Title
Photochemistry of ozone over the Western Pacific in Winter and Spring

Permalink
https://escholarship.org/uc/item/6057k69h

Journal
GEOCHIMICA ET COSMOCHIMICA ACTA, 67(18)

ISSN
0016-7037

Authors
Kondo, Y
Chen, G
Hudman, R
et al.

Publication Date
2003-09-01

License
https://creativecommons.org/licenses/by/4.0/ 4.0

Peer reviewed
Photochemistry of ozone over the western Pacific from winter to spring


Received 6 April 2004; revised 2 July 2004; accepted 20 July 2004; published 14 October 2004.

[1] Aircraft measurements of ozone (O₃) and its precursors, including NO, CO, H₂O, and nonmethane hydrocarbons (NMHCs), were made over the western Pacific in the 20°–45°N latitude range in January and April–May 2002 during the Pacific Exploration of Asian Continental Emission (PEACE)-A and B campaigns. These measurements have provided data sets that, in combination with Transport and Chemical Evolution over the Pacific (TRACE-P) data taken in March 2001, enable studies of O₃ photochemistry from winter to late spring. A photochemical box model is used to calculate ozone formation (F(O₃)) and destruction (D(O₃)) rates constrained by the observed species concentrations. The values of F(O₃) and D(O₃) are controlled directly by NO, J(O¹D) (O₃ photolysis frequency), H₂O, OH, and HO₂. Changes in HO₂ concentration cause corresponding changes in both F(O₃) and D(O₃), leading to their coupling. Concentrations of these species, which are strongly influenced by photochemistry and transport from the Asian continent, underwent large seasonal variations. In the boundary layer (0–3 km), NO was much higher in January than in April–May, because of stronger winds, lower convective activities, and lower oxidation rates by OH in winter. The net O₃ formation rate, given by P(O₃) = F(O₃) – D(O₃), was largely positive in the boundary layer at 30°–45°N (1.5 – 4 ppbv d⁻¹) in January, mainly because of high NO and low H₂O values. Net O₃ formation continued from January to the end of March, demonstrating that the western Pacific is an important O₃ source region during this season. Net O₃ formation nearly ceased by late April/May because of the decrease in NO and the increase in H₂O. In the latitude range of 20°–30°N, P(O₃) in the boundary layer was positive in January and turned negative by March. The earlier transition was mainly due to lower NO and higher H₂O concentrations, combined with weaker transport and higher temperatures than those at 30°–45°N. The upper troposphere (6–12 km) has been shown to be a region of net O₃ formation throughout most of the year because of high NO and low H₂O. The present study illustrates that a decrease in the net O₃ formation rate at 20°–45°N latitude from winter to late spring is explained systematically by the increases in J(O¹D), H₂O, OH, and HO₂ (primarily due to increases in temperature and solar radiation) and the decrease in NO (primarily due to decrease in transport from the Asian continent). Differences in the seasonal variation of O₃ photochemistry observed over the North American continent are interpreted in terms of the differences in factors controlling O₃ formation and destruction.

INDEX TERMS: 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; KEYWORDS: ozone, troposphere, western Pacific

Citation: Kondo, Y., et al. (2004), Photochemistry of ozone over the western Pacific from winter to spring, J. Geophys. Res., 109, D23S02, doi:10.1029/2004JD004871.
1. Introduction

[2] Ozone (O$_3$) in the troposphere is a principal precursor of the hydroxyl radical (OH) and nitrate radical (NO$_3$), which control the oxidizing capacity of the atmosphere [e.g., Logan et al., 1981; Thompson, 1992]. Ozone is also a major pollutant, because it has adverse effects on human health and plants at high concentrations. Ozone is chemically produced in the troposphere by OH-initiated oxidation of CO, CH$_4$, and nonmethane hydrocarbons (NMHCs). NO$_x$ (NO + NO$_2$) acts as a key catalyst in these cycles. East Asia is a region where rapidly growing industrial activities are causing large increases in the emissions of these O$_3$ precursors. Specifically, emissions of NO$_x$ in Asia are estimated to have increased by a factor of 3 between 1975 and 1998 [Akimoto, 2003]. Another study showed a nearly 40% increase from 1990 to 2002 [Streets et al., 2003]. Emissions of these pollutants from the Asian continent can significantly impact the distributions of O$_3$ over the western Pacific, downwind of the Asian continent.

[3] One of the important features of tropospheric O$_3$ is that its mixing ratios reach maximum values in late spring in many regions of the northern midlatitudes, including over the western Pacific [Logan, 1985, 1999]. The budget of seasonal variations in O$_3$ has been investigated with 3-D models [e.g., Wang et al., 1998b; Yienger et al., 1999]. However, estimates of the O$_3$ budget will remain uncertain unless predicted concentrations of related trace gases are validated by observations of key chemical species. A lack of seasonally and geographically resolved stratospheric O$_3$ flux measurements represents another major uncertainty. Budgets of reactive nitrogen and O$_3$ over the North American continent were studied by the Tropospheric Ozone Production about the Spring Equinox (TOPSE) aircraft campaign made at middle and high latitudes in winterspring [Atlas et al., 2003]. Photochemical O$_3$ processes in these regions were studied with a photochemical box model [Wang et al., 2003; Cantrell et al., 2003b] and with 3-D models [Emmons et al., 2003]. Budgets of O$_3$ over the western Pacific from early to middle spring were estimated with photochemical box model calculations using the data set obtained from February to April 2001 during the NASA Transport and Chemical Evolution over the Pacific (TRACE-P) campaign and the Pacific Exploratory Mission (PEM)-W-B [Davis et al., 2003]. However, comprehensive measurements in winter and late spring are still very limited, although some data were obtained during the Biomass Burning and Lightning Experiment (BIBLE)-T campaign of the Japan Aerospace Exploration Agency (JAXA) in late April 1998 [Miyazaki et al., 2002]. In order to improve our understanding of O$_3$ chemistry during these periods, the aircraft measurement campaigns Pacific Exploration of Asian Continental Emission (PEACE)-A and B were conducted in January and April–May 2002, respectively, within the framework of the atmospheric chemistry project of the Earth Observation Research Center (EORC) of JAXA. We have investigated the seasonal variation of the formation and destruction processes of HO$_x$ (OH + HO$_2$) and O$_3$ in the region of 20$^\circ$–45$^\circ$N latitude from winter to late spring using the same photochemical box model as used by Davis et al. [2003]. The data sets obtained by the PEACE and TRACE-P campaigns have been used as input parameters to constrain this model. Major factors controlling the budgets of O$_3$ and HO$_x$ in different seasons have been quantified by these calculations.

2. Aircraft Measurements

[4] In situ chemical data obtained on board the G-II aircraft were used for this study. The measured quantities include O$_3$, CO, NMHCs, NO, total reactive nitrogen (NO$_x$), H$_2$O, and the photolysis frequency of NO$_2$ ($J$(NO$_2$)). The instruments used for the PEACE aircraft measurements are the same as those used for BIBLE-B campaigns [Kondo et al., 2002], with an addition of an O$_3$ instrument. The techniques, uncertainties (accuracy and precision), and time resolutions of these measurements are summarized by Parrish et al. [2004, Table 1]. In addition, the $J$(NO$_2$) instrument was calibrated at Lauder, New Zealand (45$^\circ$S), using a National Institute of Water and Atmospheric Research (NIWA) spectroradiometer along with a radiative transfer model to convert irradiances from that instrument to actinic fluxes [McKenzie et al., 2003]. All necessary inputs to the model were available, and the instrumentation, analysis methods, and radiative transfer model have all been verified previously [Bais et al., 2001; McKenzie et al., 2002; Cantrell et al., 2003a]. On the basis of these calibrations, we estimate that the $J$(NO$_2$) measurement during the PEACE campaigns has an uncertainty of 7%. The O$_3$, CO, NO, NO$_x$, H$_2$O, and $J$(NO$_2$) data were then averaged using a common time base with an interval of 1 min. The NMHC data, which were obtained every 5 min on average, were interpolated to produce 1-min data, when changes in CO and altitude were small. The G-II was based in Nagoya (35.3$^\circ$N, 136.9$^\circ$E) and Kagoshima (31.6$^\circ$N, 130.5$^\circ$E) during PEACE-A. Thirteen flights were conducted during the period between 6 and 23 January 2002 as shown by Parrish et al. [2004, Table 3a]. The flight tracks are shown in Figure 1. During PEACE-B, the G-II was based in Nagoya, and 12 flights were conducted during the period between 21 April and 16 May 2002 [Parrish et al., 2004, Figure 1 and Table 3b]. The altitude of airborne sampling ranged between 0.1 and 13 km. Flights made during PEACE-A covered the latitudes between 22$^\circ$N and 42$^\circ$N. Flights during PEACE-B covered similar latitudes. However, because the quantity of data south of 30$^\circ$N was much smaller than during PEACE-A, the statistical analysis of the PEACE-B data was limited to the latitude range of 30$^\circ$–42$^\circ$N.

[5] During TRACE-P, concentrations of O$_3$ and its precursors were measured over the western Pacific on board the P-3B and DC-8 aircraft in February–April 2001 [Jacob et al., 2003]. These data were also used for the present analysis. The TRACE-P measurements covered the latitude range between 15$^\circ$–45$^\circ$N over the western Pacific, as shown in Figure 1.

3. Photochemistry of O$_3$ and Box Model

[6] For the present study, a time-dependent photochemical box model [Crawford et al., 1997; Davis et al., 2003; G. Chen et al., A diagnostic analysis of winter/spring ozone budget based on ozonesonde and airborne observations from PEACE A/B and TRACE-P, submitted to Journal of Geophysical Research, 2004, hereinafter referred to as Chen et al., submitted manuscript, 2004] was used in order to estimate radical concentrations, including NO$_x$, and to
quantitatively assess the photochemical impact on O3. This box model was applied to the analysis of O3 photochemistry using the data sets obtained during the NASA missions PEM-W-A, PEM-W-B, and TRACE-P. The key reactions for O3 photochemistry considered in this model are discussed by Crawford et al. [1997] and are listed in Table 1. HOx is initially formed by the photolysis of O3 at wavelengths of 290–320 nm (reaction (R1)). The rate of HOx formation is expressed as

$$F(\text{HO}_x) = 2k_1k_{3a}[\text{O}_3][\text{H}_2\text{O}]/(k_{10}[\text{M}] + k_{12}[\text{H}_2\text{O}])$$

$$\approx 2k_1k_{3a}[\text{O}_3][\text{H}_2\text{O}]/k_{10}[\text{M}],$$

(1)

where [ ] denotes the number density of the indicated species, $k_1$ is the reaction rate coefficient for reaction $R_5$, and $k_{3a} = J(\text{O}^1D)$ is the photolysis frequency of O3. This equation shows that the key parameters driving the HOx primary formation are solar ultraviolet (UV) radiation, O3, and H2O. At the same time, formation of HOx results in O3 loss. Net photochemical loss of HOx occurs through reactions (R9) and (R12). Under high-NOx conditions, reaction (R12) dominates as a sink of HOx; for low NOx, reaction (R9) does. NO also controls the partitioning between OH and HO2 through reaction (R4). Oxidation of CO, CH4, and NMHCs by OH leads to the formation of peroxy radicals HO2, CH3O2, and RO2 (R = C2H4 and higher organic groupings). These radicals react with NO, leading to catalytic O3 formation (reactions (R4), (R5), (R6), (R10), (R11), and (R2)). Photochemical destruction of O3 occurs through reactions (R1) + (R3a), (R7), and (R8), with reaction (R3a) being dominant for the lowest part of the troposphere. The photochemical formation ($F(\text{O}_3)$), destruction ($D(\text{O}_3)$), and net formation ($P(\text{O}_3)$) rates are expressed as

$$F(\text{O}_3) = (k_6[\text{HO}_2] + k_8[\text{CH}_3\text{O}_2] + k_9[\text{RO}_2])[\text{NO}],$$

(2)

$$D(\text{O}_3) = k_{3a}[\text{O}^1D][\text{H}_2\text{O}] + k_9[\text{OH}] + k_8[\text{HO}_2])[\text{O}_3] + k_{10}[\text{NO}][\text{O}_3] \times k_{12}[\text{NO}_2][\text{OH}]/(k_10[\text{NO}]) + k_{12}[\text{NO}_2][\text{OH}],$$

(3)

$$P(\text{O}_3) = F(\text{O}_3) - D(\text{O}_3).$$

(4)

The last term in equation (3) becomes significant only at NOx levels exceeding $\approx 500$ parts per trillion by volume (pptv). The $F(\text{O}_3)$ and $D(\text{O}_3)$ values increase linearly with [NO] and [O3], respectively (equations (2) and (3)), when concentrations of other species are unchanged.

[7] The time-dependent box model was run using the observed values of NO, CO, O3, H2O, NMHCs, $J(\text{NO}_2)$, temperature, and pressure as input parameters. The other photolysis frequencies were initially calculated with the NCAR Tropospheric Ultraviolet Visible (TUV) radiative transfer model with a DISORT four-stream implementation for clear-sky conditions. The observations of $J(\text{NO}_2)$ relative to calculated clear-sky values were used to scale these values for the cloudy conditions encountered during the sampling.

[8] Model integration was continued until the model outputs reached diurnal stationary state. For most of the present analysis, diurnally averaged values of radicals, $F(\text{O}_3)$, $D(\text{O}_3)$, and $P(\text{O}_3)$ were used. Olson et al. [2004] showed good model agreement with the observed total peroxy radical concentrations (with a median bias of 23%). Similarly, calculated NO2 concentrations at 0–7 km agreed with the observations.

**Figure 1.** Latitudes and periods covered by the PEACE-A, TRACE-P, and PEACE-B campaigns and their flight tracks.

**Table 1.** Key Reactions in O3 Photochemistry

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1)</td>
<td>O3 + hv → O2 + O(1D)</td>
</tr>
<tr>
<td>(R2)</td>
<td>O(1D) + O3 + M → O2 + O + M</td>
</tr>
<tr>
<td>(R3a)</td>
<td>O(1D) + H2O → 2OH</td>
</tr>
<tr>
<td>(R3b)</td>
<td>O(1D) + M → O(1P) + M</td>
</tr>
<tr>
<td>(R4)</td>
<td>HO2 + NO → NO2 + OH</td>
</tr>
<tr>
<td>(R5)</td>
<td>CH3O2 + NO → NO2 + CH3O</td>
</tr>
<tr>
<td>(R6)</td>
<td>RO2 + NO → NO2 + RO</td>
</tr>
<tr>
<td>(R7)</td>
<td>O3 + OH → HO2 + O2</td>
</tr>
<tr>
<td>(R8)</td>
<td>HO2 + HO2 → H2O2 + O2</td>
</tr>
<tr>
<td>(R9)</td>
<td>NO + O3 → NO2 + O2</td>
</tr>
<tr>
<td>(R10)</td>
<td>NO2 + OH → NO + O</td>
</tr>
<tr>
<td>(R11)</td>
<td>NO2 + hv → NO + O</td>
</tr>
<tr>
<td>(R12)</td>
<td>NO2 + OH + M → HNO3 + M</td>
</tr>
</tbody>
</table>
Figure 2. Mean winds at 925 and 500 hPa during PEACE-A, TRACE-P, and PEACE-B.
with those measured during TRACE-P to within 30% [Nakamura et al., 2003].

4. Meteorological Conditions in Winter and Spring

Here brief descriptions of meteorological conditions relevant to the present study are given for the western Pacific region. More detailed descriptions of the meteorological conditions are given by Fuelberg et al. [2003] for TRACE-P and by Oshina et al. [2004] for PEACE-B. Mean wind fields at 925 hPa and 500 hPa during PEACE-A, TRACE-P, and PEACE-B are shown in Figure 2. The major sampling region over the western Pacific shown in Figure 1 is also shown in Figure 2. Hereafter the months of January, March, and April–May represent the observational periods for PEACE-A, TRACE-P, and PEACE-B, respectively. Seasonal variations in meteorological conditions proceeded in a different way at different latitudes (20°–30°N and 30°–45°N), as detailed below. At 925 hPa, the mean wind direction was northwesterly, and the wind speed was highest in January, because of the dominating Siberian high-pressure system. The continental outflow reached 20°N and even farther south down to 10°N during this period. The northwesterly wind weakened noticeably by March, especially at 20°–30°N. The wind speed became very weak by April–May, associated with the weakening of the Siberian high and strengthening of Pacific high pressure. The flow was easterly or southerly in the 20°–30°N region, transporting maritime air into this region. Around (30°N, 130°E), the mean wind speeds at 925 hPa in January, March, and April–May were about 8, 6, and 2 m s⁻¹, respectively (Figure 2). The boundary layer wind fields at 30°–45°N were clearly more impacted by continental outflow than those at 20°–30°N between March and May.

Figure 3 shows 5-day back trajectories for air masses sampled at 30°–45°N below 3 km in January and April–May, calculated using the 1° × 1° gridded meteorological data from the European Centre for Medium-Range Weather Forecasts (ECMWF). In January, most of the sampled air masses were transported from the coastal region of the Asian continent in less than one day. In April–May, on the other hand, it took 3–5 days for most of the air masses to reach the aircraft sampling region after leaving the coastal region.

At 500 hPa, northwesterly winds dominated at 30°–45°N in January and March but turned westerly by April–May. At 20°–30°N, westerlies dominated throughout the period between January and May. This latitudinal variation corresponds to the location of the subtropical jet at around 30°N. In March, vertical mixing became more active because of synoptic-scale disturbances, including transport associated with frontal systems [Fuelberg et al., 2003; Miyazaki et al., 2003]. Meteorological and chemical analyses have shown that most of the uplifted transport was associated with warm conveyor belts.
(WCBs) and convective outflow. In April–May, a quasi-stationary frontal zone was formed over central China by low-altitude southerlies associated with a predominant anticyclone over the central Pacific (Figure 2). Convective activities along the frontal zone occasionally transported pollutants, most prominently CO, to 6–12 km altitudes, followed by rapid eastward transport along the subtropical jet [Oshima et al., 2004]. In addition to

Figure 4a. Vertical profiles of the median values of O₃, CO, and C₃H₈ in the latitude ranges of (left) 20°–30°N and (right) 30°–45°N during PEACE-A, TRACE-P, and PEACE-B. Horizontal bars represent central 67 percentile values.
convection, synoptic-scale disturbances also transported pollutants to the free troposphere.

5. Seasonal and Latitudinal Variations of O₃ and Its Precursors

For the present analysis, we define two latitude regions (20°–30°N and 30°–45°N) over the western Pacific at longitudes between 123°E and 145°E, considering the distinct differences in meteorological conditions between the two regions, especially in the boundary layer. In addition, both tropopause height and total O₃ column density showed abrupt changes around 30°N over the western Pacific during PEM-W-B [Crawford et al., 1997] and TRACE-P [Browell et al., 2003; Wild et al., 2003]. The latitudinal variation of the total O₃ column strongly influences the latitudinal variation of \( J(O^1D) \), which is an important controlling factor of photochemical activity. Stratospheric data were excluded by using the thermal tropopause height, which is defined as the region where the lapse rate is smaller than 2 K/2 km for a 2 km altitude range.

Profiles of the median values of O₃, CO, propane (\( C_3H_8 \)), \( H_2O \), temperature, NO, NO\(_x\) (observed NO + model-calculated NO\(_2\)), and NO\(_x\)/NO\(_y\) ratio in each latitude range are shown for January, March, and April–May in Figures 4a–4c. The top of the boundary layer, as determined from the relative humidity profile, was often located between 3 and 4 km in January [Takegawa et al., 2004]. This also corresponds to the altitudes where the median values of short-lived species, such as \( C_3H_8 \) and NO\(_x\), showed sharp decreases (Figures 4a and 4c). Data with \( NO_x/(CO + 100 \text{ parts per billion by volume (ppbv)} \) exceeding 10 pptv/ppbv in the boundary layer (0–3 km) were excluded from the present analysis. These data are considered to have been strongly influenced by local NO\(_x\) emissions and do not represent regional NO\(_x\) levels. By this selection, the median NO\(_x\) mixing ratios at 0–1 km decreased by about 30%, and they changed little at 2–3 km. Column-integrated amounts of O₃ up to the tropopause are given in Table 2. It should be noted that the median values at 20°–30°N for April–May are not representative because of the very limited quantity of the data, as mentioned above, and are therefore excluded from the present analysis. The O₃ mixing ratios in the 30°–45°N regime increased at all altitudes in the troposphere from January to April–May, with major increases occurring by March. The increase was 10–20 ppbv below 8 km, depending on altitude. The increase in the total column between January and March is \( 2.3 \times 10^{17} \) molecules cm\(^{-2} \) (28%). A similar increase
The median O₃ values were close to those observed by ozonesondes at three stations: Tateno (36.1°N, 140.1°E), Kagoshima (31.6°N, 130.6°E), and Naha (26.2°N, 127.7°E), operated by the Japan Meteorological Agency (JMA) (Chen et al., submitted manuscript, 2004), suggesting that the aircraft O₃ data are representative of this region. The O₃ mixing ratios in the boundary layer are plotted versus the CO mixing ratios for January and March in Figure 5. The April–May data are not shown because of the narrow range (100–200 ppbv in most cases) of CO values. The increase in O₃ from January to March is seen at similar CO values. This suggests the importance of photochemical formation of O₃ as the principal cause of the observed increase.

Figure 4c. Same as Figure 4a, except for vertical profiles of observed NO, NOₓ, and NOₓ/NOᵧ ratios.
increase from January to March rather than transport from the stratosphere. An increase in O$_3$ due to stratospheric transport would be accompanied by a decrease in CO in the stratospheric air [Singh et al., 1997].

The CO mixing ratios below 2 km in the 30°–45°N regime were highest in January and decreased during spring. The seasonal variation of CO is mainly driven by the seasonal variation of the chemical loss rate of CO by OH and vertical mixing. Vertical mixing dilutes the high CO boundary layer air with low-CO free tropospheric air. The vertical gradient of the CO mixing ratio was lowest in April–May, when the convection over continental regions became more frequent than in January. In fact, episodic convection associated with stationary fronts over southern China occasionally increased CO at 7–12 km in April–May, as discussed by Oshima et al. [2004]. The decrease in the mixing ratios from January to April–May is more systematic for C$_2$H$_4$ in the boundary layer and middle troposphere (3–6 km). In the boundary layer, C$_2$H$_4$ has a lifetime of about 13–28 (6–8) days in January–April–May, as compared to 55–110 (24–36) days for CO, as summarized in Table 3. For this calculation, the average OH concentration (also given in the table) was estimated by using a box model, as detailed in section 6.1.

The H$_2$O mixing ratios in the 30°–45°N regime were highest in April–May because of higher temperatures. At 0.5 km, the median temperature was 278 K (287 K) in January (April–May), and the corresponding H$_2$O saturation mixing ratios was 0.9% (1.7%). The higher H$_2$O in April–May was also due to the transport of humid air from lower latitudes, associated with strengthening of the Pacific high (see Figure 2) [Oshima et al., 2004]. The H$_2$O mixing ratios below 6 km changed little from January to March.

At 30°–45°N, NO and NO$_x$ mixing ratios at 0–2 km were highest in January. This high NO$_x$ was caused by efficient transport of NO$_x$ from the Asian continent due to strong winds and slow OH oxidation. The average lifetime of NO$_x$ determined by OH oxidation is calculated to be 2.6 days (0.6 days) for January (April–May) (Table 3). Takegawa et al. [2004] have estimated the lifetime of NO$_x$ in January to be 1.2 ± 0.4 days using the observed slope of the C$_2$H$_4$/C$_2$H$_2$ correlation and the OH concentration calculated by the box model. This lifetime is about 2 times shorter than the lifetime considering only oxidation by OH, suggesting the contribution of hydrolysis of N$_2$O$_5$ on aerosols (N$_2$O$_5$ + H$_2$O $\rightarrow$ 2HNO$_3$). The effect of this reaction has also been studied using a 3-D model combined with the TOPSE aircraft data at midlatitudes to high latitudes over the North American continent in winter–spring [Tie et al., 2003]. The relative contribution of this reaction should be greatly reduced in spring because of shorter nighttime hours and 2-to-4-times-higher OH concentrations (Table 3). In the boundary layer, the lifetime of NO$_x$ has been estimated to be 1.7 ± 0.5 days, which is longer than but still comparable to that of NO$_x$ (1.2 ± 0.4 days) [Takegawa et al., 2004]. Because of this relatively fast removal rate of NO$_x$, a NO$_x$/NO ratio as high as 0.5 below 1 km is not due simply to the freshness of the air masses. The lower NO$_x$/NO ratio in spring than in January is consistent with the longer transport time. At 3–7 km, NO showed no systematic seasonal variation. The contribution of peroxyacetyl nitrate (PAN) decomposition to the observed NO$_x$ cannot be assessed, because of the lack of PAN data during the PEACE campaigns.

The combined effect of the changes in transport time and OH concentrations can be seen from the C$_2$H$_4$/C$_2$H$_2$ and NO$_x$–CO correlations for 30°–45°N as shown in Figure 6. The lifetime of C$_2$H$_4$ in the boundary layer is 3.0 days (1.6 days) in January (March), much shorter than that of C$_2$H$_2$ (Table 3). The decrease in the C$_2$H$_4$ concentration relative to C$_2$H$_2$ indicates that air masses observed in March had undergone more processing by OH than those in winter, because of higher OH concentrations and lower wind speeds. For NO$_x$, correlation with CO was used instead of C$_2$H$_2$ because of the much higher sampling rate of CO and good correlation between C$_2$H$_2$ and CO. The general decrease in NO$_x$ from January to March is shown. The change in the NO$_x$–CO correlation from January to March, combined with that of the C$_2$H$_4$–C$_2$H$_2$ correlation, consistently shows the important role of the oxidation of NO$_x$ by OH in causing the observed seasonal variation in the NO$_x$ concentrations. Hydrolysis of N$_2$O$_5$ should have reduced the degree of the change in NO$_x$ between January and March to some extent.

6. Seasonal and Latitudinal Variations of HO$_x$ and O$_3$ Photochemistry

6.1. OH and HO$_2$

[19] The calculated values of diurnally averaged $J$(O$_1^D$), $F$(HO$_2$), OH, and HO$_2$ are shown in Figures 7a and 7b. The $J$(O$_1^D$) values increased from winter to spring associated with the decrease in the solar zenith angles (SZAs) as well
as the decrease in the total column \(O_3\) density associated with the seasonal variation of stratospheric \(O_3\). General features of the temporal and spatial variations in OH and \(HO_2\) can be understood in terms of the variations in the \(J(O_1D)\), \(O_3\), and \(H_2O\), which directly contribute to \(F(HO_x)\) (equation (1)). Because all of these parameters increased from winter to spring in both latitude ranges, corresponding increases in OH and \(HO_2\) are anticipated, as is shown from \(J(O_1D)\) and \(H_2O\) (see earlier discussion). More detailed analysis due to the increase in \(O_3\) and \(H_2O\) (see earlier discussion).

\[ \text{Equation (1)} \]

**Figure 7b.** This \(HO_x\) increase is seen to be related to the April–May/January ratios of OH and \(HO_2\) were about 3–4 from March to April–May by another factor of 2–3. The increases in OH and \(HO_2\) are anticipated, as is shown from winter to spring in both latitude ranges, corresponding to the tropospheric column-integrated \(O_3\) formation was largest, as discussed in section 6.2.

[20] The seasonal changes in photochemistry are quite evident from the increase in \(HO_x\) levels. For example, at 30°–45°N, the OH and \(HO_2\) concentrations at 0–12 km showed a general increase from January to March. In the boundary layer, the March/January ratio was about 2. The OH and \(HO_2\) concentrations showed increases also from March to April–May by another factor of 2–3. The April–May/January ratios of OH and \(HO_2\) were about 3–4 (Figure 7b). This \(HO_x\) increase is seen to be related to the seasonal increases in \(F(HO_x)\), which are driven by \(J(O_1D)\), \(O_3\) and \(H_2O\) (see earlier discussion). More detailed analysis has shown the model-predicted diel average \(HO_x\) is highly correlated with \(F(HO_x)\) (i.e., \(r^2 > 0.7\)) in all boundary layer cases, except for 30°–45°N. The lack of correlation for the latter case is due to the wide range of \(NO_x\) and NMHC levels. At the highest \(NO_x\) levels, NMHC oxidation becomes the major source of \(HO_x\), which can be seen from the tight correlation between \(CH_3O_2\) and \(HO_x\) (not shown). The ratio of \([\text{HO}_2]/(\text{[HO}_2] + \text{[CH}_3\text{O}_2] + \text{[RO}_2])\) was 0.6–0.7 in the boundary layer and increased to 0.8–0.9 at 8–12 km in winter and spring, indicating a limited contribution of NMHCs to peroxy radicals. Similar results have been obtained by Davis et al. [2003] for the TRACE-P March data.

[21] At 20°–30°N, the OH and \(HO_2\) concentrations also increased from January to March. This increase is mainly due to the increase in \(F(HO_x)\) as a result of shifts in \(J(O_1D)\) and \(O_3\), while the \(H_2O\) mixing ratios showed little changes. In March, the OH and \(HO_2\) concentrations in the boundary layer at 20°–30°N were higher than those at 30°–45°N by factors of 1.5–3. The difference in \(J(O_1D)\) and \(H_2O\) is the major reason, because the \(O_3\) concentrations were similar.

### 6.2. Net Ozone Formation

[22] Calculated values of \(F(O_3)\), \(D(O_3)\), and \(P(O_3)\) integrated for each km altitude range are shown in Figure 8 for three observation periods for each latitudinal range. The column-integrated values are given in Table 4. The \(P(O_3)\) profile at 30°–45°N in units of ppbv d\(^{-1}\) is shown in Figure 9. The relative contribution of each reaction term to \(F(O_3)\) and \(D(O_3)\) is given in Tables 5 and 6. It should be noted that \(F(O_3)\) and \(D(O_3)\) are directly connected through \(HO_2\) and indirectly through \(J(O_1D)\) and \(H_2O\), which control \(HO_x\) (equations (2) and (3)).

#### 6.2.1. The 30°–45°N Regime

**6.2.1. Boundary Layer**

[21] At 30°–45°N, \(F(O_3)\) and \(D(O_3)\) values in the boundary layer were largest in April–May, reflecting the highest photochemical activities, as represented in the \(HO_x\) concentrations. However, the \(F(O_3)\) values for January were smaller than those for April–May by only 35%, despite the difference of a factor 3 in \(HO_2\), which directly influences \(F(O_3)\) (equation (2)). This difference is compensated by the 2-times-larger \(NO_x\) mixing ratios in January. The contribution of reaction (R4) to \(F(O_3)\) is proportional to the

#### Table 3. Lifetimes of CO, NMHCs, and NO\(_x\) in the Boundary Layer Determined by the Reactions With OH for PEACE-A, TRACE-P, and PEACE-B\(^a\)

<table>
<thead>
<tr>
<th>Species</th>
<th>PEACE-A TRACE-P</th>
<th>PEACE-A TRACE-P</th>
<th>PEACE-B TRACE-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>3.18 4.92</td>
<td>3.18 4.92</td>
<td>3.18 4.92</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>3.18 4.92</td>
<td>3.18 4.92</td>
<td>3.18 4.92</td>
</tr>
<tr>
<td>C(_3)H(_4)</td>
<td>3.18 4.92</td>
<td>3.18 4.92</td>
<td>3.18 4.92</td>
</tr>
<tr>
<td>C(_4)H(_10)</td>
<td>3.18 4.92</td>
<td>3.18 4.92</td>
<td>3.18 4.92</td>
</tr>
<tr>
<td>NO(_x)</td>
<td>3.18 4.92</td>
<td>3.18 4.92</td>
<td>3.18 4.92</td>
</tr>
<tr>
<td>OH</td>
<td>3.18 4.92</td>
<td>3.18 4.92</td>
<td>3.18 4.92</td>
</tr>
</tbody>
</table>

\(^a\)Units are days. OH is given in units of 10^\(^5\) molecules cm\(^{-3}\).
Figure 6. Same as Figure 5, except for C$_2$H$_4$-C$_2$H$_2$ and NO$_x$-CO correlations. Correlations derived from the emissions of C$_2$H$_2$, CO, C$_2$H$_4$, and NO$_x$, estimated by Streets et al. [2003] for Nagoya (Japan), South Korea, northern China, and central China are also shown for comparison (thin lines).

Figure 7. (a) Same as Figure 4a, except for vertical profiles of the 24-hour average $J$(O$_1^D$) and $F$(HO$_2$); (b) OH and HO$_2$. 
[HO2]/([HO2] + [CH3O2] + [RO2]) ratio, which was 60–70% in the boundary layer, as summarized in Table 5. Although the $F(O_3)$ values showed only modest increases from winter to spring, the $D(O_3)$ values increased much more rapidly. This increase occurred most dramatically between March and April–May. The $D(O_3)$ values for January were 2 times lower than those for March and 5 times lower than those for April–May. In January, reaction (R8) made a major contribution to the total $D(O_3)$, and the contribution of reaction (R3a) to $D(O_3)$ increased to about 50% in April–May (Table 6). The largest values of $D(O_3)$ in April–May were due to the largest values of the parameters controlling $D(O_3)$ given in equation (3), namely, $O_3$, $J(O_1D)$, $H_2O$, $HO_2$, and $OH$.

Because $F(O_3)$ is proportional to $[NO]$, $F(O_3)$ and $D(O_3)$ balance at a specific level of NO, defined as the critical NO ($NO_{crit}$) [Crawford et al., 1997; Davis et al., 2003]. When the ambient NO levels are higher than $NO_{crit}$, photochemistry tends to be a net source of $O_3$. Conversely, the photochemistry is a net sink when NO is low. The value of $NO_{crit}$ depends on the value $D(O_3)$, which increases with photochemical activity and $O_3$. The calculated $NO_{crit}$ is shown in Figure 10. $NO_{crit}$ increased from January (9 pptv) to April–May (29 pptv), corresponding to the seasonal variation of the photochemical activity.

The $P(O_3)$ value in the boundary layer was largest in January, because of $F(O_3)$ comparable to that in spring and much lower $D(O_3)$. The $P(O_3)$ value decreased by 25% from January to March, and by April–May, it decreased down to about 10% of the January value (Table 4). The net $O_3$ production in the boundary layer was a major contributor to the total column production: about 80% for January and 30% for March–May (Table 4). The fact that $P(O_3)$ was positive during January–March and was much reduced in the April–May period is consistent with the largest increase in $O_3$ during the January–March period and the smaller change during the March–May period (Table 2).

6.2.1.2. Middle Troposphere

The $P(O_3)$ values were lowest in the middle troposphere (3–6 km) during all the three periods (Figures 8 and 9). Specifically in April–May, both $F(O_3)$ and $D(O_3)$ monotonically decreased with altitude, and the middle tropospheric values were smaller than those in the boundary layer by only a factor of 2–3 (Table 4). The $F(O_3)$ and $D(O_3)$ in the middle troposphere contributed 24% of the column-integrated values. However, contribution of $P(O_3)$ in this region to the total integrated value amounted to only...
Figure 8. Vertical profiles of the O\textsubscript{3} formation ($F$($O_3$)), destruction ($D$($O_3$)), and net formation ($P$($O_3$)) rates in the latitude ranges of 20°–30°N and 30°–45°N during PEACE-A, TRACE-P, and PEACE-B.
9%. The \( P(O_3) \) values were observed to be lowest in the middle troposphere also in September during PEM-W-A [Davis et al., 1996; Crawford et al., 1997].

The lifetime of \( O_3 \) in the middle troposphere at 30°/C was estimated to be 100 and 20 days, respectively, by a 3-D chemical transport model (CTM) [Wang et al., 1998b]. This is much longer than the corresponding lifetimes of 40 and 6 days in the boundary layer. Therefore \( O_3 \) in the boundary layer should tend to be closer to photochemical steady state in general. The large departure from photochemical steady state in the middle troposphere should be due to the minimal \( NO_x \) levels, owing to the lack of in situ sources and longer transport time of \( NO_x \) from source regions below and above.

### 6.2.1.3. Upper Troposphere

In the upper troposphere (6–12(±1) km), \( O_3 \) deviated from photochemical steady state as in the boundary layer. The \( F(O_3) \) values increased or remained unchanged with altitude from the middle to the upper troposphere, while the \( D(O_3) \) values decreased. The causes in the altitude changes in \( F(O_3) \) and \( D(O_3) \) are the increase in NO and the decrease in \( H_2O \) concentrations with altitude, respectively. Even in April–May, when \( H_2O \) was highest, the contribution of reaction (R3a) to \( D(O_3) \) was not dominant. As a result of these changes, \( P(O_3) \) was positive in the upper troposphere because of “excess NO” above \( NO_{crit} \) (Figure 10). The \( P(O_3) \) integrated in the upper troposphere contributed about 14% and 60% of the column-integrated \( P(O_3) \) values in January and April/May, respectively. Over the western Pacific, net \( O_3 \) formation in the upper troposphere was also observed in September and February during PEM-W-A and B [Davis et al., 1996; Crawford et al., 1997]. The median \( NO \) mixing ratios at 10–12 km during these periods were 40–100 pptv, which are similar to those observed in January, March, and April–May. The persistent net \( O_3 \) formation throughout the year has been predicted by 3-D CTMs [Wang et al., 1998b; Yienger et al., 1999].

The major sources of NO in the upper troposphere are known to be production by lightning, emissions from commercial aircraft, transport of \( NO_x \) from the boundary layer, and transport of \( HNO_3 \) from the stratosphere followed by reaction with \( OH \) and photolysis to form \( NO_x \) [World Meteorological Organization, 1999]. The NO emissions from aircraft are concentrated at northern midlatitudes, while lightning activity is highest in the tropics [e.g., Levy et al., 1999; Lamarque et al., 1996]. The effect of air traffic on upper tropospheric \( NO_x \) was indicated over the western Pacific during PEM-W-B, where air traffic is frequent [Koike et al., 1997]. High \( NO_x \) observed in the upper troposphere was often correlated with high condensation

### Table 4. Column-Integrated Values of \( F(O_3) \), \( D(O_3) \), and \( P(O_3) \)

<table>
<thead>
<tr>
<th>Altitude</th>
<th>( F(O_3) )</th>
<th>( D(O_3) )</th>
<th>( P(O_3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEACE-A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–3 km</td>
<td>42</td>
<td>25</td>
<td>14</td>
</tr>
<tr>
<td>3–6 km</td>
<td>14</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>6–11 km</td>
<td>6.7</td>
<td>2.6</td>
<td>4.2</td>
</tr>
<tr>
<td>0–11 km</td>
<td>63</td>
<td>39</td>
<td>21</td>
</tr>
<tr>
<td>TRACE-P</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–3 km</td>
<td>24</td>
<td>34</td>
<td>-4.8</td>
</tr>
<tr>
<td>3–6 km</td>
<td>15</td>
<td>17</td>
<td>-1.1</td>
</tr>
<tr>
<td>6–12 km</td>
<td>14</td>
<td>5.5</td>
<td>8.7</td>
</tr>
<tr>
<td>0–12 km</td>
<td>53</td>
<td>57</td>
<td>2.8</td>
</tr>
<tr>
<td>PEACE-B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–3 km</td>
<td>37</td>
<td>48</td>
<td>-</td>
</tr>
<tr>
<td>3–6 km</td>
<td>35</td>
<td>51</td>
<td>-</td>
</tr>
<tr>
<td>6–13 km</td>
<td>35</td>
<td>17</td>
<td>-</td>
</tr>
<tr>
<td>0–13 km</td>
<td>107</td>
<td>116</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 5. Percentage Contribution of Different Peroxy-Radicals to \( O_3 \) Formation at 30°–45°N for January, March, and April–May

<table>
<thead>
<tr>
<th>Altitude, km</th>
<th>( HO_2 )</th>
<th>( CH_3O_2 )</th>
<th>( RO_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–3 km</td>
<td>62</td>
<td>70</td>
<td>66</td>
</tr>
<tr>
<td>3–6 km</td>
<td>70</td>
<td>73</td>
<td>72</td>
</tr>
<tr>
<td>&gt;6</td>
<td>83</td>
<td>82</td>
<td>81</td>
</tr>
</tbody>
</table>

*Units are \( 10^{10} \text{ molecules cm}^{-2} \text{ s}^{-1} \).*

![Figure 9](image-url) Vertical profiles of the net formation \( (P(O_3)) \) rate at 20°–30°N and 30°–45°N in units of ppbv d{\textsuperscript{-1}}.
nuclei (CN) densities. Similar correlation was observed in the North Atlantic flight corridor during the SASS Ozone and NOx Experiment (SONEX) [Kondo et al., 1999]. This excludes a large contribution of transport of stratospheric HNO3 to the observed high NOx, because HNO3 from the stratosphere does not correlate with CN in general. This in itself does not exclude convective transport of NOx and CN from the boundary later, however. NOx-CO and NOy-CO correlations were generally poor, but occasionally significant (not shown), suggesting some effect of transport from the boundary layer. The number of data points obtained in the upper troposphere was considerably smaller than that in the boundary layer and middle troposphere. This prevents the use of statistical analysis to quantify contributions of different sources of NOx in the upper troposphere.

### 6.2.2. The 20°–30°N Regime

#### 6.2.2.1. Boundary Layer

[31] Changes in the $F(O_3)$, $D(O_3)$, and $P(O_3)$ values in the 20°–30°N regime are discussed in comparison with those in the 30°–45°N regime. In January, the $F(O_3)$ values in the boundary layer at 20°–30°N were 25% higher than those at 30°–45°N (Figure 5 and Table 3). The median NO mixing ratios at 20°–30°N were about 1–3 times lower than those at 30°–45°N, as discussed in section 5. The effect of lower NO concentrations at 20°–30°N is compensated by the 2-to-3-times-higher HO2 (Figures 4c and 7a–7b), because of much higher $F(HO_x)$ values in this latitude bin. The $D(O_3)$ values at 20°–30°N were 3 times higher than those at 30°–45°N, mostly because of the larger values of $J(O(1D))$ and H2O. The resulting $P(O_3)$ values at 20°–30°N turned out to be positive. In March, the $P(O_3)$ values became negative. The decrease in $F(O_3)$, mainly due to the decrease in NO, and the increase in $D(O_3)$ are together the major cause of the large decrease in $P(O_3)$ from January. The decrease in NO, in turn, was caused by a higher fraction of Asian NOx oxidized because of the much weaker winds, especially at 20°–30°N (Figure 2), and

<table>
<thead>
<tr>
<th>Altitude, km</th>
<th>$O(1D)$</th>
<th>HO$_2$ + O$_3$</th>
<th>OH + O$_3$</th>
<th>NO$_2$ + OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–3</td>
<td>J</td>
<td>M</td>
<td>A–M</td>
<td>J</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>30</td>
<td>49</td>
<td>47</td>
</tr>
<tr>
<td>3–6</td>
<td>15</td>
<td>26</td>
<td>39</td>
<td>64</td>
</tr>
<tr>
<td>&gt;6</td>
<td>12</td>
<td>15</td>
<td>33</td>
<td>46</td>
</tr>
</tbody>
</table>

*J, M, and A–M stand for January, March, and April–May, respectively.

**Table 6.** Percentage Contribution of Different Reactions to O$_3$ Destruction at 30°–45°N for January, March, and April–May

**Figure 10.** Vertical profiles of the median values of the observed and critical NO mixing ratios.
higher OH levels (Figures 7a–7b) than in January, as discussed in section 5. The \( P(O_3) \) value integrated over the boundary layer is \(-4.8 \times 10^{10} \) molecules cm\(^{-2} \) s\(^{-1} \).

[32] In February–March during PEM-W-B, \( P(O_3) \) was positive in the boundary layer [Crawford et al., 1997]. PEM-W-B was conducted about three weeks earlier than TRACE-P. The values of \( P(O_3), D(O_3), \) and \( P(O_3) \) integrated over 0–4 km were \( 39 \times 10^{10}, 28 \times 10^{10}, \) and \( 11 \times 10^{10} \) molecules cm\(^{-2} \) s\(^{-1} \), respectively. These values are comparable to those integrated over 0–3 km for January (Table 4). The median NO mixing ratio during PEM-W-B was about 20 pptv, which is comparable to the values in January, leading to the comparable \( F(O_3) \) values. The \( F(O_3) \) and \( D(O_3) \) during PEM-W-B were higher and lower than those in March, respectively, resulting in the difference in the sign of \( P(O_3) \). The lower \( D(O_3) \) during PEM-W-B was due mainly to the lower \( J(O^1D) \), as \( H_2O \) and \( \text{HO}_x \) concentrations were similar. By comparing the results for January, February–March, and March, it appears that \( P(O_3) \) turned from positive to negative sometime between February and March, one month earlier than at 30°–45°N. The earlier change in the sign of \( P(O_3) \) is due to the earlier decrease in NO (leading to decrease in \( F(O_3) \)) and earlier increases in \( J(O^1D) \) and \( H_2O \) (leading to increase in \( D(O_3) \)).

### 6.2.2.2. Middle and Upper Troposphere

[33] In January, \( F(O_3) \) values in the middle troposphere were larger than those at 30°–45°N, because of the higher \( \text{HO}_x \) and comparable NO levels. The \( D(O_3) \) values at 20°–30°N were 3–4 times higher than those at 30°–45°N, because of the larger values of \( J(O^1D), H_2O, \text{HO}_2, \) and \( \text{OH} \). The resulting \( P(O_3) \) values at 20°–30°N turned out to be 2 times larger. In March, the \( P(O_3) \) values in the middle troposphere became negative, similarly to the boundary layer.

[34] In January and March, the \( P(O_3) \) values in the upper troposphere at 20°–30°N were similar to those at 30°–45°N. The NO levels in both latitude regimes were similar (Figure 4c).

### 6.2.3. Influx From the Stratosphere and Surface Deposition

[35] Studies have shown that transport from the stratosphere and dry deposition on the Earth’s surface can also have significant contributions to tropospheric \( O_3 \), in addition to photochemical formation and destruction. Chemical destruction and deposition affect \( O_3 \) regardless of its origin, namely tropospheric or stratospheric. Thus it is appropriate to compare the \( O_3 \) transport term with \( F(O_3) \).

The effect of \( O_3 \) from the stratosphere on the \( O_3 \) budget has been assessed in some detail by Davis et al. [2003] by comparing \( O_3 \) fluxes estimated by previous studies with derived column-integrated \( F(O_3) \) values at 25°–45°N for the PEM-W-B (February–March) and TRACE-P (March) data. Column-integrated \( F(O_3) \) values of \( 28 \times 10^{10} \) and \( 54 \times 10^{10} \) molecules cm\(^{-2} \) s\(^{-1} \) for February–March and March, respectively, were 3–6 times larger than the \( O_3 \) flux from the stratosphere of \( 8.7 \times 10^{10} \) molecules cm\(^{-2} \) s\(^{-1} \), estimated for the latitude range of 20°–60°N by Wang et al. [1998a]. Photochemistry dominates influx from the stratosphere. The same conclusion applies to the present data sets because \( F(O_3) \) values in January and April–May in the range at 20°–30°N and 30°–45°N were between 39 \( \times 10^{10} \) and 78 \( \times 10^{10} \) molecules cm\(^{-2} \) s\(^{-1} \), which is 4–9 times higher than the flux from the stratosphere.

[36] The integrated \( D(O_3) \) at 30°–45°N were \( 10 \times 10^{10}, 24 \times 10^{10}, \) and \( 70 \times 10^{10} \) molecules cm\(^{-2} \) s\(^{-1} \) for January, March, and April–May, respectively. The average surface deposition of \( 5 \times 10^{10} \) molecules cm\(^{-2} \) s\(^{-1} \) estimated by Kawa and Pearson [1989] and Lenschow et al. [1982] becomes comparable to the chemical destruction for January, the period of the minimum photochemical activity. However, the integrated \( P(O_3) \) value of \( 28 \times 10^{10} \) molecules cm\(^{-2} \) s\(^{-1} \) for January is not significantly altered by taking the deposition into account because of the much higher value of \( P(O_3) \) than \( D(O_3) \) and surface deposition (Table 4).

### 6.3. Implications of the Present Data and Comparison With TOPSE

[37] The present data were obtained in the region about 200–2000 km distant from the coast of the Asian continent. This is the region over the Pacific most significantly influenced by anthropogenic activities in Asia, as indicated by previous studies using 3-D CTMs [e.g., Wang et al., 1998a; Yienger et al., 1999]. At farther distance from the continent, concentrations of short-lived precursors, especially \( \text{NO}_x \), are predicted to decrease greatly because of oxidation and dilution, as was observed during PEM-W-A and B [Kondo et al., 1997]. Accordingly, \( O_3 \) photochemistry, especially the \( P(O_3) \) value, should be much reduced in more remote regions of the Pacific. The seasonal variation of \( P(O_3) \) shown here, therefore, should be interpreted to represent that in the region close enough to sources, where precursor concentrations, especially \( \text{NO}_x \), are still high. The total \( O_3 \) formed within 3.5 months from January to April–May is calculated to be \( 19 \times 10^{17} \) molecules cm\(^{-2} \), assuming an average column-integrated \( P(O_3) \) of \( 21 \times 10^{10} \) molecules cm\(^{-2} \) s\(^{-1} \) during this period. This \( O_3 \) formation is 6 times larger than the observed increase in the \( O_3 \) column of \( 3.1 \times 10^{17} \) molecules cm\(^{-2} \) during this period, indicating that \( O_3 \) formed over the western Pacific was transported to regions over the Pacific outside the region of the present study. Namely, \( O_3 \) formed in this study area can cause similar seasonal increase in \( O_3 \) in a region 5 times larger than this area.

[38] Similar seasonal variation of \( P(O_3) \) can prevail downwind of other continental sources, as predicted by 3-D CTMs [e.g., Yienger et al., 1999], because the parameters \( J(O^1D), H_2O, \text{OH, HO}_2, \) and wind fields, which control \( P(O_3) \), are considered to follow similar seasonal variations.
They are mainly driven by natural seasonal variations. In this regard, there can be other regions where the seasonal variation of the O₃ chemistry is driven by natural changes in these parameters coupled with anthropogenic emissions of O₃ precursors, in a way similar to that over the western Pacific.

[39] Seasonal variations of the O₃ photochemistry from February to May over the North American continent were also calculated with a time-dependent photochemical box model using TOPSE aircraft measurement data as input parameters [Wang et al., 2003; Stroud et al., 2004], in a similar way to that of the present study. Monthly median values of F(O₃), D(O₃), P(O₃) in the boundary layer, and key parameters (NOₓ, H₂O, and J(O¹D)) controlling O₃ photochemistry are listed in Table 7 for the latitude band of 40°–60°N. TOPSE NOₓ observations at 0–3 km at midlatitudes (40°–60°N) (Table 7) did not show a large seasonal variation from January to May.

[40] The H₂O mixing ratios were also 2–3 times lower over North America, due primarily to the lower temperature. In addition, airflow over North American orography leads to much drier conditions in the boundary layer. The values of H₂O and J(O¹D) over North America increased from winter to spring, leading to increases in both F(O₃) and D(O₃) of comparable size. As a consequence, P(O₃) from February to April was stable. By contrast, over the western Pacific, a large decrease in NOₓ and increase in H₂O from winter to spring caused large decreases in P(O₃), as discussed in section 6.2.1. The F(O₃) values in the TOPSE study region were 4–8 times lower than those over the western Pacific because of the correspondingly lower NOₓ values. The P(O₃) values were about 20 times lower in the January–March period. Differences in the values of H₂O and J(O¹D) made additional contributions to the differences in P(O₃). This comparison, based on measured key parameters, demonstrates the critical role of NOₓ in controlling O₃ production on regional scales.

7. Conclusions

[41] Seasonal variations of solar UV radiation (J(O¹D)) and concentrations of key precursors (NO, H₂O, OH, and HO₂) determine the seasonal variations of chemical O₃ formation and destruction. In the boundary layer over the western Pacific (123°–145°E), H₂O and HO₂ increased primarily because of increases in temperature and solar radiation and NOₓ decreased primarily because of decrease in transport efficiency from the Asian continent from winter to spring. The changes of these key parameters are coupled in the O₃ chemistry. The complex chemical interplay over the western Pacific during this period has been assessed systematically using box model calculations constrained by the data sets obtained by aircraft observations made in the latitude regimes of 20°–30°N and 30°–45°N in January (PEACE-A), March (TRACE-P), and April–May (PEACE-B).

[42] At 30°–45°N, the OH concentration of 0.2–0.5 × 10⁶ molecules cm⁻³ in the boundary layer (0–3 km) and middle troposphere (3–6 km) almost doubled by March. It showed a factor of 2–3 increase from March to April–May, due to the increase in J(O¹D) and H₂O. This leads to a shortening of lifetimes by a factor of 4 of trace species that are removed by reaction with OH, from winter to late spring.

[43] In this latitude range, NO concentration in the boundary layer was highest in January because of the strongest outflow of dry polluted air from the Asian continent under the influence of the Siberian high. This high NO was compensated by low HO₂ due to low H₂O and J(O¹D), resulting in an O₃ formation rate (F(O₃)) comparable to that in spring. On the other hand, the O₃ destruction rate (D(O₃)) was much lower than in spring because of the lowest values of J(O¹D), H₂O, OH, and HO₂. The combination of these factors resulted in the highest net O₃ formation rate (P(O₃)) in January. This balance tends to shift as the season progresses. In March, calmer winds, combined with higher OH, reduce the NO concentrations. The increases in HO₂ and other peroxy radicals compensate for the NO reduction and maintain F(O₃) essentially unchanged. However, the destruction rate is 2 times higher because of higher J(O¹D), H₂O, OH, HO₂, and O₃, resulting in a 25% reduction in P(O₃) from January. In April–May, both F(O₃) and D(O₃) become highest because of the highest photochemical activity, but P(O₃) is lowest (negative), as the two largest terms become closer in value. The P(O₃) in the boundary layer made a large contribution to the column-integrated P(O₃), especially in winter.

[44] In the middle troposphere, P(O₃) was lowest because of the lowest NO and moderately low H₂O concentrations. This holds also in September (PEM-W-A period). O₃ was closest to photochemical steady state in this altitude region, where O₃ lifetime is 100–200 days in winter. Moderately long transport times from fresh NO emissions, located below and above, should lower the NO levels and allow O₃ to be closer to the steady state values, despite the longer O₃ lifetimes.

[45] In the upper troposphere (6–12 km), P(O₃) was positive throughout the period from January to May. The net O₃ formation in this region constituted about 14–60% of the column-integrated O₃ formation. This net O₃ formation was observed also in September 1991 and February–March 1994, indicating that O₃ is stably produced in the upper troposphere throughout most of the year. This net O₃ formation is due to the NO levels greatly exceeding the critical level. The small number of data points obtained in the upper troposphere prevents the use of statistical analysis to quantify contributions of different sources of NOₓ in the upper troposphere.

[46] At 20°–30°N, the seasonal transition of ozone chemistry in the boundary layer from winter to spring was qualitatively the same as that at 30°–45°N. However, quantitatively, NO was lower and J(O¹D), H₂O, OH, and HO₂ were higher than at 30°–45°N in January and March. A higher fraction of NOₓ emitted from the Asian continent was oxidized before reaching this region because of the higher HO and weaker outflow from the Asian continent, leading to the 3-times-lower NO levels in January at 20°–30°N than at 30°–45°N. F(O₃) in January at 20°–30°N was 25% larger than at 30°–45°N, compensated by the 2-to-3-times-higher HO₂. In March, P(O₃) turned negative, indicating that it changes sign about one month earlier than it does at 30°–45°N, because of lower F(O₃) (lower NO) and higher D(O₃).
[47] Integrated $F(O_3)$ values are 4–9 times larger than the estimated O3 influx from the stratosphere during January–April/May. It is also estimated that dry deposition of O3 should have only a small influence on the integrated $F(O_3)$ during this period.

[48] The seasonal variation shown here should be interpreted as representing that in the region close to anthropogenic sources of NOx, where NOx concentrations are still high. Similar seasonal variation of $F(O_3)$ can prevail downwind of other continental sources, because the parameters $\lambda(O_3D)$, $H_2O$, OH, HO2, and wind fields, which control $F(O_3)$, are considered to follow similar seasonal variations. In this regard, there can be other regions where seasonal variations of the O3 chemistry can be interpreted in a similar way.

[49] Comparison of the present western Pacific data with those obtained at 40°–60°N over North America shows differences in the seasonal variation in O3 photochemistry. Much lower NOx led to much lower $F(O_3)$ in the boundary layer over North America in winter and early spring, demonstrating the importance of high NOx in the higher O3 production rates over the western Pacific.

[50] Acknowledgments. We are indebted to all of the PEACE-A and B participants for their cooperation and support. Special thanks are due to the flight and ground crews of the G-II aircraft of Mitsubishi Diamond Air Service Co. Calibration of the filter radiometers was made by R. L. McKenzie of NIWA. We thank N. Toriyama and M. Kanada for their participation for their cooperation and support. Special thanks are due to J. H. Logan, J. A. Calvert, and R. Shetter (2002), Relationship between photolysis frequencies derived from spectroscopic measurements of actinic fluxes and irradiances during the IPM campaign, J. Geophys. Res., 107(D5), 4042, doi:10.1029/2001JD000601.


