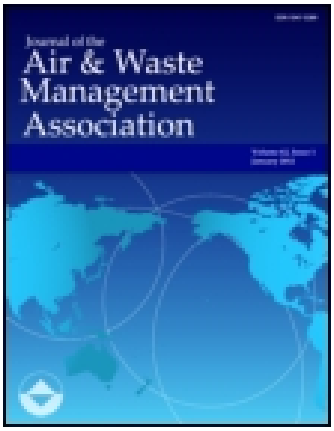

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Apportioning Visibility Degradation to Sources of $PM_{2.5}$ Using Positive Matrix Factorization

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Apportioning Visibility Degradation to Sources of $PM_{2.5}$ Using Positive Matrix Factorization

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ABSTRACT

Intensive monitoring studies of aerosol have been conducted in two regions of California with poor air quality. Winter monitoring in the Fresno area was conducted in December 2003. Two summer samplings were collected from the eastern Los Angeles Basin, from Rubidoux in 2003 and Riverside in 2005. All three of these studies featured a suite of semicontinuous aerosol monitors. The speciated aerosol data with continuous gaseous measurements from these studies were combined with continuous Automated Surface Observing System (ASOS) measurements of visibility and extinction from nearby airports and modeled aerosol water content to conduct source apportionment analyses. The data were analyzed using three different techniques. A conventional positive matrix factorization (PMF) method was used. Then a novel approach was used that coupled PMF with added extinction and modeled water data. Another technique involved integrating conventional PMF with linear regression to obtain the extinction associated with each source. The novel PMF with added extinction and modeled water data provided the most robust results. The Fresno winter study was meteorologically characterized by stagnant conditions, a shallow mixing height, and intermittent periods of fog and low clouds. Six factors were identified using PMF. The secondary nitrate and gasoline mobile combustion emission associated sources exhibited the highest extinction coefficients. PMF also identified six factors in the summer 2003 study at Rubidoux. The secondary nitrate and the ozone-related secondary semi-volatile organic material (SVOM) sources exhibited the highest extinction levels. Water associated with the aerosols plays an important role because of the marine influence and stratus clouds typically occurring in the basin during the summer months. The summer of 2005 study in Riverside lead to the identification of 11 sources. The highest contributors to extinction are associated with material transported across the basin, the relative humidity secondary source, followed by secondary nitrate.

IMPLICATIONS

Sampling aerosols continuously with negligible artifacts produces a dataset ideal for detailed source apportionment analyses. Hourly averaged speciated aerosol and gaseous data produced 24 data points plus an important diurnal signal every day. This paper analyzes short-term intensive datasets from two California regions in winter and summer. PMF analyses were exercised in three different ways to obtain source apportionment and visibility impairment associated with each factor-identified source. Combining extinction from an airport's ASOS data and modeled water content associated with sulfate and nitrate aerosols into PMF is an improved approach.

INTRODUCTION

Apportionment of visibility to particulate matter 2.5 μm in aerodynamic particle diameter (D_p) and smaller ($PM_{2.5}$) has generally focused on determining the components of this fine particulate material that is responsible for observed visibility degradation.[1,2] Frequently these analyses are centered around a linear regression analysis such as those calculated using the set of n equations.

$$Ext_{p,i} = \sum_{j=1}^{g} \alpha_j [m_{i,j}] \quad (1)$$

$Ext_{p,i}$ is the extinction due to particles for data point i, α_j is the calculated mass extinction coefficient for aerosol component j, $[m_{ij}]$ is the concentration of component j of particulate matter (e.g., sulfate, elemental carbon, etc.) for data point i, g is the total number of components, and n is the total number of data points. Occasionally this analysis has been conducted where the $m_{i,j}$ terms are the concentrations of sources identified in an apportionment analysis.[3] No previous studies have been documented where the attribution of extinction to sources was accomplished by direct inclusion of the extinction data into the apportionment analysis.

Intensive ambient field sampling programs were conducted in the Riverside area in July 2003[4] and again in July and August 2005.[5] During the summer, this populous region of Southern California (16 million residents) is known for its reduced visibility due to copious amounts of secondary and primary aerosols from various sources. The moist stratus marine cloud air mass that frequently emanates from the Pacific Ocean sea

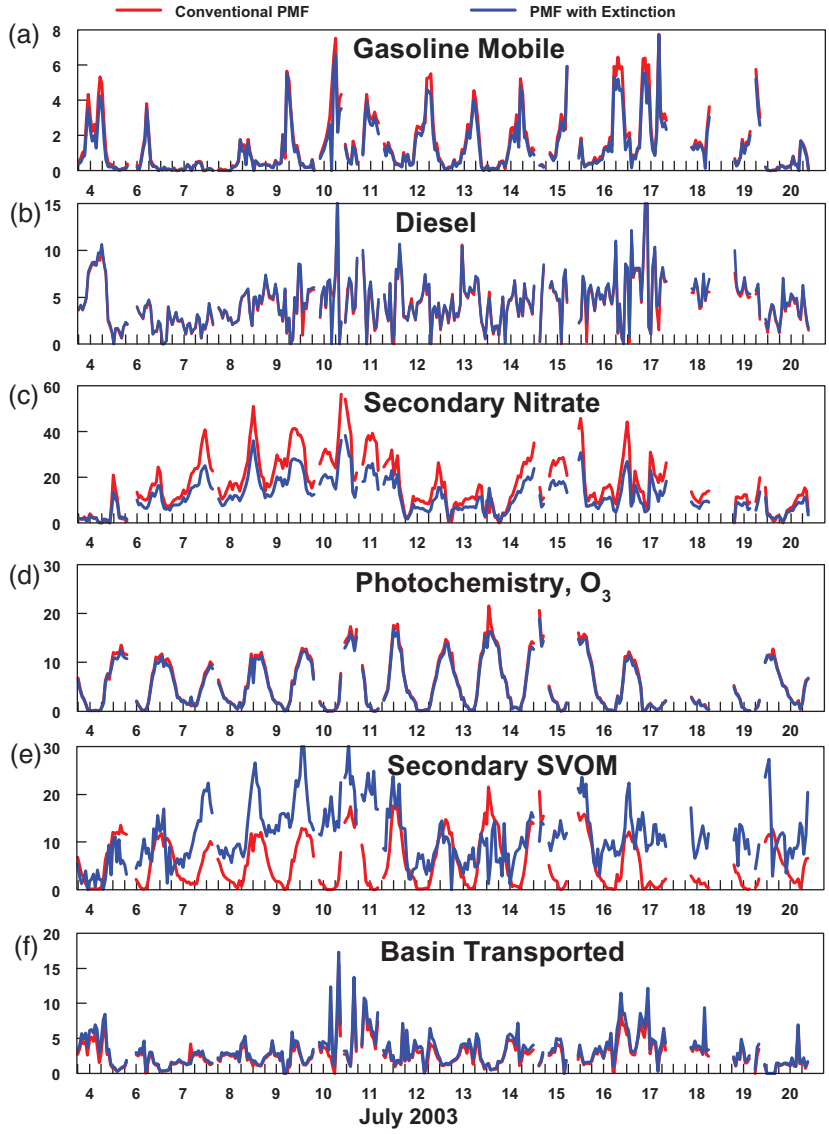

Figure 1. 2003 Rubidoux $PM_{2.5}$ data for conventional PMF and PMF with extinction. The diurnal patterns associated with each identified source are similar for the two analyses. Source concentrations are also similar except for secondary nitrate and secondary SVOM. Sources include (a) gasoline mobile, (b) diesel mobile, (c) secondary nitrate, (d) photochemistry, O_3 (e) secondary SVOM, and (f) basin-transported.

breezes causes an accelerated conversion of gas to particles and an increase in extinction due to uptake of water by the particles. Additionally, these pollutants are trapped in an average 500-m mixed layer below a strong 10 °C inversion because of high-pressure conditions dominating the region during the summer. The 1-hr average data available from these two studies[4,5] are summarized in the next section and their positive matrix factorization (PMF) analyses are discussed in papers by Grover and Eatough[6] and Eatough et al.[7]

Sampling was also conducted in December 2003 at the U.S. Environmental Protection Agency (EPA) Superfund site in Fresno; the details of the study were reported in Grover et al.[8] The Fresno area often experiences prolonged episodes of fog and low clouds during the winter; such was the case for this study. During the first half of the study, the boundary layer air mass was shallow (300 m), moist, and stagnant, with visibility sometimes reduced to a few feet. During the second half of the study, inversions were present each day, but no fog occurred. Extinction-related analyses were performed only for the 2-wk period that fog was not present. The PMF analysis of $PM_{2.5}$ sources is presented in this paper.

Each of the data points were combined with aerosol water estimated from the relative humidity (RH) measurements, particulate sulfate and nitrate concentrations (as described in the Methodology section), and airport visibility data to apportion the sources of aerosol extinction. These data can be retrieved from the National Climatic Data Center at ftp://ftp.ncdc.noaa.gov/pub/data/asos-onemin.

METHODOLOGY

Each of the datasets outlined in the introduction were analyzed by PMF[10] using three different methods. The first method, *conventional PMF*, uses all available data except for the inclusion of any extinction or modeled aerosol water content to evaluate the factors contributing to the observed measured $PM_{2.5}$. Although this approach was previously applied to the datasets from the California cities of Rubidoux (16 km west of Riverside) in 2003[6] and Riverside in 2005,[7] this paper only documents the conventional PMF analysis for the Fresno data.

The second method, a new approach, uses experimental extinction data and modeled concentrations of water in $PM_{2.5}$ for its PMF source apportionment calculations. This approach is referred to as *PMF with extinction*.

The third method used the more conventional approach and added apportionment of extinction sources to evaluate the robustness of the PMF with extinction approach. Obtaining an extinction source apportionment involves identifying sources without including extinction and water in the PMF analysis. This approach is referred to as *PMF without extinction*. For this approach, the sources responsible for visibility degradation were calculated using the conventional PMF results and modeled aerosol water concentrations[9] using a standard linear regression analysis as calculated in eq 2, where $j = 1$ and $i = 1$ to n.

$$Ext_{P,i} = \sum_{j=1}^{g} \alpha_j [s_{i,j}] \qquad (2)$$

Ext_{Pi} is the extinction due to particles, α_j is the calculated mass extinction coefficient for source j, $[s]$ is the concentration of particulate matter for source j for data point i, g is the total number of sources, and n is the total number of 1-hr average data points. The only difference between eqs 1 and 2 is the former uses experimental particulate composition data for the attribution of visibility degradation and the latter uses source apportionment results. The g sources include those sources identified in the conventional PMF analysis plus the modeled concentrations of particulate water. These analyses were performed on the datasets for Fresno 2003 (g = 6, n = 218), Rubidoux 2003 (g = 6, n = 326), and Riverside 2005 (g = 11, n = 572).

EXPERIMENTAL DATA

Rubidoux, CA, 2003 Study

The July 2003 study was conducted at the South Coast Air Quality Management District (SCAQMD) monitoring site at Rubidoux, CA. The details of the study are found in Grover et al.[4] One-hour averaged semicontinuous measurements were made with a suite of instruments to provide $PM_{2.5}$ mass and chemical composition data. Total $PM_{2.5}$ mass concentrations (nonvolatile plus semi-volatile) were measured

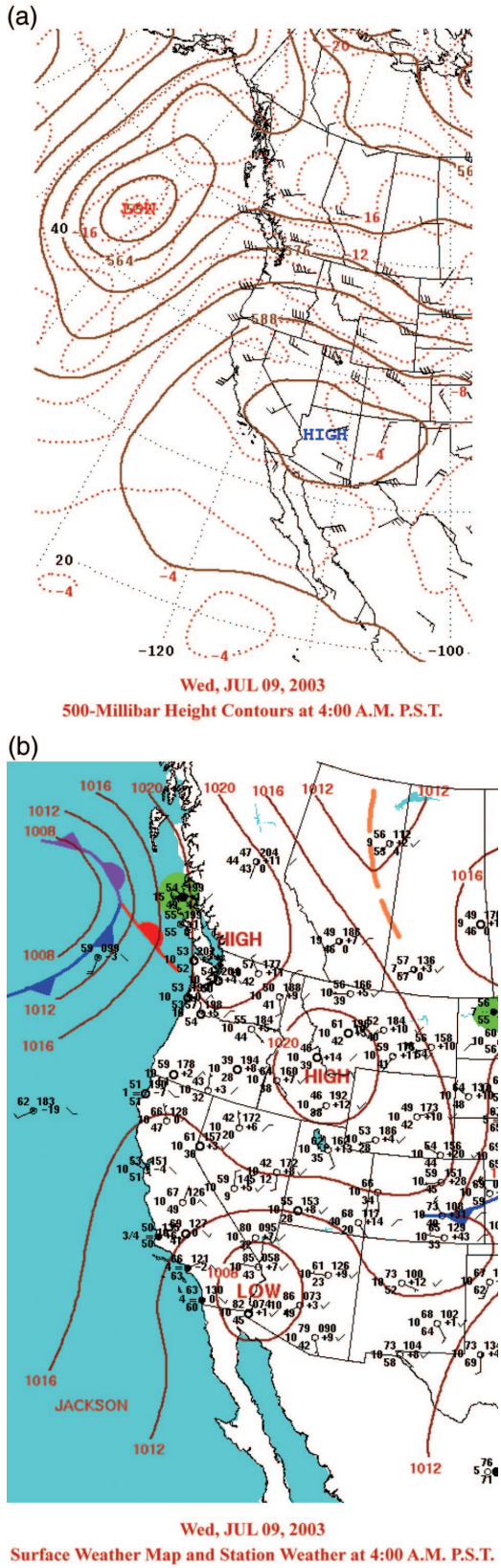

Figure 2. The synoptic meteorological pattern for the western United States on July 9, 2003. (a) 500-mb height contours at 4:00 a.m. Pacific standard time (PST). (b) Surface weather map and station weather at 4:00 a.m. PST. A strong warm ridge of high pressure was centered over the southwestern United States of 5940 m at 500 mb. At the surface, typical onshore sea breeze flow from the Pacific Ocean into the thermal low over the deserts occurs continuously. This strong high pressure results in considerable subsidence leading to relatively boundaries with low mixing heights of 300–400 m throughout the Los Angeles Basin.

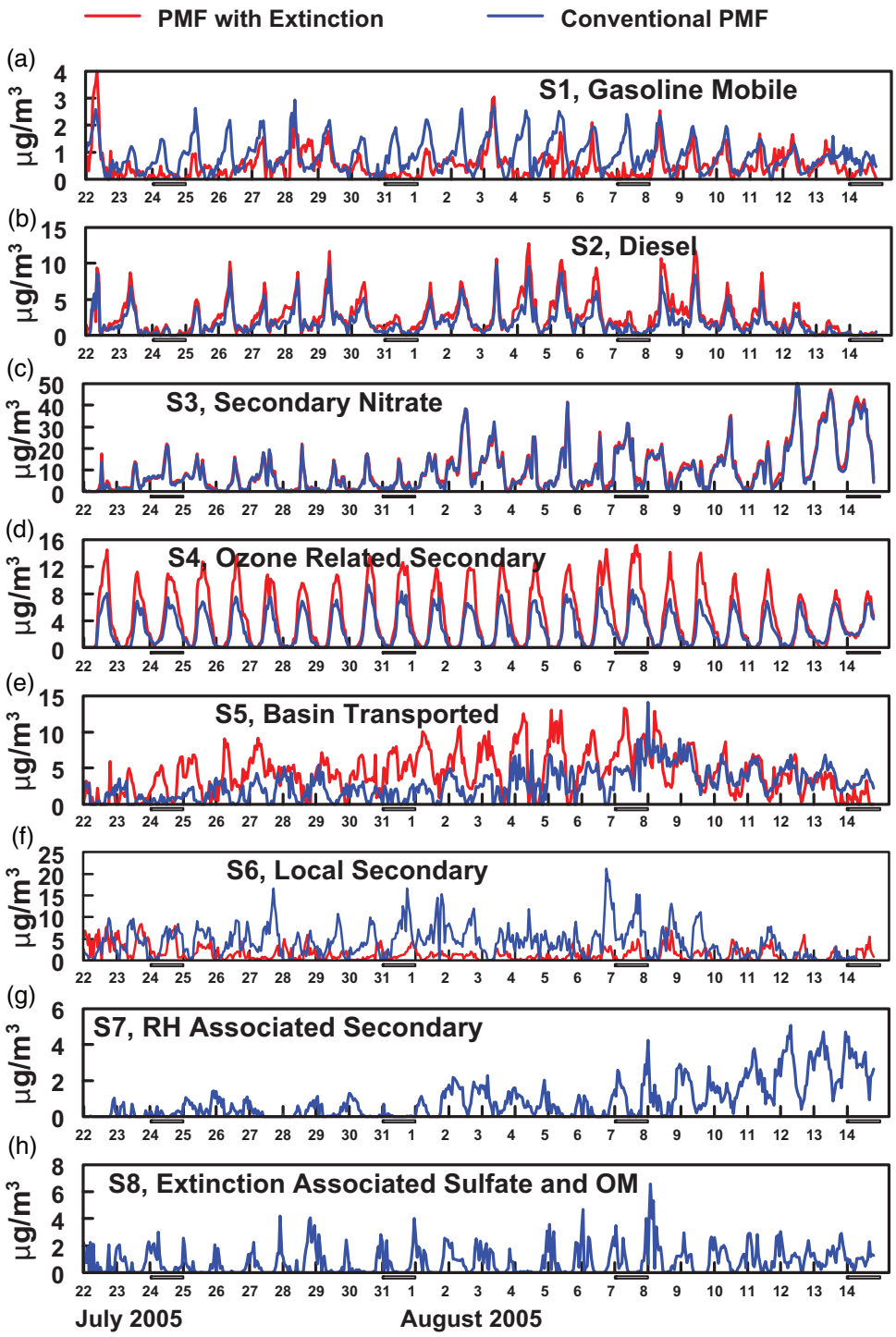

Figure 3. 2005 Riverside $PM_{2.5}$ data for the six major sources of the conventional PMF and PMF with extinction and two new sources identified by PMF with extinction. Comparing the two analyses, the diurnal patterns associated with each source are similar, and except for the basin-transported and local secondary sources, concentrations are also similar. Bars on x-axis denote weekends. Sources include (a) gasoline mobile, (b) diesel mobile, (c) secondary nitrate, (d) ozone-related secondary, (e) basin-transported, (f) local secondary, (g) RH-associated secondary; and (h) extinction-associated sulfate and OM.

with a Rupprecht and Patashnick (R&P) filterdynamic measurement system (FDMS), whereas a conventional Thermo Scientific tapered element oscillating microbalance (TEOM) monitor was used to measure nonvolatile mass concentrations. Semi-volatile material (SVM) was calculated by subtracting the TEOM-determined $PM_{2.5}$ mass from the FDMS. $PM_{2.5}$ chemical species monitors included an R&P 5400 carbon monitor, an Anderson Aethalometer, and an R&P 8400N nitrate monitor. Gas-phase data included carbon monoxide (CO), nitrogen dioxide (NO_2), oxides of nitrogen (NO_x), and ozone, which were obtained from the SCAQMD. The factors associated with

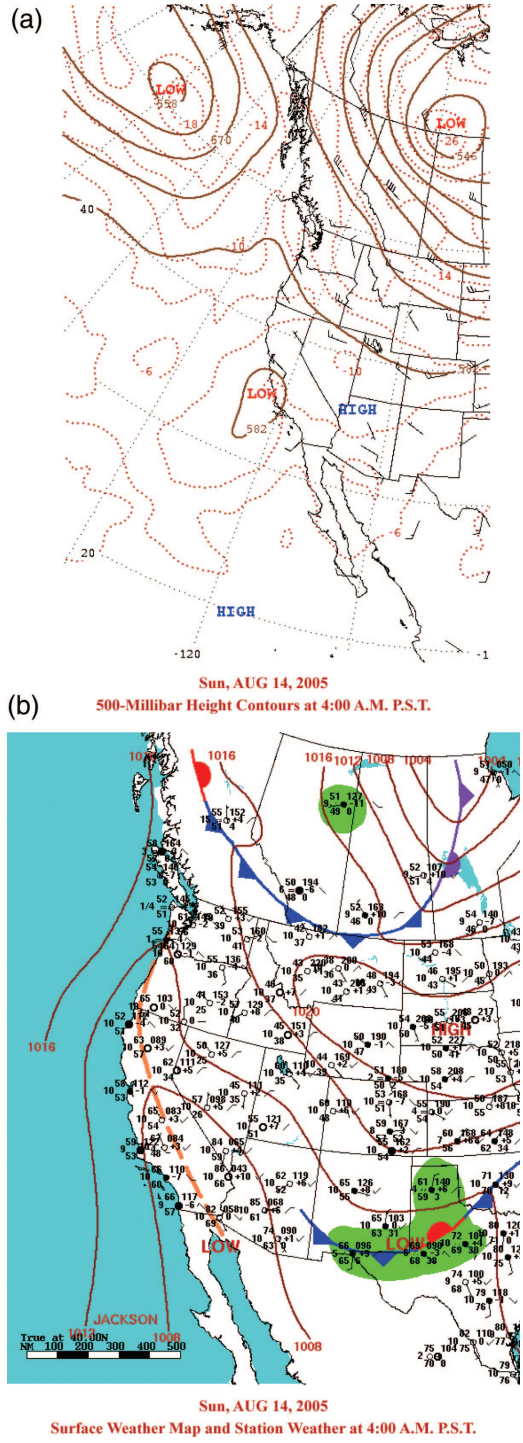

Figure 4. Synoptic meteorological description for the western United States on August 14, 2005. (a) 500-mb height contours at 4:00 a.m. Pacific standard time (PST). (b) Surface weather map and station weather at 4:00 a.m. PST. A weak upper level low of 5820 m at 500 mb is situated just off the California coast. At the surface, there is a well-developed thermal trough over the western U.S. deserts. Because of this upper low and decreased subsidence, the marine/boundary layer rose to 900–1000 m and there was a well-developed westerly sea breeze across the entire Los Angeles Basin.

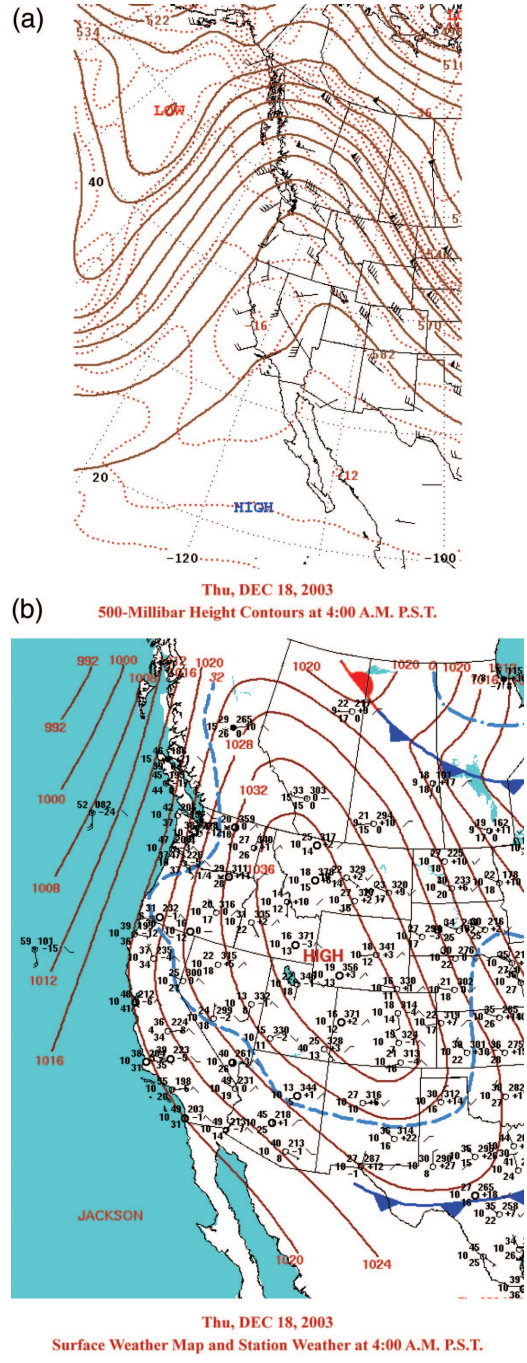

Figure 5. Synoptic meteorological setting for the western United States on December 18, 2003. (a) 500-mb height contours at 4:00 a.m. Pacific standard time (PST). (b) Surface weather map and station weather at 4:00 a.m. PST. A well-established high-pressure ridge was centered over the western United States of 5820 m at 500 mb (18,000 ft). This area of high pressure resulted in a typical winter surface high, centered over the cold Colorado Plateau. The setting led to a nearly stagnant air mass in the San Joaquin Valley, intermittent tule radiational fog, and low mixing heights of ~300 m.

the observed $PM_{2.5}$ were determined using the conventional PMF method.[6] A total of six factors were identified. The factors were assigned source names consistent with the apparent major contributor to each factor on the basis of the factor profiles and the $PM_{2.5}$ diurnal patterns. The study results are shown in Figure 1 and detailed in Grover and Eatough.[6]

The Rubidoux intensive monitoring study occurred July 4–20, 2003, at a widely used SCAQMD monitoring

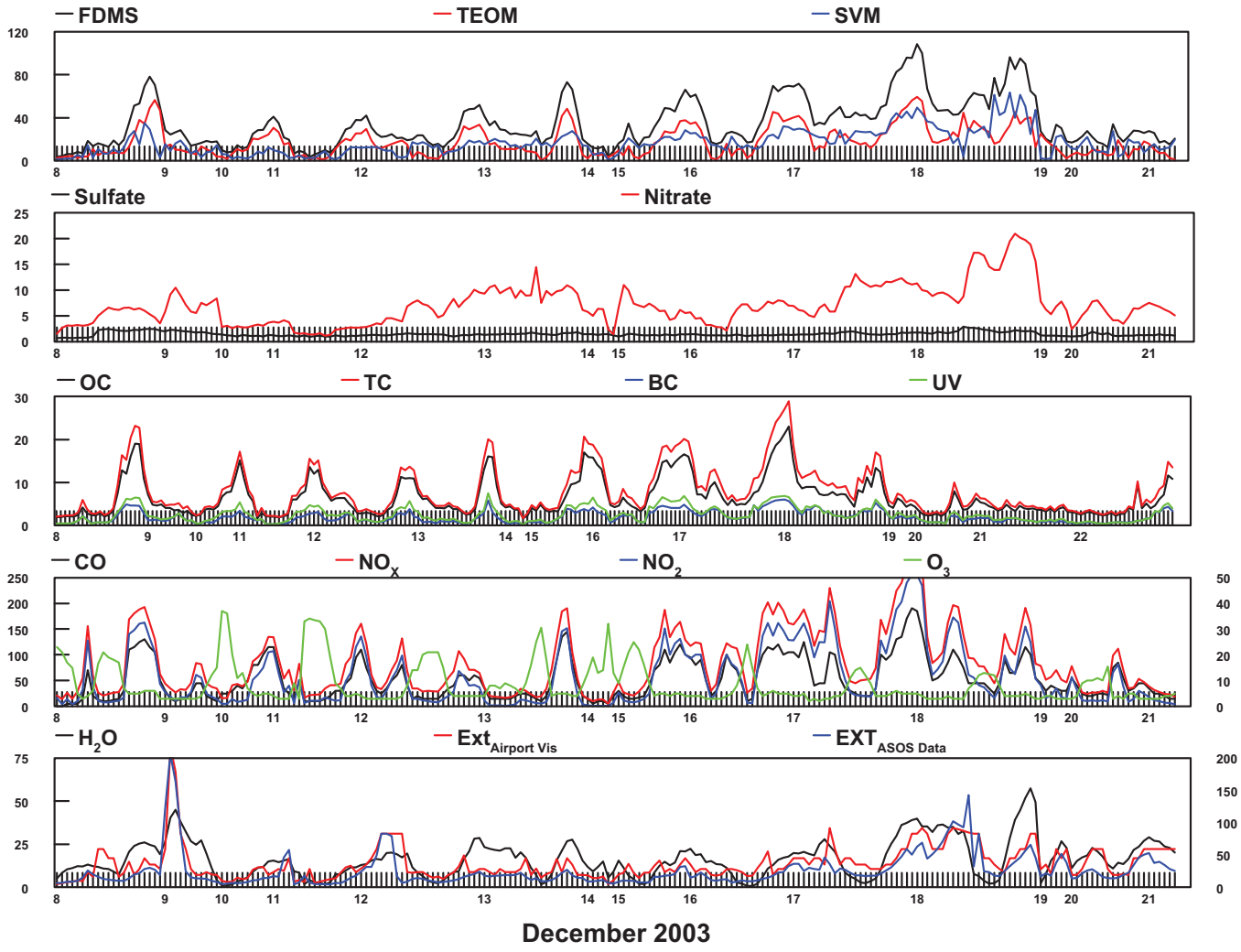

Figure 6. Concentrations of the various species used in the PMF analyses for the Fresno 2003 study. The data in the bottom chart were used for the PMF with extinction analysis. The other data were used in conventional PMF and PMF with extinction analyses. Units for all particulate components are $\mu g/m^3$. Units are parts per million (ppm) for CO and parts per billion (ppb) for the other gases. Units for both extinction values are Mm^{-1}.

site. Meteorologically, this period was characterized by a relatively strong ridge of high pressure with 500-mb heights ranging from 5905 to 5970 m as depicted in Figure 2. The air mass was somewhat warmer than normal, with 850-mb temperatures ranging from 22 to 28° C; normal for this area at this time of year is approximately 24° C. Because the Los Angeles Basin is bordered on the west by the Pacific Ocean, there is a predominant marine layer influence during the summer. This often results in stratus clouds on the west side of the basin, which burn back to the coast during the day. The deserts heat relative to the ocean (often 10° C), creating this marine layer and a strong inversion. During this particular period, the mixed/boundary layer (marine layer depth) ranged from 150 to 650 m; the average was approximately 500 m. There is always an onshore or westerly flow to the deserts across the Los Angeles Basin, increasing each afternoon and building into the evening. Even at 12 Greenwich Mean Time (GMT), the Los Angeles Airport (LAX) to Jacqueline Cochran Regional Airport (TRM) gradient ranged from a positive 2 to 8 mb. The region's maximum daily temperatures ranged from the low 20s along the coast (LAX), to 33–38° C in the Riverside area, and 40° C and higher in the southern deserts (TRM). Because of sea breeze divergence (strengthening and lowering of the inversion in the afternoon), the inversion, and thus limited mixing, remained intact throughout the entire Los Angeles Basin.

Riverside, CA, 2005 Study

The 2005 July/August study was conducted on the University of California–Riverside (UCR) campus.[5] One-hour averaged semicontinuous measurements were made with a suite of instruments to provide $PM_{2.5}$ mass and chemical composition data. Total $PM_{2.5}$ mass concentrations (nonvolatile plus semi-volatile) were measured with an R&P FDMS TEOM. Nonvolatile mass concentrations were measured with a conventional TEOM monitor. $PM_{2.5}$ chemical species monitors included a dual oven Sunset monitor to measure nonvolatile and semi-volatile carbonaceous material, an ion chromatographic-based monitor to measure sulfate and nitrate, and an Anderson Aethalometer to measure black carbon (BC) and ultraviolet (UV) absorption. Gas-phase data including CO, NO_2, NO_x, and ozone

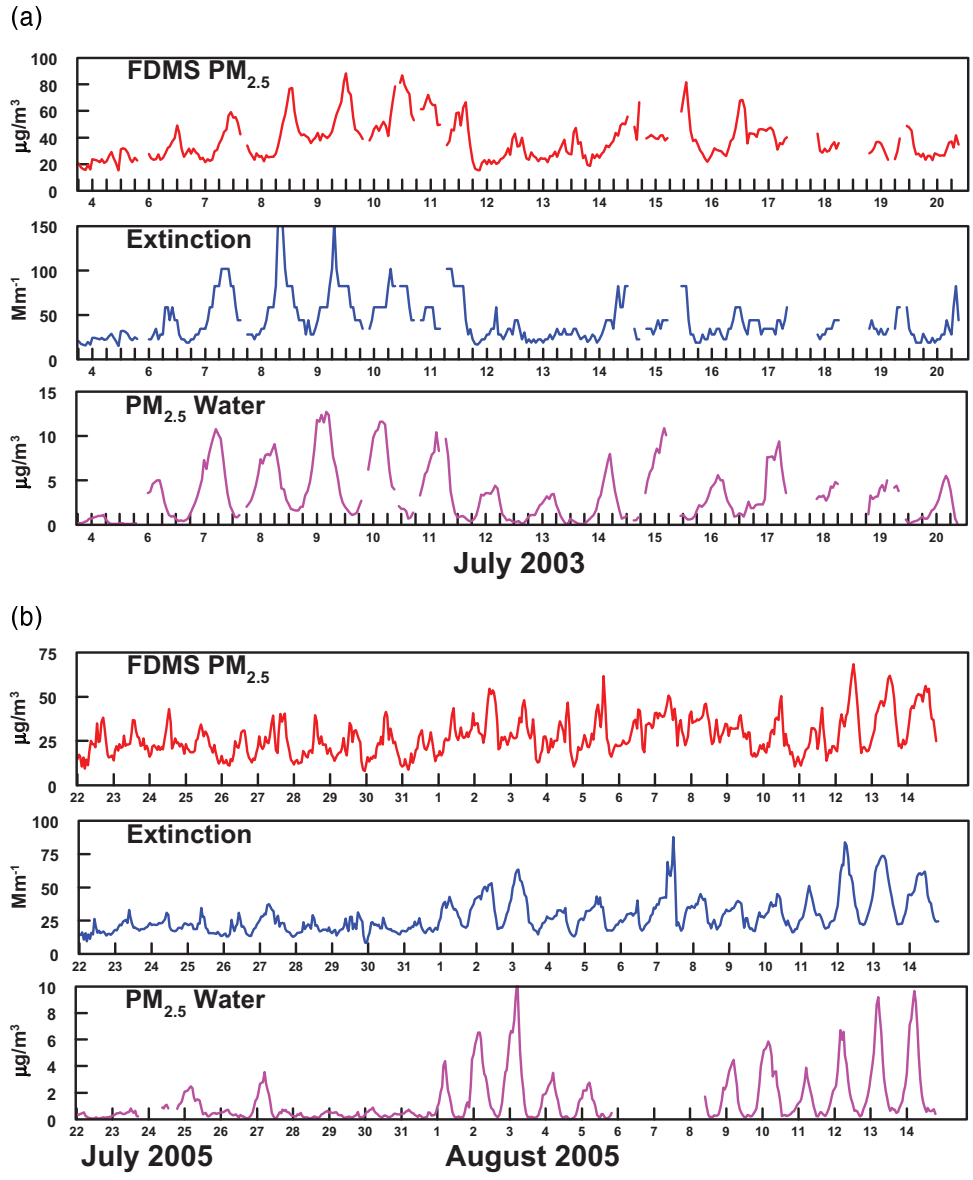

Figure 7. $PM_{2.5}$ extinction and PM water used in the PMF with extinction analysis. (a) $PM_{2.5}$ extinction for Rubidoux 2003 and (b) for Riverside 2005.

were also collected during the sampling period. In addition, single particle measurements were made using aerosol time-of-flight mass spectrometry (MS) (ATOFMS). Nineteen different particle types were identified for the PMF analysis. Finally, time-of-flight aerosol MS (TOF-AMS) provided data on markers of primary and secondary organic aerosols.[7] The factors responsible for the observed $PM_{2.5}$ were also determined for this study using the conventional PMF approach.[7] Because of an increase in the number of components included in the analysis, a total of 16 factors were identified. Six of these were the same six factors identified in the 2003 Rubidoux study (Figure 1). Ten of these factors had smaller concentrations identified from the MS data. Source names were applied to the factors using the same approach as for the Rubidoux study.[7] Results for the six major sources are shown in Figure 3.

The study was conducted from July 22 to August 15, 2005 on the UCR campus. Meteorologically, this was an interesting period because there were some synoptic pattern differences. Most of the time, relatively strong high pressure dominated (Figure 2). However, toward the end of the study, a weak upper level low formed off the coast, which increased the depth of the marine layer and inland penetration of the stratus (Figure 4). During this period, 500-mb heights ranged from 5820 to 5940 m (an average of 5910 m). The air mass was about normal, with 850-mb temperatures ranging from 20 to 25 °C. The marine layer depth varied from 300 to 1025 m. As expected, there was consistent onshore or westerly flow across the basin out to the deserts, with the 12:00 GMT LAX-TRM pressure gradient ranging from a positive 2 to 6 mb. Temperatures were about normal during this period, with daily maximums in the range of 20–25 °C along the coast (LAX), 26–39 °C in the Riverside area, and 39–43 °C in the southern deserts (TRM).

Fresno, CA, 2003 Study

In the 2003 Fresno study, $PM_{2.5}$ mass was measured using an FDMS TEOM and a GRIMM monitor. Anions (sulfate

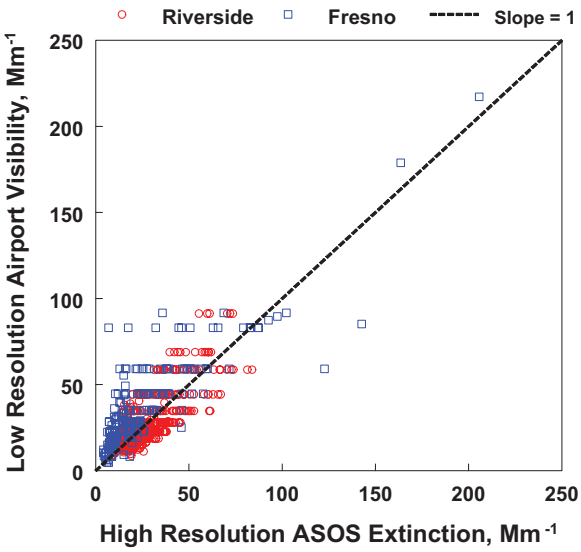

Figure 8. Comparison of high-resolution ASOS and low-resolution extinction data from the Riverside and Fresno airports. The low-resolution data originated from the airport visual range data. These data are given in mile increments, accounting for the layered nature of the comparison at higher extinction values.

and nitrate), including nonvolatile and semi-volatile components, and cations (ammonium ion) were measured using a Dionex prototype ion monitor. Organic material was measured with a Sunset Laboratory field monitor. Aethalometer-measured BC and UV absorption were also obtained. Total semi-volatile and semi-volatile organic material (SVOM) were estimated from the other data.[13] Gas-phase data, including CO, NO_2, NO_x and ozone, were also obtained from this EPA Superfund site for the period. In addition, temperature and RH data were available. All of the above data were obtained on an hourly averaged frequency.

The monitoring program was conducted from December 8 to 21, 2003 in Fresno, CA. Meteorologically, these 2 weeks were characterized by dry weather. High pressure on the surface and aloft was the dominant weather pattern. Perhaps the strongest high pressure occurred in the period around December 18 (Figure 5). Characteristic of this time of year, there was surface high pressure centered over the cold Colorado Plateau in Utah, which was under a relatively strong upper level high at 500 mb (5820 m). This pattern resulted in a strong inversion, with 850-mb temperatures of 16 °C (normal is 8 °C) and limited boundary layer mixing of no more than 300 m. There were also intermittent periods of tule radiational fog, a thick ground fog condition common in central California that forms at this time of year. At times the air mass was nearly stagnant and at other times, weak frontal systems passed to the north, flattening and weakening the ridge and leading to slightly higher boundary layers.

Extinction data were obtained from either the Riverside or Fresno municipal airports. Both are located close to the corresponding sampling sites. The ASOS dataset (ftp://ftp.ncdc.noaa.gov/pub/data/asos-onemin/) gives minute-averaged extinction measurements for each airport. These data were averaged to 1-hr values and are referred to here as *high-resolution extinction*. High-resolution extinction data were unavailable for Riverside in 2003; only the reported airport visual range was available. Airport visual range is reported every hour and referred to as *low-resolution extinction*. To allow an estimation of the uncertainty in the 2003 Riverside low-resolution extinction, hourly reported visibility data from the Riverside Airport in 2005 and Fresno Airport in 2003 were converted to extinction using the appropriate Koschmeider relationship with a 1% contrast threshold value. Although a value of 5% is used for a human observer, the value of 1% gives the best model fit for converting the instrument-measured visual range to extinction.

The concentration of water associated with the aerosol sulfate and nitrate was estimated using data obtained by Tang et al.[9] and protocols described in Malm et al.[10] and Sisler et al.[11] The uptake of water by aerosol ammonium sulfate and ammonium nitrate (Tang et al.[9]) increases significantly with increasing RH. A previously described protocol to average the hysteresis effects for pure ammonium sulfate (Malm et al.[10] and Sisler et al.[11]) was used. The effect of humidity on water content for ammonium nitrate aerosols may be slightly less pronounced.[9] Nevertheless, the same RH curve was used to describe the effects for the ammonium sulfate and ammonium nitrate aerosols.[10,11] These calculated results are referred to as *modeled aerosol water content*. Hourly averaged sulfate data were measured in the 2005 Riverside and 2003 Fresno studies, but estimated for the Rubidoux 2003 study on the basis of available 24-hr data. Hourly average nitrate data were available for all three studies. The extinction data and modeled aerosol water content for the 2003 Fresno study are given in Figure 6; data for the Rubidoux 2003 and Riverside 2005 studies are shown in Figure 7.

Table 1. The values of χ^{2}[12] and the results of the linear regression fit of the experimental $PM_{2.5}$ to the sum of the $PM_{2.5}$ attributed to the various sources in the conventional PMF (no extinction) and the PMF with extinction (either ASOS high-resolution data or airport visibility data as noted) analyses.

Site	*N*	PMF Result χ^2	Regression Fit R^2	Slope	Intercept ($\mu g/m^3$)	σ ($\mu g/m^3$)[a]	σ (%)
Fresno (no extinction)	218	1205	0.995	1.043 ± 0.005	1.0 ± 1.6	±2.1	±5.9
Fresno (ASOS extinction)	218	1534	0.994	1.029 ± 0.005	1.0 ± 1.7	±1.9	±5.5
Riverside (no extinction)[b]	572	2717	0.920	0.958 ± 0.012	0.6 ± 3.0	±2.2	±8.1
Riverside (ASOS extinction)	572	1144	0.907	0.951 ± 0.013	0.6 ± 3.3	±2.4	±8.8
Rubidoux (no extinction)[c]	326	1424	0.937	0.959 ± 0.014	1.2 ± 3.7	±2.7	±7.1
Rubidoux (airport visibility)	326	1643	0.967	0.932 ± 0.013	10.0 ± 9.2	±7.4	±19

Notes: [a]σ calculated from the equation, $\sigma = \sqrt{(1/(n-1) \times (\Sigma(x - x_i)^2 - \text{bias}^2))}$; [b]Results taken from Eatough et al.[8]; [c]Results taken from Grover and Eatough.[6]

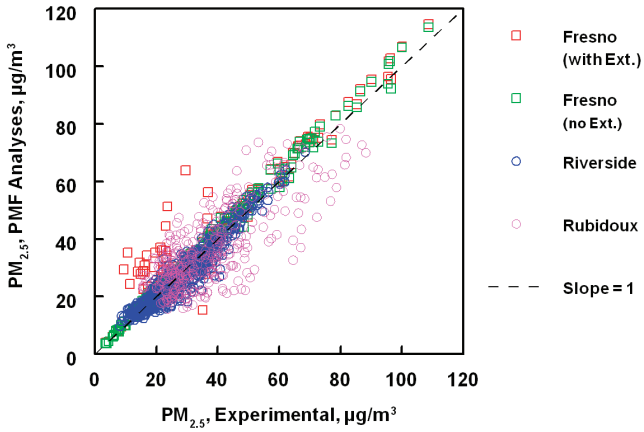

Figure 9. Experimental $PM_{2.5}$ mass compared with the calculated sum of the $PM_{2.5}$. All factors for the various PMF with extinction analyses and the conventional PMF analysis at Fresno are plotted. The linear regression results for the fit of the various datasets are found in Table 1. The greater scatter in the data for the Rubidoux site is due to increased uncertainty in the low-resolution extinction data for this site.

PMF ANALYSIS METHODS

The PMF analysis methods were identical to those previously used.[6,7] Conventional PMF analyses were performed for the Fresno data. PMF with extinction analyses were performed for each dataset with the extinction data and particulate water included. For Rubidoux (2003), the reported airport visibility low-resolution data were used. For the Riverside (2005) and Fresno (2003) studies, high-resolution ASOS data were used. Assumed uncertainties of the various particulate and gas-phase species were the same as previously reported.[6,7] The uncertainty of the calculated PM water was ±15% with a detection limit of 1 µg/m^3. For the high-resolution extinction data, the uncertainty was ±15%. The extinction data for Rubidoux were corrected for Rayleigh scattering (dispersion of electromagnetic radiation) and the uncertainty was assumed to increase with decreasing visibility (visibility is reported in 1-mi increments) from ±20 to 35%, consistent with the data given in Figure 8. The diurnal information aids substantially in the source apportionment analysis. This is true for the identification of the most reasonable number of factors and for the identification of the probable major contributing source (or secondary formation processes) associated with those factors on the basis of the PMF-determined factor profile and the diurnal variability in the concentrations for the factor.

RESULTS AND DISCUSSION

This section provides the source apportionment results for the three studies beginning with the conventional

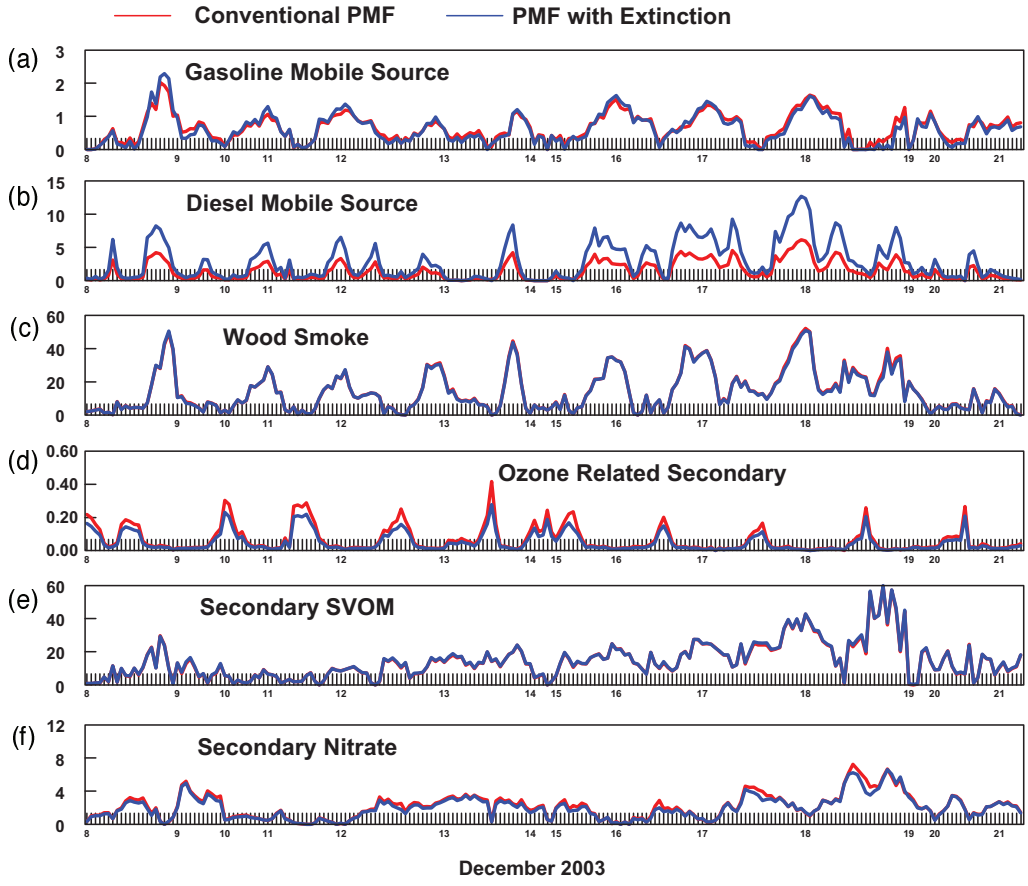

Figure 10. 2003 Fresno $PM_{2.5}$ data for the identified six sources of the conventional PMF and PMF with extinction. Comparing the two analyses, the diurnal patterns associated with each source are similar and, except for the diesel mobile source, concentrations are similar. Sources include (a) gasoline mobile, (b) diesel mobile, (c) wood smoke, (d) ozone-related secondary, (e) secondary SVOM, and (f) secondary nitrate.

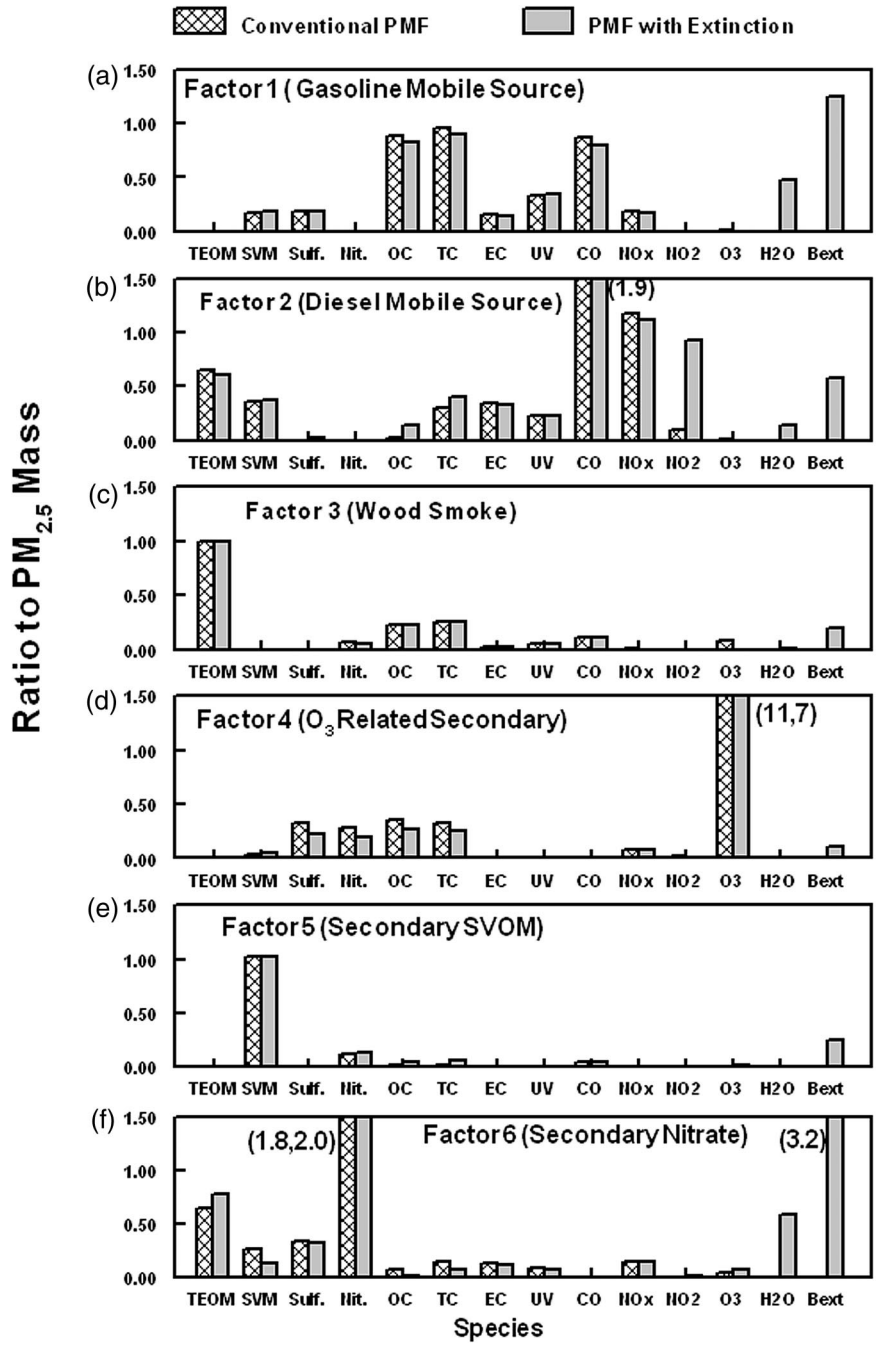

Figure 11. Factor profiles for the Fresno 2003 conventional PMF and PMF with extinction analyses. Measurement units for all particulate components are $\mu g/m^3$. Units are ppm for CO, ppb for ozone, and ppb/20 for the other gases. Units for the extinction values are Mm^{-1}. Where a ratio exceeds the *y*-axis 1.5 maximum, the values are noted at the side of the bars. The value of CO for conventional PMF is 1.5. The factor profiles for both analyses are comparable. Factors and sources include (a) factor 1, gasoline mobile; (b) factor 2, diesel mobile; (c) factor 3, wood smoke; (d) factor 4, ozone-related secondary; (e) factor 5, secondary SVOM; and (f) factor 6, secondary nitrate.

PMF analysis. The analysis is then expanded to apportion extinction to various sources using two different techniques—PMF with and without extinction.

PMF Apportionment of $PM_{2.5}$ Sources during the 2003 Fresno Study

The 2003 Fresno study used a conventional PMF analysis method similar to the Rubidoux[6] study. $PM_{2.5}$ mass, aerosol component, and gas-phase concentrations used in the PMF analyses are shown in Figure 6. Six factors were identified. The χ^2 results[10] were consistent with the degrees of freedom in the analysis (Table 1). The $PM_{2.5}$ mass obtained from the conventional PMF analysis compared well with the experimental $PM_{2.5}$ data, as shown by Table 1 and Figure 9. The named sources for each factor are based on the profile

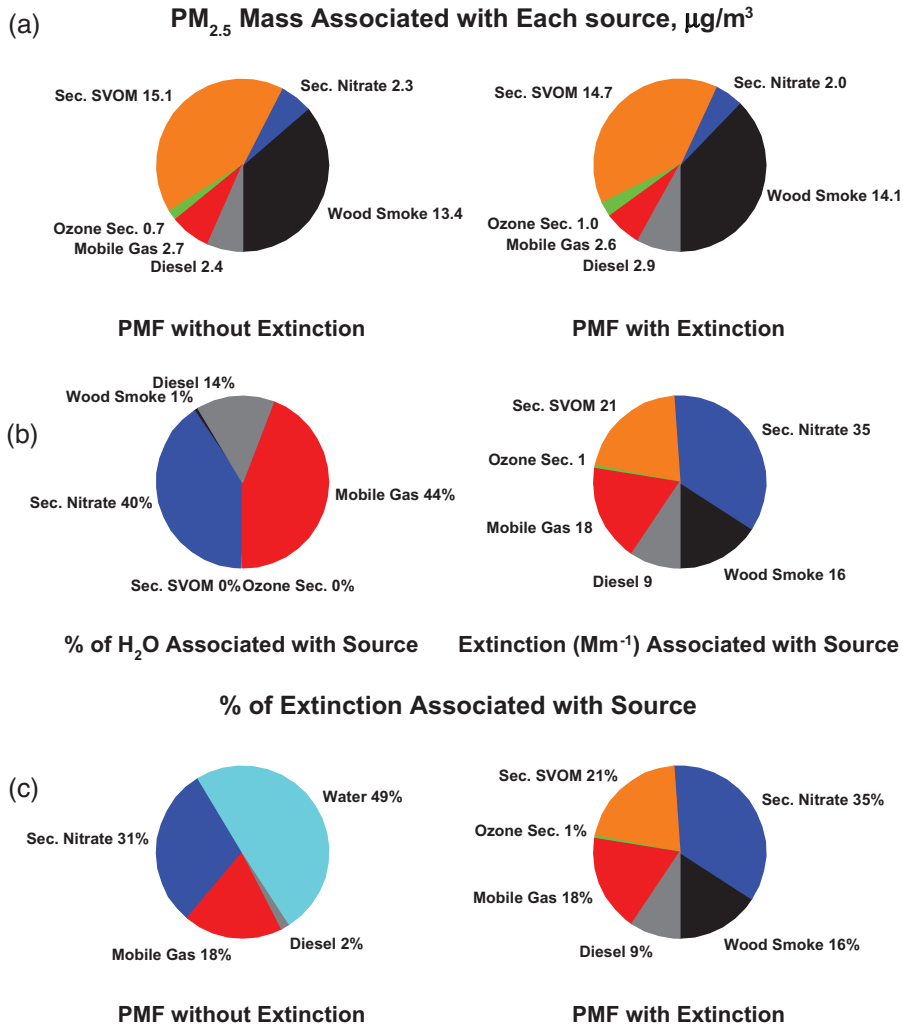

Figure 12. Pie chart comparisons using the Fresno 2003 data. Chart (a) shows the $PM_{2.5}$ mass associated with each source identified in the PMF with extinction and PMF without extinction analyses. The PMF results are from the conventional PMF. Chart (b) shows the percentage of modeled particulate water and Mm^{-1} of extinction associated with each factor for the PMF with extinction. Chart (c) shows the percentage of extinction associated with each source for the PMF without extinction and PMF with extinction.

and diurnal pattern observed using the protocols previously outlined for the Rubidoux[5] and Riverside[7] studies. The concentrations of the factors identified and the profiles obtained from the PMF analysis are given in Figures 10 and 11, respectively. Three of the sources are associated with primary emissions and three from secondary processes in the atmosphere. The gasoline mobile source profile was dominated by organic material, CO, and NO_x. The diesel mobile source profile was dominated by organic material, BC (33%), CO, and NO_x. The three secondary factors were dominated by the material indicated by the name of each secondary source (ozone-related secondary, secondary SVOM, and secondary nitrate). SVOM was not measured directly in the dataset, but is identified as the non-nitrate portion of the SVM (Figure 6),[13] which is the difference between the FDMS and conventional TEOM measurements.

The average concentrations of each factor obtained from the conventional PMF and PMF with extinction analyses are given in Figure 10. As indicated in Table 1 and Figure 10, the two analyses are in excellent agreement. Results for two PMF analyses are given in Figure 12a, with the PMF without extinction pie derived from the conventional PMF analysis. The average source mass results for the two analyses agree. The diurnal patterns were also in agreement (Figure 10). The contribution of PM water and extinction for each factor are given in Figure 12b. Two of the major contributors to extinction, the secondary nitrate and gasoline mobile factors, are also the two highest sources associated with water. As expected, some water is associated with the secondary nitrate factor. When the gasoline mobile factor and modeled aerosol water content were both high, nitrate was generally low.

PMF with extinction provides mass extinction coefficients and the extinction associated with each factor (Table 2 and Figure 12b). The water influence on these coefficients is apparent (Figure 12b). Gasoline mobile has the highest calculated mass extinction coefficient. Extinction attributions for various sources derived from the PMF with extinction and PMF without extinction analysis are

Table 2. Comparison of mass extinction coefficients (m^2/g), extinction (% of total), modeled aerosol water (% of total), and $PM_{2.5}$ ($\mu g/m^3$) associated with the various sources for the two PMF approaches for the apportionment of extinction.

	PMF with Extinction			PMF without Extinction		
Study/Source	**α (m^2/g)**	**Percent Extinction**	**Percent Water**	**α (m^2/g)**	**Percent Extinction**	**Percent Water**
Fresno 2003					(N=218,R^2=0.43)	
Gasoline mobile	5.2	18	44	11.3 ± 6.4	12	NA
Diesel mobile	0.6	9	14	0.5 ± 1.6	1	NA
Wood smoke	0.2	16	1	−0.1 ± 0.2	0[b]	NA
Ozone-related secondary	2.3	1	0		Not included in analysis	
Secondary SVOM	0.3	16	1	−0.3 ± 0.4	0[b]	NA
Secondary nitrate	3.2	35	40	5.8 ± 1.5	19	NA
Water		Not identified as a source		5.9 ± 0.9	50	100
Rubidoux 2003					(N = 326, R^2 = 0.54)	
Gasoline mobile	1.9	6	38	0.4 ± 0.7	2	NA
Diesel mobile	0.7	8	16	0.1 ± 0.4	0[b]	NA
Secondary nitrate	1.5	50	46	1.4 ± 0.1	66	NA
Ozone-related secondary	0.7	11	0	0.7 ± 0.3	11	NA
Secondary SVOM	0.6	17	0	0.7 ± 0.4	11	NA
Basin-transported	0.9	8	0	−0.5 ± 0.6	0[b]	NA
Water		Not identified as a source		1.5 ± 0.5	14	100
Riverside 2005					(N = 572, R^2 = 0.70)	
Gasoline mobile	3.7	7	0	5.7 ± 0.6	32	NA
Diesel mobile	0.1	1	0		Not included in analysis	
Secondary nitrate	0.4	18	0	0.4 ± 0.1	7	NA
Ozone-related secondary	0.2	3	0	1.0 ± 0.4	5	NA
Basin-transported	2.2	35	0	1.2 ± 0.2	18	NA
Local secondary	1.2	7	7	0.5 ± 0.1	15	NA
Other (3 sources)	2.7	6	0	3.6 ± 0.7	34	NA
RH-associated secondary	6.1	21	55		Not identified as a source	
Extinction-associated sulfate and OM	1.0	3	0		Not identified as a source	
Water		Not identified as a source		3.0 ± 1.0	2	100

Notes: [a]NA = not applicable; [b]Linear regression α value negative, attributed extinction is negligible.

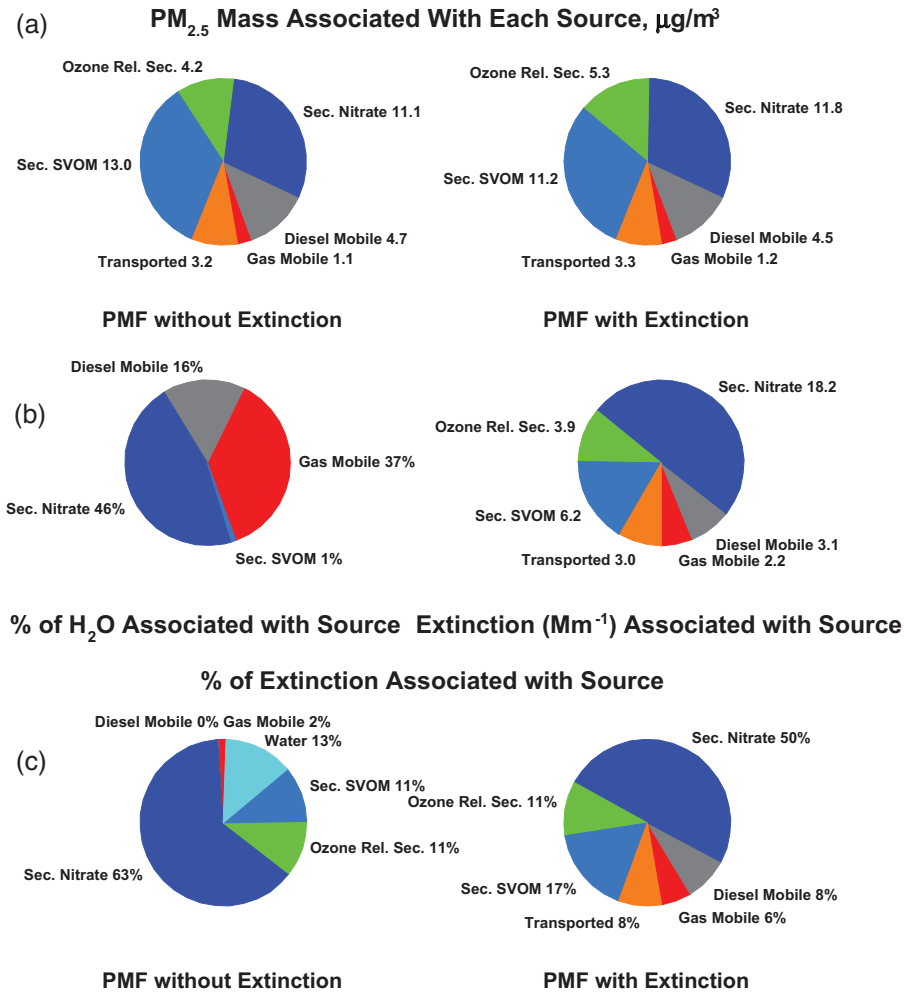

Figure 13. Pie chart comparisons using the Rubidoux 2003 data. Chart (a) shows the $PM_{2.5}$ mass associated with each source identified in the PMF with extinction and PMF without extinction analyses. The PMF results are from the conventional PMF. Chart (b) shows the percentage of modeled particulate water and Mm^{-1} of extinction associated with each factor for the PMF with extinction. Chart (c) shows the percentage of extinction associated with each source for the PMF without extinction and PMF with extinction.

summarized in Table 2 and Figure 12c. Figure 12b contains the Mm^{-1} and water contribution from PMF with extinction. Figure 12b and Table 2 help interpret the results in Figure 12c.

Source contributions using the two PMF methods are nearly identical. However, source contributions to extinction from the two approaches are different. This may result from PMF with extinction incorporating these values directly into the source apportionment analysis. The PMF without extinction assigns extinction contributions using eq 2 with quite different assumptions. Including the extinction data directly into PMF leads to a more robust result.

Contributions from secondary SVOM, ozone-related secondary, and wood smoke were omitted from the PMF without extinction pie in Figure 12c. The contributions calculated from eq 2 were negative and the uncertainty included zero (Table 2); therefore, the contribution from these sources was assigned a zero value. Thus, eq 2 gives results comparable to only a portion of the PMF with extinction sources and misses the contribution from other sources.

In Figure 12c PMF without extinction includes aerosol water because it is one of the fitting parameters in eq 2. Figure 12b suggests that this water extinction is present in gasoline mobile (44%), secondary nitrate (40%), and diesel mobile (14%). For the PMF with extinction, 42% of the extinction is associated with the gasoline mobile source and its accompanying water, 51% with secondary nitrate and its accompanying water, and 9% with the diesel mobile source and its accompanying water.

PMF Apportionment of Sources of $PM_{2.5}$ during the 2003 Rubidoux Study

The 2003 Rubidoux study was analyzed in a similar fashion to the Fresno study. Figure 1 compares the results from the conventional PMF and PMF with extinction analyses. Both methods identified six factors representing the same sources. The total measured mass is comparable to the modeled mass in the conventional

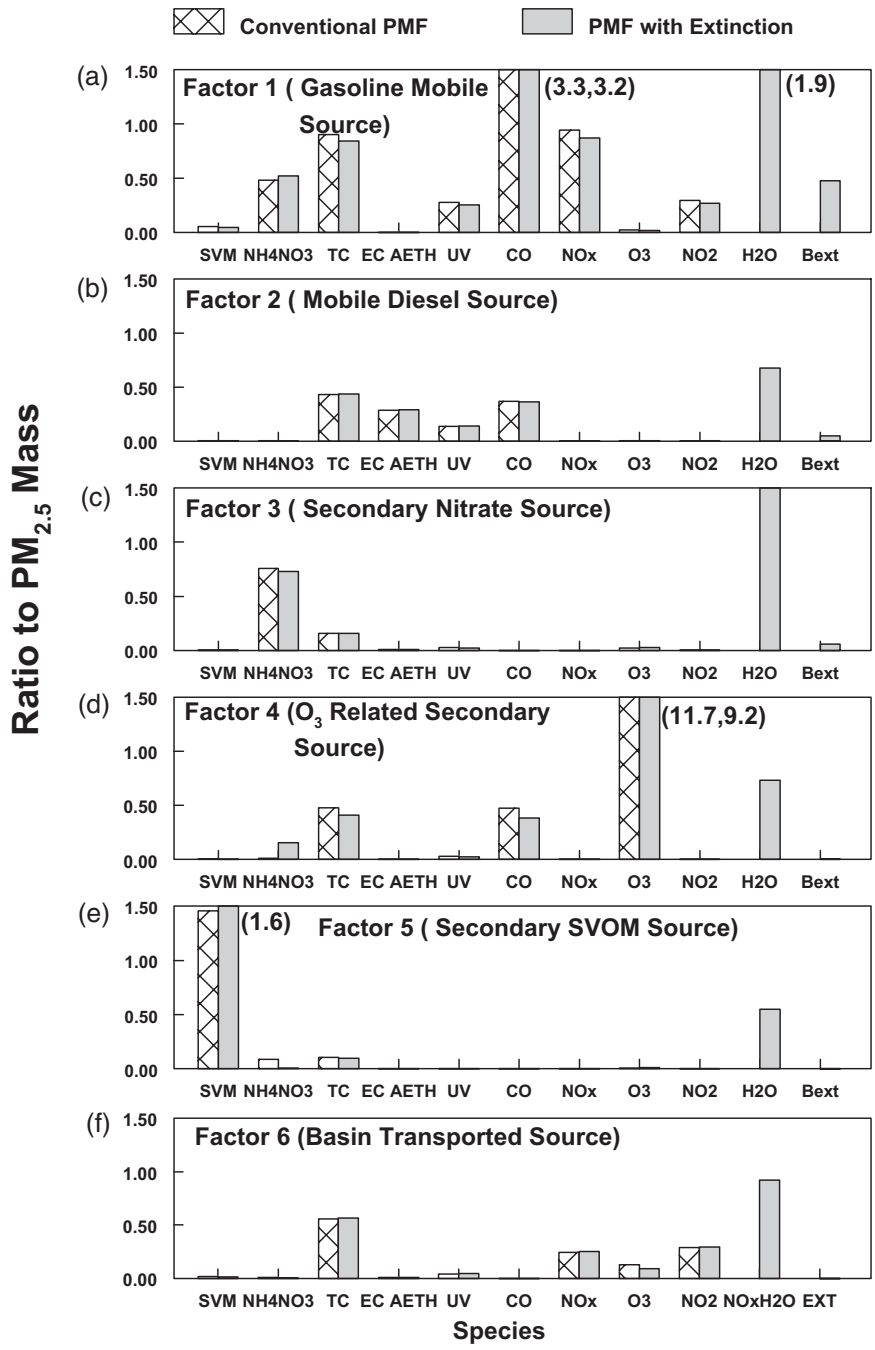

Figure 14. Factor profiles for the Rubidoux 2003 conventional PMF and PMF with extinction analyses. Units on all particulate components are $\mu g/m^3$. Units are ppm for CO, ppb for ozone, and ppb/20 for the other gases. Units for the extinction values are Mm^{-1}. Where a ratio exceeded the *y*-axis 1.5 maximum, the values are noted at the side of the bars. The factor profiles for the two analyses are comparable. Factors and sources include (a) factor 1, gasoline mobile; (b) factor 2, mobile diesel; (c) factor 3, secondary nitrate; (d) factor 4, ozone-related secondary; (e) factor 5, secondary SVOM; and (f) factor 6, basin-transported.

PMF and PMF with extinction analyses. There is somewhat poorer agreement between the PMF with extinction modeled and measured mass. This may be because of the high uncertainty of the low-resolution extinction data. Three sources—gasoline mobile, diesel mobile, and basin-transported—are associated with primary processes. Three sources—secondary nitrate, ozone-related secondary, and secondary SVOM—emanate from atmospheric secondary processes. The diurnal results and average concentrations shown in Figures 1 and 13a are nearly identical for the two PMF analyses. The PMF results for PMF without extinction being the same as the conventional PMF results except for the secondary nitrate and the secondary SVOM associated sources. This most likely is a result of the SVOM not being actually measured but inferred from the FDMS

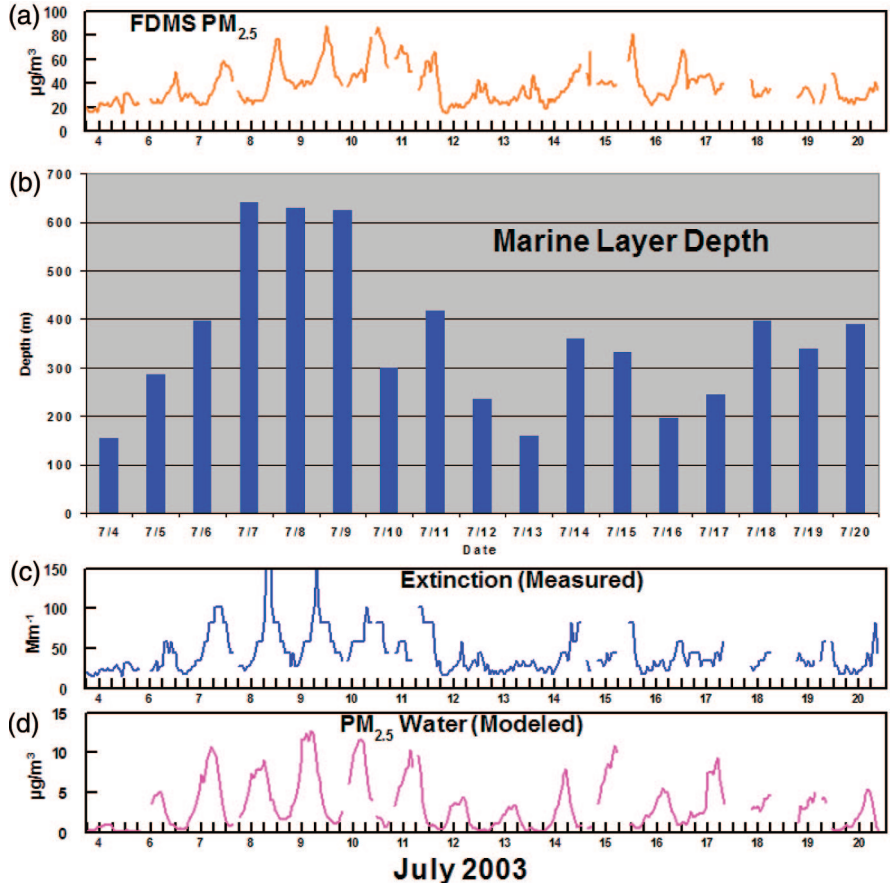

Figure 15. Four temporal graphs from July 4 to July 20, 2003 at Rubidoux. The graphs include (a) the FDMS $PM_{2.5}$, (b) marine layer depth, (c) the measured extinction converted from Riverside Municipal Airport ASOS hourly averaged visibility, and (d) the modeled $PM_{2.5}$ water associated with sulfate and nitrate aerosols. Note that when the marine layer depth deepened from July 7 to 9, the $PM_{2.5}$ mass, extinction, and modeled water also increased.

and TEOM data, making the analysis subject to the addition of the extinction and modeled aerosol water data in the PMF with extinction analysis. However, the source profiles are very comparable for the two analyses, as shown in Figure 14. The average concentrations of each factor for the two analyses are given in Figure 13a.

PM water and extinction associated with each factor for the PMF with extinction is shown in Figure 13b. Figures 1, 13a, and Table 2 show generally good agreement between the two PMF analyses. The major contributor to extinction, secondary nitrate, also had the most water. PMF with extinction provides mass extinction coefficients and the extinction associated with each factor (Table 2). Secondary nitrate and gasoline mobile have the highest calculated mass extinction coefficient.

The mass extinction coefficients from PMF with extinction (Table 1) are quite different from the Fresno study for three sources—gasoline mobile, secondary nitrate, and ozone-related secondary. The chemical compositions of these sources are similar. However, the mass extinction coefficient is a function of the particle size distribution of the aerosols, which may be quite different in the moist winter and dry summer studies. Particle size distribution is unavailable to directly confirm this hypothesis.

Figure 15 compares the boundary or mixed marine layer depth to the total $PM_{2.5}$ mass, measured extinction, and modeled water. All three variables increase as the marine layer depth increases. More stratus often leads to increased sulfate and nitrate species (heterogeneous droplet reactions). This increases the aerosol mass and extinction.

The results for the two PMF extinction budget approaches are in Figure 13c and Table 2. Figure 13b is the Mm^{-1} and water contribution using the PMF with extinction. Source apportionment results from the two approaches agree, but the extinction contributions are quite different.

PMF without extinction does not identify the transported source as a contributor to extinction. On the basis of the results obtained from the PMF with extinction (Figure 13b) assignment of the water source to the other sources in PMF without extinction attributes 7% of the extinction to the gasoline mobile source and its associated water. Likewise, 2% of the extinction is attributed to the diesel mobile source and its associated water, 69% of the extinction to secondary nitrate and its associated water,

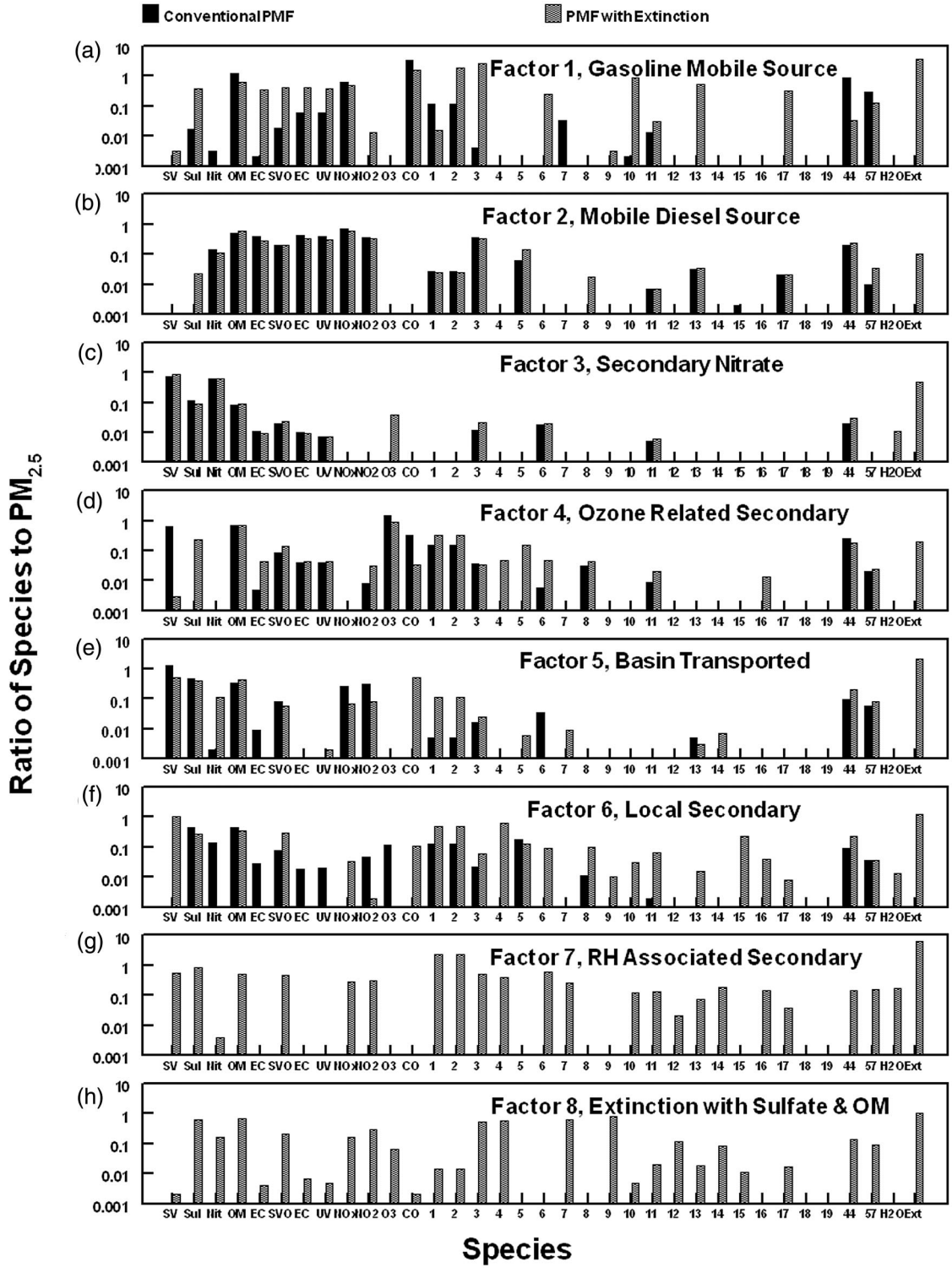

Figure 16. Factor profiles for the Riverside 2005 conventional PMF and PMF with extinction analyses. Units on all particulate components are $\mu g/m^3$. Units are ppm for CO, ppb for ozone, and ppb/20 for the other gases. Units for the extinction values are Mm^{-1}. Where a ratio exceeded the *y*-axis 1.5 maximum, the values are noted at the side of the bars. The six major source factor profiles for the two analyses are comparable. Factors and sources include (a) factor 1, gasoline mobile; (b) factor 2, mobile diesel; (c) factor 3, secondary nitrate; (d) factor 4, ozone-related secondary; (e) factor 5, basin-transported; and (f) factor 6, local secondary; (g) factor 7, RH-associated secondary; and (h) factor 8, extinction with sulfate and OM.

11% to the ozone-related secondary source, and 12% to the secondary SVOM source and its associated water. For PMF without extinction, the contribution of secondary nitrate to the total extinction is higher and the contribution of diesel mobile lower compared with the PMF with extinction analysis.

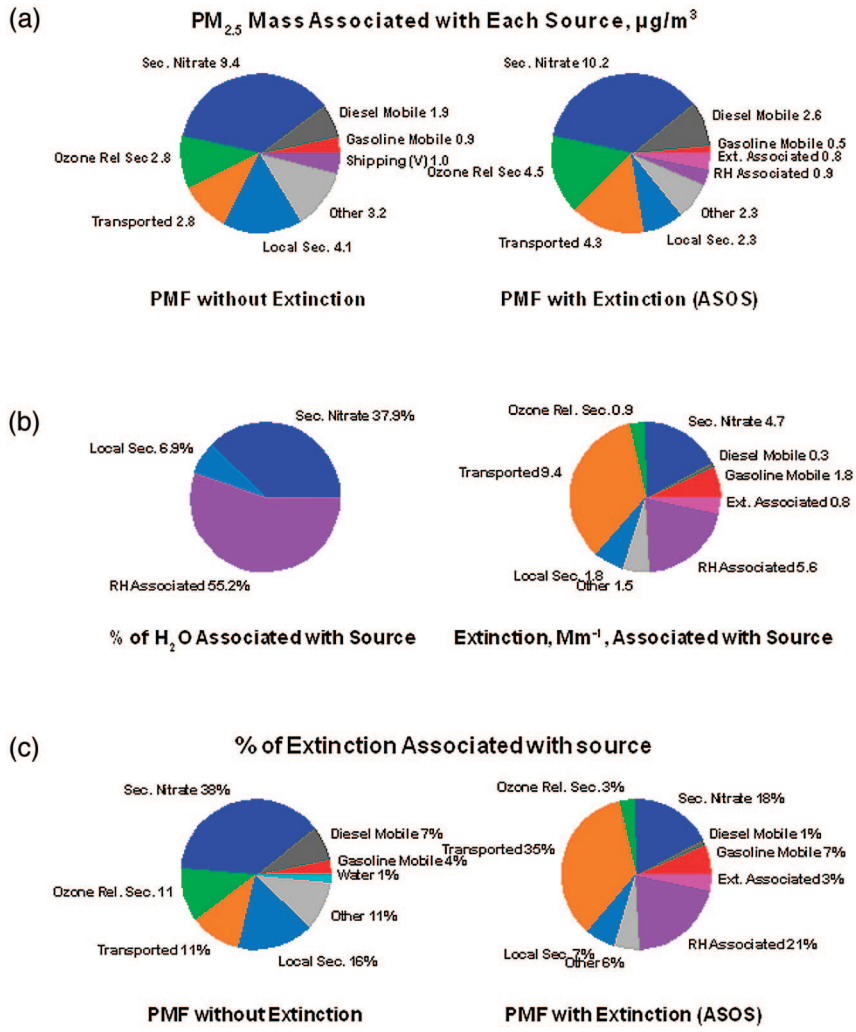

Figure 17. Pie charts comparisons using the Riverside 2005 data. Chart (a) shows the $PM_{2.5}$ mass associated with each source identified in the PMF with extinction and PMF without extinction analyses. Chart (b) shows the percentage of modeled particulate water and Mm^{-1} of extinction associated with each factor for the PMF with extinction. Chart (c) shows the percentage of extinction associated with each source for the PMF without extinction and PMF with extinction.

PMF Apportionment of $PM_{2.5}$ Sources during the 2005 Riverside Study

In the 2005 Riverside study, a total of 16 factors were identified using conventional PMF.[7] PMF with extinction missed some of the smaller sources, but added 2 new sources for a total of 11 factors. The named sources for each factor are based on the observed profile and diurnal patterns.[7] The six major factors and the two added new factors (Figure 3) had diurnal patterns and source profiles similar to the previously identified six major factors (Figure 16). However, the total mass assigned to each factor by PMF was somewhat different for the two solutions (Figures 3 and 17a). This was particularly true for the local secondary and transported sources, both with significant SVOM. Generally, these differences were associated with the specific assignment of secondary mass (especially SVOM) in the PMF solutions. The first six factors represent the same sources, with or without inclusion of the extinction and water data, and with the total measured mass agreeing with the PMF modeled mass in both analyses (Table 1).

The PMF with extinction RH secondary source is dominated by nitrate, sulfate, and organic matter (OM). These species are formed during the night, probably by heterogeneous mechanisms, when RH (and therefore fine particulate water content) is elevated. Thus, the temporal profile for the PMF with extinction S7, RH secondary, is similar to that of the extinction with sulfate and OM S8 profile, which is also associated with the modeled fine particulate water given in Figure 7.

The PMF with Extinction S7, RH secondary contains the ATOFMS aerosol types (14 and 16) that are high vanadium (V) and are probably associated with refinery or shipping emissions from operations at the Port of Los Angeles.[7] Two sources with high V were identified in conventional PMF. Because of the importance of water in these emissions, they appear as a single factor in the PMF with extinction analysis. In contrast, S8 is associated with

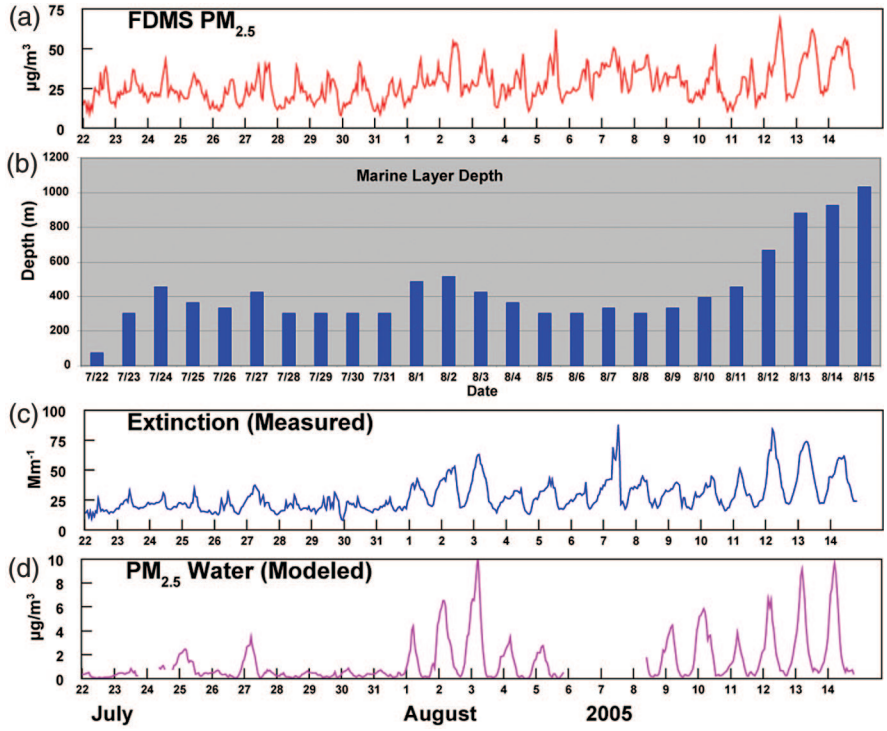

Figure 18. Four temporal graphs from July 22 to August 15, 2005 on the UCR campus. The graphs include (a) the FDMS $PM_{2.5}$, (b) marine layer depth, (c) the measured extinction, and (d) the modeled $PM_{2.5}$ water associated with sulfate and nitrate aerosols. During this period, the marine layer remained fairly constant except from August 12–15. Note the mass extinction and modeled aerosol water increases during this period.

the formation of sulfate and OM (but not nitrate) during the day when RH (and hence, fine particulate water content) is low (25–50%) and the concentrations of this source are probably due to homogeneous gas-phase photochemical formation mechanisms. The identification of these two sources on the basis of the RH and extinction data is most likely the reason three of the smaller sources defined by the ATOFMS data could not be identified in the PMF with extinction analysis.

The contribution of the various sources to the total $PM_{2.5}$ is summarized in Figure 17a, and the contribution of PM water and extinction to each factor are given in Figure 17, b and c. The two highest contributors to extinction—basin-transported and RH—probably resulted from aged emissions that originated from Los Angeles port operations. Both result from secondary species formed as they are being transported across the Los Angeles Basin.

PMF with extinction provides mass extinction coefficients and the extinction associated with each factor (Figure 1). The major contributors to extinction are basin-transported, RH secondary, and secondary nitrate.

Figure 18 compares the measured marine layer depth to the measured $PM_{2.5}$ mass, extinction, and modeled water. During most of the study, the marine layer remained relatively constant (400 m); however, toward the end of the study a weak upper low off the coast increased the marine layer depth to approximately 1000 m. The increased mixed layer led to dilution of chemical species. However, some of the highest mass and extinction were recorded during this brief period. Most likely, the increased stratus clouds throughout the basin led to accelerated production of sulfate and nitrate aerosols.

The PMF with extinction and PMF without extinction for the Riverside 2005 study are compared in Figure 17, b and c, and Table 2. PMF without extinction shows water is a minor contributor to extinction (Figure 17b). Thus, source apportionment results from the two approaches are similar, whereas the extinction contributions are quite different.

CONCLUSIONS

This study illustrates the direct incorporation of fine particulate water content and extinction data into a PMF source apportionment analysis in the 2003 and 2005 studies in the Riverside, and 2003 studies in Fresno, CA. These analyses techniques allowed direct identification of sources responsible for observed visibility degradation.

The PMF with extinction analysis provides more robust results for attribution of extinction to sources than PMF without extinction. Even using hourly average data in the source apportionment analysis to increase the robustness of the analysis, not all contributing sources can be identified by PMF without extinction using eq 2. Thus, this novel approach is superior to prior methods used to apportion extinction to sources. In contrast, the apportionment of the mass of sources is not significantly dependent on the approach used. Visibility impairment was dominated by contributions from secondary aerosols at

all three sites. The source associated with automobile emissions had a high-calculated mass extinction coefficient in all three studies. The role of water was also important at all three sites, with the contribution of water to visibility degradation being dominated by water associated with secondary aerosols. A strong correlation was found for the studies in the Los Angeles Basin between marine layer depth, modeled aerosol water content, and extinction and the formation of secondary inorganic aerosol components. Thus, the role of meteorology to extinction was observed from these results. In all three studies, the concentrations of particulate matter from diesel mobile was higher than gasoline mobile, but the predicted visibility degradation from gasoline combustion automobile sources was higher because of a higher mass absorption coefficient.

These observations illustrate the usefulness of the PMF with extinction approach. The method allows the identification of primary and secondary source contributors to extinction and identification of those sources where extinction is increased because of the influence of particulate associated water. It is recommended that experimental extinction and estimated aerosol water content should be integrated directly into source apportionment analyses when attributing modeled extinction to these sources.

Differences in the calculated mass extinction coefficients between the Rubidoux and Fresno studies reflect the various identified sources, differences in the assignment of water to sources in the richer Fresno dataset, and probable differences in particle size distribution for a given source between the two studies.

The PMF with extinction analysis including measured extinction and modeled aerosol water content studies provided the statistics for each PMF solution found in Table 1; the results are summarized in Table 2. As indicated in Figures 3, 9, and 10, and Table 1, the total experimental $PM_{2.5}$ mass was well represented by the PMF solution for the Riverside and Fresno sites. However, the uncertainty in this comparison was much higher for the Rubidoux site (Figures 1 and 9 and Table 1). This can be attributed to the much higher uncertainly in the low-resolution extinction data. In all cases, comparison of the experimental- and PMF-calculated total mass centered around the slope being equal to 1 line. Deviations between the experimental- and PMF-calculated total mass for each data point had a Gaussian distribution.

The results are comparable to those for Fresno and Rubidoux. However, the PMF with extinction analysis includes two sources that are unique to that analysis and therefore could not be identified in the PMF without extinction analysis. These are the extinction sources associated with homogeneous day formation of secondary material and the RH source associated with heterogeneous night formation of secondary material from port-related emissions.

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