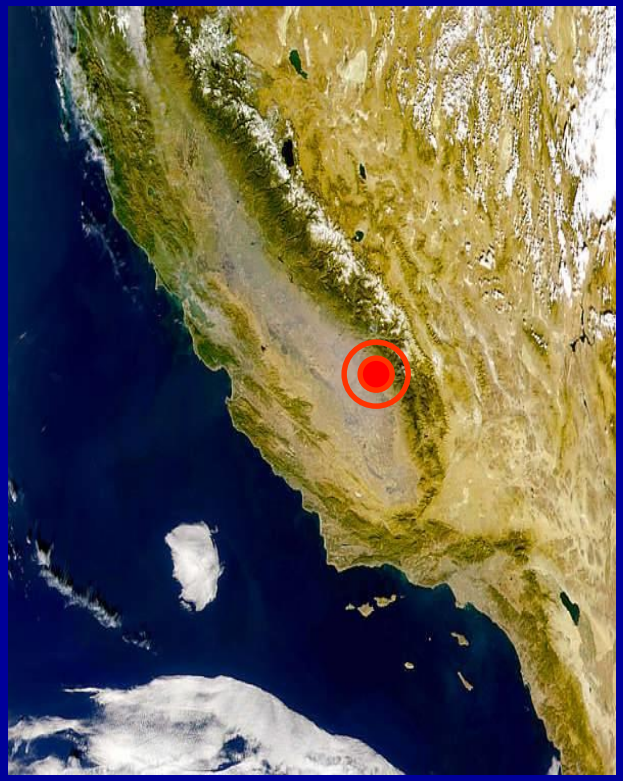
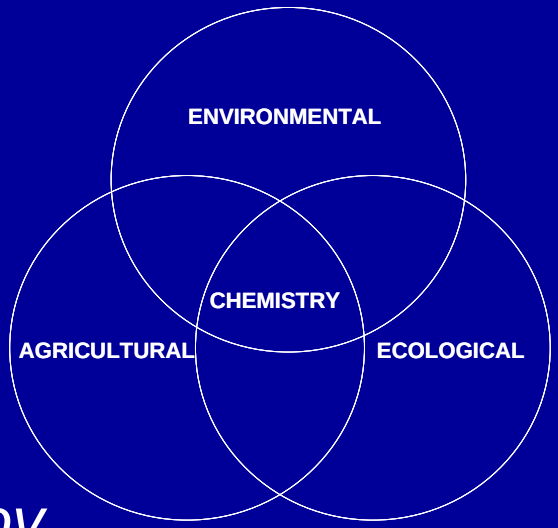
"Postharvest fumigants: residue tolerances & other registration issues"

Crop Protection & Quality Unit

Spencer S. Walse





USDA

Agricultural Research Service

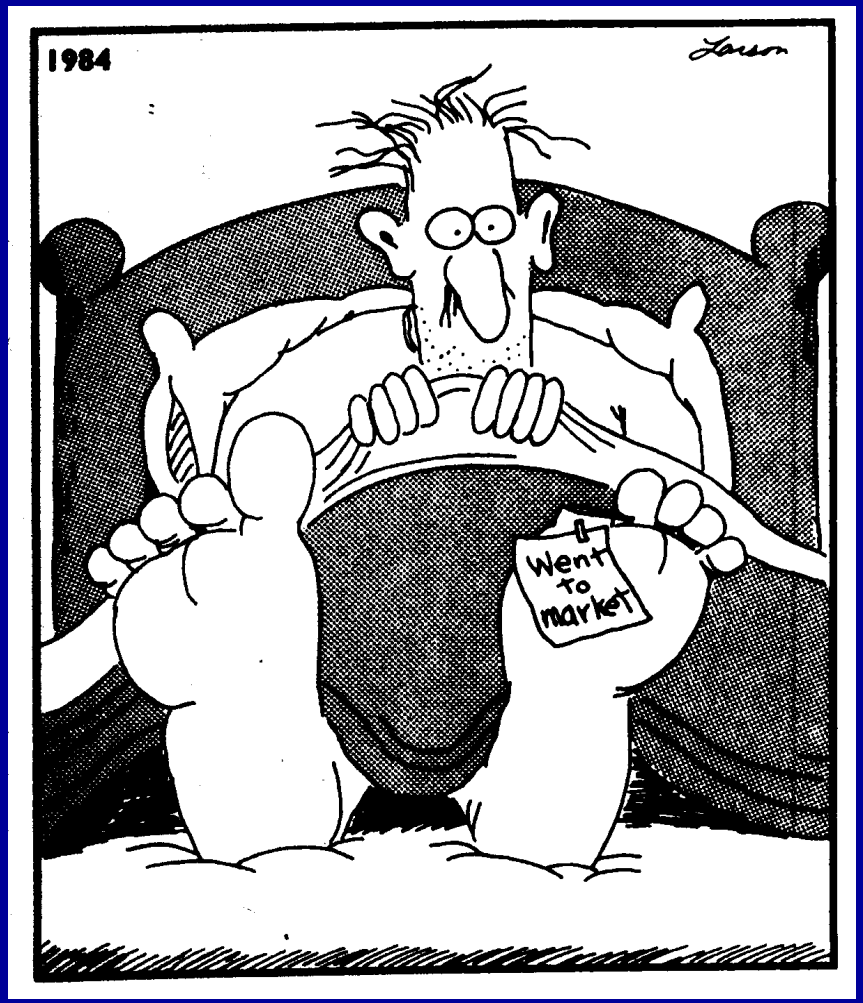
San Joaquin Valley Agricultural Sciences Center

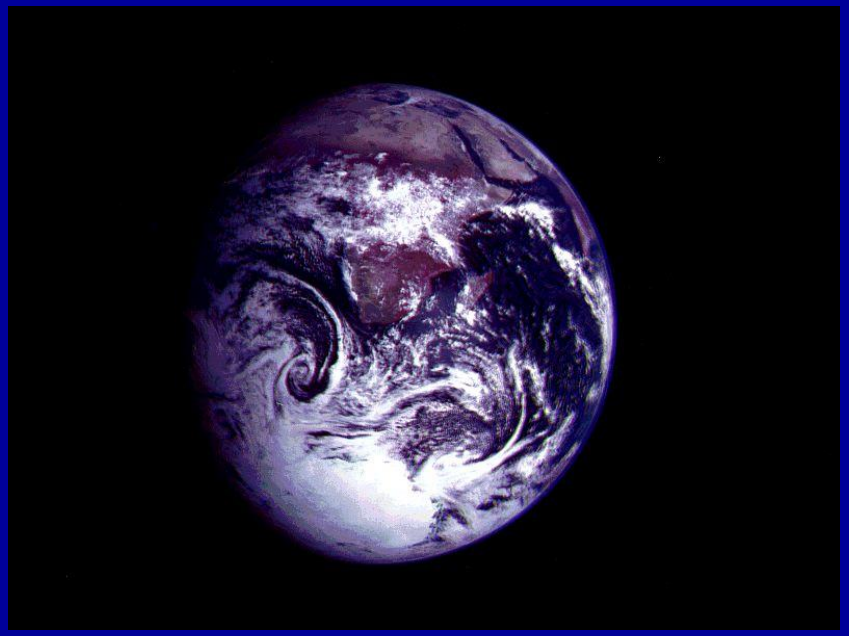
http//fresno.ars.usda.gov

http://agchem.ucdavis.edu/ UCDAVIS UNIVERSITY OF CALIFORNIA

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

(Proactively) Address Consumer & Regulatory Demands…….

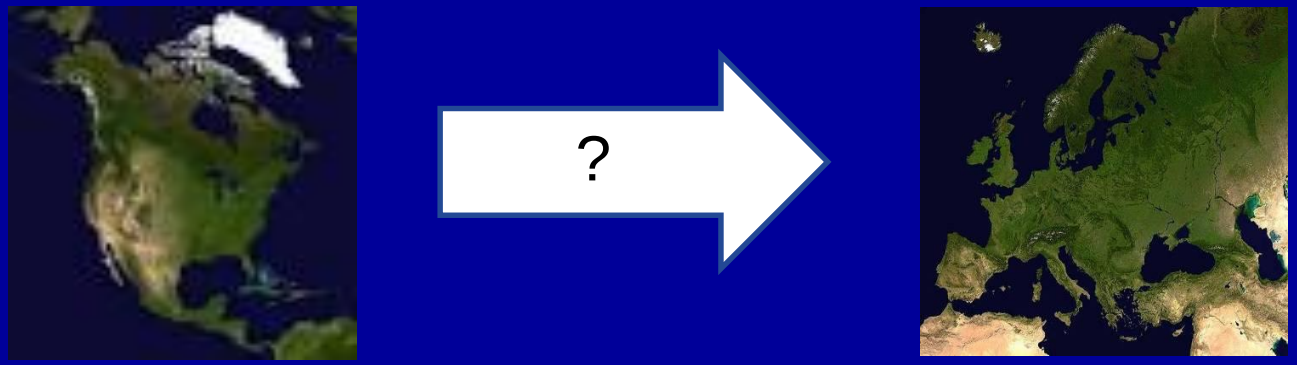




….for the Global Ag. Market

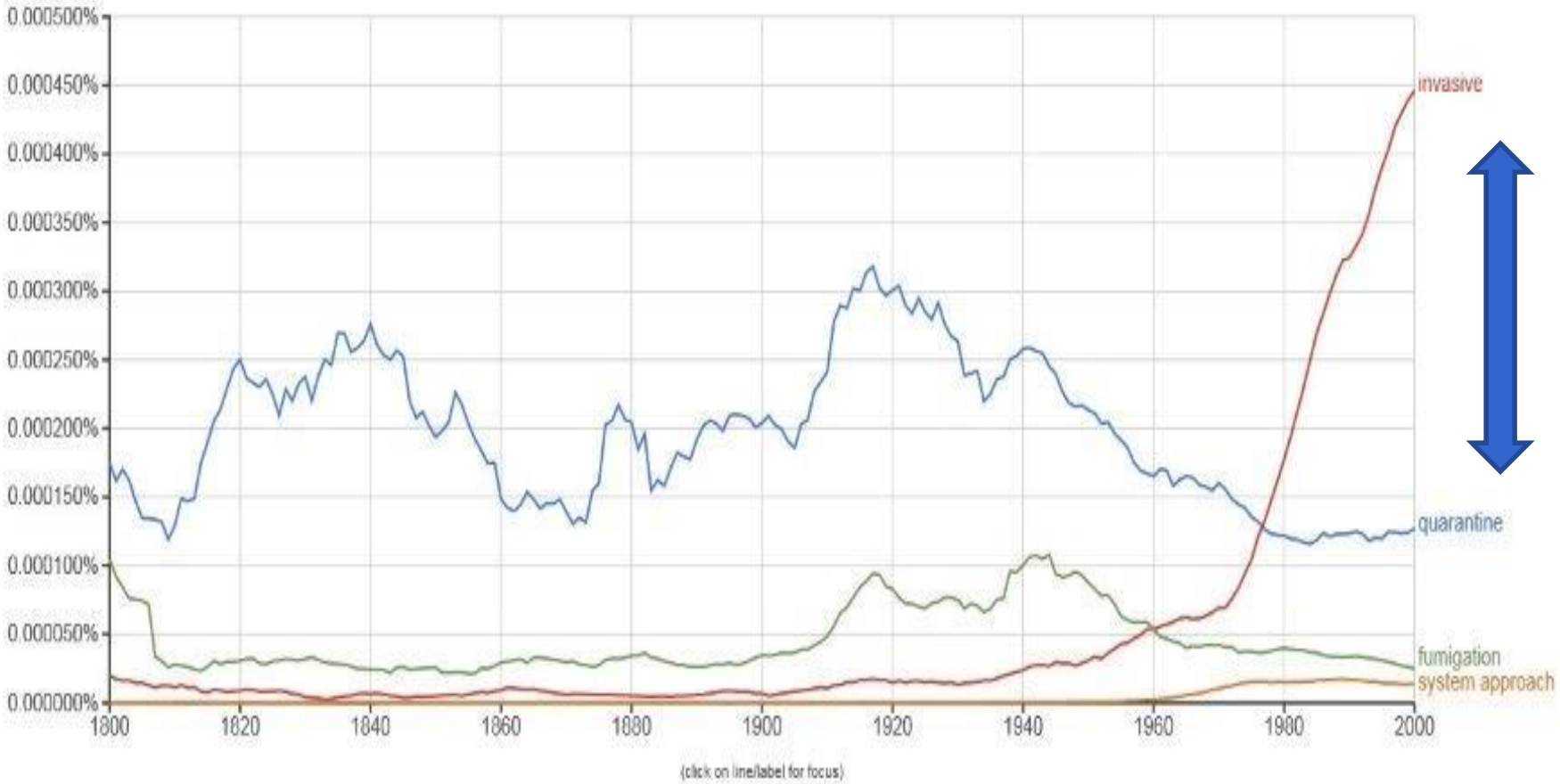
Consumer Ag. Demands (Phobias)

http://phobialist.com/#I-



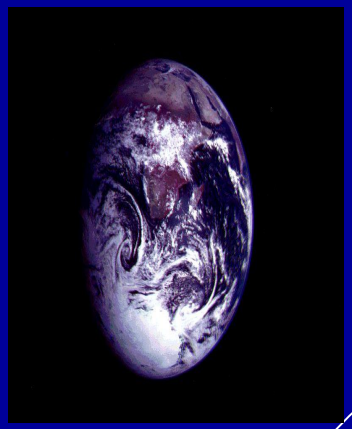
- Insectophobia – insects
- Iophobia- poison
- Radiophobia – radiation
- Microbiophobia - microbes (germs)
- Genophobia- Fear of sex (GMO)
- Chemophobia - chemicals
- Chrometophobia - $$ money
- Georgophobia - farms
- Gnosiophobia- knowledge

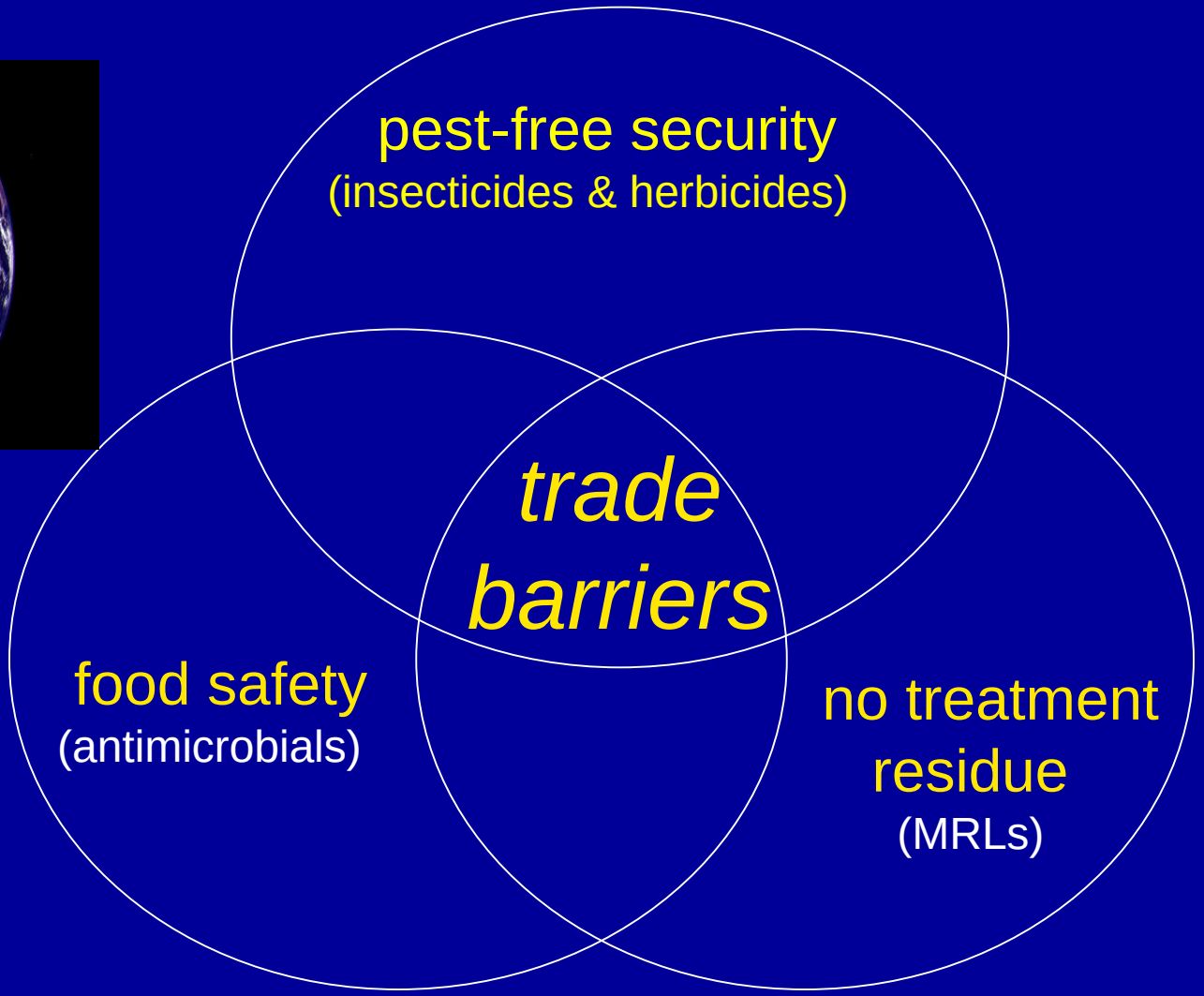
We must educate millennials (rich and poor) .....



"google" N-gram

Regulatory Ag. Demands

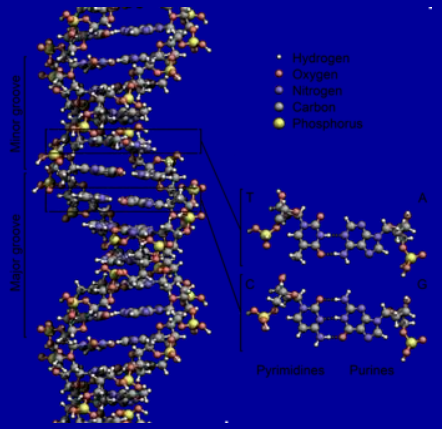




Agricultural Conundrum –

must use chemicals, but can't????

Opportunity to break trade barriers:



PREPLANT ▼ PRODUCTION ▼ POSTHARVEST

start — finish

"SYSTEMS-BASED"

tapping the "system" to negotiate the agchem conundrum

RETROspective inspiration

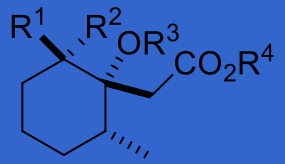
1990 Nobel Laureate
EJ Corey

ret·ro·spec·tive
/ˌretrəˈspektiv/

adjective

1. looking back on or dealing with past events or situations.
   "our survey was retrospective"
   synonyms: backdated, retroactive, ex post facto
   "the government introduced retrospective legislation"

uncertainty → certainty



acylation R^3 = Ac
cyclization

1 R^1 = $CH{=}CH_2$, R^2 = CH_3
2 R^1 = CH_3, R^2 = $CH{=}CH_2$

9 R^1 = $CH{=}CH_2$, R^2 = CH_3, R^3 = H, R^4 = *t*-Bu
10 R^1 = CH_3, R^2 = $CH{=}CH_2$, R^3 = H, R^4 = *t*-Bu

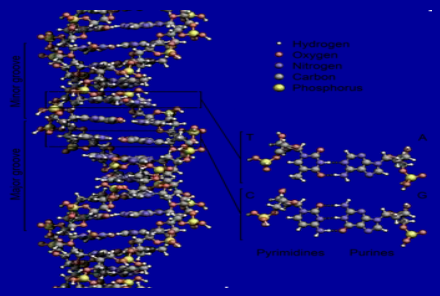
RETROspective approach

quantitative

uncertainty

certainty

"Pest control based retrospectively through the point of marketing/consumption"



PREPLANT PRODUCTION POSTHARVEST

start "SYSTEM" finish

Postharvest Fumigation Residues

red-head·ed step·child

noun US *informal*

a person or thing that is neglected, unwanted, or mistreated.
"audio has always been something of a red-headed stepchild in the PC world"

1-slide introduction.....

Complexities of Postharvest Fumigant Use

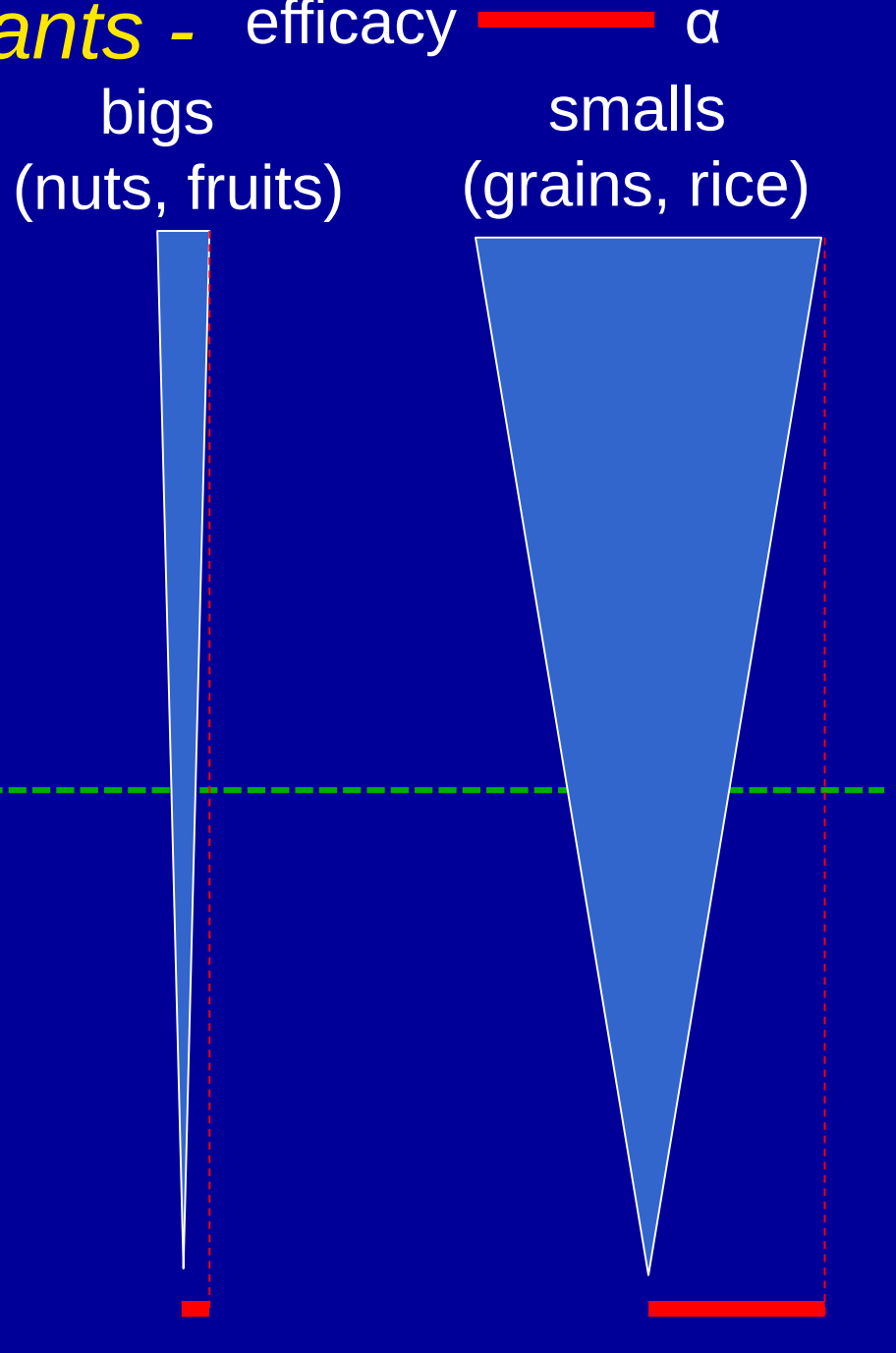
target efficacy

worker- and consumer-exposure

by-stander- and environmental-exposure

Postharvest fumigants - tools in the box

	bp °C
• phosphine	-87
• sulfuryl fluoride	-55
• sulfur dioxide	-10
• methyl bromide	4
• hydrogen cyanide	26
• propylene oxide	34
• ethyl formate	54
• Vapona (non-food)	148
• pyrethrin	170



Key (regulatory & consumer) issues

- residues
  - definition (MB & PH3)
  - methodology (MB, PPO, SO2)
- environmental
  - greenhouse (SF)
  - efficacy (PH3)
- human health
  - worker exposure (MB & PH3)
  - by-stander (SF)
- quarantine
  - procedural operations (PH3)
  - enforcement (PH3)

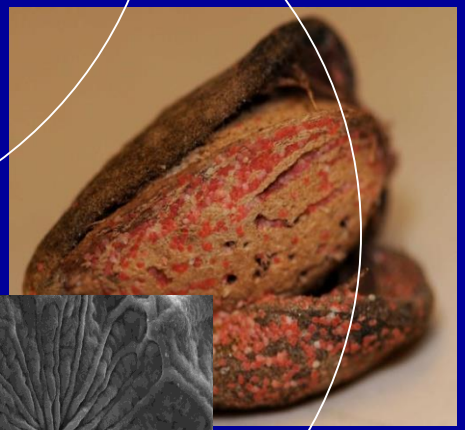
methyl bromide: the issue

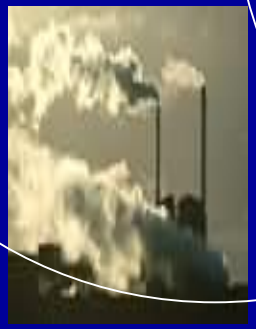
politics

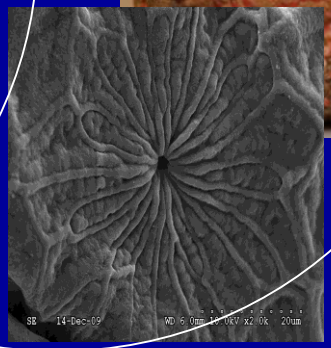
economics

science

$







§ 180.124 Methyl bromide; tolerances for residues.

* * * * *

(b) *Section 18 emergency exemptions.* Time-limited tolerances as listed in the following table are established for residues of the fumigant methyl bromide, including its metabolites and degradates, in or on the specified agricultural commodities, resulting from use of the pesticide pursuant to FIFRA section 18 emergency exemptions. Compliance with the tolerance levels specified below is to be determined by measuring only methyl bromide. These tolerances expire and are revoked on the date indicated in the table.

TOLERANCE REASSESSMENT SUMMARY

Tolerances are currently established for residues of inorganic bromides (calculated as Br) in/on raw and processed commodities that have been fumigated with the antimicrobial agent and insecticide methyl bromide [40 CFR §180.123]. The Agency has approved the replacement of inorganic bromide tolerances with tolerances for methyl bromide *per se* as supported by residue chemistry data (Letter to MBIP, A. Lindsay, 7/7/89). In conjunction with acceptance of plant metabolism data, HED subsequently recommended that methyl bromide *per se* is the residue to be regulated (DP Barcode D168913, R. Perfetti, 9/24/91).

The reassessed tolerances under 40 CFR §180.123(a) should be defined in terms of residues of methyl bromide *per se* resulting from the post-harvest, stored commodity fumigation use of products containing methyl bromide. The post-harvest designation (POST-H) following each commodity listing can be deleted.

Methyl Bromide 100
Commodity Fumigant

Commodity -- Fresh Fruits & Vegetables :	Pests Controlled	Dosage (lbs/1000ft^3)	Exposure Time (hrs)	Tolerance (ppm)
Apples	fruit flies, oriental fruit moth, codling moth, apple maggot, apple curculio, twig borer, melon fruit fly, Mediterranean fruit fly, Oriental fruit fly, cherry fruit fly, brown mite, green peach aphid, scales, thrips, ants	1-4	3	5
Apricots		1-4	3	20
Blueberries		1-4	3	20
Cherries		5	2	20
Nectarines		1-4	3	20
Peaches		1-4	3	20
Pears		1-4	3	5
Plums		1-4	3	20
Quinces		1-4	3	5
Strawberries		3	3-4	60

Methyl Bromide Quarantine Fumigant

FOR QUARANTINE/REGULATORY USE ONLY
SUPERVISION BY REGULATORY AGENT REQUIRED

Apples	Oriental fruit moth, coddling moth, apple maggot, apple curculio, twig borer, melon fruit fly, Mediterranean fruit fly, Oriental fruit fly, cherry fruit fly, brown mite, green peach aphid, scales, thrips	1.5-4	2	5
Apricots		1.5-4	2	20
Blueberries		1.5-2	2-3.5	20
Cherries		1.5-4	2	20
Nectarines		1.5-4	2	20
Peaches		1.5-4	2	20
Pears		1.5-4	2	5
Plums		1.5-4	2	20
Quinces		1.5-4	2	5

February 22, 2002

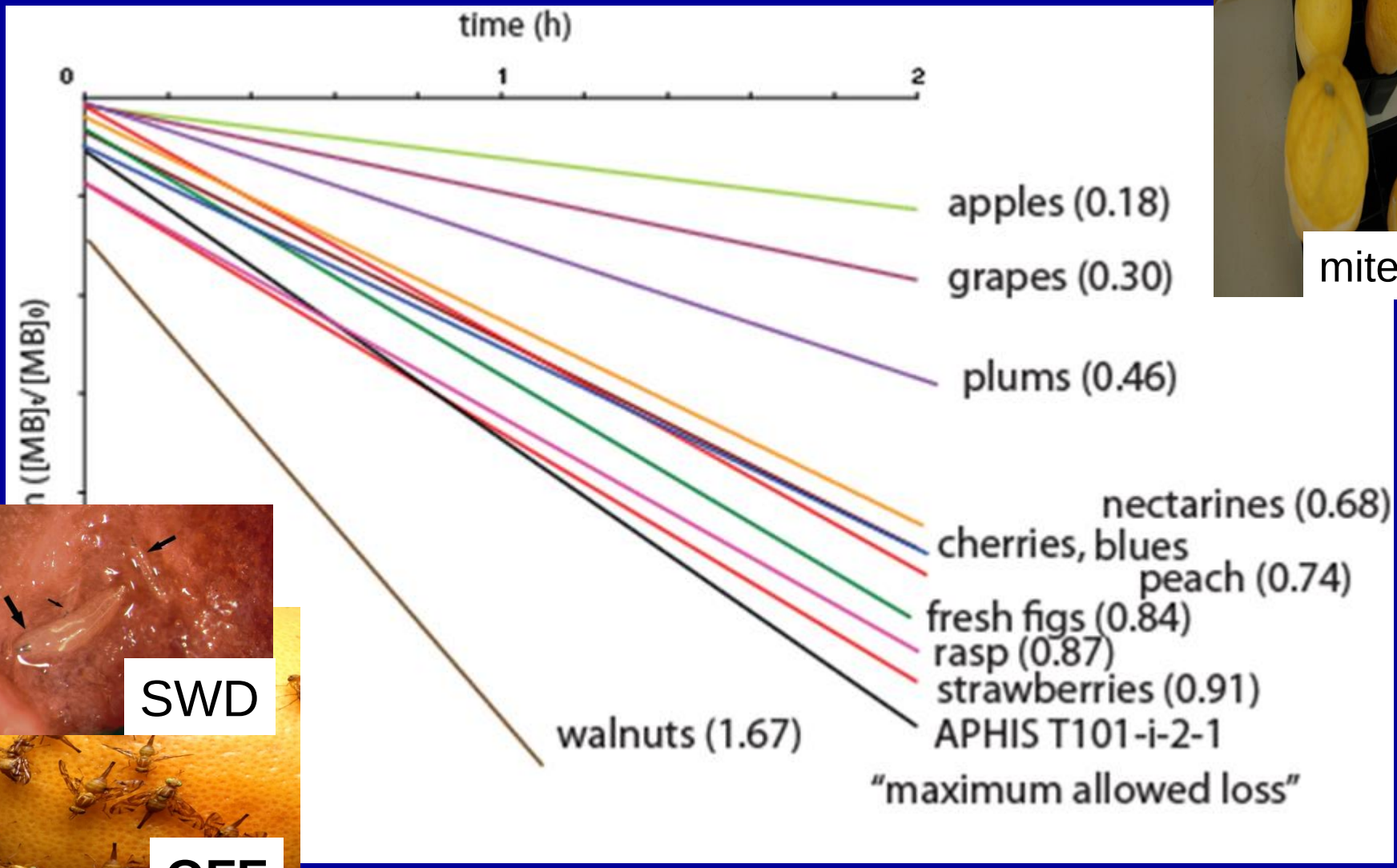
MEMORANDUM

Subject: Reregistration of **Methyl Bromide:** Product and Residue Chemistry Chapters to the Reregistration Eligibility Document; Chemical No. 53201; DP Barcode D271583

Blueberries (POST-H)	20.0	0.5 [a]	Reassign to crop group tolerance for residues in/on Berries Crop Group. Commodity fumigation trials support a decreased tolerance level for methyl bromide.
Strawberries (PRE- and POST-H)	60.0	0.05	Commodity fumigation trials support a decreased tolerance level.
Grape (POST-H)	20.0	4.0	Commodity fumigation trials support a decreased tolerance level.
Apples (POST-H)	5.0	8.0 [a]	Reassign to crop group tolerance for residues in/on the Pome Fruits Group. Commodity fumigation trials support an increased tolerance level for methyl bromide.

Br - MeBr

Relative sorption of methyl bromide into "naked" fresh produce: external versus internal feeders



mites

SWD

OFF

very important for short treatments (MB)

When does one take the measurement?

OPPTS GLN 860.1380: Storage Stability Data

Methyl bromide residues decline rapidly, e.g., 30% in rice stored in dry ice for 40 hours. For the commodity fumigation residue trials, the registrants agreed to place residue samples in impermeable containers at <3.7 C as soon as possible. HED has determined that storage stability data are not required unless samples are or have been stored for longer than 12 hours. Most of the residue data used to reassess tolerances were generated from samples stored for 12 hours or less. For some samples stored for longer intervals, results were compared with initial analyses obtained after shorter periods; the results were comparable. Therefore, there are no unresolved storage stability issues related to samples used for tolerance reassessment.

§ 180.225 Phosphine; tolerances for residues.

registered by the U.S. Environmental Protection Agency (EPA) under FIFRA. Labeling shall bear a restriction to aerate the finished food/feed for 48 hours before it is offered to the consumer, unless EPA specifically determines that a different time period is appropriate. Where appropriate, a

CODEX

Pesticides Functional Classes

The pesticide functional classes are based on ...

Below is a complete list of functional classes ...(under brackets the number of pesticides belonging to the functional classes).

- Acaricide (12)
- Acaricide, Insecticide and Nematocide
- Acaricide and Insecticide (8)
- Aphicide
- Fumigant (3)
- Fungicide (65)
- Generic
- Herbicide (26)
- Insect growth regulator (2)
- Insecticide (78)
- Nematocide (2)
- Plant growth regulator (6)
- Scald control agent
- Storage scald preventer
- Synergist
- Hydrogen Phosphide
- Methyl Bromide
- Sulfuryl fluoride

CODEX – methyl bromide

Cacao beans	5 mg/Kg	1999	Po	To apply at point of entry into a country and, in case of cereal for milling, if product has been freely exposed to air for a period of at least 24 h after fumigation and before
Cereal grains	5 mg/Kg	1999	Po	To apply at point of entry into a country and, in case of cereal for milling, if product has been freely exposed to air for a period of at least 24 h after fumigation and before
Cocoa products	0.01 mg/Kg	1999	(*) Po	To apply to commodity at point of retail sale or when offered for consumption
Dried fruits	2 mg/Kg	1999	Po	To apply at point of entry into a country and, in case of cereal for milling, if product has been freely exposed to air for a period of at least 24 h after fumigation and before
Dried fruits	0.01 mg/Kg	1999	(*) Po	To apply to commodity at point of retail sale or when offered for consumption
Milled cereals products	1 mg/Kg	1999	Po	To apply at point of entry into a country and, in case of cereal for milling, if product has been freely exposed to air for a period of at least 24 h after fumigation and before

NO fresh fruit ?!??

CODEX – bromide

Cucumber	100 mg/Kg	1997		
Dates, Dried or dried and candied	100 mg/Kg			
Dried fruits	30 mg/Kg			Except as otherwise listed.
Dried grapes (=currants, raisins and sultanas)	100 mg/Kg			
Dried herbs	400 mg/Kg			
Figs, Dried or dried and candied	250 mg/Kg			
Fruits (except as otherwise listed)	20 mg/Kg			
Garden pea (young pods)(=succulent, immature seeds)	500 mg/Kg	1997		

YES fresh fruit ?!?

CODEX – sulfuryl fluoride

218 - Sulfuryl fluoride

Functional class: Fumigant

Commodity	MRL	Year of Adoption	Symbol	Note
Bran, Unprocessed of cereal grain (except buckwheat, cañihua and quinoa)	0.1 mg/Kg	2006	Po	
Cereal bran, Processed	0.1 mg/Kg	2006	Po	
Cereal grains	0.05 mg/Kg	2006	Po	
Dried fruits	0.06 mg/Kg	2006	Po	
Maize flour	0.1 mg/Kg	2006	Po	
Maize meal	0.1 mg/Kg	2006	Po	
Rice, Husked	0.1 mg/Kg	2006	Po	
Rice, Polished	0.1 mg/Kg	2006	Po	
Rye flour	0.1 mg/Kg	2006	Po	
Rye wholemeal	0.1 mg/Kg	2006	Po	
Tree nuts	3 mg/Kg	2006	Po	
Wheat flour	0.1 mg/Kg	2006	Po	
Wheat germ	0.1 mg/Kg	2006	Po	
Wheat wholemeal	0.1 mg/Kg	2006	Po	

No timing ?!?

No fluoride ?!!??

CODEX – phosphine

46 - Hydrogen Phosphide

Functional class: **Fumigant**

Commodity	MRL	Year of Adoption	Symbol	Note
Cacao beans	0.01 mg/Kg		Po	
Cereal grains	0.1 mg/Kg		Po	
Dried fruits	0.01 mg/Kg		Po	
Dried vegetables	0.01 mg/Kg		Po	
Peanut	0.01 mg/Kg		Po	
Spices	0.01 mg/Kg		Po	
Tree nuts	0.01 mg/Kg		Po	

No fresh fruit ?!?

No timing ?!?

10 ppb ≅ no detection ≅ no residue

Phosphine (PH) – non-food use

§180.2020 Non-food determinations.

The following pesticide chemical uses do not need a tolerance or exemption from the requirement of a tolerance based on EPA's determination that they are not likely to result in residues in or on food.

Pesticide Chemical	CAS Reg. No.	Limits	Uses
Pure phosphine gas mixed with air or carbon dioxide	7803-51-2	When used for post-harvest cold storage fumigation followed by aeration and a 48 hour holding period.	Fresh fruits and vegetables

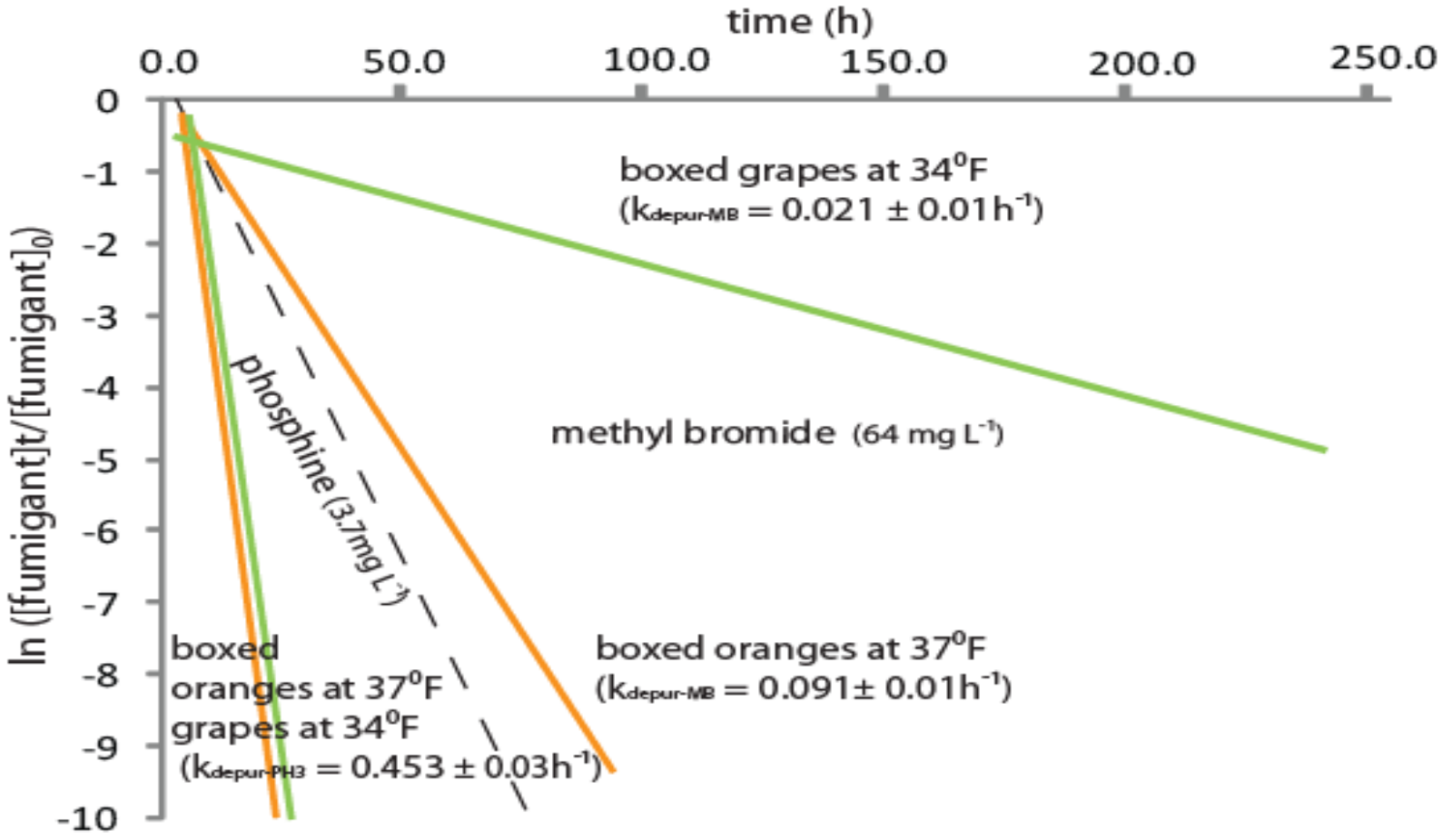
Nothing new.....

OPPTS GLN 860.1850 and 1900: Rotational Crops

These guidelines are not applicable to methyl bromide. The agricultural uses of methyl bromide are non-food uses; therefore, residues in rotational crops are also not of concern.

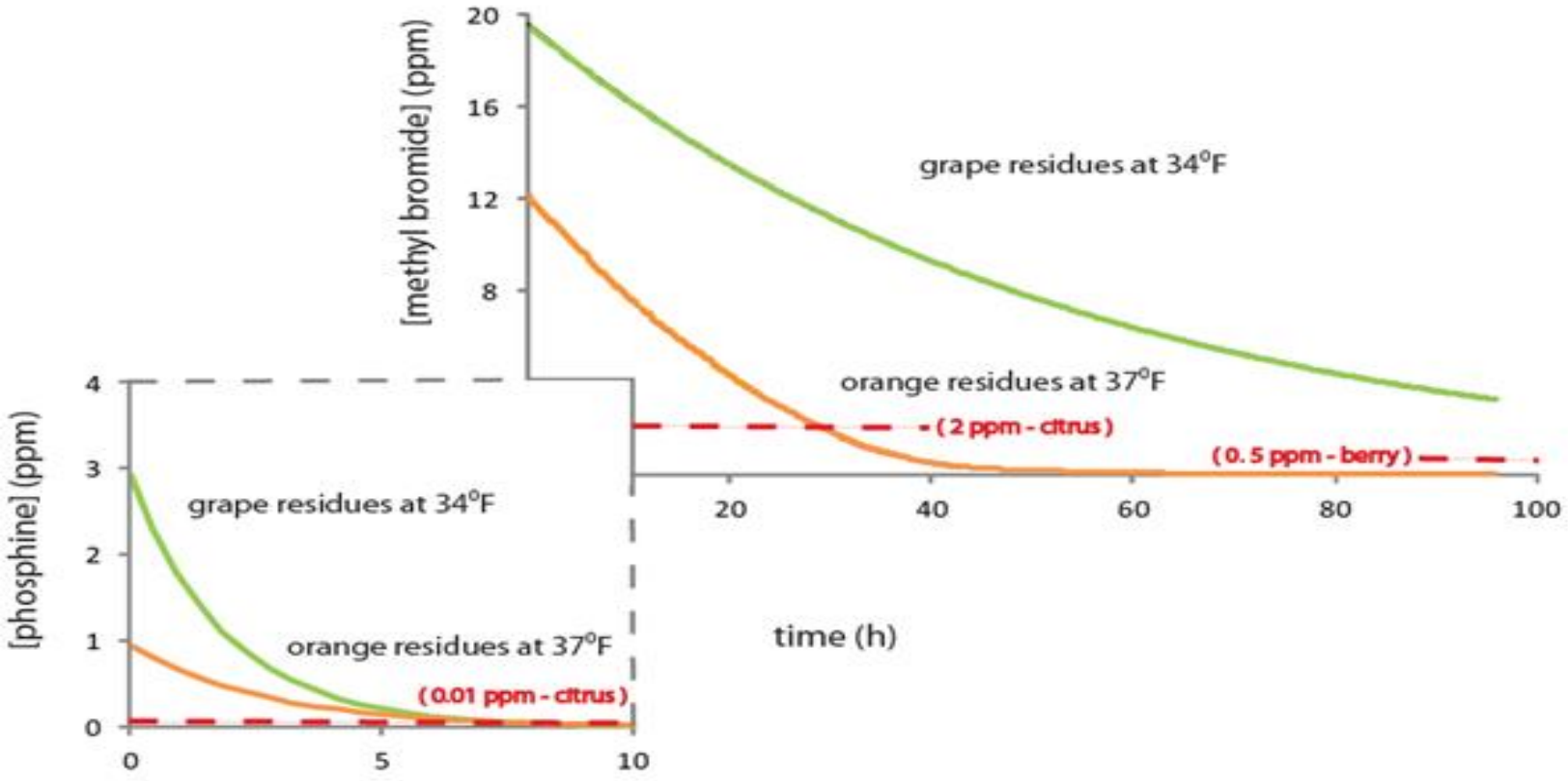
Thanks IR4 (Jerry Baron) and USEPA (Rick Keigwin)

Other factors for Korea: Worker Safety – Inhalation Exposure



Fumigants "off gas" (i.e., depurate) uniformly from boxed fruit over the course of cold storage with loss that follows first-order kinetic approximations given the applied doses and corresponding treatment temperature utilized in this study.

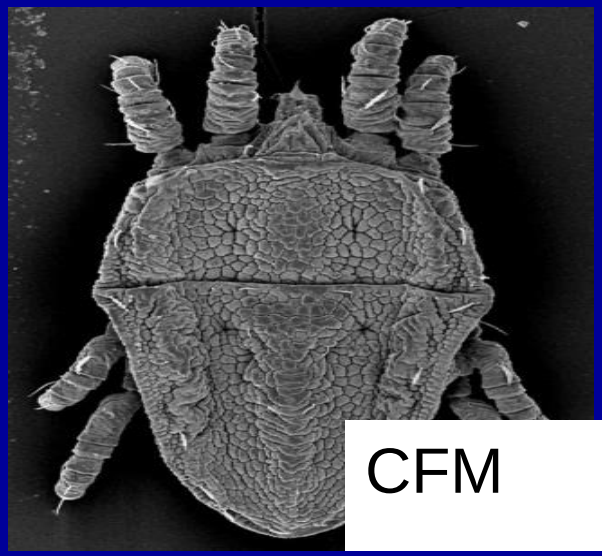
Other factors for Korea: Residues – Ingestion Exposure



"Organic" (i.e., gaseous) fumigant residues in fumigated fruit decreased uniformly over the course of cold-storage at 37 °F and 34 °F for oranges and grapes, respectively. Methyl bromide requires time-scales of days and phosphine requires timescales of hours to reach USEPA food tolerences for both methyl bromide and phosphine residues in fruit (dashed red lines).

Table grapes vs. Brevapalpus chilensis – Chilean false mite (CFM)

- Key trade barrier of US toward Chile fresh fruit
- US largest use of MB (fresh fruit)
- USEPA worker exposure issues at the dock
- Chilean exporters / US consumers want quality fruit



CFM

Winks (CSIRO) summary cartoon, adult RFB

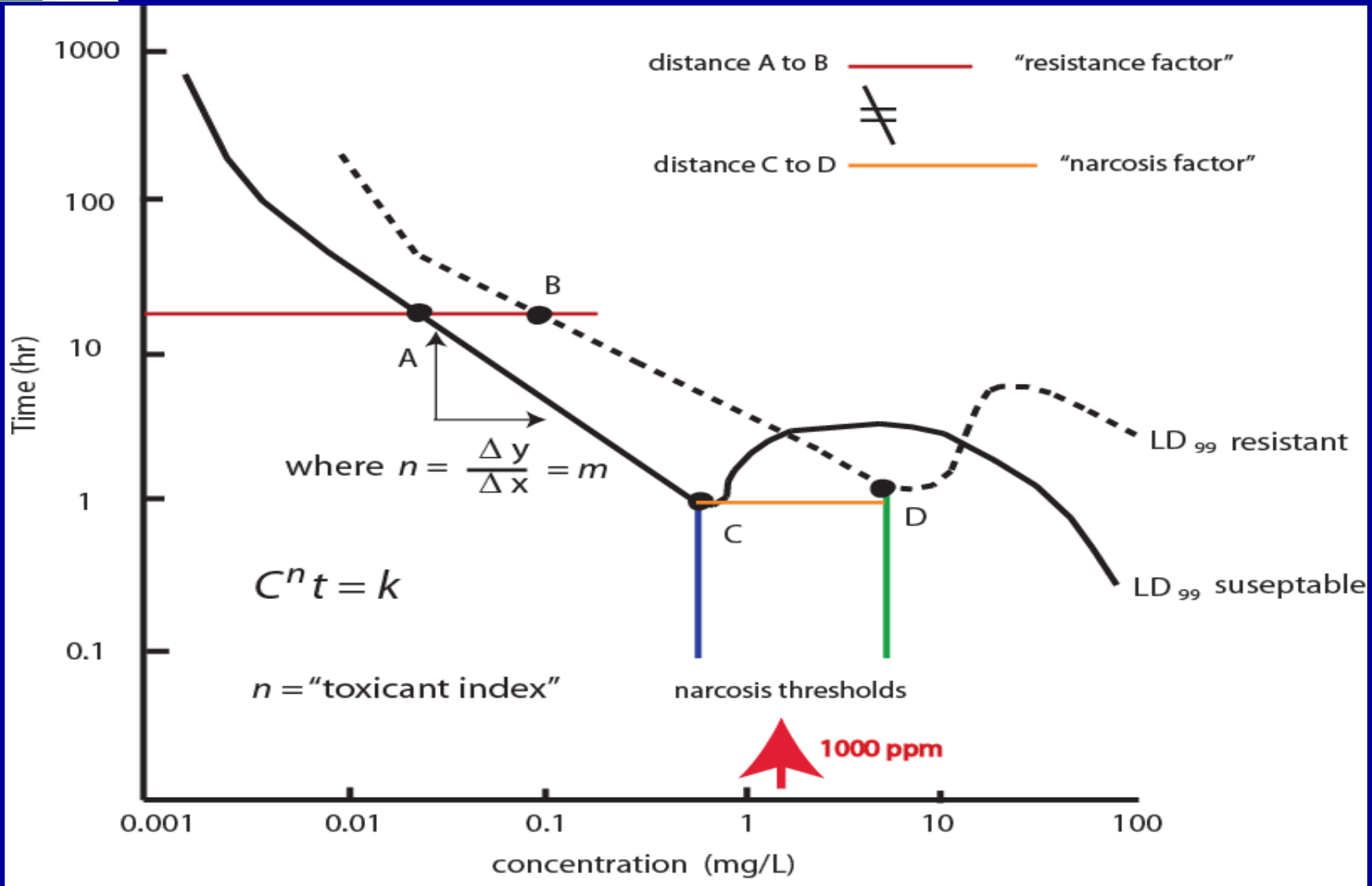
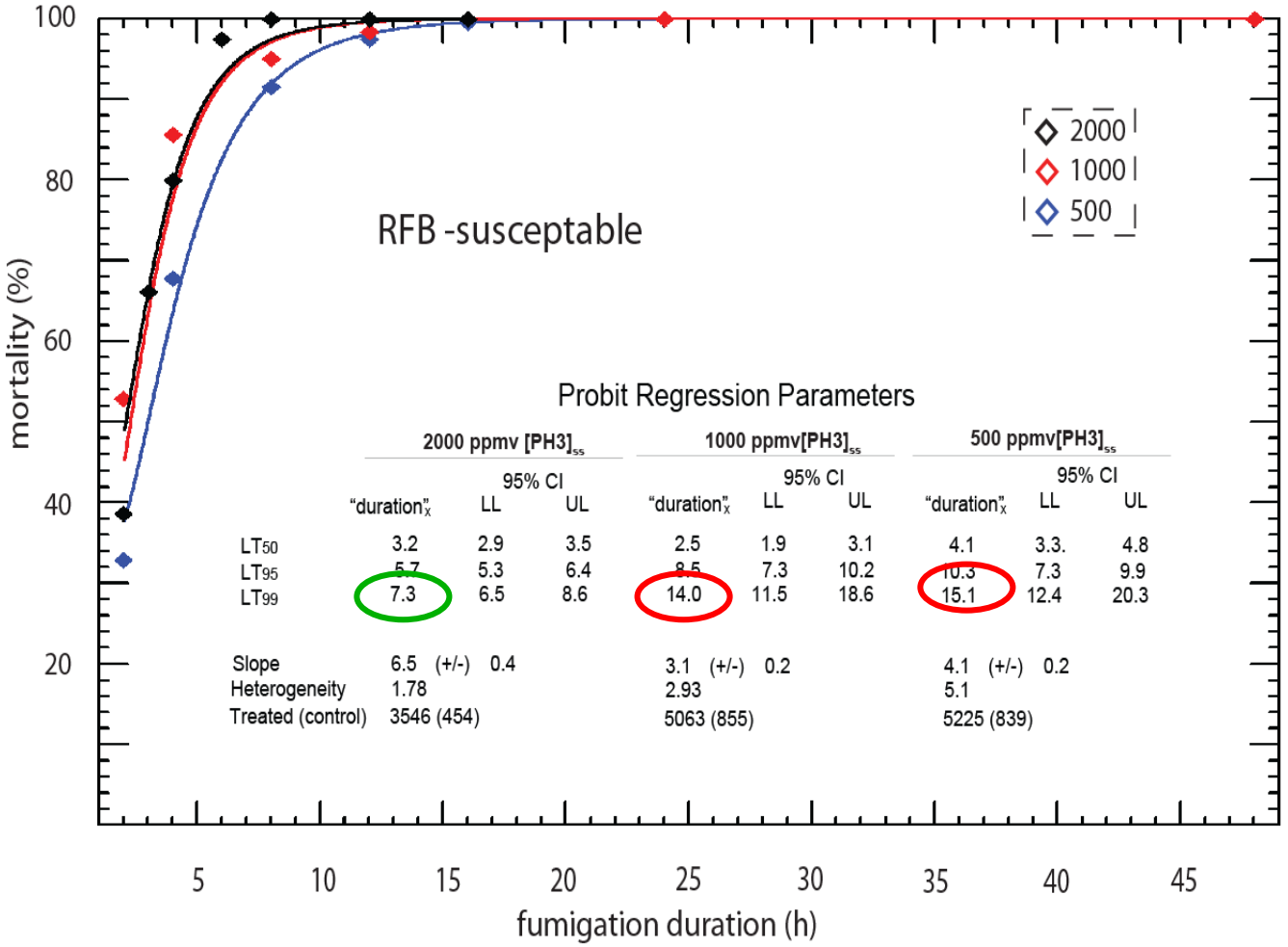
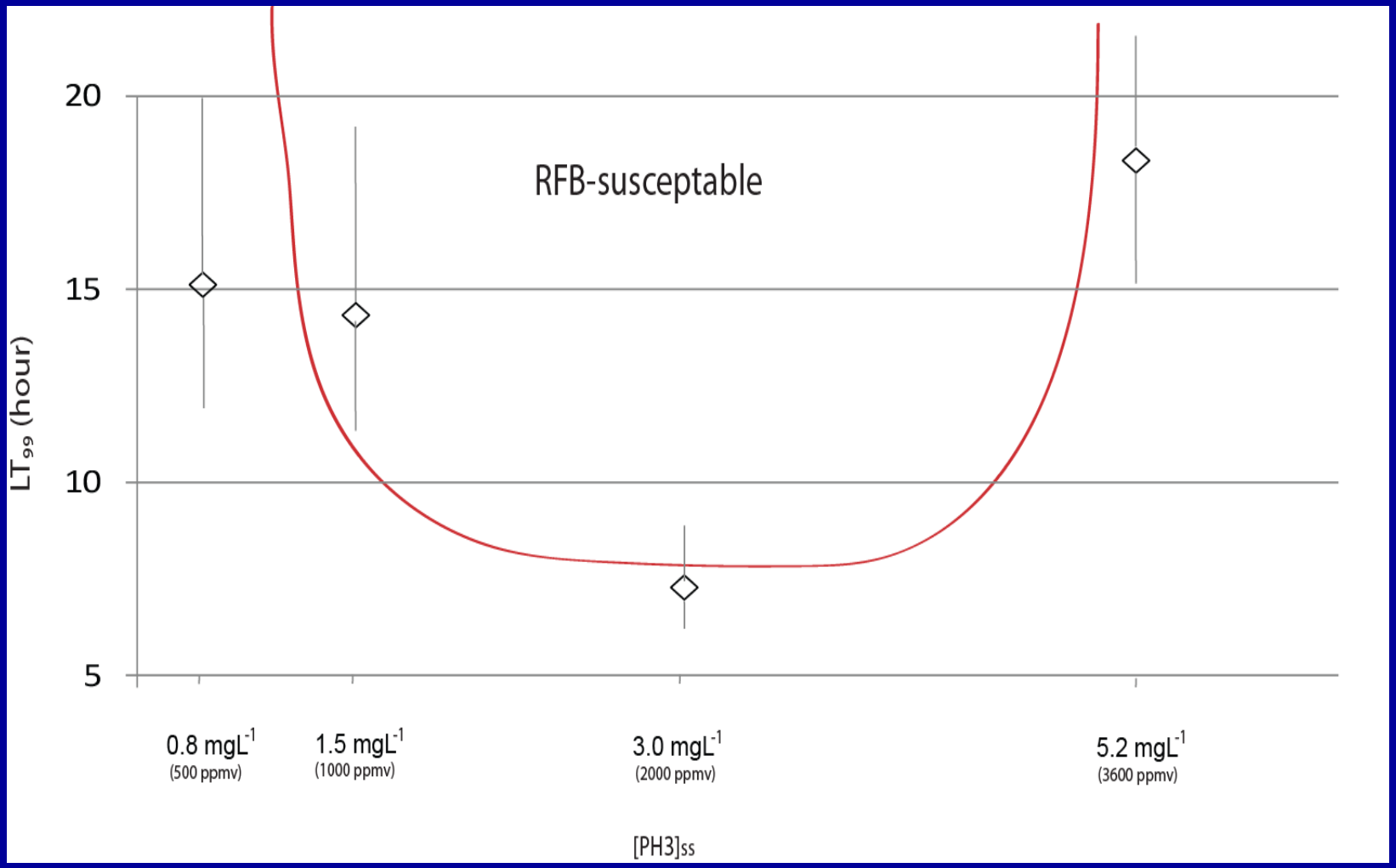


Figure 3. The realtionship between the time required for an LD_{99} at each of a range of fixed concentraions of phosphine to which RFB adults of a resistant strain CTC_{476} and a suseptable strain CTC_4 were exposed.

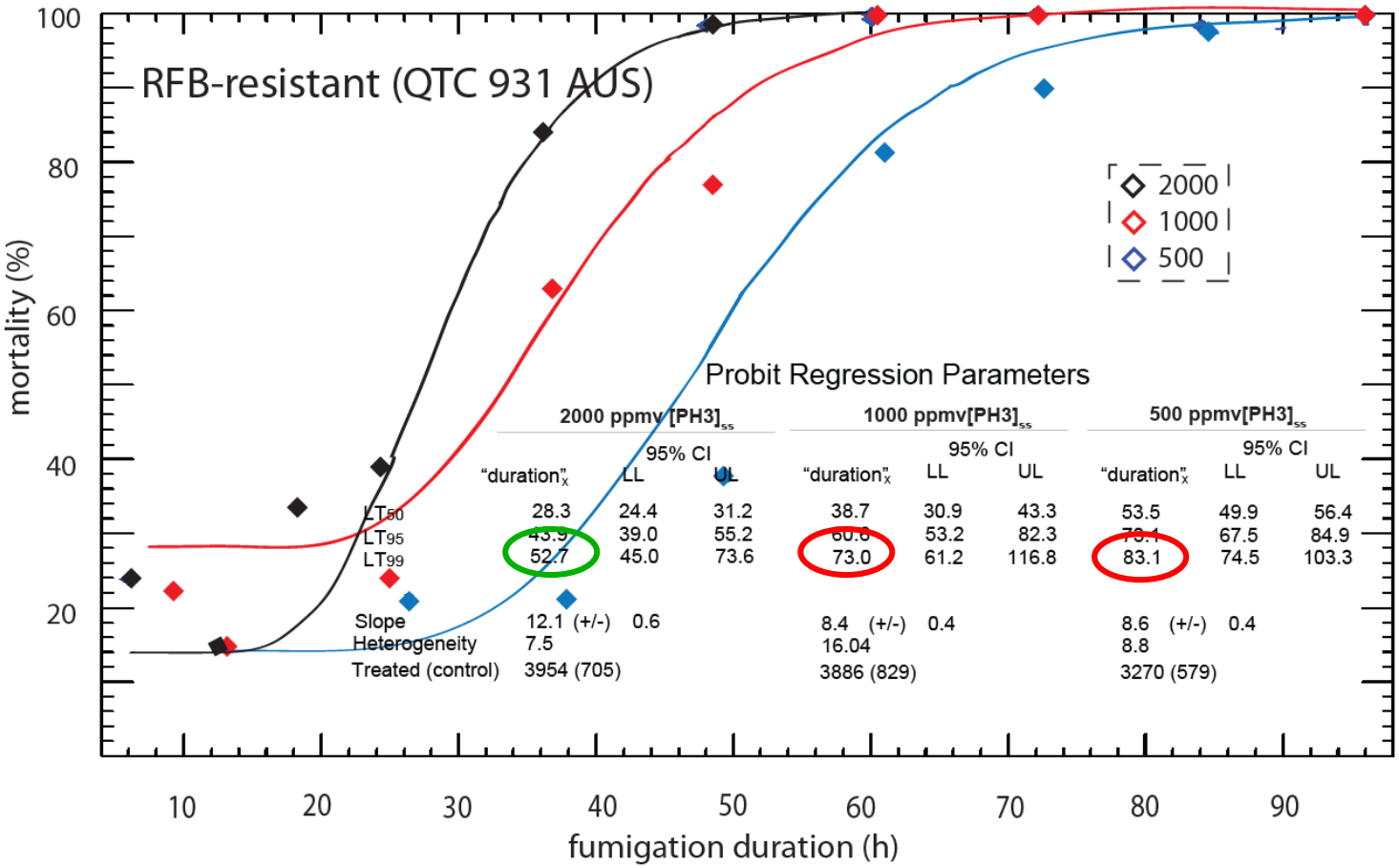
Mortality of susceptible (RFB), *Tribolium castaneum*, eggs w/ $[PH3]_{ss}$ at 70ºF



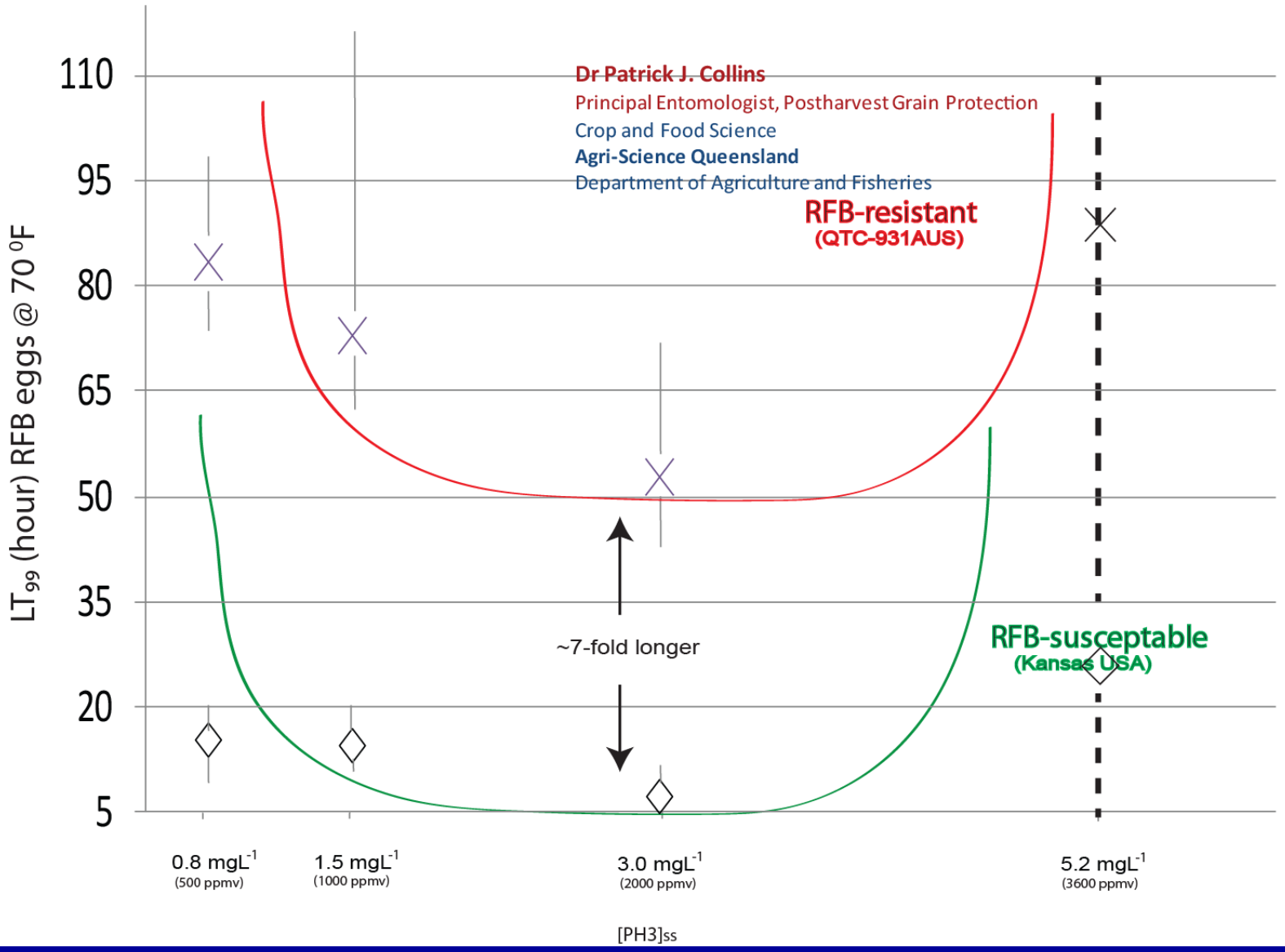
Susceptible RFB “sweet spot” @ 70°F



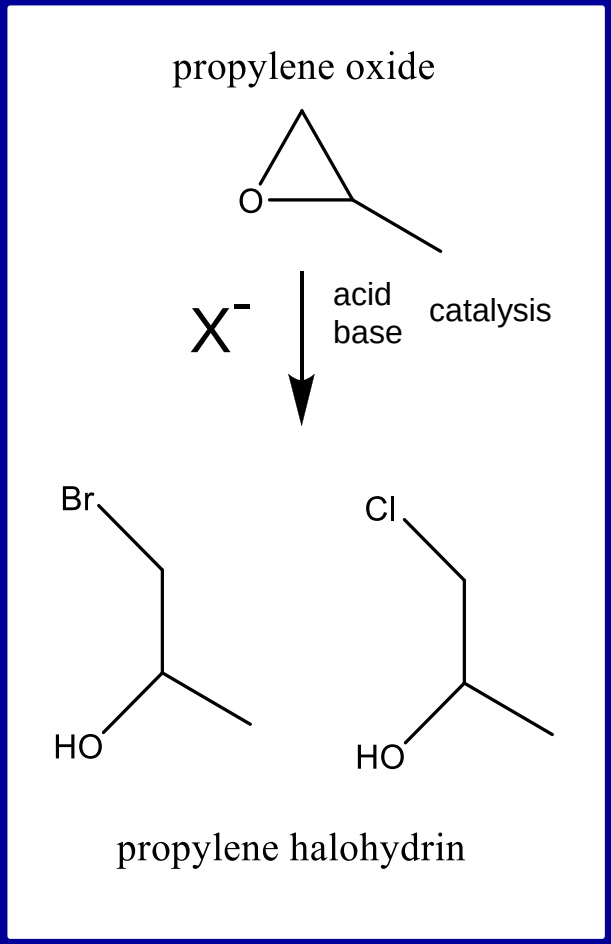
Mortality of resistant (RFB), *Tribolium castaneum*, eggs w/ $[PH3]_{ss}$ @70.0ºF



Resistance αTime >>>>[PH3]



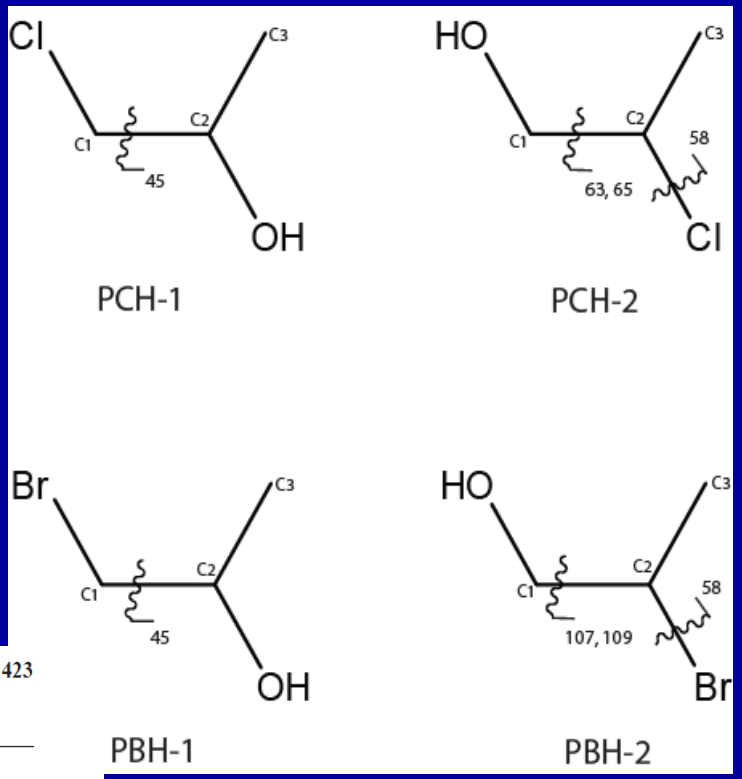
Tree nut MRL issues -propylene halohydrins & EU



- Degradation products as MRLs
  - Limited data on PCH
  - No data on PBH
- Historic perspective for concern
  - MB, bromide quantification (Br-)
  - Ozonation of drinking water

Tree nut MRL – PPO issue -getting started

- Novel Methodology
  - Existing ASTA method no work
    - "Artifactually" raises PCH and PBH
- Need isomeric resolution
  - Critically supports tox data

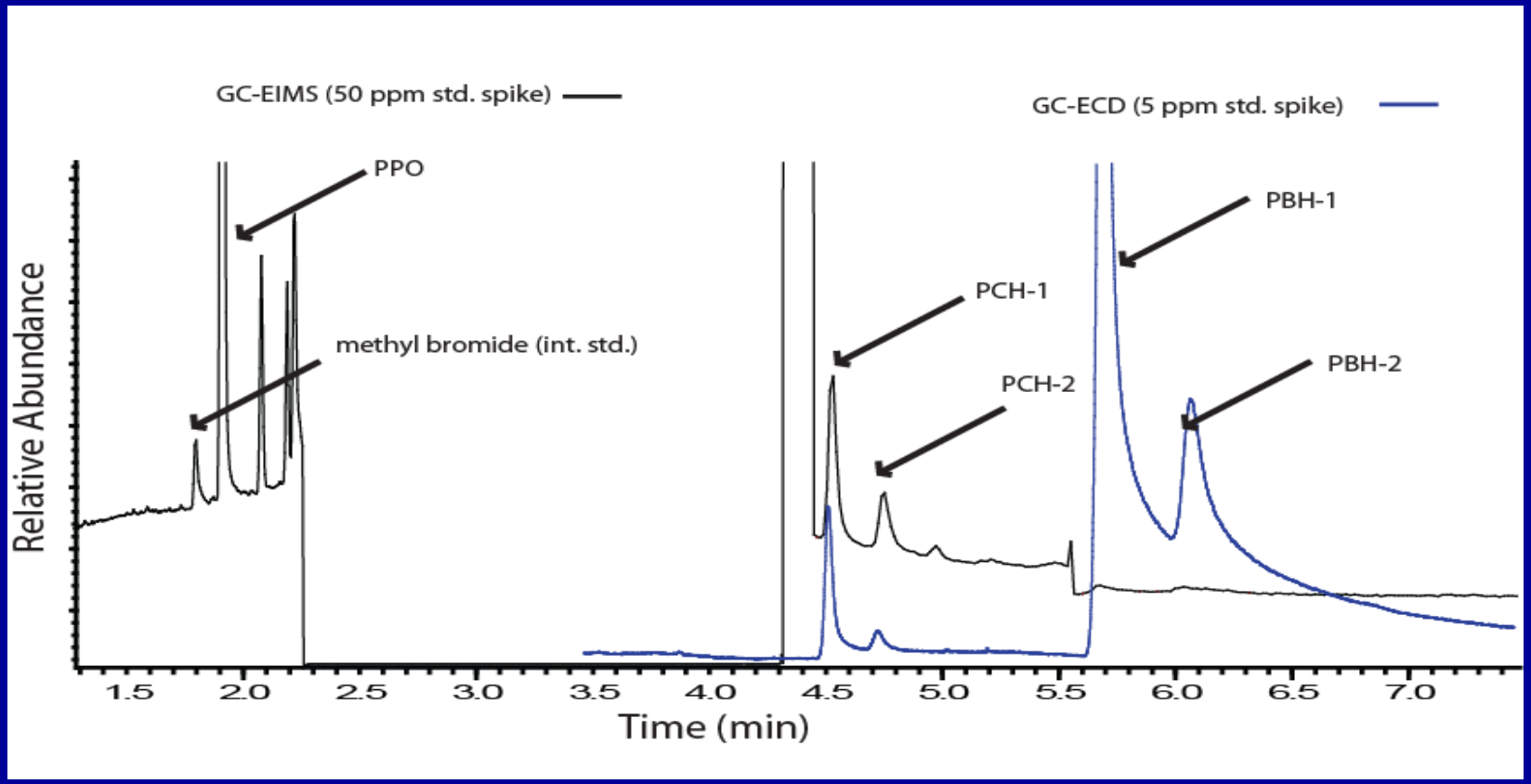


RESIDUES AND TRACE ELEMENTS

Quantifying Residues from Postharvest Propylene Oxide Fumigation of Almonds and Walnuts

Tree nut MRL – PPO issue -getting started

- Novel Methodology – GC Mass spectrometry



Mega bore GSQ (high flow of nastyness), $olvent

FAO PLANT PRODUCTION AND PROTECTION PAPER

225

Submission and evaluation of pesticide residues data for the estimation of maximum residue levels in food and feed

Storage

Samples should be analysed as quickly as possible after collection before physical and chemical changes occur. If prolonged storage is unavoidable, it is usually preferable to store the samples at a low temperature, preferably at or below –20 °C. This removes the residue from contact with enzymes which might degrade the pesticide and also prevents further possibility of residues being "bound" in the tissue. Do not store samples (whole or homogenised) for analysis unless an adequate check has been made on the stability of the residue. Fumigant residue samples need special attention and ideally should be analysed immediately on receipt at the laboratory. Storage at –20 °C is likely to be inadequate to prevent loss of fumigant residues.

USDA Agricultural Research Service

FAO PLANT PRODUCTION AND PROTECTION PAPER

225

Submission and evaluation of pesticide residues data for the estimation of maximum residue levels in food and feed

Sampling fruit and vegetables in packing houses

Where post-harvest treatments are applied to fruit and vegetables in packing houses, an adequate number of samples must be taken to determine the range of residue levels resulting from variations in the treatment process. The effects on residue levels of concentration, temperature, duration of treatment, drying (after dip treatments) and subsequent handling may need to be considered.

Post-harvest treated fruit and vegetables should be kept in, or packed in, commercial containers or punnets and stored at ambient or cool-room temperature according to normal commercial practice. Samples should then be drawn for analysis from the commercial containers at suitable intervals representing the time expected between treatment and subsequent marketing. The rate of disappearance or degradation of some residues depends on whether the commodity is held in a sealed or partly sealed container or is open to the air.

The sizes of samples to be taken are the identical as suggested in Tables V.1–V.3.

1. General recommendations

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In selecting sampling points and the sampling methods, all factors that control the residue distributions over the entire experimental plot must be considered. The best approach for any given plot can only be determined by a sufficiently trained person who is capable of recognising the importance and usefulness of the residue data sought, and who can interpret the results.

The samples must be representative to enable the analytical result to be applied to the entire experimental unit. The greater the number of plants sampled in a field plot, the more representative the sample will be. However, economics and the practical problems involved in handling large samples affect the magnitude of the sampling programme. The sample size

Detailed sampling procedures

The following recommendations refer to the sampling of mature crops at normal harvest time, unless otherwise stated. The classification of the crops is contained in Section 2 of Codex Alimentarius Volume 2A.[22]

Fruits and tree nuts

- Circle each tree or bush and select fruit from all segments of the tree or plant, high and low, exposed and protected by foliage. For small fruits grown in a row, select fruit from both sides, but not within 1 metre of the end of the row.

Miscellaneous small fruits e.g., olives, dates, figs	Group 005	1 kg from several places on 4 trees
Pineapples	Fl 0353	12 fruits
Banana, Plantain	Fl 0327	24 fruits. Take two fingers each from top, middle and lowest hand of four harvestable bunches
Tree nuts e.g., walnuts, chestnuts, almonds	Group 022	1 kg

IPPC compliance versus feedback from JMPR

Trial	location	duration, t (h)	applied $[PPO]_0$ ($g\ m^{-3}$)	$[PPO]_{t=x}$ $\bar{x} \pm s$
1	SJVASC	6	1500	554.1 ± 44.3
2	SJVASC	6	1500	547.0 ± 42.1
3	SJVASC	6	1500	535.6 ± 52.4
4	SJVASC	6	1500	583.2 ± 35.8
5	SJVASC	6	1500	541.5 ± 27.3

10% RSD

Bond, E. J. 1984. Manual of Fumigation for Insect Control: Chapter 2; Principles of Fumigation. FAO Plant Production and Protection Paper No. 54. Food and Agriculture Organization on the United Nations. Rome. pp 22-28.

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However, the Meeting also noted issues with the residue data. The laborato
analysis was a 25 g subsample for almonds and a 15 g subsample of nutmeat for
laboratory sample sizes do not correspond to the generally accepted prescribed sample s
tree nuts, see the "*FAO manual on the submission and evaluation of pesticide residue*
estimation of maximum residue levels in food and feed, 3rd edition" (2016), p 168. There is a concern that variability in residues, even for post-harvest fumigation, is such that the results may not adequately represent the average residue in the lot sampled. While the Meeting noted the difficulties presented by the analysis of a volatile fumigant such as PPO the small sample size was considered unacceptable.

Postharvest Fumigation Residues

1-slide take home.....