

Potential Air Quality Effects of Using Ethanol—Gasoline Fuel Blends: A Field Study in Albuquerque, New Mexico

JEFFREY S. GAFFNEY* AND
NANCY A. MARLEY

*Environmental Research Division, Building 203,
9700 South Cass Avenue, Argonne National Laboratory,
Argonne, Illinois 60439*

RANDAL S. MARTIN,[†] ROY W. DIXON,[‡]
LUIS G. REYES,[‡] AND CARL J. POPP[‡]

*Department of Mineral and Environmental Engineering and
Department of Chemistry, New Mexico Institute of Mining and
Technology, Socorro, New Mexico 87801*

The use of alternate fuels has been proposed as a method of improving urban air quality by reducing combustion-related pollution. One such program mandates the use of oxygenates in the wintertime to reduce CO emissions in cities such as Albuquerque, NM. A field study was conducted in Albuquerque to determine the atmospheric impacts of the use of ethanol fuels. Atmospheric concentrations of ozone, oxides of nitrogen, CO, peroxyacetyl nitrate (PAN), aldehydes, and organic acids were measured in the summer of 1993, before the use of ethanol fuels, and in the winters of 1994 and 1995, during the use of 10% ethanol fuel (>99%). Data showed increased levels of peroxyacetyl nitrate (PAN) and aldehydes in winter. The formaldehyde/acetaldehyde ratio was 1.4, indicating an anthropogenic source, and PAN and acetaldehyde levels were anti-correlated over short time periods, indicating primary acetaldehyde emissions. A comparison of data taken at rural sites south of the city indicates that although there is a significant anthropogenic component to the aldehyde concentrations during the winter, there are also contributions from the photochemical oxidation of natural hydrocarbons.

Introduction

The use of alternative fuels has been proposed as a method of improving urban air quality by reducing combustion-related pollution and minimizing U.S. dependence on foreign oil (1). In an attempt to speed progress toward urban attainment of the National Ambient Air Quality Standards, oxygenated and reformulated gasoline programs were mandated by the 1990 Clean Air Act Amendments in the worst nonattainment areas. Specifically, the oxygenated fuels program requires the use of fuels containing 2.7% oxygen by weight (e.g., methanol, ethanol, methyl *tert*-butyl ether [MTBE]) in the wintertime to reduce CO emissions while the reformulated gasoline program requires fuels containing 2% oxygen in the summer to reduce ozone formation (2).

However, it is not completely certain that these blended fuels will help to abate urban air pollution (1–7). The effects of oxygenated fuels on ambient CO concentrations are small at best. Studies have shown reductions in wintertime CO concentrations to vary from as high as 10% to as low as zero (3). In addition, some evidence indicates that the use of these fuels may lead to increased ambient levels of other air pollutants, specifically aldehydes and peroxyacyl nitrates (4–8), which are both toxic and possible animal carcinogens (9, 10). Although these pollutants are not currently regulated, their potential health and environmental effects should be considered in assessments of the impacts of alternative fuels on air quality.

The use of oxygenated fuels in motor vehicles generally decreases the total hydrocarbon and CO emissions under moderate temperatures, although the total magnitude of this reduction is uncertain (3, 7, 11). However, the 1990 Clean Air Act Amendments also directed the U.S. Environmental Protection Agency (EPA) to consider not only the total mass but also the reactivity of hydrocarbon emissions in defining low-pollution fuels (12). The combustion of ethanol and methanol in spark-ignition engines results in increased emissions of primary acetaldehyde and formaldehyde, both of which are much more reactive in the atmosphere than their parent alcohols (13). The reaction of acetaldehyde with the OH free radical in urban atmospheres leads directly to the formation of the peroxyacetyl radical, which can react with NO₂ to form PAN. Increased concentrations of PAN have been observed in Rio de Janeiro, Brazil (5, 8), and in preliminary studies in Albuquerque (6) during periods of increased use of ethanol–gasoline blends. Currently, PAN is not a criteria pollutant, nor are aldehydes; however, these compounds are known to be potent lachrymators and mutagens. In addition, PAN is a plant toxin more potent than ozone (10). The data taken at both Rio de Janeiro and Albuquerque also indicate that peroxypropionyl nitrate (PPN), a larger peroxyacyl nitrate, is apparently produced at higher levels when ethanol or MTBE is used as an oxygenated fuel (3, 4). PPN has been found to be more toxic than PAN. It is a storage medium for NO₂ and will lead to the formation of PAN, peroxides, and aldehydes upon thermal decomposition as the air mass is transported downwind. Regional ozone levels can also be affected by changes in these emissions downwind of the urban center.

Albuquerque, NM, was chosen as a field study site because it is currently mandated, like increasing numbers of U.S. urban areas, to use ethanol–gasoline fuel blends and to institute bans on wood burning in an attempt to maintain air quality during the winter months. Although the use of blended fuels containing 10% alcohol is >99% in the winter, in the summertime the use is substantially less (<5% statewide) (14). This pattern makes Albuquerque an ideal site for studying the urban and downwind effects of alternative fuel usage. Atmospheric concentrations of ozone, oxides of nitrogen, CO, peroxyacetyl nitrate (PAN), aldehydes, and organic acids were measured in the summer of 1993, before the use of ethanol fuels, and in the winters of 1994 and 1995, during the use of 10% ethanol fuel. This paper focuses on measurements of the non-criteria pollutants (PAN and aldehydes) in an initial attempt to evaluate the total air quality effects of the combustion of ethanol–gasoline mixtures in motor vehicles. The results of this study have direct implications for the use of such fuel mixtures to reduce carbon monoxide emissions and ozone formation in a number of major cities and to bring these urban centers into compliance with the Clean Air Act.

* Corresponding author telephone: 630-252-5178; fax: 630-252-8895; e-mail: jeff_gaffney@qmgate.anl.gov.

[†] Department of Mineral and Environmental Engineering.

[‡] Department of Chemistry.

Experimental Methods

Field Sites. The city of Albuquerque 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 Rio Grande on the west, and Indian reservations on the north and south. It has little heavy industry so that the major daytime source of nitrogen oxides (NO_x) is motor vehicle traffic. The terrain is ideal for periodic thermal inversions, during which substantial levels of "brown-cloud" pollution occur (15). At other times, the meteorology in the complex terrain leads to periods in which background air infiltrates the city, improving the air quality significantly.

The sampling site used in this study is located in the center of the urban area, near the two major freeways. The site is maintained by the city of Albuquerque Air Quality Control Division as part of its air quality network and contains O_3 , NO_x , CO, wind speed, and wind direction instruments that are routinely maintained. In addition, field measurements of PAN, aldehydes, and organic acids along with ultraviolet-B (UV-B) radiation and daytime temperatures were taken at the site. Data were collected for periods of 1 month during July–August 1993, 1 month in January–February 1994, and 2 weeks during January 1995.

For comparison with the samples taken in the city of Albuquerque, a limited number of samples were taken at two rural locations for aldehydes and organic acids. The first site is in the city of Socorro, NM, which is located 75 mi south of Albuquerque and has a population of about 9000. Samples were obtained at the campus of New Mexico Institute of Mining and Technology in 1993 and 1994. In the winter of 1995, the sampling site was moved to a more centrally located site that was impacted with vehicular traffic. To confirm that elevated levels of aldehydes were due to transport from Albuquerque and not local sources, samples were also taken at a second rural site in 1995. This second site is a remote mountain site at Langmuir Laboratory in the Magdalena Mountains west of Socorro.

Instrumental Methods. Peroxyacyl nitrate (PAN and PPN) measurements were taken by using PANalyzers, which are automated gas chromatographs equipped with electron capture detectors (16). The PANalyzers used ultra-high-purity nitrogen as the carrier gas and had an automated gas-sampling system consisting of a six-port solenoid valve (Rheodyne, Teflon-lined) connected to an electronic relay controller. Samples were analyzed every 30 min and reported as 1-h average values for direct comparison with the air quality data, which are reported by the city of Albuquerque as hourly averages. A recording integrator (Shimadzu CRIB) was used to collect PAN data and examine concentrations of higher analog peroxyacyl nitrates, such as PPN. Instruments were calibrated by using PAN and PPN standards synthesized from the corresponding anhydride, placed in diffusion tubes, and referenced to a calibrated NO_x analyzer (10, 17). The instruments were calibrated before and after the field measurements. The results of the two calibration procedures were averaged, and agreement was 30% or better with a daily precision of 15%. Detection limits were 30 parts per trillion.

Aldehydes were sampled with Sep-Pac C_{18} cartridges (Waters/Millipore Corp.), coated in the laboratory with acidified 2,4-dinitrophenylhydrazine (DNPH) after procedures described previously (5, 18, 19). Briefly, the cartridges were cleaned with acetonitrile, coated with DNPH, wrapped in aluminum foil, and stored in a refrigerator in dark glass containers. Air samples were pulled through the cartridges at about 1 L/min with air flow controlled by rotameters calibrated every few days with a mass flowmeter (Aalborg Corp.) or a bubble meter.

Ambient air was filtered through a 5- μm Teflon filter to remove particles. The cartridges were wrapped with alu-

minum foil during sampling, rewrapped, and stored in a dark glass bottle on ice during transport to the laboratory. All materials were handled with new latex gloves during sampling and analysis. Collection of daily field blanks resulted in 14–28 blanks, depending on the length of each sampling period. Samples were collected at Socorro for comparison with the urban samples.

Ten percent of the samples were run as duplicates; the relative error was always less than 15% and generally less than 10%. The exposed cartridges were analyzed by using high-performance liquid chromatography (HPLC) on a Waters Corp. HPLC system and a C_{18} , 5- μm column with UV detection at 360 nm. The eluent was 60:40 acetonitrile:water. Principal attention was given to formaldehyde, acetaldehyde, and acetone, although other aldehydes and ketones were examined as they relate to natural carbonyl compounds produced by the oxidation of isoprene and the monoterpenes. Standards were prepared from twice-recrystallized DNPH derivatives of the carbonyl compounds prepared (in the laboratory in the range of 1–200 ng depending on the compounds). The R^2 values for the calibration plots were always >0.99 . The sensitivities, as determined by the slope of the calibration curves were 1.83×10^4 for formaldehyde, 1.81×10^4 for acetaldehyde and 1.97×10^4 for acetone (response vs ng/10- μL sample). Collection efficiencies for this procedure have been shown to be 96, 95, and 88% for formaldehyde and 99, 99, and 92% for acetaldehyde at 71, 44, and 28% relative humidity (20). Relative humidities were always above 25% and an average of 45% for each period of study. Detection limits, determined as twice the standard deviation of the blank values, were 0.5–0.7 ppb (2–4 ng/10- μL injection) for the carbonyls. The largest detection limits were for the four carbon species (methyl ethyl ketone, methacrolein, methyl vinyl ketone, and butyraldehyde) whose chromatographic peaks were not always well resolved. Standards were analyzed every 10 samples to verify the calibration curves.

The major interference for the DNPH technique has been shown to be reaction of ozone with the hydrazones leading to low results (21). For example, in the presence of 120 ppb of O_3 , the measured formaldehyde concentrations in the range of 20–40 ppb was 34% low. At concentrations below 120 ppb of O_3 , no interference is observed with this technique. With the exception of one summertime episode (see Figure 1), ozone concentrations were below this level during each period of study.

Organic acid samples were collected at 2-h intervals during the day and at 6-h intervals at night, corresponding to the sample collection schedule for the carbonyl compounds. Water mist nebulizers (DeVibiss Model 40) were used with the procedures described by Cofer et al. (22) and modified by Popp et al. (6). Ambient air at flows of 3–5 L/min, controlled by a rotameter, was pulled through a 5- μm prefilter and then the nebulizer. Samples were collected by rinsing the nebulizer several times with distilled, deionized water (DDW) into volumetric flasks and then into dark glass bottles with Teflon-lined lids. Several drops of chloroform were added to retard bacterial growth. All samples were handled by using a new pair of latex gloves. Blanks were collected daily by rinsing the nebulizer with DDW and handling, diluting, and stabilizing as for the samples. Samples were also collected at Socorro for comparison with the urban samples.

The samples were analyzed by using ion chromatography (Dionex 2000 Si) and a Dionex AS 11 column with 35 mM $\text{K}_2\text{B}_4\text{O}_7$ as eluent. The acid detection limits, calculated from twice the deviation of the blanks, were 3–4 ppb for acetic acid, 2–2.5 ppb for formic acid, and about 1 ppb for propionic and pyruvic acid, which were detected in only about 10% of the samples. The atmospheric concentrations correspond to 0.05–0.25 ppm in solution. Averaged values for field blanks subtracted from the samples ranged from 0.05–10 ppm in

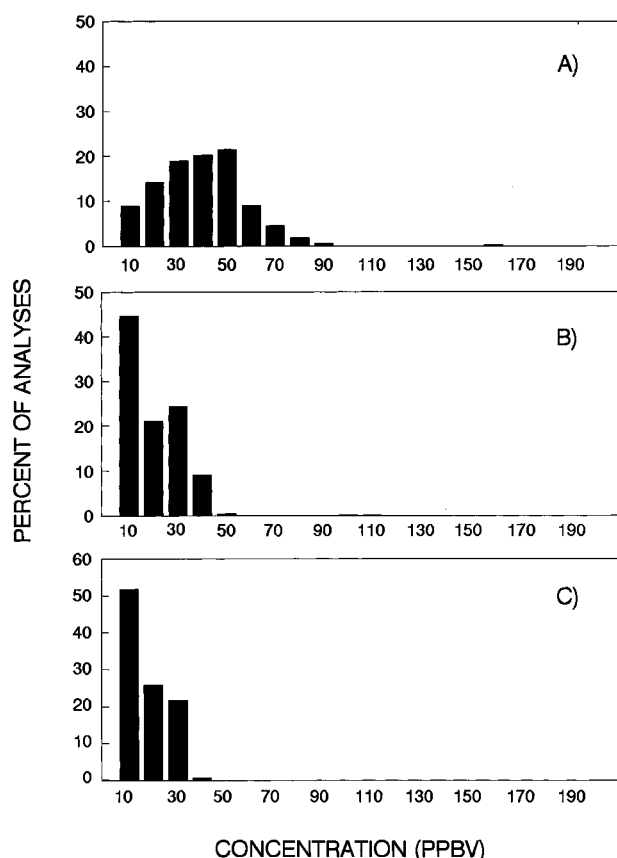


FIGURE 1. Frequency distributions for ozone analyses in Albuquerque, NM, during (A) the summer of 1993, (B) the winter of 1994, and (C) the winter of 1995.

solution for formic, propionic, and pyruvic acids to 0.20–0.30 ppm for acetic acid. Calibration solutions were made from >99.5% sodium salts (Aldrich Chemicals), and regression plots gave R^2 values better than 0.99. Standards were analyzed every six samples to verify the calibration curves.

Sensitivities as determined from the slopes of the calibration curves were 656.12 for acetic acid, 1578.03 for formic acid, and 613.68 for pyruvic acid (response vs ppm sample).

Gas analysis for NO_x , O_3 , and CO was performed by the city of Albuquerque Air Quality Control Division according to EPA-approved standard methods. The NO_x was measured by using standard ozone chemiluminescence analyzers (Monitor Labs 8440), O_3 was measured by using standard UV absorption methods (Dasibi 1003). All results are reported to the nearest 1 ppb. The CO measurements were made by nondispersive infrared spectroscopy and are reported to the nearest 1 ppm. All systems were calibrated weekly, and the data are reported as hourly averages.

A Richardson-Berger UV-B radiometer (Solar Light Co.) was used to assess the effective photochemical light intensity at the urban site during the summer of 1993 and the winter of 1994. This instrument allows direct continuous measurement of broadband ultraviolet radiation (290–320 nm) along with daytime temperatures. Measurements of both UV radiation and temperature were transferred to Lotus-123 data files at 5-min intervals during daylight hours. Since the radiometer was not used in the winter of 1995, daytime temperatures for this period were obtained from the City of Albuquerque airport weather station.

Results and Discussion

The average values obtained in the city of Albuquerque for each period of study (July 11–August 10, 1993; January 4–February 1, 1994; January 11–January 25, 1995) and the number of analyses used to obtain each value are given in Table 1. Similarly, the average values obtained at the rural sites are presented in Table 2. The average wind speeds for the three periods were quite comparable, although in 1995 the winds were more consistently from the north. Wind direction during the other two studies was more variable. The winter was relatively mild in 1994. Daytime temperatures averaged 24.7 and 10.3 °C for the summer of 1993 and winter of 1994, respectively. However, the winter of 1995 was much colder with an average temperature of 6.9 °C.

TABLE 1. Number of Analyses and Average Concentrations of Atmospheric Pollutants and Meteorological Parameters during Three Field Studies in Albuquerque, NM: summer 1993, July 11–August 10, 1993; winter 1993, January 4–February 1, 1994; winter, 1995, January 11–25, 1995

component	units	summer 1993		winter 1994		winter 1995	
		av	no.	av	no.	av	no.
wind speed	mph	5.2	710	5.7	657	5.3	340
UV-B	$\mu\text{W cm}^{-2} \text{ h}^{-1}$	9.1	408	1.8	236		
NO	ppb	6	702	62	600	57	340
NO_y^a	ppb	14	702	33	600	18	340
NO_x	ppb	20	702	94	600	75	340
ozone	ppb	35	712	15	664	11	340
CO	ppm	1	712	2	664	1	340
PAN	ppb	0.1	1388	0.4	914	0.2	366
acetic acid	ppb	6.7	133	1.3	117	0.5	43
formic acid	ppb	8.6	133	6.1	117	4.1	43
propionic acid	ppb	0.6	133	0.6	117	<1	43
pyruvic acid	ppb	0.4	133	2.1	117	<1	43
total acids	ppb	16.3	133	10.1	117	4.6	43
acetaldehyde	ppb	6.6	129	7.3	136	1.4	53
formaldehyde	ppb	13.9	129	16.8	136	3.2	53
propionaldehyde	ppb	0.7	129	<0.5	53		
total aldehydes ^b	ppb	21.2	129	24.1	136	8.2	53
acetone	ppb	4.3	128	0.3	136	1.8	53
methyl ethyl ketone	ppb	<0.7	136	0.9	53		
methacrolein	ppb	<0.7	136	<0.7	53		
total carbonyls	ppb	25.5	128	24.4	136	10.9	53

^a HNO_3 , PAN, etc. ^b May also include benzaldehyde and *p*-tolualdehyde.

TABLE 2. Number of Analyses and Average Concentrations of Atmospheric Pollutants and Meteorological Parameters during Three Field Studies in Albuquerque, NM: summer 1993, July 11–August 10, 1993; winter 1993, January 4–February 1, 1994; winter, 1995, January 11–25, 1995

component	units	Socorro, NM						Langmuir, NM	
		summer 1993		winter 1994		winter 1995		winter 1995	
		av	no.	av	no.	av	no.	av	no.
acetic acid	ppb	16.1	20	32.0	25	12.6	41	17.1	17
formic acid	ppb	3.7	20	4.4	25	1.6	41	1.5	17
propionic acid	ppb	<1	20	1.1	25	<1	41	<1	17
pyruvic acid	ppb	<1	20	<1	25	<1	41	<1	17
total acids	ppb	19.1	20	37.5	25	10.5	41	13.2	17
acetaldehyde	ppb	4.1	37	1.3	25	5.4	51	2.7	21
formaldehyde	ppb	7.6	37	1.3	25	14.2	51	10.1	21
propionaldehyde	ppb	1.0	37	0.7	25	<0.5	51	<0.5	21
total aldehydes ^a	ppb	13.0	37	3.3	25	20.2	51	11.7	21
acetone	ppb	7.6	33	1.2	24	7.1	51	11.4	21
methyl ethyl ketone	ppb	<0.7	33	3.2	24	1.4	51	1.1	21
methacrolein	ppb	<0.7	33	<0.7	24	0.8	51	1.7	21
total carbonyls	ppb	20.6	33	7.7	24	29.5	51	25.9	21

^a May also include benzaldehyde and *p*-tolualdehyde.

Average NO, NO_x, NO_y (reported as the difference between the NO and NO_x channels), and PAN levels were all substantially higher in Albuquerque in the winter. This elevation was probably caused by the boundary layer thermal inversions that occur in the winter months and act to trap these pollutants over the city. The average O₃ concentrations were lower in the winter, probably because of the reduced light intensities (accompanied by decreased photochemistry) and higher levels of NO (which reacts rapidly with O₃).

Figure 1 shows the frequency distribution for all ozone analyses taken for the Albuquerque summer and winter field studies. The summer frequency distribution clearly indicates higher levels of ozone during this more photochemically active period. However, ozone was above criteria levels during only one episode in the summer study, indicating a period of relatively clean air compared to past levels measured in Albuquerque (6).

The frequency distribution for PAN analyses in Albuquerque are presented in Figure 2. The results clearly show that urban PAN levels are higher in the winter than in the summer, despite the lower photochemical activity. Because the daytime temperatures were fairly comparable for the summer of 1993 and the winter of 1994, it appears that the higher winter values are due primarily to local production of PAN.

Mean levels of acetic acid and formic acid in Albuquerque (Table 1) were lower in winter, with total amounts of 7.4 ppb in 1994 and 4.6 ppb in 1995, while the total concentration for summer 1993 was 15.3 ppb. This falls in the concentration range observed in southern California (23, 24). Similar seasonal trends reported for remote forested areas (25, 26) have been attributed to the direct emission of organic acids from vegetation during the productive summer months. However, this concentration decrease in winter was not seen in the rural areas south of Albuquerque (Table 2). In urban areas, carboxylic acids are thought to be produced photochemically and by reaction of ozone with olefins (27). Therefore, the diminished photochemical activity during the winter could be a contributing factor to the seasonal differences in the city. The higher values for organic acids in the rural areas during the winter are likely caused by wood burning, which is occasionally banned in Albuquerque but not in the rural areas.

Total aldehyde concentrations in the rural area of Socorro were higher in the summer of 1993 and lower in the winter of 1994, indicating a biogenic source during the summer months. However, in Albuquerque, these concentrations were slightly higher in the winter of 1994, indicating an anthropogenic source for the aldehydes in the urban area.

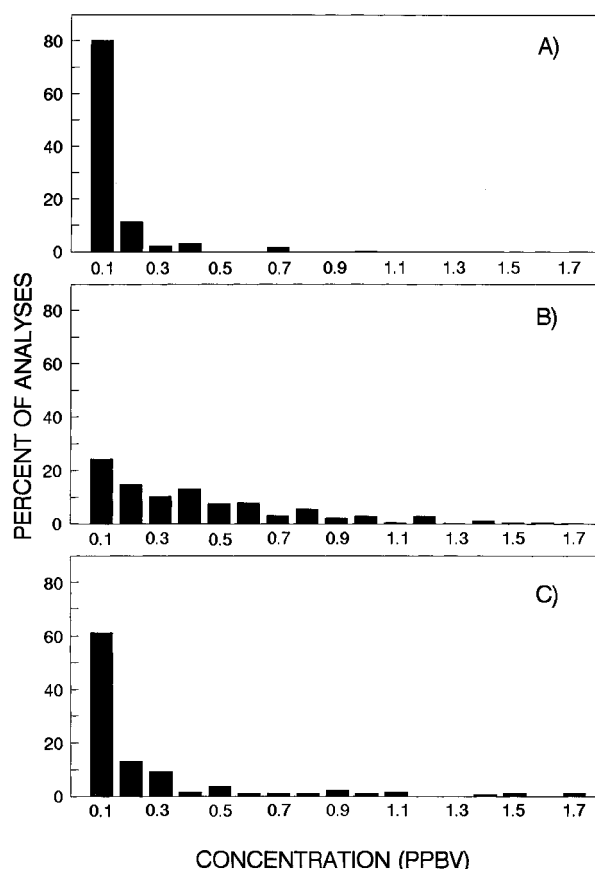


FIGURE 2. Frequency distributions for PAN analyses in Albuquerque, NM, during (A) the summer of 1993, (B) the winter of 1994, and (C) the winter of 1995.

In the winter of 1995, acetaldehyde and formaldehyde concentrations were lower in Albuquerque and significantly higher in both rural areas studied than the previous year. This is due to meteorological conditions that transported the pollutants south of the city of Albuquerque into the surrounding rural areas. Lower PAN levels in Albuquerque in the winter of 1995 than in 1994 are also indicative of downwind transport of the primary pollutants. The downwind levels of PAN are also likely to be higher than those in the city because PAN is formed from the oxidation of the primary aldehydes.

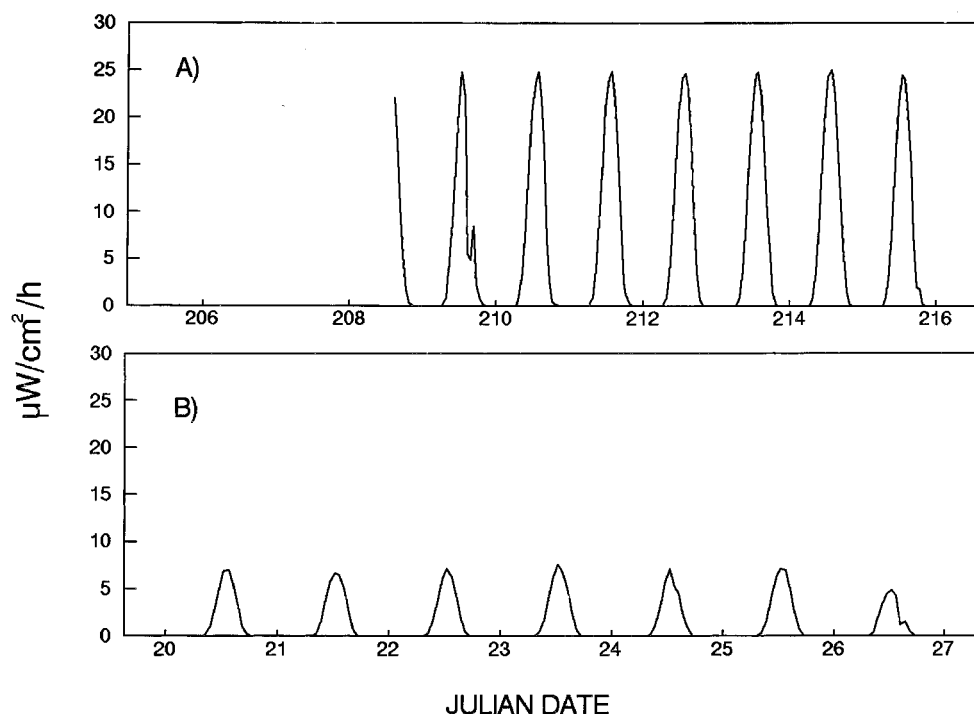


FIGURE 3. Ultraviolet-B irradiance in Albuquerque, NM, during (A) the summer of 1993 and (B) the winter of 1994.

Unfortunately, PAN levels were not obtained in Socorro for comparison.

Average acetone concentrations generally follow the same trend as the aldehydes, being higher in the summer of 1993 than in the winter of 1994, indicating a biogenic source, and also showed evidence of some downwind transport to the rural areas in 1995. Acetone is a direct biogenic emission product from many plants and has been suggested as an oxidation product of α -pinene (28). Acetone can comprise 10–70% of the total carbonyl emissions from motor vehicles; it is an intermediate product of the atmospheric oxidation of propane (28). This ketone is probably produced by both natural and anthropogenic sources. As a potentially photochemically active compound under UV-B radiation, acetone may become important if UV-B levels increase because of stratospheric ozone depletion.

Summer and Winter Air Quality. Two pollution episodes, which include 11 days during the summer of 1993 and 7 days during the winter of 1994, have been studied to compare seasonal air quality in the city of Albuquerque and to indicate possible impacts of wintertime alcohol fuel usage. Figure 3 presents the UV-B irradiance for the summer and winter during the study periods. The data for the two periods are remarkably consistent and indicate minimal effects of clouds. Doublets on day 209 of 1993 and day 26 of 1994 indicate times when local clouds moved into the area, causing a reduction in UV-B intensity because of light scattering. However, for the most part, the meteorology was very clear. Mean values for UV-B during the summer were higher by approximately a factor of 5 than during the winter. Maximum values during the summer were $28 \mu\text{W cm}^{-2} \text{ h}^{-1}$, compared to $7.6 \mu\text{W cm}^{-2} \text{ h}^{-1}$ during the winter. These data support the assumption that photochemical activity is reduced during the winter. Summertime winds were primarily from the south, southeast, and southwest (Socorro to Albuquerque), but wintertime winds were mostly from the north and might move air pollutants downwind from Albuquerque to Socorro.

As an indication of general air quality, levels of CO were generally higher during the winter. The average CO concentration for the winter of 1994 was about 2 ppm, compared to 1 ppm for the summer of 1993 (Table 1). However, the frequency of CO values above 3.0 was much higher in the

winter. In general, the number of CO exceedances in Albuquerque have been steadily decreasing since 1986, from 75 violations per year in 1984 to less than 5 since 1992 (29). The two major causes for this reduction in Albuquerque were the steady improvements in reductions of CO emissions due to the use of catalytic converters and the gradual removal of the older higher polluting vehicles with time as well the relative lack of temperature inversions caused by meteorological conditions during this period. This significant impact of meteorological conditions on CO concentrations has also been seen in Denver since 1983 (7).

Figure 4 presents hourly average concentrations for O_3 , NO, and PAN at the Albuquerque field site in the summer of 1993 and winter of 1994. The NO concentrations were much higher during the winter because of atmospheric inversions, which trap the pollutants in the boundary layer, and reduced photochemical activity in winter. Higher levels of NO were observed early and late in the day corresponding to traffic flow patterns that peak at approximately 7:30 AM and 4:30 PM. These NO concentration patterns are caused by the time-dependent daytime emissions and the subsequent atmospheric transport from the city.

In contrast to the NO data, O_3 concentrations depicted in Figure 4 show the opposite trends for summer and winter. Higher O_3 levels were observed during the summer, while much lower levels were found during the winter. This pattern is consistent with decreased light intensity (Figure 3) resulting in reduced photochemical activity in the winter, accompanied by higher levels of NO that titrates the ozone. These data sets clearly indicate the fairly good anti-correlation between ozone and NO, which occurs because NO reacts quite rapidly with ozone to produce NO_2 .

The Albuquerque PAN concentrations (Figure 4) were much lower in the summer than in the winter. In the summer, PAN concentrations exceeded 1 ppb twice for very short periods. The wintertime data set shows PAN concentration levels above 1 ppb for substantially longer periods of time, with PPN being observed on a number of occasions. The 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 the much lower photochemical reactivity in winter, PAN levels were signifi-

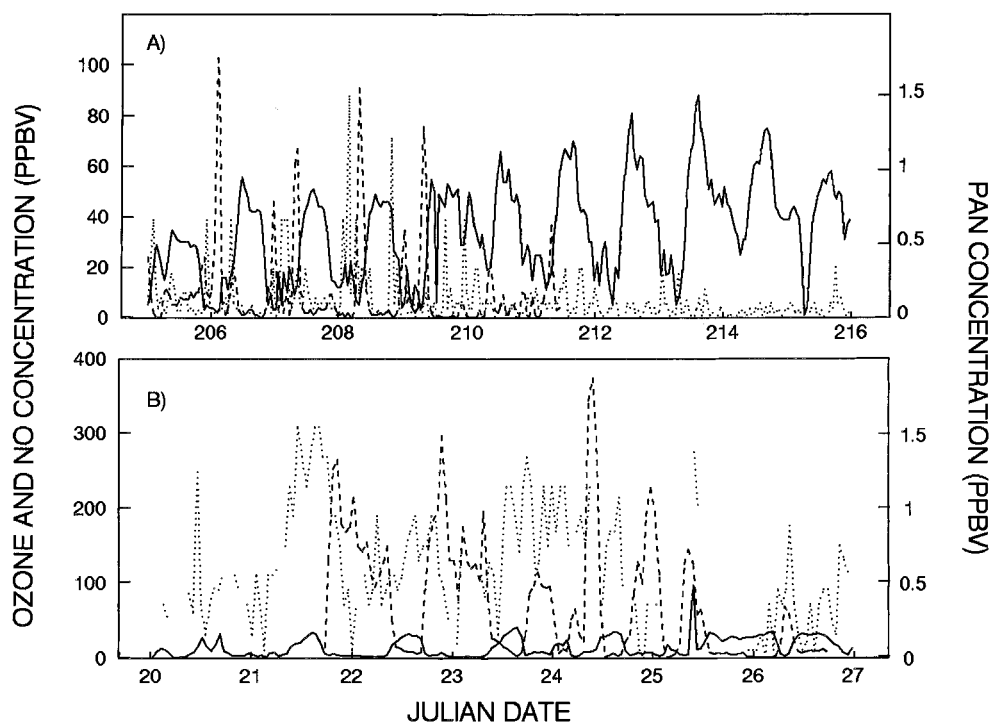


FIGURE 4. Ozone (—), NO (---), and PAN (···) concentrations in Albuquerque, NM, during (A) the summer of 1993 and (B) the winter of 1994.

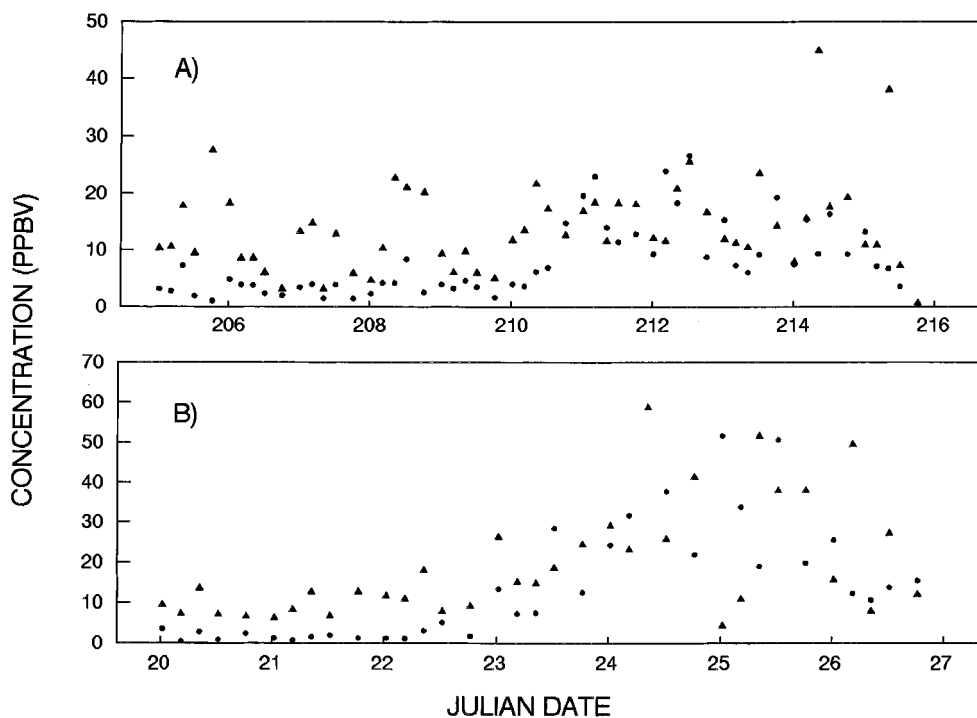


FIGURE 5. Acetaldehyde (●) and formaldehyde (▲) concentrations in Albuquerque, NM, during (A) the summer of 1993 and (B) the winter of 1994.

cantly higher in the winter than in the summer. The levels observed during this initial field study, however, were lower than those found in previous field efforts in Rio de Janeiro, where ethanol fuels were used (5, 8), perhaps because of the lower alcohol:gasoline ratios used in Albuquerque (10%) than in Brazil (30%) and because the Brazilian vehicles are not equipped with catalytic converters.

Acetaldehyde and formaldehyde levels for the summer of 1993 and the winter of 1994 are shown in Figure 5. Periods with higher acetaldehyde and formaldehyde levels occurred during the winter. The winter maximum value of acetalde-

hyde was about twice the summer maximum with a winter maximum value of approximately 50 ppb. With two exceptions, summer formaldehyde concentrations were below 25 ppb, while winter values reached 60 ppb in the later part of the period studied. More frequent episodes of high aldehyde concentrations were observed during the winter, consistent with the inversions occurring during the early morning hours. In addition, during the winter, the aldehyde concentrations were roughly anti-correlated with PAN levels (Figure 4), with days 20–24 corresponding to the highest PAN and lowest aldehyde concentrations and days 24–27 showing the op-

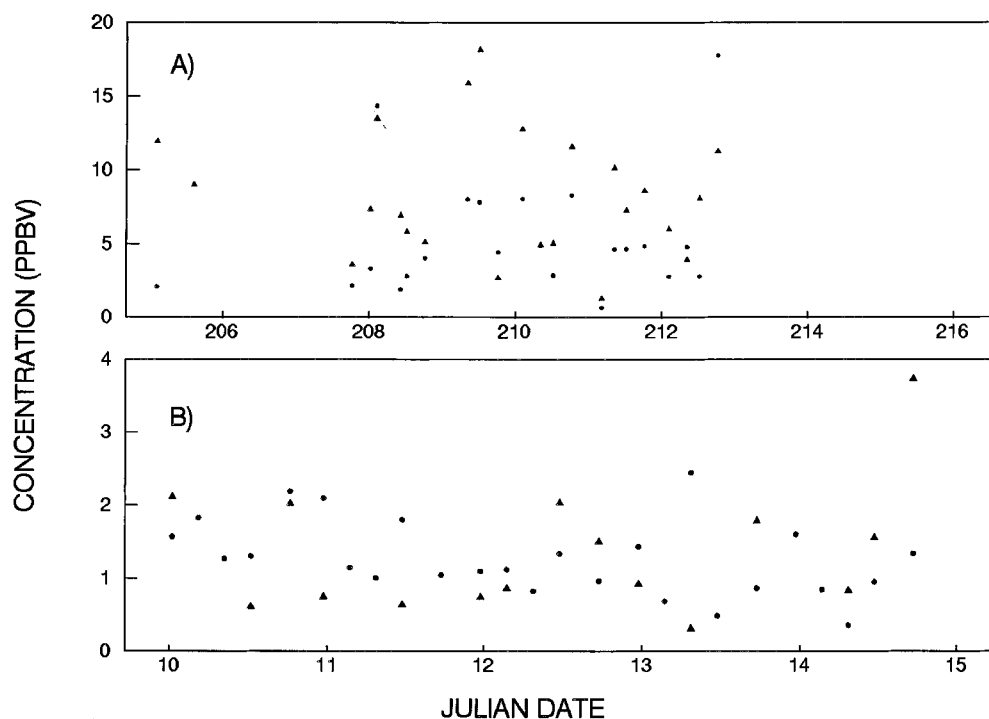


FIGURE 6. Acetaldehyde (●) and formaldehyde (▲) concentrations in Socorro, NM, during (A) the summer of 1993 and (B) the winter of 1994.

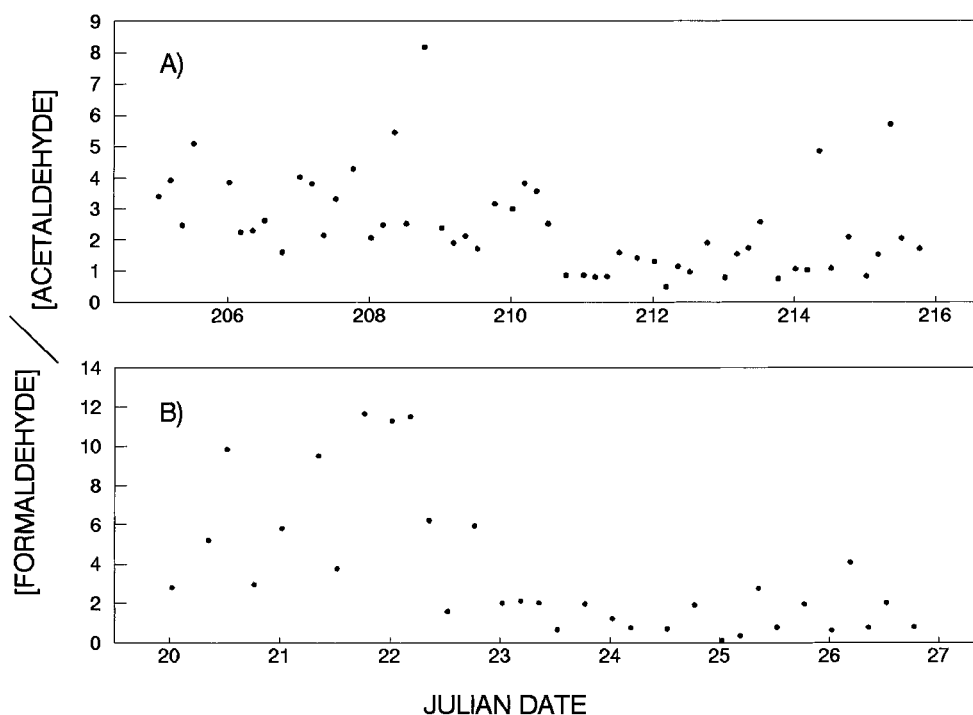


FIGURE 7. Formaldehyde/acetaldehyde concentration ratios in Albuquerque, NM, during (A) the summer of 1993 and (B) the winter of 1994.

posite trend. This pattern indicates a primary source of aldehydes in the winter.

To compare urban versus rural aldehyde levels, a limited data set was taken at New Mexico Tech in Socorro, NM. These data are presented in Figure 6. The winter aldehyde levels are quite low, while the summer levels are much higher, particularly for formaldehyde. Both of these rural data sets have concentrations much lower than the values in Albuquerque during the same periods. In addition, the rural aldehyde levels were substantially lower in the winter than in the summer. This observation suggests that the summer aldehyde levels may result from the oxidation of natural

hydrocarbons and direct emission of aldehydes from plants and trees. Likewise, appreciable amounts of aldehydes measured during the summer in Albuquerque could be coming from natural sources. Thus, aldehydes, particularly formaldehyde, could be produced from both natural and anthropogenic sources during the summer. The comparison of urban and rural wintertime data sets indicates that aldehyde levels in the winter are predominantly from anthropogenic sources.

Formaldehyde:acetaldehyde ratios can be used as a measure of anthropogenic to natural sources of these hydrocarbons in the atmosphere. This ratio is expected to be about 10 from

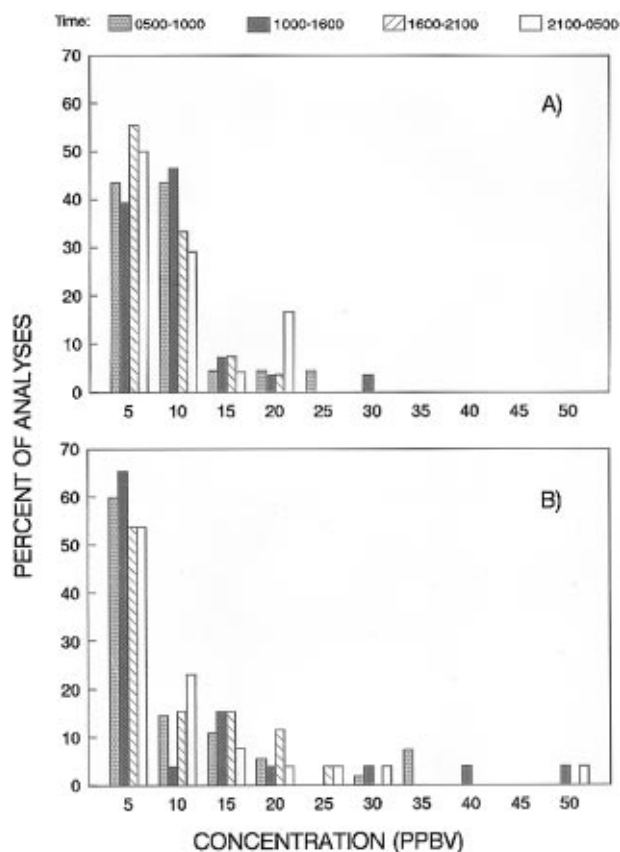


FIGURE 8. Time-dependent frequency distributions for acetaldehyde in Albuquerque, NM, during (A) the summer of 1993 and (B) the winter of 1994.

the photooxidation of isoprene alone. It has been reported as 3–4 over rural areas of central Ontario (30). For urban areas, the ratio has been reported as 2 in southern California (31) and as 0.85 in Rio de Janeiro during the use of alcohol (5). In Albuquerque, during days 23–27 in the winter of 1994, when aldehyde levels were highest, the formaldehyde:acetaldehyde ratios were lowest (see Figure 7) with an average of 1.4. This is a further indication of an anthropogenic source. During periods of low aldehyde concentrations in the winter and during the summer, the formaldehyde:acetaldehyde ratio was variable but substantially higher, indicating input from natural sources.

Frequency distributions for the summer and winter data sets as a function of time of day (Figure 8) show differences in acetaldehyde levels that could be due to use of ethanol-gasoline fuel blends. Elevated levels of acetaldehyde (above 25 ppb) occurred much more frequently during the winter months. In addition, more of the higher acetaldehyde concentrations occurred during peak traffic hours in the winter (1600–2100 and 0500–1000). 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 oxidation of natural hydrocarbons and direct natural emissions. Therefore, one would not expect aldehyde emissions to correlation with time of day during the summer.

Acetic acid and formic acid concentrations were higher in the summer than the winter during these two time periods and are not apparently correlated with aldehyde levels. This observation suggests that the acids arise from different sources than the aldehydes, possibly biogenic in the summer and from wood burning in the winter. The lower levels observed in the wintertime are due to a combination of reduced biogenic emissions and lower light levels resulting in reduced

photochemical activity, coupled with lower direct emissions from restricted wintertime wood burning.

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