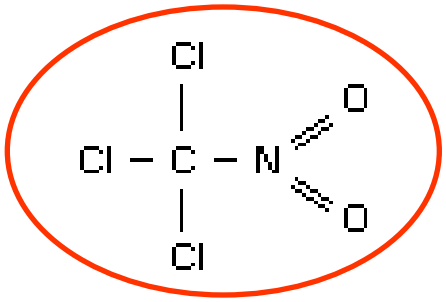
Public Exposure to Chloropicrin in California

Sheryl Beauvais
Worker Health and Safety Branch

Terrell Barry
Environmental Monitoring Branch

California Department of Pesticide Regulation

Chloropicrin: Introduction



- Trichloronitromethane
  - Colorless, volatile liquid
- Strongly and rapidly irritating to eyes and respiratory system
- Used as fumigant active ingredient (AI), alone or mixed with other fumigants (e.g., methyl bromide & 1,3-dichloropropene)
  - Primarily controls soil fungi and other pathogens, as well as nematodes
  - Controls some weeds
  - Also used as a warning agent

(Photo from Rossopf *et al*, 2005)

(Chloropicrin cylinder & pan with cotton from Cardinal Products)

Warning Agent

- What is a warning agent (WA)?
  - Has **good warning properties**, such as odor or irritation
  - **Ideally,** can detect the warning agent at concentrations below which it and co-applied chemicals are toxic
- Soil fumigations
  - Methyl bromide contains chloropicrin at **≤ 2%** (at higher concentrations, up to 55%, chloropicrin is considered an AI)
- Structural fumigations
  - 2 methyl bromide products with **0.5 - 1%** chloropicrin
  - Sulfuryl fluoride labels require use of chloropicrin, which is added separately to a pan in front of a fan (see photos)

Chloropicrin in Reevaluation at DPR

- DPR placed all products containing chloropicrin into reevaluation, based on data submitted under California's Birth Defect Prevention Act
  - DPR required submission of new studies from registrants; all required studies have been submitted
- Chloropicrin is also a candidate to be listed as a Toxic Air Contaminant (full exposure assessment to follow)
  - Focused on public airborne exposures to chloropicrin
  - **Screening estimates** for bystanders to soil, structural, and enclosed space fumigations (if screening estimates are okay, others are, too)

U.S. EPA Status

- Soil Fumigant Risk Assessments
  - Chloropicrin is one of 5 AIs with risk mitigation measures proposed by EPA in 2008 – amended documents with revised measures released in May 2009
  - Proposed mitigation measures include **buffer zones of 25 ft – ½ mile**, depending on the application method and conditions
- EPA's risk assessment only considered uses supported by the Chloropicrin Manufacturers Task Force (CMTF)
  - Other registrants must submit data to support reregistration of any uses not supported by CMTF
  - (DPR's risk assessment examines current uses)

Key Differences in Chloropicrin Exposure Assessments by DPR and U.S. EPA

- **Application rates:**
  - Maximum rates of **500** vs. **350** lbs AI/acre, based on current labels (DPR) vs. proposed maximum rates (U.S.EPA)
- **Exposure durations**
  - U.S. EPA: short-term exposures only (no annual or lifetime)
  - Shortest: 4-hour (U.S. EPA) vs. 1-hour (DPR)
- **Statistics** used to estimate exposure
  - Upper-bound and arithmetic mean vs. geometric mean
- **Model** used to estimate off-site concentrations: ISCST3 (screening, deterministic) vs. PERFUM (probabilistic)
  - U.S. EPA reported ISCST3 results in an appendix, but used PERFUM in its risk assessment

Chloropicrin Products

Active Ingredient	Number of Products Registered	Chloropicrin Concentration Range (%)	Fumigation Type
Methyl Bromide	25	0.25 – 55	
Chloropicrin – WA	(7)	0.25 – 2.0	Soil/Space/WA in Structural
Chloropicrin – 10.5%	(1)	10.5	Soil
Chloropicrin – AI	(17)	19.8 – 55	Soil/Space
Methyl Iodide*	0	2 – 75	Soil
1,3-Dichloropropene	13	15 – 60	Soil
Chloropicrin as sole AI	9	94 - 100	Soil/Space/WA in Structural
Total	47		

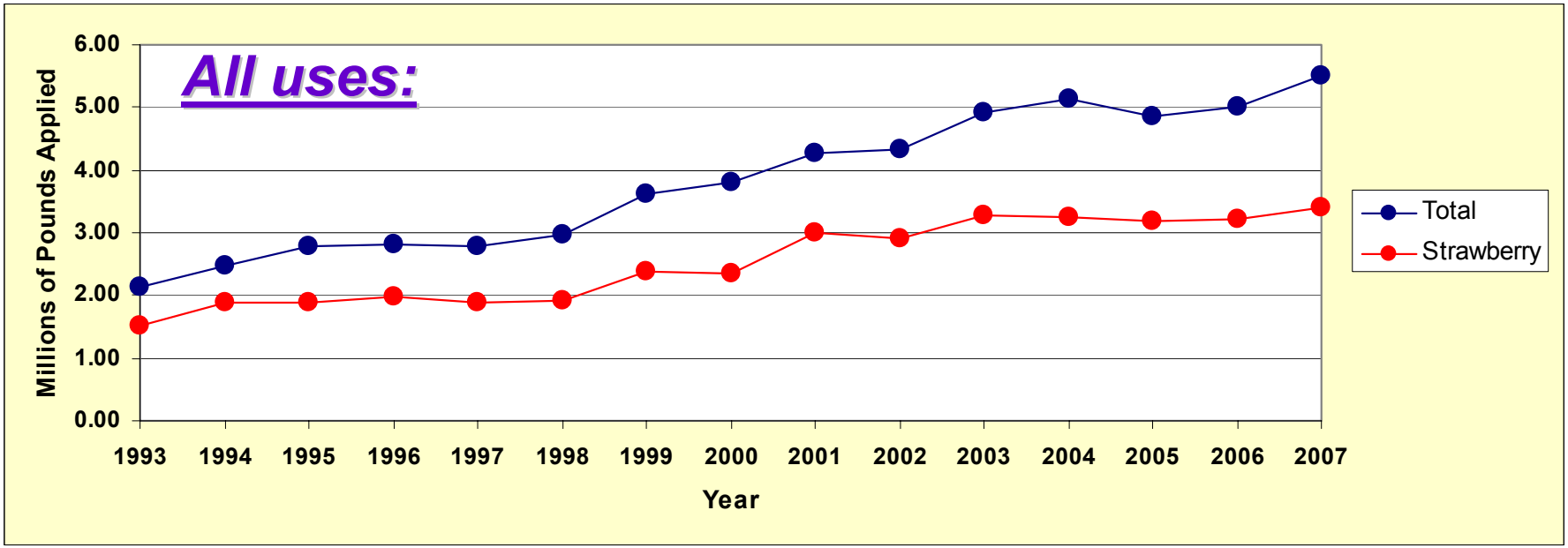
- **47** products registered in California
- Registered uses:
  - Soil/space fumigation (also warning agent for structural fumigation)

(Warning agent for sulfuryl fluoride)

** Methyl iodide is not currently registered in California*

Chloropicrin Use

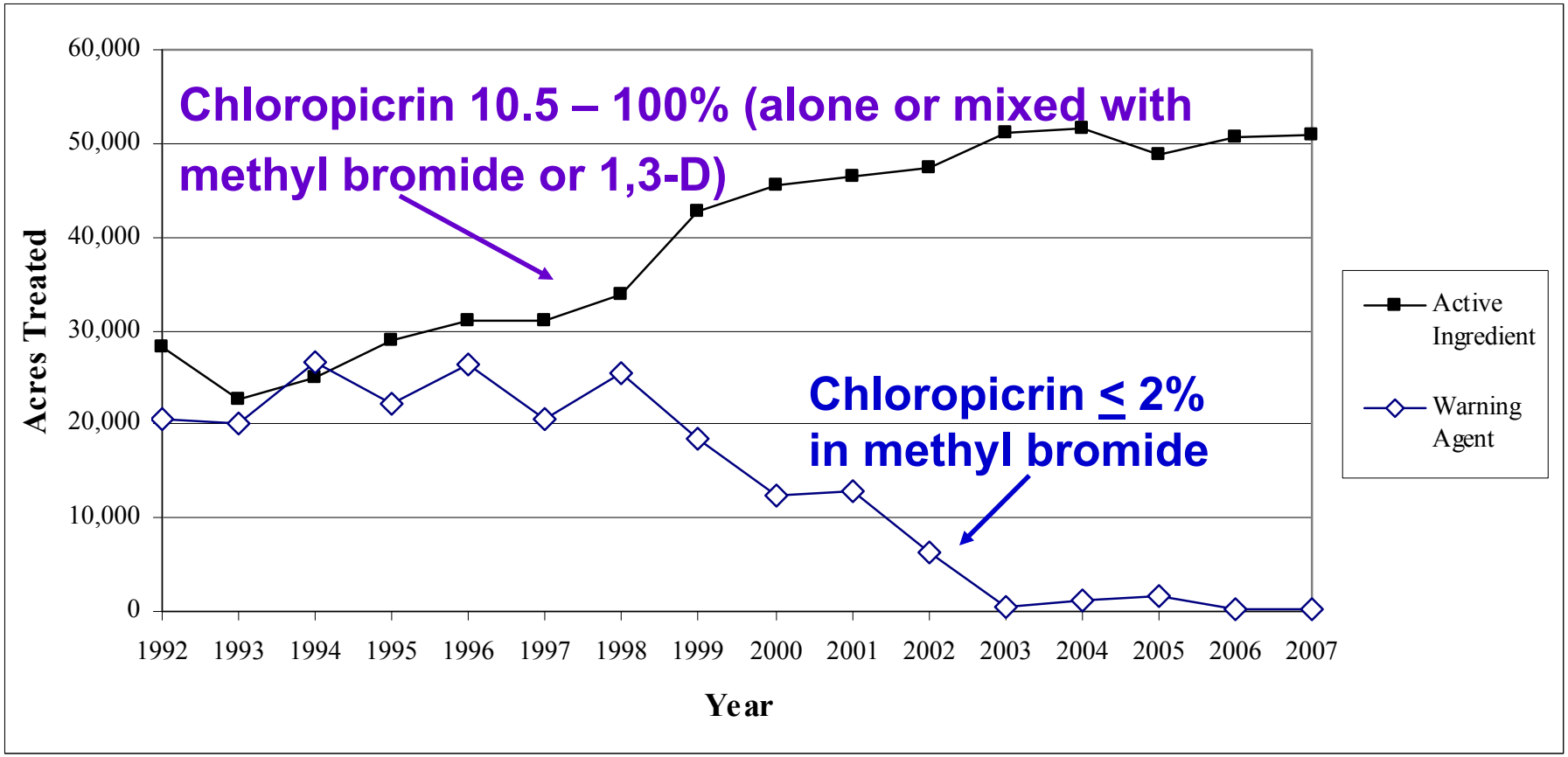
- Over the past 15 years, an average of **at least 68%** of use (lbs applied) was pre-plant for **strawberries**
  - Other top crops: nursery, tomatoes, berries, melons
  - Use approximately doubled between 1993 and 2003, hovered around 5 million lbs in 2003 – 2006, then increased to nearly 5.5 million in 2007



Warning Agent vs. AI in Soil Fumigations

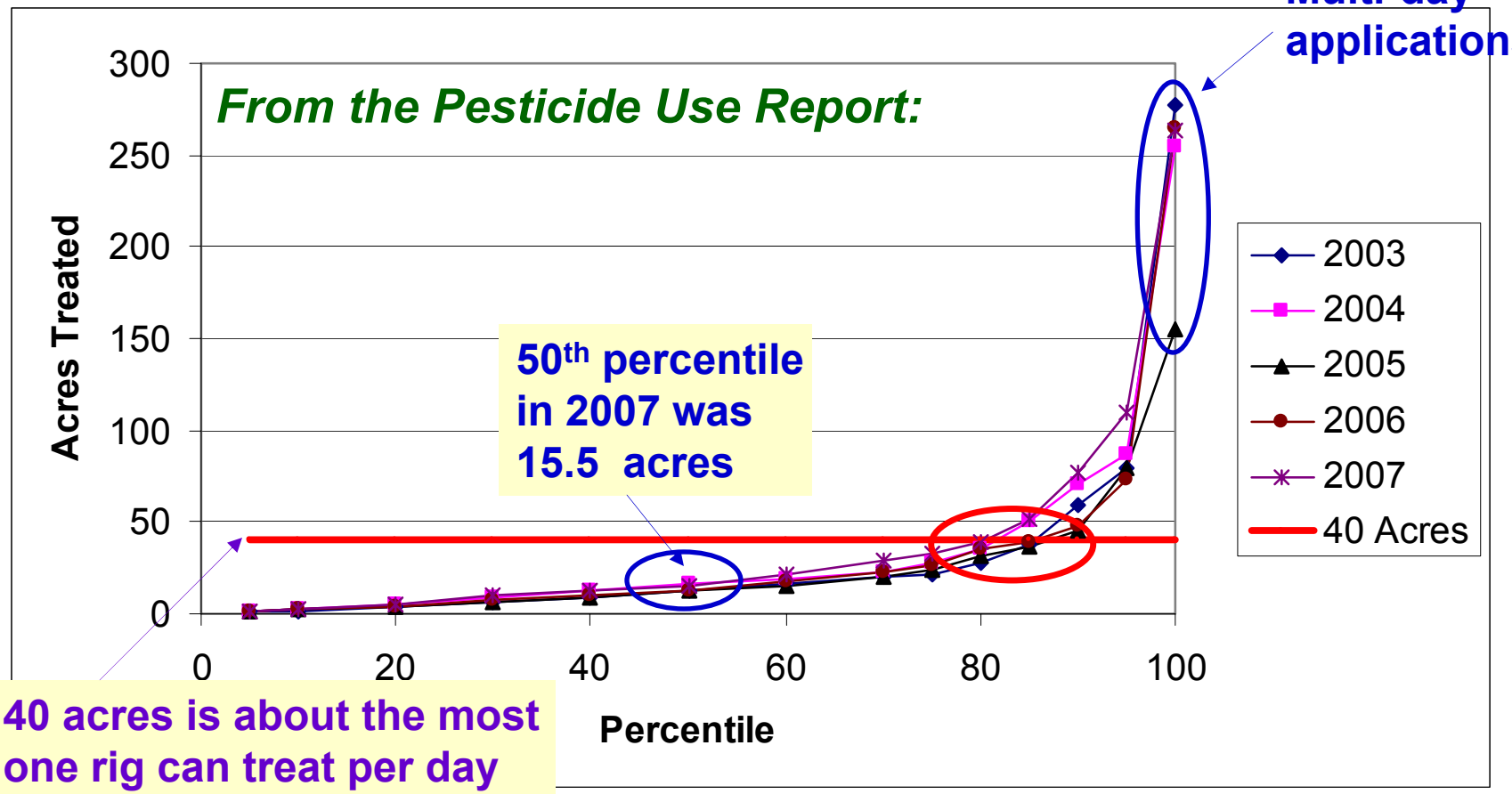
Warning agent use decreased with methyl bromide phase-out

- **Agricultural applications** reported in **acres treated**:



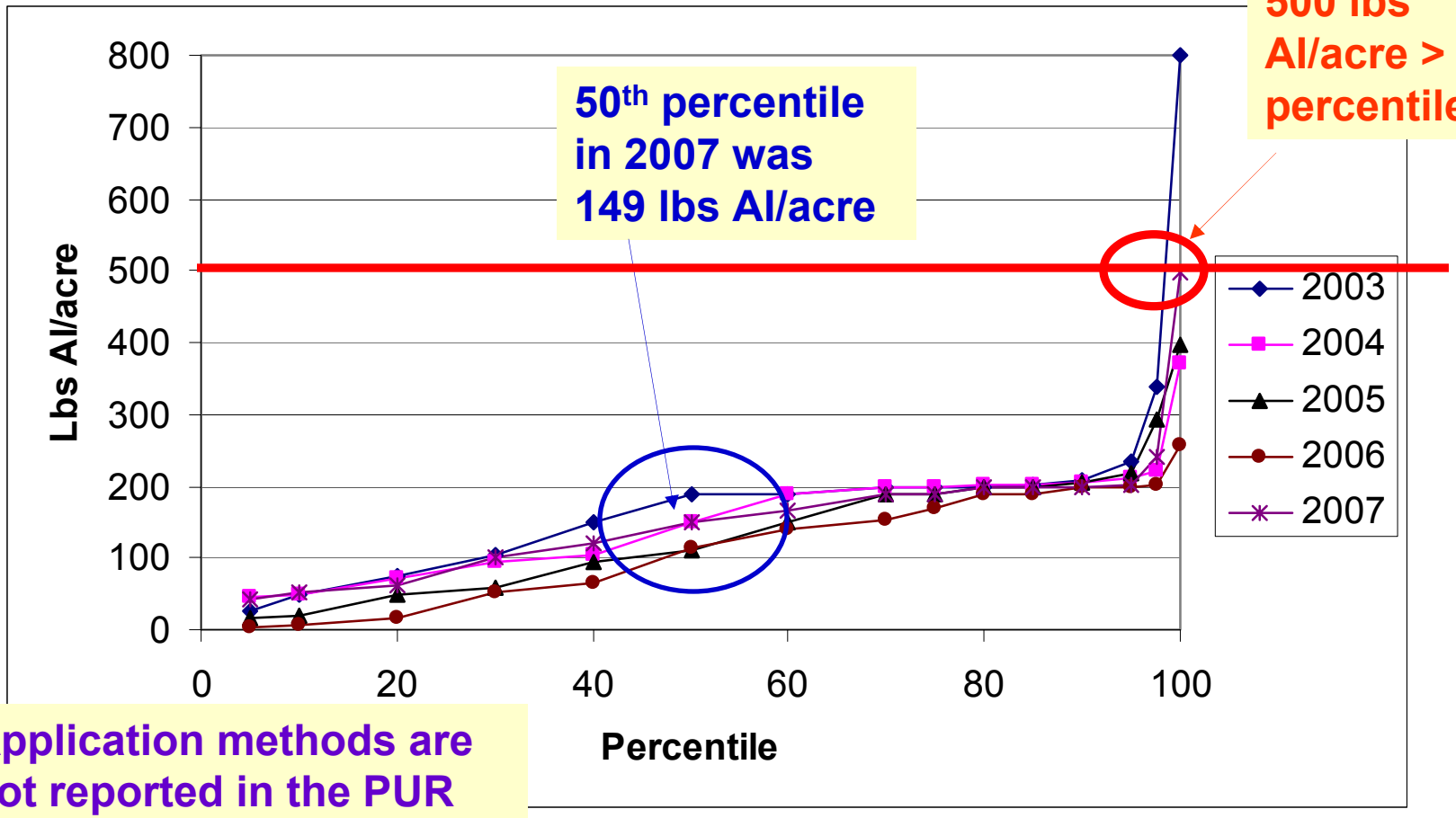
Acres Treated/Day (Reported in PUR)

- Applications reported as acres treated, chloropicrin ≥ 94%
- **40 acres** is at about the **80th - 85th percentile**



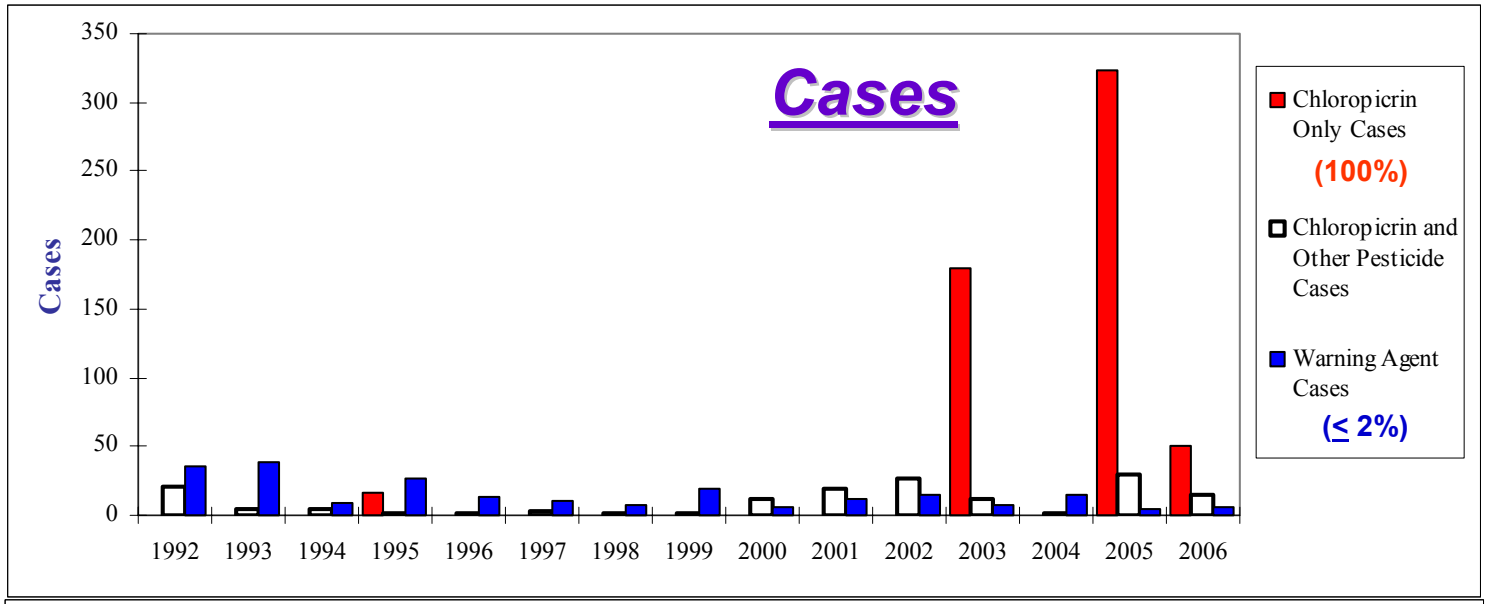
Application Rates (Reported in PUR)

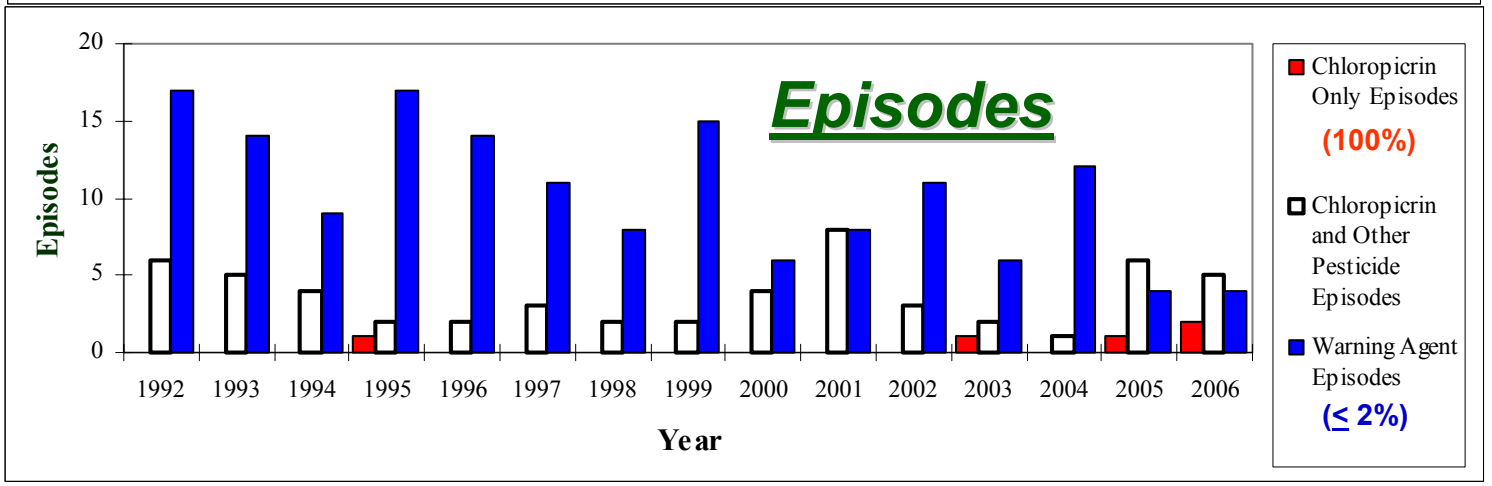
- Applications reported as acres treated, chloropicrin ≥ 94%
- **50th percentile** range: **111 – 188 lbs AI/acre**



Application methods are not reported in the PUR

Illnesses Associated with Chloropicrin



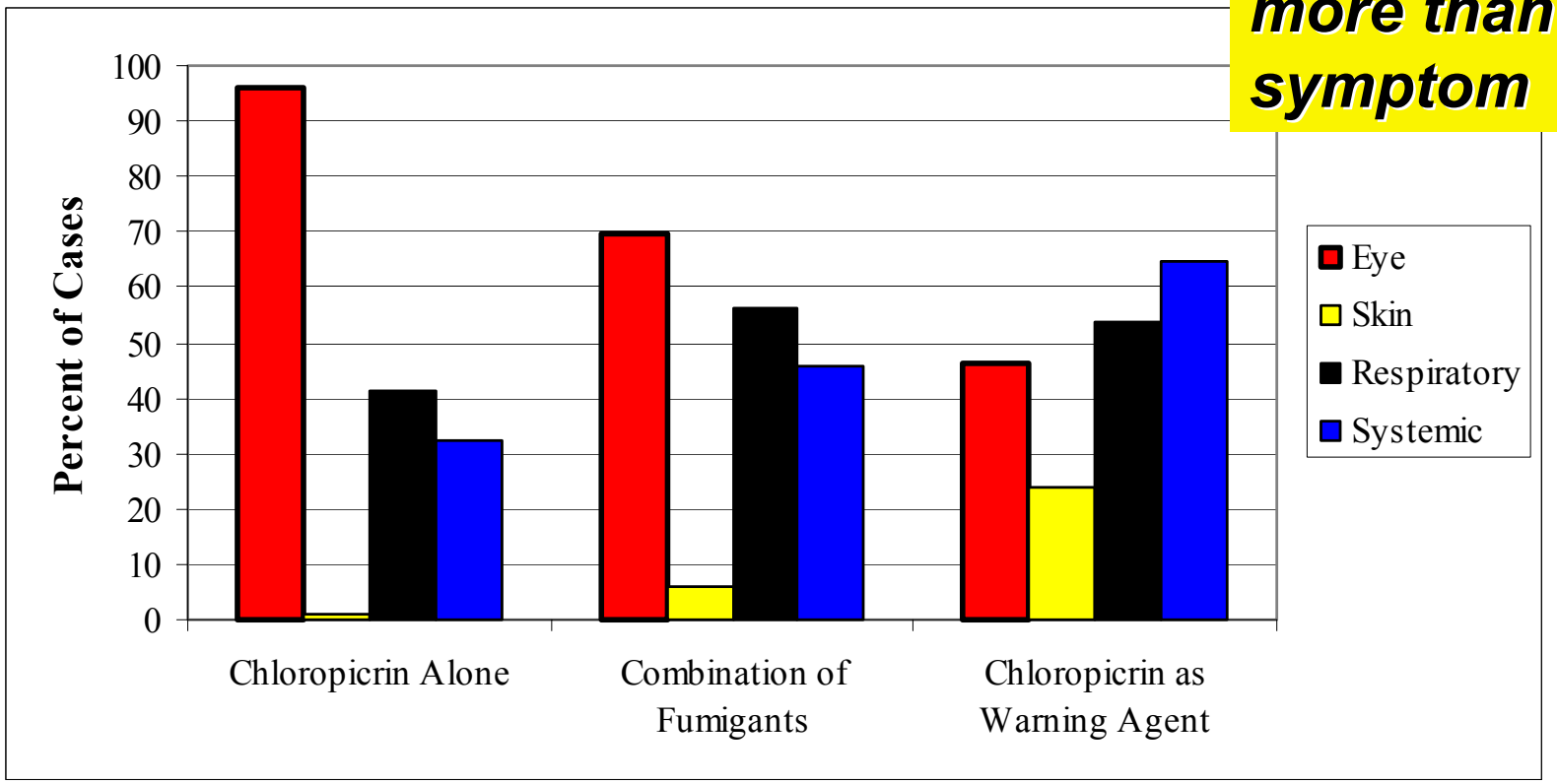


More than one case can be associated with each episode

Most cases in one episode: 324 (in 2005)

Percent of Illnesses (Cases)

560 of 1,015 cases reported more than one symptom



- Eye irritation most commonly associated with 100% chloropicrin use
- Skin and systemic symptoms most common with warning agent use

Environmental Fate

- After application, chloropicrin rapidly diffuses through the soil or structure in all directions
- **Volatilization** is the major pathway through which chloropicrin dissipates from soil
  - Over 2-week intervals, on average **61 – 69%** of chloropicrin applied by shank fumigation volatilized; **15%** of chloropicrin applied by tarped drip methods
  - Also degraded through biotic and abiotic reactions, with $T_{1/2}$ ~ 1 to 8 days in field studies
- Volatilized chloropicrin undergoes rapid photolysis by absorbing UV light
  - Predicted $T_{1/2}$ < 1 day in bright sunlight

Persistence in Soil

- Laboratory soil metabolism studies: **$T_{1/2} \leq 10$ d**
  - Longer in sterile soils (3 – 14 days vs. <1 – 4 days)
  - Longer in anaerobic and high-moisture soils
- Field dissipation studies reported degradation half-lives between 1 and 8 days
- Soil beneath a former manufacturing plant in Maine contained residues as high as 500 mg/kg 7 years after the plant was shut down
  - Suggests that in some cases residues may persist

Groundwater Contamination?

- Chloropicrin is on DPR's list of pesticides that could potentially contaminate ground water:
  - High water solubility: 2,000 mg/L at 25 °C
  - Low soil adsorption: K_{oc} = 25 cm^3/g
  - Hydrolysis $T_{1/2}$: probably > 191 days
- Between 1986 and 2003, a total of **1,719** well water samples were collected in 34 California counties: **No detects for chloropicrin**

Exposure Durations

- **Short-term**
  - Upper-bound estimate: want realistic worst case
  - **1 Hour:** Chloropicrin-associated irritation occurs rapidly
  - **8 Hours:** Occupational bystanders
  - **24 Hours:** Residential bystanders

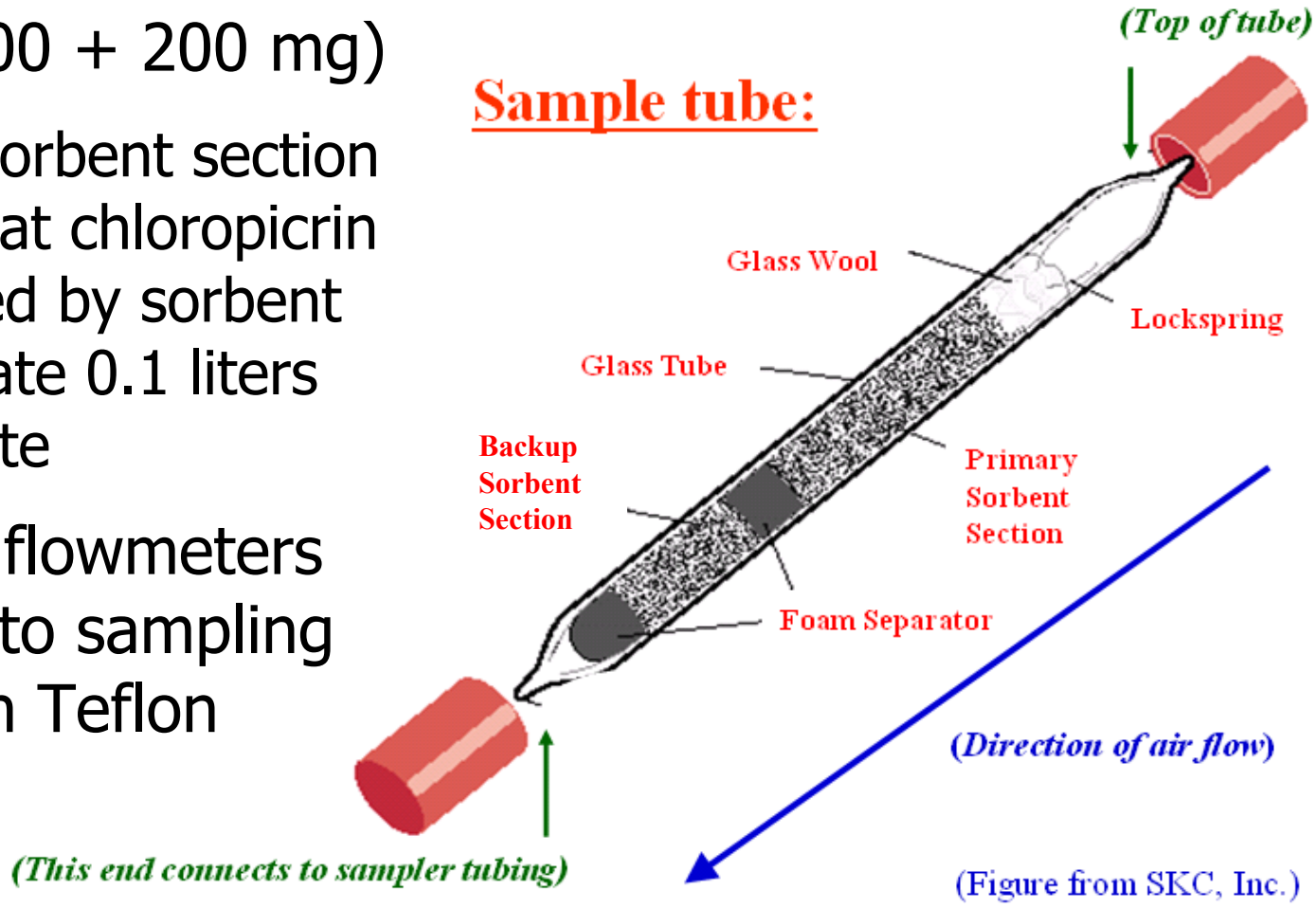
- **Seasonal**, **Annual** and **Lifetime**
  - In some agricultural areas, repeated exposure may occur from **multiple fumigations**
  - Want typical exposures – over longer intervals, individuals would not consistently have high-end exposures

Soil Fumigation Air Monitoring

- **California Air Resources Board (ARB)**
  - Ambient air and application off-site monitoring (summarized but not used to estimate exposure)
- **Chloropicrin Manufacturers Task Force (CMTF, registrants)**
  - Application site monitoring, **on-site** & off-site measurements (only **on-site** used to estimate exposure)
  - Two sets of studies (data from both were used):
    - Arizona, Florida and Washington in 1995-1996
    - California in 2003-2004

Air Samplers

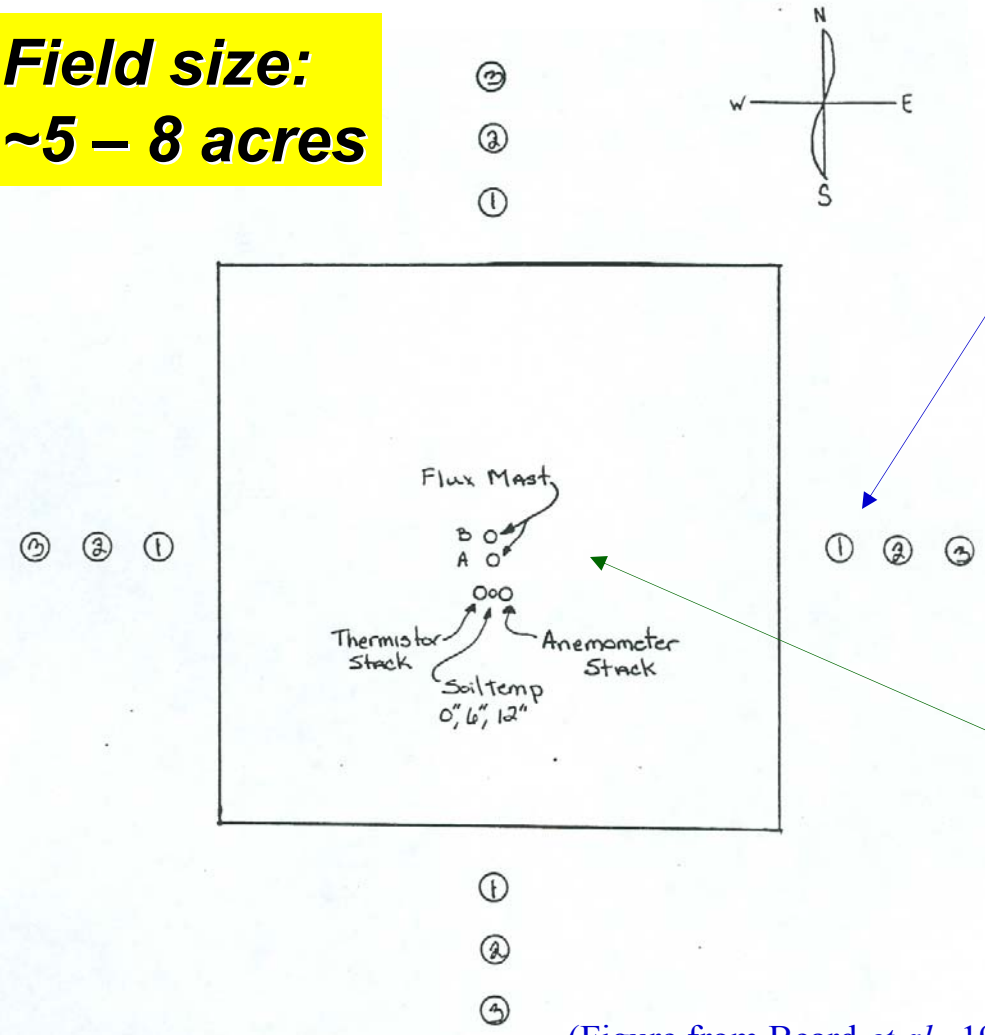
- Glass tubes with **XAD-4** sorbent (400 + 200 mg)
  - Backup sorbent section shows that chloropicrin is retained by sorbent at flow rate 0.1 liters per minute
- Tubes and flowmeters connected to sampling pumps with Teflon tubing

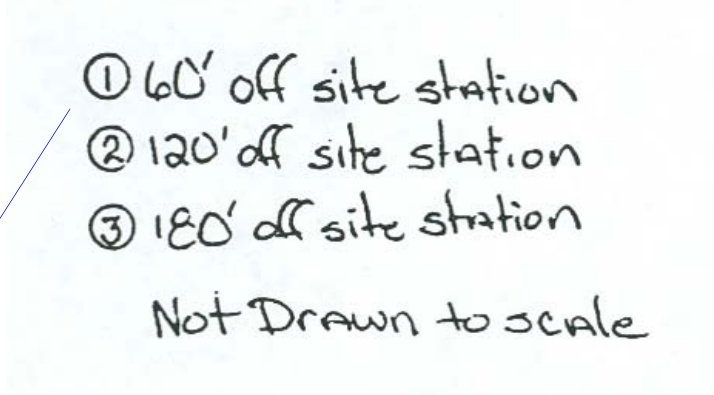


(Figure from SKC, Inc.)

CMTF: Sampler Locations

Field size:
~5 – 8 acres



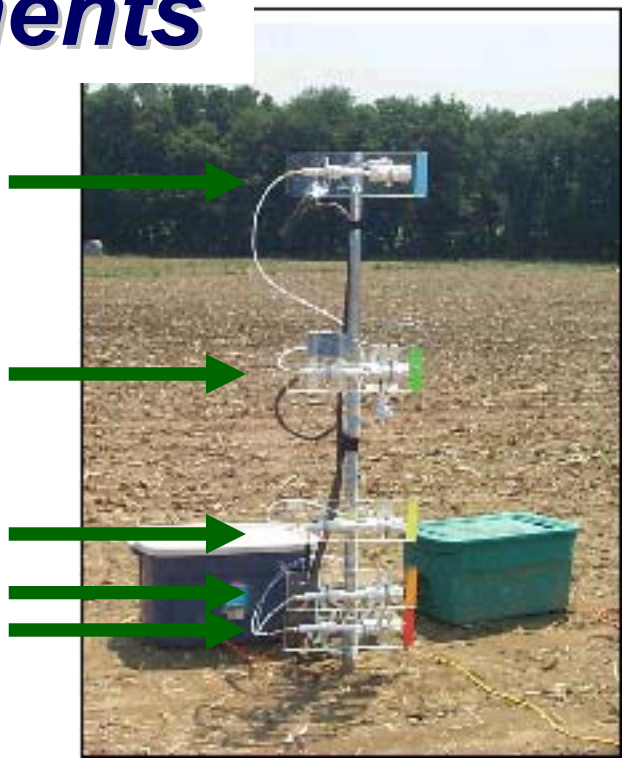


- **Off-site** samplers at 3 distances from field edge (none at edge)
  - Greenhouse (and ARB) had a single distance
- **On-site** samplers in center of field
  - ARB did not do on-site

(Figure from Beard *et al.*, 1996)

CMTF: On-Site Measurements

- Series of **air samplers** on a sampling mast at the field center
- Changes in air concentration, temperature, and wind speed with height used to calculate flux (Barry, 2008a)
- **Flux** is the amount of chemical emitted per unit area and time
  - Field volatility or emission rate



(USDA Photo from McConnell *et al.*)

- **Flux** can be used to calculate off-site concentrations
  - Results in more health-protective exposure estimates than obtained from off-site monitoring

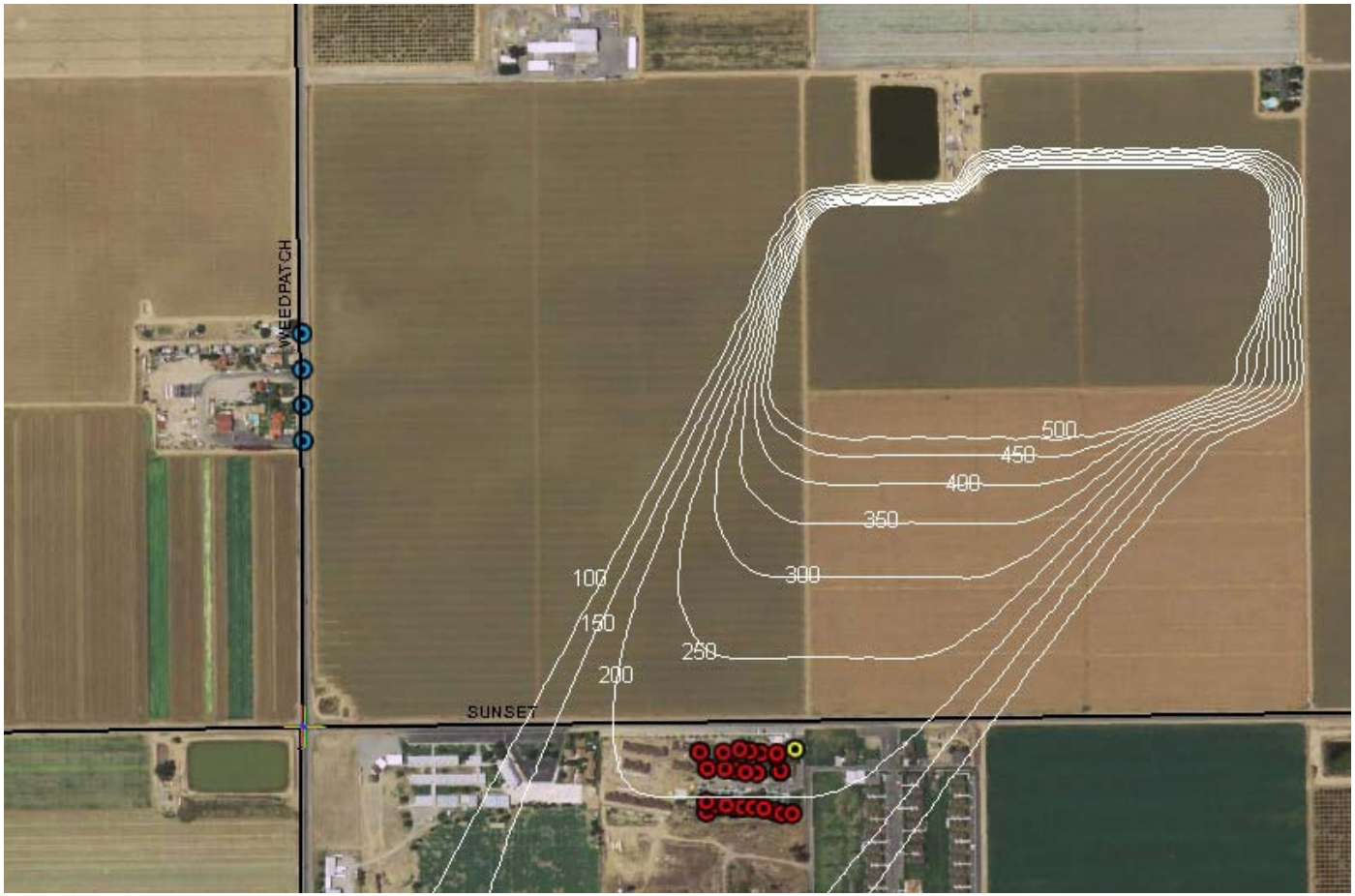
Air Dispersion Modeling

- Air dispersion models use emission information from one or more sources to estimate chemical air concentrations
- Gaussian Plume Model
- Gaussian Plume Model inputs:
  - **Field volatility** (**emission rate** or **flux**)
  - Dimensions and orientation of treated field, distance from field, urban or rural dispersion pattern
  - Temperature, wind speed, atmospheric stability
- Gaussian Plume Model Screening mode:
  - Model predicts the reasonable worst case **downwind** ground level concentrations that may occur off-site by examining a full range of meteorological conditions across all stability classes and wind speeds.

Off-Site Movement: Plume

Plume movement away from the field is affected by wind speed and direction, etc.

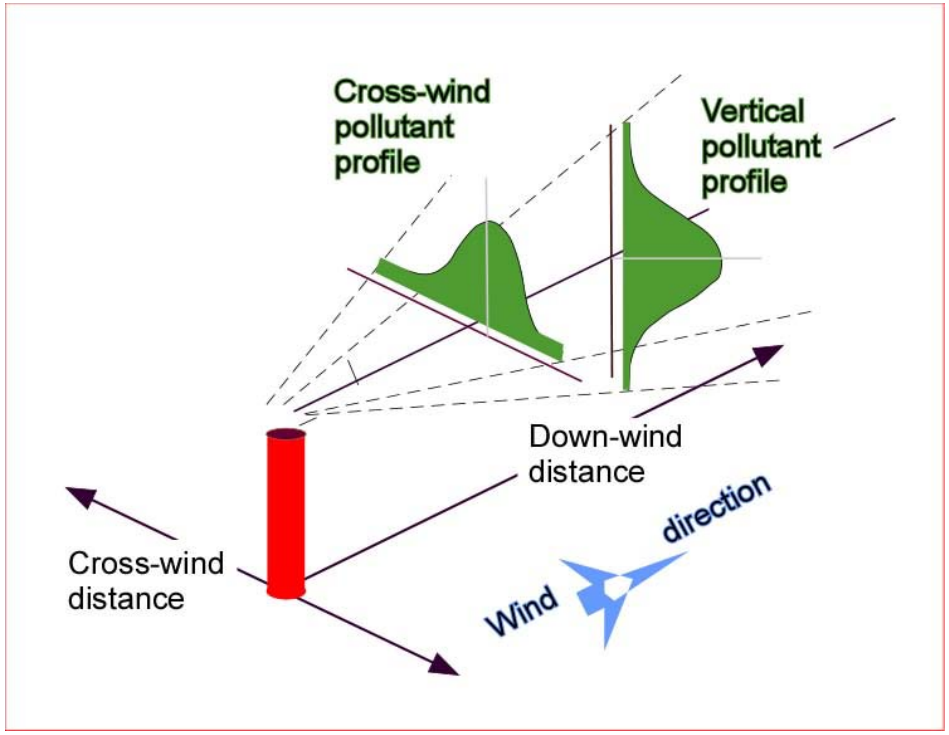
Off-Site Movement: Plume



The fumigant volatilizes, mixes with air and moves downwind.

DPR Uses the ISCST3 Model

Industrial Source Complex—Short Term, Version 3



(Figure from Univ of Colorado)

Features of ISCST3 model

- **Steady-state:** conditions do not change within a unit of time (e.g., 1 hour)
- **Gaussian plume:** chemical concentrations peak at center of plume, taper toward edges
  - Calculate concentrations along plume centerline

Computer Modeling

- Industrial Source Complex Short Term (ISCST3)
- Primary model used by DPR since 1992
- Gaussian plume model developed by U.S. EPA

$C = F \times M$

C = concentration (ug/m^3)

F = flux (ug/m^2s)

M = Function of x,y,z,meteorology (s/m)

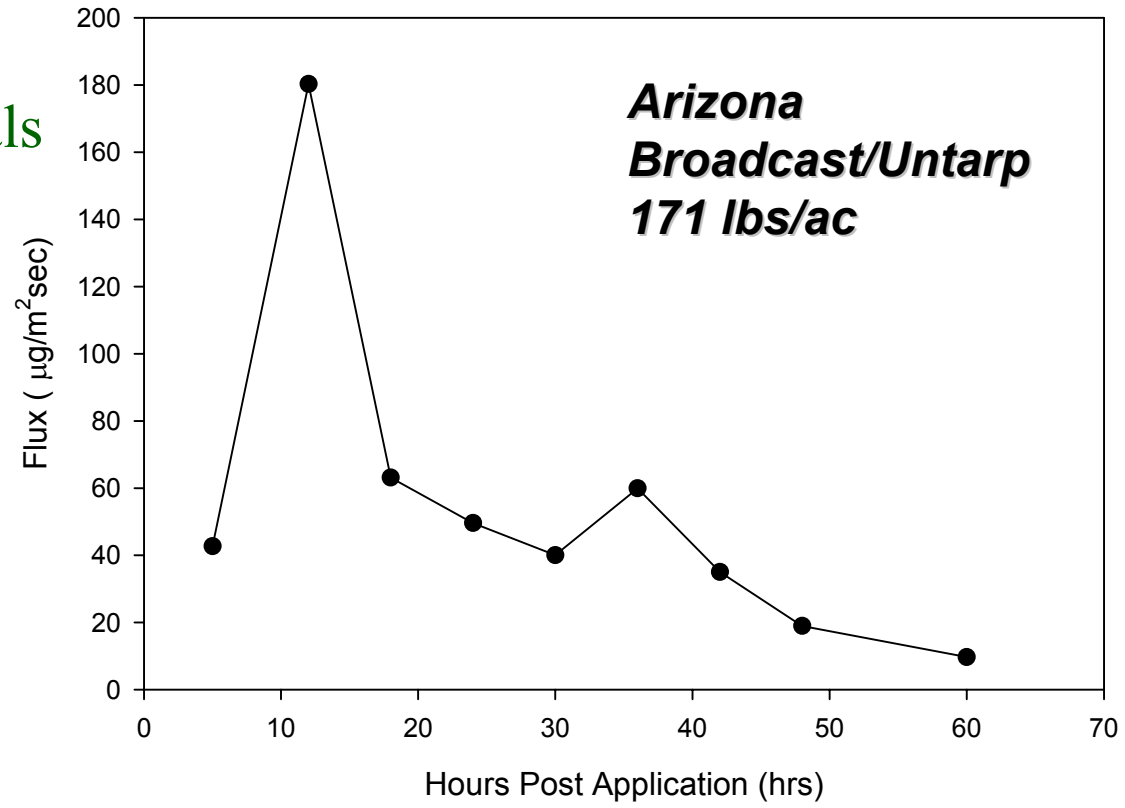
Computer Modeling

- Screening methods produce reasonable worst case air concentration estimates
- The averaging time of the air concentration is directly related to the averaging time that produced the flux estimate
- The meteorological data is considered the predominant condition for that averaging time
  - Screening meteorological conditions can and do occur in the environment
  - The wind direction is interpreted as the predominant (average) direction for the averaging time

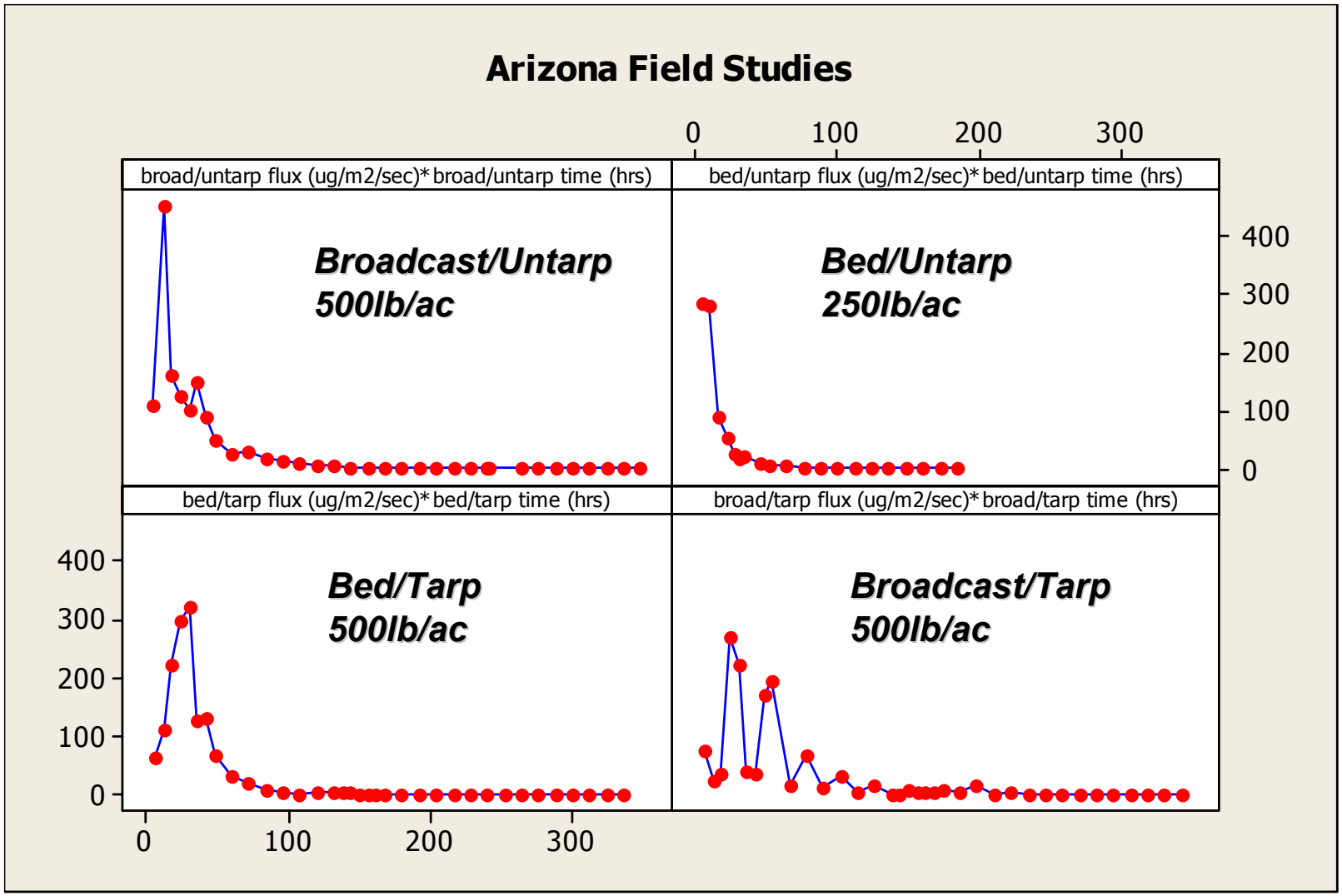
Example Flux Profile

First 9 Sampling Intervals

Each Interval = 6 hrs



Example Flux Profiles



Estimating 1-Hour Concentrations

- Shortest monitoring interval for flux in any chloropicrin study was **6 hours** (used for 8-hour exposure estimate)
- A mean concentration is the result of many short-term peak conditions and a definable relationship exists between the peaks and the mean (Singer 1961).
- Hino (1968) found that the definable relationship for air concentrations with sampling times between 10 minutes and 6 hours was the ratio of sampling times raised to the -0.5 power

Estimating 1-Hour Concentrations

- **1-hour** concentrations were estimated from the **6-hour** concentrations by employing the **peak-to-mean ratio** (Barry, 2000):

$$C_p = C_m(t_p/t_m)^{-1/2}$$

C_p = peak concentration over period of interest

C_m = mean concentration over measurement period

t_p = duration of peak period of interest (1-hour)

t_m = duration of mean measurement period (6 hours)

Thus:

$$C_{1hr} = C_{6hr}(1/6)^{-1/2} = 2.24^* C_{6hr}$$

Bystanders to Soil Fumigation

- **Short-term screening exposure estimates**: highest modeled concentration for each interval
- Assumptions: **40 acres** & **maximum** allowed application rate on current product labels (**500 lbs AI/acre**)

Duration	Concentration ($\mu g/m^3$)	Concentration (ppb)
1 Hour	**110,000**	**16,000**
8 Hours	**44,000**	**6,500**
24 Hours	**7,400**	**1,100**

For chloropicrin, ppb = (0.1487) x ($\mu g/m^3$)

For Context: 50th Percentile Exposures

- Highest modeled concentration per interval for bystanders **50 feet (15 m)** downwind from field edge
- Assumptions: **2007 - 50th percentile** application rate (**150 lbs AI/acre**) & acres treated (**15 acres**)

Duration	Concentration (µg/m³)	Concentration (ppb)
1 Hour	30,000	4,500
8 Hours	12,000	1,800
24 Hours	2,500	370

Concentrations summarized in Appendix 3

For Context: 50th %ile, ½-Mile Away

- Highest modeled concentration per interval for bystanders **½ mi (760 m)** downwind from field edge
- Assumptions: **2007 - 50th percentile** application rate (**150 lbs AI/acre**) & acres treated (**15 acres**)

Duration	Concentration (µg/m³)	Concentration (ppb)
1 Hour	**7,400**	**1,100**
8 Hours	**3,000**	**450**
24 Hours	**250**	**37**

Concentrations summarized in Appendix 3

Assumptions

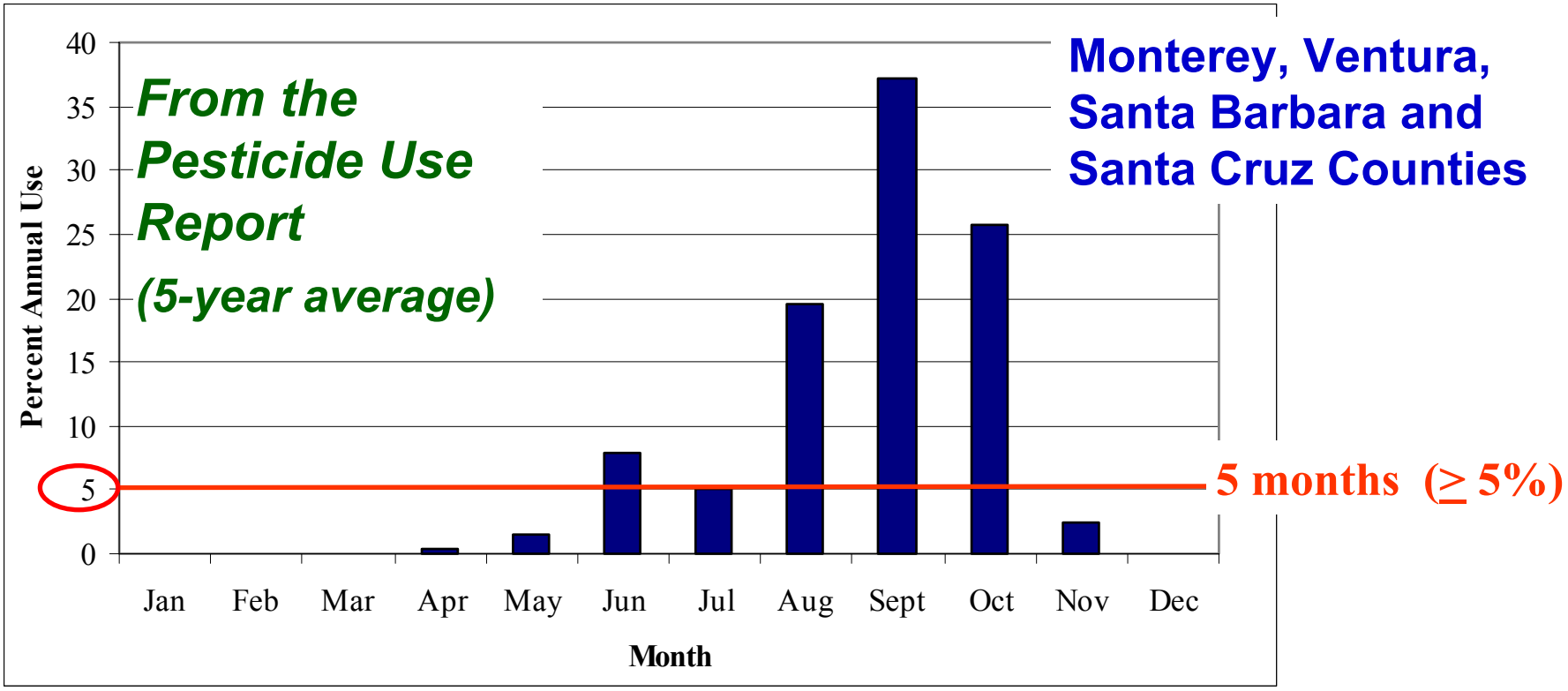
- **40 acres** treated/day is a practical maximum
  - If more than one rig is used, can treat more acres
  - PUR data suggest that 40 acres/day is about the 80th to 85th percentile of all applications (some of the applications reported in the PUR probably spanned multiple days)
- Adjustments for application rate assume that flux and concentrations are proportional to rate
  - Adjusted concentrations are outside measured range

Seasonal, Annual, Lifetime Exposures

- Monitoring in several of the CMTF studies spanned 2 weeks
  - Average 24-hour flux calculated over 2 weeks (Barry, 2008c)
  - Because wind direction is not constant over longer intervals, concentrations were adjusted with a time-scaling factor derived using peak-to-mean theory (Barry, 2008c)
  - Concentrations **not** adjusted for maximum rate
- Length of season approximated using PUR data from top 4 counties

Chloropicrin Use Pattern for Seasonal & Annual Bystander Exposures

- **Assumption:** Exposures are **less likely** during months when little use occurs (e.g., < 5% of total use each year)



Bystanders to Soil Fumigation

- **Intermediate- and long-term exposure estimates**: Seasonal exposure includes intervals of 1 week – 1 year
- Assumptions: **40 acres** treated & that applications occur about **every 2 weeks** over **5 months** each year
- Annual concentration = Seasonal concentration x (5/12 months)

Duration	Assumed Application Rate	Conc. ($\mu g/m^3$)	Conc. (ppb)
Seasonal	**350 lbs AI/acre**	**490**	**73**
Annual	**350 lbs AI/acre**	**200**	**30**
Lifetime	**150 lbs AI/acre**	**88**	**13**

Supported by registrants

50th percentile

Assumptions

- With the exception of application rate, assumptions of modeling are the same as for short-term estimates
  - 40 acres/day, distance from field, etc.
  - Not adjusted for maximum application rate, assuming that upper-bound exposures are less likely over a longer interval
- Multiple applications are possible, at least in 1-mi^2 sections
  - Frequent applications occur in some sections in Monterey County, as much as 38 days/year over a 5-month interval
  - PUR data only reported at section level; no data with better resolution are available

Structural Fumigation

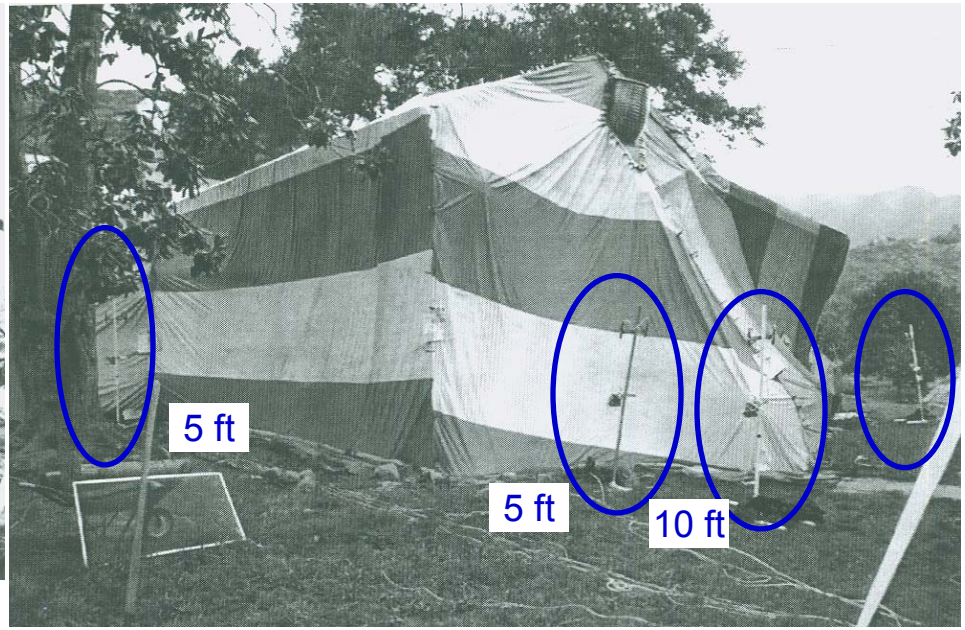
- Exposure estimates based on **measured** rather than **modeled** concentrations
  - 3 studies by ARB and one registrant study (highest chloropicrin concentrations were in this study)
- Amount of chloropicrin used is much lower for structural than soil fumigations
  - Chloropicrin is used only as a **warning agent** for structural fumigations
  - Smaller areas treated

(Photos from Texas A&M and Cardinal Products websites)

Barnekow and Byrne (2006)

(Registrant study)

- Monitored 8 fumigations, 2 in each of 4 houses
- A total of 32 outdoor samplers were set up around each house: 2 – 6 samplers on 4 corners and 4 sides
  - Also indoor samplers (discussed later)

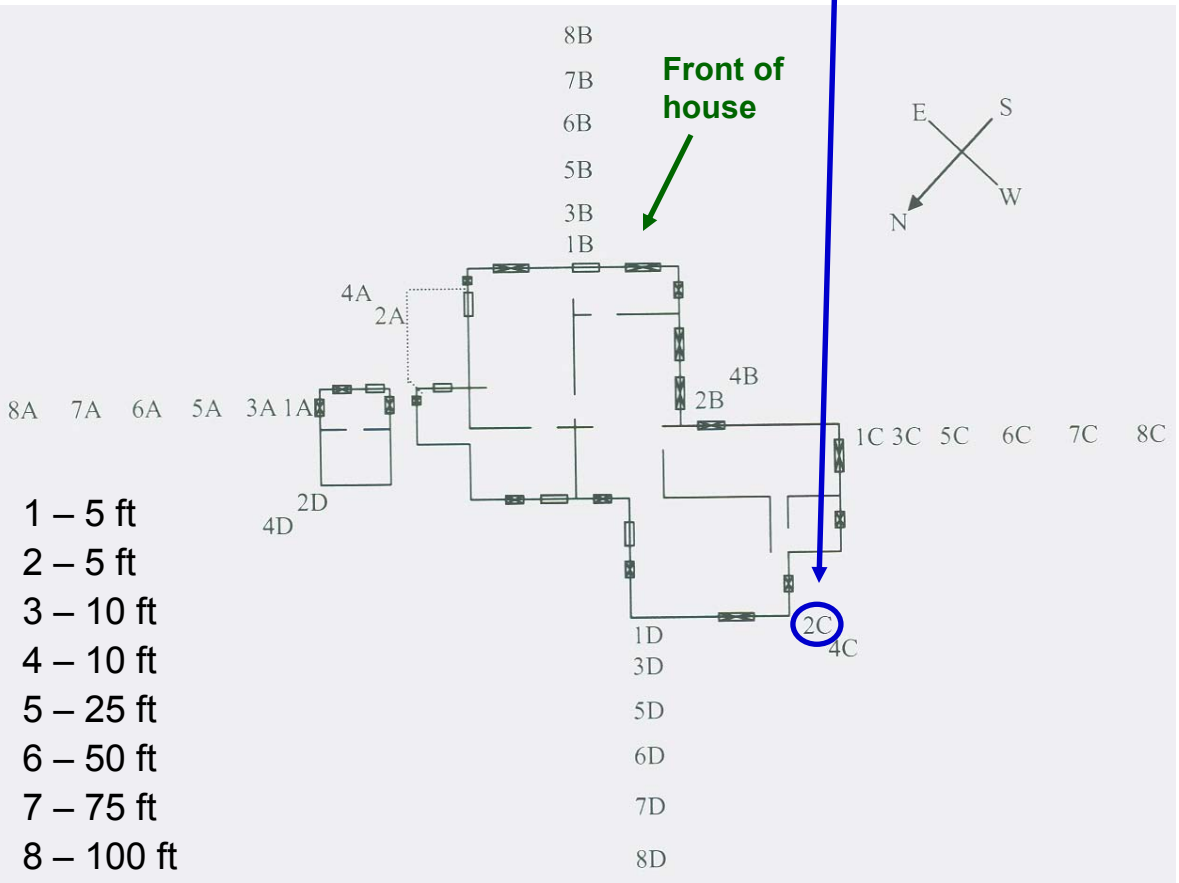


(Photos from Barnekow and Byrne, 2006)

Outdoor Samplers: Replicate 2

- Samples collected during 24-hour fumigation followed by 12-hour aeration
- **Highest outdoor chloropicrin concentrations** were measured following the 2nd fumigation of the first house, in Ventura County ~ 32,000-ft^3 (900-m^3)
- Highest concentration occurred during aeration at the sampler 5 ft west of house

244 µg/m³ (1-hour sample, 4th hour of aeration) at sampler located 5 feet from edge of house



(Figure from Barnekow and Byrne, 2006)

Bystanders to Structural Fumigation

- Results were adjusted for field spike recoveries (chloropicrin was used at maximum rate in the study)
- Seasonal, annual, or lifetime exposures are not anticipated

Duration	Concentration ($\mu g/m^3$)	Concentration (ppb)
1 Hour	**244**	**36.2**
8 Hours	**67.7**	**10.1**
24 Hours	**49.7**	**7.39**

Bystanders to Space Fumigation

- Chloropicrin can be used as an active ingredient to fumigate **enclosed spaces**
  - One product gives directions for use in fumigating empty potato storages and empty grain bins
  - U.S. EPA has received requests to **cancel** the enclosed space fumigation uses
- Maximum application rate: 0.7 lbs/1,000 ft^3 (0.3 kg/28 m^3)
- Assume twice per year: storage fumigated between crops, two crops per year
  - Annual = 24-hour concentration x (2 days/365 days)

Bystanders to Space Fumigation

- Annual and lifetime exposures assumed fumigation of potato warehouse twice each year, between crops
- No seasonal exposures (i.e., no durations 1 week - 1 year)

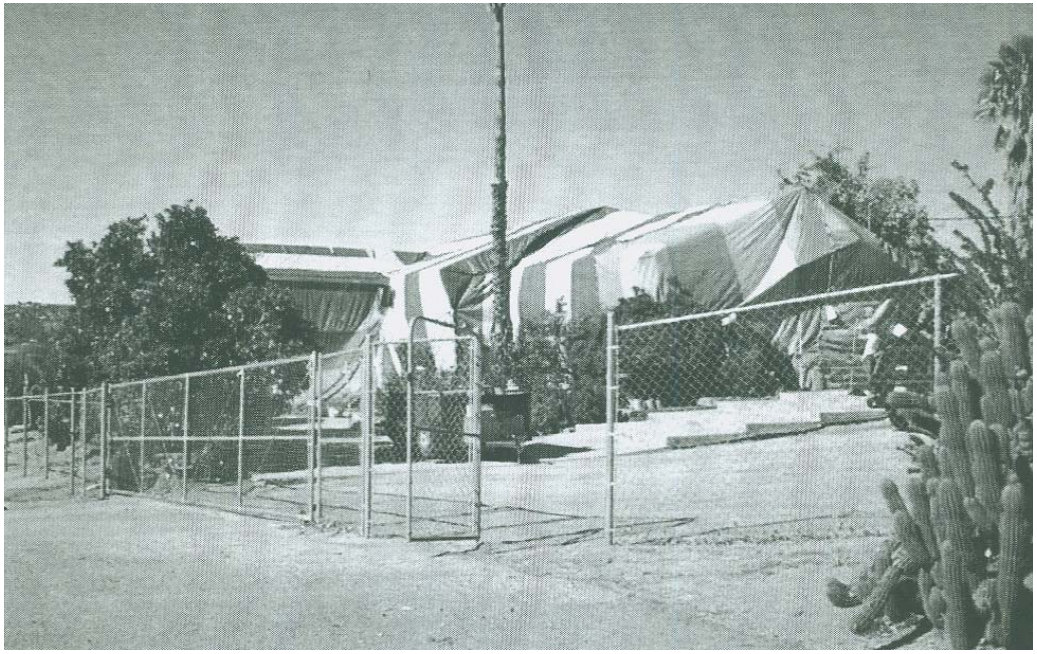
Duration	Concentration ($\mu g/m^3$)	Concentration (ppb)
1 Hour	**160,000**	**24,000**
8 Hours	**46,000**	**6,800**
24 Hours	**34,000**	**5,000**
Annual	**190**	**28**
Lifetime	**190**	**28**

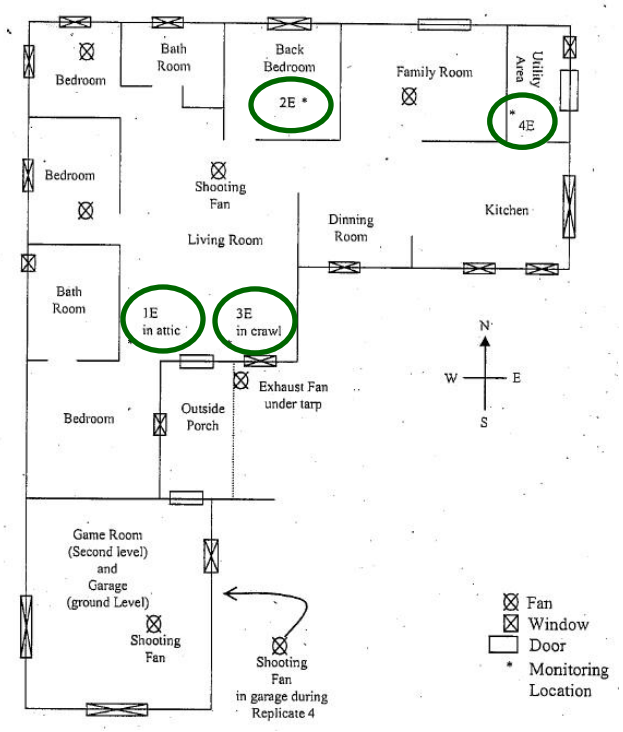
Bystander Exposures Associated with Structural/Space Fumigation

- Concentrations were based on measured off-site data, not modeling; measured concentrations are expected to be health-protective
  - Samplers were about as close to application as nearest likely bystander would be – as close as 5 feet (1.5 m)
- Corrected for field spike recovery
  - No adjustment for application size, but in all structural fumigation studies house size did not appear to correlate with off-site concentrations.

Indoor Air Concentrations

- Barnekow and Byrne (2006) collected indoor air samples at 4 locations for up to 36 hours **post-aeration** (no indoor samples during fumigation or aeration)
- These post-clearance samples represent **residents reentering a treated structure**





(Photo and figure from Barnekow and Byrne, 2006)

Indoor Air Concentrations

- Highest concentrations were in Replicate 4 (1 hour) and Replicate 5 (8 hours and 24 hours)
- Results were adjusted for field spike recoveries
- Seasonal, annual, and lifetime exposures are not anticipated

Duration	Concentration ($\mu g/m^3$)	Concentration (ppb)
1 Hour	**3,060**	**456**
8 Hours	**1,230**	**183**
24 Hours	**1,160**	**172**

Questions?

(WHS/DPR Photo)