Seasonal and Spatial Characteristics of Formic and Acetic Acids Concentrations in the Southern California Atmosphere

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Formic and acetic acids measurements made during the year 1986 are reported for eight sites in the Los Angeles basin and one remote offshore site. Formic and acetic acids concentrations measured in marine air upwind of the Los Angeles area over an 8-month period average 1.4 and 0.6 ppb, respectively, while concentrations within the Los Angeles urban area average 2.7−5.8 ppb formic acid and 2.9−4.2 ppb acetic acid. Average formic and acetic acids concentrations exceed average HNO_3 and HCl concentrations, making them the most abundant gas phase acids in the southern California atmosphere throughout the year. Formic and acetic acids concentrations near the coast change in proportion to changes in atmospheric dilution potential, as would be expected if formic and acetic acids were emitted directly from widespread area sources such as motor vehicle traffic. Downwind of Los Angeles, formic and acetic acids concentrations peak during the summer photochemical smog season, and concentration changes track both changes in atmospheric oxidant concentrations and markers for heterogeneous conversion within clouds or fog. Formic and acetic acids concentrations thus appear to arise both from direct emissions and from atmospheric chemical production, with the relative importance of these pathways varying spatially over the area surveyed.

Introduction

Formic acid (HCOOH) and acetic acid (CH_3COOH) are ubiquitous trace components of the atmosphere. These organic acids have been found to be important contributors to precipitation acidity in nonurban environments (1, 2), including the Venezuelan savanna (3) and the Brazilian central Amazon region (4). Gas phase concentrations ranging from 0.2 to 1 ppb have been reported for many remote areas around the globe (5−12).

Formic and acetic acids concentrations are enhanced in urban areas when compared to remote areas and therefore may play an important role in determining precipitation acidity, the acidity of fog and dew, and the dry deposition flux of acids in urbanized regions. Formate and acetate are found to be major constituents of Los Angeles rainwater (13), and formate is the most abundant anion present, organic or inorganic, in southern California dew (14). Grosjean (15, 16) shows that daytime summer peak 4-h average gas phase

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concentrations of formic and acetic acids in southern California urban air are in the range of 8−10 ppb, higher than the average concentrations of the major inorganic acids, HNO_3 and HCl, during the summer (17, 18).

In addition to being important in the acid deposition budget, exposure to organic acids is known to cause damage to a wide range of materials, including shells, fossils, sandstone, and lead. Organic acid vapors emitted by wooden storage containers in art museums have been observed to corrode objects made of lead or lead-containing alloys such as pewter and bronze (19). Both formic and acetic acids are primary damaging agents, reacting to form a white efflorescence or even a heavy frosting of lead formate or lead acetate crystals, causing permanent pitting and scarring. High concentrations of organic acids in outdoor urban air have the potential to cause similar damage to lead, pewter, and bronze objects, particularly within buildings that have a high air exchange rate with the outdoors.

There are many potential sources of atmospheric formic and acetic acids. However, the relative importance of the various pathways that could lead to the introduction of formic and acetic acids into the atmosphere has not yet been identified conclusively. The seasonality in concentrations observed at remote sites (2, 9) is consistent with substantial contributions from vegetative or biogenic emissions, especially during the growing season. Photochemical oxidation of isoprene in particular has been suggested to be an important biogenic source of formic acid (4, 9, 20). Known anthropogenic primary emissions sources include direct emissions from automotive exhaust (21) and combustion of coal, wood, and agricultural waste (9, 12). Acetic acid is reported to be emitted in much greater amounts than formic acid in combustion processes (9). The ozone−olefin reaction has been suggested to yield significant amounts of formic and acetic acids (22, 23), but some studies have found no evidence that this pathway is an important source (8). Atmospheric gas phase oxidation of formaldehyde by hydroperoxyl radicals also has been suggested as a source of formic acid (24), but this reaction is expected to be too slow at atmospheric concentrations to be the main contributor to atmospheric HCOOH levels (25). Acetic acid can be formed from radical recombination reactions between acetyl peroxy and other peroxy radicals (26−28). Aqueous phase oxidation of formaldehyde by hydroxyl radicals, with subsequent volatilization to the gas phase upon fog or cloud evaporation, also has been proposed as an important pathway for formic acid formation (25, 29).

Because formic and acetic acids have not been regulated as air pollutants, they have not been subject to routine monitoring. With the exception of the 15-month study of Talbot *et al.* (9) at one remote site in eastern Virginia and a year-long study by Grosjean (30) at Upland, CA, past observations have generally been limited to intensive sampling periods at a single location with a duration of at most a few days. Most of these field studies (e.g., refs 4, 10, 12, 15, and 31) have focused on determining the diurnal variation of formic and acetic acids concentrations and have usually observed that concentrations peak in the middle of the afternoon and decline at night. Rather little long-term monitoring, however, has been undertaken to define average concentrations plus seasonal and spatial variations, particularly in urban areas. In this paper, experimental data collected at nine monitoring sites throughout the Los Angeles area in 1986 will be reported to document the long-term average concentrations and spatial distribution of formic acid and acetic acid in the southern California atmosphere. To the authors' knowledge, this constitutes the largest database
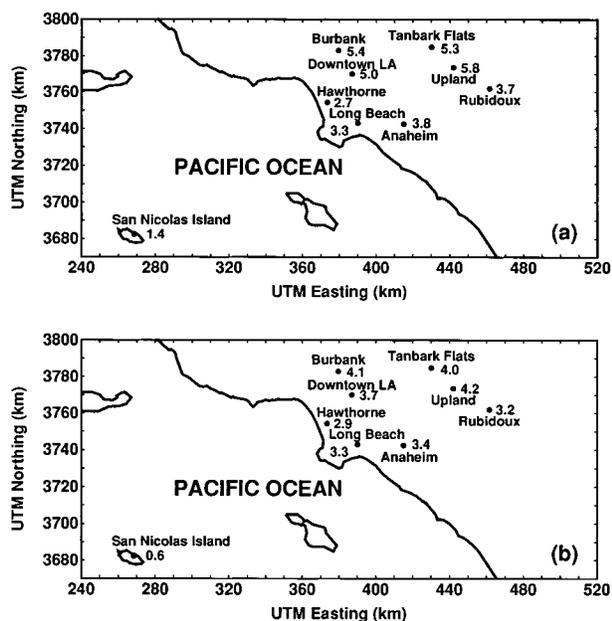
FIGURE 1. Southern California air monitoring network. Arithmetic mean 24-h average (a) formic acid and (b) acetic acid concentrations over the period May–December 1986 are given in ppb, assuming standard conditions of 25 °C and 1 atm pressure. The uncertainty in the mean concentrations over the days observed due to the experimental precision is ≤0.05 ppb for formic acid and ≤0.4 ppb for acetic acid at all sites.

reported for these species. The seasonal and spatial characteristics of these data then will be examined for clues as to the principal sources of formic and acetic acids.

Experimental Methods

During the calendar year 1986, gas phase acids, ammonia, and atmospheric particulate matter concentrations were measured at nine sampling sites in the Los Angeles area, as depicted in Figure 1. All sites except Tanbark Flats and San Nicolas Island were collocated with continuous air monitoring stations operated by the South Coast Air Quality Management District (32, 33). The Tanbark Flats site was located in the San Gabriel Mountains north of San Dimas, in the Angeles National Forest, at an elevation of approximately 870 m. The San Nicolas Island air monitoring site was located at the meteorological station on that island, approximately 140 km southwest of the Los Angeles coastline. This remote, offshore location was chosen to determine background pollutant levels entering the Los Angeles area from the upwind marine environment.

PM_{10} aerosol concentration and chemical composition as well as the concentrations of HNO_3 and HCl measured during these experiments have been described previously (17, 18, 34). Gas phase formic and acetic acids were measured over 24-h averaging times at 6-day intervals at each site using the tandem filter method. Inert polytetrafluoroethylene (PTFE) prefilters were used to remove particulate matter from the airstream prior to collection of gaseous formic and acetic acids on two KOH impregnated 47-mm diameter quartz fiber backup filters in series (Pallflex 2500 QAO). The quartz fiber filters were prebaked for at least 3 h at 750 °C before being spiked with KOH in order to reduce organic contamination. Filters were installed the day prior to and removed the day after sample collection. The nominal air flow rate through the tandem filter pack was 4.9 L/min, with flow rates monitored before and after sampling by a rotameter that had been factory calibrated with an accuracy of 1% full scale. Flow rate checks were performed to ensure that the filter holders were not leaking and to verify that filter clogging had

not occurred. After sampling, filters were stored in prelabeled Petri dishes at −25 °C until analysis.

Filters were leached by lightly shaking each of them in 10 mL of distilled, deionized water for 3 h. Formic and acetic acids were analyzed as formate and acetate using ion chromatography (Dionex Model 2020i). Concentrations of $HCOO^-$ and CH_3COO^- were determined relative to laboratory standards of known concentration prepared from ACS grade analytical reagents. Instrument detection limits were determined to be 0.9 μg/filter formate and 2.3 μg/filter acetate. Field blanks equal in number to 10% of the actual ambient samples were obtained and analyzed in the same manner. Blank values averaged 3.6 ± 1.5 μg/filter formate and 23 ± 17 μg/filter acetate. Single sample analytical precision, determined from duplicate (split filters analyzed separately) or replicate (repeat analysis of a filter extract) measurements, was found to be ±2.8% formate and ±4.6% acetate. Final error estimates were calculated by the statistical propagation of the sample, filter blank, and sampling volume precisions. The average relative precision (1σ) was ±10.4% for formic acid, while the concentration-weighted average precision was ±6.6%. Due to the higher variability of acetate in the blanks, the acetic acid measurements are less precise; the concentration-weighted average precision was ± 38.0% (typically about ±1 ppb), with the precision better than ±20% for peak concentrations greater than about 10 ppb. The uncertainty in the long-term means computed from sample sets collected over many months is of course much smaller.

In the absence of a large data base on organic acids concentrations in the Los Angeles atmosphere, the quantity of KOH used to prepare the alkaline-impregnated filters had to be estimated initially. Analysis of the earliest samples taken showed excessive breakthrough of organic acids onto the second KOH-impregnated backup filter of each set. The quantity of KOH spiked onto each filter was therefore increased to 1 mL of 0.1 M KOH in distilled, deionized water, and the subsequent collection of organic acids data proceeded without incident. Accordingly, only data from the final eight months of 1986 are reported here.

Keene et al. (35) reported that alkaline filter techniques for measuring gas phase formic acid may be subject to a significant positive interference from the reaction of aldehydes with the sampling media to generate HCOOH subsequent to collection. When excess formaldehyde was added to the airstream, they detected increased levels of formate on alkaline filters. Other investigators, however (36, 37), have performed similar experiments and concluded that the extent of artifact production of formic acid from formaldehyde is negligible. A different possible artifact that could arise during sampling is the adsorption of gas phase formic or acetic acid onto particulate matter collected on the PTFE prefilter (38). Measurements made during the August 1986 Carbon Species Methods Comparison Study (CSMCS) conducted in Glendora, CA, found that 94% of the total formate measured on PTFE plus KOH filters in a stacked filter unit and 88% of the total measured acetate were detected on the KOH filters (16). Thus, the maximum extent of this negative sampling artifact under conditions found in the South Coast Air Basin is 6% for formic acid and 12% for acetic acid even if all of the particulate formate and acetate are attributed to adsorption of gas phase formic and acetic acids. Furthermore, as part of CSMCS, Grosjean et al. (39) obtained comparable results when using both an alkaline trap-liquid chromatography method and Fourier transform infrared spectroscopy (FTIR) simultaneously to measure formic acid. Since FTIR is not subject to bias from formaldehyde and uses no PTFE particle prefilter, this provides a degree of confidence in the reliability of sampling formic acid in southern California with alkaline traps.

The decomposition of peroxyacetyl nitrate (PAN) to form acetate plus nitrite in alkaline media may constitute a source

TABLE 1. Location of Meteorological Observations for Each Site

air monitoring site	associated meteorological station
Hawthorne	Los Angeles International Airport
Long Beach	Long Beach Airport
Anaheim	USMC Air Station, Tustin
downtown Los Angeles	Burbank-Glendale-Pasadena Airport
Burbank	Burbank-Glendale-Pasadena Airport
Tanbark Flats	Tanbark Flats USFS Station
Upland	Ontario Airport
Rubidoux	March Air Force Base, Riverside

of positive interference in measuring ambient acetic acid. Grosjean and Parmar (*36*) 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 gas phase acetic acid. In this work we make no further distinction between acetate derived from true acetic acid and PAN-derived acetate and report all acetate as "acetic acid", recognizing that the values reported constitute an upper bound on the true acetic acid concentration.

For use in the data interpretation that follows, meteorological observations routinely made at local airports, including temperature, dew point, wind speed and direction, and fog observations, were obtained from the National Climatic Data Center. Data from the closest airport or other meteorological observation site were associated with each air monitoring station, as shown in Table 1. Since there are virtually no important anthropogenic sources at or upwind of San Nicolas Island, and as the formic and acetic acids concentrations there are very low, there is no reason to process the San Nicolas Island meteorological data during the later analysis of dilution effects on source emissions. For this reason, San Nicolas Island is excluded from Table 1. Temperature soundings taken at 0500 hours daily at Loyola Marymount University near Hawthorne were provided by the South Coast Air Quality Management District and were used to determine the morning mixing depth over the west Los Angeles coastal area. Incident solar radiation measurements were made at Riverside, CA, by the California Irrigation Management Information System.

Results and Discussion

Ambient Levels of Formic and Acetic Acids in Southern California. The arithmetic means of the 24-h average formic and acetic acids concentrations over the period May–December 1986 are shown in Figure 1. As a general trend, it can be seen that concentrations are lowest over the ocean at San Nicolas Island, averaging 1.4 ppb for formic acid and 0.6 ppb for acetic acid. HCOOH and CH_3COOH concentrations rise to approximately 3 ppb each at the near coastal sites at Hawthorne and Long Beach. Average formic and acetic acids concentrations increase to approximately 5 ppb HCOOH and 4 ppb CH_3COOH at areas of high traffic density (Burbank and Downtown Los Angeles) and remain at about the same level at the downwind locations at Upland and Tanbark Flats. Rubidoux is generally downwind of Anaheim in the summer (*40*); average formic acid and acetic acid concentrations are approximately the same at these two sites (3.7–3.8 ppb formic acid and 3.2–3.4 ppb acetic acid). Peak 24-h average formic and acetic acids concentrations are typically 2–3 times greater than the 8-month average concentrations for the same site, as shown in Figure 2. The highest peaks occur at the downwind locations Upland and Tanbark Flats. Peak 24-h average formic and acetic acids concentrations for the year at each monitoring site generally
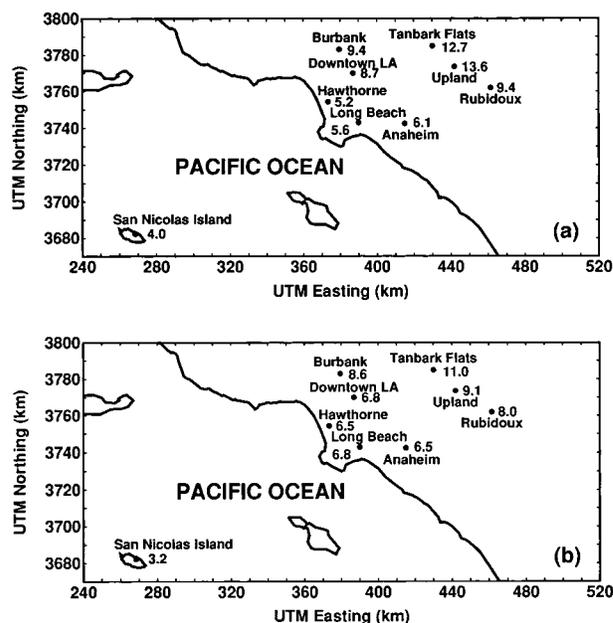

FIGURE 2. Peak 24-h average organic acids concentrations over the period May–December 1986, in ppb: (a) formic acid and (b) acetic acid.

occur on days with higher than average concentrations throughout the air basin, although peak concentrations do not all occur on the same day of the year at all sites.

Formic and acetic acids time series plots for each of the nine sites are presented in Figure 3. It can be seen that fluctuations in formic acid and acetic acid concentrations are highly correlated and that these two gas phase organic acids are present in approximately equal concentrations at the same sites on most days. No seasonal variation is evident for the coastal sites. Burbank and the three inland sites Tanbark Flats, Upland, and Rubidoux show a marked increase in organic acid levels during the summer months. The data at San Nicolas Island show that background concentrations of formic and acetic acids in marine air upwind of the city are low and nearly uniform. The higher but fairly constant levels of formic and acetic acids at the near-coastal sites at Long Beach and Hawthorne suggest a relatively constant addition of these acids from primary emissions sources. The still higher and more variable concentrations at inland sites suggest that the marine background and primary source emissions are supplemented by episodic photochemical or aqueous phase chemical production during transport to the downwind sites in the summer and sometimes the fall seasons.

Concentrations of formic and acetic acids averaged over eight sites in the Los Angeles basin (excluding San Nicolas Island) are shown in Figure 4 along with basinwide monthly average concentrations of HCl and HNO_3, the major inorganic acids species measured in this study (*17, 18*). The average concentration of acetic acid in the Los Angeles basin exhibits little seasonal variation, but average formic acid concentrations peak during the summer months. These average urban formic and acetic acids concentrations are substantially higher than annual average HNO_3 concentrations (urban annual mean 1.2–2.7 ppb) and HCl concentrations (urban annual mean 0.53–1.25 ppb). Previous observations that formic acid and acetic acid are the most abundant acids present in the atmosphere (*15, 16*) and in dew (*14*) in southern California in the summer thus apply in general over the rest of the year and over each of the large number of urban monitoring sites studied here.

Comparison with Results of Other Studies. It is important to bear in mind that the results from the present work provide 24-h and longer average values, and as such the peak values
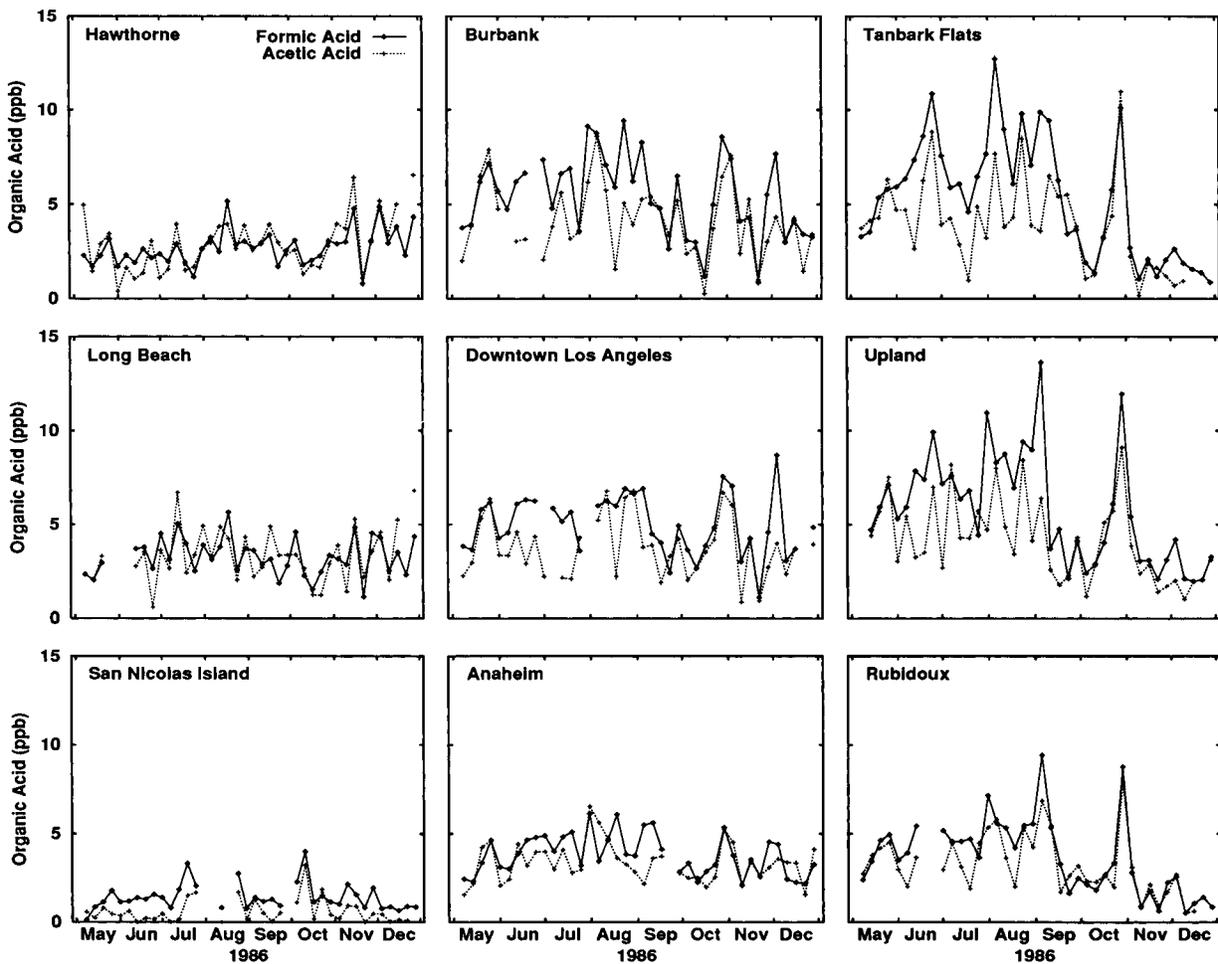
FIGURE 3. Time series of formic acid and acetic acid concentrations in southern California. Data points represent 24-h averages. Line breaks indicate missing data.
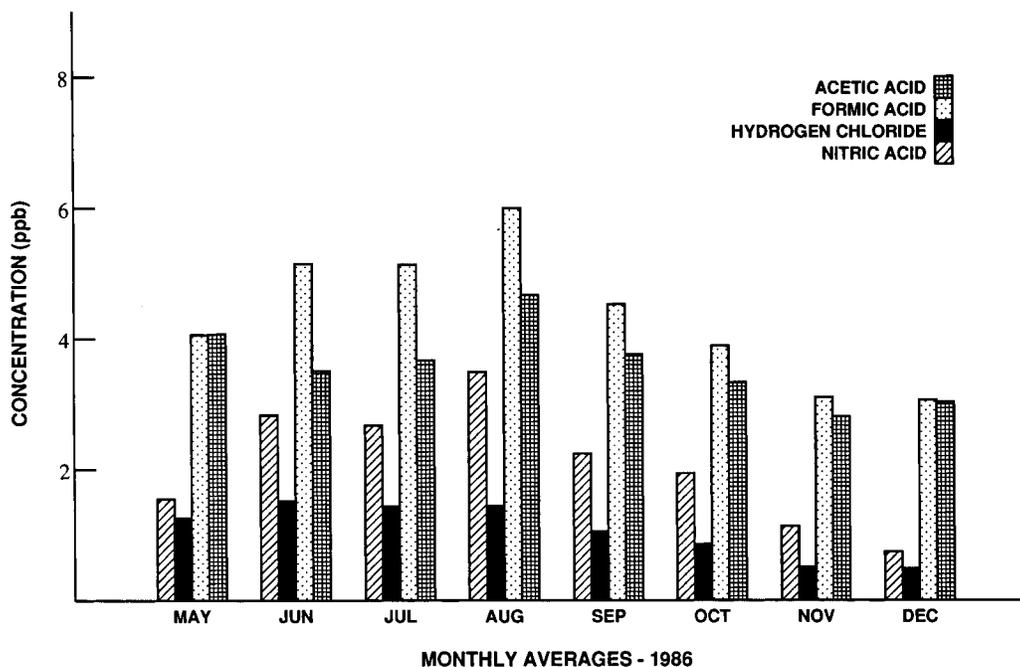

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FIGURE 4. Concentrations of gas phase acids in the Los Angeles air basin in 1986, averaged over the eight on-land air monitoring sites shown in Figure 1. HNO_3 data adapted from Solomon et al. (17); HCl data adapted from Eldering et al. (18).

from the present study should be lower than peak values seen in other studies which reported midday 4-h averages. Summertime 24-h average concentrations at the downwind receptor sites at Upland and Tanbark Flats during the present

study ranged from 4 to 14 ppb for formic acid and from 1 to 11 ppb for acetic acid. Short-term (≤5 min) average formic acid concentrations of up to 19 ppb have been measured by FTIR during summer smog episodes in Pasadena

(*41*), Riverside (*42*), and Claremont, CA (*43*), which are all located within our study area. Using an alkaline trap−ion chromatography method nearly identical to that described here, except over a 4-h time scale, Grosjean (*15*) reported 1.9−10.5 ppb formic acid and 2.5−9.5 ppb acetic acid over a 9-d period during the summer of 1985 Nitrogen Species Methods Comparison Study (NSMCS) at Claremont. As part of the 1987 Southern California Air Quality Study (SCAQS), 4-h average formic and acetic acids concentrations were measured at two sites during four 2−3-day periods in the summer and at one site during two 3-d periods in the fall (*44*). Peak 4-h average concentrations were 20 ppb formic acid during the summer at Claremont and 18 ppb acetic acid during the fall at Long Beach. Formic and acetic acids were measured over five 2−4-day periods at four sites in the western Sierra Nevada Mountains, CA (*45*). Mean daytime (10-h average) formic acid concentrations were 18 ppb at Tehachapi and 12−13 ppb at three other sites, with peak 10-h averages as high as 40 ppb. Acetic acid concentrations ranged from 0.5 to 13 ppb. These results at Tehachapi are higher than those obtained in the present study at Tanbark Flats. In a year-long study conducted at a single site at Upland, CA, in 1988−1989 (*30*), the peak 24-h average formic acid concentration observed was 8 ppb, while the annual average concentration was 2.8 ppb, somewhat lower than the results reported here for that site.

Only limited organic acid data are available for urban areas outside southern California. During a single 10-h daylight period in August, Schultz Tokos *et al.* (*31*) observed formic and acetic acids concentrations ranging from 3.1 to 12.5 ppb and from 1.8 to 7.3 ppb, respectively, over 30-min averaging times in the urban atmosphere of Yokohama, Japan. Six-hour average formic and acetic acids concentrations ranged from 1.8 to 14.8 and from 0.8 to 5.4 ppb, respectively, during a 2-month period in Boston (*46*). As can be seen from these results, the formic and acetic acids concentrations data presented here for Los Angeles in 1986 is in the range of that measured at other locations or in the same location at other time periods.

Examination of Sources and Production Pathways for Organic Acids. Several possible sources and production mechanisms have been proposed for formic and acetic acids. These include their direct emission into the atmosphere, either from biogenic sources (*2, 9*) or via anthropogenic activities (*4, 12, 21*), and atmospheric gas or aqueous phase oxidation of precursor organic compounds (*8, 12, 20, 22−29, 45*). While a mechanistic air quality model might be envisioned that would explain the cause and effect relationships between pollutant emissions and formic and acetic acids concentrations, such a model is presently beyond the state of the art. As noted in the review by Chebbi and Carlier (*47*), the emissions fluxes of carboxylic acids from vegetation and soils, the precise mechanism of all important gas phase reactions, as well as the importance of heterogeneous reactions on aerosol particles and on other surfaces in the environment are not fully understood at present. Therefore, at this time the highest use of the present data is to search for clues as to the possible sources and formation pathways for formic and acetic acids through analysis of the meteorological and co-pollutant data from the present experiment to determine whether or not fluctuations in formic or acetic acids concentrations track conditions that are indicative of a particular hypothetical source of organic acids. We adopt this approach to examine the following possible sources of organic acids: direct emissions from widespread area sources (*e.g.*, motor vehicle exhaust; decay of biological material in soils); gas phase photochemical production; and aqueous phase oxidation to form organic acids within fog, clouds, or dew.

We first examine the hypothesis that formic and acetic acids are predominantly primary pollutants, *i.e.*, that they are directly emitted from widespread area sources. Changes

TABLE 2. Pearson Correlation Coefficients between EC, CO, Formic Acid, Acetic Acid, and Dilution Parameter D^a

site	EC/CO	EC/D	EC/FA	EC/AA	FA/D	AA/D
Hawthorne	0.91[b]	0.82[b]	0.60[b]	0.61[b]	0.62[b]	0.52[b]
Long Beach	0.88[b]	0.85[b]	0.17	0.21	0.24	0.35[c]
Anaheim	0.85[b]	0.74[b]	0.00	0.10	−0.22	−0.09
downtown Los Angeles	0.94[b]	0.64[b]	0.28	0.02	−0.16	−0.19
Burbank	0.94[b]	0.63[b]	0.16	0.03	−0.21	−0.20
Tanbark Flats	n/a	−0.12	0.74[b]	0.52[b]	−0.41[c]	−0.21
Upland	0.79[b]	0.23	0.52[b]	0.30	−0.49[b]	−0.49[b]
Rubidoux	0.84[b]	0.44[b]	0.34[b]	0.32	−0.37[c]	−0.26

^{a} EC, elemental carbon; CO, carbon monoxide; D, 1/(WS × MH); WS, scalar average wind speed; MH, mixing height; FA, formic acid; AA, acetic acid; n/a, not available. ^{b} $p \leq 0.01$. ^{c} $p \leq 0.05$.

in carbon monoxide (CO) or elemental carbon (EC) concentrations from day to day are often used as indicators of the changes in dilution that influence the atmospheric concentrations of directly emitted air pollutants, since CO and EC are not formed photochemically but instead are directly emitted by combustion sources. In the Los Angeles area, both CO and EC are emitted largely from motor vehicle traffic, and daily average traffic volumes are thought to be roughly the same from day to day over the course of the year. In the present study, PM_{10} elemental carbon concentrations (EC) will be used as a surrogate tracer for the dilution of direct emissions. The EC measurements used were taken on the same days at the same locations and with the same averaging times as the organic acids data and have been reported previously by Solomon *et al.* (*34*). We note that at all sites where CO data are available from South Coast Air Quality Management District air monitoring instruments (*i.e.*, all except San Nicolas Island and Tanbark Flats) our EC values and the reported daily 1-h average CO peaks are highly correlated. Correlation coefficients range from 0.79 to 0.94, and all have a *p*-value ≤0.01 (Table 2).

Assuming that emissions patterns are similar from day to day, variations in ambient EC concentrations should track changes in the dilution volume of the air basin. Two factors closely related to the dilution volume for inert species such as EC are the scalar average wind speed (WS) and the mixing height (MH) determined from the morning temperature sounding. We define the dilution parameter D as the reciprocal of the product of the scalar average wind speed and the mixing height:

$$D = \frac{1}{WS \times MH}$$

Defined in this manner, D is inversely proportional to the effective air volume of the airshed on a given day. Table 2 lists correlation coefficients between EC and D. When changes in EC concentrations are examined as an indicator of the degree of dilution of direct emissions, it is found that EC concentrations track the dilution parameter most closely at coastal sites near the location of the lowest morning mixing depths and near where the mixing depth is measured at the coast. If we seek a signal that captures the effect of direct emissions from vehicles and other primary sources on formic and acetic acids concentrations, it is most likely to be detected at the coastal sites.

We now turn to formic and acetic acids and ask the question of whether or not fluctuations in their concentrations track changes in EC or changes in the dilution parameter. Correlation coefficients of formic and acetic acids versus EC and D are listed in Table 2. These correlation coefficients are highest at Hawthorne near the coast and suggest that much of the formic and acetic acids concentrations at that site could be attributable to local primary emissions sources. At Long

TABLE 3. Pearson Correlation Coefficients with O_3[a]

site	T_{avg}	SR	EC	FA	AA
Hawthorne	0.47[b]	0.44[c]	−0.31[c]	0.34[c]	0.15
Long Beach	0.69[b]	0.58[b]	−0.42[b]	0.50[b]	0.14
Anaheim	0.59[b]	0.45[b]	−0.27	0.59[b]	0.19
downtown Los Angeles	0.85[b]	0.68[b]	−0.36[c]	0.51[b]	0.27
Burbank	0.77[b]	0.68[b]	−0.33[c]	0.78[b]	0.47[b]
Upland	0.77[b]	0.66[b]	0.35[c]	0.87[b]	0.61[b]
Rubidoux	0.77[b]	0.65[b]	0.15	0.86[b]	0.61[b]

[a] T_{avg}, daily average temperature; SR, incident solar radiation; EC, elemental carbon; FA, formic acid; AA, acetic acid. [b] $p \leq 0.01$. [c] $p \leq 0.05$.

TABLE 4. Pearson Correlation Coefficients with SO_4^{2-} [a]

site	RH	NFOG	O_3	FA	AA
Hawthorne	0.63[b]	0.66[b]	0.30	0.02	−0.09
Long Beach	0.45[b]	0.63[b]	0.40[c]	0.10	−0.05
Anaheim	0.43[b]	0.68[b]	0.47[b]	0.57[b]	0.54[b]
downtown Los Angeles	0.74[b]	0.69[b]	0.44[b]	0.42[b]	0.62[b]
Burbank	0.76[b]	0.73[b]	0.56[b]	0.50[b]	0.58[b]
Tanbark Flats	0.57[b]	0.56[b]	n/a	0.69[b]	0.64[b]
Upland	0.61[b]	0.67[b]	0.64[b]	0.72[b]	0.68[b]
Rubidoux	0.46[b]	0.61[b]	0.69[b]	0.83[b]	0.79[b]

[a] RH, average relative humidity; NFOG, number of hours per day fog was observed; FA, formic acid; AA, acetic acid. [b] $p \leq 0.01$. [c] $p \leq 0.05$.

Beach, a weaker but consistently positive correlation between the organic acids concentrations and dilution variables also is seen. The small or negative correlations between the dilution variable and organic acids concentrations at the inland sites indicate that processes other than dilution of primary emissions are important in controlling organic acids levels at the other sites. Tanbark Flats is located in the mountains in an area with no local motor vehicle traffic. All pollutants reaching Tanbark Flats are transported to that site from upwind. The positive correlations between EC and formic and acetic acids at that site indicate that all three pollutants arrive together at Tanbark Flats whenever heavily contaminated air is advected over the site. The negative correlations between pollutant concentrations and the dilution volume parameter indicate that transport direction matters more than degree of dilution at Tanbark Flats. Upland, which is located not far from Tanbark Flats, seems to share some of these characteristics.

Next, we consider the hypothesis that formic and acetic acids are formed photochemically. Daily peak 1-h average ozone (O_3) concentration measurements made by the South Coast Air Quality Management District at seven of our sites were acquired from the California Air Resources Board (48). We use high ozone concentrations as a marker for days with high rates of gas phase photochemistry. Correlation coefficients between the 24-h average temperature, incident solar radiation, EC, formic and acetic acids, and ozone are listed in Table 3. It is evident that high O_3 concentration peaks are positively correlated with days having high temperature and high solar radiation, as expected. In the western part of the air basin, factors that produce high EC concentrations (e.g., winter air stagnation events) occur at a different time of year than high photochemical smog events, hence the negative correlations between high ozone events and high elemental carbon concentration events. At Upland and Rubidoux at the eastern end of the air basin, EC levels are higher on days with high O_3. This is due to the transport of material emitted within the Los Angeles urban core to downwind locations on high photochemical smog days rather than to dominance by local sources of EC emitted in the vicinity of Upland or Rubidoux. Most importantly, we note that there is a progressively improving correlation between formic and acetic acids and O_3 as air parcels move inland toward the downwind photochemical smog receptor sites. These results suggest that, for the eastern portion of the air basin, photochemical production during transport dominates local primary emissions of formic and acetic acids.

Finally, we consider evidence that could support or refute the hypothesis that formic and acetic acids are formed by aqueous phase oxidation within liquid fog droplets. Since it is known that in the Los Angeles basin high sulfate levels are formed primarily within liquid droplets in the presence of high relative humidity and fog (49−51), we use particulate sulfate, SO_4^{2-}, as our primary marker for the occurrence of fog processing. In addition, the average relative humidity and the number of hours that fog was observed during the day (NFOG) can be used to characterize the potential for aqueous phase transformations. However, it must be noted that if NFOG is computed only from fog observations at airports located near the air monitoring sites where the formic and acetic acids measurements were made, then those local fog observations may not capture a Lagrangian description of the conditions experienced by air parcels as they are advected across the air basin to the sampling sites. An air monitoring site at which fog was not observed during a day may sample air parcels that encountered a fog upwind near the coast earlier in the day. Accordingly, for the inland sites (i.e., all except Hawthorne and Long Beach), NFOG was determined by counting the number of hours in each day that fog was observed at some point in the Los Angeles basin. Since fog downwind of the coastal sites at Hawthorne and Long Beach does not affect pollutant levels at the coast, the NFOG parameter values for Hawthorne and Long Beach were based only on data from the local meteorological observation station representing those areas (Table 1).

The correlation coefficients of relative humidity, NFOG, peak O_3, and formic and acetic acids with SO_4^{2-} are presented in Table 4. Sulfate concentrations are positively correlated with both aqueous phase indicators at all sites. Formic and acetic acids concentrations at inland sites are highly correlated with sulfate concentrations, while at the coastal sites, Hawthorne and Long Beach, the same relationship to sulfate concentrations does not exist. This suggests that different processes are important in determining formic and acetic acids and sulfate concentrations at the coast, but that similar processes control their concentrations inland. This is consistent with the hypothesis that direct emissions sources plus marine background concentrations dominate formic and acetic acids concentrations at Hawthorne and Long Beach, but that atmospheric conversion processes are important at locations downwind.

Acknowledgments

Literature Cited

(1) Keene, W. C.; Galloway, J. N.; Holden, J. D. *J. Geophys. Res.* **1983**, *88*, 5122−5130.

(2) Keene, W. C.; Galloway, J. N. *J. Geophys. Res.* **1986**, *91*, 14466−14474.

(3) Sanhueza, E.; Elbert, W.; Rondon, A.; Arias, M. C.; Hermoso, M. *Tellus* **1989**, *41B*, 170−176.

(4) Andreae, M. O.; Talbot, R. W.; Andreae, T. W.; Harriss, R. C. *J. Geophys. Res.* **1988**, *93*, 1616−1624.

(5) Dawson, G. A.; Farmer, J. C.; Moyers, J. L. *Geophys. Res. Lett.* **1980**, *7*, 725−728.

(6) Farmer, J. C.; Dawson, G. A.; *J. Geophys. Res.* **1982**, *87*, 8931−8942.

(7) Dawson, G. A.; Farmer, J. C. *J. Geophys. Res.* **1988**, *93*, 5200−5206.

(8) Puxbaum, H.; Rosenberg, C.; Gregori, M.; Lanzerstorfer, C.; Ober, E.; Winiwarter, W. *Atmos. Environ.* **1988**, *22*, 2841−2850.

(9) Talbot, R. W.; Beecher, K. M.; Harriss, R. C.; Cofer, W. R., III *J. Geophys. Res.* **1988**, *93*, 1638−1652.

(10) Hartmann, W. R.; Santana, M.; Hermoso, M.; Andreae, M. O.; Sanhueza, E. *J. Atmos. Chem.* **1991**, *13*, 63−72.

(11) Norton, R. B. *J. Geophys. Res.* **1992**, *97*, 10389−10393.

(12) Helas, G.; Bingemer, H.; Andreae, M. O. *J. Geophys. Res.* **1992**, *97*, 6187−6193.

(13) Kawamura, K.; Kaplan, I. R. *Anal. Chem.* **1984**, *56*, 1616−1620.

(14) Pierson, W. R.; Brachaczek, W. W. *Aerosol Sci. Technol.* **1990** *12*, 8−27.

(15) Grosjean, D. *Atmos. Environ.* **1988**, *22*, 1637−1648.

(16) Grosjean, D. *Environ. Sci. Technol.* **1989**, *23*, 1506−1514.

(17) Solomon, P. A.; Salmon, L. G.; Fall, T.; Cass, G. R. *Environ. Sci. Technol.* **1992**, *26*, 1594−1601.

(18) Eldering, A.; Solomon, P. A.; Salmon, L. G.; Fall, T.; Cass, G. R. *Atmos. Environ.* **1991**, *25A*, 2091−2102.

(19) Hatchfield, P.; Carpenter, C. *Formaldehyde: How Great is the Danger to Museum Collections?*; Center for Conservation and Technical Studies, Harvard University Art Museums: Cambridge, MA, 1987.

(20) Jacob, D. J.; Wofsy, S. C. *J. Geophys. Res.* **1988**, *93*, 1477−1486.

(21) Kawamura, K.; Ng, L.; Kaplan, I. R. *Environ. Sci. Technol.* **1985**, *19*, 1082−1086.

(22) Calvert, J. G.; Stockwell, W. R. *Environ. Sci. Technol.* **1983**, *17*, 428A−443A.

(23) Atkinson, R.; Lloyd, A. L. *J. Phys. Chem. Ref. Data* **1984**, *13*, 315−444.

(24) Su, F.; Calvert, J. G.; Shaw, J. H. *J. Phys. Chem.* **1979**, *83*, 3185−3191.

(25) Jacob, D. J. *J. Geophys. Res.* **1986**, *91*, 9807−9826.

(26) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem.* **1985**, *89*, 588−591.

(27) Moortgat, G.; Veyret, B.; Lesclaux, R. *J. Phys. Chem.* **1989**, *93*, 2362−2368.

(28) Madronich, S.; Calvert, J. G. *J. Geophys. Res.* **1990**, *95*, 5697−5715.

(29) Chameides, W. L.; Davis, D. D. *Nature* **1983**, *304*, 427−429.

(30) Grosjean, D. *Environ. Sci. Technol.* **1991**, *25*, 710−715.

(31) Schultz Tokos, J. J.; Tanaka, S.; Morikami, T.; Shigetani, H.; Hashimoto, Y. *J. Atmos. Chem.* **1992**, *14*, 85− 94.

(32) *Directory of Air Quality Monitoring Sites− 1972*; EPA-450/2-73-006; U.S. Environmental Protection Agency, U.S. Government Printing Office: Research Triangle Park, NC, 1973.

(33) *Directory of Air Quality Monitoring Sites Active in 1977*; EPA-450/2-78-048; U.S. Environmental Protection Agency, U.S. Government Printing Office: Research Triangle Park, NC, 1978.

(34) Solomon, P. A.; Fall, T.; Salmon, L.; Cass, G. R.; Gray, H. A.; Davidson, A. *J. Air Pollut. Control Assoc.* **1989**, *39*, 154−163.

(35) Keene, W. C.; Talbot, R. W.; Andreae, M. O.; Beecher, K.; Berresheim, H.; Castro, M.; Farmer, J. C.; Galloway, J. N.; Hoffmann, M. R.; Li, S.; Maben, J. R.; Munger, J. W.; Norton, R. B.; Pszenny, A. A. P.; Puxbaum, H.; Westberg, H.; Winiwarter, W. *J. Geophys. Res.* **1989**, *94*, 6457−6471.

(36) Grosjean, D.; Parmar, S. S. *Environ. Sci. Technol.* **1990**, *24*, 1021−1026.

(37) Johnson, B. J.; Dawson, G. A. *J. Atmos. Chem.* **1993**, *17*, 123−140.

(38) Grosjean, D.; Williams, E.; Van Neste, A. Measurements of organic acids in the South Coast Air Basin. Final report, California Air Resources Board Agreement A5-177-32; DGA, Inc.: Ventura, CA 1988.

(39) Grosjean, D.; Tuazon, E. C.; Fujita, E. *Environ. Sci. Technol.* **1990**, *24*, 144−146.

(40) Russell, A. G.; Cass, G. R. *Atmos. Environ.* **1986**, *20*, 2011−2025.

(41) Hanst, P. L.; Wilson, W. E.; Patterson, R. K.; Gay, B. W.; Chaney, L. W.; Burton, C. S. *A spectroscopic study of California smog*; Environmental Protection Agency Publication EPA 650/4-75-006; U.S. EPA: Research Triangle Park, NC, 1975.

(42) Tuazon, E. C.; Graham, R. A.; Winer, A. M.; Easton, R. R.; Pitts, J. N., Jr.; Hanst, P. L. *Atmos. Environ.* **1978**, *12*, 865−875.

(43) Tuazon, E. C.; Winer, A. M.; Pitts, J. N. Jr. *Environ. Sci. Technol.* **1981**, *15*, 1232−1237.

(44) Grosjean, D. *Atmos. Environ.* **1990**, *24A*, 2699−2702.

(45) Harrington, R. F.; Gertler, A. W.; Grosjean, D.; Amar, P. *Atmos. Environ.* **1993**, *27A*, 1843−1849.

(46) Lawrence, J. E.; Koutrakis, P. *Environ. Sci. Technol.* **1994**, *28*, 957−964.

(47) Chebbi, A.; Carlier, P. *Atmos. Environ.* **1996**, *30*, 4233−4249.

(48) *California Air Quality Data*, Vol. 18; California Air Resources Board: Sacramento, CA, 1986.

(49) Cass, G. R. Methods for Sulfate Air Quality Management with Applications to Los Angeles, Ph.D. Thesis, California Institute of Technology, 1977.

(50) Hering, S. V.; Friedlander, S. K. *Atmos. Environ.* **1982**, *16*, 2647−2656.

(51) Meng, Z.; Seinfeld, J. H. *Aerosol Sci. Technol.* **1994**, *20*, 253−265.