FINAL REPORT

EVALUATING VOC RECEPTOR MODELS USING GRID-MODEL SIMULATIONS

CRC PROJECT A-34

Prepared for

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The authors acknowledge the assistance of Dr. H. Andrew Gray in designing photochemical model experiments to challenge the receptor model in this study.

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EXECUTIVE SUMMARY

Receptor models, such as the Chemical Mass Balance (CMB) model, are used to estimate what sources contribute to ambient levels of volatile organic compounds (VOCs). Reliable source contribution estimates (SCEs) derived from ambient data are valuable for evaluating and refining emission inventories. Emission inventories are central to air quality planning activities to comply with clean air regulations.

Important issues to understand when using the results of VOC receptor modeling are: (1) The ability of the receptor model to accurately quantify individual source contributions from ambient air samples impacted by many different sources; (2) Relationships between source contributions to air concentrations vs. emission inventories, and; (3) How to associate source signatures identified from air samples (e.g., gasoline engine exhaust) to activity categories used in emission inventories (e.g., on-road mobile vs. off-road mobile vs. stationary gasoline engines). The Coordinating Research Council (CRC) sponsored Project A-34 to evaluate the performance of VOC receptor models under realistic conditions where the actual source contributions are known.

A photochemical grid model was used to simulate the detailed VOC composition of an urban atmosphere and to keep track of the contributions of 22 source categories to 55 VOC species. The 55 VOC species were those routinely monitored by the Environmental Protection Agency's (EPA's) Photochemical Assessment Monitoring Stations (PAMS). The modeled PAMS species concentrations at several receptor locations were analyzed by VOC receptor modeling using the CMB model. The CMB SCEs were compared to the known source contributions from the photochemical grid model to permit a rigorous analysis of how well the CMB model performed. Receptor modeling was performed in several "rounds" of analysis with progressively more information being provided to the receptor modelers in each round. The receptor modelers analyzed tens of thousands of "ambient samples" using a combination of manual and automated fitting techniques.

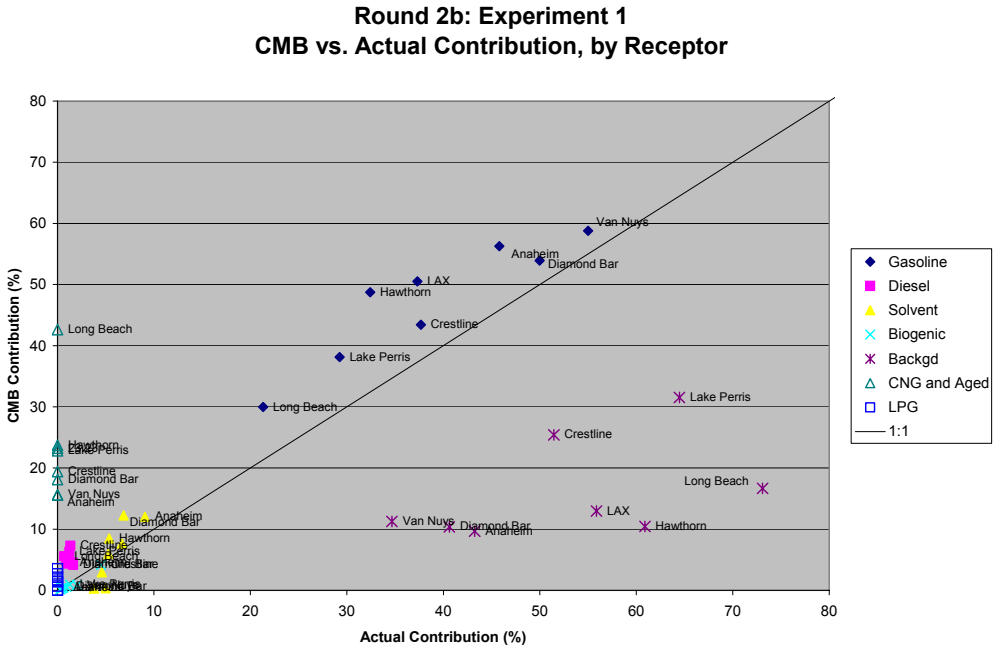
The study approach required two teams working collaboratively, but independently. The photochemical grid modeling was designed and executed by ENVIRON, whereas the Desert Research Institute (DRI) carried out the CMB receptor modeling. Dr. Warren White of the University of California at Davis provided independent assistance in the study design and the interpretation of results. This is the first study to use a grid model to quantitatively evaluate CMB, to our knowledge. The study results provide a unique opportunity to investigate how well CMB performs for VOC and what assumptions are important. Nevertheless, the results are limited by being based on a single modeling scenario.

Study Results

Example results from two "rounds" of analysis are shown in Figure ES-1. Figure ES-1(a) shows results for 8 receptors analyzed in Round 2b whereas Figure ES-1(b) shows the receptors analyzed again in Round 4. The difference between Rounds 2b and 4 was in the amount of information provided to the group performing the CMB analysis. The Round 2b CMB analysis was conducted with information typically available to a well-organized receptor modeling study; sample location and time, source profile information from a tunnel study and liquid gasoline

samples. For Round 4, the CMB modelers had complete information about all sources present including the source composition profiles. Figure ES-1 compares the actual source category contribution to the sum of PAMS species in each air sample with the source contributions inferred by the CMB analysis.

(a)



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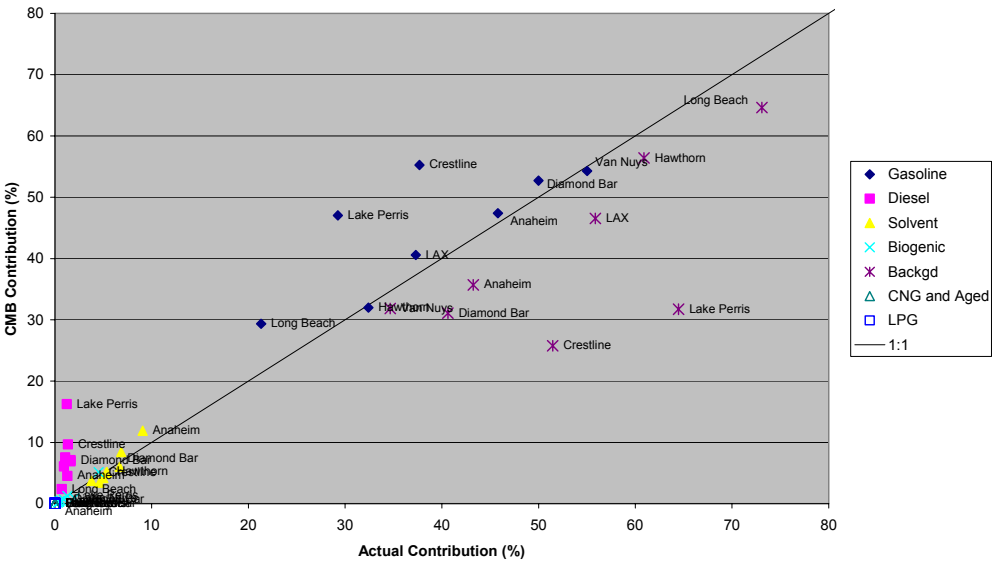


Figure ES-1. Comparison of CMB contributions to actual contributions for experiment 1 at each receptor averaged over all hours in (a) Round 2b and (b) Round 4.

Comparing the performance of CMB in Rounds 2b and 4 (Figure ES-1) lead to several findings:

- In Round 2, the CMB analysis apportioned VOCs to categories called "CNG and Aged" and "LPG" that were not actually present in the samples, illustrating that CMB category names may describe chemical characteristics (fingerprints) rather than specific activities tracked in emission inventories. CNG is compressed natural gas and LPG is liquid petroleum gas.
- CMB tended to over-estimate the contribution of gasoline emissions except when complete profile information was available in Round 4.
- CMB performance for diesel was poorer in Round 4 than Round 2 because of a decision to exclude nonane, decane and undecane as CMB fitting species in Round 4 that resulted in partial colinearity between the diesel and gasoline source profiles.

The results presented in Figure ES-1 show that CMB can achieve accurate results with adequate supporting information but that even with detailed supporting information, results can be biased by decisions made during the analysis. Consequently, it may be difficult to judge the accuracy of CMB results in each application.

The comparisons presented in Figure ES-1 are based on the actual source contributions to VOCs present in air samples. However, CMB results are frequently interpreted as measures of emission inventories. There are at least two major reasons why actual contributions may differ from emission contributions; namely chemical reaction and spatial heterogeneity in emissions.

The impacts of chemical reaction on source contributions are illustrated in Figure ES-2 for several source categories at a downwind receptor (Crestline). Figure ES-2 compares source category contributions from the photochemical model with and without chemical degradation included. Low reactivity VOCs (CNG/aged and LPG) are only slightly depleted by chemical degradation, whereas high reactivity VOCs (biogenics) are almost completely depleted during the night and highly depleted at day. Differences in VOC degradation rates introduce a bias toward low reactivity VOCs having higher contributions to actual concentrations than to emission inventories.

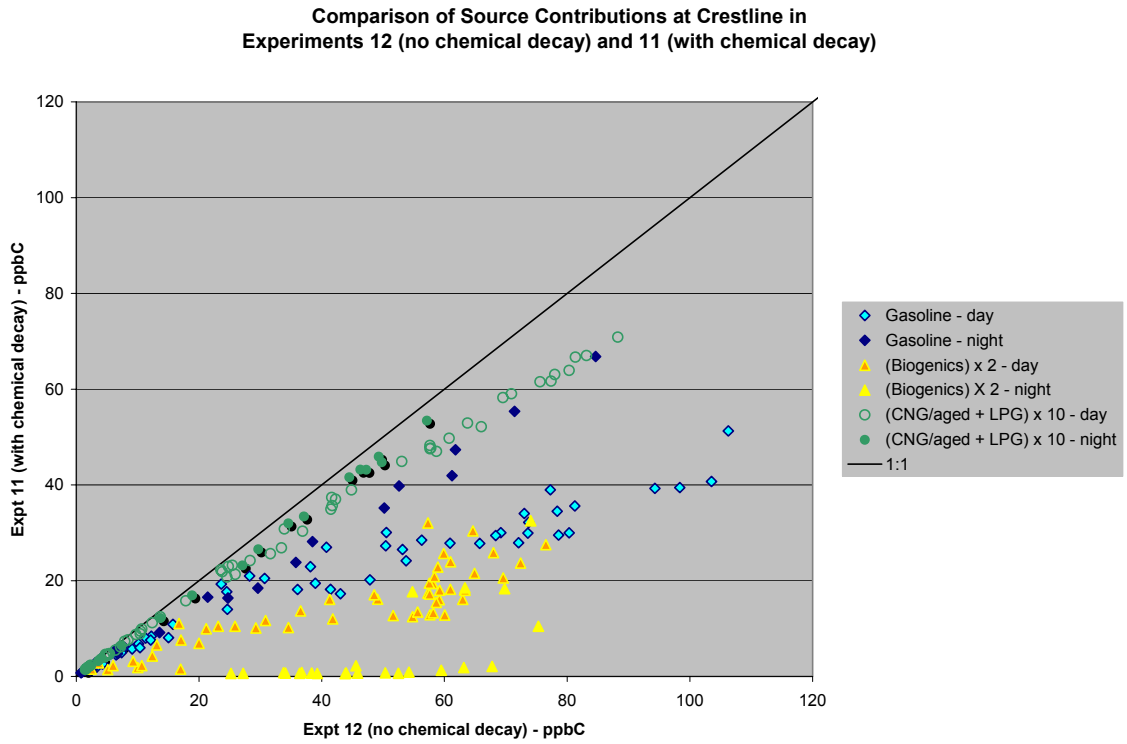


Figure ES-2. The effects of chemical reaction on concentrations of high, medium and low reactivity source categories at a downwind receptor (Crestline).

The impact of spatial heterogeneity in emissions on the relationship between actual contributions and emission contributions is illustrated n Figure ES-3. The Figure compares actual contributions in air samples to emissions contributions for 15-km square areas around 8 receptors. Points that are not along the 1:1 line are for receptors/source categories where the contributions in the air are significantly different from the local emissions inventory. The largest deviations are at downwind receptors (Crestline and Lake Perris) that have relatively low emissions near the receptor but are influenced by transport from high emission areas upwind. This is an example of spatial heterogeneity in emissions that was resolved by the 5-km gridded emissions inventory. In the real-world, there also could be fine-scale heterogeneity if, for example, a monitor is located close to a large source (e.g., a point source or freeway intersection).

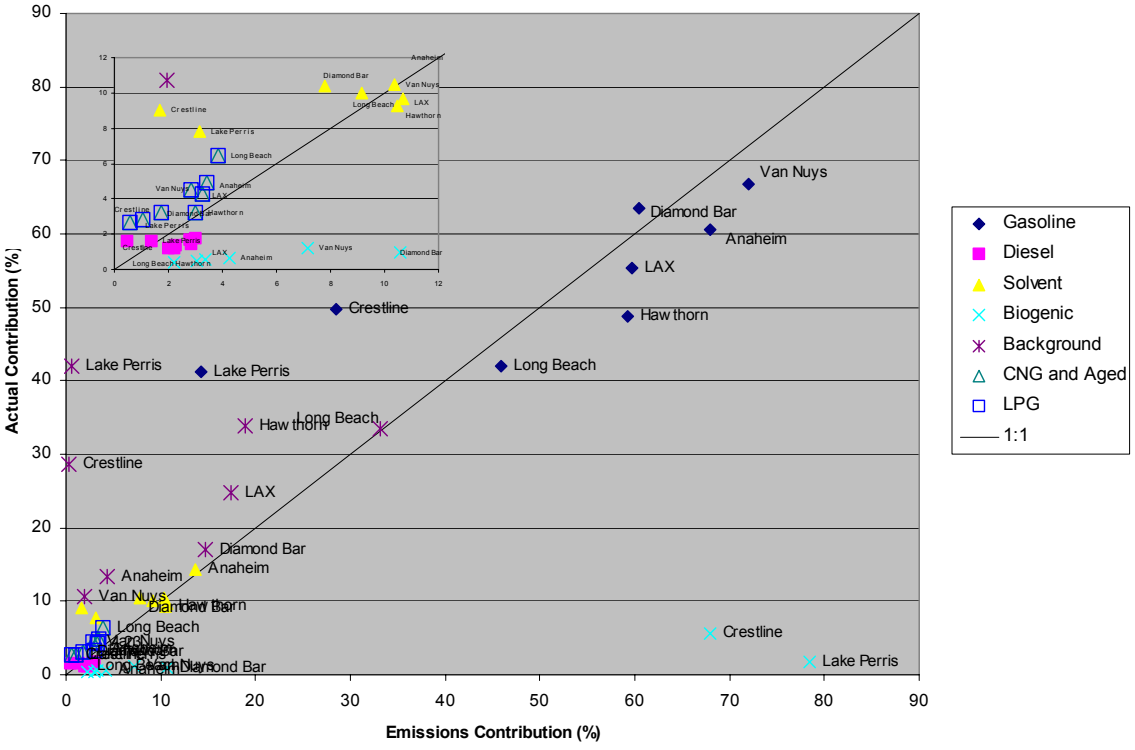


Figure ES-3. Actual and emission contributions in experiment 12 (with no chemical reactions) by receptor, averaged over all hours.

Evaluating the Stated Assumptions for CMB

The developers of CMB have identified six assumptions to be satisfied when applying the methodology for VOCs. These assumptions are evaluated based on the findings of this project.

1. *The composition of source emissions is constant over the period of ambient and source sampling.*

This study found that CMB was robust against variations in source profiles at the temporal scale (1 hour) and spatial scale (5 km) employed in the air quality model. In the real-world, samples may violate this assumption if they are influenced by single sources, such as a nearby stationary source, that are temporally varying.

2. *Chemical species do not react with each other; i.e., they add linearly.*

This assumption was met by the chemical reaction scheme for the 55 PAMS species employed in this study. There are no known reactions among the 55 PAMS species (or other VOCs) that violate this assumption for the dilute concentration levels found in ambient VOC samples.

3. All significant sources have been identified and had their emissions characterized.

Results from this study confirm that this is an important assumption for CMB. Receptor models in general, and CMB in particular, seek an optimum source apportionment of the ambient VOCs among the source profiles allowed in the model. This creates a tendency to apportion all sources to just the sources allowed in the analysis if source profiles have species in common. The resulting bias over-estimates the contributions of expected or identifiable sources.

When hypothetical industrial sources were added to the emission inventory, CMB tended to apportion the hypothetical industrial emissions to other sources, such as gasoline and solvents, resulting in an over-estimation of gasoline and solvents. The significance of this result is open to interpretation. Since the receptor modelers did not know that hypothetical sources had been added to the emission inventory, it can be argued that important sources of emissions were unidentified in the CMB because the presence of the source was unexpected, causing assumption 3 to be violated because sources were unidentified. An alternate view is that the receptor modelers knew that real industrial sources were located close to the locations of the hypothetical industrial sources, so that the hypothetical sources merely raised the importance of a known source category, causing assumption 3 to be violated because sources were incorrectly characterized. These possible interpretations lead to two conclusions: (1) That violating assumption 3 can result in biased CMB apportionments, and: (2) That assumption 3 may be violated either by failing to realize that a source exists or misunderstanding the characteristics of a source.

Characterizing emissions sources (i.e., determining the source profiles) strongly influences the outcome of CMB receptor modeling. With minimal source profile information (less than in typical real-world CMB applications) the receptor modelers were able to select profiles that fit the ambient data, in most cases resulting in source apportionments that showed some skill but also contained biases. The biases tended toward over-estimating some sources (i.e., gasoline) and under-estimating others (i.e., solvents). Some of the source category identifications (i.e., compressed natural gas and liquid petroleum gas) required careful interpretation because the names assigned by the receptor modelers described the chemical nature of the emissions (i.e., ethane and propane, respectively) but not the source of the emissions.

With typically available source profile information (e.g., a tunnel study and fuel samples) the performance of CMB was improved for solvents but degraded for diesel relative to analyses with minimal information. The major changes were for solvents and diesel due to issues of profile co-linearity and choice of fitting species. The receptor modelers eliminated nonane, decane and undecane as fitting species and the gasoline and diesel profiles became somewhat co-linear and the apportionment for diesel was degraded.

When the receptor modelers were provided with detailed information on the sources present and their source profiles (which is not a realistic scenario for the real world), the CMB results were increasingly accurate and CMB performance was limited by other factors such as the degree of profile co-linearity.

4. The number of source categories is less than the number of species; i.e., there are degrees of freedom available in the analysis.

This assumption is a mathematical requirement of the CMB methodology. In practice, the number of resolvable source categories is limited by profile co-linearity rather than available degrees of freedom. In this study, CMB resolved about 7 source categories with typically available profile information and about 13 source categories with complete source profile information. The number of categories identified (7-13) was substantially smaller than the theoretical maximum (55).

5. The source profiles are sufficiently different one from another.

Receptor models rely upon sources having uniquely identifiable fingerprints. Two consequences of profile co-linearity were observed in this study. First, CMB could not separate different categories of gasoline exhaust emissions that had similar speciation profiles; e.g., catalyst and non-catalyst vehicles, start and stabilized emissions, on-road and off-road vehicles.

A second co-linearity problem was observed for diesel exhaust. CMB was able to apportion diesel exhaust with some skill; i.e., correctly ranking high and low contributions. The accuracy of the diesel apportionments depended upon whether several heavy hydrocarbons (nonane, decane and undecane) were used as fitting species. Excluding these heavy hydrocarbons resulted in partial co-linearity between diesel and gasoline and a bias toward over-estimating diesel.

The conclusion from these findings is that severe profile co-linearity will likely be detected and accounted for by combining source categories, but less severe co-linearity may go undetected and lead to biased source contribution estimates.

6. Measurement errors are random, uncorrelated and normally distributed.

Several experiments investigated the impact of random sampling errors and confirmed that CMB is robust against realistic levels of random measurement noise. This did not mean that random sampling errors had no impact on CMB apportionments for individual samples. CMB performed better for larger groups of samples because of improved signal/noise ratio.

This study did not investigate the effects of non-random errors, such as measurement bias for specific species, on CMB performance. Because CMB relies upon ratios of species concentrations, it is evident that non-random errors could bias CMB results. For example, the CMB developers have shown that CMB apportionments are sensitive to ethylene/acetylene ratios, so biasing the ethylene or acetylene measurements is likely to bias CMB source apportionments.

Other Factors that Influence CMB

The CMB assumptions discussed above apply to source apportionment of air samples, which is a zero-dimensional (non-spatial) analysis. Other assumptions come into play when receptor models are used to analyze 4-D spatial/temporal source-receptor relationships. Issues that might affect the accuracy or interpretation of CMB receptor model results in real world (4-D) applications are source overlap, chemical degradation, heterogeneity in the spatial distribution of emissions sources, and accounting for different measures of total organic compounds.

4-D Source Overlap

The grid model experiments performed in this study investigated how CMB is influenced by source overlap in a multi-dimensional environment where sources with similar/different profiles located in similar/different locations mix in a 4-D spatial/temporal environment and are subjected to similar/different degrees of chemical reaction. In a 4-D scenario, there is potential for confounding source profiles that occur together but were emitted at different times, different places, or both different times and places. In the absence of chemical reactions, CMB performed very well in retrieving the source contributions for receptor locations ranging from upwind source areas to far downwind. This result shows that complex spatial and temporal source overlap in the 4-D environment of the grid modeling was not fundamentally more challenging than source overlap in the zero-dimensional sense considered above.

Chemical Degradation

The grid model experiments also investigated whether complex spatial/temporal source-receptor relationships were more challenging to CMB when combined with chemical degradation. Increasing oxidant levels (i.e., the amount of chemical reaction) did not degrade the ability of CMB to apportion complex source profiles. Eliminating chemistry altogether in experiments with simpler (i.e., fewer different) source profiles also had little impact on the performance of CMB. CMB performance was degraded for downwind receptors in experiments with complex source profiles. There appears to be two reasons why CMB was quite robust against the effects of chemical reaction: (1) The CMB protocols employed by the receptor modelers for this study always eliminated highly reactive species from consideration and also eliminated moderately reactive species in air samples that were identified as chemically aged using heuristic algorithms. (2) Source profiles were included for abundant low reactivity PAMS species (CNG and LPG for ethane and propane) that provided a way to account for the mass of these species. As discussed above, the names (CNG/aged and LPG) attached to these profiles needed careful interpretation because they describe chemical appearances rather than emission inventory source categories.

CMB generally was able to correctly apportion the sum of PAMS species present in the air samples even when source profiles had been altered by chemically aging. Chemical reaction also changes the relative amounts of low and high reactivity source categories. For example, high reactivity biogenic emissions were degraded much more than low reactivity CNG or LPG emissions. The impact of chemical aging on source contributions must be considered when comparing source apportionment results to emission inventories. The experimental findings were that: Source apportionment results for highly reactive emissions categories (e.g., biogenic emissions) significantly under-estimate the actual contribution due to chemical degradation. Source apportionment results for low reactivity categories (e.g. those labeled CNG or LPG) may over-estimate the real contributions of these categories due to chemical degradation. Apart from biases for high and low reactivity categories, source apportionment results for other categories are not greatly influenced by chemical degradation except at far downwind receptors.

Spatial Heterogeneity in Emissions Sources

CMB source contributions are often compared to emission inventories with the goal of evaluating and improving the emissions inventory. Air samples at a receptor location may be

dissimilar from the local emissions because of spatial heterogeneity in the distribution of emissions sources. Comparisons of the known source contributions in air samples to local emissions showed that the impacts of spatial heterogeneity were most pronounced for downwind receptors and receptors located near major point sources. The impacts of spatial heterogeneity in emission inventories were least, but not absent, for urban/suburban receptors with a mix of residential/commercial/industrial emissions.

Effects of spatial heterogeneity in emissions are likely under represented in the grid model experiments of this study compared to the real-world because (1) the grid model cannot represent micro-scale (sub 5-km) variations in emissions, and (2) grid modelers have limited information to spatially allocate emissions and so use spatial surrogates to allocate emissions (e.g., population) which simplify the texture in the emissions inventory. Micro-scale impacts present a challenge to selecting regionally representative monitoring locations in a real-world study where the goal is to characterize a regional emissions inventory.

Measure of "Total" Organic Compounds

There are several ways of defining the "total" of organic compounds for an emissions inventory or a receptor model analysis. Measures that are most appropriate for an emissions inventory (e.g. ROG, TOG) tend to be all inclusive, whereas a receptor model such as CMB is applied for a specific set of VOC species such as the PAMS list. Bridging the gap between emission inventories and receptor model results requires assumptions about relationships between different measures of total organic compounds, such as PAMS/ROG ratios. The emission inventory modeling for this revealed relationships between TOG, ROG and PAMS for 22 source category groupings. The ROG/TOG ratios ranged from 0.09 to 1.0. The PAMS/ROG ratios ranged from 0.23 to 2.4 (the sum of PAMS can be greater than ROG because ethane is included in PAMS but excluded from ROG).

Relationships between different measures of total organic compounds are more difficult to characterize for some source categories than others. Difficulties for biogenic emissions are that the PAMS species list contains only a few biogenic compounds (e.g., isoprene, ethene) and that many non-PAMS biogenic compounds require specialized measurement methods because they are oxygenated and/or heavy (e.g., 15 carbon sesquiterpenes; Guenther et al., 1999). Solvents have similar difficulties to biogenics, especially for oxygenated organics used in water-based formulations. Diesel emissions include many heavier compounds (more than 12 carbons) that require specialized measurement methods and may be difficult to classify as included or excluded from measures of volatile organics (e.g., ROG, VOC). These considerations introduce uncertainties and may result in positive or negative biases in source category contributions.

Source category contributions may vary significantly (by more than a factor of 2) depending upon how total organic compounds are measured. It follows that comparing different measures of total organic compounds between receptor modeling and emission inventories will introduce biases (either positive or negative) in comparisons of source category contributions. Corrections may be applied by assuming certain ratios (e.g., PAMS/ROG) for each category, but such assumptions are external to the receptor modeling process and must be accounted for separately. Recommendations for receptor modeling studies are: Clearly state the measure of organic compounds that is apportioned by the receptor model and define any conversion factors used to adjust this to a different basis. Conversion factors (e.g., PAMS/ROG ratios) must be consistent

with the receptor modeling source profiles (i.e., developed from the same set of detailed VOC data) and ideally should be developed specifically for each study.

1.0 INTRODUCTION

1.1 STUDY BACKGROUND

Receptor models, such as the Chemical Mass Balance (CMB) model, have been used to estimate source contributions to ambient concentrations of volatile organic compounds (Watson, Chow and Fujita, 2001). Reliable source contribution estimates (SCEs) derived from ambient data are valuable for evaluating and refining emissions inventories. Emission inventories are central to air quality planning activities to comply with clean air regulations. Air quality planning activities for ozone, fine particles (PM2.5) and air toxics all rely upon emissions inventories for volatile organic compounds (VOCs).

Important issues to understand when using the results of VOC receptor modeling are:

- The ability of the receptor model to accurately retrieve source contributions from ambient air samples where many different sources overlap.
- Differences between source contributions to air concentrations and source contributions to emission inventories.
- How to associate source signatures identified from air samples (e.g., gasoline engine exhaust) to activity categories used in emissions inventories (e.g., on-road mobile vs. off-road mobile vs. stationary gasoline engines).

The Coordinating Research Council (CRC) sponsored Project A-34 to evaluate how well VOC receptor models perform under realistic conditions where the actual source contributions are known.

1.2 STUDY OBJECTIVES

The overall objective of CRC Project A-34 was to evaluate the use receptor modeling for estimating source contributions to ambient VOCs. As discussed in more detail below, VOC receptor modeling has been used to estimate source contributions to ambient VOCs, and the receptor modeling results have been compared to emission inventories. However, there is no way to rigorously evaluate real world applications of VOC receptor models because in the real world the actual source contributions are unknowable. This study used numerical modeling to simulate ambient VOC concentrations in an urban atmosphere (the Los Angeles area) such that the source contributions to each VOC were known. The numerical simulations and receptor modeling analyses addressed the following issues:

- Quantifying the accuracy of the VOC receptor model source apportionments of ambient air samples.
- Investigating the sensitivity of receptor model apportionments to ambient conditions and modeling assumptions; e.g., relative source contributions, source profiles, photochemical oxidants.
- Quantifying relationships between air concentrations and emissions contributions, which limit the obtainable agreement between receptor model source apportionments and emissions inventories.
- Identifying sources of bias.

- Recommend approaches for applying VOC receptor models that are likely to provide the most reliable results.

1.3 VOC RECEPTOR MODELING BACKGROUND

The Chemical Mass Balance (CMB) model (Friedlander, 1973; Cooper and Watson, 1980; Gordon, 1988; Watson, 1984; Watson et al., 1984; 1990; 1991; Hidy and Venkataraman, 1996) consists of a least-squares solution to a set of linear equations that 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 VOC emissions from each source type) and the receptor concentrations, each with uncertainty estimates, serve as input data to the CMB model. The output consists of the contributions for each source type to the total ambient VOC as well as to individual VOC 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.

The CMB receptor model has been used to analyze speciated VOC samples and estimate the relative contributions of VOC source categories to the total VOC inventory. Most CMB VOC receptor model applications attribute a larger contribution of the ambient VOC concentrations to the mobile source category than is present in the emissions inventory. These results have been used to support the notion that mobile source VOC emissions are underreported in the current emission inventories. However, receptor modeling has its own limitations ranging from the representativeness of the speciation profiles to fundamental assumptions regarding temporal and spatial homogeneity of emissions, chemical reactivity, and speciation profile collinearity that have the potential to confound the receptor modeling approach. Although the statistical techniques used in receptor modeling have provisions for estimating uncertainties in the calculations, they quantify measurement uncertainties associated with the source and ambient data and do not address fundamental inaccuracies arising from potential deviations from model assumptions.

The developers of the CMB receptor model have summarized the key assumptions for CMB applied to VOCs as follows (Watson, Chow and Fujita, 2001):

1. The composition of source emissions is constant over the period of ambient and source sampling.
2. Chemical species do not react with each other, i.e., they add linearly.
3. All significant sources have been identified and had their emissions characterized.
4. The number of source categories is less than the number of species; i.e., there are degrees of freedom available in the analysis.
5. The source profiles are sufficiently different one from another.

Receptor models have been evaluated using synthetic datasets of known source contributions that have simplifications of some atmospheric processes (e.g., White, 2000). However, the full scale testing and evaluation of receptor modeling under controlled conditions using realistic "real-world" VOC concentrations of known VOC source contributions has not been done. One way to evaluate and test receptor models in this way is through use of photochemical grid modeling of known VOC speciation profiles and source contributions.

1.4 OVERVIEW OF PROJECT APPROACH

Project A-34 used the CAMx photochemical grid model (ENVIRON, 2004) to simulate an urban atmosphere with known contributions from 22 source categories to 55 individual VOC species. The VOC species selected were those routinely monitored by the Environmental Protection Agency's (EPA's) Photochemical Assessment Monitoring Stations (PAMS). The PAMS species profiles simulated for specific receptor locations were analyzed by receptor modeling using the Chemical Mass Balance (CMB) model to identify source contributions. The source contributions estimated by CMB were compared to the known source contributions simulated by the photochemical grid model to permit a rigorous analysis of how well the CMB model performed. This approach required two teams working collaboratively, but independently. The photochemical grid modeling was designed and executed by ENVIRON whereas the Desert Research Institute (DRI) carried out the CMB receptor modeling. Dr. Warren White of the University of California at Davis provided independent assistance in the study design and the interpretation of results.

The receptor model performance was evaluated in four rounds of tests. In Rounds 1, 2, and 4, the receptor modeling team analyzed the same set of 8 experiments (from Round 1) but with increasing levels of knowledge about how the ambient samples were simulated. Round 3 was designed after Round 2 had been completed to follow up on specific uncertainties in the CMB receptor modeling analysis.

Round 1: Blind Test. In the first round, ENVIRON provided DRI with virtual PAMS samples for 8 receptors, four days (August 4-7, 1997) and 8 experiments for a total of 6144 simulated air samples. DRI had no supporting information other than the sample identification number. The 8 experiments differed in modeling assumptions used to prepare the simulated air samples (e.g., relative source contributions, atmospheric reactivity, sampling noise, source profiles).

Round 2: Available Information. In Round 2, DRI reanalyzed the same set of 6144 simulated air samples as in Round 1. The difference was that for Round 2 ENVIRON provided DRI with sample location, date, time and experiment number and additional information that a receptor modeler would typically have available to support a "real-world" receptor model application. For example, a virtual tunnel study was performed to provide DRI with information on the mobile source emissions profiles.

Round 3: Uncertainty Analysis. New photochemical modeling experiments were performed in Round 3 to follow up in issues identified after Rounds 1 and 2. Four new experiments were designed (3072 simulated ambient samples) to understand how chemical decay and sampling noise influence CMB performance in situations where the receptor model should do well

Round 4: Full Information. In the final round, DRI was provided with detailed information on how the experiments in Rounds 1-3 had been performed. This included VOC speciation profiles used in the photochemical modeling emissions inventory for each major source category. This round assessed the ability of the CMB receptor model to estimate source contributions given an ideal situation in which all emissions speciation information is known.

2.0 PHOTOCHEMICAL MODELING METHODOLOGY

This section of the report describes how the photochemical grid modeling was performed to prepare synthetic air samples for receptor locations in the Los Angeles area. An overview of A-34 study design was presented in Section 1. The procedures described below were developed in modeling protocol at the outset of the study. The modeling protocol was reviewed by CRC, but not by DRI since this would have revealed critical information.

2.1 MODELS, DOMAIN, EPISODE AND RECEPTORS

The Comprehensive Air-quality Model with extensions (CAMx) photochemical modeling database for the August 3-7, 1997 Southern California Ozone Study (SCOS) episode was used for this study. This is the same database as was used in the CRC A-36-A1 Weekday/Weekend Proximate Modeling (Yarwood et al., 2002 and 2003a) and CRC A-38 EMFAC on-road vehicle emission factor model evaluation (Yarwood et al., 2003b) studies. The previous studies have found good model performance for ozone and ozone precursors in the Los Angeles are with this modeling system.

Ambient Conditions During the SCOS Episode

The August 3–7, 1997 ozone episode began with warm temperatures at the surface and aloft and weak pressure gradients directed offshore opposing onshore sea breezes. August 3 was the first model spin-up day and is not discussed. Ozone concentrations were relatively low on August 4 in most locations with the highest ozone occurring inland in the mountains and passes consistent with onshore flow. On August 5, temperatures increased reaching 29 °C at Los Angeles International Airport (LAX) and 49 °C at Palm Springs. The offshore pressure gradient increased in intensity and the episode maximum ozone concentration was 187 ppb at Riverside, consistent with continued weak onshore flow. By August 6, the offshore pressure gradients had weakened and inland temperatures cooled (43 °C at Palm Springs). The maximum ozone on August 6 occurred in the mountains at Crestline. On August 7, pressure gradients turned onshore and the onshore winds strengthened so that the highest ozone concentrations occurred far inland. The meteorological patterns during the August 3–7, 1997 period fit a typical pattern for Los Angeles ozone episodes. High ozone levels occurred because the period was relatively stagnant, tending to trap ozone and precursors within the Los Angeles basin.

Models and Modeling Domain

Photochemical ozone modeling for the August 3-7, 1997 SCOS period was performed with version 4.03 of the Comprehensive Air-quality Model with extensions (CAMx; ENVIRON, 2004). CAMx simulates the emission, dispersion, reaction, and removal of ozone precursors and ozone in a Eulerian (grid) framework. The modeling domain covered 65 by 40, 5-km grid cells as shown in Figure 2-1. This domain was selected to be consistent with past modeling for air quality management plans in the LA area (SCAQMD 1997, 1999). CAMx was run with 10 layers extending between a surface layer of 60 m and a model top at 4 km.

Meteorological input data for CAMx were developed using the Penn State/NCAR Mesoscale Model, version 5 (MM5). The MM5 is a non-hydrostatic, prognostic meteorological model that simulates atmospheric properties based on fundamental equations, but also permits assimilation of observed data to nudge the simulated meteorological fields toward the data (Dudhia, 1993). MM5 was run with assimilation of SCOS measurement data assembled by the CARB (i.e., radar wind profiler upper-air data and surface site data) and Eta Data Analysis System data from the National Centers for Environmental Prediction (NOAA-ARL, 2002). The CAMx modeling grid was closely matched to the MM5 grid and, in particular, CAMx layer interfaces exactly matched MM5 layer interfaces to facilitate direct mapping of meteorological parameters from MM5 to CAMx.

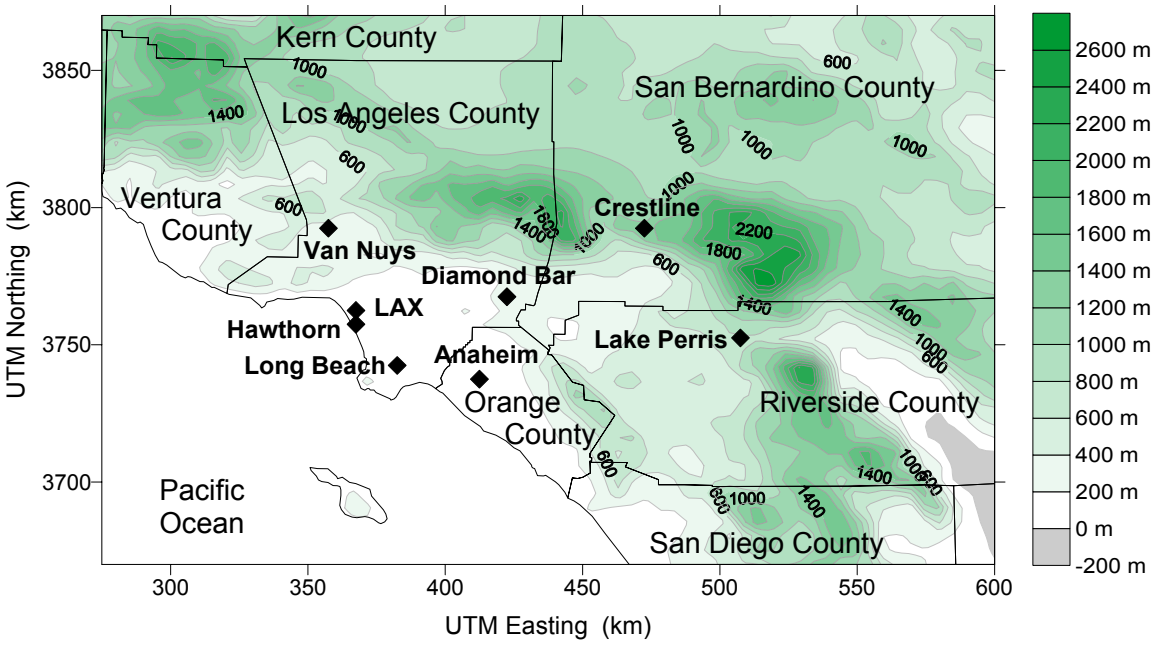


Figure 2-1. CAMx photochemical modeling domain showing terrain height (m) and receptor locations for the CMB analysis.

Selection of a Photochemical Mechanism for the Host Model

The photochemical mechanism for the host model is important because it provides the oxidant fields to chemically decay the PAMS species reactive tracers. CAMx supports both the CB4 (Gery et al., 1989) and SAPRC99 (Carter, 2000) chemical mechanisms. Emission inventories for the August 1997 SCOS episode are available for both the CB4 and SAPRC99 chemistry. The CB4 chemical mechanism was selected because, together with the other model inputs, it better replicates the observed ozone levels for the August SCOS episode than the SAPRC99 mechanism (Yarwood et al., 2003b).

Reactive Tracers (RTRAC) for PAMS Species and Source Categories

Atmospheric concentrations of specific PAMS species from specific source categories were modeled using a reactive tracer methodology (RTRAC) included in CAMx (ENVIRON, 2004). This methodology was developed and tested for modeling air toxics species in Los Angeles for

CRC project A-42-2 (ENVIRON, 2002a). In RTRAC, an arbitrary number of additional tracer species can be added to a CAMx simulation where they are emitted, transported and deposited using the core model algorithms. The core model chemistry drives the chemical decay of RTRAC tracers by reactions with OH radical, NO_3 radical, ozone and photolysis. Compared to the alternate approach of adding "live species" to the core model the RTRAC approach has several advantages for this study:

- Reactive tracers are much more computationally efficient than live species.
- The oxidant fields are decoupled from uncertainties in the chemistry of the tracers.
- The source strengths of the tracers may be varied without changing the oxidant fields allowing experiments to be more controlled.

RTRAC was used to model atmospheric concentrations of 55 PAMS species from 22 source categories giving a total of 1210 unique tracers in each simulation. The total concentration of a PAMS species at a receptor location is the sum of tracers for that species over the 22 source categories modeled, plus a background. Sampling noise was added to this total concentration as described below. The 55 PAMS species are listed in Table 2-1 along with reaction rate constants at 298 K and background concentrations. Each PAMS species was assigned a unique "A-34" number for this study. Table 2-1 also provides the short names that DRI uses for PAMS species in receptor modeling studies. Reaction rate constants at 298 K and 1 atmosphere are given in units of cm^3 $molecule^{-1}$ s^{-1} and are from Calvert et al. (2000, 2002), JPL (1997), Atkinson (1989) and Carter (2000). Temperature dependencies of rate constants also were accounted for in the modeling. The background concentrations shown in Table 2-1 are averages of data from San Nicolas Island (in the Pacific Ocean to the west of Los Angeles) collected during SCOS and provided by DRI.

Table 2-1. PAMS species included in the modeling analysis with reaction rate constants at 298 K and background concentrations.

A-34 Num	Short Name	Full Name	M.Wt. (g)	k(OH) #	k(O3) #	k(NO3) #	Background (ppbC) $
1	ETHENE	ethene	28.05	8.52E-12	1.59E-18	2.05E-16	0.503
2	ACETYL	acetylene	26.04	8.97E-13			0.475
3	ETHANE	ethane	30.07	2.68E-13			1.393
4	PROPE	propene	42.08	2.63E-11	1.01E-17	9.49E-15	0.292
5	N_PROP	n-propane	44.10	1.15E-12			0.590
6	I_BUTA	isobutane	58.12	2.34E-12			0.383
7	LBUT1E	1-butene	56.11	3.14E-11	9.65E-18	1.35E-14	0.048
8	N_BUTA	n-butane	58.12	2.54E-12			0.608
9	T2BUTE	t-2-Butene	56.11	6.40E-11	1.90E-16	3.90E-13	0.000
10	C2BUTE	c-2-butene	56.11	5.64E-11	1.25E-16	3.52E-13	0.000
11	IPENTA	isopentane	72.15	3.90E-12			0.613
12	PENTE1	1-pentene	70.13	5.14E-11	1.06E-17	1.38E-14	0.057
13	N_PENT	n-pentane	72.15	3.94E-12			0.367
14	I_PREN	isoprene	68.11	1.01E-10	1.28E-17	6.78E-13	0.000
15	T2PENE	t-2-pentene	70.13	6.70E-11	2.96E-16	3.70E-13	0.000
16	C2PENE	c-2-pentene	70.13	6.50E-11	2.09E-16	3.70E-13	0.000
17	BU22DM	2,2-dimethylbutane	86.17	2.32E-12			0.047
18	CPENTA	cyclopentane	70.13	5.16E-12			0.000
19	BU23DM	2,3-dimethylbutane	86.17	6.20E-12			0.088
20	PENA2M	2-methylpentane	86.17	5.60E-12			0.382
21	PENA3M	3-methylpentane	86.17	5.70E-12			0.152

A-34 Num	Short Name	Full Name	M.Wt. (g)	k(OH) #	k(O3) #	k(NO3) #	Background (ppbC) $
22	P1E2ME	2-methyl-1-pentene	84.16	6.30E-11	1.60E-17	3.32E-13	0.000
23	N_HEX	n-hexane	86.17	5.61E-12			0.183
24	MCYPNA	methylcyclopentane	84.16	5.68E-12			0.107
25	PEN24M	2,4-dimethylpentane	100.20	5.00E-12			0.068
26	BENZE	benzene	78.11	1.22E-12			0.280
27	CYHEXA	cyclohexane	84.16	7.49E-12			0.055
28	HEXA2M	2-methylhexane	98.19	6.89E-12			0.070
29	PEN23M	2,3-dimethylpentane	100.20	7.15E-12			0.133
30	HEXA3M	3-methylhexane	100.20	7.17E-12			0.582
31	PA224M	2,2,4-trimethylpentane	114.23	3.68E-12			0.113
32	N_HEPT	n-heptane	100.20	7.20E-12			0.113
33	MECYHX	methylcyclohexane	98.19	1.00E-11			0.077
34	PA234M	2,3,4-trimethylpentane	114.23	7.10E-12			0.037
35	TOLUE	toluene	92.14	5.63E-12			0.350
36	HEP2ME	2-methylheptane	114.23	8.31E-12			0.062
37	HEP3ME	3-methylheptane	114.23	8.59E-12			0.037
38	N_OCT	n-octane	114.22	8.68E-12			0.083
39	ETBZ	ethylbenzene	106.16	7.00E-12			0.070
40	MP_XYL	mp-xylene	106.16	1.87E-11			0.153
41	STYR	styrene	104.14	5.80E-11			0.000
42	O_XYL	o-xylene	106.17	1.36E-11			0.065
43	N_NON	n-nonane	128.26	1.02E-11			0.087
44	IPRBZ	isopropylbenzene	120.20	6.30E-12			0.000
45	N_PRBZ	n-propylbenzene	120.20	5.80E-12			0.075
46	M_ETOL	m-ethyltoluene	120.20	1.86E-11			0.067
47	P_ETOL	p-ethyltoluene	120.20	1.18E-11			0.073
48	BZ135M	1,3,5-trimethylbenzene	120.20	5.67E-11			0.178
49	O_ETOL	o-ethyltoluene	120.20	1.19E-11			0.047
50	BZ124M	1,2,4-trimethylbenzene	120.20	3.25E-11			0.443
51	N_DEC	n-decane	142.29	1.16E-11			0.092
52	BZ123M	1,2,3-trimethylbenzene	120.20	3.27E-11			0.077
53	DETBZ1	m-diethylbenzene	134.22	1.50E-11			0.000
54	DETBZ2	p-diethylbenzene	134.22	1.00E-11			0.000
55	N_UNDE	n-undecane	156.30	1.32E-11			0.105

Notes:

Rate constants are at 298 K and 1 atmosphere in units cm^3 $molecule^{-1}$ s^{-1}

$ Background concentration is the average from San Nicolas Island

Receptor Locations

Eight receptor locations were selected to represent different types of locations within the Los Angeles modeling domain. Receptors were selected at four location types:

- Fresh urban emissions: Anaheim (29,13) and Van Nuys (18,24)
- Fresh urban/industrial emissions: Long Beach (23,14), Hawthorn (20,17) and LAX (20,18)
- Mixed fresh/aged air mass: Diamond Bar (31,19)
- Downwind locations with aged air: Crestline (41,24) and Lake Perris (48,16)

Additional information on these receptor locations is given in the supporting information for Round 2, below.

2.2 EMISSION INVENTORY DATA

Emission inventory data were provided by the California Air Resources Board (ARB; Allen, 2002) as described previously by Yarwood et al., (2003b). On-road mobile emissions were based on the ARB's EMFAC 2001 emission factor model. Biogenic emissions were based on the ARB's BEIGIS model. The ARB emissions inventory staff working with the South Coast Air Quality management District (SCAQMD) developed the other emissions data.

The emission inventories were formatted for photochemical modeling using the ARB's Gridded Emissions Model (GEM; Allen, 2002). The GEM computer program performs the following major functions:

- Read gridded emissions data for total organic gases (TOG), NOx and CO.
- Apply temporal allocation profiles for emissions data are daily totals rather than hourly totals (only on-road mobile and biogenics are hourly).
- Apply chemical speciation profiles to convert organic emissions from TOG to modeling species (e.g., CB4).
- Separate emissions data for elevated sources (stacks) and ground level sources into two output files for CAMx.

Two sets of emissions inventory data were prepared for this study. The standard version of the GEM software was used to prepare CB4 emissions inventories to drive the calculation of oxidant fields by the core CAMx model. The CB4 emissions are summarized in Table 2-2. A modified version of the GEM software was created to prepare emissions of the 1210 reactive tracers species for 55 PAMS species from 22 source categories.

Table 2-2. Emission inventories (tons/day) for the CAMx-CB4 modeling of oxidant fields.

	Sunday 3-Aug-97	Monday 4-Aug-97	Tuesday 5-Aug-97	Wednesday 6-Aug-97	Thursday 7-Aug-97
NOx					
On-road Mobile	674.5	923.8	985.7	950.2	938.0
Other surface	400.8	470.5	471.1	471.1	471.1
Point source	129.1	132.9	116.2	120.5	129.6
Wildfire	4.4	0.9	47.5	234.7	105.6
Biogenic	0.0	0.0	0.0	0.0	0.0
Total	**1208.8**	**1528.1**	**1620.5**	**1776.4**	**1644.3**
CB4-ROG					
On-road Mobile	746.2	813.9	913.7	854.0	791.1
Other surface	918.4	781.6	812.8	792.4	763.7
Point source	9.0	9.2	8.6	8.8	9.2
Wildfire	24.3	4.9	260.6	1286.3	576.2
Biogenic	361.3	381.8	494.2	419.8	313.7
Total	**2059.3**	**1991.5**	**2489.8**	**3361.2**	**2453.9**

	Sunday 3-Aug-97	Monday 4-Aug-97	Tuesday 5-Aug-97	Wednesday 6-Aug-97	Thursday 7-Aug-97
CO					
On-road Mobile	6031.2	7015.6	7458.9	7277.2	6918.3
Other surface	2598.8	1157.4	1157.4	1157.4	1157.4
Point source	42.2	45.1	43.4	43.8	44.6
Wildfire	169.7	33.9	1825.7	9018.8	4058.2
Biogenic	0.0	0.0	0.0	0.0	0.0
Total	**8841.9**	**8252.0**	**10485.4**	**17497.3**	**12178.6**

Notes:
1. On-road mobile emissions are from EMFAC2001.
2. Other surface emissions include off-road mobile and area sources.
3. CB4-ROG is the sum of CB4 species assuming molecular weights of 16 per Carbon to account for average carbon/hydrogen/oxygen ratios in VOC.
4. NOx includes HONO emissions.

Reactive Tracer Emission Inventories for PAMS Species

The ARB SCOS97 emissions inventory provides organic emissions as total organic gases (TOG). The relationships between TOG and other definitions of organic gases are defined to minimize confusion later on. Reactive organic gases (ROG, equivalent to the EPA term VOC) are a subset of TOG that excludes methane, ethane, acetone, methyl acetate and many halogenated compounds. The 55 PAMS species listed in Table 2-1 are a subset of ROG except for ethane. Consequently:

- Emissions of TOG are always greater than ROG
- Emissions of ROG generally are greater than the sum of PAMS except when ethane is a significant contributor.

The ARB SCOS97 emissions inventory classifies TOG emissions from thousands of source categories that are identified by source category codes (SCCs). TOG emissions are chemical speciated using speciation profiles that apportion TOG to individual organic compounds. The ARB has a TOG speciation library containing hundreds of source profiles. Many speciation profiles are assigned by the ARB to multiple SCCs. The SCOS97 emissions inventory was analyzed to identify a manageable number (~20) of source category groupings that account for most of the organic gas emissions. The source category groupings were selected to combine emissions that have similar chemical speciation, or that receptor modelers generally assume can be represented by a characteristic speciation profile.

The SCOS97 TOG emission data were the starting point for the selection of source categories to be modeled. The emission inventory for August 5, 1997 contains 170 source categories with at least 1 ton/day of TOG emissions (Appendix A, Table A-1). These 170 source categories account for more than 96% of the total TOG emissions in the CAMx modeling domain and are mapped to 86 different chemical speciation profiles (Appendix A, Table A-2). The 170 ARB source categories were assigned to the 21 source category groups shown in Table 2-3. An additional source category was included called “hypothetical industrial operations” as described below. The top 20 speciation profiles with the highest ROG emissions (excluding wildfires) are

listed by ARB profile code in Table 2-4. These profiles account for about 80% of the ROG emissions in the RTRAC simulations of detailed VOC composition.

Table 2-3. Source category groups for the CAMx-RTRAC simulation of detailed VOC composition.

A-34 Category	Description
1	On-road Mobile Gasoline Catalyst Exhaust – start emissions
2	On-road Mobile Gasoline Catalyst Exhaust – stabilized emissions
3	On-road Mobile Gasoline Non-Catalyst Exhaust – start
4	On-road Mobile Gasoline Non-Catalyst Exhaust – stabilized
5	On-road Mobile Gasoline Evaporative – vapor
6	On-road Mobile Gasoline Evaporative – liquid fuel
7	On-road Mobile Diesel
8	Off-road Mobile Gasoline Four-Stroke
9	Off-road Mobile Gasoline Two-Stroke
10	Off-road Mobile Diesel
11	Gasoline Marketing/Refueling
12	Oil and Gas Extraction
13	Refinery Operations
14	Consumer Products
15	Architectural Coatings
16	Other Surface Coatings and Industrial Solvents
17	Degreasing
18	Biogenics
19	Wastewater Treatment
20	Industrial Engines (gas fueled)
21	Hypothetical Industrial Operations
22	Other

Notes:

Other includes wildfires, livestock, landfills, turbines, jets, plastics manufacturing, baking, pesticides, cooking (see Appendix A, Tables A-1 to A-3).

Table 2-4. Top 20 speciation profiles by ROG emissions in the ARB emissions inventory for August 5, 1997.

ARB Profile	ROG Tons/Day	TOG Tons/Day	ARB Description
419	285.0	285.0	Liquid Gasoline - MTBE 11% - Commercial Grade - MTBE/Etoh Program
806	273.0	479.1	Isoprene & Soil No
307	224.8	243.9	Forest Fires
401	205.7	205.7	Gasoline - Non-Cat - Stabilized Exhaust - ARB Ius Summer 1996
906	188.6	228.7	Gasoline - Ucberk - Headspace Vapors For MTBE 2.0 % O Gasoline
436	179.3	179.3	Gasoline - Catalyst - Stabilized Exhaust - ARB Summer 1997
807	135.0	144.2	Monoterpenes
877	97.2	149.5	Gasoline - Catalyst - Ftp Bag 1-3 Starts - ARB Ius Summer 1996
533	60.6	62.8	Daytime Biogenic Profile- Kern County Crops
919	53.7	61.1	Degreasing: Cold Cleaning (Batch, Conveyor, Spray Gun)
818	38.2	41.1	Farm Equipment - Diesel - Light & Heavy - (Ems=Actual Weight)
1901	29.0	29.3	Draft Architectural Ctgs: Solvent Borne (ARB 1998 Survey)
783	22.7	22.7	Industrial Surface Coating-Solvent Based Paint
1760	19.0	19.4	Draft Consumer Prd: Hair Spray

ARB Profile	ROG Tons/Day	TOG Tons/Day	ARB Description
402	17.9	19.4	Gasoline - Non-Cat - Ftp Bag1-3 Starts - ARB Ius Summer 1996
822	17.2	215.0	Methylbutenol
203	16.7	23.9	Animal Waste Decomposition
600	12.9	13.1	Species Unknown- All Category Composite
1902	12.6	13.0	Draft Architectural Ctgs: Water Borne (ARB 1998 Survey)
1930	11.6	13.4	Thinning Solvent/Mineral Spirits (Calpoly Slo 1996) ARB Default
Total	**1637.7**	**1981.7**	

Examining the profiles listed in Table 2-4 shows that major industrial VOC emissions sources (refineries, chemicals) are not present in the top 20 profiles. This illustrates the concern that major industrial sources are relatively less important in Los Angeles than many other urban areas due to emissions regulations. This was addressed by adding emissions from hypothetical industrial sources, as described below. Another concern was that three biogenic emissions profiles contained only the dominant compounds (isoprene, terpenes, methylbutenol) and not minor constituents that also are PAMS species. The biogenic emissions profiles were modified as described below. Finally, a speciation profile was developed for 2-stroke exhaust (A-34 category 9 in Table 2-3) by combining 80% profile 419 (liquid fuel) with 20% profile 401 (non-cat exhaust).

PAMS Speciation for Biogenic Emissions

Biogenic emissions are often modeled (e.g., by the EPA BEIS models) as isoprene, terpenes and generic "other VOCs". Since there are no terpenes among the PAMS species and the other VOCs are unspecified, this makes the conventional PAMS speciation for biogenic emissions trivial (100% isoprene) and essentially unique within CMB. In reality, biogenic emissions contain species that also are emitted by anthropogenic sources and so there is a possibility of biogenic emissions being classified as anthropogenic by CMB. The biogenic speciation profiles for this study were modified to account for potential overlap of biogenic and anthropogenic emissions for PAMS species.

A speciation approach was developed for the GloBEIS biogenic emissions model that identifies some of the "other VOCs" (ENVIRON, 2002b and Guenther et. al., 1999) as summarized in Table 2-5. This table shows estimated total biogenic emissions of various VOCs organized by emissions mechanism (table rows, not specifically identified here) and gives an overall estimate of the types and amounts of compounds emitted. The compounds other than isoprene that are in the PAMS species list are ethane, ethene, propene, butene, and possible formaldehyde and acetaldehyde. Several other compounds would likely be included in the TNMOC reported by a PAMS measurement (e.g., methylbutenol, ethanol, methanol, acetone, butanone). Table 2-5 suggests that, on average, ethene emissions might be about 5% of biogenic emissions and propene, butene, formaldehyde and acetaldehyde should be a smaller fraction. Biogenic ethene is potentially significant because the CMB is sensitive to the ethene/acetylene ratio. Five % ethene, 1% propene and 1% butene were added to the ARB biogenic emissions of terpenes and methylbutenol. This approach ensured that the added ethane/propene/butene had a different temporal/spatial distribution than isoprene which is appropriate because these emissions have different source mechanism.

Table 2-5. Estimated North American biogenic emission totals by species and organized by emissions mechanism (rows).

Emission Capacity (mg g^{-1} hr^{-1})	Annual Emissions (Tg Carbon)	Emitted Compounds
0 to 100	29.3	isoprene
0 to 60	3.2	methylbuteneol
0 to 2	4.5	a-pinene
0 to 1.5	3.2	b-Pinene
0 to 1	2	D3-Carene
0 to 0.6	0.4 to 1.1	sabinene, d-Limonene, b-phellandrene, r-cymene, myrcene
0 to 1.5	0.1 to 0.4	camphene, camphor, bornyl acetate, a-thujene, terpinolene, a-terpinene,g-terpinene, ocimene, 1,8-cineole, piperitone, a-phellandrene, tricyclene
0.6	8.4	methanol
0.3	4	carbon monoxide
0.16	2.6	hexenyl-acetate, hexenol
0.09	1.5	ethene
0.09	1.5	propene, ethanol, acetone, hexenal,
0.04	0.6	acetaldehyde, formaldehyde, butene, hexanal
0.02	0.2	butanone, ethane, acetic acid, formic acid

Hypothetical Industrial Emissions

Industrial VOC emissions were added to the emission inventory to boost the importance of major industrial sources. These are referred to as "hypothetical industrial emissions" because the sources do not really exist in Los Angeles. DRI had no knowledge that these hypothetical emissions were added to the emission inventory. The source profiles were derived from actual chemical plants and refineries in Texas. The point source emission inventory for 2000 prepared by the Texas Commission on Environmental Quality (TCEQ) was reviewed and 9 major facilities were identified as listed in Table 2-6. The TCEQ's point source database (PSDB) was chosen for this purpose because it encourages facilities to report detailed speciation data. The facilities in Table 2-6 were selected because they had high total ROG emissions with relatively complete and detailed speciation data.

Table 2-6. Major VOC emission sources from the TCEQ point source database (PSDB) for year 2000.

TCEQ Code	ROG Tons/Day	PAMS Tons/Day	Approximate description of activities
HW0018P	17.2	6.5	Refinery - Motor fuels, aviation fuel, LPG, distillates
GB0004L	12.3	4.7	Chemical plant - styrenics, aromatics, lubricants, olefins
HG0232Q	11.4	5.1	Chemical plant - olefins
HG0659W	10.4	6.3	Refinery - motor fuels, aviation fuels, ship and utility fuels
HH0042M	9.9	6.6	Chemical plant - olefins, plastics
JE00671	8.7	3.6	Chemical plant - olefins, aromatics, polyethylene, specialty
HG0033B	6.7	4.0	Chemical plant - olefins, aromatics, alkylates, MTBE
HG0048L	6.4	3.7	Refinery - motor fuels, aviation fuels, lubricants, aromatics
CB0028T	6.0	4.9	Chemical plant - chemicals, plastics and catalysts

Industrial facilities from Table 2-6 were grouped into complexes of three facilities at six locations throughout the Los Angeles area as shown in Table 2-7. Facilities were combined to provide more complicated emissions signatures at each source complex. To further complicate the emissions signatures, each facility in each complex was assigned a different temporal profile. These temporal profiles varied the emissions rate every three hours within a range spanning a factor of three. The result was that the emissions from each complex varied in composition and magnitude every hour.

Table 2-7. Industrial source complexes synthesized for six locations in the Los Angeles area.

Location Name	Grid Cell i	Grid Cell j	TCEQ Code	SCC	ROG Tons/Day	PAMS Tons/Day
Disneyland	29	16	HW0018P	1000010	39.3	17.8
			GB0004L	1000011		
			HH0042M	1000014		
Griffith Park	22	22	HG0659W	1000013	30.5	15.0
			HG0232Q	1000012		
			JE00671	1000015		
LAX/Hawthorn	20	17	HG0048L	1000017	23.0	14.3
			HH0042M	1000014		
			HG0033B	1000016		
Ontario	35	20	HW0018P	1000010	31.9	15.0
			JE00671	1000015		
			CB0028T	1000018		
Long Beach	22	14	HG0659W	1000013	29.3	14.9
			HG0033B	1000016		
			GB0004L	1000011		
El Monte	27	20	HG0048L	1000017	23.9	13.6
			CB0028T	1000018		
			HG0232Q	1000012		
Total					**177.9**	**90.6**

2.3 MEASUREMENT NOISE IN AMBIENT SAMPLES

To present the receptor model with problems that represent real-world conditions, the variability in the simulated ambient samples should be comparable to ambient data that are typically used for receptor modeling. Real-world variability is introduced by several mechanisms, including:

- Variability in source contributions.
- Variability in source profiles.
- Different amounts of chemical aging.
- Measurement errors in collecting and analyzing the ambient samples.

The photochemical modeling addressed all of these sources of variability, to some extent, except for measurement noise. Failing to account for measurement noise would give the receptor modelers a significant advantage over real-world applications because the numerical model can maintain precision in source receptor relationships down to concentration levels that are well below ambient detection limits.

An ambient data set from a 1995 DRI receptor modeling study for Los Angeles was analyzed to infer the variability in VOC measurements by VOC species type. The variability inferred from

the DRI data was consistent with variability in inter-laboratory blind comparisons (Apel et al., 1999). The simulated ambient samples from the CAMx simulations were post-processed by adding random sampling noise to obtain a target level of variability for each species. The sampling noise sometimes resulted in negative concentrations that were then treated as missing data.

We analyzed ambient data obtained by DRI in an October 1995 Los Angeles study that has been used in previous CRC projects (Fujita et. al., 1997a). The analysis focused on morning samples when variability should be most related to source variability and measurement artifacts and least related to different chemical aging. The October 1995 data set included 24 VOC canister samples that were collected at eight sites across the Los Angeles urban area from 6 to 7 am or 7 to 8 am on October 10-12, 1995 (Fujita et al., 1997). The sites included Azusa, Burbank, Lynwood, Long Beach, Los Angeles North Main and Pico Rivera. The VOC data were classified into PAMS and other species, and sum of the PAMS species compared to the total NMHC (TNMHC) in Figure 2-2. For most samples the PAMS species accounted for about 70% of TNHMC except for two samples from Pico Rivera that were excluded from further analysis. The weight fraction of the PAMS species (i.e., relative to the sum of PAMS species) was calculated for each of the remaining 22 samples. Figure 2-3 shows the mean weight fraction and the range (minimum to maximum) for the 22 samples on absolute and log scales. The log scale plot suggests that the relative variability depends both upon the species type (alkane, alkene, etc.) and the concentration level. Higher concentration species often have less relative variability than lower, but there are exceptions such as light alkanes. From examining the relationships between the standard deviations and the means for the species shown in Figure 2-3, we developed total variability targets (1 sigma) for species weight fractions as shown in Table 2-8.

Table 2-8. Target variability (1 sigma) in weight fraction for random sampling noise.

Compound	Target Variability
Alkanes	
ethane	40%
c3-c4 alkanes	35%
c5-c6 alkanes	20%
c7+ alkanes	10%
Alkenes	
ethene	15%
propene	20%
c4+ alkenes	30%
isoprene	50%
Alkynes	
acetylene	20%
Aromatics	
benzene	10%
toluene	20%
c8 aromatics	15%
styrene	50%
c9+ aromatics	25%

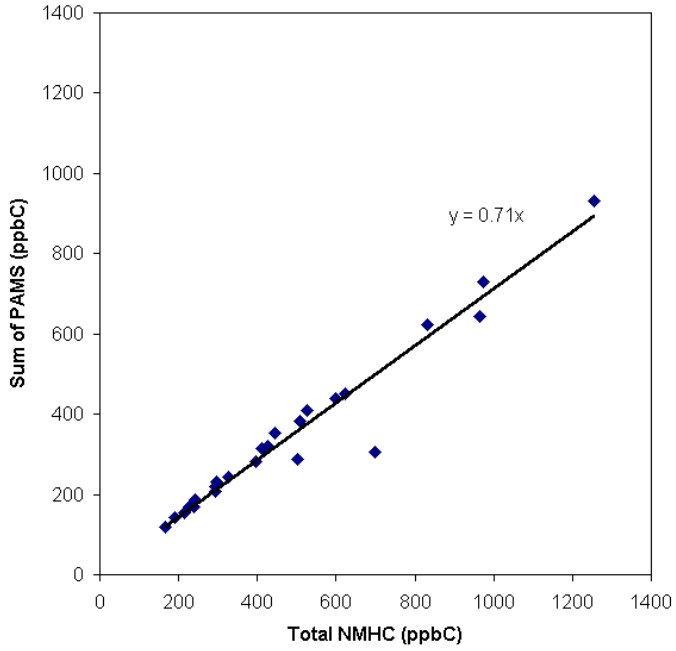


Figure 2-2. Comparison of the sum of PAMS species to Total NMHC for 24 morning samples from Los Angeles in October 1995.

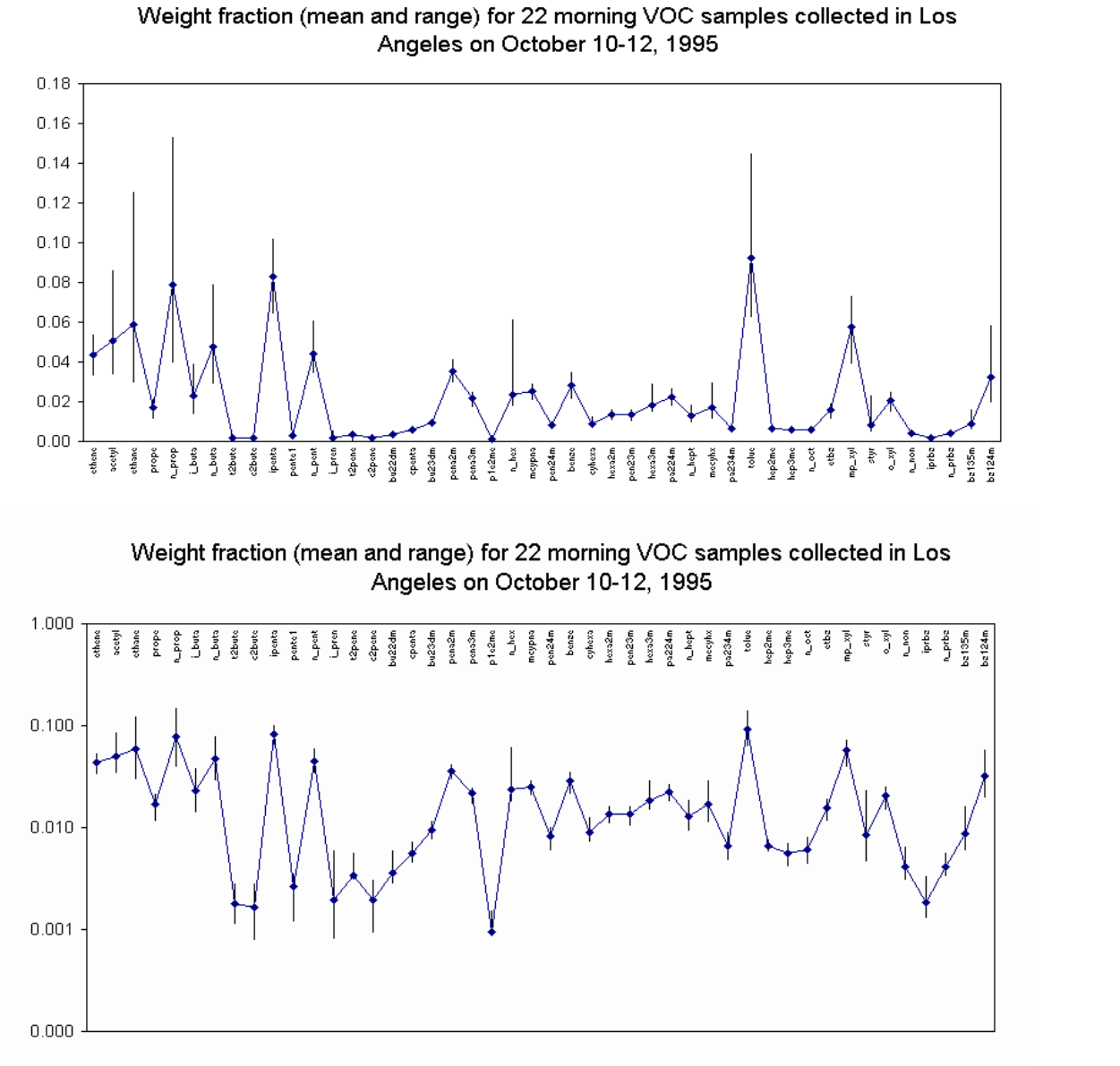


Figure 2-3. Average composition (weight percent) and range for PAMS species in 22 morning samples from Los Angeles in October 1995. Shown on an absolute scale (top) and log scale (bottom).

The random variability introduced into the ambient samples, shown in Table 2-8, is described as "measurement noise" because it was developed to address this issue. However, because of the way that the measurement noise estimates were developed from real-world data, it is likely that the random variability includes some effects of emissions source strength and source profile variability in addition to measurement noise. This is consistent with the project objectives because the photochemical model predicts concentrations that represent 25 km^2 grid cells whereas urban monitoring sites are influenced by neighborhood scale variability that is not captured by the grid model.

2.4 EXPERIMENTS FOR ROUNDS 1 AND 2

For Rounds 1 and 2, ENVIRON provided DRI with virtual PAMS samples for 8 receptors, four days (August 4-7, 1997) and 8 different experiments for a total of 6144 simulated air samples. The 8 experiments differed in modeling assumptions used to prepare the simulated air samples (e.g., relative source contributions, atmospheric reactivity, sampling noise, source profiles). For Round 1, DRI had no additional supporting information beyond the sample identification number. For Round 2, ENVIRON provided DRI with additional information that a receptor modeler would typically have available to support a real-world receptor model application. For example, a virtual tunnel study was performed to provide DRI with information on the mobile source emissions profiles.

The 8 experiments for Rounds 1 and 2 are described below and the relative emission levels for the source categories in each experiment are shown in the Table 2-9. The emission levels by source category were varied for each experiment as shown in Table 2-9 so that each experiment would be different, in some cases substantially different. The base emissions for each day shown in Table 2-10 were multiplied by the ROG percentages from Table 2-9. This conserves total ROG emission levels, but not necessarily the total TOG and PAMS emission levels as illustrated in Table 2-11 for experiment 1 on August 5, 1997.

1. **Base Case:** A simulation representing nominal 1997 weekday conditions. Random measurement noise was added to the species concentrations at each receptor.

2. **Higher Atmospheric Reactivity:** Essentially a re-run of the base case with higher ambient reactivity to produce more rapid chemical aging of VOC emissions. The 1997 base case has a relatively low VOC-NOx ratio that results in suppression of ozone (and related photochemical activity) over a wide area of the LA basin for much of the night and morning. Photochemical reactivity was enhanced by substantially reducing the NOx emission inventory (by 50% for surface emissions and 75% for point sources) to raise the VOC/NOx ratio. In addition, a 300 m deep mixed layer was maintained at night to reduce NOx titration of ozone and suppression of nocturnal chemistry. The source contributions will be varied from the base case by a moderate amount to provide a different receptor model solution without completely changing the nature of the problem. The source profiles were the same as the base case but the measurement noise will be different (but with the same form and magnitude). Random measurement noise was added to the species concentrations at each receptor with the same magnitude as the base case but initialized using a different random number. The objective of this experiment was to investigate the influence of high chemical aging on receptor model performance.

3. **Alternate Source Profiles:** Re-run the base case using alternate source profiles. Mobile source profiles were based on a Houston tunnel study and related fuel samples. The replacement of profiles is summarized in Tables 2-12 and 2-13. In total, 19 base case profiles were replaced by 7 alternate profiles affecting 53 source categories and about 50% of the ROG emissions. The source profiles were the same as the base case. The source contributions were varied from the base case by a moderate amount and the measurement noise was initialized using a different random number. The objective of this experiment was to investigate how receptor model performance is related to chemical speciation, especially for mobile sources.

4. **Reduced Species Set:** Re-run the base case with slightly different source contributions and set 20% (11) of the VOC species to missing in the receptor data. The removed species were ethene, acetylene, 2,2-dimethylbutane, 3-methylpentane, 2-methyl-1-pentene, methylcyclopentane, cyclohexane, 3-methylhexane, 2,3,4-trimethylpentane, toluene, mp-xylene. These include important species for the receptor model as well as less important species. The source profiles were the same as the base case. The source contributions were varied from the base case by a moderate amount and the measurement noise was initialized using a different random number. The objective of this experiment was to investigate the extent to which CMB results depend upon all species or a few key species.

5. **Weekend Source Mix:** The source category contributions were changed to approximate emissions changes that may occur on weekends in Los Angeles. The source profiles were the same as the base case and the measurement noise was initialized using a different random number. The objective of this experiment was to see whether the CMB could distinguish the difference between weekend and weekday emissions.

6. **High Industrial Emissions:** Include a large contribution from industrial source categories that are not typical of Los Angeles by increasing the hypothetical and real industrial emissions and lowering mobile source emissions. The source profiles were the same as the base case and the measurement noise was initialized using a different random number. The objective of this experiment was to observe CMB performance when the source attribution (solution) is very different from the other experiments and from what the receptor modelers expect for Los Angeles.

7. **Variable Source Profiles:** Source profiles were randomly varied from grid cell to grid cell around the base case profiles. Each species weight fraction was changed randomly with a sigma of 15% and then the profile was renormalized to conserve emissions mass. Since the variation was random, the average profiles should be similar to the base case. The source contributions were varied from the base case by a moderate amount and the measurement noise was initialized using a different random number. The objective of this experiment was to investigate the ability of CMB to see through random source profile variability.

8. **Poor Ambient Data:** The random measurement noise was doubled in magnitude relative to the base case. The source profiles were the same as the base case. The source contributions were varied from the base case by a moderate amount and the measurement noise was initialized using a different random number. The objective of this experiment was to investigate the ability of CMB to see through large amounts of measurement noise, corresponding to larger-than-typical measurement errors.

Table 2-9. Source category contribution (Percent of ROG) for each experiment in Rounds 1 and 2.

Experiment Number		1	2	3	4	5	6	7	8
A34 Number	**A34 Category Name**	**Base Case**	**High Reactivity**	**Alternate Source Profiles**	**Reduced Species Set**	**Weekend Source Mix**	**High Industrial Emissions**	**Variable Source Profiles**	**Poor Ambient Data**
01	Onroad Mobile Gasoline Catalyst Exhaust (start)	9	9	8	7	6	5	9	9
02	Onroad Mobile Gasoline Catalyst Exhaust (stabilized)	4	5	5	3	3	2	5	5
03	Onroad Mobile Gasoline Non-Catalyst Exhaust (start)	5	3	6	6	3	3	5	4
04	Onroad Mobile Gasoline Non-Catalyst Exhaust (stabilized)	1	1	1	1	1	1	1	1
05	Onroad Mobile Gasoline Evaporative (headspace)	11	11	11	11	8	4	12	10
06	Onroad Mobile Gasoline Evaporative (liquid)	4	4	3	3	3	2	4	4
07	Onroad Mobile Diesel	2	3	2	3	1	1	1	2
08	Offroad Gasoline Four-Stroke	3	3	3	5	4	2	3	3
09	Offroad Gasoline Two-Stroke	3	4	3	3	6	2	4	3
10	Offroad Diesel	1	1	1	1	1	1	1	1
11	Gasoline Marketing/Refueling	3	3	5	2	4	1	3	3
12	Oil and Gas Extraction	4	3	5	5	4	11	5	4
13	Refinery Operations	1	2	1	2	1	4	1	1
14	Consumer Products	4	3	6	3	4	3	4	5
15	Architectural Coatings	2	3	2	3	2	1	2	1
16	Other Surface Coatings and Industrial Solvents	3	3	2	2	3	7	3	4
17	Degreasing	4	4	3	3	4	9	4	4
18	Biogenics	17	19	15	20	21	9	14	18
19	Wastewater Treatment	0	0	0	0	0	0	0	0
20	Industrial Engines (gas fueled)	3	3	2	2	3	1	4	2
21	Hypothetical Industrial Operations	3	2	3	2	3	24	3	4
22	Other Sources	13	11	13	13	15	7	12	12
Total		**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**

Table 2-10. Total emissions of TOG, ROG and PAMS species in the base inventory used to prepare each experiments.

Day	TOG Tons/Day	ROG Tons/Day	PAMS Tons/Day	ROG/TOG Ratio	PAMS/ROG Ratio
3-Aug-97	2705	1974	1254	0.73	0.64
4-Aug-97	2666	1900	1188	0.71	0.62
5-Aug-97	2833	2066	1289	0.73	0.62
6-Aug-97	2726	1959	1223	0.72	0.62
7-Aug-97	2586	1821	1132	0.70	0.62

Table 2-11. Total emissions by source category for experiment 1 on August 5, 1997.

A-34 Category Number	TOG Tons/Day	ROG Tons/Day	PAMS Tons/Day	ROG/TOG Ratio	PAMS/ROG Ratio
1	225.5	185.9	148.8	0.82	0.80
2	88.2	82.6	62.8	0.94	0.76
3	112.0	103.3	78.6	0.92	0.76
4	22.3	20.7	15.8	0.92	0.76
5	227.3	227.2	161.2	1.00	0.71
6	82.7	82.6	59.6	1.00	0.72
7	47.1	41.3	16.5	0.88	0.40
8	71.3	62.0	47.8	0.87	0.77
9	62.9	62.0	43.7	0.99	0.70
10	23.5	20.7	8.2	0.88	0.40
11	62.0	62.0	48.0	1.00	0.77
12	704.3	82.6	98.3	0.12	1.19
13	29.7	20.7	21.1	0.70	1.02
14	94.8	82.6	19.3	0.87	0.23
15	43.5	41.3	13.2	0.95	0.32
16	67.9	62.0	35.5	0.91	0.57
17	134.1	82.6	29.9	0.62	0.36
18	374.1	351.2	234.7	0.94	0.67
19	0.0	0.0	0.0	N/A	N/A
20	677.9	62.0	147.9	0.09	2.39
21	62.0	62.0	31.6	1.00	0.51
22	1206.5	268.6	279.7	0.22	1.04
Total	**4419.6**	**2065.8**	**1602.1**	**0.47**	**0.78**

Table 2-12. Alternate speciation profiles used in experiment 3.

A-34 Code	Speciate Code	Description
9100		Liquid gasoline average composition for Houston RFG in summer 2000
9101		Gasoline headspace average composition for Houston RFG in summer 2000
9102		Washburn Tunnel profile for gasoline vehicles, Houston 2000
9103		2-stroke exhaust (0.8*9100 + 0.2*9102)
9104	2547	Composite of 10 Emission Profiles - Misc. Chemical and Refining Plants in Houston - 1993
9105	2520	Vehicle Exhaust - Tuscarora Tunnel Diesel - 1995
9106	2471 2472	Industrial Point Source, GATX Terminals, Principle Business: Bulk Storage Terminals - 1993

Table 2-13. Replacement of base case speciation profiles by alternate profiles in experiment 3 and the number of source categories (SCCs) affected.

ARB Code	ARB Description	A-34 Code	SCC Count
419	Liquid gasoline - MTBE 11% - Commercial	9100	3
906	Gasoline - UCBerk - headspace vapors for	9101	12
401	Gasoline - non-cat - stabilized exhaust	9102	8
402	Gasoline - non-cat - FTP bag1-3 STARTS	9102	1
413	Gasoline - non-cat - FTP Composite	9102	1
436	Gasoline - catalyst - stabilized exhaust	9102	1
877	Gasoline - catalyst - FTP Bag 1-3 STARTS	9102	1
9000	Project A-34: 0.2 * 401 + 0.8 * 419	9103	4
297	Crude oil evaporation- vapor composite f	9104	1
316	Refinery- pipes, valves & flanges- compo	9104	3
530	Oil & gas extraction - pump seals	9104	1
531	Oil & gas extraction - compressor seals	9104	2
818	Farm equipment - diesel - light & heavy	9105	7
520	Composite natural gas	9106	1
529	Oil & gas extraction - pipeline valves &	9106	2
551	OCS - oil seeps - volatile fraction	9106	1
756	Oil & gas production fugitives-liquid se	9106	2
757	Oil & gas production fugitives-gas servi	9106	1
758	Oil & gas production fugitives-valves-un	9106	1

Speciation Profiles for A-34 Categories in Experiment 1

As described above, the emissions for the 22 A-34 source categories in experiment 1 included 179 source categories (including hypothetical industrial emissions) represented by 95 speciation profiles. The first four A-34 categories represent a single SCC but all others are composites of multiple related SCCs (see Appendix A, Table A-3). For A-34 categories representing multiple SCCs, the source profile for the A-34 category can vary in time and space as the relative contributions of different SCCs vary. This is shown in Figure 2-4 which presents the spatial/temporal variation in source profiles for A-34 categories 1, 16 and 21 in experiment 1. The symbols show the median PAMS fraction and the vertical lines the inter-quartile range (25^{th} to 75^{th} percentiles). There is no variation for A-34 category 1 because it is a single SCC, but the other categories do have variable speciation with some species switching on/off (i.e., 25^{th} percentile PAMS fraction is zero, median is non-zero). This type of source profile variability may be expected in the real-world.

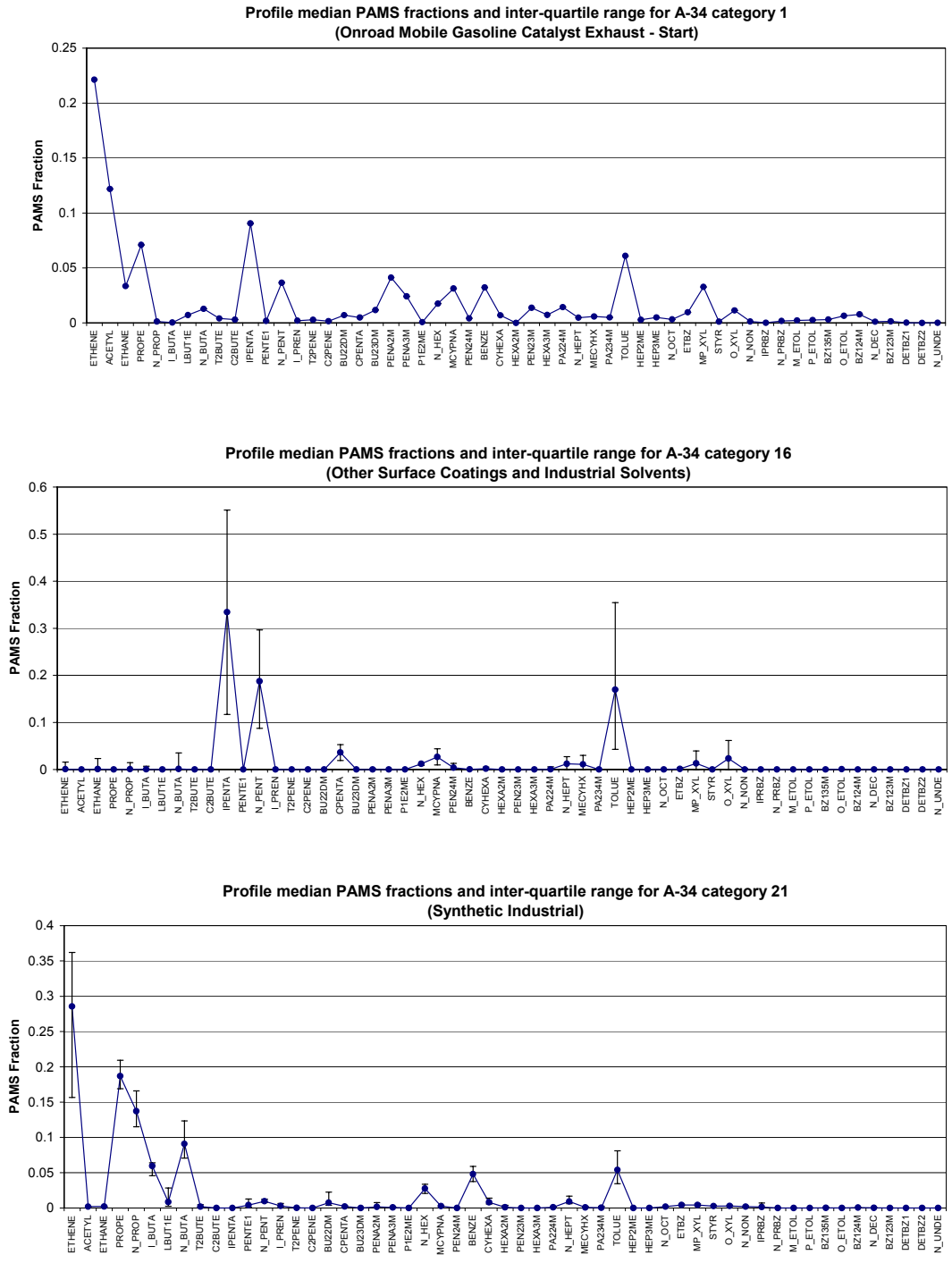


Figure 2-4. Spatial/temporal variation in source profiles for three A-34 categories (1, 16 and 21) in experiment 1. The symbols show the median PAMS fraction and the lines the inter-quartile range (25th to 75th percentiles).

The mean source profiles for all A-34 categories in experiment 1 are presented in Figure 2-5. This figure is useful in a qualitative sense to see which source profiles were similar and different. The species order from left to right is the same as Table 2-1 and the A-34 source category order

from front to back is the same as Table 2-3. The same information is given quantitatively in Table A-4 of Appendix A. Table A-5 presents mean source profiles for experiment 3, "alternate source profiles."

The on-road mobile source gasoline exhaust profiles (first four A-34 categories at the front of Figure 2-5) are similar, which they should be since all are based on similar fuel composition. We deliberately selected mobile source profiles that reflected the same type of fuel so that the experiments would be closer to real-world conditions. The source profiles for solvents, coatings and industrial sources toward the back of Figure 2-5 have peaks for many species that are low in the mobile source profiles toward the front of Figure 2-5. There also are species that are high in mobile and non-mobile source profiles such as ethane, the left most species in Figure 2-5.

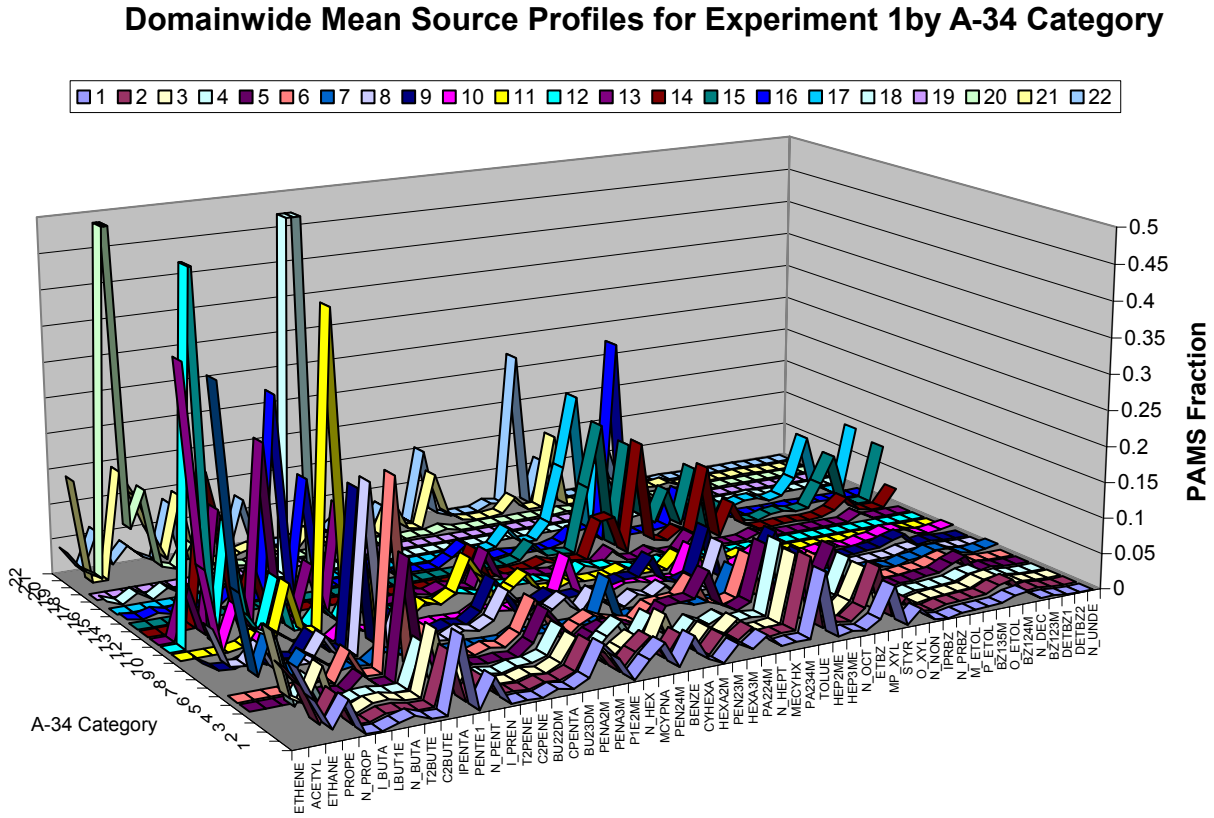


Figure 2-5. Mean source profiles for experiment 1. The profiles are for 55 PAMS species over 22 source categories. These are mean profiles because each A-34 category may combine several SCCs that have different speciation profiles.

2.5 SUPPORTING INFORMATION FOR ROUND 2

In Round 2, DRI analyzed the same experiments as in Round 1 but was provided with additional information that a receptor modeler would typically have available to support a "real-world" receptor model application. DRI requested information on:

- Receptor locations
- Source characterization
    - Tunnel study
    - Gasoline samples
    - CNG and LPG samples
    - Surface coatings
    - Background air samples
- Additional monitoring data
    - Tenax samples for heavy hydrocarbons (> C12)

ENVIRON provided information on receptor locations, a tunnel study, gasoline samples, CNG and LPG samples (although these profiles had not been utilized in the experiments) and background air composition. Data on surface coatings were not provided because very limited data are available and DRI was already using data from the same source as ENVIRON. Providing data for heavy hydrocarbons was beyond the scope of the available source profile data.

Description of Receptor Locations

The receptors were identified by the city/area where they are located. Receptors were sited to be regionally representative, meaning at least a 25 km^2 area. The receptor locations for A-34 are not the same as monitoring locations that may happen to have the same name in the real world. The expected emissions distribution for each area is:

- Anaheim and Van Nuys are densely populated mixed-use residential/commercial/light industrial areas.
- Hawthorn, Long Beach and LAX are similar to Anaheim and Van Nuys, but in addition have more heavy industry including petrochemicals (refining and chemical production).
- Diamond Bar is less densely populated than the sites described above and has a diverse mix of sources.
- Crestline and Lake Perris are downwind sites with low population density nearby. Crestline is in a forested area that is used for recreation.

Source Characterization

We conducted a virtual tunnel study in the Van Nuys tunnel. Air concentrations for the 55 PAMS species are reported in Table 2-14 for the 9 runs. The virtual tunnel study was based on data from an actual Van Nuys tunnel study described in Table 2-15. Tables 2-14 and 2-15 were provided to DRI.

The methodology for the virtual Tunnel study was as follows:

1. The fraction of vehicles older than 20 years was used as a proxy for the fraction of non-catalyst vehicles.
2. Set the g/mi hot stabilized exhaust emission rate for non-catalyst light-duty vehicles to 8 times that of catalyst vehicles (steps 1 and 2 combined give about 50% emissions from 12% non-catalyst vehicles with variation between tunnel runs).

3. Set the average diesel g/mi emission rate equal to the average for gasoline vehicle exhaust (as requested by DRI).
4. Set the running loss g/mi emission rate to 5% of gasoline exhaust on average, but vary between runs in proportion to the temperature minus 50 ºF.
5. Scale emission factors between runs in proportion to the number vehicles and to obtain an overall average of ~1.7 g/mi TNHMC as observed in the real study. The g/mi emission factors for each emissions type in each tunnel study run are shown in Table 2-16.
6. Speciate the tunnel study emissions using the same speciation profiles as for experiment 1.
7. Correct the tunnel speciation for background (as requested by DRI). No correction was necessary because no background had been introduced into the tunnel samples.
8. Introduce measurement noise into the speciation results for each run using the same algorithm as for the ambient samples. The final speciated emissions for each tunnel study run are shown in Table 2-14.

Table 2-14. Species composition data for the virtual tunnel study.

		Run1	Run2	Run3	Run4	Run5	Run6	Run7	Run8	Run9
Temperature (F)		86.2	90.1	84.2	102.0	88.3	98.8	94.6	107.8	108.9
Heavy Duty Vehicle Fraction		0.024	0.019	0.007	0.005	0.003	0.002	0.020	0.012	0.018
Species	**A34_Num**	**Tunnel Mixing Ratio (ppbC) Corrected for Background**								
ethene	1	202.2	149.2	111.0	109.4	57.1	101.6	263.6	260.3	140.1
acetylene	2	51.9	56.2	53.6	60.0	27.5	42.2	88.9	98.9	47.2
ethane	3	25.5	17.0	17.4	17.4	10.9	12.6	25.7	29.0	21.4
Propene	4	59.9	85.7	67.7	87.4	30.5	60.4	97.0	95.8	57.3
n-propane	5	1.4	1.2	1.7	0.8	0.6	0.5	2.4	1.1	1.0
isobutane	6	0.8	0.5	0.6	0.7	0.3	0.4	1.5	1.0	0.6
1-butene	7	9.3	7.9	11.7	7.7	4.2	7.1	10.9	10.2	7.9
n-butane	8	17.2	9.6	10.4	16.4	5.0	8.9	20.6	12.5	16.1
t-2-Butene	9	4.8	4.2	4.5	4.7	2.4	2.8	7.4	8.0	5.4
c-2-butene	10	3.9	4.4	3.6	3.1	1.3	2.2	4.6	4.1	4.0
isopentane	11	91.6	76.9	119.9	127.2	50.8	62.9	167.4	182.2	97.0
1-pentene	12	2.4	2.9	2.4	3.5	0.7	1.6	3.6	1.8	2.3
n-pentane	13	22.0	27.4	33.6	34.3	15.6	34.0	61.1	52.1	36.1
isoprene	14	2.5	2.2	2.9	2.4	1.2	1.9	3.5	3.4	1.9
t-2-Pentene	15	2.9	3.1	3.4	3.7	1.7	2.9	6.7	5.4	3.2
c-2-pentene	16	1.6	2.2	2.2	1.7	1.0	1.2	2.2	3.0	1.0
2,2-dimethylbutane	17	6.5	6.2	9.9	10.5	5.7	6.4	9.1	9.5	6.7
cyclopentane	18	5.3	5.1	5.4	5.4	3.1	4.4	9.8	8.4	4.9
2,3-dimethylbutane	19	20.4	22.5	17.6	20.8	10.8	17.2	24.3	20.0	14.1
2-methylpentane	20	53.6	82.3	79.0	74.9	30.9	50.3	75.6	55.8	33.0
3-methylpentane	21	40.3	33.1	31.1	33.6	20.0	27.7	49.3	36.5	22.0
2-methyl-1-pentene	22	1.3	1.3	1.0	0.9	0.4	1.1	1.4	1.1	1.1
n-hexane	23	26.0	19.6	13.9	27.0	12.4	17.7	33.6	28.4	20.3
Methylcyclopentane	24	39.4	45.2	57.8	52.0	17.6	21.6	49.0	44.0	30.9
2,4-dimethylpentane	25	7.9	8.0	9.9	11.2	4.0	6.6	6.5	10.5	10.3
benzene	26	49.8	62.2	48.1	67.5	21.6	38.8	72.4	68.0	50.9
cyclohexane	27	6.5	11.5	12.8	9.2	2.9	4.6	13.4	13.8	7.5
2-methylhexane	28	1.9	2.6	1.5	1.9	0.7	1.9	4.1	2.8	1.7
2,3-dimethylpentane	29	27.9	37.9	29.7	32.6	14.6	18.7	44.3	30.2	26.5
3-methylhexane	30	12.3	15.4	13.8	16.6	8.6	10.6	26.6	15.8	13.1
2,2,4-trimethylpentane	31	30.8	29.3	35.3	34.9	10.0	21.3	46.7	34.5	28.9
n-heptane	32	9.1	9.8	9.7	7.8	4.9	7.6	11.1	11.8	7.6
methylcyclohexane	33	8.7	10.4	11.4	9.8	3.9	6.3	14.0	10.7	8.7
2,3,4-trimethylpentane	34	9.6	9.7	11.9	11.1	3.8	8.6	13.8	15.0	9.9
toluene	35	145.2	170.2	131.3	110.8	42.7	68.3	120.9	116.7	111.4
2-methylheptane	36	5.6	5.4	5.8	6.7	2.6	4.3	7.4	8.3	4.9
3-methylheptane	37	9.7	7.8	11.9	7.4	4.3	7.7	13.5	12.4	7.9
n-octane	38	5.9	8.2	7.0	6.2	3.0	4.3	7.8	10.1	5.7
ethylbenzene	39	18.5	29.6	33.8	23.9	12.2	16.5	24.6	31.4	17.0
mp-xylene	40	88.9	92.8	90.5	80.1	26.5	44.6	125.3	102.3	56.5
styrene	41	1.6	4.5	3.2	0.5	0.9	2.2	4.0	1.8	1.8
o-xylene	42	27.2	28.0	22.8	32.9	10.3	19.0	43.4	27.2	25.8
n-nonane	43	2.7	3.5	3.4	3.5	1.5	1.8	4.6	3.8	2.7
isopropylbenzene	44	0.6	0.5	0.6	0.4	0.2	0.3	0.5	0.6	0.4
n-propylbenzene	45	6.3	5.7	4.9	5.1	1.7	2.8	4.2	4.0	2.4
m-ethyltoluene	46	6.0	4.5	7.6	5.5	3.3	3.2	10.3	5.3	8.2
p-ethyltoluene	47	9.4	8.6	5.6	9.7	3.6	3.3	14.2	10.9	4.4
1,3,5-trimethylbenzene	48	9.2	10.9	11.0	11.0	4.5	5.7	12.9	9.1	5.2
o-ethyltoluene	49	16.7	14.4	15.9	22.3	9.8	11.4	19.3	31.5	14.9
1,2,4-trimethylbenzene	50	11.4	17.1	19.3	25.3	12.2	10.3	28.2	26.2	24.2
n-decane	51	2.7	2.3	2.0	2.5	1.0	1.4	2.4	3.4	1.7
1,2,3-trimethylbenzene	52	4.7	4.2	2.8	3.0	1.6	3.5	6.4	3.7	2.3
m-diethylbenzene	53	1.1	1.5	1.3	1.0	0.5	0.8	2.1	1.7	1.0
p-diethylbenzene	54	0.1	0.1	0.2	0.1	0.0	0.1	0.2	0.2	0.1
n-undecane	55	0.5	0.7	0.4	0.5	0.1	0.3	0.8	0.7	0.3
Sum of PAMS		1231.1	1283.2	1227.9	1266.6	529.4	826.5	1724.9	1596.9	1039.1
TOG		1750.5	1806.4	1768.0	1740.0	742.1	1190.7	2538.3	2308.0	1497.1

Table 2-15. Model year distribution for vehicles in the virtual tunnel study.

MY	Run1	Run2	Run3	Run4	Run5	Run6	Run7	Run8	Run9
1997	0.0068	0.0085	0.0049	0.0038	0.002	0	0	0.0024	0.0017
1996	0.0051	0.0222	0.0049	0.0051	0.014	0.0094	0.0202	0.0097	0.0503
1995	0.0444	0.0342	0.0304	0.0609	0.0341	0.0346	0.0417	0.0181	0.0503
1994	0.0819	0.0701	0.0803	0.0761	0.0581	0.0928	0.0795	0.0593	0.0838
1993	0.0666	0.0786	0.0681	0.0673	0.0601	0.0928	0.0732	0.0568	0.0687
1992	0.0324	0.0154	0.0401	0.0444	0.0461	0.0566	0.0429	0.0302	0.0469
1991	0.0307	0.0325	0.0292	0.0254	0.0261	0.0676	0.0354	0.0447	0.0335
1990	0.07	0.0581	0.0608	0.0609	0.0621	0.0425	0.0556	0.0508	0.0151
1989	0.0802	0.0667	0.0827	0.099	0.1062	0.1053	0.0606	0.1064	0.0436
1988	0.0563	0.0821	0.0487	0.0647	0.0802	0.0503	0.0492	0.0786	0.0637
1987	0.07	0.0632	0.0779	0.0584	0.0701	0.0566	0.072	0.0665	0.0888
1986	0.0273	0.0547	0.0158	0.0254	0.0321	0.022	0.029	0.0314	0.0469
1985	0.0666	0.0564	0.0706	0.0825	0.0501	0.0393	0.0707	0.0435	0.0402
1984	0.0461	0.041	0.0426	0.0495	0.0461	0.044	0.0492	0.0387	0.0452
1983	0.0546	0.0581	0.0547	0.0406	0.0361	0.033	0.0556	0.052	0.062
1982	0.0119	0.0171	0.0182	0.0114	0.016	0.0157	0.0253	0.0326	0.0151
1981	0.0648	0.0632	0.0426	0.0406	0.0461	0.0692	0.0442	0.0617	0.0603
1980	0.0205	0.0256	0.0414	0.0431	0.0321	0.0314	0.0265	0.029	0.0168
1979	0.0137	0.0137	0.0414	0.0102	0.012	0.0094	0.0114	0.0145	0.0067
1978	0.0188	0.0103	0.0073	0.014	0.016	0.0094	0.0152	0.0339	0.005
1977	0.0171	0.0171	0.0195	0.0254	0.0361	0.0126	0.0177	0.023	0.0067
1976	0.0188	0.0205	0.0195	0.0089	0.0321	0.0173	0.0379	0.0109	0.0302
1975	0.0341	0.0188	0.0316	0.0216	0.0381	0.0267	0.0253	0.029	0.0201
1974	0.0068	0.0188	0.0049	0.0102	0.012	0.0236	0.0126	0.0133	0.0251
1973	0.0205	0.0137	0.017	0.0051	0.01	0.0126	0.0088	0.0121	0.0268
1972	0.0051	0.0068	0.0036	0	0.006	0.0047	0.0051	0.0012	0.0034
1971	0.0017	0.0068	0.0085	0.0051	0.002	0.0047	0.0088	0.0097	0.0084
1970	0.0068	0.0068	0.0122	0.014	0.002	0.0016	0.0088	0.0109	0.0117
1969	0.0102	0.0034	0.0036	0.0013	0	0.0016	0.0025	0.006	0
1968	0.0068	0	0.0049	0.0038	0.006	0.0031	0.0025	0.0073	0.005
1967	0.0017	0.0051	0.0036	0.0063	0.006	0.0047	0.0051	0.0048	0.0067
1966	0	0.0085	0.0012	0.0063	0.002	0.0031	0.0038	0.0024	0.0017
1965	0	0	0.0073	0.0089	0	0.0016	0.0025	0.006	0.0067
1964	0	0	0	0	0.002	0	0	0.0024	0.0017
1963	0.0017	0.0017	0	0	0	0	0.0013	0	0.0017
	1	1	1	1	1	1	1	1	1

Table 2-16. Emission factors (g/mi) by speciation profile developed for the virtual tunnel study.

	1	2	3	4	5	6	7	8	9	Average
Cat hot stab	0.81	0.85	0.82	0.87	0.35	0.56	1.12	1.06	0.66	0.79
Non-cat hot stab	0.86	0.87	0.88	0.71	0.38	0.53	1.32	1.13	0.95	0.85
Run loss	0.07	0.08	0.06	0.10	0.03	0.06	0.12	0.14	0.09	0.08
Diesel	0.04	0.03	0.01	0.01	0.00	0.00	0.05	0.03	0.03	0.02
Total	**1.78**	**1.83**	**1.78**	**1.69**	**0.77**	**1.16**	**2.60**	**2.36**	**1.72**	**1.74**

The data provided to DRI on gasoline samples, CNG and LPG samples and background air composition are shown in Table 2-17. The gasoline sample is simply the liquid fuel profile. The LPG and CNG profiles are representative but had not been utilized in the experiments for Rounds 1 and 2. The background air composition was the San Nicolas Island data (originally obtained from DRI) as analyzed by ENVIRON and used to set the background levels for all experiments.

Table 2-17. Fuel composition for gasoline, LPG and CNG (weight fraction) and average air composition at San Nicolas Island (ppbC).

Species	A34 Number	Gasoline	LPG	CNG	San Nicolas Island
ethene	1	0.000	0.000	0.000	0.503
acetylene	2	0.000	0.000	0.000	0.475
ethane	3	0.000	0.008	0.051	1.393
Propene	4	0.000	0.017	0.000	0.292
n-propane	5	0.000	0.953	0.010	0.590
isobutane	6	0.002	0.018	0.001	0.383
1-butene	7	0.000	0.000	0.000	0.048
n-butane	8	0.009	0.003	0.001	0.608
t-2-Butene	9	0.000	0.000	0.000	0.000
c-2-butene	10	0.000	0.000	0.000	0.000
isopentane	11	0.125	0.001	0.000	0.613
1-pentene	12	0.001	0.000	0.000	0.057
n-pentane	13	0.017	0.000	0.000	0.367
isoprene	14	0.000	0.000	0.000	0.000
t-2-Pentene	15	0.003	0.000	0.000	0.000
c-2-pentene	16	0.002	0.000	0.000	0.000
2,2-dimethylbutane	17	0.002	0.000	0.000	0.047
cyclopentane	18	0.001	0.000	0.000	0.000
2,3-dimethylbutane	19	0.012	0.000	0.000	0.088
2-methylpentane	20	0.041	0.000	0.000	0.382
3-methylpentane	21	0.020	0.000	0.000	0.152
2-methyl-1-pentene	22	0.001	0.000	0.000	0.000
n-hexane	23	0.014	0.000	0.000	0.183
Methylcyclopentane	24	0.016	0.000	0.000	0.107
2,4-dimethylpentane	25	0.017	0.000	0.000	0.068
benzene	26	0.009	0.000	0.000	0.280
cyclohexane	27	0.002	0.000	0.000	0.055
2-methylhexane	28	0.025	0.000	0.000	0.070
2,3-dimethylpentane	29	0.025	0.000	0.000	0.133
3-methylhexane	30	0.025	0.000	0.000	0.582
2,2,4-trimethylpentane	31	0.072	0.000	0.000	0.113
n-heptane	32	0.013	0.000	0.000	0.113
methylcyclohexane	33	0.010	0.000	0.000	0.077
2,3,4-trimethylpentane	34	0.016	0.000	0.000	0.037
toluene	35	0.058	0.000	0.000	0.350
2-methylheptane	36	0.009	0.000	0.000	0.062
3-methylheptane	37	0.008	0.000	0.000	0.037
n-octane	38	0.008	0.000	0.000	0.083
ethylbenzene	39	0.019	0.000	0.000	0.070
mp-xylene	40	0.054	0.000	0.000	0.153
styrene	41	0.000	0.000	0.000	0.000
o-xylene	42	0.024	0.000	0.000	0.065
n-nonane	43	0.002	0.000	0.000	0.087
isopropylbenzene	44	0.001	0.000	0.000	0.000
n-propylbenzene	45	0.003	0.000	0.000	0.075
m-ethyltoluene	46	0.003	0.000	0.000	0.067
p-ethyltoluene	47	0.005	0.000	0.000	0.073
1,3,5-trimethylbenzene	48	0.008	0.000	0.000	0.178
o-ethyltoluene	49	0.014	0.000	0.000	0.047
1,2,4-trimethylbenzene	50	0.018	0.000	0.000	0.443
n-decane	51	0.001	0.000	0.000	0.092
1,2,3-trimethylbenzene	52	0.003	0.000	0.000	0.077
m-diethylbenzene	53	0.001	0.000	0.000	0.000
p-diethylbenzene	54	0.000	0.000	0.000	0.000
n-undecane	55	0.000	0.000	0.000	0.105
Sum of PAMS		0.719	1.000	0.063	9.880
TOG		1.000	1.000	1.000	N/A

2.6 EXPERIMENTS FOR ROUND 3

Four new experiments (9-12) were developed for Round 3 after Round 2 had been completed. ENVIRON and UC Davis decided to focus Round 3 on understanding how chemical decay and sampling noise influence CMB performance in situations where the receptor model should do well.

- Conduct a factorial matrix of four experiments with chemistry and sampling noise turned on and off (Table 2-18).
- Prepare the PAMS emission inventories using source profiles that DRI had used for CMB analysis in Rounds 1 and 2 (Table 2-19).
- Instruct DRI to use the same profiles to analyze Round 3 as Rounds 1 and 2, without revealing that Round 3 was built upon these profiles.
- Turning off the chemistry means that there was no chemical decay of the PAMS tracers so the experiments were purely emissions and dispersion.
- Turning off the sampling noise means that the predicted total concentrations of PAMS species at each receptor were not altered by the sampling noise algorithm developed for this study.
- Experiment 12 should be an ideal situation for CMB because the source profiles are known, there is no chemical decay and no sampling noise.

Table 2-18. Design of experiments 9-12 for Round 3.

Experiment Number		Chemistry	
		Yes	**No**
Sampling Noise	**Yes**	9	10
	No	11	12

Table 2-19. Assignment of DRI source profiles to A-34 source categories for Round 3.

DRI Code	Description	A-34 Category Numbers
NCATsb96	Non-catalyst vehicle exhaust	1, 2, 3, 4, 8
LG_EtO96	Liquid gasoline	6, 9
EvaEtO96	Gasoline evaporative emissions	5
TuMchHDc	Tunnel diesel exhaust	7, 10
CPcomp_1	Consumer products and coatings average	14, 15, 16, 17
CNG/LPG	50/50 mixture of DRI's CNG and LPG profiles	12
Biogenic	Isoprene	18
BkgAMcom	Morning ambient air samples	13, 19, 20, 21, 22

2.7 INFORMATION PROVIDED FOR ROUND 4

In Round 4, DRI re-analyzed experiments 1-12 and could ask for any information short of the answer (the source contributions). DRI knew:

- The conceptual design of each experiment.
- The characteristics of the sampling noise algorithm.
- Average source profiles for each receptor and experiment based on the 9 cells around each receptor.

3.0 RECEPTOR MODELING METHODOLOGY

Receptor models infer contributions from different source types using multivariate measurements taken at one or more receptor locations and the abundances of chemical components in source emissions. Receptor models include the Enrichment Factors (EF), Chemical Mass Balance (CMB), eigenvector analysis (also termed Principal Component Analysis [PCA], Factor Analysis [FA], and Empirical Orthogonal Functions [EOF]), Multiple Linear Regression (MLR), neural networks, cluster analysis, Fourier Transform time series, and a number of other multivariate data analysis methods. CMB is well established for VOC apportionment and is the receptor model that is evaluated in this study. The review by Watson et al. (2001) examines how the CMB receptor model has been applied to quantify ambient volatile organic compound (VOC) source contributions to ambient concentrations of organic gases.

DRI recently prepared a protocol for applying the CMB to Photochemical Assessment Monitoring Station (PAMS) VOC data and for evaluating and interpreting model outputs (Fujita and Campbell, 2003). The guidance includes a summary of the fundamentals of CMB, descriptions of the features of CMB Version 8, and sample VOC source and ambient input data files, default source and fitting species selection files, and a current library of available source VOC composition profiles in CMB8-ready format. The applications and validation protocol provides recommended procedures for validating ambient VOC data, assigning uncertainties to ambient and source measurements, selecting and evaluating source composition profiles and fitting species, evaluating and validating model outputs, and analyzing and interpreting the CMB source contribution estimates and associated uncertainties. The document and supporting files are intended to facilitate and encourage the application of the CMB receptor model to PAMS VOC data by State and Local air pollution agencies as an evaluation of emissions inventories.

The actual profiles are available electronically. This library is a compilation of source profiles that have been used by the Desert Research Institute in prior VOC source apportionment studies. They include profiles that were newly developed for specific studies, the literature, and from the California Air Resources Boards Modeling Emissions Data System (MEDS). Studies for which profiles were newly developed include the 1993 Coast Oxidant Assessment for Southeast Texas (Fujita et al., 1995b), 1995 Boston and Los Angeles VOC Source Apportionment Study (Fujita et al. 1997a), 1995/96 Washington Ozone Transport Study (Fujita et al., 1997c), 1996 El Paso/Juarez Ozone Study (Fujita, 1998; Seila et al., 2001), and 1998 Central Texas On-Road Hydrocarbon Study (1999a), 1999 VOC Source Signatures in Houston, TX (Fujita et al., 1999b), apportionment of 1994-97 South Coast Air Basin PAMS VOC data (Fujita and Campbell, 2003b), and the 2000 Weekend Ozone Observations in the South Coast Air Basin (Fujita et al., 2003a).

3.1 FUNDAMENTALS

The CMB 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; 4) estimation of the uncertainties to both ambient concentrations and source compositions; and 5) solution of the chemical mass balance equations. The CMB model assumes that: 1) compositions of source emissions are constant over the period of ambient and source sampling; 2) chemical species do not react with each other, i.e., they add linearly; 3)

all sources with a potential for significant contribution to the receptor have been identified and have had their emissions characterized; 4) the source compositions are linearly independent of each other; 5) the number of source categories is less than or equal to the number of chemical species; and 6) measurement uncertainties are random, uncorrelated, and normally distributed. These assumptions are fairly restrictive and will never be totally complied with in actual practice. Deviations from these assumptions increase the uncertainties of the source contribution estimates.

CMB software applies the effective variance solution developed and tested by Watson et al. (1984). This method gives greater influence in the solution to chemical species that are measured more precisely in both source and receptor samples, and calculates uncertainties for source contributions from both the source and receptor uncertainties. Source contribution estimates (SCE) are the main output of the CMB model. The sum of these concentrations approximates the total mass concentrations. Negative SCE are not physically meaningful, but can occur when a source profile is collinear with another profile or when the source contribution is close to zero. When the SCE is less than its standard error, the source contribution is undetectable. Two or three times the standard error may be taken as the upper limit of the SCE in this case. There is about a 66% probability that the true source contribution is within one standard error and about a 95% probability that the true concentration is within two standard errors of the SCE.

The reduced chi square (χ^2), R^2 , and percent mass are goodness of fit measures for the least-squares calculation. The χ^2 is the weighted sum of squares of the differences between calculated and measured fitting species concentrations. The weighting is inversely proportional to the squares of the precision in the source profiles and ambient data for each species. A value of less than one indicates a very good fit to the data, while values between 1 and 2 are acceptable. χ^2 values greater than 4 indicate that one or more of the fitting species concentrations are not well-explained by the source contribution estimates. R^2 is determined by the linear regression of the measured versus model-calculated values for the fitting species. R^2 ranges from 0 to 1. The closer the value is to 1.0, the better the SCEs explain the measured concentrations. When R^2 is less than 0.8, the SCEs do not explain the observations very well with the given source profiles. Percent mass is the percent ratio of the sum of model-calculated SCEs to the measured mass concentration. This ratio should equal 100%, though values ranging from 80 to 120% are acceptable.

Normalization of Source Composition Profiles and Uncertainties

The source composition profiles used in the CMB calculations were expressed as weight percentages of the sum of the PAMS target species shown in Table 3-1 and total nonmethane hydrocarbons. The PAMS target compounds typically account for about 80 percent of the ambient hydrocarbons in urban areas. The source profile data reported in units of ppbC were converted to $\mu g/m^3$ prior to calculating the weight percentages using species-specific conversion factors. One-sigma uncertainties were derived from variations among multiple measurements for a particular source type or a nominal analytical uncertainty of 10 percent with a minimum uncertainty of 0.001. The assigned uncertainties are the larger of the two values.

Selection of Fitting Species

A prerequisite for using receptor models is that the relative proportions of chemical species change little between source and receptor. Most ambient NMHCs are oxidized in the lowest 2 km of the troposphere with tropospheric lifetimes ranging from hours to several months. Nominal afternoon summertime residence times for a reactive environment (e.g., Los Angeles) are estimated in Table 3-1. These estimates provide indications of which components are likely to remain relatively stable between source and receptor, thereby qualifying as fitting species for CMB source apportionment. An exception is isoprene, which is included as a fitting species despite its high reactivity because it serves as a marker for biogenic emissions. The source contribution estimates under-estimated the actual source contributions of biogenic emissions, i.e., they provide a lower limit to biogenic contributions.

Table 3-1 lists three sets of default fitting species, by site location and time of day, which we have used in past CMB analysis of PAMS hydrocarbon data. Compounds with potential analytical problems such as coelution of peaks during gas chromatographic analysis are also excluded as fitting species. Type 2 PAMS sites are located immediately downwind of the area of maximum precursor emissions and are typically placed near the downwind boundary of the central business district. An expanded list of hydrocarbons (36 species) are used as fitting species at Type 2 sites for samples collected in the morning hours prior to 9:00 am since the emissions are largely unreacted. A shorter list of more stable species (20 species) is used for samples collected between 9:00 am and 6:00 pm. Type 1 sites characterize upwind background and Type 3 sites monitor maximum ozone concentrations downwind from the fringe of the urban area. Type 4 sites characterize the extreme downwind transported ozone and its precursor concentrations exiting the area and are located near the downwind edge of the photochemical grid model domain. A shorter list of 11 fitting species is used for Type 1, 3 and 4 PAMS sites. Reactive species are retained in the CMB modeling as "floating species", and provide useful diagnostic information. Because the CMB model calculations are based upon non-reactive fitting species, the predicted concentrations exceed the measured values by margins that increase with increasing reactivity of the species.

3.2 APPLICATION OF CMB BY ROUND

The validity of source contribution estimates obtained from CMB depends greatly upon the selection and application of appropriate sets of source composition profiles and "fitting" species. In an actual CMB analysis, the location and time of sample collection are known. Available emission inventory data are used to determine the major emission sources that are likely to impact the receptor site. Visual surveys of the sampling location identify local sources near the sampling site that might disproportionately influence the receptor measurements. This information is then used to select an appropriate set of source composition profiles among available alternatives and identify sources for which new or updated composition profiles are needed. The location of the sampling site in relation to source and receptor areas and time of sample collection provide a basis for selecting "fitting" species that are sufficiently nonreactive so that relative proportions of chemical species change little between source and receptor. The expectation in this present experiment is that the accuracy of the source attributions from the CMB model analysis will improve as more appropriate source profiles and fitting species are applied to the simulated ambient samples. The receptor model performance was evaluated in four rounds as described in Section 1.4. This section describes DRI's approach for performing

the CMB analysis for the 6144 simulated air samples in Rounds 1, 2 and 4 and 3072 samples in Round 3.

Round 1

DRI had no information about the simulated air samples in Round 1 other than sample identification numbers. Application of CMB without regard for applicability of source profiles and effect of photochemical aging would have little relevance to an actual CMB analysis and confirm that the results would be poor. In the absence of specific information, DRI examined the parameters shown in Table 3-2 to glean some information about the simulated air samples. The samples were then sorted into seven batches according to probable extent of photochemical aging indicated by ratios of the sum of xylene isomers to benzene, varying levels of total hydrocarbons, and emissions characteristics of the corresponding modeling grid cells based upon relative abundances of source indicator species such as acetylene (mobile source), isoprene (biogenic), heavy hydrocarbons (diesel exhaust or surface coatings). The batches and the number of samples in each batch are: urban fresh (1788), suburban fresh (648), low concentration fresh (428), urban aged (1383), suburban aged (514), low concentration aged (620) and background (606).

While DRI was not aware of the specific experimental design for the four rounds, DRI was aware that the modeling database for the August 3-7, 1997 SCOS episode would be used by ENVIRON to generate the simulated air samples. Because the simulated air samples were generated for South Coast Air Basin modeling domain, the source composition profiles that were considered by DRI were those used in recent source apportionment studies in the basin. DRI was not aware during the first three rounds that emissions for hypothetical industrial sources were added by ENVIRON to the modeling inventory. Table 3-3 shows lists the source composition profiles that DRI considered during Round 1. The source composition profiles in weight percent (normalized to sum of the 55 PAMS species) are shown in Table 3-4.

The choices among alternative source profiles for major source categories are typically based upon sensitivity tests that are performed on subsets of samples from source-dominated locations. Four alternative gasoline exhaust profiles were examined on a subset of samples from the urban fresh batch. The subset of samples were selected on the basis of xylene/benzene ratio > 2.5, acetylene > 2.0 percent, NMHC > 120 ppbC. The alternative gasoline exhaust profiles were used in combination with a profile for liquid gasoline (LG_EtO96), gasoline vapor (EvaEtO96), diesel exhaust (TuMchHDc), composite of consumer products (CPcomp_1), composite of surface coatings (COATcomp), commercial natural gas (CNG), liquefied petroleum gas (LPG) and Biogenic. The effect of including a regional background profile was also examined. The results of the sensitivity tests are summarized in Figure 3-1. In the output files, the category "gasoline" is the sum of the gas exhaust, liquid, and vapor. CNG and LPG were combined in the summary since these fugitive gas sources are generally not distinguished well from other components of aged emissions.

The samples were run in batch mode using the Autofit feature in CMB8 with a default set of profiles and fitting species for each batch. Table 3-1 indicates the different sets of fitting species that were used depending on the range of xylene/benzene ratios. The batches with "fresh" samples were run with and without a regional background profile. Because of the large number of samples (~6,000), it was not possible to review and validate the apportionment for individual

samples. Spatial variations and time-series plots are effective diagnostic tools, but could not be applied because information on site location and time were not provided to us.

Round 2

In this round, DRI was provided information on receptor locations (city), sample dates, times and duration. A general description of the type of location and sources was provided with a caveat that receptor locations are sited to be representative of an area several km square. The following source composition data were also provided.

- A set of simulated tunnel experiment data with varying contributions of gasoline and diesel exhaust. DRI estimated 100% gasoline (exhaust + running evap) and diesel profiles using the regression analysis used in previous tunnel studies.
- Composition of gasoline, CNG, LPG.
- Data for grid cell corresponding to San Nicolas Island for establishing the composition upwind background.

Data from the virtual tunnel study were used to derive speciated VOC emission rates for the light-duty and heavy-duty diesel vehicles. The fleet emission rates for the nine virtual tunnel runs were correlated against the corresponding traffic composition (i.e., fraction of light duty). The linear regression of the points yielded the light-duty and heavy-duty emission rates at the two intercepts of the line. This process was conducted for each species. The utility of the virtual tunnel data was limited by the relatively small fractions of heavy-duty vehicles among the tunnel runs (0.002 to 0.024). The consequence is that while extrapolations of the regression lines to 100% light-duty emissions have reasonably small errors, extrapolation to 100% heavy-duty emissions are highly uncertain. Figure 3-2 shows that the LDV profiles derived from the virtual tunnel study is similar to the default light-duty gasoline exhaust profiles used in Round 1. The HDV profiles derived from the virtual tunnel study has extremely high uncertainties for many species and does not resemble the diesel profile used in Round 1. The LDV profile derived from the virtual tunnel study was used in Round 2, but the HDV profile was not used. New source composition profiles for gasoline exhaust, liquid gasoline, and gasoline vapor, LPG, CNG, and upwind background were created from the data provided by ENVIRON. The same profiles applied in Round 1 for diesel exhaust, consumer products, and solvents were used.

The samples were run in batch mode using the Autofit feature in CMB8 using a default set of profiles and fitting species for each batch. CMB was applied to a total of 5956 samples in batches corresponding to site categories and time periods. The different batches and number of samples, indicated by parentheses, are urban fresh (2034), suburban fresh (416), urban aged (1668), suburban aged (303), and downwind (1535). CMB could not converge to a solution for 188 samples. The sites were grouped as per the information given us by ENVIRON: Anaheim, Van Nuys, Hawthorn, Long Beach and LAX as urban, Diamond Bar is suburban, and Lake Perris and Crestline are downwind. The set of fitting species for Type 2 AM (Table 3-2) was used for urban and suburban receptor locations for 0600 to 1800 samples and Type 2 pm for 1800 to 0600 samples. The Type 1, 3 & 4 set was used for downwind receptor locations for all sampling periods.

Round 3

In Round 3, DRI was instructed to use the same profiles used in Round 1. The upwind background profile provided by ENVIRON in Round 2 was the only exception. The sets of fitting species that were applied to the simulated in Round 2 were also used in Round 3.

Round 4

In Round 4, DRI was given the 22 aggregate "A-34" source composition profiles shown in Table 2-3 and Appendix A. DRI was also informed of the conceptual design of each experiment, the characteristics of the sampling noise algorithm and the average profiles for each receptor and experiment based on the 9 cell around each receptor.

Prior to the final CMB runs for Round 4, DRI ran a series of tests to examine the sensitivity of model results on the four alternative gasoline exhaust profiles (A-34 category 1 to 4). The results, summarized in Table 3-5, show little variation among the profile, especially for the first three profiles. The final CMB runs consisted of categories 1, 5, 7, 11, 12, 13, 14, 17, 18, 21 and 22 for the default set of profiles except as noted below. The following notes also specify the default set of fitting species that were applied.

Notes on autofit CMB – Round 4

Interior Sites (DBar and VNuys) 06-09 PDT

- Used type2 fresh exhaust species set.
- Removed ethane from default species list due to excess ethane in boundary conditions which accounted for almost all of under apportionment; improved stats.
- Removed IndEngin (caused collinearity).
- exp5 - used type2 aged exhaust species set.
- exp6 - put ethane back into species list; high ethane from increased industrial emissions, especially at Vnuys.

Interior Sites (DBar and VNuys) 10-05 PDT

- Used type2 aged exhaust species set.
- Removed IndEngin.
- Removed ethane from default species list due to excess ethane in boundary conditions, which accounted for almost all of under apportionment; improved stats.
- exp3 - removed SynthInd profile due to frequent collinearity.
- exp6 - put ethane back into species list; high ethane from increased industrial emissions, especially at Vnuys.
- exp8 - many samples did not fit due to collinearity. Tried removing some solvent-related sources, and 'other' without much success. Ran with default source set.
- exp9-12 - removed ethene, acetylene, ethane and I-buta to improve fit.

Coastal Sites (LAX and Long Beach)

- Used type2 fresh exhaust species set.
- Removed IndEngin (caused collinearity).
- exp5 - used type2 aged exhaust species set.

- Removed ethane from default species list due to excess ethane in boundary conditions, which accounted for almost all of under apportionment; improved stats.
- exp6 - tried to improve fits by removing sources and species, without success.
- exp9-12 - removed ethene, acetylene, ethane, I-buta to improve fit.

Downwind sites (Lake Perris and Crestline)

- Used type 3 site default species.
- Removed IndEngin.
- Removed Paint, Solvents, and Degrease from profile list because of too few selected species in profiles.
- exp4 - used type2 aged exhaust species set (not enough species in type 3 set), and put Paint and Solvents profiles back in.
- exp9-12 - removed acetylene, ethane to improve fit.

Middle sites (Anaheim and Hawthorne)

- Used type2 fresh exhaust species set.
- Removed ethane from default species list due to excess ethane in boundary conditions, which accounted for almost all of under apportionment; improved stats.
- Removed IndEngin (caused collinearity).
- exp5 - used type2 aged exhaust species set.
- exp6 - put ethane back into species list; high ethane from increased industrial emissions, especially at Van Nuys.

Notes On Manual CMB - Round 4

- CMB run manually for Diamond Bar and Van Nuys for Experiments 1, 2, 3, 6 and 7 for hours 8,12,18 and 24 (80 samples at each site).
- Source elimination feature turned on. Highest negative SCE is automatically removed and CMB rerun until no negative SCEs remain.
- Used Type 2 fitting species for 08000 samples. Remove *ethene* in most cases.
- Use same fitting species set for other times except *ethane, n_prbz, iprbz* and *etbz* were removed.
- Species with absolute value of R/U ratio[1] greater than 2 were removed from fitting species and CMB repeated. Species with R/U occasionally greater than 2 include *mcypna, pena2m, pena3m, i_buta, n_buta, hexa3m, mecyhx*, and *bu23dm*.

[1] Ratio of Residual to Its Standard Error (RATIO R/U). This column contains the ratio of the signed difference between the calculated and measured concentration (the residual) divided by the uncertainty of that residual (square root of the sum of the squares of the uncertainty in the calculated and measured concentrations). The RATIO R/U specifies the number of uncertainty intervals by which the calculated and measured concentrations differ. When the absolute value of the RATIO R/U exceeds 2, the residual is significant. If it is positive, then one or more of the profiles is contributing too much to that species. If it is negative, then there is an insufficient contribution to that species and a source 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.

Table 3-1. PAMS target compounds.

	Mnemonics[1]	Names	Formula	AIRS Code	convert to ug/m3	MW	Group	k_{OH} at 298 K	Lifetime hours	CMB Fitting Species Type 2 AM	Type 2 PM	Types 1,3, & 4
1	ETHENE	ethene	C2H4	43203	0.5736	28.05	O	8.52	6.52	*		
2	ACETYL	acetylene	C2H2	43206	0.5325	26.04	Y	0.90	61.73	*	*	*
3	ETHANE	ethane	C2H6	43202	0.6149	30.07	P	0.27	207.30	*	*	*
4	PROPE	Propene	C3H6	43205	0.5737	42.08	O	26.30	2.11			
5	N_PROP	n-propane	C3H8	43204	0.6012	44.10	P	1.15	48.31	*	*	*
6	I_BUTA	isobutane	C4H10	43214	0.5943	58.12	P	2.34	23.74	*	*	*
7	LBUT1E	1-butene	C4H8	43280	0.5737	56.11	O	31.40	1.77			
8	N_BUTA	n-butane	C4H10	43212	0.5943	58.12	P	2.54	21.87	*	*	*
9	T2BUTE	t-2-Butene	C4H8	43216	0.5737	56.11	O	64.00	0.87			
10	C2BUTE	c-2-butene	C4H8	43217	0.5737	56.11	O	56.40	0.99			
11	IPENTA	isopentane	C5H12	43221	0.5902	72.15	P	3.90	14.25	*	*	*
12	PENTE1	1-pentene	C5H10	43224	0.5737	70.13	O	31.40	1.77			
13	N_PENT	n-pentane	C5H12	43220	0.5902	72.15	P	3.94	14.10	*	*	*
14	I_PREN	isoprene	C5H8	43243	0.5571	68.11	O	101.00	0.55	+	+	+
15	T2PENE	t-2-Pentene	C5H10	43226	0.5737	70.13	O	67.00	0.83			
16	C2PENE	c-2-pentene	C5H10	43227	0.5737	70.13	O	65.00	0.85			
17	BU22DM	2,2-dimethylbutane	C6H14	43244	0.5874	86.17	P	2.32	23.95	*	*	*
18	CPENTA	cyclopentane	C5H10	43242	0.5737	70.13	P	5.16	10.77	*	*	
19	BU23DM	2,3-dimethylbutane	C6H14	43284	0.5874	86.17	P	6.20	8.96	*		
20	PENA2M	2-methylpentane	C6H14	43285	0.5874	86.17	P	5.60	9.92	*	*	
21	PENA3M	3-methylpentane	C6H14	43230	0.5874	86.17	P	5.70	9.75	*	*	
22	P1E2ME	2-methyl-1-pentene	C6H12	43246	0.5737	84.16	O	31.40	1.77			
23	N_HEX	n-hexane	C6H14	43231	0.5874	86.17	P	5.61	9.90	*	*	
24	MCYPNA	Methylcyclopentane	C6H12	43262	0.5737	84.16	P	8.81	6.31	*		
25	PEN24M	2,4-dimethylpentane	C7H16	43247	0.5855	100.20	P	5.10	10.89	*	*	
26	BENZE	benzene	C6H6	45201	0.5324	78.11	A	1.23	45.17	*	*	*
27	CYHEXA	cyclohexane	C6H12	43248	0.5737	84.16	P	7.49	7.42	*		
28	HEXA2M	2-methylhexane	C7H16	43263	0.5737	98.19	P	6.79	8.18	*		
29	PEN23M	2,3-dimethylpentane	C7H16	43291	0.5855	100.20	P	4.87	11.41	*	*	
30	HEXA3M	3-methylhexane	C7H16	43249	0.5855	100.20	P	7.16	7.80	*	*	
31	PA224M	2,2,4-trimethylpentane	C8H18	43250	0.584	114.23	P	3.68	15.10	*	*	*
32	N_HEPT	n-heptane	C7H16	43232	0.5855	100.20	P	7.15	7.77	*		
33	MECYHX	methylcyclohexane	C7H14	43261	0.5737	98.19	P	10.40	5.34	*		
34	PA234M	2,3,4-trimethylpentane	C8H18	43252	0.584	114.23	P	7.00	7.94	*		
35	TOLUE	toluene	C7H8	43202	0.5384	92.14	A	5.96	9.32	*	*	
36	HEP2ME	2-methylheptane	C8H18	43260	0.5829	114.23	P	8.18	6.80	*	*	
37	HEP3ME	3-methylheptane	C8H18	43253	0.584	114.23	P	8.56	6.49	*		
38	N_OCT	n-octane	C8H18	43233		114.22	P	8.68	6.40	*		
39	ETBZ	ethylbenzene	C8H10	45203	0.5427	106.16	A	7.10	7.82	*		
40	MP_XYL	mp-xylene	C8H10	45109	0.5427	106.16	A	18.95	4.71			
41	STYR	styrene	C8H8	45220	0.5324	104.14	A	58.00	0.96			
42	O_XYL	o-xylene	C8H10	45204	0.5428	106.17	A	13.70	4.06			
43	N_NON	n-nonane	C9H20	43235	0.5829	128.26	P	10.20	5.45	*		
44	IPRBZ	isopropylbenzene	C9H12	45210	0.5462	120.20	A	6.50	8.55	*		
45	N_PRBZ	n-propylbenzene	C9H12	45209	0.5462	120.20	A	6.00	9.26	*		
46	M_ETOL	m-ethyltoluene	C9H12	45212	0.5462	120.20	A	19.20	2.89			
47	P_ETOL	p-ethyltoluene	C9H12	45213	0.5462	120.20	A	12.10	4.59			
48	BZ135M	1,3,5-trimethylbenzene	C9H12	45207	0.5462	120.20	A	57.50	0.97			
49	O_ETOL	o-ethyltoluene	C9H12	45211	0.5462	120.20	A	12.30	4.52			
50	BZ124M	1,2,4-trimethylbenzene	C9H12	45208	0.5462	120.20	A	32.50	1.71			
51	N_DEC	n-decane	C10H22	43238	0.582	142.29	P	11.60	4.79	*		
52	BZ123M	1,2,3-trimethylbenzene	C9H12	45225	0.5462	120.20	A	32.70	1.70			
53	DETBZ1	m-diethylbenzene	C10H14	45218		134.22	A	14.20	3.90			
54	DETBZ2	p-diethylbenzene	C10H14	45219		134.22	A	14.20	3.90			
55	N_UNDE	n-undecane	C11H24	43954		156.30	P	13.20	4.20	*		
	TNMOC											
	PAMHC											
	UNID											
	MTBE											

A = aromatic, AL = Aldehyde, O = alkene (olefin), P = parafin, Y = alkyne, K = ketone, E = ether, X = haogenated, OH = alcohol

Note: Rate constants k at 298 K for the reaction of OH radicals with VOCs.

Unit: 1012 x k cm3 molecule-1 s-1

Table 3-2. Criteria for including compounds as fitting species.

Category	Parameter	Very Low	Low	Med	High	Very High
Location	NMHC (ppb)	< 40 (background)	40-80 (rural)	80-120 (suburban)	> 120 (urban)	
Photochemical aging	xyl/ben	<1.2 (aged)	1.2 to 1.6 = 3	1.6 to 2.0 = 2	2.0 to 2.4	> 2.4 (fresh)
Contribution of vehicle exhaust	% acetylene		< 0.5	0.5 to 2.0	2.0 to 4.0	> 4.0
Catalyst vs noncatalyst vehicles/high emitter	ethene/acetylene		< 1.0 (non catalyst)	1.0 to <3.0	3.0 to <7.0 (catalyst)	
Diesel exhaust	Heavy HC n-decane + n-undecane	< .5%	5 to < 1.0	1.0 to <1.5	1.5 to <2.0	> 2.0
CNG, LPG or aged emissions	% ethane + propane		< 15	15 to 25	25 to 40	> 40
Biiogenic	% isoprene		< 1	1 to 3	3 to 5	> 5

Table 3-3. Source composition profiles used in Round 1 of CRC A-34.

PNO	Profioe	Description	Source
GASEX1	NCATsb96	Gasoline - non-cat - stabilized exhaust - ARB IUS summer 1996	ARB In-Use Vehicle Surveillance Program Testing 1994, 1996
GASEX2	NCATco96	Gasoline - non-cat - FTP Composite - ARB IUS summer 1996	CEIDARS
GASEX3	CATstb97	Gasoline - catalyst - stabilized exhaust - ARB summer 1997	ARB In-Use Vehicle Surveillance Program Testing 1994, 1996
GASEXT	TunS96	Sepulveda Tunnel, diesel subtracted, 1996	CRC Study
GASLIQ	LG_EtO96	Liquid gasoline 1996 SSD etoh 2.0% o (MTBE phaseout)	CEIDARS
GASEVA	EvaEtO96	Headspace vapors 1996 SSD etoh 2.0% o (MTBE phaseout)	CEIDARS
DIESEL	TuMchHDc	Fort McHenry Tunnel Diesel	CRC, DRI - Tunnel
CONSPR	CPcomp_1	Draft Consumer Prd: Combined Small Categories EPA Composite	1997 ARB Consumer Products survey
COATIN	COATcomp	Composite of coatings 2-11, weighted by total U.S. sales	Fujita et al. derived from Censullo et al.
CNGEVA	CNG	Commercial Natural Gas from Los Angeles	Mayrsohn et al 1976
LPGEVA	LPG	Liquefied Petroleum Gas from Los Angeles	Mayrsohn et al 1976
BIOGEN	Biogenic	100% isoprene	
BkgAMc	BkgAMcom	Composite bkgrd ambient for SoCal 0600 summer 97 - Isoprene removed	SCOS97-NARSTO VOC data
BkgPMc	BkgPMcom	Composite bkgrd ambient for SoCal 1800 summer 97 - Isoprene removed	SCOS97-NARSTO VOC data

Table 3-4. Normalized source composition profiles used in Round 1 of CRC A-34 (normalized to sum of 55 PAMS species as weight percent).

profile	NCATsb96	NCATco96	CATstb97	TuS96	LG_EtO96	EvaEtO96	TuMchHDc
ethene	13.48 ± 1.36	14.26 ± 1.44	10.67 ± 1.09	8.43 ± 1.07	0.00 ± 0.20	0.00 ± 0.20	9.92 ± 0.99
acetyl	3.53 ± 0.41	5.77 ± 0.61	5.45 ± 0.58	4.45 ± 0.96	0.00 ± 0.20	0.00 ± 0.20	1.80 ± 0.18
ethane	2.67 ± 0.33	2.28 ± 0.30	1.73 ± 0.26	2.05 ± 0.29	0.00 ± 0.20	0.00 ± 0.20	1.19 ± 0.12
prope	7.39 ± 0.77	7.12 ± 0.74	5.14 ± 0.55	4.21 ± 0.57	0.00 ± 0.20	0.00 ± 0.20	4.02 ± 0.40
n_prop	0.14 ± 0.20	0.09 ± 0.20	0.10 ± 0.20	0.77 ± 0.62	0.00 ± 0.20	0.36 ± 0.20	2.23 ± 0.22
i_buta	0.03 ± 0.20	0.01 ± 0.20	0.03 ± 0.20	0.32 ± 0.12	0.25 ± 0.20	1.67 ± 0.26	0.28 ± 0.10
lbut1e	1.00 ± 0.22	0.97 ± 0.22	0.70 ± 0.21	0.55 ± 0.10	0.01 ± 0.20	0.15 ± 0.20	2.97 ± 0.30
n_buta	1.13 ± 0.23	1.08 ± 0.23	1.28 ± 0.24	1.33 ± 0.25	1.22 ± 0.23	8.07 ± 0.83	0.64 ± 0.10
t2bute	0.53 ± 0.21	0.48 ± 0.21	0.40 ± 0.20	0.33 ± 0.10	0.01 ± 0.20	0.76 ± 0.21	0.24 ± 0.10
c2bute	0.38 ± 0.20	0.34 ± 0.20	0.29 ± 0.20	0.26 ± 0.10	0.01 ± 0.20	0.44 ± 0.20	0.30 ± 0.10
ipenta	9.89 ± 1.01	9.40 ± 0.96	11.23 ± 1.14	10.62 ± 1.25	9.53 ± 0.97	44.75 ± 4.48	1.32 ± 0.13
pente1	0.21 ± 0.20	0.15 ± 0.20	0.22 ± 0.20	0.16 ± 0.10	0.11 ± 0.20	0.28 ± 0.20	0.89 ± 0.10
n_pent	3.30 ± 0.39	3.37 ± 0.39	4.54 ± 0.50	3.13 ± 0.31	1.76 ± 0.27	9.34 ± 0.96	1.53 ± 0.15
i_pren	0.21 ± 0.20	0.25 ± 0.20	0.24 ± 0.20	0.21 ± 0.12	0.02 ± 0.20	0.00 ± 0.20	0.00 ± 0.10
t2pene	0.29 ± 0.20	0.25 ± 0.20	0.35 ± 0.20	0.32 ± 0.10	0.37 ± 0.20	0.94 ± 0.22	0.36 ± 0.10
c2pene	0.17 ± 0.20	0.12 ± 0.20	0.19 ± 0.20	0.17 ± 0.10	0.20 ± 0.20	0.38 ± 0.20	0.29 ± 0.10
bu22dm	0.77 ± 0.21	0.76 ± 0.21	1.05 ± 0.23	1.12 ± 0.21	0.23 ± 0.20	1.99 ± 0.28	2.64 ± 0.26
cpenta	0.42 ± 0.20	0.38 ± 0.20	0.59 ± 0.21	0.48 ± 0.10	0.14 ± 0.20	1.26 ± 0.24	0.32 ± 0.10
bu23dm	1.48 ± 0.25	1.42 ± 0.25	1.73 ± 0.26	0.00 ± 0.10	1.27 ± 0.24	2.50 ± 0.32	0.32 ± 0.10
pena2m	4.84 ± 0.52	4.92 ± 0.53	6.10 ± 0.64	4.48 ± 0.44	4.06 ± 0.45	7.15 ± 0.74	1.98 ± 0.20
pena3m	2.91 ± 0.35	2.91 ± 0.35	3.58 ± 0.41	2.63 ± 0.26	2.27 ± 0.30	3.93 ± 0.44	0.92 ± 0.10
p1e2me	0.09 ± 0.20	0.06 ± 0.20	0.11 ± 0.20	0.13 ± 0.10	0.10 ± 0.20	0.08 ± 0.20	0.23 ± 0.10
n_hex	1.98 ± 0.28	2.05 ± 0.29	2.60 ± 0.33	1.83 ± 0.18	1.16 ± 0.23	1.85 ± 0.27	0.97 ± 0.10
mcypna	3.32 ± 0.39	3.50 ± 0.40	4.54 ± 0.50	2.84 ± 0.28	1.50 ± 0.25	3.39 ± 0.39	0.63 ± 0.10
pen24m	0.80 ± 0.22	0.67 ± 0.21	0.71 ± 0.21	1.50 ± 0.15	4.62 ± 0.50	0.65 ± 0.21	0.36 ± 0.10
benze	5.19 ± 0.56	5.01 ± 0.54	4.33 ± 0.48	3.69 ± 0.37	1.52 ± 0.25	0.43 ± 0.20	3.21 ± 0.32
cyhexa	0.68 ± 0.21	0.76 ± 0.21	1.00 ± 0.22	1.13 ± 0.11	0.21 ± 0.20	1.23 ± 0.23	0.23 ± 0.10
hexa2m	0.00 ± 0.20	0.00 ± 0.20	0.00 ± 0.20	1.69 ± 0.16	7.01 ± 0.73	0.86 ± 0.22	0.00 ± 0.10
pen23m	2.55 ± 0.32	2.34 ± 0.31	2.36 ± 0.31	2.51 ± 0.25	7.47 ± 0.77	0.83 ± 0.22	0.91 ± 0.10
hexa3m	1.15 ± 0.23	1.14 ± 0.23	1.25 ± 0.24	1.85 ± 0.27	7.68 ± 0.79	0.95 ± 0.22	2.32 ± 0.23
pa224m	3.00 ± 0.36	2.65 ± 0.33	2.82 ± 0.35	4.00 ± 0.40	14.64 ± 1.48	1.55 ± 0.25	1.48 ± 0.15
n_hept	0.74 ± 0.21	0.78 ± 0.21	0.82 ± 0.22	1.19 ± 0.12	2.38 ± 0.31	0.50 ± 0.21	0.58 ± 0.10
mecyhx	0.75 ± 0.21	0.82 ± 0.22	1.00 ± 0.22	1.19 ± 0.13	2.01 ± 0.28	0.49 ± 0.21	0.44 ± 0.10
pa234m	0.95 ± 0.22	0.89 ± 0.22	0.98 ± 0.22	1.50 ± 0.15	3.81 ± 0.43	0.40 ± 0.20	0.32 ± 0.10
tolue	10.24 ± 1.04	10.02 ± 1.02	9.66 ± 0.99	9.04 ± 0.89	7.77 ± 0.80	2.04 ± 0.29	4.52 ± 0.45
hep2me	0.50 ± 0.21	0.50 ± 0.21	0.55 ± 0.21	0.69 ± 0.10	1.85 ± 0.27	0.15 ± 0.20	0.00 ± 0.10
hep3me	0.80 ± 0.22	0.82 ± 0.22	0.98 ± 0.22	0.87 ± 0.10	1.99 ± 0.28	0.15 ± 0.20	0.44 ± 0.10
n_oct	0.53 ± 0.21	0.56 ± 0.21	0.63 ± 0.21	0.55 ± 0.10	0.92 ± 0.22	0.06 ± 0.20	0.31 ± 0.10
etbz	2.26 ± 0.30	2.12 ± 0.29	1.76 ± 0.27	1.52 ± 0.16	2.50 ± 0.32	0.14 ± 0.20	2.86 ± 0.29
mp_xyl	6.71 ± 0.70	6.50 ± 0.68	5.98 ± 0.63	5.95 ± 0.62	6.21 ± 0.65	0.54 ± 0.21	11.05 ± 1.11
styr	0.20 ± 0.20	0.25 ± 0.20	0.21 ± 0.20	0.39 ± 0.10	0.00 ± 0.20	0.00 ± 0.20	1.86 ± 0.19
o_xyl	2.34 ± 0.31	2.24 ± 0.30	2.08 ± 0.29	2.13 ± 0.22	2.44 ± 0.32	0.15 ± 0.20	3.76 ± 0.38
n_non	0.27 ± 0.20	0.26 ± 0.20	0.29 ± 0.20	0.21 ± 0.10	0.23 ± 0.20	0.01 ± 0.20	1.13 ± 0.11
iprbz	0.08 ± 0.20	0.04 ± 0.20	0.02 ± 0.20	0.17 ± 0.10	0.07 ± 0.20	0.01 ± 0.20	0.33 ± 0.10
n_prbz	0.42 ± 0.20	0.38 ± 0.20	0.38 ± 0.20	0.35 ± 0.10	0.44 ± 0.20	0.00 ± 0.20	1.06 ± 0.11
m_etol	1.61 ± 0.26	1.49 ± 0.25	1.33 ± 0.24	1.51 ± 0.16	1.56 ± 0.25	0.05 ± 0.20	4.17 ± 0.42
p_etol	0.69 ± 0.21	0.64 ± 0.21	0.55 ± 0.21	0.66 ± 0.10	0.66 ± 0.21	0.03 ± 0.20	1.41 ± 0.14
bz135m	0.75 ± 0.21	0.70 ± 0.21	0.65 ± 0.21	0.86 ± 0.12	0.79 ± 0.22	0.00 ± 0.20	2.10 ± 0.21
o_etol	0.56 ± 0.21	0.51 ± 0.21	0.46 ± 0.21	0.46 ± 0.10	0.43 ± 0.20	0.01 ± 0.20	2.01 ± 0.20
bz124m	1.90 ± 0.28	1.77 ± 0.27	1.62 ± 0.26	2.45 ± 0.26	2.17 ± 0.30	0.00 ± 0.20	7.50 ± 0.75
n_dec	0.15 ± 0.20	0.10 ± 0.20	0.25 ± 0.20	0.10 ± 0.10	0.09 ± 0.20	0.00 ± 0.20	2.63 ± 0.26
bz123m	0.35 ± 0.20	0.29 ± 0.20	0.29 ± 0.20	0.39 ± 0.30	0.37 ± 0.20	0.01 ± 0.20	1.68 ± 0.17
detbz1	0.15 ± 0.20	0.10 ± 0.20	0.05 ± 0.20	0.09 ± 0.10	0.13 ± 0.20	0.00 ± 0.20	0.00 ± 0.10
detbz2	0.18 ± 0.20	0.12 ± 0.20	0.11 ± 0.20	0.72 ± 0.10	0.00 ± 0.20	0.00 ± 0.20	0.00 ± 0.10
n_unde	0.06 ± 0.20	0.04 ± 0.20	0.02 ± 0.20	0.00 ± 0.10	0.04 ± 0.20	0.00 ± 0.20	5.35 ± 0.54
tnmhc	128.93 ± 12.89	126.46 ± 12.65	124.83 ± 12.48	125.39 ± 12.54	143.50 ± 14.35	106.66 ± 10.67	113.14 ± 11.31

Table 3-4 (continued). Normalized source composition profiles used in Round 1 of CRC A-34 (normalized to sum of 55 PAMS species as weight percent).

profile	CPcomp_1	COATcomp	CNG	LPG	Biogenic	BkgAMcom	BkgPMcom
ethene	0.22 ± 0.20	0.00 ± 0.44	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	3.12 ± 1.68	2.89 ± 1.10
acetyl	0.00 ± 0.20	0.00 ± 0.44	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	5.20 ± 1.81	4.20 ± 1.56
ethane	0.00 ± 0.20	0.00 ± 0.44	69.19 ± 10.38	4.11 ± 0.62	0.00 ± 0.10	14.25 ± 5.00	11.79 ± 3.60
prope	0.00 ± 0.20	0.00 ± 0.44	0.00 ± 0.10	5.11 ± 0.77	0.00 ± 0.10	1.68 ± 1.08	2.02 ± 1.01
n_prop	13.18 ± 1.33	0.00 ± 0.44	21.23 ± 3.19	90.58 ± 13.59	0.00 ± 0.10	8.70 ± 4.46	5.94 ± 2.96
i_buta	42.04 ± 4.21	0.00 ± 0.44	2.09 ± 0.33	0.20 ± 0.10	0.00 ± 0.10	2.84 ± 1.41	2.27 ± 1.27
lbut1e	0.00 ± 0.20	0.00 ± 0.44	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.35 ± 0.47	0.50 ± 0.20
n_buta	7.81 ± 0.81	0.00 ± 0.44	3.10 ± 0.48	0.00 ± 0.10	0.00 ± 0.10	4.50 ± 2.50	3.61 ± 2.11
t2bute	0.00 ± 0.20	0.00 ± 0.44	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.20	0.00 ± 0.20
c2bute	0.00 ± 0.20	0.00 ± 0.44	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.20	0.00 ± 0.20
ipenta	0.00 ± 0.20	0.00 ± 0.10	0.69 ± 0.15	0.00 ± 0.10	0.00 ± 0.10	5.46 ± 2.93	4.46 ± 2.28
pente1	0.00 ± 0.20	0.00 ± 0.44	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.26 ± 0.22	0.39 ± 0.36
n_pent	0.05 ± 0.20	0.00 ± 0.44	0.69 ± 0.15	0.00 ± 0.10	0.00 ± 0.10	2.46 ± 1.91	2.22 ± 1.70
i_pren	0.00 ± 0.20	0.00 ± 0.44	0.00 ± 0.10	0.00 ± 0.10	100.00 ± 10.00	0.00 ± 1.16	0.00 ± 0.32
t2pene	0.00 ± 0.20	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.20	0.00 ± 0.20
c2pene	0.00 ± 0.20	0.00 ± 0.44	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.20	0.00 ± 0.20
bu22dm	0.00 ± 0.20	0.00 ± 0.44	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.29 ± 0.30	0.38 ± 0.48
cpenta	0.00 ± 0.20	0.00 ± 0.44	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.30 ± 0.26	0.18 ± 0.20
bu23dm	0.00 ± 0.20	0.00 ± 0.44	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.41 ± 0.27	0.55 ± 0.52
pena2m	0.05 ± 0.20	0.01 ± 0.10	0.30 ± 0.11	0.00 ± 0.10	0.00 ± 0.10	1.36 ± 0.98	1.87 ± 1.27
pena3m	0.00 ± 0.20	0.01 ± 0.10	0.10 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.90 ± 0.66	1.33 ± 1.09
p1e2me	0.00 ± 0.20	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.01 ± 0.20	0.00 ± 0.20
n_hex	4.66 ± 0.51	0.00 ± 0.44	0.40 ± 0.12	0.00 ± 0.10	0.00 ± 0.10	2.35 ± 2.93	2.47 ± 1.46
mcypna	0.00 ± 0.20	0.04 ± 0.10	0.99 ± 0.18	0.00 ± 0.10	0.00 ± 0.10	1.21 ± 0.58	1.04 ± 0.38
pen24m	0.00 ± 0.20	0.01 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.47 ± 0.44	0.38 ± 0.46
benze	0.00 ± 0.20	0.00 ± 0.44	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	2.94 ± 1.18	2.70 ± 1.11
cyhexa	0.06 ± 0.20	0.15 ± 0.23	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.46 ± 0.24	0.42 ± 0.29
hexa2m	0.13 ± 0.20	0.28 ± 1.22	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.65 ± 0.41	0.88 ± 0.79
pen23m	0.00 ± 0.20	0.12 ± 0.21	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	1.05 ± 0.49	1.28 ± 0.89
hexa3m	0.00 ± 0.20	0.34 ± 0.45	0.20 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	4.53 ± 2.47	5.92 ± 2.09
pa224m	0.00 ± 0.20	0.00 ± 0.44	0.30 ± 0.11	0.00 ± 0.10	0.00 ± 0.10	0.70 ± 0.42	0.71 ± 0.47
n_hept	3.19 ± 0.38	1.57 ± 4.82	0.20 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.81 ± 0.36	0.95 ± 0.49
mecyhx	0.18 ± 0.20	2.61 ± 9.12	0.10 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.64 ± 0.34	0.81 ± 0.60
pa234m	0.00 ± 0.20	0.05 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.12 ± 0.20	0.09 ± 0.20
tolue	19.17 ± 1.93	6.91 ± 6.86	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	6.74 ± 6.08	6.03 ± 3.63
hep2me	0.04 ± 0.20	1.36 ± 2.34	0.40 ± 0.12	0.00 ± 0.10	0.00 ± 0.10	0.33 ± 0.25	0.55 ± 0.35
hep3me	0.03 ± 0.20	0.96 ± 1.62	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.17 ± 0.20	0.25 ± 0.23
n_oct	0.07 ± 0.20	3.44 ± 5.30	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.65 ± 0.45	0.85 ± 0.49
etbz	0.33 ± 0.20	3.82 ± 2.85	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.77 ± 0.29	0.90 ± 0.46
mp_xyl	1.87 ± 0.27	15.40 ± 10.58	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	2.04 ± 1.21	2.34 ± 1.12
styr	0.05 ± 0.20	0.01 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	4.06 ± 2.01	5.05 ± 2.60
o_xyl	1.42 ± 0.25	7.18 ± 4.36	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	1.47 ± 0.89	1.77 ± 0.72
n_non	5.88 ± 0.62	4.54 ± 2.30	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.52 ± 0.29	0.70 ± 0.30
iprbz	0.00 ± 0.20	0.63 ± 0.57	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.12 ± 0.21	0.14 ± 0.20
n_prbz	0.87 ± 0.22	1.46 ± 1.46	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.66 ± 0.46	0.88 ± 0.39
m_etol	0.01 ± 0.20	0.00 ± 0.44	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	1.56 ± 1.36	1.70 ± 0.92
p_etol	0.01 ± 0.20	4.51 ± 1.66	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.79 ± 0.62	1.00 ± 0.54
bz135m	0.00 ± 0.20	4.14 ± 2.64	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	1.14 ± 0.80	1.63 ± 1.28
o_etol	0.33 ± 0.20	0.00 ± 0.44	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	1.08 ± 0.77	1.16 ± 0.51
bz124m	0.03 ± 0.20	11.13 ± 4.31	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	4.81 ± 2.69	6.66 ± 4.79
n_dec	0.08 ± 0.20	18.12 ± 6.01	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.73 ± 0.29	0.87 ± 0.62
bz123m	0.01 ± 0.20	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.98 ± 0.76	1.15 ± 0.42
detbz1	0.00 ± 0.20	0.39 ± 0.42	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.07 ± 0.20	0.10 ± 0.20
detbz2	0.00 ± 0.20	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	1.38 ± 0.98	1.91 ± 0.75
n_unde	0.08 ± 0.20	10.81 ± 8.14	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	1.00 ± 0.60	1.46 ± 1.05
tnmhc	222.46 ± 22.25	286.46 ± 28.65	100.49 ± 10.05	100.00 ± 10.00	100.00 ± 10.00	125.18 ± 9.61	139.00 ± 14.69

Table 3-5. Sensitivity of CMB performance in Round 4 with alternative mobile source profiles.

Site	conc	uconc	rsquar	chisquar	pcmass	Gasoline Exhaust	Unc	Gasoline Vapor	Unc	Diesel Exhaust	Unc
Anaheim	86.3	2.4	0.99	0.39	102.7	15.2	5.0	16.9	2.7	3.9	2.1
Diamond_Bar	71.6	2.2	0.99	0.29	104.2	15.2	4.0	14.8	2.8	2.5	2.2
Hawthorn	153.0	4.1	0.99	0.58	98.6	16.7	6.4	18.0	3.7	8.1	3.2
LAX	122.7	3.2	0.99	0.38	103.4	19.1	5.8	20.0	3.4	8.8	2.9
Long_Beach	112.0	3.5	0.98	0.42	110.9	16.5	5.7	13.7	3.5	1.8	2.4
Van_Nuys	71.7	1.9	1	0.18	102.4	19.3	4.1	16.3	2.5	2.8	1.7
Cat_CS			**0.99**	**0.37**	**103.7**	**17.0**	**5.2**	**16.6**	**3.1**	**4.7**	**2.5**
Anaheim	86.3	2.4	0.99	0.36	103.7	13.5	4.5	16.3	2.9	4.2	2.1
Diamond_Bar	71.6	2.2	0.99	0.25	103.6	13.9	3.7	13.5	3.1	3.3	2.3
Hawthorn	153.0	4.1	0.99	0.53	99.0	15.8	5.9	17.1	3.8	7.8	3.3
LAX	122.7	3.2	0.99	0.4	103.9	16.7	5.3	19.3	3.6	9.1	2.8
Long_Beach	112.0	3.5	0.98	0.41	111.6	13.7	4.8	13.3	3.7	2.4	2.2
Van_Nuys	71.7	1.9	1	0.18	103.8	17.1	3.7	15.8	2.6	3.3	1.7
Cat_HS			**0.99**	**0.36**	**104.3**	**15.1**	**4.7**	**15.9**	**3.3**	**5.0**	**2.4**
Anaheim	86.3	2.4	0.99	0.51	104.6	16.4	6.0	15.7	3.1	4.3	2.0
Diamond_Bar	71.6	2.2	0.99	0.45	107.5	16.5	4.8	14.4	2.9	2.2	2.2
Hawthorn	153.0	4.1	0.99	0.64	100.2	19.5	7.6	16.4	4.0	9.7	2.9
LAX	122.7	3.2	0.99	0.42	105.7	22.5	6.9	18.1	3.7	9.9	2.6
Long_Beach	112.0	3.5	0.98	0.63	112.4	13.0	7.3	14.2	4.1	3.9	2.3
Van_Nuys	71.7	1.9	0.99	0.43	106.0	21.2	4.7	16.0	3.1	2.0	2.2
nCat_CS			**0.99**	**0.51**	**106.1**	**18.2**	**6.3**	**15.8**	**3.5**	**5.3**	**2.4**
Anaheim	86.3	2.4	0.99	0.36	103.3	11.2	4.0	17.6	2.7	2.7	2.7
Diamond_Bar	71.6	2.2	0.99	0.22	99.9	12.2	3.3	13.9	3.1	2.3	2.6
Hawthorn	153.0	4.1	0.99	0.54	98.0	13.7	5.6	18.7	3.6	4.9	4.5
LAX	122.7	3.2	0.99	0.46	102.8	13.3	4.7	21.3	3.4	7.1	3.6
Long_Beach	112.0	3.5	0.99	0.38	110.3	11.0	3.9	14.8	3.4	0.9	2.8
Van_Nuys	71.7	1.9	0.99	0.22	102.7	13.4	3.0	17.7	2.4	2.0	1.9
nCat_HS			**0.99**	**0.36**	**102.8**	**12.5**	**4.2**	**17.3**	**3.1**	**3.3**	**3.1**

SIXcatCS	Onroad Mobile Gasoline Catalyst Exhaust (start)
SIXcatHS	Onroad Mobile Gasoline Catalyst Exhaust (stabilized)
SIXnctCS	Onroad Mobile Gasoline Non-Catalyst Exhaust (start)
SIXnctHS	Onroad Mobile Gasoline Non-Catalyst Exhaust (stabilized)

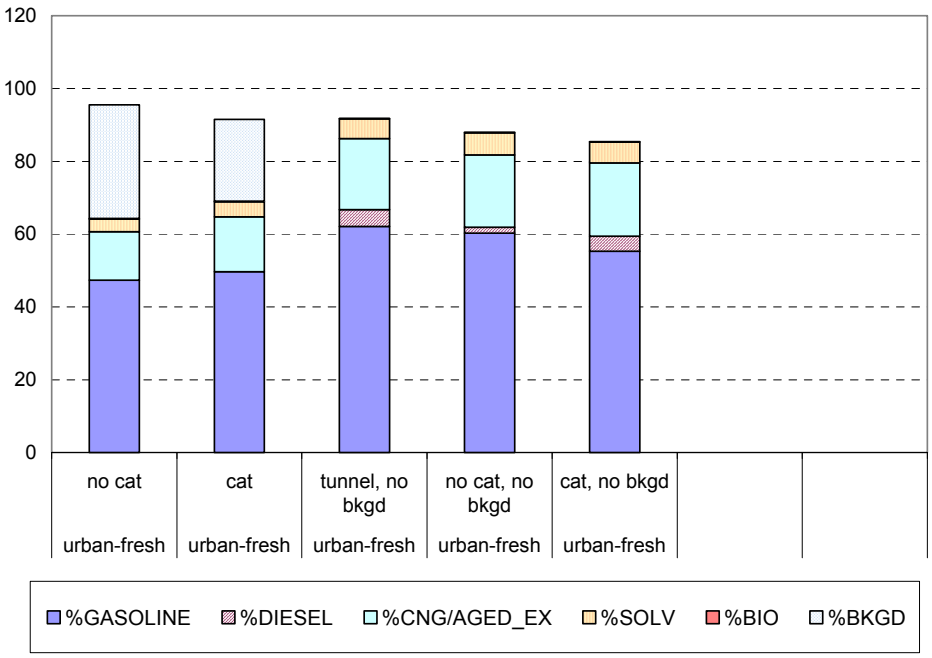


Figure 3-1. Sensitivity of source attribution to three different gasoline exhaust profile and inclusion of a regional background profile. Removing regional background shift attribution to mostly gasoline exhaust and small amount of diesel exhaust.

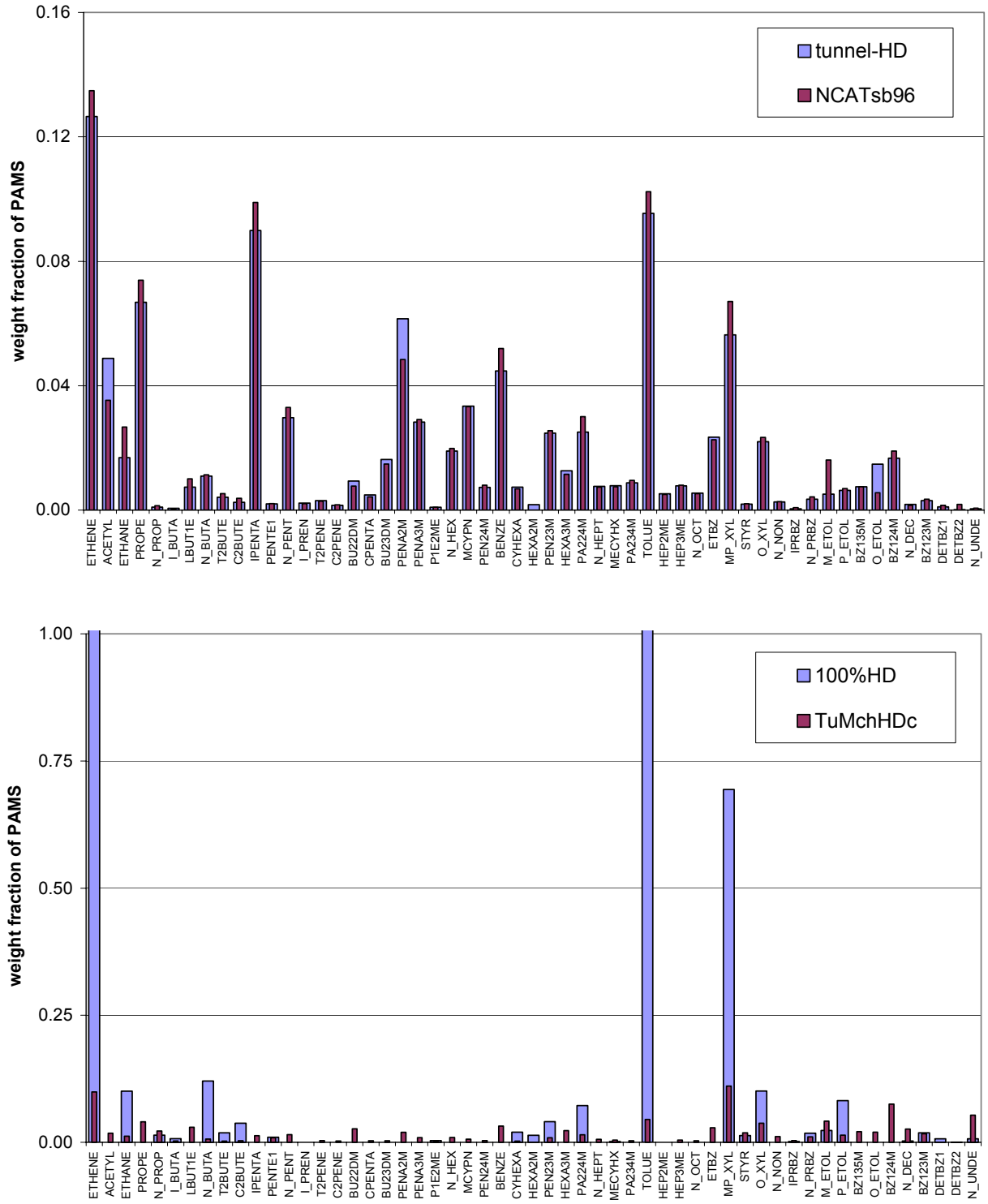


Figure 3-2. LDV and HDV profiles derived from the virtual tunnel study in comparison to the default light-duty gasoline and heavy-duty diesel exhaust profiles used in Round 1.

4.0 RESULTS

This section presents the results of experiments designed to test the ability of the CMB receptor model to source apportion ambient VOC samples. Simulated "ambient" VOC samples were prepared for several receptor locations using a photochemical grid model as described in Section 2. CMB was used to estimate the source contributions to the 55 PAMS species present in each "ambient" sample as described in Section 3. The actual source contributions for 22 source categories in each air sample were known from the photochemical modeling. The CMB source contributions were evaluated against the actual contributions in four Rounds of analyses, as described in Section 1. The actual source contributions to the "ambient" samples were compared to emissions contributions near the receptors.

4.1 EXPERIMENTS 1-8 IN ROUNDS 1, 2 AND 4

Eight experiments were conducted by ENVIRON and analyzed independently by DRI in Round 1. As discussed in Section 1, Round 1 was the "blind analysis" where DRI had minimal information about each air sample. Experiment 1 is the base case for experiments 1-8. DRI classified the concentrations of PAMS species to 7 different CMB categories as shown in Figure 4-1 for 8 receptor locations. Figure 4-1 compares CMB contributions to actual contributions for experiment 1, which are defined as follows:

- **CMB contribution**: The fraction of total PAMS species concentration (ppbC) attributed to a category by CMB, expressed as a percentage.

- **Actual contribution**: The true fraction of PAMS species concentration (ppbC) from a source category (a known quantity for each air sample) expressed as a percentage.

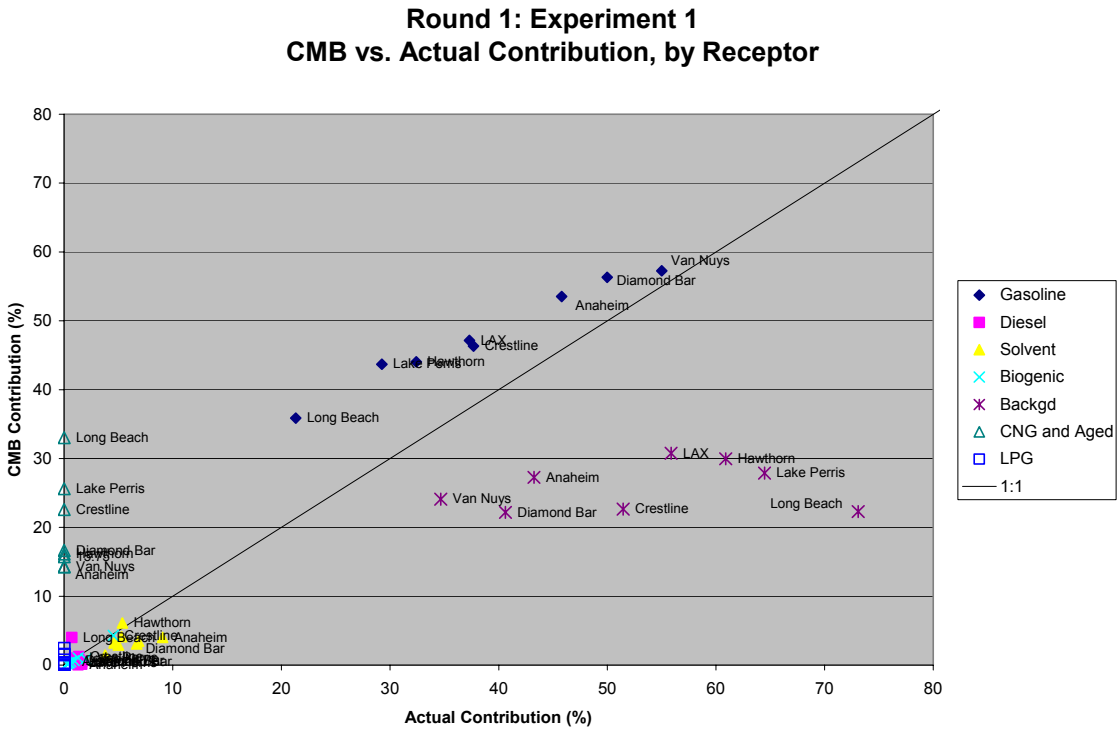
These percentages are averages over multiple "ambient" samples and are calculated as the sum of PAMS for the source category divided by the total PAMS (i.e., we avoided averaging ratios).

Most of the analyses below evaluate the ability of CMB to identify contributions to the PAMS species actually present in the simulated air samples. This approach is adopted because the only measure of CMB performance that can be evaluated rigorously is its ability to recover the actual contributions present in air samples. We considered comparing the CMB contributions to emissions contributions, defined as:

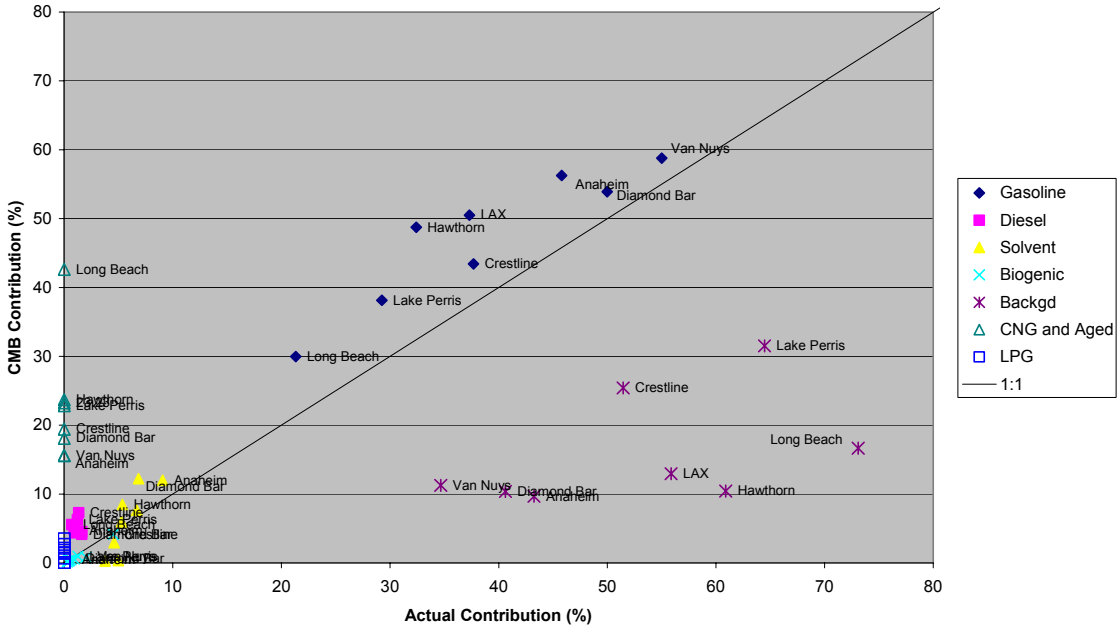
- **Emissions contribution**: The fraction of PAMS species emissions (molesC) from a source category in the 9 grid cells (15-km by 15-km) around a receptor, expressed as a percentage.

However, as shown below, the relationships between actual contributions and emissions contributions depend upon the spatial distributions of emissions sources and the area (footprint) used to characterize emissions around a receptor. Comparing CMB contributions to emissions contributions is likely to introduce compensating errors.

(a)


Round 1: Experiment 1
CMB vs. Actual Contribution, by Receptor
CMB Contribution (%)
Actual Contribution (%)
0
10
20
30
40
50
60
70
80
Van Nuys
Diamond Bar
Anaheim
LAX
Crestline
Lake Perris
Long Beach
Hawthorn
Gasoline
Diesel
Solvent
Biogenic
Backgd
CNG and Aged
LPG
1:1

(b)


Round 2b: Experiment 1
CMB vs. Actual Contribution, by Receptor
CMB Contribution (%)
Actual Contribution (%)
0
10
20
30
40
50
60
70
80
Van Nuys
Anaheim
Diamond Bar
LAX
Hawthorn
Crestline
Lake Perris
Long Beach
Gasoline
Diesel
Solvent
Biogenic
Backgd
CNG and Aged
LPG
1:1

(c)

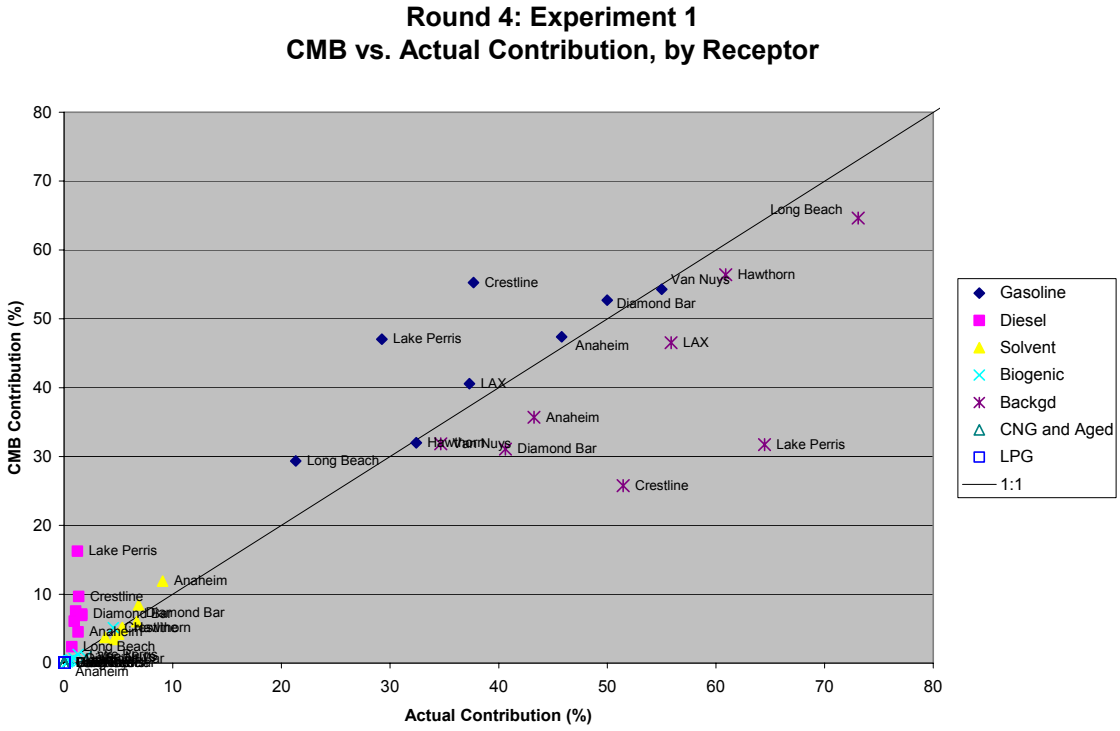


Figure 4-1. Comparison of CMB contributions to actual contributions for experiment 1 at each receptor averaged over all hours in (a) Round 1 (b) Round 2 and (c) Round 4.

DRI selected seven CMB categories for the Round 1 analysis based on criteria of good CMB performance and lack of co-linearity between source category profiles. It is important to understand that these CMB categories were identified because they had different chemical compositions that, taken together, explained the "ambient" sample composition with some success. The CMB category names should not be expected to always correspond with source categories that are used in preparing emission inventories. This is because emission inventory categories are defined around activities that generate emissions rather than the chemical composition of emissions. The seven CMB categories selected by DRI for Round 1 are described in Table 4-1. The CMB categories were matched to A-34 source categories used in preparing the simulated "ambient" air samples as shown in the right column of Table 4-1.

Table 4-1. Categories identified by CMB in experiments 1-8 of Round 1 and the way they were matched to A-34 categories actually present in the "ambient" samples.

CMB Category	Description/Interpretation	Matched to A-34 Categories
Gasoline	Emissions related to gasoline usage. Includes exhaust, whole gasoline and gasoline vapor.	1, 2, 3, 4, 5, 6, 8, 9, 11
Diesel	Diesel exhaust.	7, 10
Solvent	Solvents and/or consumer products that do not resemble gasoline.	14, 15, 16, 17,
CNG and aged	Compounds that looked like CNG, predominantly ethane.	None
LPG	Compounds that looked like LPG,	None

CMB Category	Description/Interpretation	Matched to A-34 Categories
	predominantly propane.	
Biogenic	Isoprene.	18
Background	Composite ambient background for Southern California in 1997 with isoprene removed. Morning and afternoon background profiles were used.	12, 13, 19, 20, 21, 22 + 9.88 ppbC[#]

Notes:

[#]9.88 ppbC is the background added to each "ambient" sample

Experiment 1 in Round 1

In Round 1, DRI applied CMB with minimal information to support the analysis. The results of the Round 1 analysis for experiment 1 are shown in Figure 4-1a. The main source category positively identified by CMB in experiment 1 was gasoline. CMB showed skill in correctly apportioning the amount of gasoline emissions and correctly rank ordering receptor locations from low to high gasoline contribution (Long Beach to Van Nuys). CMB systematically over-estimated the contribution of gasoline emissions. The bias was greatest when the actual gasoline contribution was low (bias > 50% at Long Beach) and least when the actual gasoline contribution was high (bias < 5% at Van Nuys). Over-estimations at Long Beach, Hawthorne and LAX were most likely due to omission of a source profile that resembles the hypothetical industrial source emissions. There is also a general tendency at downwind locations such as Lake Perris and Crestline, and with aged afternoon samples at mid-basin sites, for total predicted VOC concentrations to exceed measured levels because relatively nonreactive species are used in the CMB calculations. The average ratios of predicted and measured VOCs were 1.10 for samples having xylene/benzene ratios between 1.2 and 1.6 and 1.15 for ratios less than 1.2.

CMB correctly identified three other source categories in Round 1: biogenics, diesel and solvents. Biogenics were quantified accurately because the profile (in terms of PAMS species) was dominated by a single compound, isoprene. Solvents were generally under-estimated by CMB with a bias of about a factor of two. CMB accurately determined that the diesel contribution (to the sum of PAMS species) was small when the Type 2 am set of fitting species was used in the fit. This set includes decane and undecane, which CMB needs to apportion surface coatings and to distinguish between gasoline and diesel exhaust. CMB detected diesel exhaust in only 23% of the urban-fresh samples and most source contributions were significantly lower than the propagated 1-sigma uncertainties. In contrast, diesel exhaust was detected in 79% of the urban-aged samples and is often co-linear with gasoline exhaust. The relative contributions of diesel exhaust are larger for the urban-aged samples but so are the corresponding propagated uncertainties. The composite surface coating profile is detected in 87% of the urban-fresh samples when nonane, decane and undecane are used in the fit, but is detected in only 28% of the urban-aged samples when the heavy hydrocarbon is left out of the calculation. Biogenic emissions are detected in most samples at negligible levels in urban samples. Their contributions are substantially higher relative to total VOC in many of the low-aged samples, which are from Crestline. CMB accurately apportioned the biogenic contribution to air concentrations (in terms of PAMS species) because the profile is dominated by a single compound, isoprene. Because isoprene is reactive, the biogenic contributions reported by CMB represent lower limits of the

emissions contributions, as discussed in more detail below where relationships between emissions and air concentrations are considered.

Two CMB categories were identified by name (CNG/aged and LPG) that were not used in preparing the emissions for experiment 1 (see Table 2-9). This emphasizes that CMB category names describe the chemical characteristics of source profiles (fingerprints) rather than specific activities tracked in emission inventories.

The CNG/aged profile accounted for ambient ethane whereas the LPG profile accounted for ambient propane. The main sources of ethane and propane in the emissions for experiment 1 were oil/gas production, gas-fueled engines, refineries and hypothetical industrial emissions (see Section 2). The amount of ethane in experiment 1 (and experiments 2-8) was higher than intended because of an artifact. The emissions fraction for each A-34 source category (Table 2-9) was defined as a ROG fraction. The PAMS species are a subset of ROG species with the exception of ethane. Therefore, ethane rich source profiles (e.g., gas-fueled engines) can have PAMS/ROG ratios greater than 1 (Table 2-11). The consequence was that contributions of ethane rich source categories (PAMS/ROG > 1 in Table 2-11) to the sum of PAMS species were artificially high. DRI accounted for the high ethane and propane backgrounds using the CMB categories CNG/aged and LPG. This outcome did not perturb the study because urban samples often contain elevated ethane and propane that are explained in CMB using the same CNG/aged and LPG categories.

CMB accounted for the remaining PAMS species in the "ambient" samples using background profiles for the Los Angeles area. The real background introduced into the "ambient" samples was low (~10 ppbC) and so the CMB category "background" really corresponded to unidentified emissions. Once again, the label "background" attached to this CMB category reflects the origin of the profile rather than the identity of the emissions source. The CMB apportionments for background were biased low because the apportionments for CNG/aged and LPG (and to a lesser extent gasoline) were biased high. The background, CNG/aged and LPG categories in CMB together represent a combination of PAMS species including excess ethane and propane that cannot be explained by other source categories and CMB performance for the sum of these three categories was better than for the individual categories.

Experiment 1 in Round 2

The difference between Round 2 and Round 1 was that DRI had additional information to help identify source profiles. In particular, DRI had a tunnel study and gasoline samples to derive mobile source profiles for Round 2 which may be expected to help the apportionment of the "gasoline" CMB category. The results of the Round 2 analysis for experiment 1 are shown in Figure 4-1b. Overall, the apportionment of gasoline was similar in Round 2 to Round 1 with CMB showing skill in sorting out low/high contribution sites, but tending to over-estimate the contribution of gasoline. As mentioned in Section 3, the gasoline profile derived from the virtual tunnel study is very similar to the gasoline profile that DRI used in Round 1. CMB performance for solvents was better in Round 2 than Round 1, but CMB performance for diesel was poorer in Round 2. Performance for biogenics was the same in Round 2 as Round 1. The remaining emissions were classified as CNG/aged, LPG and background in Round 2 as in Round 1.

Overall, there was little change in CMB performance between Rounds 1 and 2. The tunnel study and other data provided in Round 2 did not improve the apportionment for gasoline emissions, but did change apportionments for solvents and diesel. The designation of "aged" sample (i.e., use of Type 2 pm set of fitting species) in Round 2 was based on site and time rather than by xylene/benzene ratios. The Type 2 am species fitting set was used for urban and suburban sites for 0600 to 1800 samples and the Type 2 pm set was used for 1800 to 0600 samples. As previously mentioned, exclusion of heavier hydrocarbons tends to result in co-linearity between gasoline and diesel with over-estimation of diesel and under-estimation of surface coatings. This demonstrates the potential for inter-dependence between CMB apportionments for different categories and the strong influence of certain key fitting species.

Experiment 1 in Round 4

In Round 4, DRI had detailed information on source categories and profiles going beyond what could ever be known in the real-world. The results of the Round 4 analysis for experiment 1 are shown in Figure 4-1c. DRI was able to fit many more source categories in Round 4 than in earlier Rounds but, to allow direct comparisons, the CMB categories have been aggregated in Figure 4-1c to the categories used in Rounds 1 and 2.

There were some clear improvements in CMB performance in Round 4 over Rounds 1 and 2. Since DRI now knew that CNG and LPG were not real emissions categories these apportionments were eliminated from the CMB analysis (resulting in points at 0,0 in Figure 4-1c) and consequently the apportionment for emissions sources in the "background" category was improved. DRI was able to dispense with the CNG/aged and LPG profiles because they had profile information to identify and account for the true sources of ethane and propane.

The Round 4 apportionments to gasoline were accurate at all sites except the downwind receptors (Crestline, Lake Perris) and at Long Beach. The apportionments to solvents also improved and were quite accurate. Biogenics remained accurately apportioned because the PAMS contribution is dominated by a single species (isoprene). The CMB apportionments for diesel showed good correlation but were too high, especially in downwind areas.

Performance for diesel systematically degraded from Round 1 to Round 4 as the source profile information improved. The tendency was to over-estimate diesel. The reasons for this were not confirmed, however diesel also was over-estimated in experiment 12 (discussed below) where conditions for CMB were nearly ideal. It appears that diesel is susceptible to systematic errors arising from profile co-linearity when only the 55 PAMS species are available. DRI encounters this issue in real-world CMB studies and accordingly prefers to have heavy hydrocarbon data (> C12) to support source apportionment of diesel emissions (DRI requested this type of information in Round 2 but ENVIRON could not provide reliable heavy hydrocarbon data from the available emissions profiles).

The Round 4 CMB apportionments were poorest at the downwind receptors (Crestline and Lake Perris) and at Long Beach. The poorer performance at downwind receptors is attributed to chemical aging of emissions during transport from upwind source regions and reliance on a smaller set of fitting species for aged air samples. A comparison of actual/emissions contributions (described below) showed that the downwind receptors were dominated by transported emissions, as expected. Experiment 2 (discussed below) investigated atmospheric

reactivity and found CMB to be quite robust against higher reactivity (oxidant levels) because of protocols that are designed to eliminate reactive species from consideration in aged air samples. However, the downwind receptors may provide a more severe test of reactivity effects than experiment 2 because the Crestline and Lake Perris receptors are always dominated by aged emissions.

The poorer CMB performance at Long Beach than other upwind and mid-basin receptors is consistent with results of experiment 6 with high industrial emission levels, discussed below. Experiment 6 showed that CMB tended to over-estimate gasoline emissions when industrial emission levels were high. Figure 4-1c shows that Long Beach had the lowest gasoline contribution and highest "background" contribution due to high industrial and oil/gas production emissions that fall under the "background" label. Therefore, the over-estimation of gasoline emissions at Long Beach in experiment 1 is attributed to incorrect classification of some industrial emissions as gasoline.

Findings From Experiment 1

- CMB category names describe chemical characteristics of source profiles (fingerprints) rather than specific activities tracked in emission inventories

- CMB tended to over-estimate the contribution of gasoline emissions except when complete profile information was available (Round 4), particularly at locations impacted by the hypothetical industrial source.

- Obtaining profile data from a Tunnel study and fuel samples (Round 2) did not improve the CMB performance for gasoline over the blind analysis (Round 1) because the profiles were substantially similar. The tunnel-derived diesel profile was highly uncertain and was not used.

- Obtaining profile data from a Tunnel study and fuel samples (Round 2) did change CMB performance for non-gasoline categories, improving performance for solvents.

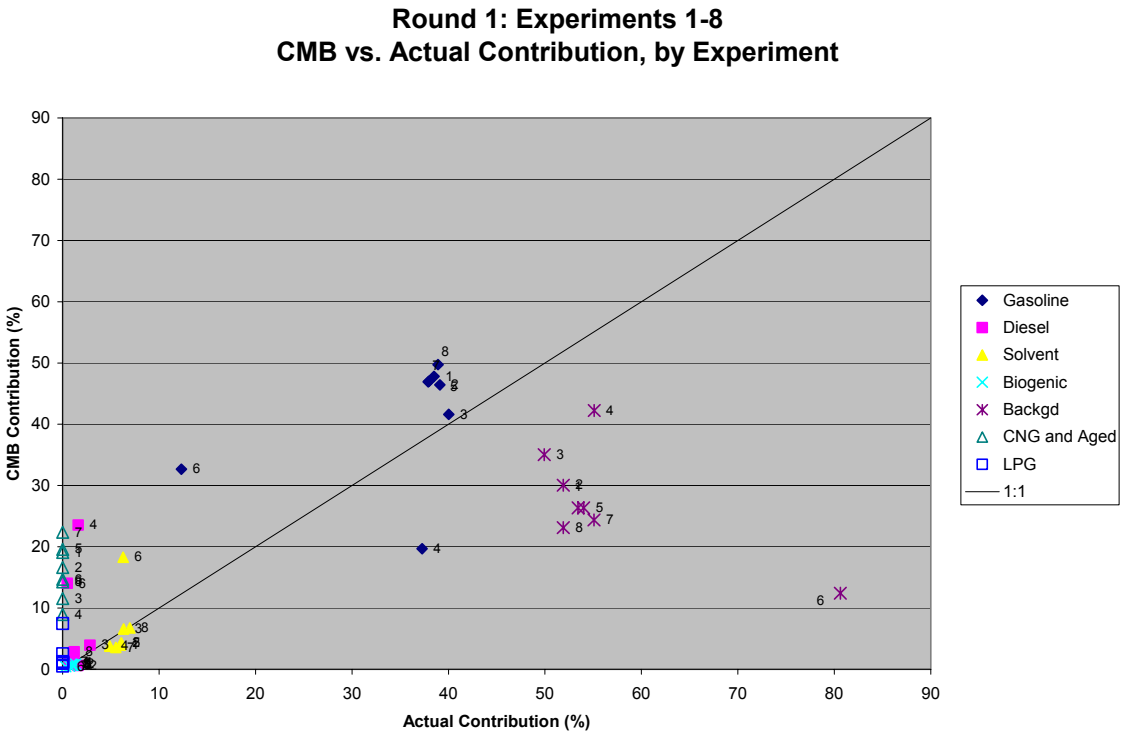
- CMB performance for diesel systematically degraded from Round 1 to Round 4 as CMB was provided with progressively more accurate source profile information and the receptor modelers made different choices for fitting species. The tendency was for CMB to over-estimate the diesel contribution. Poor performance for diesel is largely related to exclusion of nonane, decane and undecane from the set of fitting species for "aged" samples, which resulted in co-linearity between gasoline and diesel.

Experiments 2-8

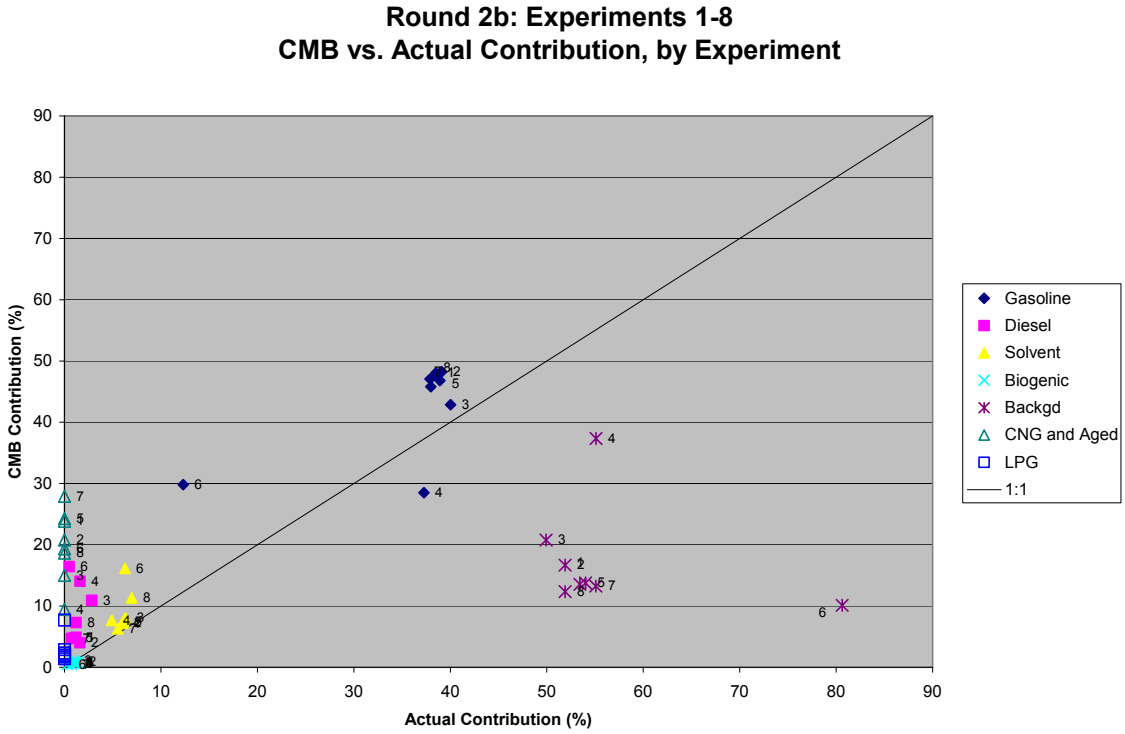
Experiments 2-8 were sensitivity tests designed to investigate uncertainties and biases relative to experiment 1 as described above in Table 2-9. Figure 4-2 compares CMB contributions to actual contributions averaged over all receptors and hours for experiments 1-8. Figure 4-2 shows that the results of experiments 2 (higher reactivity), 5 (weekend source mix), 7 (randomly varying source profiles) and 8 (higher random sampling noise) were substantially the same as experiment 1 in all Rounds. CMB performance was sensitive to using alternate speciation profiles

(experiment 3), reducing the number of species available for the CMB analysis (experiment 4) and having high industrial emission levels (experiment 6). These findings are discussed in more detail below.

(a)



(b)



(c)

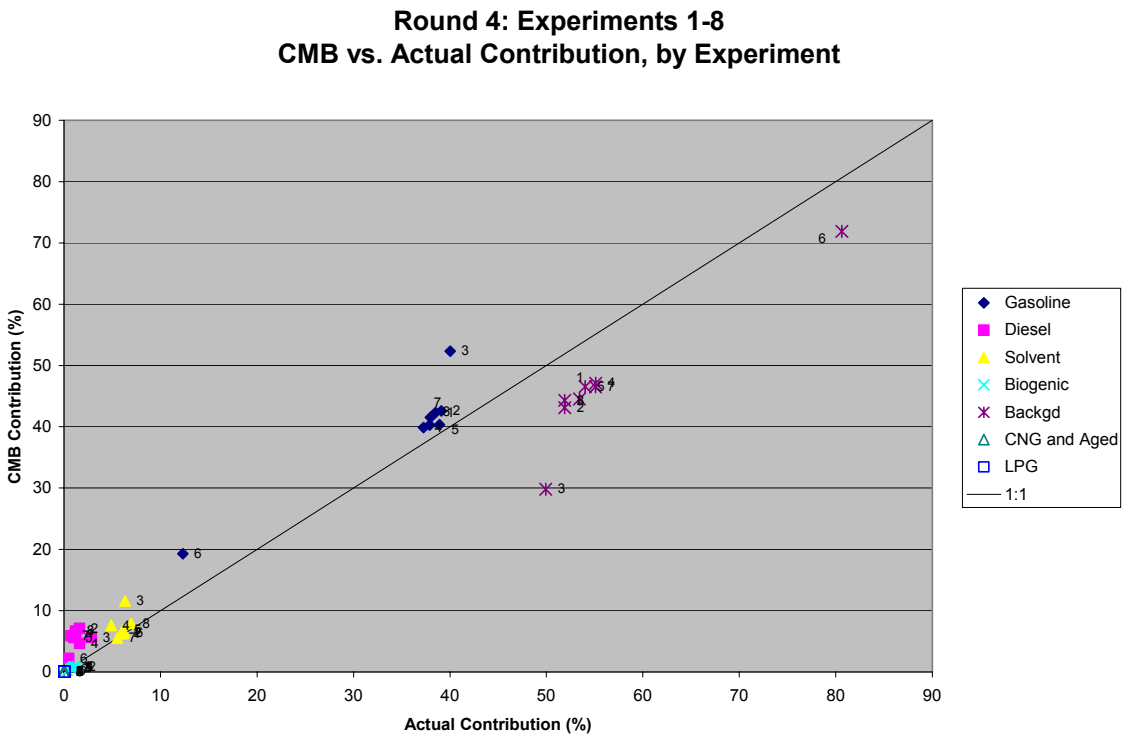


Figure 4-2. Comparison of CMB contributions to actual contributions for experiments 1-8 averaged over all receptors and hours in (a) Round 1 (b) Round 2 and (c) Round 4.

Findings From Experiments 2-8

- Overall CMB performance was relatively insensitive to higher atmospheric reactivity (experiment 2), weekend source mix (experiment 5), randomly varying source profiles (experiment 7) and higher random noise in the ambient data (experiment 8).
- The results from experiments 7 and 8 showing that random changes did not impact CMB performance on average are expected because random changes tend to cancel when averaged by the atmosphere (experiment 7) or multiple samples (experiment 8).
- CMB was robust against higher reactivity (experiment 2) because of receptor modeling protocols designed to avoid relying upon highly reactive species when ambient samples appear to be aged. However, the experiment 1 results for downwind receptors, discussed above, show that CMB performance can be degraded when air samples are highly aged at all times.
- Introducing a weekend for 2 out of 4 days (experiment 5) did not degrade CMB performance because CMB was able to quantify emissions contributions on weekend days about as well as on weekdays.
- When industrial emission levels were set to high levels (experiment 6) CMB tended to over-estimate the gasoline and solvent contributions by a factor of two, or more. Providing typically available source profile data in Round 2 did little to reduce these biases. Providing complete source profile data in Round 4 eliminated the bias for solvents and reduced the bias for gasoline to about 50%.

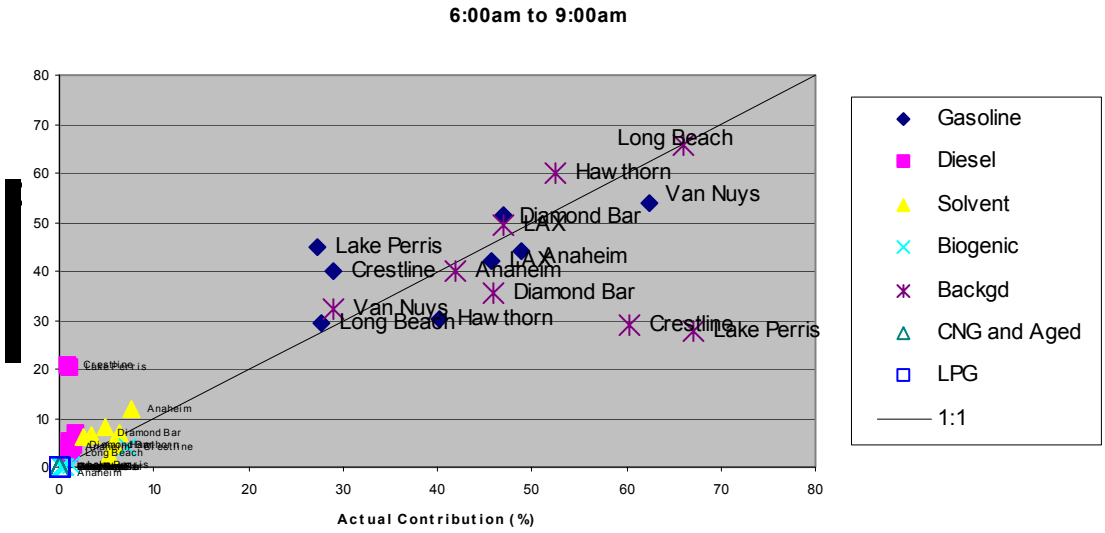
- Eliminating 20% of the species available to CMB (experiment 4) degraded performance, especially when source profiles were poorly known. Eliminating species had a substantial impact in Round 1 (blind analysis) and little impact in Round 4 (full profile information).
- Changing the speciation profiles (experiment 3) improved or degraded CMB performance depending upon whether the alternate profiles were a better or poorer fit with the profiles used in CMB.

The last finding on the effects of alternate speciation profiles seems obvious and needs further discussion. The alternate profiles used in experiment 3 included mobile source (gasoline) profiles taken from other CMB studies. In Round 1, with minimal information, DRI obtained more accurate gasoline contributions for experiment 3 than any other experiment, perhaps because the experiment 3 profiles had internal characteristics that "work well" for CMB analyses, such as lack of co-linearity. Round 4 with detailed profile information showed the opposite result of poorer gasoline apportionments for experiment 3 than any other experiment, likely because experiment 3 was the odd man out, i.e., it used profiles that differed from the "known profiles."

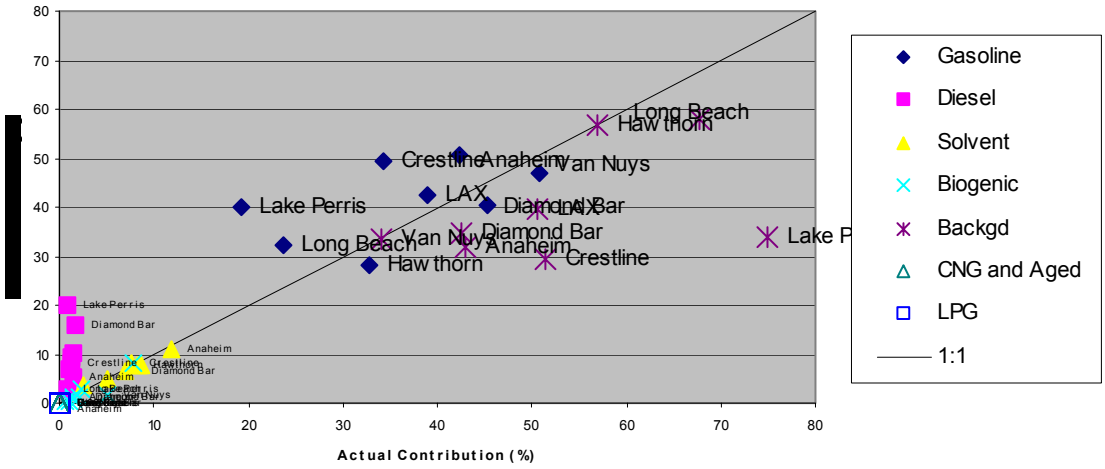
4.2 HOURLY SOURCE APPORTIONMENT RESULTS

The discussion of experiments 1-8 above focused on source contributions averaged over all hours. However, analyses of ambient data often focus on morning (6-9 am) samples to minimize effects of atmospheric dilution and chemical reaction. In contrast, afternoon (1-4 pm) samples are expected to be chemically aged and so more difficult to analyze. Figure 4-3 shows the results for experiment 1 in Round 4 at each receptor for three averaging times: 6-9 am, 1-4 pm and all hours. The results for all hours were shown above (Figure 4-1c) and it was concluded that CMB performed well for gasoline, solvents and biogenics at most receptors. Figure 4-3 shows that there was more scatter in the CMB apportionments for gasoline, solvents and biogenics in 6-9 am samples than for all hours. Similarly, the CMB apportionments for 1-4 pm were more scattered than for all hours, but were no worse than for 6-9 am. The degraded performance of CMB for restricted time periods may be due to the reduction in sample size (averages over 12 samples rather than 96) in these experiments where only 4 days were simulated. This difficulty could be avoided for real-world conditions if many more days are sampled (e.g., data from a PAMS auto-GC site). However, the results obtained here show no evidence that focusing on 6-9 am samples will improve the accuracy of CMB. Correspondingly, analyzing afternoon samples did not degrade the performance of CMB.

(a)


6:00am to 9:00am
Actual Contribution (%)
Gasoline
Diesel
Solvent
Biogenic
Backgd
CNG and Aged
LPG
1:1
Long Beach
Haw thorn
Van Nuys
Diamond Bar
LAX
Lake Perris
Crestline
Anaheim

(b)


1:00pm to 4:00pm
Actual Contribution (%)
Gasoline
Diesel
Solvent
Biogenic
Backgd
CNG and Aged
LPG
1:1
Long Beach
Haw thorn
Crestline
Anaheim
Van Nuys
LAX
Lake Perris
Diamond Bar

(c)

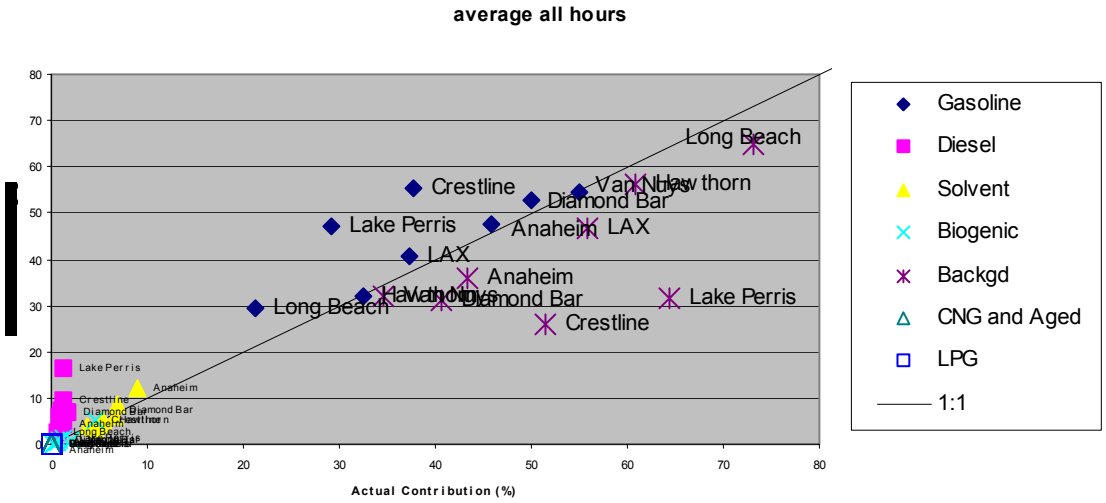
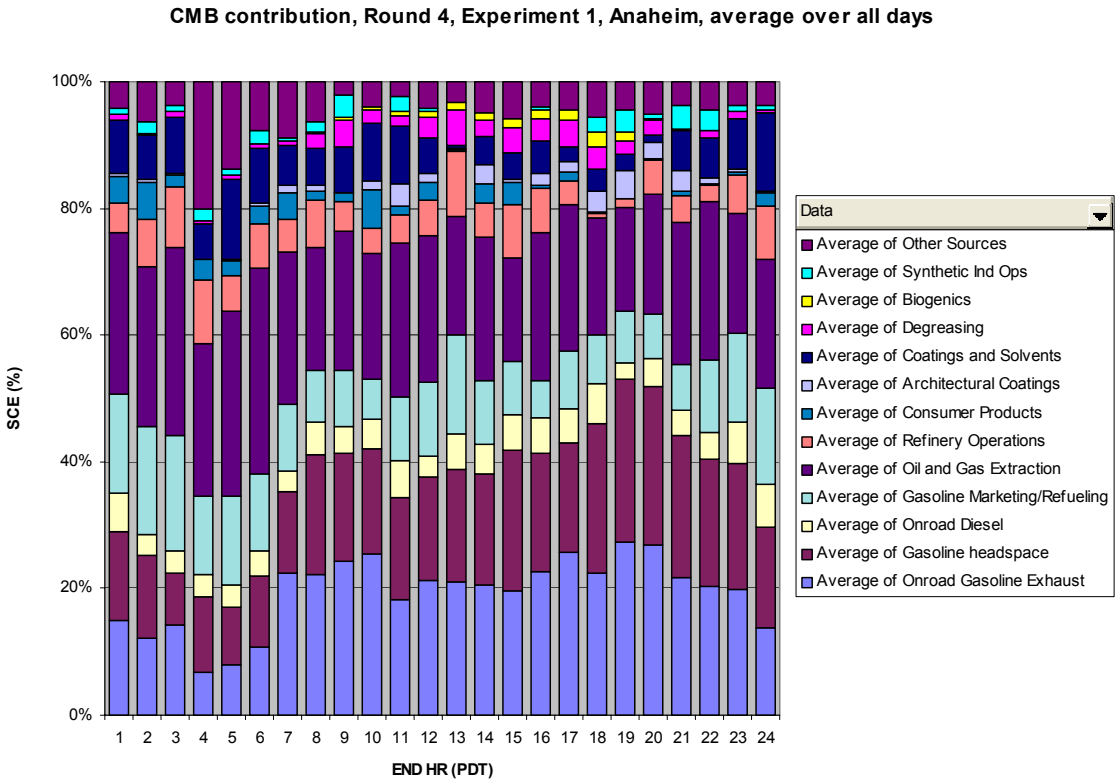


Figure 4-3. Comparison of CMB contributions to actual contributions for experiment 1 in Round 4 at each receptor averaged over (a) 6-9 am (b) 1-4 pm and (c) all hours.

Hourly source apportionment results are compared in greater detail in Figures 4-4 for experiment 1 at Anaheim in Round 4. Anaheim was one of the better performing sites for CMB in Round 4. Figure 4-4a shows all of the 13 source categories that CMB reported for this case in Round 4. CMB was able to resolve a large number of categories in Round 4 because detailed source profiles were available. Figure 4-4b shows the actual contributions aggregated to match Figure 4-4a. CMB was able to follow some major temporal features in the actual contributions such as (1) the rush hour for on-road, gasoline-powered vehicle emissions, (2) the afternoon peak in biogenics and (3) the daytime peak in degreasing. However, many of the other hour-to-hour variations reported by CMB are noisy or incorrect. A large part of this noise likely results from the sampling noise introduced into the "ambient" samples. With only four sampling days, each hour is averaged over just 4 samples. These comparisons show that with the size of dataset considered here (four days of continuous samples) CMB performance is much better for daily average source contributions than for individual hours.

(a)


CMB contribution, Round 4, Experiment 1, Anaheim, average over all days
100%
80%
60%
40%
20%
0%
SCE (%)
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
END HR (PDT)
Data
Average of Other Sources
Average of Synthetic Ind Ops
Average of Biogenics
Average of Degreasing
Average of Coatings and Solvents
Average of Architectural Coatings
Average of Consumer Products
Average of Refinery Operations
Average of Oil and Gas Extraction
Average of Gasoline Marketing/Refueling
Average of Onroad Diesel
Average of Gasoline headspace
Average of Onroad Gasoline Exhaust

(b)

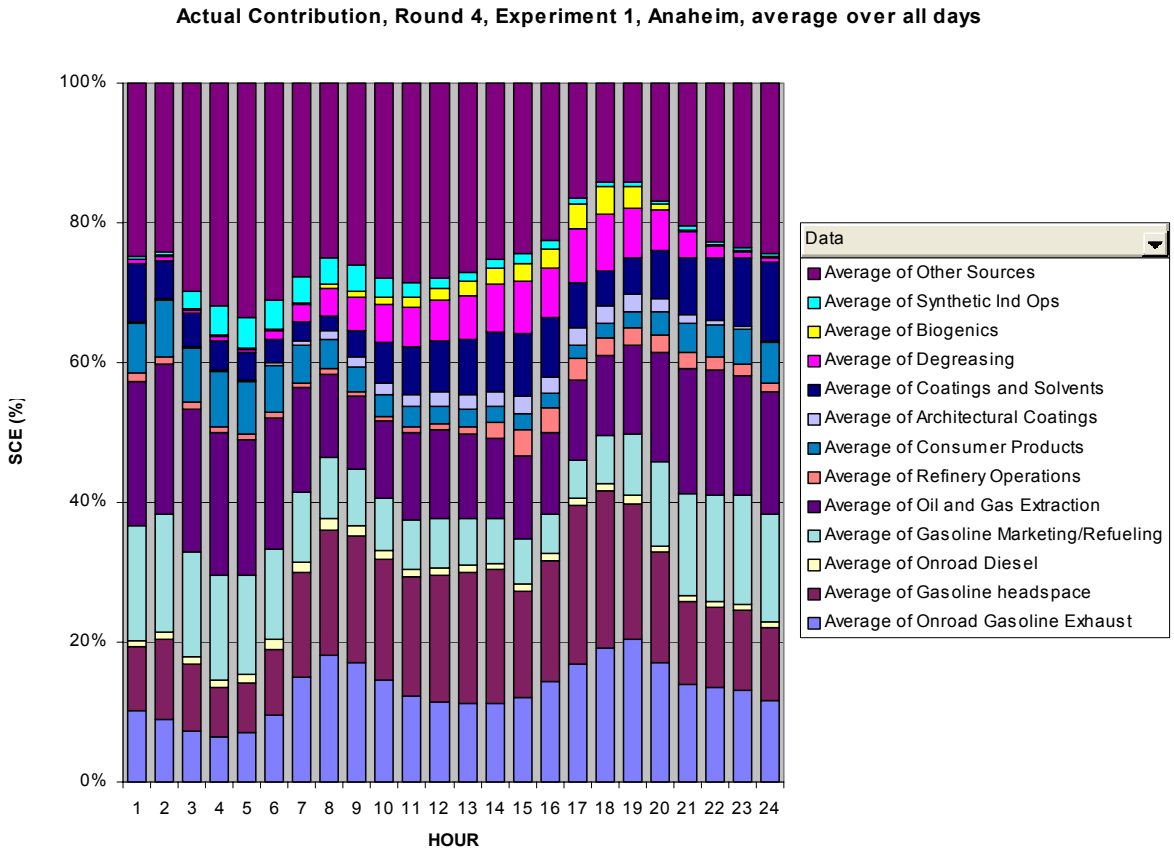


Figure 4-4. Comparison of detailed source contributions for experiment 1 in Round 4 at Anaheim by hour of day: (a) CMB and (b) actual.

Findings from Hourly Analyses

- Focusing on morning (6-9 am) samples did not clearly improve the accuracy of CMB. Correspondingly, focusing on afternoon samples (1-4 pm) did not clearly degrade the performance of CMB, especially for samples in areas of high emissions density. Problems for downwind samples are largely independent of the time of day.
- Reducing the number of samples at each receptor from 48 to 12 in order to restrict the time-period of analysis did degrade CMB performance.
- CMB performance is more reliable for daily average source contributions than for individual hours.

4.3 EXPERIMENTS 9-12: APPROACHING IDEAL CONDITIONS

Experiments 9-12 were designed after preliminary analysis of experiments 1-8 in Rounds 1 and 2. Experiments 9-12 were designed to investigate how chemical decay and sampling noise

influence CMB performance in situations where the receptor model should do well. The experiment design was shown above in Table 2-18.

To provide near-ideal conditions for CMB, the emission inventories for experiments 9-12 were prepared using source profiles that DRI had used for CMB analysis in Rounds 1 and 2 (Table 2-19). DRI was instructed keep the same profile set for the Round 3 analysis of experiments 9-12. Experiment 12 should be an ideal situation for CMB because the source profiles are known, the source profiles tend to avoid co-linearity, there is no chemical decay and no sampling noise. Lack of co-linearity in the Round 3 source profiles follows from the fact that DRI had previously been able to obtain CMB solutions with the chosen set of source profiles.

Experiment 12: Ideal Conditions

Figure 4-5 compares CMB contributions to actual contributions for experiment 12 in Round 3, averaged over all hours. Figure 4-5 shows excellent agreement for all source categories and receptors, except for diesel. The results shown in Figure 4-5 are discussed below. CMB performance for experiments 9-12 did not improve in Round 4 and so the Round 4 results are not discussed.

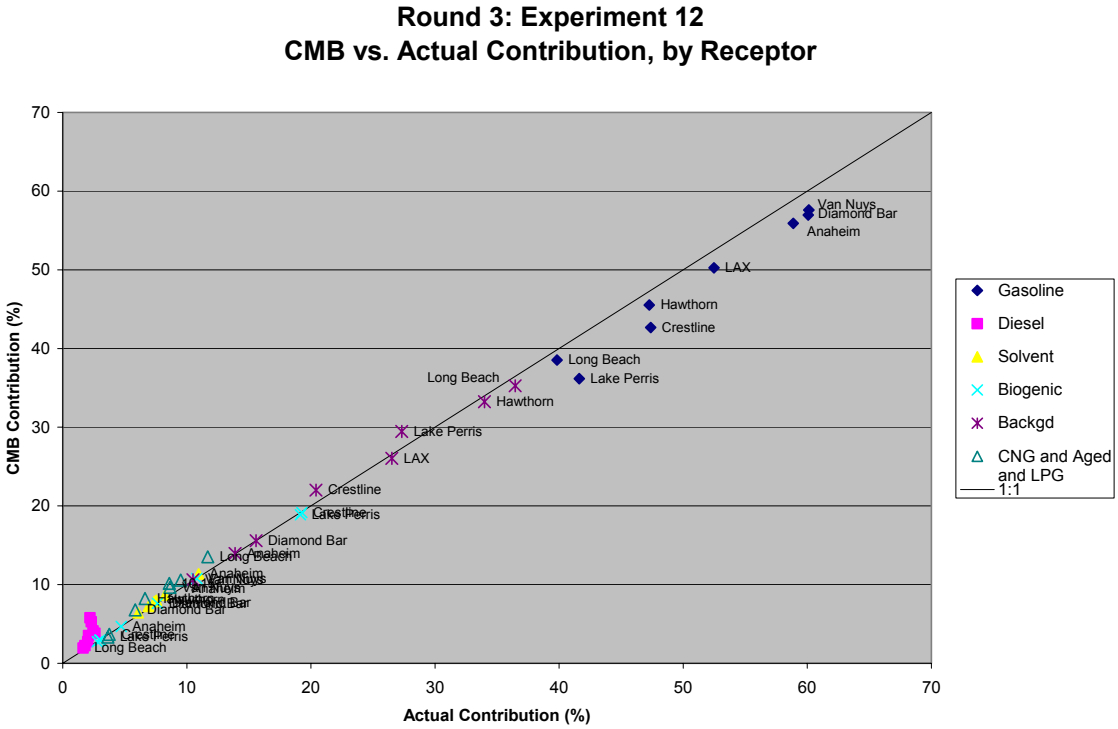


Figure 4-5. Comparison of CMB contributions to actual contributions for experiment 12 in Round 3 by receptor averaged over all hours.

The results shown in Figure 4-5 demonstrate that CMB can resolve several different source categories simultaneously in a 3-D environment under ideal conditions. However, the errors for diesel contributions in Figure 4-5 show that there are limitations to CMB performance, which

appear to originate from source profiles approaching co-linearity due to exclusion of nonane, decane and undecane from the fit for "aged" samples.

Several of the source categories accurately resolved by CMB in Figure 4-5 have rather trivial source profiles (CNG/aged, LPG and biogenics) and therefore are relatively immune to errors resulting from co-linearity. The skill demonstrated by CMB in Figure 4-5 is in simultaneously resolving the gasoline, background and diesel contributions despite overlap between profiles for many species. The CMB apportionment for diesel shows fair correlation with the actual contribution, but diesel is over-estimated by CMB. Figure 4-6 shows in detail the diesel and gasoline apportionments (with diesel multiplied by 10) and shows that the CMB diesel over-estimates are correlated with gasoline under-estimates, i.e., the deviations from 1:1 are largest for both gasoline and diesel at Crestline/Lake Perris and smallest at Hawthorn/Long Beach. This suggests that the CMB bias for diesel originates from a degree of co-linearity with the gasoline profile. This is generally true when nonane, decane and undecane are left out of the fit.

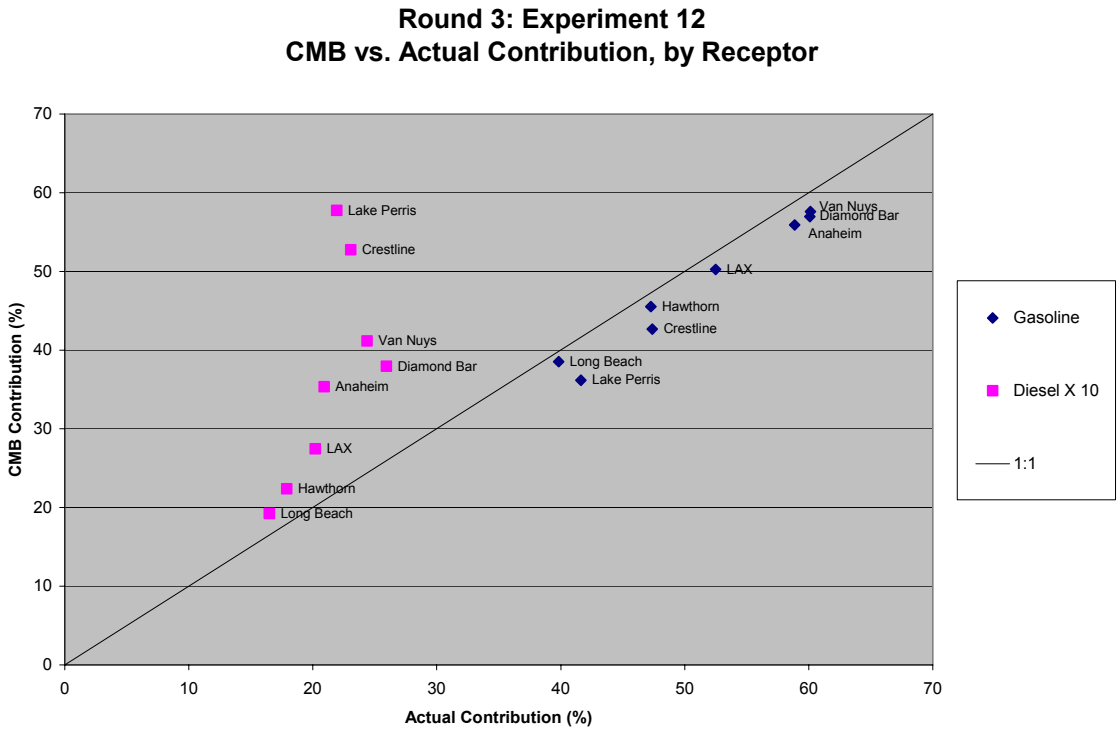


Figure 4-6. Comparison of gasoline and diesel (multiplied by 10) contributions in experiment 12 of Round 3.

Experiments 9-11: Chemical Processing and Measurement Noise

Experiments 9-11 were similar to experiment 12 but introduced the complicating effects of chemical processing (experiments 9 and 11) and measurement uncertainties (9 and 10). Figure 4-7 compares CMB contributions to actual contributions for experiments 9-12 in Round 3, averaged over all receptors and hours.

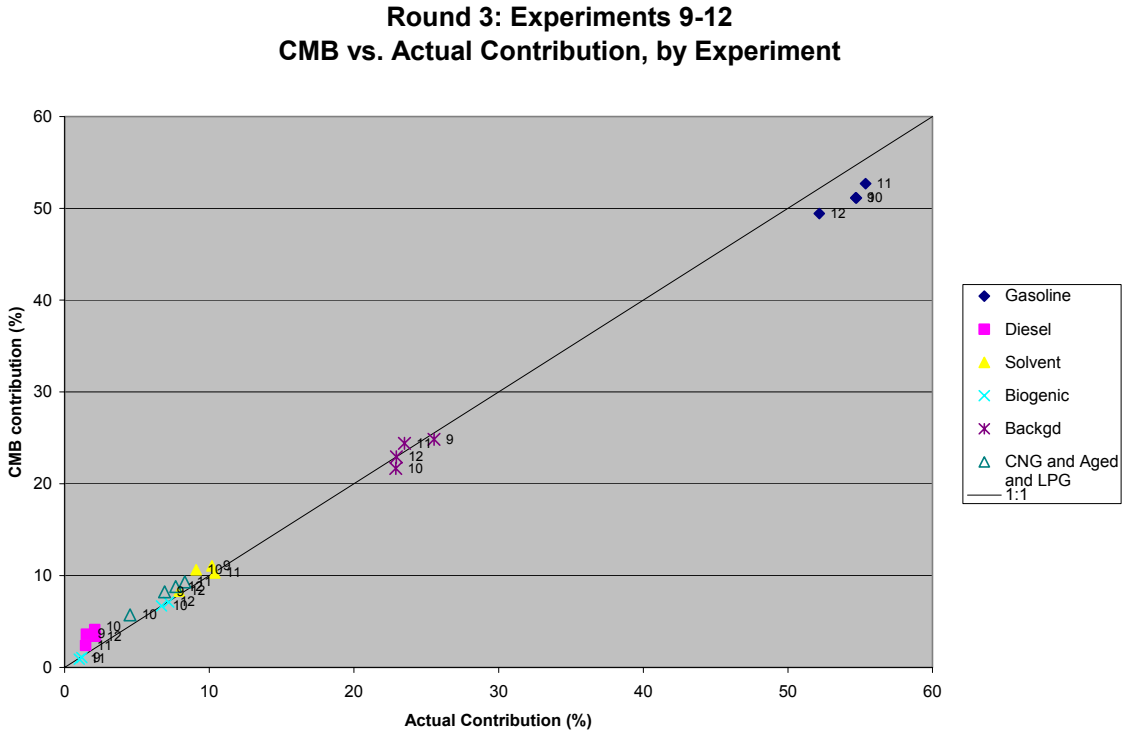


Figure 4-7. Comparison of CMB contributions to actual contributions for experiments 9-12 in Round 3 averaged over all hours and receptors.

The results in Figure 4-7 show that, on average, chemical processing and sampling noise had very little impact on CMB performance in these experiments. The lack of impact from sampling noise is consistent with the results of experiment 8, discussed above, where increasing the sampling noise also had little impact on the average source contributions determined by CMB. The small impact of chemical processing was a surprising result because a significant amount of chemical degradation was occurring as demonstrated below.

Figure 4-8 shows the effects of chemical reaction on simulated ambient concentrations for high, medium and low reactivity source categories at a mid-basin receptor, Diamond Bar. Differences in emissions strength introduced by the design of experiments 11 and 12 have been corrected for in Figure 4-8. Points lying on the 1:1 line in Figure 4-8 are unaffected by chemical aging whereas points lying below the line show effects of chemical decay. The highly reactive emissions category (biogenics) shows substantial chemical aging in both day and nighttime hours (shown by different symbols). In contrast, the low reactivity source category (CNG/aged) shows almost no chemical loss at night and only a small amount of degradation in daylight hours. The gasoline category (comprising exhaust, liquid fuel and gasoline vapors) shows some chemical loss at night (about 10%) and greater loss during the day (about 10% to 40%). These results show that a significant amount of chemical removal was occurring in the grid model experiments, and that the amount of removal varied widely by source category. For source categories that contained high and low reactivity species, the amount of chemical removal would vary with species effectively changing the source signature (profile) as aging occurred.

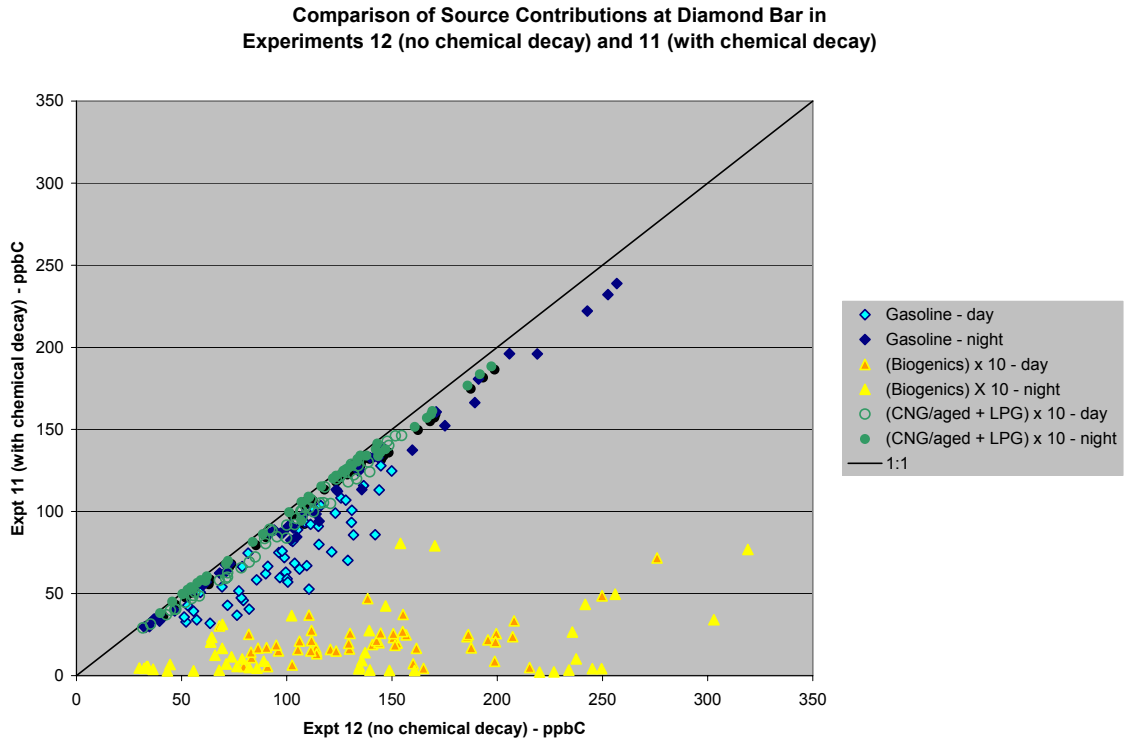


Figure 4-8. The effects of chemical reaction on concentrations of high, medium and low reactivity source categories at a mid-basin receptor (Diamond Bar).

Figure 4-9 shows the effects of chemical reaction on simulated ambient concentrations at a downwind site, Crestline. As for Diamond Bar, the most heavily depleted source category is biogenic emissions, which are almost completely removed at night. However, biogenic emissions are less depleted at Crestline than Diamond Bar during the day because there are stronger local sources of biogenic emissions at Crestline. The gasoline and CNG/aged categories are more depleted by reaction at Crestline than Diamond Bar indicating that at Crestline these emissions are being transported from far upwind which allows time for even a low reactivity category such as CNG/aged (ethane) to lose about 10% to chemical reaction. The differences in the amount of chemical processing of emissions between Diamond Bar and Crestline and day vs. night show that it will be difficult to adjust a receptor model to account for chemical reactions.

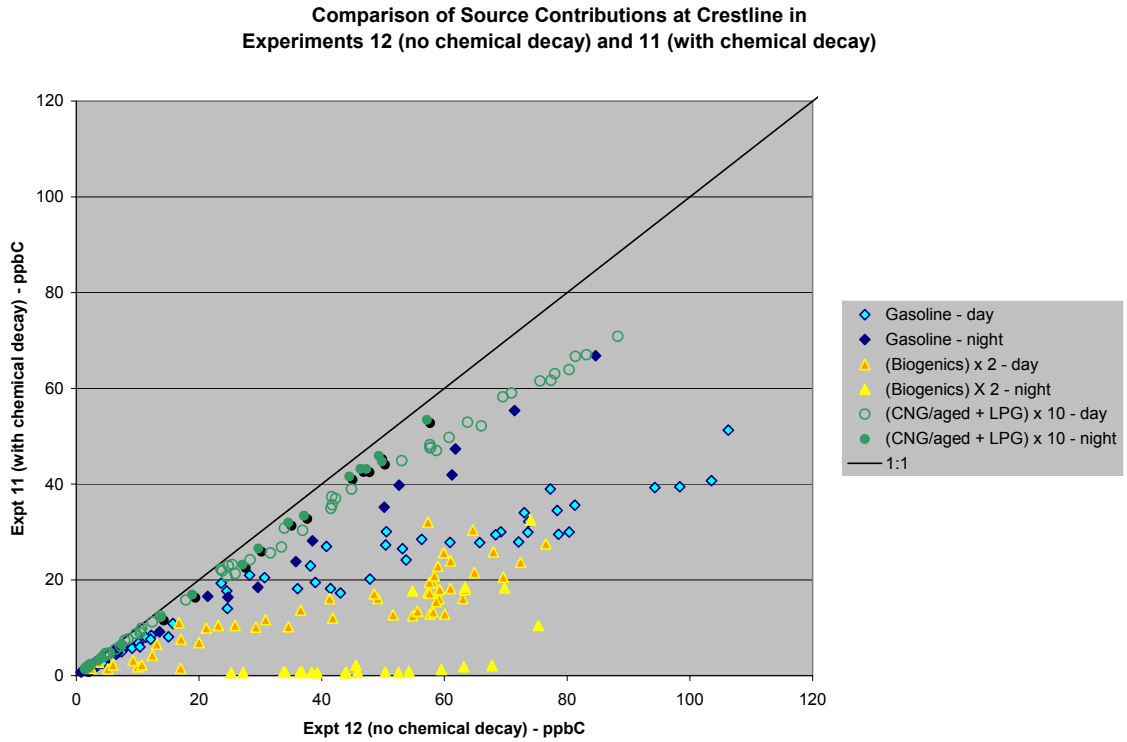


Figure 4-9. The effects of chemical reaction on concentrations of high, medium and low reactivity source categories at a downwind receptor (Crestline).

Findings from Experiments 9-12

- CMB performs very well for 3-D cases under ideal conditions where source profiles are well characterized, source profiles are not co-linear, there is no chemical decay, and no sampling noise.
- Limitations to CMB performance in ideal 3-D cases are more related to co-linear source profiles than either chemical decay or random measurement noise.
- CMB performance was very robust against effects of chemical decay in an ideal case with fairly simple source contributions.
- The experiments performed leave open a possibility that chemical decay could be a greater impediment to CMB in more complex cases with more sources that are more co-linear or for source categories with greater dependence on more reactive species to properly apportion the source..
- CMB performance was very robust against random sampling noise in an ideal case with fairly simple source contributions. Experiment 8 showed that CMB performance also was robust against random sampling noise with more complex sources and profiles.

4.4 ACTUAL VERSUS EMISSIONS CONTRIBUTIONS

Source apportionment methods are often used to gain insight into the real-world sources of emissions in order to evaluate emission inventories. Therefore, the relationships between actual contributions and emissions contributions (defined above as emissions from the 9 5-km grid cells centered on the receptor) are of interest. The actual contributions present in an air sample could differ from the local emissions contributions for two main reasons:

- The emissions inventory is spatially inhomogeneous. Air samples integrate source contributions over some upwind area (footprint) that depends upon wind direction/speed and atmospheric dispersion properties.

- Emissions from different source categories have different photochemical removal rates according to their VOC speciation (e.g., see Figures 4-8 and 4-9, above).

The actual emissions contributions for each receptor in experiments 1 on August 5, 1997 are shown in Figure 4-10 and Table 4-2. The emissions are summarized by the A-34 categories, which are listed in Table 4-2. Figure 4-10 shows qualitatively that the distributions of emissions by source category varied substantially among the receptor locations, with the exception of Hawthorn and LAX. The same information is provided quantitatively in Table 4-2.

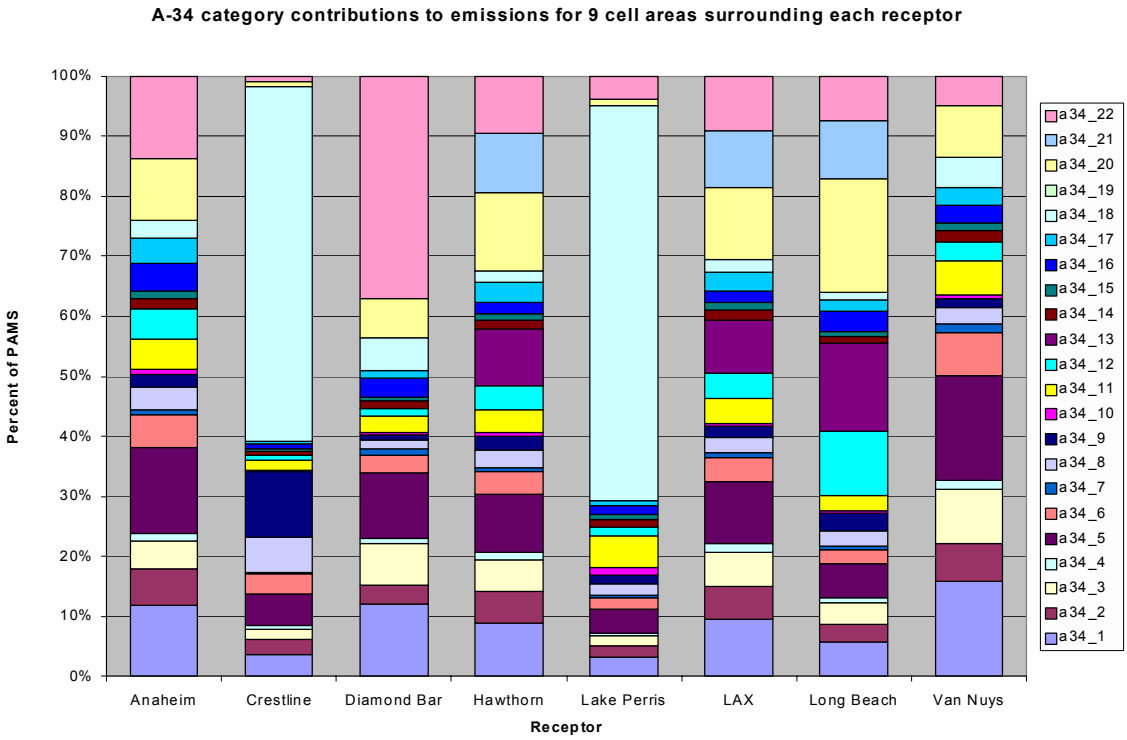


Figure 4-10. Source category contributions to the sum of PAMS emissions for 9 cell areas surrounding each receptor in experiment 1 on August 5, 1997.

Table 4-2. Source category contributions to the sum of PAMS emissions for 9 cell areas surrounding each receptor in experiment 1 on August 5, 1997.

A34 Number	Category Description	Anaheim	Crestline	Diamond Bar	Hawthorn	Lake Perris	LAX	Long Beach	Van Nuys
1	On-road Mobile Gasoline Catalyst Exhaust Stabilized	11.8%	3.7%	12.1%	8.8%	3.3%	9.6%	5.8%	15.8%
2	On-road Mobile Gasoline Catalyst Exhaust Start	6.1%	2.4%	3.1%	5.3%	1.9%	5.5%	3.0%	6.4%
3	On-road Mobile Gasoline Non-Catalyst Exhaust Stabilized	4.7%	1.7%	7.0%	5.3%	1.7%	5.7%	3.5%	9.0%
4	On-road Mobile Gasoline Non-Catalyst Exhaust Start	1.3%	0.7%	0.8%	1.4%	0.5%	1.4%	0.8%	1.6%
5	On-road Mobile Gasoline Evaporative	14.2%	5.3%	11.0%	9.5%	3.9%	10.4%	5.6%	17.4%
6	On-road Mobile Gasoline Evaporative	5.4%	3.2%	2.9%	3.8%	1.9%	3.9%	2.3%	7.3%
7	On-road Mobile Diesel	0.9%	0.3%	1.1%	0.8%	0.5%	0.8%	0.7%	1.3%
8	Off-road Gasoline Four-Stroke	3.8%	5.8%	1.4%	2.8%	1.9%	2.6%	2.6%	2.7%
9	Off-road Gasoline Two-Stroke	2.1%	10.9%	0.8%	2.4%	1.5%	1.8%	3.0%	1.5%
10	Off-road Diesel	0.9%	0.2%	0.4%	0.5%	1.2%	0.5%	0.3%	0.6%
11	Gasoline Marketing/Refueling	5.0%	1.7%	2.9%	4.0%	5.2%	4.2%	2.7%	5.7%
12	Oil and Gas Extraction	5.0%	0.8%	1.2%	4.0%	1.6%	4.2%	10.7%	3.1%
13	Refinery Operations	0.0%	0.0%	0.1%	9.4%	0.0%	8.9%	14.7%	0.0%
14	Consumer Products	1.9%	0.7%	1.1%	1.5%	1.2%	1.7%	1.1%	2.0%
15	Architectural Coatings	1.2%	0.5%	0.7%	1.1%	0.9%	1.2%	0.7%	1.4%
16	Other Surface Coatings and Industrial Solvents	4.6%	0.9%	3.1%	1.8%	1.5%	1.9%	3.4%	2.9%
17	Degreasing	4.2%	0.3%	1.3%	3.5%	0.8%	3.2%	1.9%	2.9%
18	Biogenics	3.0%	59.0%	5.5%	1.8%	65.9%	2.0%	1.2%	5.1%
19	Wastewater Treatment	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
20	Industrial Engines (gas fueled)	10.3%	1.0%	6.6%	13.0%	1.2%	12.0%	19.1%	8.6%
21	Synthetic Industrial	0.0%	0.0%	0.0%	9.9%	0.0%	9.4%	9.6%	0.0%
22	Other	13.7%	0.8%	37.0%	9.6%	3.7%	9.2%	7.4%	4.8%
Total PAMS Emissions (Tons/day)		**48.0**	**7.4**	**27.2**	**50.3**	**1.9**	**53.0**	**54.1**	**39.9**

Experiments 11 and 12 were analyzed to investigate the relative importance of these effects. Figure 4-11 compares the actual and emissions contributions in experiment 12 (without chemical reactions) at all receptors. Deviations from a 1:1 line in Figure 4-11 show cases where the actual contributions are not representative of the nearby emissions contributions. The downwind

receptors (Crestline and Lake Perris) stand out as having ambient contributions that are unrelated to the local emissions. This is because their local emissions are dominated by biogenic sources (> 65%) whereas the actual contribution of biogenics in the air is less than 10%. This is not due to chemical removal of biogenic VOCs because experiment 12 was designed to have no chemical degradation. The reason is that the air concentrations at the downwind receptors are dominated by transport of emissions (primarily the gasoline and background categories in experiment 12) from upwind locations. Other receptors show the same type of effects but smaller in magnitude.

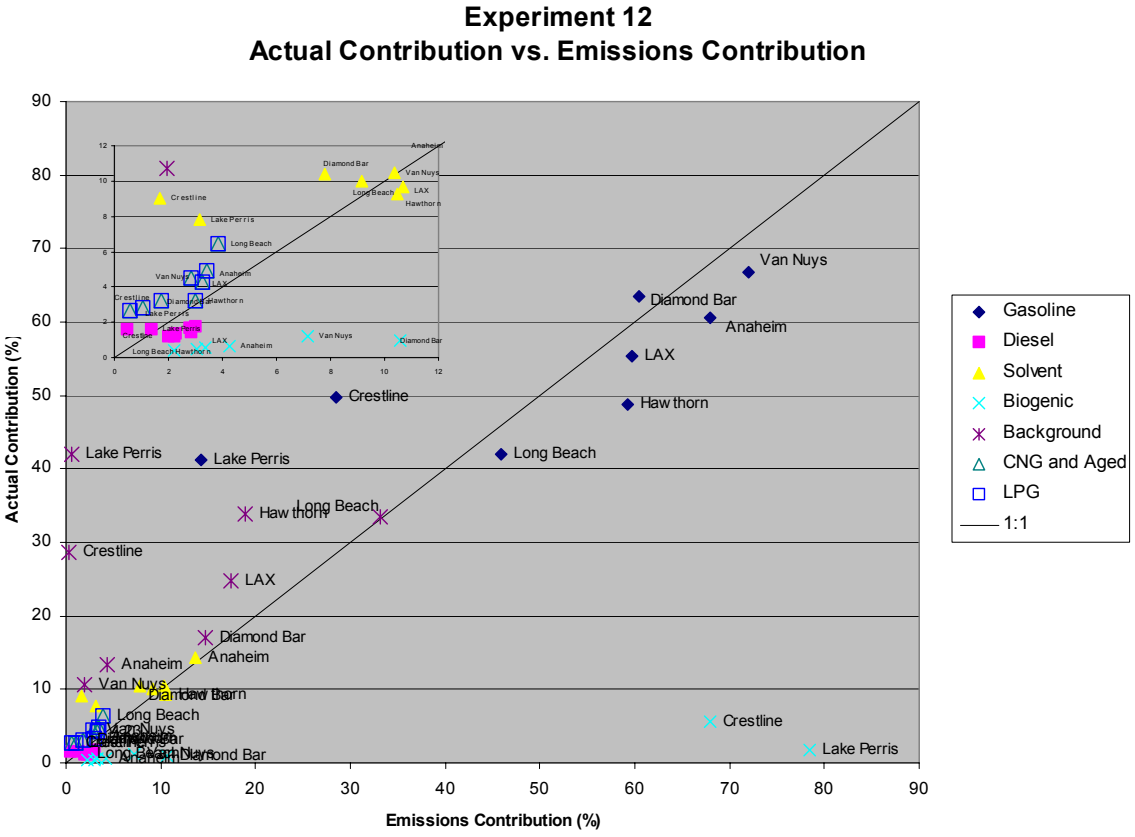


Figure 4-11. Actual and emissions contributions in experiment 12 (with no chemical reactions) by receptor, averaged over all hours.

The Hawthorn and LAX receptors provide an interesting comparison in Figure 4-11. These receptors are located in adjacent grid cells and have similar emissions contributions (Figure 4-10). The actual contributions at Hawthorn and LAX differ more than the emissions contributions, as seen from Figure 4-11 for the gasoline and background categories. This shows that averaging emissions over 9 grid cells (i.e., a 15-km square) centered on the receptor does not describe differences in air composition between LAX and Hawthorn. This discrepancy must be because the upwind footprint influencing the Hawthorn and LAX receptors is not a 15-km square around the receptor.

Figure 4-12 compares the actual and emissions contributions in experiment 11, which is similar to experiment 12 but includes chemical decay. The patterns of deviation from a 1:1 relationship are very similar in Figures 4-12 and Figure 4-11. This shows that the main reason for actual

contributions being different from the local emissions contribution is spatial heterogeneity in the emission inventory, not chemical reaction. Effects of spatial heterogeneity in emissions are likely under represented in these grid model experiments compared to the real-world, (1) because the grid model cannot represent neighborhood scale (sub 5-km) variations in emissions, and (2) because grid modelers have limited information to spatially allocate emissions and so use spatial surrogates to allocate emissions (e.g., population) which simplify the texture in the emissions inventory.

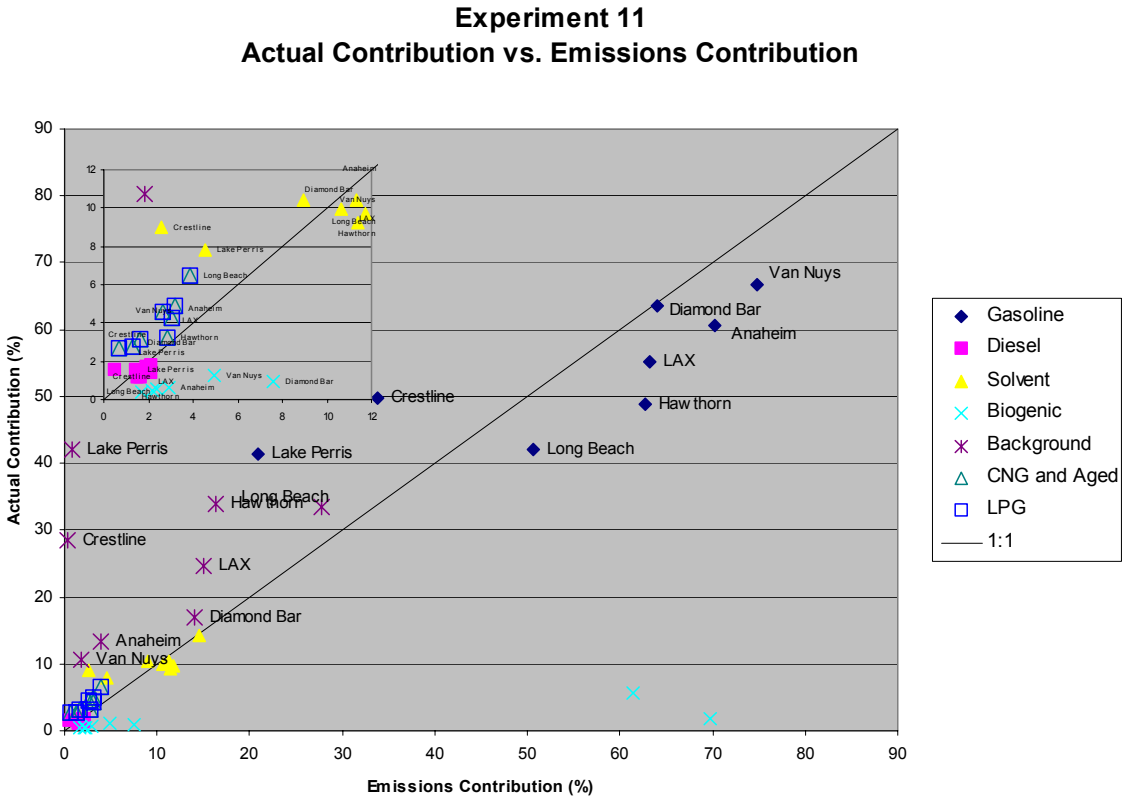


Figure 4-12. Actual and emissions contributions in experiment 11 (with chemical reactions) by receptor, averaged over all hours.

The effects of spatial heterogeneity in emissions were largest at downwind receptors, as discussed above. The corresponding bias in actual vs. emissions contributions is smaller and mostly negative for the gasoline contributions at the upwind and mid-basin receptors (Figure 4-11). Figures 4-1b showed that CMB tended to have a positive bias relative to the actual contributions for gasoline at the upwind and mid-basin receptors. Therefore, if CMB contributions in Figure 4-1b were compared to emissions contributions (rather than actual contributions) the agreement would tend to improve because two opposing biases would tend to cancel. However, this would be a coincidence and would not indicate an ability of CMB to uncover the emissions contributions underlying the actual concentrations because the opposing biases are unrelated: The bias in Figure 4-11 is spatial heterogeneity in emissions whereas the analysis (and therefore the bias) shown in Figure 4-1b is non-spatial (i.e., for a point).

Findings on Emissions vs. Actual Contributions

- The source category composition of air samples at a receptor location may be dissimilar from the contribution of local emissions because of spatial heterogeneity in the emissions inventory.
- Source apportionment results for biogenic emissions significantly under-estimate the real contribution of biogenic emissions due to chemical degradation.
- Source apportionment results labeled CNG or LPG will over-estimate the real contributions of these categories due to chemical degradation and because the category labels are misleading.
- Apart from biases for biogenics, CNG and LPG, source apportionment results for other source categories are not greatly influenced by chemical degradation except at far downwind receptors.
- The impacts of spatial heterogeneity in emissions inventories were most pronounced for downwind receptors and receptors located near major point sources.
- The impacts of spatial heterogeneity in emissions inventories were least, but not absent, for urban/suburban receptors with a mix of residential/commercial/industrial emissions.
- Spatial heterogeneity in emissions inventories had a greater impact than atmospheric chemical degradation on the differences between the source category contributions found in ambient air and local emissions.

4.5 DEFINING "TOTAL ORGANIC COMPOUNDS"

There are several ways of defining "total organic compounds" and differences between definitions must be considered when comparing receptor modeling to emissions inventories. Three definitions are used in this study, namely ROG, TOG and PAMS:

> ROG – "reactive organic gasses" is a measure used by the California Air Resources Board (ARB) for ozone precursors. ROG is comparable to the EPA's VOC (volatile organic compounds). ROG includes volatile hydrocarbons and other (e.g., oxygenated) organic compounds with the exception of specific compounds that have been determined to be of low photochemical reactivity (e.g., methane, ethane, acetone) and therefore not significant as ozone precursors.
>
> TOG – total organic gasses is similar to ROG but includes the low reactivity compounds that are excluded from ROG.
>
> PAMS – the sum of the 55 species measured by PAMS monitors.

Other definitions used with ambient measurements such as TNMHC, THC and TNMOC are operationally defined and are not considered here.

Results from the emission inventory preparation (Section 2) shows the relationships between TOG, ROG and PAMS (see Table 2-11). The ROG/TOG ratios for the 22 source categories used in the receptor modeling experiments ranged from 0.09 to 1.0. ROG is always smaller than TOG, by definition, and the ROG/TOG approaches zero for emissions categories that are dominated by low reactivity species such as methane. The PAMS/ROG ratios ranged from 0.23

to 2.4 over the A-34 source categories. ROG tends to be greater than PAMS for many emissions categories because PAMS is includes only 55 species and therefore omits many species (e.g., oxygenated and heavier compounds) that are part of ROG. However, PAMS can be greater than ROG because ethane is included in PAMS but excluded from ROG (and VOC) on the basis of low reactivity.

The ROG/TOG and PAMS/ROG ratios in Table 2-11 show that source category contributions may vary significantly (by more than a factor of 2) depending upon how total organic compounds are measured. It follows that comparing different measures of total organic compounds between receptor modeling and emissions inventories will introduce biases (either positive or negative) in comparisons of source category contributions. If source category contributions are compared on a relative basis (e.g., percent of total) then a bias for one category affects all others. Corrections may be applied by assuming certain PAMS/ROG ratios for each category, but such assumptions are external to the receptor modeling process and the experiments performed here are unable to characterize the resulting biases. These findings are summarized as follows:

Findings on Measures of Total Organic Compounds

- Comparing different measures of total organic compounds (e.g., PAMS, ROG) between receptor modeling and emissions inventories will introduce biases (either positive or negative) in comparisons of source category contributions.
- Receptor modeling studies should state the measure of organic compounds that is apportioned by the receptor model and define any conversion factors used to adjust this to a different basis (e.g., PAMS/ROG ratios for each source category).
- If adjustment factors are used (e.g., PAMS/ROG ratios) they must be consistent with the source profiles used for the receptor modeling and ideally should be developed specifically for the study along with source profiles; i.e., the adjustment factors and source profiles should be developed from the same set of detailed VOC measurements.

5. CONCLUSIONS

The experiments conducted for CRC Project A-34 are the first to test quantitatively the ability of a receptor model to source apportion VOCs under simulated "real-world" conditions. Important features of the experiments were:

- The presence of 4-D spatial/temporal source-receptor relationships simulated using the photochemical grid model with mass-consistent and mass-conservative meteorological fields.
- Known source contributions of 22 source categories to 55 VOC species monitored by the EPA's Photochemical Assessment Monitoring Stations (PAMS).
- Photochemical decay of VOCs by reactions with OH radicals, ozone and NO_3 radicals.

Experiments investigated how receptor model performance depended upon modeling assumptions and simulated "ambient" conditions.

The receptor model evaluated was the Chemical Mass Balance (CMB) model version 8. The CMB model has been applied to VOC source apportionment in numerous studies (Watson, Chow and Fujita, 2001). The CMB developers have presented six assumptions (Watson, Chow and Fujita, 2001) that underlie the application of the model for VOCs:

1. The composition of source emissions is constant over the period of ambient and source sampling.
2. Chemical species do not react with each other, i.e., they add linearly.
3. All significant sources have been identified and had their emissions characterized.
4. The number of source categories is less than the number of species, i.e., there are degrees of freedom available in the analysis.
5. The source profiles are sufficiently different one from another.
6. Measurement errors are random, uncorrelated and normally distributed.

Similar assumptions apply to other receptor models except that factor analysis methods do not rely upon the third assumption, but make other assumptions (Watson and Chow, 2004).

The findings from the experiments conducted for this study are summarized below and then compared to the six assumptions listed above. We consider whether the experimental results confirm the CMB assumptions, whether there are other CMB assumptions that need to be considered, how well these assumptions were met for the conditions of our experiments, and whether there are other factors external to the CMB analysis that should be considered when interpreting the results.

5.1 REVIEW OF FINDINGS

The findings developed throughout Section 4 are presented here so that they may be considered together.

Experiment 1: Base Case

1. CMB category names may describe chemical characteristics of source profiles (fingerprints) rather than specific activities tracked in emission inventories.
2. CMB tended to over-estimate the contribution of gasoline emissions except when complete profile information was available (Round 4), particularly at locations impacted by the hypothetical industrial source.
3. Obtaining profile data from a Tunnel study and fuel samples (Round 2) did not improve the CMB performance for gasoline over the blind analysis (Round 1) because the profiles were substantially similar. The tunnel-derived diesel profile was highly uncertain and was not used.
4. Obtaining profile data from a Tunnel study and fuel samples (Round 2) did change CMB performance for non-gasoline categories, improving performance for solvents.
5. CMB performance for diesel systematically degraded from Round 1 to Round 4 as CMB was provided with progressively more accurate source profile information. The tendency was for CMB to over-estimate the diesel contribution. Poor performance for diesel is largely related to exclusion of nonane, decane and undecane from the set of fitting species for "aged" samples, which resulted in co-linearity between gasoline and diesel.

Experiments 2-8: Sensitivity Studies

6. Overall, CMB performance was relatively insensitive to higher atmospheric reactivity (experiment 2), weekend source mix (experiment 5), randomly varying source profiles (experiment 7) and higher random noise in the ambient data (experiment 8).
7. The results from experiments 7 and 8 showing that random changes did not impact CMB performance on average are expected because random changes tend to cancel when averaged by the atmosphere (experiment 7) or multiple samples (experiment 8).
8. CMB was robust against higher reactivity (experiment 2) because of receptor modeling protocols designed to avoid relying upon highly reactive species when ambient samples appear to be aged. However, the experiment 1 results for downwind receptors, discussed above, show that CMB performance can be degraded when air samples are highly aged at all times due partly to restrictions on the species that could be included in the fit.
9. Introducing a weekend for 2 out of 4 days (experiment 5) did not degrade CMB performance because CMB was able to quantify emissions contributions on weekend days about as well as on weekdays.
10. When industrial emission levels were set to high levels (experiment 6) CMB tended to over-estimate the gasoline and solvent contributions by a factor of two, or more, because an appropriate industrial profile was not included in the CMB calculation during Rounds 1 and 2. Providing typically available source profile data in Round 2 did little to reduce these biases. Providing complete source profile data in Round 4 eliminated the bias for solvents and reduced the bias for gasoline to about 50%.
11. Eliminating 20% of the species available to CMB (experiment 4) degraded performance, especially when source profiles were poorly known. Eliminating species had a substantial impact in Round 1 (blind analysis) and little impact in Round 4 (full profile information).
12. Changing the speciation profiles (experiment 3) improved or degraded CMB performance depending upon whether the alternate profiles were a better or poorer fit with the profiles used in CMB.

Hourly vs. Average Results

13. Focusing on morning (6-9 am) samples did not clearly improve the accuracy of CMB. Correspondingly, focusing on afternoon samples (1-4 pm) did not clearly degrade the performance of CMB, especially for samples in areas of high emissions density. Problems for downwind samples are largely independent of the time of day.
14. Reducing the number of samples at each receptor from 48 to 12 in order to restrict the time-period of analysis to 3 hours (e.g., 6-9 am) did degrade CMB performance.
15. Looking at hourly CMB results degraded performance even more than looking at 3-hourly results because the sample size was further reduced from 12 to 4.
16. The hourly CMB analysis could discern major features of temporal variations in emissions (e.g., rush hour) but not minor features.

Experiments 9-12: Approaching Ideal Conditions

17. CMB performs very well for 3-D cases under ideal conditions where source profiles are well characterized, source profiles are not co-linear, there is no chemical decay, and no sampling noise.
18. Limitations to CMB performance in ideal 3-D cases are more related to co-linear source profiles than either chemical decay or random measurement noise.
19. CMB performance was very robust against effects of chemical decay in an ideal case with fairly simple source contributions.
20. The experiments performed leave open a possibility that chemical decay could be a greater impediment to CMB in more complex cases with more sources that are more co-linear.
21. CMB performance was very robust against random sampling noise in an ideal case with fairly simple source contributions. Experiment 8 showed that CMB performance also was robust against random sampling noise with more complex sources and profiles.

Emissions Contribution vs. Ambient Contribution

22. The source category composition of air samples at a receptor location may be dissimilar from the contribution of local emissions because of spatial heterogeneity in the emissions inventory.
23. Source apportionment results for biogenic emissions significantly under-estimate the real contribution of biogenic emissions due to chemical degradation.
24. Source apportionment results labeled CNG or LPG will over-estimate the real contributions of these categories due to chemical degradation and because the category labels are misleading.
25. Apart from biases for biogenics, CNG and LPG, source apportionment results for other source categories are not greatly influenced by chemical degradation except at far downwind receptors.
26. The impacts of spatial heterogeneity in emissions inventories were most pronounced for downwind receptors and receptors located near major point sources.
27. The impacts of spatial heterogeneity in emissions inventories were least, but not absent, for urban/suburban receptors with a mix of residential/commercial/industrial emissions.

28. Spatial heterogeneity in emissions inventories had a greater impact than atmospheric chemical degradation on the differences between the source category contributions found in ambient air and local emissions.

Measures of Total Organic Compounds

29. Comparing different measures of total organic compounds (e.g., PAMS, ROG) between receptor modeling and emissions inventories will introduce biases (either positive or negative) in comparisons of source category contributions.
30. Receptor modeling studies should state the measure of organic compounds that is apportioned by the receptor model and define any conversion factors used to adjust this to a different basis (e.g., PAMS/ROG ratios for each source category).
31. If adjustment factors are used (e.g., PAMS/ROG ratios) they must be consistent with the source profiles used for the receptor modeling and ideally should be developed specifically for the study along with source profiles; i.e., the adjustment factors and source profiles should be developed from the same set of detailed VOC measurements.

5.2 EVALUATION OF STATED ASSUMPTIONS FOR CMB

The stated assumptions for CMB applied for VOCs (Watson, Chow and Fujita, 2001) are evaluated based on the findings of this project.

1. *The composition of source emissions is constant over the period of ambient and source sampling.*

The need for this assumption is obvious. In general, this assumption is likely to be satisfied when VOC samples are collected so as to average many individual sources of the same type: E.g., the source profiles for individual cars may vary, but averages over sub-populations of cars in an urban area are similar. Because the modeling experiments in this study had 5-km grid cells they tended to provide "regionally representative" ambient samples where many sources had been averaged. Real-world VOC samples may be influenced by single sources, such as a nearby stationary source, where averaging over multiple sources does not tend to eliminate temporal variability in source profiles.

Experiment 7 varied the source profiles for all source categories randomly in time (hour to hour) and space (grid cell to grid cell). CMB was robust against this random variation in source profiles (findings 6 and 7) because the modeled atmosphere (diffusion and advection) and averaging results over samples tended to average out the random perturbations.

2. *Chemical species do not react with each other, i.e., they add linearly.*

This assumption was met by the chemical reaction scheme for the 55 PAMS species employed in this study. There are no known reactions among the 55 PAMS species (or other VOCs) that violate this assumption for the dilute concentration levels found in ambient VOC samples.

3. All significant sources have been identified and had their emissions characterized.

Results from this study confirm the importance of this assumption to CMB source apportionments. Receptor models in general, and CMB in particular, seek an optimum source apportionment of the ambient VOCs among the source profiles allowed in the model. This creates a tendency to apportion all sources present to just the sources allowed in the analysis if the omitted source(s) contain species in common with the included sources. The resulting bias over-estimates the contributions of expected or identifiable sources. However, the study results showed that source profile errors also can lead to under-estimated as well as over-estimated source contributions.

The hypothetical industrial sources added to the emission inventory in this study demonstrate that assumption 3 may be difficult to fulfill (finding 10). In Round 1, CMB tended to apportion the hypothetical industrial emissions to other sources, such as gasoline and solvents, resulting in an over-estimation of gasoline and solvents. This bias was most noticeable at the most heavily impacted receptors (Long Beach, LAX and Hawthorn) and when industrial emissions were increased to high levels. This bias was corrected in Round 4 when the hypothetical sources were known to exist and their profiles fully characterized. Round 2 corresponded most closely to a real-world CMB application and the results were more similar to Round 1 than Round 4, i.e., the industrial emissions were wrongly attributed to gasoline and solvents. The interpretation of the Round 2 result is open to interpretation. In round 2 the receptor modelers did not know that the hypothetical sources had been added to the emission inventory, and so it can be argued that important sources of emissions were unidentified in the CMB because the presence of the source was unexpected, violating assumption 3. An alternate view is that since the receptor modelers knew that real industrial sources were located near the Long Beach, Hawthorn and LAX receptors, the addition of hypothetical industrial emissions raised the importance of a known source category rather than added a new category, which does not violate assumption 3. The hypothetical industrial emissions had comparable magnitude to ”real” industrial emissions in the 9 grid cells around the three impacted receptors (Table 4-2). These possible interpretations lead to two conclusions: (1) That violating assumption 3 can result in biased CMB apportionments, and: (2) That assumption 3 may be violated either by failing to realize that a source exists or misunderstanding the importance of a source (e.g., because an emissions inventory suggests it is less important than in reality).

Characterizing emissions sources (i.e., determine source profiles) has a strong influence on the outcome of CMB receptor modeling. Changes in CMB apportionments through Rounds 1, 2 and 4 showed how increasing profile knowledge influenced CMB results. With minimal knowledge in Round 1, the receptor modelers were able to select profiles that fit the ambient data in most cases resulting in source apportionments that showed some skill but also contained biases (finding 2). The biases tended toward over-estimating some sources (i.e., gasoline) and under-estimating others (i.e., solvents). Some source category identifications (i.e., CNG, LPG) must be interpreted with care because the names assigned by the receptor modelers described the chemical nature of the emissions (i.e., ethane and propane, respectively) but not the source of the emissions (finding 1).

With typically available source profile information in Round 2 the performance of CMB was improved for solvents but degraded for diesel relative to Round 1 (findings 4 and 5). The gasoline apportionment changed little between Rounds 1 and 2 (finding 3) because the

composition derived from the virtual tunnel study for gasoline exhaust was similar to that used in Round 1. The major changes to apportionments occurred for solvents and diesel due to profile co-linearity and choice of fitting species. When nonane, decane and undecane were excluded as fitting species in Round 2 the gasoline and diesel profiles became somewhat co-linear and the apportionment for diesel was degraded.

Round 4 provided the receptor modelers with complete knowledge of the sources present and their source profiles, which is not a realistic scenario for the real world. The CMB results for Round 4 show that receptor model apportionments become increasingly accurate as assumption 3 is better satisfied (finding 2). This conclusion was confirmed by Round 3 (findings 17-19 and 21) where the experiment design provided CMB with accurate source profiles. With complete source profile information CMB performance was limited by other assumptions such as the absence of profile co-linearity (findings 5 and 18).

4. *The number of source categories is less than the number of species, i.e., there are degrees of freedom available in the analysis.*

This assumption is a mathematical requirement of the CMB methodology. In practice, the number of resolvable source categories is limited by profile co-linearity rather than available degrees of freedom. In this study CMB resolved about 7 source categories in Round 2 with typically available profile information and about 13 source categories in Round 4 with complete source profile information.

5. *The source profiles are sufficiently different one from another.*

Receptor models rely upon sources having uniquely identifiable fingerprints. Two consequences of profile co-linearity were observed in this study. First, CMB could not separate different categories of gasoline exhaust emissions that had different speciation profiles: catalyst and non-catalyst vehicles, start and stabilized emissions, on-road and off-road vehicles. This result is expected because these categories all have very similar source profiles.

A second co-linearity problem was observed for diesel exhaust. CMB was able to apportion diesel exhaust with some skill (correctly ranking high and low contributions) in all of the experiments from Rounds 1 to 4. Exclusion of the heavy hydrocarbons nonane, decane and undecane from the fit resulted in co-linearity with gasoline and a bias toward over-estimating diesel. This bias is particularly noticeable at the downwind sites.

The conclusion from these findings is that severe profile co-linearity will likely be detected and be accounted for by combining source categories, but less severe co-linearity may go undetected and lead to biased source contribution estimates.

6. *Measurement errors are random, uncorrelated and normally distributed.*

Several experiments investigated the impact of random sampling errors and confirmed that CMB is robust against realistic levels of random measurement noise (findings 21, 7 and 6). This did not mean that random sampling errors had no impact on CMB apportionments for individual samples. CMB performed better for larger groups of samples because of improved signal/noise ratio (findings 14 and 15).

This study did not investigate the effects of non-random errors, such as measurement bias for specific species, on CMB performance. Because CMB relies upon ratios of species concentrations it is evident that non-random errors could bias CMB results. For example, Fujita et. al. (1994) have shown that CMB apportionments are sensitive to ethylene/acetylene ratios, so biasing the ethylene or acetylene measurements is likely to bias CMB source apportionments.

5.3 EMISSIONS vs. AMBIENT CONTRIBUTIONS IN 4-D ENVIRONMENTS

The CMB assumptions discussed above apply to source apportionment of air samples, which is a zero-dimensional (non-spatial) analysis. Other assumptions come into play when receptor models are used to analyze 4-D spatial/temporal source-receptor relationships. A 1-D trajectory model (Lagrangian) scenario introduces the potential complication of source contributions varying in time and a 4-D grid model (Eulerian) scenario is even more complex because source contributions may vary in both time and space. For example, a receptor model based on analysis of spatial/temporal variability (Henry, 1997) confounded near and distant sources with the same chemical signature (White, 1999). CMB differs from the case discussed by White (1999) because CMB uses chemical profiles to discriminate between sources. Issues that might affect the accuracy or interpretation of CMB receptor model results in real world (4-D) applications are source overlap, chemical degradation, heterogeneity in the spatial distribution of emissions sources, and accounting for different measures of total organic compounds.

4-D Source Overlap

The grid model experiments performed in this study investigated how CMB is influenced by source overlap in a multi-dimensional environment where sources with similar/different profiles located in similar/different locations mix in a 4-D spatial/temporal environment and are subjected to similar/different degrees of chemical reaction. In the absence of chemical reactions, CMB performed very well in retrieving the source contributions for receptor locations ranging from upwind source areas to far downwind (finding 17). This result shows that complex spatial and temporal source overlap in the 4-D environment of the grid modeling was not fundamentally more challenging than source overlap in the zero-dimensional sense considered above.

Chemical Degradation

The experiments also investigated whether complex spatial/temporal source-receptor relationships were more challenging to CMB when combined with chemical degradation. Increasing oxidant levels (i.e., the amount of chemical reaction) did not degrade the ability of CMB to apportion complex source profiles (finding 8). Eliminating chemistry altogether in experiments with simpler (i.e., fewer different) source profiles also had little impact on the performance of CMB (finding 19). CMB performance was degraded for downwind receptors in experiments with complex source profiles. There appear to be two reasons why CMB was quite robust against the effects of chemical reaction: (1) The CMB protocols employed by the receptor modelers for this study always eliminated highly reactive species from consideration and also eliminated moderately reactive species in air samples that were identified as chemically aged using heuristic algorithms. (2) Source profiles were included for abundant low reactivity PAMS

species (CNG and LPG for ethane and propane) that provided a way to account for the mass of these species. As discussed above, the names (CNG/aged and LPG) attached to these profiles needed careful interpretation because they describe chemical appearances rather than emission inventory source categories.

Analyses of the grid model experiments revealed the extent to which source contributions were degraded by chemical reaction. The extent of chemical degradation varied with source profile and receptor location: high reactivity categories (e.g., biogenics) were depleted by up to 90% whereas low reactivity categories (e.g., CNG, LPG) were depleted ~10% by chemical reaction. As expected, the extent of chemical degradation was greater at downwind receptors.

The experimental findings reviewed above show that CMB generally was able to correctly apportion the sum of PAMS species present in the air samples even when source profiles had been altered by chemically aging. Chemical reaction also changes the relative amounts of low and high reactivity source categories. For example, high reactivity biogenic emissions were degraded much more than low reactivity CNG or LPG emissions. The impact of chemical aging on source contributions must be considered when comparing source apportionment results to emission inventories. The experimental findings were that: Source apportionment results for highly reactive emissions categories (e.g., biogenic emissions) significantly under-estimate the actual contribution due to chemical degradation (finding 23). Source apportionment results for low reactivity categories (e.g. those labeled CNG or LPG) may over-estimate the real contributions of these categories due to chemical degradation (finding 24). Apart from biases for high and low reactivity categories, source apportionment results for other categories are not greatly influenced by chemical degradation except at far downwind receptors (finding 25).

Spatial Heterogeneity in Emissions Sources

CMB source contributions are often compared to emission inventories with the goal of evaluating and improving the emissions inventory. Air samples at a receptor location may be dissimilar from the local emissions because of spatial heterogeneity in the distribution of emissions sources. Comparisons of the known source contributions in air samples to local emissions showed that the impacts of spatial heterogeneity were most pronounced for downwind receptors and receptors located near major point sources (findings 23 and 24). The impacts of spatial heterogeneity in emissions inventories were least, but not absent, for urban/suburban receptors with a mix of residential/commercial/industrial emissions.

Effects of spatial heterogeneity in emissions are likely under represented in the grid model experiments of this study compared to the real-world because (1) the grid model cannot represent micro-scale (sub 5-km) variations in emissions, and (2) grid modelers have limited information to spatially allocate emissions and so use spatial surrogates to allocate emissions (e.g., population) which simplify the texture in the emissions inventory. Micro-scale impacts present a challenge to selecting regionally representative monitoring locations in a real-world study where the goal is to characterize a regional emissions inventory.

Measure of "Total" Organic Compounds

There are several ways of defining the "total" of organic compounds for an emissions inventory or a receptor model analysis. Measures that are most appropriate for an emissions inventory (e.g. ROG, TOG) tend to be all inclusive whereas a receptor model such as CMB is applied for a specific set of VOC species such as the PAMS list. Bridging the gap between emission inventories and receptor model results requires assumptions about relationships between different measures of total organic compounds, such as PAMS/ROG ratios. The emission inventory modeling for this revealed relationships between TOG, ROG and PAMS for 22 source category groupings. The ROG/TOG ratios ranged from 0.09 to 1.0. The PAMS/ROG ratios ranged from 0.23 to 2.4 (the sum of PAMS can be greater than ROG because ethane is included in PAMS but excluded from ROG).

Relationships between different measures of total organic compounds are more difficult to characterize for some source categories than others. Difficulties for biogenic emissions are that the PAMS species list contains only a few biogenic compounds (e.g., isoprene, ethene) and that many non-PAMS biogenic compounds require specialized measurement methods because they are oxygenated and/or heavy (e.g., 15 carbon sesquiterpenes; Guenther et al., 1999). Solvents have similar difficulties to biogenics, especially for oxygenated organics used in water-based formulations. Diesel emissions include many heavier compounds (more than 12 carbons) that require specialized measurement methods and may be difficult to classify as included or excluded from measures of volatile organics (e.g., ROG, VOC). These considerations introduce uncertainties and may result in positive or negative biases in source category contributions.

Source category contributions may vary significantly (by more than a factor of 2) depending upon how total organic compounds are measured (finding 29). It follows that comparing different measures of total organic compounds between receptor modeling and emissions inventories will introduce biases (either positive or negative) in comparisons of source category contributions. Corrections may be applied by assuming certain ratios (e.g., PAMS/ROG) for each category, but such assumptions are external to the receptor modeling process and must be accounted for separately. Recommendations for receptor modeling studies are: Clearly state the measure of organic compounds that is apportioned by the receptor model and define any conversion factors used to adjust this to a different basis (finding 30). Conversion factors (e.g., PAMS/ROG ratios) must be consistent with the receptor modeling source profiles (i.e., developed from the same set of detailed VOC data) and ideally should be developed specifically for each study (finding 31).

REFERENCES

Allen, P. 2002. Personal communication from Paul Allen, California Air Resources Board, Sacramento, CA.

Apel, E.C., J.G. Calvert, T.M. Gilpin, F.C. Fehsenfeld, D.D. Parrish and W.A. Lonneman. 1999. "The Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE): Task 3." *J. of Geophysical Research*, 104 (D21), 26069-26086.

Atkinson, R. 1989. " Kinetics qnd Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds*". J. of Physical and Chemical Reference Data* (Monograph No. 1).

Carter, W.P.L. 2000. "Programs and Files Implementing the SAPRC-99 Mechanism and its Associated Emissions Processing Procedures for Models-3 and Other Regional Models." Center for Environmental Research and Technology, University of California, Riverside, CA. http://pah.cert.ucr.edu/~carter/SAPRC99/s99files.htm.

Calvert, J.G., R. Atkinson, K.H. Becker, R.M. Kamens, J.H. Seinfeld, T.H. Wallington and G. Yarwood. 2002. "The Mechanisms of Atmospheric Oxidation of the Aromatic Hydrocarbons." Oxford University Press.

Calvert, J.G., R. Atkinson, J.A. Kerr, S. Madronich, G.K. Moortgat, T.J. Wallington, and G. Yarwood. 2000. "The Mechanisms of Atmospheric Oxidation of the Alkenes." Oxford University Press.

Cooper, J.A. and J.G. Watson. 1980. Receptor oriented methods of air particulate source apportionment. JAPCA 30, 1116-1125.

Dudhia, J.A. 1993. "Nonhydrostatic Version of the Penn State-NCAR Mesoscale Model: Validation Tests and Simulation of an Atlantic Cyclone and Cold Front." *Monthly Weather Review*, Vol. 121, pp.1493-1513.

ENVIRON. 2004. "User's Guide, Comprehensive Air Quality Model With Extensions (CAMx) Version 4.00." ENVIRON International Corp., Novato, CA. Available from http://www.camx.com.

ENVIRON. 2002a. "Development, Application, and Evaluation of an Advanced Photochemical Air Toxics Modeling System." Report for Project A-42-2 prepared for the Coordinating Research Council, 3650 Mansell Road, Alpharetta, GA 30022. Available at http://www.crcao.com.

ENVIRON. 2002b. "User's Guide to the Global Biosphere Emissions and Interactions System, Version 3." Available from http://www.globeis.com.

Friedlander, S.K. 1973. "Chemical Element Balances and Identification of Air Pollution Sources." Environ. Sci. Technol., 1:235-240.

Fujita, E.M. and D.E. Campbell. 2003. "Validation and Application Protocol for Source Apportionment of Photochemical Assessment Monitoring Stations (PAMS) Ambient Volatile Organic Compound (VOC) Data." Executive Summary Report. EPA Grant #GR826237-01-0. August 31.

Fujita, E.M., D.E. Campbell, B. Zielinska, J.C. Sagebiel, J.L. Bowen, W.S. Goliff, W.R. Stockwell, and D. R. Lawson. 2003a. Diurnal and Weekday Variations in the Source Contributions of Ozone Precursors in California's South Coast Air Basin. *J. Air & Waste Manage. Assoc.,* 53, 844-863.

Fujita, E.M., R.E. Keislar, J.L. Bowen, W. Goliff, F. Zhang, L.H. Sheetz, M.D. Keith, J.C. Sagebiel, and B. Zielinska. 1999a. 1998 Central Texas On-Road Hydrocarbon Study. Draft final report prepared for the Texas Department of Transportation, Austin, TX under subcontract to PBS&J, Austin, TX, March, 1999

Fujita, E.M. 1999b. VOC Source Signatures in Houston, TX Phase 1: Sample Collection. Prepared for the Texas Natural Resource Conservation Commission (Contract No. 980069300) under subcontract to MCNC-North Carolina Supercomputing Center, Research Triangle Park, NC

Fujita, E.M. 1998. Hydrocarbon Source Apportionment for the 1996 Paso del Norte Ozone Study. EPA Contract No. 68-D3-0030. Final report prepared for U.S. Environmental Protection Agency, Dallas, TX., March 1998.

Fujita, E.M., Z. Lu, L. Sheetz, G. Harshfeld, and B. Zielinska. 1997. "Determination of Mobile Source Emission Fraction Using Ambient Field Measurements." Report available from the Coordinating Research Council, 215 Perimeter Center Parkway, Atlanta, GA. .

Fujita, E.M., Z. Lu, L. Sheetz, G. Harshfield, and B. Zielinska. 1997a. Determination of Mobile Source Emission Source Fraction Using Ambient Field Measurements. Final Report prepared for the Coordinating Research Council, Atlanta, GA, July 1997.

Fujita, E.M., Z. Lu, L. Sheetz, G. Harshfield, T. Hayes, and B. Zielinska. 1997c. Hydrocarbon Source Apportionment in Western Washington. Report prepared for the State of Washington Department of Ecology, Lacy, WA, September, 1997.

Fujita, E.M., Z. Lu, J. Sagebiel, N.F. Robinson, and J.G. Watson. 1995b. VOC Source Apportionment for the Coast Oxidant Assessment for Southeast Texas. Final report prepared for the Texas Natural Resource Conservation Commission, August 1995.

Fujita, E.M., J.G. Watson, J.C. Chow and Z. Lu. 1994. "Validation of the Chemical Mass Balance Receptor Model Applied to Hydrocarbon Source Apportionment in the Southern California Air Quality Study." *Environ. Sci. Technol*., 28, 1633-1649.

Gery, M.W., G.Z. Whitten, J.P. Killus, and M.C. Dodge. 1989. "A photochemical kinetics mechanism for urban and regional scale computer modeling." *J. Geophysics Res*. Vol.94, pp.12,925-12,956.

Gordon, G.E. 1988. Receptor models. Environ. Sci. Technol. 22, 1132-1142.

Guenther, A., B. Baugh, G. Brasseur, J. Greenberg, P. Harley, L. Klinger, D. Serca, and L. Vierling. 1999. "Isoprene emission estimates and uncertainties for the Central African EXPRESSO study domain." *J. of Geophysical Research*, 104, 30625-30639.

Henry, R.C. 1997. "Receptor model applied to patterns in space (RMAPS) part I -model description." *J. Air & Waste Manage. Assoc.* 47:216-225.

Hidy, G.M. and C. Venkataraman. 1996. The chemical mass balance method for estimating atmospheric particle sources in Southern California. *Chem. Eng. Comm*. 151, 187-209.

JPL. 1997. W.B. DeMore, S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Kolb, and M.J. Molina. "Chemical Kinetics and Photochemical Data for use in Atmospheric Studies, Evaluation Number 13", NASA Jet Propulsion Laboratory, December. Available from http://jpldataeval.jpl.nasa.gov/download.html.

NOAA Air Resources Laboratory (ARL). 2002. "Gridded NCEP Meteorological Data Archives." Silver Spring, MD. http://www.arl.noaa.gov/ss/transport/archives.html.

Seila, R.L., H.H. Main, J.L. Arriaga, G. Martinez, and A.B. Ramadan. 2001. "Atmospheric volatile organic compound measurements during the 1996 Paso del Norte Ozone Study." *The Science of the Total Environment*, no. 276(1-3), Aug 10, 2001:pp. 153-69.

South Coast Air Quality Management District (SCAQMD). 1999. "Final 1999 Amendment to the 1997 Ozone SIP Revision for the South Coast Air Basin." SCAQMD, Diamond Bar, CA. December. Available from, http://www.aqmd.gov/aqmp/99amend2.html.

South Coast Air Quality Management District (SCAQMD). 1997. "1997 Air Quality Management Plan, Appendix V, Modeling and Attainment Demonstrations." SCAQMD, Diamond Bar, CA. November. Available from, http://www.aqmd.gov/aqmp/97aqmp/.

Watson, J.G., J.C. Chow. 2004. "Receptor Models for Air Quality Management." *Environmental Manager*, pp.15-24, October.

Watson, J.G., J.C. Chow, and E.M. Fujita. 2001. "Review of Volatile Organic Compound Source Apportionment by Chemical Mass Balance." *Atmos. Environ*., 35(9), 1567-1584.

Watson, J.G., J.C. Chow, T.G. Pace. 1991. Chemical mass balance. In Receptor Modeling for Air Quality Management, Hopke, P.K., Ed. Elsevier Press, New York, NY, pp. 83-116.

Watson, J.G., Robinson, N.F., Chow, J.C., Henry, R.C., Kim, B.M., Pace, T.G., Meyer, E.L., and Nguyen, Q. 1990. The USEPA/DRI chemical mass balance receptor model, CMB 7.0. ENVIRON. Software 5, 38-49.

Watson, J.G. 1984. Overview of receptor model principles. JAPCA 34, 619-623.

Watson, J.G., and N.F. Robinson. 1984. "A Method to Determine Accuracy and Precision Required of Receptor Model Measurements." In Quality Assurance in Air Pollution Measurements. Air Pollution Control Association, Pittsburgh, PA.

White, W.H. 2000. Memorandum from Warren White. August 6, 2000. *True source contributions for "ambient" data.*

White, W. H. 1999. "Phantom Spatial Factors: An Example." *J. Air & Waste Manage. Assoc.*, 49:345-349.

Yarwood, G. T.E. Stoeckenius, J.G. Heiken, and A.M. Dunker. 2003a. "Modeling Weekday/Weekend Ozone Differences in the Los Angeles Region for 1997." *J. Air & Waste Manage. Assoc.* Vol. 53, No. 7, July.

Yarwood, G., C. Tran, S. Lau, E. Fujita. 2003b "Impact of Updates to On-Road Mobile Source Emission Factor Models (EMFAC) for the Los Angeles Region: Ozone Model Sensitivity and Ambient/Inventory Reconciliation." Report for Project A-38 prepared for the Coordinating Research Council, 3650 Mansell Road, Alpharetta, GA 30022. Available at http://www.crcao.com.

Yarwood, G., T. Stoeckenius, J. Heiken. 2002. "Proximate modeling of Weekday/Weekend Differences for Ozone." Report for Project A-36-A1 prepared for the Coordinating Research Council, 3650 Mansell Road, Alpharetta, GA 30022. Available at http://www.crcao.com.

APPENDIX A

Supplemental Modeling Results

Table A-1. 170 source categories (SCCs) with more than 1 Ton/Day of TOG emissions in the emission inventory for August 5, 1997 and assignments to speciation profiles.

SCC Description	TOG Ton/Day	%TOG	Cumu-lative	Profile Code
Unplanned Fires Wildfires Timber & Brush	394.6	12.8%	12.8%	307
Biogenic Emissions - Isoprene	273.0	8.9%	21.7%	806
Waste Disposal Biodegradation Municipal Wastes	223.2	7.2%	28.9%	1401
On-Road Vehicles TOG Cat Hot Exhaust	217.5	7.1%	36.0%	436
On-Road Vehicles TOG Running Evaporatives	212.0	6.9%	42.8%	419
Farming Operation Livestock Waste	209.0	6.8%	49.6%	203
Biogenic Emissions - Monoterpenes	135.0	4.4%	54.0%	807
On-Road Vehicles TOG Non-Cat Hot Exhaust	117.7	3.8%	57.8%	401
On-Road Vehicles TOG Cat Cold Exhaust	103.8	3.4%	61.2%	877
Misc.Processes Natural Sources Vegetative	93.2	3.0%	64.2%	533
Gas Distribution Transmission Losses Nat.Gas Distribution	77.2	2.5%	66.7%	520
On-Road Vehicles TOG Hot Soak	69.2	2.2%	69.0%	419
On-Road Vehicles TOG Diurnal	65.2	2.1%	71.1%	906
Degreasing Cold Cleaning Petroleum Solvents	55.6	1.8%	72.9%	919
Fuel Combustion Industrl Ic Engines Natural Gas	40.1	1.3%	74.2%	719
Fuel Storage/Handling gasoline Cans Gasoline (Evap)	39.9	1.3%	75.5%	906
Recreational Boats Recreational Boats Gasoline (Unspec) Two-Stroke	34.8	1.1%	76.6%	401
On-Road Vehicles TOG Resting Evaporatives	34.5	1.1%	77.7%	906
Gasoline Disp. Facil. vehicle Refueling Vapor Displacement	26.3	0.9%	78.6%	906
Off-Road Equipment Lawn And Garden Gasoline (Unspec) Two-Stroke	20.2	0.7%	79.2%	401
On-Road Vehicles TOG Non-Cat Cold Exhaust	19.4	0.6%	79.9%	402
Solvent Use Consumer Products Hair Spray	19.4	0.6%	80.5%	1760
Off-Road Equipment Construct And Mining diesel (Unspecified)	18.3	0.6%	81.1%	818
Biogenic Emissions - 3-Methyl-2-Buten-1-Ol	17.2	0.6%	81.7%	822
Recreational Boats Recreational Boats Gasoline (Unspec) Four-Stroke	16.9	0.5%	82.2%	401
On-Road Vehicles TOG Diesel Exhaust	14.2	0.5%	82.7%	818
Internl combustion Industrial Natural Gas Reciprocating	12.6	0.4%	83.1%	719
Solvent Use Architectural Cleanup & Thinning	12.0	0.4%	83.5%	1930
Solvent Use Consumer Products Comb Small Categorys	10.6	0.3%	83.8%	1799
Solvent Use Adhesive & Sealent Solvent Based	10.1	0.3%	84.1%	714
Organic Solvent Surface Coating Wood Furniture Coating Operation	8.6	0.3%	84.4%	783
Off-Road Equipment Lawn And Garden Gasoline (Unspec) Four-Stroke	8.6	0.3%	84.7%	401
Solvent Use Architectural Oil-Based Coating Industrial Maint.	8.2	0.3%	85.0%	1901
Off-Road Equipment Lawn And Garden Gasoline (Evap) Four-Stroke	7.9	0.3%	85.2%	906
Solvent Use Consumer Products Multipurpose Solvent	7.2	0.2%	85.5%	1580
Solvent Use Commercial Auto Refinishing	6.7	0.2%	85.7%	1448
Solvent Use Architectural Water-Based Coating Flat Coatings	6.6	0.2%	85.9%	1902
Internl combustion Electric Generatn Natural Gas Turbine	6.5	0.2%	86.1%	719
Off-Road Equipment Light Comm Equip Gasoline (Unspec) Four-Stroke	6.3	0.2%	86.3%	401
Internl combustion Industrial Natural Gas Turbine-Cogenertn	5.3	0.2%	86.5%	719
Gasoline Disp. Faciltanks Tank Working Losses Underground	5.1	0.2%	86.6%	906
Off-Road Vehicles Recreational Motorcycles	5.1	0.2%	86.8%	401
Solid Waste Displ Government Landfill Area Method	5.0	0.2%	87.0%	1401
Solvent Use Architectural Water-Based Coating Med Gloss Nonflat	4.8	0.2%	87.1%	1902
Off-Road Equipment Industrial Equipmentnatural Gas	4.5	0.1%	87.3%	719
Internlcombustion Industrial Natural Gas Turbine	4.5	0.1%	87.4%	719
Off-Road Vehicles Recreational Atv	4.4	0.1%	87.5%	401

SCC Description	TOG Ton/Day	%TOG	Cumu-lative	Profile Code
Solvent Use Consumer Products Personal Fragrance Fragrance <= 20%	4.2	0.1%	87.7%	1750
Off-Road Equipment Industrial Equipment gasoline (Unspec) Four-Stroke	4.2	0.1%	87.8%	401
Solvent Use Consumer Products Aerosol Coatings Nonflat Coatings	4.2	0.1%	88.0%	1804
Degreasing Handwiping Petroleum Solvents	4.1	0.1%	88.1%	920
Solvent Use Consumer Products Gen Purpose Cleanersnon-Aerosols	4.0	0.1%	88.2%	1652
Solvent Use Consumer Products Crawl Bug Insecticide aerosols	4.0	0.1%	88.3%	1615
Solvent Use Consumer Products Rubbing Alcohol	4.0	0.1%	88.5%	1780
Solvent Use Consumer Products Auto Windshld Washer	4.0	0.1%	88.6%	1560
Chemical Processes Fabrication Fiberglass	3.9	0.1%	88.7%	600
Natural Sources Petroleum Related Oil Seep	3.8	0.1%	88.9%	551
Solvent Use Industrial Coating (Unspecified)	3.8	0.1%	89.0%	783
Gasoline Disp. Facilvehicle Refueling Spillage	3.8	0.1%	89.1%	419
Degreasing Handwiping Alcohols	3.7	0.1%	89.2%	918
Solvent Use Consumer Products Paint Remover/Stripr	3.7	0.1%	89.3%	1571
Government Aircraft Military Jet Aircraft	3.6	0.1%	89.5%	586
Solvent Use Architectural Oil-Based Coating Primer/Sealer/Under	3.5	0.1%	89.6%	1901
Oil & Gas Prodn Crude Oil Prodn Wells-Rod Pumps	3.5	0.1%	89.7%	756
Farm Equipment Agricultural Equip Diesel (Unspecified)	3.4	0.1%	89.8%	818
Solvent Use Consumer Products Disinfectants	3.3	0.1%	89.9%	1590
Internlcombustion Industrial Natural Gas Engine-Cogeneratn	3.2	0.1%	90.0%	719
Baking Commercial Bakeries	3.2	0.1%	90.1%	211
Solvent Use Consumer Products Carb/Fuel Inj Clean	3.2	0.1%	90.2%	1552
Solvent Use Consumer Products Auto Brake Cleaners	3.2	0.1%	90.3%	1551
Solvent Use Architectural Oil-Based Coating Quick Dry Prime/Seal	3.1	0.1%	90.4%	1901
Degreasing Handwiping Ketones	3.1	0.1%	90.5%	916
Petroleum Indry Fugitive Hc Emis Drains All Streams	3.1	0.1%	90.6%	297
Pesticide Applicatn. Agricultural Non-Methyl Bromide	3.0	0.1%	90.7%	76
Organic Solvent Surface Coating Misc. Metal Parts Coating Operation	3.0	0.1%	90.8%	783
Organic Solvent Surface Coating Miscellaneous Other	3.0	0.1%	90.9%	600
Internl combustion Fixed Wing Aircraft Military Fixed Wing: Jp-5	3.0	0.1%	91.0%	586
Degreasing Handwiping Trichloroethane	2.9	0.1%	91.1%	87
Oil & Gas Extraction fugitive Losses Gas Stripping	2.9	0.1%	91.2%	531
Solvent Use Architectural Oil-Based Coating Stains - Semitrans	2.8	0.1%	91.3%	1901
Internl combustion Electric Generatn Natural Gas Reciprocating	2.7	0.1%	91.4%	719
Organic Solvent Cold Cleaning Other/Not Classfd Specify Solvent	2.7	0.1%	91.5%	515
Oil Production Fugitive Losses Valves	2.6	0.1%	91.5%	529
Pesticide Applicatn.Agricultural Methyl Bromide	2.6	0.1%	91.6%	796
Degreasing Vapor Degreasing Trichloroethane	2.5	0.1%	91.7%	87
Trains Locomotives Hauling	2.5	0.1%	91.8%	818
Solvent Use Architectural Oil-Based Coating Quick Dry Enamel	2.4	0.1%	91.9%	1901
Cooking Commercial Charbroiling	2.4	0.1%	91.9%	600
Food/Agriculture Miscellaneous Not Classified Other	2.3	0.1%	92.0%	600
Solvent Use Consumer Products Multi-Purp Lubricant	2.3	0.1%	92.1%	1700
Mineral Products Nonmetallic Minrl Mixing & Blending	2.3	0.1%	92.2%	1411
Organic Solvent Surface Coating Thinning Solvent Other	2.3	0.1%	92.2%	96
Degreasing Handwiping Misc Solvent Blends	2.3	0.1%	92.3%	932
Solvent Use Consumer Products Air Fresheners Double Phase Aerosol	2.2	0.1%	92.4%	1711
Organic Solvent Surface Coating Misc.Metal Parts Clean/Pretreatmnt	2.2	0.1%	92.5%	783
Solvent Use Printing & Publish Printing	2.2	0.1%	92.5%	517

SCC Description	TOG Ton/Day	%TOG	Cumu-lative	Profile Code
Solvent Use Consumer Products Flyin Insct Inscide Aerosols	2.1	0.1%	92.6%	1611
Oil & Gas Prodn Crude Oil Prodn Valves General	2.1	0.1%	92.7%	758
Internl combustion Commercl-Instutnl Natural Gas Reciprocating	2.1	0.1%	92.7%	719
Off-Road Equipment Construct And Mining gasoline (Unspec) Four-Stroke	2.1	0.1%	92.8%	401
Commercial Jet Taxi	2.1	0.1%	92.9%	586
On-Road Vehicles TOG Multi-Day Diurnal	2.0	0.1%	92.9%	906
Petroleum Indry Petroleum Refng Hydrogen Generation General	2.0	0.1%	93.0%	1412
Rubber/Plastics Fab. Plastic Prod Fiberglass Resin General-Roll On	2.0	0.1%	93.1%	753
Rubber/Plastics Fab. Plastic Prod Fiberglass Resin General-Spray On	2.0	0.1%	93.1%	600
Solvent Use Architectural Oil-Based Coating Lacquer - Clear	1.9	0.1%	93.2%	1901
Solvent Use Consumer Products Herbicides/Defoliant non-Selective	1.9	0.1%	93.3%	1600
Mobile Equipment Refrigeration Units Diesel	1.9	0.1%	93.3%	818
Solvent Use Dry Cleaning Perchloroethylene	1.9	0.1%	93.4%	85
Solvent Use Consumer Products Charcoal Lighter Mat	1.9	0.1%	93.5%	1720
Solvent Use Industrial Miscellaneous	1.9	0.1%	93.5%	600
Internl combustion Industrial Propane Reciprocating	1.9	0.1%	93.6%	719
Rubber/Plastics Fab. Plastic Prod Fiberglass Resin Product-General	1.8	0.1%	93.6%	600
Off-Road Equipment Lawn And Garden Gasoline (Evap) Two-Stroke	1.8	0.1%	93.7%	906
Printing/Publish Printing Process Letterpress Cleaning Solution	1.8	0.1%	93.7%	517
On-Road Vehicles TOG Multi-Day Resting	1.7	0.1%	93.8%	906
Off-Road Equipment Industrial Equipment diesel (Unspecified)	1.7	0.1%	93.9%	818
Petroleum Indry Fugitive HC Emis Pipeline Valves Gas Streams	1.7	0.1%	93.9%	316
Recreational Boats Recreational Boats Gasoline (Evap) Two-Stroke	1.7	0.1%	94.0%	906
Oil Production Fugitive Losses Fittings	1.6	0.1%	94.0%	529
Solvent Use Industrial Coating Paper	1.6	0.1%	94.1%	783
Solvent Use Consumer Products Laundry Detergent	1.6	0.1%	94.1%	1790
Solvent Use Architectural Oil-Based Coating	1.5	0.0%	94.2%	1901
Off-Road Equipment Light Comm Equip Diesel (Unspecified)	1.5	0.0%	94.2%	818
Recreational Boats Recreational Boats Gasoline (Evap) Four-Stroke	1.5	0.0%	94.3%	906
Chemical Processes Manufacturing Synthetic Rubber	1.5	0.0%	94.3%	274
Organic Solvent Surface Coating Adhesive General	1.5	0.0%	94.4%	714
Solvent Use Architectural Oil-Based Coating Bituminous Coatings	1.5	0.0%	94.4%	1901
Solvent Use Consumer Products Hvy Dty Hand Cleaner	1.5	0.0%	94.5%	1792
Oil & Gas Prodn Natural Gas Prodn Wells	1.4	0.0%	94.5%	757
Solvent Use Consumer Products Floor Wax Strippers	1.4	0.0%	94.6%	1650
Off-Road Equipment Light Comm Equip Gasoline (Unspec) Two-Stroke	1.4	0.0%	94.6%	401
Solvent Use Architectural Oil-Based Coating Varnish - Clear	1.4	0.0%	94.6%	1901
Off-Road Vehicles Recreational Four-Wheel Drive	1.4	0.0%	94.7%	401
Solvent Use Architectural Oil-Based Coating Wtrproof Seal/Clear	1.4	0.0%	94.7%	1901
Solvent Use Consumer Products Glass Cleaners Non-Aerosols	1.4	0.0%	94.8%	1656
Solvent Use Consumer Products Aerosol Coatings Grd/Traffic/Marking	1.4	0.0%	94.8%	1811
Solvent Use Architectural Water-Based Coating Low Gloss Nonflat	1.4	0.0%	94.9%	1902
Pesticide Applicatn. Structural Non-Methyl Bromide	1.4	0.0%	94.9%	76
Oil & Gas Prodn Crude Oil Prodn Flanges & Connectns	1.3	0.0%	95.0%	756
Solvent Use Industrial Coating Wood Furnit. & Fixt	1.3	0.0%	95.0%	783
Solvent Use Architectural Oil-Based Coating Hi Gloss Nonflat	1.3	0.0%	95.0%	1901
Petroleum Indry Fugitive Hc Emis Flanges All Streams	1.3	0.0%	95.1%	316
Solvent Use Consumer Products Engine Degreasers Aerosol	1.3	0.0%	95.1%	1553
Solvent Use Industrial Coating Marine	1.3	0.0%	95.2%	783

SCC Description	TOG Ton/Day	%TOG	Cumu-lative	Profile Code
Extcomb Boiler Electric Generatn Natural Gas >100Mmbtu/Hr Extf	1.3	0.0%	95.2%	3
Internl combustion Electric Generatn Landfill Gas Reciprocating	1.2	0.0%	95.3%	719
Degreasing Cold Cleaning Alcohols	1.2	0.0%	95.3%	917
Organic Solvent Surface Coating Autos/Light Truck Repair Topcoat	1.2	0.0%	95.3%	783
Solvent Use Architectural Oil-Based Coating Traffic Coatings	1.2	0.0%	95.4%	1901
Fuel Combustion Residential Nat Gas Water Heatn	1.2	0.0%	95.4%	3
Solvent Use Consumer Products Underarm Antiperspir aerosols	1.2	0.0%	95.4%	1730
Internl combustion Commercl-Instutnl Natural Gas Turbine	1.1	0.0%	95.5%	719
Solid Waste Displ Government Landfill Gas Collctn Sys Othr	1.1	0.0%	95.5%	1401
Degreasing Cold Cleaning Terpenes	1.1	0.0%	95.6%	926
Solvent Use Consumer Products Rubber/Vinyl Protectnon-Aerosols	1.1	0.0%	95.6%	1537
Secondary Metals Sec. Aluminum Not Classified Other	1.1	0.0%	95.6%	600
Petroleum Indry Fugitive Hc Emis Pipeline Valves Lt Liq/Gas Stream	1.1	0.0%	95.7%	316
Petroleum Indry Fugitive Hc Emis Compressor Seals Heavy Liqd Stream	1.0	0.0%	95.7%	531
Solvent Use Consumer Products Air Fresheners Solid/Gel	1.0	0.0%	95.7%	1714
Solvent Use Adhesive & Sealent Water Based	1.0	0.0%	95.8%	717
Petroleum Indry Fugitive Hc Emis Pump Seals Heavy Liqd Stream	1.0	0.0%	95.8%	530
Solvent Use Consumer Products Underarm Antiperspir non-Aerosols	1.0	0.0%	95.8%	1731
Internl combustion Fixed Wing Aircraft Civil Fixed Wing: Av Gas	1.0	0.0%	95.9%	413
Solvent Use Consumer Products Astringents/Toners	1.0	0.0%	95.9%	1740
Chemical Mfg Pharmaceuticals General Processes Coating	1.0	0.0%	95.9%	1404
Degreasing Cold Cleaning Misc Solvent Blends	1.0	0.0%	96.0%	930
Solvent Use Architectural Oil-Based Coating Med Gloss Nonflat	1.0	0.0%	96.0%	1901
Internl Combustion Commercl – Institutl digester Gas Reciprocating	1.0	0.0%	96.0%	719
Gasoline Disp. Facil tanks Breathing Losses Underground	1.0	0.0%	96.1%	906
Other Categories	121.4	3.9%		
Total	**3081.4**	**100.0%**		

Table A-2. Speciation profiles assigned to the 170 source categories (SCCs) listed in Table A-1.

ARB Profile Number	TOG %Total	% TOG Cumula-tative	SCC Count	ARB Profile Description
307	12.8%	12.8%	1	Forest Fires
419	9.2%	22.1%	3	Liquid Gasoline - Mtbe 11% - Commercial Grade - Mtbe/Etoh Program
806	8.9%	30.9%	1	Isoprene & Soil No
1401	7.4%	38.4%	3	Landfills, Usepa Landfill Emission Model
401	7.2%	45.6%	12	Gasoline - Non-Cat - Stabilized Exhaust - Arb Ius Summer 1996
436	7.1%	52.7%	1	Gasoline - Catalyst - Stabilized Exhaust - Arb Summer 1997
203	6.8%	59.4%	1	Animal Waste Decomposition
906	6.1%	65.6%	12	Gasoline - Ucberk - Headspace Vapors For Mtbe 2.0 % O Gasoline
807	4.4%	69.9%	1	Monoterpenes
877	3.4%	73.3%	1	Gasoline - Catalyst - Ftp Bag 1-3 Starts - Arb Ius Summer 1996
533	3.0%	76.3%	1	Daytime Biogenic Profile- Kern County Crops
719	2.8%	79.1%	13	Ice-Reciprocating-Natural Gas
520	2.5%	81.6%	1	Composite Natural Gas
919	1.8%	83.4%	1	Degreasing: Cold Cleaning (Batch, Conveyor, Spray Gun)
818	1.4%	84.9%	7	Farm Equipment - Diesel - Light & Heavy - (Ems=Actual Weight)
1901	1.0%	85.9%	13	Draft Architectural Ctgs: Solvent Borne (Arb 1998 Survey)
783	0.7%	86.6%	8	Industrial Surface Coating-Solvent Based Paint
402	0.6%	87.2%	1	Gasoline - Non-Cat - Ftp Bag1-3 Starts - Arb Ius Summer 1996
1760	0.6%	87.9%	1	Draft Consumer Prd: Hair Spray
600	0.6%	88.5%	8	Species Unknown- All Category Composite
822	0.6%	89.0%	1	Methylbutenol
1902	0.4%	89.4%	3	Draft Architectural Ctgs: Water Borne (Arb 1998 Survey)
1930	0.4%	89.8%	1	Thinning Solvent/Mineral Spirits (Calpoly Slo 1996) Arb Default
714	0.4%	90.2%	2	Industrial Surface Coating-Composite Adhesive
1799	0.3%	90.6%	1	Draft Consumer Prd: Combined Small Categories Epa Composite
586	0.3%	90.8%	3	Composite Jet Exhaust Jp-5 (Epa 1097-1099)
1580	0.2%	91.1%	1	Draft Consumer Prd: Multipurpose Solvents
1448	0.2%	91.3%	1	Auto Refinishing (Us Epa #2402)
87	0.2%	91.5%	2	1,1,1-Trichloroethane Cleaning Solvent
756	0.2%	91.6%	2	Oil & Gas Production Fugitives-Liquid Service
76	0.1%	91.8%	2	Pesticide Use- Composite Domestic & Commercial
529	0.1%	91.9%	2	Oil & Gas Extraction - Pipeline Valves & Fittings
1750	0.1%	92.0%	1	Draft Consumer Prd: Personal Fragrance Product (Fragrance <= 20%)
1804	0.1%	92.2%	1	Draft Aerosol Ctgs: Nonflat Coatings (Unspecified)
920	0.1%	92.3%	1	Degreasing: Handwiping
316	0.1%	92.4%	3	Refinery- Pipes, Valves & Flanges- Composite
1652	0.1%	92.6%	1	Draft Consumer Prd: General Purpose Cleaners - Non-Aerosols
1615	0.1%	92.7%	1	Draft Consumer Prd: Crawling Bug Insecticides - Aerosols
1780	0.1%	92.8%	1	Draft Consumer Prd: Rubbing Alcohol
1560	0.1%	93.0%	1	Draft Consumer Prd: Automotive Windshield Washer Fluids
517	0.1%	93.1%	2	Printing Evaporation Loss- General
531	0.1%	93.2%	2	Oil & Gas Extraction - Compressor Seals
551	0.1%	93.3%	1	Ocs - Oil Seeps - Volatile Fraction
918	0.1%	93.5%	1	Degreasing: Handwiping
1571	0.1%	93.6%	1	Draft Consumer Prd: Paint Removers Or Strippers
1590	0.1%	93.7%	1	Draft Consumer Prd: Disinfectants

ARB Profile Number	TOG %Total	% TOG Cumula-tative	SCC Count	ARB Profile Description
211	0.1%	93.8%	1	Beer Fermentation- Ethanol
1552	0.1%	93.9%	1	Draft Consumer Prd: Carburetor Or Fuel-Injection Air Intake Cleaners
1551	0.1%	94.0%	1	Draft Consumer Prd: Automotive Brake Cleaners
916	0.1%	94.1%	1	Degreasing: Handwiping
297	0.1%	94.2%	1	Crude Oil Evaporation- Vapor Composite From Fixed Roof Tanks
515	0.1%	94.3%	1	Composite Industrial Degreasers
796	0.1%	94.4%	1	Methyl Bromide
3	0.1%	94.4%	2	External Combustion Boiler - Natural Gas
1700	0.1%	94.5%	1	Draft Consumer Prd: Multi-Purpose Lubricant
1411	0.1%	94.6%	1	Mineral Products - Average (Epa 9011)
96	0.1%	94.7%	1	Surface Coating Solvent- General
932	0.1%	94.7%	1	Degreasing: Handwiping
1711	0.1%	94.8%	1	Draft Consumer Prd: Double Phase Aerosol Air Fresheners
1611	0.1%	94.9%	1	Draft Consumer Prd: Flying Insect Insecticide - Aerosols
758	0.1%	95.0%	1	Oil & Gas Production Fugitives-Valves-Unspecified
1412	0.1%	95.0%	1	Petroleum Industry - Average (Epa 9012)
753	0.1%	95.1%	1	Styrene
1600	0.1%	95.1%	1	Draft Consumer Prd: Non-Selective Herbicides/Defoliants
85	0.1%	95.2%	1	Perchloroethylene Cleaning Solvent
1720	0.1%	95.3%	1	Draft Consumer Prd: Charcoal Lighter Materials
1790	0.1%	95.3%	1	Draft Consumer Prd: Laundry Detergent
274	0.0%	95.4%	1	Synthetic Rubber Auto Tire Production
1792	0.0%	95.4%	1	Draft Consumer Prd: Heavy Duty Hand Cleaner Or Soap
757	0.0%	95.5%	1	Oil & Gas Production Fugitives-Gas Service
1650	0.0%	95.5%	1	Draft Consumer Prd: Floor Wax Strippers
1656	0.0%	95.6%	1	Draft Consumer Prd: Glass Cleaners - Non-Aerosols
1811	0.0%	95.6%	1	Draft Aerosol Ctgs: Ground/Traffic/Marking Coatings
1553	0.0%	95.6%	1	Draft Consumer Prd: Engine Degreasers - Aerosols
917	0.0%	95.7%	1	Degreasing: Cold Cleaning (Batch, Conveyor, Spray Gun)
1730	0.0%	95.7%	1	Draft Consumer Prd: Underarm Antiperspirants - Aerosols
926	0.0%	95.8%	1	Degreasing: Cold Cleaning (Batch, Conveyor, Spray Gun)
1537	0.0%	95.8%	1	Draft Consumer Prd: Rubber And Vinyl Protectants - Non-Aerosols
1714	0.0%	95.8%	1	Draft Consumer Prd: Solid/Gel Air Fresheners
717	0.0%	95.9%	1	Architectural Surface Coating-Water Based Paint
530	0.0%	95.9%	1	Oil & Gas Extraction - Pump Seals
1731	0.0%	95.9%	1	Draft Consumer Prd: Underarm Antiperspirants - Non-Aerosols
413	0.0%	96.0%	1	Gasoline - Non-Cat - Ftp Composite - Arb Ius Summer 1994
1740	0.0%	96.0%	1	Draft Consumer Prd: Astringents/Toners
1404	0.0%	96.0%	1	Chemical Manufacturing - Average (Epa 9004)
930	0.0%	96.1%	1	Degreasing: Cold Cleaning (Batch, Conveyor, Spray Gun)
Total	**96.1%**		**170**	

Table A-3. Assignment of source categories (SCCs) to 22 emission categories for project A-34.

A-34 Number	SCC Code	SCC Description
1	3#	On-Road Vehicles Tog Cat Hot Exhaust
2	2#	On-Road Vehicles Tog Cat Cold Exhaust
3	5#	On-Road Vehicles Tog Non-Cat Hot Exhaust
4	4#	On-Road Vehicles Tog Non-Cat Cold Exhaust
5	9#	On-Road Vehicles Tog Running Evaporatives
5	7#	On-Road Vehicles Tog Diurnal
5	12#	On-Road Vehicles Tog Multi-Day Diurnal
6	6#	On-Road Vehicles Tog Hot Soak
6	10#	On-Road Vehicles Tog Resting Evaporatives
6	11#	On-Road Vehicles Tog Multi-Day Resting
7	8#	On-Road Vehicles Tog Diesel Exhaust
8	84086411000040	Recreational Boats Recreational Boats Gasoline (Unspec) Four-Stroke
8	86088311000040	Off-Road Equipment Lawn And Garden Gasoline (Unspec) Four-Stroke
8	86088311000041	Off-Road Equipment Lawn And Garden Gasoline (Evap) Four-Stroke
8	86088511000040	Off-Road Equipment Light Comm Equip Gasoline (Unspec) Four-Stroke
8	86088601100000	Off-Road Equipment Industrial Equipmentnatural Gas
8	85087411000000	Off-Road Vehicles Recreational Atv
8	86088611000040	Off-Road Equipment Industrial Equipmentgasoline (Unspec) Four-Stroke
8	86088711000040	Off-Road Equipment Construct And Mininggasoline (Unspec) Four-Stroke
8	84086411000041	Recreational Boats Recreational Boats Gasoline (Evap) Four-Stroke
8	85087611000000	Off-Road Vehicles Recreational Four-Wheel Drive
9	84086411000020	Recreational Boats Recreational Boats Gasoline (Unspec) Two-Stroke
9	86088311000020	Off-Road Equipment Lawn And Garden Gasoline (Unspec) Two-Stroke
9	85087211000000	Off-Road Vehicles Recreational Motorcycles
9	86088311000021	Off-Road Equipment Lawn And Garden Gasoline (Evap) Two-Stroke
9	84086411000021	Recreational Boats Recreational Boats Gasoline (Evap) Two-Stroke
9	86088511000020	Off-Road Equipment Light Comm Equip Gasoline (Unspec) Two-Stroke
10	86088712100000	Off-Road Equipment Construct And Miningdiesel (Unspecified)
10	87089312100000	Farm Equipment Agricultural Equip Diesel (Unspecified)
10	82082012100000	Trains Locomotives Hauling
10	86088412100000	Mobile Equipment Refrigeration Units Diesel
10	86088612100000	Off-Road Equipment Industrial Equipmentdiesel (Unspecified)
10	86088512100000	Off-Road Equipment Light Comm Equip Diesel (Unspecified)
11	89089511000041	Fuel Storage/Hndlinggasoline Cans Gasoline (Evap)
11	33037811000000	Gasoline Disp. Facilvehicle Refueling Vapor Displacement
11	33037411000000	Gasoline Disp. Faciltanks Tank Working Losses Underground
11	33038011000000	Gasoline Disp. Facilvehicle Refueling Spillage
11	33037611000000	Gasoline Disp. Faciltanks Breathing Losses Underground
12	33031801100000	Gas Distribution Transmission Losses Nat.Gas Distributio
12	92092016000000	Natural Sources Petroleum Related Oil Seep
12	31000103	Oil & Gas Prodn Crude Oil Prodn Wells-Rod Pumps
12	31099501000000	Oil & Gas Extractionfugitive Losses Gas Stripping **
12	31030216000000	Oil Production Fugitive Losses Valves
12	31000124	Oil & Gas Prodn Crude Oil Prodn Valves General
12	31030416000000	Oil Production Fugitive Losses Fittings
12	31000204	Oil & Gas Prodn Natural Gas Prodn Wells
12	31000127	Oil & Gas Prodn Crude Oil Prodn Flanges & Connectns
13	30600821	Petroleum Indry Fugitive Hc Emis Drains All Streams
13	30601801	Petroleum Indry Petroleum Refng Hydrogen Generation General
13	30600811	Petroleum Indry Fugitive Hc Emis Pipeline Valves Gas Streams
13	30600816	Petroleum Indry Fugitive Hc Emis Flanges All Streams
13	30600812	Petroleum Indry Fugitive Hc Emis Pipeline Valves Lt Liq/Gas Stream
13	30600820	Petroleum Indry Fugitive Hc Emis Compressor Seals Heavy Liqd Stream
13	30600818	Petroleum Indry Fugitive Hc Emis Pump Seals Heavy Liqd Stream
14	51050667600000	Solvent Use Consumer Products Hair Spray
14	51050669000000	Solvent Use Consumer Products Comb Small Categorys

A-34 Number	SCC Code	SCC Description
14	51050665800000	Solvent Use Consumer Products Multipurpose Solvent
14	51050667500000	Solvent Use Consumer Products Personal Fragrance Fragrance <= 20%
14	51050090600000	Solvent Use Consumer Products Aerosol Coatings Nonflat Coatings
14	51050666520000	Solvent Use Consumer Products Gen Purpose Cleanersnon-Aerosols
14	51050666150000	Solvent Use Consumer Products Crawl Bug Insecticidaerosols
14	51050667800000	Solvent Use Consumer Products Rubbing Alcohol
14	51050665600000	Solvent Use Consumer Products Auto Windshld Washer
14	51050665710000	Solvent Use Consumer Products Paint Remover/Stripr
14	51050665900000	Solvent Use Consumer Products Disinfectants
14	51050665520000	Solvent Use Consumer Products Carb/Fuel Inj Clean
14	51050665510000	Solvent Use Consumer Products Auto Brake Cleaners
14	51050667000000	Solvent Use Consumer Products Multi-Purp Lubricant
14	51050667110000	Solvent Use Consumer Products Air Fresheners Double Phase Aerosol
14	51050666110000	Solvent Use Consumer Products Flyin Insct Inscide Aerosols
14	51050666000000	Solvent Use Consumer Products Herbicides/Defoliantnon-Selective
14	51050667200000	Solvent Use Consumer Products Charcoal Lighter Mat
14	51050667900000	Solvent Use Consumer Products Laundry Detergent
14	51050667920000	Solvent Use Consumer Products Hvy Dty Hand Cleaner
14	51050666500000	Solvent Use Consumer Products Floor Wax Strippers
14	51050666560000	Solvent Use Consumer Products Glass Cleaners Non-Aerosols
14	51050090770000	Solvent Use Consumer Products Aerosol Coatings Grd/Traffic/Marking
14	51050665530000	Solvent Use Consumer Products Engine Degreasers Aerosol
14	51050667300000	Solvent Use Consumer Products Underarm Antiperspiraerosols
14	51050665370000	Solvent Use Consumer Products Rubber/Vinyl Protectnon-Aerosols
14	51050667140000	Solvent Use Consumer Products Air Fresheners Solid/Gel
14	51050667310000	Solvent Use Consumer Products Underarm Antiperspirnon-Aerosols
15	52052283000000	Solvent Use Architectural Cleanup & Thinning
15	52052091720000	Solvent Use Architectural Oil-Based Coating Industrial Maint.
15	52052092590000	Solvent Use Architectural Water-Based Coating Flat Coatings
15	52052092620000	Solvent Use Architectural Water-Based Coating Med Gloss Nonflat
15	52052091050000	Solvent Use Architectural Oil-Based Coating Primer/Sealer/Under
15	52052091060000	Solvent Use Architectural Oil-Based Coating Quick Dry Prime/Seal
15	52052091340000	Solvent Use Architectural Oil-Based Coating Stains - Semitrans
15	52052091530000	Solvent Use Architectural Oil-Based Coating Quick Dry Enamel
15	52052091550000	Solvent Use Architectural Oil-Based Coating Lacquer - Clear
15	52052091000000	Solvent Use Architectural Oil-Based Coating
15	52052091640000	Solvent Use Architectural Oil-Based Coating Bituminous Coatings
15	52052091420000	Solvent Use Architectural Oil-Based Coating Varnish - Clear
15	52052091140000	Solvent Use Architectural Oil-Based Coating Wtrproof Seal/Clear
15	52052092630000	Solvent Use Architectural Water-Based Coating Low Gloss Nonflat
15	52052091610000	Solvent Use Architectural Oil-Based Coating Hi Gloss Nonflat
15	52052091760000	Solvent Use Architectural Oil-Based Coating Traffic Coatings
15	52052091620000	Solvent Use Architectural Oil-Based Coating Med Gloss Nonflat
16	25029282020000	Solvent Use Adhesive & Sealent Solvent Based
16	40201901	Organic Solvent Surface Coating Wood Furniture Coating Operation
16	23021890000000	Solvent Use Commercial Auto Refinishing
16	23099590000000	Solvent Use Industrial Coating (Unspecified)
16	40202501	Organic Solvent Surface Coating Misc.Metal Parts Coating Operation
16	40299995	Organic Solvent Surface Coating Miscellaneous Other
16	30509202	Mineral Products Nonmetallic Minrl Mixing & Blending
16	40200998	Organic Solvent Surface Coating Thinning Solvent Other
16	40202502	Organic Solvent Surface Coating Misc.Metal Parts Clean/Pretreatmnt
16	24099580000000	Solvent Use Printing & Publish Printing
16	29999580000000	Solvent Use Industrial Miscellaneous
16	23022290000000	Solvent Use Industrial Coating Paper
16	40200710	Organic Solvent Surface Coating Adhesive General
16	23023290000000	Solvent Use Industrial Coating Wood Furnit. & Fixt

A-34 Number	SCC Code	SCC Description
16	23022090000000	Solvent Use Industrial Coating Marine
16	40201620	Organic Solvent Surface Coating Autos/Light Truck Repair Topcoat
16	30400199	Secondary Metals Sec. Aluminum Not Classified Other
16	25029282500000	Solvent Use Adhesive & Sealent Water Based
16	51050667400000	Solvent Use Consumer Products Astringents/Toners
17	22020405000000	Degreasing Cold Cleaning Petroleum Solvents
17	22020805000000	Degreasing Handwiping Petroleum Solvents
17	22020830220000	Degreasing Handwiping Alcohols
17	22020832040000	Degreasing Handwiping Ketones
17	22020833440000	Degreasing Handwiping Trichloroethane
17	40100398	Organic Solvent Cold Cleaning Other/Not Classfd Specify Solvent
17	22020633440000	Degreasing Vapor Degreasing Trichloroethane
17	22020881060000	Degreasing Handwiping Misc Solvent Blends
17	21020033000000	Solvent Use Dry Cleaning Perchloroethylene
17	40500215	Printing/Publish Printing Process Letterpress Cleaning Solution
17	22020430220000	Degreasing Cold Cleaning Alcohols
17	22020433330000	Degreasing Cold Cleaning Terpenes
17	22020481060000	Degreasing Cold Cleaning Misc Solvent Blends
18	24[$]	Biogenic Emissions - Isoprene
18	25[$]	Biogenic Emissions - Monoterpenes
18	91091202500000	Misc.Processes Natural Sources Vegetative
18	32[$]	Biogenic Emissions - 3-Methyl-2-Buten-1-ol
19	12012202420000	Waste Disposal Biodegradation Municipal Wastes
20	5004001100000	Fuel Combustion Industrl Ic Engines Natural Gas
20	20200202	Internlcombustion Industrial Natural Gas Reciprocating
20	20200204	Internlcombustion Industrial Natural Gas Engine-Cogeneratn
20	20100202	Internlcombustion Electric Generatn Natural Gas Reciprocating
20	20300201	Internlcombustion Commercl-Instutnl Natural Gas Reciprocating
20	20201001	Internlcombustion Industrial Propane Reciprocating
20	20100802	Internlcombustion Electric Generatn Landfill Gas Reciprocating
21	1000010*	Synthetic industrial emissions for project A-34: TCEQ code HW0018P
21	1000011*	Synthetic industrial emissions for project A-34: TCEQ code GB0004L
21	1000012*	Synthetic industrial emissions for project A-34: TCEQ code HG0232Q
21	1000013*	Synthetic industrial emissions for project A-34: TCEQ code HG0659W
21	1000014*	Synthetic industrial emissions for project A-34: TCEQ code HH0042M
21	1000015*	Synthetic industrial emissions for project A-34: TCEQ code JE00671
21	1000016*	Synthetic industrial emissions for project A-34: TCEQ code HG0033B
22	62061802620000	Farming Operation Livestock Waste
22	20100201	Internlcombustion Electric Generatn Natural Gas Turbine
22	20200203	Internlcombustion Industrial Natural Gas Turbine-Cogenertn
22	50100403	Solid Waste Displ Government Landfill Area Method
22	20200201	Internlcombustion Industrial Natural Gas Turbine
22	41040350180000	Chemical Processes Fabrication Fiberglass
22	81080814000000	Government Aircraft Military Jet Aircraft
22	42041260120000	Baking Commercial Bakeries
22	53053057020000	Pesticide Applicatn.Agricultural Non-Methyl Bromide
22	27501015	Internlcombustion Fixed Wing Aircraft Military Fixed Wing: Jp-5
22	53053032250000	Pesticide Applicatn.Agricultural Methyl Bromide
22	69068060000000	Cooking Commercial Charbroiling
22	30299998	Food/Agriculture Miscellaneous Not Classified Other
22	125	Commercial Jet Taxi
22	30800723	Rubber/Plastics Fab. Plastic Prod Fiberglass Resin General-Roll On
22	30800724	Rubber/Plastics Fab. Plastic Prod Fiberglass Resin General-Spray On
22	30800720	Rubber/Plastics Fab. Plastic Prod Fiberglass Resin Product-General
22	41040250620000	Chemical Processes Manufacturing Synthetic Rubber
22	53054057020000	Pesticide Applicatn.Structural Non-Methyl Bromide
22	10100601	Extcomb Boiler Electric Generatn Natural Gas >100Mmbtu/Hr Extf

A-34 Number	SCC Code	SCC Description
22	61060801100000	Fuel Combustion Residential Nat Gas Water Heatn
22	20300202	Internlcombustion Commercl-Instutnl Natural Gas Turbine
22	50100406	Solid Waste Displ Government Landfill Gas Collctn Sys Othr
22	27505001	Internlcombustion Fixed Wing Aircraft Civil Fixed Wing: Av Gas
22	30106011	Chemical Mfg Pharmaceuticals General Processes Coating
22	20300702	Internl Combustion Commercl - Institutldigester Gas Reciprocating

Notes

[#] SCC codes 2-12 are used by ARB for on-road emissions.

[$] SCC codes 24, 25 and 32 are used by ARB for biogenic emissions.

* SCC codes for synthetic industrial emissions (A-34 number = 21) are arbitrary.

Table A-4. Mean source profiles (PAMS fraction) for experiment 1 on August 5, 1997.

	A-34 Source Category Number							
	1	2	3	4	5	6	7	8
ETHENE	0.2213	0.2053	0.2700	0.2341	0.0000	0.0000	0.5587	0.1700
ACETYL	0.1218	0.1416	0.0761	0.2105	0.0000	0.0000	0.1782	0.0481
ETHANE	0.0335	0.0220	0.0498	0.0201	0.0000	0.0000	0.0205	0.0418
PROPE	0.0710	0.0690	0.0986	0.0602	0.0000	0.0000	0.0673	0.0628
N_PROP	0.0013	0.0014	0.0017	0.0007	0.0006	0.0027	0.0046	0.0047
I_BUTA	0.0003	0.0003	0.0003	0.0001	0.0056	0.0118	0.0229	0.0080
LBUT1E	0.0072	0.0084	0.0100	0.0064	0.0004	0.0011	0.0129	0.0071
N_BUTA	0.0129	0.0086	0.0109	0.0067	0.0311	0.0593	0.0020	0.0441
T2BUTE	0.0041	0.0038	0.0053	0.0029	0.0012	0.0047	0.0038	0.0070
C2BUTE	0.0030	0.0035	0.0038	0.0031	0.0008	0.0027	0.0018	0.0044
IPENTA	0.0906	0.0663	0.0770	0.0514	0.2085	0.3074	0.0091	0.2128
PENTE1	0.0018	0.0018	0.0017	0.0009	0.0024	0.0026	0.0050	0.0021
N_PENT	0.0366	0.0295	0.0257	0.0221	0.0396	0.0618	0.0026	0.0505
I_PREN	0.0020	0.0028	0.0017	0.0030	0.0002	0.0001	0.0000	0.0011
T2PENE	0.0029	0.0033	0.0023	0.0038	0.0078	0.0086	0.0006	0.0050
C2PENE	0.0016	0.0015	0.0013	0.0008	0.0042	0.0041	0.0005	0.0023
BU22DM	0.0071	0.0058	0.0050	0.0044	0.0050	0.0098	0.0008	0.0093
CPENTA	0.0049	0.0052	0.0034	0.0057	0.0037	0.0075	0.0002	0.0069
BU23DM	0.0117	0.0102	0.0096	0.0089	0.0204	0.0208	0.0000	0.0138
PENA2M	0.0412	0.0381	0.0316	0.0331	0.0641	0.0631	0.0050	0.0418
PENA3M	0.0242	0.0231	0.0190	0.0204	0.0358	0.0350	0.0015	0.0240
P1E2ME	0.0008	0.0006	0.0006	0.0004	0.0016	0.0013	0.0000	0.0006
N_HEX	0.0176	0.0180	0.0129	0.0160	0.0181	0.0173	0.0020	0.0138
MCYPNA	0.0314	0.0310	0.0221	0.0277	0.0249	0.0269	0.0019	0.0246
PEN24M	0.0041	0.0048	0.0045	0.0048	0.0211	0.0147	0.0002	0.0046
BENZE	0.0322	0.0282	0.0373	0.0287	0.0158	0.0113	0.0279	0.0250
CYHEXA	0.0069	0.0079	0.0045	0.0075	0.0042	0.0068	0.0003	0.0067
HEXA2M	0.0000	0.0003	0.0000	0.0000	0.0325	0.0223	0.0013	0.0023
PEN23M	0.0137	0.0153	0.0143	0.0134	0.0339	0.0230	0.0008	0.0112
HEXA3M	0.0073	0.0082	0.0064	0.0077	0.0349	0.0240	0.0038	0.0066
PA224M	0.0144	0.0150	0.0148	0.0113	0.0582	0.0393	0.0029	0.0129
N_HEPT	0.0048	0.0059	0.0041	0.0059	0.0200	0.0136	0.0007	0.0039
MECYHX	0.0059	0.0072	0.0043	0.0069	0.0095	0.0072	0.0008	0.0040
PA234M	0.0050	0.0060	0.0047	0.0049	0.0152	0.0102	0.0001	0.0039
TOLUE	0.0609	0.0703	0.0624	0.0652	0.0887	0.0603	0.0174	0.0451
HEP2ME	0.0028	0.0038	0.0025	0.0034	0.0073	0.0049	0.0005	0.0019
HEP3ME	0.0050	0.0064	0.0039	0.0050	0.0079	0.0052	0.0000	0.0028
N_OCT	0.0032	0.0043	0.0026	0.0034	0.0067	0.0042	0.0013	0.0018
ETBZ	0.0096	0.0130	0.0120	0.0107	0.0244	0.0152	0.0031	0.0079
MP_XYL	0.0328	0.0435	0.0355	0.0364	0.0608	0.0384	0.0073	0.0237
STYR	0.0012	0.0021	0.0011	0.0011	0.0000	0.0000	0.0006	0.0007
O_XYL	0.0114	0.0150	0.0124	0.0124	0.0238	0.0149	0.0034	0.0082
N_NON	0.0013	0.0020	0.0012	0.0017	0.0015	0.0009	0.0020	0.0008
IPRBZ	0.0001	0.0005	0.0004	0.0002	0.0006	0.0004	0.0007	0.0003
N_PRBZ	0.0019	0.0028	0.0020	0.0023	0.0038	0.0023	0.0017	0.0012
M_ETOL	0.0022	0.0033	0.0026	0.0020	0.0037	0.0023	0.0018	0.0017
P_ETOL	0.0027	0.0039	0.0032	0.0027	0.0057	0.0035	0.0006	0.0021
BZ135M	0.0032	0.0045	0.0035	0.0033	0.0068	0.0041	0.0023	0.0022
O_ETOL	0.0064	0.0091	0.0075	0.0064	0.0134	0.0083	0.0028	0.0049
BZ124M	0.0078	0.0113	0.0089	0.0075	0.0187	0.0113	0.0048	0.0056
N_DEC	0.0010	0.0008	0.0006	0.0003	0.0005	0.0003	0.0041	0.0004
BZ123M	0.0014	0.0022	0.0016	0.0015	0.0032	0.0020	0.0017	0.0011
DETBZ1	0.0002	0.0007	0.0006	0.0002	0.0010	0.0006	0.0004	0.0004
DETBZ2	0.0000	0.0001	0.0001	0.0000	0.0002	0.0001	0.0011	0.0000
N_UNDE	0.0001	0.0004	0.0002	0.0001	0.0002	0.0001	0.0018	0.0001

Table A-4 (continued).

	A-34 Source Category Number							
	9	10	11	12	13	14	15	16
ETHENE	0.0529	0.5587	0.0000	0.0000	0.0000	0.0004	0.0000	0.0106
ACETYL	0.0149	0.1782	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETHANE	0.0098	0.0205	0.0000	0.7146	0.1442	0.0014	0.0000	0.0156
PROPE	0.0193	0.0673	0.0000	0.0000	0.0032	0.0024	0.0000	0.0000
N_PROP	0.0022	0.0046	0.0059	0.1364	0.2218	0.3545	0.0000	0.0097
I_BUTA	0.0085	0.0229	0.0210	0.0210	0.1005	0.1488	0.0000	0.0046
LBUT1E	0.0027	0.0129	0.0020	0.0000	0.0001	0.0000	0.0000	0.0001
N_BUTA	0.0451	0.0020	0.1015	0.0486	0.2458	0.0858	0.0000	0.0236
T2BUTE	0.0042	0.0038	0.0098	0.0000	0.0000	0.0000	0.0000	0.0000
C2BUTE	0.0026	0.0018	0.0057	0.0000	0.0000	0.0000	0.0000	0.0000
IPENTA	0.2456	0.0091	0.4549	0.0130	0.0576	0.0000	0.0000	0.3208
PENTE1	0.0024	0.0050	0.0030	0.0000	0.0000	0.0000	0.0000	0.0000
N_PENT	0.0510	0.0026	0.0948	0.0189	0.1166	0.0000	0.0000	0.1797
I_PREN	0.0004	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T2PENE	0.0073	0.0006	0.0099	0.0000	0.0000	0.0000	0.0000	0.0000
C2PENE	0.0036	0.0005	0.0041	0.0000	0.0000	0.0000	0.0000	0.0000
BU22DM	0.0081	0.0008	0.0169	0.0007	0.0010	0.0000	0.0000	0.0002
CPENTA	0.0060	0.0002	0.0131	0.0012	0.0055	0.0000	0.0000	0.0337
BU23DM	0.0186	0.0000	0.0215	0.0014	0.0019	0.0000	0.0000	0.0003
PENA2M	0.0571	0.0050	0.0616	0.0050	0.0066	0.0000	0.0000	0.0011
PENA3M	0.0320	0.0015	0.0338	0.0029	0.0038	0.0000	0.0000	0.0006
P1E2ME	0.0012	0.0000	0.0007	0.0000	0.0000	0.0000	0.0000	0.0000
N_HEX	0.0166	0.0020	0.0160	0.0047	0.0326	0.0368	0.0004	0.0108
MCYPNA	0.0256	0.0019	0.0298	0.0035	0.0047	0.0001	0.0002	0.0257
PEN24M	0.0138	0.0002	0.0052	0.0028	0.0018	0.0003	0.0016	0.0072
BENZE	0.0172	0.0279	0.0046	0.0034	0.0036	0.0000	0.0000	0.0003
CYHEXA	0.0059	0.0003	0.0107	0.0010	0.0022	0.0015	0.0039	0.0028
HEXA2M	0.0196	0.0013	0.0070	0.0009	0.0006	0.0053	0.0265	0.0002
PEN23M	0.0231	0.0008	0.0067	0.0065	0.0042	0.0007	0.0034	0.0000
HEXA3M	0.0224	0.0038	0.0076	0.0041	0.0026	0.0006	0.0030	0.0000
PA224M	0.0377	0.0029	0.0111	0.0036	0.0011	0.0000	0.0000	0.0036
N_HEPT	0.0128	0.0007	0.0040	0.0017	0.0115	0.0379	0.1034	0.0156
MECYHX	0.0070	0.0008	0.0038	0.0004	0.0014	0.0399	0.2016	0.0173
PA234M	0.0100	0.0001	0.0028	0.0008	0.0002	0.0003	0.0016	0.0001
TOLUE	0.0655	0.0174	0.0179	0.0019	0.0051	0.1121	0.1630	0.2310
HEP2ME	0.0048	0.0005	0.0011	0.0005	0.0001	0.0076	0.0386	0.0004
HEP3ME	0.0054	0.0000	0.0011	0.0007	0.0002	0.0048	0.0244	0.0003
N_OCT	0.0043	0.0013	0.0005	0.0000	0.0111	0.0135	0.0683	0.0006
ETBZ	0.0161	0.0031	0.0015	0.0000	0.0000	0.0073	0.0150	0.0023
MP_XYL	0.0416	0.0073	0.0049	0.0000	0.0009	0.0664	0.0932	0.0377
STYR	0.0002	0.0006	0.0000	0.0000	0.0000	0.0001	0.0029	0.0000
O_XYL	0.0159	0.0034	0.0015	0.0000	0.0004	0.0292	0.0375	0.0366
N_NON	0.0011	0.0020	0.0001	0.0000	0.0033	0.0060	0.0184	0.0040
IPRBZ	0.0004	0.0007	0.0001	0.0000	0.0000	0.0008	0.0042	0.0000
N_PRBZ	0.0025	0.0017	0.0001	0.0000	0.0000	0.0005	0.0008	0.0006
M_ETOL	0.0026	0.0018	0.0002	0.0000	0.0000	0.0014	0.0062	0.0003
P_ETOL	0.0038	0.0006	0.0003	0.0000	0.0000	0.0015	0.0076	0.0001
BZ135M	0.0045	0.0023	0.0001	0.0000	0.0000	0.0004	0.0041	0.0000
O_ETOL	0.0090	0.0028	0.0006	0.0000	0.0000	0.0011	0.0056	0.0008
BZ124M	0.0121	0.0048	0.0004	0.0000	0.0000	0.0050	0.0348	0.0002
N_DEC	0.0004	0.0041	0.0000	0.0000	0.0040	0.0122	0.0616	0.0006
BZ123M	0.0021	0.0017	0.0001	0.0000	0.0000	0.0021	0.0106	0.0001
DETBZ1	0.0007	0.0004	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DETBZ2	0.0001	0.0011	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
N_UNDE	0.0002	0.0018	0.0000	0.0000	0.0000	0.0114	0.0578	0.0006

Table A-4 (concluded).

	A-34 Source Category Number				
	17	18	20	21	22
ETHENE	0.0000	0.0196	0.0346	0.2721	0.0887
ACETYL	0.0000	0.0000	0.0190	0.0018	0.0195
ETHANE	0.0000	0.0305	0.7175	0.0021	0.1435
PROPE	0.0000	0.0000	0.0619	0.1860	0.0161
N_PROP	0.0002	0.0208	0.1017	0.1400	0.0537
I_BUTA	0.0001	0.0000	0.0114	0.0562	0.0172
LBUT1E	0.0000	0.0000	0.0074	0.0159	0.0043
N_BUTA	0.0001	0.0000	0.0265	0.0961	0.0999
T2BUTE	0.0000	0.0000	0.0036	0.0029	0.0001
C2BUTE	0.0000	0.0000	0.0006	0.0001	0.0010
IPENTA	0.0000	0.0000	0.0017	0.0000	0.0411
PENTE1	0.0000	0.0022	0.0002	0.0062	0.0028
N_PENT	0.0000	0.0000	0.0037	0.0101	0.0693
I_PREN	0.0000	0.9199	0.0000	0.0040	0.0000
T2PENE	0.0000	0.0000	0.0002	0.0002	0.0000
C2PENE	0.0000	0.0000	0.0000	0.0000	0.0000
BU22DM	0.0000	0.0000	0.0002	0.0143	0.0024
CPENTA	0.0000	0.0000	0.0006	0.0022	0.0084
BU23DM	0.0000	0.0000	0.0000	0.0000	0.0047
PENA2M	0.0001	0.0000	0.0001	0.0037	0.0169
PENA3M	0.0000	0.0000	0.0004	0.0010	0.0095
P1E2ME	0.0000	0.0000	0.0004	0.0000	0.0000
N_HEX	0.0000	0.0000	0.0004	0.0283	0.0243
MCYPNA	0.0003	0.0000	0.0008	0.0025	0.0118
PEN24M	0.0019	0.0000	0.0003	0.0001	0.0001
BENZE	0.0000	0.0000	0.0022	0.0470	0.0818
CYHEXA	0.0044	0.0000	0.0002	0.0100	0.0060
HEXA2M	0.0304	0.0000	0.0000	0.0019	0.0000
PEN23M	0.0039	0.0000	0.0003	0.0000	0.0002
HEXA3M	0.0035	0.0000	0.0003	0.0001	0.0001
PA224M	0.0253	0.0000	0.0001	0.0012	0.0051
N_HEPT	0.1176	0.0000	0.0003	0.0124	0.0036
MECYHX	0.2307	0.0000	0.0003	0.0012	0.1522
PA234M	0.0072	0.0000	0.0000	0.0012	0.0000
TOLUE	0.1086	0.0020	0.0007	0.0557	0.0412
HEP2ME	0.0473	0.0000	0.0000	0.0000	0.0000
HEP3ME	0.0331	0.0000	0.0003	0.0000	0.0000
N_OCT	0.0781	0.0000	0.0003	0.0020	0.0001
ETBZ	0.0103	0.0017	0.0002	0.0043	0.0005
MP_XYL	0.0391	0.0012	0.0003	0.0047	0.0425
STYR	0.0004	0.0000	0.0000	0.0030	0.0050
O_XYL	0.0117	0.0005	0.0002	0.0032	0.0215
N_NON	0.0371	0.0000	0.0001	0.0020	0.0036
IPRBZ	0.0046	0.0000	0.0000	0.0033	0.0000
N_PRBZ	0.0034	0.0000	0.0000	0.0000	0.0006
M_ETOL	0.0081	0.0000	0.0001	0.0000	0.0003
P_ETOL	0.0087	0.0000	0.0000	0.0000	0.0000
BZ135M	0.0023	0.0015	0.0003	0.0004	0.0000
O_ETOL	0.0064	0.0000	0.0001	0.0000	0.0001
BZ124M	0.0265	0.0000	0.0001	0.0007	0.0001
N_DEC	0.0705	0.0000	0.0001	0.0003	0.0004
BZ123M	0.0121	0.0000	0.0001	0.0000	0.0000
DETBZ1	0.0000	0.0000	0.0000	0.0000	0.0000
DETBZ2	0.0000	0.0000	0.0000	0.0000	0.0000
N_UNDE	0.0661	0.0000	0.0000	0.0000	0.0004

Table A-5. Mean source profiles (PAMS fraction) for experiment 3 on August 5, 1997.

	A-34 Source Category Number							
	1	2	3	4	5	6	7	8
ETHENE	0.1942	0.1941	0.1942	0.1942	0.0000	0.0000	0.2440	0.1213
ACETYL	0.1167	0.1167	0.1167	0.1167	0.0000	0.0000	0.0680	0.0729
ETHANE	0.0411	0.0411	0.0411	0.0411	0.0002	0.0008	0.0272	0.0384
PROPE	0.0609	0.0609	0.0609	0.0609	0.0001	0.0006	0.0658	0.0394
N_PROP	0.0031	0.0031	0.0031	0.0031	0.0002	0.0011	0.0348	0.0045
I_BUTA	0.0035	0.0035	0.0035	0.0035	0.0041	0.0098	0.0033	0.0091
LBUT1E	0.0045	0.0045	0.0045	0.0045	0.0016	0.0031	0.0364	0.0049
N_BUTA	0.0205	0.0205	0.0205	0.0205	0.0234	0.0507	0.0077	0.0471
T2BUTE	0.0065	0.0065	0.0065	0.0065	0.0054	0.0112	0.0030	0.0115
C2BUTE	0.0064	0.0064	0.0064	0.0064	0.0058	0.0115	0.0036	0.0114
IPENTA	0.1087	0.1087	0.1087	0.1087	0.1527	0.2278	0.0126	0.1928
PENTE1	0.0057	0.0057	0.0057	0.0057	0.0081	0.0114	0.0088	0.0095
N_PENT	0.0327	0.0327	0.0327	0.0327	0.0503	0.0663	0.0146	0.0534
I_PREN	0.0043	0.0043	0.0043	0.0043	0.0009	0.0010	0.0000	0.0031
T2PENE	0.0119	0.0119	0.0119	0.0119	0.0201	0.0260	0.0036	0.0201
C2PENE	0.0063	0.0063	0.0063	0.0063	0.0107	0.0137	0.0029	0.0105
BU22DM	0.0041	0.0041	0.0041	0.0041	0.0057	0.0063	0.0211	0.0052
CPENTA	0.0038	0.0038	0.0038	0.0038	0.0077	0.0084	0.0031	0.0058
BU23DM	0.0012	0.0012	0.0012	0.0012	0.0018	0.0016	0.0025	0.0011
PENA2M	0.0319	0.0319	0.0319	0.0319	0.0672	0.0664	0.0159	0.0434
PENA3M	0.0203	0.0203	0.0203	0.0203	0.0436	0.0417	0.0073	0.0267
P1E2ME	0.0020	0.0020	0.0020	0.0020	0.0045	0.0043	0.0018	0.0027
N_HEX	0.0191	0.0191	0.0191	0.0191	0.0410	0.0372	0.0077	0.0232
MCYPNA	0.0121	0.0121	0.0121	0.0121	0.0263	0.0232	0.0051	0.0142
PEN24M	0.0053	0.0053	0.0053	0.0053	0.0112	0.0094	0.0025	0.0057
BENZE	0.0280	0.0280	0.0280	0.0280	0.0161	0.0137	0.0283	0.0210
CYHEXA	0.0026	0.0026	0.0026	0.0026	0.0063	0.0052	0.0019	0.0029
HEXA2M	0.0126	0.0126	0.0126	0.0126	0.0283	0.0222	0.0000	0.0124
PEN23M	0.0053	0.0053	0.0053	0.0053	0.0113	0.0089	0.0063	0.0052
HEXA3M	0.0132	0.0132	0.0132	0.0132	0.0286	0.0223	0.0160	0.0127
PA224M	0.0275	0.0275	0.0275	0.0275	0.0642	0.0490	0.0090	0.0262
N_HEPT	0.0095	0.0095	0.0095	0.0095	0.0206	0.0155	0.0039	0.0087
MECYHX	0.0053	0.0053	0.0053	0.0053	0.0139	0.0105	0.0031	0.0051
PA234M	0.0110	0.0110	0.0110	0.0110	0.0300	0.0217	0.0019	0.0099
TOLUE	0.0566	0.0566	0.0566	0.0566	0.1054	0.0761	0.0338	0.0460
HEP2ME	0.0036	0.0036	0.0036	0.0036	0.0093	0.0066	0.0027	0.0031
HEP3ME	0.0047	0.0047	0.0047	0.0047	0.0116	0.0082	0.0027	0.0039
N_OCT	0.0041	0.0041	0.0041	0.0041	0.0099	0.0068	0.0019	0.0033
ETBZ	0.0087	0.0087	0.0087	0.0087	0.0148	0.0100	0.0186	0.0062
MP_XYL	0.0259	0.0259	0.0259	0.0259	0.0483	0.0324	0.0718	0.0187
STYR	0.0028	0.0028	0.0028	0.0028	0.0000	0.0000	0.0123	0.0018
O_XYL	0.0099	0.0099	0.0099	0.0099	0.0191	0.0127	0.0244	0.0071
N_NON	0.0022	0.0022	0.0022	0.0022	0.0051	0.0033	0.0061	0.0016
IPRBZ	0.0008	0.0008	0.0008	0.0008	0.0020	0.0013	0.0019	0.0006
N_PRBZ	0.0020	0.0020	0.0020	0.0020	0.0041	0.0027	0.0061	0.0014
M_ETOL	0.0077	0.0077	0.0077	0.0077	0.0135	0.0087	0.0239	0.0052
P_ETOL	0.0033	0.0033	0.0033	0.0033	0.0056	0.0036	0.0081	0.0022
BZ135M	0.0042	0.0042	0.0042	0.0042	0.0073	0.0047	0.0121	0.0028
O_ETOL	0.0026	0.0026	0.0026	0.0026	0.0041	0.0026	0.0115	0.0018
BZ124M	0.0109	0.0109	0.0109	0.0109	0.0168	0.0108	0.0430	0.0073
N_DEC	0.0011	0.0011	0.0011	0.0011	0.0014	0.0009	0.0128	0.0007
BZ123M	0.0025	0.0025	0.0025	0.0025	0.0041	0.0026	0.0096	0.0017
DETBZ1	0.0008	0.0008	0.0008	0.0008	0.0013	0.0008	0.0000	0.0005
DETBZ2	0.0032	0.0032	0.0032	0.0032	0.0042	0.0027	0.0000	0.0020
N_UNDE	0.0007	0.0007	0.0007	0.0007	0.0008	0.0005	0.0236	0.0005

Table A-5 (continued).

	A-34 Source Category Number							
	9	10	11	12	13	14	15	16
ETHENE	0.0351	0.2440	0.0000	0.0016	0.0000	0.0004	0.0000	0.0106
ACETYL	0.0211	0.0680	0.0000	0.0005	0.0000	0.0000	0.0000	0.0000
ETHANE	0.0080	0.0272	0.0017	0.0105	0.0238	0.0014	0.0000	0.0156
PROPE	0.0114	0.0658	0.0013	0.0024	0.0305	0.0024	0.0000	0.0000
N_PROP	0.0013	0.0348	0.0024	0.0353	0.0959	0.3545	0.0000	0.0097
I_BUTA	0.0076	0.0033	0.0184	0.0584	0.1561	0.1488	0.0000	0.0046
LBUT1E	0.0031	0.0364	0.0053	0.0002	0.0001	0.0000	0.0000	0.0001
N_BUTA	0.0404	0.0077	0.0924	0.3742	0.3732	0.0858	0.0000	0.0236
T2BUTE	0.0093	0.0030	0.0201	0.0062	0.0125	0.0000	0.0000	0.0000
C2BUTE	0.0095	0.0036	0.0202	0.0049	0.0098	0.0000	0.0000	0.0000
IPENTA	0.1929	0.0126	0.3425	0.1199	0.0229	0.0000	0.0000	0.3208
PENTE1	0.0098	0.0088	0.0164	0.0266	0.0076	0.0000	0.0000	0.0000
N_PENT	0.0574	0.0146	0.0906	0.0450	0.0913	0.0000	0.0000	0.1797
I_PREN	0.0016	0.0000	0.0011	0.0231	0.0000	0.0000	0.0000	0.0000
T2PENE	0.0224	0.0036	0.0350	0.0065	0.0120	0.0000	0.0000	0.0000
C2PENE	0.0118	0.0029	0.0182	0.0030	0.0060	0.0000	0.0000	0.0000
BU22DM	0.0058	0.0211	0.0072	0.0040	0.0077	0.0000	0.0000	0.0002
CPENTA	0.0074	0.0031	0.0094	0.0029	0.0065	0.0000	0.0000	0.0337
BU23DM	0.0015	0.0025	0.0011	0.0000	0.0002	0.0000	0.0000	0.0003
PENA2M	0.0603	0.0159	0.0653	0.0002	0.0032	0.0000	0.0000	0.0011
PENA3M	0.0382	0.0073	0.0389	0.0079	0.0176	0.0000	0.0000	0.0006
P1E2ME	0.0039	0.0018	0.0040	0.0000	0.0000	0.0000	0.0000	0.0000
N_HEX	0.0346	0.0077	0.0315	0.0783	0.0331	0.0368	0.0004	0.0108
MCYPNA	0.0218	0.0051	0.0185	0.0061	0.0153	0.0001	0.0002	0.0257
PEN24M	0.0090	0.0025	0.0068	0.0015	0.0035	0.0003	0.0016	0.0072
BENZE	0.0167	0.0283	0.0100	0.0496	0.0193	0.0000	0.0000	0.0003
CYHEXA	0.0049	0.0019	0.0036	0.0299	0.0032	0.0015	0.0039	0.0028
HEXA2M	0.0216	0.0000	0.0129	0.0001	0.0013	0.0053	0.0265	0.0002
PEN23M	0.0087	0.0063	0.0054	0.0000	0.0001	0.0007	0.0034	0.0000
HEXA3M	0.0218	0.0160	0.0128	0.0015	0.0044	0.0006	0.0030	0.0000
PA224M	0.0479	0.0090	0.0259	0.0011	0.0016	0.0000	0.0000	0.0036
N_HEPT	0.0153	0.0039	0.0078	0.0225	0.0073	0.0379	0.1034	0.0156
MECYHX	0.0101	0.0031	0.0052	0.0005	0.0023	0.0399	0.2016	0.0173
PA234M	0.0212	0.0019	0.0090	0.0002	0.0005	0.0003	0.0016	0.0001
TOLUE	0.0778	0.0338	0.0314	0.0207	0.0193	0.1121	0.1630	0.2310
HEP2ME	0.0065	0.0027	0.0024	0.0003	0.0011	0.0076	0.0386	0.0004
HEP3ME	0.0081	0.0027	0.0030	0.0003	0.0011	0.0048	0.0244	0.0003
N_OCT	0.0069	0.0019	0.0022	0.0024	0.0011	0.0135	0.0683	0.0006
ETBZ	0.0106	0.0186	0.0026	0.0053	0.0019	0.0073	0.0150	0.0023
MP_XYL	0.0340	0.0718	0.0081	0.0058	0.0001	0.0664	0.0932	0.0377
STYR	0.0005	0.0123	0.0000	0.0069	0.0000	0.0001	0.0029	0.0000
O_XYL	0.0134	0.0244	0.0029	0.0179	0.0030	0.0292	0.0375	0.0366
N_NON	0.0034	0.0061	0.0006	0.0014	0.0002	0.0060	0.0184	0.0040
IPRBZ	0.0013	0.0019	0.0002	0.0141	0.0011	0.0008	0.0042	0.0000
N_PRBZ	0.0028	0.0061	0.0004	0.0001	0.0001	0.0005	0.0008	0.0006
M_ETOL	0.0094	0.0239	0.0014	0.0000	0.0000	0.0014	0.0062	0.0003
P_ETOL	0.0039	0.0081	0.0005	0.0000	0.0000	0.0015	0.0076	0.0001
BZ135M	0.0050	0.0121	0.0007	0.0000	0.0001	0.0004	0.0041	0.0000
O_ETOL	0.0029	0.0115	0.0004	0.0000	0.0000	0.0011	0.0056	0.0008
BZ124M	0.0119	0.0430	0.0016	0.0002	0.0022	0.0050	0.0348	0.0002
N_DEC	0.0010	0.0128	0.0001	0.0000	0.0002	0.0122	0.0616	0.0006
BZ123M	0.0029	0.0096	0.0004	0.0000	0.0000	0.0021	0.0106	0.0001
DETBZ1	0.0009	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000
DETBZ2	0.0030	0.0000	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000
N_UNDE	0.0006	0.0236	0.0001	0.0000	0.0000	0.0114	0.0578	0.0006

Table A-5 (concluded).

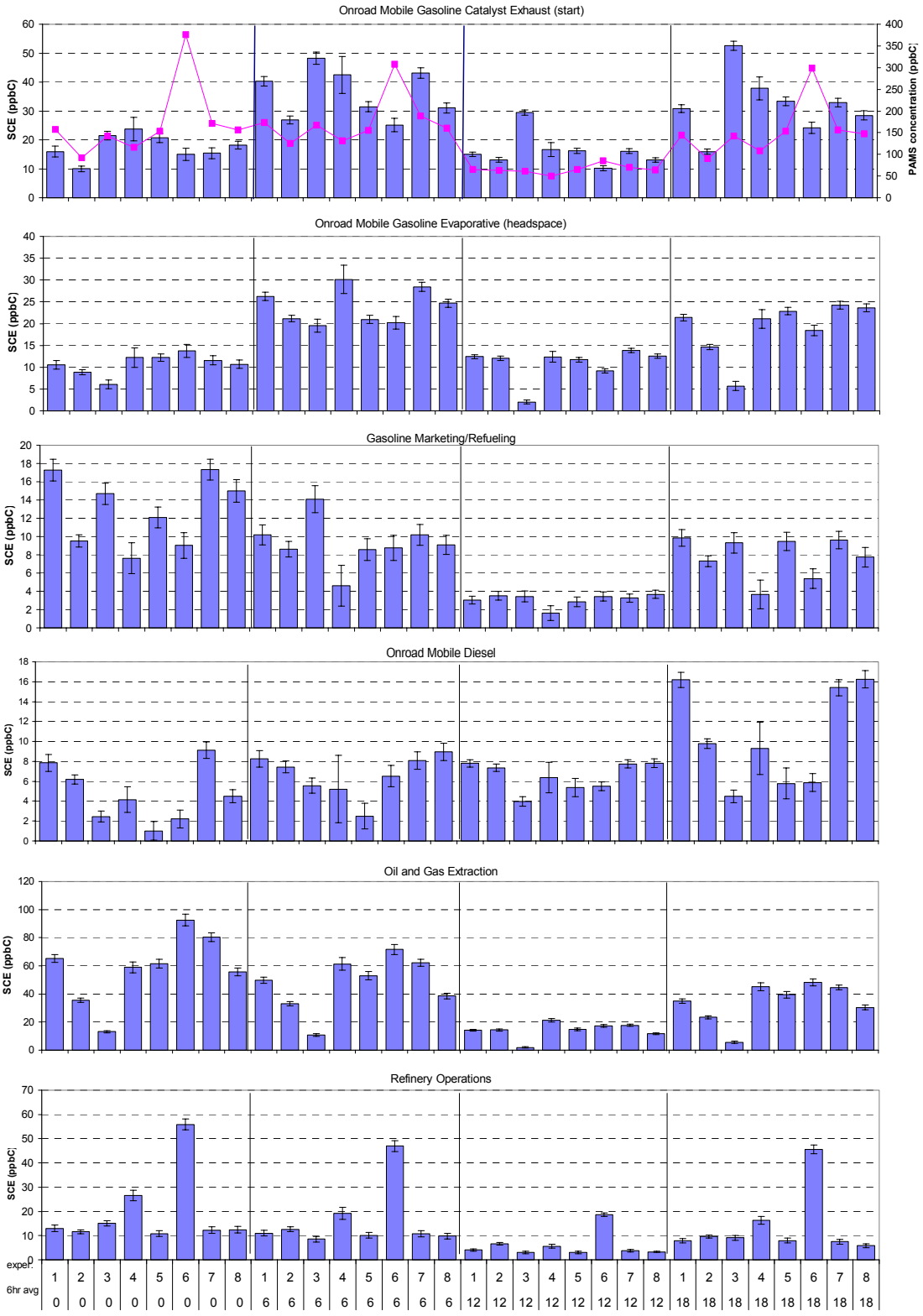
	A-34 Source Category Number				
	17	18	20	21	22
ETHENE	0.0000	0.0196	0.0346	0.2721	0.0882
ACETYL	0.0000	0.0000	0.0190	0.0018	0.0195
ETHANE	0.0000	0.0305	0.7175	0.0021	0.1436
PROPE	0.0000	0.0000	0.0619	0.1860	0.0159
N_PROP	0.0002	0.0208	0.1017	0.1400	0.0537
I_BUTA	0.0001	0.0000	0.0114	0.0562	0.0172
LBUT1E	0.0000	0.0000	0.0074	0.0159	0.0042
N_BUTA	0.0001	0.0000	0.0265	0.0961	0.1000
T2BUTE	0.0000	0.0000	0.0036	0.0029	0.0001
C2BUTE	0.0000	0.0000	0.0006	0.0001	0.0010
IPENTA	0.0000	0.0000	0.0017	0.0000	0.0414
PENTE1	0.0000	0.0022	0.0002	0.0062	0.0028
N_PENT	0.0000	0.0000	0.0037	0.0101	0.0694
I_PREN	0.0000	0.9199	0.0000	0.0040	0.0000
T2PENE	0.0000	0.0000	0.0002	0.0002	0.0001
C2PENE	0.0000	0.0000	0.0000	0.0000	0.0000
BU22DM	0.0000	0.0000	0.0002	0.0143	0.0024
CPENTA	0.0000	0.0000	0.0006	0.0022	0.0084
BU23DM	0.0000	0.0000	0.0000	0.0000	0.0046
PENA2M	0.0001	0.0000	0.0001	0.0037	0.0170
PENA3M	0.0000	0.0000	0.0004	0.0010	0.0095
P1E2ME	0.0000	0.0000	0.0004	0.0000	0.0000
N_HEX	0.0000	0.0000	0.0004	0.0283	0.0243
MCYPNA	0.0003	0.0000	0.0008	0.0025	0.0117
PEN24M	0.0019	0.0000	0.0003	0.0001	0.0000
BENZE	0.0000	0.0000	0.0022	0.0470	0.0817
CYHEXA	0.0044	0.0000	0.0002	0.0100	0.0060
HEXA2M	0.0304	0.0000	0.0000	0.0019	0.0001
PEN23M	0.0039	0.0000	0.0003	0.0000	0.0000
HEXA3M	0.0035	0.0000	0.0003	0.0001	0.0001
PA224M	0.0253	0.0000	0.0001	0.0012	0.0052
N_HEPT	0.1176	0.0000	0.0003	0.0124	0.0037
MECYHX	0.2307	0.0000	0.0003	0.0012	0.1523
PA234M	0.0072	0.0000	0.0000	0.0012	0.0001
TOLUE	0.1086	0.0020	0.0007	0.0557	0.0411
HEP2ME	0.0473	0.0000	0.0000	0.0000	0.0000
HEP3ME	0.0331	0.0000	0.0003	0.0000	0.0000
N_OCT	0.0781	0.0000	0.0003	0.0020	0.0001
ETBZ	0.0103	0.0017	0.0002	0.0043	0.0005
MP_XYL	0.0391	0.0012	0.0003	0.0047	0.0423
STYR	0.0004	0.0000	0.0000	0.0030	0.0050
O_XYL	0.0117	0.0005	0.0002	0.0032	0.0214
N_NON	0.0371	0.0000	0.0001	0.0020	0.0036
IPRBZ	0.0046	0.0000	0.0000	0.0033	0.0000
N_PRBZ	0.0034	0.0000	0.0000	0.0000	0.0006
M_ETOL	0.0081	0.0000	0.0001	0.0000	0.0003
P_ETOL	0.0087	0.0000	0.0000	0.0000	0.0000
BZ135M	0.0023	0.0015	0.0003	0.0004	0.0000
O_ETOL	0.0064	0.0000	0.0001	0.0000	0.0000
BZ124M	0.0265	0.0000	0.0001	0.0007	0.0001
N_DEC	0.0705	0.0000	0.0001	0.0003	0.0004
BZ123M	0.0121	0.0000	0.0001	0.0000	0.0000
DETBZ1	0.0000	0.0000	0.0000	0.0000	0.0000
DETBZ2	0.0000	0.0000	0.0000	0.0000	0.0000

Table A-6. DRI source profiles (PAMS fraction) for Round 3 experiments.

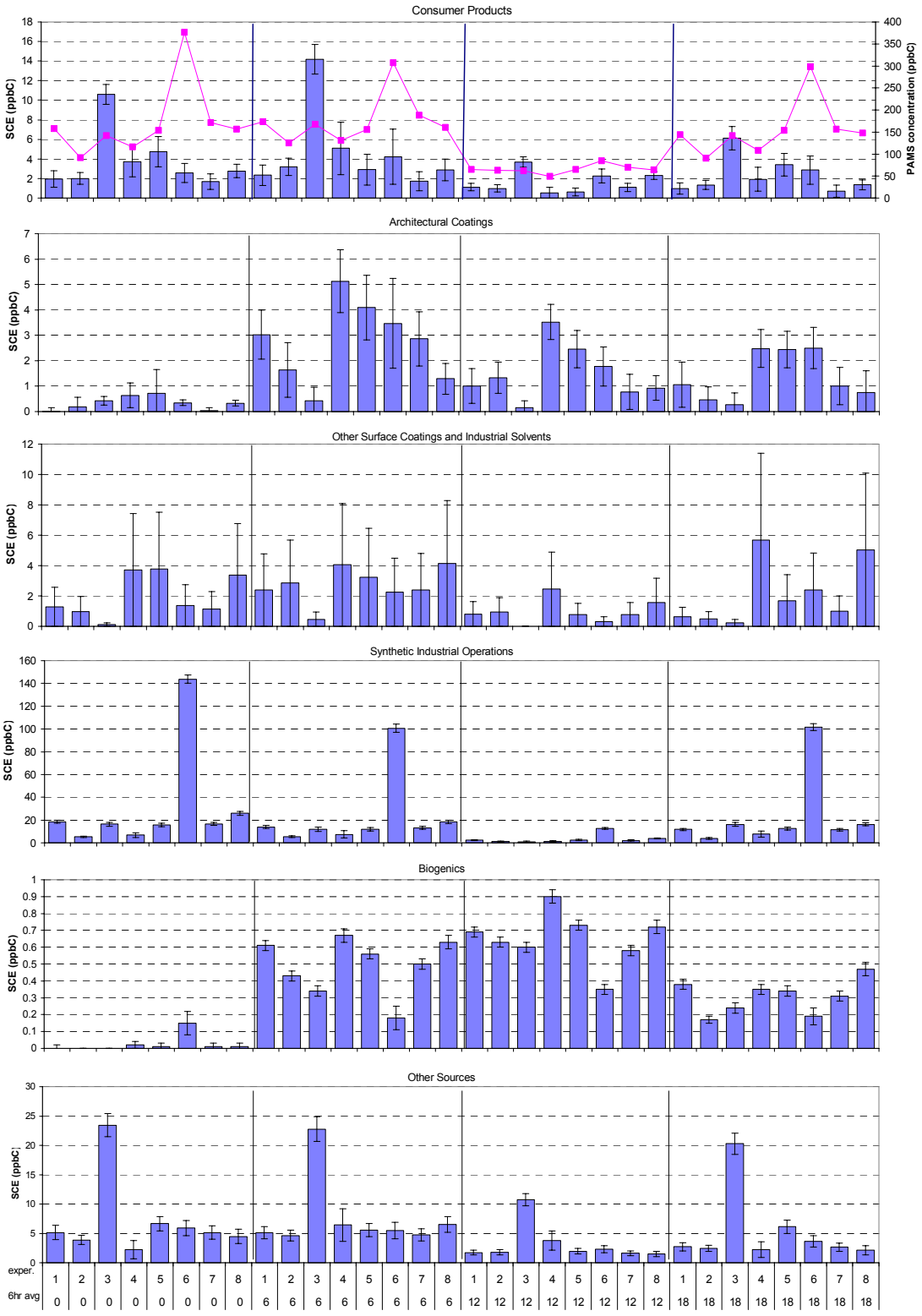
Name	NCATsb96	LG_EtO96	EvaEtO96	TuMchHDc	CPcomp_1	CNG/LPG	Biogenic	BkgAMcom
ETHENE	0.100	0.000	0.000	0.070	0.001	0.000	0.000	0.007
ACETYL	0.026	0.000	0.000	0.013	0.000	0.000	0.000	0.012
ETHANE	0.020	0.000	0.000	0.008	0.000	0.036	0.000	0.032
PROPE	0.055	0.000	0.000	0.028	0.000	0.003	0.000	0.004
N_PROP	0.001	0.000	0.003	0.016	0.048	0.056	0.000	0.019
I_BUTA	0.000	0.002	0.016	0.002	0.154	0.001	0.000	0.006
LBUT1E	0.007	0.000	0.001	0.021	0.000	0.000	0.000	0.001
N_BUTA	0.008	0.009	0.076	0.005	0.029	0.002	0.000	0.010
T2BUTE	0.004	0.000	0.007	0.002	0.000	0.000	0.000	0.000
C2BUTE	0.003	0.000	0.004	0.002	0.000	0.000	0.000	0.000
IPENTA	0.074	0.071	0.422	0.009	0.000	0.000	0.000	0.012
PENTE1	0.002	0.001	0.003	0.006	0.000	0.000	0.000	0.001
N_PENT	0.025	0.013	0.088	0.011	0.000	0.000	0.000	0.005
I_PREN	0.002	0.000	0.000	0.000	0.000	0.000	0.900	0.000
T2PENE	0.002	0.003	0.009	0.003	0.000	0.000	0.000	0.000
C2PENE	0.001	0.001	0.004	0.002	0.000	0.000	0.000	0.000
BU22DM	0.006	0.002	0.019	0.019	0.000	0.000	0.000	0.001
CPENTA	0.003	0.001	0.012	0.002	0.000	0.000	0.000	0.001
BU23DM	0.011	0.009	0.024	0.002	0.000	0.000	0.000	0.001
PENA2M	0.036	0.030	0.067	0.014	0.000	0.000	0.000	0.003
PENA3M	0.022	0.017	0.037	0.007	0.000	0.000	0.000	0.002
P1E2ME	0.001	0.001	0.001	0.002	0.000	0.000	0.000	0.000
N_HEX	0.015	0.009	0.017	0.007	0.017	0.000	0.000	0.005
MCYPNA	0.025	0.011	0.032	0.004	0.000	0.000	0.000	0.003
PEN24M	0.006	0.034	0.006	0.003	0.000	0.000	0.000	0.001
BENZE	0.039	0.011	0.004	0.023	0.000	0.000	0.000	0.007
CYHEXA	0.005	0.002	0.012	0.002	0.000	0.000	0.000	0.001
HEXA2M	0.000	0.052	0.008	0.000	0.000	0.000	0.000	0.001
PEN23M	0.019	0.055	0.008	0.006	0.000	0.000	0.000	0.002
HEXA3M	0.009	0.057	0.009	0.016	0.000	0.000	0.000	0.010
PA224M	0.022	0.108	0.015	0.010	0.000	0.000	0.000	0.002
N_HEPT	0.006	0.018	0.005	0.004	0.012	0.000	0.000	0.002
MECYHX	0.006	0.015	0.005	0.003	0.001	0.000	0.000	0.001
PA234M	0.007	0.028	0.004	0.002	0.000	0.000	0.000	0.000
TOLUE	0.076	0.058	0.019	0.032	0.070	0.000	0.000	0.015
HEP2ME	0.004	0.014	0.001	0.000	0.000	0.000	0.000	0.001
HEP3ME	0.006	0.015	0.001	0.003	0.000	0.000	0.000	0.000
N_OCT	0.004	0.007	0.001	0.002	0.000	0.000	0.000	0.001
ETBZ	0.017	0.019	0.001	0.020	0.001	0.000	0.000	0.002
MP_XYL	0.050	0.046	0.005	0.078	0.007	0.000	0.000	0.005
STYR	0.001	0.000	0.000	0.013	0.000	0.000	0.000	0.009
O_XYL	0.017	0.018	0.001	0.027	0.005	0.000	0.000	0.003
N_NON	0.002	0.002	0.000	0.008	0.022	0.000	0.000	0.001
IPRBZ	0.001	0.001	0.000	0.002	0.000	0.000	0.000	0.000
N_PRBZ	0.003	0.003	0.000	0.007	0.003	0.000	0.000	0.001
M_ETOL	0.012	0.012	0.000	0.029	0.000	0.000	0.000	0.003
P_ETOL	0.005	0.005	0.000	0.010	0.000	0.000	0.000	0.002
BZ135M	0.006	0.006	0.000	0.015	0.000	0.000	0.000	0.003
O_ETOL	0.004	0.003	0.000	0.014	0.001	0.000	0.000	0.002
BZ124M	0.014	0.016	0.000	0.053	0.000	0.000	0.000	0.011
N_DEC	0.001	0.001	0.000	0.019	0.000	0.000	0.000	0.002
BZ123M	0.003	0.003	0.000	0.012	0.000	0.000	0.000	0.002
DETBZ1	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000
DETBZ2	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.003
N_UNDE	0.000	0.000	0.000	0.038	0.000	0.000	0.000	0.002
Sum PAMS	**0.883**	**0.786**	**0.948**	**0.786**	**0.466**	**0.997**	**1.000**	**0.439**
Sum ROG	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**

APPENDIX B

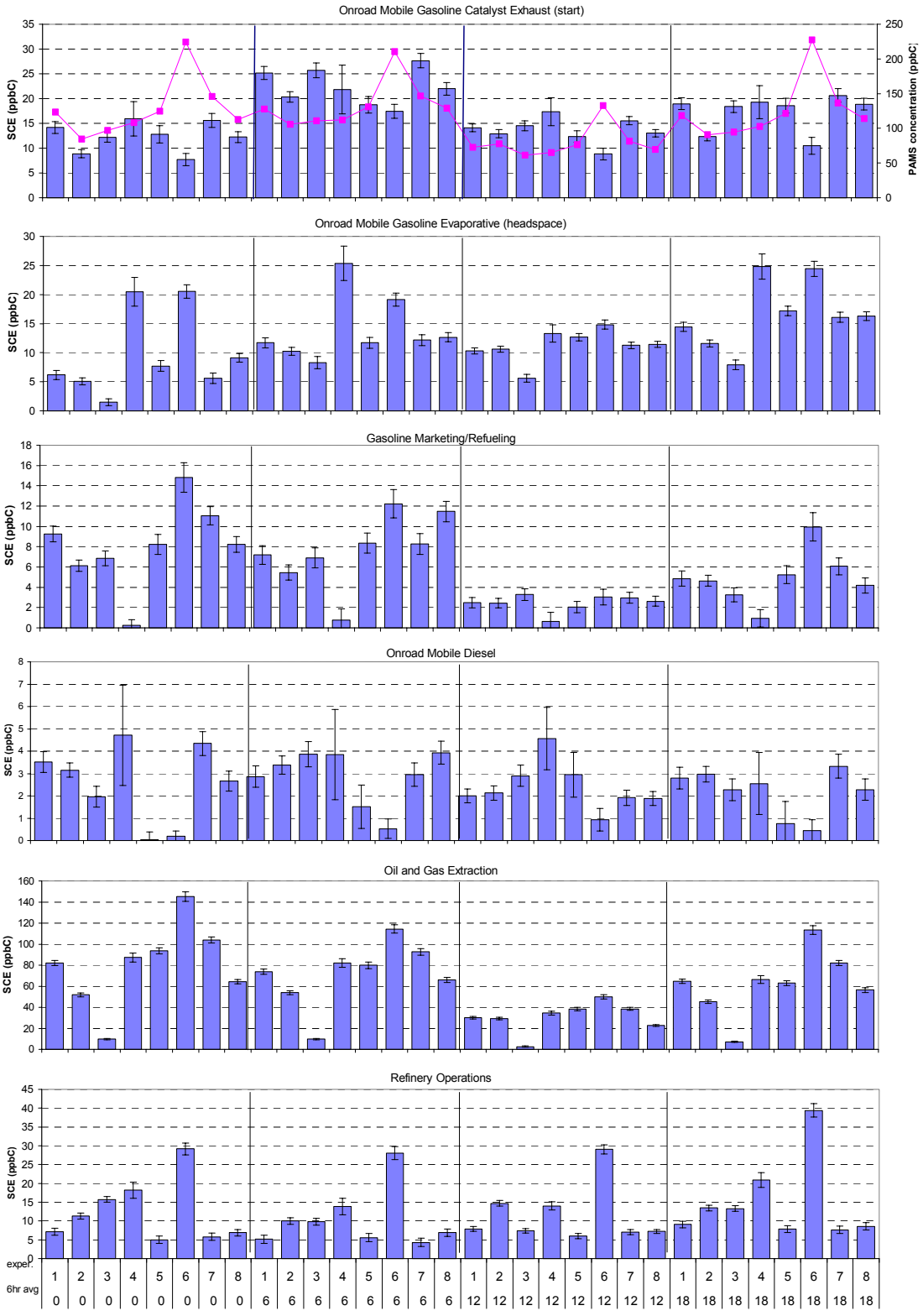
CMB-Derived Source Contribution Estimates for Round 4 by Receptor Location and Time of Day and Experiment



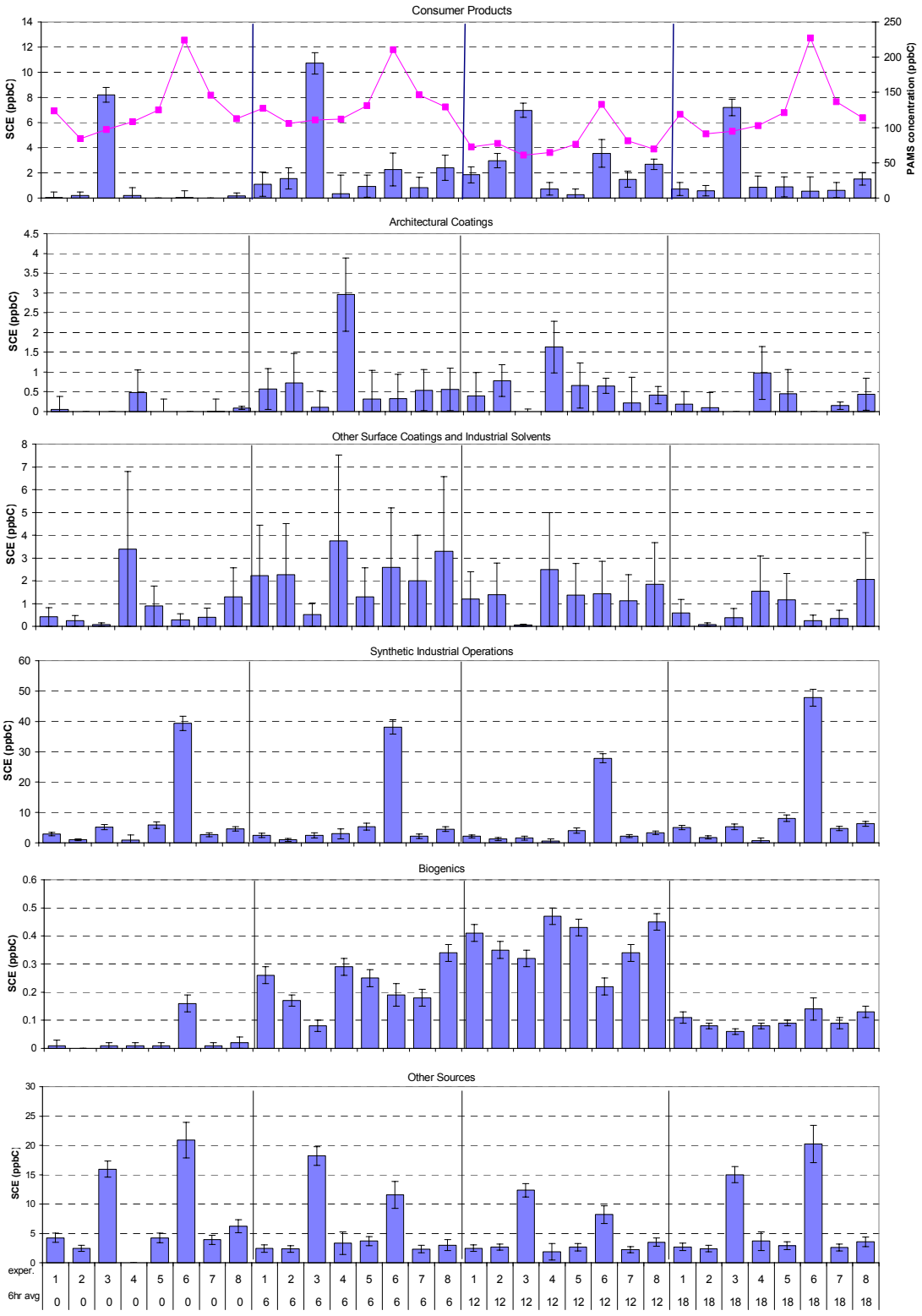
Mean source contribution estimates at LAX by 6-hour period. Start hour (PDT) is indicated.



Mean source contribution estimates at LAX by 6-hour period, cont'd.

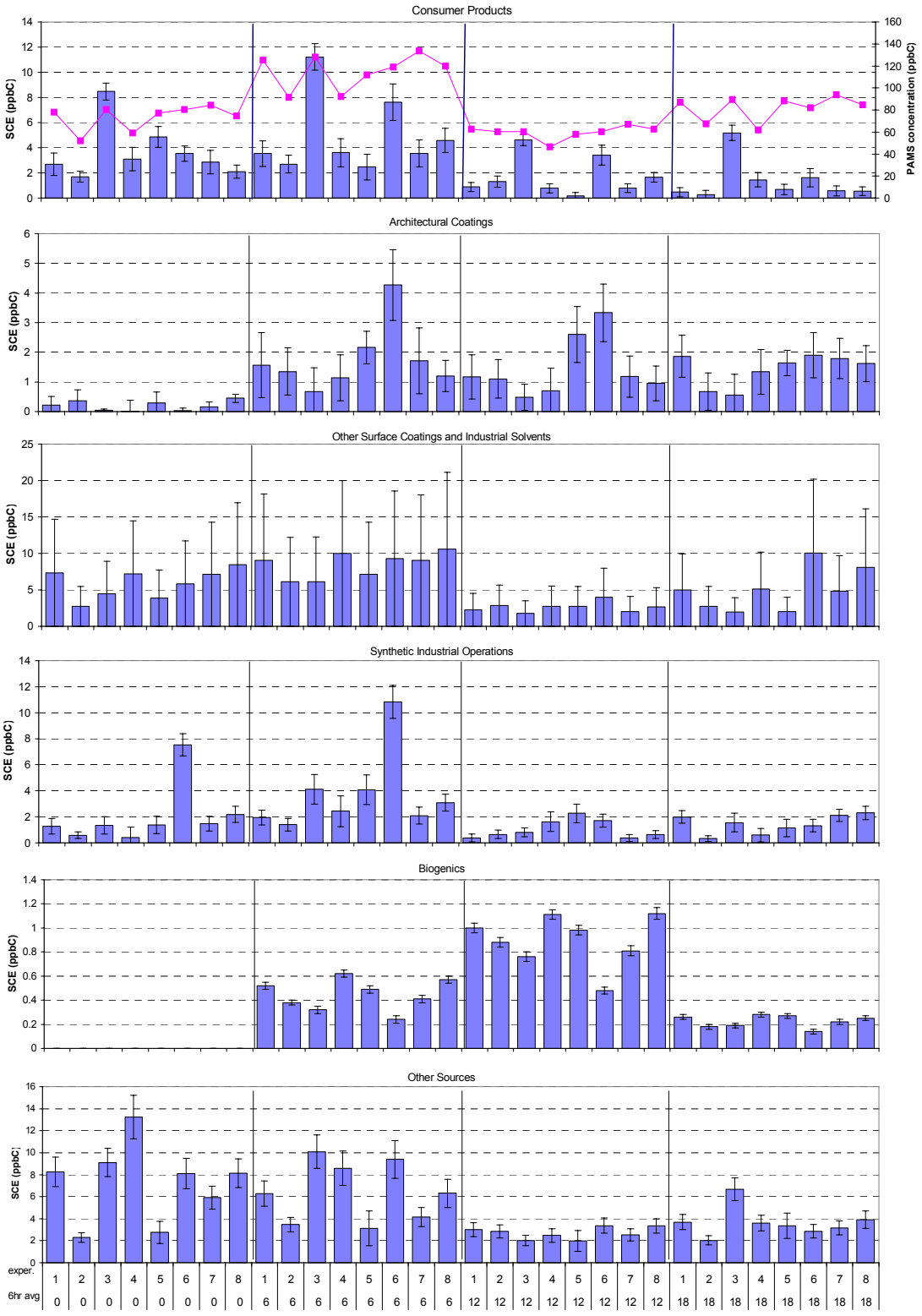


Mean source contribution estimates at Long Beach by 6-hour period. Start hour (PDT) is indicated.

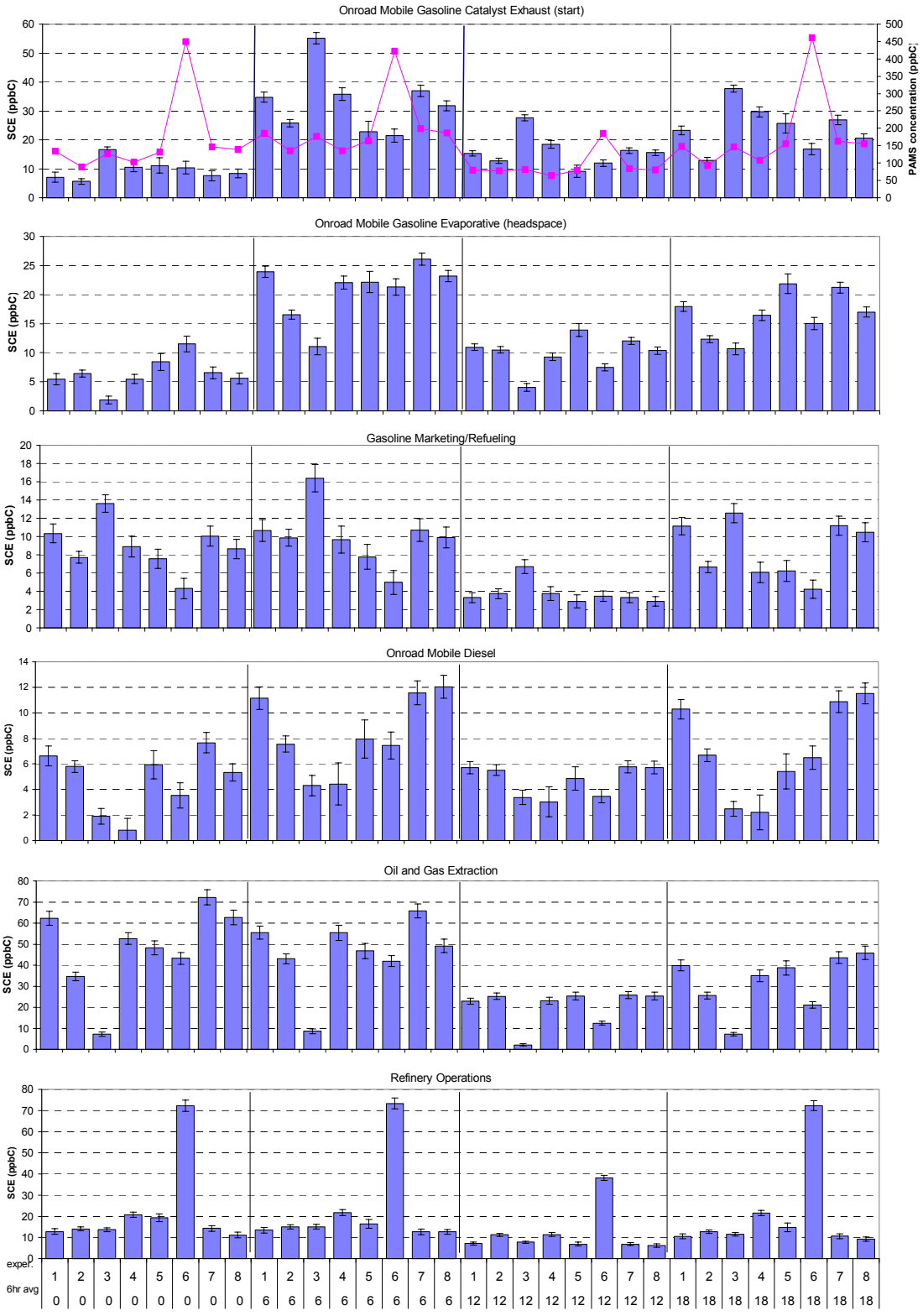


Mean source contribution estimates at Long Beach by 6-hour period, cont'd.

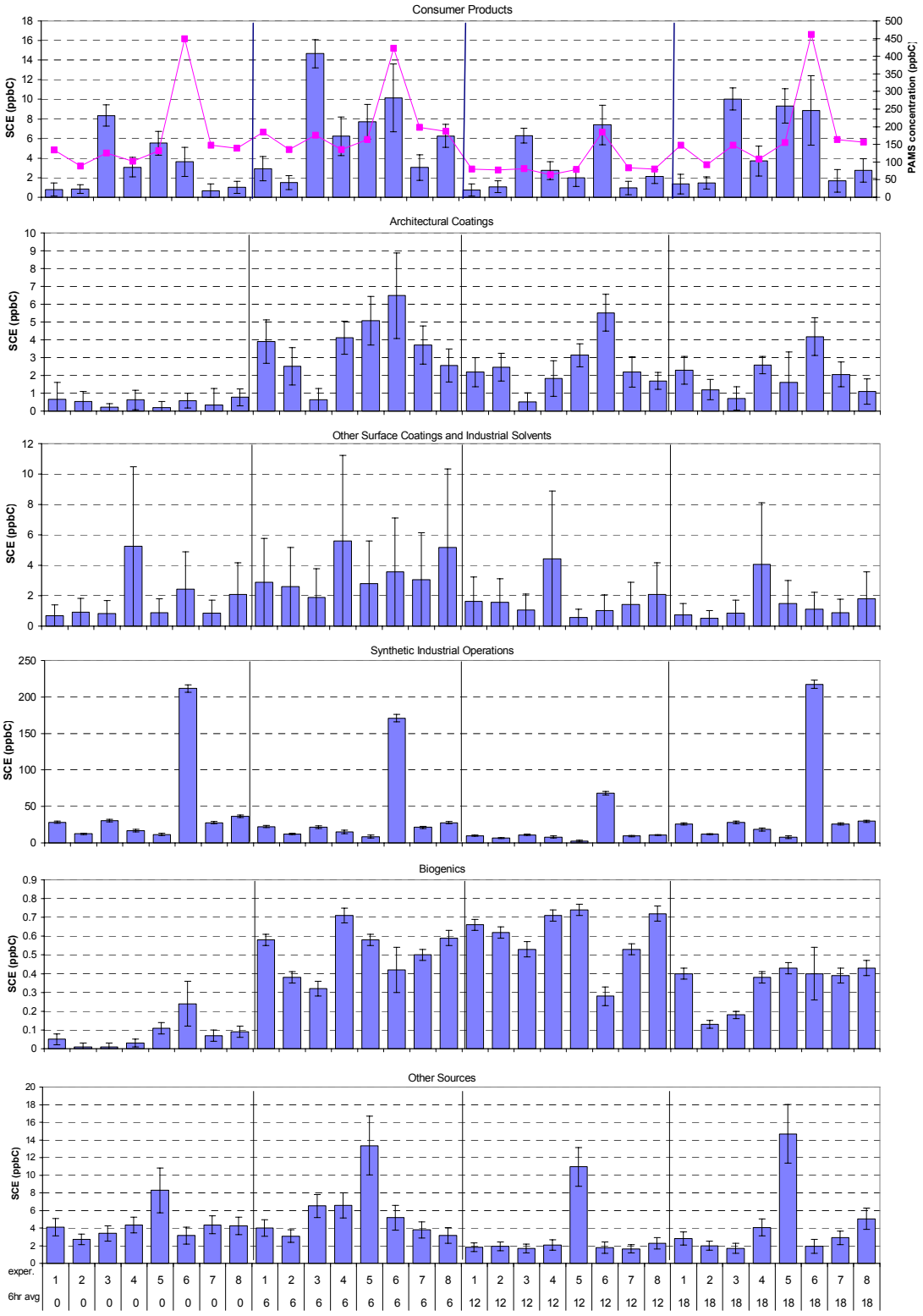
Mean source contribution estimates at Anaheim by 6-hour period. Start hour (PDT) is indicated.



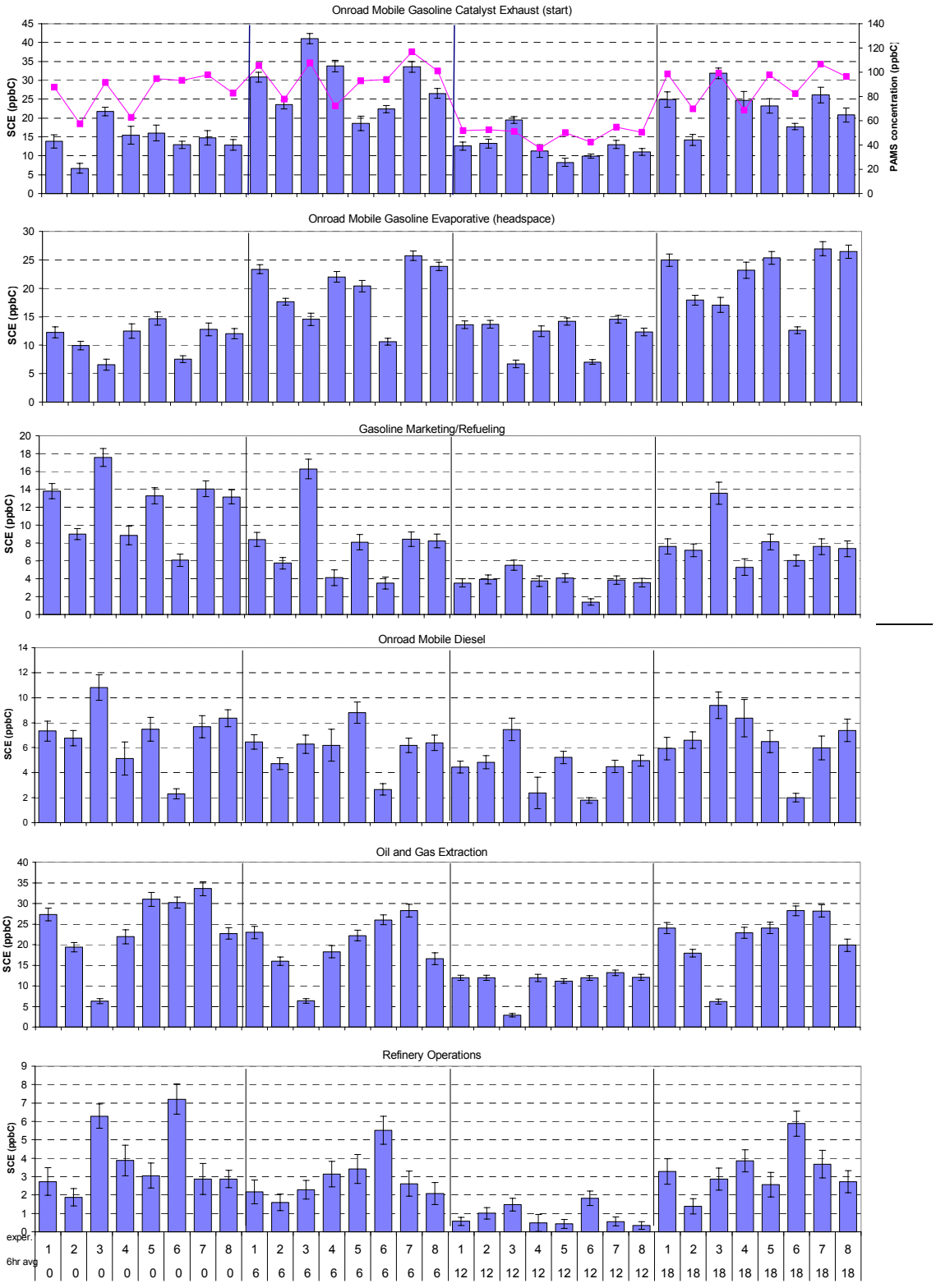
Mean source contribution estimates at Anaheim by 6-hour period, cont'd.



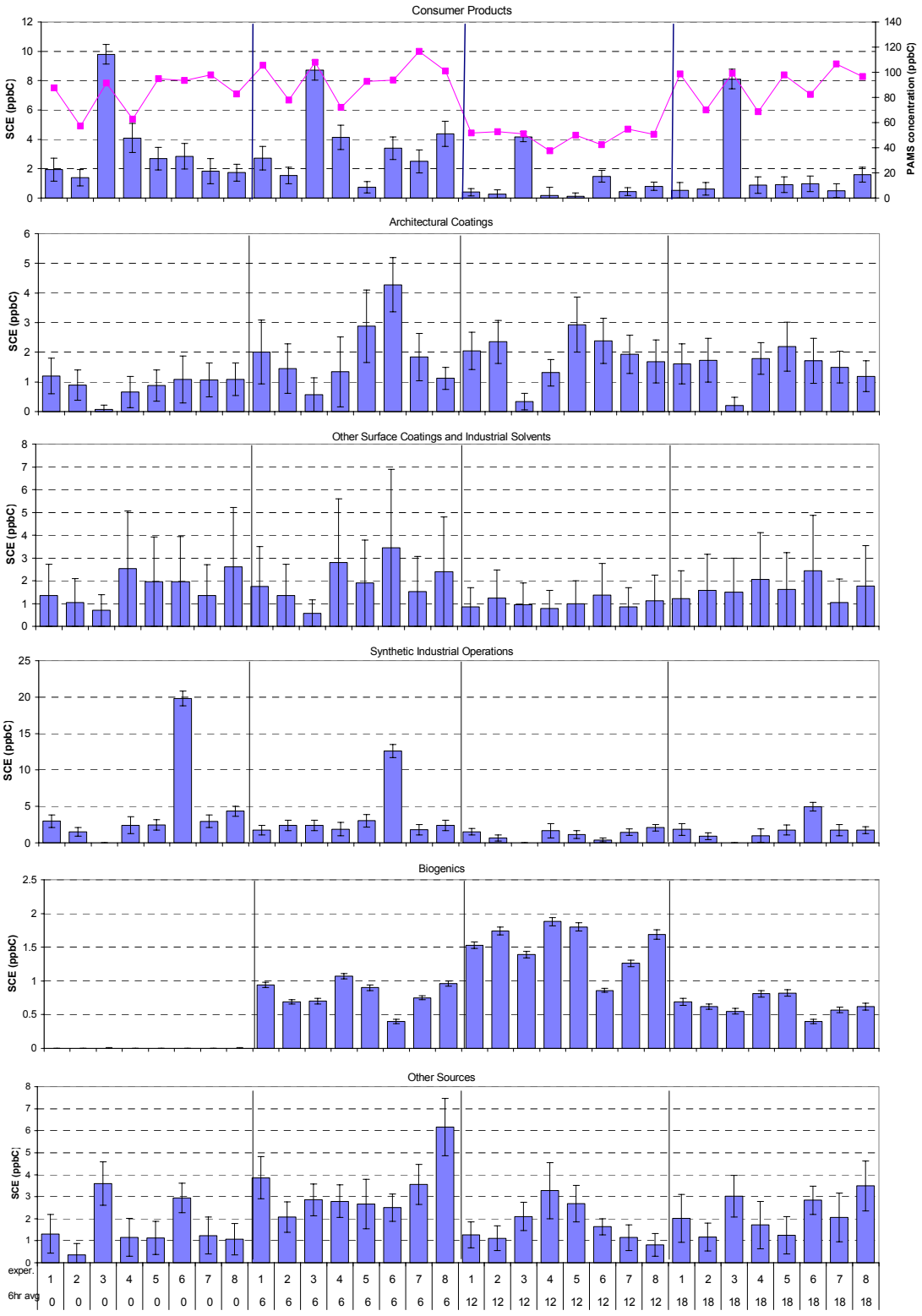
Mean source contribution estimates at Hawthorne by 6-hour period. Start hour (PDT) is indicated.



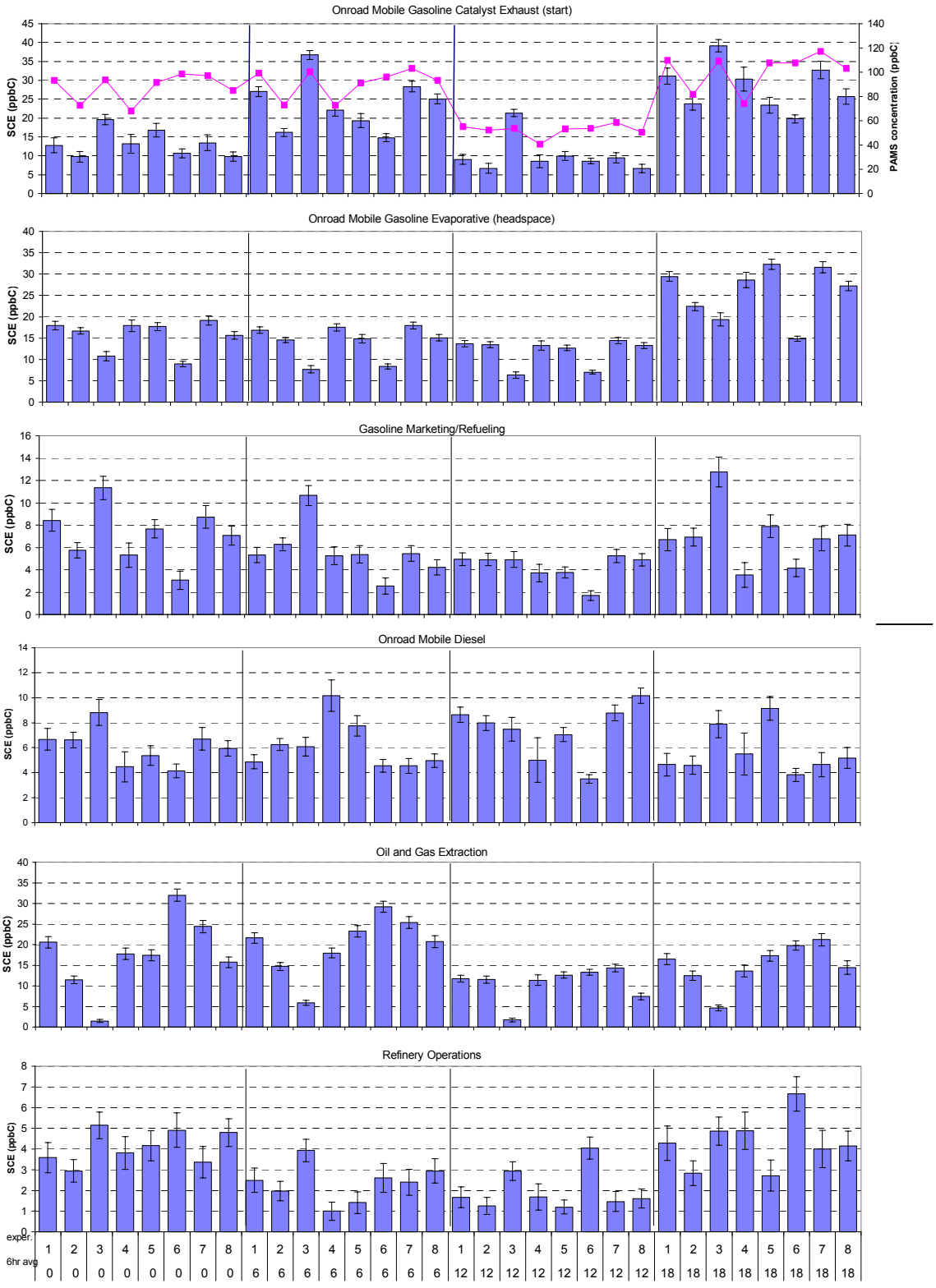
Mean source contribution estimates at Hawthorne by 6-hour period, cont'd.



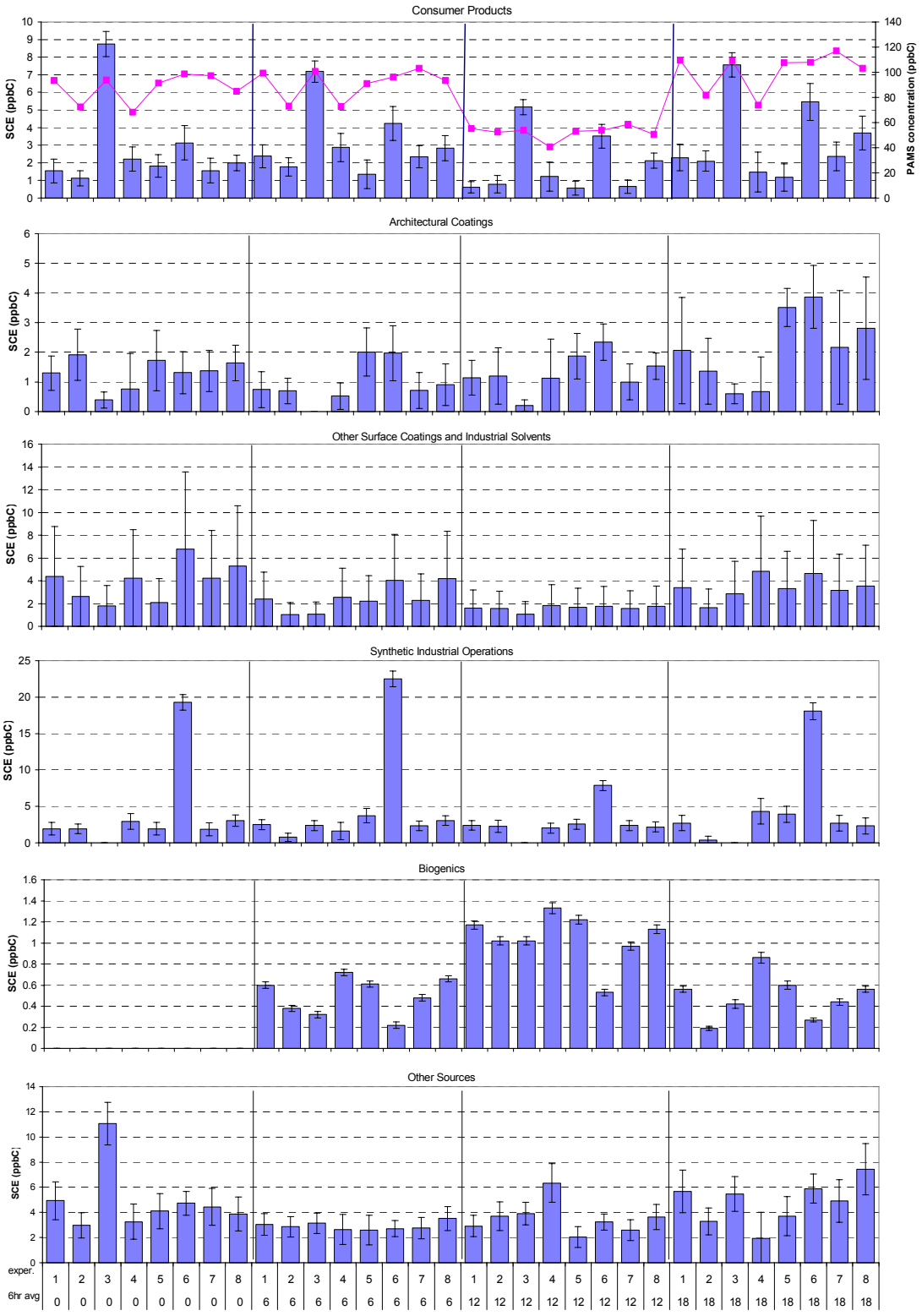
Mean source contribution estimates at Van Nuys by 6-hour period. Start hour (PDT) is indicated.



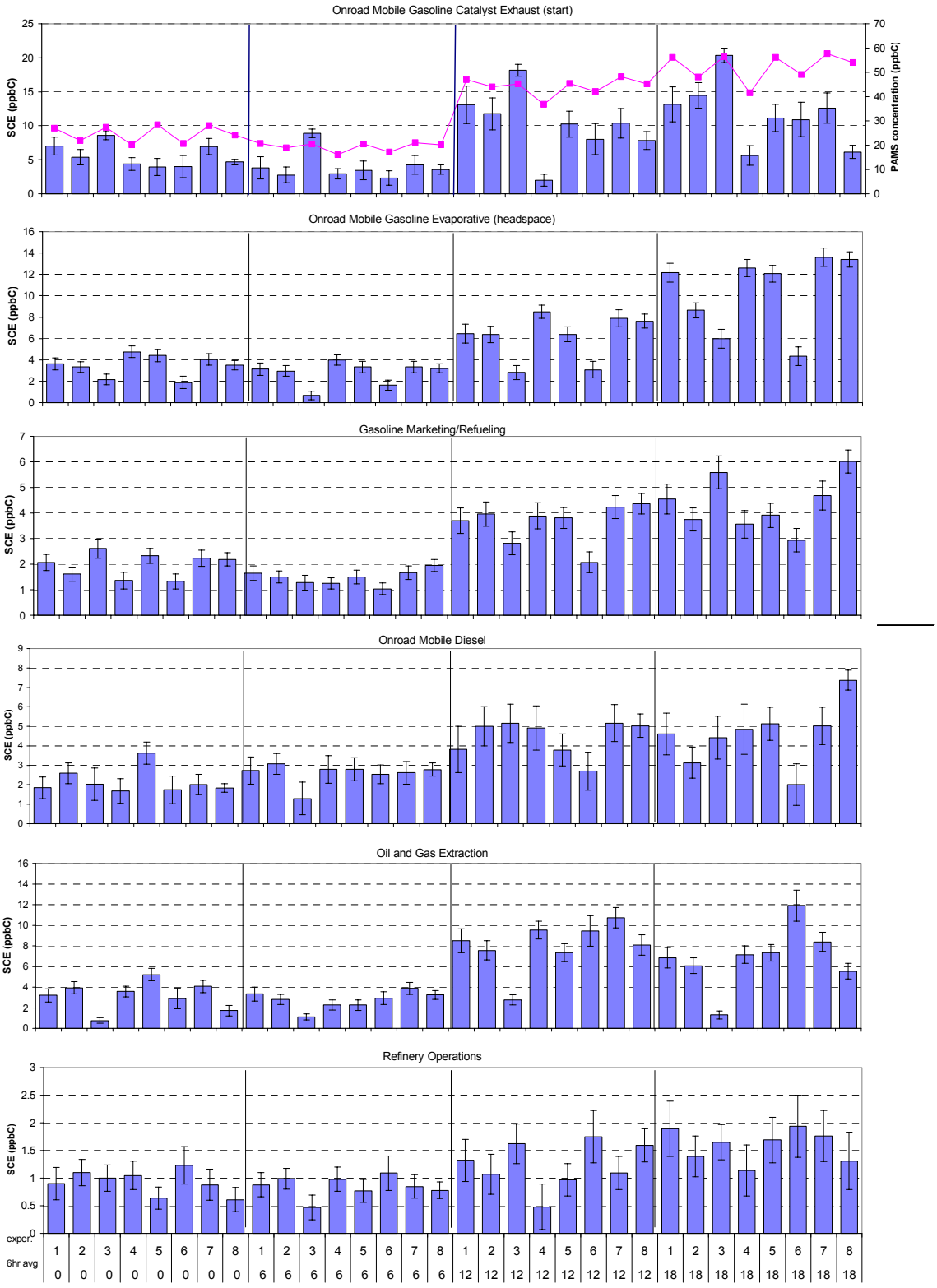
Mean source contribution estimates at Van Nuys by 6-hour period, cont'd.



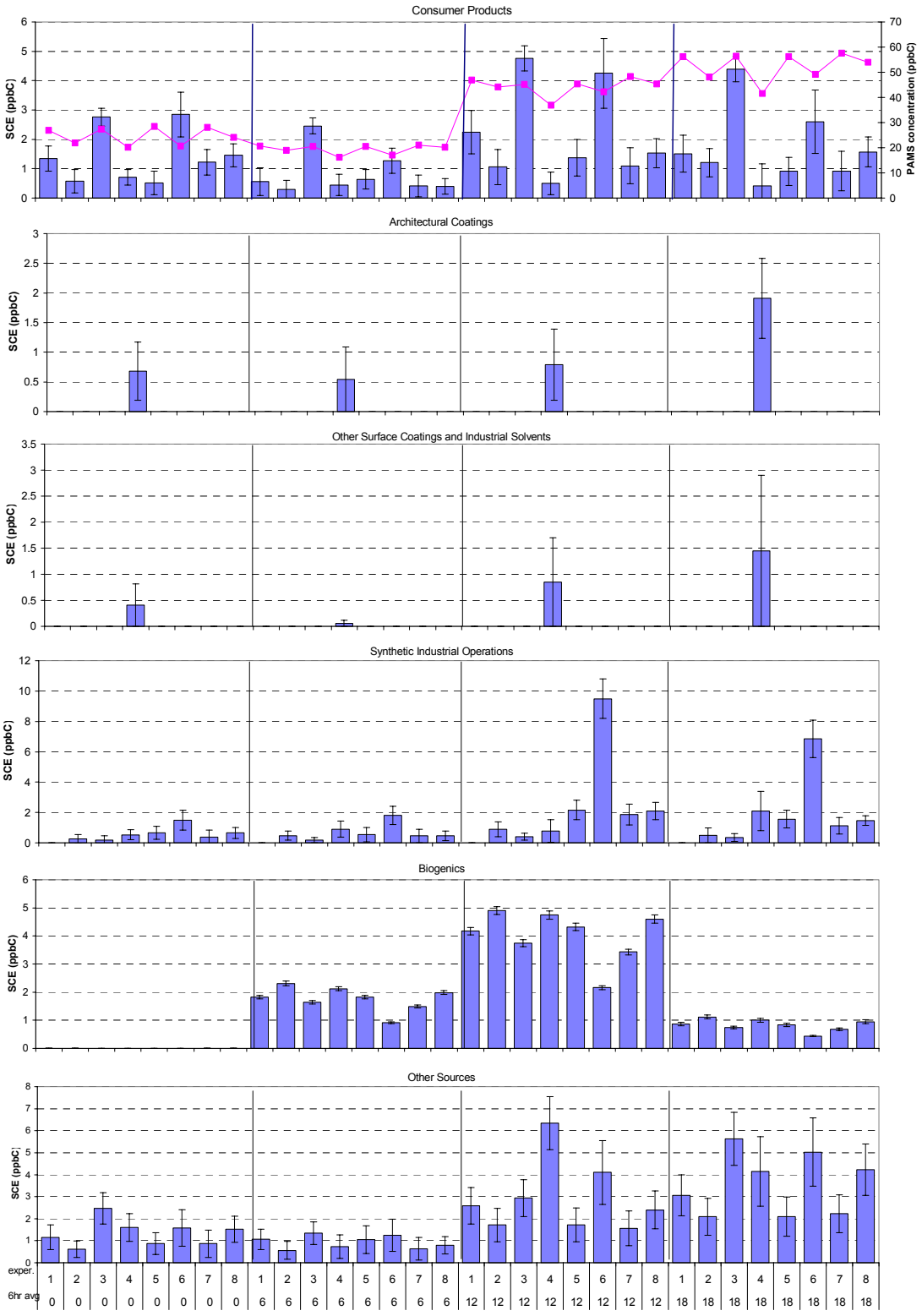
Mean source contribution estimates at Diamond Bar by 6-hour period. Start hour (PDT) is indicated.



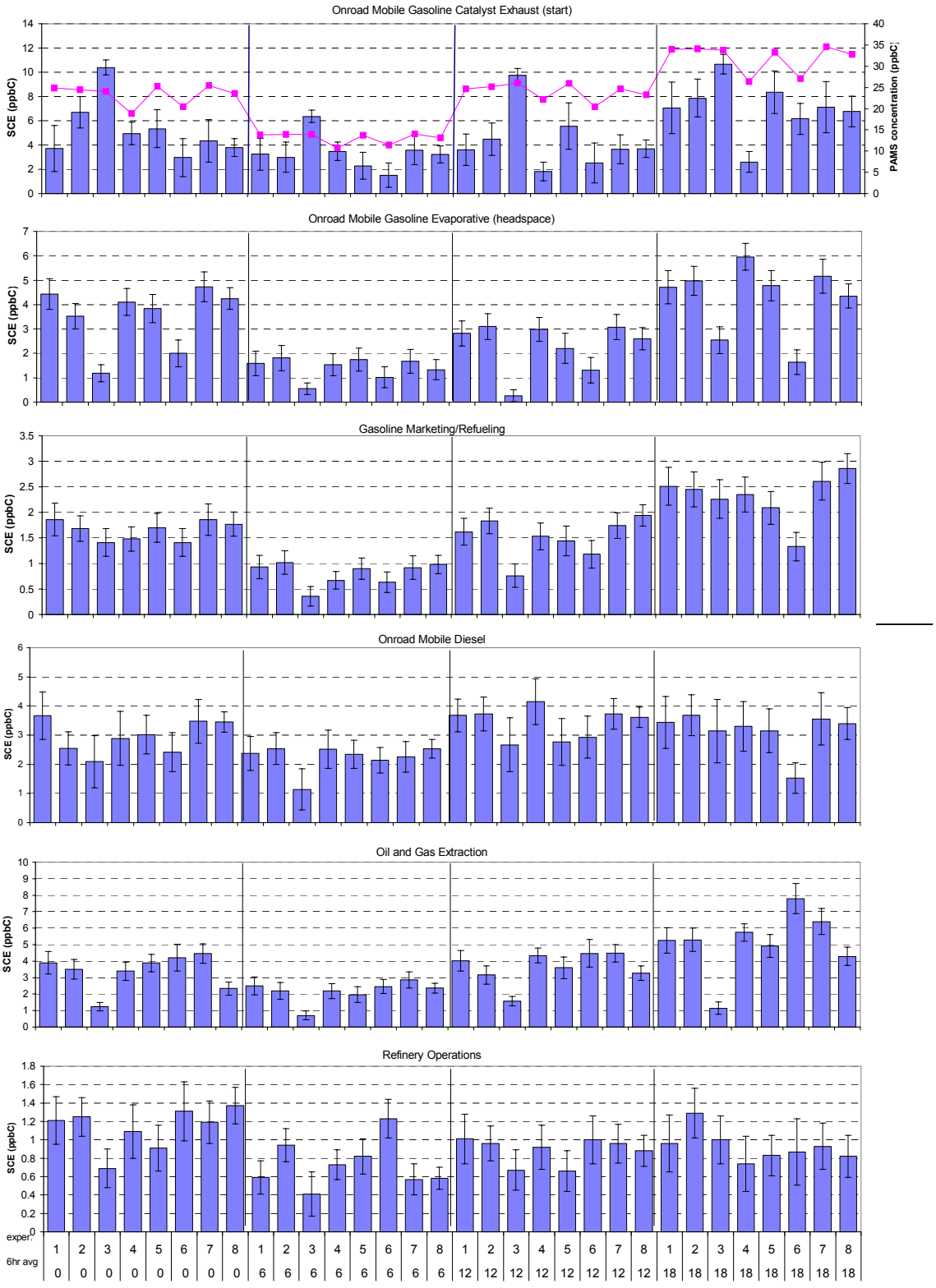
Mean source contribution estimates at Diamond Bar by 6-hour period, cont'd.



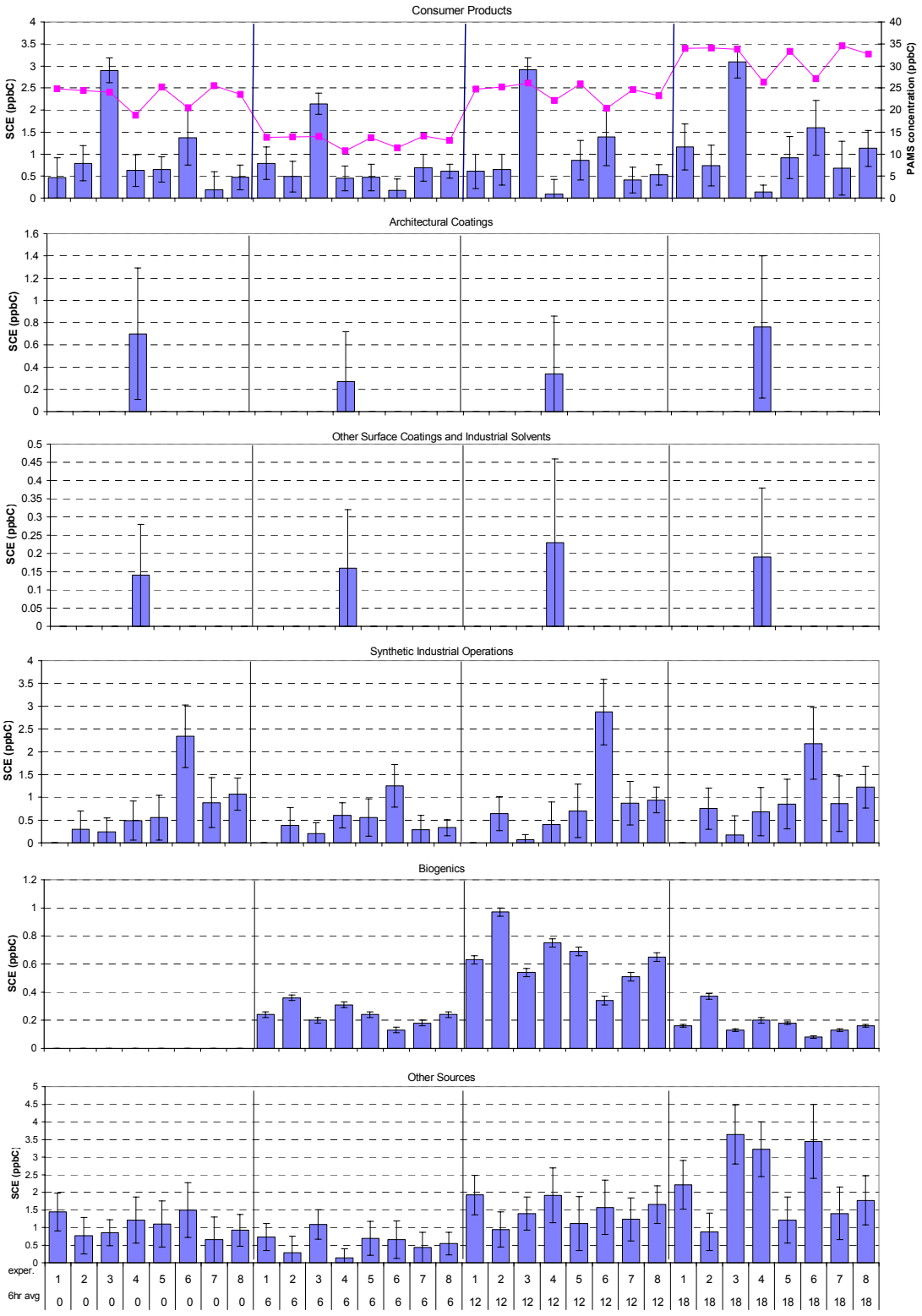
Mean source contribution estimates at Crestline by 6-hour period. Start hour (PDT) is indicated.



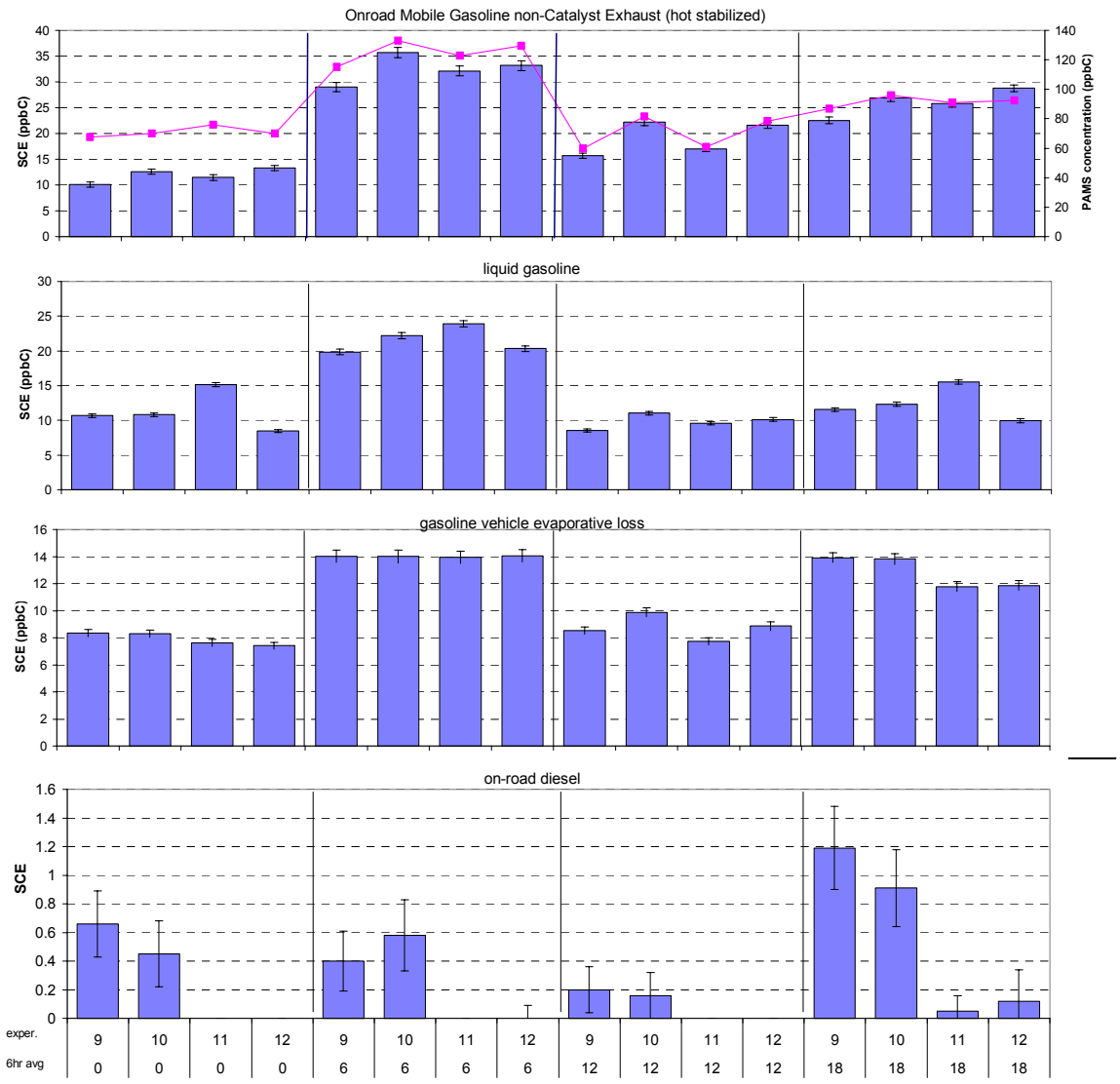
Mean source contribution estimates at Crestline by 6-hour period, cont'd.



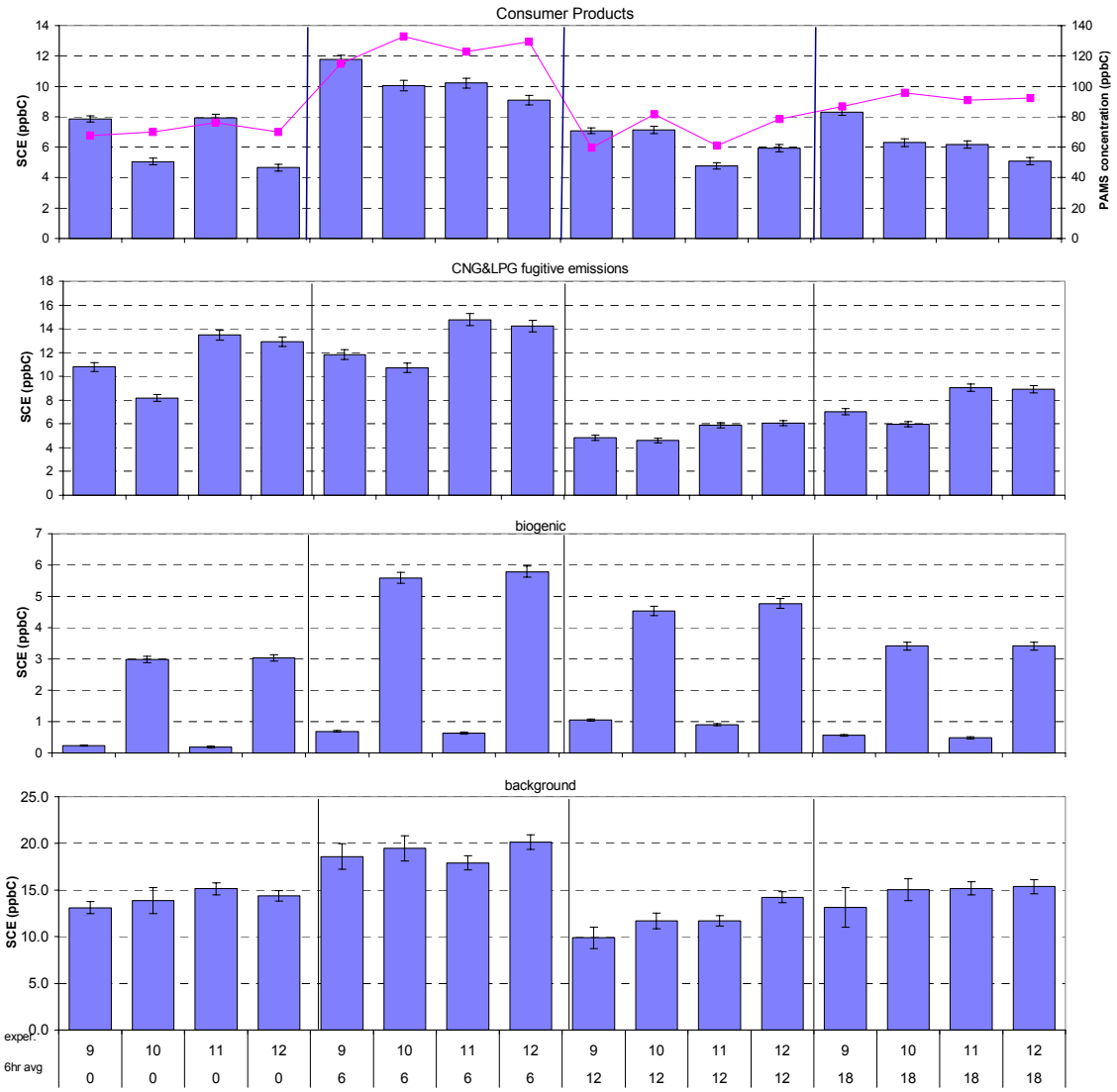
Mean source contribution estimates at Lake Perris by 6-hour period. Start hour (PDT) is indicated.



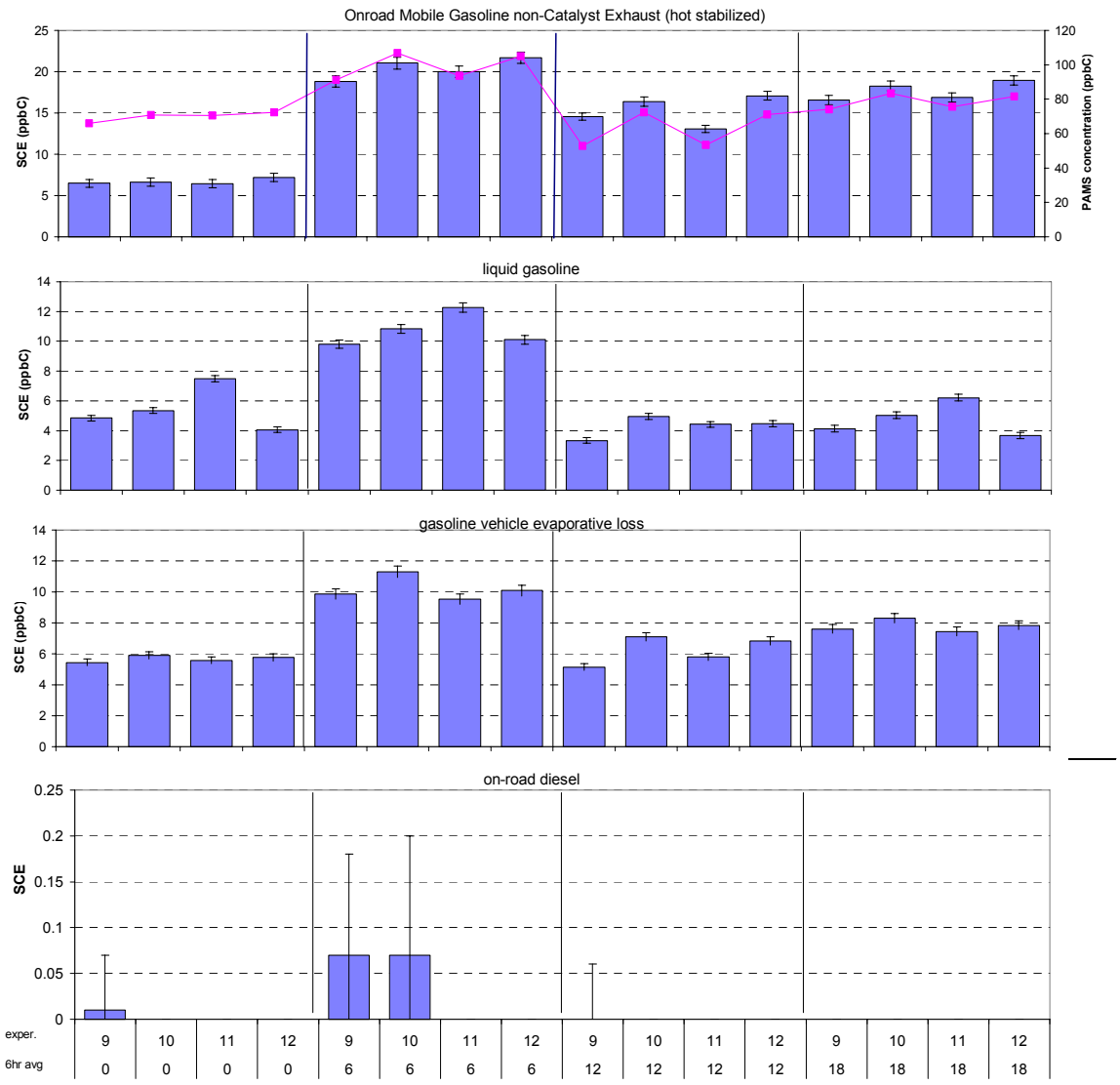
Mean source contribution estimates at Lake Perris by 6-hour period, cont'd.



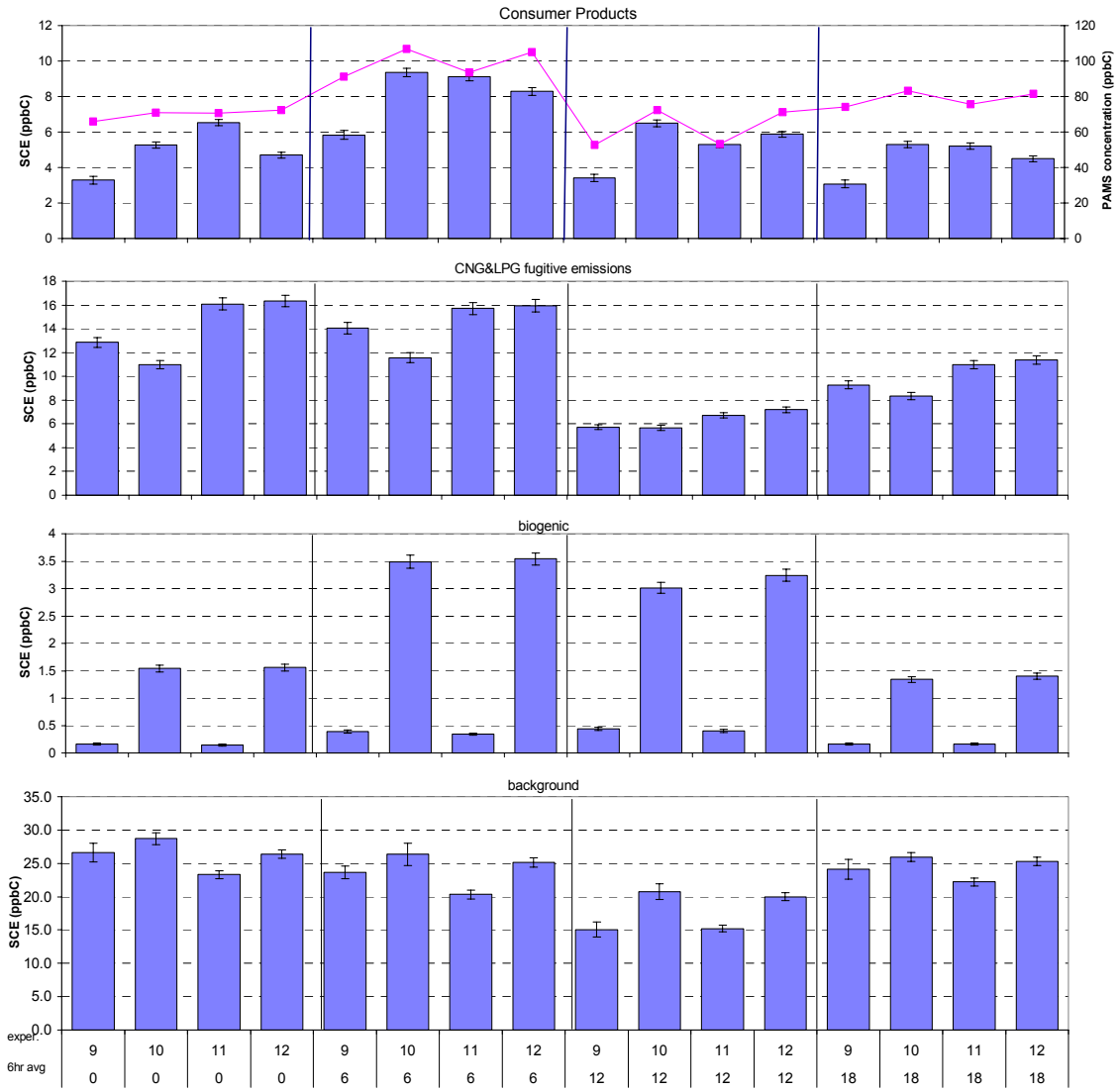
Mean source contribution estimates at LAX by 6-hour period. Start hour (PDT) is indicated.



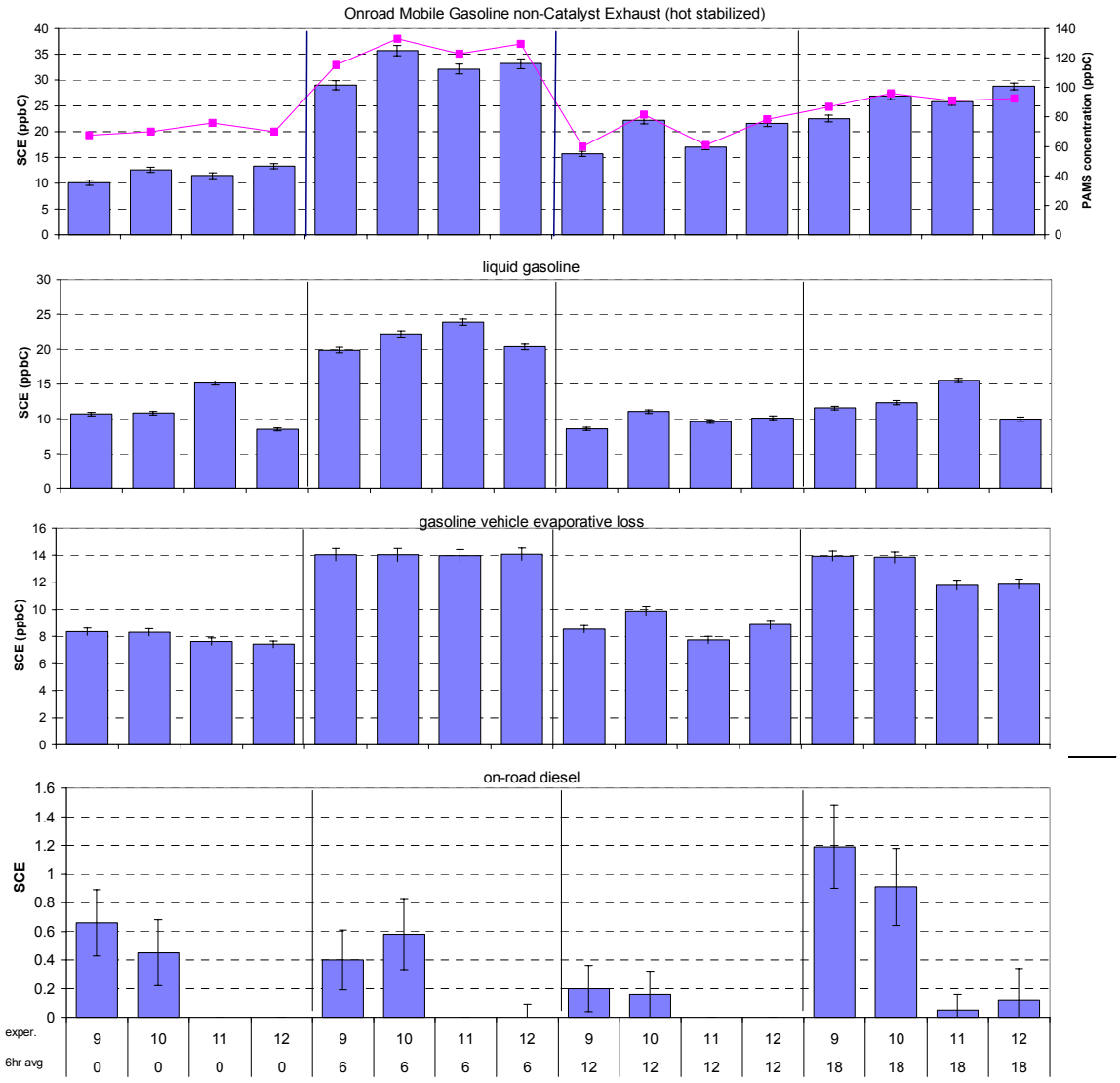
Mean source contribution estimates at LAX by 6-hour period, cont'd.



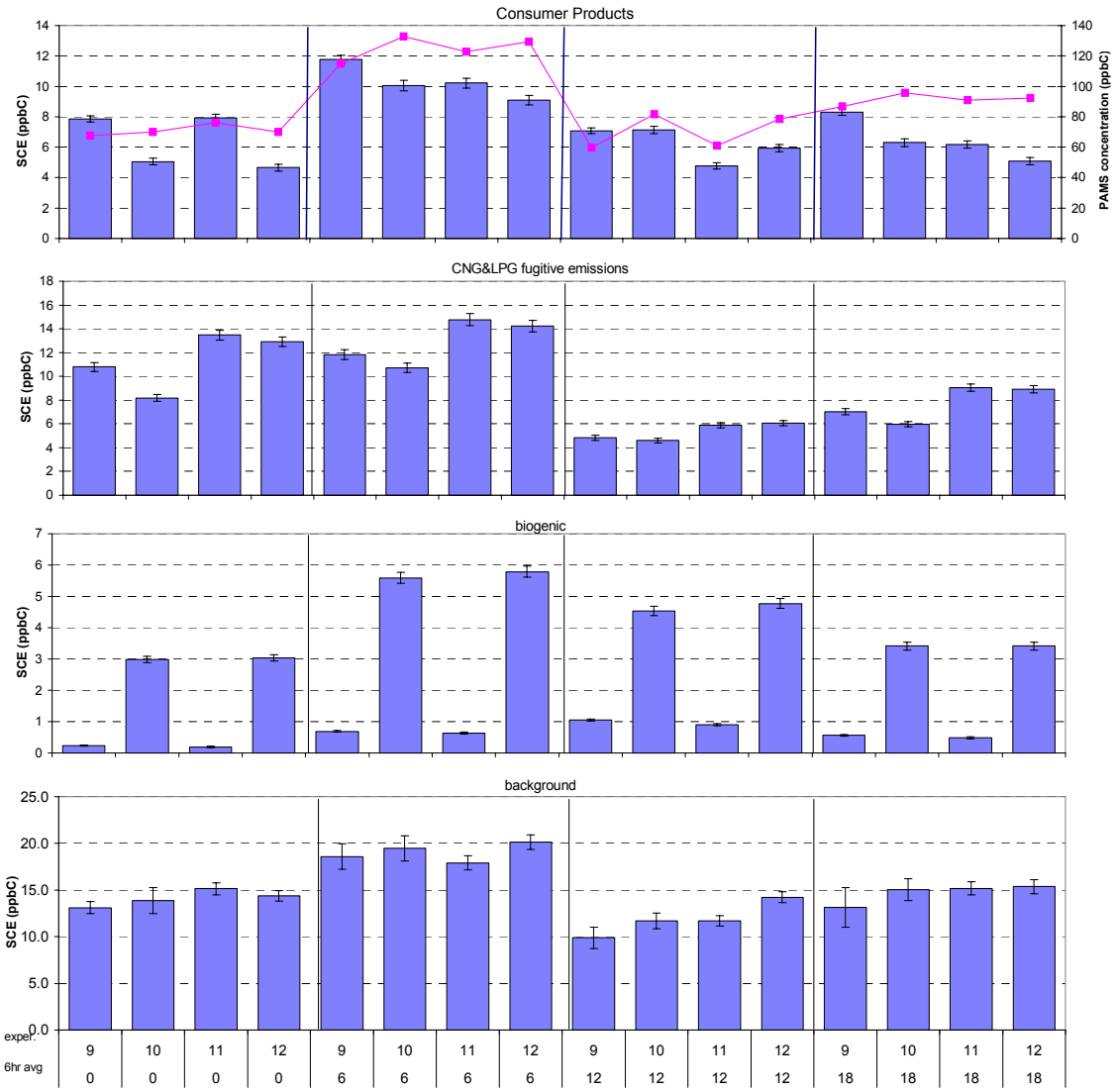
Mean source contribution estimates at Long Beach by 6-hour period. Start hour (PDT) is indicated.



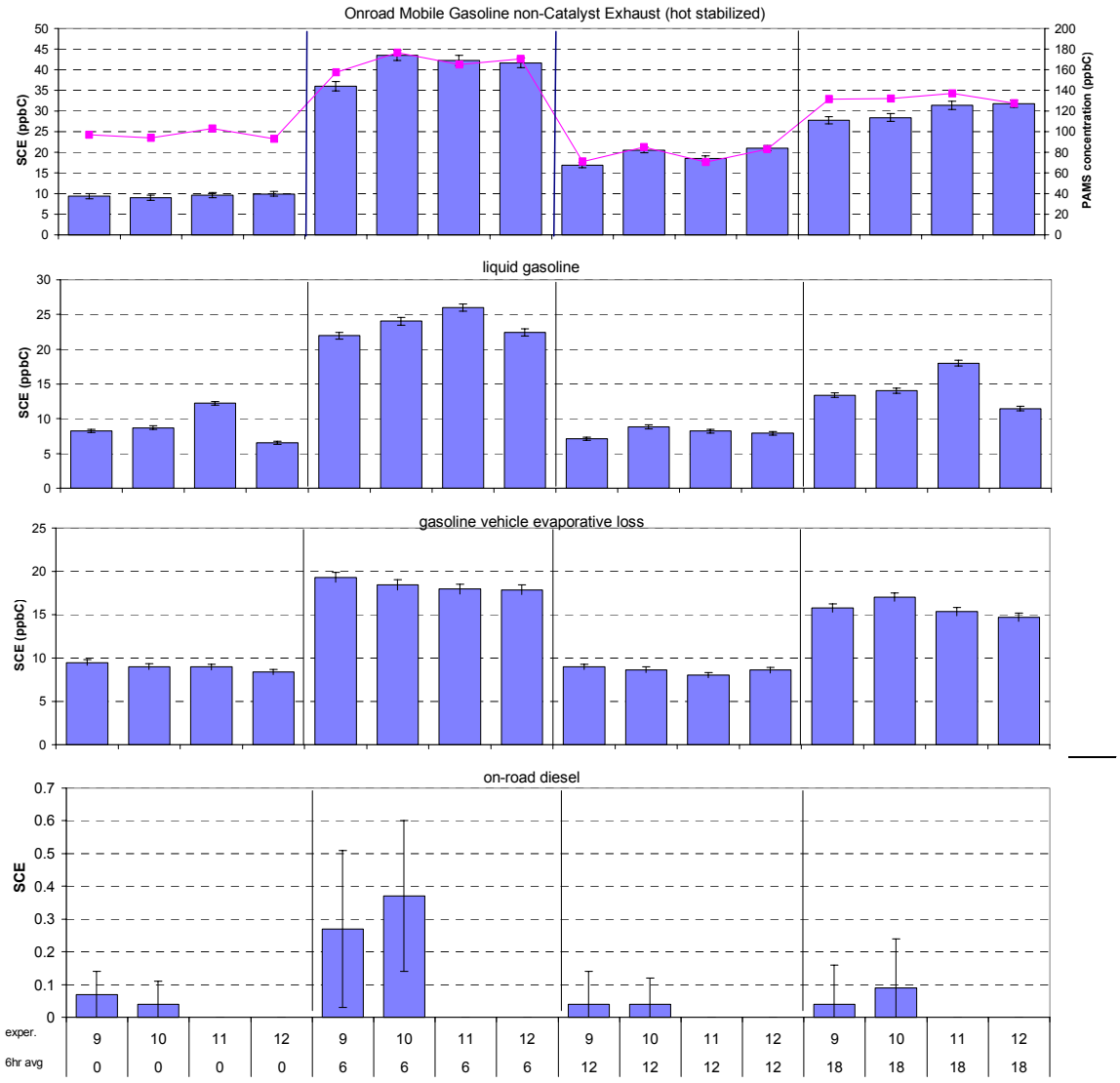
Mean source contribution estimates at Long Beach by 6-hour period, cont'd.



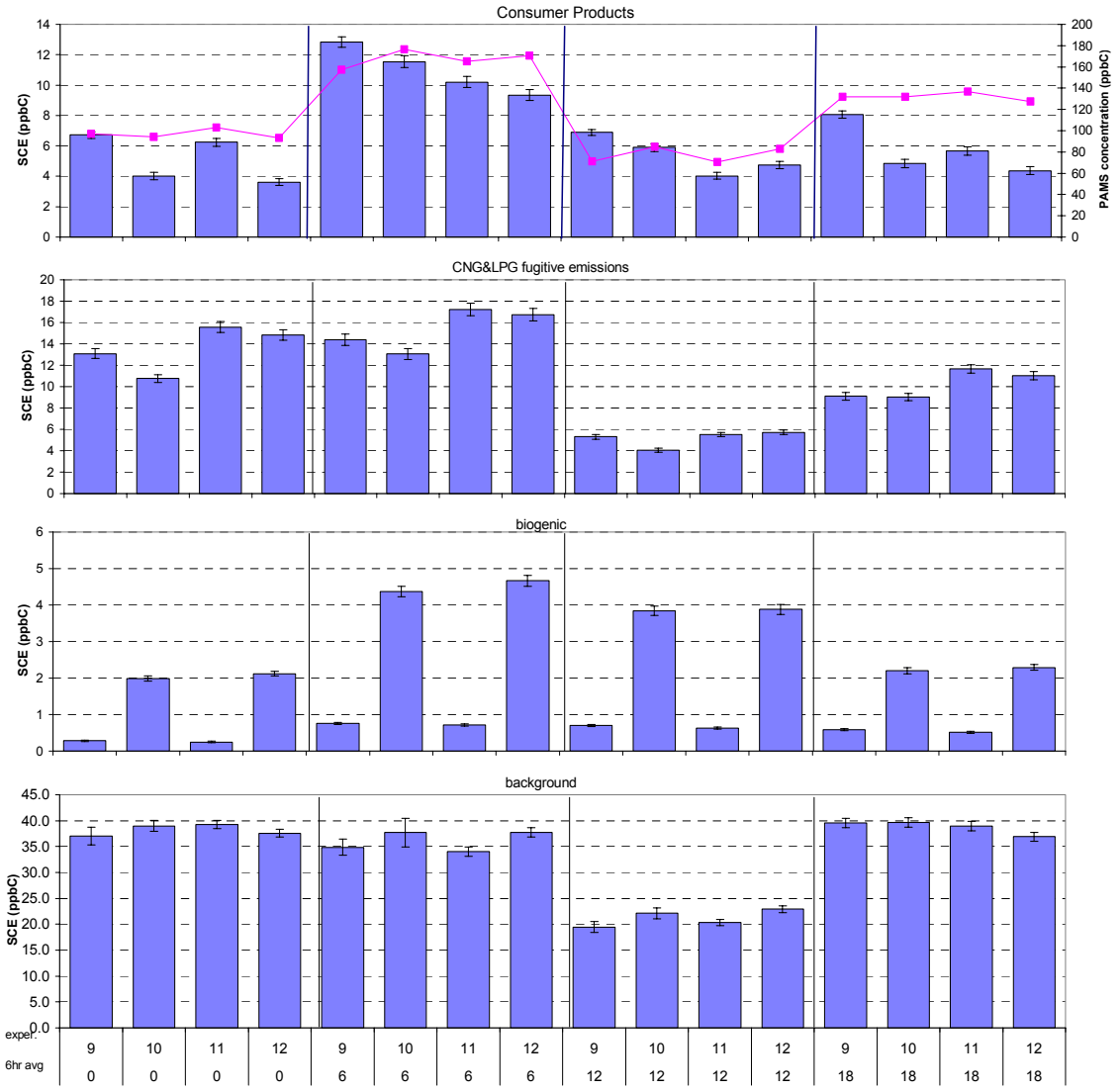
Mean source contribution estimates at Anaheim by 6-hour period. Start hour (PDT) is indicated.



Mean source contribution estimates at Anaheim by 6-hour period, cont'd.

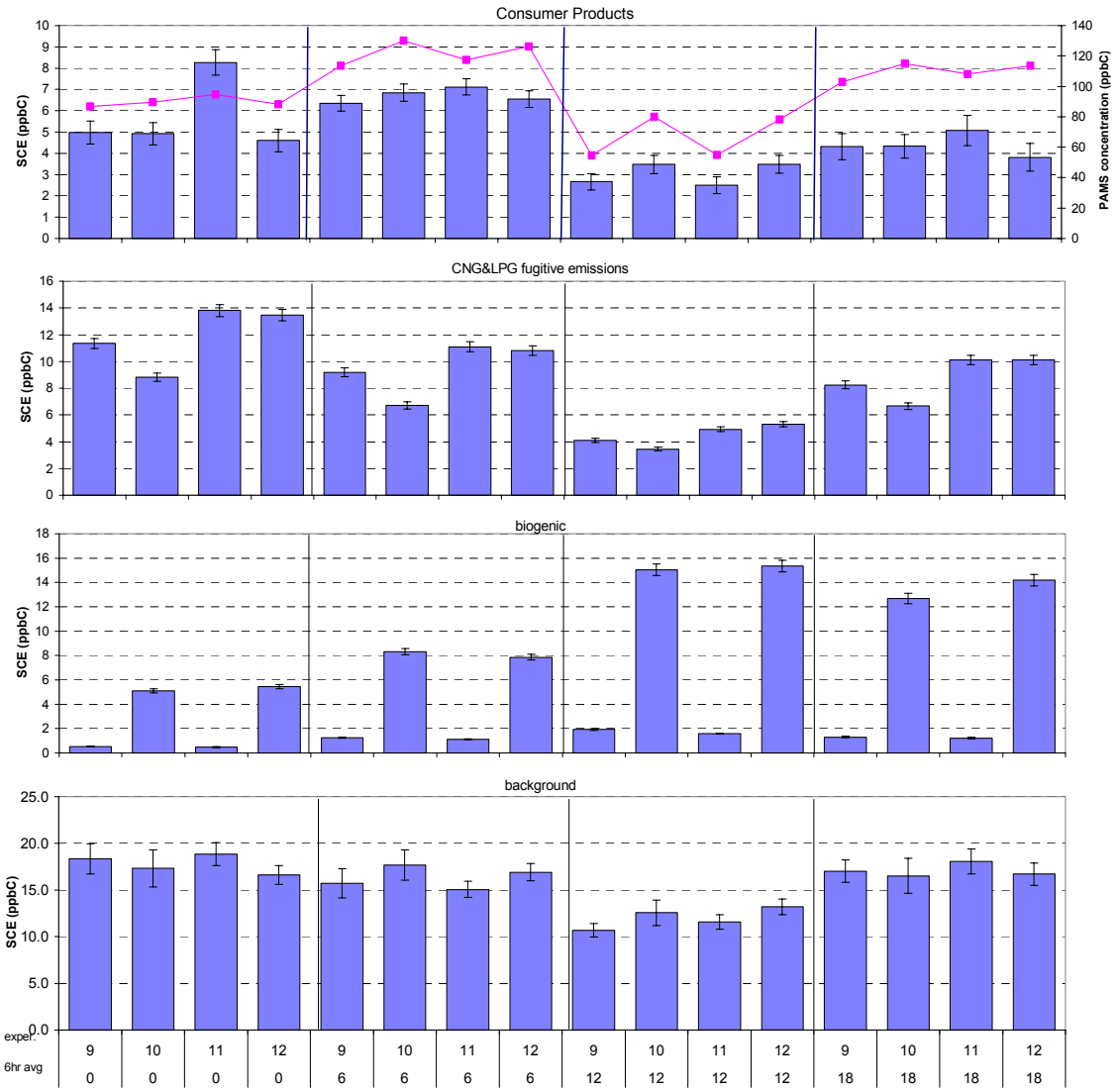


Mean source contribution estimates at Hawthorne by 6-hour period. Start hour (PDT) is indicated.

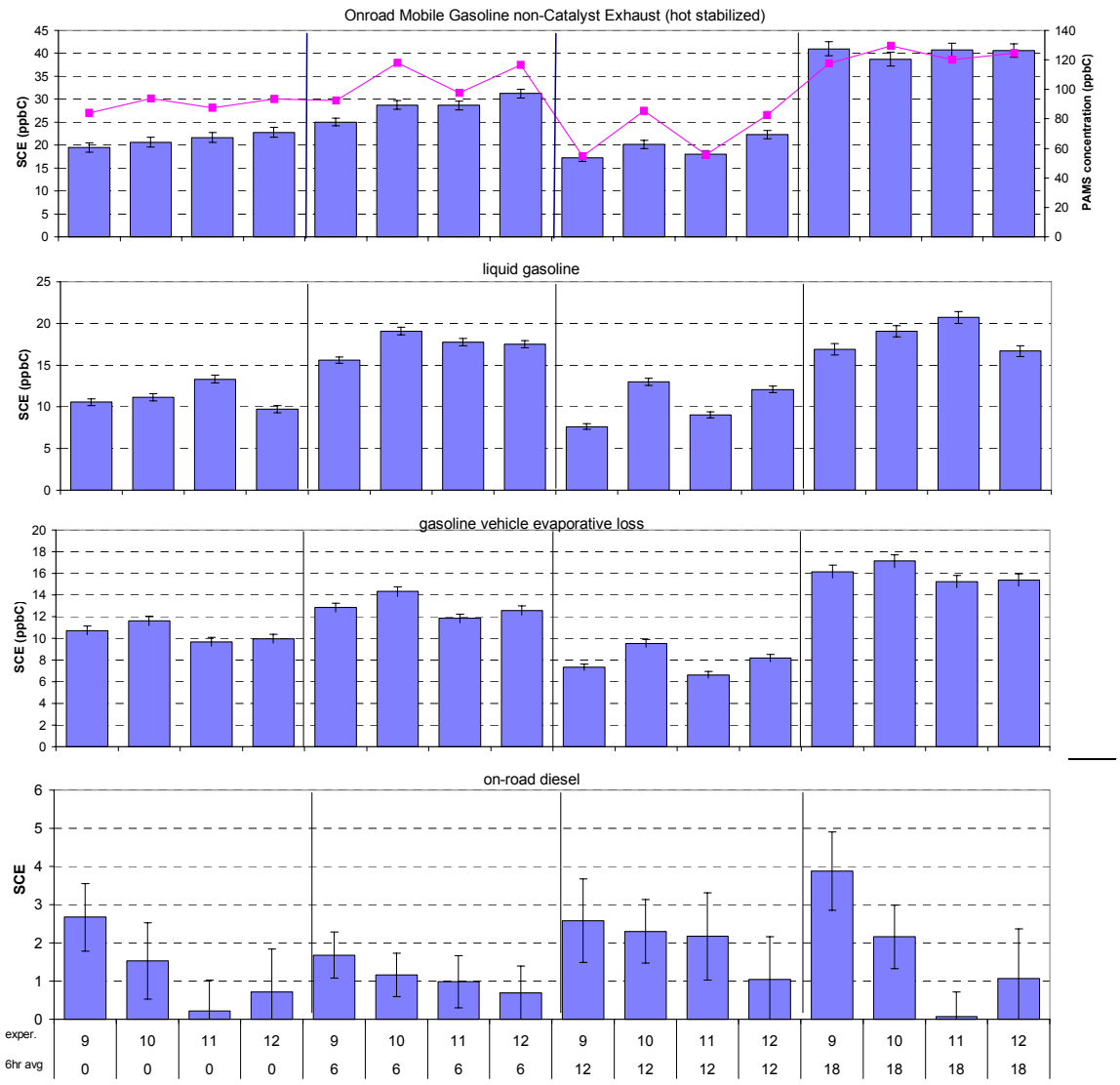


Mean source contribution estimates at Hawthorne by 6-hour period, cont'd.

Mean source contribution estimates at Van Nuys by 6-hour period. Start hour (PDT) is indicated.

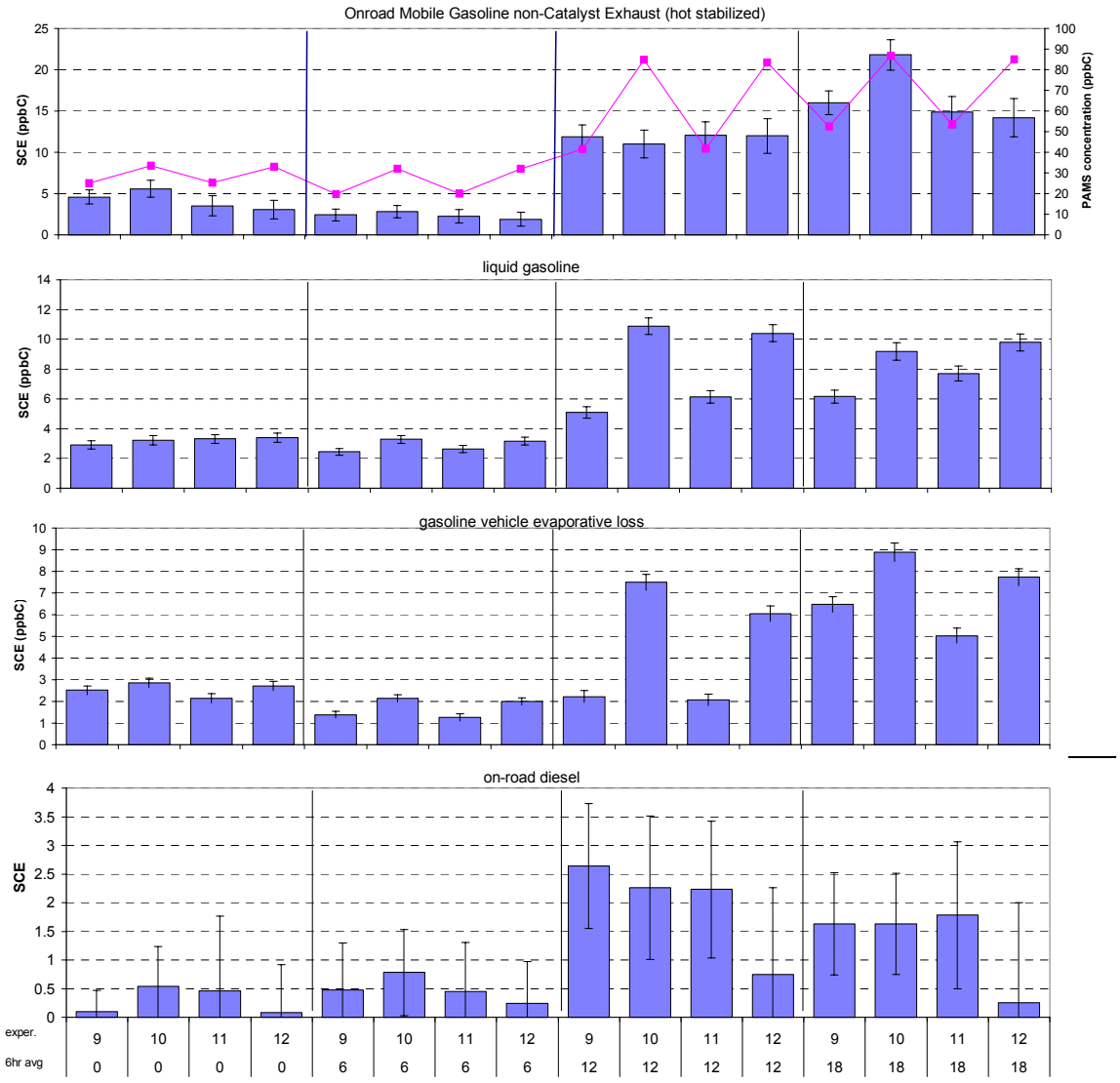


Mean source contribution estimates at Van Nuys by 6-hour period, cont'd.

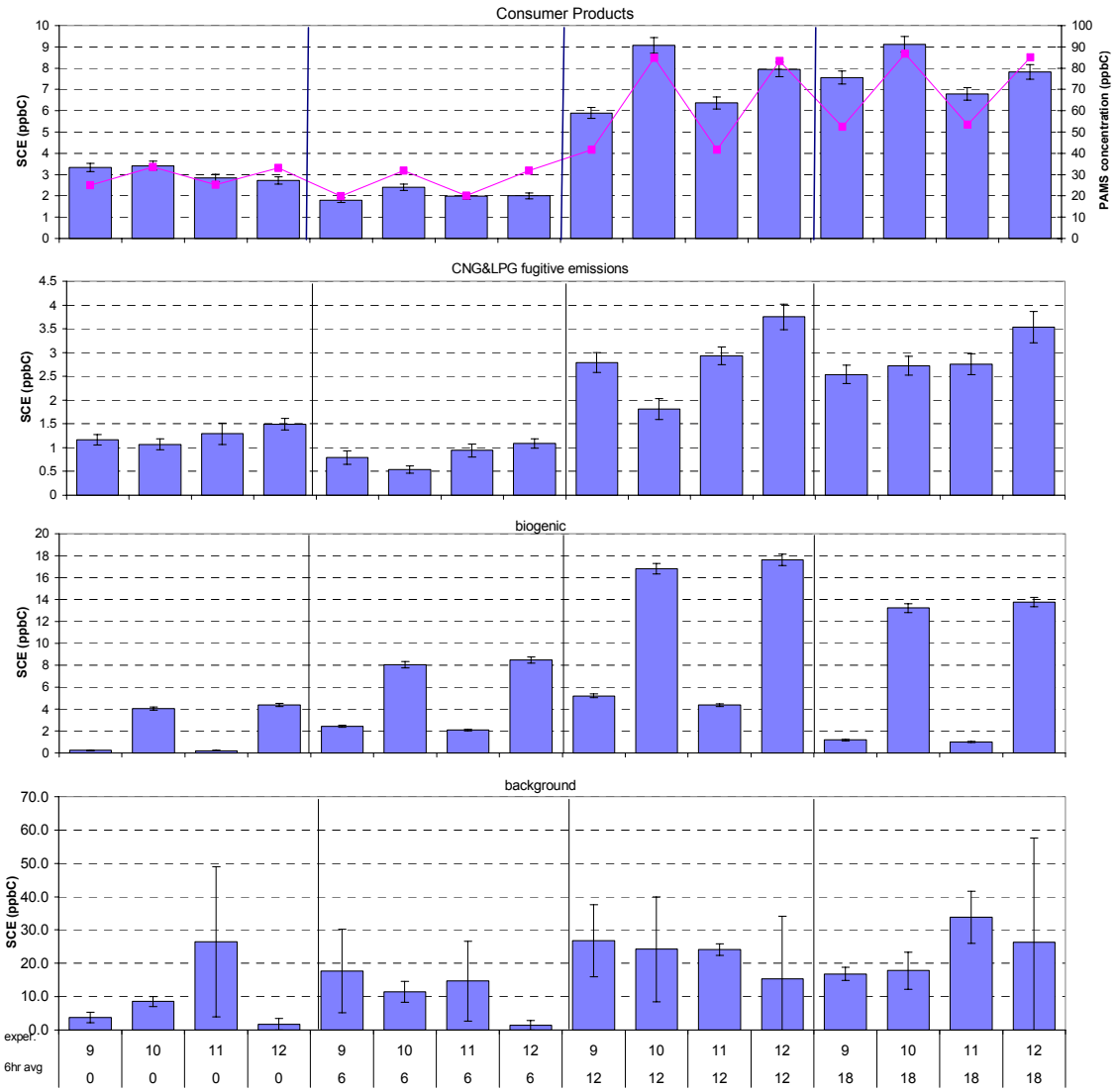


Mean source contribution estimates at Diamond Bar by 6-hour period. Start hour (PDT) is indicated.

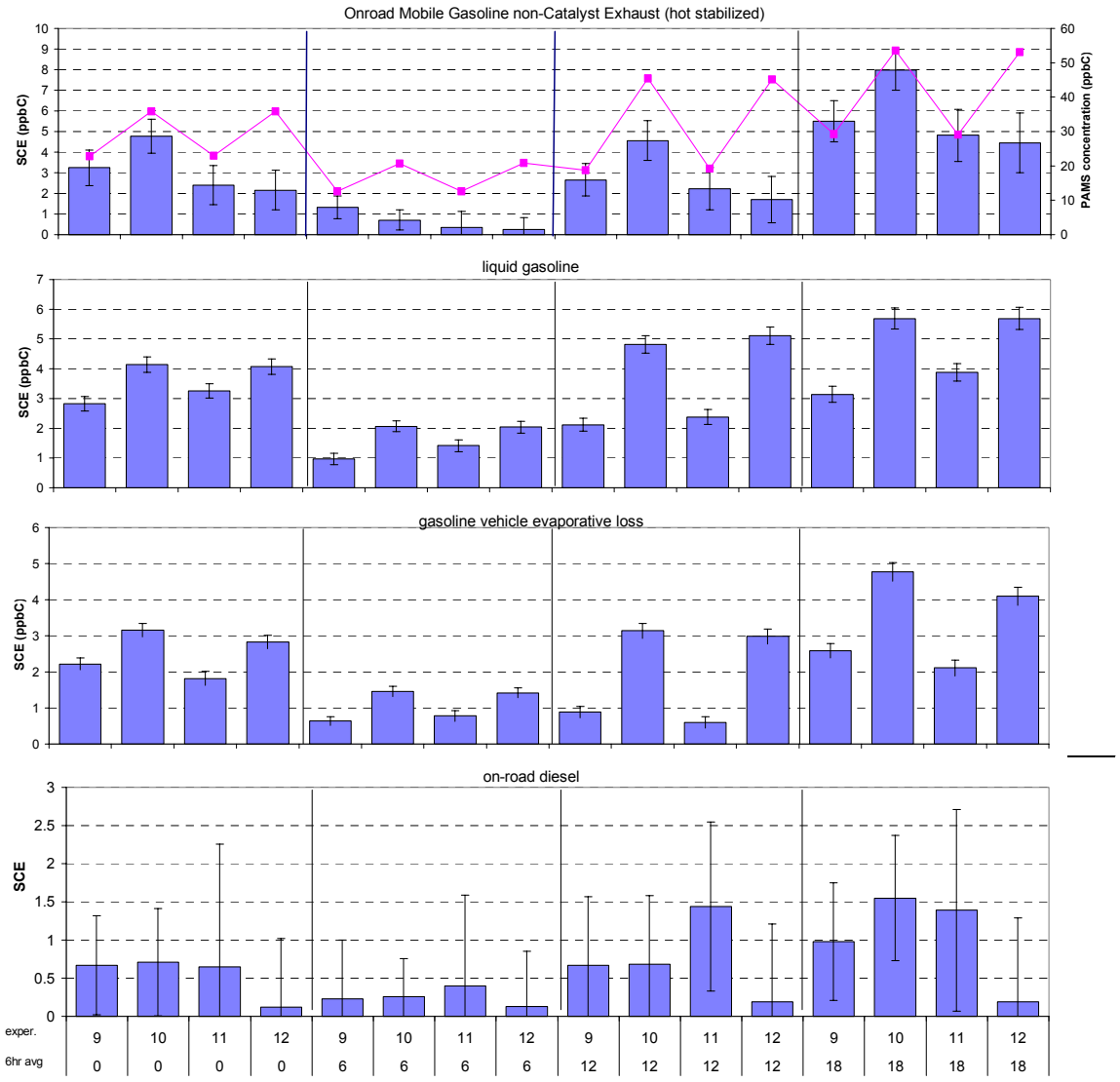
Mean source contribution estimates at Diamond Bar by 6-hour period, cont'd.



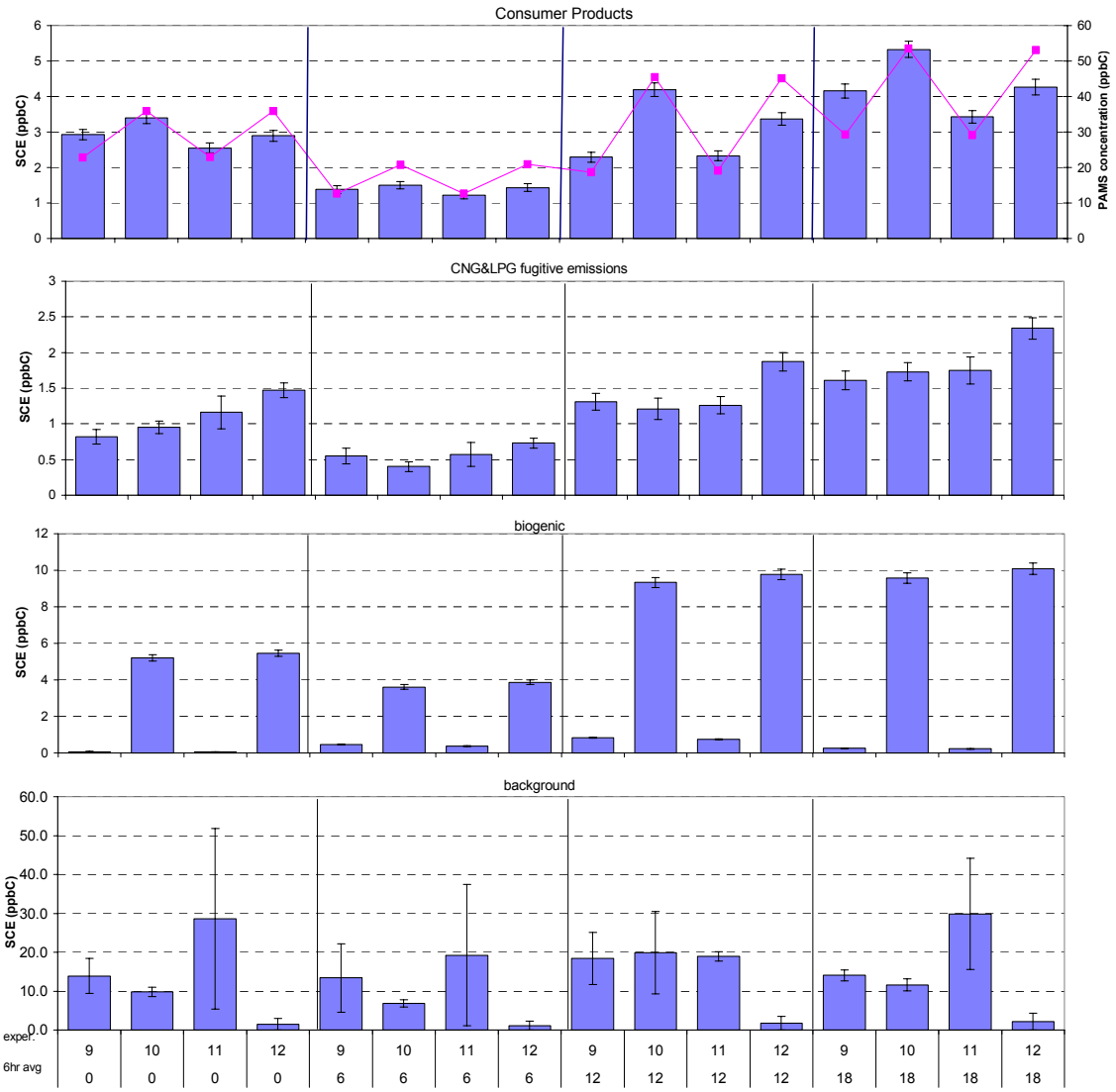
Mean source contribution estimates at Crestline by 6-hour period. Start hour (PDT) is indicated.



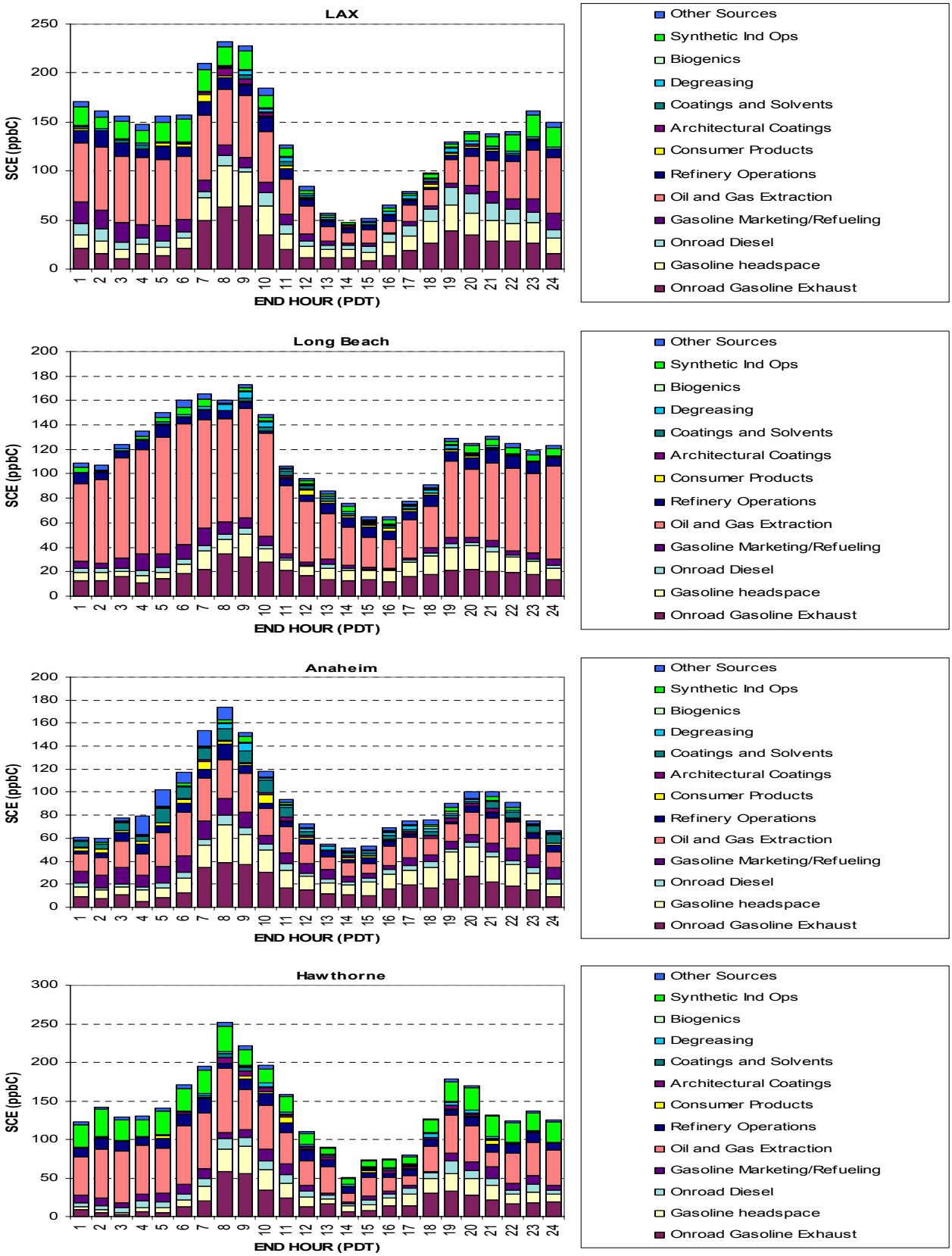
Mean source contribution estimates at Crestline by 6-hour period, cont'd.



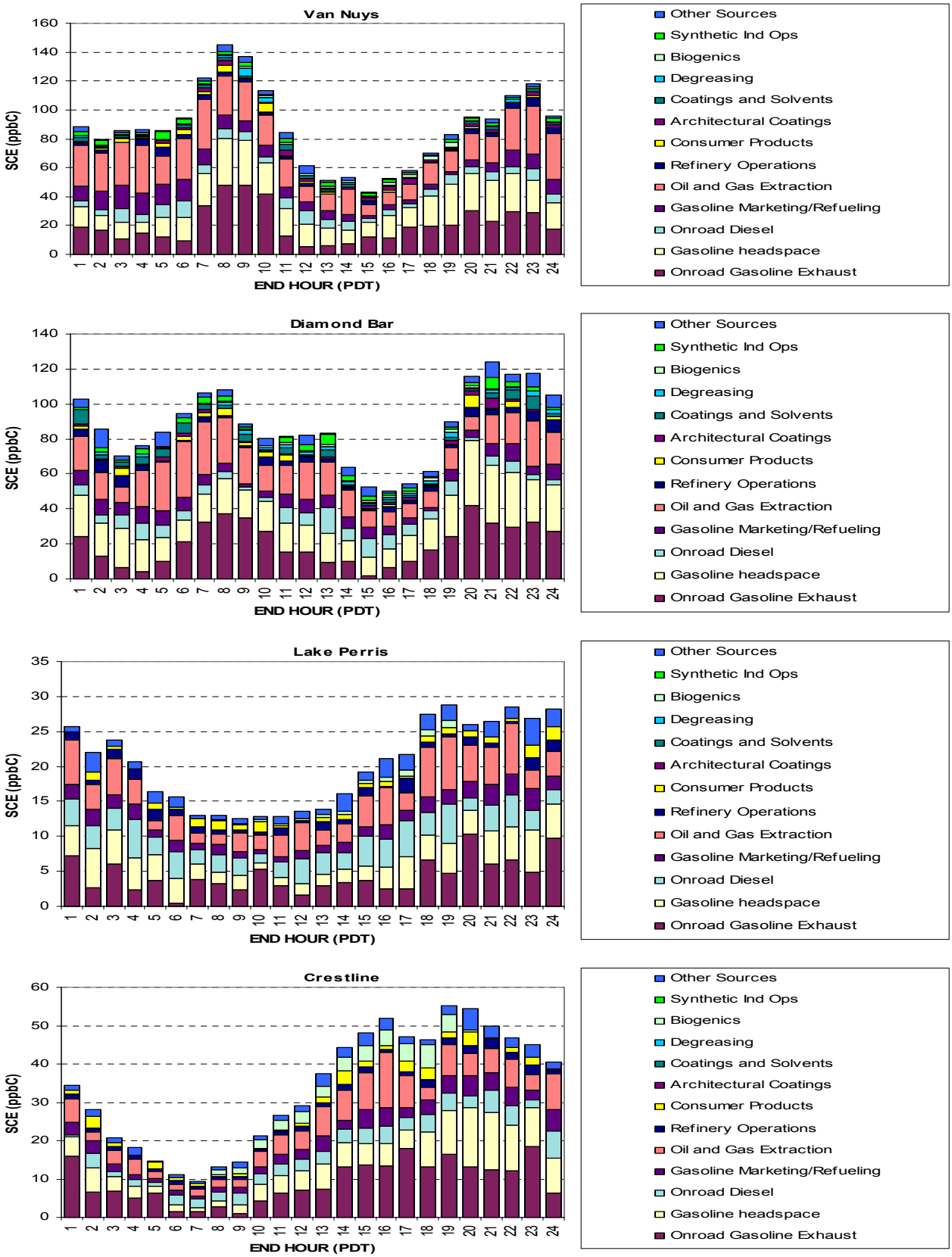
Mean source contribution estimates at Lake Perris by 6-hour period. Start hour (PDT) is indicated.



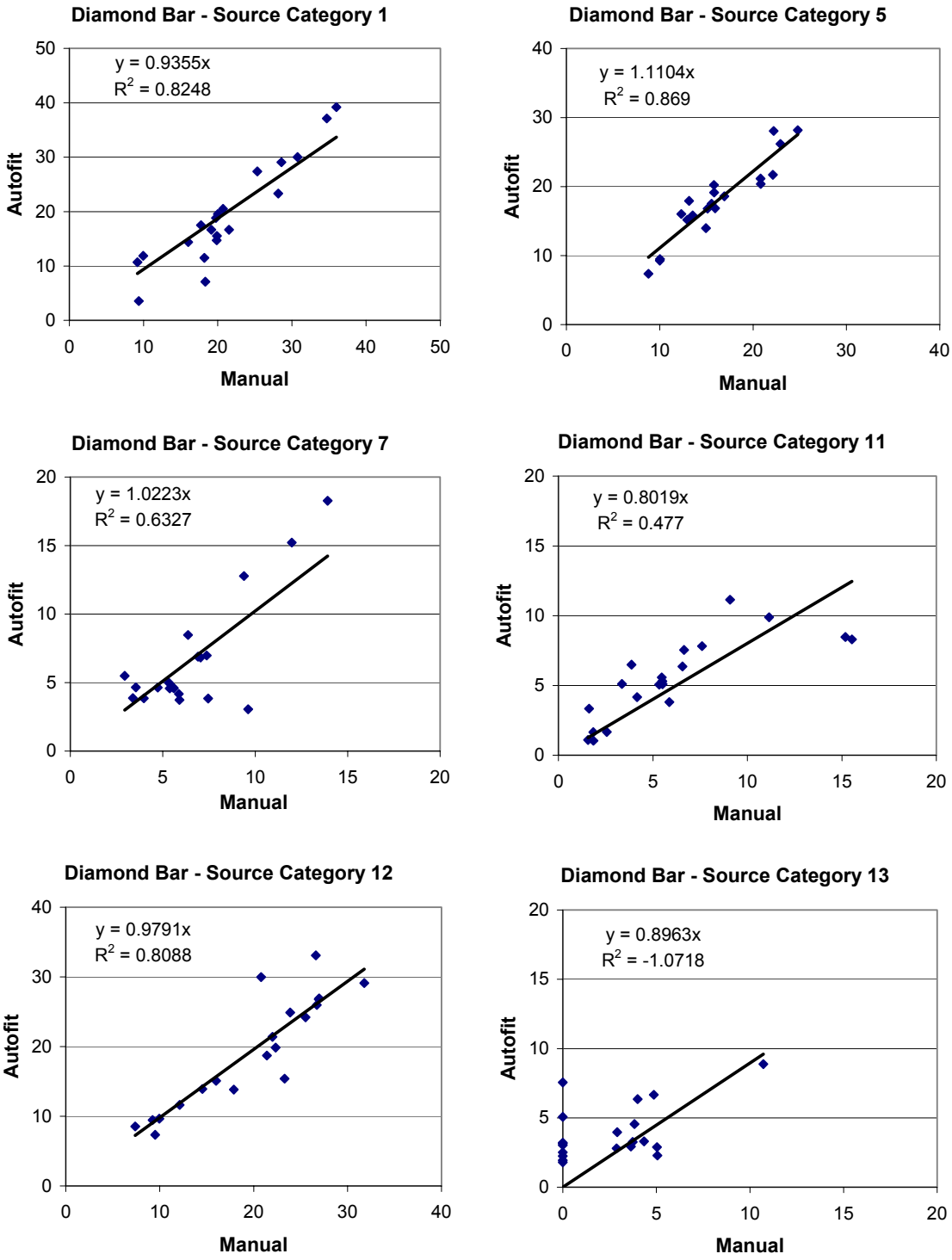
Mean source contribution estimates at Lake Perris by 6-hour period, cont'd.



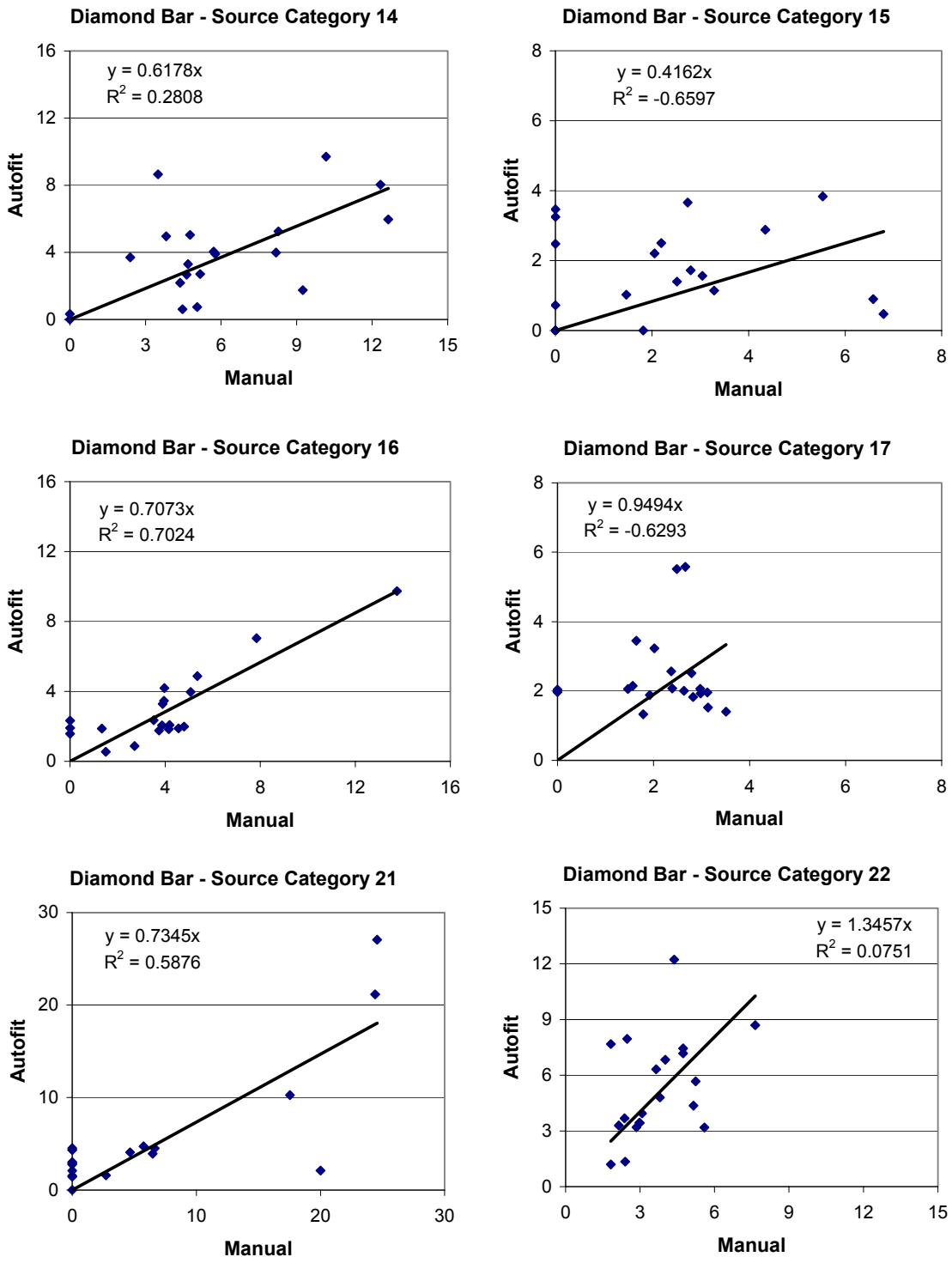
Time series plots of mean source apportionment by site for experiment 1.



Time series plots of mean source apportionment by site for experiment 1, cont'd.



Comparisons of source contributions estimates from manual versus autofit CMB for Diamond Bar.



Comparisons of source contributions estimates from manual versus autofit CMB for Diamond Bar.