Comparison of Ambient Measurements to Emissions Representations in Modeling

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Presented to:
The CCOS Technical Committee
Sacramento, CA
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Statement of Work – Phase 1

- Task 1 – Kickoff meeting, workplan, and EI data and EI documentation gathering
- Task 2 – Identify available air quality data
- Task 3 – Review ARB chemical speciation profiles
- Task 4 – Workshop to justify and discuss merits of Phase 2

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Task 3 – Review Speciation Profiles (1 of 18)

Summary of Findings:

- In general, ARB speciation profiles for key source categories are up-to-date
- A handful of speciation profiles were identified that need updating
- Updates would likely result in a slight lowering of the reactivity of the organic gas inventory

Task 3 – Review Speciation Profiles (2 of 18)

ARB TOG Speciation Profile Database

- 425 available organic gas profiles
- 252 profiles applied to the 2002 CCOS placeholder EI
- Individual profiles prioritized by summing TOG, ROG, and reactivity-weighted emissions associated with each profile

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Task 3 – Review Speciation Profiles (3 of 18)

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* =

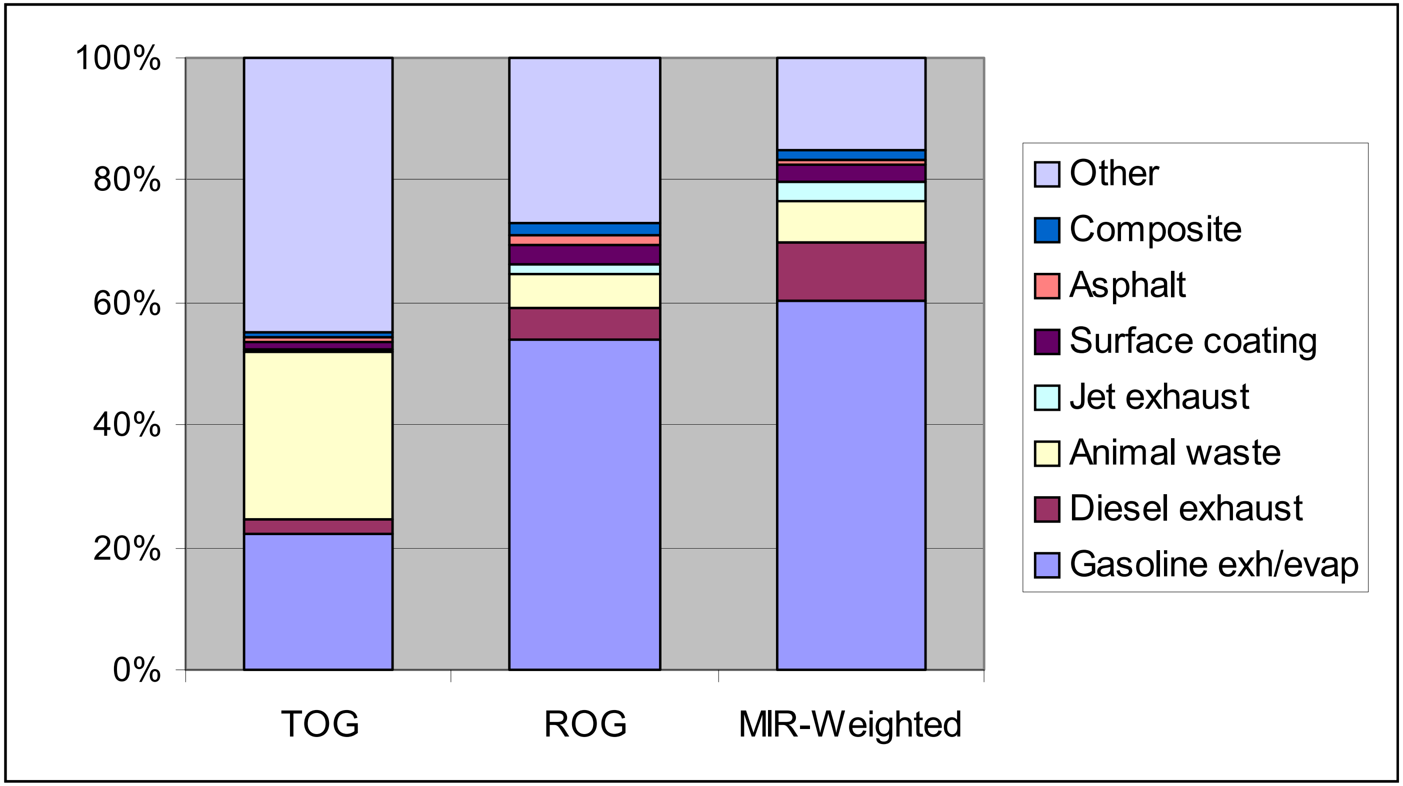
$$TOG_x \times R_x$$

Task 3 – Review Speciation Profiles

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%	---

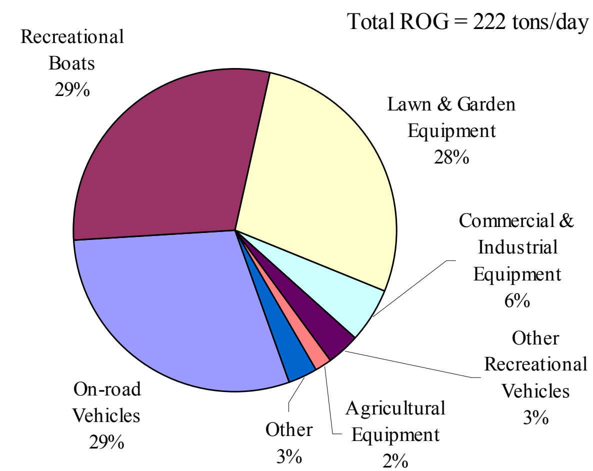
Task 3 – Review Speciation Profiles (5 of 18)

Percent of Emissions by Profile Group



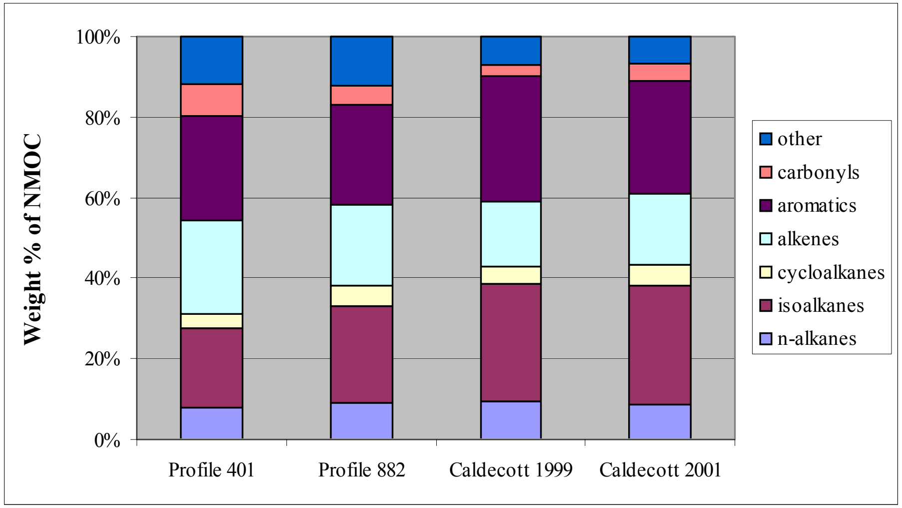
ARB gasoline exhaust profiles

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

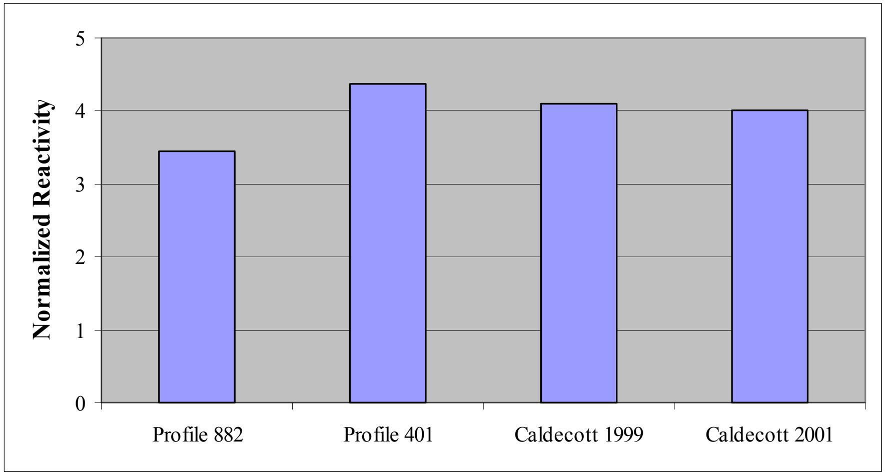


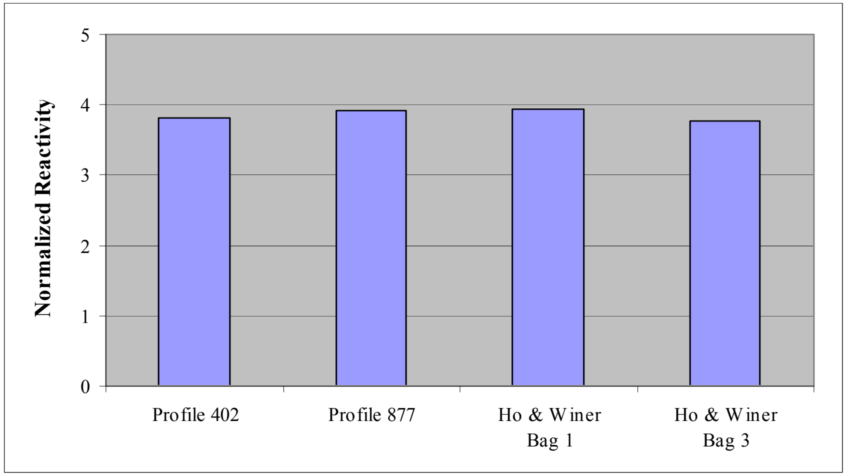
Emissions associated with Profile 401

Task 3 – Review Speciation Profiles (7 of 18)



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





Weighted reactivity of various profiles for gasoline-fueled vehicles

Task 3 – Review Speciation Profiles

ARB gasoline evaporative profiles

Rank	Profile #	Profile Name	Application	Source	Vintage
3	422	Hot soak emissions - CA light-duty vehicles	Running and hot soak evaportive emissions from light-duty gasoline vehicles	19 SHED tests conducted in 1999 and 2000	2000
8	906	Diurnal and resting evaporatives	Diurnal and resting evaporatives from on-road gasoline vehicles	Study of gasoline samples collected at Berkeley service stations	1996
9	419	Liquid gasoline - MTBE 11% - commercial	Vehicle refueling and petroleum storage and marketing operations	ARB study of gasoline blends containing MTBE and ethanol	1997

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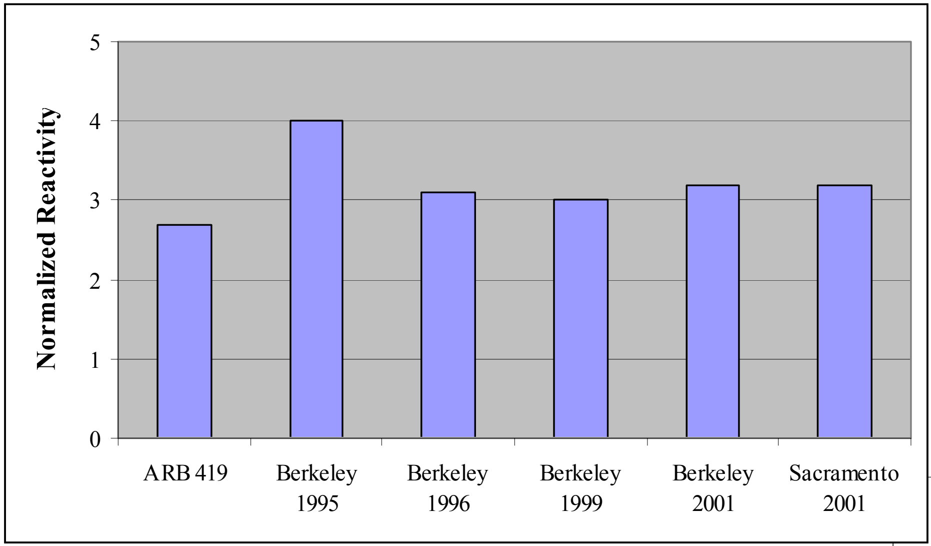
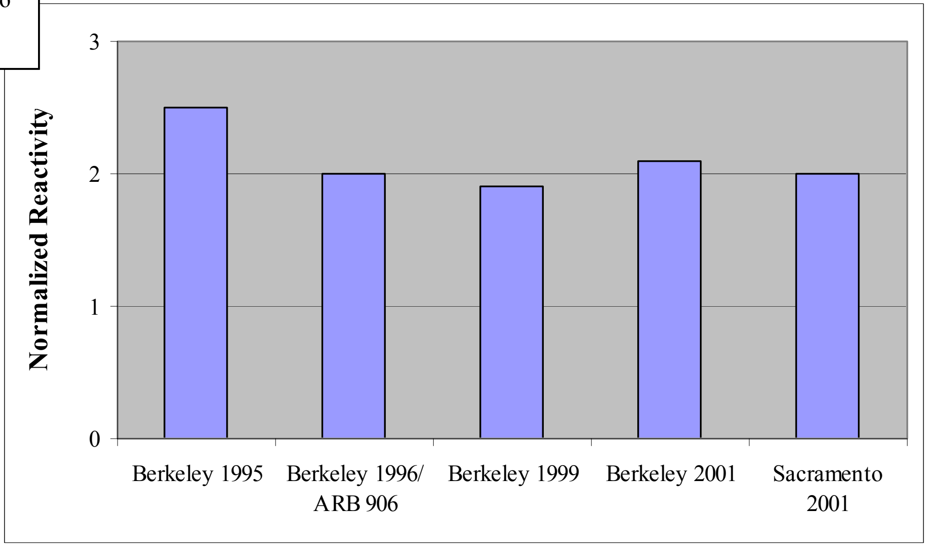


Weighted reactivity of liquid gasoline speciation profiles

Weighted reactivity of gasoline headspace speciation profiles



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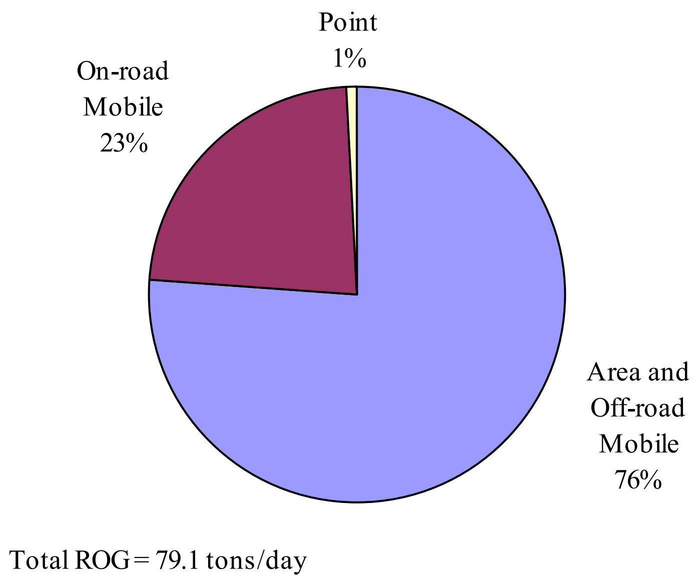
ARB diesel exhaust profile

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

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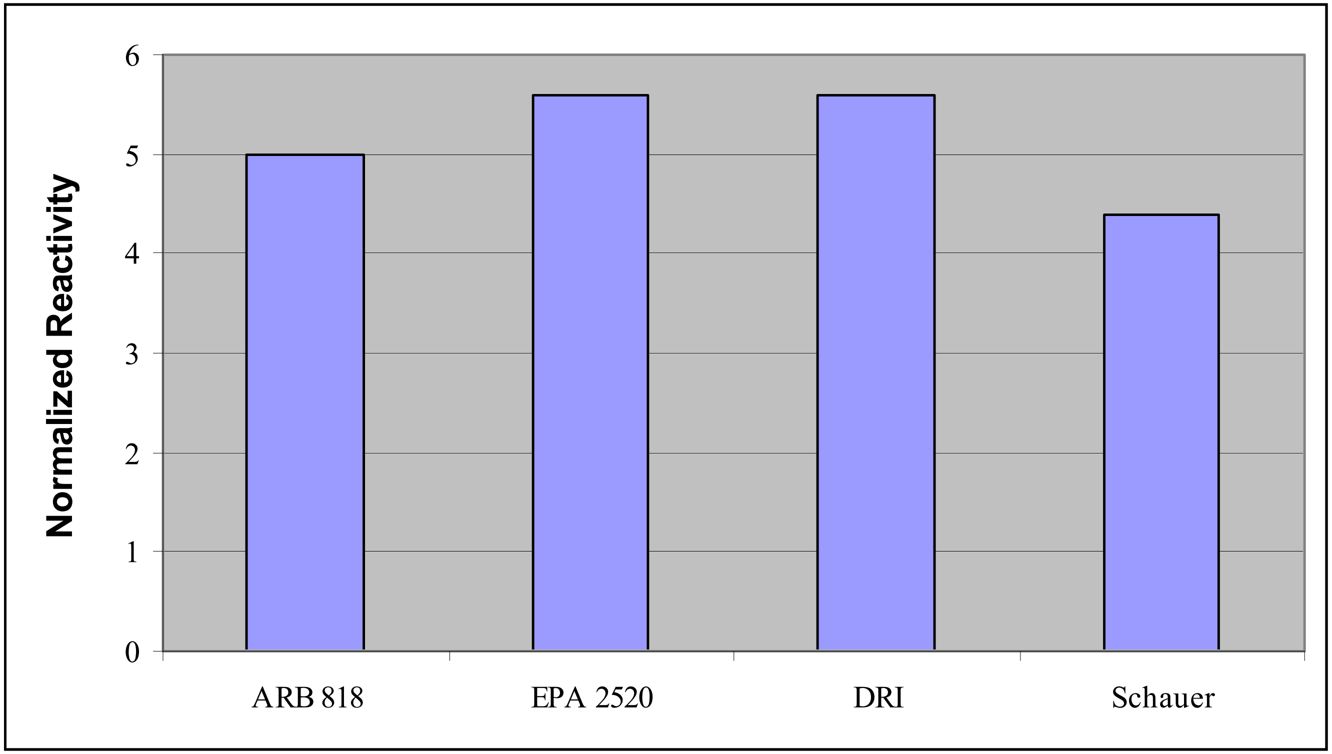
Reactivity of various diesel exhaust profiles



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ARB 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

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

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Task 3 – Review Speciation Profiles (13 of 18)

Dairy organic gas emissions by process type (Schmidt, et al., 2005)

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%

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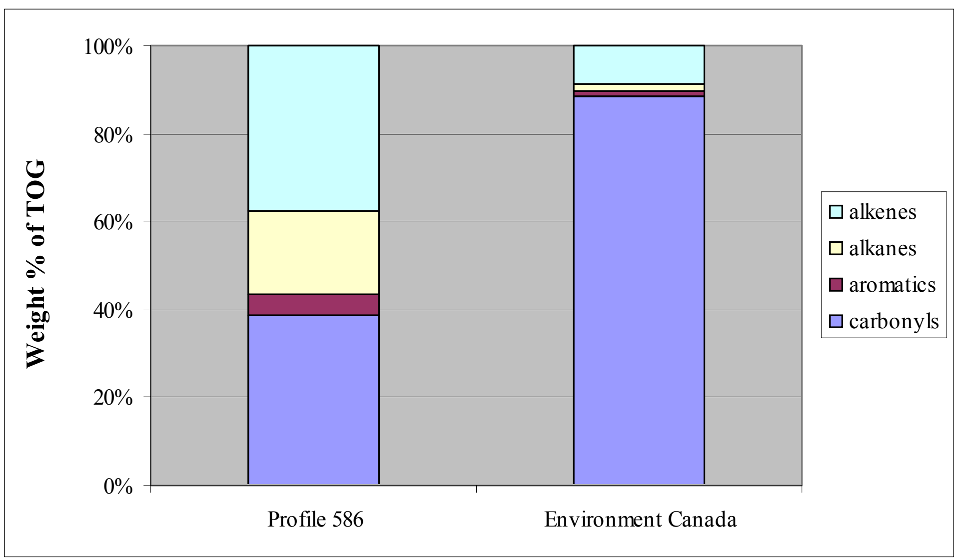
Task 3 – Review Speciation Profiles (14 of 18)

ARB 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

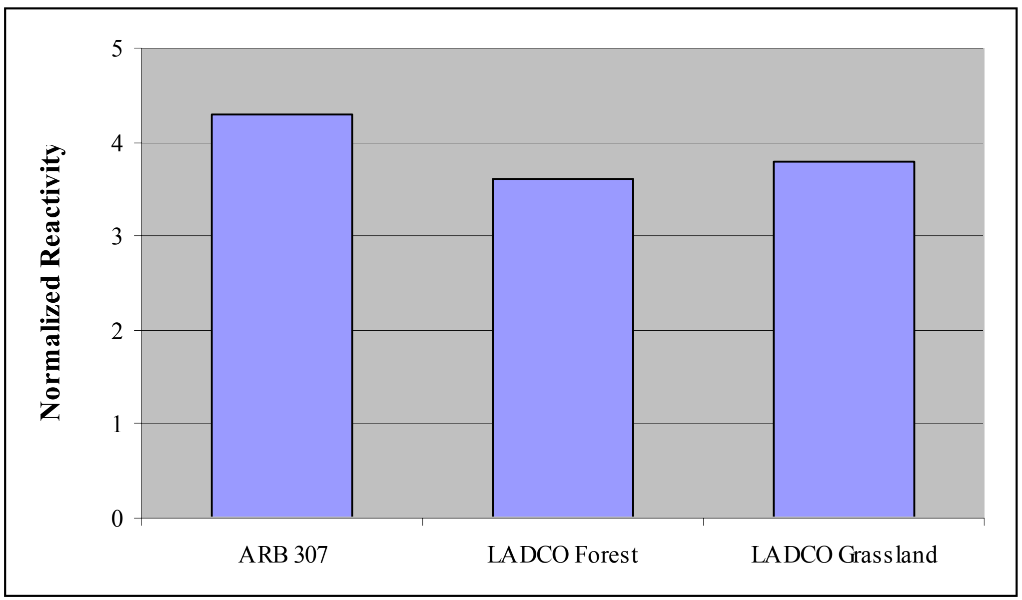


Comparison of jet exhaust profiles

Task 3 – Review Speciation Profiles (15 of 18)

ARB wildfire profile

Rank	Profile #	Profile Name	Application	Source	Vintage
--	307	Forest fires	Unplanned fires on grasslands and forested lands	EPA's SPECIATE 3.2 database - based on literature search	1975



Reactivity of various wildfire profiles

Task 3 – Review Speciation Profiles (16 of 18)

Findings & Recommendations

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

Task 3 – Review Speciation Profiles (17 of 18)

Findings & Recommendations (cont'd)

- 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 ARB for this source category.
- ARB industrial surface coating, medium-cure asphalt, and all-category composite profiles need to be updated (new industrial coating profiles identified).

Task 3 – Review Speciation Profiles (18 of 18)

Findings & Recommendations (cont'd)

- 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 4,922 tpd).

Task 2 – Identify Available Air Quality Data (1 of 13)

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 PAMS sites
- CCOS supplemental sites

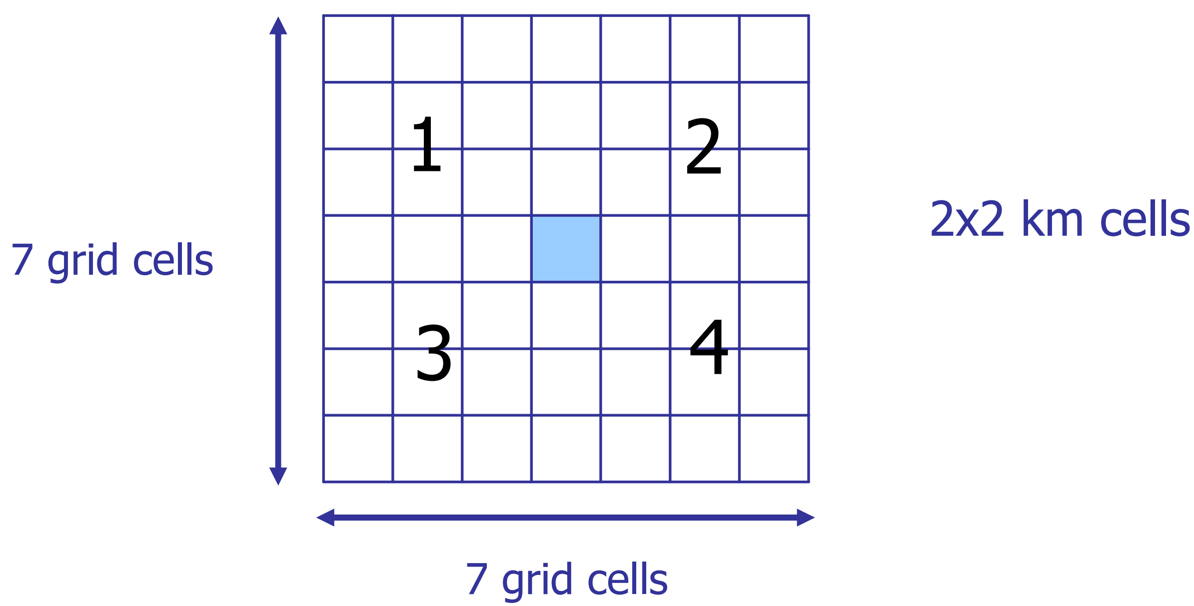
Task 2 – Identify Available Air Quality Data

Ambient data collection

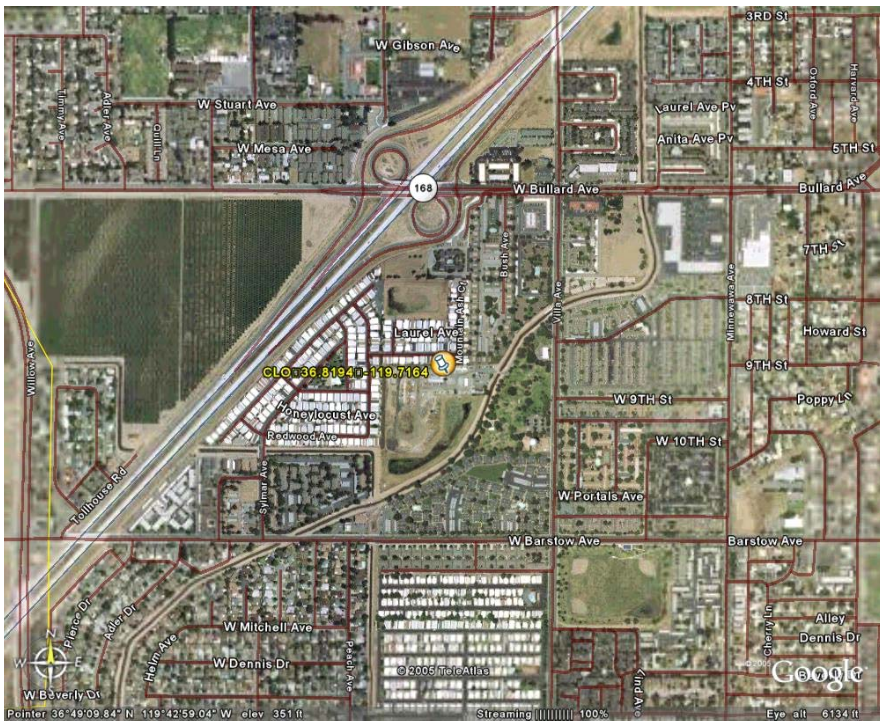
- Speciated VOC
  > 3-hour samples collected every third day
  > Episodic measurements on forecast basis
  > 30-37 samples per site expected
- NO_x, CO, wind
  > Hourly measurements
  > 750 samples per site expected

Emissions evaluation by site

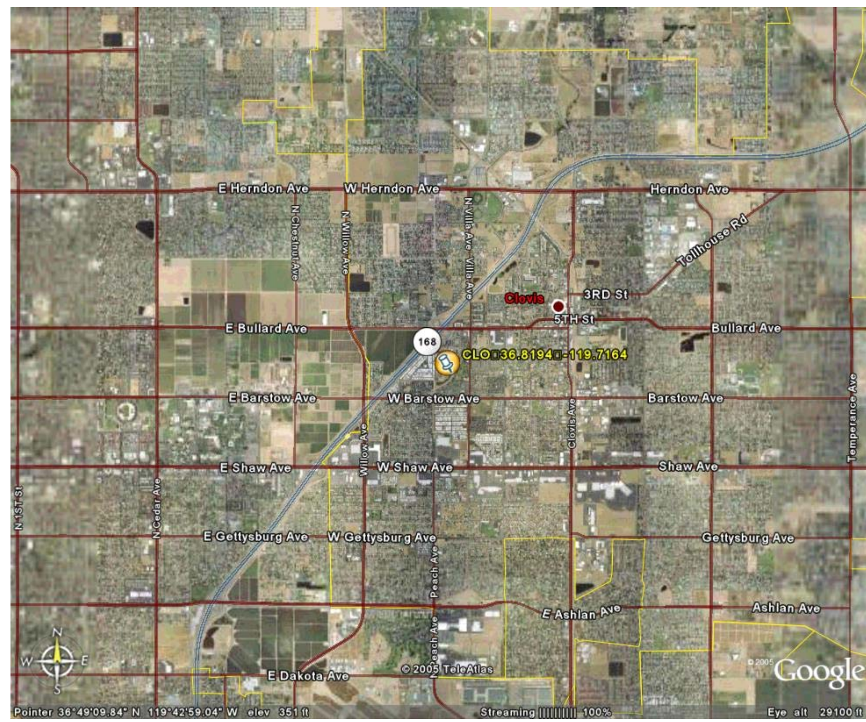
- Summed TOG and NOx emissions for a 14x14 km area around each site



Emissions evaluation by site (cont'd)



Clovis Station (2-km width)



Clovis Station (10-km width)

Task 2 – Identify Available Air Quality Data (6 of 13)

Monitoring site rankings

- Tier 1 – VOC, NO_x, CO, wind data; high local emissions
- Tier 2 – VOC, NO_x, wind data; some local emissions
- Tier 3 – VOC, NO_x, wind data; low local emissions
- Tier 4 - NO_x, CO, wind data; high local emissions
- Tier 5 – Missing one Tier 4 criteria

Task 2 – Identify Available Air Quality Data (7 of 13)

Site	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	1	27	103	752	76	53	Urban	Local	191	24
CLO	1	21	78	750	199	46	Urban	Local		22
FSF	1	29	92	746	210	49	Urban	Local	246	20
NAT	1	26	85	756	65	53	Rural	Mixed		24
SDP	1	20	65	756	93	67	Urban	Local		19
SUN	1	30	343	756	94	37	Rural	Regional		527
FLN	2	24	33	569	46	28	Urban	Local		
PLR	2	25	42	751	63	18	Rural	Regional		
ARV	3	21	37	750	11	9	Rural	Regional	88	
ELK	3	11	50	751	10	20	Rural	Regional		
SJ4	3	6	151		137	85	Urban	Local		32
M29	3	25	81	748	32	15	Rural	Regional		
BODB	3	11	NOy only	756	2	1	Rural	Regional	1	NA
TSM	3	7	89	756	65	25	Urban	Local		18
BAC	4		86	754	69	49	Urban	Local	49	18
ELM	4		64	753	41	19	Rural	Regional	33	8
FSS	4		59	749	171	41	Rural	Mixed		13
M14	4		79	756	155	29	Urban	Local		21
ROS	4		68	644	75	45	Urban	Local		15
S13	4		103	755	79	59	Urban	Local		24
SIM	4		109	749	36	20	Urban	Local	28	33
SOH	4		110	687	61	41	Urban	Local		24
VCS	4		68	753	81	19	Urban	Local		15
CHM	5		65	756	13	9	Urban	Local		20
DVP	5		18	756	37	5	Rural	Regional		6
DVS	5		58	739	13	15	Rural	Mixed		6
FSD	5		93		188	44	Urban	Local		21
GNF	5		45	691	34	13	Urban	Local		11
LOM	5		35	748	14	4	Urban	Local		14
LWP	5		91	755	21	14	Urban	Local		25
SBC	5		75	756	32	12	Urban	Local		22
SHA	5		101	752	14	12	Urban	Mixed	239	
SLM	5		57	756	17	7	Urban	Local		13
SNH	5		58		92	63	Urban	Local		20
YAS	5		72	683	17	15	Urban	Mixed		15

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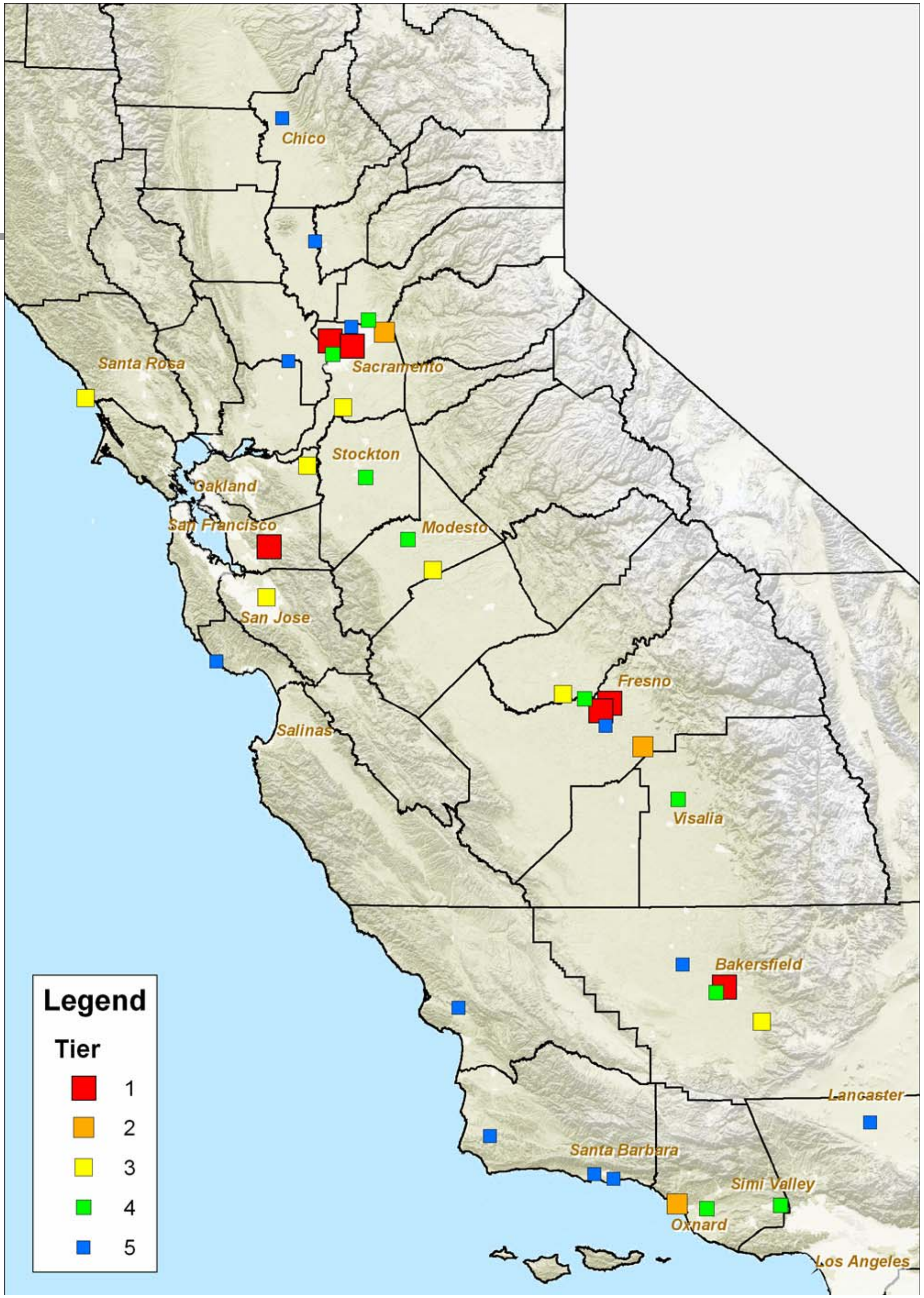
Site map with Tier designations



Task 2 – Identify Available Air Quality Data (9 of 13)

July VOC

Site	Tier	Total Count	7/1/2000	7/2/2000	7/3/2000	7/4/2000	7/5/2000	7/6/2000	7/7/2000	7/8/2000	7/9/2000	7/10/2000	7/11/2000	7/12/2000	7/13/2000	7/14/2000	7/15/2000	7/16/2000	7/17/2000	7/18/2000	7/19/2000	7/20/2000	7/21/2000	7/22/2000	7/23/2000	7/24/2000	7/25/2000	7/26/2000	7/27/2000	7/28/2000	7/29/2000	7/30/2000	7/31/2000
FSF	1	29		X			X			X						X			X			X					X	X			X		
BGS	1	27		X			X			X			X			X			X			X			X			X			X		
NAT	1	27		X			X						X			X			X			X			X			X			X		
CLO	1	22					X			X			X			X			X												X		
SDP	1	21																										X			X		
VTE	2	32								X			X			X			X			X			X			X			X		
FLN	2	27		X			X			X			X			X						X			X			X			X		
PLR	2	27		X			X			X			X			X			X			X			X			X			X		
M29	3	26		X												X			X						X			X			X		
ARV	3	23		X			X			X			X			X			X			X			X			X			X		
ELK	3	11					X																										

Aug. VOC

Site	Tier	Total Count	8/1/2000	8/2/2000	8/3/2000	8/4/2000	8/5/2000	8/6/2000	8/7/2000	8/8/2000	8/9/2000	8/10/2000	8/11/2000	8/12/2000	8/13/2000	8/14/2000	8/15/2000	8/16/2000	8/17/2000	8/18/2000	8/19/2000	8/20/2000	8/21/2000	8/22/2000	8/23/2000	8/24/2000	8/25/2000	8/26/2000	8/27/2000	8/28/2000	8/29/2000	8/30/2000	8/31/2000
FSF	1	29	X			X			X			X			X			X			X			X			X			X			X
BGS	1	27	X			X			X			X			X			X			X			X			X			X			X
NAT	1	27	X			X			X			X			X			X			X			X									X
CLO	1	22				X			X			X			X			X			X						X			X			X
SDP	1	21	X			X			X			X			X			X			X			X									X
VTE	2	32	X			X			X			X			X			X			X			X			X			X			X
FLN	2	27	X			X						X			X			X			X			X									X
PLR	2	27	X			X			X			X			X			X						X			X			X			X
M29	3	26	X			X			X			X			X			X			X			X			X			X			X
ARV	3	23										X			X			X			X			X			X			X			X
ELK	3	11																X						X									X

Task 2 – Identify Available Air Quality Data (10 of 13)

Sept. VOC

Site	Tier	Total Count	9/1/2000	9/2/2000	9/3/2000	9/4/2000	9/5/2000	9/6/2000	9/7/2000	9/8/2000	9/9/2000	9/10/2000	9/11/2000	9/12/2000	9/13/2000	9/14/2000	9/15/2000	9/16/2000	9/17/2000	9/18/2000	9/19/2000	9/20/2000	9/21/2000	9/22/2000	9/23/2000	9/24/2000	9/25/2000	9/26/2000	9/27/2000	9/28/2000	9/29/2000	9/30/2000
FSF	1	29			X			X						X			X			X			X			X			X			X
BGS	1	27			X			X			X			X						X			X									
NAT	1	27			X			X			X			X			X		X	X	X	X										
CLO	1	22			X			X			X			X						X									X			X
SDP	1	21			X			X			X			X			X		X	X	X	X	X									
VTE	2	32			X			X			X						X			X						X			X			X
FLN	2	27			X			X			X			X			X		X	X	X	X	X									
PLR	2	27			X									X						X			X			X			X			X
M29	3	26						X			X			X			X			X			X			X			X			X
ARV	3	23						X			X						X			X			X									
ELK	3	11						X			X			X			X		X	X	X											

Task 2 – Identify Available Air Quality Data (11 of 13)

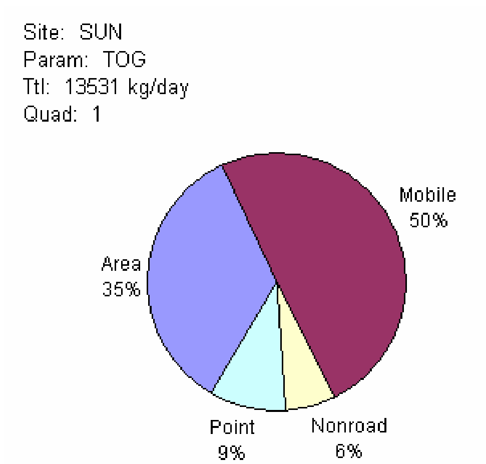
Dominant emission source types by wind quadrant

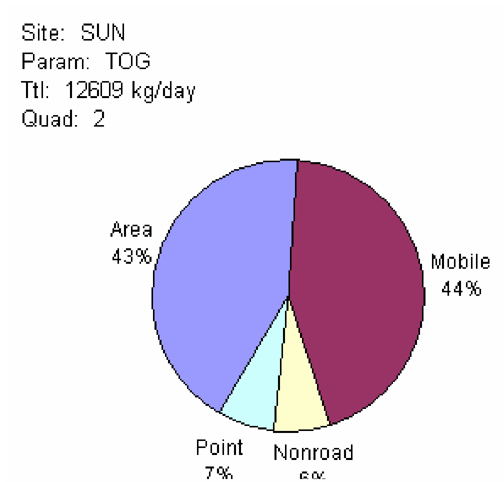
		Wind Quadrant			
Site	Tier	1	2	3	4
BGS	1	A	A	A	A
CLO	1	A	A	A	A
FSF	1	A	A	A	A
NAT	1	A,M	A	A	A
SDP	1	A	A	A	A
SUN	1	M	A,M	P	M
FLN	2	A	A	A	A
PLR	2	A	A	A	A
ARV	3	A	A	A	P
ELK	3	M	A,M	M	M
SJ4	3	A	A	A,M	A,M
M29	3	A	A	A	A
BTI	3	A	N	A	A
BODB	3	N	A	N	N
TSM	3	A	A	A	A

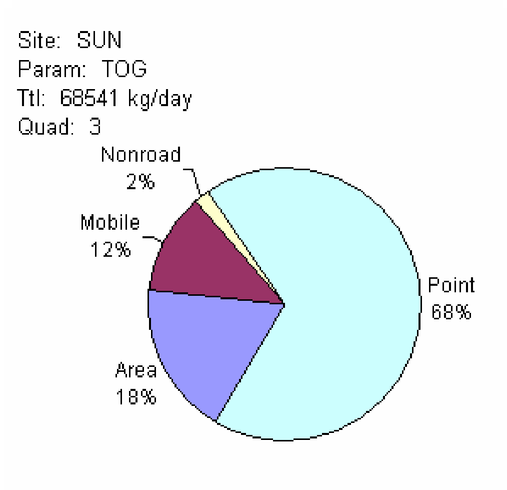
Legend:
- A = Area
- M = Mobile (on-road)
- N = Non-road
- P = Point

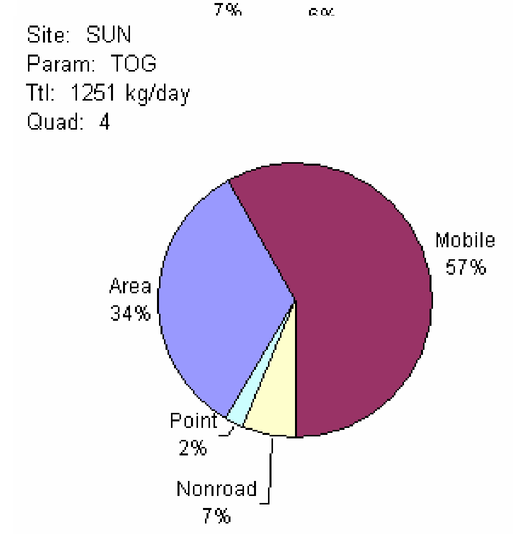
Task 2 – Identify Available Air Quality Data (12 of 13)

Dominant emission source types by wind quadrant



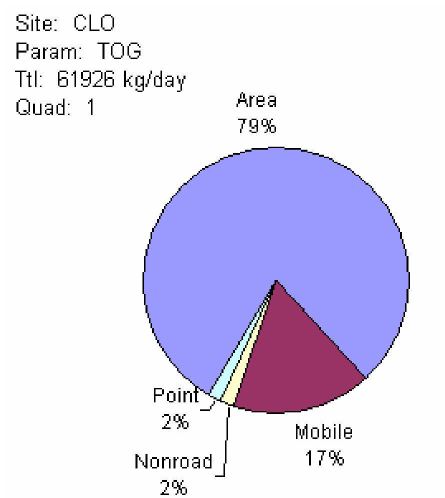


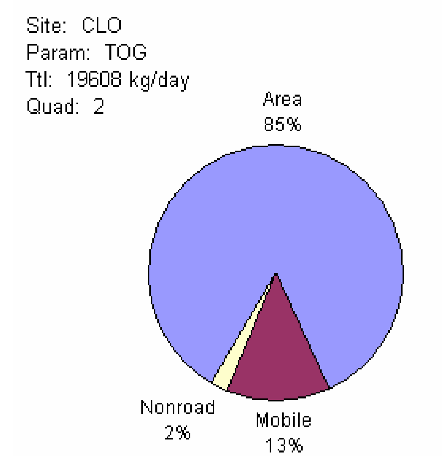


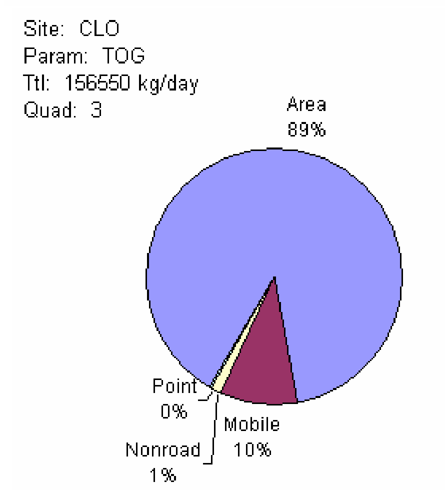


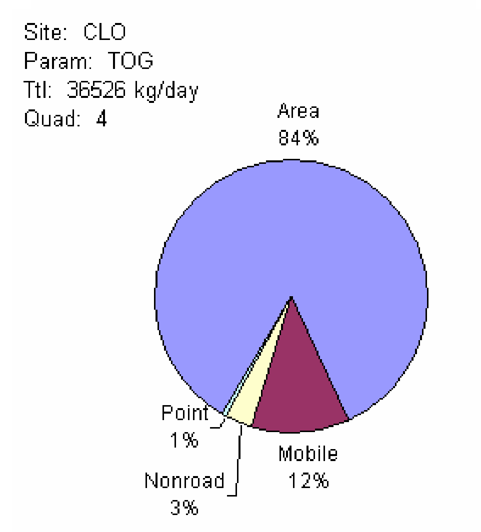
Task 2 – Identify Available Air Quality Data (13 of 13)

Dominant emission source types by wind quadrant









Phase 1 Summary

12 monitoring sites identified with sufficient data to perform Phase 2 analyses that have a high probability of identifying specific biases/uncertainties in the emission inventory that will lead to improved air quality modeling results.

Phase 2 – Objective (1 of 2)

To gather corroborative evidence using different analysis techniques that will result in recommendations for specific, meaningful improvements to the CCOS emission inventory.

Phase 2 – Objective (2 of 2)

Sample questions (example outcomes in red):

- Do the methods used to characterize wildfires in the EI adequately represent the spatial and temporal dimensions of large fire events? (e.g., development of a new temporal profile for wildfires by pollutant species.)
- Do any discrepancies exist between ambient data and emissions data for those species with strong diurnal patterns? What are the likely sources of those differences? (e.g., recommendations for adjustments to the temporal distribution of biogenic emissions.)

STI

Original Phase 2 Techniques

- Integrate the results of previous research
- Perform EI reconciliation with pollutant ratios (VOC/NO_x, CO/NO_x)
- Perform EI reconciliation with speciated VOCs (ratios, TNMOC composition)
- Perform VOC source apportionment (e.g., factor analysis, CMB, PMF)

STI

Revised Phase 2 Techniques

- Review of previous findings
- Analysis methods
  - Ratio comparisons (VOC/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

Review Previous Findings

Literature review to identify previous, relevant work

- For example
  - SJV Emissions Reconciliation (STI)
  - DRI advanced data analysis study

Key Questions

Does the current EI preparation methodology incorporate the latest results from available research (e.g. speciation profiles, temporal profiles, emission factors, etc.)?

Analysis Methods

- Ratio Comparisons
  - Convert emission inventory (EI) from mass to moles and compare VOC/NO_x ratios in EI to ambient data ratios by hour and wind quadrant
  - Individual species ratios by hour and wind quadrant (e.g., acetylene/benzene, benzene/toluene, benzene/xylene)

Key Questions

How do pollutant ratios derived from the EI compare with those from ambient data? How do these ratios vary by site/wind quadrant due to the influence of various emission sources?

Analysis Methods (2 of 5)

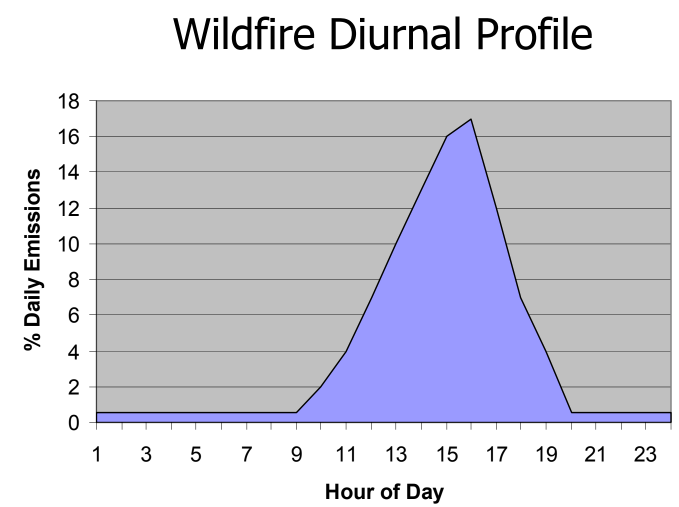
- Fingerprint analyses
  - Comparison of speciated emissions to speciated VOCs in ambient air by hour and wind quadrant

Key Questions

How does the EI-predicted VOC species composition compare with the ambient data? Do any variations appear to be a result of differences in mass, speciation, or both?

Analysis Methods (3 of 5)

- Wildfire analyses
  - 2,000 tpd of TOG on July 31, 2000 EI (33% of total TOG)
  - Manter fire consumed 74,000 acres over an 18-day period
  - Flaming and smoldering emissions generated



Key Questions

Do the methods used to characterize wildfires in the EI adequately represent the spatial and temporal dimensions of large fire events?

Analysis Methods (4 of 5)

- Analysis of species that vary temporally
  - Identify and assess those species such as isoprene that exhibit diurnal patterns (i.e., isoprene, evaporative VOCs)
  - Analyze morning and afternoon data for selected abundant species

Key Questions

Do any discrepancies exist between ambient data and emissions data for those species with strong diurnal patterns? What are the likely sources of those differences?

STI

Analysis Methods (5 of 5)

- Source apportionment
  - Chemical mass balance (CMB) or positive matrix factorization (PMF)
  - Use as a tool to corroborate findings from previous analyses

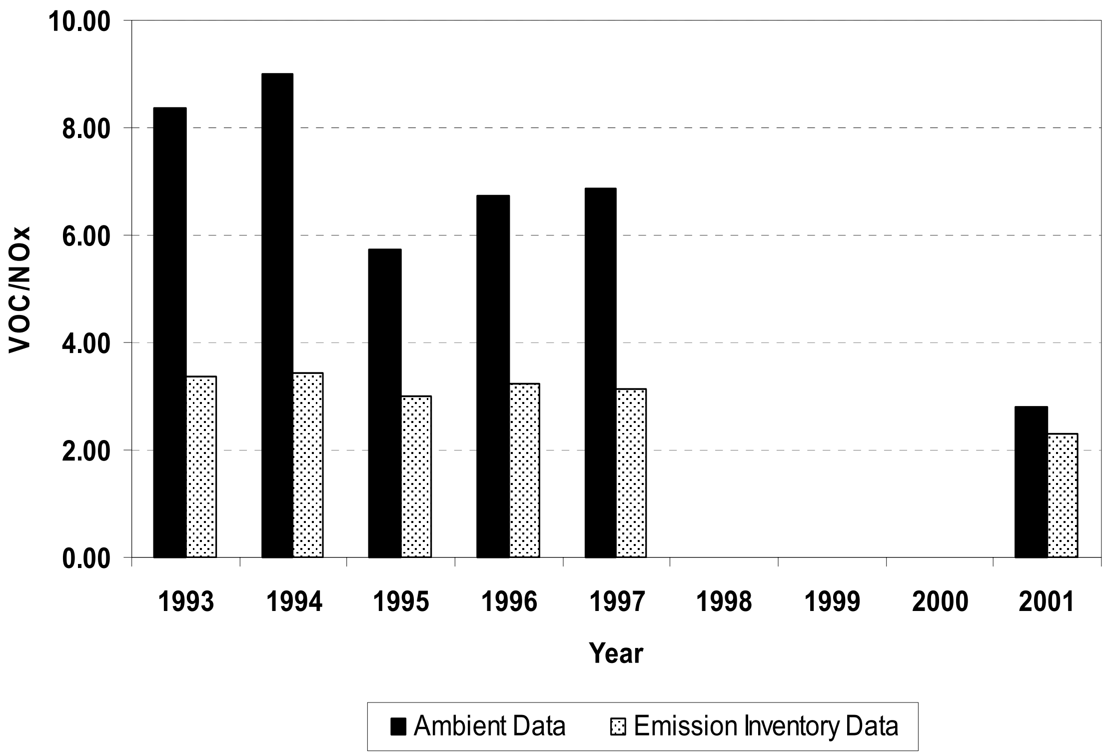
Key Questions

Does the source mix produced by source apportionment tools match up with the mix calculated from the EI? How does this analysis corroborate the findings of other techniques?

Develop Recommendations

- Synthesize Findings
  - Formulate overarching conclusions
  - Summarize the apparent strengths and weaknesses of the EI including a discussion of possible biases in the EI
  - Make recommendations for “corroborative adjustments” to the EI

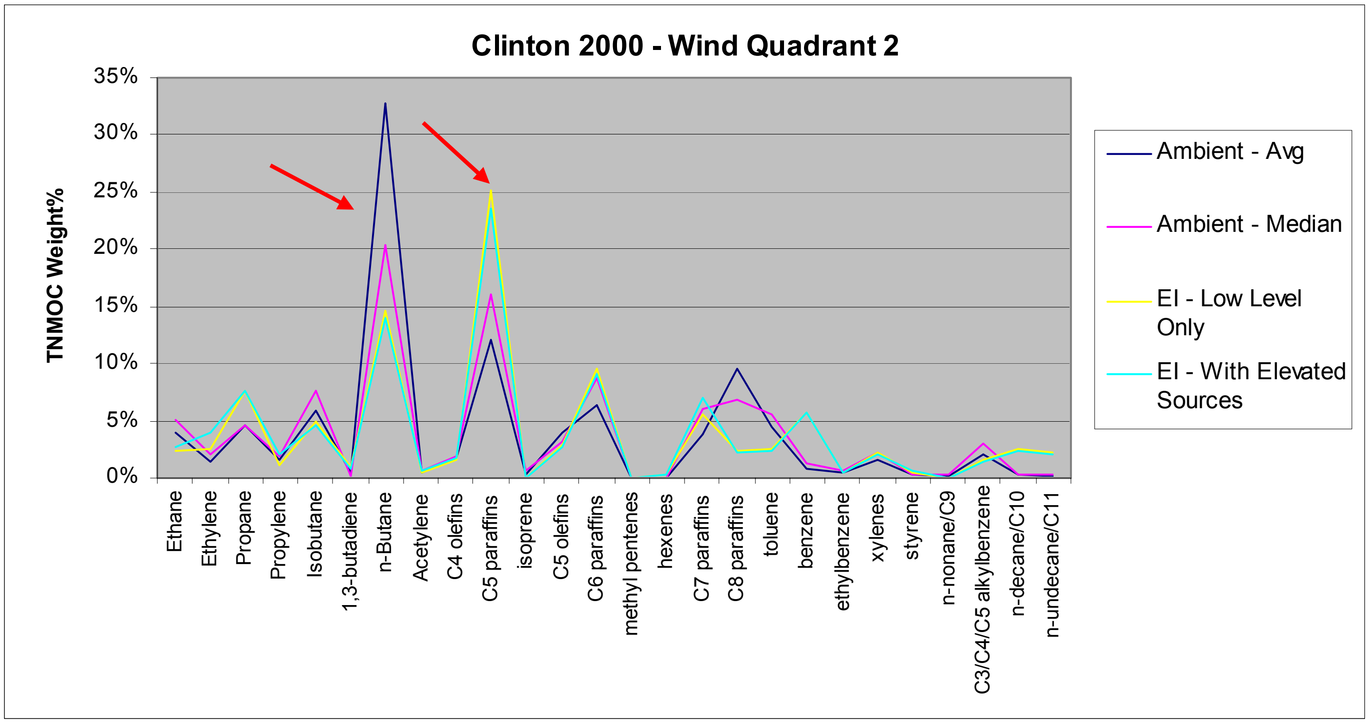
Examples



Emission inventory- and ambient-derived VOC/NOx ratios at Los Angeles North Main during summer mornings.

Results can be used to explore segments of the inventory that may be underestimated.

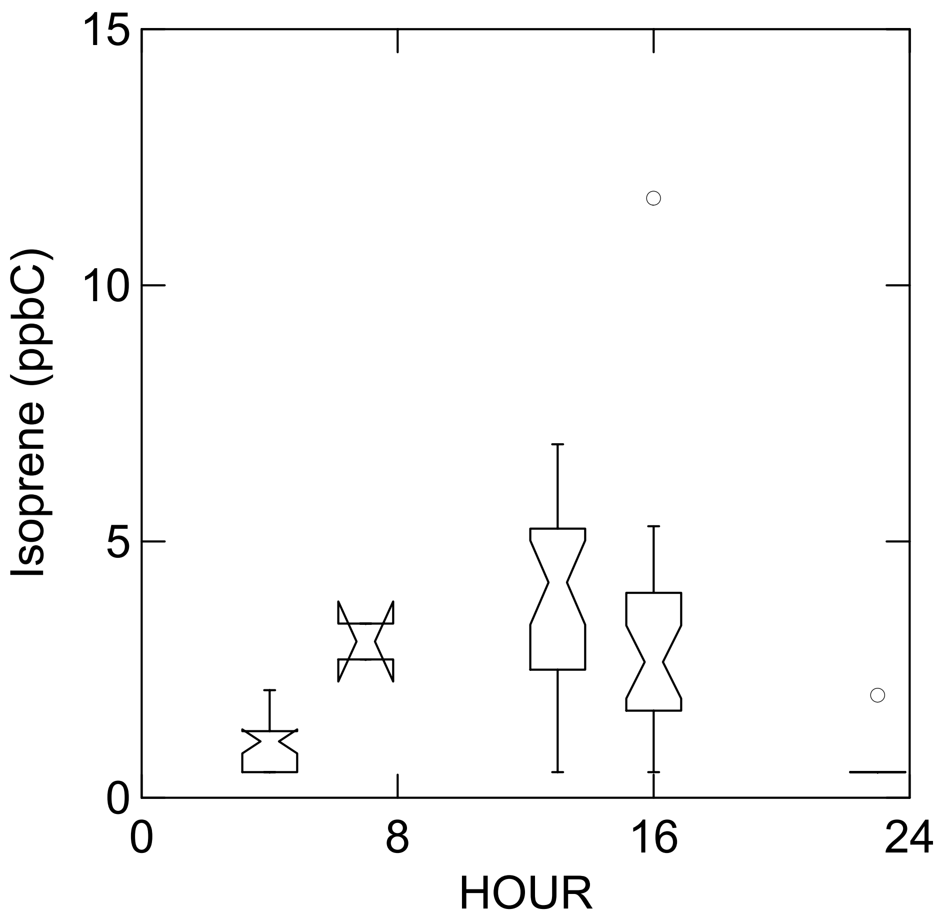
Examples



Houston area EI reconciliation spike in ambient concentrations of n-butane when winds were from the southeast.

Results can be used to identify the speciation profiles that are need revision.

Examples

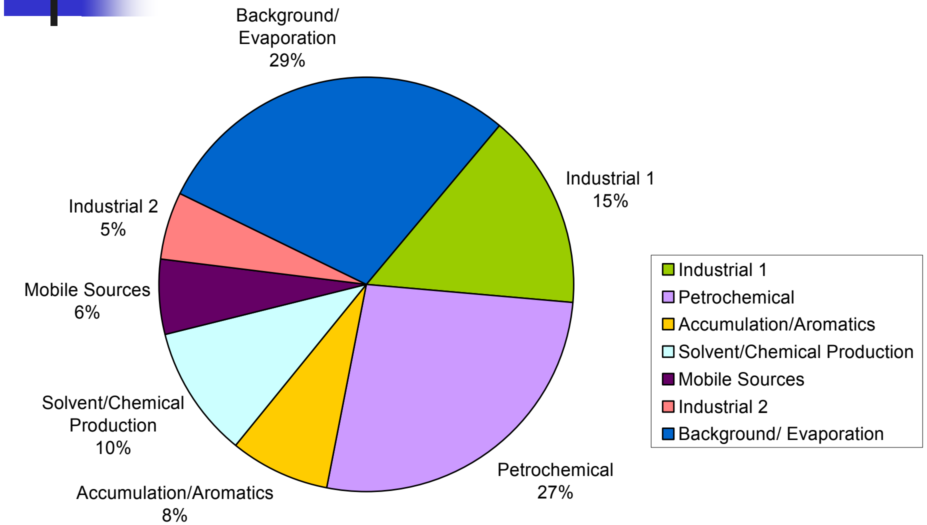


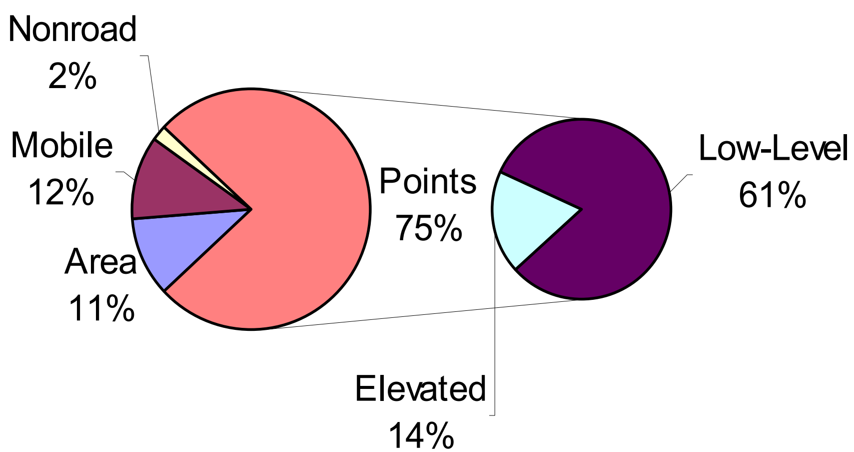
3-hr duration isoprene concentrations at Clovis in 2001

Reconciliation of some speciated VOCs such as isoprene will require looking at concentrations during the daytime, rather than in the morning.

Isoprene concentrations are highest during the day, due to the higher emissions from biogenics.

Examples





Source apportionment (PMF) used for multiple Houston sites to provide a breakdown of emissions from various sources.

The EI appears to be overestimating mobile source emissions at this site by a factor of 1.5 (15% in the EI vs. 6% in the PMF results).