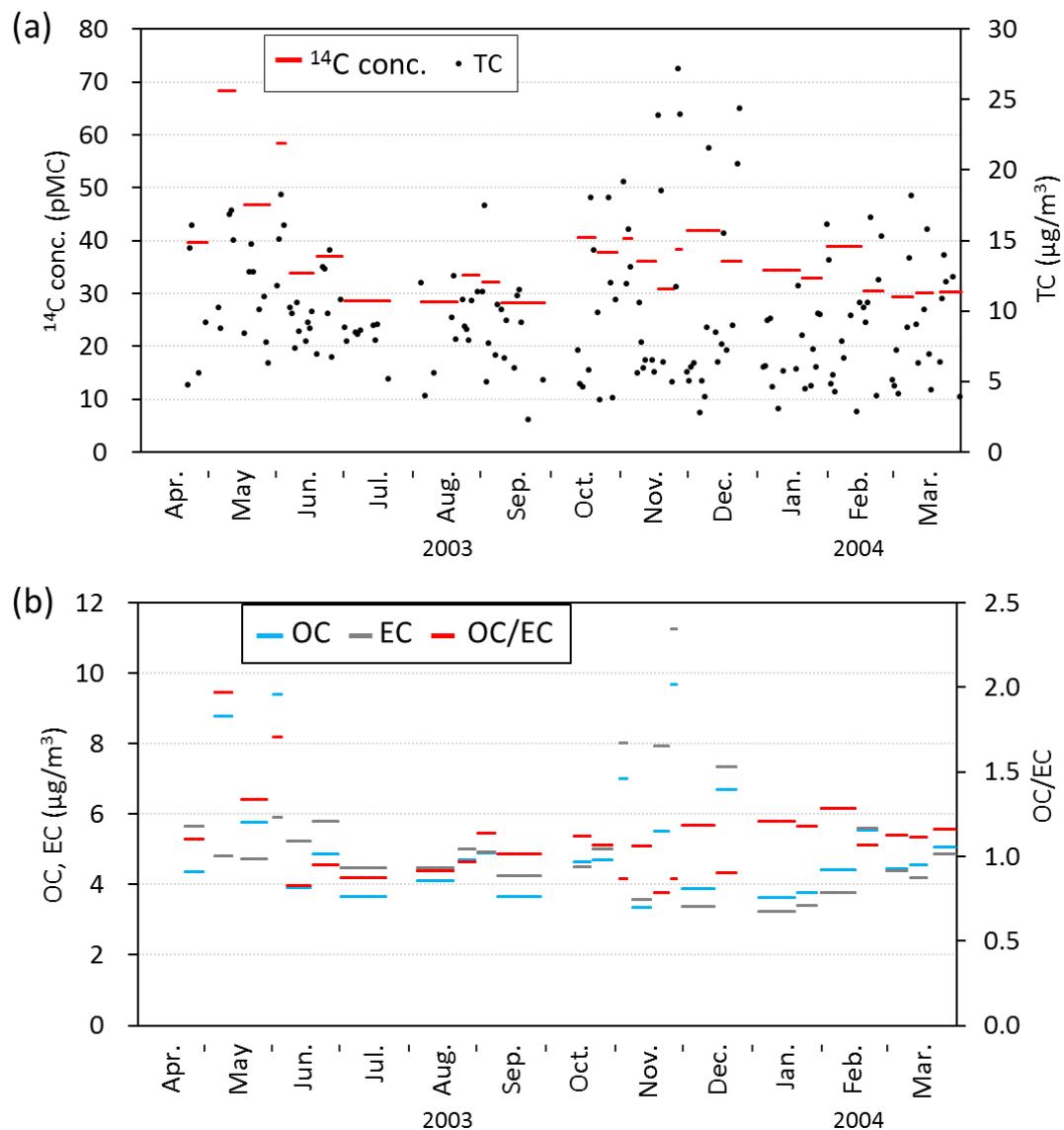
Fig. 2.2. (a) Plots of radiocarbon (^{14}C) concentrations for pooled samples and total carbon (TC) concentrations for daily data, and (b) organic carbon (OC) and elemental carbon (EC) concentrations and OC/EC ratios of pooled samples from April 2003 to March 2004.

Table 2.3.

Radiocarbon (^{14}C), organic carbon (OC), and elemental carbon (EC) concentrations in addition to OC/EC ratios of pooled samples (from April 2003 to March 2004). ^{14}C values represent value ± measurement error; values for the totals and other elements represent the average ± S.D.

Sample time	n[a]	^{14}C conc. (pMC)	OC (μg/m^3)	EC (μg/m^3)	OC/EC
Apr	5	39.8 ± 0.2	4.38 ± 1.49	5.66 ± 4.27	1.10 ± 0.66
May-P1	5	68.4 ± 0.2	8.80 ± 4.59	4.82 ± 0.80	1.97 ± 1.18
May-P2	8	47.0 ± 0.2	5.77 ± 1.74	4.73 ± 1.74	1.34 ± 0.62
Jun-P1	4	58.6 ± 0.2	9.40 ± 0.77	5.91 ± 1.96	1.71 ± 0.47
Jun-P2	9	33.9 ± 0.1	3.93 ± 1.42	5.24 ± 1.26	0.83 ± 0.44
Jun-P3	7	37.1 ± 0.2	4.89 ± 2.22	5.80 ± 2.15	0.95 ± 0.55
Jul	9	28.7 ± 0.1	3.66 ± 0.47	4.50 ± 1.04	0.88 ± 0.31
Aug-P1	6	28.5 ± 0.1	4.13 ± 1.99	4.49 ± 1.65	0.92 ± 0.36
Aug-P2	6	33.5 ± 0.1	4.72 ± 1.41	5.02 ± 0.80	0.97 ± 0.37
Sep-P1	6	32.3 ± 0.1	4.90 ± 2.06	4.93 ± 2.54	1.14 ± 0.47
Sep-P2	9	28.3 ± 0.2	3.67 ± 1.32	4.25 ± 2.00	1.02 ± 0.44
Oct-P1	6	40.6 ± 0.2	4.65 ± 2.79	4.52 ± 2.96	1.12 ± 0.42
Oct-P2	6	37.9 ± 0.2	4.71 ± 2.51	5.01 ± 3.02	1.07 ± 0.33
Nov-P1	4	40.4 ± 0.2	7.01 ± 1.89	8.02 ± 1.42	0.87 ± 0.12
Nov-P2	7	36.2 ± 0.2	3.36 ± 0.43	3.60 ± 1.62	1.06 ± 0.38
Nov-P3	4	30.9 ± 0.1	5.53 ± 3.51	7.94 ± 5.83	0.79 ± 0.20
Nov-P4	3	38.4 ± 0.2	9.69 ± 3.68	11.28 ± 4.49	0.87 ± 0.04
Dec-P1	11	41.9 ± 0.2	3.89 ± 2.61	3.40 ± 2.45	1.19 ± 0.18
Dec-P2	6	36.1 ± 0.2	6.70 ± 3.67	7.35 ± 3.62	0.90 ± 0.09
Jan-P1	9	34.5 ± 0.2	3.64 ± 1.17	3.26 ± 1.59	1.21 ± 0.24
Jan-P2	7	32.9 ± 0.2	3.77 ± 0.94	3.43 ± 1.33	1.18 ± 0.27
Feb-P1	10	38.9 ± 0.2	4.43 ± 2.10	3.78 ± 2.22	1.29 ± 0.33
Feb-P2	7	30.5 ± 0.1	5.56 ± 1.90	5.62 ± 2.39	1.07 ± 0.26
Mar-P1	7	29.4 ± 0.1	4.46 ± 2.17	4.41 ± 3.15	1.13 ± 0.20
Mar-P2	6	30.2 ± 0.1	4.57 ± 1.98	4.22 ± 2.07	1.11 ± 0.18
Mar-P3	6	30.4 ± 0.1	5.07 ± 1.83	4.89 ± 2.20	1.16 ± 0.42
Total	173	37.1 ± 9.2	4.86 ± 2.44	4.88 ± 2.62	1.11 ± 0.45

Table 2.4.

(a) Organic carbon/total carbon (OC/TC) ratios and (b) ^{14}C concentrations of pooled samples collected at Nagoya (from May-P1 to Jun-P1, and in Apr and from Jun-P2 to Mar-P3).

(a)

OC/TC	Sample number	Ave. ± S.D.	Range
May-P1 to Jun-P1	3	0.60 ± 0.05	0.55–0.65
Apr and Jun-P2 to Mar-P3	23	0.48 ± 0.03	0.41–0.54

(b)

^{14}C conc. (pMC)	Sample number	Ave. ± S.D.	Range
May-P1 to Jun-P1	3	58.0 ± 10.7	47.0–68.4
Apr and Jun-P2 to Mar-P3	23	34.4 ± 4.4	28.3–41.9

2.3.3. Estimation of the source region of PM$_{2.5}$ emissions with high ^{14}C and OC concentrations observed in Nagoya from May-P1 to Jun-P1

To estimate the source regions of PM$_{2.5}$ emissions with higher ^{14}C and OC concentrations from May-P1 to Jun-P1 in 2003, backward air mass trajectories were calculated. These trajectories were plotted with fire events from Apr to Jun-P2 2003 in Fig. 2.3(a)-1 to (a)-5; the trajectories are shown as lines and the fire locations are shown as red dots. The colors of the trajectories indicate the values of the OC/EC ratios that were measured for the respective PM$_{2.5}$ samples. The fire data, which were from the Moderate-Resolution Imaging Spectroradiometer (MODIS) Fire Information for Resource Management System (FIRMS), indicated that the fire events were prevalent in East Siberia during this time frame. The air mass containing PM$_{2.5}$ with high values of OC/EC ratios in Nagoya in May-P1

and Jun-P1 appeared to have passed through East Siberia (Fig. 2.3(a)). OC concentrations and OC/EC ratios of 11–13 µg/m^3 and 2.5–3.3, respectively, were higher on 11–13 May (May-P1 in Fig. 2.3(b)-2) when the air mass arrived at Nagoya through East Siberia (red trajectories in May-P1, Fig. 2.3(a)-2). However, OC concentrations were lower on 6 May (5.2 µg/m^3) and 7 May (2.7 µg/m^3), and likewise, OC/EC ratios were lower on 6 May (1.0) and 7 May (0.45) (May-P1 in Fig. 2.3(b)-2), at the time when the air mass appeared to have originated from the oceanic area (green trajectories in May-P1, Fig. 2.3(a)-2). The OC concentrations and the OC/EC ratios also showed higher values of 8.3–10 µg/m^3 and 1.2–2.3, respectively, in Jun-P1 (Fig. 2.3(b)-4) than those in other periods, similar to the results on 11–13 May. The backward trajectories showed that the air mass in Jun-P1 also passed through East Siberia (Jun-P1 in Fig. 2.3(a)-4). ^{14}C concentrations showed high values from May-P1 to Jun-P1, as shown in Section 2.3.2, whereas the ^{14}C concentrations in Jun-P2 showed lower values than those from May-P1 to Jun-P1 (Fig. 2.2(a), Table 2.3). The backward trajectories showed that the air mass in Jun-P2 did not originate from Siberia; instead, it came from other regions (Jun-P2 in Fig. 2.3(a)-5). Some studies have shown that large forest fires occurred in Siberia during the spring and summer of 2003 (e.g. Nedelec *et al.*, 2005), the smoke of which reached to Korea (Lee *et al.*, 2005), Japan (Jeong *et al.*, 2008; Kaneyasu *et al.*, 2007; Murayama *et al.*, 2004), and North America (Bertschi and Jaffe, 2005; Jaffe *et al.*, 2004). The OC/EC ratio of biomass burning emissions (Saarikoski *et al.*, 2008) is higher than that of diesel vehicle emissions (Pio *et al.*, 2011). From such data, it is concluded that the high values of ^{14}C in those periods were caused

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by non-FC transported from the Siberian which forest fires were occurred.

Secondary organic aerosols (SOA) can be formed via VOCs emitted from forest fires (Akagi *et al.*, 2013; Andreae and Merlet, 2001). Akagi *et al.* (2013) showed that not only organic and inorganic aerosols but also large amounts of VOCs are simultaneously emitted during the biomass burning. They also demonstrated that large amounts of terpene compounds were emitted by wildland fires. They concluded that the monoterpenes amounted to 0.4–27.9% of non-methane organic compounds and 21% of the organic aerosol mass in some South Carolina biomass burning plumes. From their results, it was concluded that the large forest fire in East Siberia released a huge amount of carbonaceous particles and VOCs. These gaseous organic compounds were likely transformed to particles through oxidative reactions during the long distance transport. Although forest fires were prevalent in East Siberia in Apr and portions of the air mass that arrived at Nagoya during the interval passed through East Siberia (Fig. 2.3(a)-1), the ^{14}C concentration during this period was lower than that from May-P1 to Jun-P1 (Fig. 2.2(a), Table 2.3). The OC/TC ratio in Apr was also lower than that from May-P1 to Jun-P1 and it was almost similar to that in Jun-P2, which is the period when the transportation of air masses originating from East Siberia was insignificant (Table 2.5).

To investigate the diffusion and transport of carbonaceous components emitted by the Siberian forest fire, transport of OM in East Asia was simulated using SPRINTARS (Fig. 2.4). The simulation showed that abundant OM from East Siberia was spread over East Asia including Japan, shown in the data set of May-P1 and Jun-P1. From the above analysis, it

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was concluded that high OC and ^{14}C concentrations observed in Nagoya from May-P1 to Jun-P1 were caused by non-FC that emitted by the huge forest fire in East Siberia and then transported over long distances to Japan.
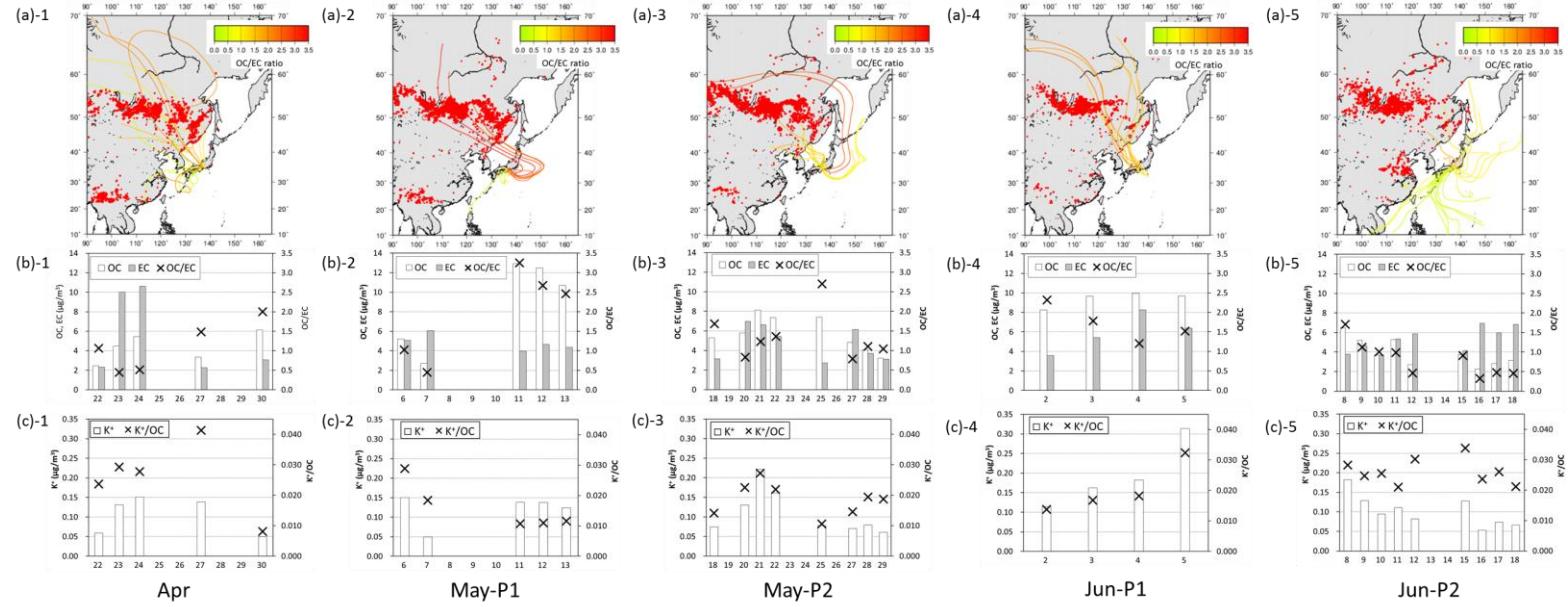
Fig. 2.3. (a) Fire occurred locations (red dots) and backward air mass trajectories (lines) from Apr to Jun-P2 in 2003. The data was obtained from the National Aeronautics and Space Administration (NASA) website (http://earthdata.nasa.gov/data/near-real-time-data/firms). Those data with possibilities ranging from 80% to 100% in the five separate periods of 17–30 April (Apr), 1–13 May (May-P1), 13–29 May (May-P2), 27 May–5 June (Jun-P1), and 3–18 June (Jun-P2) in 2003 were used in this study. Air mass back trajectories at 1500 m for five-day intervals from Apr to Jun-P2 were calculated every 12 h using the HYSPLIT model. The color of the trajectories indicates the value of organic carbon/elemental carbon (OC/EC) ratios in $PM_{2.5}$. (b) Variations of OC, EC, and OC/EC in $PM_{2.5}$ for daily samples from Apr to Jun-P2 in 2003. (c) Variations of K^+ and K^+/TC in $PM_{2.5}$ for daily samples from Apr to Jun-P2 in 2003.
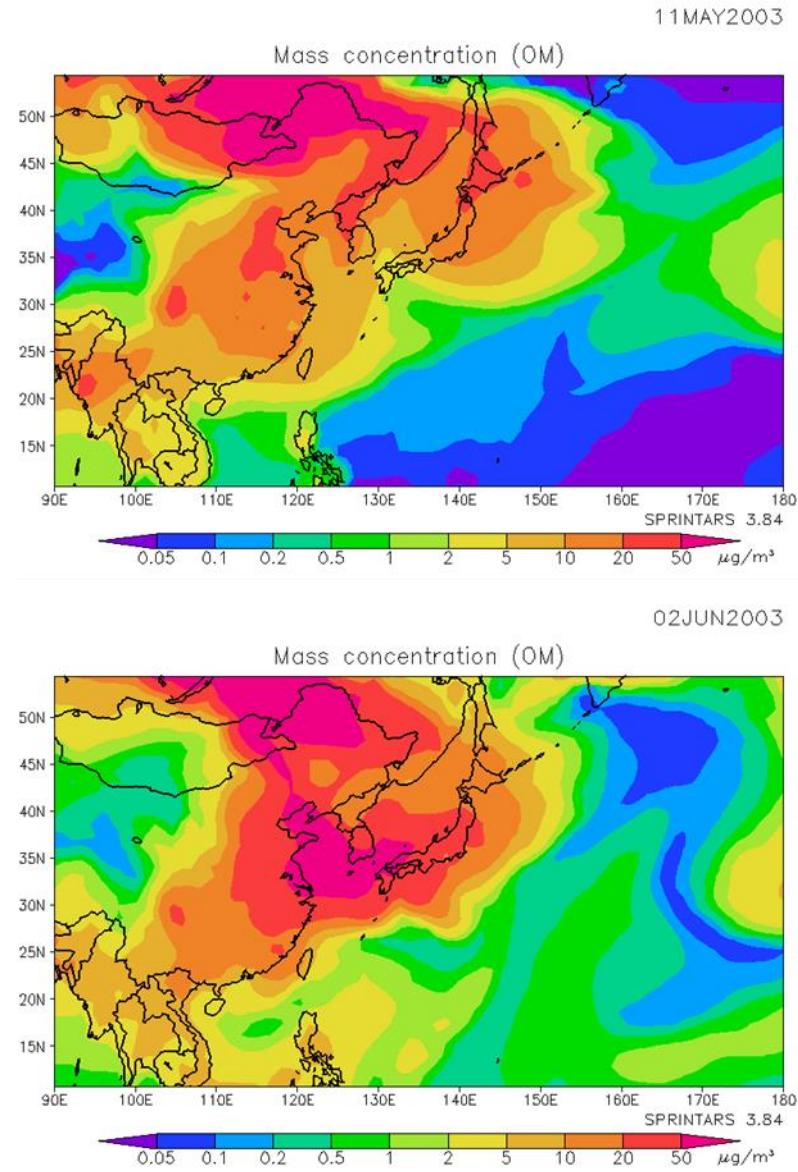
Fig. 2.4. Simulations of diffusion and transport of organic matter (OM) in East Asia. The OM concentrations were simulated by the SPRINTARS model on 11 May 2003 and 2 June 2003 when high organic carbon (OC) concentrations and OC/elemental carbon (EC) ratios were observed at Nagoya.

Table 2.5. Organic carbon/total carbon (OC/TC) ratios of pooled samples (from Apr to Jun-P2).

Month	OC/TC
Apr	0.44
May-P1	0.65
May-P2	0.55
Jun-P1	0.61
Jun-P2	0.43

2.3.4. Other possibilities for increasing ^{14}C values from May-P1 to Jun-P1

One of the factors that can cause increased ^{14}C concentrations is emissions from biomass burning, which can be traced by water-soluble potassium (K^+; Cachier *et al.*, 1995; Chow, 1995; Duan *et al.*, 2004). Duan *et al.* (2004) suggested that a high K^+/OC ratio indicated large emissions from biomass burning. K^+ is also considered as a tracer for aerosols emitted by forest fires in mid- and high-latitude regions (Hudson *et al.*, 2004; Owega *et al.*, 2004). The variations of K^+ concentrations and K^+/OC ratios in $PM_{2.5}$ for daily samples from Apr to Jun-P2 in 2003 are shown in Fig. 2.3(c)-1 to (c)-5. The observations of high OC concentrations and OC/EC ratios on 11−13 and 25 May and on 2 and 3 June did not coincide with high K^+ concentrations. Kaneyasu *et al.* (2007) demonstrated that dense smoke aerosols at the summit of Mt. Fuji, the highest mountain in Japan, in 2003 were transported from huge forest fire occurred sites in Siberia. They also suggested that the difference in K^+ concentrations between smoke and non-smoke days was not as prominent as that in black carbon (BC). They

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suggested that K^+ was not always an effective tracer for large-scale boreal forest fire emissions. In Japan, aerosol emissions from biomass burning were significant during the fall and winter in the Kanto areas (Kumagai *et al.*, 2010; Minoura *et al.*, 2012; Takahashi *et al.*, 2007). In fact, the correlation between OC and K^+ from Oct-P1 to Feb-P2 was much more significant than that from May-P1 to Jun-P1, with respective values of r = 0.83, n = 80, and *p* <0.01 and r = 0.55, n = 17, and *p* <0.05 (Fig. 2.5). These results suggest that OC from Oct-P1 to Feb-P2 was apparently influenced by domestic biomass emissions than that from May-P1 to Jun-P1 in this study. Nakayama *et al.* (2014) also showed that the contribution of biomass burning (including biofuel and agricultural residue burning) in winter was larger than that in summer in Nagoya, and their results were derived by measuring the optical properties of aerosols.

The BVOCs such as isoprene, monoterpenes, and sesquiterpenes are important to distinguish the emission sources of non-FC (Kleindienst *et al.*, 2007; Pavuluri *et al.*, 2013). Kleindienst *et al.* (2007) estimated that SOA formed from both BVOC (isoprene, α-pinene, and β-caryophyllene) and toluene contributed significantly to the OC component by quantitative analysis for potential tracer compounds. They suggested that the substantial SOA was derived from isoprene in the summer, although the contribution was minor and negligible for other seasons. Saito *et al.* (2009) reported on the concentrations of non-methane hydrocarbons (NMHCs) and propylene equivalents (PEs), which are used to estimate the production efficiency of SOA at Nagoya. Their results indicate that the PE concentrations of isoprene were high during the summer at Nagoya because of emissions from

vegetation and the formation of SOAs (48 different kinds of NMHCs were measured in their study). Our observed results showed that OC and ^{14}C concentrations in summer were relatively lower than the ones in other seasons (Fig. 2.3 (a); Table 2.3). These results suggest that SOA formed via BVOC emissions from local vegetation did not contribute significantly to TC at Nagoya. Pavuluri *et al.* (2013) demonstrated that the emissions of pollen in spring, fungal spores from soil in summer to autumn, and SOA formation from BVOC in summer to autumn were responsible for the increased ^{14}C concentrations. Our observations of enhanced ^{14}C and OC values in PM$_{2.5}$ in spring showed insignificant influence by pollen because the diameter of pollen is generally larger than 2.5 μm (Shibata *et al.*, 2004).
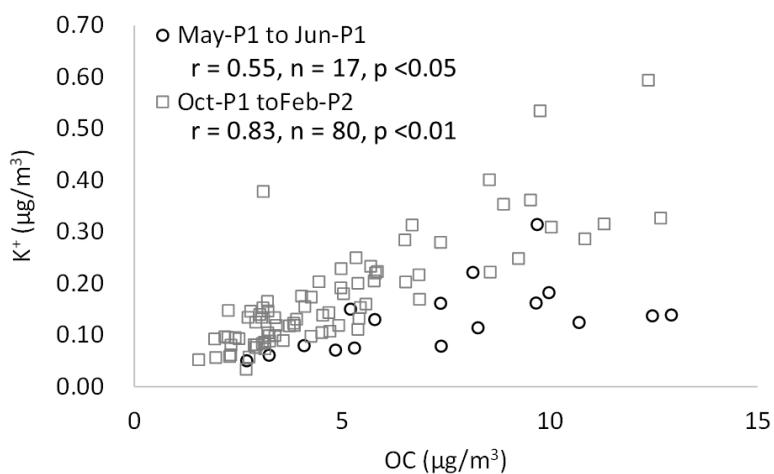

Fig. 2.5. Relationship between organic carbon (OC) and K$^+$ for daily samples at Nagoya in spring (May-P1 to Jun-P1 in 2003) and from autumn to winter (Oct-P1 in 2003 to Feb-P2 in 2004).

3. Seasonal variation and source analysis of carbonaceous aerosol at urban site in Nagoya using radiocarbon

3.1. Introduction

To clarify the emission sources of carbonaceous aerosols, the measurements of ^{14}C and organic components have been conducted and used for source analysis and estimation of their relative contribution to carbonaceous aerosols. The source analysis of non-FC and the estimation of the relative contribution of each source to non-FC have been conducted using ^{14}C and levoglucosan which is known to be produced in the pyrolysis of cellulose (Gelencsér *et al.*, 2007, Szidat *et al.*, 2009b, Zhang *et al.*, 2015). Zhang *et al.* (2015) measured the concentrations of ^{14}C in both OC and EC, and concluded that non-FC amounted to about a half of TC and OC at four mega cities in China (Xi'an, Beijing, Shanghai and Guangzhou). They also estimated that 40−65% of non-FC was emitted from biomass burned area based on an assessment of levoglucosan concentration and the source information of biomass burning. These results suggested that the relative contribution of non-FC to carbonaceous aerosols is prominent, and carbonaceous aerosols emitted by biomass burning dominate non-FC. Further, they reported that non-FC fractions, except for the contribution of biomass burning, increased in the period of high concentration of PM$_{2.5}$.

It is apparent that the research of non-FC is remarkably important in the source identification of carbonaceous aerosols. However, ^{14}C and organic compounds of carbonaceous aerosols are not sufficiently

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investigated. In Japan, the ^{14}C concentration have been measured in the specific seasons and restricted to studies of short time campaign (Fushimi *et al.*, 2011; Minoura *et al.*, 2012; Takahashi *et al.*, 2007; Yamamoto *et al.*, 2007). Levoglucosan concentrations were already measured at the Kanto regions, around Tokyo in Japan (Hagino *et al.*, 2006; Kumagai *et al.*, 2010; Ueno *et al.*, 2012). However, these reports were limited in Kanto region.

It is expected that the emission sources of non-FC are different in each season, but the studies determining the relative contribution of each source to non-FC are not sufficiently performed. To clarify the seasonal variation of emission sources of carbonaceous aerosols, especially non-FC, the measurements of ^{14}C and levoglucosan concentrations, and source analysis of carbonaceous aerosols were performed on total suspended particulate matter (TSP) collected at Nagoya in a year from November 2010 to September 2011.

3.2. Methods

3.2.1. Sampling location and methods

Two or three weekly TSP samples for month were collected on quartz filter (ADVANTEC, QR-100, 20.3×25.4 cm^2) at the Higashiyama campus of Nagoya University ($35^°09'$N, $136^°58'$E) using a high-volume air sampler (Kimoto) from November 2010 to September 2011. The flow rate was set at 810 L/min. Before the sampling, the quartz filters were heated at $1000^°$C for 3 hours to remove carbonaceous contaminants. After the sampling, aerosol samples on the filters were stored in a desiccator at room

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temperature before the analysis.

It is well known that the particle size is different with the origins of carbonaceous aerosols. For examples, the fine particles of SOA and aerosols were emitted directly from diesel, industry and biomass burning, the other hand, particle sizes of pollen and soil are larger than those of SOA and biomass burning. The source information of carbonaceous aerosol can be given by comparing fine with large size particles. To compare the carbonaceous components, $PM_{2.5}$ were collected on the quartz and PTFE filters at the Nagoya city institute for environmental sciences, 7.5 km southwest of the Higashiyama campus of Nagoya University. The daily samplings of $PM_{2.5}$ were conducted from November 2010 to September 2011 using two FRM samplers. Three to six samples for a week were collected. The flow rate was set at 16.7 L/min. Before the sampling, the quartz filters were not heated.

3.2.2. Measurements of concentrations for OC, EC, potassium and calcium ions, and levoglucosan

The concentrations of both OC and EC in TSP and $PM_{2.5}$ were measured by OC/EC analyzer (Sunset lab.) with IMPROVE protocol and TOR correction. These concentrations were corrected by the values obtained for blank filters. To extract K^+ and Ca^{2+}, ultrasonic extraction was conducted for the sample filters with ultrapure water (10 mL). After removal of residuals, the concentrations of K^+ and Ca^{2+} were measured by ion chromatography. To measure the levoglucosan concentration, $^{13}C6$-levoglucosan solution as an internal standard was added to the filters.

Ultrasonic extraction was conducted for the sample filters and distilled water (10 mL). After the removal of residuals, the concentrations of levoglucosan were measured by high-performance anion-exchange chromatography with positive electrospray ionization mass spectrometry (HPAEC-positive ESI-MS) (Asakawa *et al.*, 2015).

3.2.3. Radiocarbon analysis

An aliquot of the quartz filter with TSP was vacuum-sealed into a pre-heated quartz tube with CuO and Ag wires and then heated at 900°C for 6 h. CO_2 in the resultant gas was separated and purified in a vacuum line, and then, it was reduced to graphite with H_2 on an iron powder catalyst in a sealed quartz tube at 650°C for 8 h. The ^{14}C concentration of the graphite was measured with a Tandetron accelerator mass spectrometry system (AMS, Model-4130, HVEE) at the Centre for Chronological Research, Nagoya University (Nakamura *et al.*, 2004). In this study, ^{14}C concentration is expressed as percent modern carbon (pMC), which is the fraction in percent of the $^{14}C/^{12}C$ ratio in samples normalized to the ^{14}C concentration reference from 1950 (Stuiver and Polach, 1977). ^{14}C concentrations for each sample were calculated using the following equation:

^{14}C concentration (pMC) = ($^{14}C/^{12}C$)sample / [(0.7459 × ($^{14}C/^{12}C$)HOxII)]

× 100   (3.1)

where HOxII is a ^{14}C standard material (oxalic acid, SRM-4990C), that was used as the ^{14}C concentration reference supplied from National Institute of

Standards and Technology (NIST). Mass-fractionation in the carbon isotopes was corrected by the $\delta^{13}C$ value, which was measured by the AMS system with an error of less than $\pm 1‰$; this error includes the effects from both machine instability and graphite production (Nakamura *et al*., 2004). In addition, the ^{14}C decrease caused by the decay of the reference material from 1950 until the sampling date was also corrected for (Stuiver and Polach, 1977).

3.2.4. *Estimation of contents of non-fossil carbon and fossil carbon in TC*

Contents of fossil carbon and non-fossil carbon in TC for each sample were estimated using ^{14}C concentrations by the following equation:

$$TC_{nf} = TC \times (R \, / \, 101.5) \tag{3.2}$$

$$TC_f = TC - TC_{nf} - CC \tag{3.3}$$

^{14}C concentration of a 1950-yr reference is defined as 100 pMC (Stuiver and Polach, 1977). However, ^{14}C concentration of CO_2 in atmosphere has shown a higher value than 100 pMC since the middle of 1950, because of the influence of nuclear bomb tests (Levin and Kromer, 2004). ^{14}C concentration of CO_2 in the year collecting the samples is used to estimate FC and non-FC (Lewis and Stiles, 2006). A constant (101.5) used in equation (3.2) is a ^{14}C concentration of a leaf collected near the Higashiyama campus of Nagoya University (unpublished data). The value is

equal to ^{14}C concentration in atmospheric CO_2 during the sampling date in this study. Carbonate carbon (CC) in soil is distributed in large particle size. The large amounts of CC may be collected in TSP samples during *Kosa* events. To estimate the contribution of carbonate carbon (CC) in soil to TC, CC in each TSP sample were calculated by the concentration of non-sea salt Ca^{2+}. This carbon component has possibility of influencing to ^{14}C value in TSP samples. ^{14}C concentration of CC is postulated to be 0 pMC and may induce an overestimation of FC in TC (TC_f). Therefore, non-Fossil carbon and CC are subtracted from TC to estimate TC_f value (eq. (3.3)). Recently, Chen *et al.* (2015) reported the ^{14}C concentration of carbonate in dust. The ^{14}C concentration of the dryland dust carbonates in northeastern China indicated a narrow range of 60.9± 4.0 pMC. However, the influence of using 60.9 pMC as ^{14}C concentration of CC is insignificant because the contribution of CC to TC is small.

3.3. Results and Discussion

3.3.1. Seasonal variations of OC, EC, and ^{14}C concentrations in TSP

The OC concentration in the aerosol samples collected at the Higashiyama campus of Nagoya University in summer to early fall (S–EF) (from June to September 2010) was 2.9 µg/m^3 (Table 3.1). The averaged concentration was lower in S–EF than in late fall to winter (LF–W) (from November 2010 to February 2011, 3.9 µg/m^3) and those in spring (from March to May 2011, 3.8 µg/m^3) as shown in Table 3.1. The seasonal value

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of the EC concentration in LF–W was 2.1 μg/m^3. It was higher than those in spring (1.5 μg/m^3) and those in S–EF (1.5 μg/m^3) in Table 3.1. OC concentration is higher than EC during the whole sampling interval (Fig. 3.1). The correlation coefficients between OC and EC were 0.93 in LF–W, −0.47 in spring, and 0.84 in S–EF, respectively. Lower correlation coefficient in spring indicates that the sources of OC and EC were different in this season.

The averaged concentration of ^{14}C was lower in LF–W (47.1 pMC) than in spring (56.4 pMC) and in S–EF (57.4 pMC). This result indicates that non-FC is major component of TC in spring and in S–EF, in comparison to in LF–W. Especially, ^{14}C concentration showed the highest value in April (about 70 pMC) (Fig. 3.1). The variations of airborne pollen counts (APC, measured at both Aichi Environmental Research Center (AERC), Aichi Shinshiro Health Center-Shitara Branch (ASHC) in Shinshiro) and OC(TSP)/OC(PM$_{2.5}$) ratio are shown in Fig. 3.2. OC(TSP)/OC(PM$_{2.5}$) ratio increased in March and showed the highest value from April to May. The coincidence in the period showing high values for both ^{14}C concentrations and OC(TSP)/OC(PM$_{2.5}$) ratio suggested that the increase of OC concentration in large particle size was related to the increase of ^{14}C concentration in TSP in spring. The correlation between OC and EC was weak in spring. These results suggested that there are multiple emission sources of OC in spring. The electron micrograph of the sample with the highest ^{14}C concentration in this study (April 13–19) is shown in Fig. 3.3. Many pollen particles are observed in this electron micrograph and are identified as beech family. The particles were also observed from February

to May by APC (Fig. 3.2). The contributions of pollen to high ^{14}C concentration of coarse or fine particles have been reported previously. Shibata *et al.* (2004) measured ^{14}C concentrations and took the electron micrograph of different particle sizes collected at Tokyo. They reported that the ^{14}C concentrations of large particles (>7.9 µm) in spring and fall showed higher values than those of fine particles. Pavuluri *et al.* (2013) measured the concentrations of ^{14}C and sucrose used as organic tracer for pollen in TSP collected at Sapporo of Hokkaido Island in Japan. The high concentrations were observed in spring. They concluded that the pollens were responsible to increase ^{14}C concentration of TSP. Our results also suggested that the carbon originated from the biogenic source (e.g. pollens) contributed to high concentrations of ^{14}C in spring.
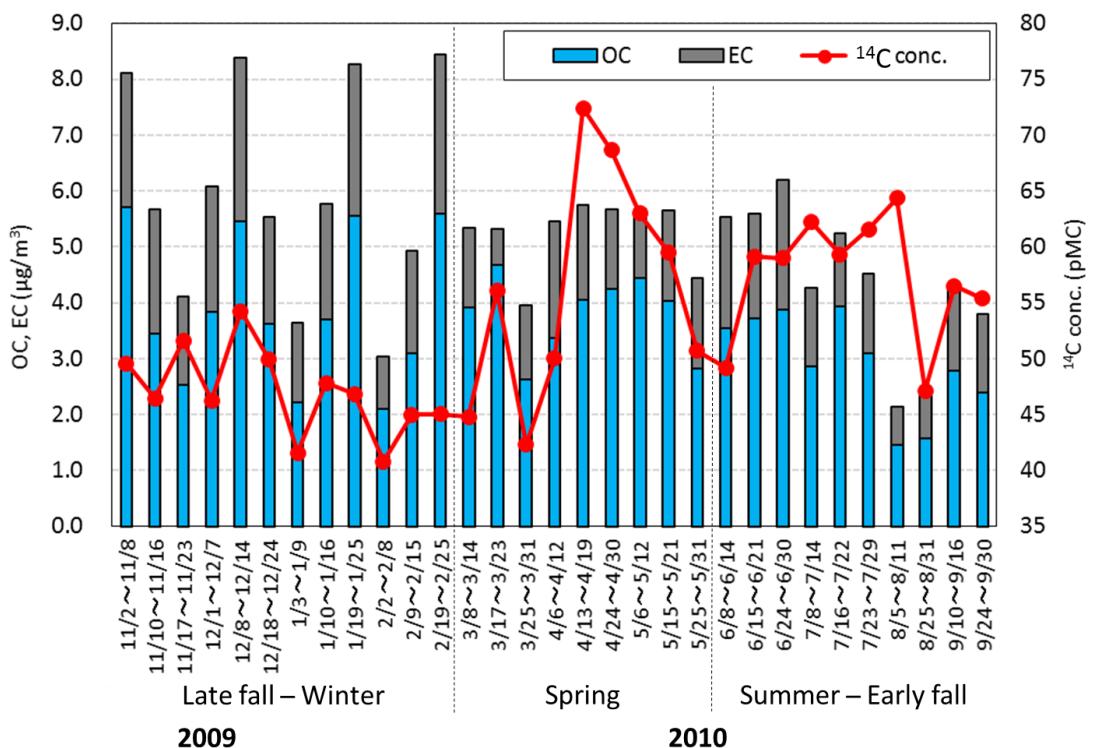
Fig. 3.1. Variations of OC, EC, and ^{14}C concentrations in TSP collected at

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the Higashiyama campus, Nagoya University, from November 2009 to September 2010.
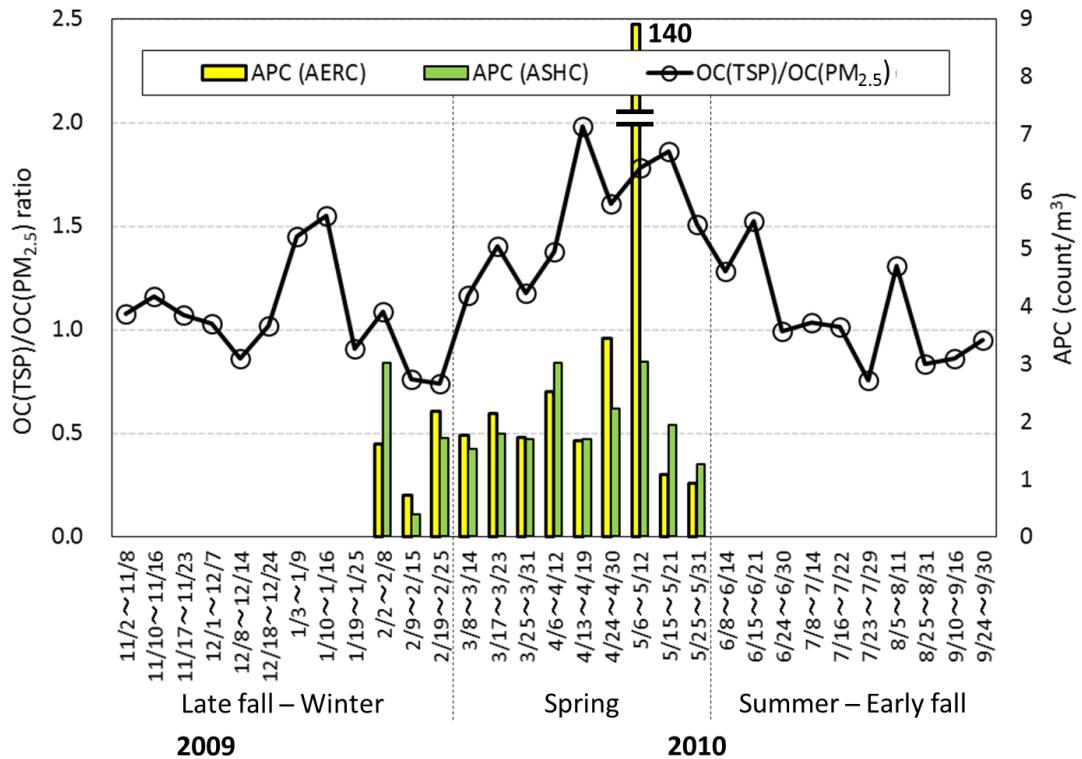
Fig. 3.2. Variations of airborne pollen counts (APC) and OC(TSP)/OC(PM$_{2.5}$) ratio. Airborne pollen counts were measured at Aichi Environmental Research Center (AERC) in Nagoya, and Aichi Shinshiro Health Center-Shitara Branch (ASHC) in Shinshiro. TSP were collected at the Higashiyama campus of Nagoya University. PM$_{2.5}$ were collected at the Nagoya city institute for environmental sciences, 7.5 km southwest of the Higashiyama campus of Nagoya University.
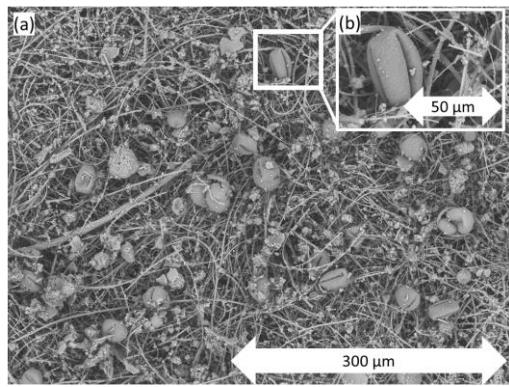
Fig. 3.3 (a) Electron micrograph of the TSP sample with the highest ^{14}C concentration (April 13–19) in this study. (b) Part of the photograph with pollen is expanded.

Table 3.1. Seasonal averages and ranges in concentrations of OC, EC, TC, ^{14}C, TC_{nf}, TC_f, CC, and levoglucosan in TSP samples, collected at the Higashiyama campus, Nagoya University, from November 2009 to September 2010.

Season (Sample number)	Late fall–Winter[a] (12)	Spring[b] (9)	Summer–Early fall[c] (10)	Annual (31)
OC (μg/m^3)	3.9 (2.1 – 5.7)	3.8 (2.6 – 4.7)	2.9 (1.5 – 3.9)	3.6 (1.5 – 5.7)
EC (μg/m^3)	2.1 (0.94 – 2.9)	1.5 (0.65 – 2.1)	1.5 (0.68 – 2.3)	1.7 (0.65 – 2.9)
TC (μg/m^3)	6.0 (3.0 – 8.4)	5.3 (4.0 – 5.8)	4.4 (2.1 – 6.2)	5.3 (2.1 – 8.4)
^{14}C concentration (pMC)	47.1 (40.8 – 54.3)	56.4 (42.3 – 72.4)	57.4 (47.1 – 64.3)	53.1 (40.8 – 72.4)
TC_{nf} (μg/m^3)	2.8 (1.2 – 4.5)	3.0 (1.6 – 4.1)	2.5 (1.1 – 3.6)	2.7 (1.1 – 4.5)
TC_f (μg/m^3)	3.0 (1.7 – 4.4)	2.1 (1.5 – 2.7)	1.8 (0.74 – 2.7)	2.3 (0.74 – 4.4)
CC (μg/m^3)	0.2 (0.10 – 0.31)	0.25 (0.13 – 0.60)	0.09 (0.04 – 0.19)	0.17 (0.04 – 0.60)
Levoglucosan (ng/m^3)	68.2 (23.0 – 132.6)	23.9 (4.9 – 50.5)	6.9 (1.9 – 19.0)	35.6 (1.9 – 132.6)

Average (range)

[a] November 2009–February 2010, [b] March–May 2010, [c] June–September 2010

3.3.2. Seasonal variations of TC_{nf}, TC_f, and levoglucosan concentrations, and the main seasonal sources in TC_{nf}

The temporal variations and seasonal averages of TC_{nf}, TC_f,

levoglucosan concentration and CC are shown in Fig. 3.4 and Table 3.1, respectively. The averaged data of TC_{nf} were 2.8 µg/m^3 (in LF–W), 3.0 µg/m^3 (in spring), 2.5 µg/m^3 (in S–EF), respectively. Although the ^{14}C concentration was lower in LF–W than in spring and in S–EF, TC was high in LF–W and TC_{nf}, estimated by equation (3.2) in LF–W, was a similar value in spring. The TC_{nf} concentration in LF–W fluctuated largely in each sample, on the other hand, TC_{nf} showed high values in the interval from mid-April to mid-May. As mentioned in section 3.3.1, the pollens contributed to the high concentration of TC_{nf} in spring.

Levoglucosan concentration showed clear seasonal variations (Fig. 3.4 and Table 3.1). The concentration of levoglucosan in LF–W (68.2 ng/m^3) showed the highest value following by those in spring (23.9 ng/m^3) and those in S–EF (6.9 ng/m^3). Levoglucosan concentrations measured in Saitama (Hagino *et al.*, 2006), Maebashi (Kumagai *et al.*, 2010) and Tokyo (Ueno *et al.*, 2012) were already reported. Levoglucosan concentrations in Maebashi and Tokyo showed higher values in winter than in summer, similar to the seasonal trend observed in this study. The main emission source of levoglucosan in the Kanto region (include Maebashi and Saitama) was considered as a field burning of plant residues. The emission of the field burning at Nagoya and/or from surrounding regions is probably associated with levoglucosan measured in this study. The ratio between levoglucosan and mannnosan (L/M) which is the isomer of levoglucosan, shows different values according to the species of burning plants, and are used for classifying the emission source (Verma *et al.*, 2015). To estimate the detailed vegetation type of biomass burning, L/M is considered as a

useful tracer. Hagino *et al*. (2006) demonstrated that both levoglucosan and K^+ in fine particles showed a good correlation, and both were useful tracers of biomass burning. However, TSP contains large particles such as sea salt. To remove the influence of K^+ originated from sea salt, the concentration of non-sea salt K^+ (nss-K^+) is calculated. The seasonal data of correlation coefficients between levoglucosan and K^+ showed the highest value in LF−W (0.70, p <0.05), followed by those in spring (0.10) and those in S−EF (-0.37). K^+ is contained in pollens (Gilardoni *et al*., 2011). Pollens contributed to high concentrations of ^{14}C in spring in this study (mentioned 3.3.1). These results suggest that a weak correlation with levoglucosan in spring is introduced by K^+ in pollens. The weak correlation between levoglucosan and K^+ was recognized in summer. It may be explained that the aerosol emissions from biomass burning in summer are relatively smaller than in other season. The K^+ emitted by biomass burning in summer are small, and K^+ emitted from other sources can be associated with nss-K^+. It is considered to cause a weak correlation between levoglucosan and K^+ by volatilization and degradation of levoglucosan in summer, as proposed by Hoffmann *et al*. (2010), May *et al*., (2012), Mochida *et al*.(2010), Xie *et al*. (2014). May *et al*. (2012) demonstrated that levoglucosan is a semi-volatile compound and about 10% is distributed in the gas phase at 25 ℃. The daily mean of atmospheric temperature during the observation term in summer was 26.6 ℃ (max: 30.5 ℃, min: 21.0 ℃). The estimation of the degradation degree of levoglucosan during the observation term in summer is difficult, but there is a possibility of lowering the concentration of levoglucosan by high temperature in summer. An additional research is needed to reveal the

potential degradation of atmospheric levoglucosan in summer.

The correlation coefficients between TC_{nf} and levoglucosan concentration show the highest value in LF–W (0.83, p <0.01), followed by those in S–EF (0.12) and those in spring (-0.14). Some organic compounds emitted by biomass burning possess an ability of absorption of UV (Chen and Bond, 2010). Nakayama $et\ al.$ (2014) reported that light-absorbing carbonaceous aerosols were more abundant in winter than in summer using a photoacoustic spectrometer. They suggested that the aerosol emissions by biomass burning were larger in winter than in summer. These results also suggested that the relative contribution of the aerosol emission by biomass burning to TC_{nf} was more important in winter than in summer. Meanwhile, the biogenic aerosols such as pollens were considered to be responsible for a lower correlation coefficient between TC_{nf} and levoglucosan in spring.

TC_f concentration in LF–W (3.0 µg/m^3) showed the highest value, followed by those in spring (2.1 µg/m^3) and in S–EF (1.8 µg/m^3). The CC concentration was lower than other carbonaceous components, and the annual mean ratio of it to TC was 3.2%. However, the sample collected from 17 to 23 March 2010 showed high CC concentration (0.60 µg/m^3), being 2–14 times of those for other samples. Large amounts of $Kosa$ particle were transported from the Asia continent to Japan from 20 to 21 March 2010. The Meteorological Agency in Japan announced that $Kosa$ was observed at 51 meteorological stations. SPM concentration per an hour measured at Nagoya was over 100 µg/m^3 at the early morning. $Kosa$ was considered as the source for high concentration of CC, because CC is a component of soil particle (Wang $et\ al$., 2005).
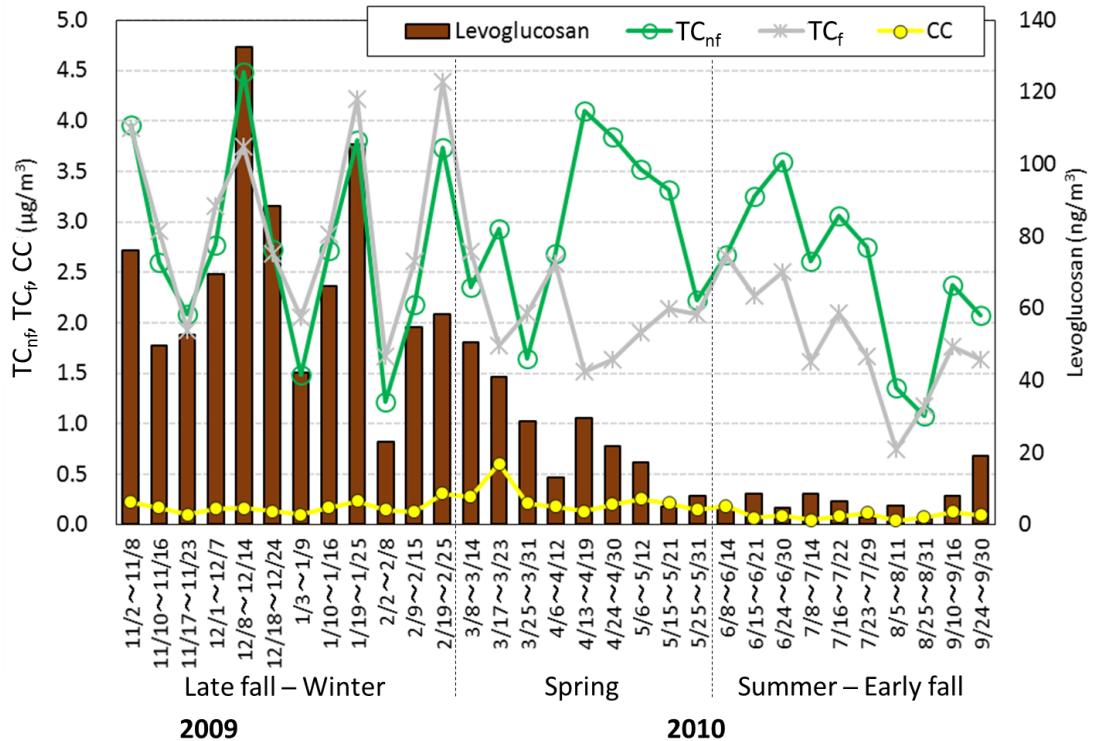
Fig. 3.4.

Temporal variations of TC_{nf}, TC_f, levoglucosan concentration, and CC of TSP collected at the Higashiyama campus, Nagoya University, from November 2009 to September 2010.

3.3.3 Estimation of carbon emitted from biomass burning, and the contributions of that to TC_{nf} and TC

The concentration of carbon emitted by biomass burning was roughly estimated with the levoglucosan concentration in TSP discussed in section 3.3.1. This estimation has been conducted in the published previous reports, for example, that discussed aerosol issues in Maebashi (Kumagai *et al.*, 2010). Moreover, the estimation of non-FC concentration to OC and EC

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by using levoglucosan and ^{14}C concentrations has been conducted in Europe (Szidat *et al.*, 2009b; Gelencsér *et al.*, 2007) and China (Zhang *et al.*, 2015). These estimated results are dependent on emission data of biomass burning. However, the concentrations of carbon components of biomass burning emission are dependent on moisture and species of plants that are burnt (Hayashi *et al.*, 2014, Sullivan *et al.*, 2008). Szidat *et al.* (2009b) used lower and higher limits of parameters of emission sources, and attempted to estimate these concentrations. The concentrations of OC and EC are also dependent on these measurement protocols. These uncertainties of emission data cause calculation error.

Sullivan *et al.* (2008) reported the biomass burning emission data of 96 species. These data included the concentrations of various components such as OC, EC and levoglucosan. The emission data of OC ($OC_{(Source)}$), EC ($EC_{(Source)}$) and levoglucosan ($Lev_{(Source)}$) per a mass of burned plants were used in this study. The concentrations of OC and EC emitted from biomass burning (OC_{bb} and EC_{bb}, respectively) were calculated in many reports. However, $OC_{(Source)}$ and $EC_{(Source)}$ were summed to calculate $Lev_{(Source)}/TC_{(Source)}$ ratios used in equation (3.4), because these emission data of OC and EC from Sullivan *et al.* (2008) were not analyzed with the IMPROVE protocol that was used in this study. The errors induced by using different analytical protocols are removed by this calculation. The 25 (0.0378), medium (0.0609) and 75 (0.0781) percentile of ($Lev_{(Source)}/TC_{(Source)}$) in 96 emission data were used to estimate TC emitted from biomass burning (TC_{bb}) by equation (3.4).

$$TC_{bb} = Lev_{(TSP)} / (Lev_{(Source)}/TC_{(Source)}) \qquad (3.4)$$

TC_{bio} was estimated by using TC_{nf} calculated in equation (3.2) in equation (3.5),

$$TC_{bio} = TC_{nf} - TC_{bb} \qquad (3.5)$$

The variations of TC_{bb} and TC_{bio} concentrations are shown in Figs. 3.5(a) and (b), respectively. TC_{bb} concentration showed higher concentration in LF−W than in other seasons. These concentrations decreased from spring to summer as similar to levoglucosan concentration. The TC_{bb} concentration in summer might be underestimated, as the results of volatilization and degradation. TC_{bio} originated from pollens and spores. Further, TC_{bio} was also generated in secondary reactions from BVOC in the atmosphere. TC_{bio} showed a high concentration in spring and summer. More detailed data of emission sources and burned species are needed to reduce the uncertainty in those estimations. Estimated seasonal means for both TC_{bb} and TC_{bio} concentrations by equation (3.4) and (3.5) by using the medium value of $Lev_{(Source)}/TC_{(Source)}$ ratio (0.0609) are shown in Table 3.2. The distributions of the ratios against TC are shown in Table 3.3. The average concentration of TC_{bb} in S−EF showed the lowest value in the three seasons. The value in S−EF was one-tenth of that in LF−W. The contribution of TC_{bb} to TC in S−EF is also the lowest value in the three seasons. Meanwhile, TC_{bio} in TC amounts to around 50% in spring and S−EF. As mentioned in section 3.3.1 and 3.3.2, the influence of pollens to TC_{nf} was significant in spring, and that

was a main factor of increasing of TC_{nf} and TC_{bio} concentrations. The pollens were also considered to influence to TC_{bio} concentration in June, because OC(TSP)/OC(PM$_{2.5}$) ratio showed relatively large values similar to those in spring. On the other hand, the contribution of pollens was decreasing in summer, because OC(TSP)/OC(PM$_{2.5}$) ratio showed a decreasing trend after June (Fig. 3.2). Saito *et al.* (2009) measured non-methane hydrocarbons at Nagoya, and showed that the large amounts of isoprene were emitted by plant from May to September. Their results indicated that isoprene had a strong effect to produce aerosols in atmosphere. Takahashi *et al.* (2011) evaluated both non-FC and FC in each primary and secondary aerosol in PM$_{2.5}$ collected in Maebashi using ^{14}C concentration. They demonstrated that non-FC accounted for 70% of secondary OC. This result proved that non-FC was significant precursor of secondary formation. These reports and the results in the variation of OC in this study supported that secondary organic aerosol (SOA) produces from BVOC was very important components to TC_{bio} in S−EF. The relative contributions of SOA generated from BVOC to TC_{bio} increase in the interval between May to September (Saito *et al.*, 2009). However, it is difficult to consider the period when the concentration of TC_{bio} originated from BVOC increases, because of pollens as a part of to TC_{bio} in spring. The application of the methods used in this study to the samples of different particle size might give us more clear insight about of the period of pollen contributions. The results in this section indicate that the contributions of TC_{bb} and TC_{bio} to TC_{nf} were different dependent on a season.
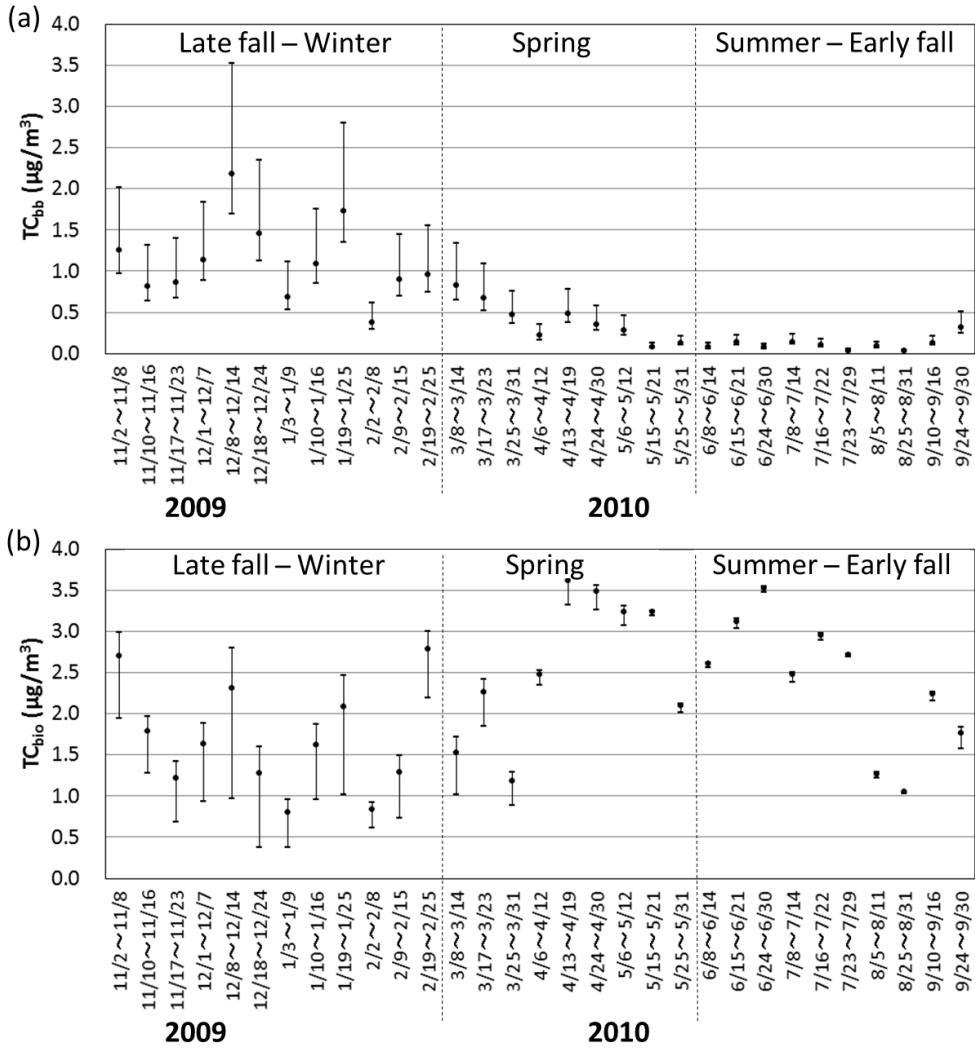
Fig. 3.5. Variations of TC_{bb} (a) and TC_{bio} (b) in TSP collected at the Higashiyama campus, Nagoya University, from November 2009 to September 2010. These values were calculated by Eqs. (4) and (5). Uncertainty bars represent the limiting values of TC_{bb} and TC_{bio} calculated by using 25 (0.0378) and 75 (0.0781) percentiles of $Lev_{(Sourse)}/TC_{(Sourse)}$. Black circles represent the values calculated by using the median value (0.0609) of $Lev_{(Sourse)}/TC_{(Sourse)}$ ratio.

Table 2. Seasonal averages of TC_{bb} and TC_{bio} in TSP.

Season	Late fall - Winter[a]	Spring[b]	Summer - Early fall[c]
TC_{bb}	1.1	0.39	0.11
TC_{bio}	1.7	2.6	2.4

unit: $\mu g/m^3$

[a] November 2009–February 2010

[b] March–May 2010

[c] June–September 2010

Table 3. Seasonal average values of the ratios (TC_{bb}/TC, TC_{bio}/TC, and TC_f/TC) and concentrations of levoglucosan in Nagoya.

Season	Late fall - Winter	Spring	Summer - Early fall
TC_{bb}/TC (%)	19	8	3
TC_{bio}/TC (%)	28	48	54
TC_f/TC (%)	51	40	41
Levoglucosan ($\mu g/m^3$)	0.07	0.02	0.01

3.3.4 Carbonaceous fraction attributing seasonal change in TC concentration

To control the emission of particle matter, it is important to understand the carbonaceous fraction associating with the high concentration of TC. To reveal the carbonaceous fraction attributing increased TC concentration in each season, carbonaceous fractions were classified in each season in the periods of high (HC) and low (LC) concentrations of TC defined by seasonal average (Fig. 3.6). All fractions showed larger values in HC than in LC in LF−W. The average wind speed is

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2.6 m/s in HC and 3.1 m/s in LC. This difference of wind speed indicates that low diffusion of atmospheric particles caused the increasing of all carbonaceous fractions in HC in LF−W. Meanwhile, the difference of TC concentrations between HC and LC was smaller in spring than in other season. However, TC_{bio} concentration showed larger value in HC than in LC, and TC_{bio} was considered to be the main source in the case of high concentration in spring. As mentioned in section 3.3.1, the pollens influenced to TC_{bio} concentrations in spring. The averages of $OC(TSP)/OC(PM_{2.5})$ ratio were 1.6 in HC and 1.3 in LC, respectively. These ratios supported that the presence of OC in large size particles was larger in HC than in LC, and pollens contributed to increase the TC concentration in spring. Both TC_{bio} and TC_f concentration were higher in HC than in LC in S−EF. The influence of underestimation of TC_{bb} caused by volatilization and decompose of levoglucosan, is insignificant because the difference of mean temperature between in HC (26.8 ℃) and in LC (26.4 ℃) is small. The pollens are considered as a significant emission source to TC_{bio} in HC, because the periods classified as HC showed high ratio of $OC(TSP)/OC(PM_{2.5})$ in early June. The average ratios of OC/EC in HC and LC were 2.6 in HC and 1.9 in LC in S−EF. The differences of these ratios both in HC and LC were small in the seasons of both in LF−W (HC:2.0 and LC:2.2) and spring (HC:2.1、LC : 2.3). These indicated that there was a specific emission source of OC in $PM_{2.5}$ in HC in S−EF. As mentioned in section 3.3, SOA originated from BVOC is a significant emission source of TC_{bio} in S−EF. These results supported large contribution of SOA to TC_{bio} in HC in S−EF. Moreover, TC_f concentration, showing an increase in HC in

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S–EF, contributed to high concentration of TC. There are large industries along the seaports at the southern part, and large traffic in Nagoya city. The primary emission and SOA originated from fossil fuels were considered to contribute to the TC_f increase. The results in this section indicate that the main source of high concentration of TC is different in each season.
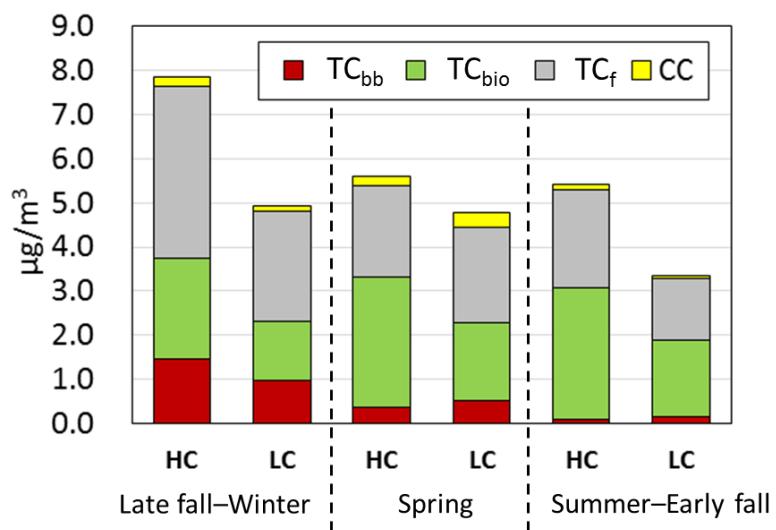

Fig. 6. Comparison of the season specific sources in TC with high (HC) and low (LC) concentrations. HC was defined as the samples with more than average value of TC in each season. LC was defined as the samples with less than average value of TC in each season.

4. Conclusions and outlooks

4.1. Conclusions

To understand the sources of the non-fossil carbonaceous aerosol, the analyses of ^{14}C and chemical components in aerosols collected at Nagoya were conducted in this study. In the first section, the influence of huge Siberian forest fires on the OC concentrations in $PM_{2.5}$ at an urban site in Nagoya was discussed. The OC concentrations during the forest fire events in 2003 showed the highest value. Moreover, OC/TC ratios and ^{14}C concentrations in this interval were higher by 10% and >20 pMC, respectively than those averaged from April 2003 to March 2004. These results indicate that the abundant OC fraction in Nagoya during the forest fire events consisted of non-FC. Backward air mass trajectories also showed that the air mass containing $PM_{2.5}$ with high values in OC concentrations and OC/EC ratios at Nagoya appeared to have passed through East Siberia. In contrast, backward trajectories showed that the air mass in January originated from various regions. After that, ^{14}C concentrations showed lower values than those during the forest fire events. From the above analyses, it was concluded that high OC and ^{14}C concentrations observed at Nagoya in May 2003 were caused by non-FC emitted from the Siberian forest fire.

In the second section, seasonal variation and sources of non-fossil carbonaceous aerosols collected at Nagoya were discussed. The concentrations of OC, EC, ^{14}C and levoglucosan in TSP collected on filters from November 2010 to September 2011 in Nagoya were measured. Seasonal means of ^{14}C were lower in LF–W (47.1 pMC) than in spring (56.4

pMC) and S–EF (57.4 pMC). The ^{14}C concentration especially showed high value (about 70 pMC) in April. These results indicated that non-FC contributed to TC in these periods, and pollens were considered as the source attributing to the higher ^{14}C values. Levoglucosan concentration showed higher value in LF–W than in other seasons. These results indicate that the emission from biomass burning was larger in late fall to winter than in other seasons. TC_{nf} and TC_f were estimated using by ^{14}C concentration. Further, TC_{bb} and TC_{bio} were estimated by ^{14}C, TC_{nf} and levoglucosan concentration. The seasonal concentrations of those fractions demonstrated that the contribution of TC_{bb} and TC_{bio} to TC_{nf}, and the main factor of high concentration of TC, were significantly different in each season.

These results clarify the sources of the non-fossil carbon at Nagoya in the urban site. The non-fossil carbon emitted from biomass burning influenced on seasonal and eventic changes of non-fossil carbon at Nagoya. On other hand, the additional study on the non-fossil carbon from biogenic carbon except for biomass burning is needed to clarify the sources.

4.2. Outlooks

^{14}C concentration and chemical components in PM were measured in this study. The measurement of ^{14}C required an amount of carbon more than 1 mg in this study. Therefore, the collection of aerosol samples using a low-volume air sampler with long time or using high-volume (HV) air sampler to collect a large amount of carbonaceous aerosols was needed. Especially, the collection of large amount of $PM_{2.5}$ was difficult due to

technical problems. Recently, an impactor of collecting $PM_{2.5}$ with a HV air sampler has been developed, and enabled us to collect a large amount of $PM_{2.5}$ (Kaneyasu *et al.*, 2010). Moreover, the measurements of ^{14}C with smaller carbon amount have been achieved (Minami *et al.*, 2013, Ruff *et al.*, 2007). Those improvements of sample collection and ^{14}C measurement enable us to analyze the samples collected at high temporal resolution (less than 1 day). The analyzing of aerosol samples collected in a short time would provide us the source information of carbonaceous aerosols in detail. Further, ^{14}C measurement with the small-size carbon enables us to analyze the lower carbon concentration samples, for example, collected at the mountain sites such as Mt. Fuji, and at the remote sites such as Fukue and Tsushima Island. To understand the regions from which aerosols are transported, the measurements of both ^{14}C and various components in aerosols collected in as a short time as possible at those sites are important. The measurement of ^{14}C was applied only to TC in this study. Our results suggested that the measurements of ^{14}C of both carbonaceous fractions (e.g. OC, EC and WSOC) and organic compounds that are one of molecular tracers of emission source, are desired to reveal and understand the emission sources of carbonaceous aerosols more in detail. The estimation of the carbon concentration emitted by biomass burning using ^{14}C and levoglucosan needs to identify the emission sources in higher spatial resolution, because there were the large uncertainty in the present estimation of both TC_{bb} and TC_{bio}. Moreover, TC_{bio} should be divided to more different kinds of sources using other organic molecular tracers, because TC_{bio} includes sea spray, biological materials such as pollens, plant

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fragments, microorganisms, and secondary organic carbon originated from BVOC. These studies would contribute to understand the sources and their relative contribution to aerosols, to keep the atmosphere clean from the pollution by aerosols, and to establish the national standards to protect us from $PM_{2.5}$ problems.

Acknowledgments

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Measurement of Polycyclic Aromatic Hydrocarbons in PM$_{2.5}$ Collected by Impactor for High Volume Air Sampler.

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Source apportionment of carbonaceous matter in PM$_{2.5}$ at NOTO peninsula using ^{14}C analysis.

Reina Yamada, **Fumikazu Ikemori**, Toshio Nakamura, Minami Masayo,

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Ambient nanoparticles characterization by East and Southeast Asia nanoparticle monitoring network.

Mitsuhiko Hata, Masami Furuuchi, Surui Dong, Worradorn Phairuang, Hui Ge, Tong Zhang, Daishi Onizuka, Atsushi Matsuki, Kensaku Kakimoto, Ning Tang, Akira Toriba, Fumie Hosokawa, Kazuhiko Sekiguchi, Nobuyoshi Yamashita, **Fumikazu Ikemori**, Kyung Hwan Kim, Xin Gang Liu, Jun Han, Yunhe Bai, Seingheng Hul, Sophal Try, Porsry Ung, Peou Hang, Perapong Tekasakul, Pattaraporn Saetiew, Wongpun Limpaseni, Sirima Panyametheekul, Panwadee Suwattiga, Sirikalaya Suvachittanont, Thunyapat Thongyen, Wladyslaw W. Szymanski, Rawiwan Maniratanachote, Khajornsak Sopajaree, Thaneeya Chetiyanukornkul, Tanachai Pankasemsuk, Thanyarat Chuesaard, Mikinori Kuwata, Bang Quoc Ho, Nguyen Thi Khanh Tuyen, Nghiem Trung Dung

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