

## Changes in the photochemical environment of the temperate North Pacific troposphere in response to increased Asian emissions

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Received 1 May 2004; revised 14 September 2004; accepted 28 September 2004; published 8 December 2004.

[1] Measurements during the Intercontinental Transport and Chemical Transformation 2002 (ITCT 2K2) field study characterized the springtime, eastern Pacific ozone distribution at two ground sites, from the National Oceanic and Atmospheric Administration WP-3D aircraft, and from a light aircraft operated by the University of Washington. D. Jaffe and colleagues compared the 2002 ozone distribution with measurements made in the region over the two previous decades and show that average ozone levels over the eastern midlatitude Pacific have systematically increased by  $\sim 10$  ppbv in the last two decades. Here we provide substantial evidence that a marked change in the photochemical environment in the springtime troposphere of the North Pacific is responsible for this increased  $O_3$ . This change is evidenced in the eastern North Pacific ITCT 2K2 study region by (1) larger increases in the minimum observed ozone levels compared to more modest increases in the maximum levels, (2) increased peroxyacetyl nitrate (PAN) levels that parallel trends in  $NO_x$  emissions, and (3) decreased efficiency of photochemical  $O_3$  destruction, i.e., less negative  $O_3$  photochemical tendency (or net rate of  $O_3$  photochemical production;  $P(O_3)$ ). This changed photochemical environment is hypothesized to be due to anthropogenic emissions from Asia, which are believed to have substantially increased over the two decades preceding the study. We propose that their influence has changed the springtime Pacific tropospheric photochemistry from predominately ozone destroying to more nearly ozone producing. However, chemical transport model calculations indicate the possible influence of a confounding factor; unusual transport of tropical air to the western North Pacific during one early field study may have played a role in this apparent change in the photochemistry. **INDEX TERMS:** 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; **KEYWORDS:** ozone, photochemistry, troposphere

**Citation:** Parrish, D. D., et al. (2004), Changes in the photochemical environment of the temperate North Pacific troposphere in response to increased Asian emissions, *J. Geophys. Res.*, 109, D23S18, doi:10.1029/2004JD004978.

### 1. Introduction

[2] Ozone ( $O_3$ ) plays a central role in the photochemistry of the troposphere, both as a precursor of the hydroxyl radical and as a product of the photochemical cycles. The background surface  $O_3$  levels (i.e., average levels in marine air undisturbed by North American continental influences) in air arriving at the west coast of North America in spring have increased by about 30% over the past two decades [Jaffe *et al.*, 2003]. Such a change in  $O_3$  levels may indicate a profound change in the photochemical environment of a relatively remote portion of the troposphere. In eastern Asia, nitrogen oxides ( $NO_x$ ) emissions grew by approximately 5.6%/yr between 1985 and 1997, but since that time have leveled off and may have even dropped [Streets *et al.*, 2003]. Jaffe *et al.* [2003] suggest that the increased  $NO_x$  emissions in the upwind Asian continent are likely responsible for the increased  $O_3$  levels in North Pacific air masses reaching North America. In this paper we examine the few

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**Table 1.** Data Sets Utilized

Site/Study	Species	Dates	Latitude, Longitude	Elevation, m	Data Source
CITE-1C	O <sub>3</sub>	20 April to 9 May 1984	see text	<7900	NASA GTE Data Archive
Point Arena, California	O <sub>3</sub> , PAN alkanes	24 April to 5 May 1985	38°57'N, 123°44'W	20	<i>Parrish et al.</i> [1992]
Redwood National Park	O <sub>3</sub>	1988–1995	41°34'N, 124°05'W	235	NPS Air Resources Division
Point Reyes National Seashore	O <sub>3</sub>	1988–1992	38°07'N, 122°55'W	76	NPS Air Resources Division
PEM-West B	O <sub>3</sub> , alkanes	8 February to 14 March 1994	see text	<12,000	NASA GTE Data Archive
Cheeka Peak, Washington	O <sub>3</sub> , PAN alkanes	March–April 1997–1998; March–May 2001–2002	48°18'N, 124°36'W	480	<i>Jaffe et al.</i> [2001], this work
PHOBEA	O <sub>3</sub> , PAN alkanes	March–May 1997–1999; 2001–2002	≈48°N, ≈124°W	<7300	<i>Kotchenruther et al.</i> [2001a], this work
TRACE-P	O <sub>3</sub> , alkanes	26 February to 10 April 2001	see text	<12,000	NASA GTE Data Archive
Trinidad Head, California	O <sub>3</sub> alkanes	19 April to 18 May 2002	41°03'N 124°09'W	100	this work
ITCT 2K2	O <sub>3</sub> , PAN alkanes	22 April to 19 May 2002	see text	<8000	this work

data sets that have been collected in the North Pacific region in spring over the last two decades to elucidate how increased Asian NO<sub>x</sub> emissions may have influenced the photochemical environment of the North Pacific troposphere leading to the increased O<sub>3</sub> levels. We focus on spring since it is the season with the strongest outflow of Asian emissions to the Pacific, and with the most extensive observational database.

[3] The photochemistry of the troposphere is largely driven by the oxidation of reduced carbon species: carbon monoxide, methane and other volatile organic compounds. This oxidation proceeds via a complex series of reactions, some of which produce O<sub>3</sub> and others that destroy O<sub>3</sub>. Whether  $P(O_3)$ , the O<sub>3</sub> photochemical tendency or the net rate of O<sub>3</sub> photochemical production, in an air parcel is positive or negative depends upon the NO<sub>x</sub> levels in the air parcel [see, e.g., *Crutzen*, 1973; *Chameides and Walker*, 1973]. Consequently, O<sub>3</sub> levels in the North Pacific troposphere can be expected to respond to changes in the NO<sub>x</sub> levels. Further, NO<sub>x</sub> sources are limited in the remote troposphere so transport of NO<sub>x</sub> from the relatively abundant Asian continental sources may exert a controlling influence on NO<sub>x</sub> levels over the Pacific.

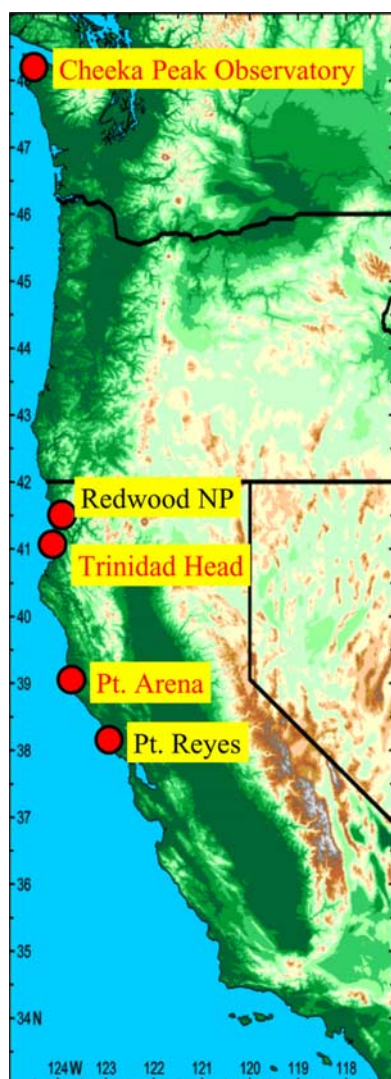
[4] Our goal in this paper is to examine evidence for a direct link between increased Asian NO<sub>x</sub> emissions and increased O<sub>3</sub> levels. We focus on the temporal trends in three aspects of the North Pacific troposphere: the distribution of the observed O<sub>3</sub> levels,  $P(O_3)$  itself and peroxyacetyl nitrate (PAN) levels. This last aspect is of interest because PAN is formed in regions where NO<sub>x</sub> and reactive organic species are emitted. Once formed, PAN can be transported long distances in the colder regions of the middle and upper troposphere. Upon descent to lower, warmer altitudes it can release NO<sub>x</sub> through thermal dissociation [*Singh et al.*, 1986; *Moxin et al.*, 1996; *Yienger et al.*, 1999]. In the following, section 2 details the data sets examined, section 3 presents and discusses the three temporal trends, and section 4 evaluates the results and reaches conclusions regarding their implication for the photochemical environment of the North Pacific troposphere. Some of the discussion relies upon photochemical aging patterns of hydrocarbons; Appendix A discusses in detail relevant aspects of this aging.

[5] The studies of the photochemistry in the North Pacific troposphere during the last two decades are unfortunately very limited. However the issue of significant changes in tropospheric photochemistry is very important from several

points of view, so in this paper we examine all of the relevant data sets that are available. The data limitation does weaken the statistical robustness of the conclusions, but nevertheless changes of substantial significance are discussed. Caveats regarding the robustness of the conclusions are given where appropriate. The analysis is formulated as linear temporal trends over the period covered by available data sets. We do not intend to imply that the trends can be extrapolated further back in time, can necessarily be expected to continue into the future, or that they actually occurred in simple linear temporal fashion. Linear trends are discussed because they provide the simplest mathematical function for representing temporal changes over a time interval, and they provide a convenient means of comparing changes derived from data sets covering differing time periods.

## 2. Data Sets and Methods Utilized

[6] In this section, we briefly describe the available data sets, and discuss how the data are selected and used. Table 1 summarizes species investigated, dates, site locations, and data sources for the ten data sets that we have identified for this season and region. In general we select all data that are available for the months of March through May. Six intensive research campaigns spanning 18 years provide measurements in the eastern North Pacific and along the U.S. West Coast. Coastal, surface measurements were made at Point Arena, California, in 1985, at Cheeka Peak, Washington, in 1997, 1998, 2001 and 2002 and at Trinidad Head, California, during the Intercontinental Transport and Chemical Transformation study in 2002 (ITCT 2K2) [*Millet et al.*, 2004; *Goldstein et al.*, 2004]. Three aircraft research campaigns were conducted: the National Aeronautics and Space Administration (NASA) Global Tropospheric Experiment (GTE) Chemical Instrumentation and Evaluation (CITE) 1C study in 1984 [*Beck et al.*, 1987], the Photochemical Ozone Budget of the Eastern North Pacific Atmosphere (PHOBEA) studies in 1999, 2001, and 2002 and the ITCT 2K2 study in 2002. The U.S. National Park Service monitored ambient ozone at two relatively remote locations on the west coast of California (Redwood National Park and Point Reyes National Seashore) that are not greatly influenced by local emissions and have coincident meteorological measurements for selection of marine air masses. Figure 1 shows the locations of the coastal surface sites.



**Figure 1.** Map of the North American west coast showing location of coastal surface sites. The colors indicate relative elevations.

Finally, NASA conducted two GTE field studies in the western North Pacific: the Pacific Exploratory Mission-West Phase B (PEM-West B) [Hoell *et al.*, 1997] in 1994 and Transport and Chemical Evolution over the Pacific (TRACE-P) in 2001 [Jacob *et al.*, 2003].

[7] We examine  $O_3$  and, when available, light alkane and PAN measurements from all of these studies. All  $O_3$  measurements from the surface sites were made using standard UV-absorption analyzers. The National Park Service has employed a consistent calibration procedure based on U.S. EPA methods. The intensive research campaigns have followed careful data validation procedures. The aircraft campaigns made high-frequency  $O_3$  measurements with chemiluminescence instruments that were calibrated against standard UV-absorption instruments. All of the  $O_3$  data sets are believed to be accurate to within  $\pm 3\%$ . During the 2002 study we compared  $O_3$  measurements through interaircraft comparisons and through aircraft flybys of ground sites. All comparisons agreed to within  $\pm 2$  ppbv. The earliest  $O_3$  data from 1985 were collected by

one of the groups involved in the 2002 study. We are confident that systematic errors in the  $O_3$  measurements make negligible contributions to the temporal trend reported by Jaffe *et al.* [2003]. The precision of the data points used here is within  $\pm 2\%$  or 1 ppbv, whichever is greater.

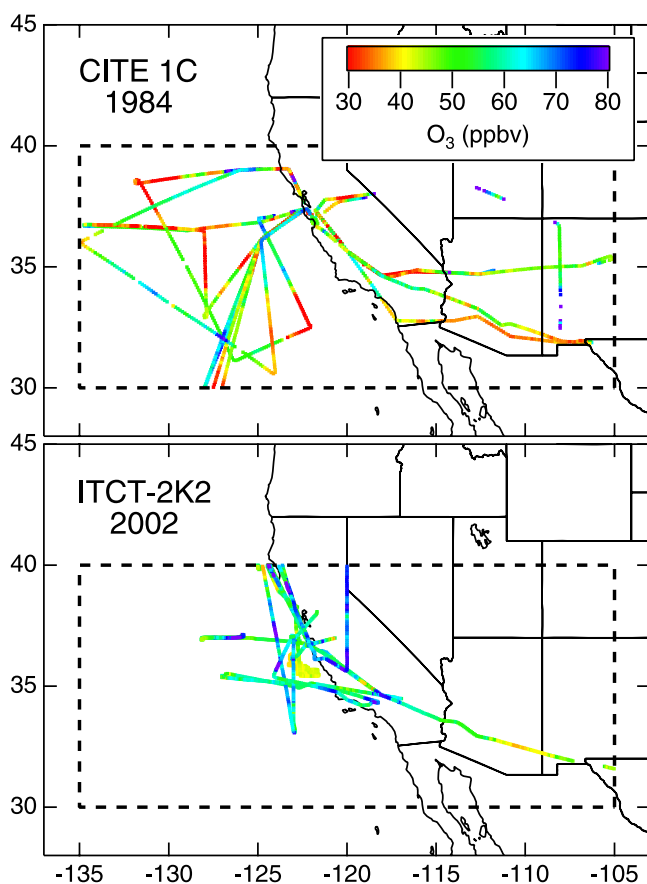
[8] The accuracy and precision of the alkane measurements are not well defined, since no formal intercomparison of ambient measurements in remote environments such as the Pacific troposphere has been reported. Nominal reported accuracies and precisions are, e.g.,  $\pm 5\%$  and the larger of  $\pm 1\%$  or 2 pptv, respectively, for the PEM-West B study [Hoell *et al.*, 1997]. Further details can be found in the original papers describing the alkane measurement techniques: Point Arena [Singh *et al.*, 1988], PEM-West B [Blake *et al.*, 1997], PHOBEA [Jaffe *et al.*, 2001; Price *et al.*, 2003], TRACE-P [Blake *et al.*, 2003], Trinidad Head [Millet *et al.*, 2004], and ITCT 2K2 [Schauffler *et al.*, 1999, 2003].

[9] Experimental details regarding the various PAN data sets are reported by Parrish *et al.* [1992], Jaffe *et al.* [2001], Kotchenruther *et al.* [2001a], and Roberts *et al.* [2004], who estimated accuracies from 15 to 30% depending upon the study and the PAN levels. The 1985 study represent the only relatively early measurements, but fortunately two, well-respected measurement groups simultaneously measured PAN, and the results agreed well [Parrish *et al.*, 1992].

## 2.1. Data Selection at Coastal Sites

[10] At coastal surface sites continental influences affect the ambient  $O_3$  levels, at least to some extent, as air comes ashore from the Pacific. These influences include deposition to the ground and other surfaces (most importantly vegetation), removal by reaction with local emissions, and photochemical production from precursors emitted over North America. To minimize such potentially confounding effects and to determine marine  $O_3$  levels, we select periods of relatively high onshore wind (1-hour average wind speed greater than 3 m/s and direction  $225^\circ$  to  $360^\circ$  at all sites except  $150^\circ$  to  $300^\circ$  at Cheeka Peak). Since this wind selection window includes the prevailing wind direction, a major fraction of the data (44 to 61% for all but one site) is usually included, but only 13% is retained at Redwood NP, which is a site evidently more protected from the prevailing wind. More details of this data selection are given by Jaffe *et al.* [2003]. The alkane and PAN measurements made along with  $O_3$  at Point Arena, Cheeka Peak and Trinidad Head were selected in the same manner.

[11] The magnitude of North American influences and the effectiveness of the wind selection criteria can be judged from the Trinidad Head data set. In that study, many species emitted on the North American continent were measured. The mean  $\pm$  standard deviation of the total  $O_3$  data set is  $38.1 \pm 7.3$  ppbv. For the 43% of data selected by the wind window, the corresponding values are  $40.9 \pm 5.6$  ppbv. This is the value we take as representative of the near surface background  $O_3$  in spring 2002. One alternative selection criterion is the level of methyl-*t*-butyl ether (MTBE), a gasoline additive in use primarily in North America. The minimum, median and maximum measured MTBE values were 0.3, 2.1 and 37 parts-per-trillion by volume (pptv), respectively. Selection of data with MTBE below 2 pptv (47% of the total data set) gives  $O_3$  values of  $41.5 \pm 4.7$  ppbv. A second alternative selection is the level of carbon dioxide



**Figure 2.** Map of flight tracks selected for analysis of  $O_3$  levels from two airborne studies conducted in the eastern North Pacific. The colors indicate the observed  $O_3$  levels as indicated by the annotated scale.

( $CO_2$ ), which is emitted and taken up by vegetation and emitted by combustion sources. The minimum, median and maximum values measured were 375, 380 and 409 parts-per-million by volume (ppmv), respectively. Selection of data with  $CO_2$  below 380 ppmv (51% of the total data set) gives  $O_3$  values of  $42.2 \pm 4.5$  ppbv. These comparisons show that the North American influences can have relatively small but significant effects on  $O_3$  levels at the low-elevation marine boundary layer sites, and that the three criterion for selecting background  $O_3$  values give results that span only 1.3 ppbv. This result gives us confidence in the wind selection window at sites lacking more extensive chemical measurements.

## 2.2. Data Selection for Aircraft Campaigns

[12] Depending upon the parameter or relationship of interest, different selections of the data sets are made. The 1984 CITE 1C and 2002 ITCT 2K2 campaigns were conducted in the same season and region, but there were some differences in time of year and regional coverage. To make the comparison of observed  $O_3$  levels as direct as possible, we select data from the overlapping time period (20 April to 11 May; see Table 1) and region covered ( $30^\circ$ – $40^\circ$ N latitude and  $105^\circ$ – $135^\circ$ W longitude) for the same altitude range (from the surface to 8 km over the ocean and from 2 to 8 km over land). Figure 2 indicates the collection locations for the selected data. In addition, we eliminate

data with  $O_3$  levels above 100 ppbv, to minimize the effects of identifiable stratospheric intrusions.

[13] For a given aircraft campaign all of the light alkane data are included, since the relationships among these species are remarkably constant over each campaign. However, the dependence of  $O_3$  upon the alkane levels is very sensitive to stratospheric influence, so we select data from only the lowest 1 km altitude in marine regions for the investigation of this relationship in section 3.2 below. Also, our focus is on the photochemistry of the relatively unpolluted troposphere over the Pacific. Since some of legs of the PEM-West B and TRACE-P flights investigated the outflow of urban plumes, we exclude data with CO above 400 ppbv or *n*-butane above 1 ppbv. Discussions of airborne PAN data include only those from the lowest 1 km altitude in marine regions. Finally, the PHOBEA airborne data are selected for marine air as described by Kotchenruther *et al.* [2001a].

## 2.3. Data Treatment

[14] Our focus is on the photochemical environment of the troposphere over the temperate North Pacific Ocean, a region predominately free of sources. Here photochemical removal is expected to be predominately responsible for the variability of the concentrations of trace atmospheric species investigated here ( $O_3$ , alkanes and PAN). The expected kinetics are pseudo first order with respect to those concentrations. Consequently, we will investigate the relationships between measured concentrations of different species through logarithmic plots and perform linear, least squares fits to log transformed concentrations.

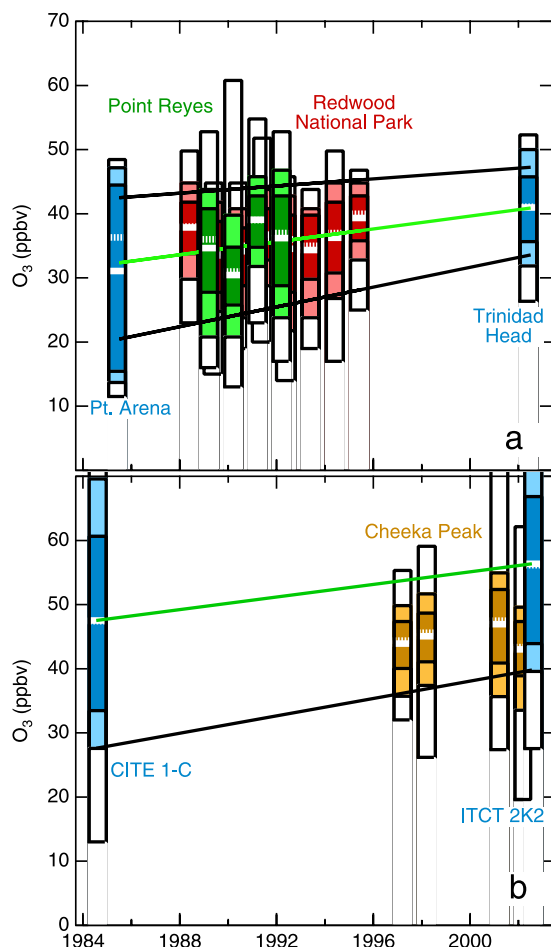
## 3. Temporal Trends of the Springtime North Pacific Troposphere

### 3.1. Background Ozone Levels

[15] Figure 3 shows the coastal marine  $O_3$  measurements discussed by Jaffe *et al.* [2003], who concluded that the  $O_3$  levels in air arriving at the U.S. West Coast have increased by about 30% over the past two decades. This increase is evident in the slopes of the temporal trend lines in Figure 3, which are summarized in Table 2.

[16] The mean  $O_3$  levels of the coastal, sea level sites in Figure 3a define a positive trend that is significant at the 95% confidence level indicated in Table 2. This trend is heavily weighted by the Point Arena and Trinidad Head data, but even if either of those sites is omitted, a significant positive trend is still found. Excluding Trinidad Head, the 1985–1996 data yield a slope of  $0.54 \pm 0.58$  ppbv/yr, and excluding Pt Arena, the 1988–2002 data yield a slope of  $0.44 \pm 0.42$  ppbv/yr. The confidence limits indicate each fit it is still significant at  $\geq 92\%$  confidence level with consistent slopes. Figure 3b includes data from a coastal site at an elevation of 0.5 km, and from two airborne campaigns. The  $O_3$  mixing ratios observed at Cheeka Peak are significantly higher than those from the sea level sites of Figure 3a. Inclusion of these data in the linear, least squares fit of Figure 3a would increase the slope and strengthen the correlation. However,  $O_3$  levels increase with altitude as illustrated below, so the Cheeka Peak data are not strictly comparable to the sea level data.

[17] Only two points are available to define the trend for the aircraft data in Figure 3b, since there have been only two



**Figure 3.** Temporal trends of background ozone mixing ratios in the eastern North Pacific (a) at the four coastal marine boundary layer sites and (b) at higher altitudes from two airborne campaigns and the higher-altitude surface site. 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. In Figure 3a the linear least squares fits to the 5th percentiles, the means, and the 95th percentiles are plotted, and in Figure 3b similar lines connect the corresponding parameters for the two aircraft campaigns.

directly comparable aircraft campaigns conducted in this region in spring. Hence the trend is highly dependent upon anomalous  $O_3$  levels in either of those years. In Figure 3b, the Cheeka Peak  $O_3$  mixing ratios are lower than the aircraft data because the latter cover altitudes from 0 to 8 km. The Cheeka Peak data do indicate, however, that 2002 was perhaps anomalously low, rather than high, so the positive aircraft trend cannot be attributed to anomalies in 2002. We have no independent check on the representativeness of the 1984 aircraft data, since we know of no other marine  $O_3$  measurements made that early.

[18] *Jaffe et al.* [2003] largely based their conclusion on data from Lassen Volcanic National Park, a rural elevated inland site with a 15-year  $O_3$  record. The trend from that site is in excellent agreement with the trends in Figure 3 and

Table 2, and they agree that  $O_3$  levels in 2002 were not unusually high. The Lassen data are not investigated further here.

[19] Figure 3 presents some evidence that the  $O_3$  temporal trend is more pronounced at the minimum mixing ratios, and less pronounced at the maximum. In Figure 3a the slope of the linear fit to the 5th percentiles of the data sets is three times larger than the slope of the fit to the 95th percentiles, although the two slopes do agree within their 95% confidence limits (see Table 2). The trend lines in Figure 3b, which simply connect the respective points in the two aircraft distributions, are also consistent with this difference. Examination of the distributions shown in Figure 3 suggests that eastern North Pacific  $O_3$  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.

[20] The two aircraft data sets offer further supporting evidence. It is notable that the difference between the two studies is evident throughout the studied region and altitude range. The color-coding in Figure 2 shows that  $O_3$  levels below 40 ppbv were widespread in 1984, but infrequently encountered in 2002. Figure 4 shows that at all altitudes above 2 km, the 2002 data were higher than the 1984 data by at least one standard deviation. (Below 2 km, too few data were collected in 1984 to adequately define the average levels; these data are discussed further in section 3.2.) The average difference in the six 1-km increment averages above 2 km is 15 ppbv. This difference is larger than the difference in the campaign averages (10 ppbv) shown in Figure 3, because the 1984 measurements were concentrated at higher altitudes. The variability in levels was also greater in 1984 than 2002; the average of the six standard deviations of the data points above 2 km in Figure 4 are  $13 \pm 1.1$  ppbv versus  $9.0 \pm 1.2$  ppbv. These lower average values and greater variability in 1984 reflects the significantly lower minimum  $O_3$  levels observed in 1984.

### 3.2. $O_3$ Photochemical Tendency

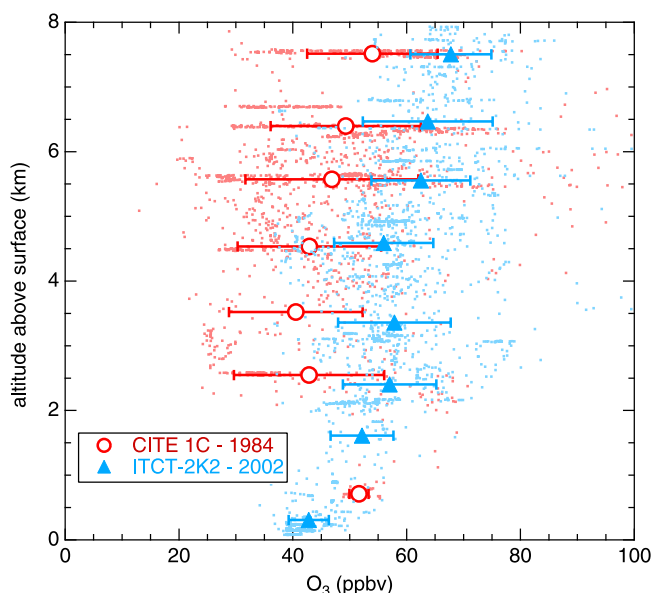
[21] The instantaneous value of  $P(O_3)$  in a given air parcel can be evaluated from photochemical models. However, the uncertainty is often large because  $P(O_3)$  is the difference between two, generally much larger terms: the gross  $O_3$  production and the gross  $O_3$  loss rates. To minimize this uncertainty, models are often constrained by measured concentrations of the most critical species [see, e.g., *Chameides et al.*, 1987]. Table 3 summarizes the results of such calculations carried out for four springtime studies in the North Pacific troposphere. One limitation of these calculations is that they yield  $P(O_3)$  only at the specific time and location of the measurements.

**Table 2.** Slopes of Linear Least Squares Fits to Temporal Variations in  $O_3$  Levels

Data Sets	5th Percentile	Mean	95th Percentile
Coastal marine boundary layer sites	$0.84 \pm 0.66^a$	$0.50 \pm 0.36^a$	$0.28 \pm 0.41^a$
Eastern North Pacific airborne campaigns	$0.66^b$	$0.51^b$	$0.36^b$

<sup>a</sup>Ninety-five percent confidence limits are indicated.

<sup>b</sup>No confidence limits are available, since only two points define the trend.



**Figure 4.** Altitude dependence of observed  $O_3$  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.

[22] Parrish *et al.* [1992] use the relationship between  $O_3$  and hydrocarbon aging patterns to evaluate the sign and qualitatively estimate the magnitude of  $P(O_3)$ . They focused on the photochemical processing of MBL air masses sampled during the spring 1985 Point Arena study. A wide range was found in the degree of photochemical processing of the sampled air masses, as indicated by the observed ratios of light alkanes, particularly propane to ethane. They also found that the concentration of  $O_3$  decreased with the extent of photochemical processing, and concluded that the photochemistry over the North Pacific Ocean acted to remove, rather than produce  $O_3$ , i.e., that negative values of  $P(O_3)$  dominated the photochemistry. An advantage of this qualitative evaluation of  $P(O_3)$  is that it provides an integrated view of the photochemistry that has influenced the  $O_3$  and alkane levels over a time span of the order of the

lifetime of the alkane ( $\approx 10$  days for propane) and the spatial region traversed by the sampled air parcels.

[23] In view of the identified increase in background  $O_3$  levels, it is of interest to see if the relationship of  $O_3$  with hydrocarbon aging has changed. In Appendix A we examine several hydrocarbon data sets collected over the North Pacific in spring. This examination leads to three conclusions. First, the photochemical aging processes of the alkanes are very similar throughout the Pacific troposphere. There is no indication for varying oxidation pathways such as chlorine atoms versus hydroxyl radicals. Second, the photochemical processing pattern is not strongly distorted by hydrocarbon sources with divergent alkane emission ratios. Third, the absolute propane concentration and the ratio of propane to ethane concentrations are both robust indicators of photochemical processing. Each can be used at least for qualitative analyses, and analyses that are consistent for both indicators can proceed with reasonable confidence. In the remainder of this section, we examine this qualitative indicator of  $P(O_3)$ , and where possible compare with model calculated  $P(O_3)$ .

[24] Figure 5 illustrates how  $O_3$  varied with changing alkane levels during two four-day periods, 17 years apart, at Point Arena in 1985 and at Trinidad Head in 2002. These two periods, which happened to span the same calendar dates, contained two of the most pronounced periods of low  $O_3$  and alkanes in the respective studies. The measurements were similar at these two coastal sites, except that ethane was not measured at Trinidad Head. In general the alkane levels varied in phase at the two sites, and the reactivity of the alkane correlates with the factor by which it varied. These features are expected from the aging patterns discussed in Appendix A. Similar  $O_3$  levels were present at the highest alkane levels in both studies. However, in air masses with similarly low alkanes,  $O_3$  was markedly lower in the earlier study.

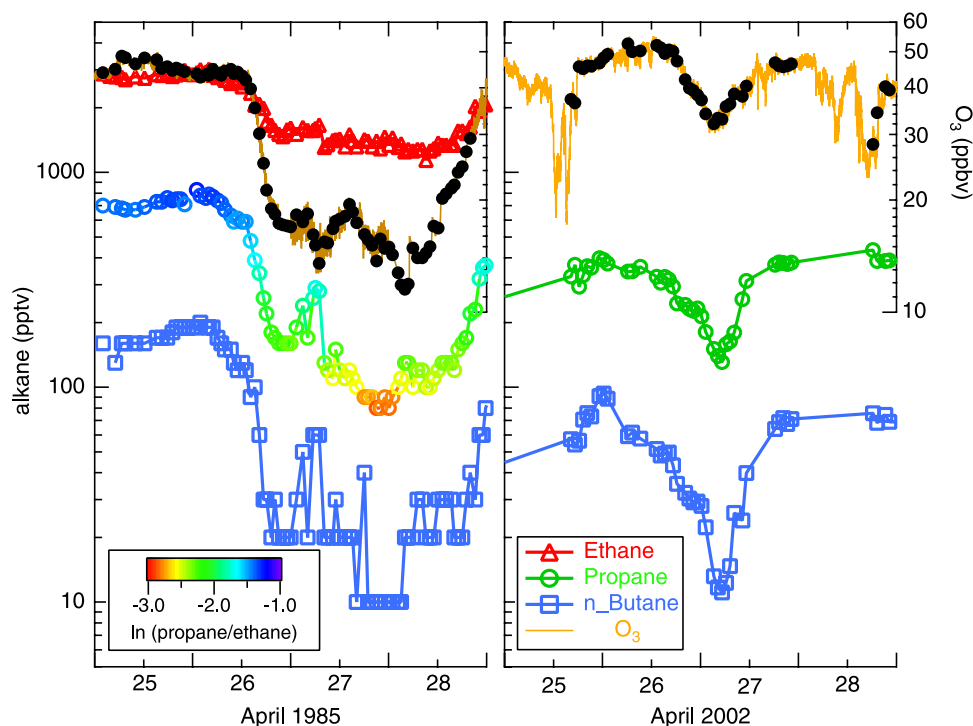
[25] Figure 6 shows that the contrasting behaviors exemplified in Figure 5 are consistent throughout the data sets collected in 1985 and 2002. Here the log-transformed  $O_3$  data are plotted versus both of the alkane aging indicators discussed in Appendix A. The Point Arena data and the marine boundary layer data collected from the aircraft in ITCT 2K2 are included in both plots. Since ethane was not

**Table 3.** Model Evaluations of  $P(O_3)$ , the Net Rate of  $O_3$  Photochemical Production or the  $O_3$  Photochemical Tendency, in the Temperate North Pacific Troposphere

Dates, Latitude, and Study	Altitude Range, km	NO, pptv	$O_3$ , ppbv	$P(O_3)^a$	Reference
<i>Eastern North Pacific</i>					
30 April to 9 May 1984, 24°–40°N, CITE-1C	0–2	5	52	−0.7 <sup>b</sup>	Chameides <i>et al.</i> [1989]
	4–8	10	48	−0.25	Chameides <i>et al.</i> [1989]
26 March to 28 April 1999, 39°–48°N, PHOBEA	0–2	9.5	47	−0.83	Kotchenruther <i>et al.</i> [2001b]
	4–6	12.5	72	−0.24	Kotchenruther <i>et al.</i> [2001b]
	6–8	12.9	79	−0.11	Kotchenruther <i>et al.</i> [2001b]
<i>Western North Pacific</i>					
21 February to 13 March 1994, 25°–45°N, PEM-West B	0–1	30	41	1.3	Davis <i>et al.</i> [2003]
	4–8	14	46	0.14	Davis <i>et al.</i> [2003]
3 March to 3 April 2001, 25°–45°N, TRACE-P	0–1	44	57	3.1	Davis <i>et al.</i> [2003]
	4–8	24	63	0.69	Davis <i>et al.</i> [2003]

<sup>a</sup>Units: 24-hour average ppbv/d except as noted.

<sup>b</sup>Units: instantaneous value near solar noon in ppbv/h.



**Figure 5.** Semilog plots of measured alkane and  $O_3$  levels over 4-day periods at two U.S. West Coast sites: Point Arena in 1985 and Trinidad Head in 2002. The Point Arena propane data are color-coded according to the natural log of the propane to ethane ratio as indicated by the annotated color scale.  $O_3$  levels are given as 1-min averages (gold trace) and as averages over the alkane sample periods for high-wind periods only (black circles).

measured at Trinidad Head, these data are included only on the right-hand plot. A relatively steep, positive slope, implying large negative  $P(O_3)$ , with a strong correlation is found in both plots for the 1985 Point Arena data. The Trinidad Head slope is essentially zero, and the two slopes for the ITCT 2K2 data are much smaller than for Point Arena. Clearly very different relationships between  $O_3$  and the photochemical processing of the alkanes were observed in 1985 and 2002.

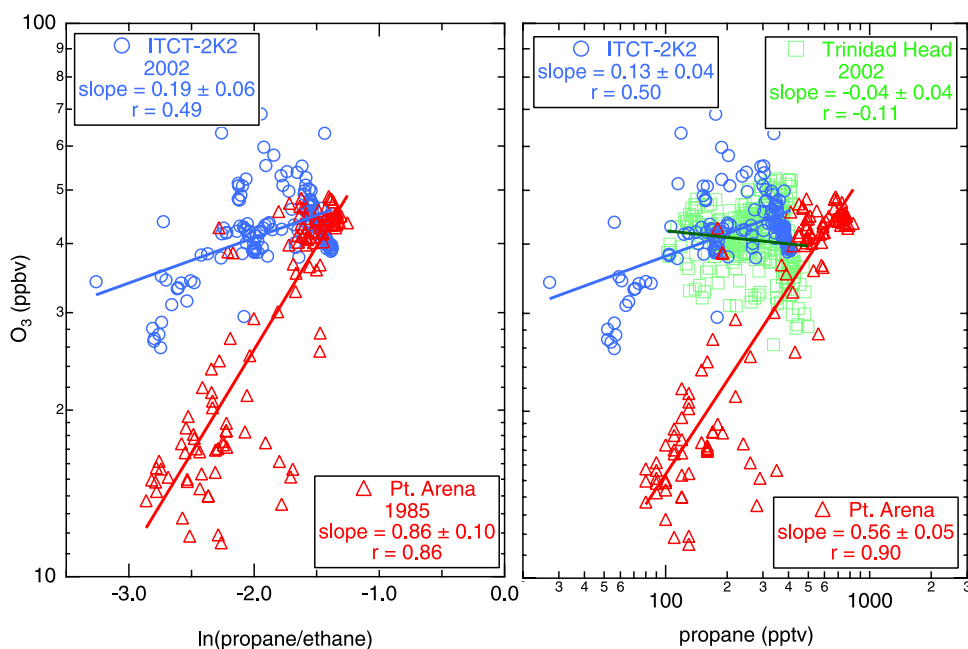
[26] One interpretation of Figure 6 is that the present tropospheric photochemistry of the North Pacific, as exemplified by the 2002 study, is characterized by less efficient  $O_3$  destruction (i.e., smaller negative average  $P(O_3)$  values) than was the case in 1985. This interpretation implies that the increasingly rare low  $O_3$  levels, or equivalently increasing minimum  $O_3$  levels, discussed in the preceding section, result from the increasingly less efficient photochemical destruction. These minimum  $O_3$  levels are observed in highly aged air masses, which are those that have resided for long periods in the North Pacific troposphere. In 1985 the higher  $O_3$  levels were observed only in relatively fresh air masses that had been rapidly transported across the Pacific [Parrish *et al.*, 1992]; these higher  $O_3$  levels have not changed as significantly in the intervening years. Tests of this interpretation constitute the remainder of this section.

[27] The Cheeka Peak and PHOBEA data sets provide evidence for reasonably consistent  $O_3$ -alkane relationships over the latter five years of the studied time interval. Figure 7 shows that all of the available data fall within the scatter about the fits with the relatively small slopes

found for the 2002 data in Figure 6. Although coincident  $O_3$  and alkane data from the MBL are relatively limited in these studies, there is no indication of statistically significant interannual variation in the aging relationships. Evidently the hypothesized change in tropospheric photochemistry largely occurred before the beginning of these studies.

[28] The PEM-West B and TRACE-P studies provide the opportunity to investigate the  $O_3$ -alkane relationships throughout the North Pacific basin in the springs of 1994 and 2001. Figure 8 shows where alkane samples were collected in the MBL during these two studies. These locations are color-coded according to the measured propane concentration to illustrate the patterns of Asian emission outflow to the Pacific. It is clear that this outflow is generally toward the northeast, and concentrated at latitudes above  $20^\circ N$ . Relatively clean air was sampled south of this outflow region. Figure 9 shows the  $O_3$ -alkane relationships for the data of Figure 8, color-coded according to latitude. Separate fits to the data of each study are shown for latitudes north and south of  $25^\circ N$ .

[29] The correlations of Figure 9 provide useful comparisons and contrasts to those of Figure 6. The slope of the TRACE-P fit for the northern latitudes agrees well with the corresponding slope for ITCT 2K2. This agreement is present even though both the  $O_3$  levels and the alkane ratios are higher in the TRACE-P data, which is consistent with their collection closer to the Asian sources. The PEM-West B fit for the northern latitudes contrasts somewhat with those of TRACE-P and ITCT 2K2. The negative slope



**Figure 6.** Correlation of log transformed  $O_3$  levels with the natural log of the propane to ethane ratio and log transformed propane levels for the Point Arena, Trinidad Head, and ITCT 2K2 marine boundary layer 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.

indicates that  $O_3$  was photochemically produced, not destroyed, as the alkanes were removed. This is consistent with the conclusions of Crawford *et al.* [1997], whose analysis indicates strong net photochemical  $O_3$  production within the Asian outflow sampled during the PEM-West B study. At the southern latitudes, the slope is positive in each of the two studies, similar to but not as steep as the slope for Point Arena in Figure 6.

[30] It is notable that the relationships in Figure 6 are consistent for both photochemical processing indicators. The relationships for the data sets in Figures 7 and 9 are consistent for both aging indicators as well, although plots for only  $\ln(\text{propane/ethane})$  are shown here. This consistency demonstrates that photochemical aging is indeed responsible for the observed relationships, and that the potential confounding factors discussed in Appendix A must play no more than minor roles.

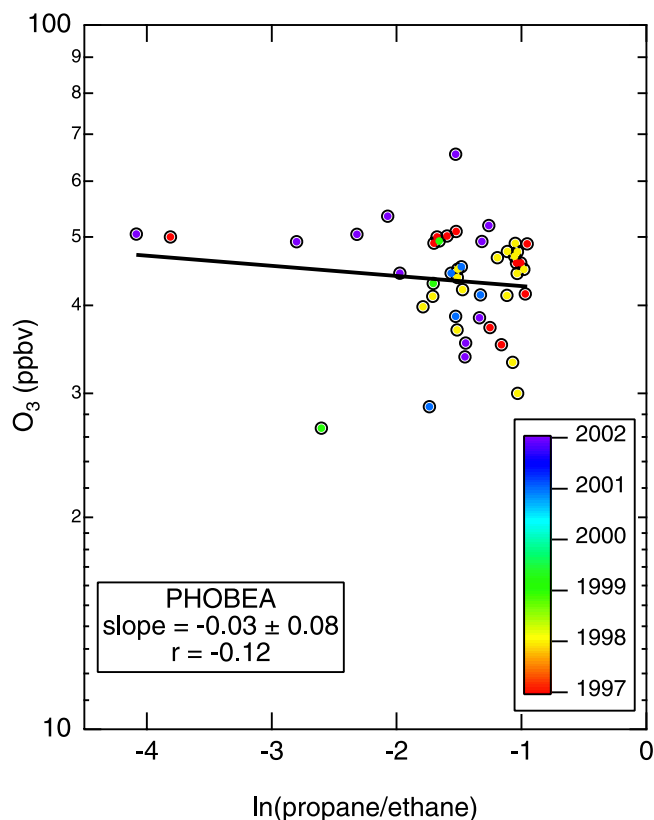
[31] The  $O_3$ -alkane relationships in Figures 6, 7, and 9 are broadly consistent with the limited photochemical modeling that has been reported for the North Pacific MBL (Table 3). For the eastern North Pacific two studies have derived values for  $P(O_3)$  from photochemical box models constrained with observations from field studies 15 years apart. In the MBL near solar noon Chameides *et al.* [1989] found very rapid net destruction,  $P(O_3) = -0.7$  ppbv/h (approximately  $-4$  ppbv/d) in 1984, while Kotchenruther *et al.* [2001b] found values a factor of nearly 5 smaller in 1999. It should be noted that the former value must be treated with caution; only one flight sampled the MBL in this study, and that air may have had some continental influence as indicated by the relatively high  $O_3$  levels apparent in the CITE 1C data below 1 km in Figure 4. This marked difference between 1984 and 1999 is qualitatively consistent with the marked difference in the  $O_3$ -alkane relationships between 1985 and

2002 in Figure 6. In the 4–8 km range, average  $P(O_3)$  was more negative in 1984 ( $-0.25$  ppbv/d) than in 1999 ( $-0.18$  ppbv/d), but this difference is much less pronounced. For the western North Pacific [Davis *et al.*, 2003] the positive values of  $P(O_3)$  are consistent with the  $>25^\circ\text{N}$  fit for PEM-West B in Figure 9, but not for the corresponding fit for TRACE-P. However, Figure 8 shows that much of the alkane- $O_3$  data were collected in the eastern North Pacific, outside the modeling domain. The positive slopes, from the  $<25^\circ\text{N}$  fits for both studies in Figure 9, are consistent with the negative values of  $P(O_3)$  for the MBL in the  $5^\circ$ – $25^\circ\text{N}$  region of the western North Pacific. However, positive  $P(O_3)$  values were found above 4 km in this region for both studies.

[32] Despite the encouraging agreement between the two approaches to investigating  $P(O_3)$ , it should be noted that the uncertainty in the model derived  $P(O_3)$  estimates is large. For example, the striking difference between the two western MBL results arises largely from differences in the measured NO levels: 5 pptv in 1984 and 9.7 pptv in 1999. The magnitude and sign of  $P(O_3)$  depends on the difference between the measured NO level and the NO level where gross photochemical production and loss of  $O_3$  are in balance. This difference is only of the order of a few pptv in remote regions. Measurements of NO at these low levels are extremely difficult to perform precisely and accurately without confounding artifacts. In the four studies summarized in Table 3, five different instruments from five different institutions on four different aircraft were involved over an 18-year period. Thus the comparability of all of the NO data sets at the  $\leq 20$  pptv level important in Table 3, is far from certain.

[33] In summary, notwithstanding the caveats regarding the various uncertainties discussed above, the pattern and





**Figure 7.** Correlation of log transformed  $O_3$  levels with the natural log of the propane to ethane ratio for the Cheeka Peak (1997 and 1998) and PHOBEA (1999, 2001, and 2002) marine boundary layer data. The format is the same as Figure 6, except the data are color-coded according to year of the study.

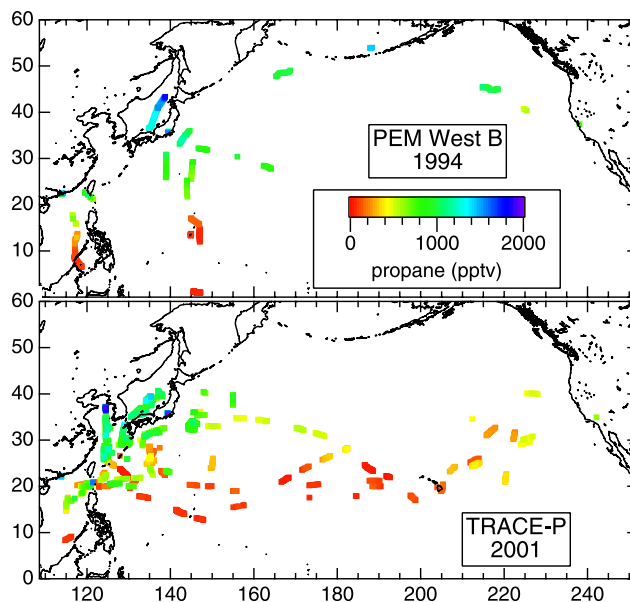
trend of the  $O_3$  tendency over the temperate North Pacific are consistent with the occurrence of a significant change in the photochemical environment of the region. In the eastern Pacific MBL the 1984 and 1985 studies found strong net  $O_3$  destruction, while the 1999 and 2002 studies found much weaker destruction. In the 4 to 8 km altitude range of the free troposphere the 1984 study found modestly stronger  $O_3$  destruction than was found in 1999. In the continental outflow region in the western Pacific the 1994 study found much weaker  $O_3$  production than was found in 2001, both in the MBL and the midtroposphere. *Davis et al.* [2003] attribute this latter difference largely to a seasonal difference. However, as shown in Table 3, the center of the study periods differed by only about 16 days, so it is difficult to attribute the large differences in Table 3 to solely seasonal trends; a long-term trend may well play a significant or even dominant role.

### 3.3. Background PAN Levels

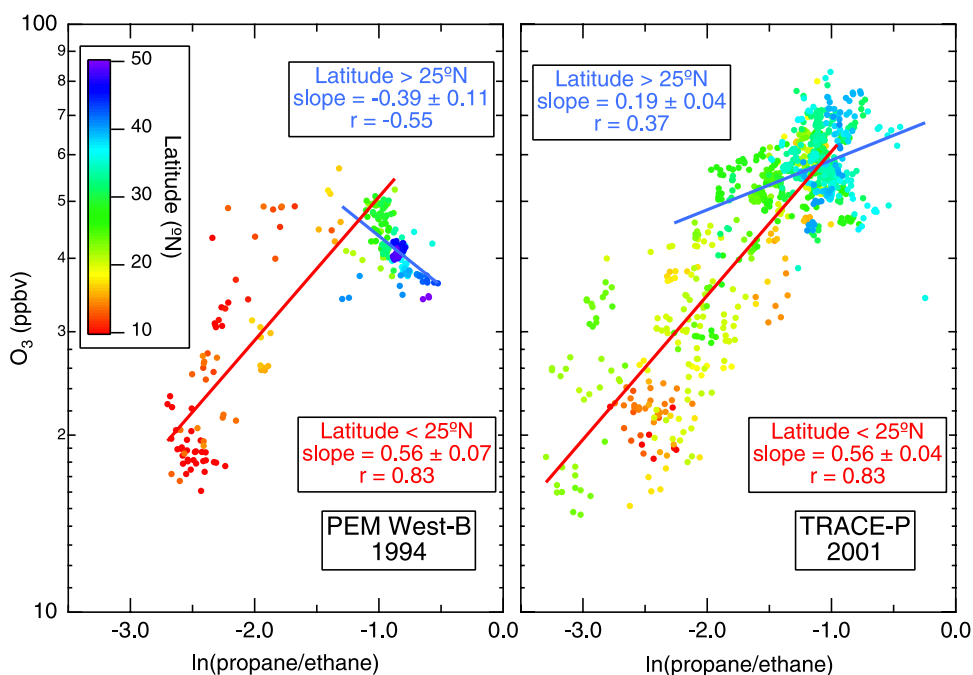
[34] A possible cause of the photochemical trend suggested above is the marked increase of Asian  $NO_x$  emissions that occurred over the last two decades [*Streets et al.*, 2003]. A large increase in Asian  $NO_x$  emissions transported to the Pacific is consistent with increased  $O_3$  levels, particularly at the minima, which are determined by the extent of photochemical destruction.

[35] Ideally, a history of  $NO_x$  measurements would provide a critical test for a causal link between increasing Asian  $NO_x$  emissions and increasing  $O_3$  levels in the eastern North Pacific. The trend in  $O_3$  photochemical tendency summarized in Table 3 is primarily due to the parallel trend in  $NO$  levels included there. However, as discussed above, the ability of the measurements to accurately determine such low values is uncertain. A more extensive data record of  $NO_x$  measurements is lacking. The two early 1984 and 1985 field studies [*Chameides et al.*, 1989; *Parrish et al.*, 1992] cannot define  $NO_x$  levels in those years. The 1984 data are very limited and  $NO_2$  was not measured. The 1985 data were collected in the MBL along the west coast of North America, and relatively local sources, presumably ship emissions, dominated the observed levels. Thus it is not possible to use direct measurements to define the temporal trends of  $NO_x$  levels in the North Pacific troposphere.

[36] The temporal history of PAN concentrations, which play a central role in tropospheric photochemistry, particularly relating to  $O_3$  formation in the remote troposphere, can give an indication of the temporal trend of  $NO_x$  levels. PAN is formed in regions of elevated  $NO_x$  and reactive organic species concentrations. Once formed, it can be transported long distances in the colder regions of the middle and upper troposphere. Upon descent to lower, warmer altitudes it can release  $NO_x$  through thermal dissociation [*Singh et al.*, 1986; *Moxin et al.*, 1996; *Yienger et al.*, 1999]. *Roberts et al.* [2004] have discussed the importance of this mechanism for the springtime eastern North Pacific. Figure 10 shows the PAN measurements collected in the eastern North Pacific MBL in spring. Although the temporal coverage is very sparse, it does indicate a significant increase ( $\approx 3$  to 4%/yr) in PAN over 18 years, which is similar to the inventoried increase in Asian  $NO_x$  emissions (5%/yr for the values shown in Figure 10). This increase in PAN levels in step with increasing Asian emissions suggests that a



**Figure 8.** Locations of alkane samples collected in the MBL during two NASA airborne studies. The data are color-coded according to the measured propane levels.



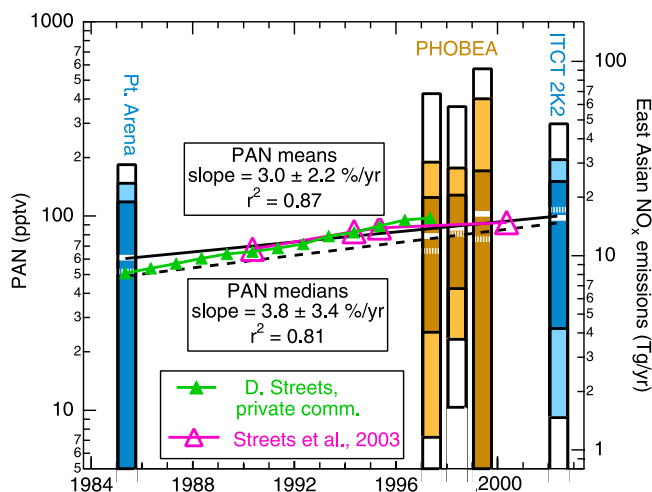
**Figure 9.** Correlation of log transformed  $O_3$  levels with the natural log of the propane to ethane ratio. The MBL data from the two NASA airborne studies are shown. The format is the same as Figures 6 and 7, except the data are color-coded according to latitude, and the linear least squares fits are given for the two indicated latitude ranges.

concurrent increase in  $NO_x$  levels, may indeed play a dominant role in the increase in background  $O_3$  levels.

#### 4. Discussion and Conclusions

[37] In the previous section we presented suggestive, but not definitive, evidence for the occurrence of a marked change in the springtime photochemical environment of the North Pacific troposphere, specifically the following: (1) The temporal trend in  $O_3$  levels that has been found over the eastern North Pacific [Jaffe *et al.*, 2003] is more pronounced at the minimum observed levels, and less pronounced at the maximum. (2) The present photochemistry, as exemplified by the ITCT 2K2 studies in 2002, is characterized by less efficient  $O_3$  destruction (less negative  $P(O_3)$ ) than was the case in 1984 and 1985. (3) These changes can be attributed to changing  $NO_x$  levels related to changing PAN levels that parallel increasing Asian  $NO_x$  emissions [Streets *et al.*, 2003]. It would be highly desirable to more critically test these hypotheses. Unfortunately, we know of no other data sets that have been collected in this region and season that can provide further tests.

[38] Alternative explanations can be posited for increasing  $O_3$  and PAN concentrations, and for the changed  $O_3$  photochemical tendency. Here we will discuss available evidence regarding two of these. First is the occurrence of anomalous conditions during a particular field study. The quantification of the  $O_3$  (Figure 3a) and PAN (Figure 10) trends and the demonstration of a change in the relationship between  $O_3$  and hydrocarbon aging (Figure 6) are all strongly dependent upon the data from the Point Arena study. This study was of short duration, only 10 days in April and May 1985. It is conceivable that tropical air, such



**Figure 10.** Temporal trends of PAN mixing ratios in the eastern North Pacific MBL compared to east Asian  $NO_x$  emissions. Data are from two coastal surface sites (Point Arena and Cheeka Peak in 1985 and 1998) and from two airborne campaigns (PHOBEA in 1999 and ITCT 2K2) at altitudes less than approximately 1 km. Each bar shows the range of the data observed in a given year, 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 means and medians are plotted, and their slopes with 95% confidence limits and correlation coefficients are annotated. The east Asian  $NO_x$  emissions are given by the green [Streets *et al.*, 2001] and violet [Streets *et al.*, 2003] lines with symbols, where the former points are divided by 1.207 to normalize to the 1990 and 1995 points of the latter.

as sampled during the PEM-West B and TRACE-P campaigns at southerly latitudes (Figure 9), was transported to the 39°N latitude location of Point Arena, bringing anomalously low levels of O<sub>3</sub> and PAN and highly aged alkanes that distort the measured distributions for such a short study. The trajectory analysis presented by Parrish *et al.* [1992] does not suggest such transport, and such transport is evidently quite unusual, since such low O<sub>3</sub> levels have not been observed in more recent studies at temperate latitudes. Also, Figure 3 suggests that low (<20 ppbv) O<sub>3</sub> levels were relatively common before about 1990, but are now less common. Finally the 1984 determinations of  $P(O_3)$  support rapid O<sub>3</sub> destruction in the mid-1980s.

[39] To test the possibility of anomalous transport in 1985 further, the global chemical transport model MOZART-2 (Model of ozone and related tracers, version 2) [Horowitz *et al.*, 2003] was run for 1985 and 2002 using the NCEP reanalysis winds [Kalnay *et al.*, 1996; Kistler *et al.*, 2001] for the respective years, but with the same emissions (valid for 1997) for both years. These calculations indicate that there are infrequent incursions of tropical or subtropical air to the west coast of North America, and that one reached Point Arena at a time in reasonable correspondence to the period of low O<sub>3</sub> shown in Figure 5. Simulated slopes of O<sub>3</sub> versus ln (propane/ethane) during this event do have the character of the 1985 Pt Arena data, although neither the O<sub>3</sub> levels nor the propane to ethane ratios were as low as actually observed in 1985. When the model is sampled at Point Arena in 1985 and Monterey in 2002 the minimum simulated 24-hour averaged O<sub>3</sub> levels are 22.3 to 29.5 ppbv, respectively. However, the difference in the mean ozone between Point Arena in 1985 and Monterey in 2002 is less than 1.5 ppbv and the difference in mean PAN is between 30 and 40% depending on exactly where the comparison is made. The overall conclusions of the model simulation is that: (1) changes in meteorology between the Point Arena and Trinidad Head measurements do not explain the increase in the measured means of PAN and O<sub>3</sub>, (2) meteorological differences can account for significant differences in the minimum ozone levels observed in 1985 and 2002, and (3) changes in the O<sub>3</sub> hydrocarbon aging relationship must be interpreted with due consideration of air mass transport patterns.

[40] A second possible alternative explanation is that the increasing O<sub>3</sub> and PAN trends may reflect local conditions along the North American coast, rather than a North Pacific wide phenomenon. Roberts *et al.* [2004] discuss the very significant increase in shipping traffic that has occurred in the eastern North Pacific coastal region, and they and G. Chen (An investigation of the chemistry of ship emission plumes during ITCT 2002, submitted to *Journal of Geophysical Research*, 2004) show that both O<sub>3</sub> and PAN are produced from these precursors. However, in one concentrated ship plume studied over a period of time long enough for the emitted NO<sub>x</sub> concentration to drop by 82%, modeled maximum O<sub>3</sub> and PAN increases were modest, 3 ppbv and 60 pptv, respectively. Thus it is unlikely that photochemical production of PAN and O<sub>3</sub> can substantially increase average ambient levels as MBL air flows through the region of the shipping lanes, since this occurs in at most a few hours time. Furthermore, Figure 4 indicates that the O<sub>3</sub> increase is not confined to the ship influenced MBL, but

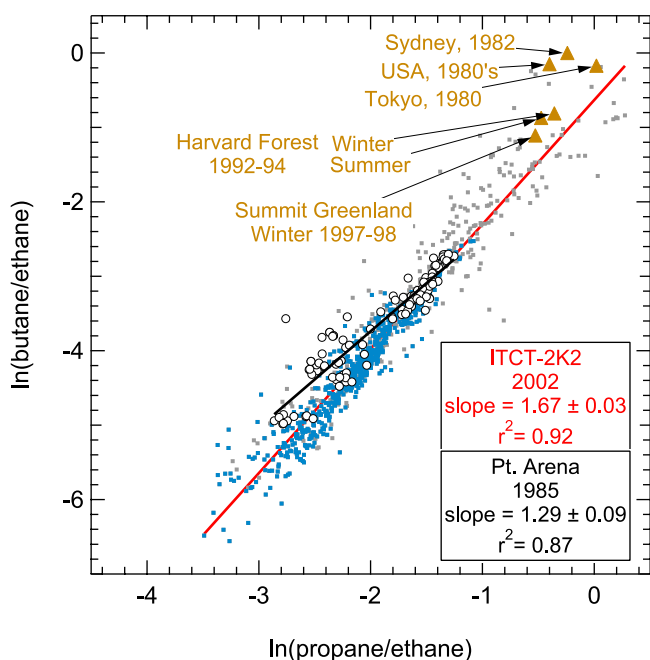
has occurred throughout the lower and middle troposphere, and Table 3 indicates that  $P(O_3)$  is less negative in the midtroposphere as well as in the MBL.

[41] In summary, it has been established that the background O<sub>3</sub> levels have increased in the North Pacific troposphere. All of the available data are consistent with the hypothesis that increasing Asian NO<sub>x</sub> emissions cause the O<sub>3</sub> trend. However, the available data provide only limited evidence, and intriguing questions remain. Comprehensive model calculations will be required to develop a thorough understanding of the photochemical trends in the North Pacific. Ultimately, these will only come from chemical transport models with sufficient resolution, realistic meteorology, and accurate emission inventories that can reproduce the observed trends in O<sub>3</sub> and PAN, can accurately and precisely derive  $P(O_3)$  from the underlying photochemistry, and can reproduce the measured O<sub>3</sub>-alkane relationships. Developing such models will be challenging, particularly with regard to accurately describing the changing emissions over the time span of the measurements, but current and evolving models can be looked to for critical insights.

## Appendix A: Photochemical Aging Pattern of Alkanes

[42] Hydrocarbon concentrations in an isolated air parcel decrease with time because of reaction with atmospheric oxidants. The ratio of the concentration of a rapidly reacting hydrocarbon to that of a more slowly reacting hydrocarbon then decreases over time. Typically a ratio of two hydrocarbon concentrations is examined to minimize the effects arising from differing quantities of hydrocarbons initially injected into different air parcels and differing degrees of dilution among air parcels. These differences affect ratios of hydrocarbon concentrations to a lesser extent than the absolute concentrations. In the absence of complicating effects (discussed below), a given hydrocarbon ratio in an air parcel decreases from the ratio of the initial emissions according to approximately first-order decay kinetics. Thus the logarithm of the ratio provides an approximate, linear measure of the degree of photochemical processing in that air parcel [see, e.g., Roberts *et al.*, 1984, 1985; Rudolph and Johnen, 1990].

[43] Parrish *et al.* [1992] used two alkane ratios, ln (propane/ethane) and ln (*n*-butane/ethane), for studying photochemical processing during trans-Pacific transport of Asian emissions that reached Point Arena. Figure A1 compares the evolution of these two ratios, both for the 1985 Point Arena data and for the 2002 ITCT 2K2 data collected from NOAA WP-3D aircraft. The triangles in the upper right represent the ratios in fresh emissions in three urban areas [Parrish *et al.*, 1992], average emission ratios for North America estimated from Harvard Forest data [Goldstein *et al.*, 1995], and for the Northern Hemisphere [Swanson *et al.*, 2003]. The reactivity of the three alkanes included in Figure A1 increases from ethane to propane to butane. Hence both ratios decrease from the estimates of initial values to the most aged air masses at lower left. In both data sets the two measures of the photochemical processing are well correlated, and are consistent with a decay of the fresh emission ratio through several e-foldings.



**Figure A1.** Correlation of the natural logarithms of two alkane concentration ratios for all samples collected during the ITCT 2K2 study (dots) and at Point Arena in 1985 (circles). The Point Arena data include only samples without North American influence [Parrish *et al.*, 1992], and the blue dots indicate the fraction of the ITCT 2K2 data that were collected in the marine environment before possible North American influence. The lines show standard linear least squares fits to the respective data sets, and the slopes with 95% confidence limits and correlation coefficients of those fits are annotated. The triangles give estimates of average emission ratios discussed in text.

The similarity of the correlations in Figure A1 indicates that the aging pattern of hydrocarbons has remained constant over the intervening seventeen years. There is a significant difference in the slope of the linear regression, but the Point Arena data lie within the scatter of the ITCT 2K2 marine data.

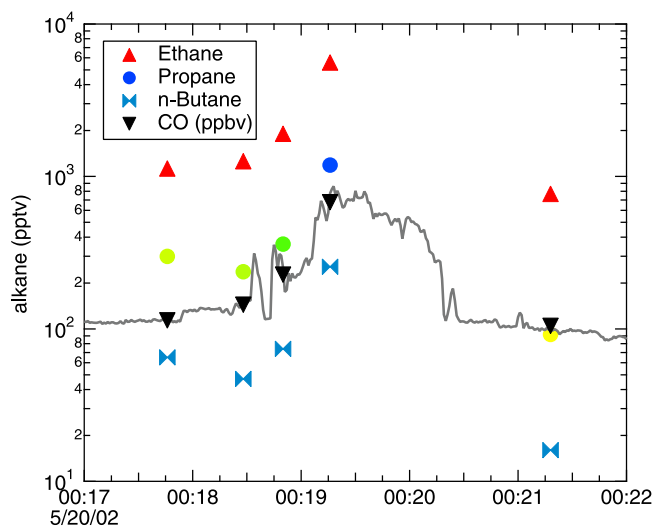
[44] Despite the strong and consistent correlations shown in Figure A1, the simple aging interpretation presented up to this point is oversimplified in at least two respects. First, the slope in Figure A1 (1.67 for the ITCT 2K2 data) is significantly smaller than expected from the kinetic rate constants (2.77) for reaction solely with hydroxyl radicals [Parrish *et al.*, 1992]. This difference is generally attributed to the effects of dilution and of mixing of air masses with hydrocarbons of different ages [Parrish *et al.*, 1992; McKeen and Liu, 1993], but it has also been suggested that competing reactions with chlorine atoms could play a role [Finlayson-Pitts, 1993; Parrish *et al.*, 1993]. These effects complicate the interpretation of observed hydrocarbon ratios as quantitative measures of hydrocarbon aging, but they do not prevent their application as qualitative linear measures of that aging.

[45] A second concern is discussed by Swanson *et al.* [2003]. The discussion up to this point implicitly assumes that the light alkanes measured in the atmosphere come

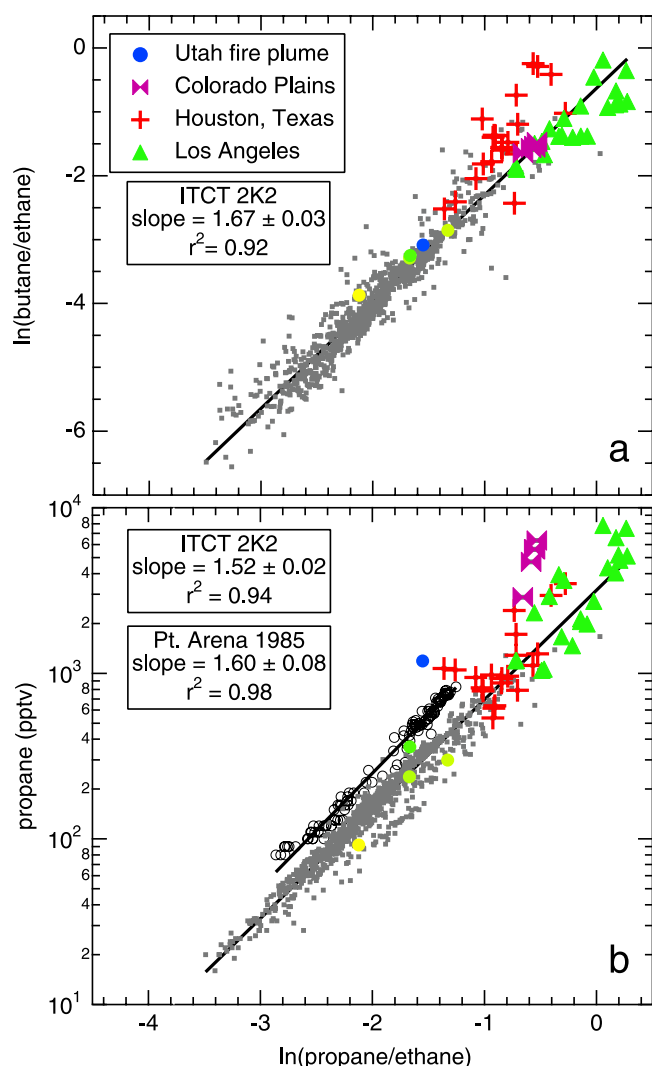
from sources with relatively uniform emission ratios. In Figure A1, these emission ratios are represented by the triangles in the upper right corner. However, Swanson *et al.* [2003] note that the manifold of important light alkane sources can have quite divergent emission ratios that span a large fraction of the observed range of the ambient ratios. Moreover, the alkane ratios of the fresh emissions tend, on average, to fall on or near the correlation line in Figure A1. Consequently, a data point lying to the lower left of the average emissions given by the triangles could represent aged average emissions, or alternatively could represent relatively fresh emissions from a source particularly rich in ethane, which would account for the low measured ratios. Since we wish to use the alkane ratios as at least qualitative indicators of the degree of photochemical aging of the air parcel in which they were measured, we must now consider this influence of varying alkane source emission ratios.

[46] Figure A2 shows one example of a source relatively rich in ethane. The NOAA WP-3D aircraft intercepted a forest fire plume with CO concentrations approaching 1 ppmv over Utah during the transit flight at the completion of the ITCT 2K2 study. The alkane concentrations were a factor of 4–10 higher in the center of the plume than in the air on either side. Figure A3a highlights these fresh forest fire emissions in the full ITCT 2K2 data set, and shows that these data indeed do fall on the aging trend line, but at significantly lower ratios than fresh emissions from other sources. Hence it is not possible to distinguish fresh forest fire emissions from, for example, aged urban emissions on the basis of these alkane ratios alone.

[47] Also highlighted by different symbols in Figure A3a are three other source categories: emissions from Los Angeles, California, from the Houston, Texas, area, and from petroleum and natural gas fields that lie on the



**Figure A2.** Alkane and CO mixing ratios measured during the transect of a forest fire plume. The symbols indicate the different alkanes and CO measured in canisters, and the gray, continuous trace gives the sequential, 1-s averages from the continuous CO measurement. The propane symbols are shown in different colors for identification of respective samples in Figure A3.

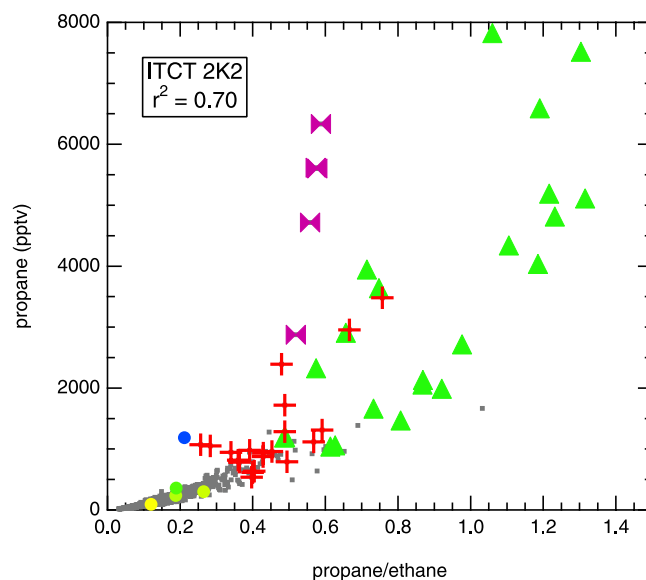


**Figure A3.** (a) ITCT alkane data in the format of Figure A1, with data influenced by four particular sources indicated by different symbols as annotated. The colors of the propane data in Figure A2 indicate those same samples in this figure. (b) Propane plotted as a function of the natural logarithm of the propane to ethane ratio. The data from Figure A3a are plotted with the same symbols, and the Point Arena data from Figure A1 are included. The lines show standard linear least squares fits to the respective data sets, and the slopes with 95% confidence limits and correlation coefficients of those fits are annotated.

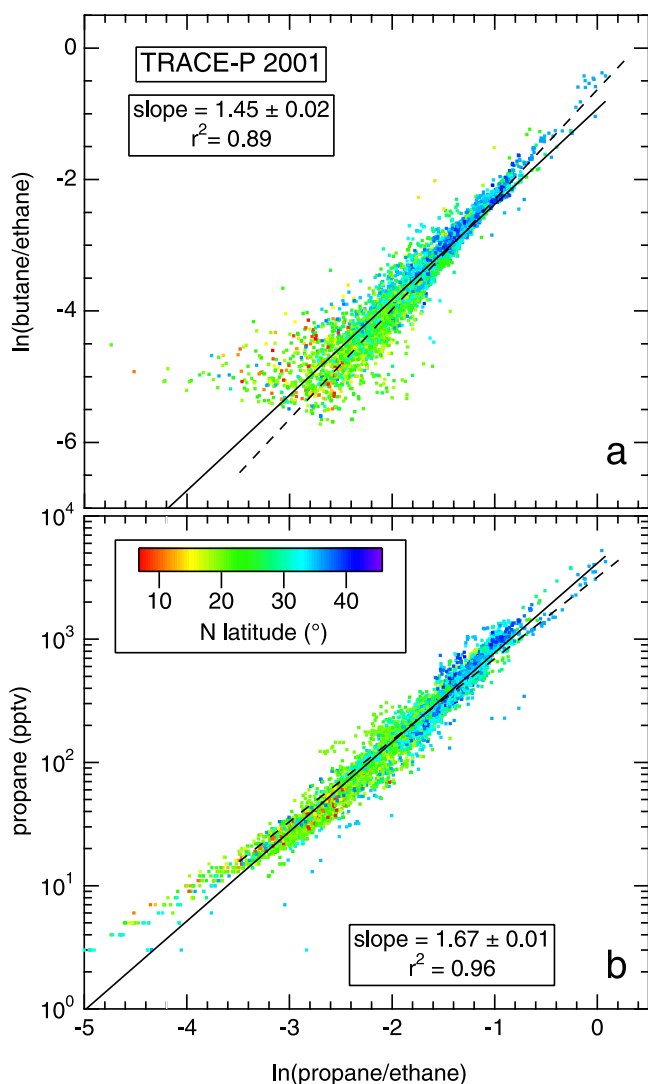
Colorado plains east of Denver. A typical U.S. mobile source mix dominates Los Angeles emissions, which approach the U.S. 1980s point in Figure A1. The Houston area has similar mobile source emissions plus a strong contribution from petrochemical industrial emissions [Brock *et al.*, 2004; Ryerson *et al.*, 2003]. These data lie to the left of the Los Angeles data, which indicates that the Houston petrochemical emissions are richer in butane relative to propane compared to either the Los Angeles data or the average source ratios given in Figure A1. The petroleum and natural gas field emissions observed over the Colorado Plains are rich in ethane; these data include the four highest

ethane concentrations observed during the study. The inflow of such emissions to Boulder, Colorado, has been suggested as the large, unidentified propane source that is important in that urban area [Goldan *et al.*, 1995]. Katzenstein *et al.* [2003] have shown the widespread influence of such emissions in the southwestern United States. These data fall on the trend line in Figure A3a, but appear at somewhat lower alkane to ethane ratios than the average source ratios. Examination of these four source types shows that sources with divergent alkane emission ratios can lead to scatter about the average source ratios (i.e., Los Angeles versus Houston data) and can lead to fresh emissions that appear to be aged (i.e., the petroleum and natural gas field emissions and especially the forest fire emissions.) A large influence from these two effects, particularly the latter, would limit the unambiguous interpretation of alkane ratios as a quantitative measure of the degree of photochemical processing of sampled air parcels. A careful assessment of the magnitude of this influence would be required before making such an interpretation.

[48] Figure A3b illustrates the discrimination of different source ratios from the effects of photochemical aging. It plots the concentration of propane on a logarithmic scale, versus the logarithm of the propane to ethane ratio. Perhaps surprisingly, the log-transformed propane concentration (subject to variability in emission loading and stronger dilution effects) nevertheless correlates strongly with the logarithm of the concentration ratio, in fact even more strongly than the correlation between the logs of the two concentration ratios. Undoubtedly, this strong correlation is largely due to the strong dependence of both variables on propane. Notably, however, in Figure A3b the samples dominated by forest fire and petroleum and natural gas field emissions are identified as outliers above the trend line, because high propane levels identify fresh emissions regardless of the emission ratio. In the analysis in this paper we use both the logarithm of the propane concentration and the logarithm of the propane to ethane ratio as indicators of



**Figure A4.** ITCT 2K2 data from Figure A3b plotted on linear axes.



**Figure A5.** Alkane data from the NASA TRACE-P study plotted in the format of Figure A3. The data are color-coded according to latitude as indicated by the annotated color scale, which spans the latitude range of the samples. The dashed lines indicate the linear regression fits from Figure A3.

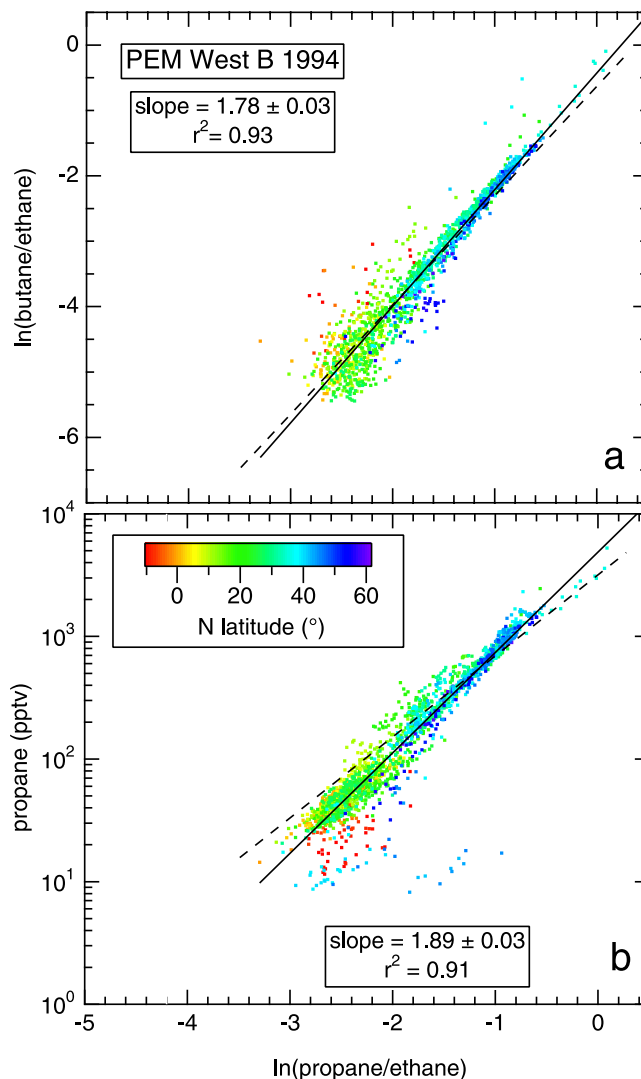
the degree of photochemical processing of a sampled air parcel. A consistent result from both of these two indicators indicates that sources with divergent emission ratios do not have a strong influence upon the analysis.

[49] Figure A4, which shows how Figure A3b appears when plotted on linear axes, more clearly illustrates the effect of different sources. A linear plot is appropriate for examining the contribution of various sources to observed alkane levels, since concentrations are linearly dependent upon mixing. Here the scatter in the data due to variation in sources dominates the variability. However, in the log-transformed data in Figure A3b this source-specific variability is much less important, because the lower several e-foldings (which are due to photochemical processing) dominate the variability of the log-transformed data. All of these data pile up near the origin on the linear plot. This demonstrates the importance of using log-transformed data

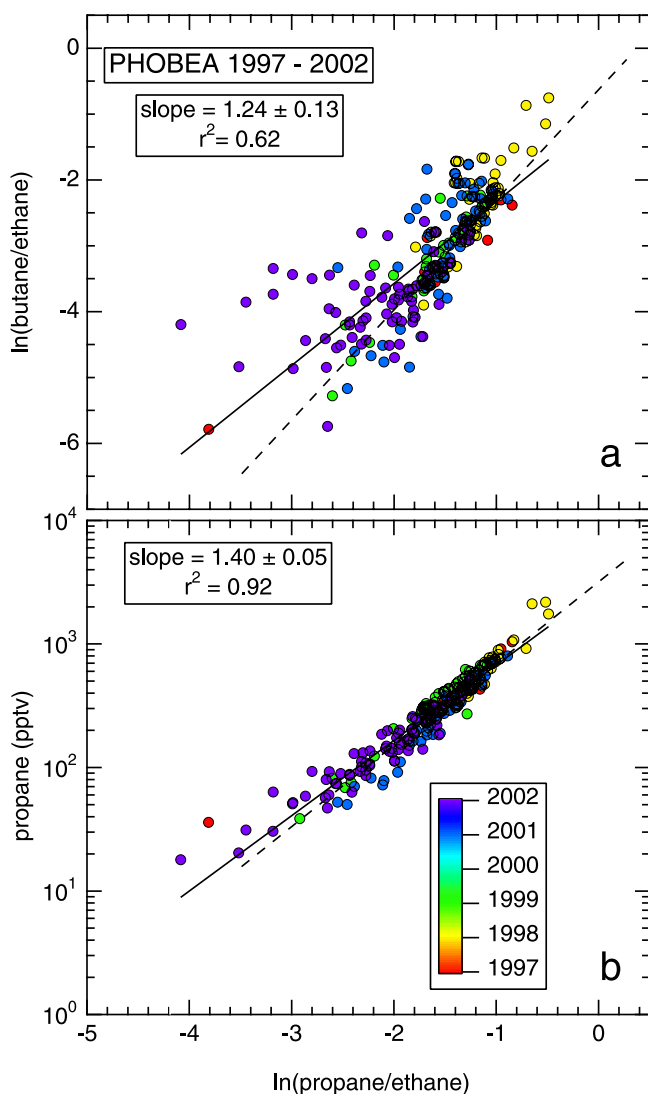
to examine photochemical removal, which is linear in log space.

[50] An interesting feature of Figures A1 and A3b is the comparison of the Point Arena and ITCT 2K2 data sets. In Figure A3b the Point Arena data are offset to lower propane to ethane ratios, even though the slopes are statistically identical, while Figure A1 shows no such offset. This is consistent with a calibration error of about 40% for the Point Arena ethane data. Also in Figure A1, the somewhat smaller slope of the Point Arena correlation is consistent with imprecision in the measurement of butane at the lowest observed levels. Indeed, the minimum levels were 10 pptv, and were quantified to  $\pm 10$  pptv. Such experimental problems are not unexpected for these measurements, which were some of the earliest accomplished at such low ambient levels.

[51] Figures A5–A7 show plots analogous to Figure A3 for three other data sets collected in the spring over the North Pacific. For reference, the linear correlations for the ITCT 2K2 data sets are included as dashed lines in these figures. In general, the correlations of the different data sets are very similar. Small differences in scatter or slopes of



**Figure A6.** Alkane data from the NASA PEM-West B study plotted in the format of Figure A5.



**Figure A7.** Alkane data collected during the five PHOBEA studies. The format is the same as Figure A5, except the data are color-coded according to year of the study.

correlations may indicate slight differences in source mix or aging patterns, or may simply indicate experimental differences between the techniques used in the measurements. At any rate the similar correlations with little scatter in the freshest emissions have two major implications. First, the photochemical aging processes of the alkanes are very similar throughout the Pacific troposphere. There is no indication for varying oxidation pathways such as chlorine atoms versus hydroxyl radicals. Second, there is no major influence from sources with divergent alkane emission ratios. These features lead us to conclude that both propane and the propane to ethane ratio are robust photochemical processing indicators that can be used with reasonable confidence for qualitative analyses.

[52] Other minor features to note in Figures A5–A7 include the following. First, in the NASA GTE data sets, collected predominately in the western Pacific off the Asian mainland during the TRACE-P and PEM-West B studies, the alkanes are most aged at low latitudes, where relatively

clean tropical air flows into the region, and the freshest emissions at high latitude where Asian emissions flow out to the Pacific during that season. This outflow ages as it is transported across the Pacific to the coast of North America where the more aged alkane mix was observed in the inflow to North America. Second, in Figure A6b there are some curious outliers at the lowest propane levels but relatively high propane to ethane ratios. The high-latitude (blue) points were collected in air with strong stratospheric influence as indicated by the  $O_3$  levels, which were above 280 ppbv, and the low-latitude (red) points were collected in the Southern Hemisphere. These few data may indicate that the hydrocarbon aging relationships defined here may not apply in the stratosphere, or in the Southern Hemisphere. Those data are not considered further in this paper. Finally, in Figure A7a, the relatively poor correlation indicates that the precision in the butane measurements from the PHOBEA study is lower than in the other data sets. These butane data also are not considered further.

[53] **Acknowledgments.** The Climate and Global Change Program of the National Oceanic and Atmospheric Administration (NOAA) largely funded this research. The University Corporation for Atmospheric Research (UCAR) operates the National Center for Atmospheric Research (NCAR) under the sponsorship of the National Science Foundation (NSF). The data from The NASA CITE 1C, PEM-West B, and TRACE-P studies were obtained from the NASA GTE Data Archive (available at [http://www-gte.larc.nasa.gov/gte\\_arch.htm](http://www-gte.larc.nasa.gov/gte_arch.htm)). The data from Redwood National Park and Point Reyes National Seashore were obtained from the National Park Service (Gaseous Pollutant Monitoring Network, Air Resources Division, Denver, Colorado, 2002; available at <http://www2.nature.nps.gov/ard/gas/>). The authors are grateful to Brian Ridley, Melody Avery, Don Blake, and Nicola Blake for providing data and helpful discussions. The ITCT 2K2/PEACE campaigns were conducted under the framework of the International Global Atmospheric Chemistry (IGAC) project (<http://www.igac.noaa.gov/>).

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