

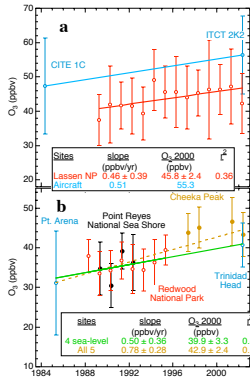
Changes in the Photochemical Environment of the North Pacific Troposphere: A Response to Increasing Asian Emissions

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1. Introduction

Measurements of atmospheric O₃ concentrations have been made over the temperate North Pacific for two decades. During that period, NO_x emissions from the upwind East Asian continent have increased dramatically. Our goal here is to examine the available data to determine if these increased emissions have changed the photochemical environment of the North Pacific troposphere. This discussion is limited to springtime when the measurements and outflow from Asia are maximized.

2. Background O₃ increase

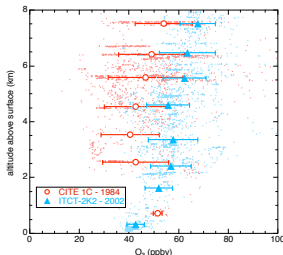


Measurements of background O₃ in the temperate North Pacific are surprisingly limited. Surface data include several short intensive studies, short records at two national park sites, and one relatively long record at Lassen Volcanic National Park. Two extensive air borne studies have been conducted: CITE 1C and ITCT 2K2. The intensive surface and aircraft studies were all conducted in springtime.

Conclusion:
 • Over the past 2 decades springtime O₃ in the eastern North Pacific troposphere has increased by 0.5 ppbv/year, or about 30% total.

Figure 1. Spring mean ± 1σ background O₃ at (a) Lassen Volcanic NP and two aircraft datasets, and (b) five MBL sites with linear regression lines. Slopes and intercept at the year 2000 are indicated. (Jaffe et al., *Geophys. Res. Letters*, 30, 2003)

3. O₃ increase through troposphere



The aircraft data are selected for the same season (20 April - 11 May) and region (30-40°N and 105-120°W). O₃ data above 100 ppbv were excluded to minimize stratospheric influences. Above 2 km, in 2002 the O₃ levels were higher than those in 1984 by at least 1 σ. The average difference above 2 km was 15 ppbv. The variability of the data above 2 km in 2002 (9 ppbv average σ) was smaller than in 1984 (13 ppbv average σ).

Conclusion:
 • The increase in O₃ extends through the depth of the lower troposphere; it is not confined to the MBL

Figure 2. Altitude dependence of observed O₃ levels from the airborne studies conducted in the eastern North Pacific. The larger symbols give the means and standard deviations for 1 km increments of altitude.

4. Lowest O₃ levels have disappeared

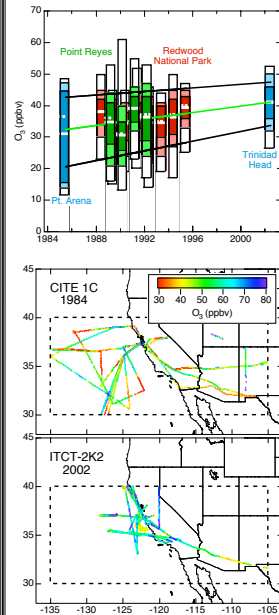


Figure 3. Temporal trends of background O₃ levels at four coastal marine boundary layer sites. Each bar shows the range of the data observed in a given spring, with the heavier and lighter colors indicating the central 67% and central 90% of the data, respectively. In each bar the solid and dotted heavy lines give the mean and median, respectively. The linear least-squares fits to the 5th percentiles, the means, and the 95th percentiles are plotted.

In Figure 3 the slope of the linear fit to the 5th percentiles of the data sets (0.84±0.7) is three times larger than the slope of the fit to the 95th percentiles (0.28±0.4), although the two slopes do agree within their 95% confidence limits. In the MBL levels below 20 ppbv were relatively common in the early years of the data record, but such low levels have become less common in the later years. Figure 4 shows that free troposphere O₃ levels below 40 ppbv were widespread in 1984, but infrequently encountered in 2002. Figure 2 shows that the O₃ variability was lower in 2002 than 1984.

Conclusion:
 • The increase in O₃ levels is greater at the minima and less at the maxima.

Figure 4. Maps of flight tracks from the two aircraft studies color coded according to the observed O₃ levels.

5. PAN levels have paralleled Asian NO_x emissions

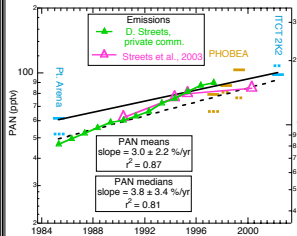


Figure 5. Temporal trends of PAN in the eastern North Pacific MBL compared to East Asian NO_x emissions. Data are from two coastal sites (Pt. Arena and Cheeka Peak in 1997 and 1998) and from two airborne campaigns (PHOBEA in 1999 and ITCT-2K2) for altitudes < 1 km. The solid and dotted bars give mean and median PAN, respectively. The linear least-squares fits to the means and medians are plotted. The East Asian NO_x emissions estimated by Streets et al. are given by the green and violet lines with symbols.

Transport of PAN from Asia is a mechanism by which increasing Asian emissions can increase O₃ precursors downwind. Measurements of PAN in the temperate North Pacific are limited to the five studies in Figure 5. They indicate an increase in PAN of 3 to 4 % per year.

Conclusion:
 • Transport of PAN to the North Pacific parallels the increase in Asian NO_x emissions, and provides the mechanism by which background O₃ levels increase.

6. MBL Photochemistry has evolved from O₃ destruction to ≈ O₃ neutral

The ratio of propane to ethane concentrations and the absolute propane concentration are both robust indicators of photochemical processing. Figure 6 shows the O₃ level dependence upon these two indicators in 1984 and 2002. A relatively steep slope, implying strong photochemical O₃ destruction, with a strong correlation is found in both plots for the 1985 Pt. Arena data. The Trinidad Head slope is near zero, and the two slopes for the ITCT-2K2 data are much smaller than for Pt. Arena. These dependencies indicate that the present tropospheric photochemistry of the North Pacific, as exemplified by the 2002 study, is characterized by less efficient O₃ destruction than in 1985. This implies that the increasingly rare low O₃ levels discussed above result from this increasingly less efficient photochemical destruction.

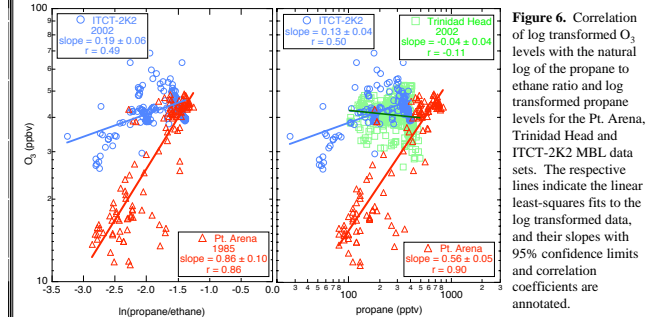


Figure 6. Correlation of log transformed O₃ levels with the natural log of the propane to ethane ratio and log transformed propane levels for the Pt. Arena, Trinidad Head and ITCT-2K2 MBL data sets. The respective lines indicate the linear least-squares fits to the log transformed data, and their slopes with 95% confidence limits and correlation coefficients are annotated.

7. Conclusions and Summary

All of the available data indicate that increasing Asian NO_x emissions have led to a marked change in the photochemical environment in the springtime troposphere of the North Pacific. This change is evidenced by:

- 1) Increasing O₃ levels with larger increases in the minima and more modest increases in the maxima,
- 2) Increasing PAN levels that parallel trends in NO_x emissions, and provide the mechanism by which the Asian emissions increase O₃ precursors over the North Pacific,
- 3) Decreasing efficiency of photochemical O₃ destruction due to higher North Pacific NO_x levels.

Caveat: Many of the relationships discussed are dependent upon the very short 1985 study. Chemical transport model calculations indicate that unusual transport of tropical air to that site may have some influence on those data.