Potential Impacts on Air Quality of the Use of Ethanol as an Alternative Fuel

A Final Report

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Introduction

The use of ethanol/gasoline mixtures in motor vehicles has been proposed as an alternative fuel strategy that might improve air quality while minimizing U.S. dependence on foreign oil. New enzymatic production methodologies are being explored to develop ethanol as a viable, economical fuel. In an attempt to reduce urban carbon monoxide (CO) and ozone levels, a number of cities are currently mandating the use of ethanol/gasoline blends. However, it is not at all clear that these blended fuels will help to abate urban pollution. In fact, the use of these fuels may lead to increased levels of other air pollutants, specifically aldehydes and peroxyacyl nitrates (Gaffney and Marley 1990; Tanner, et al. 1988). Although these pollutants are not currently regulated, their potential health and environmental impacts must be considered when assessing the impacts of alternative fuels on air quality. Indeed, formaldehyde has been identified as an important air pollutant that is currently being considered for control strategies by the State of California..

This report focuses on measurements taken in Albuquerque, New Mexico during the summer of 1993 and the winter of 1994 as an initial attempt to evaluate the air quality effects of ethanol/gasoline mixtures. The results of this study have direct implications for the use of such fuel mixtures as a means to reduce CO emissions and ozone in a number of major cities and to bring these urban centers into compliance with the Clean Air Act.

The use of ethanol may lead to small decreases in CO emissions and nonmethane hydrocarbons (NMHCs) as measured by nondispersive infrared and flame ionization detection, respectively. However, ethanol combustion in spark-ignition engines results in increased primary acetaldehyde and formaldehyde emissions. The reaction of acetaldehyde with the OH radical in urban atmospheres leads directly to the formation of the peroxyacetyl radical, which can react with nitrogen dioxide (NO_2) to form peroxyacetyl nitrate (PAN).

Indeed, increased PAN levels have been observed in Rio de Janeiro, Brazil, and in preliminary studies in Albuquerque during periods of increased use of ethanol/gasoline blends. PAN is not currently a criteria pollutant, nor are aldehydes; however, these compounds are known to be potent lachrymators and mutagens. PAN is also a plant toxin more potent than ozone.

Data taken at both Rio de Janeiro and Albuquerque (Tanner, et al. 1988; Popp, et al. 1993) also indicate that the larger peroxyacyl nitrate, peroxyproprionyl nitrate (PPN), is apparently produced in higher levels when ethanol or methyl-t-butyl ether is used as an oxygenated fuel. PPN has been found to be more toxic than PAN. It is a storage medium for NO_2 and will lead to the formation of PAN, peroxides, and aldehydes upon thermal decomposition, i.e., as an air mass is transported downwind. Peroxides produced from these aldehyde emissions can cause increased oxidation of sulfur dioxide to sulfate resulting in decreased visibility and increased acidic deposition. Regional ozone levels may also be affected by changes in these emissions downwind of the urban center.

The available data from preliminary studies and from related research in Denver indicate that the use of ethanol/gasoline blends may not be as beneficial to overall air quality as first proposed. Albuquerque was chosen as a field study site because it is currently mandated to use these fuels and institute wood-burning bans in an attempt to maintain air quality during the winter months. Albuquerque is an ideal site for studying the urban and downwind effects of alternative fuel usage. The city has a population of approximately 450,000 and is isolated from any other population center. It is located in the Rio Grande Valley and is bordered by the Sandia Mountains on the east. The terrain is ideal for periodic thermal inversions, during which substantial levels of "brown-cloud" pollution can occur. At other times, meteorology in the complex terrain leads to periods where background air infiltrates the city, improving the air quality. Thus, Albuquerque is an excellent site to evaluate the impact of ethanol usage on air quality.

Field Measurements

Field measurements of PAN, ozone, formaldehyde, acetaldehyde, and formic and acetic acids were taken for periods of 1 month during July-August 1993 and 1 month in January-February 1994 at the downtown air quality monitoring station operated by the City of Albuquerque (Figure 1). To perform these studies most efficiently, atmospheric chemistry students from New Mexico Tech in Socorro, New Mexico collected samples and performed routine data collection and instrument maintenance at the field site, under the supervision of Dr. Carl J. Popp and the principal investigators.

Details of the field analytical measurements are provided in the following section.

Field Measurement Methods

PAN Measurements

The measurements were taken using PANalyzers, which are automated gas chromatographs equipped with electron capture detectors (Gaffney, et al. 1989). The PANalyzers used ultra-high-purity nitrogen as the carrier gas and made use of an automated gas sampling system consisting of a six-port solenoid valve connected to an electronic relay controller. Samples were analyzed every 30 minutes and reported as 1-hour average values for comparison with other air quality data. A recording integrator was used to collect PAN data and examine higher analog peroxyacyl nitrate concentrations such as PPN.

Instruments were calibrated using PAN standards in diffusion tubes which were referenced to a calibrated NO_x analyzer (Gaffney, et al. 1984). The instruments were calibrated before and after the field measurements, and were found to be quite stable during these field efforts.

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New Mexico Tech support staff changed chart paper and carrier gas tanks as necessary during the field studies. Once the strip charts were collected, Argonne evaluated and the data placed them into Lotus-123 files for analysis.

Aldehyde Measurements

Aldehydes were sampled with commercially available dinitrophenylhydrazine (DNPH) cartridges (Sepak C-18, Waters) and air sampling pumps. Samples were collected at 4-hour intervals during the day and 6-hour intervals during the night. Each cartridge sample was collected for a 2-hour period and the results represent an average value over the 2 hours. New Mexico Tech personnel collected the samples and labeled them with the date, collection time interval, and volume of air sampled. Researchers also collected samples at Socorro, New Mexico, a rural site 75 miles south of Albuquerque, as a comparison to the urban samples.

The exposed cartridges were analyzed at New Mexico Tech using high-performance liquid chromatography (HPLC) with ultraviolet-visible detection. Principal attention was given to formaldehyde and acetaldehyde, although data for other aldehydes were examined, particularly as they related to natural emissions of isoprene from local hardwood trees during the summer.

Organic Acid Measurements

Organic acid samples were collected at 2-hour intervals during the day and 6-hour intervals at night using a water mist nebulizer (Popp, et al. 1993). The samples were analyzed at New Mexico Tech using ion chromatography. These data were placed into Lotus 123 data files for analysis. Samples were also collected at Socorro to compare with the urban samples. These data are detailed in the results and discussion section.

Gas Analysis

Gas analysis for NO_x ozone, and CO was performed by the City of Albuquerque air quality monitoring station (Figure 1). The NO_x measurement is based on ozone chemiluminescent reaction with NO. Ozone is measured using standard ultraviolet absorption methods, and CO measurements are made with nondispersive infrared spectroscopy. Data from these instruments were recorded as hourly averages.

Actinic Radiation Measurements

Researchers used a Richardson-Berger ultraviolet-B (UV-B) radiometer to assess the effective photochemical light intensity at the urban site. This instrument allows direct measurement of ultraviolet radiation, along with daytime temperatures, which should be useful information for future modeling efforts of regional air quality impacts due to the use of ethanol blends in Albuquerque.

Results and Discussion

Figure 1 is a map of Albuquerque which shows the location of the sampling station for data obtained in this field study. The station is maintained by the City of Albuquerque as part of its air quality network. The site is centrally located, fenced, and contains ozone, oxides of nitrogen, CO, wind speed, and wind direction instruments. All systems are calibrated on a weekly basis, and the data are reported as hourly averages. These data were obtained from the city and used as part of this study to minimize cost.

Acetic acid, formic acid, propionic acid, pyruvic acid, acetaldehyde, formaldehyde, propionaldehyde, PAN, UV-B radiation, and daytime temperatures were also measured at this

site using the methods described previously. Table 1 gives the average values for these data observed during the two field efforts in the summer of 1993 and the winter of 1994, as well as UV-B radiation levels measured using a Richardson-Berger (RB) radiometer. During the summer, the use of 10% gasohol blends was less than 5%, compared to the winter when the City of Albuquerque was mandated to use 100% ethanol/gasoline blends.

Table 1 shows that the daytime temperatures and wind speed for the two periods were quite comparable, due to a relatively mild winter in 1994. UV-B was substantially reduced in the winter, as expected. NO, NO_y (the difference between the NO and NO_x channels), and NO_x along with CO and PAN levels were all substantially higher in the winter. This was likely caused by the boundary layer thermal inversions which occur in the winter months and act to trap these pollutants over Albuquerque.

The increased PAN levels correlate with increased acetaldehyde and formaldehyde levels observed during the winter. This could result from use of 10% ethanol fuel blends, as the ethanol will be cracked directly to acetaldehyde, particularly during cold starts of the motor vehicles. It is interesting to note that ozone levels were lower in the winter, probably due to reduced light intensities and higher levels of NO, which reacts rapidly with ozone. Mean levels of acetic acid and formic acid were dramatically reduced in winter, possibly due to reduced photochemical activity along with the substantial reduction in potential natural hydrocarbon sources (isoprene) reduced during the winter when hardwoods are dormant.

Graphic Comparison of the Hourly Data for Summer and Winter

Nitrogen Oxide

Figures 2 and 3 present hourly averages for NO at the Albuquerque field site for Summer 1993 and Winter 1994, respectively. The graphs are presented on the same scale to clearly indicate the much higher levels found during the winter. These higher levels are due to atmospheric inversions and the reduced photochemical activity in winter.

Total NO_x hourly averages given in Figures 4 and 5 for summer and winter, respectively, show the same behavior. Higher levels of NO_x and NO were observed during the early part of the day and later in the day corresponding to traffic flow patterns that peak at approximately 7:30 am and 4:30 pm. The diurnal patterns are caused by the time dependent daytime emissions followed by atmospheric transport from the city during the day and night.

NO_y levels, the difference between the NO_x and NO concentrations, which includes NO_2, PAN, and nitric acid are shown in Figures 6 and 7. The data show a similar pattern to that described above. Wintertime levels of NO_y are higher due to the atmospheric inversions.

Carbon Monoxide

Like the nitrogen oxide data, the CO data (Figures 8 and 9) indicate generally higher levels of CO during the winter with the exception of two high values measured during the summer. These values were observed for 1-hour periods only, and may have been caused by a diesel truck or other motor vehicles that were observed to be parked near the station for short times. The mean CO levels for the winter were about 1.6 ppm, compared to 1.0 for the summer (see Table 1). However, the frequency of CO values above 3.0 was much higher in the winter.

Ozone

In contrast to the nitrogen oxide and CO data, the ozone data depicted in Figures 10 and 11 for summer and winter, respectively, show the opposite trends: higher ozone levels were observed during the summer, while much lower levels were found during the winter. The data show one episode during the summer where ozone rose above 120 ppb. The wintertime data set contains two periods where the ozone exceeded 80 ppb. These data are consistent with the decreased light intensity and higher levels of NO in the winter which act to titrate the ozone.

Figures 12 and 13 show the time comparison of the NO and ozone data for the summer and winter field efforts, respectively. These data sets clearly indicate the fairly good anti-correlation between ozone and NO. This is due to the fact that the NO reacts quite rapidly with ozone. Ozone is formed from the photolysis of NO_2, which is produced from the primary NO emitted from the mobile sources in the Albuquerque area. The reactions involved are summarized below:

$$NO_2 + hv \longrightarrow NO + O \qquad\qquad [1]$$

$$O + O_2 + M \longrightarrow O_3 + M \qquad\qquad [2]$$

$$NO + O_3 \longrightarrow NO_2 + O_3 \qquad\qquad [3]$$

In order to produce ozone, NO needs to be converted to NO_2 by peroxy radicals. These can be formed by the reaction of OH radicals with organics or the direct photolysis of aldehydes. Again, note that the NO levels are substantially higher in the winter than in the summer. Alternately, the ozone levels are substantially higher in the summer than in the winter, as expected due to the higher level of photochemical activity produced by the higher light levels in the summer.

PAN Data

PAN data for the summer and winter months are given in Figures 14 and 15, respectively. PPN concentrations are also indicated for the winter data, but were found to be below detection limits (30 ppbv) during the summer studies. The PAN levels were found to be quite low in the summer, with the exception of a few periods where PAN was measured at levels above 0.5 ppbv. The highest level measured in the summer was approximately 1.5 ppbv. The wintertime data set shows higher PAN levels with PPN observed on a number of occasions. The highest levels of PAN were approximately 1.7 ppbv. It should be noted that PAN is expected to form from the oxidation of acetaldehyde via OH abstraction and the subsequent reaction of the peroxyacetyl radical with NO_2. Despite much lower photochemical reactivity in winter, PAN levels were found to be significantly higher in the winter than in the summer. The levels observed during this initial field study, however, are lower than those found in previous field efforts in Rio de Janeiro (Tanner, et al. 1988). This may be due to the lower alcohol/gasoline ratios used in Albuquerque (10%) than in Brazil (30%), and to the fact that the Brazilians are not using catalytic converters.

Ultraviolet-B Radiation (UV-B)

UV-B data are presented in Figures 16 and 17 for the summer and winter, respectively. The data for both periods are remarkably consistent and indicate minimal effects due to clouds. Doublets in some of the daily measurements indicate times when local clouds did move into the area, causing a reduction in UV-B light due to light scattering; however, for the most part, the meteorology was very clear. Mean values for UV-B during the summer were approximately a factor of 5 higher than winter means. Maximum values during the summer were 28 $\mu W/cm^2/hr$, compared to 7.6 $\mu W/cm^2/hr$ during the winter. These data support the assumption that photochemical activity is reduced during the winter.

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Aldehydes

Total aldehyde levels for the summer of 1993 and the winter of 1994 are shown in Figures 18 and 19. Overall total aldehyde levels were comparable during both field efforts, with slightly higher levels measured during the winter.

Plots of the acetaldehyde and formaldehyde measurements are shown in Figures 20 and 21 for summer and winter, respectively. Periods of higher acetaldehyde and formaldehyde levels were found during the winter. Maximum values of acetaldehyde were found to be about twice as high during the winter than the summer, with a maximum winter value of approximately 50 ppbv. Highest values for formaldehyde were comparable for both periods, with the maximum values at approximately 60 ppbv. More frequent episodes of high aldehyde concentrations were observed during the winter, consistent with the inversion situation during the early morning hours. The one period of high acetaldehyde values in the winter (days 23-25) also showed higher PAN levels.

Propionaldehyde was detected during the summer study but not during the winter study. This may be due to a natural source of propionaldehyde from deciduous vegetation in the Albuquerque area.

To compare urban versus rural aldehyde levels, a limited data set was taken at New Mexico Tech in Socorro, New Mexico (population 10,000). These data are presented in Figures 22 (Summer 1993) and 23 (Winter 1994) for acetaldehyde, formaldehyde, and propionaldehyde. As the figures clearly show, the winter data values are quite low, while the summer data indicate much higher levels, particularly for formaldehyde. While both these rural data sets are much lower than the values in Albuquerque during the same periods, they are substantially lower in the winter than in the summer. This suggests that the summer

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aldehyde levels may be due to the oxidation of natural hydrocarbons (isoprene) and direct emission of aldehydes from plants and trees. Likewise, appreciable amounts of aldehydes measured during the summer in Albuquerque may be coming from these deciduous plants and trees. Thus, aldehydes, particularly formaldehyde, may be produced from both natural and anthropogenic sources during the summer. The comparison of wintertime data sets indicates that aldehyde levels in the winter are from predominantly anthropogenic sources.

Organic Acids

Total organic acid levels are plotted for the summer and winter studies in Figures 24 and 25, respectively. These plots show the organic acid levels to be quite variable, but reaching appreciable concentrations (i.e., 50-90 ppbv). The data indicate organic acid levels are much higher in summer than in winter. This is likely due to the combination of higher emissions of these compounds from natural sources in the summer and increased oxidation of aldehydes caused by higher photochemical activity.

Specific values measured for acetic, formic, propionic, and pyruvic acids are shown in Figures 26 and 27 for the summer and winter studies. As can be seen from these figures and from the mean values for these sampling periods (Table 1), acetic acid and formic acid were higher in the summer, propionic acid levels were very comparable for the two periods, and pyruvic acid was higher in the winter. Pyruvic acid in the atmosphere is likely caused by natural sources and by wood burning, the latter being elevated during colder winter nights. Acetic acid levels were found to be appreciable, averaging 17.9 ppbv during the summer and 7.4 ppbv during the winter.

In an attempt to evaluate the input from natural sources of organic acids, measurements of these species were also taken at the Socorro rural site. These data are given in Figures 28 and

29 for the summer and winter, respectively. Organic acid levels in the summer were much lower in Socorro than in Albuquerque, particularly for acetic acid. This indicates that photochemical oxidation of organics in the urban samples led to higher levels of these acids. Formic acid was slightly higher in the urban air shed, except for a few episodes where the data were approximately a factor of four higher in the rural samples. Propionic acid levels also were higher at the urban site in summer. In contrast, during acetic acid levels were found to be appreciably higher at the rural site in winter. This may be due to the transport and transformation of some of the aldehydes from Albuquerque to downwind Socorro. Formic acid levels also were found to be higher at Socorro in winter, while propionic acid levels were comparable at the two sites. This may be due to the formation of these organic acids from wood burning sources.

Acetone

Acetone measurements for Albuquerque are presented in Figures 30 and 31. Acetone values were typically highly variable and found to be higher during the summer than the winter. This ketone is likely produced by both natural and anthropogenic sources. Because it is potentially photochemically active under UV-B radiation, acetone may become an important compound if UV-B levels increase due to stratospheric ozone depletion.

Acetone measurements at Socorro are given in Figures 32 and 33 for summer and winter, respectively. Again the levels are highly variable but can reach values in the 20-30 ppbv range, similar to those measured in Albuquerque. Acetone levels were higher at the urban site during the winter. Methyl ethyl ketone (MEK) values also were taken in the winter field study in an attempt to evaluate natural sources (i.e. isoprene) and wood burning impacts at the Socorro site.

Frequency Distributions

Acetaldehyde

Frequency distributions were determined for the summer and winter data sets to better evaluate the differences in acetaldehyde levels that could be due to ethanol/gasoline fuel usage. These data analyses are shown in Figures 34 and 35. The occurrences of elevated levels of acetaldehyde (i.e., those above 35 ppbv) appear to occur much more frequently during the winter months. As noted above, the Socorro aldehyde data strongly suggest that a substantial amount of the formaldehyde and acetaldehyde observed in the urban air shed during the summer is due to natural hydrocarbon oxidation and direct natural emissions.

Ozone

Ozone frequency distributions are presented in Figures 36 and 37 for the summer and winter field studies. Note that the summer frequency distribution clearly indicates higher levels of ozone, as expected for this more photochemically active period. However, ozone was above criteria levels during only one episode in the summer study. This indicates a relatively clean air period compared to past levels measured in Albuquerque.

PAN

The PAN frequency distribution analyses are presented in Figures 38 and 39 for summer and winter, respectively. This analysis clearly shows that the PAN levels in the urban winter are higher than those in the summer, despite the lower photochemical activity due to lower light intensities. Because the daytime temperatures were fairly comparable for both sampling periods, it appears that the higher winter values are primarily due to local production of PAN.

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Downwind levels of PAN are likely to be higher, because PAN is slowly titrated by NO and the conversion of NO to NO_2 during transport would increase PAN formation rates.

Daytime Temperature

The daytime temperature frequency distributions are shown for Summer 1993 and Winter 1994 in Figures 40 and 41. Daytime temperatures during the winter were very consistent and mild. The summer data show more variability, with some temperatures above 25.5 C. These warmer conditions cause PAN to decompose somewhat faster, leading to PAN losses. However, the production of PAN from photochemical reactions also is expected to be higher in the summer, thus compensating for the thermal decomposition and reaction with NO in the urban atmosphere:

$$PAN \text{------------>} CH_3CO_3 + NO_2 \qquad [4]$$
$$CH_3CO_3 + NO + O_2 \text{----->} CH_3O_2 + NO_2 + CO_2 \qquad [5]$$
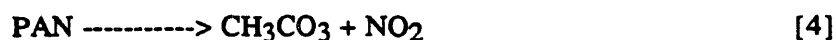
In general, the summer and winter periods showed fairly consistent daytime temperatures which is reflected in the mean values (Table 1). The cooler periods in the summer resulted from appreciable cloud cover and cooler temperatures during monsoon thunderstorms.

Conclusions and Recommendations for Future Study

The data in this study were obtained during periods of relatively clean air at the urban site for both the summer of 1993 and the winter of 1994. The use of alcohol/gasoline blend fuel during the summer was less than 5% statewide, while the Albuquerque usage in winter was mandated at 100% (State of New Mexico 1993; 1994).

This study examined the concentrations of various pollutants to determine if levels of aldehydes are affected by the wintertime use of ethanol fuels and if increased levels of

acetaldehyde may lead to increased production of organic oxidants (i.e., PAN) and acids. The data showed increased levels of PAN and aldehydes in winter, while levels of acids appeared to be lower.

A comparison of data taken at the Socorro rural site with data from the Albuquerque urban site indicates that while emission levels are higher at the urban site, significant amounts of aldehydes and acids are likely being produced from the photochemical oxidation of natural hydrocarbons and from primary emissions. This is an important finding and should be evaluated further to determine the relative role of motor vehicle emissions compared to natural hydrocarbon emissions in the formation of aldehydes, oxidants, and acids. Future studies should make use of the natural isotopic variations of carbon-13 (C-13) to differentiate corn-derived alcohol products (C-4 plants; $-12^o/_{oo}$) from the natural plant derived products and wood-burning (C-3 plants; $-26^o/_{oo}$). The following section outlines the development of methods to accomplish this goal.

Future studies also need to address the downwind photochemical impacts of increased levels of NO_x and aldehydes observed during the wintertime. These pollutants will likely lead to increased regional ozone and oxidant levels which could damage crops and affect the health of suburban inhabitants. NO_x and aldehyde levels should be measured at a downwind site as well as the original urban site for comparison. It would be useful for these future studies to be performed in summer and winter so that results could be directly compared with the data gathered and presented here. Meteorological data, along with a relatively simple chemical computer model could be used to evaluate potential downwind effects of using alcohol fuels in an urban center. These data would be useful in determining the potential for increased levels of organic oxidants, aldehydes, and organic acids, as well as for evaluating the effectiveness of fuel blend usage in abating criteria pollutants (i.e., ozone, CO, etc.).

Although the PAN and aldehyde levels were somewhat lower in this study than in previous field studies in Brazil (Tanner, et al. 1988), they are still high enough to indicate that ethanol/gasoline fuel blends may cause excessive aldehyde and organic oxidant levels in urban and regional sites.

We presented preliminary results from the acid and aldehyde comparisons at the American Chemical Society (ACS) National Meeting (Popp, et al. 1994) and plan to publish most of the results from this study in the peer-reviewed literature, most likely in the ACS journal *Environmental Science & Technology*. These manuscripts will be sent to NREL for review for approval before submission, and published copies will be made available to NREL.

Use of C-13 Isotopes to Determine Aldehyde Sources

Aldehydes are produced from wood burning and from the oxidation of natural hydrocarbon emissions from trees and other vegetation as well as from ethanol/gasoline emissions. It would be advantageous to be able to differentiate the various sources of aldehydes to give a more direct measure of the impact of ethanol/gasoline fuel on air quality. One possible approach is to measure the stable carbon isotope ratios ($^{13}C/^{12}C$) that naturally label these materials.

Carbon exists naturally as two stable isotopes, carbon-12 and carbon-13. C-12 is the and accounts for approximately 99% of the carbon on the planet. The amount of C-13 varies due to fractionation by biochemical and physiochemical processes.

The conventional method for determining the $^{13}C/^{12}C$ ratio is to use an isotope ratio mass spectrometer. The stable carbon isotope ratios are determined on samples by converting them to carbon dioxide (CO_2) and examining the 44, 45, and 46 m/e intensities. These samples are compared to a standard sample (usually a limestone), and $^{13}C/^{12}C$ is reported as

the difference from the standard in parts per thousand. The usual standard is PDB, a limestone from the PeeDee Belemnite formation. Most samples are depleted in C-13 when compared to PDB, so the reported ratios are often negative.

Figure 42 provides some carbon isotope ratios relative to PDB for terrestrial plants. Plants are known to make use of two types of biochemical pathways to fixate CO_2 from the atmosphere. One pathway has been referred to as the C_4 or the Hatch and Slack mechanism. In this biochemical mechanism four carbon atoms are fixed in the initial carboxylic diacid and the initial CO_2 is not appreciably fractionated from the atmospheric value of -7 $^o/_{oo}$.

The figure shows terrestrial plants are typically in the range of -12 $^o/_{oo}$. The other more common pathway is the C_3 mechanism (the Calvin-Benson cycle). This biochemical mechanism fixes three carbon dioxide molecules in the initial diacid and is more selective in its use of carbon isotopes, preferring the lighter C-12 to C-13. Thus, the C_3 plants have a typical carbon isotope ratio of -25 $^o/_{oo}$. Some examples of C_4 and C_3 grains are also given in Figure 42. Note that corn, sugar cane, and sorghum are readily distinguished from oats, rice, barley, and wheat by their biochemically driven stable carbon isotope ratios. Fossil fuels are usually derived from the more common C_3 biochemistry which is reflected in their ratios ranging from -22 to -32 $^o/_{oo}$.

Note that this is the principal fractionation process in the formation of the stable isotope ratio for any carbon containing material. Carbon ratios in animals including humans, reflects their diet. Previous work by Gaffney, et al (1978; 1979) used the stable carbon isotopes to differentiate human populations and to identify the source of black pulmonary pigment found in human thoracic lymph nodes. Products from the primary labeled materials reflect their source and will be similar in carbon isotopic ratio (Slatkin, et al. 1978). Thus, ethanol from corn will be naturally labeled in C-13 and easily distinguished from gasoline, which is

derived from petroleum. Aldehydes derived from wood burning or from the oxidation of natural hydrocarbons also would be differentiated because they are derived from C_3 plants with lower $^{13}C/^{12}C$ ratios.

Therefore, this natural labeling technique holds promise for directly determining the source of aldehydes and the extent of input from ethanol/gasoline blends.

One of the problems with using the isotope mass spectrometric method is that at least 0.1 milligram of sample material is typically required and must be combusted and measured as CO_2. Improvements in high-resolution Fourier-transform spectroscopy and the application of infrared laser techniques (Sauke, et al. 1994), particularly CO_2 lasers (Murnick and Peer 1994), need to be explored to determine if carbon isotopic ratios of aldehydes can be directly examined by measuring specific isotopic infrared transitions that are caused by C-13 and C-12 isotopes. In principal, these spectroscopic techniques also could be used on combusted samples and would likely have higher sensitivities than the mass spectrometric methods (i.e., low microgram levels).

Preliminary studies using an automobile fueled with ethanol/gasoline blends are needed to obtain samples for spectroscopic testing. The isotope ratio of a corn-based ethanol should be determined and compared to the ratio measured in gasoline. Isotope ratio measurements for several different ethanol/gasoline blends are needed to evaluate the potential of the mass-balance approach before it is applied in field studies.

Determining the source of aldehydes from their isotope ratios would enable researchers to evaluate the actual impacts of ethanol use on total acetaldehyde levels. C-14 measurements also should be evaluated as a means to determine the relative input of natural and fossil hydrocarbons to total aldehyde levels in the Albuquerque air shed since fossil fuels are void

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of C-14. The isotopic approach may aid considerably in determining the impact of alcohol/gasoline blends on air quality.

Acknowledgments

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Table 1. AVERAGE VALUES, ALBUQUERQUE, NM

Criteria	Unit of Measurement	Summer 1993	Winter 1994
Temperature	°C	24.7	25.0
Wind Speed	mph	5.2	5.7
UV-B	$\mu W/cm^2/hr$	9.1	1.8
NO	ppbv	6.5	61.6
NO_y	ppbv	13.8	32.8
NO_x	ppbv	20.3	94.5
Ozone	ppbv	34.8	14.7
CO	ppm	1.0	1.6
PAN	ppbv	0.1	0.4
Acetic Acid	ppbv	17.9	7.4
Formic Acid	ppbv	7.7	1.6
Propionic Acid	ppbv	0.6	0.6
Pyruvic Acid	ppbv	0.4	2.1
Total Acids	ppbv	26.9	9.3
Acetaldehyde	ppbv	6.6	7.5
Formaldehyde	ppbv	13.9	16.7
Propionaldehyde	ppbv	0.7	ND
Total Aldehydes	ppbv	21.0	24.0

FIGURE 1.

Map cf Albuquerque

1 - SITE OF SAMPLING STATION
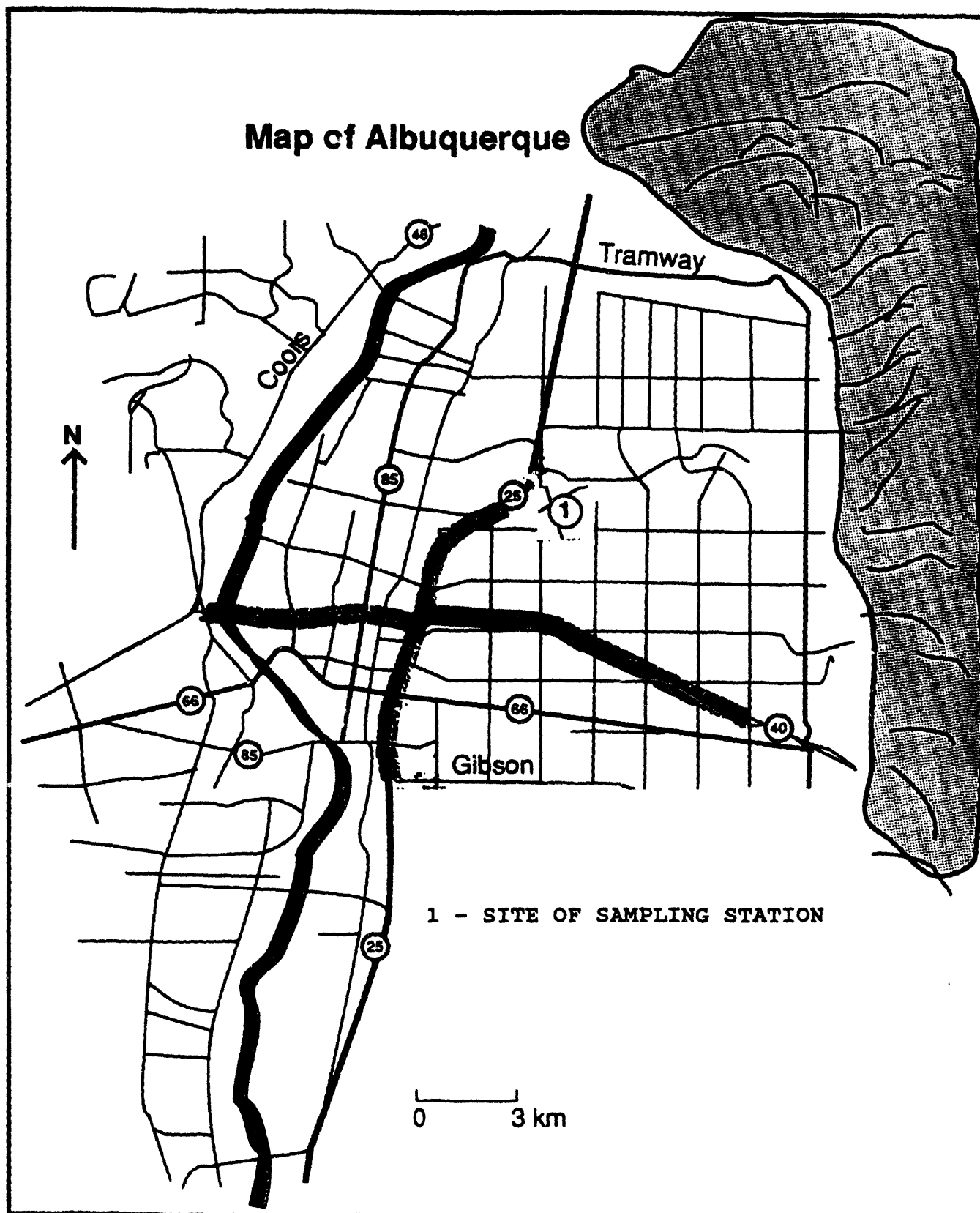
FIGURE 2.

NO
Albuquerque, NM — Summer 1993
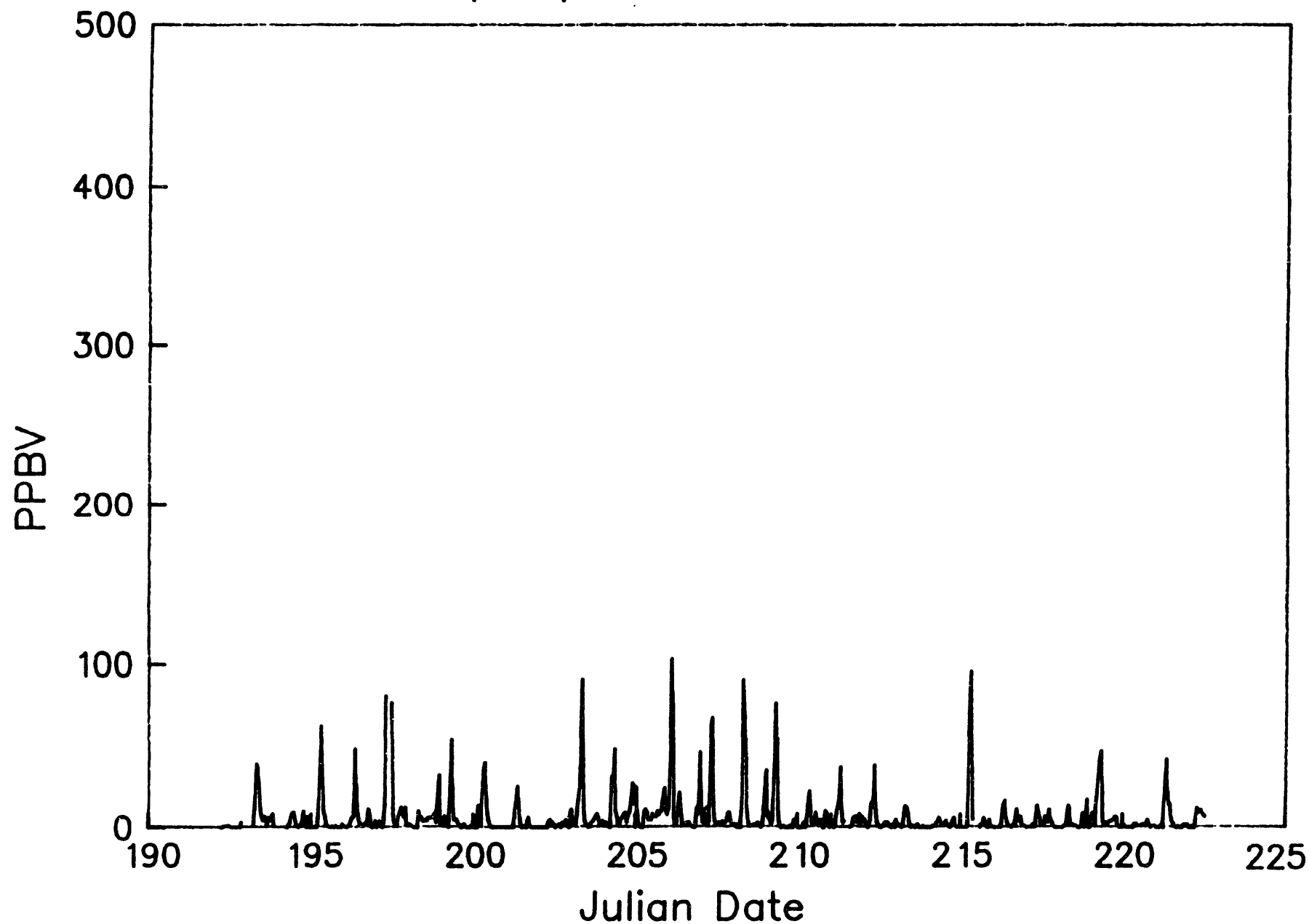
FIGURE 3.

NO
Albuquerque, NM — Winter 1994
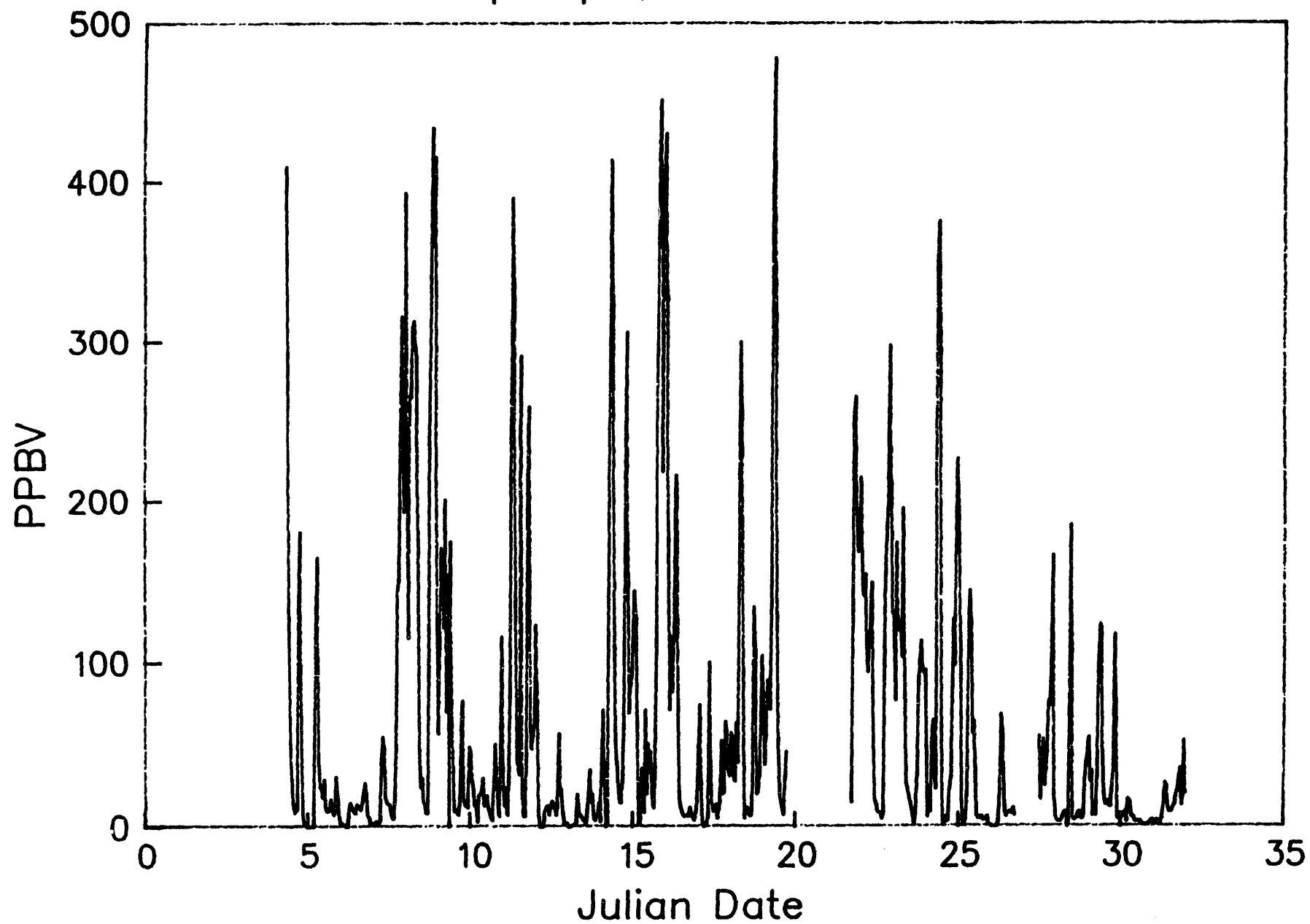
FIGURE 4.

NOx
Albuquerque, NM — Summer 1993
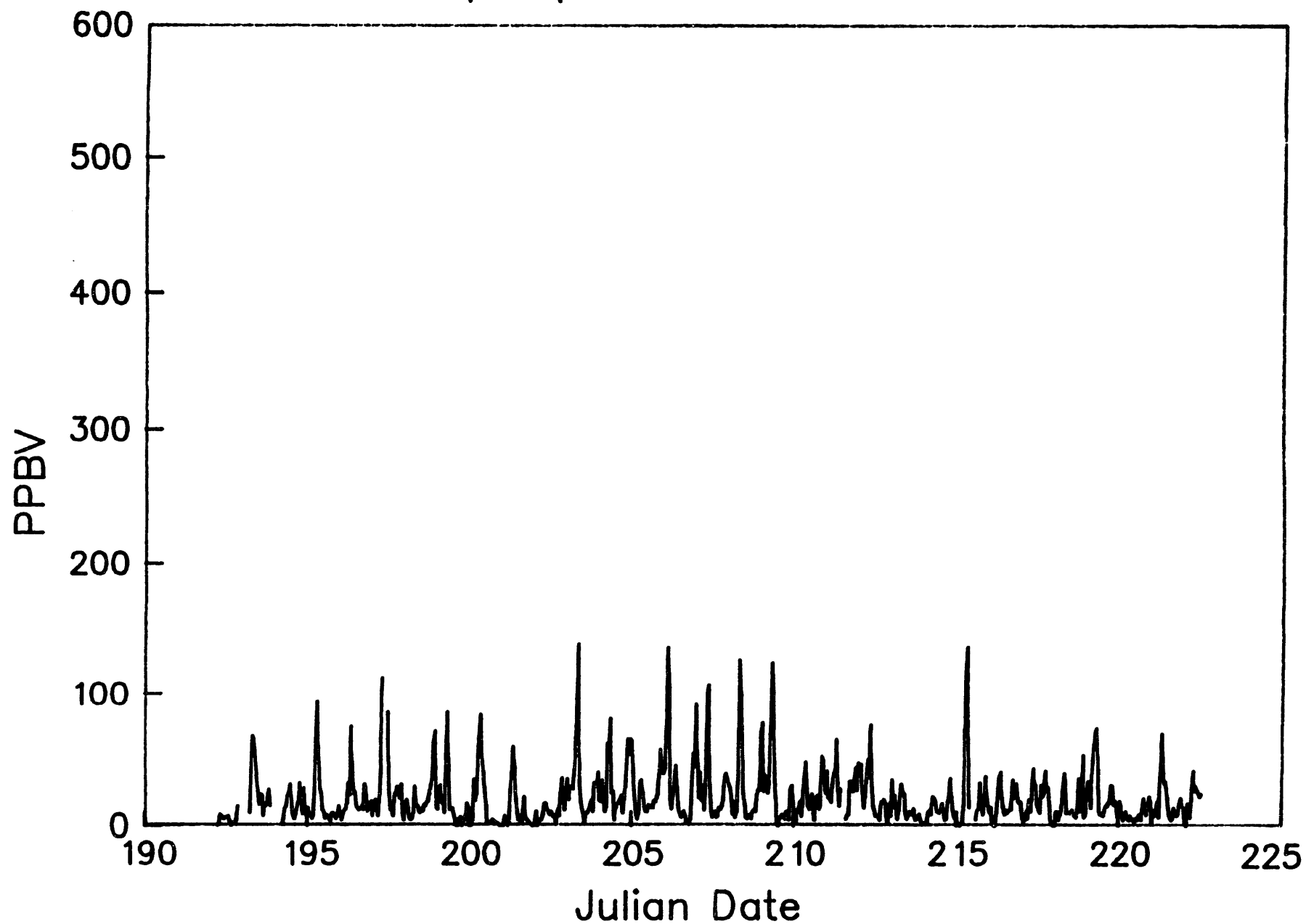
FIGURE 5.

NOx
Albuquerque, NM — WINTER 1994
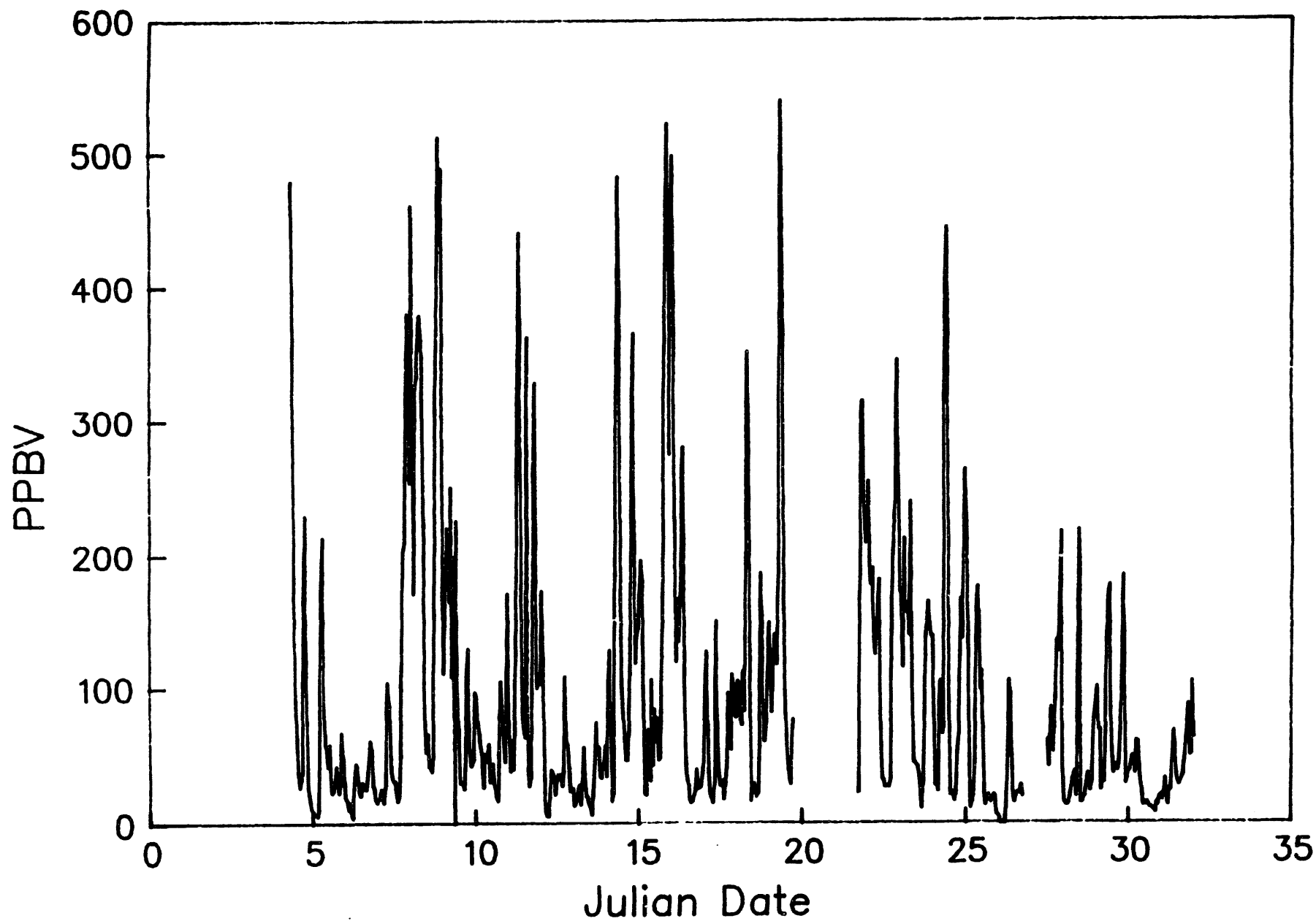
FIGURE 6.

NOy
Albuquerque, NM — Summer 1993
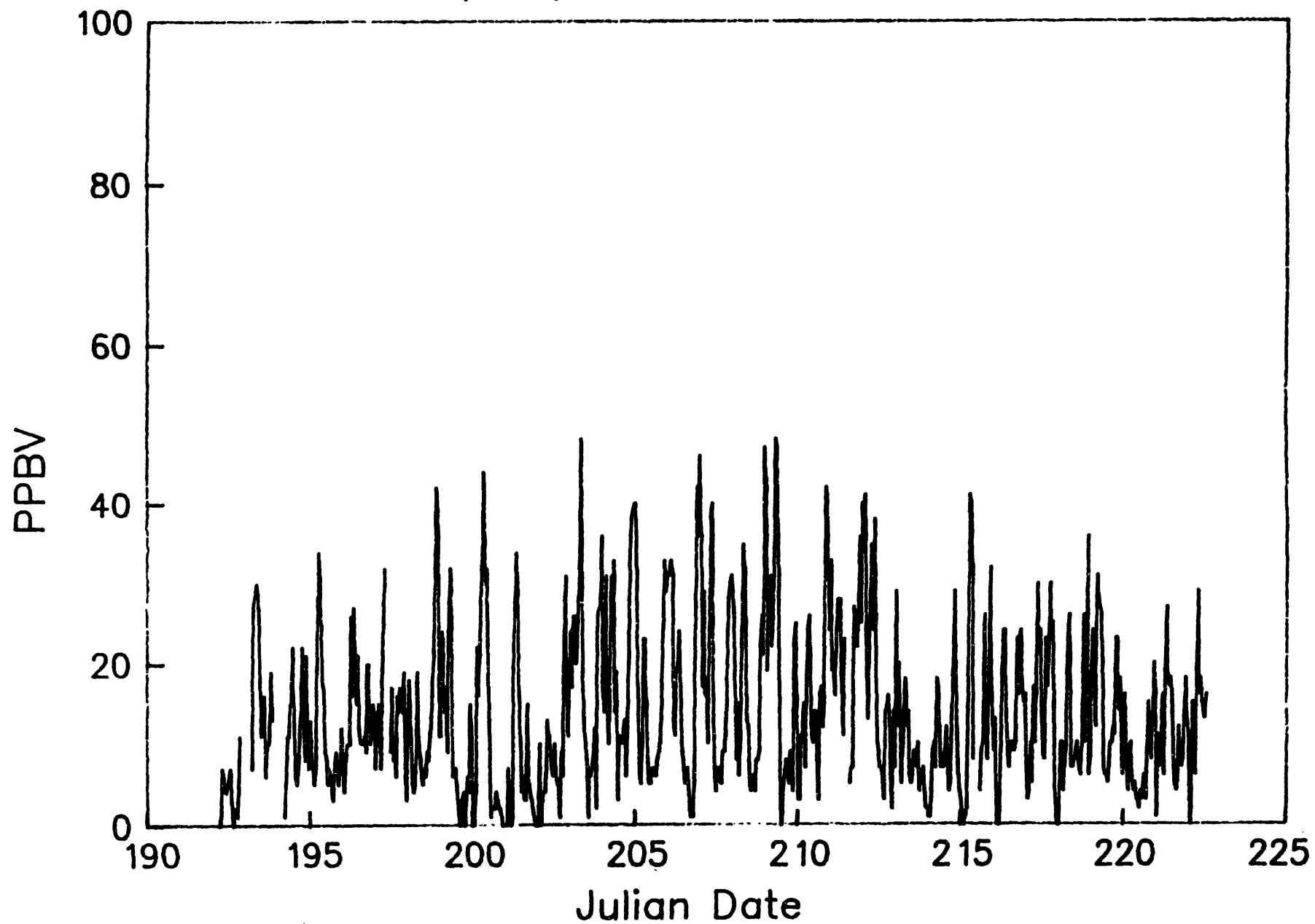
FIGURE 7.

NOy
Albuquerque, NM — Winter 1994

FIGURE 8.

CO
Albuquerque, NM — Summer 1993
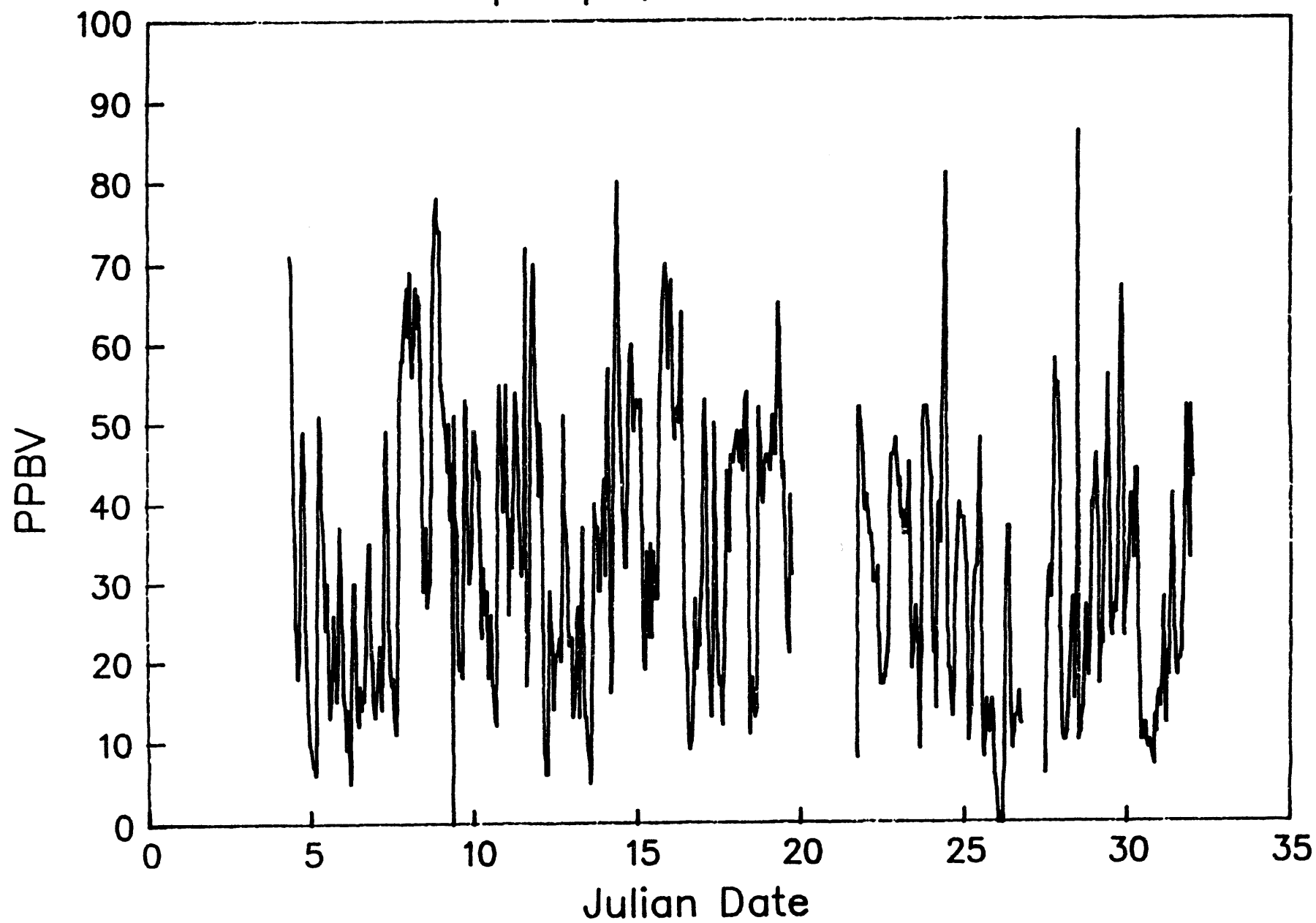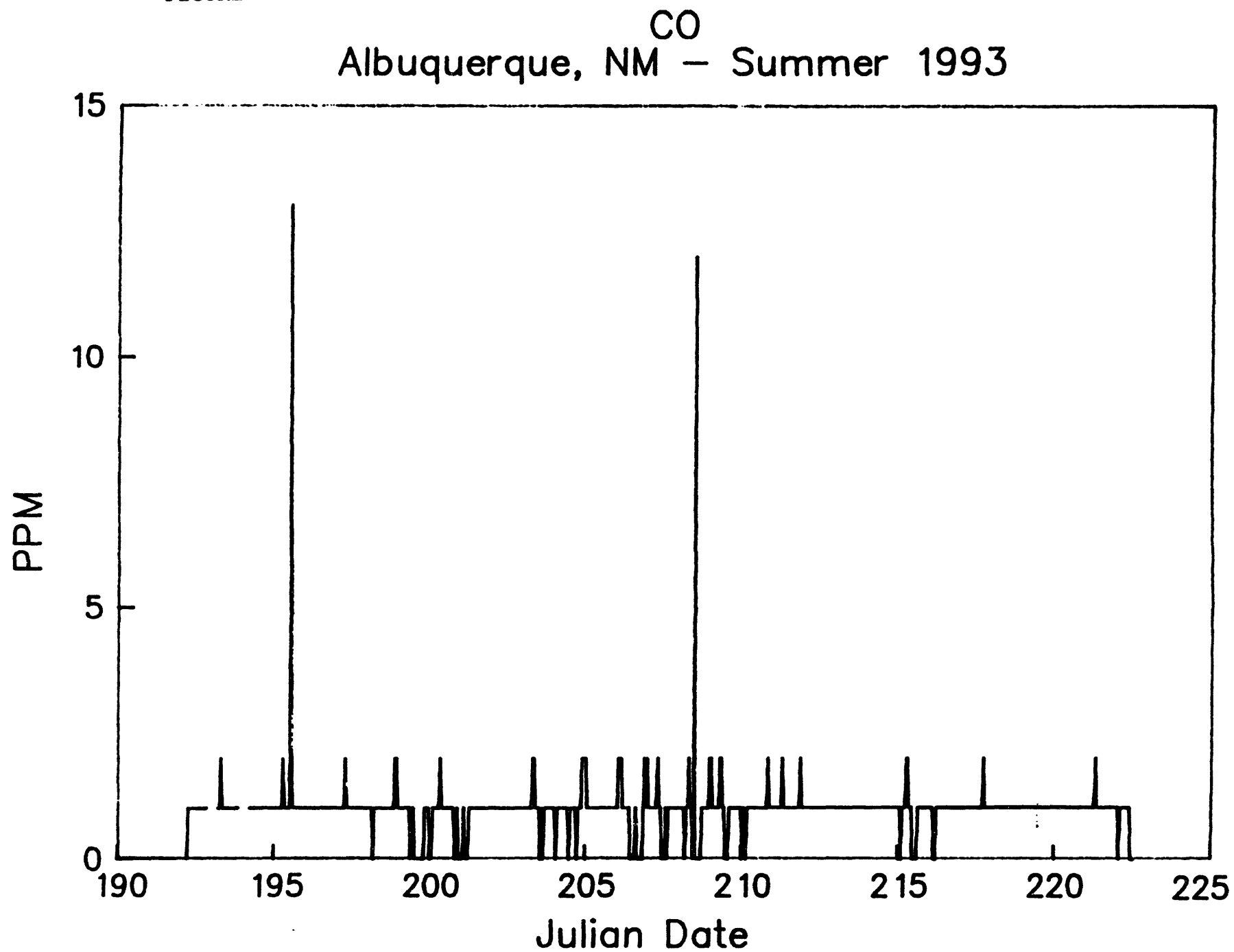
FIGURE 9.

CO
Albuquerque, NM — Winter 1994
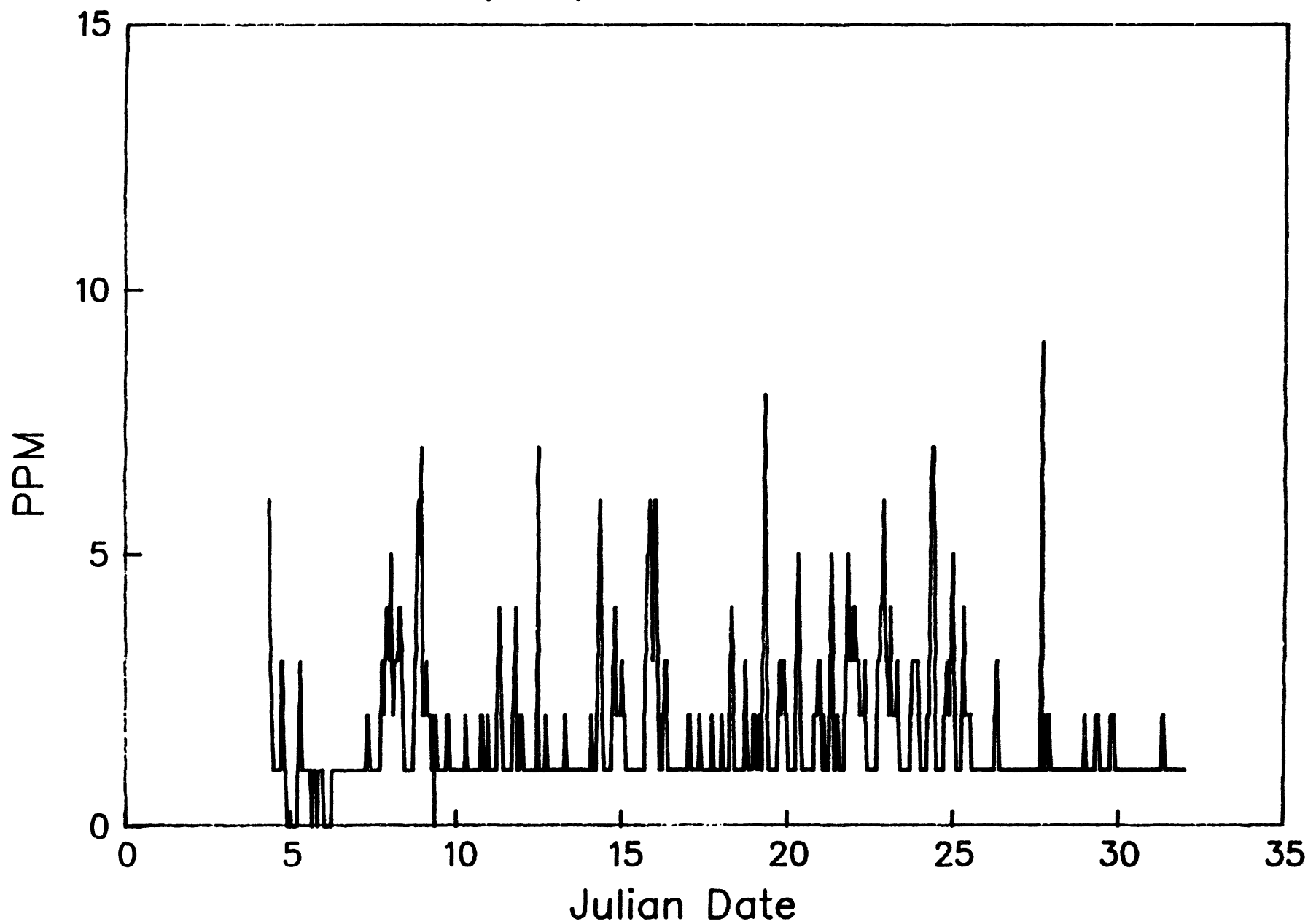
FIGURE 10.

OZONE
Albuquerque, NM — Summer 1993
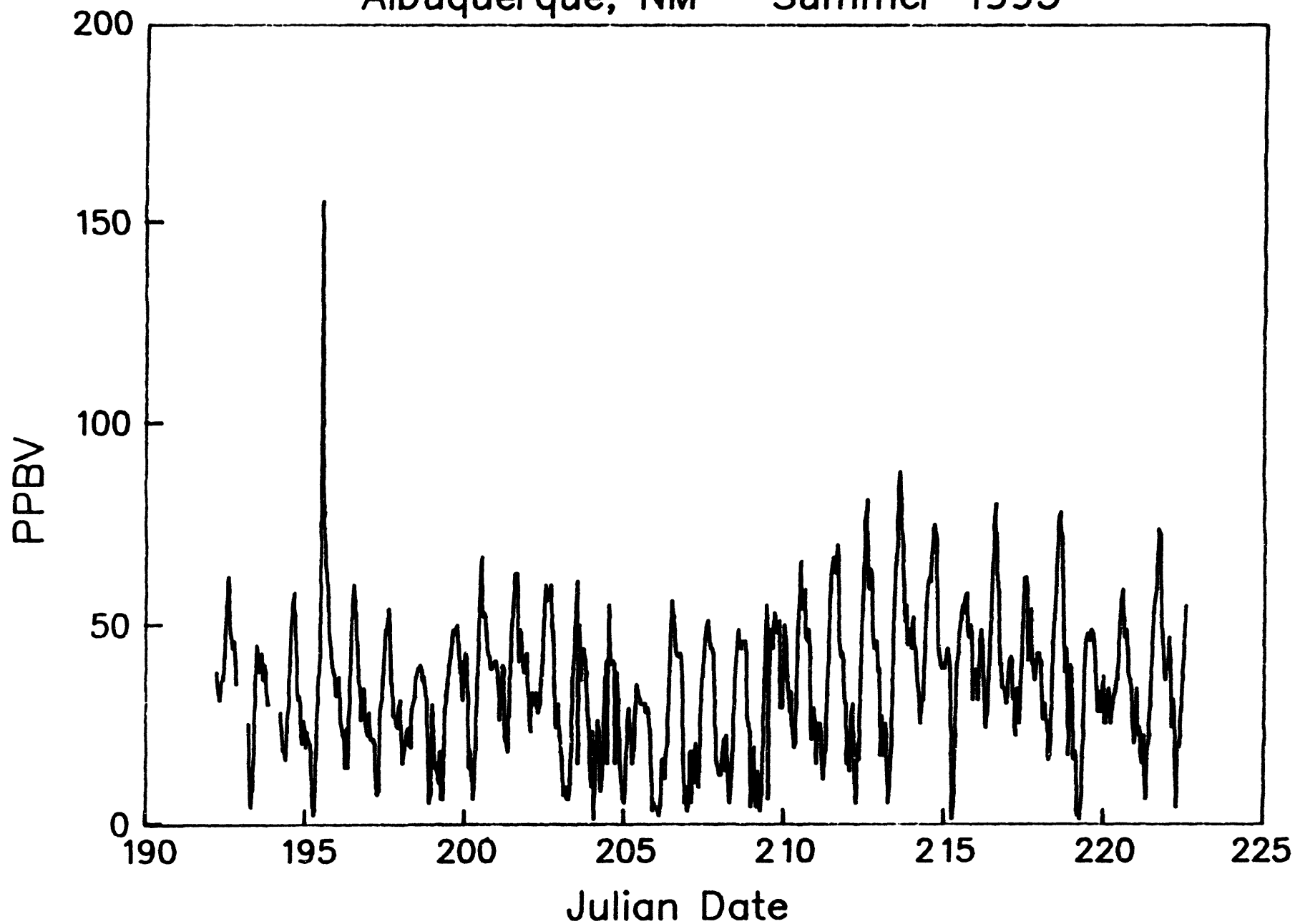
FIGURE 11.

OZONE
Albuquerque, NM — Winter 1994
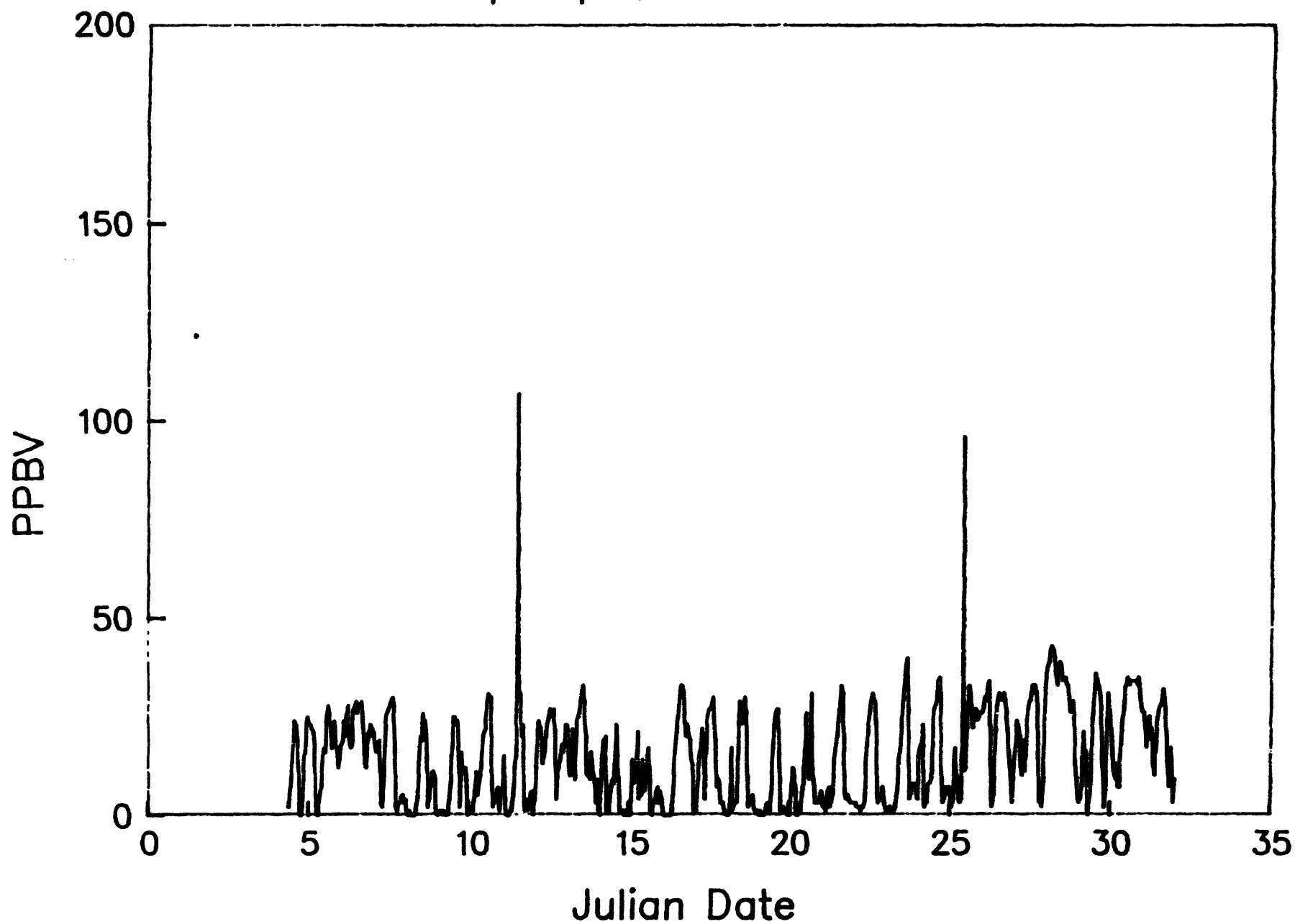
FIGURE 12.

OZONE AND NITRIC OXIDE HOURLY MEANS
Albuquerque, NM — Summer 1993
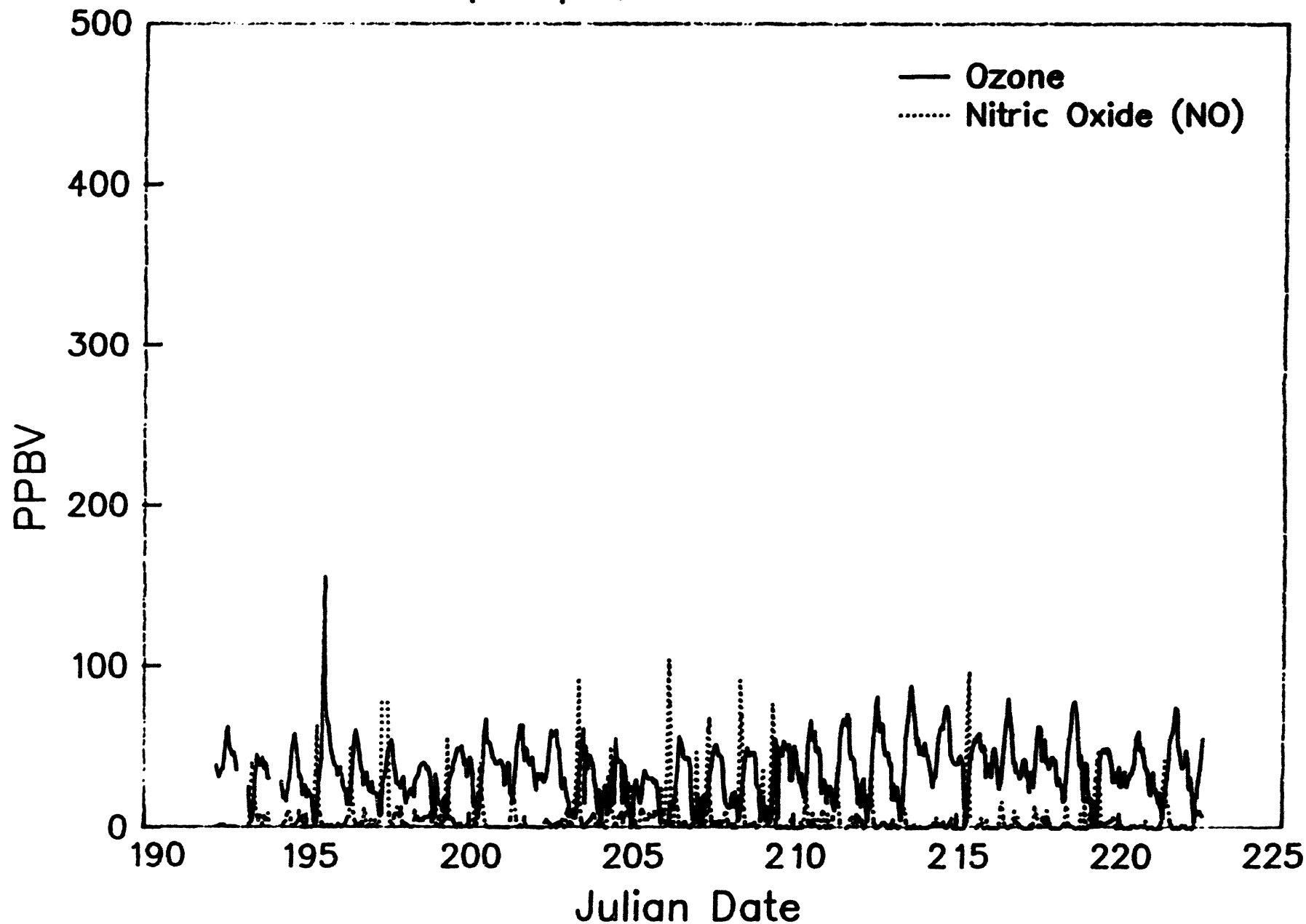
FIGURE 13.

OZONE AND NITRIC OXIDE HOURLY MEANS
Albuquerque, NM — Winter 1994
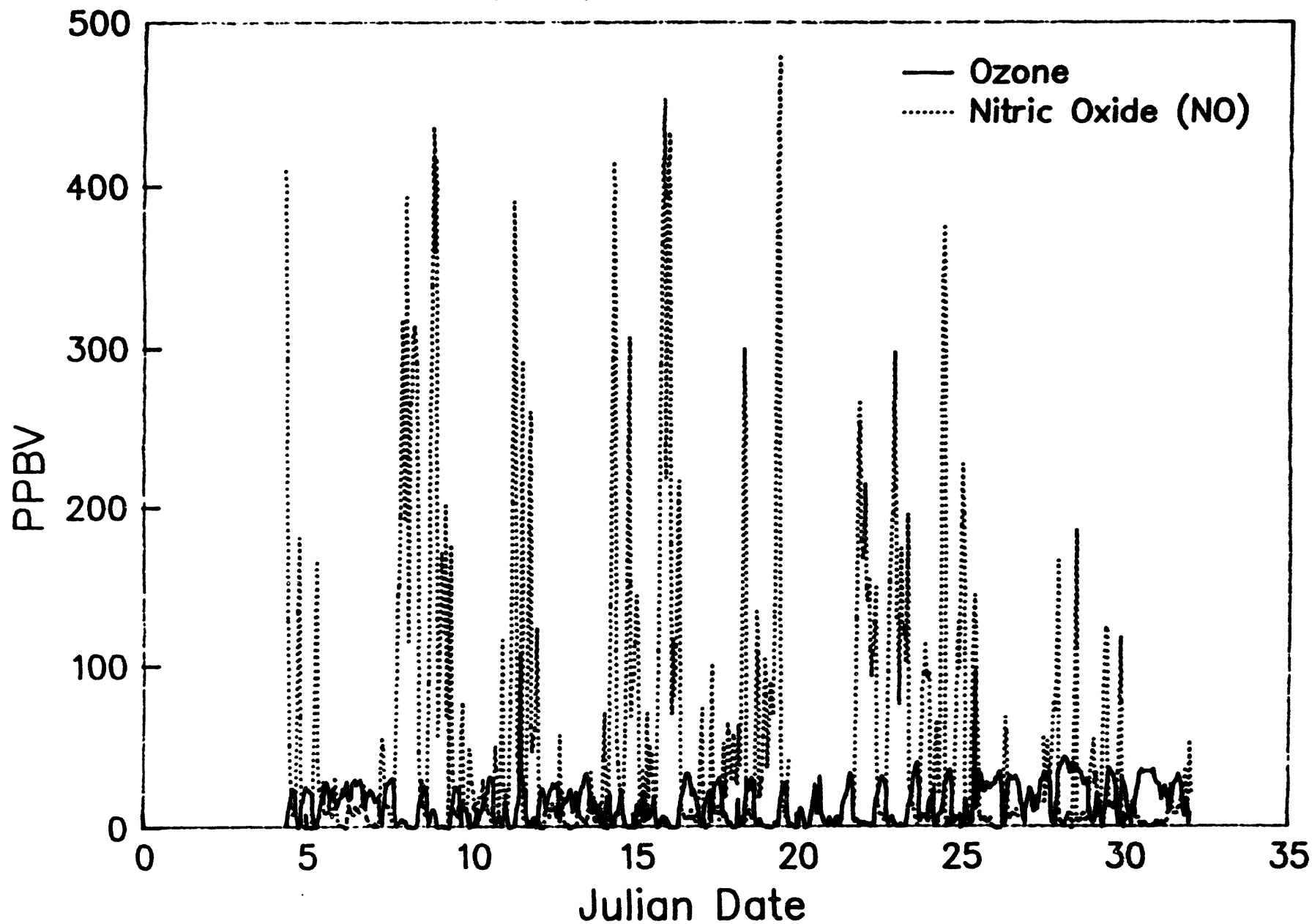
FIGURE 14.

PAN
Albuquerque, NM — Summer 1993
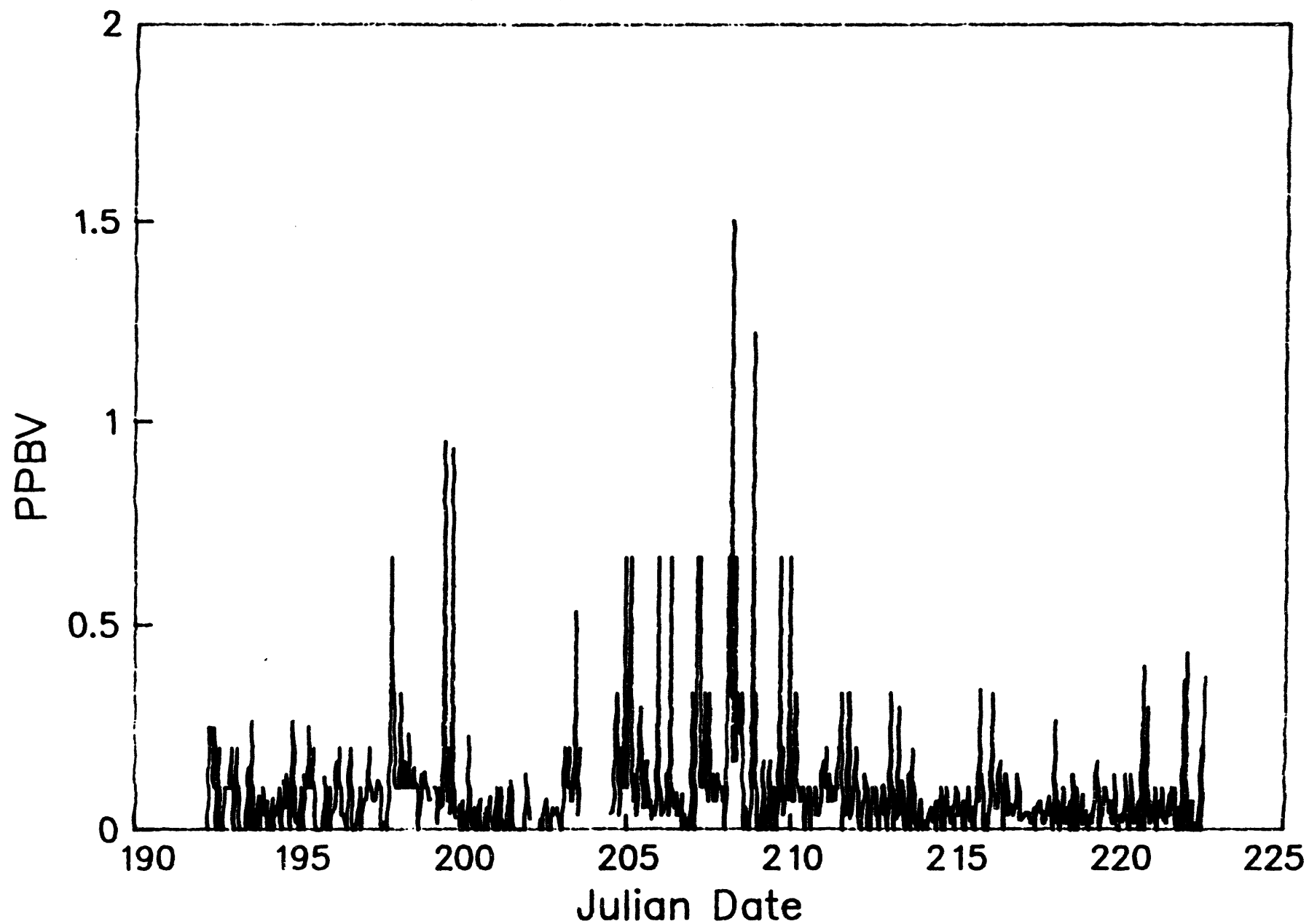
FIGURE 15.

PAN
Albuquerque, NM — Winter 1994
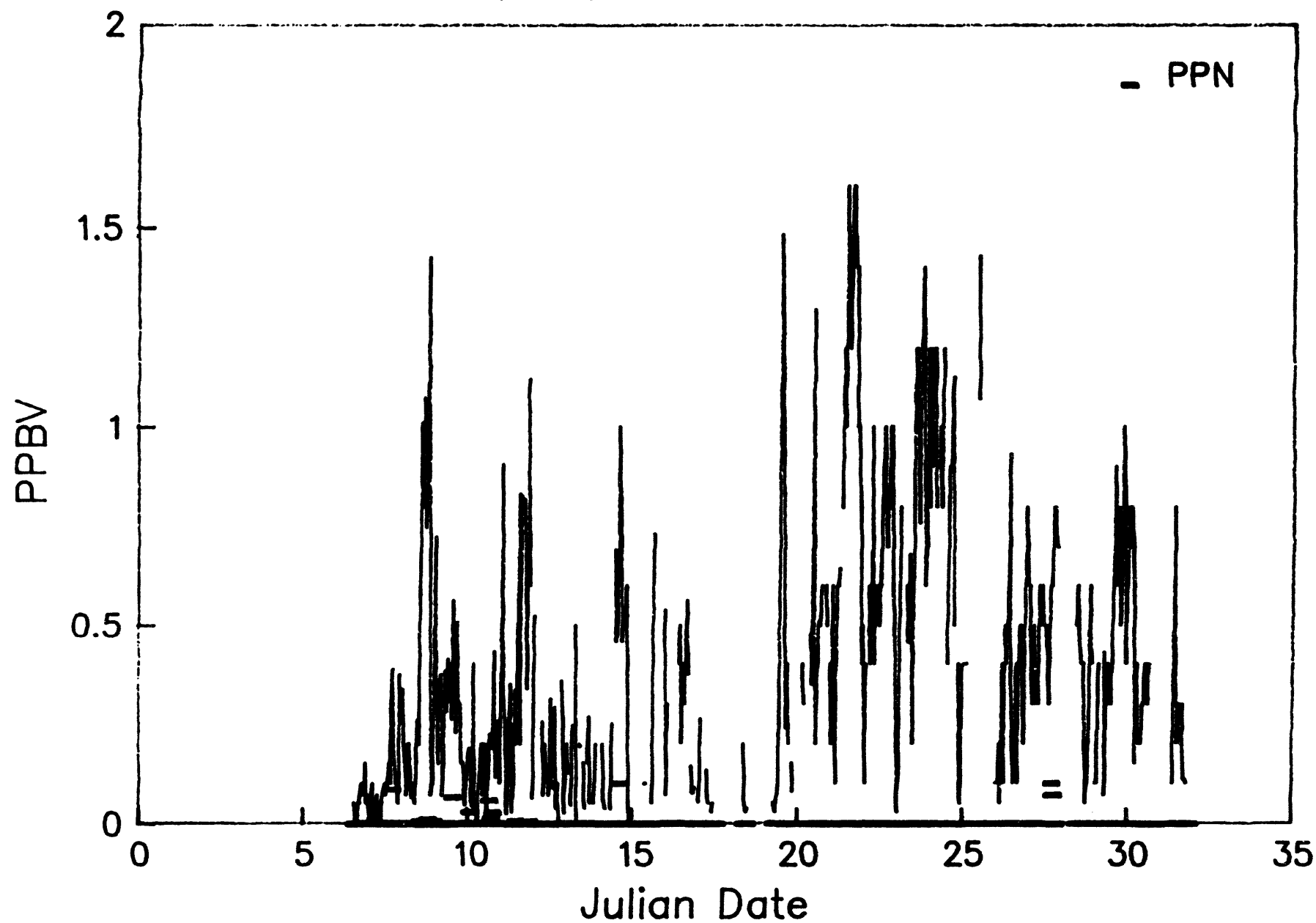
FIGURE 16.

UVB
Albuquerque, NM — Summer 1993
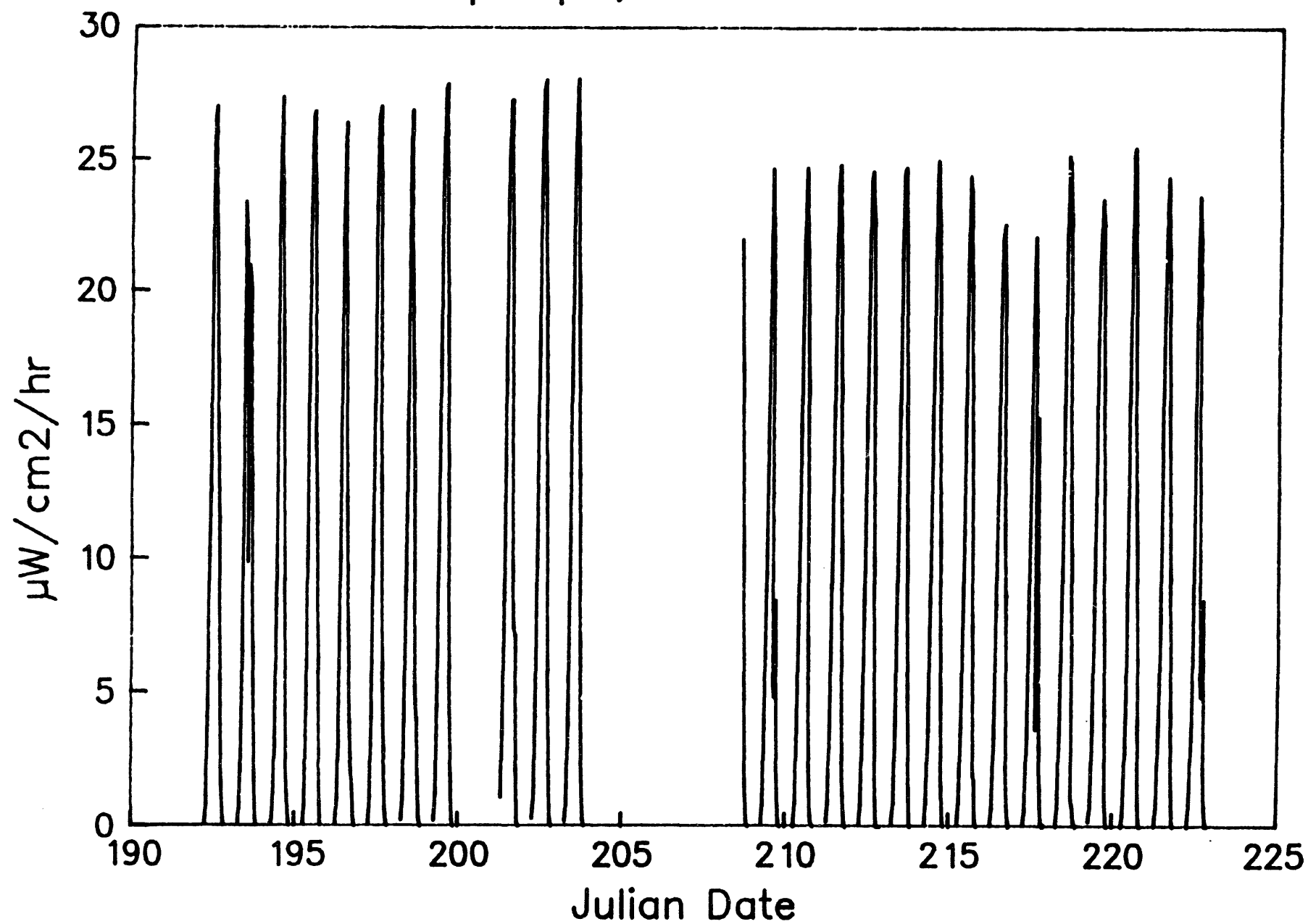
FIGURE 17.

UVB
Albuquerque, NM — Winter 1994
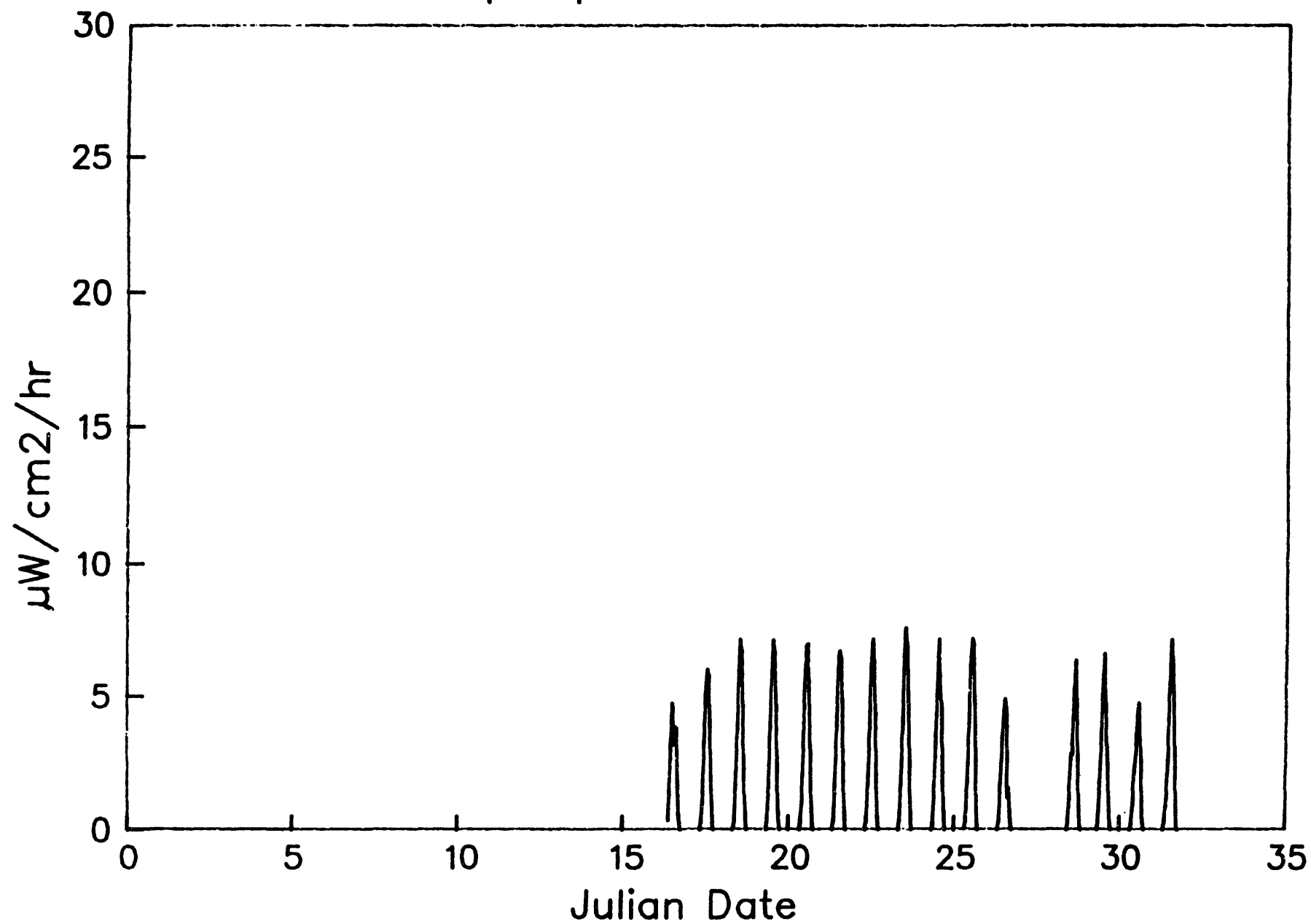
FIGURE 18.

ALDEHYDES
Albuquerque, NM — Summer 1993
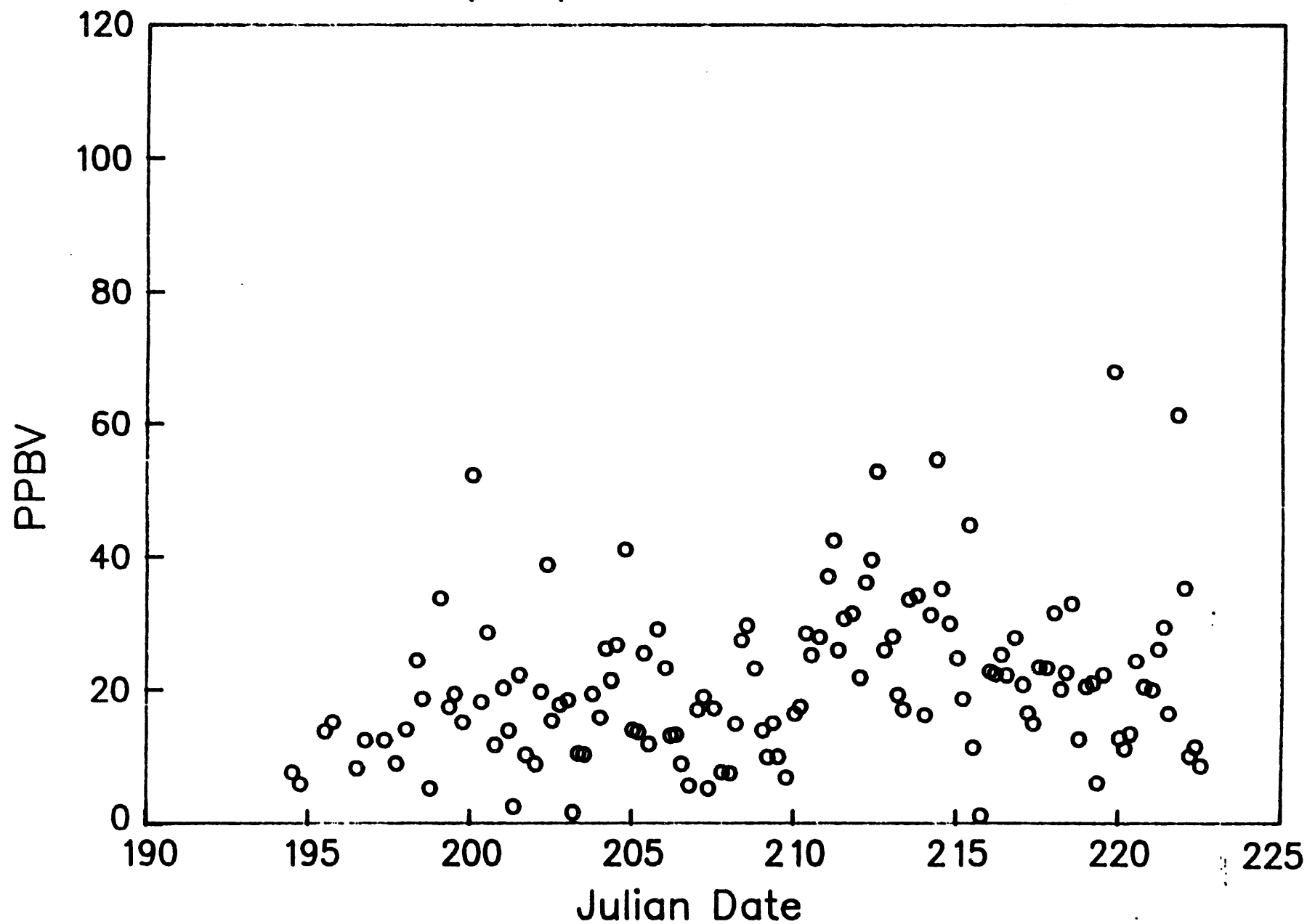
FIGURE 19.

ALDEHYDES
Albuquerque, NM — Winter 1994
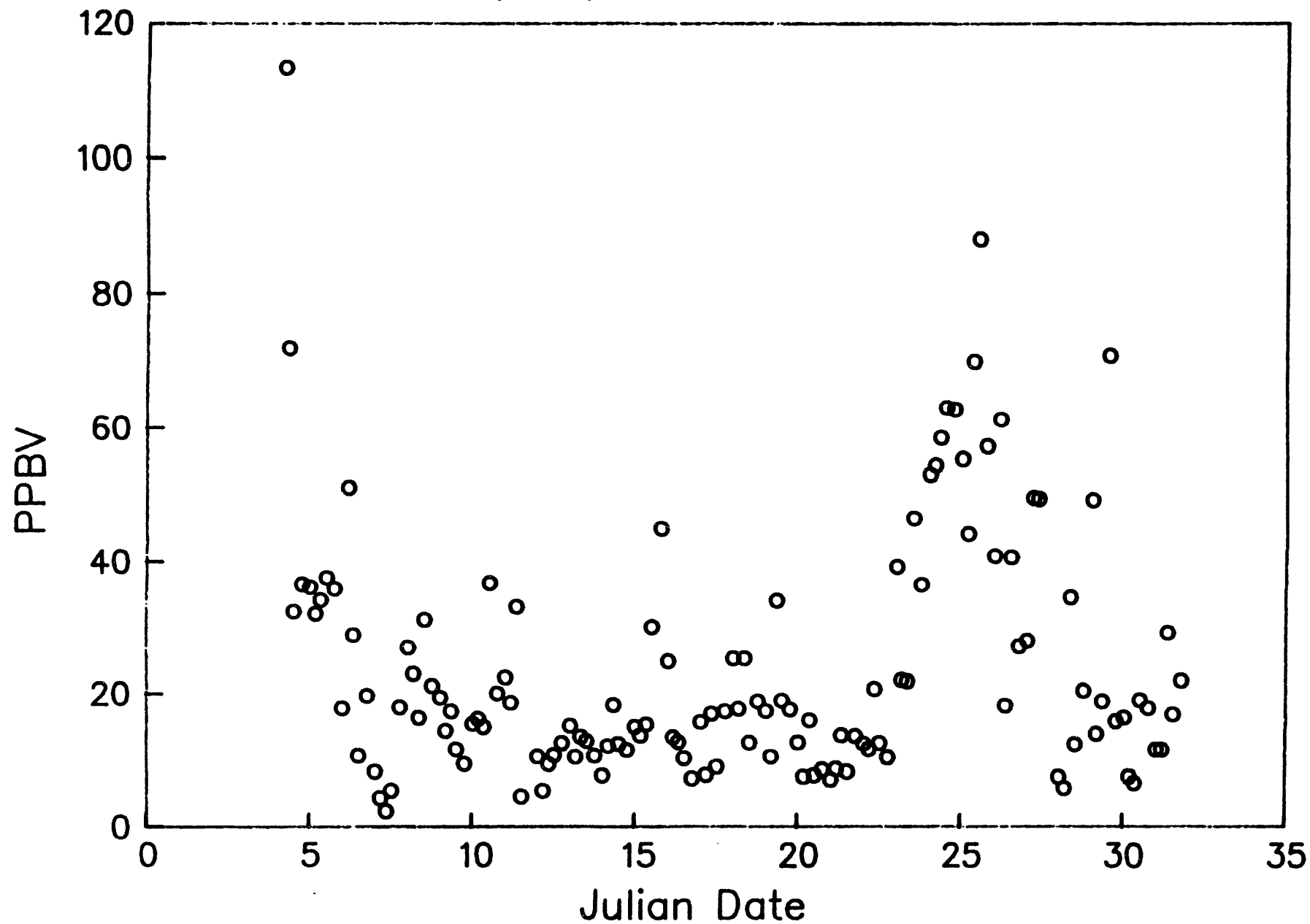
FIGURE 20.

ALDEHYDES
Albuquerque, NM — Summer 1993

Legend: △ Acetaldehyde ○ Formaldehyde

Y-axis: PPBV
X-axis: Julian Date
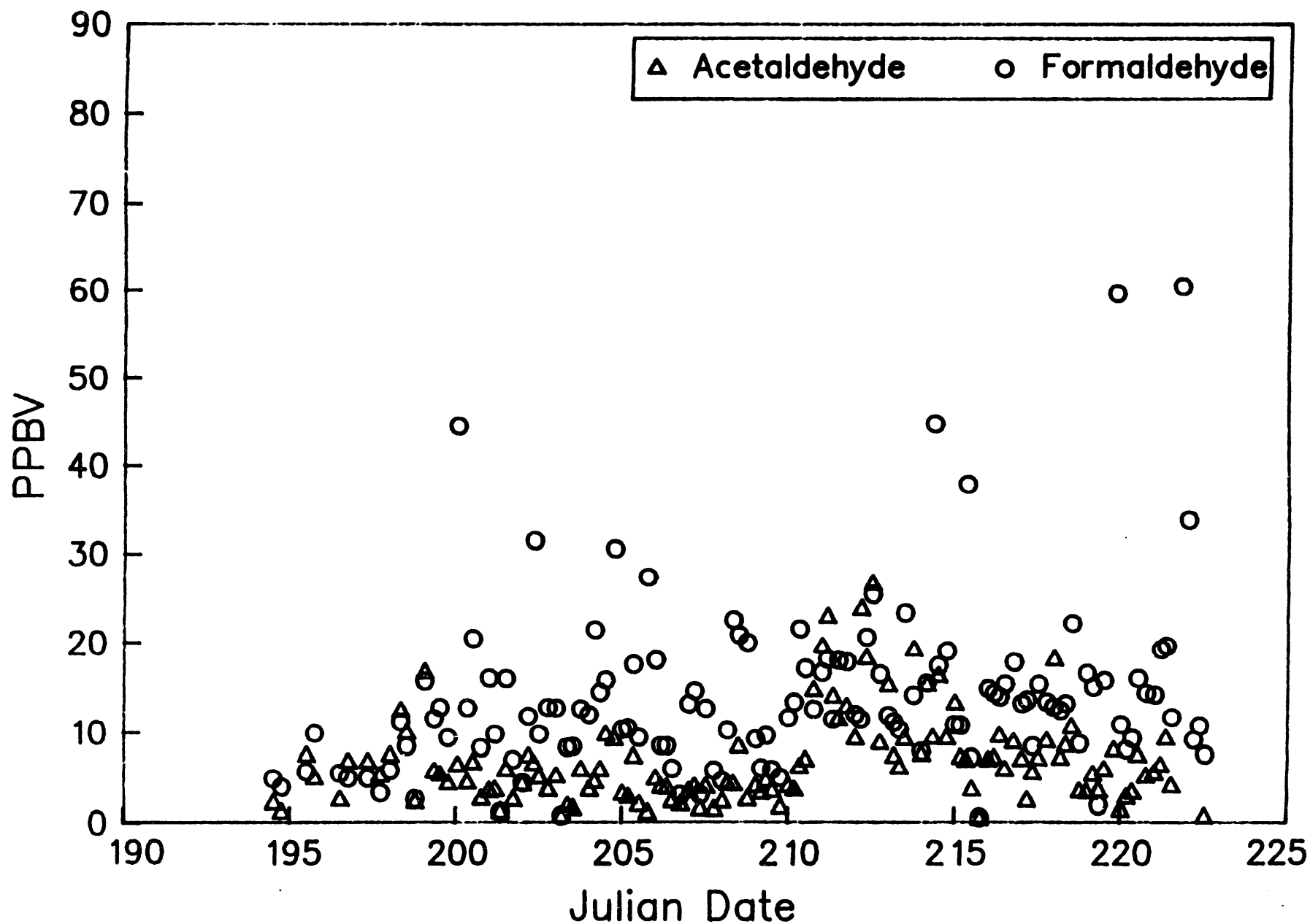
FIGURE 21.

ALDEHYDES
Albuquerque, NM — Winter 1994
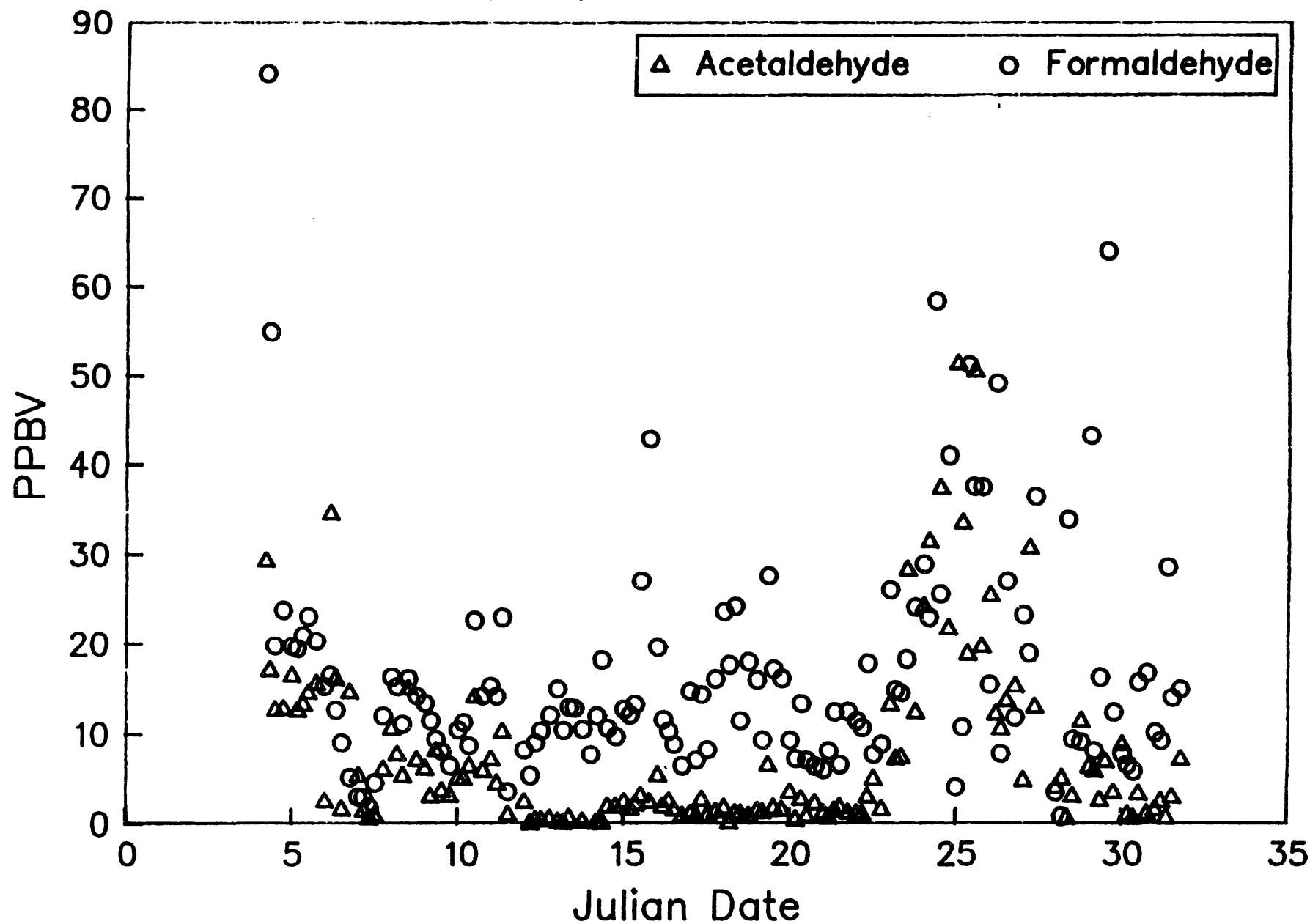
FIGURE 22.

ALDEHYDES
Socorro, NM — Summer 1993
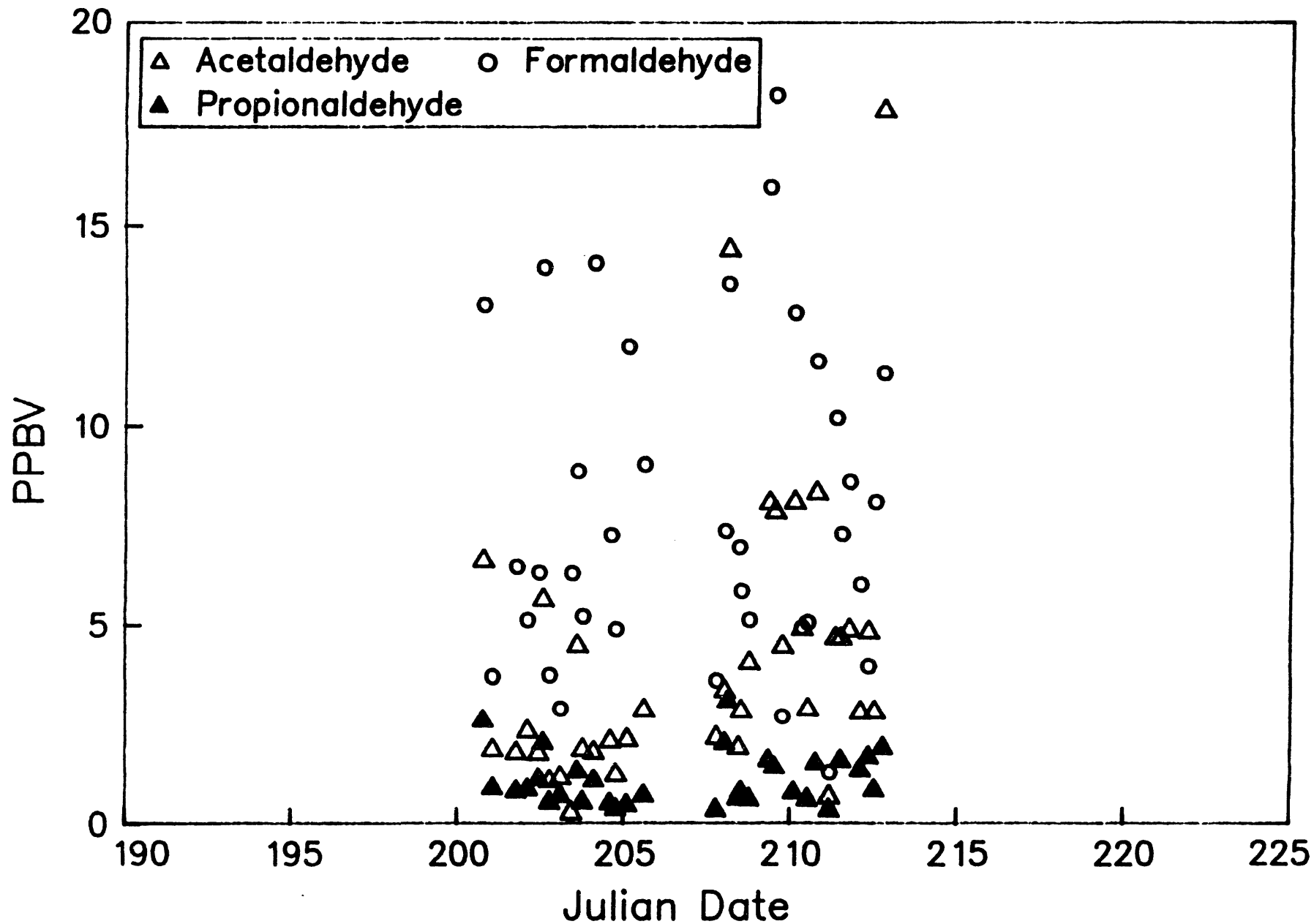
FIGURE 23.

ALDEHYDES
Socorro, NM — Winter 1994

Legend:
- △ Acetaldehyde
- ▲ Propionaldehyde
- ○ Formaldehyde

Y-axis: PPBV (0 to 20)
X-axis: Julian Date (0 to 35)
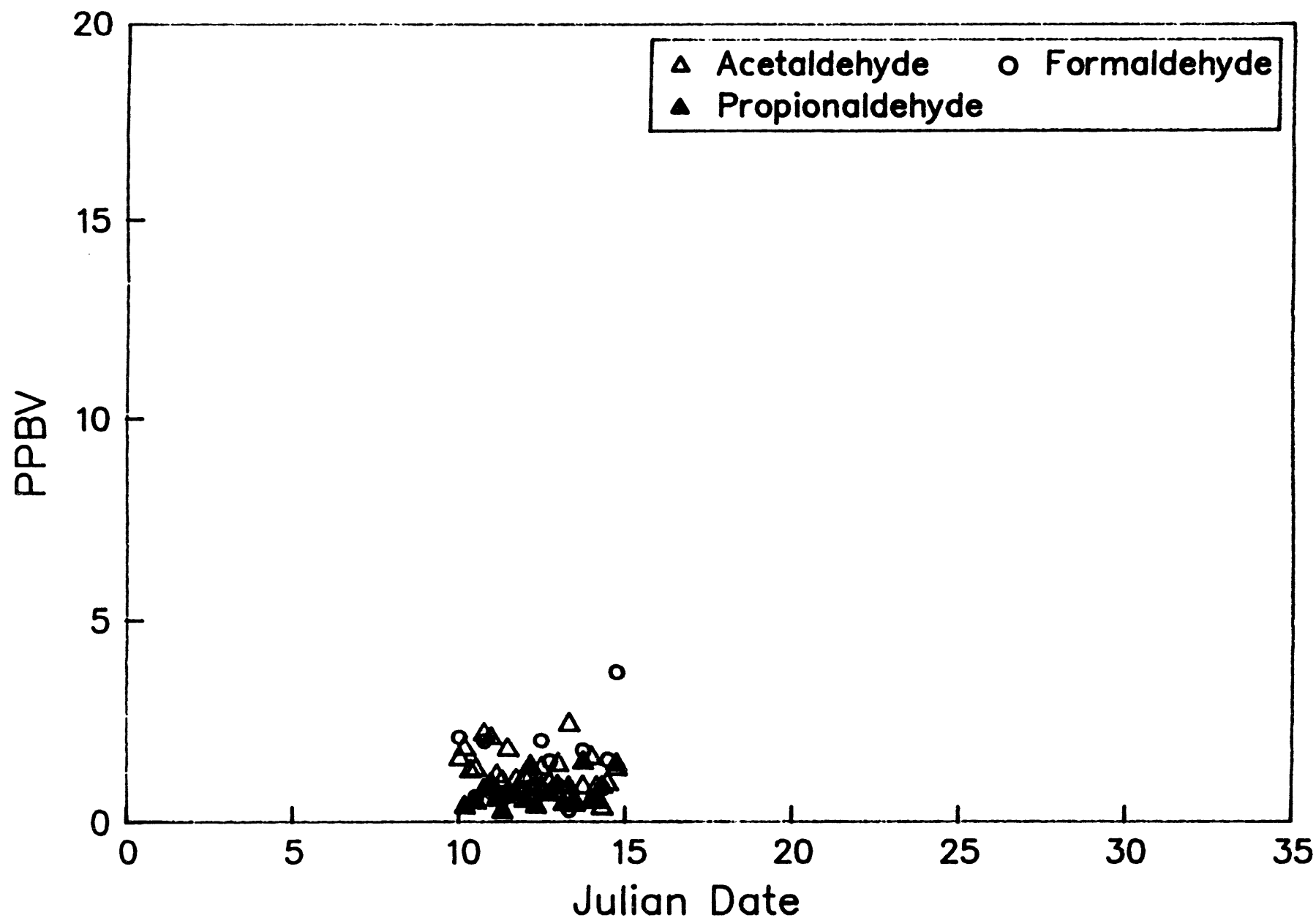
FIGURE 24.

ORGANIC ACIDS
Albuquerque, NM — Summer 1993
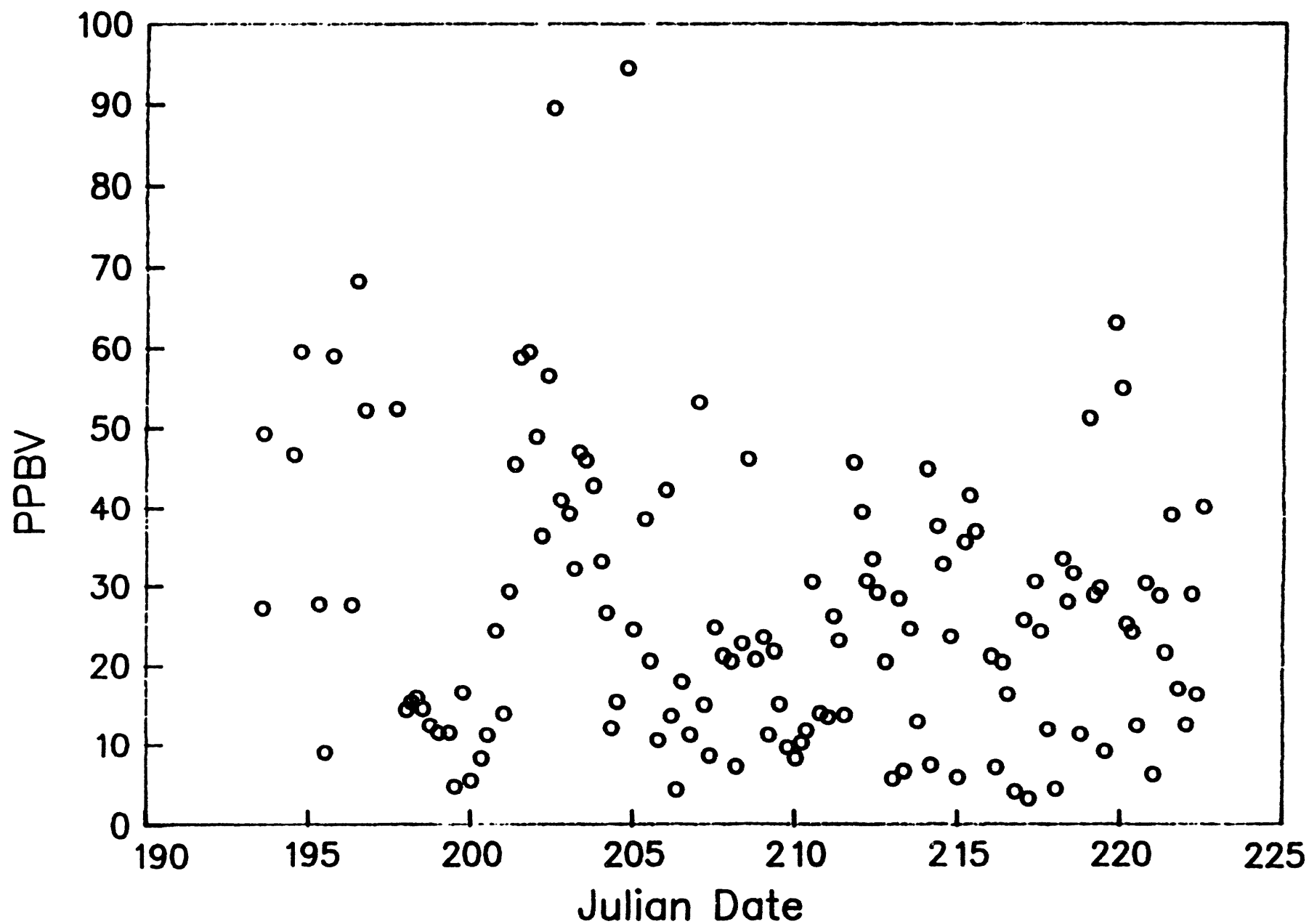
FIGURE 25.

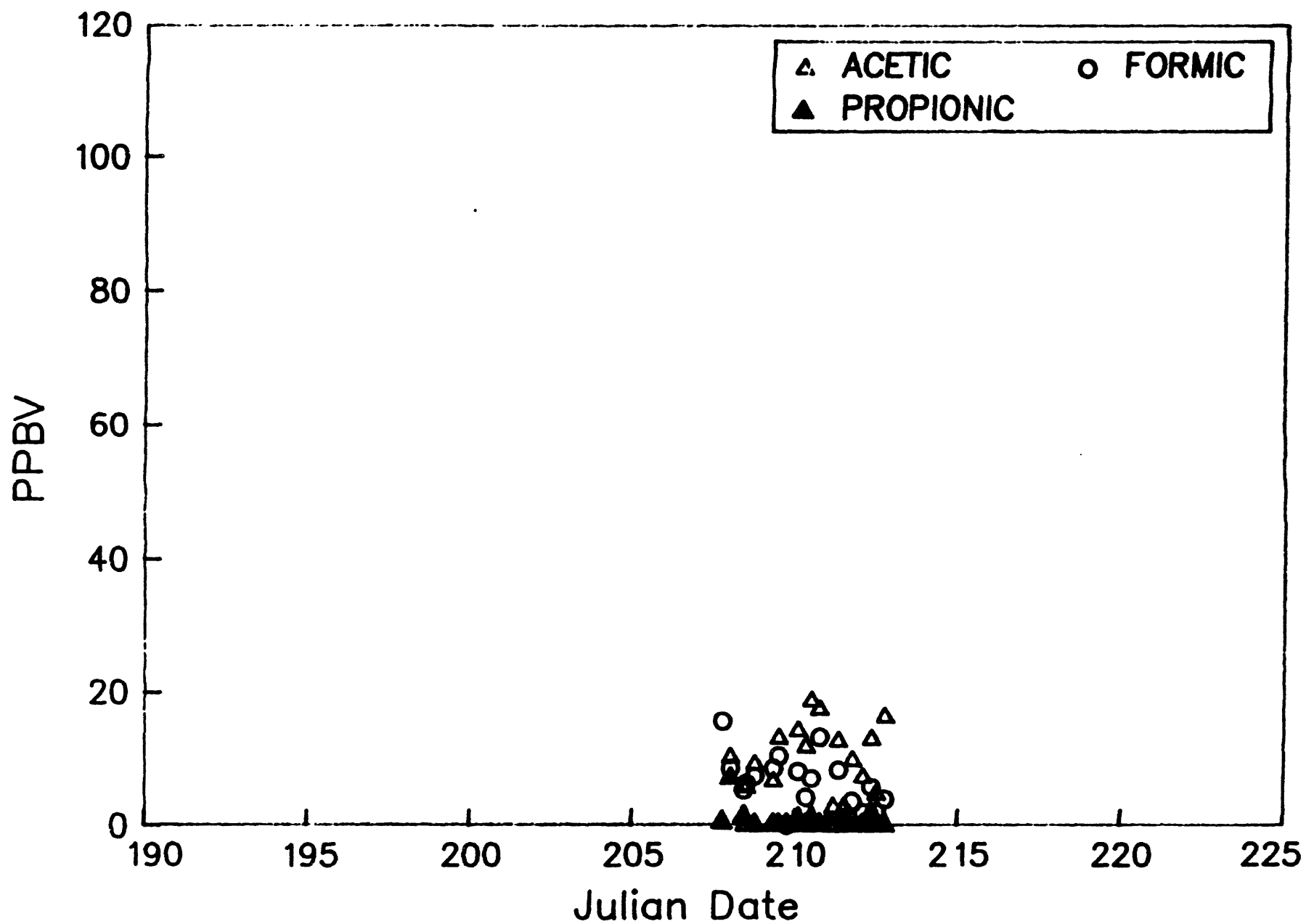ORGANIC ACIDS
Albuquerque, NM — Winter 1994
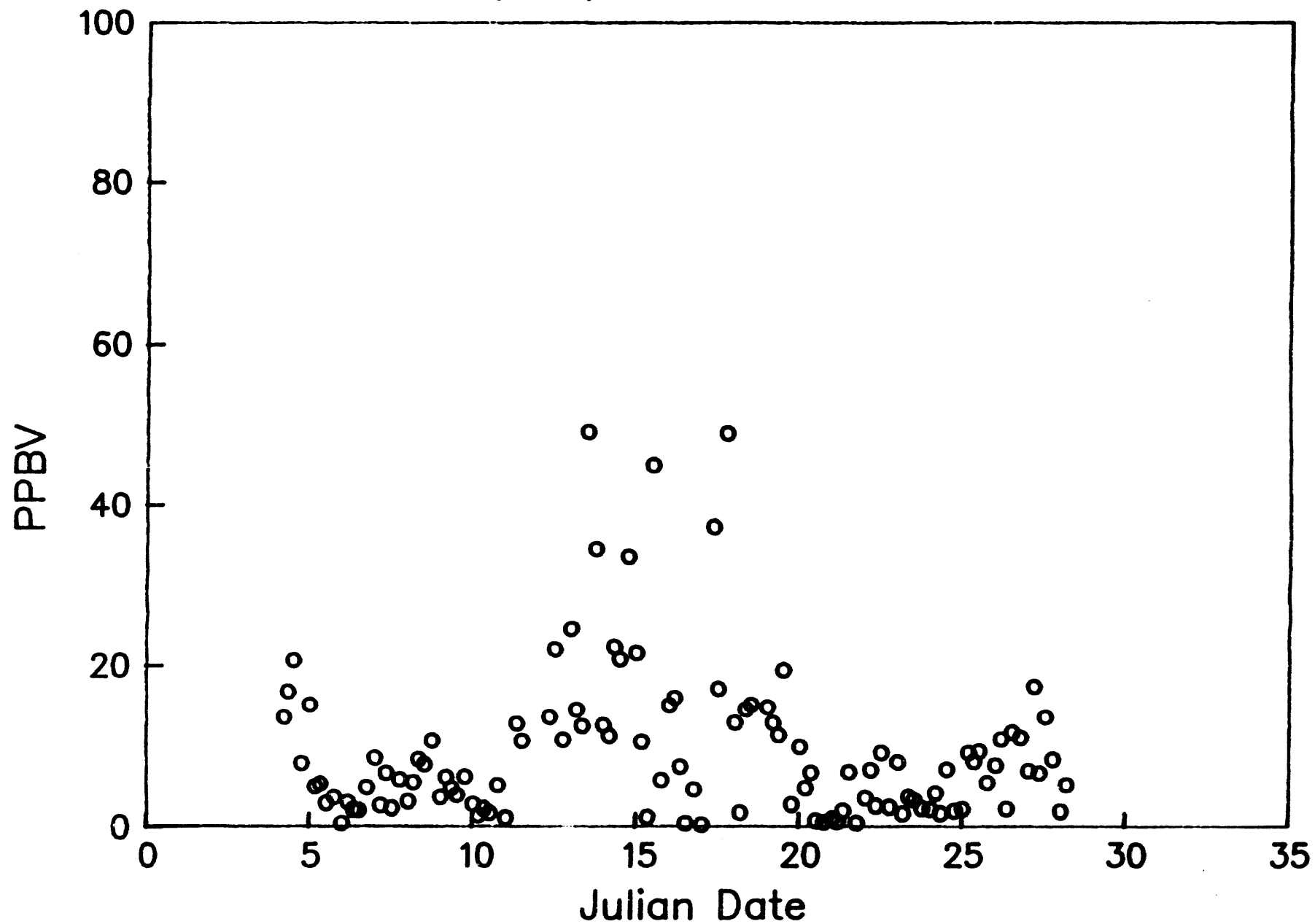
FIGURE 26.

ORGANIC ACIDS
Albuquerque, NM — Summer 1993
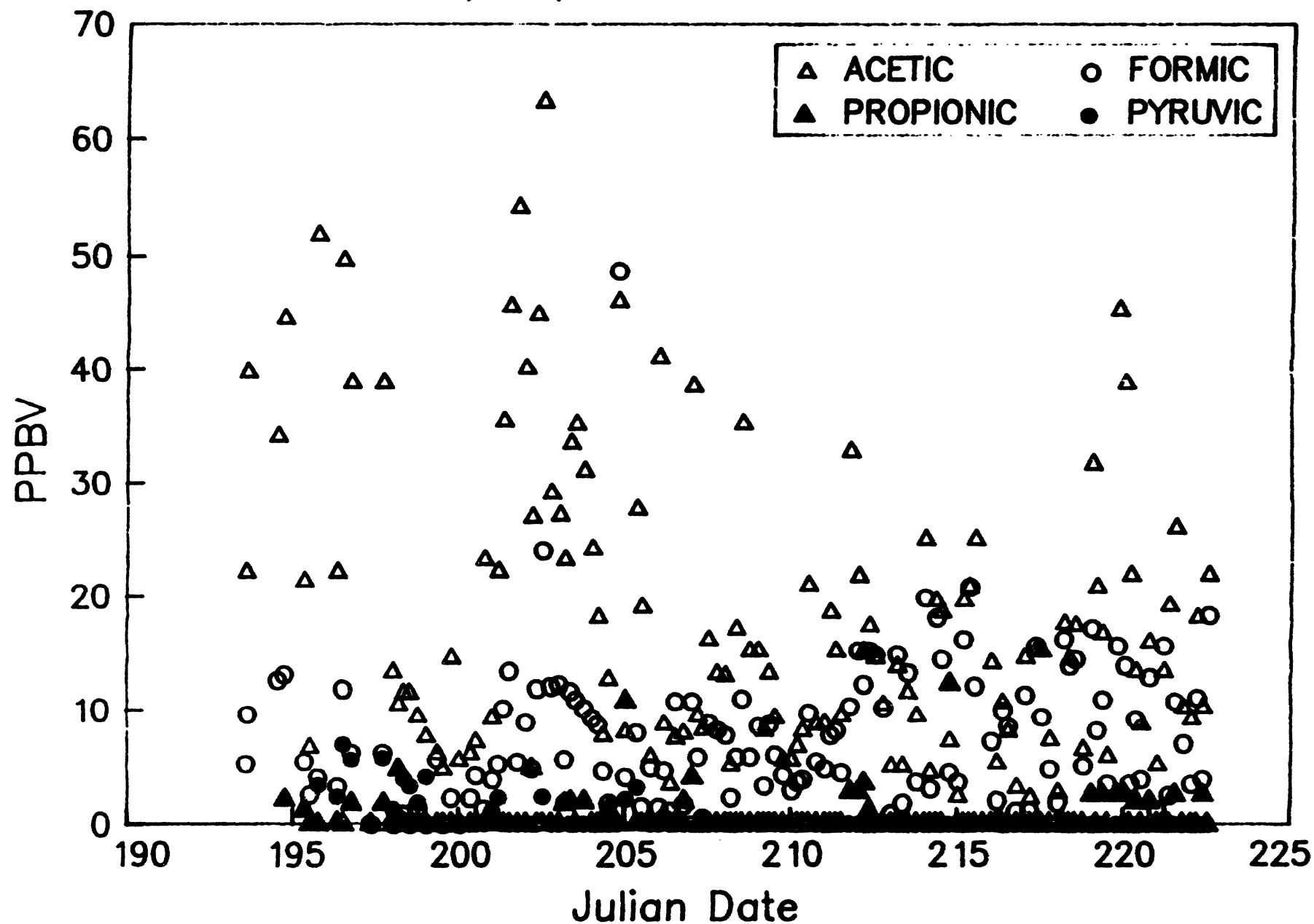
FIGURE 27.

ORGANIC ACIDS
Albuquerque, NM — Winter 1994
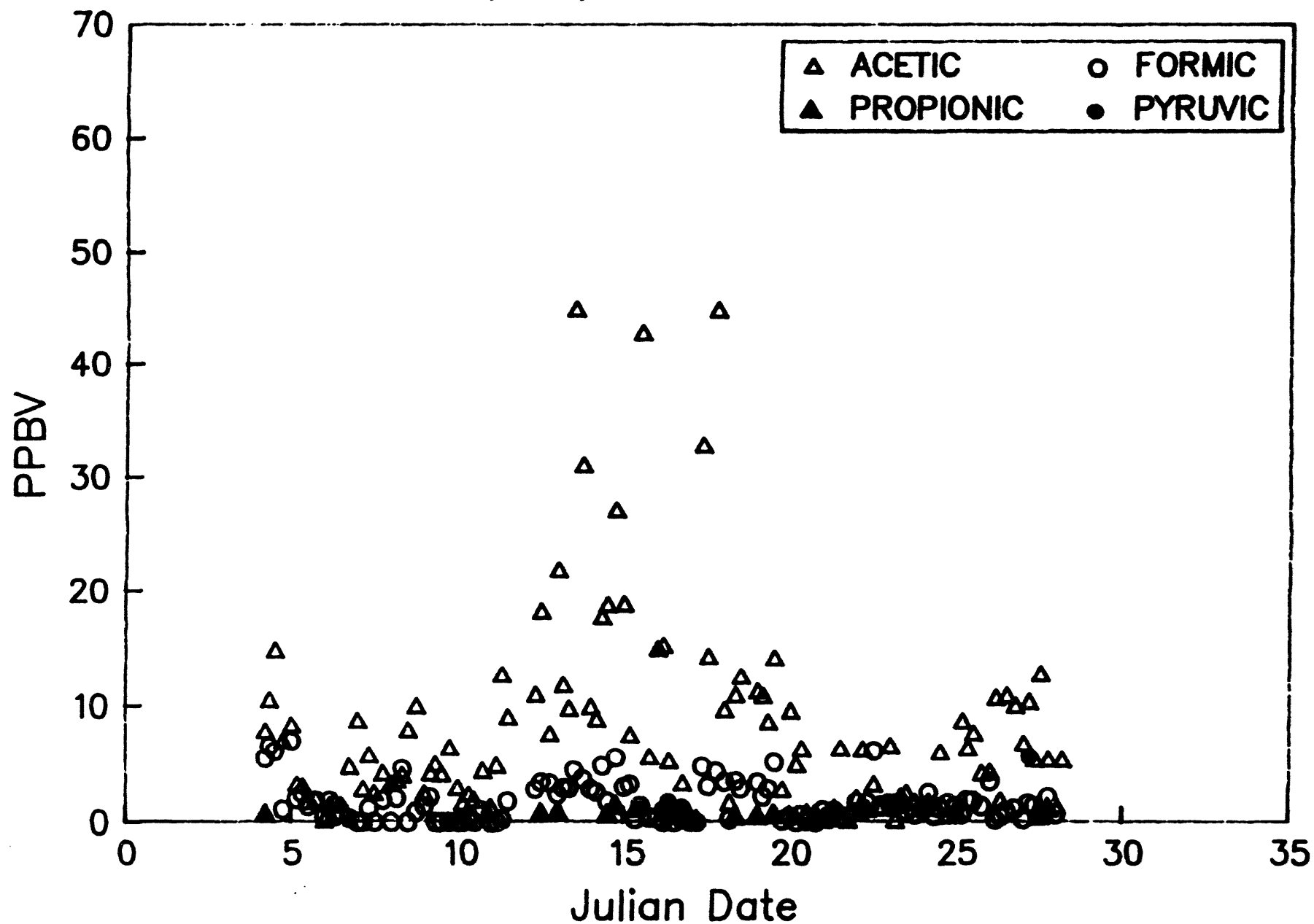
FIGURE 28.

ACIDS
Socorro, NM — Summer 1993

FIGURE 29.

ACIDS
Socorro, NM — Winter 1994

Legend:
△ ACETIC   ○ FORMIC
▲ PROPIONIC

Y-axis: PPBV (0, 20, 40, 60, 80, 100, 120)
X-axis: Julian Date (0, 5, 10, 15, 20, 25, 30, 35)
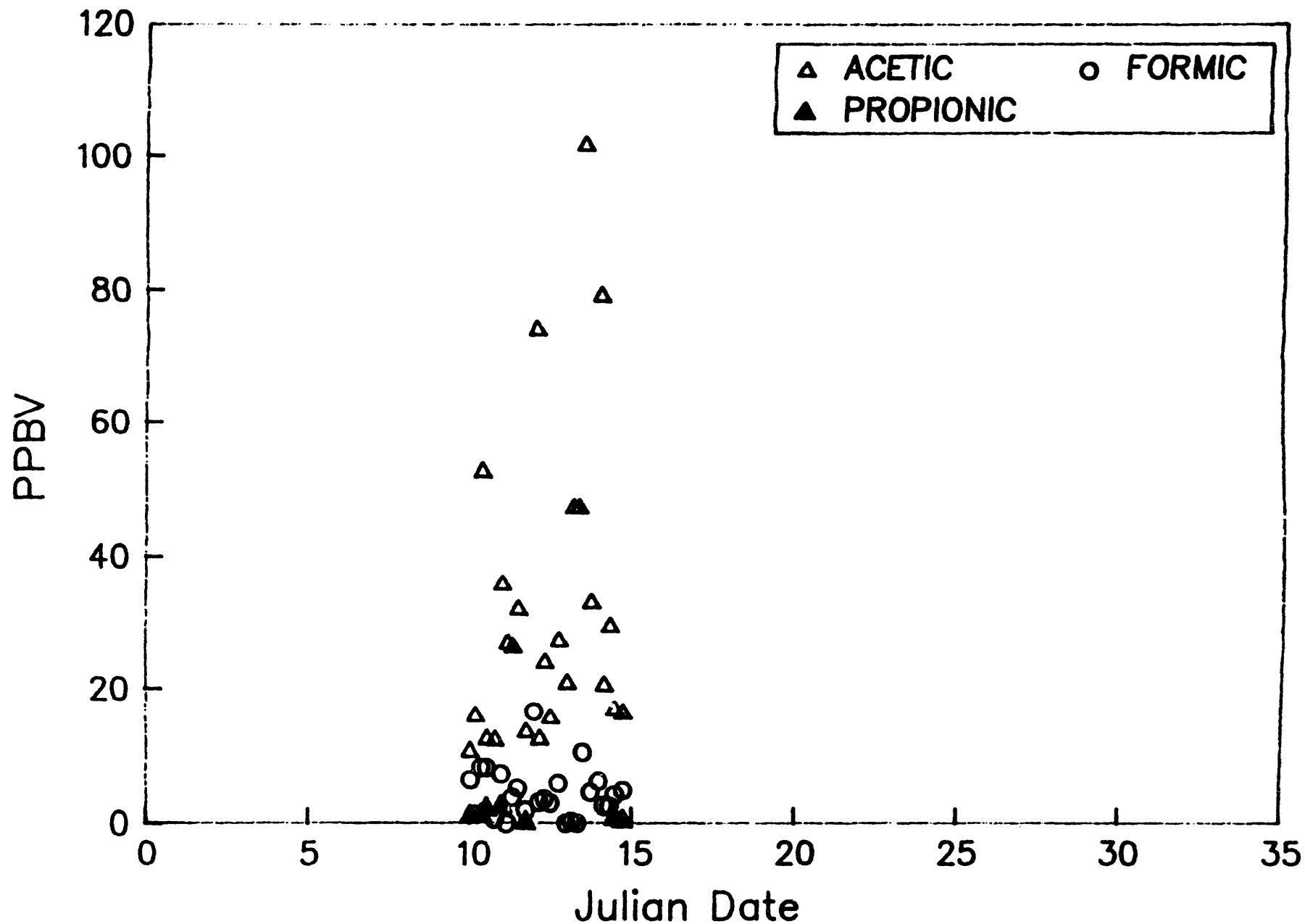
FIGURE 30.

ACETONE
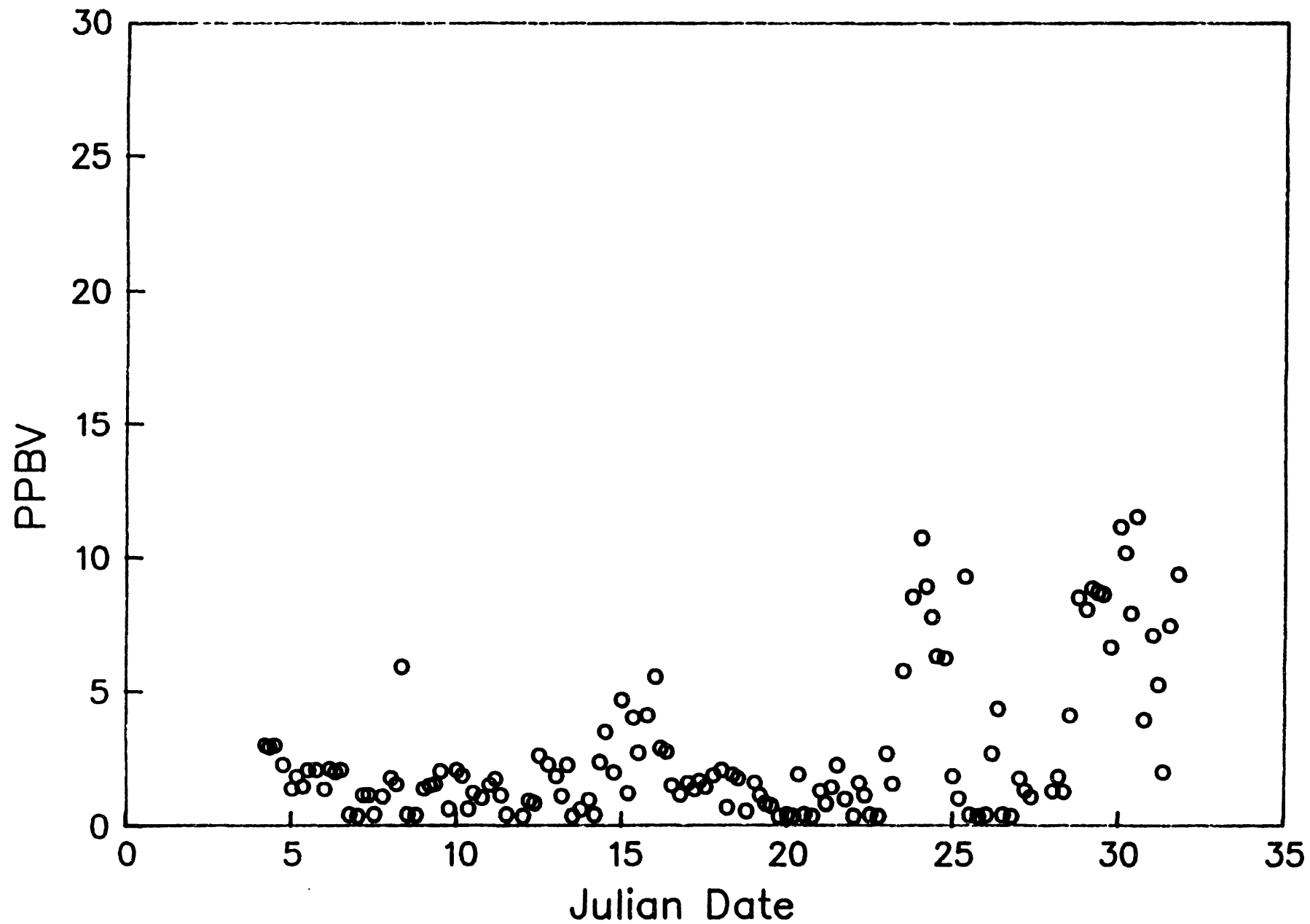Albuquerque, NM — Summer 1993
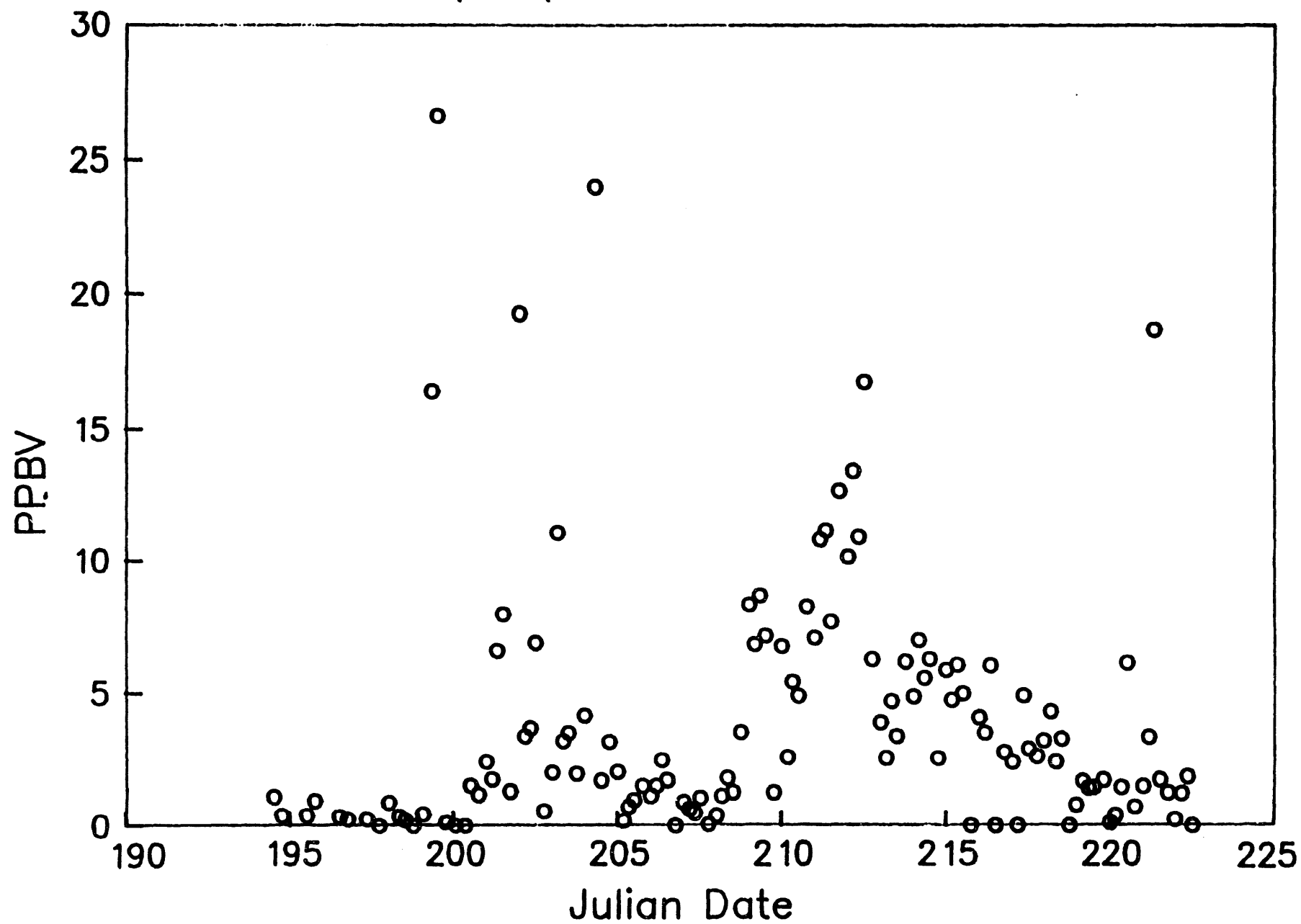
FIGURE 31.

ACETONE
Albuquerque, NM — Winter 1994
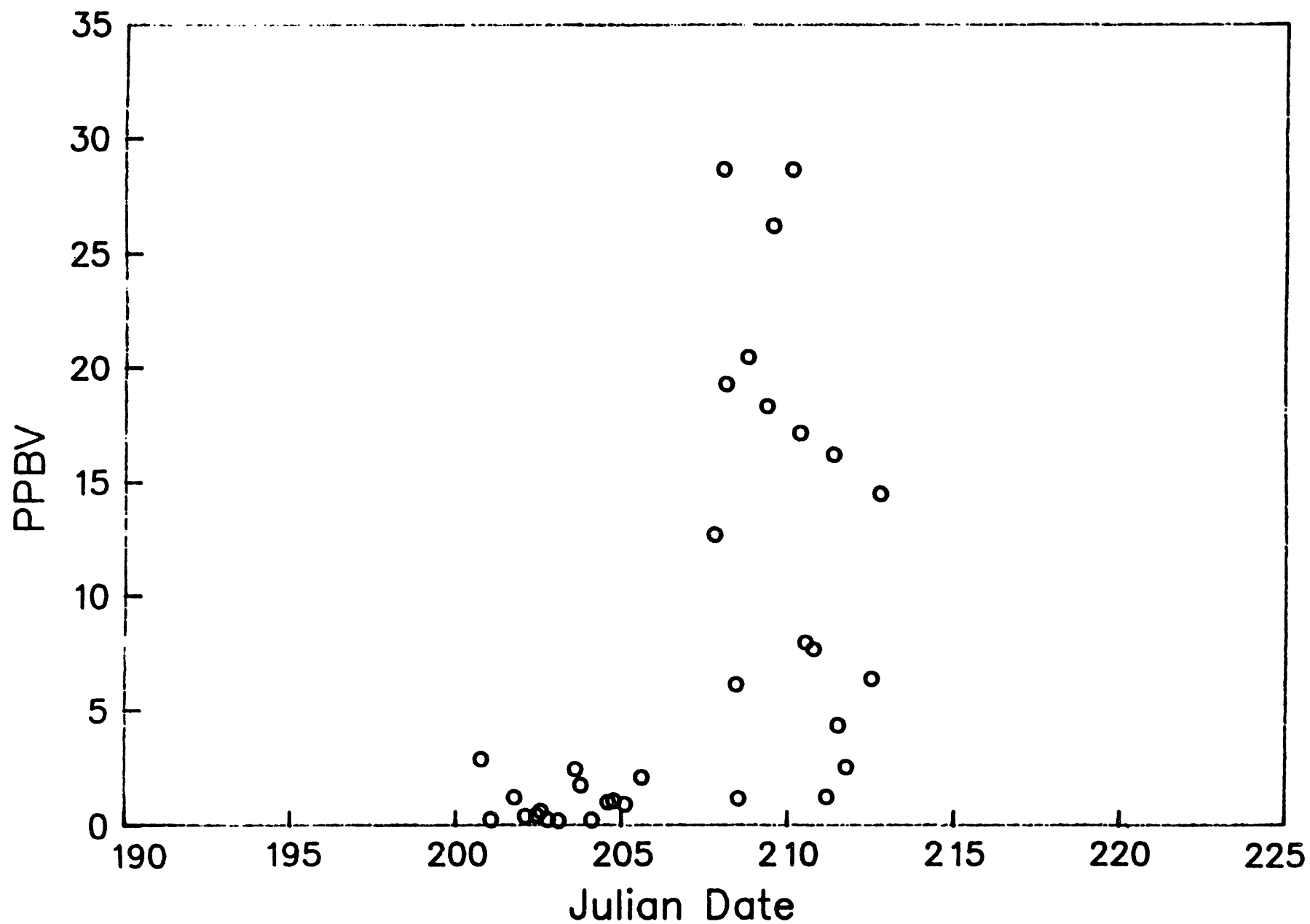
FIGURE 32.

ACETONE
Socorro, NM — Summer 1993

FIGURE 33.
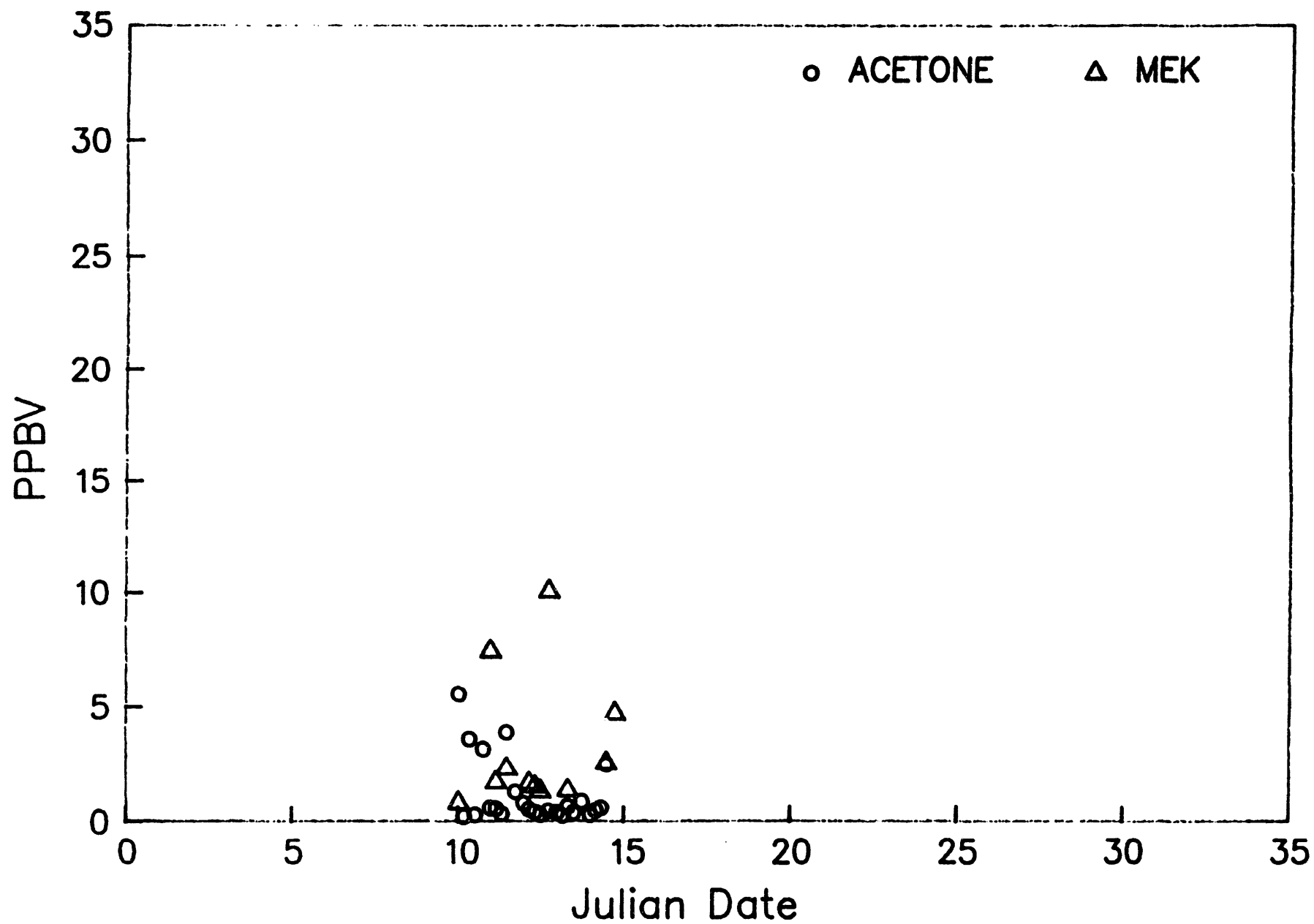
ACETONE
Socorro, NM — Winter 1994

FIGURE 34.

ACETALDEHYDE FREQUENCY DISTRIBUTION
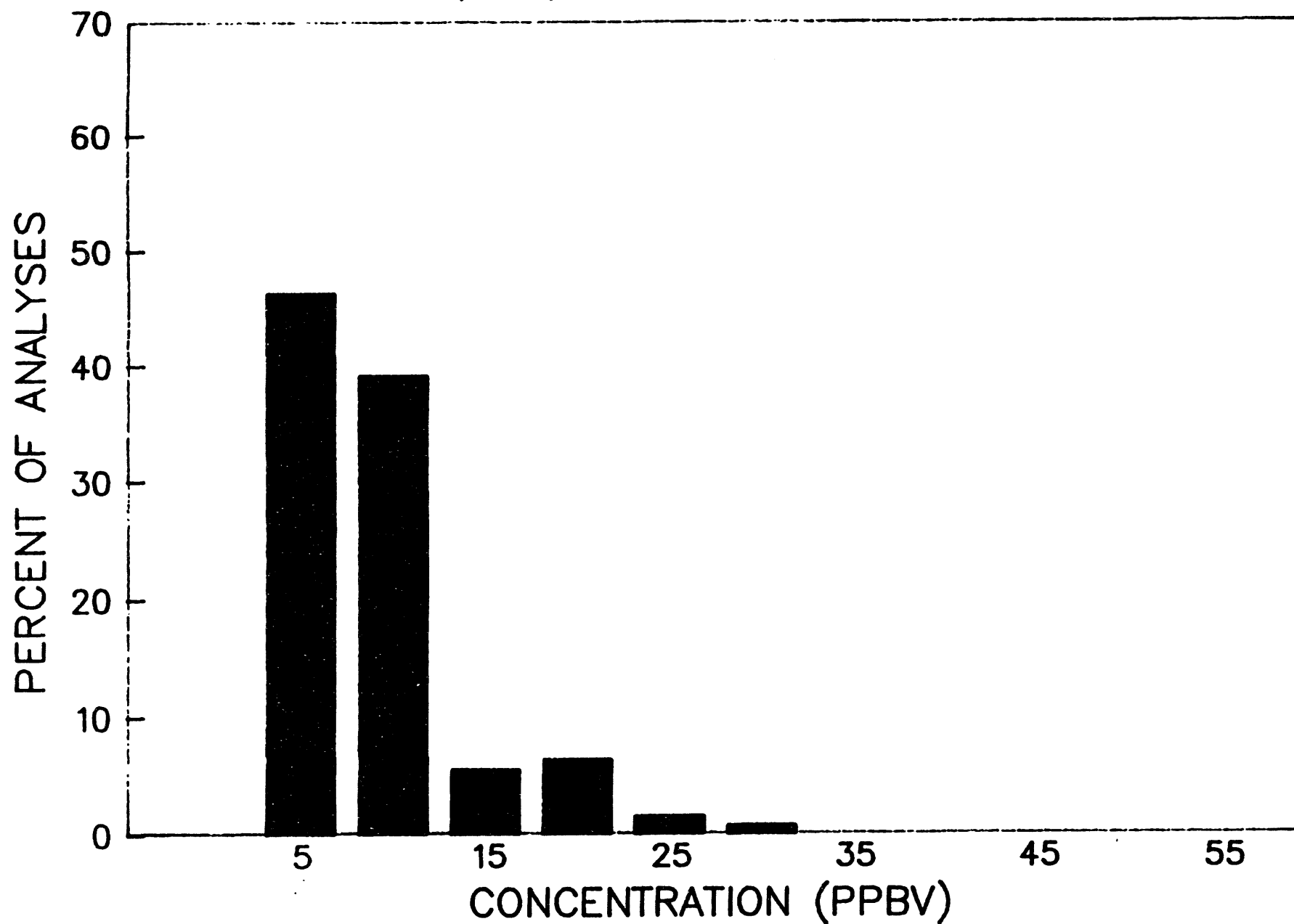## Albuquerque, NM — Summer 1993

FIGURE 35.

ACETALDEHYDE FREQUENCY DISTRIBUTION
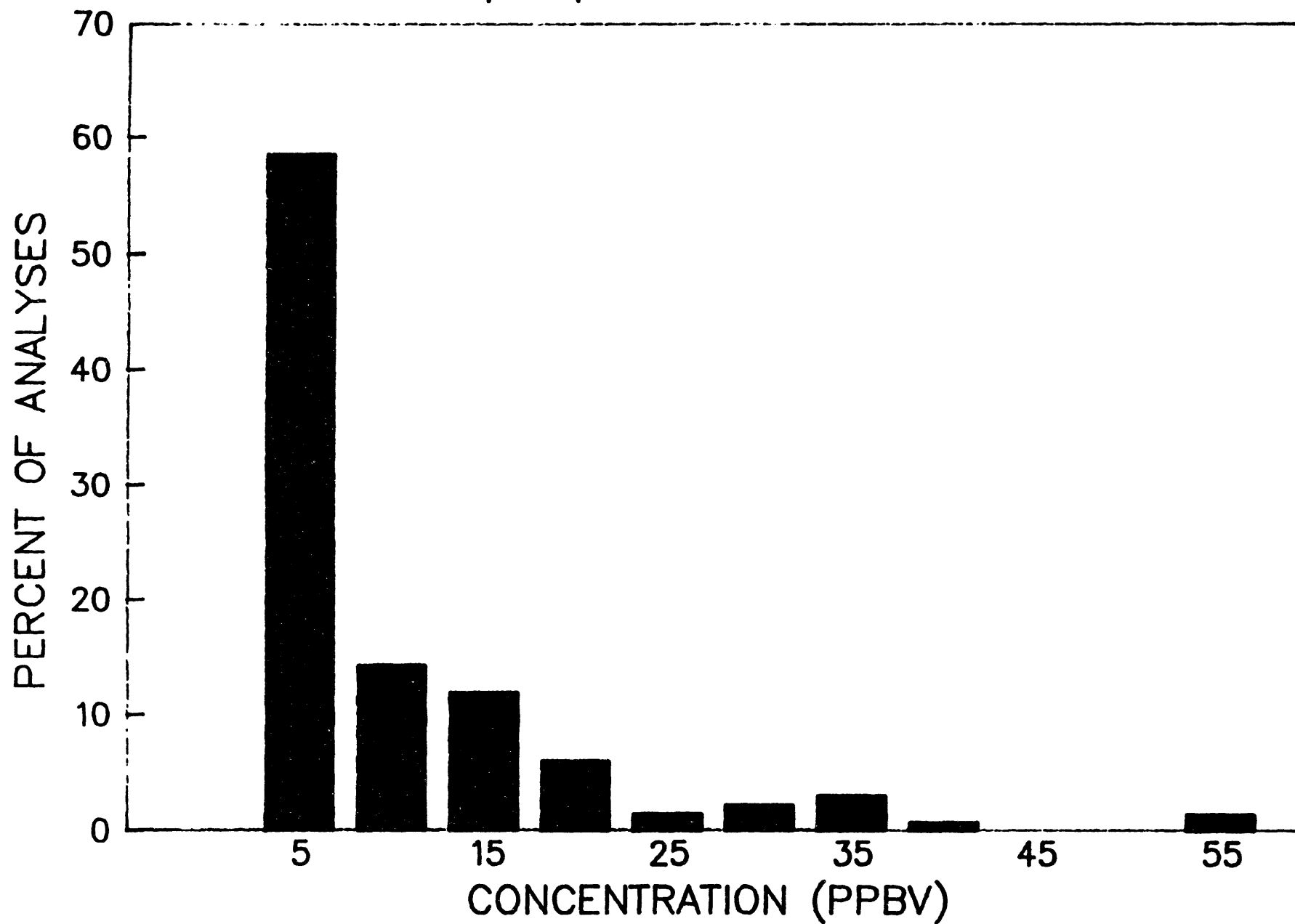Albuquerque, NM — Winter 1994

FIGURE 36.

OZONE FREQUENCY DISTRIBUTION
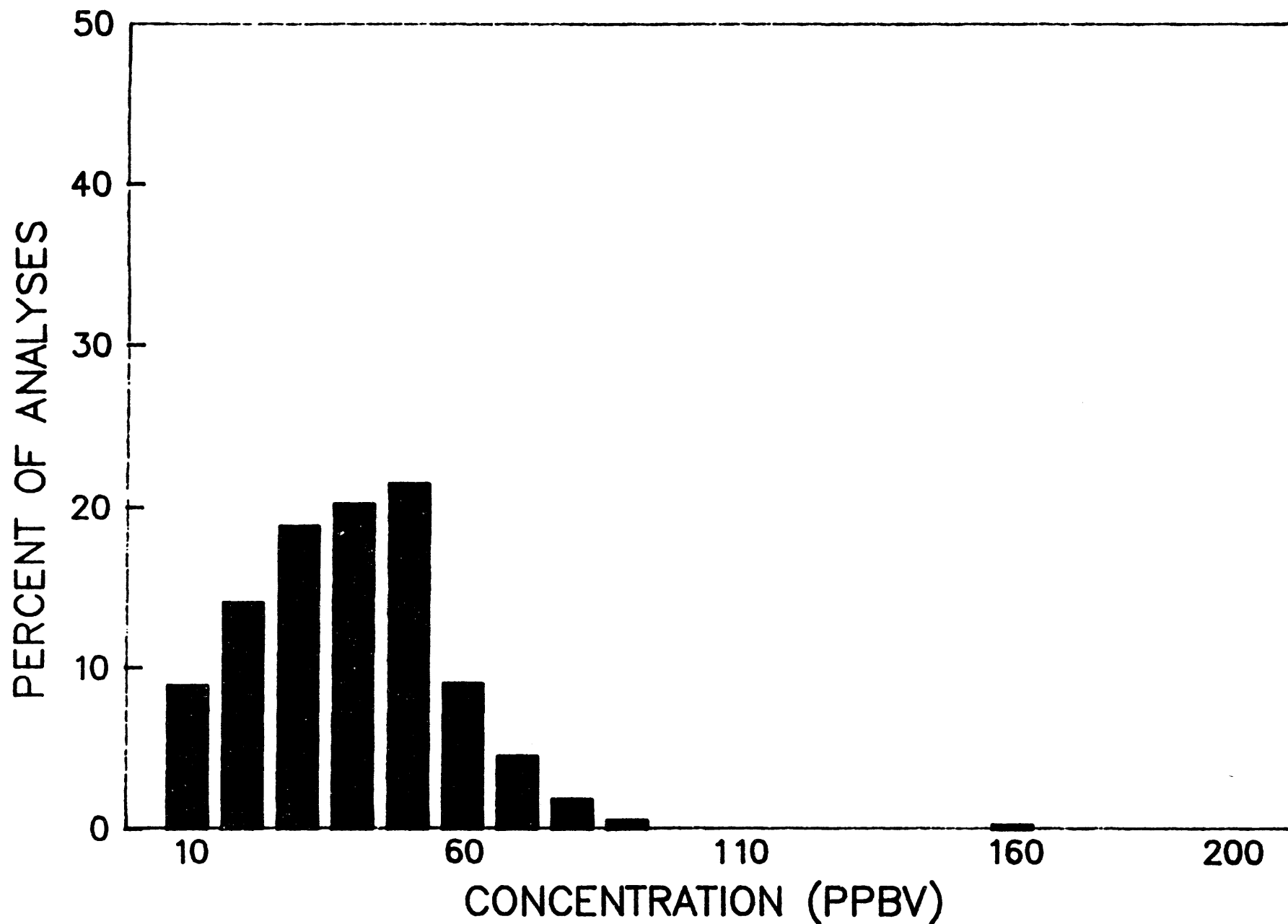Albuquerque, NM — Summer 1993

FIGURE 37.

OZONE FREQUENCY DISTRIBUTION
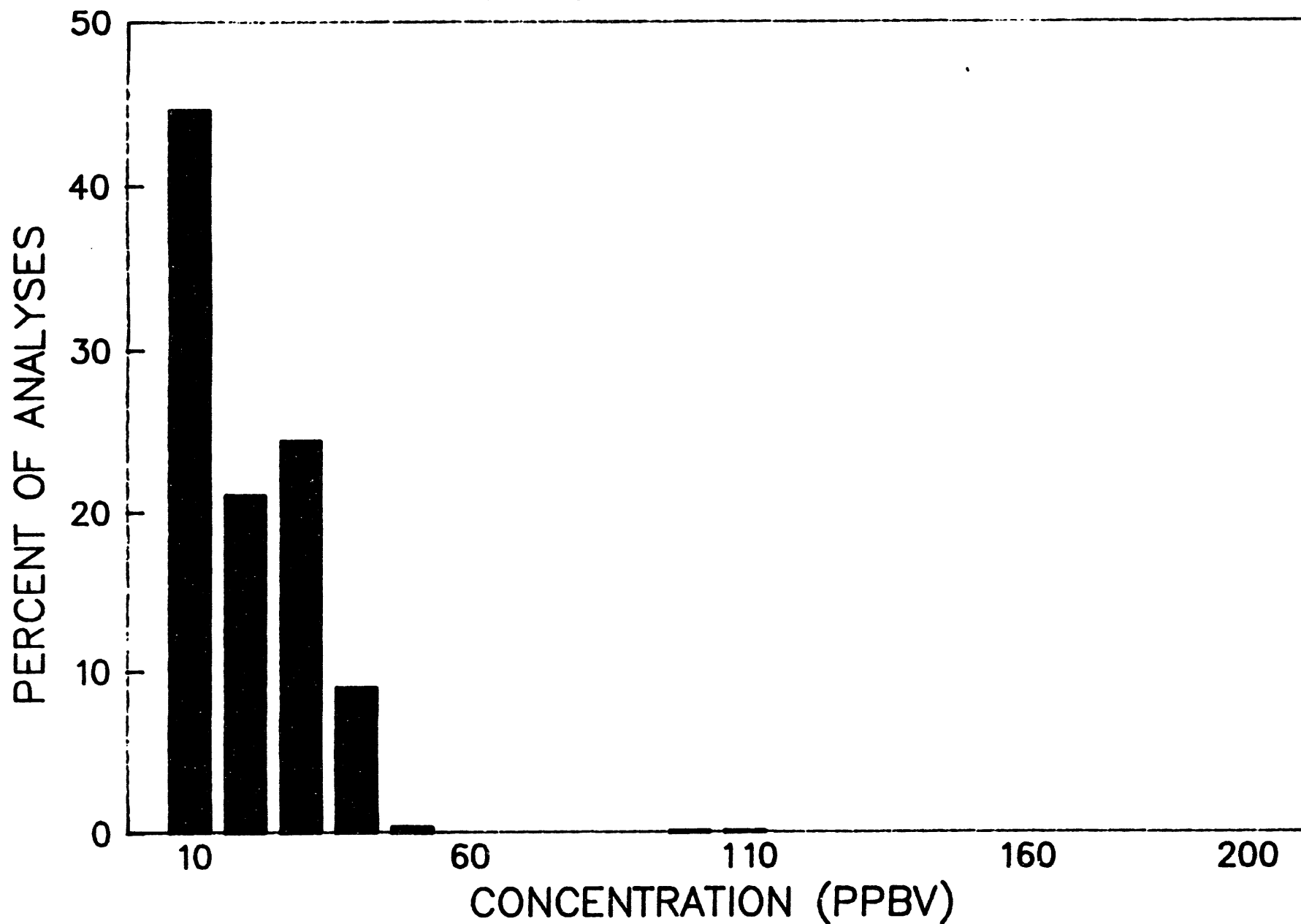Albuquerque, NM — Winter 1994

FIGURE 38.

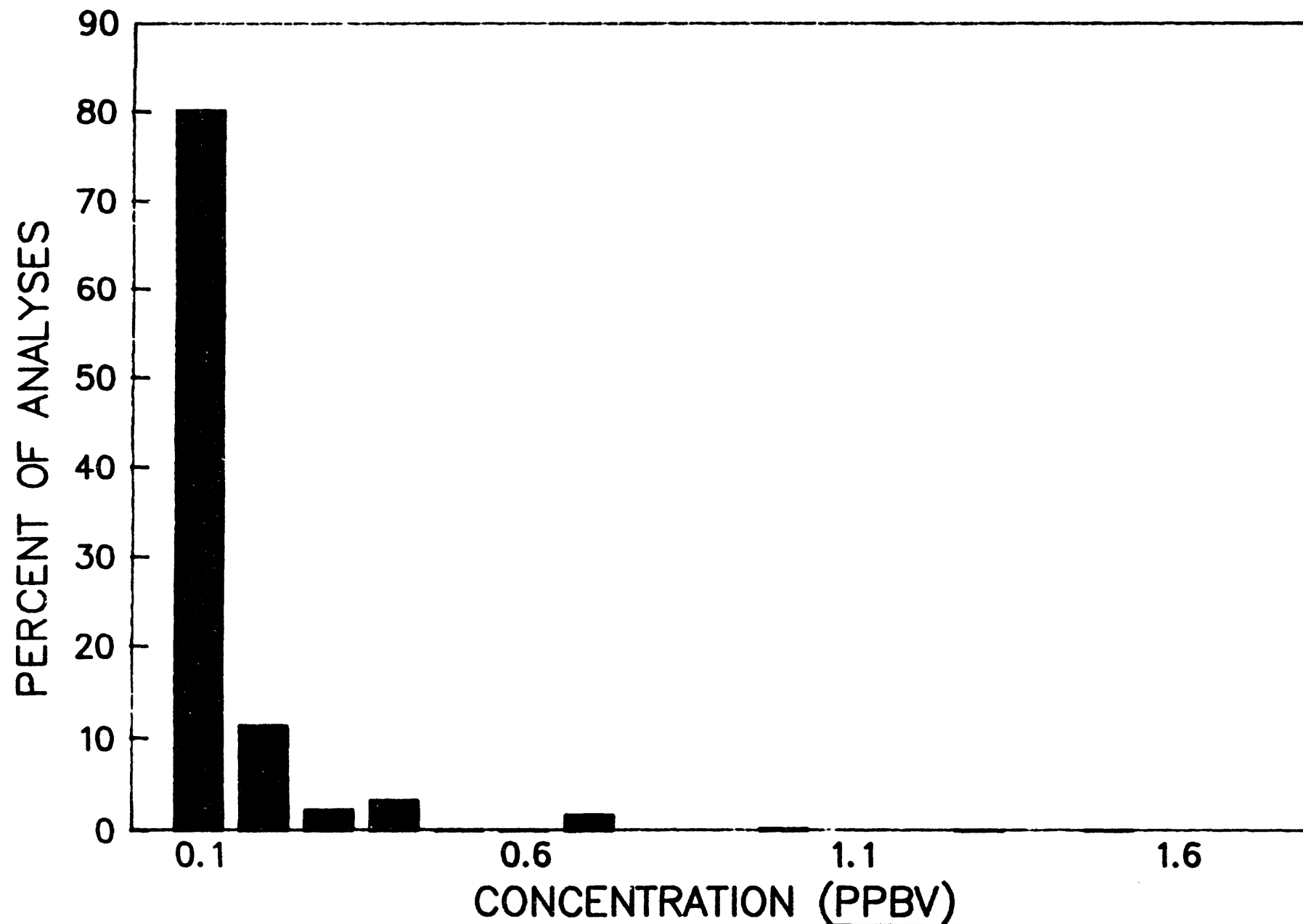PAN FREQUENCY DISTRIBUTION
Albuquerque, NM — Summer 1993

FIGURE 39.   PAN FREQUENCY DISTRIBUTION
Albuquerque, NM — Winter 1994
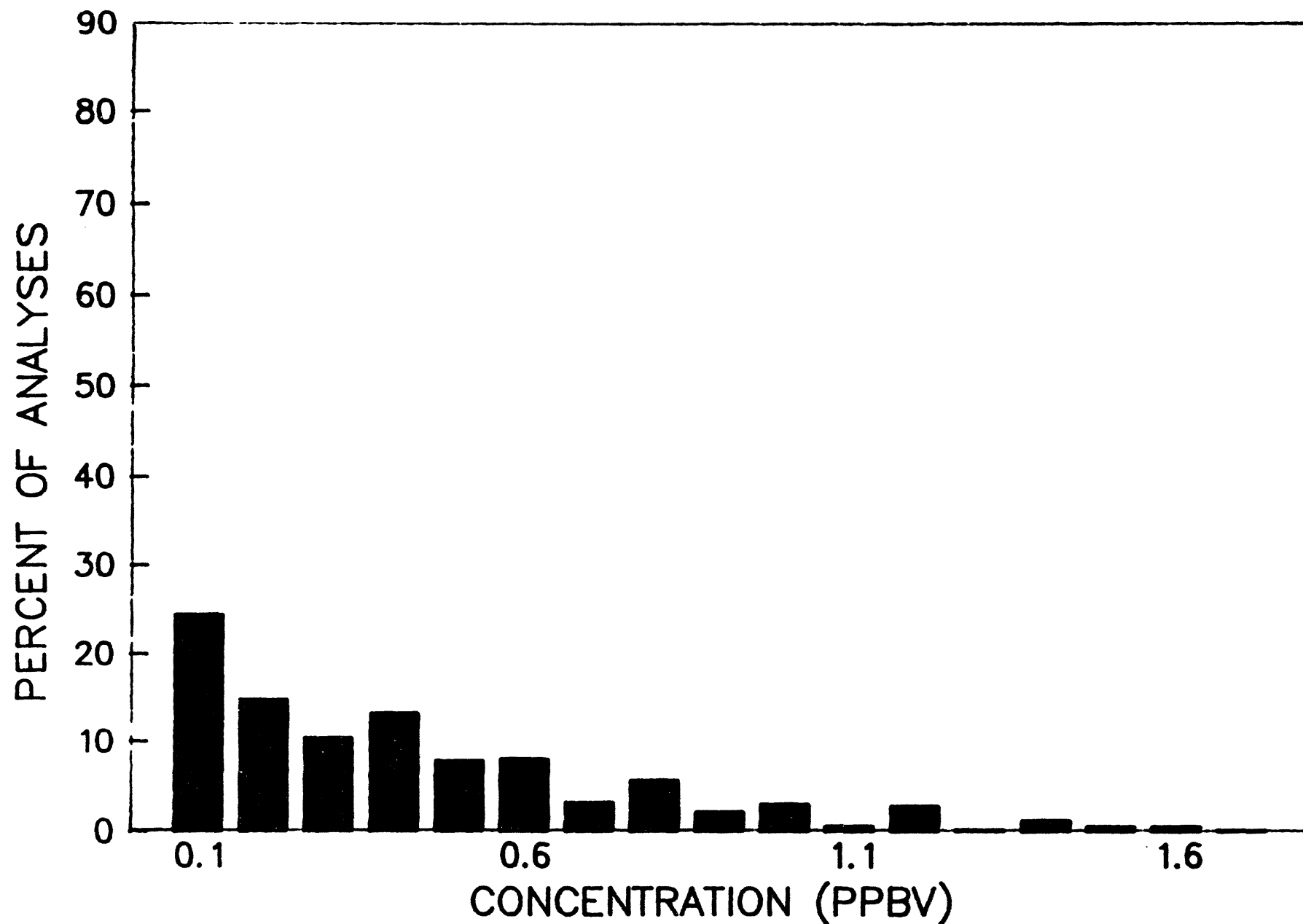
FIGURE 40.

DAYTIME TEMPERATURE FREQUENCY DISTRIBUTION
Albuquerque, NM — Summer 1993
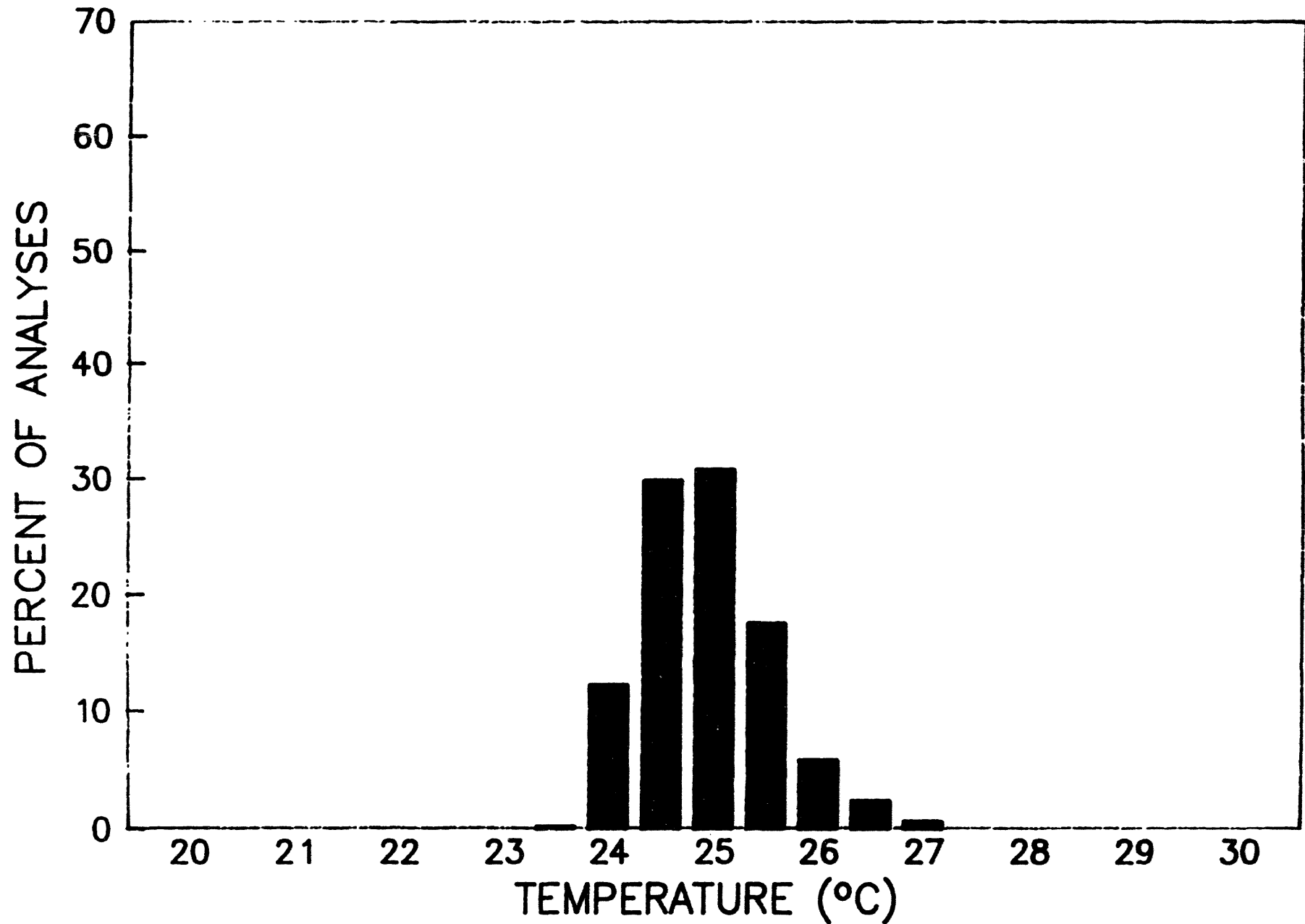
FIGURE 41.

DAYTIME TEMPERATURE FREQUENCY DISTRIBUTION
Albuquerque, NM — Winter 1994
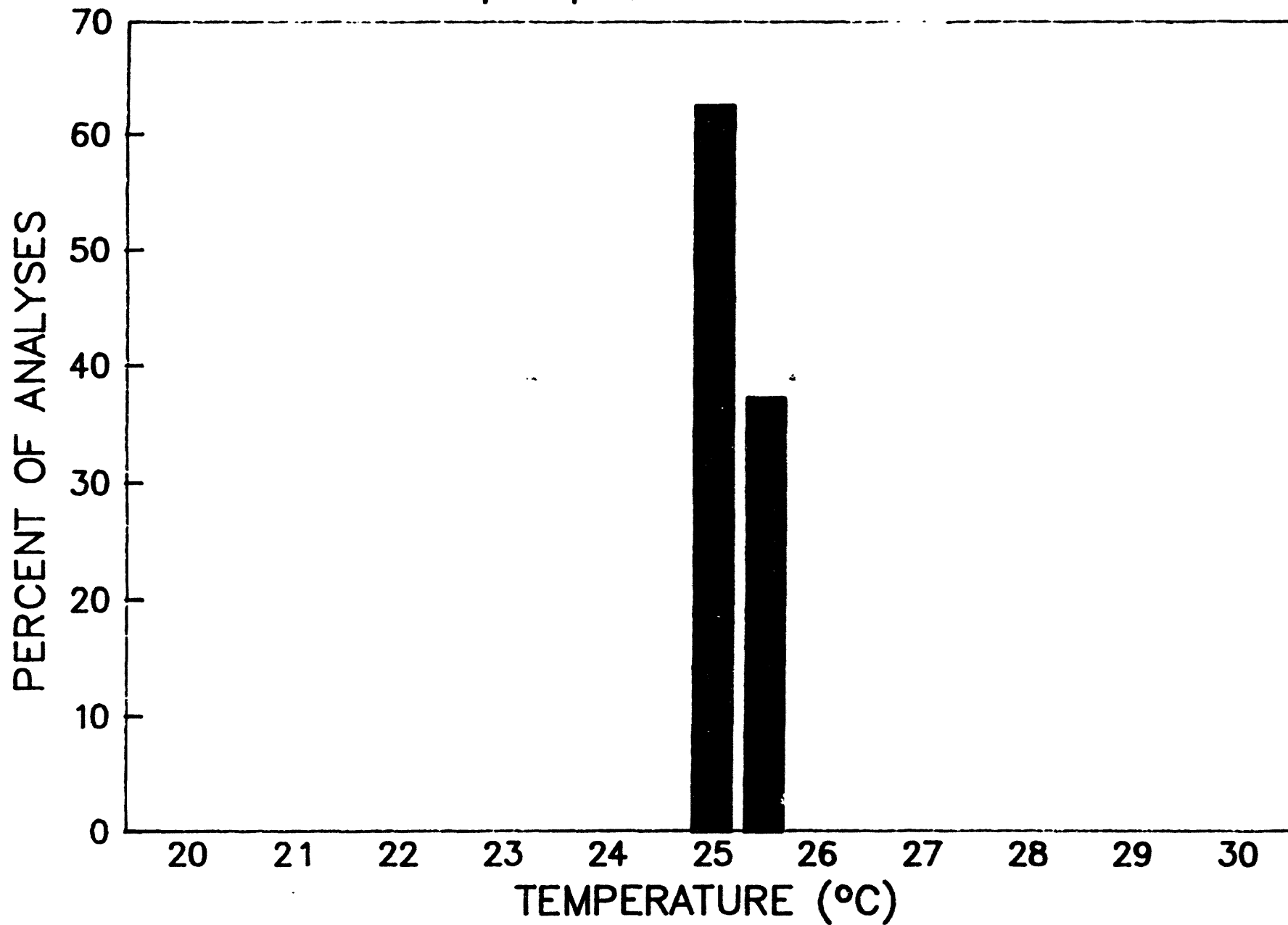
FIGURE 42.

RELATIVE CARBON ISOTOPIC RATIOS COMPARED TO PDB LIMESTONE.
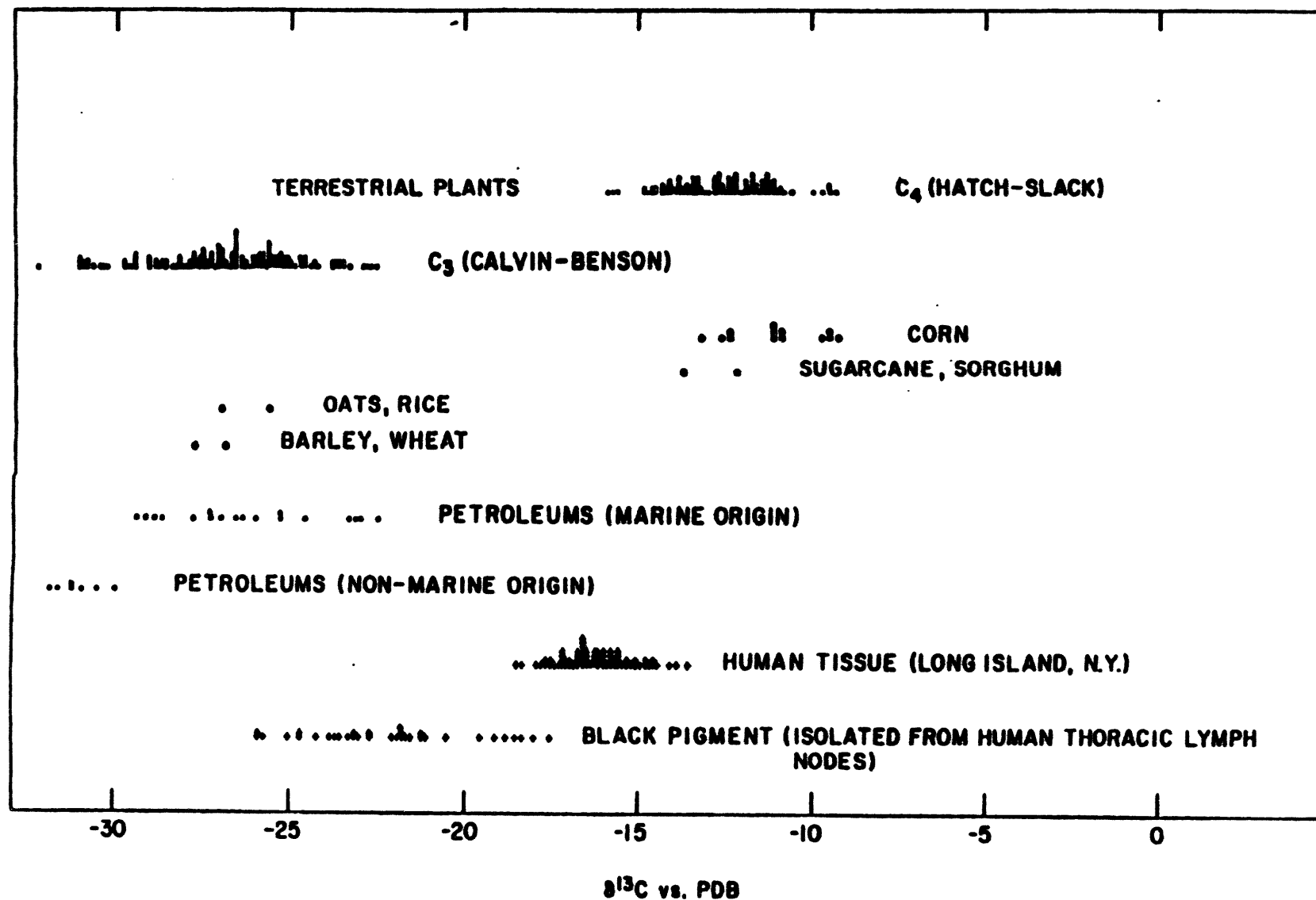
TERRESTRIAL PLANTS C_4 (HATCH-SLACK)

C_3 (CALVIN-BENSON)

CORN

SUGARCANE, SORGHUM

OATS, RICE

BARLEY, WHEAT

PETROLEUMS (MARINE ORIGIN)

PETROLEUMS (NON-MARINE ORIGIN)

HUMAN TISSUE (LONG ISLAND, N.Y.)

BLACK PIGMENT (ISOLATED FROM HUMAN THORACIC LYMPH NODES)

-30   -25   -20   -15   -10   -5   0

$\delta^{13}C$ vs. PDB

Potential Impacts on Air Quality of the Use of Ethanol as an Alternative Fuel
DAC-3-13252-01

Reporting Period: June, 1994
ANL Activity # 85858

Date: 7/18/94
Principal Investigator: J. Gaffney
(708) 252-5178

MONTHLY COST DETAIL

	Budget*	Total Cost	4/93	5/93	6/93	7/93	8/93	9/93	10/93	11/93	12/93	1/94	2/94	3/94	4/94	5/94	6/94
Staff Man-months		10.19	0.00	0.72	1.49	1.57	0.19	0.20	0.26	0.38	0.59	0.81	0.87	1.47	1.16	0.48	0.00
Cost:																	
EFFORT RELATED COST	83,060	93,511	0	6678	14110	12464	1823	1189	2487	3676	5547	7698	8240	13986	11059	4554	0
TRAVEL	11,138	3,714	0	0	0	2800	183	0	0	731	0	0	0	0	0	0	0
EDITING/MEDIA SERVICES	2,200	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
BIOMETER	3,495	3,515	0	0	3515	0	0	0	0	0	0	0	0	0	0	0	0
SUBCONTRACT	31,176	31,175	0	0	0	0	0	8082	5840	3500	3000	3000	0	0	10191	3598	-6036
MISC. SUPPLIES & SERV.	4,000	1,314	0	0	254	1034	8	0	0	0	0	0	14	0	4	0	0
G&A	34,931	34,143	0	1989	5324	4854	600	1154	1487	1759	2035	2676	2458	4165	4597	1816	-771
TOTAL	170,000	167,372	0	8,667	23,203	21,152	2,614	10,425	9,814	9,666	10,582	13,374	10,712	18,151	25,851	9,968	-6,807

*Budget figures per Contract Pricing Proposal dated March 1993

Prepared by C. Doyle, ER Division
(708) 252-5969

Potential Impacts on Air Quality of the Use of Ethanol as an Alternative Fuel
DAC-3-13252-01

Reporting Period: 6/1/94-6/30/94

ANL Activity 85858
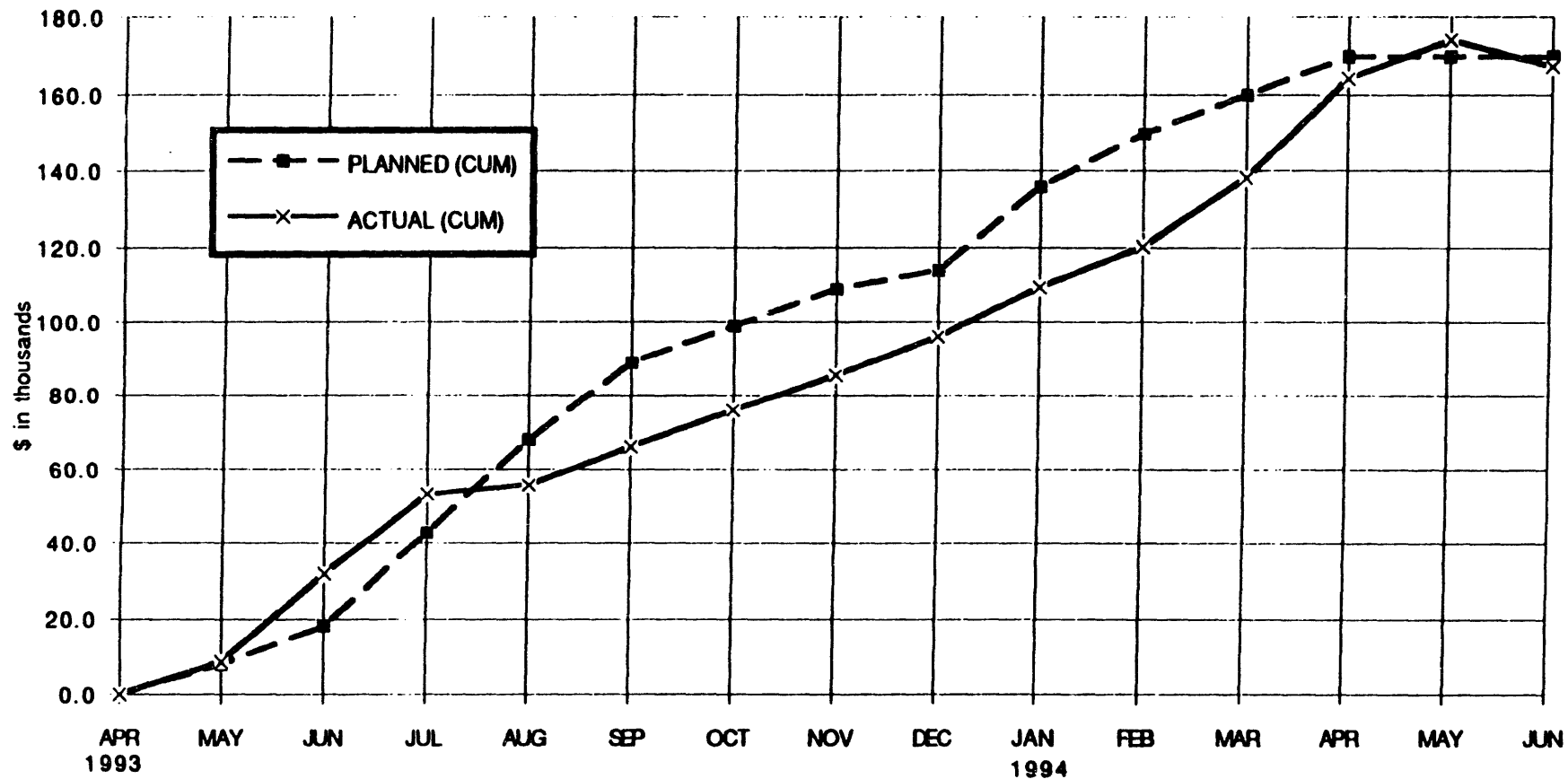
COST STATUS

Date: 7/18/94

Principal Investigator: J. Gaffney

(708) 252-5178

COST STATUS (In $1000)

	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN
PLANNED (CUM)	0.0	8.0	18.0	43.0	68.0	89.0	99.0	109.0	114.0	136.0	150.0	160.0	170.0	170.0	170.0
ACTUAL (CUM)	0.0	8.7	31.9	53.0	55.6	66.1	76.9	85.5	96.1	109.5	120.2	138.3	164.2	174.2	167.4