experiments. It also greatly increased the rate of hydrocarbon consumption. For a second strain, significant degradation of the same two hydrocarbons occurred in the presence of the surfactant, but degradation was negligible in its absence.

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Peroxyacyl Nitrates at Southern California Mountain Forest Locations

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■ Ambient levels of the peroxyacyl nitrates [RC(O)-OONO$_2$] PAN (R = CH$_3$) and PPN (R = C$_2$H$_5$) have been measured at two southern California mountain forest locations impacted by urban photochemical smog. The highest levels recorded were 22 ppb for PAN and 4.3 ppb for PPN; 24-h averages were 2–10 ppb for PAN and 0.25–1.7 ppb for PPN. PPN and PAN were highly correlated, with PPN/PAN ratios of 0.28 (August–October 1989), 0.18 (August–September 1990), and 0.14 and 0.19 (August–September 1991). Diurnal and seasonal variations in PAN/ozone, PPN/ozone, and PPN/PAN ratios are discussed in terms of formation and removal processes for PAN and PPN. The relative contribution of olefins, aromatics, carbonyls, and paraffins to the observed PPN PAN ratios has been estimated. Other peroxyacyl nitrates measured included PnBN (R = n-C$_3$H$_7$), which was frequently observed at one location at levels of 0.2–0.4 ppb. With a detection limit of 0.2 ppb, the isoprene oxidation product MPAN [R = CH$_2$ = C(CH$_3$)] was only observed in a few instances at one location but was observed more frequently at the other at levels of 0.3–1.2 ppb.

Introduction

Photochemical oxidants that may adversely impact vegetation include ozone and peroxyacyl nitrates [RC-(O)OONO$_2$]. The two most abundant peroxyacyl nitrates are peroxyacetyl nitrate (PAN, R = CH$_3$) and peroxy-propionyl nitrate (PPN, R = C$_2$H$_5$). While the adverse effects of ozone on forests and crops are well documented, less information is available regarding the phytotoxic properties of peroxyacyl nitrates (*1–3*). The phytotoxicity of PAN has been demonstrated in several studies (*1–3*), and there is limited evidence suggesting that PPN and higher molecular weight peroxyacyl nitrates may be even more phytotoxic than PAN (*1*). In addition, ambient levels of peroxyacyl nitrates, while required to obtain a realistic assessment of photochemical oxidant damage to vegetation, have been seldom measured at locations where observations of severe oxidant damage have been recorded.

In a recent study, we carried out detailed measurements of the ambient levels of peroxyacyl nitrates at a southern California mountain forest location (*4*). This study included the first set of quantitative measurements of PPN in ambient air and described the diurnal and seasonal variations of PAN and PPN along with those of ozone at a mountain forest site severely impacted by photochemical air pollution (*5, 6*). In this study, we have measured the ambient levels of the two most abundant peroxyacyl nitrates, PAN and PPN, during the 1990 and 1991 smog seasons. These measurements were carried out at two southern California mountain forest locations including the one surveyed in 1989 as part of our earlier study (*4*). The two C$_3$-substituted peroxyacyl nitrates, namely, peroxy-n-butyryl nitrate (PnBN, R = n-C$_3$H$_7$) and peroxy-

methacryloyl nitrate [MPAN, R = CH_2=C(CH_3)] have also been measured and were present at ambient levels substantially lower than those of PAN and PPN. The results, together with those obtained in our earlier study, include peroxyacyl nitrate measurements carried out during three consecutive smog seasons and are discussed in terms of formation and removal processes for PAN and PPN.

Experimental Methods

Field Locations. Ambient levels of peroxyacyl nitrates were measured at two southern California mountain forest sites, Tanbark Flat and Franklin Canyon. Tanbark Flat (San Dimas Experimental Forest, USDA Forest Service), elevation 800 m, is located 35 km northeast of Los Angeles in the San Gabriel Mountains, a mountain range bordering the northeast side of the Los Angeles urban area. The surrounding vegetation is mostly chaparral and Coulter pine. Franklin Canyon (Santa Monica Mountains National Park), elevation 200 m, is located 25 km west of Los Angeles in the Santa Monica Mountains, a coastal mountain range bordering the northwest side of the Los Angeles urban area. The surrounding vegetation is mostly chaparral and sage. Both sampling locations are impacted by air pollution originating from vehicle and stationary source emissions in the Los Angeles area.

Measurement Method. The peroxyacyl nitrates PAN [$RC(O)OONO_2$, R = CH_3], PPN (R = C_2H_5), PnBN (R = n-C_3H_7), and MPAN [R = CH_2=C(CH_3)] were measured on site by electron capture gas chromatography (EC-GC) using and SRI Model 8610 GC and a Valco Model 140 BN EC detector (4). The column used was a 70 cm × 3 mm Teflon-lined stainless steel column packed with 10% Carbowax 400 on Chromosorb P, acid washed, and treated with dimethyldichlorosilane. The column and detector temperatures were 36 and 60 °C, respectively. The carrier gas was ultrahigh-purity nitrogen. The column flow rate was 58 mL/min. Ambient air was sampled about 4 m above ground level and was continuously pumped through a 25-mm-diameter, 1.2-μm pore size Teflon filter, a 6.4 m × 6 mm Teflon sampling line, and a 6.7-mL stainless steel loop housed in the GC oven. Laboratory experiments carried out with ppb levels of alkyl nitrates and peroxyacyl nitrates in purified air showed negligible loss at the Teflon filter inlet (<0.1, 0.73, 1.1, and 1.5% for methyl nitrate, ethyl nitrate, PPN, and MPAN, respectively). The residence time in the sampling line was 20 s. Ambient air was injected every 30 min with a timer-activated 10-port sampling valve. Retention times relative to that of PAN were typically 1.24, 1.70, and 1.92 for PPN, MPAN, and PnBN, respectively. The detection limits were 0.01 ppb for PAN, 0.02 ppb for PPN, 0.2 ppb for MPAN, and 0.10 ppb for PnBN. Additional details regarding the measurement protocol have been reported previously (4, 7). Methyl nitrate, other alkyl nitrates, and several halogenated hydrocarbons are detected by EC-GC and elute on the type of column employed in this study to measure peroxyacyl nitrates (4, 8). We have verified in previous work that these compounds do not interfere under the conditions employed when peroxyacyl nitrates are measured in ambient air (4, 8). As an additional test, ambient air samples were drawn through a heated tube inserted upstream of the EC–GC instrument, and the tube temperature was set at temperatures of 130–160 °C at which peroxyacyl nitrates, but not alkyl nitrates, are thermally decomposed (4, 8). The heights of the peaks corresponding to PAN, PPN, and either MPAN or PnBN (see Discussion) decreased by 70, 88, and 100%, respectively, at 135 °C and by 92, 94, and 100%, respectively, at 157 °C. For com-parison, laboratory tests with ppb levels of methyl nitrate, ethyl nitrate, PAN, PPN, and MPAN gave peak heights decreases of 6, 4, 80, 99, and 100%, respectively, at 190 °C.

Instrument Calibration. To calibrate the EC-GC instrument, we prepared pure PAN, PPN, MPAN, and PnBN in n-dodecane by nitration of the appropriate peracid (e.g., peracetic acid for PAN) following synthesis of the peracids from the corresponding commercially available anhydrides (4, 9, 10). Another method was used to prepare ppb levels of the peroxyacyl nitrates in order to confirm their identity and their retention times. This method involves sunlight irradiation, in a 3.5-m^3 Teflon chamber, of 0.2 ppm nitric oxide and 1 ppm of an olefin or aldehyde in purified air (4). Using this in-situ method, we have prepared PAN from acetaldehyde or from 2-methyl-2-butene, PPN from propanal, PnBN from n-butanal, mixtures of PAN and PPN from trans-2-pentene, and mixtures of MPAN and PAN from isoprene and from methacrolein.

Calibrations were carried out using ppb concentrations of PAN, PPN, MPAN, and PnBN in purified air. For the calibrations carried out in 1990, ppb levels of PAN and PPN were obtained by passing purified air over impingers containing dilute solutions of PAN or PPN in n-dodecane. The air stream was directed to a 45-L Plexiglas chamber lined with Teflon film, and purified dilution air was added to the chamber at a flow rate of 1.6 L/min. For the calibrations carried out in 1991, a constant output of PAN, PPN, or MPAN was obtained by filling a diffusion vial with a solution of PAN or PPN in n-dodecane, maintaining the diffusion vial at low temperature (2 ± 1 °C) in the freezer compartment of a small refrigerator, and diluting the output of the diffusion vial with purified air. A silica gel trap was placed upstream of the diffusion vial to minimize water condensation in the purified air stream. The impinger method described above for the 1990 PAN and PPN calibrations was also used for the PnBN calibrations, which were carried out after the field studies were completed.

In all calibrations, peroxyacyl nitrates were measured every 30 min by EC-GC, and the corresponding NO_x concentration was monitored continuously with a calibrated chemiluminescence NO_x analyzer (Monitor Labs 8840). Since chemiluminescence analyzers that use surface converters to convert oxides of nitrogen to NO respond quantitatively to peroxyacyl nitrates (11), the NO_x value from the chemiluminescence analyzer was used to quantitate the PAN, PPN, MPAN, and PnBN peak height from the GC chromatograms. Peak height vs concentration plots were constructed, and plots of peroxyacyl nitrate peak height as well as NO_x analyzer response vs 1/dilution were constructed to verify the range of linear response of the EC detector (12). Regression analysis of the linear region of the experimental data yielded the slopes, i.e., calibration factors, listed in Table I. Also given in Table I are the ratios of the calibration factors obtained for PAN and PPN. These ratios ranged from 1.23 to 1.37; i.e., the EC-GC is less sensitive to PPN than to PAN on a peak height basis. This is not unexpected since PAN elutes before PPN under our EC-GC conditions, thus yielding higher (sharper) peaks than PPN for a given concentration. In the same way, the small year-to-year changes in calibration factors reflect small changes in PAN and PPN retention times in the corresponding calibration experiments.

Results and Discussion

Ambient Levels of PAN and PPN. Ambient levels of PAN and PPN were measured at Tanbark Flat from

Table I. Electron Capture Gas Chromatograph Calibration Factors for PAN and PPN

year	calibration factor, ppt/mm[a] PAN	PPN	corr coeff PAN	PPN	ratio of calibration factors, PPN/PAN	linearity of EC-GC response, ppb[b] PAN	PPN
1989[c]	11.9 ± 0.2	15.2 ± 0.3	0.988	0.993	1.28	26	16
1990	16.9 ± 0.2	20.7 ± 0.3	0.999	0.999	1.23	60	60
1991	16.1 ± 0.3	22.2 ± 0.7	0.988	0.993	1.37	30	22

[a] ppt, parts per trillion; peak height, mm, on attenuation setting 3; least squares forced through origin, slope ± one standard deviation. [b] Upper limit tested. [c] From ref 4, included for comparison.

Table II. Lowest, Highest, and 24-h Averaged PAN and PPN Concentrations, Tanbark Flat, August 3–September 5, 1990

date	PAN, ppb lowest	highest	24-h av	PPN, ppb lowest	highest	24-h av
8/3	2.7	8.0	5.3	0.4	1.5	0.89
8/4	1.4	9.2	4.5	0.1	1.5	0.58
8/5	1.0	6.1	2.9	0.1	1.0	0.38
8/6	0.6	7.0	2.7	0.0	1.2	0.36
8/7	0.5	8.4	2.7	0.1	1.2	0.34
8/8	1.0	11.4	4.3	0.1	2.0	0.70
8/9	2.1	12.7	6.3	0.2	2.5	0.99
8/10	1.1	10.3	4.4	0.1	1.7	0.68
8/11	0.6	7.8	3.0	0.0	1.5	0.44
8/12	1.7	9.2	4.8	0.2	1.5	0.75
8/13	1.1	7.0	4.6	0.1	1.2	0.68
8/14	1.1	5.9	2.6	0.1	0.9	0.31
8/15	0.5	4.1	2.1	0.1	0.5	0.25
8/16	3.0	15.3	6.5	0.3	2.7	0.95
8/17	4.6	22.0	7.7	0.6	3.5	1.22
8/18	2.6	9.7	5.4	0.4	1.5	0.81
8/19	0.8	4.6	2.5	0.1	0.6	0.33
8/20	0.5	5.4	2.6	0.1	0.9	0.36
8/21	2.3	11.1	5.2	0.3	2.3	0.87
8/22	3.4	13.5	5.5	0.5	2.5	0.92
8/23	2.3	10.1	6.1	0.4	2.0	1.00
8/24	1.3	7.8	3.6	0.2	1.3	0.55
8/25	1.3	8.7	3.6	0.2	1.5	0.56
8/26	0.9	12.0	4.8	0.2	2.2	0.79
8/27	1.3	10.0	3.7	0.2	2.0	0.60
8/28	0.2	14.9	3.6	0.0	3.2	0.62
8/29	0.9	13.8	6.1	0.1	2.8	1.09
8/30	5.7	21.6	10.3	1.0	2.5	1.62
8/31	3.7	14.7	9.1	0.5	3.0	1.69
9/1	1.9	22.0	8.2	0.3	4.1	1.49
9/2	1.6	22.0	7.2	0.2	4.3	1.31
9/3	1.1	15.1	5.3	0.2	3.2	0.91
9/4	0.9	14.3	4.5	0.2	2.8	0.75
9/5	1.1	3.9	2.1	0.2	0.5	0.28

Table III. Lowest, Highest, and 24-h Averaged PAN and PPN Concentrations, Tanbark Flat and Franklin Canyon, 1991

date	PAN, ppb lowest	highest	24-h av	PPN, ppb lowest	highest	24-h av
			Tanbark Flat			
8/5	1.0	2.3	1.4	0.09	0.31	0.16
8/6	0.9	5.0	2.5	0.09	0.75	0.29
8/7	0.7	6.8	2.6	0.04	1.07	0.31
8/8	0.2	10.6	3.3	0[a]	2.04	0.46
8/9	0.6	12.8	4.0	0	2.66	0.62
8/10	0.4	7.2	2.6	0	1.11	0.35
8/11	0.6	5.6	2.4	0	0.93	0.31
8/12	0.3	2.3	1.3	0	0.31	0.13
8/13	0.3	3.2	1.4	0	0.44	0.16
8/14	0.2	2.5	1.0	0	0.27	0.09
8/15	0.2	6.8	2.1	0	1.02	0.26
8/16	1.1	7.0	4.0	0.18	1.33	0.64
8/17	2.3	9.6	5.1	0.31	1.86	0.83
8/18	1.6	7.0	3.9	0.22	1.20	0.56
8/19	0.6	9.4	3.4	0.04	1.86	0.52
8/20	0.6	7.2	3.4	0	1.42	0.54
8/21	0.4	5.9	2.8	0	1.07	0.41
8/22	0.7	11.1	3.9	0	2.22	0.64
8/23	0.4	8.9	3.1	0	1.86	0.46
8/24	1.2	9.0	4.0	0.13	1.95	0.64
8/25	1.4	8.8	4.1	0.18	1.60	0.6
8/26	1.0	4.3	2.7	0.13	0.67	0.4
			Franklin Canyon			
9/4	0.5	3.8	1.5	0.04	0.31	0.13
9/5	0.3	4.8	1.9	0.04	0.49	0.18
9/6	0.2	5.9	1.8	0	0.80	0.19
9/7	0.2	2.4	1.2	0	0.27	0.13
9/8	0.4	6.8	2.6	0.04	1.15	0.37
9/9	0.2	2.0	1.1	0	0.22	0.10
9/10	0.1	2.7	1.1	0	0.22	0.09
9/11	0.3	3.1	1.3	0	0.40	0.16
9/12	0.1	7.0	2.1	0	1.15	0.26

[a] 0, below detection limit of 0.02 ppb.

August 3 to September 5, 1990, and from August 5 to August 29, 1991, as well as at Franklin Canyon from September 4 to September 12, 1991, thus yielding some 2500 observations for each peroxyacyl nitrate. These observations have been compiled elsewhere (12, 13) and are summarized in the frequency distribution plots shown in Figure 1 for PAN and in Figure 2 for PPN.

Lowest, highest, and 24-h averaged concentrations of PAN and PPN are summarized in Table II (Tanbark Flat, 1990) and in Table III (Tanbark Flat and Franklin Canyon, 1991). The highest concentrations observed in 1990 were 22 ppb for PAN and 4.3 ppb for PPN. In 1991, the highest concentrations observed at Tanbark Flat were 13 ppb for PAN and 2.7 ppb for PPN; those recorded at Franklin Canyon were 7 ppb for PAN and 1.2 ppb for PPN. These values are consistent with those we recorded during the 1989 smog season, i.e., >16 ppb for PAN and 5.1 ppb for PPN (4). The corresponding 24-h averages, which are relevant to vegetation exposure to phytotoxic pollutants, were 2.1–10.3 ppb for PAN (0.25–1.7 ppb for PPN) at Tanbark Flat in 1990, 1.0–5.1 ppb for PAN (0.1–0.8 ppb for PPN) at Tanbark Flat in 1991, and 1.1–2.6 ppb for PAN (0.1–0.4 ppb for PPN) at Franklin Canyon.

Diurnal Variations. Time series plots of 24-h averaged concentrations, illustrated in Figure 3 for 1990 at Tanbark Flat, indicate identical variations for PAN and PPN with high values corresponding to smog episodes of 2–4-days duration. Diurnal variations of PPN followed closely those of PAN, as expected since the two compounds have similar formation and removal processes (see discussion below). Diurnal profiles were identical to those observed in 1989 (4) and included in all cases midafternoon maxima that coincided with those of ozone and reflected transport, to the two mountain forest locations, of photochemically polluted air from the Los Angeles urban area. These diurnal variations have been discussed in detail before and reflect the contribution of "horizontal" transport from the Los Angeles urban area, of "vertical" transport up the mountain slopes, and possibly of biogenic hydrocarbons
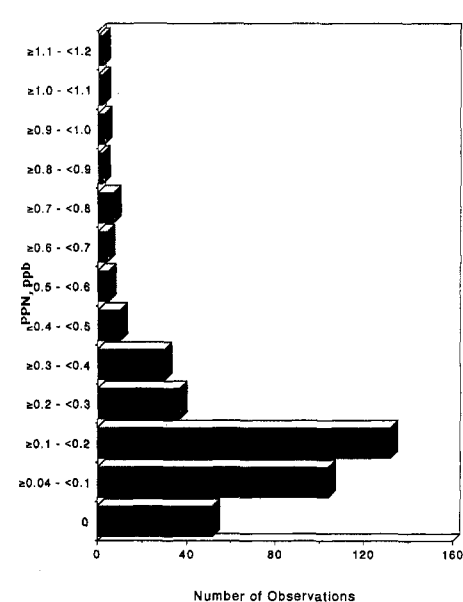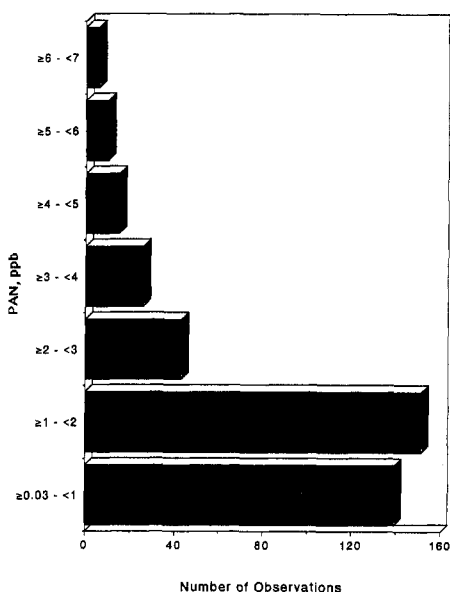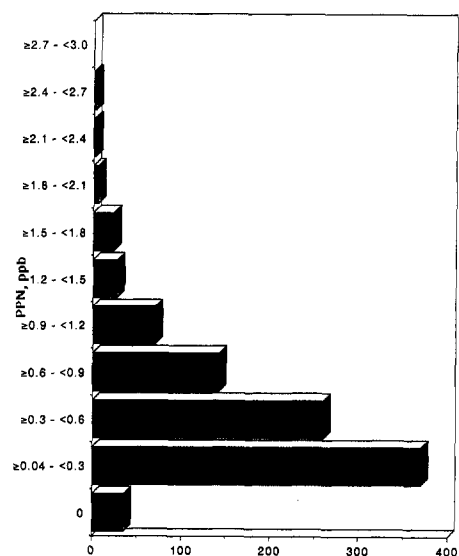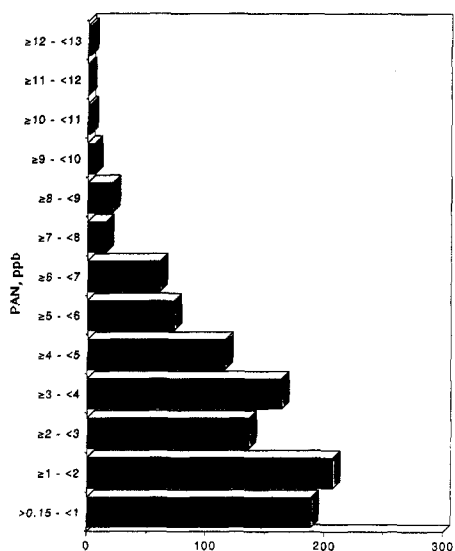
Figure 1. PAN frequency distributions: Tanbark Flat, 1990 (a, top), Tanbark Flat, 1991 (b, middle), and Franklin Canyon, 1991 (c, bottom).
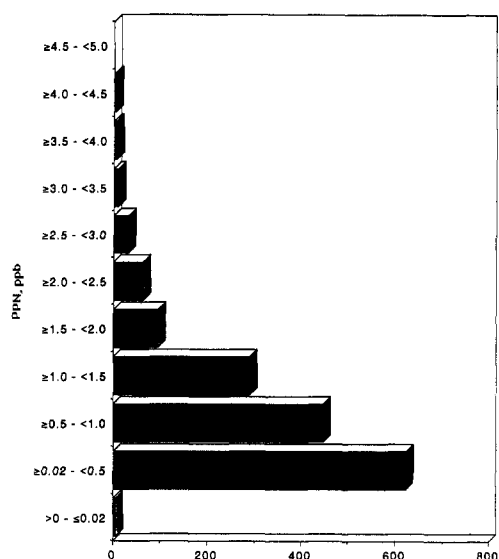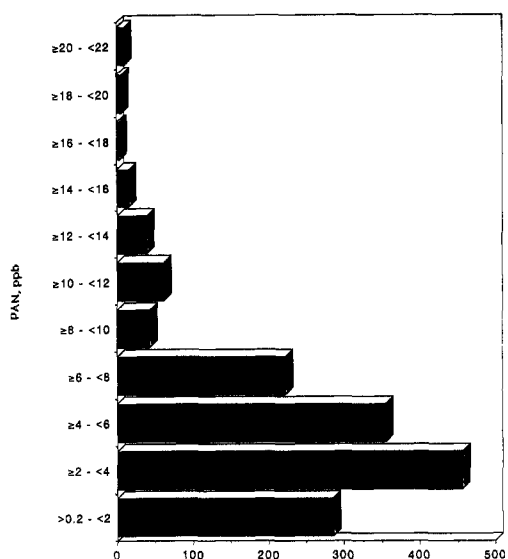

Figure 2. PPN frequency distributions: Tanbark Flat, 1990 (a, top), Tanbark Flat, 1991 (b, middle), and Franklin Canyon, 1991 (c, bottom).

to the observed diurnal variations of PAN and PPN (4).

Composite diurnal profiles, i.e., diurnal profiles averaged over all days during which round-the-clock measurements were made, are shown in Figure 4. PAN and PPN max-

ima at Tanbark Flat occurred several hours later than those at Franklin Canyon, as expected since Tanbark Flat is further downwind than Franklin Canyon. Comparison of the composite diurnal profiles for PAN and PPN at
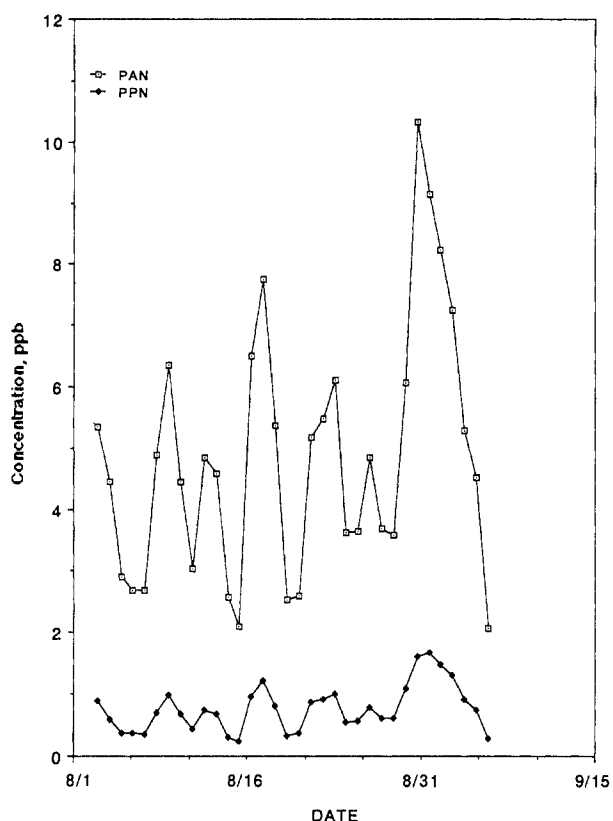
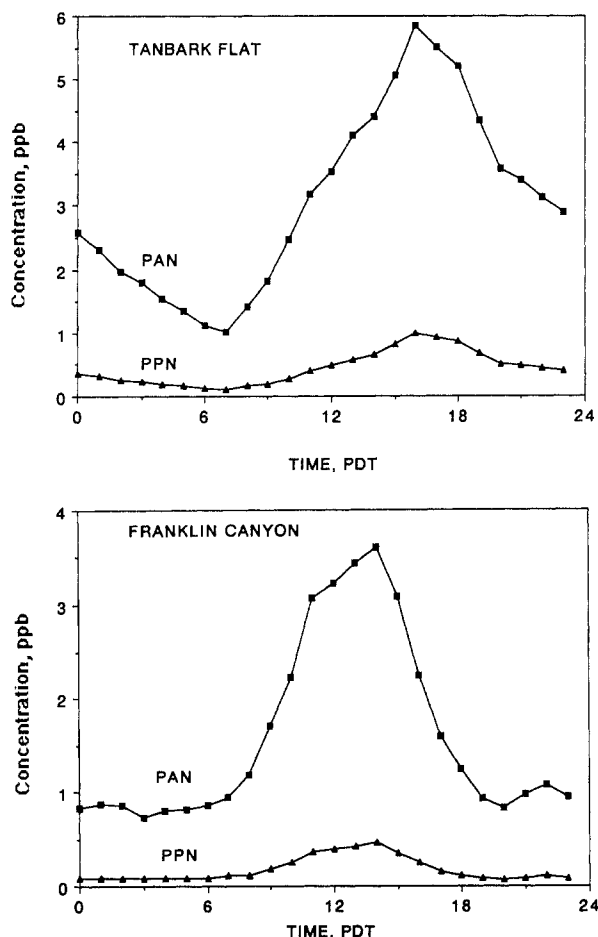**Figure 3.** Time series plot of 24-h averaged PAN and PPN concentrations, Tanbark Flat, 1990.

Table IV. Frequency Distribution of PPN/PAN Concentration Ratios, 1991

| | no. of observations | |
PPN/PAN	Tanbark Flat Aug 5–26	Franklin Canyon Sept 5–12
0.02–0.039	2	0
0.04–0.059	19	13
0.06–0.079	25	43
0.08–0.099	85	90
0.10–0.119	177	90
0.12–0.139	227	47
0.14–0.159	191	37
0.16–0.179	107	7
0.18–0.199	57	5
0.20 and greater	11	6

Tanbark Flat for 1989, 1990, and 1991 indicates that the time of maximum PAN (and PPN) was the same during the three consecutive smog seasons. Thus, on the average, polluted air mass transport times from the urban area to the mountain forest location were the same from one year to the next.

PPN/PAN Concentration Ratios. Since PPN may be more phytotoxic than PAN (1) it is of interest to examine PPN/PAN concentration ratios at both mountain forest locations. In addition, spatial, temporal, and diurnal variations of this ratio may reflect differences and similarities in formation and removal processes for the two peroxyacyl nitrates.

Individual ratios for paired observations of PAN and PPN in 1990 at Tanbark Flat have been compiled else-
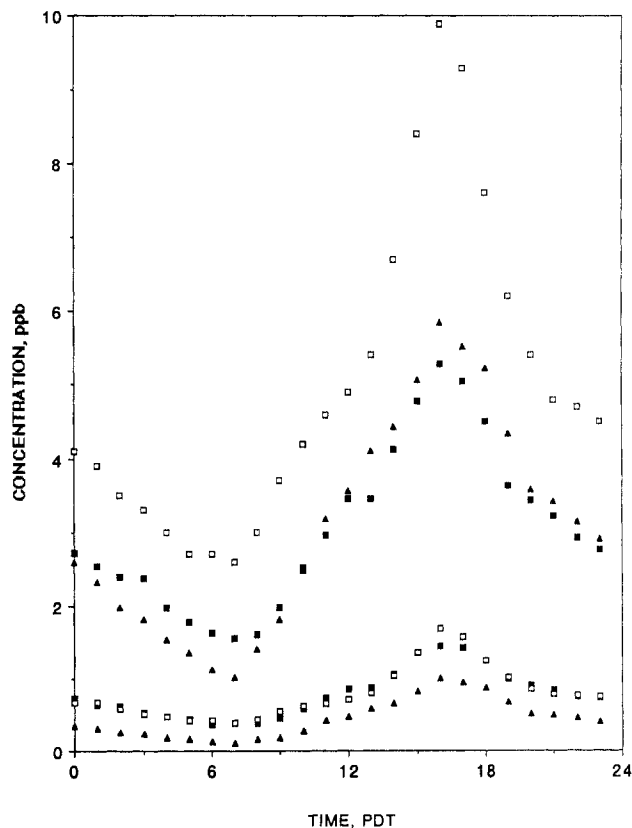

Figure 4. Composite diurnal profiles for PAN and PPN: (a, left) comparison of 1991 data for Tanbark Flat (top) and Franklin Canyon (bottom); (b, right) comparison of PAN (upper curves) and PPN (lower curves) in 1989 (dark squares), 1990 (open squares), and 1991 (dark triangles) at Tanbark Flat.

Table V. Summary of PPN/PAN Concentration Ratios

| location	date	PPN/PAN concn ratio (ppb/ppb)
Tanbark Flat, 1989 (4)	Aug 8–Sept 23	0.310 ± 0.002 (R = 0.965)
	Sept 23–Oct 16	0.230 ± 0.002 (R = 0.930)
	overall (Aug 8–Oct 16)	0.280 ± 0.002 (R = 0.943)
Tanbark Flat, 1990 (this study)	Aug 3–Sept 5	0.182 ± 0.001 (R = 0.966)
Tanbark Flat, 1991 (this study)	Aug 5–Aug 26	0.187 ± 0.001 (R = 0.979)
Franklin Canyon, 1991 (this study)	Sept 4–Sept 12	0.140 ± 0.002 (R = 0.964)
Palms Springs, 1989 (17)	Aug 23–25	0.125–0.135
Perris, 1989 (17)	Aug 25–27	0.135–0.182
Edison,[a] 1990 (unpublished data, Grosjean and Williams, DGA, Inc.)	July 21–26	0.11 ± 0.03

[a] Near Bakersfield in California's San Joaquin Valley.
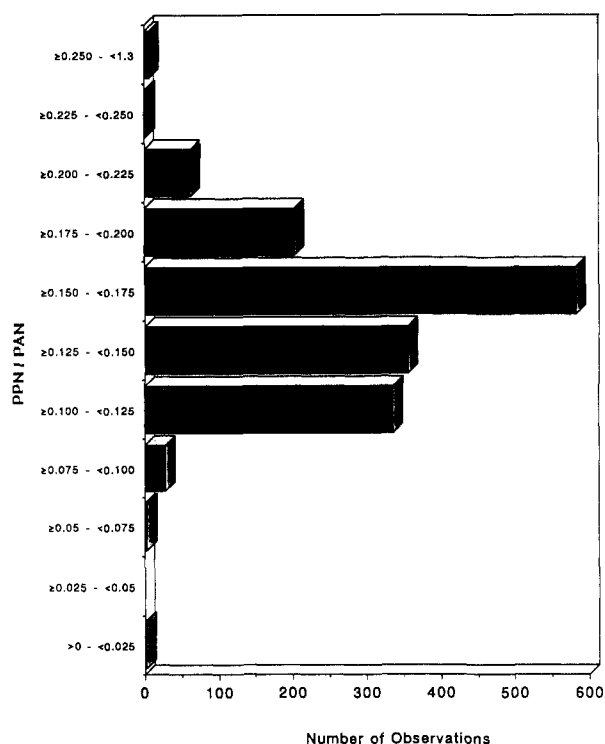
Figure 5. Frequency distribution of PPN/PAN concentration ratios, Tanbark Flat, Aug 3–Sept 5, 1990.

Figure 6. Scatterplot and linear regression of PPN vs PAN, Tanbark Flat, Aug 5–26, 1991.

where (12, 13) and are summarized as frequency distributions in Figure 5 (Tanbark Flat, 1990) and in Table IV (Tanbark Flat and Franklin Canyon, 1991). The data suggest that, for each location and each sampling season, the PPN/PAN concentration ratio was essentially constant. Indeed, least squares linear regression of all paired observations of PPN and PAN yielded near-zero intercepts and correlation coefficients ranging from 0.96 to 0.98 (Table V). A linear regression plot of PPN vs PAN is illustrated in Figure 6 for Tanbark Flat. On the average, PPN/PAN ratios exhibited spatial and year-to-year variations. In 1991, the PPN/PAN ratio was higher at Tanbark Flat than at Franklin Canyon, 0.19 vs 0.14. At Tanbark Flat, the average PPN/PAN ratio was lower in 1990 (0.18) and in 1991 (0.19) than during the 1989 smog season (0.28, see ref 4).

Variations of the PPN/PAN ratio from one smog season to the next may reflect changes in air mass transport time, changes in the abundance of hydrocarbons that are precursors to PAN relative to those that are precursors to PPN, or changes in photochemical activity during transport. Other factors that may influence the PPN/PAN ratio include their relative thermal stability, their relative removal by dry deposition, and their relative removal by
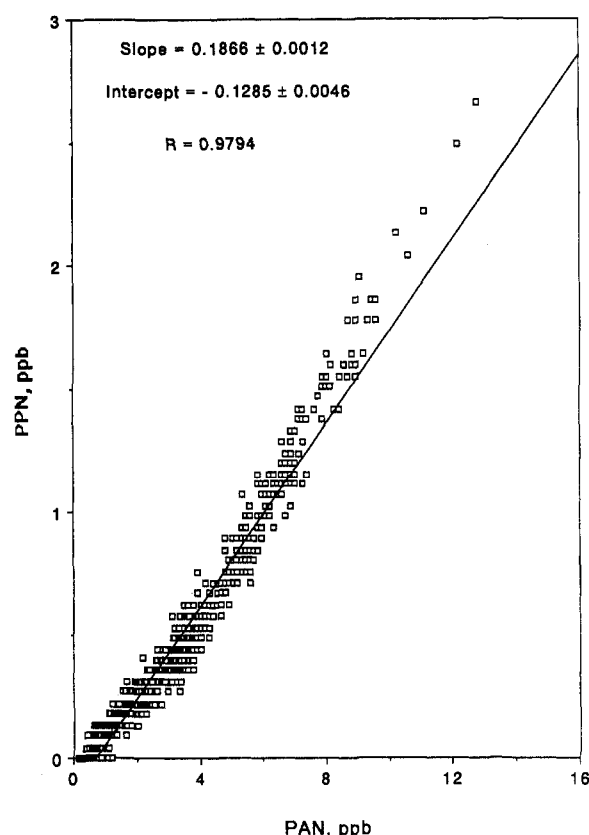
chemical reaction with the hydroxyl radical. PAN and PPN have almost identical thermal stabilities (14, 15). They presumably have similar deposition velocities (16). Unlike PAN, PPN contains two secondary C–H bonds and is therefore expected to react faster with OH than PAN does (4, 16), thus resulting in a more rapid removal during long-range transport. However, removal of PPN by reaction with OH is probably not of major importance in view of the short transport times (a few hours) typical of the two mountain forest locations. Substantial changes in air mass transport times from one smog season to the next appear to be ruled out on the basis of the diurnal profiles shown earlier in Figure 4. This leaves two parameters, i.e., differences in photochemical activity and changes in emissions of hydrocarbons that are precursors to PAN and PPN.

In the absence of input data, i.e., detailed hydrocarbon emission inventories for the years 1989–1991, the hypothesis of changes in precursor hydrocarbon emissions cannot be tested, but substantial changes in emissions during this 2-year period are unlikely. The role of pho-
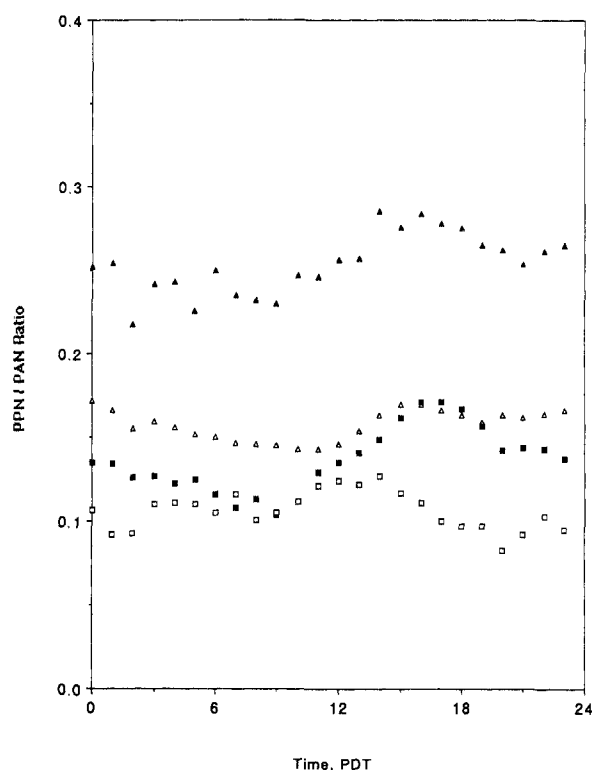
Figure 7. Diurnal variations of PPN/PAN concentration ratios: Franklin Canyon 1991 (open squares) and Tanbark Flat 1989 (dark triangles), 1990 (open triangles), and 1991 (dark squares).

Figure 8. Daily average PPN/PAN ratios vs PAN concentration, Tanbark Flat, Aug 5–Sept 26, 1991.

tochemical activity on PPN/PAN concentration ratios can be tested, at least qualitatively, if we assume that no major changes in emissions of precursor hydrocarbon occurred during the 1989–1991 period. Composite diurnal variations of the PPN/PAN ratio are shown in Figure 7. These ratios exhibit maxima that coincide with the maximum PAN, PPN, and ozone concentrations; i.e., PPN/PAN ratios are highest during the period of greater photochemical activity at both locations and for all three consecutive smog seasons.

Taking now PAN as an indicator of in-situ photochemical activity during air mass transport, we have plotted the PPN/PAN ratios as a function of the corresponding PAN concentrations for all three subsets of data, i.e., Tanbark Flat, 1990, Tanbark Flat, 1991, and Franklin Canyon, 1991. As is shown in Figure 8, the three scatterplots exhibited a clear trend of increasing PPN/PAN ratios with increasing PAN concentrations. Thus, both PPN/PAN diurnal profiles and PPN/PAN vs PAN scatterplots are consistent with a higher in-situ production rate for PPN, relative to PAN, during episodes of higher photochemical activity. This trend would indeed be expected if precursors of PPN are, on the average, more reactive than those of PAN, thus resulting in a higher production rate for PPN relative to PAN during smog episodes. Because of the short air mass transport time involved, this higher production rate is not substantially offset by the removal process involving faster (relative to PAN) reaction of PPN with OH. Removal of PPN by OH is expected to become more important when longer air mass transport times are involved. Indeed, we have observed low PPN/PAN concentration ratios at two downwind locations, Perris and Palm Springs, which are 90 and 120 km, respectively, east and downwind of Los Angeles (17).

Another factor that may contribute to lowering the PPN/PAN ratio downwind of urban areas is the involvement of biogenic hydrocarbons including isoprene and terpenes. Atmospheric oxidation of isoprene yields PAN
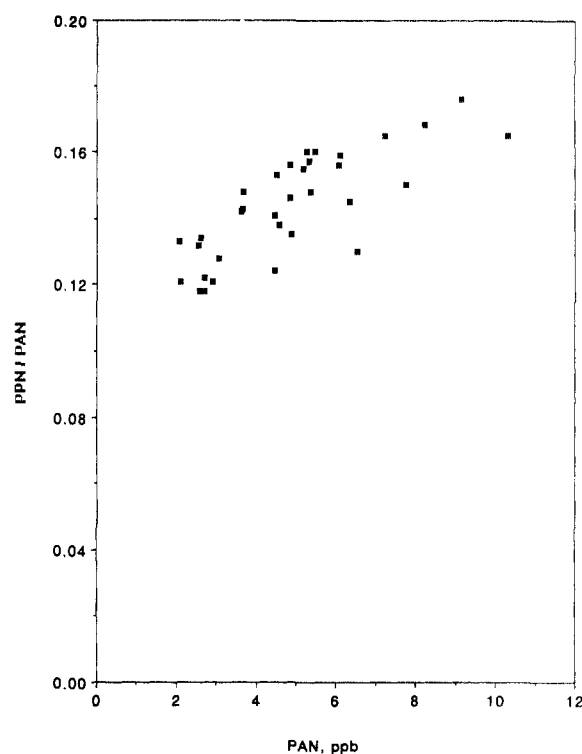
and MPAN [$CH_2{=}C(CH_3)C(O)OONO_2$] but not PPN (18); oxidation of the most abundant terpenes, e.g., α-pinene, β-pinene, and d-limonene, also yields PAN but little or no PPN (19).

Relative Abundance of Photochemical Oxidants: PAN, PPN, and Ozone. Since ozone and PAN have a common photochemical origin and are both phytotoxic, it is of interest to compare their concentrations and diurnal variations at mountain forest sites that are impacted by urban smog. Ambient levels of ozone reached up to 170, 240, and 250 ppb at Tanbark Flat during our 1989, 1990, and 1991 field studies, respectively. Levels of PAN at Tanbark Flat, up to 22 ppb on several days, are comparable to those measured earlier at other southern California locations. Indeed, examination of the data summarized in Table VI, which compiles maximum PAN levels recorded in southern California and elsewhere over the last 25 years, indicates that the highest PAN level recorded at Tanbark Flat during this study ranks third among PAN maxima measured in southern California since 1980.

During the periods studied, the average ozone and PAN concentrations at Tanbark Flat were 69 and 5 ppb, respectively, in 1990 and 65 and 3 ppb, respectively, in 1991. The corresponding average ozone/PAN concentration ratios were 14 in 1990 and 22 in 1991. Ozone PAN concentration ratios at the time of maximum ozone (and maximum PAN) were in the range 15–19. As is shown in Table VII, these ratios are consistent with those of 10–22 calculated from data for other locations in southern California during the smog season, i.e., summer and early fall. During the late fall and winter, lower temperatures result in substantially less thermal decomposition for PAN and therefore markedly lower ozone/PAN ratios, e.g., ratios of only 4–9 at five southern California locations in November–December 1987 (7).

The effect of temperature on the stability of peroxyacyl nitrates, and therefore on the corresponding ozone/PAN and ozone/PPN concentration ratios, is shown in Figure 9 as scatterplots of 24-h averaged concentration ratios vs

Table VI. Urban Levels of PAN (maximum, ppb)

location	PAN	location	PAN
Southern California[a]			
Riverside, 1967	58	Burbank, 1987	17
Los Angeles, 1968	65	Los Angeles, 1987	13
Riverside, 1968	38	Anaheim, 1987	19
Pasadena, 1973	53	Long Beach, 1987	16
West Covina, 1973	46	Hawthorne, 1987	16
Riverside, 1975	25	Los Angeles, 1988	14
Riverside, 1976	32	Los Angeles (south-central), 1988	5
Riverside, 1977	27	Los Angeles (west), 1988	9
Riverside, 1978	42	Los Angeles (west-central), 1988	10
Claremont, 1978	37	Westwood, 1988	3
Claremont, 1979	10	Malibu, 1988	7
Los Angeles, 1979	17	Ventura, 1988	4
Claremont, 1980	47	Pasadena, 1988	12
East Los Angeles, 1980	16	Highland Park, 1988	10
Riverside, 1980	42	Griffith Park, 1989	8
Downey, 1984	7	Palm Springs, 1989 (17)	3
Claremont, 1985	20	Perris, 1989 (17)	7
Glendora, 1986	35	Tanbark Flat, 1989 (4)	16
Claremont, 1987	30	Tanbark Flat, 1990[b]	22
Azusa, 1987	13	Tanbark Flat, 1991[b]	13
Rubidoux, 1987	14	Franklin Canyon, 1991[b]	7
Other Urban Locations[a]			
Hoboken, NJ, 1970	9	Calgary, 1981–1982	7
St. Louis, MO, 1973	19–25	Athens, 1985	4
Dayton, OH, 1974	10	Rio de Janeiro, 1985	5
Houston, TX, 1976	11	Paris, 1985	9
Houston, TX, 1984	8	Rome, 1987	10
Phoenix, AZ, 1979	4	Edmonton, 1984	7
Oakland, CA, 1979	2	Bonn, 1980	2
Denver, CO, 1984	2	Tokyo, 1972–1973	7–31
Staten Island, NY, 1983	5	London, 1975	16
Philadelphia, PA, 1983	4		

[a] From refs 7 and 20–22 unless otherwise indicated. [b] This study.

Table VII. Summary of PAN/Ozone Concentration Ratios

location and date[a]	av ozone/PAN ratio at ozone maximum[b] (ppb/ppb)	
	smog season	late fall
Claremont, Sept 19–Oct 8, 1980 (23)	13.3 (11)	
Glendora, Aug 12–20, 1986 (24)	10.0 (9)	
Anaheim, Nov 11–Dec 11, 1987		6.0 (6)
Azusa, June 19–Sept 3, 1987	21.0 (11)	
Burbank, June 19–Sept 3, 1987	21.0 (11)	
Burbank, Nov 11–Dec 11, 1987		4.6 (6)
Claremont, June 19–Sept 3, 1987	20.0 (11)	
Hawthorne, Nov 11–Dec 11, 1987		8.9 (6)
Long Beach, June 19–Sept 3, 1987	16.0 (11)	
Long Beach, Nov 11–Dec 11, 1987		9.4 (6)
Los Angeles, June 19–Sept 3, 1987	16.0 (11)	
Los Angeles, Nov 11–Dec 11, 1987		6.5 (6)
Rubidoux, Nov 11–Dec 11, 1987	22.0 (11)	
Tanbark Flat, Aug 8–Oct 16, 1989 (4)	19.1 (59)	
Tanbark Flat, Aug 3–Sept 5, 1990 (this study)	14.7 (34)	
Tanbark Flat, Aug 5–26, 1991 (this study)	19.2 (18)	

[a] From ref 7 unless otherwise indicated. [b] Number of days in parentheses.

temperature at Tanbark Flat for the period August 3–September 5, 1990. Both PAN/ozone and PPN/ozone ratios decreased substantially with increasing temperature. The same trend was observed for maximum PAN (PPN)/maximum ozone ratios (not shown).

Diurnal Variations of PAN/Ozone and PPN/Ozone Concentration Ratios. Using the data obtained in 1990 at Tanbark Flat as an example, diurnal variations in ozone, PAN, and PPN concentrations and in the cor-

responding PAN/ozone and PPN/ozone ratios are shown in Figure 10. The PAN/ozone and PPN/ozone concentration ratios track each other closely, with nightime maxima and morning minima. Diurnal variations of these ratios reflect several factors that influence the relative abundance of ozone and peroxyacyl nitrates: temperature (the thermal decomposition of PAN and PPN is slower at the lower temperatures generally prevailing at night), deposition velocities (ozone is lost more rapidly than PAN, and presumably PPN, by dry deposition), relative rates of formation by chemical reactions (i.e., hydrocarbon–NO_x reactions involving OH during the day, and possibly reaction of aldehydes with NO_3 at night), and relative rates of removal by chemical reactions (mostly scavenging by NO in air masses transported to the mountain slopes in the early morning). A more detailed analysis of these diurnal profiles would require computer kinetic simulations and would not be possible with current computer kinetic models since these models "lump" all peroxyacetyl nitrates together, with the exception of the Carter mechanism (25), which treats PAN (but not PPN) separately.

Precursors of PAN and PPN. Formation rates for PAN and PPN are proportional to the emission rates and chemical reactivity of their precursor hydrocarbons. Even if reliable hydrocarbon emission inventories were available (26, 27), precise calculations of PAN and PPN formation rates would require, for each hydrocarbon, a detailed knowledge of photooxidation pathways, of the relative importance of these pathways, and of the corresponding PAN and PPN yields. This information is not available for most hydrocarbons. However, estimates of the relative production rates of PAN and PPN can be made by simply taking the product of the hydrocarbon emission rate and of some measure of its chemical reactivity. Such estimates
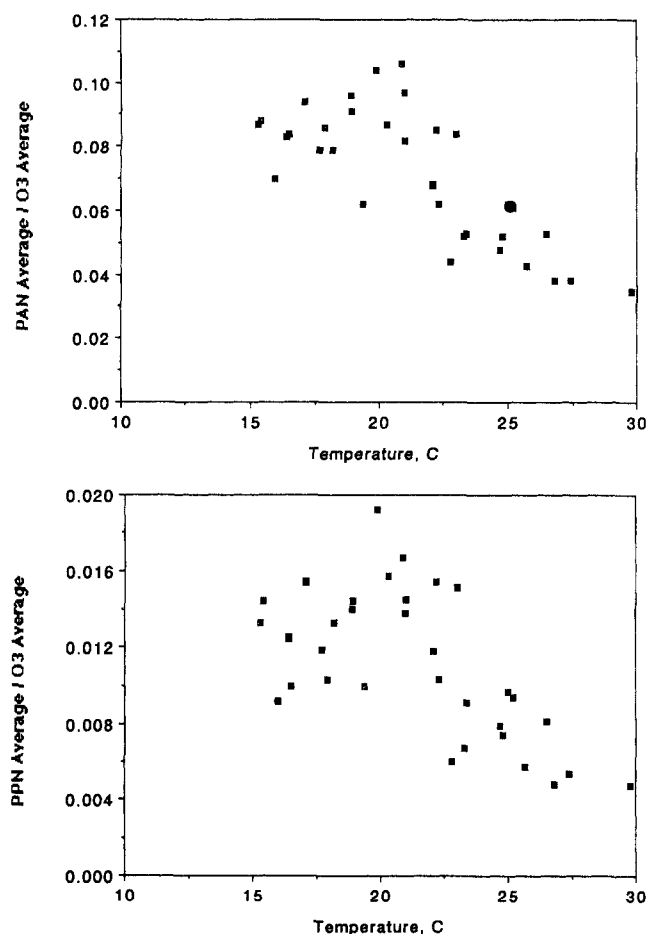
Figure 9. Scatterplots of PAN/ozone (top) and PPN/ozone (bottom) ratios of 24-h averaged concentrations vs 24-h averaged temperature, Tanbark Flat, 1990.

Figure 10. Composite diurnal profiles (top) and PAN/ozone (open squares) and PPN/ozone (dark squares) concentration ratios (bottom), Tanbark Flat, 1990.

are presented in Table VIII.

The emission rates given in Table VIII are those for the California South Coast Air Basin updated and modified by Grosjean and Seinfeld (27). Since all hydrocarbons react with the OH radical, we take the OH–hydrocarbon reaction rate constant as a measure of the hydrocarbon reactivity. These OH rate constants include experimental data compiled from the literature as well as estimates made on the basis of structure–reactivity relationships (27–29). For olefins, a correction factor has been applied to take into account the ozone–olefin reaction, which competes with the OH–olefin reaction especially for the more reactive olefins (27). This correction factor, e.g., 0.53 for 1-butene, is calculated from the known rate constants for the olefin–ozone and olefin–OH reactions and by taking the ozone and OH concentrations to be typical for a smog episode, e.g., $[O_3]$ = 100 ppb and $[OH]$ = 1.0×10^6 molecules/cm^3. The use of this correction factor leads to conservative estimates of olefins as precursors of PAN and PPN since (a) some OH is formed in the ozone–olefin reaction, (b) disubstituted Criegee biradicals formed in the ozone–olefin reaction lead to dicarbonyls (30) that are precursors to PAN (e.g., CH_3COCHO) and PPN (e.g., C_2H_5COCHO), and (c) some of the carbonyl products of the ozone–olefin reaction also lead to PAN and PPN. For aromatics, paraffins, and carbonyls, reaction with ozone is negligibly slow and only their reaction with OH is of importance. For aromatics, a correction factor has also been applied to account for aromatic ring-retaining reaction pathways. The fraction of the total OH–aromatic hydrocarbon reaction that leads to ring-opening products, i.e., to dicarbonyls that are precursors of PAN and PPN,
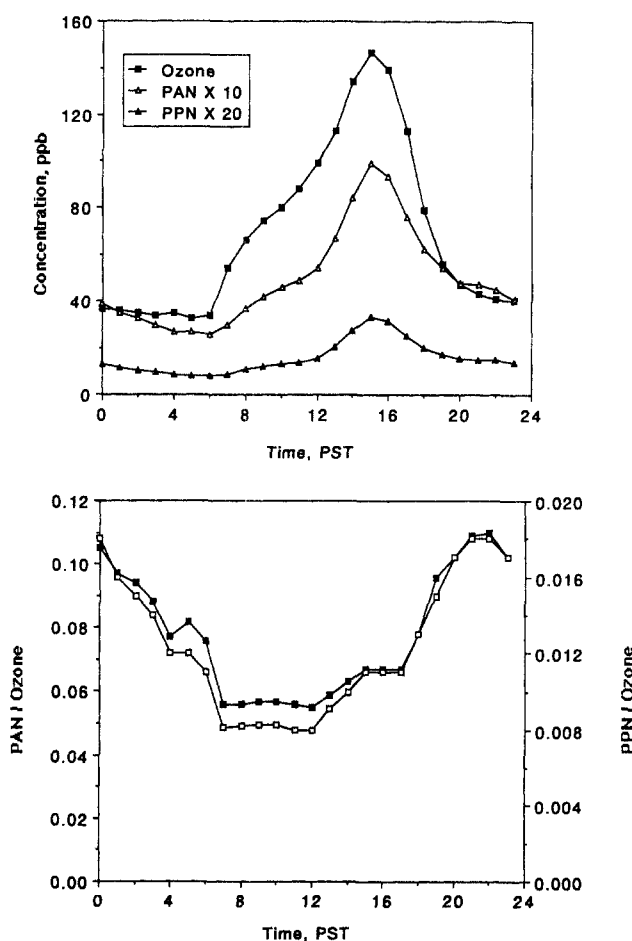
has been estimated using the dicarbonyl yields of Tuazon et al. (31) for toluene, xylenes, and ethylbenzenes, e.g., 0.42 for o-xylene (0.24 methylglyoxal + 0.18 biacetyl). For diethylbenzenes and ethyltoluenes, for which no data exist, the fraction of ring-opening products has been arbitrarily taken to be 0.5. As for olefins, the use of a correction factor for aromatics results in conservative estimates of their contribution to PAN and PPN. This is because some of the ring-retaining products, e.g., cresols and other phenols, also react with OH to yield dicarbonyls and subsequently PAN (32) and PPN. For paraffins, no correction factor was applied, and our estimates are limited to those 16 alkanes that are among the 25 most abundant hydrocarbons consistently observed in Los Angeles ambient air (33). For carbonyls, no correction factor has been applied; i.e., we have neglected in first approximation carbonyl photolysis which competes with the OH–carbonyl reaction.

With these assumptions, the PAN-forming and PPN-forming potentials listed in Table VIII indicate that olefins account for more than 50% of the total precursors for both PAN and PPN. The most important precursors of PAN include three alkenes, i.e., propene, 2-methyl-1-butene, and isobutene, along with the paraffin isopentane. Two of these hydrocarbons, 2-methyl-1-butene and isopentane, are, along with 1-butene, the most important precursors of PPN. In terms of relative abundance of PAN and PPN, the calculated PPN/PAN ratios given in Table VIII vary substantially from one category of hydrocarbons to the next, being 0.12 for carbonyls, 0.16 for aromatics, 0.55 for olefins, and 0.88 for paraffins.

Consequently, PPN/PAN ratios measured downwind of an urban area with a given mix of hydrocarbon emissions

Table VIII. Relative Importance of PAN and PPN Precursors

hydrocarbon	emission rate, metric tons/day	$10^{11} \times$ OH reaction rate const, cm^3 molecule^{-1} s^{-1}	PAN	PPN
Olefins				
propene	34.6	2.6	43.2	
2-methyl-2-butene	27.7	6.9	11.5	
2-methyl-1-butene	22.5	6.1	91.2	91.2
1-butene	19.0	3.1		31.2
cis-2-butene	15.6	5.6	13.1	
trans-2-butene	13.8	6.4	9.7	
isobutene	12.1	5.1	38.9	
2,3-dimethyl-1-butene	5.2	5.5	18.6	
cis-2-pentene	2.6	6.5	1.8	1.8
trans-2-pentene	2.2	6.7	1.2	1.2
trans-3-methyl-2-pentene	1.0	9.4	0.3	0.3
2-ethyl-1-butene	0.5	5.6		1.8
2,4,4-trimethyl-1-pentene	4.0	3.5	5.0	
2-methyl-2-pentene	1.4	6.9	0.6	0.6
cis-3-hexene	1.4	6.3		1.4
Aromatics				
toluene	105.5	0.6	9.4	
ethylbenzene	8.5	0.7		3.0
xylenes				
ortho	19.8	1.3	10.9	
meta	12.0	2.3	8.8	
para	12.0	1.4	1.7	
trimethylbenzenes				
1,2,3	3.3	3.3	5.1	
1,2,4	3.3	3.2	4.3	
1,3,5	4.6	5.7	15.7	
diethylbenzene				
1,2	0.17	2.9		0.25
1,3	0.17	2.9		0.25
1,4	0.17	2.9		0.25
ethyltoluenes				
1,2	4.0	1.2	2.4	2.4
1,3	2.8	1.9	2.6	2.6
1,4	2.7	1.2	1.6	1.6
Carbonyls				
acetaldehyde	10.5	1.6	16.8	
propanal	0.5	2.0		1.0
acetone	13.0	0.02	0.3	
2-butanone	11.1	0.1	1.1	1.1
Paraffins				
isopentane	89.5	0.39	34.9	34.9
n-butane	66.7	0.25	16.7	16.7
propane	26.2	0.11	2.9	
ethane	59.7	0.02	1.2	
n-pentane	20.8	0.39	8.1	8.1
1,2,4-trimethylpentane	20.0	0.5	10.0	10.0
2-methylpentane	4.0	0.56	2.2	2.2
isobutane	22.4	0.23	5.1	
2,4-dimethylpentane	2.6	0.51	1.3	
3-methylpentane	4.8	0.57		2.7
n-hexane	19.6	0.56	10.9	10.9
3-methylhexane	10.0	0.6	6.0	6.0
2,2,4-trimethylpentane	4.3	0.37	1.6	1.6
n-heptane	9.9	0.71	7.2	7.2
2,3-dimethylbutane	5.0	0.63	3.1	
2-methylhexane	5.0	0.6	3.0	

Summary

	forming potential, % of total PAN	forming potential, % of total PPN	PPN/PAN ratio		forming potential, % of total PAN	forming potential, % of total PPN	PPN/PAN ratio
olefins	54.6	53.5	0.55	carbonyls	4.3	0.9	0.12
aromatics	14.5	4.2	0.16	paraffins	26.6	41.4	0.88

[a] Product of emission rate, OH reaction rate constant, and dimensionless correction factor; see text.

are expected to vary as a function of transport time, i.e., as a function of the overall reactivity of the remaining hydrocarbon mix. For short transport times, the PPN/PAN ratio should reflect to a large extent the relative forming potential of the most reactive precursors, i.e., olefins. For intermediate transport times, e.g., 6 h and longer, olefins are substantially depleted and the PPN/PAN ratio is expected to decrease as aromatics and aldehydes replace olefins as the most reactive compounds in the air mass. Further downwind, the PPN/PAN ratio may increase when the air mass contains mostly the less reactive precursors, i.e., paraffins. Finally, one may expect the PPN/PAN ratio to decrease again when the least reactive compounds, e.g., ethane and acetone, which form PAN but not PPN, become the predominant non-methane hydrocarbons. The estimates given in Table VIII and the corresponding predictions of PPN/PAN ratios are consistent with the PPN/PAN ratios measured at Tanbark Flat and Franklin Canyon (this study, short transport times; olefins are the predominant precursors), at Palm Springs and Perris [further downwind, lower ratios since olefins are depleted (17)], and at more remote locations [importance of ethane and acetone, low PPN/PAN ratios (16)].

Other Peroxyacyl Nitrates. Chromatograms of ambient air at both mountain locations often included a peak

that eluted after those of PAN and PPN. In our earlier study (4), this peak was assigned to peroxy-n-butyryl nitrate (PnBN) on the basis of two sets of tests. First, the compound decomposed when ambient air is passed through a heated tube, as expected for a peroxyacyl nitrate but not for an alkyl nitrate (this was verified experimentally; see Experimental Section). Second, the retention time of this compound in chromatograms of ambient air matched well that of PnBN prepared in the laboratory by two methods, liquid-phase synthesis and sunlight irradiation of n-butanal–NO mixtures (Table IX).

Two peroxyacyl nitrates bearing a C_3 substituent may have retention times similar to that of PnBN: peroxyisobutyryl nitrate [(CH$_3$)$_2$CHC(O)OONO$_2$, PiBN] and the peroxyacyl nitrate observed to form by photooxidation of isoprene and of isoprene's oxidation product methacrolein, i.e., CH$_2$=C(CH$_3$)C(O)OONO$_2$ (MPAN). Our attempts to synthesize PiBN in earlier work were not successful (4). Therefore, the contribution of PiBN to the peak assigned to its isomer PnBN cannot be ruled out. The other peroxyacyl nitrate, MPAN, has been characterized in the laboratory (18, 34) and has been tentatively observed in ambient air (35). We have prepared MPAN by three methods, one involving synthesis of MPAN in the liquid phase (18) and the others involving sunlight irradiation, in a 3.5-m^3 all-Teflon outdoor chamber, of isoprene–NO

Table IX. Retention Times of MPAN and PnBN and Comparison with Field Observations

	retention time, rel to PAN[a]		
	PPN	MPAN	PnBN
laboratory experiments			
isoprene–NO (b)		1.69 ± 0.05 (78)	
methacrolein–NO (b)		1.69 ± 0.02 (34)	
MPAN in pure air (c)		1.71 ± 0.02 (49)	
MPAN–ozone mixture (c)		1.69 ± 0.02 (34)	
mixture of PAN, PPN, and MPAN (c)	1.23 ± 0.01 (24)	1.71 ± 0.01 (24)	
mixture of PPN and MPAN	1.24 ± 0.01 (12)	1.68 ± 0.01 (12)	
mixture of PAN, PPN, MPAN, and PnBN (c)	1.24 ± 0.01 (6)	1.7 ± 0.05 (6)	1.92 ± 0.02 (6)
n-butanal–NO (b)			1.92 ± 0.01 (4)
PnBN in pure air (c)			1.92 ± 0.01 (10)
ambient observations			
Tanbark Flat, 1989 (d)	1.24 ± 0.01 (e)		2.05 ± 0.12 (e)
Tanbark Flat, 1990 (f)	1.24 ± 0.01 (796)	1.77 ± 0.02 (11)	1.97 ± 0.06 (785)
Tanbark Flat, 1991 (g)	1.26 ± 0.1 (102)	1.61 ± 0.10 (8)	2.15 ± 0.30 (93)
Franklin Canyon, 1991 (h)	1.25 ± 0.02 (9)	1.64 ± 0.10 (11)	2.01 ± 0.15 (3)

[a] Mean ± one standard deviation; number of measurements given in parentheses. [b] In sunlight. [c] In the dark. [d] From ref 4. [e] From about 100 chromatograms taken at random from the 3000 chromatogram data base. [f] This study, Aug 3–Sept 5. [g] This study, Aug 5–29. [h] This study, Sept 4–12.

and methacrolein–NO mixtures in purified air (18). The EC-GC retention time of MPAN was established, and its ratio to that of PAN was 1.70 ± 0.02 as compared to 1.92 ± 0.02 for authentic samples of PnBN (Table IX).

A systematic examination of the retention time of the third peak observed in chromatograms of ambient air was carried out. Retention time ratios relative to that of PAN were calculated and are summarized in Table IX. Comparison of these ratios to those measured for authentic samples of MPAN and PnBN indicates that, at one of the mountain forest locations studied (Tanbark Flat), PnBN was frequently observed (98% of the time) while MPAN was seen in only 18 of the 900 chromatograms recorded. At the other location (Franklin Canyon), the third peak was present in only 14 chromatograms (as compared to some 400 observations for PAN); MPAN accounted for 11 of these observations and PnBN for the remaining 3.

Ambient levels of PnBN were up to 2.8, 0.7, and 1.3 ppb at Tanbark Flat in 1989, 1990, and 1991, respectively, with typical values of 0.2–0.4 ppb. The only three observations of PnBN at Franklin Canyon corresponded to levels of 0.65, 0.65, and 0.20 ppb on September 6, 8, and 11, 1991, respectively. Ambient levels of MPAN were 0.6–1.9 ppb at Tanbark Flat in 1990 (average 1.2 ppb, n = 11) and 0.3–0.4 ppb in 1991 (n = 7); they ranged from 0.2 to 2.3 ppb (average 1.0 ppb, n = 11) at Franklin Canyon in 1991.

MPAN is formed along with PAN in the atmospheric oxidation of isoprene (18). Therefore, its presence in ambient air at the two mountain forest locations probably reflects local biogenic emissions. While MPAN was only observed on a few occasions and at levels that were much lower than those of PAN and PPN, the contribution of biogenic emissions relative to that of transported urban smog may be higher than that suggested by the observed low MPAN/PAN (or PPN) concentration ratios. This is because MPAN, while having about the same thermal stability as PAN and PPN (35, 36), may have additional loss processes. Unlike PAN and PPN, MPAN contains an unsaturated carbon–carbon bond and therefore reacts faster than PAN and PPN with the hydroxyl radical and with ozone (18, 35).

In addition, observations of more rapid (relative to PAN and PPN) losses of MPAN on surfaces (33, 35) suggest that the deposition velocity of MPAN may be higher than those of PAN and PPN. These two removal processes, i.e., chemical reactions and dry deposition, may explain why MPAN was not detected frequently, and this only at low

levels, at the two mountain forest locations.

Acknowledgments

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Field Comparison of an Eddy Accumulation and an Aerodynamic-Gradient System for Measuring Pesticide Volatilization Fluxes

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■ The field experiment reported here applied the relaxed eddy accumulation (REA) technique to the measurement of triallate (TA) and trifluralin (TF) volatilization from fallow soil. A critical analysis of the REA system used in this experiment is done, and the fluxes are compared to those obtained by the aerodynamic-gradient (AG) technique. The measured cumulative volatilization losses, corrected for the effective upwind source area (footprint), for the AG system were higher than with the REA system. The differences between the methods over the first 5 days of the experiment were 27 and 13% for TA and TF, respectively. A mass balance based on the amount of parent compounds volatilized from soil during the first 5 days of the experiment showed a 110 and 70% and a 79 and 61% accountability for triallate and trifluralin by the AG and REA methods, respectively. These results also show that the non-footprint-corrected AG flux values underestimated the volatilization flux by approximately 16%. The footprint correction model used in this experiment does not presently have the capability of accounting for changes in atmospheric stability. However, these values still provide an indication of the most likely upwind area affecting the evaporative flux estimations. The soil half-lives for triallate and trifluralin were 9.8 and 7.0 days, respectively.

Introduction

There is a variety of techniques that can be used to measure the postapplication volatilization rates of pesticides from agricultural fields, each with its associated advantages and disadvantages (*1*). The aerodynamic-gradient (AG) method is the most frequently used technique for determining field pesticide volatilization rates, but the methodology has not been standardized. This technique has been developed by analogy with the molecular diffusion processes, and its applicability to atmospheric turbulent-transfer processes has been questioned when larger size eddies are present in the flow (*2, 3*). Questions have also been raised about the molecular weight and structure contribution of the pesticide to it's dispersion in turbulent air (*4*). Several investigators have reported good accountability when using the AG technique in pesticide mass balance field experiments (*5, 6*). However, others have indicated that this technique may underpredict the evaporation rate (*7, 8*).

In contrast, the eddy correlation (EC) technique has long been recognized as a more direct approach for measuring atmospheric fluxes of sensible heat, water vapor, and carbon dioxide (*9–13*). Due to the lack of fast-response sensors for agrochemicals it has not been possible to use this technique for estimating pesticide fluxes. Desjardins (*14*) suggested an alternative, the eddy accumulation technique (EA), to overcome this limitation. EA is based on the conditional sampling of air at a rate proportional to the vertical wind velocity. One air sampling inlet collects vapors or particulates associated with updrafts, and the other, vapors or particulates associated with downdrafts. Despite the intrinsic appeal, this technique has not yet been successfully used in the field due to problems related to biased vertical wind velocity measurements, limited accuracy of volume and chemical analysis measurements, and difficulty in controlling the proportional sampling

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