

Figure 7.1 Peak concentrations of PAN in Southern California, 1960 - 2003

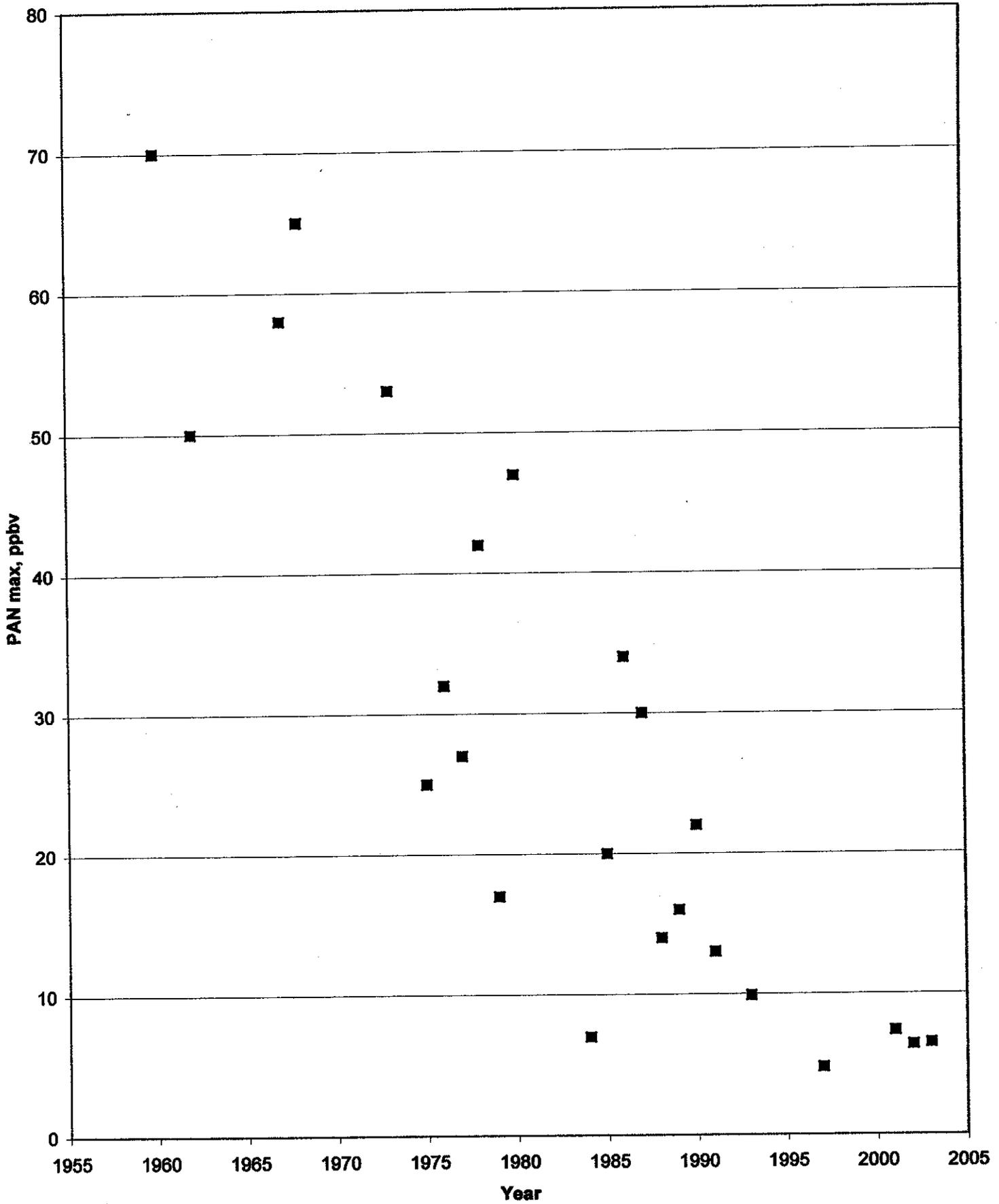


Figure 7.2 Highest 24 hour-averaged PAN concentrations in Southern California

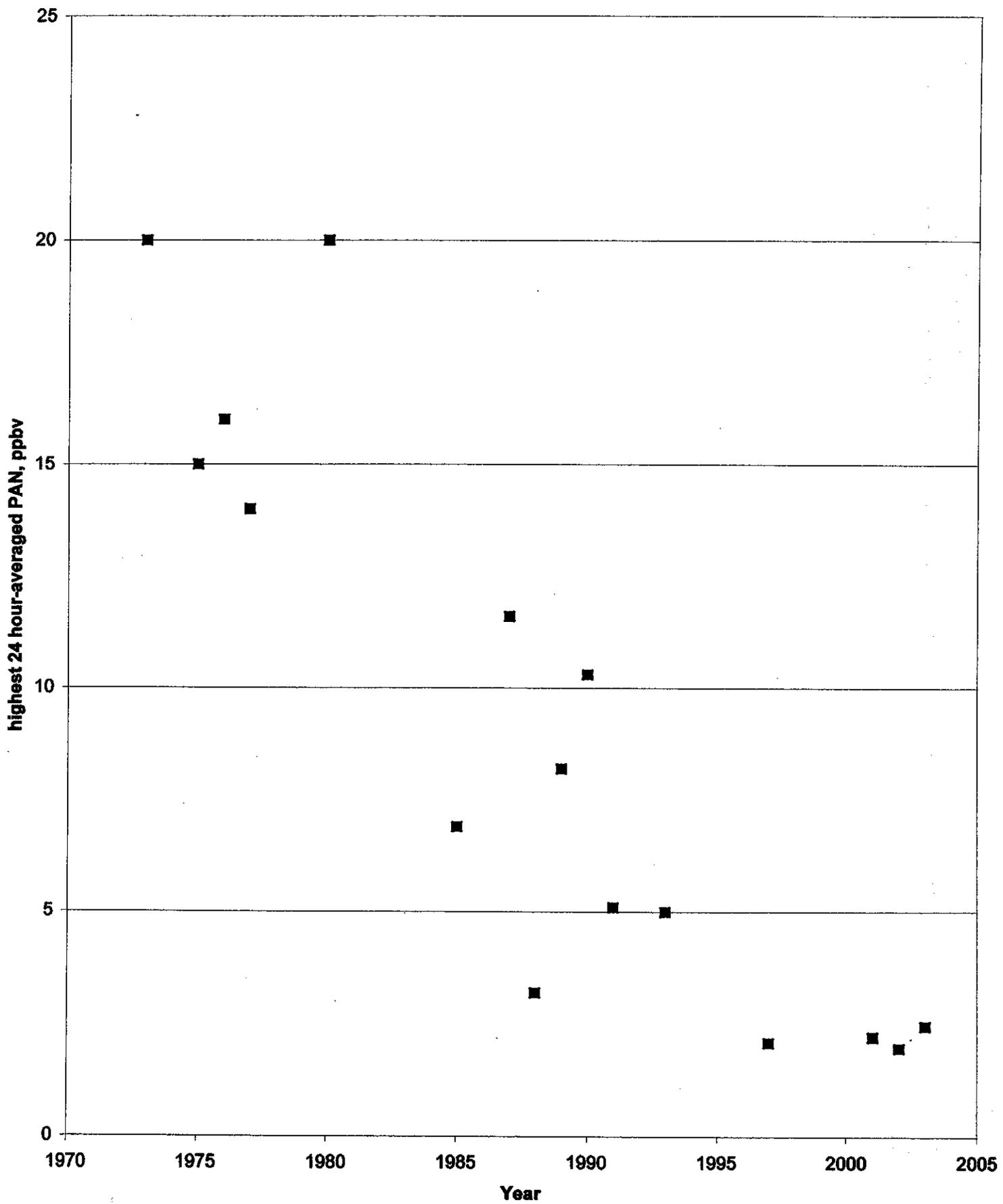


Figure 7.3 Highest monthly-averaged PAN concentrations in Southern California

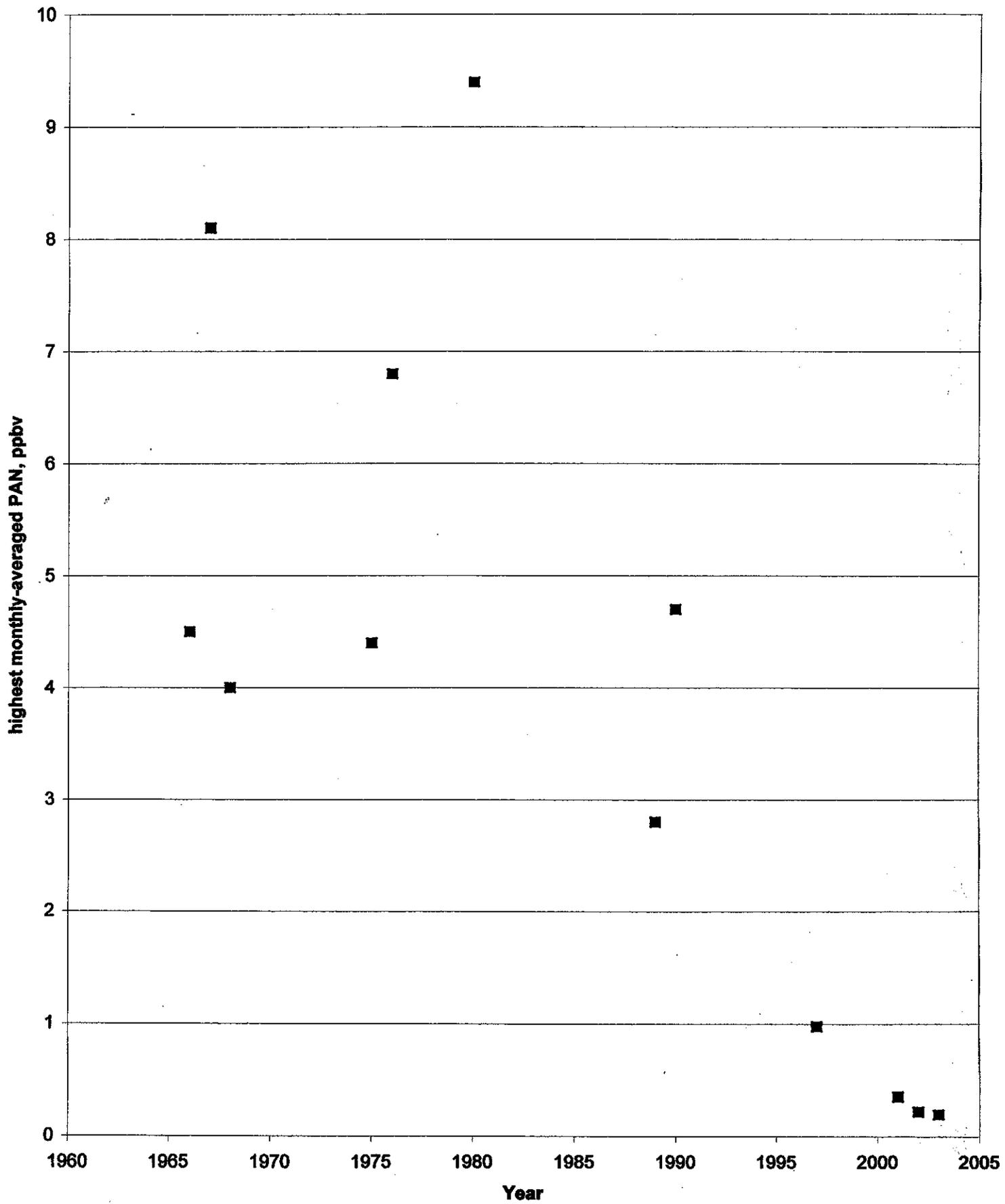


Figure 7.4 Composite diurnal profiles of ambient PAN concentrations measured in Azusa in 1987, 1993, 1997 and 2001 – 2003

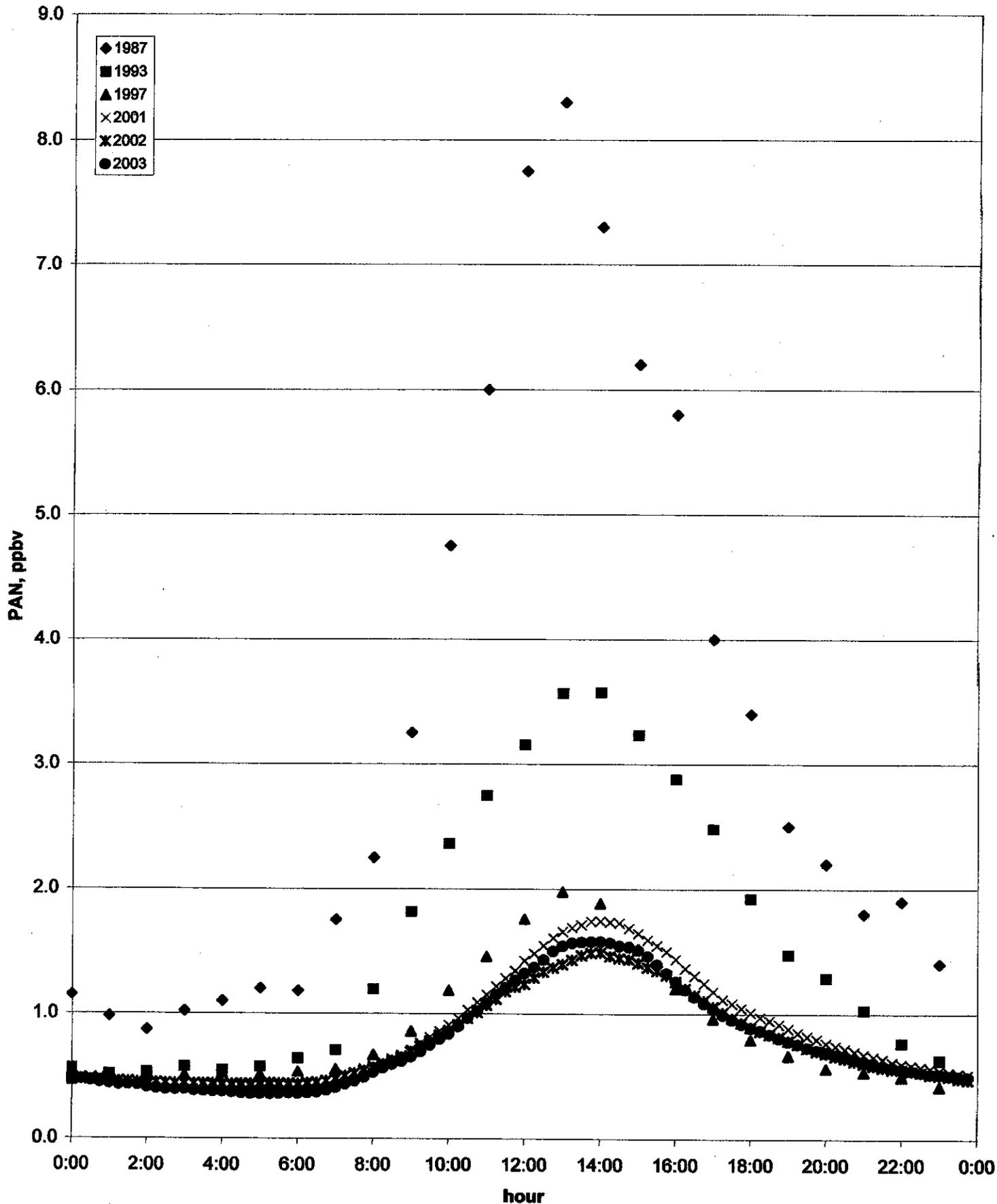


Figure 7.5 Seasonal variations of peak PAN concentrations in 1967 – 68, 1975 – 76, 1980 and 2001 – 2003

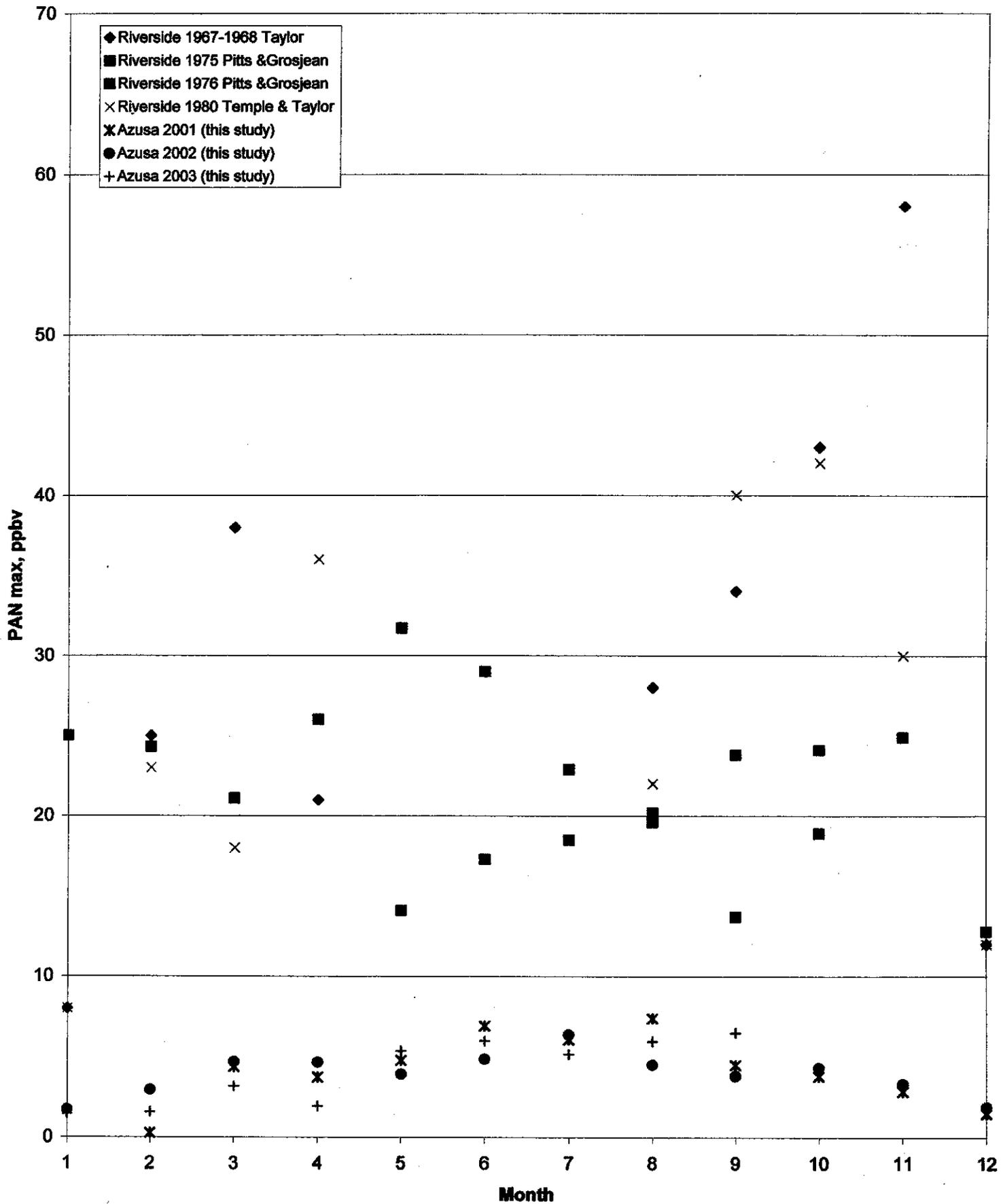


Figure 7.6 Seasonal variations of monthly-averaged PAN concentrations in 1967 – 68, 1975 – 76, and 2001 – 2003

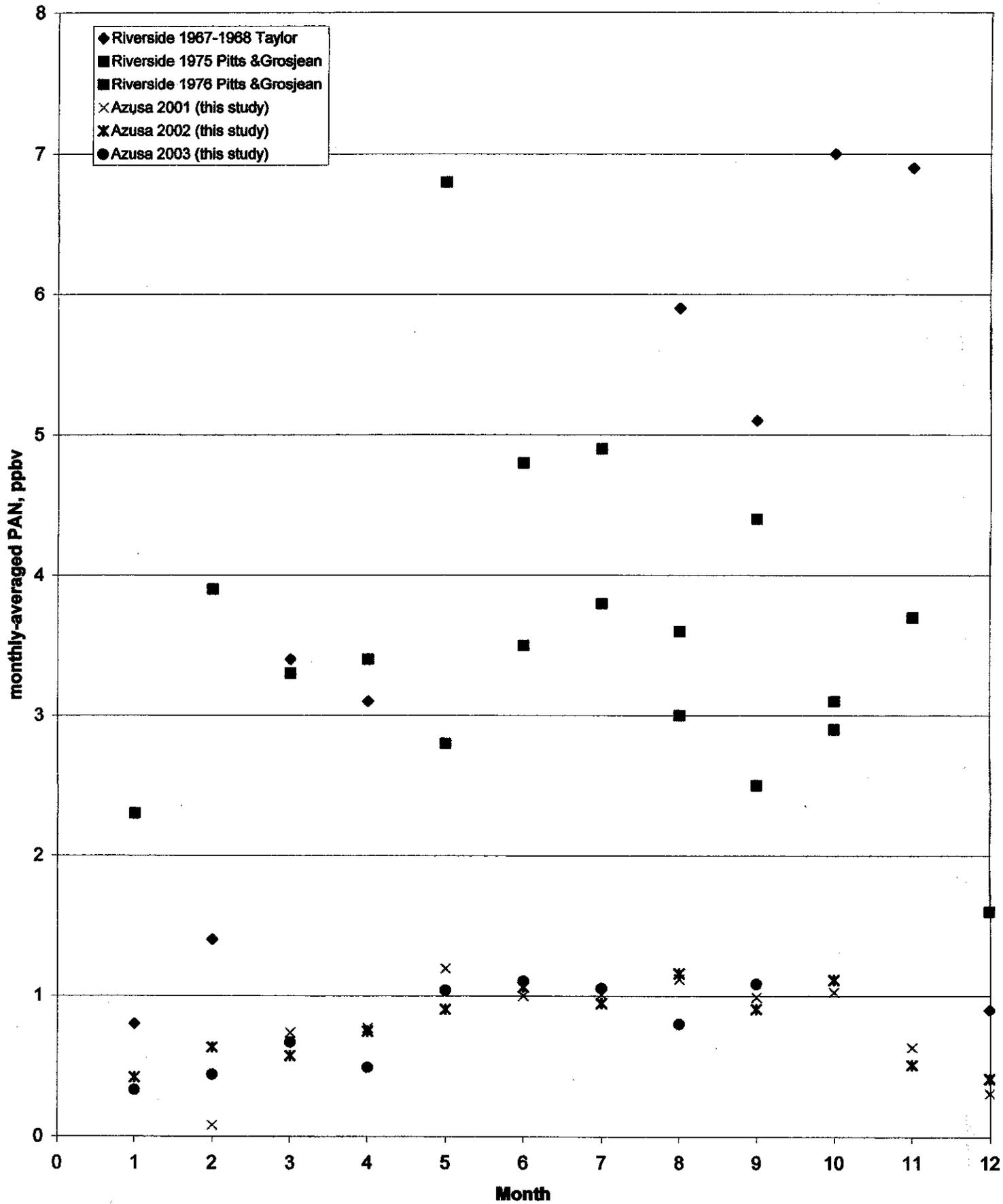


Figure 7.7 Peak PPN concentrations and highest 24 hour-averaged PPN concentrations in Southern California, 1989 - 2003

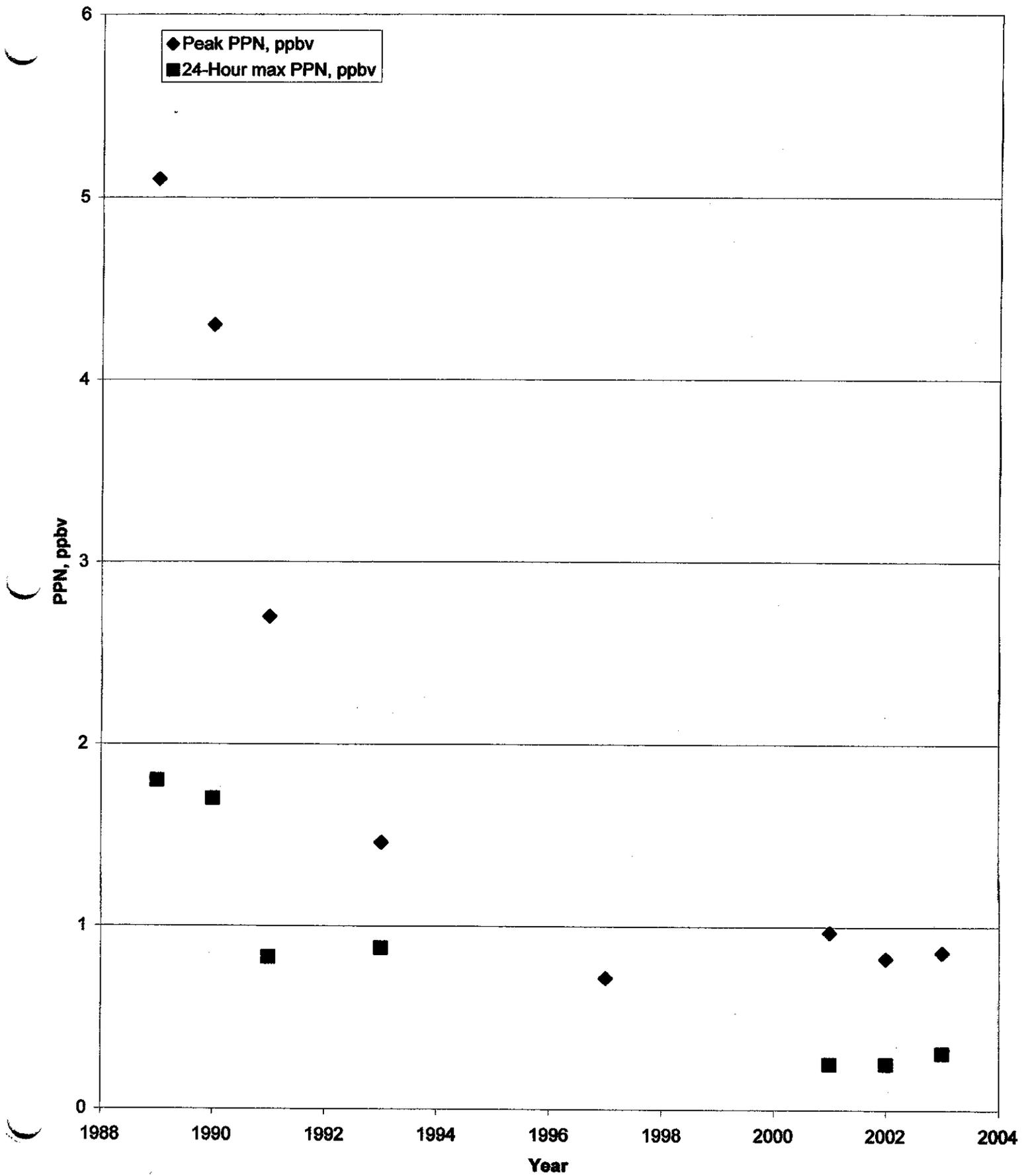


Figure 7.8 PPN/PAN ambient concentration ratio, 1989 - 2003

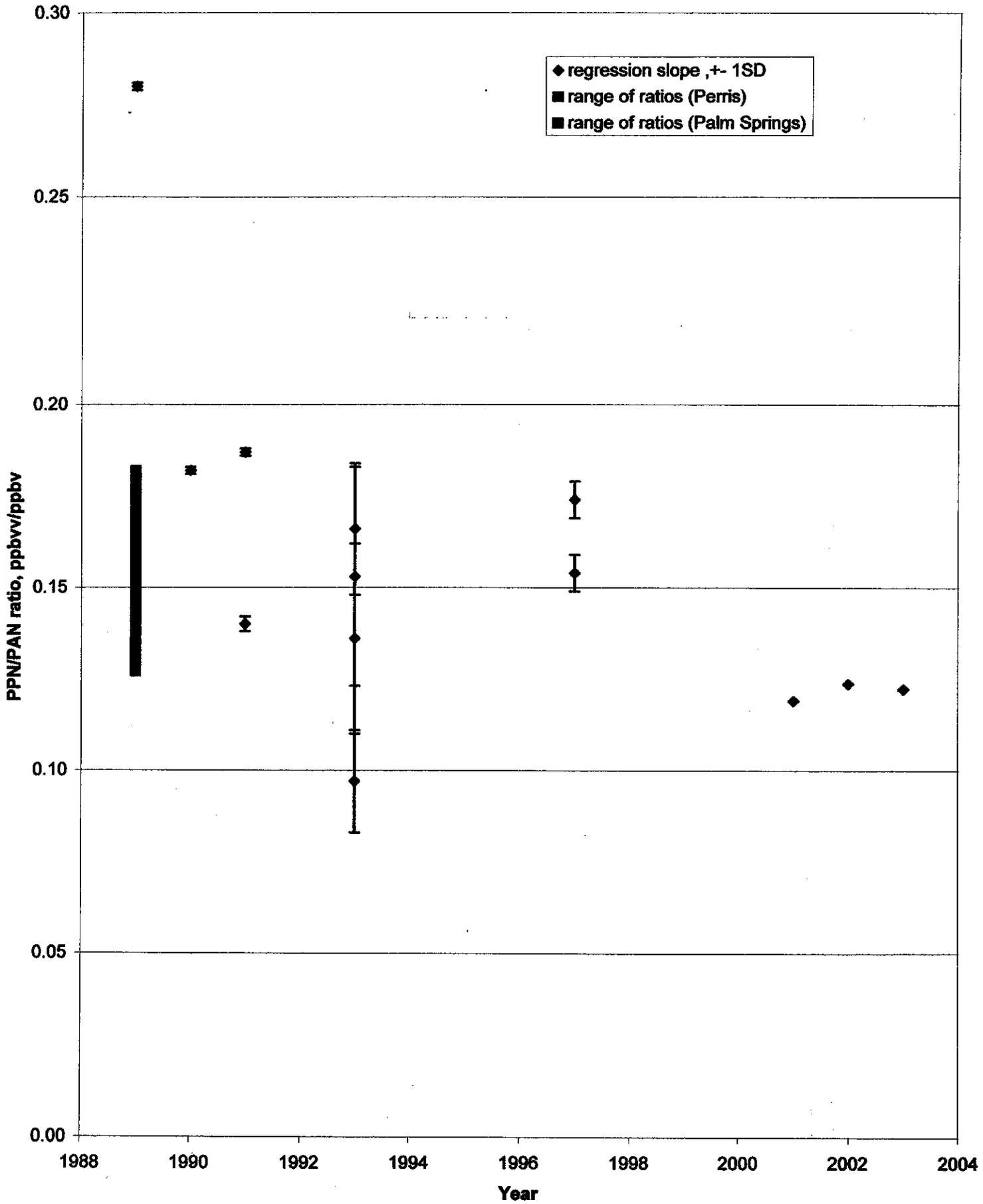


Figure 8.1 Time series plot of one-hour ambient ozone concentrations, Azusa, 2002

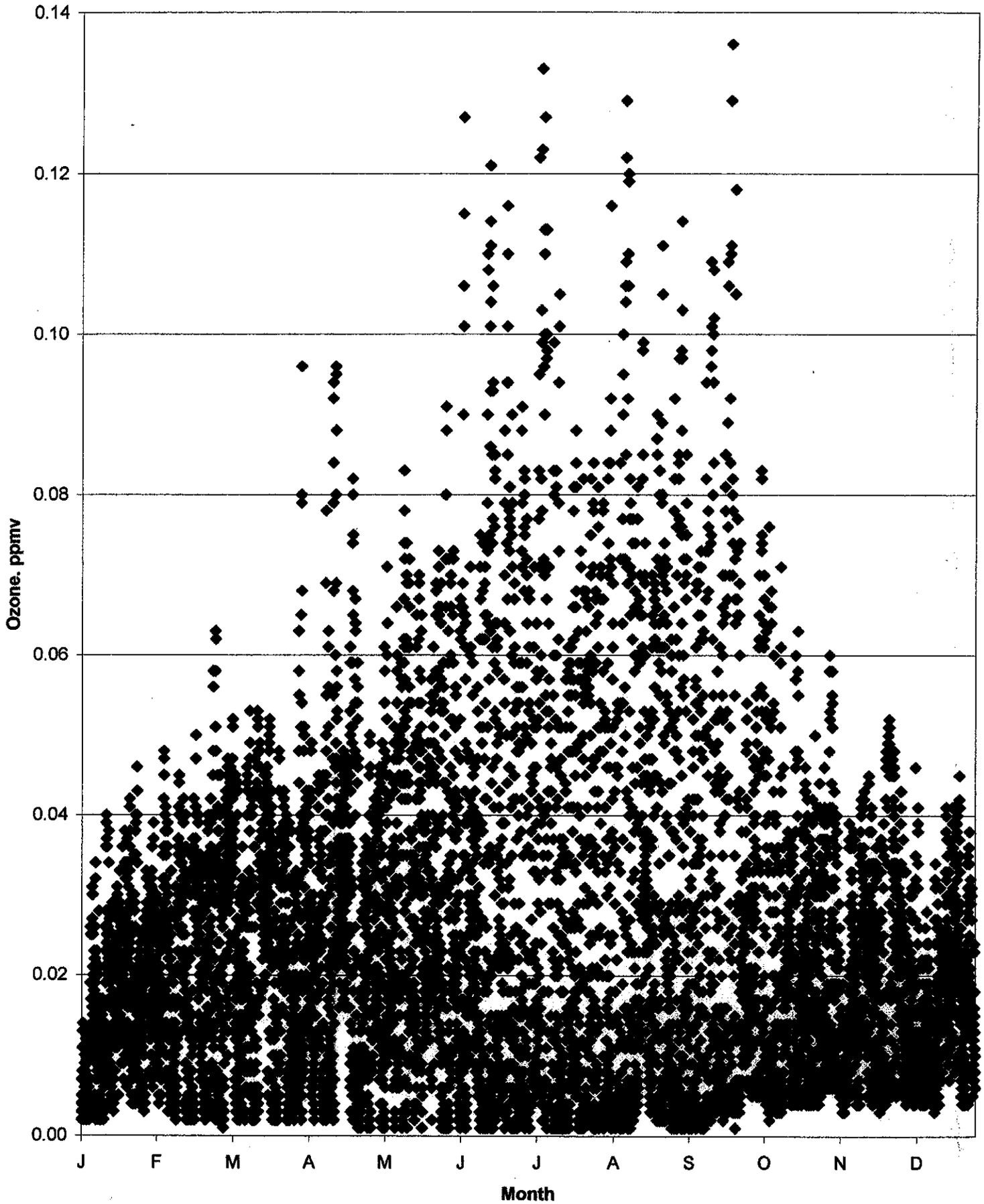


Figure 8.2 Time series plot of daily one-hour ozone maxima, Azusa, 2001 - 2003

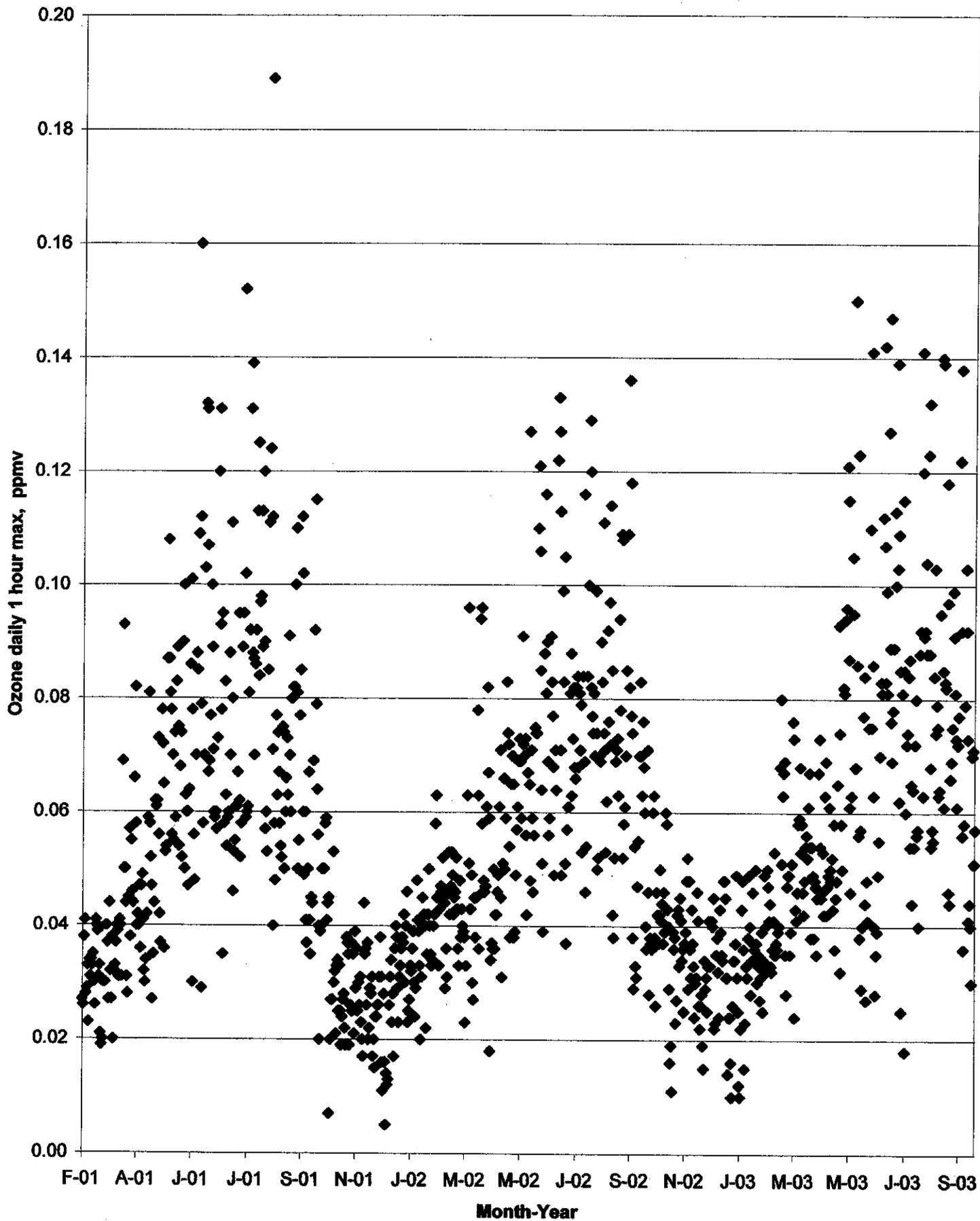


Figure 8.3 Ozone concentrations vs. time of day, Azusa, 2002

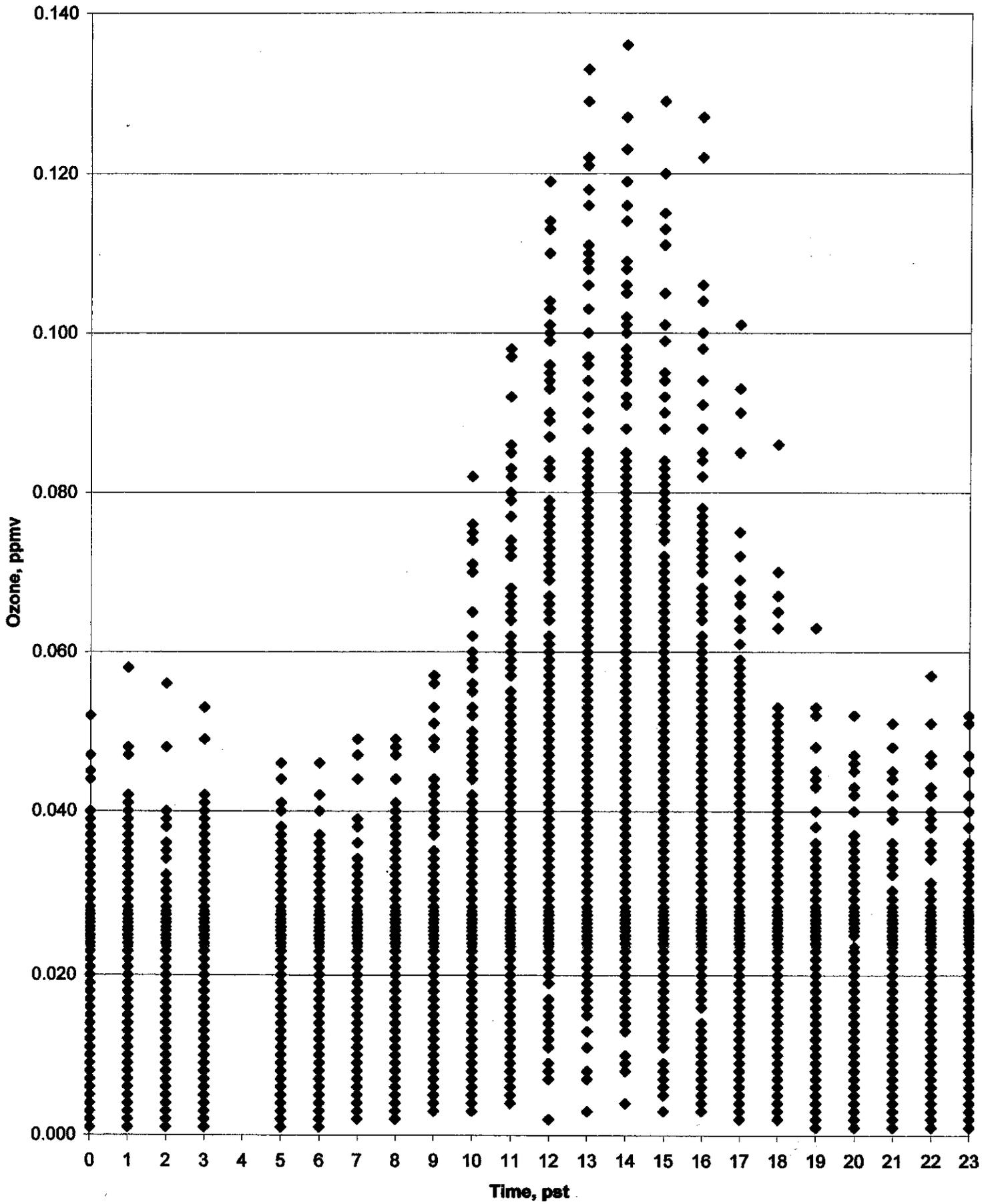


Figure 8.4 Composite diurnal profiles for ambient PAN and ambient ozone, Azusa, 2002

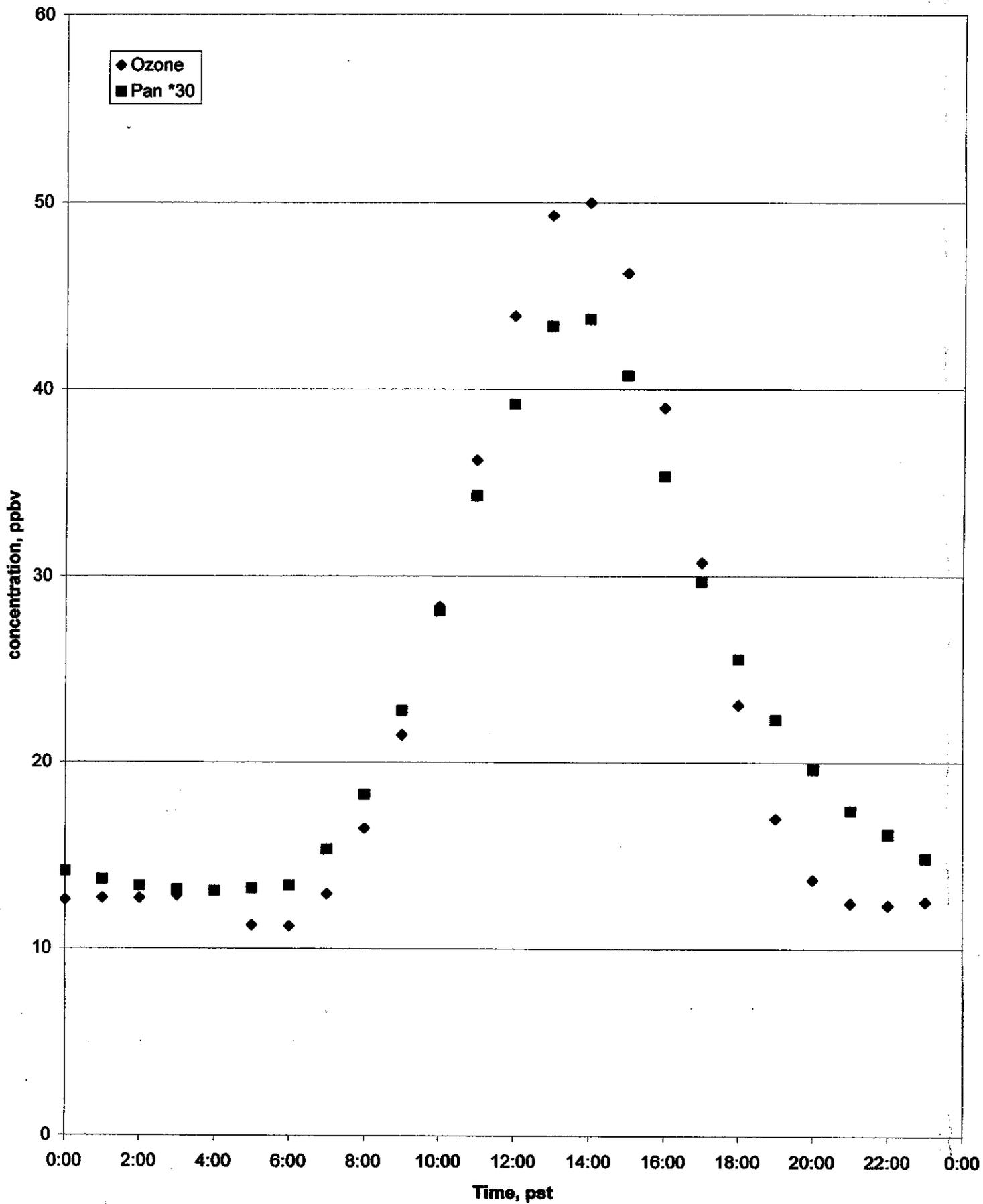


Figure 8.5 Scatterplot of ambient PAN vs. ambient ozone, Azusa, 2002

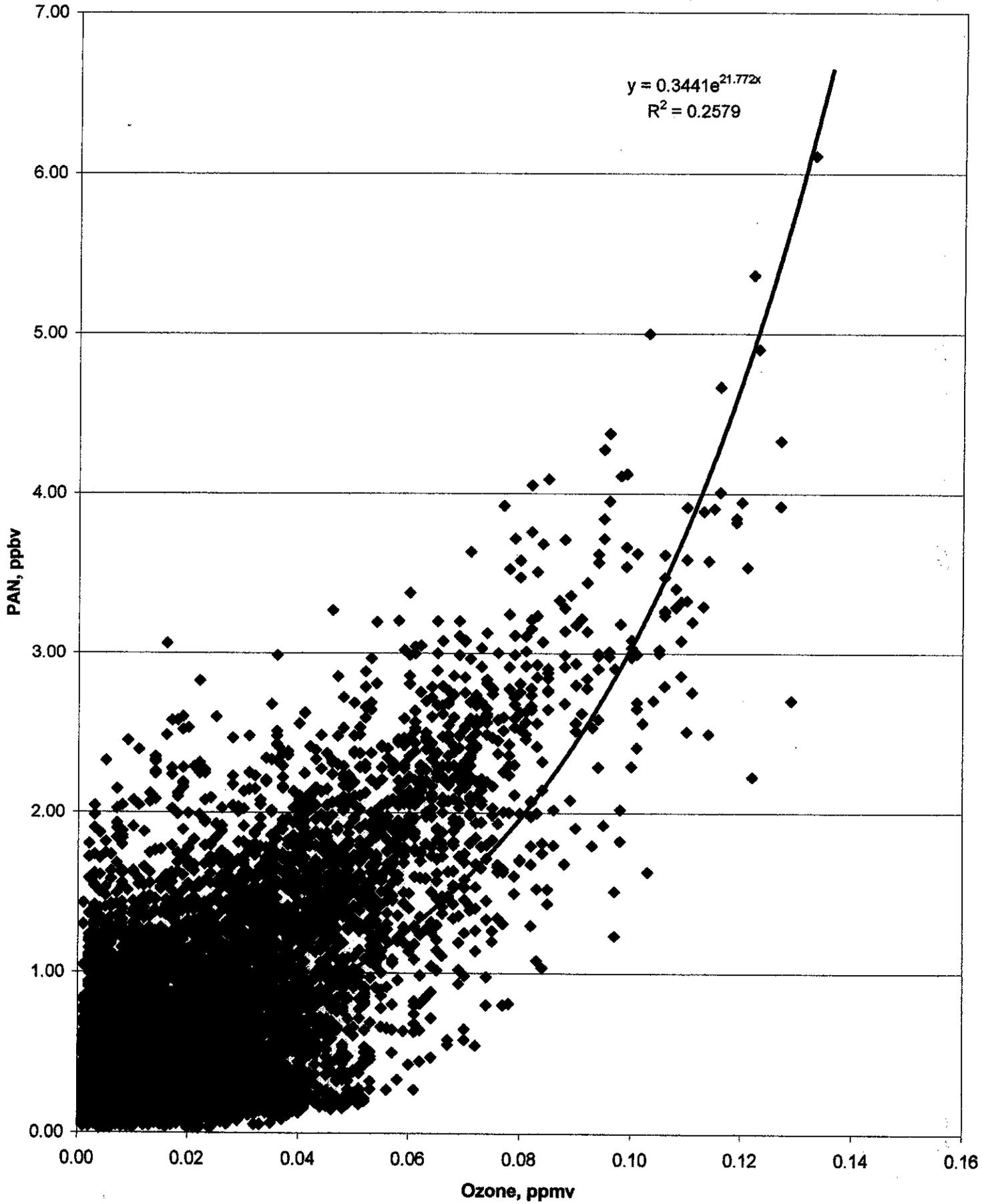


Figure 8.6 Scatterplot of daily log (maximum one-hour ozone) vs. log (maximum PAN), Azusa, 2001

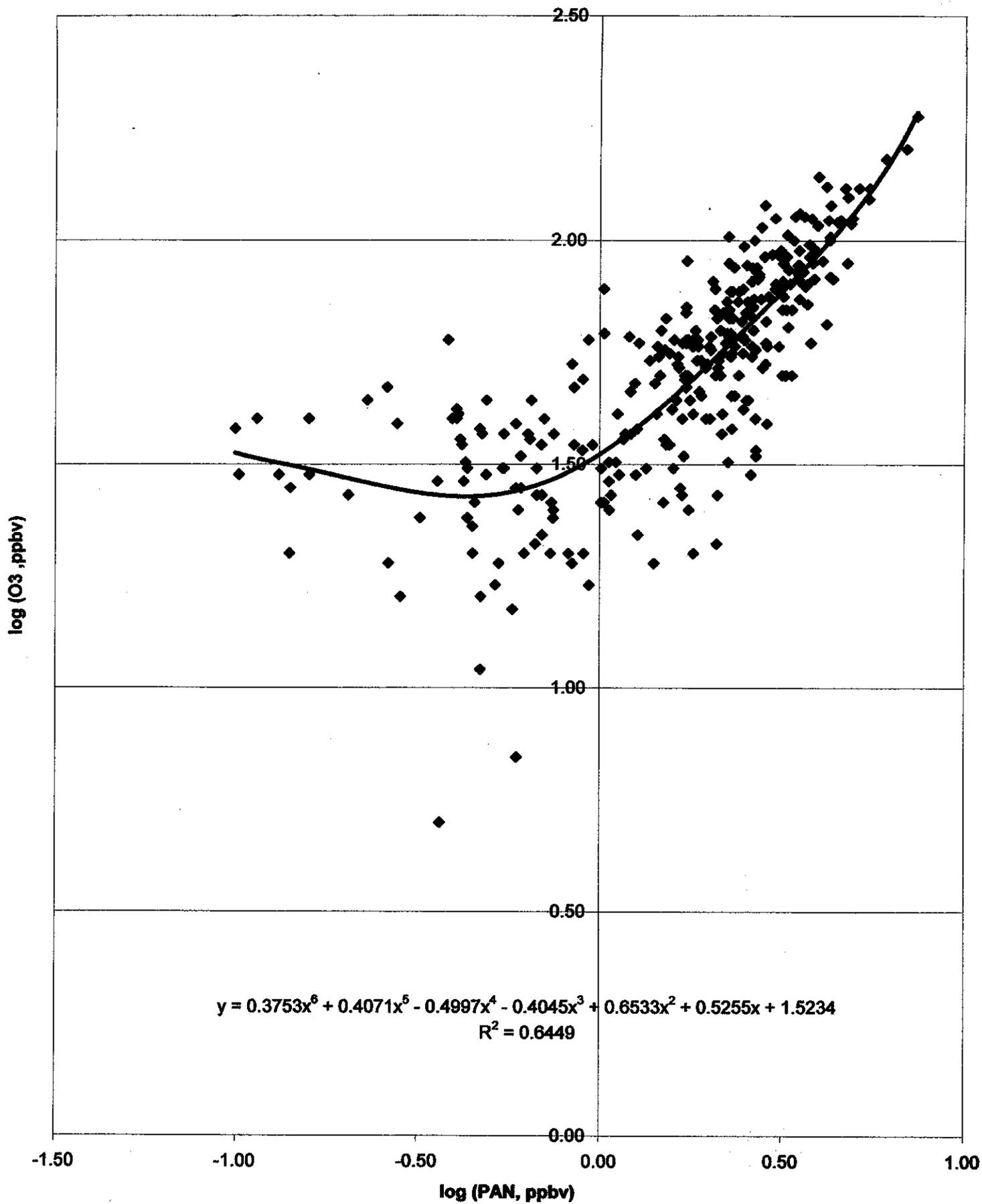


Figure 8.7 Time series plots of daily maximum one-hour ozone and daily maximum PAN concentrations, Azusa, 2001

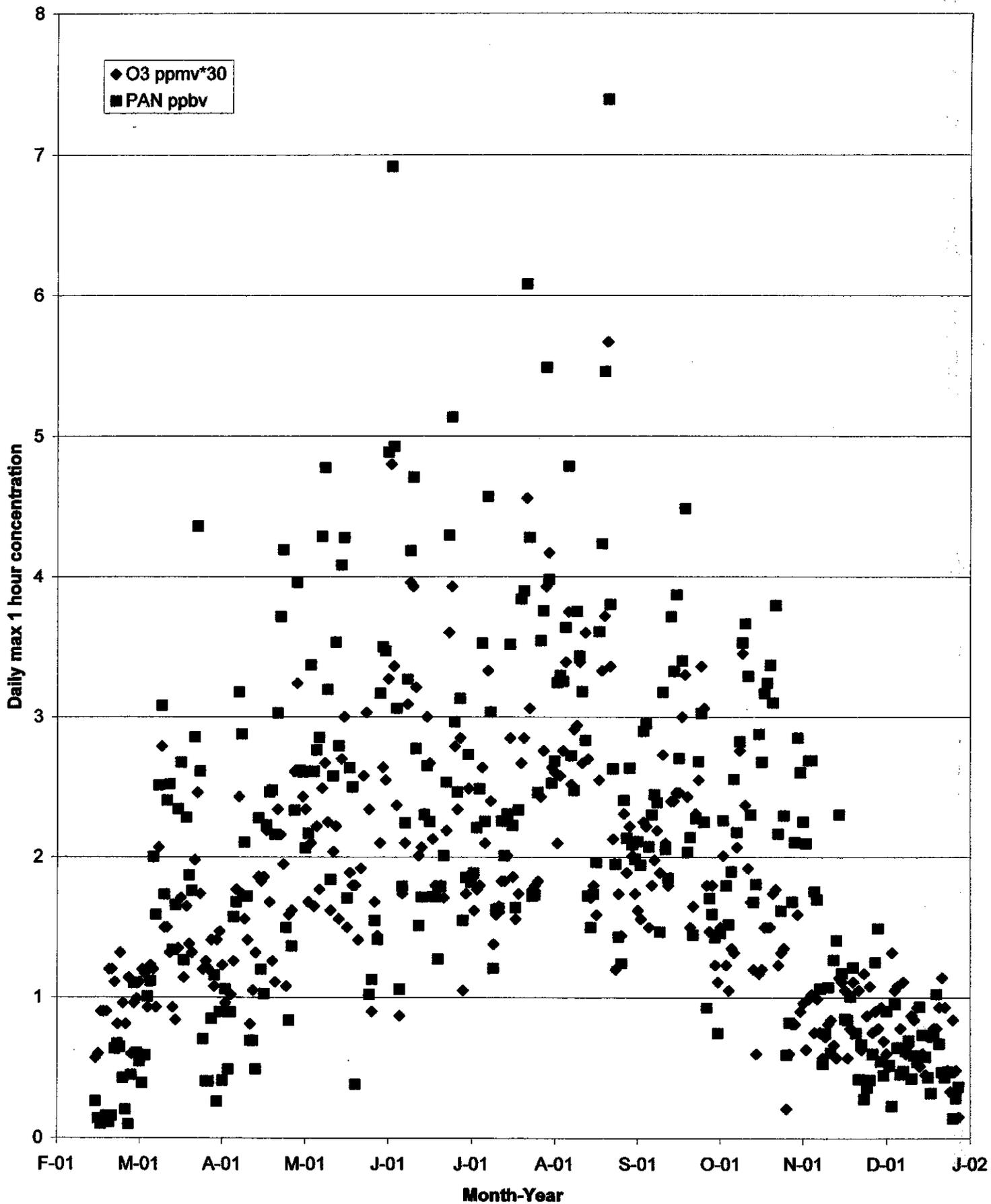


Figure 8.8 Time series log plots of daily maximum one-hour ozone and daily maximum PAN concentrations, Azusa, 2001

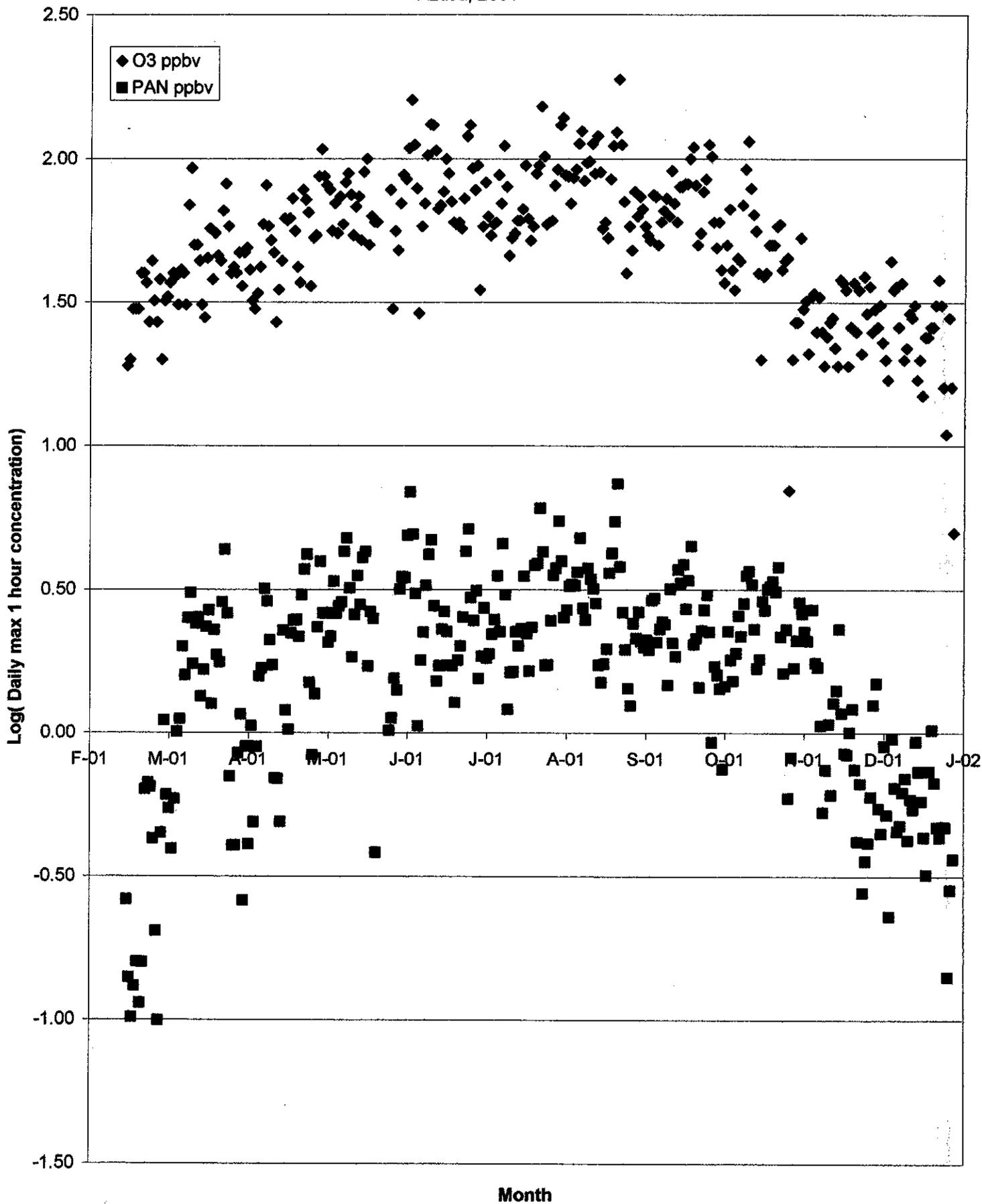


Figure 8.9 Scatterplot of daily maximum PAN vs. daily maximum one-hour ozone, Azusa, 2001

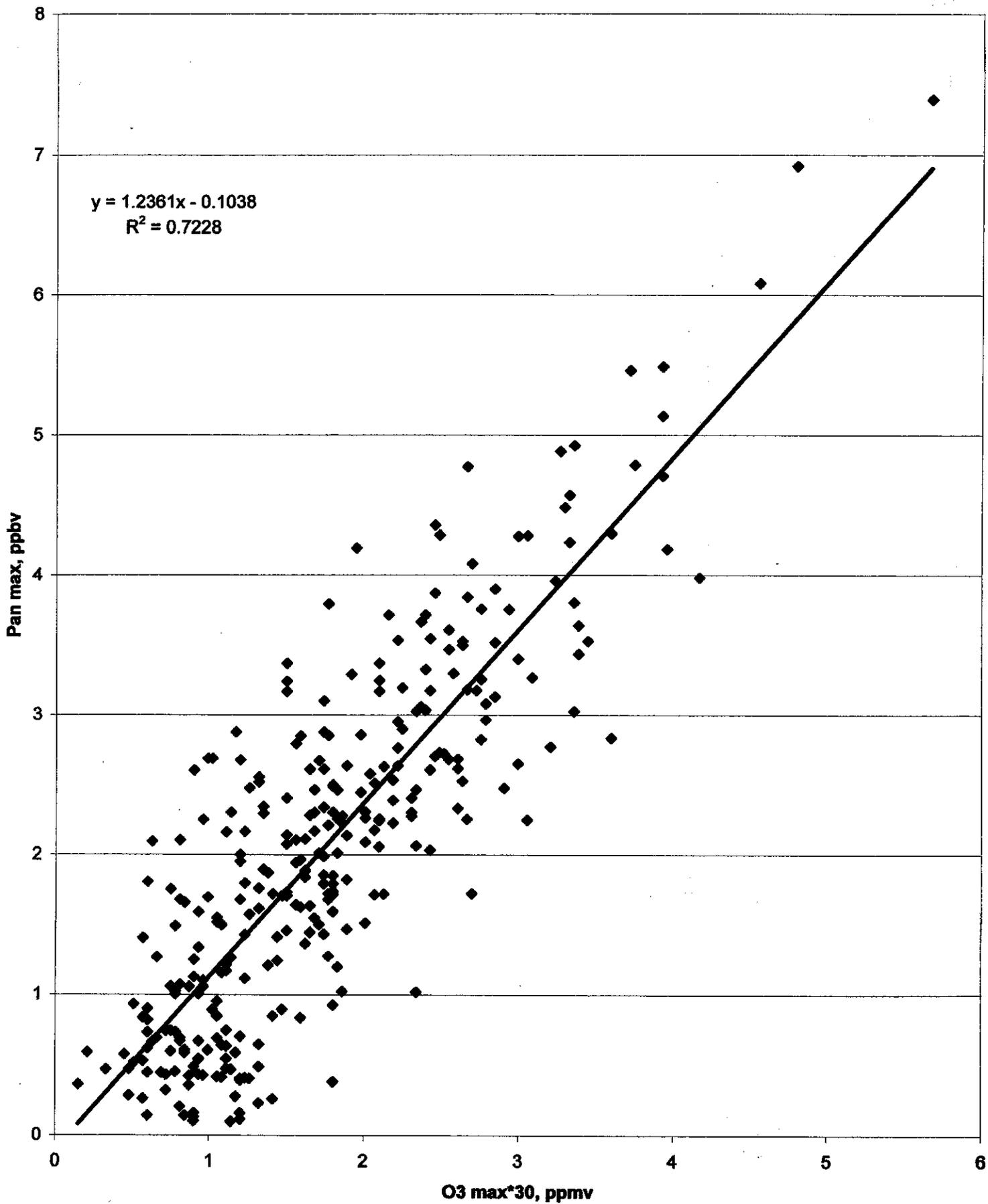


Figure 8.10 Time series plot of the PAN/ozone ambient concentration ratio, Azusa, 2002

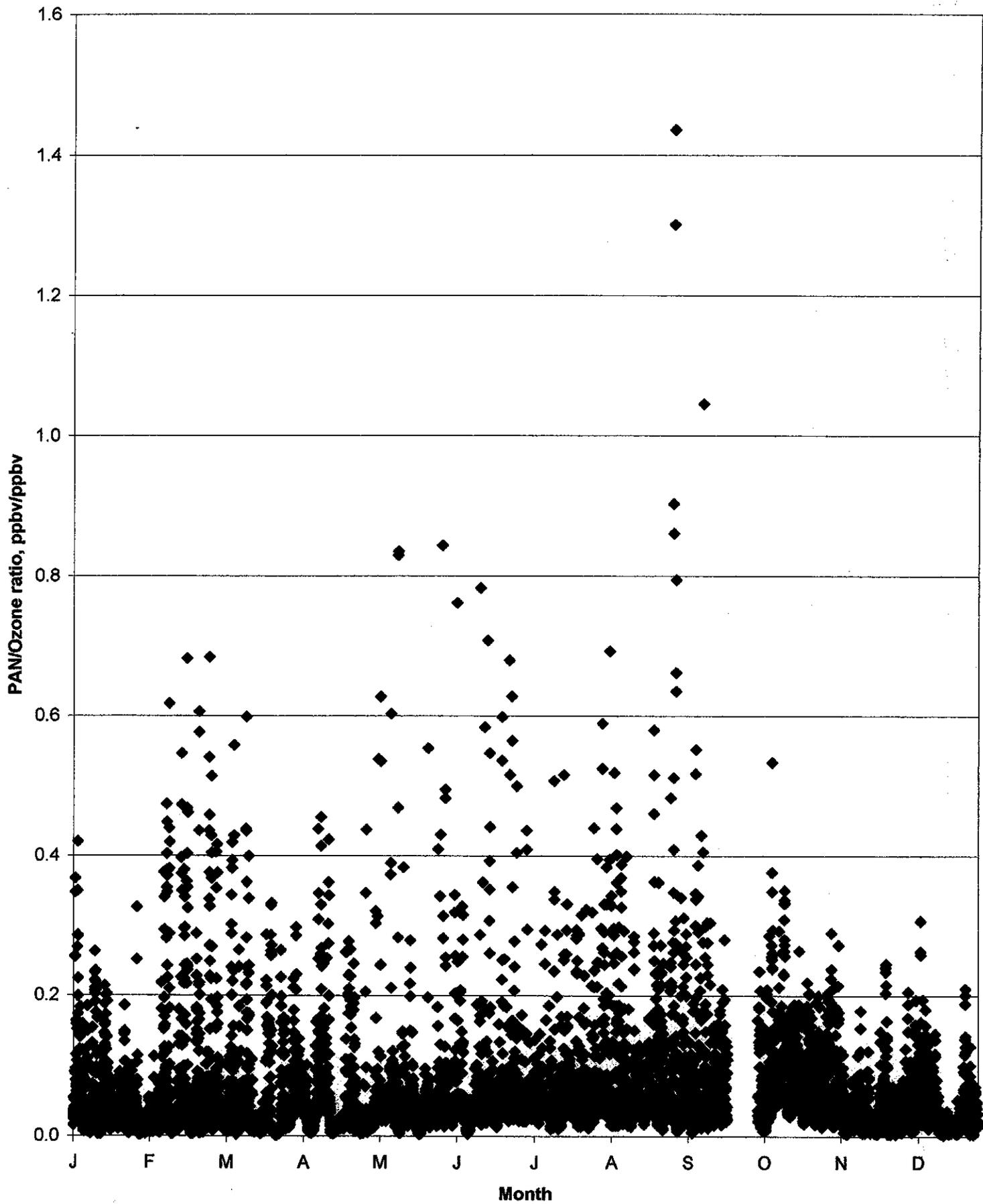


Figure 8.11 Diurnal variations of the PAN/ozone ambient concentration ratio, July 7, 2002

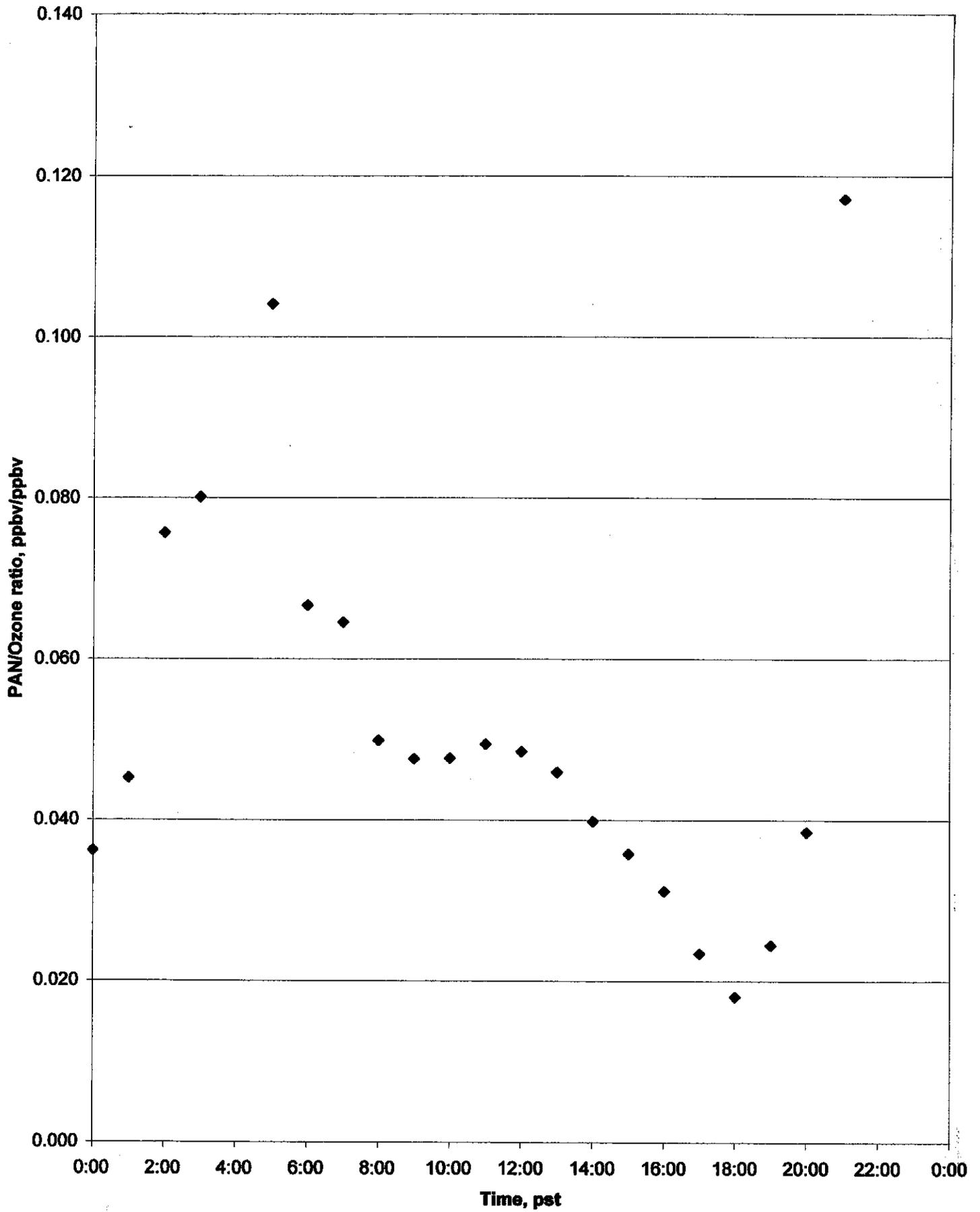


Figure 8.12 Diurnal variations of the PAN/ozone ambient concentrations ratio, August 30 – 31, 2002

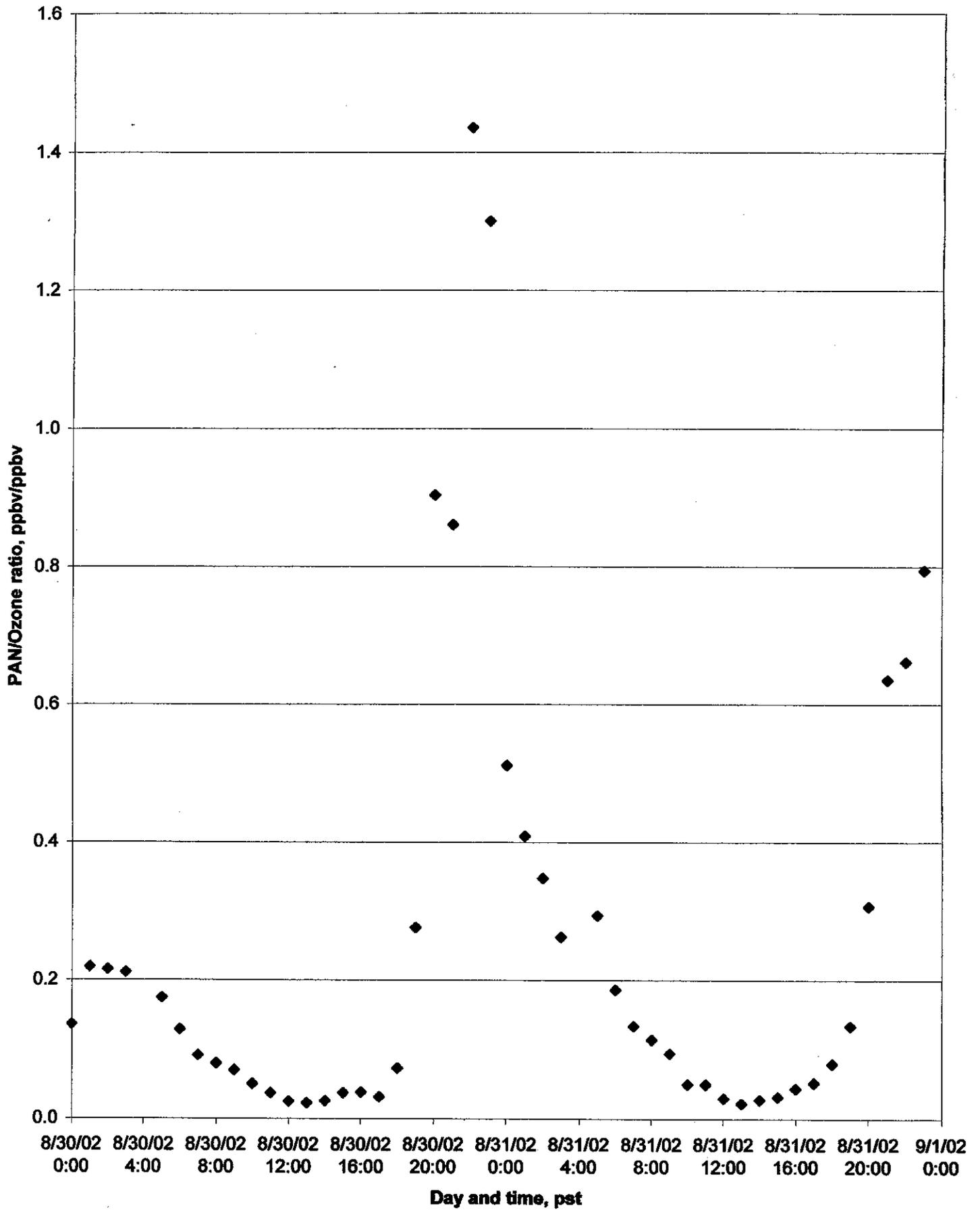


Figure 8.13 Diurnal variations of the PAN/ozone ambient concentration ratio, March 23 – 24, 2002

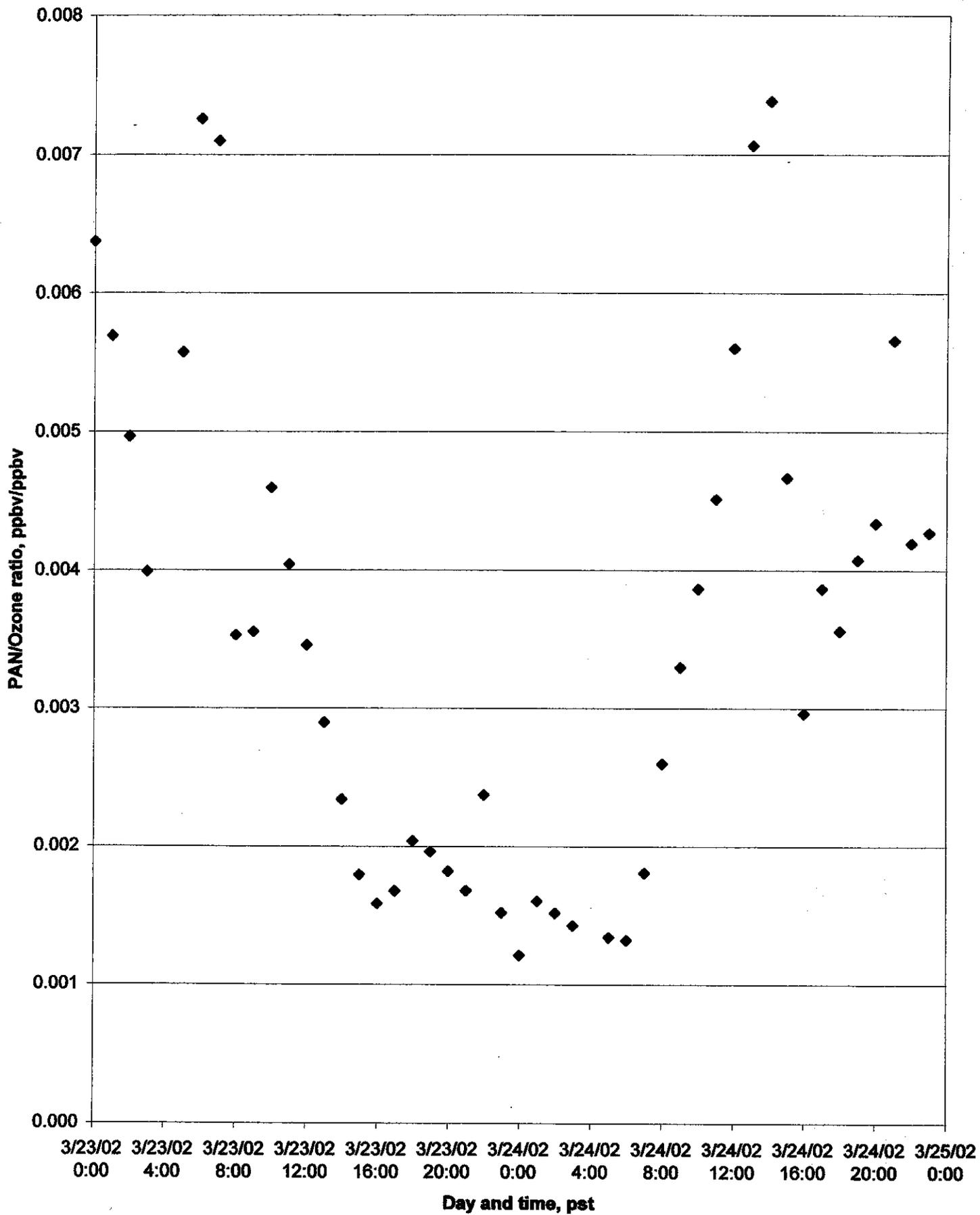


Figure 8.14 Plot of the PAN/ozone ambient concentration ratio vs. time of day, Azusa, 2002

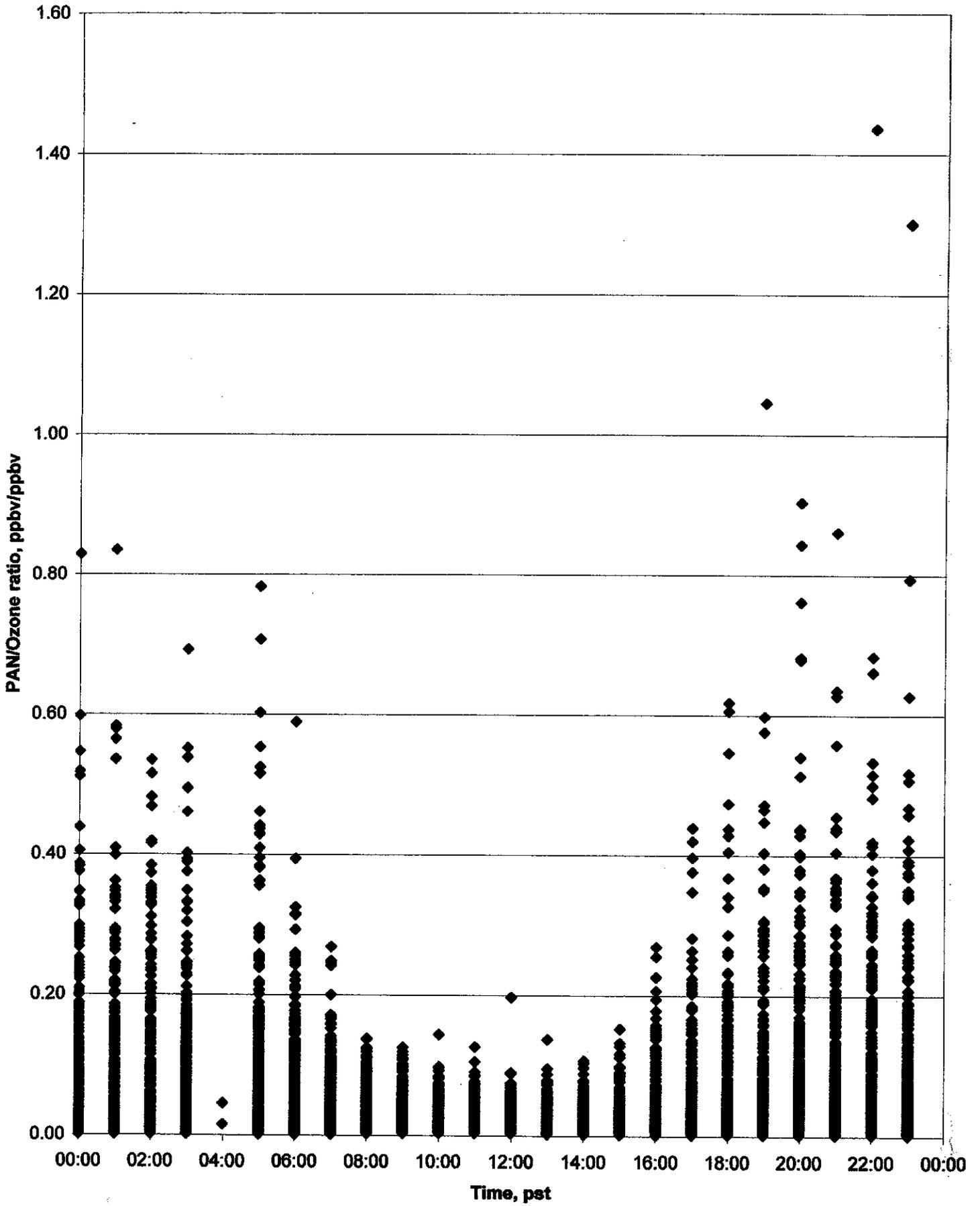


Figure 8.15 Composite diurnal profiles of the PAN/ozone and PPN/ozone ambient concentration ratios, Azusa, 2002

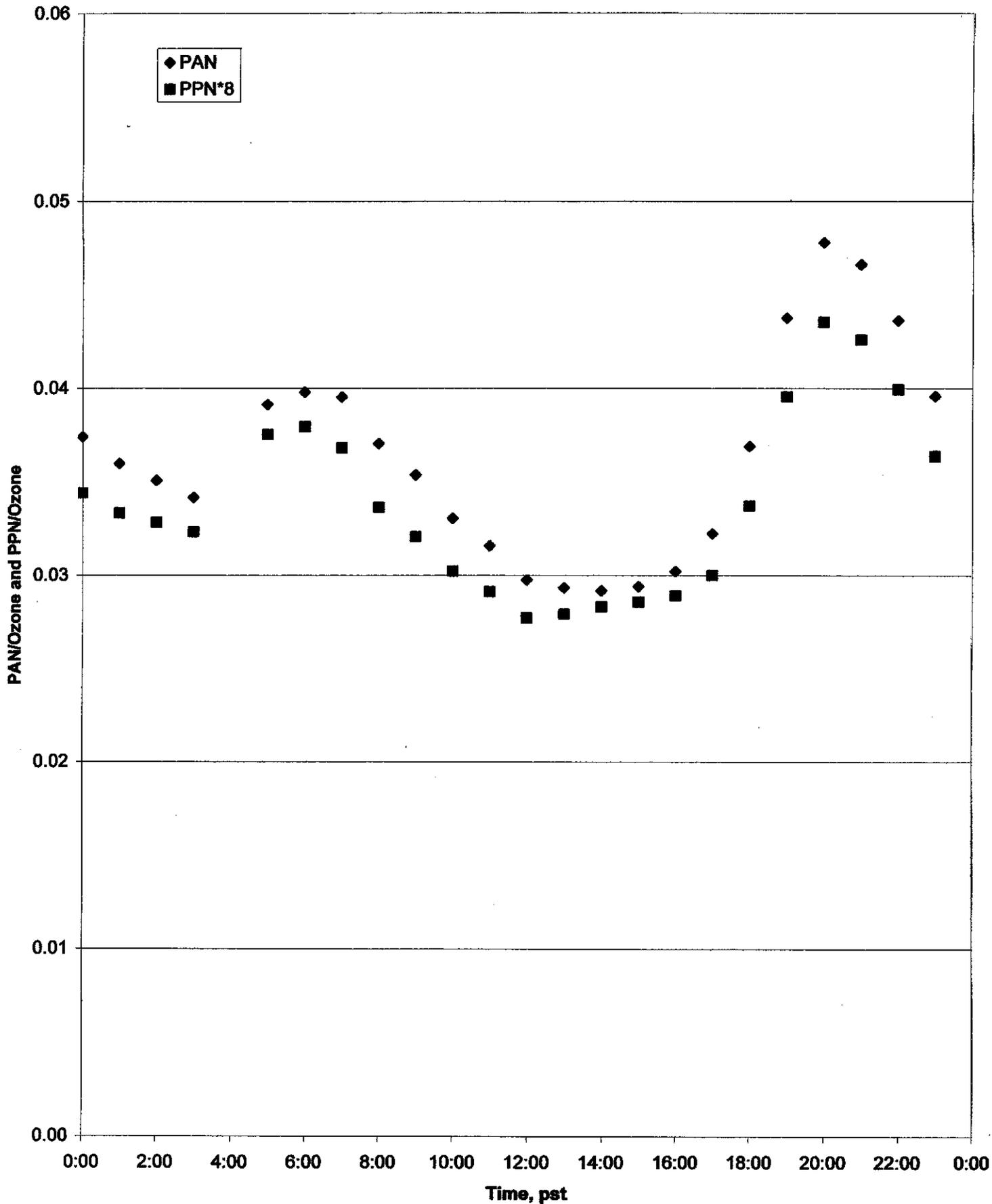
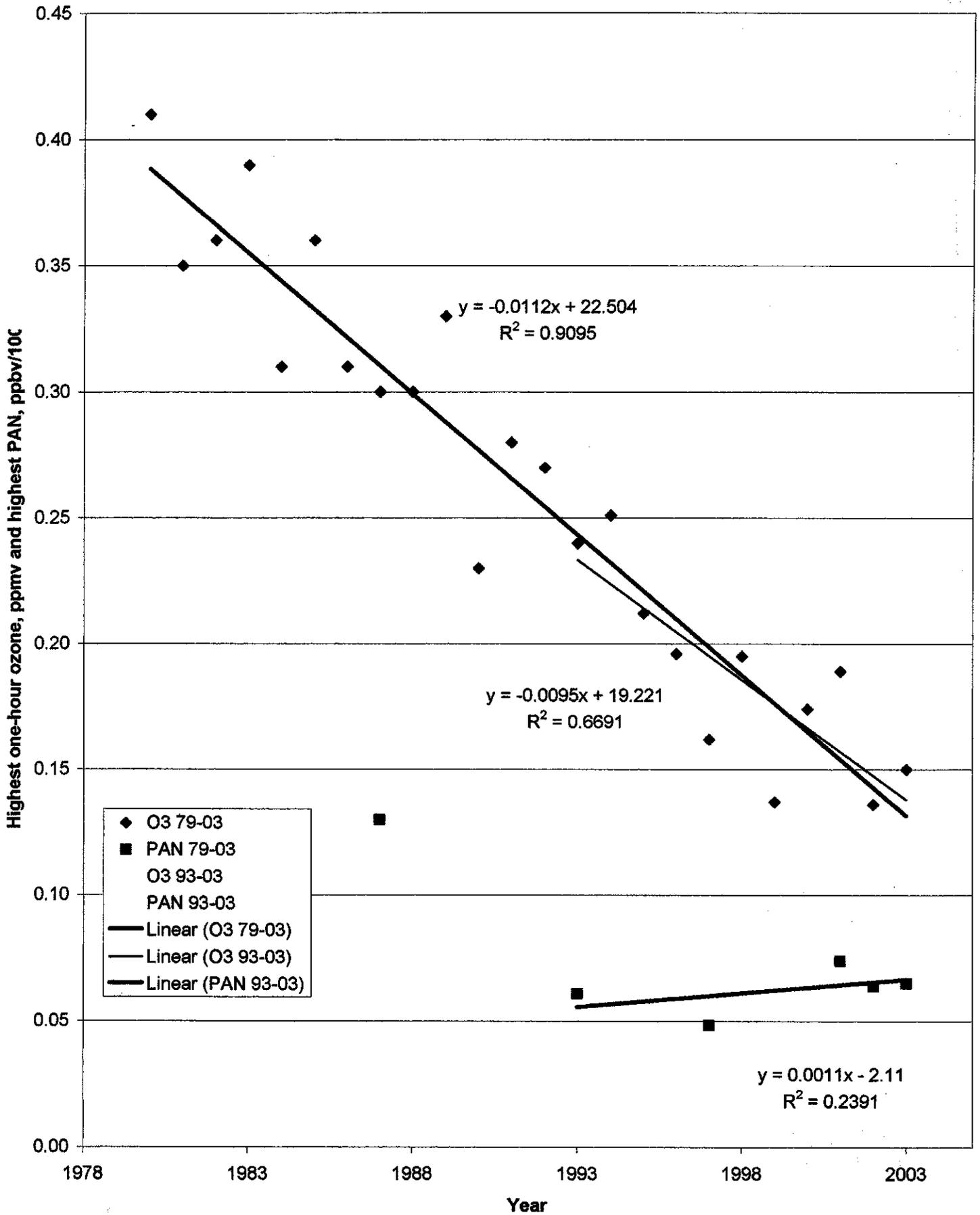


Figure 8.16 Long-term trends in highest one-hour ozone and highest PAN concentrations, Azusa, 1980 – 2003



APPENDIX A

Peroxyacetyl Nitrate and Peroxypropionyl Nitrate during SCOS 97-NARSTO

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Peroxyacyl nitrates [RC(O)OONO₂] play an important role in urban air quality and tropospheric chemistry. They also receive attention as mutagens, phytotoxins, and possible air quality indicators of changes in vehicle fuel composition. Ambient concentrations of PAN (R = CH₃) and PPN (R = C₂H₅) have been measured during summer 1997 at two southern California locations, Azusa (July 14–October 16) and Simi Valley (June 18–October 16). The highest concentrations were 4.8 ppb for PAN and 0.72 ppb for PPN in Azusa and 3.0 ppb for PAN and 0.28 ppb for PPN in Simi Valley. Ambient levels of PAN and PPN during summer 1997 were lower than those measured in the last three studies carried out in southern California in the summers of 1990, 1991, and 1993. Average PPN/PAN concentration ratios were about the same in Azusa (0.142 ± 0.025, *n* = 132) and in Simi Valley (0.135 ± 0.028, *n* = 138). The PPN/PAN ratio measured in Azusa was the same as that measured at that location in 1993 prior to the introduction in 1996 of California Phase 2 reformulated gasoline. Diurnal variations of PAN and PPN generally followed those of ozone with respect to time of day but not with respect to amplitude. The PAN/ozone ratio was lower in Simi Valley than in Azusa, and daytime minima were recorded at both locations. The amount of PAN lost by thermal decomposition accounted for large fractions of the amount of PAN formed (measured + decomposed) during daytime hours at both locations. The amount of PAN lost by thermal decomposition was higher in Azusa and was up to ca. 8.5 ppb, i.e., 4–5 times more than that measured, when afternoon temperatures were ca. 40 °C.

Introduction

Peroxyacetyl nitrate [PAN, CH₃C(O)OONO₂] and other peroxyacyl nitrates [RC(O)OONO₂] play an important role in urban and regional air quality and in tropospheric chemistry. Peroxyacyl nitrates have no known direct emission sources and are formed in situ by photochemical reactions involving volatile organic compounds (VOC) and oxides of nitrogen (1). They have received regulatory attention as eye irritants, mutagens, and phytotoxins (1–4). PAN has also received attention as a precursor to formaldehyde and to free radicals

(5), as an interferent in the measurements of NO₂ by chemiluminescence (6), and for its important role in the atmospheric transport of reactive nitrogen on regional and global scales (7). There is also regulatory interest in PAN in the context of oxygenated fuel policies. The photochemical oxidation of ethanol leads to acetaldehyde (8), and the photochemical oxidation of acetaldehyde leads to PAN (1). At issue is whether gasolines that contain ethanol lead to significantly more ambient PAN than gasolines that do not (9, 10). This issue is receiving attention in the State of California where methyl *tert*-butyl ether (MTBE) will be phased out by the end of 2002 (11) and may be replaced by ethanol (12). Despite its importance, PAN is not included in urban air quality monitoring networks, and long-term trends can only be examined from data obtained in brief studies carried out several years apart. The last study of ambient PAN and PPN in southern California was carried out in summer 1993 (13) prior to the introduction in 1996 of California Phase 2 reformulated gasolines.

We report ambient concentrations of PAN and of peroxypropionyl nitrate [PPN, CH₃CH₂C(O)OONO₂] measured as part of the Southern California Ozone Study (SCOS 97-NARSTO), a comprehensive study of ozone air quality carried out from mid-June to mid-October 1997 in the entire southern region of California (14). The overall objectives of SCOS 97-NARSTO and the study design are described in ref 14 and at <http://www.arb.ca.gov/SCOS>. We measured PAN and PPN at two locations, Azusa in Los Angeles County and Simi Valley in Ventura County. Measurements at Azusa, a near-downwind smog receptor site east of Los Angeles, could be compared to those made in 1993 (13) and before that in 1987 (15) at the same location. Simi Valley was a suitable location to characterize transport of polluted air from Los Angeles to Ventura County following a smog episode in that airshed (14). In the following sections, we summarize the overall results, describe temporal variations of PAN and PPN, and discuss PPN/PAN and PAN/ozone concentration ratios. High daytime temperatures (up to 41 °C) were recorded during summer 1997, and we calculated the magnitude of the loss of PAN resulting from thermal decomposition.

Experimental Methods

Ambient levels of PAN and PPN were measured by electron capture gas chromatography (EC-GC) using Scientific Research Instruments model 8610 gas chromatographs and Valco model 140 BN electron capture detectors. The measurement protocol was essentially identical to that described in ref 13 except that 75 cm long × 3 mm diameter Teflon columns were used instead of Teflon-lined stainless steel columns. The column temperature was 30 °C. To calibrate the EC-GC instruments, PAN was synthesized in the liquid phase, and parts per billion (ppb) levels of PAN in the gas phase were obtained by flowing purified air over an impinger containing solutions of PAN in dodecane. Calibrations involved collocated measurements of PAN by EC-GC and by chemiluminescence (13). Prestudy calibrations were carried out in the laboratory using a ca. 3.5-m³ all-Teflon chamber. These calibrations involved simultaneous measurements of PAN (five concentrations) by EC-GC (using the two EC-GC units to be deployed in the field) and by chemiluminescence (Monitor Labs model 8840 NO_x analyzer). The NO_x analyzer was calibrated in our laboratory using a certified cylinder of NO in nitrogen (Air Liquide America Corp.) and an EnviroNics model 100 calibrator. The ozone generator of the calibrator was used to titrate the NO from the cylinder to NO₂, which was then used to calibrate the NO₂ and NO_x channels of the

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TABLE 1. Summary of Ambient Concentrations of PAN and PPN

	Azusa, Los Angeles County	Simi Valley, Ventura County
	PAN, ppb^a	
detection limit	0.028	0.038
hourly measurements		
range ^{b,c}	0.05–4.84 (0.06–4.06)	0.06–2.99 (0.06–2.15)
average ^{b,d}	0.880 ± 0.742 (0.936 ± 0.743)	0.608 ± 0.433 (0.515 ± 0.410)
no. of measurements ^b	2194 (393)	2694 (401)
24-h averaged concns:		
range	0.17–2.08	0.15–1.30
average	0.87 ± 0.34	0.60 ± 0.23
no. of days	95	118
	PPN, ppb^a	
detection limit	0.042	0.049
hourly measurements		
range	0.075–0.719	0.053–0.278
average ^d	0.253 ± 0.124	0.127 ± 0.069
no. of measurements	132	138

^a Measured from July 14 to Oct 16, 1997, in Azusa and from June 18 to Oct 16, 1997, in Simi Valley. ^b Values given in parentheses are for SCOS 97-NARSTO days of intensive operations. ^c The highest values were recorded on Oct 5 in Azusa and on Oct 1 in Simi Valley. ^d ± 1 SD. ^e From data for SCOS 97-NARSTO days of intensive operations.

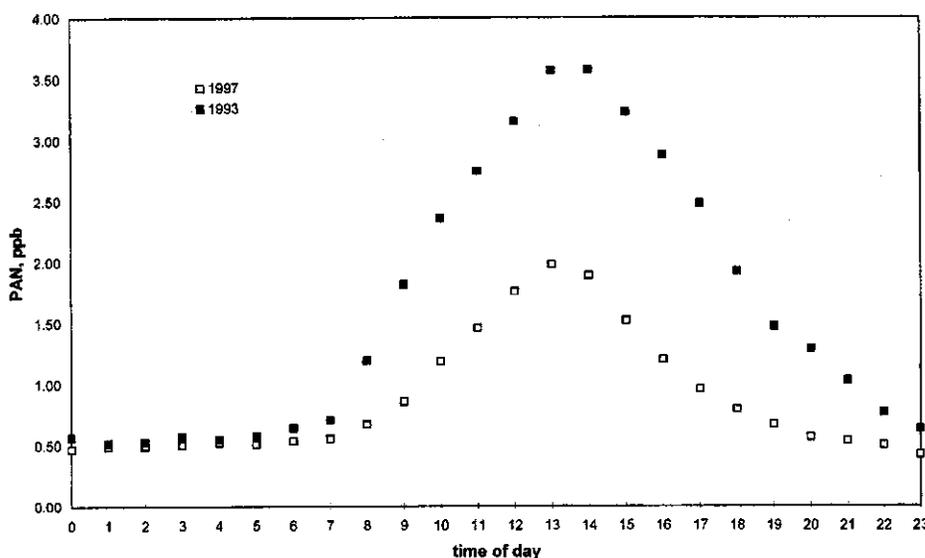


FIGURE 1. Composite diurnal profiles for ambient PAN in Azusa, summer 1993 and summer 1997.

NO_x analyzer. The converter efficiency was found to be the same for PAN as for NO₂ by thermally decomposing PAN using a heated tube at 150 °C and measuring the response of the NO_x analyzer. The EnviroNics calibrator was compared to a CSI model 1700 calibrator transfer standard maintained by the Ventura County Air Pollution Control District, with excellent agreement (±1%) for both NO and NO₂ calibrations. The ozone generator of the CSI calibrator was used to calibrate the ozone generator of the EnviroNics calibrator, and the mass flow controllers of the EnviroNics calibrator were calibrated using a NIST-traceable Humonics model 650 electronic bubble flowmeter. Field calibrations carried out in Simi Valley involved collocated measurements of PAN (ppb levels in a 125-L Teflon bag) by EC-GC and by chemiluminescence (TECO model 42 NO_x analyzer operated by the Ventura County Air Pollution Control District). To minimize decomposition of PAN, the 125-L Teflon bag was covered with black plastic and was cooled using the vehicle's air conditioning during trips from the laboratory to the field locations. Two comparisons were made of PAN concentrations measured using the Monitor Labs model 8840 NO_x analyzer and the TECO model 42 NO_x analyzer. Good agreement was obtained in both cases, with relative standard

deviations of 3.5% (PAN = 8 ppb) and 6.7% (PAN = 14 ppb). For field calibrations in Azusa, the 125-L Teflon bag containing ppb levels of PAN and used to carry out calibrations at Simi Valley was taken to Azusa to measure PAN by EC-GC and returned to Simi Valley for collocated measurements of PAN by EC-GC and by chemiluminescence. In this way both EC-GC units could be calibrated using the same chemiluminescence NO_x analyzer, i.e., the one operated in Simi Valley. The wall loss rate of PAN in the 125-L Teflon bag was measured in four separate trips from Simi Valley to Azusa and back to Simi Valley and averaged 1% h⁻¹. This value was used to correct the Azusa EC-GC calibration data. Calibrations (eight in Simi Valley and seven in Azusa) were carried out ca. every 2 weeks.

The calibrations yielded PAN response factors (peak height, mm, on attenuating setting 4 vs concentration, ppb) of 7.55 ± 0.53 in Azusa and 7.04 ± 0.42 in Simi Valley. These response factors were used to convert measured peak heights in the chromatograms to ambient concentrations. The measured response factors for PAN and PPN and the PPN/PAN response factor ratios were entirely consistent with those measured in previous work carried out with the same EC-GC units (13). Detection limits were 28 ppt for PAN in Azusa, 38

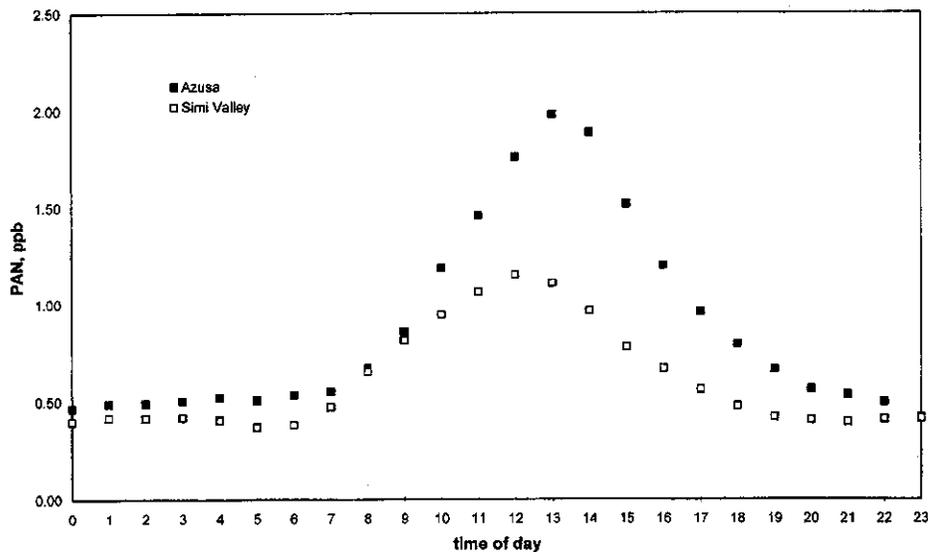


FIGURE 2. Composite diurnal profiles for ambient PAN in Azusa and in Simi Valley, summer 1997.

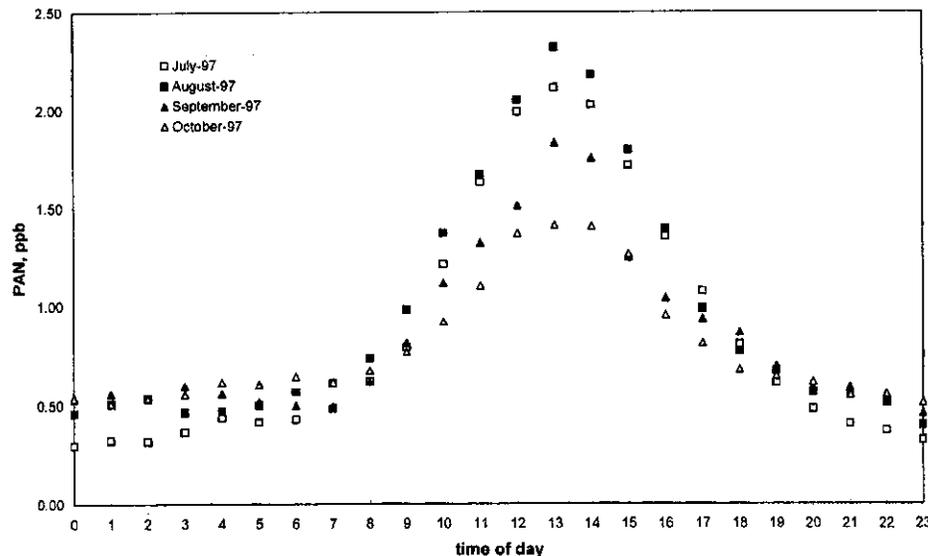


FIGURE 3. Monthly composite diurnal profiles for ambient PAN in Azusa.

ppt for PAN in Simi Valley, 42 ppt for PPN in Azusa, and 49 ppt for PPN in Simi Valley.

Because of air conditioning failure at Azusa, the EC-GC column temperature increased to 45 °C on August 5–6. Calibrations were carried out at three temperatures in the range of 30–45 °C and were used to correct ambient concentrations.

Proper operating conditions were verified every 2–7 days. The retention time of PAN was 7.21 ± 0.27 min (RSD = 3.3%) in Azusa and 6.28 ± 0.20 min (RSD = 3.2%) in Simi Valley. The ratio of the retention time of PPN to that of PAN was 1.25 ± 0.04 in Azusa (RSD = 3.2%) and 1.25 ± 0.03 in Simi Valley (RSD = 2.4%). We verified at both locations that no loss of PAN (<1%) occurred in the sampling lines (1/4 in. diameter Teflon tubing: 7.8 m long in Azusa and 5.1 m long in Simi Valley) and on the inlet Teflon filters. These tests were carried out at the sampling flow rates used during the study, i.e., 275 ± 10 mL/min in Azusa and 350 ± 10 mL/min in Simi Valley. We verified, by inserting a heated tube ($T = 150$ °C) in the sampling line upstream of the EC-GC unit operated in Azusa, that the PAN peak height decreased due to thermal decom-

position of PAN (measured peak height decrease = 96%). We also verified, by inserting a nylon filter upstream of the chemiluminescent NO_x analyzer operated in Simi Valley, that the Teflon bag used for field calibrations and containing ppb levels of PAN in purified air did not contain nitric acid (no change in NO_x reading to $\pm 0.5\%$), which if present would have introduced a bias in our field calibrations. Methyl nitrate was found as a minor impurity (1–2%) resulting from decomposition of PAN in the liquid phase, and the calibrations were corrected accordingly. Repeat injections were made at both locations from the Teflon bag containing ppb levels of PAN in pure air. The corresponding PAN peak heights were within $\pm 1\%$ of each other. Taking all uncertainties into account, we estimate the overall uncertainty to be $\pm 15\%$ for ambient PAN and PPN.

Ambient concentrations of PAN and PPN were measured from June 18 to October 16, 1997, in Simi Valley (121 days) and from July 14 to October 16, 1997, in Azusa (95 days). Injections of ambient air were made every 60 min (every 30 min in Azusa on July 14), and ca. 2700 and 2200 valid chromatograms were obtained in Azusa and Simi Valley,

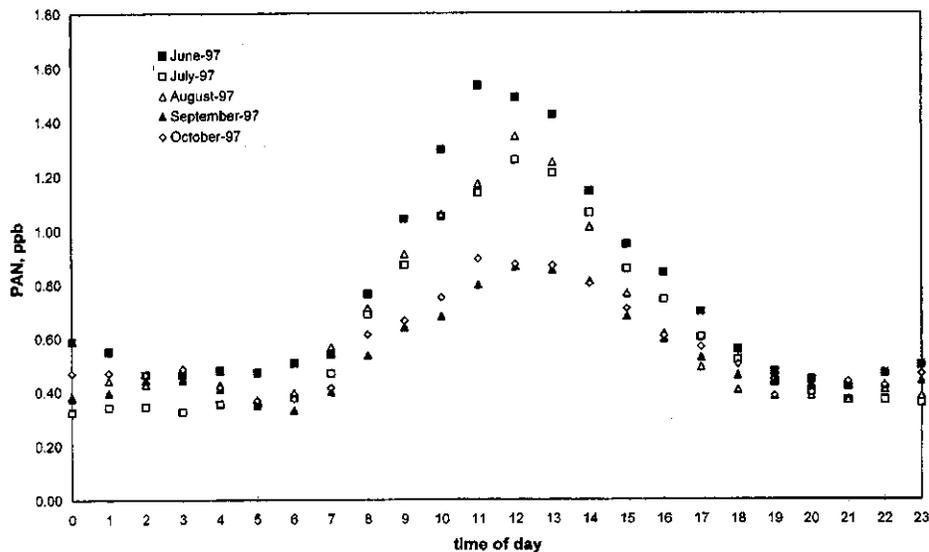


FIGURE 4. Monthly composite diurnal profiles for ambient PAN in Simi Valley.

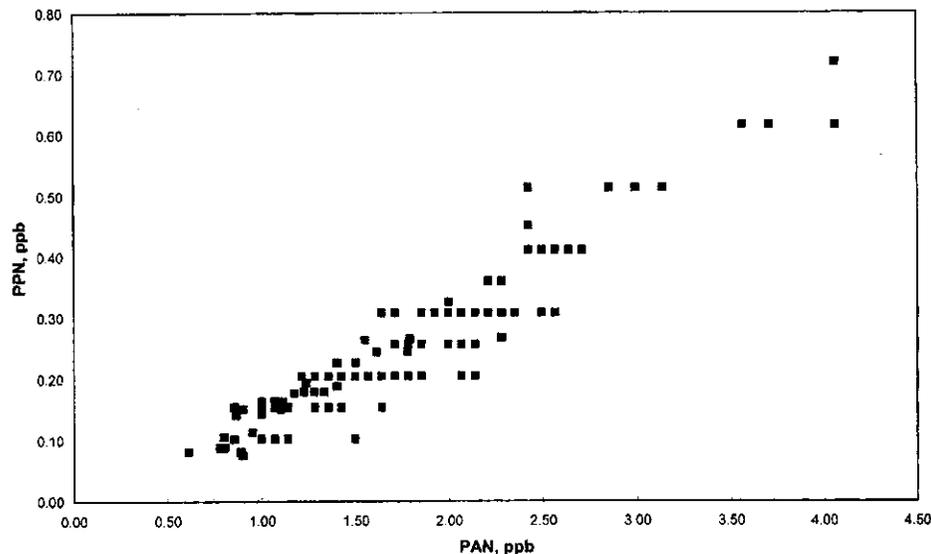


FIGURE 5. Scatterplot of ambient PPN vs ambient PAN, Azusa.

respectively (data capture >94%). Concentrations of PAN were calculated for all chromatograms. Concentrations of PPN were calculated only for the chromatograms recorded on the 17 days scheduled for SCOS 97-NARSTO intensive field operations (i.e., July 14; August 4–6, 21–23, and 26–28; September 4–6, 28, and 29; and October 3 and 4, 1997). Individual results are not listed and are available (electronic version) from the study sponsor.

Results and Discussion

Ambient Concentrations of PAN and PPN. Ambient concentrations of PAN and PPN measured in Azusa and Simi Valley during summer 1997 are summarized in Table 1. The highest concentrations recorded were 4.8 ppb for PAN and 0.72 ppb for PPN in Azusa and 3.0 ppb for PAN and 0.28 ppb for PPN in Simi Valley. Ambient concentrations of PAN and PPN during summer 1997 were lower than those measured earlier at southern California locations. Prior to this study, ambient PAN and PPN have been measured in the 1990s at two southern California mountain locations, Tanbark Flat (San Gabriel Mountains) in summer 1990 and summer 1991

and Franklin Canyon (Santa Monica Mountains) in summer 1991 (16–18), and at four southern California urban locations during summer 1993: Azusa, Claremont, Long Beach, and downtown Los Angeles (13). The highest concentrations measured in these studies were 5.5–22 ppb for PAN and 0.84–4.3 ppb for PPN (13, 16–18). The 24-h averaged PAN and PPN concentrations measured in summer 1997 (Table 1) were also lower than those measured in summers of 1990, 1991, and 1993 (not listed; see refs 13 and 16–18). Composite diurnal profiles (study-averaged hourly values vs time of day) are shown in Figure 1 for PAN in Azusa in summer 1993 and summer 1997. Figure 1 shows that nighttime levels measured in 1997 matched well those measured in 1993 and that 1993 levels were higher during the daytime. Higher daytime temperatures were recorded in 1997, i.e., thermal decomposition of PAN and PPN may have been more important in 1997 than in 1993 (see discussion below). Other differences between summer 1993 and summer 1997 include significant changes in vehicle fuel composition that resulted from the mandated use of California Phase 2 reformulated gasolines in 1996 (19–22). These changes were likely to impact the

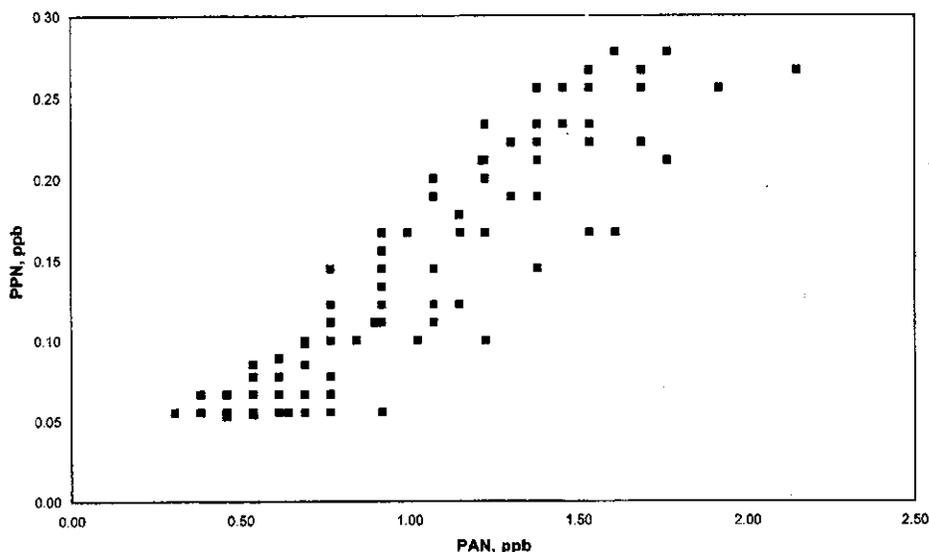


FIGURE 6. Scatterplot of ambient PPN vs ambient PAN, Simi Valley.

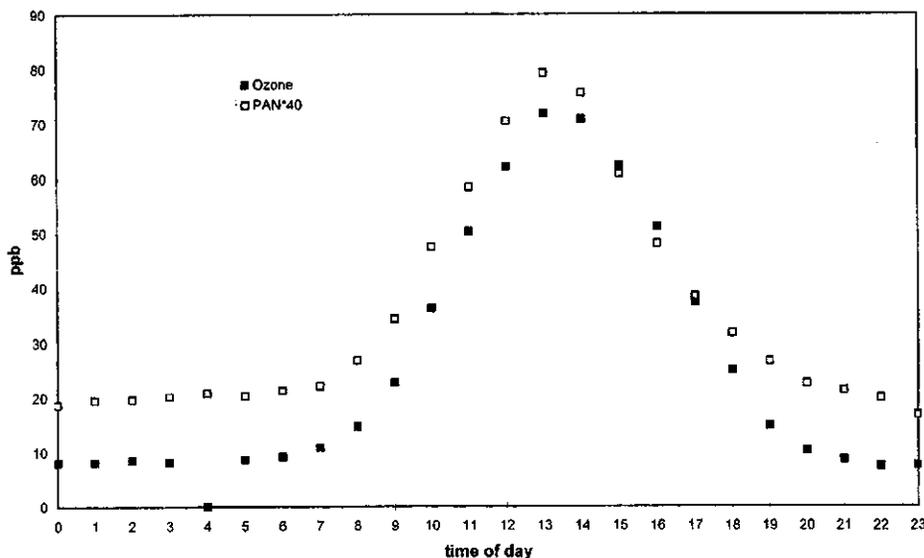


FIGURE 7. Composite diurnal profiles for ozone and PAN, Azusa.

nature and magnitude of vehicle emissions of oxides of nitrogen (NO_x) and of volatile organic compounds (VOC) that are precursors to PAN and PPN.

Diurnal variations of PAN and PPN generally included midday maxima and nighttime minima. Diurnal variations for specific days are not shown due to space limitations. Examples have been given in earlier studies carried out at southern California locations (13, 15–18). Composite diurnal profiles are shown in Figure 2 for PAN at Azusa and at Simi Valley. On the average, daytime concentrations of PAN were higher at Azusa. The midday maxima occurred ca. 1 h earlier in Simi Valley (ca. 12:30 PST) than in Azusa (ca. 13:30 PST, as was also the case in Azusa in 1993, see ref 13). The average diurnal variations shown in Figure 2 were not always observed, and on several instances, relatively elevated concentrations of PAN and PPN were recorded at night (e.g., PAN levels of ca. 1.2–1.6 ppb on August 27–29, August 30–September 2, and September 13–15 in Azusa and September 22–23 in Simi Valley).

While ambient PAN has been measured many times in southern California, most studies have been of short duration

(from several days to a few weeks), and the 3 (Azusa) and 4 months (Simi Valley) of measurements during summer 1997 constitute the longest studies since that carried out by Pitts and Grosjean in Riverside in 1975–1976 (23). Monthly composite diurnal profiles for ambient PAN are shown in Figures 3 (Azusa) and 4 (Simi Valley). In Azusa, the lowest daytime concentrations were recorded in October. In Simi Valley, there were substantial variations from one month to the next, daytime peak values were twice as high in June as they were in September and October, and maximum PAN concentrations occurred ca. 1 h earlier in June and October than in July–September.

Ambient PPN vs Ambient PAN. Diurnal variations of ambient PPN (not shown) followed closely those of ambient PAN at both locations. On the average, ambient levels of PPN were ca. 7 times lower than those of PAN. The concentration ratios PPN/PAN (units: ppb) when PPN could be detected ranged from 0.069 to 0.212 and averaged 0.142 ± 0.025 ($n = 132$) in Azusa and ranged from 0.060 to 0.190 and averaged 0.135 ± 0.028 ($n = 138$) in Simi Valley. Scatterplots of ambient PPN vs ambient PAN are shown in

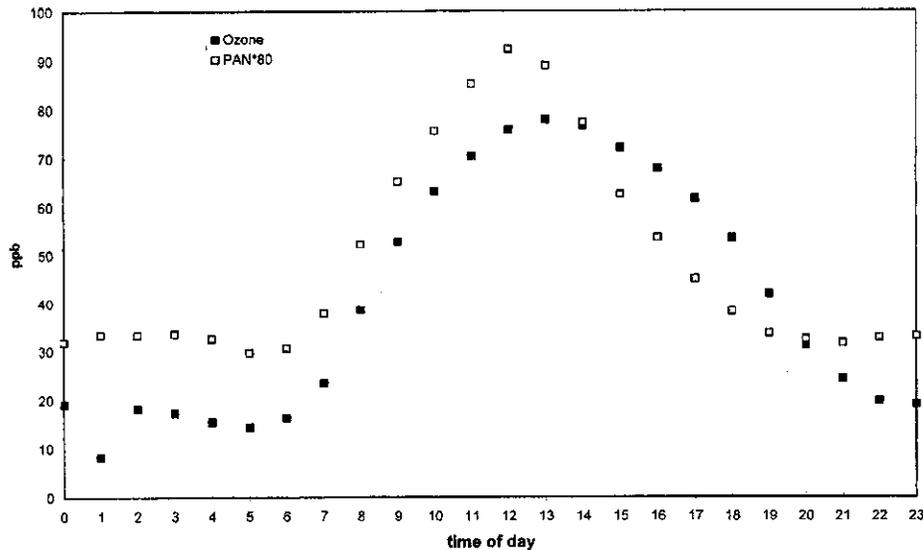


FIGURE 8. Composite diurnal profiles for ozone and PAN, Simi Valley.

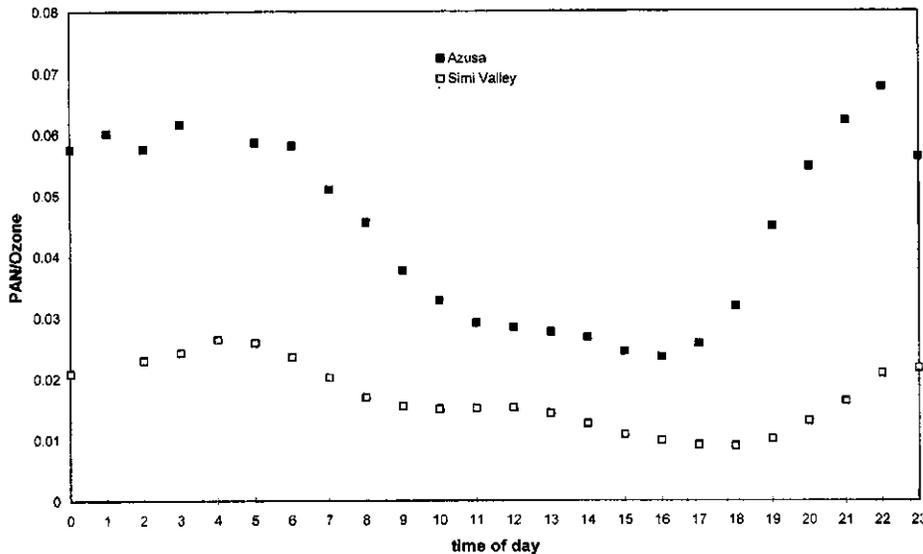


FIGURE 9. Composite diurnal profiles for the ambient PAN/ambient ozone concentration ratios, Azusa and Simi Valley.

Figure 5 for Azusa and in Figure 6 for Simi Valley. These scatterplots indicate a reasonable degree of correlation, as would be expected since PAN and PPN have a common (photochemical) origin. The scatter in Figures 5 and 6 reflects measurement uncertainties, especially for PPN whose ambient concentrations were often near detection. PAN and PPN have different VOC precursors, i.e., PAN forms from VOC that lead to the acetyl peroxy radical (CH_3CO_3) and PPN forms from VOC that lead to the propionyl peroxy radical ($\text{CH}_3\text{-CH}_2\text{CO}_3$). Thus, some of the scatter in Figures 5 and 6 may reflect temporal variations in the relative abundance of VOC that are precursors to PAN and PPN. Linear least squares regression of the data shown in Figures 5 and 6 (unit-weighted, not forced through the origin, no outliers omitted) yielded the following relations:

$$\text{PPN}_{\text{AZ}} = (0.174 \pm 0.005), \text{PAN}_{\text{AZ}} = (0.051 \pm 0.010), R = 0.943 \quad (n = 132) \quad (1)$$

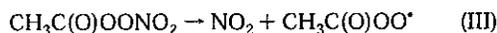
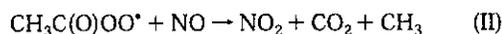
$$\text{PPN}_{\text{SV}} = (0.154 \pm 0.005), \text{PAN}_{\text{SV}} = (0.015 \pm 0.006), R = 0.924 \quad (n = 138) \quad (2)$$

where the subscripts AZ and SV stand for Azusa and Simi Valley, respectively, and the uncertainties of the slopes and intercepts are one standard deviation. In Azusa, the slope in eq 1 is essentially the same as that of 0.166 ± 0.018 ($n = 331$) measured in summer 1993 (13). Thus, changes in vehicle fuel composition and vehicle emissions between 1997 and 1993, including those that resulted from the introduction of California Phase 2 reformulated gasoline in 1996 (19-22), have had no measurable effect on the abundance of the VOC that are precursors to PPN relative to that of the VOC that are precursors to PAN.

Ambient PAN vs Ambient Ozone. Diurnal variations of ambient PAN generally followed those of ambient ozone with respect to time of day but not with respect to amplitude. Diurnal variations of PAN and ozone for specific days are not shown due to space limitations. Examples have been given in earlier studies (13, 15-18). Composite diurnal profiles for ozone and PAN are shown in Figure 7 for Azusa and in Figure 8 for Simi Valley. In Azusa, peak concentrations of ozone and PAN occurred at the same time, and the ozone/PAN concentration ratio (units: ppb) at that time averaged 36

($n = 95$). In Simi Valley, peak concentrations of PAN on the average preceded those for ozone by ca. 1 h, and the ozone/PAN concentration ratios averaged 70 at the time of maximum ozone and 66 at the time of maximum PAN ($n = 121$). The O_3 /PAN ratios were substantially higher in Simi Valley than in Azusa. At both locations, the O_3 /PAN ratios increased from nighttime to daytime, from 15 to 43 on the average in Azusa and from 20 to 112 on the average in Simi Valley. As is shown in Figure 9, the amplitude of the diurnal variations of the PAN/ O_3 concentration ratios was more pronounced in Azusa than in Simi Valley. This observation may reflect changes in wind direction, differences in dry deposition (24, 25), and differences in chemical formation and in chemical loss processes. With changes in wind direction, the instruments at both locations are sampling air parcels that may differ in chemical composition. If dry deposition is a dominant loss process, the data shown in Figure 9 would require the unlikely assumption that the PAN/ O_3 ratio of daytime dry deposition velocities is much higher in Azusa than in Simi Valley. There are differences in chemical formation, i.e., ozone forms from virtually all reactive VOC whereas PAN forms only from those VOC that are precursors to the radical CH_3CO_3 . There are also differences in chemical removal i.e., ozone is removed by reaction with NO and with unsaturated VOC while PAN is removed by decomposition, which increases with increasing temperature, and at a given temperature with increasing NO/ NO_2 concentration ratio (26, 27). Daytime temperatures during summer 1997 were often higher in Azusa than in Simi Valley. As a result, more PAN could be lost by thermal decomposition in Azusa than in Simi Valley, and this would explain in part why PAN/ O_3 concentration ratios decreased more in Azusa than in Simi Valley during daytime hours. The magnitude of PAN loss by thermal decomposition is examined below.

Thermal Decomposition of PAN. The net production (formation minus removal) of PAN in the atmosphere is described by reactions I–III:



From reactions I–III, the loss of PAN due to decomposition is given by

$$-d(\ln[\text{PAN}])/dt = (k_2 k_3 [\text{NO}]) / (k_2 [\text{NO}] + k_1 [\text{NO}_2]) \quad (3)$$

where [PAN], [NO], and [NO₂] are concentrations; k_3 (s^{-1}) = $2.52 \times 10^{16} e^{(-13573/T)}$; and $k_2/k_1 = 1.95 \pm 0.28$, independent of temperature in the range $T = 283\text{--}313\text{ K}$ (27). Rearranging eq 3 with $k_2/k_1 = 1.95$ gives

$$-d(\ln[\text{PAN}])/dt = k_3 / (1 + ([\text{NO}_2]/1.95[\text{NO}])) \quad (4)$$

Using measured concentrations of PAN, NO, and NO₂ and ambient temperature as input data, we have calculated using eq 4 the amount of PAN lost by thermal decomposition in Azusa and in Simi Valley. These calculations have been carried out for the ca. 15 days of SCOS 97-NARSTO intensive operations. The data presented below are for the two days August 5 and October 4, 1997, which are representative examples of high and moderate ambient temperature, respectively (up to 41 °C in Azusa and 37 °C in Simi Valley on August 5 and up to 29 °C in Azusa and 25 °C in Simi Valley on October 4). Figure 10 shows measured concentrations of PAN and those calculated to be lost by thermal decomposition (labeled TPAN). On October 4, PAN measured in Azusa reached 3.7 ppb, calculated TPAN reached 0.9 ppb, and

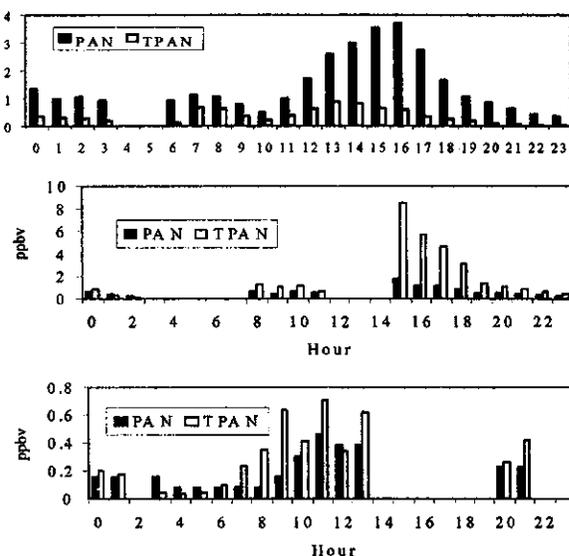


FIGURE 10. Thermal decomposition of PAN in Azusa, October 4, 1997 (top); Azusa, August 5, 1997 (middle); and Simi Valley, August 5, 1997. PAN, measured ambient concentration. TPAN, calculated concentration of PAN lost by thermal decomposition.

decomposition accounted for a modest fraction (29% or less) of the total (PAN + TPAN) concentration. On August 5, PAN measured in Azusa reached 1.8 ppb, calculated TPAN reached 8.5 ppb, and decomposition accounted for a large fraction (up to 83% in the afternoon) of the total (PAN + TPAN) concentration. Thus, the amount of PAN formed in Azusa in the afternoon of August 5 was up to ca. 4–5 times that measured. On that day, decomposition also accounted for a substantial fraction of the total (PAN + TPAN) concentration in Simi Valley but less so than in Azusa. The examples shown in Figure 10 together with the results of similar decomposition of PAN was important during the hot, El Niño-influenced summer 1997, and this more so in Azusa than in Simi Valley. As a result, the decomposition of PAN accounted for much of the difference between the daytime O_3 /PAN concentration ratios measured in Azusa and those measured in Simi Valley (see Figures 7–9). Taking thermal decomposition into account, the amount of PAN formed in Azusa in 1997 was closer to that formed at the same location in 1993, i.e., measured PAN was lower in 1997 but calculated TPAN was lower in 1993 (1993 values of TPAN are given in ref 13). Thermal decomposition may also explain why the highest peak values during summer 1997 were recorded in June (Simi Valley) and October (both locations), i.e., on relatively cooler days. The thermal decomposition of PAN leads to CO₂, NO₂, and CH₃ (see reaction II). In turn, the methyl radical leads to HO₂ and formaldehyde ($CH_3 + O_2 \rightarrow CH_3O_2$, $CH_3O_2 + NO \rightarrow NO_2 + CH_3O$, $CH_3O + O_2 \rightarrow HO_2 + HCHO$), which contribute to photochemical smog reactions including ozone formation. Formaldehyde also continues to receive regulatory attention as a toxic air contaminant.

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APPENDIX B



PERGAMON

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Ambient PAN and PPN in southern California from 1960 to the SCOS97-NARSTO

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Abstract

We examine long-term trends in ambient levels of peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) in southern California from the first measurements made in 1960 to those made in 1997 as part of SCOS97-NARSTO. We analyze peak concentrations, 24-h averages and monthly averages. Although the data record is incomplete with respect to frequency and duration of measurements and is limited with respect to seasonal and spatial variations, peak concentrations have decreased from ca. 60–70 ppb to ca. 5–10 ppb for PAN and from ca. 5–6 to 1 ppb or less for PPN. Twenty-four-hour averages and monthly averages also show downward trends in ambient PAN and PPN. The PPN/PAN concentration ratios range from 0.10 to 0.28 and the limited data record give no indication of a long-term temporal trend. The downward trend in peak PAN concentrations is similar to that of peak ozone concentrations during the same 37-year period and is likely to result from increasingly stringent controls on emissions of oxides of nitrogen and of volatile organic compounds that are precursors to ozone, PAN, PPN and other photochemical oxidants.

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Keywords: Peroxyacetyl nitrate; Peroxypropionyl nitrate; Long-term trends; Urban air quality; Oxygenated fuels

1. Introduction

1.1. Study objective

We analyze ambient levels of peroxyacetyl nitrate (PAN, $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$) and peroxypropionyl nitrate (PPN, $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OONO}_2$) in southern California. Our study is motivated in part by the decision to ban, in the State of California, the use of methyl-*tert*-butyl ether (MTBE) as an oxygenated additive to gasoline (Davis, 1999). Thus, gasolines sold in California after 31 December 2003 will no longer contain MTBE. This mandated change in gasoline composition may result in changes in vehicle emissions and may therefore impact air quality (California Air Resources Board, 1999). Possible indicators of changes in air quality include

ambient PAN, ambient PPN, and the PPN/PAN ambient concentration ratio, see Section 1.2. To assess the possible impact of the mandated phase-out of MTBE from California gasolines on PAN and PPN air quality, the California Air Resources Board has initiated several studies, one of which focuses on long-term measurements of ambient PAN and PPN at a smog receptor location within the urban Los Angeles area. This study began in early 2001 and is scheduled to last several years. To place the results of this new study in perspective, it is important to gather, review and analyze available information on past ambient levels of PAN and PPN in California. Thus, we analyze data from ca. 35 studies that span ca. 37 years, from the first measurements of PAN and PPN in ambient air in 1960 to those made in summer 1997 as part of SCOS97-NARSTO. The focus of our study is on the urban region that has been most severely impacted by photochemical smog, i.e., southern California, where PAN and PPN

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have been first detected and were measured more frequently than anywhere else in the world.

Peroxyacyl nitrates (RC(O)OONO₂) including PAN and PPN have long received attention for their importance in urban, regional and global atmospheric chemistry. They have been studied for their adverse effects including eye irritation, mutagenic activity, and phytotoxicity (Stephens et al., 1959; Darley et al., 1963a; Mudd, 1966; Heuss and Glasson, 1968; Stephens, 1969; Taylor, 1969; Peak and Belser, 1969; Lovelock, 1977; Temple and Taylor, 1983; Kleindienst et al., 1990; Heddle et al., 1993). They have received attention as photochemical oxidants, as precursors to photochemically reactive species including carbonyls and free radicals, as interferents when measuring ambient NO₂ by chemiluminescence, and for their important role in the long-range transport of reactive nitrogen in the troposphere (e.g., US Department of Health, Education and Welfare, 1970; Carter et al., 1981; Singh and Hanst, 1981; Grosjean, 1983; Grosjean and Harrison, 1985; Singh et al., 1985, 1986; Ridley et al., 1990; Kanakidou et al., 1991; Grosjean et al., 2001a, b). The properties, formation, reactions and ambient levels of peroxyacyl nitrates have been the object of several reviews (Stephens, 1969; Eschenroeder, 1977; Heck et al., 1977; Altschuller, 1983, 1993; Gaffney et al., 1989; Roberts, 1990).

1.2. PAN, PPN and oxygenated fuel policies

Peroxyacyl nitrates have begun to receive attention as possible indicators of air quality changes that may result from changes in vehicle fuel composition and vehicle emissions. Peroxyacyl nitrates have no known direct sources and form in situ in atmospheric photochemical reactions that involve volatile organic compounds (VOC) and oxides of nitrogen (Stephens, 1969). Vehicle emissions are a major source of VOC in urban air. Vehicle emissions of VOC depend on fuel composition, engine technology, and emission control devices. Vehicle fuels in many countries currently consist of oxygenated gasolines, i.e., gasoline-ethanol blends and/or gasolines that contain MTBE. Oxygenated fuel policies continue to receive much attention for their impact on air quality (Bravo et al., 1991; Anderson et al., 1996; US National Research Council, 1996; US National Science and Technology Council, 1997; Mannino and Etzel, 1996; Dolislager, 1997; Gaffney et al., 1999; Franklin et al., 2000; Gaffney and Marley, 2000). Emissions of VOC from vehicles fueled with oxygenated gasolines that contain MTBE or ethanol have been characterized in dynamometer tests (e.g., Hoekman, 1992; Stump et al., 1996; Gabele, 1995; Black et al., 1998). In California, on-road emissions of VOC by vehicles fueled with gasolines that contain MTBE have been measured in several highway tunnels (e.g., Kirchstetter et al., 1996,

1999a, b; Fraser et al., 1998; Gertler et al., 1999; Kean et al., 2001).

The phasing out of MTBE now mandated in California, is also under consideration at the federal level in the United States (Hogue, 2001) and in other countries (e.g., Schifter et al., 2001). Gasolines that no longer contain MTBE may contain ethanol, among other options. Emissions of vehicles fueled with gasoline-ethanol blends include ethanol (exhaust and evaporative emissions) and, for exhaust emissions, include more acetaldehyde than is the case for gasolines that contain no ethanol (e.g., Stump et al., 1996; Gabele, 1995; Black et al., 1998). The photochemical oxidation of ethanol leads to acetaldehyde (Carter et al., 1979) and the oxidation of acetaldehyde leads to PAN (Stephens, 1969). Hence, ethanol, acetaldehyde and hydrocarbons emitted by vehicles fueled with gasoline-ethanol blends contribute to the formation of PAN. At issue is whether gasolines that contain ethanol lead to more ambient PAN than gasolines that do not (e.g., Gaffney et al., 1997; Whitten, 1998).

Further complicating this issue is the possible impact of MTBE on PAN formation. The photochemical oxidation of MTBE does not lead to PAN (Japar et al., 1990; Tuazon et al., 1991a; Smith et al., 1991). The combustion of MTBE leads to exhaust products that include formaldehyde and isobutene (Siegl et al., 1992; Zervas et al., 1999). Zielinska et al. (1997a, b) have noted an increase in ambient levels of isobutene in the Los Angeles, CA, area following the introduction in 1996 of reformulated gasoline that contains MTBE. Grosjean et al. (2001b) have reported a substantial decrease in ambient levels of isobutene in Porto Alegre, Brazil, when MTBE was replaced by ethanol as the oxygenated additive to gasoline. The atmospheric oxidation of isobutene leads to formaldehyde, acetone, methylglyoxal and other products (Carter, 1990; Atkinson, 1997; Grosjean and Grosjean, 1998; Tuazon et al., 1997, 1998). Acetone and methylglyoxal are precursors to PAN (Carter, 1990; Atkinson, 1997). Hence, removing MTBE from gasoline is likely to result in lower vehicle emissions of isobutene, i.e., less ambient PAN would form via isobutene oxidation. Thus, it appears that the impact, on ambient PAN, of replacing MTBE by ethanol in oxygenated gasoline depends on many parameters including MTBE content, ethanol content, nature and abundance of hydrocarbons in gasoline (including hydrocarbons that are precursors to PAN), and changes in vehicle engine technology and exhaust control devices that may affect emissions of unburned fuel VOC (MTBE, ethanol, hydrocarbons) and/or combustion products (including acetaldehyde and isobutene).

Ethanol, MTBE and their incomplete combustion products including acetaldehyde and isobutene do not lead to PPN. Thus, ambient levels of PPN are expected

to be affected by changes in oxygenated fuel policies only to the extent that such changes may affect vehicle emissions of VOC (unburned fuel and combustion products) that are precursors to PPN. As a result, ambient PPN and the ambient PPN/ambient PAN concentration ratio may be used, along with ambient PAN, as diagnostic tools to assess air quality changes that may accompany changes in vehicle fuel policies.

Taken together, the above considerations underline the importance of reviewing existing data for ambient PAN, ambient PPN and their ratio in the context of assessing the air quality impact of mandated changes in vehicle fuel composition.

2. Ambient levels of PAN in southern California

PAN was first identified as “compound X” and subsequently characterized by Stephens and coworkers in the mid-1950s (Stephens et al., 1956a, b, 1959, 1961; Scott et al., 1957; Stephens, 1961). A lively account of early smog studies carried out in the 1950s, including laboratory and ambient air studies pertaining to PAN, is given by Stephens (1987). The first observations of ambient PAN were made in 1956 in South Pasadena (Scott et al., 1957). The Franklin Institute Laboratories (Philadelphia, PA) researchers W.E. Scott, E.R. Stephens, P.L. Hanst and R.C. Doerr brought their instrumented trailer to South Pasadena in August 1956 and began to measure PAN (then thought to be a peroxyacyl nitrite, RC(O)OONO), ozone and other ambient pollutants using long-path infrared spectroscopy. Fig. 3 in the paper of Scott et al. (1957) shows observations of ambient PAN on 18 and 26 September 1956; Fig. 6 in the same paper includes diurnal profiles for PAN (arbitrary concentration units) and ozone (up to ca. 520 ppb) on 12 November 1956, under what the authors described as “mild smog” conditions! The instrumented trailer was moved to Riverside in late 1958, and measurements of ambient PAN continued at that location (Stephens, 1987). The first quantitative ambient measurements of PAN reported in the peer-reviewed literature appear to be those of Renzetti and Ryan (1961), who measured ambient PAN in downtown Los Angeles (South San Pedro Street) on 10 days in summer and fall 1960. Grab samples of ambient air collected in downtown Los Angeles were analyzed by long-path infrared spectroscopy at the Stanford Research Institute facility in South Pasadena. The highest PAN concentrations reported were 70 ppb on 18 August 1960, 50 ppb on 18, 19 and 22 July and 6 and 26 September 1960, and 40 ppb on 18 August, 7 September and 4 October 1960 (Renzetti and Ryan, 1961).

The first quantitative measurements of PPN appear to be those of Darley et al. (1963b) who, using electron capture gas chromatography, measured ca. 6 ppb of

PPN along with ca. 50 ppb of PAN in one sample of Riverside air taken during a heavily polluted afternoon (presumably in 1962). Since then, ambient PAN and PPN have been measured many times, first in southern California and subsequently throughout the world. The results discussed below are for southern California locations and are from the ca. 35 studies carried out between 1960 (Renzetti and Ryan, 1961; Darley et al., 1963b) and SCOS97-NARSTO in 1997 (Grosjean et al., 2001a).

2.1. Highest PAN concentrations

The highest ambient concentrations of PAN at southern California locations are listed in Table 1. The early measurements of ambient PAN, made in the 1960s in Riverside and in Los Angeles (Renzetti and Ryan, 1961; Darley et al., 1963b; US Department of Health, Education and Welfare, 1970; Taylor, 1969; Lonneman et al., 1976), yielded the highest PAN concentrations measured in ambient air, i.e., 70 ppb in 1960 in Los Angeles (Renzetti and Ryan, 1961), 50 ppb in 1962 in Riverside (Darley et al., 1963b), 58 ppb in 1967 in Riverside (Taylor, 1969) and 65 ppb in 1968 in Los Angeles (Lonneman et al., 1976). To put these high PAN concentrations in perspective, we note that the highest ozone concentrations recorded in southern California during the 1960s were 500–650 ppb (South Coast Air Quality Management District, 1997). The severity of the smog problem in southern California has been documented as early as 1943 with the first media reports of a “gas attack” on 26 July (South Coast Air Quality Management District, 1997). Measurements of ambient ozone in Los Angeles began in 1955. The highest concentration measured that year, 680 ppb, remains the highest ever measured in southern California. Thus, it is likely that even higher levels of ozone went unrecorded in previous years. Similarly, ambient levels of PAN may well have exceeded 100 ppb before PAN was first measured in 1960.

Several early articles (Stephens, 1969; Taylor, 1969; Lonneman et al., 1976; Altschuller, 1983) cite an unpublished communication of Mayrsohn and Brooks (1965), who reportedly measured 214 ppb of PAN in Los Angeles County in September–October 1965. Since the highest ozone concentration recorded in 1965 in southern California was ca. 570 ppb, the PAN concentration reported by Mayrsohn and Brooks (1965) would correspond to a low (and perhaps unlikely) ozone/PAN concentration ratio of ca. 2.7.

2.2. Averaged PAN concentrations

Reports from studies of ambient PAN in southern California have often included some measure of average PAN concentrations, i.e., 24-h averages, monthly

Table 1
Highest PAN concentrations in southern California^a

Year	Location	Study period	Range of daily PAN maxima (ppb)	Reference
1960	Los Angeles	9 days in July–October	40–70	Renzetti and Ryan (1961)
1962?	Riverside	Date not reported	50 (1 sample)	Darley et al. (1963b)
1966	Riverside	1 June–31 December	> 10 ^b	US Department of Health, Education and Welfare (1970)
1967	Riverside	1 January–30 June	> 10 ^b	US Department of Health, Education and Welfare (1970)
		1 August–31 December	12–58	Taylor (1969)
1968	Los Angeles	Several days, September to November	65	Lonneman et al. (1976)
	Riverside	1 January–30 April	8–38	Taylor (1969)
1973	Pasadena	Several days in July and August	53	Hanst et al. (1975)
	West Covina	24 August–28 September	46	Spicer (1977a, b)
1975	Riverside	1 May–31 December	13–25	Pitts and Grosjean (1979)
1976	Riverside	1 January–31 October	14–32	Pitts and Grosjean (1979)
	Riverside	4–6 October	18	Tuazon et al. (1978)
1977	Riverside	16–21 February	11–27	Pitts and Grosjean (1979)
	Riverside	21, 25 July, 10–12 August and 3, 4, 11, 14, 17 October	18	Tuazon et al. (1980)
1978	Claremont	9–13 October	37	Tuazon et al. (1981)
	Riverside	Several days, May to July	42	Pitts and Grosjean (1979)
1979	Claremont	27 August–3 September	10	Spicer et al. (1982) ^c
	East Los Angeles (California State University, Los Angeles)	9–21 April	17	Singh and Hanst (1981)
1980	Riverside	1 January–30 April and 1 August–31 December	8–42	Temple and Taylor (1983)
	East Los Angeles (California State University, Los Angeles)	26–27 June	16	Hanst et al. (1982)
	Claremont	19 September–8 October	3.5–47	Grosjean (1983)
1982	Pasadena	30 and 31 August	9, 11	Russell et al. (1988)
	Riverside	31 August	22	Russell and Cass (1986) ^d
1984	Downey	18–27 February	7	Singh and Salas (1989)
1985	Claremont	11–19 September	20	Grosjean (1988) ^e
1986	Glendora	12–20 August	34	Grosjean et al. (1988)
1987	Several locations listed below (SCAQS)	Summer: 19, 24, 25 June, 13–15 July, 27–31 August and 1–3 September; Fall: 11–13 November and 3, 10, 11 December		
	Anaheim	Summer	7	Williams and Grosjean (1990)
		Fall	19	Williams and Grosjean (1990)
	Azusa	Summer	13	Williams and Grosjean (1990)
	Burbank	Summer	13	Williams and Grosjean (1990)
		Fall	19	Williams and Grosjean (1990)
	Claremont	Summer	30	Williams and Grosjean (1990)
			24	Lonneman and Seila (1989)
	Hawthorne	Summer	< 4–9	Williams and Grosjean (1990)
		Fall	16	Williams and Grosjean (1990)
	Long Beach	Summer	16	Williams and Grosjean (1990)
		Fall	15	Williams and Grosjean (1990)
	Los Angeles	Summer	11	Williams and Grosjean (1990)

Table 1 (continued)

Year	Location	Study period	Range of daily PAN maxima (ppb)	Reference
1988	Rubidoux	Fall	13	Williams and Grosjean (1990)
	San Nicolas Island	Summer	14	Williams and Grosjean (1990)
	Los Angeles, downtown (Olveira Street)	Summer	1	Williams and Grosjean (1990)
	Los Angeles, downtown (Exposition Park)	18–27 July	14	Hisham and Grosjean (1991a)
	Los Angeles, west (Westwood, UCLA campus)	22 August–2 September	5	Hisham and Grosjean (1991a)
	Los Angeles, west (Wilshire, George C. Page Museum)	7–16 September	9	Hisham and Grosjean (1991a)
	Los Angeles, west (Wilshire, LA County Museum of Art)	29 August–7 September	10	Hisham and Grosjean (1991a)
	Los Angeles, north (Southwest Museum)	1–15 August	9	Hisham and Grosjean (1991a)
	San Marino	16 September–12 October	10	Hisham and Grosjean (1991a)
	Malibu (J. Paul Getty Museum)	9–22 August	12	Hisham and Grosjean (1991a)
1989	Ventura	12–19 September	7	Hisham and Grosjean (1991a)
	Los Angeles, north (Griffith Park)	26 July–5 August	4	Hisham and Grosjean (1991a)
	Perris	7–20 August	8	Hisham and Grosjean (1991b)
	Palm Springs	25–27 August	7	Grosjean and Williams (1992)
	Tanbark Flat (San Gabriel Mountains)	23–25 August	3	Grosjean and Williams (1992)
	Tanbark Flat	8 August–16 October	1.5–16	Williams and Grosjean (1991)
1990	Tanbark Flat	3 August–5 September	3.9–22	Grosjean et al. (1993a)
1991	Tanbark Flat	5–26 August	2.3–12.8	Grosjean et al. (1993a)
	Franklin Canyon (Santa Monica Mountains)	4–12 September	2.0–7.0	Grosjean et al. (1993a)
1993	Azusa	28 August–13 September	1.9–6.1	Grosjean et al. (1996)
	Claremont	1–11 September	2.4–9.9	Grosjean et al. (1996)
	Claremont	1–25 September	4.2	Mackay (1994)
	Long Beach	29 August–13 September	0.2–5.5	Grosjean et al. (1996)
	Los Angeles	30 August–11 September	0.2–6.9	Grosjean et al. (1996)
1997	Azusa	14 July–16 October	4.8	Grosjean et al. (2001a)
	Simi Valley	12 June–16 October	3.0	Grosjean et al. (2001a)

^aPAN was measured using the following methods: long-path infrared spectroscopy (Renzetti and Ryan, 1961; Hanst et al., 1975, 1982; Tuazon et al., 1978, 1980, 1981; Spicer et al., 1982), coulometry (Singh and Hanst, 1981; results deemed tentative by the authors), luminol (Mackay, 1994) and electron capture gas chromatography, EC-GC (all other studies).

^bDaily maxima not reported; monthly means of daily maxima were up to 10 ppb (September 1966 and July 1967).

^cFT-IR PAN data of Tuazon and co-workers (Spicer et al., 1982).

^dPAN data from U.C. Riverside (Russell and Cass, 1986).

^eEC-GC PAN data of Holdren and co-workers (Grosjean, 1988).

averages, or averages for the period studied. These averages are compiled in Table 2. Because of length limitations generally prescribed by peer-reviewed journals, authors have often omitted individual measurements from their articles. As a result, we have calculated several of the averages listed in Table 2 using data from

tables and figures that appeared in non-peer-reviewed technical reports. Twenty-four-hour averaged PAN concentrations as high as 15–20 ppb have been reported in West Covina (1973), Riverside (1975–1976) and Claremont (1980). After 1980, lower 24-h averages have been measured, the highest values being ca. 5–12 ppb in

Table 2
Averaged PAN concentrations in southern California

Year	Location	Date	Range of monthly averages (ppb)	Study average (ppb)	Range of 24-h averages (ppb)	Reference
1966	Riverside	1 June–31 December	1.5–4.5			US Department of Health, Education and Welfare (1970)
1967	Riverside	1 January–30 June	1.5–7.0			US Department of Health, Education and Welfare (1970)
1968	Riverside	1 August–31 December	1.2–8.1	5.2 ^a		Taylor (1969)
1971	Riverside area	1 January–30 April	1.0–4.0	2.2 ^a		Taylor (1969)
		ca. 10 days between 12 July and 15 November	—	3.0–9.6 ^b	—	Thompson et al. (1973)
1973	West Covina	24, 31 August, 3–14 September and 17–28 September		9.4	1–20	Spicer (1977a, b)
1975	Riverside	1 May–31 December	1.6–4.4	3.3 ^a	1–15	Pitts and Grosjean (1979)
1976	Riverside	1 January–31 October	2.3–6.8	3.8 ^a	1–16	Pitts and Grosjean (1979)
1977	Riverside	16–21 February		9 ^c	6–14 ^b	Pitts and Grosjean (1979)
1979	East Los Angeles	9–12 April		5.0 ± 4.5		Singh et al. (1981)
1980	Claremont	19 September–8 October			1–20 ^b	Grosjean (1983)
	Riverside	1 January–30 April	0.4–5.5 ^c	2.3 ^{a,d}		Temple and Taylor (1983)
	Riverside	1 August–31 December	1.6–9.4 ^c	5.9 ^{a,d}		Temple and Taylor (1983)
1984	Downey	18–27 February		1.2 ± 1.1	0.3–6.9	Singh and Salas (1989)
1985	Claremont	14–18 September				Grosjean (1988)
1986	Glendora	12–21 August		13.7		Grosjean et al. (1988)
1987 (SCAQQS)	Long Beach	Summer			0.8–2.9	Williams and Grosjean (1990)
		Late fall			1.0–5.0	Williams and Grosjean (1990)
	Los Angeles	Summer			1.3–3.7	Williams and Grosjean (1990)
		Late fall			0.9–5.2	Williams and Grosjean (1990)
	Anaheim	Late fall			1.0–9.0	Williams and Grosjean (1990)
	Burbank	Summer			1.0–4.6	Williams and Grosjean (1990)

1988	Azusa	Late fall	1.3–7.1	Williams and Grosjean (1990)
		Summer	1.7–4.8	Williams and Grosjean (1990)
1989	Claremont	Summer	2.7–11.6	Williams and Grosjean (1990)
		18 July–12 October	0.2–3.1	Hisham and Grosjean (1991a)
		9–22 August	1.6–3.2	Hisham and Grosjean (1991a)
		12–19 September	0.5–2.9	Hisham and Grosjean (1991a)
		26 July–5 August	0.4–1.4	Hisham and Grosjean (1991a)
		7–20 August	0.3–2.6	Hisham and Grosjean (1991b)
1990	Tanbark Flat	8 August–16 October	0.9–8.2	Williams and Grosjean (1991)
		3 August–5 September	2.1–10.3	Grosjean et al. (1993a)
		5–26 August	1.0–5.1	Grosjean et al. (1993a)
		4–12 September	1.1–2.6	Grosjean et al. (1993a)
		28 August–13 September	0.53–2.96	Grosjean et al. (1996)
		1–11 September	0.81–4.96	Grosjean et al. (1996)
		29 August–13 September	0.9±0.9	Grosjean et al. (1996)
		30 August–11 September	1.1±1.3	Grosjean et al. (1996)
		14 July–16 October	0.88±0.74	Grosjean et al. (2001a)
		18 June–16 October	0.61±0.43	Grosjean et al. (2001a)
1991	Tanbark Flat	2.2 (August 8–31)	2.9 ^f	
		4.7 (August 3–31)	4.8 ^f	
1993	Franklin Canyon		3.0 ^f	
			1.6 ^f	
1997	Azusa	0.98±0.83 (August)	0.88±0.74	
		0.85±0.68 (September)		
		0.62±0.43 (July)		
		0.63±0.47 (August)		
		0.53±0.34 (September)		
		(av = 0.87±0.34, n = 95)		
		(av = 0.60±0.23, n = 118)		

^a Average of monthly averages.

^b Range of averages measured at 11 locations as part of an indoor/outdoor study.

^c Estimated from data reported by authors as figures.

^d From measurements taken from 8 a.m. to 8 p.m.

^e Combining data from the 6 locations listed in Table 1.

^f Average of 24-h averaged values.

1985–1990 and ca. 2–5 ppb thereafter. The most recent 24-h averages, measured in summer 1997 during SCOS97-NARSTO (Grosjean et al., 2001a), were 0.17–2.08 ppb in Azusa and 0.15–1.30 ppb in Simi Valley.

Little information is available regarding monthly averages. Most of this information is for only one location, Riverside, from studies made in 1966–1967 (US Department of Health, Education and Welfare, 1970), 1967–1968 (Taylor, 1969), 1975–1976 (Pitts and Grosjean, 1979) and 1980 (Temple and Taylor, 1983). Monthly averages were 1.5–7.0 ppb in 1966–1967, 1.0–8.1 ppb in 1967–1968, 1.6–6.8 ppb in 1975–1976, and ≤ 0.4 –9.4 ppb in 1980. Only three of the more recent studies have been sufficiently long to calculate monthly averages. Monthly averages in Tanbark Flat were ca. 2–5 ppb, i.e., 2.2 ppb in August 1989, 2.8 ppb in September 1989, and 4.7 ppb in August 1990 (Williams and Grosjean, 1991; Grosjean et al., 1993a). Monthly averages in 1997 were 0.5–1.0 ppb, i.e. 0.98 ± 0.83 ppb (August) and 0.85 ± 0.68 ppb (September) in Azusa and 0.62 ± 0.43 ppb (July), 0.63 ± 0.47 ppb (August) and 0.53 ± 0.34 ppb (September) in Simi Valley (Grosjean et al., 2001a).

2.3. Highest and average PPN concentrations

Measurements of ambient PPN in southern California have been less frequent than those of ambient PAN. Singh et al. (1981) have carried out two short studies, one in 1979 in Los Angeles and the other in 1984 in Downey (Singh and Salas, 1989). Two studies have been carried out in 1989, one involving measurements for 2 months at a mountain location, Tanbark Flat (Williams and Grosjean, 1991) and the other involving brief surveys of ca. 2 days each in Perris and Palm Springs (Grosjean and Williams, 1992). PPN was also measured at Tanbark Flat during the 1990 and 1991 smog seasons, and at another mountain location, Franklin Canyon in the Santa Monica Mountains, during the 1991 smog season (Grosjean et al., 1993a). Spatial variations of PPN in the Los Angeles area were first studied in 1993 by measuring PPN simultaneously at four locations (Azusa, Claremont, Long Beach and Los Angeles) during a ca. 2-week period that included severe smog episodes (Grosjean et al., 1996). More recently, simultaneous measurements of PPN have been carried out at two locations, Azusa and Simi Valley, during SCOS97-NARSTO (Grosjean et al., 2001a).

The results of the studies cited above are summarized in Table 3, which includes highest, study-averaged, and 24-h averaged PPN concentrations. Highest concentrations of PPN range from up to ca. 5–6 ppb in the earlier studies to ca. 1 ppb or less in recent years. Twenty-four-hour averaged concentrations range from ca. 0.1 to 1.8 ppb, with the lower values being those reported in recent years.

2.4. Ambient PPN/ambient PAN concentration ratios

As discussed in more detail previously (Grosjean et al., 1993a), spatial and temporal variations in the ambient PPN/ambient PAN concentration ratio reflect the combined influence of several parameters including emissions and reactivities of the VOC that are precursors to PPN (i.e., those leading to the $\text{CH}_3\text{CH}_2(\text{O})$ -radical) and of the VOC that are precursors to PAN (i.e., those leading to the $\text{CH}_3(\text{O})$ -radical). For a given study at a given southern California location, the PPN/PAN ratio has been observed to be approximately constant (Singh et al., 1981; Singh and Salas, 1989; Williams and Grosjean, 1991; Grosjean and Williams, 1992; Grosjean et al., 1993a, 1996, 2001b). Ambient PPN/ambient PAN concentration ratios for all studies carried out in southern California are listed in Table 4. Table 4 includes linear least squares regression parameters (slope ± 1 S.D., intercept ± 1 S.D., and correlation coefficient) when reported by the authors and, for the earlier and more limited studies, average PPN/PAN concentration ratios. The data in Table 4 indicate that PPN and PAN are generally related in a linear fashion. The slopes given in Table 4 are for studies carried out during the smog season and range from ca. 0.10 to 0.28 (PPN/PAN, both in ppb units). Data for different years are available for only two locations, Tanbark Flat (San Gabriel Mountains) and Azusa (east of Los Angeles). At Tanbark Flat, a mountain forest location, the PPN/PAN ratio may be influenced not only by upslope transport of smog from the Los Angeles basin (e.g., Lu and Turco, 1996) but also by biogenic hydrocarbons (e.g., Reissell and Arey, 2001). For example, PAN forms from isoprene (Tuazon and Atkinson, 1990; Grosjean et al., 1993b; Carter and Atkinson, 1996) and from several terpenes (Grosjean et al., 1992) and PPN forms from *cis*-3-hexen-1-ol (Grosjean et al., 1993c). At Azusa, the regression slope calculated from the 1997 data was essentially the same as that calculated from the 1993 data. This suggests that the introduction, in 1996, of California Phase 2 reformulated gasoline had little effect on VOC that are precursors to PPN relative to VOC that are precursors to PAN.

3. Long-term trends in ambient PAN, ambient PPN and the PPN/PAN concentration ratio

3.1. Limitations

In spite of their importance, PAN and PPN are not included in any federal, state or local air quality monitoring network, in the US or elsewhere. As a result, examination of long-term trends in ambient concentrations must rely on a patchy record. The data in Tables 1–4 are limited with respect to frequency of

Table 3
Ambient concentrations of PPN in southern California

Year	Location and dates	PPN (ppb) ^a			Reference
		Range of daily maxima	Study average	Range of 24-h averages	
1962	Riverside (date not reported)	ca. 6 ^b			Darley et al. (1963b)
1979	East Los Angeles 9–21 April	Up to 2.7	0.72 ± 0.67		Singh et al. (1981) ^{c,d}
1984	Downey 18–27 February	Up to 0.4	0.060 ± 0.067		Singh and Salas (1989) ^d
1989	Tanbark Flat 8 August–16 October	0.4–5.1	0.75	0.09–1.8	Williams and Grosjean (1991)
	Palm Springs 23–25 August	0.42			Grosjean and Williams (1992)
	Perris 25–27 August	0.73			Grosjean and Williams (1992)
1990	Tanbark Flat 3 August–5 September	0.5–4.3	0.69 ^e	0.25–1.7	Grosjean et al. (1993a)
1991	Tanbark Flat 5–26 August	0.3–2.7	0.43 ^e	0.1–0.83	Grosjean et al. (1993a)
	Franklin Canyon 4–12 September	0.3–1.2	0.18 ^e	0.09–0.37	Grosjean et al. (1993a)
1993	Azusa 28 August–11 September	0.26–1.46	0.47 ± 0.24	0.19–0.88	Grosjean et al. (1996)
	Claremont 1–11 September	0.17–1.20	0.31 ± 0.17	0.17–0.69	Grosjean et al. (1996)
	Long Beach 29 August–13 September	0.20–0.86	0.25 ± 0.15	0.14–0.42	Grosjean et al. (1996)
	Los Angeles 30 August–11 September	0.33–1.04	0.24 ± 0.18	0.07–0.32	Grosjean et al. (1996)
1997	Azusa 17 days in July–October ^f	Up to 0.72	0.25 ± 0.12		Grosjean et al. (2001b)
	Simi Valley 17 days in July–October ^f	Up to 0.28	0.13 ± 0.07		Grosjean et al. (2001b)

^a Measured by electron capture gas chromatography except in one study (see footnote).

^b One sample collected during a smoggy afternoon.

^c Measured by coulometry, results deemed tentative by the authors.

^d Instrument not calibrated for PPN, concentrations of PPN reported assuming the same response factor as for PAN.

^e Mean of 24-h averaged values.

^f 17 July, 4–6, 21–23 and 26–28 August, 4–6, 28 and 29 September, and 3 and 4 October.

measurements, spatial distribution, duration of measurements and information on seasonal variations.

- Frequency of measurements: no data are available for many years, including 6 years in the 1990s. For example, PAN and PPN have not been measured between summer 1993 and summer 1997 and between fall 1997 and February 2001.
- Spatial distribution: information on spatial distribution of PAN within southern California was first obtained in 1987 during SCAQS (Lawson, 1990), which included simultaneous measurements of PAN at up to nine locations during summer and at five locations during late fall (Williams and Grosjean, 1990). PAN and PPN have been measured at four locations in summer 1993 (Grosjean et al., 1996) and at two locations in summer 1997 (Grosjean et al., 2001a). No measurements have been made since summer 1991 at mountain forest locations, which as a result of eastward and upslope transport often

experience the highest levels of ozone measured in southern California.

- Duration of measurements: many of the studies listed in Table 1 are short-term studies that have lasted only a few days or a few weeks. Long-term studies (ca. 1 year or longer) have been carried out at only one location, Riverside, and this prior to 1981 (Taylor, 1969; US Department of Health, Education and Welfare, 1970; Pitts and Grosjean, 1979; Temple and Taylor, 1983; Grosjean et al., 1984). Long-term studies are very valuable and have been carried out outside of California (Lewis et al., 1983) and in other countries (e.g., Guicherit and Schulting, 1985; Brice et al., 1988; Dollard et al., 1991; Tsalkani et al., 1991; Bottenheim et al., 1994; Ciccioli et al., 1995; Beine and Krognes, 2000).
- Seasonal variations: all studies conducted after 1987 have been carried out during summer with focus on ozone episodes. As a result, seasonal variations in ambient PAN are sparsely documented and those of

Table 4
Summary of PPN/PAN concentration ratios

Year	Location and dates	PPN/PAN (ppb/ppb)					Reference
		Ratio	Slope	Intercept (ppt) ^a	<i>n</i>	<i>R</i>	
1962?	Riverside date not reported	0.12 ^b					Darley et al. (1963b)
1979	East Los Angeles 9–21 April	0.145 ^c 0.163 ^d					Singh et al. (1981) ^e
1984	Downey 18–27 February	0.05 ^c 0.06 ^d					Singh and Salas (1989) ^e
1989	Tanbark Flat 8 August– 16 October		0.280 ± 0.001	–73 ± 2	3,000	0.943	Williams and Grosjean (1991)
	Perris 25–27 August	0.135–0.182 ^f		—	—	—	Grosjean and Williams (1992)
	Palm Springs 23–25 August	0.127–0.135 ^f		—	—	—	Grosjean and Williams (1992)
1990	Tanbark Flat 3 August– 5 September		0.182 ± 0.001	–115 ± 7	1,400	0.966	Grosjean et al. (1993a)
1991	Tanbark Flat 5–26 August		0.187 ± 0.001	–128 ± 5	900	0.979	Grosjean et al. (1993a)
	Franklin Canyon 4–12 September		0.140 ± 0.002	–46 ± 4	338	0.964	Grosjean et al. (1993a)
1993	Azusa 28 August– 11 September		0.166 ± 0.018	–24 ± 23	331	0.786	Grosjean et al. (1996)
	Claremont 1–11 September		0.097 ± 0.014	–4 ± 7	403	0.925	Grosjean et al. (1996)
	Long Beach 29 August–13 September		0.153 ± 0.030	92 ± 8	354	0.793	Grosjean et al. (1996)
	Los Angeles 30 August–11 September		0.136 ± 0.026	48 ± 7	319	0.897	Grosjean et al. (1996)
1997	Azusa several days in July–October ^g	0.142 ± 0.025	0.174 ± 0.005	–51 ± 10	132	0.943	Grosjean et al. (2001b)
	Simi Valley several days in July–October ^g	0.135 ± 0.023	0.154 ± 0.005	–15 ± 6	138	0.924	Grosjean et al. (2001b)

^a 1 ppt = 0.001 ppb.

^b PPN/PAN ratio (one sample).

^c Average PPN/average PAN.

^d Highest PPN/highest PAN.

^e See footnotes c and d in Table 3.

^f Range of ratios at the time of maximum PPN concentration.

^g Days are listed in footnote (f) in Table 3.

ambient PPN have not been studied. Data from earlier long-term studies are not supportive of a simple scenario in which PAN concentrations, like those of ozone, peak during the summer months. In fact, high levels of PAN have often been recorded outside of the “traditional” smog season (Taylor, 1969; Pitts and Grosjean, 1979; Singh et al., 1981;

Temple and Taylor, 1983; Williams and Grosjean, 1990).

3.2. Trends in ambient levels of PAN

With the caveat that only incomplete information is available, see above, ambient levels of PAN in

southern California have declined between 1960 and 1997 (Fig. 1). Peak concentrations were 50–70 ppb in the 1960s, 40 ppb or more until 1980 and less than 40 ppb after 1980 (including 34 ppb in summer 1986 in Glendora and 30 ppb in summer 1987 during SCAQS). Peak concentrations have not exceeded 22 ppb since 1990, 13 ppb since 1991, and 10 ppb thereafter (even though the measurements made in 1993 included the most severe smog episodes for that year). To put the recent southern California data in perspective, the highest PAN concentrations recorded in 1993 (5–10 ppb) and 1997 (3 and 5 ppb) are lower than those measured in the 1990s in other urban areas, e.g., 12 ppb in 1991 in Tokyo, Japan (Kaneyasu et al., 1995), 40 ppb in 1992 in Montelibretti near Rome, Italy (Ciccioli et al., 1995), 12 ppb in 1994 in Athens, Greece (Suppan et al., 1998) and more than 30 ppb (along with up to 6 ppb of PPN) in Mexico City, Mexico (Gaffney et al., 1999).

Consistent with the trend indicated by peak concentrations, 24-h averaged and monthly averaged PAN concentrations (Table 2) indicate a decrease in ambient PAN since 1960. Thus, the highest 24-h averaged PAN concentrations were ca. 15–20 ppb until 1980, 5–12 ppb in 1985–1991 (including SCAQS in 1987), 2–5 ppb in 1993, and 2.1 and 1.3 ppb in Azusa and Simi Valley, respectively, during SCOS97-NARSTO. Data for monthly averages, although more limited, show a similar decrease: ca. 7.0 ppb in Riverside in 1967–1968, 1975–1976 and 1980, 2.8 ppb in Tanbark Flat in

1989, and, in 1997, 1 ppb in Azusa and 0.6 ppb in Simi Valley.

3.3. Trends in ambient levels of PPN

Available data are even more limited for PPN than for PAN. The daily maxima, 24-h averages and study averages listed in Table 3 indicate that ambient levels of PPN in southern California have declined in a manner similar to those of PAN. For example, peak levels of PPN have decreased by a factor of ca. six between the early 1960s (5–6 ppb) and the late 1990s (1 ppb or less). The PPN/PAN concentration ratios (Table 4) range from 0.10 to 0.28 and give no indication of a long-term temporal trend. We stress that no firm conclusions can be made regarding trends in ambient PPN on account of the paucity of data. However, the results given in Tables 3 and 4 are of value as baseline data and for comparison with current, longer-term measurements that may be used to assess changes in ambient concentrations that may accompany mandated changes in vehicle fuel composition.

4. Possible causes for the observed decline in ambient levels of PAN in southern California

We speculate in this section on possible reasons for the decrease in ambient levels of PAN and PPN in southern California between 1960 and 1997.

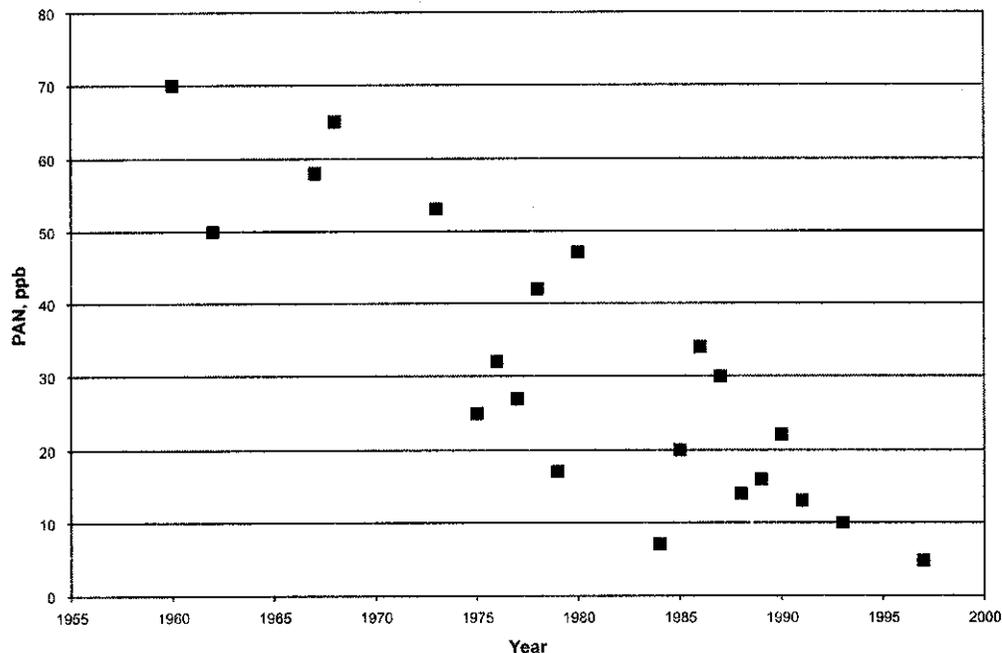


Fig. 1. Peak concentrations of PAN at southern California locations, 1960–1997 (from data in Table 1).

4.1. Comparison of long-term trends for PAN to those for ozone

Ozone and PAN have a common (photochemical) origin, and it is of interest to compare long-term trends in ambient levels of PAN to those of ozone. Ambient ozone in southern California has been reported since 1955 (e.g., South Coast Air Quality Management District, 1985, 1997, and <http://www.aqmd.gov>), although measurements made until the late 1960s using the KI method included other photochemical oxidants (such as PAN and PPN) and therefore overstated actual ozone concentrations. Trends in ozone concentrations have been analyzed numerous times (e.g., California Air Resources Board, 1992; Davidson, 1993; Fiore et al., 1998; Wolff et al., 2001; Fujita, 2001). In the South Coast Air Basin, peak ozone concentrations were ca. 680 ppb in 1958, ca. 540 ppb in 1960 (the year ambient PAN was first measured) and 210 ppb in summer 1997. Overall, peak ozone concentrations have decreased by a factor of roughly 3 in the second half of the 20th century (Fig. 2), reflecting increasingly stringent controls on emissions of VOC and NO_x by stationary and mobile sources. Increased controls of VOC and NO_x emissions have undoubtedly resulted in lower PAN concentrations as well as in lower ozone concentrations.

4.2. VOC reactivity considerations

While long-term data indicate a downtrend in ambient levels of the photochemical oxidants ozone and PAN, it appears that ambient levels of PAN (and possibly PPN) have decreased faster than those of ozone. While ozone forms by oxidation of virtually all VOC, PAN forms only from those VOC whose oxidation lead to the acetyl radical. Mandated controls, first intended to reduce the magnitude of the emissions of ozone precursors, have more recently focused on reducing the photochemical reactivity of emitted VOC (e.g., Carter, 1994, 1995). California Phase 1 and Phase 2 reformulated gasolines are examples of such mandated controls of the reactivity of VOC emitted by mobile sources. It is plausible that VOC controls implemented over the years have lead to a larger decrease in emissions of VOC that are precursors to PAN as compared to the decrease in emissions of VOC that do not produce PAN. To test this hypothesis, it would be necessary to have long-term, detailed information on speciated ambient VOC, including PAN precursors (these include aromatics, alkenes, alkanes, and acetaldehyde). This information is only available for recent years (since the inception of the PAMS monitoring program for hydrocarbons and of Air Toxics programs for acetaldehyde) and is not sufficient to examine long-term trends in

emissions and ambient levels of VOC that are precursors to PAN.

4.3. Thermal decomposition of PAN

The thermal decomposition of PAN increases rapidly with increasing temperature and is a major loss process for PAN in the troposphere (Bridier et al., 1991; Tuazon et al., 1991b, and references cited therein). It is relevant to examine briefly the importance of PAN thermal decomposition in the context of long-term trends. Calculations of the amount of PAN lost by thermal decomposition have been made using results for summer 1993 and summer 1997 at southern California locations (Grosjean et al., 1996, 2001a). These calculations indicate that, on summer afternoons, the amount of PAN lost by thermal decomposition is comparable in magnitude to the amount of PAN measured in ambient air.

On account of higher than usual temperatures during summer 1997 (up to 41°C), the amount of PAN lost by thermal decomposition was particularly high during SCOS97-NARSTO (Grosjean et al., 2001a). However, the total amount of PAN formed (i.e., the sum of ambient PAN and PAN lost by thermal decomposition) during SCOS97-NARSTO was about the same as that formed in summer 1993 (Grosjean et al., 1996). Thus, the lower ambient levels of PAN (and PPN, whose thermal decomposition is similar to that of PAN) measured in 1997, as compared to 1993, most likely resulted from higher temperatures in 1997 and not from a factor of ca. 2–3 decrease, between 1993 and 1997, in emissions of VOC that are precursors to PAN and PPN.

5. Concluding comments

We have compiled and analyzed available information regarding ambient concentrations of peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) in southern California where PAN was first observed in the mid-1950s and measured in 1960. The data record, contained in ca. 35 studies carried out between 1960 and 1997 (SCOS97-NARSTO), is limited with respect to frequency and duration of measurements, spatial distribution, and information on seasonal variations. Nevertheless, peak concentrations, 24-h averaged concentrations and monthly and/or study averages all indicate a decrease in ambient PAN and a decrease in ambient PPN in southern California during the period 1960–1997. For example, peak values for PAN have decreased from 60–70 ppb in the 1960s to 5–10 ppb in the 1990s, and peak values for PPN have decreased from 5–6 to 1 ppb or less during the same period. The observed downward trend is a likely result of increasingly stringent controls of emissions of the precursors to

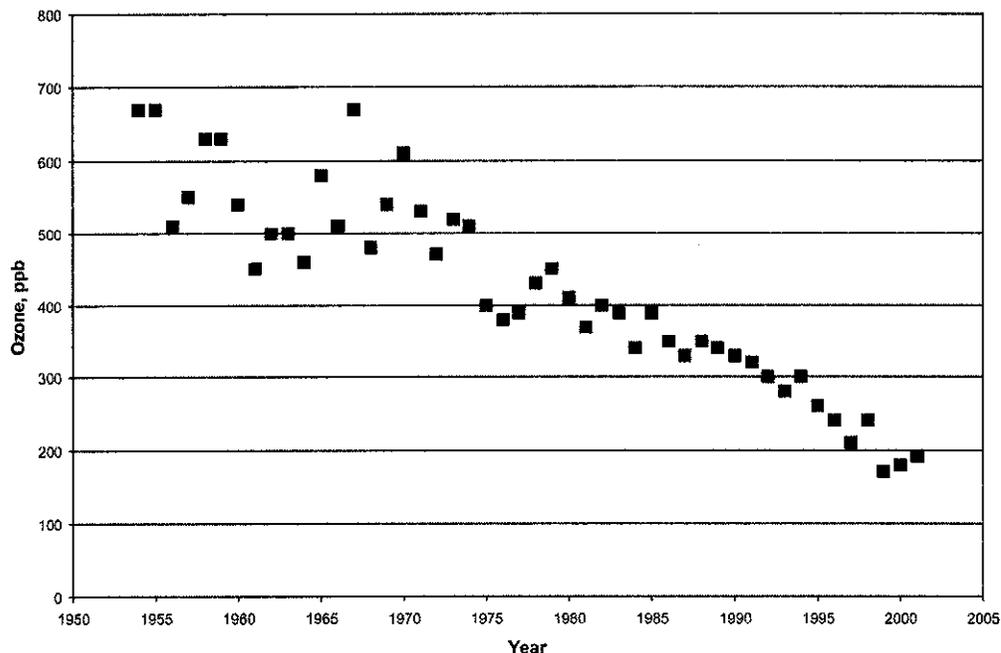


Fig. 2. Peak concentrations of ozone in the California South Coast Air Basin, 1955–2001 (constructed from South Coast Air Quality Management District, 1985 and www.aqmd.org).

PAN and PPN, i.e., volatile organic compounds and oxides of nitrogen. PPN/PAN concentration ratios range from 0.10 to 0.28 and the limited data record gives no indication of a long-term temporal trend.

After 31 December 2003, gasolines distributed in California will no longer contain MTBE, which may be replaced by ethanol. The possible impact of MTBE and ethanol on ambient PAN and PPN is outlined in this article and will be examined in more detail using the results of an on-going, long-term campaign of measurements that started in early 2001. The historical record presented here will be of value when analyzing the results of the new campaign with respect to the impact of mandated changes in oxygenated fuel policies on ambient photochemical oxidants including PAN and PPN.

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