Diagnosis of Photochemical Ozone Production Rates and Limiting Factors in Continental Outflow Air Masses Reaching Fukue Island, Japan: Ozone-Control Implications

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ABSTRACT

Asian continental outflow air masses reach western Japan in the springtime, carrying high levels of ozone produced over the Asian continent, and facilitating in-situ production. In this study, in-situ production was highlighted; the rate and limiting factors of net ozone production were diagnosed at Fukue Island, a remote island west of Japan, on 17 days during May–June 2009, when the continental outflow air mass arrived, using an observation-based modeling approach. The average ozone production was estimated to be 6.8 ppb per day. Information on the chemical status of the arriving air mass is important, because it affects how further ozone production in the air mass occurs after precursor addition from Japanese domestic emissions. The main limiting factor of ozone production for such air masses was usually nitrogen oxides (NOx), suggesting that domestic NOx emission control is important in reducing further ozone production. Volatile organic compounds (VOCs) also increased the ozone production rate, and occasionally (14% of time) became the dominant controlling factor. This analysis implies that the VOC reduction legislation recently enacted by the Japanese government should be effective. VOC-limited conditions occurred particularly when the air mass traveled within 6–8 h, via the Korean Peninsula. The uncertainty in the radical chemistry mechanism governing ozone production had a non-negligible impact, but the main conclusion relevant to policy was not altered. When chain termination was augmented by HO2 + NO/NO2 reactions in the presence of H2O and by heterogeneous loss of HO2 on aerosol particle surfaces, as recently verified or hypothesized, the daily ozone production rate decreased by up to 24%, and the fraction of hours when the VOC-limited condition occurred varied from 14% to 13–26%.

Keywords: In-situ ozone photochemistry; East Asia; Policy implications; Observation-based model.

INTRODUCTION

The health issues related to elevated concentrations of tropospheric ozone over the Pacific Rim region of East Asia are of concern, because photochemical production of ozone has recently been strengthened by increased emissions of nitrogen oxides (NOx) and volatile organic compounds (VOCs). Ozone formation is most efficient over cities and the surrounding areas where precursors are emitted, but continues as the plume is transported to downwind areas over a long range (of the order of 1000 km), until the NO concentration is depleted or diluted to the critical level of ~10–30 ppt (Crawford et al., 1997; Kondo et al., 2004) at which the net photochemical trend in ozone changes from production to loss. For the Asian continental outflow air mass that travels along the westerly wind in spring, Parrish et al. (2004) suggested that such a transition could occur over the Pacific Ocean, because the net rate was positive in the west North Pacific and negative in the east North Pacific. Japan therefore lies on the side of net ozone production in springtime (Pochanart et al., 1999, 2002; Kondo et al., 2004). The air mass originating from the Asian continent and intruding into western Japan can contain hazardous levels of ozone, reaching ~100 ppb, composed of (1) the fraction

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produced over the continent on previous days and (2) the fraction produced on the day of air mass arrival. After intrusion, ozone may be (3) further produced in the same air mass, driven by Japanese domestic emissions of NO$_x$ and VOCs. Studies clarifying all these aspects of ozone production are needed to reveal the whole picture of ozone pollution over Japan and to develop effective countermeasures.

Past studies conducted in the context of regional-scale air pollution at remote sites in Japan did not distinguish between (1) and (2). Pochanart et al. (1999) reported that ozone levels were enhanced in the springtime at Oki Island when the air mass traveled over the coastal, industrialized region of the Asian continent, and attributed the enhancement (~12 ppb in May) from the background level to “regional” photochemical ozone formation. Yamaji et al. (2006) used a regional-scale atmospheric chemistry transport model and showed that about 10–20 ppb of ozone (about 20–30% of the total) was attributable to regional production in April–May over western Japan. Naja and Akimoto (2004) and Tanimoto et al. (2005, 2009) investigated the overall influence of the expanding Asian economy on ozone levels over Japan. They all looked at the entire regional production of ozone without discriminating between (1) and (2).

The daytime increases in the average diurnal variations in the ozone concentrations observed at remote sites in Japan would be a useful indicator for the determination of (2), although other factors (such as vertical mixing and deposition) also affect (2). More specifically, in-situ ozone production rates can be assessed based on a photochemical box model calculation, constraining the precursor concentrations to observations [observation-based model (OBM)]. This methodology, originally established for the study of urban photochemistry in the United States (e.g., Cardelino and Chameides, 1995; Kleinman, 2000), has been applied to Asian megacities (Zhang et al., 2008; Shao et al., 2009) and suburban and rural areas (e.g., Kanaya et al., 2009; Kim et al., 2014). The rates were also determined for the Asian outflow captured by aircraft-borne observations over the western Pacific region during Pacific Exploration of Asian Continental Emission campaigns (Kondo et al., 2004) and near California during the Intercontinental Transport and Chemical Transformation 2002 campaign (Hudman et al., 2004). However, the rates have not been examined for the regions in between (e.g., western Japan).

Determination of the limiting factor of ozone production, i.e., NO$_x$- or VOC-limited production, is also important, not only as a diagnosis of chemistry, but also for clarifying policy implications. Past studies have mainly focused on urban regions (Sillman, 1999; Kanaya et al., 2008), but assessment of regional-scale ozone pollution would also be meaningful. From this perspective, we studied the rates and limiting factors of ozone pollution at the top of Mt. Tai (Kanaya et al., 2009) and at Rudong, Jiangsu, more than 100 km from Shanghai (Pan et al., 2015).

In this paper, the investigation of in-situ ozone photochemistry at Fukue Island (Fig. 1(a)), one of the westernmost remote islands of Japan, which directly receives Asian continental outflow in spring, is described. At this island, the term (3) mentioned above could be negligible because the influence from Japanese domestic emissions was minimal. The ozone production rates and limiting factors were determined using the OBM approach. The sensitivity model runs performed to determine a regime, in which the NO$_x$ or non-methane hydrocarbon (NMHC) concentration levels were artificially increased, were regarded as hypothetical cases where small domestic emissions are added to the Asian outflow air masses. This was done to determine whether reductions in the domestic emissions of NO$_x$ or VOCs should be recommended, to avoid further production of ozone in the air mass arriving from the continent. In Japan, VOC emission reduction was tightened nationally in 2006, in addition to those of NO$_x$, and the effectiveness of the policy in reducing ozone has to be assessed (Photochemical Oxidant Survey Committee, 2014). The policy was applied uniformly across Japan, including megacities such as Tokyo and western rural regions where the influence from the continental outflow is important. This study attempts to determine whether such VOC emission reductions are meaningful in the western region. Photochemical ozone production rates and the limiting factors were investigated for southern Taiwan (Shiu et al., 2007) under westerly wind conditions (i.e., the influence of air from the Asian continent), but the analysis was performed after the domestic influence became dominant. The limiting factor for an air mass that has just arrived could be different from that after the effect of domestic emissions becomes dominant. A separate study for such conditions is therefore required to examine the three factors mentioned above individually and to obtain policy-relevant information on the limiting factor, applicable to areas where the perturbation is smaller (e.g., from rural areas to small towns). As Fig. 1(b) shows, in small towns in the Kyushu area of Japan, daytime hourly ozone concentrations reached the warning level (120 ppb) for which in-situ production (partly affected by local emissions in this case) was overlaid on the accumulation for the previous day. In order to examine which reduction of NO$_x$ or VOC emission is recommended for such cases, clarification of the chemical status at the point of air mass arrival is essential, because the status affects how subsequent ozone production occurs, fueling small local emissions.

This paper is structured as follows: in the next two sections, observations at Fukue Island and the photochemical box model simulations used to study the net ozone production rates and their limiting factors during May–June 2009 are outlined. In the results and discussion section, we first examine the representativeness of the year of study (2009) in the context of interannual variations in the ozone and NO$_x$ concentration levels observed for a longer period (2009–2014). And then the base model run results of the radical concentrations and the ozone production rate are presented. The results from the sensitivity model runs where NO$_x$ and VOC concentrations are artificially shifted are presented to determine the controlling factor. Last, results from further model sensitivity runs are presented, in which the chemical mechanism is altered to ensure that the influence of its uncertainty is small and that the derived conclusion in the previous sections is robust.
Fig. 1. (a) Location of Fukue Island, shown with backward trajectories on 17 days (shades in (b)) when continental air mass arrived at the island. (b) Time series of observed ozone concentrations. Data at additional five rural sites within Kyushu Main Island are also shown. The sites (Black circles in the inset map) are Itoshima (label 1 in the map, 33.56°N, 130.21°E), Karatsu (label 2, 33.46°N, 129.96°E), Yukiura (label 3, 32.92°N, 129.67°E), Minamata Health Center (HC) (label 4, 32.21°N, 130.40°E), and Environmental Radiation Monitoring Center (ERMC) (label 5, 31.81°N, 130.30°E). They are away from large cities (gray circles).

OBSERVATIONS AND MODEL SIMULATION INPUTS

The observations were made at the Observatory of the Atmospheric Environment on Fukue Island (32.75°N, 128.68°E) (Takami et al., 2005; Kanaya et al., 2013) from May 1 to June 5, 2009. The island is located between the main Japanese islands and the Asian continent (Fig. 1(a)). The observatory is located in the northwest part of the island, about 20 km from the main residential area in the southeast. Under typical continental outflow conditions with a westerly wind, the site is free from domestic local emissions of ozone precursors and suitable for testing ozone production before the influence of domestic emissions becomes large. Table 1 lists the observed species and parameters relevant to the study of ozone photochemistry; aerosol and other observations (elemental and organic carbon, black carbon, PM$_{2.5}$, water-soluble composition of PM$_{2.5}$, CO$_2$, particle size distribution, and aerosol scattering coefficient) were made simultaneously. Ozone and CO were measured using standard ultraviolet and non-dispersive infrared absorption. NO/NO$_2$/NO$_x$ were sequentially measured using a chemiluminescence instrument equipped with two converters (a blue light converter and a molybdenum converter) located outdoors to minimize the loss on the sampling tube (Inomata et al., 2010). NMHCs were determined using an automated gas chromatograph-flame ionization detector (GC-FID) system coupled with cryogenic preconcentration. Ambient air sampled 5 m above the ground was first dried with a Nafion tube and then passed through a microtrap (1/16"OD × 35 mm, Carboxene 14 mg + Carbopak 2 mg) in a freezer. After thermal decomposition, the NMHCs (C$_2$–C$_8$) were again concentrated on a trap of smaller volume and then analyzed using a GC-FID with two columns (Al$_2$O$_3$/Na$_2$SO$_4$ plot, 0.32 mm ID × 30 m) and HP-1 (methylsiloxane, 0.32 mm ID × 60 m × 1 µm). Specifically, the measured species were ethane (ETH; the model name species in RACM2, see below), propane (HC3), isobutane (HC3), n-butane (HC3), acetylene (ACE), isopentane (HC5), n-pentane (HC5), and n-hexane (HC5). Hourly observations were automatically made with standard sample measurements conducted every 12 h. Alkenes [ethylene (ETE), propylene (OLT), 1-butene (OLT), and cis-2-butene (OLI)], and aromatics [toluene (TOL), ethylbenzene (TOL), m-/p-xylene (equally divided to XYM and XYP), and o-xylene (XYO)] were not quantified accurately during this period; therefore their concentrations were inferred from those observed during April–June 2010. The concentrations of these individual NMHCs observed in
Table 1. Observed species or parameters and instruments used during intensive measurement period from May 1 to June 5, 2009 at Fukue Island.

<table>
<thead>
<tr>
<th>Observed species or parameters</th>
<th>Instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Dylec 1100 (switched to Thermo 49C on Oct 2010 for long-term observations)</td>
</tr>
<tr>
<td>CO</td>
<td>Horiba APMA-360</td>
</tr>
<tr>
<td>NO/NO&lt;sub&gt;x&lt;/sub&gt;/NOy</td>
<td>Thermo42CTL coupled with BLC/Molybdenum converters</td>
</tr>
<tr>
<td>NMHCs</td>
<td>Cryogenic pre-concentration GC-FID</td>
</tr>
<tr>
<td>Aromatics and OVOCs</td>
<td>PTR-MS</td>
</tr>
<tr>
<td>Spectral actinic flux/J values</td>
<td>Spectroradiometer</td>
</tr>
</tbody>
</table>

2010 were regarded as the sum of 1) background concentrations that linearly decrease with time as the season proceeds to summer, representing more intensive oxidative loss, and 2) a term that is proportional to the acetylene concentration where the proportional factor is decaying exponentially with the traveling time taken for the air mass to take to reach the observatory from the edge of the Asian continent. For 1), 8-day moving five-percentile values were assumed as the background values and were linearly fitted. For 2), the difference from the background value for each NMHC [ANMHC(i)] was divided by that for the less reactive C<sub>2</sub>H<sub>2</sub> (ΔC<sub>2</sub>H<sub>2</sub>), plotted against the traveling time and fitted by an exponential decay function. The fitting parameters were used to estimate the concentrations in 2009. The traveling time from the edge of the continent was calculated with the backward trajectories outlined in the first part of the results and discussion section. Benzene concentrations estimated in this way agreed well (median estimated/observed ratio = 0.92, R<sup>2</sup> = 0.68) with those independently observed using proton-transfer reaction mass spectrometry (PTR-MS; Ionicon Analytik GmbH, Austria) during May–June 2009. The PTR-MS measurements provided the concentrations of benzene (m/z = 79, BEN), formaldehyde (m/z = 31, HCHO), acetaldehyde (m/z = 45, ACD), acetone/propanal (m/z = 59, ACT), methyl ethyl ketone (m/z = 73, MEK), methacrolein and methyl vinyl ketone (m/z = 71, assumed MACR and MVK gave 50% contributions), and methanol (m/z = 33, MOH) used in the model simulations. The concentrations of benzene, acetaldehyde, acetone, MVK, and methanol was calibrated by using a ten-VOC premixed standard gas containing toluene (4.98 ppmv), 1,3,5-trimethybenzene (1.01 ppmv), acetonitrile (4.95 ppmv), acetaldehyde (5.04 ppmv), methanol (5.05 ppmv), benzene (5.01 ppmv), acetonitrile (4.99 ppmv), isopropene (4.99 ppmv), p-xylene (4.99 ppmv), and MVK (5.00 ppmv) balanced with N<sub>2</sub>. Formaldehyde concentrations were determined by using the detection sensitivity reported previously (Inomata et al., 2014). Isoprene (ISO) concentrations were not determined previously (Inomata et al., 2008). For MEK, the volume mixing ratio was calculated theoretically from the equation-obtained signal intensity, rate constant, and reaction time for its protonation reaction (Inomata et al., 2010; Kudo et al., 2014). Isoprene (ISO) concentrations were not determined in 2009 and were estimated from 2010 data, parameterized as a function of solar light intensity and ambient temperature. The isoprene concentrations in the study period were low and their contributions to ozone production were small. The spectral actinic flux (2πsr) in the wavelength range 274–698 nm was observed using a spectrometer (Metcon) equipped with a one-dimensional photodiode array detector. Calibration and conversion to J values were performed as described by Kanaya et al. (2009). A multiplication factor of 1.05 was used to account for upwelling fractions of J values.

After this intensive field campaign, ozone measurements at the Fukue site have continued until the present. The observed data from May 2010 to 2014 will also be presented. A different ozone instrument (Thermo 49C) was used after October 2010. NO<sub>2</sub> remote-sensing observations based on multi-axis differential optical absorption spectroscopy (MAX-DOAS) have also been continuously conducted at the site since March 2009. Details of the observations can be found elsewhere (Kanaya et al., 2014). The retrieved NO<sub>2</sub> partial column density at an altitude layer of 0–1 km will also be shown. The long-term ozone and NO<sub>2</sub> data indicate the representativeness of the intensively studied period during spring 2009.

**BOX MODEL SIMULATIONS**

Our previous photochemical box model based on the regional atmospheric chemistry mechanism (RACM) was updated to RACM2 (Goliff et al., 2013). Apparent errors in the rate coefficients of key reactions were corrected; the updated equations are (1.0 × 10<sup>-14</sup>)exp(−490/T) for the O<sub>3</sub> + HO<sub>2</sub> reaction, (3.2 × 10<sup>-11</sup>)exp(67/T) for O(1D) + O<sub>2</sub>, and (2.15 × 10<sup>-13</sup>)exp(110/T) for O(1D) + N<sub>2</sub>, where T is the ambient temperature in kelvin. As in our previous studies (Kanaya et al., 2007, 2009, 2013), the box model calculation was conducted in a time-dependent manner, with concentrations of ozone, NO, NO<sub>2</sub>, H<sub>2</sub>O, CO, NMHCs, oxygenated VOCs (OVOCs), and J values constrained to observations. The OH, HO<sub>2</sub>, and RO<sub>2</sub> radical concentrations were simulated and then the net oxidant production rate, F–D(O<sub>x</sub>), where O<sub>x</sub> represents ozone and NO<sub>2</sub>, was calculated based on the calculated radical concentrations, using the following equation:

\[
F - D(O_x) = \sum_{i} k_i[H_2O] + \sum_{j} \phi[J_2[RO_2]]/[NO] - k_i[O(D)][H_2O] - k_i[O_3][OH] - k_i[O_3][HO_2] - \Sigma_{k_i}[olefin][O_3] - k_i[OH][NO_2],
\]

where \(k_{i,7}\) and \(\phi\) are the reaction rate coefficient and the NO<sub>2</sub> yield, respectively. Here, ozone and NO<sub>2</sub> are grouped together as O<sub>x</sub>, and their net production is used, to cancel out the effect of rapid interconversion between them.
The model calculation was conducted for each day individually. For each day, 24 h calculations starting from 0000 LT were repeated five times and the values during the last 24 h were used as output. The concentrations of unmeasured (and therefore unconstrained) organic species were estimated simultaneously, considering their chemistry and dry deposition. Their diurnal variations reached steady state after 5 days of model runs. The assumed deposition velocities were 1.1, 2.0, 0.5, 0.2, 1.1, and 0.55 cm s\(^{-1}\) for \(\text{H}_2\text{O}_2\), \(\text{HNO}_3\), carbonyl species, peroxyacetyl nitrates, nitrates, and organic peroxides, respectively, and the boundary layer heights were 100 and 1000 m during nighttime and daytime, respectively.

Table 2 lists the model runs performed in this study. As variants of the base run (R0), sensitivity runs where the NO\(_x\) or NMHC concentrations were multiplied by a factor of 1.1 were conducted (R0_NO\(_x\) and R0_NMHCs). Also, because of the possibility that NMHC concentrations were underestimated by at most a factor of 2, another set of model runs (R1, R1_NO\(_x\), and R1_NMHCs) were conducted based on doubled NMHC concentrations. Other sets of model runs (R2a and b, R3, and R4) were also conducted to study the impact of the newly proposed radical chemistry mechanism: the R2a run was performed to study the impact of accelerated \(\text{HNO}_3\) production from water adduct formation of \(\text{HO}_2\) (Butkovskaya et al., 2009). R2b artificially increased the \(\text{HNO}_3\) production rate by a factor of 10. The R3 run assumed \(\text{HONO}\) formation from the reaction \(\text{HO}_2 + \text{NO}_2\) in the presence of \(\text{H}_2\text{O}\) proposed by Li et al. (2014). The R4 run added heterogeneous loss of \(\text{HO}_2\) on the aerosol particle surface. Detailed information will be given later.

**RESULTS AND DISCUSSION**

**Ozone Concentration Levels in Spring**

In this subsection, the observed ozone climatology and diurnal variations are shown to characterize the spring period studied in 2009, before presenting detailed results for the ozone production rates. Fig. 2(a) shows the seasonal variations in the years 2009–2014. Here, spring and autumn peaks were evident, under the influence of continental outflow. The highest concentrations occurred in April or May, with monthly averages exceeding 60 ppb for more than half of the years. Table S1 provides numerical data for monthly average mixing ratios. Fig. 3(a) is a box-whisker diagram showing the distribution of hourly average values in May for individual years. The highest 10% of hourly averages ranged between 90 percentiles (72–81 ppb) and the maximum (92–118 ppb) for the studied years, suggesting that ozone pollution was significant. Fig. 2(b) shows average diurnal variations in the observed ozone concentrations. The ozone concentration increased from the morning to the afternoon, indicating that the net photochemical production rate, \(F-D(O_3)\), was positive. The amplitude was similar from year to year. Fig. 3(b) shows that the partial \(\text{NO}_2\) columns in the altitude range 0–1 km were similarly distributed for the years 2009–2013. These analyses suggest that the results for the period of intensive study of the ozone production

**Table 2. Model simulations performed in this study. For each run, two sensitivity runs were performed, in which concentrations of NO\(_x\) or NMHCs were multiplied by a factor of 1.1.**

<table>
<thead>
<tr>
<th>Model Run</th>
<th>Explanation</th>
<th>Average ozone production (ppb) per day</th>
<th>VOC-limited hours (out of 255 hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base (R0)</td>
<td>Base run, constraining (\text{O}_3), (\text{H}_2\text{O}), (\text{NO}), (\text{NO}_2), (\text{CO}), NMHCs, OVOCs, and (J) values to observations</td>
<td>6.8</td>
<td>35 (14%)</td>
</tr>
<tr>
<td>R1</td>
<td>NMHCs × 2</td>
<td>8.4</td>
<td>33 (13%)</td>
</tr>
<tr>
<td>R2a</td>
<td>(\text{HO}_2 + \text{NO} + \text{H}_2\text{O} \rightarrow 0.07\text{HNO}_3 + 0.93 (\text{OH} + \text{NO}_2))</td>
<td>6.7</td>
<td>35 (14%)</td>
</tr>
<tr>
<td>R2b</td>
<td>(\text{HO}_2 + \text{NO} + \text{H}_2\text{O} \rightarrow 0.7\text{HNO}_3 + 0.3 (\text{OH} + \text{NO}_2))</td>
<td>4.3</td>
<td>67 (26%)</td>
</tr>
<tr>
<td>R3</td>
<td>(\text{HO}_2 + \text{NO}_2 (\text{+H}_2\text{O}) \rightarrow \text{HONO})</td>
<td>5.4</td>
<td>30 (12%)</td>
</tr>
<tr>
<td>R4</td>
<td>(\text{HO}_2 + \text{aerosol surface} \rightarrow \text{lost (γ = 0.25)})</td>
<td>5.2</td>
<td>41 (16%)</td>
</tr>
</tbody>
</table>

**Fig. 2.** (a) Seasonal variations in monthly average ozone concentrations at Fukue Island. (b) Average diurnal variations in May in different years, shown as deviations from monthly averages. Diurnal variations are separately shown for continental air mass cases and other cases for 2009.
rate (May–June 2009) were typical, showing the general features of ozone trends during springtime.

Fig. 1(a) includes the backward trajectories (CGER-METEX, http://db.cger.nies.go.jp/metex/trajecory.html, for 5-days duration from altitude 500 m at 1500 LT using kinematic vertical wind) on 17 days out of the 36 days of the study period (May 1 to June 5, 2009), when the air mass originated from the continent (hereafter referred to as continental outflow days). The traveling time from the edge of the continent ranged from 8 to 87 h, with a median of 25 h. The average daytime (0500–2000 LT) ozone concentration (66 ppb) for the continental outflow days was clearly larger than that (56 ppb) for the other 19 days of the study period. The average daytime (0500–2000 LT) ozone concentration variations (Fig. 2(b)). On May 8 and 9, when high average ozone levels of 91 and 85 ppb were observed over the period 0500–2000 LT, the concentrations of photochemical ozone produced were 13 and 3.1 ppb per day, respectively, suggesting that in-situ production of ozone on the day of arrival was important, although production in the upstream regions on previous days was dominant.

**Base Run Results**

Fig. 5 shows the average diurnal variations in the concentrations of OH, HO2, RO2, and F–D(O1D) calculated in the base model run on the continental outflow days. The average daytime peak of OH was 7.4 × 106 radicals cm−3, and HO2 and RO2 peaked at 24 and 16 pptv, respectively. The F–D(O1D) value peaked earlier (1000–1100 LT), at ~1.6 ppb h−1, when NO was present at higher concentrations. Integration from 0500 to 2000 LT gave estimated average daily productions of 6.8 ppb. This was almost consistent with the daytime increase in average diurnal ozone concentration variations (Fig. 2(b)). On May 8 and 9, when high average ozone levels of 91 and 85 ppb were observed over the period 0500–2000 LT, the concentrations of photochemical ozone produced were 13 and 3.1 ppb per day, respectively, suggesting that in-situ production of ozone on the day of arrival was important, although production in the upstream regions on previous days was dominant.

**Sensitivity Model Run Results and Regime Evaluation**

Fig. 7(a) shows the average diurnal variations in F–D(O1D) in the base run (R0) and the sensitivity runs, R0_NMHCs and R0_NOx, with the NMHC and NOx concentrations multiplied by a factor of 1.1, for the continental outflow days. The average integrated F–D(O1D) values were 7.4 and 7.0 ppb per day for R0_NOx and R0_NMHCs, respectively, compared with 6.8 ppb per day in the base run (R0). Here, we define VOC limited as the case where the VOC increase resulted in a larger F–D(O1D) than that in the case where NOx increases. On average, the increase from the base run was larger for R0_NMHCs than for R0_NOx, during the period 0700–1000 LT, suggesting VOC limited, whereas that for R0_NOx was larger for the other hours, suggesting NOx limitation.
limited. This implies that VOC reduction was meaningful as well as NO\textsubscript{x} reduction. Typical examples were on the mornings of May 13 and 14 (Fig. 7(b)); during the periods 0500–1000 and 0500–1200 LT on each day, the NMHC increase resulted in higher $F$–$D$(O\textsubscript{x}) values than did the NO\textsubscript{x} increase. In this case, VOC reduction should be prioritized to avoid additional ozone production. We found 35 h of VOC-limited cases from a total of 255 h (0500–2000 LT) on the 17 days with continental outflow.

The results may be affected by the uncertainty in the precursor concentrations used as model input. In particular, the NMHC concentrations could have been underestimated, because only 18 species (see Fig. 4(c)) were determined or estimated and taken into account in the model simulation. To test the impact of this underestimation, we used the R1 run and its variants, R1_NO\textsubscript{x} and R1_NMHCs, where the NMHC concentrations were doubled. The average integrated $F$–$D$(O\textsubscript{x}) values were 8.4, 9.1, and 8.6 ppb per day for the R1, R1_NO\textsubscript{x}, and R1_NMHCs scenarios, respectively. The basic NO\textsubscript{x}-limited feature did not change; 33 h were judged to be VOC limited. Based on the above analyses, we concluded that the regime was mostly NO\textsubscript{x} limited, and occasionally (~14% of time) VOC limited. The policy implication is that the VOC reduction legislation recently enacted by the Japanese...
Fig. 5. Average diurnal variations in modeled OH, HO$_2$, and RO$_2$ radical concentrations and F–D(Ox) values on continental outflow days in base run R0. Those estimated for May 8 and 9, 2009, are shown individually.

government in addition to NO$_x$ emission control should be effective, to avoid further production of ozone in the air mass arriving from the continent.

The chemical features of the VOC-limited cases were investigated. The VOC-limited cases were associated with relatively high NO$_x$/NO$_y$ ratios (Fig. 8(a)), implying the influence of relatively fresh pollution from the continent. Similar results were obtained for the analysis of ozone production regimes at the top of Mt. Tai, Shandong Province, China (Kanaya et al., 2009). The backward trajectories from 0900 LT on May 8, 13, 14, 31, and June 1, when VOC-limited conditions occurred at that hour in the morning, were mostly traced back to the Korean Peninsula within 6–8 h, with the exception of June 1, when the air mass came directly from the North China Plain region, with a transport time of 43 h. NO$_x$ was probably emitted in the continental region, including the Korean Peninsula, and transported to Fukue Island before conversion to NO$_y$ species. Fig. 8(b) shows that the NMHCs/NO$_x$ ratio was low when the VOC-limited conditions occurred. The border between the VOC-limited and NO$_x$-limited regimes seemed to lie at around 10 ppbC/ ppb, almost consistent with the results for previous theoretical studies (Milford et al., 1994) and studies conducted in Tokyo (Kanari, 2006; Kanaya et al., 2008; Sadanaga et al., 2012). Impact of Modified Radical Chemistry

We also studied how the recently proposed HO$_2$ radical reaction pathway, which is not included in the standard tropospheric chemistry mechanism, influenced the ozone production rates. Three different mechanisms were individually tested. Fig. 9 shows the average diurnal variations in the OH and HO$_2$ radical concentrations and F–D(Ox) in the base run and the sensitivity runs (R2a, b, R3, and R4).

First, a mechanism in which the HNO$_3$ yield was increased by the HO$_2$ + NO reaction in the presence of H$_2$O (Butkovskaya et al., 2009) was tested (R2a). In RACM2, such an HNO$_3$ production channel was considered from the HO$_2$ + NO reaction, but only under dry conditions (Butkovskaya et al., 2007). Here, we assumed equilibrium between HO$_2$ and HO$_2$-H$_2$O (Archibald et al., 2011) and that HO$_2$-H$_2$O reacted with NO, yielding 7% HNO$_3$ (and 93% OH and NO$_2$), with the same rate coefficient as for the original HO$_2$ reaction (Butkovskaya et al., 2009). All other HO$_2$-H$_2$O reactions were the same as that of HO$_2$. The shown HO$_2$ amount included the HO$_2$-H$_2$O fraction. The R2a model showed that the HO$_2$ radical concentrations was reduced by only < 0.5% and the average daily integrated F–D(Ox) decreased only slightly to 6.7 ppb per day, from 6.8 ppb per day in the base run. Although the introduced process reduced the efficiency of the radical propagation reaction, the influence was limited. A sensitivity run (R2b) in which the HO$_2$-H$_2$O reaction yielded 70% HNO$_3$, 10 times higher than in the R2a run, HO$_2$ decreased by 4–15% and F–D(Ox) decreased to 4.3 ppb per day. Although not supported by laboratory experiments, such large losses were necessary to produce recognizable changes in the calculated ozone production rate.

Second, the HO$_2$ + NO$_2$ reaction was assumed to be accelerated by HO$_2$-H$_2$O adduct formation and to produce HONO instead of HNO$_4$ (Li et al., 2014). This process was hypothesized based on HONO measurements made onboard a Zeppelin airship. In this case, HO$_2$-H$_2$O was assumed to react with NO$_2$ at a rate 3.5 times faster than HO$_2$, and to produce HONO at a yield of unity (Li et al., 2014). The results (R3 run) show that the OH peak increased to $8.3 \times 10^6$ radicals cm$^{-3}$, the HO$_2$ peak decreased to 21 ppt, and the average integrated F–D(Ox) value decreased to 5.4 ppb per day. The assumed perturbation was large enough to reduce the ozone formation rate by 21%.

Third, heterogeneous loss of HO$_2$ on the aerosol particle surface was introduced at an uptake coefficient of 0.25 (Kanaya et al., 2009; Taketani et al., 2012). The process was assumed to give no products. We used the aerosol number size distribution measured using an optical particle counter...
Fig. 6. Breakdown of $F$–$D(O_3)$ into the reaction terms. MO2, ACO3, ETHP, and ISOP in RACM2 indicate methyl peroxy radical, acetyl peroxy radical, ethyl peroxy radical, and peroxy radical from isoprene oxidation.

Fig. 7. (a) Average diurnal variations in $F$–$D(O_3)$ in runs R0, R0_NMHCs, and R0_NOx. (b) Values for May 13 and 14, 2009, are shown separately.

(LASX-II, Particle Measurement Systems, Boulder, CO, USA) covering the size range 90–3000 nm. The calculated heterogeneous loss rate of HO$_2$, $k$, was $(4.2 \pm 1.9) \times 10^{-3}$ s$^{-1}$, and showed a close correlation with PM$_{2.5}$ ($k = 1.61 \times 10^{-3} \text{[PM}_{2.5} \text{(µg/m}^3\text{)]} - 5.90 \times 10^{-4}$; $R^2 = 0.82$; PM$_{2.5}$ ranged from 4 to 85 µg m$^{-3}$, with an average of 22 µg m$^{-3}$).

In run R4, the OH and HO$_2$ peaks decreased to $6.7 \times 10^6$ radicals cm$^{-3}$ and to 19 ppt, whereas the RO$_2$ peaks were similar (~16 ppt). The $F$–$D(O_3)$ value decreased to 5.2 ppb per day. Apart from run R2b, this sensitivity run gave the largest impact on the ozone production rate, implying that heterogeneous loss, the impact of which was studied in Tokyo and at the top of Mt. Tai (Kanaya et al., 2007, 2009), can be important in a regional scale. More studies of the overall uptake coefficient of HO$_2$ and the chemical mechanism are therefore necessary. The presence of aerosols can also affect ozone photochemistry through $J$ value modification. However, in the single scattering albedo range ~0.95, measured around Fukue Island, the impact was not large even if the aerosol optical depth changed from 0 to 0.5, as tested using the Tropospheric Ultraviolet-Visible ver. 4.6 radiative transfer model (Madronich and Flocke, 1997).

For the R2a, R2b, R3, and R4 runs, sensitivity runs with 10% increases in NO$_x$ or NMHCs concentrations were conducted. The VOC-limited periods were 35, 67, 30, and 41 h, respectively, compared with 35 h in the base case (R0). This implies that the uncertainty in the radical chemistry could affect determination of the limiting factor of ozone.
Fig. 8. Time series of NO\textsubscript{x}/NO\textsubscript{y} and NMHCs/NO\textsubscript{x} ratios. Shaded days are continental outflow days. Circles indicate hours judged to be VOC limited.

Fig. 9. Average diurnal variations in OH, HO\textsubscript{2}, and RO\textsubscript{2} concentrations and \(F-D(O_x)\) for runs R0, R2a, R2b, R3, and R4, with differences among radical chemistry reactions.

production; more study is therefore necessary. However, the conclusion here that ozone production was mainly limited by NO\textsubscript{x} and less frequently by VOCs is unchanged. From these analyses, we conclude that VOC reduction and NO\textsubscript{x} reduction are both significant in reducing additional production of ozone fueled by local (domestic) precursor emissions in the relatively clean western Japan region.

SUMMARY

Asian continental outflow clearly raised the daytime ozone concentrations at Fukue Island, west of Japan, during May–June 2009 to 66 ppb, from 56 ppb on the days under the influence of other air mass type. The OBM approach used to assess the \textit{in-situ} ozone production rates and regimes in the continental outflow air masses suggested that not only production on previous days over the continent, but also \textit{in-situ} or in-travel production was as much as 6.8 ppb per day, and raised the ozone levels. Diagnosis of the chemical state suggested that the limiting factor in ozone production was usually NO\textsubscript{x}, although VOCs occasionally dominated. The conclusion was robust in that the modified assumption in the radical chemistry that dominated the estimation of the ozone production rates had a limited degree of influence. The analysis here supports the ongoing, intensified VOC emission reduction enforced for the whole of Japan since 2006, in addition to continuous efforts to reduce NO\textsubscript{x} emissions to avoid further ozone production fueled by domestic emissions of precursors in the air masses arriving from the Asian continent.

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SUPPLEMENTARY MATERIALS

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

REFERENCES


