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An assessment of ozone photochemistry in the extratropical western North Pacific: Impact of continental outflow during the late winter/early spring

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Abstract. This study examines the influence of photochemical processes on tropospheric ozone distributions over the extratropical western North Pacific. The analysis presented here is based on data collected during the Pacific Exploratory Mission-West Phase B (PEM-West B) field study conducted in February-March 1994. Sampling in the study region involved altitudes of 0-12 km and latitudes of 10°S to 50°N. The extratropical component of the data set (i.e., 20-50°N) was defined by markedly different photochemical environments north and south of 30°N. This separation was clearly defined by an abrupt decrease in the tropopause height near 30°N and a concomitant increase in total O3 column density. This shift in overhead O3 led to highly reduced rates of O3 formation and destruction for the 30-50°N latitude regime. Both latitude ranges, however, still exhibited net O3 production at all altitudes. Of special significance was the finding that net O3 production prevailed even at boundary layer and lower free tropospheric altitudes (e.g., < 4 km), a condition uncommon to Pacific marine environments. These results reflect the strong impact of continental outflow of O3 precursors (e.g., NO and NMHCs) into the northwestern Pacific Basin. Comparisons with PEM-West A, which sampled the same region in a different season (September-October), revealed major differences at altitudes below 4 km, the altitude range most influenced by continental outflow. The resulting net rate of increase in the tropospheric O3 column for PEM-West B was 1-3% per day, while for PEM-West A it was approximately zero. Unique to the PEM-West B study is the finding that even under wintertime conditions substantial column production of tropospheric O3 can occur at subtropical and mid-latitudes. While such impacts may not be totally unexpected at near coast locations, the present study suggests that the impact from continental outflow on the marine BL could extend out to distances of more than 2000 km from the Asian Pacific Rim.

1. Introduction

The importance of O3 in tropospheric photochemistry is well established. It is central to determining the oxidative capacity of the atmosphere. The photolysis of this species (λ<320 nm) initiates the formation of the OH radical, and it is the follow-on free radical chemistry that is responsible for the removal of atmospheric pollutants. This free radical chemistry also contains feedbacks that can both produce as well as further destroy O3 [e.g., Chameides and Walker, 1973; Crutzen, 1973; Liu et al., 1980]. Depending on the environment, the combined effect of these feedbacks can result in either a net photochemical loss or gain of ozone. In studies of the global budget of tropospheric O3, an issue of continuing interest has been determining the importance of photochemical sources and sinks relative to transport of O3 from the stratosphere and surface loss [e.g., Fabian, 1974; Chasfield and Harrison, 1976; Fabian and Pruchniwicz, 1977; Fishman et al., 1979; Liu et al., 1980; Gidel and Shapiro, 1980; Mahlman et al., 1980; Chameides and Tan, 1981; Logan et al., 1981; Logan, 1985; Isaksen and Hov, 1987; Hough and Derwent, 1990; Hough, 1991; Davis et al., 1996; Jacob et al., 1996; Thompson et al., 1996; Crawford et al., this issue].
In an effort to expand the observational data base for evaluating the tropospheric O₃ budget, aircraft campaigns such as those sponsored by NASA's Global Tropospheric Experiment (GTE) have become centrally important. The Pacific Exploratory Mission in the western North Pacific (PEM-West) represents one of the most recent missions. It was conducted in two phases [Hoell et al., 1996, this issue]. In the fall of 1991, PEM-West Phase A (PEM-A) sampled the western Pacific during a period when the mean flow was toward the Asian continent. Thus, it afforded an opportunity to observe this region under minimal anthropogenic influence. By contrast, PEM-West Phase B (PEM-B) was conducted during the winter of 1994 and sampled at a time during which there was maximum continental outflow. This outflow was mainly confined to extratropical latitudes (i.e., >20°N) although on occasion it penetrated as far south as 13°N [Crawford et al., this issue; Merrill et al., this issue].

In a companion paper we discuss the tropical component of PEM-B [Crawford et al., this issue]. This paper will focus on the extratropical latitudes. Specific objectives will include (1) to assess the relative importance of the ozone-controlling chemical factors such as NO, NMHCs, H₂O, and peroxy radicals, (2) to assess the impact of photochemistry on the regional ozone budget, and (3) to evaluate seasonal differences in the photochemistry of the extratropical western Pacific through comparison with the first phase program, PEM-A.

2. Observational Database

2.1. Measurements

The basic suite of chemical species and physical variables measured during PEM-B was essentially unchanged from PEM-A [Hoell et al., 1996]. Parameters specifically used to constrain the model calculations for this analysis are listed in Table 1. Specific details on individual measurement techniques as well as changes/improvements to previously employed instrumentation are given by Hoell et al. [this issue].

As in PEM-A, NO was measured using two independent techniques. The first group, from Georgia Institute of Technology, used a laser detection technique labeled by these investigators as "two-photon laser-induced fluorescence" (TPLIF). The second group, associated with Nagoya University, employed the more common method of O₃ chemiluminescence. The results from these two approaches compared quite well for all PEM-B flights. A standard regression analysis of approximately 5000 paired NO measurements (30 s sample integration) gave a slope of 1.25 ± 0.01, an intercept of 1.2 ± 0.2 pptv, and an R² value of 0.95. On average, the Nagoya University NO data were found to be higher than those measured by Georgia Tech. Although this comparison only involved data with mixing ratios in the range of 0-200 pptv, these data constituted nearly 99% of the total data set. Given this good agreement, the modeling analysis presented here used NO values reported by both groups. For time periods where both groups reported NO values, the average was taken.

The analysis described in this work has been based on time-dependent box model calculations. These calculations have used median chemical and physical conditions for specific altitude/latitude sampling bins. A merged data set based on 30 s sampling time intervals was used to establish these median values. Before estimating these median values, however, the data set was filtered so as to include only data for solar zenith angles less than 60°. This restriction was imposed in an effort to deal with the fact that NO₂ measurements were not available. Since the partitioning of NOₓ (NO+NO₂) changes rapidly during early morning and late afternoon, the exclusion of high zenith angle data tended to ensure that median NO values could be used with high confidence to infer values for median NO₂. Finally, data were filtered to include only data points for which valid measurements of all critical constituents (e.g., NO, O₃, CO, and H₂O) were present. Concerning NMHCs, concurrent measurements were available for only 37% of the data. For most of the remaining time periods, NMHC values were interpolated from measurements that bracketed the empty data slot (typically 4 min. or less). In these cases the continuity in O₃ and CO as well as NMHC levels themselves were used as criteria to determine whether the interpolation was reasonable. In cases where interpolation could not be justified (16%), median NMHC values for the appropriate altitude/latitude bin were used.

2.2 Geographic Distribution of Critical Species

Figure 1 shows the geographic distribution of samples taken during PEM-B. Symbols indicate the location of the more than 6800 observations (i.e., 30 s time intervals). For this analysis, these observations were assigned to one of three analysis regimes. The first division involved a separation of the data into tropical and extratropical regimes based on meteorological data which showed significant continental outflow (via frontal passage) into marine areas north of 20°N [Merrill et al., this issue]. The extratropical region, north of 20°N, was then further separated into two subregimes encompassing the latitude ranges of 20-30°N and 30-50°N. The latter separation reflects the abrupt change observed in both the tropopause height and total O₃ column density. Plate 1 depicts the latitude-altitude distribution of O₃ as derived from the PEM-B UV-DIAL data and clearly shows the abrupt drop in tropopause height from ~16 km to 8-9 km near 30°N.

| Chemical Variables |
|---------------------|
| O₃, CO, NO, C₂H₆, C₃H₈, >C₄ alkanes, C₂H₆, >C₃ alkenes, C₃H₆ aromatics, acetone, methanol, ethanol, formic acid, acetic acid, HNO₃, PAN |

| Physical Variables |
|---------------------|
| latitude, longitude, altitude, temperature, pressure, dew point, O₃ column density (Meteor-3 TOMS, version 7) |
Also associated with this change was an increase in the median total \( O_3 \) column density of \( \sim 150 \) D.U. based on Meteor-3 TOMS data (Version 7).

Still other information justifying the proposed separation into two latitude regimes can be found in the latitude trends of several chemical species. For example, Figures 2a-2f show distributions of \( O_3 \), CO, NO, dew point, \( C_2H_6 \), and \( C_3H_8 \) for altitude ranges of 0-4, 4-8, and 8-12 km. As seen from Figure 2a, \( O_3 \) levels decrease southward from \( 20^\circ \)N at all altitudes. However, north of \( 20^\circ \)N there is no discernable gradient below 8 km. The increase in \( O_3 \) between 20 and \( 30^\circ \)N for altitudes of 8-12 km most likely reflects the increasing influence of stratospheric intrusions. North of \( 30^\circ \)N at 8-12 km, \( O_3 \) values less than 100 ppbv were observed mostly between 8-9 km. Quite consistent with the remote UV-DIAL data, two-thirds of the in situ \( O_3 \) data above 9 km ranged from 100-600 ppbv and are not seen in Figure 2a. As shown in Figure 2b, CO exhibits a rather abrupt change in its mixing ratio in the vicinity of \( 20^\circ \)N, most likely reflecting the influence of continental outflow. Below 8 km, the highest values occur in the 20-30°N range; whereas, above 8 km, extreme values of CO are observed north of \( 30^\circ \)N. The latter values were primarily recorded between 8-9 km during flight 16 which was intended to sample continental outflow behind a recent frontal passage. Above 9 km there was a high frequency of stratospheric CO values with typical mixing ratios in the 50 ppbv or less range.

In Figure 2c, NO increases dramatically north of \( 20^\circ \)N in the 0-4 km altitude range. North of \( 30^\circ \)N, the average value appears to drop by nearly a factor of 2. For intermediate altitudes (4-8 km) a significant decrease in both the variability and average mixing ratio is seen for latitudes north of \( 30^\circ \)N. At the highest altitudes (8-12 km) some of the highest mixing ratios of NO observed throughout the entire mission are seen over the latitude interval of \( 20-30^\circ \)N. Although high values are also seen north of \( 30^\circ \)N for this altitude range, it is important to note that these high NO mixing ratios are not coincident with the high CO values observed. Instead, the high CO values are correlated with unusually high PAN levels.
approaching 1 ppbv; whereas, PAN levels less than 100 pptv were observed for periods of elevated NO. As expected, Figure 2d shows decreasing values for the dew point as more northern latitudes are reached. Like CO, the trends in NMHCs, as shown in Figures 2e and 2f, reveal abrupt increases when moving from tropical to extratropical latitudes and steadily increase with latitude north of 20øN. Unlike CO, however, there appears to be an absence of extreme values for NMHC's in the latitude range of 20-30øN.

Figures 3a-3f give the median observations as a function of altitude for the extratropical regimes of 20-30øN and 30-50øN. These values were used in time-dependent model calculations discussed later in the text. No median values are shown for the 30-50øN latitude range above 8 km because the tropopause height at these latitudes was only 8-9 km. The median data in these figures clearly show that the trends in CO and O3 are very modest relative to those for NO and H2O. For example, both NO and H2O exhibit gradual changes with altitude at 20-30øN; whereas, for altitudes above 2 km they undergo a sudden decrease at 30-50øN.

The most striking difference in the median values for the two latitude regimes are those displayed by the NMHC species (figures 3e and 3f). Both C2H6 and C3H8 are significantly elevated for 30-50øN relative to 20-30øN. This most
likely reflects greater continental outflow at the higher latitudes; however, another contributing factor could be the longer photochemical lifetime for NMHCs north of 30°N. Recall, there was a difference in median total O₃ of ~150 Dobson units between the two regimes. The impact of this shift on the level of photochemical activity is discussed in detail in section 3.3.

While the PEM-B data were not formally segregated longitudinally, they were examined for evidence of long range transport of pollutants into the open Pacific from the Pacific Rim. For the 20-30°N sampling regime the bulk of the data were collected during six flights covering a longitudinal range of 115° to 165°E. Altitudes for which the sampling covered the greatest longitudinal range were 0-1 and 8-10 km; however, even at these two altitudes major longitudinal gaps existed. In the case of 0-1 km, continental pollution in the form of elevated NO levels was found to be quite evident near 120°E, just off the coast of Taiwan; however, relatively high BL values (e.g., 20-40 pptv) persisted out to 145 and 165°E, a distance of more than 2000 km from the Asian Pacific Rim. Similarly, near the coast of Taiwan, CO mixing ratios of 250 ppbv were recorded, but again values in the 150-175 ppbv range were observed at 145 and 165°E. The latter observations at 165°E were all from flight 16, a flight that was specifically intended to sample the extent to which continental outflow behind a front could move out into the Pacific. Thus, the above findings clearly demonstrate that anthropogenic emissions of O₃ precursors can extend far out into the Pacific at this time of year.

3. Data Analysis
3.1. Ozone Photochemistry

The critical photochemical processes that control the rate of formation and destruction of O₃ have been previously discussed [Davis et al., 1996; Crawford et al., this issue] and are summarized in Table 2. On the basis of these reactions the photochemical formation and destruction of ozone can be defined as

\[
F(O_3) = \{k_4[HO_2] + k_5[CH_3O_2] + k_6[RO_2]\}[NO] \tag{1}
\]

\[
D(O_3) = k_310[O(D)][H_2O] + \{k_7[OH] + k_8[HO_2]\}[O_3] \tag{2}
\]

The net effect of all photochemical processes on O₃ (the photochemical ozone tendency) can then be defined as the difference between formation and destruction.

\[
P(O_3) = \{k_4[HO_2] + k_5[CH_3O_2] + k_6[RO_2]\}[NO] - (k_310[O(D)][H_2O] + \{k_7[OH] + k_8[HO_2]\}[O_3]) \tag{3}
\]

From a chemical point of view, equation (3) is most appropriate for remote global regions involving low to modest levels of NOx (e.g., <500 pptv). As noted by other authors [e.g., Chameides et al., 1987; Liu, 1977], under these conditions the additional O₃ loss reaction sequence defined by (R10) and (R12) is insignificant. For much higher levels of NOx, (R10) and (R12) result in an additional destruction term in equation (3):

\[
k_{10}[NO][O_3][k_{12}[NO_2][OH]/\{k_{11}[NO_2] + k_{12}[NO_2][OH]\}] \tag{4}
\]

3.2. Model Description

All O₃ photochemical evaluations presented in this analysis have been based on output from a time-dependent (TD) photochemical box model. Details concerning this model have been previously described by Davis et al. [1993, 1996] and Crawford et al. [this issue]. Specifically, this model was used to calculate diurnal profiles for both radical species and the modeling products F(O₃), D(O₃), and P(O₃). As noted earlier in the text, input used to constrain the model consisted of median values for O₃, CO, H₂O, NO, and NMHCs for
specific altitude/latitude bins (see Figures 3a-3f) as well as median values for the parameters listed in Table 1. With the exception of NO, all variables were assumed to be constant over a 24-hour period. In the case of NO, the source flux was adjusted to match the median NO value.

The initial values for all photolysis rates (J-values) were those calculated for clear-sky conditions using a two-stream radiative transfer model (see Crawford et al., 1996 and references therein). J-values were then further adjusted to simulate actual solar/cloud conditions encountered during sampling using a cloud correction factor (CCF) based on in-flight UV measurements from both an Eppley radiometer and a J(NO2) radiometer [Junkerman et al., 1989]. Both instruments, however, exhibit a systematic difference from the two-
stream model calculations for clear-sky flight periods. This problem was first documented during PEM-A [Crawford et al., 1996] with the further complication that these differences have changed considerably between past NASA-GTE campaigns. Furthermore, the range in these systematic differences (e.g., factors of 1.04 to 1.53) has been too large to justify through any natural differences in atmospheric conditions such as aerosol loading. This inconsistency has led to an additional correction for these data which has involved normalizing the radiometer data with the clear-sky radiometer-to-model ratio. For PEM-B this ratio was determined to be 1.53. This normalization allows for corrections due to cloud variability without allowing the systematic difference to impact on the model calculations. It also adds consistency to comparisons between results for different NASA-GTE campaigns such as that presented here with those from PEM-A which had a clear-sky radiometer-to-model ratio of 1.35. The normalized median CCF values used to constrain the TD model for the current set of calculations are listed in Table 3.

To evaluate the potential magnitude of any systematic error in model calculations related to rate constant uncertainties, we have performed Monte Carlo calculations similar to those described by Thompson and Stewart [1991] and also reported by Davis et al. [1993]. These calculations have assumed uncertainties in gas phase and photolytic reactions as specified by DeMote et al. [1994]. Since many of these uncertainties are temperature dependent, calculations were performed for median conditions for two different altitude ranges (i.e., 0-1 and 10-12 km) within the 20-30°N regime. Results of these calculations showed that the 1σ potential systematic error for HO2 should be within ±18% and ±35% for 0-1 and 10-12 km, respectively. Similarly, the potential systematic error in F(O3) should be within ±23% and ±38%, and for D(O3) it should be within ±28% and ±64%.

3.3. Formation, Destruction, and Tendency of O3

Modeling results for F(O3), D(O3), and P(O3) are shown in Table 4. Values cited here are diurnal average rates. For
Table 4. Diurnal Averaged Rates for O₃ Formation, Destruction, and Tendency

| Latitude Range, 20-30°N | F(O₃), molec/cm³/s | D(O₃), molec/cm³/s | P(O₃), molec/cm³/s | P(O₃), ppbv/day | F(O₃), molec/cm³/s | D(O₃), molec/cm³/s | P(O₃), molec/cm³/s | P(O₃), ppbv/day |
|-------------------------|--------------------|--------------------|--------------------|-----------------|--------------------|--------------------|--------------------|-----------------|
| 0-1                     | 1.01E+06           | 8.15E+05           | 1.94E+05           | 0.68            | 3.63E+05           | 9.55E+04           | 2.67E+05           | 0.88            |
| 1-2                     | 9.88E+05           | 8.04E+05           | 1.84E+05           | 0.72            | 3.43E+05           | 9.36E+04           | 2.49E+05           | 0.93            |
| 2-4                     | 9.51E+05           | 6.09E+05           | 3.42E+05           | 1.54            | 7.34E+04           | 4.36E+04           | 2.98E+04           | 0.13            |
| 4-6                     | 3.67E+05           | 2.99E+05           | 6.75E+04           | 0.37            | 5.99E+04           | 3.36E+04           | 2.64E+04           | 0.14            |
| 6-8                     | 2.10E+05           | 8.11E+04           | 1.29E+05           | 0.93            | 3.95E+04           | 2.01E+04           | 1.94E+04           | 0.24            |
| 8-10                    | 2.32E+05           | 3.18E+04           | 2.00E+05           | 1.85            | 3.12E+04           | 1.96E+04           | 1.94E+04           | 0.24            |
| 10-12                   | 1.56E+05           | 1.58E+04           | 1.40E+05           | 1.61            | 1.50E+04           | 1.48E+04           | 1.96E+04           | 0.24            |

Read 1.01E+06 as 1.01x10⁶.

Both regimes the values of F(O₃) and D(O₃) decrease with altitude, reflecting in large part reductions in H₂O levels with altitude. Even so, O₃ formation rates for 20-30°N exceed those for 30-50°N for all altitudes examined. The magnitude of this difference varies with altitude being nearly a factor of 3 for 0-1 km, but ranging up to factors of 5 to 13 at altitudes of 2-8 km. The difference in O₃ destruction is even more pronounced with 20-30°N exceeding 30-50°N by a factor of 8.5 at 0-1 km and factors of 4 to 14 at altitudes of 2-8 km. These dramatic differences in both F(O₃) and D(O₃) have been found in large part to be due to the highly reduced actinic flux calculated for the 30-50°N regime. This reduction is primarily a result of the large increases in the total overhead O₃ column density. Model simulations indicate that nearly two-thirds of this difference can be attributable to differences in total overhead O₃ with the remaining one-third coming from differences due to shifts in latitude (e.g., solar zenith angle) and the degree of cloudiness (see Table 3). Figure 4 compares model-calculated diurnal-average rates for production of O(1D) (i.e., J(O1D)) for each regime. Photolysis rates for 20-30°N are shown to be 5-10 times greater than those for 30-50°N.

Although Table 4 indicates that major differences exist between the two regimes for F(O₃) and D(O₃), the results for P(O₃) show that both regimes exhibit net photochemical O₃ production at all altitudes. This finding is quite surprising in that previous studies have typically found that the marine boundary layer and the lower free troposphere are regions of net O₃ destruction [Chameides et al., 1987; Davis et al., 1996; Chen, 1995; Jacob et al., 1996; Crawford et al., this issue]. It can be argued that within the uncertainties associated with the Monte Carlo calculations described earlier that P(O₃) at 20-30°N below 4 km could in fact be slightly negative. Nonetheless, any such systematic error in reaction rates would similarly impact earlier assessments and does not diminish the importance of the differences between these results and those of earlier marine studies.

4. Discussion

4.1. Ozone Chemical Controlling Factors

Figure 5 shows the magnitude of the different reaction channels contributing to the photochemical destruction and formation of O₃ as represented by equation (3). For the latitude range 20-30°N and an altitude of 0-1 km (Figure 5a), formation is dominated by reaction (R4), HO₂ + NO, (e.g., 60%). The importance of this process increases with altitude reaching 84% at 10-12 km. This shift primarily reflects the steady decrease in the relative importance of peroxy radicals as derived from the oxidation of CH₄ and NMHCs. At the lowest altitudes NMHCs account for only a very modest contribution to F(O₃) with reaction (R6) contributing 20% at 0-1 km, decreasing to 10% at altitudes < 4 km. The contribution from NMHCs was dominated by >C₄ alkanes and aromatics which collectively accounted for 70-80% of the RO₂ formed, and hence 70-80% of the RO₂ + NO reaction rate. For 30-50°N (Figure 5b), F(O₃) is also dominated by reaction (R4), which accounts for 60-70% of the total at all altitudes. NMHCs play a somewhat larger role in defining the value of F(O₃) for the 30-50°N regime, contributing 20% from 0-4 km and ~10% at all other altitudes. Again, 70-80%
of the NMHC contribution was from >C₄ alkanes and aromatics.

D(O₃) for 20-30°N and altitudes below 4 km (Figure 5a) is dominated by reaction (R3), O¹(D)+H₂O; however, reactions (R7) (OH + O₃) and (R8) (HO₂ + O₃) still make up ~47% of the total. Above 4 km, reaction (R8) becomes dominant reflecting rapid decreases in H₂O levels, but (R7) also increases and on reaching 10-12 km becomes comparable to (R8). At this altitude each is found to contribute ~46%. In no case is any reaction found to define more than 60% of the total destruction rate, and typically the contribution is less than 50%. By contrast, O₃ destruction at 30-50°N (Figure 5b) is dominated by reaction (R8) at all altitudes (e.g., 73-89%). Also at these latitudes, the sharp reduction in O¹(D) due to reduced actinic flux limits the importance of reaction (R3) to less than 20% at all altitudes.

The importance of specific elementary reactions to ozone photochemistry can only be evaluated using a photochemical box model. It is also important to explore the extent to which O₃ formation and destruction can be understood in terms of simpler empirical equations based only on measured chemical and radiative parameters. In earlier work reported by Davis et al. [1996], two empirical equations were developed to see if model-calculated diurnal-average rates of O₃ destruction and formation could be related to the critical variables O₃, H₂O, and NOₓ.

\[
D(O_3) = 1.03 \times 10^{10} \left( \frac{O_3}{M} \right) [H_2O]^{-0.767} \\
F(O_3) = \left( \frac{NO_x}{M} \right) (2.87 \times 10^{17} \ln \left( \frac{H_2O}{O_3} \right) - 2.47 \times 10^{18})
\]

where D(O₃) and F(O₃) have units of ppbv/day, O₃ has units of ppbv in equation (5) and molecules/cm³ in equation (6), H₂O and M have units of molecules/cm³ in both equations, and NOₓ has units of pptv.

These equations were based on model calculations for the 13 altitude/latitude sampling bins from PEM-A. Adding
PEM-B model calculations for the tropics [Crawford et al., this issue] and extratropics (See Table 4), this database is expanded to 37 altitude/latitude sampling bins. When applied to the expanded database, equation (5) was successful in predicting D(O₃) values to within ±50% for all cases but five, all of which were in the PEM-B 30-50°N regime. Application of equation (6) proved to be considerably less successful. In this case, not only were the predictions for 30-50°N significantly in error, but those for some high-altitude data bins even generated negative values.

That these equations were unable to predict reasonable values of F(O₃) and D(O₃) for the 30-50°N latitude regime is quite understandable since they contained no variable which could account for large changes in radiative conditions. Recall that it was in this latitude zone that a major enhancement in total overhead O₃ column density was observed. Expanding the earlier relationship to account for large changes in radiative conditions requires one to address not only changes in O₃ column density but also seasonal effects, latitude changes, shifts in daily solar insolation, and variations in cloud conditions. Estimating the impact of clouds requires the use of a model; however, O₃ column density and seasonal/latitudinal changes in solar insolation can be more easily incorporated into empirical equations of the type of (5) and (6). For O₃ column density the variable "TOMS" was adopted signifying the use of data derived from the Total Ozone Mapping Spectrometers which have been placed in orbit on a number of satellites (e.g., Meteor-3, Nimbus-7, etc.). To account for seasonal/latitudinal impacts, the cosine of the high noon solar zenith angle (θ_HN) was adopted. This value is easily calculated given only the latitude and day of the year.

Incorporating these new variables, the following updated version of equation (5) was developed.

\[
D(O₃) = 1.03 \times 10^{-1} \frac{[O_3][H_2O]^{0.6}\cos(θ_HN)}{\text{TOMS}}
\]

Here D(O₃) is in ppbv/day, O₃ is in ppbv, H₂O is in ppmv, and TOMS is in Dobson units. Both equations (5) and (7) illustrate the linear dependence of D(O₃) on O₃ and the near square root dependence on H₂O. The linear dependence on O₃ comes from the fact that it appears explicitly in two O₃ destruction terms (see Equation 2) and is linearly related to the concentration of O(¹D) in the remaining term. The sublinear dependence on H₂O is a result of its explicit appearance in only one term. HO₂ (OH + HO₂) radicals in the other terms are indeed derived from H₂O; but increases in H₂O do not typically result in linear increases in HO₂. The cos(θ_HN)/TOMS term indicates a linear influence from radiative conditions which directly impacts on the production of O(¹D) through O₃ photolysis.

A correlation plot of D(O₃) determined from equation (7) versus model-estimated values is shown in Figure 6a. This equation predicted D(O₃) to within ±25% for 30 of the 37 model calculations. Of the remaining seven, all but two were within ±50%. The worst source of error came from those bins associated with the 0-1 and 1-2 km data for 30-50°N. In this case the errors were +150 and +80%, respectively. A large part of the latter discrepancy appears to be the result of not including a variable that deals with cloudiness.

A further modification of the empirical equation for F(O₃) resulted in the following form:

\[
F(O₃) = 2.19 \times 10^7 [NO] \sqrt{\frac{[H_2O][O_3]\cos(θ_HN)}{[M]\text{TOMS}}}
\]

Here F(O₃) is in ppbv/day, NO is in pptv, O₃ is in ppbv, H₂O is in ppmv, M is in molecules/cm³, and TOMS is in Dobson units. The form of equation (8) reflects the fact that F(O₃) should be proportional to the product of NO and peroxy radicals. Since peroxy radicals are derived primarily from the OH oxidation of CO and hydrocarbons, the square root terms...
Figure 7. Critical NO (shaded area) and median measured NO (symbols) versus altitude for (a) 20-30°N and (b) 30-50°N. Error bars encompass the inner quartiles.

Critical NO (NO$_{\text{crit}}$) is defined as the level of NO at which O$_3$ formation and destruction are in balance (i.e., P(O$_3$) = 0). As noted earlier, the net O$_3$ production observed in the lower troposphere was primarily a result of elevated NO levels from continental outflow. A comparison of NO$_{\text{crit}}$ with observed NO can provide a measure of the sensitivity of P(O$_3$) to small changes in NO. PEM-B simulations using median conditions show that NO$_{\text{crit}}$ values ranged from 4-18 pptv. Figure 7 shows NO$_{\text{crit}}$ and median observed NO with respect to altitude for both 20-30°N and 30-50°N. What is seen here is that ΔNO (NO$_{\text{obs}}$ - NO$_{\text{crit}}$) undergoes major variations within a given regime as a function of altitude and also differs considerably between regimes. For 20-30°N, below 6 km, the difference is quite small (e.g., 10-20%); whereas, above this altitude ΔNO is a factor of 2.5 to 20. For 30-50°N the value of ΔNO over all altitudes is between a factor of 2 to 6, but the largest differences are below 2 km. The latter observation reflects the major impact resulting from continental outflow. That NO$_{\text{crit}}$ values should differ so dramatically between regimes (i.e., 5 versus 20 for altitudes <2 km) raises an interesting question related to what determines these "break even" values? To explore this question we return to equations...
photochemical source is only a factor of two greater than the much smaller (10 x 10^6 molecules/cm²/s). In this case the deposition, e.g., 37 x 10^6 versus 5 x 10^6 (Kawa and Pearson, about 7 times greater than estimates of the average surface local stratospheric source of O₃ is probably larger than that (3.8 x 10^6) falls just below values for surface deposition. The average stratospheric flux. This suggests that at 30-50°N the total tropospheric column-integrated rate. Model results for in this simplified view.

4.3. Ozone Budgets

Diurnal-average column-integrated rates of O₃ destruction, formation, and tendency for 20-30°N and 30-50°N are shown in Figures 9a-9c. Also given in each figure legend is the total tropospheric column-integrated rate. Model results show F(O₃) for the 20-30°N regime (58 x 10^10 molecules/cm²/s) to be more than an order of magnitude greater than the average NH stratospheric flux of ~5 x 10^10 [Gidel and Shapiro, 1980; Mahlman et al., 1980]. However, given the latitude and season, the local stratospheric flux was likely to be substantially larger than the NH average. Even so, we estimate that it would still fall well short of the value cited for photochemical formation. For 30-50°N, F(O₃) is much smaller (10 x 10^10 molecules/cm²/s). In this case the photochemical source is only a factor of two greater than the average stratospheric flux. This suggests that at 30-50°N the local stratospheric source of O₃ is probably larger than that from photochemistry. Ozone destruction for 20-30°N is about 7 times greater than estimates of the average surface deposition, e.g., 3 x 10^10 versus 5 x 10^10 [Kawa and Pearson, 1989; Lenschow et al., 1982]; while at 30-50°N, D(O₃) (3 x 10^10) falls just below values for surface deposition. The cited photochemical destruction rates lead to estimated photochemical lifetimes for the tropospheric O₃ column of 16 and 120 days, respectively, for 20-30°N and 30-50°N.

As noted by Crawford et al. [this issue] in their analysis of the PEM-B tropical data and Davis et al. [1996] in their analysis of the tropical and extratropical data of PEM-A, the level of photochemical activity within the tropospheric O₃ column can be a strong function of altitude. In the current analysis at 20-30°N, 67% of formation and 77% of the destruction occurred below 4 km. For 30-50°N the corresponding values were 81 and 72% below 4 km. These results suggest that for these latitudes and for wintertime conditions, F(O₃) and D(O₃) are quite sensitive to changes in lower tropospheric conditions. Thus, strong low-altitude Asian continental outflow for the late winter and early spring months can greatly amplify the photochemical impact on local O₃ levels.

Estimates of the net O₃ tendency for 20-30°N and 30-50°N indicate that for the PEM-B sampling period the respective tropospheric O₃ columns increased by 2.1 x 10^10 and 6.7 x 10^10 molecules/cm²/s. As a percentage change, these rates are approximately 2 and 1% per day, respectively. From a regional/hemispheric perspective, it could be argued that these large net positive values for F(O₃) are what is needed to offset the rather large net negative values observed for the tropics (e.g., ~1.4 x 10^10 molecules/cm²/s) [Crawford et al., this issue]. The possibility that O₃ rich extratropical air is transported into the tropics to balance the net photochemical destruction in the tropics was raised by Crawford et al. in their analysis of the PEM-B tropical data as well as by Davis et al. [1996] in their analysis of the tropical PEM-A data. If this type of transport were to occur, it obviously would also tend to reduce the impact from photochemical O₃ production on the extratropics.

Given the seasonal climatology of tropospheric ozone (1979-1989) as derived from satellite observations [Fishman et al., 1992], the tropospheric O₃ column in the PEM-B extratropical region should have experienced a seasonal increase of 30-40%. This might lead one to conclude that the estimated photochemical increases of 1 to 2% per day are unrealistically high. On further reflection, however, it is unlikely that these estimated rates could be sustained over any significant period of time. For example, it must be recognized that the PEM-B mission was planned in order to sample the western Pacific Rim region during maximum continental outflow. Thus, the overall levels of precursors (particularly NO and NMHCs) were near a maximum and would be expected to gradually decrease with time, especially in the marine boundary layer. There is also a natural leveling effect that would occur with increasing O₃ concentrations since destruction increases linearly with increasing O₃ but formation increases only by the square root of the O₃ level as illustrated in equations (7) and (8). Additionally, with a steady increase in temperature due to the onset of spring, one would predict increases in H₂O with corresponding higher values of D(O₃) and most likely higher values for NOcrit. Concurrent with increases in the critical level of NO, increased levels of OH and longer days would decrease the photochemical lifetime of NO₃. Increasing temperatures would also result in a decrease in the levels of PAN. Under cooler conditions this thermally labile nitrogen species can be advected out over the Pacific and thus serve to sustain elevated levels of NO₃ at large distances from the source of NOₓ. For all of the above
Figure 9. Diurnal-average column-integrated values of (a) F(O₃), (b) D(O₃), and (c) P(O₃). Values are calculated from median conditions for the latitude ranges of 20-30°N and 30-50°N. Total tropospheric column values are annotated at the bottom of the figure.
reasons, it can be argued that the very high rates of \( O_3 \) production estimated for the extratropics based on PEM-B data would be significantly moderated in time. Even so, the above calculations also suggest that under near wintertime conditions, photochemistry in this region of the Pacific can have a very large impact on local and regional \( O_3 \) budgets when perturbed by a major outflow of anthropogenic continental emissions.

4.4. Comparison With PEM-A

During PEM-A there was no abrupt drop in the tropopause height at extratropical latitudes. Thus the entire PEM-A
region of 18 to 42°N can be characterized as consisting of a single regime [Davis et al., 1996]. This "Pacific Rim" regime was, in fact, not all that dissimilar from the PEM-B 20-30°N sampling region in that nearly 75% of the Pacific Rim PEM-A data were recorded south of 30°N. Most importantly, during PEM-A, no significant latitudinal gradient in the total O_3 column density was present. This is reflected in the observation that for the latitude ranges given, J(O_1D) values were quite similar for both field programs. (Note, both programs took place near solar equinox conditions.)

Figures 10a-10f provide a comparison of several PEM-B (20-30°N) and PEM-A (18-42°N) critical photochemical parameters as a function of altitude. These include median mixing ratio values for O_3, CO, NO, H_2O, C_2H_6, and C_3H_8. Among the differences seen in these data is the contrast in O_3 below 4 km. Ozone levels in PEM-B exceed those in PEM-A by more than a factor of 1.5 and for the BL this difference reaches a factor of 4. This low-altitude enhanced O_3 in PEM-B is a product of the continental outflow of O_3 and its precursors which are still actively producing O_3. This outflow was almost totally absent during PEM-A. Strong evidence of this outflow is also seen in the distributions of CO and NMHCs. At altitudes below 6 km, levels in PEM-B exceed those in PEM-A by factors of 1.5 to 2 for CO, 1.5 to 5 for C_2H_6, and 6 to 10 for C_3H_8. In contrast to this low altitude scenario, above 8 km, PEM-A has only slightly higher CO and NMHC levels. As discussed by Davis et al. [1996], the latter observation is in concert with a northern hemisphere, and specifically a Pacific Rim region, that experienced large amounts of deep convection during PEM-A.

A comparison of NO shows PEM-B levels below 4 km exceeding those in PEM-A by factors of 3-5. Even at altitudes above 8 km, PEM-B values still exceed PEM-A values by a factor of approximately 1.5. Observed values for H_2O at high altitude support the view that PEM-A was more influenced by deep convection than PEM-B. Above 6 km PEM-A values are systematically higher by a factor of 2-5 times over those in PEM-B.

Differences in the photochemical O_3 budgets for PEM-A and B are shown in Figures 11a-11c. Rates in these figures are diurnal-average column-integrated values with total tropospheric column rates annotated in each figure legend. The results show that below 4 km O_3 formation in PEM-B exceeds that for PEM-A by a factor of 3. By contrast, above 4 km the difference between PEM-A and B is less than 10%. Overall, this means that O_3 formation in PEM-B exceeded that for PEM-A by nearly a factor of 2. Differences in O_3 destruction are much smaller. PEM-B has slightly larger values in the lower atmosphere, due mostly to higher levels of O_3, but overall the tropospheric column destruction for the two field programs differ by only 15%, PEM-B being greater.

As noted several times earlier in the text, the elevated O_3 formation rate in PEM-B primarily reflects the impact of elevated NO levels from continental outflow. Additionally, however, some enhancement resulted from NMHC oxidation (i.e., NO + RO_2). The latter was significantly larger in the case of PEM-B for altitudes below 4 km. This impact is shown more quantitatively in Table 5 which displays the results from several sensitivity calculations for PEM-B. These sensitivity calculations for PEM-B were based on substituting PEM-A median values for NO, CO, or NMHCs. Results show the largest difference generated is that for F(O_3) at low altitudes. For altitudes less than 4 km F(O_3) values during PEM-B would have been 3-4 times lower given PEM-
Figure 11. Diurnal-average column-integrated values of (a) \( F(O_3) \), (b) \( D(O_3) \), and (c) \( P(O_3) \). Values are calculated from median conditions for PEM-West A (18-42°N) and PEM-West B (20-30°N). Total tropospheric column amounts are annotated at the bottom of the figure.
A NO levels. Minor differences are also seen in D(O$_3$) due to the secondary effects from HO$_x$ levels. For NMHCs the impact on F(O$_3$) using PEM-A levels is 15% or less. Perhaps the most surprising result is at high altitude (10-12 km) where the NMHC levels of PEM-A resulted in a 21% increase in PEM-B F(O$_3$) values. Because of the extensive deep convection during PEM-A [Davis et al., 1996], NMHC levels were significantly higher at 10-12 km than in PEM-B. This result makes the point that oxidation of NMHCs at high altitudes can provide a significant source of HO$_x$ as evidenced in the 12% increase in D(O$_3$). Again, C$_4$ alkanes were the most prominent source of reactive NMHCs. The smallest impact from the substitution of PEM-A input data into PEM-B was found for the variable CO.

When examined in terms of P(O$_3$), the difference between the two field programs is primarily limited to the lower troposphere with PEM-B showing significant positive values and PEM-A being significantly negative. As previously noted, tropospheric O$_3$ column rates of formation and destruction are more sensitive to changes in lower atmospheric conditions. For PEM-B, higher NO levels in addition to elevated RO$_2$ from NMHCs resulted in the net production of O$_3$.

4.5. NO$_x$ Sources

As is now well documented in the literature, NO$_x$ plays a pivotal role in the photochemical formation of O$_3$; thus, understanding the NO$_x$ budget is a centrally important issue. The components of this budget include both surface primary sources (i.e., fossil fuel combustion, biomass burning, and soil emission) as well as upper free tropospheric sources (i.e., aircraft emissions, lightning, and stratospheric intrusions). Secondary sources are defined as NO$_x$ recycled from HNO$_3$, PAN, or other NOy species. For regions having very weak primary sources the latter source type can become the dominant one.

Figure 12 shows the distribution of NO$_x$ for PEM-B (20-30°N) and PEM-A (18-42°N). Although this summary data indicate that at all altitudes NO$_x$ mixing ratios for PEM-B exceeded those for PEM-A, the difference for altitudes above 4 km is quite modest, that is, typically a factor of 1.6 or less. For the lower troposphere the large NO$_x$ difference has already been addressed in terms of the major influence from continental outflow. The chemical make-up of this outflow was dominated by anthropogenic emissions. As this continental air mass was advected out into the western Pacific at low altitudes, high levels of NO$_x$ were maintained by the recycling of NO$_x$ from PAN (~200 pptv). Model simulations suggest that as much as 50% of the observed NO$_x$ for altitudes of 0-1 km and 20% at 1-2 km could have been derived from PAN. Above 2 km this source was found to be negligibly small.

For the upper free troposphere the relative amounts of different NO$_x$ sources represent a far more complex issue. A more detailed analysis of high-altitude sources for both PEM-A and PEM-B is in progress and will be published independently (D.D. Davis et al., unpublished results, 1997). Model calculations suggest that for PEM-B as much as 32% of the upper free tropospheric NO$_x$ could be explained by the recycling of NO$_x$ through HNO$_3$ (~120 pptv) with virtually no contribution coming from PAN (~60 pptv). The remaining high-altitude NO$_x$ appears to be made up of a combination of primary sources. Chemical fingerprints identified in time series plots of the high-altitude data suggest that the primary sources include aircraft emissions, stratospheric intrusions, transport of surface emissions to high altitudes, and even some small contribution from lightning.

**Table 5. Sensitivity Calculations for PEM-West B Conditions When Substituting PEM-West A Levels of NO, CO, and NMHCs**

| Altitude | NO F(O$_3$) Change | CO D(O$_3$) Change | NMHCs F(O$_3$) Change | CO D(O$_3$) Change |
|----------|-------------------|--------------------|-----------------------|--------------------|
| 0-1 km   | 0.37              | 1.08               | 0.85                  | 0.94               |
| 1-2 km   | 0.25              | 1.04               | 0.85                  | 0.93               |
| 2-4 km   | 0.39              | 1.00               | 0.93                  | 0.96               |
| 4-6 km   | 0.79              | 0.99               | 0.96                  | 0.98               |
| 6-8 km   | 0.86              | 1.00               | 1.03                  | 0.99               |
| 8-10 km  | 0.72              | 1.02               | 1.06                  | 0.96               |
| 10-12 km | 0.73              | 1.04               | 1.21                  | 0.96               |

[Figure 12. Median altitude distribution of NO$_x$ for PEM-West A (18-42°N) and PEM-West B (20-30°N).]
Although climatological data based on long term satellite further demonstrated the impact of continental outflow during with the comparable PEM-A latitude zone of 18-42øN has due to springtime reductions in continental outflow as well as erably greater than expected. Even so, it is unlikely that these observations would argue that for this season modest increases much smaller, e.g., factors of 2 and 0.8, respectively.

Diurnal-average O3 formation rates for 20-30øN exceeded those for 30-50øN by factors of 3-13. For O3 destruction the difference was even greater, involving factors of 4-14. In spite of these large differences, both regimes still exhibited net photochemical production of O3 at all altitudes. This first of its kind observation for a large segment of the northwestern Pacific is quite unusual, both because the lower marine troposphere is typically a region found to exhibit net photochemical destruction and because the season of the year was late winter/early spring. As noted above, the low-altitude outflow of continental emissions was a critical factor in creating conditions in which net O3 production prevailed for both regimes. This was apparent in the observed elevated levels of NO and CO as well as numerous NMHCs. It was also evident in the contribution to O3 formation from organic peroxy radicals (RO2) of 10-20% for altitudes less than 4 km.

Despite the much lower values for O3 formation and destruction at 30-50øN, net O3 production below 2 km was still estimated to be as large as that calculated at 20-30øN. This result strongly reflects the influence of having much lower values of NOcrit at 30-50øN than at 20-30øN. For example, even though NO levels in both regimes were in the 20-50 pptv range, 30-50øN had an excess of 20 pptv NO (above NOcrit), while for 20-30øN the excess was only 4 pptv.

For both latitude ranges a significant fraction of O3 formation and destruction took place at altitudes below 4 km. The values were 67 and 81% for O3 formation and 77 and 72% for O3 destruction at 20-30øN and 30-50øN, respectively. The diurnal-average column-integrated rate of tropospheric O3 formation for the 20-30øN regime exceeded the NH average stratospheric flux by an order of magnitude, while tropospheric column O3 destruction exceeded surface deposition by a factor of 7. For 30-50øN the differences were much smaller, e.g., factors of 2 and 0.8, respectively.

Values for the tropospheric column-integrated O3 tendency (e.g., 6.7x1010 and 21.4x1010 molecules/cm2/s at 30-50øN and 20-30øN, respectively) suggest that the tropospheric O3 column density was increasing at the rates of 1 and 2%/day. Although climatological data based on long term satellite observations would argue that for this season modest increases should occur, the increases estimated in this work are considerably greater than expected. Even so, it is unlikely that these rates could be sustained over any significant period of time due to springtime reductions in continental outflow as well as leveling effects driven by a linear dependence of D(O3) on ozone levels. In addition, one would expect a shortened lifetime for O3 with increasing spring temperatures.

A comparison of the 20-30øN sampling regime of PEM-B with the comparable PEM-A latitude zone of 18-42øN has further demonstrated the impact of continental outflow during PEM-B. Most of this impact, however, was confined to altitudes below 4 km. For these altitudes, PEM-B ozone formation exceeded that for PEM-A by a factor of nearly 4. Integrated over all altitudes it was a factor of 2. Differences in ozone destruction were much smaller, amounting to only 15% overall, PEM-B being slightly higher.

A survey of both primary and secondary PEM-B NOx sources indicated that below 4 km, continental outflow of anthropogenic emissions was clearly the dominant source; however, model simulations also suggest that recycling of NOx from PAN could have contributed as much as 50% of the NOx at altitudes below 1 km and as much as 20% between 1 and 2 km. For altitudes above 8 km, recycling of HNO3 was estimated to account for one-third of the observed NOx. In an independent study of the high-altitude PEM-B data, D.D. Davis et al. (unpublished results, 1997) have indicated that several primary NOx sources contributed to the observed levels of NOx including aircraft emissions, stratospheric intrusions, vertical transport of surface emissions, and a small contribution from lightning.

The results from this work are important in establishing that significant net production of O3 can occur at extratropical latitudes even under wintertime conditions. Equally significant is the finding that these conditions can be found in a marine environment at low altitudes, an atmospheric domain typically dominated by net O3 destruction. In the current study, outflow from the Asian continent maintained elevated levels of NOx, CO, and NMHCs creating ideal conditions for O3 production. While this impact is not totally unexpected in the near-coastal areas of a continent, this study has shown that outflow in some cases impacted on the western North Pacific at distances of 2000 km from the Asian Pacific Rim.

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