LIBRARY - AIR RESOURCES BOARD

MEASUREMENTS OF ORGANIC ACIDS IN THE SOUTH COAST AIR BASIN

Agreement A5—177—32

Final Report
September 1988

Prepared for:

Research Division
State of California Air Resources Board
P.O. Box 2815, Sacramento, CA 95812

Prepared by:

Daniel Grosjean
Edwin Williams
Antoinette Van Neste

Daniel Grosjean and Associates, Inc.
Suite 205, 4526 Telephone Road
Ventura, CA 93003

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO. ARB/R-88/375	2.	3. Recipient's Accession No. PB89145411

4. Title and Subtitle
MEASUREMENTS OF ORGANIC ACIDS IN THE SOUTH COAST AIR BASIN

5. Report Date
July 31, 1988

6.

7. Author(s)
Daniel Grosjean, Edwin L. Williams II and Antoinette Van Neste

8. Performing Organization Rept. No.

9. Performing Organization Name and Address
DGA, INC.
4526 Telephone Road, Suite 205
Ventura, CA 93003

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.
(C) A5-177-32
(G)

12. Sponsoring Organization Name and Address
Air Resources Board
State of California
P.O. Box 2815
Sacramento, CA 95812

13. Type of Report & Period Covered
Final Report

14.

15. Supplementary Notes

16. Abstract (Limit: 200 words)

Ambient levels of formic acid (up to 13 ppb) and acetic acid (up to 16 ppb) have been measured at a Southern California smog receptor site. The results are discussed with respect to emission sources, in-situ formation in the atmosphere, and removal processes for organic acids in urban atmospheres. Mobile sources contribute an estimated 20,000 kg per day of organic acids in the Los Angeles area. In-situ formation by ozone-hydrocarbon reactions contributes another 20,000 kg per day. Removal involves mostly dry deposition, with estimated deposition fluxes of 70 nmol m^{-2} $year^{-1}$ for formic acid and acetic acid. Ambient levels of organic acids were higher than those of inorganic acids (nitric acid, HCl) and exceeded those of ozone 50% of the time, i.e. for 12 hours at night. Sampling and analytical methods, gas-aerosol phase partition, diurnal variations and relationships with other air quality parameters and earlier literature data are examined in detail.

17. Document Analysis a. Descriptors

Organic acids
Formic acid
Acetic acid
Air Pollution

b. Identifiers/Open-Ended Terms

c. COSATI Field/Group

18. Availability Statement
Release Unlimited. Available from National Technical Information Service, 5285 Port Royal Road Springfield, VA 22161

19. Security Class (This Report)

20. Security Class (This Page)

21. No. of Pages
100

22. Price
$21.95

DISCLAIMER

The statements and conclusions in this report are those of Daniel Grosjean and Associates, Inc. (DGA) and not necessarily those of the State Air Resources Board. The mention of commercial products, their sources or their use in connection with material reported here is not to be construed as actual or implied endorsement of such products.

ACKNOWLEDGMENTS

Dr. Sucha Parmar (DGA) contributed to the laboratory analyses of chloride and organic acid samples and to the development of the corresponding analytical protocols. Mr. Eric Grosjean (California State University, Northridge) had major responsibility in carrying out the field operations. As field manager of the CSMCS project, Dr. Suzanne Hering provided logistical assistance during the field component of this project. Dr. Carol Ellis of Southern California Edison (SCE) agreed to have the DGA PAN analyzer installed in the SCE Mobile Air Quality Laboratory (MAQL) for the duration of CSMCS. Dr. Andrew Huang and Ms. Laura Games of SCE provided assistance and made available MAQL air quality data. Dew samples were made available by Dr. William Pierson (Ford Motor Co.), who also provided draft results on dew chemistry. Ms. Jennifer Felix (DGA) typed the several drafts and final version of this report. Dr. Douglas Lawson and Mr. Eric Fujita (Air Resources Board) provided advice and made available ARB air quality data.

This report was submitted in fulfillment of Agreement A5—177—32 entitled "Measurements of Organic Acids in the South Coast Air Basin" under the sponsorship of the California Air Resources Board. Work was completed as of April 1988.

TABLE OF CONTENTS

Disclaimer i
Acknowledgments ii
List of Figures iv
List of Tables v
Summary, Conclusions and Recommendations vi

1. Introduction: Project Scope and Objectives 1
2. Sampling and analytical methods 2
   2.1. Scope of field measurements 2
   2.2. Sampling configuration 2
   2.3. Sample handling and storage 2
   2.4. Sample analysis: general approach 6
   2.5. Organic acids 6
   2.6. Nitric acid and hydrogen chloride 7
   2.7. Peroxyacetyl nitrate (PAN) 7
   2.8. Dew samples 17
   2.9. Aldehyde denuder 17
   2.10. Sampling and analytical performance 18

3. Results and Discussion 20
   3.1. Ambient concentrations (gas phase) 20
   3.2. Diurnal variations 20
   3.3. Comparison with literature data 20
   3.4. Gas-particle distribution 27
   3.5. Air quality indicators 30
   3.6. Direct emissions of organic acids 35
   3.7. Estimates of vehicle emissions of organic acids 39
   3.8. Atmospheric formation of organic acids 42
   3.9. Ozone-olefin reaction 42
   3.10. Aldehyde-HO_2 reaction 46
   3.11. Phenol-OH reaction 46
   3.12. Aldehyde oxidation in clouds 49
   3.13. Removal processes 49
   3.14. Comparison of emissions, in-situ formation and removal processes 56
   3.15. Positive bias due to aldehydes 56
   3.16. Positive bias due to peroxyacetyl nitrate 59
   3.17. Collection efficiency of nylon filters 60
   3.18. Relative abundance of organic and inorganic acids in the South Coast Air Basin atmosphere 64

4. References 72
Appendix A: Aldehydes and organic acids in dew samples
Appendix B. Peroxyacetyl nitrate ambient concentrations

LIST OF FIGURES

Figure 1. Map of South Coast Air Basin and sampling location.

Figure 2. Calibration curves for formate and acetate. Non-suppressed size exclusion ion chromatography on resin column, 0.5 mM H_2SO_4 eluent, ultraviolet detection at 210 nm, forward detection mode (non-absorbing eluent).

Figure 3. Size exclusion chromatography-ultraviolet detection analysis of formate,acetate, nitrite and bicarbonate in ambient air sample collected on alkaline-impregnated filter in Teflon-KOH filter pack.

Figure 4. Calibration curves for nitrate and chloride. Non-suppressed ion exchange (partition) chromatography on resin column, phthalic acid and sodium tetraborate eluent, ultraviolet detection at 248 nm, negative detection mode (non-absorbing analyte in uv-absorbing eluent).

Figure 5. Ion exhange chromatography-ultraviolet detection of nitrate in ambient air sample collected on nylon filter in Teflon-nylon filter pack.

Figure 6. Diurnal variations of ambient levels of gas phase formic acid and acetic acid, Glendora, CA, August 12-21, 1986.

Figure 7. Diurnal variations of gas-particle concentration distributions of formic acid and acetic acid.

Figure 8. Diurnal variations of ozone, carbon monoxide, sulfur dioxide, and formaldehyde, Glendora, CA, August 12-21, 1986.

Figure 9. Composite diurnal profiles for nitric oxide, nitrogen dioxide, and ozone, Glendora, CA, August 12-21, 1986.

Figure 10. Nitrogen dioxide concentration ratios; data from ARB chemiluminecence analyzer (reference), SCE chemiluminescence analyzer, and ARB visible light absorption photometer.

Figure 11. Diurnal variations of formic acid and formaldehyde, Glendora, CA, August 12-21, 1986.

Figure 12. Production of the keto acid pyruvic acid by photooxidation of ortho cresol.

Figure 13. Diurnal variations of PAN and of the acetate to formate concentration ratio, Glendore, CA, August 12-21, 1986.

LIST OF TABLES

Table 1. Sampling configuration
Table 2. Sampling flow rate and volumes of air sampled
Table 3. List of organic acids tested for analysis by liquid chromatography
Table 4. Conditions for the analysis of organic acids
Table 5. Selected examples of LC methods for organic acids and co-analytes
Table 6. Selected liquid chromatography methods for negative photometry analysis of chloride and nitrate
Table 7. Sampling and analytical performance
Table 8. Ambient levels (gas phase) of formic acid and acetic acid
Table 9. Concentration-frequency distribution of gas phase formic acid and acetic acid
Table 10. Formic acid to acetic acid gas phase concentration ratios
Table 11. Gas phase carboxylic acids in the non-urban troposphere
Table 12. Gas phase carboxylic acids in urban air
Table 13. Gas-particle distribution of formic acid and acetic acid
Table 14. Vapor pressure of monocarboxylic and dicarboxylic acids
Table 15. Organic acids identified in urban particulate matter
Table 16. Air quality parameters used in data analysis
Table 17. Averaged concentrations of gas phase pollutants, Glendora, CA, 8/12-21/86
Table 18. Diurnal variations of formic acid/CO and acetic acid/CO concentrations ratios
Table 19. Estimates for mobile source emissions of formic and acetic acids in the South Coast Air Basin
Table 20. Estimated emission inventory for organic acids in the South Coast Air Basin
Table 21. Olefins whose reaction with ozone leads to formic acid and acetic acid
Table 22. Rate constants for OH-carbonyl and OH-organic acid reactions in the aqueous phase
Table 23. Organic acids in hydrometeors
Table 24. Input data for deposition calculations
Table 25. Deposition fluxes for organic acids
Table 26. Summary of emission, atmospheric formation and removal data for organic acids
Table 27. Summary of studies relevant to the conversion of aldehydes to carboxylic acids on alkaline substrates
Table 28. Nitrite concentrations from samples collected on alkaline filters
Table 29. PAN interference in acetic acid measurements
Table 30. Side-by-side measurement of formate on Teflon-alkaline and nylon-alkaline filter packs
Table 31. Ambient concentrations of nitric acid, Glendora, CA, August 12—21, 1986.
Table 32. Ambient concentrations of hydrogen chloride, Glendora, CA, August 12-21, 1986
Table 33. Literature data for ambient levels of HCl
Table 34. Relative abundance of inorganic and organic acid, Glendora, CA, August 12-21, 1986.

Table A-1 Aldehydes and organic acids in dew samples.

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Much of the research and regulatory efforts concerning acid deposition in California and elsewhere have focused in the past on the strong inorganic acids, sulfuric and nitric; organic acids have received much less attention. The main objective of this project was to contribute measurements that would augment the data base from which the role of organic acids in urban pollution and acid deposition could be better assessed. The major components of this project included (a) the development of cost-effective measurement methods for airborne acids, (b) the application of these methods to intensive measurements carried out at a California South Coast Air Basin smog receptor site, Glendora, and closely coordinated with the ARB-sponsored Carbon Species Methods Comparison Study (CSMCS), and (c) data interpretation with emphasis on ambient levels, diurnal variations, phase distribution, emissions, formation and removal of organic acids in urban air. In addition, the relative abundance of organic and inorganic acids was determined for the first time from simultaneous measurements carried out at the Glendora study site. Major findings are as follows:

Measurement methods

Filter packs involving Teflon and alkaline-impregnated filters are suitable for quantitative collection of airborne organic acids. The use of a biocide is mandatory to avoid analyte loss during sample storage. Sample bicarbonate content and pH measurements indicate rapid "neutralization" of alkaline-impregnated filters by atmospheric CO_2. Filters directly impregnated with carbonate had collection efficiencies comparable to those obtained with alkaline filters. Nylon filters failed to collect airborne formic acid and acetic acid under the conditions of our study.

Recent progress in liquid chromatography (LC) technology has made it possible to analyse organic acids on LC hardware with detection limits exceeding our "target" limit for this study, one part per billion (ppb.) A number of analytical protocols tested were successful for several classes of organic acids. Two of these protocols were applied to the analysis of the field samples, one involving ion exhange (partition) chromatography with ultra violet detection in the negative mode (non-absorbing analyte in uv-absorbing eluent) and the other involving size-exclusion chromatography with dilute acid eluent and direct ultraviolet detection. These protocols are suitable for a number of inorganic species (chloride, nitrate, nitrite, bicarbonate) as well as for organic acids.

Field experiments with annular denuders to remove gas phase aldehydes showed no indication, in agreement with laboratory literature data, that aldehyde oxidation to acids on alkaline media introduces a positive bias when measuring airborne organic acids. Alkaline decomposition of peroxyacetyl nitrate (PAN) to acetate was examined on the basis of direct measurements of PAN, nitrite, and other possible nitrite precursors such as NO_2. The levels of nitrite measured on alkaline traps corresponded to 2-4 ppb of nitrous acid at night, and to only 2.6—4.1% of NO_2 and to less than 6.4% of PAN during daytime. In turn, PAN contributed up to 20-35% of the measured acetic acid concentration, with an average of 22.5%

Levels, diurnal variations and phase distribution of organic acids

Formic acid and acetic acid are by a substantial margin the most abundant organic acids in the Basin atmosphere. Levels of formic acid were in the range 1---13 ppb (4 hr. and 8 hr. averaged values); those of acetic acid ranged from 2 to 16 ppb. On the average, formic acid levels exceeded those of acetic acid, though by a small margin (average ratio of 1.1). Both

acid exhibited nighttime maxima. Levels of formic acid and acetic acid each exceeded those of ozone during the twelve-hour period, 8 p.m. to 8 a.m. Consistency with literature data was examined from a comprehensive survey of both tropospheric and urban air studies.

While particulate phase samples often contained measurable amounts of formate and acetate, gas-particle partition data clearly indicate that formic acid and acetic acid are present in the Basin atmosphere mostly in the gaseous form. Overall, 94% and 88% of the total measured formate and acetate were present as gas phase formic acid and gas phase acetic acid, respectively. Literature data, vapor pressure considerations and sampling artifact scenarios were examined together with measured gas-particle distribution ratios. This analysis suggests that some formate and acetate are retained on alkaline particles during sampling.

Sources, in-situ production and removal of organic acids

Descriptive analysis of the ambient organic acid data base and of the corresponding air quality tracers (CO, SO_2, O_3, PAN, formaldehyde, NO_x) indicates that ambient levels of organic acids reflect both direct emissions and in-situ formation. Estimates are proposed for emissions from mobile sources and are as follows: 6,500 kg/day for formic acid (range 1,200-13,000 kg/day), 9,000 kg/day for acetic acid, 2,900 kg/day for other monocarboxylic acids, 400 kg/day for aliphatic dicarboxylic acids, and 1,000 kg/day for aromatic acids, for a total of ~ 20,000 kg/day. No emission rates could be derived for stationary sources.

In-situ formation of organic acids in urban air may involve aldehyde oxidation in the gas phase and in cloudwater, phenol photooxidation, and the ozone-olefin reaction. Detailed considerations of the mechanisms and kinetic data for these reactions, and of the chemical structure and emission rates of the possible acid precursors point out to the ozone-olefin reaction as a major source of organic acids in the atmosphere, with acid production rates consistent with both ambient acid levels and their diurnal variations. In-situ reactions produce more formic acid than acetic acid, along with lesser amounts of other carboxylic acids. Net (in-situ production not corrected for simultaneous removal, see below) in-situ production rates are comparable to emission rates from motor vehicles, i.e. ~15,000-20,000 kg/day.

Removal of organic acids from the atmosphere by chemical reactions is negligible. The two important removal processes are dry deposition (gas phase acids) and removal by rain (particulate phase acids). Overall, dry deposition is about 14 times more important than removal by rain and accounts for 92% of the total organic acid deposition budget. In turn, removal by rain is twice that estimated for dew collected in Glendora during the study period. Deposition fluxes, in nmol m^{-2} $year^{-1}$, are 67.0 for formic acid (of which 95% is by dry deposition), 70.00 for acetic acid (91% dry deposition), and 6.7 for propionic acid (95% dry deposition).

Comparison is made of direct emissions, in-situ formation and removal processes. Removal estimates exceed production estimates by a factor of about 2—4. This discrepancy may reflect an overestimate of dry deposition velocities, and underestimate of production processes (direct emissions and/or in-situ formation), or both.

Finally, simultaneous measurements of major organic (formic, acetic) and inorganic acids (nitric acid, hydrogen chloride) clearly showed the former category to be more abundant. During the study period, formic acid accounted for 24—49% (volume basis) or 20—44% (mass concentration basis) of the total gas phase acids in the Basin atmosphere. Formic

and acetic acid each exceeded the sum of the inorganic acids during the 16 hour period 8 p.m. to 12 noon, and together accounted for 73.5% (volume basis) of the total gas phase acids during the study period. These results underline the importance of including organic acids when assessing the atmospheric acid burden including acid deposition in the South Coast Air Basin.

Recommendations

In the area of sampling and analytical protocols, we recommended that our estimates of the positive bias due to PAN when measuring acetate (acetic acid) be refined by carrying out limited field work with selective denuders (e.g. that remove PAN but not acetic acid, or vice versa). Meanwhile, PAN should be measured whenever measuring acetic acid, as was done in this study, in order to correct the measured acetic acid for positive PAN bias.

In the area of data interpretation, descriptive analysis would greatly benefit from shorter time resolution, e.g. 1 hour samples, than that afforded by our ARB-prescribed 4-hour and 8-hour sampling schedule. Ambient levels of organic acids do vary substantially over short time increments, as do those of other air pollutants including those that can be used to estimate organic acid emission, in-situ formation, and removal rates.

Mobile sources of organic acids should be better characterized, preferentially using "integrated" methods (e.g. tunnels, parking garage, truck stations, etc.) which provide information of much more value than individual vehicle emissions rates. In the same way, stationary source emissions of organic acids should be characterized.

Estimates of in-situ formation would benefit from product studies of the ozone-olefin reaction, with obvious emphasis on organic acid yields. The importance of this and other reactions could be further delineated by descriptive analysis of field data from intensive studies. This data base already exists for the South Coast Air Basin (1985 Nitrogen study, 1986 CSMCS, i.e. this work, and 1987 SCAQS) but has yet to be exploited.

Dry deposition estimates should be refined, using additional field data. Our estimates involved the choice of a conservative value for organic acid dry deposition velocities, i.e. 2—3 times lower than that measured for nitric acid. If the actual deposition flux of organic acids is higher than the value estimated in this study, emission and in-situ formation rates would also have to be revised upwards.

Finally, the magnitude of our emission and deposition estimates, together with the abundance of organic acids relative to inorganic acids, would justify additional studies of organic acids in the South Coast Air Basin. Their spatial and seasonal variations are unknown (even though the 1987 SCAQS study, which involved summer measurements at two sites, and summer and winter measurements at one site, may shed modest light on this issue). The analytical protocols employed in this study are suitable for more routine and long-term studies. With the possible future use of methanol as a fuel in California, and considering that methanol toxicity involves formic acid as the toxic metabolite, it would seem prudent to gather baseline data on current population exposure to ambient levels of formic acid and other organic acids.

1. INTRODUCTION: PROJECT SCOPE AND OBJECTIVES

Much of the research and regulatory efforts concerning acid deposition have focused in the past on the strong inorganic acids, sulfuric and nitric, and on their respective precursors sulfur dioxide and oxides of nitrogen. Organic acids have received much less attention. However, recent studies of precipitation chemistry have shown that organic acids may account for a large fraction, up to 64%, of the total acidity in samples collected in nonurban environments (e.g. Keene et al, 1983). Indeed, organic acids including formic acid and acetic acid now appear ubiquitous in the atmosphere (e.g. Dawson et al 1980, Farmer and Dawson, 1982, Norton 1985, Galloway et al 1982, Andreae et al 1988, Talbot 1988).

Few studies of organic acids have been carried out in urban areas including the South Coast Air Basin. Several studies of limited scope include reports of organic acids in engine exhaust, ambient air (gas phase and particle-bound), and precipitation samples (e.g. Hanst et al 1975, 1982, Tuazon et al 1978, 1981, Grosjean et al 1978, Kawamura et al 1985a, Grosjean 1988). Pierson and Brachaczek (1987) measured organic acids in dew collected at Glendora, CA. Formate was the most abundant of all anions present, organic or inorganic. The main objective of the present study was to contribute additional measurements that would augment the data base from which the role of organic acids in urban pollution and acid deposition could be better understood. Specific issues to be addressed included:

- the nature and ambient levels of organic acids in the South Coast Air Basin.
- the diurnal variations of ambient concentrations for the most abundant organic acids.
- the phase distribution of these acids, i.e. gas phase vs. particulate matter.
- the relative abundance of organic and inorganic acids in the Basin's atmosphere.
- the relationships between organic acids and other indicators of air quality.
- the performance and limitations of the corresponding sampling and analytical methods.

Accordingly, the major components of this project include (a) laboratory studies, focusing on the investigation of cost-effective sampling and analytical methods for airborne organic acids, (b) a field study, closely coordinated with the ARB-sponsored Carbon Species Method Comparison Study (CSMCS) and (c) data analysis, focusing on ambient levels of organic acids vs. other air quality parameters.

2. SAMPLING AND ANALYTICAL METHODS

2.1. Scope of field measurements

This study was closely coordinated with the ARB-sponsored CSMCS Project which took place August 11-21, 1986, on the Citrus College Campus, Glendora, CA, (Figure 1). Our ARB-prescribed sampling schedule was identical to that of most CSMCS participants and involved the collection of five sets of samples per day, i.e. 08:00 - 12:00, 12:00 - 16:00, 16:00 - 20:00, 20:00 - 24:00 (periods #1-4) and 00:00 - 08:00 PDT (period #5).

2.2. Sampling configuration

All samples were collected on a 120 x 10 ft. platform raised 3 ft. above ground. Sampling was carried out using open face, 47 mm diameter dual filter holders mounted on tripods 5 ft. above the platform, upstream side down for protection against rain and direct sunlight, and with the sampling units maintained in the shade during daylight hours. Each sampling unit was connected to a dual head Barnant Air Cadet sampling pump. Each set of samples consisted of six dual filter units (Table1). Particulate phase organic acids were collected on Teflon filters (upstream), and gas phase organic acids on alkaline-impregnated filters (downstream). Nitric acid and hydrogen chloride were collected on nylon filters and carbonate-impregnated filters, respectively, downstream of Teflon filters. The fourth sampling unit consisted of a Teflon-alkaline filter pack mounted downstream of an aldehyde denuder (see description below) in order to investigate sampling artifacts i.e., aldehyde oxidation to acid during sample collection. The fifth sampling unit consisted of a nylon-alkaline filter pack. As nylon filters are known to retain nitric acid (e.g. Grosjean 1982) and oxalic acid (Norton et al 1983, Grosjean 1988), their potential to collect other acids could be investigated by comparing Teflon-alkaline and nylon-alkaline filter packs. Finally, a sixth sampling unit was operated on a rotating schedule to provide replicate samples of all five filter pack configurations.

All filter pack samples were collected at flow rates of 8-14 liters per minute depending upon filter pack configuration (each type of filter has a different resistance to air flow). Flow rates were measured during each sampling period using a specially made calibration plate that provided a leak-free seal on top of the open face filter holder andwhose single opening (a 1/4 inch diameter hole in the center of the plate) was connected to a flowmeter that had been calibrated in the laboratory using a mass flow controller. Independent flow checks out by the CSMCS field management team showed our calibration flowmeter to be within 8% of the audit value. Sampling flow rates and volumes of air sampled are summarized in Table 2.

2.3. Sample handling and storage

Teflon and nylon filters (both in their original boxes), alkaline-impregnated filters, and carbonate-impregnated filters (both individually stored in 47 mm petri dishes sealed with Parafilm) were shipped to the sampling site in a dark, refrigerated container and were stored at the site in a small refrigerator located underneath the sampling platform. Immediately after sampling, all filters were placed in dark (amber) glass tubes with Teflon-lined screw caps and containing 10 mL of deionized water and 40 uL of HPLC grade chloroform added as a biocide. The addition of a biocide is critical to the stability, during storage, of analytes including formate and acetate (e.g. Herliky et al, 1987). Rapid loss of analyte, even in

FIGURE 1. MAP OF SOUTH COAST AIR BASIN AND SAMPLING LOCATION

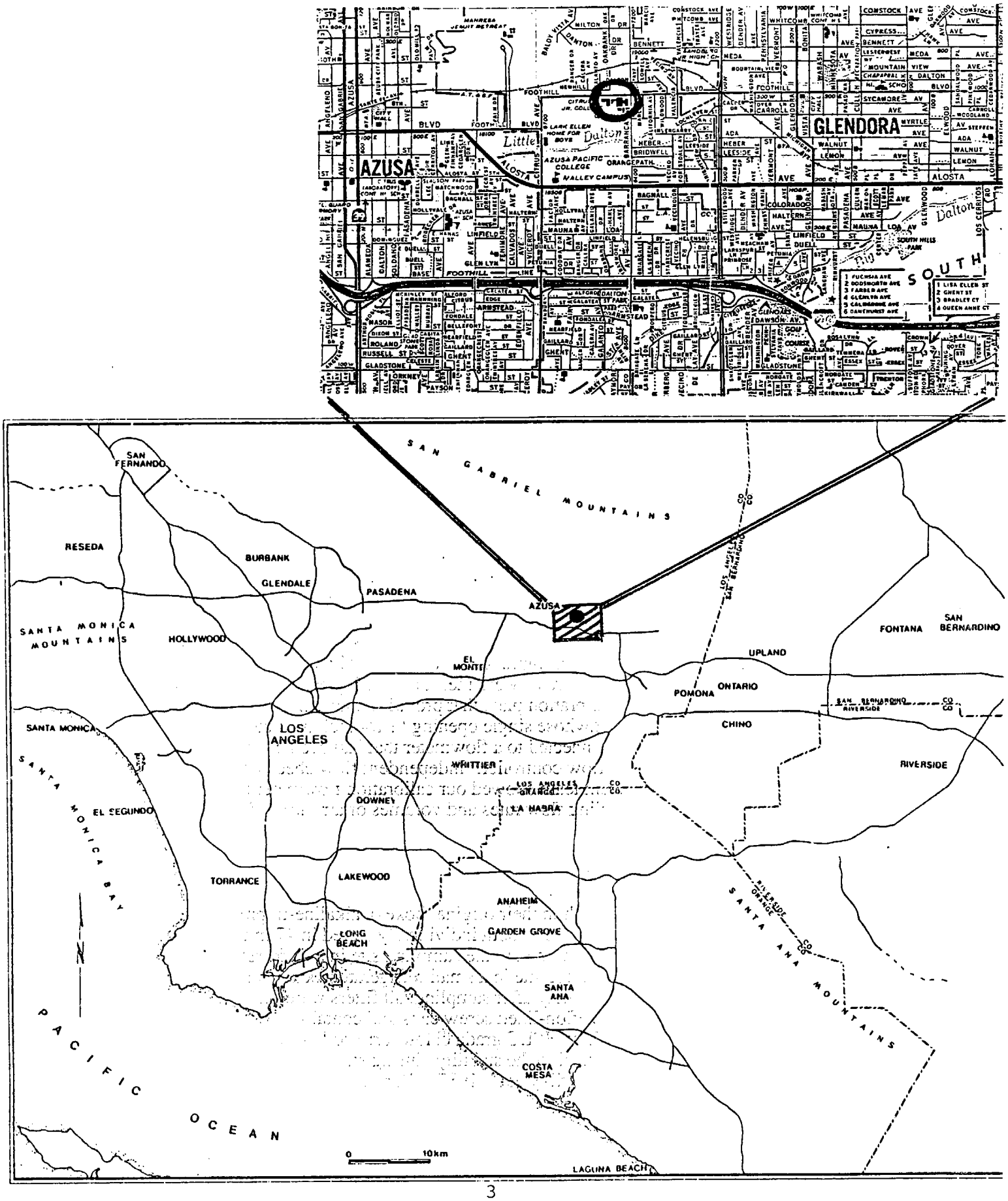


TABLE 1. SAMPLING CONFIGURATION

Unit Code	Filter pack (all 47 mm diameter filters, upstream filter listed first)	Filter type	Analyte(s), comments
A	Teflon Alkaline	Sartorius, 1.2 μm pore size Gelman AE glass filter with 0.05N KOH	Particulate phase organic acids Gas phase organic acids
B	Teflon Alkaline	same as A same as A	same as A, downstream of aldehyde denuder (a) same as A, downstream of aldehyde denuder (a)
C	Nylon Alkaline	Sartorius, 0.45 μm pore size Gelman AE glass filter with 0.05N KOH	nylon filter-collected organic acids (b) gas phase organic acids
D	Teflon Carbonate	same as A Whetman 41 filter with 2% sodium carbonate	particulate phase organic acids (c) hydrogen chloride
E	Teflon Nylon	same as A same as C	particulate phase organic acids (c) nitric acid
G	Replicates	A,B,C,D or E(d)	same as A,B, C,D or E

(a) during sampling period #3, 16:00-20:00 PDT.
(b) particulate phase acids plus any gas phase acid retained by nylon filter.
(c) analyzed for aromatic acids.
(d) rotating schedule of replicates as follows: Teflon-alkaline (A and B) on days #2 (8/12/86) and #7, Nylon-alkaline (C) on days #3 and #8 , Teflon-carbonate (D) on days #4 and #9, and Teflon-nylon (E) on day #5.

TABLE 2. SAMPLING FLOW RATES AND VOLUMES OF AIR SAMPLED

Filter pack (upstream filter listed first)	Mean sampling flow rate, liters per minute	Volume of air sampled, m3	
		Periods 1-4 (sampling time 3 hr 55 min.)	Period 5 (sampling time 7 hr 55 min.)
Teflon-KOH	14.1	3.31	6.70
Teflon-KOH with aldehyde denuder	11.1	2.61	5.27
Nylon-KOH	11.7	2.76	5.57
Teflon-carbonate	11.9	2.80	5.65
Teflon-nylon	8.25	1.91	3.86

samples stored in the dark at low temperature, has been observed when no biocide is added (Galloway 1985, Chapman et al 1986, Grosjean et al, unpublished results 1985, 1986). Chloroform was selected in this study after verifying that its presence in the samples does not interfere with the several analytical protocols employed.

Once placed in biocide-containing vials, all samples were returned to the field refrigerator, then returned to the DGA laboratory on blue ice in a dark container, and stored at refrigerator temperature prior to analysis. Shortly before analysis, the samples were sonicated for 20 minutes at room temperature and the extracts were filtered on 0.2 um filters mounted directly on the syringe used for sample injection into the liquid chromatograph's sampling loop.

2.4. Sample analysis: general approach

Two methods have been widely used for the identification of organic acids in environmental samples, namely ion chromatography (IC) and gas chromatography-mass spectrometry (GC-MS). GC-MS and direct MS methods are complex, time-consuming and expensive. Their application to atmospheric samples has yielded much information concerning particulate phase organic acids (e.g. Schuetzle et al 1973, 1975, Grosjean et al 1978). However, gas phase organic acids, which constitute the bulk of the total organic acids in the atmosphere, are not easily amenable to MS analysis. For these lower molecular weight organic acids, IC has become increasingly popular (e.g. Grosjean and Nies 1984, Norton 1985), due in part to its relative simplicity and cost-effectiveness. IC analysis, however, is essentially limited to formic acid and acetic acid. Its application to other low molecular weight monoacids (e.g. propionic, butyric, pyruvic) and diacids (e.g. oxalic, malonic) has been fraught with difficulties including incomplete resolution and poor detection limits.

Our search for more suitable methods has focused on liquid chromatography (LC). With the recent progress in LC column technology, separation of ionic species with acidic or alkaline aqueous eluents (the counterpart of conventional IC) is now possible using LC equipment (e.g. Okada and Kuwamoto 1983). In addition, ultraviolet detectors, which can be operated at one or more wavelengths in the range 190-600 nm, provide much more selectivity than the conductivity detector used in conventional IC analysis (Willison and Clarke, 1984). Another expensive and troublesome feature of conventional ion chromatography, the suppressor column, is no longer needed with new resin-based ion exchange columns and ultraviolet detection. Finally, ultraviolet detection allows not only to detect uv-visible-absorbing analytes in a non-absorbing eluent, but also to detect non-absorbing analytes using a strongly absorbing eluent. Specific examples of applications are given in the next section.

2.5. Organic acids

The matrix of exploratory investigations of analytical protocols for LC separation of organic acids involved five types of columns, two types of detection (uv-visible and conductivity), and two modes of detection (positive, e.g. absorbing analyte in non-absorbing eluent, or negative,e.g. non-absorbing analyte in absorbing eluent). The hardware employed included a SSI model 300 pump, a Perkin Elmer LC 75 uv-visible detector (190-600 nm), a Waters Co. conductivity detector, a Valco injection valve, and a Hitachi D-2000 integrator.

A list of the organic acids tested is given in Table 3. The specific conditions investigated are listed in Table 4 and were selected after a comprehensive review of literature data. Selected results are listed in Table 5 and include, for each set of conditions tested, retention times and detection limits where appropriate. Several of the more promising methods were studied more systematically in order to optimize resolution and sensitivity. For example, the size exclusion, direct photometry method involving H_2SO_4 as eluent was optimized with respect to detection wavelength (studied in the range 190-250 nm), eluent concentration (range 0.25 - 5.0 mM), eluent flow rate, and addition of an organic modifier (methanol and acetonitrile) which accelerates the elution of slow-eluting analytes. On the basis of these results, several of the methods tested were employed to analyze the samples collected during the Citrus College field study. As an example, calibration curves are given in Figure 2 for formate and acetate. The criteria for selection included detection limits and, perhaps more importantly, the resolution of organic acids from other ions unavoidably present in air samples collected on alkaline substrates, i.e. chloride (from HCl), nitrate (from HNO_3), nitrite (from NO_2), sulfate, and carbonate/bicarbonate (from CO_2). Figure 3 shows resolution of strong ions, formate, acetate, nitrite and bicarbonate in a field sample collected on a KOH-impregnated filter. The other methods listed in Table 4 and Table 5 may have potential usefulness for a wide range of environmental analytical applications.

2.6. Nitric acid and hydrogen chloride

Nitric acid and hydrogen chloride were analyzed as nitrate and chloride, respectively, using negative photometry liquid chromatography. As for organic acids, a number of methods were tested, of which several gave good resolution and suitable detection limits (Table 6).

Aqueous extracts of nylon filters were analyzed directly for nitrate after sonication and extract filtration. Aqueous extracts of carbonate-impregnated filters contained large amounts of carbonate/bicarbonate whose presence in the sample resulted in poor baseline stability. Baseline stability was restored by dilution of the samples (1:10) prior to analysis. Comparision of aqueous and carbonate-containing chloride standards indicated a lower detector response to chloride in the presence of carbonate. Thus, all calibration curves were prepared with chloride standards containing the same amount of carbonate as the impregnated filters employed for sampling of ambient HCl (aqueous Na_2CO_3, 2% by weight). Examples of calibration curves are given in Figure 4 for nitrate and chloride. A typical field sample chromatogram is shown in Figure 5.

2.7. Peroxyacetyl nitrate (PAN)

Peroxyacetyl nitrate was measured using a Shimadzu GC Mini 2 gas chromatograph equipped with a ^{63}Ni detector, an automated 5 cm^3 sampling loop, a 1/8 inch x 3 ft. Teflon column packed with 10% Carbowax 400 on Chromosorb W, 60/80 mesh, and ultra high purity nitrogen as carrier gas. The chromatograph was housed in the Southern California Edison Mobile Laboratory located near the sampling platform and within 10 ft. of the DGA filter pack samplers. Ambient air was sampled about 12 ft. above ground using a 1/4 inch diameter Teflon line. The instrument was operated in the isothermal mode with the column, injector and detector temperatures maintained at 30°C. Timer-activated injections of ambient air were made at 20 minute intervals. On-site calibration was carried out using the DGA PAN generator, a portable photochemical flow reactor in which parts per

TABLE 3. LIST OF ORGANIC ACIDS TESTED FOR ANALYSIS BY LIQUID CHROMATOGRAPHY

aliphatic monocarboxylic acids	
formic acid	HCOOH
acetic acid	CH3 COOH
propionic acid	CH3CH2 COOH
butyric acid	CH3(CH2)2 COOH
valeric acid	CH3(CH2)3 COOH
hexanoic acid	CH3(CH2)4 COOH
aliphatic dicarboxylic acids	
oxalic acid	COOH-COOH
malonic acid	COOH CH2 COOH
succinic acid	COOH (CH2)2 COOH
glutaric acid	COOH (CH2)3 COOH
adipic acid	COOH (CH2)4 COOH
other aliphatic acids	
glyoxylic acid	CHO COOH
pyruvic acid	CH3COCOOH
methane sulfonic acid	CH3SO3H
aromatic acids	
benzoic acid	C6H5 COOH
phenyl acetic acid	C6H5 CH2 COOH
hydroxy benzoic acid	OH-C6H4 COOH
toluic acid	CH3-C6H4 COOH

TABLE 4. CONDITIONS FOR LC ANALYSIS OF ORGANIC ACIDS

COLUMNS

reverse phase	Whatman Partisphere C18 cartridge, 5 µm, carbon loading 11%
silica column, strong anions	Whatman Partisphere SAX cartridge, 5 µm, quarternary amino groups
silica column, weak anions	Whatman Partisphere WAX cartridge, 5 µm
resin-based column, low capacity anion exchange:	Hamilton PRP-X-100, 10 µm, poly (styrene-divinylbenzene)-trimethylammonium
resin-based ion exclusion column:	Hamilton PRP-X-300, 10 µm, polystyrene-divinylbenzene sulfonate

ELUENTS

phthalic acid, 1.5-8 mM, with and without sodium tetraborate buffer

benzoic acid, 1.3-2.7 mM

potassium hydroxide, 0.8-15 mM

sulfuric acid, 0.5-5 mM, with and without methanol or acetonitrile added as organic modifier

nitric acid, pH 2.5

water-acetonitrile, 95:5 by volume

sodium bicarbonate, 0.15 mM

TABLE 5. SELECTED EXAMPLES OF LC METHODS FOR ORGANIC ACIDS AND GO-ANALYTES

Column (a)	Eluent and conditions (a)	Analyte	Retention time, min.	Detection limit, µg/mL uv(b)	conductivity
WAX	phthalic acid + sodium tetraborate, pH 4.0	formate	6.8	1.8(248)	1.0
		acetate	2.1	15	2.4
		chloride	8	0.5	0.5
		nitrate	9	0.9	0.9
		sulfate	22	-	-
		phosphate	15	-	-
		bicarbonate	25	13	-
PRP-X-100	phthalic acid + sodium tetraborate pH 4.0	formate	5.1	6 (248)	6
		acetate	4.8	35	35
		chloride	8.1	0.6	1.2
		nitrate	12	0.8	1.4
		bicarbonate (c)	5.5	-	-
PRP-X-300	0.5 mM H2SO4	formate	1.0	0.25 (210)	120
		acetate	2.4	0.4	110
		chloride	0.45	-	-
		nitrate	0.45	-	-
		sulfate	0.54	-	-
		hydroxide	0.43	-	-
		oxalate	0.52	0.4	0.4
		glyoxylate	0.60	14	-
		malonate	1.1	8.6	-
		pyruvate	0.84	1.0	-
		succinate	4	24	-
		others (d)	10 - 22	-	-
PRP-X-300	0.25 mM H2SO4 + 5% CH3OH	succinate	2.0	0.5 (210)	-
		propionate	6.1	1.7	-
		glutarate	4.5	1.4	-
		adipate	18	-	-
PRP-X-300	95:5 water-acetonitrile	valerate	9	0.2 (210)	-
		benzoate	3	0.4	-
		phenylacetate	3.8	0.6	-
		hydroxybenzoate	1.5	0.4	-

Table 5. Selected examples of LC methods for organic acids (continued)
Page 2

Column (a)	Eluent and conditions (a)	Analyte	Retention time, min.	Detection limit, µg/mL uv(b)	conductivity
PRP-X-300	phthalic acid + sodium tetraborate, pH 4	formate	1.9	0.5 (248)	-
		acetate	4	6	-
		chloride	1.8	0.008	-
		benzoate	7.2	4	-
		pyruvate	7.0	0.25	-
		nitrate	7.3	0.02	-
		oxalate	7.1	1.2	-

(a) see Table 4
(b) detection wavelength indicated in parentheses
(c) negative peak
(d) other organic acids tested: propionic, butyric, methane sulfonic, glutaric, adipic, benzoic, hydroxybenzoic, phenylacetic

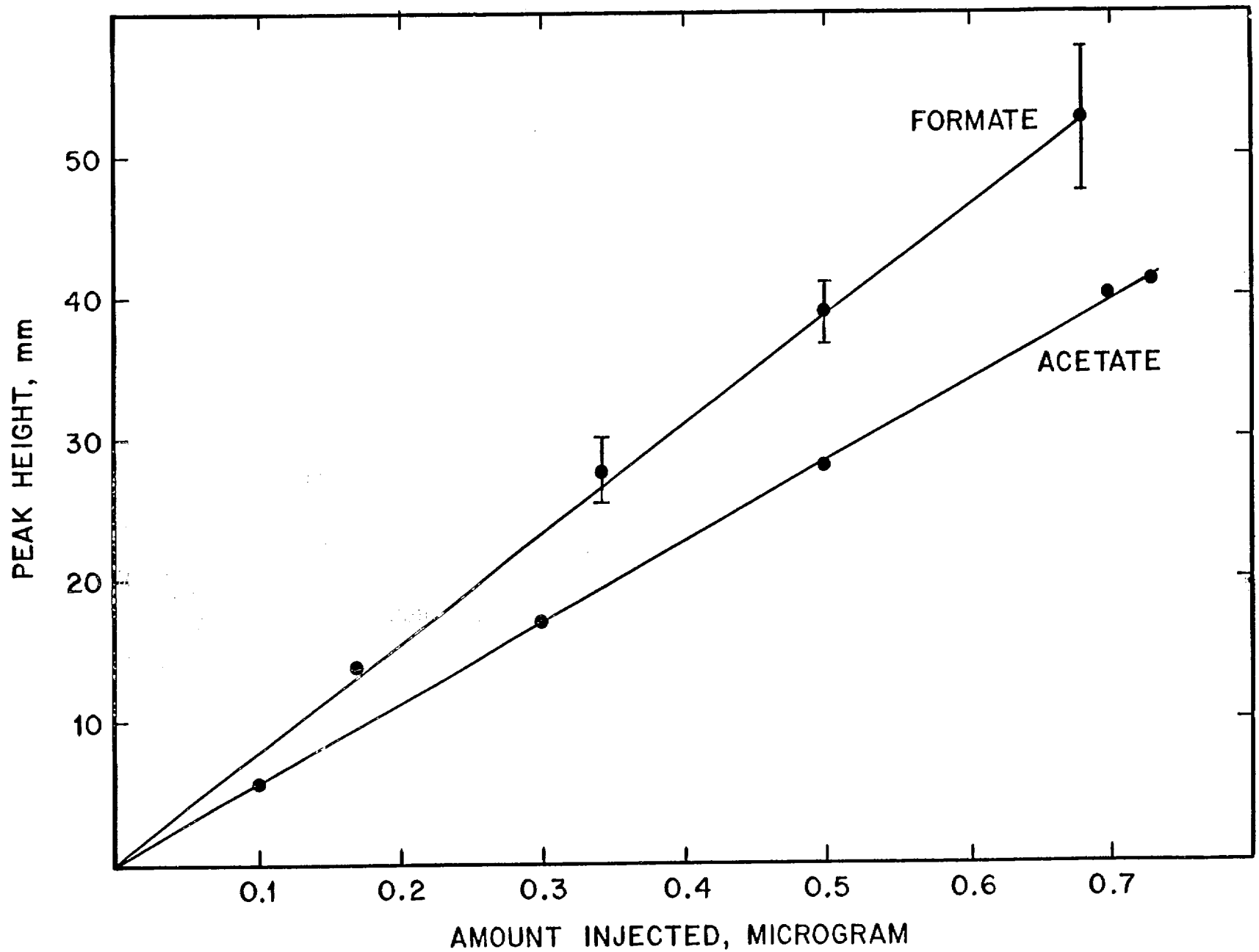


Figure 2. Calibration curves for formate and acetate. Non-suppressed size exclusion ion chromatography on resin column, 0.5 mM H_2SO_4 eluent, ultraviolet detection at 210 nm, forward detection mode (non-absorbing eluent)

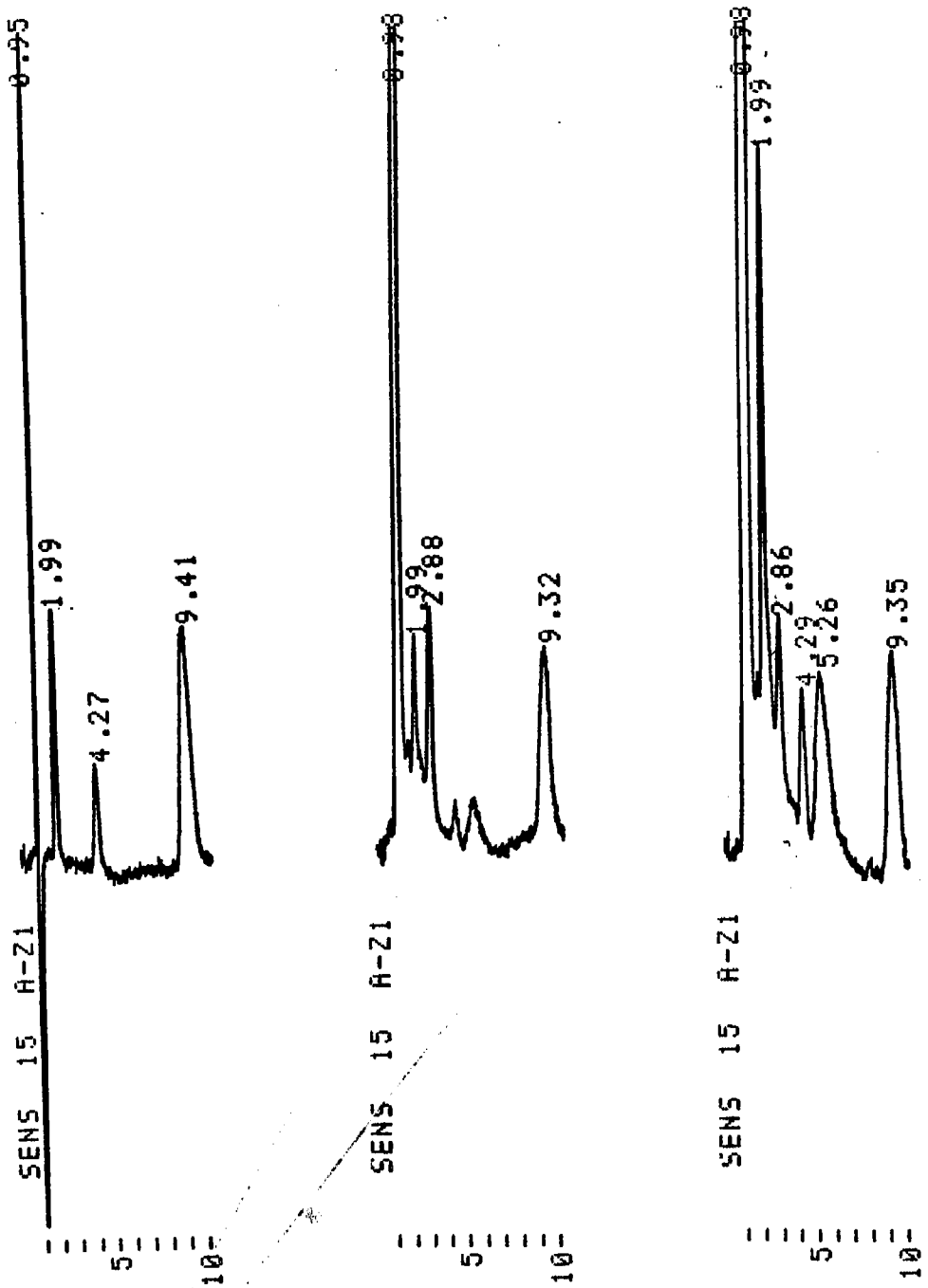


Figure 3. Size exclusion chromatography-ultraviolet detection analysis of formate, acetate, nitrite and bicarbonate in ambient air sample collected on alkaline-impregnated filter in Teflon-KOH filter pack

TABLE 6. SELECTED LIQUID CHROMATOGRAPHY METHODS FOR NEGATIVE PHOTOMETRY ANALYSIS OF CHLORIDE AND NITRATE

Column (a)	Eluent (a)	Analyte	Retention time (min.)	Detection limit, ug/mL uv(nm)	conductivity
SAX	2mM phthalic acid	chloride	19	12.5 (247)	-
		nitrate	28	12.5 (247)	-
SAX	2.6 mM benzoic acid	chloride	6	8.5 (247)	-
		nitrate	8	8.0 (247)	-
WAX	phthalic acid + sodium tetraborate, pH 4.0	chloride	8	0.5 (248)	0.5
		nitrate	9	0.9 (248)	0.9
PRP-X100	phthalic acid + sodium tetraborate, pH 4.0	chloride	8	0.6 (248)	1.2
		nitrate	12	0.8 (248)	1.4
PRP-X-300	phthalic acid + sodium tetraborate, pH 4.0	chloride	1.8	0.008 (248)	-
		nitrate	7.3	0.02 (248)	-

(a) see Tables 4 and 5.

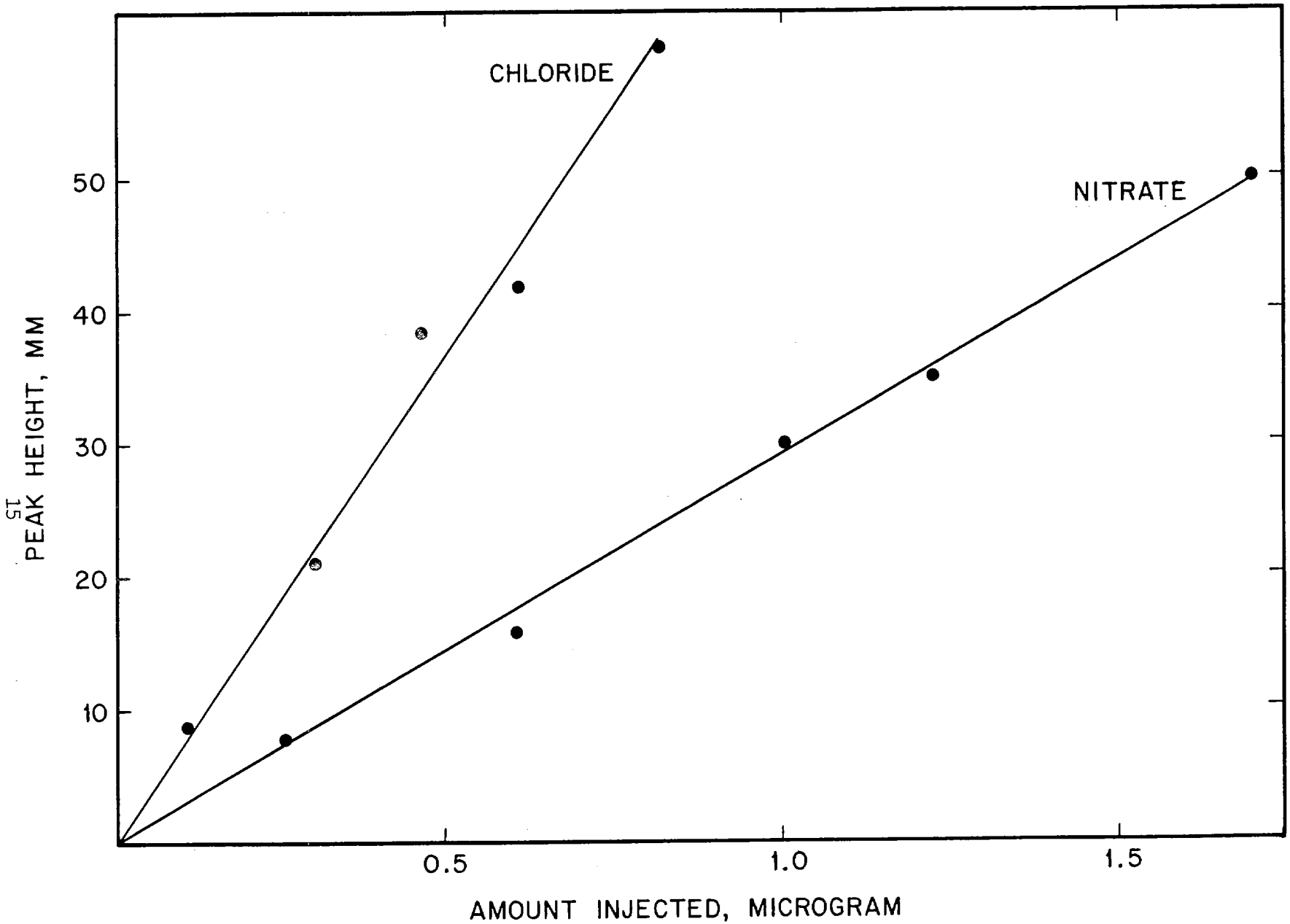


Figure 4. Calibration curve for nitrate and chloride. Non-suppressed ion exchange (partition) chromatography on resin column, phthalic acid and sodium tetraborate eluent, ultraviolet detection at 290 nm, negative detection mode (non-absorbing analyte in uv-absorbing eluent)

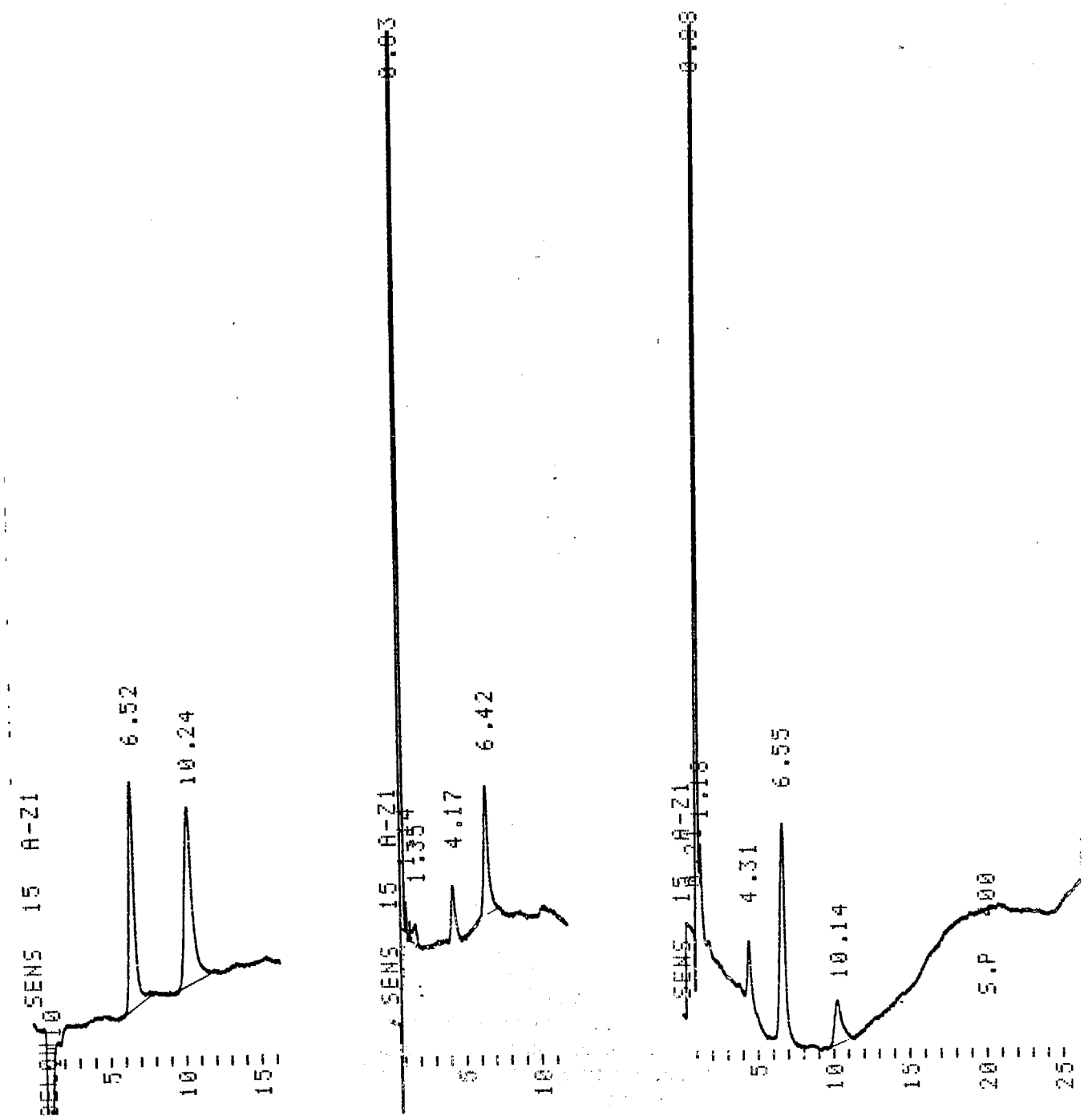


Figure 5. Ion exchange chromatography ultraviolet detection of nitrate in ambient air sample collected on nylon filter in Teflon-nylon filter pack. Left: standard solution of chloride (6.5 min.) and nitrate (10.2 min.). Middle: nylon filter blank with high formate (4.3 min.) and chloride blank, see text. Right: ambient sample, 8/15/86, 12 noon-4 p.m.

billion (ppb) levels of PAN are produced by irradiation of mixtures of acetaldehyde, chlorine and nitrogen dioxide (Grosjean et al, 1984). The output of the generator was measured as acetate following alkaline hydrolysis of PAN in an impinger containing 10 mL of aqueous KOH or on a small resin cartridge (Sep-Pak, Waters Co.) impregnated with KOH. Acetate was determined using the size exclusion-ultraviolet photometry detection method also employed for the analysis of acetate in ambient samples.

At the completion of the field study, the instrument was re-calibrated in the laboratory under identical operating conditions, and was also compared to another GC unit used as "reference" for calibration of nine ECD-GC units that were being prepared for field measurements of PAN in the South Coast Air Basin (SCAQS project).

2.8. Dew samples

Aliquots of dew samples collected during the CSMCS project were made available by Dr. Pierson (Pierson and Brachaczek, 1987). Initially, the dew samples were to serve as a basis for comparison of formate and acetate concentrations measured using two methods, i.e.ion chromatography with conductivity detection (Pierson and Brachaczek 1987) and liquid chromatography with ultraviolet detection (this study). We also decided to analyze the dew samples for aldehydes, which play important role in dew chemistry.

Sample handling and analytical protocols were as follows. After collection, dew samples were saturated with chloroform and stored at refrigerator temperature. Towards the end of the study (i.e. up to 10 day after collection), 1 mL aliquots given by Dr. Pierson were added to glass vials with Teflon-lined screw caps and containing either 1 mL of 5 x 10^{-3}N KOH and 4 uL of chloroform or 1 mL of deionized water + 50 uL of a saturated solution of dinitrophenylhydrazine (DNPH) in acetonitrile + 10 uL of 6 N HCl. The aliquot volumes were determined by gravimetry. Blanks and field controls were included for each type of sample. The samples added to KOH-chloroform were analyzed for formate and acetate by liquid chromatography on a size exclusion column and with ultraviolet detection at 210 nm. Experimental conditions were identical to those described earlier for the analysis of the air samples collected on filter packs. The samples added to acidic DNPH were analyzed for formaldehyde and acetaldehyde (as their DNPH derivatives) using the liquid chromatography method described by Grosjean (1982, 1988). This method involves separation of carbonyl hydrazones on a C18 reverse phase column with acetonitrile-water as eluent and quantitation with an ultraviolet-visible detector at 360 nm.

Under the conditions employed, the measured aldehyde concentrations in dew are expected to be only those of the "free" aldehydes, with little or no contribution from the aldehydes combined as hydroxyalkane sulfonic acids (aldehyde-bisulfite adducts).

2.9. Aldehyde denuder

The denuder prepared for this study consisted of an acidic aqueous solution of acidic DNPH with added glycerol and coated inside an annular denuder, 21.7 cm long x 2.8 cm outside diameter, with an annular gap of 1 mm (inside diameter of

outer tube 24 mm, outside diameter of inner tube 22 mm). DNPH removes selectively gas phase aldehydes, which combine with DNPH on the denuder walls to form 2,4-dinitrophenylhydrazones. The removal efficiency of the denuder has been established in tests carried out in this laboratory and elsewhere (Possanzini et al 1987). The annular denuder was mounted upstream of a Teflon-alkaline filter pack and the entire unit was operated side-by-side with a Teflon-alkaline filter pack without denuder. Differences in measured organic acids between the two units were taken to reflect alkaline substrate-mediated oxidation of aldehydes to organic acids during sampling.

2.10. Sampling and analytical performance

A number of quality assurance steps were built into our sampling and analytical protocol. These included:

- replicate samples, i.e. sampling side-by-side with two identical filter packs.
- replicate analyses, i.e. repeat injections of aliquots of the same sample, for each type of filter pack and analyte.
- determination and daily checks of analytical detection limits.
- analysis of procedural controls which consisted for each type of filter, of filters brought to the field, mounted onto the dual filter holder, taken off the filter holder after activating the sampling pump for a few seconds, placed in vials containing deionized water and chloroform, and stored and analyzed along with actual field samples.
- determination of sampling detection limits, i.e. the lesser of analytical detection limits or analyte concentration in procedural controls.
- daily preparation and analysis of calibration standards.

For each type of filter, the number of replicate samples, replicate analyses, and procedural controls was at least 10% of the number of samples.

Results of these protocol performance studies are summarized in Table 7 for the major analytes studied, i.e. formate, acetate, nitrate, chloride, and nitrite. Our target detection limits of 1 part per billion were exceeded for all analytes, e.g. 0.29 ppb for formic acid and 0.45 ppb for acetic acid in 4 hour samples (sampling periods #1-4) and 0.14 ppb and 0.22 ppb for the same analytes in the 8 hour sample (period #5).

Filter pack collection efficiencies were not investigated in this study but have been well documented in previous work. Grosjean (1988) reported collection efficiencies of 88.4 ± 6.6% for formic acid and of 90.1 ± 6.4% for acetic acid on Teflon-alkaline filter packs identical to those employed here, and operated at even higher flow rates than those used in this study (16-19 vs. 11-14 lpm). In the same way, a collection efficiency of ≥ 99% was obtained for nitric acid on nylon filters in Teflon-nylon filter packs (Grosjean 1982, 1988). Norton (1983) obtained quantitative collection of oxalic acid on nylon filters. Kawamura et al (1985) have reported collection efficiencies of ≥ 98% for formic and acetic acid and of ≥ 91% for the C_3-C_6 monocarboxylic acids on KOH-impregnated filters operated at 10 lpm. Quantitative collection of hydrogen chloride on carbonate-impregnated filters has also been documented (e.g. Okita and Ohta 1979). For each type of filter pack, the sampling flow rates employed in this study were within the range of literature flow rates reported to yield quantitative collection.

TABLE 7. SAMPLING AND ANALYTICAL PERFORMANCE

	Analyte		
	Formate	Acetate	Nitrite
Slope of calibration curve, peak height (mm) per µg of analyte	160	56	163
Analytical detection limit, nanogram per injection (100 µL injected)	12	36	12
Content of procedural controls, nanogram per injection (100 µL injected)	18	<36	<12
Sampling detection limit, µg per sample	1.8	3.6	1.2
µg m^{-3}, periods 1-4 (4 hr) (a)	0.54	1.1	0.36
µg m^{-3}, period 5 (8 hr) (b)	0.27	0.54	0.18
ppb, periods 1-4 (4 hr)	0.29	0.45	0.19
ppb, period 5 (8 hr)	0.14	0.22	0.1
Replicate analyses relative standard deviation, % (n)			
standards	2.0(15)	3.0(15)	3.0(15)
samples, alkaline filters	7.3(10)	8.5(9)	8.3(8)
samples, Teflon filters	10.2(9)	11.3(9)	-

(a) calculated for sampling volumes of 1.91(nitrate), 2.80 (chloride) and 3.31 m3 (other analytes)
(b) calculated for sampling volumes of 3.86 (nitrate), 5.65 (chloride) and 6.70 m3 (other analytes)

3. RESULTS AND DISCUSSION

3.1. Ambient concentrations (gas phase)

Formic and acetic acids were observed in all samples at levels exceeding our "target" concentration of 1 ppb. Ambient levels of other organic acids, which were occasionally seen in a few samples were below 1 ppb. Ambient concentrations for each sampling period are listed in Table 8, along with the corresponding averages. Levels of formic acid ranged from 1.3 to 13 ppb; those of acetic acid ranged from 1.9 to 16 ppb. Sampling period-averaged values (4 hr or 8 hr averages) ranged from 3.4 to 6.3 ppb for formic acid, from 2.8 to 5.5 ppb for acetic acid and from 6.2 to 11.9 ppb for the sum of formic and acetic acids (13.1 to 25.0 $\mu g\ m^{-3}$). Also listed in Table 8 are the period-averaged concentrations of ozone. It is interesting to note that, during the entire study, levels of formic acid and acetic acid each exceeded those of ozone during the twelve hour period 8 p.m. to 8 a.m. Concentration-frequency distributions are given in Table 9 and exhibit frequency maxima at 3—5 ppb. On the average, levels of formic exceeded those of acetic acid, though by a small margin. Concentration ratios are given in Table 10 for each sampling period. Averaged formic acid to acetic acid concentration ratios ranged from 1.00 to1.14.

3.2. Diurnal Variations

These are plotted in Figure 6 and are seen to exhibit nighttime maxima. This diurnal behavior has been reported before by Grosjean (1988) for both formic acid and acetic acid in Claremont, CA, during the Sept. 1985 NSMCS study. Diurnal variations of ozone, which exhibit daytime maxima, are also included in Figure 6 for comparison.

3.3. Comparison with literature data

A summary of the literature data regarding ambient levels of gas phase carboxylic acids is given in Tables 11 and 12 for the non-urban troposphere and for urban air, respectively. Formic, acetic and pyruvic acid have been identified in non-urban air. Typical concentrations are up to a few ppb for formic and acetic acids, whose sources include the oxidation of isoprene emitted by vegetation as well as biomass burning. Oxidation of isoprene yields formic acid but not acetic acid (Jacob and Wolfsy 1988). In contrast, biomass burning yields substantially more acetic acid than formic acid (Talbot et al 1988). Pyruvic acid (Andreae et al 1987) may also originate from isoprene oxidation. All three acids may form by oxidation of hydrocarbons in plumes from forest fires.

Turning now to urban air, it is evident that little data are available regarding atmospheric levels of gas phase organic acids (Table 12). Hoshika (1982) has measured the C_2- C_5 aliphatic monoacids in Nagoya, Japan. Typical concentrations were 2.5 ppb for acetic acid, 0.3 ppb for propionic acid, and 4-50 x 10^{-3} ppb each for the C_4 and C_5 isomers (butyric, isobutyric, valeric and isovaleric). Dawson et al (1980) have measured up to 3 ppb of formic acid and up to 6 ppb of acetic acid in Tucson, Arizona.

Studies carried out in the South Coast Air Basin include the FT-IR measurements of Hanst et al (1975, 1982) and Tuazon et al (1978, 1981). Only formic acid can be detected by FT-IR, with a detection limit of 4 ppb for about 1 km optical path length. Hanst et al (1975) first reported up to 72 ppb of formic acid in Pasadena, CA, during the severe 7/25/73 smog episode. These results were subsequently

TABLE 8. AMBIENT LEVELS (GAS PHASE) OF FORMIC ACID AND ACETIC ACID

Date (1986)	Sampling period									
	8 - 12		12 - 16		16 - 20		20 - 24		0 - 8	
	F(a)	A(b)	F	A	F	A	F	A	F	A
8/12- 13	4.5	7.0	2.3	3.0	1.8	3.5	3.5	3.0	3.7	3.4
8/13- 14	1.6	3.5	2.7	2.9	1.3	3.4	2.2	4.1	2.7	2.6
8/14- 15	-	4.7	1.3	3.4	3.8	5.1	4.1	4.4	7.5	2.8
8/15- 16	5.5	4.4	6.8	4.1	5.7	4.5	3.6	3.3	3.3	3.3
8/16- 17	5.5	5.0	3.0	2.2	5.0	2.8	2.7	3.6	5.3	5.0
8/17- 18	4.7	4.1	4.5	2.9	4.1	3.2	4.6	3.8	4.4.	4.1
8/18- 19	5.3	2.2	3.1	2.5	2.0	1.9	3.5	2.1	7.2	4.1
8/19- 20	5.6	4.1	3.2	2.1	3.0	2.4	5.5	4.2	13.0	8.7
8/20- 21	8.0	5.9	4.0	2.5	3.6	2.4	2.2	3.2	10.0	16

averages:

formic acid, ppb	5.10	3.40	3.36	3.53	6.34
acetic acid, ppb	4.54	2.84	3.24	3.52	5.55
formic & acetic	9.64	6.24	6.60	7.05	11.89
ozone, ppb	48	171	89	3.5	5.1

(a) F = formic acid, ppb (1 ppb = 1.88 $\mu g\ m^{-3}$)
(b) A = acetic acid, ppb (1 ppb = 2.45 $\mu g\ m^{-3}$), not corrected for possible positive bias due to alkaline decomposition of PAN, see Table 29

TABLE 9. CONCENTRATION FREQUENCY DISTRIBUTIONS OF GAS PHASE FORMIC ACID AND ACETIC ACID

Concentration range, ppb	Number of observations	
	Formic acid	Acetic acid
0-1	0	0
1.1-2	5	1
2.1-3	8	15
3.1-4	10	11
4.1-5	8	13
5.1-6	7	2
6.1-7	1	1
7.1-8	3	0
8.1-9	0	1
>9	2	1

TABLE 10. FORMIC ACID TO ACETIC ACID
GAS PHASE CONCENTRATION RATIOS

	Concentration ratios, ppb/ppb				
DAY	8 - 12	12 - 16	16 - 20	20 - 24	0 - 8
8/12- 13	0.64	0.77	0.51	1.17	1.09
8/13- 14	0.46	0.93	0.38	0.54	1.04
8/14- 15	-	0.38	0.74	0.93	2.68
8/15- 16	1.25	1.66	1.27	1.09	0.98
8/16- 17	1.10	1.36	1.78	0.75	1.08
8/17- 18	1.15	1.55	1.28	1.21	1.07
8/18- 19	2.41	1.24	1.05	1.67	1.77
8/19- 20	1.33	1.52	1.25	1.31	1.49
8/20- 21	1.35	1.60	1.50	0.69	0.62
Sampling Period average	**1.12**	**1.2**	**1.04**	**1.00**	**1.14**

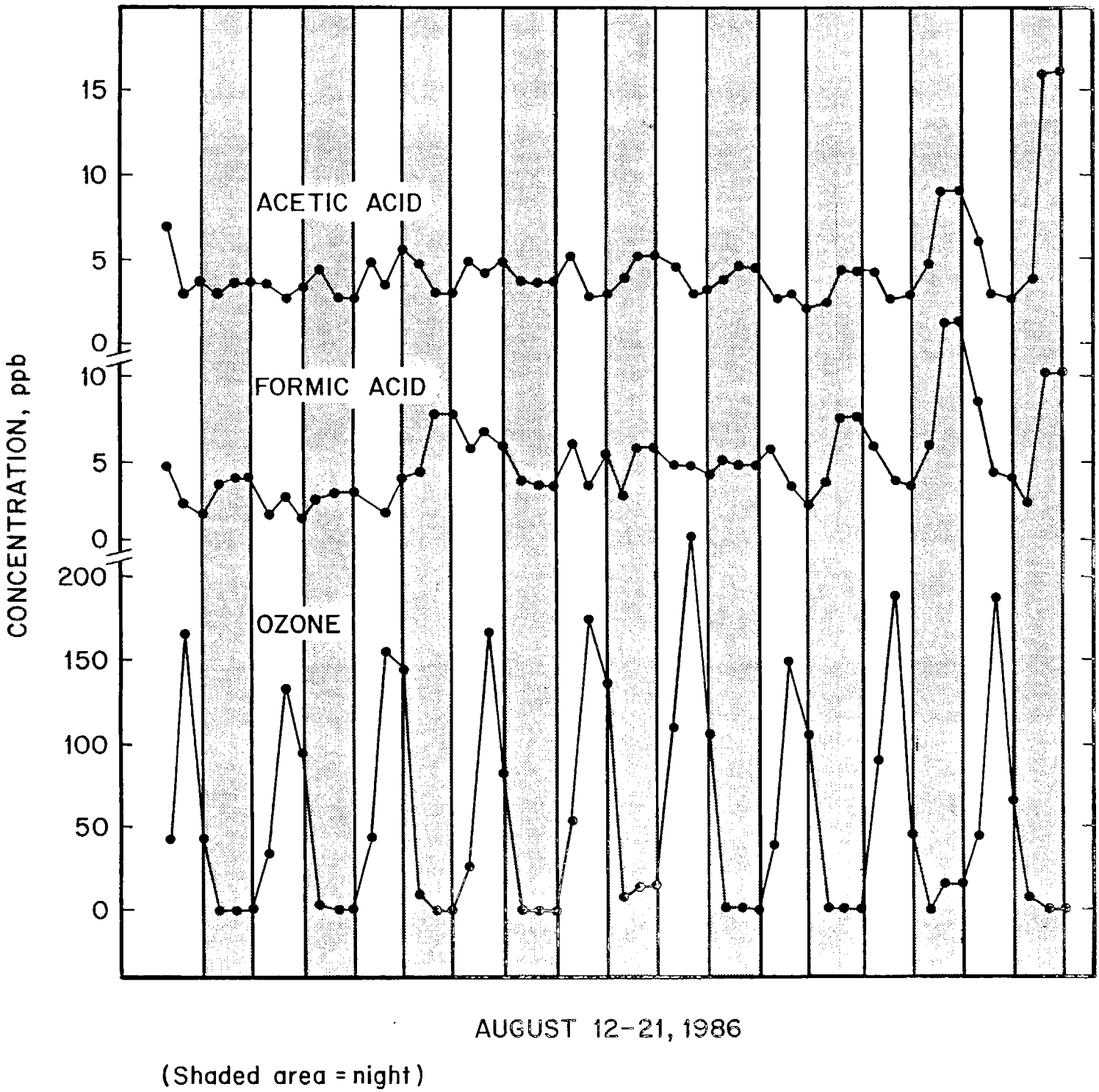


Figure 6. Diurnal variations of ambient levels of gas phase formic acid and acetic acid, Glendora, CA, August 12 - 21, 1986

TABLE 11. GAS PHASE CARBOXYLIC ACIDS IN THE NON-URBAN TROPOSPHERE

Location	Formic acid (ppb)	Acetic acid (ppb)	Other acids (ppb)	Reference
Amazon forest	1.6 ± 0.6	2.2 ± 1.0	-	Andreae et al, 1988
Amazon forest	-	-	pyruvic, 0.01-0.4	Andreae et al, 1987
Hampton, VA	1.9 ± 1.2	1.3 ± 0.9	-	Talbot et al, 1988
Saguaro Nat. Monument, AZ	1.0	0.5		Dawson et al, 1980
Sells, AZ	0.8	0.6		Dawson et al, 1980
Near Tucson, AZ	1.5	1.0		Dawson et al, 1980

TABLE 12. GAS PHASE CARBOXYLIC ACIDS IN URBAN AIR (Units: ppb)

Location	Formic acid	Acetic acid	Other acids	Reference
Nagoya, Japan	-	2.4	propionic 0.3 butyric isobutyric valeric isovaleric, each 4-50 x 10^{-3}	Hoshika, 1982
Tucson, AZ	2.5	4.0	-	Dawson et al, 1980
Pasadena, CA, 1973	up to 19	-	-	Hanst et al, 1975
Riverside, CA, 1977	4 - 19	-	-	Tuazon et al, 1978
Claremont, CA, 1978	4 - 19	-	-	Tuazon et al, 1981
Los Angeles, CA, 1980 (Cal State Los Angeles Campus)	4 - 10	-	-	Hanst et al, 1982
Los Angeles, CA, 1984	0.07 - 3.0	0.3 - 3.9	propionic 0.02 - 0.3 C4-C10 monoacids, each about 10 x 10^{-3} benzoic acid, 1-26 x 10^{-3}	Kawamura et al, 1985
Claremont, CA, 1985	1.9 - 10.5	2.5 - 8.1	-	Grosjean, 1988

corrected and reduced by a factor of four following re-determination of the absorption coefficient (Tuazon et al, 1981, Hanst 1982). Formic acid levels measured by FT-IR are in the range < 4 (detection limit)-19 ppb. Another method, involving sampling with alkaline traps, has been employed by Kawamura et al (1985) who reported up to 3 ppb of formic acid, 4 ppb of acetic acid, 0.3 ppb of propionic acid, 10 x 10^{-3} ppb each of the C_4-C_{10} aliphatic monacids, and 1-26 x 10^{-3} ppb each of the C-C_{10} aliphatic monoacids, and 1-26 x 10^{-3} ppb of benzoic acid. Grosjean (1988) also used an alkaline trap method and reported up to 10 and 8 ppb of formic and acetic acid, respectively.

From the data summarized above, it appears that (a) formic and acetic acids are, by a substantial margin, the most abundant organic acids in the Basin's atmosphere, (b) FT-IR and alkaline trap methods give comparable results for formic acid, (c) urban/non-urban concentration ratios are typically in the range 3—10, (d) there is no apparent long-term trend in ambient levels in the Basin during the period 1973—1985 (the alkaline trap results in Table 12 appear lower than the FT-IR data but correspond to 4—24 hour averaged samples) and (e) there is a distinct increase in organic acid levels from coastal to smog receptor sites. This increase may reflect in-situ formation by atmospheric oxidation processes. Direct emissions and in-situ formation are discussed in detail in Sections 3.6 to 3.12 of this report.

It should be emphasized here that all the studies cited above have been intensive, short-term studies of at most a few days duration at a single location. The present study, even though limited to nine consecutive days at one location, represents one of the most comprehensive efforts so far to measure ambient levels of organic acids in the Basin. No data are available regarding the seasonal and spatial variations of organic acids in the South Coast Air Basin.

3.4. Gas-particle distribution

Results for formic acid and acetic acid concentrations in Teflon-alkaline filter pack samples are listed in Table 13. The observed phase distributions, taken as the ratios of the concentrations measured on Teflon filters (particulate phase) to those measured on alkaline-impregnated filters (gas phase), clearly indicate that both formic acid and acetic acid are present in the Basin's atmosphere in the gaseous form. Overall, 94% of the total measured formate was present as gas phase formic acid, and 88% of the total measured acetate was present as gas phase acetic acid.

These findings are consistent with literature data and with vapor pressure considerations. In the non-urban troposphere, ≥ 98% of both formic acid and acetic acid exist in the gaseous form (Andreae et al 1988, Talbot et al 1988). Small amounts of formate and acetate were found to be associated with the coarse aerosol fraction, probably reflecting adsorption on alkaline particles (Andreae et al 1988, Talbot et al 1988). Similar observations have been made in urban air, where ≥ 95% of the measured formic acid and acetic acid were found in the gas phase (Kawamura et al 1985, Grosjean 1988). Vapor pressures for organic acids are listed in Table 14 and indicate that not only formic acid and acetic acids, but also all monocarboxylic acids up to about C_{10}-C_{12} should be expected to accumulate in the gas phase under typical atmospheric conditions. Cautreels and Van Cauwenberghe (1978) have determined the phase distribution of organic compounds including carboxylic acids in ambient air in Antwerp, Belgium. C_7-C_{11} monocarboxylic acids were found in the gas phase, and C_{12}-C_{18} monocarboxylic acids were found

TABLE 13. GAS/PARTICLE PHASE DISTRIBUTION OF FORMATE AND ACETATE FROM SAMPLES COLLECTED ON TEFLON-ALKALINE FILTER PACKS

	SAMPLING PERIOD									
	8 - 12		12- 16		16- 20		20- 24		0- 8	
	F(a)	A	F	A	F	A	F	A	F	A
8/12 T(b)	0	0								
KOH	27	54								
Gas phase, %	**100**	**100**								
8/13 T	0	4	4	4	3	7	1	5	6	7
KOH	7	20	17	23	8	27	13	32	32	41
Gas phase, %	**100**	**83**	**81**	**85**	**73**	**79**	**93**	**86**	**84**	**85**
8/15 T			2	5						
KOH			41	32						
Gas phase,%			**95**	**86**						
8/16 T	0	6	0	0	0	0	2	0	0.3	3
KOH	38	45	21	20	32	23	19	31	69	83
Gas phase, %	**100**	**88**	**100**	**100**	**100**	**100**	**90**	**100**	**99**	**96**
8/17 T									0	18
KOH									61	74
Gas phase, %									**100**	**80**
8/18 T									1	11
KOH									95	70
Gas phase, %									**99**	**86**
8/19 T	4	11	5	7	3	14	6	16	5	9
KOH	36	34	23	20	19	20	36	34	174	150
Gas phase, %	**90**	**75**	**82**	**74**	**86**	**59**	**86**	**68**	**97**	**94**
8/20 T	0	0	1	0	0	4	0	0	1	4
KOH	52	49	28	23	23	20	14	27	137	286
Gas phase, %	**100**	**100**	**96**	**100**	**100**	**83**	**100**	**100**	**99**	**99**
Average	**98**	**89**	**91**	**89**	**90**	**80**	**92**	**88**	**96**	**90**

(a) F = formate, A = acetate, both in micrograms per sample. Trace amounts of oxalic and benzoic acid were also seen in a few Teflon filter samples.
(b) T = Teflon (upstream), KOH = alkaline trap (downstream), gas phase = KOH/(T + KOH).

Table 14. Vapor Pressures of Monocarboxylic and Dicarboxylic Acids (a)

Monocarboxylic Acids, RCOOH

C_1	Formic Acid	40
C_2	Acetic Acid	18
C_3	Propionic Acid	4
C_4	Butyric Acid	1.15
	Isobutyric Acid	2.25
C_5	Valeric Acid	0.29
	Isovaleric Acid	0.52
C_6	Hexanoic Acid	0.036
C_7	Heptanoic Acid	0.022
C_8	Octanoic Acid	7.7×10^{-3}
C_9	Nonanoic Acid	2.3×10^{-3}
C_{12}	Lauric Acid	1.2×10^{-3}
C_{14}	Myristic Acid	1.5×10^{-4}
C_{16}	Palmitic Acid	1.3×10^{-4}
C_{18}	Stearic Acid	0.2×10^{-4}

Dicarboxylic Acids, $COOH-(CH_2)_n-COOH$

C_2	Oxalic Acid	2.5×10^{-4}
C_3	Malonic Acid	2.6×10^{-3}
C_4	Succinic Acid	2.9×10^{-7}
C_5	Glutaric Acid	1.2×10^{-5}
C_6	Adipic Acid	6.4×10^{-5}

Other Aliphatic Carboxylic Acids

C_3	Pyruvic Acid, $CH_3COCOOH$	1.5×10^{-4}
C_4	Maleic Acid, COOHCH=CHCOOH	1.0×10^{-4}

Aromatic Acids

C_7	Benzoic Acid	4×10^{-3}
C_8	Terephthalic Acid	2×10^{-5}
C_8	Isophthalic Acid	10^{-5}
C_8	Phenylacetic Acid	6×10^{-3}

(a) Adapted From Grosjean 1977; units = mm Hg, at 25°C.

in the condensed phase (aerosol), in agreement with vapor pressure considerations. Also in agreement with vapor pressure considerations, the numerous organic acids that have been identified in urban aerosols are those with very low vapor pressures, see Table 15 and references therein.

Even though most of the formic acid and acetic acid measured in this study were found in the gas phase, the small but measurable amounts of particulate formate and acetate are worthy of consideration since gas phase and particle bound organic acids have different atmospheric residence times. The diurnal variations in gas phase/total concentration ratios are shown in Figure 7 and exhibit daytime minima for both acids. Particulate phase acids may be present as free acids in aerosol droplets, as carboxylate ammonium salts (by reaction with ambient ammonia), as monovalent or divalent cation salts (by displacement of CO_2 from particles containing carbonate, e.g. Na_2CO_3), or simply by adsorption onto alkaline particles. In addition, bias during sampling (artifact) may include adsorption of gas phase formic (acetic) acid on deposited particles (adsorption on the Teflon filter itself is negligible), displacement of particle-bound formate (acetate) by stronger gas phase acids such as HNO_3 and HCl, decompositon of PAN to acetate on alkaline particles (see section 3.16 for details), and oxidation of aldehydes to carboxylic acids. Changes in aerosol droplet acidity will result in gas-liquid phase partition shifts. Finally, changes in temperature, humidity, and gas phase concentration during sampling may also result in gas-condensed phase partition shifts. The observed daytime minima in gas phase/total concentration ratios are consistent with one or more of the processes listed above, but air quality data available to us for the period of interest are not sufficient to carry out a more detailed analysis. Additional studies are needed, preferably with a better time resolution (e.g. 1 hour) than that afforded by our ARB-prescribed sampling schedule in 4—8 hour increments. At the minimum, the magnitude of sampling artifact effects (and their contribution to particulate formate (acetate) should be investigated using denuders that would remove gas phase organic acids upstream of Teflon-alkaline filter packs.

3.5. Air quality indicators

Diurnal variations of organic acid levels reflect the complex interplay of emissions, in-situ formation and removal processes. In order to gain some insight on the relative importance of these processes, we have analyzed these variations vs. those of other indicators of air quality. To this end, we have compiled air quality data gathered by other investigators at Citrus College during CSMCS for the period August 11—21, 1986. Parameters selected and their origin are listed in Table 16. Carbon monoxide and sulfur dioxide were used as indicators of primary emissions from mobile and stationary sources, respectively. Ozone and peroxyacetyl nitrate (PAN) were used as indicators of photochemical activity. Other parameters compiled for their relevance to one or more aspects of this study include nitric oxide, nitrogen dioxide, formaldehyde, and other aldehydes. Sampling period-averaged values were calculated from the original data, which were typically given as one-hour averages.

Data from several sources and/or from different measurement methods were compared whenever available. Data for ozone, carbon monoxide, formaldehyde and sulfur dioxide are shown in Figure 8. Ozone data obtained from ARB and SCE were in excellent agreement, with the exception of several hours on 8/17. Ozone data from nearby monitoring stations were consistent with those reported by the ARB instrument during this period. Overall, ozone levels gradually increased from 8/12 to 8/17 and remained high until 8/21. Instantaneous maxima of 246—292 ppb

TABLE 15. CARBOXYLIC ACIDS IN PARTICULATE MATTER

Reference (sampling location)	Acids and their ambient concentrations
Schuetzle et al, 1973, 1975 (West Covina, CA and other ACHEX sites in SCAB)	Aromatic acids (benzoic, etc.), up to 1.5 $\mu g\ m^{-3}$ Aliphatic diacids, C3-C7, 3 $\mu g\ m^{-3}$
Cronn et al, 1977 (South Coast Air Basin)	Aliphatic diacids, C3-C7
Cautreels and Van Cauwenberghe, 1978 (Antwerp, Belgium)	Aliphatic monoacids, C12-C24 Aromatic acids
Grosjean et al, 1978 (Riverside, CA)	Aliphatic diacids, C3-C10, linear and branched, 0.2 - 0.5 $\mu g\ m^{-3}$
Wauters et al, 1979 (Ghent, Belgium)	
Brewer et al, 1983 (Duarte, CA)	Aliphatic monoacids, C11-C24, 16-39 ng m^{-3} each Aliphatic diacids, C4-C12, up to 90 ng m^{-3}
Barbenkus et al, 1983 (rural sites in Indiana and Ohio)	Aliphatic diacids, C3-C5, 2-50 ng m^{-3} each
Yokouchi and Ambe, 1986 (Nagoya, Japan)	Aliphatic monoacids, C16 and up Aliphatic diacids, C2-C16, 170 ng m^{-3} Tetrahydrofuroic acid
Kawamura and Kaplan, 1986 (Los Angeles, CA)	Aliphatic diacids, C2-C10, linear, branched and unsaturated, 5-20 nanomoles m^{-3} each Aromatic diacids (phthalic)

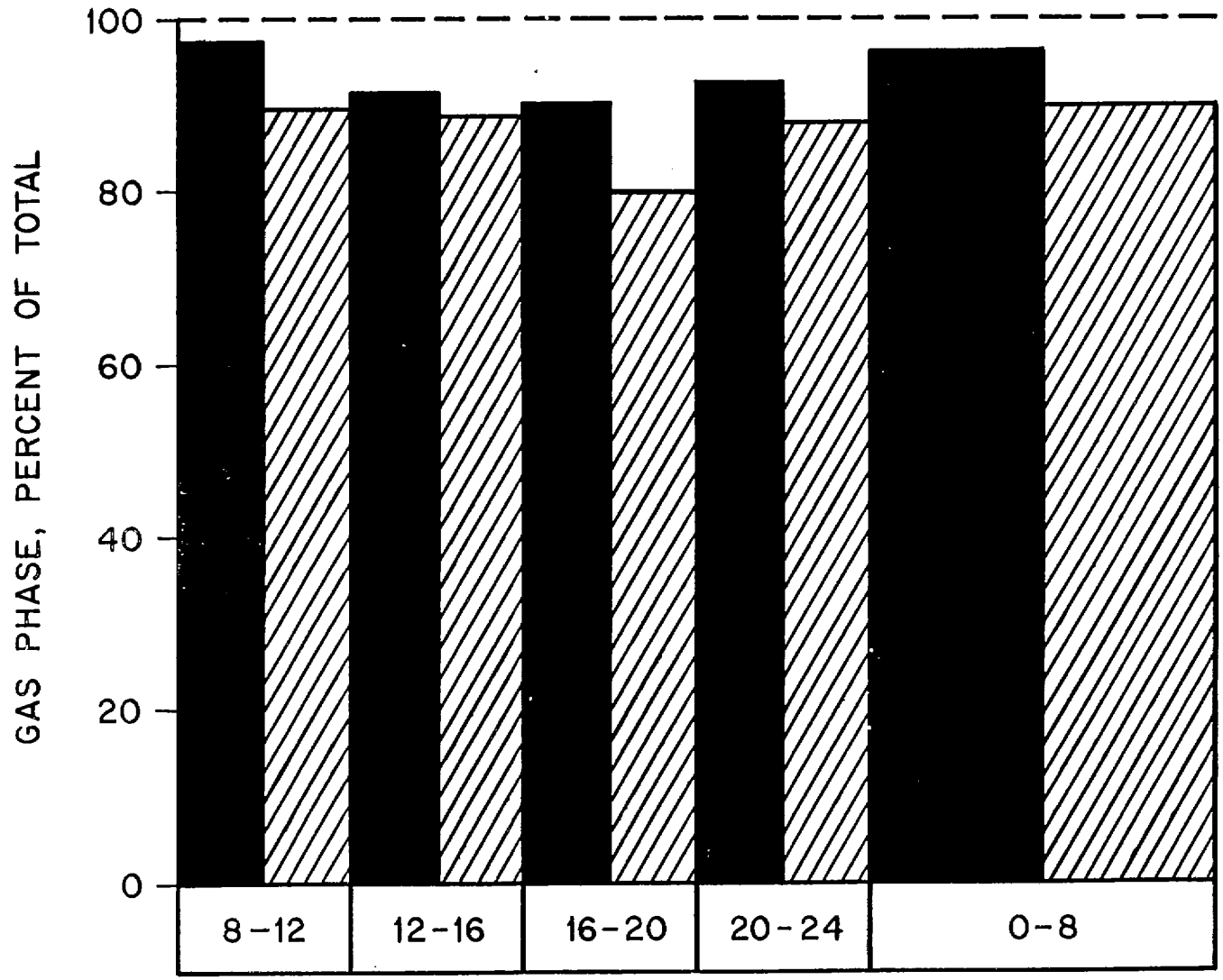


Figure 7. Diurnal variations of gas-particle concentration distribution of formic acid (solid bars) and acetic acid

TABLE 16. AIR QUALITY PARAMETERS USED IN DATA ANALYSIS

Parameter	Source	Measurement method and comments
Ozone	ARB	ultraviolet photometry
	SCE	ultraviolet photometry
Carbon monoxide	ARB	infrared
	SCE	infrared
Nitric oxide	ARB	chemiluminescence
Nitrogen dioxide	ARB	chemiluminescence
	SCE	chemiluminescence (CSI)
	DGA	chemiluminescence (Teco 14 BE)
	ARB	visible light absorption photometry
Sulfur dioxide	SCE	pulsed fluorescence
Formaldehyde	ARB	ARB-averaged values from several groups using several methods
	DGA	DNPH-liquid chromatography
Peroxyacetylnitrate (PAN)	DGA	electron capture gas chromatography

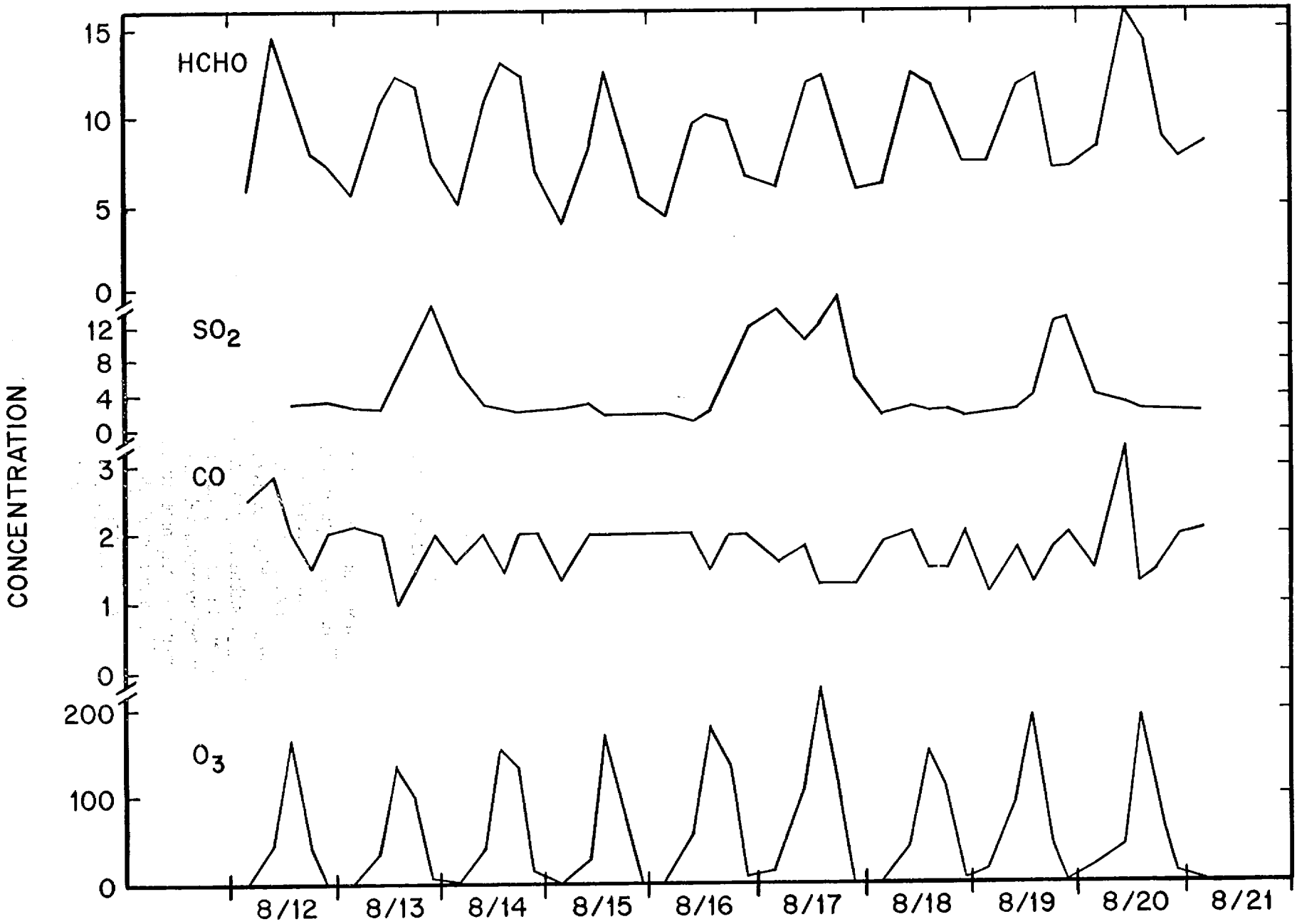


Figure 8. Diurnal variations of ozone, carbon monoxide, sulfur dioxide, and formaldehyde, Glendora, CA, August 12-21, 1986

were recorded on four days by the SCE instrument. One-hour averaged ozone maxima of at least 200 ppb were recorded on all but one day (8/13). Carbon monoxide data from ARB and SCE were only in rough agreement, a probable reflection of the poor performance of current CO instruments. Data for sulfur dioxide exhibit four maxima of 12—14 ppb, three at night on 8/13—14, 8/16—17, and 8/19—20 and one during daytime on 8/17.

Composite diurnal profiles for the study period (8/12—8/21) are shown in Figure 9 for the oxides of nitrogen, NO and NO_2, as measured by chemiluminescence; ozone is also shown for comparison. Levels of NO_2 substantially exceeded those of NO. These conditions are favorable to PAN formation and stability.

Data for nitrogen dioxide are shown in Figure 10 as concentration ratios. The two chemiluminescence instruments (ARB and SCE) are in reasonable agreement but the trend towards increasing ratios over the 9-day period suggest a 20% drift for one or both instruments. NO_2 levels measured by visible light photometry are considerably lower than those recorded by the two chemiluminescence instruments, which are known to suffer from positive bias from other nitrogenous pollutants including PAN and nitric acid.

Concentrations of the major pollutants of interest are listed in Table 17 as averages for the entire study period (8/12—21, 1986). Also given in Table 17 is a comparison of "daytime" and "nighttime" values, i.e. 8 a.m. to 8 p.m. vs. 8 p.m. to 8 a.m. Population exposure during daytime was, in decreasing order, to CO (1800 ppb), ozone (103 ppb), NO_2 (45 ppb), PAN (14.3 ppb), followed by formaldehyde, NO, formic acid, SO_2, and acetic acid. Nighttime exposure values were 1,800 ppb for CO (~ same as daytime) followed by NO_2 (48 ppb), NO (20 ppb), PAN (13 ppb), and about 6 ppb each of formic acid, formaldehyde, SO_2 and acetic acid.

3.6. Direct emissions of organic acids

Emission inventories for the South Coast Air Basin include two California Air Resources Board compilations of emission rates for individual organic compounds. The first inventory, which applies to the year 1974, gives daily emission rates for some 180 compounds. No organic acids are listed. The more recent inventory, which applies to the year 1982 on the basis of a 1979 forecast, lists some 220 compounds and includes a single organic acid, benzoic acid (SAROAD 45502, 12.0 kg/day).

In the absence of emission data, we examined air quality indicators of mobile and stationary sources. There is no apparent correlation between SO_2 and organic acids (compare diurnal profiles in Figures 6 and 8, respectively). In particular, no special trend in organic acid levels can be observed during the four sampling periods corresponding to elevated ambient levels of SO_2. While it is likely than organic acids are emitted in <u>all</u> combustion processes, no strong correlation can be identified with stationary sources. In contrast, there is limited but convincing evidence that organic acids are emitted by motor vehicles as incomplete products of fuel combustion. They may also originate from their use as fuel additives (Courtney and Newhall 1979). Kawamura et al (1985) measured formic acid and acetic acid in the exhaust from a single car; they also measured C2-C10 dicarboxylic acids in the exhaust of gasoline— and diesel—powered automobiles (Kawamura and Kaplan, 1986). Talbot et al (1988) measured formic acid and acetic acid in a tunnel near Hampton, Va. (~10^5 vehicles per day). Plots of ambient formic (acetic)

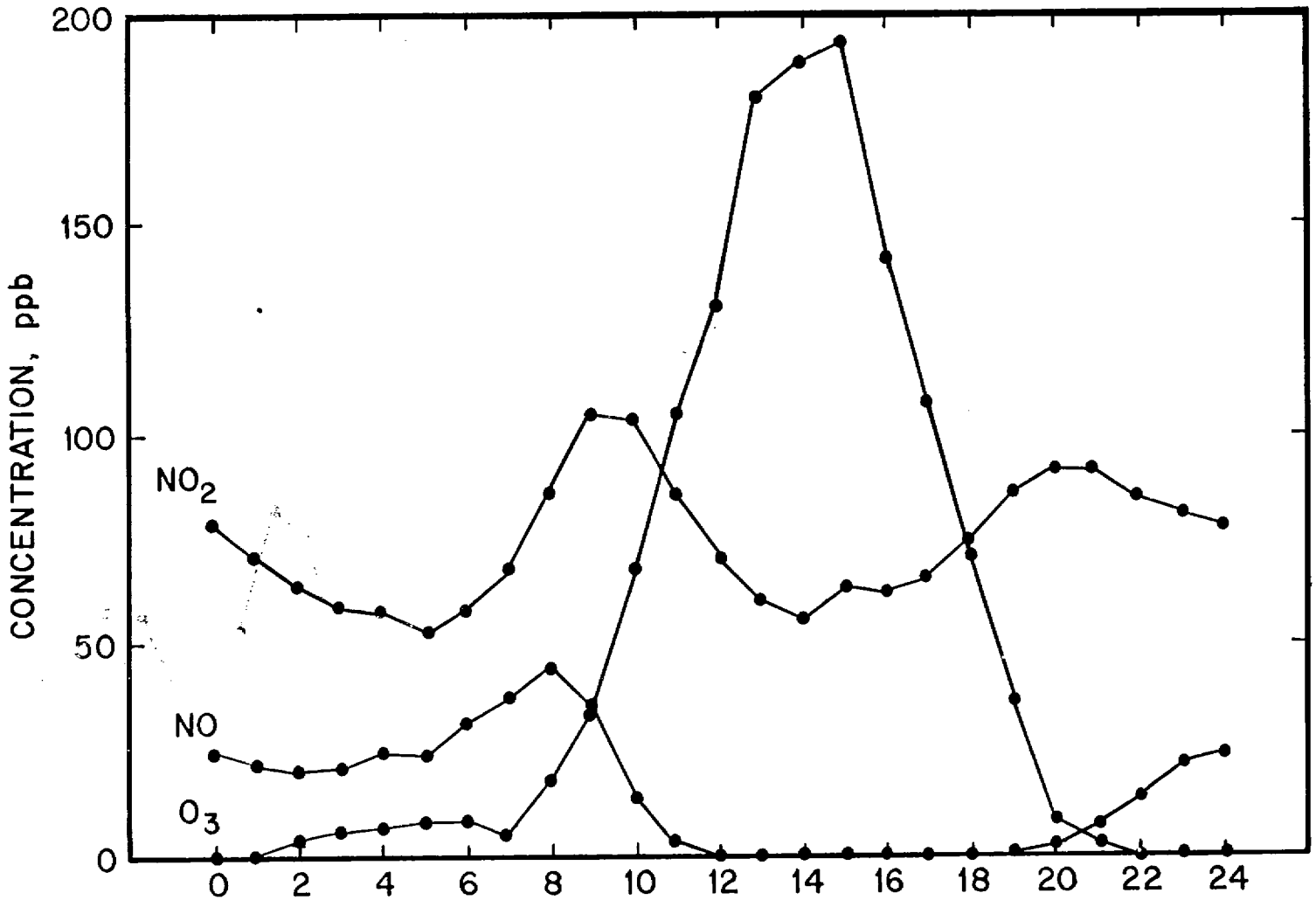


Figure 9. Composite diurnal profiles for nitric oxide, nitrogen dioxide and ozone (ppb), Glendora, CA, August 12-21, 1986

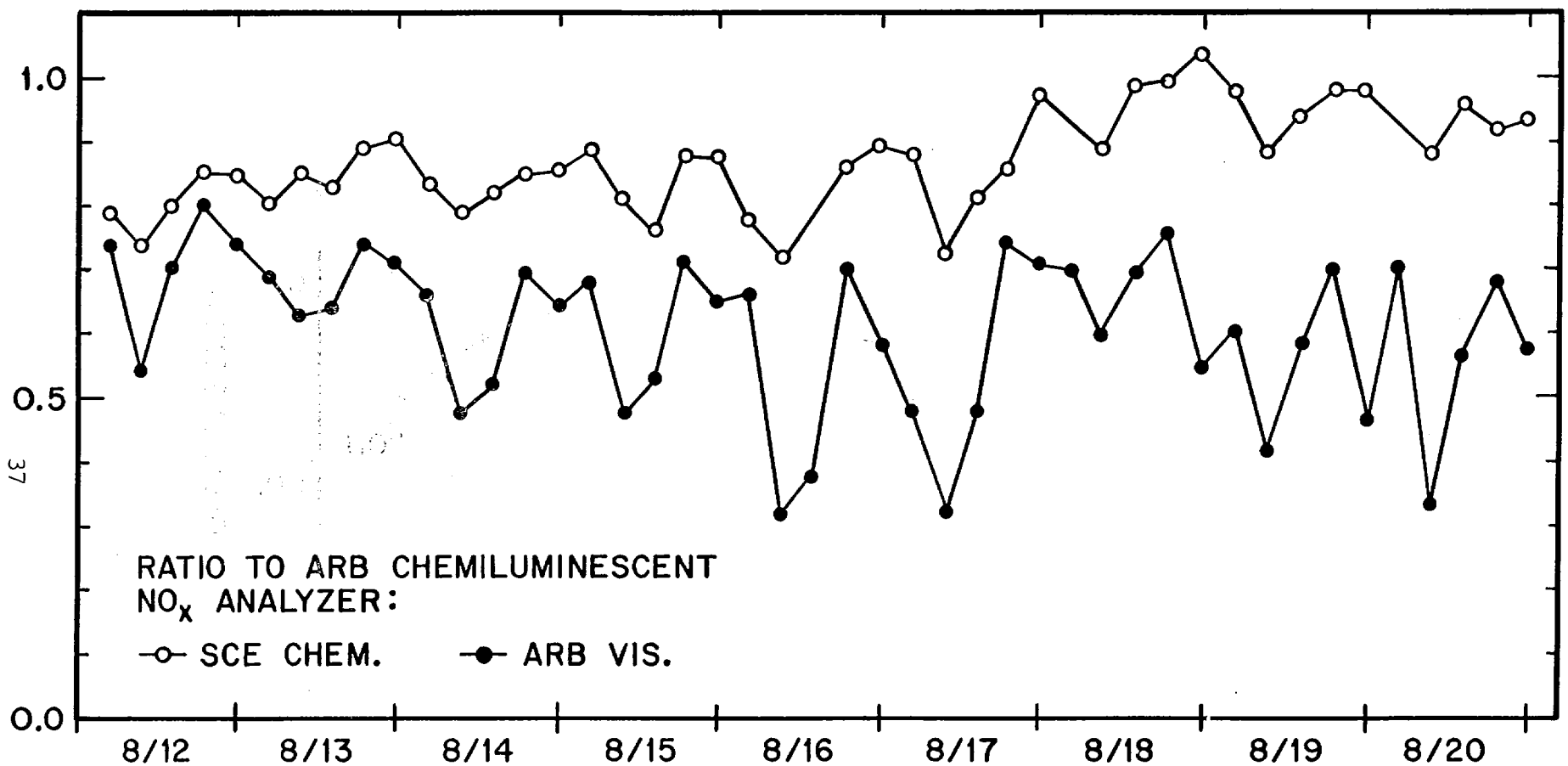


Figure 10. Nitrogen dioxide concentration ratios; data from ARB chemiluminescence analyzer (reference), SCE chemiluminescence analyzer, and ARB visible light absorption photometer

TABLE 17. AVERAGED CONCENTRATIONS OF GAS PHASE POLLUTANTS, GLENDORA, CA, 8/12 to 21/86

Pollutant	average concentration, ppb		
	day (8 a.m.—8 p.m.)	night (8 p.m.— 8 a.m.)	average, 8/12-8/21/86
carbon monoxide:			
ARB	1790	1770	1780
SCE	1780	1740	1760
ozone:			
ARB	103	4	53
SCE	103	4	53
nitrogen dioxide:			
ARB chemiluminesence	78	72	75
ARB visible light abs.	45	48	47
peroxyacetyl nitrate:	14.3	13.1	13.7
nitric acid:	4.0	0.5	2.3
formaldehyde:	11.3	6.3	7.8
formic acid:	4.0	5.4	4.7
acetic acid:	3.5	4.9	4.2
hydrogen chloride:	1.3	0.7	1.0
sulfur dioxide:	4.0	5.8	4.9
nitric oxide:	8.0	20	14

acid/CO ratios also give a strong indication that vehicles are a major source of organic acids (Grosjean, 1988). Diurnal variations of ambient aldehyde/CO and organic acids/CO ratios are consistent with two major sources, i.e. emission from vehicles and in-situ production in the atmosphere (Grosjean 1988). The organic acids/CO ratios obtained in this study are listed in Table 18 and show diurnal variations also consistent with vehicle emissions and in-situ production. Emission estimates and in-situ production estimates are presented in the next two sections.

3.7. Estimates of vehicle emissions of organic acids

Estimates of the Basin-wide emission rates of formic and acetic acid for mobile sources can be made by extrapolation of relevant CO data. These estimates are summarized in Table 19 and have been derived from the single exhaust study, the single tunnel study, and the several ambient acid/CO ratios cited in the preceding section. In the absence of other data, we assume that the results of these very limited studies can serve as a basis for basinwide emission estimates. We also assume that CO is a non-reactive tracer of mobile sources, i.e. we neglect its photochemical formation during air mass transport. CO emissions are set at 5,850 x 10^3 kg per day, of which 91.5% is contributed by mobile sources (5,357 x 10^3 kg/day). We further assume that acid/CO ratios in ambient air at the time of the automobile traffic peak (CO and NO peak) reflect the corresponding emission ratios, i.e. we neglect possible differences in dry deposition rates.

With these assumptions in mind, we estimate basinwide emissions from mobile sources of about 1.0 to 13.0 metric tons/day for formic acid and of 3.0 to 15.0 metric tons/day for acetic acid. The range of estimates given for both acids reflect the differences in reported acid/CO ratios (factors of 10 and 5 for formic acid acetic acid, respectively). The use of ambient ratios at smog receptor sites (Pasadena, Claremont, Glendora) may overestimate direct emissions, since the measured acid concentrations may already include a photochemical component (O_3 levels are low at the time of the traffic peak, but NO is rapidly converted to NO_2). We note that both tunnel and exhaust studies indicate that more acetic acid than formic acid is emitted by mobile sources. The reason for this is unknown, but biomass burning yields even higher acetic acid/formic acid emission ratios (~10 vs. 2—3 for mobile sources, Talbot et al 1988).

TABLE 18. DIURNAL VARIATIONS OF FORMIC ACID/CO AND ACETIC ACID/CO CONCENTRATION RATIOS

	Formic acid/CO, ppb/ppm				
	8—12	12—16	16—20	20—24	0—8
8/12—13	1.45	1.28	1.20	1.75	2.05
8/13—14	0.69	1.80	0.81	1.10	1.63
8/14—15	-	0.90	2.11	2.38	5.36
8/15—16	2.75	3.78	2.71	1.71	1.54
8/16—17	2.39	1.87	2.50	1.17	2.65
8/17—18	2.14	2.25	2.28	2.30	2.31
8/18—19	2.20	2.31	1.51	2.19	6.04
8/19—20	3.10	2.67	2.50	3.23	8.67
8/20—21	2.42	3.08	3.00	1.47	4.76
Average, formic acid	2.33	2.28	2.00	1.84	3.75
Average, acetic acid	2.07	1.91	1.93	1.83	3.28

TABLE 19. ESTIMATES FOR MOBILE SOURCES EMISSIONS OF FORMIC AND ACETIC ACIDS IN THE SOUTH COAST AIR BASIN

	Concentration ratios, ppb/ppm		Emission rate, kg/day	
	Formic acid/CO	Acetic acid/CO	Formic acid	Acetic acid
Tunnel (a):	0.21	0.42	1,170	3,060
Car exhaust (b):	0.14 (c)	0.47 (c)	780	3,424
Ambient air at or near traffic peak (d):				
Pasadena (e)	1.6(2)	-	8,900	-
East Los Angeles (f)	0.38 (2)	-	2,120	-
Claremont (g)	2.1(4)	2.0(4)	11,700	14,600
Glendora (h)	2.33(9)	2.07(9)	12,980	15,080

(a) Talbot et al 1988. Tunnel wtih 10^5 cars per day near Hampton, VA; emissions not necessarily representative of vehicles operated in California.
(b) Kawamura et al, 1985. Toyota Corolla, after idling for 30 minutes.
(c) CO not measured, estimated from author's ratio of 17 for exhaust vs. ambient air organic acids.
(d) Number of days in parentheses.
(e) Hanst et al 1975. Formic acid concentation corrected downward, see text.
(f) Hanst et al, 1982.
(g) Grosjean 1988.
(h) This work.

Using the mid-range values in Table 19 for formic and acetic acid emissions, the exhaust data of Kawamura et al (1985, 1986), and the ambient aerosol composition data of earlier literature (see Table 15 and references therein) we can estimate basinwide emissions of other carboxylic acids, stressing again that these estimates only represent the contribution of mobile sources. These estimates are listed in Table 20. Total estimated emissions are about 20,000 kg per day, of which formic and acetic acid together account for 78%, all other aliphatic monocarboxylic acids 15%, aromatic acids 5%, and aliphatic dicarboxylic acids 2%.

An independent consistency check on the emission rates given in Table 20 was carried out by comparing the formaldehyde/formic acid ratio measured during the Citrus College Study to the aldehyde emission inventory developed by Grosjean et al (1983). In its present state, the organic acid emission inventory given in Tables 19 and 20 is admittedly approximate, but no more so than emission data for other categories of organics that are included in current state or county emission inventories. This inventory could be improved by including stationary source emission rates and by obtaining better data for the organic acid/CO ratios in mobile source emissions (e.g. by carrying out a few "traffic-integrated" measurements in tunnels, parking garages, bus stations, etc.)

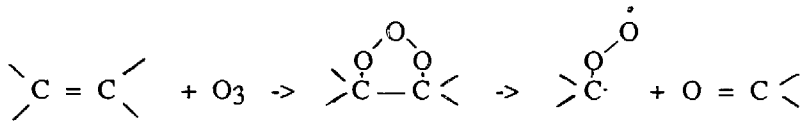
3.8. Atmospheric formation of organic acids

Chemical reactions that produce organic acids in the atmosphere include gas phase and liquid phase processes. Because gas phase formic and acetic acid are by far the most abundant organic acids in the Basin's atmosphere, our discussion will focus on reactions that produce these two acids in the gas phase. These reactions include:

- the gas phase reaction of ozone with olefins.
- the gas phase reaction of aldehydes with the HO_2 radical.
- the gas phase reaction of phenols (cresols) with the hydroxyl radical.
- the aqueous phase reaction of aldehydes in cloud water.

3.9. Ozone-olefin reaction

The reaction of ozone with olefins is reasonably well understood (e.g. Atkinson and Carter, 1984) and proceeds by electrophilic addition of ozone on the unsaturated carbon-carbon bond followed by unimolecular decomposition of the trioxolane adduct to yield a carbonyl and the Criegee biradical:



Further reactions of the Criegee biradical include several decomposition pathways as well as isomerization to form the corresponding carboxylic acid, e.g.:

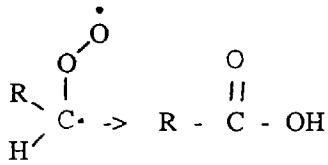
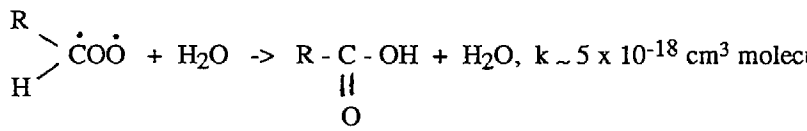


TABLE 20. ESTIMATED EMISSION INVENTORY FOR ORGANIC ACIDS IN THE SOUTH COAST AIR BASIN

Organic acid	Emission rate, kg/day
1. Aliphatic monocarboxylic	
formic	6,500 (a)
acetic	9,000(a)
propionic	1370
butyric	136
iso butyric	136
valeric	158
iso valeric	158
hexanoic	180
heptanoic	200
octanoic	222
nonanoic	244
decanoic	250
Subtotal:	**18,418**
2. Aliphatic dicarboxylic (b)	
oxalic	87
malonic	52
succinic	52
glutaric	52
adipic	52
C7-C10	75
Subtotal	**370**
3. Aromatic acids	
benzoic	310
phthalic	300
phenylacetic	250
toluic (3 isomers)	120
Subtotal	**980**
	Total: 19,768

(a) mid-range of values given in Table 19.
(b) gasoline-powered vehicles; diesel-powered vehicles emissions are about five times greater (Kawamura and Kaplan, 1986).

The relative importance of the isomerization pathway increases with the size of the substituent, i.e., only small amounts of formic acid are produced in the ethylene-ozone reaction, and larger yields of organic acid are formed from higher molecular weight olefins. In addition, Hatakeyama et al. (1981) have shown that the isomerization of the Criegee biradical to carboxylic acid also results from reaction with water vapor:



$$\begin{matrix} R \\ H \end{matrix}\!\!>\dot{C}O\dot{O} + H_2O \rightarrow R-\underset{\underset{O}{\|}}{C}-OH + H_2O, \; k \sim 5 \times 10^{-18}\ cm^3\ molecule^{-1}\ sec^{-1}$$

Thus, higher yields of organic acids are expected to form at high humidity from the ozone-olefin reaction.

A list of olefins whose reaction with ozone is expected to produce formic acid, acetic acid and other organic acids is given in Table 21 along with the corresponding emission rates and ozone-olefin rate constants. The olefins are listed in order of decreasing emission rates. It is evident from Table 21 that organic acids have distinctly different source strengths. Of the $\sim 230 \times 10^3$ kg of olefins emitted everyday, $\sim 190 \times 10^3$ may yield formic acid, and 56, 36, 20, 18, and 5 may yield acetic, propionic, isovaleric, n-butanoic and iso-butanoic acids, respectively. Of course, these olefins react with ozone at widely different rates which span a 300 fold increase from ethylene to 2-methyl-2 butene.

In addition, and perhaps more importantly for organic acids formation, olefins also react with the hydroxyl radical (daytime: OH levels are low at night) and with the nitrate radical (nighttime: NO_3 photolyses rapidly in sunlight). These two reactions, which compete with the olefin-ozone reaction, lead to products other than organic acids. The relative importance of the three reactions may be estimated from the relation:

$$-d\,(olefin)\,/\,dt = (olefin)\ [\,k_{OH}\,(OH) + k_{O3}\,(O_3) + k_{NO3}\,(NO_3)\,]$$

where (OH), (O_3) and (NO_3) are ambient concentrations and k_{OH}, kO_3 and k_{NO3} are the corresponding reaction rate constants. For example, for a typical daytime situation, O_3 = 100 ppb, OH = 10^6 molecules cm^{-3} (4×10^{-5} ppb) and NO_3 = O, the kinetic data in Table 21 indicate that the least reactive olefin, ethylene, will be removed primilarily by reaction with OH (66% vs. 33% for removal by reaction with ozone). In contrast, the more reactive olefins, such as 2-methyl-2-butene, will react mostly with ozone (93% vs. 7% with OH) under the same conditions.

For conditions where reaction with ozone is a major loss process for olefins, the production rate of organic acids by the ozone-olefin reaction is consistent with the measured ambient concentrations. Taking for example O_3 = 100 ppb, olefin = 10 ppb, (Grosjean and Fung, 1984) and making allowance for the fact that the thermalized Criegee biradical only accounts for a fraction of the products (e.g. 40% for ethylene), the production rate of organic acids range from $\sim$ 0.2 to 6 ppb per hour depending upon olefin reactivity. At night, higher humidity will favor the Criegee biradical-water reaction which leads to higher yields of organic acids, as observed by Hatakeyama (1981) under laboratory conditions. In addition, OH

TABLE 21. OLEFINS WHOSE REACTION WITH OZONE LEADS TO FORMIC ACID AND ACETIC ACID

Olefin (a)	Acid Product			SCAB	Reaction rate constants, cm^{-3} $molecule^{-1}$ sec^{-1}		
	Formic	Acetic	Other(b)	Emission rate, 10^3 kg/day (c)	10^{18} kO_3	10^{11} kOH	10^{15} k NO_3
Ethylene	+			71	1.6	0.8	0.06
Propene	+	+		20	12.6	2.5	4.2
3 Me 1 pentene	+		iso C5	20	-	-	-
1 pentene	+		n C4	18	10.7	2.9	-
2 Me 2 butene		+		16	493	8.7	5,100
1,3 butadiene	+			15	8.4	-	-
2 Me 1 butene	+			13	-	6.5	
1 butene	+		C3	11	12.6	2.9	5.4
cis 2 butene		+		9	161	5.5	190
trans 2 butene		+		8	288	7.0	210
isobutene	+			7	12.0	5.5	1.7
cyclohexene			adipic	7	204	6.4	280
3 Me 1 butene	+		iso C4	5	-	3.1	-
Mecyclopentene			Meglutaric	3	-		-
2,3 di Me 1 butene	+			3	-		-
cis 2 pentene		+	C3	1.5	-	6.2	-
trans 2 pentene		+	C3	1.3	-	6.8	-
cis 3 hexene			C3	0.8	-	-	-
2 Me 2 pentene			C3	0.8	-	-	-
trans 3 Me 2 pentene		+		0.6	563	-	-
1-hexene	+		C5	0.3	12.1	3.1	-
2-Et-1 butene	+			0.3	-	-	-
TOTAL							

(a) Me = methyl, Et = ethyl
(b) C3 = propionic acid, C4 = butyric acid, C5 = valeric acid
(c) 1974 ARB emission inventory

concentrations drop to low levels at night, thus eliminating the OH-olefin reaction as a competing pathway for olefin removal. Thus, while production of organic acids may take place day and night, the production rate is expected to increase at night, in agreement with ambient observations.

3.10. Aldehyde-HO_2 reaction

A second gas phase pathway for organic acid formation may involve the gas phase reaction of aldehydes with HO_2 (Su et al 1979, Veyret et al 1982), e.g.:

$$HO_2 + HCHO \longrightarrow O_2CH_2OH \qquad k = 7 \times 10^{-14}\ cm^3\ molecule^{-1}\ sec^{-1}$$
$$O_2CH_2OH + NO \longrightarrow NO_2 + OCH_2OH \qquad k = 7.6 \times 10^{-12}\ cm^3\ molecule^{-1}\ sec^{-1}$$
$$OCH_2OH + O_2 \longrightarrow HO_2 + HCOOH$$

During daytime, aldehydes react rapidly with OH and also photolyze, so that conversion to organic acids by reaction with HO_2 is probably of minor importance. The above reaction may, however, be of some importance at night even though aldehydes are also removed by nighttime reaction with NO_3. Ambient levels of formaldehyde in the Basin are typically 5—25 ppb (Grosjean 1982). They were in the range 6—16 ppb during CSMCS and their diurnal variations show little similarity to those of formic acid (Figure 11). On several days the formic acid peak followed the formaldehyde peak with a lag time of several hours, as observed before (Tuazon et al 1981, Grosjean 1988), thus indicating a possible relation between the two pollutants. On most days formaldehyde and formic acid had opposite diurnal variations, with daytime maxima for HCHO and nighttime maxima for HCOOH. With the rate constant given above and HCHO = 10 ppb, a formic acid production rate of 2 ppb hr^{-1} would require HO_2 concentrations of ~ 8×10^8 molecules cm^{-3}. HO_2 levels were not measured during CSMCS; they could be estimated with computer kinetic modeling of the appropriate input data. The importance of the HO_2-aldehyde reaction as a pathway for organic acid formation is uncertain at this time.

3.11. Phenol-OH reaction

The reaction of the hydroxyl radical with aromatic hydrocarbons involves a complex sequence of pathways (e.g., Leone et al 1985) which include opening of the aromatic ring and the formation of aliphatic dicarbonyl products. The reaction of OH with phenols proceeds in a similar manner, with one of the dicarbonyl products retaining the initial OH substituent, i.e., a carboxylic acid is formed (more specifically a keto acid). Thus, the OH-initiated photooxidation of ortho cresol yields products including pyruvic acid, as is shown in Figure 12 (Grosjean 1984). Since phenols are themselves produced in the reaction of OH with aromatic hydrocarbons, all aromatic hydro-carbons are potential precursors of ketoacids. Aromatic hydrocarbons now account for a large fraction of the reactive hydrocarbon burden in the South Coast Air Basin (Grosjean and Fung 1984). Phenols also react rapidly with the NO_3 radical at night; the reaction products are unknown but probably do not include organic acids.

The formation rate of keto acids can be estimated, using the o-cresol-OH reaction as an example. For o-cresol = 1 ppb, OH = 10^6 molecule cm^{-3}, and $k = 1 \times 10^{-11} cm^3$ $molecule^{-1}$ sec^{-1}, pyruvic acid is produced at the slow rate of 36×10^{-3} ppb/hr. In

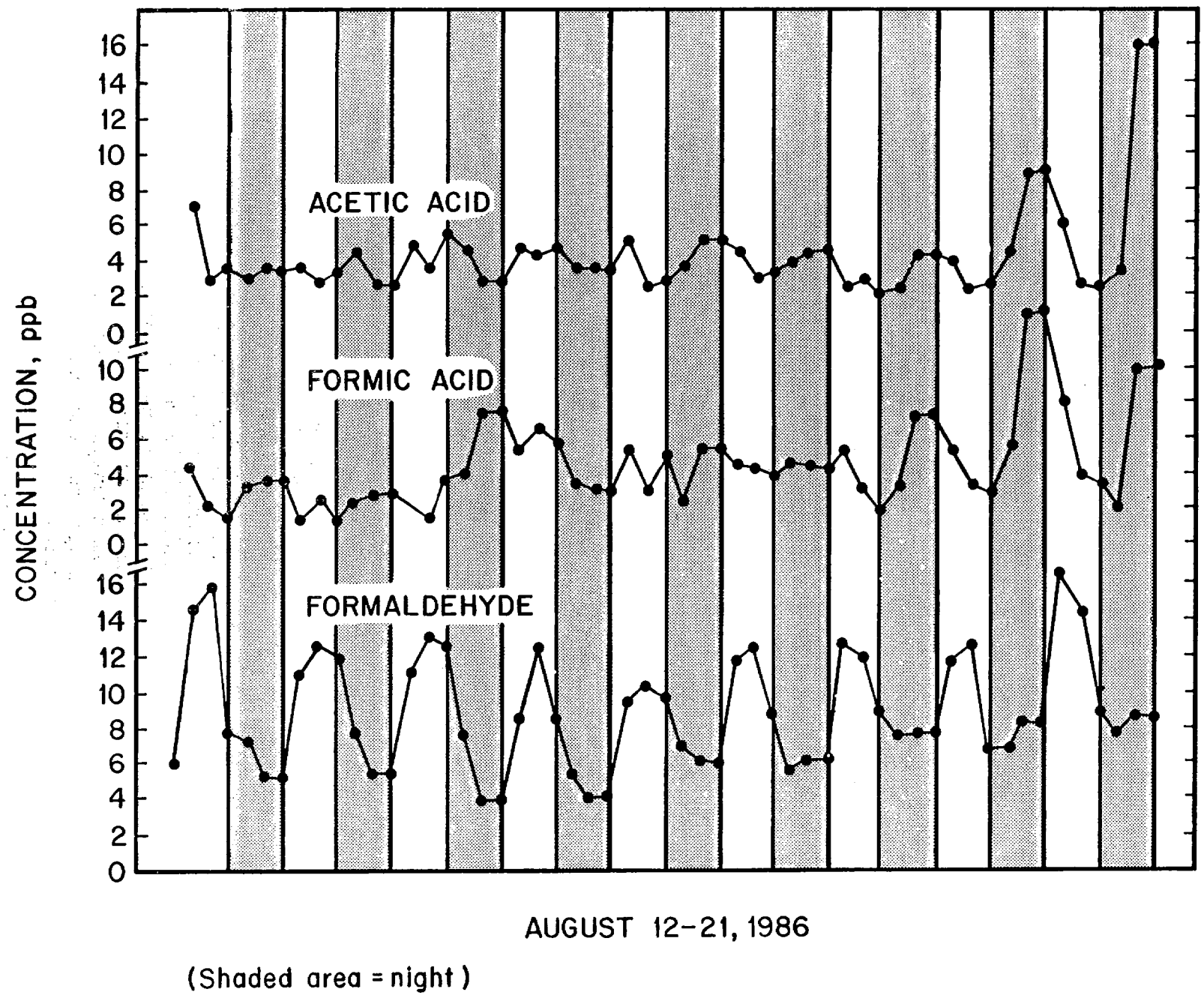


Figure 11. Diurnal variations of organic acids and formaldehyde, Glendora, CA, August 12-21, 1986

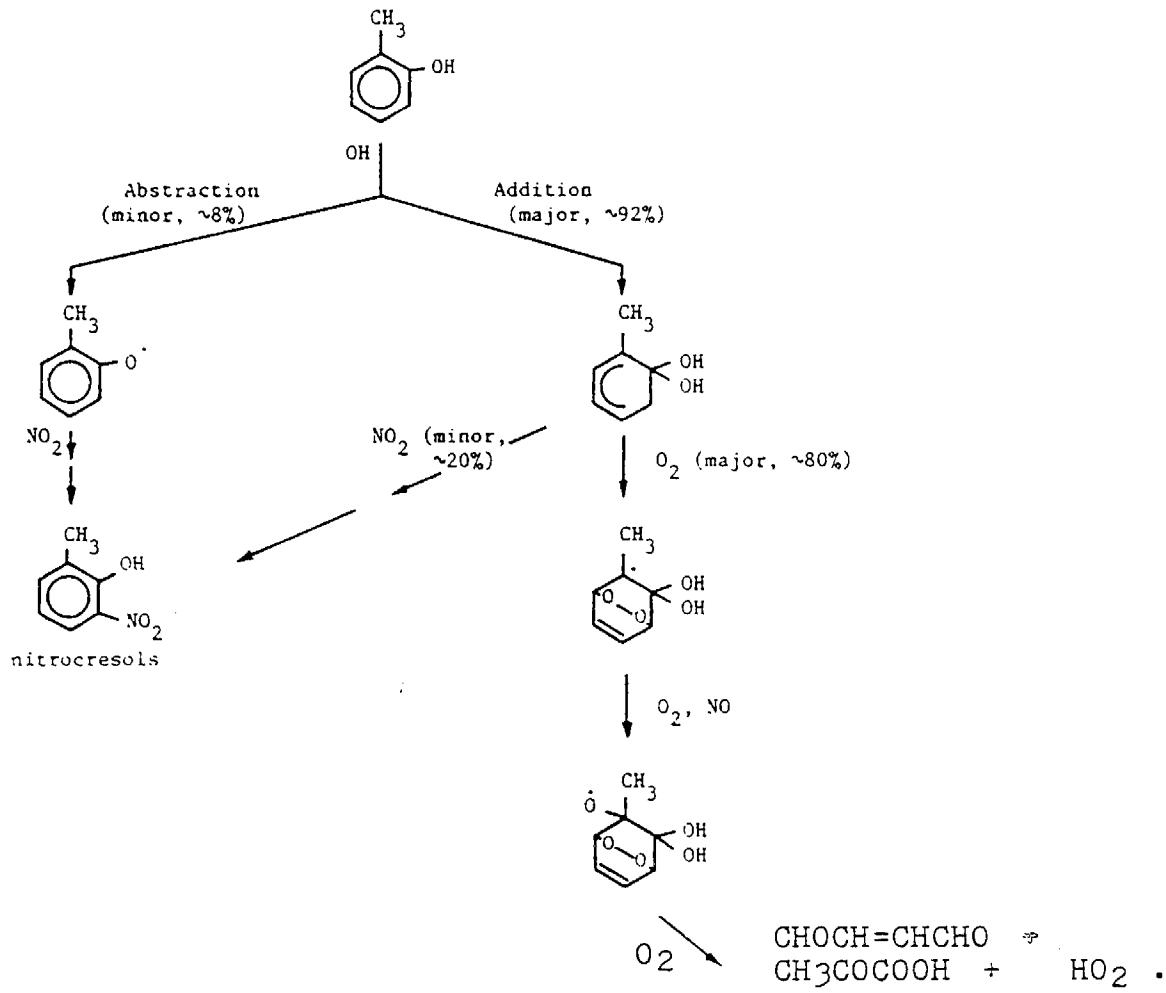


Figure 12. Production of the oxoacid pyruvic acid by photooxidation of ortho-cresol.

turn, pyruvic acid photolyzes in sunlight to yield products other than organic acids, i.e. acetaldehyde and CO_2 (Grosjean 1983). Thus, the OH-initiated oxidation of phenols is of negligible importance as a route for organic acid formation in the atmosphere.

3.12. Aldehyde oxidation in clouds

Liquid phase formation processes that may take place in hydrometeors are also relevant to the gas phase budget of organic acids provided that some of the acid formed in the aqueous droplet is transferred to the gas phase. Jacob (1986) has described the OH-initiated oxidation of formaldehyde to formic acid in cloudwater. Mass transfer and acid-base considerations indicate that, if the acidity of the cloud droplet increases (e.g. scavenging of nitric acid, SO_2, etc.), the gas-liquid partition of any organic acid will shift towards the gas phase when the cloudwater pH is lower than the pKa of the acid of interest. Thus, acidic cloudwater may be a source of gas phase acetic acid if pH $<$ 4.7, of gas phase formic acid if pH $<$ 3.7 and so on. However, organic acids formed by aldehyde oxidation in the aqueous phase are in turn rapidly consumed by reaction with OH. In fact, literature data for aqueous phase reactions, although not always available for the range of pH of interest, indicate that formaldehyde and formic acid are removed by reaction with OH at comparable rates (Table 22). Thus, reaction with OH will severely compete with gas-liquid partition. While cloudwater chemistry cannot be ruled out as a source of gas phase organic acids, we have no evidence that this pathway contributed to the observed levels of gas phase acids during CSMCS.

3.13. Removal processes

With the exception of keto acids (see below), organic acids are not significantly removed from the atmosphere by gas phase reactions: their only removal pathway is by slow reaction with the hydroxyl radical; the corresponding reaction rate constants are 0.35—0.46, 0.73, 1.2, and 2.0 x 10^{-12} cm^3 $molecule^{-1}$ sec^1 for formic, acetic propionic and isobutyric acid, respectively (Dagaut et al, 1988 and references therein). These rates correspond to atmospheric residence times of several weeks.

The keto acids also react slowly with OH, but are removed rapidly by photolysis (Grosjean 1983, Yamamoto and Back 1985). Thus, the daytime persistence of glyoxylic, pyruvic, and oxalic acid is not expected to exceed a few hours. Another reaction of possible interest involves the reaction of organic acids with ammonia, to form carboxylate ammonium salts:

$$RCOOH + NH_3 \rightleftarrows RCOONH_4$$

This reaction, if actually taking place in the atmosphere, would not represent a removal process. It would, however, shift the gas-aerosol distribution of the acid towards the condensed phase. In the bulk phase, carboxylate ammonium salts hydrolyze to form amides:

$$RCOONH_4 \leftrightarrows H_2O + RCONH_2$$

While amides have indeed been identified in Los Angeles aerosols (e.g., Cronn et al 1977), the sequence of reactions involving organic acids and ammonia is only speculative at this time. Ammonium salts of the strong acids (NH_4NO_3, NH_4 Cl)

TABLE 22. RATE CONSTANTS FOR OH-CARBONYL AND OH-ORGANIC ACID REACTIONS IN THE AQUEOUS PHASE

Compound	Rate constant, $cm^3\ mol^{-1}\ sec^{-1}$ (pH in parentheses)	
formaldehyde	1.14×10^{-12}	(1)
acetaldehyde	8.3×10^{-13}	(1)
n-butanal	6.3×10^{-12}	(2)
octanal	7.3×10^{-12}	(9)
acetone	1.5×10^{-13}	(7)
other ketones	$1.5—3.0 \times 10^{-12}$	(6—7)
formic acid	1.0×10^{-12}	(1)
acetic acid	3.3×10^{-14}	(1)
propionic acid	3.3×10^{-13}	(1)
	8.3×10^{-13}	(2)

have limited thermal stability under atmospheric conditions; ammonium salts of the weaker organic acids, if formed, would be expected to be of even lower stability. A possible exception may be oxalic acid (pK = 1.27) which may form stable ammonium salts or displace carbonate, etc. from coarse particles.

Physical processes for removal of atmospheric organic acids include scavenging by hydrometeors (cloud, fog, and rain) as well as dry deposition. Organic acids are soluble in water; indeed, there are numerous reports concerning organic acids in rainwater, snow, cloudwater, fog, and mist. The literature relevant to this project is summarized in Table 23. Formate and acetate are the most abundant organic acids in hydrometeors. Their concentrations range from ~ 10-30 μM in non-urban precipitation (e.g. Galloway et al 1982) up to several hundreds μM in urban fog (Jacob et al 1986, Munger et al 1988). Oxalic, pyruvic, and propionic acid have also been reported in non-urban samples. Kaplan and coworkers (references in Table 23) have identified many mono and diacids in Southern California rain and fog water.

Removal of organic acids by dry deposition (including deposition to dew) has received little attention to date. Pierson and Brachaczek (1987) have identifed formate, acetate, propionate, oxalate and benzoate at concentrations of 118, 52, 2.8, 2.1 and 0.4 μM, respectively, in dew samples collected at Glendora during CSMCS.

They estimated a deposition flux to dew of ~ 4 millimole/m^2/year for titratable acidity. Since species observed in dew may not always be those actually deposited (e.g. deposited formaldehyde may be oxidized to formic acid in dew), the flux given above is probably an upper limit for the actual contribution of organic acids. Talbot et al (1988) measured much lower amounts of formate (~ 1 μM) and acetate (10 μM) in dew samples collected in Hampton, Va. They also determined the dry deposition flux of formate and acetate on Teflon plates, and obtained very small values of ~20 nmol cm^{-2} $year^{-1}$.

Dry deposition velocities of formic acid, acetic acid and other organic acids have not been determined. Both Talbot et al (1988) and Pierson and Brachaczek (1987) suggest that a deposition velocity of 1 cm sec^{-1} is probably reasonable, i.e. organic acids are assumed to have deposition velocities comparable to that of nitric acid. For comparison, the dry deposition velocity of nitric acid on grass is 2.5 ± 0.9 cm sec^{-1} (Huebert and Robert, 1985).

In the absence of data, we have set the dry deposition velocity for all gas phase organic acids at v = 1.0 cm sec^{-1}, and estimated the contribution of dry deposition and wet deposition to the removal of organic acids in the Basin. Input data for these estimates are listed in Table 24. Organic acid concentrations in the gas phase and in rainwater were taken from mid-range values of literature data for the Basin. Oxalic acid was assumed to be associated with fine particles with a deposition velocity of 0.1 cm sec^{-1}. Rainwater values may include a contribution from in-droplet reactions.

Results of these calculations are given in Table 25. For the gas phase organic acids, dry deposition far exceeds removal by rain and accounts for 95% (formic and propionic) and 91% (acetic) of the acid deposition budget. This probably holds true for all other gas phase organic acids, some of which are present in the Basin's atmosphere at levels much lower than those of formic and acetic acid. For oxalic

TABLE 23. ORGANIC ACIDS IN HYDROMETEORS (μM)

Location	Formate	Acetate	Others	Reference
Rainwater, non-urban				
Amazon forest	40	22	pyruvic 1.2 oxalic 6.2	Andreae et al, 1988
Hampton, VA	5.4	4.8	-	Talbot et al, 1988
Niwot Ridge, CO	up to 90	1—30	oxalic 0.1—20 malonic, succinic	Norton 1985
Amsterdam Island	10	4	-	Galloway et al, 1982
Katherine, Australia	22	7	-	ibid
San Carlos, Venezuela	14	3	-	ibid
rural Wisconsin	1—56	1—33	propionic, oxalic, malonic	Chapman et al, 1986
Waseca, MN	trace	4	propionic 0.10 adipic, lactic or glyocolic	Guiang et al, 1984
Rainwater, urban				
Los Angeles, CA	0.04	0.04	propionic, valeric	Barcelona et al, 1980
Los Angeles, CA	8.7	24	-	Kawamura & Kaplan, 1984
Los Angeles, CA (UCLA)			oxalic 4—30 glyoxylic, pyruvic, alpha-keto glutaric	Steinberg et al, 1985
			C2–C10 diacids (linear, branched and unsaturated)	Kawamura et al, 1985
Fog, cloud and mist				
Los Angeles, CA (Henninger Flats)	-	-	oxalic, 4—30 pyruvic 4—30 glyoxylic 4—30 alpha-ketoglutaric 4—30	Steinberg et al, 1985

Table 23 (continued)

Location	Formate	Acetate	Others	Reference
Fog, cloud and mist (continued)				
Los Angeles, CA (Henninger Flats)			C2—C10 diacids (linear, branched, and unsaturated)	Kawamura et al, 1985
Riverside, CA	1500	500	-	Munger et al, 1988
San Joaquin Valley, CA (four sites)	22—144	3—155	propionic 0—9 lactic 2—15	Jacob et al, 1986
Southern California (San Pedro, Laguna Peak, Ventura, Casitas Pass)	20—60	10—30	-	Munger et al, 1988
Dew				
Los Angeles, CA (Glendora)	118	52	propionic 2.3 oxalic 2.1 benzoic 0.4	Pierson and Barachzek, 1988
Hampton, VA	0.1—1	1—10	-	Talbot et al, 1988

TABLE 24. INPUT DATA FOR DEPOSITION CALCULATIONS

	Formic acid	Acetic acid	Propionic acid	Oxalic acid
Rainwater concentration, μM	10	20	1	5
Amount of rain, mm/year	300	300	300	300
Gas phase concentration, ppb	5	5	0.5	0
Particulate phase concentration, $\mu g\ m^{-3}$	0	0	0	0.5
Deposition velocity, cm/sec	1.0	1.0	1.0	0.1

TABLE 25. DEPOSITION FLUXES FOR ORGANIC ACIDS

(nmol m^{-2} $year^{-1}$)

	Formic	Acetic	Propionic	Oxalic	Total
Wet	3.0	6.0	0.3	1.5	10.8
Dry	64.0	64.0	6.4	0.18	134.6
Total	67.0	70.0	6.7	1.7	145.4
Dry deposition, % of total	95	91	95	11	92.5

acid, and probably all other trace particulate phase organic acids, wet deposition is more important by virtue of the lower dry deposition velocity for fine particles. Overall, dry deposition is estimated to be ~ 14 times more important than removal by rain, accounting for ~ 92% of the total organic acid deposition budget. In turn, removal by rain is about twice that estimated for dew collected during CSMCS. Of course, the estimates given in Table 25 are highly dependent on the values assigned to dry deposition velocities. For example, a ten-fold decrease from 1.0 to 0.1 cm sec^{-1} would make dry deposition and removal by rain equally important. Actual measurements of dry deposition are obviously needed to refine the deposition budget of organic acids in the South Coast Air Basin.

3.14. Comparison of emissions, in-situ formation and removal processes

A summary of our estimates is given in Table 26. Emission data are from Table 19, with only the mid-range value given for clarity. In-situ formation estimates are from extrapolation of diurnal variations in organic acid/CO concentration ratios. In-situ formation may account for as much as direct emissions from mobile sources, with the same range of uncertainty. As removal competes with atmospheric formation, the "net" in-situ formation values given in Table 26 are lower limits for actual formation rates. Removal data are from wet and dry deposition fluxes given in Table 26 and taking the Basin's area to be $6 \times 10^3 km^2$ (120 x 50 km).

It is evident from Table 26 that removal estimates exceeds production (emissions plus in-situ formation) estimates by a factor of about 4 (3.4 for formic acid, 4.8 for acetic acid). Using the upper range values for emission rates (i.e. those estimated from this study, see Table 19), and using the corresponding increase in atmospheric formation rates (formation and emission vary together with a fixed ratio) would bring the removal/production ratio down to about 2 (1.7 for formic acid, and 2.7 for acetic acid). The discrepancy still remaining may indicate an overestimate of dry deposition velocities, an underestimate of direct emissions (and the associated underestimate of in-situ formation), an underestimate of in-situ formation relative to direct emissions, or any combination thereof. Emission and deposition data are clearly needed to refine our budget of organic acids in the Basin's atmosphere.

3.15. Positive bias due to aldehydes

In the bulk liquid and in strongly alkaline solutions, aldehydes undergo a disproportionation reaction (the Cannizzaro reaction) leading to the corresponding alcohol and carboxylic acid:

$$2\,RCHO + OH^- \longrightarrow RCH_2OH + RCOO^-$$

The possible role of this reaction as a positive bias when sampling atmospheric carboxylic acids has been investigated; the corresponding literature data have been reviewed by Grosjean (1988) and are summarized in Table 27. For the two aldehydes studied, acetaldehyde and benzaldehyde, the literature data show no evidence of positive bias from these two aldehydes when measuring acetic acid and benzoic acid, respectively. In addition, Irgum (1985) reports that formaldehyde at concentrations of up to 0.05 M is quite stable in 0.5 M aqueous sodium hydroxide.

Since all previous literature data were from laboratory studies, we set out to verify their validity under actual field conditions. Our approach involved side-by-side sampling of ambient air with two identical Teflon-alkaline filter pack units, one of which was sampling ambient air downstream of a DNPH-coated annular denuder

TABLE 26. SUMMARY OF EMISSION, ATMOSPHERIC FORMATION AND REMOVAL DATA FOR ORGANIC ACIDS

	Formic acid kg/day	Acetic acid kg/day	All organic acids kg/day
Emissions			
- stationary sources	ND (a)	ND	ND
- mobile sources	6,500 (b)	9,000 (c)	19,800 (d)
In-situ formation			
- ozone-olefin reaction	+++	++	+
- HO2-aldehyde reaction	?	?	?
- OH-phenol reaction	0	0	small, oxoacids only (e)
- aldehyde oxidation in clouds	?	?	?
- net, estimated from ambient RCOOH/CO data (f)	8,000 (g)	5,000 (g)	~15,000
Removal processes			
- gas phase reaction with OH	negligible	negligible	negligible
- photolysis	negligible	negligible	negligible except for oxoacids (e)
- removal by rain	minor, 2,200	minor, 5,800	minor except for particle-bound acids
- dry deposition	major, 47,000	major, 61,600	major except for particle-bound acids

(a) no data
(b) range 1,000-13,000, see Table 19.
(c) range 3,000-15,000, see Table 19.
(d) from Table 20.
(e) oxoacids = glyoxylic, pyruvic, etc.
(f) net = not corrected for loss by deposition which competes with in-situ formation.
(g) with same range of uncertainty as the one for direct emissions, see Table 19.

Table 27. Summary of Studies Relevant to the Conversion of Aldehydes to Carboxylic Acids on Alkaline Substrates

Aldehyde	Reference	Test Summary
Acetaldehyde	Grosjean, et al. 1984	PAN from irradiated CH_3CHO-Cl_2-NO_2 mixtures quantitatively converted to acetate in KOH impingers.
		Sampling with KOH of 1 ppm CH_3CHO in pure air: no acetate detected.
		Sampling with KOH of 0.1 ppm CH_3CHO + 0.14 ppm ozone: no acetate detected.
		Sampling with KOH of 0.1-1.0 ppm CH_3CHO + 0.1-0.5 ppm NO_2: no acetate detected.
	Grosjean, 1986 (a)	Sampling with KOH of 3.0 ppm CH_3CHO in pure air: acetate detected, $\leq$2.7% of initial CH_3CHO concentration.
Benzaldehyde	Fung and Grosjean 1985	Sampling with KOH of 6.4 ppb benzaldehyde in pure air: no benzoic acid detected.
		Sampling with KOH of 1 ppm benzaldehyde in pure air: $\leq$0.6% converted to benzoic acid.
		Sampling with KOH of 1 ppm benzaldehyde + 0.45 ppm ozone in pure air: $\leq$2.8% converted to benzoic acid.
		Sampling, with KOH saturated with benzaldehyde, of pure air containing 120 ppb ozone: no benzoic acid detected.
		Sampling with KOH of air with 6.4 ppb benzaldehyde and effluent from PAN generator (b): no benzoic acid detected.

(a) Unpublished results.
(b) Effluent contained 250 ppb NO_2, 30 ppb PAN, 10 ppb nitric acid, ozone, chlorine, HCl.

which retains formaldehyde, acetaldehyde, and other carbonyls. This experiment was repeated every day during CSMCS sampling period #3 (16:00—20:00) during which aldehyde levels were high (HCHO = 7—12 ppb) and carboxylic acid levels were low (2—5 ppb), therefore maximizing the positive aldehyde bias, if any. Analysis of formate and acetate in alkaline filters of filter packs operated with and without the aldehyde denuder were in agreeement, within 8 ± 4% for formate and 5 ± 4% for acetate (n=9). This compares to 10 ± 3% and 6 ± 6% for formate and acetate in two filter pack units operated side-by-side, both without aldehyde denuder. These results fail to indicate any positive bias from ambient aldehydes when sampling ambient formic acid and acetic acid under our experimental conditions.

Several observations are supportive of the experimental results. First, formic acid levels of up to 19 ppb have been measured at several of the Basin's smog receptor sites using a method which does not involve the use of alkaline traps, i.e. FT-IR (Hanst et al 1975, 1982, Tuazon et al 1978, 1981). Second, the alkaline-impregnated filter is rapidly "neutralized" by retention of atmospheric CO_2 (as carbonate and bicarbonate), SO_2, nitric acid, and hydrogen chloride. Since the Cannizzaro reaction is first order with respect to [OH^-], and second order with respect to [RCHO], the rapid decrease in filter OH content, together with the low (ppb) aldehyde concentration, combine to yield a negligible rate of aldehyde disproportionation during sampling.

Evidence for collection and retention of atmospheric CO_2 was seen in all KOH-impregnated filter samples, whose chromatograms exhibited a well-resolved bicarbonate peak corresponding to concentrations of 12—60 mg/sample. For atmospheric CO_2= 350 ppm and sampling flow rates of 11—14 lpm, the measured bicarbonate concentrations are equivalent to neutralization by CO_2 in 0.3 to 1.7 minutes, i.e. in 0.06—0.7% of the total sampling duration. Indeed, the pH of randomly selected extracts was 5.6 - 5.9 for seven alkaline filter samples and 5.7 for four Teflon filter samples. Finally, formate, acetate and nitrite were determined in five samples initially impregnated with sodium carbonate for collection of hydrogen chloride (see experimental section). The results were in good agreement with those obtained on KOH-impregnated filters.

To summarize, experimental evidence obtained in the field during this study is consistent with earlier laboratory findings and indicates no positive bias in organic acid sample content from the alkaline-mediated disproportionation of ambient aldehydes during sampling.

3.16. Positive bias due to peroxyacetyl nitrate

PAN decomposes in alkaline solutions to yield nitrite and acetate:

$$CH_3C(O)OO\,NO_2 + 2OH^- \longrightarrow CH_3COO^- + NO_2^- + O_2 + H_2O$$

This well-known reaction serves as a basis for a calibration method for PAN analyzers, with the effluent from a PAN generator being sampled in KOH impingers (Grosjean et al 1984) or on KOH-impregnated Sep-Pak cartridges (DGA, unpublished results) and subsequently analyzed for acetate and/or nitrite by size exclusion liquid chromatography (see experimental section for details of analytical protocol). PAN is quantitatively collected and decomposed at low flow rates using both KOH impingers (0.1—1 lpm) and KOH-impregnated Sep-Paks

(1—2 lpm). If PAN also decomposes to acetate and nitrite when sampling ambient air on KOH-impregnated filters at higher flow rates of 11—15 lpm, the measured acetic acid concentration will include a positive bias due to PAN.

The first step in our analysis was to compare ambient levels of PAN, formic acid, and acetic acid. Since PAN is an interferent for acetic acid but not for formic acid, and since PAN exhibit strong diurnal variations, a substantial PAN interference would be reflected in the diurnal variations of the acetate/formate ratios. The data shown in Figure 13 do not suggest a close association between PAN and acetate/formate ratios.

The next item to be considered is the actual collection efficiency of alkaline filters for PAN. Unlike liquid-filled impingers or impregnated resin traps which are operated at low flow rates and provide relatively long contact times between PAN and the alkaline medium, impregnated filters operated at higher flow rates afford only brief contact between PAN and the alkaline medium. In addition, the alkaline filter is rapidly "neutralized" by atmospheric CO_2, as discussed in detail in the preceeding section, and the neutral to slightly acidic medium is no longer favorable to the decomposition of PAN to acetate.

To clarify this, we have analyzed all alkaline filter field samples for their nitrite content. The results are listed in Table 28 and are expressed in units of ppb, on the assumption that all measured nitrite originates from collection of the three gases PAN, NO_2 and nitrous acid. There is little doubt that nitrous acid, a weak acid like formic and acetic acid, is likewise collected quantitatively on alkaline or carbonate filters. Its presence in the nighttime atmosphere (HONO photolyses rapidly in sunlight) is reflected in the increase in nitrite levels measured during periods 4 and 5 (8 p.m.—8 a.m.). The difference between nighttime and daytime measurements indicate $HONO_2$ levels of up to 2—4 ppb at night during CSMCS. The daytime nitrite values are contributed by PAN and NO_2 The removal efficiency of various traps for NO_2 is 20% for KOH impingers, 20% for water impingers (Grosjean et al 1984) and about 15% for alkaline Sep-Pak cartridges (DGA unpublished results, 1987). We expect the removal of NO_2 on carbonate filters to be even lower, again from contact time considerations. Indeed, nitrite/NO_2 ratios calculated for daytime samples are in the range 2.6—4.1% (Table 28).

Neglecting now this small contribution of NO_2 to the measured nitrite, we calculate the nitrite/PAN ratios (see Table 28) and use the mean of the daytime values, 6.4%, as upper limit for the extent of decomposition of PAN to nitrite. Since the decomposition of PAN yields equal amounts of nitrite and acetate (molar basis), we can now correct the measured acetic acid concentrations for the positive bias contributed by PAN decomposition to acetate. The results are listed in Table 29. Our upper limits for PAN interference in acetic acid measurements range from 19.8 to 34.8%, and averages 22.5%. Careful laboratory studies should be carried out to refine these estimates. In the meantime, we recommend direct simultaneous measurements of PAN, as was done in this study, whenever attempting to measure acetic acid using alkaline filters. Conversely, denuders may be developed that remove PAN but not acetic acid (or vice versa) to alleviate potential bias.

3.17. Collection efficiency of nylon filters

Because of the potential interference problems associated with the use of alkaline traps, we also investigated during this study the possible use of nylon filters to collect formic, acetic and other organic acids in ambient air. Should nylon filters

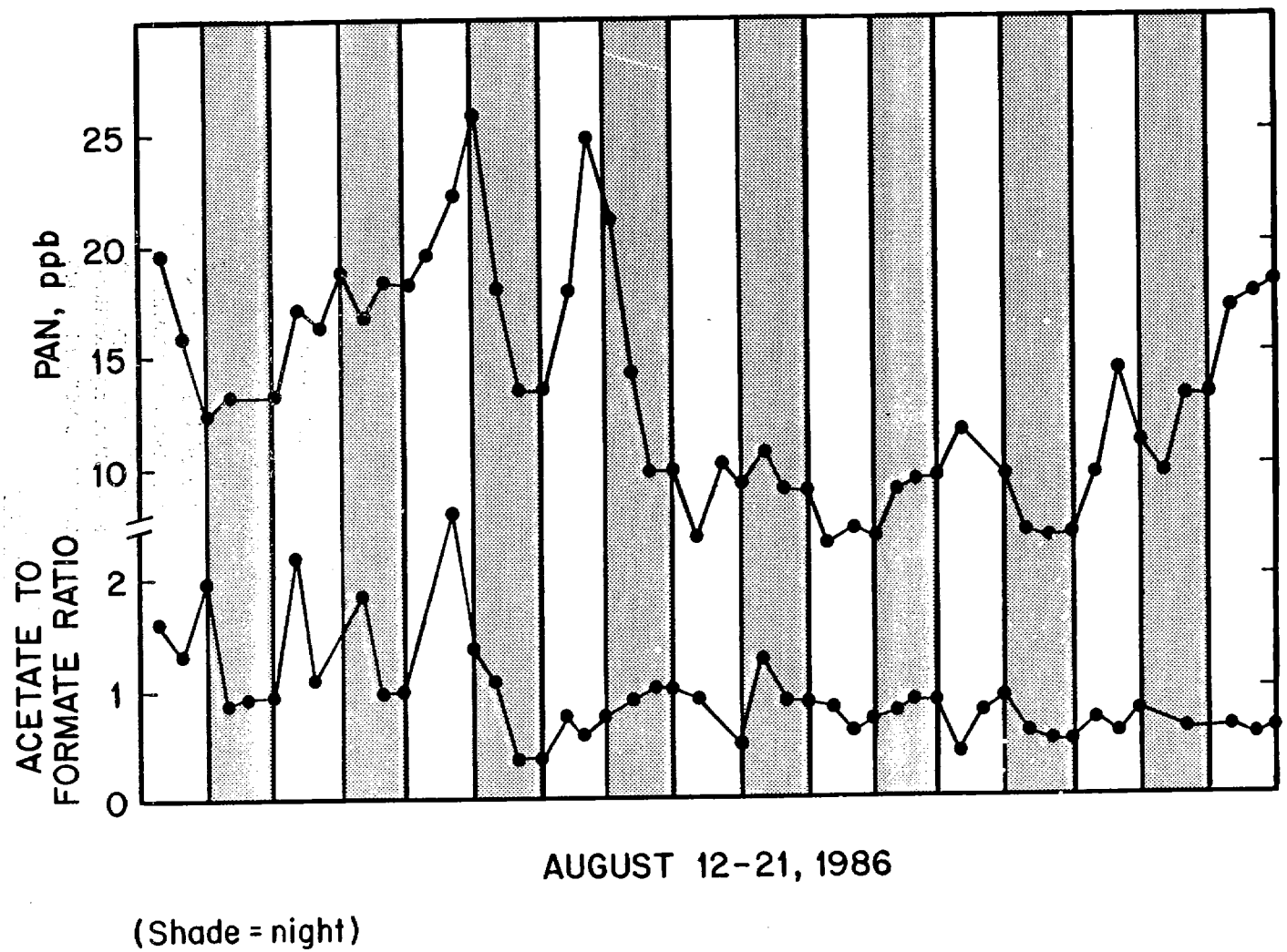


Figure 13. Diurnal variations of PAN and of the acetate to formate concentration ratio, Glendora, CA, August 12-21, 1986

TABLE 28. NITRITE CONCENTRATIONS (ppb) FROM SAMPLES COLLECTED ON ALKALINE FILTERS

	Sampling period				
Date	8—12	12—16	16—20	20—24	0—8
8/12—13	2.5	1.7	1.0	2.4	4.2
8/13—14	2.5	1.4	1.0	2.8	4.8
8/14—15	2.4	1.5	0.41	4.6	6.3
8/15—16	4.5	2.2	2.3	3.8	6.9
8/16—17	4.7	0.35	0.57	1.3	5.3
8/17—18	<0.1	<0.1	1.9	2.6	0.5
8/18—19	4.1	0.7	1.4	2.2	2.2
8/19—20	<0.1	<0.1	0.95	3.2	6.8
8/20—21	3.8	1.0	<0.1	3.2	10.1
Average	2.7	1.0	0.9	2.9	5.2
NO_2^-/ NO , ppb/ppb (a)	4.1	2.8	2.6	4.6	14.1
NO_2^- / PAN, ppb/ppb	13.4	6.4	6.7	21.1	40.6

(a) NO_2 from ARB visible light absorption instrument.

TABLE 29. PAN INTERFERENCE IN ACETIC ACID MEASUREMENTS

	Sampling period				
	8—12	12—16	16—20	20—24	0—8
Measured acetic acid, ppb	4.54	2.84	3.24	3.52	5.55
PAN interference, ppb (a,b)	0.90	0.99	0.86	0.88	0.82
Corrected acetic acid, ppb	3.64	1.85	2.38	2.64	4.73
Relative bias, % of measured value (b)	19.8	34.8	26.5	25.0	14.7

(a) from measured nitrite and nitrite/PAN ratio.
(b) this is an upper limit for actual PAN interference, see text.

prove efficient for organic acid collection, their use would obviously alleviate any concern regarding collection of organic acids on alkaline traps. Nylon filters are known to collect strong acids and have been extensively tested for their performance in sampling nitric acid (Grosjean 1982) and oxalic acid, pK = 1.27 (Norton 1983). These acids are apparently retained on the free amino groups ($-NH_2$) and amide groups ($-CONH_2$ and/or - CONH-) within the nylon matrix. Since these functional groups are strong bases, it was hoped that their use could be extended to the collection of weaker acids.

Our experimental protocol involved side-by-side sampling, every study day during sampling period 3 (16:00—20:00), with Teflon-alkaline and nylon-alkaline filter packs (see experimental section for detail). Sampling flow rates were in the range of 12—14 lpm. Formate and acetate were measured on all four filters. Filter blanks and field controls were included. Teflon and alkaline filters have low formate and acetate blanks, as described in the experimental section. In contrast, nylon filters have a high formate content, 17 ± 4 (n = 5) µg/filter. This observation was taken as an encouraging sign with respect to the nylon filter's ability to collect formate. In fact, the results summarized in Table 30 demonstrate that nylon filters do not retain weak organic acids. As expected, the formate content of the Teflon filter was small or below detection. The formate content of the nylon filters had also dropped to below detection, i.e. not only nylon filters did not collect any formate but the large initial formate content had been lost during sampling. Comparison of the alkaline filters for each paired experiment indicates that alkaline traps behind nylon filters collected more formate than their counterparts behind Teflon filters. The constant difference, 16.8 ± 4.6 µg/filter, n=9, closely matches the initial formate content of the nylon filters, 17 ± 4 µg/filter. Formate was obviously displaced from the nylon filters during sampling (by evaporation if loosely bound, and/or displacement by stronger acids such as nitric acid) and was re-collected on the downstream alkaline filters.

On the basis of these experiments, nylon filters do not appear suitable for collection of weak organic acids in ambient air. If the observed loss of formate is due to displacement by stronger acids, field applications appear to be severely limited since ambient air unavoidably contains acids stronger than carboxylic acids, e.g. HNO_3, HCl, SO_2. Collection of organic acids in pure air (laboratory conditions) may be more successful. Since nylon filters collect oxalic acid (pK = 1.27) but neither formic acid (pK = 3,7) nor the weaker acids (e.g. acetic, pK = 4.7), it would be interesting to determine the "pK_a cut-off" for quantitative collection of atmospheric organic acids and other acidic pollutants on nylon filters.

3.18. Relative abundance of organic and inorganic acids in the South Coast Air Basin atmosphere

In order to assess the relative abundance of ambient organic and inorganic acids, nitric acid and hydrogen chloride were measured along with carboxylic acids and according to the same sampling schedule. For sampling using Teflon-nylon filter packs, the convention of Grosjean (1982) is adopted, i.e. nylon filter-collected nitrate is construed to be an upper limit for gas phase nitric acid. This definition makes allowance for the possible decomposition of particulate nitrate during sampling:

$$NH_4NO_3 \rightleftarrows NH_3 + HONO_2$$

TABLE 30. SIDE-BY-SIDE MEASUREMENTS OF FORMATE ON TEFLON-ALKALINE AND NYLON-ALKALINE FILTER PACKS

Date (b)	Formate, µg/filter (a)		
	A alkaline filter behind Teflon filter (c)	B alkaline filter behind nylon filter (c)	Difference B-A
8/12—13	11	28	17
8/13—14	8	31	23
8/14—15	23	42	19
8/15—16	27	48	21
8/16—17	32	46	14
8/17—18	26	37	8
8/18—19	14	27	13
8/19—20	19	39	20
8/20—21	23	39	16
			mean: 16.8 ± 4.6 (d)

(a) corrected for mean of field controls content.
(b) sampling period 3, 16:00—20:00.
(c) formate content of Teflon and nylon filter samples is not listed, was small or below detection for all 9 sets.
(d) compares to formate content of nylon filters, 17 ± 4 µg/filter.

which would be lost from the upstream Teflon filter, collected on the downstream nylon filter, and thus measured as nitric acid. We adopt the same convention for hydrogen chloride collected on Teflon-carbonate filter packs, i.e. the carbonate-collected chloride is an upper limit for gas phase HCl. In this case, allowance is made for the possible decomposition of particulate chloride during sampling:

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

Both equilibria are strongly temperature-dependent, with ammonium chloride being even less stable than ammonium nitrate at ambient temperatures (equilibrium constants of ~ 73 ppb^2 and ~ 27 ppb^2, respectively, at 25°C). Thus, the positive bias from salt decomposition during sampling may be more important for hydrogen chloride than for nitric acid. A detailed discussion of the advantages and limitations of filter packs and other methods for the determination of ambient nitric acid is given by Hering et al (1988). The corresponding analysis of filter pack performance for measuring ambient HCl has yet to be carried out.

With these operational definitions in mind, we have listed in Table 31 and Table 32 the ambient concentrations of nitric acid and hydrogen chloride, respectively. Four-hour and eight-hour-averaged nitric acid levels ranged from less than 1 ppb to 16.6 ppb. Nitric acid levels exhibited strong diurnal variations with mid-afternoon maxima and nighttime minima. These concentrations and their diurnal variations are consistent with those measured at other smog receptor sites (e.g. Grosjean 1983, Grosjean 1988, Hering et al, 1988, and references therein) and reflect photochemical production as well as gas-particle phase partition, the equilibrium being shifted toward particulate nitrate at lower temperature and higher humidity, i.e. at night.

Ambient levels of hydrogen chloride ranged from 0.05 to 2.68 ppb (four-hour and eight-hour averaged values). Literature data regarding ambient HCl are sparse and are summarized in Table 33.

Our results appear to be consistent with literature values. It has been suggested that the reaction of nitric acid with sea-salt sodium chloride is a source of HCl in the South Coast Air Basin:

$$NaCl + HONO_2 \longrightarrow NaNO_3 + HCl$$

The HCl thus displaced may react with ammonia to form ammonium chloride as indicated above or react at the surface of coarse alkaline particles. The net result may be a shift from coarse chloride ($NaCl + Cl^-$ from the reaction of HCl with coarse particles) to fine chloride (NH_4Cl) plus gaseous chloride (HCl), as observed by Wall et al (1988). However, ambient levels of HCl in Hampton, Va. (Cofer et al 1983) and Tucson, Ariz. (Farmer and Dawson, 1984) are comparable (~ 2 ppb) to those measured in the Basin, and suggest that sources of HCl other than sea salt are likely to exist.

Table 34 summarizes the relative abundance of inorganic and organic acids in Glendora during the period August 12—21, 1986. To our knowledge, simultaneous measurement of inorganic and organic acids over a consecutive 10-day period have not been carried out before in the South Coast Air Basin. It is evident from Table 34 that organic acids always account for a large fraction of the total gas phase acids in the Basin atmosphere. Formic acid accounts for 24—49%

TABLE 31. AMBIENT CONCENTRATIONS OF NITRIC ACID (ppb)
GLENDORA, CA., AUGUST 12-21, 1986

Date	Sampling period 8—12	12—16	16—20	20—24	0—8
8/12—13	1.83	1.8	2.5	0.75	0
8/13—14	1.71	6.1	4.2	1.33	0.51
8/14—15	0.63	7.3	5.8	1.34	1.1
8/15—16	0.8	8.7	7.0	1.0	0.5
8/16—17	2.5	16.6	3.8	0.1	0.16
8/17—18	2.4	6.6	5.9	1.70	0.27
8/18—19	1.0	3.5	1.0	0	0
8/19—20	3.3	2.6	1.45	0.3	0.53
8/20—21	1.3	5.1	2.9	0.9	0.69
Average, ppb:	1.72	6.48	3.84	0.82	0.42

TABLE 32. AMBIENT CONCENTRATIONS OF HYDROGEN CHLORIDE (ppb), GLENDORA, CALIF., AUGUST 12-21, 1986

	Sampling period				
Date	8—12	12—16	16—20	20—24	0—8
8/12—13	1.77	1.93	0.77	1.48	0.71
8/13—14	1.01	0.93	0.98	0.12	0.05
8/14—15	2.53	1.99	0.91	0.69	0.22
8/15—16	2.45	1.26	0.48	0.53	0.14
8/16—17	0.57	0.32	1.40	0.24	0.85
8/17—18	0.55	-	1.35	1.27	0.52
8/18—19	2.68	2.65	0.50	1.90	0.61
8/19—20	-	0.87	1.20	1.46	0.63
8/20—21	0.83	1.15	1.82	1.62	0.79
Average, ppb:	1.55	1.39	1.04	1.03	0.50

TABLE 33. LITERATURE DATA FOR AMBIENT LEVELS OF HCl

Location	HCl, ppb	Reference
over Atlantic Ocean	0.05—0.1	Rudolph et al, 1985
rural Ohio	0.4	Spicer et al, 1986
Hampton, VA.	0.7—2.1	Cofer et al, 1983
Tucson, AZ	up to 2	Farmer and Dawson, 1984
Tokyo, Japan	0.5-2	Okita, 1979
Claremont, CA	0.1—1.0	Wall et al, 1988
Los Angeles, CA	0.14—2.9	Appel et al, 1987
Glendora, CA	0.05—2.68 (mean 1.00, n=45)	this work

TABLE 34. RELATIVE ABUNDANCE OF INORGANIC AND ORGANIC ACIDS, GLENDORA, CALIF., AUGUST 12-21, 1986

	Sampling period				
Volume basis (ppb)	8—12	12—16	16—20	20—24	0—8
HCl	1.55	1.39	1.04	1.03	0.50
HONO2	1.72	6.48	3.84	0.82	0.42
HCOOH	5.10	3.43	3.36	3.53	6.34
CH3COOH	4.54	2.84	3.24	3.52	5.55
Total	12.9	14.1	11.5	8.9	12.8
Organic acids, % of total	74.7	44.3	57.5	79.2	92.8
Mass basis ($\mu g\ m^{-3}$)					
HCl	2.25	2.01	1.51	1.49	0.72
HONO2	4.35	16.39	9.71	2.07	1.06
HCOOH	9.59	6.45	6.32	6.64	11.92
CH3COOH	11.13	6.96	7.95	8.63	13.61
Total	27.3	31.8	25.5	18.8	27.3
Organic acids, % of total	75.8	42.2	56.0	81.1	93.4

(volume basis, ppb) or 20—44% (mass concentration basis, $\mu g\ m^{-3}$) or the total acids. In the same way, the sum of formic acid and acetic acids accounts for 44—93% (volume basis) and 42-93% (mass basis) of the total acids. The relative contribution of organic acids to the total gas phase acid burden of the atmosphere is lowest in the mid-afternoon (~ 43%), and highest at night (93%). Formic acid and acetic acid <u>each</u> exceed the sum of the inorganic acids during the 16-hour period 8 p.m. to 12 noon. Formic and acetic acid together accounted for 73.5% (ppb basis) of the total gas phase acids during the study period. These results, while limited to a short (but representative) period at only one smog receptor site, underline the importance of including organic acids when assessing the atmospheric acid burden in the South Coast Air Basin.

4. REFERENCES

Andreae, M.O., R.W. Talbot and S.M.Li, 1987. Atmospheric measurements of pyruvic acid and formic acid, J. Geophys. Res., 92, 6635-6641.

Andreae, M.O. R.W. Talbot, T.W. Andreae and R.C. Harris 1988. Formic and acetic acid over the central Amazon region, Brazil. I. Dry season. J. Geophys. Res. 93D, 1616-1624.

Atkinson, R.A. and W.L.P. Carter 1984. Kinetics and mechanisms of the gas phase reactions of ozone with organic compounds under atmospheric conditions. Chem. Reviews, 84, 437-470.

Barcelona, M.J., H.M. Liljestrand and J.J. Morgan 1980. Determination of low molecular weight volatile fatty acids in aqueous samples. Anal. Chem. 52, 321-325.

Barkenbus, B.D., C.S. MacDougall, W.H. Griest and J.E. Caton 1983. Methodology for the extraction and analysis of hydrocarbons and carboxylic acids in atmospheric particulate matter. Atmos. Environ. 8, 1537-1543.

Brewer, R.L., R.J. Gordon, W.M. Ip, I.R. Kaplan, C.C. Lee and S.T. Pau 1983. Characterization of organic aerosols from the Southern California air basin. Global Geochemistry Corp., Canoga Park, Calif., June 1983.

Cautreels, W. and K. Van Cauwenberghe 1978. Atmos. Environ., 12, 1133-1141.

Chapman, E.G., D.S. Sklarew and J.S. Flickinger 1986. Organic acids in springtime Wisconsin precipitation. Atmos. Environ. 20, 1717-1725.

Cronn, D.R., R.J. Charlson, R.L. Knights, A.L. Crittenden and B.R. Appel 1977. Atmos. Environ., 11, 929-937.

Courtney, R.L. and H.K. Newhall 1979. Automotive fuels for the 1980s. Society of Automotive Engineers Paper #790809.

Dagaut, P., T.J. Wallington, R. Liu and M.J. Kurylo 1988. The gas phase reactions of hydroxyl radicals with a series of carboxylic acids over the temperature range 240-440K. Int. J. Chem. Kinetics, 20, 331-338.

Dawson, G.A., J.C. Farmer, and J.G. Moyers, Formic and acetic acids in the atmosphere of the southwest U.S.A., Geophys. Res. Letter., 7, 725-728,1980.

Farmer, J.C., and G.A. Dawson, Condensation sampling of soluble atmospheric trace gases, J. Geophys. Res., 87, 8931-8942, 1982.

Galloway, J. N., G.E. Likens, W.C. Keene, and J.M. Miller, The composition of precipitation in remote areas of the world, J. Geophys. Res., 87, 8771-8786, 1982.

Galloway, J.N. 1985. Environ. Sci. Technol., 19, 1157-1159.

Grosjean, D. 1977. Aerosols. Chapter 3 in Ozone and Other Photochemical Oxidants, National Academy of Sciences, Washington, DC, pp. 45-125.

Grosjean, D., D. Van Cauwenberghe, J.P. Schmid, P.E. Kelley and J.N. Pitts, Jr., 1978. Environ. Sci. Technol., 12, 313-317.

Grosjean, D. 1982. Formaldehyde and other carbonyls in Los Angeles ambient air. Environ. Sci. Technol. 16, 254-262.

Grosjean, D. 1982. Quantitative Collection of Total Inorganic Atmospheric Nitrate on Nylon Filters. Anal. Letters, 15, 785-796.

Grosjean, D. 1983. Atmospheric reactions of pyruvic acid. Atmos. Environ.,17, 2379-2382.

Grosjean, D., R.D. Swanson and C. Ellis 1983. Carbonyls in Los Angeles air: contribution of direct emissions and photochemistry. Sci. Total Environ. 28, 65-85.

Grosjean, D. 1983. Distribution of atmospheric nitrogenous pollutants at a Los Angeles area smog receptor site. Environ. Sci. Technol., 17, 13-19.

Grosjean, D. and J.D. Nies 1984. Sampling and analysis of pyruvic acid and methane sulfonic acid in air. Anal. Letters, 17, 89-96.

Grosjean, D. and K. Fung 1984. Hydrocarbons and carbonyls in Los Angeles air. J. Air Pollut. Control Assoc., 34, 537-543.

Grosjean, D., D. Fung, J. Collins, J. Harrison and E. Breitung 1984. Portable generator for on-site calibration of peroxyacetylnitrate analyzers. Anal. Chem., 56, 569-573.

Grosjean, D. 1988. Aldehydes, carboxylic acids and inorganic nitrate during NSMCS. Atmos. Environ. 22, 1637-1648.

Guiang, S.R., III, S.V. Krupa, and G.C. Pratt, Measurements of S(IV) and organic anions inMinnesota rain, Atmos. Environ. 18, 1677-1682, 1984.

Hanst, P.L., W.E. Wilson, R.K. Patterson, B.W. Gay, L.W. Chaney and C.S. Burton 1975. A spectroscopic study of California smog. U.S. EPA report EPA 650/4-75-006, Research Triangle Park, NC.

Hanst, P.L., N.W. Wong and J. Bragin 1982. A long-path infrared study of Los Angeles Smog. Atmos. Environ., 16, 969-981.

Hatakeyama, S., H. Bandow, M. Okuda and H. Akimoto 1981. J. Phys. Chem., 85, 2249-2254.

Herliky, L.J., J.N. Galloway and A.L. Mills 1987. Bacterial utilization of formic and acetic acids in rainwater. Atmos. Environ. 21, 2397-2402.

Holdren, M.W., C.W. Spicer, and J.M. Hales. Peroxyacetyl nitrate solubility and decomposition rate in acidic water. Atmos. Environ. 18, 1171-1173, 1984.

Hoshika, Y. 1982. Gas chromatographic determination of lower fatty acids in air at parts per trillion levels. Anal. Chem., 54, 2433-2437.

Huebert, B.J., and C.H. Robert. The dry deposition of nitric acid to grass. J. Geophys. Res. 90, 2085-2090 (1985).

Irgum, K. 1985. Anal. Chem., 57, 1334-1338.

Jacob, D. J., The chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate, J. Geophys. Res., 91, 9807-9826, 1986.

Jacob, D.J., J.W. Munger, J.M. Waldman and M.R. Hoffman 1986. The H_2SO_4-HNO_3-NH_3 system at high humidities and in fogs. I. Spatial and temporal patterns in the San Joaquin Valley of California. J. Geophys. Res. D91, 1073-1088.

Jacob, D. J. and S.C. Wolfsy 1988. Photochemistry of biogenic emissions over the Amazon forest. J. Geophys. Res. 93D, 1477-1486.

Japar, S.M., W.W. Brachaczek, R.A. Gorse, Jr., J.M. Norbeck, and W.R. Pierson. Dry deposition of nitric acid and sulfur dioxide to a nylon surrogate surface. International Symposium on Acid Precipitation, Muskoka,Ontario, September 16-20, 1985.

Kawamura, K. and I.R. Kaplan 1983. Organic compounds in the rainwater of Los Angeles. Environ. Sci. Technol., 17, 497-501.

Kawamura, K. and Kaplan, I.R. (1984). Capillary gas chromatography determination of volatile organic acids in rain and fog samples. Analyt.Chem. 56, 1616-1620.

Kawamura, K., S. Steinberg and I.R. Kaplan 1985a. Capillary GC determination of short-chain dicarboxylic acids in rain, fog and mist. Int. J. Environ. Anal. Chem., 19, 175-188.

Kawamura, K., L.L. Ng and I.R. Kaplan 1985. Determination of organic acids (C_1-C_{10}) in the atmosphere, motor exhausts and engine oils. Environ.Sci. Technol., 19, 1082-1086.

Kawamura, K. and Kaplan, I.R. (1986a). Biogenic and anthropogenic organic compounds in rain and snow samples collected in Southern California. Atmos. Environ., 20, 115-124.

Kawamura, K. and Kaplan, I.R. (1986b). Compositional change of organic matter in rainwater during precipitation events. Atmos. Environ. 20, 527-535.

Kawamura, K. and Kaplan, I.R. (1987). Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air. Environ. Sci.Technol. 21, 105-110.

Keene, W. C., J.N. Galloway and J.D. Holdren, Jr. 1983. Measurement of weak organic acidity in precipitation from remote areas in the world. J.Geophys. Res. C9, 5122-5130.

Keene, W. C., and J.N. Galloway, Organic acidity in precipitation of North America, Atmos. Environ., 18, 2491-2498, 1984.

Keene, W. C., and J.N. Galloway, Considerations regarding sources for formic and acetic acids in the troposphere, J. Geophys. Res., 91, 14,466-14,474, 1986.

Keene, W.C. et al 1987. Intercomparison of measurement systems for vapor and particulate phase concentrations of formic and acetic acids. Preprint.

Leone, J.A., R.C. Flagan, D. Grosjean, and J.H. Seinfeld 1985. Int. J. Chem.Kinetics, 17, 177-216.

Likens, G.E., E.S. Edgerton and J.N. Galloway 1983. The composition and deposition of organic carbon in precipitation. Tellus, 35B, 16-24.

Likens, G.E., W.C. Keene, J.M. Miller and J.N. Galloway 1987. Chemistry of precipitation from a remote, terrestrial site in Australia. J. Geophys. Res. 92, 13299-13314.

Lunde, G., J. Gether, N. Gjos and M.B. Stobet-Lande 1977. Organic micro-pollutants in precipitation in Norway. Atmos. Environ., 11, 1007-1014.

Munger, J.W., J. Collett, Jr., B. C. Daube, Jr., and M. R. Hoffmann 1987. Carboxylic acids and carbonyl compounds in Southern California clouds and fogs. Tellus, submitted for publication.

Norton, R.B., J.M. Roberts and B.J. Huebert 1983. Tropospheric oxalate. Geophys. Res Letters. 10, 517-520.

Norton, R.B., Measurements of formate and acetate in precipitation at Niwot Ridge and Boulder, Colorado, Geophys. Res. Lett., 12, 769-772, 1985.

Okaka, T. and T. Kuwamoto 1983. Anal. Chem., 55, 1001-1004.

Okita, T. and S. Ohta 1979. Chap. 17 in Nitrogenous Air Pollutants: Chemical and Biological Implications. D. Grosjean, edit. Ann Arbor Sci. Pub., Ann Arbor, MI, pp. 282-306.

Pierson, W. R. and W.W. Brachaczek 1987. Dew chemistry and acid deposition in Glendora, CA, during the 1986 Carbonaceous Species Methods Comparison Study. Preprint.

Pierson, W.R., Brachaczek, W.W., Gorse, R.A., Jr., Japar, S.M. and Norbeck, J.M. (1986a). On the acidity of dew. J. Geophys. Res. 91, 4083-4096.

Plum, C.N., E. Sanhueza, R. Atkinson, W.P.L. Carter and J.N. Pitts, Jr., 1983. OH radical rate constants and photolysis rates of alpha-dicarbonyls. Environ. Sci. Technol., 17, 479-484.

Possanzini M., P. Ciccioli, V. Di Palo, and R. Draisci 1987. Determination of low boiling point aldehydes in air and exhaust gases by using annular denuders combined with HPLC techniques. Chromatographia, November (preprint obtained from Dr. Ciccioli, 10/87).

Schuetzle, D., A.L. Crittenden and R.J. Charlson 1973. J. Air Pollut. Control Assoc., 23, 704-709.

Schuetzle, D., D. Cronn, A.L. Crittenden and R.J. Charlson 1975. Environ. Sci. Technol., 9, 838-845.

Steinberg, S., K. Kawamura and I.R. Kaplan 1985. The determination of alpha-ketoacids and oxalic acid in rain, fog and mist by HPLC. Int. J. Environ. Anal. Chem., 19, 251-260.

Su, F., J.G. Calvert and J.H. Shaw 1979. J. Phys. Chem., 83, 3185-3190.

Talbot, R. W., K.M. Beecher, R.C. Harriss and W.R. Cofer III, 1988. Atmospheric Geochemistry of Formic and Acetic acids at a mid-latitude temperate site. J. Geophys. Res. 93D, 1638-1652.

Tokos, J., Jr. and R.A. Duce 1987. Formic and acetic acids in rain and aerosol particles over the central north Pacific Ocean. Tellus, submitted for publication.

Tuazon, E.C., R.A. Graham, A.M. Winer, R.R. Easton, J.N. Pitts, Jr. and P.L. Hanst 1978. A kilometer pathlength Fourier-transform infrared system for the study of trace pollutants in ambient and synthetic atmospheres. Atmos. Environ., 12, 865-875.

Tuazon, E.C., A.M. Winer and J.N. Pitts, Jr. 1981. Trace pollutant concentrations in a multiday smog episode in the California south coast air basin by long path length Fourier transform infrared spectroscopy. Environ. Sci. Technol., 15, 1232-1237.

Veyret, B., J.C. Rayez and R. Lesclaux 1982. J. Phys. Chem., 86, 3424-3430.

Wauters, E., F. Vangaever, P. Sandra and M. Verzele 1979. Polar organic fraction of air particulate matter. J. Chromatog. 170, 133-138.

Williamson, M.J. and A.G. Clarke 1984. Anal. Chem., 56, 1037-1039.

Yamamoto, S. and R.A. Back 1985. The gas phase chemistry of oxalic acid. J. Phys. Chem., 89, 622-625.

APPENDIX A.
ALDEHYDES AND ORGANIC ACIDS IN DEW SAMPLES

Aliquots of dew samples collected at the Glendora site (Pierson and Brachaczek 1987) were obtained from Dr. Pierson and were analyzed for formaldehyde, acetaldehyde, formate and acetate using the analytical protocols described in Section 2.8. The corresponding results are listed in Table A-1. Aldehyde concentrations are those of the "free" carbonyls, i.e. do not include aldehydes combined as hydroxyalkane sulfonic acids (aldehyde-bisulfite adducts).

Formaldehyde and acetaldehyde concentrations in dew were in the range 4-24 ug/mL (140-810 uM) and 4-12 ug/mL (57-300 uM), respectively. The average formaldehyde to acetaldehyde ratio was 1.8 (ug/mL units), but two of the ten samples contained more acetaldehyde than formaldehyde.

Formate concentrations were in the range 5-17 ug/mL (115-380 uM). Dew samples with and without addition of a biocide before collection gave similar formate values. Three consecutive short-term samples and the corresponding longer-term sample also yielded comparable formate levels. Acetate was present in all samples at concentrations of 50-200 uM.

On the average, there was slightly more formaldehyde than formic acid in dew (11.6 vs. 10.6 ug/mL) and about as much acetaldehyde as acetic acid. A detailed discussion of this data set and of the importance of aldehydes and organic acids in Southern California dew is given by Pierson and Brachaczek (1987).

TABLE A-1. POLAR ORGANICS IN GLENDORA DEW SAMPLES

Date collected	Sample number (a)	Formaldehyde		Acetaldehyde		Formate		Acetate	
		µg/mL	µM	µg/mL	µM	µg/mL	µM	µg/mL	µM
8–12 to 8–13	2.1	6.7	225	12.2	305	17.2	382	-	(b)
	2.2	8.2	272	6.2	155	10.7	237	5.4	90
8–14 to 8–15	4.1	8.5	283	5.1	127	6.5	145	6.8	114
	4.2	4.2	139	4.5	113	5.2	115	-	
8–16 to 8–17	6 bio (c)	12.6	421	8.4	210	11.4	254	-	
	6 i (d)	11.8	395	2.3	57	15.0	333	-	
	6 ii (d)	15.5	516	9.6	239	8.1	179	-	
	6 iii (d)	14.1	470	4.9	123	13.9	309	-	
	6	24.2	806	5.3	132	11.6	259	-	
8–21	10	9.9	332	5.2	131	6.8	151	-	
	Average	11.57	-	6.37		10.64			
	Detection limit	0.37		0.12		0.44		0.5	

(a) same number as in Pierson and Brachaczek (1987).
(b) incompletely resolved from larger unidentified peak. Acetate was present in all samples not listed at concentrations of 50-200 µM. The large unknown peak is not chloride, sulfate, nitrate, bicarbonate, hydroxyde, or any of the following organic acids: oxalic, glyoxylic, malonic, pyruvic, succinic, propionic, butyric, valeric, hexanoic, glutaric, adipic, benzoic, phenylacetic, and methanesulfonic.
(c) with added biocide, same sampling time as sample 6.
(d) three consecutive short-term samples, total sampling time same as for samples 6 and 6 bio.

APPENDIX B
PEROXYACETYL NITRATE AMBIENT CONCENTRATIONS

Ambient levels of peroxyacetyl nitrate (PAN) at the Citrus College site are compiled in tabular form and as concentration-time profiles according to date (from 8/12 to 8/21), time (PST) and PAN concentration (units: ppbv). PAN diurnal profiles are consistent with those obtained in previous studies. "Typical" profiles closely following those for ozone and with well-defined mid-afternoon maxima were observed on several days, e.g. 8/15 and 8/19/86. Another typical profile, with a sharp concentration increase corresponding to the arrival of the smog front at the site, was also observed, e.g. 8/12 (afternoon), 8/14 and 8/20/86. On the four remaining days, 8/13, and 8/16-18/86, the PAN diurnal profiles exhibit few distinct features: high NO2/NO ratios on those days were conducive to the stability of PAN throughout the smog episodes. Finally, early morning "spikes" were observed on several days. These spikes are probably due to smog-laden air being "backflushed" over the site in the early morning hours.

Citrus College PAN Data

Date	Time / PST	PAN Conc. / ppbv
8/12/86	7:50	23
8/12/86	8:07	19
8/12/86	8:15	23
8/12/86	8:49	22
8/12/86	9:03	19
8/12/86	9:33	21
8/12/86	10:07	26
8/12/86	11:30	14
8/12/86	11:55	14
8/12/86	12:35	13
8/12/86	12:51	13
8/12/86	13:07	13
8/12/86	13:22	14
8/12/86	13:52	14
8/12/86	14:22	14
8/12/86	14:51	25
8/12/86	15:21	21
8/12/86	15:52	16
8/12/86	16:23	16
8/12/86	16:53	12
8/12/86	17:24	10
8/12/86	17:53	9
8/12/86	18:23	11
8/12/86	18:53	14
8/12/86	19:23	14
8/12/86	19:53	13
8/12/86	20:23	14
8/12/86	20:53	15
8/12/86	21:23	14
8/12/86	21:53	13
8/12/86	22:23	12
8/12/86	22:53	13
8/12/86	23:23	16
8/12/86	23:53	11
8/13/86	0:23	13
8/13/86	0:53	13
8/13/86	1:23	12
8/13/86	1:53	12
8/13/86	2:23	14
8/13/86	2:53	15
8/13/86	3:23	13
8/13/86	3:53	12
8/13/86	4:23	13
8/13/86	4:53	12
8/13/86	5:23	11
8/13/86	5:53	11
8/13/86	6:23	14

Citrus College PAN Data

Date	Time / PST	PAN Conc. / pptv
8/13/86	6:53	11
8/13/86	7:23	15
8/13/86	7:53	20
8/13/86	8:23	14
8/13/86	8:53	15
8/13/86	9:23	17
8/13/86	9:53	18
8/13/86	10:23	20
8/13/86	10:53	19
8/13/86	11:14	18
8/13/86	11:44	17
8/13/86	12:14	16
8/13/86	12:44	18
8/13/86	13:14	18
8/13/86	13:44	19
8/13/86	14:14	14
8/13/86	14:44	14
8/13/86	15:14	14
8/13/86	15:44	18
8/13/86	16:14	18
8/13/86	16:44	20
8/13/86	17:14	21
8/13/86	17:44	20
8/13/86	18:14	19
8/13/86	19:14	18
8/13/86	19:44	17
8/13/86	20:14	18
8/13/86	20:44	18
8/13/86	21:14	17
8/13/86	21:44	16
8/13/86	22:14	14
8/13/86	22:44	15
8/13/86	23:14	17
8/13/86	23:44	19
8/14/86	0:14	24
8/14/86	0:44	18
8/14/86	1:14	21
8/14/86	1:44	16
8/14/86	2:14	19
8/14/86	2:44	19
8/14/86	3:14	22
8/14/86	3:44	23
8/14/86	4:14	18
8/14/86	4:44	16
8/14/86	5:14	16
8/14/86	5:44	16
8/14/86	6:14	16

Date	Time / PST	PAN Conc. / ppbv
8/14/86	6:44	15
8/14/86	7:14	16
8/14/86	7:44	18
8/14/86	8:14	18
8/14/86	8:44	23
8/14/86	9:14	18
8/14/86	9:44	19
8/14/86	10:14	18
8/14/86	10:44	18
8/14/86	11:14	24
8/14/86	11:44	21
8/14/86	12:14	21
8/14/86	12:44	25
8/14/86	13:14	19
8/14/86	13:44	18
8/14/86	14:14	20
8/14/86	14:44	19
8/14/86	15:14	24
8/14/86	15:44	32
8/14/86	16:14	29
8/14/86	16:44	27
8/14/86	17:14	26
8/14/86	17:44	25
8/14/86	18:14	25
8/14/86	18:44	24
8/14/86	19:14	27
8/14/86	19:44	26
8/14/86	20:14	22
8/14/86	20:44	19
8/14/86	21:14	20
8/14/86	21:44	18
8/14/86	22:14	18
8/14/86	22:44	16
8/14/86	23:14	16
8/14/86	23:44	16
8/15/86	0:14	15
8/15/86	0:44	14
8/15/86	1:14	14
8/15/86	1:44	14
8/15/86	2:14	13
8/15/86	2:44	12
8/15/86	3:14	14
8/15/86	3:44	13
8/15/86	4:14	13
8/15/86	4:44	14
8/15/86	5:14	13
8/15/86	5:44	15

Citrus College PAN Data

Date	Time / PST	PAN Conc. / ppbv
8/15/86	6:14	14
8/15/86	6:44	14
8/15/86	7:14	14
8/15/86	7:44	13
8/15/86	8:14	14
8/15/86	8:44	16
8/15/86	9:14	18
8/15/86	9:44	15
8/15/86	10.14	16
8/15/86	10:44	17
8/15/86	11:14	24
8/15/86	11:44	24
8/15/86	12:14	25
8/15/86	12:44	20
8/15/86	13:14	22
8/15/86	13:44	19
8/15/86	14:14	23
8/15/86	14:44	26
8/15/86	15:14	33
8/15/86	15:44	34
8/15/86	16:14	29
8/15/86	16:44	26
8/15/86	17:14	22
8/15/86	17:44	19
8/15/86	18:14	19
8/15/86	18:44	20
8/15/86	19:14	17
8/15/86	19:44	18
8/15/86	20:14	16
8/15/86	20:44	17
8/15/86	21:14	17
8/15/86	22:44	10
8/15/86	23.2	11
8/16/86	0:04	11
8/16/86	0:33	11
8/16/86	1:03	11
8/16/86	1:33	7
8/16/86	2:03	9
8/16/86	2:33	11
8/16/86	3:03	7
8/16/86	3:33	8
8/16/86	4:03	11
8/16/86	4:33	8
8/16/86	5:03	8
8/16/86	5:33	11
8/16/86	6:03	12
8/16/86	6:33	11

Date	Time / PST	PAN Conc. / ppbv
8/16/86	7:03	11
8/16/86	7:33	12
8/16/86	8:03	11
8/16/86	9:03	4
8/16/86	9:33	5
8/16/86	10:03	9
8/16/86	10:33	7
8/16/86	11:03	6
8/16/86	11:33	5
8/16/86	12:03	11
8/16/86	12:33	11
8/16/86	13:03	10
8/16/86	13:33	9
8/16/86	14:02	9
8/16/86	14:32	10
8/16/86	15:02	10
8/16/86	15:32	12
8/16/86	16:02	11
8/16/86	16:32	11
8/16/86	17:02	9
8/16/86	17:32	9
8/16/86	18:02	6
8/16/86	18:32	8
8/16/86	19:02	11
8/16/86	19:32	9
8/16/86	20:32	10
8/16/86	21:02	11
8/16/86	21:32	11
8/16/86	22:15	10
8/16/86	22:45	10
8/16/86	23:15	12
8/16/86	23:45	12
8/17/86	0:15	9
8/17/86	0:45	9
8/17/86	1:15	8
8/17/86	2:15	10
8/17/86	2:45	9
8/17/86	3:15	9
8/17/86	3.45	9
8/17/86	4:15	11
8/17/86	4:45	9
8/17/86	5:15	12
8/17/86	5:45	9
8/17/86	6:15	7
8/17/86	7:45	8
8/17/86	8:15	8
8/17/86	8:45	5

Citrus College PAN Data

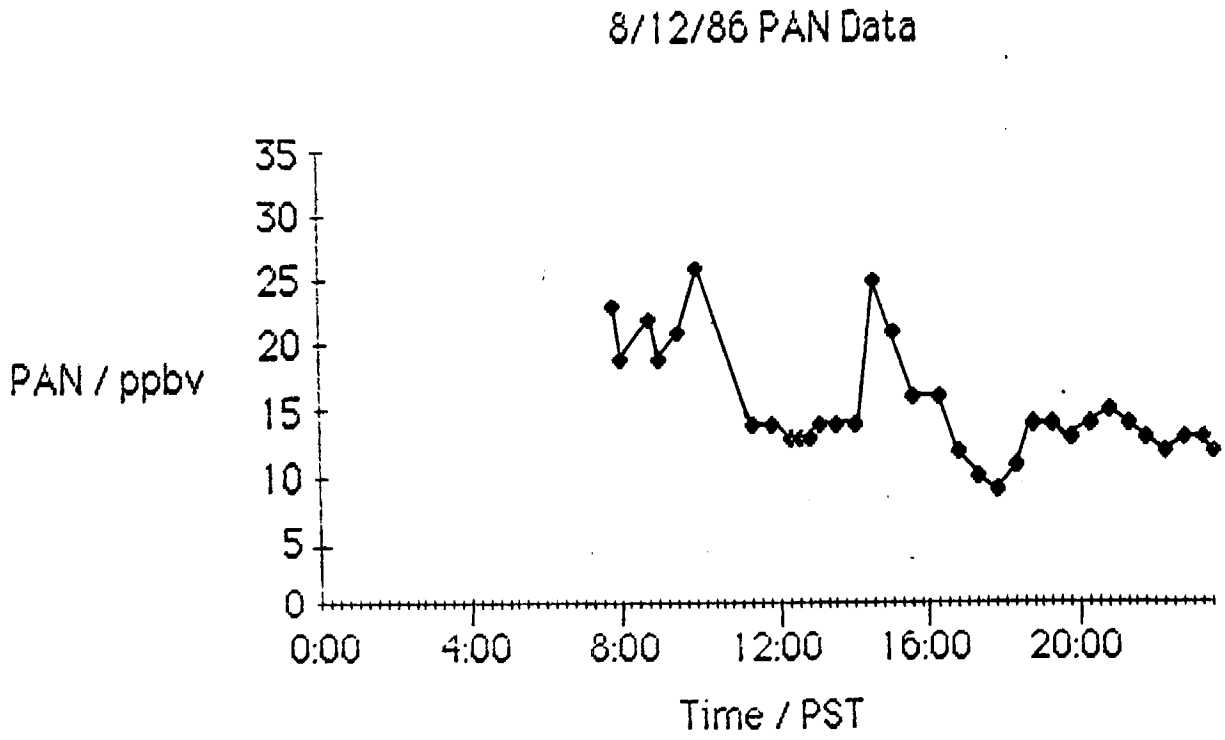
Date	Time / PST	PAN Conc. / ppbv
8/17/86	9:15	8
8/17/86	9:45	7
8/17/86	10:15	5
8/17/86	10:45	7
8/17/86	11:15	5
8/17/86	11:45	6
8/17/86	12:15	6
8/17/86	12:45	7
8/17/86	13:15	8
8/17/86	13:45	11
8/17/86	14:15	7
8/17/86	14:45	6
8/17/86	15:15	7
8/17/86	15:45	7
8/17/86	16:15	8
8/17/86	16:45	7
8/17/86	17:15	6
8/17/86	17:35	5
8/17/86	18:35	8
8/17/86	19:05	8
8/17/86	19:35	7
8/17/86	20:05	6
8/17/86	20:35	10
8/17/86	21:05	8
8/17/86	21:35	9
8/17/86	22:05	11
8/17/86	23:05	12
8/17/86	23:35	8
8/18/86	0:05	8
8/18/86	0:35	7
8/18/86	1:05	10
8/18/86	1:35	8
8/18/86	2:05	11
8/18/86	2:35	12
8/18/86	3:05	11
8/18/86	3:35	10
8/18/86	4:05	9
8/18/86	4:35	11
8/18/86	5:05	8
8/18/86	5:35	18
8/18/86	6:05	7
8/18/86	6:35	7
8/18/86	7:05	8
8/18/86	7:35	9
8/18/86	8:05	9
8/18/86	8:35	5
8/18/86	9:05	9

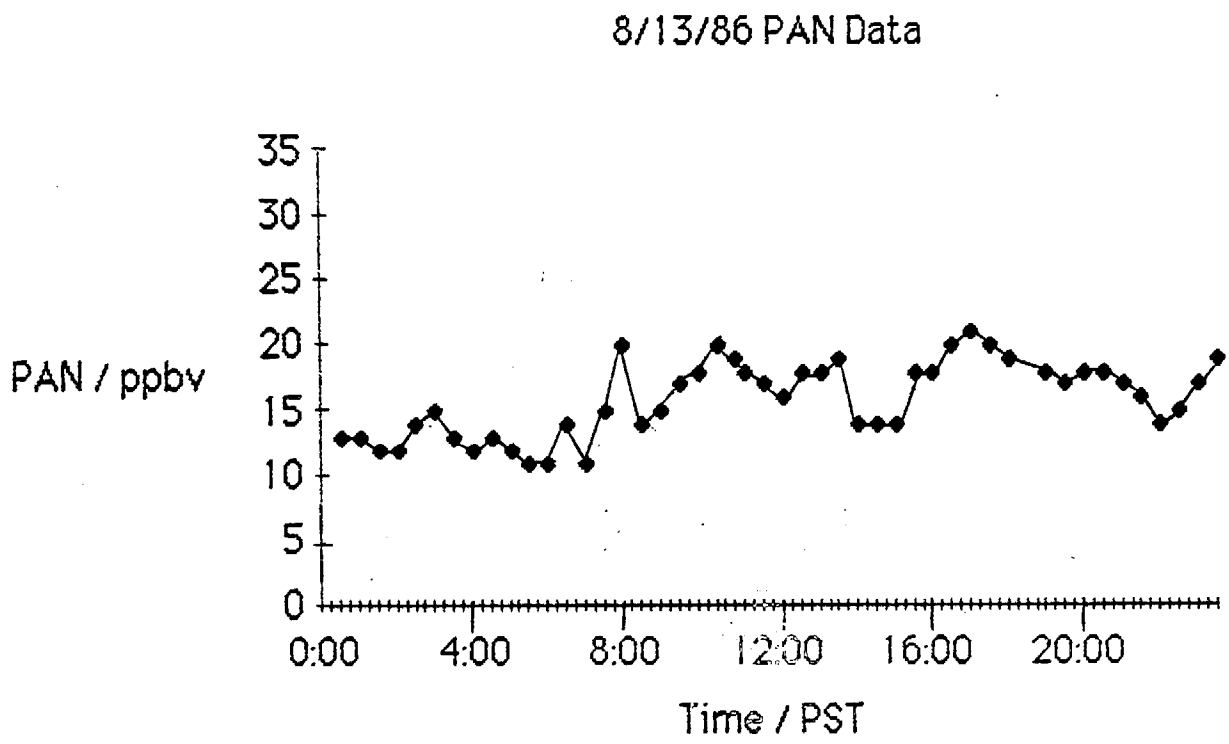
Date	Time / PST	PAN Conc. / ppbv
8/18/86	9:35	18
8/18/86	10:35	15
8/18/86	11:05	13
8/18/86	11:35	15
8/18/86	12:05	10
8/18/86	12:35	8
8/18/86	13:05	8
8/18/86	13:35	7
8/18/86	14:05	7
8/18/86	17:35	10
8/18/86	18:05	11
8/18/86	19:05	11
8/18/86	19:35	7
8/18/86	20:05	7
8/18/86	20:35	7
8/18/86	21:05	7
8/18/86	21:35	8
8/18/86	22:05	8
8/18/86	22:35	7
8/18/86	23:05	7
8/18/86	23:35	7
8/19/86	0:05	8
8/19/86	0:35	7
8/19/86	1:05	7
8/19/86	1:35	9
8/19/86	2:05	8
8/19/86	2:35	6
8/19/86	3:05	7
8/19/86	3:35	7
8/19/86	4:05	7
8/19/86	4:35	7
8/19/86	5:05	6
8/19/86	5:35	6
8/19/86	6:05	6
8/19/86	6:35	8
8/19/86	7:05	8
8/19/86	7:35	7
8/19/86	8:35	7
8/19/86	9:35	11
8/19/86	10:05	10
8/19/86	10:35	9
8/19/86	11:05	9
8/19/86	11:35	12
8/19/86	12:05	11
8/19/86	12:35	11
8/19/86	13:05	11
8/19/86	13:35	14

Date	Time / PST	PAN Conc. / ppbv
8/19/86	14:05	19
8/19/86	14:35	19
8/19/86	15:05	14
8/19/86	15:35	16
8/19/86	16:05	14
8/19/86	16:35	11
8/19/86	17:05	14
8/19/86	17:35	11
8/19/86	18:05	10
8/19/86	18:35	11
8/19/86	19:35	8
8/19/86	20:05	11
8/19/86	20:35	11
8/19/86	21:05	9
8/19/86	21:35	9
8/19/86	22:05	7
8/19/86	22:35	11
8/19/86	23:05	11
8/20/86	0:35	10
8/20/86	1:05	8
8/20/86	2:05	17
8/20/86	2:35	18
8/20/86	3:35	11
8/20/86	4:05	16
8/20/86	4:35	9
8/20/86	6:35	9
8/20/86	7:05	13
8/20/86	8:05	10
8/20/86	8:35	16
8/20/86	9:05	16
8/20/86	9:35	15
8/20/86	10:05	19
8/20/86	10:35	22
8/20/86	11:05	14
8/20/86	11:35	11
8/20/86	12:05	12
8/20/86	12:35	14
8/20/86	13:05	16
8/20/86	13:35	15
8/20/86	14:05	17
8/20/86	14:35	18
8/20/86	15:17	34
8/20/86	16:03	22
8/20/86	16:33	19
8/20/86	17:32	15
8/20/86	18:03	16
8/20/86	18:51	18

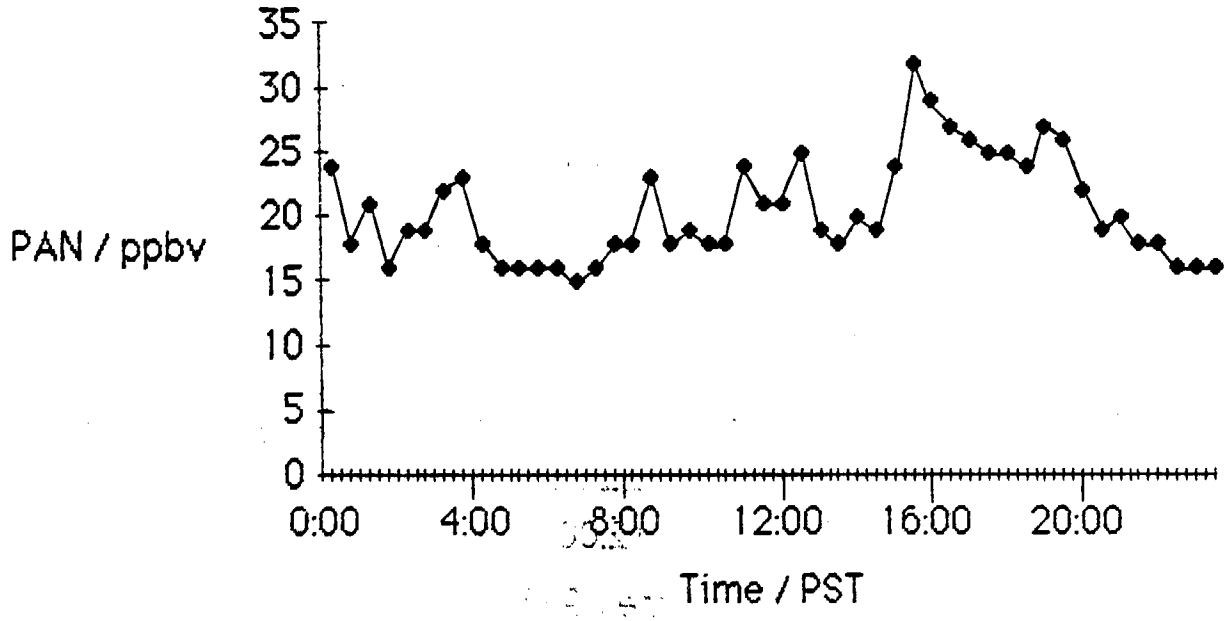
Citrus College PAN Data

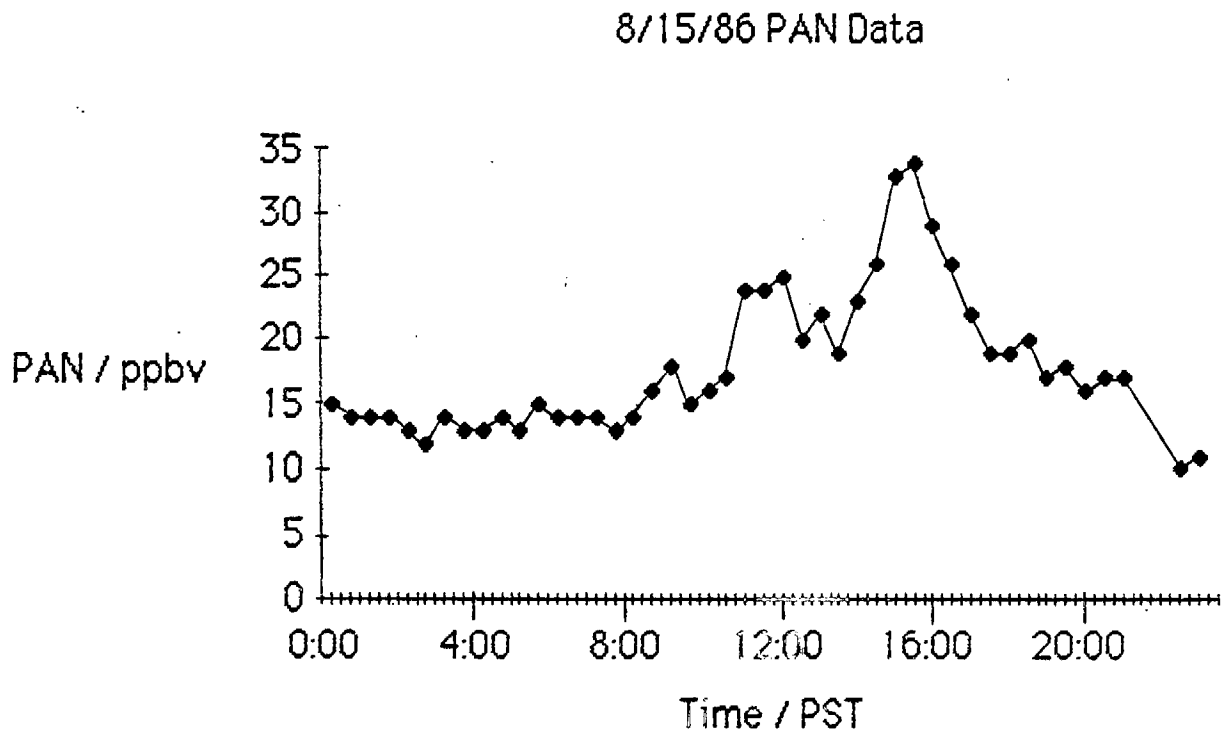
Date	Time / PST	PAN Conc. / ppbv
8/20/86	19:21	21
8/20/86	19:51	19
8/20/86	20:21	19
8/20/86	20:51	21
8/20/86	21:21	22
8/20/86	21:51	21
8/20/86	22:22	28
8/20/86	22:51	24
8/20/86	23:21	27
8/20/86	23:51	28
8/21/86	0:21	21
8/21/86	0:51	29
8/21/86	1:21	21
8/21/86	1:51	21
8/21/86	2:21	20


8/12/86 PAN Data
PAN / ppbv
35
30
25
20
15
10
5
0
0:00
4:00
8:00
12:00
16:00
20:00
Time / PST

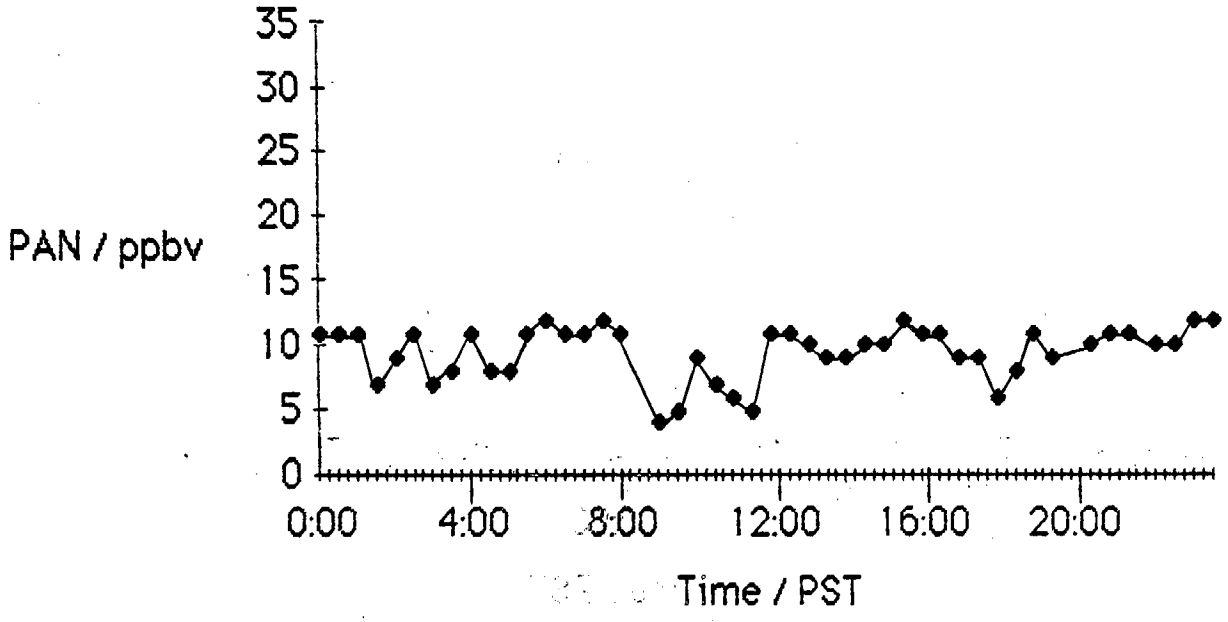

8/13/86 PAN Data
PAN / ppbv
35
30
25
20
15
10
5
0
0:00
4:00
8:00
12:00
16:00
20:00
Time / PST

8/14/86 PAN Data

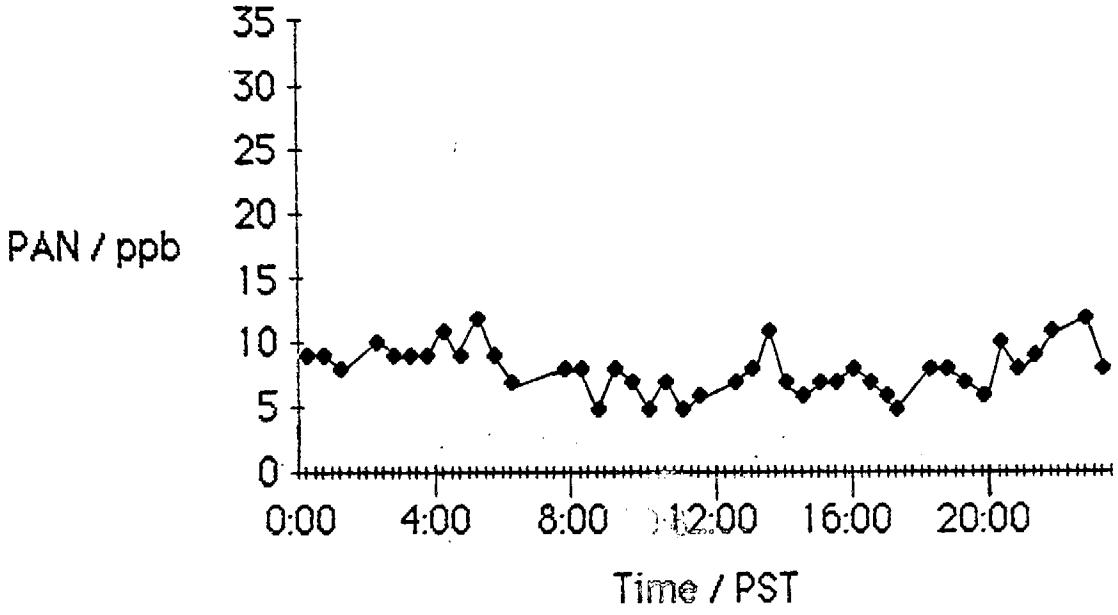



8/15/86 PAN Data
PAN / ppbv
35
30
25
20
15
10
5
0
0:00
4:00
8:00
12:00
16:00
20:00
Time / PST

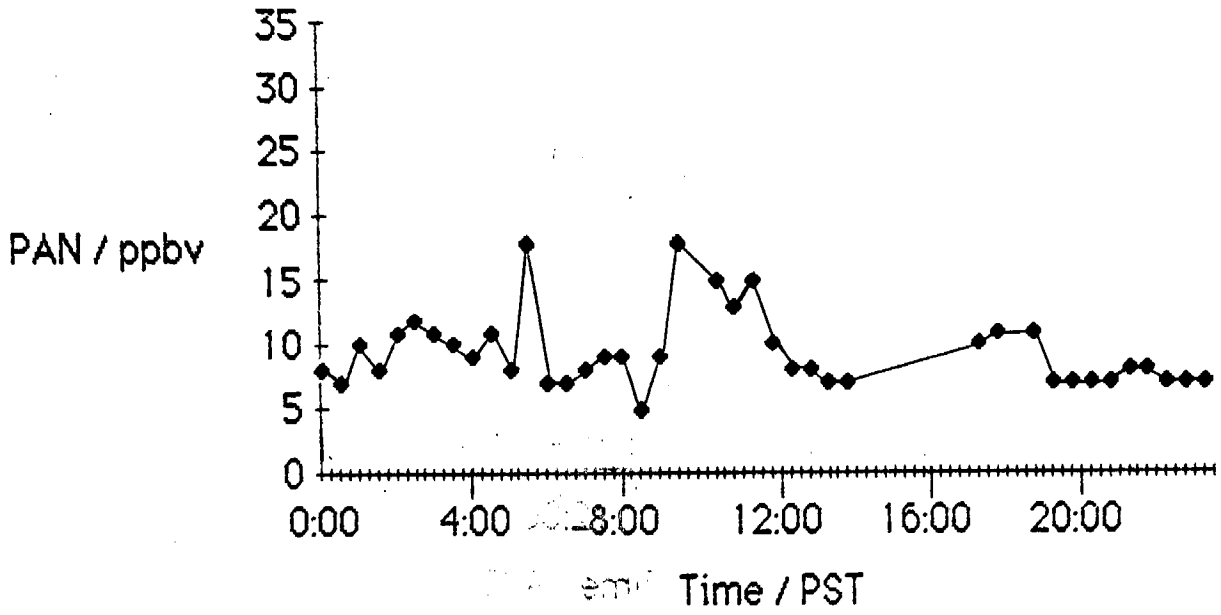
8/16/86 PAN Data

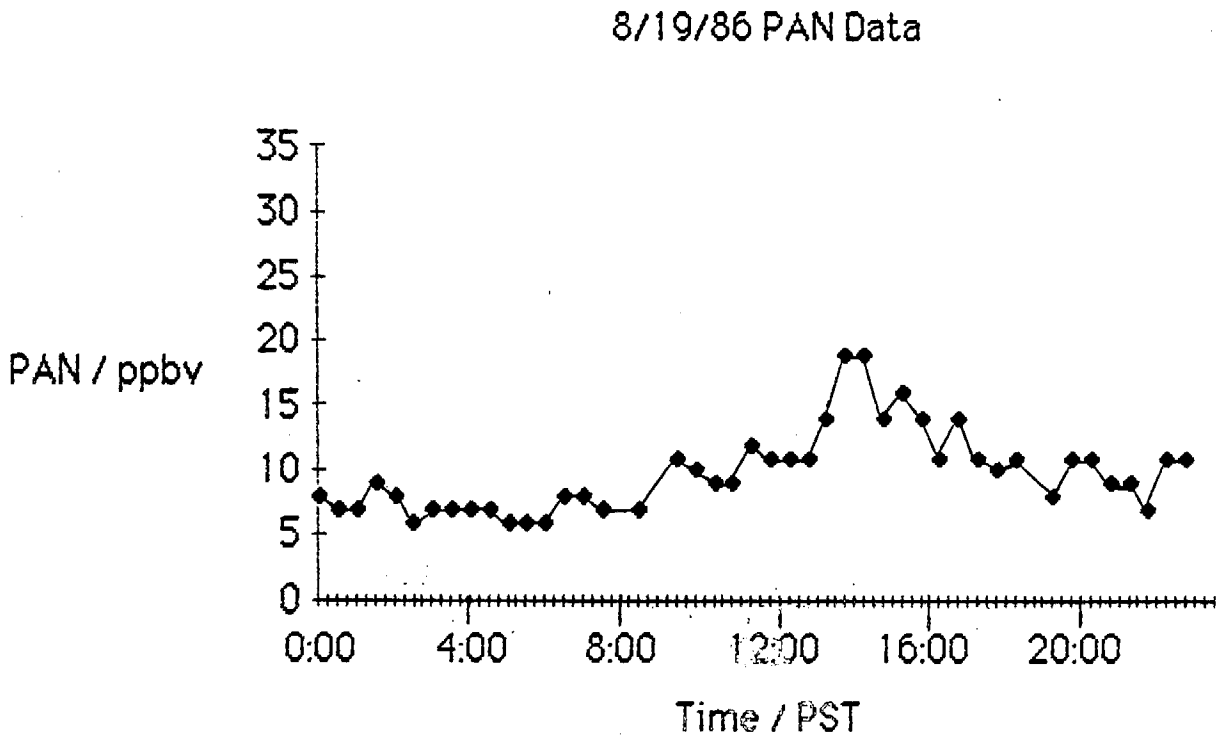


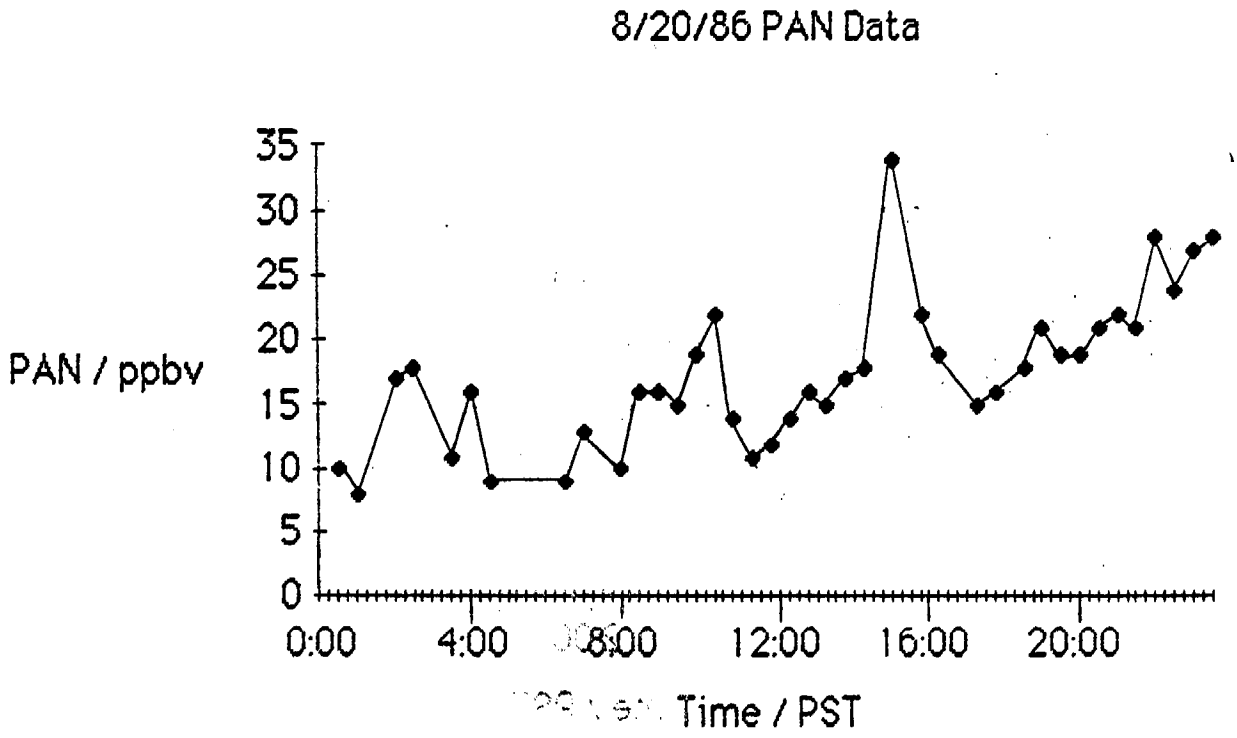
8/17/86 PAN Data



8/18/86 PAN Data




8/19/86 PAN Data
PAN / ppbv
35
30
25
20
15
10
5
0
0:00
4:00
8:00
12:00
16:00
20:00
Time / PST


8/20/86 PAN Data
PAN / ppbv
35
30
25
20
15
10
5
0
0:00
4:00
8:00
12:00
16:00
20:00
Time / PST

00000109
ASSET