4.0 SAMPLING AND ANALYSIS OF ORGANIC ACIDS

Ambient concentrations of formic acid and acetic acid were made at the four forested sites situated along the western slope of the Sierra Nevada (see Figure 1-1). This section discusses the measurements of formic acid and acetic acid and compares the results with those of earlier studies.

4.1 Experimental Methods

4.1.1 Sampling Protocol

Samples were collected on alumina cartridges (Sep-Pak, Waters-Millipore) coated with an alkaline solution (Grosjean, 1990; 1991). Each cartridge was sealed with Teflon tape, wrapped in aluminum foil, and placed in a glass vial with a Teflon-lined screw cap. The cartridges were shipped and stored refrigerated in the dark before and after sampling. The storage containers consisted of zip-lock plastic bags. These plastic bags contained alkaline-coated 47 mm diameter glass fiber filters that collect (by passive diffusion) any organic acids present in the bag air, thus protecting the cartridges from contamination. Samples were collected by connecting each cartridge to a timer-activated sampler using 1/4 inch diameter plastic tubing. Each sampler housed a sampling pump, calibrated flow meter, vacuum gauge, 7 day timer, power cord, and the corresponding air flow and electrical connections. The flow meters were calibrated prior to the field operations and were re-calibrated upon return of the samplers to the laboratory (Grosjean and Williams, 1990).

4.1.2 Liquid Chromatography Analysis

The cartridges were eluted with 3 ml of deionized water containing 40 μL of HPLC-grade chloroform added as a biocide to prevent analyte loss. Aliquots of the eluate were analyzed for formate and acetate by liquid chromatography with ultraviolet detection. The column employed was a Hamilton PRP-X-100, 4.1 x 250 mm, the eluent was 1.0 mM KHP in deionized water (pH = 4.5) containing 5% HPLC-grade CH_3CN, the eluent flow rate was 2.0 mL/min at a column pressure of 1,700 psi, the detection wavelength was 280 nm, and the injection volume was 150 μL. Under these conditions, acetate and formate elute at 2.2 and 3.5 min, respectively. Quantitative analysis involved the use of external standards consisting of dilute aqueous solutions of reagent grade sodium formate and sodium acetate. Calibration factors, i.e., the slopes of plots of peak height (absorbance) vs. analyte concentration, were verified using fresh standards each day samples were analyzed (Grosjean and Williams, 1990). The analytical detection limits (signal to noise ratio = 5) were equivalent to 50 and 100 ng per cartridge for formate and acetate, respectively. For a typical volume of air sampled, 0.6 m^3, this corresponded to detection limits of 0.05 ppb for formic acid and 0.07 ppb for acetic acid.

4.1.3 Method Performance

The relative standard deviations (RSD) for multiple injections of standards were in the range 1.2 to 17.4% for formate and 1.7 to 6.0% for acetate, with averages of 8.3% for formate and 3.7% for acetate. Replicate analyses of 30 field samples yielded RSD's of 0 to 12% for formate and 0 to 8% for acetate, with averages of 2.3% for formate and 1.8% for acetate.

Analyte recovery, determined by performing two consecutive elutions of the same cartridge, was 95.2 +/- 5.1% for formate and 91.7 +/- 7.0% for acetate (average of 22 field samples).

Sampling efficiency under field conditions was measured by sampling ambient air using two cartridges in series and analyzing them for formate and acetate. The results for nine sets of field samples yielded an average collection efficiency of 0.730 +/- 0.103 for formate and 0.822 +/- 0.137 for acetate (Grosjean and Williams, 1990). Accordingly, organic acid concentrations reported in this paper have been corrected upward by factors of 1.37 for formic acid and 1.22 for acetic acid.

An estimate of the overall precision of the sampling and analytical protocol was obtained by analysis of formate and acetate in two sets of collocated samplers. For formic acid, the RSD's were in the range 0.4% to 4.5% and averaged 2.7%. For acetic acid, the RSD's were in the range 5.9 to 16.5% and averaged 11.0%.

4.1.4 Sampling Periods

Sampling intervals to corresponded to periods of predicted high photochemical air pollution in the San Joaquin Valley, which borders on the western slopes of the Sierra Nevada. The sampling periods were 7/13 - 7/14/90, 7/21 - 7/22/90, 7/27 - 7/29/90, 8/3 - 8/6/90, and 8/22 - 8/24/90, for a total of 14 sampling days. Two samples were collected daily, one from 0700 to 1700 and the other from 1700 to 0700 PDT.

4.2 Results and Discussion

4.2.1 Ambient Levels of Formic Acid and Acetic Acid

Formic acid concentrations ranged from approximately 1 ppb to 40 ppb; those of acetic acid ranged from approximately 0.5 ppb to 13 ppb. Mean formic acid concentrations were 18 ppb at Tehachapi and between 12 and 13 ppb at the three other sites. Mean acetic acid concentrations ranged from 3.9 ppb at Blodgett to 8.0 ppb at Yosemite (Table 4-1). Formic acid was more abundant at all sites except Yosemite (Table 4-2). Figures 4-1 and 4-2 show the average daytime and nighttime formic and acetic acid concentrations for each of the five sampling periods. Each point on Figures 4-1 and 4-2 represents the average of 1 to 4 samples depending on how many days the sampling period lasted. The August 3 to 6 sampling interval was a period of particularly high carboxylic acid levels throughout the region. Histograms of the data (Figures 4-3 and 4-4) present a more detailed picture of the distribution of the data. The ratios between formic and acetic acid at each site and the ratio between daytime and nighttime levels at each site are given in Table 4-2. The greater diurnal fluctuation of formic acid is reflected in the bimodal appearance of Figure 4-3, where the lower peak around 9 ppb consists mainly of nighttime measurements, and the higher peak around 15 ppb consists mainly of daytime measurements. The acetic acid histogram does not show bimodality, and Table 4-2 accordingly indicates that diurnal variations in acetic acid were less pronounced than those of formic acid.

Table 4-1 Summary of ambient concentrations (ppbv).

Location	Formic Acid					Acetic Acid			
	N	mean	SD	max.	min.	mean	SD	max.	min.
Blodgett	28	12.7	6.4	29.4	0.9	3.9	1.8	9.6	1.8
Yosemite	32	12.8	7.1	26.3	1.1	8.0	2.5	13.3	3.5
Giant Forest	31	12.3	6.1	23.5	1.7	5.1	2.0	13.2	2.0
Tehachapi	33	18.1	8.8	39.6	3.6	4.6	2.5	12.4	0.6

Table 4-2 Ratios of acetic to formic acid concentrations, and daytime to nighttime ratios for formic and acetic acid.

Location		Day/Night	
	Acetic/Formic	Formic	Acetic
Blodgett	0.51	1.68	1.19
Yosemite	1.27	1.81	1.91
Giant Forest	0.61	2.03	1.21
Tehachapi	0.28	1.96	1.05

Figure 4-1a Daytime formic acid level at sampling sites. Sample period durations indicated at bottom.

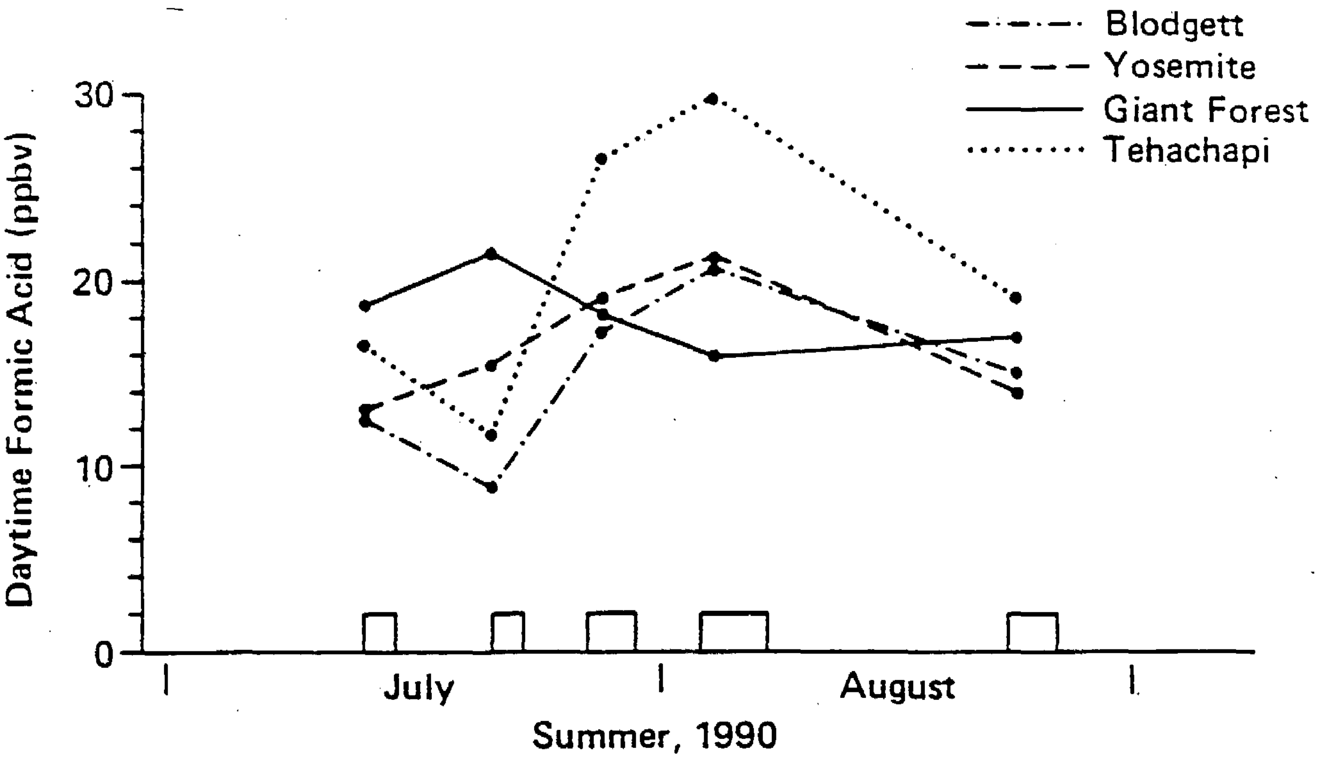


Figure 4-1b Nighttime formic acid level at sampling sites. Sample period durations indicated at bottom.

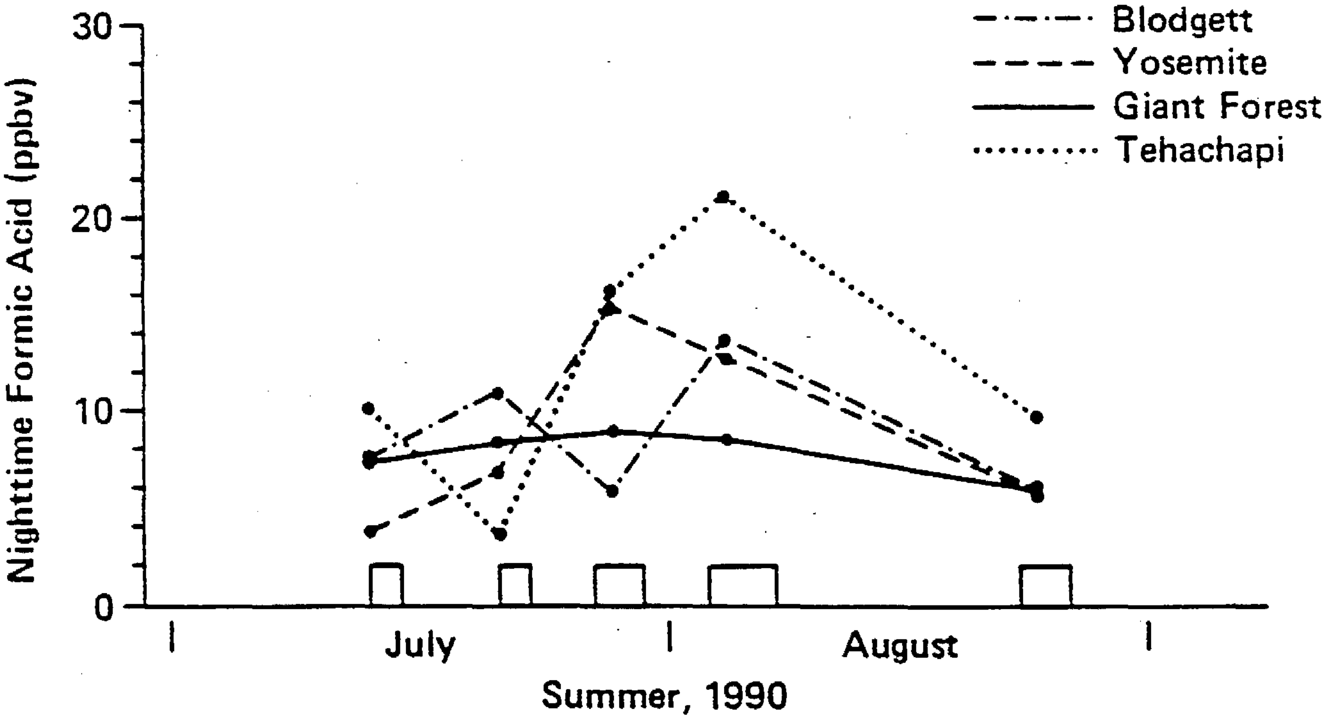


Figure 4-2a Daytime acetic acid levels at sampling sites. Sample interval durations indicated at bottom.

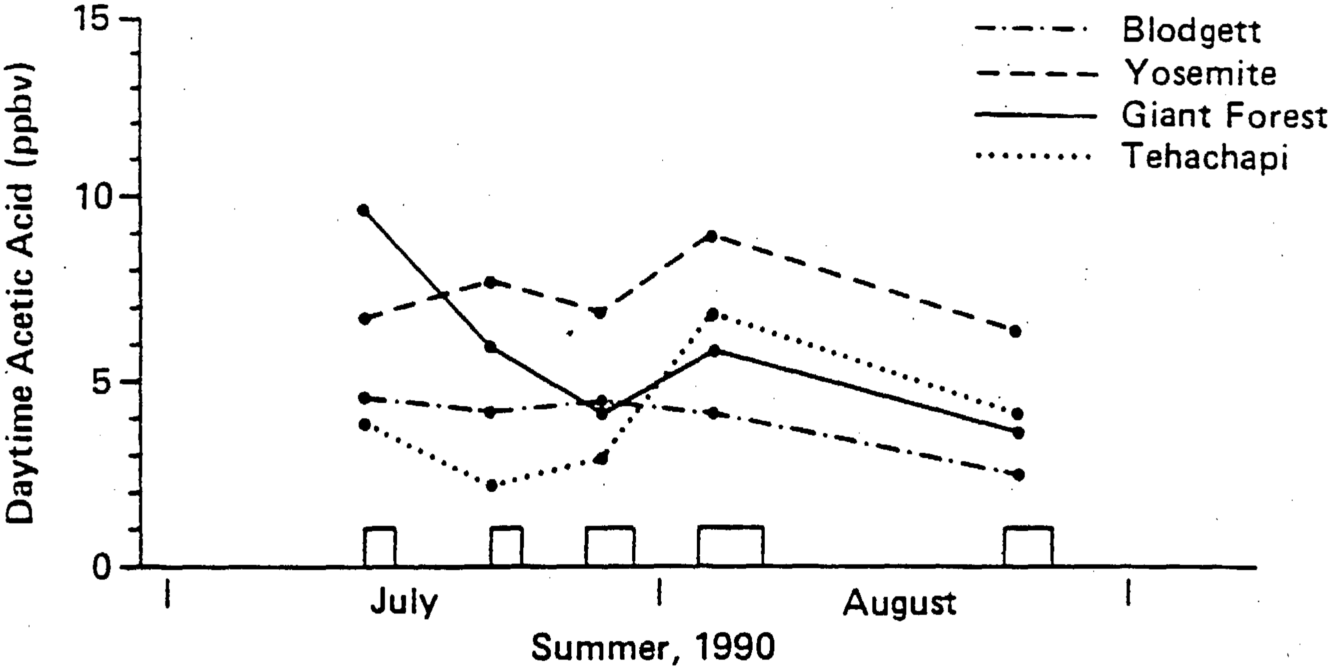


Figure 4-2b Nighttime acetic acid levels at sampling sites. Sample interval durations indicated at bottom.

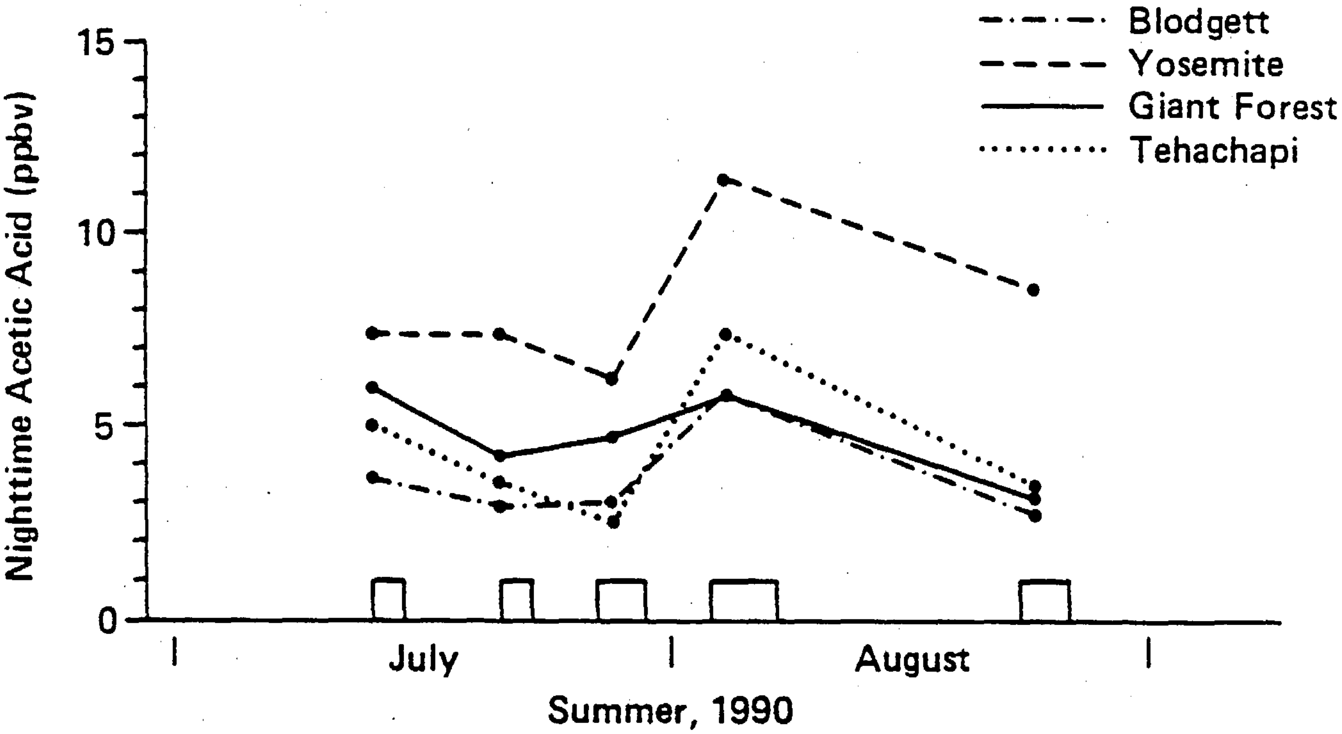


Figure 4-3 Histogram of formic acid concentrations for all sites.

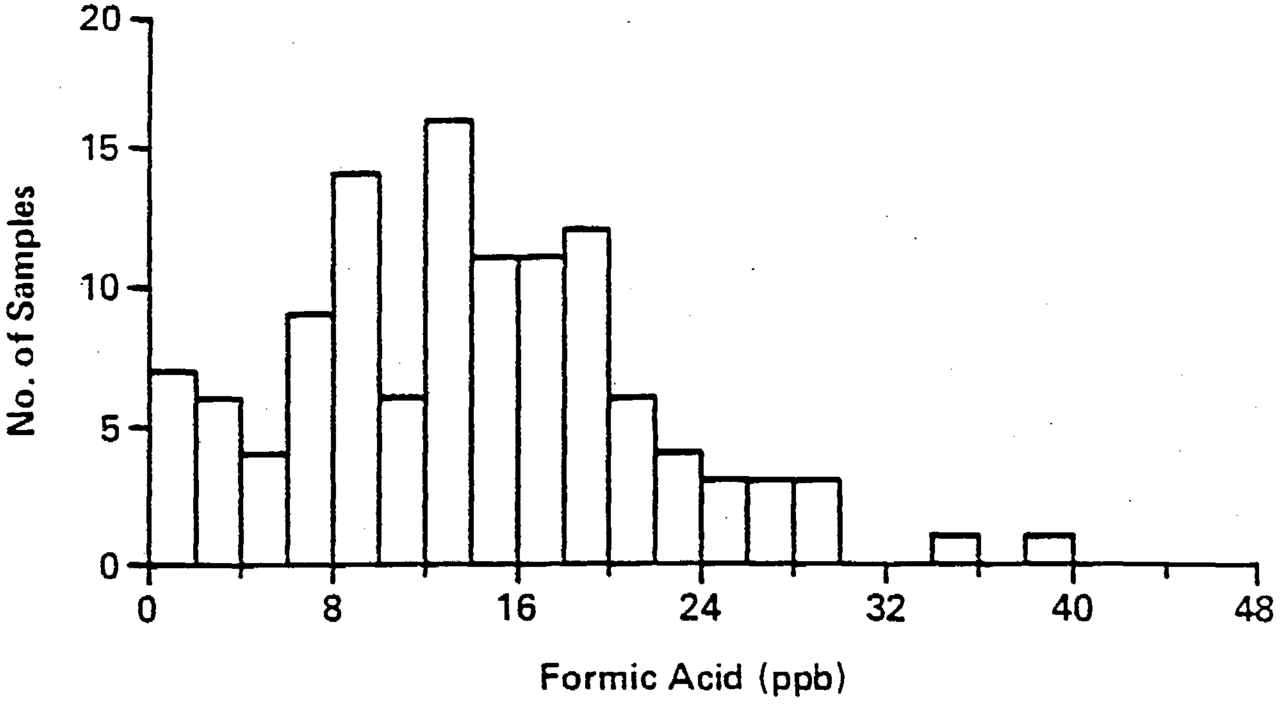
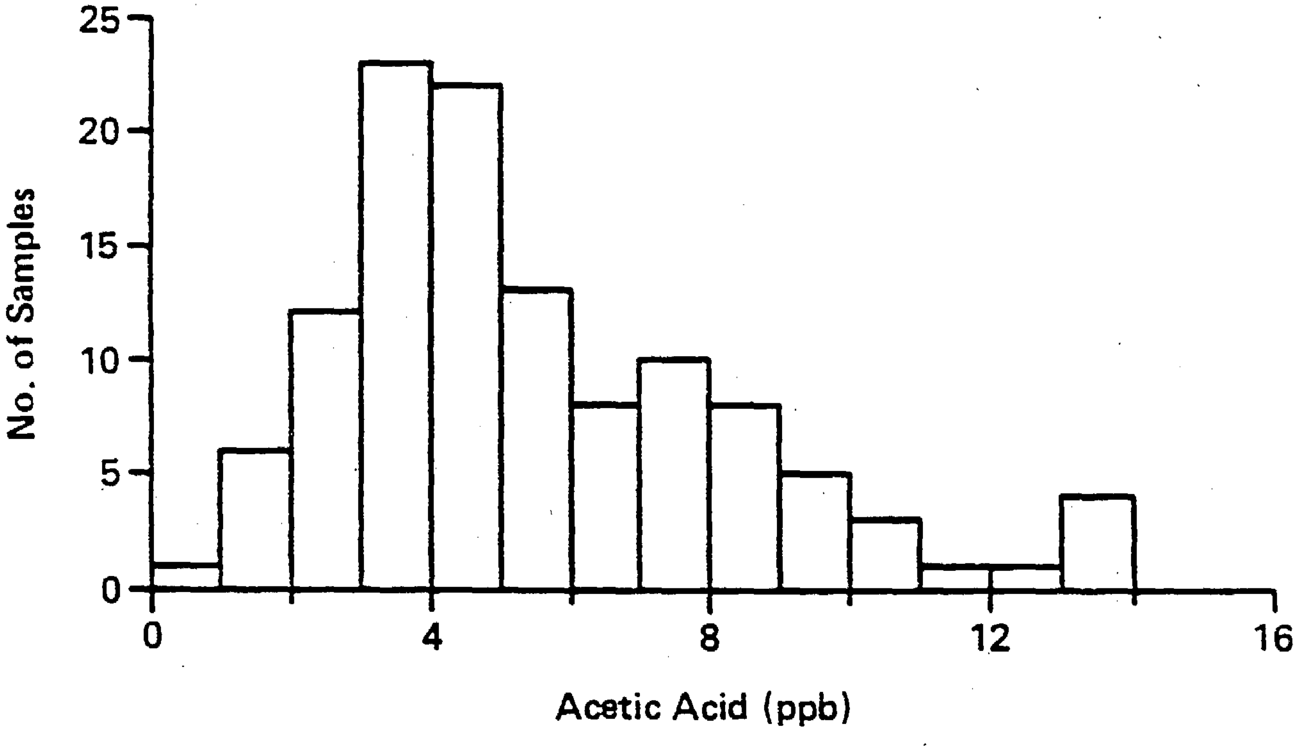


Figure 4-4 Histogram of acetic acid concentrations for all sites.



4.2.2 Comparison with Other Studies

When comparing results from the western Sierra Nevada (Table 4-1) with those of other studies (Table 4-3), it is important to note that our sampling periods were chosen to capture intervals when the ozone concentration in the San Joaquin Valley region of California (i.e., the most likely source region for pollutants impacting at the forested sites) exceeded ambient air quality standards (greater than 0.12 ppm), while other studies have focused on measuring seasonal variability (Talbot et al., 1988) or background levels (Puxbaum et al., 1988; Dawson et al., 1980) or on quantifying diurnal variations (Talbot et al., 1988; Puxbaum et al., 1988); therefore, concentrations observed in one study might not be directly comparable to those from another. Results of the current study are more appropriately compared to the previous studies of Grosjean (1989 and 1990), since these also focused on high pollution events, and the sampling and analytical procedures were the same as those employed in this work.

Comparison of Table 4-1 with Table 4-3 indicates that carboxylic acid levels we measured in the Sierra Nevada are higher than those measured in past studies. In many cases, average concentrations of both formic and acetic acids observed during this study were greater than the maxima observed in other studies. The highest formic acid levels cited in other studies (Table 4-3) are those of Tuazon et al. (1978), who reported mean concentrations of 8.2 ppb with a maximum of 19 ppb for urban sites in Southern California. High formic acid concentrations were also reported by Grosjean (1990) at Palm Springs, but these are still lower than those reported here for Sierra Nevada locations. Many of the values listed in Table 4-3 for formic acid (Hanst et al., 1982; Andreae et al., 1987; Puxbaum, 1988; Kawamura, 1985) are one-third

Table 4-3 Summary of previous studies of atmospheric formic and/or acetic acids.

			Concentration (ppbv)					
Location[1]	Date	Method[2]	Sampling time (h)	Formic acid		Acetic acid		Reference
				mean	max.	mean	max.	
Riverside, CA (U)	August-October, 1976	FT-IR	0.5	8.2	19	—	—	Tuazon et al., 1978
Claremont, CA (U)	October, 1978	FT-IR	0.5	4.6	19	—	—	Tuazon et al., 1981
Tucson, AZ (U)	December, 1979 - January, 1980	WF-IC	?	2.5	3.4	4	6.5	Dawson et al., 1980
Sells, AZ (R)	January, 1980	WF-IC	?	0.7	1.0	0.6	0.8	ibid.
Los Angeles, CA (U)	June, 1980	FT-IR	0.5	4.0	10	—	—	Hanst et al., 1982)
Los Angeles, CA (U)	August, 1984	AT-GC	4-24	1.0	3	1.4	4	Kawamura et al., 1985
Manaus, Brazil (R)	July-August, 1985	AS-IC	0.3	2	3	—	—	Andreae et al., 1987
Charlottesville, VA (U)	June, 1986	AS-IC	4-5	1.8	2	—	—	ibid.
Hampton, VA (U)	September, 1985-December, 1986	MC-IC	0.3-1	1.5	5	1.0	3	Talbot et al., 1988
Exelberg, Austria (SR)	July, 1986-August, 1987	DD-IC	12	1.7	3.8	0.5	0.8	Puxbaum et al., 1988
Raasdorf, Austria (SR)	July, 1986-August, 1987	DD-IC	12	1.0	1.8	0.6	0.8	ibid.
Schoeneben, Austria (R)	March-September, 1987	DD-IC	12	0.9	1.2	0.3	0.4	ibid.
Long Beach, CA (U)	June-December, 1987	AT-LC	4-8	2.8	12	4.7	17	Grosjean, 1990
Palm Springs, CA (SR)	July-September, 1987	AT-LC	4-7	7.8	13	4.5	11	ibid.
Claremont, CA (U)	June-September 1987	AT-LC	4-7	5.5	19	3.5	13	ibid.
Upland, CA (U)	September, 1988-September, 1989	AT-LC	24	2.8	8.0	—	—	Grosjean, 1991

1. (U) = urban site, (R) = rural site, (SR) = semirural site.

2. FT-IR = Fourier transform infrared spectroscopy, WF-IC = Water film ion chromatography, AT-GC = Alkaline scrubber ion chromatography, MC-IC = Mist chamber ion chromatography, DD-IC = Diffusion denuder ion chromatography, AT-LC = Alkaline trap liquid chromatography.

to one-tenth as high as those reported here. Acetic acid levels comparable to levels measured at Sierra Nevada sites were reported by Grosjean (1990) at urban sites in Southern California.

Explanations for the observed high levels of formic acid and acetic acid may include: (a) an artifact of sampling or analytical methods, (b) the presence of local sources of organic acids, and/or (c) high levels of regional air pollution. These are addressed next.

Our sampling and analytical methods were identical to those employed in past studies, including three of the studies cited in Table 4-3. If there is a bias, it is systematic and should be reflected in the data reported in those studies (Grosjean, 1989; Grosjean et al., 1990; Grosjean, 1990). Comparison of Table 4-1 with Table 4-3 shows the observed concentrations of formic and acetic acids are substantially higher than those observed in studies that used the same measurement method. Furthermore, this method gave results that were comparable to those obtained with an in-situ method, FTIR, when performing collocated measurements of ambient formic acid in the urban Los Angeles area (Grosjean et al., 1990). Therefore the high levels reported here cannot be attributed simply to sampling and analytical artifacts.

To investigate the possibility that local sources of organic acids could account for the variability between sites, Spearman rank-order correlation coefficients were calculated to compare the data from each site with the data from other sites. The Spearman rank-order correlation coefficient is used here because it is more robust than the more commonly used linear (Pearson's) correlation coefficient in the event of non-normally distributed data (Press et al., 1986). The assumption is that positive correlations between sites is due to regional meteorological effects and emission patterns that influence all sites, whereas an absence of correlation is due to each site being perturbed by local sources and hence uncorrelated. These statistics should be treated cautiously because a significant correlation does not necessarily require a causal relationship, nor does a real causal relationship necessarily impart a strong correlation. Correlation coefficients for the entire organic acid data set (Table 4-4) suggest a weak positive correlation between formic acid concentrations at all sites. Acetic acid concentrations are less correlated than the formic acid concentrations, but the correlation is still positive, and formic versus acetic acid concentrations appear to be uncorrelated. In order to eliminate correlations simply due to diurnal variations, Spearman's rank-order correlation coefficients for daytime and nighttime formic acid levels (Table 4-5) were calculated separately, again revealing a weak positive correlation for daytime concentrations between all sites except Giant Forest.

Considering the variability of vegetation, topography, and exposure to local mobile source emissions, it seems unlikely that local or biogenic sources present at each site could account for the high concentrations observed. Therefore, it appears the data presented here are representative of regional formic and acetic acid levels found throughout the western Sierra Nevada, with some additional contributions from local sources. High formic acid concentrations observed at Tehachapi might reflect additional sources in southern California. High acetic acid concentrations at Yosemite might be due to more localized sources such as emissions from the nearby Fresno area, traffic into Yosemite Valley, or biogenic emissions.

The organic acid levels recorded in the western Sierra Nevada were similar to those for Palm Springs (Table 4-3) in that the levels were high, and the acetic to formic acid concentration ratio was low compared to those reported elsewhere. These observations are consistent with the suggestion of Grosjean (1990) for the Palm Springs observations that formic acid levels are high

Table 4-4 Spearman's rank-order correlation coefficients for formic (for) and acetic (ace) acid at Forest Study sites. A small significance level in parentheses indicates a significant correlation.

		Blodgett		**Yosemite**		**Giant Forest**		**Tehachapi**	
		for	ace	for	ace	for	ace	for	ace
Blodgett	for	—	.31(.66)	.49(.00)	.08(.71)	.43(.00)	.22(.53)	.49(.00)	.28(.58)
	ace	—	—	.21(.53)	.17(.53)	.16(.54)	.44(.00)	.30(.60)	.21(.53)
Yosemite	for	—	—	—	.06(.74)	.60(.00)	.35(.00)	.64(.00)	.11(.63)
	ace	—	—	—	—	-.31(.00)	.20(.53)	.18(.53)	.29(.62)
Giant Forest	for	—	—	—	—	—	.23(.55)	.41(.00)	-.17(.53)
	ace	—	—	—	—	—	—	.32(.01)	.37(.01)
Tehachapi	for	—	—	—	—	—	—	—	.37(.00)
	ace	—	—	—	—	—	—	—	—

Table 4-5 Spearman's rank-order correlation coefficients for daytime and nighttime formic and acetic acids. In parentheses is the probability that the correlation coefficient would have been larger in the event of uncorrelated data, thus, a small probability indicates a significant correlation.

Formic acid

	Daytime				Nighttime			
	Blodgett	Yosemite	Giant Forest	Tehachapi	Blodgett	Yosemite	Giant Forest	Tehachapi
Blodgett	—	.49(.03)	-.16(.65)	.47(.03)	—	.30(.54)	.20(.58)	.03(.93)
Yosemite	—	—	.00(.99)	.64(.01)	—	—	.61(.00)	.53(.01)
Giant Forest	—	—	—	-.41(.59)	—	—	—	.36(.58)
Tehachapi	—	—	—	—	—	—	—	—

Acetic acid

	Daytime				Nighttime			
	Blodgett	Yosemite	Giant Forest	Tehachapi	Blodgett	Yosemite	Giant Forest	Tehachapi
Blodgett	—	.01(.97)	.48(.03)	-.18(.62)	—	.30(.54)	.40(.61)	.77(.00)
Yosemite	—	—	.26(.54)	.08(.80)	—	—	.09(.73)	.39(.62)
Giant Forest	—	—	—	.08(.81)	—	—	—	.63(.00)
Tehachapi	—	—	—	—	—	—	—	—

at sites downwind from emission sources due to photochemical formation during atmospheric transport from source areas. Under this hypothesis, formic acid is a secondary product of anthropogenic emissions, therefore formic acid is more prevalent at sites where precursors of formic acid have had ample time to react.

Another hypothesis is that biogenic emissions contribute significantly to the observed high levels of formic and acetic acids. Under this hypothesis, formic and acetic acids are produced from emissions by vegetation, while formic acid is also produced by photochemical oxidation of isoprene, which is emitted by plants (e.g., Jacob and Wofsy, 1986). This hypothesis is supported by the work of Keene and Galloway (1986) in which it was concluded that natural and not anthropogenic emissions were major contributors to formic and acetic acid levels in precipitation (and by extrapolation to ambient concentrations of those species). Similarly, Talbot et al. (1988) observed higher formic to acetic acid ratios during the growing season than during the nongrowing season and attributed this to seasonal changes in the relative contributions of biogenic and anthropogenic emissions. While this hypothesis was not tested directly, given the significant differences in vegetative covering at the four sites (Table 4-6), the weak Spearman's rank-order correlation coefficients (Table 4-4) argue against biogenic emissions being the source of the high organic acid concentrations observed.

Levels of carboxylic acids can be compared to concentrations of strong acids measured at two locations included in our study, Yosemite and Giant Forest from October, 1986 to September, 1987 (Watson et al., 1990). At Yosemite, annual nitric acid concentrations averaged 0.20 ppb during the day, and 0.06 ppb at night, and at Giant Forest, nitric acid averaged 0.17 ppb during the day, and 0.05 ppb at night. Sulfate and sulfur dioxide concentrations at both

Table 4-6 Description of sampling locations.

Site	Elevation (m)	Topography	Vegetation
Blodgett	1330	rolling hills on divide between major drainages	heavily forested mixed conifer
Yosemite	670	near bottom of steep walled canyon	foothill forest and chaparral
Giant Forest	1900	ridge overlooking steep canyon	open conifer forest
Tehachapi	1200	open flat	chaparral

sites were of the same order of magnitude. Thus, the formic acid concentrations of approximately 1 ppb to 40 ppb and acetic acid concentrations of 0.5 ppb to 13 ppb observed in this study suggest formic and acetic acid are significant contributors to the overall flux of ambient acidity in the western Sierra Nevada.

4.3 Summary

High ambient levels of formic acid and acetic acid have been measured at the four forest locations in the California Sierra Nevada during episodes of severe regional air pollution in the nearby San Joaquin Valley. In relation to levels of strong acids previously measured at Sierra Nevadan sites, organic acids appear to be significant contributors to the overall acidity. Statistical analysis of the data suggests that formic acid and acetic acid levels are influenced by regional emissions possibly coupled to additional local inputs. The contribution of biogenic and local emissions to the observed levels of formic acid and acetic acid and the lack of meteorological, hydrocarbon, and oxidant data suggests that further work is warranted to better understand the role of organic acids in the atmospheric environment and their effects on the Sierra Nevada.

5.0 MEASUREMENT AND ANALYSIS OF ATMOSPHERIC ORGANIC ACIDS

Based on the results presented in Section 4, questions arose regarding the accuracy and routine applicability of current methods for collection and analysis of atmospheric organic acids. Collection efficiencies were good (0.730 ± 0.103 for formate and 0.822 ± 0.137 for acetate), but variable. Because of the low levels of other pollutants such as PAN and aldehydes in this region, minimal interferences were expected. This section discusses these issues which are important for future studies and offers recommendations for the collection and analysis of atmospheric organic acids.

5.1 Background

There have been a number of studies over the past few years which focused on the measurement of organic acids in the gas phase and in hydrometeors. Most of these studies were the result of concern over the potential contribution of organic acids to wet and dry acidic deposition. It has been established that the principal organic acids found in both gaseous and precipitation samples are the C_1 and C_2 monocarboxylic acids, formic acid and acetic acid, although smaller amounts of propionic, pyruvic and benzoic acids have been quantified. Further, in remote and some rural areas, formic and acetic acids contribute a major portion of the acidity in rain, comparable to or greater than the major inorganic acidic species (sulfuric and nitric acids).

Other organic acids of lower volatility have been found predominantly in the particulate phase, e.g., oxalic, succinic and other dicarboxylic acids, benzoic acid, and some C_{20}-C_{40} monocarboxylic acids. These species, however, being present at levels which are small compared to inorganic acids, have generated less concern and have thus been the object of fewer measurements. A list of observed organic acids and their observed phase distributions is shown in Table 5-1.

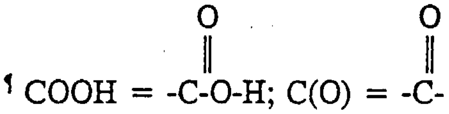
Limited data sets on organic acid levels in gaseous and precipitation samples (mostly formic and acetic acids) exist for a number of areas--Austria (Puxbaum et. al., 1988), Germany (Hartmann et al., 1989), Italy (Facchini et al., 1992), and the Netherlands (Keuken, 1989) in Europe, tropical areas of South America (Sanhueza et al., 1989, 1992; Andreae et al., 1988), and Africa (Helas et al., 1992), Japan, various remote areas (Keene et al., 1983; Keene and Galloway, 1984; Norton, 1992), as well as eastern, midwestern and southwestern areas of the USA (Hoffman, 1985; Bachman and Peden, 1987; Norton, 1985; Dawson and Farmer, 1988; Harrington et al., 1993). Several sites within the South Coast Air Basin (Los Angeles area) have been the focus of more intensive sampling campaigns (Grosjean, 1988, 1989, 1990, 1991, 1992; Pierson and Brachaczek, 1990). A major intercomparison study was conducted of sampling and analysis methods (Keene et al., 1989) and a second, more limited comparison of cartridge samplers and a real-time spectroscopic technique was reported by Grosjean et al. (1990). Strong correlations between ambient levels of formic and acetic acids have been observed. Organic acid levels are usually decoupled from those of most other pollutants, specifically the inorganic acids.

Despite the extent of these previous studies, there are still some major uncertainties in the assessment of the role of organic acids in atmospheric chemistry. These uncertainties relate to a variety of issues, ranging from problems with sampling techniques for their collection, preservation techniques needed to get collected samples unaltered to the analysis lab, sensitivity and selectivity of analysis techniques, as well as uncertainties in emission factors, atmospheric

Table 5-1

Organic Acids Commonly Found in Atmospheric Samples

Name	Formula[1]	Predominant Phase
Formic Acid	$HCOOH$	Gas, Pptn
Acetic Acid	CH_3COOH	Gas, Pptn
Glycolic Acid	$HOCH_2COOH$	Unknown
Glyoxylic Acid	$HC(O)COOH$	Unknown
Oxalic Acid	$(COOH)_2$	Aerosol, Pptn?
Propionic Acid	CH_3CH_2COOH	Gas, Pptn
Lactic Acid (dl)	$CH_3CHOHCOOH$	Aerosol, Pptn
Pyruvic Acid	$CH_3C(O)COOH$	Gas, Aerosol, Pptn?
Citric Acid	$HOC(CH_2COOH)_2COOH$	Aerosol?, Pptn
Benzoic Acid	C_6H_5COOH	Aerosol, Pptn?
Other Monocarboxylic Acids	$RCOOH$	Aerosol
Other Dicarboxylic Acids (e.g.,succinic)	$R(COOH)_2$	Aerosol, Pptn



[1] $COOH = -\overset{\overset{O}{\|}}{C}-O-H;\ C(O) = -\overset{\overset{O}{\|}}{C}-$

secondary formation mechanisms and rates, and sink process rates, all of which are needed for source apportionment activities. A thorough evaluation of these uncertainties is overdue in light of the need for monitoring of long-term trends in, and short-term variability of weak organic acid concentrations at a variety of receptor sites. Vertical distributions and levels in free tropospheric air have not generally been measured, with the exceptions of some aircraft data from Germany (Hartmann et al., 1989) and nighttime free tropospheric data from Mauna Loa (Norton, 1992). There is some urgency in doing such a review since the relative contribution from organic acids to acidic deposition will increase in the USA as the Clean Air Act-mandated reductions in emissions of precursors to inorganic acids take place. The ecological effects of weak acid deposition are not well known, but could impact areas with little acid neutralizing capacity.

In the review which follows, we emphasize the area of organic acid collection and analysis, highlighting the uncertainties which exist and the prospects for using current techniques to obtain validated monitoring data sets with known uncertainties. We then briefly discuss these measurement science aspects in the context of observed ambient concentrations, sources and sinks of organic acids, and the current state of source apportionment efforts.

5.2 Summary of Collection Methods

A variety of methods have been used to collect organic acids from the atmosphere, since these acids may exist in gaseous, particulate or hydrometeor phases, depending on atmospheric conditions. Methods applicable to particulate and hydrometeor phases have generally required few modifications from conventional techniques, hence most of the emphasis in this section is on gas-phase collection methods, with some discussion of the relative ease with which methods could be used in routine monitoring networks.

5.2.1 Gas-Phase Collection

Methods for collection of organic acids from the gas phase at atmospheric concentrations are mostly integrative (sampling periods from 3 to 24 hr), and may be conveniently differentiated by the means of retention: filters or cartridges containing basic material which convert the acid molecules to their alkali salts. Particulate acids are removed from the air stream by pre-filters, or discriminated in the collection process using diffusion denuder tubes, usually in the annular denuder configuration. Alternate approaches include condensation of gaseous species to a cold surface, or uptake to aqueous (mist) droplets. Direct measurement of formic acid by an infrared (IR) spectroscopic technique has also been reported.

5.2.1.1 Impregnated Filters

Quartz filters impregnated with Na_2CO_3 (Norton, 1985) and cellulose filters impregnated with K_2CO_3 (Andreae et al., 1987) have been used to collected gaseous formic, acetic, and pyruvic acids from air. The principal considerations in this approach are the type of filter, the concentration of the impregnating solution, and the potential for interferences. These two filter methods have been compared (Keene et al., 1989) and some systematic differences were found. The cellulose filters impregnated with 1.8M K_2CO_3 gave higher results than the quartz filters with 0.02M Na_2CO_3, but it was not clear whether the differences were due to the higher concentration of extractant in the former, or the lower collection efficiency (reported to be $\approx 70\%$) or different storage conditions (refrigeration vs. freezing) used with the latter.

Two groups have used KOH-impregnated quartz filters for gaseous organic collection with comparable success (Kawamura et al., 1985; Grosjean, 1988). The collection efficiencies reported by Grosjean (1988) were in the range of 70-85%.

5.2.2.2 Impregnated Cartridges and Sorbents

Grosjean et al. (1989) give a detailed description of a KOH-coated cartridge method for organic acids. The devices used are small Sep-Pak C18 cartridges, which are impregnated with a $\approx$0.1N solution of KOH in methanol and allowed to dry in a vacuum dessicator. The cartridges thus prepared contain about 10 mg KOH, and are kept sealed from ambient air until use in the field. This method has been evaluated with respect to interferences, and its overall precision and accuracy determined. Typically, sampling is performed at up to 2.0 Lpm for 4-24 hr; with total sample volumes of 0.5-1.0 m^3, limits of detection for formic and acetic acids are $\approx$0.3 and $\approx$0.6 ppbv, respectively.

Field application of KOH-coated cartridges for organic acid collection has been widespread in the Los Angeles basin and other California sites. During the Southern California Air Quality Study (SCAQS), KOH-coated cartridges were used at 2 sites, KOH-coated filters at 2 others, preceded by Teflon filters in both cases, with equivalent results (Grosjean, 1990). This same cartridge method was used to collect day and night samples at 4 sites in the Sierra Nevada mountains of California in the summer of 1990 (Harrington et al., 1993). However, questions remain with respect to accuracy due to analytical interferences, as discussed below.

Florisil sorbent has been used for carboxylic acid collection in industrial hygiene applications (Simon et al., 1989), but collection efficiencies and sample recoveries have not been evaluated at ambient levels.

5.2.2.3 Coated Denuder Tubes

NaOH-coated annular denuders for collection of gaseous organic acids were introduced by Puxbaum and co-workers (Winiwarter et al., 1988; Rosenberg et al., 1988; Puxbaum et al., 1988). Annular denuder sampling with coarse particles ($>5\mu m$) removed was conducted as part of the intercomparison reported by Keene et al. (1989). Carbonate-coated denuders have also been used to determine ambient levels of formic and acetic acids by Norton (1992). Limits of detection (LOD) of 0.05 ppbv for formic and 0.3 ppbv for acetic with 3-hr samples using the annular denuder technique have been reported by Puxbaum et al. (1988).

5.2.1.4 Other Sampling Methods

A complete description of the mist chamber technique as applied to collection of organic acids is given by Talbot et al. (1988). Gases are scavenged in a chamber in which a mist of micrometer-sized aqueous droplets has been generated. Collection efficiencies are high for species with high Henry's Law constants such as formic and acetic acids. Particles are removed by a pre-filter, and it is usually necessary to buffer the recirculated solution used to generate the mist. However, results from this technique appear to agree well with an annular denuder-based collection method (slope = 1.06, intercept = -20 nmole/m^3, r = 0.86, reported in Keene et al., 1989). As a result of this comparison, the mist chamber has been widely used for surface (and, more recently, airborne) measurements in Europe, Africa and South America (Andreae et al., 1988; Hartmann et al., 1989; Helas et al., 1992b). Facchini et al. (1992) used an automated mist chamber with Teflon pre-filter for gaseous formic, acetic, and pyruvic acids. Sanhueza et al. (1992) also used a mist chamber with Teflon pre-filter for gaseous sampling in a tropical mountain cloud site.

A condensation collection technique has been pioneered by Dawson and co-workers, in which soluble gaseous species are condensed on a cold surface, and the condensate is then analyzed for dissolved species. Its use for formic and acetic acids is reported by Dawson and Farmer (1988), and in the absence of species which rapidly convert other soluble species to the acids, or decompose the acids themselves, the method appears to work reasonably well. A version of this technique was deployed in the intercomparison reported by Keene et al. (1989) and performed well, albeit with some unexplained anomalous results. A variation of the condensation technique with a cold finger for collection, has been used by Willey and Wilson (1993) to measure gaseous formic and acetic acid levels at an east coast, US, site.

5.3 Particle-Phase Collection

Teflon or quartz filters have been used largely as pre-filters in various sampling schemes for collection of gaseous organic acids, or independently of gaseous collection for later analysis of organic acids thought to be mostly in the particulate phase (Kawamura et al., 1985). Filters are used downstream of annular denuder stages to capture the particulate phase, and these filters can be analyzed for particulate organic acids. In some cases these "pre-filters" have also been analyzed for organic acids and the distribution between phases reported. No reports of the use of impactors for evaluation of the size distribution of organic species have been found, although an impactor stage was used to remove coarse particles during annular denuder sampling (Winiwarter et al., 1988), and a stacked filter inlet was used by Andreae et al. (1987) for particle sizing.

Kawamura et al. (1985) used a quartz prefilter (with an alkaline-coated quartz backup for gaseous acids) to collect particulate acids in the LA basin. Teflon pre-filters are used with the mist chamber (Talbot et al., 1988) to remove particulate-phase acids. Problems related to the distribution of organic acids between gaseous and aerosol particulate phases, and the potential for disturbing this distribution during sampling, analogous to problems observed for nitrate and nitric acid (Stelson et al., 1979), have generally been ignored. This has probably occurred because formic and acetic acids are found almost entirely in the gas phase, while other acids of interest, e.g., oxalic and other dicarboxylic acids, are found almost entirely in the particulate phase.

5.4 Dew, Fog and Precipitation Collection

Dew samples were collected by condensation onto inert, passive plates in the Carbonaceous Species Methods Comparison Study (CSMCS) by Pierson and Brachaczek (1990); levels of formic and acetic acids were determined, as well as the much lower levels of propionic, oxalic and benzoic acids. Sanhueza et al. (1992) collected dew by the same method, also fog by a passive string collector, with formic and acetic acid quantified in both types of samples. Winiwarter et al. (1988) analyzed liquid fog samples without preservation immediately in the field.

Precipitation samples--both event samples and sequential samples--have been analyzed in a significant number of studies, following the finding (Keene et al., 1983; Keene and Galloway, 1984) that preservation of formate and acetate in collected samples required addition of a biocide (usually chloroform). Sanhueza et al. (1988; 1992), for example, added μL-quantities of $CHCl_3$ as a preservative to samples collected in remote savannah and tropical forest sampling sites.

5.5 Sampling Method Deficiencies--A Summary

Sampling problems identified in the collection of organic acids as described above are of serious concern in the design of an apparatus which can be effectively used for multi-site monitoring networks. These problems will be discussed in further detail below but consist at minimum of the following:

- interferences from PANs and aldehydes (+) and possibly ozone (-);
- collection efficiencies and their variation with sampling rates and throughputs;
- sample preservation problems.

Problems of interferences and uncertainties in collection efficiencies appear to be confined to sampling from the gas-phase. That is, no experimental evidence that particulate- or hydrometeor-phase organic acids are formed or destroyed **during sampling** has to our knowledge been published. However, the sample preservation problem may be of concern for gas- and particulate-phase, as well as hydrometeor-phase samples.

5.6 Summary of Analytical Methods for Organic Acids

5.6.1 Separation Methods for Organic Acids

A summary of the methods used for collection and analysis of species in gas, aerosol and precipitation samples is given in Table 5-2.

There are only two types of columns which have been widely used to separate the weak acids (as their anions) in gas and particulate sample extracts, and in precipitation samples:

- anion exchange columns (basic eluent) which separate anions based on their exchange capacities;
- ion exclusion columns (acidic eluent) which retain un-dissociated weak acid species, but do not retain ionized species such as nitrate or sulfate.

Organic acids which have been identified and when present above the MDL, quantified in atmospheric samples include, in addition to formic and acetic acids, propionic acid in gas phase samples, benzoic, oxalic and succinic acids in particulate samples, propionic, oxalic and benzoic acids in dew samples, and lactic and citric acids in precipitation samples.

When analyzing gaseous samples eluted from an impregnated cartridge or extracted from a filter, some pretreatment may be necessary. The sampling medium may also affect the choice of analytical separation column, for example, carbonate interferes with organic acid separation on IC columns.

Eluents for ion chromatographic exclusion (ICE) columns are millimolar solutions of strong acids, whereby carboxylic acids and other weak organic acids found in the atmosphere are separated in the free acid form. Less common eluents used for ICE columns include octanesulfonic acid, benzoic acid, and pH-adjusted n-octylammonium chloride. Eluents for ion

Table 5-2

Summary of Measurement Methods for Atmospheric Organic Acids

Ref Code	Sample Phases	Sample Method	Analysis Method	Formic Acid	Acetic Acid	Other Acids
A	L	NA	HPICE	Y	Y	N
B	L	NA	HPICE	Y	Y	N
C	L	NA	HPICE	Y	Y	?
D	L	F,CO_3,	IC, ICE	Y	Y	N
E	G,P	F	Der-GC	Y	Y	19,incl oxalic
F	L	NA	ICE,C	Y	Y	Citrc
G	G,P	F,CO3, MC	IC,C	Y	N	Pyruv.
H	G,P	F,CO3, MC	IC,C	Y	N	Pyruv.
I	G,P	F,KOH	ICE,UV	Y	Y	N
J	G,L	D, KOH	IC	Y	Y	N
K	G	Cond	IC,C	Y	Y	N
L	G,A	C, KOH	ICE,UV	Y	Y	N
M	G,P	Var	Var	Y	Y	N
N	G	MC	IC,C	Y	Y	N
O	G	C&F, KOH	ICE,UV	Y	N	N
P	G	C,KOH; FTIR	ICE,UV; FTIR	Y	N	N
Q	G	C&F, KOH	ICE,UV	Y	Y	N
R	D	IP	ICE,UV	Y	Y	Prp,Ox Benz
S	G	C,KOH	ICE,UV	Y	Y	N
T	G	MC	IC,C	Y	Y	Pyruv.
U	G	C,KOH	ICE,UV	Y	Y	Not quant
V	G,L	Cond	IC,C	Y	Y	N

Reference Code

A: Keene et al., 1983; B: Keene and Galloway, 1984: C: Hoffman and Tanner, 1985; D: Norton, 1985; E: Kawamara et al., 1985, 1987; F: Bachman and Peden, 1987; G: Andreae et al., 1987; H: Andreae et al., 1988; I: Grosjean, 1988; J: Winiwarter et al., 1988; K: Dawson and Farmer, 1988; L: Grosjean et al., 1989; M: Keene et al., 1989; N: Hartmann et al., 1989; O: Grosjean, 1990; P: Grosjean et al., 1990; Q: Grosjean and Parmer, 1990; R: Pierson and Brachczek, 1990; S: Grosjean, 1991; T: Helas et al., 1992; U: Harrington et al., 1993; V: Willey and Wilson, 1993.

Sample Phase Code

G: gas-phase samples; P: particulate samples; L: precipitation; D: dew; F: fog.

Method Codes

Sampling: MC: mist chamber; F: impregnated filter; C: cartridge; D: denuder; Cond: condensation; CO_3: carbonate impregnant; KOH: alkali impregnant; FTIR: in situ spectroscopy. Analysis: IC: anion exchange column; ICE: ion exclusion column; C: conductivity detection; UV: UV absorbance detection.

chromatographic (IC) columns (anion exchange with/without suppression) include $\approx$0.5-2 mM HCO_3^-/CO_3^{2-} solutions, or 0.1-0.2 mM sodium tetraborate solutions. Limits of detection for formic and acetic acids with 0.1-0.25 mL samples are generally of the order of 0.1-1 μM in the aqueous phase, corresponding to gas-phase LODs of 0.1 ppbv or less for integrated filter or cartridge samples of several hours.

5.6.2 Detection Methods

There are generally only two types of detectors which have been used to analyze the effluents of columns used to separate the organic acids of atmospheric interest:

- conductivity detection with or without suppression in a manner analogous to the detection of inorganic ions by "suppressed" or "single-column" ion chromatography, with the organic acid species necessarily in the anion form;
- UV absorbance detection, usually at 210 nm, with the organic acid species in either the neutral acid or anion form.

Conductivity detectors are nearly universally used for effluents from IC and ICE columns. Most of the information on the use of UV absorbance detection has been obtained by Grosjean and co-workers (c.f., Grosjean et al., 1989).

5.6.3 Gas Chromatographic Methods With and Without Derivatization

Gas chromatographic (GC) methods can easily separate the common acids found in various atmospheric samples, especially if capillary columns are used. However, the most common universal GC detectors, particularly flame ionization, are inconveniently insensitive for many trace gas analysis applications, and some difficulties in transferring trace quantities of free acids through GC systems have been experienced. As a result, GC methods for atmospheric samples usually require the conversion of the acid to a more inert derivative which can be detected with higher sensitivity. One of the most useful techniques for carboxylic acids (RCOOHs) was reported by Kawamura et al. (1985), in which C_1-C_{10} RCOOHs + benzoic acid were converted to their p-bromophenacyl esters and analyzed by capillary GC and GC-mass spectrometry (GC-MS). Recoveries are 70-85% and minimum detectable limits (MDLs) were about 1-2 nmoles.

5.6.4 Other Analytical Methods

Long-path Fourier-transform infrared (FTIR) spectroscopy has been used to detect gaseous formic acid in the atmosphere (see Tuazon et al., 1981). The results from a direct comparison with an integrated sampling technique (cartridge collection with LC/UV absorption) have been reported in Grosjean et al. (1990). Agreement was good between the methods but with a lot of scatter. As used for the measurement of other gas-phase species, the main strength of the FTIR method is its unequivocal identification of the species being quantified, and its principal weakness is its limited sensitivity (MDLs generally 2-10 ppbv).

5.6.5 Analytical Method Deficiencies--A Summary

Andreae et al. (1988) have conducted interference studies showing that the carbonate matrix (from extracts of impregnated filters) interferes with anion chromatography, so ion exclusion columns (e.g., HPICE-AS1) with millimolar strong acid eluents need to be used for baseline separation of formate, acetate, and pyruvate. Keene et al. (1989) also indicate difficulty in separating acetate and lactate on IC columns. These columns (e.g., HPIC-AS4) can be used with mist chamber samples with equivalent results.

Puxbaum (personal communication, 1993) indicates that the single column IC method described in Tsidouridou and Puxbaum (1987) is not generally sensitive enough for organic acids in atmospheric samples.

5.7 Sampling Method Deficiencies

5.7.1 Interferences During Collection

5.7.1.1 Peroxyacetyl Nitrate (PAN) Interference with Acetic Acid Determination

The most complete description of laboratory experiments on PAN interferences is found in Grosjean and Parmer (1990), and laboratory and field tests (the latter from CSMCS) are reported in Grosjean et al. (1988). These workers conclude that PAN interferes positively with acetate determinations (+15-35% bias found in Grosjean et al., 1988), but this bias can be corrected for if PAN is simultaneously measured, since it does not appear to depend on PAN concentration. In Grosjean and Parmer (1990), conversion of PAN to acetate varied with the collection device, being 11-17% for carbonate- and KOH-coated filters, 16-27% for carbonate cartridges, and 100% for KOH cartridges. Clearly, carbonate-impregnated filters are the most suitable choice for network operations in which PAN cannot be routinely monitored.

5.7.1.2 Aldehyde Interference with Formic and Acetic Acid Determination

Grosjean et al. (1988) observed that differences in measured acid concentrations with and without an aldehyde denuder were $8\pm4\%$ for formic and $4\pm4\%$ for acetic acid, compared with $10\pm3\%$ and $6\pm6\%$ for co-located filter packs. Ergo, no interferences were found. Data from the same study show that KOH-coated filters become carbonate-coated filters via reaction (1) after

$$2OH^- + CO_2 \rightarrow CO_3^{2-} + H_2O \qquad (1)$$

$<1\%$ of the sample volume (2.6-2.8 m^3, at a flow rate of 11-14 Lpm) had passed through the filter. In other work, Winiwarter et al. (1988) observed no gaseous formaldehyde conversion to formate at [HCHO] up to 2μmole/m^3 (50 ppbv). The experiments reported in Keene et al. (1989) with the impregnated filter technique of Andreae et al. (1987), however, clearly show that formaldehyde can be converted to formate during collection. Further evaluation of this problem seems warranted, to see if it is wholely a matter of how much impregnant is used, or if there are other problems.

5.7.1.3 Other Potential Interferences

Grosjean (1988) found no interference from ozone in smog chamber tests of carboxylic acid collection and analysis. No other reported laboratory studies have confirmed interferences from other compounds likely present in the atmosphere. Artifacts from sampling cartridges containing Chromosorb 103 are discussed by Keene et al. (1989).

5.7.2 Collection Efficiencies and Their Variability

Efficiencies for formic and acetic on KOH-coated filters (71-82%) are reported by Kawamura et al. (1985). Grosjean (1988) discusses in detail efficiencies for formic and acetic on KOH-coated and nylon filters. Keene et al. (1989) also found low efficiencies with nylon (Gelman Nylasorb) filters. Grosjean et al. (1989) report efficiencies for KOH-coated cartridges of about 90% for formic and acetic acids.

Grosjean and Parmer (1990) report losses of formic and acetic acids in aqueous impingers due to acidification of the solution during collection. Similar considerations for sampling using the mist chamber are discussed by Talbot et al. (1988) and Keene et al. (1989).

5.7.3 Storage Problems and the Use of Biocides

5.7.3.1 Gaseous and Particulate Samples

It appears that there have been few systematic studies documenting (a) the extent of loss of sorbed gaseous **and** particulate organic acids with time; (b) whether and how rapidly microbial decomposition takes place; and (c) how effective treating with a biocide is in preserving samples. For example, Keene et al. (1989) reported "significant bias....for particulate phase measurements by participating groups [in an intercomparison]", and attributed the bias to "differences in sample storage and handling subsequent to collection." However, the nature of these artifacts could not be assessed in that study. Norton (1992) preserved extracts from gaseous collection by denuder until analysis. Filters for gas and particulate formic and acetic acids collected by Grosjean et al. (1988) were stored in sealed vials at 4°C with 10 mL water and 40 μL chloroform. In another study, Grosjean et al. (1989) found that particle and cartridge-retained gaseous samples were stable against decomposition for several months.

Several different storage and preservation schemes were employed by participants in the intercomparison reported in Keene et al. (1989). Condensate samples collected according to Dawson and Farmer (1988) were treated with chloroform and refrigerated at 5°C. Particulate filters and Chromosorb 103 cartridges collected by Keene, particulate filters collected by Munger, and nylon filters collected by Pszenny were stored sealed and frozen at -4°C. Filter extracts derived from the method of Andreae et al. (1987) were preserved with chloroform and analyzed immediately, as were the mist chamber collections (Talbot et al., 1988). Samples extracted from base-coated denuders were analyzed for formate immediately, then preserved with chloroform for later analysis of acetate.

5.7.3.2 Hydrometeor Samples

Samples of rain (or snow), fogs, and dew are nearly always preserved with chloroform (or occasionally, another biocide). This follows Keene et al. (1983) and Keene and Galloway (1984), who showed for the 1st time both the loss with time of formate and acetate in precipitation, and also the effectiveness of chloroform in preserving these acids in precipitation samples from rural and remote sites. Indeed, Herlihy et al. (1987) demonstrated that bacteria in precipitation samples can mediate the loss of formate and acetate, likely for the purpose of growth, and that these microbes are omnipresent in the atmosphere, although rapid reduction of formate and acetate levels is observed only in liquid samples.

Bachman and Peden (1987), using 0.2% chloroform as a preservative, also demonstrated formate and acetate losses and how to prevent them. In the dew samples collected by Pierson and Brachaczek (1990), 0.3 mL of $CHCl_3$ per sample was used as a preservative. Winiwarter et al. (1988) and Facchini et al. (1992) analyzed fog samples immediately, without the use of preservatives. Willey and Wilson (1993) preserved both condensate and rain samples with $CHCl_3$.

5.8 Ambient Atmospheric Data for Organic Acids

5.8.1 Data on Formic, Acetic and Other Organic Acids in the Gas Phase

Most of the available data on concentrations of weak organic acids are for formic and acetic acids, and can be summarized according to geographical areas: (a) Europe; (b) tropical areas of South America and Africa; (c) temperate locations in North America; (d) southwest USA; and (e) southern California (especially the Los Angeles basin). We summarize the data below on this geographical basis, taking special note of information on diurnal and seasonal variation, and of vertical profiles, where available. This data is also summarized in Table 5-3, Summary section.

European Data

Hartmann et al. (1989) collected airborne data over Germany, 0.15-3.0 km in the boundary layer; with strong westerly advection, concentrations were 0.17 ± 0.06 and 0.72 ± 0.08 ppbv for formic and acetic acids, respectively; in a more stagnant anticyclone, up to 2.76 and 2.20 ppbv formic and acetic acids, respectively, were observed.

Puxbaum et al. (1988), in a semirural area near Vienna, observed formic = 1.4±0.2 ppbv; in a rural area in north central Austria, formic = 0.9±0.3 ppbv, with the ratio, formic/acetic ≈ 1.5. Winiwarter et al. (1988) obtained fall-winter data in the Po valley of Italy, and found variable concentrations of gaseous formic and acetic acids from 0.1-3.5 ppbv.

Tropical Continental and Marine

Andreae et al. (1988) observed mean gas-phase formic and acetic acid levels = 1.6±0.6 and 2.2±1.0 ppbv, respectively, at ground level at a central Amazon site in the dry season. Sanhueza et al. (1992) found mean gas-phase formic and acetic acid concentration = 1.7±0.5 and 1.4±0.6 ppbv, respectively, in the dry season, and = 0.79±0.24 and 0.54±0.20 ppbv in the rainy season. Helas et al. (1992b) measured organic acids over equatorial Africa during the DECAFE study and found much higher levels aloft (> 3 ppbv) than at the surface (< 1 ppbv). Norton (1992) found during the MLOPEX study (Mauna Loa, HI) mean daytime levels in the marine boundary layer = 0.45 and 0.37 ppbv for formic and acetic acids, respectively; mean nighttime free troposphere levels = 63 and 94 pptv, respectively.

Temperate North America

Talbot et al. (1988) observed mean monthly levels at a Virginia site, ranging from 0.5 (winter) to 3 ppbv (summer) for formic acid, and from 0.6 (winter) to 2 ppbv (summer) for acetic acid; ratios of formic to acetic acids, F/A, ranged from <1 in winter to 1.5±0.5 in summer. Keene et al. (1989) reported ambient data taken by several methods during an intercomparison in June at a Virginia site. Willey and Wilson (1993) show data for spring and fall in the range of 0.9-3.4 ppbv for formic and acetic acids, with the ratio F/A=1.7-2.7, at an east coast, US, site.

Southwest USA

Dawson and Farmer (1988) measured mean concentrations at several SW USA sites, finding average formic and acetic acid levels = 1-2 ppbv at 7 sites but 3-5 ppbv at 4 other sites.

Harrington et al. (1993), in summertime sampling at 4 mountain sites, found mean formic acid levels = 12-13 ppbv, except 18 ppbv at the Tehachapi site; mean acetic acid varied from 3.9 ppbv at the Blodgett site to 8.0 ppbv at Yosemite. Levels of formic and acetic acids were much larger than those of co-measured nitric acid. Day/night ratios for formic acid were 1.6-2.0 (depending on site) and for acetic acid, 1.0-1.9.

Southern California

Tuazon et al. (1981), measuring formic acid by FTIR for a 1980 smog episode, found daily averages = 2-11 ppbv, and a maximum concentration = 19 ppbv at an LA basin smog receptor site. Kawamura et al. (1985) found 0.4-7.4 ppbv total gas-phase C_1-C_{10} RCOOH, with >80% being the C_1 & C_2 acids, but measurable amounts of propionic and benzoic acids were observed.

Grosjean (1988), in late summer results from the southern California air basin, observed mean formic acid = 5.4 ppbv, and mean acetic acid = 5.5 ppbv (N=21); propionic and pyruvic were observed at low levels but not quantified. Grosjean et al. (1988), during the CSMCS in the LA basin in late summer, observed gaseous formic and acetic acid medians ≈ 4 and 3.5, respectively, F/A ratios ≈ 1.1, no diurnal variation in ratios, and highest concentrations at night. Grosjean (1990), in summertime Southern California Air Quality Study (SCAQS) sampling in the LA basin, found a mean of 0.6 ppbv at the control site (San Nicholas Island), and maxima of 13-19 ppbv at inland receptor sites, with the ratio, F/A, increasing from coastal to inland sites. Levels at the coastal site (Long Beach) were higher in late fall than in summer. Grosjean (1991), in a year-long study of formic acid (and HCHO, CH_3CHO) at 6 sites in the LA basin (1 sample every 6th day), found up to 8 ppbv HCOOH, with the location average for formic acid = 2.8 ppbv.

5.8.2 Data on Less Volatile Organic Acids Found in Particles

Data have been reported for oxalic acid, other dicarboxylic acids, benzoic acid, and some higher molecular weight RCOOHs. Almost all of this data is for the USA, mostly for southern California.

Kawamura et al. (1985) observed that particulate C1-C10 carboxylic acids + benzoic acid are usually <10% of total gas + particle phase acids. Kawamura and Kaplan (1987) found 19 dicarboxylic acids in LA air, with the total concentration = 12.3±6.1 nmole/m^3 (0.3 ppbv ±50%); oxalic acid was the dominant species, but succinic, malonic, maleic, glutaric, adipic, and phthalic were also found. Talbot et al. (1988) measured aerosol formic + acetic acids, but only in the 5-25 pptv range at a Virginia site. Grosjean (1988) reported particulate oxalate data from NSMCS.

5.8.3 Data on Organic Acids in Dew, Fogs, Clouds and Precipitation

5.8.3.1 Dew, Fogwater and Cloudwater

Pierson and Brachaczek (1990) measured the constituents of dew during the CSMCS. Winiwarter et al. (1988) observed formic and acetic acids at higher levels (11-175μM and 10-269μM, respectively) in fogs than in precipitation. Sanhueza et al. (1989) measured mean formic and acetic = 8.4 and 4.5 μM, respectively, in the Venezuelan savannah. Sanhueza et al. (1992) measured dew and fog, and cloudwater at a Venezuelan tropical cloud forest site, and give ranges of formic and acetic acid levels = 8.1-69.5 μM and 4.3-15.3 μM, respectively, in the collected cloud water.

Weathers et al. (1988) gives the best summary available of cloudwater formate and acetate levels from a 2-yr study at 10 non-urban sites in North America; less regional differences were observed than for inorganic ions.

5.8.3.2 Precipitation

Keene et al. (1983) and Keene and Galloway (1984) are the first major works showing a significant contribution of formic and acetic acids to free acidity of precipitation at rural and remote sites. Keene et al. (1983) report formic and acetic acid data, calculated indirectly from NADP and MAP3S network precipitation samples, indicating that 18-35% and 16% of the free acidity, respectively, was derived from sum of these organic acids. Keene and Galloway (1984) report levels of 6-30 μM formate and acetate, which contributed 60-65% of acidity of samples from a Katherine, Australia site.

Keene and Galloway (1986) report precipitation data from 14 global sites: higher concentrations of formate and acetate were found during the growing season, as well as higher total formate/total acetate ratios. Main sources suggested are volatile vegetative sources over continents, and a weaker source over continental and marine areas. What is keeping formate/acetate ratios so constant at background sites is still a mystery.

Hoffman and Tanner (1985) reported winter-spring levels in precipitation of <1 to 20 μM formate, <1 to 10μM acetate, and other acids below MDL at a Long Island, NY site. Talbot et al. (1988) report formate and acetate in precipitation <3 μM in winter to >10 μM in summer at an east coast, US, site. Norton (1985) show levels in precipitation at Niwot and Boulder, CO, as molar ratios relative to nitrate: formate/nitrate = 0.2-1; acetate/nitrate $\approx$ 5-30%; oxalate/nitrate = 5% or less.

Sanhueza et al. (1989) report mean formic and acetic = 8.4 and 4.5 μM respectively, in the Venezuelan savannah; Sanhueza (1992) indicate a range of formic and acetic = 8.1-69.5 μM and 4.3-15.3 μM respectively, in precipitation collected at a Venezuelan tropical cloud forest site. An exhaustive search for other tropical rainfall data on formate and acetate was beyond the scope of this review.

5.8.4 Phase Distribution of Atmospheric Organic Acids

Overview--Models

Helas et al. (1992a) describe a model of phase partitioning of formic and acetic between gas and hydrometeor. Modeling of phase distributions is also developed in Facchini et al. (1992), in which possible mass transfer limitations are discussed.

Temperate

Winiwarter et al. (1988) report gaseous and fog data for fall and winter conditions in northern Italy, in which formic acid is found to be undersaturated in fogs in which pH>5. Facchini et al. (1992), in a continuation of this work, also found formic and acetic acids undersaturated in fog at higher pH (conditions in which most of these acids should be partitioned into the aqueous phase), and they suggest that limitations to mass transport are the cause of this undersaturation.

Andreae et al. (1987) found 10-20% of total pyruvate in particle phase, a larger fraction than for total formate and acetate.

Tropical and Remote Marine

Andreae et al. (1988) found that formic and acetic in gas ≈100x that in particles measured over a central Amazon site in the dry season. Norton (1992), in reporting MLOPEX aerosol data from Mauna Loa, HI, showed that levels in the particulate phase were 10-100x less than gas phase levels for formic and acetic acids.

Southern California

Grosjean (1988) reported that essentially all formate and acetate was found on the alkaline-coated filters behind the particulate filter (i.e., % particulate formate and acetate levels are very low). Conversely, oxalate levels are low and essentially all in the particulate phase. Later work by Grosjean (1989) showed that an average 93% and 87% of formic and acetic acid, respectively, was found in gas phase, with the remainder in airborne particles.

The conclusions from reported work are that most of the weak organic acidity in the atmosphere is found in the gas phase (little in the particle phase), and that it consists of species (mostly formic and acetic acids) which are highly soluble in clouds and raindrops, hence are rapidly removed from the atmosphere by both wet and dry deposition.

5.9 Primary and Secondary Sources of Organic Acids

5.9.1 Direct Emissions of Weak Acids

Kawamura et al. (1985) and Kawamura and Kaplan (1987) discuss in some detail the nature of primary (anthropogenic) sources of weak acids in the LA basin. Andreae et al. (1987) suggest that formic and pyruvic acids are formed in the atmosphere in major part from natural sources (e.g., isoprene oxidation). Keene and Galloway (1986) discuss in some detail the mechanisms by which formate and acetate in precipitation might obtain their observed values, and their close correlation with each other. Seasonal variations observed by Talbot et al. (1988) suggested to these authors that natural sources of formic and acetic acids might be dominant in rural and remote areas, especially the photodecomposition of isoprene and other biogenic hydrocarbons.

5.9.2 Mechanisms of Formation of Secondary Organic Acids

Grosjean (1989) gives details on *in situ* formation mechanisms of organic acids in urban smoggy atmospheres. He identifies four principal mechanisms by which formic and acetic acids are formed in the gas phase:

- the gas-phase reaction of ozone with olefins, with rearrangement of the Kriegee biradical intermediate (2,3):

$$R_1CH{=}CHR_2 + O_3 \rightarrow R_1CH(OO^{\cdot})CH(O^{\cdot})R_2 \qquad (2)$$

$$R_1CH(OO^{\cdot})CH(O^{\cdot})R_2 \rightarrow R_1COOH\ R_2CHO \qquad (3)$$

- the gas-phase reaction of aldehydes with the HO_2 radical (4-6):

$$HCHO + HO_2 \rightarrow O_2CH_2OH \tag{4}$$

$$O_2CH_2OH + NO \rightarrow OCH_2OH + NO_2 \tag{5}$$

$$OCH_2OH + O_2 \rightarrow HCOOH + HO_2 \tag{6}$$

- the reaction of phenols with OH radicals;
- aldehyde oxidation in clouds.

It has been suggested that the olefin-ozone reaction may produce higher yields of carboxylic acids at high humidities. There are uncertainties to date as to whether the sum of these four mechanisms is sufficient to explain the observed urban concentrations of formic and acetic acids.

5.9.3 Source Apportionment of Organic Acids

Grosjean (1989, 1992) has attempted a weak acid source apportionment for the Los Angeles basin. In addition, Kawamura and Kaplan (1987) indicate that the major sources of dicarboxylic acids are motor vehicle emissions. Preliminary estimates indicate that primary emissions of and *in situ* formation processes forming formic and acetic acids are of comparable magnitude, but there is a large uncertainty in the latter. Loss of weak organic acids by dry deposition is calculated to greatly exceed wet deposition for the LA basin. Other loss processes--photolysis and reaction with OH radicals--are negligible compared with wet and dry deposition, with the exception of photolysis of oxoacids (e.g., pyruvic acid). Improvements in estimates of the rates of formation and loss of organic acids are greatly needed for apportionment studies in urban, rural and remote areas.

5.10 Summary and Recommendations

Common Collection Methods

Common collection methods for weak organic acids consist of base-impregnated filters, cartridges, or denuder tubes. Alternate methods includes mist chambers and condensation collection. The only *in situ* method is long-path FTIR spectroscopy.

Common Analytical Methods

Common analytical methods for weak organic acids include ion chromatrography with anion exchange or ion chromatorgraphic exclusion columns, with conductivity or UV absorption detection. An alternate approach is derivatization-GC with GC-MS for identification.

Range of Observed Concentrations

A summary of observed concentrations for weak organic acids in gas-phase, particulate and precipitation samples is given in Table 5-3. Comparison of the maximum levels of these species indicates that they are found at levels comparable to those of inorganic acids, nitric acid and (partially neutralized) sulfuric acid, except under episodic conditions for the latter.

Outstanding Issues

- interference from PAN, although quantified for cartridges and filters in one laboratory, warrants further study with other filter and annular denuder methods;
- interferences from aldehydes and ozone are uncertain and need verification;
- instability of hydrometeor samples after collection is known, but comparable data for gaseous and particulate organic acids is scarce for most methods;
- data on diurnal variability of acid concentrations are inconsistent;
- data on seasonal variability are not generally available;

Table 5-3

Ambient Gaseous Concentrations of Atmospheric Organic Acids

Ref Code	Location	Season, Diurnal	Mean FA, (Range)	Mean AA, (Range)	Other Concns
A	LA Basin	Su,F	0.1-3.0	0.3-3.9	C_2-C_{10}, Benz
B	Virginia	Su	≈2	N	Py: ≈0.1
C	Amazon	Dry	1.6±0.6	2.2±1.0	N
D	LA Basin	late Su	4.4	4.5	Py,Pr low
E	LA basin	Su, Diurnal	≈4.0	3.5	N
F	Virginia	Su,W	Su: 1.9±1.2; W: 0.7±0.4	1.3±0.9; 0.7±0.4	N
G	N. Italy	F	(0.1-3.5)	(0.3-1.4)	N
H	SW USA	All Seasons	(0.7-3.5)	(0.6-4.5)	N
I	Austria	Su, F; 3 sites	1.7; 1.0; 0.9	0.5; 0.6; 0.3	N
J	Virginia	Summer, Yes	≈2.7, 0.5-7	≈2.2, 0.7-5	N
K	Germany, airborne	early F	0.17±0.06, max ≈2.8	0.72±0.08, max ≈2.2	N
L	Bkgd Site, LA Basin,	Su, 4 sites	0.6; 2.2; 5.5; 7.8	0.6; 2.7; 3.5; 4.5	N
M	LA Basin	All Seasons	2.8 (mas ≈8)	N	N
N	Congo, Africa	Dry	sfc:0.5±0.6 BL: 3.7±1.0	0.6±0.7 2.7±0.9	N
O	N. Italy	F	(<0.2-6.1)	(<0.4-3.9)	Py: ≈0.1
P	Venezuela	Dry, rainy	1.7±0.5, 0.79±0.24	1.4±0.6, 0.54±0.20	N
Q	Mauna Loa	Marine, FT	0.45, 0.063	0.37, 0.094	N
R	LA Basin	Su (smog)	(2-11), max ≈19	N	N
S	Artic Bkgd	Su	0.07	0.07	N
T	Sierra Nevada Mountains	Su, 4 sites	12.7±6.4; 12.8±7.1; 12.3±6.1; 18.1±8.8	3.9±1.8; 8.0±2.5; 5.1±2.0; 4.6±2.5	N
U	N. Carolina	Su, F	3.1±1.5	1.5±1.2	N

Reference Code

A: Kawamara et al., 1985; B: Andreae et al., 1987; C: Andreae et al., 1988; D: Grosjean, 1988; E: Grosjean et al. 1988; F: Talbot et al., 1988; G: Winiwarter et al., 1988; H: Dawson and Farmer, 1988; I: Puxbaum et al. 1988; J: Keene et al., 1989; K: Hartmann et al., 1989; L: Grosjean, 1990; M: Grosjean, 1991; N: Helas et al., 1992b; O: Facchini et al., 1992; P: Sanhueza et al. 1992; Q: Norton, 1992; R: Tuazon et al., 1981; S: Talbot et al., 1992; T: Harrington et al., 1993; U: Willey and Wilson, 1993.

Acid Nomenclature Codes

FA = formic acid; AA = acetic acid; Py = pyruvic acid, C_2-C_{10} = monocarboxylic acids with 2-10 carbons; pr = propionic acid; benz = benzoic acid. N indicates that the acid in question was not quantified.

- there are very limited long-term data at any given site;
- emission rates, source factors, secondary formation mechanisms, and dry deposition velocities all have significant uncertainties.

The results of this review of the literature have led to the following general statements:

- existing data sets for formic and acetic acids in air and precipitation for rural and remote areas vary widely, but suggest, in some cases, that wet and dry deposition of these organic acids are significant relative to deposition of inorganic acids.
- sampling of common organic acids on alkaline filters, cartridges, denuders, etc. is relatively simple. Preserving the samples until analysis, and demonstrating the absence of interferences for specific acids is still difficult and problematical.
- analytical methods using ion exchange, ion exclusion, and related chromatographic techniques are well developed, but issues concerning the resolution of common organic acids on existing columns (hence potential interferences) remain.
- sources of primary emissions of organic acids are still not well characterized in most areas. Mechanisms of secondary acid formation are generally known but not quantified for given atmospheric conditions.

Recommended Research

A moderate research effort is required to improve sampling and analysis methods to the point at which a monitoring network for gaseous- and hydrometeor-phase formic and acetic acids could be established.

Verification of collection efficiencies as a function of impregnating solution concentration, sampling velocity, and humidity conditions needs to be done.

Interferences from PAN, ozone, and aldehydes need to be quantified for any method being considered for routine monitoring.

Investigation of the stability toward microbial decomposition of particulate and gaseous samples collected on filters and by cartridges under field conditions needs to be investigated prior to these methods being applied for routine field measurements.

Other areas requiring further investigation include primary sources and *in situ* secondary formation processes of weak organic acids and investigation of the contributions of natural vs. anthropogenic sources of organic acids (using, e.g., isotope ratio approaches).

6.0 CMB RECEPTOR MODELING

A discussion of the receptor modeling methods used to apportion the sources of pollutants observed in the forested regions of the Sierra Nevada is presented in this section. Included in the discussion are descriptions of the source profiles used for the receptor model, the model itself, and the model predictions.

6.1 Source Profiles

Receptor modeling applied to source apportionment requires information about the chemical characteristics of the emissions sources which are likely to affect pollutant concentrations at a receptor. For the Chemical Mass Balance (CMB) receptor model, the required information is the fractional composition of each chemical species in the source emissions and an estimate of the variability of those compositions.

In a study to evaluate the feasibility of source apportionment of utility emissions, Javitz and Watson (1988) concluded that the major weakness of all receptor models is inadequate source composition data. They identified the following deficiencies in currently available source profiles: 1) the species measured are more often those which are convenient rather than those which differentiate among sources; 2) the types of species and size fractions measured are not the same for different source types and are not equivalent to the types of measurements made at receptors; 3) measurement methods are non-standard and do not give equivalent results for the same species; 4) source characteristics, fuels, and operating parameters are inadequately documented; 5) data are of poor or unknown quality; 6) source profile uncertainties are not reported; 7) source samples are not representative of source profiles as they appear at the receptor; and 8) data are not available in formats which can be conveniently interfaced to modeling software.

Javitz and Watson (1988) recommended the development of a standardized approach to sampling and analyzing particulate and gaseous emissions which would minimize these concerns with respect to future source profile measurements. Such a protocol was subsequently developed and applied for California Air Resources Board (ARB) source characterization studies of suspended particulate matter (Ahuja *et al.*, 1989; Houck *et al.*, 1989, 1990). This protocol has not been applied to particulate emitters in the SJV. These profiles can be supplemented with profiles measured in other studies which are expected to have a strong similarity to emissions profiles from the SJV.

6.1.1 Particulate Source Types

The potential source types which contribute to primary $PM_{2.5}$ and PM_{10} in the Sierra Nevada and lead to deposition in the Sierra Nevada are: 1) geological material (fugitive dust from agriculture, paved and unpaved roads, vacant land, and construction); 2) motor vehicle exhaust (from cars, trucks, and buses fueled with diesel, leaded gasoline, and unleaded gasoline); 3) marine aerosol transported from the Pacific Ocean; 4) secondary particles (ammonium sulfate, ammonium nitrate, and residual organic carbon); and 5) vegetative burning (from campfires, forest fires, and agricultural burning). A "source type" does not necessarily correspond to a particular emitter. For the primary contributors, several source sub-types may exist within some of these categories which are not easily distinguishable from each other by receptor models using commonly measured chemical species. The source type perceived at a receptor may be a mixture of these different sub-types, and the profile which best explains the receptor measurement should represent this mixture. Several different profiles are examined in each of the following sub-sections to determine whether or not they possess enough differences to allow them to be distinguished as separate source types by the CMB receptor model.

Table 6-1 lists the source types, a short identifier for each specific profile, and a brief description of the ten source profile applied in the Sierra Nevada particulate data base. The short identifiers are used to refer to these particulate profiles in the subsequent discussion.

6.1.1.1 Geological Source Profile

Table 6-2 lists the geological source profile used in the apportionment. The profile was formed by collecting agricultural soil samples in the vicinity of Bakersfield, sieving the dried material, resuspending it into a chamber and sampling the resuspended dust through PM_{10} and $PM_{2.5}$ inlets. Cooper *et al.* (1987) found that typically less than 10% of the PM_{10} was in the $PM_{2.5}$ fraction, and the PM_{10} and coarse particle (PM_{10} minus $PM_{2.5}$) source profiles are nearly identical. Both $PM_{2.5}$ and coarse particle source profiles are listed in Table 6-2, and though there are some minor differences between them, these differences do not result in large differences in CMB source contribution estimates. Each individual profile results from the average of several samples (typically three) taken around each measurement location.

In addition to Si and Al, organic carbon (OC) is one of the more abundant species, accounting for approximately 3% of total mass. Organic carbon usually exceeds elemental carbon (EC) in these samples by factors of 15 to 20. When one considers the typical contributors to geological material, this finding is not surprising. Dust on a paved road surface

Table 6-1

Source Profiles Applied in Sierra Nevada $PM_{2.5}$ and PM_{10} Receptor Modeling

Source Type	Data Base Identifier	Description of Source Profile
Primary Geological	SOIL10	Bakersfield Agricultural Soil (Sandy)
Primary Motor Vehicle	PHRD	Phoenix Motor Vehicle: Roadside Emissions
Marine Aerosol	MARO	Aged Marine Aerosol: 100% Chloride Replaced With Nitrate
Secondary Ammonium Sulfate	AMSUL	Secondary Ammonium Sulfate
Secondary Ammonium Nitrate	AMNIT	Secondary Ammonium Nitrate
Secondary Organic Carbon	OC	Secondary Organic Carbon
Wood Smoke	BAMAJC	Bakersfield Fireplace
Wood Smoke	WFIREC	Composite of Two Denver Fireplaces
SJV Regional	EDI4	Lower San Joaquin Valley Regional Profile
SJV Regional	ACA1	Mid San Joaquin Valley Regional Profile

Table 6-2A
Geological Source Profile
SOIL10 - $PM_{2.5}$

	Conc. (%)	Uncert. (%)
Cl-	0.3295	0.3332
NO3-	0.1102	0.9632
SO4=	0.0000	0.3478
NH4+	0.0000	0.0159
Na+	0.1303	0.1106
K+	0.0941	0.0847
OC	2.8260	1.8500
EC	0.0000	0.4484
Al	10.0237	1.1397
Si	24.9847	2.8383
P	0.2184	0.0385
S	0.2407	0.1182
Cl	0.3295	0.3332
K	2.3425	0.2663
Ca	2.7301	0.3295
Ti	0.5248	0.0751
V	0.0332	0.0267
Cr	0.0330	0.0055
Mn	0.1403	0.0159
Fe	5.7636	0.7654
Ni	0.0117	0.0015
Cu	0.0443	0.0133
Zn	0.0459	0.0038
Se	0.0007	0.0038
Br	0.0024	0.0030
Rb	0.0158	0.0024
Sr	0.0266	0.0055
Zr	0.0098	0.0062
Ba	0.1023	0.1936
Pb	0.0210	0.0074
Sum	50.4708	3.8681

Table 6-2B
Geological Source Profile
SOIL10 - PM_{10} and $PM_{2.5}$

	Conc. (%)	Uncert. (%)
Cl-	0.4708	0.4847
NO3-	0.0410	0.5699
SO4=	0.1638	0.2838
NH4+	0.0000	0.0094
Na+	0.2056	0.1822
K+	0.1322	0.0521
OC	3.4457	1.1152
EC	0.0000	0.2656
Al	9.6520	1.3639
Si	24.9250	2.7993
P	0.1699	0.0558
S	0.2035	0.0572
Cl	0.4708	0.4847
K	2.1965	0.2462
Ca	3.7852	0.7504
Ti	0.5134	0.0702
V	0.0299	0.0150
Cr	0.0275	0.0031
Mn	0.1132	0.0150
Fe	5.1412	0.6055
Ni	0.0090	0.0011
Cu	0.0325	0.0135
Zn	0.0350	0.0027
Se	0.0009	0.0023
Br	0.0033	0.0007
Rb	0.0155	0.0017
Sr	0.0290	0.0057
Zr	0.0110	0.0019
Ba	0.0716	0.1008
Pb	0.0154	0.0044
Sum	51.1039	3.5628

builds up by being tracked out from unpaved areas such as construction sites, unpaved roads, parking lots, and shoulders; by spills from trucks carrying dirt and other particulate materials; by transport of dirt collected on vehicle undercarriages; by wear of vehicle components such as tires, brakes, clutches, and exhaust system components; by wear of the pavement surface; by deposition of suspended particles from many emissions sources; and by water and wind erosion from adjacent areas.

The abundance of total potassium (K) in geological materials has been found in other studies (Houck *et al.*, 1989) to be approximately 10 times that of soluble potassium (K^+) in these profiles. This is an important difference, since soluble potassium is one of the key markers for vegetative burning. It is partly because soluble potassium is not very abundant in geological material that vegetative burning can be distinguished from other sources when K^+ is measured in receptor samples.

The abundances of lead (Pb) and bromine (Br) in paved road dust are also higher than might be expected in pristine soil, which demonstrates the presence of tailpipe exhaust from vehicles burning leaded fuels. Enrichments in species from clutch and brake wear are absent in these paved road dust profiles. These are often composed of asbestos and/or semi-metal carbon composites. Ondov (1974) measured abundances of ~14% magnesium (Mg), ~2% calcium (Ca), ~4% iron (Fe), and ~1% barium (Ba) in asbestos brake shoes, while Anderson *et al.* (1973) reported silicon (Si) abundances of ~10%. Cooper *et al.* (1987) examined the elemental composition of semi-metal brake shoes and found abundances of ~45% iron (Fe), ~2% copper (Cu), ~0.5% tin (Sn), ~3% barium (Ba), and ~0.5% molybdenum (Mo). None of these species is found in the SoCAB paved road dust profiles at levels which are significantly in excess of their abundances in the other geological sub-types.

Approximately 50% of the mass is unaccounted for in this profile. This is due to presence of oxygen in oxides which is not measured directly by the measurement methods which were applied.

When the percent composition for a species is several times larger than its uncertainty, then that species is a good marker for that source type. When few other source profiles contain this species, then it is very probable that the source types which these profiles represent can be distinguished from each other by CMB modeling. The high concentrations, low uncertainties, and uniqueness with respect to other source types of Al, Si, Ca, Ti and Fe make it likely that this geological profile can be easily distinguished from other source types. Paved road dust, agricultural soil, and windblown dust profiles are too similar to each other to be distinguished.

6.1.1.2 Particulate Motor Vehicle Exhaust Profiles

Mobile source particulate emissions are among the most difficult to measure with respect to emission rate and chemical composition. This difficulty arises from: 1) the large number of mobile source types (passenger cars, light duty trucks, diesel trucks, diesel buses, etc.); 2) a large number of individual emitters within each type; 3) fuel-use characteristics which have radically changed over the past decade (e.g., the phase-out of lead in gasoline); 4) a large variety of undefined (and probably undefinable) operating conditions; 5) a variety of emissions points on each vehicle (i.e., tailpipe, resuspended dust, fuel evaporation, tire wear, brake wear); and 6) a large fraction of emissions which are probably semi-volatile or are secondary particle precursors.

Watson (1979) and Pierson and Brachaczek (1976, 1983) summarize studies of motor vehicle exhaust particulate source profiles measured in the 1960's and 1970's, but these profiles are not relevant to exhaust emissions found during SJVAQS/AUSPEX. Only a few post-1985 measurements of these profiles have been conducted. Watson *et al.* (1988) obtained six roadside samples under a freeway overpass, in a city bus yard, and near busy intersections in Reno, NV during 1986. These profiles provided good fits to the ambient $PM_{2.5}$ and PM_{10} in combination with profiles from geological material and residential wood combustion (Chow *et al.*, 1988).

Watson *et al.* (1990) report the results from dynamometer tests of eight unleaded, three leaded, and three light- to medium-duty diesel vehicles tested in the SCENIC Denver Study during 1987. The Federal Test Procedure (FTP) driving cycle was applied to vehicles which had been prepared at cold temperatures (<40 °F) similar to those found in wintertime Denver. These profiles have been used in PM_{10} source apportionment studies in support of State Implementation Plans in Colorado, Utah, and Idaho as well as to apportion light extinction in Denver (Watson *et al.*, 1988).

Houck *et al.* (1989) took three samples of heavy-duty diesel truck exhaust at a roof monitor over the Wheeler weigh station near Bakersfield, CA during 1987 in support of PM_{10} State Implementation Plans in California's San Joaquin Valley.

Cooper *et al.* (1987) measured profiles from vehicle exhaust in the SoCAB during 1986. Exhausts from 11 unleaded gasoline vehicles, 3 leaded-gasoline vehicles, and 2 heavy-duty diesel trucks operating on laboratory dynamometers were sampled. The Federal Test Procedure (FTP) and a steady-state test at 35 miles per hour (mph) were followed for the gasoline-fueled tests. The diesel trucks were tested under modified FTP and steady-state conditions. Cooper *et al.* (1987) also took three roadside samples in a tunnel under the Los Angeles Airport.

Watson *et al.* (1993) report profiles taken during 1988 in Phoenix, AZ, at: 1) a centralized dynamometer inspection and maintenance station for passenger cars; 2) a centralized dynamometer inspection and maintenance station for heavy duty diesel trucks and buses; 3) a dynamometer station for city buses; and 4) alongside urban roadsides.

There are significant similarities and differences between the chemical composition of these different motor vehicle profiles measured in different areas. For example, the SCENIC Denver diesel profiles have a much higher abundance of elemental carbon (74±21%) than the SoCAB (52±5%), Wheeler Station (43±8%), or the Phoenix diesel (33±8%) profiles. This difference may be due to differences in the test procedures, sampling methods, vehicles tested, or carbon analysis methods. Watson *et al.* (1989) used several of the profiles from other studies, including those from the SoCAB in CMB modeling of Phoenix PM_{10}. None of the SoCAB profiles reproduced the measured concentrations as well as the roadside motor vehicle profiles measured in Phoenix.

When Countess (1991) used the Phoenix and SoCAB profiles to apportion PM_{10} in Santa Barbara County during 1989, he also found that the Phoenix profiles explained the ambient data better than the SoCAB profiles. Countess (1990) observed that the majority of fuel in Phoenix arrives by pipeline from Santa Barbara County's Gaviota Terminal, and that vehicle types, driving patterns, and inspection and maintenance are similar in Arizona and in southern

California. Countess (1991) therefore concluded that the Phoenix profiles were reasonable representatives for southern California emissions. Lowenthal *et al.* (1992) confirmed this in CMB sensitivity and collinearity tests on the Santa Barbara samples.

Table 6-3 lists the PHRD profile which was found to best describe emissions in the source region impacting on the Sierra Nevada. Cooper *et al.* (1987) and Houck *et al.* (1989) found that more than 90% of vehicle exhaust was in the $PM_{2.5}$ size fraction, so the $PM_{2.5}$ profiles are used to represent contributions in both $PM_{2.5}$ and coarse material. It is believed that most of the motor vehicle contributions to the coarse particle fraction are really $PM_{2.5}$ particles which are removed in the $PM_{2.5}$ inlet of the ambient sampler.

The "PHRD" profile (Table 6-3) was created from roadside samples taken in Phoenix, AZ during 1988 (Watson *et al.*, 1993). Though these samples were taken through a $PM_{2.5}$ inlet, they were also affected by vehicle-related resuspended road dust. Contributions to the mass and chemical species concentrations were estimated for each sample using the CMB model with road dust as the only contributing source with Al, Si, Ca, and Fe as fitting species. As noted above, these species are very abundant in geological material and are depleted in directly emitted motor vehicle exhaust. This method assumes that ~100% of these species measured in the roadside samples originates in suspended road dust. The contributions of road dust to all remaining (non-fitting) species concentrations were calculated by the CMB model and subtracted from the measured concentrations, including the mass. The remaining species concentrations were then divided by the remaining mass to obtain profiles for the non-road dust motor vehicle exhaust samples. These individual roadside sample profiles were then averaged and their standard deviations calculated to obtain the "PHRD" profile. It is assumed that contributions from

Table 6-3
Motor Vehicle Source Profile
PHRD - $PM_{2.5}$

	Conc. (%)	Uncert. (%)
Cl-	1.1573	0.7545
NO3-	11.0254	10.4066
SO4=	6.0125	2.0920
NH4+	4.1064	2.7397
Na+	0.0000	0.1000
K+	0.7588	2.3147
OC	39.0031	18.6177
EC	36.4646	10.9899
Al	0.0723	0.5250
Si	0.0828	1.1319
P	0.0837	0.1327
S	2.0156	0.6026
Cl	0.5624	0.4085
K	0.2150	0.2294
Ca	0.1253	0.9805
Ti	0.0872	0.4008
V	0.0233	0.2011
Cr	0.0187	0.0402
Mn	0.1782	0.1142
Fe	0.9341	0.5294
Ni	0.0189	0.0149
Cu	0.3558	0.1351
Zn	0.5054	0.3873
Se	0.0042	0.0335
Br	0.0580	0.0339
Rb	0.0019	0.0331
Sr	0.0042	0.0476
Zr	0.0100	0.0631
Ba	0.2002	1.5018
Pb	0.2700	0.1261
Sum	100.4236	24.3575

sources other than motor vehicle exhaust are negligible (<10%) in this profile, and this assumption is valid for the source-dominated sampling sites and short (~2 hr) sample durations.

The most abundant species are OC (39±10%), EC (36±11%), nitrate (11±10%), sulfate (6±2%), and ammonium (4±3%). The nitrate, sulfate, and ammonium abundances are more than twice those of the dynamometer profiles. This is probably due to the longer residence time of the motor vehicle exhaust in the air being sampled at the roadside when compared to that sampled from a dynamometer.

6.1.1.3 Marine Aerosol Source Profile

It is known that the marine aerosol will react rapidly with nitric acid in the environment, and that pure sea salt will probably never be found as a contributor to suspended particles in the SoCAB (though it probably will be found at San Nicolas Island). Several different marine profiles have been constructed to represent different levels of reaction between marine aerosol and nitric acid. The bulk seawater composition of Pytkowicz and Kester (1971) was selected as a pure marine aerosol and reacted with nitric acid. This liberates the chloride and replaces it with nitrate. "MAR0" (Table 6-4) represents the profile when 100% of the original marine aerosol reacted with nitric acid. Given the transport distance and reaction time over the SJV prior to impacting on the Sierra Nevada this profile was used to model the contribution from marine aerosols.

Table 6-4
Marine Aerosol Source Profile
MARO - $PM_{2.5}$

	Conc. (%)	Uncert. (%)
Cl-	0.0000	0.0300
NO3-	70.4532	8.7677
SO4=	5.5425	0.6898
NH4+	0.0000	0.1000
Na+	22.1700	2.7590
K+	0.8211	0.1022
OC	0.0000	0.1000
EC	0.0000	0.1000
Al	0.0000	0.0000
Si	0.0062	0.0008
P	0.0001	0.0000
S	1.8475	0.2299
Cl	0.0000	0.0000
K	0.8211	0.1022
Ca	0.8457	0.1053
Ti	0.0000	0.0000
V	0.0000	0.0000
Cr	0.0000	0.0000
Mn	0.0000	0.0000
Fe	0.0000	0.0000
Ni	0.0000	0.0000
Cu	0.0000	0.0000
Zn	0.0000	0.0000
Se	0.0000	0.0000
Br	0.1375	0.0171
Rb	0.0002	0.0000
Sr	0.0162	0.0020
Zr	0.0000	0.0000
Ba	0.0000	0.0000
Pb	0.0000	0.0000
Sum	99.9928	9.2203

6.1.1.4 Secondary Sulfate, Nitrate, and Organic Source Profiles

Because species such as nitrate (NO_3^-), sulfate ($SO_4^=$), and organic carbon (OC) can be formed through gas-to-particle transformation in the atmosphere, they cannot be entirely accounted for by primary emissions. Secondary source profiles are included in Tables 6-5a, 6-5b, and 6-5c which consist of "pure" ammonium sulfate, ammonium nitrate, and organic carbon to apportion remaining ammonium (NH_4^+), sulfate ($SO_4^=$), nitrate (NO_3^-), and organic carbon (OC) which is not apportioned to the primary particle profiles.

6.1.1.5 Vegetative Burning Profile

Besides the source profiles described above, several other profiles were included due to the unique nature of the forested sites. Key profile were those for vegetative burning to apportion the impact of campfires, forest fires, and agricultural burning. Table 6-6a and 6-6b contain profiles developed from burning two different types of wood.

6.1.1.6 Other Source Profiles

In addition to the commonly applied source profiles described above, two other composite profiles were developed to account for regional transport from different areas of the SJV. These profiles, ACA1 and EDI4 (Table 6-7a and 6-7b), represent regional sources from the mid (SJVAQS/AUSPEX Academy site) and lower (SJVAQS/AUSPEX Edison site) parts of the SJV. These profiles were necessary to account for the well mixed and complex nature of the air masses impacting on the forested sites.

Table 6-5A
Secondary Sulfate Source Profile
AMSUL - $PM_{2.5}$

	Conc. (%)	Uncert. (%)
Cl-	0.0000	0.0000
NO3-	0.0000	0.0000
SO4=	72.7000	7.2700
NH4+	27.3000	2.7300
Na+	0.0000	0.0000
K+	0.0000	0.0000
OC	0.0000	0.0000
EC	0.0000	0.0000
Al	0.0000	0.0000
Si	0.0000	0.0000
P	0.0000	0.0000
S	24.2700	2.4270
Cl	0.0000	0.0000
K	0.0000	0.0000
Ca	0.0000	0.0000
Ti	0.0000	0.0000
V	0.0000	0.0000
Cr	0.0000	0.0000
Mn	0.0000	0.0000
Fe	0.0000	0.0000
Ni	0.0000	0.0000
Cu	0.0000	0.0000
Zn	0.0000	0.0000
Se	0.0000	0.0000
Br	0.0000	0.0000
Rb	0.0000	0.0000
Sr	0.0000	0.0000
Zr	0.0000	0.0000
Ba	0.0000	0.0000
Pb	0.0000	0.0000
Sum	100.0000	7.7657

Table 6-5B
Secondary Ammonium Nitrate Profile
AMNIT - $PM_{2.5}$

	Conc. (%)	Uncert. (%)
Cl-	0.0000	0.0000
NO3-	77.5000	7.7500
SO4=	0.0000	0.0000
NH4+	22.5500	2.2550
Na+	0.0000	0.0000
K+	0.0000	0.0000
OC	0.0000	0.0000
EC	0.0000	0.0000
Al	0.0000	0.0000
Si	0.0000	0.0000
P	0.0000	0.0000
S	0.0000	0.0000
Cl	0.0000	0.0000
K	0.0000	0.0000
Ca	0.0000	0.0000
Ti	0.0000	0.0000
V	0.0000	0.0000
Cr	0.0000	0.0000
Mn	0.0000	0.0000
Fe	0.0000	0.0000
Ni	0.0000	0.0000
Cu	0.0000	0.0000
Zn	0.0000	0.0000
Se	0.0000	0.0000
Br	0.0000	0.0000
Rb	0.0000	0.0000
Sr	0.0000	0.0000
Zr	0.0000	0.0000
Ba	0.0000	0.0000
Pb	0.0000	0.0000
Sum	100.0500	8.0714

Table 6-5C
Secondary Organic Carbon Source Profile
OC - $PM_{2.5}$

	Conc. (%)	Uncert. (%)
Cl-	0.0000	0.0000
NO3-	0.0000	0.0000
SO4=	0.0000	0.0000
NH4+	0.0000	0.0000
Na+	0.0000	0.0000
K+	0.0000	0.0000
OC	100.0000	30.0000
EC	0.0000	0.0000
Al	0.0000	0.0000
Si	0.0000	0.0000
P	0.0000	0.0000
S	0.0000	0.0000
Cl	0.0000	0.0000
K	0.0000	0.0000
Ca	0.0000	0.0000
Ti	0.0000	0.0000
V	0.0000	0.0000
Cr	0.0000	0.0000
Mn	0.0000	0.0000
Fe	0.0000	0.0000
Ni	0.0000	0.0000
Cu	0.0000	0.0000
Zn	0.0000	0.0000
Se	0.0000	0.0000
Br	0.0000	0.0000
Rb	0.0000	0.0000
Sr	0.0000	0.0000
Zr	0.0000	0.0000
Ba	0.0000	0.0000
Pb	0.0000	0.0000
Sum	100.0000	30.0000

Table 6-6A
Woodsmoke Source Profile
BAMAJC - $PM_{2.5}$

	Conc. (%)	Uncert. (%)
Cl-	1.9083	0.6396
NO3-	0.4624	0.1228
SO4=	1.4231	0.4234
NH4+	0.0852	0.0573
Na+	0.1434	0.0520
K+	3.9926	1.2397
OC	44.5991	7.9412
EC	15.8891	5.8031
Al	0.0019	0.0273
Si	0.0000	0.0148
P	0.0000	0.0223
S	0.5211	0.1761
Cl	1.9083	0.6396
K	3.9926	1.2397
Ca	0.0659	0.0554
Ti	0.0009	0.0162
V	0.0005	0.0067
Cr	0.0000	0.0016
Mn	0.0007	0.0010
Fe	0.0006	0.0009
Ni	0.0001	0.0006
Cu	0.0001	0.0004
Zn	0.0866	0.0355
Se	0.0004	0.0009
Br	0.0096	0.0023
Rb	0.0042	0.0012
Sr	0.0007	0.0012
Zr	0.0000	0.0019
Ba	0.0095	0.0497
Pb	0.0043	0.0033
Sum	68.6892	9.9445

Table 6-6B
Woodsmoke Source Profile
WFIREC - $PM_{2.5}$

	Conc. (%)	Uncert. (%)
Cl-	0.2874	0.0404
NO3-	0.2025	0.0156
SO4=	0.4553	0.0359
NH4+	0.1132	0.0140
Na+	0.0000	0.0438
K+	0.5208	0.0795
OC	49.4961	5.4810
EC	21.1455	4.5813
Al	0.0034	0.0103
Si	0.0443	0.0167
P	0.0000	0.0051
S	0.1533	0.0173
Cl	0.2874	0.0404
K	0.6346	0.1008
Ca	0.0664	0.0165
Ti	0.0010	0.0120
V	0.0007	0.0050
Cr	0.0003	0.0012
Mn	0.0030	0.0013
Fe	0.0038	0.0017
Ni	0.0002	0.0005
Cu	0.0002	0.0007
Zn	0.0762	0.0054
Se	0.0001	0.0008
Br	0.0029	0.0011
Rb	0.0007	0.0007
Sr	0.0006	0.0009
Zr	0.0000	0.0014
Ba	0.0093	0.0369
Pb	0.0031	0.0018
Sum	72.5508	7.1447

Table 6-7A
Regional SJV Source Profile
ACA1 - $PM_{2.5}$

	Conc. (%)	Uncert. (%)
Cl-	0.3000	0.6400
NO3-	2.0800	1.9500
SO4=	17.6200	4.9700
NH4+	6.8100	2.2200
Na+	0.8900	0.8100
K+	0.8300	0.2000
OC	31.3200	13.0700
EC	9.0300	2.6100
Al	3.0500	1.4100
Si	5.0600	1.8500
P	0.0000	0.0000
S	7.6800	1.9400
Cl	0.1100	0.1600
K	1.5900	0.4400
Ca	0.9600	0.4400
Ti	0.0700	0.0700
V	0.0100	0.0100
Cr	0.0000	0.0100
Mn	0.0400	0.0200
Fe	1.9200	0.6800
Ni	0.0100	0.0000
Cu	0.0300	0.0300
Zn	0.0900	0.0300
Se	0.0000	0.0000
Br	0.0300	0.0100
Rb	0.0100	0.0100
Sr	0.0100	0.0100
Zr	0.0000	0.0100
Ba	0.3300	0.3400
Pb	0.0300	0.0200
Sum	81.1000	14.7694

Table 6-7B
Regional SJV Source Profile
EDI4 - $PM_{2.5}$

	Conc. (%)	Uncert. (%)
Cl-	0.7600	1.6700
NO3-	2.5600	0.6800
SO4=	7.1700	5.0000
NH4+	2.3500	1.8900
Na+	1.2400	1.3600
K+	0.9100	0.3300
OC	22.7400	19.7200
EC	7.8200	7.2600
Al	3.7000	0.7500
Si	10.0100	2.3500
P	0.0900	0.0800
S	2.8000	2.1100
Cl	0.9500	2.4100
K	2.5400	0.6800
Ca	2.1800	0.4600
Ti	0.3200	0.1000
V	0.0100	0.0100
Cr	0.0000	0.0000
Mn	0.0700	0.0100
Fe	3.9200	0.9700
Ni	0.0100	0.0100
Cu	0.0200	0.0200
Zn	0.0500	0.0100
Se	0.0000	0.0000
Br	0.0200	0.0200
Rb	0.0100	0.0000
Sr	0.0200	0.0100
Zr	0.0100	0.0000
Ba	0.1100	0.1200
Pb	0.0200	0.0300
Sum	67.9400	22.0457

6.2 Particulate Source Apportionment

Both source-oriented dispersion models and receptor models have been used to apportion atmospheric constituents to sources. Current scientific understanding is that both approaches are necessary, either operating independently (U.S. EPA, 1987) to engender the reconciliation of model results, or operating together (Chow, 1985; Freeman *et al.*, 1987; Watson *et al.*, 1987) so that the strengths of one type of model can compensate for the weaknesses of the other. This section addresses the chemical mass balance receptor modeling of $PM_{2.5}$ and PM_{10} in the forested regions of the Sierra Nevada.

Types of receptor models include: 1) chemical mass balance (CMB); 2) principal components analysis (PCA, otherwise known as factor analysis); and 3) multiple linear regression (MLR). Extensive discussions of each of these models, operating separately and together, are given by Watson *et al.* (1984), Chow (1985), Hopke (1985), Watson *et al.* (1987), and Javitz and Watson (1988). The CMB model, as specified by U.S. EPA guidance for State Implementation Plan (SIP) development (Pace and Watson, 1987), is applied here. Different variations of PCA models are being applied in other SCAQS data analysis studies (Henry, 1992; Hopke, 1992).

6.2.1 Chemical Mass Balance Receptor Model

The CMB model consists of a least-squares solution to a set of linear equations which expresses each receptor concentration of a chemical species as a linear sum of products of source profile species and source contributions. The source profile species (the fractional amount of the species in the emissions from each source type) and the receptor concentrations, each with realistic uncertainty estimates, serve as input data to the CMB model. The output consists of the contributions for each source type to the total ambient aerosol mass as well as to individual chemical species concentrations. The model calculates values for contributions from each source and the uncertainties of those values. Input data uncertainties are used both to weight the relative importance of the input data to the model solution and to estimate uncertainties of the source contributions.

CMB software currently in use (Watson *et al.*, 1990) applies the effective variance solution developed and tested by Watson *et al.* (1984) because: 1) it calculates realistic uncertainties of source contributions from both the source and receptor uncertainties; and 2) chemical species measured more precisely in both source and receptor samples are given greater influence in the solution than are less precisely measured species.

Watson (1979) observed that individual sources with similar source profiles, such as different soils and road dusts, would yield unreliable source strength estimates if used in the same CMB. Henry (1982; 1992) proposed a quantitative method of identifying this interference among similar source compositions, which is known as "collinearity." Henry's "singular value decomposition" defines an "estimable space in which resolvable sources should lie" (Henry, 1982; 1992). The source types which do not fall into this estimable space are collinear, or too similar to be resolved from a combination of one or more of the source types which do lie within the estimable space. Henry (1982; 1992) further proposed that linear combinations of source contributions resulting from collinear source compositions would be more representative of the summed contributions of these sources. Analytical measures of collinearity and Henry's linear combination method are available in the U.S. EPA/DRI Version 7.0 of the CMB model (Watson *et al.*, 1990).

6.2.2 CMB Application and Validation

The CMB modeling procedure requires: 1) identification of the contributing source types; 2) selection of chemical species to be included; 3) estimation of the fractions of each chemical species contained in each source type (i.e., the source profiles); 4) estimation of the uncertainties of both ambient concentrations and source compositions; and 5) solution of the chemical mass balance equations.

These procedures are described in an applications and validation protocol (Watson *et al.*, 1991) which has been assembled for PM_{10} source assessment. Since this study is not being done specifically for PM_{10} SIP development, there is no requirement that this protocol be followed. The protocol does provide a regimen which makes the results from this source apportionment study comparable with those from other PM_{10} non-attainment areas, so it will be applied to the Sierra Nevada aerosol source apportionment.

The CMB applications and validation protocol consists of seven steps: 1) determination of model applicability; 2) initial source contribution estimates; 3) examination of model outputs and performance measures; 4) identification of deviations from model assumptions; 5) identification and correction of model input errors; 6) verification of the consistency and stability of source contribution estimates; and 7) evaluation of the results of the CMB analysis with respect to other source assessment methods. The activities carried out for each of these steps are described in this section.

6.2.2.1 CMB Model Applicability

The requirements for CMB model applicability are as follows: 1) a sufficient number of receptor samples are taken with an accepted method to evaluate compliance with standards; 2) samples are analyzed for chemical species which are also present in source emissions; 3) potential source contributors have been identified and chemically characterized; and 4) the number of non-collinear source types is less than the number of measured species.

Samples were taken through well-characterized $PM_{2.5}$ and/or PM_{10} inlets during the Sierra Nevada field program. All of these samples were submitted to analysis for mass, elements, carbon, and ion concentrations, as discussed in Section 2 of this report. All major source types in the SJV have been identified, sampled, and analyzed, as reported in the first part of this chapter. The examination of chemical profiles described previously showed significant differences among profiles for major source types such as primary geological material, primary motor vehicle exhaust, primary marine aerosol, and secondary sulfates and nitrates. The number of species measured in source and receptor samples is greater than the number of non-collinear sources.

The Sierra Nevada data set was not randomly obtained over a one-year period, and it should not be used to evaluate compliance with the annual average particulate standard. However, since meteorological conditions on sampled days reflect the conditions most conducive to high particulate concentrations, and since several cases were observed for which the particulate levels were relatively high (>50 $\mu g/m^3$, with no violations of the standard), the Sierra data set can be used to determine source contributions to the high loadings.

There do appear to be negative biases in the x-ray fluorescence and carbon data. Since mass closure was not found for the chemical species measured in Sierra, it is not anticipated for the CMB source contribution estimates. These biases will probably affect the source contributions from motor vehicle exhaust and geological material, which account for most of the organic carbon and trace elements in SJV sources.

6.2.2.2 Initial Source Contribution Estimates

A number of samples in both the $PM_{2.5}$ and PM_{10} size fractions were used to calculate initial source contribution estimates. These initial tests were intended to determine which profiles best explain the data at each site. Profiles which represent the following source types were used in different combinations to reproduce the ambient concentrations: 1) geological material (different samples of soil and road dust); 2) regional transport (based on SJVAQS/AUSPEX particulate sampling); 3) motor vehicle exhaust (roadway tests from Phoenix); 4) vegetative burning (from an earlier study in the SJV); 5) particles formed from the transformation of gases in the atmosphere (ammonium sulfate, $(NH_4)_2SO_4$, ammonium nitrate, NH_4NO_3, and organic carbon); and 6) aged marine aerosol (assuming different displacements of chloride by nitrate from the reaction of sodium chloride with nitric acid). These source types were found in many samples.

Several initial CMB runs were performed at each site, and the CMB performance measures were examined to determine how well the ambient concentrations were explained by the source contribution estimates. These performance measures are described in the next sub-section, and examples of their use to test model outputs are shown.

The initial source apportionments also examined the fitting species which would provide the best indication of the presence or absence of sources. Many of the trace elements were omitted as fitting species (phosphorous [P], chromium [Cr], manganese [Mn], cobalt [Co], copper [Cu], zinc [Zn], arsenic [As], selenium [Se], strontium [Sr], molybdenum [Mo], cadmium [Cd], tin [Sn], antimony [Sb], cesium [Cs], barium [Ba], platinum [Pt], and mercury [Hg]) because Section 3 found their concentrations to be less than or close to their lower quantifiable limits and because Section 5 did not find great abundances of these species in SoCAB sources. Sulfate was used in place of sulfur and chloride was used in place of chlorine as fitting species owing to the suspected bias in the elemental data and because the soluble fractions of these species are more typical of secondary sulfate and marine sources than the total elemental fractions. Ammonium and nitrate were also included as initial fitting species to account for ammonium nitrate, as were aluminum, silicon, potassium, calcium and iron as indicators of soils. Vanadium and nickel were also retained, even though their concentrations were very low, for residual oil combustion to be sought.

Initial CMB calculations used both organic carbon (OC) and elemental carbon (EC) as fitting species. It was found that OC was always overpredicted and EC was always underpredicted. This often moved performance measures significantly away from their targets and biased the motor vehicle exhaust source contributions. This discrepancy is due to the incompatibility of the carbon measurements in the ambient data and in the source profiles. After several trials, it became apparent that only total carbon (TC) was consistent between source and receptor samples. Using TC instead of OC and EC has major consequences for the apportionment of motor vehicle exhaust. Lowenthal *et al.* (1992) show that the OC and EC abundances are crucial to separating gasoline-fueled exhaust from diesel exhaust. When OC and EC are included in the apportionment of other data sets, it is often possible to assign excess OC to secondary organic carbon.

6.2.3 Model Outputs and Performance Measures

Pace and Watson (1987) define several performance measures which are examined with each CMB to eliminate many combinations of profiles from further consideration. There may be more than one combination of profiles which attain the performance criteria to the same extent. When this is the case, it is necessary to group these individual sources into source types which are not specific to individual sources.

Evaluations of several different combinations of profiles were made for every $PM_{2.5}$ and coarse particle sample in this data set. An example of the process is given here to illustrate the evaluation process and the grouping of similar profiles into source types. The selected model outputs, ambient concentrations, source profiles, and modeling software are available from the authors for other researchers to reproduce these tests on this example and for all data reported in this study.

Tables 6-8 and 6-9 show examples of the CMB7 output format which are examined with every initial source apportionment and every change in source/fitting species configuration. A separate output is obtained for $PM_{2.5}$ and coarse particle apportionments. These outputs contain every specification for the configuration under which the model was applied. The upper part of the display shows the source profiles included in each model application. The lower part of

Table 6-8
Example CMB Output for $PM_{2.5}$ Collected at Sequoia on August 8, 1990 Between 0000 and 0700 PST

```
SOURCE CONTRIBUTION ESTIMATES -  SITE: SLK          DATE: 08/06/90    CMB7 33889
SAMPLE DURATION        7       START HOUR        00        SIZE:    F
       R SQUARE      .93     PERCENT MASS     105.1
     CHI SQUARE      .61               DF        14

  SOURCE
     * TYPE     SCE(UG/M3)    STD ERR      TSTAT
---------------------------------------------
61     BAMAJC       1.5777      .7377    2.1387
81     AMSUL        1.1245      .2775    4.0516
91     OC           4.5573     1.8352    2.4832
101    ACA1         2.5577      .7495    3.4125
---------------------------------------------

MEASURED CONCENTRATION FOR SIZE: F
       9.3+-     1.2

       UNCERTAINTY/SIMILARITY CLUSTERS    CMB7 33889     SUM OF CLUSTER SOURCES
-------------------------------------------------------------------------------

-------------------------------------------------------------------------------

SPECIES CONCENTRATIONS -  SITE: SLK          DATE: 08/06/90    CMB7 33889
SAMPLE DURATION        7       START HOUR        00        SIZE:    F
       R SQUARE      .93     PERCENT MASS     105.1
     CHI SQUARE      .61               DF        14

SPECIES-------I---MEAS------------------CALC-------------RATIO C/M----RATIO R/U
MTGC   MTGU   T   9.34190+-  1.24860  9.81715+-   1.86432   1.05+-  .24      .2
CLIC   CLIU   *    .00020<    .02200   .03778<     .01923  *****< *****     1.3
N3IC   N3IU   *    .14900+-   .05070   .06050+-    .04991    .41+-  .36    -1.2
BKN3IC BKN3IU      .04890<    .05520   .06855<     .03274   1.40<  1.72      .3
HNDDGC HNDDGU      .66560+-   .12460   .35655+-    .50004    .54+-  .76     -.6
S4IC   S4IU   *   1.32970+-   .09340  1.29060+-    .15128    .97+-  .13     -.2
GSS4IC GSS4IU      .04200<    .17670   .41589<     .11459   9.90< 41.75     1.8
N4CC   N4CU   *    .43800+-   .09700   .48250+-    .06455   1.10+-  .29      .4
GSN4CC GSN4CU     1.97890+-   .20760  1.60984+-    .75735    .81+-  .39     -.5
NAAC   NAAU        .01640<    .02690   .02503<     .02073   1.53<  2.80      .3
KPAC   KPAU        .05880+-   .01990   .08422+-    .02022   1.43+-  .59      .9
OCTC   OCTU   *   6.06200+-  1.12580  6.06200+-   1.41303   1.00+-  .30      .0
ECTC   ECTU   *   1.21060+-   .40160   .48164+-    .11331    .40+-  .16    -1.7
ALXC   ALXU   *    .03040<    .03890   .07804<     .03607   2.57<  3.49      .9
SIXC   SIXU   *    .13030+-   .03630   .12942+-    .04732    .99+-  .46     -.0
PHXC   PHXU        .00000<    .02840   .00000<     .00035    .00<   .00      .0
SUXC   SUXU        .49900+-   .02870   .47756+-    .05670    .96+-  .13     -.3
CLXC   CLXU        .00000<    .03450   .03292<     .01089    .00<   .00      .9
KPXC   KPXU   *    .10500+-   .02240   .10366+-    .02257    .99+-  .30     -.0
CAXC   CAXU   *    .02690+-   .01720   .02559+-    .01129    .95+-  .74     -.1
TIXC   TIXU   *    .00000<    .07370   .00180<     .00181    .00<   .00      .0
VAXC   VAXU        .00000<    .03890   .00026<     .00028    .00<   .00      .0
CRXC   CRXU        .00000<    .01160   .00000<     .00026    .00<   .00      .0
MNXC   MNXU   *    .00000<    .00640   .00103<     .00051    .00<   .00      .2
FEXC   FEXU   *    .03770+-   .02450   .04912+-    .01739   1.30+-  .96      .4
NIXC   NIXU   *    .00000<    .00300   .00026<     .00001    .00<   .00      .1
CUXC   CUXU        .00000<    .00510   .00077<     .00077    .00<   .00      .1
ZNXC   ZNXU        .00320<    .00350   .00367<     .00095   1.15<  1.29      .1
SEXC   SEXU        .00000<    .00420   .00001<     .00001    .00<   .00      .0
BRXC   BRXU   *    .00380+-   .00280   .00092+-    .00026    .24+-  .19    -1.0
RBXC   RBXU   *    .00000<    .00340   .00032<     .00026    .00<   .00      .1
SRXC   SRXU   *    .00060<    .00380   .00027<     .00026    .44<  2.85     -.1
ZRXC   ZRXU        .00000<    .00590   .00000<     .00026    .00<   .00      .0
BAXC   BAXU        .12630+-   .12590   .00859+-    .00873    .07+-  .10     -.9
PBXC   PBXU   *    .00000<    .01070   .00084<     .00051    .00<   .00      .1
-------------------------------------------------------------------------------
```

Table 6-9

Example CMB Output for PM_{10} Collected at Sequoia on August 8, 1990 Between 0000 and 0700 PST

```
SOURCE CONTRIBUTION ESTIMATES -  SITE: SLK          DATE: 08/06/90     CMB7 33889
SAMPLE DURATION        7       START HOUR        00        SIZE:    C
       R SQUARE      .94     PERCENT MASS      93.1
     CHI SQUARE      .26               DF        16

  SOURCE
     * TYPE     SCE(UG/M3)    STD ERR      TSTAT
---------------------------------------------
10     SOIL10       4.3837      .6338     6.9168
90     MARO          .4228      .1115     3.7920
---------------------------------------------

MEASURED CONCENTRATION FOR SIZE: C
       5.2+-     1.9

       UNCERTAINTY/SIMILARITY CLUSTERS    CMB7 33889     SUM OF CLUSTER SOURCES
--------------------------------------------------------------------------------

--------------------------------------------------------------------------------

SPECIES CONCENTRATIONS -  SITE: SLK          DATE: 08/06/90    CMB7 33889
SAMPLE DURATION        7       START HOUR        00        SIZE:    C
       R SQUARE      .94     PERCENT MASS      93.1
     CHI SQUARE      .26               DF        16

SPECIES-------I---MEAS------------------CALC-------------RATIO C/M----RATIO R/U
MTGC   MTGU   T   5.16210+-   1.88910  4.80640+-    .64169   .93+-   .36     -.2
CLIC   CLIU   *     .00000<    .04620    .02064<    .02125    .00<   .00      .4
N3IC   N3IU   *    .29780+-    .06480   .29964+-    .04470  1.01+-   .27      .0
BKN3IC BKN3IU       .00000<    .11050    .00000<    .00000    .00<   .00      .0
HNDDGC HNDDGU   -99.00000+--99.00000   .00000+-    .00000   .00+-   .00     1.0
S4IC   S4IU   *     .00000<    .12100    .03061<    .01278    .00<   .00      .3
GSS4IC GSS4IU   -99.00000+--99.00000   .00000+-    .00000   .00+-   .00     1.0
N4CC   N4CU   *     .05240<    .10350    .00000<    .00059    .00<   .01     -.5
GSN4CC GSN4CU   -99.00000+--99.00000   .00000+-    .00000   .00+-   .00     1.0
NAAC   NAAU         .03520<    .03790    .10274<    .01414   2.92<  3.17     1.7
KPAC   KPAU         .01020<    .02500    .00927<    .00232    .91<  2.24     -.0
OCTC   OCTU   *     .00000<   1.56990    .15105<    .04889    .00<   .00      .1
ECTC   ECTU   *     .00000<    .60800    .00000<    .01165    .00<   .00      .0
ALXC   ALXU   *    .58010+-    .21290   .42311+-    .05979   .73+-   .29     -.7
SIXC   SIXU   *   1.28790+-    .47030  1.09265+-    .12271   .85+-   .32     -.4
PHXC   PHXU         .00000<    .04550    .00745<    .00245    .00<   .00      .2
SUXC   SUXU        .21320+-    .08840   .01673+-    .00269   .08+-   .03    -2.2
CLXC   CLXU         .00000<    .05330    .02064<    .02125    .00<   .00      .4
KPXC   KPXU   *    .15900+-    .04780   .09976+-    .01080   .63+-   .20    -1.2
CAXC   CAXU   *    .19530+-    .04560   .16951+-    .03290   .87+-   .26     -.5
TIXC   TIXU   *     .02230<    .10280    .02251<    .00308   1.01<  4.65      .0
VAXC   VAXU         .00150<    .04940    .00131<    .00066    .87< 28.78      .0
CRXC   CRXU         .00020<    .01410    .00121<    .00014   6.03< *****      .1
MNXC   MNXU   *     .00520<    .00770    .00496<    .00066    .95<  1.42     -.0
FEXC   FEXU   *    .17520+-    .03550   .22537+-    .02654  1.29+-   .30     1.1
NIXC   NIXU   *     .00000<    .00430    .00039<    .00005    .00<   .00      .1
CUXC   CUXU        .01130+-    .00580   .00142+-    .00059   .13+-   .08    -1.7
ZNXC   ZNXU        .00810+-    .00470   .00153+-    .00012   .19+-   .11    -1.4
SEXC   SEXU         .00000<    .00610    .00004<    .00010    .00<   .00      .0
BRXC   BRXU   *     .00130<    .00390    .00073<    .00008    .56<  1.68     -.1
RBXC   RBXU   *     .00190<    .00500    .00068<    .00007    .36<   .94     -.2
SRXC   SRXU   *     .00120<    .00560    .00134<    .00025   1.12<  5.21      .0
ZRXC   ZRXU         .00000<    .00850    .00048<    .00008    .00<   .00      .1
BAXC   BAXU         .00000<    .22200    .00314<    .00442    .00<   .00      .0
PBXC   PBXU   *     .00000<    .01540    .00068<    .00019    .00<   .00      .0
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```

may be missing. The sum of the squared RATIO R/U for fitting species divided by the degrees of freedom yields the CHI-SQUARE. The highest RATIO R/U values for fitting species are the cause of high CHI SQUARE values. The RATIO R/U for most species is within the target range for each example.

- Ratio of Calculated to Measured Species (RATIO C/M). The column entitled RATIO C/M shows the ratio of calculated to measured concentration and the standard error of that ratio for every chemical species with measured data. The ratios should be near 1.00 if the model has accurately explained the measured concentrations. Ratios which deviate from unity by more than two uncertainty intervals indicate that an incorrect set of profiles is being used to explain the measured concentrations. The RATIO C/M for most species is within the target range for each example.

6.2.4 Deviations from Model Assumptions

The basic assumptions of the CMB model (Watson, 1979) are: 1) compositions of source emissions are constant over the period of ambient and source sampling; 2) chemical species do not react with one another (i.e., they add linearly); 3) all sources which may significantly contribute to the receptor have been identified and their emissions characterized; 4) the number of source categories is less than or equal to the number of chemical species; 5) the source profiles are linearly independent (i.e., they are statistically different); and 6) measurement uncertainties are random, uncorrelated, and normally distributed.

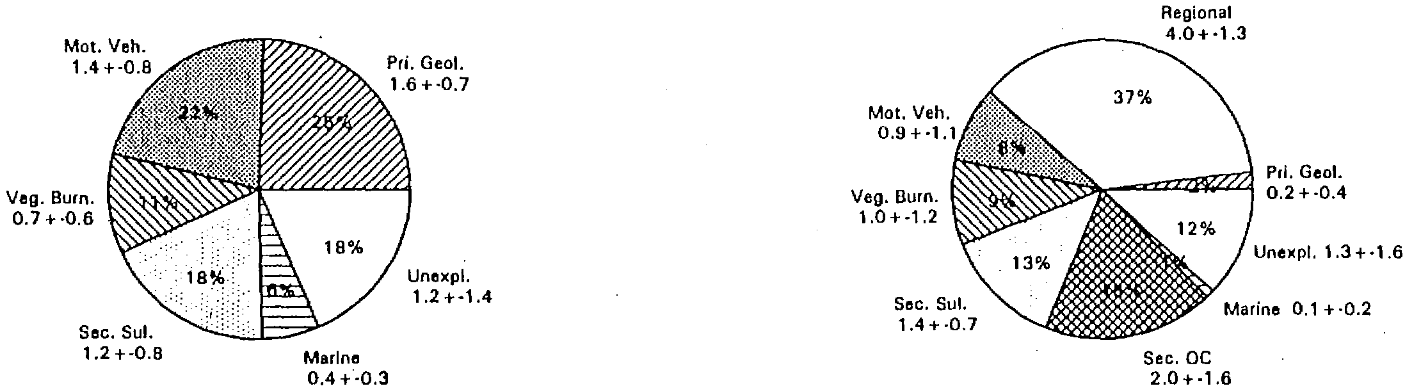
The degree to which these assumptions are met in practice depends to a large extent on the types and quality of chemical measurements made at the sources and receptor. The CMB model has been subjected to a number of tests to determine its ability to tolerate deviations from the model assumptions (e.g., Watson, 1979; Gordon *et al.*, 1981; Henry, 1982; Currie *et al.*, 1984; Dzubay *et al.*, 1984; Watson and Robinson, 1984; DeCesar *et al.*, 1985; Watson *et al.*, 1985; Watson *et al.*, 1987; Javitz and Watson, 1988).

The first part of this Section shows that there is substantial variability among individual profiles, and even among similar profiles from different source types, and that Assumption 1 is never completely met. Previous studies have shown (Chow et al., 1993) that the primary motor vehicle exhaust source contribution estimate is not very sensitive to the selection of a particular profile, nor is it sensitive to the removal of lead or organic carbon. This is in spite of substantial uncertainties assigned to the abundances in these profiles.

With respect to Assumption 2, all of the source types are treated as non-reactive. This is definitely the case for primary emissions from motor vehicle exhaust and vegetative burning, in which little change is expected between source and receptor. By apportioning PM_{10} and $PM_{2.5}$ to secondary ammonium nitrate and secondary ammonium sulfate, rather than to their ammonia, sulfur dioxide, and oxides of nitrogen precursors, the CMB problem has been linearized for the reactive precursors. Watson *et al.* (1991) demonstrate how chemical equilibrium modeling might be applied to these secondary species to determine how emissions reductions in their precursors might affect their ambient concentrations.

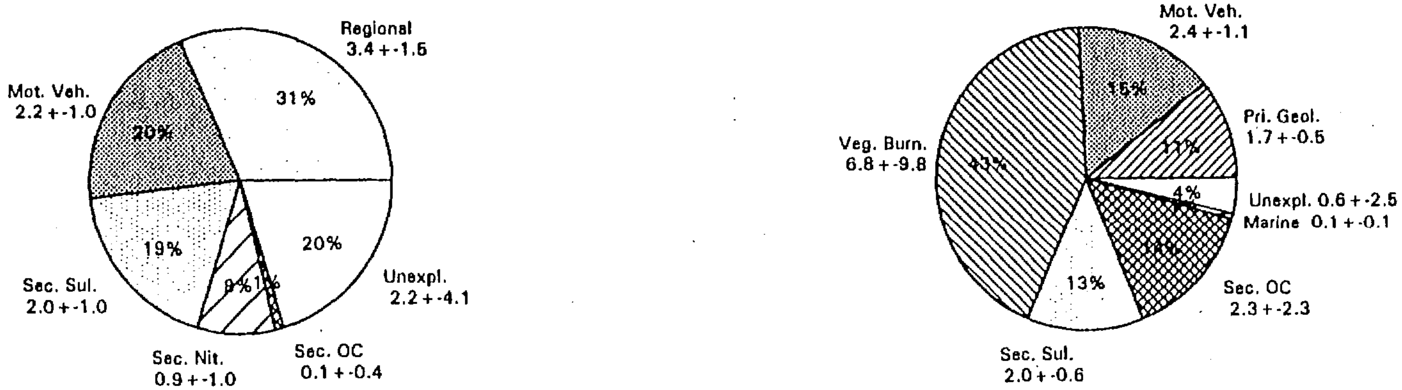
With respect to Assumption 3, it appears from the lower than target PERCENT MASS performance measures for the majority of the CMBs that there is mass which is unaccounted for by the included sources. However, it has been amply demonstrated that the carbon and elemental data are negatively biased, and this is a valid explanation for the mass which has not been accounted for.

With respect to Assumption 4, 16 chemical species and up to 6 source profiles were used in each calculation. The number of chemical species always exceeded the number of source types.



Average 24-hr PM2.5 Source Contributions
at Blodgett

Average 24-hr PM2.5 Source Contributions
at Sequoia



Average 24-hr PM2.5 Source Contributions
at Tehachapi

Average 24-hr PM2.5 Source Contributions
at Yosemite

Figure 6-1. Pie charts of 24-hour $PM_{2.5}$ source contributions for Sierra Nevada forest sites.

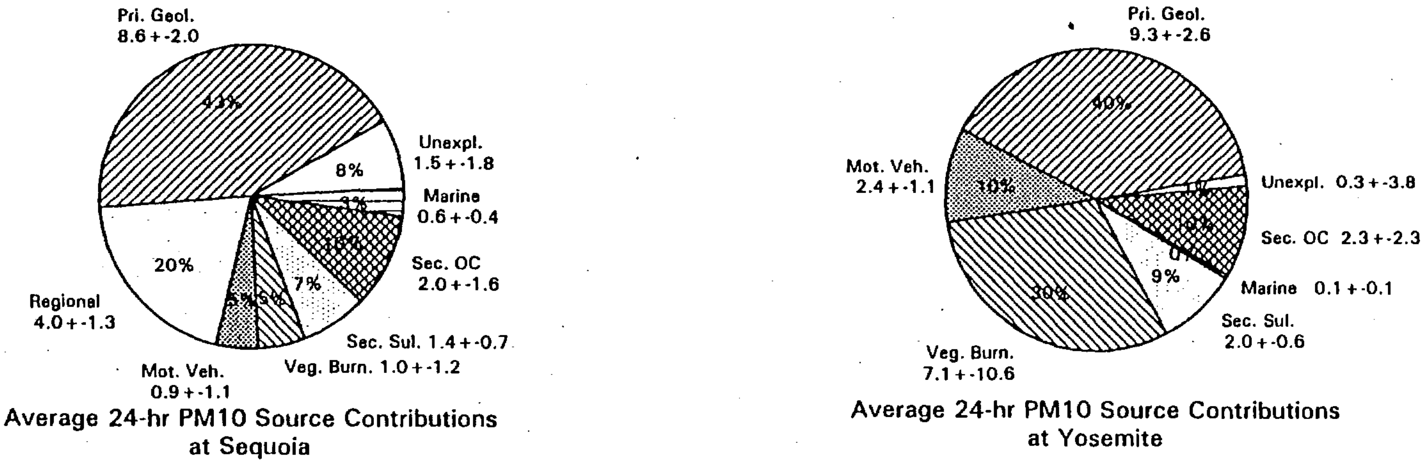


Figure 6-2. Pie charts of 24-hour PM_{10} source contributions for Sierra Nevada forest sites.

on the sampling period and day. Unlike any of the other sites, secondary ammonium nitrate accounted for 8% of the $PM_{2.5}$ mass.

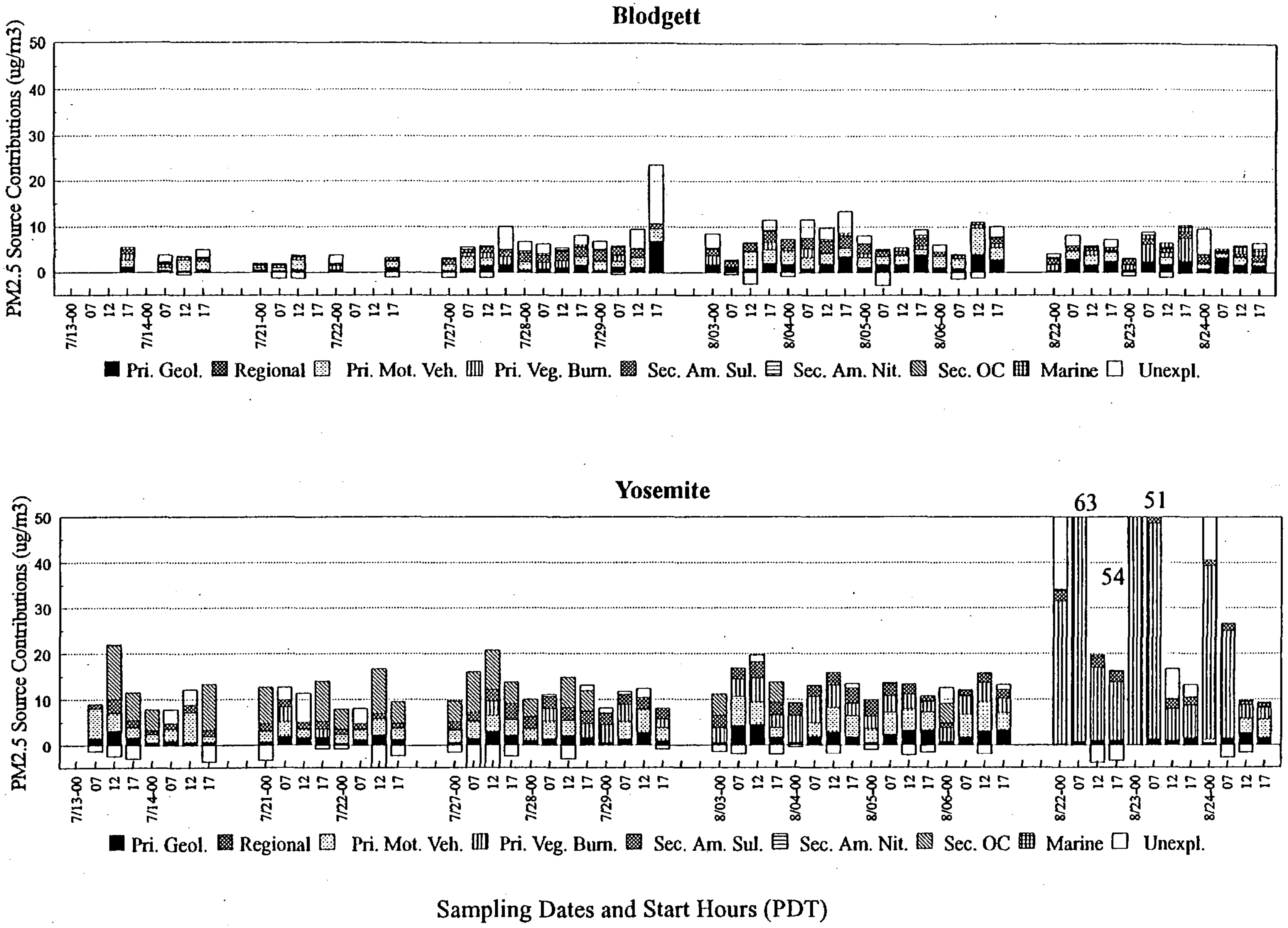
For the PM_{10} averages at Sequoia and Yosemite, the major difference was the increased contribution of primary geological material. This source accounted for 43% of the mass at Sequoia and 40% of the mass at Yosemite.

6.4 Individual Source Contribution Estimates

Spatial and temporal patterns can be more easily observed by plotting histograms of the individual source apportionments and these are shown in Figures 6-3 and 6-4. For the most part, these distributions show the same distribution of source contributions and differences and similarities among sampling sites. The most striking difference is the impact of the Yosemite fire on the 8/22 - 8/24 results.

Average source contribution estimates of $PM_{2.5}$ were low for all sites, varying from 6.5 $\mu g/m^3$ at Blodgett to 15.8 $\mu g/m^3$ at Yosemite. When the effect of vegetative burning is excluded from Yosemite, this decreases to 9.0 $\mu g/m^3$, a value close to the 10.9 and 10.8 $\mu g/m^3$ results from Sequoia and Tehachapi.

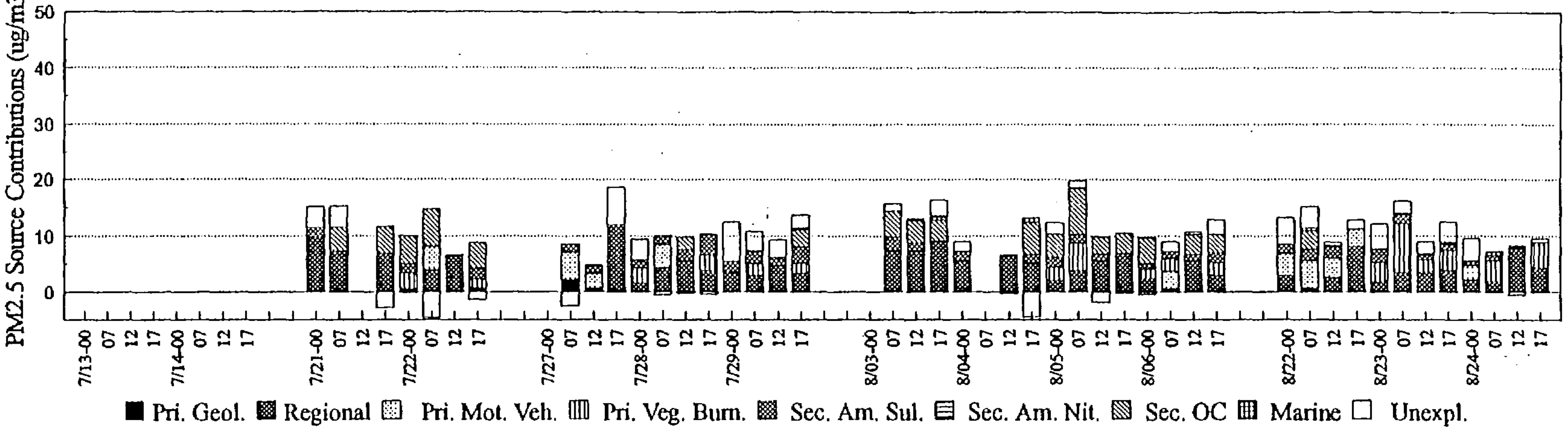
One way of visualizing day/night differences in source contributions is to compare pie charts of the average day time and average night time contributions for the sites Figures 6-5 to 6-8). For Blodgett, primary motor vehicle and primary geological sources were substantially larger during the day, contributing 30% and 28% vs. 17% and 23%, respectively. This type of diurnal pattern with the highest contributions generally found in the morning samples


Blodgett

Yosemite

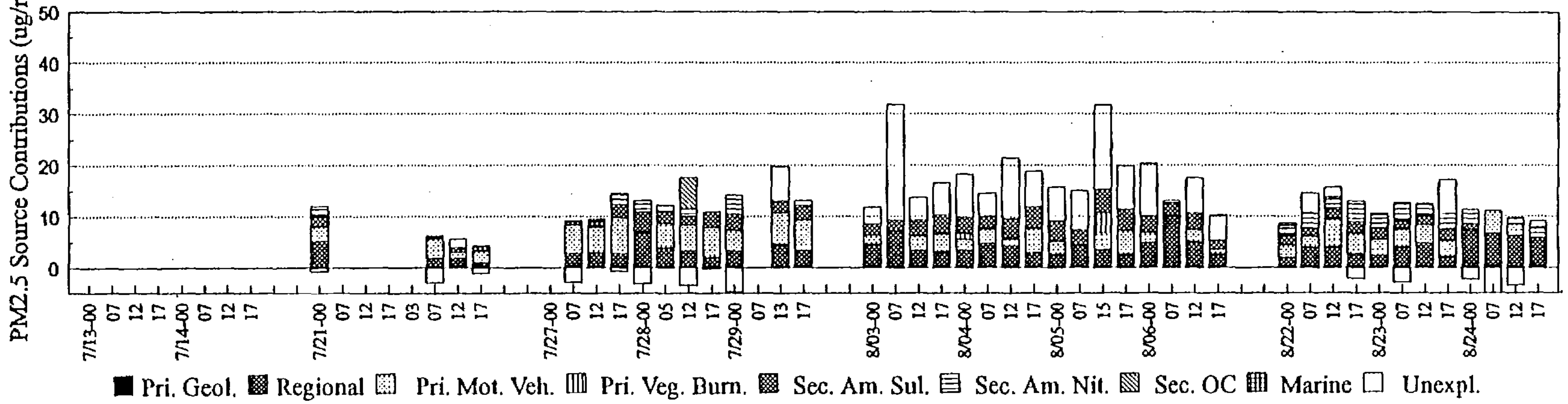
Figure 6-3. Diurnal source contributions to $PM_{2.5}$ at Sierra Nevada forest sites.

Sequoia Lower Keweah



Tehachapi

(Intensive Sampling Days)



Sampling Dates and Start Hours (PDT)

Figure 6-3 (continued)

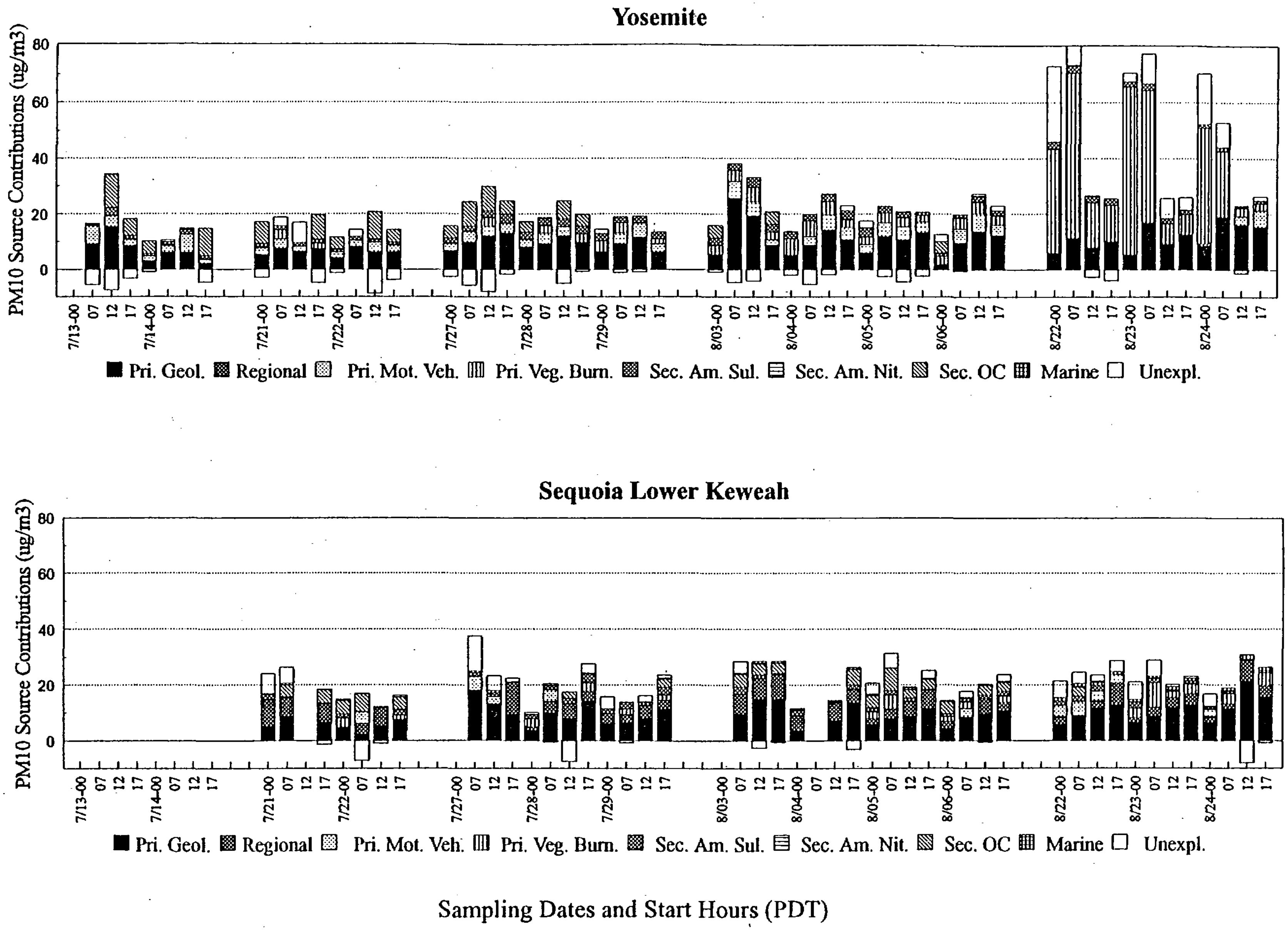
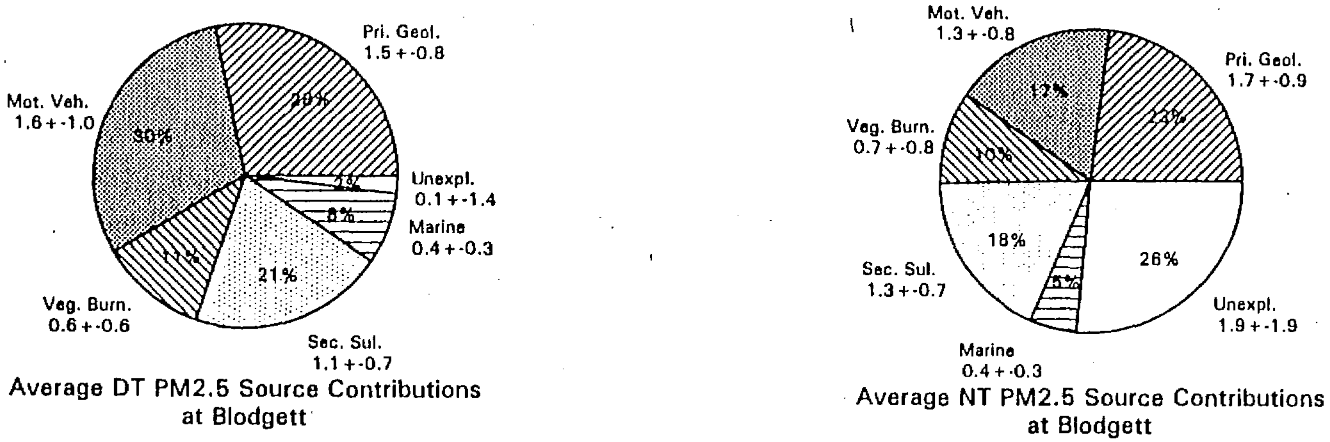


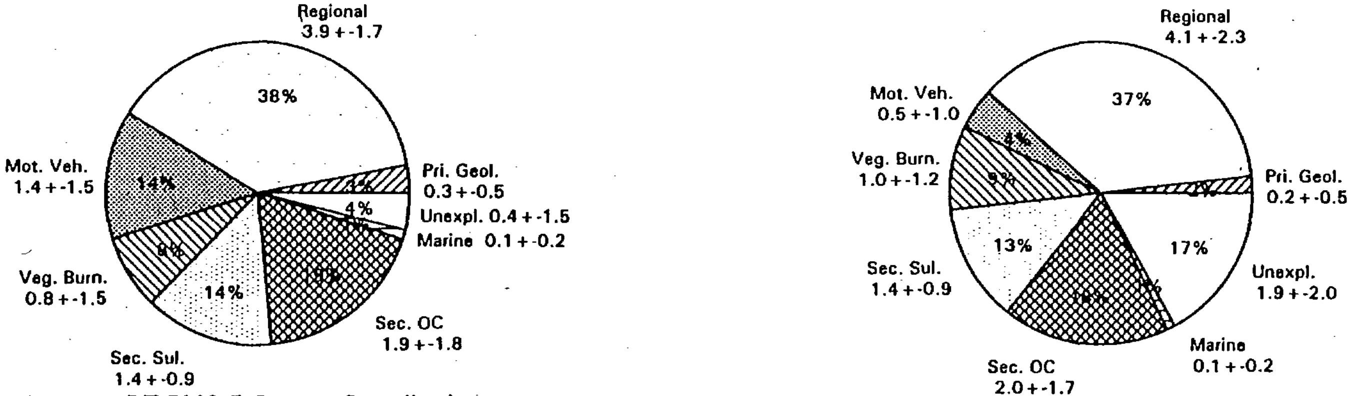
Figure 6-4. Diurnal source contributions to PM_{10} at Yosemite and Sequoia.



Average DT PM2.5 Source Contributions at Blodgett

Average NT PM2.5 Source Contributions at Blodgett

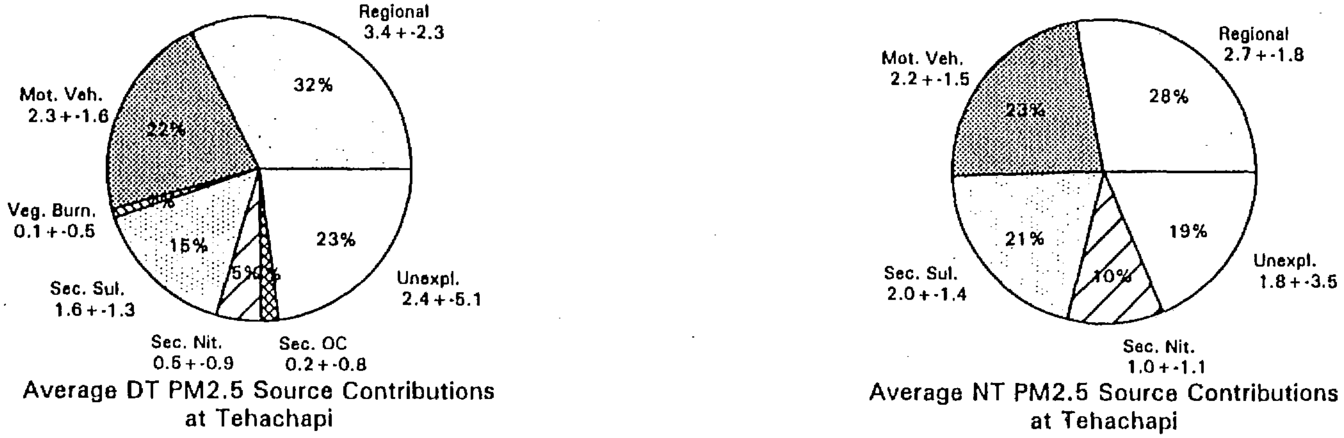
Figure 6-5. Pie charts of diurnal $PM_{2.5}$ source contribution estimates for Blodgett.



Average DT PM2.5 Source Contributions
at Sequoia

Average NT PM2.5 Source Contributions
at Sequoia

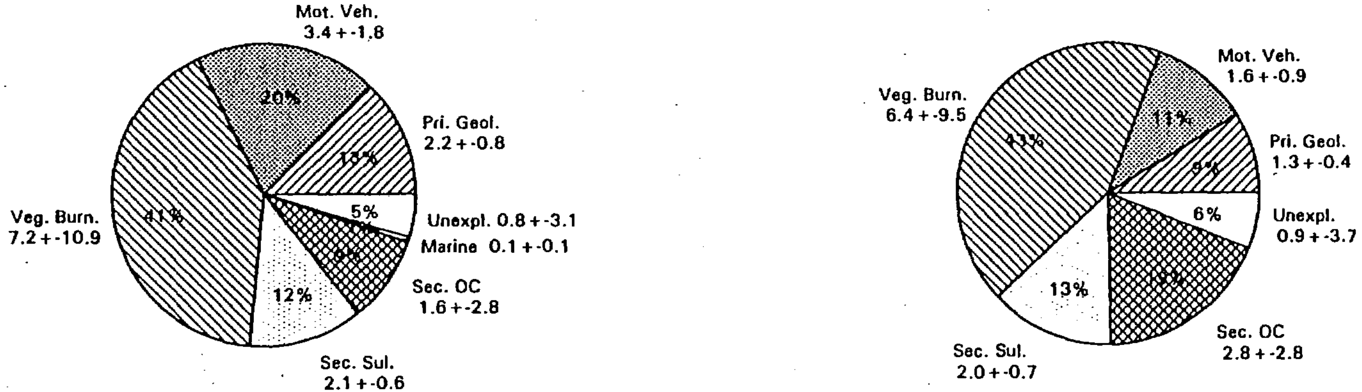
Figure 6-6. Pie charts of diurnal $PM_{2.5}$ source contribution estimates for Sequoia.



Average DT PM2.5 Source Contributions
at Tehachapi

Average NT PM2.5 Source Contributions
at Tehachapi

Figure 6-7. Pie charts of diurnal $PM_{2.5}$ source contribution estimates for Tehachapi.



Average DT PM2.5 Source Contributions
at Yosemite

Average NT PM2.5 Source Contributions
at Yosemite

Figure 6-8. Pie charts of diurnal $PM_{2.5}$ source contribution estimates for Yosemite.

corresponds to local activity and is consistent with emissions somewhat proportional to traffic volume and other activity factors.

For Sequoia (Figure 6-6), the major day/night difference was in the contribution of the motor vehicle source. As was observed at Blodgett, this source contribution was greatest during the day time period. Overall, the site was consistently impacted by secondary and regional sources indicative of transport.

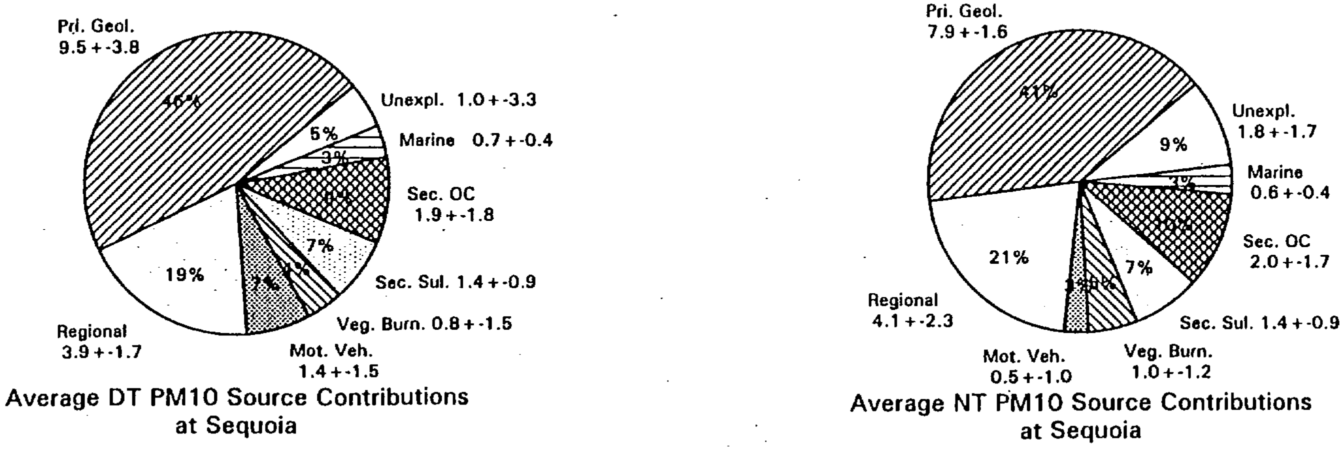
Unlike the other sites, the major diurnal change observed at Tehachapi (Figure 6-7) was the increased contribution secondary sulfate and nitrate at night. This pattern is consistent with emissions in nearby regions coupled with transport and transformation to the impacted area. Because of Tehachapi's proximity to the SoCAB, these species may have originally been emitted in that source region rather than in the SJV.

Excluding the contribution of vegetative burning at Yosemite, the impact of local activity on the day/night contributions is observed. Primary motor vehicle and geological sources are greatest during the day time periods.

For the two sites with PM_{10} data (Sequoia and Yosemite) the typical day/night variation in primary motor vehicle and geological sources is again seen. These are greater during the day than at night (Figures 6-9 and 6-10).

6.5 Source Sub-Types

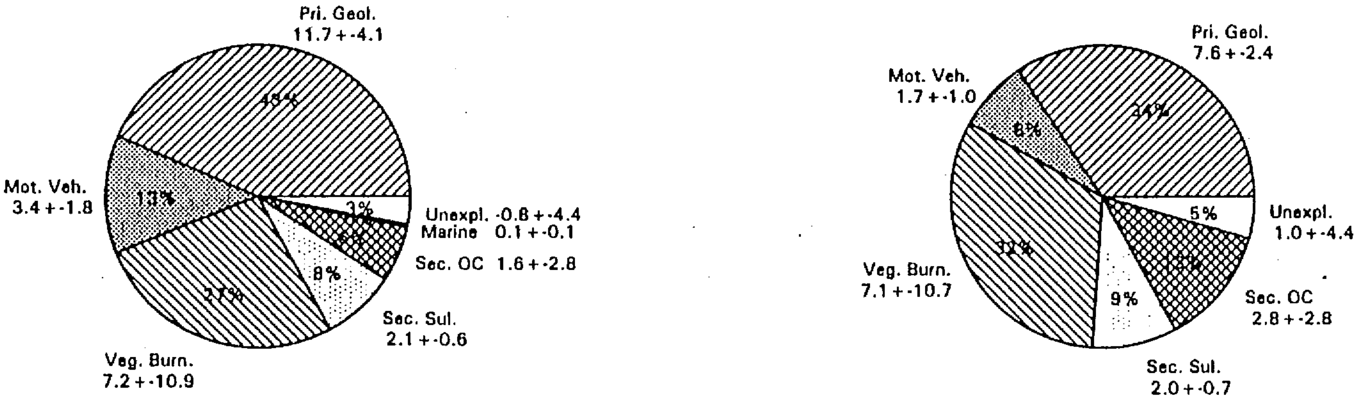
To develop emissions control strategies, the major source types must be related to specific types of emitters. The impact of local sources such as primary motor vehicle and geological sources while large on a percent basis was generally low for all cases. The only



Average DT PM10 Source Contributions at Sequoia

Average NT PM10 Source Contributions at Sequoia

Figure 6-9. Pie charts of diurnal PM_{10} source contribution estimates for Sequoia.



Average DT PM10 Source Contributions
at Yosemite

Average NT PM10 Source Contributions
at Yosemite

Figure 6-10. Pie charts for diurnal PM_{10} source contribution estimates for Yosemite.

exception was the extraordinary event of the forest fire at Yosemite. Controls over these sources would be unlikely to have an impact on the observed particulate loadings.

The other sources tended to be secondary or regional in nature. Estimates of their influence can be made, however, by examining the CMB source apportionments in light of knowledge of the meteorology, emissions, spatial distribution, and temporal distribution of source contributions.

Secondary ammonium nitrate was a major contributor on many occasions. The sources of its precursors are nitrogen oxides from motor vehicle exhaust (with some from gas-fired power plants and home heating) and ammonia from agricultural operations. The major source of sulfur dioxide is also primary motor vehicle exhaust. Reductions in sulfur dioxide precursor emissions will probably result in reductions in ambient sulfate concentrations. Similarly, the two regional profiles are based on primary emissions coupled with transport and transformation followed by deposition at the forested sites.