Environ. Sci. Technol. **1999**, *33,* 540−545

Gas Phase C_2−C_{10} Organic Acids Concentrations in the Los Angeles Atmosphere

CHRISTOPHER G. NOLTE,
MATTHEW P. FRASER,[†] AND
GLEN R. CASS*
Environmental Engineering Science Department,
California Institute of Technology, Pasadena, California 91125

The atmospheric concentrations of gas-phase C_2−C_{10} monocarboxylic and benzoic acids are reported in samples collected during a severe Los Angeles area photochemical smog episode. Average urban concentrations are 10−50 × greater than concentrations observed at a remote background location, indicating an anthropogenic origin for these compounds. Average urban concentrations during the episode were 16.1 $\mu g\ m^{-3}$ (6.6 ppb) for acetic acid and 1.67 $\mu g\ m^{-3}$ (0.55 ppb) for propionic acid, with progressively lesser amounts as the carbon chain length of the acids is increased. Spatial and diurnal variations in atmospheric organic acids concentrations point to the importance of both direct emissions from primary sources and formation by photochemical reaction of precursor compounds.

Introduction

Much of the research on atmospheric carboxylic acids has focused on formic and acetic acids, both in remote environments (*1*−*4*) and in urban areas (*5*−*10*). Formate and acetate are found to be major constituents of rain (*11*, *12*) and dew (*13*) in Los Angeles. Formic and acetic acids have been measured in automotive emissions (*3, 14*) and in the smoke from biomass combustion (*3*). Higher molecular weight acids also are reported in motor vehicle exhaust (*14*, *15*). Several chemical reaction mechanisms have been proposed for the formation of organic acids in the atmosphere. These include the reaction of ozone with olefinic hydrocarbons (*16*, *17*), particularly isoprene (*3, 18, 19*), aldehyde oxidation by hydroxyl radicals (*20, 21*), and radical recombination reactions between acetyl peroxy and other peroxy radicals (*22*). Little is known, however, about the relative importance of these various chemical reaction mechanisms versus direct emissions from anthropogenic and biogenic sources.

Substantial attention has been given to measurements of the atmospheric concentrations of particle-phase carboxylic acids, including aliphatic dicarboxylic acids (*12*, *23*−*26*), higher molecular weight alkanoic acids (*26, 27*), and aromatic polycarboxylic acids (*26*, *27*). This work instead focuses on gas-phase carboxylic acids > C_2. Due to the analytic difficulty in quantifying trace levels of volatile polar compounds, relatively few measurements of the ambient concentrations of these species have been reported. One approach to making such measurements is to use a free fatty acid phase (FFAP) gas chromatographic (GC) column to effect the separation of the homologous series of the alkanoic acids. Hoshika (*28*) used such a technique to determine the gas-phase concentrations of C_2−C_5 alkanoic acids in ambient urban air and in air near a poultry manure pen. Various derivatization techniques also have been employed to make the organic acids less polar and thus amenable to analysis using standard GC columns. Kawamura et al. (*14*) used such a derivatization technique to measure gas-phase C_1−C_{10} monocarboxylic acids plus benzoic acid in atmospheric samples taken in 1984 at a single site in West Los Angeles. To the authors' knowledge, comprehensive measurements of the gas-phase concentrations of organic acids > C_2 have never been made over a network of air monitoring stations during an extended urban smog episode.

The present study reports the gas-phase concentrations of C_2−C_{10} monocarboxylic acids and benzoic acid during a severe photochemical smog event in the Los Angeles area during which peak ozone concentrations reached 0.3 ppm. These data have been collected as part of a larger study of vapor-phase, semivolatile, and particle-phase organic compounds (*29*).

Experimental Methods

Sample Collection. During the summer of 1993, a field experiment was conducted to measure simultaneously the concentrations of as many individual vapor-phase, semivolatile, and particle-phase organic compounds as possible (*29*). The purpose of the experiment was to acquire a comprehensive data set for the evaluation of air quality models that predict the concentrations of individual organic species in the atmosphere. Samples were collected at five sites in Southern California during a 2-day photochemical smog episode on September 8−9, 1993. The sampling locations used in the study are shown in the map of Figure 1. Samples of 4 h duration centered within consecutive 6 h periods were collected at four sites in the Los Angeles basin (Long Beach, Central Los Angeles, Azusa, and Claremont). Samples of somewhat longer duration (8−11 h) were collected at San Nicolas Island, a remote offshore site intended to characterize clean background conditions prevailing upwind of the city. The severity of the photochemical smog episode and the overall experimental design are more fully described by Fraser et al. (*29*).

Organic acids were collected by two separate sampling methods: a high-volume dichotomous sampler that used quartz fiber filters followed by polyurethane foam (PUF) cartridges, plus a low-volume particulate matter sampler in which two potassium hydroxide (KOH) impregnated 47-mm diameter quartz fiber filters were placed in series downstream of a Teflon particle prefilter. Particle-phase and high molecular weight vapor-phase organic acids were collected with the high-volume dichotomous sampler filters and PUF cartridges, respectively, while the KOH impregnated filters deployed with the low-volume (10 L min^{-1}) sampler were used to measure the low molecular weight vapor-phase acids, which are present at much higher concentrations. The KOH impregnated filters have a lower *n*-alkanoic acids blank value than is the case for the PUF material. The high-volume quartz fiber filter and PUF samples are discussed elsewhere (*26*, *30*); only the low molecular weight gas-phase acids collected on the KOH impregnated filters are reported here. The quartz fiber filters were prebaked at 550 ° C for at least 8 h in order to reduce organic contamination and were then spiked with 1.0 mL of 0.1 M KOH solution. Filters were stored and transported in individual Petri dishes lined with annealed aluminum foil and sealed with Teflon tape. At the end of

---

* Corresponding author phone: (626)395-6888; Fax: (626)395-2940; e-mail: glen@eql.caltech.edu.

[†] Current address: Environmental Science and Engineering Department, Rice University, Houston, TX 77005.

10.1021/es980626d CCC: $18.00

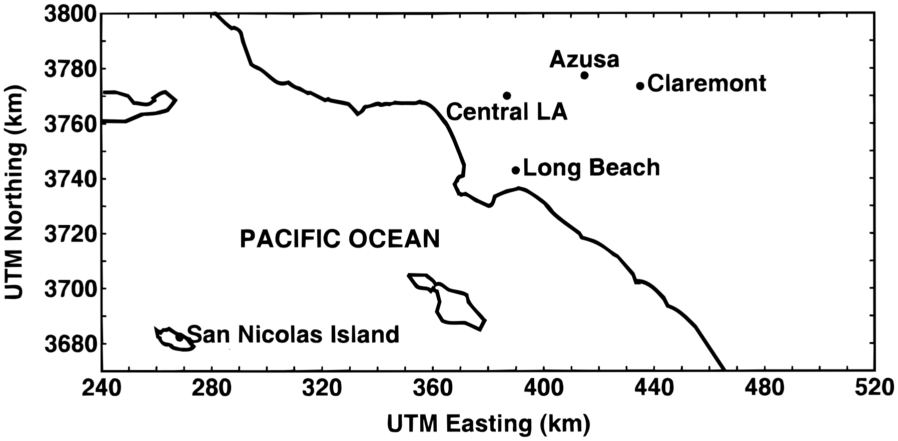

FIGURE 1. Map of Southern California showing the locations of the air monitoring stations used.

TABLE 1. Average Concentrations (μg m^{-3}) at Background and Urban Sites during the Photochemical Smog Episode of September 8−9, 1993

compound	San Nicolas Island	Long Beach	Central Los Angeles	Azusa	Claremont	urban av[a]	ref *14*[b]
acetic acid	1.76 ± 0.64	11.1 ± 1.5	14.7 ± 1.6	19.8 ± 2.2	16.8 ± 1.8	16.1 ± 0.9	3.42
propionic acid	0.08 ± 0.01	0.95 ± 0.05	1.55 ± 0.07	2.03 ± 0.09	1.96 ± 0.08	1.67 ± 0.04	0.31
isobutyric acid	0.02 ± 0.00	0.17 ± 0.00	0.25 ± 0.00	0.32 ± 0.01	0.35 ± 0.01	0.28 ± 0.00	0.04
butyric acid	0.01 ± 0.00	0.30 ± 0.01	0.52 ± 0.02	0.68 ± 0.02	0.75 ± 0.02	0.58 ± 0.01	0.11
pentanoic acid	0.00 ± 0.01	0.15 ± 0.02	0.28 ± 0.02	0.34 ± 0.02	0.24 ± 0.02	0.26 ± 0.01	0.06
hexanoic acid	0.02 ± 0.01	0.32 ± 0.03	0.48 ± 0.04	0.52 ± 0.04	0.27 ± 0.02	0.41 ± 0.02	0.10
heptanoic acid	0.00 ± 0.01	0.14 ± 0.02	0.18 ± 0.02	0.23 ± 0.02	0.16 ± 0.01	0.18 ± 0.01	0.04
octanoic acid	0.00 ± 0.01	0.08 ± 0.01	0.10 ± 0.01	0.12 ± 0.01	0.08 ± 0.01	0.10 ± 0.00	0.06
nonanoic acid	0.01 ± 0.01	0.09 ± 0.01	0.11 ± 0.01	0.14 ± 0.01	0.13 ± 0.01	0.12 ± 0.01	0.04
decanoic acid	0.00 ± 0.00	0.04 ± 0.01	0.06 ± 0.01	0.05 ± 0.01	0.07 ± 0.01	0.06 ± 0.00	0.02
benzoic acid	0.01 ± 0.02	0.16 ± 0.04	0.36 ± 0.04	0.28 ± 0.04	0.38 ± 0.04	0.30 ± 0.02	0.05

[a] Average across the four urban sites Long Beach, Central Los Angeles, Azusa, and Claremont. [b] Measurements made at a single site in 1984 at West Los Angeles; adapted from ref *14*.

each sampling period, filters were promptly removed from the samplers and refrigerated until being returned to the laboratory, where they were placed in freezers at − 21 ° C until analysis.

The decomposition of peroxyacetyl nitrate (PAN) to form acetate plus nitrite in alkaline media may constitute a source of positive interference in measuring ambient acetic acid. Grosjean and Parmar (*6*) investigated the extent of this potential artifact by determining the NO_2^-/PAN ratio in daytime summer Southern California ambient air samples, using an alkaline trap to measure the gas-phase nitrite concentrations. Assuming that all of the nitrite collected was due to PAN decomposition in the alkaline trap, they derived an estimate of 11−17% as an upper limit for the positive bias due to PAN in measuring acetic acid. PAN and peroxypropionyl nitrate (PPN) were measured as part of the present field experiment. During this study period, 48-h average PAN concentrations ranged from 1.35−3.76 ppb between the four urban monitoring sites, while PPN ranged from 0.28−0.58 ppb (*32*).

Analytical Methods. Prior to extraction, each sample was spiked with a constant amount of a recovery standard containing deuterated propionic, hexanoic, and benzoic acids. The quantity of the spike used was chosen to be comparable to the concentrations of the actual organic acids that were expected to be present in a typical atmospheric sample. The two KOH filters from each sample were extracted together three times by mild sonication in 5 mL of HPLC grade water for 10 min. Organic acids concentrations were determined by the method first used by Kawamura and Kaplan (*11, 14*) that will be described briefly here. The extracts were combined and passed through a polypropylene column packed with a cation-exchange resin (Bio-Rad Poly-Prep, AG 50W-X8 resin, 100−200 mesh, K^+ form). The solution pH was adjusted to 8.0−9.0 with 1 M HCl, and the solution was dried in a rotary evaporator. Potassium carboxylates ($RCOO^-K^+$) were dissolved in 5 mL of acetonitrile and converted to bromophenacyl esters by addition of 2,4′-dibromoacetophenone (reagent, 40 μL of 0.2 M solution in CH_2Cl_2) and dicyclohexano-18-crown-6 (catalyst, 25 μL of 0.03 M solution in acetonitrile) and heating in a water bath at 80 °C for 1 h. Following derivatization, the solution was again dried in a rotary evaporator and redissolved in a 2:1 mixture of hexane/CH_2Cl_2. The samples were concentrated to a final volume of 100−250 μL under nitrogen before analysis by gas chromatography/mass spectrometry (GC/MS).

Samples were analyzed with a Hewlett-Packard GC/MS system (GC Model 5890; MSD Model 5972) using a 30 m DB-5MS column (0.25 mm ID, 0.25 μm film thickness; J&W Scientific). The gas chromatographic conditions used were as follows: (1) splitless injection of 1 μL sample at 200 °C; (2) constant He carrier gas flow rate of 1.0 mL min^{-1}; (3) GC oven temperature hold at 40 °C for 6 min.; (4) oven temperature ramp at 30 °C min^{-1} to 160 °C; (5) temperature ramp at 8 °C min^{-1} to 290 °C; and (6) isothermal hold at 290 °C for 3 min. The mass spectrometer scanned from 45 to 400 Da twice per second. 1-Phenyldodecane was used as a co-injection standard to monitor the response of the instrument. An authentic standard containing each of the compounds studied here as well as the alkenoic acids acrylic acid and crotonic acid was spiked onto KOH filters and derivatized in the same manner as described above for the atmospheric samples, ensuring accurate peak identification and com-

TABLE 2. Urban Average Concentrations of Monocarboxylic Acids and Aldehydes (ppbv) in Southern California during the Photochemical Smog Episode of September 8–9, 1993

carbon no.	acid	aldehyde[a]
C_2	6.6	4.0
C_3	0.55	0.79
C_4	0.16	0.71
C_5	0.06	0.41
C_6	0.09	0.42
C_7	0.03	0.64
C_8	0.02	0.53[b]
C_9	0.02	1.09[b]
C_{10}	0.01	0.53[b]
benzoic	0.06	0.22

[a] Data adapted from Grosjean et al. (*36*). [b] Measured only at Long Beach and Azusa, 6–10 a.m. and 12–4 p.m. on September 9, 1993.

pound response factors. Peaks in the single ion GC/MS traces were manually integrated for each of the compounds of interest. The amounts of acids in the samples were quantified relative to the known amounts of deuterated acids spiked onto the filters before extraction. The recovery of the compounds in the deuterated spike was found to be reasonably uniform across all of the samples.

Calibration and Detection Limits. The authentic standard suite was analyzed nine times at concentrations spanning 2 orders of magnitude (ca. 1–100 ng injected), bracketing the range of concentrations observed in the atmospheric samples. A constant amount of the deuterated acids internal standard was spiked onto all samples. For all compounds studied here, the instrumental response (peak area relative to deuterated acid peak area) was linearly related to the compound mass spiked onto the filter. Relative response factors calculated from these standard runs were determined with a precision of 10–20%.

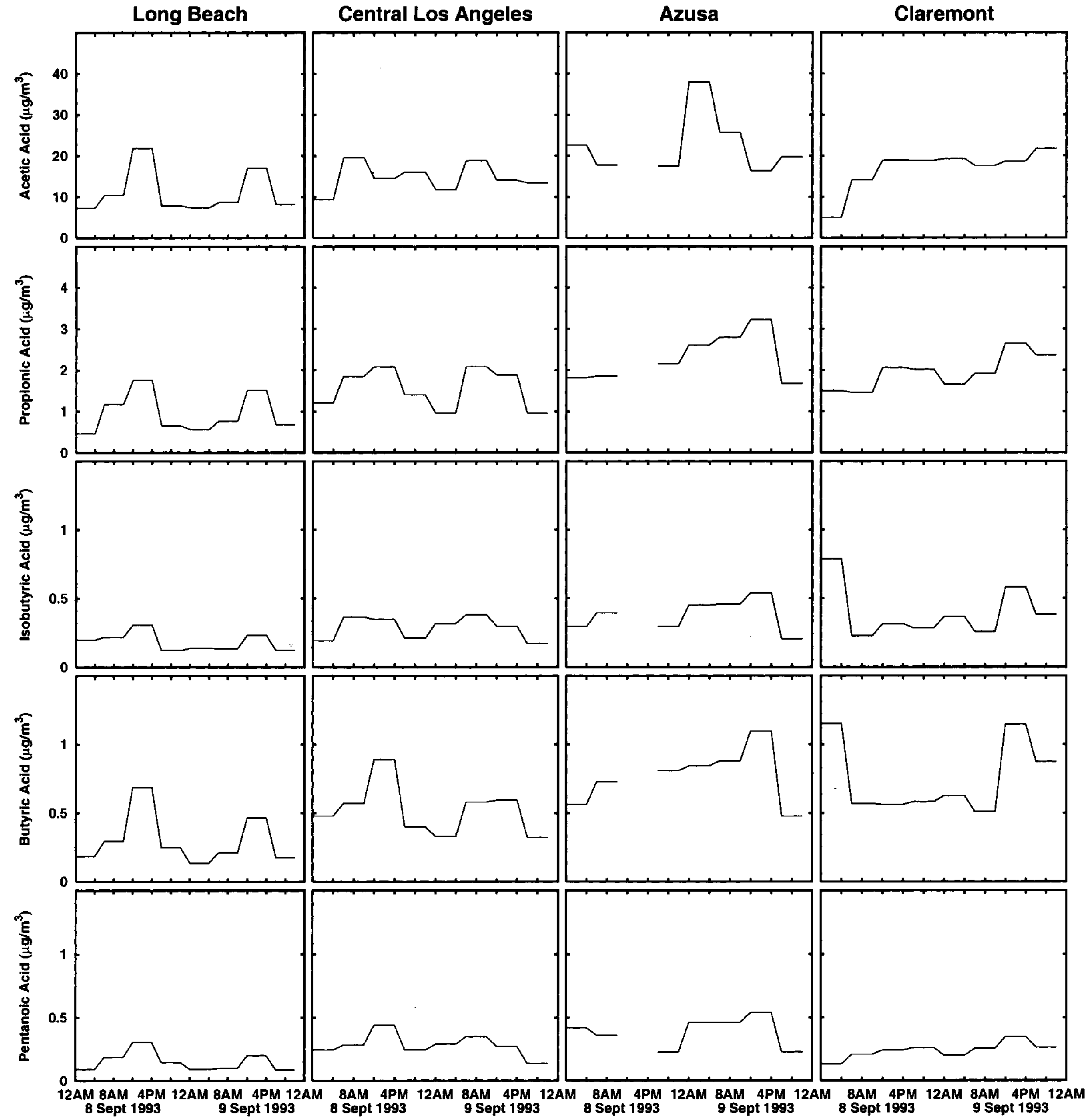

FIGURE 2. The diurnal variation of C_2–C_5 *n*-alkanoic acids in the Southern California atmosphere during the severe photochemical smog episode of September 8–9, 1993.

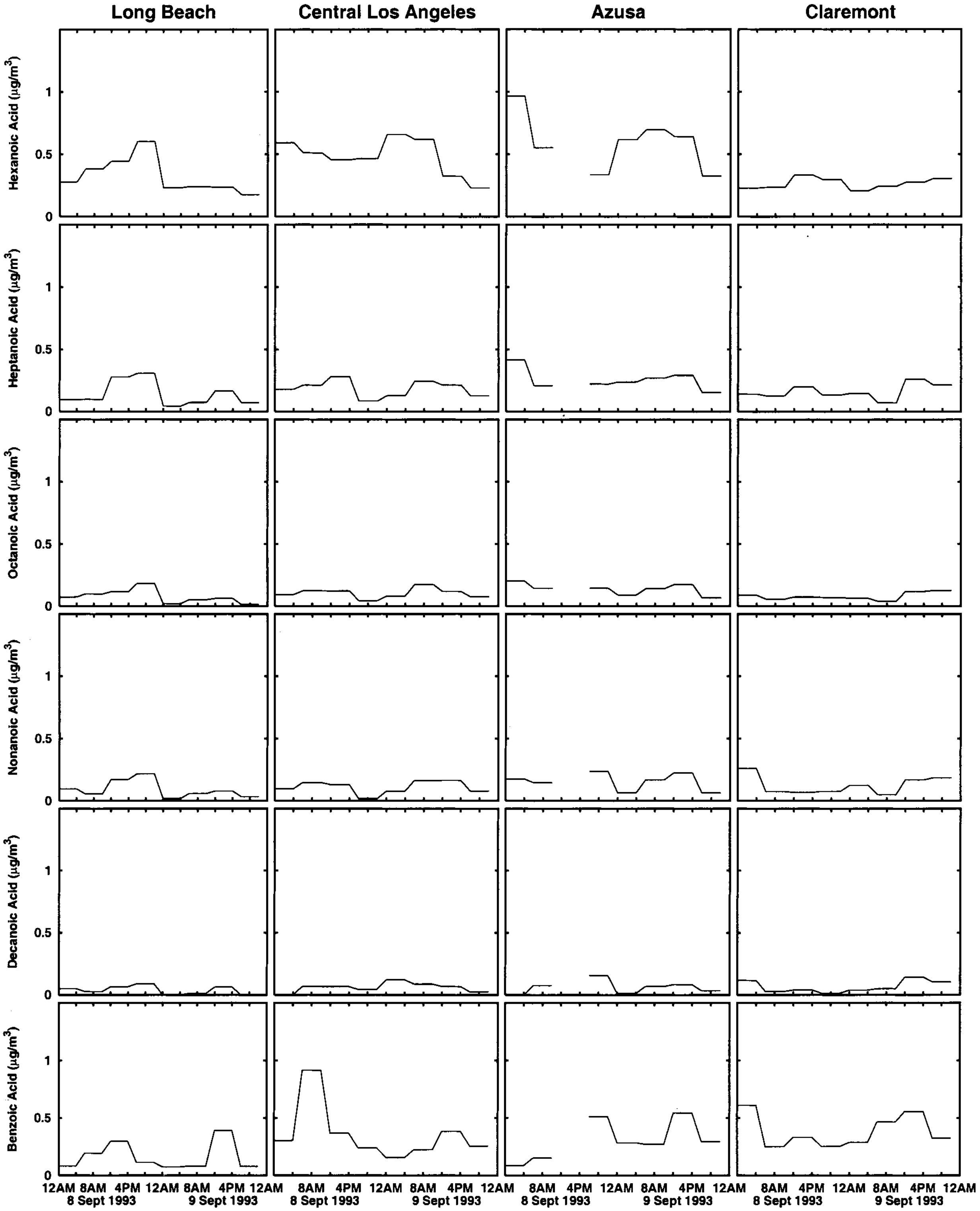

FIGURE 3. The diurnal variation of C_6-C_{10} *n*-alkanoic and benzoic acids in the Southern California atmosphere during the severe photochemical smog episode of September 8–9, 1993.

Procedural blanks were analyzed by the same extraction and quantification methods described above. The recovery of formic acid was found to be highly variable. Accordingly, formic acid concentrations were not quantified. The alkenoic acids acrylic acid and crotonic acid were not found in any of the atmospheric samples. It is possible, however, that acrylic and crotonic acids may have been present in the atmosphere but reacted with ozone while trapped on the alkaline filter. Acids on the blank filters mainly consisted of minor amounts of acetic acid and were generally low compared to values in the urban atmospheric samples. Atmospheric concentration data presented below have been corrected by subtraction of the values observed in the blanks. Error bounds were determined from statistical propagation of analytic uncertainties and the variability of the blanks.

Results and Discussion

Atmospheric Samples. Average gas-phase carboxylic acids concentrations at each air monitoring site over the 2-day episode are presented in Table 1. Acetic acid concentrations at the remote offshore site at San Nicolas Island are low compared to concentrations seen at the urban sites but are still significantly above the filter blank values. Propionic acid concentrations in the San Nicolas Island samples are only slightly greater than the blank values, while the levels of the other acids $> C_3$ are virtually indistinguishable from the blanks. All of the acids studied here are detected at much higher concentrations in the urban atmospheric samples than at San Nicolas Island, with generally progressively increasing concentrations as air masses are advected from the coast (e.g., Long Beach) to Central Los Angeles and Azusa. This indicates that these acid species arise from either direct emissions from local primary sources in the urban area or are formed in the atmosphere by chemical reaction of locally emitted precursor volatile organic compounds (VOC). The diurnal variation of the acids concentrations is examined below in an attempt to assess the relative importance of direct emissions versus atmospheric formation.

Acetic acid is by far the most abundant carboxylic acid species studied at all sites, with average concentrations ranging from 1.8 $\mu g\ m^{-3}$ (0.7 ppb) at San Nicolas Island to 19.8 $\mu g\ m^{-3}$ (8.1 ppb) at Azusa. These concentrations are in the range of those previously reported for the Southern California atmosphere (*5, 6, 33−35*). Propionic acid is the next most abundant species, with generally lesser quantities of acids as carbon chain length is increased. Included for comparison in Table 1 are compound concentrations measured by the same technique at a single location in West Los Angeles in 1984 (*14*). The atmospheric concentrations observed during the severe photochemical smog episode studied here are approximately 2−7 times higher than those reported earlier at West Los Angeles in the 1980s, though the relative distribution of the various acid species is similar. We note that the concentrations of C_4-C_9 *n*-alkanoic acids in the gas phase are much greater than the concentrations of the C_8-C_{24} *n*-alkanoic acids in the particle phase reported by Fraser et al. (*26, 30*). Simultaneous measurements reported by Fraser et al. using PUF cartridges (*26, 30*) show close agreement for benzoic acid, the only gas-phase species measured by both methods.

As part of this study, atmospheric C_1-C_{14} carbonyls concentrations were measured at the same sampling sites over the same sampling period (*36*). Average C_2-C_{10} aldehydes and monocarboxylic acids concentrations as well as average benzaldehyde and benzoic acid concentrations are listed for comparison in Table 2. It is evident that the low molecular weight carboxylic acids $> C_3$ are present at much lower concentrations than their corresponding aldehydes while acetic acid is more abundant than acetaldehyde.

Diurnal Variation. Time-series plots of the ambient concentrations of low molecular weight organic acids are shown in Figures 2 and 3. As a generalization, the diurnal patterns for most of the acids track each other at a given site, especially at Long Beach, indicating that they travel together as a group and probably have a common origin. The highest molecular weight alkanoic acids studied have nearly constant concentrations throughout the day and exhibit no clear diurnal behavior. The concentration profile of acetic acid is very similar to that of acetaldehyde, both in absolute magnitude and in diurnal variation (*36*). The diurnal variations of propionic and higher acids are also similar to those of their corresponding aldehydes, though the acid/aldehyde ratio decreases with increasing carbon number.

In the case of acetic acid and benzoic acid at Central Los Angeles, modest peaks at the time of heaviest early morning traffic (during the 6:00−10:00 a.m. sampling period) are evident, suggesting at least some contribution from direct motor vehicle exhaust, consistent with previous studies which have found that motor vehicle exhaust is an important source of acetic acid (*3*). The morning rush hour peak during this experiment is much more pronounced, however, for compounds such as the hopanes and steranes, whose atmospheric concentrations are dominated by automotive exhaust [see Figure 4 in reference 37]. Using the ratio of acetic acid to carbon monoxide reported by Talbot et al. in a highway tunnel (*3*) and scaling the carbon monoxide concentrations observed during the present field experiment by that ratio, we find that direct emissions from motor vehicles can account for no more than 13−28% of the average levels of acetic acid observed in the atmosphere. The large nighttime acetic acid peak seen at Azusa is accompanied by a similar spike in the concentrations of the industrial solvents acetone and 2-butanone, which were measured independently and which have been reported previously (*36*). This suggests that acetic acid may also be emitted from industrial processes in or near Azusa.

Acknowledgments

We thank the 13 California Institute of Technology graduate students and staff who participated in air monitoring site operations for their assistance; William Bope (South Coast Air Quality Management District) for logistics support in Azusa, Long Beach, and Los Angeles; and Lowell Ashbaugh (California Air Resources Board), Eric Grosjean (DGA Incorporated) and Gervaise McKay (Unisearch Associates) for logistics support in Claremont. This research was supported by the Electric Power Research Institute under Agreement RP3189-03 and by the Caltech Center for Air Quality Analysis.

Literature Cited

(1) Norton, R. B. *J. Geophys. Res.* **1992**, *97*, 10389−10393.
(2) Hartmann, W. R.; Santana, M.; Hermoso, M.; Andreae, M. O.; Sanhueza, E. *J. Atmos. Chem.* **1991**, *13*, 63−72.
(3) Talbot, R. W.; Beecher, K. M.; Harriss, R. C.; Cofer, W. R. *J. Geophys. Res.* **1988**, *93*, 1638−1652.
(4) Harrington, R. F.; Gertler, A. W.; Grosjean, D.; Amar, P. *Atmos. Environ.* **1993**, *27A*, 1843−1849.
(5) Grosjean, D. *Environ. Sci. Technol.* **1989**, *23*, 1506−1514.
(6) Grosjean, D. *Atmos. Environ.* **1990**, *24A*, 2699−2702.
(7) Grosjean, D. *Environ. Sci. Technol.* **1991**, *25*, 710−715.
(8) Puxbaum, H.; Rosenberg, C.; Gregori, M.; Lanzerstorfer, C.; Ober, E.; Winiwarter, W. *Atmos. Environ.* **1988**, *22*, 2841−2850.
(9) Schultz Tokos, J. J.; Tanaka, S.; Morikami, T.; Shigetani, H.; Hashimoto, Y. *J. Atmos. Chem.* **1992**, *14*, 85−94.
(10) Chebbi, A.; Carlier, P. *Atmos. Environ.* **1996**, *30*, 4233−4249.
(11) Kawamura, K.; Kaplan, I. R. *Anal. Chem.* **1984**, *56*, 1616−1620.
(12) Kawamura, K.; Steinberg, S.; Kaplan, I. R. *Atmos. Environ.* **1996**, *30*, 1035−1052.
(13) Pierson, W. R.; Brachaczek, W. W. *Aerosol Sci. Technol.* **1990**, *12*, 8−27.
(14) Kawamura, K.; Ng, L.-L.; Kaplan, I. R. *Environ. Sci. Technol.* **1985**, *19*, 1082−1086.
(15) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **1993**, *27*, 636−651.
(16) Calvert, J. G.; Stockwell, W. R. *Environ. Sci. Technol.* **1983**, *17*, 428A−443A.
(17) Atkinson, R.; LLoyd, A. C. *J. Phys. Chem. Ref. Data* **1984**, *13*, 315−444.
(18) Andreae, M. O.; Talbot, R. W.; Andreae, T. W.; Harriss, R. C. *J. Geophys. Res.* **1988**, *93*, 1616−1624.
(19) Jacob, D. J.; Wofsy, S. C. *J. Geophys. Res.* **1988**, *93*, 1477−1486.
(20) Jacob, D. *J. Geophys. Res.* **1986**, *91*, 9807−9826.
(21) Chameides, W. L.; Davis, D. D. *Nature* **1983**, *304*, 427−429.
(22) Madronich, S.; Calvert, J. G. *J. Geophys. Res.* **1990**, *95*, 5697−5715.
(23) Grosjean, D. In *Ozone and Other Photochemical Oxidants*; National Academy of Sciences: Washington, DC, 1977; pp 45−125.
(24) Kawamura, K.; Kaplan, I. R. *Environ. Sci. Technol.* **1987**, *21*, 105−110.
(25) Kawamura, K.; Ikushima, K. *Environ. Sci. Technol.* **1993**, *27*, 2227−2235.
(26) Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T.; Rasmussen, R. A. Manuscript in preparation.
(27) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. *Atmos. Environ.* **1993**, *27A*, 1309−1330.

(28) Hoshika, Y. *Anal. Chem.* **1982**, *54*, 2433−2437.
(29) Fraser, M. P.; Grosjean, D.; Grosjean, E.; Rasmussen, R. A.; Cass, G. R. *Environ. Sci. Technol.* **1996**, *30*, 1731−1743.
(30) Fraser, M. P. Ph.D. Dissertation, California Institute of Technology, 1998.
(31) Grosjean, D. *Environ. Sci. Technol.* **1990**, *24*, 1021−1026.
(32) Grosjean, E.; Grosjean, D.; Fraser, M. P.; Cass, G. R. *Environ. Sci. Technol.* **1996**, *30*, 2704−2714.
(33) Tuazon, E. C.; Winer, A. M.; Pitts, J. N., Jr. *Environ. Sci. Technol.* **1981**, *15*, 1232−1237.
(34) Grosjean, D. *Atmos. Environ.* **1988**, *22*, 1637−1648.
(35) Nolte, C. G.; Solomon, P. A.; Fall, T.; Salmon, L. G.; Cass, G. R. *Environ. Sci. Technol.* **1997**, *31*, 2547−2553.
(36) Grosjean, E.; Grosjean, D.; Fraser, M. P.; Cass, G. R. *Environ. Sci. Technol.* **1996**, *30*, 2687−2703.
(37) Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T.; Rasmussen, R. A. *Environ. Sci. Technol.* **1997**, *31*, 2356−2367.

Received for review June 18, 1998. Revised manuscript received November 11, 1998. Accepted November 13, 1998.

ES980626D