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Formation and transport of oxidized reactive nitrogen, ozone, and secondary organic aerosol in Tokyo

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Measurements of the major reactive nitrogen species (NOx), NOy, peroxycylic nitrates, HNO3, and particulate nitrate (NO3-), total reactive nitrogen (NOx), volatile organic compounds, OH and HO2, and organic aerosol were made near the urban center of Tokyo in different seasons of 2003–2004 to study the processes involving oxidized forms of reactive nitrogen and O3. Generally, NOx constituted the dominant fraction of NOx throughout the seasons. The NOy/NOx and HNO3/NOx ratios were lowest and highest, respectively, in summer, owing to the seasonally high OH concentration. The fraction of NO3- that remained in the atmosphere after emission (RNO3-) decreased with the decrease in the NOy/NOx ratio in summer and fall. It is likely that the median seasonal-diurnal variations of O3 + NO2 were controlled by those of the background O3 levels, photochemical O3 formation, and vertical transport. O3 showed large increases during midday under stagnant conditions in mid-August 2004. Their in situ production rates calculated by a box model were too slow to explain the observed increases. The high O3 was likely due to the accumulation of O3 from previous days in the upper part of the boundary layer (BL) followed by transport down to the near the surface by mixing after sunrise. Considering the tight correlation between O3 and secondary organic aerosol (SOA), it is likely that SOA also accumulated during the course of sea-land breeze circulation in the BL.


1 Introduction

Large amounts of reactive gases, in particular NOx and volatile organic carbons (VOCs), 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 O3 levels [Guttikunda et al., 2005; Ramanathan et al., 2007]. In urban areas, O3 is mainly produced by reactions between NO and peroxy radicals generated from oxidation of carbon monoxide (CO) and VOCs initiated by reaction with OH [e.g., Thornton et al., 2002; Kleinman et al., 2005]. The oxidation of NOx can lead to the formation of nitric acid (HNO3), nitrate aerosol (NO3-), and peroxycylic nitrates (PANs). Oxidation of VOCs also leads to the formation of secondary organic aerosol (SOA) [e.g., de Gouw et al., 2005; Sullivan et al., 2006; Takegawa et al., 2006b], although the chemical species contributing to the O3 and SOA formation are different [e.g., Odum et al., 1997; Hoffmann et al., 1997; Griffin et al., 1999]. SOA generally constitutes the major fraction of fine-mode aerosol mass concentration. Reactive nitrogen, O3, and SOA play important roles in the atmospheric environment, including acid deposition, effects on human health, visibility, and climate. In order to assess the impacts of NOx and VOCs emitted from local sources on surrounding areas, we need to understand quantitatively the key processes involved in their oxidation and the fate of the oxidized species near the source regions.

The abundance of NOx is controlled by its emission, oxidation, and transport. During daytime, NOx is oxidized to HNO3 via oxidation of nitrogen dioxide (NO2) by the hydroxyl radical (OH):

\[ \text{(R1)} \quad \text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}. \]
where M represents a third body (usually N₂ or O₂). During the nighttime, HNO₃ is formed via oxidation of NO₂ followed by hydrolysis of N₂O₅ in aqueous-phase H₂O (H₂O (aq)) [e.g., Tieg et al., 2003; Takegawa et al., 2004]:

\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O}(\text{aq}) \rightarrow 2\text{HNO}_3. 
\]

HNO₃ reacts with gas-phase NH₃ to form ammonium nitrate (NH₄NO₃) aerosol:

\[
\text{HNO}_3(g) + \text{NH}_3(g) \rightarrow \text{NH}_4\text{NO}_3(\text{aerosol}) + \text{H}_2\text{O}(\text{aerosol}). 
\]

[4] HNO₂ and NO₃ are lost through wet and dry deposition. The deposition velocity of NO₃ is an order of magnitude smaller than that of HNO₃ [e.g., Morino et al., 2006, and references therein].

[5] NO₂ is also oxidized by peroxyacyl radicals (RC(O)O₂) to form PANs (RC(O)O₂NO₂ = peroxyacetyl nitrate (PAN) + peroxypropionyl nitrate (PPN) + peroxy-n-butyryl nitrate (PbBN) + peroxy-i-butyryl nitrate (PiBN) + peroxyacryl nitric anhydride (APAN) + peroxymethylacryloyl nitrate (MPAN)) [e.g., Tanimoto et al., 1999; Tanimoto and Akimoto, 2001; Roberts et al., 2001]:

\[
\text{RC(O)O}_2 + \text{NO}_2 \rightarrow \text{RC(O)O}_2\text{NO}_2. 
\]

RC(O)O₂ is produced by oxidation of VOCs by OH. Acyl radicals formed from aldehydes and alcohols quickly add oxygen to form peroxyacyl radicals. PANs are thermally unstable and decompose back to NO₂ quickly at high temperatures. In addition, alkyl nitrates (RONO₂) have been observed to constitute a significant portion of oxidized reactive nitrogen [Day et al., 2003].

[6] Chemical processes of reactive nitrogen inside megacities control fluxes of NOx and oxidized reactive nitrogen to surrounding regions. A number of studies have been made to understand oxidation processes of NOx and the resulting partitioning of total reactive nitrogen, NOy (=NO + NO₂ + PANs + HNO₃ + HONO + HO₂NO₂ + NO₃ + N₂O₅ + organic nitrate + NO₅), in urban and suburban air through field observations at various locations, mainly over the U.S. and Europe [e.g., Fahey et al., 1986; Singh et al., 1986; Parrish et al., 1993, 1998, 2002; O’Brien et al., 1997; Ridley et al., 1998; Neuman et al., 2002; Day et al., 2003]. These observations identified NOy, HNO₃, and PANs to be dominant components of NOy, although their fractions showed large temporal and spatial variations. However, quantitative understanding of the reactions involving these species is still limited partly because of the difficulty in deploying a suite of instruments for accurate and time-resolved measurements of relevant parameters throughout the seasons. On the other hand, the rate-limiting reactions for O₃ formation are

\[
\begin{align*}
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2, \\
\text{RO}_2 + \text{NO} & \rightarrow \text{RO} + \text{NO}_2.
\end{align*}
\]

[7] The processes of oxidation of NOx and VOCs via OH are closely coupled with the O₃ formation processes via formation of HO₂ and RO₂, as can be seen from reactions (R1)–(R6) [e.g., Kanaya et al., 2007, 2008]. Therefore, it is useful to elucidate the relationships of the reactive nitrogen, HO₂ (OH and HO₂) radicals, and O₃ for an improved understanding of O₃ formation, especially near urban areas, where reactions leading to its formation are active. In addition, SOA have been observed to correlate well with O₃ in summertime in the TMA [Takegawa et al., 2006a; Miyakawa et al., 2008]. O₃, together with OH and NO₃, oxidize VOCs, initiating a number of chemical and physical processes leading to SOA formation [e.g., Kalberer et al., 2000]. Therefore, SOA-O₃ correlations should also be useful in understanding the chemistry of these species.

[8] In addition to the chemical processes, the levels of reactive nitrogen and O₃ are subject to transport processes. In the TMA, it has been suggested that accumulation of formed O₃ in the boundary layer (BL) plays an important role in elevating surface O₃ levels under stagnant conditions in summer [Wakamatsu et al., 1983, 1996, 1999]. However, these studies are limited to O₃ variations. Simultaneous measurements of oxidized reactive nitrogen and SOA will give us further insights on transport processes of the oxidized species in this area.

[9] Intensive measurements of reactive nitrogen, together with other precursors of O₃ and PM₁ aerosol (aerosol with diameters smaller than 1 μm) chemical composition were made for the first time in Tokyo, Japan, in 2003–2004, as a part of the series of the Integrated Measurement Program for Aerosol and Oxidant Chemistry in Tokyo (IMPACT) campaigns, which were conducted within the framework of the International Global Atmospheric Chemistry Project (IGAC), Mega-Cities: Asia. Using these data, we investigate the seasonal and diurnal variations of reactive nitrogen species, especially in relation to HO₂ radicals and O₃ near the urban center of Tokyo. The relationship between O₃ and SOA in summer is also discussed.

2. Observations

2.1. Location and NOx Sources

[10] NOy, individual NOx compounds, and PM₁ aerosol were measured near the urban center of Tokyo during the periods of 24 July to 13 August and 1–15 October in 2003 and 20 January to 2 February, 16 June to 7 July, and 26 July to 14 August in 2004. Air samplings were made about 20 m above ground level from a building on the Research Center of Advanced Science and Technology (RCAST) campus of the University of Tokyo (Komaba; 35.66°N, 139.66°E) in Japan. RCAST is located 57 m above sea level and about 2 km from major roads or highways, near the southeastern edge of the Kanto Plain, about 20 km from Tokyo Bay [Kondo et al., 2006; Takegawa et al., 2006a; Morino et al., 2006], as shown in Figure 1.

[11] Figure 1 also shows the distribution of NOx emissions in the TMA by Kannari et al. [2004]. The TMA is defined as the area over seven prefectures labeled in Table 1. Motor vehicles are estimated to be the dominant contribution (55%) to NOx emissions in the TMA. Emissions from diesel vehicles are estimated to be particularly important to NOx emissions in the TMA (38%). RCAST is located within a high-NOx emission area. How-
ever, the measurements presented here were not significantly influenced by emissions from highly localized sources, as discussed in section 3.1.

2.2. Instrumentation

Table 2 summarizes the measurements used for the present study, including accuracies, precisions, and time resolutions. The key measurements at RCAST are described in brief below. NO, NO₂, and NOy were measured using a NO-O₃ chemiluminescence detector [Kondo et al., 1997; Nakamura et al., 2003; Miyazaki et al., 2005]. The ambient air was sampled through a 2-m-long perfluoroalkoxy (PFA) hose with a 4.6-cm inner diameter (ID) at a flow rate of 1200 standard liter per minute (slm). From the center of the unheated hose, a small portion of the ambient air was drawn up into the NO, NO₂, and NOy instrument by way of a 6.35-mm outer-diameter (OD) PFA tube (1 m long) heated to 35°C. NO₂ was catalytically converted to NO on the surface of a gold tube heated to 300°C. The conversion efficiency of particulate NH₄NO₃ (boiling point 210°C) was measured to be 91 ± 9%, while the conversion efficiencies for KNO₃, NaNO₃, and Ca(NO₃)₂ were 1, 2, and 3% respectively [Miyazaki et al., 2005]. The overall collection efficiency of NH₄NO₃ should be close to 1, because of high flow in the PFA hose, heated PFA tube, and high conversion efficiency. On the other hand, NaNO₃ in sea salt is excluded from NOy because of the conversion efficiency close to zero. NO₂ was converted to NO by a photolytic converter (Droplet Measurement Technologies, Inc., USA) with a conversion efficiency of about 30–40%. Systematic errors of the measurements of NO, NO₂, and NOy were 10, 16, and 12%, respectively. The random errors of the NO, NO₂, and NOy measurements with 1-min time averaging were ±4 parts per trillion by volume (pptv), ±9 pptv, and ±68 pptv, respectively, for their typical ambient mixing ratios.

HNO₃ was measured by a chemical ionization mass spectrometer (CIMS) using the selective ion-molecule reaction of SiF₅ with HNO₃ [Kita et al., 2006; Morino et al., 2006]. We used the same PFA hose, as that used for the NOy measurements, for ambient air sampling. The detection limit for a 10-s integration was 19 pptv, and the overall accuracy was about 9% at an HNO₃ mixing ratio of 1 part per billion by volume (ppbv). Interference of particulate NO₃ to the HNO₃ measurements was negligible [Kita et al., 2006].

Particulate NO₃, predominantly in the form of NH₄NO₃, was measured using an Aerodyne Aerosol Mass Spectrometer (AMS) with a time resolution of 10 min [Takegawa et al., 2005; Morino et al., 2006]. Organic aerosol (OA) was also measured by AMS [Takegawa et al., 2005]. The sample line from the inlet to the AMS consisted of a PM2.5 (2.5 µm) cyclone and a 1-mm-inner-diameter stainless steel tube (6 m long). The AMS measurements were compared extensively with a particle-into-liquid sampler combined with an ion chromatography analyzer (inorganic components) and a Sunset Laboratory semicontinuous thermal-optical carbon analyzer (organics). The detection limits of nitrate and OA were 0.02 and 0.3 µg m⁻³, respectively [Takegawa et al., 2005]. The actual size cut of the AMS was determined to be nearly PM₁ (1 µm) by the more restrictive transmission characteristics of the aerodynamic lens.

Each species of PANs (=PAN + PPN + PiBN + PiAN + APAN + MPAN) was measured every 15 min using a gas chromatograph with a negative ion chemical ionization mass spectrometer [Tanimoto et al., 1999, 2002]. The detection limit for PAN, a dominant species of PANs, was 15 pptv with an overall measurement uncertainty of 20%. VOCs, including alkyl nitrates and nonmethane hydrocarbons (NMHCs) (RONO₂; C₁-C₅) were measured using whole air sampling followed by laboratory analysis using gas chromatography [Blake et al., 2003a, 2003b; Simpson et al., 2003, and references therein]. Although the sampling interval was 2–6 h, the actual integration time was 5–10 s for each sample. The whole air sample data were merged with the other data without further averaging or smoothing. The RONO₂ data were available only for the summer period. The temporal variations of C₂-C₇ VOCs are shown by Shirai et al. [2007].

CO was measured using a nondispersive infrared absorption (NDIR) instrument (Model-48, Thermo Environmental Instruments (TEI), USA). The overall precision and accuracy of the 1-min CO data were estimated to be 4 ppbv and 20 ppbv, respectively, at a CO mixing ratio of 400 ppbv [Kondo et al., 2006]. O₃ was measured using an ultraviolet spectrometer (CIMS) using the selective ion-molecule reaction of HNO₃ with O₃ [Morino et al., 2005]. O₃ was measured using an ultraviolet absorption (NDIR) instrument (Model-48, Thermo Environmental Instruments (TEI), USA). The overall precision and accuracy of the 1-min CO data were estimated to be 4 ppbv and 20 ppbv, respectively, at a CO mixing ratio of 400 ppbv [Kondo et al., 2006]. O₃ was measured using an ultraviolet spectrometer (CIMS) using the selective ion-molecule reaction of HNO₃ with O₃ [Morino et al., 2005].

Table 1. NOy Emissions in Tokyo and the TMA

<table>
<thead>
<tr>
<th>Source</th>
<th>Tokyo¹ (Gg/a)</th>
<th>TMA² (Gg/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy industries</td>
<td>153 (100)</td>
<td>337 (100)</td>
</tr>
<tr>
<td>Manufacturing industries and construction</td>
<td>25 (16)</td>
<td>66 (20)</td>
</tr>
<tr>
<td>Transport (total)</td>
<td>74 (48)</td>
<td>187 (55)</td>
</tr>
<tr>
<td>Transport (gasoline)</td>
<td>14 (9)</td>
<td>35 (11)</td>
</tr>
<tr>
<td>Transport (diesel)</td>
<td>46 (30)</td>
<td>129 (38)</td>
</tr>
<tr>
<td>Transport (others)</td>
<td>14 (9)</td>
<td>23 (6)</td>
</tr>
<tr>
<td>Other sectors (commercial, etc.)</td>
<td>13 (8)</td>
<td>26 (8)</td>
</tr>
<tr>
<td>Waste incineration</td>
<td>7 (4)</td>
<td>15 (5)</td>
</tr>
</tbody>
</table>

¹Relative contribution in percent is given in parentheses.
Table 2: Systematic and Random Errors in the Mixing Ratios of Measured Trace Gases, Aerosols, and Meteorological Parameters

<table>
<thead>
<tr>
<th>Species</th>
<th>Technique</th>
<th>Accuracy (%)</th>
<th>Time Resolution</th>
<th>Integration Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>chemiluminescence (CL)</td>
<td>10 (at 2 ppbv)</td>
<td>1 min</td>
<td>1 min</td>
</tr>
<tr>
<td>NO₂</td>
<td>CL with photolysis converter</td>
<td>16 (at 13 ppbv)</td>
<td>1 min</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td>NOy CL with heated gold converter</td>
<td>12 (at 21 ppbv)</td>
<td>1 min</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td>HNO₃ chemical ionization mass spectrometer</td>
<td>9 (at 1 ppbv)</td>
<td>1 min</td>
<td>1 min</td>
</tr>
<tr>
<td></td>
<td>PANs gas chromatography</td>
<td>19 (at 50 pptv)</td>
<td>1 min</td>
<td>1 min</td>
</tr>
<tr>
<td></td>
<td>HONO diffusion scrubber/ion chromatography</td>
<td>20</td>
<td>1 min</td>
<td>1 min</td>
</tr>
<tr>
<td></td>
<td>O₃ UV absorption</td>
<td>5</td>
<td>1 min</td>
<td>1 min</td>
</tr>
<tr>
<td></td>
<td>(NO₂) spectroradiometer</td>
<td>20</td>
<td>2 min</td>
<td>2 min</td>
</tr>
</tbody>
</table>
|                  | Wind, temperature, RH                           | 4 (at 10% in the diffuse component of the full hemisphere, resulting in an underestimation of approximately 10% in the diffuse component of the radiation field. The direct sun was sometimes blocked in the morning up to solar elevations of 20°. However, at those solar elevations, the actinic flux is dominated by the diffuse skylight component, and the overall reduction in actinic fluxes due to horizon obscuration was generally less than 10%. Taking all of the above uncertainties into consideration, we estimate the overall uncertainty in the derived photolysis rates to be ±20%. Most of the data described above (gases, aerosols, and actinic flux) were merged into time intervals of 10 min for the present analysis.

In addition to the measurements at RCAST, concentrations of inorganic aerosol were measured by collecting aerosol particles on quartz fiber filters using a high-volume filter sampler (Model 130, Kimoto, Osaka, Japan), followed by analysis using an ion chromatography analyzer at the
Etchujima campus (35.66°N, 139.80°E) of the Tokyo University of Marine Science and Technology (TUMSAT). TUMSAT is located 10 km east of RCAST (Figure 1). The sampling of aerosol particles was made in two size ranges using an impactor with diameters larger than 2 μm (coarse mode) and smaller than 2 μm (PM2) [Murayama et al., 1999].

2.3. Box Model

In this work we used a photochemical box model to calculate RO2 (organic peroxy) radical concentrations to derive ozone formation (F(O3)), destruction (D(O3)), and net formation (P(O3)) rates. The O3 formation processes include reactions (R5) and (R6). F(O3) and D(O3) are expressed as

\[
F(O_3) = \left( k_{OH2+NO}[HO2] + \sum k_{RO2+NO}[RO2] \right) [NO],
\]

where [ ] denotes the number density of the indicated species, k is the reaction rate coefficient of the corresponding reaction indicated by the suffix, and \( \varphi \) is the yield of NO2 from reaction (R6):

\[
D(O_3) = k_{O1D+HO}[O1D][H_2O] + (k_{OH+O3}[OH] + k_{HO2+O3}[HO2]
+ \sum k_{olefin+O3}[olefin])[O3] + k_{OH+NO2}[NO2][OH],
\]

\[
P(O_3) = F(O_3) - D(O_3).
\]

Observed HO2 concentrations and model-calculated RO2 were used in equations (1) and (2). Briefly, the box model takes into account the Regional Atmospheric Chemistry Mechanism (RACM) [Stockwell et al., 1997] with updated kinetic parameters. The heterogeneous loss of HO2 is not taken into account in the standard runs. For constraining the model, we used the observed concentrations and parameters (O3, CO, H2O, SO2, NO, NO2, CH4, NMHCs, PANs, temperature, ambient pressure, and \( J \) values) in the analysis of the winter and summer data. In total, 54 NMHCs were taken into account in the 11 model categories, as described by Kanaya et al. [2007]. For winter, the measured concentrations of HONO, HCHO, and CH3CHO were also used to constrain the model. Summertime concentrations of HONO were calculated by the model. HCHO and CH3CHO concentrations estimated empirically from CO and (O3 + NO2) concentrations were used for the summer period. All of the other oxygenated species were calculated in the model, with an assumption that dilution occurred with a time constant of 6 h to represent horizontal advection of air masses influenced by urban emissions.

We compared the model-calculated HO2 values with the observed values to check the reliability of the calculated RO2 used in calculating P(O3). For winter, the model-calculated OH and HO2 levels during the daytime agreed better with observations when the concentrations of internal olefin (OLI in RACM) and reactive alkanes (HC8) were increased by factors of 3 and 5, respectively (run 2), above the standard-run hydrocarbon levels. Therefore, the calculated RO2 from run 2 and the observed HO2 were used to calculate P(O3).
For summer, increased OLI and HC8 concentrations lead to a significant overestimation of HO2 by the model. Therefore the calculated RO2 from the standard run and the observed HO2 were used for the P(O3) calculations, although the effect of using the different levels of RO2 on P(O3) was not significant. More detailed descriptions of the model and the comparisons between calculated and observed OH and HO2 radical concentrations have been given by Kanaya et al. [2007].

The same box model was used to simulate temporal variations of PAN in summer, with slightly different settings. In this case, the constraint on PAN concentrations was removed and its concentrations were predicted considering photochemical processes included in RACM, a deposition term with a velocity of 0.2 cm s$^{-1}$, and a dilution term with a time constant of 6 h. The BL height was assumed to be 1000 m in the daytime and 100 m in the nighttime to calculate the loss rate owing to surface deposition. The model-calculated PAN concentrations are compared with those observed in section 6.1.

3. Temporal Variations of Reactive Nitrogen and Oxidants

3.1. Spatial Uniformity of the Observational Data

Figure 2a shows a 1-h resolution time series of NOx, O3, and NO2 measured at RCAST and of NOy and O3 at routine monitoring stations of the Atmospheric Environmental Regional Observation System (AEROS) (http://soramame.taiki.go.jp/) at Setagaya (5 km southwest of RCAST) and at a site very close to TUMSAT during the summertime period to illustrate the spatial uniformity of these species near the urban center of Tokyo. Here Ox represents oxidants O3 + NO2, taking into account conversion of O3 to NO2 (O3-NO titration). The nighttime decrease of Ox was significantly smaller than that of O3, because Ox is better conserved than O3. Figure 2a also shows time series of HNO3, NO3, PANs, and NOy. NOy represents reactive nitrogen measured using molybdenum converters with particulate filters mounted upstream of chemiluminescence NO detectors. The conversion efficiencies of molybdenum converter for NO2, HNO3, and PAN were observed to be close to those for gold catalytic converter [Fehsenfeld et al., 1987]. However, the unheated filter and metal plumbing parts removed HNO3 and particulate nitrate, although the removal efficiencies were not quantified. The NOy levels measured at RCAST during a different period were found to be between the NOx and NOy levels (not shown). It is likely that NOy represents NOx + organic nitrates. Temporal variations of NOx and NOy measured at RCAST and Setagaya were similar, indicating that the air masses observed at RCAST were not significantly affected by localized sources. The differences in the NOx variations between Setagaya and TUMSAT were larger than those between RCAST and Setagaya, although the average NOx levels were similar. It is likely that the larger differences between Setagaya and TUMSAT reflect the relatively short lifetime of NOx (about 8 h) and differences in the accumulated amounts of NOx along trajectories of air masses sampled at these sites, as discussed in detail in Appendix A. The temporal variations of the O3 concentration at the three sites were very similar. These features of NOx and O3 were basically the same for other seasons, suggesting their spatial
uniformity near the urban center of Tokyo throughout the seasons.

3.2. Reactive Nitrogen and P(O3)

[25] Figure 2b shows time series of NO, HO2, P(O3), and NO3/NOx and NO/NOx ratios at RCAST during the latter part of the summertime period. The whole summertime observation period of 31 July to 14 August in 2004 was classified into two phases according to meteorological conditions, as discussed in previous studies [Takegawa et al., 2006b; Miyakawa et al., 2008]. Detailed meteorological analyses in relation to concentrations of VOCs and CO have been given by Shirai et al. [2007]. Phase 1 is from 31 July to 9 August, when persistent southerly wind flows (wind speed > 2 m s\(^{-1}\)) were dominant, as shown in Figure 3 of Shirai et al. [2007]. The concentrations of O\(_3\) were relatively low because clean maritime air was transported from the Tokyo Bay to RCAST.

[26] Phase 2 is from 10 August to 15 August, when sea-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. The diurnal change in the wind direction over the TMA is shown in Figure 4 of Shirai et al. [2007]. During this phase,

the concentrations of O\(_3\), HNO3, and PANs showed large increases in the daytime, especially during the period of 12–14 August. SOA also showed simultaneous increases during this period [Kondo et al., 2007; Miyakawa et al., 2008].

[27] The difference in the circulation between phases 1 and 2 is clearly reflected in the trajectories of air masses sampled at RCAST at 1400 LT on 2 and 13 August, as shown in Figure 3. The backward trajectories were calculated using the wind data obtained at RCAST. The high-emission areas in the study region are marked in red. A more detailed description of the trajectory calculation is given in Appendix A. The air originating from RCAST at 0400 LT moved southward and returned to the original site at 1400 LT on 13 August. On 2 August, air originating near the coast of the Tokyo Bay reached RCAST in about 2 h.

[28] Figure 4 shows time series of O\(_3\), NO\(_x\), NO\(_y\), HNO\(_3\), NO\(_3\), PANs, O\(_3\), NO, HO2, and P(O3) at RCAST for the winter period. The nighttime decrease of O\(_3\) was much smaller than that of O\(_x\), similar to summer. In winter, HNO3 levels were much lower and NO\(_3\) levels were much higher than in summer as discussed by Morino et al. [2006]. PANs showed stable background levels with some daytime increases. However, the level of the daytime enhancements was much lower than that in phase 2 in summer. NO\(_3\) and NO\(_y\) concentrations showed increases with a period of about 3–4 days, lasting for about 2 days. Primary organic aerosol (POA) and SOA showed correlated increases, as shown in Figure 3 of Kondo et al. [2007]. Weak wind conditions favored accumulation of all these species. On a larger perspective, the periodic synoptic-scale cyclonic activity typical for this season set these conditions (Y. Morino et al., manuscript in preparation, 2008).

4. Median Diurnal and Seasonal Variations

4.1. \(J(O^1D)\), OH, and HO2

[29] For a statistical analysis of NO\(_x\) oxidation and O\(_3\) formation processes, the observed data sets were classified into two categories on the basis of \(J(O^1D)\) values. High-\(J(O^1D)\) (HJ) days were defined as days when the maximum values of \(J(O^1D)\) within the day exceeded a threshold value, which was determined as half of the maximum value of \(J(O^1D)\) in each season. The rest of the data were classified as low-\(J(O^1D)\) (LJ) days. The threshold values and the numbers of HJ and LJ days are summarized in Table 3. The HJ and LJ days generally represent sunny and cloudy days, respectively. Figure 5 shows the diurnal variations of the median \(J(O^1D)\) values on HJ and LJ days in the three seasons and the median OH and HO2 concentrations on HJ days in two seasons. \(J(O^1D)\) was a good indicator of

<table>
<thead>
<tr>
<th>Number of High- and Low-(J(O^1D)) Days</th>
<th>Maximum (Threshold) Values of (J(O^1D))</th>
<th>Number of High-(J(O^1D)) Days</th>
<th>Number of Low-(J(O^1D)) Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer 2003</td>
<td>36 (18) (\times) (10^{-6})</td>
<td>18</td>
<td>2</td>
</tr>
<tr>
<td>Fall 2003</td>
<td>22 (11) (\times) (10^{-6})</td>
<td>11</td>
<td>2</td>
</tr>
<tr>
<td>Winter 2004</td>
<td>13 (7) (\times) (10^{-6})</td>
<td>16</td>
<td>2</td>
</tr>
<tr>
<td>Summer 2004</td>
<td>39 (20) (\times) (10^{-6})</td>
<td>19</td>
<td>0</td>
</tr>
</tbody>
</table>

*Threshold values were defined as about half of the maximum values of \(J(O^1D)\) for each season and are given in parentheses.*
photochemical activity, judging from the correspondence between the $J(\text{O}_1\text{D})$ values and the OH concentrations. On HJ days between 1000 and 1500 local time (LT) the daytime $J(\text{O}_1\text{D})$ values in winter were about 3–5 times lower than those in summer. The daytime $J(\text{O}_1\text{D})$ values for LJ days between 1000 and 1500 LT were about 2–3 times lower than those for HJ days. The number of HJ days was much larger than that of LJ days. In addition, precipitation occurred only on one day both in summer and winter. Therefore, when averaged over all HJ and LJ days, the median and average values of the species discussed in this paper are very close to those for HJ days.

[30] OH and HO$_2$ reached maximum values during daytime in summer and winter. However, in winter, HO$_2$ showed high values from late afternoon throughout the nighttime comparable to those during midday. Detailed discussion of the temporal variations of OH and HO$_2$ has been made by Kanaya et al. [2007].

[31] The e-folding lifetimes of NO$_x$ oxidation (reaction (R1)) on HJ days were calculated using the observed OH concentrations (Table 4). They are estimated to be 6–10 h and 25–39 h during daytime in summer and winter, respectively. For LJ days, when OH data were not available, the NO$_x$ lifetime was estimated using the OH concentrations calculated by the parameterization method given by Ehhalt and Rohrer [2000]. The ratios of [calculated OH]/[observed OH] were 0.98 ± 0.62 in summer and 1.0 ± 0.56 in winter for HJ days between 1000 and 1500 LT, indicating the reliability of the calculated OH. The lifetimes of NO$_x$ for LJ days are estimated to be 6–8 times longer than those for HJ days.

4.2. NO$_y$ and NO$_x$

[32] Figure 6 shows the diurnal variations of the median values of NO, NO$_2$, NO$_x$, NO$_y$, NO$_x$/NO$_y$ ratio, O$_3$, and O$_x$ in three seasons and P(O$_3$) in two seasons for HJ days. The seasonal and diurnal variations of NO$_x$ are consistent with the column NO$_2$ measurements derived from the spectroradiometer [McKenzie et al., 2008]. The NO$_x$/NO$_y$ ratios for LJ days are also shown. These values are summarized in Table 4.

**Figure 5.** Diurnal variations of the median values of $J(\text{O}_1\text{D})$ on (a) high-$J(\text{O}_1\text{D})$ (HJ) days in summer (closed squares), fall (open triangles), and winter (open circles) and (b) low-$J(\text{O}_1\text{D})$ (LJ) days in summer (closed squares), fall (open triangles), and winter (open circles). (c) The OH concentration on HJ days in summer and winter. (d) The HO$_2$ concentration on HJ days in summer and winter. Bars represent 1σ values.

Table 4. Average Daytime OH Concentrations and the Corresponding NO$_x$ Lifetimes

<table>
<thead>
<tr>
<th></th>
<th>1000–1500 LT</th>
<th></th>
<th>0600–1800 LT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[OH] (cm$^{-3}$)</td>
<td>Lifetime (hours)</td>
<td>[OH] (cm$^{-3}$)</td>
</tr>
<tr>
<td>Winter 2004 (HJ)</td>
<td>1.2 × 10$^6$ (observed)</td>
<td>25</td>
<td>0.77 × 10$^6$</td>
</tr>
<tr>
<td>Winter 2004 (LJ)</td>
<td>0.17 × 10$^6$ (calculated)</td>
<td>180</td>
<td>0.095 × 10$^6$</td>
</tr>
<tr>
<td>Summer 2004 (HJ)</td>
<td>5.5 × 10$^6$ (observed)</td>
<td>6.3</td>
<td>3.5 × 10$^6$</td>
</tr>
<tr>
<td>Summer 2004 (LJ)</td>
<td>0.96 × 10$^6$ (calculated)</td>
<td>35</td>
<td>0.58 × 10$^6$</td>
</tr>
</tbody>
</table>
Table 5 together with the values of other reactive nitrogen species. The median NOy (NOx) concentrations ranged over 20–42 (16–39) ppbv. The NOy concentrations were generally negatively correlated with wind speed, as has been found for CO and elemental carbon (EC) [Kondo et al., 2006]. The average wind speeds were generally higher during the daytime than during the nighttime, and the frequency of wind speeds exceeding 3 m/s was highest in summer. The BL height also increased after sunrise. Ceilometer observations showed that the top of the BL typically increased from 0.4 km at midnight to 1.5 km at midday. The vertical mixing during the daytime also contributed to the decrease in the concentrations of species emitted from the surface [Kondo et al., 2006; Morino et al., 2006].

Reflecting these dynamic conditions, the NOx and NOy concentrations were generally lower during the daytime than during the nighttime, and they were higher in winter than in summer on average.

In addition to these variations caused by the meteorology, the NOx concentrations peaked in the early morning during summer and fall. In winter, NOx and NOy peaked around midnight, in addition to the peak in the early morning, likely owing to the accumulation of these species in the shallow nocturnal wintertime BL. Peaks in EC at the same local times have been ascribed to the emissions from diesel vehicles [Kondo et al., 2006]. It is also very likely that these NOy peaks were due to enhanced NOx emissions from heavy-duty diesel vehicles, which are known to emit NOx and EC much more efficiently than gasoline vehicles [Miguel et al., 1998; Sawyer et al., 2000; Marr et al., 2002].

On HJ days, the median NOx/NOy ratios showed significant diurnal variation (Figure 6). The ratios were systematically higher during the nighttime than during the daytime throughout the year. The ratios were lower in summer and fall (0.63–0.89) than those in winter (0.83–0.95). The NOx/NOy ratios differed little between summer and fall in spite of the difference in the $J(0^1D)$ values. This is because of the larger removal of NOy in summer than in fall associated with larger HNO3/NOy ratios, as discussed in more detail in section 5.

On LJ days, the median NOx/NOy ratios showed little diurnal variation and remained high (mostly above 0.8), irrespective of season. These temporal variations are consistent with the longer lifetimes of NOx on LJ days.

4.3. HNO3 and Particulate NO3

The seasonal-diurnal variations of the median values of NOx species other than NOx (i.e., HNO3, NO3 (PM1), total nitrate (TN = HNO3 + NO3)), and PANs) and their
ratios to NO$_3$ for HJ days are shown in Figures 7 and 8, respectively. They are also summarized in Table 5.

[37] The temporal variations of HNO$_3$, NH$_3$, and NO$_3$ were discussed in detail by Morino et al. [2006], in terms of chemistry and vertical transport. Here, we discuss the important points relevant to the present analysis. The median HNO$_3$ concentrations were highest in summer (0.58 ppbv) and lowest in winter (0.06 ppbv). By contrast, the nitrate concentrations were lowest (0.16 ppbv) in summer and highest in winter (1.1 ppbv). The seasonal variation of TN was much reduced compared with each component of TN, that is, HNO$_3$ and NO$_3$. The seasonal variations of HNO$_3$ and NO$_3$ were due to the seasonal variation of the HNO$_3$-NO$_3$ partitioning. The high (low) temperatures in summer (winter) shifted the HNO$_3$-NO$_3$ partitioning to the gas (aerosol) phase.

[38] In summer and fall, the median HNO$_3$ concentrations showed a distinct diurnal variation: they started to increase...
soon after sunrise, reaching maximum values in the early afternoon, and decreased rapidly toward sunset. This diurnal pattern is similar to those for O₃ and $J(O^1D)$, suggesting that the concentrations of HNO₃ in urban air were mainly controlled by in situ photochemical production via reaction (R1) and removal-transport processes with similar time constants. The similarity of the production and accumulation between O₃ and HNO₃ was also shown in Figure 2. In winter, the

<table>
<thead>
<tr>
<th>Uncertainty (%)</th>
<th>Summer Median (1σ)</th>
<th>Average</th>
<th>Fall Median (1σ)</th>
<th>Average</th>
<th>Winter Median (1σ)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOₓ</td>
<td>11–12</td>
<td>16 (9.5–26)</td>
<td>19 ± 12</td>
<td>24 (13–49)</td>
<td>30 ± 19</td>
<td>39 (18–68)</td>
</tr>
<tr>
<td>NO₃</td>
<td>12</td>
<td>20 (13–33)</td>
<td>24 ± 14</td>
<td>29 (18–54)</td>
<td>35 ± 20</td>
<td>42 (21–75)</td>
</tr>
<tr>
<td>HNO₃</td>
<td>11–34</td>
<td>0.58 (0.13–2.0)</td>
<td>1.2 ± 1.6</td>
<td>0.17 (0.07–0.49)</td>
<td>0.33 ± 0.45</td>
<td>0.06 (0.02–0.13)</td>
</tr>
<tr>
<td>PANs</td>
<td>20</td>
<td>0.14 (0.02–0.64)</td>
<td>0.45 ± 1.0</td>
<td>no data</td>
<td>0.47 (0.28–0.68)</td>
<td>0.48 ± 0.22</td>
</tr>
<tr>
<td>NOₓ</td>
<td>26</td>
<td>0.16 (0.05–0.66)</td>
<td>0.37 ± 0.55</td>
<td>0.37 (0.10–1.5)</td>
<td>0.71 ± 0.84</td>
<td>1.1 (0.33–2.8)</td>
</tr>
<tr>
<td>TN</td>
<td>20–31</td>
<td>0.92 (0.25–2.7)</td>
<td>1.6 ± 1.9</td>
<td>0.63 (0.30–2.0)</td>
<td>1.0 ± 0.97</td>
<td>1.2 (0.38–2.8)</td>
</tr>
<tr>
<td>NOₓ/NO₃</td>
<td>16–18</td>
<td>0.84 (0.69–0.92)</td>
<td>0.80 ± 0.14</td>
<td>0.84 (0.74–0.89)</td>
<td>0.82 ± 0.09</td>
<td>0.91 (0.87–0.96)</td>
</tr>
<tr>
<td>HNO₃/NOₓ</td>
<td>16–37</td>
<td>0.03 (0.01–0.10)</td>
<td>0.05 ± 0.07</td>
<td>0.01 (0.00–0.02)</td>
<td>0.01 ± 0.02</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>PANs/NOₓ</td>
<td>31</td>
<td>0.01 (0.00–0.03)</td>
<td>0.02 ± 0.04</td>
<td>no data</td>
<td>0.01 (0.00–0.02)</td>
<td>0.02 ± 0.01</td>
</tr>
<tr>
<td>NOₓ/NO₃</td>
<td>30–31</td>
<td>0.01 (0.00–0.02)</td>
<td>0.01 ± 0.01</td>
<td>0.01 (0.00–0.04)</td>
<td>0.02 ± 0.02</td>
<td>0.03 (0.01–0.06)</td>
</tr>
<tr>
<td>TN/NOₓ</td>
<td>23–33</td>
<td>0.04 (0.01–0.12)</td>
<td>0.07 ± 0.07</td>
<td>0.01 (0.00–0.05)</td>
<td>0.03 ± 0.03</td>
<td>0.03 (0.01–0.06)</td>
</tr>
<tr>
<td>ΔNOₓ</td>
<td>102–273</td>
<td>2.1 (1.5–2.8)</td>
<td>2.4 ± 1.6</td>
<td>no data</td>
<td>1.6 (1.1–2.6)</td>
<td>2.8 ± 3.4</td>
</tr>
<tr>
<td>TN/NOₓ</td>
<td>84–176</td>
<td>0.23 (0.16–0.30)</td>
<td>0.24 ± 0.16</td>
<td>no data</td>
<td>0.32 (0.23–0.42)</td>
<td>0.35 ± 0.18</td>
</tr>
<tr>
<td>PANs/NOₓ</td>
<td>87–176</td>
<td>0.06 (0.03–0.09)</td>
<td>0.08 ± 0.07</td>
<td>no data</td>
<td>0.13 (0.09–0.18)</td>
<td>0.16 ± 0.12</td>
</tr>
<tr>
<td>ΔNOₓ/NOₓ</td>
<td>132–323</td>
<td>0.69 (0.59–0.78)</td>
<td>0.67 ± 0.19</td>
<td>no data</td>
<td>0.50 (0.40–0.60)</td>
<td>0.49 ± 0.22</td>
</tr>
<tr>
<td>CO</td>
<td>5</td>
<td>260 (150–480)</td>
<td>300 ± 170</td>
<td>330 (230–490)</td>
<td>360 ± 160</td>
<td>480 (320–760)</td>
</tr>
<tr>
<td>O₃</td>
<td>6–9</td>
<td>14 (2.8–39)</td>
<td>21 ± 22</td>
<td>17 (2.9–34)</td>
<td>20 ± 17</td>
<td>11 (1.7–27)</td>
</tr>
</tbody>
</table>

Number of data (n)

4126
2056
2584

Table 5. Median and Average Values of NOₓ, NOₓ, HNO₃, PANs, NO₃, Total Nitrate, NOₓ/NOₓ, HNO₃/NOₓ, PANs/NOₓ, NOₓ/NOₓ, TN/NOₓ, TN/NOₓ, PANs/NOₓ, ΔNOₓ/NOₓ, CO, O₃, and the Number of Data

*aAll the species concentrations units are in ppbv. The values in parentheses are 1σ values (central 67%).

Figure 7. (a–d) Diurnal variations of the median values of the HNO₃, NOₓ, TN = HNO₃ + NOₓ, and PANs concentrations on HJ days in summer, fall, and winter. Bars represent 1σ values.
HNO₃ concentration showed little diurnal variation, with a median HNO₃ concentration of ~0.2 ppbv. It also showed little difference between HJ and LJ days (not shown).

In contrast to the relatively regular diurnal variation of HNO₃, the NO₃ concentrations showed rather irregular variations. In summer, NO₃ peaked in the morning (0.3 ppbv), reached a minimum of < 0.1 ppbv in the late afternoon, and then increased again during the nighttime. The NO₃ concentrations were much lower than those of HNO₃, especially during daytime. In fall, the diurnal patterns of HNO₃ and NO₃ were similar to those in summer, although NO₃ showed a broader peak (about 0.5–0.8 ppbv) from midnight to early afternoon. The HNO₃ concentration on LJ days (not shown) was lower than that on HJ days by a factor of 2, reflecting lower photochemical activity. In winter, the median NO₃ concentrations (0.6–1.7 ppbv) were much higher than those of

Figure 8. (a–c) Same as Figure 7 but for the HNO₃/NOy, NO₃/NOy, TN/NOy, PANs/NOy, and Σ(NOy)/NOy ratios.
HNO₃ (≈0.2 ppbv). The NO₃⁻ concentrations on LJ days were comparable to or higher than that on HJ days. On HJ days, the HNO₃/NOy and NO₃⁻/NOy ratios showed diurnal and seasonal variations similar to those for HNO₃, NO₃⁻, and TN, as discussed above. Here we define NOz = NOy − NOx to represent the oxidized form of NOx. As discussed in section 4.2, NOx constituted a dominant fraction of NOy. The uncertainty of NOz is estimated to be as large as 82–174% owing to the subtraction of the two large terms. The median TN/NOz ratios for summer and winter are shown in Table 5, together with their uncertainties. The median TN/NOz ratios in winter were higher than those in summer. In summer HNO₃ > NO₃⁻ and the median HNO₃/NOz = 0.23. In winter, NO₃⁻ > HNO₃ and the median NOz/NO₂ = 0.32.

4.4. NO₃⁻ in Sea-Salt Particles

Uptake of HNO₃ onto sea-salt particles (NaCl) has been suggested to be an important pathway of NOy removal in marine and coastal areas [e.g., Davies and Cox, 1998; Spokes et al., 2000]:

\[
\text{HNO}_3(g) + \text{NaCl}(s, \text{aq}) \rightarrow \text{NaNO}_3(s, \text{aq}) + \text{HCl}(g).
\] (R7)

The uptake coefficient of HNO₃ onto sea-salt particles (dominated by NaCl) measured by laboratory experiments using an aerosol flow tube was 0.5 ± 0.2, which is much higher than that for mineral dust [Guimbaud et al., 2002].

Figure 9a shows variations of the concentrations of NO₃⁻ in the coarse mode (diameter larger than 2 μm), hereinafter denoted as coarse-NO₃⁻, and NO₃⁻ (PM₂) measured at TUMSAT in summer 2004. The HNO₃ and NO₃⁻ (PM₁) concentrations measured at RCAST are also shown for comparison. The fine-mode NO₃⁻ (PM₁ and PM₂) was similar at these sites. It is likely that HNO₃ concentrations at TUMSAT were similar to those at RCAST considering that NO₃⁻ (PM₁) was nearly in equilibrium with HNO₃ at RCAST [Morino et al., 2006]. PM₁-NO₃⁻ is nearly in equilibrium with HNO₃ and is a minor fraction of total nitrate during the daytime because of the high temperature.

The coarse-NO₃⁻ concentrations showed distinct diurnal variations, with a peak in the early afternoon. They increased with the increase in HNO₃ and were much higher than PM₁-NO₃⁻ under high-HNO₃ conditions. This is seen more clearly by the correlation between coarse-NO₃⁻ and HNO₃ for 1200 LT, shown in the left plot of Figure 9b.

The good correlation between HNO₃ and coarse-NO₃⁻ indicates that the flux of HNO₃ molecules onto sea-salt particles increased approximately in proportion to the HNO₃ concentrations, as predicted theoretically [Seinfeld and Pandis, 2006]. HNO₃ and coarse-NO₃⁻ will be correlated as long as the rate of HNO₃ deposition onto sea-salt particles does not far exceed the HNO₃ formation rate. The good correlation between HNO₃ and coarse-NO₃⁻ suggests that the concentration of sea-salt particles was also a limiting factor for the uptake of HNO₃.
on sea-salt particles, especially at low-wind conditions. Except for these periods, the median coarse-NO$_3$/HNO$_3$ ratios were about 0.83 (1σ = 0.41–1.3), indicating significant removal of HNO$_3$ by uptake onto sea-salt particles. A large removal of HNO$_3$ by sea-salt particles was also suggested by a modeling study for Appleford Island, Maine, USA [Fischer et al., 2006]. The uptake of HNO$_3$ onto sea-salt particles led to net NO$_y$ removal, because coarse-NO$_3$ was not included in NO$_y$, as discussed in section 2.2.

4.5. PANs

[46] The PANs concentrations and PANs/NO$_y$ ratios underwent diurnal variations reaching maximum values in the afternoon on HJ days in summer and winter, as shown in Figures 7 and 8. The maximum median PANs/NO$_y$ ratio was lower in winter (0.025) than in summer (0.04). The production rate of PANs is considered to have been higher in summer than in winter. However, the lifetime of PANs due to decomposition was shorter in summer (35 min) than in winter (14 h) for typical afternoon conditions. These compensating effects led to reduced seasonal variations of PANs. This point is discussed in more detail in section 5.

[47] The median PANs/NO$_y$ ratios for summer and winter are shown in Table 5. The median PANs/NO$_y$ ratios in winter (0.13) were higher than those in summer (0.06), opposite to the PANs/NO$_y$ ratio.

4.6. $\Sigma$(NO$_y$)$_i$

[48] Here we compare the sum of the measured individual NO$_y$ species (NO$_y$)$_i$ with the directly measured total NO$_y$ to understand pathways of NO$_y$ oxidation in some more detail. The sum is defined as

$$\Sigma$(NO$_y$)$_i$ = NO$_y$ + HNO$_3$ + NO$_3$ + PANs, 

and unmeasured NO$_y$ (ΔNO$_y$) (or “missing NO$_y$”) is defined as

$$\Delta$NO$_y$ = NO$_y$ - $\Sigma$(NO$_y$)$_i$.

The uncertainties of $\Sigma$(NO$_y$)$_i$ and ΔNO$_y$ in the three seasons were estimated to be about 13% and 103–273%, respectively, by combining possible errors of the individual measurements. The uncertainty of $\Sigma$(NO$_y$)$_i$ was derived as a root-sum-square of the uncertainty of each (NO$_y$)$_i$ species, weighted by its relative abundance. The much larger uncertainty of ΔNO$_y$ is due to the subtraction of the two large terms in equation (5), similar to the PANs/NO$_y$ ratio.

[49] $\Sigma$(NO$_y$)$_i$ was found to be highly correlated with NO$_y$, with linear regression slopes of 0.94 and 0.90 for the winter and summer periods, respectively. The average median $\Sigma$(NO$_y$)$_i$/NO$_y$ ratios were 0.89 ± 0.03 and 0.96 ± 0.02 (Figure 8). The $\Sigma$(NO$_y$)$_i$/NO$_y$ ratios showed a decrease during the daytime, and the minimum ratio was lower during summer than in winter. The seasonal variations of the median ΔNO$_y$ and ΔNO$_y$/NO$_y$ ratios are summarized in Table 5. The ratios of the sum of RONO$_2$ identified by gas chromatography ($\Sigma$(RONO$_2$)$_i$) to NO$_y$ were less than 0.44%. The good correlation between ΔNO$_y$ and NO$_y$ (r$^2$ = 0.64) (not shown) suggests that ΔNO$_y$ was produced photochemically. Both TN/NO$_y$ and PANs/NO$_y$ ratios were lower in summer than those in winters (Table 5), suggesting higher fraction of oxidized reactive nitrogen other than TN and PANs in summer. However, it should be stressed that the uncertainties of the ΔNO$_y$/NO$_y$ ratios are very large (>100%), and quantitative discussion of ΔNO$_y$ is not feasible.

[50] Total alkyl nitrates (ΣANs) have been measured using thermal dissociation followed by laser-induced fluorescence detection of NO$_2$ at rural and suburban sites in California and an urban site in Houston, Texas [Day et al., 2002, 2003; Rosen et al., 2004; Cleary et al., 2005]. At the suburban and urban sites, the ΣANs/NO$_y$ ratios were 0.1–0.25 in summer. The observed ΣANs were generally much higher than the sum of identified alkyl nitrates ($\Sigma$(RONO$_2$)$_i$) observed previously [e.g., O’Brien et al., 1997] constituting a large fraction of the missing NO$_y$. Considering this, it is possible that ΣANs constituted a significant fraction of ΔNO$_y$ also in the present observations.

[51] The oxidation of NO$_y$ to ΣANs can significantly reduce NO$_y$ lifetimes as compared with those estimated by considering only reaction (R1). In fact, lifetimes of NO$_y$ in power plant and urban plumes were derived to be 2–5 h from the decay of NO$_y$ in the plumes [Ryerson et al., 1998, 2003; Nunnermacker et al., 2000].

4.7. O$_3$ and P(O$_3$)

[52] According to the analysis by Kanaya et al. [2008], the predominant term in F(O$_3$) is $k_{\text{HONO}}$ + [NO][NO] in general. The HO$_2$ concentration has been observed to be relatively stable at NO lower than 300 pptv decreasing with NO at higher NO as predicted for steady state conditions [Kanaya et al., 2007] and predicted theoretically [Seinfeld and Pandis, 2006]. The observed dependence of HO$_2$ on NO also agreed with that predicted by the box model for the summer period. Because of this relationship, the dependence of $k_{\text{HONO}}$ on [NO][NO] on NO is much reduced with a broad maximum at NO mixing ratios of a few ppbv [Kanaya et al., 2008]. However, for winter, the model underestimated the observed HO$_2$ at high NO. Therefore P(O$_3$) estimated using the model-calculated HO$_2$ underestimated that derived using the observed HO$_2$, especially at NO mixing ratios larger than 10 ppbv. The P(O$_3$) values shown in Figures 5 and 6 are those calculated using the observed HO$_2$.

[53] The O$_3$ concentrations showed maximum values in the early afternoon reaching close to zero just before sunrise in three seasons. However, the amplitudes of the diurnal variations of O$_3$ were significantly smaller than that of O$_3$, because most of O$_3$ was converted to NO$_2$ during the nighttime, as seen from Figure 6. The importance of nighttime O$_3$ loss by NO$_x$ titration in urban centers is well understood [e.g., Siliman, 1999]. It is likely that the seasonal variation of the regional background in O$_3$, which should be close to O$_3$, contributed to the seasonally different levels of the nighttime O$_3$. The surface O$_3$ at remote sites located at similar latitudes in Japan were reported to be about 40–50 ppbv in fall and winter and reach minimum values of about 25–35 ppbv [e.g., Tanimoto et al., 2005; Kondo et al., 2008]. In fall and winter, the background O$_3$ in the BL over Japan is strongly influenced by the Asian outflow and in summer it is influenced by inflow of cleaner maritime air. The daytime-nighttime difference in O$_3$ is
largest in summer (about 30 ppbv) and smallest in winter (about 5 ppbv). Photochemical \(O_3\) production during the daytime significantly contributed to the daytime increase in \(O_3\), particularly in summer, as detailed below.

[54] The median of the daily peak \(P(O_3)\) in winter was smaller than that in summer by only a factor 1.5 (about 12 ppbv h\(^{-1}\) versus 8 ppbv h\(^{-1}\)) despite the difference in \(HO_2\) by about a factor of 6. This difference is due to the difference in \(NO\) by a factor of 3 around midday between winter and summer. The steady state \([NO]/[NOy]\) ratio is expressed to a good approximation as

\[
\frac{[NO]}{[NOy]} = \frac{([NO]/[NOy])([NOy]/[NOy])}{(J([NOy]/[NOy] + k_{NOy>0})(O_3))([NOy]/[NOy])}. \tag{6}
\]

In winter, \(NO_x\) and the \(NO_x/NO_y\) ratio were higher than in summer while \(O_3\) was lower, leading to higher \(NO\). It should be noted that if model-calculated \(HO_2\) for winter is used, the compensating effect is much smaller and \(P(O_3)\) used the \(NO_y\) and \(CO\) data for LJ days in winter, when \(NO_y\) should be least oxidized. As discussed in section 3.1, the lifetime of \(NO_x\) on LJ days in winter was estimated to be about 7 days or longer. In fact, the median \(NO_x/NO_y\) ratios on LJ days in winter were as high as 0.89 even during the daytime. \(ER(NO_x/CO)\) was estimated from (1) the median values of the \(NO_y/CO\) ratios and the slopes were derived for the other seasons using the LJ data. The results are summarized in Table 7. There were no LJ days in the summer of 2004.

5. \(NO_x\) Oxidation and \(NO_y\) Removal

5.1. Estimate of \(NO_x\) Removal

[56] Here we estimate the remaining fractions of \(NO_y\) (\(R_{NOy}\)) in air masses sampled at RCAST, after transport from emission areas. For this purpose, \(CO\) was used as a tracer because \(CO\) is emitted simultaneously with \(NO_x\) and has a relatively long lifetime of 1–2 months. \(R_{NOy}\) is given as the ratio of the \(NO_y/CO\) correlation slope to the \(NO_x/CO\) emission ratio (\(ER(NO_y/CO)\)) [Nunnermacker et al., 1998, 2000; Koike et al., 2003; Kondo et al., 2004]:

\[
R_{NOy} = \frac{(NO_y/\Delta CO)}{ER(NO_x/CO)}. \tag{7}
\]

[57] As discussed in section 2.1, \(NO_x\) is estimated to be emitted predominantly from motor vehicles, especially heavy-duty diesel vehicles in the TMA. \(ER(NO_x/CO)\) was derived to be 0.24 for the TMA from the emission rates of \(NO_x\) and \(CO\) compiled by Koike et al. [2000; Kondo et al., 2003] for diesel vehicles has previously been reported to be much higher than that for gasoline vehicles [Sawyer et al., 2000; Marr et al., 2002]. The traffic density of diesel vehicles in the TMA generally reaches a maximum in the early morning [Kondo et al., 2006]. Therefore, \(ER(NO_x/CO)\) may undergo diurnal variations. Scatter in the slope of the \(NO_y/\Delta CO\) correlation in Figure 10 includes this effect, and the \(1\sigma\) variability given in Table 5 gives the uncertainty in the derived \(ER(NO_y/CO)\).

[58] In addition to the winter data, the median values of the \(NO_y/\Delta CO\) ratios and the slopes were derived for the other seasons using the LJ data. The results are summarized in Table 7.

**Table 7.** Estimates of the \(NO_y/CO\) Emission Ratio

<table>
<thead>
<tr>
<th>Season</th>
<th>Median (NO_y/\Delta CO)</th>
<th>(n)</th>
<th>Slope of (NO_y/\Delta CO)</th>
<th>(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer</td>
<td>0.14 (0.12–0.23)</td>
<td>163</td>
<td>0.15</td>
<td>0.60</td>
</tr>
<tr>
<td>Fall</td>
<td>0.14 (0.11–0.18)</td>
<td>106</td>
<td>0.13</td>
<td>0.82</td>
</tr>
<tr>
<td>Winter</td>
<td>0.14 (0.12–0.18)</td>
<td>211</td>
<td>0.14</td>
<td>0.65</td>
</tr>
</tbody>
</table>

\(a\) The values in parentheses are \(1\sigma\) values (central 67%) on \(NO_y/\Delta CO\).
emissions from diesel trucks are important sources of NOy. There was generally much less traffic. As stated above, vehicles in Tokyo was much lower during this period, when likely explanation is that the ratio of diesel trucks to total vehicles in 2004, than those for the rest of the summer 2004 period. A factor 2 during the Bon holiday period of 12–14 August.

Figure 11. Correlation between the remaining fractions of NOx (RNOx) and the NOx/NOy (TN/NOy) ratios for 0830–1730 LT on HJ days in summer (circles), fall (triangles), and winter (squares). The approximate TN/NOy ratios, corresponding to the NOy/NOx ratios, are given for reference.

All the values are nearly identical irrespective of season, indicating that the value of 0.14 ppbv/ppbv is a valid estimate for ER(NOx/CO).

[59] It was found that ∆EC/∆CO ratios were lower by a factor 2 during the Bon holiday period of 12–14 August 2004, than those for the rest of the summer 2004 period. A likely explanation is that the ratio of diesel trucks to total vehicles in Tokyo was much lower during this period, when there was generally much less traffic. As stated above, emissions from diesel trucks are important sources of NOy and EC in the TMA. A correction to ER(NOx/EC) was made using the change in the diesel trucks/total vehicles ratio estimated from the changes in the ∆EC/∆CO ratio, in a similar way to that described by Kondo et al. [2006]. The correction amounted to about 12%.

[60] The RNOx estimated from equation (7) is plotted as a function of the NOx/NOy ratios for the daytime on HJ days in Figure 11. The data were binned according to the NOx/NOy ratio and the median RNOx for each bin was derived from the NOy/NOx correlation. The approximate TN/NOy ratios are also shown for reference. The median values of RNOx for each season are summarized in Table 8. The slope of the RNOx-NOx/NOy correlation depends strongly on the relative rate of the depositional removal of HNO3 to the NOy oxidation rate. Generally, faster HNO3 removal leads to a steeper slope, which therefore can be sensitive to dry deposition rates of HNO3.

[61] RNOx decreased with the decrease in the NOx/NOy ratio in summer and fall. Because the NOx/NOy ratio decreased from early morning to the early afternoon, the change in RNOx in Figure 11 also represents the diurnal variation of RNOx in each season. On average between 0830 and 1730 LT, the RNOx values were estimated to be 0.78, 0.90, and 1.0 for the summer, fall, and winter periods, respectively.

[62] The systematic decrease in RNOx with the decrease (increase) in the NOx/NOy (TN/NOy) ratios in summer is likely due to the removal of NOx through production of HNO3 and its subsequent removal (high HNO3/TN ratios). The removal of HNO3 can occur by dry deposition and uptake on sea-salt particles. Precipitation occurred only on one day both in summer and winter. The coarse-NOx/NOy ratio was about 7% under weak wind conditions in summer, suggesting that the uptake of HNO3 on sea-salt particles contributed to the removal of NOx by a similar degree. In fall, a similar trend was seen, although the range of the TN/NOy ratios was narrower. In winter, NOx/NOy ratios were about 0.9 and the RNOx was close to 1. The uncertainties in RNOx were largely due to the diurnal variation of ER(NOx/CO), which reached maximum and minimum values in the early morning and afternoon, respectively (not shown).

5.2. Estimate of NOx Oxidation

[63] Here we derive the NOx oxidation, formation of NOz, and removal of NOx for summertime conditions, relative to the NOx emitted. For this purpose, we first estimate NOx mixing ratios uninfluenced by irreversible removal (NOx*). The RNOy was close to 1. The uncertainties in RNOy were largely due to the diurnal variation of ER(NOx/CO), which reached maximum and minimum values in the early morning and afternoon, respectively (not shown).

\[
\text{NOx} = \Delta \text{CO} \times \text{ER(NOx/CO)}.
\]

The ratio of removed NOx (δNOx) to NOx is given as

\[
\frac{\delta \text{NOx}}{\text{NOx}} = 1 - \text{RNOx}.
\]

\[\text{ER} \left(\frac{\text{NOx}}{\text{CO}}\right) = \frac{\text{NOy}}{\text{NOy}^*} = \frac{\Delta \text{CO}}{\text{ER} \left(\frac{\text{NOy}}{\text{CO}}\right)} \frac{\text{NOy}}{\text{NOx}} = \frac{\Delta \text{CO}}{\text{ER} \left(\frac{\text{NOx}}{\text{CO}}\right)} \frac{\text{NOy}}{\text{NOx}}
\]

Figure 12 shows the median NOx/NOy*, NOy/NOy*, and δNOx/NOy* ratios as functions of the NOx/NOy ratio. The approximate residence time (RT), as derived in Appendix A is also shown as a reference. On LJ days in summer, the NOx/NOy ratios were about 0.89, as discussed in section 3 (Figure 6). In these air masses, about 89% (100%) of the emitted NOx (NOy) remained. These data represent less-processed air.

[64] On HJ days, the median NOx/NOy ratios were about 0.89 in the morning and late afternoon (around 1000 and 1700 LT), representing moderately processed air. During daytime (1000–1700 LT), the ratios decreased to about 0.78, representing highly processed air. The remaining portions of NOx (NOy) were about 76% (86%) and 66% (84%) of moderately and highly processed air, respectively. In highly processed air, 18% of the emitted NOx remained as NOy, and 16% of NOy was removed.

[65] During the stagnant conditions of 12–14 August, with an RT of 8–10 h (Appendix A), the NOx/NOy ratios decreased to as low as 0.44. Substantial oxidation of NOx (69%) and removal of NOy (30%) occurred in this extremely processed air. These results indicate that most of the

Table 8. Remaining Fractions of NOx (RNOx) During the Daytime and the Nighttime on HJ Days

<table>
<thead>
<tr>
<th>Period</th>
<th>0830–1730 LT</th>
<th>1730–0830 LT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer</td>
<td>0.78 (0.62–0.94)</td>
<td>0.86 (0.67–1.02)</td>
</tr>
<tr>
<td>Fall</td>
<td>0.90 (0.70–1.06)</td>
<td>0.96 (0.75–1.12)</td>
</tr>
<tr>
<td>Winter</td>
<td>1.00 (0.84–1.26)</td>
<td>0.93 (0.77–1.16)</td>
</tr>
</tbody>
</table>
emitted NOx was lost within 10 h even in urban areas in summer.

[67] By contrast, in winter little NOx was removed during any conditions within the error of the estimate (Figure 12), although about 15% of the emitted NOx was converted to NO2 during the daytime of HJ days. The majority of the TN was in the form of NO3 owing to the low temperature, leading to significantly reduced NOx removal.

6. Formation of O3, PAN, TN, and SOA in Summer

6.1. High O3, PANs, and SOA During Phase 2

[68] Here we investigate key processes that caused enhanced O3 and PANs on 12–14 August, when a stagnant sea-land circulation developed. Both PANs and O3 mixing ratios were much higher than those during the preceding period, as discussed in section 3.2. HO2 also showed a large increase during the daytime as predicted by the increase in O3. P(O3) reached maximum values of about 10–15 ppbv h⁻¹ around midday on these days. However, P(O3) did not show significant variability throughout phases 1 and 2 because NO was low in the early afternoon when HO2 reached maximum (Figure 2b). As a result, the P(O3) values on the high-O3 days are close to the median value for the summertime. The low NO in the early afternoon was mainly due to the reduced NOx/NOy and NOx/NOy ratios (Figure 2b). The high O3 mainly lowered the NOx/NOy ratios. The low NOx/NOy ratios (as low as 0.3) could have been due to oxidation of NOx in stagnant air near the surface and partly due to downwash transport of aged air by vertical mixing, and the reduced NOx emissions due to the

Bon holidays (section 5.1). The NO levels on these days were significantly lower than those on the other days for comparable levels of VOCs [Kanaya et al., 2008, Figure 7] and P(O3) was NOx-limited in these cases.

[69] As anticipated from the trajectories shown in Figure 3, the air mass sampled in the early afternoon accumulated primary pollutants from the previous night. In fact peaks in NOx (Figure 2a) and VOCs (C2H4 and C2H6) [Shirai et al., 2007] were seen during the peak in O3. However, it is very unlikely that the enhanced levels of these species led to significant increases in P(O3), as discussed above. Considering that air masses stayed at locations close to RCAST, the diurnal variation of P(O3) shown in Figure 2b should be close to that for air masses sampled in the early afternoon. Accumulation of O3 produced after sunrise is insufficient to explain the observed O3 increase by up to 104–116 ppbv from 0500 to 1300 LT [Kanaya et al., 2008]. Instead, it is likely the high O3 was due to the accumulation of O3 from previous days at higher altitudes in the BL and to transport down to near the surface by mixing. The very low NOx/NOy ratios could have been due, at least partly, to downward transport of aged air by vertical mixing, although its relative importance is not quantified.

[70] The enhancement of O3 occurred not only at RCAST but also over a wide region of the TMA on 12–14 August. In Kisai and the northern part of the TMA, midday O3 exceeded 80 ppbv after 9 August [Miyakawa et al., 2008], two days earlier than at RCAST. Considering that P(O3) was rather insensitive to the NOx level and following the same reasoning discussed above, the observed high O3 (>80 ppbv) in Kisai also cannot be explained solely by in situ O3 formation. The wind fields shown by Shirai et al. [2007] suggest that the air over the entire TMA was under the influence of sea-land breeze circulation. Wakamatsu et al. [1983, 1996, 1999] have shown the effect of accumulation of O3 in elevating its concentrations over the TMA under sea-land breeze circulation conditions using field observations and modeling studies. In particular, they observed O3 mixing ratios exceeding 80 ppbv above the surface (0.2–1.2 km) over a wide region of TMA under the stagnant conditions in summer of 1978.

[71] In Figure 13, the observed concentration of saturated PANs (PAN + PPN + PiBN + PnBN) is compared with model simulations. The model predicted the observed PANs quite well during phase 1. However, the model underestimated enhanced PANs concentrations observed during phase 2, especially on 12–14 August. Model calculations were also made by varying the ALD (acetaldehyde and higher aldehydes in RACM) concentrations to estimate the sensitivity of the calculated PANs to ALD, because the ALD concentrations can be highly uncertain. The calculated PANs with the ALD tripled still cannot explain the observations. The ALD concentrations calculated without the ALD constraint was about 70% of the ALD concentrations used for the standard model run, suggesting that the uncertainty in ALD concentrations is smaller than a factor of 3. In the model, ACO3 (acetyl peroxy and higher saturated acyl peroxy radicals in RACM) is the precursor of PAN. It is mainly produced by the ALD-OH reaction and photolysis of MGLY (methylglyoxal and other α-carbonyl aldehydes). In turn, ALD was mainly produced from
oxidation of olefins and alkanes (including alcohols) and MGLY originating from oxidation of aromatics.

The daytime maximum concentrations on the highest PANs days were reproduced by the model by employing temperatures 9°C lower than at ground level (corresponding to 0.9 km), increasing ALD concentrations by a factor of 3, and increasing time constant for dilution (48 h) simultaneously. The longer time constant may represent the stagnant conditions (increased horizontal homogeneity in the BL). Considering these comparisons, it may be possible that the high PANs concentrations observed at the surface were due to downward transport of the upper BL with lower temperatures and augmented aldehyde concentrations due to stagnation.

6.2. O₃-PANs-TN-SOA Correlations

Correlations between the species photochemically produced are shown in Figure 14. The correlations were tighter for Oₓ than O₃ (not shown). The slope of the PANs-Oₓ correlation for Oₓ lower than 60 ppbv, mainly during phase 1, was lower than that for Oₓ higher than 80 ppbv. A similar feature was observed for TN. At lower Oₓ (higher wind speed), the local productions and loss should control the PANs and TN concentrations. At higher Oₓ (lower wind speed), accumulated aldehydes (section 6.1) and TN in the entire BL may have caused steeper slopes of the PANs-Oₓ and TN-Oₓ correlations.

Both oxygenated organic aerosol (OOA) and OA correlated well with Oₓ (r² = 0.74 and 0.79, respectively). 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.

Figure 13. Temporal variations of observed (black line) and simulated (gray line) PANs concentrations in the summer of 2004. The results from two model runs are included: one with the acetaldehyde and higher aldehydes (ALD) concentrations constrained at standard levels (solid line) and the other with those tripled (dotted line). See text for more details.

Figure 14. Correlations of PAN, total nitrate (TN), oxygenated organic aerosol (OOA), and organic aerosol (OA) with Oₓ = O₃ + NO₂ in summer 2004.
About 90% of OOA was estimated to be water soluble for summer and winter, indicating that OOA represents SOA. In summer, OA and OOA were tightly correlated ($r^2 = 0.95$), and the OOA/OA ratio was about 0.8 owing to high levels of photochemical activity, which led to active formation of SOA. Correlation of OA with O$_3$ at RCAST in summer has been reported by Takegawa et al. [2006a]. Figure 14 demonstrates tighter correlations of OA and OOA with O$_3$ but with O$_3$. More importantly, the OA-O$_3$ correlation was linear throughout the whole O$_3$ range. This is because OA is more highly conserved than PANs and TN owing to its much slower dry deposition velocity. The tight OA-O$_3$ correlation indicates that the accumulation and mixing processes led to simultaneous increases in O$_3$ ($\approx$80 ppbv) and SOA (>15 µg m$^{-3}$).

7. Summary and Conclusions

Simultaneous measurements of major components of reactive nitrogen (NO$_x$, PANs, HNO$_3$, and NO$_3$ (PM$_{10}$)), total reactive nitrogen (NOy), VOCs, and HO$_x$ were made at RCAST, located near the urban center of Tokyo in summer, fall, and winter 2003–2004 to study the processes involving oxidized forms of reactive nitrogen and O$_3$. The median NO$_x$ concentrations were about 20–42 ppbv during these periods. On average, the $\Sigma$(NO$_x$)/NO$_y$ ratios were 0.96 ± 0.02 and 0.89 ± 0.03 in winter and summer, respectively, confirming the overall validity of the measurements of the NO$_x$ species.

The median NO$_2$/NO$_y$ ratios underwent distinct diurnal variations in each season reaching minimum values in the early afternoon on HJ days, owing to the oxidation of NO$_y$ by OH (reaction (R1)). The daily minimum NO$_2$/NO$_y$ ratios were lower in summer (about 0.7) than those in winter (about 0.85), reflecting faster oxidation of NO$_x$ due to the higher OH concentrations. On LJ days, the median NO$_2$/NO$_y$ ratios showed little diurnal variation and remained high (mostly above 0.8), irrespective of season, consistent with the longer lifetime of NO$_x$.

In summer, the dominant form of TN was HNO$_3$, with a maximum at 1400 LT. The coarse-NO$_3$ concentrations, which were not included in NO$_x$, increased nearly in proportion to the HNO$_3$ concentrations. This implies that a significant fraction of HNO$_3$ was taken up by sea-salt particles. In winter, NO$_3$ was the dominant form of TN. The lower HNO$_3$ and higher NO$_3$ in winter were due to the shift of the HNO$_3$-NO$_3$ partitioning to NO$_3$ at low temperatures.

The nighttime levels of O$_3$ were much higher in fall and winter than those in summer reflecting the seasonal variation of the background O$_3$. The daytime-nighttime difference in O$_3$ was largest in summer (about 30 ppbv) and smallest in winter (about 5 ppbv) in winter. Photochemical O$_3$ production during the daytime partly contributed to the daytime increase in O$_3$, consistent with the estimated P(O$_3$). In addition to the O$_3$ formation, dry deposition of O$_3$ during the daytime and transport in vertical and horizontal directions should have played some roles in controlling the seasonal-diurnal variation of O$_3$.

The remaining fraction of NO$_x$ ($R_{NO_x}$) was estimated from the decrease in the slope of the observed NO$_y$/CO correlation from the estimated NO$_y$/CO emission ratios. $R_{NO_x}$ decreased with the decrease in the NO$_y$/NO$_x$ ratio in summer and fall. The systematic decrease in $R_{NO_x}$ with the decrease in the NO$_y$/NO$_x$ ratios was likely due to the removal of NO$_y$ through production of HNO$_3$ and its subsequent removal. The removal of HNO$_3$ could have occurred by dry deposition and uptake on sea-salt particles. On average during 0830–1730 LT, the $R_{NO_x}$ values were 0.78 and 0.90 for summer and fall, respectively. Little NO$_y$ was removed in winter owing to the suppressed HNO$_3$ production.

The mean NO$_x$/NO$_y$ ratios of 0.89 (LJ days), 0.89 (morning and late afternoon–nighttime on HJ days), 0.78 (daytime on HJ days), and 0.44 (daytime under stagnant conditions in summer) represent air masses with different degrees of photochemical processing. The remaining fractions of NO$_x$ (NO$_x$) in these air masses were estimated to be about 89 (100), 76 (86), 66 (84), and 31 (70) %, respectively. These remaining NO$_x$ amounts give initial conditions that control the transport of NO$_x$ from the urban center of the TMA to its surrounding regions.

SOA was highly correlated with O$_3$. It is likely that O$_3$ and SOA accumulated during the course of sea-land breeze circulation above the surface in the BL and were transported to the surface together with O$_3$. The identification of the importance of vertical transport for high O$_3$ (>80 ppbv) and other oxidants is important in predicting secondary oxidants in the TMA and their future reductions.

Appendix A: Oxidation of NO$_x$

We have shown in section 4 that reaction (R1) and oxidation to PAN were the major pathways of the oxidation of NO$_x$ during the daytime. In this section, we interpret the decrease in NO$_x$ observed in summer more quantitatively by taking into account the oxidation process during transport that occurred prior to sampling air masses at RCAST. Changes in NO$_x$ concentrations due to reaction (R1) are expressed as

$$\frac{d[NO_x]}{dt} = -k_{OH+NO_2}[OH][NO_2]$$

$$= -k_{OH+NO_2}[OH][NO_2]([NO_2]/[NO_x]).$$

Here we neglect the effect of PAN formation for simplicity and discuss this point in the interpretation of the results. The NO$_x$ concentrations at time $t$ (NO$_x(t)$) after NO$_x$ emissions beginning at $t = 0$ can be expressed by

$$NO_x(t)/NO_x(0) = \exp(-\int k_{OH+NO_2}[OH]([NO_2]/[NO_x])dt).$$
If average OH concentrations and \([\text{NO}_2]/[\text{NO}_x]\) ratios are used for simplicity, equation (A2) is reduced to

\[
\text{NO}_x(t)/\text{NO}_x(0) = \exp(-k_{\text{H}_2\text{O}+\text{NO}_2}\text{[OH]}/[\text{NO}_2]/[\text{NO}_x])t). \tag{A3}
\]

For the present calculations, the reaction time \(t\) was given as the residence time \((RT)\) of the sampled air mass in the high-\(\text{NO}_x\) emission areas. Spatial variability of the \(\text{NO}_x\) emission rates in the high-emission areas is relatively small and is not a large source of uncertainty. However, considering that \(\text{NO}_x\) was injected into the sampled air masses continuously during their transport, the \(RTs\) derived in this way may be overestimates.

Figure 3 shows typical backward trajectories of air masses arriving at RCAST during summer, overlaid with the emission rates of \(\text{NO}_x\). The backward trajectories were calculated using the wind data obtained at RCAST, because the winds in summer were generally southerly during the daytime owing to the sea breeze in the high-\(\text{NO}_x\) area. The high-emission areas in the study region are marked in red. Spatial inhomogeneity of wind fields within the high-\(\text{NO}_x\) areas introduced some errors in the trajectory calculations.

The wind speeds measured by Japan Meteorological Agency at Yokohama (30 km south of RCAST) and Nerima (10 km north of RCAST) were stronger and weaker by factors 2.2 and 0.65, respectively than those at RCAST on these days on average. The wind directions at Yokohama and Nerima were to within ±28° of those at RCAST. However, it is very difficult to estimate errors in \(RT\) by this inhomogeneity, because of the complexity of a wind system of this scale.

The backward trajectory for 2 August is typical for the observational period from 1–9 August 2004. Air masses arriving at RCAST remained in the high-emission areas for a few hours. On the other hand, the backward trajectory for 13 August is typical for 10–14 August. The air masses stagnated owing to the development of the sea-land breeze circulation, and the air masses sampled at RCAST remained in the emission areas for about 10 h. The \(RT\) values estimated for the summer period typically range over 1.5–60 h.

The photochemical ages \((PA)\) of air masses can be estimated using the ratio of alkyl nitrates to their parent hydrocarbons \([\text{Bertman et al., 1995}]\). For the present analysis, the ratio of 2-pentyl nitrate (2-PeONO\(_2\)) to n-pentane \((n-\text{C}_5\text{H}_{12})\) was chosen \([\text{Simpson et al., 2003; Takegawa et al., 2006b}]\). The 2-PeONO\(_2/n-\text{C}_5\text{H}_{12}\) ratio and \(PA\) (or \(t\)) are related as

\[
\frac{[\text{2-PeONO}_2]}{[n-\text{C}_5\text{H}_{12}]} = \frac{\beta k_d}{(k_B - k_A)} \left(1 - e^{(k_A-k_B)t}\right), \tag{A4}
\]

where \(\beta\) is the fractional yield, and \(k_A\) and \(k_B\) are the pseudo-first-order rate coefficients for the formation and destruction of 2-PeONO\(_2\), respectively. Values of these parameters for typical midlatitude surface conditions during spring were given by Simpson et al. [2003]. The coefficient \(k_B\) is a function of [OH]. We assumed average values of [OH] = 5.5 \times 10^6 \text{ cm}^{-3} \ (1000–1500 \text{ LT}) and 3.1 \times 10^6 \text{ cm}^{-3} \ (0500–1900 \text{ LT})

which gave \(RT/\text{PA}\) ratios of 1.6 ± 0.80 and 1.2 ± 0.6, respectively, with \(r^2 = 0.31\) for the \(RT/\text{PA}\) correlation. The results showing \(RT/\text{PA}\) ratios larger than 1 are consistent with the possible overestimation of \(RT\), although other factors, including effects of vertical mixing, also introduce additional uncertainties. These results suggest \(RT\) can be used as a qualitative measure of air mass age. The uncertainties discussed above will be greatly reduced if the plumes are well defined, as has been done for aircraft studies of plumes from power plants \([\text{e.g., Nunnermacker et al., 1998, 2000; Neuman et al., 2002, 2004}]\).

Using the \(RT\), we investigate the validity of equation (A3). If \(\text{NO}_x\) is conserved, \(\text{NO}_x(0) = \text{NO}_x\). Figure A1 shows the relationships between the observed \(\text{NO}_3/\text{NO}_x\) ratios with the \(\exp(-k_{\text{H}_2\text{O}+\text{NO}_2}\text{[OH]}/[\text{NO}_2]/[\text{NO}_x])\) value calculated for the average [OH] = 5.5 \times 10^6 \text{ cm}^{-3} \ (1000–1500 \text{ LT}). The data points for which the \(PA\) values were obtained are depicted as triangles. The median \(\text{NO}_3/\text{NO}_x\) ratios for each bin are correlated well with \(\exp(-k_{\text{H}_2\text{O}+\text{NO}_2}\text{[OH]}/[\text{NO}_2]/[\text{NO}_x])\) \((r^2 = 0.96)\) with a slope of 0.82. The scatter of the correlation can arise partly from the uncertainties in the estimate of \(RT\), as discussed above.

Some fractions of \(\text{NO}_x\) were found to have been removed during transport, as discussed in section 6.1. A \(\text{NO}_3\) value that was corrected for this removal, denoted \(\text{NO}_3^e\), was also used for \(\text{NO}_x(0)\) for comparison. Using the \(\text{NO}_3^e\) values did not significantly alter the correlation \((r^2 = 0.91)\) and slope \((=0.85)\). The correction by \(\text{NO}_3^e\) becomes important for the lowest \(\text{NO}_x/\text{NO}_x\) ratios. Because the fraction of these data is small, the \(\text{NO}_3^e\) correction is not important in this case. It should be noted that \(\text{NO}_x\) lost to PANs is not considered in equation (1). The time constant of PAN formation is different from \(\text{HNO}_3\) formation, although reactions of OH with VOCs are involved in PANs formation. In addition, formation of alkyl nitrate is also an important pathway for \(\text{NO}_x\) oxidation \([\text{e.g., Day et al.,}]\).
2003), as discussed in section 4.6. Therefore, the term \( \text{exp}(-\text{AH}_1 + \text{NO}_2\cdot[\text{NO}_2]) \) should be considered to represent a qualitative measure of chemical aging of \( \text{NO}_x \), rather than a quantitative measure of \( \text{NO}_x \) oxidation. In practice, the reasonably good correlation of this term with the \( \text{NO}_2/\text{NO}_x \) ratios and the slope of 0.82 suggests that the \( \text{NO}_2/\text{NO}_x \) ratios approximately represent air mass ages due to oxidation along trajectories.

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