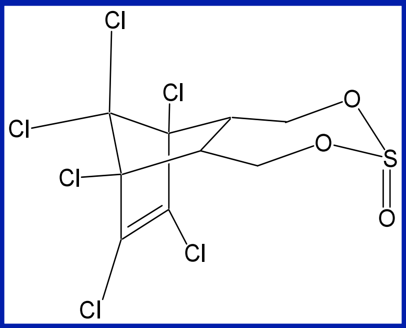
Postharvest Technologies for Residue Remediation

MRL Harmonization Workshop – 4 June 2015

San Joaquin Valley Agricultural Sciences Center

Specialty Crop Chemist – Primary Focus

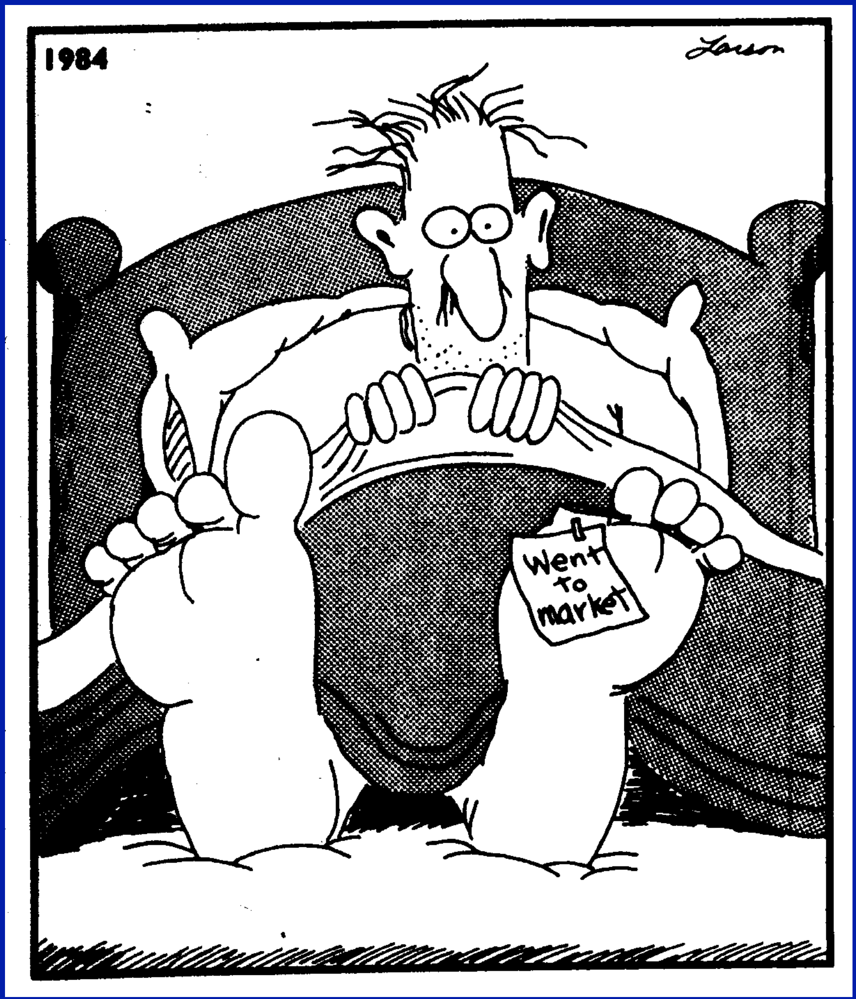
Spencer Walse

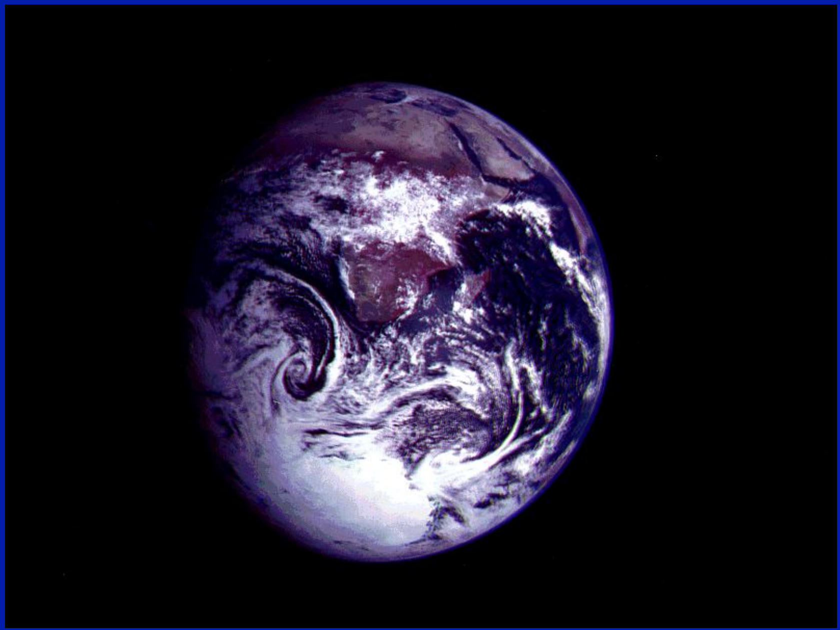


- **QPS scenario & methyl bromide**
  - **low-emission fumigations**
  - **alternatives**
    - **PH3, SF**
- **Break specialty crop trade barriers**
  - **pests (insects), microbes, residues**
  - **systems-based approaches**
  - **mathematical modeling**
  - **method/process development**

30,000 ft view – what do we want to do?

(Proactively) Address Consumer & Regulatory Demands…..





….for the Global Market

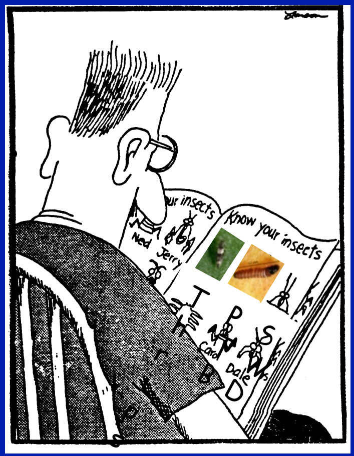
Agricultural Conundrum – must use chemicals, but can't????

pest-free security
(insecticides & herbicides)

food safety
(antimicrobials)

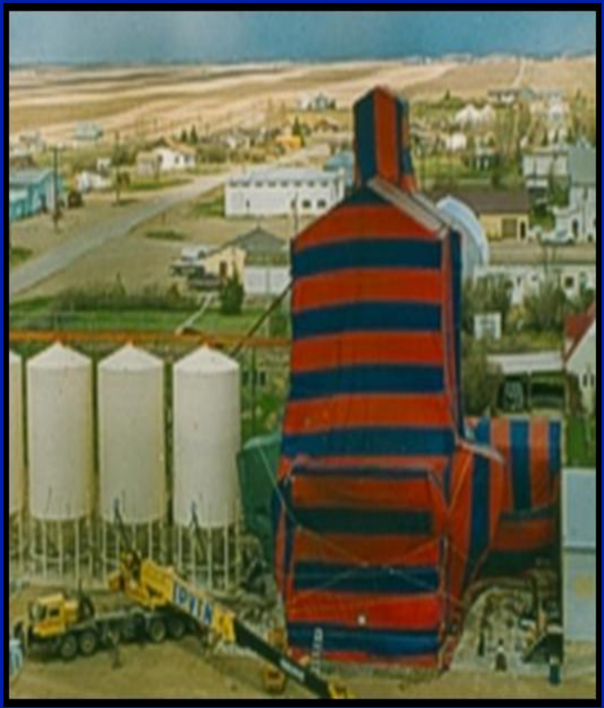
no treatment residue
(MRLs)

trade barriers



So many chemicals are involved

- **Plant & insect biomolecules**
- **What can you use?**
- **How much can you use?**
- **How much do you need?**
- **How long do they last?**
- **When to apply – rotate use?**
- **Does use impact global marketing?**



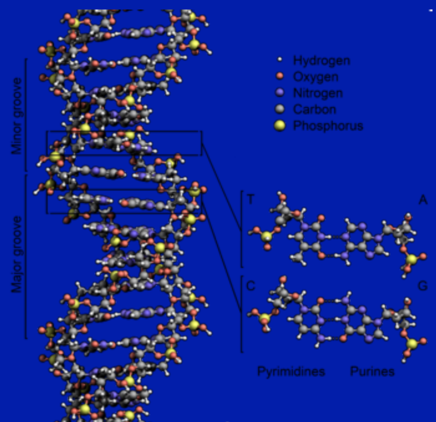
Where there are chemicals……

there is a need for chemical analysis

<u>& getting rid of them</u>

Opportunity to impact chemically-related trade barriers

"SYSTEMS-BASED"



PREPLANT ▼ PRODUCTION ▼ POSTHARVEST

decay curves

start

finish

any tool along the line is welcome & embraced!

Opportunity to impact chemically-related trade barriers

- Traditional logistics/ infrastructure
  - Imports → proximity to port terminals
  - Exports → packing, processing facilities
  - Domestic → hybrid of above

Postharvest is key!

Retrospective analysis – why not MRLs?

- Systems alternatives to methyl bromide
  - OFF in cherries
  - SWD in table grapes
  - ACP in citrus
  - Medfly in green tomatoes

“ACP packinghouse project” domestic implications

Systems evaluation: where we sit now

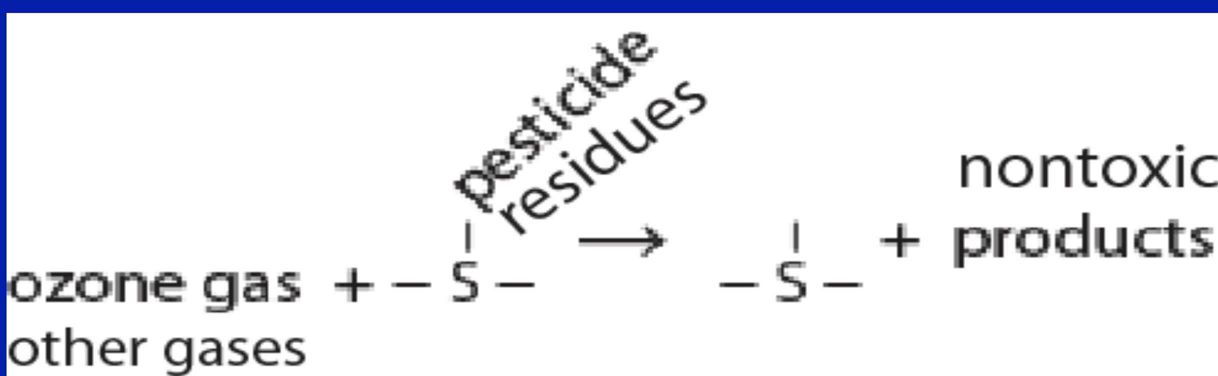
joint events	% mort. (95% LOC)	$P(E_1+E_2+E_n)$ (95% LOC)	probit (95% LOC)
Σ soak + brushes	99.999560	4.4 E-6	9.44
Σ soak + rollers	99.999577	4.2 E-6	9.45
Σ soak + dryer-135s	99.998520	1.5 E-5	9.18
Σ soak + brushes + dryer-135s	99.999987	1.3 E-7	10.15
Σ soak + rollers+ dryer-135s	99.999987	1.3 E-7	10.16

Exceeding "Probit 9" benchmark without postharvest fumigation

Cherry trade barriers: (necessitate use of chemicals)

Cherry MRL trade barriers: key markets jeopardized by residues

industry needs:
- better detection & better records of detection
- ways to minimize, <u>or ELIMINATE</u>, residues



Our recent advances in ozone fumigation enable residue removal : many improvements possible

ENVIRONMENTAL Science & Technology

ARTICLE

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Remediation of Fungicide Residues on Fresh Produce by Use of Gaseous Ozone

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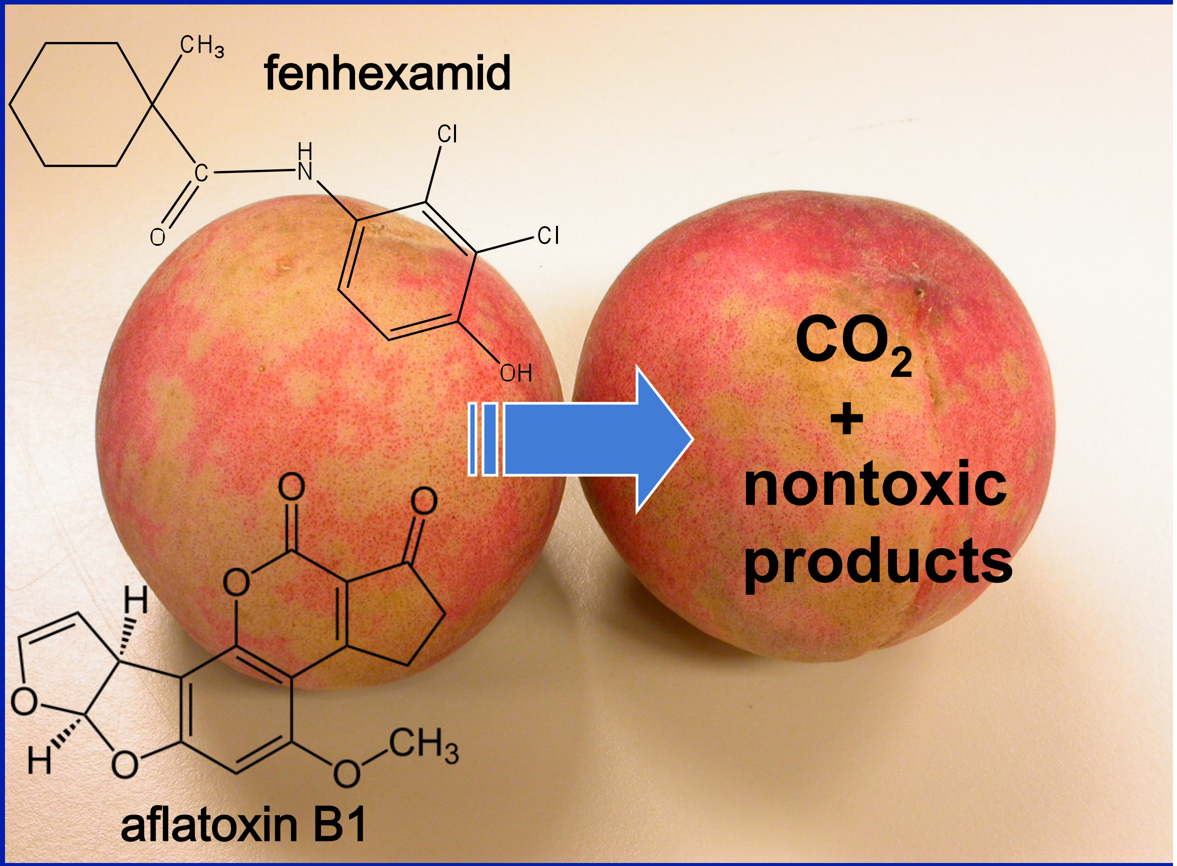
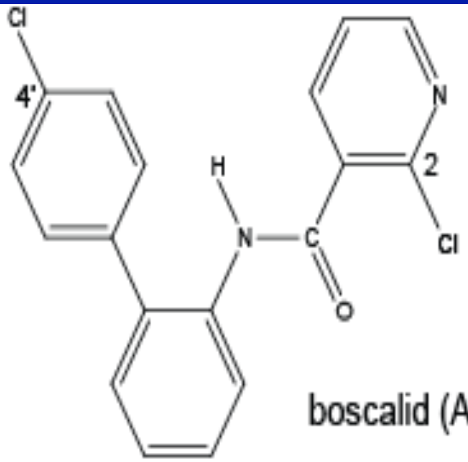
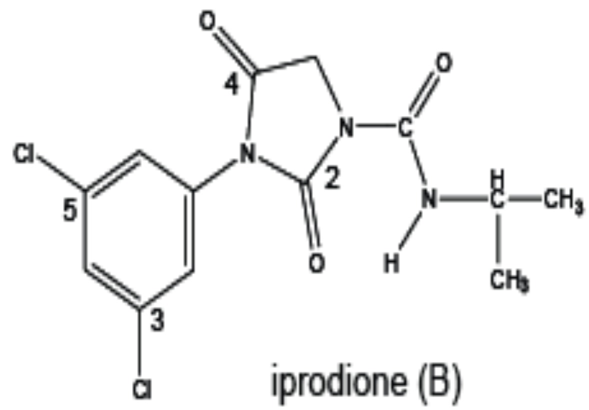
Supporting Information

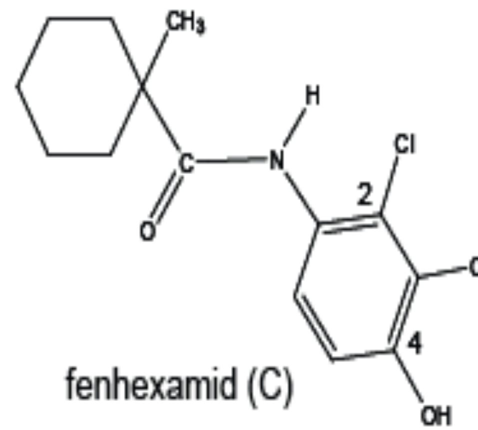
ABSTRACT: Ozone fumigation was explored as a means for degrading organic fungicide residues on fresh produce. Fungicides sorbed onto model abiotic glass surfaces or onto grape berries were fumigated separately in a flow-through chamber. Gaseous ozone at a constant concentration of 150 ± 10 ppmv (μL·L^{-1}) selectively oxidized fungicides sorbed to model surfaces. Over 140 min, boscalid and iprodione levels did not change significantly based on a single-factor analysis of variance (ANOVA) at the 95% level of confidence (p = 0.05); however, pseudo-first-order losses resulted in observable rate constants of ozonolysis, $k_{ozonolysis}$ (min^{-1}), of 0.0233 ± 0.0029 ($t_{1/2}$ ≈ 29.7 min), 0.0168 ± 0.0028 ($t_{1/2}$ ≈ 41.3 min), and 0.0127 ± 0.0010 ($t_{1/2}$ ≈ 54.6 min) for fenhexamid, cyprodinil, and pyrimethanil, respectively. The relative degradation of fungicides on berries at gaseous ozone concentrations of 900 ± 12 ppmv (μL·L^{-1}) over 2 h was similar to that on glass; decreases in residue concentration were observed for only fenhexamid (~64%), cyprodinil (~38%), and pyrimethanil (~35%) with corresponding $k_{ozonolysis}$ (min^{-1}) of 0.0085 ± 0.0021 ($t_{1/2}$ ≈ 81.5 min), 0.0039 ± 0.0008 ($t_{1/2}$ ≈ 177.7 min), and 0.0036 ± 0.0007 ($t_{1/2}$ ≈ 192.5 min). Heterogeneous rate constants of gaseous ozone reacting with a sorbed fungicide, k_{O_3} (M^{-1}·min^{-1}), were calculated for both surfaces and indicate losses proceed ~15-fold slower on grapes. The kinetics and mechanism of fungicide removal, supported by gas chromatography– and liquid chromatography–mass spectrometry product analyses, is discussed in the context of facilitating compliance with maximum residue level (MRL) tolerances for fresh produce.

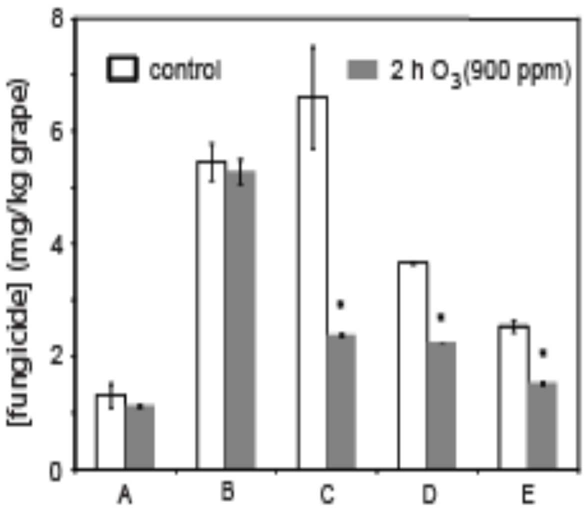


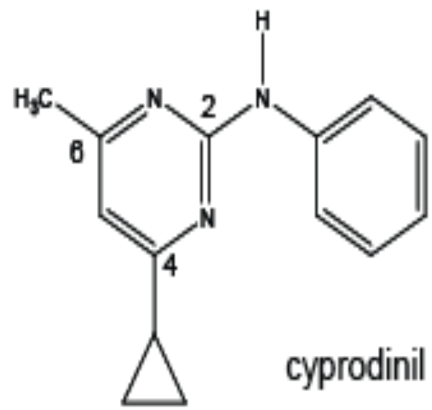
Residue remediation w/ O3: structurally selective

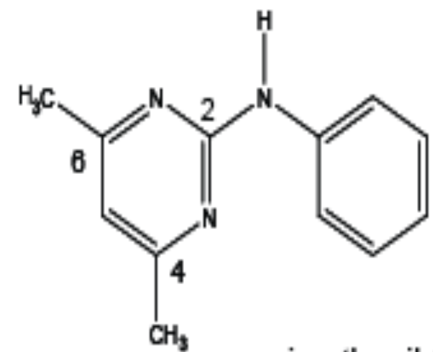

boscalid (A)


iprodione (B)

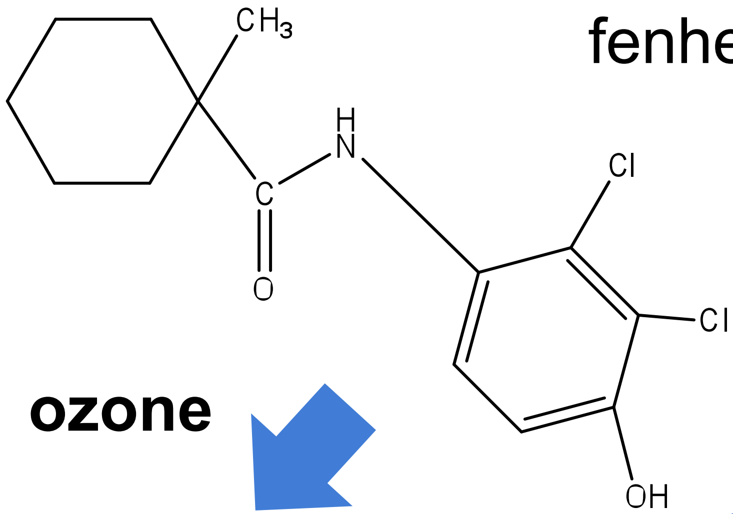

fenhexamid (C)




cyprodinil (D)


pyrimethanil (E)

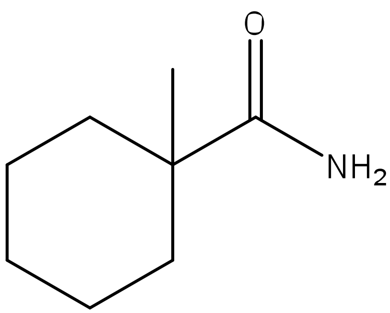
~2 ~2 64 38 40 % degradation



fenhexamide

ozone

ideal



1-methylcyclohexanecarboxamide

small bits & chunks + CO2

-can this be sold as a band-aid?
-can this be sold as a civil service?

Considerable regulatory precedence AOPs

ozone vs. chlorine (amination)

Ozone fumigation

Will my product look worse?
Situation dependent

Cherries?

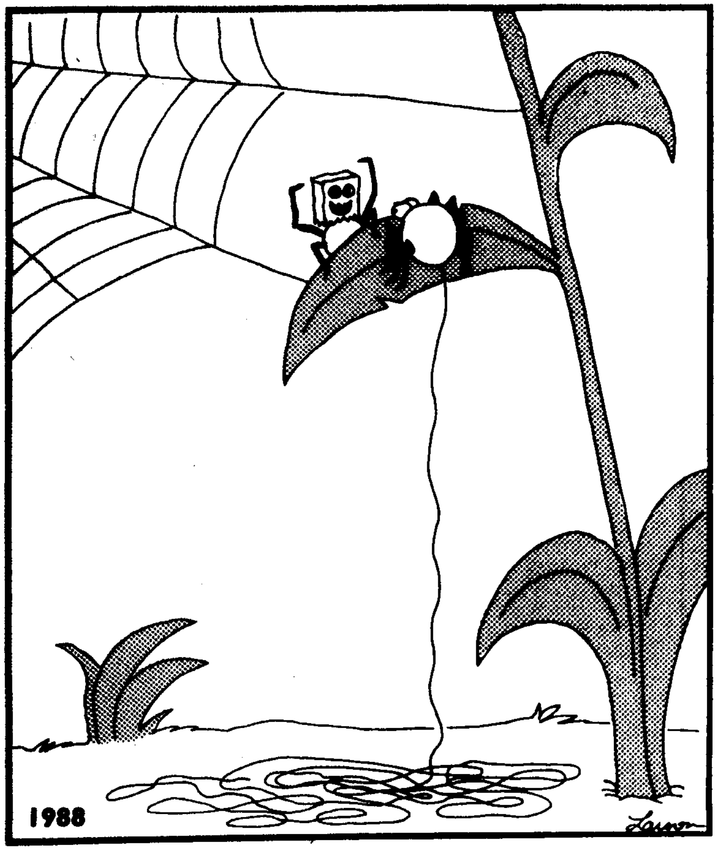
ozone treated

not treated

Ozone fumigation

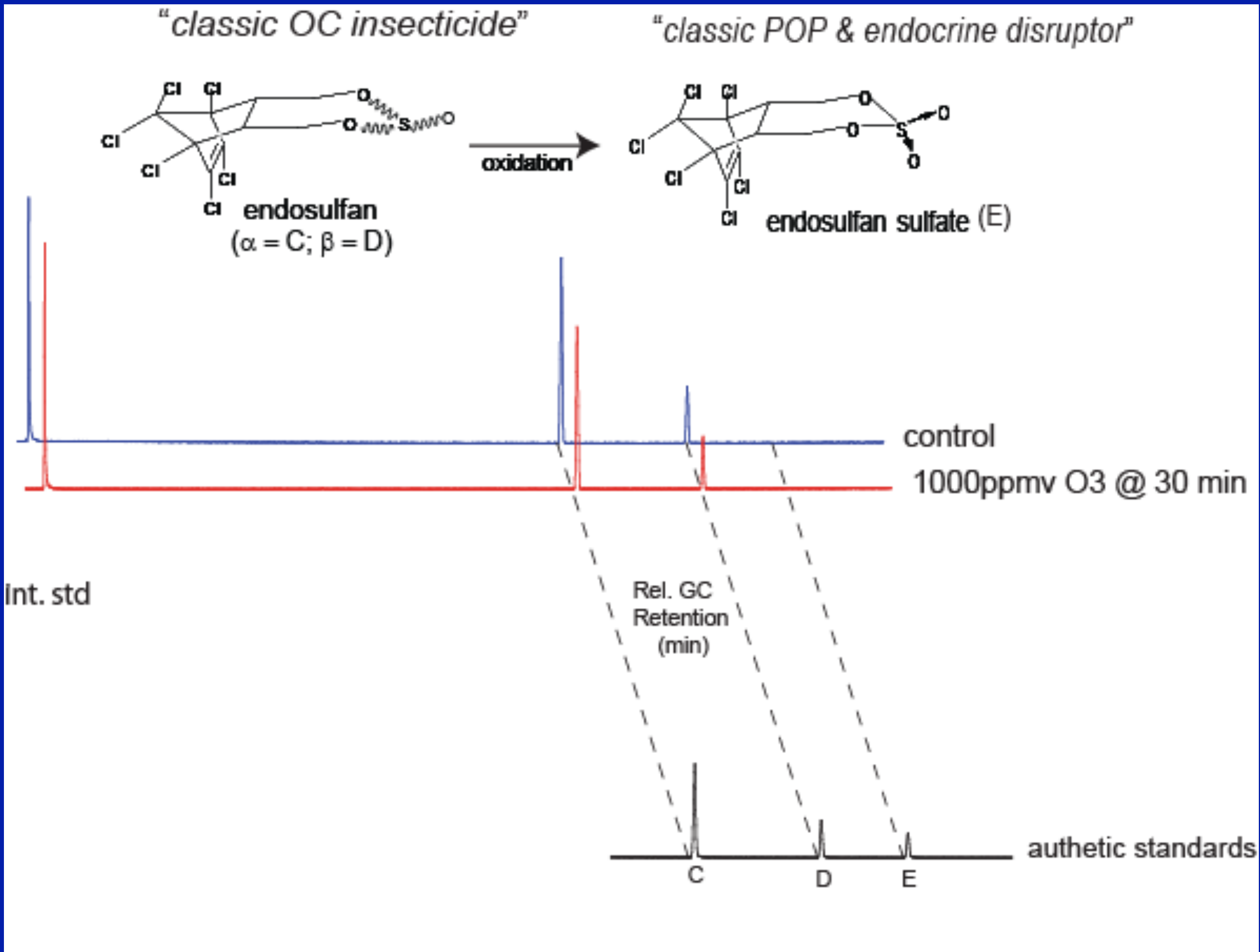
Will worse products form?
more polar = less toxic (ozone)

- Endocrine disruptors
  - endosulfan and sulfate
- POPs
  - paraoxon and parathion

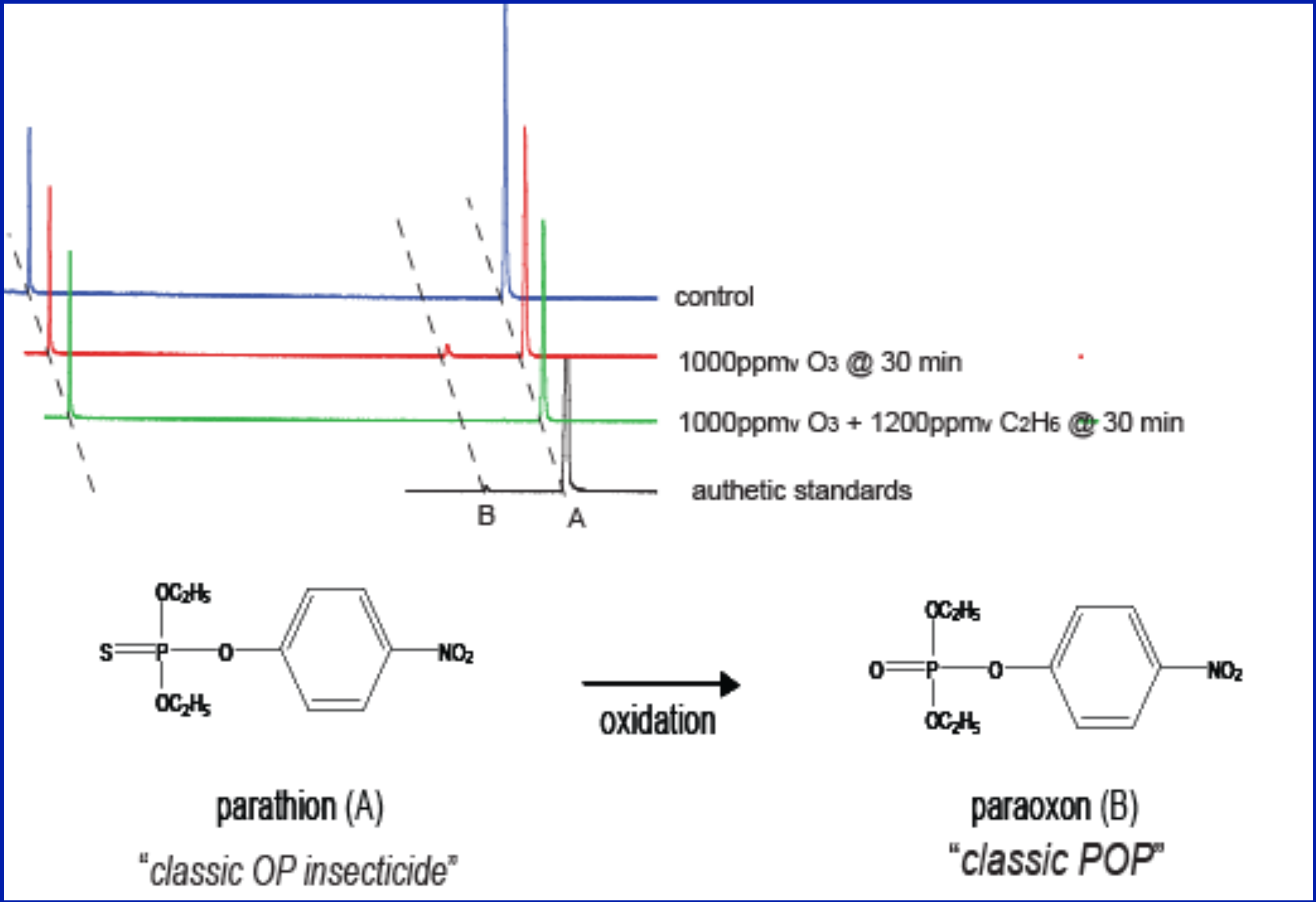


"Hey, Bob ... did I scare you or what?"

endosulfan story

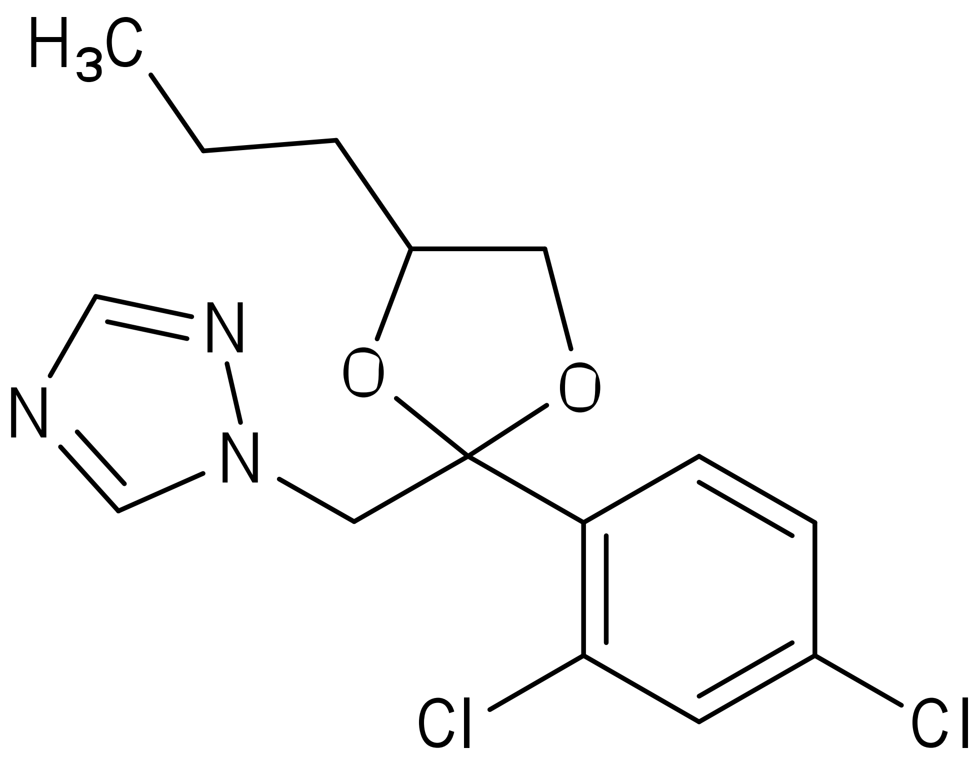


parathion story



Optimized fumigation blend

(mineralization of key targets)



propiconazole

We assembled a trusted team to research residue science via USDA-FAS-TASC program

USDA

Agricultural Research Service

San Joaquin Valley Agricultural Sciences Center

Spencer Walse

fumigation development
residue detection & tech transfer

Northwest Horticultural Council & WTFRC

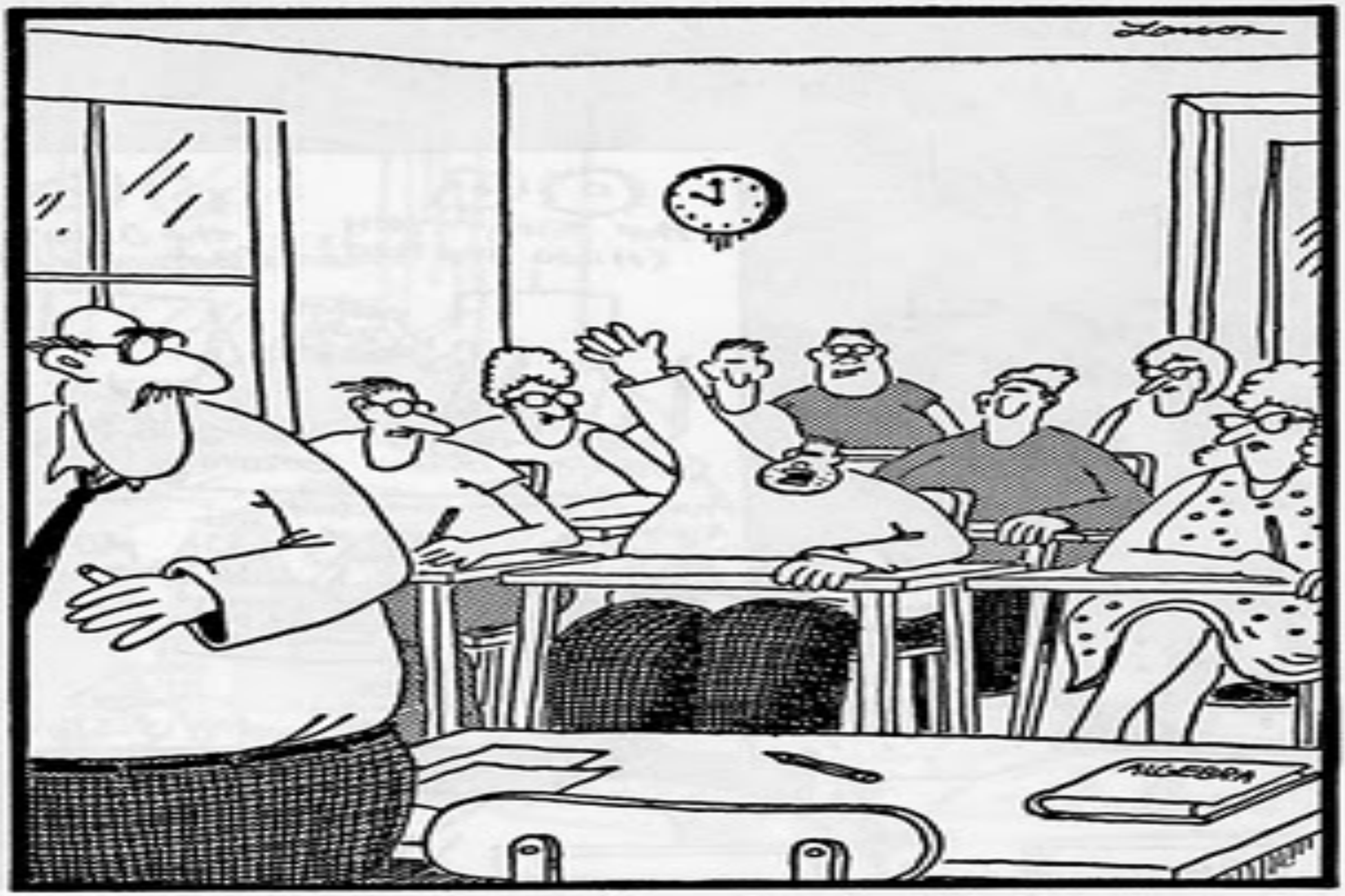
residue indexing
& forecasting

University of South Carolina

John Ferry
S.M. Angel

fumigation development &
in-field / in-shed real-time
residue detection

Thank you!



"Mr. Osborne, may I be excused? My brain is full."