

# Impacts of Volatile Organic Compounds from Compost on Ozone Formation

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Funding: CASA, CalRecycle, and previously from  
StopWaste.org, Composting Businesses, and USDA.<sup>1</sup>

# My interests and background

- Air quality, and also water quality as well
- All areas of Environmental Chemistry:  
Agriculture, transportation, ecology, clinical, mines...
- Recent VOC-ozone projects -- 7 papers published  
(plus 2 reports.)
  - Insecticide solvents and oil pesticides
  - Dairy and livestock studies: animals, fresh waste, feeds
  - Green scrap compost, biosolids co-composting
- Finding Solutions – practical, cost-effective, sustainable



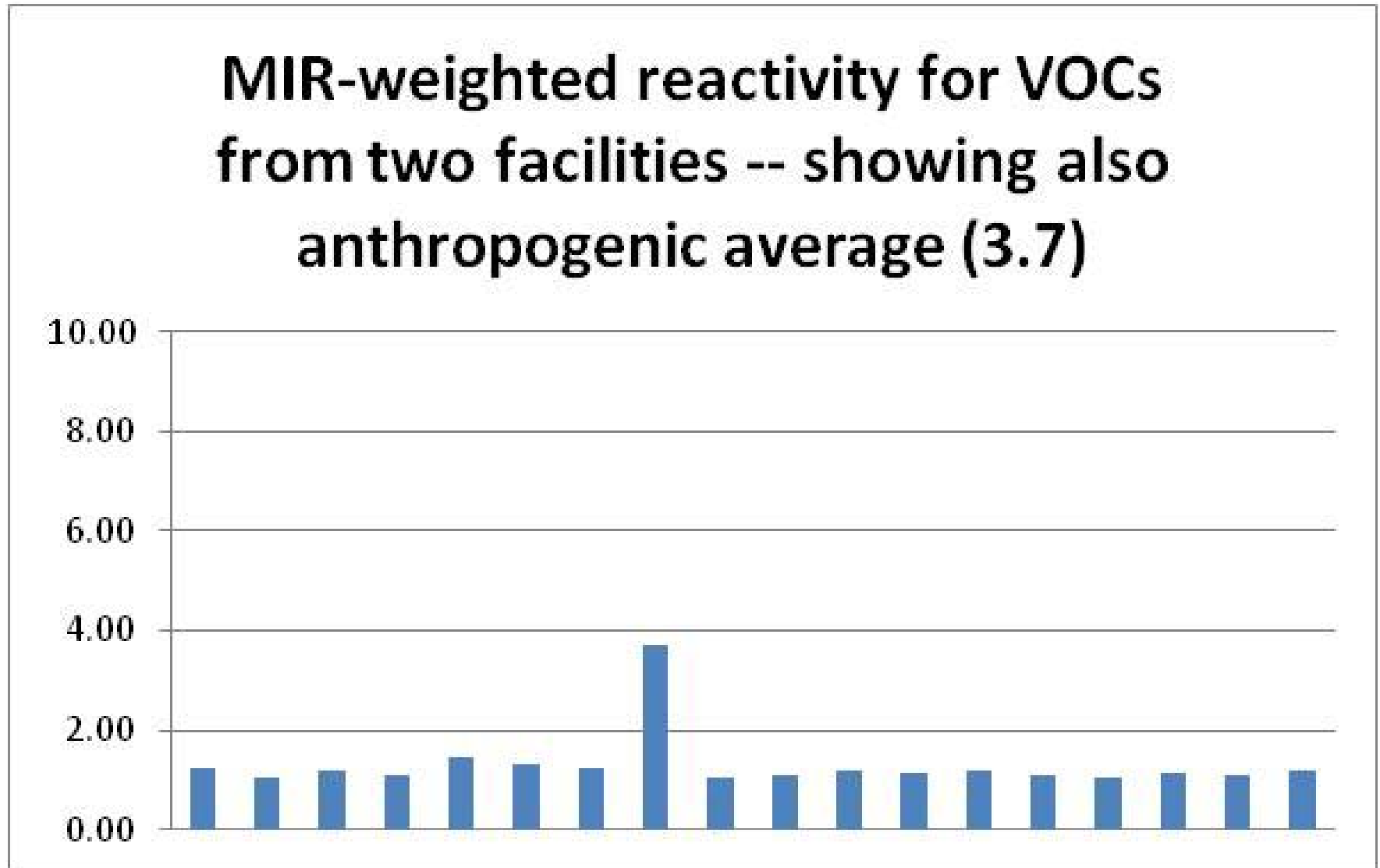
## **Field Team and Apparatus for VOC-to-ozone**

Spring 2010, studying VOCs from post-composting over-sized material

City of Santa Rosa  
Biosolids co-composting  
Facility – lava rock biofilter



One figure to summarize the main conclusion:  
compost VOCs are generally weak



# Good ozone vs. bad ozone -- and where does bad ozone come from?

Ozone in the stratosphere (higher than airplanes) is good -- it protects us from the strongest ultraviolet light from the sun

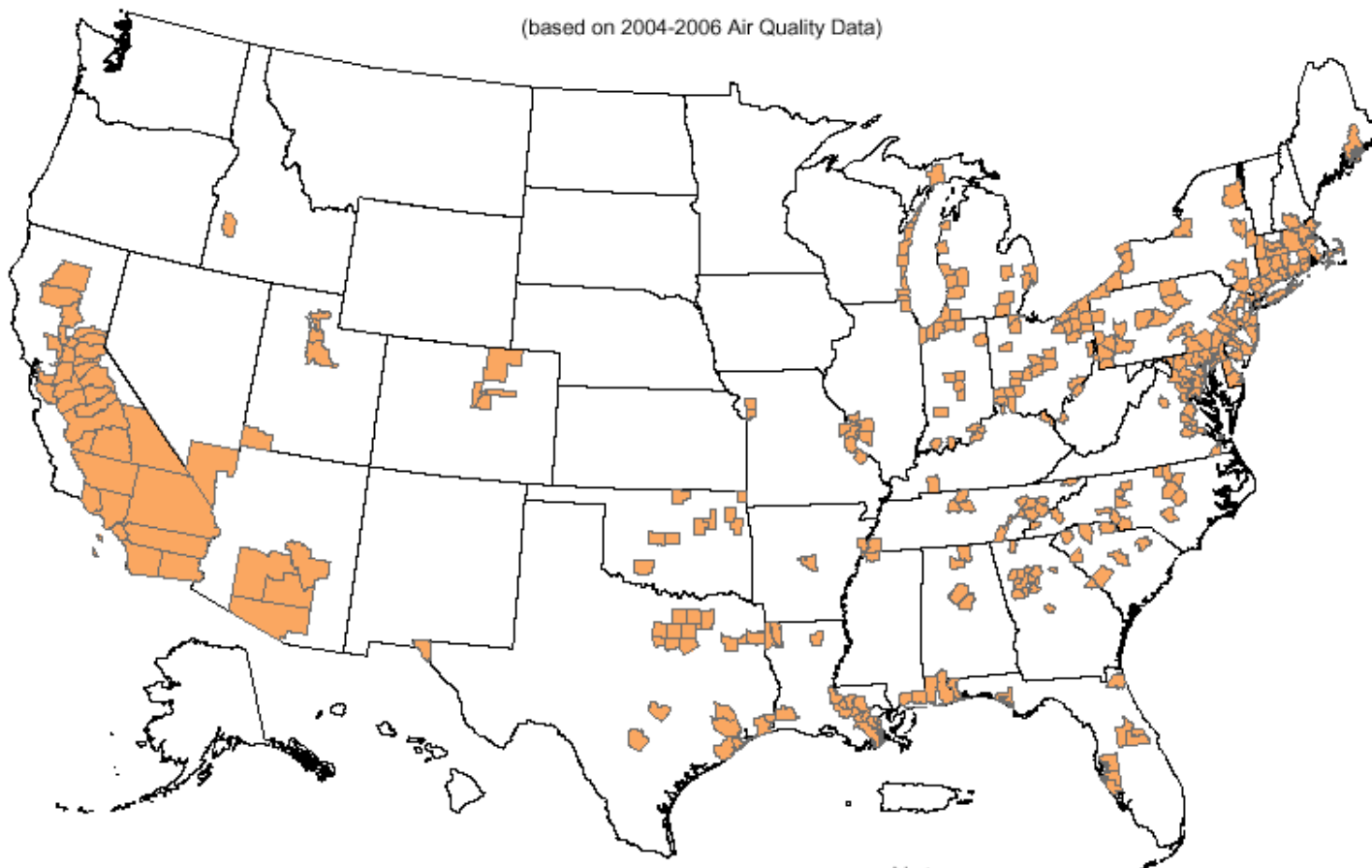
Ozone at ground level hurts our lungs, and comes from reactions between sunlight and 2 pre-cursors:

nitrogen oxides ( $\text{NO}_x$ ),

and volatile organic compounds (VOCs)

## Counties with Monitors Violating the 2008 8-Hour Ozone Standard of 0.075 parts per million (ppm)

(based on 2004-2006 Air Quality Data)

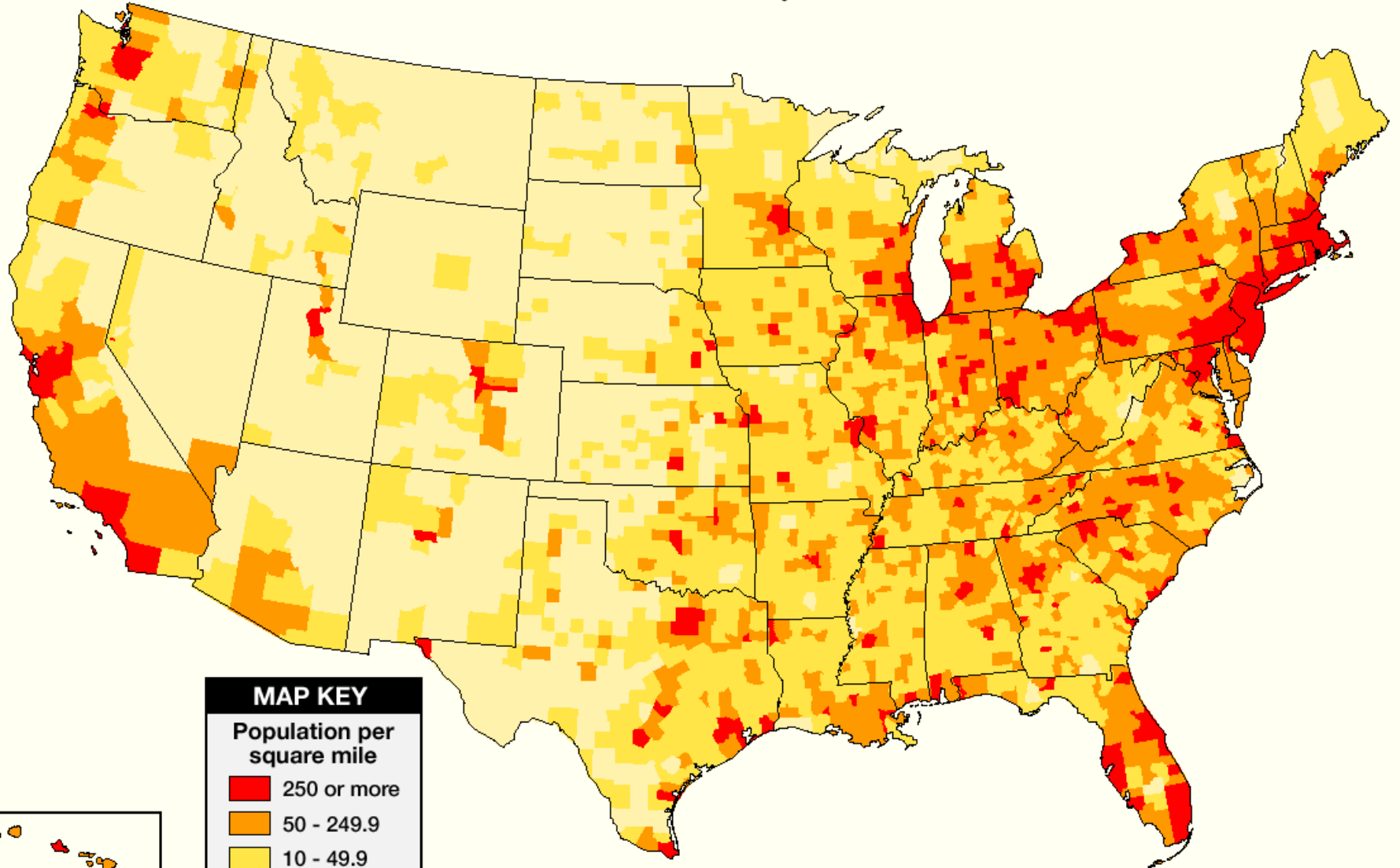


Notes:

<sup>1</sup> 345 monitored counties violate the 2008 8-hour ozone standard of 0.075 parts per million (ppm).

<sup>2</sup> Monitored air quality data can be obtained from the AQS system at <http://www.epa.gov/ttn/airs/airsaqs/>

# U.S. Population Density (By Counties)



## MAP KEY

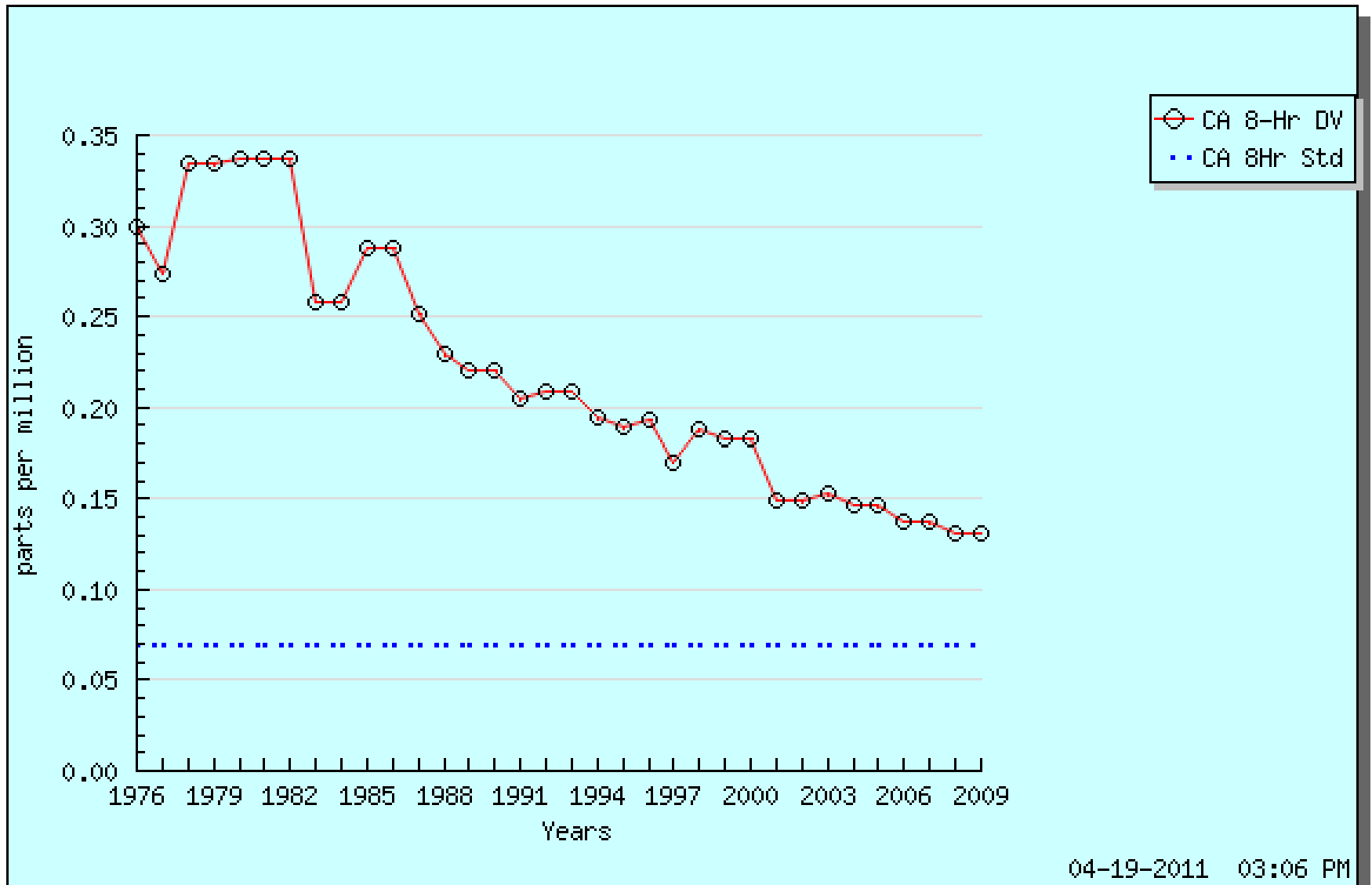
Population per  
square mile

- 250 or more
- 50 - 249.9
- 10 - 49.9
- less than 10

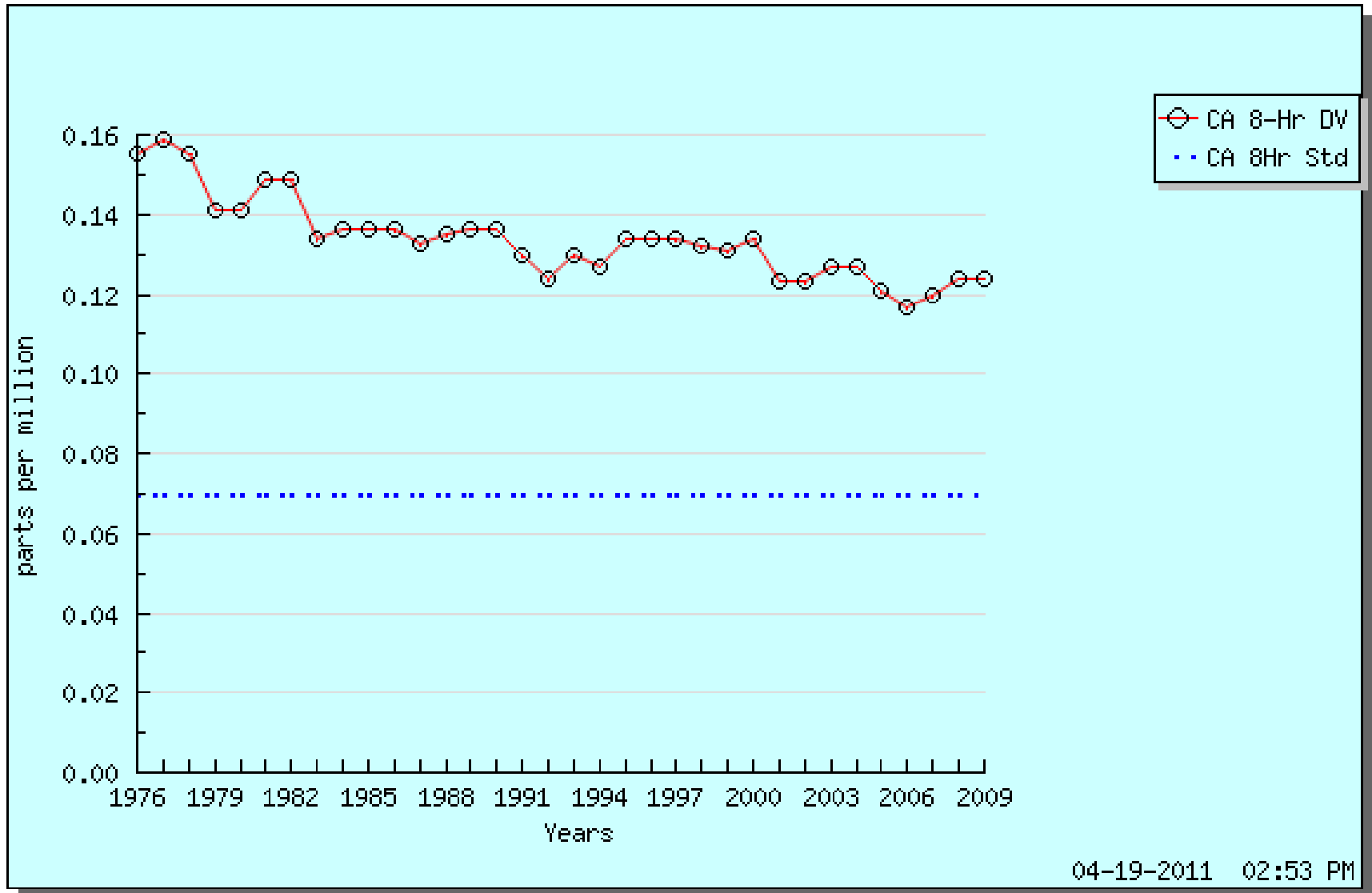
## California's efforts so far:

- Develop an inventory of all VOC and NO<sub>x</sub> sources
- Large reductions in VOCs from urban sources
- Also reductions in VOCs from non-urban sources
- Reductions in NO<sub>x</sub> from cars
- New focus on NO<sub>x</sub> reductions from diesel engines

# 8-hour average O<sub>3</sub>, max, South Coast



# 8-hour average ozone, max, SJV



# Complexity of ozone formation

- Diverse mixture of VOCs, some unknown
- Even with multiple measurement techniques, there is **no** ‘total’ VOC
- Regulations treat all reactive VOCs equally on a pound-for-pound basis
- (Methane and a few others are exempt.)
- However, different VOCs are *different* molecules – they react *differently*
- Hence, Ozone Formation Potential

Great variation in formation potential (lbs. ozone per lb. VOC) even among similarly volatile molecules

<b>Molecule</b>	<b>Boiling Point, C</b>	<b>MIR</b>
<b>acetic acid</b>	<b>118</b>	<b>0.5</b>
<b>butyl acetate (n-)</b>	<b>118</b>	<b>0.89</b>
<b>octane</b>	<b>126</b>	<b>1.11</b>
<b>butanol (n-)</b>	<b>125</b>	<b>3.34</b>
<b>octene (1-)</b>	<b>121</b>	<b>3.45</b>
<b>toluene</b>	<b>111</b>	<b>3.97</b>
<b>xylene (para,ortho,meta)</b>	<b>139</b>	<b>4.2,7.5,10.6</b>

Also considerable variation within a family of VOCs, e.g. alcohols, etc...

From a regulator: Unfortunately, this may be one issue where the legal system hinders [progress]. We are legally required ...  
the inventory is calculated based on mass not reactivity.

# What VOCs come from where?

## Microbial fermentation:

wood input leads to wood alcohol  
(low subsequent reactivity)

## Internal combustion engines:

leads to aromatics and aldehydes  
(high subsequent reactivity)

# Mobile Ozone Chamber Assay (MOChA)



Graduate students Cody Howard and Doniche Derrick.

# Mobile Ozone Chamber Assay (MOChA)



Separate lamp unit, with fans to aid temperature control.

# Mobile Ozone Chamber Assay (MOChA)



We measure VOCs with multiple techniques.

We assess the amount of ozone they actually form (over a few hours), directly at the source.

Then match with a photo-chemical model calculation – to assert we have successfully accounted for the overall reactivity.

# VOCs found from compost

Propane  
Butane  
Pentane & isomers  
3 Methyl hexane  
Dimethyl hexane isomer  
Trimethyl hexane  
Epoxy cyclooctane  
≥ C7 straight and cyclic HC

Propene  
2 Methyl 1-propene  
Butene & isomers  
2 Methyl 1,3-butadiene (Isoprene)  
2 Methyl 3-butene 2-ol  
2 Methyl 1,3 pentadiene  
2,4-Heptadienal  
Acetyl cyclomethylpentene  
2 Ethyl 3-hexen 1-ol  
Methyl hexyne  
Methyl cycloheptene  
Acetyl methylcyclohexene  
Other alkenes

Benzene  
Toluene  
Xylene isomers  
Styrene  
C-3 Benzene isomers  
C-4 Benzene isomers  
Isopropenyl toluene  
4 Methyl benzenemethanol  
Naphthlene  
Dichlorobenzene isomers  
Trichlorobenzene isomers

α-Pinene  
β-Pinene  
4 Carene  
3 Carene  
Camphene  
Terpinene  
Terpinolene  
Limonene  
Adamantane  
α-Phellandrene  
β-Phellandrene  
L-Fenchone  
Copaene  
Camphor  
cis-Linalool oxide  
trans-Linalool oxide

2 Pinen-3 one  
Thujen-2-one (Umbellulone)  
Verbenone  
trans-Verbenol  
Linalool  
Eucalyptol  
Terpineol  
Borneol  
Allylanisole  
Safrol (1,3-Benzodioxole, 5-(2-propenyl))

Formaldehyde  
Acetaldehyde  
Propionaldehyde  
Crotonaldehyde (2-Butenal)  
Butyraldehyde  
Isovaleraldehyde  
Valeraldehyde  
2 Methyl pentenal  
Hexanal  
Hexenal  
Heptanal  
Heptenal  
Octanal  
Nonanal  
Decanal  
Dimethyl octenal  
Benzaldehyde

Furan  
3 Methyl furan  
2 Methyl furan  
2,5 Dimethyl furan  
2 Ethyl 5-methyl furan  
2 Butyl furan  
2 Pentyl furan  
Methyl hexanone isomers

Methanol  
Ethanol  
2 Propanol  
1 Propanol  
2 Butanol  
1 Butanol  
2 Methyl 1-butanol & isomer  
Pentanol  
Hexanol  
2,3 Butanediol  
Pentanol  
Hexanol  
2,3 Butanediol

Acetone  
2 Butanone  
2 Pentanone  
3 Pentanone  
3,3 Dimethyl 2-butanone  
Methyl isobutylketone (MIBK)  
3 Pentene 2-one  
3 Methyl 2-pentanone  
2 Hexanone  
Methyl hexanone isomers  
Octanone  
Nonanone  
2 Butanedione (Diacetyl)  
1 Hydroxy 2-propanone  
3 Hydroxy 2-butanone  
Methyl phenylethanone

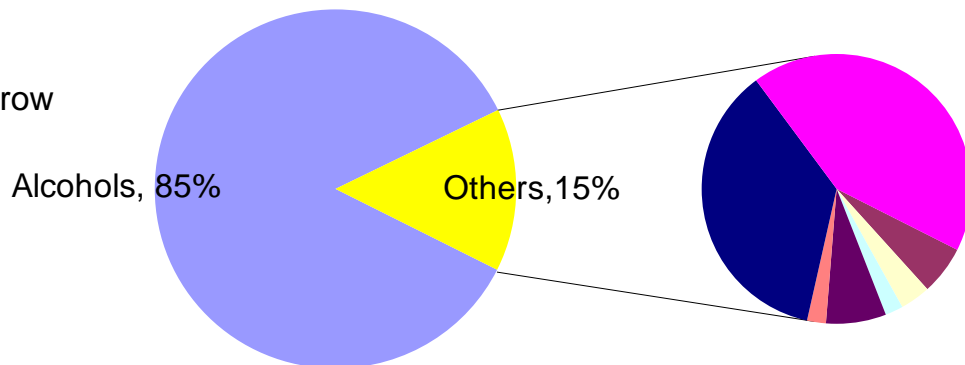
Methyl acetate  
Ethyl acetate  
Propyl acetate  
Isoamyl acetate  
Methyl butylacetate  
Bornyl acetate  
Methyl isobutanoate  
Methyl butanoate  
Methyl isopentanoate  
Ethyl butanoate  
Methyl pentanoate  
Propyl butanoate  
Methyl hexanoate  
Butyl butanoate  
Isomer of butylbutanoate  
Heptyl hexanoate  
Other ester

Acetic acid  
Propionic acid  
Methyl propionic acid  
Butanoic acid  
Methyl butanoic acid  
Pentanoic acid  
Hexanoic acid  
Acetyl benzoic acid

Dimethyl disulfide

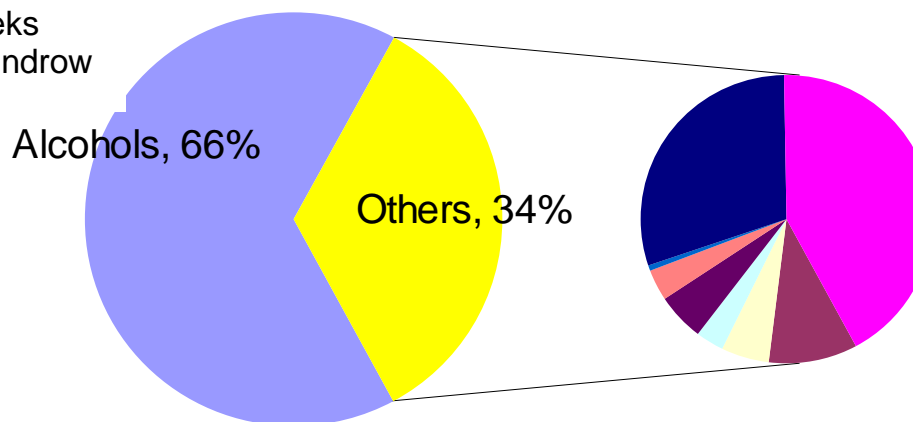
Methylthymyl ether  
Dichlorodifluoro methane  
Chloro difluoro methane  
Trichloromonofluoromethane

3-6 Days  
old windrow



- Alkenes / Alkynes,  $0.9 \pm 0.2\%$
- Aromatic Hydrocarbons,  $0.3 \pm 0.1\%$
- Ketones,  $0.3 \pm 0.3\%$
- DMDS,  $< 0.1\%$
- Acid / Esters / Others  $6.3 \pm 4.3\%$
- Alkanes / Cyclic alkanes,  $0.5 \pm 0.3\%$
- Aldehydes,  $1.1 \pm 0.5\%$
- Furans,  $< 0.1\%$
- Biogenic Hydrocarbons,  $5.4 \pm 2.2\%$

2-3 Weeks  
old windrow



- Alkenes / Alkynes,  $3.3 \pm 1.1\%$
- Aromatic Hydrocarbons,  $1 \pm 0.8\%$
- Ketones,  $1.2 \pm 1.0\%$
- DMDS,  $0.1 \pm 0.1\%$
- Acid / Esters / Others  $14.6 \pm 6.0\%$
- Alkanes / Cyclic alkanes,  $1.9 \pm 0.6\%$
- Aldehydes,  $1.8 \pm 1.9\%$
- Furans,  $0.2 \pm 0.2\%$
- Biogenic Hydrocarbons,  $10.3 \pm 3.8\%$

From our recently accepted paper in Atmos. Environment.

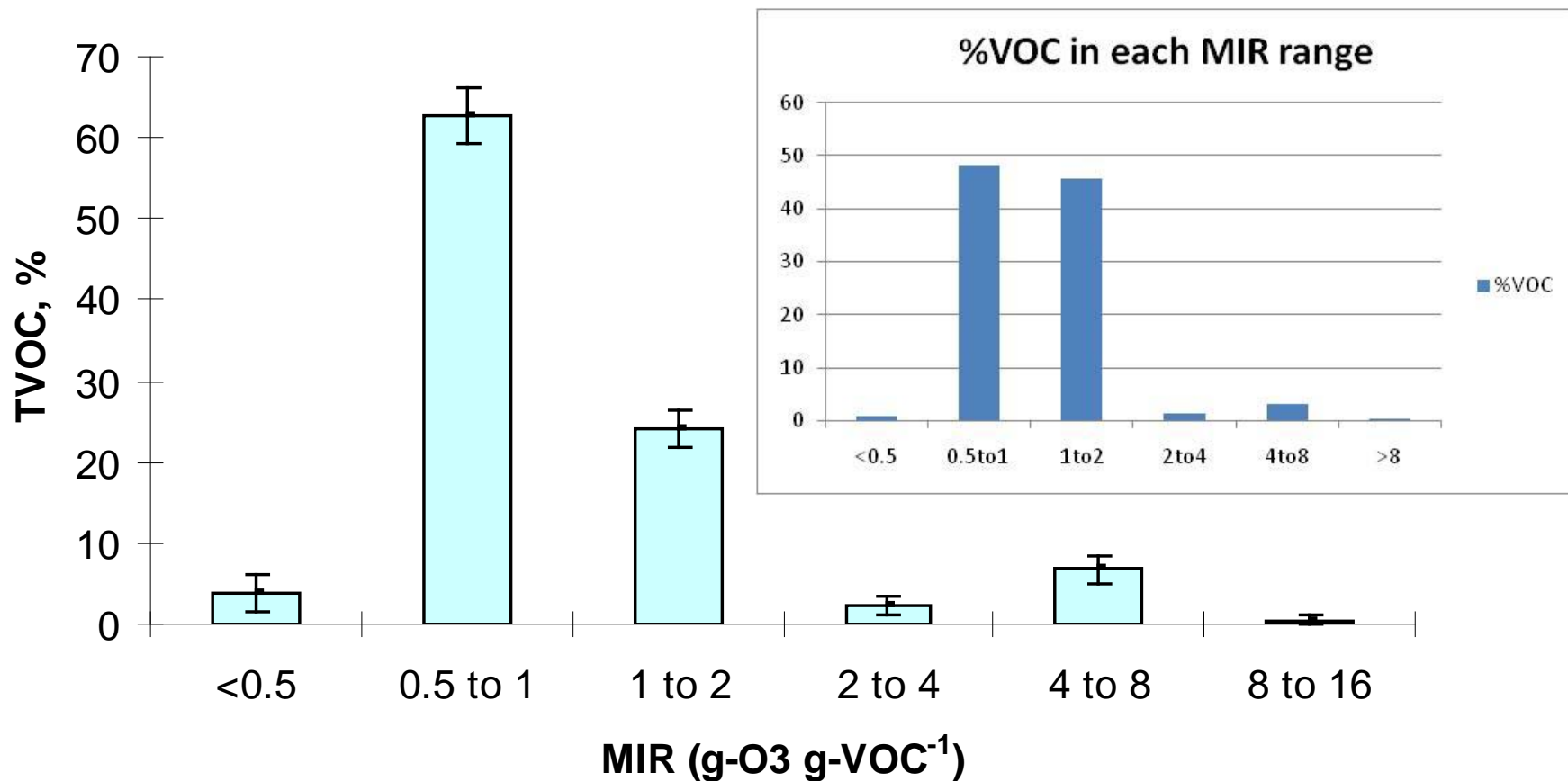
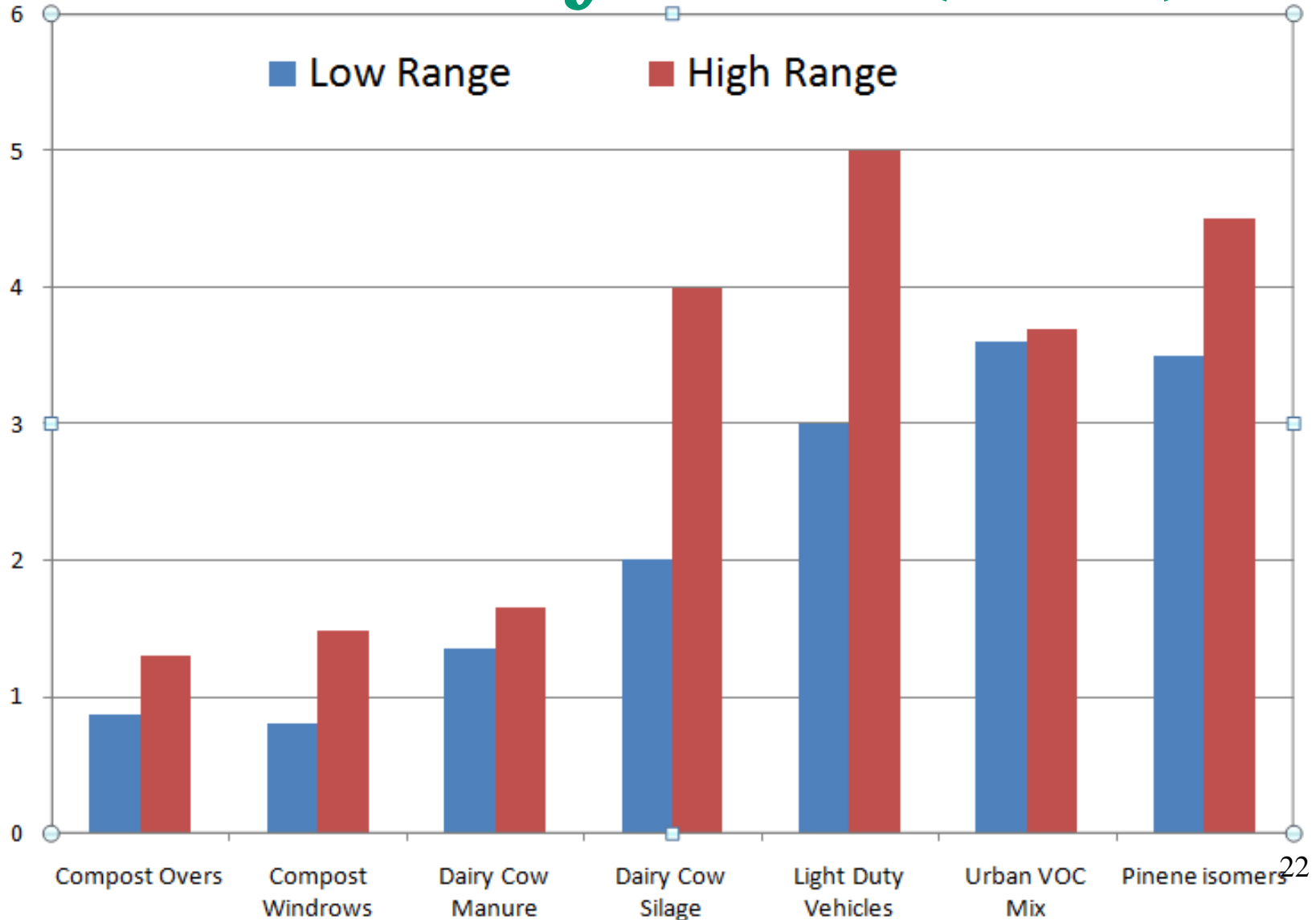


Figure 3. Average contribution of VOC into the ozone formation according to their reactivity. (Urban VOC average is 3.6 to 3.7, depending on latest model revisions.)

# Maximum Incremental Reactivity scale (MIR)



# Conclusions

- Compost VOC emissions are dominated by low reactivity compounds
- All VOC sources can have a role in improving air quality – however some may be more important to manage for NO<sub>x</sub>
- The relative value of VOC reductions is higher in urban areas vs. non-urban
- Future regulations (e.g. state implementation plans) will use reactivity more realistically

# Additional Results

The use of a cap of oversized material (from sieving previously finished compost) reduces OFP from VOCs by 25% to 40%.

This could be a cost-effective mitigation, using otherwise un-sold material (which could go to grinder, or to landfill) and which adds compost microbes and aeration when mixed in during turning.

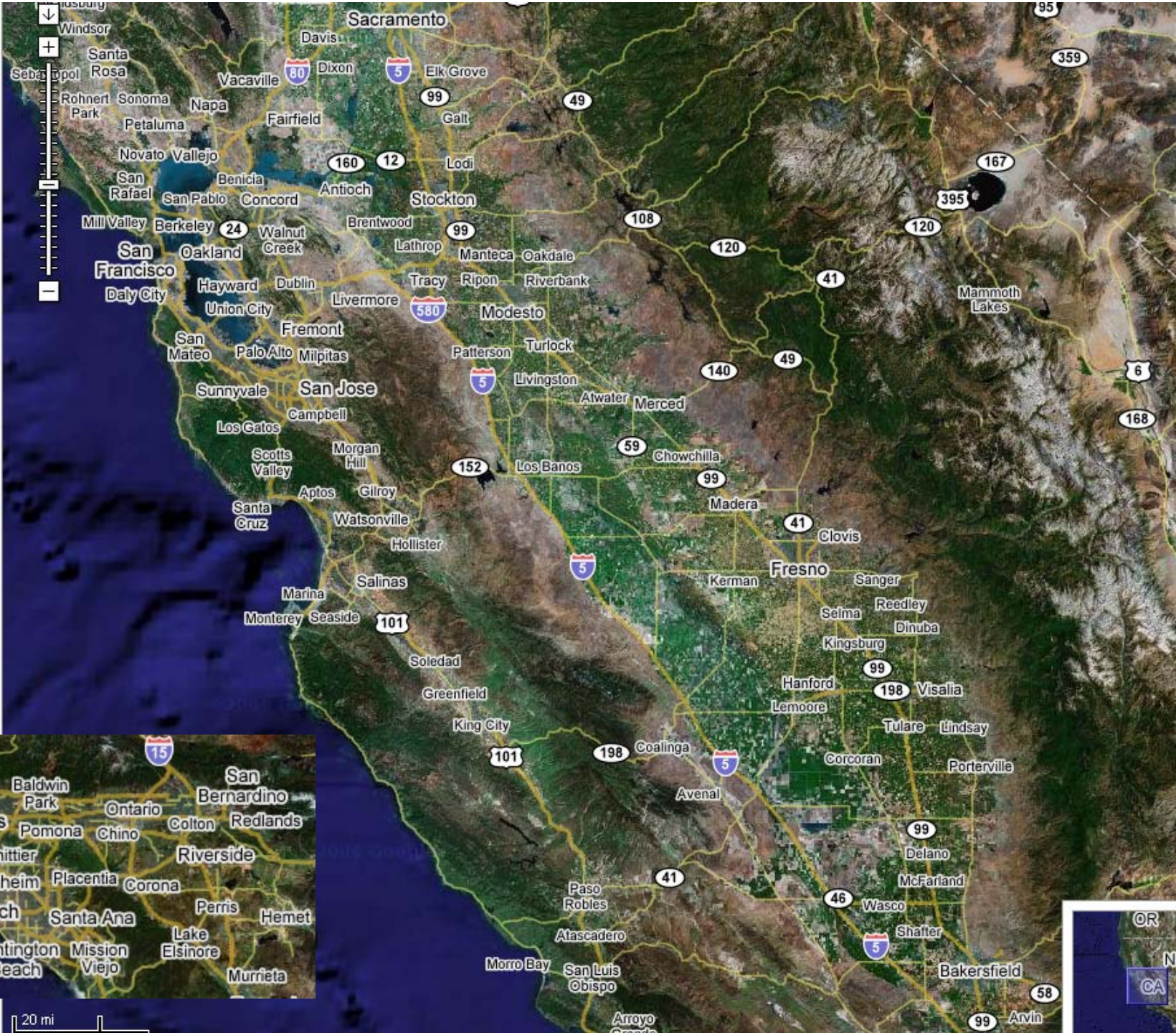
Biosolids co-composting generally shows similar VOCs, with minor differences not significantly affecting ozone formation.

Thank you, and questions?

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San  
Joaquin  
Valley  
and  
Los  
Angeles  
Calif.  
(same  
scale)



20 mi

# Ozone Cycle and the Dependence on NO<sub>x</sub> and VOC:

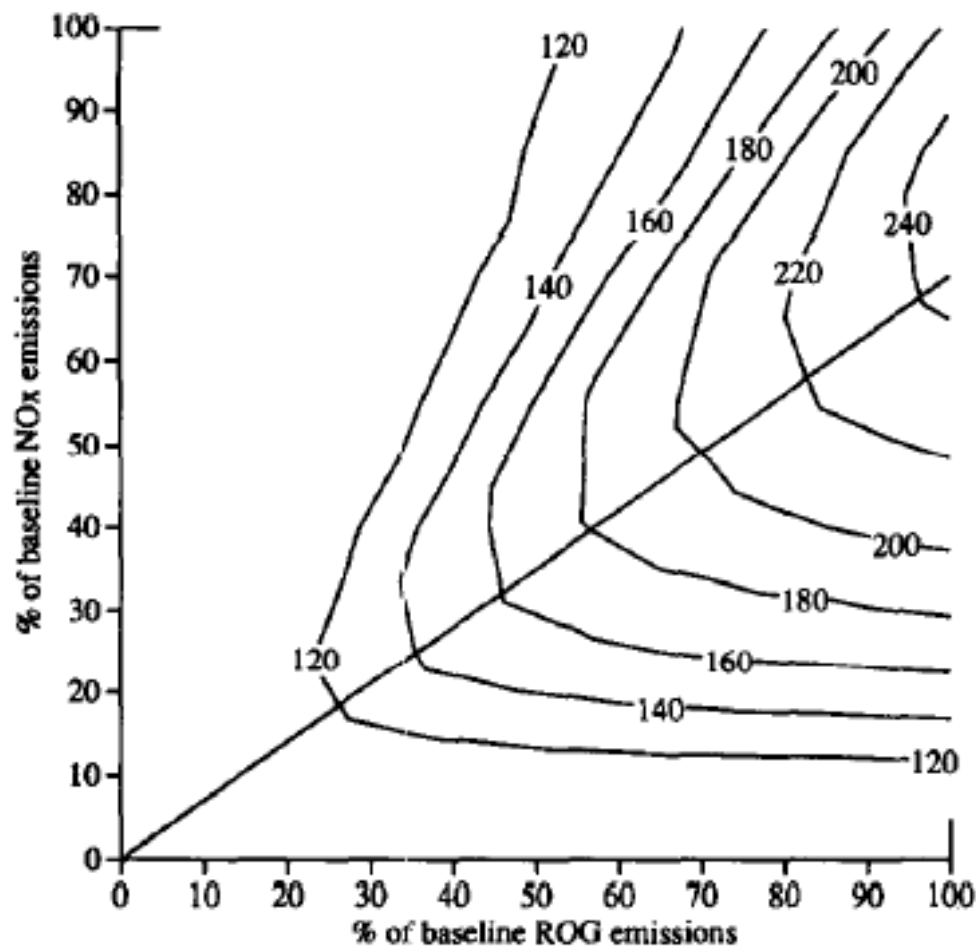
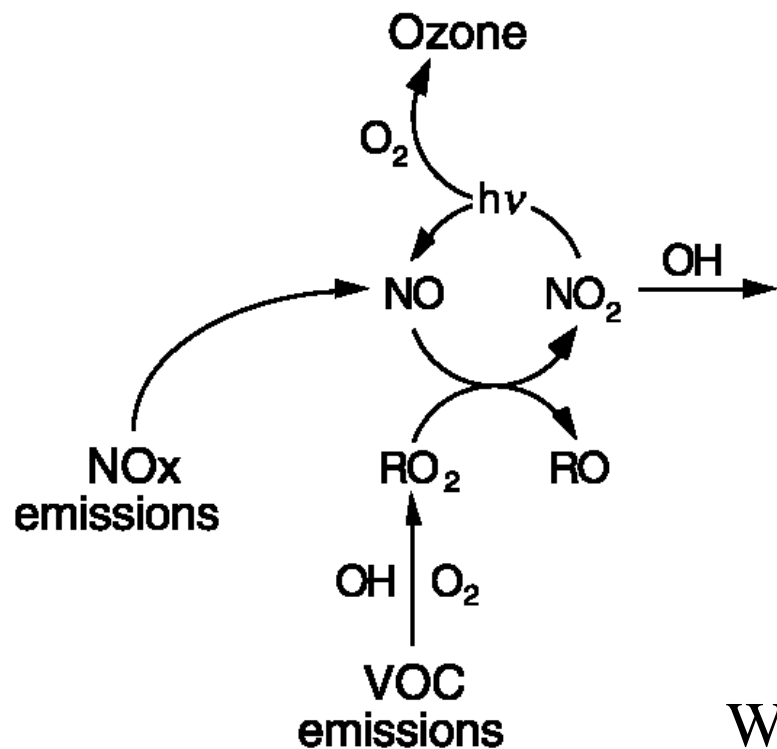
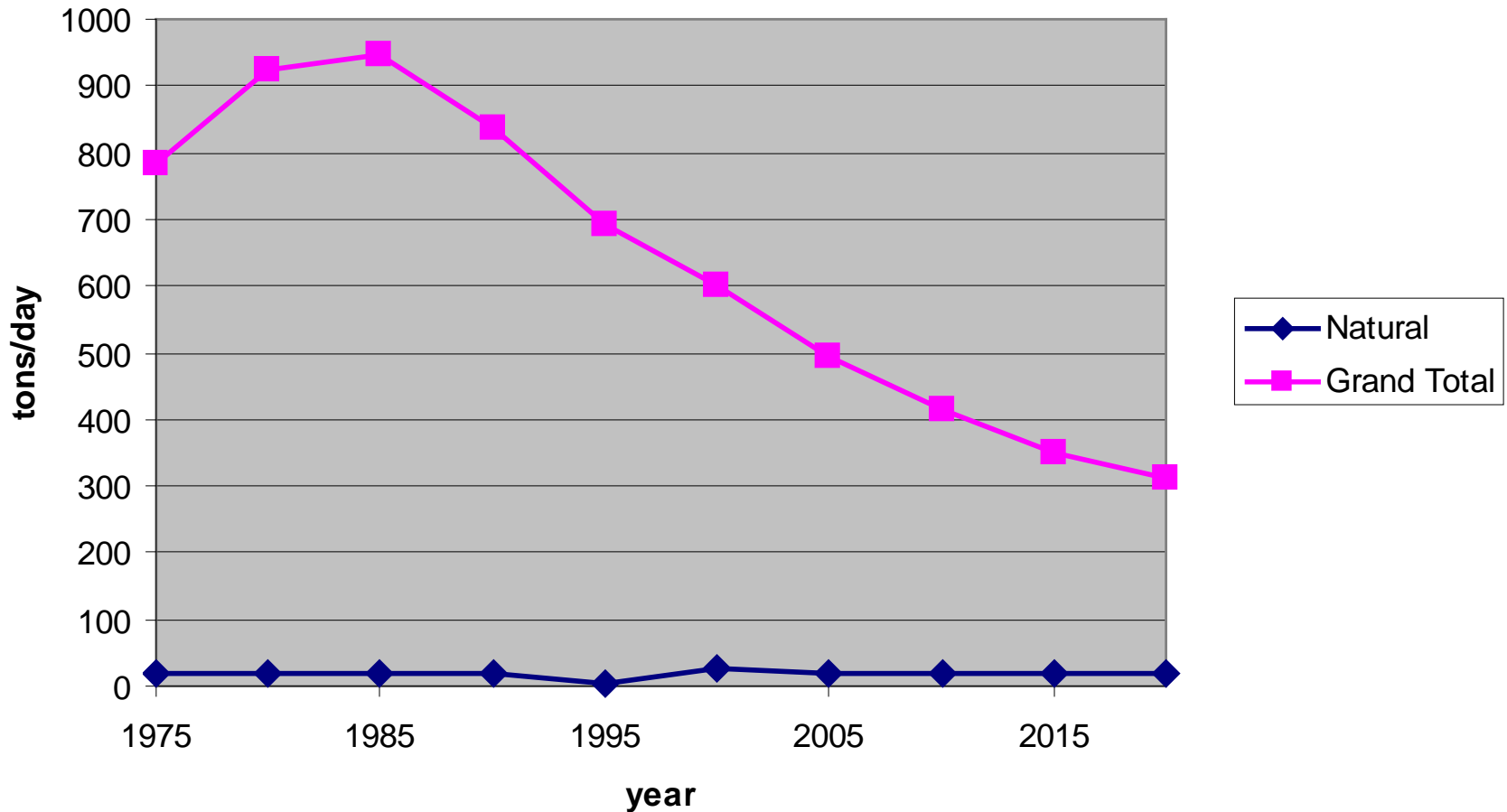


Fig. 1. Ozone isopleth diagram showing the hypothetical response of peak 1 h average ozone concentrations within an air basin to changed levels of anthropogenic ROG and NO<sub>x</sub> emissions. Contour lines are lines of constant ozone concentration (ppb).

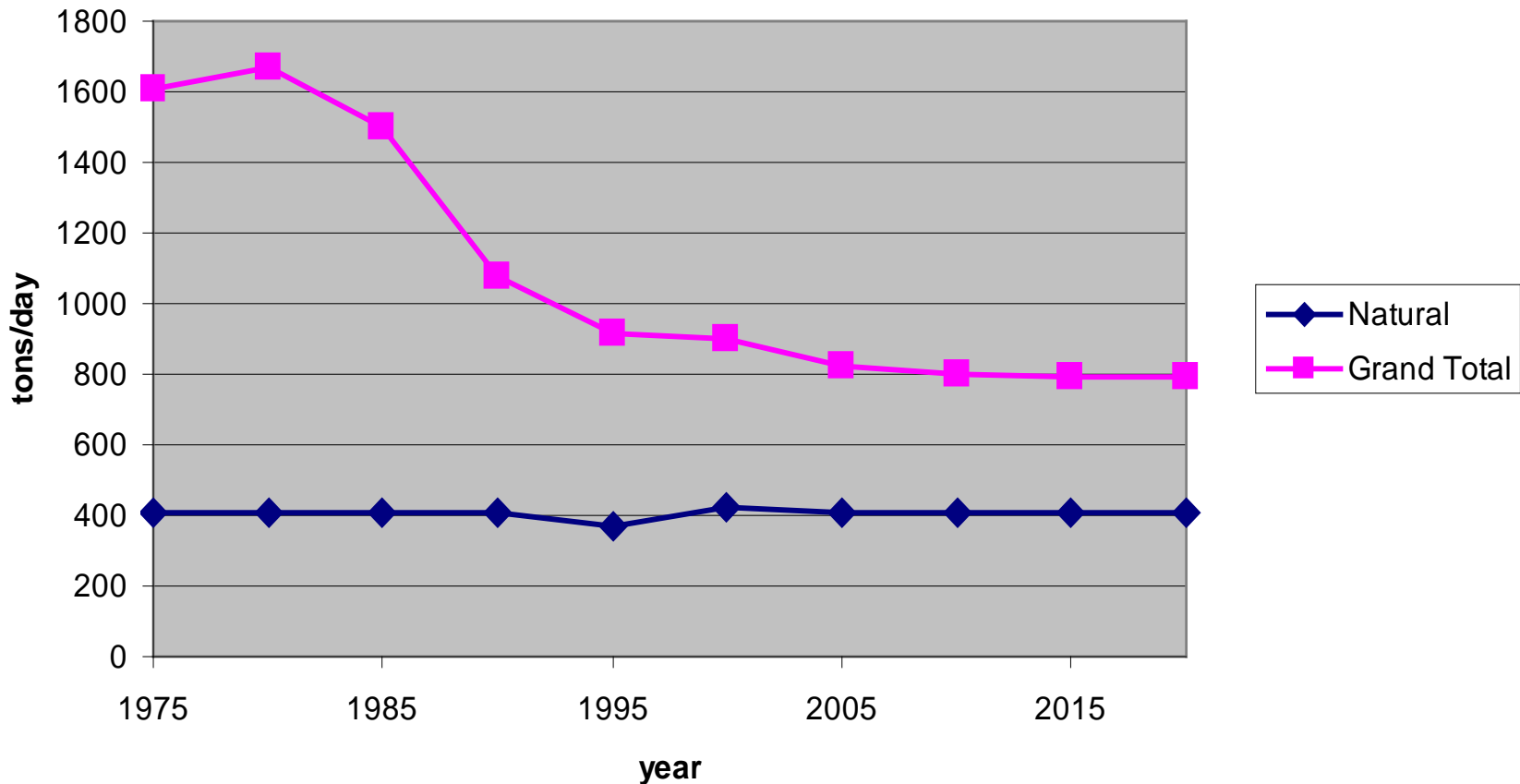
NOx show a delayed trend/forecast  
-- and monitoring data suggests may be slower

**SJV Summer Emissions Inventory for NOx**



# Total Reactive Organic Gases (non-exempt VOCs) have actually been quite greatly reduced.

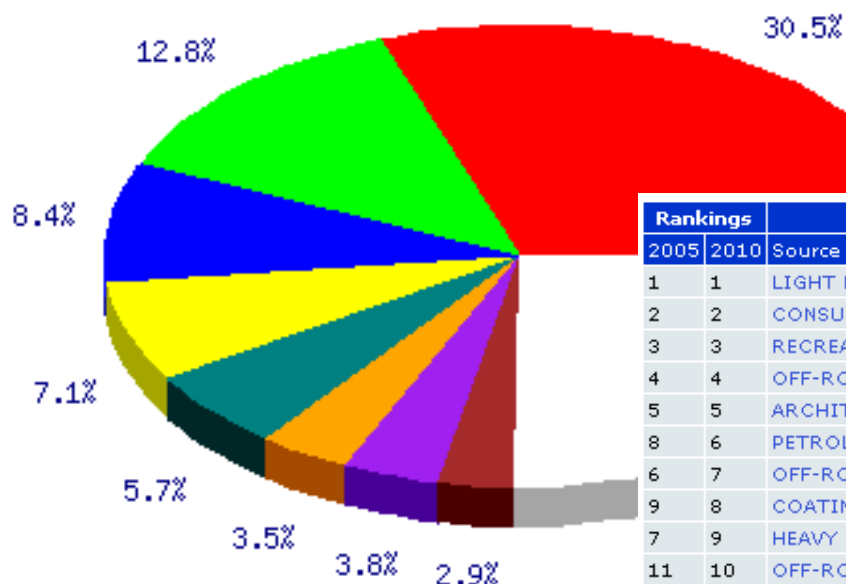
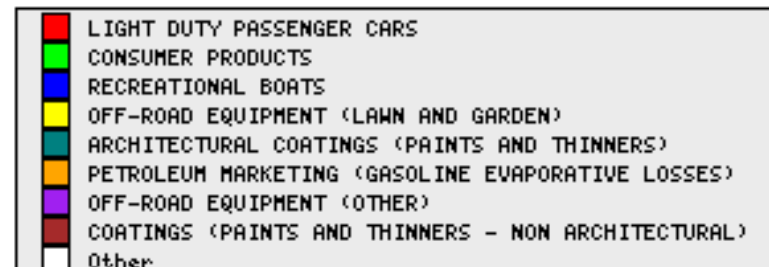
### SJV Summer Emissions Inventory for ROG (non-exempt VOC)



# Los Angeles VOC inventory

2005

-- and forecast

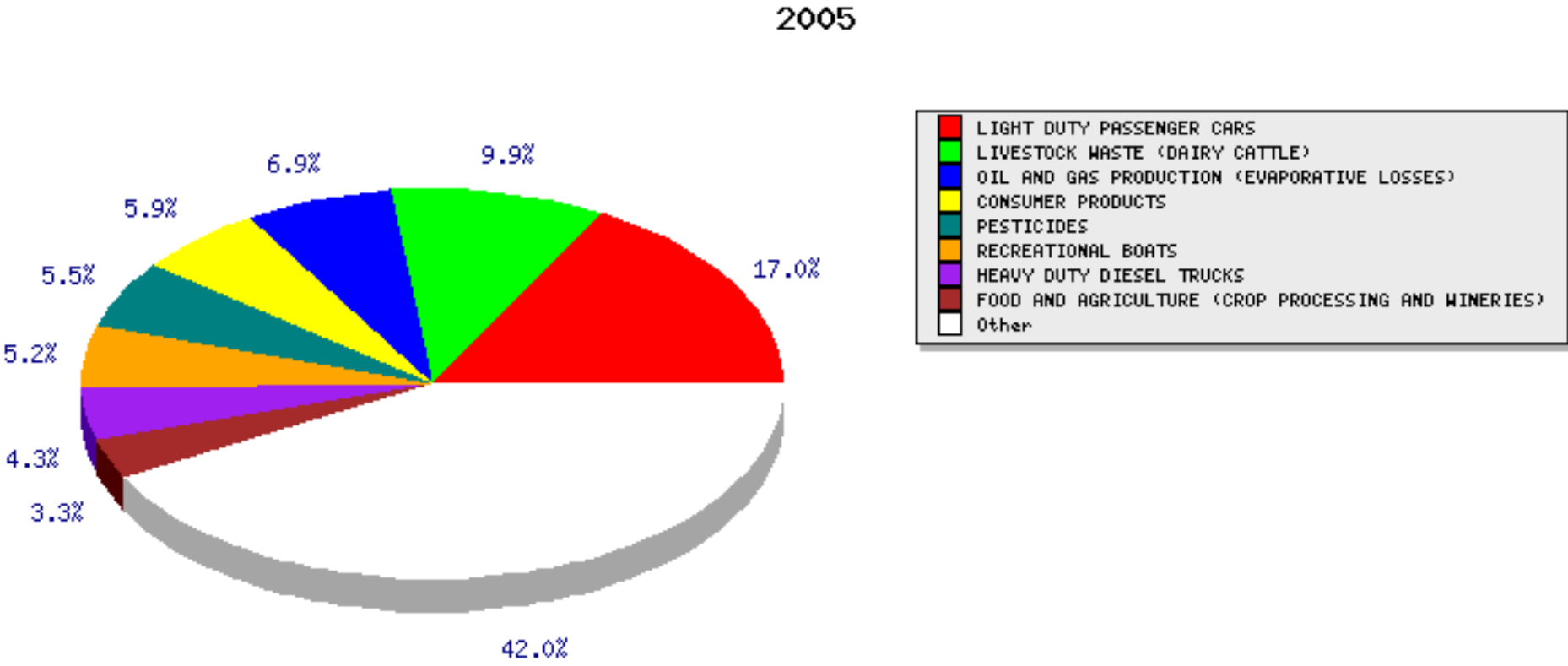


Rankings		Source Category	Summer 2005		2010	
2005	2010		ROG (tpd)	% of Total	ROG (tpd)	% of Total
1	1	LIGHT DUTY PASSENGER CARS	237.15	30.5%	142.82	23.5%
2	2	CONSUMER PRODUCTS	99.68	12.8%	102.57	16.9%
3	3	RECREATIONAL BOATS	65.56	8.4%	57	9.4%
4	4	OFF-ROAD EQUIPMENT (LAWN AND GARDEN)	54.93	7.1%	45.27	7.5%
5	5	ARCHITECTURAL COATINGS (PAINTS AND THINNERS)	44.58	5.7%	31.89	5.3%
8	6	PETROLEUM MARKETING (GASOLINE EVAPORATIVE LOSSES)	27.13	3.5%	26.96	4.4%
6	7	OFF-ROAD EQUIPMENT (OTHER)	29.69	3.8%	20.4	3.4%
9	8	COATINGS (PAINTS AND THINNERS - NON ARCHITECTURAL)	22.77	2.9%	20.39	3.4%
7	9	HEAVY DUTY GAS TRUCKS	29.63	3.8%	16.09	2.7%
11	10	OFF-ROAD EQUIPMENT (CONSTRUCTION AND MINING)	20.84	2.7%	15.54	2.6%
12	11	HEAVY DUTY DIESEL TRUCKS	15.7	2%	13.12	2.2%
10	12	GAS CANS	22.21	2.9%	13.09	2.2%
13	13	MOTORCYCLES	14.99	1.9%	12.19	2%
14	14	DEGREASING	9.09	1.2%	10.2	1.7%
16	15	CHEMICAL (PROCESS AND STORAGE LOSSES)	8.85	1.1%	9.67	1.6%
15	16	OFF-ROAD RECREATIONAL VEHICLES	9.08	1.2%	9.16	1.5%
17	17	AIRCRAFT*	*	*	*	*
19	18	PRINTING	6.54	0.8%	6.86	1.1%
18	19	OTHER (WASTE DISPOSAL)	7.45	1%	6.68	1.1%
21	20	ADHESIVES AND SEALANTS	3.15	0.4%	3.84	0.6%
22	21	PETROLEUM REFINING (EVAPORATIVE LOSSES)	3.1	0.4%	3.07	0.5%
23	22	FOOD AND AGRICULTURE (CROP PROCESSING AND WINERIES)	2.61	0.3%	2.7	0.4%
24	23	TRAINS	2.55	0.3%	2.45	0.4%
26	24	LIVESTOCK WASTE (LAYERS)	2.36	0.3%	2.36	0.4%
25	25	PESTICIDES	2.45	0.3%	2.09	0.3%
-	-	All other Sources	35.51	4.6%	30.42	5%
-	-	<b>Total</b>	777.59	100%	606.82	100%

Note: Natural Sources not included

Data Source: 2007 Almanac published by the California Air Resources Board.

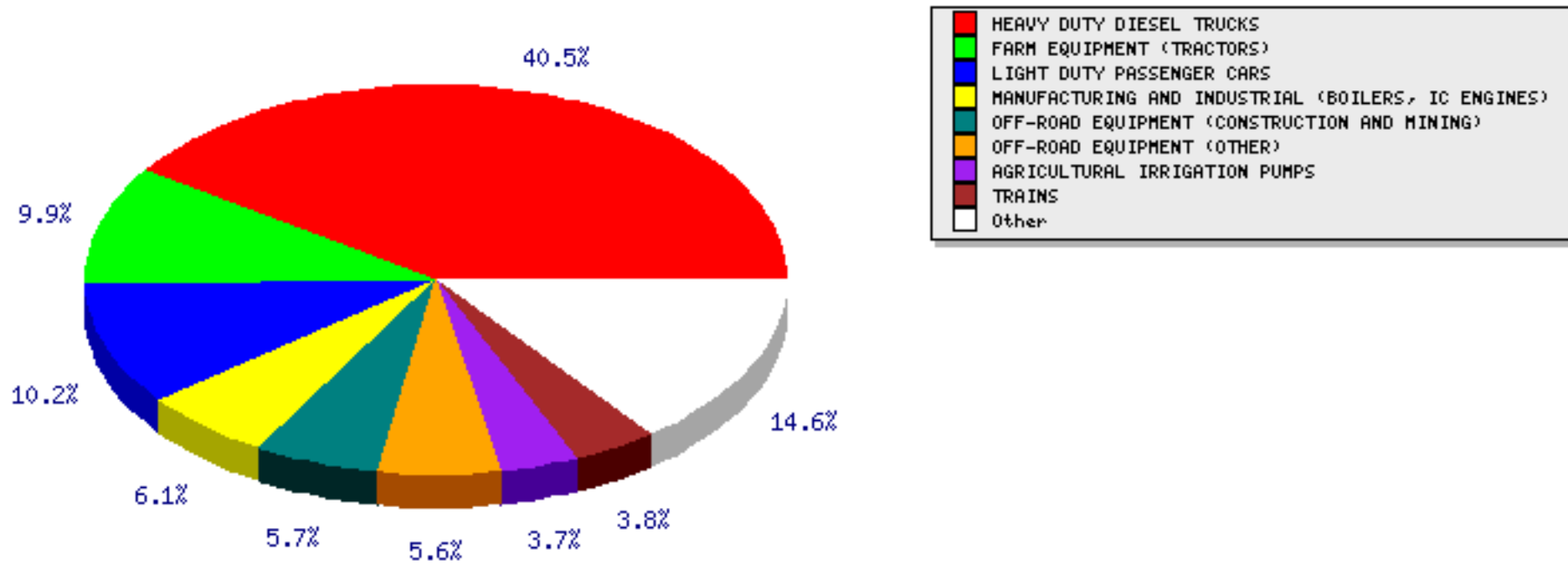
# The San Joaquin Valley is different from Los Angeles.



State has authority over stationary sources, not transportation.

# San Joaquin Valley NOx emissions inventory, summer season

2005



# Ground-level ozone improving, but slowly

## Days Exceeding Ozone Standard -- San Joaquin Valley

