

Ratios of Peroxyacetyl Nitrate to Active Nitrogen Observed During Aircraft Flights Over the Eastern Pacific Oceans and Continental United States

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During August and September 1986, 11 aircraft flights were made over the eastern Pacific Ocean and continental United States. The suite of observations included simultaneous measurements of peroxyacetyl nitrate (PAN) and active nitrogen ($\text{NO}_x = \text{NO} + \text{NO}_2$). At altitudes of 4.5-6.1 km in the middle free troposphere, PAN was usually 5-6 times NO_x in maritime air masses and 2-4 times NO_x in continental air masses. In air masses of tropical origin, or in the marine boundary layer, both PAN and NO_x were typically less than 20-30 parts per trillion by volume, and the PAN to NO_x ratio was less than one. The observations show that PAN can be a major component of the odd nitrogen budget in the middle free troposphere and strongly reinforce earlier views that the abundance is mainly governed by long-range transport processes including formation during transport and continental boundary layer to free tropospheric exchange of PAN and its precursors. Unlike reservoir HNO_3 , PAN can be transformed to active nitrogen and peroxy radicals by a variety of physical atmospheric processes that lead to air mass warming. Since NO_x plays a critical role in determining photochemical O_3 production, which in turn determines the oxidative power of the atmosphere, the observed large ratios of reservoir PAN to active NO_x imply an important photochemical and dynamical role for PAN in the eastern Pacific remote free troposphere.

1. INTRODUCTION

Peroxyacetyl nitrate or PAN ($\text{CH}_3\text{C}(\text{O})\text{OONO}_2$) formation in urban atmospheres by photochemical reactions involving nonmethane hydrocarbons (NMHC) and active nitrogen ($\text{NO}_x = \text{NO} + \text{NO}_2$) has long been understood since its identification in Los Angeles smog [Stephens *et al.*, 1956]. Numerous measurement programs in urban or near-urban regions have shown PAN to be present at levels comparable to NO and HNO_3 [Spicer, 1977; Tuazon *et al.*, 1981; Spicer *et al.*, 1983; Singh *et al.*, 1985]. Like O_3 and HNO_3 , PAN is a good indicator of photochemical activity, and a reservoir of active nitrogen, but also one much more susceptible to thermal forcing.

The free tropospheric atmospheric lifetime of PAN is ultimately limited to about 4 months due to photolysis [Serum *et al.*, 1984] or to reaction with OH [Wallington *et al.*, 1984]. Deposition in the boundary layer is also slow [Garland and Penkett, 1976]. For shorter times, and assuming no competing production or destruction of peroxyacetyl radicals ($\text{PA} = \text{CH}_3\text{C}(\text{O})\text{OO}\cdot$), the PAN lifetime is governed by the processes



The rate coefficients are $k_1 = 2.0 \times 10^{16} \exp(-13543/T)$, $k_2 = 4.8 \times 10^{-12}$, and $k_3 = 3.7 \times 10^{-12} \exp(240/T)$ [Atkinson and Loyd, 1984]. Rate coefficient k_2 is not well known. The lifetime depends sensitively on temperature and weakly on the NO_2/NO ratio and is given by [Cox and Roffey, 1977]

$$\tau_{\text{PAN}} = (1/k_1)(1 + k_2[\text{NO}_2]/k_3[\text{NO}]) \quad (4)$$

For example, with daytime NO_2/NO ratios of 2.5 and no NO present at night the lifetimes at 0 km (299 K), 4 km (277 K), and 6 km (266 K) are approximately 1.6 hours, 5 days, and 34 days, respectively. At very low daytime NO_x mixing ratios, reactions of PA with HO_2 or organic peroxy radicals may compete with reaction (3).

A global role for PAN was outlined a number of years ago by Crutzen [1979], who proposed that with exchange of PAN from continental production regions to the colder free troposphere, PAN could serve as a carrier for the global or at least hemispheric redistribution of active nitrogen and PA

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radicals by long-range transport. An analogous process would be exchange of PAN precursors to the free troposphere and subsequent production by photochemistry along air mass trajectories [Hov, 1984; Brice *et al.*, 1984]. Because the lifetime of NO_x in the summertime lower free troposphere is considerably shorter (1-2 days in summer), and more independent of temperature, than the lifetime of PAN in the middle troposphere, the ratio of PAN to NO_x should increase rapidly as the air mass ages. Some direct evidence for this has been reported for remote and aged continental near-surface air masses in which PAN and NO_x were measured concurrently [Singh *et al.*, 1985; Fahey *et al.*, 1986].

In contrast, Singh and Hanst [1981] proposed that ubiquitous NMHCs like ethane are sufficiently abundant globally [Robinson, 1978; Rudolph and Ehhalt, 1981; Singh and Salas, 1982; Greenberg and Zimmerman, 1984; Ehhalt *et al.*, 1985] to allow significant in situ production rates of PAN provided NO_x precursors are available. However, more recent NO and NO_x measurements in remote maritime areas (see Fehsenfeld *et al.* [1988] for a recent review) suggest that NO_x may often be limited, especially in the lower troposphere. Modeling studies [Aikin *et al.*, 1982, 1983; Fishman and Carney, 1984; Isaksen *et al.*, 1985; Kasting and Singh, 1986], although constrained by a paucity of NO_x measurements, support a significant fraction of active nitrogen in reservoir PAN in the remote free troposphere. In this case, expectations for the PAN to NO_x ratio are not as clear. The ratio will depend sensitively on temperature and the distribution and source strengths of PAN precursors.

Latent active nitrogen in the form of PAN can affect computed O₃ in the troposphere, but long-range transport and in situ production have important and different implications for the free tropospheric O₃ budget. When active nitrogen is sequestered as PAN the O₃ generation potential of NO_x emissions near source regions or during long-range transport is reduced. Ultimately, however, PAN will release active nitrogen, perhaps in remote regions where NO_x levels are usually less than 100 parts per trillion by volume (pptv) and where the O₃ production efficiency is greater [Liu *et al.*, 1987] or perhaps in regions where the NO_x level is so low that net photochemical destruction of O₃ remains in effect even with some release of NO_x from PAN. With in situ production of PAN in remote regions to levels comparable to or greater than NO_x, models incorporating PAN formation will have to increase source strengths of NO_x to maintain the observed levels compared to versions without PAN chemistry. Such changes will necessarily affect calculated O₃ abundances in remote regions depending upon the O₃ and PAN formation rates as a function of altitude and season.

There is little doubt that both scenarios contribute to the global distribution of PAN and ultimately NO_x in the free troposphere. A few measurements of PAN have been made in the eastern Pacific region. Aircraft measurements by Singh *et al.* [1986] gave values of 50 pptv or less near 5 km in August and 50-500 pptv in February. Shipboard measurements showed values averaging 38 pptv in the northern hemisphere and much lower values (≤ 10 pptv) in the southern hemisphere. Summertime measurements (B. Gandrud, J. Shetter, and B. A. Ridley, unpublished work, 1989) made during 10 flights of the NCAR Electra during the Dynamics and Chemistry of Marine Stratocumulus (DYCOMS) experiment [Lenschow *et al.*, 1988] averaged 8 ± 5 pptv just

above and 15 ± 11 just below the top of the marine boundary layer. At 3.1 km the average was 50 ± 41 pptv, while between 3.2 and 6 km the average was 135 ± 40 pptv. The most extensive set of free tropospheric measurements was made by Rudolph *et al.* [1987] over the Atlantic Ocean in both hemispheres. In the western Atlantic at mid-latitudes in the northern hemisphere, reported mixing ratios were rarely above 60 pptv at 5 km. In the southern hemisphere Atlantic region, mixing ratios above 10 pptv were rare at any altitude up to 12 km.

In July and August 1986 the second phase of the NASA Global Tropospheric Experiment Chemical Instrumentation Test and Evaluation program (GTE/CITE) was carried out, using the NASA Wallops Electra aircraft. The flights were designed to provide instrument intercomparisons of NO, NO₂, HNO₃, and PAN and to examine some aspects of the budget and interconversion of nitrogen compounds through simultaneous measurements [Hoell *et al.*, this issue]. Here the relative abundances of reservoir PAN and active NO_x are examined.

2. OBSERVATIONS

Figure 1 summarizes the flight paths and gives the altitudes flown from within the boundary layer to a maximum of 6.1 km. Except for two across-continent transits the flights were about 5 hours in duration, and most flights were also centered about local noon. Only flight 9 (August 23, 24) was made at night. The scalloped vertical lines in Figure 1 denote confined spiral ascents or descents of the aircraft at a rate of 0.15 km min⁻¹ used to determine local concentration profiles. The maximum range from the California coast west over the Pacific Ocean was only about 800 km. Table 1 gives the averages and median values of O₃, CO, total odd nitrogen (NO_y), temperature, and dew point (DPT) for each flight, but only for altitudes greater than 4.5 km, where the majority of measurements were made.

The NO_x data file used here is based on measurements of NO by chemiluminescence by NASA Wallops [Torres and Buchan, 1988], of NO₂ by tunable diode laser spectrometer measurements by York University [Schiff *et al.*, this issue], of NO and NO₂ by laser-induced fluorescence by the Georgia Institute of Technology [Davis *et al.*, 1987; Sandholm *et al.*, this issue], or by chemiluminescence and photolysis combined with chemiluminescence by the National Oceanic and Atmospheric Administration/National Center for Atmospheric Research (NOAA/NCAR) [Ridley *et al.*, 1987, 1988a; Carroll *et al.*, this issue]. The NO_x data used here is discussed in detail by Gregory *et al.* [this issue (a)]. Only NO_x data overlapping the period required to collect a PAN sample are used here in discussing PAN to NO_x ratios.

The PAN data file is based on 271 samples collected by the group from NCAR and 189 samples collected by the group from the NASA Ames Research Center (Ames). Each group estimated its overall experimental uncertainty prior to the flights at $\pm 20\%$ for ambient levels well above the detection limits of a few pptv. Gregory *et al.* [this issue (b)] have presented a detailed assessment of the relative agreement between the results from the two groups for samples collected simultaneously or nearly so. The relative agreement was within the combined uncertainty for only about 50% of the simultaneously collected samples, demonstrating ample opportunity for improvement. Since no program-sponsored independent standards were provided

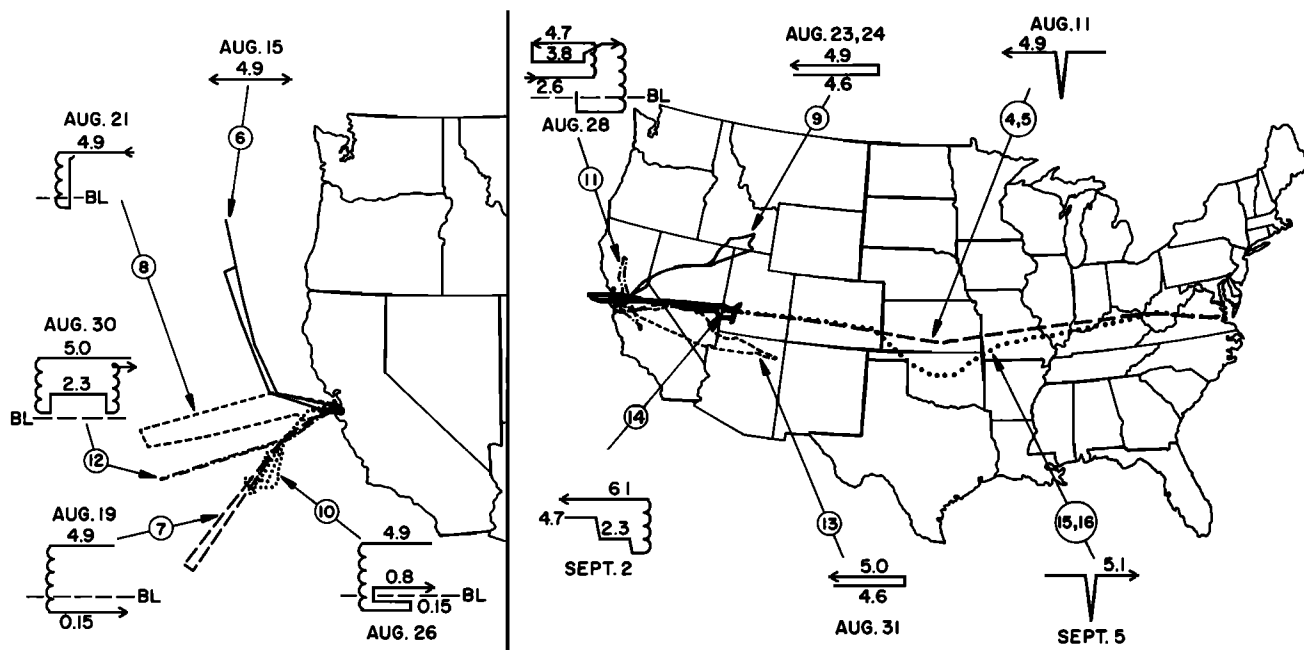


Fig. 1. The flight paths and altitudes flown over the continent and eastern Pacific. The circled numbers denote the flight number. The scalloped lines denote confined spiral ascents or descents of the aircraft. The numbers on the profiles give the altitude in kilometers. BL identifies the height of the marine boundary layer.

for the PAN instrument intercomparison, as was done for the CITE NO, NO₂, and HNO₃ intercomparisons, and because the Ames group had some difficulty in establishing its instrument calibration [Gregory *et al.*, this issue (b)], it is impossible to assess the real likely uncertainty of the measurements. Thus each group's data were taken at face value and simply merged to provide as large a data base as

possible for comparison with the NO_x data. When PAN sample collections overlapped in time, the average of the two reports was taken.

Table 2 presents a statistical summary of the individual and merged data files for an arbitrary division into results from flights above and within the boundary layer over the ocean or continent. The table includes all samples, the

TABLE 1. CITE 2 Average and Median Values at Altitudes of 4.5-6.1 km

Flight	Date	Type*	O ₃ , ppbv	CO, ppbv	NO _y , pptv	Temperature, °C	DPl, °C
4,5	Aug. 11	C, T	51.5 ± 16	108 ± 20	no data	-3.2 ± 1.1	-17 ± 10
			54 (451)	104 (53)		-3.0 (463)	-20 (483)
6	Aug. 15	O	62 ± 14	85 ± 17	816 ± 398	-4.7 ± 0.7	-16 ± 5
			68 (242)	79 (85)	954 (676)	-4.9 (250)	-17 (250)
7	Aug. 19	O	26 ± 3	59 ± 15	149 ± 42	-3.7 ± 0.7	-18 ± 2
			26 (120)	58 (24)	150 (343)	-3.8 (148)	-18 (148)
8	Aug. 21	O	48 ± 12	98 ± 14	218 ± 94	-3.2 ± 0.8	-22 ± 7
			48 (198)	98 (29)	199 (449)	-3.2 (198)	-22 (198)
9	Aug. 23, 24	C, N	45 ± 13	104 ± 25	622 ± 382	-2.2 ± 1.0	-10 ± 4
			50 (266)	108 (82)	492 (416)	-1.9 (256)	-9 (167)
10	Aug. 26	O	53 ± 11	94 ± 15	308 ± 74	-4.4 ± 0.6	-9 ± 1
			54 (77)	90 (32)	321 (223)	-4.4 (77)	-9 (89)
11	Aug. 28	C	47 ± 18	97 ± 25	230 ± 94	-3.5 ± 0.4	-16 ± 7
			57 (71)	102 (22)	235 (175)	-3.5 (71)	-13 (77)
12	Aug. 30	O	47 ± 10	87 ± 9	246 ± 65	-4.9 ± 1.2	-22 ± 7
			46 (129)	85 (33)	241 (157)	-5.4 (129)	-19 (129)
13	Aug. 31	C	54 ± 8	105 ± 18	497 ± 206	-5.2 ± 1.8	-19 ± 7
			54 (269)	104 (84)	434 (495)	-5.3 (271)	-20 (271)
14	Sept. 2	C	46 ± 12	102 ± 10	209 ± 108	-9.8 ± 4.3	-23 ± 7
			45 (154)	99 (43)	199 (467)	-10.5 (158)	-22 (158)
15, 16	Sept. 5	C,T	38 ± 11	91 ± 23	303 ± 188	-6.6 ± 10.	-21 ± 7
			42 (396)	84 (125)	259 (1307)	-6.8 (425)	-21 (425)

The first row gives the average and standard deviation, and the second row gives the median and the number of samples, in parentheses.

*C, continental flight; T, transit flight; O, ocean flight; N, nighttime flight.

TABLE 2. PAN Data Intercomparison

	Altitude, km	Merged Data	NCAR	Ames
Ocean	4.5-5.0	137 ± 102	121 ± 95	154 ± 103
		117	97	145
		(84)	(54)	(49)
Ocean	0.6	6.8 ± 4	4.3 ± 3	9.3 ± 4
		6	4	10
		(13)	(8)	(7)
Continental	4.6-6.1	149 ± 100	128 ± 79	177 ± 115
		141	120	156
		(195)	(131)	(91)
Continental	≤2.6	172 ± 216	185 ± 239	176 ± 237
		127	127	52
		(29)	(23)	(10)

All mixing ratios are in units of pptv. The first row gives the average and standard deviation, the second row the median, third row the number of samples. The data were not always taken at same time, so the differences also include real variabilities in the atmospheric abundance of PAN.

majority of which were not collected simultaneously, so that averages from the individual data files do not have to agree because of both atmospheric and instrumental variability. The degree of atmospheric variability is exemplified by the large standard deviations, particularly in the continental mixing layer flights where larger PAN levels were measured, not unexpectedly. Air mass inhomogeneity and different sampling frequencies in the continental mixing layer can account for the large difference in average values in Table 2. However, the averages for the ocean and continental middle free troposphere and the continental mixing layer are within or close to being within the combined uncertainty expected for the two groups of measurements. Thus the conclusions based on the merged data file are likely reasonable in spite of the larger than expected disagreement found sometimes between the measurements by the two groups [Gregory *et al.*, this issue (b)]. In the ocean boundary layer the averages or medians differ by over a factor of 2, but at very low ambient mixing ratios, only several times instrument detection limits.

3. RESULTS AND DISCUSSION

Other papers [LeBel *et al.*, this issue; Huebert *et al.*, this issue; Singh *et al.*, this issue; Carroll *et al.*, this issue; G. Hübler *et al.*, Airborne measurements of reactive nitrogen oxides, submitted to *Journal of Geophysical Research*, 1990] have addressed the detailed behavior and distribution of HNO₃, PAN, NO_x, and total odd nitrogen, NO_y, observed during these flights. Here the focus is on the broader relationship of PAN within the odd nitrogen budget. To provide a reference for the magnitude of the mixing ratios, Figures 2 and 3 summarize the observations on a flight-by-flight basis. Figures 2a and 2b present the NO_x and PAN data, respectively, from over the continent (C) or ocean (O) at altitudes above 4.5 km but below 6.1 km. (All altitudes

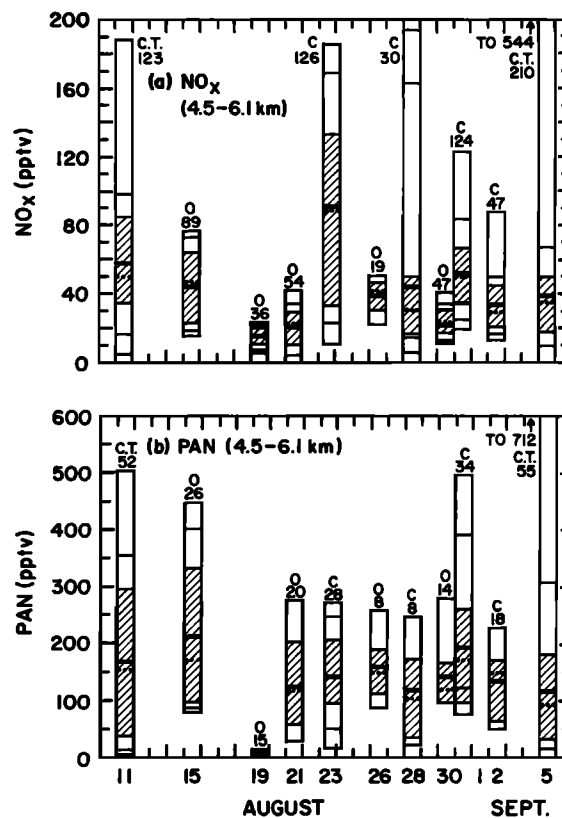


Fig. 2. The flight by flight mixing ratios in the middle free troposphere. (a) NO_x over the ocean (O) and continent (C). T denotes the continental transit flights. The number of samples is given near the top of each bar. The bar represents the range, the next inner rectangle is the central 90%, and the shaded region is the central 67% of the observations. The average is represented by the bold line, and the median by the dotted line. (b) PAN.

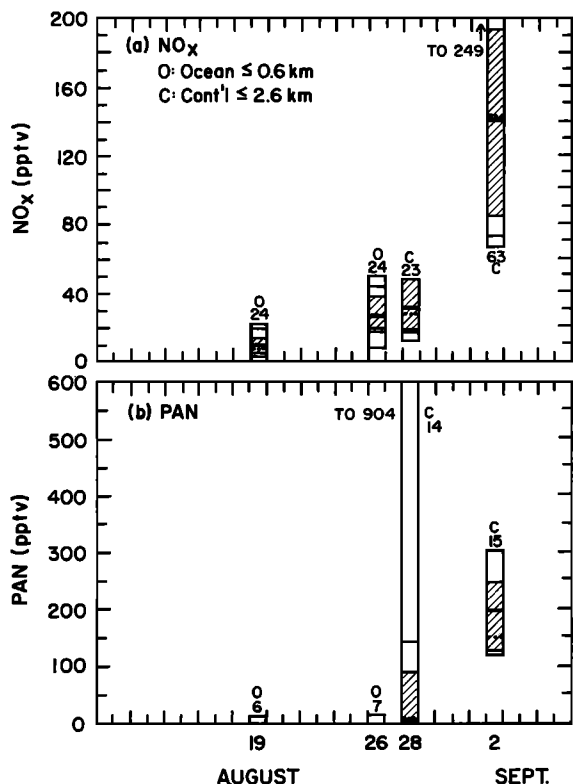


Fig. 3. Same format as Figure 2 but for portions of the maritime flights below 0.6 km, or for continental flights below 2.6 km above mean sea level.

over the ocean or continent referenced here are pressure altitudes or altitudes above mean sea level.) Figures 3a and 3b present the data obtained within the marine boundary layer at altitudes below 0.6 km or, if over the continent, for altitudes below 2.6 km. All of the NO_x observations are included, not just those coincident with the measurements of PAN. In these figures the longest open rectangle represents the range of the measurements, the next inner rectangle is the central 90% of the measurements, and the next shaded rectangle is the central 67%. The average is given by the bold horizontal line, and the median by the bold dotted line. Clearly, the figures and Table 1 reveal the real-world atmospheric variability of the trace species encountered during the whole program and during most individual flights.

On the flights made in the middle free troposphere over the ocean, NO_x did not exceed 80 pptv and was usually less than 40 pptv. Such low values were expected from the earlier CITE flights [Davis et al., 1987; Ridley et al., 1987, 1988a, b, 1989]. Over the continent, above 4.4 km, the average or median values were near or below 50 pptv except during the nighttime flight 9 (August 23, 24), but the range of values was usually much larger than those observed over the ocean. Values of NO_x (and PAN) as low as those over the ocean were also observed during the continental transit flights 15, 16 (September 5). Excursions to larger mixing ratios were expected due to penetration of the mixing layer or due to stochastic injection of near-surface emissions by convective activity. One example is given by flight 14 of September 2 (Figure 3a), where the range of NO_x at lower altitudes is significantly larger than that above 4.5 km (Figure 2a). A second example is given in flight 10 (August

28). Figure 3a apparently shows that the range of NO_x values for this continental flight was small. However, the NO_x instruments were shut off to avoid excessive contamination when the polluted boundary layer over the San Joaquin valley was penetrated. In the boundary layer, PAN was near 1 part per billion by volume (ppbv), as shown in Figure 3b.

At altitudes above 4.5 km the PAN mixing ratios over the ocean or continent were usually larger than NO_x, but rarely above 400 pptv. Note that the ordinates of Figures 2b and 3b are 3 times those of Figures 2a and 3a. There is also not as sharp a contrast in the range of PAN mixing ratios between the continental and oceanic flights. Surprisingly, the PAN levels measured here over the eastern Pacific ocean were considerably larger than those measured over the Atlantic ocean [Rudolph et al., 1987], where a greater influence from continental North America might have been expected. Very small mixing ratios, usually less than 20 pptv of PAN (or NO_x), were found in the eastern Pacific marine boundary layer.

Although remarkably low mixing ratios of PAN and NO_x were observed during portions of the transit flight back to Wallops, flight 7 (August 19) stands out by having consistently the lowest mixing ratios of PAN and NO_x of all the flights, and with apparently little difference between the middle free troposphere and the marine boundary layer. Possible reasons for this difference are discussed later.

To give the general altitude trends observed for PAN, Figure 4 summarizes PAN measurements made by NCAR during the confined spiral ascents or descents (Figure 1) over

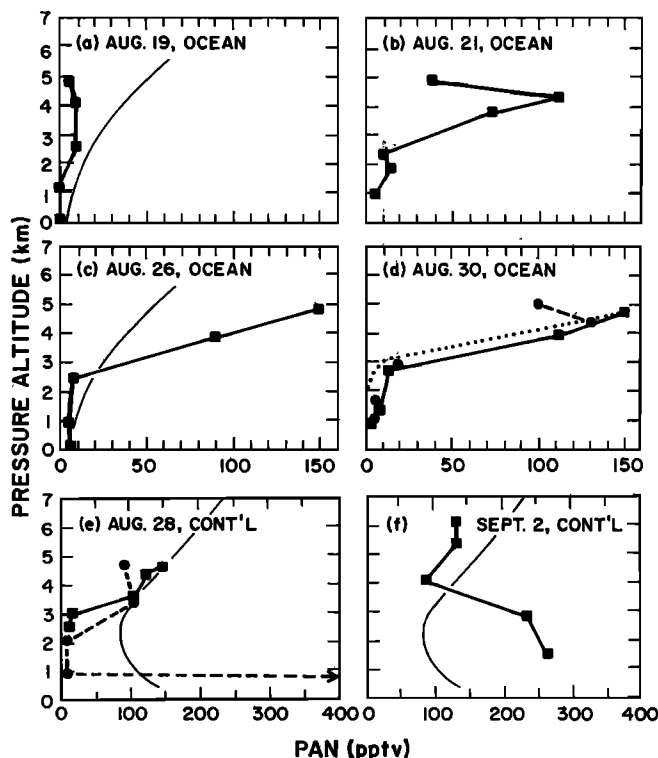


Fig. 4. Altitude profiles of PAN during the confined spiral ascents or descents. The dotted line in Figure 4d is discussed in the text. The result from the Kasting and Singh [1986] model for the summer ocean region and the continental region is given as the solid light line in Figures 4(a), 4(c), 4(e) and 4(f).

the ocean or continent. Over the ocean, PAN mixing ratios decreased rapidly with decreasing altitude and warming except for flight 7 (August 19). It is not clear from the few profile observations whether PAN might continue to increase with higher altitudes or whether the standard flight pressure altitude of the Electra was near a maximum in PAN. Future flights will be required to investigate this important aspect, although *Singh et al.* [this issue] present reasonable evidence that PAN maintains high abundances at higher altitudes. Over the continent the observations were more variable, but as expected, larger values were usually observed within the mixing layer due to higher precursor concentrations and active photochemical production of PAN. NO_x also usually decreased with decreasing altitude, although layers of higher mixing ratios were sometimes observed with these instruments, which had faster sampling rates than the PAN instrumentation.

For presentation and discussion of the simultaneous measurements of NO_x and PAN the observations are separated into those made over the ocean and those made over the continent. Most observations were made at constant pressure altitudes between 4.5 and 6.1 km in the middle free troposphere to provide optimum conditions for the instrument intercomparison objectives of CITE 2. Only a few excursions to higher altitudes or to the boundary layer were made. Consequently, simultaneous measurements in the lower free troposphere and marine boundary layer are quite limited.

Trajectory analyses [*Shipham et al.*, this issue] reveal that this simple geographic division also at least separates those flights which were made in air masses of maritime origin where no continental influence occurred for at least the period of the trajectory analysis (2.5 days). The only exception was a portion of flight 6, August 15, where the trajectory analysis indicated a possible contribution of air from over the continent, but not from the continental mixing layer. The actual period of no continental influence for the remaining ocean flights was likely 2-3 times this 2.5-day period, based on the origin of the back-trajectories. Thus the majority of flights over the ocean can be considered to have been in air masses aged a week or more photochemically with respect to the last chance for significant precursor or secondary photochemical product input from continental regions. However, the lifetime of PAN in the 4.5- to 6-km region is longer than a week, so the trajectory analyses do not rule out continental sources of PAN or precursors, only recent continental influence.

MARITIME FLIGHTS

Middle Free Troposphere

Figure 5 gives the ratio of coincident observations of PAN to NO_x for the ocean data set for the middle free troposphere. The NO_x measurements have been averaged over the 2- to 4-min sampling integration period required for the PAN measurements. On four of the five flights, where reservoir PAN strongly dominates active nitrogen, the median or average values of the ratio all lie between 4.7 and 5.8. (Portions of two flights made over the continent that are discussed later were also within maritime air masses, and these supported similarly high values of the ratio.) The range for the ratios on any given flight was also substantial except for flight 7, August 19. Some of the largest ratios, above about 10, are not very accurate because NO_x approached,

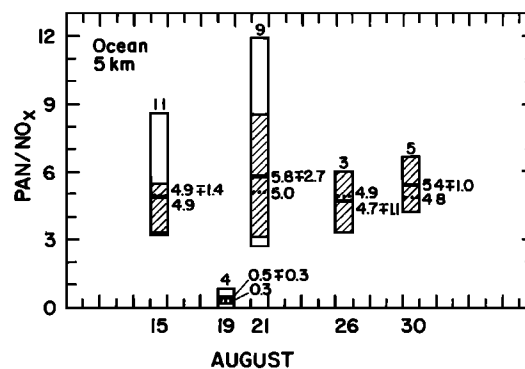


Fig. 5. The PAN/NO_x ratios from simultaneous measurements over the ocean at 5 km. The format is the same as for Figure 2. The average, standard deviation, and median are labeled to the side of each bar. The number of samples is given at the top of each bar.

while PAN remained well above, the instrument detection limits. The magnitude of the ratios was a surprise. On the basis of the very low mixing ratios of NO and NO₂ observed in this region on the previous two CITE missions in fall 1983 and spring 1984, we had become accustomed to considering this a pristine region with respect to odd nitrogen with photochemically more stable HNO₃ being the dominant form [*Huebert and Lazrus, 1980; Huebert, 1980; Galasyn et al., 1987*].

Figure 5 also shows that the number of concurrent PAN and NO_x measurements was not large. However, the dominant trend of large PAN to NO_x ratios is maintained if the ratio of average or median values derivable from Figures 2a and 2b is considered.

The importance of the roles of in situ photochemistry versus long-range transport for the maritime middle free troposphere, discussed in the introduction, can be addressed from the concurrent measurements. By comparison with available atmospheric models for the region it is unlikely that the high PAN to NO_x ratios and the large mixing ratios of PAN can be sustained by in situ production from the background precursor mixing ratios in the eastern Pacific free troposphere. By background we mean mixing ratios near the average for NMHCs and NO_x measured during these and earlier CITE 1 flights. For example, *Kasting and Singh [1986]* formulated a one-dimensional model to address the role of PAN in the eastern Pacific. The model was tuned to have NMHC and NO_x levels representative of CITE observations and had stratospheric and lightning sources of NO_x. The model-calculated summertime profile of PAN is compared to the confined profile data in Figures 4a and 4c. Model abundances of PAN are much lower than the majority of the data in the 4- to 5-km region. An exception, when the model profile is in better agreement with the observations, is flight 7 (August 19), where PAN and most other trace species were significantly lower than observed on the other maritime flights. From the model, for August at 5.5 km, and with temperatures several degrees colder than those measured during the present flights the steady state PAN to NO_x ratio was only about 1.3, and the PAN mixing ratio was only about 60 pptv. Both the ratio and abundance are significantly lower than the minimum values of Figures 2 and 5 for the flights of August 15, 21, 26, and 30. Both comparisons show that the model precursor abundances were

too low to give a large enough formation rate of PAN, even though the PAN destruction rate at these altitudes and temperatures is very small. Calculations by R. Chatfield (private communication, 1988) using a different model give similarly low ratios and mixing ratios for typical background conditions. Thus unless the PAN over the ocean results from collective sporadic high precursor abundances of NO_x from the stratosphere or lightning and NMHCs, possibly from ocean sources, the results from the bulk of the maritime free troposphere flights imply other sources, presumably long-range transport of PAN or its precursors from continental regions. Over the continent, and at the same altitude, the Kasting and Singh model predicted a PAN abundance near 200 pptv (see Figure 4e) and larger PAN to NO_x ratios of 3-4 due to greater PAN production from much larger near-surface fluxes of precursors. The model results for the continent are in better agreement with the maritime observations (and continental observations to be described), a result that also supports a long-range transport source of PAN or precursors to the ocean region. The observations do not imply that in situ photochemical formation of PAN from background precursor levels is unimportant in model simulations of the eastern Pacific but that it is often outweighed by continental influences.

The relatively large mixing ratios of PAN and the large ratios of PAN to NO_x are supportive of either the theory that PAN results primarily from long-range transport from continental production regions or that PAN was formed from precursor injection earlier in the air mass history. Clearly, precursor injection over continents allows continued photochemical partitioning of NO_x to reservoir species including PAN along the trajectory, but the bulk of the transformation would occur within a few days of injection. Thus both processes are considered here to be a long range transport source of PAN to the Pacific maritime middle free troposphere. The average temperatures for the four high-ratio flights of Figure 5 were in the range of 268-270 K (see Table 1). Using the observed NO₂ to NO ratios [Carroll *et al.*, this issue] the lifetime of PAN (equation (4)) at these altitudes was 14-21 days, much longer than the 1- to 2-day lifetime of NO_x. Consequently, and provided the air mass remained near or below these temperatures, PAN and NO_x are well decoupled photochemically; NO_x transformed to PAN is essentially locked into the PAN reservoir. In the long-range transport case the PAN abundance is then governed by its rate of injection, or the rate of injection of precursors, and subsequent formation rates, from source regions over the continent and by atmospheric mixing. Remaining NO_x would continue to be transformed to reservoir species such as HNO₃, PAN or other organic nitrates, and HO₂NO₂ with an overall time constant of 1-2 days, resulting in an increase in the PAN to NO_x ratio but with relatively smaller increases in the PAN abundance since so little NO_x remains. With such disparate lifetimes, only a few days are required to give large ratios of PAN to NO_x and correspondingly low mixing ratios of NO_x, even if the initial PAN to NO_x ratio was near or less than unity, as is typical of continental boundary layer regions in summer [Singh *et al.*, 1985; Fahey *et al.*, 1986].

Further support for the importance of long-range transport as opposed to gradual production from background alkanes results from the observations that PAN mixing ratios correlate significantly and positively with precursor NO_x and measured NMHCs and with photochemically produced

counterparts, O₃ and HNO₃ [Singh *et al.*, this issue]. In particular, during the high-ratio flights over the ocean there was a significant correlation of PAN with CO and chlorofluorocarbon 11 from continental source regions. It is also likely that the correlation with precursor NO_x results from photochemistry along trajectories after continental source influences, although the correlation with NO_x and with O₃ could be reinforced by upper tropospheric/lower stratospheric sources if the PAN mixing ratio does continue to increase with altitude above the flight level. However, the majority of middle free troposphere flights show that the PAN to NO_x ratios were high and that simultaneously the NO_x mixing ratios were very low, usually less than 40-50 pptv. Since NO_x levels are a good indicator of the age of an air mass, the chemical observations also imply that the ocean middle free troposphere air masses were well aged photochemically. By comparison with the age derived from the back-trajectory analyses, PAN to NO_x ratios of about 5, and low NO_x, are likely typical of isolated maritime middle free tropospheric air masses of an age of 1 week. Clearly, these air masses could not have suffered much vertical motion to altitudes where the PAN lifetime was short or there was significant mixing with warmer air masses prior to the measurements.

The interpretation given above is substantiated by Figure 6, where the PAN to NO_x ratios for altitudes above 4.5 km over the ocean and the continent are considered. The format is the same as that used in presentation of ground-based studies at Niwot Ridge, Colorado [Singh *et al.*, 1985]. The ratio is plotted as a function of the NO_x mixing ratio, which is used as an indicator of the age of the air masses involved. The crosses represent a 12-point average with the range required given by the horizontal line and the standard deviation given by the vertical line. A filter has been applied in the averaging to exclude PAN mixing ratios less than 25 pptv, or all of the data from the flight of August 19 and portions of the return transit flight of September 5. As is discussed later, we believe the history of these air masses was quite different from the majority and most likely of tropical or low-altitude origin. The solid lines represent the expected relationship for constant PAN mixing ratios of 100

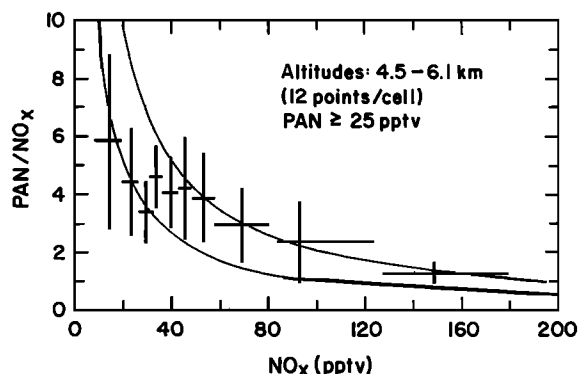


Fig. 6. The PAN/NO_x ratio versus the NO_x mixing ratio for the middle free troposphere over the ocean or continent. Each cross is the average of 12 samples. The vertical line is the standard deviation, and the horizontal line is the range required for the 12 samples. PAN mixing ratios below 25 pptv have been excluded (see text). The upper and lower solid curves are for constant PAN mixing ratios of 200 and 100 pptv, respectively.

and 200 pptv. There remains a clear trend of increasing PAN to NO_x ratio with decreasing NO_x levels, a result consistent with increasing age from source locations and consistent with photochemical decoupling of PAN and NO_x. Figure 4, or a comparison of Figure 2a with Figure 2b, shows that the lower ratios were usually found over the continent, not so much because PAN was significantly lower but because the NO_x mixing ratios were larger, an observation readily attributable to the proximity of source regions. Singh *et al.* [1985] observed a similar trend for ground-based summertime measurements at Niwot Ridge, Colorado. However, the largest ratios observed in that study for summer conditions were about 1.3 at NO_x levels of just over 100 pptv. Ratios at least 5 times larger were observed in the summertime middle free troposphere, a result of isolation, aging, and much colder air temperatures. Indeed, values for the ratio of 3-4 were observed in ground-based studies in autumn at Niwot Ridge and in early spring at Alert, in northern Canada [Bottenheim *et al.*, 1986], when ambient temperatures were closer to the aircraft measurements.

The evidence for a long-range transport source of PAN is also supported by the large range observed for the PAN/NO_x ratio even during the high average ratio flights. Clearly, there must also be contributions to the range from air mass components where PAN and NO_x levels are closer to background steady state model simulations, such as was encountered during the August 19 flight. However, the range also likely reflects the differences revealed by the 60-hour back-trajectory calculations [Shipham *et al.*, this issue], although an even earlier time and temperature history would be very relevant. Flight 6 (August 15) sampled a variety of air masses having either maritime polar or maritime tropical character, as well as a mixture of both types including components from the upper troposphere over the west coast. Flight 8 (August 21) sampled air that 60 hours earlier was from just northeast of Hawaii or between 30° and 40°N near 150°W. Flight 10 (August 26) received air from the south near 20°N and 130°W during the early portion of the outbound leg at 4.9 km, while for the rest of this leg the air came from the north in the vicinity of 40°-50°N and 140°-160°W. Flight 12 (August 30) received air that 60 hours earlier had been predominantly in the north central Pacific near 40°-45°N, 140°W. In these flights, O₃, CO, and NO_y (Table 1) exhibited considerable variability at 4.9 km, also likely reflecting differences in history. However, at the time of the measurements the air masses were likely sufficiently aged with respect to odd nitrogen from continental source regions to have essentially depleted most active nitrogen originating from continental sources. The NO_x observed during the flights then was not just residuals from continental injection, but also was from the stratosphere, lightning activity, commercial aircraft, and slow transformation of reservoir PAN, HO₂NO₂, HNO₃, N₂O₅, and other organic nitrates. Thus if the present observations are applicable to a much broader region of the Pacific, it is moot to question which continents are providing the sources of PAN or precursors. Instead, odd nitrogen stochastically injected from source regions can be locked in the PAN reservoir and distributed hemispherically. Furthermore, the bulk of the maritime observations made here have an important implication for the North American continental middle free troposphere. Clearly, many of the ocean air masses encountered in these flights will travel eastward, so

that PAN levels measured there in the continental middle free troposphere will not necessarily have originated from near-surface sources.

An exception to the dominance by high ratios of PAN to NO_x in the middle free troposphere maritime data is found in flight 7, August 19. This flight is notable because it may be more representative of the lower-latitude central Pacific region. On this flight the ratio (Figure 5) was low with a median value near 0.3 (The low ratio is also not very accurate since both the NO_x and PAN instruments were operating near detection limits. However, the ratio is certainly much less than the other four flights.) The low ratio is not due to a shorter lifetime for PAN. The air temperature (Table 1) was similar to the other four flights. A PAN/NO_x ratio near unity would be expected for recent primary or secondary species injection. However, this was certainly not the case for this flight. First, the observed mixing ratios were much too low for recent injections. From Figure 2, both the mixing ratios of PAN and NO_x and their range were considerably smaller for this flight. Second, the trajectory analysis does not show anything particularly distinguishing for this flight relative to the four high-ratio flights. At 4.9 km the air 60 hours earlier was in the north central Pacific, 35°-40°N, 150°-160°W. At lower altitudes, near 3-4 km, the air was mostly from the south in the vicinity of 25°-30°N, 125°-135°W. In the marine boundary layer it was from the north near 40°-45°N, 130°-135°W. Furthermore, Table 3 shows that all of the mixing ratios of trace species measured at 4.9 km were low and typical of the south central Pacific region, as revealed in the CITE 1 fall program. The range observed for each species was also considerably narrower than that observed on most other flights. This uniformity, indicative of a well-mixed air mass, and especially the low mixing ratios, suggests that the air mass previously originated predominantly from the marine boundary layer, cycled through or near the boundary layer where odd nitrogen species were removed, or at least suffered substantial descent and warming to dissociate PAN prior to the aircraft encounter. Air mass ascent from the near-equatorial central Pacific and descent in the eastern Pacific are a frequent synoptic pattern in summer [Danielsen *et al.*, 1987]. Another possibility is that the air mass motion was such that continental injections had not been received for a very long period of time. Indeed the observations suggest that this air mass was likely the oldest

TABLE 3. Average and Median Values at 4.9 km for Flight 7, August 1

	Median	Average	Range	Number of Samples
PAN, pptv	8	8.3 ± 3	3-15	15
NO _x , pptv	15	15 ± 4	6-24	36
NO, pptv	8	8 ± 5	0-18	51
HNO ₃ , pptv	95	98 ± 25	60-140	8
NO _y , pptv	150	149 ± 42	84-252	343
CO, ppbv	58	59 ± 2	58-63	24
O ₃ , ppbv	26	26 ± 3	17-32	120
T, C	-3.8	-3.7 ± 0.7	0.2 to -5.3	148
Dpt, C	-18	-18 ± 2	-13 to -24	148

of all of those sampled over the ocean in view of the very low CO.

There were other examples of maritime middle free tropospheric air masses supporting PAN/NO_x ratios near unity. These examples were only of short duration but are given so as not to unduly bias the frequency of large PAN/NO_x ratios shown in Figure 5. During the continental nighttime flight 9 (August 23, 24), while at 4.6 km and west of the Sierra Nevada mountains, very "clean" air was encountered with O₃ ~ 15-20 ppbv, NO_y ~ 80 pptv, NO_x ~ 10-20 pptv, and PAN ~ 20 pptv. The trajectory analysis for this portion of the flight [Shipham *et al.*, this issue] showed the air to be of maritime tropical origin that 60 hours earlier had been almost due west well out over the eastern Pacific.

Another example was provided by flight 11 (August 28), which was made at several altitudes over the San Joaquin and Sacramento valleys of California. At the highest altitude of 4.7 km, maritime polar air was encountered, and PAN/NO_x ratios were high and near 5 (Figure 8). Above the mixing layer, and at 2.6 km, very clean air was still encountered with mixing ratios similar to those given just above for the clean portion of flight 9 (August 23, 24) and with a PAN/NO_x ratio near unity. Here the trajectory analysis again revealed air of maritime tropical origin similar to flight 7 (August 19). However, a lower PAN/NO_x ratio is also consistent with the shorter lifetime of PAN at air temperatures ranging from 283 to 288 K at 2.6 km.

Lower Free Troposphere and Marine Boundary Layer

Although Figure 4 gives local altitude profiles of PAN, the number of concurrent measurements of NO_x was very limited. Consequently, overall altitude variations of the PAN to NO_x ratio for all of the ocean flights is given in Figure 7. Included in the figure is the steady state ratio predicted by the *Kasting and Singh* [1986] model, which, as discussed previously, is unable to account for the majority of the high-altitude observations. Although there is considerable variability in the ratio, especially at the higher altitudes, there is a clear trend of decreasing ratio with decreasing altitude because the PAN mixing ratios decreased more

rapidly than did NO_x. The trend is as expected. The PAN pseudoequilibrium of equations (1) and (2) shifts to favor NO_x and PA radicals, a shift that illustrates the importance of PAN in the remote atmosphere. Since NO_x is so low, PA radicals can be transformed photochemically to other oxygenated hydrocarbons and NO_x can lead to an increased rate of O₃ production or suffer a net conversion to HNO₃, since hydroxyl concentrations are expected to increase with decreasing altitude. Although HNO₃ has a long photochemical lifetime, its near-surface or near-boundary layer lifetime is short due to wet deposition or incorporation in cloud droplets. The low-altitude observations are consistent with the marine boundary layer, or air masses which have descended (and warmed) to near the marine boundary layer, being cleansed of odd nitrogen.

Figure 1 shows that three flights penetrated the marine boundary layer. Of these, flight 8, made on August 21, allowed but a short time for measurements. Consequently, the number of observations, especially coincident observations of PAN and NO_x, was very limited. NO_x in the marine boundary layer was usually very low, less than or near 20 pptv (see Figure 3a), an expected result based upon observations reported from the CITE 1 programs mentioned previously. PAN was also very low with mixing ratios less than 20 pptv (Figure 3b), similar to the measurements made during the DYCOMS project but significantly lower than the average of 38 pptv reported by *Singh et al.* [1986] for the ship-based measurements mentioned earlier. Whether this difference for the latter measurements is a seasonal trend or due to the proximity of the ship to the coast with the possibility of continental contamination is unclear.

During flight 7, August 19, three coincident samples gave a median PAN/NO_x ratio of 0.2 and a range of 0-0.4. This median value is very close to the median of 0.3 observed at 4.9 km during this flight. (Figure 4 implies a more or less constant mixing ratio of PAN with decreasing altitude. However, the air mass during the descent was not uniform. The top of a subsidence inversion at 3.4 km [Shipham *et al.*, this issue] supported strong increases in O₃, NO_x, and NO_y [Carroll *et al.*, this issue; G. Hübler, submitted manuscript, 1990], but no PAN sample was taken during this spike.) Five

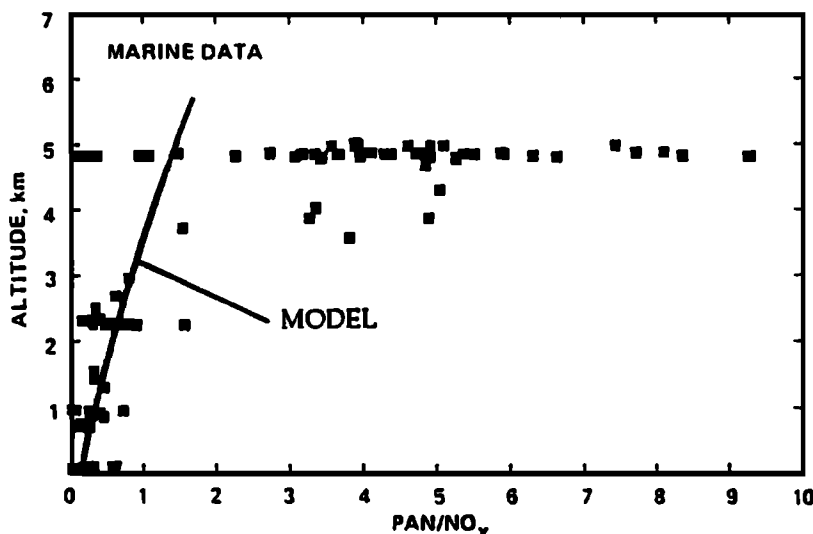


Fig. 7. The altitude variation of the PAN/NO_x ratio for all of the flights over the ocean. The solid curve is from the model of *Kasting and Singh* [1986].

coincident samples in the marine boundary layer during flight 10, August 26, gave a similarly low median of 0.3 for the PAN to NO_x ratio with a range of 0.2-0.4.

Although these medians are not very accurate for reasons given previously, the marine boundary layer ratios are (1) much smaller than the majority of maritime middle free troposphere results, (2) characterized by small mixing ratios of both species, and (3) characterized by a narrow range of values. The narrow range is expected for the well-mixed marine boundary layer. The low mixing ratios of NO_x signify both an aged marine boundary layer and one in which in situ production of PAN cannot be important because it is NO_x precursor limited. Because the temperatures in the marine boundary layer at 0.15-0.3 km were typically near 288 K, the PAN lifetime was only about 8 hours. The net effect of a rapid dissociation of PAN to NO_x and PA radicals and precursor-limited production is a small steady state abundance of PAN. Indeed it is possible that a significant fraction of the small NO_x abundance in the marine boundary layer is due to PAN to NO_x conversion.

The contrast in abundances of PAN and NO_x and their ratio between the middle free troposphere and the marine boundary layer is illustrated by the altitude profiles of PAN given in Figure 4. The profiles of Figure 4d were measured under the influence of large-scale subsidence in the flight region, a frequent synoptic condition for this region of the Pacific ocean. In fact, many of the flights were made under these conditions to ensure high photochemical activity at the flight altitudes. The rapid decline in the PAN mixing ratio with decreasing altitude is readily rationalized by the decrease in photochemical lifetime with increasing temperature in a region where photochemical production is limited. With subsidence at velocity v_s the mixing ratio of PAN at altitude z ($0 \leq z \leq 4.9$ km) is approximated by

$$\text{PAN}(z) = \text{PAN}(4.9 \text{ km}) \exp -z^{4.9} (\tau_{\text{PAN}} v_s)^{-1} dz \quad (5)$$

The dashed curve of Figure 4d, which reproduces the major features of the observed profile, was calculated from (5) using the observed temperature profile, a constant NO₂ to NO ratio of 2.5, and a reasonable value for v_s of 0.25 cm s⁻¹. Clearly, downward advection and warming will decrease the PAN abundance, add NO_x and PA radicals to the lower troposphere, and decrease the PAN to NO_x ratio. Analogous processes would occur for transport from cool high latitudes to warm low latitudes. Furthermore, reservoir PAN acts like other sources of odd nitrogen in the remote troposphere. The stratosphere, lightning, commercial aircraft, PAN, and HO₂NO₂ can all contribute to a downward flux of active nitrogen.

Peroxyacetyl Radicals (PA)

An upper limit estimate of the daytime concentration of PA radicals in the maritime air masses can be made by ignoring reaction (3) and production of PA radicals and assuming reactions (1) and (2) are balanced. Then,

$$[\text{PA}] = k_1 [\text{PAN}]/k_2[\text{NO}_2] \sim 1.4k_1[\text{PAN}]/k_2[\text{NO}] \quad (6)$$

since the daytime NO₂/NO ratios were typically near 2.5 [Carroll *et al.*, this issue]. With middle free troposphere temperatures near 268 K, and PAN/NO_x near 5, the PA concentration estimate is 3×10^7 cm⁻³ or just over 2 pptv. Since representative model calculations [Carroll *et al.*, this issue] for the flights in the middle free troposphere predict

HO₂ concentrations of 15-25 pptv and CH₃O₂ concentrations of 10-20 pptv, PA radicals could typically account for a maximum of 10-20% of the oxidizing power of HO₂ or CH₃O₂ upon NO to produce O₃. In the marine boundary layer a similar calculation yields just over 10⁷ cm⁻³ or 0.4 pptv of PA radicals, which results in an insignificant contribution to NO oxidation compared to HO₂ and CH₃O₂ species. Nevertheless, if the PAN levels measured here in the middle free troposphere over the ocean are typical of much larger maritime regions, then PAN and PA chemistry obviously cannot be ignored in atmospheric models of remote regions. This is particularly true for questions of O₃ production, which is often nearly in balance with O₃ loss in this region of the atmosphere [Chameides *et al.*, 1987, 1989; Ridley *et al.*, 1987, 1989].

CONTINENTAL FLIGHTS

Middle Free Troposphere

The largest number of concurrent measurements of NO_x and PAN was made in the continental middle free troposphere at pressure altitudes between 4.6 and 6.1 km. The PAN to NO_x ratios are given in Figure 8. Here the average and median values range from 1.4 to 5.7 with the lowest values occurring during the nighttime flight 9 (August 23, 24). The other flights have medians ranging from 2.7 to 5.7, apparently a broader range of medians than was observed over the ocean. Many of the PAN/NO_x ratios remain remarkably large, indicating substantial photochemical aging for all but the nighttime flight.

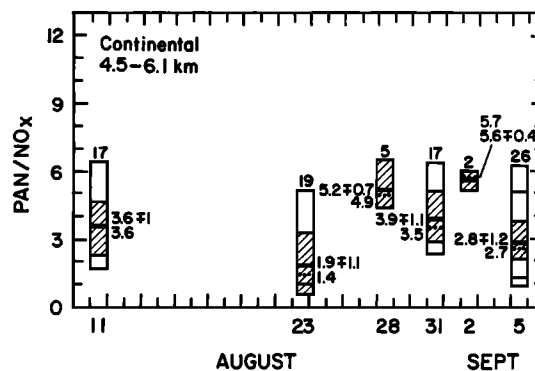


Fig. 8. Same as Figure 5 but for the middle free troposphere over the continent.

In part the range of median values observed in the continental middle free troposphere is an artifact of the simple geographic separation of the flights. Flight 11 (August 28) was flown at various altitudes above the Sacramento and San Joaquin valleys of California. At middle free troposphere altitudes the air was of maritime origin [Shipham *et al.*, this issue] and should have been included with the ocean data set. Clearly, the median ratio of 4.9 compares favorably with the majority of the ratios for the ocean middle free troposphere flights of Figure 4. The higher median of 5.7 for flight 14 (September 2) is explained similarly.

Ignoring the nighttime flight 9 (August 23, 24) for the moment, the remaining median ratios range from 2.7 to 3.5,

lower than observed in the maritime air masses. As well, minimum values of the ratio for any continental flight were predominantly smaller than minimums measured over the ocean. The explanation is trivial. As discussed previously with reference to Figure 6, on average, NO_x was larger in the continental flights, as expected for nearby sources in the mixing layer and exchange to the middle free troposphere, while the range of PAN levels was much the same as that over the ocean. Consequently, the ratios are smaller as a result of mixing with less photochemically aged air over the continents.

The nighttime flight is a clear example. For the first part of this flight, up until near the Sierra Nevada mountains, NO_x (or NO₂) values were typically 25-40 pptv, and PAN/NO_x ratios were 4-5, typical of most of the maritime air masses discussed previously. During and after crossing the mountains, for about another hour of the flight, turbulence due to convective activity and likely orographic lifting was encountered. The planetary boundary layer was above the flight pressure altitude of 4.6 km, and NO_x peaked at 200 pptv, while PAN reached 200-250 pptv. Near the turnaround point over Idaho, both species mixing ratios decreased as the planetary boundary layer (PBL) was cleared, and the ratio increased to near 4. Frequent lightning flashes were observed some 30-50 km distant in this area. The lightning is referenced not because we believe NO_x was larger in the vicinity due to electrical activity (although it is possible), but as an indicator of large-scale convection in the flight region. However, with photochemical activity stopped, exchange and mixing of fresher NO₂ or penetration of the PBL accounts for the low flight average or median PAN to NO_x ratio observed during this flight. Figure 2a shows that average NO_x was significantly larger during the flight and that aged middle free troposphere air was being rejuvenated with new odd nitrogen emissions.

Lower Troposphere

Figures 4e and 4f present local profiles of PAN measured over the continent. As noted previously, PAN levels in the middle free troposphere are not very different from those observed over the ocean. As expected, larger mixing ratios were observed at lower altitudes within or near the

continental boundary layer due to net photochemical production near precursor source areas. Because of the paucity of concurrent measurements during the confined spiral ascents or descents the PAN to NO_x ratios for all of the continental flights are shown versus altitude in Figure 9. Here, with higher precursor concentrations over the continent, the model-calculated ratio of *Kasting and Singh* [1986], which is given by the solid line, is in good agreement with the observations. A comparison of Figure 9 with Figure 7, and although the number of observations is limited, shows that larger ratios of PAN to NO_x are evident in the 1 to 3 km altitude range over the continent. Since the temperatures at these altitudes were similar over the ocean and the continent and warm enough to allow rapid dissociation of PAN, the larger ratios reflect greater in situ photochemical production rates due to larger precursor abundances over the continent.

Figure 4e also shows some very large mixing ratios of PAN determined within the continental boundary layer, but concurrent NO_x measurements were unavailable. Clearly, ground-based studies like those described by *Singh et al.* [1985], *Fahey et al.* [1986], and *Bottenheim et al.* [1986] provide much more detailed information.

Continental Transit Flight 15/16, September 5

A variety of middle free troposphere conditions were reflected in the trace species measurements during this flight [*Singh et al.*, this issue, *LeBel et al.*, this issue]. The flight is discussed here to illustrate that the lowest mixing ratios of odd nitrogen and small PAN/NO_x ratios were not just found over the ocean. Figure 8 shows that the flight average PAN/NO_x was typical of the other continental flights. However, the figure shows also that smaller minimum ratios near unity were observed. These were due to two episodes of remarkably clean air with respect to odd nitrogen. The first was encountered for about 20 min over the eastern plains of Colorado. The second was found over Missouri. In both episodes, O₃, NO_y, NO_x, and PAN mixing ratios were about 20 ppbv, 50 pptv, 10-15 pptv, and 20 pptv, respectively. The 60-hour back-trajectories calculated for a number of positions along the flight path revealed continental polar air originating from central and northern British Columbia.

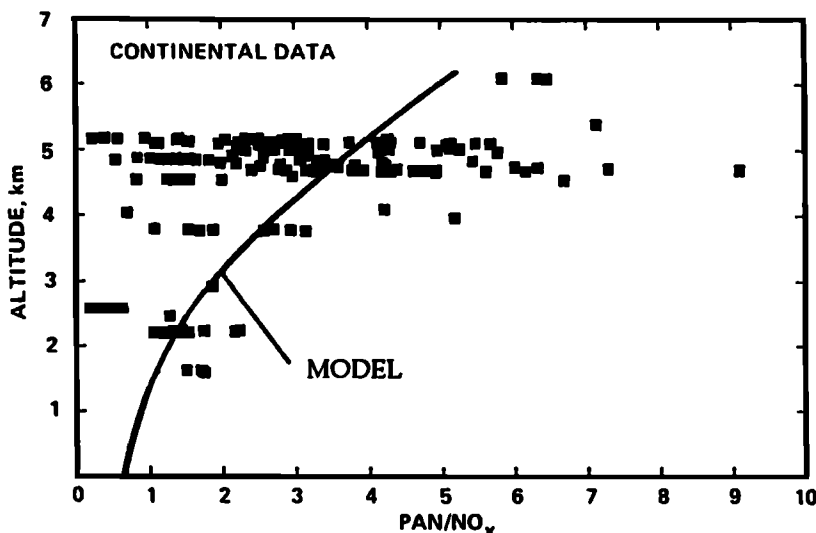


Fig. 9. Same as Figure 7 for the flights over the continent.

They also revealed nothing to distinguish these clean episodes from the rest of the flight. However, during the flight, either turbulence due to convective activity or convective cumulus cells were often noted, but not during the clean episodes. Thus it seems fairly obvious that the very clean air mass, which may well have been of maritime origin earlier in the air mass history, was suffering episodic continental injection.

SUMMARY

The flights of the CITE 2 program have shown that PAN is one of the major components of total odd nitrogen in the remote maritime and the continental middle free troposphere. In the majority of flights in the middle free troposphere, reservoir PAN dominated active odd nitrogen by average factors of 4.7-5.8 in eastern Pacific air masses and by average factors of 1.9-3.9 over the continental United States. Most important, the suite of measurements presents a strong case for the importance of long-range transport and hemispheric redistribution of PAN and ultimately active nitrogen and peroxy radicals. The observations clearly show that PAN cannot be neglected in models of the remote or background troposphere. They also exemplify the complexity of NMHC/NO_x/organic nitrate chemistry and the importance of continental boundary layer to free tropospheric exchange and, consequently, present a challenge for modeling efforts for even remote regions.

HNO₃ was also a major component of the odd nitrogen budget during these flights [LeBel *et al.*, this issue; Huebert *et al.*, this issue]. However, HNO₃ is only very slowly photolyzed to active nitrogen in the free troposphere and is therefore nearly a permanent sink of odd nitrogen, ultimately being removed by wet and dry deposition. In contrast, PAN can readily release PA radicals and NO_x through dynamic processes that cause air mass warming. Because NO_x is such a critical species in determining net photochemical O₃ production, which in turn determines the oxidative potential of the atmosphere, the observed large ratios of PAN to active NO_x guarantee an important photochemical and dynamical role for PAN in the eastern Pacific free troposphere. In addition, release of PA radicals in the lower troposphere and boundary layer under NO_x-limited conditions leads to the formation of oxygenated hydrocarbons [Calvert and Madronich, 1987].

In the marine boundary layer, these and previous CITE flights have shown that NO_x and PAN are only a few pptv. Certainly, PAN formation in the ocean boundary layer is NO_x limited. In fact, the PAN altitude profiles observed over the ocean strongly suggest that PAN decomposition may be a major source of NO_x and PA radicals to the lower free troposphere and boundary layer. Thus PAN and presumably other reservoir organic and inorganic nitrate reservoir species contribute to the downward flux of active nitrogen from the stratosphere, lightning, and aircraft over ocean regions.

There was also limited evidence that tropical air masses may have much smaller ratios of PAN to NO_x, and much lower mixing ratios of both NO_x and PAN, due to having survived a much longer time since continental influence or because of the temperature history. The present flights were limited to distances less than 800 km from the west coast of North America, and many of the measurements were made in subsiding air masses to guarantee high photochemical activity for the instrument intercomparison objectives of the

program. Consequently, the high frequency of large PAN/NO_x ratios may not be applicable to much broader and especially near-equatorial regions of the Pacific. For example, during the CITE 1 fall program, where about one half of the flights were based from Hawaii, the average O₃ mixing ratio in the middle and upper free troposphere was 27 ppbv, significantly lower than the average of 47 ppbv for the present oceanic flights. Since NO_x and PAN correlated positively with O₃ in the present flights [Singh *et al.*, this issue; Carroll *et al.*, this issue], lower mixing ratios of each species may be anticipated for the central and southern regions of the Pacific. Whether the PAN/NO_x ratio there remains frequently high, as observed in many of the present flights in the middle free troposphere, and whether the upper free troposphere contains proportionately larger abundances of PAN will have to await future experiments.

In the continental middle free troposphere, lower median PAN to NO_x ratios were observed compared to the ocean region, a result readily explained by episodic boundary layer to free tropospheric injection of younger air masses. However, the observations do show that North American continental production or precursors are not the sole source of PAN in the middle free troposphere over the United States. Significant fractions also come from other northern hemisphere sources by long-range transport.

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