Formation and Transport of Aerosols in Tokyo in Relation to Their Physical and Chemical Properties: A Review

Yutaka KONDO, Nobuyuki TAKEGAWA, Hitoshi MATSUI

Research Center for Advanced Science and Technology, University of Tokyo, Tokyo, Japan

Takuma MIYAKAWA

Development Department, Sibata Scientific Technology LTD., Soka, Japan

Makoto KOIKE

Department of Earth and Planetary Science, Graduate School of Science, University of Tokyo, Tokyo, Japan

Yuzo MIYAZAKI

Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan

Yugo KANAYA

Research Institute for Global Change, Japan Agency for Marine-Earth Science and Technology, Yokohama, Japan

Michihiro MOCHIDA

Institute for Advanced Research, Nagoya University, Nagoya, Japan

Mikinori KUWATA

School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA

Yu MORINO

Asian Environment Research Group, National Institute for Environmental Studies, Tsukuba, Japan

and

Manabu SHIRAIWA

Max Planck Institute for Chemistry, Biogeochemistry Department, Mainz, Germany

(Manuscript received 22 October 2009, in final form 26 February 2010)
Abstract

Large amounts of reactive gases and aerosols are emitted from urban areas. Megacities, including the Tokyo Metropolitan Area (TMA), are very large, concentrated sources of these species affecting local, regional, and global ozone (O3) and aerosol levels. Emissions strongly influence air quality and climate on these scales. In 2003–2004, we made intensive measurements of O3 and chemical composition of aerosol particles with diameters less than 1 μm (PM1 aerosol) together with their precursors for the first time in Tokyo, Japan, as a part of the series of Integrated Measurement Program for Aerosol and Oxidant Chemistry in Tokyo (IMPACT) campaigns. Using these data, we investigated the formation and transport processes of O3 and PM1 aerosols through the analysis of their temporal variations near the urban center of Tokyo and regions downwind. Key findings obtained in these studies are reviewed in this paper.

1. Overview of O3 and aerosol studies performed in the Tokyo Metropolitan Area

Large amounts of reactive gases and aerosols are emitted from urban areas. Megacities, including the Tokyo Metropolitan Area (TMA), are very large, concentrated sources of these species, which affect ozone (O3) and aerosol levels on local, regional, and global scales (e.g., Molina and Molina 2004; Ramanathan et al. 2007). The uncertainties in emission estimates of these species are generally large for Asia (Streets et al. 2006; Ohara et al. 2007) or are not assessed in the TMA (Kannari et al. 2007).

The increased levels of pollutants have a large impact on regional air quality, nutrient deposition patterns, and climate. In order to assess the impacts of anthropogenic species emitted from these megacities on surrounding areas, we need to understand quantitatively the key processes involved in the oxidation of primary species and the fate of the oxidized species near the source regions (Fig. 1). In addition, clusters of megacities lead to the accumulation of O3 and aerosol through large-scale mixing. Reactive species with elevated concentrations in urban outflows can also interact with species emitted from natural sources surrounding the mega cities. It should be noted here that O3 and aerosol levels are coupled due to similar sources, photochemical interactions (e.g., UV changes by aerosol), and transport.

In the 1980s and 1990s, regional increases in photochemical pollution, including high levels of O3, occurred in the TMA (Wakamatsu et al. 1996, 1999). As discussed below in more detail, photochemical pollution continued to increase through 2000s under certain conditions, as typically shown in Fig. 2 (Miyakawa et al. 2008). The TMA is one of the most densely populated megacities in the world (population density of about 5800 people km⁻² in 2007 (http://metro.tokyo.jp/ENGLISH/PROFILE/overview03.htm)). From 1978 to 1990, the concentrations of nitrogen oxides (NOx) have increased due to the increase in the numbers of vehicles (Wakamatsu et al. 1996). On the contrary, the non-methane hydrocarbon (NMHC) concentration and therefore NMHC/NOx ratio decreased during this period. According to model predictions, these emission changes could alter the location where the maximum O3 is observed over the TMA (Wakamatsu et al. 1996). This is consistent with the fact that the location of the daily maximum oxidant concentration moved farther away from the major emission areas.

From 1991 to 2004, both NOx and NMHCs showed continued decreases (Tokyo Metropolitan Government 2005) (Fig. 3), due to regulations to reduce the emissions of these species. The concentrations of these species in the TMA are considerably lower than those in megacities in developing Asian countries (Molina and Molina 2004). Despite the decreases of the precursors, the average O3 concentration in the TMA during the summer season (June–August) increased during this period. According to Japanese air quality standards (AQS), hourly O3 mixing ratios are required to be lower than 60 parts per billion by volume (ppbv). The frequency of exceeding the Japanese AQS for O3 has increased, especially since 2000. For example, the fraction of days when the hourly O3 mixing ratios exceeded 120 ppb (i.e., 2 × AQS) increased, as shown in Fig. 4 (Miyakawa 2008).

According to the Tokyo Metropolitan Government (2005), the observed increase in the frequency of high-O3 days over the TMA cannot be explained by year-to-year variations in meteorological parameters, such as solar radiation and temperature. Thus, further understanding of the factors controlling O3 concentrations—for example, relationships between NOx and NMHCs, formation efficiency, and amounts of O3 transported from source areas...
Fig. 1. Schematic diagram of key processes of ozone, aerosols, and their precursor gases near megacity regions.

Fig. 2. Map of the Tokyo Metropolitan Area. This figure shows the locations of two sites, RCAST (square) and CESS (cross), where IMPACT measurements were conducted, and air quality monitoring stations (circles) maintained by the atmospheric environmental regional observation system (AEROS), Ministry of Environment. The area bounded by shaded lines depicts the approximate urban boundary. These 361 monitoring sites are color-coded by the mixing ratio of ozone obtained by AEROS (2004/8/13 1500 LT).
Fig. 3. Annual average hourly mixing ratios of NO\textsubscript{x} (black, left axis) and total NMHCs (shaded, right axis) measured at about 30 sites in Tokyo from 1991–2004. The original data used in this figure were provided by National Institute for Environmental Studies.

Fig. 4. Three-month summertime (June–August) percentages of days with hourly ozone mixing ratios exceeding 120 ppb at 41 sites in Tokyo (filled circles) and 57 sites in Saitama (open circles). The original data used in this figure were provided by the National Institute for Environmental Studies.
of NO\textsubscript{x} and NMHCs—are needed in order to assess effective ways to lower the levels of photochemical pollution over the TMA.

The mass concentrations of particles in fine mode in Tokyo decreased since 1996 (Minoura et al. 2006). Previous studies have shown that organic compounds constitute a substantial fraction of the total fine particle mass at various urban locations (Zhang et al. 2007). However, the chemical composition and formation mechanisms of organic aerosols are not completely understood because organic aerosols consist of numerous chemical species with a very wide range of chemical and thermodynamic properties.

Emissions from motor vehicles (gasoline and diesel) can be important sources of primary organic aerosol (POA) in urban areas. Secondary organic aerosol (SOA) is formed via oxidation of volatile organic compounds (VOCs) followed by condensation on existing particles or by homogeneous nucleation, as discussed in detail in recent reviews (Kanakidou et al. 2005; Fuzzi et al. 2006; Hullquist et al. 2009). Smog chamber experiments have shown that aromatic hydrocarbons (toluene, xylene, etc.,) from gasoline vapor can be a significant source of SOA in urban air (Odum et al. 1997). Biogenic hydrocarbons also contribute substantially to SOA in some urban areas (Szidat et al. 2004). Atmospheric measurements in urban areas have identified a large amount of water-soluble organic carbon (WSOC), which is likely the major constituent of SOA. WSOC generally consists of oxygenated organic compounds containing various functional groups such as alcohols, carboxyls, and dicarboxylic acids.

Black carbon (BC) particles, sometimes called elemental carbon (EC), which are emitted by incomplete combustion (Streets et al. 2003; Bond et al. 2004), alter the global radiation budget by absorbing solar visible radiation (Jacobson 2001; IPCC 2007) and, when deposited in polar regions, by changing snow albedo (Hansen and Nazarenko 2004). BC particles are often mixed with toxic compounds such as polycyclic aromatic hydrocarbons (PAH) and heavy metals upon emission and thus act as efficient carriers of these compounds to the human respiratory system (Samet et al. 2004; Somers et al. 2004).

An assessment of the contributions of primary emissions and secondary formation to ambient organic aerosol loadings in urban areas is important for developing regulatory strategies for particulate matter (PM) control. It is also important for estimating the direct/indirect climate forcing of organic aerosols because hygroscopic properties of organic aerosols depend upon chemical composition (Carslaw et al. 2009).

2. Integrated Measurement Program for Aerosol and oxidant Chemistry in Tokyo

Studies on characterizing primary emission and secondary formation of aerosols in the TMA have to date been very limited. Further observational studies of aerosols, especially organic aerosols (OA), near source areas are required in order to improve understanding of the amounts and chemical composition of aerosols exported from this large source area. Recognizing this, we conducted the Integrated Measurement Program for Aerosol and oxidant Chemistry in Tokyo (IMPACT) campaign with the specific goal of improving our understanding of atmospheric chemistry in the TMA. IMPACT was conducted within the framework of the International Global Atmospheric Chemistry Project (IGAC), Mega-Cities: Asia. The major objectives of IMPACT were:

- Characterizing the temporal and spatial changes of aerosols, oxidants, and their precursors, primarily through surface measurements near and downwind of urban centers.
- Characterizing the composition, mixing state, and physical properties of aerosols in urban air.
- Evaluating emission inventories of trace gases (e.g., NO\textsubscript{x}, SO\textsubscript{2}, NH\textsubscript{3}, and VOCs) through comparisons of ratios of concentrations of trace species observed in urban air.

The instruments used during IMPACT have been described in detail elsewhere (Kondo et al. 2006; Takegawa et al. 2006a). The acronyms used for instruments discussed here are summarized in Table 1. The observation sites were located at the Research Center for Advanced Science and Technology (RCAST), Komaba, Tokyo (35\degree39’N, 139\degree40’E), and the Center for Environmental Science in Saitama (CESS), Kisai, Saitama prefecture (36\degree05’N, 139\degree33’E), which is located about 50 km north of Tokyo (Fig. 2). They concern chemical processes of HO\textsubscript{x} radicals and O\textsubscript{3} formation (Kanaya et al. 2007, 2008) and emissions and transformation of primary aerosol, especially BC (Kondo et al. 2006; Shiraiwa et al. 2007), secondary aerosol, cloud condensation nuclei (CCN) activity, and the hygroscopicity of aerosol (Kuwata et al.
Table 1. Summary of acronyms used for instrumentation

<table>
<thead>
<tr>
<th>Terminology</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIMS</td>
<td>Chemical ionization mass spectrometer</td>
</tr>
<tr>
<td>AMS</td>
<td>Aerodyne aerosol mass spectrometer</td>
</tr>
<tr>
<td>PILS</td>
<td>Particle-into-liquid sampler</td>
</tr>
<tr>
<td>TOC analyzer</td>
<td>Total organic carbon analyzer</td>
</tr>
<tr>
<td>SP2</td>
<td>Single particle soot photometer</td>
</tr>
<tr>
<td>DMA</td>
<td>Differential mobility analyzer</td>
</tr>
<tr>
<td>APM</td>
<td>Aerosol particle mass analyzer</td>
</tr>
<tr>
<td>VTDMA</td>
<td>Volatility tandem DMA</td>
</tr>
<tr>
<td>VTAPM</td>
<td>Volatility tandem APM</td>
</tr>
<tr>
<td>HTDMA</td>
<td>Hygroscopicity tandem DMA</td>
</tr>
</tbody>
</table>

2007; Kuwata and Kondo 2008; Mochida et al. 2006; 2008). A summary of the definitions concerning OAs is provided in Table 2. Important findings recorded by IMPACT are summarized in Table 3.

3. OH and HO2 observations in relation to aerosol characterization

The OH radical is central to the oxidizing capacity of the troposphere and has a large effect on tropospheric composition, including secondary aerosol levels. Oxidation of SO2 and NOx by OH in the gas phase produces sulfuric and nitric acids, which can enter the particulate phase. Oxidation of VOCs leads to the formation of less-volatile organic species, significantly contributing to the particulate burden. Heterogeneous uptake of OH (Robinson et al. 2007) and possibly HO2 (Taketani et al. 2010) on preexisting organic aerosols will lead to composition changes of organic in the particle phase.

The concentrations of OH and HO2, a reservoir species of OH, were measured by laser-induced fluorescence at Komaba, an urban site, from January–February and July–August 2004 (Kanaya et al. 2007). They showed diurnal variations with daytime maxima (e.g., Fig. 5 for summer). In addition, HO2 in winter showed a secondary maximum in the evening (1800–2100 LT), likely produced by dark reactions of unsaturated hydrocarbons with O3 and NO3. The median values of the daytime peak concentrations of HO2 were 1.1 and 5.7 parts per trillion by volume (pptv) for the winter and summer periods, respectively, while the values for OH were 1.5 x 10^6 and 6.3 x 10^6 cm^-3. High HO2 mixing ratios (>50 pptv) were observed on a day in summer when O3 mixing ratios exceeded 100 ppbv. The 24-h average concentrations of OH as calculated from hourly median values were 5 x 10^5 and 2 x 10^6 cm^-3 in winter and summer, respectively.

A photochemical box model was constrained by ancillary observations, which include hydrocarbons directly measured and those indirectly estimated by taking previous studies into account. The model reproduced daytime OH concentrations to within 20% on average for the summer and winter periods (Kanaya et al. 2007), suggesting that the set of known reactions implemented in the model is able to describe the levels and variations of the oxidative capacity of the urban atmosphere. The model calculated HO2 concentrations agree with those observed to within 30% on average for summer and winter (Kanaya et al. 2007). However, the model significantly underestimated HO2 levels at high NO mixing ratios. Overall, the model underestimated the daytime HO2/OH ratio by a factor of 1.8 in winter and overestimated it by a factor of

Table 2. Summary of terminology used to describe organic aerosols (OA) in this study

<table>
<thead>
<tr>
<th>Terminology</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>OA</td>
<td>Organic aerosol, which is approximately equal to OOA + HOA</td>
</tr>
<tr>
<td>m/z 44</td>
<td>Equivalent mass concentration of OA represented by m/z 44 (a)</td>
</tr>
<tr>
<td>POA</td>
<td>Primary organic aerosol, OA component linearly correlated with CO (b)</td>
</tr>
<tr>
<td>SOA</td>
<td>Secondary organic aerosol = OA – POA – background OA (b)</td>
</tr>
<tr>
<td>OOA</td>
<td>Oxygenated OA obtained from AMS mass spectra (a)</td>
</tr>
<tr>
<td>HOA</td>
<td>Hydrocarbon-like OA obtained from AMS mass spectra (a)</td>
</tr>
<tr>
<td>OC</td>
<td>Total carbon of OA measured by thermal optical technique</td>
</tr>
<tr>
<td>WSOC</td>
<td>Total carbon of OA that is water-soluble, collected by PILS-WSOC (c)</td>
</tr>
<tr>
<td>WIOC</td>
<td>Total carbon of OA that is water-insoluble, not collected by PILS-WSOC (b), (c); WIOC = OC – WSOC</td>
</tr>
<tr>
<td>Org.-eq.</td>
<td>Organic equivalent mass concentration of an AMS m/z (a)</td>
</tr>
</tbody>
</table>

1.6 in summer. These issues require further experimental and modeling investigation.

Matsui et al. (2009) made three-dimensional (3-D) regional model calculations (MM5/CMAQ) by employing MADRID2 as the aerosol chemistry module, as discussed in Section 9. The OH levels observed during the summer of 2004 agreed with those calculated for the summer of 2003, although a possible reduction in actinic flux to produce OH due to high aerosol loading in Tokyo was not taken into account. Thus, it is expected that the simulation of secondary formation of organic, sulfuric, and nitric aerosols in the model is reasonable from the viewpoint of the oxidation rate by OH. The model, however, significantly underestimated the mass concentrations of SOA. Matsui et al. (2009) attributed this to unidentified NMHCs that might have produced more condensable species upon oxidation by OH.

The observed OH concentration was used to calculate the photochemical age of air masses from the concentration ratios of n-pentane and its oxidative product, 2-pentyl nitrate, observed at Kisai, a site downwind of Tokyo (Takegawa et al. 2006b), as discussed in more detail in Section 6.4. The calculated age ranged between 0 and 16 hours, when using the daytime (0600–1800 LT) average OH concentration of $4 \times 10^6$ cm$^{-3}$. It was verified that the observed NO$_x$/NO$_2$ ratio decreased exponentially with the calculated age. The decreasing rate is well explained by the OH oxidation of NO$_x$, suggesting the validity of determining

<table>
<thead>
<tr>
<th>Topic</th>
<th>Major findings</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrumentation</td>
<td>A HNO$_3$-CIMS with a new calibration/zero system was developed. Performance of an Aerodyne AMS was evaluated based on intercomparison with a PILS-IC and Sunset OC. A new method to quantify BC coating was developed using an SP2.</td>
<td>Kita et al. (2006) Takegawa et al. (2005) Moteki and Kondo (2007, 2008)</td>
</tr>
<tr>
<td>OH/HO$_2$/O$_3$</td>
<td>Measured OH was reproduced by a box model in winter and summer. Measured HO$_2$ was underestimated by the model in the high-NO$_x$ regime.</td>
<td>Kanaya et al. (2007) Kanaya et al. (2008)</td>
</tr>
<tr>
<td>VOCs</td>
<td>Seasonal variation of C$_2$–C$_7$ nonmethane hydrocarbons was quantified.</td>
<td>Shirai et al. (2007)</td>
</tr>
<tr>
<td>BC</td>
<td>Diesel emissions were identified as a major source of BC in Tokyo.</td>
<td>Kondo et al. (2006) Shiraia et al. (2007)</td>
</tr>
<tr>
<td>Nitrate</td>
<td>Nitrate-HNO$_3$ partitioning in summer was influenced by vertical mixing.</td>
<td>Morino et al. (2006)</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Only a small fraction (3% in winter and 18% in summer) of SO$_2$ emitted was converted to sulfate.</td>
<td>Miyakawa et al. (2007)</td>
</tr>
<tr>
<td>Organic aerosol</td>
<td>Seasonal and diurnal variation of POA and SOA was quantified. Most SOA (OOA) was found to be water soluble.</td>
<td>Takegawa et al. (2006a, 2007) Miyazaki et al. (2006) Kondo et al. (2007, 2008) Matsui et al. (2009)</td>
</tr>
<tr>
<td>Hygroscopicity and CCN</td>
<td>Hygroscopicity and CCN activity were perturbed by organics. BC can act as CCN with a small amount of coating material.</td>
<td>Mochida et al. (2006, 2008) Kuwata et al. (2007) Kuwata and Kondo (2008)</td>
</tr>
<tr>
<td>Outflow from Tokyo</td>
<td>Significant formation of organics and alteration of BC mixing state took place within ~0.5 days in summer</td>
<td>Takegawa et al. (2006b) Shiraia et al. (2007) Miyakawa et al. (2008)</td>
</tr>
</tbody>
</table>
photochemical age by this method (Takegawa et al. 2006b). The OA concentrations observed using an Aerodyne aerosol mass spectrometer (AMS) showed a strong positive dependence on age (Takegawa et al. 2006b; Miyakawa et al. 2008). It has been estimated that OA levels increased from 3.6 to 16.4 µg m\(^{-3}\) after 8–16 h of photochemical processing, with a rate of increase of 0.8–1.6 µg m\(^{-3}\) h\(^{-1}\) (Takegawa et al. 2006b). Miyakawa et al. (2008) examined the time evolution of individual mass-to-charge ratio (m/z) peaks of organic compounds. They also noted that the time evolution of sulfate

Fig. 5. (a) OH and (b) HO\(_2\) concentrations observed at RCAST in summer (open circles) compared with a model (gray lines). Shaded vertical bars associated with open circles indicate the ranges of 1-min data included in the 10-min intervals. Gray rectangles indicate nighttime periods (SZA > 85).
cannot be explained solely by the gas-phase oxidation of \(\text{SO}_2\) by \(\text{OH}\), suggesting the importance of aqueous-phase oxidation, consistent with current understanding of sulfur chemistry (Seinfeld and Pandis 2006).

4. General features of aerosol

The seasonally averaged mass concentrations of total \(\text{PM}_1\) aerosol (aerosol with diameters less than 1 \(\mu\)m) did not show significant seasonal variation during the measurement period, ranging between 17 and 20 \(\mu\)g m\(^{-3}\) (Takegawa et al. 2005). Non-refractory \(\text{PM}_1\) aerosol was measured using an AMS. Measurements of BC were made simultaneously with organic carbon (OC), using a semicontinuous thermooptical EC-OC analyzer (Sunset Laboratory, Inc.). Figure 6 shows the \(\text{PM}_1\) fraction of chemical composition measured at RCAST in summer and winter. Nitrate and sulfate were observed to be the major inorganic compounds in Tokyo. Sulfate dominated in summer while nitrate was more abundant in winter. Organic compounds were found to be the dominant component throughout the year (median 6–7 \(\mu\)g m\(^{-3}\), 40–60\% of the total). In summer, secondary aerosol (inorganic aerosol + SOA) constituted 40–90\% of the total \(\text{PM}_1\) mass concentration (Fig. 6). In winter, the fraction of secondary aerosol was even somewhat higher (50–90\%). It should be stressed that significant reductions in secondary aerosol levels are required in order to improve air quality in the TMA throughout the year.

5. Inorganic aerosol

5.1 Nitrate

Ground-based measurements of gas-phase HNO\(_3\) and particulate NO\(_3^-\) (PM\(_1\)) were made using chemical ionization mass spectrometer (CIMS) (gas-phase species) and AMS (particulate species) instruments with time resolutions of approximately 1 min (CIMS) and 10 min (AMS) (Morino et al. 2006). The thermodynamic equilibrium model ISORROPIA (Nenes et al. 1998) was coupled with a 1-D model to investigate the effect of vertical mixing during daytime on the partitioning of HNO\(_3\) and NO\(_3^-\). It was found that the time scales of thermodynamic equilibrium (\(\tau_e\)) and vertical mixing (\(\tau_m\)) were comparable (~10 min) (Morino et al. 2006). \(\tau_m\) was calculated using the ratio of the boundary layer depth to the convective velocity. \(\tau_e\) was calculated from gas-to-particle mass transfer flux by the following equation.

\[
\tau_e = \left( \frac{2\pi D_{\text{HNO}_3} \int_{-\infty}^{\infty} dN/d \log d \cdot \frac{1}{2\lambda_{\text{HNO}_3} \log d + 1} \, d \log d}{\beta_{\text{HNO}_3} C_{\text{HNO}_3}} \right)^{-1}
\]

Here, \(d\) represents particle diameter (m), \(dN/d \log d\) is the number size distribution of particles (m\(^{-3}\)), \(D_{\text{HNO}_3}\) is the diffusivity (m\(^2\) s\(^{-1}\)), \(\lambda_{\text{HNO}_3}\) is the mean free path (m), and \(\beta_{\text{HNO}_3}\) is the mass accommodation coefficient (dimensionless) of HNO\(_3\).

Thus, vertical mixing can increase the \(\text{NO}_3^-/\text{total nitrate}\) ratio at the surface beyond that predicted when only including thermodynamic equilibrium processes. Here, total nitrate TNO\(_3\) is defined as \(\text{HNO}_3 + \text{NO}_3^-\). The 1-D model reproduced the \(\text{NO}_3^-/\text{TNO}_3\) ratios observed during the daytime, whereas the equilibrium model significantly underestimated these ratios under daytime conditions in summer and autumn when vertical mixing affected the \(\text{NO}_3^-/\text{TNO}_3\) ratios, as shown in Fig. 7. The \(\text{NO}_3^-/\text{TNO}_3\) ratios were generally reproduced (within 13\%) by the 1-D model over the observed temperature (1–34°C) and relative humidity (RH) (18–95\%) ranges (Fig. 7). This study suggests that accounting for vertical mixing can greatly reduce the overestimation (underestimation) of daytime HNO\(_3\) (\(\text{NO}_3^-\)) by equilibrium models that has been reported in previous studies.

5.2 Sulfate

The formation of \(\text{SO}_4^{2-}\) and removal of \(\text{SO}_x = \text{SO}_2 + \text{SO}_4^{2-}\) were investigated using measurements of \(\text{SO}_2\), \(\text{SO}_4^{2-}\), and CO (Miyakawa et al. 2007). The \(\text{SO}_4^{2-}/\text{SO}_x\) ratio, which is a good indicator for the formation of \(\text{SO}_4^{2-}\), varies significantly with season; mean values were 0.45–0.50 for the summer period and 0.10–0.15 for the winter period. In order to assess the removal of \(\text{SO}_x\), the average remaining fraction of \(\text{SO}_x\) (\(\text{RSO}_x\)) was estimated by the following equation

\[
\text{RSO}_x = \frac{\text{Slope}_{\text{SO}_x/\text{CO}}}{\text{ERSO}_{\text{SO}_x/\text{CO}}},
\]

where \(\text{Slope}_{\text{SO}_x/\text{CO}}\) is the linear regression slope of the \(\text{SO}_x/\text{CO}\) correlation and \(\text{ERSO}_{\text{SO}_x/\text{CO}}\) is the emission ratio of \(\text{SO}_2\) to CO in Tokyo. Here, \(\text{RSO}_x\) represents the \([\text{Observed } \text{SO}_x]/[\text{Estimated } \text{SO}_x \text{ uninfluenced by removal}]\) ratio.

The average values of \(\text{RSO}_x\) were estimated to be 0.40 and 0.21 for the summer and winter periods.
respectively. Using the average values of $SO_2^+ / SO_x$ and $R SO_x$, the average formation efficiency of $SO_2^+ (e_{av})$ was estimated. Here, $e_{av}$ is the average molar ratio of the observed $SO_4^2-$ to the total SO$_2$ emitted. The $e_{av}$ value for the summer period (0.18) was much greater than that for the winter period (0.03). These results suggest that during summer (winter) about 60% (80%) of SO$_x$ was removed in
the boundary layer within about a day and about 20% (3%) of SO$_2$ formed SO$_3$ over Tokyo. The seasonal variations of these parameters are likely due to those of the boundary layer height and SO$_2$ oxidation rate.

6. Organics

6.1 Secondary organic aerosol

It is difficult to identify the chemical composition of OA from AMS mass spectra. However, it is possible to classify the approximate chemical composition corresponding to functional groups using characteristic mass/charge ($m/z$) ratios. For example, $m/z$ 44 (mostly COO$^+$) is a good marker of oxygenated organic compounds (dicarboxylic acids), and $m/z$ 57 (mostly C$_2$H$_7^+$) is a marker of aliphatic compounds. Therefore, the fraction of $m/z$ 57 is expected to be higher in chemically unprocessed aerosols and the fraction of $m/z$ 44 increases with aging (chemical processing). In fact, it has been shown that the $m/z$ 44/OA ratio was anti-correlated with the $m/z$ 57/OA ratio and the NO$_x$/NO$_2$ ratio (Takegawa et al. 2006a, 2006b).

CO is a good tracer for incomplete combustion, from which POA is also produced. POA and SOA were classified using their correlation with CO. This method is similar to the BC-tracer method used by Turpin and Huntzicker (1995). The lower envelope of OA-CO scatter plots mostly consist of the data obtained at 2200–0800 LT with $m/z$ 44/OA ratios lower than 0.05 and $m/z$ 57/OA ratios higher than 0.05, suggesting that most of OA in this regime was POA. The slope of the linear regression of these data (OA mass versus CO) is considered to represent the average POA/CO emission ratio (ER), which was estimated to be 0.011–0.014 $\mu$g $m^{-3}$ ppbv$^{-1}$. POA was defined using the ER as POA = ER × ΔCO, where ΔCO is the difference between the observed and background CO mixing ratios. SOA was given as SOA = OA − POA − BG, where BG is background OA (1–2 $\mu$g $m^{-3}$). BG was defined as the average of the lowest 5% OA values for each measurement period.

On an average, the POA did not exhibit a distinct diurnal variation, while the SOA showed a clear diurnal pattern (daytime peak at ~1300 LT) for the summer (Fig. 8), fall, and winter periods. At the daytime peak, the SOA concentration was nearly the same as POA for all periods, suggesting that significant SOA formation occurred in...
daytime throughout the measurement period. A second peak in SOA was found at \( \sim 2100 \) LT in summer and winter. This result suggests significant SOA formation even after sunset or a shift in the gas-particle equilibrium of SOA compounds after sunset.

6.2 Water-soluble organic carbon

Water-soluble organic carbon (WSOC) can significantly alter the hygroscopicity of aerosols and can be important in determining the ability of particles to act as cloud condensation nuclei (CCN) (Novakov and Penner 1993; Facchini et al. 1999). It is generally believed that under certain conditions (e.g., lack of biomass burning influence), total SOA is nearly equivalent to WSOC because SOA particles have oxygenated chemical functional groups (e.g., carboxylic groups) that lead to polar molecules with resulting water affinity (Saxena and Hildemann 1996). However, this point had not been experimentally demonstrated for ambient air. Semicontinuous measurements of submicron WSOC aerosol were made every 6 min in the Tokyo urban area, using a particle-into-liquid sampler (PILS) (Weber et al. 2001) with a total organic carbon (TOC) analyzer (Sullivan et al. 2004; Miyazaki et al. 2006, 2009). Comparison of the PILS-WSOC measurements with WSOC concentrations manually extracted from 12-h-integrated quartz filters for a 6-d period in Tokyo showed agreement within 12% (Miyazaki et al. 2006). In the following descriptions, the term WSOC is technically defined as particles sampled by the PILS and detected by the TOC analyzer after penetrating through a liquid filter.

Figure 9 shows diurnal variations of WSOC, OC, and WSOC/OC averaged for the winter and summer periods. The water-soluble fraction of OC is a useful parameter in understanding the composition and chemical processes of OA. The WSOC concentrations and WSOC/OC ratios showed diurnal variations similar to that for SOA, with peaks at 1200–1400 LT in summer and at 1400–1800 LT in winter. The observed WSOC levels could be interpreted as resulting from a combination of locally produced WSOC and that transported from an upwind region.

In summer, WSOC concentrations correlated well with those of \( \text{O}_3 \) \( (r^2 = 0.62) \) and the \( r^2 \) value increased to as high as 0.72 during daytime \((0600–1800 \text{ LT})\). The increase in WSOC was often observed under conditions of low wind speed \((< 2 \text{ m s}^{-1})\) and intense solar radiation. These results suggest that a major fraction of WSOC in summer was locally produced within TMA by photochemical processes that are also linked to \( \text{O}_3 \) production.

In winter, surface winds were dominated by northerlies (Miyazaki et al. 2006), which transported air from inland of the Kanto plain. WSOC increased in the late afternoon similar to CO, and WSOC was poorly correlated with \( \text{O}_3 \) \( (r^2 < 0.01) \). These results indicate that the elevated WSOC levels in winter were more strongly controlled by the transport of anthropogenic WSOC from an upwind region rather than in situ photochemical production near the sampling site.

The average WSOC/OC ratios were 0.20 and 0.35 \( \mu \text{gC}/\mu \text{gC} \) for winter and summer/fall, suggesting that the air masses sampled in summer and fall were more photochemically processed than those in winter. In general, the WSOC/OC ratios obtained in Tokyo were lower than those found at other urban and rural sites in previous studies (e.g., De cesari et al. 2001; Kiss et al. 2002). The WSOC/OC ratios depend on various factors, including chemical composition of organic compounds emitted.
from various sources and the degree of chemical processing. The observed lower WSOC/OC ratios compared to those reported in previous studies may reflect a smaller [WSOC precursors]/[POA] emission ratio in Tokyo. Most of POA is considered to be water-insoluble organic carbon (WIOC = OC - WSOC). It is also possible that the production of WSOC from biogenic VOCs was low in urban Tokyo.

6.3 Oxygenated organic aerosol (OOA)

Oxygenated organic aerosol (OOA) and hydrocarbon-like organic aerosol (HOA) were quantified from AMS mass spectral time series using an algorithm based on a custom principal component analysis (Kondo et al. 2007). In summer, about 80% of organic aerosols were oxygenated due to high levels of photochemical activity, which lead to the active formation of chemically processed OA. In winter, the fraction decreased to 39% because of the lower degree of oxidation. The slopes of the OA-OC correlations (OA/OC ratios) were 2.22 and 1.72 mg/mgC in summer and winter, respectively (Kondo et al. 2007). The seasonal variations of the OA/OC ratios were driven by those of OOA, because of relatively small seasonal variations in HOA.

In 2004, time series of AMS m/z 44 (m/z 57), a good marker for OOA (HOA), were highly (poorly) correlated with WSOC in winter and summer. The slope of the m/z 44—WSOC correlation was nearly constant at 0.423 ± 0.016 org.-eq. µg/µgC over the year—i.e., showing only 4% variability across the winter and summer seasons. The signal at m/z 44 is therefore an excellent marker for WSOC, given the high m/z 44-WSOC correlation and the stable m/z 44/WSOC ratio, independent of season. OOA was even more strongly correlated ($r^2 = 0.87–0.93$) with WSOC, despite the significant variabilities in the HOA/OOA and HOA/WSOC ratios, especially in winter. The average OOA/WSOC ratio was 3.24 ± 0.08 µg/µgC, also showing only 2% seasonal variability, as shown in Fig. 10. About 88 (69–100)% of OOA was estimated to be water soluble for both winter and summer from a comparison of WSOC with derived carbon mass concentrations of OOA.

In summer 2004, both OOA and OA correlated well with O$_x$ (¼ NO$_2$ + O$_3$) ($r^2 = 0.74$ and 0.79, respectively), as shown in Fig. 11. The OA-O$_x$ correlation was linear throughout the whole O$_x$ range, indicating that accumulation of photochemical products and their transport, including mixing processes, led to simultaneous increases in O$_3$ (>about 80 ppbv) and OOA (>15 µg m$^{-3}$).

6.4 Formation of OA during transport from the urban center

AMSs were deployed in conjunction at an urban site (RCAST) and a suburban site (CESS at Kisai in Saitama prefecture) 50 km north of Tokyo (Fig. 2) in the summer of 2004 to study the evolution of submicron OA in polluted air exported from Tokyo by the sea breeze (Fig. 12). As seen from this figure, the western part of the TMA is bounded by mountains (green color). The sea breeze combined with this topography to form a stable corridor (orange color) of northward transport of pollutants emitted from Tokyo. OA and SO$_4^{2-}$ were found to be the major constituents of PM$_{10}$ aerosols (40–50% and
20–30%, respectively) at both sites during the observation period. A large increase in OA was found at the site downwind of Tokyo, suggesting a significant formation of SOA with air mass aging (Takegawa et al. 2006b; Miyakawa et al. 2008). OA (normalized by C$_2$H$_2$ or BC to correct for the dilution effect) increased from ~4 to ~16 µg m$^{-3}$ in processed air (photochemical age of 8–16 h), corresponding to a growth rate of 0.8–1.6 µg m$^{-3}$ h$^{-1}$, as shown in Fig. 13 (Takegawa et al. 2006b). The NO$_x$/NO$_y$ ratios were also used to estimate aging of air, as discussed in Section 3. These results could

Fig. 11. Correlations of oxygenated organic aerosol (OOA) and organic aerosol (OA) with O$_x$ = O$_3$ + NO$_2$ at RCAST in summer 2004. Phase 1 is from July 31 to August 9, when persistent southerly wind flows (wind speed > 2 m s$^{-1}$) were dominant. Phase 2 is from August 10 to August 15, when sea-land breeze circulation was dominant. Generally, the wind speed was weaker than during phase 1, and the wind was southerly or southeasterly in the afternoon and mostly northerly or northeasterly in the night and early morning.

Fig. 12. Transport of pollutants from the urban center (Tokyo) to suburban areas by the sea breeze.
be useful for the validation of SOA formation and OA aging in chemical transport models.

The temporal evolution of OA mass spectra was also investigated using the AMS data (Miyakawa et al. 2008). The m/z peaks of organic compounds (and therefore their concentrations) relative to BC mass generally showed increasing trends with air mass aging. However, the trends varied significantly for different m/z peaks, suggesting the complexity of the temporal evolution of organic functional groups. The m/z 44 and 45 peaks, which are good markers of carboxylic groups in organic particles, showed larger increases than any other m/z peaks, suggesting an efficient formation of carboxylic functional groups on a time scale of hours during the measurement period.

7. Black carbon

7.1 Temporal variations of BC concentrations

BC concentrations and ΔBC/ΔCO were measured on an hourly basis at RCAST between May 2003 and February 2005 (Kondo et al. 2006). The median BC value was 1.8 ± 1.8 (central 67% values) μg m⁻³. BC and CO were well correlated throughout the measurement period due to a similarity in sources. BC generally decreased with increasing wind speed, indicating the importance of dilution by vertical mixing and horizontal transport in controlling its near-surface concentration. BC and ΔBC/ΔCO values showed diurnal variation, peaking in the early morning and reaching minimum values around midnight. This diurnal pattern
is similar to that of the traffic density of diesel trucks. ∆BC/∆CO for Sundays was lower by about 50% than weekday values, in reasonable agreement with changes in truck traffic. These results indicate that diesel trucks, especially heavy-duty trucks, are the dominant sources of BC in Tokyo.

∆BC/∆CO showed a seasonal variation, reaching broad maximum values in spring-autumn and reaching minimum values in midwinter, following the seasonal variation in temperature (Fig. 14). This may be due to an increase in CO emission from motor vehicles at colder temperature in winter, as observed in Beijing (Han et al. 2009). The overall dependence of ∆EC/∆CO on temperature was estimated to be 0.17 ng m⁻³/ppbv°C in the temperature range of 2–25°C.

More stringent regulation of emissions of particles from diesel vehicles was started in the TMA in October 2003. The ∆BC/∆CO values did not change, however, exceeding the natural variability (10%) after one year from the start of the new regulations, when the temperature dependence (or seasonal variation) is taken into account. This indicates the need for continued measurements to quantify the effect of regulation of particle emissions in the TMA in reducing BC concentrations.

7.2 Size distribution and mixing state of BC

The total instantaneous energy absorption rate \( A_{BC} \) of BC is expressed as

\[
A_{BC} = \int_{D_{BC}} \left( \frac{hc}{\lambda} \right) C_{\text{abs}}(D_{BC}, \lambda) \times (dN_{BC}/d \log D_{BC}) F_\lambda d\lambda d \log D_{BC},
\]

where \( h, c, \lambda, D_{BC}, C_{\text{abs}}(D_{BC}, \lambda), dN_{BC}/d \log D_{BC} \), and \( F_\lambda \) are Planck constant (6.63 × 10⁻³⁴ J s), the speed of light (3.0 × 10⁸ m s⁻¹), wavelength (nm), BC core diameter (nm), photo absorption cross section of BC (m⁻²), number size distribution (m⁻³), and solar actinic flux (photons m⁻² s⁻¹ nm⁻¹), respectively (Gao et al. 2008). \( C_{\text{abs}}(D_{BC}, \lambda) \) depends on refractive index, particle shape, and mixing state (Bond et al. 2006; Shiraiwa et al. 2010; Moteki et al. 2010; Moteki and Kondo 2010). In addition, the CCN activity of BC depends on the mixing state, as discussed in Section 8.2. Therefore, it is critically important to understand the microphysical properties (size distribution and mixing state) of BC in source regions and their evolution during transport to improve our understanding of the climatic impacts of BC.

The size distribution and mixing state of BC were
measured using a single-particle soot photometer (SP2) at Kisai (Shiraiwa et al. 2007). Polluted air was transported there from Tokyo under southerly wind conditions. The BC emissions were estimated to be greatest near the center of Tokyo (20 × 20 km²), rapidly decreasing toward suburban areas (Kannari et al. 2007). Consequently, Kisai is an appropriate site to investigate the evolution of the mixing state of BC aerosols transported from Tokyo.

The size distributions of BC measured using the SP2 at 0000 LT and 0900 LT on August 13, 2004 are shown in Fig. 15, as fit by mono-modal lognormal functions with mass median diameters of 145 (±9) and 150 (±10) nm, respectively. These peaks in the mass size distribution are in a similar range (100–200 nm) to those obtained previously in polluted urban areas of Tokyo (Kondo et al. 2006).

For mixing state, the number fraction of thickly coated BC (shell-to-core ratio > about 2) was obtained using the delay time (Δt) between the occurrence of the peaks of the scattering signal and the incandescence signal obtained by SP2. Figure 16 shows the relationship between the number fraction of the thickly coated BC with $D_{BC} = 180$ (±5) nm—relative to the total number of BC particles with the same $D_{BC}$—and photochemical age during August 11–12 and 13–14.

As the photochemical age advanced, the number fraction of thickly coated BC increased steadily because of formation of condensable gases by photochemical processes followed by condensation on BC. During August 11–12, the thickly coated BC and photochemical age were highly correlated ($r^2 = 0.84$). The number fraction of thickly coated BC increased from 7%–25% in about 12 h, resulting in the increase rate ($R_{coat}$) of the fraction of thickly coated BC for $D_{BC} = 180$ nm of 1.9 (±0.3)% h⁻¹. During the night of August 13, the number fraction of the thickly coated BC increased considerably from 0.12 (2300 LT, August 12) to 0.28 (0900 LT, August 13), although the photochemical age remained almost the same. A large increase was also observed during the evening of August 14. These events are likely attributable to the condensation of sulfate, nitrate, and organics on BC at lower temperatures and/or higher humidity during the night. As shown in Fig. 16, the intercepts of the fitted lines were approximately 0.07 (±0.02) during August 11–12, which indicates that about 7 (±2)% of BC particles were thickly coated initially.

Positive matrix factorization (PMF) (Paatero and Tapper 1993) was applied to investigate the time-dependent contributions of different coating
materials using the mass concentrations of sulfate, nitrate, and organics measured using an aerosol mass spectrometer. PMF is a factor analysis that imposes a non-negativity constraint on the resulting factors. Results show that, at $D_{BC} = 180$ nm, factors in which sulfate and organics dominated accounted for 90 (±7)% of the coating on BC during the daytime, indicating that the main coating materials were sulfate and organics. This is consistent with the observed increases in OA/BC and SO$_2^-$/BC ratios with photochemical aging as discussed in Section 6.4 (Miyakawa et al. 2008). Nitrate formed from HNO$_3$ and N$_2$O$_5$ also contributed substantially to coatings during the nighttime (2300–0600 LT) under high-RH conditions.

Evolution of the BC mixing state with time was simulated using a detailed box model (Oshima et al. 2009a; 2009b). Therefore, a fraction of thickly coated BC mass observed by SP2 was generally well reproduced. Model calculations showed that enhancements of mass absorption efficiency and CCN activity with a time scale of about a day.

In global scale 3-D models, BC particles are expressed in much simpler ways. For example, they are classified into two groups: hydrophobic and hydrophilic (e.g., Cooke and Wilson 1996; Chung and Seinfeld 2005; Park et al. 2005). In some of these models, the e-folding time of the transformation from hydrophobic to hydrophilic is assumed to be about 1 day, without observational evidence. The observations showed significant changes in the BC mixing state in 12 h in urban plumes. These results, together with the results discussed in Section 8.2 (CCN activity of BC), will improve our understanding of the key microphysical processes of BC. This will, in turn, lead to improved assessment of the effects of BC on climate by 3-D models.

8. Aerosol hygroscopicity and CCN activity of aerosols in Tokyo

8.1 Hygroscopicity

The aerosol hygroscopicity in Tokyo was measured using a hygroscopicity tandem differential mobility analyzer (HTDMA) (Rader and McMurry 1986; Mochida and Kawamura 2004) in August and November 2004, and the hygroscopicity data were analyzed with the AMS-derived chemical composition and CCN activity (Mochida et al. 2006; 2008). In summer, in addition to highly and slightly hygroscopic particles that were commonly found in the urban atmosphere (McFiggans et al. 2006; Mochida et al. 2006), aerosol particles showing intermediately hygroscopic growth appeared sporadically in accordance with the build-up of OOA (Fig. 17) (Mochida et al. 2008). This result suggests that the condensation of secondary organics, which has also been discussed on an aerosol mass basis (Takegawa et al. 2006a; Miyakawa et al. 2008), strongly alters aerosol hygroscopic properties. A rapid decrease in the hygroscopic growth factor under persistent southerly wind conditions (cf., Miyakawa et al. 2008) implies that aerosols entering the TMA change hygroscopicity by the condensation of organics. This sheds light on the importance of megacities not only as the aerosol source regions but also as the regions where pre-existing aerosols transported from the surrounding areas are strongly modulated.

In the time periods longer than those discussed in Mochida et al. (2008) (i.e., over several hours), formation of sulfate, which is highly hygroscopic, might counteract the lowering of aerosol hygroscopicity due to the condensation of secondary organics. Further, the condensed organics possibly change their hygroscopicity by chemical aging processes. These effects need to be investigated further in order to understand the evolution of aerosol hygroscopicity in the TMA and its outflow.

The relationship between hygroscopicity and CCN activity was assessed in November 2004 (Mochida et al. 2006). A new instrument setup, an HTDMA and a CCN counter (CCNC) connected in series, was used for the simultaneous measurement of these two properties. The particles for the CCN measurement were segregated by hygroscopicity as well as dry diameter to deal with Tokyo aerosols with complex mixing states. The correlation between the hygroscopicity and the CCN fraction of particles was successfully obtained and the possible role of the organic fraction, which perturbs the CCN activity of particles via both solute and surface tension effects, was inferred. Note that a hygroscopicity measurement under subsaturated RH conditions is currently accepted as a useful measure of the CCN activity, as shown by the kappa-Köhler theory (Petters and Kreidenweis 2007). While the CCN activity of less-hygroscopic particles in Tokyo was not assessed in detail by Mochida et al. (2006), combination of the volatility measurements with the HTDMA-CCNC measurements has revealed that the coating thickness on non-volatile cores (likely BC) strongly controls the CCN activity of less-hygroscopic particles (Kuwata et al. 2007), as discussed in Section 8.2.
Fig. 17. Time series of (a) hygroscopic growth factors, (b) chemical composition (50 < \(d_{wa}\) < 200 nm (\(d_{wa}\): vacuum aerodynamic diameter)), OO: oxygenated organics, HO: hydrocarbon-like organics, and the number concentrations of 100-nm particles with (c) slightly, (d) intermediately, and (e) highly hygroscopic properties (squares) measured at RCAST. The mass concentration of oxygenated organics is also presented (triangles in 1c–1e). Reproduced by permission of American Geophysical Union, Mochida M., T. Miyakawa, N. Takegawa, Y. Morino, K. Kawamura, Y. Kondo, 2008: Significant alteration in the hygroscopic properties of urban aerosol particles by the secondary formation of organics. Geophys. Res. Lett., 35, L02804, doi:10.1029/2007GL031310.
8.2 CCN activity of black carbon

a. Theoretical considerations

In discussing the CCN activity of BC particles, it is useful to calculate the CCN activity of a particle composed of an insoluble spherical core and a single soluble component coating the core on the basis of Köhler theory. This idealized model ignores some characteristics of real BC particles (e.g., particle morphology and complexity in the chemical composition of condensed compounds); however, it still captures some important features of their CCN activity.

The equilibrium vapor saturation ratio of water ($s$) for particles with a dry diameter of $d_{\text{dry}}$ and insoluble core diameter of $d_{\text{core}}$ is expressed as a function of the diameter of the droplet ($D_p$) (Seinfeld and Pandis 1998; Kuwata et al. 2007).

$$\ln s = \frac{A}{D_p} - \frac{B(d_{\text{dry}}^3 - d_{\text{core}}^3)}{D_p^3 - d_{\text{dry}}^3} \left( \frac{4M_w \sigma}{RT \rho_w} B \equiv \nu \frac{M_w \rho_s}{\rho_w M_s} \right),$$

(4)

where $\sigma$ is the surface tension, $M_w$ and $M_s$ are the molecular weights of water and solute, $\rho_w$ and $\rho_s$ are the densities of water and solute, respectively; $\nu$ is the stoichiometric number of ions and molecules, and $\psi$ is the osmotic coefficient.

The first term on the right-hand side of equation (4) represents the Kelvin effect. The Kelvin effect increases the equilibrium vapor pressure of water because of the surface tension of the droplet. The second term on the right-hand side shows Raoult’s effect. Raoult’s effect decreases the equilibrium vapor pressure due to the mixing of solute. When we consider a single particle, $d_{\text{dry}}$ and $d_{\text{core}}$ are constants. In this case, $s$ depends strongly on $D_p$, because the variabilities of $A$ and $B$ are relatively small. The calculated $s$ as a function of $D_p$, the so-called Köhler curve, reaches a maximum value ($S_{\text{max}}$) at a certain $D_p$. The supersaturation ($S$) corresponding to this value is called the critical supersaturation (critical $S = (S_{\text{max}} - 1)$). The balance between the Kelvin and Raoult’s effects determines the critical $S$.

Figure 18 shows the critical $S$ of $d_{\text{dry}} = 100$-nm particles as a function of $d_{\text{core}}$. The calculations were made for an insoluble core coated with ammonium sulfate and glutaric acid. The parameter $B$ in equation (4) is a function of the chemical properties of the coating material ($M_s$ and $\rho_s$). Consequently, the critical $S$ depends on the chemical composition of the coating material. The volume fraction of the core ($V_{\text{core}}/V_{\text{total}}$) is also shown in Fig. 18 as a function of $d_{\text{core}}$. When $d_{\text{core}} < 80$ nm, the volume fraction of the coating material is larger than $V_{\text{core}}/V_{\text{total}}$, and the critical $S$ does not strongly depend on $d_{\text{core}}$. In this region, the critical $S$ is mainly determined by the chemical composition of the coating material. When $d_{\text{core}} > 80$ nm, $V_{\text{core}}/V_{\text{total}}$ exceeds the volume fraction of the coating material and the critical $S$ increases with the increase in $d_{\text{core}}$. In this region, $S$ is sensitive to the amount of coating. This theoretical calculation
indicates that the CCN activity of BC particles strongly depends on the amount of condensed compounds and their chemical composition. Atmospheric observations employing novel instruments were made in Tokyo to understand the CCN activities of atmospheric BC particles within this framework, as discussed in detail below.

b. Dependence of CCN activity on the amount of condensed compounds

Because various kinds of aerosol particles exist in the atmosphere, it is critically important to classify fresh BC particles in order to investigate their CCN activity. It has been shown that the HTDMA can select particle type on the basis of hygroscopicity. McMurry et al. (1996) showed that less-hygroscopic particles are likely soot particles and more-hygroscopic particles are mainly composed of secondary compounds such as sulfate. In addition, recent studies showed that a differential mobility analyzer (DMA)-aerosol particle mass analyzer (APM) system can classify particle type by effective density \( \rho_{\text{eff}} \), which is defined by the following equation:

\[
m_p = \frac{\pi}{6} \rho_{\text{eff}} d_m^3.
\]

where \( m_p \) is the particle mass selected by the APM, and \( d_m \) is the mobility diameter classified by the DMA (McMurry et al. 2002). An HTDMA was employed by Kuwata et al. (2007), and a DMA-APM was used by Kuwata et al. (2009).

The volatility technique is one of the most important methods that are currently available to measure BC mixing state in connection with CCN activity. The volatility technique employs a heater to volatilize condensed compounds on BC such as ammonium sulfate, ammonium nitrate, and organic compounds (Kondo et al. 2006). By placing the heater in between two particle classifiers such as DMAs, it is possible to detect the change in particle size caused by volatilization. This system is called a volatility tandem DMA (Sakurai et al. 2003; Philippin et al. 2004; Kuwata et al. 2007). A volatility tandem APM (VTAPM) can quantify the amount of compounds coating BC (Kuwata et al. 2009).

The instrumental setup to investigate the CCN activity of BC particles was described by Kuwata et al. (2009). In short, particles were selected on the basis of their \( d_m, m_p, \) and \( \rho_{\text{eff}} \) using the DMA-APM system. Selected particles were examined by VTAPM, VTDMA, and CCN counter. The VTAPM measured the mass of condensed compounds on BC \( \Delta m \) and the VTDMA was employed to determine the number fraction of fresh BC particles. CCN activity was measured by employing a CCN counter (CCNC).

Figure 19 shows the relationship between the mass of condensed compounds and the CCN activity of BC particles observed in Tokyo (Kuwata et al. 2009). \( (\text{CCN/CN})_{\text{BC}} \) denotes the number fraction of CCN-active BC particles. It is clear that CCN activity strongly depends on \( \Delta m \). \( (\text{CCN/CN})_{\text{BC}} \) increases with increasing \( \Delta m \). \( (\text{CCN/CN})_{\text{BC}} \) is equal to 0.5 at \( \Delta m = 0.18 \) fg (femto gram, \( 10^{-15} \) g) for particles with a diameter of 100 nm at \( S = 0.9\% \). This value can be considered as the criterion separating hydrophobic BC and hydrophilic BC. Kuwata et al. (2009) further explored the chemical composition of condensed compounds and found that organic compounds are the major component of the condensed compounds in their measurements in Tokyo.
c. Relationship between BC mixing state and size-resolved CCN spectra

Kuwata et al. (2008) measured the CCN size distribution and BC mixing state simultaneously. A VTDMA was employed to measure the BC mixing state in Tokyo. BC particles were categorized into two types on the basis of the VTDMA measurements. One group was less-volatile (thinly coated) BC particles and another group was more-volatile (thickly coated) particles. The observations were conducted in January 2007.

Figure 20 shows the high correlation between the CCN-inactive fraction (100 nm, \( S = 0.6\% \)) and number fractions of thinly coated BC particles measured at RCAST. This good correlation shows that it is a good approximation to regard CCN-inactive particles under these conditions (100 nm, \( S = 0.6\% \)) as thinly coated BC particles.

\[
\text{DMA1} = 100 \text{ nm (SS = 0.60\%)}
\]

\[
\text{Slope} = 0.91 \\
\text{r}^2 = 0.85
\]

Fig. 20. Correlation between the CCN-inactive fraction (100 nm, \( S = 0.6\% \)) and number fractions of thinly coated BC particles measured at RCAST. This good correlation shows that it is a good approximation to regard CCN-inactive particles under these conditions (100 nm, \( S = 0.6\% \)) as thinly coated BC particles.

\[
\text{all particles} \\
\text{CCN (0.6\%)} \\
\text{Thinly coated BC} \\
\text{Thinly coated BC + POA}
\]

\[
\text{CCN inactiv} \\
\text{Thinly coated BC}
\]

Fig. 21. Number size distributions of all aerosol particles, CCN, and thinly coated BC particles measured at RCAST in Tokyo in winter 2007. For large (>100-nm) particles, the number concentration of CCN-inactive particles is almost equal to that of thinly coated particles.

9. 3-D chemistry transport model calculations of \( O_3 \) and \( PM_1 \) aerosols

For a systematic understanding of formation, transport, and removal processes of aerosols around the TMA, studies using a 3-D regional chemistry transport model (CTM) (MM5 and CMAQ-MADRID2) were made (Matsui et al. 2009). Figure 22 shows the model-calculated daytime \( O_3 \) and SOA distributions for August 4, 2003, as an example. The model calculations generally reproduced well diurnal variations of the spatial distribution of \( O_3 \) around the TMA in summer observed by the atmospheric regional observation system (AEROS), maintained by local governments. A sea breeze developing during the daytime brought precursor gases emitted within the urban center to the north, causing \( O_3 \) enhancements in downwind areas (50–100 km distant) in the afternoon. A relatively small normalized mean bias (NMB = 24%)
and a high correlation coefficient \( r = 0.68 \) of daytime averages (statistics for 610 AEROS stations) indicate that day-to-day variations of the spatial \( O_3 \) distribution were also captured by the model calculations. Sulfate and ammonium aerosol concentrations observed at RCAST were also well reproduced (within 25%, Figs. 23a, 23b), although nitrate concentrations were overestimated by a factor of two, suggesting that important factors controlling inorganic aerosol concentrations are generally understood.

On the other hand, as shown in Fig. 23c, model calculations of SOA significantly underestimated AMS-derived OOA concentrations at RCAST; they are a factor of 5 or less, on average. Within the factor-of-5 underestimation, the underestimation of the organic carbon concentration is a factor of 3.4, while that in the ratio of oxygen and hydrogen to carbon is a factor of 1.5. A possible cause of SOA underestimation was examined from the viewpoint of a shortage of precursor VOCs. At RCAST, total carbon amounts of identified NMHCs (\( C_2-\text{C}_{10} \) NMHCs) accounted for only half of those that appeared in GC chromatograms. Although model calculations generally reproduced identified NMHCs well, they also underestimated observed total carbon concentrations by a factor of 2. Unidentified high-molecular-weight NMHCs can be a potential source of SOA. A sensitivity simulation has shown that the observed OOA amounts can be reproduced by assuming SOA yields of the unidentified NMHCs that are approximately a factor of 2.4 greater on average than those of identified NMHCs. This shows the importance of reliable measurements of high-molecular-weight NMHCs.

In spite of severe underestimations, features of the observed temporal variation of OOA, such as diurnal and day-to-day variations, were reproduced by model calculations reasonably well \( (r = 0.59 \) and 0.67 for hourly and daytime average values, respectively) (Fig. 23c), suggesting that initial oxidation processes of precursor VOCs largely control the temporal variation of SOA. Furthermore, a clear positive correlation was found between OOA and \( O_3 + NO_2 \) for both observations (Kondo et al. 2008) and model calculations. Considering regional enhancements of daytime \( O_3 \) over the large area around the TMA \((200 \times 200 \text{ km}^2)\) in summer (Fig. 22), it is expected that enhancements of OOA concentrations are regional phenomena (Fig. 23c), causing regional impacts on air quality and possibly the radiation field.

Fig. 22. Spatial distribution of concentrations at the surface: (a) \( O_3 \) concentrations observed by AEROS, (b) simulated \( O_3 \) concentrations, and (c) simulated SOA concentrations. Values at 1400 LT on August 4, 2003 are shown.
10. Perspectives and future studies

The methodology used for IMPACT is schematically shown in Fig. 24. First, a combination of a limited number of fully instrumented observational sites (super sites) and monitoring stations of fundamental species has been proven to be cost-effective for megacity studies. During the IMPACT experiments, two super sites were set up (Fig. 12); one was located near the urban center of Tokyo (RCAST) and the other was about 50 km downwind (CESS). Because of the typical transport time of 3–7 h, time-resolved measurements provided quite useful information on the chemical evolution of polluted air. Second, instrumentation for vertical sounding, including lidar, were also useful, because changes in the boundary layer height cause corresponding changes in the concentrations of various species measured at the surface. Third, regional-scale model calculations were evaluated by the data obtained by the system mentioned above. Model calculations are useful in improving our understanding of chemistry and transport processes over the entire TMA.

Together with the scientific findings obtained through the studies in the TMA, the framework used in this study will be very useful for understanding chemistry and transport in other megacities in Asia, especially considering that many of them are also located in coastal areas, i.e., Beijing, Shanghai, Hong Kong, Guangzhou, and Seoul.

Fig. 23. Time series of hourly observed (dots) and calculated (line) fine aerosol concentrations at RCAST: (a) sulfate, (b) ammonium, and (c) observed OOA (left axis) and calculated SOA (right axis). Dotted vertical lines denote every 0000 LT.
Acknowledgments

This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), strategic international cooperative program of Japan Science and Technology Agency (JST), and the global environment research fund of the Japanese Ministry of the Environment (B-083). This study was conducted as a part of the Megacities: Asia Task under the framework of the International Global Atmospheric Chemistry (IGAC) project. We thank L. Sahu in assisting in the revision of the manuscript.

References


Bond, T. C., G. Habib, and R. W. Bergstrom, 2006: Limit-
ations in the enhancement of visible light absorp-


Chung, S. H., and J. H. Seinfeld, 2005: Climate re-
response of direct radiative forcing of anthropo-

Cooke, W., and J. Wilson, 1996: A global black car-


Facchini, M. C., M. Mircea, S. Fuzzi, and R. J. Charl-
son, 1999: Cloud albedo enhancement by surface-

Fuzzi, S., et al., 2006: Critical assessment of the current state of scientific knowledge, terminology, and re-

Gao, R. S., et al., 2008: Calculations of solar shortwave heating rates due to black carbon and ozone ab-


Szidat, S., et al., 2004: Radiocarbon (C-14)-deduced biogenic and anthropogenic contributions to organic carbon (OC) of urban aerosols from Zurich, Switzerland. *Atmos. Environ.*, 38, 4035–4044.


