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

Stephen B. Reid
Steven G. Brown
Michael C. McCarthy
Lyle R. Chinkin
Sonoma Technology, Inc.
Petaluma, CA

U.S. EPA 15th Annual Emission Inventory Conference
New Orleans, LA

May 18, 2006

Background

The Central California Ozone Study (CCOS) consists of a field program, data analysis, emission inventory development, and modeling. The study was designed to gather corroborative evidence, using different analysis techniques, that will result in recommendations for specific, meaningful improvements to the CCOS emission inventory.

Summary of Analyses

- California Air Resources Board (CARB) chemical speciation profiles review
- Identification of available air quality data
- CCOS Phase 2, ongoing analyses

Speciation Profile Review (1 of 14)

Summary of Findings

- Ten CARB speciation profiles account for 80% of the reactivity-weighted total organic gas (TOG) emissions in the CCOS modeling domain
- In general, speciation profiles for key source categories are up to date
- A handful of speciation profiles that need updating were identified
- Updates will likely result in a slight lowering of the reactivity of the organic gas inventory

Speciation Profile Review (2 of 14)

CARB TOG Speciation Profile Database

- 425 available organic gas profiles
- 252 profiles applied to the preliminary year-2000 CCOS emission inventory
- Individual profiles prioritized by summing TOG, reactive organic gases (ROG), and reactivity-weighted emissions associated with each profile

Speciation Profile Review (3 of 14)

Reactivity-Weighted Emission Calculation

$$R_x = \sum(MIR)_y w_y$$

where:

R_x = weighted reactivity for profile *x*

$(MIR)_y$ = maximum incremental reactivity for species *y*

w_y = weight fraction of species *y* in profile *x*

Reactivity-weighted emissions for profile *x* = $TOG_x \times R_x$

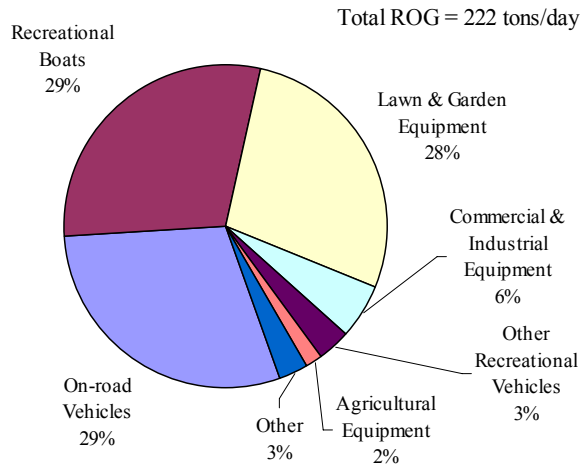
Speciation Profile Review (4 of 14)

Rank	Profile Number	Profile Name	TOG (tons/day)	ROG (tons/day)	Weighted Reactivity	MIR-Weighted TOG	MIR-Weighted TOG %	∑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%
---	Other	Various	1,794	418	0.4	754	15%	100%
		Total	4,017	1,540	---	4,946	100%	---

Speciation Profile Review (5 of 14)

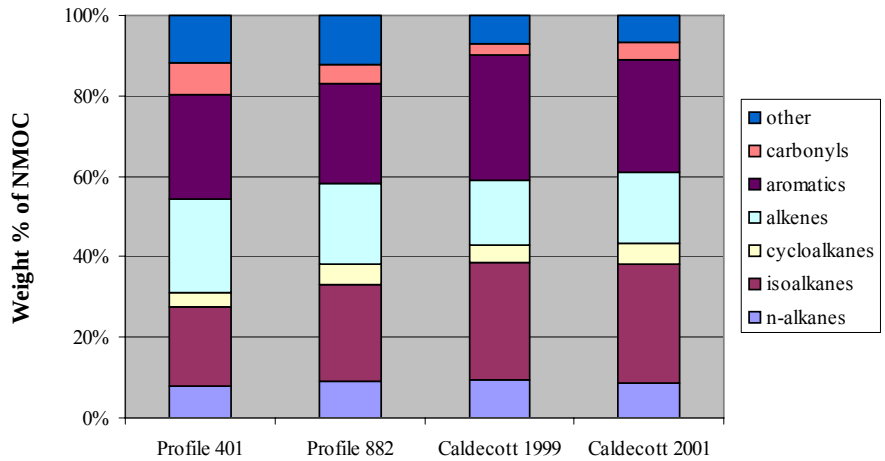
CARB gasoline exhaust profiles

Rank	Profile Number	Profile Name	Application	Source	Vintage
1	401	Non-catalyst - stabilized exhaust	Non-catalyst on-road vehicles; gasoline-powered off-road equipment	CARB's in-use vehicle surveillance program	1996
2	882	Catalyst - stabilized exhaust	Catalyst on-road vehicles	CARB's in-use vehicle surveillance program	1996
5	877	Catalyst – FTP bag 1-3 starts	Cold start emissions from catalyst on-road vehicles	CARB's in-use vehicle surveillance program	1996
10	402	Non-catalyst – FTP bag 1-3 starts	Cold start emissions from non-catalyst on-road vehicles	CARB's in-use vehicle surveillance program	1996

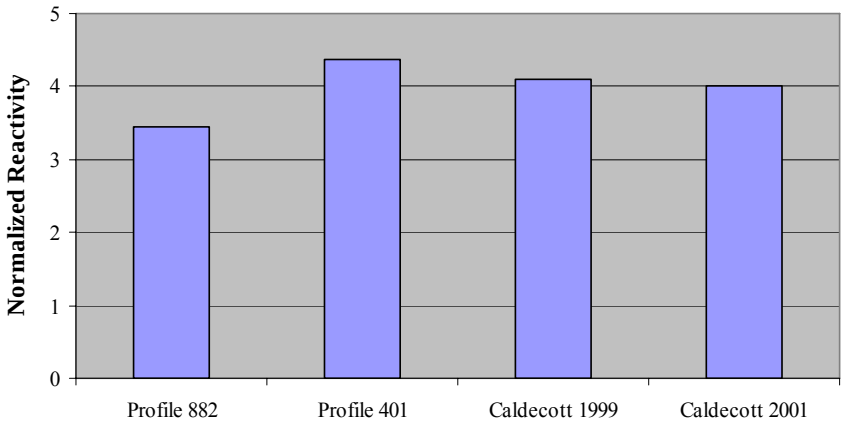


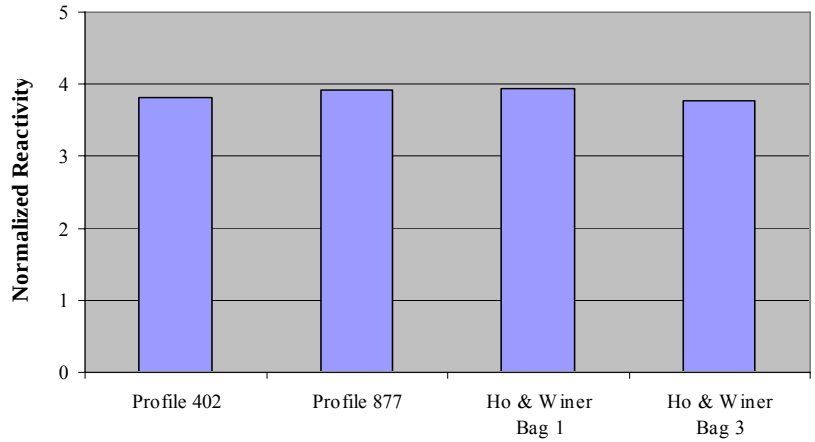
Emissions associated with profile 401

Speciation Profile Review (6 of 14)



Composition of organic gas emissions from gasoline-fueled vehicles by species group



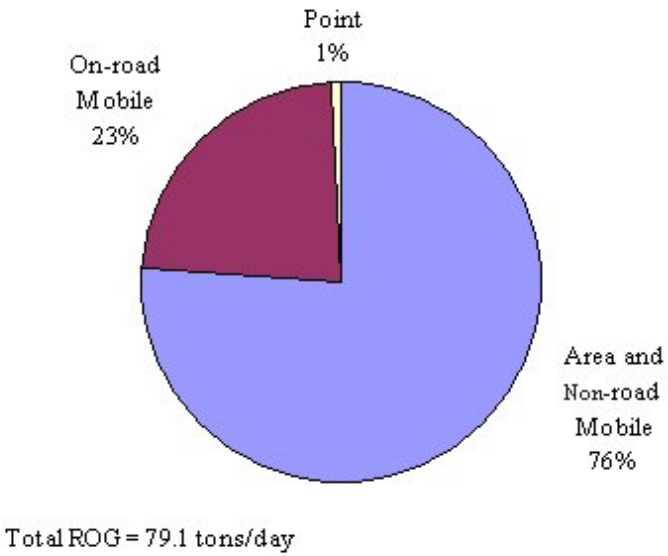


Weighted reactivity of various profiles for gasoline-fueled vehicles

Speciation Profile Review (7 of 14)

CARB diesel exhaust profile

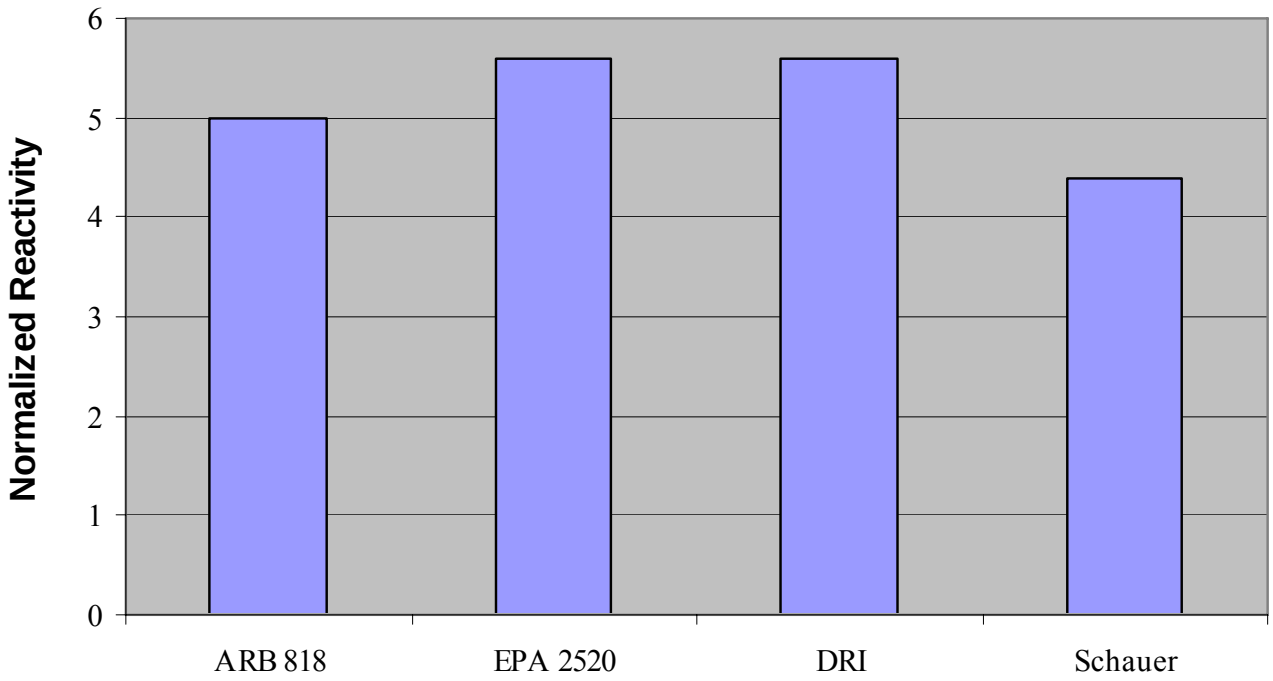
Rank	Profile #	Profile Name	Application	Source	Vintage
4	818	Diesel Farm Equipment	Exhaust emissions from on-road diesel vehicles and off-road diesel equipment	Cal Poly heavy-duty diesel equipment engine tests	1991



Emissions associated with profile 818

Speciation Profile Review (8 of 14)

Reactivity of various diesel exhaust profiles



Speciation Profile Review (9 of 14)

CARB animal waste decomposition profile

Rank	Profile #	Profile Name	Application	Source	Vintage
6	203	Animal waste decomposition	Livestock husbandry operations	EPA's SPECIATE 3.2 database - based on 1978 study in SOCAB	1978

Fraction of reactive organic gas (FROG) for profile 203 = 8%

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

Speciation Profile Review (10 of 14)

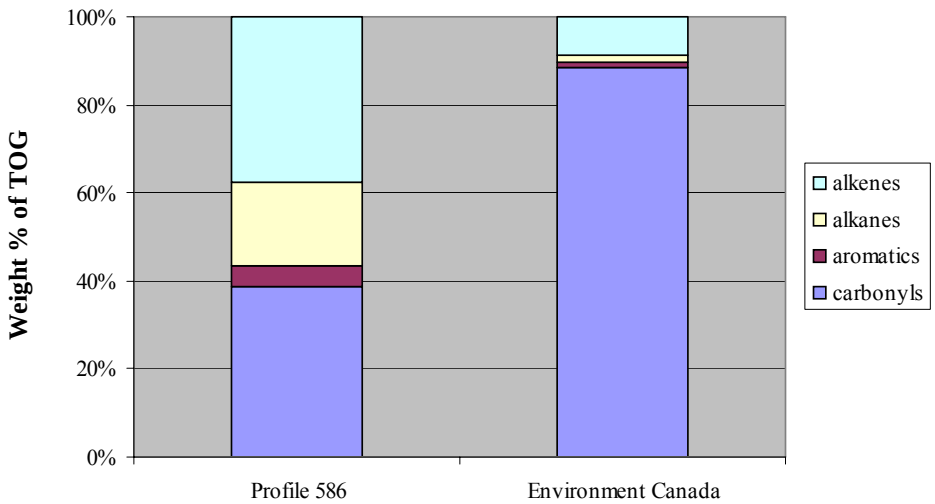
Dairy organic gas emissions by process type

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%

Speciation Profile Review (11 of 14)

CARB jet exhaust profile

Rank	Profile #	Profile Name	Application	Source	Vintage
7	586	Composite jet exhaust	Military, commercial, and civil jet aircraft	Composite of 3 EPA profiles developed from engine tests	1984



Comparison of jet exhaust profile 586

Speciation Profile Review (12 of 14)

Findings and Recommendations (1 of 3)

- Gasoline exhaust and evaporative profiles appear to be appropriate for on-road vehicles in California in 2000.
- A 1997 lawnmower-based profile is more appropriate for non-road gasoline equipment than the current CARB profile (401).
- A Schauer speciation profile is more appropriate for on-road diesel vehicles than CARB's current farm equipment-based profile (818).
- Further study of the reactivity of animal waste emissions is needed.

Speciation Profile Review (13 of 14)

Findings and Recommendations (2 of 3)

- Further study of the composition of organic gas emissions from jet exhaust is needed.
- Wildfires can be a significant ROG source on given days; a new California-specific profile should be developed to replace the current EPA profile used by CARB for this source category.
- CARB industrial surface coating, medium-cure asphalt, and all-category composite profiles need to be updated (new industrial coating profiles were identified).

Speciation Profile Review (14 of 14)

Findings and Recommendations (3 of 3)

- Application of the recommended profiles is likely to result in a slight decrease in MIR-weighted TOG emissions for the CCOS domain (from 4,946 tpd to 4,895 tpd).

Available Air Quality Data (1 of 11)

Site selection based on

- Data availability (distinct counts of VOC, NO_x, CO, wind measurements)
- Ambient concentration levels (VOC > 50 ppbC; NO_x > 10 ppb; CO > 0.15 ppm)
- Presence of local emissions sources
- Spatial distribution of sites
- Temporal distribution of the data

Sites evaluated

- Regular Photochemical Assessment Monitoring Stations (PAMS) sites
- CCOS supplemental sites

Available Air Quality Data (3 of 11)

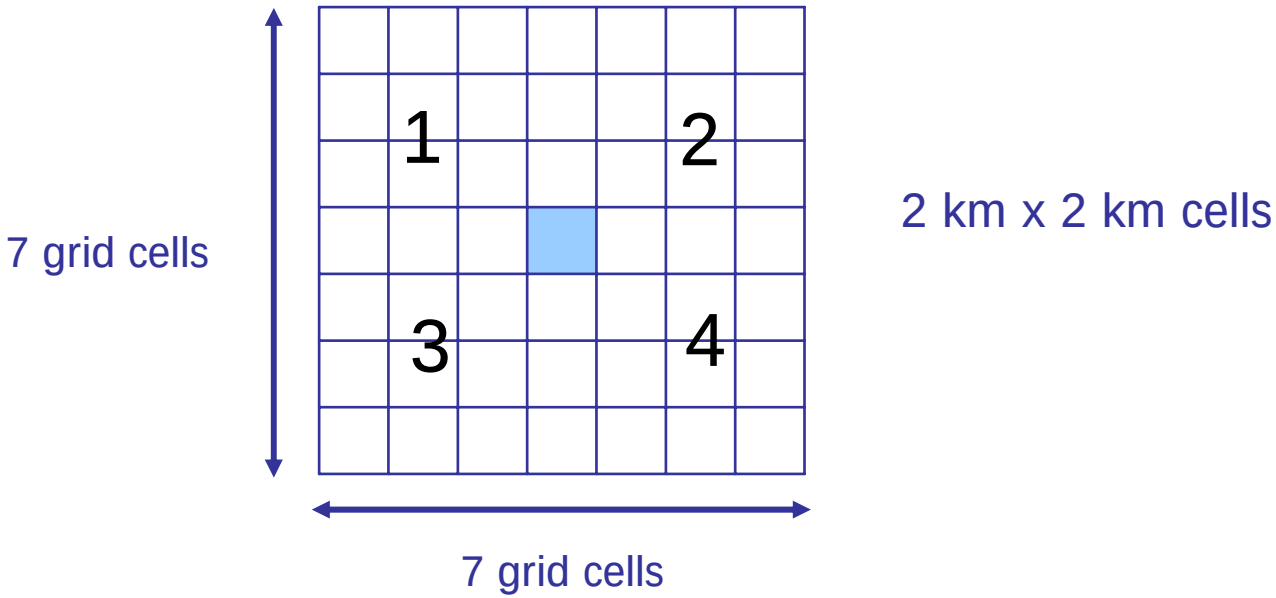
Ambient data collection

- Speciated VOC
  - > 3-hr samples collected every third day
  - > Episodic measurements on forecast basis
  - > 30-37 samples per site expected
- NO_x, CO, wind
  - > Hourly measurements
  - > 750 samples per site expected

Available Air Quality Data (4 of 11)

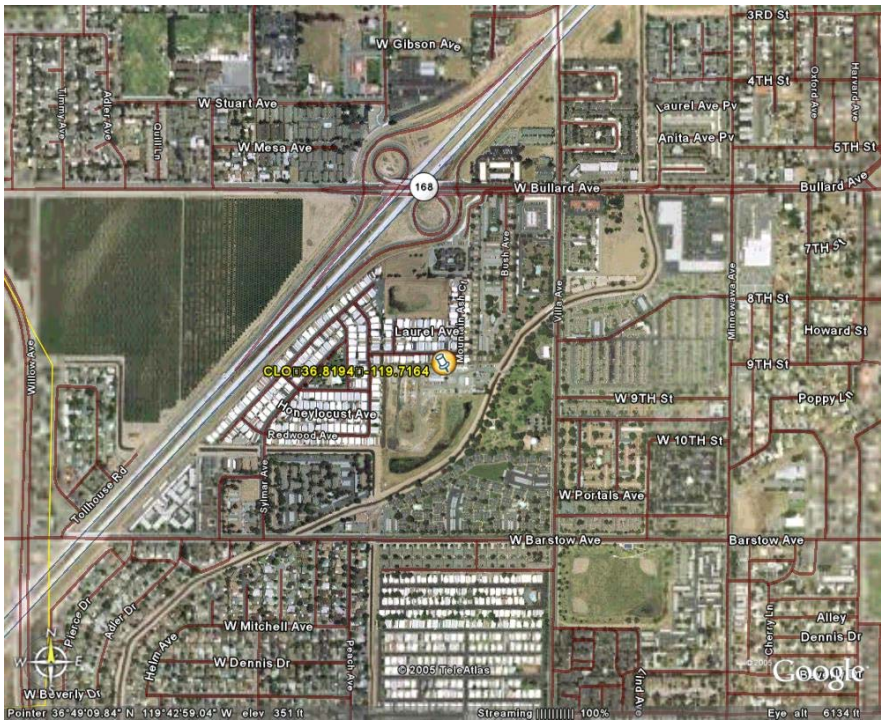
Emissions evaluation by site

- Summed TOG and NO_x emissions for a 14 km x 14 km area around each site

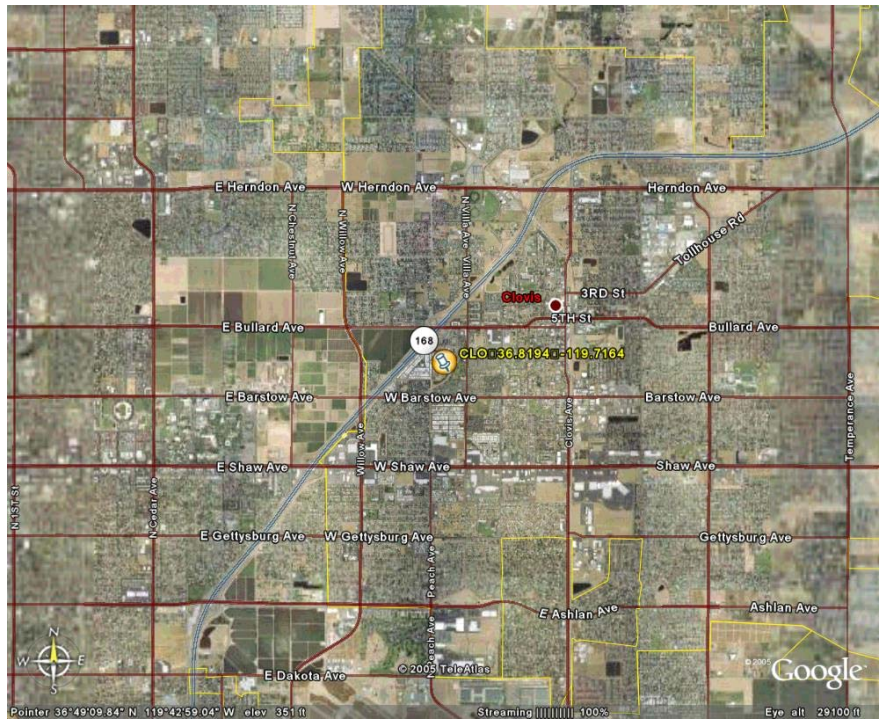


Available Air Quality Data (5 of 11)

Emissions evaluation by site



Clovis Station (2-km width)



Clovis Station (10-km width)

Available Air Quality Data (6 of 11)

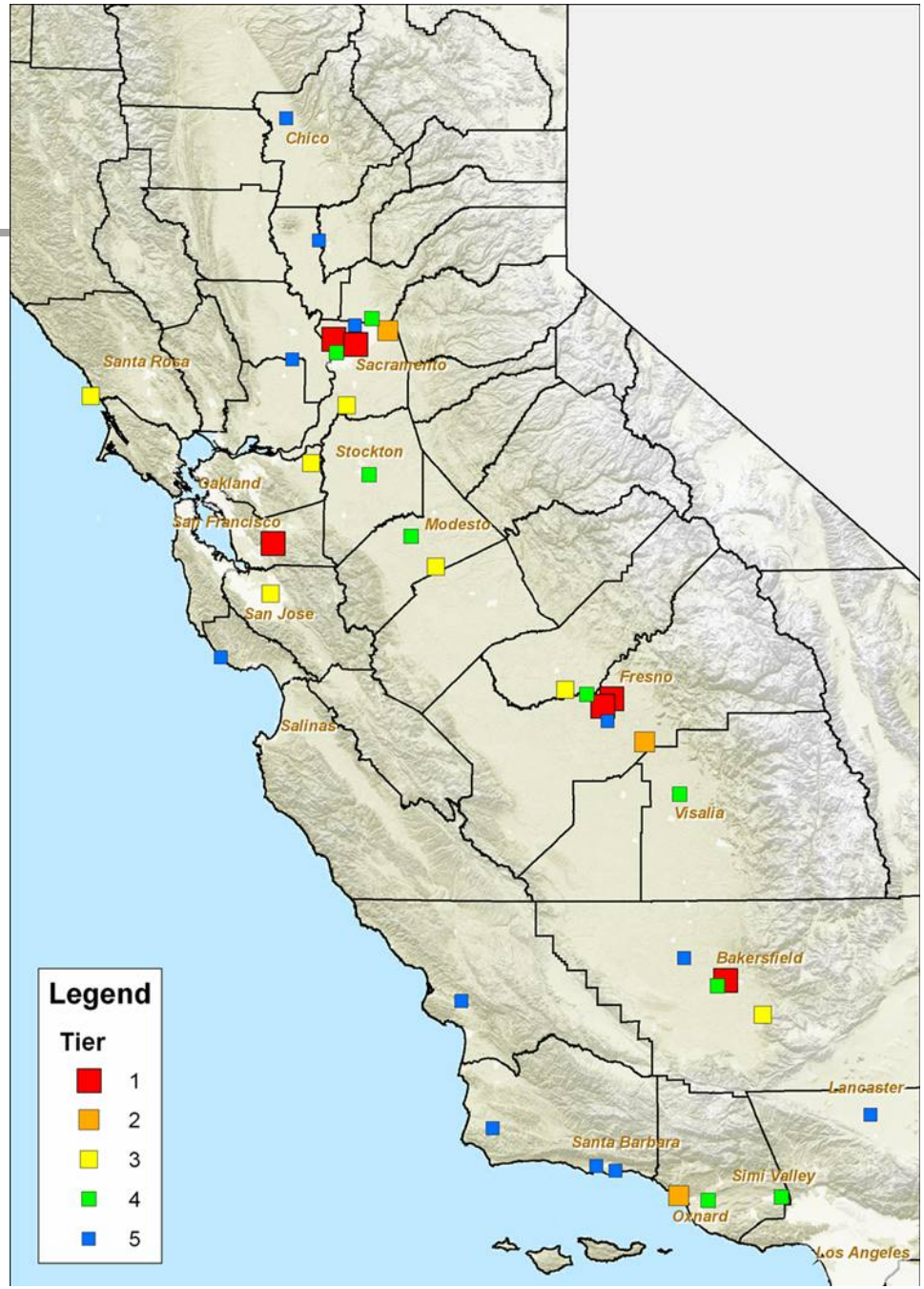
Monitoring site rankings by criteria

- Tier 1 – VOC, NO_x, CO, wind data; significant local emission sources
- Tier 2 – VOC, NO_x, wind data; some local emission sources
- Tier 3 – VOC, NO_x, wind data; insignificant local emission sources
- Tier 4 - NO_x, CO, wind data; significant local emission sources
- Tier 5 – Missing one Tier 4 criteria

Available Air Quality Data (7 of 11)

Site	Air District	Tier	# Speciated VOC > 50 ppbC Samples	# NOx > 10 ppb Samples	# Wind Direction Samples	TOG Emissions (tons/day)	NOx Emissions (tons/day)	Designation	Local or Regional Emissions	# TNMOC > 50 ppbC Samples	# CO > 0.15 ppm Samples
BGS	San Joaquin	1	27	103	752	76	53	Urban	Local	191	24
CLO	San Joaquin	1	21	78	750	199	46	Urban	Local		22
FSF	San Joaquin	1	29	92	746	210	49	Urban	Local	246	20
NAT	Sacramento	1	26	85	756	65	53	Rural	Mixed		24
SDP	Sacramento	1	20	65	756	93	67	Urban	Local		19
SUN	Bay Area	1	30	343	756	94	37	Rural	Regional		527
FLN	Sacramento	2	24	33	569	46	28	Urban	Local		
PLR	San Joaquin	2	25	42	751	63	18	Rural	Regional		
SHA	San Joaquin	3	20	101	752	14	12	Urban	Mixed	239	
ARV	San Joaquin	3	21	37	750	11	9	Rural	Regional	88	
ELK	Sacramento	3	11	50	751	10	20	Rural	Regional		
SJ4	Bay Area	3	6	151		137	85	Urban	Local		32
M29	San Joaquin	3	25	81	748	32	15	Rural	Regional		
BTI	Bay Area	3	35	41	623	15	15	Rural	Regional		8
BODB	No. Sonoma	3	11	NO_y only	756	2	1	Rural	Regional	1	NA
TSM	San Joaquin	3	7	89	756	65	25	Urban	Local		18
BAC	San Joaquin	4		86	754	69	49	Urban	Local	49	18
FSS	San Joaquin	4		59	749	171	41	Rural	Mixed		13
M14	San Joaquin	4		79	756	155	29	Urban	Local		21
ROS	Placer	4		68	644	75	45	Urban	Local		15
S13	Sacramento	4		103	755	79	59	Urban	Local		24
SOH	San Joaquin	4		110	687	61	41	Urban	Local		24
VCS	San Joaquin	4		68	753	81	19	Urban	Local		15
CHM	Butte	5		65	756	13	9	Urban	Local		20
DVP	Monterey Bay	5		18	756	37	5	Rural	Regional		6
DVS	Yolo Solano	5		58	739	13	15	Rural	Mixed		6
FSD	San Joaquin	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
SLM	San Luis Obispo	5		57	756	17	7	Urban	Local		13
SNH	Sacramento	5		58		92	63	Urban	Local		20
YAS	Feather River	5		72	683	17	15	Urban	Mixed		15

Site map with tier designations



Available Air Quality Data (9 of 11)

Dominant emission source types by wind quadrant

		Wind Quadrant			
Site	Tier	1	2	3	4
BGS	1	A	A	A	A
CLO	1	A	A	A	A
FSF	1	A	A	A	A
NAT	1	A,M	A	A	A
SDP	1	A	A	A	A
SUN	1	M	A,M	P	M
FLN	2	A	A	A	A
PLR	2	A	A	A	A
ARV	3	A	A	A	P
ELK	3	M	A,M	M	M
SJ4	3	A	A	A,M	A,M
M29	3	A	A	A	A
BTI	3	A	N	A	A
BODB	3	N	A	N	N
TSM	3	A	A	A	A

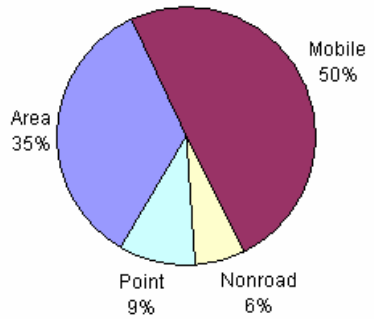
Legend:

- A = Area
- M = Mobile (on-road)
- N = Non-road
- P = Point

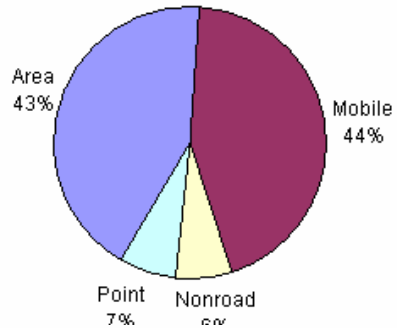
Available Air Quality Data (10 of 11)

Dominant emission source types by wind quadrant

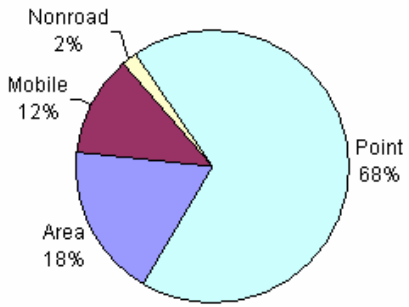
Site: SUN
Param: TOG
Ttl: 13531 kg/day
Quad: 1



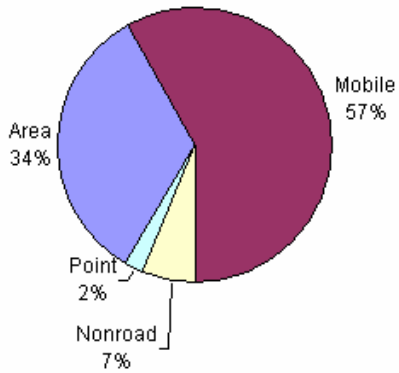
Site: SUN
Param: TOG
Ttl: 12609 kg/day
Quad: 2



Site: SUN
Param: TOG
Ttl: 68541 kg/day
Quad: 3



Site: SUN
Param: TOG
Ttl: 1251 kg/day
Quad: 4



Available Air Quality Data (11 of 11)

Summary of Findings

- 16 monitoring sites yielded sufficient data to perform CCOS Phase 2 analyses
- Phase 2 analyses have a high probability of identifying specific biases/uncertainties in emission inventory
- Improved emission inventory will improve air quality modeling results

Ongoing Analyses

CCOS Phase 2

- Ratio comparisons (VOC/NO_x, CO/NO_x, and individual species)
- Fingerprint analyses
- Wildfire analyses
- Analysis of species that vary temporally
- Source apportionment (e.g., CMB and PMF) as a corroborative tool