

AIR QUALITY STUDIES IN ALBUQUERQUE, NEW MEXICO

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ABSTRACT

The objectives of this project were to upgrade instrumentation by analyzing species present in the atmosphere, train students in the area of air quality analysis parameters and provide an opportunity to determine baseline atmospheric concentrations of potential pollutants in the urban atmosphere of Albuquerque, New Mexico. Matching funds provided through this project and New Mexico Institute of Mining and Technology (New Mexico Tech) have allowed considerable upgrade of equipment available to measure air quality parameters. To meet the training objectives, six students were involved in the project (two graduate students and four undergraduate students). The two graduate students have based their M.S. thesis projects on this study and one student has completed her thesis during fall of 1992. The four undergraduate students have learned techniques and procedures related to atmospheric analyses. A suite of inorganic and organic chemicals were analyzed over a one year period in Albuquerque, New Mexico to determine baseline conditions for organic pollutants, and, coupled with analyses of inorganic species, a snapshot of conditions under the current air pollution control parameters has been obtained. Concentrations of low molecular weight carbonyl compounds are relatively high compared with highly polluted areas such as Los Angeles. In addition, ratios of peroxypropionyl nitrate to peroxyacetylnitrate are higher than expected and may be related to the use of oxygenated fuels which are used to mitigate CO concentrations. More detailed studies are needed to determine the specific relationship between the use of oxygenated fuels and the composition of the atmosphere over Albuquerque, New Mexico.

Keywords: air pollution, atmospheric processes, organic compounds

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NATURE, SCOPE AND OBJECTIVES

This project's objectives are to enhance educational training and research capabilities in the area of environmental air pollution problems in New Mexico. Traditionally, environmental studies in New Mexico have centered around surface and groundwater quality/supply issues. This is not surprising given the scarcity of water in New Mexico's arid landscape. However, it is usually taken for granted that clean air and magnificent vistas will always be a part of New Mexico's quality of life. This concept is quickly shattered when one encounters the city of Albuquerque's 'brown cloud'. Many of the air quality-related virtues which attract a growing population are now degrading, partly as a consequence of growth. New Mexico Tech, through its research and teaching programs in atmospheric physics and chemistry and in environmental engineering, has provided air quality education and research for many years. The thrusts of this project have been to enhance and acquire specialized equipment used for atmospheric measurements for both teaching and research and to provide research support for urban air quality studies in Albuquerque.

Urban air pollution has developed into a serious problem in many areas of the United States with mobile sources of pollutants playing a major role. Pollutants presenting potential health hazards include carbon monoxide (CO) and ozone (O₃) as well as more exotic species such as peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN). Oxides of nitrogen (NO_x = NO + NO₂) can contribute to acidic rains and fogs, and particulates and NO₂ can cause visibility problems often resulting in the 'brown cloud' phenomenon common in many cities during wintertime temperature inversions, especially prevalent in the western U.S. The

inversions trap not only components responsible for visibility degradation but all pollutants resulting in a series of complex chemical reactions perpetuating the formation of higher concentrations of pollutants and subsequent transport from the pollution source. Such urban air pollution problems have become more severe in recent years in Albuquerque and are beginning to occur in other developing urban areas in the state such as Las Cruces and Santa Fe.

In order to mitigate the problems associated with increased emission rates in urban centers, many municipalities have adopted various measures such as required emission checkups on motor vehicles, bans and limitations on activities such as wood burning, and the use of oxygenated fuels in the wintertime. At this time, six large urban areas in the West (Albuquerque, New Mexico; Denver, Colorado; Phoenix, Arizona; Las Vegas, Nevada; Reno, Nevada; and Tucson, Arizona) have adopted the use of oxygenated fuels in the winter as one step toward reducing CO pollution (Miller, 1992). As observed by Gaffney and Marley (1990) in an article entitled "The search for clean alternate fuels: There's no such thing as a free lunch," a number of issues and unanswered questions have been raised including emission of increased levels of aldehydes and PAN and the ultimate net effect of using alternative fuels has on the chemistry of urban atmospheres. Typical strategies for using oxygenated fuels containing such additives as ethanol, methanol, and ethers [methyl tertiarybutyl ether (MTBE) as an example] are directed at reducing CO emissions. Using such blended fuels (or pure alcohols) has the potential to increase atmospheric concentrations of low molecular weight, photochemically active organic compounds that, in turn, may increase concentrations of ozone, hydrogen peroxide, and/or organic oxidants.

Sampling and chemically analyzing air samples requires specialized training and equipment not normally available in academic institutions with traditional curricula and research emphases. At New Mexico Tech, courses in environmental and atmospheric chemistry include laboratory experience, and ongoing research programs in atmospheric chemistry and physics provide training in atmospheric science. It is necessary to upgrade laboratory equipment in this non-traditional area to enhance the training potential for students and the effectiveness of atmospheric chemistry research programs.

Objectives

A comprehensive program was developed to analyze air samples in Albuquerque for low molecular weight carbonyl compounds, PAN, nitric acid (HNO_3), NO_x , CO, and O_3 during both winter and summer. The field data collected during the study was used to predict changes in atmospheric concentrations of pollutants resulting from the use of alternative fuels, especially oxy-fuels. Collaboration with researchers at Argonne National Laboratory (ANL) was established. The City of Albuquerque Air Quality Control Division (CAAQCD) agreed to provide data and access to sample sites. Study results will be applicable to other growing urban centers in New Mexico such as Las Cruces and Santa Fe which are already experiencing problems similar to Albuquerque's, although to a lesser extent.

Specific objectives are to:

- Upgrade equipment used to monitor atmospheric species
- Provide undergraduate and graduate students training in the use of atmospheric monitoring equipment

- Sample air quality in Albuquerque, New Mexico for one year to provide a database for the evaluation of air pollution control strategies (especially the use of oxygenated fuels) adopted by the City of Albuquerque

METHODS, PROCEDURES AND FACILITIES

Study Area - General Description

The primary study area is the city of Albuquerque, which has a metropolitan population of about 500,000 and is located along the Rio Grande Valley at an altitude of 5000 feet (1524 m) in central New Mexico (Figure 1). The city is typical of many growing urban centers in the West and is experiencing environmental problems associated with growth.

Albuquerque is located 75 miles (120 km) north of New Mexico Tech in Socorro making it convenient to respond to study opportunities based on the changing meteorological conditions. Air samples collected and analyzed in Socorro provide a comparison with a low-population site removed from urban influences, but located in a similar geographic and meteorological setting.

Sample Sites and General Sampling Protocol

Two sampling sites in Albuquerque were selected to coincide with air quality sampling sites operated by the CAAQCD and are shown as 1 (2R) and 2 (2ZM) on figure 1. Site 2ZM was selected because it was the only site where NO and NO₂ (NO_x) are analyzed. The CAAQCD also monitors ozone (O₃), carbon monoxide (CO), wind speed and wind direction at both sites. Site 2ZM is located near the center of the highest traffic density (35,000-55,000 vehicles/day) in Albuquerque (Appendix A) and should be representative of direct emissions

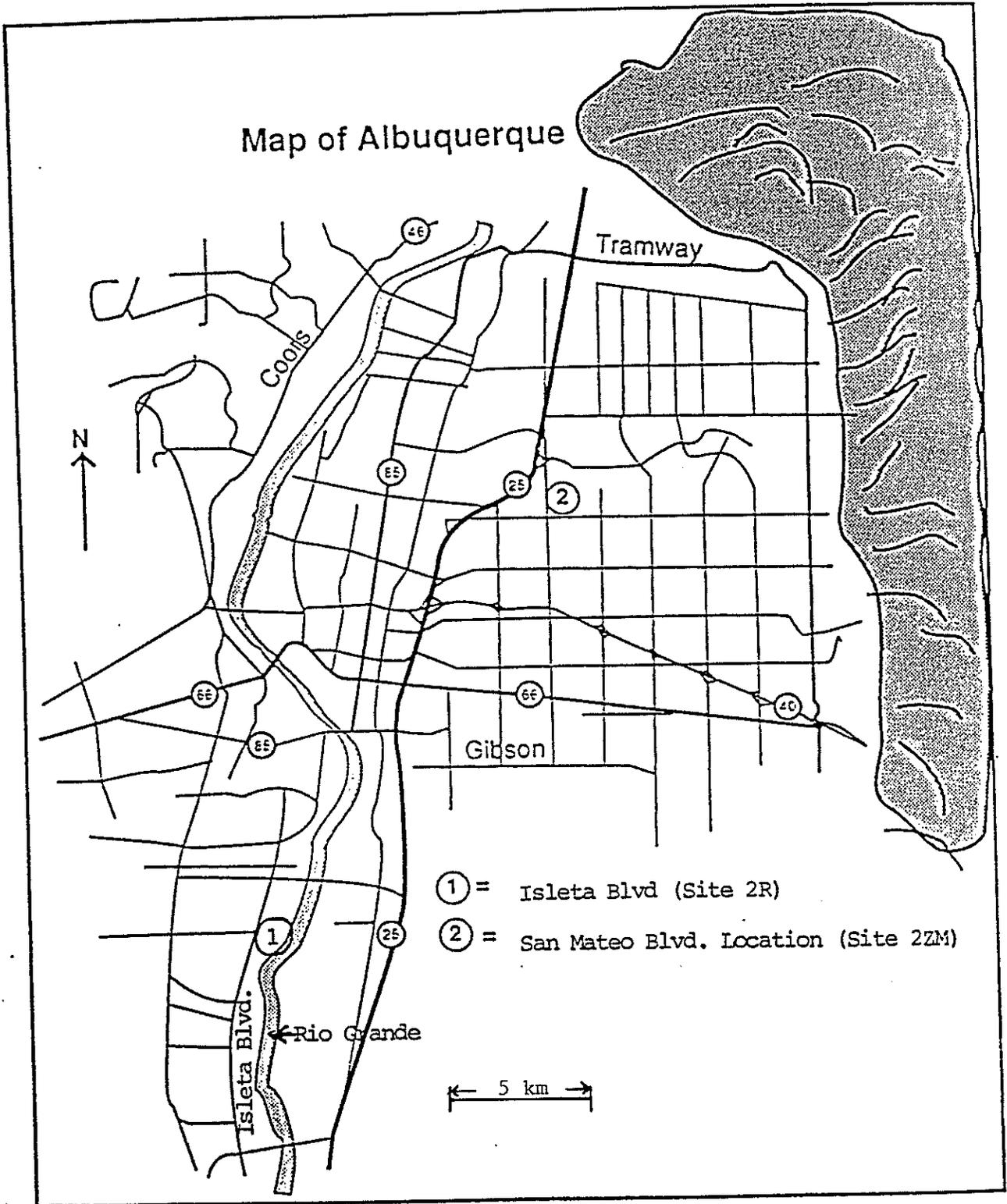


Figure 1. Map of Albuquerque Showing Sampling Sites

while site 2R is located in the more rural south valley with much lower traffic densities. The distance from 2ZM to 2R is 9 miles (14.4 km). Because down-valley air drift is common during winter temperature inversions, it was hoped that photochemical and oxidation reactions would have time to take place as primary emissions (presumably generated at 2ZM) react to form secondary emission products. Samples were also collected on the New Mexico Tech campus.

In order to determine any differences in the atmospheric composition of trace pollutants, samples were taken during wintertime when oxy-fuels use is mandated in Albuquerque and during spring, summer and fall when the use of such fuels is not required. All sampling times involved simultaneous measurement of NO_x , O_3 , CO, low molecular weight oxygenated hydrocarbons, and PAN. Nitric acid and SO_2 gases were collected and analyzed using filter packs during the March 1992 sampling period (Hall 1985).

NO_x and Ozone Analysis

NO_x and O_3 were analyzed using standard chemiluminescent oxides of nitrogen analyzers and ultraviolet ozone analyzers. A variety of instruments are available through New Mexico Tech and the City of Albuquerque and include Dasibi 1003 O_3 analyzers and Monitor Labs 8440 and Thermoelectron Corp. NO_x Analyzers. New Mexico Tech's NO_x analyzer was calibrated with certified cylinders of NO in nitrogen that are checked yearly at the National Oceanic and Atmospheric Administration Aeronomy Lab in Boulder, Colorado. To check conversion efficiencies of the NO_x analyzer, NO_2 permeation tubes were used. Ozone analyzers were calibrated using a Thermo Environmental Instruments, Inc. Model 49PS ozone calibrator or similar equipment.

PAN Analysis

PAN and PPN were analyzed by gas chromatography using an electron capture detector and gas chromatograph (Shimadzu Mini II) equipped with a chromosorb W-HP/10% carbowax column and automatic sampling valve and timer to collect and analyze samples every one-half hour. The analysis procedure and calibration follows that described by Tanner et al. (1988) and Gaffney et al. (1989). Calibration of PAN was attained by analyzing for NaOH-scrubbed acetate using ion chromatography (Dionex 2000 Si/AS 10 column) and both PAN and PPN were calibrated using a chemiluminescent NO_x analyzer with flow split from a PAN or PPN loaded diffusion tube. Both PAN and PPN were prepared by the acid oxidation of the appropriate anhydrides as described by Gaffney et al. 1989 and/or by splitting the PAN and PPN flow from a diffusion tube through NaOH with subsequent spectrophotometric analysis of nitrite (Saltzman 1954).

Meteorology

Meteorological stations located on site recorded wind velocity and direction during sampling periods. Temperatures were noted for Ideal Gas Law calculations.

Oxygenated Hydrocarbons

Formaldehyde and acetaldehyde are generally the most abundant and most photochemically active aldehydes in ambient air. These and other aldehydes and ketones are collected efficiently by pulling air through 2,4 dinitrophenylhydrazine-coated Sep-Pak C18 microcolumns (Waters Associates or Millipore Corp.) followed by elution with acetonitrile and analysis of the 2,4 dinitrophenylhydrazines using high-performance liquid chromatography (HPLC) as described by Tanner et al. (1988), Zhou and Mopper (1990), and Grosjean

(1991a). Organic acids can be both primary and secondary pollutants with formic and acetic acids (analogous to the aldehydes) being the most common. Organic acids can be efficiently scrubbed from the air using fine mists following a procedure described by Cofer et al. (1985). A 1 m Teflon prefilter was placed upstream from the nebulizer to trap particulates and air was pulled through the nebulizer at about 1 L/min. Flow rates for air sampling were monitored by rotameters calibrated using a bubble meter. The distilled water in the nebulizer (~7 mL) was diluted to 25 mL in a volumetric flask and stored under refrigeration after about three drops of chloroform were added to discourage bacterial degradation of the organic acids. Analysis was accomplished using ion chromatography (Dionex 2000 Si) and an AS10 column with NaOH eluent. Because of an unknown source of contamination of acetic acid, data are only reported for formic acid. No formic acid contamination was observed.

RESULTS AND DISCUSSION

Equipment Upgrades

Equipment upgrades have taken two pathways; purchase of new equipment and renovation of current equipment. New equipment purchased include a portable gas chromatograph (SRI Research Model 8610) equipped with electron capture detection, an integrator (Spectra Physics Chromejet) for gas and high performance liquid chromatographic analysis, and a Teflon-lined six-port sampling valve. Upgrades and repairs were made on Dasibi 1003A O₃ analyzers and a Shimadzu Mini-II gas chromatograph. In addition, construction of an eight-channel, computer controlled data logging system is in process for use

on field- or lab-based equipment from equipment purchased through the grant and matching funds.

Student Involvement

Two graduate students, Michelle Cash and Lin Zhang, and four undergraduate students, Casey Caddell, Kirk Ferdig, Matt Hind, and Melissa York, were directly involved in sampling, analysis and data reduction. The graduate students have based their M.S. thesis projects on this research and will probably complete requirements during the summer or fall of 1992. The two graduate students presented papers at the Southwest Regional American Chemical Society Meeting (RM²) in Albuquerque on June 10, and copies of their abstracts are included in the Appendix B. The four undergraduate students were involved in various aspects of the project. Matthew Hind received his B.S. in chemistry in May 1992 and has been admitted to the M.S. program in Chemistry at New Mexico Tech to continue atmospheric chemistry research.

Carbonyl Compounds

Formic acid and low molecular weight aldehydes and ketones (formaldehyde, acetaldehyde, propionaldehyde and acetone) were collected in Albuquerque and Socorro beginning in August 1991 (raw data for all samples are summarized in Appendix C). Samples were collected in early August 1992, and during mid-December 1991, mid-February 1992 and mid-March 1992 in Albuquerque and at similar times if possible in Socorro for comparison (figures 2-5). As expected, formic acid concentrations peaked from mid-day to late afternoon corresponding to increased photochemical activity and increases in oxidants such as O₃ and organic oxide and peroxide radicals (as shown later, O₃ concentrations peak from mid-morning

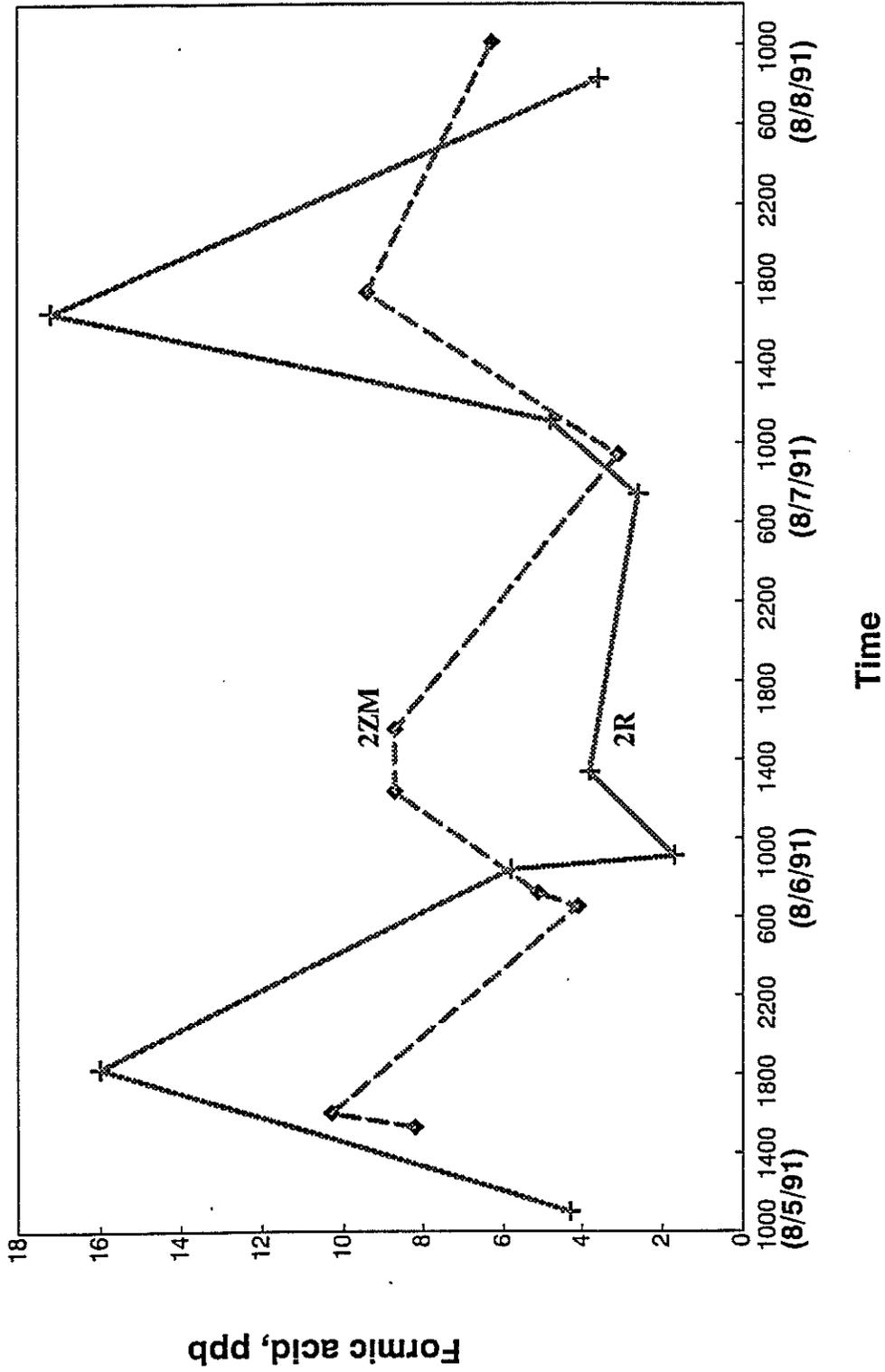


Figure 2 Concentrations of gas-phase formic acid during August 5, 6, 7 and 8 of 1991 in 2ZM and 2R at Albuquerque

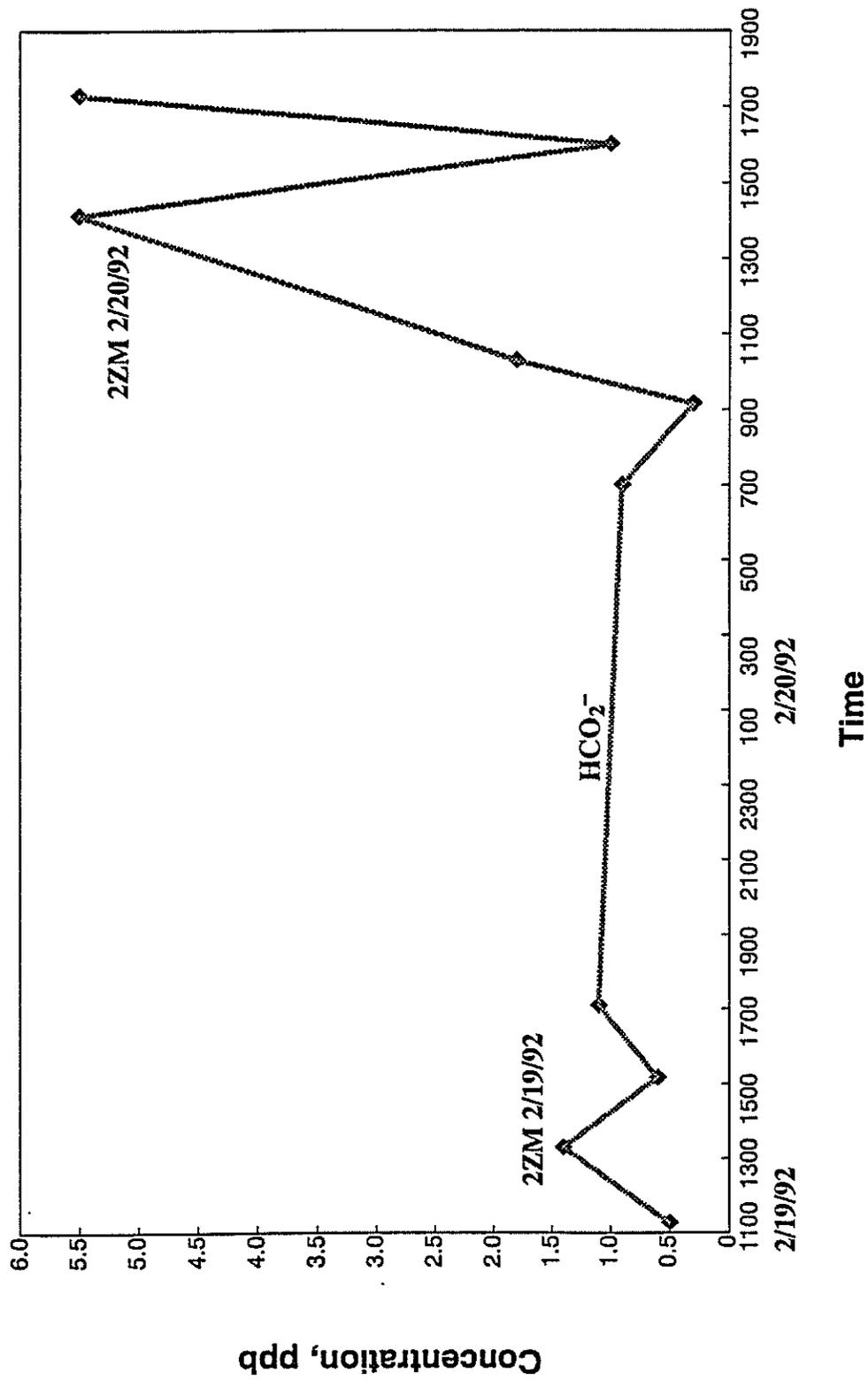


Figure 3. The concentrations of formic acid during February 19-20, 1992 at 2ZM, Albuquerque, NM

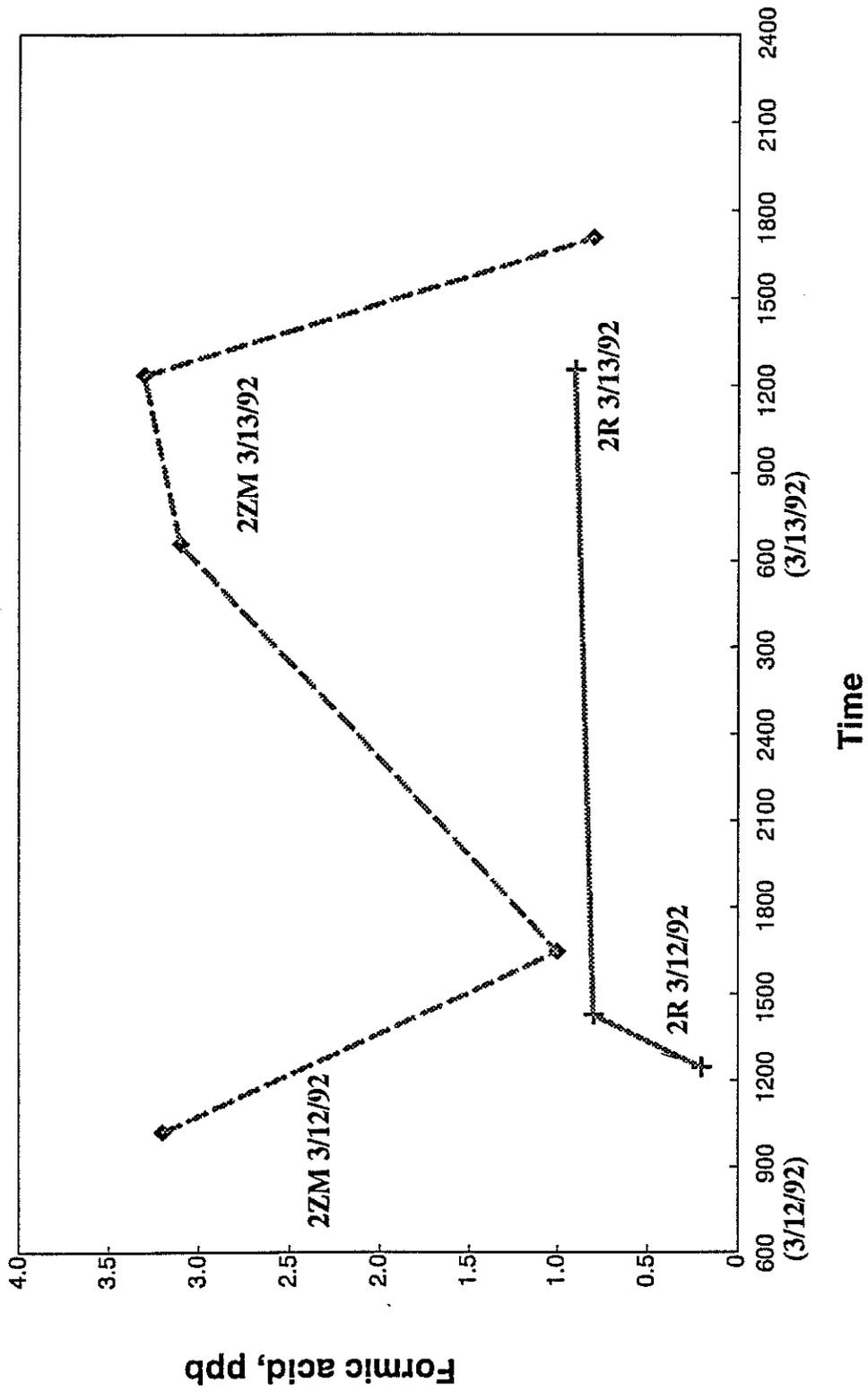


Figure 4. Concentrations of gas-phase formic acid during March 12 and 13 of 1992 in 2ZM and in 2R at Albuquerque

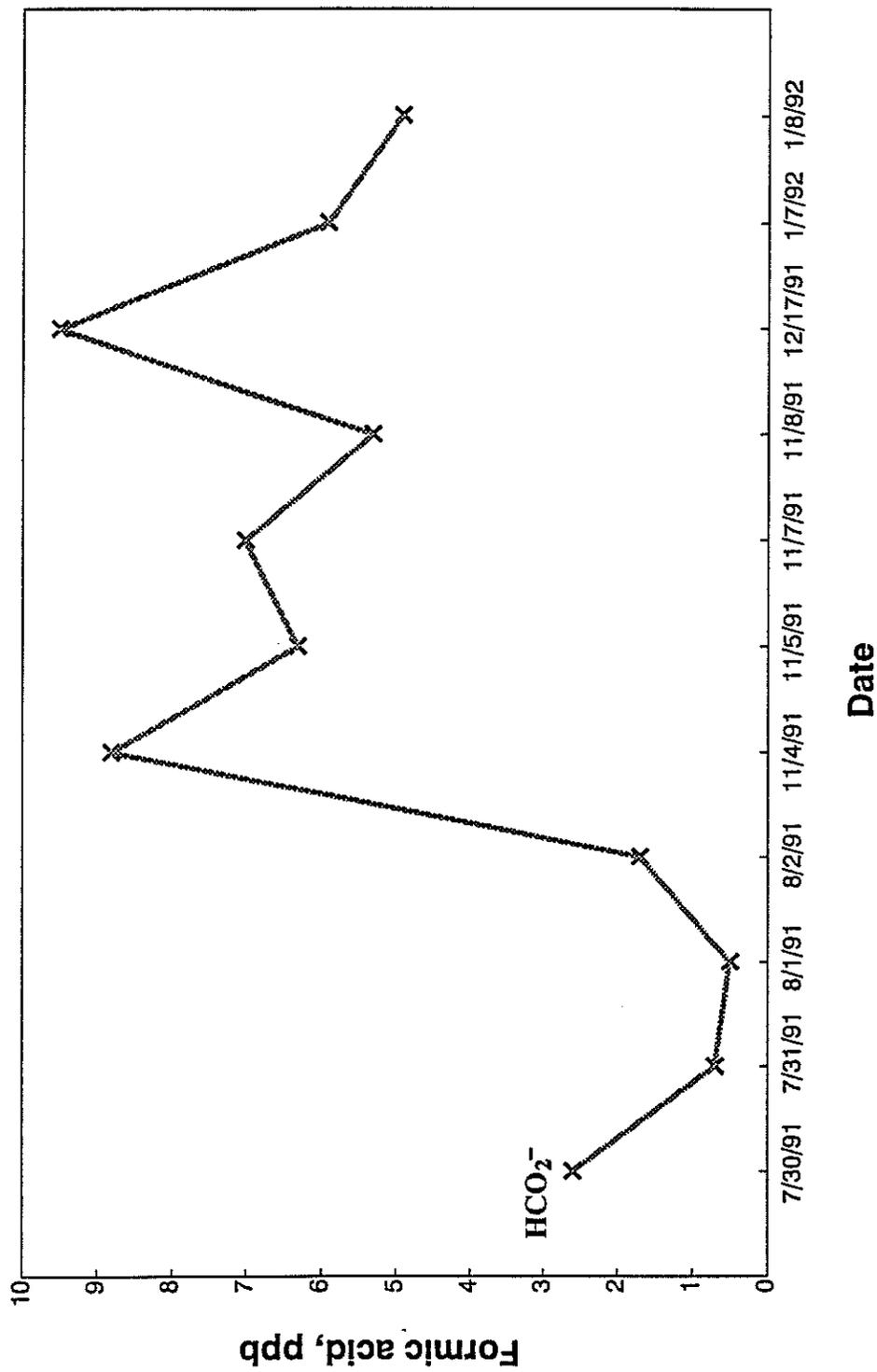


Figure 5. Concentrations of gas-phase formic acid during July of 1991 to January of 1992 at Socorro.
 All samples between 1030 -- 1727 except 8/5/91(0920)

to late afternoon also). Precursors to the formation of formic acid are formaldehyde and compounds such as plant emissions (i.e. isoprene, terpenes) which must undergo photolytic decomposition to form formaldehyde which then must be oxidized to formic acid. The time necessary for these processes is of the order of hours. The highest concentrations of formic acid 10-17 ppbv in Albuquerque (figure 2) occurred in August at the South Valley site (2R) where vegetation probably contributes to relatively high biogenic emissions of isoprene which rapidly degrades through oxidation and photochemical processes to formaldehyde, a precursor of formic acid. The two sites showed parallel behavior in August but at the San Mateo and Montgomery, high traffic density site (2ZM) formic acid concentrations were lower, again probably related to lower biogenic isoprene emissions (figure 1). The highest formic acid concentrations in December (Table 1) and February (figure 3) were 16 ppbv and 5.5 ppbv, respectively. The December samples averaged 8.9 ppbv and were unusual because for several days the city was subject to continual cloudiness, fog and drizzle with no sunshine during the sample period. As a consequence, O₃ was extremely low and air quality was generally very good. This together with almost no photochemical activity apparently led to a buildup of formic acid while in February (figure 3) and March (figure 4), the formic acid concentrations peaked at 5.5 and 3.5 ppbv, respectively, at site 2ZM. In contrast to Albuquerque, formic acid concentrations in Socorro were highest in winter, 5-10 ppbv, and lowest in summer, 0.5-3 ppbv (figure 5). The biogenic emissions in summer might be expected to be similar in Socorro and Albuquerque but much greater anthropogenic organic emissions in Albuquerque might account for higher concentrations of formic acid precursors in the city. It is not clear why wintertime formic acid concentrations are relatively high in Socorro except for the effects of

diminished photochemical activity and lower winter temperatures increasing the lifetime of formic acid (similar to the December sampling in Albuquerque when formic acid was also high).

Data for low molecular weight aldehydes and acetone are shown in figures 6 and 7 for individual samples for Socorro and the 2ZM site in Albuquerque from December and February in Socorro (figure 6) and in Albuquerque (figure 7). Average values for each sampling period are summarized in Table 1. Samples collected in December were generally lower in

Table 1. Average values for the concentrations of acetaldehyde (Acet), acetone (Act), formaldehyde (Form), propionaldehyde (Prop) and formic acid (F.A.) in Socorro and Albuquerque air. Concentrations are in the gaseous phase expressed in ppbv.

Site	Acet	Act	Form	Prop	F.A.
Socorro					
August	--	--	--	--	1.4
November-Jan	--	--	--	--	6.8
December	1.0	1.5	2.4	25 ^a	5
February	20.0	33.0	74.0	8.8	7
Albuquerque (2ZM)					
August	--	--	--	--	6.6
December	2.0	0.8	7.9	1.3	8.9
February	26.0	25.0	112.0	26.0	2.1
March	--	--	--	--	2.0
Compared to other sites:					
Site	Date	Acet	Form	F.A.	
Upland, California ^b	9/88	3.9	5.3	2.8	
Carribbean Sea ^c	10/88	BDL	.1-.9	--	
Rio de Janeiro ^d	7/85	13.5	9.8	--	
Amazon (Brazil) ^e	7/85	--	--	1.6	
Tucson, Arizona ^f	7/85	--	--	1.5-2.5	

^aPossible anomolous data as a result of construction activity at the sampling site.

^bGrosjean 1991b

^cZhou and Mopper 1990

^dTanner et al 1988

^eAndreae 1988

^fDawson et al 1980

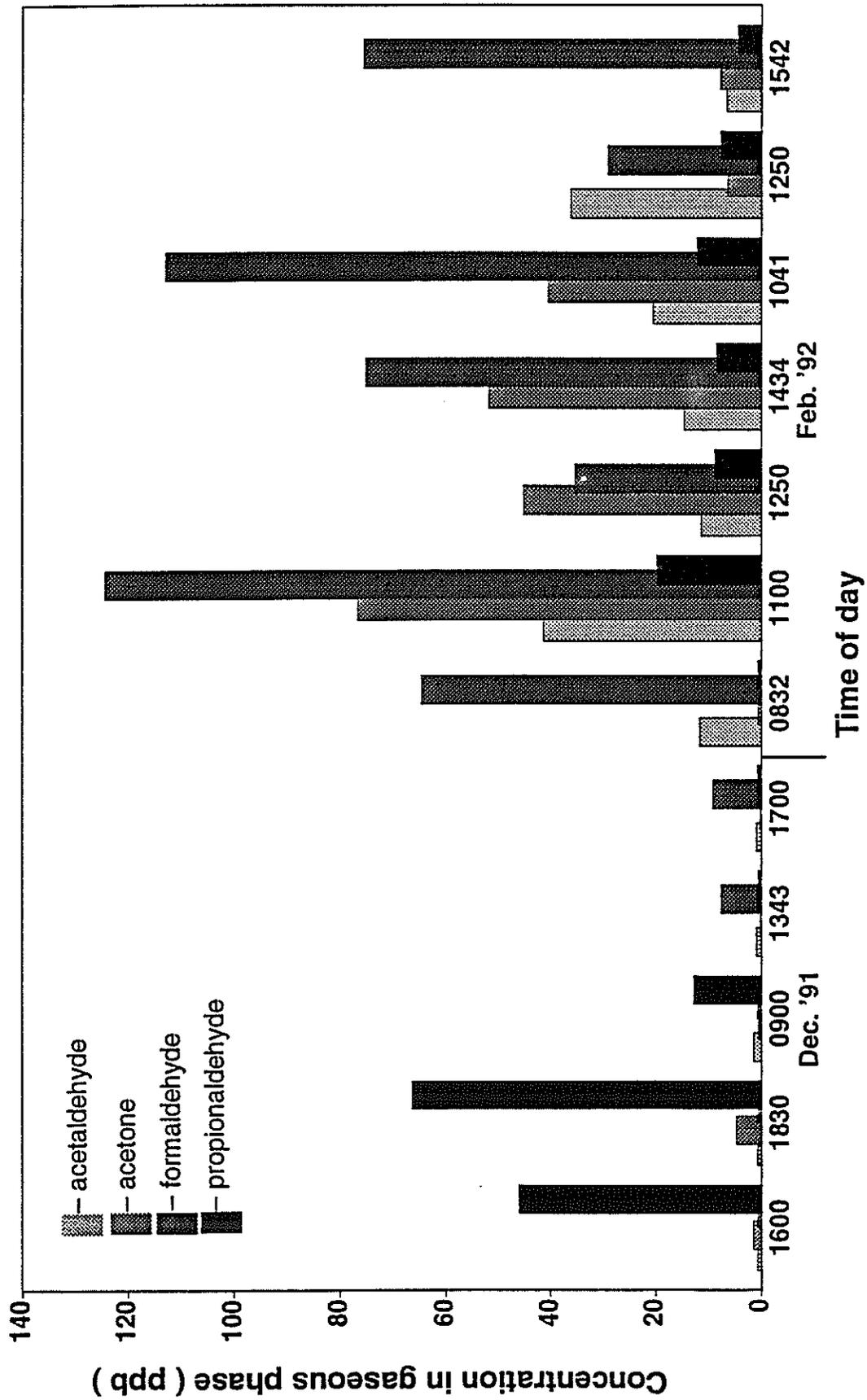


Figure 6. Aldehyde/Ketone concentrations. Socorro (New Mexico Tech).

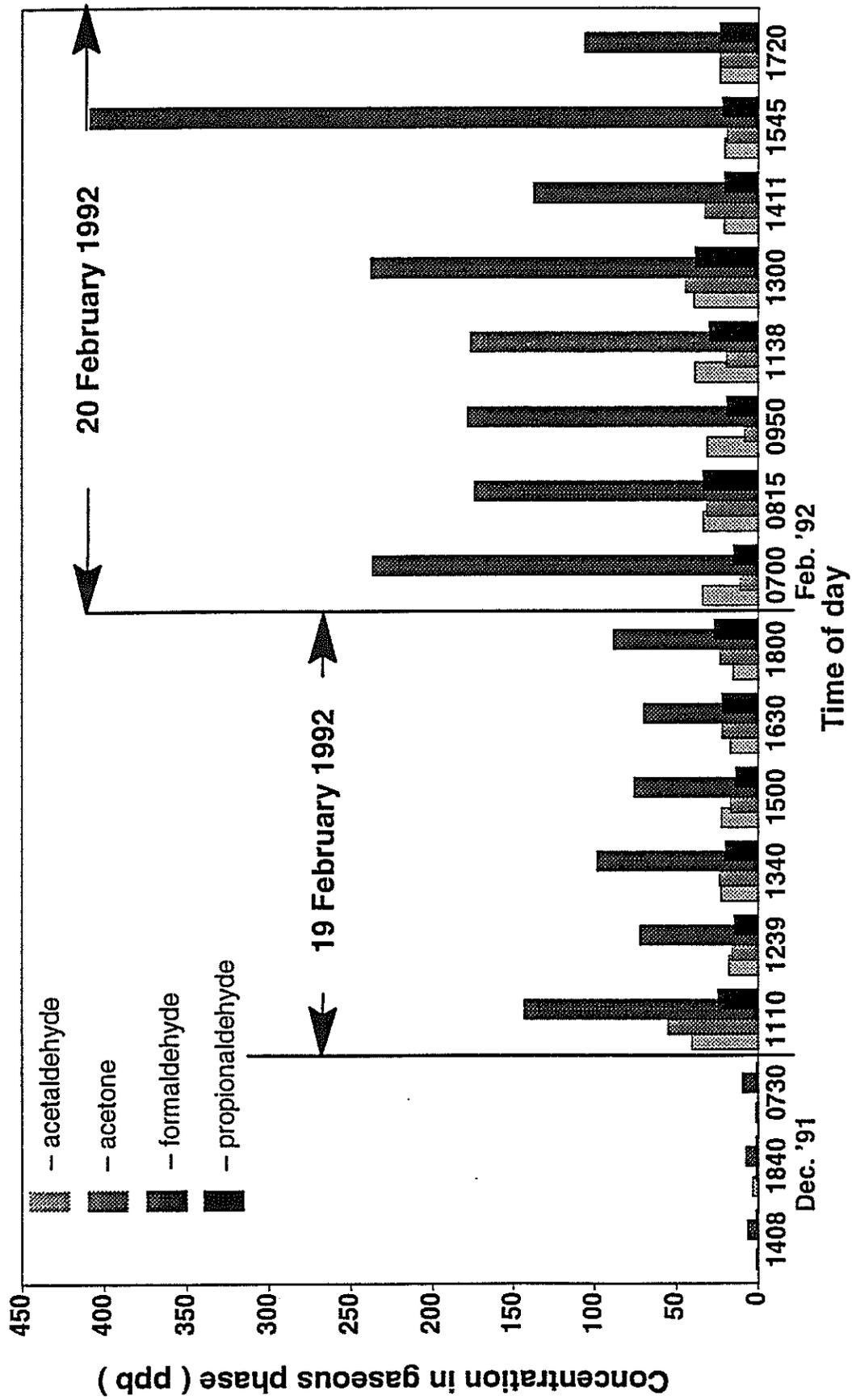


Figure 7. Aldehyde/Ketone concentrations. Albuquerque, New Mexico, Site 2ZM.

aldehyde/acetone carbonyl compound concentrations than samples collected in February, both in Socorro and Albuquerque while formic acid concentrations were high in December both in Socorro and Albuquerque, low in Socorro in August and low in Albuquerque in February and March. The sampling period in December coincided with cold, foggy, wet, sunless days which may have severely reduced concentrations of these species by reducing photochemical reactions and thermal decomposition because of slower kinetics. Also, the moisture may have scrubbed soluble pollutants from the air. In contrast, warmer, clear and sunny weather in February and March may have increased concentrations of these species. Data for February 19, 20 for O₃, formic acid and formaldehyde plotted on figure 8 illustrate that even for similar O₃ values, PAN, formaldehyde and formic acid concentrations can vary greatly from day to day in this case with lower concentrations of organics on the 19th and much higher concentrations on the 20th. The thermal and photochemical sensitivity to degradation of PAN is shown on the afternoon of the 20th with an afternoon decrease while formic acid and formaldehyde peaks are shown at the same time. PAN concentrations remain low until O₃ increases (and presumably other oxidants as well) later in the day. The PAN and formaldehyde and formic acid peaks at noon and in the late afternoon may indicate primary emissions from automobiles. The relationships among O₃, formic acid and PAN in August in Albuquerque are shown in figure 9 for the south valley (2R) and uptown (2ZM) sites (PAN was determined only at site 2ZM). The organics (PAN and formic acid) again peak at the same time as O₃ in mid-to-late afternoon.

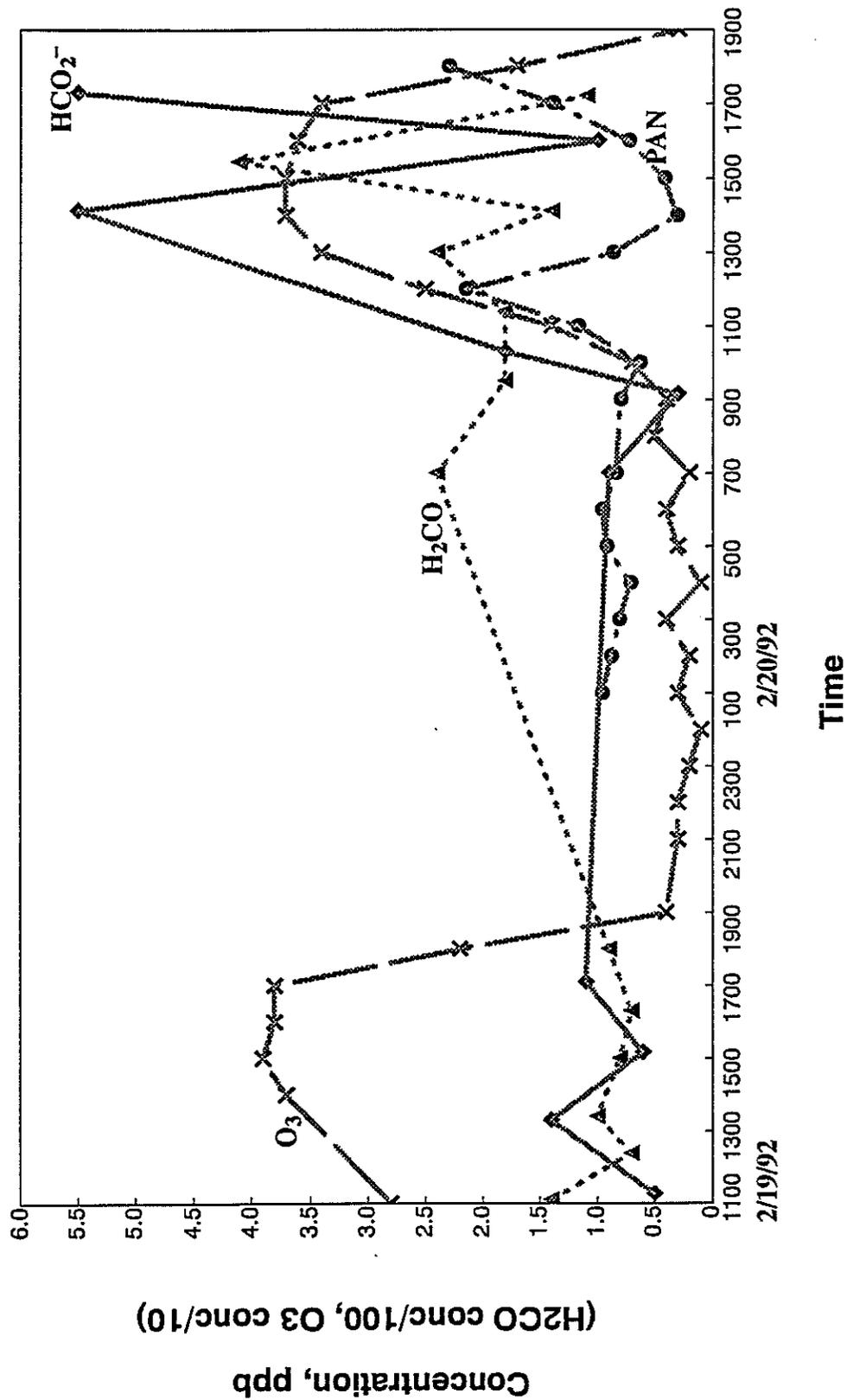


Figure 8. The concentrations of formic acid, ozone, formaldehyde and PAN during February 19–20, 1992 at ZMZ, Albuquerque, NM

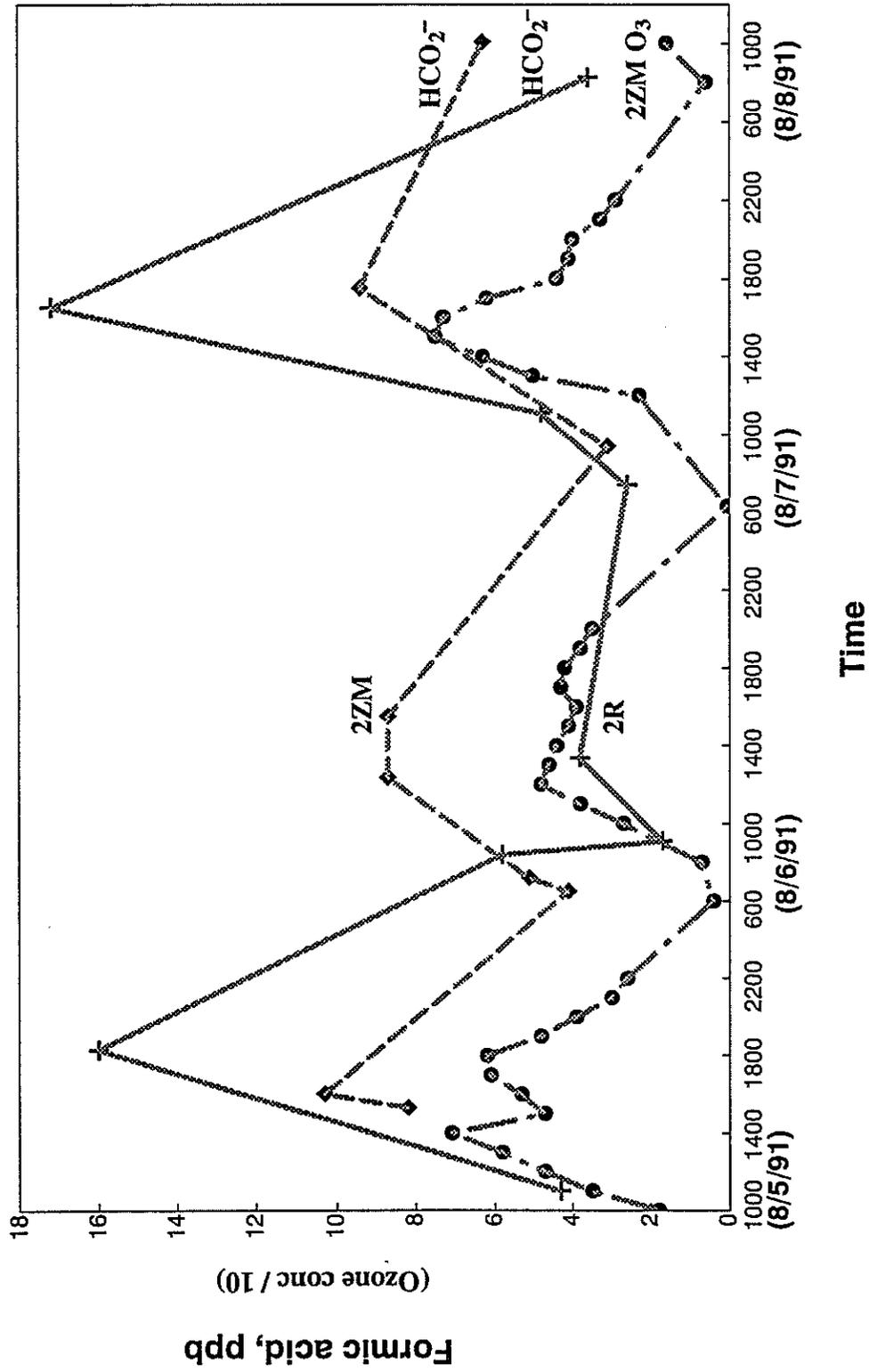


Figure 9. Concentrations of gas-phase formic acid and O₃ during August 5, 6, 7 and 8 of 1991 in 2ZM and 2R at Albuquerque

Peroxyacetyl and Peroxypropionyl Nitrates

PAN and PPN concentrations are shown on a diurnal basis for the four sampling periods (August, December, February and March) in figures 10-13, respectively. PPN concentrations are lower than PAN concentrations but concentrations of the two species correlate well indicating similar sources of organic precursors. The lowest PAN concentrations (0.5 ppbv) are during the December sampling which correlates well with the other organics and again is probably a function of the weather conditions. When sunlight and O₃ are present, PAN concentrations reached maximums near 6 ppbv (figures 10, 13). The only historical PAN data for Albuquerque was obtained in February 1988 by Dr. J. Gaffney of Los Alamos National Laboratory. The average PAN concentration for the February 1988 sampling was 0.74 ± 0.52 ppbv and in February 1992 an average value of 1.1 ± 0.5 ppbv was obtained. This slight increase in PAN concentrations for data obtained before and after the implementation of the oxygenated fuels program is insufficient evidence to suggest that levels of PAN precursors may be increasing. It is suggested (Tanner et al. 1988, Grosjean 1991b) that the PPN/PAN ratio may change when the mix of organic precursors changes. In Table 2, PPN/PAN ratio data are summarized. All data are normalized to take into account the fact that some authors assumed that the electron capture detector (ECD) response to PAN and PPN were similar and only PAN response was calibrated. However, Grosjean (1991b) has shown that PPN is about 82% as sensitive as PAN. Additionally, our calibrations showed a similar factor of 78% when both PAN and PPN were subject to calibration. For comparison purposes, all data from other authors in Table 2 (except Grosjean 1991b and Shepson et al. 1992) are corrected by 1.28.

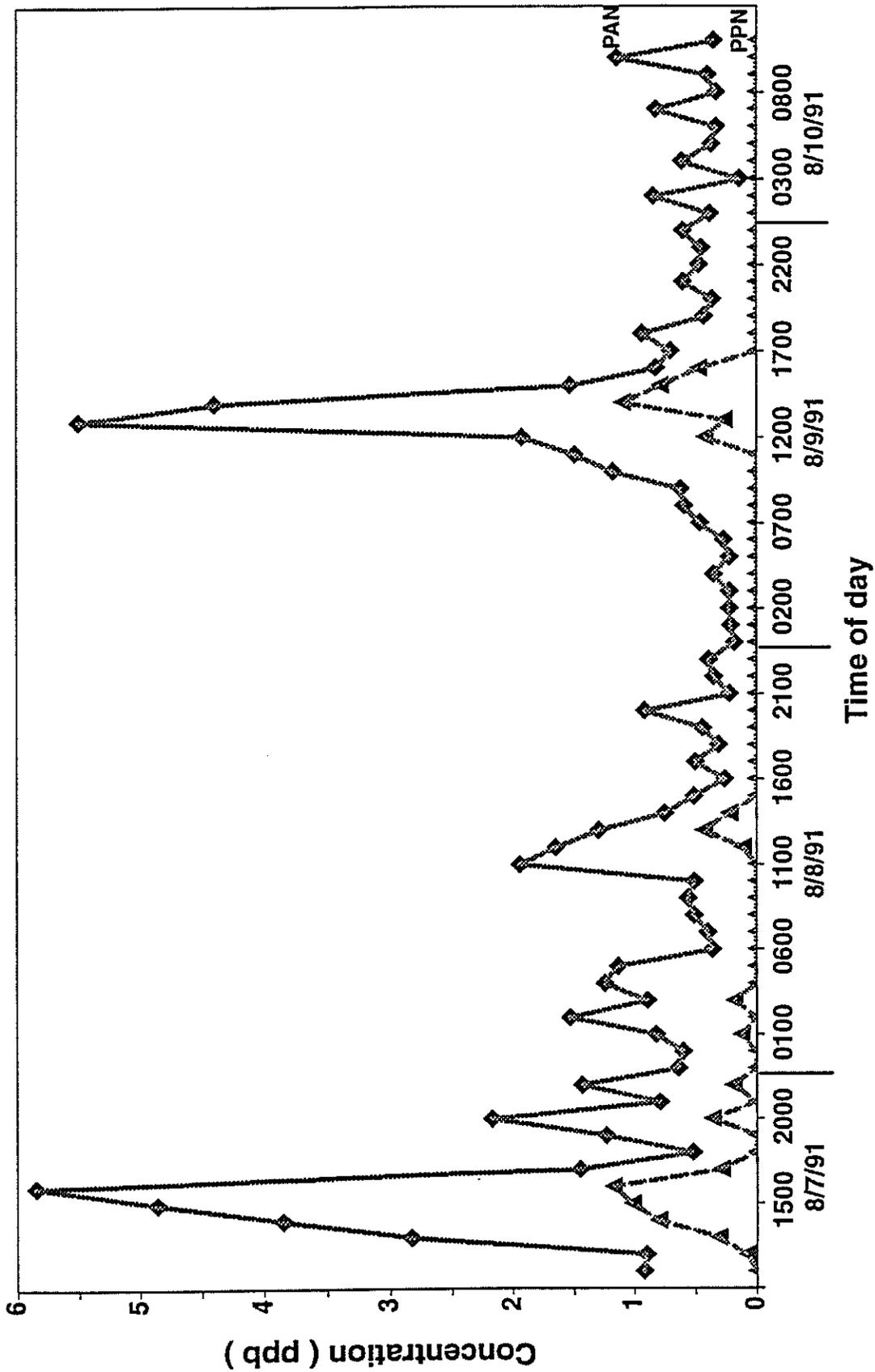


Figure 10. PAN and PPN concentrations during August 7–10, 1991, Albuquerque, New Mexico. Site 2ZM.

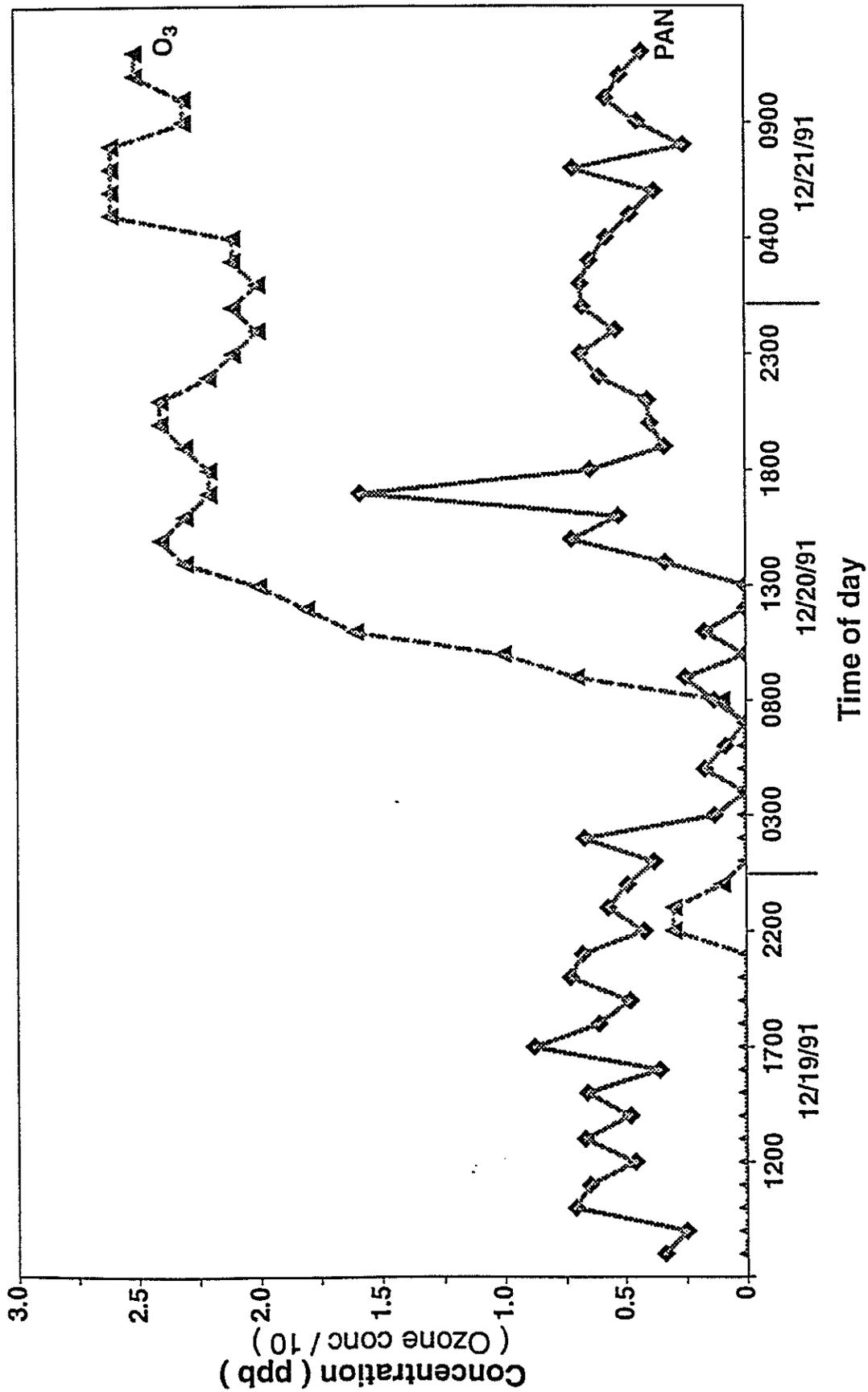


Figure 11. PAN and O₃ concentrations during December 19-21, 1991, Albuquerque, New Mexico. Site 2R.

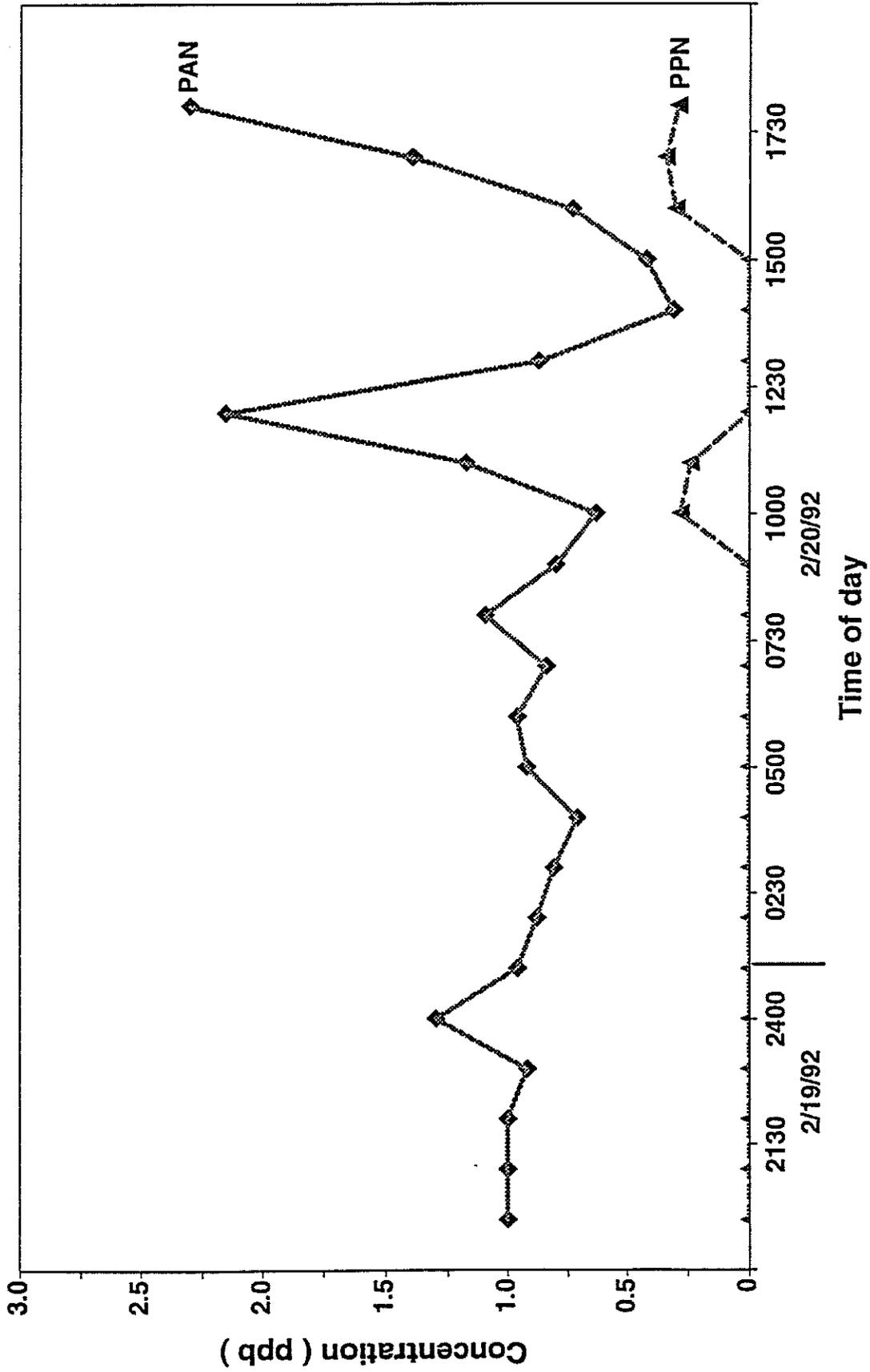


Figure 12. PAN and PPN concentrations during February 19-20, 1992, Albuquerque, New Mexico. Site 2ZM.

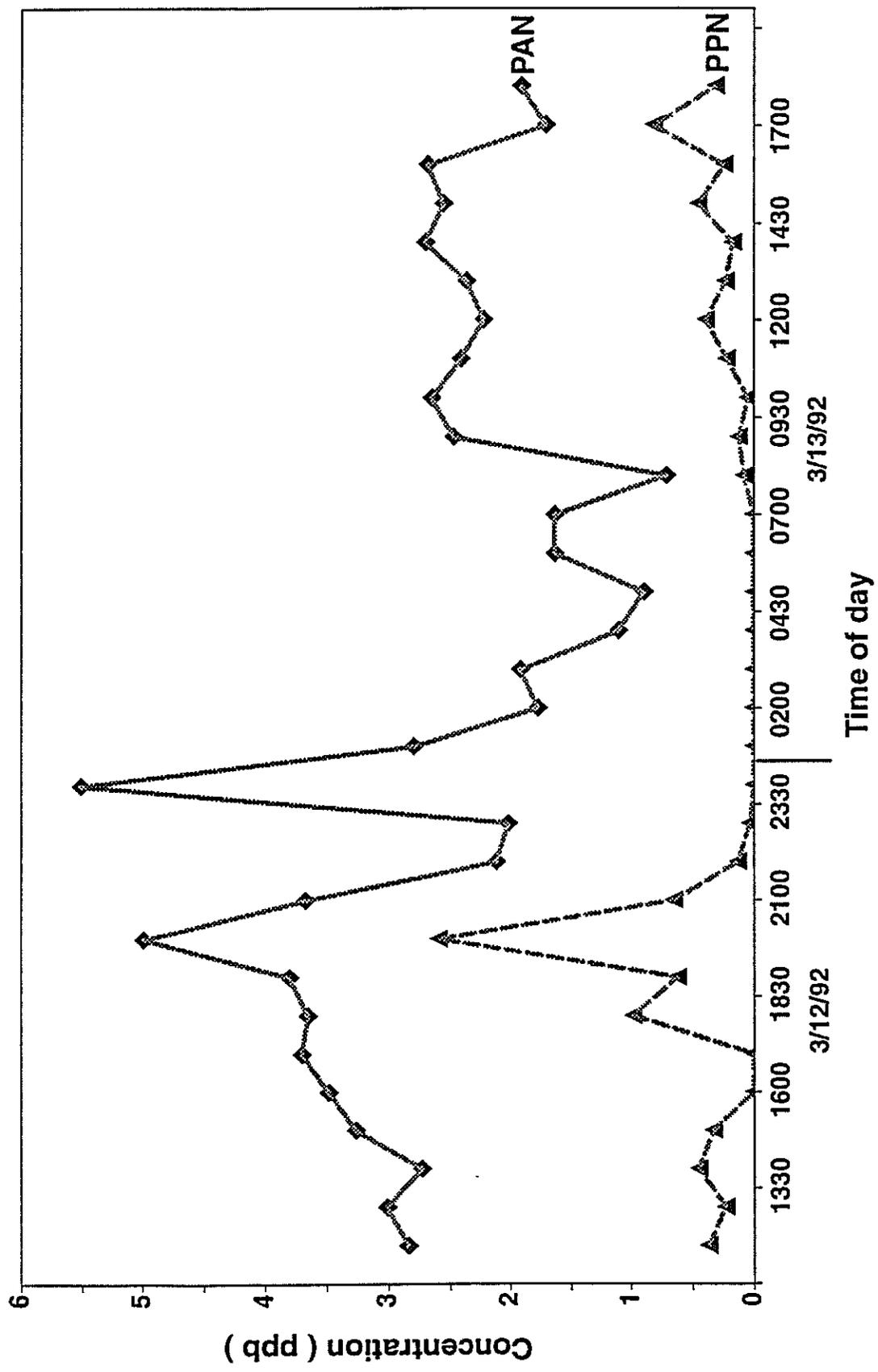


Figure 13. PAN and PPN concentrations during March 12-13, 1992, Albuquerque, New Mexico. Site 2ZM.

Table 2. PPN/PAN x 100 at various sites. Ratios are in ppbv units.

<u>Site/Date</u>	<u>PPN/PAN x 100</u>
Albuquerque 1988 (Feb.) ^a	9.3
Albuquerque 1992 (Feb.) ^b	28.7
Albuquerque 1991-1992 (2 dates) ^c (August, March)	18.0
Rio de Janeiro ^d	25.6
Urban Eastern USA ^e	16.5
Urban Western USA ^e	6.4
Remote Western USA ^e	7.7
Southern California Mountains ^f	28.0
Ontario, Canada ^g	8.9

^aGaffney and Popp, unpublished data

^bThis study

^cThis study - August, December, February, March average

^dTanner et al. 1988

^eSingh and Salas 1989

^fGrosjean 1991b

^gShepson et al. 1992

A large increase in the percentage of PPN/PAN appears to have occurred between February 1988 and February 1992 (9.3 →28.7) suggesting an increase in primary emissions of propionyl precursors relative to acetyl precursors. The effect is more evident in February (PPN/PAN x 100 = 28.5) than March (17.0), or August (19.3). Because the percentage of PPN/PAN averages for August and March are also lower than the values found in February, the data suggest that oxygenated fuels (mandated in February but not in August or March) may be playing a role in causing high ratios such as those found by Tanner et al. (1988) in Brazil where ethanol-enhanced fuel (30% ethanol) was also used. However, because the PPN/PAN

ratios seem to be generally higher on a year round basis, other anthropogenic PPN source(s) may also be important.

PAN concentrations correlate well with O₃ concentrations and PAN/O₃ plots for the four sampling periods (figures 14 - 17). The unusual decrease in PAN on the afternoon of February 20, 1992 (figure 17) may be due to photochemical and thermal degradation after an initial increase by early afternoon. When temperatures cool and the evening rush hour begins, PAN again increases.

Ozone and NO_x Correlations

Variations of the concentrations of O₃ with NO and NO₂ are shown for the four sample periods in figures 18-21. Higher summertime concentrations of O₃ are expected due to longer daylight hours and more intense sunlight and the presence of higher concentrations of organic compounds which contribute to O₃ formation. The highest O₃ concentrations were found in the summer, as expected, and reached a concentration maximum of 75 ppbv (figure 18). The USEPA limit is 120 ppbv. As a primary emission product of automobiles, NO concentrations peak early and late in the day during the rush hours and the NO is then converted to NO₂ during the day which photolyzes back to NO and O, thereby producing an oxidant for making organic radicals and producing O₃ again in the cycle. Of particular interest is the high concentration for NO of 350 ppbv shown on figure 19. This was an extremely smoggy period brought on by a temperature inversion and the NO and NO₂ titrated out the O₃. Ozone also shows a typical urban trend with respect to NO in that an inverse relationship exists between the two species as follows:

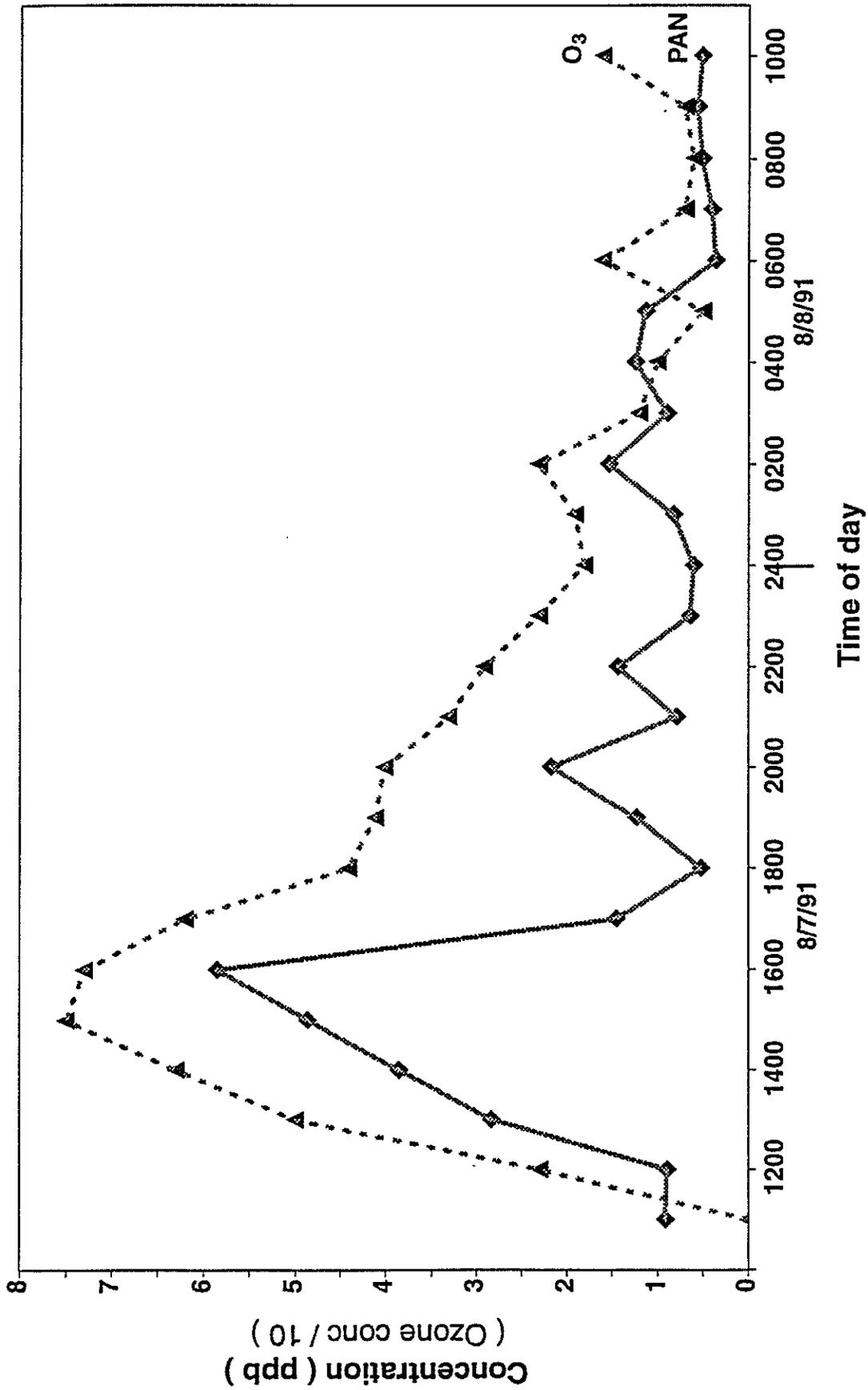


Figure 14. PAN and O₃ concentrations during August 7-8, 1991, Albuquerque, New Mexico. Site 2ZM.

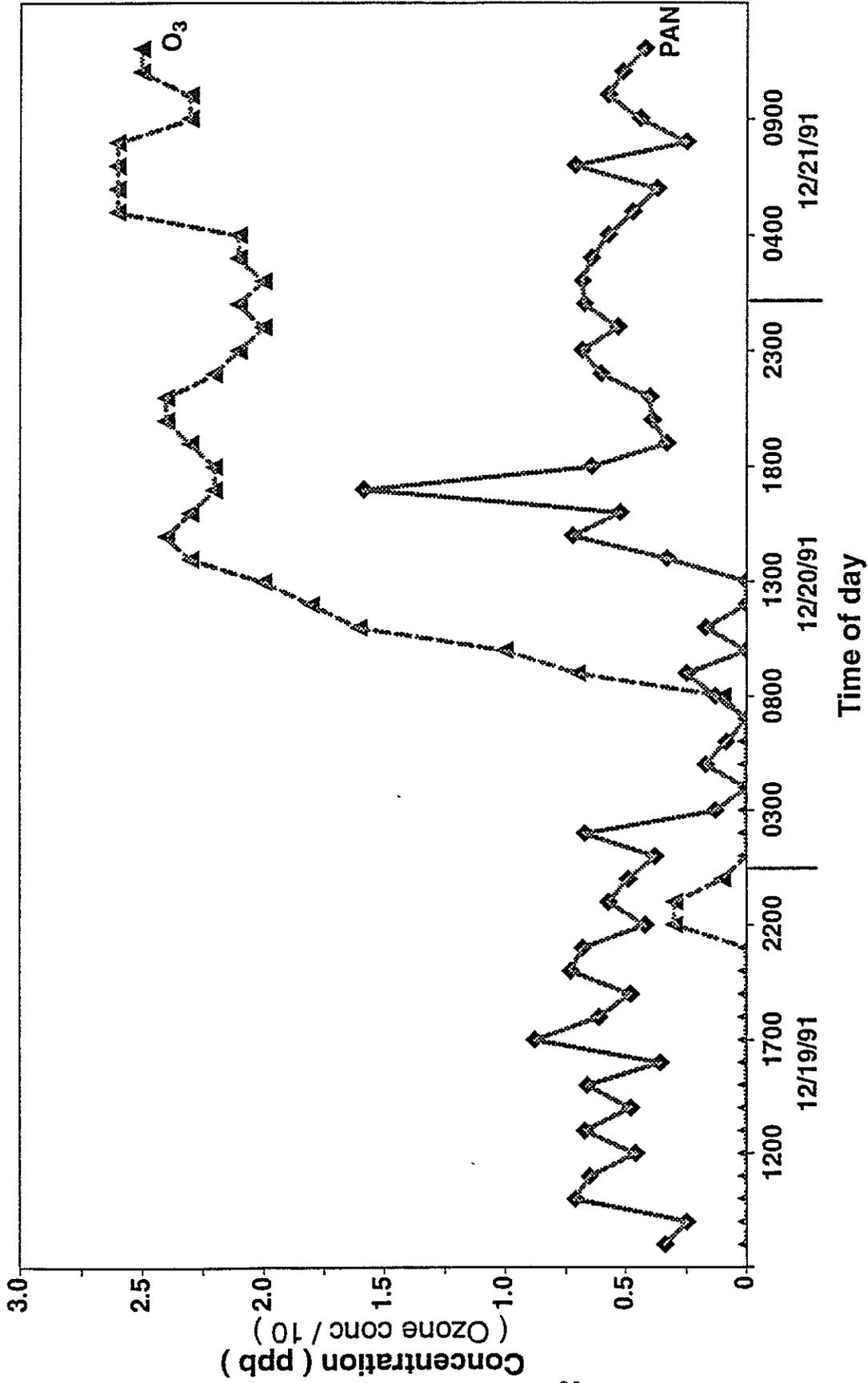


Figure 15. PAN and O₃ concentrations during December 19–21, 1991, Albuquerque, New Mexico. Site 2R.

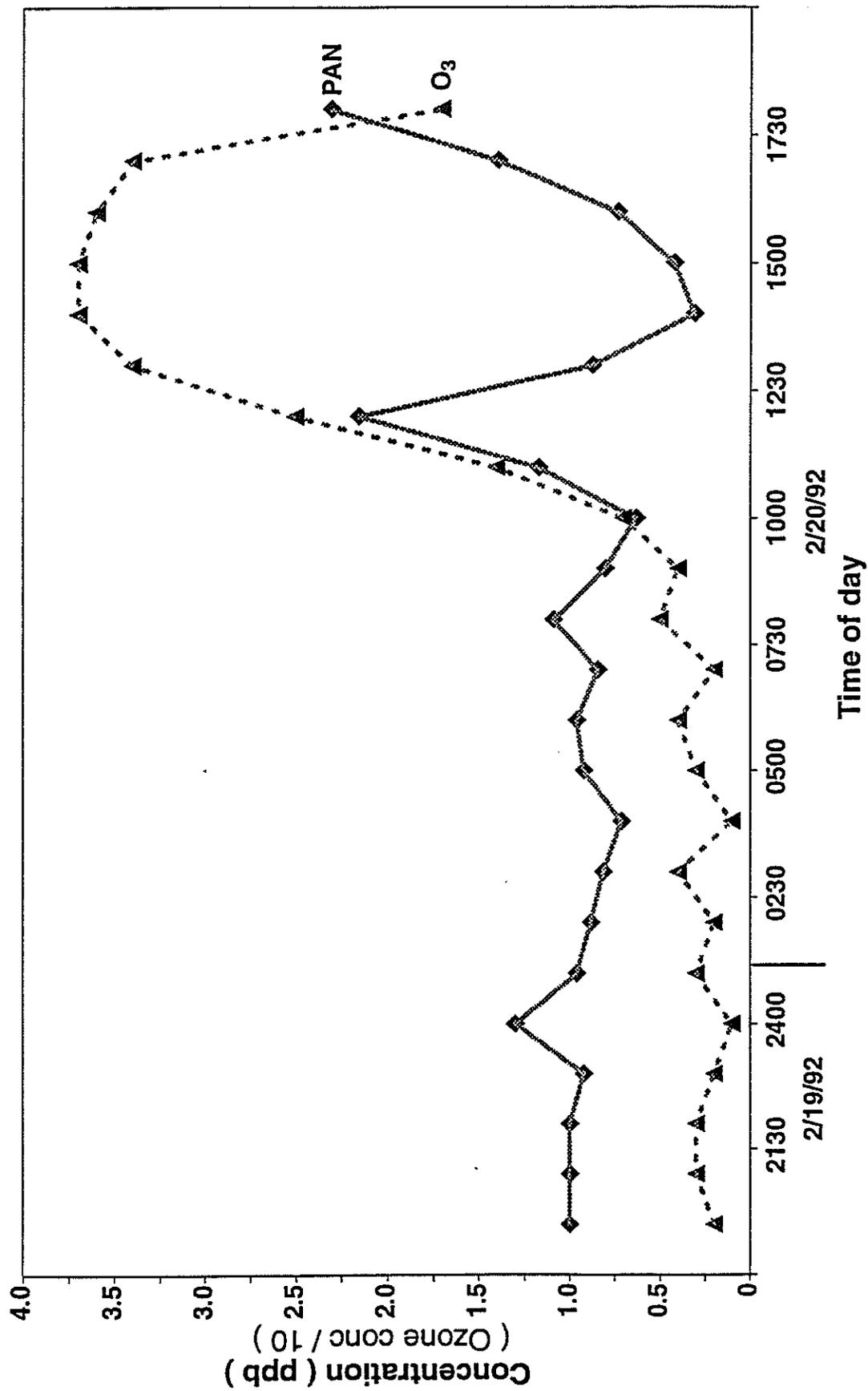


Figure 16. PAN and O₃ concentrations during February 19-20, 1992, Albuquerque, New Mexico. Site 2ZM.

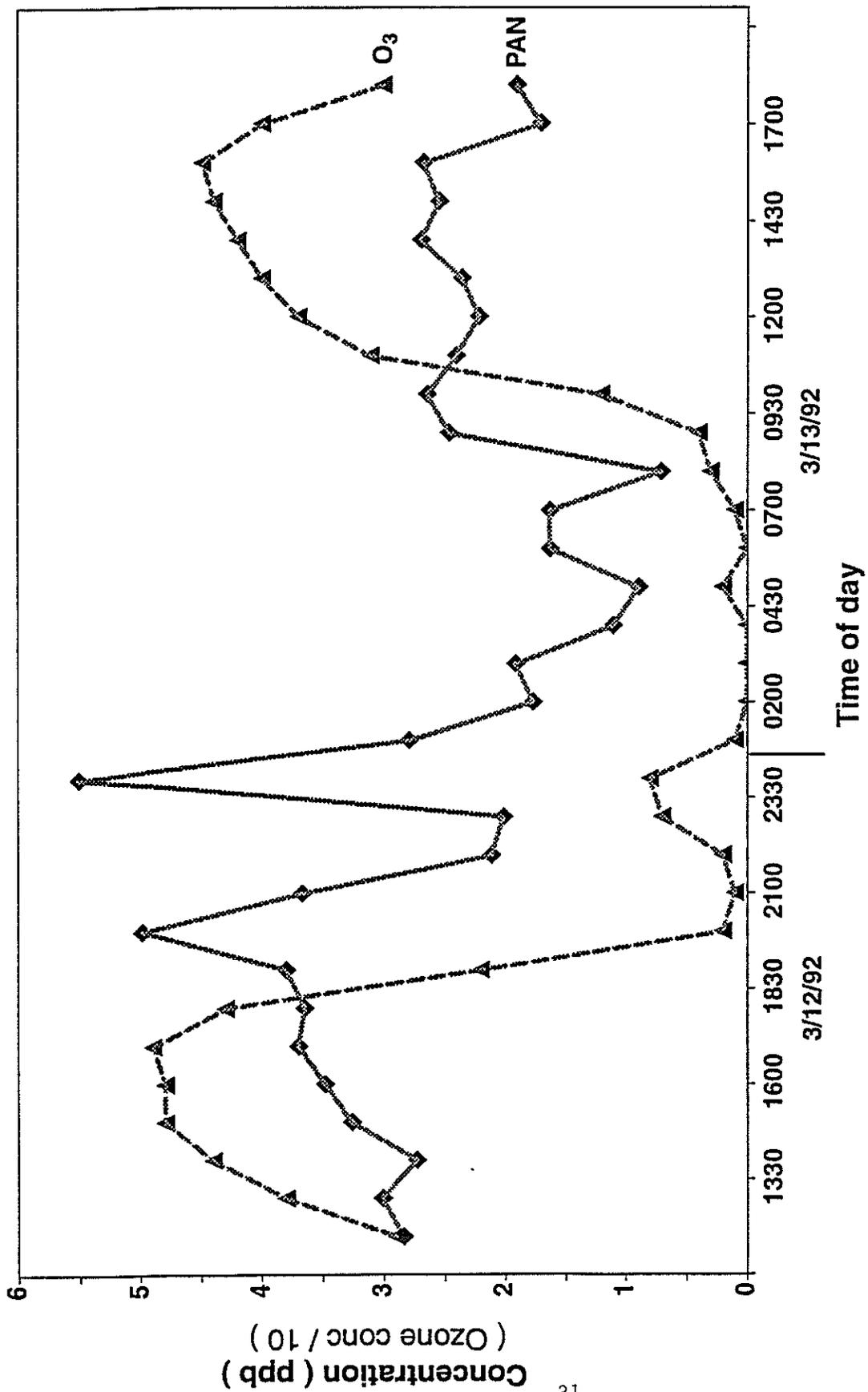


Figure 17. PAN and O₃ concentrations during March 12-13, 1992, Albuquerque, New Mexico. Site 2ZM.

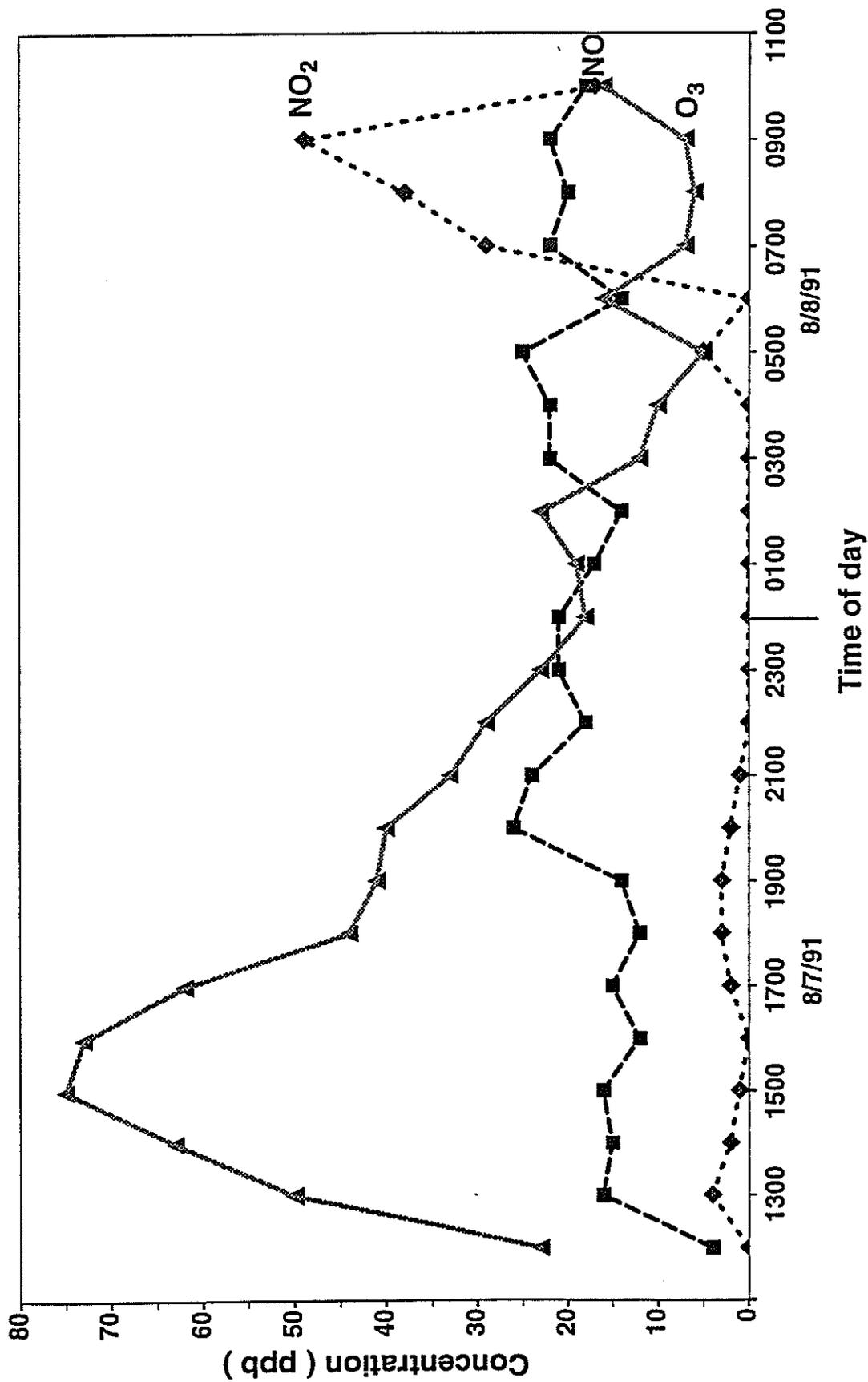


Figure 18. O₃, NO, and NO₂ concentrations for August 7-8, 1991, Albuquerque, New Mexico. Site 2ZM.

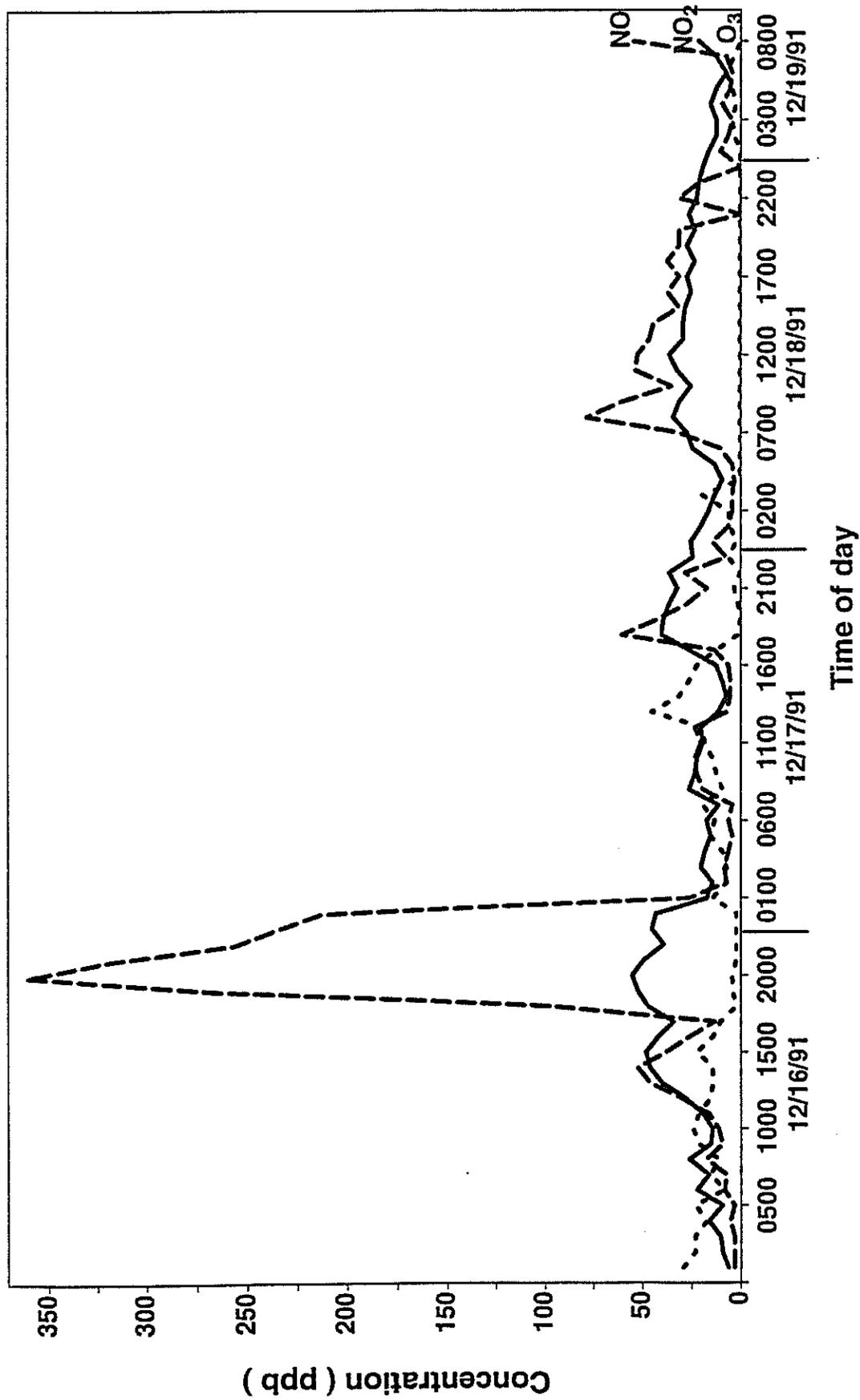


Figure 19. O₃, NO, and NO₂ concentrations during December 16–19, 1991, Albuquerque, New Mexico. Site 2ZM.

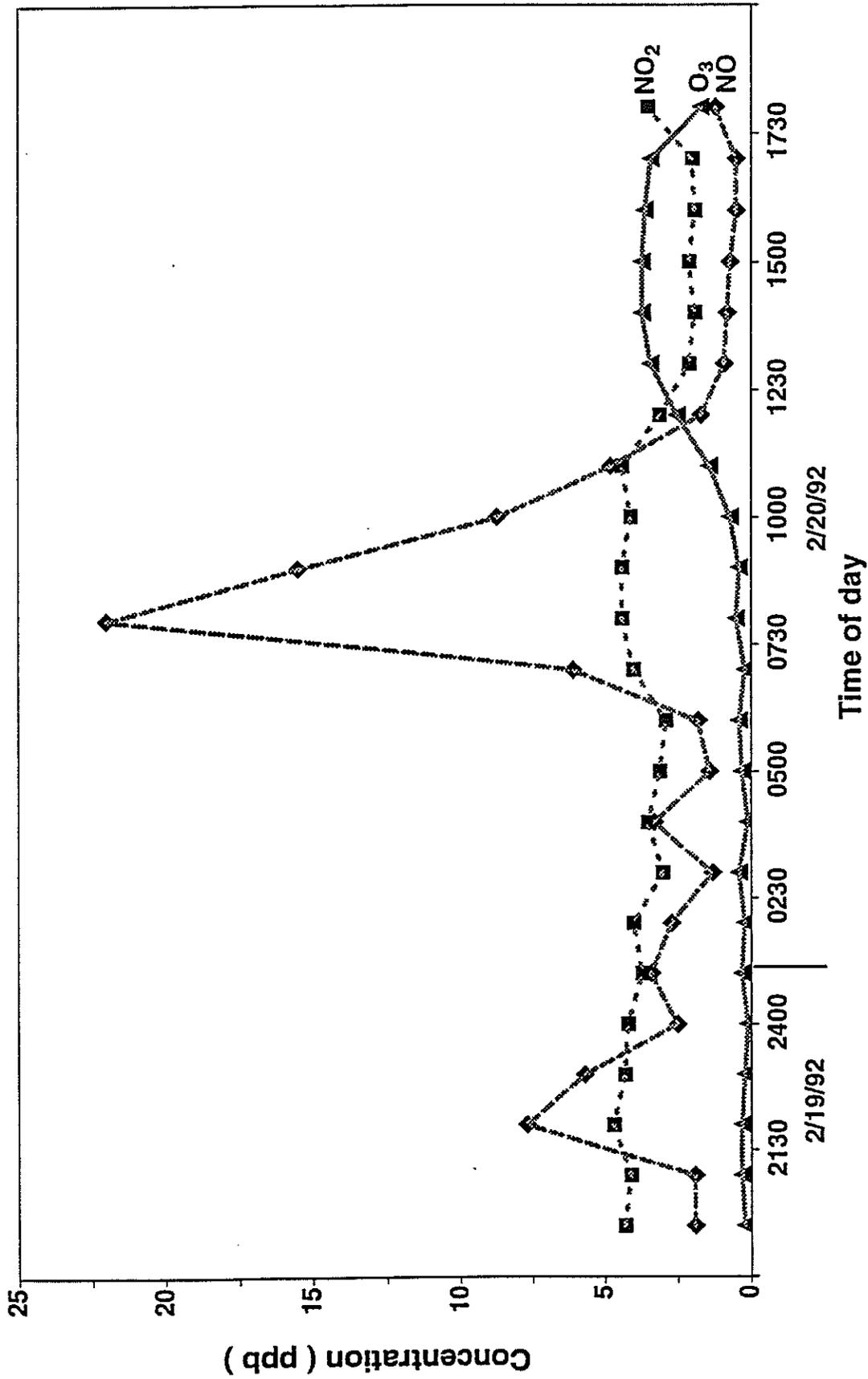


Figure 20. O₃, NO, and NO₂ concentrations during February 19–20, 1992, Albuquerque, New Mexico. Site 2ZM.

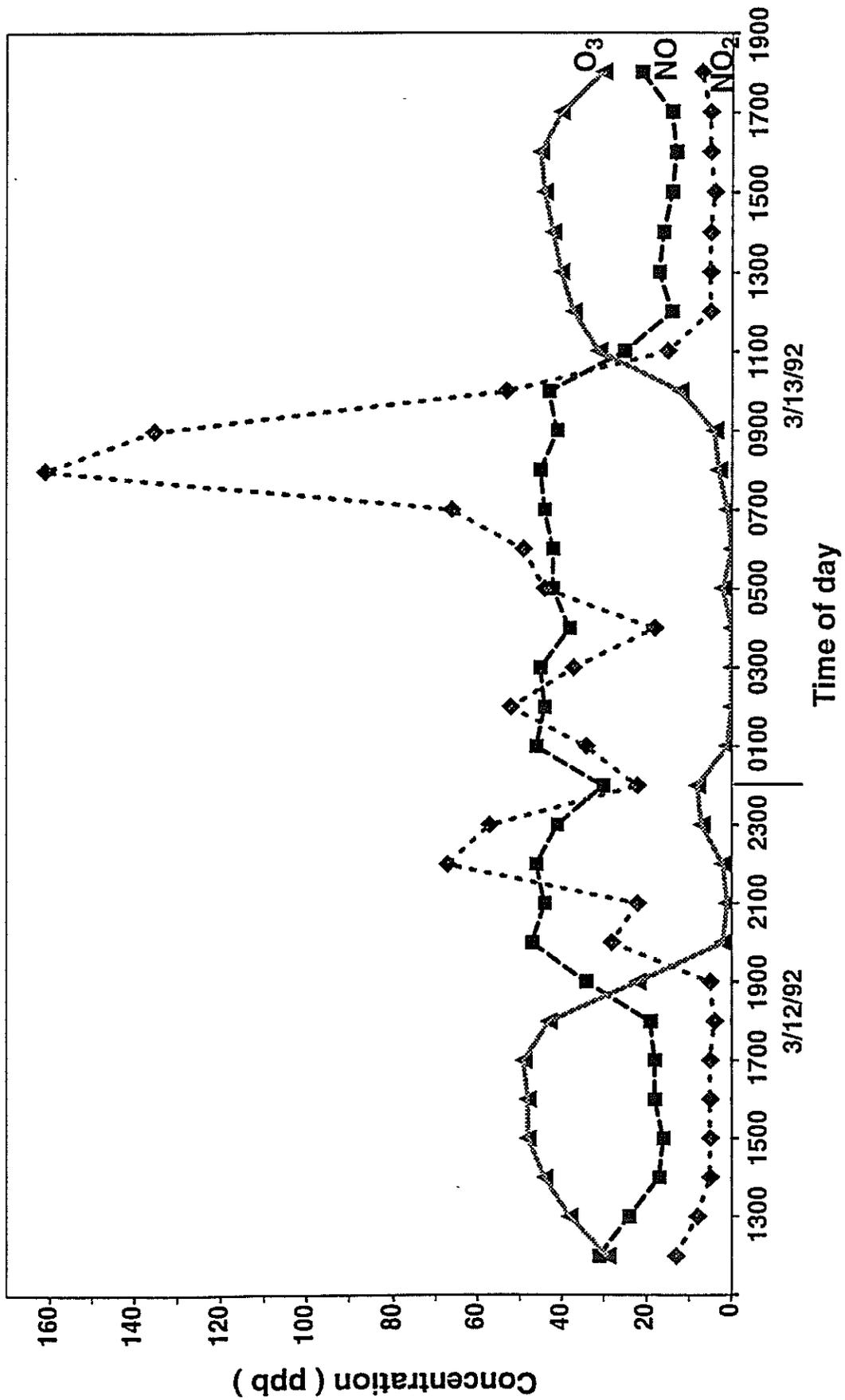
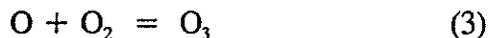
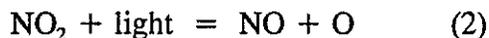
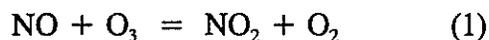


Figure 21. O₃, NO, and NO₂ concentrations during March 12–13, 1992, Albuquerque, New Mexico. Site 2ZM.



That is, when O_3 and NO are present, NO is oxidized to NO_2 [eq. (1)] and reduces O_3 concentrations but sunlight then breaks NO_2 down to NO and O [eq. (2)] and O then reacts with O_2 to produce O_3 which can then recycle. The buildup of O_3 is due to organic oxygenated radicals taking the place of O_3 in reaction (1) thereby allowing O_3 to accumulate, i.e.



CONCLUSIONS

The training potential for students has been successfully addressed with the involvement of six students on the project including two graduate students and four undergraduate students. In addition, instrumentation has been improved and upgraded with the addition of a field-adaptable gas chromatograph and detector, an automatic sampling valve, an electronic controller interface, an eight-channel digital data logger and upgrades to ozone and NO_x analyzers.

The concentrations of low molecular weight aldehydes, acetone and formic acid have been determined in Albuquerque as a function of season. These compounds exhibit higher concentrations than found at a control site in Socorro, New Mexico suggesting that anthropogenic sources in the urban environment may contribute to levels of organic compounds. These organic compounds may eventually lead to increases in urban ozone concentrations. PAN concentrations have increased slightly since 1988 but, of possibly greater

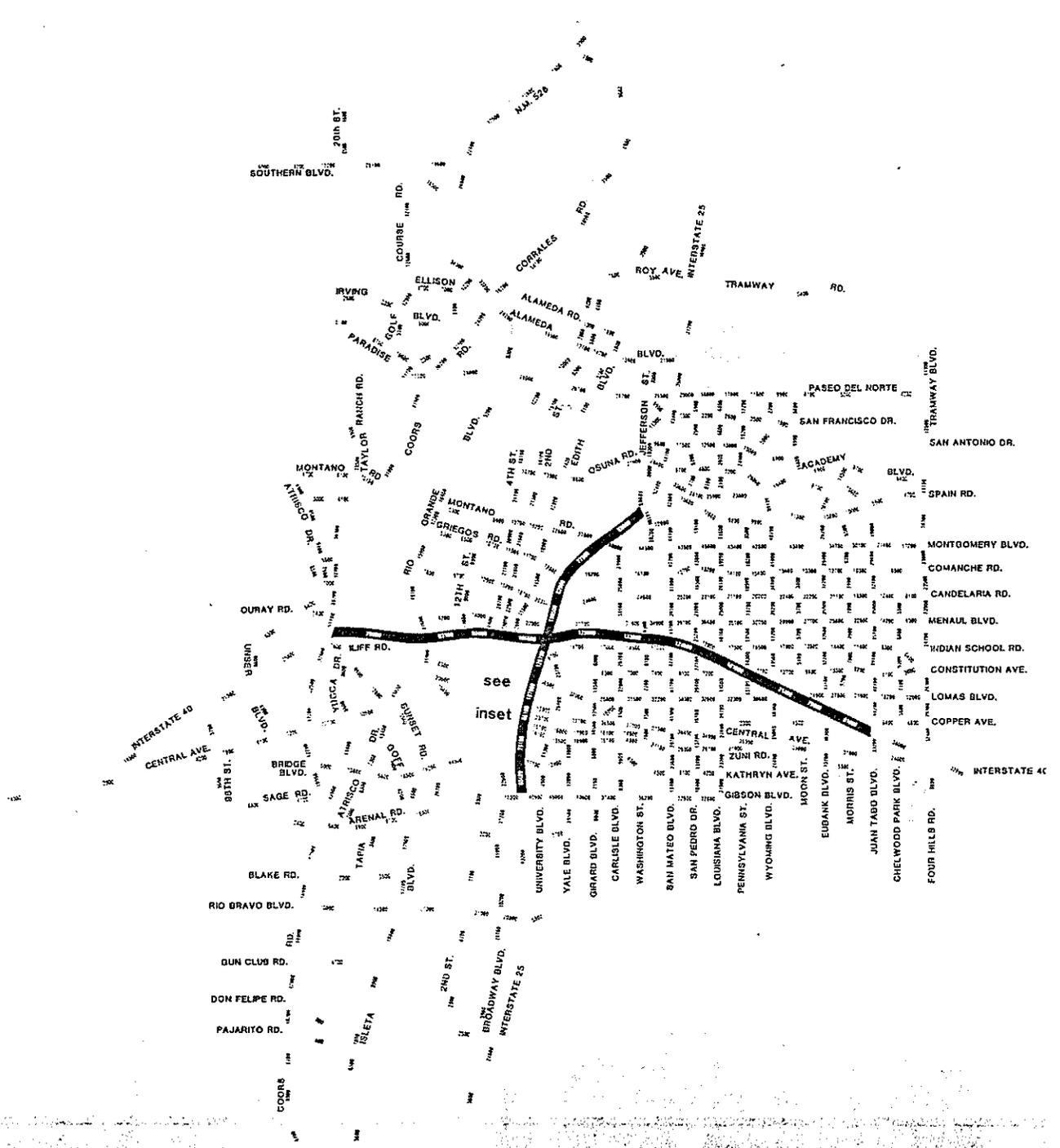
significance, has been a large increase in the PPN/PAN ratio that suggests an increasing primary source of organic pollutants. Further, detailed studies are necessary to ascertain specific cause and effect relationships. More long-term, diurnal measurement need to be performed during summer when no oxygenated fuels are used and in winter when the oxygenated fuel program is in place. In addition, analysis of non-methane hydrocarbons needs to be performed in conjunction with other analysis to help establish the role of plant emissions in the process.

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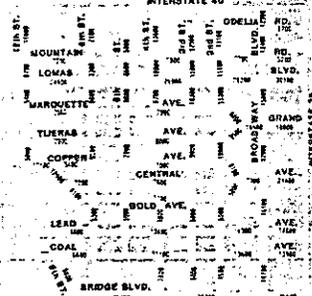
APPENDIX A



Average Weekday Traffic Flows

1000	4800
5000	14900
15000	24900
25000	34900
35000	44900
45000	54900
55000	134900

inset



1988 TRAFFIC FLOWS

for the

GREATER ALBUQUERQUE AREA

prepared by
Middle Rio Grande Council of Governments
 and
New Mexico State Highway and Transportation Department

In cooperation with the local governments
 in the Albuquerque Urban Area and
 U.S. Department of Transportation,
 Federal Highway Administration



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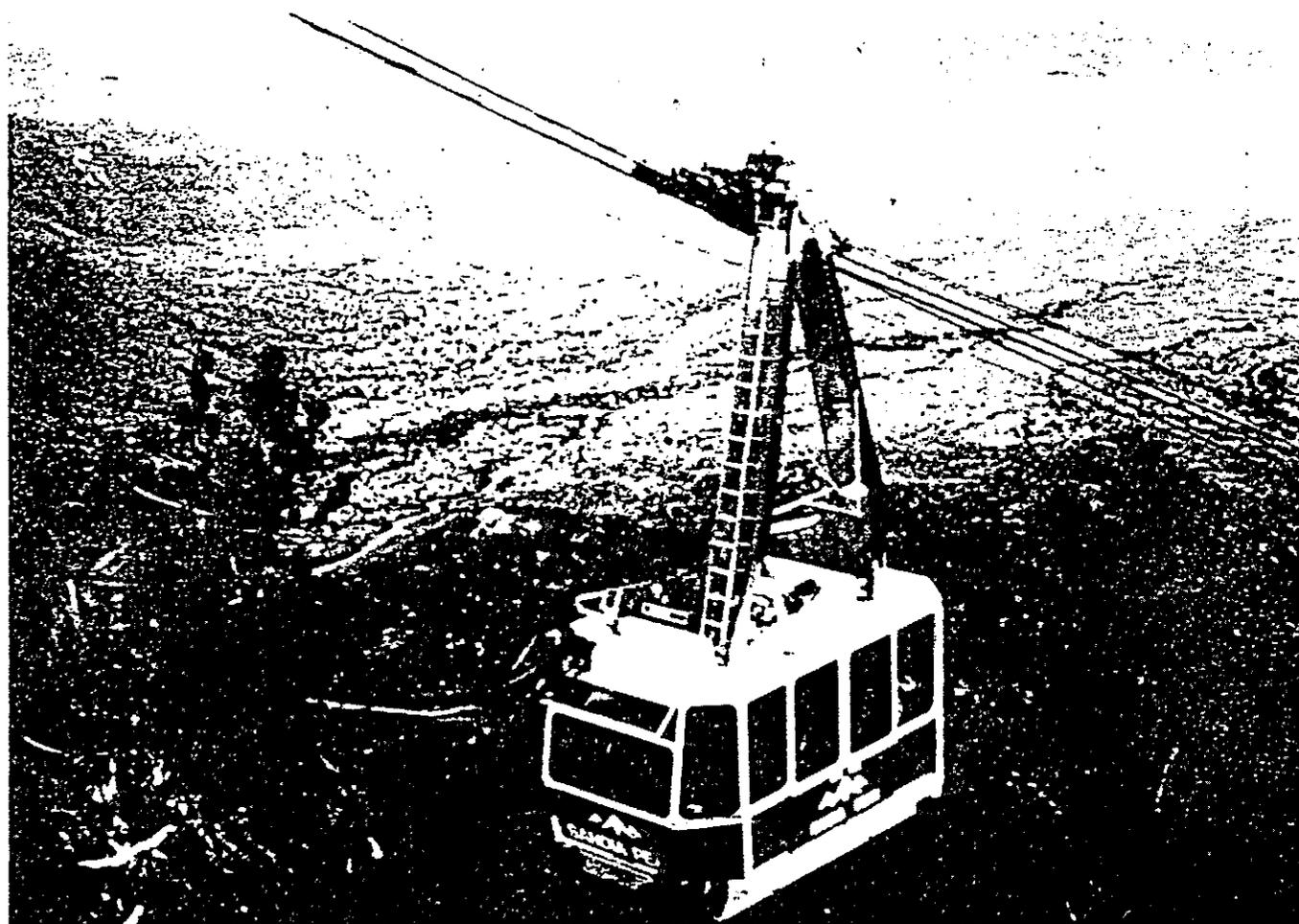
NOTE: Traffic flow data was obtained from a survey conducted by the New Mexico State Highway and Transportation Department and the Federal Highway Administration. The data is for the year 1988.

APPENDIX B

11th Rocky Mountain Regional Meeting

American Chemical Society

Program and Abstracts



June 10-12, 1992
Four Seasons Quality Hotel
Albuquerque, New Mexico

76 CONCENTRATIONS OF LOW MOLECULAR WEIGHT CARBONYL COMPOUNDS IN ALBUQUERQUE AIR;
Michelle Whetten-Cash and Carl J. Popp, Department of Chemistry, New Mexico
Institute of Mining and Technology, Socorro, New Mexico 87801

A study of the composition of Albuquerque, New Mexico air has been initiated to study the effects of the mandatory oxygenated fuels program on the concentrations of a variety of trace atmospheric species, including low molecular weight aldehydes and ketones. Albuquerque faces problems similar to other cities in that the ambient levels of ozone (O_3) and carbon monoxide (CO) can approach or exceed EPA limits. The oxygenated fuels program is one attempt to alleviate the potential violation of EPA standards. A possible side effect may be to increase the release of oxygenated organic emissions. Average concentrations for compounds identified to date in Albuquerque for combined summer and winter samples are: Formaldehyde (6.0 ppb), acetaldehyde (21.2 ppb), propionaldehyde (0.72 ppb) and acetone (0.80 ppb) while concentrations in air in more rural Socorro were 3.7, 0.86, 25. and 1.4 ppb respectively. Acetaldehyde concentrations are much higher in summer in Albuquerque which may reflect contributions from vegetation. The sampling method utilizes a Sep-pak cartridge which has been treated with 2,4-dinitrophenylhydrazine. The corresponding hydrazones are eluted with acetonitrile, separated by High Performance Liquid Chromatography, and detected using a UV-Vis detector.

77 FORMATE AND ACETATE CONCENTRATIONS IN AIR, PRECIPITATION AND PARTICULATES AT
URBAN AND RURAL SITES IN NEW MEXICO; Lin Zhang and Carl J. Popp, Department of
Chemistry, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801

Formate, acetate and inorganic anions (Cl^- , NO_3^- and SO_4^{2-}) were measured in rain, snow, air, aerosol, and dry deposition in Socorro and Albuquerque, New Mexico and in the Magdalena Mountains during the summer of 1991 and winter of 1991-1992. All samples were analyzed by ion chromatography. The ratio of acetate to formate was 0.8 and 1.7 in rain and snow samples respectively during the winter of 1991 in Socorro. At ground level the average concentrations of gas-phase samples of HCO_2^- , Cl^- , NO_3^- and SO_4^{2-} were 1.4 ppb, 195 ppb, 49.2 ppb, and 16.8 ppb respectively during the summer of 1991 in Socorro with average concentrations of gas-phase samples of the same species were 6.4-7.1 ppb, 132-177 ppb, 69-55ppb and 26-17 ppb at two sites in Albuquerque during the same period. The average concentrations of formate were 4.3 ppb in an open area and 8.8 ppb under trees in air samples collected during the summer of 1991 at the high mountain site. Acetic acid samples in gas-phase collection were subject to contamination in deionized water and lab air. Contributions to organic and inorganic acids can be from mobile emission, vegetative sources and chemical reactions in the atmosphere. Urban formate concentrations in the winter are similar to values found at a remote site in the summer when deciduous trees can contribute. Concentrations of formate in wet and dry deposition were 0.46 ppm and 22.2 ppm and for acetate were 0.49 ppm and 301 ppm respectively in Socorro during the winter of 1991.

78

SOLVENT ENHANCEMENT USING SUPERCRITICAL CO_2 IN
THE CLEANING OF MACHINE OILS, Wayne Bongiani
Los Alamos Nat'l Lab., MS E549, Los Alamos,
NM 87545

Solvents used in cleaning, such as the degreasing of machined parts, are usually volatile organic compounds, VOC's. Generally, VOC's represent an occupational hazard, most are flammable, and their disposal represents an environmental problem. Using a supercritical fluid, as a cosolvent dilutant, increases the cleaning effectiveness of the VOC and minimizes the amount of waste requiring disposal. This paper proposes a cosolvent cleaning model and presents recent data on the rate and effectiveness of supercritical CO_2 alone and with a VOC cosolvent.

APPENDIX C

All Concentrations in ppbv

Site	Date	Time	PAN	PPN	O3	NO	NO2	Form	Actl	Prop	Act	F.A.		
2ZM	8/5/91	0700			4	25	17							
		0800			6	28	19							
		0900			8	41	25							
		1000			18	22	25							
		1100			35	9	19							
		1200			47	4	14							
		1300			58	2	15							
		1400			71	1	12							
		1500			47	1	8							
		1600			53	0	5	6.5	94.7	<0.5		9.3		
		1700			61	1	6							
		1800			62	1	7							
		1900			48	0	6							
		2000			39	0	10							
		2100			30	0	16							
		2200			26	3	17							
		2300			28	0	13							
		2400			22	1	18							
		8/6/92	8/6/92	0100			23	0	15					
				0200			19	0	16					
				0300			16	0	16					
				0400			22	0	8					
				0500			11	2	17					
				0600			4	7	23					
0700					6	7	19	7.9	50.1	4.6		4.6		
0800					7	29	21							
0900					8	46	24							
1000					27	7	14							
1100					38	7	21							
1200					48	4	14							
1300					46	3	11					8.7		
1400					44	3	8							
1500					41	1	9							
1600					39	6	13					8.7		
1700					43	3	9							
1800					42	3	12							
1900					38	4	17							
2000					35	2	9							
8/7/91	8/7/91			0700										4.8
				1000										3.1
				1100	0.92									
				1200	0.9	0.08	23	0	4					
		1300	2.83	0.31	50	4	16							
		1400	3.85	0.8	63	2	15							
		1500	4.86	1.01	75	1	16							
		1600	5.85	1.17	73	0	12							
		1700	1.45	0.29	62	2	15							
		1800	0.52		44	3	12							
		1900	1.23		41	3	14							

	2000	2.17	0.36	40	2	26	
	2100	0.79		33	1	24	
	2200	1.43	0.19	29	0	18	
	2300	0.64		23	0	21	
	2400	0.6		18	0	21	
8/8/91	0100	0.82	0.12	19	0	17	
	0200	1.53		23	0	14	
	0300	0.89	0.18	12	0	22	
	0400	1.24		10	0	22	
	0500	1.13		5	5	25	
	0600	0.36		16	0	14	
	0700	0.4		7	29	22	
	0800	0.51		6	38	20	
	0900	0.56		7	49	22	
	1000	0.51		16	17	18	6.3
	1100	1.94					
	1200	1.65	0.03				
	1300	1.29	0.43				
	1400	0.75	0.22				
	1500	0.51					
	1600	0.26					
	1700	0.5					
	1800	0.31					
	1900	0.44					
	2000	0.91					
	2100	0.22					
	2200	0.35					
	2300	0.39					
	2400	0.18					
8/9/91	0100	0.21					
	0200	0.22					
	0300	0.22					
	0400	0.35					
	0500	0.22					
	0600	0.27					
	0700	0.46					
	0800	0.59					
	0900	0.62					
	1000	1.17					
	1100	1.49					
	1200	1.92	0.42				
	1300	5.5	0.26				
	1400	4.39	1.09				
	1500	1.53	0.78				
	1600	0.82	0.47				
	1700	0.7					
	1800	0.93					
	1900	0.43					
	2000	0.36					
	2100	0.6					
	2200	0.47					

		2300	0.45						
		2400	0.6						
	8/10/91	0100	0.38						
		0200	0.84						
		0300	0.14						
		0400	0.61						
		0500	0.37						
		0600	0.33						
		0700	0.82						
		0800	0.33						
		0900	0.4						
		1000	1.14						
		1100	0.35						
2R	8/5/91	0900			1	13			
		1000		29	3	12			
		1100		43	1	12			4.3
		1200		48	0	18	5.3	1200 <0.5	
		1300		48	1	10			
		1400		51	1	8			
		1500		50	1	10			
		1600		50	0	6			
		1700		49	1	4			
		1800		48	2	6	6.4	25.2 <0.5	16
		1900		48					
		2000		51	0	12			
		2100		34	0	12			
		2200		30	1	12			
		2300		24	1	24			
		2400		14	4	75			
	8/6/91	0100		10	3	43			
		0200		6	4	63			
		0300		2	7	68			
		0400		2	4	50			
		0500		1	8	61			
		0600		0	33	50			
		0700		0	os	os			
		0800		7	48	52			
		0900		14	28	43			3.8
		1000		27	22	43	5.2	85.9 <0.5	
		1100		60	2	16			
		1200		45	0	10			
		1300		44	2	6			
		1400		44					3.8
		1500		52					
		1600		41					
		1700		41					
		1800		43					
		1900		39	1	5			
		2000		34	13	1			
		2100		30	10	1			
		2200		28	1	20			

	2300	17	0	25	
	2400	19	0	19	
8/7/91	0100	18	1	11	
	0200	11	1	15	
	0300	15	2	11	
	0400	12	5	10	
	0500	11	6	9	
	0600	5	8	16	
	0700	1	22	33	
	0800	36	27	40	2.6
	0900	13	34	28	
	1000	21	26	13	
	1100	36	12	10	4.8
	1200	62	7	4	
	1300	51	9	0	
	1400	52	9	0	
	1500	63	7	2	
	1600	69	7	4	
	1700	77	7	8	17.2
	1800	80	13	2	
	1900	50	16	18	
	2000	63	14	1	
	2100	32	11	3	
	2200	28	13	0	
	2300	19	12	4	
	2400	7	18	13	
8/8/91	0100	0	27	32	
	0200	1	21	21	
	0300	1	16	10	
	0400	0	17	10	
	0500	0	29	6	
	0600	0	27	14	
	0700	0	56	14	
	0800	2	28	25	3.6
	0900	2	44	26	
2ZM 12/16/91	0100	29	3	6	
	0200	23	3	9	
	0300	23	3	10	
	0400	17	5	16	
	0500	23	3	9	
	0600	8	8	22	
	0700	15	7	16	
	0800	11	17	26	
	0900	21	9	15	
	1000	24	11	14	
	1100	21	16	19	
	1200	15	30	28	
	1300	14	46	40	
	1400	14	52	46	
	1500	22	38	48	
	1600	14	26	42	

	1700	10	13	34					
	1800	2	96	47					
	1900	4	263	52					
	2000	4	361	55					
	2100	2	319	49					
	2200	2	256	39					
	2300	2	235	45					
	2400	2	213	43					
12/17/91	0100	14	26	17					
	0200	7	7	14					
	0300	7	8	20					
	0400	9	6	18					
	0500	15	4	15					
	0600	13	6	17					
	0700	19	4	11					
	0800	9	19	26					
	0900	12	22	23					
	1000	14	23	22					
	1100	18	20	19					
	1200	19	23	20					
	1300	45	7	11					
	1400	31	5	7					
	1500	26	5	9					
	1600	22	6	12					
	1700	12	13	26					
	1800	1	60	40					
	1900	0	42	39					
	2000	1	27	36					
	2100	3	17	32					
	2200	0	28	36					
	2300	6	7	24					
	2400	2	14	25					
12/18/91	0100	5	6	20					
	0200	6	4	16					
	0300	19	4	13					
	0400	0	3	9					
	0500	0	4	13					
	0600	0	10	24					
	0700	0	31	27					
	0800	0	78	34					
	0900	0	60	31					
	1000	0	35	25					
	1100	0	53	32					
	1200	0	52	36					
	1300	0	46	29					
	1400	0	44	29	7.7	2.3	1.8	0.7	7.7
	1500	0	31	28					
	1600	0	37	25					
	1700	0	31	27					
	1800	0	37	23					
	1900	0	31	27	5	2.3	1.8	3.1	

	1500	0.66	0		
	1600	0.36	0		
	1700	0.88	0		
	1800	0.61	0		
	1900	0.48	0		
	2000	0.73	0		
	2100	0.68	0		
	2200	0.42	3		
	2300	0.57	3		
	2400	0.49	1		
12/20/91	0100	0.38	0		
	0200	0.67	0		
	0300	0.13	0		
	0400		0		
	0500	0.17	0		
	0600	0.084	0		
	0700		0		
	0800	0.13	1		
	0900	0.25	7		
	1000		10		
	1100	0.17	16		
	1200		18		
	1300		20		
	1400	0.33	23		
	1500	0.72	24		
	1600	0.52	23		
	1700	1.58	22		
	1800	0.64	22		
	1900	0.33	23		
	2000	0.39	24		
	2100	0.4	24		
	2200	0.6	22		
	2300	0.68	21		
	2400	0.53	20		
12/21/91	0100	0.67	21		
	0200	0.68	20		
	0300	0.64	21		
	0400	0.57	21		
	0500	0.47	26		
	0600	0.37	26		
	0700	0.71	26		
	0800	0.25	26		
	0900	0.44	23		
	1000	0.57	23		
	1100	0.51	25		
	1200	0.42	25		
2ZM 2/18/92	1800		17	13	28
	1900		14	12	28
	2000		20	4	21
	2100		27	4	14
	2200		16	4	22

	0700	1	17	34
	0800	5	33	40
	0900	15	31	32
	1000	26	7	20
	1100	29	6	16
	1200	35	5	11
	1300	36	5	10
	1400	36	6	13
	1500	36	6	13
	1600	37	5	14
	1700	35	4	11
	1800	25	6	17
	1900	17	4	21
	2000	3	17	30
	2100	9	10	21
	2200	5	17	24
	2300	3	11	25
	2400	2	11	27
3/10/92	0100	2	8	24
	0200	8	4	14
	0300	13	4	10
	0400	8	4	13
	0500	9	4	11
	0600	8	5	10
	0700	2	15	21
	0800	3	38	26
	0900	7	23	22
	1000	10	30	24
	1100	24	9	17
	1200	30	6	11
	1300	33	5	9
	1400	37	5	9
	1500	37	4	9
	1600	36	4	10
	1700	30	6	12
	1800	23	8	19
	1900	8	21	34
	2000	10	14	34
	2100	4	9	34
	2200	0	15	36
	2300	15	26	37
	2400	0	19	35
3/11/92	0100	3	9	29
	0200	3	5	24
	0300	11	4	17
	0400	17	3	12
	0500	16	3	10
	0600	17	3	9
	0700	5	12	21
	0800	2	40	34
	0900	14	26	30

		1300	2.35	0.23	40	5	60.3	4.9	3.7	3.3	
		1400	2.69	0.17	42	5					
		1500	2.54	0.45	44	4					
		1600	2.67	0.24	45	5					
		1700	1.7	0.81	40	5				0.8	
		1800	1.9	0.27	30	7					
2R	3/12/92	1300								0.2	
		1400			45		58	7.4	2.6	0.8	
		1500			41						
		1600			43						
		1700			46		67.9	9.1	<0.7		
		1800			45						
		1900			41						
		2000			11						
		2100			9						
		2200			4						
		2300			1						
		2400			0						
	3/13/92	0100			0						
		0200			0						
		0300			0						
		0400			0						
		0500			0						
		0600			0						
		0700			0						
		0800			10						
		0900			8						
		1000			20		55.4	8.3	<0.7		
		1100			28						
		1200			34						
		1300			38						
		1400			36						
		1500			36		85	11.9	<0.7	3.8	
		1600			35						
Weir	7/30/91	1030								2.6	
NMT	7/31/91	1030								0.7	
	8/1/91	1030								0.5	
	8/2/91	1030								1.7	
	11/4/91	1030								8.8	
	11/5/91	0920								5.5	
	11/5/91	1530								7	
	11/6/91	1545					60	14	2.5		
	11/7/91	1420								7	
	11/8/91	1420								5.3	
	12/12/91	1600					<.7	<.9	46	1.6	
	12/13/91	1830					<.9	<.9	66	4.6	
	12/17/91	0900					<.9	1.4	13	0.5	
	12/17/91	1343					7.5	0.9	0.7	0.3	11.1
	12/17/91	1700					9.1	0.9	0.8	0.3	7.8
	12/18/91	1100					124				
	12/18/91	1408					44				

1/7/92	1100						7
1/7/92	1405						8.1
1/7/92	1712	11					2.6
1/8/92	1727						4.9
1/30/92	0630		21				
1/30/92	1230		25				
2/12/92	0832	75	21				
2/12/92	1100	109	34	15	87		
2/12/92	1250	66	15	14	85		
2/12/92	1434	91	19	8	47		
2/18/92	1041	90	24	13	56		
2/18/92	1250	29	36	72	17		
2/18/92	1542	75	7	4	8		
6/24/92	1020	27					
6/24/92	1600	25					
6/25/92	1330	10					
6/25/92	1640	7					