Emission Regulations Altered the Concentrations, Origin, and Formation of Carbonaceous Aerosols in the Tokyo Metropolitan Area

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ABSTRACT

To investigate the effects of the regulations of diesel and non-methane hydrocarbon (NMHCs) emissions in the Tokyo metropolitan area (TMA) on the characteristics of carbonaceous aerosols (organic carbon (OC) and elemental carbon (EC)), we conducted field observations to characterize carbonaceous aerosols in the TMA in the summer of 2004 and 2014 (the end of July–middle of August). Following the enforcement of diesel emission regulations, EC concentrations showed a four-fold decrease from 2004 to 2014. However, OC concentrations showed no significant decrease in the last decade. Multiple chemical analyses revealed the differences in the impacts of the contribution of oxygenated fraction, biogenic NMHCs on OC, and the secondary organic aerosol–Ozone relationship between 2004 and 2014. Further investigations into the emission inventory for recent years, especially in terms of precursor gases, are needed for better prediction of OC in the TMA using chemical transport models.

Keywords: Emission regulations; Carbonaceous aerosols; SOA; Biogenic carbons.

INTRODUCTION

Carbonaceous materials, including organic and elemental carbons (OC and EC, respectively), are one of the most important constituents of aerosols and are ubiquitous across various atmospheric environments (e.g., Kanakidou *et al.*, 2005). In particular, understanding the sources and secondary processes of carbonaceous aerosols is of great importance in considering their climatic and environmental impacts in the atmosphere. In October 2003, the Tokyo Metropolitan Government began regulating on-road diesel emissions with a view to reducing the concentrations of EC aerosols in Tokyo with the cooperative efforts to the regulation in the surrounding three prefectures (Kondo *et al.*, 2012). Since then, additional regulations were implemented in 2006 and

2011 to further regulate off-road diesel emissions and to strengthen the existing regulations. In addition to the regulations of particulate matter emitted from mobile sources, non-methane hydrocarbons (NMHCs) emissions from all stationary sources in Japan have been regulated since April 2006. It is expected that the characteristics of carbonaceous aerosols in the Tokyo metropolitan area (TMA) will have significantly varied since the introduction of these regulations. Yamamoto *et al.* (2007) compared the concentrations and origins of carbonaceous aerosols in Tokyo before and after the implementation of the first diesel vehicle regulation in the fall of 2003. Their results revealed no substantial decrease in the concentrations of carbonaceous aerosols, and only slight changes in their origins between 2003 and 2004. Biogenic carbon made up 34% of the total carbon mass of fine aerosols (< 1.1 µm) in TMA in the summer of 2004 (Yamamoto *et al.*, 2007). Fushimi *et al.* (2011) investigated the impacts of biogenic carbon on the mass of secondary organic aerosols (SOA) as well as their diurnal variations at sites outflow from the TMA in the summer of 2007. Additionally, Kondo *et al.* (2012) conducted continuous measurements of EC/BC

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concentration in the TMA during 2003–2005 and 2007–2010. These revealed that the annual mean mass concentrations of EC in TMA decreased from 2.6 µgC m^{-3} to 0.6 µgC m^{-3} between 2004 and 2010. Akimoto *et al.* (2015) recently reported that despite substantial decreases of around 50% for both nitrogen oxides (NO$_x$) and non-methane hydrocarbons (NMHCs), ozone (O$_3$) increased in TMA during 1990–2010. The concentrations of O$_3$ and SOA are strongly correlated in the daytime during summer season; the results indicate possible changes in SOA formation processes in the TMA (Kondo *et al.*, 2008). To the best of our knowledge, the concentrations and origins of recent carbonaceous aerosols in the TMA have not yet been investigated. Such information is critical for a continuing understanding of the effects of emission reduction attempts on the characteristics of carbonaceous aerosols in the TMA.

We conducted ground-based measurements of trace gas mixing ratios and chemical composition of fine aerosols in the TMA during the summer of 2004 (Kondo *et al.*, 2008; Miyakawa *et al.*, 2008) and 2014 (this study) using either the same or consistent analytical methods. We also conducted aerosol sampling in the industrial area (Yokosuka), which is located at the southern boundary of the TMA in the fall of 2014 in order to understand the spatial variations in carbonaceous aerosol characteristics. Multiple analytical techniques, including in-situ aerosol mass spectrometry (AMS) and radiocarbon (^{14}C) analyses, were applied to the atmospheric OC and EC aerosols in order to fully investigate the concentrations, compositions, and origin of carbonaceous aerosols in TMA. We report their observed changes between 2004 and 2014 and thus reveal the effect of regulations of diesel and NMHCs emissions in the TMA.

METHODS

Atmospheric Observations in the TMA in the Summers of 2004 and 2014

Intensive field measurements were conducted at two sites in the TMA, Komaba (35.65°N, 139.67°E) and Hongo (35.71°N, 139.76°E) sites, during the summers of 2004 and 2014, respectively. The locations of the observation sites are shown in Fig. 1, and the measurements made during the two observation periods are summarized in Table 1. The details of the Komaba site and the experimental setups for the observations in the summer of 2004 (from July 26 to August 15) have been presented in previous studies (Kondo *et al.*, 2008; Miyakawa *et al.*, 2008). It is important to indicate that the analysis methods used in the previous study are basically the same as or consistent with those used in the summer of 2014. We therefore describe here the atmospheric observation in the summer of 2014 (from July 27 to August 15). The Hongo site is located within the campus of the University of Tokyo in the center of the TMA. This site is located around 10 km northeast of the Komaba site. The spatial homogeneity of atmospheric trace gases and aerosols concentrations in the TMA has been discussed in previous
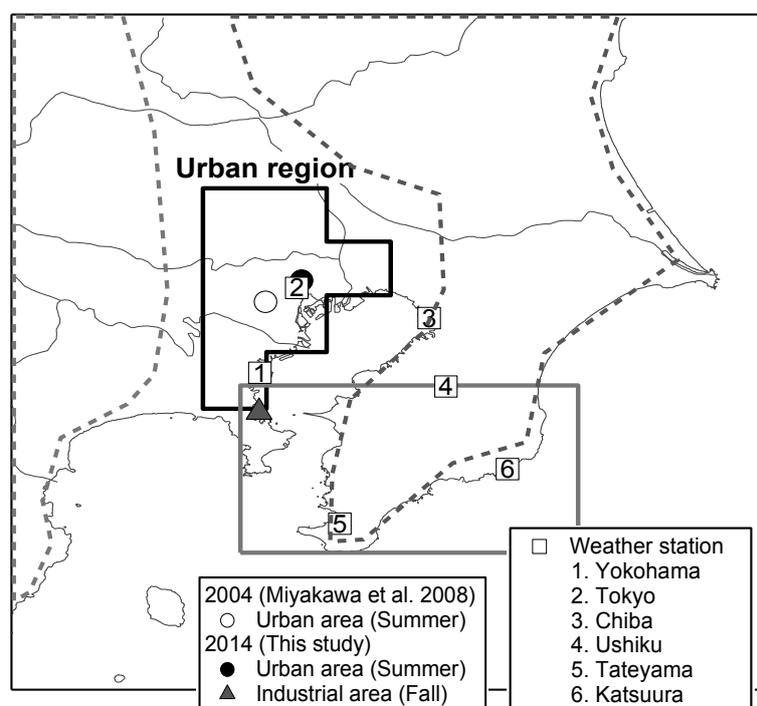

Fig. 1. Distribution of the atmospheric observation sites used in this study: Komaba site (open circle), Hongo site (Filled circle), and Yokosuka site (filled triangle). The locations of AMeDAS stations are shown as open squares with the number representing the station name; 1. Yokohama, 2. Tokyo, 3. Chiba, 4. Ushiku, 5. Tateyama, and 6. Katsuura. The regions enclosed by dashed lines are approximate forest area inferred from the satellite-derived land use data. The regions enclosed by bold black and shaded lines represent TMA and the area where net primary productivity was analyzed for assessing the biogenic impact to the TMA (see text for details), respectively.

Table 1. Summaries of the ground-based measurements in this study.

Summer of 2004 (Komaba[a])

	Online analysis	**Sites**	Reference
Inorganic aerosol Organic aerosol (OM)	Q-Aerodyne Aerosol Mass Spectrometer	Komaba	Miyakawa *et al.* (2008), Kondo *et al.* (2008)
Organic carbon Elemental carbon	semicontinuous EC/OC analyzer (NIOSH)	Komaba	Kondo *et al.* (2008)
CO	NDIR	Komaba	Miyakawa *et al.* (2008), Kondo *et al.* (2008)
O_3	UV-absorption	Komaba	Miyakawa *et al.* (2008), Kondo *et al.* (2008)

Summer and Fall of 2014 (Hongo[b] and Yokosuka[c])

	Online analysis	Sites	Reference
Inorganic aerosol Organic aerosol (OM)	Q-Aerodyne Aerosol Mass Spectrometer	Hongo	-
$CO/CO_2/CH_4$	Cavity ring down	Hongo	-
O_3	UV-absorption	Hongo	Kondo *et al.* (2008)

	Offline analysis	Sites	Reference
Inorganic aerosol	Ion chromatography	Hongo, Yokosuka	Miyakawa *et al.* (2015; 2016)
Oragnic carbon Elemental carbon	EC/OC analyzer (NIOSH)	Hongo, Yokosuka	Miyakawa *et al.* (2016)
$^{14}C/^{12}C$	Accelarator Mass Spectrometer	Hongo, Yokosuka	-

[a, b] Observation sites in the TMA (July–August, 2004 and 2014);
[c] Observation site near the Tokyo-Yokohama industrial area (November, 2014).

studies (Kondo *et al.*, 2006; Miyakawa *et al.*, 2015), and therefore, we assumed that there is no significant difference between the air masses at the Komaba and Hongo sites. The sample air was aspirated from the building rooftop (~40 m above ground level) in the lab at the top floor of the building. Real-time measurements of aerosol microphysics and chemical compositions were carried out, using a scanning mobility particle sizer (differential mobility analyzer 3081 and condensation particle counter 3022, TSI Inc., US), an ultra-high sensitivity aerosol spectrometer (UHSAS, Droplet Measurement Technologies, Inc., US), an Aerodyne Quadrupole Aerosol Mass Spectrometer (Q-AMS, Aerodyne Research, Inc., US), and a Single Particle Soot Photometer (SP2, Droplet Measurement Technologies, Inc., US). Positive matrix factorization (PMF) was used to analyze the organic mass spectra measured using the Q-AMS (Lanz *et al.*, 2007; Ulbrich *et al.*, 2009). Total organic aerosol (OA) was classified into hydrocarbon-like organic aerosol (HOA) and oxygenated organic aerosol (OOA) in this study. The analyses of organic mass spectra using the PMF method and their results are shown in the supporting information (SI). In this study, we analyzed OOA mass concentrations in relation to O_3 as a measure of SOA formation processes. A tandem series of Nafion tube dryers (MD-070-12, Perma Pure LLC., USA) was placed in front of all instruments for drying the sample air to a typical relative humidity of ~50%.

A high volume air sampler (HV500F, Sibata Scientific Technology, Ltd., Japan) was placed at the rooftop of the building. The sampler was equipped with a $PM_{2.5}$ impactor with a sampling flow rate of 500 liter per minute (L min^{-1}).

During the observation period, sampling (for almost a day) was carried out, on a 110-mm pre-combusted (900°C for 3 h) quartz filter (QR-100, Advantec Toyo Kaisha Ltd., Japan). Pieces, 16 mm in diameter, were punched out of the filters and analyzed by thermal-optical analysis using an EC/OC analyzer (Sunset Laboratory, Inc., US) following the National Institute for Occupational Safety and Health (NIOSH) protocol (Birch and Cary, 1996). According to Turpin *et al.* (1994), the carbon mass of organic gases adsorbed on quartz filters was estimated to be about 3 μgC at maximum per a punched filter for the EC/OC analysis, which typically accounts only for ~5% of OC. Water soluble ions were analyzed using ion chromatography (Dionex ICS1000, Thermo Fisher Scientific K.K., Japan). The radioisotope analysis for carbonaceous aerosols collected on the quartz filters will be described in a later section.

Trace gases, carbon monoxide (CO) and O_3, were measured in a laboratory on the sixth floor of the same building (around 20 m above ground level). Ambient air was drawn into the laboratory via Teflon tubes for trace gas measurements. The mixing ratio of CO was measured using a cavity ring-down spectroscopy gas analyzer (G2401, Picarro Inc., USA). The effect of water vapor on the concentrations of CO was corrected by a method provided by the manufacturer. Finally, the O_3 mixing ratio was measured through UV absorption (Model 1150, Dylec, Inc., Japan).

Atmospheric Observation in an Industrial Area

The air sampling and subsequent ion and carbon analysis were performed at the head quarter of the Japan Agency

for Marine-Earth Science and Technology in Yokosuka (35.32°N, 139.65°E) during the fall of 2014 (from November 11 to 21). The Yokosuka site is located near an industrial emission source region, Tokyo-Yokohama industrial area, which is one of the largest industrial areas in the TMA (Kanaya *et al.*, 2014; Miyakawa *et al.*, 2016). The atmospheric observations made at this site are summarized in Table 1. Although the observation at the Yokosuka site was made during a different season to the two observations in the TMA, the data sets for the Yokosuka site are only used to discuss the horizontal scale of the effects of the emission regulations.

Radioisotope Ratio Analysis for Carbonaceous Aerosols

We conducted an analysis of radioisotope ratios ($^{14}C/^{12}C$) for the TC of aerosols collected at Hongo and Yokosuka sites in 2014. As the half-lifetime of ^{14}C is 5730 (± 40) yrs, $^{14}C/^{12}C$ decrease in fossil fuels which have no interaction with atmospheric CO_2. The $^{14}C/^{12}C$ for aerosols therefore has been used for the investigation of origins (fossil or modern) of carbons in aerosols (e.g., Currie, 2000; Szidat *et al.*, 2006). Sample preparation and quantification of ^{14}C concentrations for TC were performed at the laboratory in the Institute of Accelerator Analysis Ltd. We hereby present brief descriptions of the analysis for carbonaceous aerosols collected on the quartz filters. Sample filters (quarter of 110-mm quartz filters) were put to a quartz tube with copper oxide and Sulfix (consisting of cobalt and silver oxides), and evacuated. Based on the results of TO analysis, typical carbon mass in each filter sample was 500–1000 µgC, which was considered to be much higher than the carbon mass derived from organic gases adsorbed on quartz filters. The maximum carbon amount of the adsorbed organic gases on the quarter of a filter was estimated to be around 30 µgC. The carbon samples in the evacuated quartz tube were combusted at 500°C for 0.5 h and 850°C for 2 h and were oxidized to CO_2. Evolved CO_2 samples were purified and reduced to make a graphite target for the ^{14}C analysis by hydrogen using iron as a catalyst. The graphite sample was measured in terms of ^{13}C concentration ($^{13}C/^{12}C$) and ^{14}C concentration ($^{14}C/^{12}C$), using an accelerator mass spectrometry system at the Institute of Accelerator Analysis Ltd. All results of $^{13}C/^{12}C$ and $^{14}C/^{12}C$ are related with those at the reference year 1950 (Reimer *et al.*, 2004) by using a standard oxalic acid (HOXII (SRM4990c)) provided by the National Institute of Standards and Technology (NIST). The percent modern carbon, pMC (Stuiver and Polach, 1977), of the samples are defined as the following Eq. 1.

$$pMC = \frac{134.07}{\left(^{14}C/^{12}C\right)_{HOxII}} \cdot \left(^{14}C/^{12}C\right)_{Sample} \qquad (1)$$

The value of 134.07 in this equation represents the pMC for HOxII. All results are reported as the fraction modern, $F^{14}C$ (= pMC/100) (Reimer *et al.*, 2004). All the values of $F^{14}C$ corrected for ^{13}C fractionation in this study. $F^{14}C$ of atmospheric CO_2 has been altered by emissions of fossil CO_2 (Suess effect) and productions of ^{14}C from nuclear bomb

tests in 1950s–1960s (Bomb effect). Levin *et al.* (2013) investigated the long-term variations of $^{14}CO_2$ at two sites in the middle latitude of the Northern Hemisphere. They found that permil-deviations of $^{14}CO_2$ from that in 1850 in summer season decreased from ~75‰ to ~35‰ between 2002 and 2012. The typical contributions of EC mass to TC mass in 2014 were minor (around 10%), indicating that the derived values of $F^{14}C$ of TC ($F^{14}C_{TC}$) were nearly equivalent to the $F^{14}C$ of OC.

Analysis of Interannual Summertime Meteorology and Biogenic Activity

We analyzed the meteorological data sets at selected meteorological monitoring sites in Japan, which are maintained by the Automated Meteorological Data Acquisition System (AMeDAS), in order to investigate the trends of temperature and solar radiation in summer season (July–August) that affect the biogenic activity (Guenther *et al.*, 1995) in the TMA and surrounding regions. As the solar radiation was not measured at all of the sites, we analyzed sunshine duration as a proxy of solar radiation. We analyzed the AMeDAS data sets at one site and found that sunshine duration showed a good correlation with global solar radiation ($r^2 = 0.89$) in summer (July–August, 2002–2014). The locations of the sites are shown in Fig. 1. The Yokohama and Tokyo sites represent those in the TMA. The Chiba site is located to the coastal urban region. The others (4–6 in Fig. 1) represent those located over the forest region south and southeast to the TMA. The net primary production (NPP) derived from Moderate Resolution Imaging Spectroradiometer (MODIS) – on the Terra was also analyzed to elucidate temporal changes in the biogenic photosynthetic activities over the forest area south and southeast to TMA. NPP can alter the emissions of BVOCs through the modulation of foliar density. Although the emission of carbon as BVOCs related to NPP is region-dependent (Guo *et al.*, 2013; and references therein), BVOCs emissions are generally correlated with NPP variations.

RESULTS AND DISCUSSION

OC and EC Mass Concentrations

Fig. 2(a) depicts the averaged mass concentrations of OC and EC during the observation periods. The average mass concentrations of OC in the summer of 2014 did not differ significantly from the summer of 2004 in the TMA. With the exception of the period when the values of $F^{14}C_{TC}$ were higher than 0.7 (high $F^{14}C_{TC}$ period), the average mass concentration of OC at the Hongo site showed a slight decrease from 2.7 µgC m^{-3} to 2.2 µgC m^{-3}. However, EC decreased by a factor of 4, from 1.6 µgC m^{-3} to 0.4 µgC m^{-3}, between 2004 and 2014, resulting in a significant increase in the slope of OC-EC correlations over this period (Fig. 2(b)). It is therefore suggested that the use of the OC/EC tracer method for the estimation of secondary OC should be discouraged as the emission ratio of primary OC to EC in the TMA has increased associated with the emission regulations. EC at the Yokosuka site showed similar mass concentrations to those in the TMA. The emission regulations in the
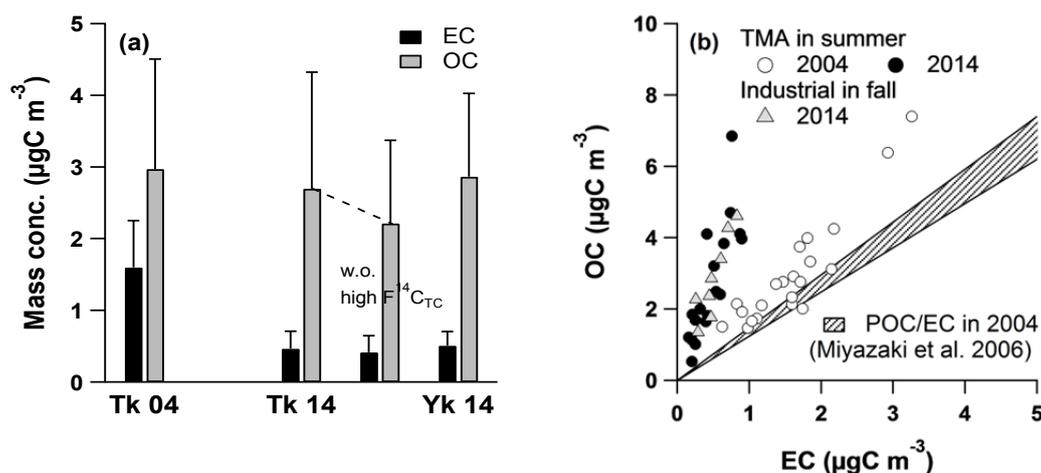
Fig. 2. (a) Averaged mass concentrations of EC (black bars) and OC (gray bars) for the three observation periods (Tk04 and Tk14, within TMA during the summers of 2004 and 2014, respectively; Yk14, near the industrial sources during the fall of 2014). (b) Correlation between OC and EC for the three observation periods: open and filled circles for the summers of 2004 and 2014 in the TMA, respectively, and triangles for the industrial sources during the fall 2014. OC/EC for the primary emission during the summer of 2004 (estimated by Miyazaki *et al.*, 2006) was overlaid as a shaded region.

surrounding prefectures also significantly affected the mass concentrations of EC. Fig. 3(a) (3b) depicts the correlations of CO and OC (EC). The slope of the EC/CO correlation in 2014 decreased substantially from that in 2004, whereas those of OC/CO correlations did not show any significant difference between 2004 and 2014. The reduced EC mass concentrations and EC/CO ratios suggest that the emission regulations have affected the abundance of EC in the TMA during this decade, while changes in weather conditions have had no significant impact.

Evolution of Compositions and Origins of Carbonaceous Aerosols with Air Mass Aging

Fig. 4 illustrates a diagnosis of the changes in the properties of carbonaceous aerosols with air mass aging. Miyakawa *et al.* (2008) showed that mass ratio of sulfate aerosol (SO4) to black carbon in the TMA increased by a factor of ~2 with air mass aging (< 1 d) in summer. In this study, SO4 normalized by EC, SO4/EC, is used as an indicator to assess the impact of secondary formation of aerosols. The mass spectrometric signal at mass-to-charge (m/z) ratio of 44 is a good marker for oxygenated fraction of organic aerosols in the TMA (e.g., Miyakawa *et al.*, 2008). The mass concentration ratios of m/z 44 (nitrate-equivalent) to total organics (f44) were compared with SO4/EC in the summer of 2004 and 2014 (Fig. 4(a)). The f44 value of diesel exhaust aerosols (Mohr *et al.*, 2009), which is almost zero, is included in this figure for the comparison. f44 increased with air mass aging and showed a similar trend during both periods. The average value of f44 in the summer of 2014 (0.085 ± 0.029) is higher than in the summer of 2004 (0.060 ± 0.027).

Fig. 4(b) depicts the relationship between $F^{14}C_{TC}$ and SO4/EC ratio at the Hongo and Yokosuka sites in the summer and fall of 2014, respectively. Values of $F^{14}C_{TC}$ greater than 0.7 (markers enclosed by dashed circles) were observed in the summer of 2014 (July 28–30, 2014), even in the center of the metropolitan region, as mentioned earlier.

The f44 values for this high $F^{14}C_{TC}$ period were higher than during other periods in the same year, indicating that chemical compositions of OC (e.g., oxidation state) were strongly affected by modern carbon sources during this period. These findings will be discussed in detail in the later sections. With the exception of these data points, the $F^{14}C_{TC}$ values observed at the Hongo and Yokosuka sites were ranging from 0.4 to 0.6, with an average of around ~0.5, showing a slight increase as SO4/EC increased. This suggests that the contributions of modern carbons to OA are enhanced in aged air masses. The $F^{14}C_{TC}$ values in 2014 were higher than that in Tokyo during the summer of 2004 (0.34, Yamamoto *et al.*, 2007).

Discussion on Changes in the Origins of Carbon in Aerosol Particles in TMA

Shibata *et al.* (2004) investigated the seasonal variation in the origin of fine carbonaceous aerosols in Tokyo from April 2002 to February 2003 (Fig. 1 of Shibata *et al.*, 2004). We collated and synthesized their data with our observations to illustrate the interannual changes in summertime $F^{14}C_{TC}$ for fine aerosols in the TMA and its outflow region (Fig. 5(a)). These results show an increase in summertime $F^{14}C_{TC}$ from less than 0.3 to around 0.5 between 2002 and 2014, indicating that biogenic contributions to carbonaceous aerosols in the summer were enhanced in this decade. The observed increase in $F^{14}C_{TC}$ is converse to recent decrease of atmospheric $^{14}CO_2$ from ~75‰ to ~35‰ (deviations from 1850) in summer season as discussed earlier (Levin *et al.*, 2013).

In order to interpret the trend, we analyzed meteorological parameters relevant to the emission of BVOCs in addition to NPP ($mgC\ m^{-2}\ d^{-1}$), daily maximum temperature (T_{max}, in °C) and sunshine duration (SD, in h) at the selected AMeDAS sites. The NPP values were averaged for the selected region located south and southeast to the TMA (Fig. 1). Their standardized relative variations of the 2-monthly (July–
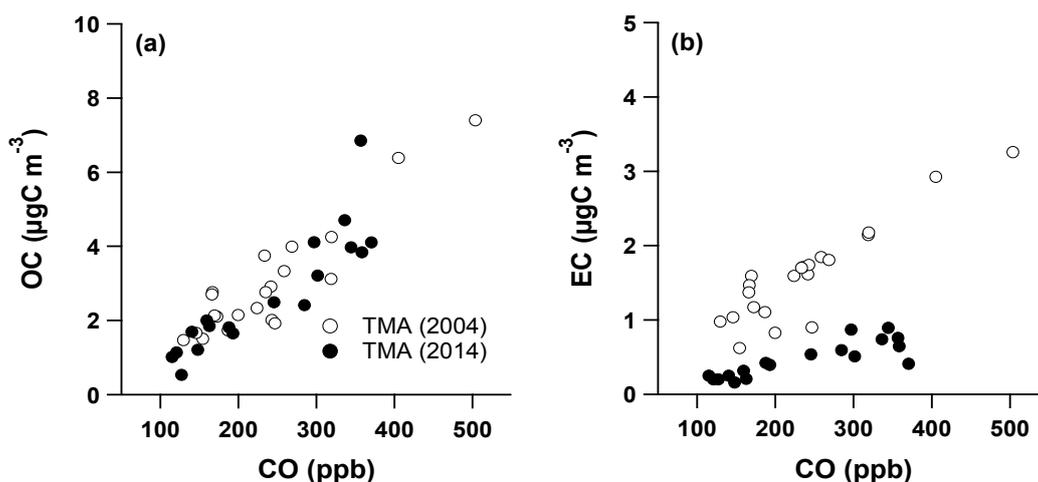
Fig. 3. Correlation of (a) OC and (b) EC with CO in the TMA during the summers of 2004 (open circles) and 2014 (filled circles).
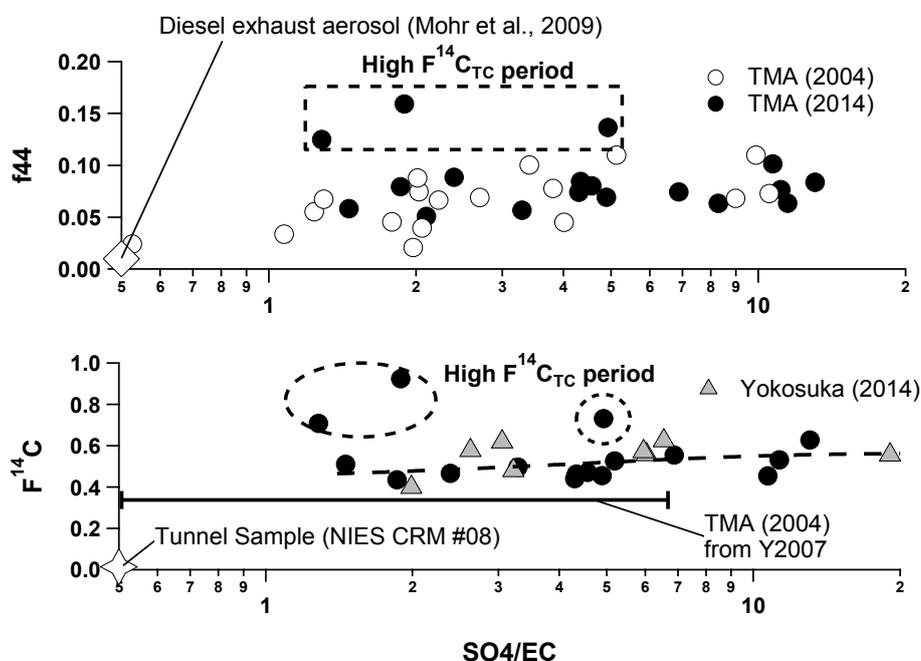

Fig. 4. Characteristics of carbonaceous aerosols as a function of SO4/EC. Variations in (a) f44 (see text for details) and (b) $F^{14}C_{TC}$ are shown as a function of SO4/EC in the TMA for the summer of 2004 (open circles) and 2014 (filled circles) and the industrial sources in the fall of 2014 (triangles). These parameters are shown for vehicle exhaust aerosol particles (see text for details) as open diamond and star markers in (a) and (b), respectively. The black bar in (b) represents the $F^{14}C_{TC}$ (from Yamamoto *et al.* (2007), see text for details) with the observed range of SO4/EC in the TMA during the summer of 2004. The data points enclosed by the dashed rectangle and circles are belonging to the high $F^{14}C_{TC}$ period (see text for details).

August) mean parameters, X (X = NPP, T_{max}, and SD), *SRV*, are defined as follows.

$$SRV = \frac{\left(X - X_{avg}\right)}{X_{avg}}, \qquad (2)$$

where X_{avg} represents values of the parameters X averaged for 2002–2014. The *SRV* for NPP, T_{max}, and SD between

2002 and 2014 are shown in Fig. 5(b). There is no clear increasing trend for the three parameters which can account for the increase in $F^{14}C_{TC}$ in the TMA. Further to this, a dip in *SRV*s for all parameters was found in the summer of 2003, indicating the lower activity of biogenic sources at that year. There is no significant change in $F^{14}C_{TC}$ related to such reduced biogenic activity in the summer of 2003 (Fig. 5(a)). These results suggest that biogenic NMHCs was not major to that derived from fossil sources during the
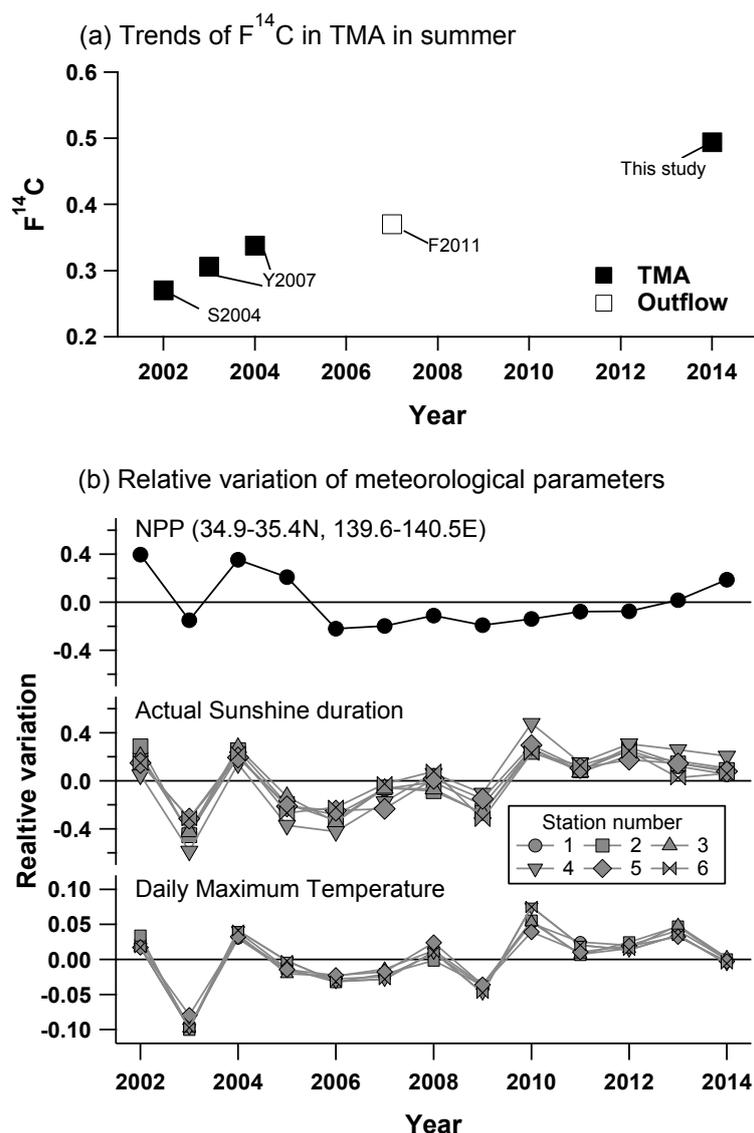
Fig. 5. (a) Changes in the summertime $F^{14}C_{TC}$ for fine aerosols in the TMA and its outflow region. Values of $F^{14}C_{TC}$ in the TMA in the summers of 2002, 2003, and 2004 and in an outflow region in the summer of 2007 were derived from Shibata *et al.* (2004) (S2004) and Yamamoto *et al.* (2007) (Y2007), and Fushimi *et al.* (2011) (F2011), respectively. (b) Changes in the SRV of NPP for the selected area (34.9–35.4N, 139.6–140.5E) (upper panel), and SD and T_{max} at the selected AMeDAS sites in the summers of 2002-2014 (see the text for details of the sites).

earlier period (2002–2004), and that the increasing trend of $F^{14}C_{TC}$ from 2004 to 2014 can be attributed to the regulation-induced reduction of NMHCs from fossil sources.

Case Study for the High $F^{14}C_{TC}$ Period in TMA in the Summer of 2014

High values of $F^{14}C_{TC}$ (0.7–0.9) were observed during the summer of 2014, even in the center of the metropolitan region, as shown in Fig. 4(b). In order to clarify the sources of modern carbons during such period, we need to consider the contributions of both biomass burning-OA and biogenic SOA. The analysis of mass spectral signals such as combination of m/z 44 and 60 (Cubison *et al.*, 2011) suggests that major sources of carbonaceous aerosol during the high $F^{14}C_{TC}$ period were not biomass burning, and that

such high $F^{14}C_{TC}$ values were likely caused by the formation of biogenic SOA. Details of the discussion on this analysis and the results are given in section S2 of SI. Satellite-derived NPP was analyzed in order to investigate the photosynthetic activity across the TMA and its surrounding region. The spatial distributions of MODIS-derived NPP during two periods, July 28–August 4 and August 5–12, 2014 (UT), are shown in Figs. 6(a) and 6(b), respectively. It should be noted that the former period includes the identified high $F^{14}C_{TC}$ period. Forested areas are found to the west and southeast of the TMA. The NPP over the southeastern region of the TMA showed higher values, by a factor of around 2, during the former period (Fig. 6(a)) than in the latter period (Fig. 6(b)). NPP averaged for July–August, 2014 (NPP_{JA14}) were subtracted from those for both periods (Dif_NPP) to
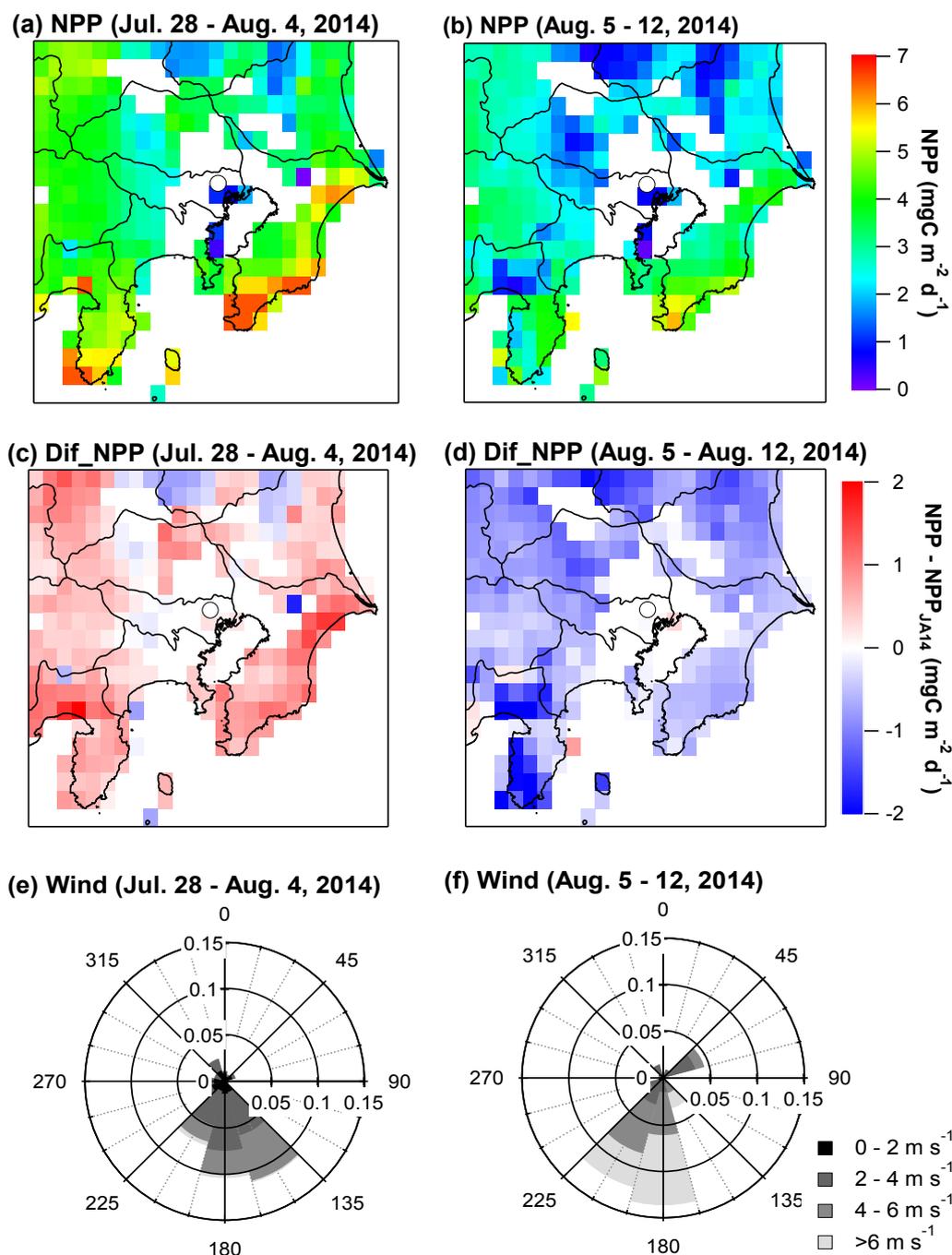
Fig. 6. Distribution of NPP and Dif_NPP (see text for details) over the TMA and surrounding regions during July 28–August 4 (a and c, respectively), and August 5–12 (b and d, respectively), 2015. The open circles in (a)–(d) represent the location of the Hongo site. The wind flow pattern during July 28–August 4 (e), and August 5–12 (d), 2015, are represented as wind rose plots.

clarify the variations of NPP. (Figs. 6(c) and 6(d)) The distribution of Dif_NPP in Figs. 6(d) (6c) also suggests more reduced (enhanced) biogenic activity for the latter (former) period than the seasonal average in 2014. This is likely caused by the cloudy (August 8 and 12, 2014) and typhoon a (August 9–10, 2014) conditions over the TMA and surrounding region during the latter period. Horizontal wind flow patterns for the former and latter periods are represented as wind rose plots in Figs. 6(e) and 6(f), respectively. While

southerly and south-southeasterly winds with moderately high speeds (2–6 m s^{-1}) prevailed during the former period, southerly and south-southwesterly winds with the higher speeds (> 4–6 m s^{-1}) occurred during the latter period. It is suggested that the biogenic activity and meteorological conditions including solar radiation and horizontal wind flow conditions affected the impacts of biogenic sources on the origins of carbonaceous aerosols in the summer of 2014, especially during the high F^{14}C$_{TC}$ period.

SOA Formation Processes in Terms of the Relationship with O_3

To investigate the effects of emission regulations on the formation of SOA with respect to the formation cycle of daytime O_3, we compared the relationships between SOA and O_X (O_3 + nitrogen dioxide) in the daytime (10:00–16:00LT) of 2004 and 2014. In this study, the SOA materials are regarded as co-products of O_3 formation in the daytime (Herndon *et al.*, 2008; Wood *et al.*, 2010). OOA derived from the PMF analysis of Q-AMS data sets were used as a proxy for SOA. The daytime OOA/O_X correlations in the summers of 2004 and 2014 are shown in Fig. 7(a). The differences between observed and estimated background concentrations (calculated as the average of observed concentrations lower than 5 percentile) were calculated for both OOA and O_X (ΔOOA and ΔO_X). The concentrations of OOA were not particularly well correlated with those of O_X during the summer of 2014; however a strong correlation were found between OOA and O_X during the summer of 2004. Fig. 7(b) illustrates the frequency distributions of the ratios of ΔOOA to ΔO_X (ΔOOA/ΔO_X) during the summers of 2004 and 2014. The modal value for ΔOOA/ΔO_X ratio during the summer of 2014 was almost half of that during the summer of 2004. The histogram of the ΔOOA/ΔO_X ratio during the high $F^{14}C_{TC}$ period of the summer of 2014 is also overlaid on Fig. 7(b), and can be seen to correspond to higher ΔOOA/ΔO_X ratios. These results suggested that biogenic sources significantly altered the ΔOOA/ΔO_X ratios in the TMA during the summer of 2014.

Possible Changes in NMHC$_S$ Composition in TMA

The OOA/O_X correlation can be affected significantly by changes in the types of air masses and the composition of NMHCs, as discussed by Henrdon *et al.* (2008) and Wood *et al.* (2010). Morino *et al.* (2015) used OOA/O_X correlations in the TMA during the summer of 2004 to diagnose the performance of the chemical transport model (CTM). The observed difference in OOA/O_X correlations between 2004 and 2014 suggests that the composition of NMHC$_S$ has altered significantly as a result of the implementation of emission regulations. We found the OOA/O_X correlation to have lower slope in 2014 than in 2004, while the range of O_X concentrations remained similar across both measurement periods. This finding suggests a decrease in the concentrations of larger NMHCs, which generate SOA more efficiently through the photochemical reactions (with the hydroxyl (OH) radical in the daytime) than smaller NMHCs (e.g., Odum *et al.*, 1997). The diesel exhaust regulations could act to reduce the concentrations of larger NMHCs, which can be generated through the evaporation of primary OA (POA) during the dilution process (i.e., particle-to-gas conversion) and be effective anthropogenic SOA precursors (Lipsky and Robinson, 2006; Robinson *et al.*, 2007). Furthermore, a modeling study has suggested that SOA formed from anthropogenic HMW-NMHCs (ASOA) can potentially account for the substantial fraction of SOA mass observed in the TMA during the summer of 2004 (Matsui *et al.*, 2009). This result highlights the need for extensive investigations into the emission inventory of both aerosol and precursor
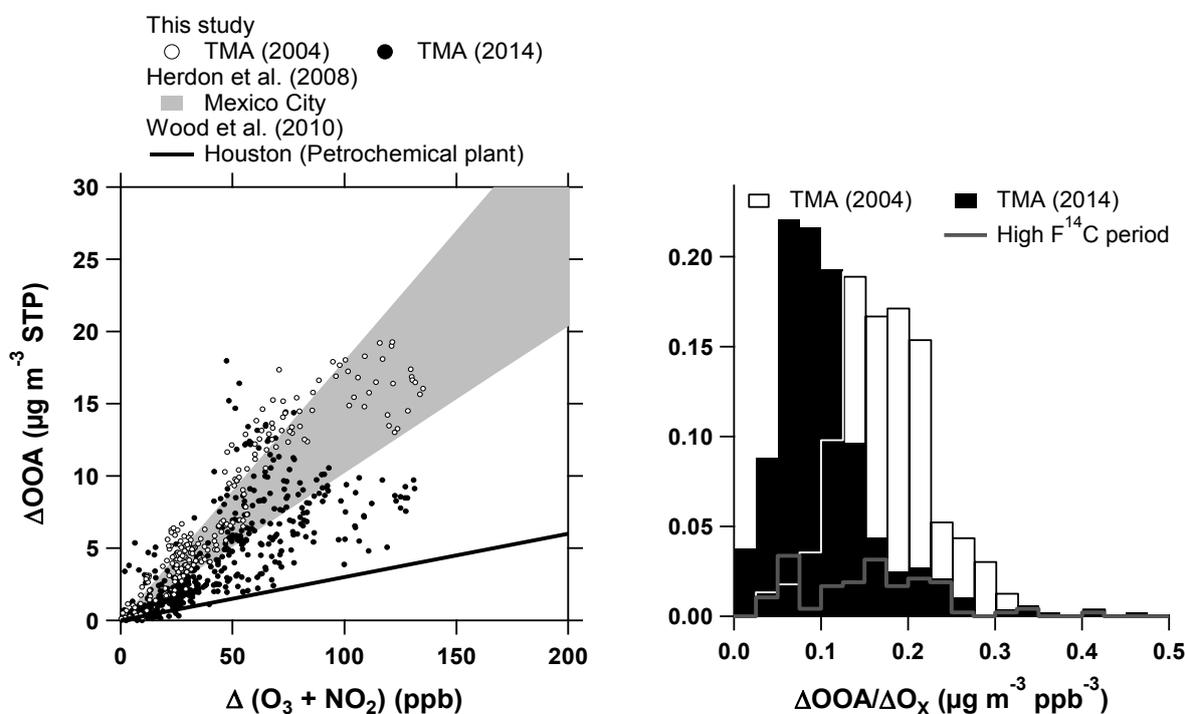

Fig. 7. (a) Correlations of ΔOOA and ΔO_X in the summers of 2004 (open circles) and 2014 (filled circles) in the TMA. The shaded band represents the range of ΔOOA-ΔO_X observed in Mexico City (Herndon *et al.*, 2008), while the ΔOOA-ΔO_X in air masses affected by petrochemical plants in Houston (Wood *et al.*, 2010) is shown as a black line. (b) Probability density function (PDF) of the ratio of ΔOOA to ΔO_X (ΔOOA/ΔO_X) in the TMA in the summers of 2004 (open bars) and 2014 (filled bars). Contribution of ΔOOA/ΔO_X during high $F^{14}C_{TC}$ period in the summer of 2014 is shown as a bold gray line.

gases in recent years in the TMA for the better prediction of the atmospheric environment of the TMA using CTMs. In particular, quantitative information about compositions and biogenic contributions of $NMHC_S$ will be critical in assessing the abundances and formation mechanisms of SOA in the TMA in recent years.

CONCLUSIONS

We conducted intensive field campaigns to characterize carbonaceous aerosols within the TMA during the summers (from the end of July to middle of August) of 2004 and 2014, in order to investigate the effects of the enforced emission regulations for the diesel exhaust and NMHCs in the TMA on the characteristics of carbonaceous aerosols in this region. As the diesel emissions were regulated, EC mass concentrations have decreased from ~1.6 μg m^{-3} to ~0.4 μg m^{-3} (75% reduction) between 2004 and 2014. In contrast, OC mass concentrations did not show significant variation during this decade. These changes cannot be attributed to variations in the meteorological conditions such as horizontal wind speed, as similar trends were observed in the correlation slopes of EC and OC with CO. Multiple chemical analyses revealed the differences in: (1) the contribution of oxygenated fraction (higher f44 values in 2014 than 2004); (2) the impacts of BVOCs on OA (~15% increase from 2004 to 2014); and (3) the formation processes of SOA relative to O_3 (~50% less efficient production of SOA to O_3 on average in 2014 than in 2004). Together, these results suggest that extensive investigations of the emission inventory in recent years both for aerosols and precursor gases, especially NMHCs, in TMA are critically needed for the better prediction of recent carbonaceous aerosols using CTMs.

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

REFERENCES

Birch, M.E. and Cary, R.A. (1996). Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Sci. Technol.* 25: 221–241.

Cubison, M.J., Ortega, A.M., Hayes, P.L., Farmer, D.K., Day, D., Lechner, M.J., Brune, W.H., Apel, E., Diskin, G.S., Fisher, J.A., Fuelberg, H.E., Hecobian, A., Knapp, D.J., Mikoviny, T., Riemer, D., Sachse, G.W., Sessions, W., Weber, R.J., Weinheimer, A.J., Wisthaler, A. and Jimenez, J.L. (2011). Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies. *Atmos. Chem. Phys.* 11: 12049–12064.

Currie, L.A. (2000). Evolution and multidisciplinary frontiers of ^{14}C aerosol science. *Radiocarbon* 42: 115–126.

Fushimi, A., Wagai, R., Uchida, M., Hasegawa, S., Takahashi, K., Kondo, M., Hirabayashi, M., Morino, Y., Shibata, Y., Ohara, T., Kobayashi, S., and Tanabe, K. (2011). Radiocarbon (^{14}C) diurnal variations in Fine particles at sites downwind from Tokyo, Japan in summer. *Environ. Sci. Technol.* 45: 6784–6792.

Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J. and Zimmerman, P. (1995). A global model of natural volatile organic compound emissions. *J. Geophys. Res.* 100: 8873–8892.

Guo, P., Guo, K., Ren, Y., Shi, Y. Chang, J., Tani, A. and Ge, Y. (2013). Biogenic volatile organic compound emissions in relation to plant carbon fixation in a subtropical urban-rural complex. *Landsc. Urban Plan.* 119: 74–84.

Herndon, S., Onasch, T., Wood, E.C., Kroll, J.H., Canagaratna, M., Jayne, J., Zavala, M., Knighton, W.B., Mazzoleni, C., Dubey, M.K., Ulbrich, I., Jimenez, J.L., Seila, R., de Gouw, J. A., De Foy, B., Fast, J., Molina, L., Kolb, C.E. and Worsnop, D.R. (2008). The correlation of secondary organic aerosol with odd oxygen in Mexico City. *Geophys. Res. Lett.* 35: L15804, doi: 10.1029/20 08GL034058.

Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G. and Wilson, J. (2005). Organic aerosol and global climate modelling: A review. *Atmos. Chem. Phys.* 5: 1053–1123.

Kanaya, Y., Irie, H., Takashima, H., Iwabuchi, H., Akimoto, H., Sudo, K., Gu, M., Chong, J., Kim, Y.J., Lee, H., Li, A., Si, F., Xu, J., Xie, P.H., Liu, W.Q., Dzhola, A., Postylyakov, O., Ivanov, V., Grechko, E., Terpugova, S. and Panchenko, M. (2014). Long-term MAX-DOAS network observations of NO_2 in Russia and Asia

(MADRAS) during the period 2007-2012: instrumentation, elucidation of climatology, and comparisons with OMI satellite observation and global model simulations. *Atmos. Chem. Phys.* 14: 7909–7927.

Kondo, Y., Komazaki, Y., Miyazaki, Y., Moteki, N., Takegawa, N., Kodama, D., Deguchi, S., Nogami, M., Fukuda, M., Miyakawa, T., Morino, Y., Koike, M., Sakurai, H. and Ehara, K. (2006). Temporal variations of elemental carbon in Tokyo. *J. Geophys. Res.* 111: D12205, doi: 10.1029/2005JD006257.

Kondo, Y., Morino, Y., Fukuda, M., Kanaya, Y., Miyazaki, Y., Takegawa, N., Tanimoto, H., McKenzie, R., Johnston, P., Blake, D.R., Murayama, T. and Koike, M. (2008). Formation and transport of oxidized reactive nitrogen, ozone, and secondary organic aerosol in Tokyo. *J. Geophys. Res.* 113: D21310, doi: 10.1029/2008JD010134.

Kondo, Y., Ram, K., Takegawa, N., Sahu, L., Morino, Y., Liu, X. and Ohara, T. (2012). Reduction of black carbon aerosols in Tokyo: Comparison of real-time observations with emission inventories. *Atmos. Environ.* 54: 242–249.

Lanz, V.A., Alfarra, M.R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prévôt, A.S.H. (2007). Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra. *Atmos. Chem. Phys.* 7: 1503–1522.

Levin, I., Kromer, B. and Hammer, S. (2013). Atmospheric $\Delta^{14}CO_2$ trend in Western European background air from 2000 to 2012. *Tellus Ser. B* 65: 20092, doi: 10.3402/tellusb.v65i0.20092.

Lipsky, E.M. and Robinson, A. (2006). Effects of Dilution on Fine Particle Mass and Partitioning of Semivolatile Organics in Diesel Exhaust and Wood Smoke. *Environ. Sci. Technol.* 40: 155–162.

Matsui, H., Koike, M., Takegawa, N., Kondo, Y., Griffin, R.J., Miyazaki, Y., Yokouchi, Y. and Ohara, T. (2009). Secondary organic aerosol formation in urban air: Temporal variations and possible contributions from unidentified hydrocarbons. *J. Geophys. Res.* 114: D04201, doi: 10.1029/2008JD010164.

Miyakawa, T., Takegawa, N. and Kondo, Y. (2008). Photochemical evolution of submicron aerosol chemical composition in the Tokyo megacity region in summer. *J. Geophys. Res.* 113: D14304, doi: 10.1029/2007JD009493.

Miyakawa, T., Kanaya, Y., Taketani, F., Tabaru, M., Sugimoto, N., Ozawa, Y. and Takegawa, N. (2015). Ground-based measurements of fluorescence aerosol particles in Tokyo in the spring of 2013: Potential impacts of non-biological materials on autofluorescence measurements of airborne particles. *J. Geophys. Res.* 120: 1171–1185, doi: 10.1002/2014JD022189.

Miyakawa, T., Kanaya, Y., Komazaki, Y., Taketani, F., Pan, X., Irwin, M. and Symonds, J. (2016). Intercomparison between a single particle soot photometer and evolved gas analysis in an Industrial Area in Japan: Implications for the Consistency of Soot Aerosol Mass Concentration Measurements. *Atmos. Environ.*, 127: 14–21.

Miyazaki, Y., Kondo, Y., Takegawa, N., Komazaki, Y., Fukuda, M., Kawamura, K., Mochida, M., Okuzawa, K. and Weber, R.J. (2006). Time-resolved measurements of water-soluble organic carbon in Tokyo. *J. Geophys. Res.* 111: D23206, doi: 10.1029/2006JD007125.

Mohr, C., Huffman, J.A., Cubison, M.J., Aiken, A.C., Docherty, K.S., Kimmel, J.R., Ulbrich, I.M., Hannigan, M. and Jimenez, J.L. (2009). Characterization of primary organic aerosol emissions from meat cooking, trash burning, and motor vehicles with high-resolution aerosol mass spectrometry with ambient and chamber observations. *Environ. Sci. Technol.* 43: 2443–2449.

Morino, Y., Tanabe, K. Sato, K. and Ohara, T. (2014). Secondary organic aerosol model intercomparison based on secondary organic aerosol to odd oxygen ratio in Tokyo. *J. Geophys. Res.* 119: 3489–13505, doi: 10.1002/2014JD021937.

Odum, J.R., Jungkamp, T.P.W., Griffin, R.J., Flagan, R.C., and Seinfeld, J.H. (1997). The atmospheric aerosol-forming potential of whole gasoline vapor. *Science* 276: 96–99.

Reimer, P., Brown, T. and Reimer, R. (2004), Discussion: Reporting and calibration of post-bomb ^{14}C data. *Radiocarbon* 46: 1299–1304.

Robinson, A.L., Donahue, N.M., Shrivastava, M.K., Weitkamp, E.A., Sage, A.M., Grieshop, A.P., Lane, T.E., Pierce, J.R. and Pandis, S.N. (2007). Rethinking organic aerosols: Semivolatile emissions and photochemical aging. *Science* 315: 1259–1262.

Shibata, K., Endo, M. Yamamoto, N., Yoshinaga, J., Yanagisawa, Y., Endo, M., Goto, S., Yoneda, M., Shibata, Y. and Morita, M. (2004). Temporal variation of radiocarbon concentration in airborne particulate matter in Tokyo. *Radiocarbon* 46: 485–490.

Stuiver, M. and Polach, H.A. (1977). Discussion: Reporting of ^{14}C data. *Radiocarbon* 19: 355–363.

Szidat, S., Jenk, T.M., Synal, H.A., Kalberer, M., Wacker, L., Hajdas, I., Kasper-Giebl, A. and Baltensperger, U. (2006). Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by ^{14}C. *J. Geophys. Res.* 111: D07206, doi: 10.1029/2005JD006590

Turpin, B.J., Huntzicker, J.J. and Hering, S.V. (1994). Investigation of organic aerosol sampling artifacts in the Los Angels basin. *Atmos. Environ.* 28: 3061–3071.

Ulbrich, I.M., Canagaratna, M.R., Zhang, Q., Worsnop, D.R. and Jimenez, J.L. (2009). Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data. *Atmos. Chem. Phys.* 9: 2891–2918.

Yamamoto, N., Muramoto, A., Yoshinaga, J., Shibata, K., Endo, M., Hirabayashi, M., Tanabe, K., Goto, S., Yoneda, M. and Shibata, Y. (2007). Comparison of Carbonaceous Aerosols in Tokyo before and after Implementation of Diesel Exhaust Restrictions. *Environ. Sci. Technol.* 41: 6357–6362.

Wood, E.C., Canagaratna, M.R., Herndon, S.C., Onasch, T.B., Kolb, C.E., Worsnop, D.R., Kroll, J.H., Knighton, W.B., Seila, R., Zavala, M., Molina, L.T., DeCarlo, P.F., Jimenez, J.L., Weinheimer, A.J., Knapp, D.J., Jobson, B.T., Stutz, J., Kuster, W.C. and Williams, E.J. (2010). Investigation of the correlation between odd oxygen and

secondary organic aerosol in Mexico City and Houston.
Atmos. Chem. Phys. 10: 8947–8968.