Implications of large scale shifts in tropospheric NOx levels in the remote tropical Pacific

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Abstract. A major observation recorded during NASA's western Pacific Exploratory Mission (PEM-West B) was the large shift in tropical NO levels as a function of geographical location. High-altitude NO levels exceeding 100 pptv were observed during portions of tropical flights 5-8, while values almost never exceeded 20 pptv during tropical flights 9 and 10. The geographical regions encompassing these two flight groupings are here labeled "high" and "low" NOx regimes. A comparison of these two regimes, based on back trajectories and chemical tracers, suggests that air parcels in both were strongly influenced by deep convection. The low NOx regime appears to have been predominantly impacted by marine convection, whereas the high NOx regime shows evidence of having been more influenced by deep convection over a continental land mass. DMSP satellite observations point strongly toward lightning as the major source of NOx in the latter regime. Photochemical ozone formation in the high NOx regime exceeded that for low NOx by factors of 2 to 6, whereas O3 destruction in the low NOx regime exceeded that for high NOx by factors of up to 3. Taking the tropopause height to be 17 km, estimates of the net photochemical effect on the O3 column revealed that the high NOx regime led to a small net production. By contrast, the low NOx regime was shown to destroy O3 at the rate of 3.4% per day. One proposed mechanism for offsetting this projected large deficit would involve the transport of O3 rich midlatitude air into the tropics. Alternatively, it is suggested that O3 within the tropics may be overall near self-sustaining with respect to photochemical activity. This scenario would require that some tropical regions, unsampled at the time of PEM-B, display significant net column O3 production, leading to an overall balanced budget for the "greater" tropical Pacific basin. Details concerning the chemical nature of such regimes are discussed.

1. Introduction

To understand the photochemistry of tropospheric ozone, the distribution of NO and NOx (NO + NO2) must be understood. It is the cycling of NOx as facilitated by peroxy radicals that governs the photochemical formation of ozone [Chameides and Walker, 1973; Crutzen, 1973]. For example, even though both stratospheric-tropospheric exchange and surface deposition contribute to the tropospheric O3 budget, photochemical formation and destruction typically make much larger contributions to the budget [e.g., Fishman et al., 1979; Liu et al., 1980; Fehsenfeld and Liu, 1993; Davis et al., 1996a]. However, considerable uncertainty remains in the quantitative evaluation of these photochemical components, particularly as related to the distribution of NOx.

Estimating the tropospheric distribution of NOx presents a significant challenge for several reasons. Among these are the fact that primary sources for this species are very diverse in nature, ranging from surface emissions (both anthropogenic and natural in origin) to lightning, aircraft emissions, and stratospheric injections [e.g., Hameed et al., 1981; Liu et al., 1980; Logan, 1983; Levy and Maxin, 1989; Penner et al., 1991; Kasibhatla et al., 1991; Beck et al., 1992; Wuebbles et al., 1993; Davis et al., 1996a; Jacob et al., 1992, 1996]. Further complicating this picture is the role played by secondary sources of NOx. The origin of the latter source involves the chemical recycling of longer-lived nitrogen species such as HNO3 and PAN as well as other potential NOx species [e.g., Liu et al., 1987; Chafield and Delany, 1990; Singh et al., 1992; Jacob et al., 1992, 1996; Davis et al., 1996a]. Still further complicating the NOx distribution picture is the highly
variable lifetime of this species. This can vary from less than 1 day at BL altitudes to nearly 2 weeks at very high altitudes.

Using source inventory data with different types of models, several groups have undertaken the goal of generating estimates of the global tropospheric NOx distribution [e.g., Ehhalt et al., 1992; Kasibhatla et al., 1993; Levy et al., 1996]. Unfortunately, the scarcity of observations, especially at high altitudes and in remote areas such as the tropics, have made it difficult to substantiate significant components of these studies. Regional campaigns attempting to obtain measurements of NO and NO2 over a substantial altitude range have included the Stratospheric Ozone III campaign (STRATOZ) [Drummond et al., 1988] and NASA's Global Tropospheric Experiment (GTE). The latter program has encompassed field studies in the Amazon River Basin (Amazon Boundary Layer Experiment (ABLE) 2A and 2B [Harris et al., 1988, 1990]); the Arctic and sub-Arctic (Arctic Boundary Layer Expedition, ABLE 3A and 3B [Harris et al., 1992, 1994]); the western North Pacific (Pacific Exploratory Mission (PEM)-West A [Hoell et al., 1996]); and the tropical Atlantic (Transport and Atmospheric Chemistry Near the Equatorial Atlantic (TRACE A) [Fishman et al., 1996]). In most cases individual measurements in these campaigns have shown large variablity in NO levels; however, median values from one region to another have generally exhibited more modest/gradual variations [J. Bradshaw, manuscript in preparation, 1996]. By contrast, during PEM-West B, recorded NO values in the tropics exhibited not only large variability in individual NO measurements but also showed large systematic shifts in regional median values, e.g., approaching an order of magnitude on the regional scale. This paper examines the large shift in median NO values in the tropical Pacific. The primary focus will be identifying the factors responsible for this shift and evaluating the photochemical consequences of this shift.

2. Observational Data

2.1. NO and Other Photochemical Measurements

While atmospheric NO measurements over the last decade have shown a trend of increasing reliability [Hoell et al., 1985, 1987, 1996; Gregory et al., 1990], observations from independent instruments still serve to increase one's confidence in unexpected findings. In the case of PEM-West B, measurements were reported by two groups: Georgia Institute of Technology and Nagoya University. The former group used the two-photon laser-induced fluorescence (TP-LIF) technique, while the latter group employed the more common NO detection method of O3 chemiluminescence. The results from these two approaches compared quite well for all PEM-West B flights. For example, based on 30-s sampling intervals, a standard regression analysis of almost 5000 paired NO measurements gave a regression line having a slope of 1.25 ± 0.01, an intercept of 1.2 ± 0.2 pptv, and an R^2 value of 0.95 with Nagoya (the dependent variable) having the higher NO values. 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. For further details concerning the experimental hardware and measurement methodology, the reader is referred to Hoell et al. [this issue].

The measurement techniques employed for all other critical photochemical parameters (e.g., CO, H2O, O3, NMHCs, and UV irradiance) as well as aerosol parameters (e.g., CN and size/# density) have been summarized by Hoell et al. [this issue]. Also reported for each of these methodologies are the data sampling rate, precision, accuracy, and nominal limit of detection (LOD).

Since no observed values of NO2 were recorded during PEM-West B, NO2 mixing ratios were estimated from photochemical box-model calculations (see later discussion in section 3.2.1.). Thus the values of the photochemical quantity NOx (NO + NO2) used throughout this analysis are those estimated from (NO)mean and (NO2)calc.

2.2. Sampling Region

On the basis of meteorological considerations the PEM-B sampling region has been separated into two large regional areas as illustrated in Figure 1. These regions are defined by the large-scale outflow from the Asian continent. Latitudes north of 20°N were heavily impacted by continental outflow [Merrill, et al., this issue]. By contrast, to the south of this latitude and east of 120°E, continental influences were found to be minimal, leading to our tentative conclusion that this region was representative of a remote tropical-marine environment. It is the latter region that exhibited the large shifts in NO and is the focus of this paper. As shown in Figure 2, the remote tropical component of the PEM-B flight track contained all or portions of flights 5-10. During flights 5-8 the free tropospheric mixing ratios of NO were found to be highly elevated (e.g., often in excess of 100 pptv), whereas during flights 9 and 10 levels almost never exceeded 20 pptv. The former sequence of flights will be defined hereafter as the "high" NOx regime, while the latter flight sequence (i.e., 9 and 10) will be referred to as "low" NOx. Note also that although geographically in the tropics, the near-coast portions of flight 10 and all of flight 11 (i.e., longitudes west of 120°E) have not been included in this analysis because both showed evidence of having been significantly influenced by low and medium

![Figure 1. Overview of mean winds and synoptic conditions during the PEM-West B sampling period. Also shown are primary cold frontal zones with the dotted line representing the southernmost extent of cold frontal movement during PEM-West B.](image-url)
altitude continental outflow, e.g., CO levels often in excess of 200 pptv. Talbot et al. [this issue] have also examined the tropical PEM-B region in terms of continental and aged marine air masses. While their designations are in many ways similar to ours, differences exist since their data separation is based predominantly on isentropic trajectories; also, they include those portions of flights 10 and 11 that we have omitted.

In order to facilitate a statistical comparison of the two regimes, all flight data falling within a solar zenith angle window of 0-60° were grouped into altitude bins of 0-1, 1-2, 2-4, 4-6, 6-8, and 8-10 km. Comparisons between regimes therefore are based on median conditions for each altitude block for each regime. Table 1 presents the distribution of data available for this analysis. In this case, the number of data points (i.e., 30-s averages) as well as the number of flights contributing data are listed for each altitude block in each regime. Since the high NOx regime had more flights that contributed data, this regime is clearly more robust than the low NOx regime. For example, only for the altitude range of 8-10 km are both regimes nearly equal in terms of total available data. This can be largely attributed to the fact that low "NOx" flight 10 sampled almost exclusively at 9.5 km between 120° and 145°E. Strictly speaking, therefore, the flight map shown in Figure 2 should be viewed as primarily providing the geographical range spanned by both regimes at high altitudes (i.e., 8-10 km). For lower altitudes the in situ data for the two regimes are more restricted as the bulk of these data come from a longitudinal band spanning 143-153°E.

Figure 3 shows a comparison of median NO mixing ratios as a function of altitude for the "high" and "low" NOx regimes. These results show that NO levels are considerably larger for the high NOx regime at all free tropospheric altitudes. The difference between the two regimes is seen to range from a factor of 2.5 for altitudes of 2-4 km to nearly 1 order of magnitude (e.g., 6 versus 60 pptv) at altitudes of 8-10 km. Quite noteworthy also is the observation that for all altitude blocks above 2 km the median values for the two regimes differ by more than one quartile. Interestingly, NO levels for the low NOx regime remain essentially constant with altitude; therefore, the large differences observed between the two regimes at the higher altitudes are seen to be entirely due to increases in NO in the high NOx regime.

As shown in Figure 4, the trends in NOx deviate only slightly from those shown for NO in Figure 3. The steady increase of NOx with altitude in the high NOx regime is similar to the trend for NO but is somewhat less pronounced since at low altitudes there is a significant amount of NOx present as NO2. At the higher altitudes, NOx is predominantly in the form of NO due to a significant decrease in the reaction rate between NO and O3 and a modest increase in the rate of NO2 photolysis. In sharp contrast to the NOx profiles shown for the high NOx re-
hemisphere. This is true not only for those trajectories shown in Figure 5 but for all isentropic trajectories calculated for altitudes above 2 km. Furthermore, approximately 80% of the trajectories for the high NO$_x$ regime are indicated to have recently passed over the Asian continent (i.e., within 2-3 days of sampling). By contrast, the trajectories associated with the low NO$_x$ regime are seen as being exclusively from the southern hemisphere. Again, this is not only true for the examples shown in Figure 5 but for all trajectories above 2 km. Approximately 50% of the low NO$_x$ trajectories track back to remote South Pacific points of origin. The remaining 50%, although from the southern hemisphere, pass over New Guinea.

For purposes of comparison with the isentropic trajectories of Figure 5, a set of 6 day kinematic trajectories were provided by S. McKeen (private communication, 1996). For both regimes, these trajectories tended to travel more slowly covering roughly half the distance of the isentropic trajectories per day. For the high NO$_x$ regime the two methods compared quite well. Both indicated air parcels being transported eastward from southeastern Asia at high altitude. In the case of low NO$_x$ the kinematic trajectories differed somewhat in that they did not cross the equator or remain at high altitude. Instead, air parcels were shown rising steadily from altitudes as low as 2 km while at the same time being transported westward from the tropical, central Pacific. Thus the kinematic trajectories offer a somewhat different perspective on the origin of the air parcels sampled in the low NO$_x$ regime; however, they do not alter the earlier conclusion, based on the isentropic trajectories, that this regime was predominantly influenced by marine sources.

While back trajectories are much less reliable for BL conditions, especially after more than 2 days, it is still noteworthy that near-surface isentropic trajectories do not follow the pattern of those in the free troposphere. For both regimes, most of the trajectories have the central North Pacific as a source region.

2.3.2. Chemical tracers. As noted above, chemical tracer data can also be an indicator of the origin and/or history of a sampled air parcel. With the notable exceptions of NO$_x$ and O$_3$, the source of many chemical tracers at high altitudes is the direct result of the coupling between vertical transport and the release of a species at or near the surface. In these cases, one of the more important vertical mixing processes can be deep convection. During PEM-B the tropics was convectively quite active as evidenced by numerous visual as well as satellite observations. Evidence supporting the notion that deep convection was indeed important in the redistribution of several tracers can be found in many of their altitude profiles. As illustrative of this, Figure 6a shows median values versus altitude for "fine" aerosol particles as expressed as CN (condensation nuclei) number density. These data clearly indicate that for both the high and the low NO$_x$ regimes, median CN values significantly increase with altitude. As suggested by other investigators [Clarke et al., 1993; Thornton et al., 1996] a likely explanation for this observation is that for tropical conditions, significant amounts of volatile surface sulfur (e.g., volcanic, anthropogenic, and/or biogenic) are pumped to high altitudes via deep convection. At high altitudes this reduced sulfur can be oxidized by OH radicals, and the resulting sulfuric acid, at very cold temperatures and in the absence of significant populations of larger particles, leads to the formation of new particles via nucleation processes. Thus, these data support the hypothesis that both the high and the low NO$_x$ regimes experienced the effects of deep convection. That deep convection occurring over both environments could lead to elevated high-altitude sulfur levels and hence CN levels is
not all that surprising since significant sulfur sources exist over both continental and marine regions of the tropics.

Other chemical tracers can help point toward whether the convection was over continental or marine regions. For example, CH$_3$I is considered an excellent tracer for BL marine air. This species has predominantly an ocean source and its lifetime is only a day or two in the tropics [Chameides and Davis, 1980; Solomon et al., 1995; Davis et al., 1996b; Chen et al., 1996]. As shown in Figure 6b, the altitude distribution of CH$_3$I for the low NO$_x$ regime shows a significant enhancement over that for the high NO$_x$ case. At 8-10 km this results in median CH$_3$I mixing ratios that are more than twice that for the high NO$_x$ regime. In fact, for all altitudes above 2 km, the lower quartile for the low NO$_x$ regime exceeds the upper quartile value for the high NO$_x$. These results thus are consistent with the hypothesis that the low NO$_x$ regime was more heavily influenced by marine convection. Although dimethylsulfide (DMS) might also be considered as a useful tracer of marine convection, the measured median concentration levels for this species were found to be too near the limit of detection (LOD) to justify a detailed quantitative comparison between the two regimes. Even so, quite relevant to the above argument were those DMS observations recorded for the highest-altitude data bin at 8-10 km. In this case, the upper quartile value for the low NO$_x$ regime was nearly a factor of 3 higher than the LOD for DMS. By comparison, the high NO$_x$ upper quartile DMS value was still at the LOD level. Thus the DMS results are qualitatively consistent with those for CH$_3$I.

Just as CH$_3$I and DMS may be viewed as excellent tracers of marine BL air, CO and NMHCs can be considered equally good tracers of surface continental air. As shown in Figure 6c the median values for CO versus altitude indicate that above 2 km the difference between the two NO$_x$ regimes averages less than 7 ppbv and never exceeds 11 ppbv. Not surprisingly, the respective median values also fall within one quartile of each other. Thus these results suggest that neither regime was preferentially influenced by continental emissions. The median levels for the high and low NO$_x$ regimes (i.e., ranging from 83 to 97 ppbv) would also argue that the source strength of CO from combustion that had been advected into both regions was relatively low. However, in contrast to CO the results for several NMHC species did show a systematic difference. A likely reason for this is that the latter species have very low background levels in the upper atmosphere relative to CO. This characteristic can be attributed to their having typically shorter atmospheric lifetimes versus CO and their having sources which are limited to the surface only. As illustrated in Figure 6d, a significant difference is seen in the mixing ratios of C$_3$H$_8$ for the two regimes. Differences between 4-8 km are larger than one quartile; but for the 8-10 km range, where C$_3$H$_8$ is roughly 1.5 times higher for high NO$_x$, median values actually fall within one quartile. This reflects the greater variability in C$_3$H$_8$ levels at high altitude as one might expect due to its short lifetime and surface source. Differences reflecting a similar trend were also observed for the NMHC species C$_2$H$_6$, C$_2$H$_2$, and C$_6$H$_6$.

Lead 210 and the organic acids HC(O)OH and CH$_3$C(O)OH represent still other tracers that can be associated with surface continental sources [Dibb et al., this issue]. Quite significant in this case is the fact that $^{210}$Pb is the daughter of $^{222}$Rn, a species naturally emitted mainly over continental areas. As shown in Figure 6e, the high NO$_x$ regime clearly shows a much stronger influence from continental sources than the low NO$_x$ regime. (The authors note that the sparseness of this database reflects the long integration times required for the low levels of $^{210}$Pb.) In the case of the organic acids, although only a 20% difference was found in the levels of HC(O)OH, for CH$_3$C(O)OH the trend observed at high altitudes was similar to
that for $^{210}$Pb in that the high NO$_x$ regime showed significantly higher levels, on the average being nearly a factor of 2 larger than those recorded for low NO$_x$.

O$_3$ is typically not considered a simple tracer of either continental or marine surface air because of its high photochemical reactivity and its highly variable mixing ratio as a function of altitude. In cases, however, where independent data suggest that a given air parcel was influenced by deep convection over a marine region versus having been more influenced by deep convection over a continental area, some
general arguments can be developed concerning the type of $O_3$ profile that might be observed. For example, in the context of strong vertical mixing over a remote tropical-marine region, transport of air out of the marine BL (where photochemical destruction of $O_3$ dominates formation) would most likely lead to rather low and uniform levels of $O_3$ at all altitudes. By contrast, because of elevated levels of NO$_x$ and hence a tendency toward net photochemical $O_3$ production, continental BL air transported to high altitudes and then advected out over the ocean would tend to generate less uniformity in $O_3$ levels and most likely lead to higher than average levels of free tropospheric $O_3$. As shown in Figure 6f, low uniform levels of ozone observed in the low NO$_x$ regime are consistent with a picture involving marine convection of BL air. For the high NO$_x$ case, elevated and nonuniform $O_3$ levels are observed. Ozone profiles similar to those of the low NO$_x$ regime were also found in the tropical Pacific during AASE 2 (Airborne Arctic Stratospheric Expedition) [Folkins et al., 1995], PEM-West A [Davis et al., 1996a], and CEPEX (Central Equatorial Pacific Experiment) [Kley et al., 1996]. These investigators also attributed their observations to deep convection over a marine region involving $O_3$ poor BL air.

3. Discussion

3.1. Origin of NO$_x$ Sources

The back trajectories and chemical tracer data have shown that while there are a few similarities between the low and the high NO$_x$ regimes, there are far more dissimilarities. These differences can be most easily understood in terms of the impact of deep convection in relationship to source regions. The isentropic back trajectories indicate that much of the air associated with the low NO$_x$ regime remained over the tropical South Pacific for several days before crossing the Intertropical Convergence Zone (ITCZ) and entering the northern hemisphere. While kinematic trajectories do not cross the ITCZ, they do indicate rising air transported westward from remote parts of the tropical central Pacific. The tracer species CH$_3$I also provides evidence indicating a preponderance of marine convection in this regime. For instance, at altitudes of 8-10 km the low NO$_x$ regime had CH$_3$I levels more than twice as high as that recorded for the high NO$_x$. (For comparison purposes, BL values of CH$_3$I in both the high and the low NO$_x$ regimes were within 20% of each other and were also within a similar margin of the tropical CH$_3$I data from PEM-A.)

Observations in the high NO$_x$ regime, by contrast, suggest the strong influence of deep convection over a landmass. In this case, the isentropic trajectories were all positioned in the northern hemisphere, and 80% of these trajectories indicate that the parcel had passed over a land mass within 2-3 days of the sampling time. The kinematic and isentropic trajectories were found to be in good agreement. Tracers of continental origin (i.e., NMHCs, $^{210}$Pb, and organic acids) also suggest a significant degree of interaction between the surface and the upper free troposphere.

Collectively, the above results suggest that two distinctively different surface environments, via deep convection, mixing, and transport, resulted in dramatically different impacts on what have been labeled here as high and low NO$_x$ regimes. It is centrally important to differentiate between these two environments since their influence on free tropospheric levels of NO$_x$ could be expected to be quite different. Not only would they differ in the levels of NO$_x$ that might be transported out of the boundary layer, but they could also differ significantly in the expected level of electrical activity and hence lightning generated NO$_x$. As shown in previous lightning-flash satellite data [Turner and Edgar, 1982; Orville and Henderson, 1986;
Goodman and Christian, 1993], marine convection is generally associated with much lower levels of electrical activity than continental convection, leading to the expectation of smaller contributions of NO\textsubscript{x} from lightning in the low NO\textsubscript{x} regime.

In the absence of both lightning generated NO\textsubscript{x} and a surface source of this species, one would expect marine convection to pump rather low levels of NO\textsubscript{x} from BL altitudes to the upper free troposphere [e.g., McFarland et al., 1979; Thompson et al., 1993; Davis et al., 1987, 1996a]. In contrast to the minimal NO\textsubscript{x} effects from deep convection over marine areas, deep convection over a continental land mass can influence NO\textsubscript{x} by both lightning and vertical transport of surface emissions. During PEM-B the potential impact from lightning can be seen in the form of Figures 7a and 7b. Figure 7a shows a latitudinal lightning frequency distribution for the months of February and March 1994 (S. Goodman, NASA Marshall Space Flight Center and the University of Colorado, unpublished data). These data were derived from the near local midnight (1030-1130) passes of the Defense Meteorological Satellite (DMSP) based on the F10 satellite optical linescan system (OLS) visible band imagery. This distribution shows a maximum of about 1600 lightning flashes near the equator. (Note that the DMSP OLS system detects only a small fraction of the total lightning (e.g., 2\% or less), but over the course of 1 month provides a reasonably realistic depiction of the most active thunderstorm regions [Goodman and Christian, 1993].) While falling off more rapidly in the northern hemisphere, it is quite noteworthy that the latitude range of 0-15\degree N still shows lightning flash levels that are nearly as intense as those in the southern hemisphere. Nevertheless, as discussed earlier, the effects from this distribution do not show up in the form of elevated NO values for the low NO\textsubscript{x} regime. This apparent inconsistency largely disappears when the geographical distribution of the DMSP lightning data is considered. For example, as shown in Figure 7b those regions having the highest flash density in both the northern and the southern hemispheres are those located near significant landmasses. The lowest flash rates are seen for areas far removed from land over the open Pacific. The latter setting is indicated in over half of the low NO\textsubscript{x} isentropic back trajectories, whereas nearly 80\%
of the high NO\textsubscript{x} regime isentropic trajectories involve passage over an extensive landmass.

Although the DMSP lightning flash data together with trajectory and tracer data suggest that a major source of NO\textsubscript{x} in the high NO\textsubscript{x} regime could have been lightning, the possible contribution from surface emissions still requires some investigation. In the text that follows we explore this question from several points of view. The first of these involves the observed trends in the trace gas CO. Recall that earlier in the text, when presenting the comparison of CO values, we found only a very modest difference between the two regimes. If surface combustion were a significant contributor to the elevated levels of NO\textsubscript{x}, one might expect that the difference in CO levels between regimes should have been much larger. On the other hand, the fact that there were significant differences recorded in the levels of C\textsubscript{3}H\textsubscript{8} at high altitudes does suggest some contribution from surface emissions. In an effort to semiquantitatively evaluate the possible magnitude of this source, we have used the ratio of C\textsubscript{3}H\textsubscript{8} to NO\textsubscript{x} as reported by Davis et al. [1996a]. These authors have suggested that under conditions this ratio can provide an upper limit estimate of the NO\textsubscript{x} fraction attributable to surface emissions when the trajectory and tracer data suggest that a major source of NO\textsubscript{x} in the high NO\textsubscript{x} regime could have been lightning. They have assumed that the photochemical lifetime of NO\textsubscript{x} is shorter than that for C\textsubscript{3}H\textsubscript{8}. If so, use of the 3:1 ratio or a value close to this tends to provide an upper limit for the amount of surface NO\textsubscript{x}. However, in the event of significant recycling of NO\textsubscript{x} from reservoir NO\textsubscript{y} species (e.g., HNO\textsubscript{3}, PAN, etc.) the atmospheric residence time of NO\textsubscript{x} could approach or exceed that of C\textsubscript{3}H\textsubscript{8}. Under these conditions, high altitude NO\textsubscript{x} levels could also end up being elevated relative to that expected from surface emissions. For the high NO\textsubscript{x} regime, though, the observed 148 pptv of HNO\textsubscript{3} and 55 pptv of PAN could only explain approximately 20-30\% of the NO\textsubscript{x}. Even so, we cannot at this time totally rule out the possibility of either yet unidentified recycling pathways (e.g., other than photolysis and reaction with OH) or the presence of yet unidentified NO\textsubscript{y} species, both of which might lead to the additional generation of recycled NO\textsubscript{x}. Some investigators, in fact, have concluded that recycling played a major role in the NO\textsubscript{x} budget in the tropical South Atlantic during NASA's TRACE A field study [e.g., Jacob et al., 1996; Smyth et al., 1996]. Possible mechanisms by which more rapid recycling of NO\textsubscript{x} might take place have been proposed by Chatfield [1994] and Fan et al. [1994] and have encompassed heterogeneous reactions involving HNO\textsubscript{3} and CH\textsubscript{2}O.

During PEM-B median HNO\textsubscript{3} mixing ratios in the high NO\textsubscript{x} regime exceed those in low NO\textsubscript{x} by only about a factor of 2. By contrast, median PAN levels above 4 km ranged from 5 to 10 pptv in the low NO\textsubscript{x} regime but reached levels of 50-65 pptv for high NO\textsubscript{x}. Thus given the small difference in HN\textsubscript{3}Q and the large difference in PAN, it could be argued that other organic nitrate species were transported with the PAN and might have been responsible for the observed high NO\textsubscript{x} mixing ratios as a result of recycling. While we acknowledge this possibility, we believe that a far more plausible explanation for the elevated NO\textsubscript{x} is that it was simply the product of lightning and that the NO\textsubscript{x} had not yet fully converted to HNO\textsubscript{3}. Recall that isentropic trajectories indicate that most of the air parcels that encountered the elevated NO\textsubscript{x} levels at between 2 and 6 TgN. Assuming a median global value of 3 TgN/y, Levy et al.'s results suggest that even during winter months lightning would contribute from 50 to 80\% of all upper tropospheric NO\textsubscript{x} in the tropical North Pacific.

In another study, Kumar et al. [1995] estimated the global distribution of NO based on satellite lightning sensor data (Ionospheric Sounding Satellite, ISS-b) and theoretical estimates of the lightning production rate as estimated by Borucki and Chameides [1984]. The product from this exercise was a
seasonally adjusted global distribution for NO from lightning. For the period of December to February the most significant region of NO production in the northern hemisphere was that located in the tropics over southeastern Asia and Indonesia. Recall that nearly 80% of the trajectories associated with the high NO$_x$ regime passed through this region.

While an understanding of the large-scale tropical processes driving the NO$_x$ shift is of considerable importance, equally important is the closely coupled question concerning which of these regimes might be the dominant one in the tropical western North Pacific. This issue is particularly important in the context of global modeling efforts that require a "representative" tropical NO$_x$ database. In this context, even though the high NO$_x$ regime was found to be much more robust in terms of the number of flights and amount of data (see Table 1), one cannot assume that this equates to this regime being temporally and/or spatially the most dominant. To further illustrate this point, Plate 1 shows the longitudinal distribution of O$_3$ at low latitudes (20°N to 10°S) as derived from UV DIAL data and supplemented by more limited in situ O$_3$ data, particularly that in the marine BL. This represents the most robust spatial coverage obtainable for any constituent measured during PEM-West B. While there is some longitudinal overlap between the high and the low NO$_x$ regimes as described earlier, it is still rather apparent from these data that there is a significant reduction in O$_3$ levels at nearly all altitudes west of 140°E, a picture that is consistent with Figure 6f. This represents the best evidence available, which suggests that the two NO$_x$ regimes did span a longitudinal band at altitudes below 8 km which was comparable with that at 8-10 km where the bulk of the in situ data was recorded. In fact, it is quite possible that these two regimes persisted in their respective regional dimensions for the duration of the tropical sampling time period; but it is also possible that temporal changes did occur. For example, sampling of the high NO$_x$ regime took place over the time period of February 8-17, 1994, and that for the low NO$_x$ was February 19-21, 1994. Thus it is also possible that each NO$_x$ regime spatially spanned the entire tropical-western North Pacific sampling region during its respective time period. Quite obviously, it is also possible that the real answer involved some combination of spatial and temporal separation. Further exploration of this important issue should be a target for future field programs in the tropical Pacific.

### 3.2. Ozone Photochemistry

Radical formation in the troposphere is initiated by the photolysis of O$_3$ in the wavelength range 290-320 nm.

\[ \text{O}_3 + hv \rightarrow \text{O}(^1\text{D}) + \text{O}_2 \]  

Most of the O(\text{I}D) produced in (R1) is collisionally quenched to form \text{O}(\text{P}). This \text{O}(\text{P}) then recombines with \text{O}_2 to reform \text{O}_3.

\[ \text{O}(^3\text{P}) + \text{O}_2 \rightarrow \text{O}_3 \]  

Most importantly, a small portion of the O(\text{I}D) also reacts with water to produce hydroxyl radicals.
The resulting product NO2 rapidly photolyzes to produce O(3p) NO to produce NO2.

These peroxy radical species may then react with which combines with an oxygen molecule to produce O3 as in HO2.

Destruction of O3 can take place by reaction of O3 with OH and oxidation of CO, CH4, and nonmethane hydrocarbons (NMHCs) via OH leads to the formation of the peroxy radical species HO2, CH3O2, and RO2 (R=CH2 and higher organic groupings). These peroxy radical species may then react with NO to produce NO2.

While (R4)-(R6) lead to the formation of O3, further destruction of O3 can take place by reaction of O3 with OH and HO2.

Still another fate for peroxy radicals is self-reaction, (R9). This process becomes particularly important in regions of low NO.

On the basis of reaction sequences listed above, the photochemical formation and destruction of ozone (F(O3) and D(O3)) can be defined as

\[
F(O_3) = \{k_3[HO_2] + k_4[CH_3O_2] + k_5[RO_2]\}[O_3] \quad (1)
\]

\[
D(O_3) = k_3[O(3D)][H_2O] + \{k_7[OH] + k_8[HO_2]\}[O_3] \quad (2)
\]

These expressions clearly indicate the importance of both NO and H2O in determining the balance between photochemical formation and destruction of O3. The net effect of all photochemical processes on O3 (the photochemical ozone tendency) can then be defined as the difference between formation and destruction.

\[
P(O_3) = \{(k_4[HO_2] + k_5[CH_3O_2] + k_6[RO_2])[NO] \} - (k_3[O(D)][H_2O] + \{k_7[OH] + k_8[HO_2]\}[O_3]) \quad (3)
\]

It should be noted that equation (3) is most appropriate for remote global regions involving low to modest levels of NOx. As noted by other authors [e.g., Chameides et al., 1987; Liu, 1977], under these conditions the additional O3 loss reaction sequence such as (R10) and (R11) is insignificant:

\[
\begin{align*}
(R10) & & NO + O_3 \rightarrow NO_2 + O_2 \\
(R11) & & NO_2 + OH + M \rightarrow HNO_3
\end{align*}
\]
should have been greater. The reason it is not is due to the much higher water vapor levels associated with the low NOx regime (see Figure 8). Elevated levels of H2O result in higher predicted peroxy radical concentrations which tend to offset the effects of higher NO mixing ratios associated with the high NOx regime. Accordingly, the difference in F(O3) between the two regimes is seen to increase with altitude much slower than might be expected based on the difference in NO levels. Thus these results further demonstrate the important joint role of NO and H2O in the photochemical formation of ozone [Chameides et al., 1987; Ridley et al., 1992; Davis et al., 1996a].

When evaluated in terms of an integrated column quantity rather than in situ formation, the difference in F(O3) between the two regimes is seen to be rather modest. As shown in Figure 9, the column-integrated F(O3) values are 25.5x10^10 and 16.1x10^10 molecules/cm²/s for the high and low NOx regimes, respectively. This means that the column integrated values differ by only a factor of 1.6. Much of this leveling effect reflects the strong influence of large values of F(O3) at altitudes below 2 km. For example, 30% of the total column integrated O3 formation for the high NOx regime and 44% for the low NOx regime occurs in the lowest 2 km.

In both regimes the reaction of NO with hydroperoxy radicals, (R4), constituted the major formation pathway. Within the BL the contributions from (R4) in the high and low NOx regimes were 54 and 50%, respectively. Above 2 km the contribution from (R4) gradually increased with altitude, reaching 80% at 8-10 km. By comparison, O3 formation due to NMHC chemistry, (R6), never exceeded 8%.

The diurnal average rates for photochemical ozone destruction, D(O3), are also given in Table 2. In this case, the

### Table 2. Diurnal Averaged Rates for O3 Formation, Destruction, and Tendency

| Altitude Range, km | F(O3) molec/cm²/s | D(O3) molec/cm²/s | P(O3) molec/cm³/s | Median O3, ppbv | F(O3) molec/cm²/s | D(O3) molec/cm²/s | P(O3) molec/cm³/s | Median O3, ppbv |
|-------------------|-------------------|-------------------|-------------------|-----------------|-------------------|-------------------|-------------------|-----------------|
| 0-1               | 4.07E+05          | 8.95E+05          | -4.89E+05         | -1.77           | 3.41E+05          | 8.86E+05          | -5.45E+05         | -2.00           |
| 1-2               | 3.67E+05          | 9.12E+05          | -5.44E+05         | -2.23           | 3.68E+05          | 8.47E+05          | -4.78E+05         | -1.92           |
| 2-4               | 1.86E+05          | 2.08E+05          | -0.23E+05         | -0.11           | 2.12E+05          | 6.65E+05          | -4.53E+05         | -2.19           |
| 4-6               | 2.84E+05          | 2.22E+05          | 0.62E+05          | 0.35            | 1.26E+05          | 2.74E+05          | -1.48E+05         | -0.90           |
| 6-8               | 2.08E+05          | 0.75E+05          | 1.32E+05          | 0.99            | 0.81E+05          | 1.78E+05          | -0.97E+05         | 0.07            |
| 8-10              | 2.10E+05          | 0.37E+05          | 1.73E+05          | 1.62            | 0.33E+05          | 0.26E+05          | 0.07E+05          | 0.07            |

Read 4.07E+05 as 4.07x10^5.

When evaluated in terms of an integrated column quantity rather than in situ formation, the difference in F(O3) between the two regimes is seen to be rather modest. As shown in Figure 9, the column-integrated F(O3) values are 25.5x10^10 and 16.1x10^10 molecules/cm²/s for the high and low NOx regimes, respectively. This means that the column integrated values differ by only a factor of 1.6. Much of this leveling effect reflects the strong influence of large values of F(O3) at altitudes below 2 km. For example, 30% of the total column integrated O3 formation for the high NOx regime and 44% for the low NOx regime occurs in the lowest 2 km.

In both regimes the reaction of NO with hydroperoxy radicals, (R4), constituted the major formation pathway. Within the BL the contributions from (R4) in the high and low NOx regimes were 54 and 50%, respectively. Above 2 km the contribution from (R4) gradually increased with altitude, reaching 80% at 8-10 km. By comparison, O3 formation due to NMHC chemistry, (R6), never exceeded 8%.

The diurnal average rates for photochemical ozone destruction, D(O3), are also given in Table 2. In this case, the
trend in D(O3) is seen as being completely out of phase with that of formation. When the two regimes differ significantly, it is the low NOx regime that tends to have the higher D(O3) value despite having lower ambient O3 levels. For altitudes below 2 km this difference is seen as being quite small, whereas above this altitude, D(O3) values for the low NOx regime are a factor of 2 to 3 times larger than those estimated for the high NOx regime. This difference in D(O3) is primarily driven by the large difference in H2O levels (see Figure 8) with the low NOx regime having much higher concentrations. This point is further illustrated in the finding that (R3) (O(D) + H2O) was the dominant O3 loss pathway (e.g., 75-80%) for the low NOx regime at all altitudes. By contrast, for the high NOx regime, only for BL conditions was (R3) dominant. At altitudes above 2 km, (R3) accounted for only 30% of the loss, while (R7) (HO2 + O3) defined 52-64% of the total. As mentioned earlier, NOx levels in the tropics were found to be substantially lower than that required for the destruction of O3 via (R11) to become significant.

As shown in Figure 10, the column-integrated values for D(O3) are 28.9x10^10 and 40.2x10^10 molecules/cm^2/s for the high and low NOx regimes, respectively. As discussed for F(O3), the closeness of the column integrated values of D(O3) is in large part a reflection of the major influence of D(O3) in the lowest 2 km. For the high NOx regime this amounted to 62% of the total column destruction. For the low NOx regime this value was 43%.

Figure 10. Diurnal-averaged, column-integrated values of D(O3). Values are those calculated from TD box model runs based on median conditions for high and low NOx regimes. Net column effects are annotated at the bottom of the figure.

Figure 11. Critical NO (shaded area) and median measured NO (symbols) versus altitude for the (a) high NOx regime and (b) low NOx regime. Error bars encompass the inner quartiles.

Although not explicitly shown in equation (2), the possible destruction of O3 from iodine reactions was also examined. Davis et al. [1996b] previously explored this possibility in the case of the tropical PEM-A data. These investigators estimated the iodine chemistry sink to be no larger than 1.8x10^10 molecules/cm^2/s or approximately 6% of the total O3 loss. Scaling this estimate to the PEM-B low NOx regime, with
adjustments for the differences in CH$_3$I levels, results in an estimated increase in D(O$_3$) of ~ 4%. This estimate would be shifted still lower for the high NO$_x$ regime since the latter regime had lower CH$_3$I concentrations.

The net effect of all photochemical processes as related to in situ O$_3$ levels, P(O$_3$), has been estimated from equation (3). These results are again provided in Table 2. Quite evident from these is the effect of combining a larger formation rate from the high NO$_x$ regime with a larger destruction rate from the low NO$_x$ regime. In summary, the difference between the two regimes, as expressed in terms of P(O$_3$) values, becomes greatly amplified. For the high NO$_x$ regime, the impact of P(O$_3$) on in situ O$_3$ levels is greatest for the 0-2 km altitude range, reflecting the highest values of D(O$_3$) and the lowest in situ levels of O$_3$. The loss of ozone at these altitudes reaches 7% per day. For altitudes in the 2-8 km range, in situ O$_3$ changes were ±2% or less per day, thus indicating a near photochemical balance. At still higher altitudes (i.e., 8-10 km), O$_3$ levels are seen increasing at a rate of nearly 4% per day. In sharp contrast the low NO$_x$ regime shows a rather consistent trend of O$_3$ destruction with in situ O$_3$ levels in the boundary layer decreasing at the high rate of 10% per day but then gradually falling off with increasing altitude, reaching -4% per day at 6-8 km. Only at 8-10 km is the low NO$_x$ regime observed to be in near photochemical balance. To further illustrate the important role of NO in influencing the trends in P(O$_3$), we show plotted in Figures 11a and 11b the mixing ratio of this species as a function of altitude and on the same plot have also included the "critical" NO level, i.e., the level of NO at which destruction is balanced by formation. In these figures the solid lines indicate the critical NO, and the symbols show the median measured NO. In this case, both regimes are seen exhibiting a similar trend in critical NO with values starting just above 15 pptv in the BL and then decreasing to less than 10 pptv at 8-10 km. The observations, however, show NO in the high NO$_x$ regime exceeding the critical level by significant amounts above 5 km. By contrast, in the low NO$_x$ regime, NO mixing ratios remain below the critical level until 8-10 km where the two are essentially equal.

In Figure 12, P(O$_3$) values are shown expressed in terms of column-integrated quantities. From this figure the low NO$_x$ regime is seen as having values that are significantly negative at all altitudes but 8-10 km (i.e., P(O$_3$) = 0). This translates into a net ozone column destruction rate of -24x10$^{10}$ molecules/cm$^2$/s. For comparison purposes, this is a value that is 5 times larger than the O$_3$ deposition flux to the ocean [Kawa and Pearson, 1989; Lenschow et al., 1982]. In contrast to the very negative integrated O$_3$ picture for low NO$_x$, the high NO$_x$ regime crosses over to positive values at 4-6 km. Thus the net column effect on O$_3$, while still destruction, is quite modest, e.g., -3.5x10$^{10}$ molecules/cm$^2$/s.
When the above values are placed in the context of a percent change per day by folding in the column ozone densities for both regimes (i.e., 2.9x10^17 and 6.5x10^17 molecules/cm^2, low versus high), the previously cited net column P(O3) values convert to -7.2% and -0.5%/day, respectively. However, this picture of net destruction in all regimes is altered if instead of using 0-10 km as the column height, the full tropopause height of 0-17 km is considered. For example, Davis et al. [1996a] found in their analysis of the PEM-A tropical data that ozone formation in the 10-17 km altitude range maximized when NO levels approached approximately 150 pptv. This new limitation reflects the effects on the chemistry from having a limited supply of HO_x. Levels of NO as high as 150 pptv are not inconsistent with the limited observations of NO at altitudes above 10 km during both PEM-A and B.

If for purposes of this analysis we accept the same assumptions as employed by Davis et al., the summary calculations illustrated in Figure 13 indicate that there results a net balance in O_3 formation and destruction for the high NO_x regime (e.g., 0.1x10^10 molecules/cm^2/s) but that there still remains a large net destruction for low NO_x of ~2.6x10^10 molecules/cm^2/s. Further changes were made by including acetone chemistry at levels of 0.5 ppbv [see Singh et al., 1995], as again assumed by Davis et al., but using updated quantum yield data for acetone photolysis that included a dependence on pressure [A. Ravishankara, private communication]. Based on this new quantum yield data, estimated photolysis rates at 10 km increased by around a factor of 2. The inclusion of acetone leads to a further positive O_3 shift in each regime of 2.8x10^10 molecules/cm^2/s due to the availability of an additional HO_x source. Thus, after all adjustments are made to the original chemical environment, the low NO_x regime still ends up with an estimated large negative net O_3 column-integrated flux of -17.9x10^10 molecules/cm^2/s.

On the basis of the seasonally adjusted O_3 column observations reported by Fishman et al. [1992], the tropospheric column density for the tropical western Pacific over the seasonal period December-February to March-May should have experienced an increase of as much as 30%. This suggests that the tropospheric O_3 column should have been undergoing a gradual systematic increase. If viewed in this context, the near balance in O_3 formation and destruction, together with the uncertainties associated with F(O_3) in the 10-17 km altitude range, would argue that the O_3 column budget estimated for the high NO_x regime is reasonably consistent with the (TOMS) data analysis of Fishman et al. [1992]. It does, however, raise a major question concerning the source of O_3 required to offset the deficit in the low NO_x regime. At these low latitudes it is unlikely that any direct flux from the stratosphere could balance the current estimated deficit of 18-24x10^10 molecules/cm^2/s. For example, the average strength of the stratosphere-to-troposphere O_3 flux in the northern hemisphere is estimated at only 5x10^10 molecules/cm^2 [Gidel and Shapiro, 1980; Mahlman et al., 1980].

Given a similar O_3 budget problem in the analysis of the PEM-A data, Davis et al. [1996a] proposed that an alternative to stratospheric O_3 might be the transport of O_3 rich midlatitude tropospheric air into the tropical region. It would seem that a similar argument could also be made for the case of the PEM-B low NO_x regime. For example, during PEM-B the midlatitude sector was a region with average free tropospheric levels of O_3 that were nearly twice those found at comparable altitudes in the low NO_x regime.

Still a second alternative to the transport of stratospheric O_3 into the tropics is the possibility that within the "greater" tropical Pacific basin, O_3 was self-sustaining through photochemistry, thus leading to a balanced budget. Such was the case for the tropical South Atlantic basin investigated during TRACE A [Jacob et al., 1996]; see discussion later in text. During PEM-B, only a brief snapshot of the tropical Pacific was recorded, and this was limited to only the western North Pacific. We may ask, therefore, how representative the low and high NO_x regimes might have been as related to the western Pacific region and also in relationship to the "greater" tropical Pacific. For instance, what might the high NO_x regime have looked like earlier in time? Equally important, were there other geographical regions in the tropical Pacific that might have been more favorably influenced by transport of lightning/surface NO_x emissions from the continent (e.g., via Walker circulation)? Quite possibly, NO_x levels in the high NO_x regime, if sampled earlier in time, would have been even higher than those sampled at the time of PEM-B. If so, this regime could have defined a region of significant net O_3 production.

In the absence of observations at other times and at other locations, several model simulations were run to assess the question of how different conditions would have had to be in order to shift a marine area such as our labeled high NO_x regime which was near steady state in O_3 to a significant O_3 source regime. In these simulations an enhancement in NO_x was implemented at altitudes between 4 and 10 km to represent the high altitude outflow of convected air over southeastern Asia into a remote marine environment. Enhancements were increased until the net column production reached a magnitude large enough that it would exceed the possible uncertainties in F(O_3) and D(O_3) (e.g., ~30% of F(O_3) or 10x10^10 molecules/cm^2/s). The results from these runs indicate that the addition of only 30 pptv to median NO_x levels would lead to significant net column production of O_3. Furthermore, time dependent model calculations indicate that it would take just over 1 day between 4-8 km and 2 days at 8-10 km for these enhanced values to decay to the observed median values. Thus the enhancement of 30 pptv would seem to be reasonable based on the isentropic trajectories which suggest that the air parcels sampled in the high NO_x regime were 2-3 days removed from the Pacific Rim.

While the trajectories do not indicate that BL air came from the Pacific Rim, we also explored the possible impact of a 30 pptv enhancement between the BL and the 4 km. In this case, the enhanced NO levels decayed to the observed median values within about 5 hours below 2 km and within 1 day from 2 to 4 km; however, the faster photochemistry at these altitudes resulted in an equivalent impact on the column F(O_3) value. This suggests that an enhancement of only 15 pptv in NO_x at all altitudes would have roughly the same impact on the O_3 column as a 30 pptv enhancement above 4 km. Whether such regimes were actually present in the tropical Pacific at the time of PEM-B is unknown, but clearly, the answer to this question is centrally important to our understanding of the tropical tropospheric O_3 budget.

3.2.3. Comparison with PEM-West A. Although the PEM-A and PEM-B field programs took place in different
seasons, the tropical components of each of these programs appear to share some commonality in terms of their chemical characteristics. For example, on the basis of the analysis of TOMS satellite data for the tropics [Fishman et al., 1992], we estimate that values for the integrated \( \text{O}_3 \) column should have been similar for both PEM-B (February - March) and PEM-A (September - October). In fact, upon comparing actual in situ \( \text{O}_3 \) field observations, the column amounts in the PEM-A tropical regime (0-18\(^\circ\)N, 120-170\(^\circ\)E) were found to compare most favorably (i.e., within 5\%) with those observed in the PEM-B low \( \text{NO}_x \) regime, the latter regime being a factor of 2 lower than that observed for high \( \text{NO}_x \). Figure 14a shows the comparison of median \( \text{O}_3 \) levels for PEM-B low \( \text{NO}_x \) and PEM-A tropics for the altitude range of 0-10 km. These data
by excess levels of low altitude O_3 in PEM-B low NO_x. (Com-
posite UV DIAL O_3 profiles from PEM-A further support the
representativeness of the in situ O_3 data for PEM-A displayed
in Figure 14a.)

The PEM-A tropical data also compare more favorably with
PEM-B low NO_x for the critical photochemical species NO and
H_2O. For instance, Figures 14b and 14c show comparisons of
the median values of NO and H_2O. These data indicate that
PEM-A NO levels increase gradually with altitude from 5 pptv
in the BL to 15 pptv at 8-10 km. This high altitude value falls
far below the 60 pptv observed in PEM-B high NO_x but is only
8 pptv greater than that shown for the low NO_x regime. PEM-
A H_2O levels are also similar to those recorded for the low
NO_x regime, agreeing within a factor of 1.5 at all altitudes.

Despite the cited similarities, the model evaluated
photochemical O_3 trends in PEM-A tropical and PEM-B low
NO_x were found to be significantly different. These are shown
in Figure 15. (Note that the difference in the nocturnal solar
zenith angles for these two data sets was <4°). In this case we
see that the diurnal-averaged column-integrated P(O_3) values,
over the altitude range of 0-10 km, are -12.4x10^{10}
molecules/cm^2/s (-3.5%/d) for PEM-A tropics and -24.1x10^{10}
molecules/cm^2/s for PEM-B low NO_x. Further analysis
revealed that this disparity is largely due to a difference in
D(O_3) values. For example, the column-integrated D(O_3)
values were -28.4x10^{10} and -40.2x10^{10} molecules/cm^2/s, re-
spectively. By comparison, column integrated F(O_3) values for
PEM-A and PEM-B low NO_x were essentially identical, i.e.,
16.0x10^{10} and 16.1x10^{10} molecules/cm^2/s.

A key element in understanding the difference between these
two data sets lies in the vertical distribution of O_3. As noted
above, although O_3 column amounts were found to be almost
identical, median O_3 levels differed significantly at some
altitudes. In PEM-A, median values increase with altitude from
9 ppbv in the BL to 25 ppbv at 8-10 km. O_3 levels for PEM-B
low NO_x remain fairly uniform throughout the troposphere,
varying between 17 and 21 ppbv (see Figure 14a). As argued
earlier, this uniform O_3 distribution is suggestive of rapid
vertical mixing. In this specific case, the photochemical by-
product of this mixing is that a larger fraction of the O_3 column
gets placed at low altitudes, where in combination with high
H_2O levels, O_3 destruction is very high. (Recall that the 0-2
km altitude range dominated the column O_3 destruction in the
low NO_x regime, contributing 43% to the total.) These results
are quite significant in that they indicate that for two
environments having near-identical O_3 column amounts, the
vertical distribution of the ozone can have a profound impact on
the photochemical O_3 budget. They further suggest that
satellite tropospheric O_3 residual maps for tropical marine
regions must be interpreted with considerable caution.

While the comparison of PEM-A tropics with PEM-B low
NO_x has provided some interesting insights concerning the
differences between the two sampling periods, a more
quantitative comparison of the regional ozone budget for PEM-
A and PEM-B necessarily must include both the low and the
high NO_x regimes. As stated earlier, in the absence of any
evidence indicating that one of these two regimes was
dominant, we have simply assigned equal weight to both and
taken the mathematical mean. The result from this averaging
fave a value for P(O_3) of -14x10^{10} molecules/cm^2/s for PEM-B
which can be compared to PEM-A tropics, as reported by
Davis et al. [1996a], whose value was -12x10^{10}
molecules/cm^2/s. Thus when looked at in terms of the total
tropical western Pacific, the net effect on the O_3 budget during
each campaign was not significantly different. It is still
noteworthy, though, that both column formation and destruction
rates in PEM-B exceed those in PEM-A by 30% and 21%,
respectively. This is primarily due to the higher NO_x levels at
high altitude and higher ozone levels at low altitudes in PEM-B.

3.2.4. Comparison with other high altitude tropical data.
Of the other available major tropical data sets (e.g., NASA
GTE CITE-1, ABLE-2A/B, and TRACE A), only TRACE A
was found to encompass both a comprehensive suite of
chemical measurements and a sampling that involved high
altitudes. It must be noted, however, that the emphasis of the
TRACE program differed from that of PEM-B in that it focused
on a region that typically experienced large seasonal influxes of
biomass burning emissions (i.e., the South Atlantic basin)
[Thompson et al., 1996; Jacob et al., 1996]. Additionally, the
TRACE A database encompassed sampling of both continental
and marine regions. Despite these differences, both this study
and TRACE A have concluded that deep convection in
conjunction with transport of NO_x via the Walker circulation
were major factors in controlling the tropical ozone budget. A
similar hypothesis was put forward earlier by Davis et al.
[1996a] in their analysis of the PEM-A data.

For the upper free troposphere (i.e., 6-10 km), NO levels
observed in TRACE A were somewhat higher than those found.
for the PEM-B high NO\textsubscript{x} regime. This is not unexpected in that additional contributions to the NO\textsubscript{x} burden were present due to biomass burning. Ozone levels at these altitudes were also higher by nearly a factor of 1.6, indicating higher net photochemical O\textsubscript{3} production. At lower altitudes, differences in both NO and O\textsubscript{3} were even more pronounced (i.e., factors of 2 or more). Collectively, these differences resulted in column-integrated formation and destruction rates that exceeded PEM-B tropics (high/low NO\textsubscript{x}) by factors of 5 and 3, respectively. Not surprisingly, the TRACE A modeling results produced an overall photochemical O\textsubscript{3} picture which involved a balanced budget. Recall that a similar situation was found for the high NO\textsubscript{x} PEM-B regime.

To illustrate the major controlling influence of photochemistry on the levels of O\textsubscript{3} in the tropics, Plates 2a and 2b show the relationship between O\textsubscript{3} and NO\textsubscript{x} for the tropical-marine free troposphere (e.g., 20\textdegree N-20\textdegree S, 4-8 and 8-12 km) as observed during GTE missions PEM-West A and B and TRACE A. The trend in these data strongly suggests (e.g., R\textsuperscript{2} = 0.67, Plate 2a and R\textsuperscript{2} = 0.41, Plate 2b) that O\textsubscript{3} levels in the tropics at middle and upper free tropospheric altitudes are regulated by photochemistry. The small fraction of data in Plate 2b showing O\textsubscript{3} uncorrelated with increasing levels of NO\textsubscript{x} comes from PEM-B flight 6. These data represent a case of significant local injection of NO\textsubscript{x} due to lightning-generated NO, the latter being further documented by onboard storm
understood in terms of air masses which have been influenced by injections of high levels of NOx into the upper troposphere. Such parcels would have high O3 formation rates; and, given long transport times, would result in significant net production of O3. By contrast, the lower end of the correlation plot would seem to reflect convection of marine BL air into the upper troposphere. Given the intense destruction of O3 in the tropical marine BL, such air would necessarily be poor in O3 and NOx. As noted already, data from flight 6 depart from the normal trend revealed in Plate 2 in that there were high NOx levels associated with low O3. This represents a case where known fresh injections of NOx from lightning had insufficient time to photochemically produce O3. Given that most lightning generated NOx tends to be concentrated near the continents, this represents a less common condition in the tropical marine upper troposphere.

One condition not observed in Plate 2 is high O3 in the presence of low NOx. Such air parcels would represent conditions where the NOx responsible for the buildup of O3 has been removed via reaction of NOx with OH, leaving elevated O3 behind. That such air parcels are not observed is most likely an indication of the strong role of vertical mixing in the tropical marine troposphere. In addition to bringing low O3 up from the marine BL, this mixing process also delivers O3 rich air from the upper troposphere to lower altitudes where higher H2O levels lead to rapid destruction. This appears to happen with such high frequency that NOx typically does not have sufficient time to reach its full potential for O3 production.

This interpretation of the relationship between NOx-O3 in the tropics is undoubtedly an oversimplification of the complex interplay between dynamics and photochemistry. It does make the point, however, that any critical assessment of the O3 budget for the "greater" tropical Pacific will require an examination of the tropical troposphere over both a wide range of altitudes and an expansive range of latitudes. Based on PEM-B results, it is unlikely that such an assessment can be carried out in any simple way using currently available satellite observations of O3. The strong relationship between NOx and O3 also underlines the continuing need for further improvement in our understanding of NOx sources in the tropics. More than any other factor it is pivotal to our reaching a comprehensive understanding of the tropical O3 budget.

4. Summary and Conclusions

PEM-B flights in tropical regions of the western Pacific (i.e., 10øS - 20øN) revealed large shifts in observed NO levels as a function of geographical location. This shift was most pronounced over the altitude range 8-10 km where the median NO level for flights 5-8 was found to exceed that from flights 9 and 10 by 1 order of magnitude (i.e., 60 versus 6 pptv). The geographical regions encompassing these two flight groupings define what have been labeled "high" and "low" NOx regimes. Isentropic back trajectories indicate a clear difference in the source regions for these two regimes. Air parcels from the low NOx regime appear to track back to the remote South Pacific, whereas the high NOx regime involves parcels that originated in the northern hemisphere and that tend to track back to the Asian continent. Further differences were found when comparing chemical tracers in each regime. The low NOx regime saw enhancements in CH4 and DMS in conjunction with depressed but uniformly mixed O3 levels. These observations are seen as being most consistent with marine convection. Thus it is not surprising that this region also revealed little evidence of lightning-generated NOx. In sharp contrast the high NOx regime showed significant enhancements in C3H8, 210Pb, and organic acids such as CH3C(O)OH. These observations are more consistent with air parcels having experienced deep convection over a continental landmass. The observed high altitude levels of C3H8, when ratioed against estimated values of NOx, tend to argue that the major source of NOx in this regime was lightning, not transport of surface emissions. This conclusion was also found to be consistent with DMSP satellite observations recorded during the PEM-B sampling period. Even so, we cannot at this time rule out the possibility that much of the NOx was being generated by the efficient recycling of unidentified NOy species through yet unknown/nondocumented mechanisms.

Time-dependent photochemical box-model simulations revealed large differences between the two regimes as related to their respective photochemical O3 budgets. These differences mainly could be attributed to the large differences between the two regimes in the levels of NO and H2O. For free tropospheric altitudes, in situ O3 formation in the high NOx regime exceeded that for low NOx by factors of 2-6. By contrast, in situ O3 destruction for the low NOx regime exceeded that estimated for the high NOx regime by as much as a factor of 3. The latter difference was primarily driven by high H2O levels associated with the low NOx regime.

The column integrated values of F(O3) and D(O3) were found to be dominated by photochemical activity in the lowest 2 km. For this altitude range both regimes had somewhat similar conditions; thus, differences in the column integrated values were smaller than what might have been expected. Even so, the higher value for F(O3) for the high NOx regime, in combination with a lower value for D(O3), resulted in an amplification of the overall photochemical effect. Thus estimates of P(O3) indicate that the low NOx regime was one of strong destruction (i.e., -24x1010 molecules/cm²/s or -7.2%/d), whereas high NOx showed only weak destruction (i.e., -3.5x1010 molecules/cm²/s or -0.5%/d) when evaluated over an altitude range of 0-10 km. When evaluated for a 0-17 km tropopause height with added acetone chemistry, the high NOx regime switched signs and became a small net O3 producer (2.9x1010 molecules/cm²/s). The low NOx regime, on the other hand, remained strongly destructive, but the rate dropped to -17.9x1010 molecules/cm²/s.

The large rate of O3 destruction in the low NOx regime was found to be inconsistent with seasonally averaged tropospheric TOMS data, which suggest that tropical O3 levels should either have been at steady state or have been increasing with the onset of the spring season. Two basic mechanisms were proposed to reconcile this situation. The first involved the transport of O3 rich midlatitude air into the tropics from midlatitudes. Analysis of the PEM-B midlatitude data base has revealed that this
region was both O$_3$ and NO$_x$ rich. The second mechanism allowed for the existence of still other high NO$_x$ regimes in the "greater" tropical Pacific as well as other low NO$_x$ regions. It was proposed that this ensemble of regimes might lead to near-self-sustaining states of column O$_3$ in the tropics. Thus in the latter scenario O$_3$ would be predominantly controlled by photochemistry. Obviously, combinations of mechanisms 1 and 2 would also be possible.

Expanding on the earlier hypothesis by Davis et al. [1996a], the existence of Pacific high NO$_x$ regimes as well as possibly "super" NO$_x$ regimes (i.e., regimes showing significant positive P(O$_3$) values) are viewed here as regions uniquely modified by transport processes. They are regions that most likely experienced the effects of long-range transport (e.g., Walker circulation) of air parcels that originated over a landmass that had experienced significant deep convection. The photochemical effects from these parcels can be most clearly seen at high altitudes, but they also become evident in those regions where sinking motion brings these NO$_x$-energized parcels (i.e., due to lightning and/or surface NO$_x$ emissions) down to lower altitudes. This process in combination with the countereffects resulting from deep marine convection along the ITCZ now appear to be the major components impacting on the photochemical O$_3$ budget of the tropical Pacific. However, the database from which this expanded hypothesis is based is still far too limited, and new observations at different geographical locations and times of year are needed.

Evidence supporting the notion that photochemistry in the tropics routinely has a major impact on the levels of O$_3$ was demonstrated in our finding a strong correlation between O$_3$ and NO$_x$ levels at free tropospheric altitudes for the Pacific field programs PEM-A and PEM-B and also for the South Atlantic study TRACE A. In addition, these observations again point to the long-standing critical need of a comprehensive understanding of both primary and secondary sources of NO$_x$ for purposes of understanding the tropical O$_3$ budget.

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