

## **APPENDIX VII**

### **PM<sub>2.5</sub> Source Apportionment for the South Coast Air Basin Using Chemical Mass Balance Receptor Model**

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#### I. Introduction

Fine particulate matter (PM<sub>2.5</sub>) is a public health concern. Due to its small size (less than 2.5 micrometers in diameter), PM<sub>2.5</sub> can deposit into the lungs. Recent studies have associated PM<sub>2.5</sub> exposure with increased mortality and morbidity due to cardio-respiratory diseases and lung cancer (Laden et al, 2000, Wichmann et al., 2000, Borja-Aburto et al., 1998). Recent studies also characterize gasoline and diesel exhaust as one of the major sources of PM<sub>2.5</sub> mass concentrations; however, their contributions vary from area to area and from time to time (Zheng et al., 2002, Lough et al., 2006, and Chow et al., 2007).

With the projected increase in population and growth in sources, in addition to secondary PM<sub>2.5</sub> formation and new, more stringent PM<sub>2.5</sub> federal and state standards, a regulatory program that reflects an understanding of PM<sub>2.5</sub> source contributions to ambient air is critical. While numerous Chemical Mass Balance (CMB) studies on PM<sub>2.5</sub> source apportionment have appeared in the literature during the last ten years, these studies either applied limited or outdated ambient air sampling data, or their analyses are not directly applicable to the South Coast Air Basin (Basin) (Schauer et al., 2002, Lough et al., 2006, Lee, 2006, and Chow et al., 2007). A study using the most recent and intensive PM<sub>2.5</sub> air sampling to differentiate major sources of PM<sub>2.5</sub> in ambient air, especially mobile source diesel and gasoline exhaust, is necessary for the Basin. Due to the uncertainty from multiplying the elemental carbon (EC) concentrations by a factor of 1.04 to estimate diesel particulate matter for cancer risk assessment in the previous Multiple Air Toxic Exposure Study (MATES II), the SCAQMD Air Toxic Study Technical Review Group recommended the use of Chemical Mass Balance (CMB) and Positive Matrix Factorization (PMF) receptor models to estimate diesel contributions.

In this study, PM<sub>2.5</sub> source apportionment for the Basin was conducted using the CMB receptor model 8.2 approved by the US EPA and the MATES III ambient data collected over a two-year period from March 2004 to April 2006 at various fixed stations across the Basin. In particular, gasoline and diesel-vehicle contributions were differentiated with the use of organic compounds (Chow et al., 2007). However, in this context, the contributions of other primary sources to ambient PM<sub>2.5</sub> mass concentrations: biomass burning, cooking operations, sea salt, geological, residual oil burning, and limestone were also estimated.

#### MATES III Source Apportionment

##### CMB Model

The CMB model was first developed by Miller et al. (1972) and further refined by Friedlander (1973) and Watson (1979). The CMB model, which uses selected chemical species as mass balance fitting species, is a tool to estimate source contributions. The ambient concentration of chemical species *i* is expressed as a linear equation:

$$C_i = \sum_{j=1}^p a_{ij} S_j, i=1,n$$

Where  $a_{ij}$  is fractional concentration of chemical species  $i$  in source  $j$ ,  $S_j$  is total mass concentration contributed by source  $j$ ,  $p$  is number of sources, and  $n$  is number of species.

Since the number of chemical species,  $n$ , is usually larger than the number of sources,  $p$ , the system is over-determined and the least-squares fitting approach is applied. The model requires the identification of emission sources, the selection of chemical species and source profiles and the estimation of ambient data and source profile uncertainty. Input uncertainty is critical to the model since it determines the importance of input data to the model solutions (EPA, 2004).

### **MATES III Ambient Data**

In this study, monthly-averaged ambient data from samples collected at the ten fixed MATES III sites [Wilmington (WI), Long Beach (LB), Compton (CP), Huntington Park (HP), Pico Rivera (PR), Los Angeles (LA), Burbank (BU), Fontana (FO), Rubidoux (RU), and Anaheim (AN)] were utilized. Sampling was conducted every three days over a two-year period from March 2004 to April 2006. Since October 2004 through February 2005 (with 56 rainy days and 24.2 to 33.9 inches of rain in Los Angeles and Long Beach per National Climatic Data Center) was not considered a typical winter season for the Basin, MATES III sampling program was extended one more year to April 2006. During the second year (2005-2006), sampling was not conducted in Pico Rivera and Huntington Park for a full year. EC, organic carbon (OC), ions, metals, and monthly-composite organics samples were analyzed. Details of the sites and sampling protocols are given in Chapter 2.

### **Selected Source Profiles**

Before selecting the source profiles, available and pertinent previous studies were reviewed. Great care was made to ensure that the chosen source profiles represented the Basin and therefore were most applicable for this study. The following source profiles for the MATES III source apportionment model and their basis for selection are as follows:

- Ammonium Nitrate and Ammonium Sulfate Profiles:

The secondary ammonium nitrate and sulfate profiles developed for use in the Fresno Supersite Study (Chow et al., 2007).

- Biomass Burning Profile:

A biomass burning profile developed for the Basin (Schauer, 1998) was based on the testing of residential fireplaces burning oak wood. The mass fraction of levoglucosan in this profile ( $0.138 \pm 0.0001$ ) is similar to the level of levoglucosan in Fine's combined profile (Fine, 2002) for fireplace and woodstove combustion ( $0.126 \pm 0.0002$ ).

In addition, another biomass burning profile that was developed by Desert Research Institute (DRI) for use in the Fresno Supersite Study (Chow et al., 2007) was also applied to the Los Angeles, Wilmington, and Rubidoux CMB source apportionment for comparison purposes.

- **Meat Cooking Profile:**

A meat cooking profile developed by Zielinska et al. (1998) for the Northern Front Range Air Quality Study (NFRAQS) to characterize ambient emissions in North Colorado. However, this profile was based on testing conducted in the Basin. This profile contains average data from charbroiling chicken with skin on.
- **Diesel-Vehicle Exhaust Profile:**

A diesel motor-vehicle profile developed during summer 2001 for the Basin (Fujita et al., 2006), and was normalized to PM<sub>2.5</sub> mass for use in the Fresno Supersite Study (Chow et al., 2007). This profile was based on the testing of 34 diesel vehicles of various vehicle weights and model years operated under various cycles.
- **Gasoline-Vehicle Exhaust Profile:**

A gasoline motor-vehicle profile developed for the Basin (Fujita et al., 2006) and was normalized to PM<sub>2.5</sub> mass (Chow et al., 2007). This profile was based on the testing of 57 gasoline vehicles of various model years and mileages operated under various cycles.

In addition, another profile (Zielinska et al., 1998) developed during summer 1996 for the NFRAQS was also selected. This profile was based on the testing of 111 gasoline vehicles under various operating cycles. Since mobile source emissions vary upon ambient temperature (Mathis et al., 2005), fuel use, engine, driving modes, and lubricating oil (Lough and Schauer, 2005), the differences in fleet composition and ambient temperature were recognized. Therefore, both gasoline profiles were utilized for the analysis and a range for motor gasoline exhaust contribution was provided.
- **Sea Salt Profile:**

An “aged” sea salt profile developed by Chow et al., (1996), which reflects a reaction of sea salt and nitric acid (HNO<sub>3</sub>) where 0.5 mole of chlorine (Cl) was replaced by one mole of nitrate (NO<sub>3</sub><sup>-</sup>).
- **Geological Profile:**

A geological profile developed by Chow et al. (2003) from paved road suspended dust samples collected in the San Joaquin Valley. The mass fractions (0.052 ± 0.01) of iron (Fe) and (0.035 ± 0.01) of calcium (Ca) in this profile are similar to those in Cooper et al.’s profile (1987) developed for the Basin (0.052 ± 0.02 for Fe and 0.035 ± 0.01 for Ca). Fe and Ca were two of the three selected fitting species for geological apportionment in the MATES III CMB.
- **Residual Oil Burning Profile:**

A residual oil burning profile developed for the Basin (1987) based on samples collected from a residual oil-fired boiler at a power plant in the Basin. Residual oil burning is mainly used in ships (Corbett and Fischbeck, 1997). Although vanadium concentration in residual oil is minimal compared to that of sulfur, vanadium is a unique species to characterize ship PM emissions.

### Selected Fitting Species

Fitting species were pre-selected based on information from previous studies and further screened based on their correlation coefficients and ambient concentrations. Species with higher ambient concentrations than their uncertainties and species with high correlation coefficients (correlation coefficients  $\geq 0.8$ ) were selected; however, the ambient concentration criteria was not strictly applied to levoglucosan, cholesterol, palmitoleic acid, coronene, indeno [123-cd]pyrene, and benzo(ghi) perylene, which often have low ambient concentrations.

The following were selected fitting species for the MATES III source apportionment categorized by their major sources:

- Ammonium nitrate and ammonium sulfate:  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$ ;
- Biomass burning: Levoglucosan and potassium (K);
- Meat cooking: Cholesterol and palmitoleic acid;
- Diesel-vehicle exhaust EC;
- Gasoline-vehicle exhaust;
- Indeno[123-cd]pyrene, benzo(ghi)perylene, coronene;
- Steranes 48 and 49;
- Hopanes 17,19, 24, and 26;
- Sea salt: sodium ( $\text{Na}^+$ ) and chlorine ( $\text{Cl}^-$ );
- Geological: Silica (Si), calcium (Ca), and iron (Fe); and
- Residual oil burning: Vanadium (V) and nickel (Ni).

Organic carbon (OC) was not used in the CMB analysis because measured ambient OC is believed to be significantly biased. The flow rate of OC measurement (6.7 lpm) for the new PM sampler, SASS used in the MATES III, was approximately three times slower than that (20 lpm) of the Multi-Channel Fine Particulate (MCFP) sampling system, which was designed to properly account for positive organic artifact formation during sampling for the  $\text{PM}_{10}$  Technical Enhancement Program (PTEP) and previous MATES II. Slower flow rate in SASS sampler reduces pressure drop through the sampler and increases the adsorption of organic vapor on filter medium; therefore, OC measured by SASS sampler is significantly higher than that measured by the MCFP sampler. While  $\text{PM}_{2.5}$  mass decreased 20 – 40% in 2004 compared to the 1995 ambient data, EC decreased 50 – 57%, nitrate decreased 30 – 54%, and sulfate decreased 11-25%, only organic carbon increased 13 to 50%. Since the SASS sampler was not designed to account for positive OC artifact, this bias was not corrected. In addition, since the quartz filters were not baked prior to their use, additional small amount of OC was added to the already high OC concentration in MATES III.

## II. Results and Discussion

The following  $\text{PM}_{2.5}$  source apportionment was conducted independently for both years, but using the same source profiles and fitting species.

***April 2004 – March 2005 (First Year) PM<sub>2.5</sub> Source Apportionment***

As stated earlier, gasoline profiles for both the NFRAQS and the Basin were used in two CMB estimates, holding all other source profiles the same.

Monthly CMB source apportionment for the ten fixed sites were conducted by targeting R<sup>2</sup> values of 0.8 to 1.0, Chi<sup>2</sup> values of less than 4.0, and differences between calculated and measured PM<sub>2.5</sub> mass of less than 20%.

The MPIN (modified pseudo-inverse matrix) diagnostic, an option to identify influential chemical species (Kim and Henry, 1989) shows that EC (with normalized MPIN absolute value of 1.0) is the most influential chemical species for diesel-vehicle exhaust, while the three PAHs (with absolute values  $\geq 0.5$ ): indeno [123-cd]pyrene, benzo(ghi) perylene, and coronene found in used gasoline motor oil, and sterane 48 found in engine lubricating oil (Fujita et al., 2006) are most influential species to gasoline-vehicle exhaust in this model.

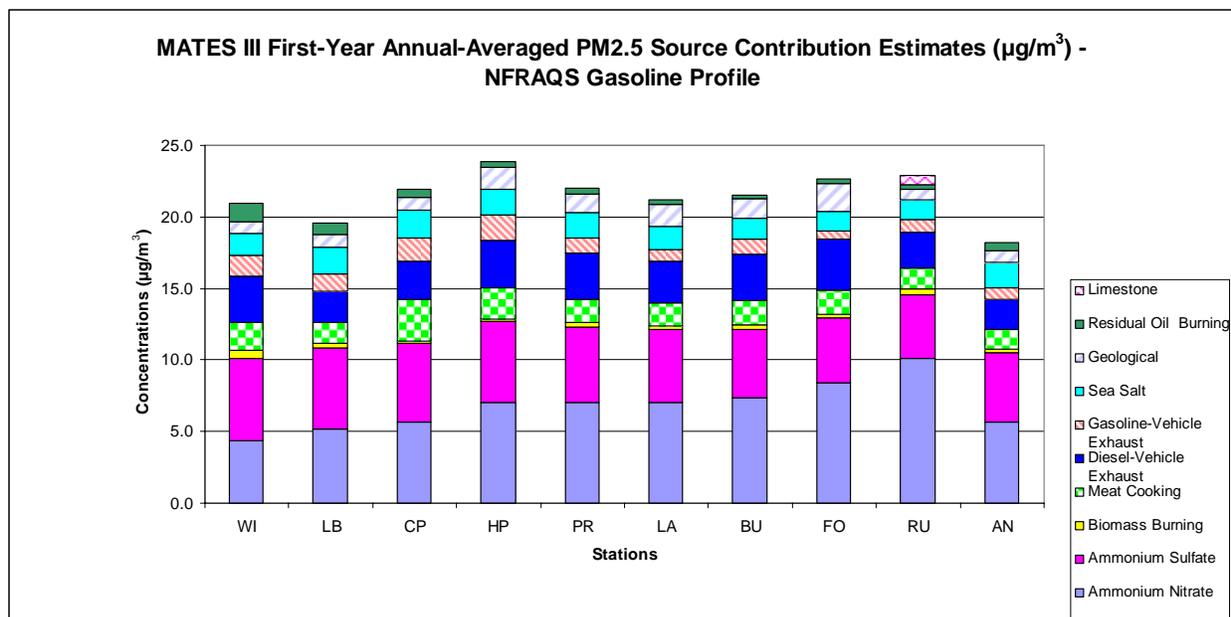
***With the NFRAQS Gasoline Profile***

The annual-averaged source contribution estimates of major PM<sub>2.5</sub> source categories and their percentages of the total predicted mass are summarized in Table 1 and Figure 1.

**Table 1**  
**MATES III First-Year Annual-Averaged PM<sub>2.5</sub> Source Contribution Estimates in  $\mu\text{g}/\text{m}^3$  –**  
**NFRAQS Gasoline Profile**

	WI	LB	CP	HP	PR	LA	BU	FO	RU	AN	10-Site Ave.
Ammonium Nitrate	4.40 (21.0)	5.14 (26.2)	5.69 (26.0)	7.00 (29.3)	7.03 (32.0)	7.04 (33.2)	7.33 (34.0)	8.43 (37.2)	10.08 (44.0)	5.70 (31.3)	6.78 (30.7)
Ammonium Sulfate	5.73 (27.4)	5.71 (29.1)	5.47 (25.0)	5.73 (24.0)	5.25 (23.9)	5.09 (24.0)	4.78 (22.2)	4.55 (20.1)	4.51 (19.7)	4.82 (26.5)	5.16 (23.3)
Biomass Burning	0.56 (2.7)	0.28 (1.4)	0.20 (0.9)	0.15 (0.6)	0.34 (1.6)	0.28 (1.3)	0.33 (1.5)	0.22 (1.0)	0.38 (1.6)	0.22 (1.2)	0.30 (1.3)
Meat Cooking	1.93 (9.2)	1.49 (7.6)	2.88 (13.2)	2.17 (9.1)	1.59 (7.2)	1.61 (7.6)	1.76 (8.2)	1.72 (7.6)	1.44 (6.3)	1.39 (7.6)	1.80 (8.1)
Diesel-Vehicle Exhaust	3.25 (15.5)	2.20 (11.2)	2.67 (12.2)	3.34 (14.0)	3.30 (15.0)	2.85 (13.4)	3.18 (14.8)	3.51 (15.5)	2.54 (11.1)	2.10 (11.5)	2.89 (13.1)
Gasoline-Vehicle Exhaust	1.42 (6.8)	1.24 (6.3)	1.63 (7.4)	1.75 (7.3)	1.05 (4.8)	0.87 (4.1)	1.06 (4.9)	0.60 (2.7)	0.85 (3.7)	0.83 (4.6)	1.13 (5.1)
Sea Salt	1.58 (7.5)	1.84 (9.4)	1.90 (8.7)	1.79 (7.5)	1.76 (8.0)	1.64 (7.7)	1.47 (6.8)	1.33 (5.9)	1.38 (6.0)	1.76 (9.7)	1.64 (7.4)
Geological	0.79 (3.8)	0.87 (4.5)	0.95 (4.3)	1.49 (6.3)	1.26 (5.8)	1.49 (7.0)	1.35 (6.3)	2.00 (8.8)	0.78 (3.4)	0.85 (4.7)	1.19 (5.4)
Residual Oil Burning	1.28 (6.1)	0.83 (4.2)	0.52 (2.4)	0.43 (1.8)	0.39 (1.8)	0.33 (1.5)	0.29 (1.4)	0.28 (1.2)	0.27 (1.2)	0.53 (2.9)	0.51 (2.3)
Limestone									0.71 (3.1)		0.71 (3.1)
Predicted Mass	20.94	19.59	21.91	23.85	21.98	21.20	21.55	22.64	22.93	18.20	22.12
Measured Mass	17.72	18.41	19.34	22.20	20.60	19.38	21.21	21.35	23.54	17.55	20.13

Italic, bold values in ( ) are the percentages of predicted mass



**Figure 1**

The CMB estimated PM<sub>2.5</sub> mass contributions range from 18.20 to 23.85 µg/m<sup>3</sup> across the Basin. Major source contributors are ammonium nitrate (4.40 – 10.08 µg/m<sup>3</sup>, 21 - 44%), ammonium sulfate (4.51 – 5.73 µg/m<sup>3</sup>, 19.7 – 27.4%), biomass burning (0.15 – 0.56 µg/m<sup>3</sup>, 0.6 – 2.7%), cooking operations (1.39 – 2.88 µg/m<sup>3</sup>, 7.6 – 13.2%), diesel-vehicle exhaust (2.10 – 3.51 µg/m<sup>3</sup>, 11.6 – 15.5%), gasoline-vehicle exhaust (0.6 – 1.75 µg/m<sup>3</sup>, 2.7 – 7.3%), sea salt (1.33 -1.9 µg/m<sup>3</sup>, 5.9 – 8.7%), geological (0.78 – 2.0 µg/m<sup>3</sup>, 3.4 – 8.8%), residual oil burning (0.27 – 1.28 µg/m<sup>3</sup>, 1.2 – 6.1%), and limestone (0.71 µg/m<sup>3</sup>, 3.1%).

Ammonium nitrate displays a strong spatial variation, with high contributions inland and low contributions in coastal areas. Ammonium nitrate varies between 4.4 µg/m<sup>3</sup> (21%) in Wilmington and 10.08 µg/m<sup>3</sup> (44%) in Rubidoux. Nitric acid concentration increases to the highest level at Diamond Bar that is located upwind of a dense array of dairy ammonia source (Kim et. al., 2000). Then most of the nitric acid is neutralized by ammonia while transported to downwind locations that results in high ammonium nitrate contribution in Rubidoux.

Ammonium sulfate also shows a strong spatial variation, but in opposite to ammonium nitrate, with high contributions in coastal areas and low contributions inland. Ammonium sulfate varies between 5.73 µg/m<sup>3</sup> (27.4%) in Wilmington and 4.51 µg/m<sup>3</sup> (19.7%) in Rubidoux. Greater relative humidity (RH ≥ 75%) at the coastal sites and the importance of the aqueous-phase sulfate chemistry at high RH may explain the higher sulfate contributions at coastal sites.

Biomass burning does not show a clear spatial variation. The highest contribution is observed at Wilmington (0.56 µg/m<sup>3</sup>, 2.7%) and the lowest contribution is observed at Huntington Park (0.15 µg/m<sup>3</sup>, 0.6%). Annual-averaged biomass burning contributions across the Basin (1.4 – 5.2 % of total anthropogenic primary PM<sub>2.5</sub> mass) are lower than the 2005 AQMP's annual-averaged inventory (7.5 % of total primary PM<sub>2.5</sub> emissions).

Another biomass burning profile that was developed by DRI for use in the Fresno Supersite study was applied to the CMB analysis for comparison purposes. In general, contributions of all

source categories are affected slightly by this profile, except biomass burning. Figures 2, 3, and 4, respectively show that biomass burning contributions for Los Angeles, Wilmington, and Rubidoux using the DRI profile are approximately two times greater than the current contributions using the Basin profile (Schauer, 1998). However, the CMB model performance statistic, that is the chi-square values generated from using the DRI profile, are roughly 1.5 times greater than that from using the Basin profile. The biomass burning contribution of  $0.72 \mu\text{g}/\text{m}^3$  in Rubidoux using the DRI profile (vs.  $0.38 \mu\text{g}/\text{m}^3$  using the Basin profile) is similar to the  $0.79 \mu\text{g}/\text{m}^3$  estimated by the PMF for data collected between 2001 and 2004 at USEPA Speciation Trends Network monitoring site in Rubidoux (Kim and Hopke, 2007). However, the four-month averaged biomass burning contribution of  $0.84 \mu\text{g}/\text{m}^3$  from November to February in Rubidoux using the DRI profile (vs.  $0.36 \mu\text{g}/\text{m}^3$  using the Basin profile) is lower than ARB's  $1.8 - 2.2 \mu\text{g}/\text{m}^3$  estimated by their 1995 CMB and 2005 PMF models, respectively (ARB, 2007).

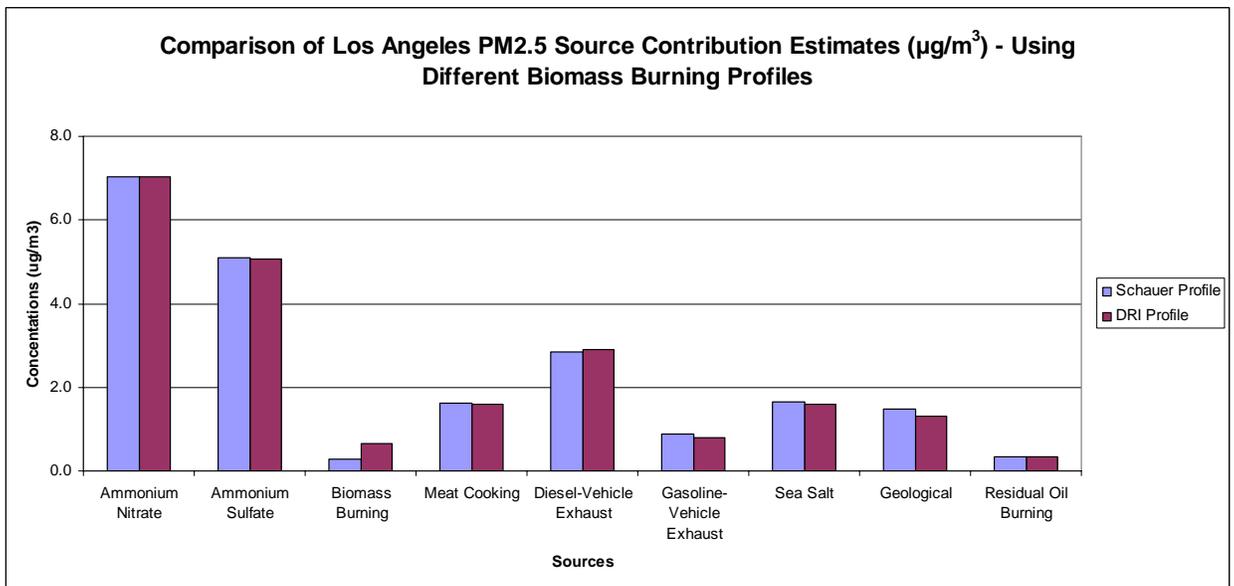


Figure 2

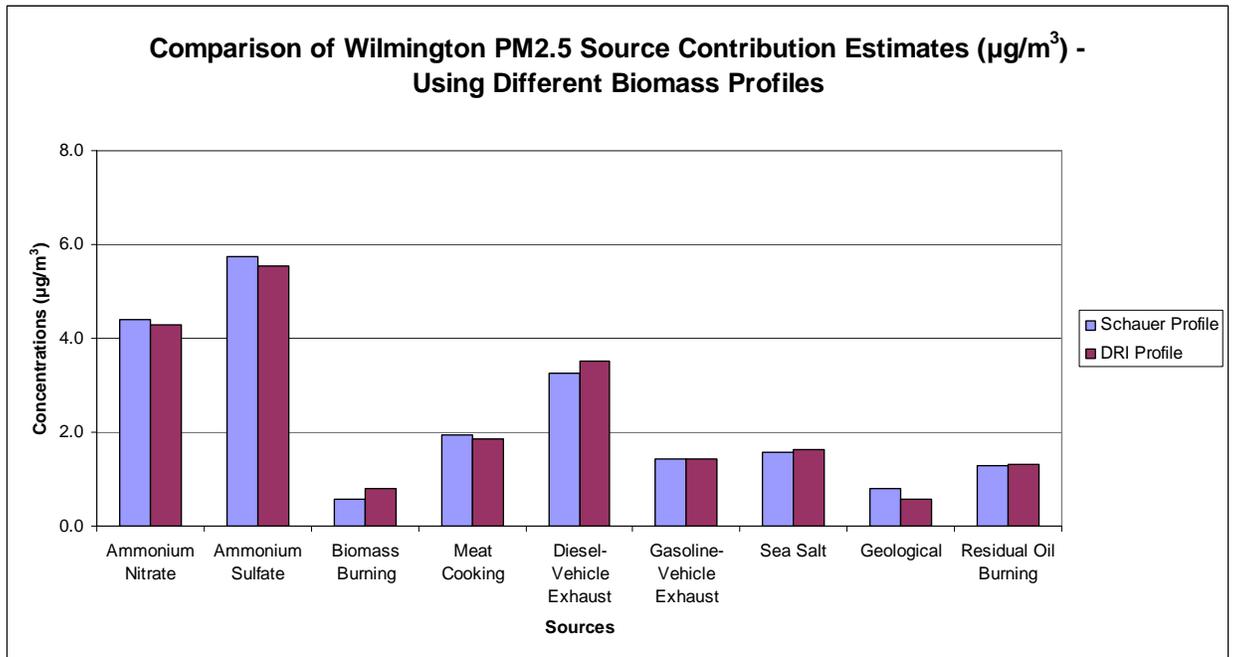


Figure 3

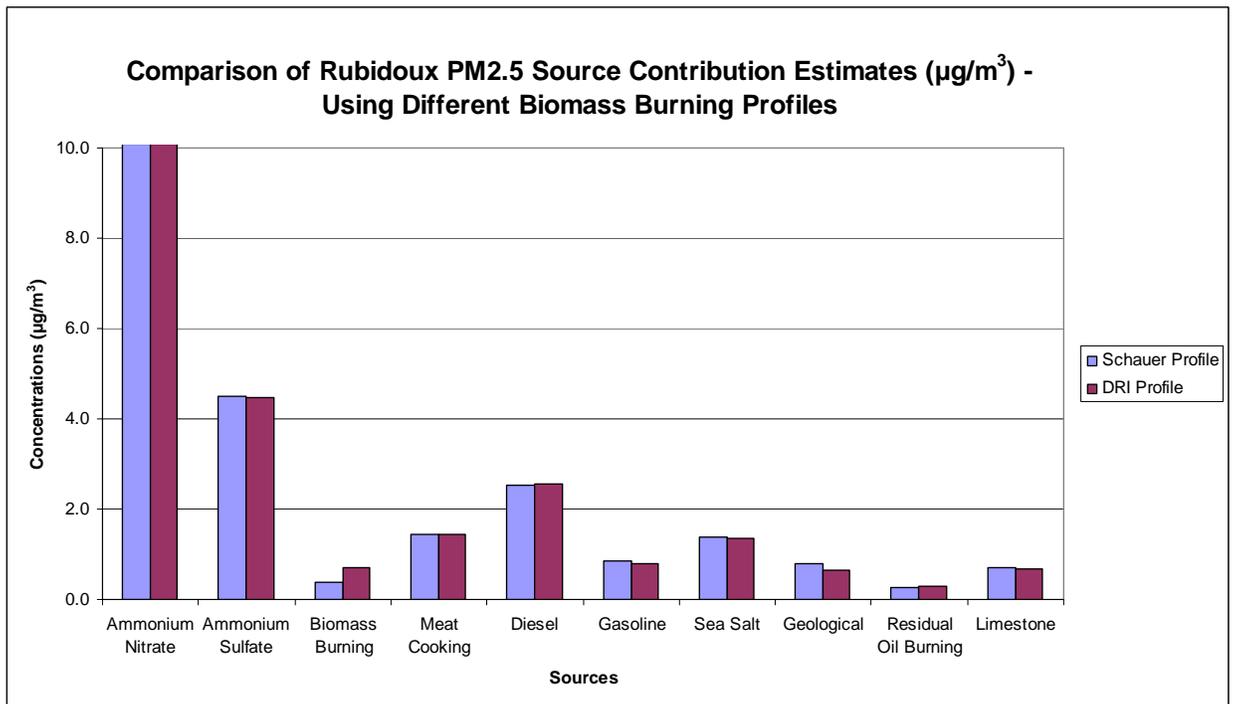


Figure 4

Meat cooking operations do not display a clear spatial variation either. The highest contribution is observed at Compton (2.88 µg/m³, 13.2%) and the lowest contribution is observed at Anaheim (1.39 µg/m³, 7.6%). The highest cooking concentration at Compton may be biased since the

monitoring station is located above the county fire station where cooking activities might occur during the sampling period.

Diesel-vehicle exhaust displays high contributions in Wilmington ( $3.25 \mu\text{g}/\text{m}^3$ , 15.5%), which is within close proximity to the ports and cargo distribution centers, and at industrial areas, such as Huntington Park ( $3.34 \mu\text{g}/\text{m}^3$ , 14%), Burbank ( $3.18 \mu\text{g}/\text{m}^3$ , 14.8%), Fontana ( $3.51 \mu\text{g}/\text{m}^3$ , 15.5%), and Pico Rivera ( $3.3 \mu\text{g}/\text{m}^3$ , 15%) where heavy diesel-truck traffic occurs. The lowest diesel contribution is observed at Anaheim ( $2.10 \mu\text{g}/\text{m}^3$ , 11.5%).

The highest gasoline-vehicle exhaust contribution is observed at Huntington Park ( $1.75 \mu\text{g}/\text{m}^3$ , 7.3%) and the lowest contribution is observed at Fontana ( $0.60 \mu\text{g}/\text{m}^3$ , 2.7%). Gasoline-vehicle exhaust displays higher contributions at the ports and in more urbanized areas where dense population and heavy gasoline-vehicle traffic are located. Gasoline exhaust estimate for Los Angeles ( $0.87 \mu\text{g}/\text{m}^3$ , 4.1%) is relatively lower than other urbanized areas.

The ratios of diesel to gasoline-vehicle contributions across the Basin vary from 1.64 in Compton to 5.80 in Fontana. The average diesel to gasoline ratio for all stations is 2.56, which is within the range of the 2007 AQMP diesel-gasoline emissions ratio of 1.90 and the ratio of 2.68 calculated from Fujita et al.'s (2006) emission factors.

Sea salt contributions show a spatial variation with high contributions in coastal areas and low contributions inland. The highest contribution is observed at Compton ( $1.90 \mu\text{g}/\text{m}^3$ , 8.7%) and the lowest contribution is observed in Fontana ( $1.33 \mu\text{g}/\text{m}^3$ , 5.9%).

Geological contributions show a strong spatial variation with low contributions in coastal areas and high contributions inland. Lowest contribution is observed at Wilmington ( $0.79 \mu\text{g}/\text{m}^3$ , 3.8%) and highest contribution ( $2.0 \mu\text{g}/\text{m}^3$ , 8.8%) is observed at Fontana where high levels of construction activity occur in addition to higher winds causing more re-suspended soil dust. Limestone is the only other source contributing to  $\text{PM}_{2.5}$  mass at Rubidoux. The geological source alone was not sufficient to explain the high measured ambient calcium concentrations in Rubidoux. Addition of limestone source in the CMB analysis accounted the excess calcium. These findings are consistent with earlier studies (Chow et al., 1992; Kim et al., 1992).

Residual oil burning displays a strong spatial variation. The highest residual oil burning contribution ( $1.28 \mu\text{g}/\text{m}^3$ , 6.1%) is observed in Wilmington where shipping activities occur. The contributions remain higher in the surrounding coastal areas in relation to the inland. The lowest contribution is observed at Rubidoux ( $0.27 \mu\text{g}/\text{m}^3$ , 1.2%).

### ***With the Basin Gasoline Profile***

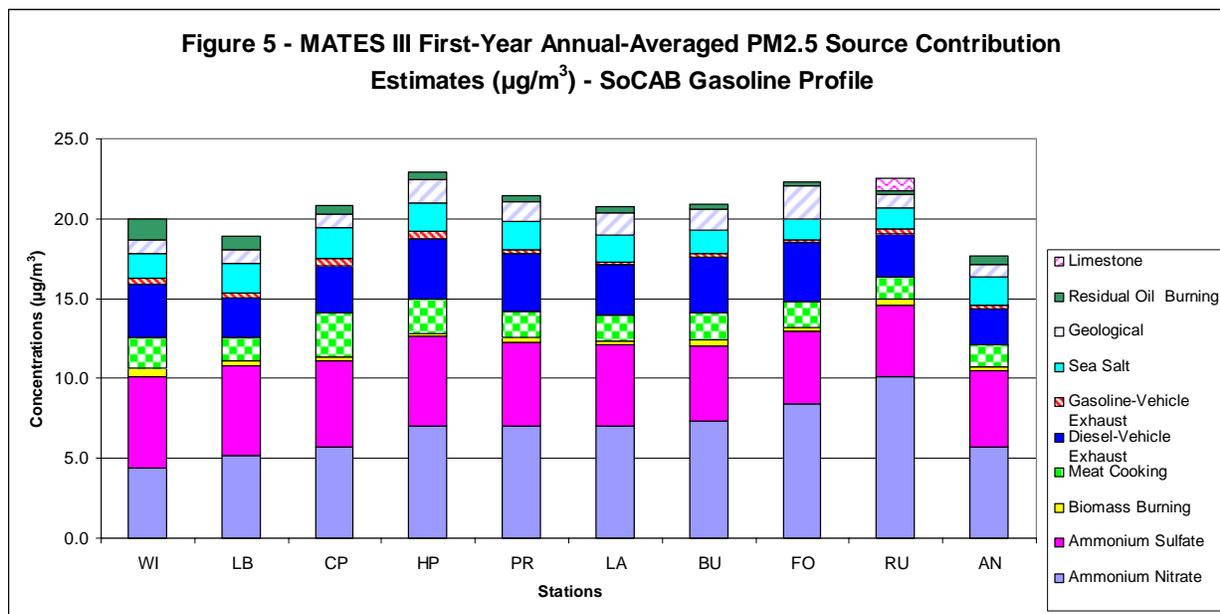
A Basin gasoline-vehicle profile used in the Fresno Supersite study (Chow et al., 2007) was applied to the CMB analysis for comparison purposes.

The annual-averaged source contribution estimates of major  $\text{PM}_{2.5}$  source categories and their percentages of the total predicted mass are summarized in Table 2 and Figure 5.

**Table 2**  
**MATES III First-Year Annual-Averaged PM<sub>2.5</sub> Source Contribution Estimates in µg/m<sup>3</sup> – Basin Gasoline Profile**

	WI	LB	CP	HP	PR	LA	BU	FO	RU	AN	10-Site Ave.
Ammonium Nitrate	4.39 <i>(22.0)</i>	5.14 <i>(27.2)</i>	5.68 <i>(27.3)</i>	6.99 <i>(30.5)</i>	7.03 <i>(32.8)</i>	7.04 <i>(34.0)</i>	7.33 <i>(35.0)</i>	8.42 <i>(37.7)</i>	10.08 <i>(44.8)</i>	5.70 <i>(32.3)</i>	6.78 <i>(31.6)</i>
Ammonium Sulfate	5.68 <i>(28.5)</i>	5.68 <i>(30.0)</i>	5.43 <i>(26.1)</i>	5.68 <i>(24.8)</i>	5.22 <i>(24.4)</i>	5.06 <i>(24.4)</i>	4.75 <i>(22.7)</i>	4.53 <i>(20.3)</i>	4.49 <i>(19.9)</i>	4.81 <i>(27.3)</i>	5.13 <i>(23.9)</i>
Biomass Burning	0.57 <i>(2.8)</i>	0.28 <i>(1.5)</i>	0.20 <i>(1.0)</i>	0.15 <i>(0.7)</i>	0.34 <i>(1.6)</i>	0.28 <i>(1.3)</i>	0.33 <i>(1.6)</i>	0.22 <i>(1.0)</i>	0.38 <i>(1.7)</i>	0.22 <i>(1.3)</i>	0.30 <i>(1.4)</i>
Cooking Operations	1.93 <i>(9.6)</i>	1.47 <i>(7.8)</i>	2.78 <i>(13.4)</i>	2.13 <i>(9.3)</i>	1.59 <i>(7.4)</i>	1.60 <i>(7.7)</i>	1.74 <i>(8.3)</i>	1.65 <i>(7.4)</i>	1.43 <i>(6.4)</i>	1.37 <i>(7.8)</i>	1.77 <i>(8.2)</i>
Diesel-Vehicle Exhaust	3.35 <i>(16.8)</i>	2.47 <i>(13.1)</i>	2.93 <i>(14.1)</i>	3.77 <i>(16.5)</i>	3.61 <i>(16.9)</i>	3.11 <i>(15.0)</i>	3.43 <i>(16.4)</i>	3.70 <i>(16.6)</i>	2.72 <i>(12.1)</i>	2.22 <i>(12.6)</i>	3.13 <i>(14.6)</i>
Gasoline-Vehicle Exhaust	0.36 <i>(1.8)</i>	0.37 <i>(2.0)</i>	0.51 <i>(2.4)</i>	0.51 <i>(2.2)</i>	0.26 <i>(1.2)</i>	0.22 <i>(1.1)</i>	0.29 <i>(1.4)</i>	0.16 <i>(0.7)</i>	0.24 <i>(1.0)</i>	0.24 <i>(1.3)</i>	0.31 <i>(1.5)</i>
Sea Salt	1.57 <i>(7.9)</i>	1.84 <i>(9.7)</i>	1.92 <i>(9.2)</i>	1.80 <i>(7.8)</i>	1.76 <i>(8.2)</i>	1.64 <i>(7.9)</i>	1.47 <i>(7.0)</i>	1.33 <i>(6.0)</i>	1.38 <i>(6.1)</i>	1.77 <i>(10.1)</i>	1.65 <i>(7.7)</i>
Geological	0.83 <i>(4.2)</i>	0.83 <i>(4.4)</i>	0.87 <i>(4.2)</i>	1.45 <i>(6.3)</i>	1.23 <i>(5.7)</i>	1.45 <i>(7.0)</i>	1.32 <i>(6.3)</i>	2.03 <i>(9.1)</i>	0.81 <i>(3.6)</i>	0.80 <i>(4.6)</i>	1.16 <i>(5.4)</i>
Residual Oil Burning	1.30 <i>(6.5)</i>	0.82 <i>(4.4)</i>	0.51 <i>(2.5)</i>	0.43 <i>(1.9)</i>	0.39 <i>(1.8)</i>	0.33 <i>(1.6)</i>	0.29 <i>(1.4)</i>	0.28 <i>(1.3)</i>	0.27 <i>(1.2)</i>	0.52 <i>(2.9)</i>	0.51 <i>(2.4)</i>
Limestone									0.72 <i>(3.2)</i>		0.72 <i>(3.2)</i>
Predicted Mass	19.98	18.89	20.83	22.89	21.42	20.73	20.93	22.33	22.50	17.65	21.46
Measured Mass	17.72	18.41	19.34	22.2	20.6	19.38	21.21	21.35	23.54	17.55	20.13

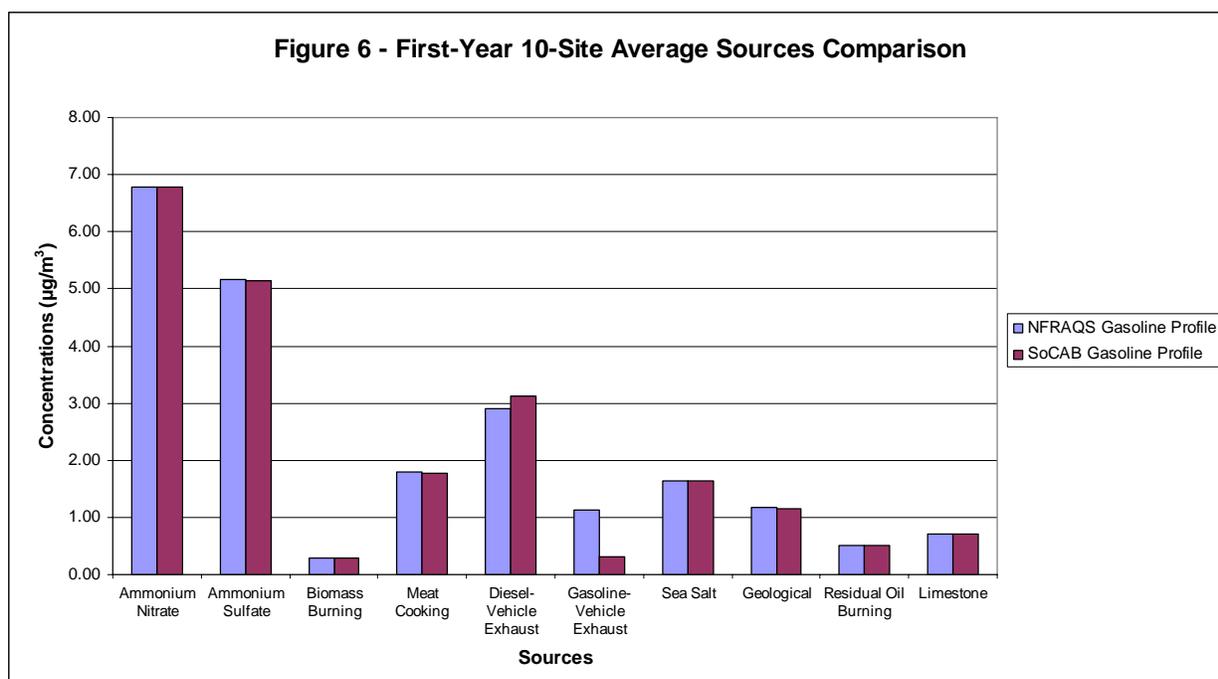
Italic, bold values in ( ) are the percentages of predicted mass



**Figure 5**

The CMB estimated PM<sub>2.5</sub> mass contributions range from 17.65 to 22.89 µg/m<sup>3</sup> across the Basin. Major source contributors are ammonium nitrate (4.39 – 10.08 µg/m<sup>3</sup>, 22 – 44.8%), ammonium sulfate (4.49 – 5.68 µg/m<sup>3</sup>, 19.9 – 30%), biomass burning (0.15 – 0.57 µg/m<sup>3</sup>, 0.7 – 2.8%), cooking operations (1.37 – 2.78 µg/m<sup>3</sup>, 7.8 – 13.4%), diesel-vehicle exhaust (2.22 – 3.77 µg/m<sup>3</sup>, 12.6 – 16.5%), gasoline-vehicle exhaust (0.16 – 0.51 µg/m<sup>3</sup>, 0.7 – 2.4%), sea salt (1.33 - 1.92 µg/m<sup>3</sup>, 6.0 – 9.2%), geological (0.80 – 2.03 µg/m<sup>3</sup>, 4.6 – 9.1%), residual oil burning (0.27 – 1.28 µg/m<sup>3</sup>, 1.2 – 6.5%), and limestone (0.72 µg/m<sup>3</sup>, 3.2%).

Applying the Basin gasoline profile affects other sources only slightly, but tremendously impacts gasoline exhaust contributions as shown in Figure 6, which compares the contributions of major sources averaged among ten sites, using both NFRAQS and Basin gasoline profiles.



**Figure 6**

The ratios of diesel to gasoline-vehicle contributions across the Basin vary from 5.78 in Compton to 23.16 in Fontana. The average diesel-gasoline ratio for all stations is 9.97, which is significantly higher than the 2007 AQMP diesel-gasoline emissions ratio of 1.90 and the ratio of 2.68 calculated from Fujita et al.'s (2006) emission factors.

Using the Basin gasoline profile also results in similar spatial contribution pattern as using the NFRAQS profile.

#### ***April 2005 to April 2006 (Second-Year) PM<sub>2.5</sub> Source Apportionment***

Since the year 2005 was not considered a typical year for the Basin due to the heavy rain, MATES III sampling was extended to April 2006. The following PM<sub>2.5</sub> source apportionment was conducted independently for second year, but using the same source profiles and fitting species.

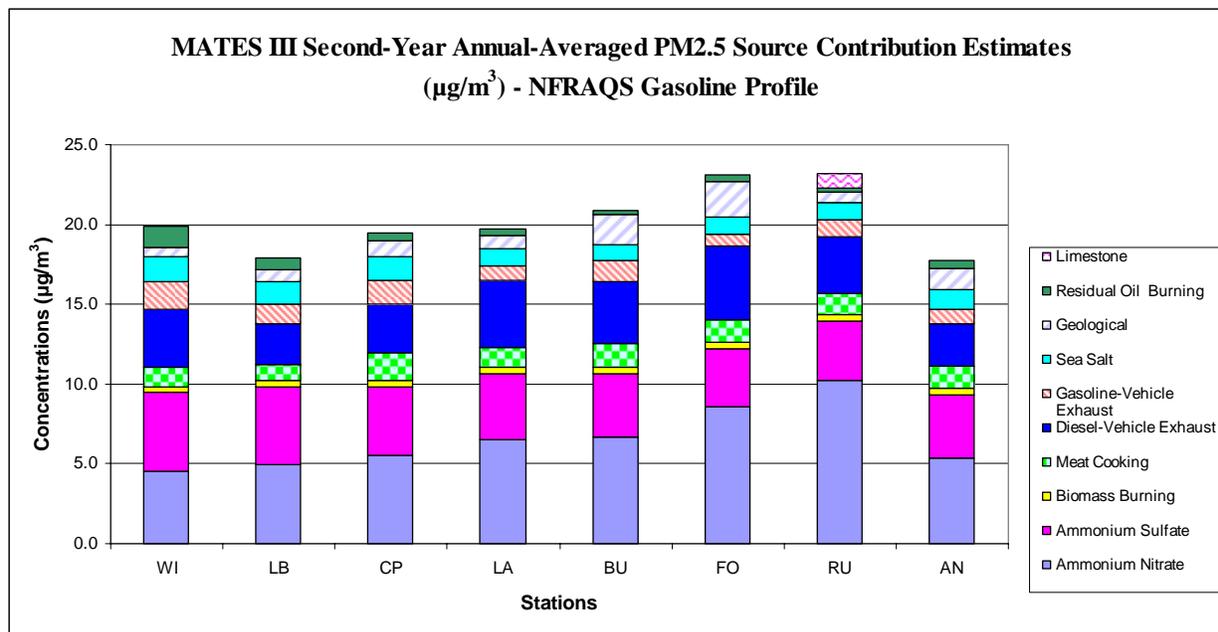
*With the NFRAQS Gasoline Profile*

The annual-averaged source contribution estimates of major PM<sub>2.5</sub> source categories and their percentage of the total predicted mass are summarized in Table 3 and Figure 7. The second-year spatial contribution pattern is similar to that of the first year.

**Table 3**  
**MATES III Second-Year Annual-Averaged PM<sub>2.5</sub> Source Contribution Estimates in**  
**µg/m<sup>3</sup> – NFRAQS Gasoline Profile**

	WI	LB	CP	LA	BU	FO	RU	AN	8-Sites Average
Ammonium Nitrate	4.56 <i>(22.9)</i>	4.92 <i>(27.5)</i>	5.50 <i>(28.2)</i>	6.55 <i>(33.3)</i>	6.69 <i>(32.0)</i>	8.55 <i>(37.1)</i>	10.24 <i>(44.2)</i>	5.39 <i>(30.4)</i>	6.55 <i>(31.2)</i>
Ammonium Sulfate	4.94 <i>(29.4)</i>	4.92 <i>(27.5)</i>	4.35 <i>(22.3)</i>	4.06 <i>(20.6)</i>	3.94 <i>(18.8)</i>	3.65 <i>(15.8)</i>	3.72 <i>(16.0)</i>	3.92 <i>(22.1)</i>	4.19 <i>(20.0)</i>
Biomass Burning	0.32 <i>(1.6)</i>	0.38 <i>(2.1)</i>	0.42 <i>(2.1)</i>	0.42 <i>(2.1)</i>	0.46 <i>(2.2)</i>	0.39 <i>(1.7)</i>	0.43 <i>(1.9)</i>	0.39 <i>(2.2)</i>	0.40 <i>(1.9)</i>
Meat Cooking	1.21 <i>(6.1)</i>	0.98 <i>(5.5)</i>	1.66 <i>(8.5)</i>	1.26 <i>(6.4)</i>	1.49 <i>(7.1)</i>	1.47 <i>(6.4)</i>	1.33 <i>(5.8)</i>	1.44 <i>(8.1)</i>	1.36 <i>(6.5)</i>
Diesel-Vehicle Exhaust	3.64 <i>(18.3)</i>	2.60 <i>(14.6)</i>	3.09 <i>(15.9)</i>	4.19 <i>(21.3)</i>	3.86 <i>(18.5)</i>	4.63 <i>(20.1)</i>	3.49 <i>(15.1)</i>	2.65 <i>(15.0)</i>	3.52 <i>(16.8)</i>
Gasoline-Vehicle Exhaust	1.75 <i>(8.8)</i>	1.19 <i>(6.7)</i>	1.52 <i>(7.8)</i>	0.91 <i>(4.6)</i>	1.27 <i>(6.1)</i>	0.73 <i>(3.2)</i>	1.07 <i>(4.6)</i>	0.86 <i>(4.8)</i>	1.16 <i>(5.5)</i>
Sea Salt	1.53 <i>(7.7)</i>	1.45 <i>(8.1)</i>	1.43 <i>(7.3)</i>	1.14 <i>(5.8)</i>	1.01 <i>(4.8)</i>	1.07 <i>(4.6)</i>	1.10 <i>(4.7)</i>	1.30 <i>(7.3)</i>	1.25 <i>(6.0)</i>
Geological	0.64 <i>(3.2)</i>	0.71 <i>(4.0)</i>	1.01 <i>(5.2)</i>	0.80 <i>(4.1)</i>	1.89 <i>(9.0)</i>	2.23 <i>(9.7)</i>	0.68 <i>(2.9)</i>	1.30 <i>(7.3)</i>	1.16 <i>(5.5)</i>
Residual Oil Burning	1.29 <i>(6.5)</i>	0.72 <i>(4.0)</i>	0.51 <i>(2.6)</i>	0.38 <i>(1.9)</i>	0.30 <i>(1.4)</i>	0.35 <i>(1.5)</i>	0.26 <i>(1.1)</i>	0.48 <i>(2.7)</i>	0.54 <i>(2.6)</i>
Limestone							0.85 <i>(3.7)</i>		0.85 <i>(3.7)</i>
Predicted Mass	19.89	17.88	19.49	19.70	21.16	23.07	23.16	17.74	20.97
Measured Mass	18.10	16.74	17.66	17.40	19.97	20.98	21.8	16.8	18.68

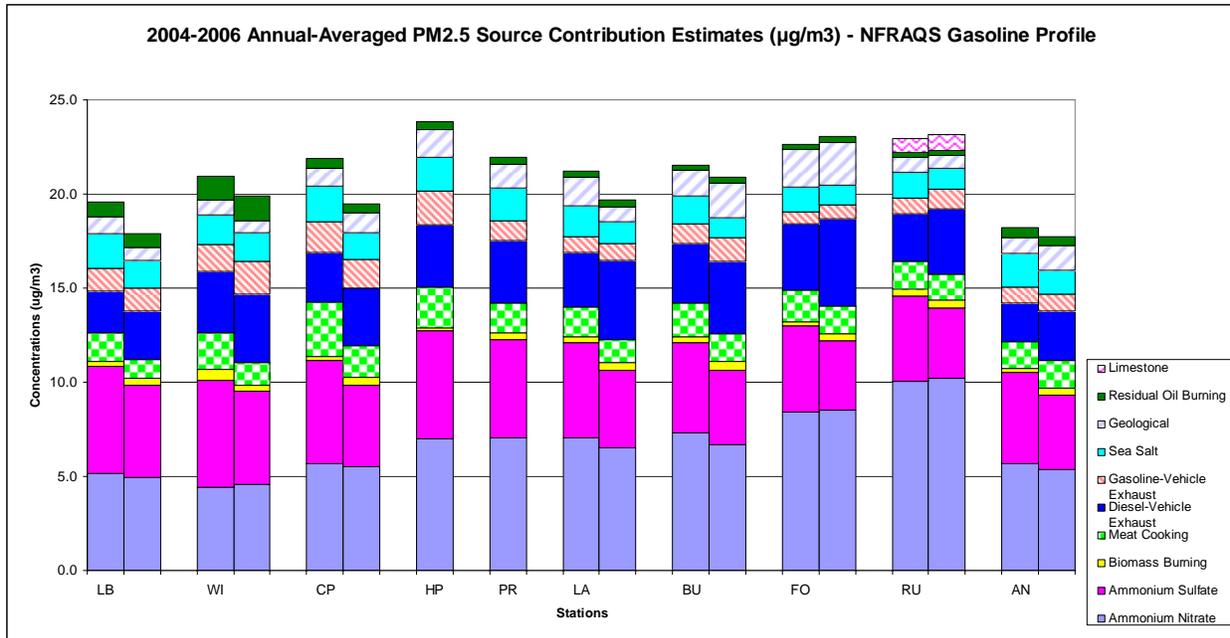
Italic, bold values in ( ) are the percentages of predicted mass



**Figure 7**

The CMB estimated PM<sub>2.5</sub> mass contributions range from 17.74 to 23.16  $\mu\text{g}/\text{m}^3$  across the Basin. Major source contributors are ammonium nitrate (4.56 – 10.24  $\mu\text{g}/\text{m}^3$ , 22.9 – 44.2%), ammonium sulfate (3.65 – 4.94  $\mu\text{g}/\text{m}^3$ , 15.8 – 29.4%), biomass burning (0.32 – 0.46  $\mu\text{g}/\text{m}^3$ , 1.6 – 2.2%), cooking operations (0.98 – 1.66  $\mu\text{g}/\text{m}^3$ , 5.5 – 8.5%), diesel-vehicle exhaust (2.6 – 4.63  $\mu\text{g}/\text{m}^3$ , 14.6 – 20.1%), gasoline-vehicle exhaust (0.73 – 1.75  $\mu\text{g}/\text{m}^3$ , 3.2 – 8.8%), sea salt (1.01 -1.53  $\mu\text{g}/\text{m}^3$ , 4.8 – 7.7%), geological (0.64 – 2.23  $\mu\text{g}/\text{m}^3$ , 3.2 – 9.7%), residual oil burning (0.26 – 1.29  $\mu\text{g}/\text{m}^3$ , 1.1 – 6.5%), and limestone (0.85  $\mu\text{g}/\text{m}^3$ , 3.7%).

Figure 8 compares major source contributions at all stations during the two years for the NFRAQS gasoline profile. Second-year source contributions are very similar to the first year source contributions except diesel-vehicle contributions. PM<sub>2.5</sub> mass is slightly decreased in the second year. However, elemental carbon (EC) concentration is increased in the second year; and this resulted in the increase of diesel-vehicle contributions. Higher EC concentrations were traced back to increased diesel trucking activities during the second year. Per ARB's EMFAC data (2007), the vehicle-mile-traveled (VMT) for diesel vehicles in 2004 was 16,398,000 while in 2005, the VMT was increased to 18,608,000, representing a 13% increase.



**Figure 8**

The ratios of diesel to gasoline-vehicle contributions across the Basin vary from 2.03 in Compton to 6.33 in Fontana, which is higher than the first-year ratio due to the higher second-year diesel distribution. The average diesel-gasoline ratio for all stations is 3.03, which is slightly higher than the 2007 AQMP diesel-gasoline emissions ratio of 1.90 and the ratio of 2.68 calculated from Fujita et al.’s (2006) emission factors.

***With the Basin Gasoline Profile***

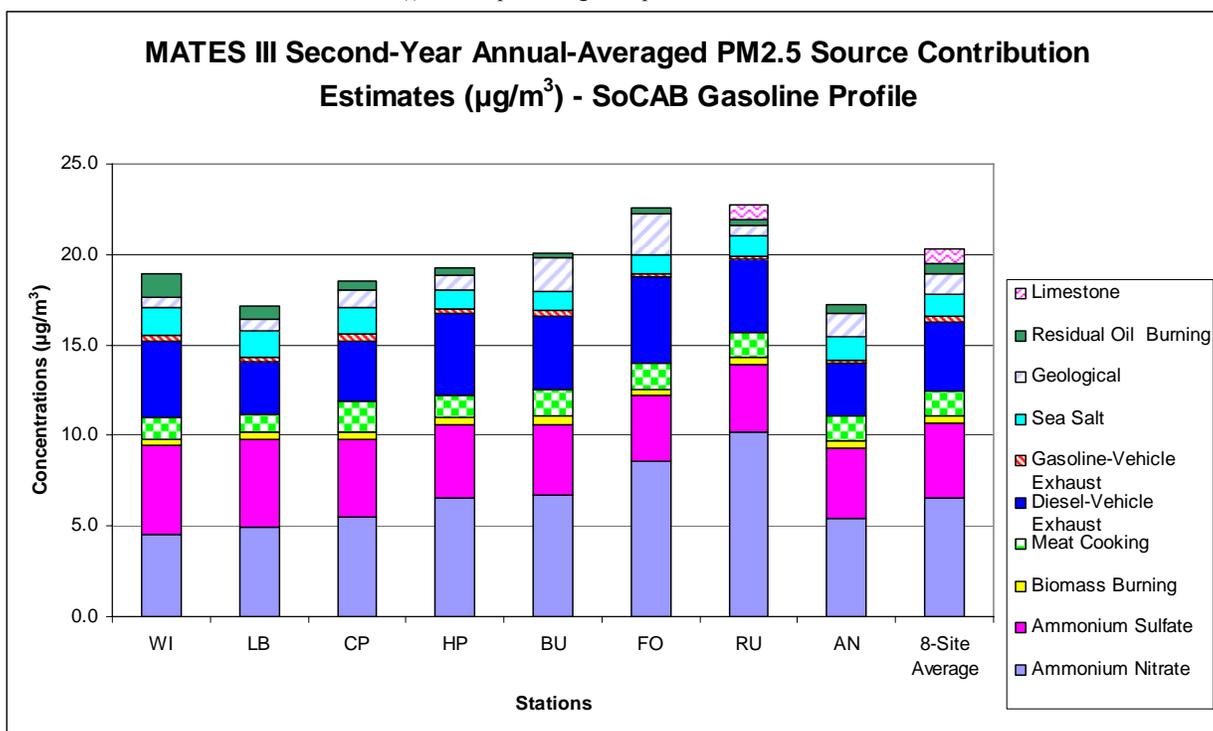
The estimated annual-averaged concentrations (in µg/m<sup>3</sup>) of PM<sub>2.5</sub> major sources in the Basin and their percentage contributions (to the total predicted mass) are summarized in Table 4 and Figure 9.

**Table 4**  
**MATES III Second-Year Annual-Averaged PM<sub>2.5</sub> Source Contribution Estimates in  $\mu\text{g}/\text{m}^3$  – Basin Gasoline Profile**

	WI	LB	CP	LA	BU	FO	RU	AN	8-Site Average
Ammonium Nitrate	4.56 <i>(24.0)</i>	4.92 <i>(28.6)</i>	5.50 <i>(29.6)</i>	6.55 <i>(34.0)</i>	6.69 <i>(33.3)</i>	8.55 <i>(37.9)</i>	10.23 <i>(45.0)</i>	5.39 <i>(31.2)</i>	6.55 <i>(32.2)</i>
Ammonium Sulfate	4.94 <i>(25.9)</i>	4.90 <i>(28.5)</i>	4.31 <i>(23.3)</i>	4.04 <i>(21.0)</i>	3.91 <i>(19.5)</i>	3.63 <i>(16.1)</i>	3.68 <i>(16.2)</i>	3.90 <i>(22.6)</i>	4.16 <i>(20.5)</i>
Biomass Burning	0.32 <i>(1.7)</i>	0.38 <i>(2.2)</i>	0.42 <i>(2.2)</i>	0.42 <i>(2.2)</i>	0.46 <i>(2.3)</i>	0.39 <i>(1.7)</i>	0.43 <i>(1.9)</i>	0.39 <i>(2.3)</i>	0.40 <i>(2.0)</i>
Meat Cooking	1.21 <i>(6.4)</i>	0.98 <i>(5.7)</i>	1.63 <i>(8.8)</i>	1.24 <i>(6.4)</i>	1.47 <i>(7.3)</i>	1.45 <i>(6.4)</i>	1.34 <i>(5.9)</i>	1.43 <i>(8.3)</i>	1.34 <i>(6.6)</i>
Diesel-Vehicle Exhaust	4.25 <i>(22.4)</i>	2.90 <i>(16.9)</i>	3.34 <i>(18.0)</i>	4.46 <i>(23.2)</i>	4.09 <i>(20.4)</i>	4.77 <i>(21.1)</i>	4.02 <i>(17.7)</i>	2.89 <i>(16.7)</i>	3.84 <i>(18.9)</i>
Gasoline-Vehicle Exhaust	0.30 <i>(1.6)</i>	0.25 <i>(1.4)</i>	0.45 <i>(2.4)</i>	0.24 <i>(1.3)</i>	0.31 <i>(1.5)</i>	0.16 <i>(0.7)</i>	0.21 <i>(0.9)</i>	0.19 <i>(1.1)</i>	0.26 <i>(1.3)</i>
Sea Salt	1.50 <i>(7.9)</i>	1.46 <i>(8.5)</i>	1.43 <i>(7.7)</i>	1.11 <i>(5.8)</i>	1.01 <i>(5.0)</i>	1.07 <i>(4.7)</i>	1.09 <i>(4.8)</i>	1.30 <i>(7.5)</i>	1.25 <i>(6.1)</i>
Geological	0.62 <i>(3.2)</i>	0.68 <i>(3.9)</i>	0.97 <i>(5.2)</i>	0.82 <i>(4.3)</i>	1.86 <i>(9.2)</i>	2.21 <i>(9.8)</i>	0.62 <i>(2.7)</i>	1.28 <i>(7.4)</i>	1.13 <i>(5.6)</i>
Residual Oil Burning	1.31 <i>(6.9)</i>	0.72 <i>(4.2)</i>	0.51 <i>(2.7)</i>	0.38 <i>(1.9)</i>	0.30 <i>(1.5)</i>	0.35 <i>(1.6)</i>	0.27 <i>(1.2)</i>	0.48 <i>(2.8)</i>	0.54 <i>(2.6)</i>
Limestone							0.87 <i>(3.8)</i>		0.87 <i>(3.8)</i>
Predicted Mass	18.96	17.18	18.55	19.27	20.08	22.58	22.76	17.25	20.34
Measured Mass	18.10	16.74	17.66	17.40	19.97	20.98	21.80	16.81	18.68

*Italic,*

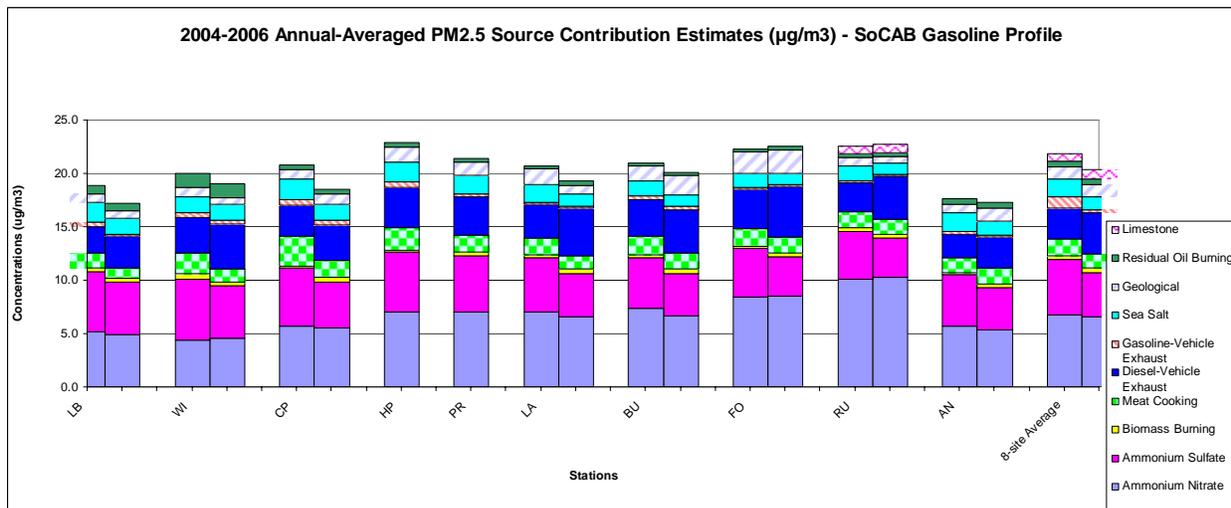
bold values in ( ) are the percentages of predicted mass



**Figure 9**

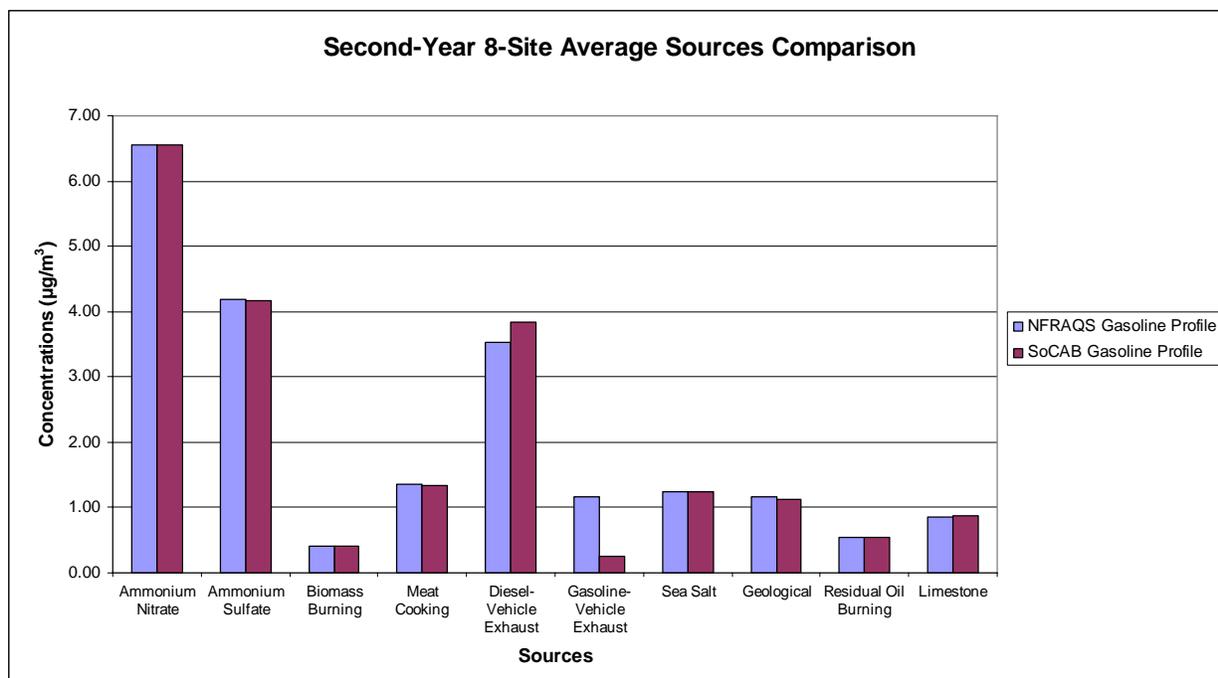
Major source contributors are ammonium nitrate (4.56 – 10.23  $\mu\text{g}/\text{m}^3$ , 24.0 – 45.0%), ammonium sulfate (3.63 – 4.94  $\mu\text{g}/\text{m}^3$ , 16.1 – 28.5%), biomass burning (0.32 – 0.46  $\mu\text{g}/\text{m}^3$ , 1.7 – 2.3%), cooking operations (0.98 – 1.63  $\mu\text{g}/\text{m}^3$ , 5.7 – 8.8%), diesel-vehicle exhaust (2.89 – 4.77  $\mu\text{g}/\text{m}^3$ , 16.7 – 21.1%), gasoline-vehicle exhaust (0.16 – 0.45  $\mu\text{g}/\text{m}^3$ , 0.7 – 2.4%), sea salt (1.01 – 1.5  $\mu\text{g}/\text{m}^3$ , 5.0 – 7.9%), geological (0.62 - 2.21  $\mu\text{g}/\text{m}^3$ , 2.7 – 9.8%), (residual oil burning (0.27 – 1.31  $\mu\text{g}/\text{m}^3$ , 1.2 – 6.9%), and limestone (0.87 $\mu\text{g}/\text{m}^3$ , 3.8%).

Figure 10 compares major source contributions at all stations during the two years for the Basin gasoline profile. Second-year source contributions are very similar to the first year source contributions except diesel-vehicle contributions.



**Figure 10**

Similar to the first-year results, applying the Basin gasoline profile slightly affects other source categories, but has a large impact on gasoline exhaust estimates as shown in Figure 11, which compares the contributions of major sources averaged among eight sites, using both NFRAQS and Basin gasoline profiles.



**Figure 11**

The ratios of diesel to gasoline-vehicle contributions across the Basin vary from 7.4 in Compton to 30.7 in Fontana. The average diesel to gasoline ratio for all stations is 14.6, which is higher than the first-year ratio of 10.0, and significantly higher than the 2007 AQMP diesel-gasoline emissions ratio of 1.90 and the ratio of 2.68 calculated from Fujita et al.'s (2006) emission factors.

### III. Summary

In summary, the use of different gasoline profiles slightly affects other source categories but has a large impact on gasoline contributions. The NFRQS gasoline profile results in gasoline exhaust contributions that are approximately 3 to 5 times higher than those generated by the Basin profile. Gasoline exhaust contributions range from 0.60 µg/m<sup>3</sup> to 1.75 µg/m<sup>3</sup> for the first year and 0.73 µg/m<sup>3</sup> to 1.75 µg/m<sup>3</sup> for the second year with the NFRQS, and from 0.16 µg/m<sup>3</sup> to 0.51 µg/m<sup>3</sup> for the first year and 0.73 µg/m<sup>3</sup> to 1.75 µg/m<sup>3</sup> for the second year. Diesel is greater in the second year due to the higher second-year diesel exhaust contribution, which is driven by the higher EC ambient concentrations.

The use of different biomass burning profile also slightly affects other sources and results in biomass burning contributions that are approximately 2 times greater than the current contributions.

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