Alternative Methods for Obtaining Field-Relevant Emission Estimates

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- Dow Agrosciences, LLC
- California Strawberry Commission
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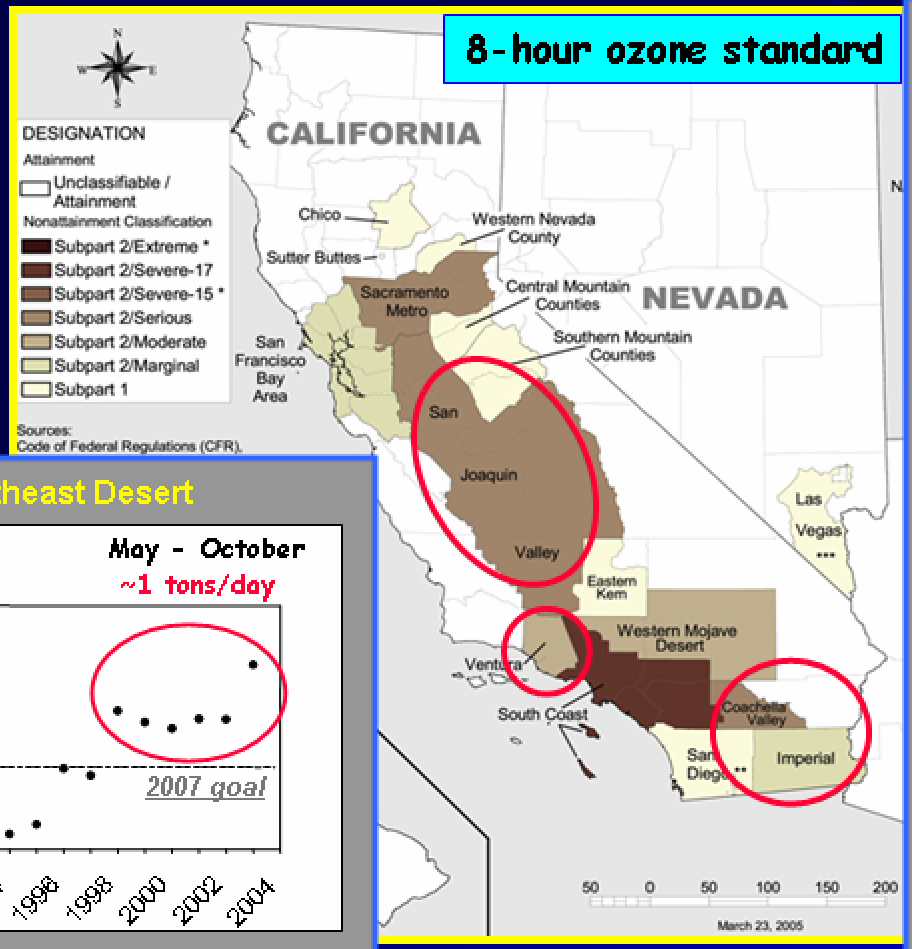
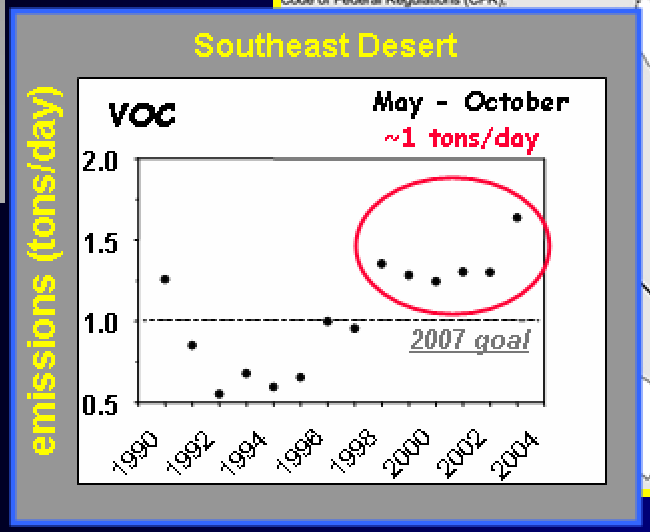
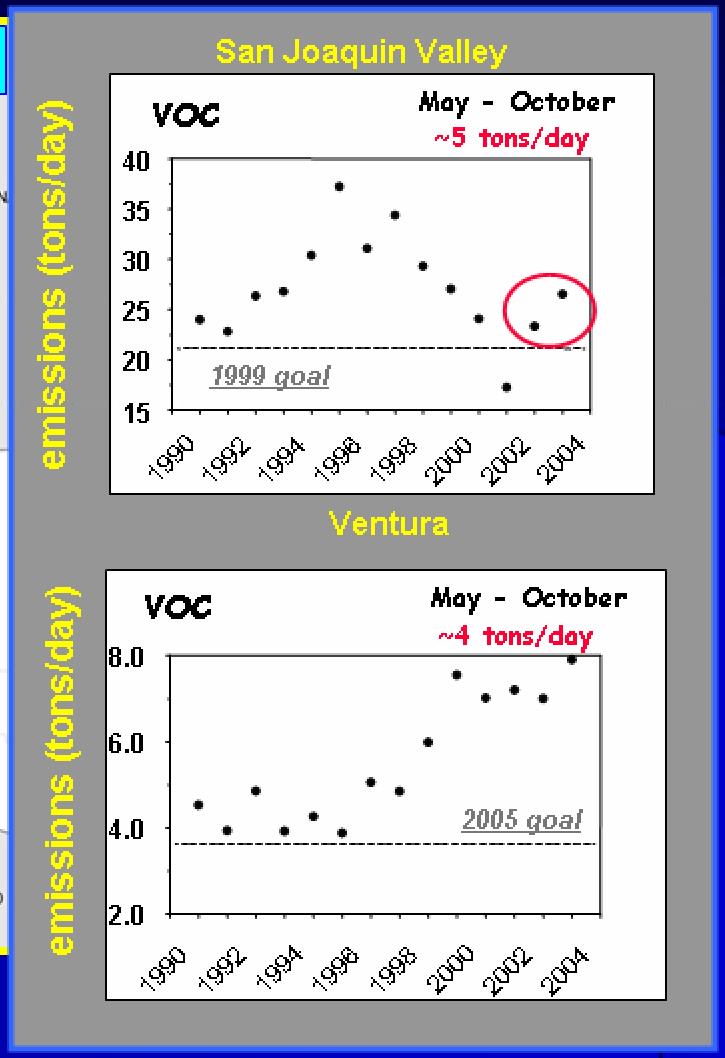
NAAQS Non-attainment Areas (O_3)







Emission estimates and pesticide use report data

Major VOC Sources (San Joaquin Valley, 2004)

	Source	Emissions, %
	Livestock Waste (Dairy Cattle)	9.6
✓	Light And Medium Duty Trucks	9.1
✓	Light Duty Passenger Cars	8.3
	Prescribed Burning	7.5
✓	Oil And Gas Production	7.4
	PESTICIDES	6.3
✓	Consumer Products	6.2

Data from www.cdpr.ca.gov (R. Segawa)

- 54% of all sources
- 12% of listed sources

Pesticide Chemical	Million Pounds Used
1. Sulfur	53.61
2. Petroleum Oil	17.67
3. Metam-Na	15.52
4. Methyl Bromide	6.59
5. Glyphosate	5.63
6. Telone	5.41
7. Mineral Oil	5.04
8. Chloropicrin	4.34
9. Sulfuryl Fluoride	3.05
10. Copper Sulfate	2.92
Soil Fumigants	32 M

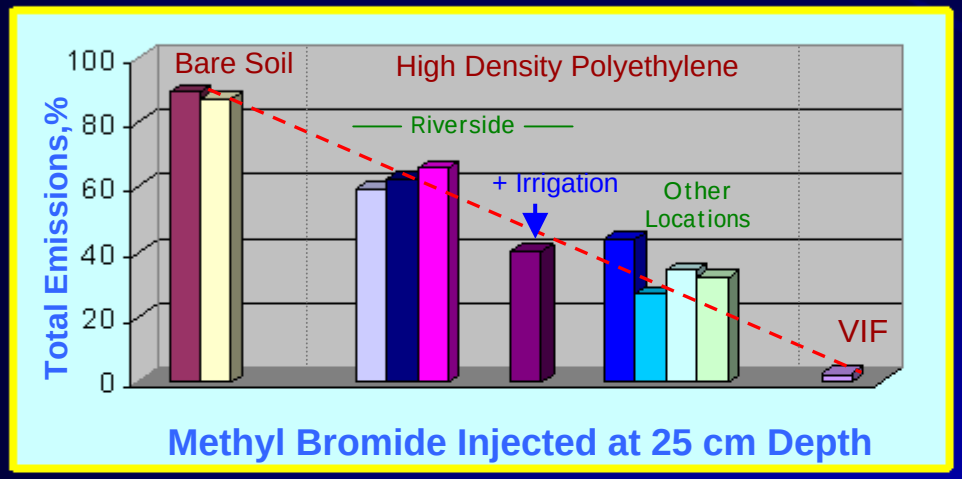
- 44 tons/day

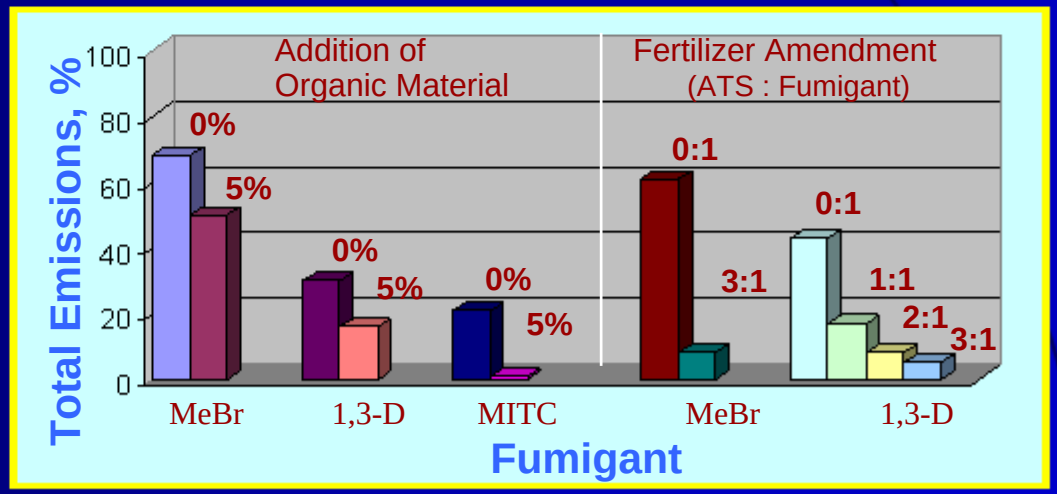
Research Available

- Emission rates and ratios (field, plot, laboratory).
- Understanding of processes and mechanisms affecting fumigant/pesticide fate and transport.
- Methods to reduce emissions have been developed:
  - Improved Containment (i.e., VIF tarps, water seals, compaction, etc.)
  - Soil Amendments (i.e., Organic matter, thiosulfate, thiourea, etc.)
  - Improved Delivery (drip application, improved shank, etc.)
- Improved transport models have been developed.
- Investigate the uncertainties of large-scale field experimentation and compare to the uncertainties of simplified experimental methodologies and modeling.

Current Activity

Fumigant Emissions In the Field





Goals

- Show an example of how experimental error and uncertainty can introduce artifacts into regulations.
  - Artifacts make rules appear theoretically incorrect, arbitrary and ineffective
- Demonstrate that simple experimental methods can provide meaningful fumigant emission estimates.
- Demonstrate that mathematical models provide meaningful fumigant emission estimates.
- Show that the uncertainties of large-scale field experiments are equal or greater than the differences in emissions estimates from simple experimental methods and modeling.

GUIDANCE MANUAL **12/8/04**
Methyl Bromide (With Chloropicrin)
Field Soil Fumigation

TABLE 1. METHYL BROMIDE FIELD SOIL FUMIGATION METHODS AND EMISSION RATIOS

Each methyl bromide fumigation must conform to all requirements specific to a Fumigation Method listed below. An applicator may not "mix-and-match" the requirements of two or more fumigation methods. Equipment and fumigation requirements are described in section 6450.3(a).

Section 6450.3(a)	Fumigation Method	Injection Type	Injection Depth (in.)	Injection Spacing (in.)	Tractor Implements	Dilution Fan	Max Rate (lbs/ac)	Emission Ratio
(1)	Nontarp/Shallow/Bed	Rearward chisel	10 - 15	40 or less	Closing shoes & bed shaper *	Yes	200	0.40
(2)(B)1	Nontarp/Deep/Broadcast	Forward chisel	20+	68 or less	None	Yes	400	0.40
(2)(B)2	Nontarp/Deep/Broadcast	Forward chisel	24+	68 or less	Closing shoes, compaction roller	No	400	0.40
(3)(B)1	Tarp/Shallow/Broadcast	Horizontal V-shaped blades	10 - 15	12 or less	None	Yes	400	0.25
(3)(B)1	Tarp/Shallow/Broadcast (STRIP FUMIGATION)**	Horizontal V-shaped blades	10 - 15	12 or less	None	Yes	400	0.40
(3)(B)2	Tarp/Shallow/Broadcast	Rearward chisel	10 - 15	12 or less	Closing shoes, compaction roller	No	400	0.80
(4)(B)1	Tarp/Shallow/Bed	Rearward chisel	6 - 15	12 or less	Closing shoes, compaction roller	No	250	0.80
(4)(B)2	Tarp/Shallow/Bed	Rearward chisel	6 - 15	12 or less	Bed shaper	No	250	0.80
(4)(B)3	Tarp/Shallow/Bed	Rearward chisel	6 - 15	12 or less	Bed former and bed shaper	No	250	0.80
(5)(B)1	Tarp/Deep/Broadcast	Forward chisel	20+	66 or less	None	Yes	400	0.25
(5)(B)1	Tarp/Deep/Broadcast (STRIP FUMIGATION)**	Forward chisel	20+	66 or less	None	Yes	400	0.40
(5)(B)2	Tarp/Deep/Broadcast	Forward chisel	20+	66 or less	Closing shoes, compaction roller	No	400	0.25
(5)(B)2	Tarp/Deep/Broadcast (STRIP FUMIGATION)**	Forward chisel	20+	66 or less	Closing shoes, compaction roller	No	400	0.40
(6)	Drip System-Hot Gas	Drip tubing	1+	NA	NA	NA	225	1.0

* Optionally, closing shoes and a compaction roller can be used.
** Similar to bed fumigations, strip fumigations have alternating treated and untreated rows. In many cases, the untreated sections are fumigated on a later date.

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Artifacts

Lower emissions for bare soil?

No effect from deep injection?

Higher emissions for strip fumigation?

The emission ratio from all types of fumigation in California can be reduced to one of 4 levels (*i.e., 25, 40, 80 and 100%*).

Why Field Experiments Aren't Definitive

Variations in Field Conditions (Space & Time)

- soil & environmental conditions, application methods
- generalization from field to regional scales
- even adjacent fields

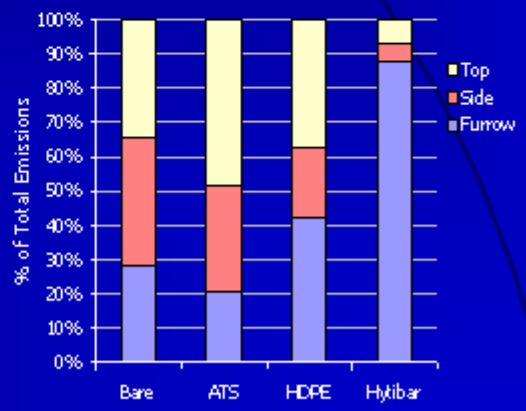
Cultural Factors

- fumigation type, tarp material, pre- and post management

Changes in Emission Patterns

- modifications to fumigation can lead to changes in emission pattern
- measurement method important

Propargyl Bromide



Why Field Experiments Aren't Definitive

Uncertainty in Methods to Obtain Flux

- experimental uncertainty (measurement/analysis)
- mathematics of the flux model
  - basic assumptions, approach
- variability and changes in surface conditions
- site disturbance during sampling

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Other sources of Uncertainty

- supplied materials (i.e., HDPE, SIF, VIF, etc)

Beware!

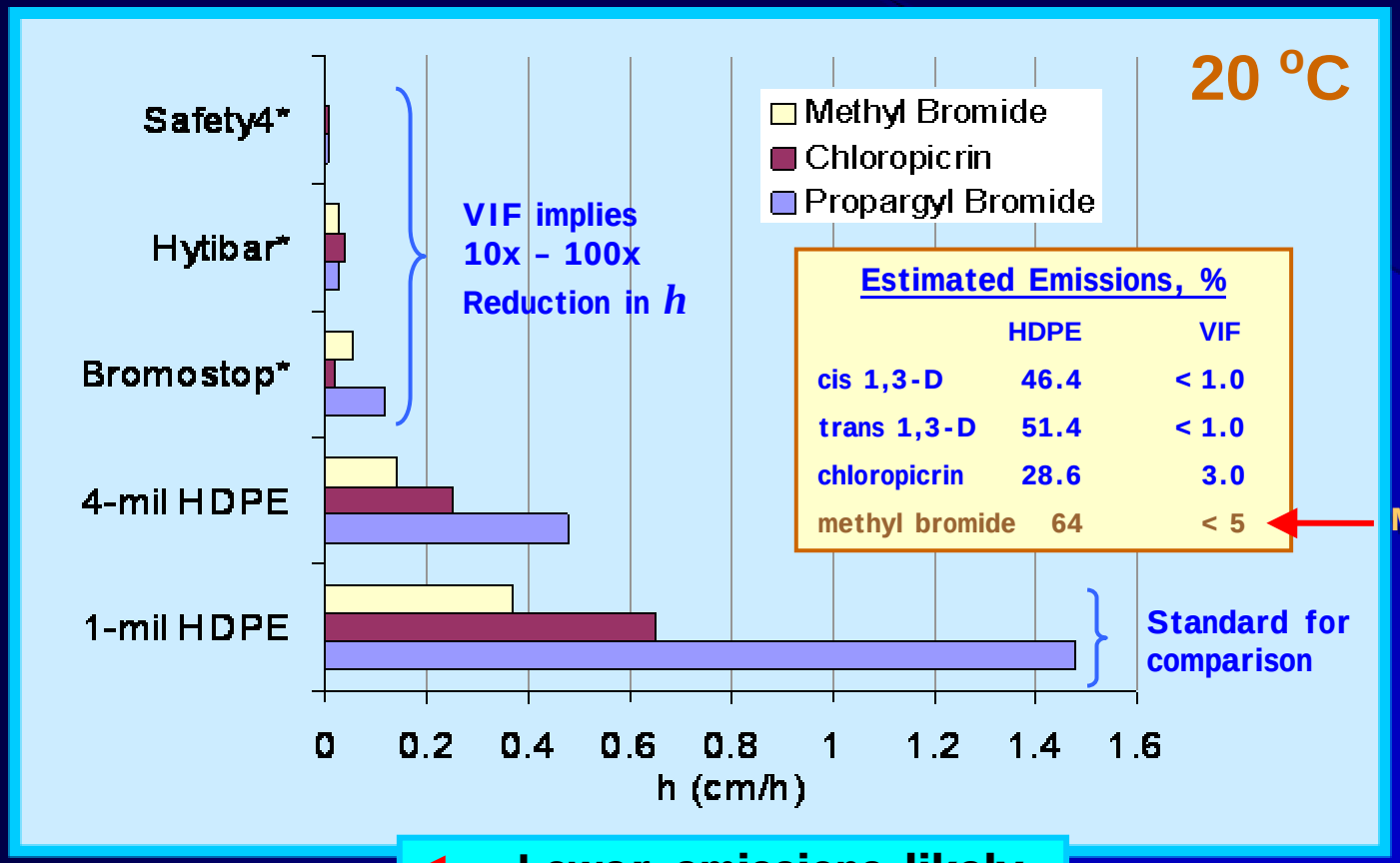
Film Permeability (mass transfer coefficient, cm/hr)

Film type	¶ HDPE	HDPE	HDPE	SIF	VIF	VIF	Estimated* emissions, %
cis	–	–	3.2	3.8	3.0	2.7	58.6 – 62.4
trans	–	–	5.5	5.9	4.7	4.8	66.6 – 68.8
chloropicrin	1.1	1.9	1.2	1.2	0.84	0.97	32.5 – 43.8

¶ Embossed

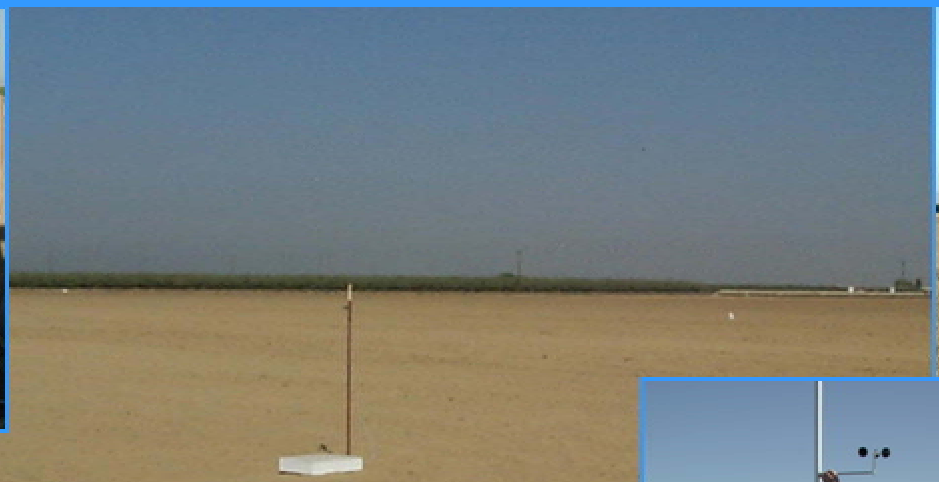
* For a shallow shank injection

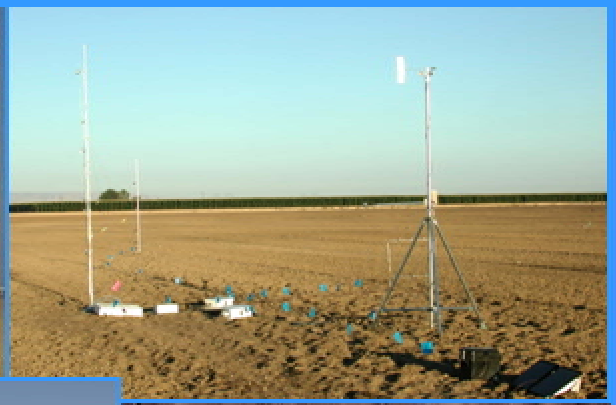
What is *h* for a Virtually Impermeable Film?



Lower emissions likely

Field Experiments are Necessary





Methods are highly developed

- Aerodynamic method
- Integrated horizontal flux
- Theoretical profile shape
- Eddy correlation/accumulation
- Residual mass
- Back calculation (ISCST3)

Experiments are expensive

Methods are complex and time consuming

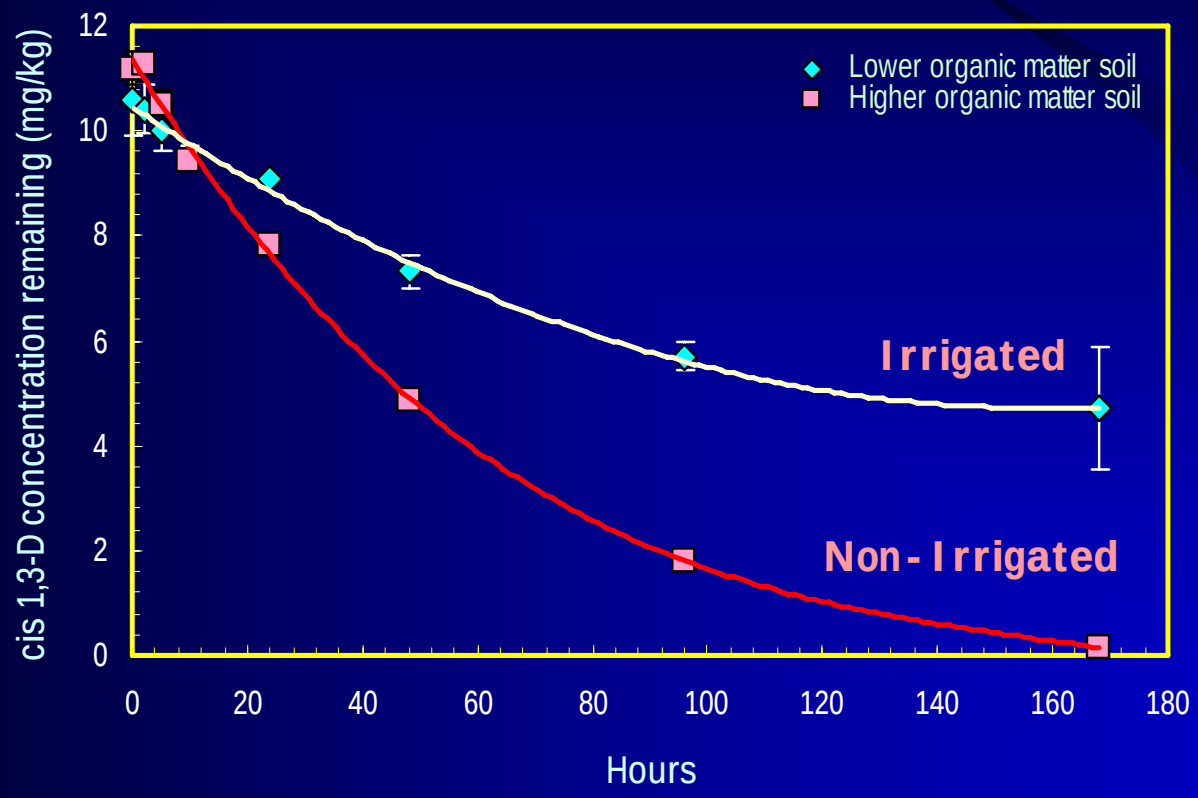
Large experimental uncertainty

Field Site Near Buttonwillow, CA

Variability

Winds

Soil Degradation



Variations in organic matter affecting degradation rate

Study Goals

a) Obtain cumulative and period (e.g., hourly) emission rates for standard and an emission reduction method
   - traditional sealing vs. intermittent water seals,
   - traditional sealing vs. surface amendment (e.g., thiosulfate),
   - to be determined

b) Compare methods to estimate emissions

c) Determine the accuracy of the back-calculation method

d) Determine effectiveness of emission-reduction strategies

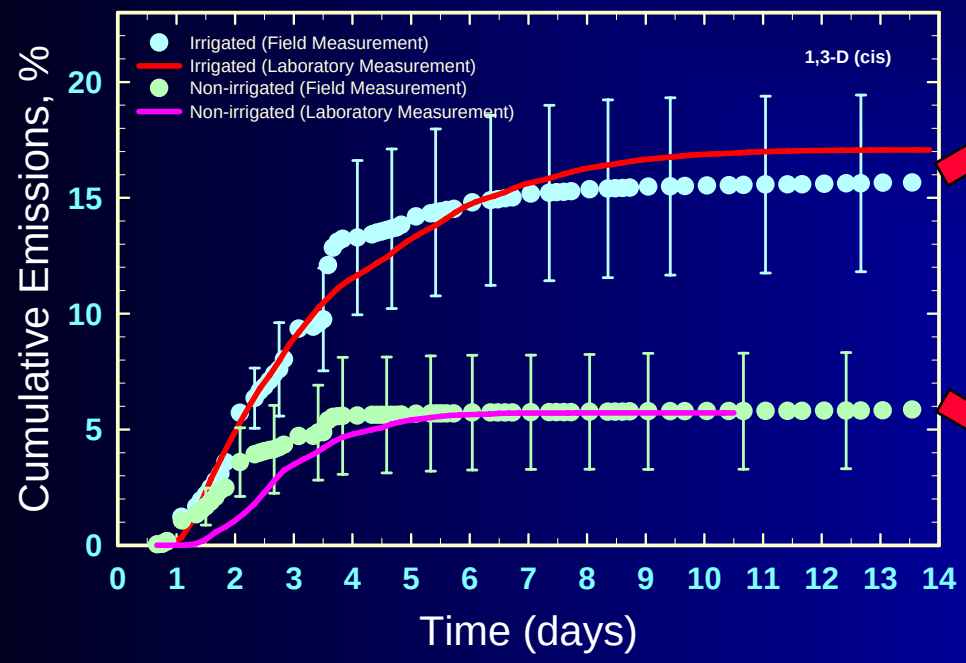
e) Collect data to allow, future, numerical simulation

f) Verify field results by conducting laboratory experiments

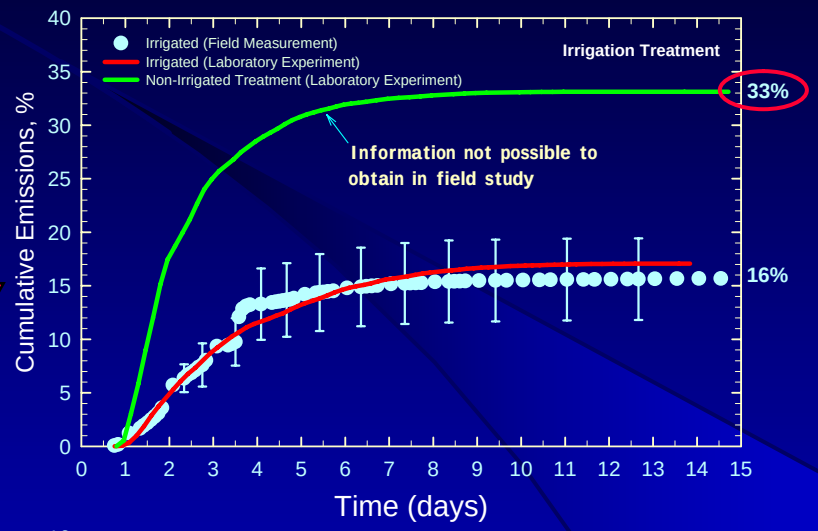
g) Extend field results by conducting laboratory experiments

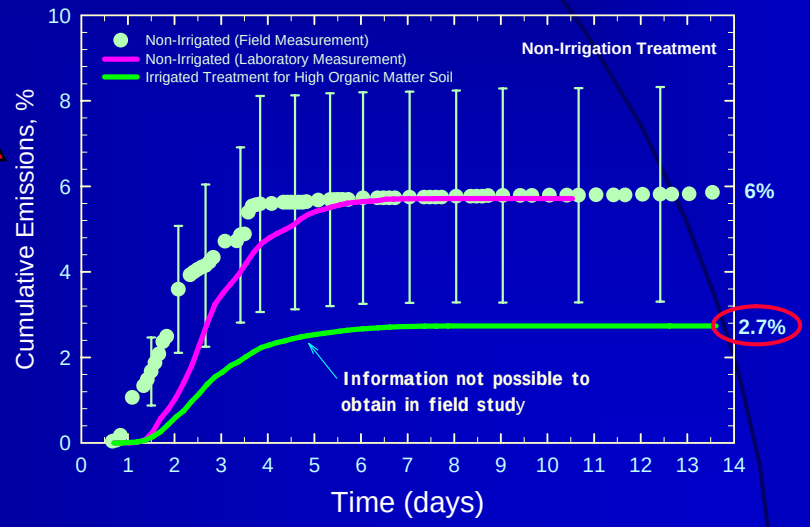
h) Determine if laboratory, field-plot, and simulation results can be used as surrogates for field measurements

Comparison of Laboratory And Field Emissions



Additional Laboratory Information





Comparison of Experimental Approaches for Estimating Emissions, MeBr

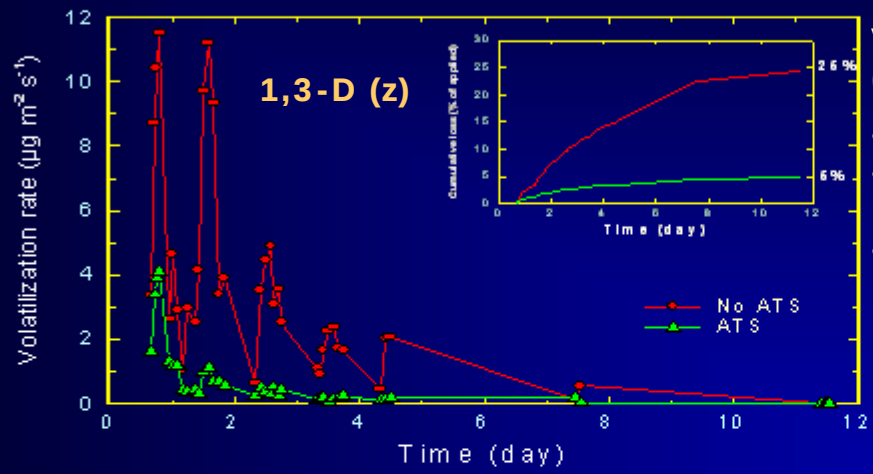
Table 1. Effects of Surface Cover on Total Emissions for shallow injection (20–35 cm) of Methyl Bromide.

Surface Barrier	Laboratory Experiments [a]		Field Plot Experiments [b]		Field Experiments		Simulation		
	Cover period (d)	Total emission (%)	Cover period (d)	Total emission (%)	Cover period (d)	Total emission (%)	Cover period (d)	Total emission (%)	
Bare Soil	–	90	–	87	–	89 [c]	–	81	81 – 90%
HDPE	5	59	5	59 - 64	5	58 - 70	5	58 - 65[e]	58 – 70%
Hytibar (VIF)	8	2[d]	15	<5	–	–	15	18[f]	2 – 18%

[a] Gan et al. (1996, 1997a, 1998d, 2000b);
[c] Majewski et al. (1995)
[e] Used a numerical solution (comprehensive model).
[b] Conducted in small field plots (Wang et al., 1997a);
[d] Cumulative emissions at 8 days.
[f] Used an analytical solution (simple model).

Simple Model

Comparison of 1,3-D Emissions



Volatilization from tarped (HDPE) beds

- sub-surface drip
- Telone EC (6.0 g a.i. m^{-2})
- ATS at 32 g m^{-2} (4:1 molar ratio)

Surface Barrier	Laboratory Experiments Shank [a]	Laboratory Experiments Drip [b]	Field Plot Experiments Drip [c]
Bare Soil (sandy loam)	Total emission (%)	Total emission (%)	Total emission (%)
1,3-D	30-43	22	32
1,3-D + ATS	17	–	16
HDPE Tarp			
1,3-D	–	–	24
1,3-D + ATS	–	–	7

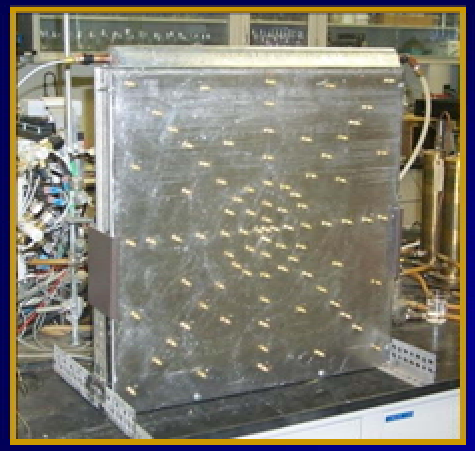
Independent Studies

[a] 3.7:1 molar ratio (ATS : 1,3D), 30 cm depth [b] 20 cm depth [c] 4:1 molar ratio (ATS : 1,3D), 10 cm depth

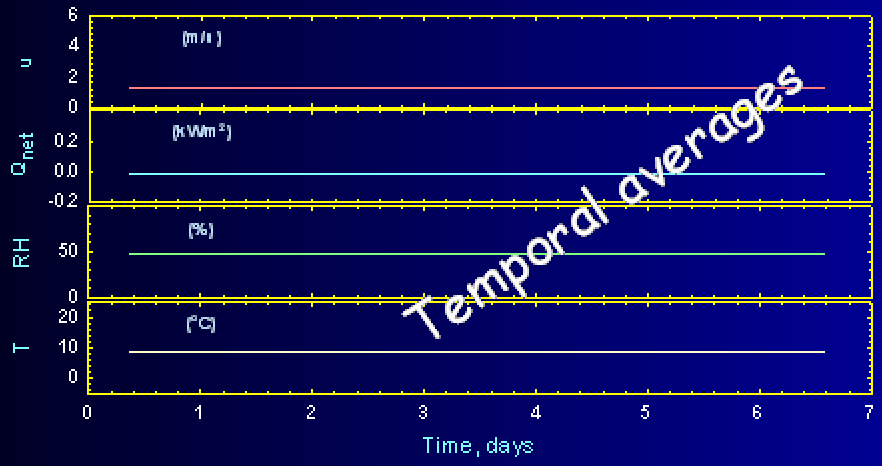
Other Approaches to Consider

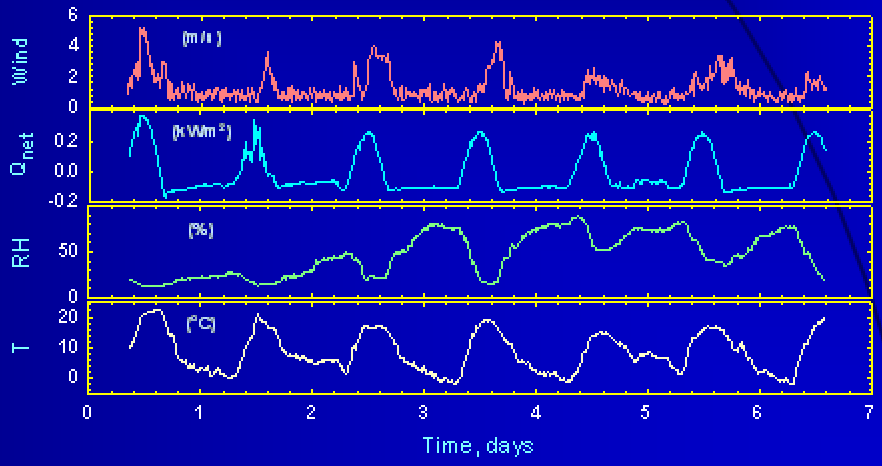
- **Detailed Laboratory Experimentation**
  - Include important processes affecting emissions
  - Experiments that better match field conditions.
- **Simple Modeling Approach**
  - Isothermal models that simulate the transport of volatile chemicals using an advection-dispersion equation, and volatilization is simulated with stagnant boundary layer theory.
- **Detailed Modeling Approach**
  - Models that include spatial and temporal variations in water, heat and chemical transport, and that couple soil and atmospheric processes to simulate the volatilization from soil.

Simple Model Approach



Detailed Model Approach





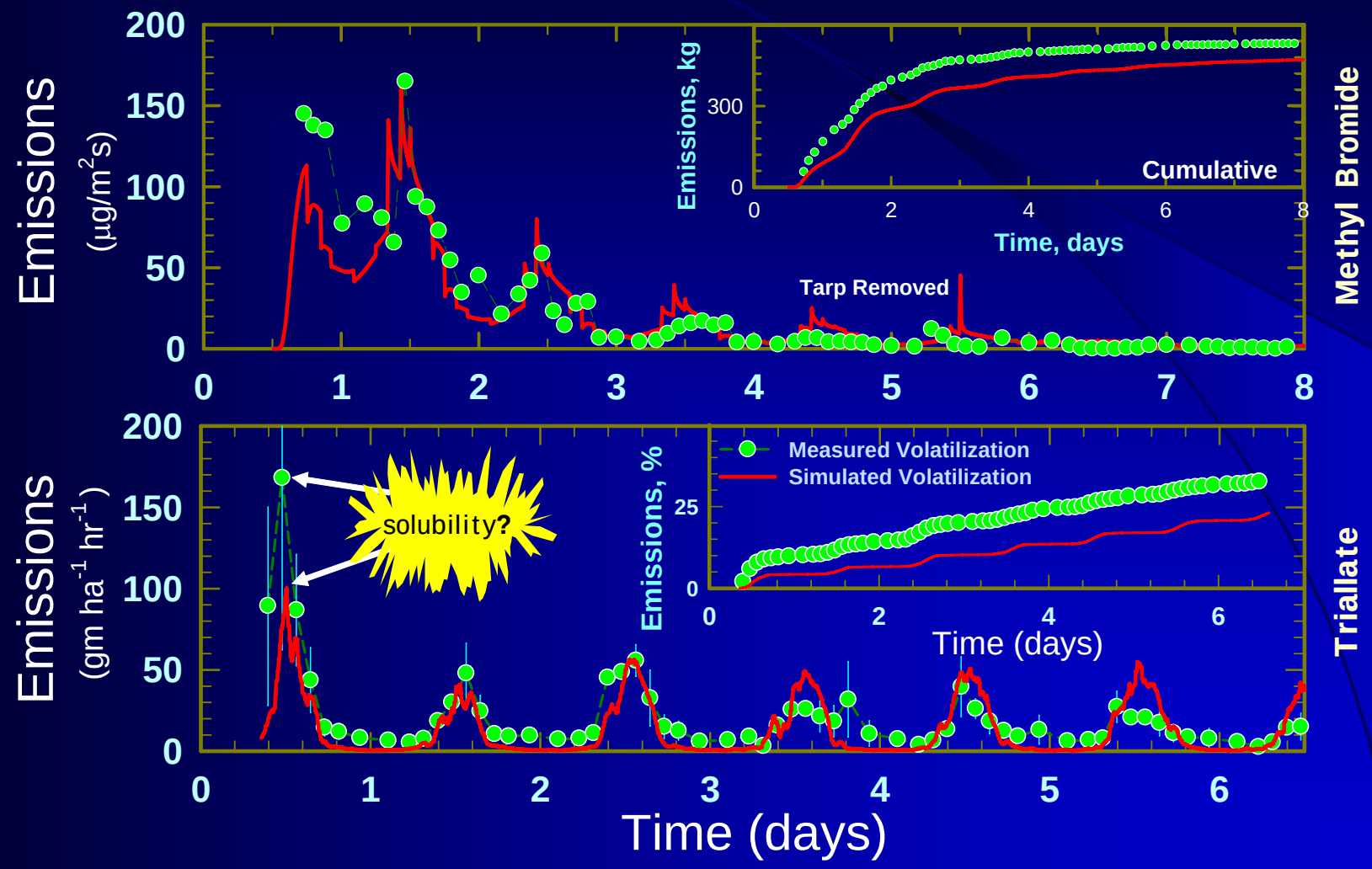
Comparison of Measured and Simulated (Predicted) Total Emissions

Field Study	Field Measured Emissions*	Simulated Emissions	
		Simple Model	Detailed Model
MeBr (1996) Broadcast tarp application	64 ± 10%	65%	58%
1,3-D (2005) Shank application	8% to 18%	11%	n/c
Triallate (1989) Bare soil surface application	30 ± 13%	27%	23% 37%

* % of applied material that volatilized during experiment

(Temporal averaged values)

Predicting Emissions



Research Needs

- More information is needed when conducting experiments (i.e., film permeability, etc.). All experiments should be verified.
- Lack sufficient information for many emission-reduction strategies. Additional study is needed to test other data sources.
- Simplified approaches provide useful information that should be considered in the regulatory decision making process. Research is needed to determine how this can be optimized.
  - Emission fractions appear insensitive to methodology
  - Difficult to isolate a single experimental variable in field studies
  - Comparisons between treatments not always meaningful
  - Theoretical transport relationships should be preserved in regulations.
- Models could be used to check consistency and screen out unrealistic patterns in a regulation. Additional research is needed.
  - Emission fractions should follow theoretical behavior (credibility issue)
- A procedural framework is needed to ensure that alternative approaches are utilized in an efficient, accurate, and accepted manner.