Methods to Reduce Fumigant Emissions

Husein Ajwa
haajwa@ucdavis.edu
Soil Fumigants and application methods
Conventional Soil Fumigation
(Acres, California 2007):

Methyl Bromide/Chloropicrin: 40,000
Telone/Chloropicrin: 17,000
Telone II: 37,000
Chloropicrin alone: 6,000
Metam sodium: 77,000

TOTAL: ~ 180,000 acres annually
Strawberry: Verticillium wilt

- Pathogen is *Verticillium dahliae*
- Survives in the soil as microsclerotia
  - These can survive for long periods of time in the soil
- *V. dahliae* has a broad host range
- Strawberry is very susceptible, 3-12 microsclerotia/g soil can cause significant losses.
- Symptom expression starts in the spring as the temperatures begin to warm up
Macrophomina problems are increasing on fields treated consecutively via drip fumigation (or low application rates). Growers will need to rotate drip applications with broadcast treatments to keep these fields viable for crop production.
Emission Reduction Methods

- **Application Methods:**
  - Deep injection
  - Subsurface drip fumigation
  - Local area treatment (strip or spot applications)

- **Surface Treatment:**
  - Plastic film (tarp) (impermeable film)
  - Irrigation (water treatment/seal)
  - Organic amendment (compost, manure, etc.)
  - Chemical treatment (e.g., K-thiosulfate)
Use of “Plastic Mulch” or Tarp for Soil Fumigation
“Agricultural Film”

- Reduces/delays fumigant volatilization losses
  - Less emissions rates and smaller buffer zone
  - Less total fumigant emissions (total flux)
- Enhances the efficacy of reduced rates by keeping fumigants in soil for a longer time
- Maintains and possibly enhances yield by warming/cooling the soil, moisture, etc…
Agricultural Film Types

“Standard” polyethylene tarp (HDPE or LDPE)

“Semi-impermeable” Tri-extruded LDPE

“Virtually impermeable (VIF)” LDPE + Nylon barrier

“Totally impermeable (TIF)” 5-layer EVOH resin barrier
5 layer TIF

Pink Mulch Film

100x ME Alcohol

Distance = 13.8604
Distance = 11.4568
Distance = 11.3487

PE/EVOH/PE
Plastic Permeability Measurement
Mass Transfer Coefficient

- Plastic film is mounted between two chambers
- Fumigant is applied to the lower chamber
- The cells are kept at a known temperature
Diffusion of MB through standard LDPE

Source (lower) chamber

Receiving (top) chamber
Diffusion of MB through metalized film

Source (lower) chamber

Receiving (top) chamber

Relative con'c

Time [hr]

S-Modeled
R-Modeled
S-Measured
R-Measured
Diffusion of MB through Bromostop VIF

Source (lower) chamber

Receiving (top) chamber

Relative con/c

Time [hr]
# Mass Transfer Coefficients (cm/h)
(Before and After Tarping)

<table>
<thead>
<tr>
<th>Film type</th>
<th>Cis 1,3-D Before</th>
<th>Cis 1,3-D After</th>
<th>Chloropicrin Before</th>
<th>Chloropicrin After</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pliant embossed, 1.25 mil</td>
<td>14.61</td>
<td>16.38</td>
<td>17.32</td>
<td>18.22</td>
</tr>
<tr>
<td>PolyPak Std, 1.5 mil</td>
<td>3.23</td>
<td>3.79</td>
<td>5.15</td>
<td>5.65</td>
</tr>
<tr>
<td>PolyPak SIF, 2.0 mil</td>
<td>1.42</td>
<td>1.53</td>
<td>1.51</td>
<td>1.71</td>
</tr>
<tr>
<td>Blockade, 1.25 mil</td>
<td>0.86</td>
<td>0.88</td>
<td>1.65</td>
<td>1.74</td>
</tr>
<tr>
<td>Bromostop VIF, 1.38 mil</td>
<td>0.07</td>
<td>0.27</td>
<td>0.09</td>
<td>0.42</td>
</tr>
<tr>
<td>Eval/Mitsui TIF, 1.38 mil</td>
<td>0.00</td>
<td>0.02</td>
<td>0.001</td>
<td>0.07</td>
</tr>
</tbody>
</table>
## Various Film Structures

### Film Structures

<table>
<thead>
<tr>
<th>Mono-Layer Blend</th>
<th>Mono-Layer Blend</th>
<th>PE &amp; Tie</th>
<th>PE</th>
<th>PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE, MDPE, &amp; REPRO</td>
<td>LLDPE &amp; MDPE</td>
<td>Nylon</td>
<td>TIE</td>
<td>EVOH or Nylon</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PE &amp; Tie</td>
<td>TIE</td>
<td>TIE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PE</td>
<td>TIE</td>
<td>TIE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PE</td>
<td>PE</td>
<td>PE</td>
</tr>
</tbody>
</table>

### Physical Properties

<table>
<thead>
<tr>
<th>STD</th>
<th>STD</th>
<th>3-layer VIF</th>
<th>5-layer VIF</th>
<th>5-layer TIF</th>
<th>7-layer VIF or TIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>POOR</td>
<td>POOR</td>
<td>MEDIUM</td>
<td>MED/HIGH</td>
<td>MED/HIGH</td>
<td>HIGH</td>
</tr>
<tr>
<td>GOOD</td>
<td>HIGH</td>
<td>POOR</td>
<td>MEDIUM</td>
<td>POOR</td>
<td>HIGH</td>
</tr>
</tbody>
</table>

### Fumigant Barrier

<table>
<thead>
<tr>
<th>STD</th>
<th>STD</th>
<th>3-layer VIF</th>
<th>5-layer VIF</th>
<th>5-layer TIF</th>
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<tr>
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<td>POOR</td>
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<td>POOR</td>
<td>HIGH</td>
</tr>
</tbody>
</table>
## Approved Tarps for Products Containing Midas

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Trade Name</th>
<th>Tarp Thickness (mil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadillac</td>
<td>Cadillac VIF</td>
<td>1.25</td>
</tr>
<tr>
<td>Filmtech</td>
<td>Grozone VIF</td>
<td>1.15</td>
</tr>
<tr>
<td>Ginegar</td>
<td>Ozgard (black) VIF</td>
<td>1.25</td>
</tr>
<tr>
<td>IPG</td>
<td>Bromostop VIF</td>
<td>1.30</td>
</tr>
<tr>
<td>Klerks</td>
<td>Hytibar VIF</td>
<td>1.30</td>
</tr>
<tr>
<td>Olefina</td>
<td>Guardian VIF</td>
<td>1.20</td>
</tr>
<tr>
<td>Pliant</td>
<td>Blockade VIF</td>
<td>1.25</td>
</tr>
<tr>
<td>Raven</td>
<td>VaporSafe TIF</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Concerns about using retentive films:

- Does retentive film (TIF and VIF) reduce fumigant volatilization losses (flux rate and total mass loss) from agricultural fields?
- Does retentive tarp improve fumigant distribution (vertical/horizontal) in soil?
- Does retentive tarp enhance the efficacy of lower fumigant application rates? 
  
  *(concentration x time)*
Methyl Bromide/Chloropicrin 50:50 with soil moisture at 70% field capacity

Field 1: Shallow (12”) broadcast under PE

Field 2: Shallow (12”) broadcast under TIF

Field 3: Shallow (12”) broadcast under TIF with KTS spray

Field 4: Deep (18”) strip (50% treated) under TIF

Field 5: Deep (18”) broadcast under TIF
Field layout showing locations of the monitoring stations

- Off-Field Air Quality Monitoring Stations
- Meteorological Monitoring Stations
• Peak for TIF was 51% less than for PE, and occurred during application (fugitive emissions).

• Post-Application peak on TIF field was 84% reduction from peak of PE field.
Chloropicrin Drip Studies
Emission reduction with TIF and potassium thiosulfate

<table>
<thead>
<tr>
<th>Field #</th>
<th>Tarp material</th>
<th>Water seal</th>
<th>Potassium Thiosulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Standard LDPE</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>2</td>
<td>TIF (Eval/Mitsui)</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>3</td>
<td>Standard LDPE</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>4</td>
<td>Standard LDPE</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>
Chloropicrin Emission Rates, Salinas, 2007

- Standard PE Tarp
- TIF (5 layers, Eval/Mitsui)
- Standard PE Tarp plus Thiosulfate
- Standard PE Tarp plus water treatment
Waiting period before tarp cutting and removal

1,3-Dichloropropene and Chloropicrin Retention under Standard Tarp (PE) and Totally Impermeable Film (TIF)

Chloropicrin and 1,3-Dichloropropene were shank injected at 12” under TIF and Std PE
1,3-D Total Emissions, Ventura, CA 2009

Total mass loss relative to amount applied (%)

Field 1: standard PE tarp
Field 2: TIF

Tarp cutting
1,3-dichloropropene Emission Rates

Lost Hills Flux Study, 2011

- Field 1 (16 days)
- Field 2 (10 days)
- Field 3 (5 days)
Chloropicrin Emission Rates

Lost Hills Flux Study, 2011

- Field 1 (16 days)
- Field 2 (10 days)
- Field 3 (5 days)
Cumulative Mass Loss of Chloropicrin

Lost Hills Flux Study, 2011

- Field 1 (16 days)
- Field 2 (10 days)
- Field 3 (5 days)
Current Chloropicrin Field Volatility Dataset: 36 flux studies

Good Agricultural Practices (GAPs)

All 26 GAP-compliant shank studies had peak flux rates lower than tarped drip, regardless of tarp/non-tarp, deep/shallow, broadcast/bed.

Only one study had a higher peak than Tarped Drip: Non-Tarped Buried Drip

Since GAPs are now mandatory on labels, USEPA no longer has “pre-GAP” buffer zones on labels.
USEPA Buffers distances are subjectively large; want users to utilize emissions reduction strategies. Developed Buffer Zone Reduction Credits.

<table>
<thead>
<tr>
<th>Condition</th>
<th>% Reduction in Chloropicrin Buffer Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use of specific high barrier tarp</td>
<td>20% (metalized films), 40% (nylon VIFs), or 60% (high-end VIFs and all TIFs)</td>
</tr>
<tr>
<td>Organic matter content</td>
<td>10% (OM ≥ 1% - 2%), 20% (OM &gt;2 – 3%), 30% (OM &gt; 3%)</td>
</tr>
<tr>
<td>Clay content &gt; 27%</td>
<td>10%</td>
</tr>
<tr>
<td>Soil temp ≤ 50°F (shank)</td>
<td>10%</td>
</tr>
<tr>
<td>Potassium thiosulfate</td>
<td>15%</td>
</tr>
<tr>
<td>Water seal</td>
<td>15%</td>
</tr>
<tr>
<td>Max reduction</td>
<td>80%</td>
</tr>
</tbody>
</table>
Summary

☑ Low permeability tarps (TIF and VIF) can significantly reduce emissions as well as improve efficacy because it can retain high fumigant concentration under that tarp.

☑ Delayed tarp cutting will reduce peak flux and total emissions:

- ~10 days chloropicrin
- ~15 days 1,3-D (Telone)
Acknowledgement

- California Strawberry Commission
- Cal-EPA (DPR)
- USEPA
- USDA-ARS, Area Wide Project
- Almond Board of California
- TriCal, Inc.
Thank you very much

Husein Ajwa

1636 East Alisal Street, Salinas, CA 93905

Phone (831) 755-2823

FAX (831) 755-2844

haajwa@ucdavis.edu