Speciation, Ozone Formation Potential and Mitigation of VOCs from Compost

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Funding: finishing from CASA, recently from CalRecycle, and previously from StopWaste.org, and Composting Businesses.

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 -- 6 papers published (plus 1 under revision, 1 in preparation, 1 being planned.)
  - Insecticide solvents and oil pesticides
  - Dairy and livestock studies: animals, fresh waste, feeds
  - Green waste compost, biosolids co-composting

- <u>Finding Solutions</u> – 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
Facilty – lava rock biofilter

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 (NOx),

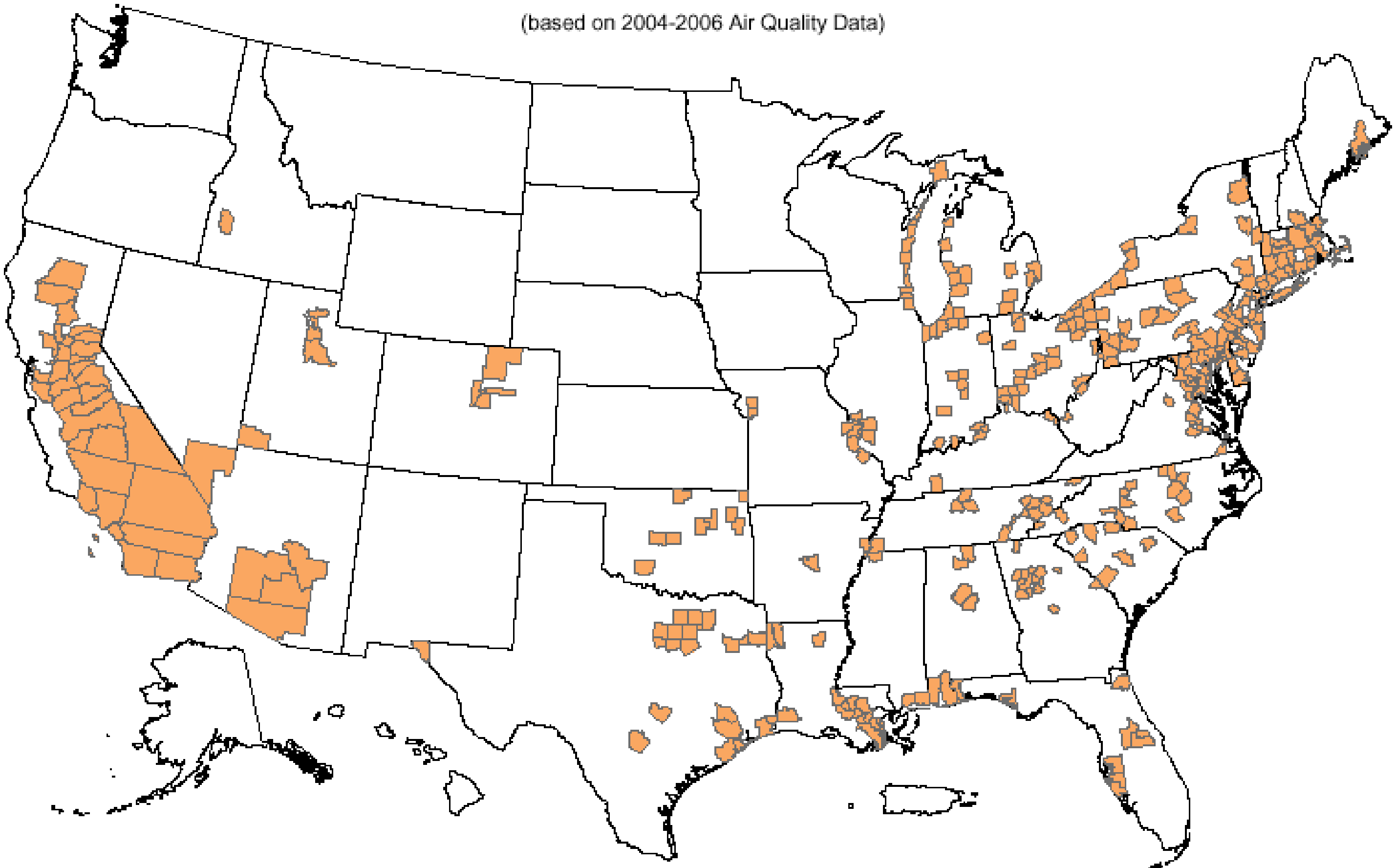
and volatile organic compounds (VOCs)

EPA United States Environmental Protection Agency

Estimates are based on the most recent data (2004 – 2006). EPA will not designate areas as nonattainment on these data, but likely on data from 2006 – 2008 or later, which we expect to show improved air quality.

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

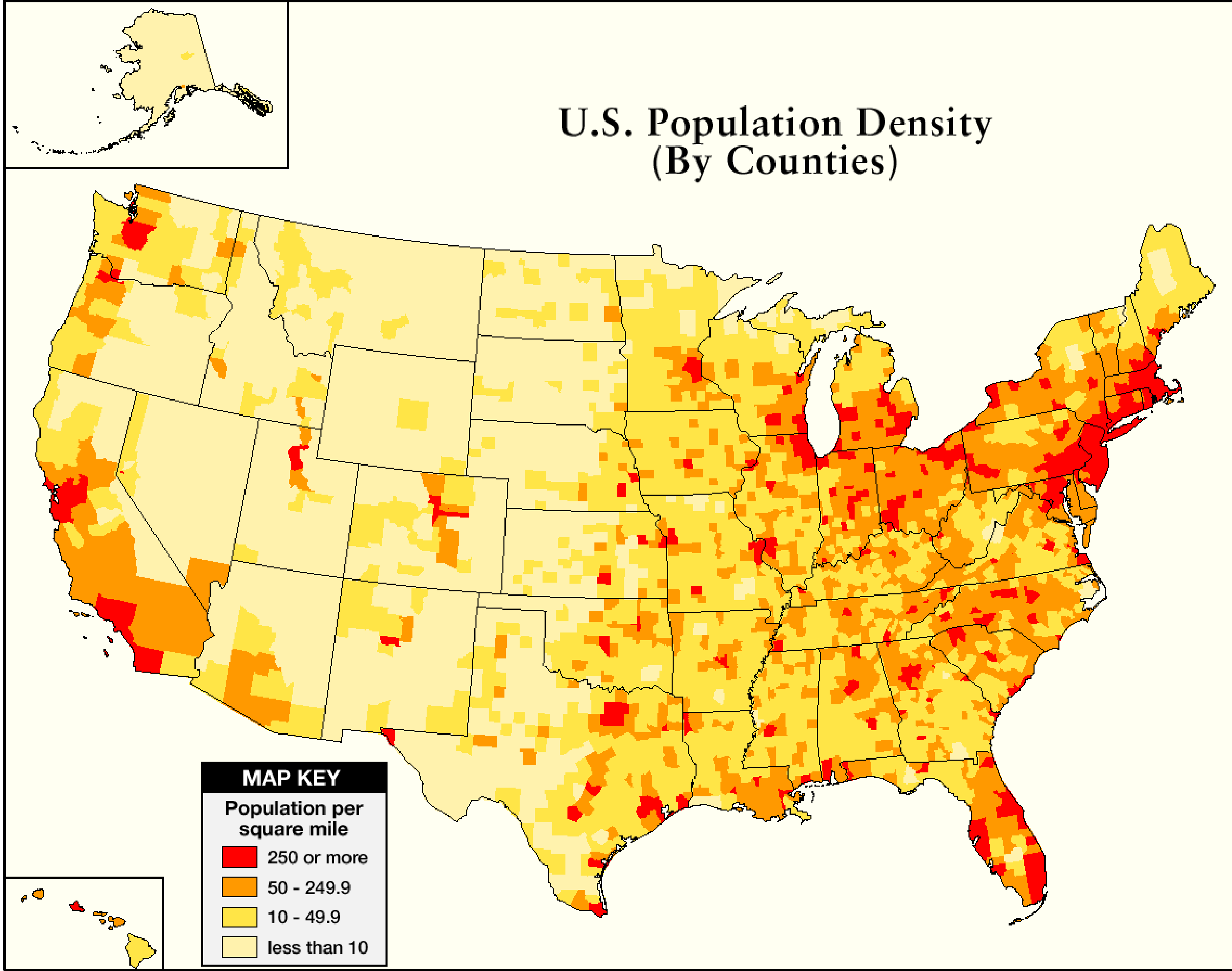
(based on 2004-2006 Air Quality Data)



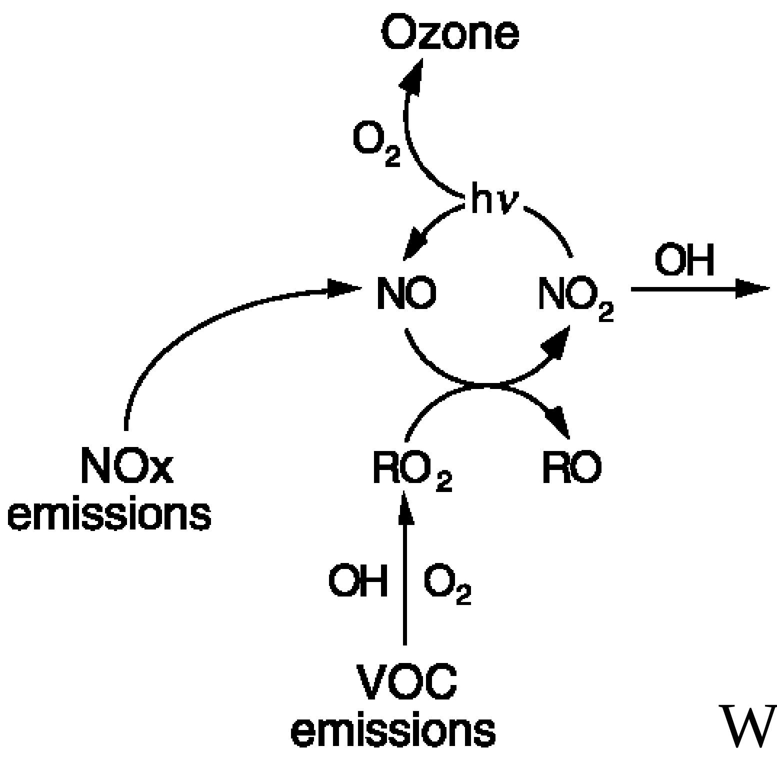
Notes:

[1] 345 monitored counties violate the 2008 8-hour ozone standard of 0.075 parts per million (ppm).

[2] 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

Ozone Cycle and the Dependence on NOx and VOC:



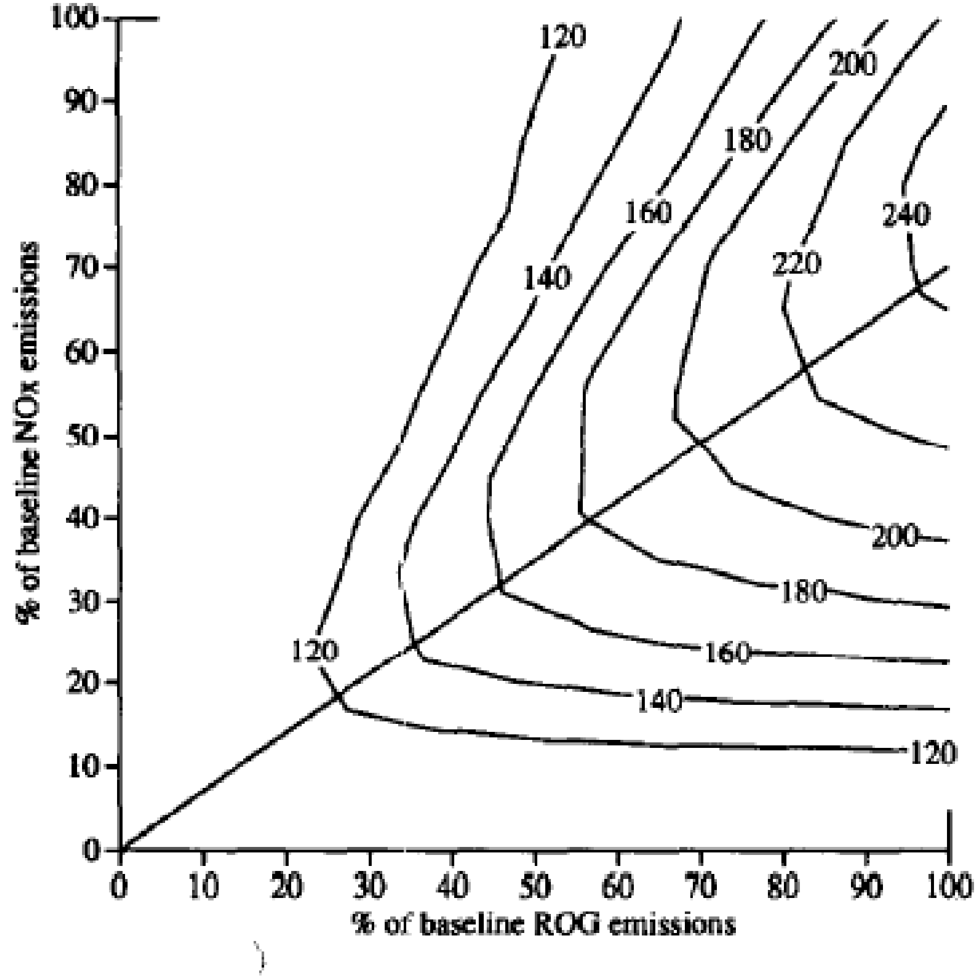
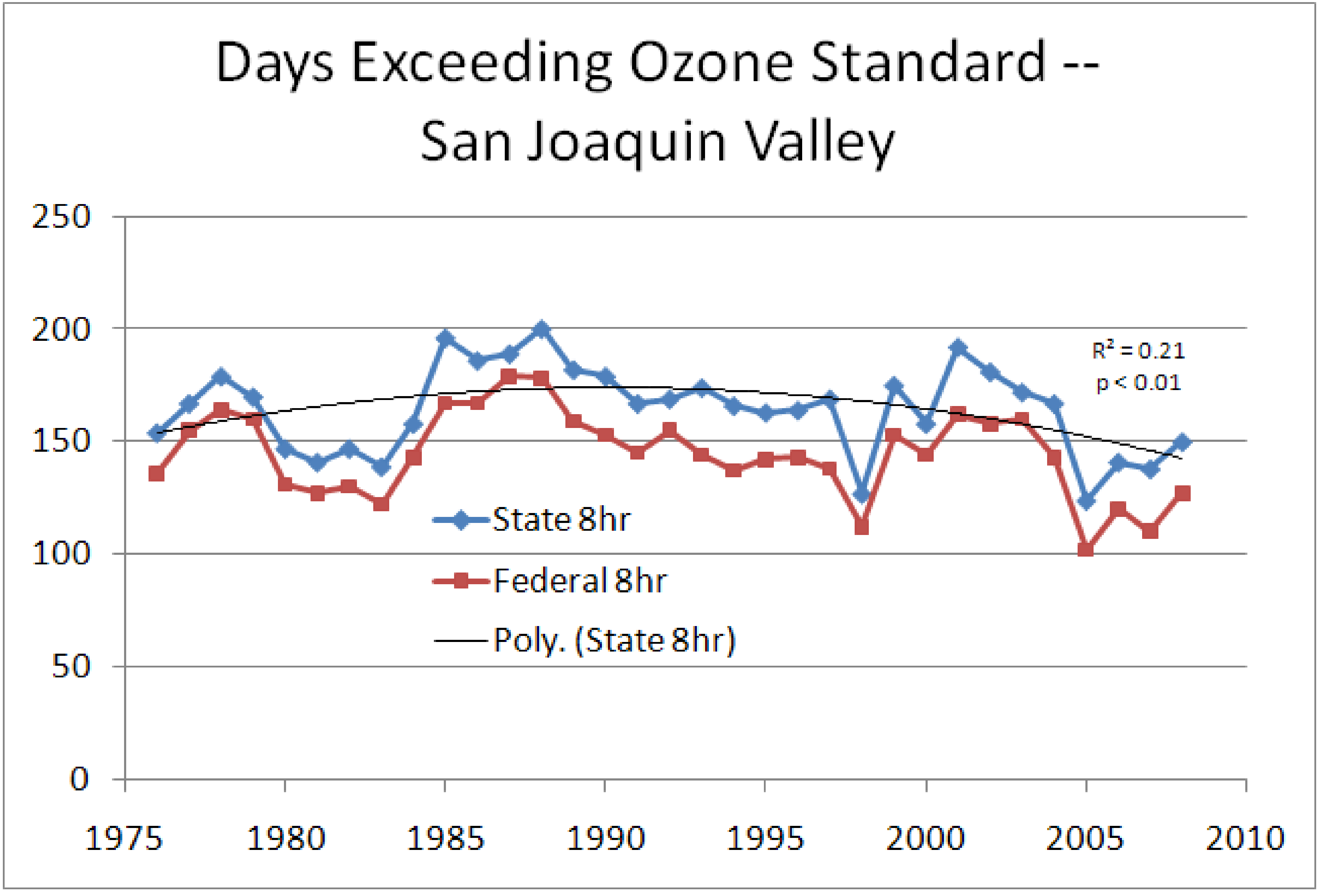


Fig. 1. Ozone isopleth diagram showing the hypothetical response of peak 1 h average ozone concentrations within an air basin to changed levels of anthropogenic ROG and NO_x emissions. Contour lines are lines of constant ozone concentration (ppb).

Winner, Cass and Harley, Atmos. Env. 1995

Ground-level ozone improving, but slowly

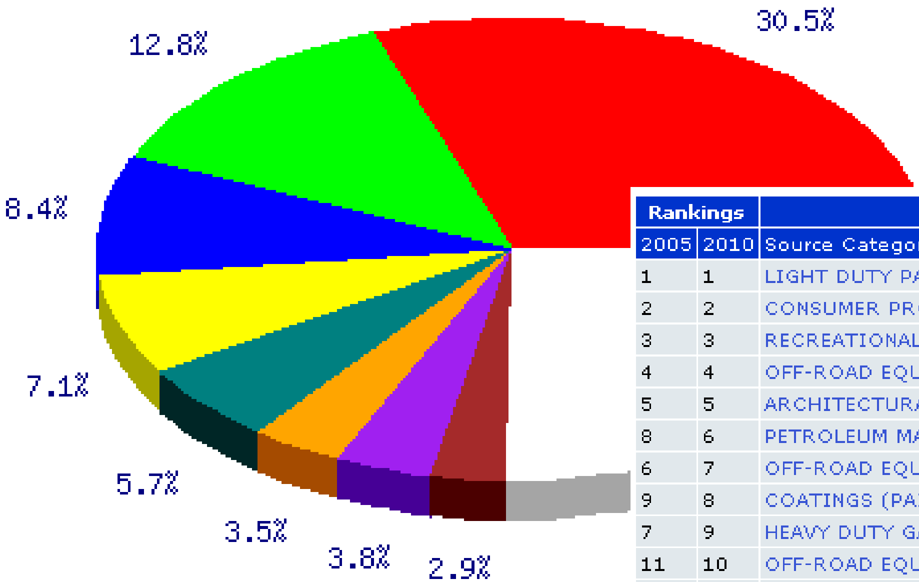


California's efforts so far:

- Develop an inventory of all VOC and NOx sources
- Large reductions in VOCs from urban sources
- Also reductions in VOCs from non-urban sources
- Reductions in NOx from cars
- New focus on NOx reductions from diesel engines

Los Angeles VOC inventory -- and forecast

2005

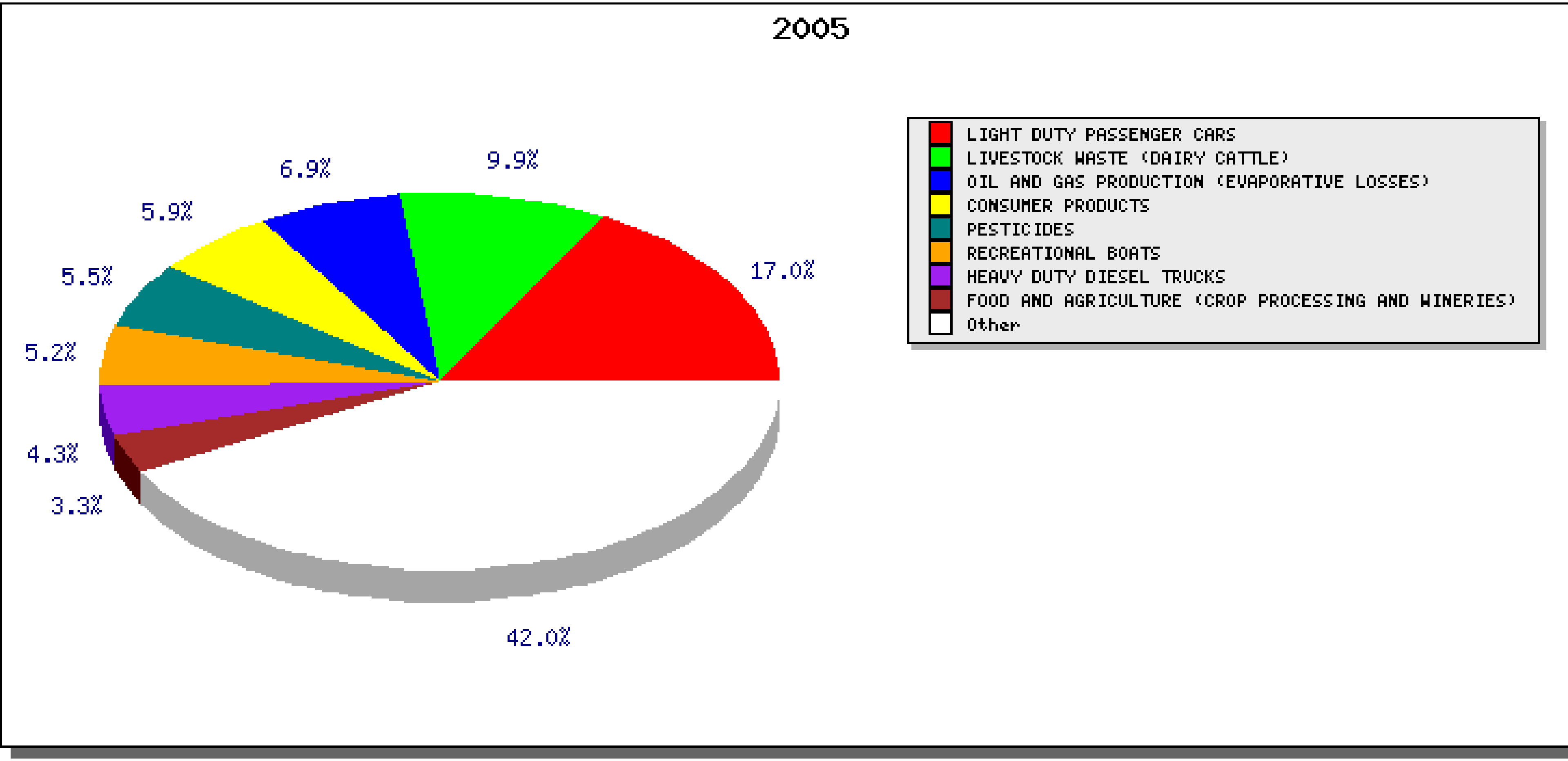


Rankings		Summer	2005		2010	
2005	2010	Source Category	ROG (tpd)	% of Total	ROG (tpd)	% of Total
1	1	LIGHT DUTY PASSENGER CARS	237.15	30.5%	142.82	23.5%
2	2	CONSUMER PRODUCTS	99.68	12.8%	102.57	16.9%
3	3	RECREATIONAL BOATS	65.56	8.4%	57	9.4%
4	4	OFF-ROAD EQUIPMENT (LAWN AND GARDEN)	54.93	7.1%	45.27	7.5%
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%
-	-	**Total**	777.59	100%	606.82	100%

Note: Natural Sources not included

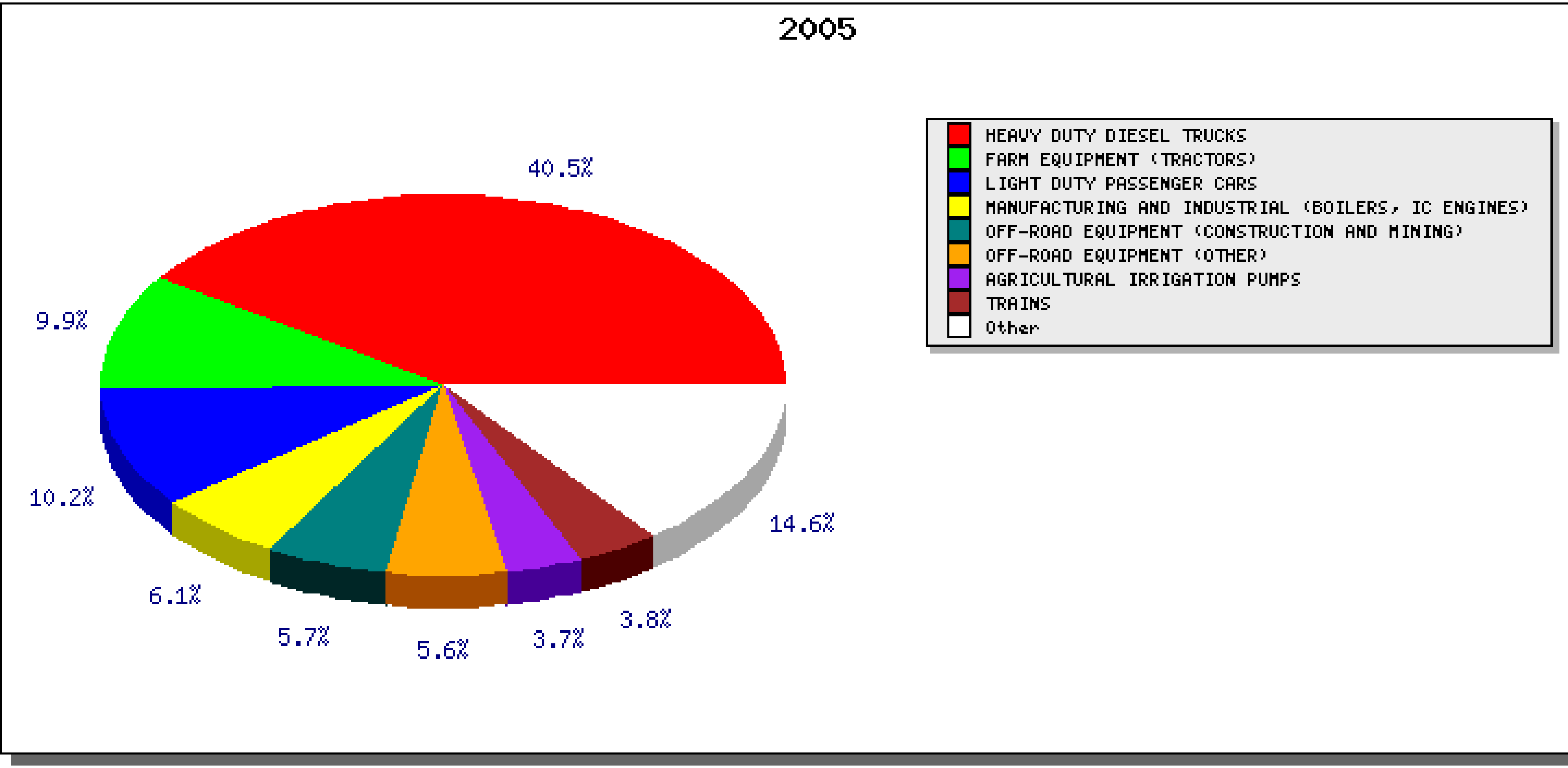
Data Source: 2007 Almanac published by the California Air Resources Board.

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



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, <u>Ozone Formation Potential</u>

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

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

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.

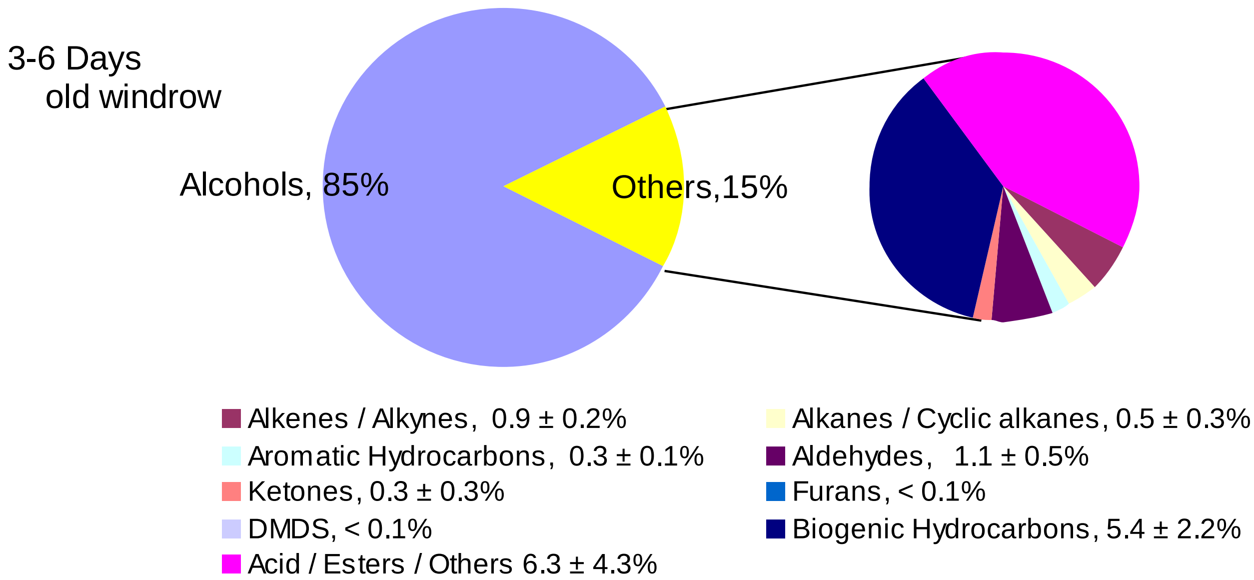
What VOCs come from where?

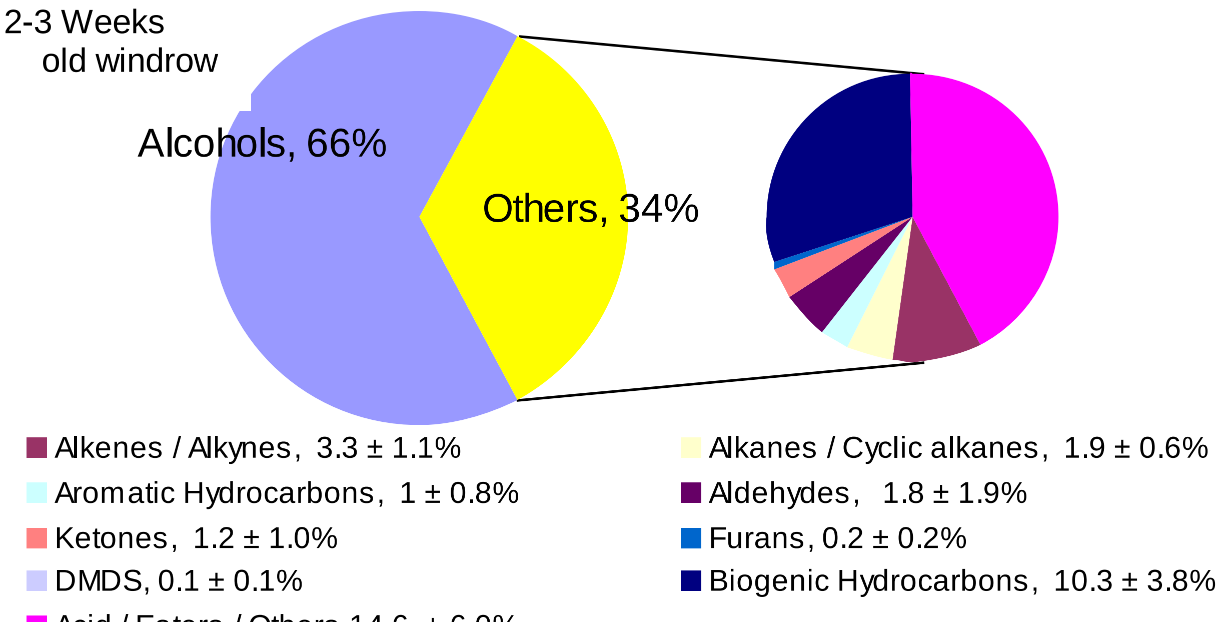
Microbial fermentation:
wood input leads to wood alcohol
(low subsequent reactivity)

Internal combustion engines:
leads to aromatics and aldehydes
(high subsequent reactivity)

VOCs found from compost

Propane	2 Pinen-3 one	Acetone
Butane	Thujen-2-one (Umbellulone)	2 Butanone
Pentane & isomers	Verbenone	2 Pentanone
3 Methyl hexane	trans-Verbenol	3 Pentanone
Dimethyl hexane isomer	Linalool	3,3 Dimethyl 2-butanone
Trimethyl hexane	Eucalyptol	Methyl isobutylketone (MIBK)
Epoxy cyclooctane	Terpineol	3 Pentene 2-one
≥ C7 straight and cyclic HC	Borneol	3 Methyl 2-pentanone
	Allylanisole	2 Hexanone
Propene	Safrol (1,3-Benzodioxole, 5-(2-propenyl))	Methyl hexanone isomers
2 Methyl 1-propene		Octanone
Butene & isomers	Formaldehyde	Nonanone
2 Methyl1,3-butadiene(Isoprene)	Acetaldehyde	2 Butanedione (Diacetyl)
2 Methyl 3-butene 2-ol	Propionaldehyde	1 Hydroxy 2-propanone
2 Methyl 1,3 pentadiene	Crotonaldehyde (2-Butenal)	3 Hydroxy 2-butanone
2,4-Heptadienal	Butyraldehyde	Methyl phenylethanone
Acetyl cyclomethylpentene	Isovaleraldhyde	
2 Ethyl 3-hexen 1-ol	Valeraldehyde	Methyl acetate
Methyl hexyne	2 Methyl pentenal	Ethyl acetate
Methyl cycloheptene	Hexanal	Propyl acetate
Acetyl methylcyclohexene	Hexenal	Isoamyl acetate
Other alkenes	Heptanal	Methyl butylacetate
	Heptenal	Bornyl acetate
Benzene	Octanal	Methyl isobutanoate
Toluene	Nonanal	Methyl butanoate
Xylene isomers	Decanal	Methyl isopentanoate
Styrene	Dimethyl octenal	Ethyl butanoate
C-3 Benzene isomers	Benzaldehyde	Methyl pentanoate
C-4 Benzene isomers		Propyl butanoate
Isopropenyl toluene	Furan	Methyl hexanoate
4 Methyl benzenemethanol	3 Methyl furan	Butyl butanoate
Naphthlene	2 Methyl furan	Isomer of butylbutanoate
Dichlorobenzene isomers	2,5 Dimethyl furan	Heptyl hexanoate
Trichlorobenzene isomers	2 Ethyl 5-methyl furan	Other ester
	2 Butyl furan	
α-Pinene	2 Pentyl furan	Acetic acid
β-Pinene	Methyl hexanone isomers	Propionic acid
4 Carene		Methyl propionic acid
3 Carene	Methanol	Butanoic acid
Camphene	Ethanol	Methyl butanoic acid
Terpinene	2 Propanol	Pentanoic acid
Terpinolene	1 Propanol	Hexanoic acid
Limonene	2 Butanol	Acetyl benzoic acid
Adamantane	1 Butanol	
α- Phellandrene	2 Methyl 1-butanol & isomer	Dimethyl disulfide
β- Phellandrene	Pentanol	
L-Fenchone	Hexanol	Methylthymyl ether
Copaene	2,3 Butanediol	Dichlorodifluoro methane
Camphor	Pentanol	Chloro difluoro methane
cis-Linalool oxide	Hexanol	Trichloromonofluoromethane
trans-Linalool oxide	2,3 Butanediol	


3-6 Days
old windrow
Alcohols, 85%
Others,15%
Alkenes / Alkynes, 0.9 ± 0.2%
Alkanes / Cyclic alkanes, 0.5 ± 0.3%
Aromatic Hydrocarbons, 0.3 ± 0.1%
Aldehydes, 1.1 ± 0.5%
Ketones, 0.3 ± 0.3%
Furans, < 0.1%
DMDS, < 0.1%
Biogenic Hydrocarbons, 5.4 ± 2.2%
Acid / Esters / Others 6.3 ± 4.3%


2-3 Weeks
old windrow
Alcohols, 66%
Others, 34%
Alkenes / Alkynes, 3.3 ± 1.1%
Alkanes / Cyclic alkanes, 1.9 ± 0.6%
Aromatic Hydrocarbons, 1 ± 0.8%
Aldehydes, 1.8 ± 1.9%
Ketones, 1.2 ± 1.0%
Furans, 0.2 ± 0.2%
DMDS, 0.1 ± 0.1%
Biogenic Hydrocarbons, 10.3 ± 3.8%
Acid / Esters / Others 14.6 ± 6.0%

From our recently accepted paper in Atmos. Environment.

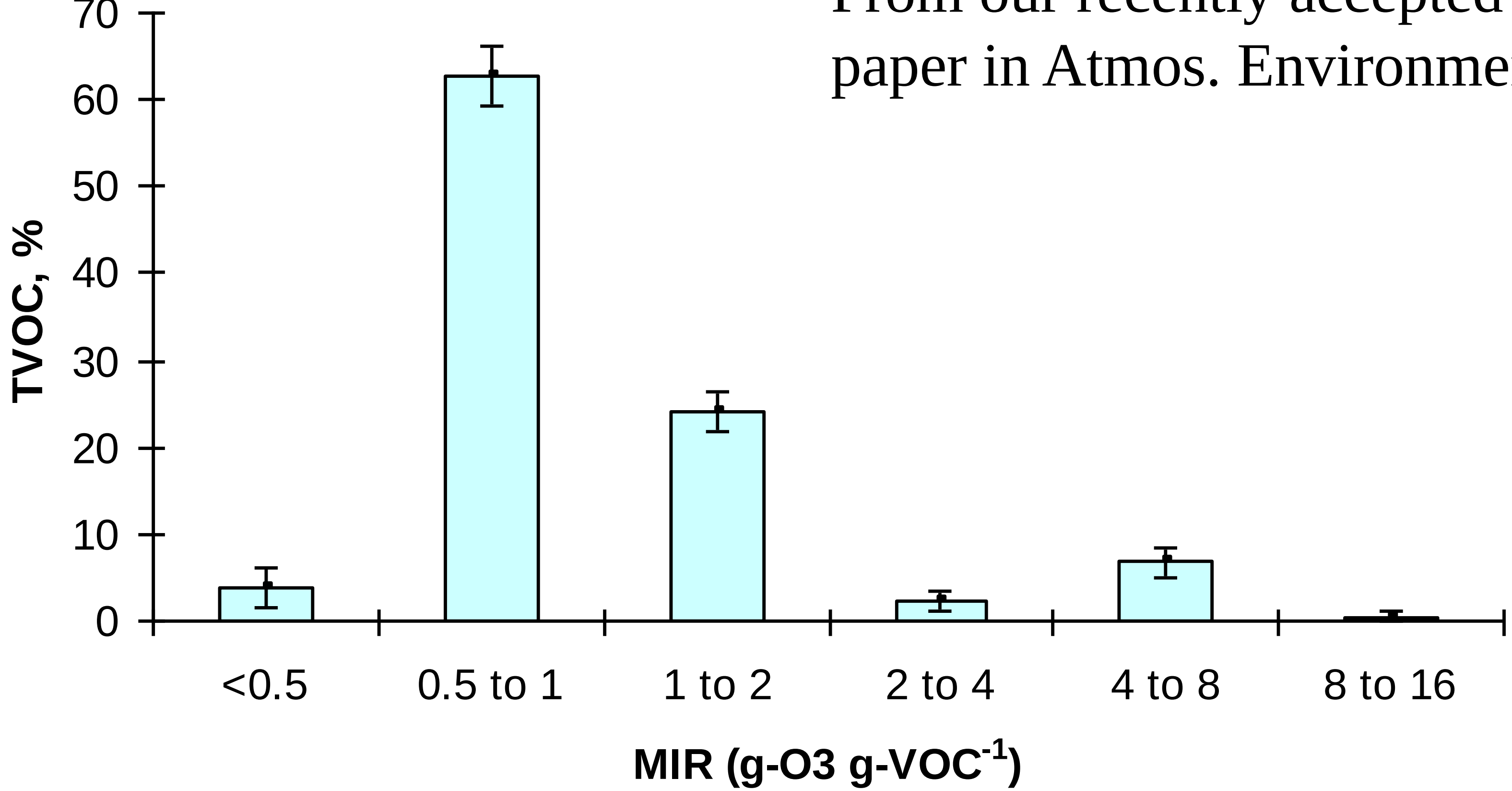
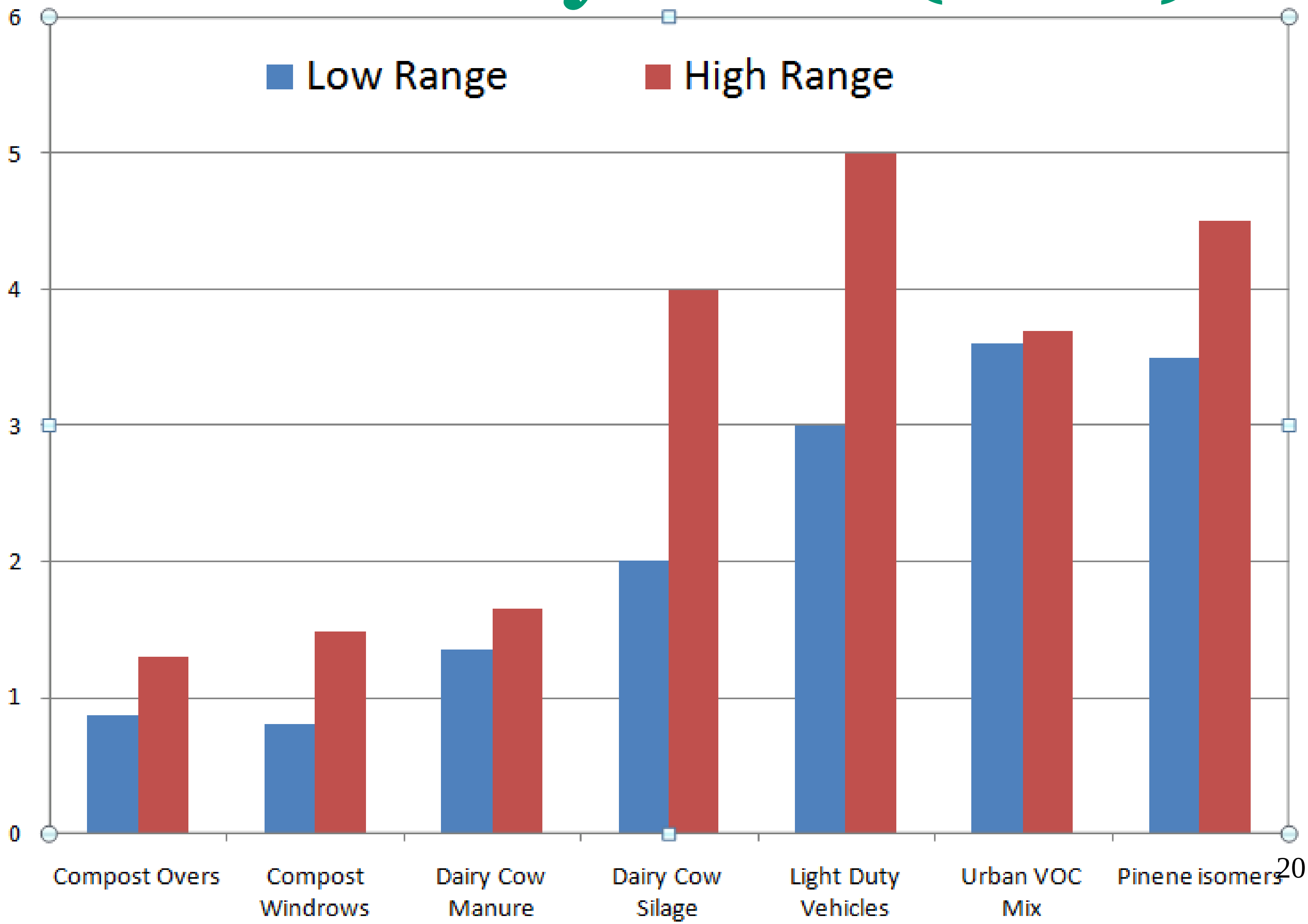


Figure 3. Average contribution of VOC into the ozone formation according to their reactivity.
(Urban VOC average is 3.6 to 3.7, depending on latest model revisions.)

Maximum Incremental Reactivity scale (MIR)



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.

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 NOx and/or GHGs
- 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

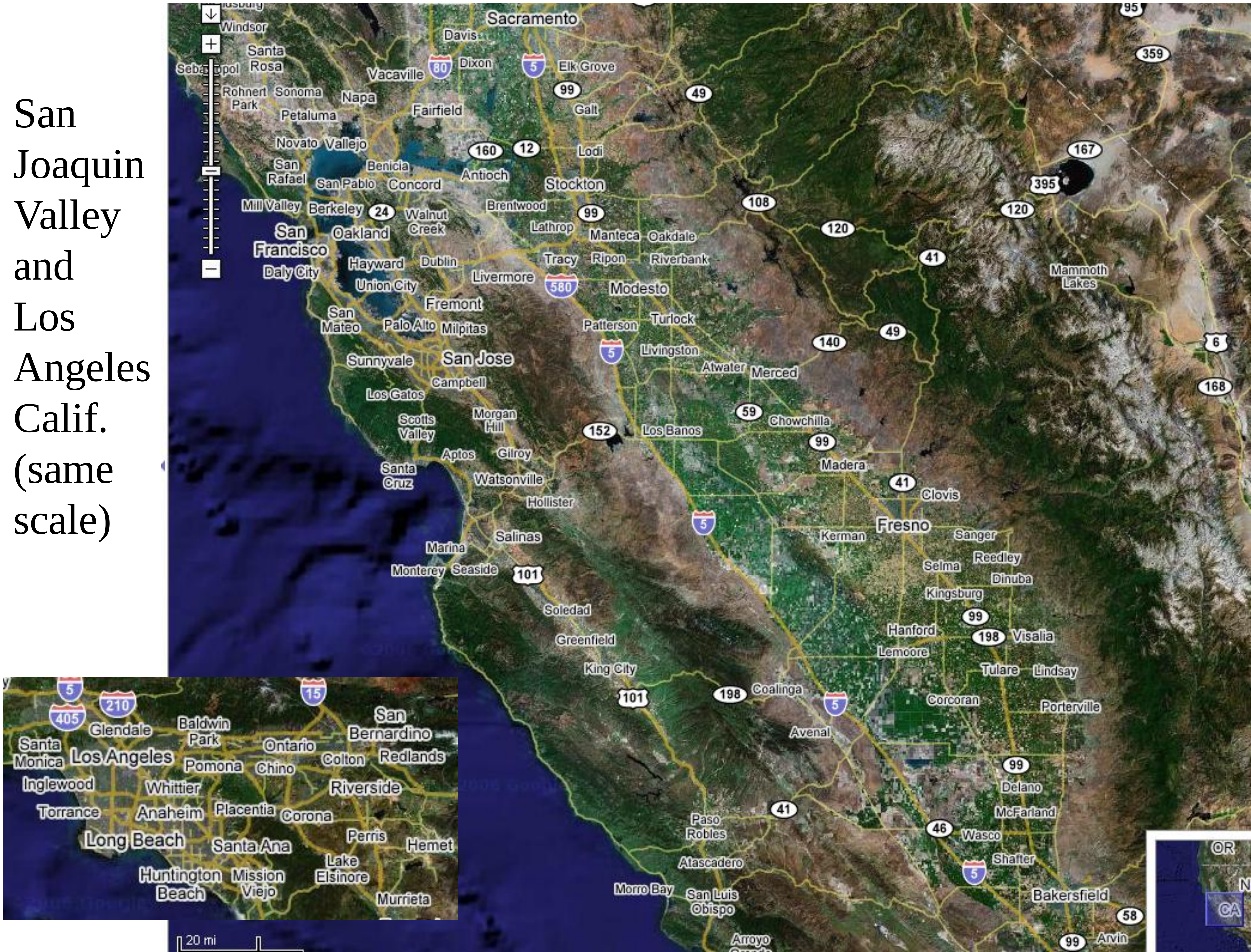
The use of a cap of oversized material (from sieving previously finished compost) may reduce OFP from VOCs by 10% to 40%.

This could be a very 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.

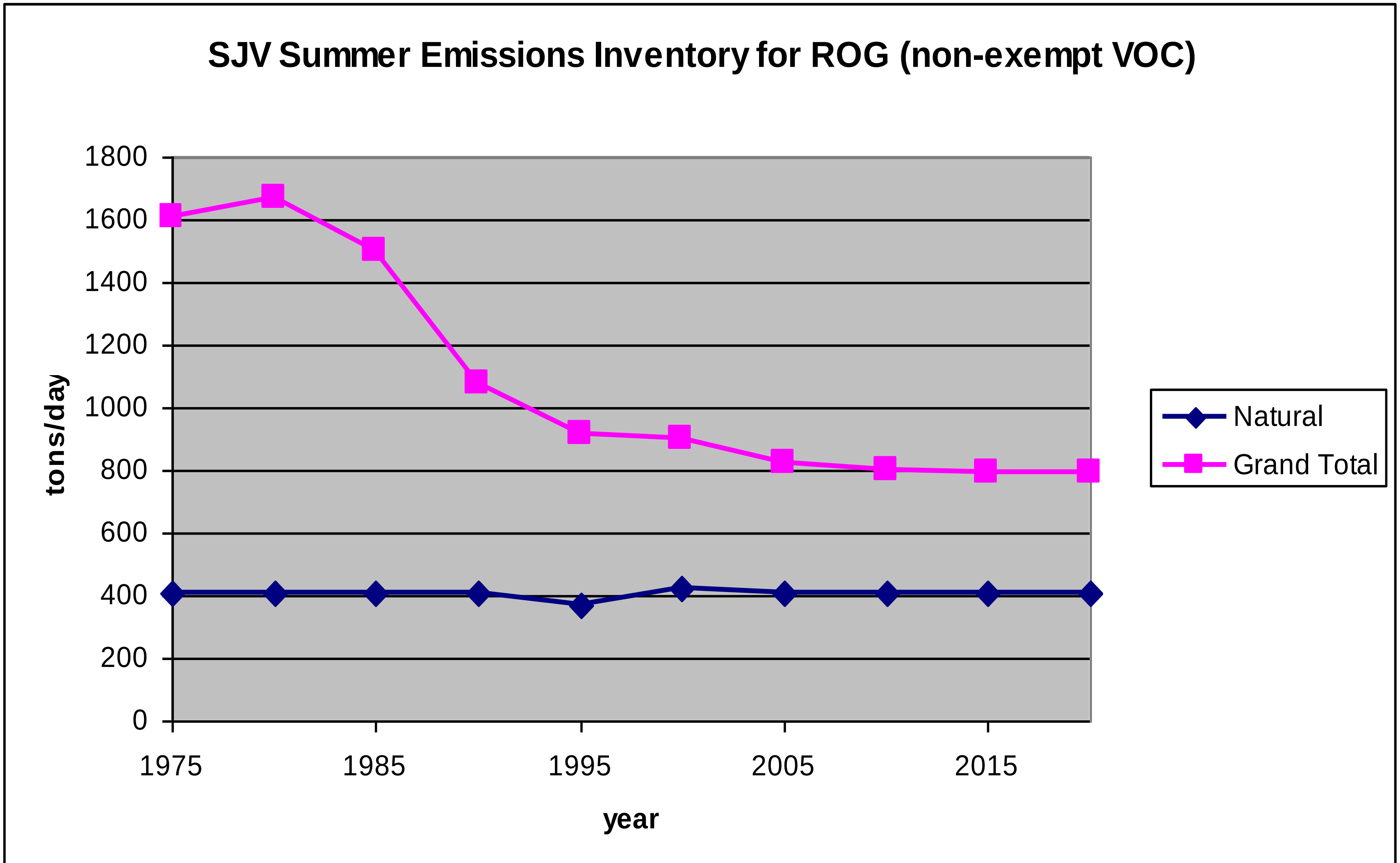
Biosolids co-composting generally shows similar VOCs, with minor differences not significantly affecting ozone formation.

Thank you, and questions?

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



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



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