Postharvest Fumigation Research at USDA-ARS-SJVASC

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http://fresno.ars.usda.gov
Update on Postharvest Fumigation

- QPS scenario & methyl bromide
  - low-emission fumigations
  - alternatives
    - PH3, SF
- breaking specialty crop trade barriers
  - pests (insects)
  - systems/processing-based
  - mathematical modeling
  - residues
Trade Barriers
Postharvest Conundrum

- Pest-free security
- Trade barriers
- Food safety
- No residue
Navel Orangeworm to EU
Mathematical modeling of fumigation
(insect-, fumigant-, commodity-specific)

<table>
<thead>
<tr>
<th>Factor (original units)</th>
<th>Factor levels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-2</td>
</tr>
<tr>
<td>$x_1$: dose (mg/L)</td>
<td>0</td>
</tr>
<tr>
<td>$x_2$: temp (°C)</td>
<td>5</td>
</tr>
<tr>
<td>$x_3$: duration (h)</td>
<td>1</td>
</tr>
<tr>
<td>$x_4$: pressure (inch. Hg)</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a0 =$ center point

Central-composite design (matrix comparison)

$y = \beta_0 + \beta_1 x_1 + \beta_{11} x_1^2 + \beta_2 x_2 + \beta_{22} x_2^2 + \beta_3 x_3 + \beta_{33} x_3^2 + \beta_4 x_4 + \beta_{44} x_4^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4$

$y = $ egg survivability $\quad y = $ SF depuration
Multifactorial Modeling fumigant residues: SF-walnuts

Initial residues (30 min post fum.):

\[ y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 \]

\[ (r^2 = 0.76) \]

\[ y = 1.36 + 0.87x^1 - 0.51x^2 \]

SF depuration rates:

- attempts to model failed, relative to an average rate
- ave. rate of 0.59 d^{-1}, half-life of 1.17 d ± 20%
-125 mg/L max dose @ 60F, SF below 3ppm MRL in ~30 min
Peach Twig Borer vs. AUS
Residues: MB & T104-a-1

**Graph 1:**
- **Y-axis:** \( \ln \left( \frac{[MB]}{[MB]_0} \right) \)
- **X-axis:** time (hours)
- Lines showing semi-logarithmic decay with half-lives: \( t_{1/2} = 0.93 \) and \( t_{1/2} = 0.47 \)
- Text: "plums sorb slower"

**Graph 2:**
- **Y-axis:** methyl bromide residues (ppm)
- **X-axis:** post-fumigation time (day)
- Data points indicating sorption and desorption of MB with "plums desorb slower"
MB sorption

![Graph showing the sorption of MB dye by different fruits, with time on the x-axis and In ([MB]_t/MB) on the y-axis.

- apples: 0.18
- grapes: 0.30
- plums: 0.46
- cherries
- nectarines: 0.78
- peach: 0.83
- walnuts: 1.67
- strawberries: 0.95
- APHIS T104-a-1

"maximum allowed loss"
Systems-based approaches: future?

CUMULATIVE JOINT PROBABILITIES
New Pest: back to MB (preserve MB)
Development of low-emission chamber fumigations

Collaborators:
Joe Pignatello (Yale)
William Mitch (Yale)
David Zilberman (UC Berkeley)
Gary Knapp (consultant)
Jim Leesch (ARS retired)
Scott Wood (APHIS-TQAU)

Note log scale

Fumigation period

Begin Aeration

16,000 ppm

Switch to bypass at 500 ppm

~5 ppm from fumigation bay

~1 ppm from adsorber exhaust

Terminate aeration at 5 ppm

Enclosure

Stack

MeBr Concentration, ppm

Time, Minutes

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pest-free security

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food safety

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Residue remediation
Soak tanks (HOCl, O3)
- oxidant-induced color changes
- other cosmetic damage
- shallow pitting on fruit surfaces
- natural organic matter competition
- inadequate activity of O3 against surface-sorbed residues (low water sol.)
- disinfection byproducts (DBPs!)
REMEDIATION OF FUNGICIDE RESIDUES ON FRESH PRODUCE USING GASEOUS OZONE

Environmental Science & Technology, 2011, in press

1000 ppm O3

Hakan Karaca, Joe Smilanick
Residue remediation w/ O3: structurally selective

~2   ~2   64     38   40
% degradation
Ozone fumigation

Will my product look worse?
Situation dependent
Ozone fumigation

Will worse products form?
more polar = less toxic (ozone)

- Endocrine disruptors
  - endosulfan and sulfate
- POPs
  - paraoxon and parathion
Case studies: endocrine disruptor (ES) and POP

Endosulfan

 oxidation

 Endosulfan sulfate

 Parathion

 Oxidation

 Paraoxon

 t=0

t=30 min
Next steps

• Develop structurally indiscriminate techs.
  – Free radical processes (•OH, •OOR)
• Obtain funding/agreements
• Tailor to commercial needs
“Think about it, Ed. ... The class Insecta contains 26 orders, almost 1,000 families, and over 750,000 described species—but I can’t shake the feeling we’re all just a bunch of bugs.”