Comparison of Ambient Measurements to Emissions Representations for Modeling in California's San Joaquin Valley

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ABSTRACT

As part of the Central California Ozone Study (CCOS), the San Joaquin Valleywide Air Pollution Study Agency (SJVAPSA) is seeking to improve preliminary photochemical modeling results. To further this goal, Sonoma Technology, Inc. (STI) is conducting several analyses of emissions and ambient data for the purpose of recommending meaningful improvements to emission inventories that will enhance subsequent photochemical ozone modeling results.

Work completed to date includes a review of the organic gas speciation profiles used to prepare emissions for input to the photochemical model and an analysis of available ambient data. Speciation profiles were analyzed in terms of reactivity and the organic gas emission totals associated with each profile, and it was determined that 14 speciation profiles account for 85% of the reactivity-weighted organic gas emissions in the CCOS modeling domain. For the most part, these 14 speciation profiles are associated with mobile sources and solvent usage, and specific recommendations were made for improving these high-priority profiles.

In addition, ambient measurements collected in Central California during summer 2000 were analyzed to identify monitoring sites with valid 1-hr or 3-hr speciated volatile organic compounds (VOCs), oxides of nitrogen (NO_x), and carbon monoxide (CO), and meteorological data. An assessment was also made of the emission sources likely impacting each site. Each monitoring site was assigned a ranking of 1 through 5 based on the quality of data available for that site, and the results of these analyses were used to select sixteen sites that would be used for subsequent comparisons of ambient to emissions data.

INTRODUCTION

The Central California Ozone Study (CCOS) is a multi-year program of meteorological and air quality monitoring, emission inventory development, data analysis, and air quality simulation modeling. The goals of CCOS are to

- obtain suitable aerometric and emission databases to update, evaluate, and improve model applications for representing urban- and regional-scale ozone episodes in central and northern California to meet the regulatory requirements for state and federal 1-hr and federal 8-hr ozone standards;
- determine the contributions of transported and locally generated ozone and the relative benefits of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) emission controls in upwind and downwind areas; and
- assess the relative contributions of ozone generated from emissions in one air basin to federal and state exceedances in neighboring air basins.

Photochemical modeling studies are being carried out using both the Comprehensive Air Quality Model with Extensions (CAMx) and the Community Multiscale Air Quality (CMAQ) model. Recent performance evaluations of the photochemical modeling have shown that the models tend to underpredict peak ozone concentrations both at the surface and aloft, particularly in the southern San Joaquin Valley (SJV).

The purpose of this study is to improve preliminary CCOS photochemical modeling results by using emissions and ambient data to examine hourly patterns in the CCOS emission inventories. The results of this investigation are being used to recommend meaningful improvements to emission inventories that will enhance photochemical ozone modeling results.

Specific tasks being undertaken in this study include a review of the organic gas speciation profiles used to prepare emissions data for input to the photochemical model, an analysis of available ambient data, and a variety of comparisons of ambient to emissions data. The speciation profile review and analysis of available ambient data are complete, and the comparisons of ambient to emissions data are ongoing.

TECHNICAL APPROACH

Speciation Profile Review

Speciation profiles provide a detailed breakdown of the individual chemical species emitted by a specific source category. When an emission inventory is being prepared for use in an air quality model, each source category is assigned a speciation profile to disaggregate total organic gas (TOG) emissions into individual chemical compounds. Incorrect assignments of speciation profiles to emissions sources and/or speciation profiles that do not accurately represent the chemical composition of emissions can cause inaccuracies that will impact photochemical modeling results.

The California Air Resources Board (CARB) provided Sonoma Technology, Inc. (STI) with the library of TOG speciation profiles used in the preliminary CCOS modeling efforts. Each profile consists of a list of Storage and Retrieval of Aerometric Data (SAROAD) codes identifying individual chemical species and the weight fraction of TOG emissions assigned to each species. The CARB also provided a cross-reference file that matches each source category in the CCOS emission inventory with a TOG speciation profile and lists the fraction of reactive organic gas (FROG) associated with each profile. Background material on the CARB speciation profiles and cross-reference file was obtained from the CARB web site.[1] This information was used to evaluate the vintage of each profile and the appropriateness of the profile-to-source category assignments selected by the CARB for application to the year-2000 CCOS inventory.

The CARB speciation profile library contains 425 organic gas profiles, making a detailed analysis of each profile impractical. Therefore, an effort was made to prioritize the profiles by the magnitude of emissions assigned to each profile and relative ozone reactivity so that analyses could be focused on the most important profiles. The emissions associated with each profile were determined using a preliminary gridded, weekday emission inventory for July 31, 2000, provided by the CARB. For assessing speciation profiles, the CARB provided STI with the anthropogenic emission inventory developed for the CCOS study domain. In that inventory, TOG emissions were disaggregated using 252 speciation profiles. To determine priorities for further evaluation, we converted TOG emissions to reactive organic gas (ROG) emissions by using the FROG values listed in the CARB speciation cross-reference file. We then summed the ROG emissions across source categories assigned to each profile to obtain total ROG emissions by speciation profile.

The reactivity of each profile was estimated using published maximum incremental reactivity (MIR) values that are used to represent the ozone formation potential of various organic compounds.[2] Weighted reactivity values for each profile were calculated as follows:

Equation (1) $$R = \sum_{i=1}^{n} (MIR)_i w_i$$

where:

R = weighted reactivity
$(MIR)_i$ = maximum incremental reactivity for species *i*
w_i = weight fraction of species *i* in a given profile

The resulting reactivity values for each speciation profile were multiplied by the total TOG emissions associated with each profile to produce total reactivity-weighted emissions by profile. Table 1 shows the total TOG-, ROG-, and MIR-weighted emissions by speciation profile for those profiles with the highest contribution to total MIR-weighted emissions. As shown in Table 1, the top 10 profiles—which are mostly associated with mobile source exhaust and evaporative emissions—account for 80% of the MIR-weighted TOG emissions in the CCOS domain (as well as 52% of the total TOG emissions and 66% of the total ROG emissions). These results suggest that focusing on as few as 10 (or 4%) of the 252 speciation profiles used in the CCOS inventory would address the speciation of 80% of the MIR-weighted TOG emissions. Adding the next four profiles account for an additional 5% of the MIR-weighted emissions. The remaining 238 speciation profiles account for the remaining 15% of emissions.

Analysis of Available Ambient Data

A CCOS field measurement program was conducted during the four-month period from June 1 to October 2, 2000. During this period, existing Photochemical Assessment Monitoring Stations (PAMS) in Central California were supplemented with a network of meteorological and air quality monitoring stations, and additional measurements were made during "intensive operating periods" (IOPs) when meteorological conditions were conducive to ozone formation. As part of this study, STI analyzed all available ambient data from PAMS or CCOS supplemental monitoring sites to identify sites collecting ambient data of sufficient quality and quantity for comparison with emission inventory data. The pollutants and parameters of interest include ozone precursors (e.g., hydrocarbons and NO_x) as well as carbon monoxide (CO) and meteorological data. In addition, TOG and NO_x emissions data from a 14-km^2 area around each monitoring site were extracted from a preliminary gridded CCOS emission inventory to assess the likelihood that the site was being influenced by nearby emissions sources. (CARB is currently working on a final CCOS emission inventory that will be used for all upcoming analyses comparing ambient and emissions data.)

Table 1. Anthropogenic TOG-, ROG-, and MIR-weighted TOG emissions by speciation profile.

Rank	Profile Number	Profile Name	TOG (tons/day)	ROG (tons/day)	Weighted Reactivity	MIR-Weighted TOG	MIR-Weighted TOG %	Cumulative MIR-Weighted TOG %
1	401	Gasoline - non-catalyst - stabilized exhaust	241	222	4.4	1,053	21%	21%
2	882	Gasoline - catalyst - stabilized exhaust	179	145	3.4	618	12%	34%
3	422	Hot soak emissions - California light-duty vehicles	198	197	2.4	475	10%	43%
4	818	Farm equipment - diesel – light and heavy- duty vehicles	95	79	5.0	470	10%	53%
5	877	Gasoline - catalyst - FTP bag 1-3 (starts)	102	96	3.9	401	8%	61%
6	203	Animal waste decomposition	1,095	88	0.3	322	7%	67%
7	586	Composite jet exhaust JP-5	25	22	7.0	172	3%	71%
8	906	Gasoline - diurnal & resting evaporatives	87	86	2.0	172	3%	74%
9	419	Liquid gasoline - MTBE 11% - commercial grade	57	57	2.7	152	3%	78%
10	402	Gasoline - non-cat - FTP bag 1-3 (starts)	31	28	3.8	116	2%	80%
11	783	Industrial surface coating - solvent based paint	28	28	2.8	79	2%	81%
12	600	Species unknown - all category composite	42	29	1.5	61	1%	83%
13	716	Medium cure asphalt	22	22	2.4	53	1%	84%
14	1902	Architectural coatings - water borne	24	24	2.0	48	1%	85%
—	All Other	Various	1,794	418	0.4	754	15%	100%
		Total	4,017	1,540	—	4,946	100%	—

To help prioritize the monitoring sites for possible inclusion in the CCOS Phase II analyses, we considered the following criteria for 36 air quality sites in the CCOS domain:

- Availability of speciated VOC measurements
- Availability of NOx measurements
- Availability of wind direction measurements
- Sufficient density of TOG and NOx emissions
- Availability of CO or total nonmethane organic compounds (TNMOC) measurements
- Number of distinct counts of VOC, NOx, and CO (i.e., how many unique levels are reported for these measurements; fewer distinct reported levels are less suitable for analysis)
- Number of values above detection limit and background thresholds. For this analysis, we used VOC > 50 ppbC, NOx > 10 ppb, and CO > 0.150 ppm.
- Visual inspection of monitoring sites using imagery from "Google™ Earth". Sites were examined for visual evidence of local emissions.

Examination of the site measurements relative to the criteria resulted in grouping the sites into five distinct groups. All sites that collected speciated VOC data and NO_x measurements were classified as Tier 1, 2, or 3 (the most suitable sites for comparisons with emission inventory data). Only six sites met all the criteria listed above and they were denoted Tier 1. Two sites failed one of these criteria and were denoted Tier 2. Eight sites failed two of the criteria and were denoted Tier 3. Tiers 2 and 3 sites are typically less suitable for comparison because of fewer emissions near the site or insufficient measurements.

Sites from which no speciated VOC data were collected or available but that made some CO or TNMOC measurements were also considered less suitable. Sites that made more than 10 CO or TNMOC measurements, NO_x measurements, meteorological measurements, and urban-like emissions levels of TOG and NO_x were considered Tier 4. Those sites that failed one of these criteria were considered Tier 5.

Comparisons of Ambient Data and Emissions Data

During the CCOS second phase, ambient data collected at the sites categorized as Tier 1, 2, or 3 will be compared with emissions data from the final version of CARB's gridded CCOS emission inventory for summer 2000 (this inventory was not available in time to present comparison results in this paper). The purpose of these emission inventory reconciliation analyses will be to identify components of the emission inventory that warrant further investigation and improvement by making quantitative comparisons of emission inventory- and ambient-derived molar pollutant ratios (e.g., VOC/NO_x) and chemical speciation profiles. Several analyses are planned:

- Comparison of emission inventory- and ambient-derived ratios of VOC/NOx and CO/NOx for morning hours when emission rates tend to be high and chemical reaction rates tend to be low, increasing the likelihood that monitoring sites are being influenced by fresh, local emissions. These comparisons will be refined by calculating emission inventory-derived ratios by hour and for grid quadrants around each monitoring site, corresponding to the prevailing upwind direction (specific emission sources impacting a monitoring site can vary by wind direction).

- Comparison of emission inventory- and ambient-derived ratios of individual hydrocarbon species such as acetylene/benzene, ethylene/acetylene, and benzene/toluene by hour and by wind quadrant.
- "Fingerprint analyses" comparing ambient- and emission inventory-derived TNMOC compositions by wind quadrant (a means of evaluating the speciation profiles used to produce the chemically resolved emission inventory).
- The application of source apportionment tools such as positive matrix factorization (PMF) and chemical mass balance (CMB) to corroborate the findings from other analyses by comparing the mix of emissions sources produced by source apportionment tools with the mix calculated from the gridded emission inventory.

RESULTS

Speciation Profile Review

A major finding of these analyses is that, while the CARB organic gas profile database contains hundreds of speciation profiles, only a handful of them appear to be significantly affecting the preparation of the CCOS emission inventory for modeling. Ten profiles (or 4% of the total number of profiles applied to the CCOS inventory) account for 80% of the MIR-weighted TOG emissions in the CCOS inventory. This greatly narrows the focus for pending speciation profile research and improvements. Specific findings and recommendations related to these 10 high-priority (and other) profiles are listed below.

Profiles 401 and 882, Gasoline-fueled Vehicles – Stabilized Exhaust

CARB profiles 401 and 882 are used to speciate exhaust emissions from on-road gasoline vehicles (non-catalyst and catalyst, respectively). In addition, profile 401 is applied to various types of gasoline-powered non-road equipment, such as recreational boats and lawn and garden equipment. These profiles were derived from tests conducted during 1994 and 1996 through the CARB's in-use vehicle surveillance program. The objective of this ongoing test program is to determine a fleet "snapshot" of baseline mobile source emissions, including the development of exhaust and evaporative speciation profiles for in-use vehicles.[3]

Recent studies have shown that the introduction of reformulated gasoline (RFG) in California has affected the reactivity of exhaust organic gas emissions from motor vehicles. Measurements made in bore two of the Caldecott Tunnel (where heavy-duty trucks are not allowed) in the San Francisco Bay Area as part of a University of California (UC), Berkeley study show a 6% reduction in the reactivity of tunnel non-methane organic compound (NMOC) emissions between 1995 and 1996, the year when Phase 2 RFG requirements first took effect (reactivity assessments were made using the maximum incremental reactivity scale).[4]

The CARB speciation profiles for exhaust emissions from gasoline-fueled vehicles appear to reflect these changes to California fuels. Figure 1 shows weighted reactivity values for CARB profiles for stabilized emissions from non-catalyst (401) and catalyst (882) vehicles and for profiles derived from tunnel measurements in 1999 and 2001. The reactivity values derived from tunnel measurements fall between the values for these two CARB profiles, which is expected because tunnel measurements reflect a mixture of gasoline vehicle types. Figure 2 shows the composition of these profiles by species group; the figure shows good general agreement between the CARB profiles and the profiles developed from tunnel measurements. Differences between the profiles, such as the higher fraction of isoalkanes in the

tunnel profiles, can likely be explained by the presence of running loss evaporative emissions as well as exhaust emissions in the tunnel measurements.

Figure 1. Weighted reactivity of various profiles for gasoline-fueled vehicles.

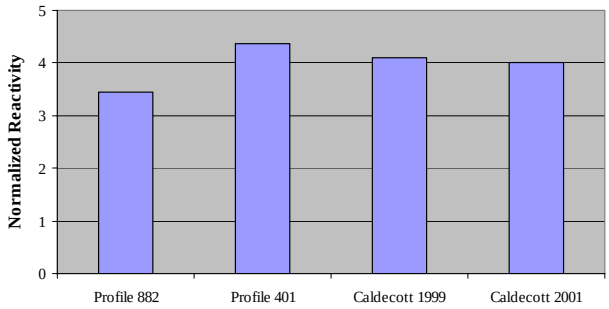
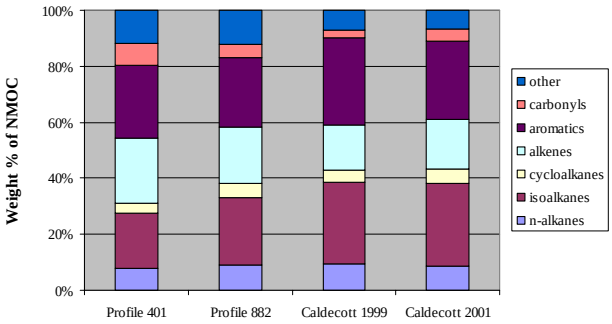


Figure 2. Composition of emissions from gasoline-fueled vehicles by species group.

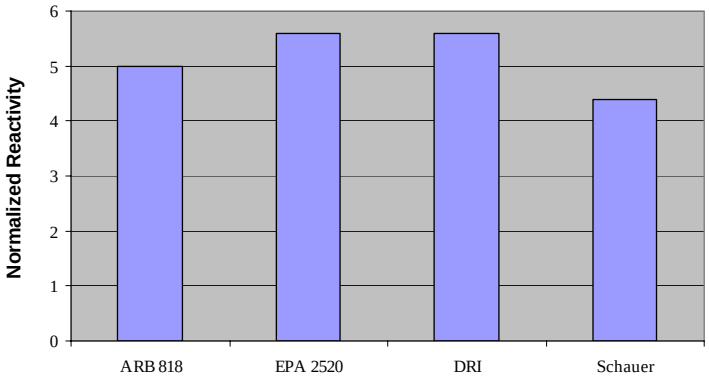


Overall, CARB profiles 401 and 882 appear to be appropriate for year-2000 exhaust emissions from gasoline-fueled on-road mobile sources in California. However, profile 401 also applied to non-road mobile sources such as recreational boats and lawn and garden equipment, and over 70% of the organic gas emissions associated with this profile are attributable to these non-road sources. To investigate possible differences in the composition of organic gas emissions from on-road and non-road mobile sources, a literature search was conducted to identify exhaust speciation profiles for non-road sources. A speciation profile developed from source tests conducted on non-road equipment (lawnmowers) using California RFG[5] was discovered to contain significantly higher fractions of methane and acetylene than does CARB profile 401 and has a slightly lower reactivity value than the CARB profile (4.2 versus 4.4). It was recommended that the Gabele profile be utilized for gasoline-powered non-road mobile sources.

CARB Profile 818, Diesel-fueled Vehicles – Exhaust

In the CCOS emission inventory, CARB profile 818 is applied to exhaust emissions from both on-road and non-road diesel vehicles. The profile is based on a 1991 study conducted at California Polytechnic State University, San Luis Obispo, in which engine exhaust emissions were collected from heavy-duty diesel equipment, such as tractors.[6] However, the chemical composition of emissions from on-road and non-road diesel engines may vary because of differing regulatory requirements, operating modes, and maintenance schedules,[7] so the applicability of profile 818 to on-road diesel vehicles is questionable. Therefore, a number of organic gas speciation profiles for on-road diesel vehicles were identified through a literature search and compared to profile 818. U.S. Environmental Protection Agency (EPA) profile 2520 was derived from measurements of vehicle exhaust taken at the Tuscarora Tunnel in Pennsylvania in 1995.[8] During a recent receptor modeling study conducted for CCOS, the Desert Research Institute (DRI) used a diesel exhaust profile derived from 1996 tunnel measurements in Baltimore and New York.[9] A recent Lake Michigan Air Directors Consortium (LADCO) study cites an organic gas profile for on-road diesel engines developed by Schauer in 1999[10] through the use of dynanometer testing of two medium-duty diesel trucks from the 1996 in-use vehicle fleet in Southern California. These trucks were fueled with California reformulated diesel fuel. Figure 3 shows the weighted reactivity for each of these profiles, along with CARB profile 818. The reactivity of the CARB profile is 12% lower than the EPA and DRI profiles and 12% higher than the Schauer profile. However, the Schauer profile contained a significant fraction of unidentified species; therefore, this reactivity value may not be accurate.

Figure 3. Weighted reactivity of various diesel exhaust speciation profiles.



Because the Schauer profile was developed from tests on trucks from California's vehicle fleet using California reformulated diesel fuel, it was recommended that this profile be used to speciate on-road diesel emissions for future CCOS modeling efforts. However, the Schauer profile contains a significant fraction of unidentified compounds (18%), and it may be necessary to disaggregate this unidentified fraction to likely known compounds.

CARB Profile 203, Animal Waste Decomposition

CARB profile 203 is applied to organic gas emissions from livestock husbandry operations in the CCOS domain. Almost half these emissions are associated with dairies and another 25% are associated with range cattle. Profile 203 is taken from the EPA's SPECIATE 3.2 database and is based on a 1978 study in California's South Coast Air Basin.[8]

Over 1,000 tons per day of TOG, but only 88 tons per day of ROG, emissions are associated with profile 203 (see Table 1). The FROG assumed for this profile is extremely important, as a change of only 1% in the FROG value would result in a change of over 10 tons per day in ROG emissions from animal waste decomposition. Profile 203 is shown in Table 2, and the species methane, ethane, and acetone are judged to be non-reactive by the CARB, resulting in a FROG value of 8% for this profile.

Table 2. CARB TOG profile for animal waste decomposition.

Species Name	CAS Code	Weight Percent	MIR
Methane	74-82-8	70	0.0139
Ethane	74-84-0	20	0.31
Acetone	67-64-1	2	0.43
Isopropyl alcohol	67-63-0	2	0.71
Propyl acetate	109-60-4	2	0.86
Ethanol	64-17-5	2	1.69
Trimethyl amine	75-50-3	1	7.06
Ethyl amine	75-04-7	1	7.79

The CCOS group recently sponsored a field study at a northern California dairy to evaluate emissions of TOG and ROG.[11] Measurements were made for a variety of processes on a summer day when 3,442 cows were present at the facility. Table 3 shows TOG and ROG emission rates by process and the fraction of reactive organic gas value for each process. The FROG value varied widely among

the processes and, overall, the ratio of ROG-to-TOG was 0.8%, or one-tenth of the fraction assumed for profile 203.

Table 3. Dairy organic gas emissions by process (based on a population of 3,442 cows).

Process Type	Process	Emissions (lbs/day)		ROG Percent
		TOG	ROG	
Milk Cow	Bedding	1.3	0.5	38.5%
	Flush Lane	10.5	1.4	13.3%
	Feeding	5.7	5.4	94.7%
	Turnout	500.5	2.1	0.4%
Dry Cow	Bedding	0.0	0.0	0.0%
	Flush Lane	0.1	0.1	100.0%
	Feeding	0.5	0.4	80.0%
	Turnout	0.7	0.7	100.0%
Solids Piles	Fresh	3.1	0.0	0.0%
	Aged	873.4	0.0	0.0%
	Bedding Storage	0.5	0.3	60.0%
Lagoon	Lagoon	164.1	1.1	0.7%
Milk Parlor	Effluent Stream	0.2	0.2	100.0%
Total	All Processes	1560.6	12.2	0.8%

Significant uncertainty exists in the composition of emissions from animal waste decomposition, and further study of this source category is needed. California State University at Fresno is currently under contract with the CARB to evaluate reactive organic gas emissions at California dairies. This project involves the chemical speciation of TOG samples collected at dairies, and project completion is expected in December 2005.[12] It was recommended that the results of this study be evaluated for inclusion to the CARB speciation database and that, in the meantime, CARB profile 203 continue to be applied to animal waste decomposition emissions.

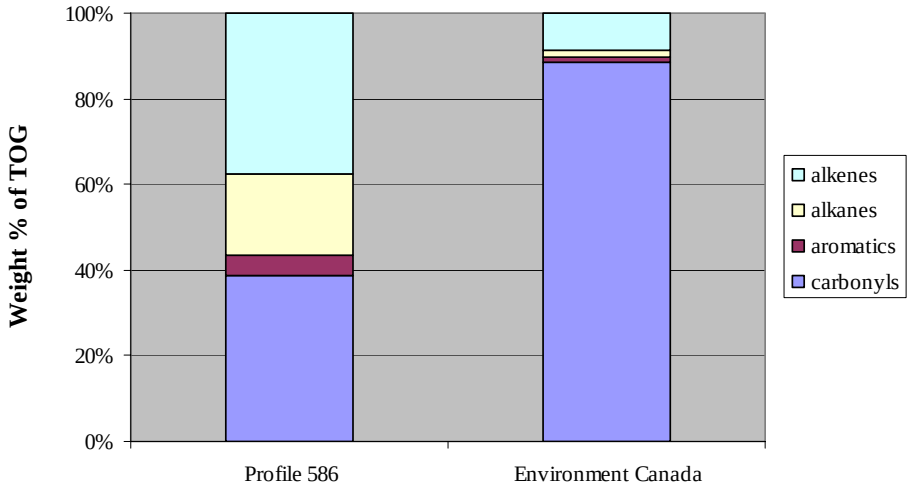
CARB Profile 586, Jet Exhaust

CARB profile 586 is applied to emissions from military, commercial, and civil jet aircraft in the CCOS inventory. Profile 586 is a composite of three EPA profiles (1097-1099) that were developed from engine tests conducted in 1984 on a Compilation of air pollutant emission factorsCFM-36 jet engine fired with JP-5 fuel at various power settings. Data collected were combined according to average landing-and-takeoff (LTO) cycle times published in AP-42.[13] JP-5 fuel is primarily used in military aircraft, whereas commercial aircraft use Jet A (United States) or Jet A-1 fuel (outside the United States), although all three fuels are kerosene-type fuels differing mostly in their flashpoints and freezing points.[14]

Environment Canada (EC) compiled a composite emissions profile for jet aircraft engines based on engine exhaust stream measurements made at Macdonald-Cartier International Airport in Ottawa, Canada, in 1993 and 1994.[15] These tests were conducted at various engine speeds on aircraft using Jet A-1 fuel. Figure 4 shows a comparison of CARB profile 586 and the EC profile by species group. About 20% of both profiles is composed of the carbonyl compounds, formaldehyde and acetaldehyde, but carbonyl acetone makes up 64% of the EC profile—making carbonyls the dominant species group. The CARB profile contains fractions of alkenes (especially ethylene) and alkanes (especially methane)

larger than those in the EC profile. Also, the weighted reactivity of the EC profile is only 3, compared to 7 for the CARB profile—largely because of the low reactivity of acetone. These differences may reflect changes in the composition of jet fuels produced since the mid-1990s.[15]

Figure 4. Composition of organic gas emissions from jet aircraft engines by species group.



The CARB profile used for jet engine exhaust dates to 1984 and is based on source tests conducted with a fuel that is not in use among commercial aircraft. The more recent Canadian study suggests that fuel composition changes may have significantly altered the makeup of emissions from jet engines since the mid-1980s, although this Canadian study was performed at an airport rather than under laboratory conditions. Further research is needed to determine the composition of TOG emissions from jet engines using fuels common to California in 2000. It was recommended that CARB profile 586 continue to be applied to jet exhaust emissions until better data is available.

Other CARB Speciation Profiles

Findings and recommendations for other speciation profiles analyzed during this study were developed:

- Speciation profiles applied to hot soak (profile 422), cold-start (profiles 877 and 402), and diurnal and resting evaporative (profiles 906 and 419) emissions from gasoline-fueled vehicles appear to be appropriate for conditions in California in 2000.
- Wildfires can be a significant source of ROG emissions on specific days, and the speciation profile for this source category dates to 1975. It was recommended that a new profile be developed based on vegetation types common to California, similar to the process recently undertaken by LADCO.[16]
- The CARB profile used for industrial surface coatings is based on a 1985 study, and recent work by LADCO[16] suggests that the composition of such coatings has changed significantly since the mid-1980s, resulting in a lowering of the reactivity of emissions from industrial surface coatings by as much as 30%. It was recommended that the LADCO profiles be used for future CCOS modeling efforts, although some adjustment to these profiles may be required to reflect conditions in California.
- The CARB profile used for medium-cure asphalt is based on a 1985 study that relied on the analysis of asphalt samples later determined to have been purposely altered at a refinery before shipment. It was recommended that a new speciation profile for this source category be developed from current asphalt samples.

- CARB's all-category composite speciation profile is applied to a wide variety of source categories in the CCOS inventory. However, Table 1 shows that the weighted reactivity of speciation profiles for fuel combustion processes tends to be higher than the reactivity of profiles for evaporative sources. Therefore, it was recommended that multiple composite profiles be developed according to broad source types such as fuel combustion and solvent usage.

To assess the potential impact of such changes, the anthropogenic emission inventory shown in Table 1 was re-weighted using MIR values from recommended profiles that could be immediately incorporated into the CCOS modeling efforts. Results showed that the total MIR-weighted TOG emissions were reduced slightly from 4,946 tons per day to 4,895 tons per day. This study using MIR values also showed that the reactivity of other profiles recommended for further study—including animal waste decomposition, jet exhaust, and wildfires—is likely to decrease when those profiles are updated with more recent data. This finding indicates that the overall effect of suggested updates to the CARB speciation profile library will be a decrease in the reactivity of the CCOS organic gas inventory. Recent model performance analyses have suggested that the mass and/or the reactivity of the CCOS ROG inventory are underestimated;[17] therefore, this finding may indicate that the problem likely lies with the mass of ROG emissions.

Analysis of Available Ambient Data

Table 4 lists the number of morning (0400 to 1000 PST) VOC, NO_x, CO, TNMOC, and wind direction samples collected from all sites during the 2000 summer ozone season in the CCOS domain. In addition, Table 4 provides the TOG and NO_x emissions from a 14-km^2 area around each monitoring station from a preliminary gridded CCOS emission inventory. All sites are categorized as Tier 1 through Tier 5—Tiers 1, 2, and 3 sites are the most suitable for analyses comparing ambient data with emissions data. Figure 5 shows a map with the location and tier designation for each site in Table 1. The most suitable sites for this analysis are all located in the San Francisco Bay Area or in the three major urban areas in the Central Valley (e.g., Sacramento, Fresno, and Bakersfield).

Comparisons of Ambient Data and Emissions Data

During the CCOS second phase, ambient data collected at Tiers 1, 2, and 3 sites will be compared with emissions data from the final version of CARB's gridded CCOS emission inventory for summer 2000. However, this inventory was not available in time to present comparison results in this paper.

Table 4. Summary of measurement sites collecting data considered for comparison with emission inventory data.

Site	Air District	Tier	Number[a] of Speciated VOC samples > 50 ppbC	Number[b] of NO_x samples > 10 ppb	Number of Wind[b] samples	TOG Emissions (tons/day)	NOx Emissions (tons/day)	Designation[c]	Local or Regional Emissions[d]	Number[b] of TNMOC samples > 50 ppbC	Number[b] of CO samples > 0.15 ppm
BGS	San Joaquin Valley Unified	1	27	103	752	76	53	Urban	Local	191	24
CLO	San Joaquin Valley Unified	1	21	78	750	199	46	Urban	Local		22
FSF	San Joaquin Valley Unified	1	29	92	746	210	49	Urban	Local	246	20
NAT	Sacramento Metro	1	26	85	756	65	53	Rural	Mixed		24
SDP	Sacramento Metro	1	20	65	756	93	67	Urban	Local		19
SUN	San Francisco Bay Area	1	30	343	756	94	37	Rural	Regional		527
FLN	Sacramento Metro	2	24	33	569	46	28	Urban	Local		
PLR	San Joaquin Valley Unified	2	25	42	751	63	18	Rural	Regional		
ARV	San Joaquin Valley Unified	3	21	37	750	11	9	Rural	Regional	88	
ELK	Sacramento Metro	3	11	50	751	10	20	Rural	Regional		
SJ4	San Francisco Bay Area	3	6	151		137	85	Urban	Local		32
M29	San Joaquin Valley Unified	3	25	81	748	32	15	Rural	Regional		
BTI	San Francisco Bay Area	3	35	41	623	15	15	Rural	Regional		8
BODB	Northern Sonoma	3	11	NO_y only	756	2	1	Rural	Regional	1	NA
TSM	San Joaquin Valley Unified	3	7	89	756	65	25	Urban	Local		18
BAC	San Joaquin Valley Unified	4		86	754	69	49	Urban	Local	49	18
ELM	Ventura	4		64	753	41	19	Rural	Regional	33	8
FSS	San Joaquin Valley Unified	4		59	749	171	41	Rural	Mixed		13
M14	San Joaquin Valley Unified	4		79	756	155	29	Urban	Local		21
ROS	Placer	4		68	644	75	45	Urban	Local		15
S13	Sacramento Metro	4		103	755	79	59	Urban	Local		24
SIM	Ventura	4		109	749	36	20	Urban	Local	28	33
SOH	San Joaquin Valley Unified	4		110	687	61	41	Urban	Local		24
VCS	San Joaquin Valley Unified	4		68	753	81	19	Urban	Local		15
CHM	Butte	5		65	756	13	9	Urban	Local		20

[a] Approximately 30-37 samples are expected based on 30 regular samples (3-hr duration, once every third day) and special episode predicted samples.

[b] Approximately 750 samples are expected based on hourly measurements.

[c] Urban and rural designations are based on site designations in the CCOS database.

[d] Local, mixed, or regional emissions designations were made using visual site inspections from Google™ Earth. Local sites showed clear emissions sources near the monitor; regional sites showed no obvious local emissions sources.

Table 4. Summary of measurement sites collecting data considered for comparison with emission inventory data.

Site	Air District	Tier	Number[a] of Speciated VOC samples > 50 ppbC	Number[b] of NO_x samples > 10 ppb	Number of Wind[b] samples	TOG Emissions (tons/day)	NOx Emissions (tons/day)	Designation[c]	Local or Regional Emissions[d]	Number[b] of TNMOC samples > 50 ppbC	Number[b] of CO samples > 0.15 ppm
DVP	Monterey Bay Unified	5		18	756	37	5	Rural	Regional		6
DVS	Yolo Solano	5		58	739	13	15	Rural	Mixed		6
FSD	San Joaquin Valley Unified	5		93		188	44	Urban	Local		21
GNF	Santa Barbara	5		45	691	34	13	Urban	Local		11
LOM	Santa Barbara	5		35	748	14	4	Urban	Local		14
LWP	Antelope Valley	5		91	755	21	14	Urban	Local		25
SBC	Santa Barbara	5		75	756	32	12	Urban	Local		22
SHA	San Joaquin Valley Unified	5		101	752	14	12	Urban	Mixed	239	
SLM	San Luis Obispo	5		57	756	17	7	Urban	Local		13
SNH	Sacramento Metro	5		58		92	63	Urban	Local		20
YAS	Feather River	5		72	683	17	15	Urban	Mixed		15

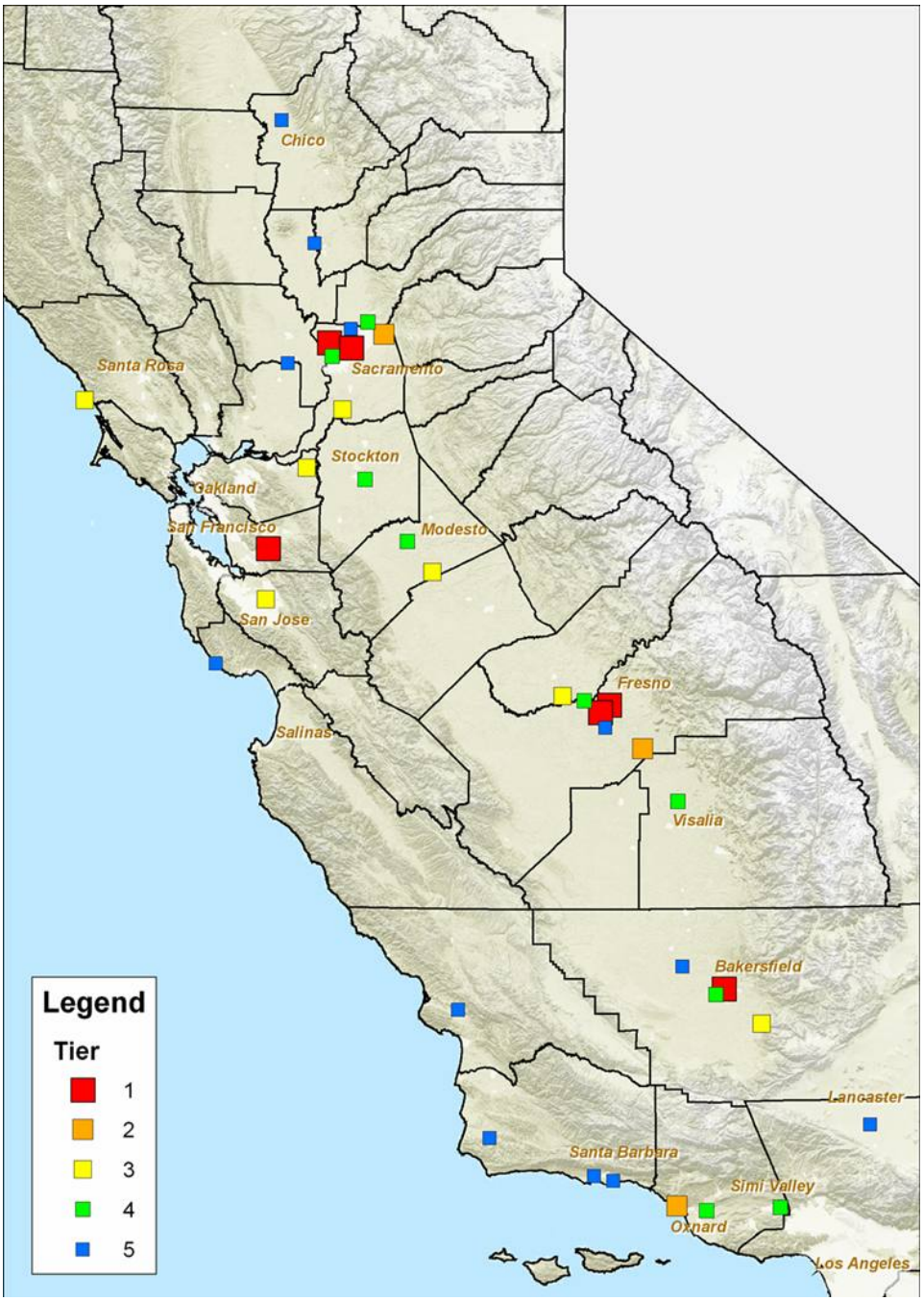
[a] Approximately 30-37 samples are expected based on 30 regular samples (3-hr duration, once every third day) and special episode predicted samples.

[b] Approximately 750 samples are expected based on hourly measurements.

[c] Urban and rural designations are based on site designations in the CCOS database.

[d] Local, mixed, or regional emissions designations were made using visual site inspections from Google™ Earth. Local sites showed clear emissions sources near the monitor; regional sites showed no obvious local emissions sources.

Figure 5. Map of sites and tier designations. Tier 1 sites are the most suitable sites for emission inventory reconciliation; Tier 5 sites are the least suitable.



CONCLUSIONS

During the first phase of the CCOS, a review of the CCOS speciation profile library used to prepare the preliminary CCOS emission inventory for use in photochemical modeling applications showed that 10 of the 252 profiles used to speciate the inventory account for 80% of the MIR-weighted TOG emissions in the CCOS inventory. An evaluation of these 10 high-priority profiles resulted in several recommendations for updates to the CARB speciation profile library. Analysis indicates that the

overall effect of suggested updates to the CARB speciation profile library will be a slight decrease in the reactivity of the CCOS organic gas inventory.

In addition, available ambient data from 36 monitoring sites in the CCOS domain were analyzed to identify sites collecting ambient data of sufficient quality and quantity for subsequent comparison with emission inventory data during the CCOS second phase. It was determined that 16 sites are suitable for subsequent emission inventory comparisons, and these sites are located in urbanized areas around San Francisco, Sacramento, Fresno, and Bakersfield.

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