Compost Volatile Organic Compounds and Ozone Formation

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Current funding from CASA, and (finishing) from CalRecycle. Also last year 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 -- 5 papers published (plus 2 under revision and 1 in preparation.)
  - 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, long-term

Field Team and Mobile Ozone Chamber Apparatus for VOC-to-ozone studies

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

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),

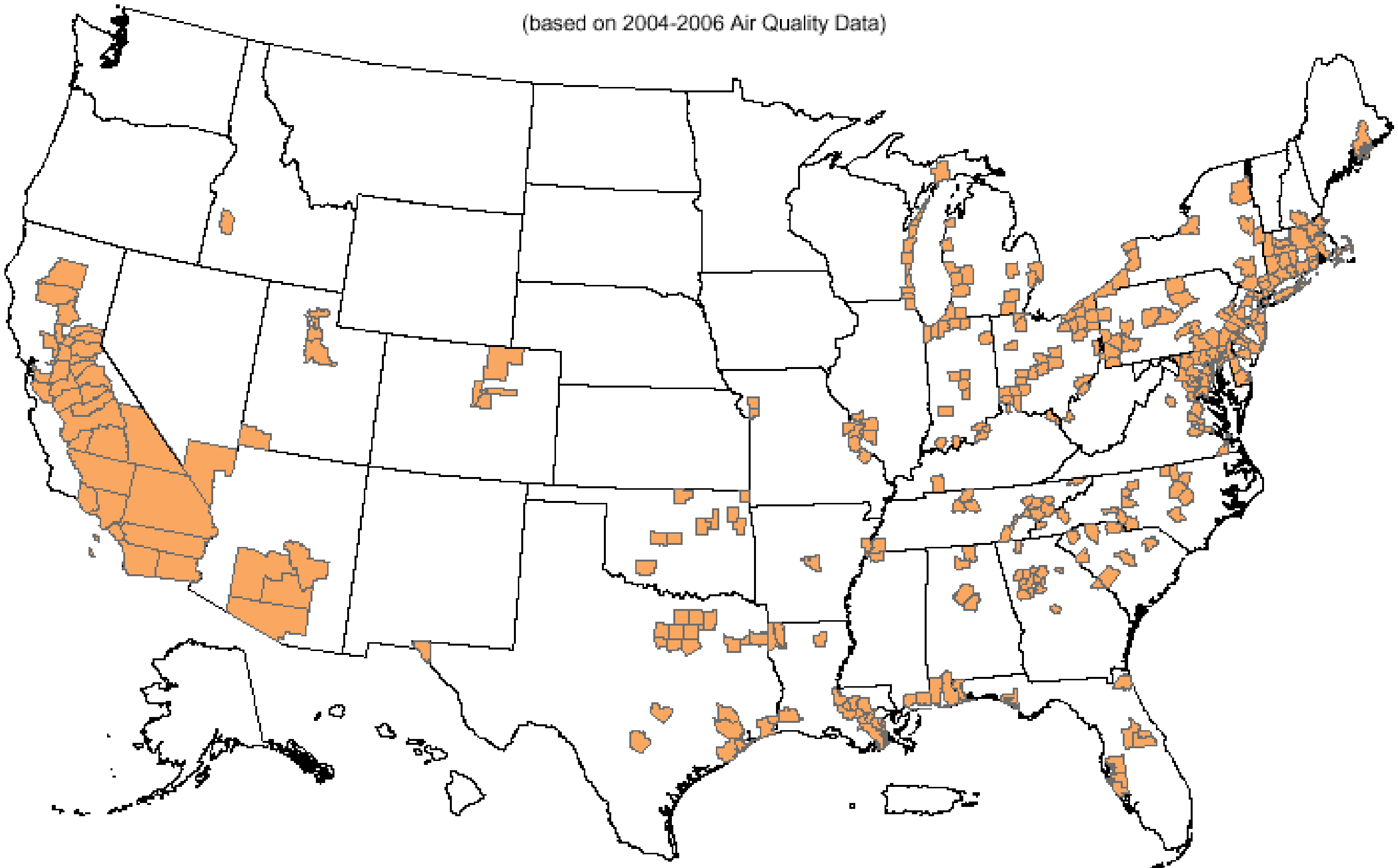
and volatile organic compounds (VOCs)

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)

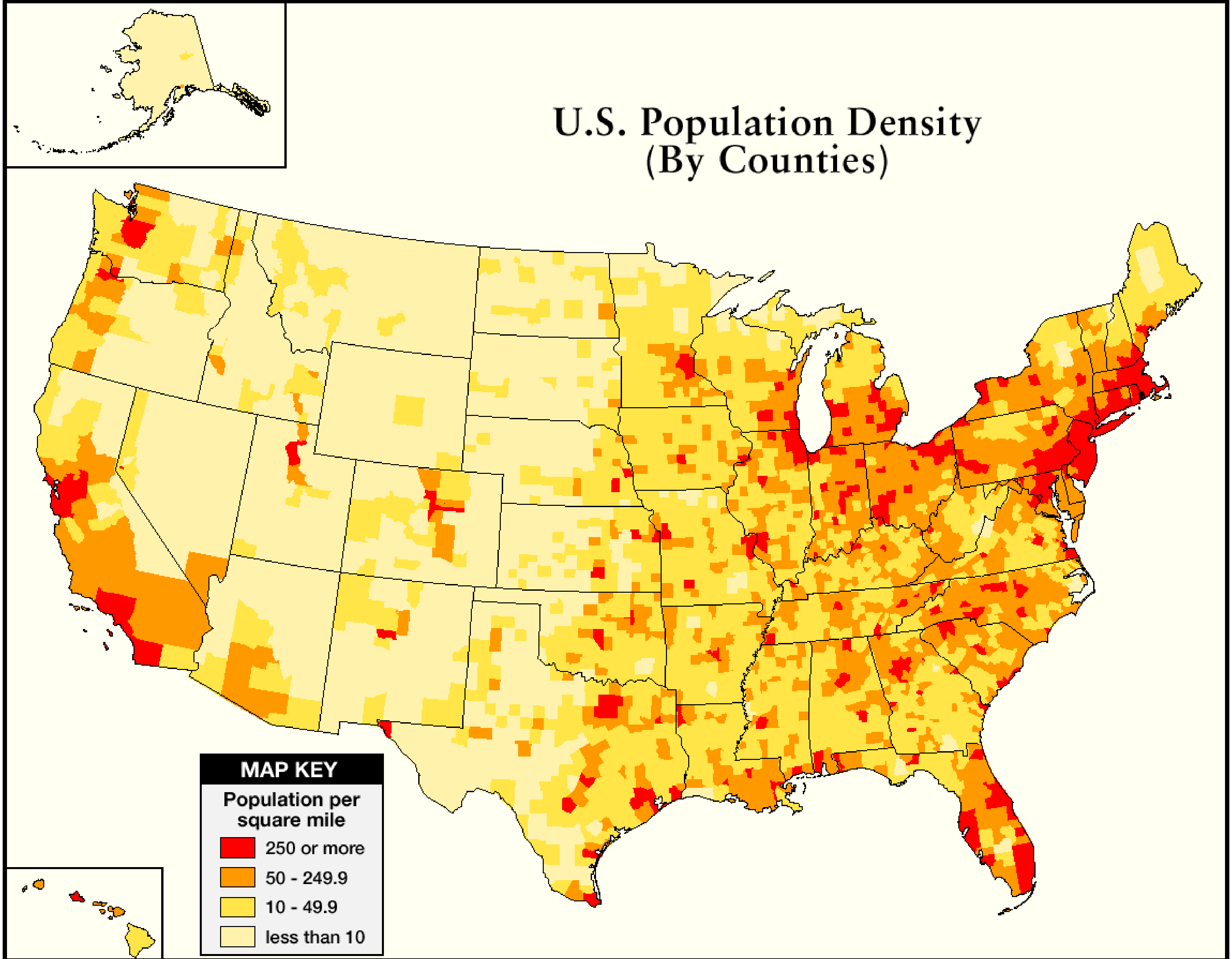
(based on 2004-2006 Air Quality Data)



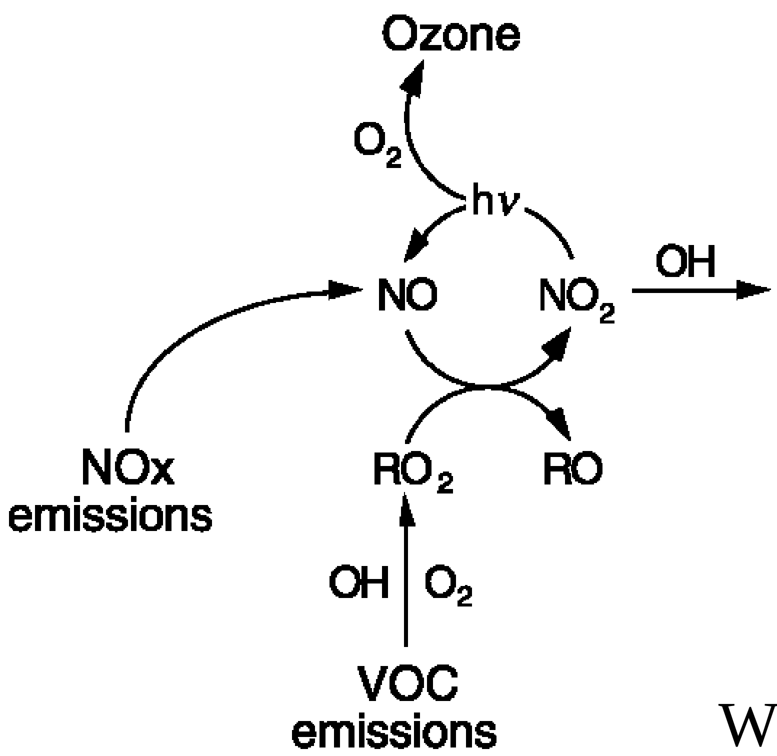
Notes:

[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:



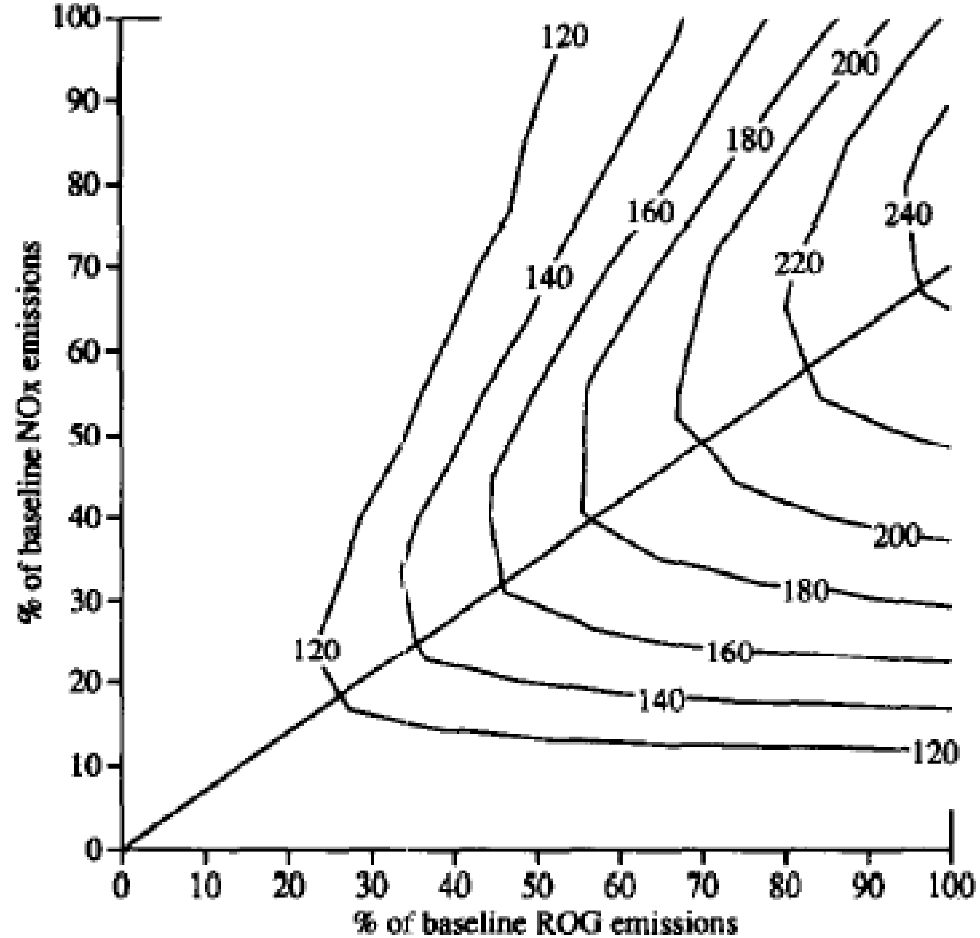
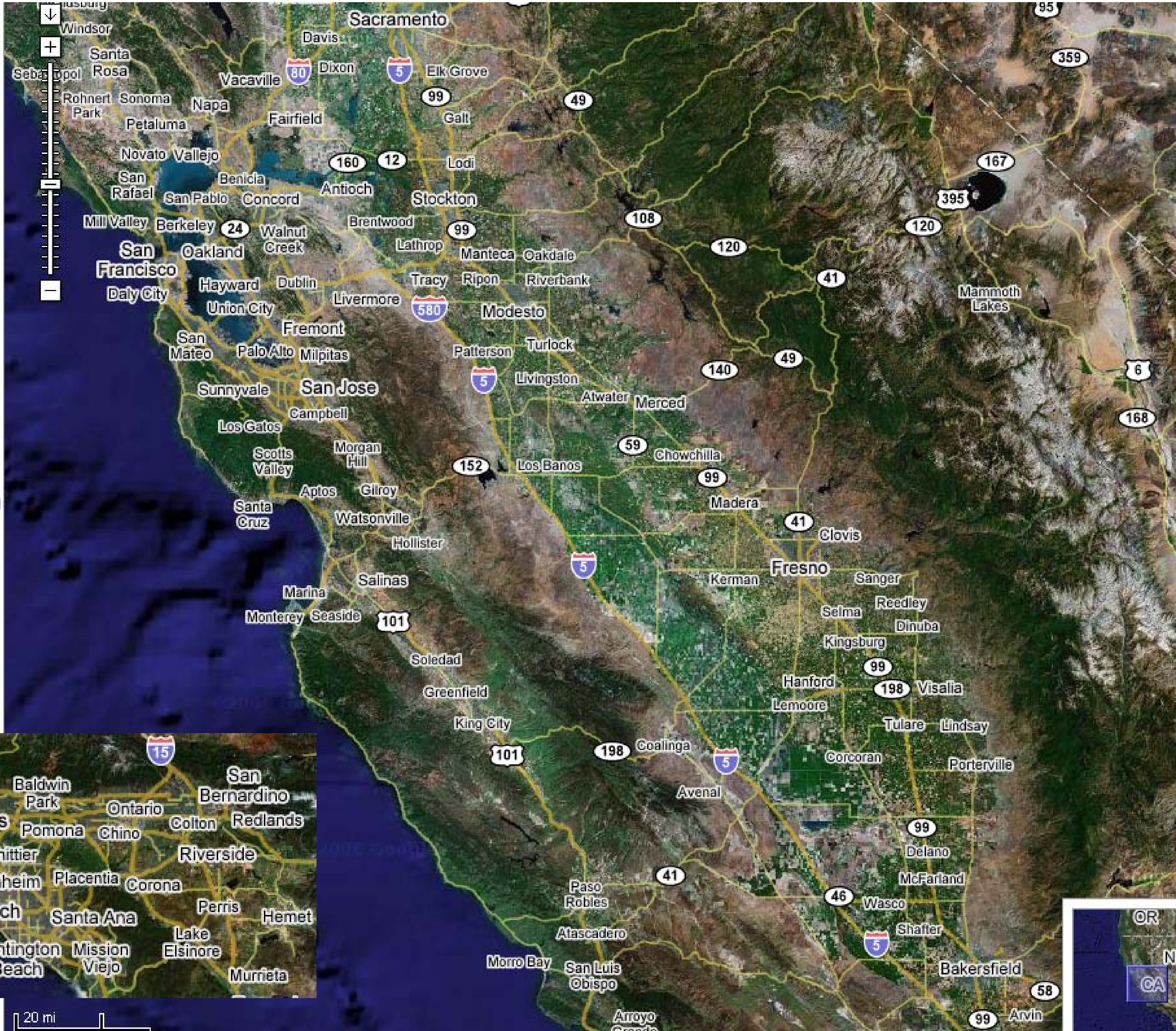


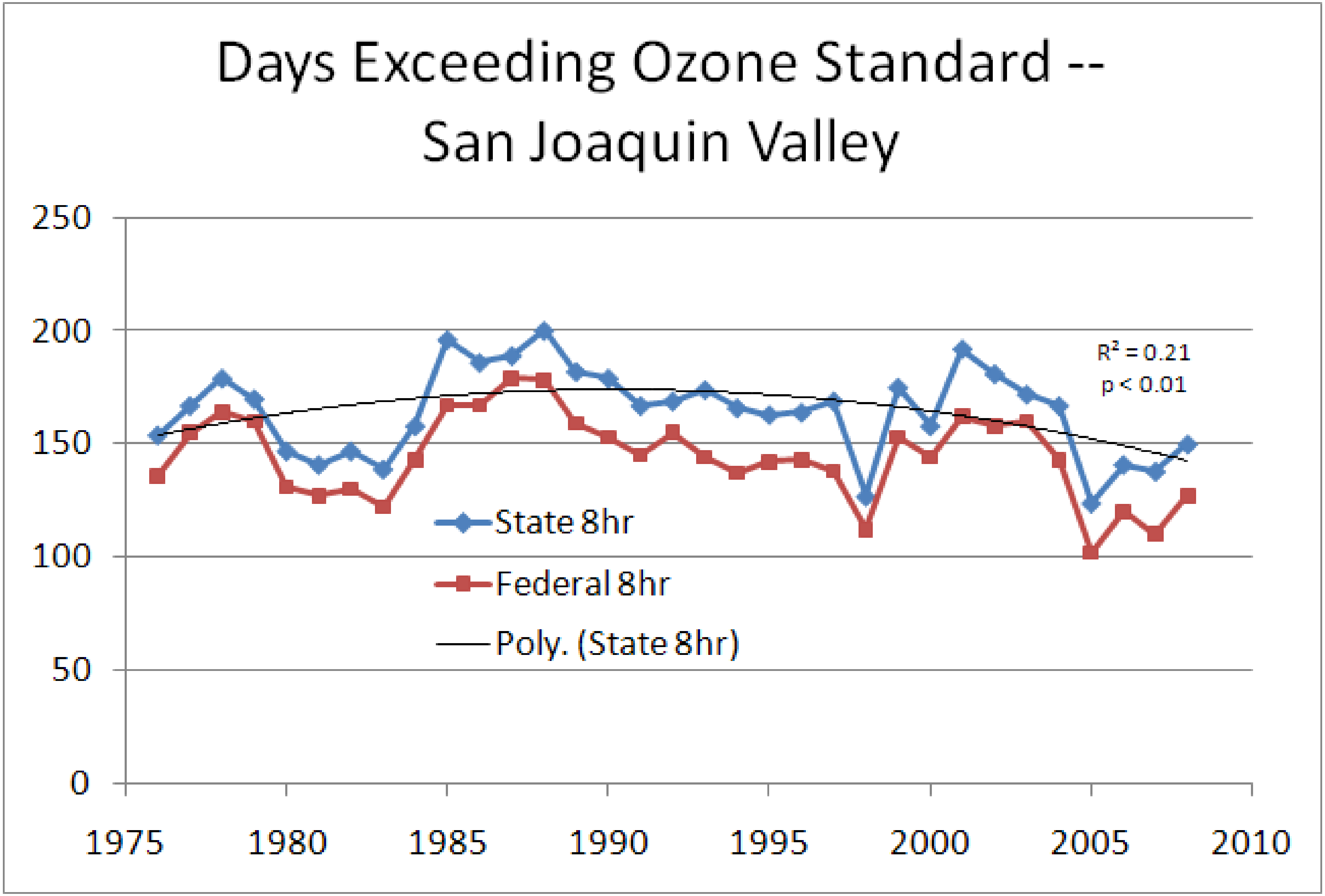
Fig. 1. Ozone isopleth diagram showing the hypothetical response of peak 1 h average ozone concentrations within an air basin to changed levels of anthropogenic ROG and NO_x emissions. Contour lines are lines of constant ozone concentration (ppb).

Winner, Cass and Harley, Atmos. Env. 1995

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



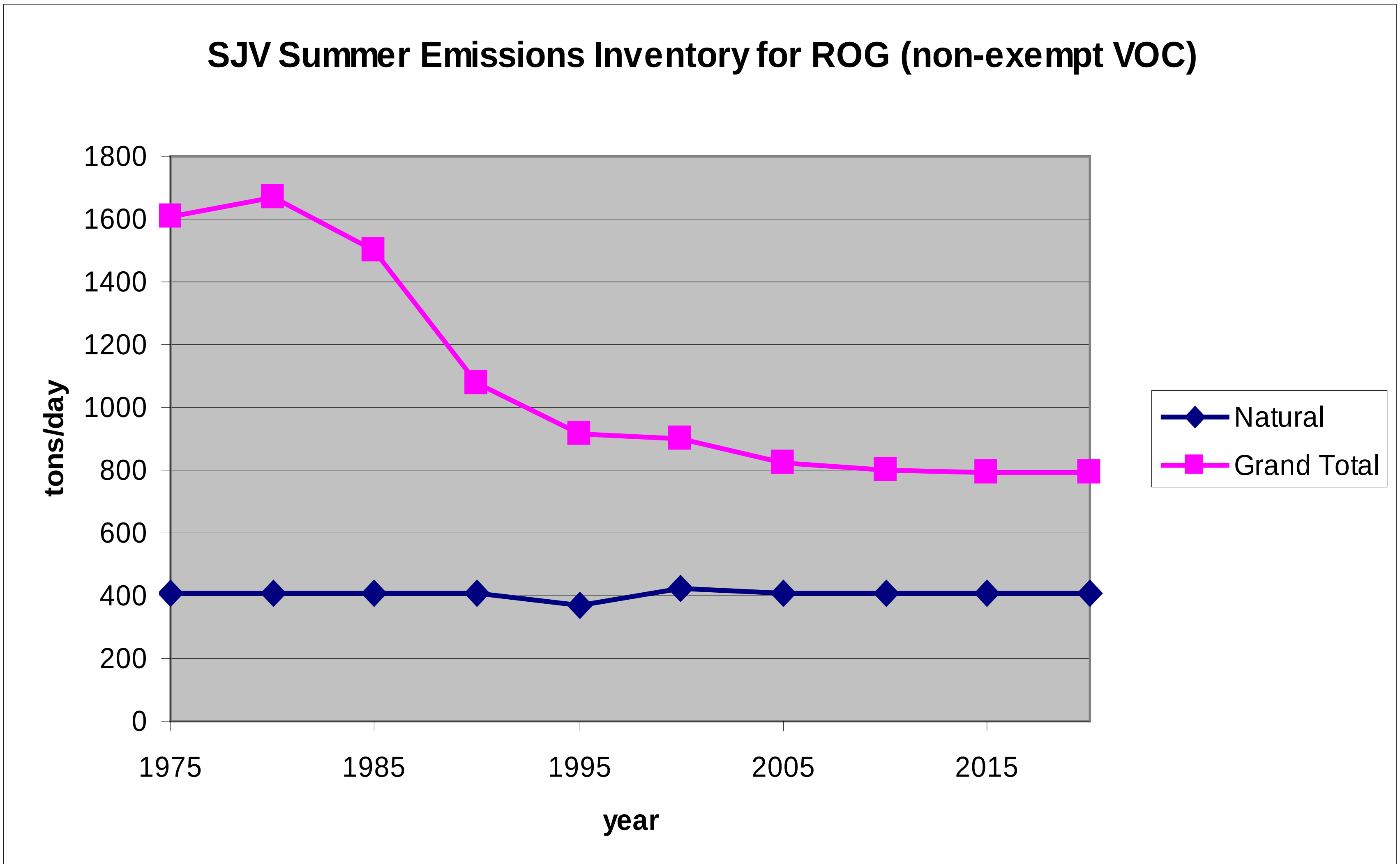
Ground-level ozone improving, but slowly



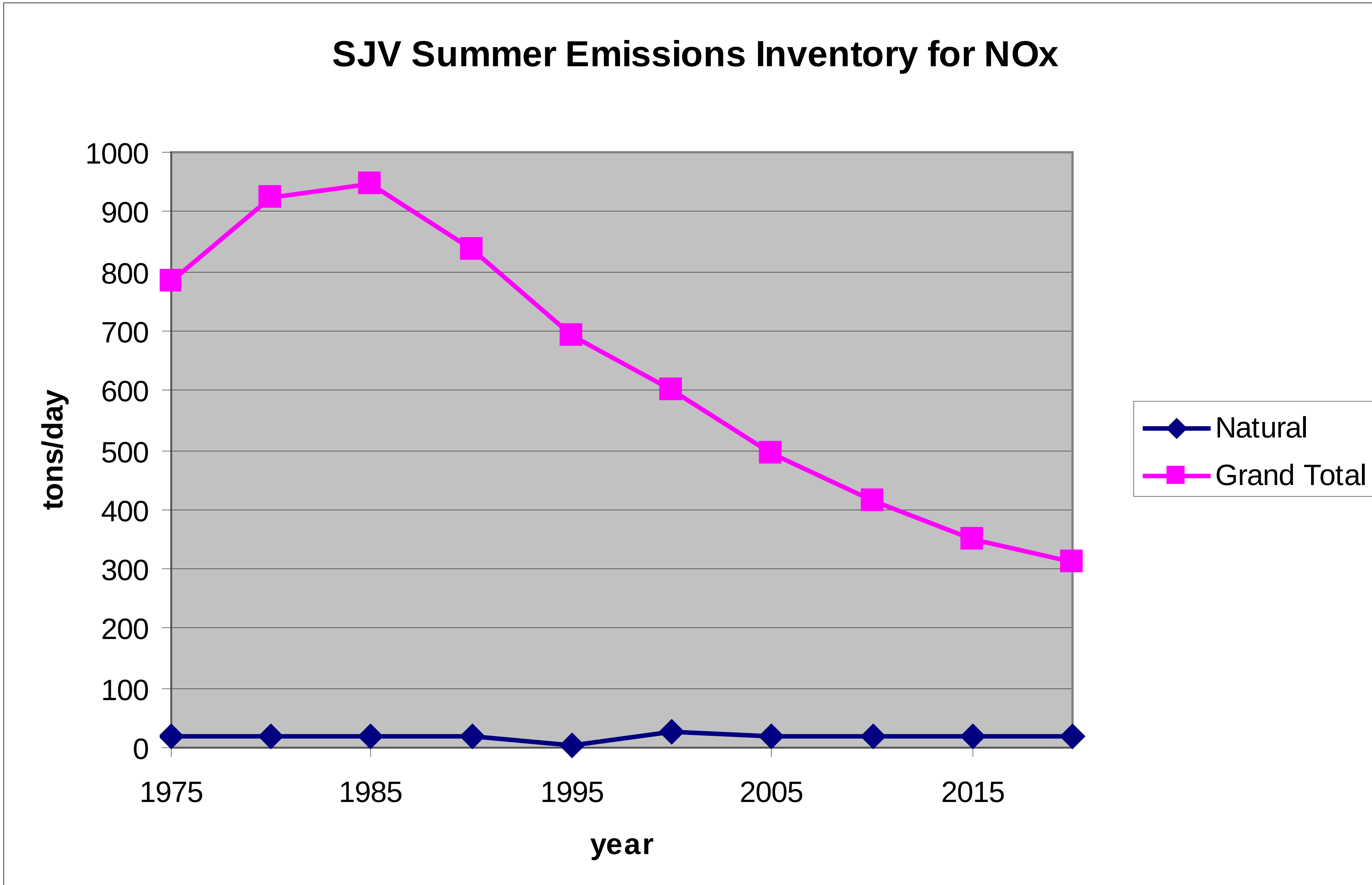
California's efforts so far:

- 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

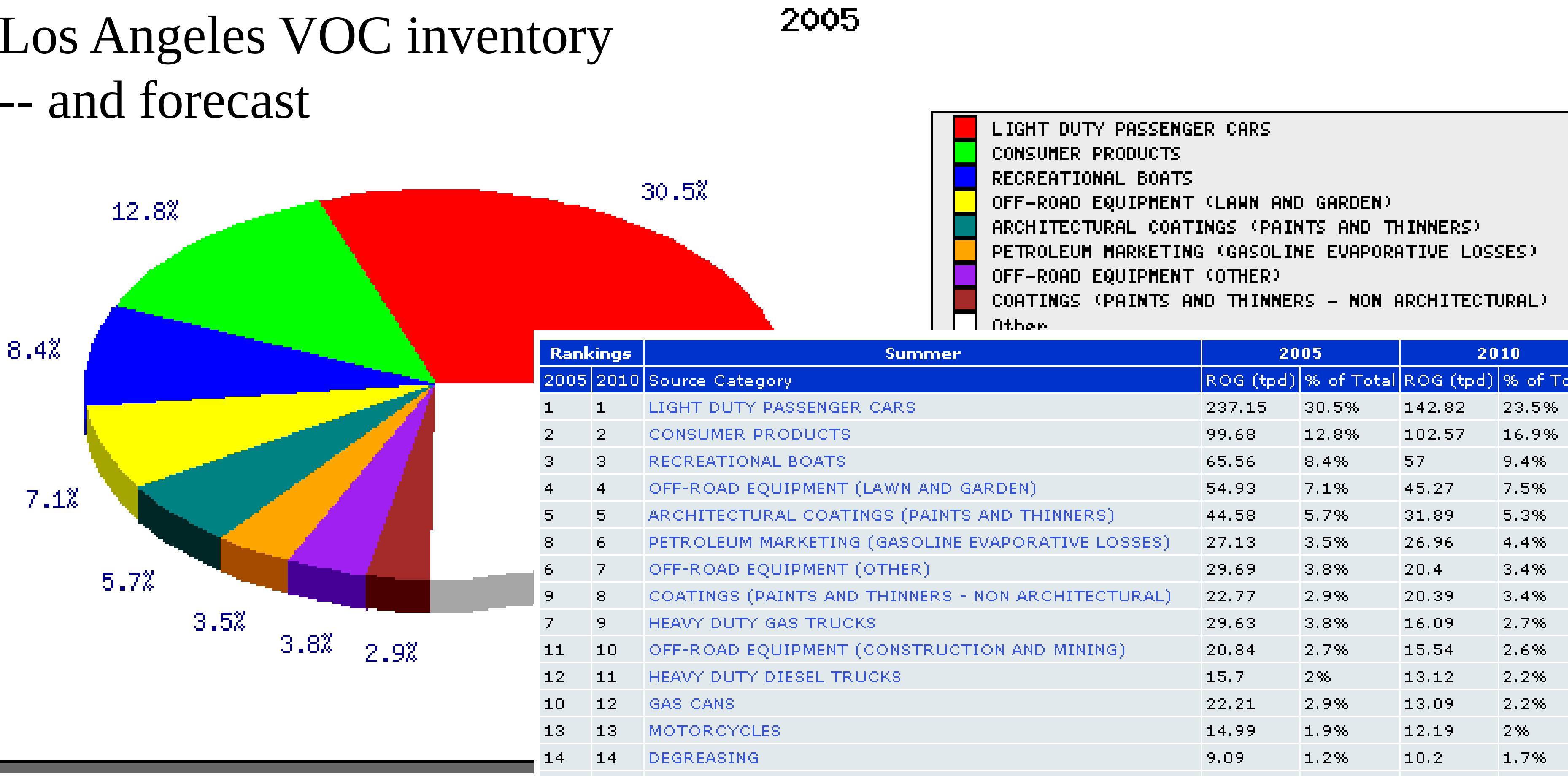
Total Reactive Organic Gases (non-exempt VOCs) have actually been quite greatly reduced.



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



Los Angeles VOC inventory -- and forecast

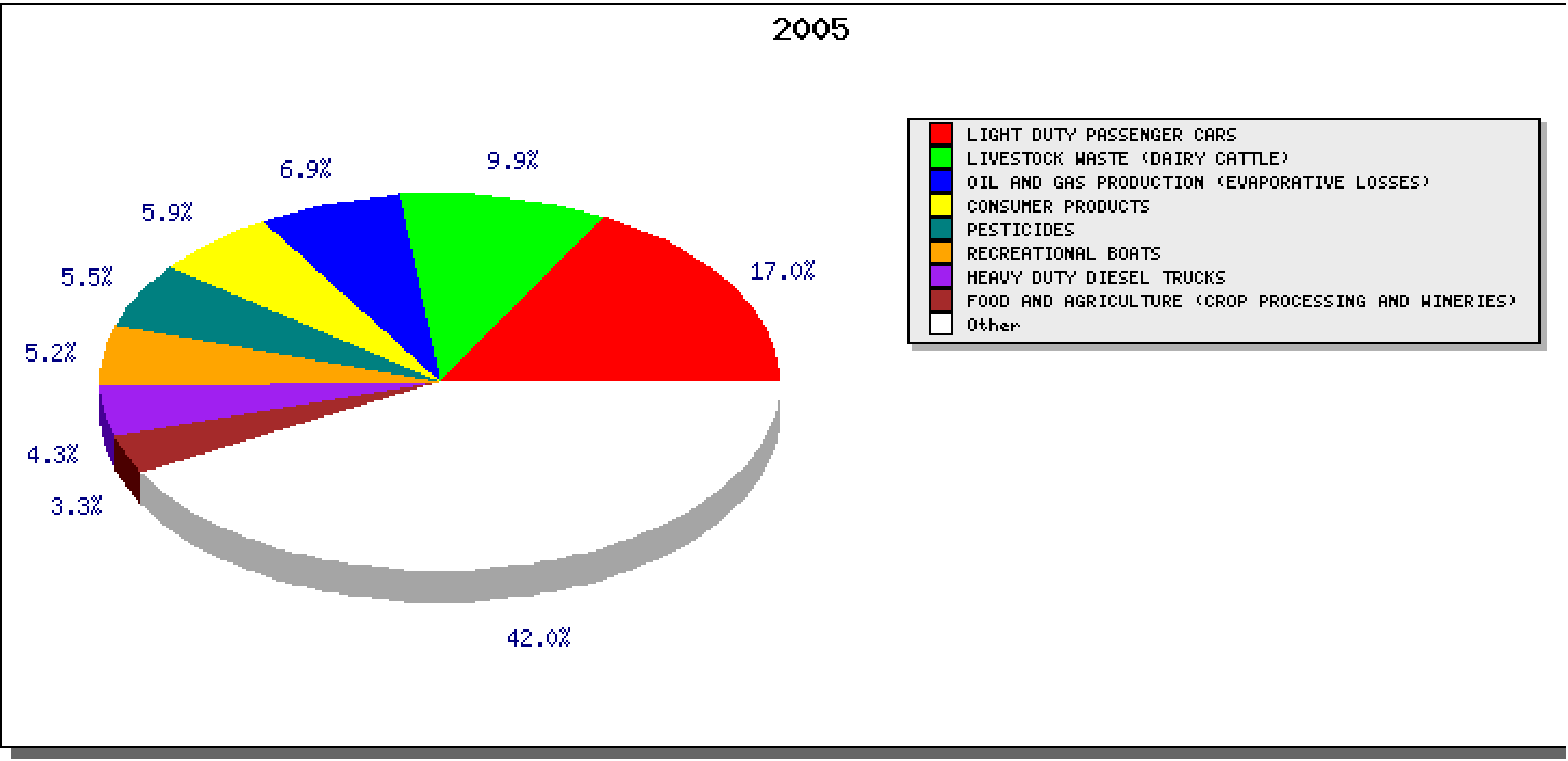


Rankings		Summer	2005		2010	
2005	2010	Source Category	ROG (tpd)	% of Total	ROG (tpd)	% of Total
1	1	LIGHT DUTY PASSENGER CARS	237.15	30.5%	142.82	23.5%
2	2	CONSUMER PRODUCTS	99.68	12.8%	102.57	16.9%
3	3	RECREATIONAL BOATS	65.56	8.4%	57	9.4%
4	4	OFF-ROAD EQUIPMENT (LAWN AND GARDEN)	54.93	7.1%	45.27	7.5%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

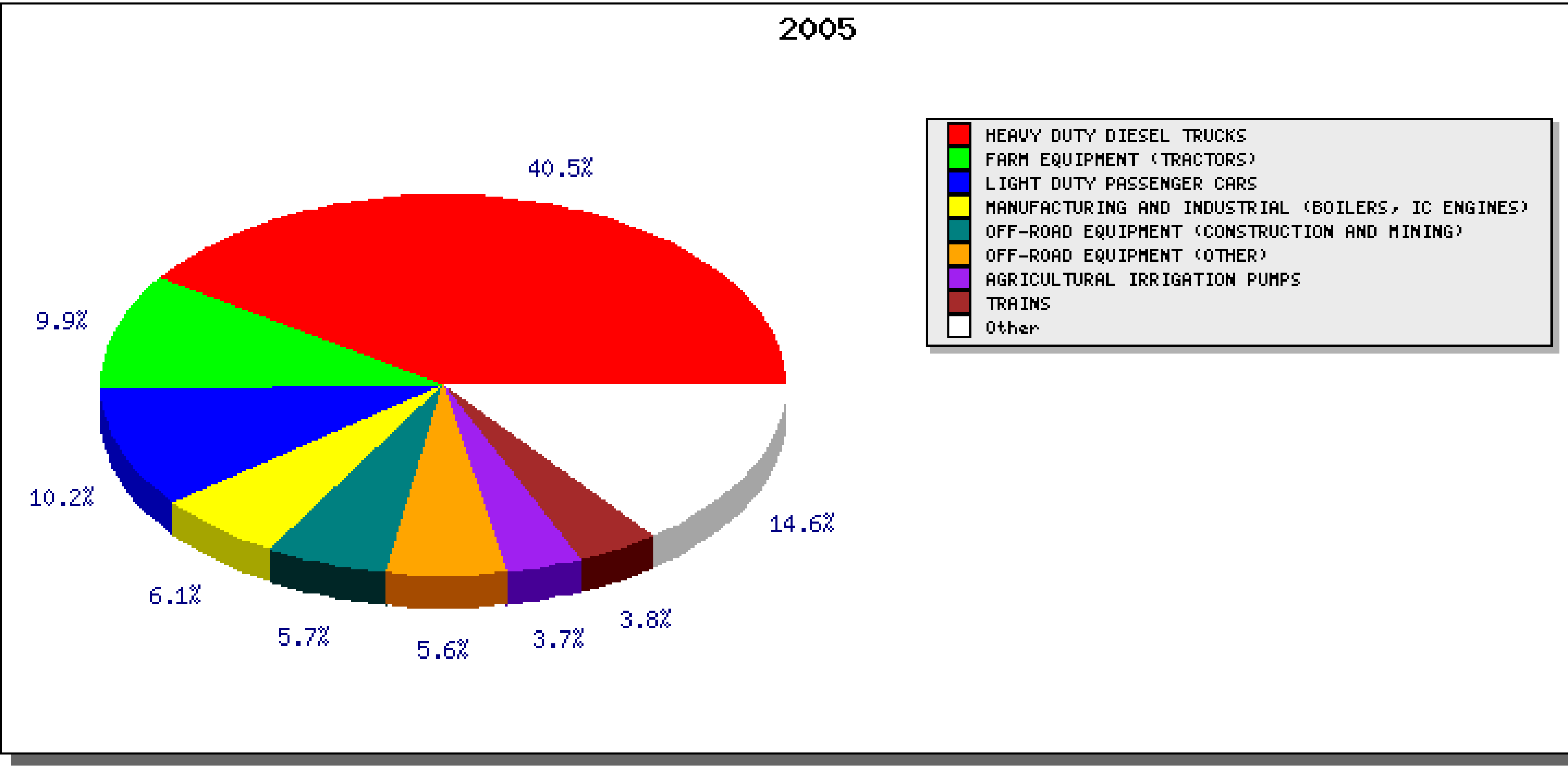
Data Source: 2007 Almanac published by the California Air Resources Board.

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>

<u>Great variation</u> 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.

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
Isovaleraldhyde
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

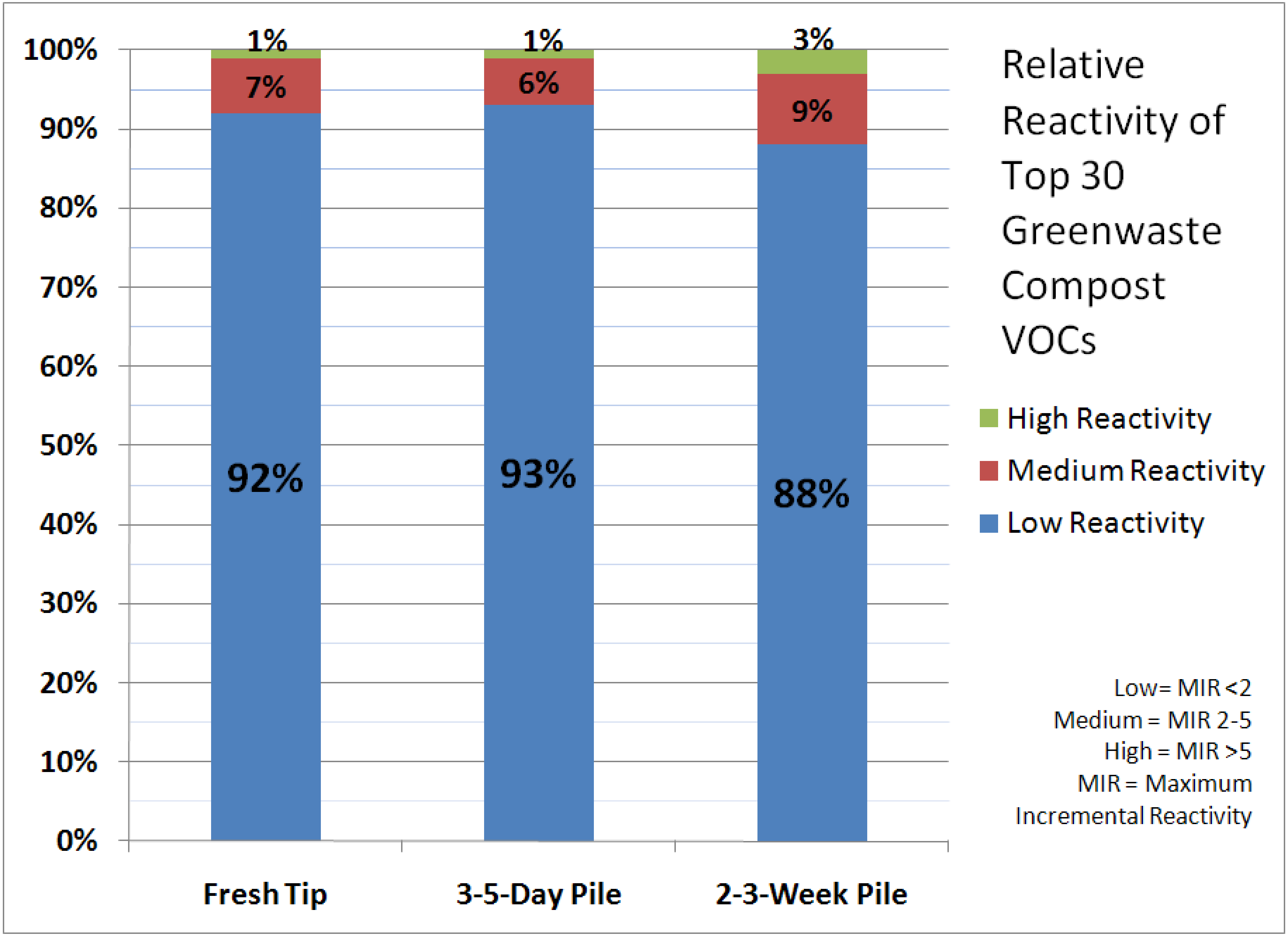
Acetone
2 Butanone
2 Pentanone
3 Pentanone
3,3 Dimethyl 2-butanone
Methyl isobutylketone (MIBK)
3 Pentene 2-one
3 Methyl 2-pentanone
2 Hexanone
Methyl hexanone isomers
Octanone
Nonanone
2 Butanedione (Diacetyl)
1 Hydroxy 2-propanone
3 Hydroxy 2-butanone
Methyl phenylethanone

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



Relative Reactivity of Top 30 Greenwaste Compost VOCs
High Reactivity
Medium Reactivity
Low Reactivity
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Fresh Tip
3-5-Day Pile
2-3-Week Pile
1%
7%
92%
1%
6%
93%
3%
9%
88%
Low= MIR <2
Medium = MIR 2-5
High = MIR >5
MIR = Maximum Incremental 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 than in non-urban
- Future regulations (e.g. state implementation plans) can use reactivity more realistically

Additional Result (Preliminary)

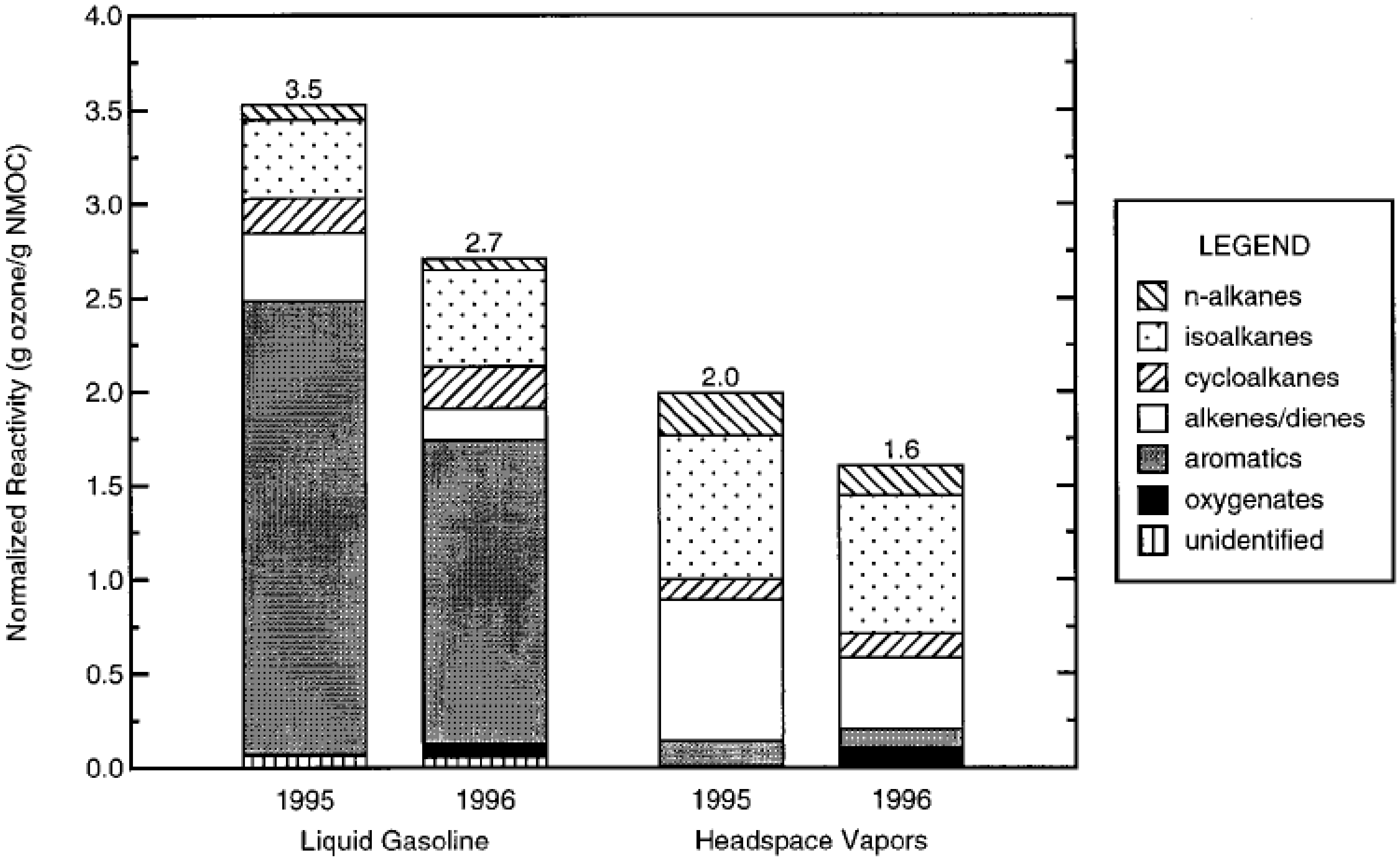
The use of a cap of oversized material (from sieving previously finished compost) may reduce OFP from VOCs by 10% to 40%.

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.

Remember: reducing total pounds of VOCs doesn’t necessarily lead to less ozone – but reducing reactivity-weighted pounds will.

Gasoline reformulation made good use of reactivity

ES&T 1999 Kirchstetter et. al.



Global summer-time ozone. 'Leaf' symbols where damage is visible.

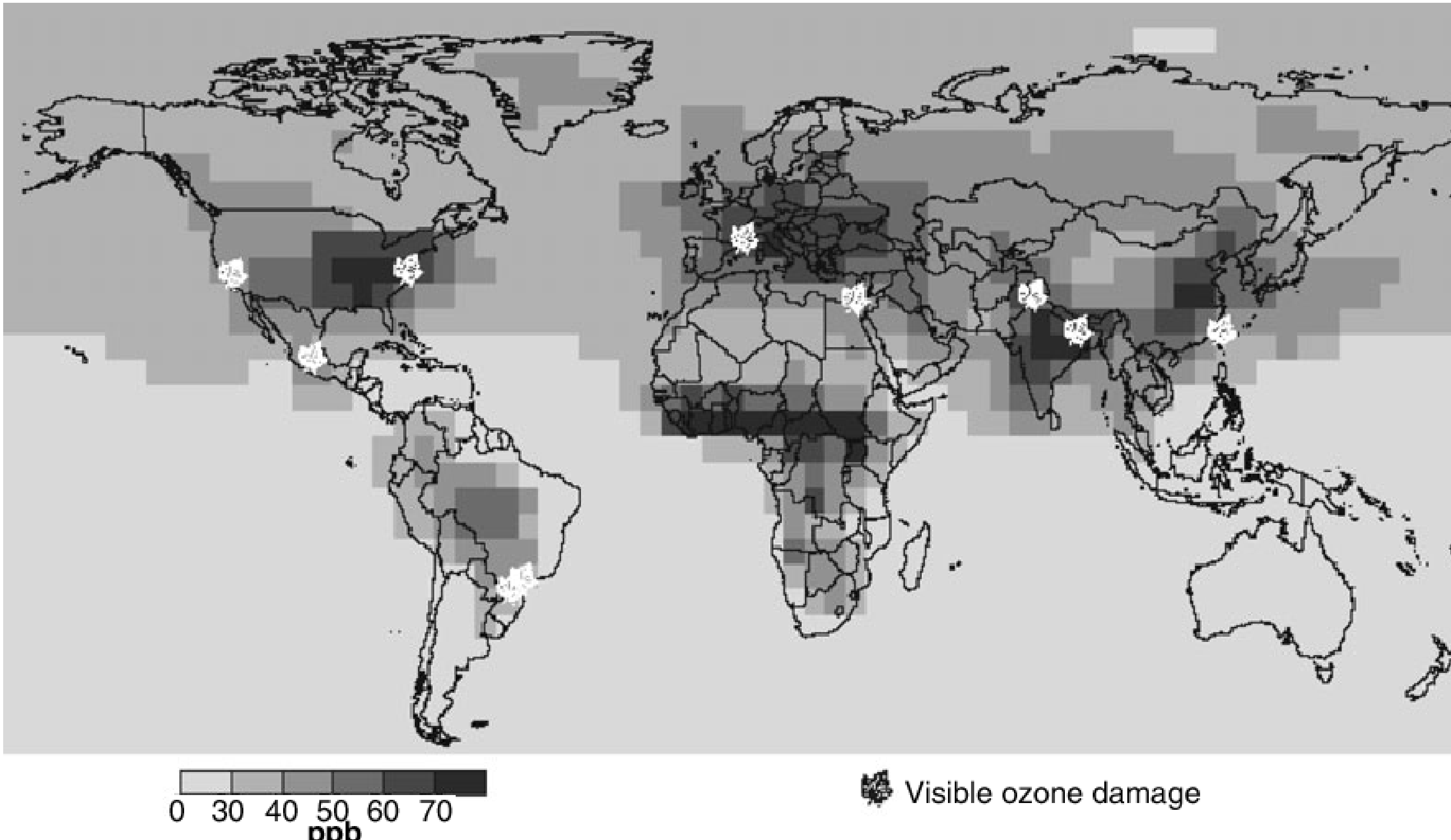


Figure 2. Global distribution of mean maximum growing season ozone concentrations based on 1990 emissions, using the global three-dimensional atmospheric chemistry model of Collins *et al*. (2000). The leaf symbols indicate regions where visible injury or yield reductions caused by ozone have been demonstrated. From Emberson *et al*. (2003).

Plant Cell and Environment, 2005.

Global average ozone: past, present and future.

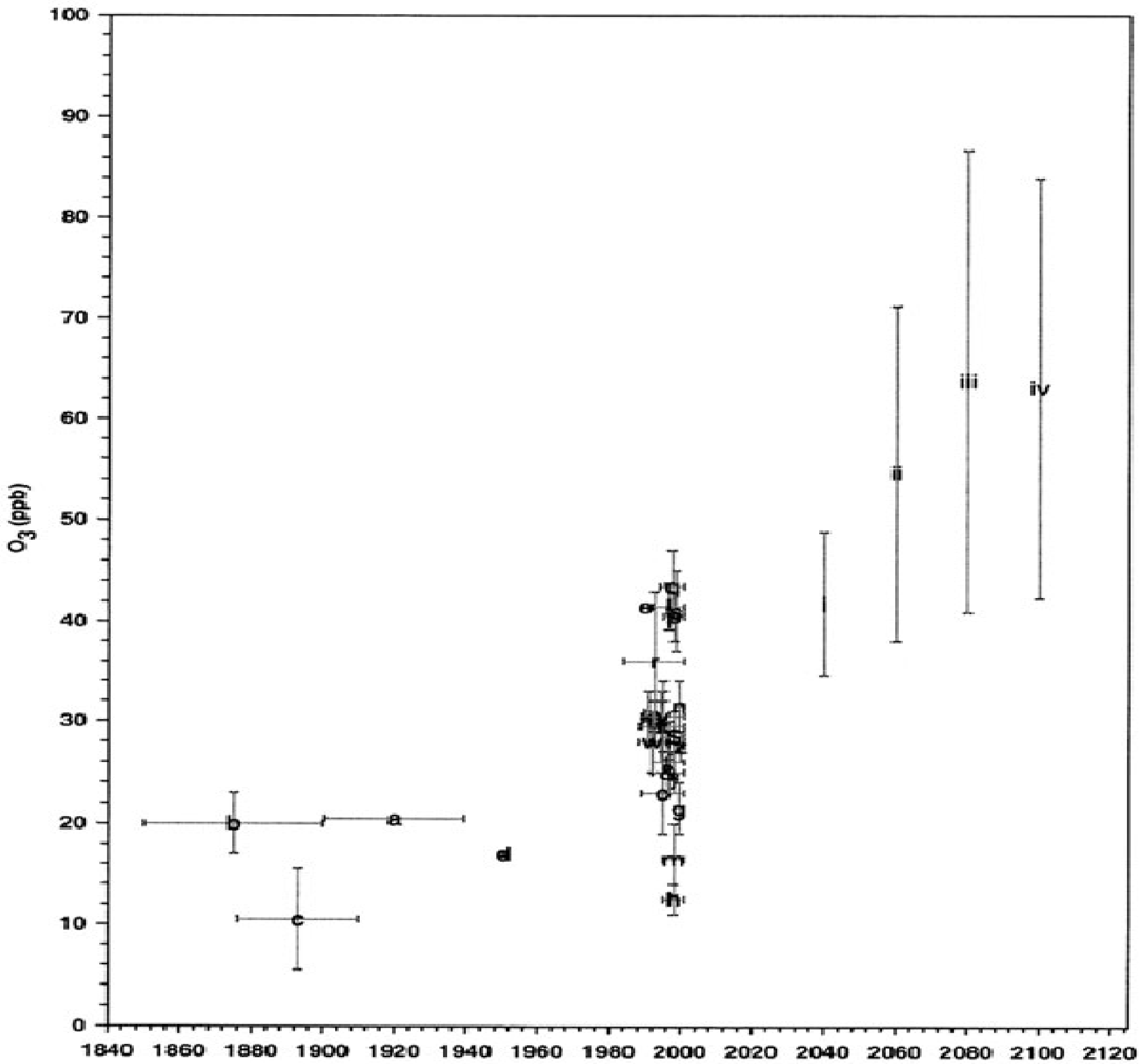


Figure 1. Historical, current and projected global background surface ozone annual mean concentrations. The range of projected concentrations reflects the range of different IPCC scenarios. From Vingarzan (2004).

Plant Cell and Environment, 2005.

GEOPHYSICAL RESEARCH LETTERS,
VOL. 30, NO. 12, 1613,
doi:10.1029/2003GL017024, 2003

"Increasing Background Ozone During Spring on the West Coast of North America"

D.Jaffe, H.Price, D.Parrish, A.Goldstein and J.Harris

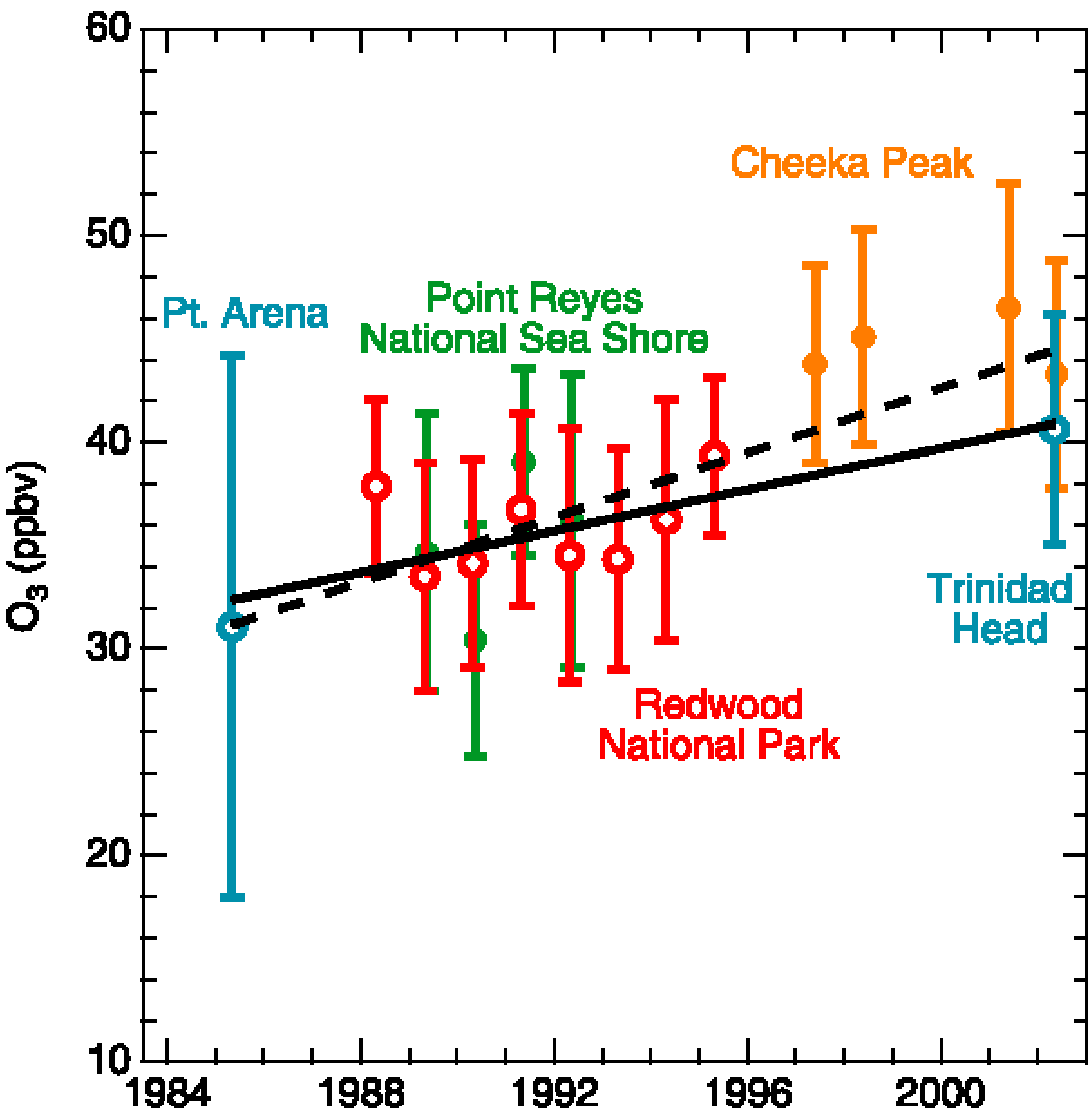


Figure 2. Spring mean mixing ratio ±1 standard deviation for background O_3 at 5 MBL sites with linear regression lines. The data have been selected by local wind direction