47th Annual

Florida Pesticide Residue Workshop

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James N. Seiber
Department of Food Science & Technology, UC Davis
Editor, *Journal of Agricultural and Food Chemistry*

PESTICIDE RESIDUES

Basic Principles for Quantitative Determination

FRANCIS A. GUNTHER and ROGER C. BLINN
University of California Citrus Experiment Station, Riverside, Calif.

The widespread use of synthetic organic pesticides has emphasized a number of analytical problems previously not significant. One of these problems involves the establishment of the magnitudes of persisting residues of these pesticides on and in foodstuffs. Present approaches to this residue problem are largely empirical. In the present paper, the basic analytical approaches to residue determinations are considered to be evaluation by direct measurement (selective) and isolation followed by measurement (nonselective). The latter approach interrelates physical separation with reaction separation. These logical approaches to devising analytical methods for pesticide residues are illustrated from the field of insecticides. Even though every foodstuff containing pesticide residues must be individually investigated as to performance in the final residue method, there is real **promise of systematization and standardization of efforts in new applications.**

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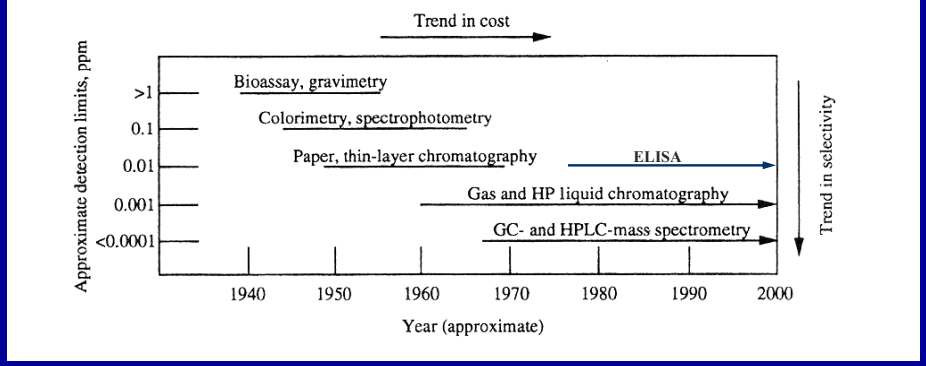


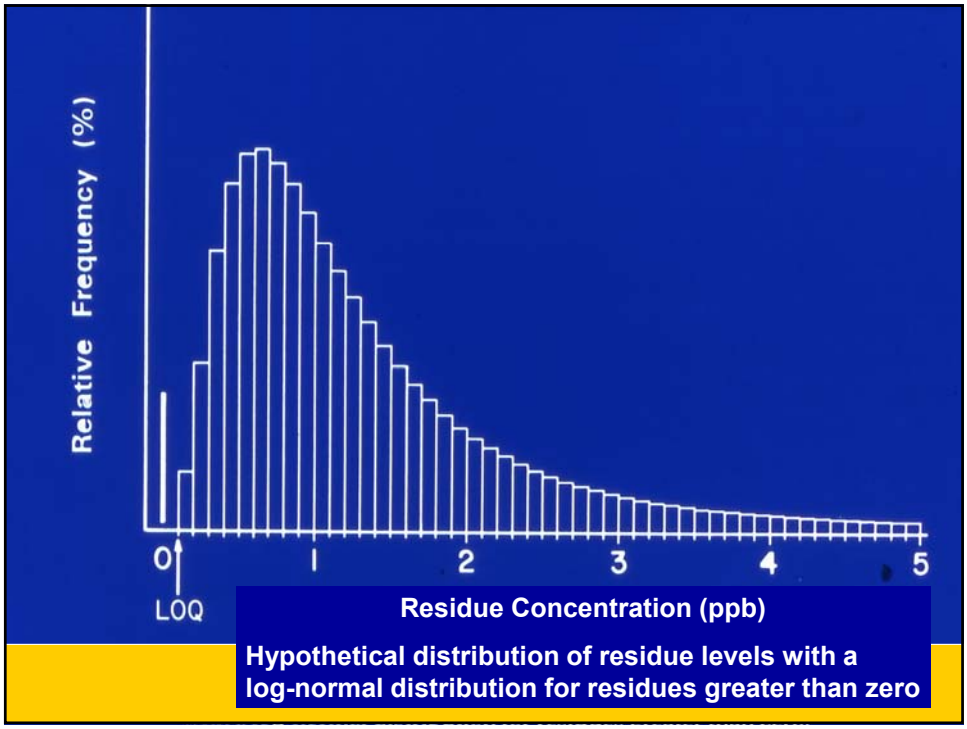
Advantages of Mass Spectrometry

DIOXIN ANALYSIS

Samples	Approximate Detection Limit	Techniques	Reference
Bird	50 ppb	Chemical Treatment Column Chromatography EC-GLC	Woolson et al, 1973
Beef (liver) Fish Crustaceans	20 ppt	Chemical Treatment Prep GLC HR Mass Spec	Baughman and Meselsohn, 1973
Trout	10 ppt	Chemical Treatment Column Chromatography (Multiple) HPLC GC/MS	Lamparski et al, 1979
Milk	1 ppt	Chemical Treatment Column Chromatography (Multiple) HPLC (2) GC/MS	Langhorst and Shadoff, 1980

ANALYSIS COSTS, 114 PRORITY POLLUTANTS

Method	Cost/Analysis
GC	$ 557
GC/MS	$ 328



Hypothetical distribution of residue levels with a log-normal distribution for residues greater than zero

RESIDUE CHEMISTRY: FOOD SAFETY

- Removal/replacement of OCs and some OPs
- Low rate, low residual chemicals and biorationals
- Better education, enforcement
- Passage of FQPA

FOOD MONITORING (CA)

Marketplace Surveillance

No detectable residue	77.94%
Within tolerance	21.35%
Over tolerance	0.71%
(0.22% exceeded tolerance; 0.49% no tolerance)	

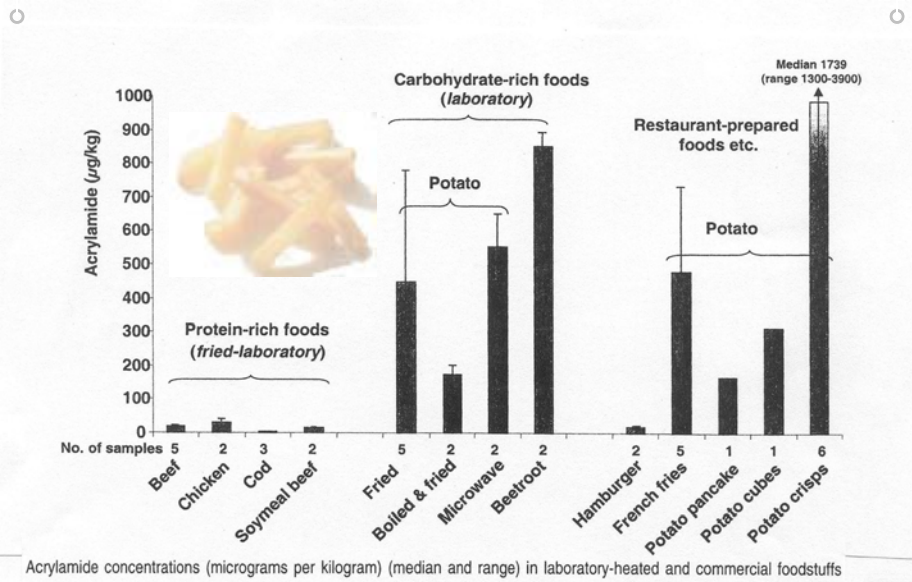
Priority pesticide

Number of targeted pesticide	36
No detectable residues	90%
Within tolerance	9.9%
Over tolerance	1 sample

Produce destined for processing

No detected residues	91%
Within tolerance	9%
Over tolerance	0%

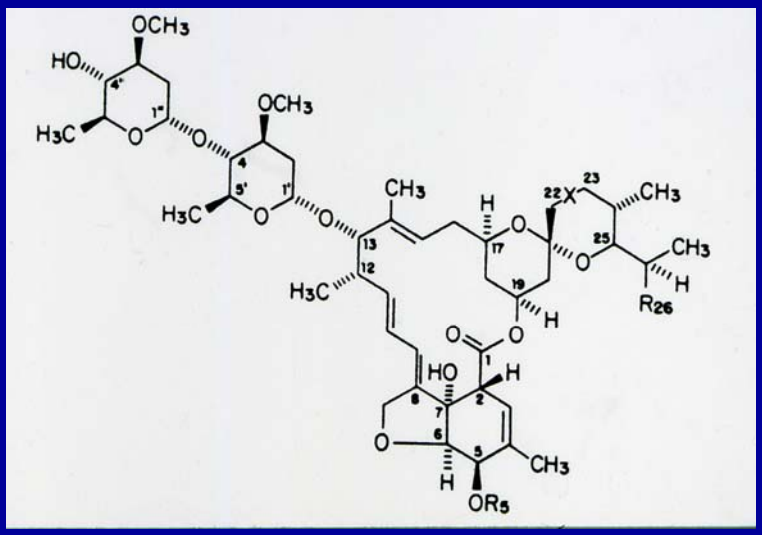
Fong, 1999



Acrylamide concentrations (micrograms per kilogram) (median and range) in laboratory-heated and commercial foodstuffs

Tareke et al. 2002

Avermectin—Miracle Drug



Dr. Linda Aston

RESIDUE CHEMISTRY AND IMPROVED WORKER SAFETY

- Reduced-risk pesticides
- Better spray technology
- Better education
- Better protection

WORKER SAFETY

RESIDUE CHEMISTRY : IMPROVED ENVIRONMENTAL SAFETY

- Better understanding of fate processes
- Better pre-market screening
- Lower risk pesticides

DETECTING AIRBORNE MOLINATE IN MAXWELL, CA

Vapor Pressures of Common Soil Fumigants

Fumigant	Structure	VP (Pa)
Methyl Bromide	CH_3Br	1.9×10^5
Chloropicrin	Cl_3CNO_2	2,266
MITC	$CH_3N=C=S$	2,533
1,3-D	$ClCH_2CH=CHCl$	3,733

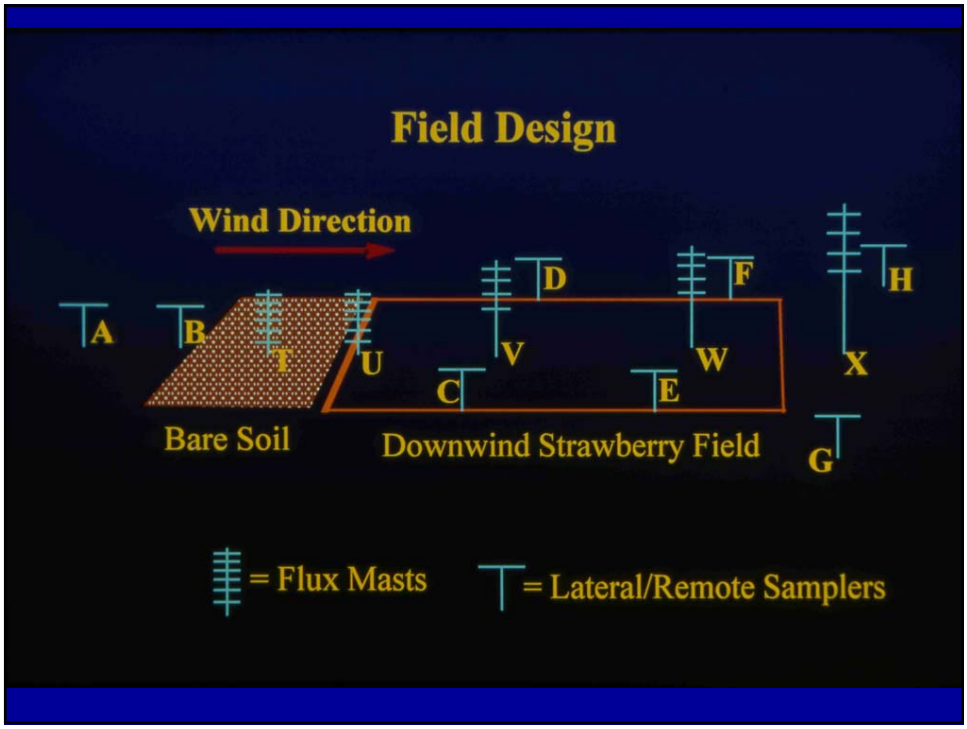
COMPARISON OF ESTIMATED WITH MEASURED SOIL FUMIGANT EMISSION RATES

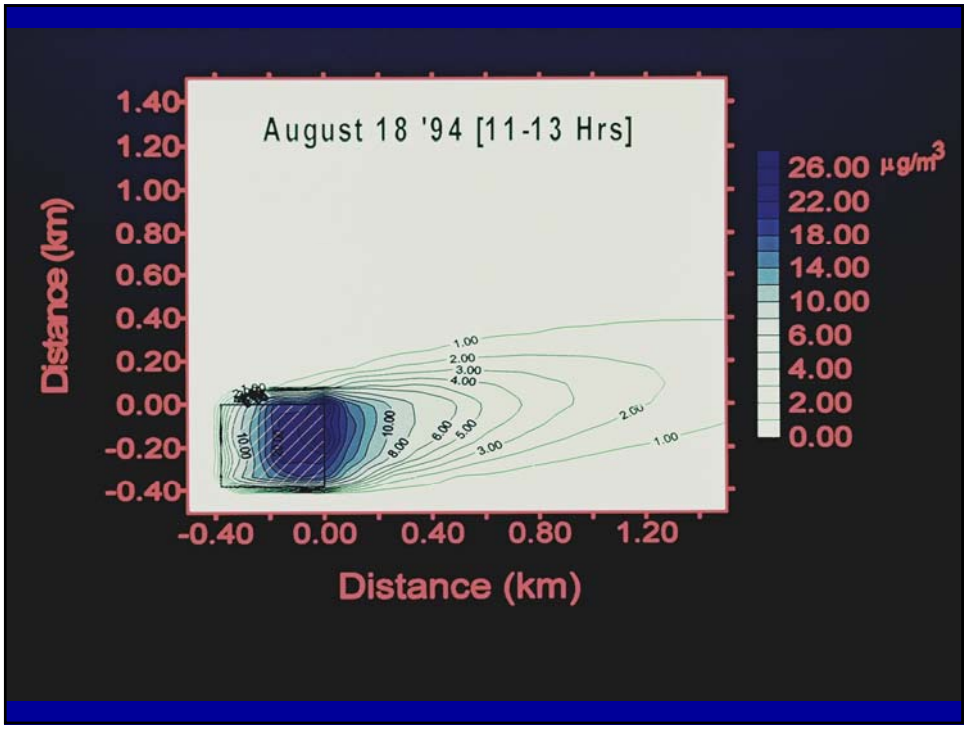
Emission ($\mu g/m^2/s$)

Fumigant	Measured	Estimated
MeBr	76-86	80
Chloropicrin	113	109
1,3-D	6.9 – 9.7	8.4
MITC	1-5	3.7

Dispersion Model:
Industrial Source Complex - Short Term 2

- Is built on straight-line, steady state Gaussian plume equation
- Applicable to:
  - Industrial source complexes
  - Rural or urban areas
  - Flat or rolling terrain
  - Transport distances less than 50 kilometers
  - One hour to annual averaging times


Field Design
Wind Direction
A
B
T
U
C
V
D
E
W
F
X
H
G
Bare Soil
Downwind Strawberry Field
= Flux Masts
= Lateral/Remote Samplers

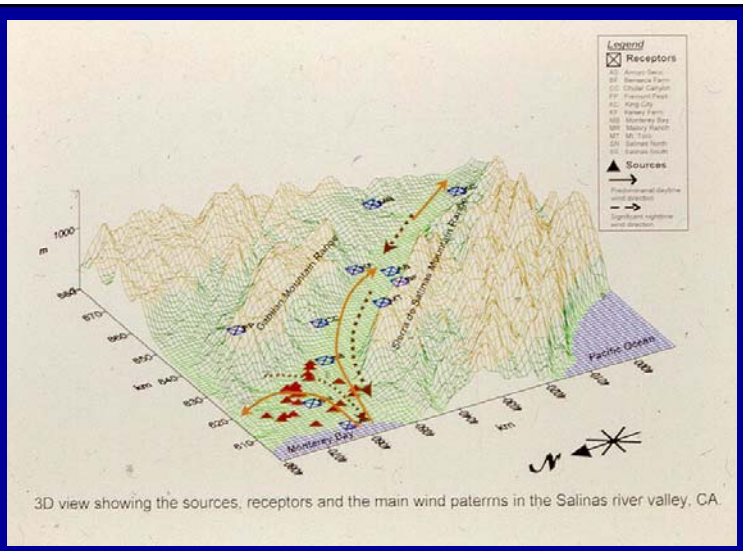

August 18 '94 [11-13 Hrs]
Distance (km)
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
-0.20
-0.40
-0.40
0.00
0.40
0.80
1.20
Distance (km)
26.00 µg/m3
22.00
18.00
14.00
10.00
6.00
4.00
2.00
0.00

AMBIENT CONCENTRATIONS OF METHYL BROMIDE IN THE SALINAS VALLEY, CA ($\mu g/m^3$)

	Salinas North	Salinas South	Arroyo Seco	King City
Highest 24 h Avg. Conc. Measured	5.68	5.94	1.65	0.51
Annual Time Wt. Avg. Conc. (WAC)	2.48	2.51	0.76	0.29
Worst Case (ISCST3)=2xWAC	4.96	5.02	1.52	0.58
Worst Case (CALPUFF) =1.66xWAC	4.12	4.17	1.26	0.48

NOAEL
=81600 $\mu g/m^3$
(Lim, 1992)

LOAEL (HEC)
=480 $\mu g/m^3$
(IRIS, 1997)



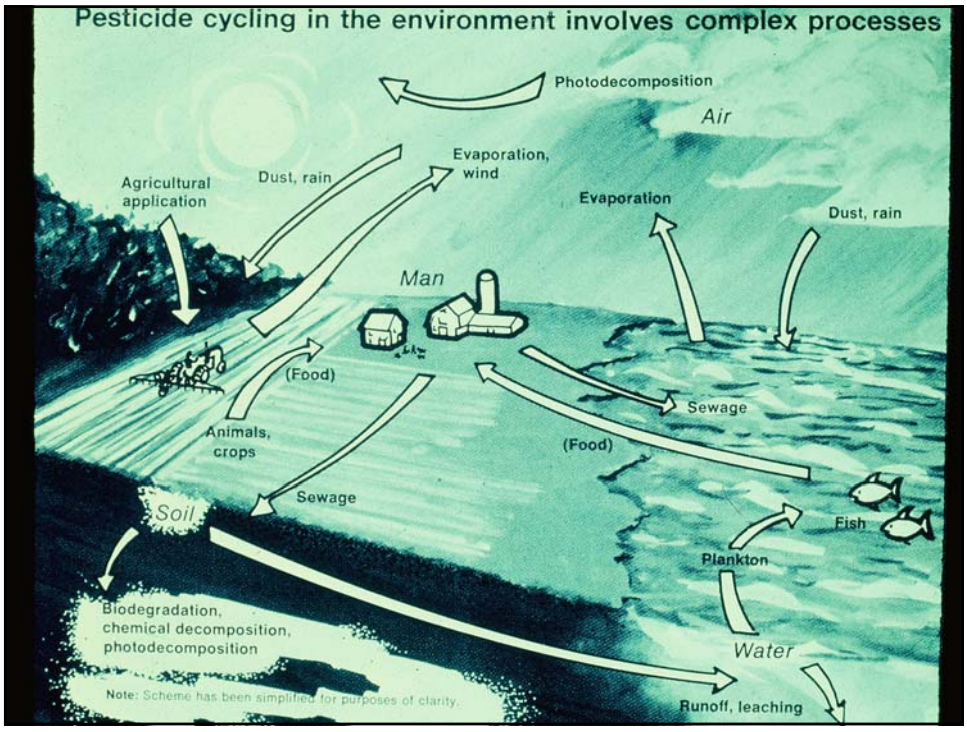
3D view showing the sources, receptors and the main wind paterms in the Salinas river valley, CA

RESIDUE DISTRIBUTION STUDY
(MeBr in THE SALINAS VALLEY)

Honaganahalli and Seiber, 2000.

Risk Management for Fumigants

- Application Rates/Methods
- Barriers to Volatilization
- Buffer Zones (Sensitive to Wind, Contours, etc.)
- Switch to Alternative Controls



Exposure Pathways for Hawks in Orchards

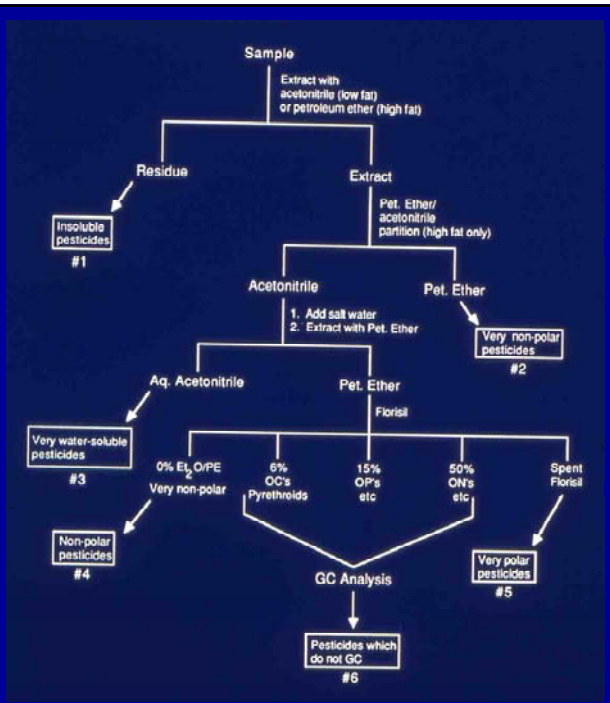
Calculating Maximum Daily Exposure of Hawks Inside Recently Treated Orchard (Example)

	Concentration		Max Daily Exposure
	Mean	***Max***	
Foot wash	7 µg/bird	70 µg/bird	70 µg/bird
Feathers	2.5 ppm	25 ppm	1000 µg/bird
Air	1.6 µg/m^3	15 µg/m^3	30 µg/bird

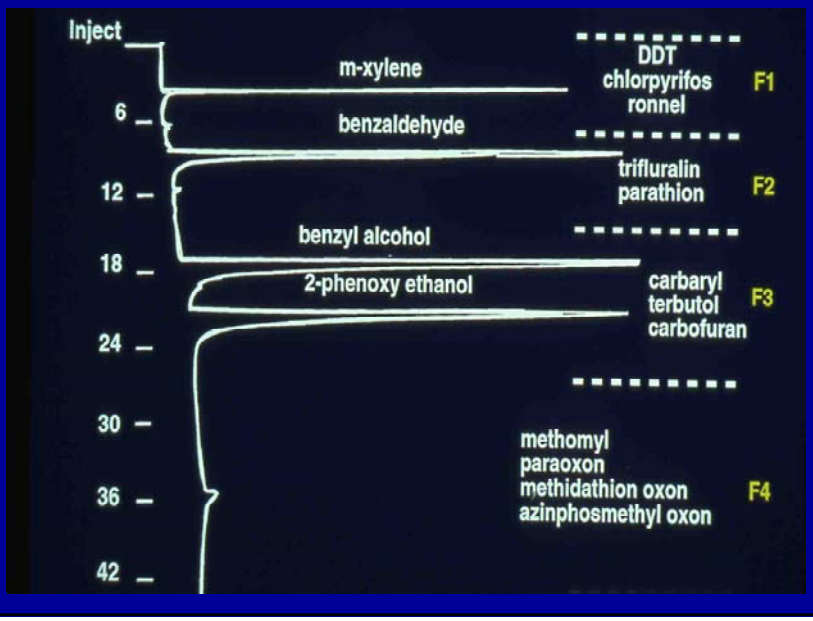
Total 1100 µg/bird
Or 1.1 mg/kg/day

Fog Sampler

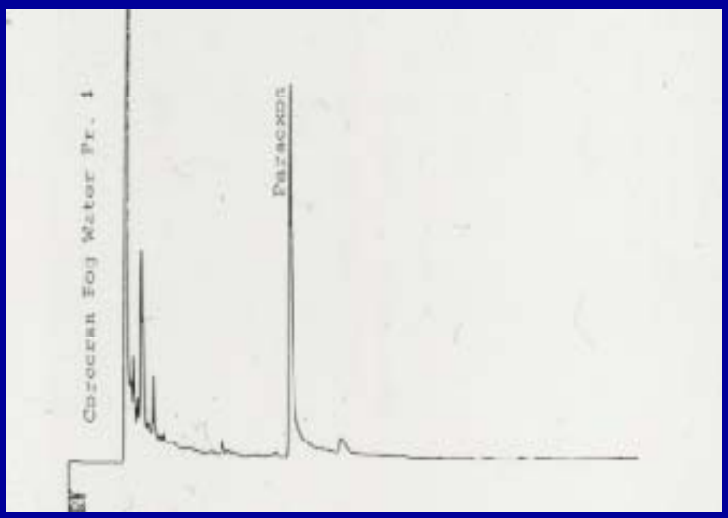
Figure 3.
Mills Procedure (PAM)



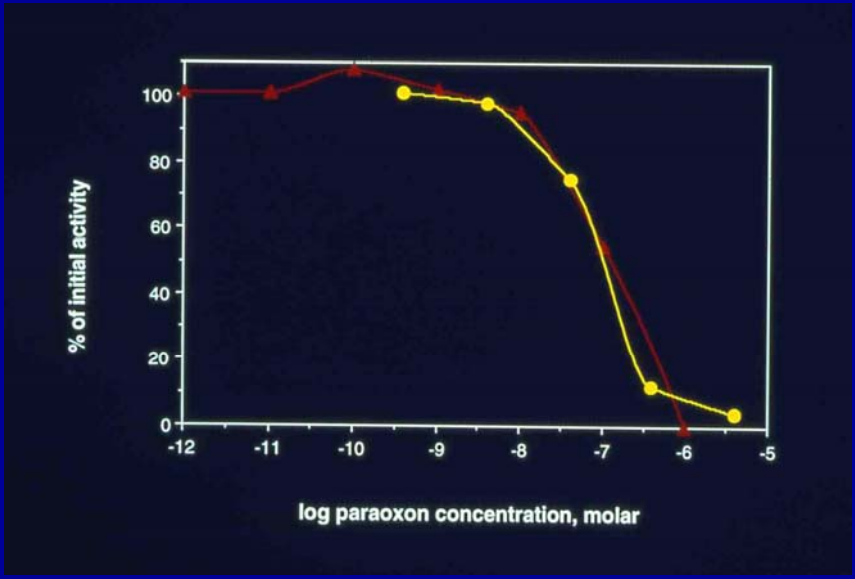
HPLC chromatogram showing organic marker standards, fraction zones, and example pesticides



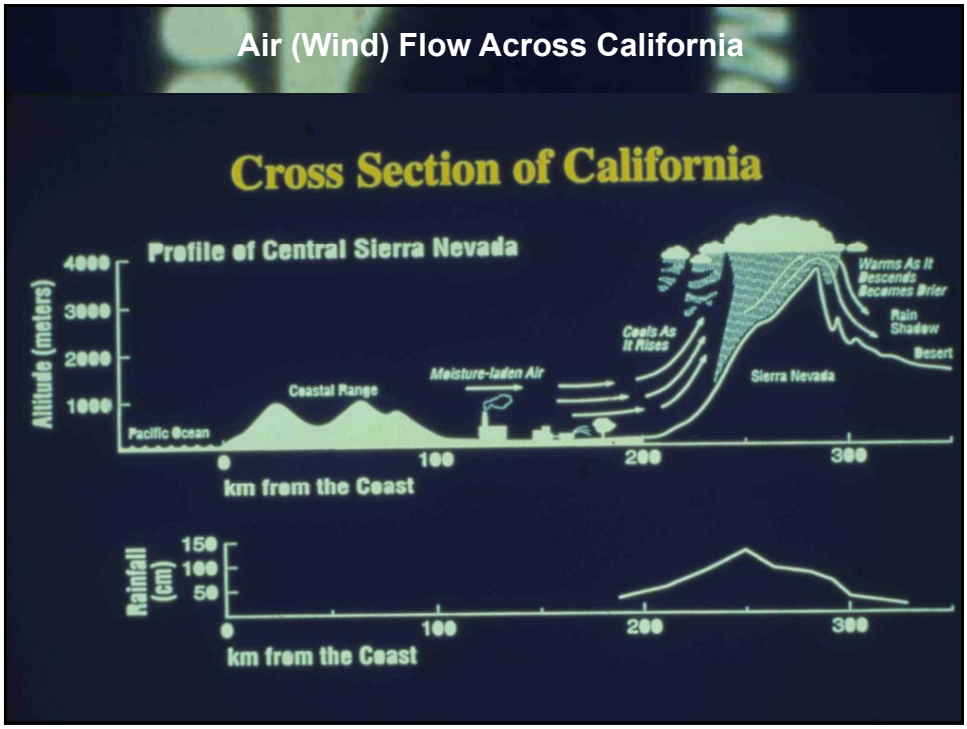
Fog Sample -- Results

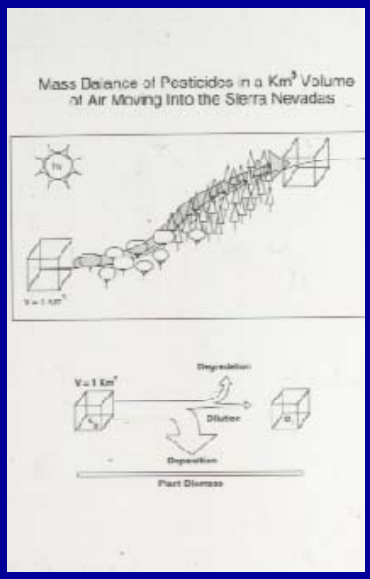


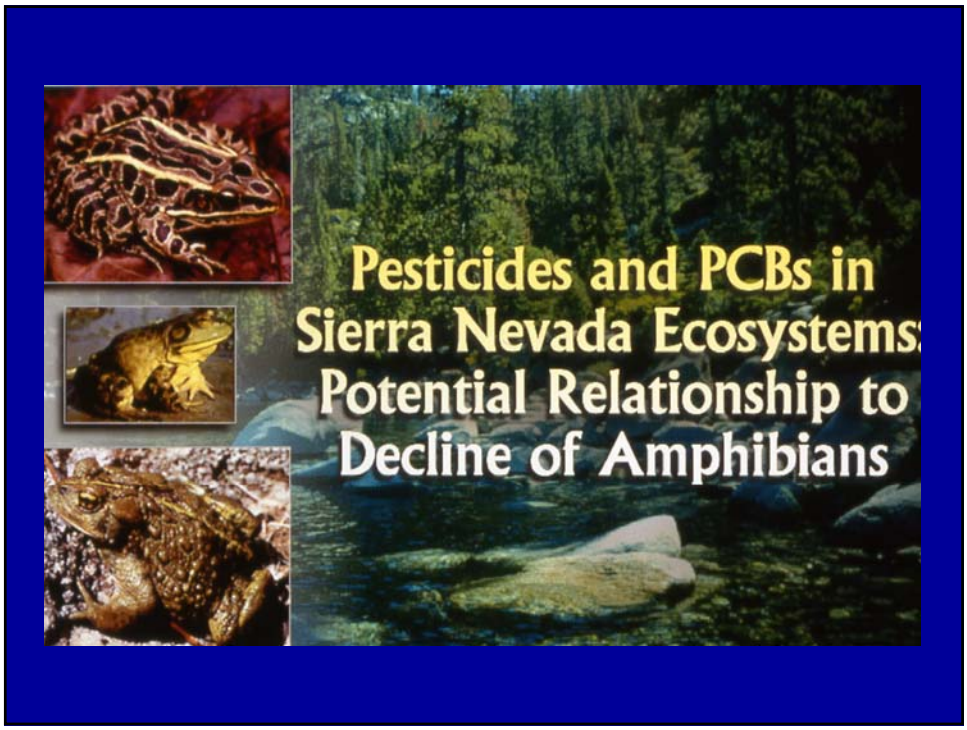
Cholinesterase inhibition of Lodi Fog

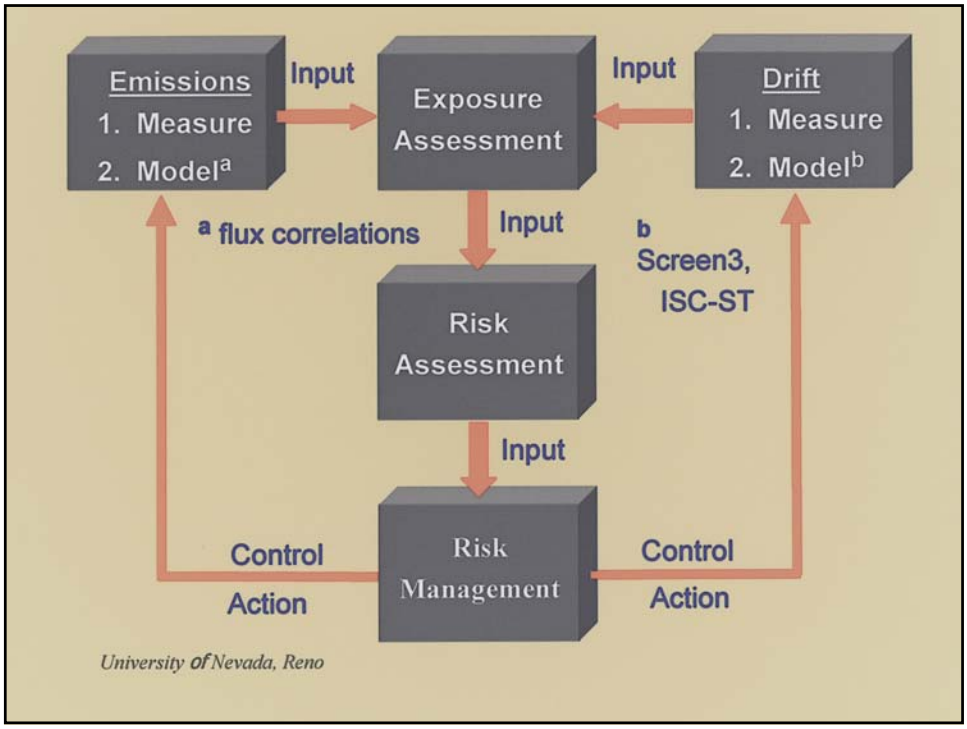


Air (Wind) Flow Across California






Pesticides and PCBs in
Sierra Nevada Ecosystems:
Potential Relationship to
Decline of Amphibians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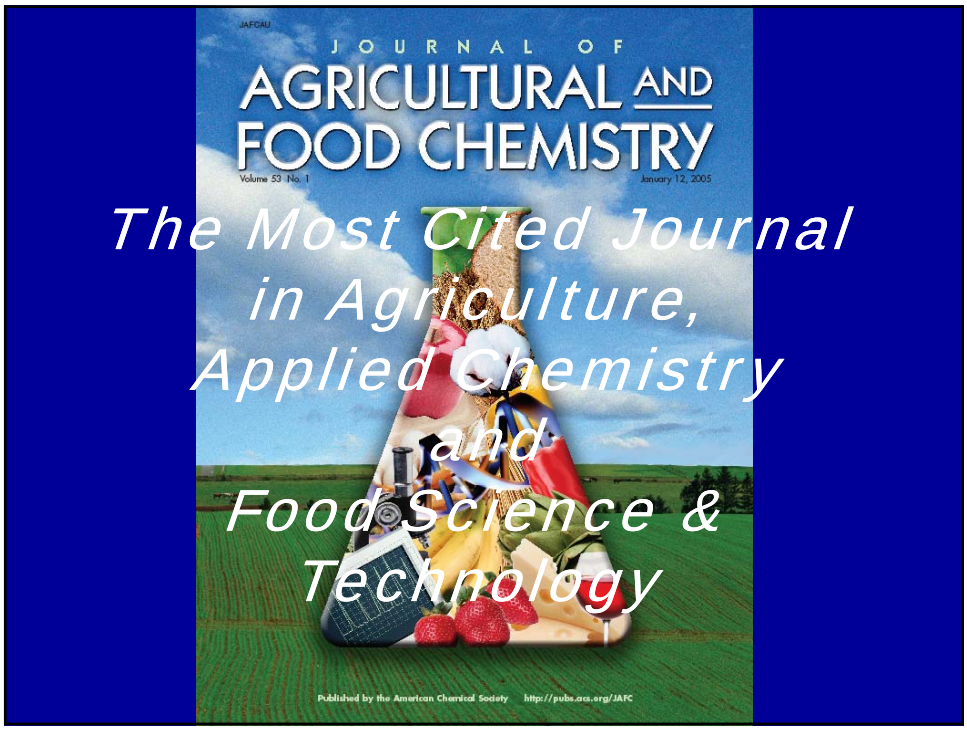
2. Model[a]
Input
Exposure Assessment
Input
Drift
1. Measure
2. Model[b]
[a] flux correlations
Input
[b] Screen3, ISC-ST
Risk Assessment
Input
Control Action
Risk Management
Control Action
University of Nevada, Reno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