California Environmental Protection Agency
Department of Pesticide Regulation

Pesticide Volatile Organic Compound Emission Inventory

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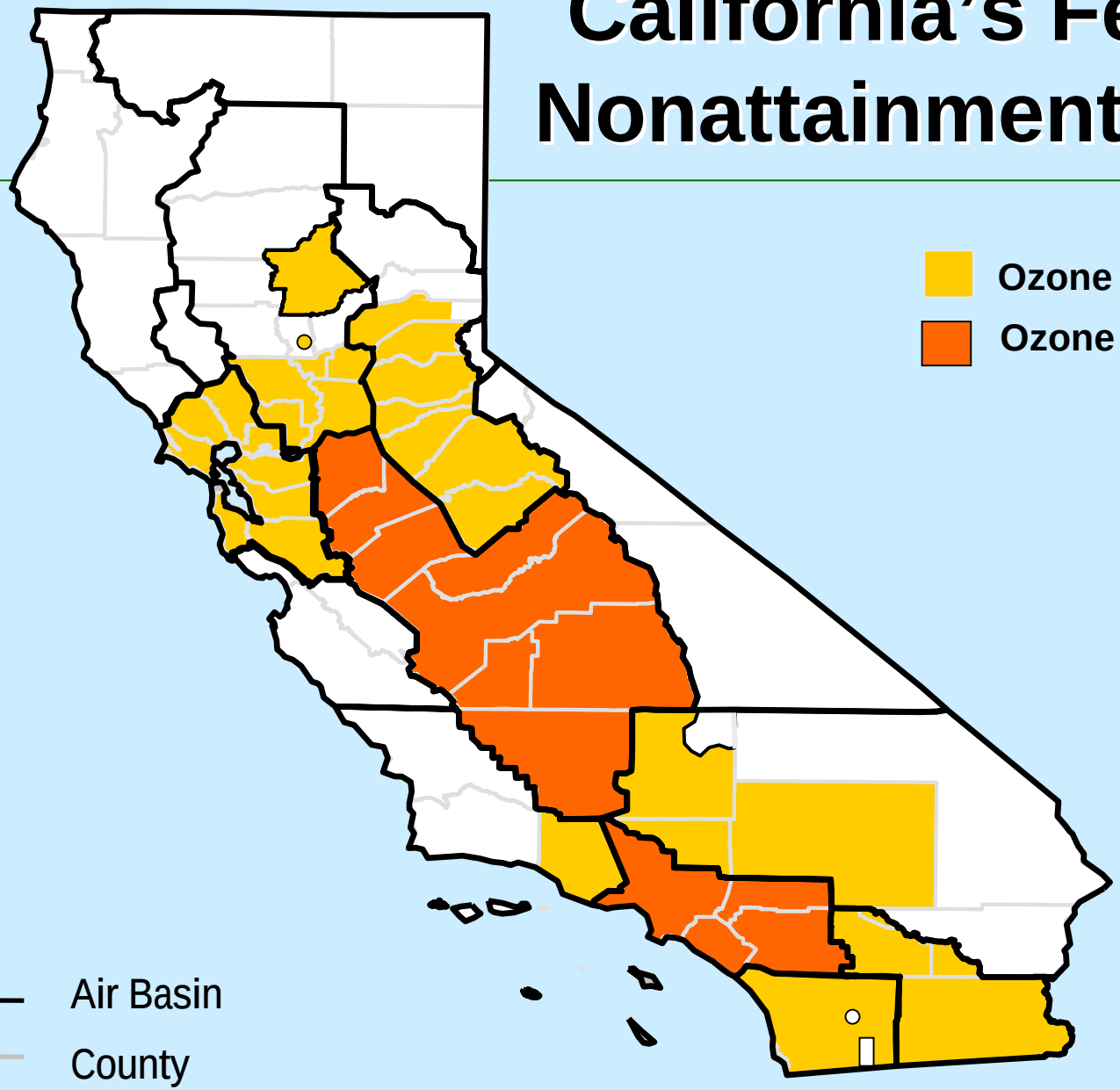
Agenda

- Overview of air pollution and VOCs
- Overview of pesticide regulation and pesticide VOCs
- Pesticide VOC emission inventory methodology
  - Estimating pesticide use
  - Estimating VOC content of pesticides
  - Estimating emissions under field conditions
- Emission inventory uncertainties and research
- Latest emission inventory estimates

Air pollution

- Volatile organic compounds (VOCs) contribute to air pollution
- VOCs and nitrogen oxides react with sunlight to form ozone, a common air pollutant
- Regions that do not meet air quality standards are nonattainment areas (NAAs)
- State Implementation Plans (SIPs) describe the actions to achieve air quality standards
  - Air Resources Board (ARB) and Air Pollution Control Districts (APCDs) are the lead agencies for CA SIPs
  - SIPs are mandated by the Federal Clean Air Act

California's Federal Nonattainment Areas



Emission inventories

- Emission inventory: list of sources and amounts of pollutants released to the air
- ARB maintains inventories for many pollutants to
  - Track trends
  - Estimate air pollutant concentrations, emission reductions needed to attain air quality standards
  - Develop mitigation strategies
  - Determine compliance with SIP obligations
- DPR provides a pesticide VOC inventory to ARB for inclusion in the overall emission inventory

Pesticide contribution to VOC inventory (2006)

Nonattainment Area	Rank
Sacramento Metro	15th
San Joaquin Valley	6th
Southeast Desert	16th
South Coast	26th
Ventura	3rd

Major Sources of VOCs (San Joaquin Valley, 2006)

Category	% of Emissions
Passenger vehicles	14
Other (waste disposal/composting)	13
Livestock waste (dairy cattle)	9
Oil and gas production (evaporative losses)	6
Consumer products	5
Pesticides	**5**
Heavy duty diesel trucks	4
Food and ag (crop processing and wineries)	4

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Pesticide background

- California legal definition of a pesticide:
  - Any substance, or mixture of substances which is intended to be used for defoliating plants, regulating plant growth, or for preventing, destroying, repelling, or mitigating any pest, which may infest or be detrimental to vegetation, man, animals, or households, or be present in any agricultural or nonagricultural environment whatsoever
  - Any spray adjuvant
- Examples: insecticides, herbicides, disinfectants, plant growth regulators, spray adjuvants
- Pesticide products contain active ingredients and inert ingredients
- DPR regulates sale and use of pesticide products

Regulating pesticide sales – registration

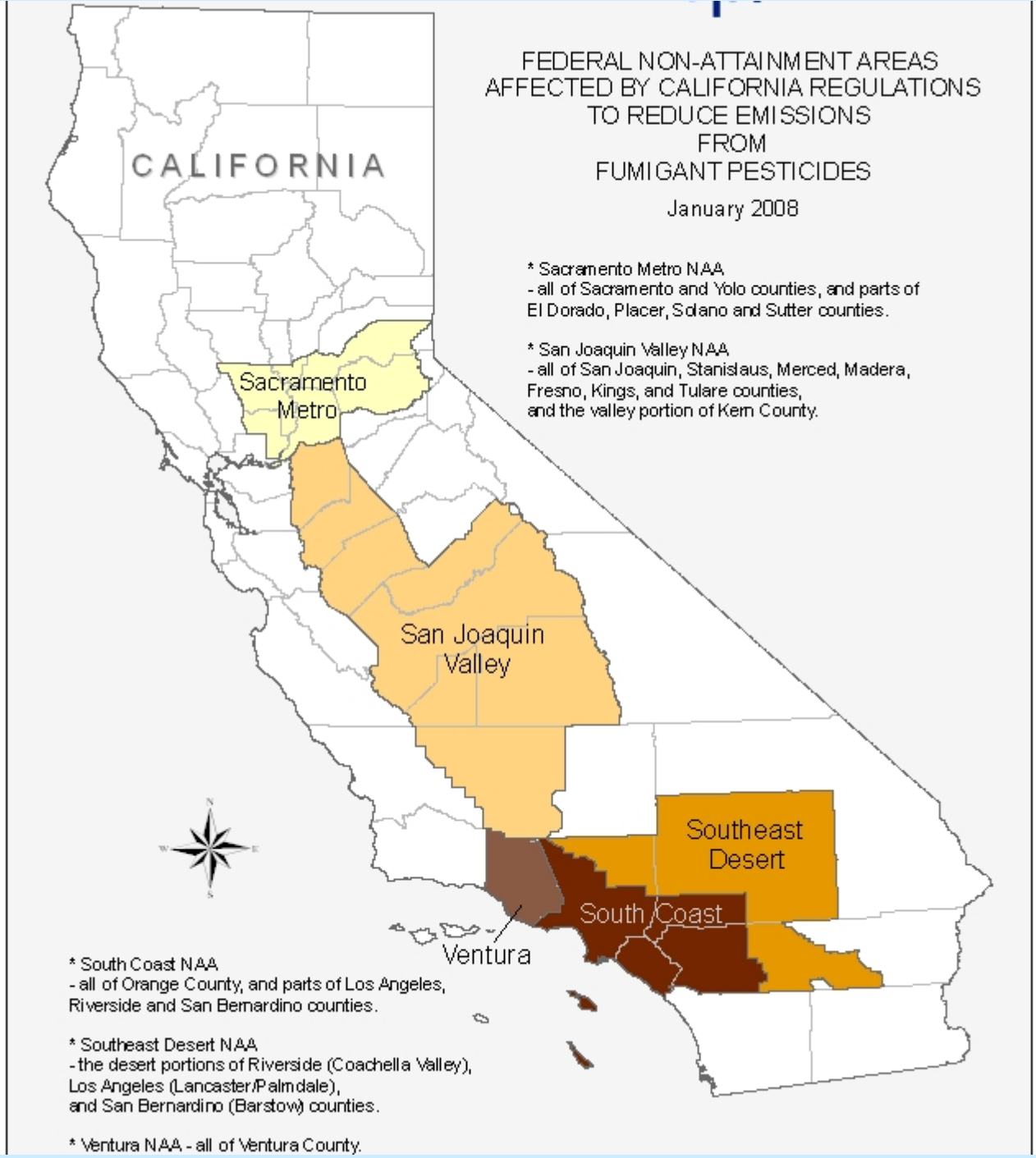
- EPA and DPR evaluate and license (register) all pesticide products prior to sale and use
- Types of EPA product registrations under FIFRA
  - Section 3: standard registration
  - Section 5: experimental use
  - Section 18: emergency exemption
  - Section 24(c): Special Local Need
  - Section 25(b): minimal risk exemption
- DPR registers additional products
  - Adjuvants
  - Structural pest control devices

Regulating pesticide use

- EPA and DPR approve pesticide product labeling that describes legal use requirements, such as
  - Maximum amounts allowed
  - Methods of application
  - Crops/sites
  - Safety requirements
- DPR state regulations (more restrictive than labeling)
  - Use requirements for certain pesticides
  - Restricted materials require permit and certified applicator
- County requirements (more restrictive than regulations)
  - Agricultural commissioner issues permits for restricted materials
  - CAC evaluates local situations and conditions permits

Pesticide VOCs

- Many pesticide active and inert ingredients are VOCs
- No pesticide products contain nitrogen oxides
- CA only state with a SIP pesticide element
- Pesticide element of SIP requires DPR to
  - Develop and maintain an emission inventory to track pesticide VOC emissions
  - Reduce emissions up to 20% from base year in five NAAs


FEDERAL NON-ATTAINMENT AREAS
AFFECTED BY CALIFORNIA REGULATIONS
TO REDUCE EMISSIONS
FROM
FUMIGANT PESTICIDES
January 2008
CALIFORNIA
* Sacramento Metro NAA
- all of Sacramento and Yolo counties, and parts of
El Dorado, Placer, Solano and Sutter counties.
* San Joaquin Valley NAA
- all of San Joaquin, Stanislaus, Merced, Madera,
Fresno, Kings, and Tulare counties,
and the valley portion of Kern County.
Sacramento
Metro
San Joaquin
Valley
Southeast
Desert
South Coast
Ventura
* South Coast NAA
- all of Orange County, and parts of Los Angeles,
Riverside and San Bernardino counties.
* Southeast Desert NAA
- the desert portions of Riverside (Coachella Valley),
Los Angeles (Lancaster/Palmdale),
and San Bernardino (Barstow) counties.
* Ventura NAA - all of Ventura County.

Scope of pesticide VOC inventory

- DPR estimates VOC emissions from agricultural and commercial structural pesticide applications
- ARB estimates VOC emissions from other sources (including pesticidal consumer products)
- DPR calculates emissions for each year beginning with 1990, and updates annually based on most recent data
- Inventory focuses on:
  - May – Oct (peak ozone period) for each year
  - 5 nonattainment areas

Method for estimating pesticide VOCs

- VOC emission from a pesticide product is calculated by multiplying:
  - Amount of product applied
  - VOC fraction in product (emission potential, EP)
- Fumigants are adjusted by an additional factor to account for emissions under field conditions
  - Emission rating varies with fumigant and application method

Nonfumigant calculation example

- Farmer Joe applies 100 pounds of “Pesticide 4E” to his orchard
- Emission potential of Pesticide 4E is 51.32%
- VOC emissions

  = 100 x 0.5132

  = 51.32 pounds

Fumigant calculation example

- Farmer Joe applies 1000 pounds of “Fumigant-X” using drip chemigation prior to planting a strawberry field
- Emission potential of Fumigant-X is 94%
- Fumigant-X emits 12% of the applied VOCs when using drip chemigation
- VOC emissions

  = 1000 x 0.94 x 0.12

  = 113 pounds

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Estimating pesticide use

- DPR's inventory includes agricultural and commercial structural pesticide applications
- Agricultural and structural use defined by law and regulations
- Depends on the crop/site and who makes the application

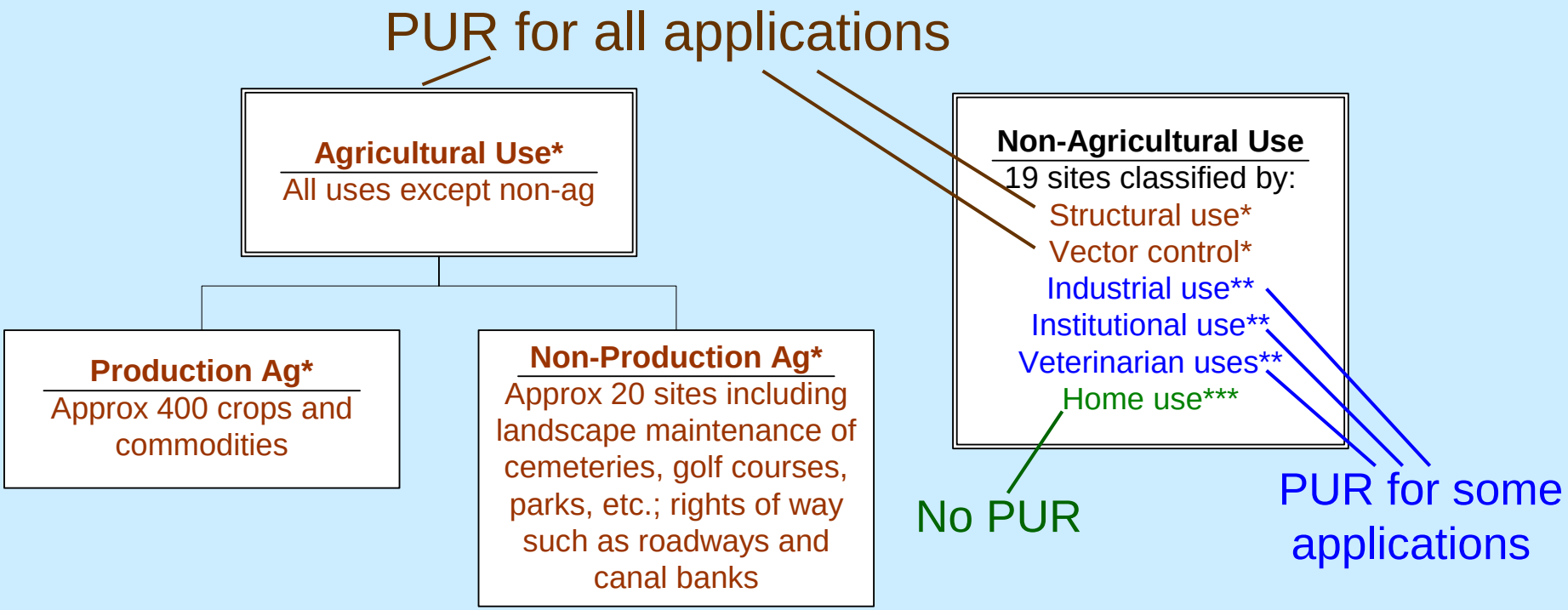
Types of pesticide use

- Agricultural use includes all applications except
  - Structural use
  - Home use
  - Industrial use
  - Institutional use
  - Vector control
  - Veterinarian uses
- Production agricultural use are crops/commodities
- Non-production agricultural use includes cemeteries, golf courses, parks, rights of way, etc.
- Structural use includes all applications by structural pest control businesses, regardless of site treated

Pesticide use reports (PURs)

- Since 1990, regulations require the following applications of registered products to be reported:
  - All applications for agricultural use
  - All applications by pest control businesses
  - All applications that use restricted materials
  - Pesticides applied for industrial post-harvest commodities
  - Certain pesticides applied for outdoor institutional or industrial uses (ground water issues)
- Memorandum of Understanding requires vector control agencies to report all applications
- PURs submitted to county agricultural commissioners and compiled by DPR

Scope of pesticide use reporting



* All ag, structural, and vector control use reported
** Partial use reporting for industrial, institutional, vet uses
*** No use reporting for home use

Key information included in pesticide use reports

Information	Production Ag Reports (each application)	Non-Production Ag and Non-Ag Reports (monthly summary)
Product applied	Yes	Yes
Crop/site treated	Yes	Yes
Amount applied	Yes	Monthly total
Date applied	Date and time	Month
Application method	Yes	No
Acres/units treated	Yes	Monthly total
Location	Tnshp/rng/sec	County

Pesticide use estimates for monthly summary data

- Applications to non-production ag and non-ag sites reported as totals for county
- 7 counties partially within NAAs
- Use surrogate data to allocate use
  - Structural and landscape use based on proportion of population
  - Rights of way use based on proportion of roadways, waterways, power lines
  - Commodity fumigation use based on agricultural commissioner information

Pesticide use report error checks

- Approx 2,500,000 PUR records each year
- DPR software includes approx 50 checks for data validity
- Outlier screens for high application rates
  - Nonfumigant application rate >200 lbs/ac
  - Fumigant application rate >1000 lbs/ac
  - Application rate >50x median for product-site
  - Neural network (scientific judgment of frequency distributions)
- PURs with suspected errors sent to agricultural commissioner for checking; approx 1% of records sent for error checking

Label database

- PUR contains information on pesticide applications
- Label database contains information on registered pesticide products
  - EPA registration number
  - Registrant (manufacturer, importer, distributor)
  - Type of pesticide (e.g., insecticide)
  - Name and % active ingredient(s)
  - Product density
  - Formulation type (e.g., dust, liquid concentrate)
  - Crops/sites registered

Pesticidal consumer products

- Pesticidal consumer products included in ARB's inventory
- DPR screens out consumer products using
  - Label database formulation type
  - PUR site codes
  - Registration list
- DPR and ARB consult on "dual" use products
  - Consumer products with ag or structural uses
  - Ag or structural products can have home (consumer) uses

Pesticide uses and products included in the inventory

Type of Use and Product Registration	Applied by Pest Control Business (ag or structural)	Not Applied by PCB (e.g., grower, homeowner)
Agricultural use (Sec 3, 18, 24c)	**DPR**	**DPR**
Structural use (Sec 3, 18, 24c)	**DPR**	Does not occur
Home use (Sec 3, 18, 24c)	Does not occur	**ARB**
Institutional use (Sec 3, 18, 24c)	Not included	**ARB (some)**
Industrial use (Sec 3, 18, 24c)	**DPR/APCD (some)**	**DPR/APCD (some)**
Vector control use (Sec 3, 18, 24c)	Not included	Not included
Veterinary use (Sec 3, 18, 24c)	Not included	Not included
Experimental product (Sec 5)	No PUR, not included?	No PUR, not included?
Exempt product (Sec 25b)	No PUR, not included	**ARB (some)**
Adjuvant/structural device products	Not included	Not included

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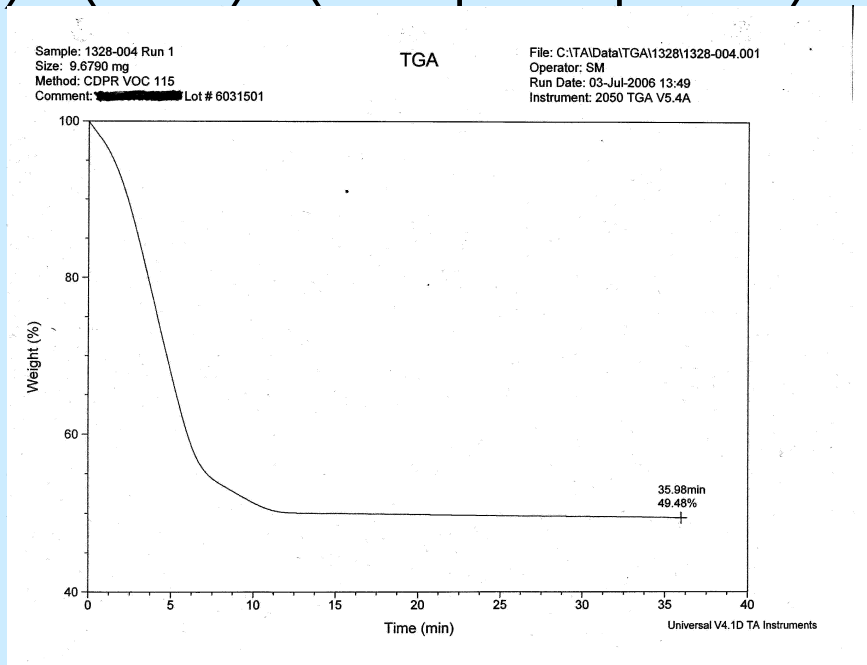
Estimating VOC content

- Methods for estimating VOC content (emission potential)
  - Lab test (thermogravimetric analysis), current best method
  - Evaluate confidential statements of formula
  - Default value for formulation category
  - Special default values

Emission potentials by thermogravimetric analysis (TGA)

- DPR method similar to EPA method 24 and ARB method 310
- Thermogravimetric analyzer is an environmental chamber containing a scale and heater
- Sample heated to 115 C (239 F) and weight loss reaches threshold
- Maximum test time: 80 minutes
- EP = (mass loss) – (water) – (exempt compounds)



Emission potentials by confidential statements of formula

- Alternative method if no TGA data available
- Confidential statement of formula lists all of the active and inert ingredients in a pesticide product
- EP = (product mass) – (water, other inorganic chems)

- Confidential statement of formula also used determine if product is identical to another product with TGA data

Default emission potentials by formulation category

- Alternative method when no TGA data available
- Different formulation types have different VOC contents (e.g., liquids have more VOCs than solids)
- Default values based on TGA data grouped by formulation category
- Prior to 2002: defaults were highest TGA value
  - Incentive for registrants to provide TGA data
- Since 2002: defaults are median TGA value
  - More representative estimate of emissions
- Special default values for certain products

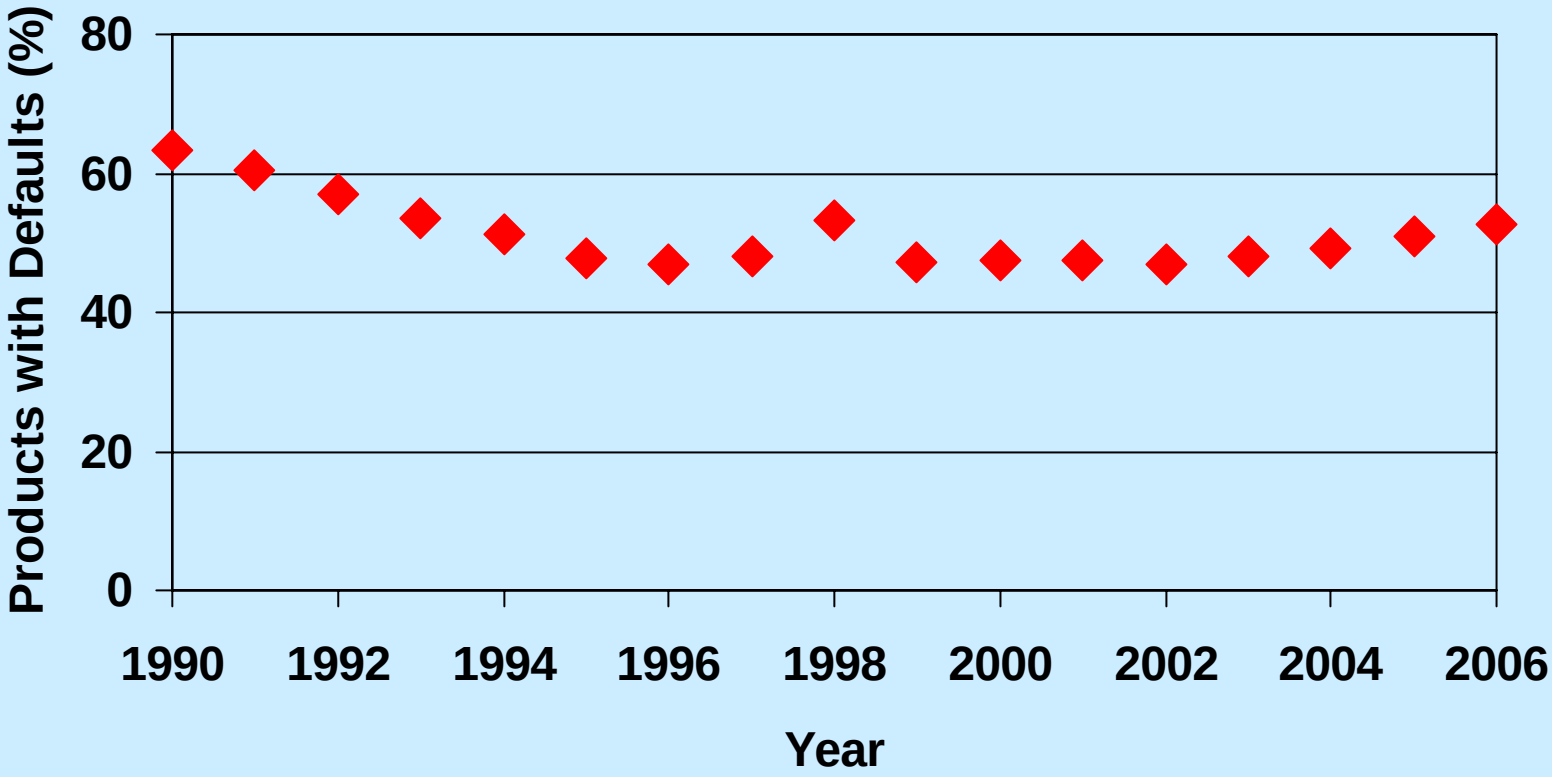
Default emission potentials by formulation category (%)

Formulation Category	Revised	Original
DUST/POWDER	1.53	59.7
EMULSIFIABLE CONCENTRATE	39.15	98.7
FLOWABLE CONCENTRATE	4.80	95.8
GRANULAR/FLAKE	3.70	20.3
PELLET/TABLET/CAKE/BRIQUET	5.18	8.2
PRESSURIZED PRODUCTS	100.00	100.0
SOLUBLE POWDER	1.15	5.3
SOLUTION/LIQUID (READY-TO-USE)	7.30	99.9
WETTABLE POWDER	1.85	9.2
SUSPENSION	5.71	9.4
DRY FLOWABLE	1.02	5.8
LIQUID CONCENTRATE	5.71	97.3

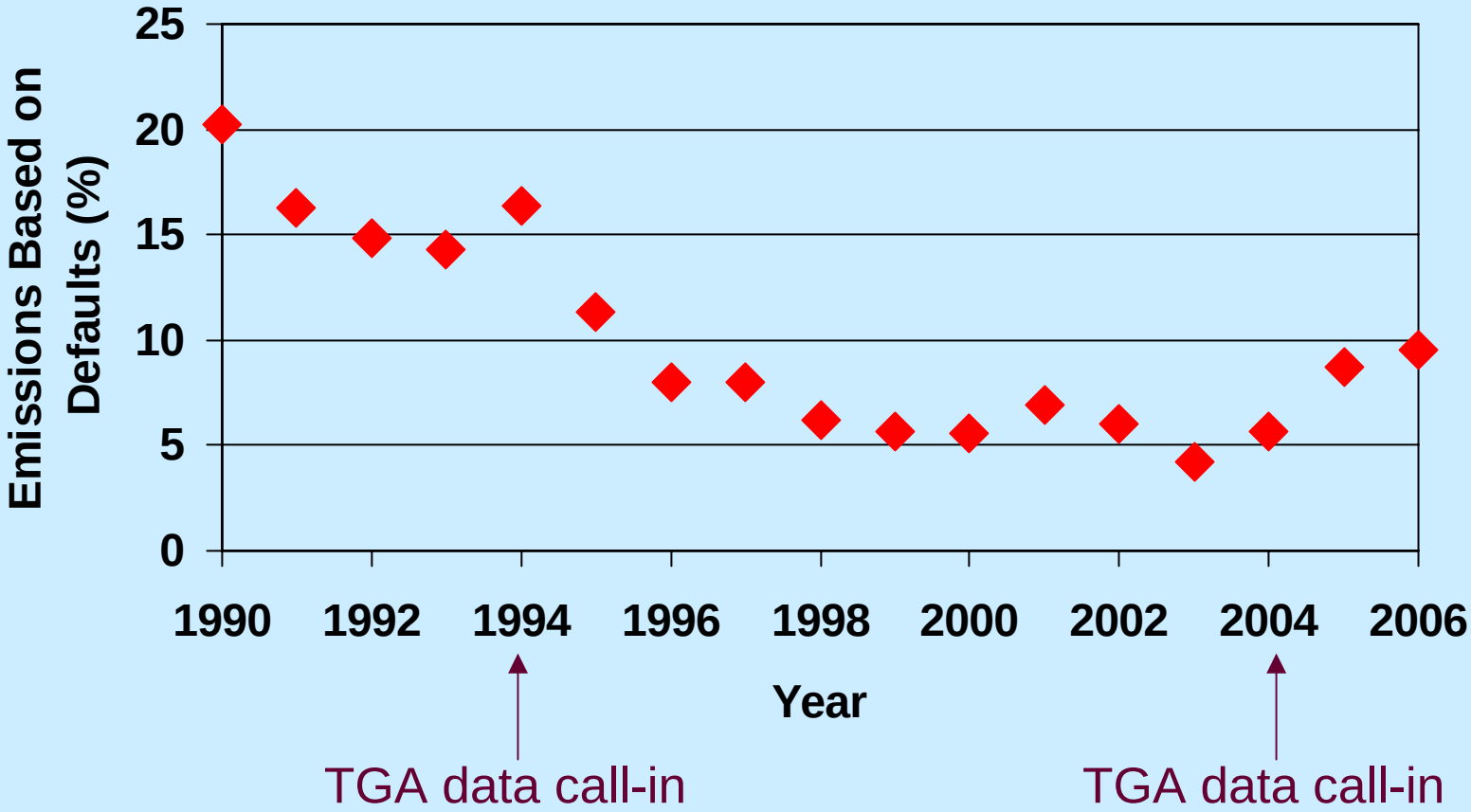
Special default emission potentials

Product	EP (%)
Sodium chlorate	0
Metam	MITC equivalent
Sodium tetrathiocarbonate	Carbon disulfide equivalent
Sulfur dusts	0
Other sulfur products	0.6
Oils	1.53

Percent of products with default EPs (statewide)



Estimated percent emissions from products with default EPs (San Joaquin Valley)



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Field fumigation methods

Emissions under field conditions – fumigants

- Several dozen field studies for fumigants
  - Data for methyl bromide, chloropicrin, 1,3-dichloropropene, metam, dazomet, sodium tetrathiocarbonate
  - Emissions vary with fumigant and fumigation method
  - Emissions range from 9 to 100% of the amount applied (emission rating or application method adjustment factor)
  - Fumigations with tarps, water treatments, or drip chemigation generally have lower emissions
  - Field data for approx one-half of the methods used in NAAs; rely on surrogate data for remainder

Methods for measuring emissions under field conditions

- Preferred methods, with demonstrated reliability
  - Off-site air monitoring (back-calculation)
  - On-field air monitoring using aerodynamic flux or integrated horizontal flux
- Other methods, with uncertain reliability, particularly at field scale
  - On-field air monitoring using chambers
  - Laboratory soil column tests
  - Computer modeling

Off-site and on-field flux monitoring studies

Off-site monitoring

On-field flux monitoring

On-field chamber studies

Photos courtesy of Suduan Gao

Soil column study

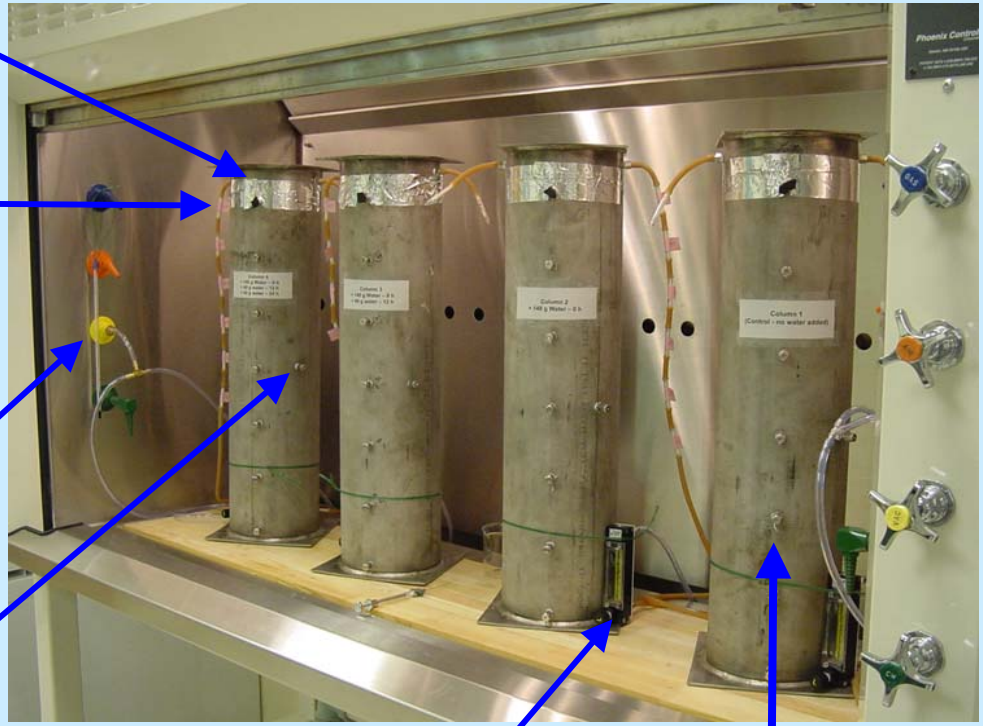

Photo courtesy of Suduan Gao

Computer modeling

chemical data soil data weather data application data

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}[K(\frac{\partial h}{\partial x} + \cos\alpha)] - S$$

$$\frac{\partial \theta c_1}{\partial t} + \frac{\partial \rho s_1}{\partial t} + \frac{\partial a_v g_1}{\partial t} = \frac{\partial}{\partial x}\left(\theta D_1^w \frac{\partial c_1}{\partial x}\right) + \frac{\partial}{\partial x}\left(a_v D_1^g \frac{\partial g_1}{\partial x}\right) - \frac{\partial q c_1}{\partial x} - Sc_{r,1} -$$

$$-(\mu_{w,1} + \mu'_{w,1})\theta c_1 - (\mu_{s,1} + \mu'_{s,1})\rho s_1 - (\mu_{g,1} + \mu'_{g,1})a_v g_1 + \gamma_{w,1}\theta + \gamma_{s,1}\rho + \gamma_{g,1}a_v$$

repeat

validation:
compare to field study data

refine model

Method use fractions

- Emission ratings range from 9% to 100% depending on fumigant and fumigation method
- Until 2008, PUR did not include method of fumigation
- Frequency each fumigation method used estimated by
  - Township cap data (1,3-dichloropropene)
  - PUR data by crop (methyl bromide, chloropicrin)
  - Survey (metam)

Emissions under field conditions – nonfumigants

- No field studies for nonfumigants
- Studies need to include
  - VOC emissions of active ingredients
  - VOC emissions of inert ingredients
  - VOC emissions of major VOC breakdown products
  - VOC emissions measured for days to weeks

Pesticide emission inventory methodology summary

- Amount of pesticide products applied estimated from pesticide use reports
- Emission potential estimated from TGA or confidential statement of formula
- Fumigant emissions adjusted for field conditions, based on monitoring data

Pesticide emission inventory history

- 1990: Began full-use reporting
- 1994: Pesticide element included in SIP
- 1994: Initiated 1st data call-in for TGA data
- 1996: Published 1st DPR inventory (1990-1993 data)
- 1999: Began PUR outlier checks (1990-1997 data)
- 2002: Changed default values (1990-2000 data)
- 2005: Initiated 2nd data call-in for TGA data
- 2007: Incorporated fumigant field emission adjustments (1990-2004 data)

Emission inventory statistics (May-Oct 2006)

NAA	Number of Products	Number of PUR Records
Sacramento Metro	1,800	125,688
San Joaquin Valley	2,780	827,678
Southeast Desert	1,701	105,671
Ventura	1,210	80,348
South Coast	2,006	124,323
TOTAL	----	1,263,708

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Emission inventory uncertainties

- Pesticide use reports and label database
  - Reporting and data entry errors
  - Uncertain reporting compliance (sales vs. use)
- Emission potentials (VOC content)
  - TGA data unavailable for some products, use defaults
  - Uncertain representation of field conditions
  - Do not reflect ozone creation
- Emission ratings for field conditions
  - No emission ratings for nonfumigants
  - Incomplete data for fumigants, use surrogate data
  - Some fumigant data may not be representative
- Several uncertainties addressed through research

Reactivity and VOC exemptions

- Different VOCs create different amounts of ozone
  - Maximum incremental reactivity (MIR) measures grams ozone produced per gram VOC
- US EPA has sole legal authority to exempt chemicals as VOCs
  - Normally use ethane as the standard, MIR = 0.27
- US EPA considering exemptions for
  - Methyl bromide (MIR = 0.03)
  - Iodomethane, not registered in CA (negative MIR)
- MITC MIR = 0.35

Adjust inventory for reactivity?

- Reactivity-based inventory reflects better science
- Almost all pesticide products have unknown reactivity
- May not be possible to determine reactivity of products used in base year

Emission inventory research

- DPR data requests
- DPR data evaluation
- VOC emissions from sulfur products
- Bayer lab test method

DPR data requests

- TGA data requested for all liquid ag products
- Fumigant emission studies requested for fumigation methods with no field data
  - Some studies in progress
  - Registrants proposing computer modeling of emissions to fulfill some data requirements

DPR data evaluation in progress

- Oil products
  - High use (#2 reported use)
  - Specific product originally assigned default of 1.53%
  - TGA data measured EP of 24%
  - TGA data invalid, reassigned default EP of 1.53%
- Post-harvest commodity fumigations
  - Propylene oxide are all industrial uses, reported by APCDs, removed from DPR's inventory
  - Methyl bromide has agricultural and industrial uses, some emissions reported by DPR and APCD

VOC emissions from sulfur products

- Sulfur default EP = 0.6%, based on median TGA value for 27 products
- Sulfur VOC emissions still significant for some NAAs due to high use (#1 reported use)
- 2008 USDA study identified water as the volatile chemical from 6 high-use sulfur products
- Most sulfur dust products assigned EP = 0

Bayer lab test method

- Bayer and others are developing lab method closer to field conditions
- Separate methods for soil and foliage
- Issues
  - Methods for ingredients, not products
  - Need to estimate drift loss
  - Need to test base year products
  - Can’t differentiate soil or foliage applications in PUR
  - Need comparison to TGA
  - Need field comparison to check for underestimation

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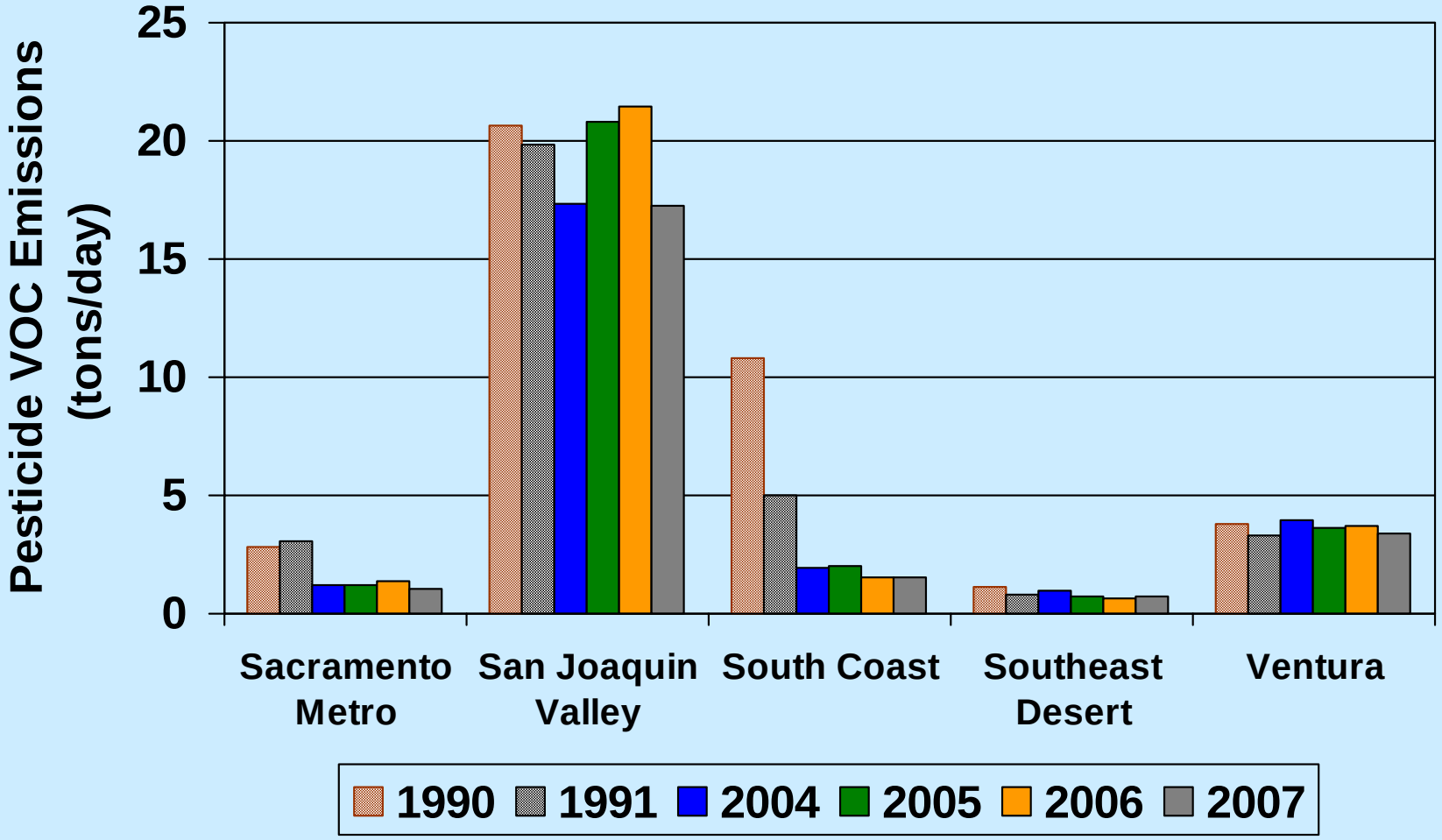
Pesticide VOC emission trends

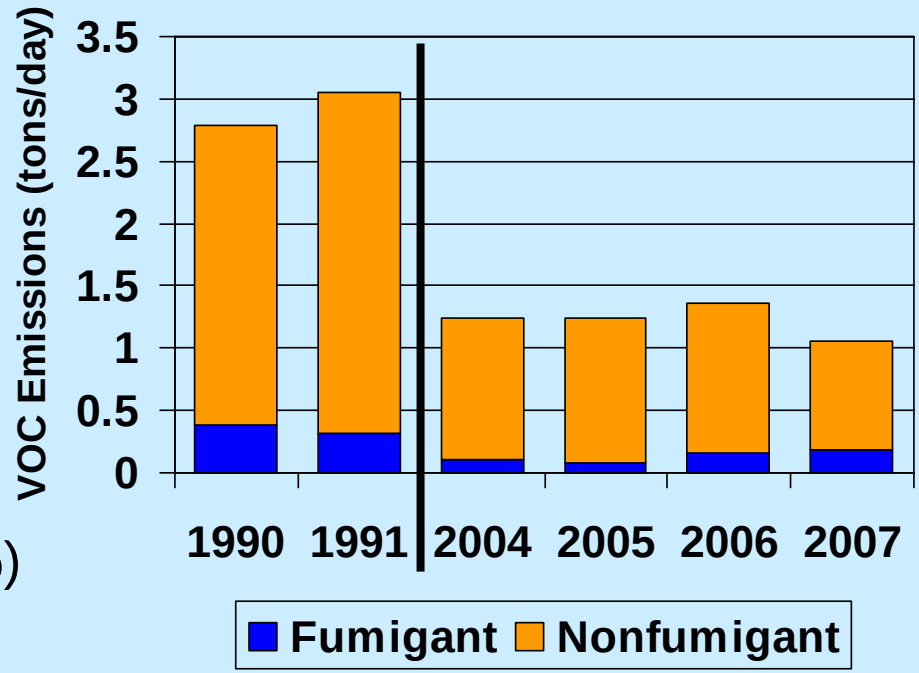
- 2007 emissions lower than 2004 in all five NAAs
- Fumigants continue to contribute a significant portion of the pesticide VOCs, even after accounting for field conditions
- Emulsifiable concentrates are major contributors, particularly in San Joaquin Valley

Pesticide VOC emission estimates (May-Oct)



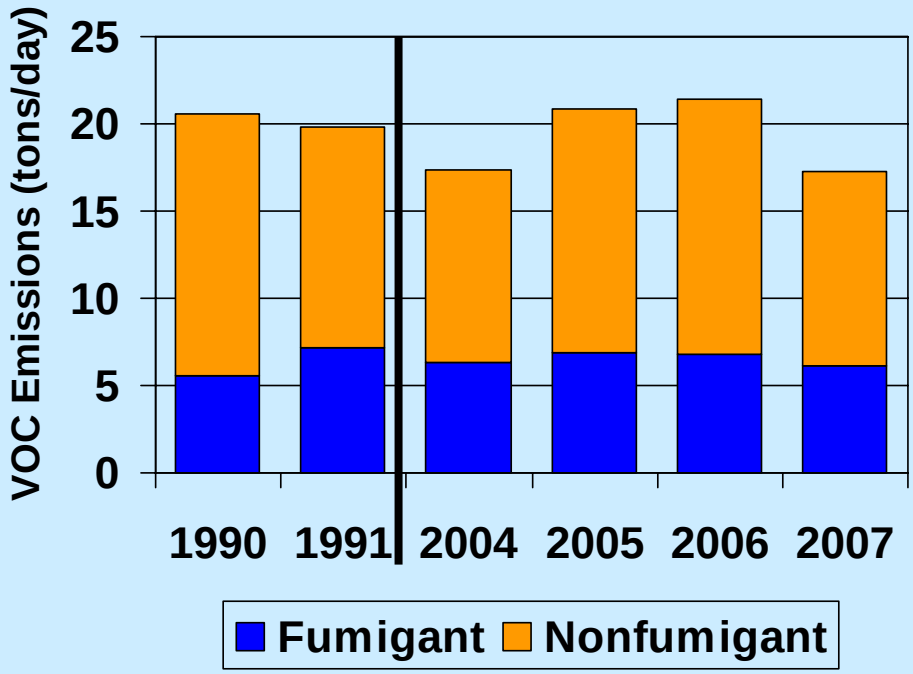
Draft pesticide VOC inventory for Sacramento Metro (May-Oct)

- Top active ingredients (% of 2007 pesticide emissions)
  - Chlorpyrifos (11.0%)
  - 1,3-dichloropropene (10.3%)
  - Trifluralin (5.4%)
  - Methyl bromide (5.2%)
  - Dimethoate (4.7%)
- Top application sites
  - Walnut (23.9%)
  - Rice (12.7%)
  - Tomato (11.4%)
  - Rights of way (6.0%)
  - Structural pest control (5.3%)



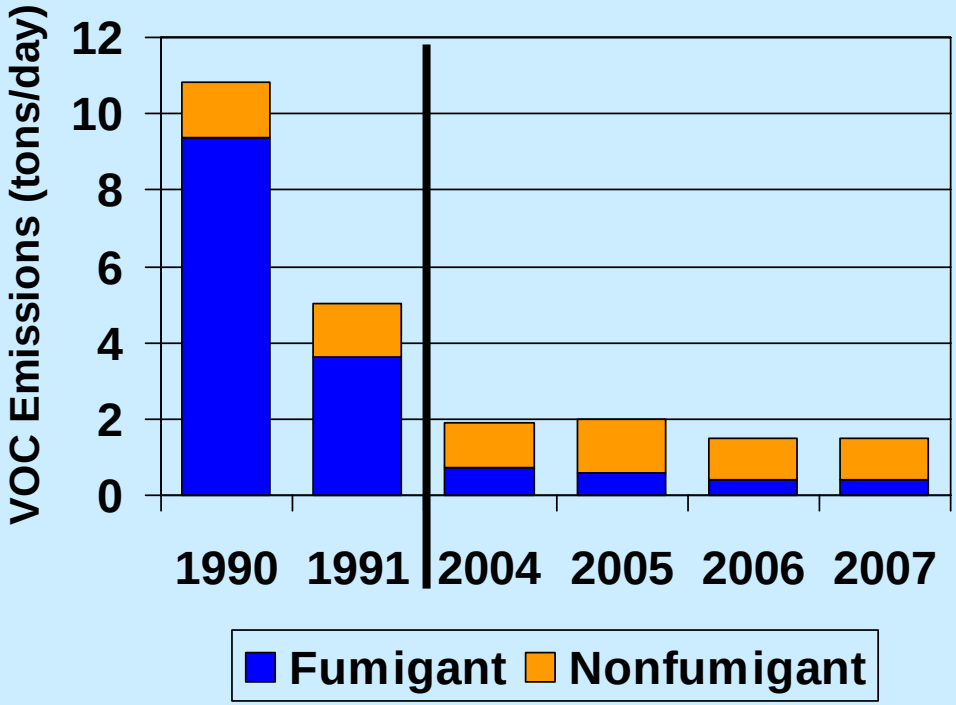
Draft pesticide VOC inventory for San Joaquin Valley (May-Oct)

- Top active ingredients (% of 2007 pesticide emissions)
  - Chlorpyrifos (13.1%)
  - 1,3-dichloropropene (12.6%)
  - Metam-sodium (12.1%)
  - Methyl bromide (5.8%)
  - Oxyfluorfen (5.5%)
- Top application sites
  - Carrot (15.9%)
  - Almond (15.8%)
  - Grape (5.6%)
  - Orange (5.3%)
  - Nursery-outdoor (4.3%)
  - Cotton (4.2%)



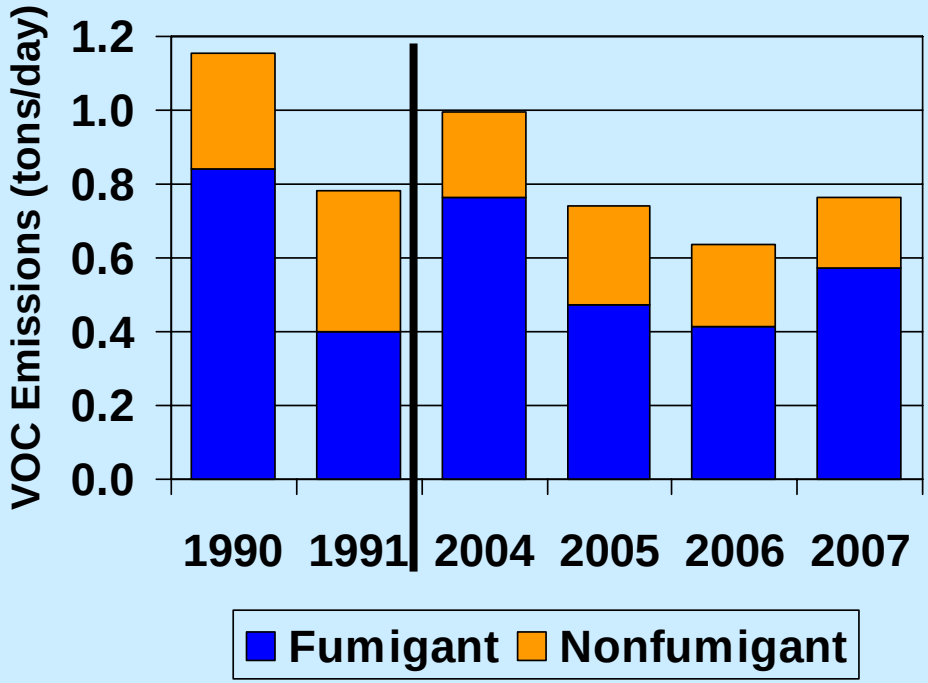
Draft pesticide VOC inventory for South Coast (May-Oct)

- Top active ingredients (% of 2007 pesticide emissions)
  - Permethrin (18.4%)
  - Methyl bromide (15.7%)
  - Limonene (8.1%)
  - Chloropicrin (7.1%)
  - Bifenthrin (5.1%)
- Top application sites
  - Structural (39.9%)
  - Strawberry (38.2%)
  - Landscape maint (8.2%)
  - Fumigation (2.9%)
  - Nursery-outdoor (2.2%)



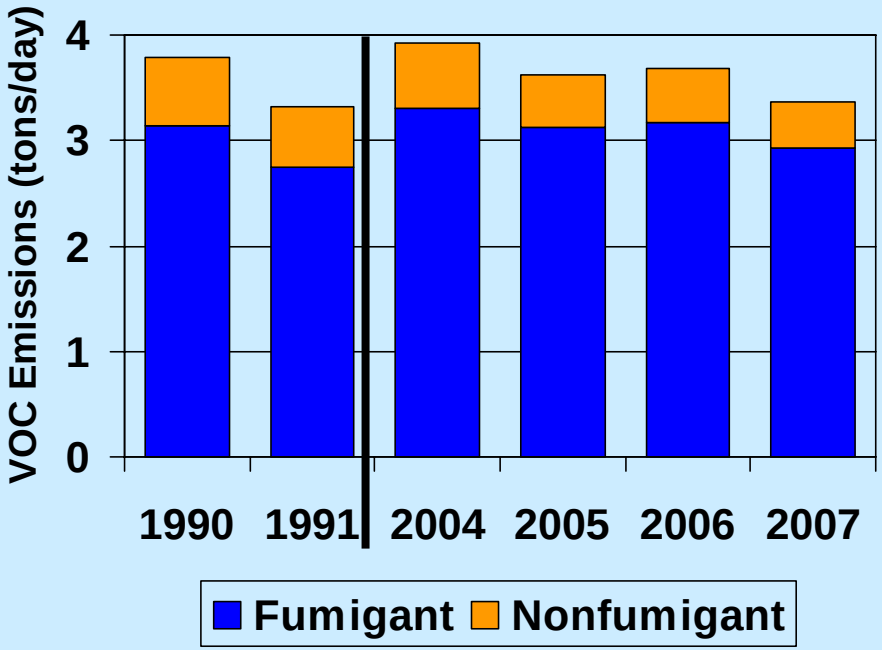
Draft pesticide VOC inventory for Southeast Desert (May-Oct)

- Top active ingredients (% of 2007 pesticide emissions)
  - Metam-sodium (42.3%)
  - Methyl bromide (22.2%)
  - 1,3-dichloropropene (4.7%)
  - Permethrin (2.7%)
  - Bensulide (2.1%)
- Top application sites
  - Pepper (24.4%)
  - Turf/sod (16.2%)
  - Strawberry (14.4%)
  - Potato (9.5%)
  - Uncultivated (6.5%)



Draft pesticide VOC inventory for Ventura (May-Oct)

- Top active ingredients (% of 2007 pesticide emissions)
  - Chloropicrin (37.3%)
  - Methyl bromide (27.8%)
  - 1,3-dichloropropene (20.0%)
  - Metam-sodium (2.1%)
  - Chlorpyrifos (1.3%)
- Top application sites
  - Strawberry (56.3%)
  - Soil fumigation (38.1%)
  - Lemon (1.7%)
  - Tomato (1.1%)
  - Raspberry (0.6%)



Key points

- Pesticide VOCs contribute to formation of ozone
- Pesticide emissions estimated based on VOC content (emission potential) of products and reported use
- Default emission potentials account for 5-10% of emissions for most years in San Joaquin Valley
- Emission rating accounts for emissions under field conditions for fumigants
- Research in progress to improve the emission inventory
- 2007 emissions lower than 2004 in all five NAAs

Additional information

- For more information
  - www.cdpr.ca.gov
  - Click on “Air” under Quick Finder
  - Link to “Volatile Organic Compounds”

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