Environmental Fate of Pesticides

Part 2 – case studies

- organochlorines and organohalogens – a persistent legacy
- diazinon – a frequent surface water contaminant, dormant spray use
- synthetic pyrethroids – history, reevaluation and data requirements

- 10 min break-

- VOCs, NOx and ozone – chemistry, reactivity and speciation
- rice herbicides – DPR's mitigation success story

- 10 min break-

- CFC age-dating and probabilistic modeling of herbicide transport to groundwater
- closing comments on emerging chemistries/problems/issues

Stockholm Convention on Persistent Organic Pollutants (POPs)

global treaty to protect human health and the environment

POPs:

- persist for exceptionally long periods of time (many years);
- widely distributed throughout the environment as a result of natural processes
- bioaccumulate
- toxic to both humans and wildlife.

Original 12 POPs

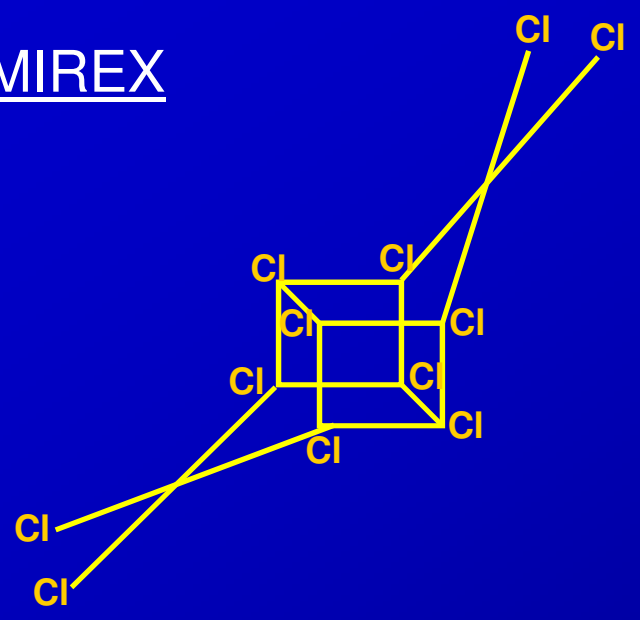
Aldrin,
Chlordane,
DDT,
Dieldrin,
Endrin,
Heptachlor,
Hexachlorobenzene,
Mirex,
Polychlorinated Biphenyls,
Polychlorinated dibenzo-*p*-dioxins,
Polychlorinated dibenzofurans,
Toxaphene

POPs added 2009

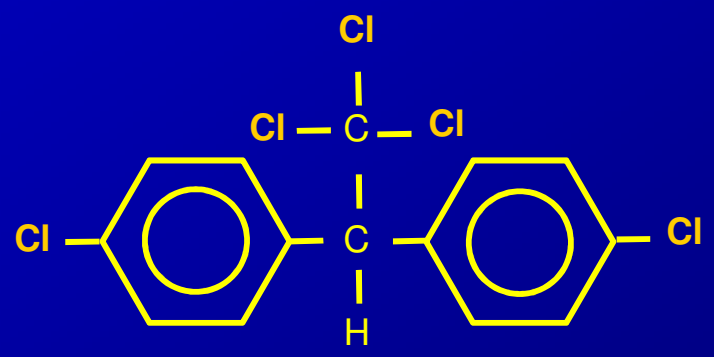
α-hexachlorocyclohexane,
β- hexachlorocyclohexane,
Chlordecone,
Commercial octabromodiphenyl ether,
Commercial pentabromodiphenyl ether,
Hexabromobiphenyl,
Lindane,
Pentachlorobenzene,
Perfluorooctane sulfonic acid (PFOS) & salts,
Perfluorooctane sulfonyl fluoride (PFOS-F)

legacy organochlorine pesticides

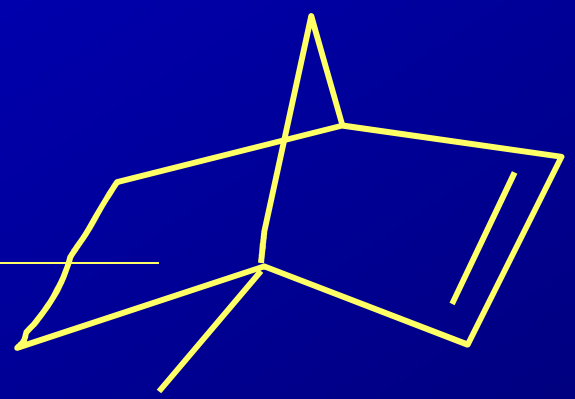
MIREX



DDT

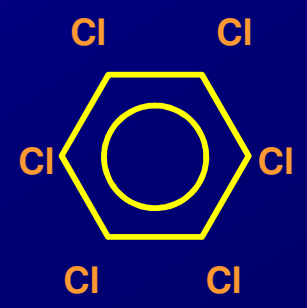


6 – 10 Cl



TOXAPHENE

HEXACHLOROBENZENE



legacy organochlorines

possess extreme properties

	DDT	mirex
MW	355	546
Soly	.008	.00007
K_{OC}	430000	1,000,000
FD $t_{1/2}$	2-15 yrs	~10 years
v.p.	.0002 torr	.0008
H'	.01	0.3

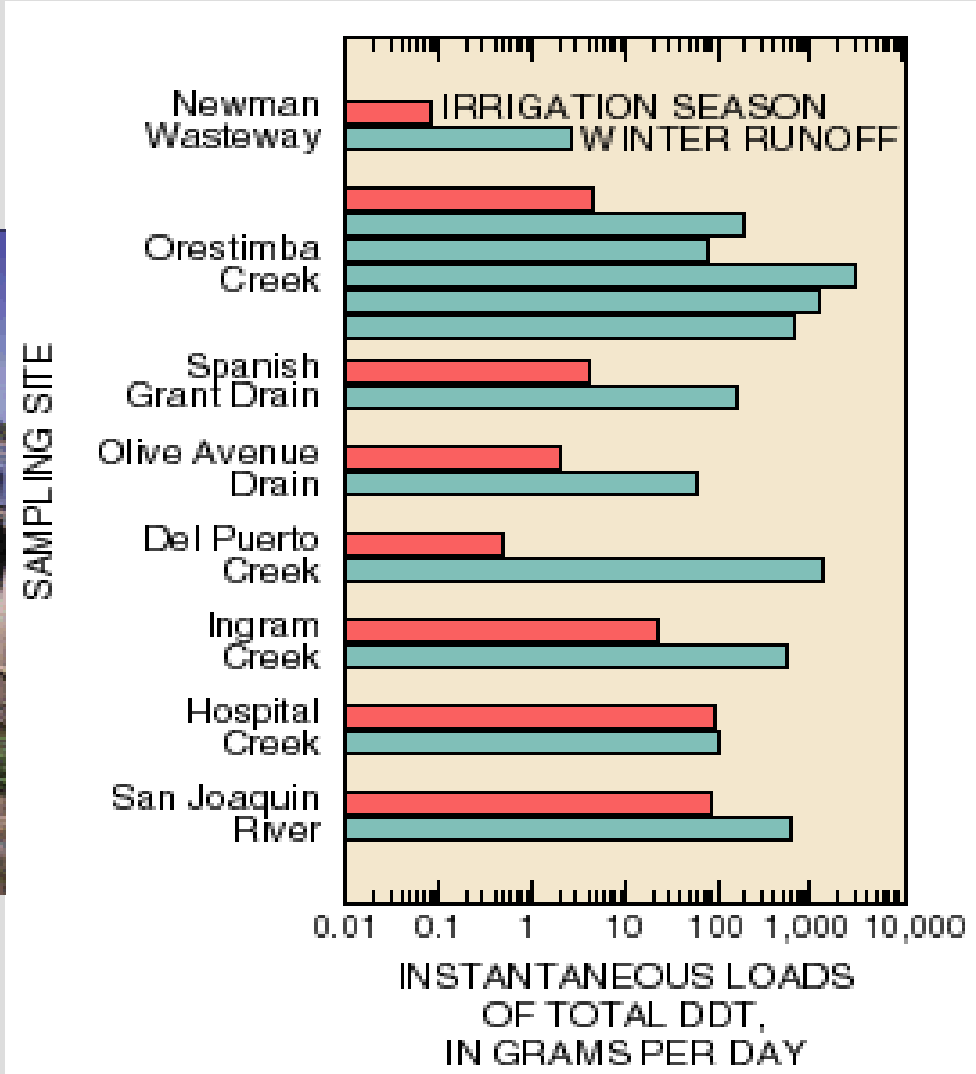
low solubility, extreme hydrophobicity
extreme persistence
extreme sorption
tendency to volatilize

→ global redistribution – wet + dry deposition
→ bioaccumulation

DDT use: widespread 1940s – 1960s

The accumulation of DDT inside birds' tissue disrupts calcium control mechanism during egg formation. The egg shells are so fragile that they crack and do not survive until hatching.

DDT surface water loads ~ 20+ years after cancellation



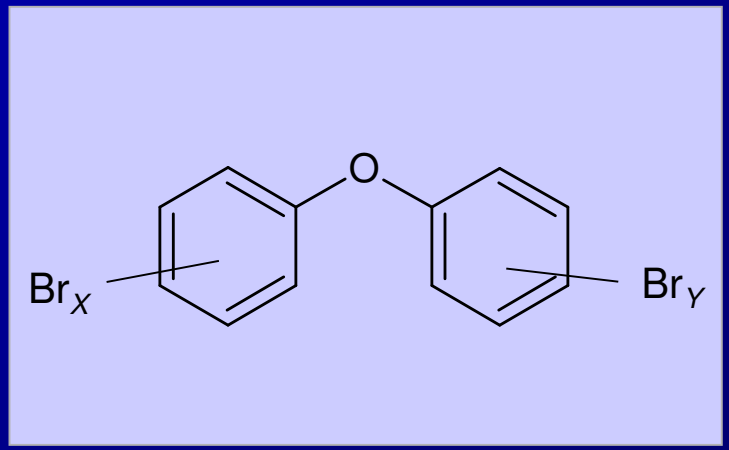
Dubrovsky, N.M., Kratzer, C.R., Brown, L.R., Gronberg, J.M., and Burow, K.R., 1998, Water Quality in the San Joaquin-Tulare Basins, California, 1992-95: U.S. Geological Survey Circular 1159

Other Halogenated Contaminants
polybrominated diphenyl ethers - PBDEs

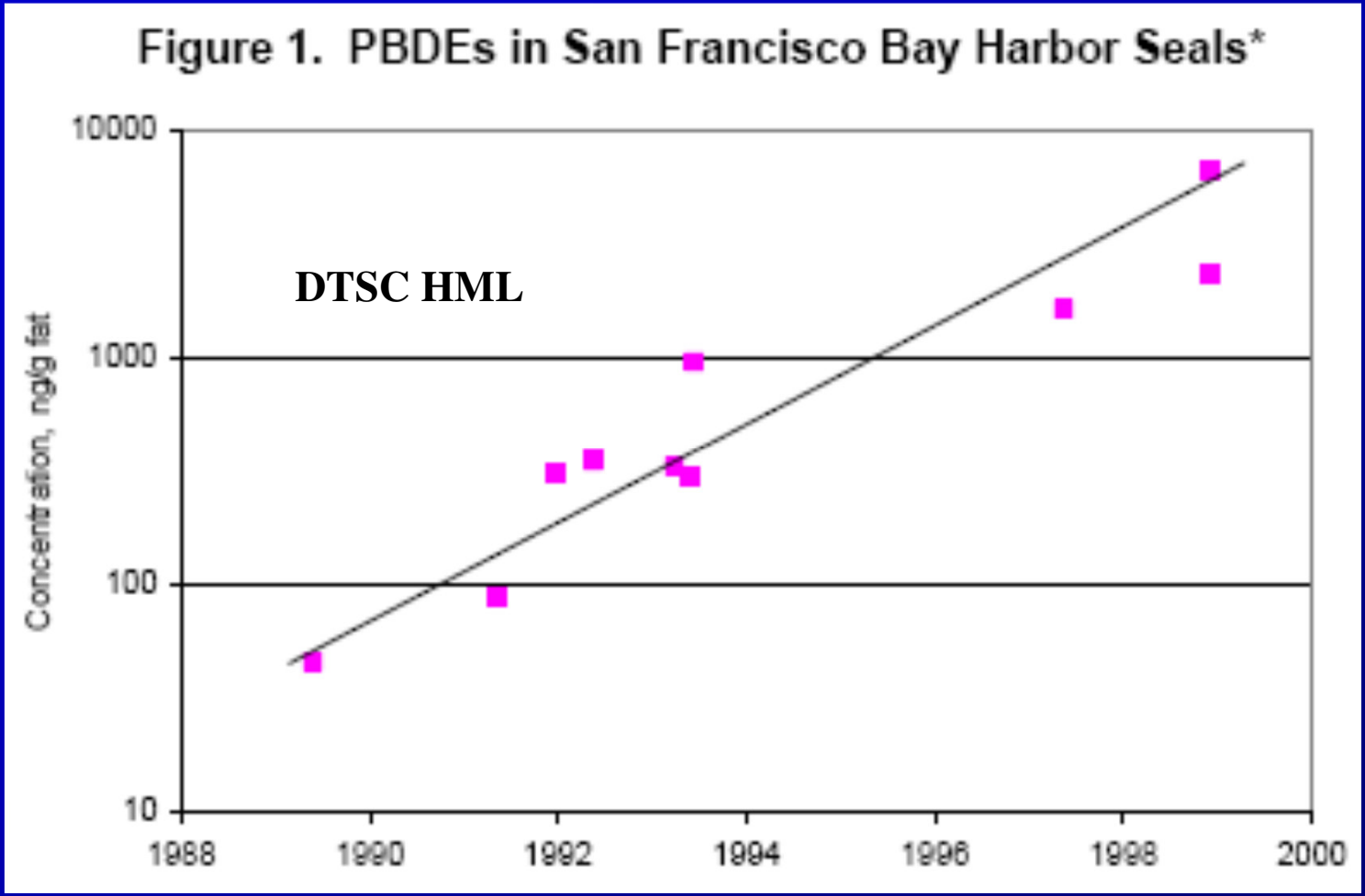
BACKGROUND

- penta- and octa-BDEs: wide use as flame retardants, ubiquitous
- half-lives in humans ~ *O* (years)
- some carcinogenic, other congener-specific effects in rats
- measured [PBDE] in Ca humans and wildlife among highest in world

$C_{12}H_{(10-x)}Br_xO$ (x = 1, 2, ..., 10 = m + n)



polybrominated diphenyl ethers - PBDEs



She, J., Petreas, M., Winkler, J, Pasita, P., McKinney, M and D. Kopec. 2002. PBDEs in the San Francisco Bay Area: measurements in harbor seal blubber and human breast adipose tissue. Chemosphere 46:697-707

Take home message:

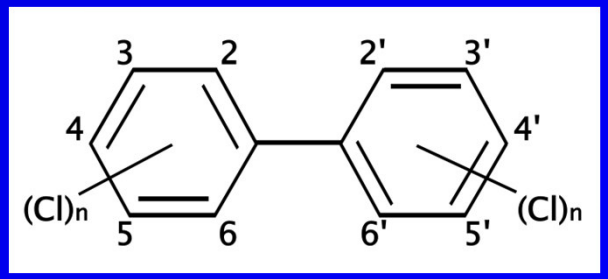
1. High degree of halogenation is a potential problem.

tendencies

persistence, hydrophobicity/lipophilicity ➔ bioaccumulation

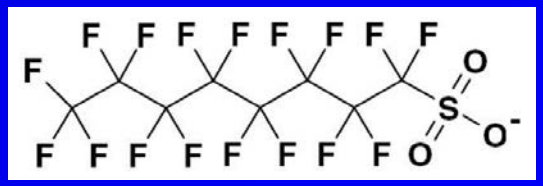
2. Several other chems listed as POPs by Stockholm Convention

polychlorinated biphenyls



PCBs
dielectric, coolant fluids

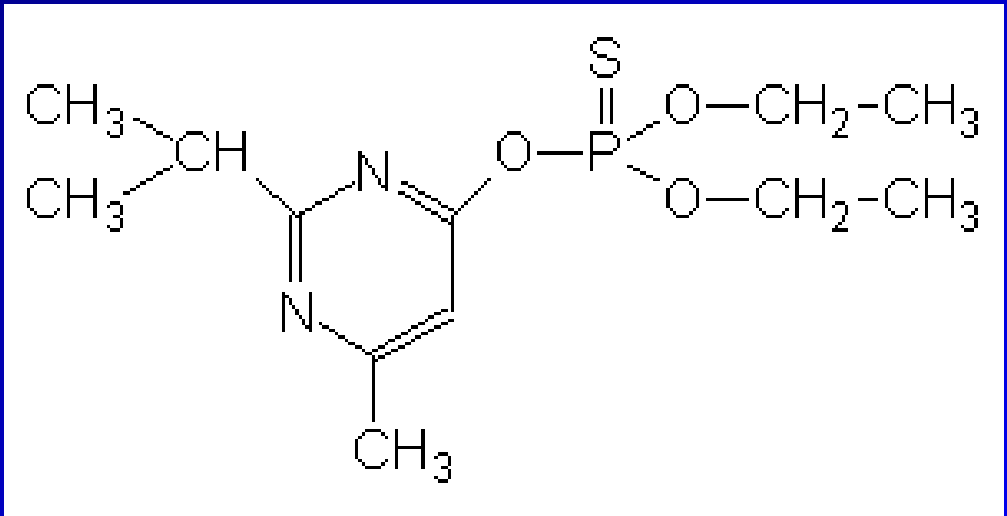
perfluoro- compounds



PFOS
fire-fighting foams,
stain resistant fabrics

3. Many POPs are either suspect carcinogens, linked to endocrine disruption, are teratogenic, cause neurotoxicity, etc.

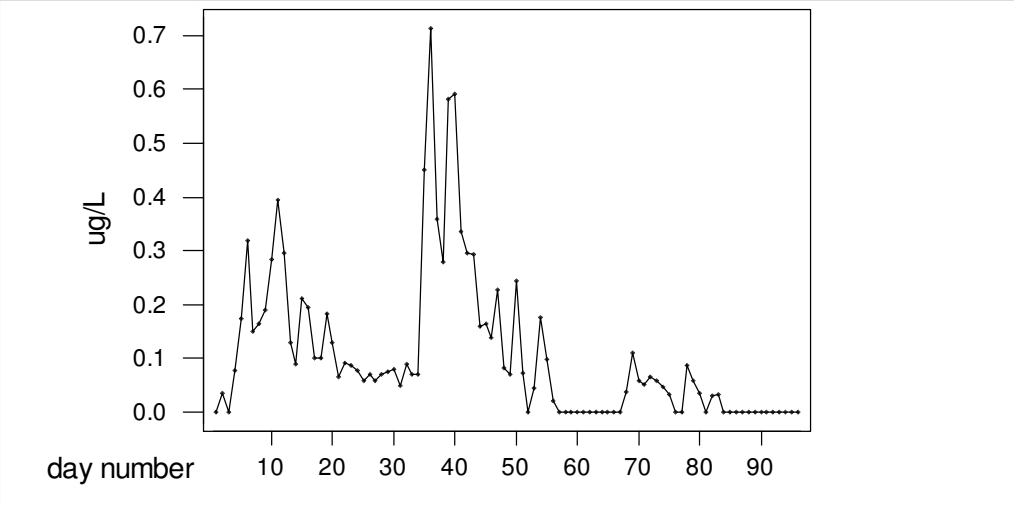
Diazinon contamination of surface water



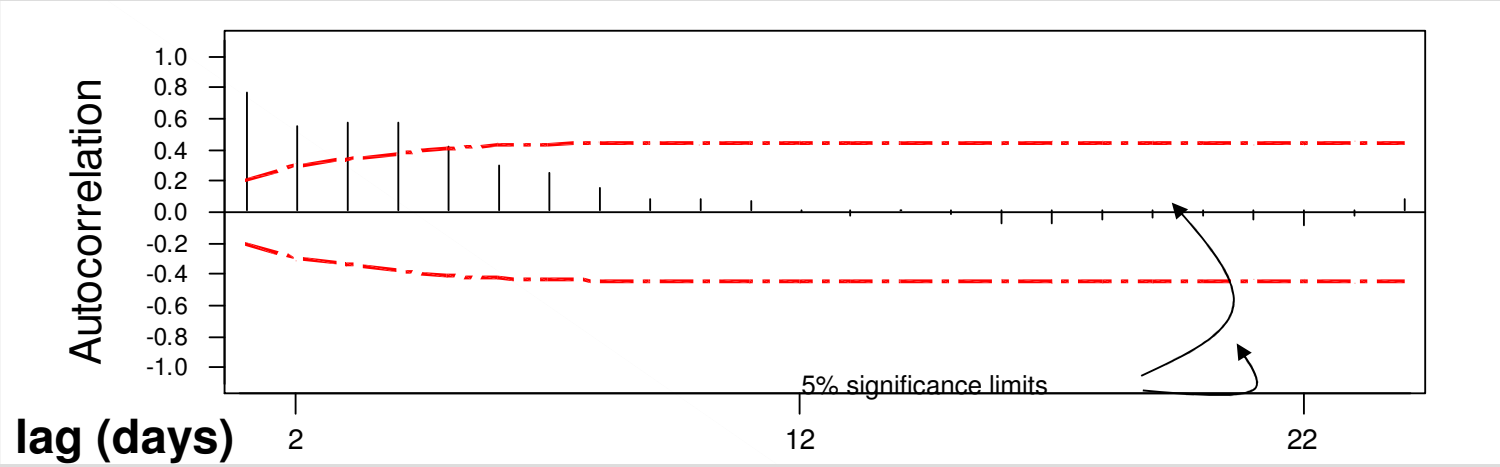
diazinon

DIAZINON		
Criterion ug L^{-1} (ppb)	Type	Recurrence period
0.10	chronic aquatic tox	4-day average; not to be exceeded more than once in 3 years.
0.16	acute aquatic tox	1-hour average; not to be exceeded more than once in 3 years.
0.436	96 hour *Ceriodaphnia dubia* LC_{50}	N/A
0.6	Drinking water health-based guidance level	N/A - Lifetime Health Action Advisory Level

Diazinon time series plot, San Joaquin River at Vernalis 1/6/93 to 4/9/93, nondetections assigned value of zero

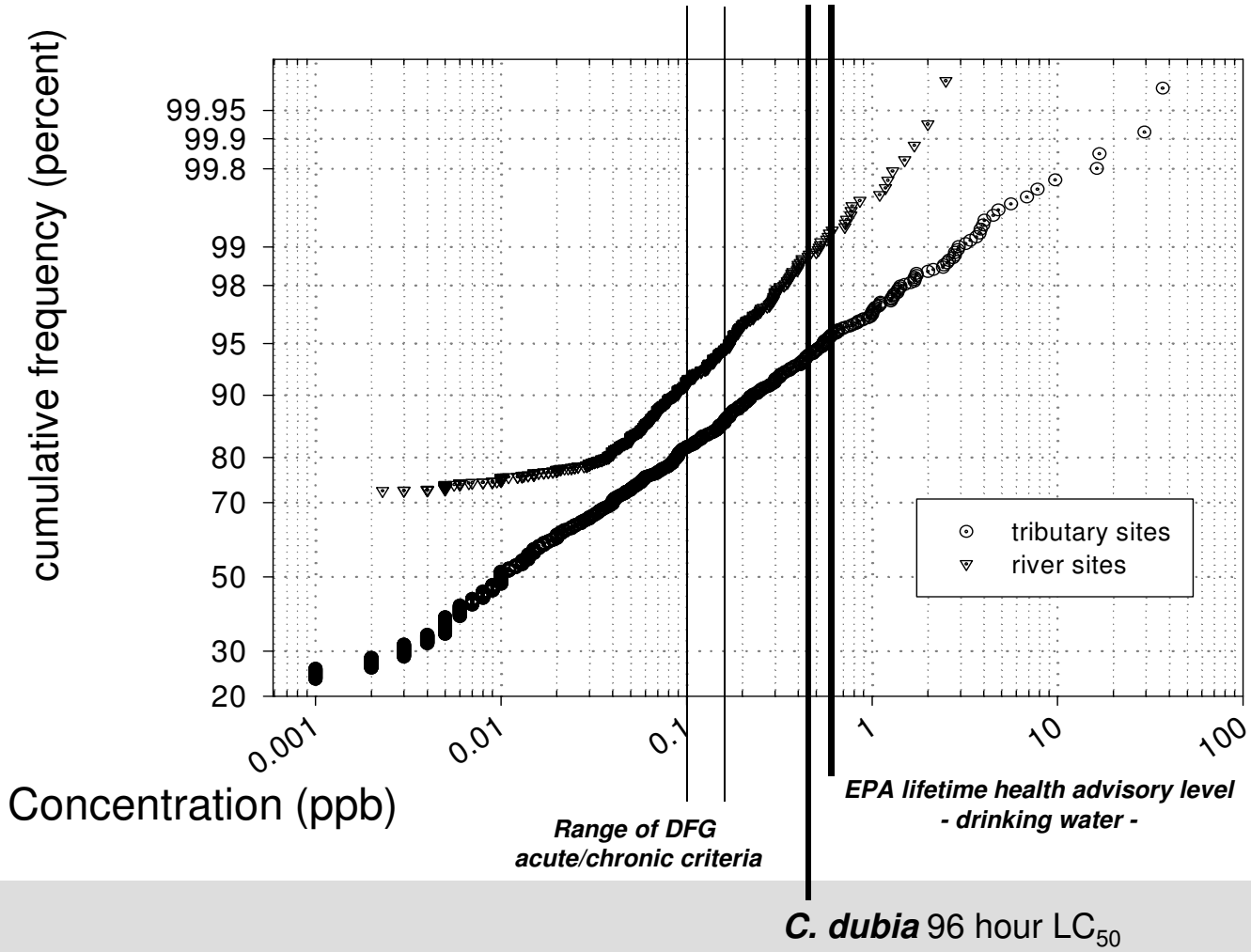


Autocorrelation function for diazinon data, San Joaquin River, Vernalis 1/6/93 to 4/9/93, nondetections assigned value of zero



Diazinon concentrations in river (n=2130) and tributary (n=1834) samples, 1991-2000

in river and tributary sampling sites



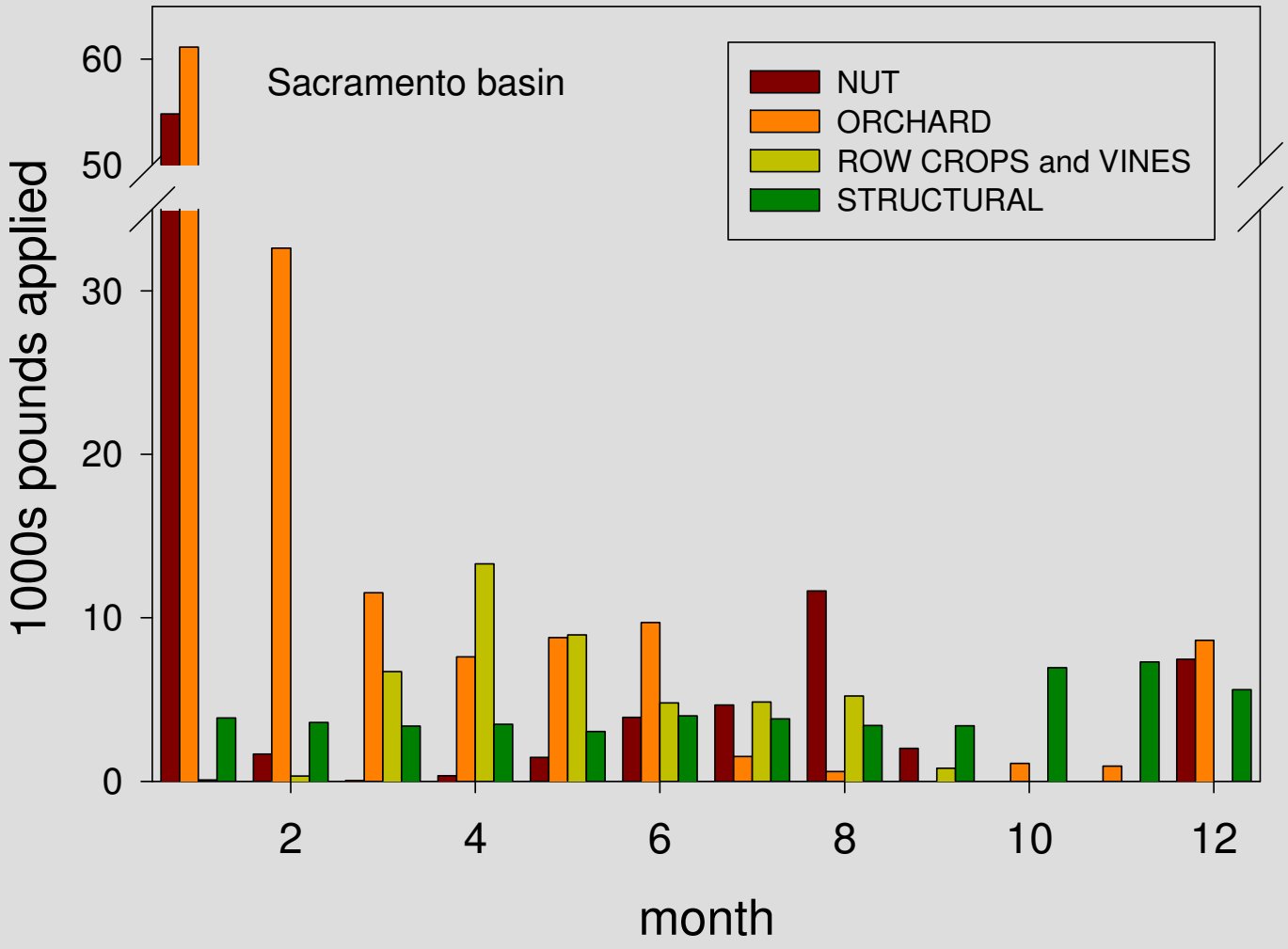
Spurlock, F. 2002. Analysis of Diazinon and Chlorpyrifos Surface Water Monitoring and Acute Toxicity Bioassay Data, 1991- 2001. EH01-01

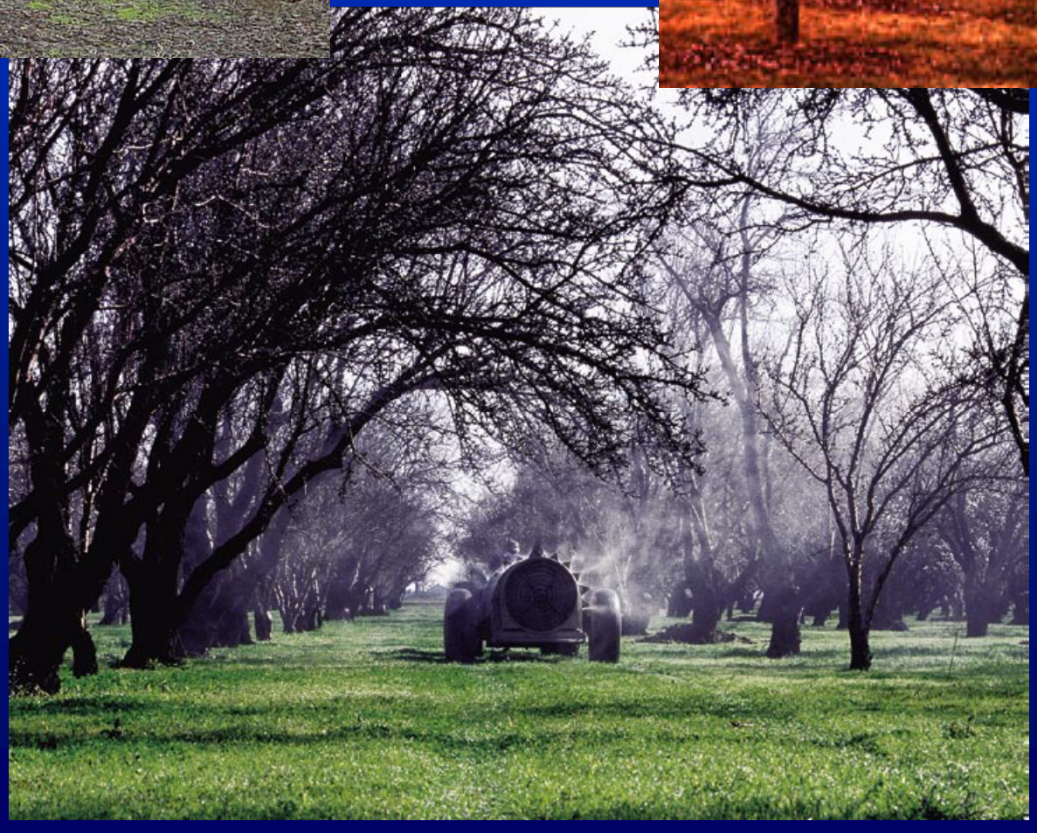
PROPERTIES

	Diazinon
Soly	60
K_{OC}	640
K_{OW}	1100
H'	3×10^{-5}
FD $t_{1/2}$	3-13d
Hydrol $t_{1/2}$	138d(?)

relatively water soluble – low to moderate sorption
low - moderate persistence
low volatility
why such common surface water contaminant ??

1998-2000 diazinon use in Sacramento River Basin



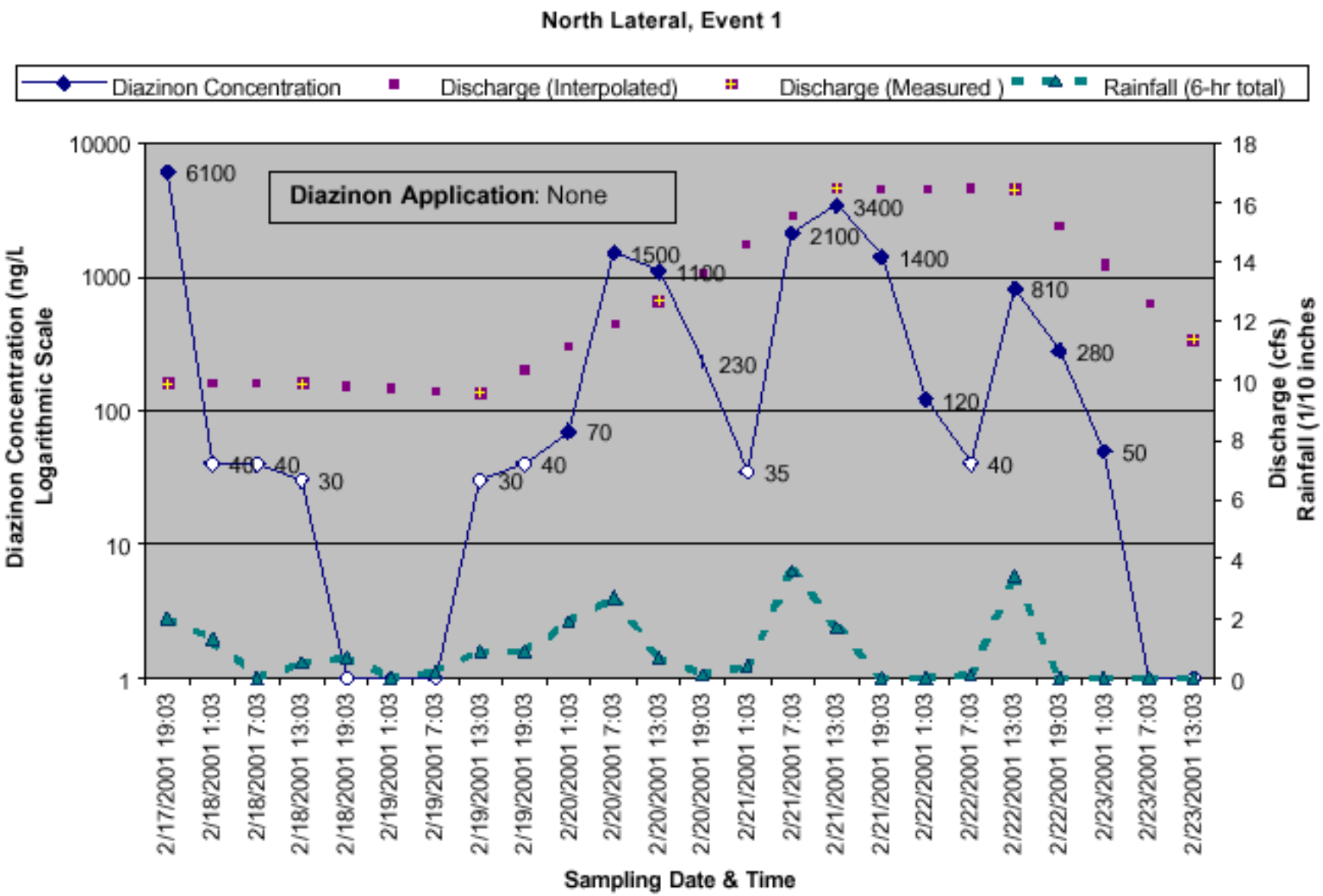


air blast sprayers

low deposition on trees

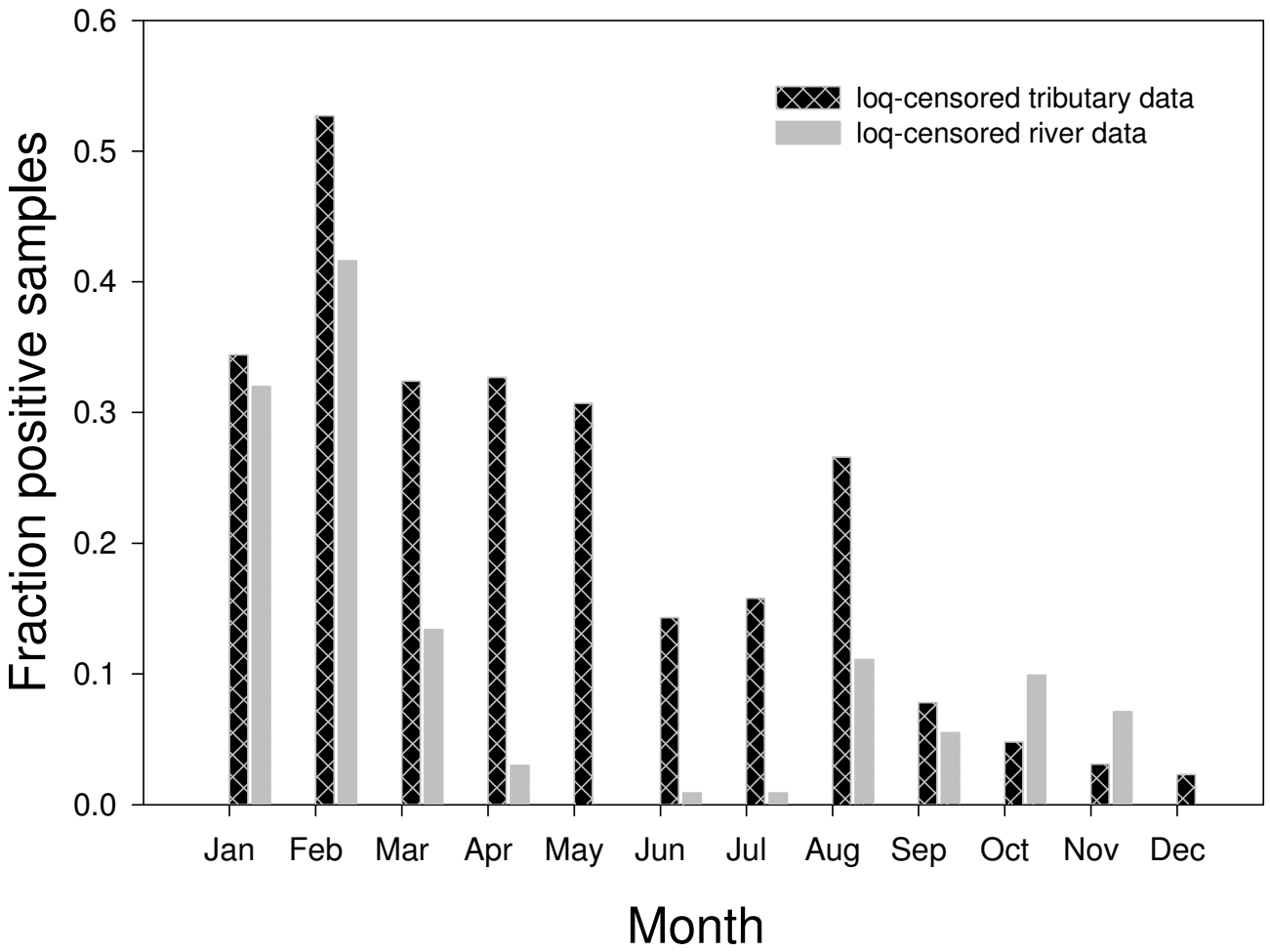
~ O (5 - 10%)

DIAZINON AND RAINFALL

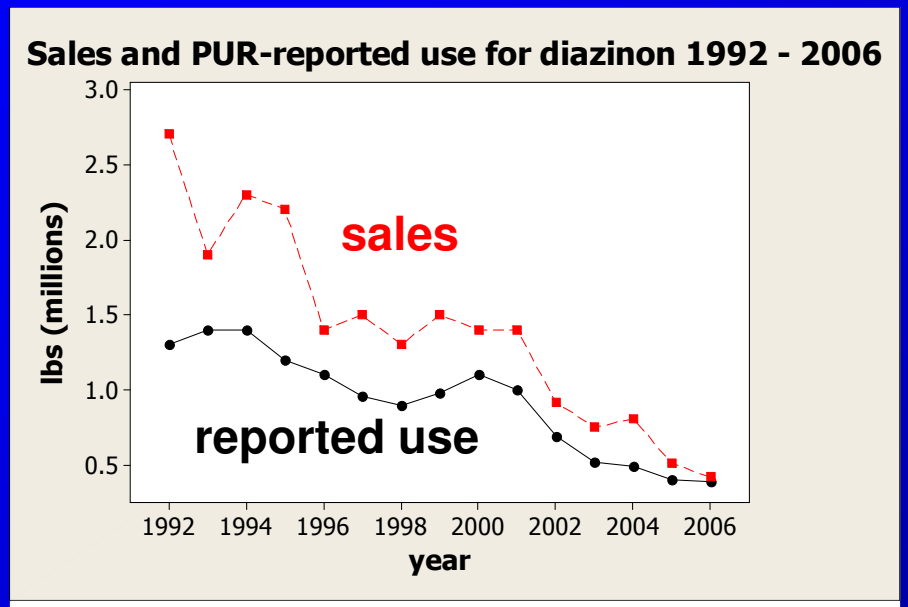


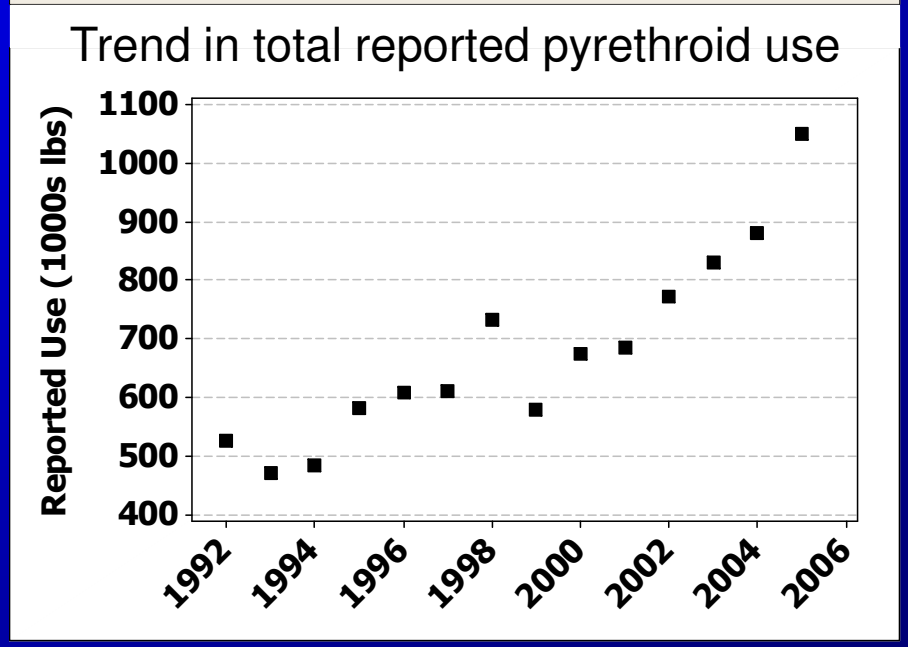
Diazinon “limit-of-quantitation” censored detection frequencies

[censoring level = 0.04 ug/L]

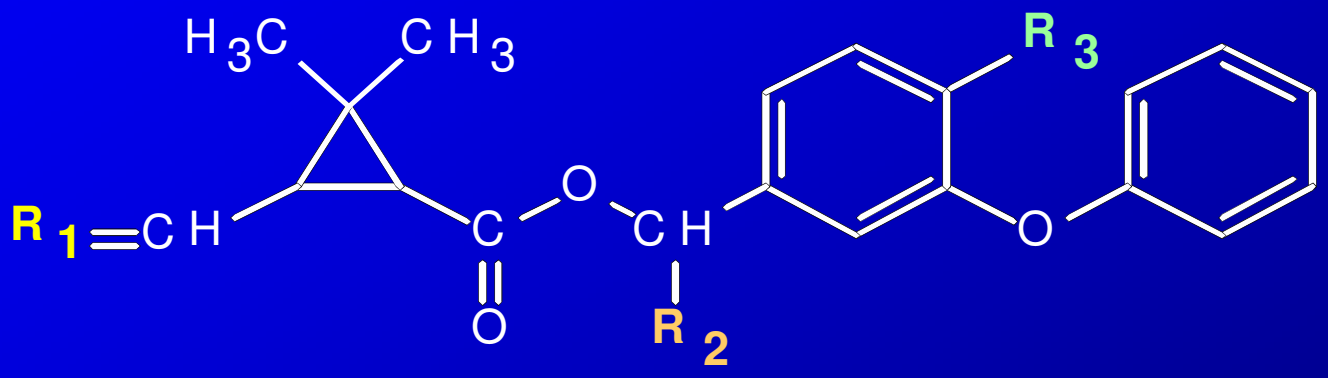


Diazinon and Synthetic Pyrethroid Use Trends

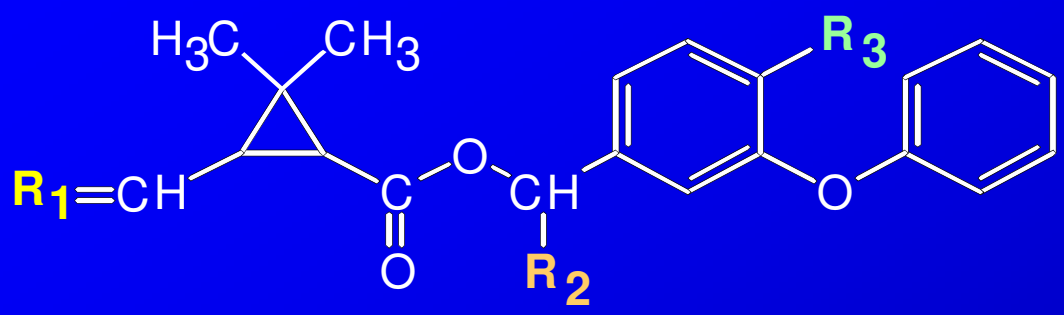




Synthetic Pyrethroids and Sediment Toxicity



Synthetic Pyrethroids



R_1	R_2	R_3	
CCl2	CN	F	**cyfluthrin**
CCl2	CN	H	**cypermethrin**
CClCF3	CN	H	**cyhalothrin**
CCl2	H	H	**permethrin**

1. highly toxic, broad spectrum insecticides ~ 20 registered
2. highly hydrophobic – associated **primarily** with soils/sediment in aquatic systems
3. sensitive organism used in bioassays is *Hyalella azteca*
4. **common mode of action**

Synthetic Pyrethroids

1. **organic-carbon normalization reduces LC50 variability***

   esfenvalerate – *H. azteca* – 96 hr exposure

	$LC50_{sed}$	$LC50_{sed} / f_{OC}$
	ug (g sediment)$^{-1}$	ug (g OC)$^{-1}$
sediment 1	14.1	1.02
sediment 2	10.4	0.92
sediment 3	48.3	0.74
% CV	86	16

***==> as expected from equilibrium partitioning theory: environmental fate, part 1**

Amweg, E.L., D.P. Weston, N.M. Ureda. 2005. Use and toxicity of pyrethroid pesticides in the Central Valley, California. Environ. Toxicol. Chem. 24:966-972

Synthetic Pyrethroids

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Amweg et al., 2006

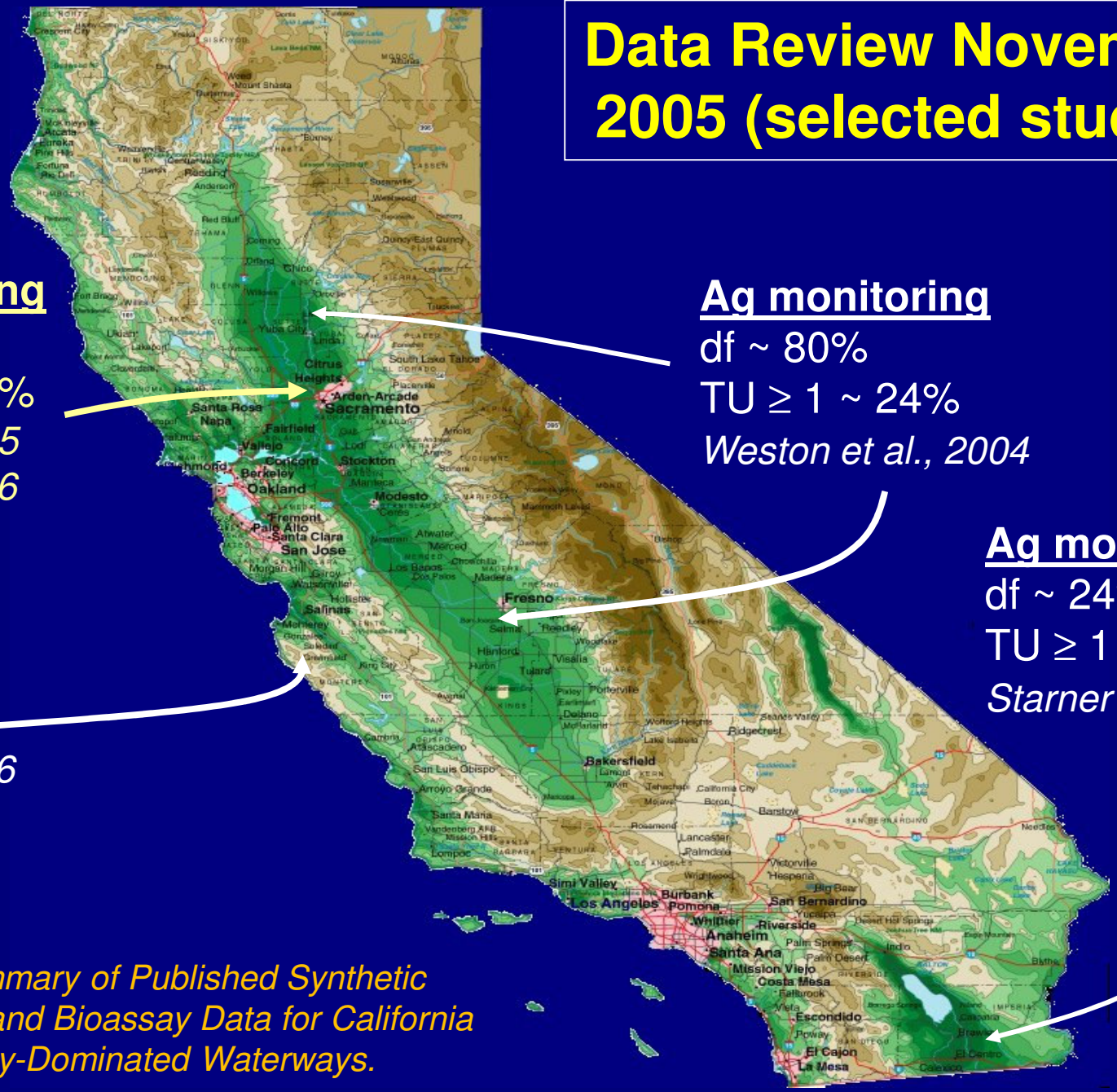
2. **common mode of action ➔ additive toxicities, "Toxic Unit" concept**

example sediment analytical data

analyte	OC- normalized Conc[A] ug (gm OC)$^{-1}$	LC50 ug (g OC)$^{-1}$	TU (=LC50 equivalents)
bifenthrin	0.1	0.2	0.5
esfenvalerate	0.45	0.9	0.5
permethrin	0.49	4.9	0.1
			Σ= 1.1 TU

[A] Dry wt conc in sediment divided by f_{OC}

Data Review November 2005 (selected studies)



Urban monitoring
df ~ 100%
TU ≥ 1 ~ 80-100%
Weston et al., 2005
Amweg et al., 2006

Ag monitoring
df ~ 80%
TU ≥ 1 ~ 24%
Weston et al., 2004

Ag monitoring
df ~ 85%
TU ≥ 1 ~ 40%
Starner et al., 2006

Ag monitoring
df ~ 24%
TU ≥ 1 ~ 19%
Starner et al., 2006

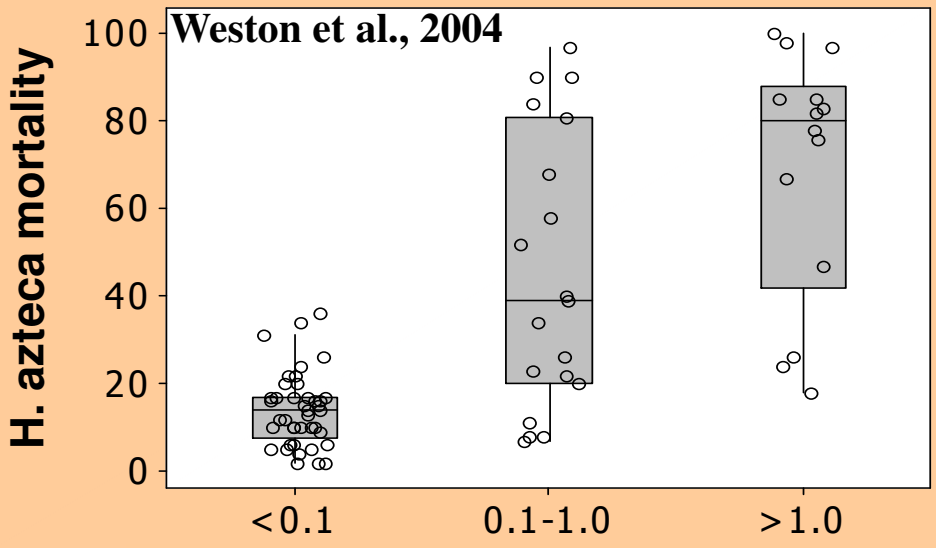
Spurlock, F. 2005. Summary of Published Synthetic Pyrethroid Monitoring and Bioassay Data for California Urban and Agriculturally-Dominated Waterways.

DPR conclusions

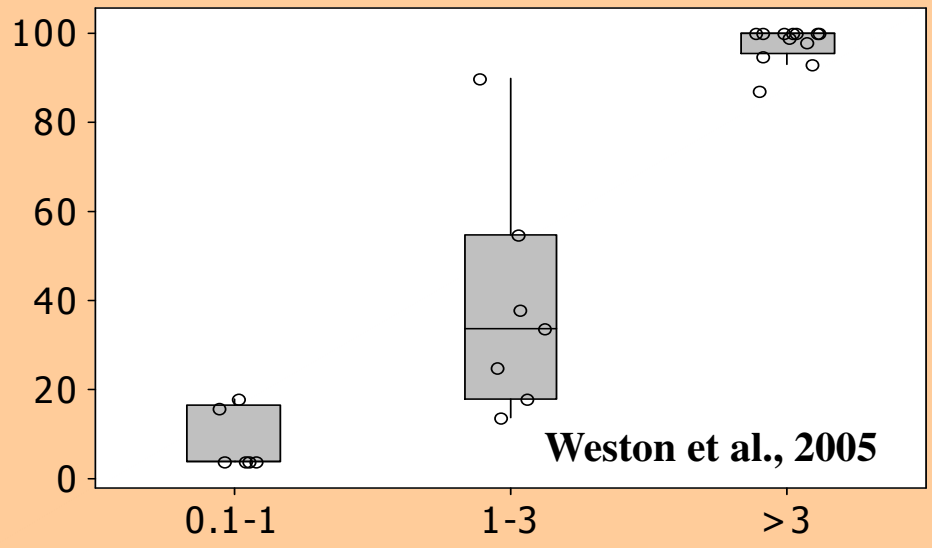
I. Detection of pyrethroids frequent and widespread in sediments of ag and urban waterways

II. In most cases total pyrethroid concentration (toxic equivalents) correlated with observed bioassay mortality

AG DATA



URBAN DATA



total pyrethroid concentration – toxic equivalents (TU)

DPR conclusions

III. No other chemical agents generally responsible

IV. Multiple detections frequent, variety of pyrethroids detected

V. Pyrethroid environmental fate characteristics similar

.....

DPR response

<u>DPR</u>

- pyrethroids "may have caused, or were likely to cause, a significant adverse impact...."

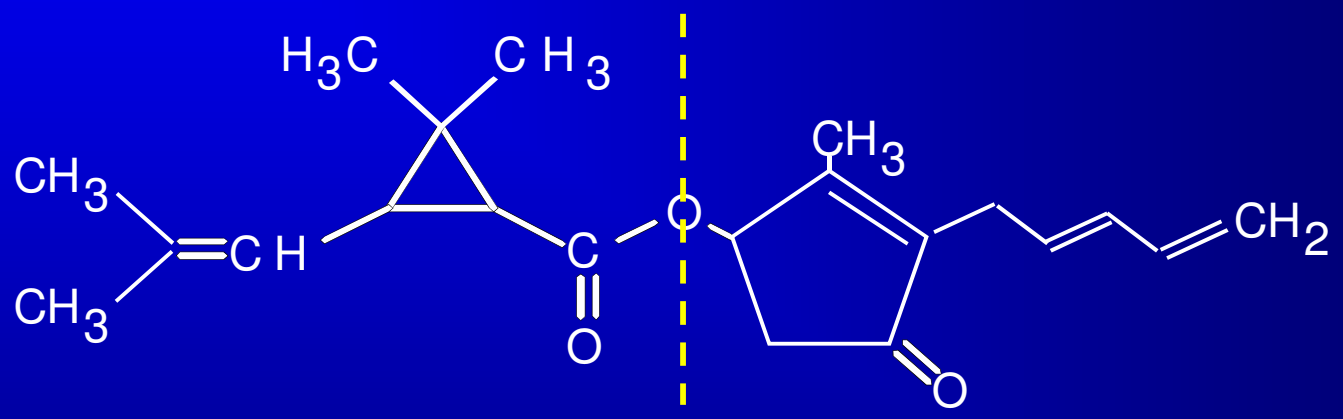
- REEVALUATION of 608 products containing 20 various pyrethroid active ingredients, 123 registrants

Data Requirements?

……use patterns and properties……

Use patterns and characteristics

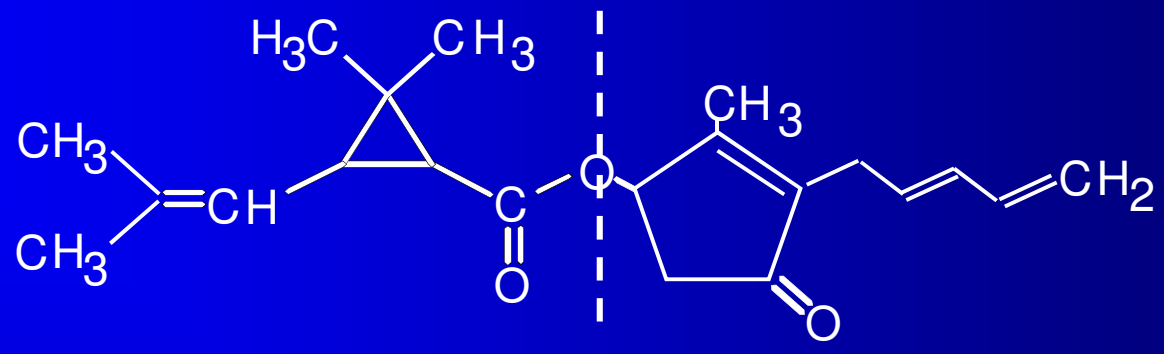
pyrethrin I



chrysanthemic acid

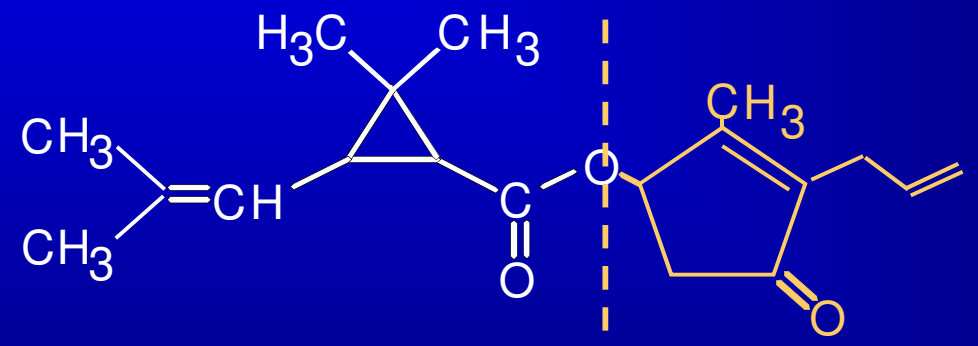
pyrethrolone (alcohol)

Early syntheses: alcohol substitutions



pyrethrin I

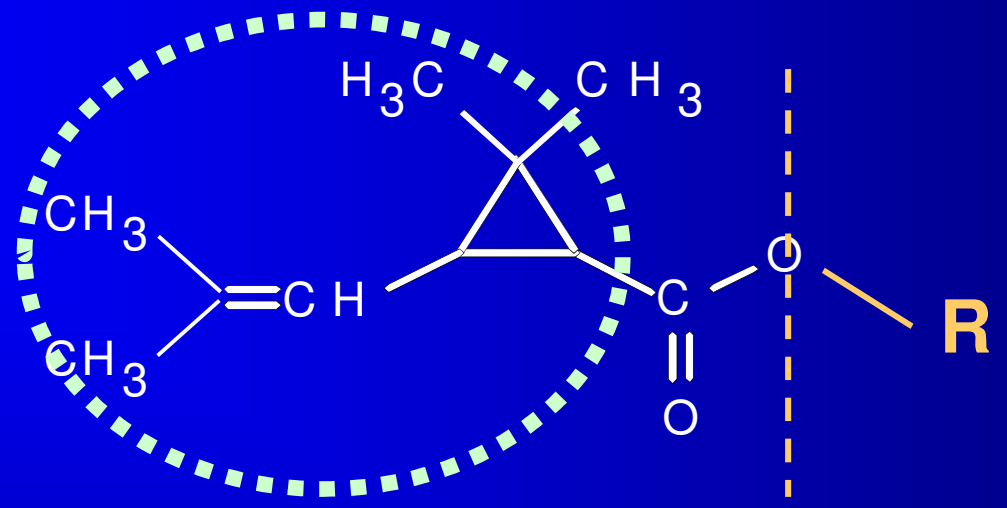
~1949



allethrin

phenothrin

Early syntheses: alcohol substitutions



allethrins
cyphenothrin
imiprothrin
prallethrin
phenothrin
resmethrin
tetramethrin

~8% Ca sales

*** PHOTOLABILE ***

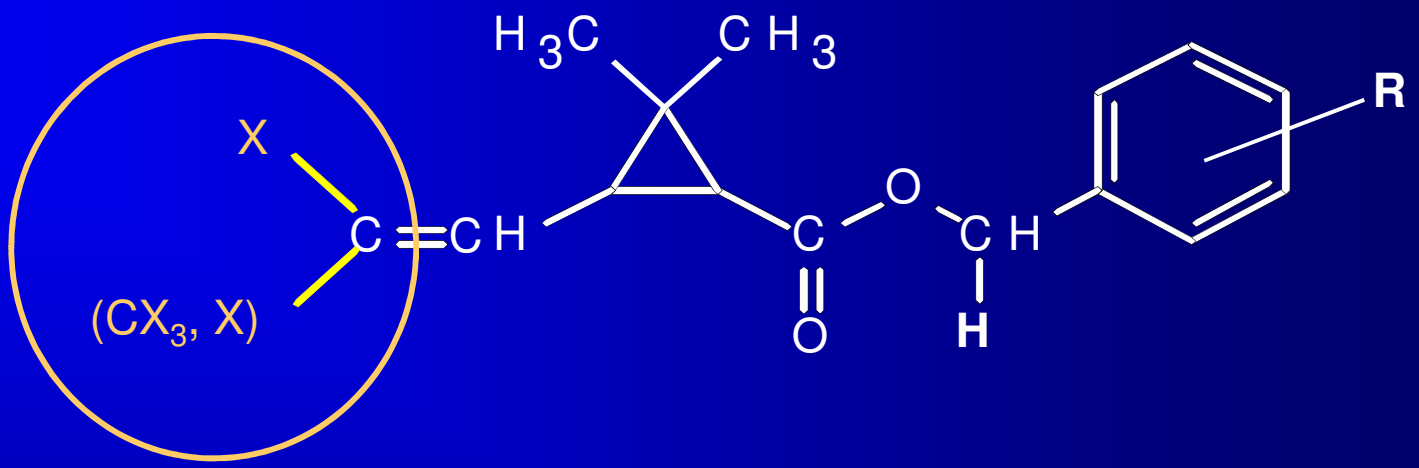
$t_{1/2}$ ~ hours

<u>Nonag uses:</u>

aerosol ant/roach sprays
fly/wasp sprays
indoor foggers
carpet/upholstery sprays
pet products
commercial/institutional
crack/crevice

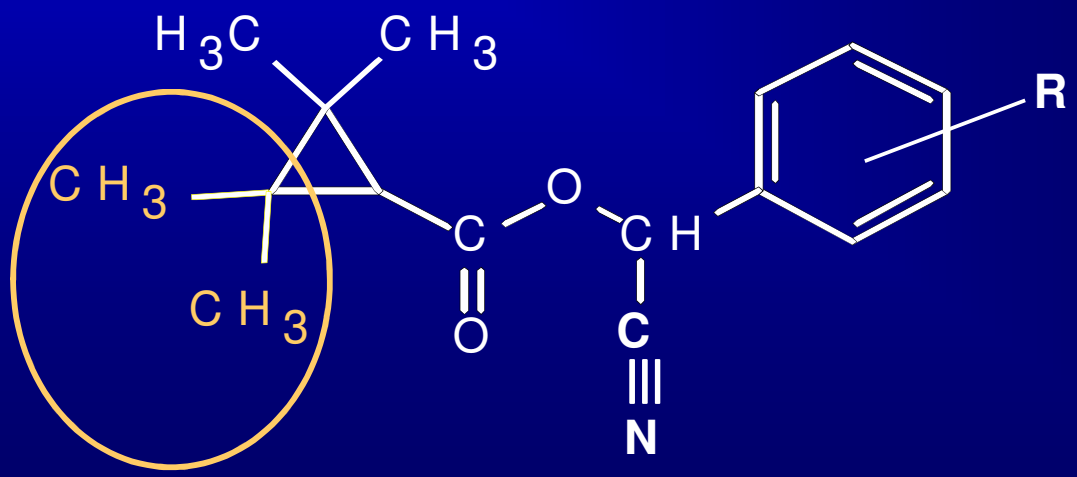
Later syntheses

vinylic halogens

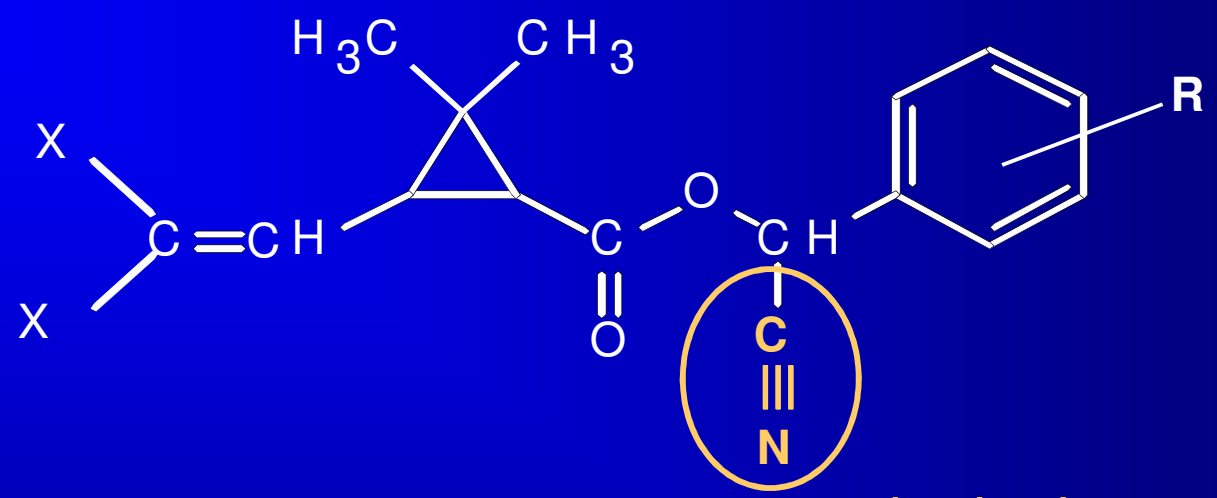


improved photostability

tetra-alkylcyclopropane ester

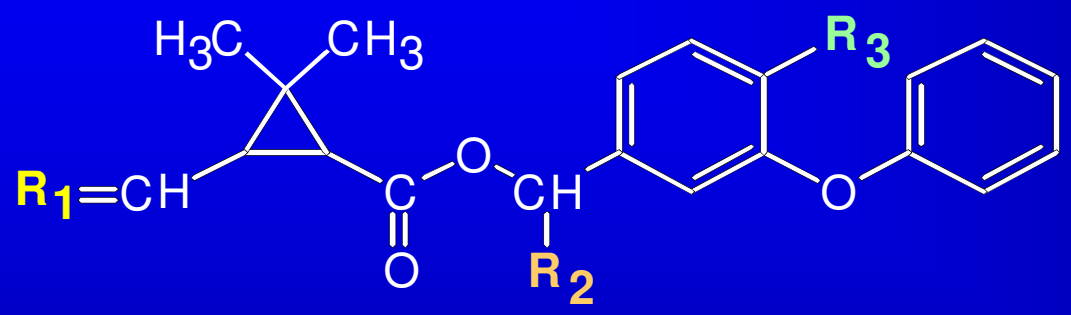


Later syntheses (cont)

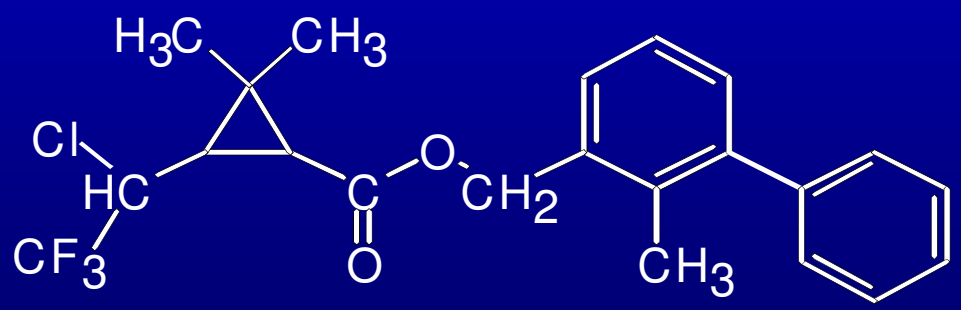


α-cyano substitution marked increase in insecticidal activity (“type II” pyrethroids)

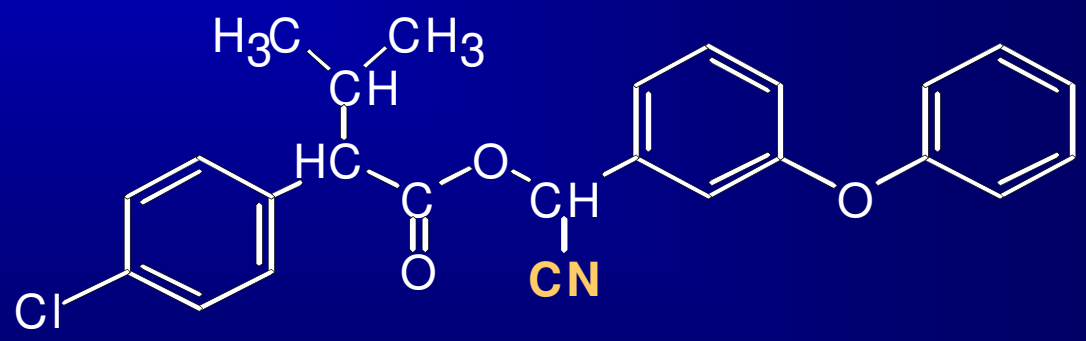
Examples of photo-stable type I and II pyrethroids



R_1	R_2	R_3	
CCl2	CN	F	cyfluthrin
CCl2	CN	H	cypermethrin
CClCF3	CN	H	cyhalothrin
CCl2	H	H	permethrin



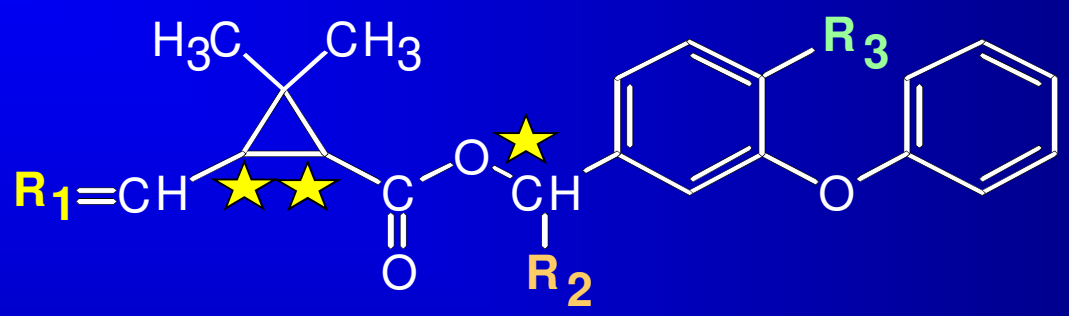
bifenthrin



fenvalerate

Pyrethroids: rich stereochemistry

cypermethrin



R_1	R_2	R_3
CCl2	CN	H

★ = cypermethrin chiral centers

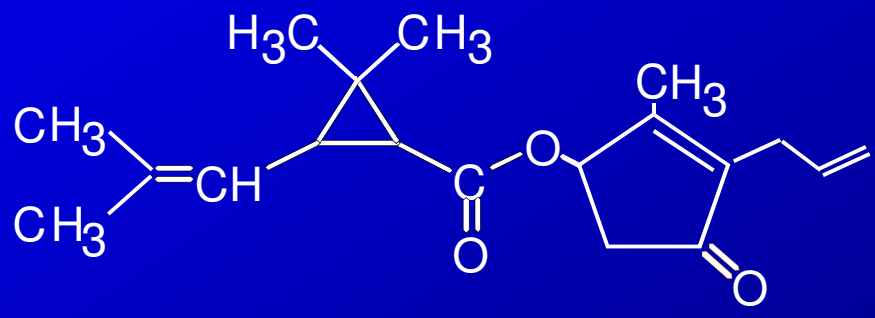
Most synthetic pyrethroids are mixtures of different isomers

Stereoisomers of a given pyrethroid differ primarily in their toxicity
ex\: cypermethrin and S-cypermethrin, fenvalerate and esfenvalerate, cyhalothrin, lambda-cyhalothrin, gamma-cyhalothrin

Two general classes of pyrethroids

I. Early photosensitive pyrethroids

- almost no agricultural use
- home/garden and indoor use
- less active than ag-use pyrethroids
- probably much less persistent but little or no fate data available



allethrin, 1949

Two general classes of pyrethroids

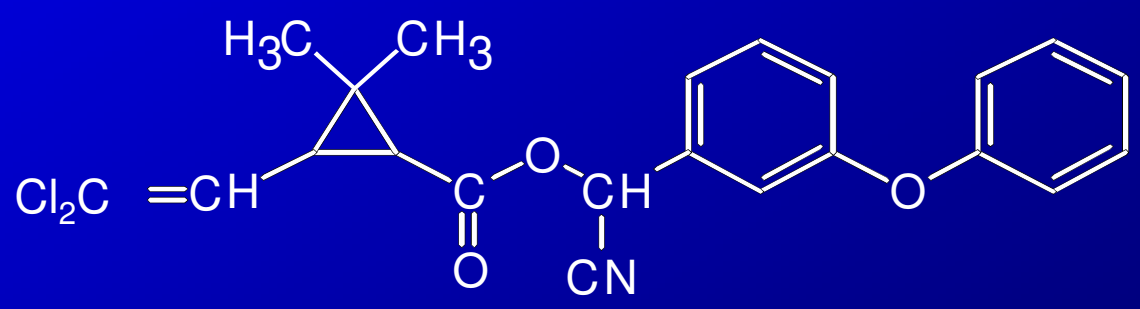
I. early photosensitive pyrethroids

II. More recent photostable pyrethroids

- ~90% total CA pyrethroid use - all use patterns

- more persistent than photosensitive pyrethroids

- most have been detected in CA sediments



cypermethrin, ~1973

Groups for reevaluation data requirements

pyrethroid	group	pyrethroid	group
bioallethrin	1	(S)-cypermethrin	3
D-allethrin	1	beta-cyfluthrin	3
imiprothrin	1	bifenthrin	3
phenothrin	1	cyfluthrin	3
prallethrin	1	cypermethrin	3
resmethrin	1	deltamethrin	3
tetramethrin	1	esfenvalerate	3
		gamma-cyhalothrin	3
tau-fluvalinate	2	lambda-cyhalothrin	3
tralomethrin	2	permethrin	3

Group 1. photosensitive

Group 2. photostable, no monitoring data

Group 3. photostable, detected in CA sediment

Reevaluation data requirements by data group

Group 1. photosensitive pyrethroids

- environmental fate data
  - solubility
  - K_{OW}
  - K_{OC}
  - hydrolysis
  - photolysis
  - aerobic soil degradation
  - anaerobic soil degradation

Reevaluation data requirements by data group

Group 1. photo- sensitive pyrethroids

EFATE data

Group 2. photostable pyrethroids, <u>no</u> monitoring data

- sediment half-life data (aerobic/anaerobic)
- sediment acute and chronic toxicity
  Chironomus tentans, Hyalella azteca
- sediment analytical method
- monitoring in areas where used

Reevaluation data requirements by data group

Group 1. photosensitive pyrethroids

- EFATE data

Group 2. photostable pyrethroids, <u>no</u> monitoring data

- sediment persistence/tox data
- monitoring

Group 3. photostable pyrethroids with sediment detections

- sediment persistence/tox data **as in Group 2**
- identify off-site movement mechanism
- management practices reduce off-site movement
- environmental monitoring in certain use patterns (e.g. permethrin, POTWs)

Novel aspects of the pyrethroid re-evaluation

- **Scope** – >600 products
- **Entire chemical family**
- **Broad range of uses** – production ag, commercial structural, urban
- **Consortium of registrants & industry representatives**
  - PWG (Pyrethroid Working Group)
  - CSPA (Consumer Specialty Products Association)
- **Numerous stakeholders** invited to comment on data requirements, workplans and study protocols
  - CASQA (stormwater)
  - Tri-TAC (POTWs)
  - State and Regional Boards
  - USEPA OPP and Region IX

Outcome of the pyrethroid re-evaluation

- Group 1 – Environmental fate data req't satisfied
  - **nonpersistent and low risk use patterns**

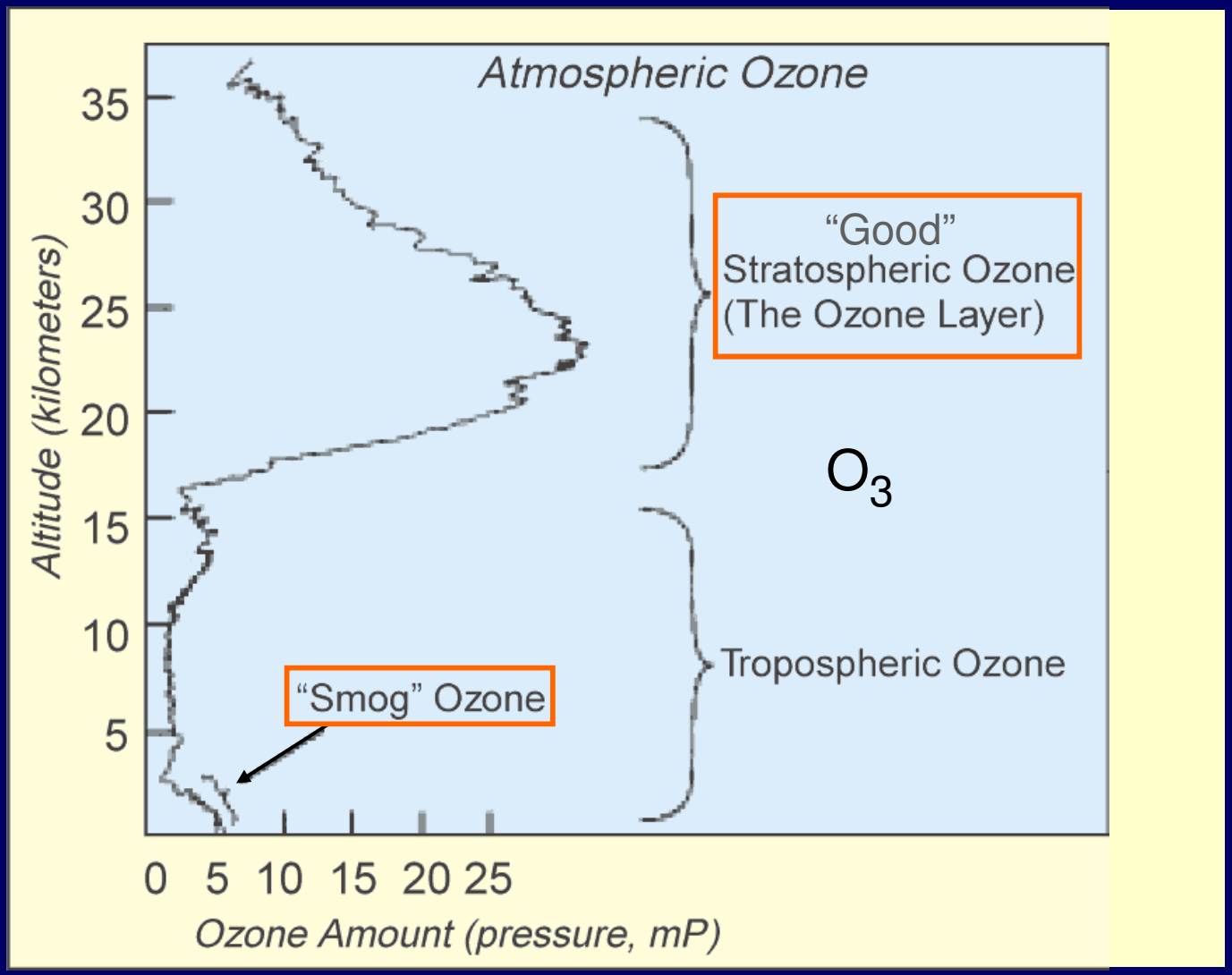
- Group II – data req't waived
  - **extremely low and declining use, low risk use patterns, low persistence.**

- Group III
  - **urban transport studies: ==> new label restrictions significantly reduce off-site movement**
  - **ag monitoring continues, continuing toxicity may trigger an "ag – focused" re-evaluation**

“Whiskey is for drinking; water is for fighting over.”
- Mark Twain

10 min break

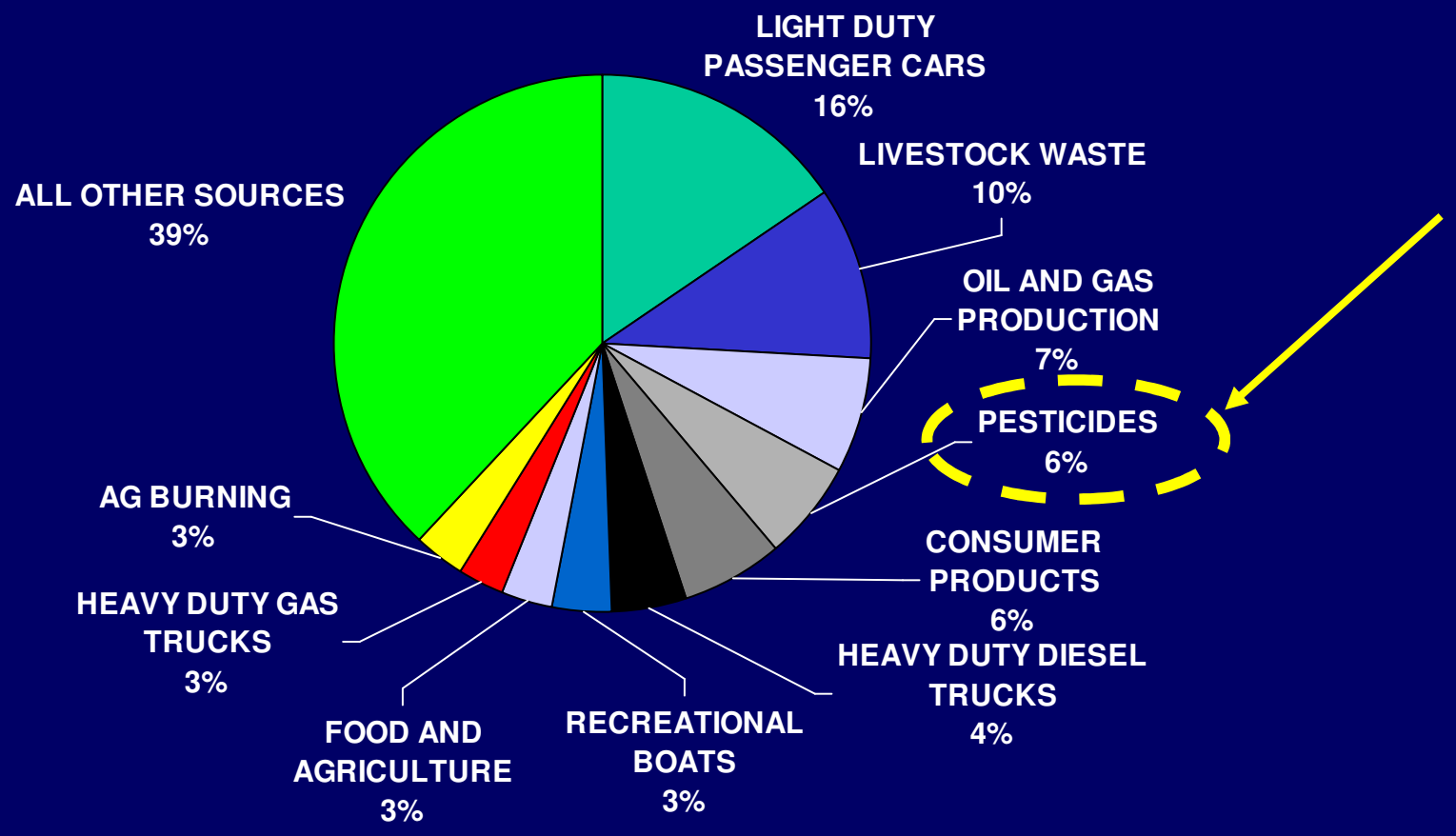
Ozone, NOx and VOCs



Pesticide contribution to VOCs is relatively small

- few other sources are regulated using reactivity -

VOC sources in San Joaquin Valley (2005)



A simplified mechanism: ozone formation, role of NOx and VOCs

... <u>only one</u> significant ozone forming reaction in lower atmosphere.....

photolysis of NO_2

$NO2 + h\nu \rightarrow O^{\bullet} + NO$	photolysis
$O^{\bullet} + O2 \rightarrow O3$	ozone formation
$O3 + NO \rightarrow NO2 + O2$	reverse reaction (rapid)

W.P.L. Carter. 1994. Development of Ozone Reactivity Scales for Volatile Organic Compounds. J. Air Waste Manag. Assoc. 44:881

A VERY simplified mechanism: ozone formation, role of NOx and VOCs

... only one significant ozone forming reaction in lower atmosphere.....

photolysis of NO_2

$NO2 + h\nu \rightarrow O^{\cdot} + NO$	photolysis
$O^{\cdot} + O2 \rightarrow O3$	ozone formation
$O3 + NO \rightarrow NO2 + O2$	reverse reaction (rapid)

if VOCs present

$VOC + OH \rightarrow ROO + products$	VOC forms peroxy radical
$ROO + NO \rightarrow NO2 + radicals$	peroxy “scrubs” NO
$radicals \rightarrow OH + products$	regenerate hydroxyl

after Carter, 1994

Illustrative example: NOx controlled vs VOC controlled conditions

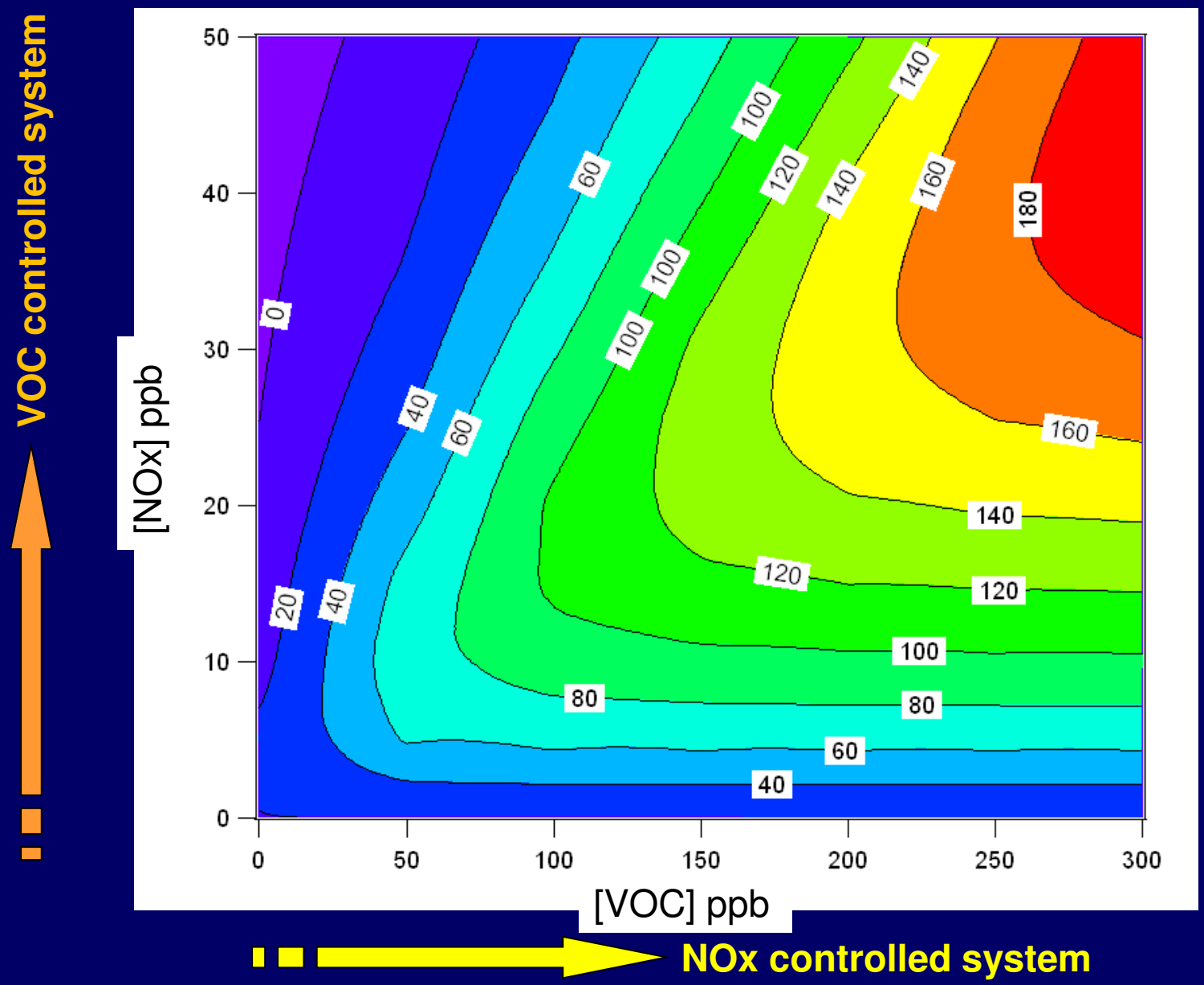


figure courtesy
Peter Green, UCD

Key Points

O3 ⇔ VOC ⇔ NOx

1. rate of ozone formation proportional to sunlight intensity
- i.e. May-Oct "ozone season"

2. rate of O3 formation depends on BOTH $[VOC],[NOx]$

3. VOCs do not participate directly in O3 formation
- VOC radicals scavenge NO, reducing O3 degradation

4. Not all VOCs are created equal WRT O3 formation potential
- radical formation = *f*(VOC type)

Maximum Incremental Reactivities

Approach:

1. 100,000L Reaction Chamber, high O_3 formation conditions (high NOx, low surrogate VOC)
2. Add chemical of interest, measure ΔO_3
3. Provides relative measure of O_3 formation potential called MIR

Photographs of Chamber and Lights

Looking Towards Reactors (from light)

Looking Towards Lights and Air Inlet

Maximum Incremental Reactivities (MIR)

Chemical or mixture	MIR gm O_3 / gm VOC
acrolein	7.6
1,3-dichloropropene	4.6
ambient emissions mixture - urban	4.3
methyl isobutyl ketone	3.6
chloropicrin	1.9
EPTC	1.6
kerosene	1.5
MITC	0.3
ethane*	**0.3**
carbon disulfide	0.2
methyl bromide	0.03

*** previously used by EPA as the standard to define "negligible" reactivity**

Data from: Carter, W.P. L. and I. L. Malkina, 2007. Investigation of Atmospheric Impacts of Selected Pesticides. Report to CARB on contract 04-0334.

Current VOC Calculation Procedure

Potential VOC emissions = lbs product applied x EP

Pesticide Use Report (PUR)

Emission Potential from thermogravimetric analysis (TGA)

→ **REACTIVITY??**

Oros, D. and Spurlock, F. 2011a&b. Estimating Pesticide Product Volatile Organic Compound Ozone Reactivity.

Part 1: Speciating TGA-Based Volatile Organic Compound Emissions Using Confidential Statements of Formula.

Part 2: Reactivity-Weighted Emissions.

Maximum Incremental Reactivities

how to calculate for mixtures?

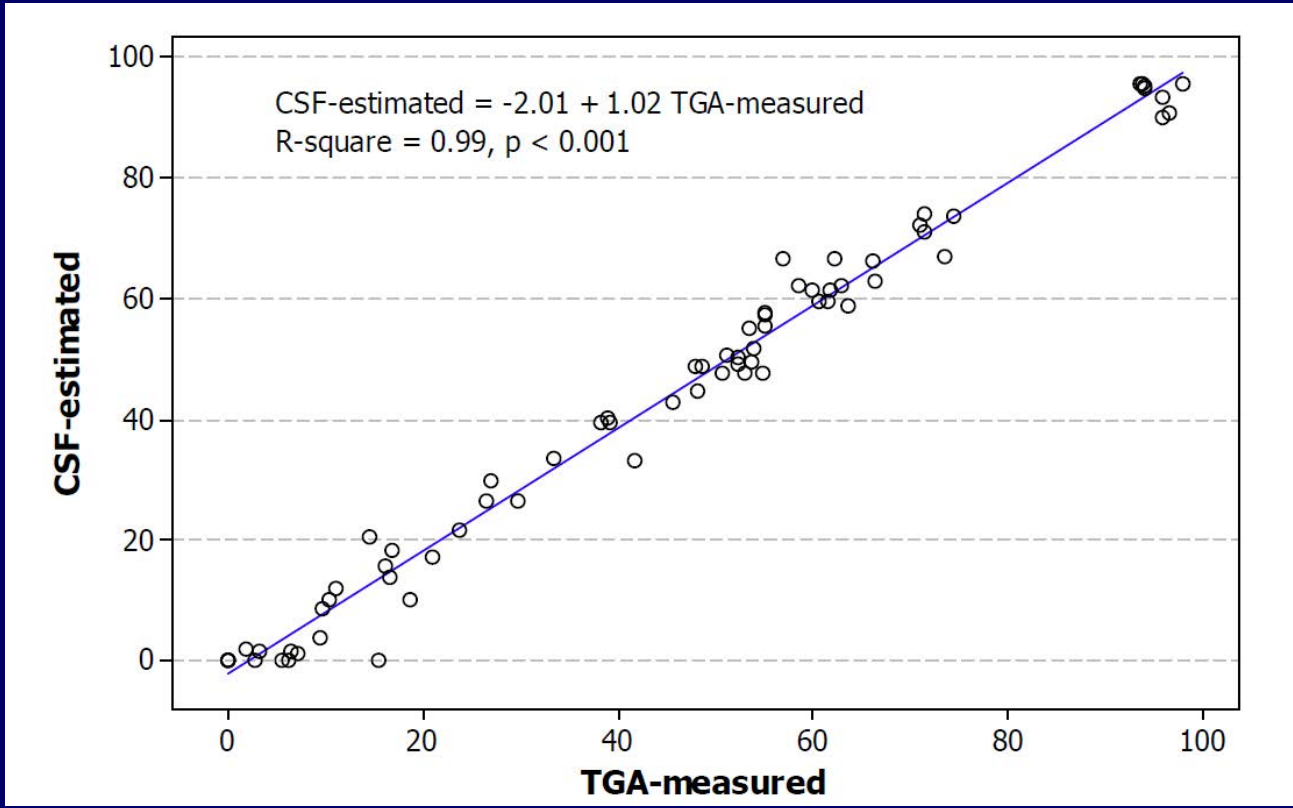
Ingredient	percent composition
Semi-volatile Active Ingredient (AI)	43.0
unknown inerts from AI	1.7
Aromatic 200 solvent	49.8
alternate: Naphthalene depleted Aromatic 200	
Antifoam A (proprietary formula)	1 ppm
Agent 1658-7 emulsifier	5.5
alternate: Sponto-T-2001	
alternate:DV 3998	

speciation:
what exactly is volatilizing?

52% C11 alkylnaphthalenes
20% C12 alkylnaphthalenes
8% C13 alkylnaphthalenes
6% Indans/tetrahydronaphthalenes
<%5 each:
C8-C11 alkylbenzenes

Speciation

Comparison of CSF-estimated to TGA-measured Emission Potential for 134 products - assumed VP cutoff = 0.05 Pa

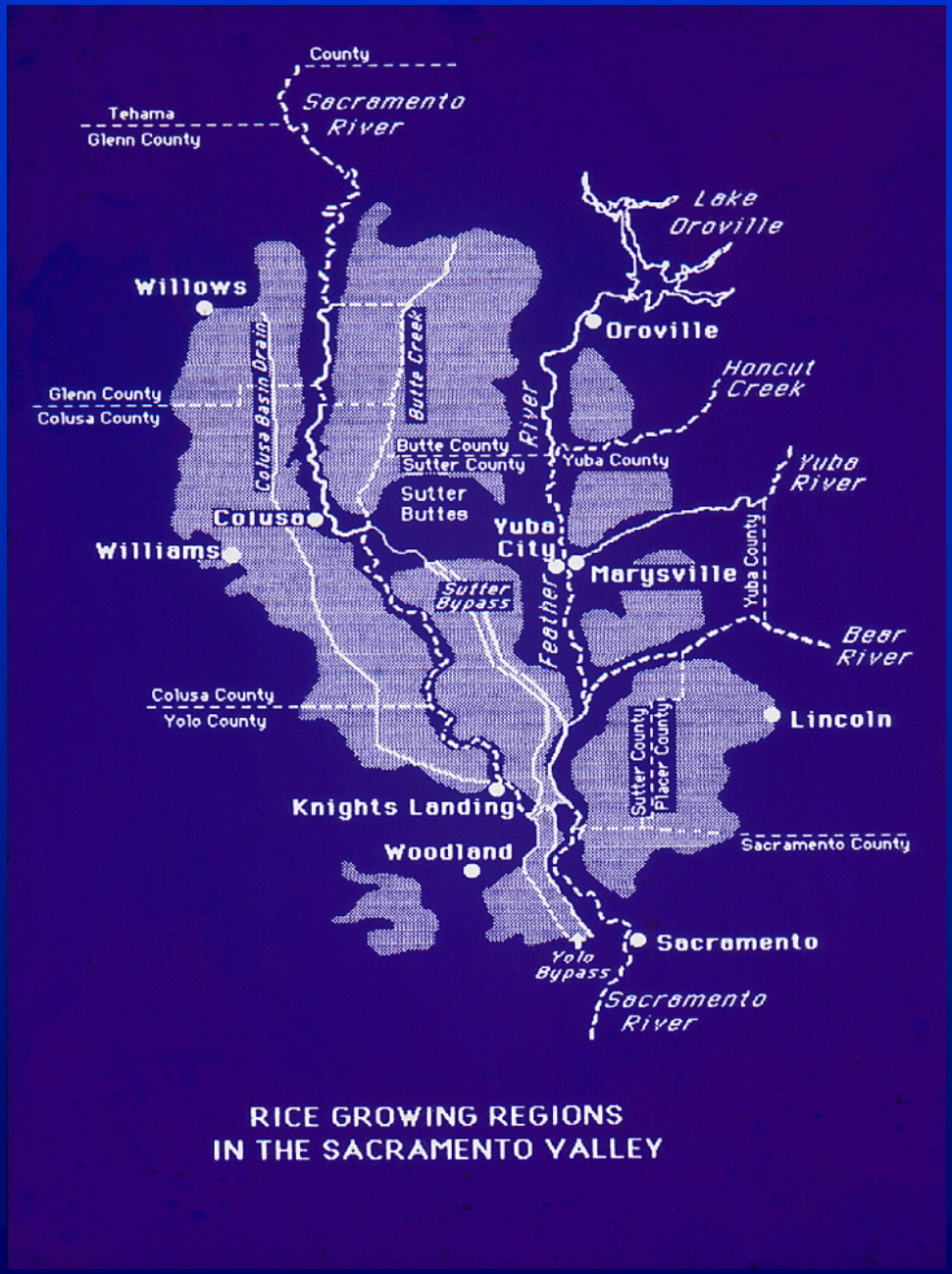


Rice Production and Water Quality

Northern Sacramento Valley

> 90% California's rice production -

> 500,000 acres (2007)

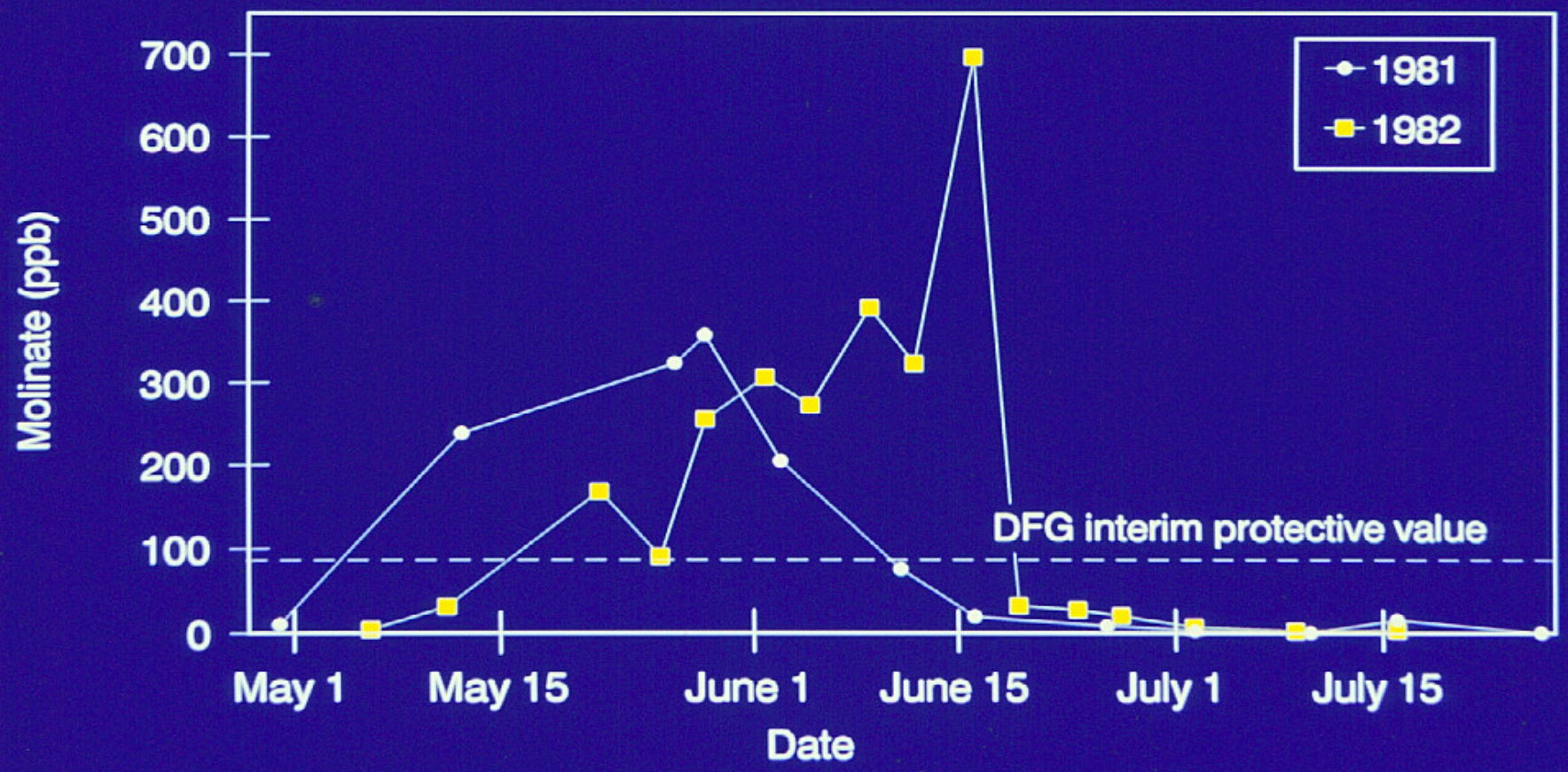


RICE GROWING REGIONS
IN THE SACRAMENTO VALLEY

Fish Kills in Rice Drains – early 1980s

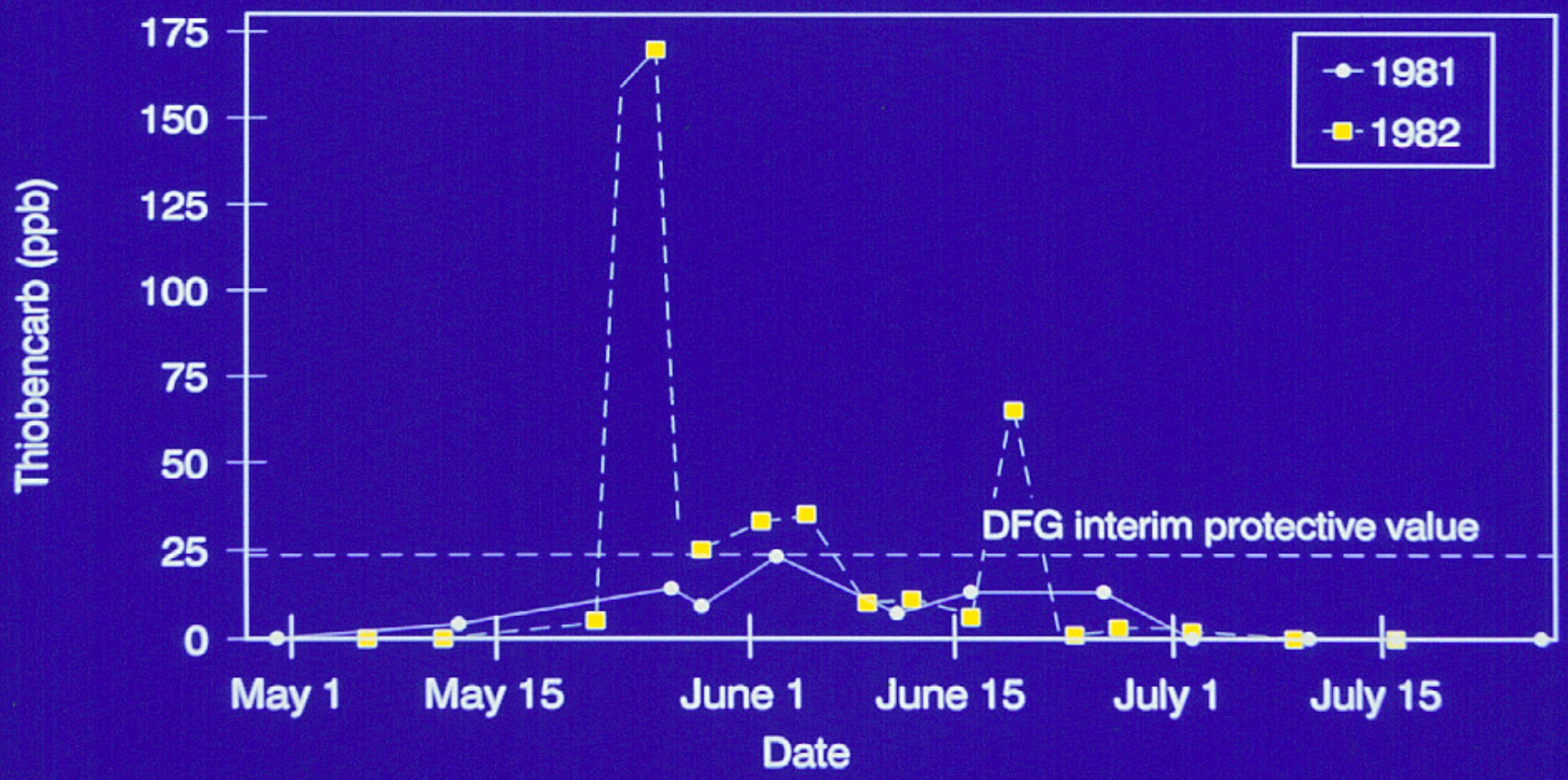
1982 DFG Evaluation

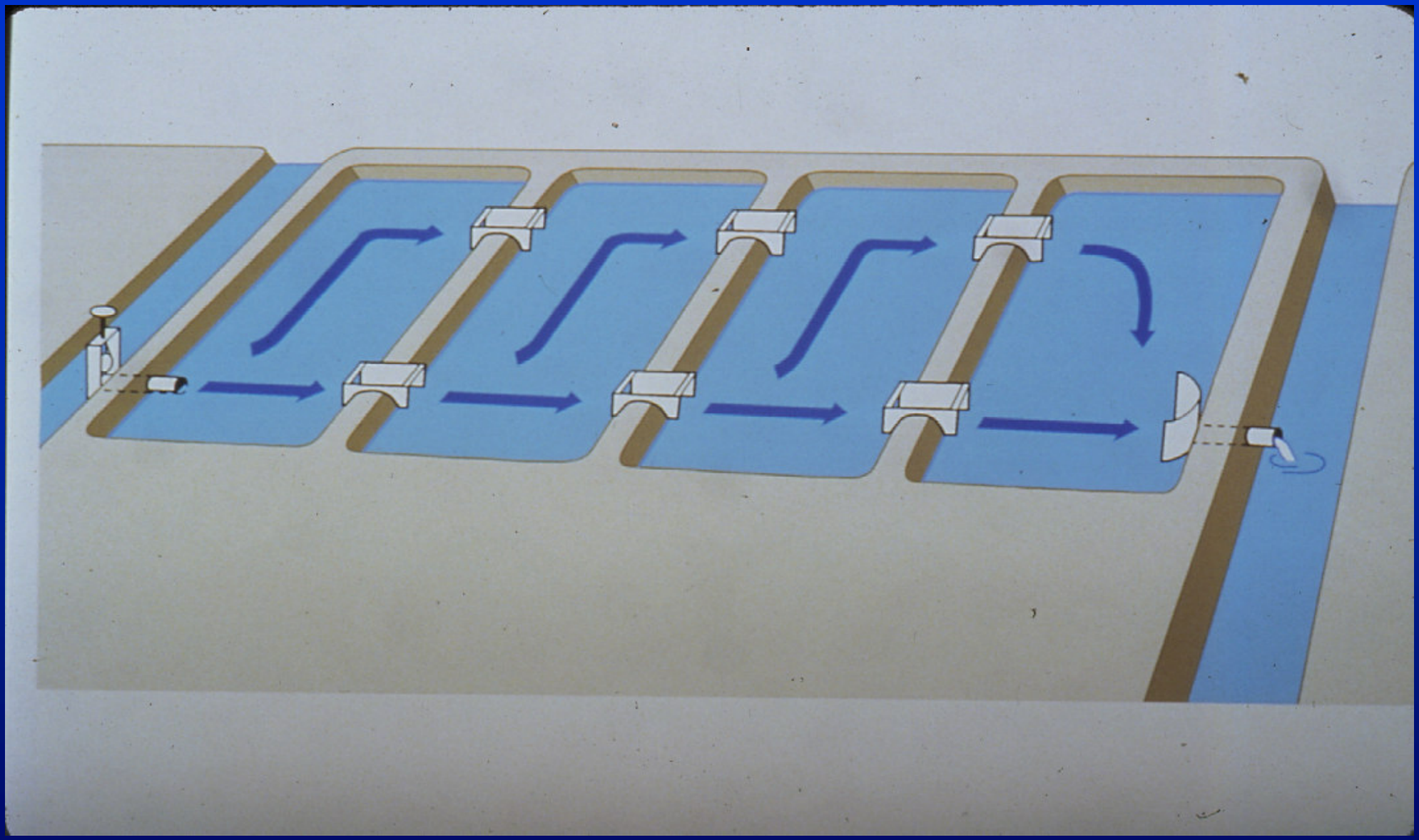
Molinate Concentrations in CBD near SR 20



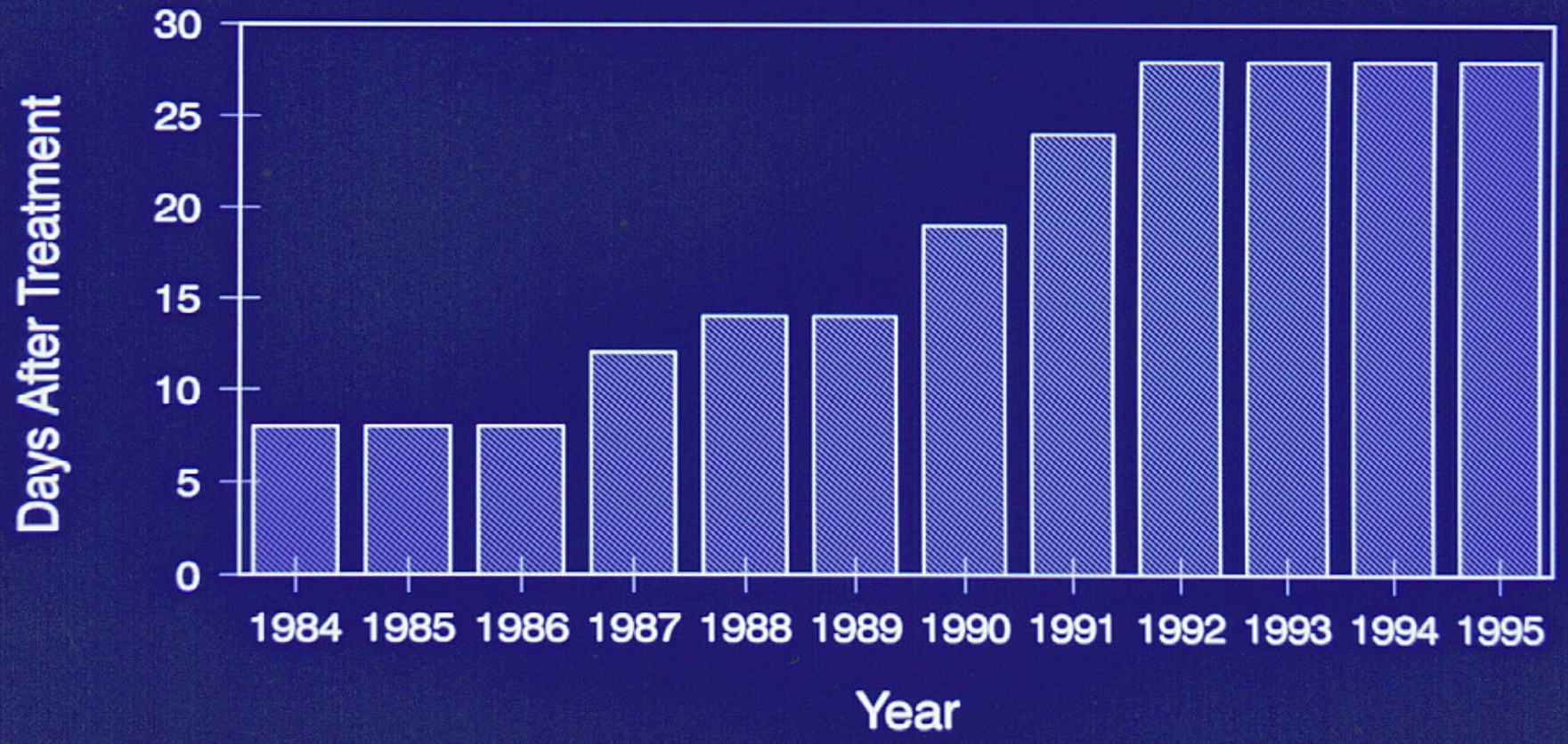
1982 DFG Evaluation

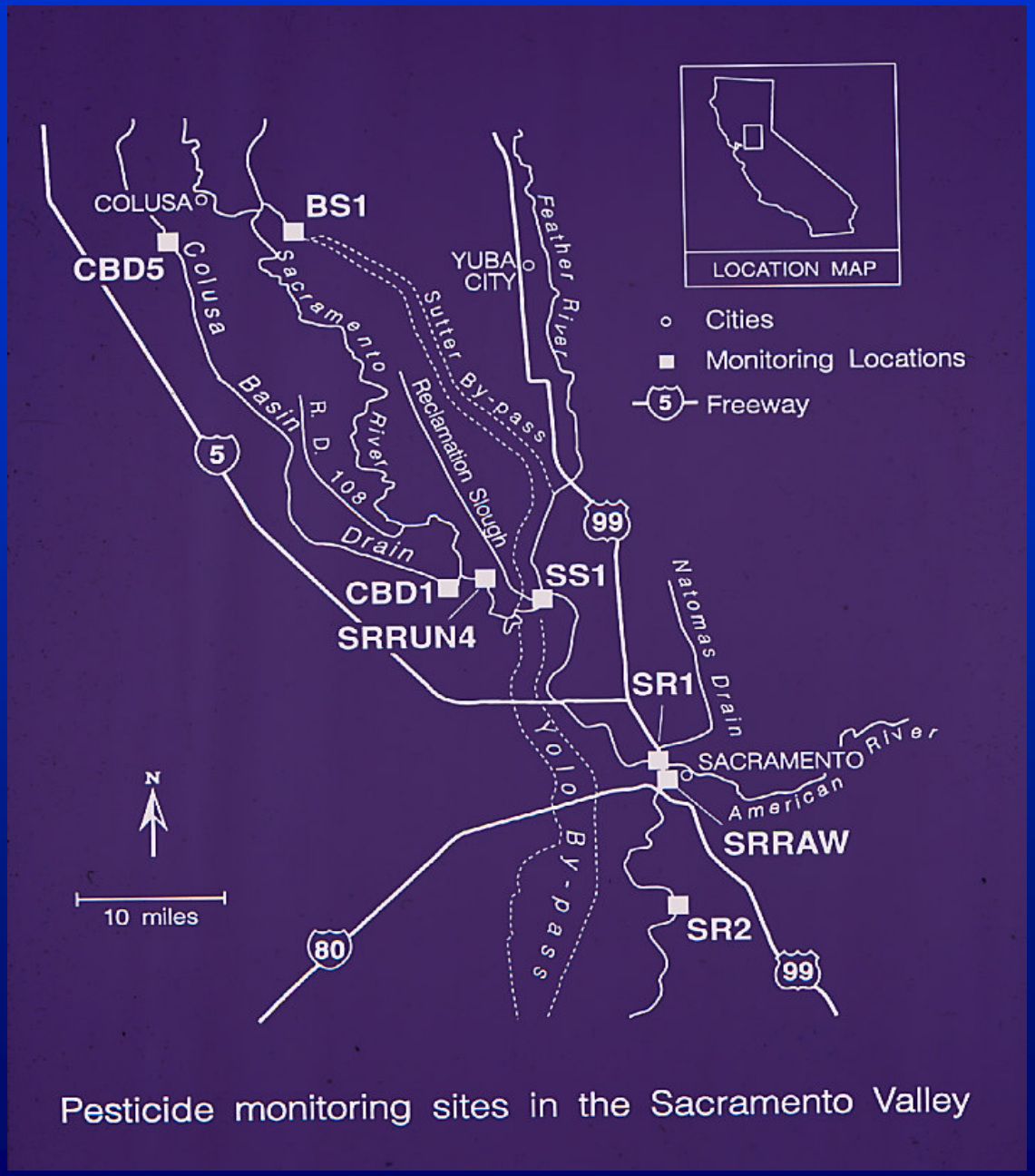
Thiobencarb Concentrations in CBD near SR 20





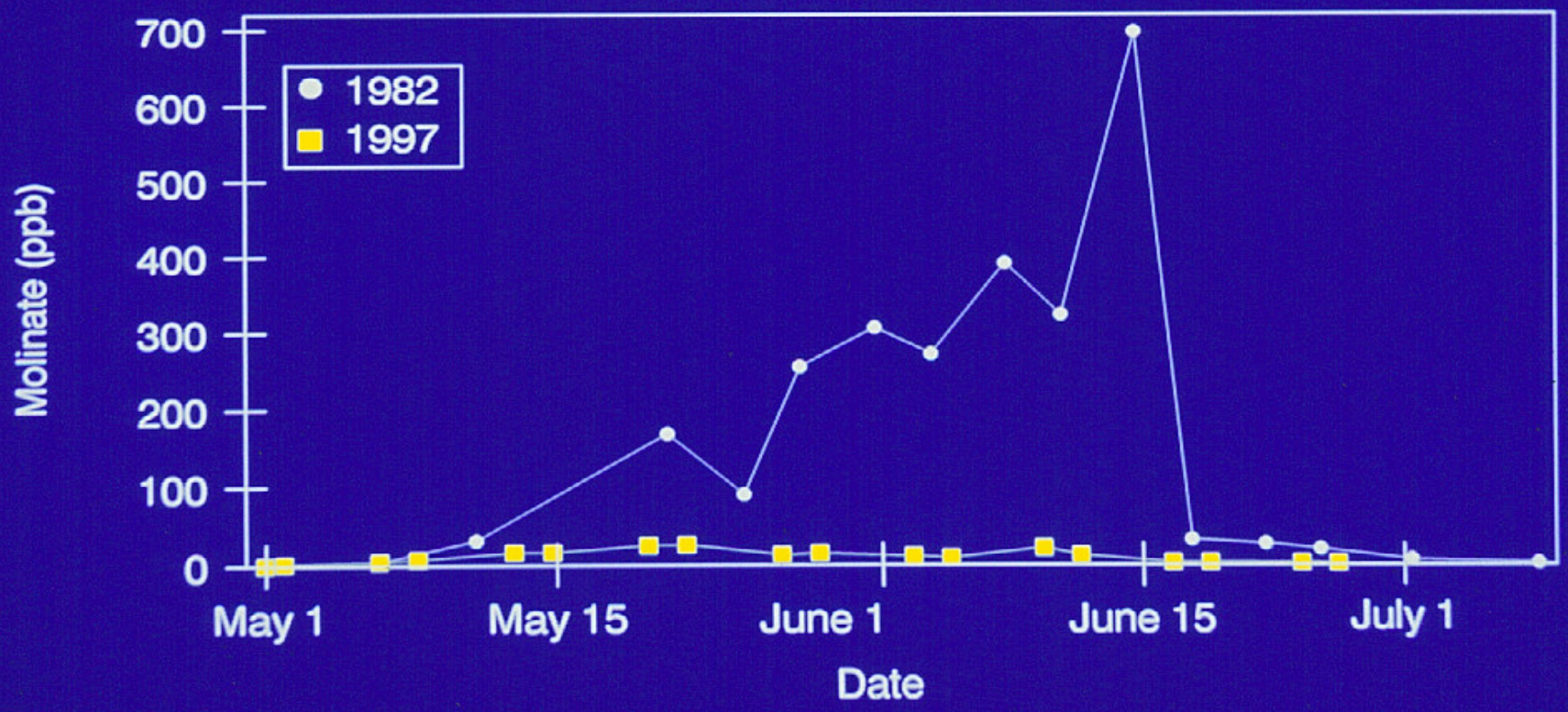
Holding Times for Fields Treated with Molinate



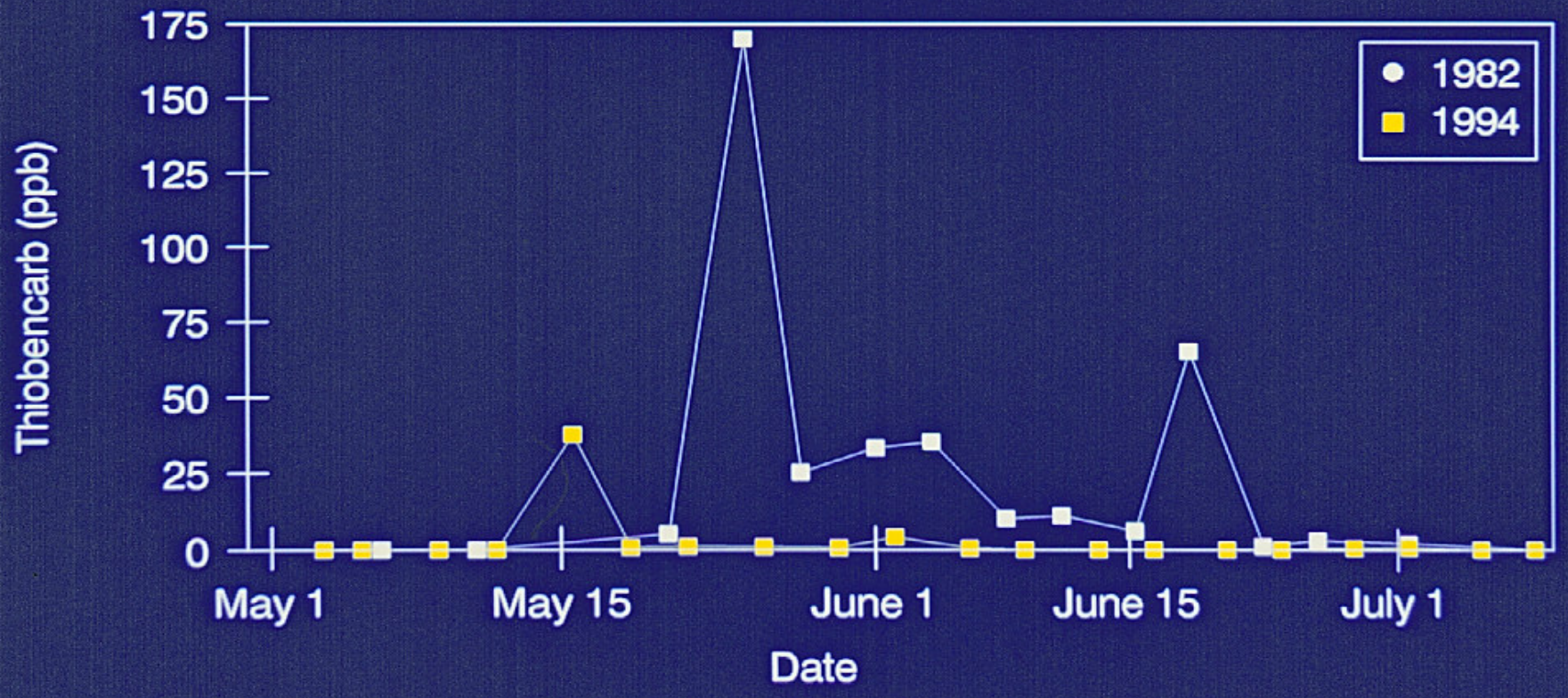


Pesticide monitoring sites in the Sacramento Valley

Molinate Concentrations in the Colusa Basin Drain near SR20 1982 and 1997



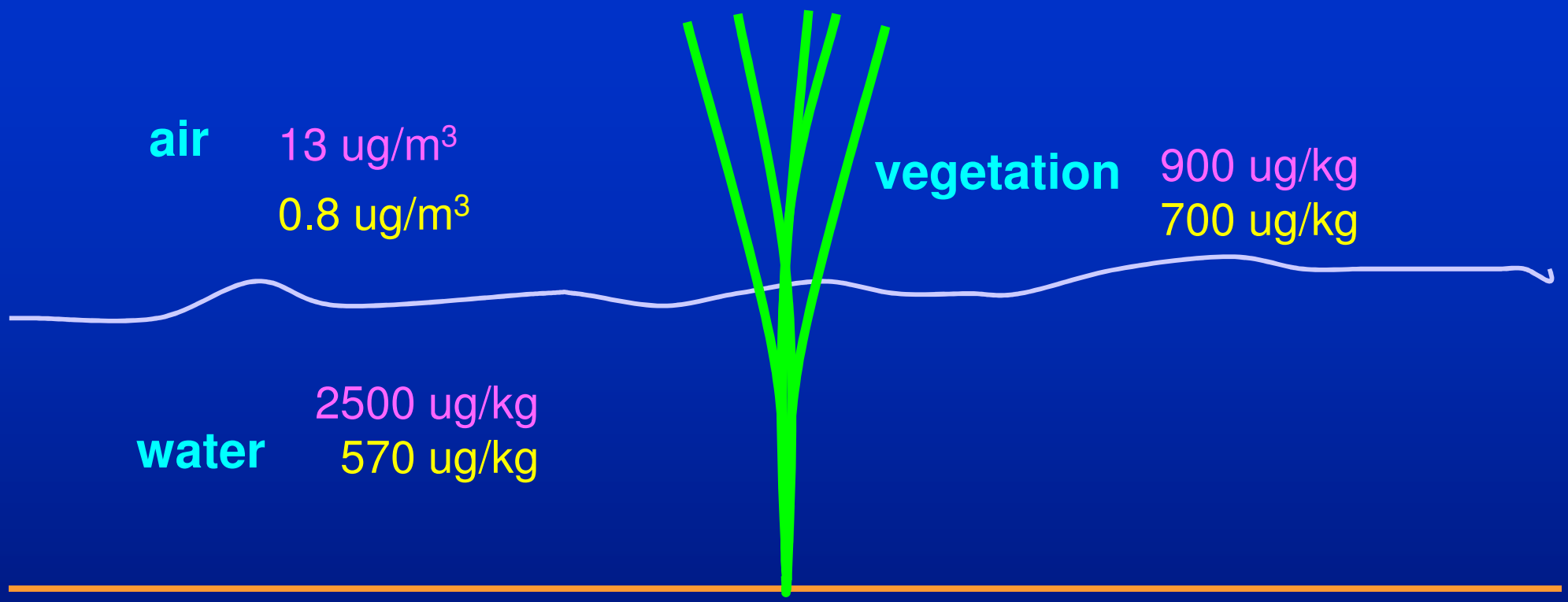
Thiobencarb Concentrations in the Colusa Basin Drain near SR20 1982 and 1994



Rice herbicide partitioning data

Property	molinate	thiobencarb
solubility (mg/l)	970	30
vapor pressure (mPa)	670	2.9
Henry's law - H'	1.7×10^{-4}	1×10^{-5}
K_{OC}	120	900
log K_{OW}	3.21	3.40

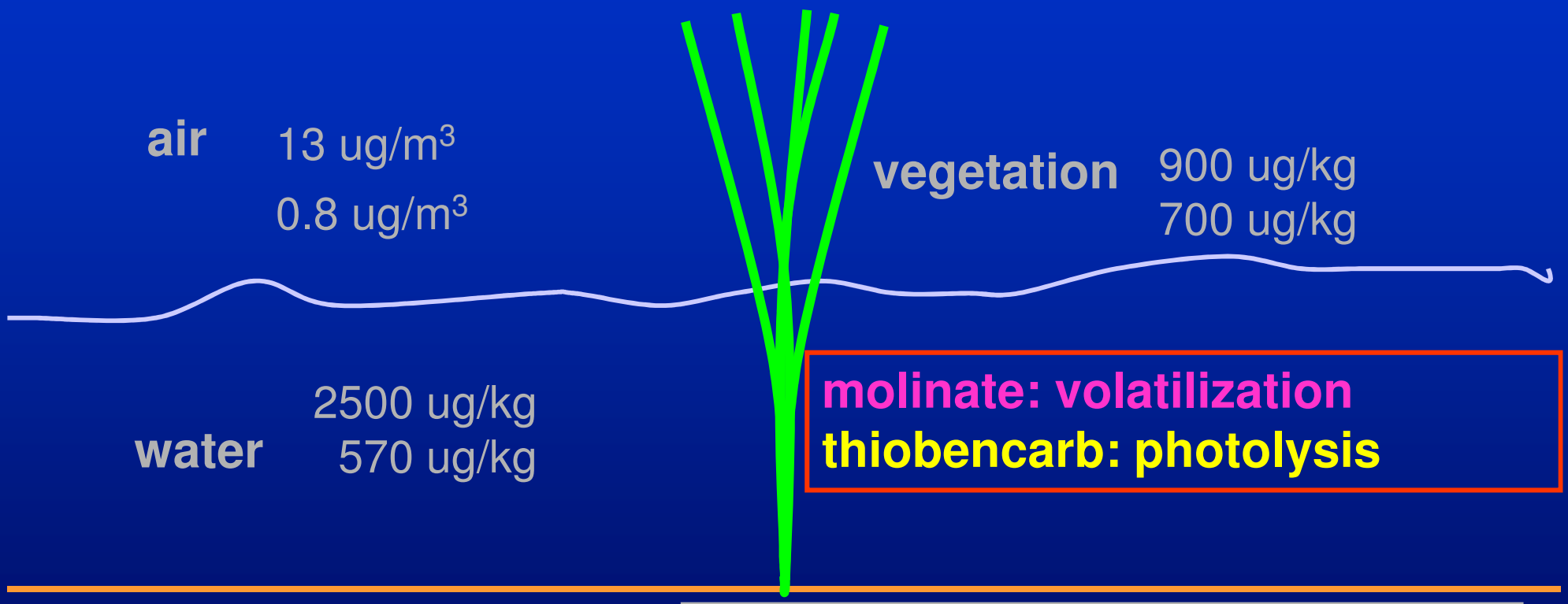
Mean concentrations two days after application



applied **molinate**:	3.1 kg/ha
applied **thiobencarb**:	4.4 kg/ha

Ross, L.J. and R.J. Sava. 1986. Fate of Thiobencarb and Molinate in Rice Fields. J. Environ. Qual. 15(3): 220-225.

Principal **dissipation** routes



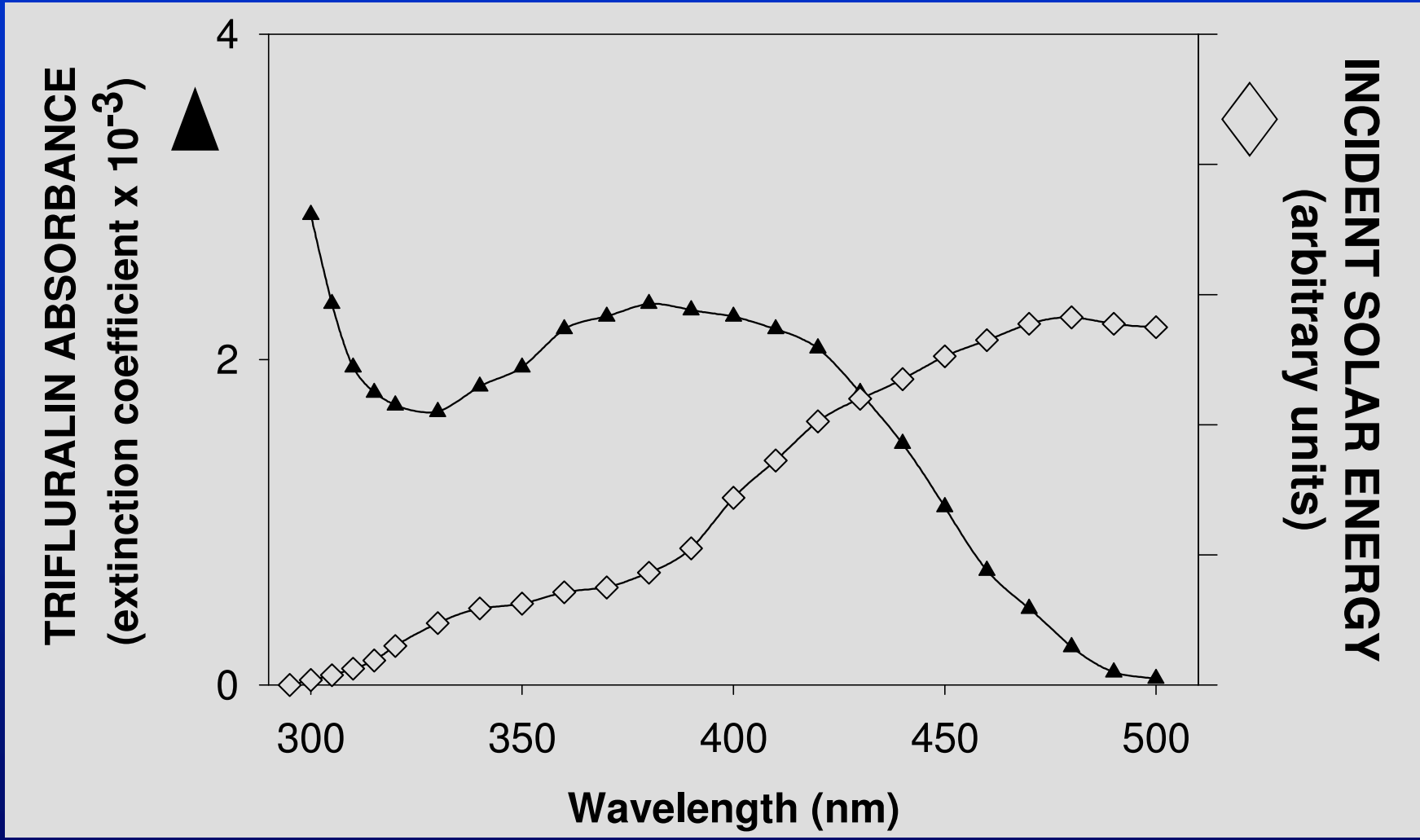
applied **molinate**:	3.1 kg/ha
applied **thiobencarb**:	4.4 kg/ha

Rice herbicide degradation data

Property	molinate	thiobencarb
solubility (mg/l)	970	30
vapor pressure (mPa)	670	2.9
Henry's law - H'	6.3×10^{-5}	1×10^{-5}
K_{OC}	120	900
aq. photolysis $t_{1/2}$ (days)	> 100	**> 100** ?????
hydrolysis $t_{1/2}$ (days)	> 100	> 100
aerobic soil $t_{1/2}$ (days)	40	40
anaerobic soil $t_{1/2}$ (days)	120	300
field dissipation $t_{1/2}$ (days)	21	21

DIRECT PHOTOLYSIS

example: trifluralin – $t_{1/2}$ ~ 9 hours



DIRECT PHOTOLYSIS

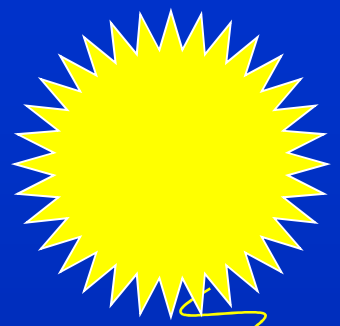
1st law of photochemistry

"light must be absorbed before there can be a chemical reaction"

Thiobencarb - λ_{MAX} = 269 nm

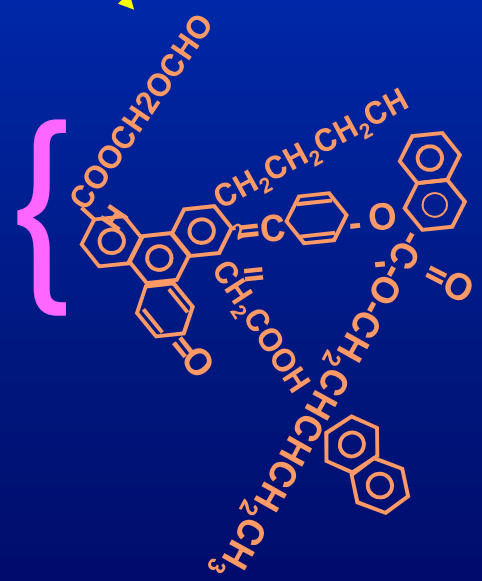
- *very weak absorbance above 290 nm*

Indirect photolysis



hν

dissolved organic matter - fulvic and humic acids



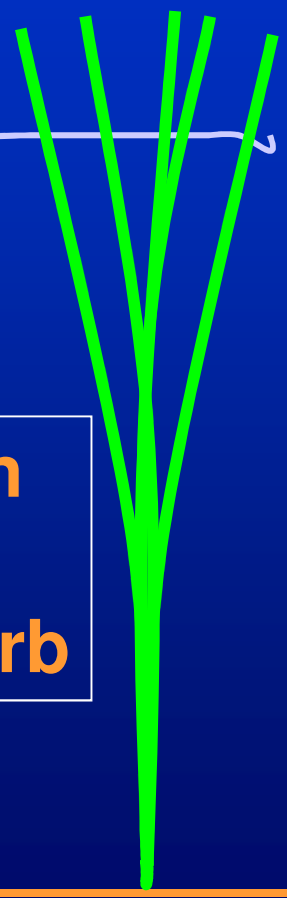
•OH

•OOH

$^1O_2$

reactive species

oxidation of thiobencarb

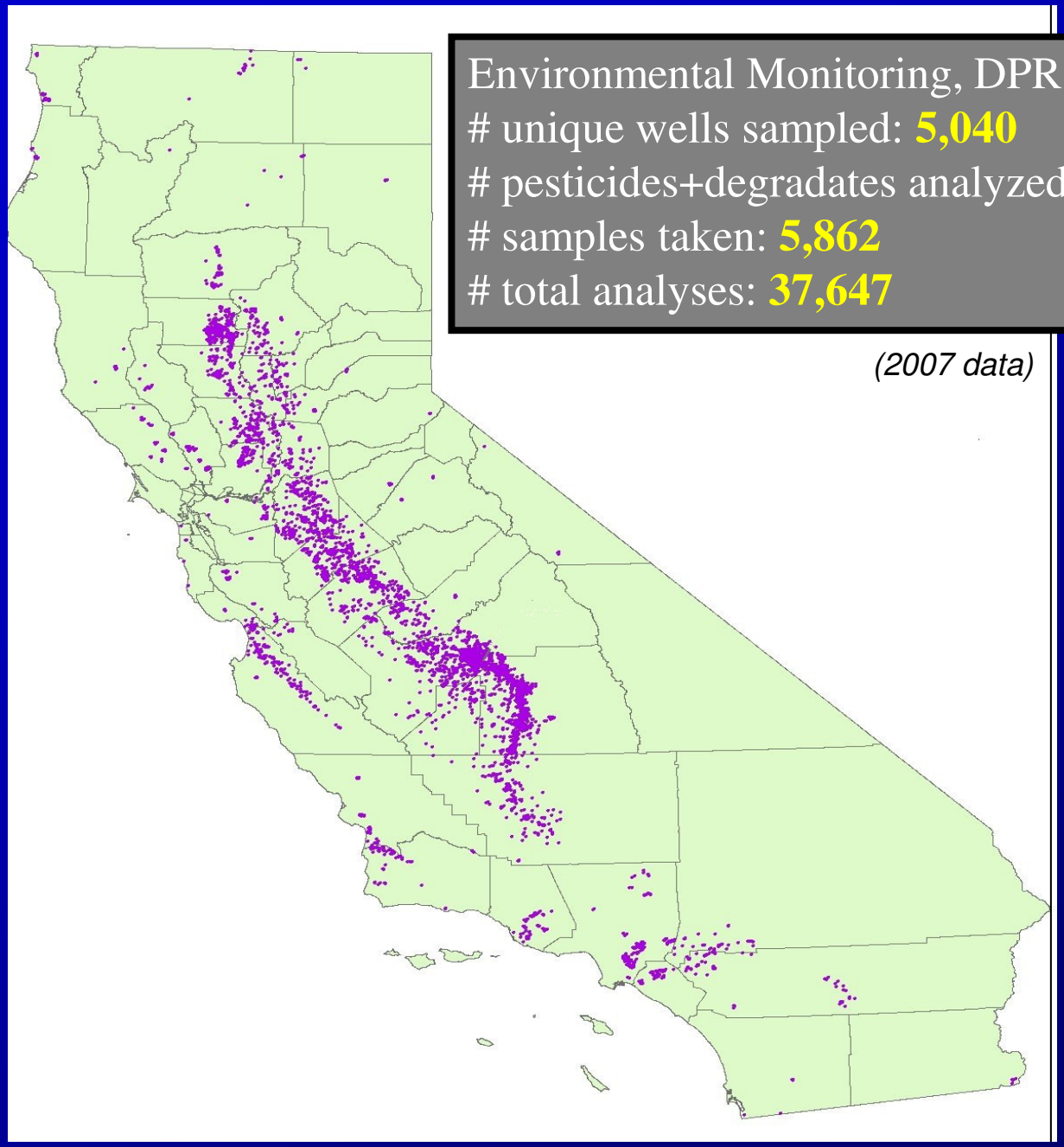


Herbicide Contamination of Ground Water

CFC Dating of Contaminated Ground Water

Probabilistic Modeling of Herbicide Movement to Ground Water

10 min break


Environmental Monitoring, DPR
unique wells sampled: 5,040
pesticides+degradates analyzed: 160
samples taken: 5,862
total analyses: 37,647
(2007 data)

Ground water contamination

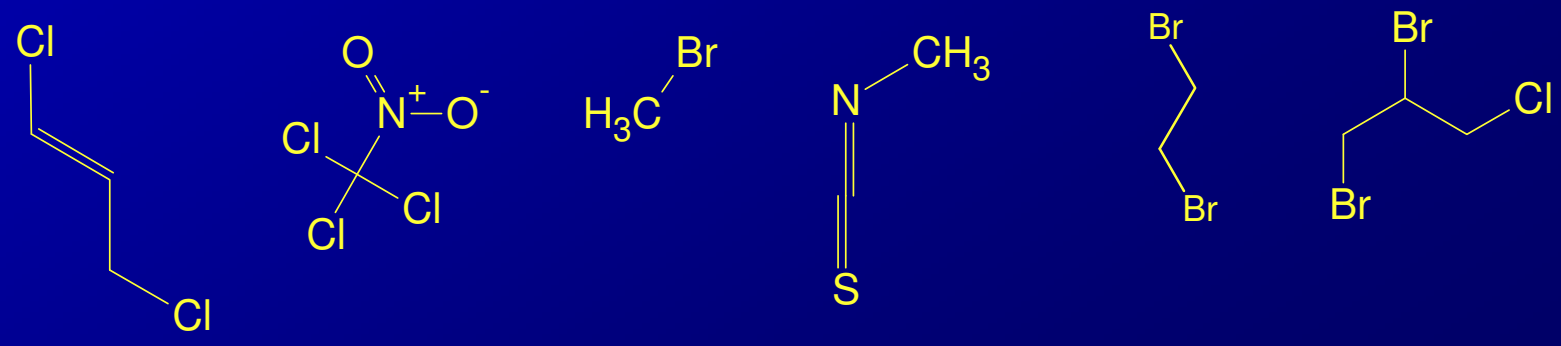
Confirmed pesticide detections in California ground water (DPR well inventory database)

pesticide	Number confirmed detections in WIDB	
TRIAZINE HERBICIDES & DEGRADATES	975	preemergent herb
DBCP, EDB, 1,2-D	728	fumigants
DIURON	376	preemergent herb
BROMACIL	202	preemergent herb
BENTAZON	70	rice herbicide
CHLORTHAL DIMETHYL & DEGRADATES	58	preemergent herb
ALDICARB & DEGRADATES	53	insecticide
PROMETON	25	preemergent herb
NORFLURAZON	12	preemergent herb
HEXAZINONE	7	preemergent herb
other	21	various

Fumigants and selected properties

why are EDB and DBCP ground water contaminants?

property	1,3-D	chloropicrin	MeBr	MITC	EDB	DBCP
State, BP(C)	L, 108C	L, 112C	G, 4C	S, MP=36C	L, 131C	L, 196C
MW	111	164	95	73	188	236
Sol, ppm	2485	10000	13200	8940	4300	1230
VP (Pa)	3700	27	190000	1740	150	120
H'	0.15	0.13	1.5	0.01	0.11	0.01
Hydrol $t_{1/2}$ (d)	7.2	STABLE	12	50	2900	14,000
log KOW	1.9	2.5	1.9	1.4	1.8	2.6
KOC	34	81	39	36	34	88
soil $t_{1/2}$ (lab,d)	9.3	15.4	1	5.2	44	7
field $t_{1/2}$ (d)	7	3	55	2.1	100	203

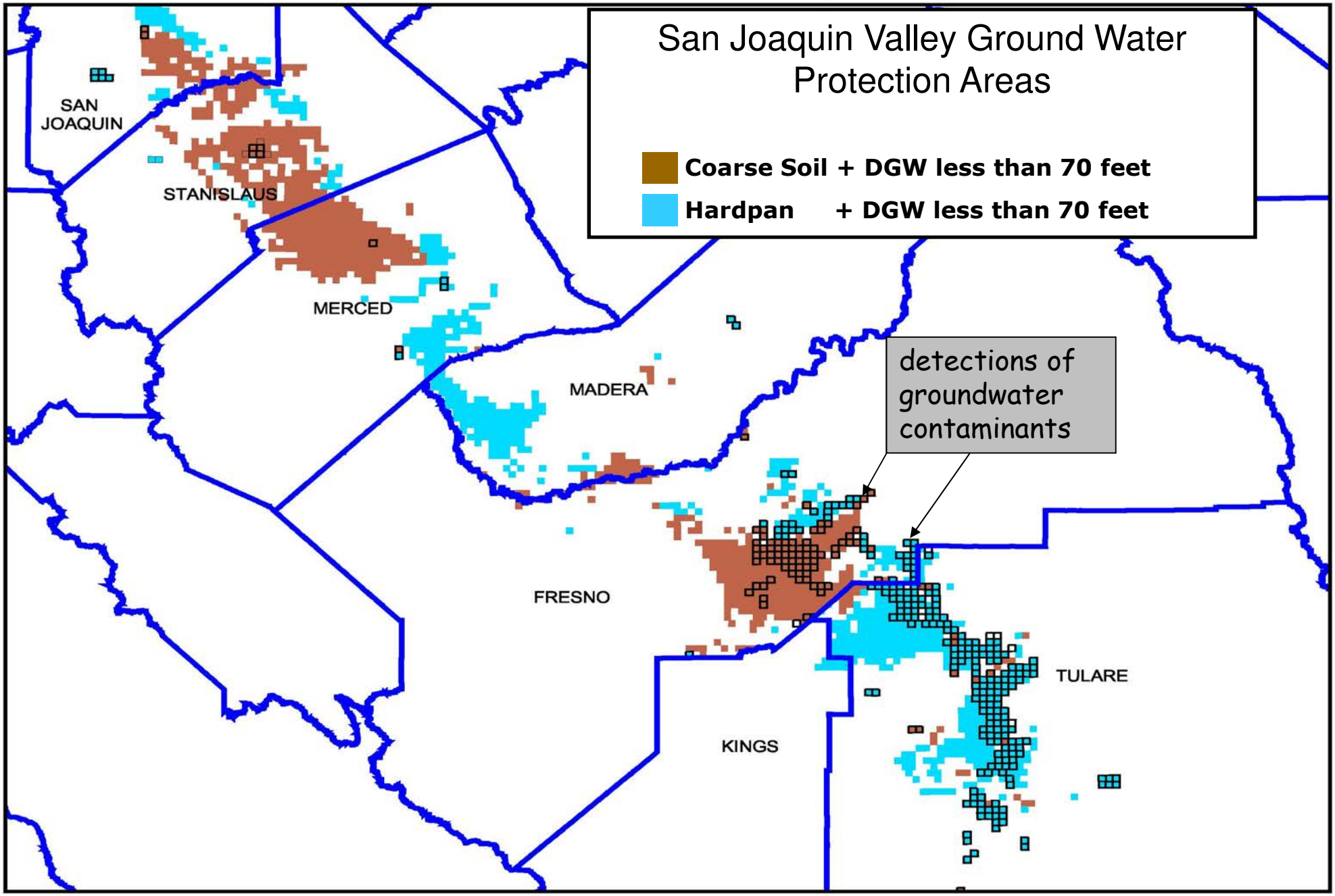


Two common ground water contaminants

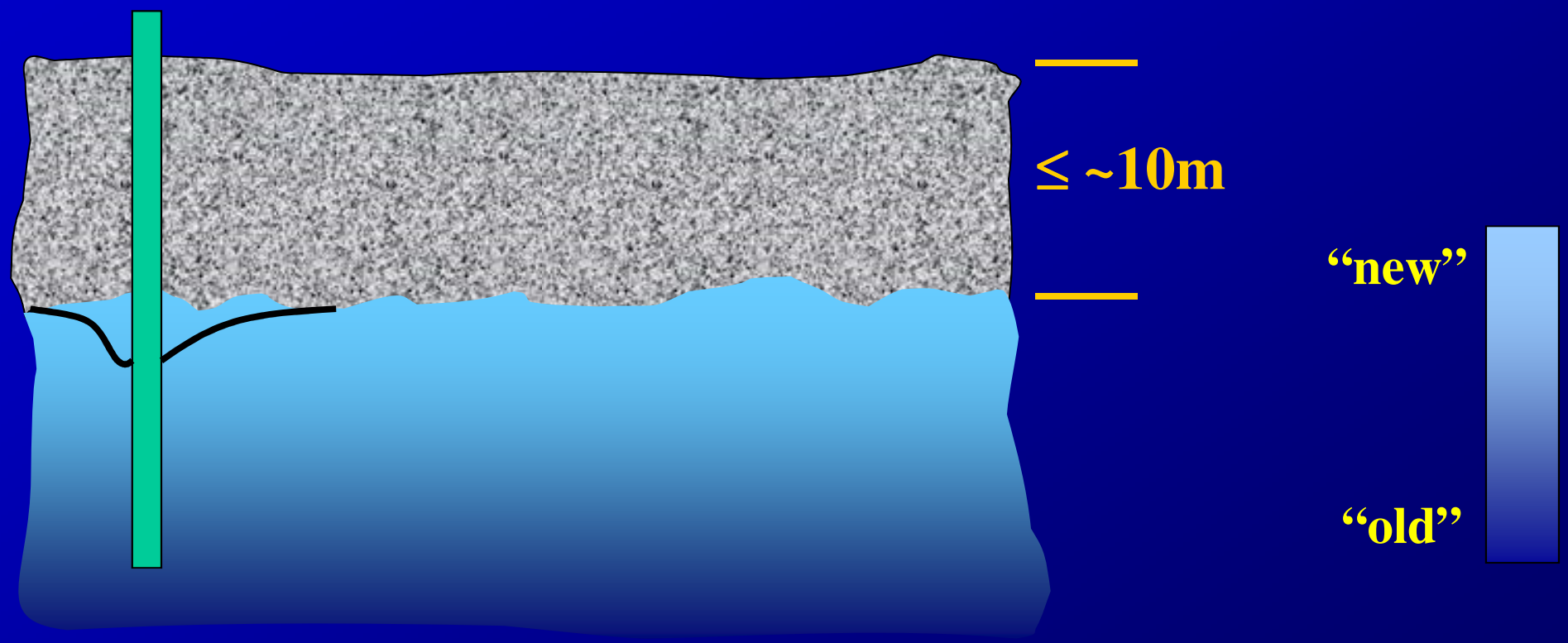
preemergent herbicides

	DIURON	**BROMACIL**
Soly	42	800
K_{OC}	480	32
K_{OW}	630	76
H'	5.4×10^{-8}	3.7×10^{-8}
FD $t_{1/2}$	90d	207d
Hydrol $t_{1/2}$	>30d	>30d

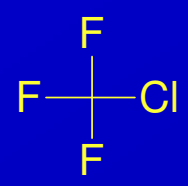
relatively water soluble, low sorption, nonvolatile
soil-applied, heavily used, moderate persistence


San Joaquin Valley Ground Water Protection Areas
Coarse Soil + DGW less than 70 feet
Hardpan + DGW less than 70 feet
SAN JOAQUIN
STANISLAUS
MERCED
MADERA
FRESNO
KINGS
TULARE
detections of groundwater contaminants

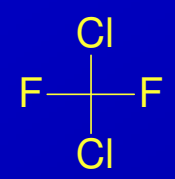
Are detections related to recent applications (~ last 10 yrs), or are they from historical applications (e.g. > 20 years ago) ?



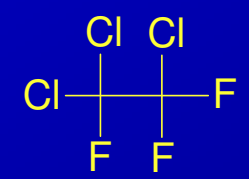
chlorofluorocarbon Henry's law constants well characterized



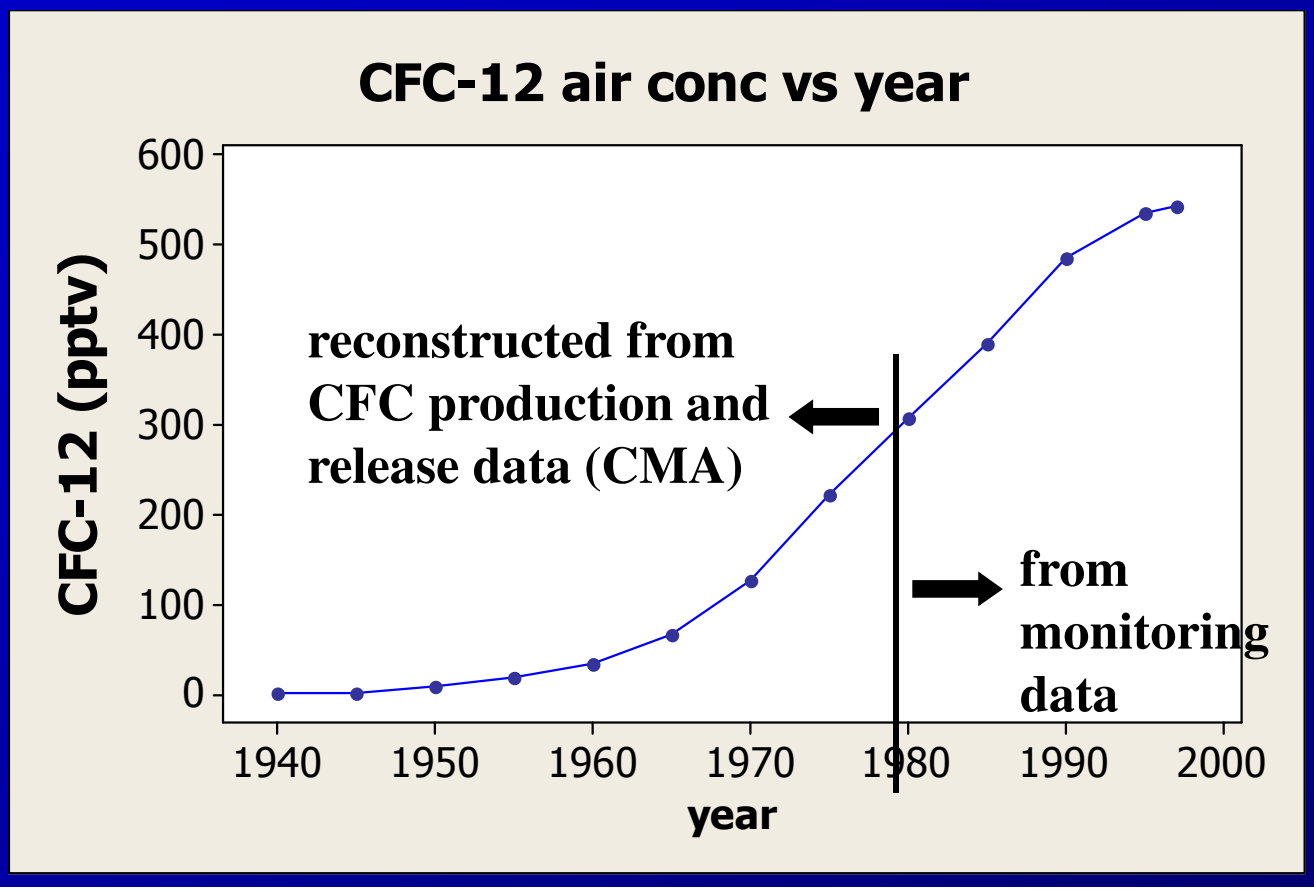
CFC-11



CFC-12



CFC-113



1. sample CFCs in well water, obtain $[CFC]_{aq}$

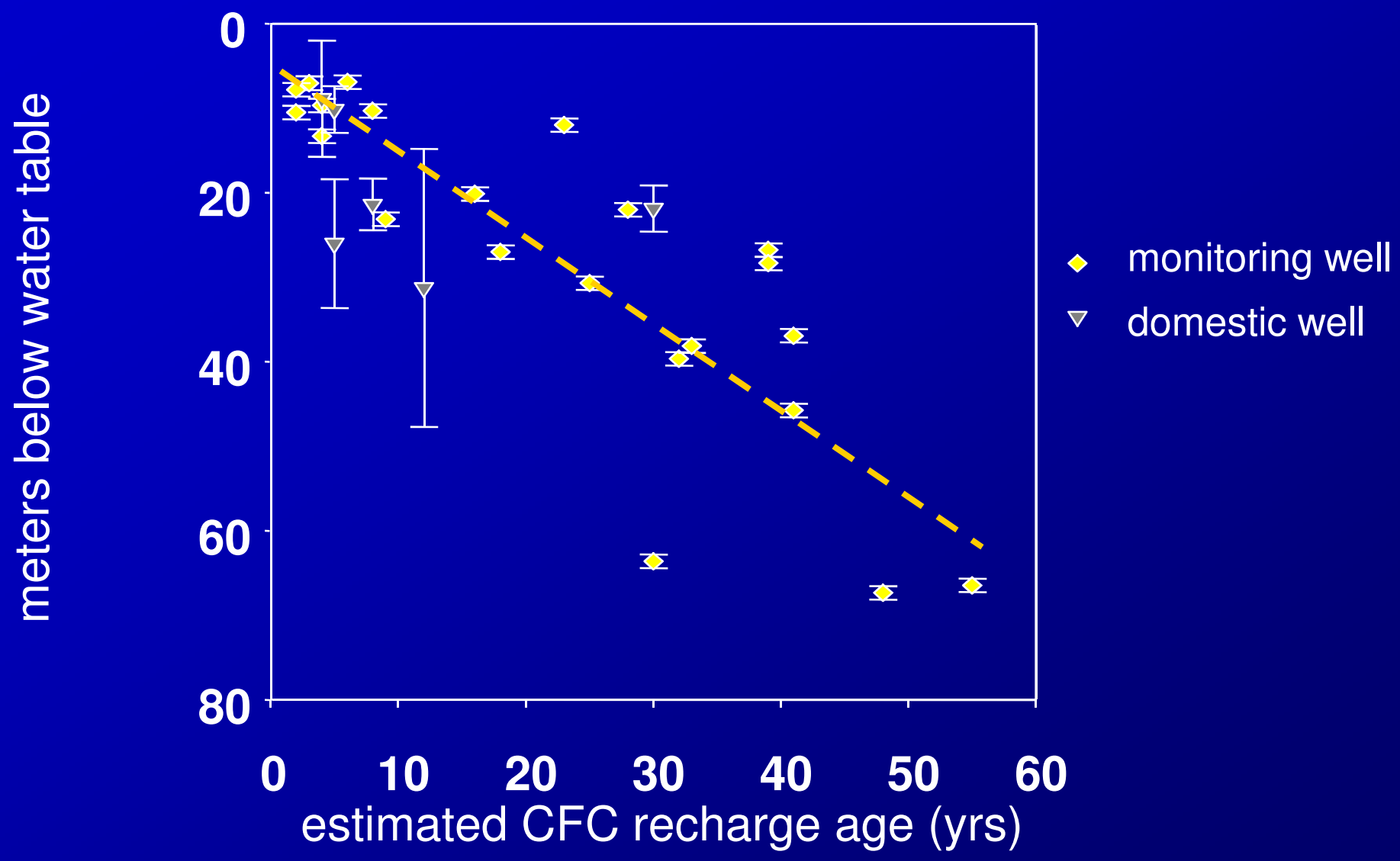
2. $$H = \frac{[CFC]_{air}}{[CFC]_{aq}}$$

   or

   $$[CFC]_{air} = [CFC]_{aq} \times H$$

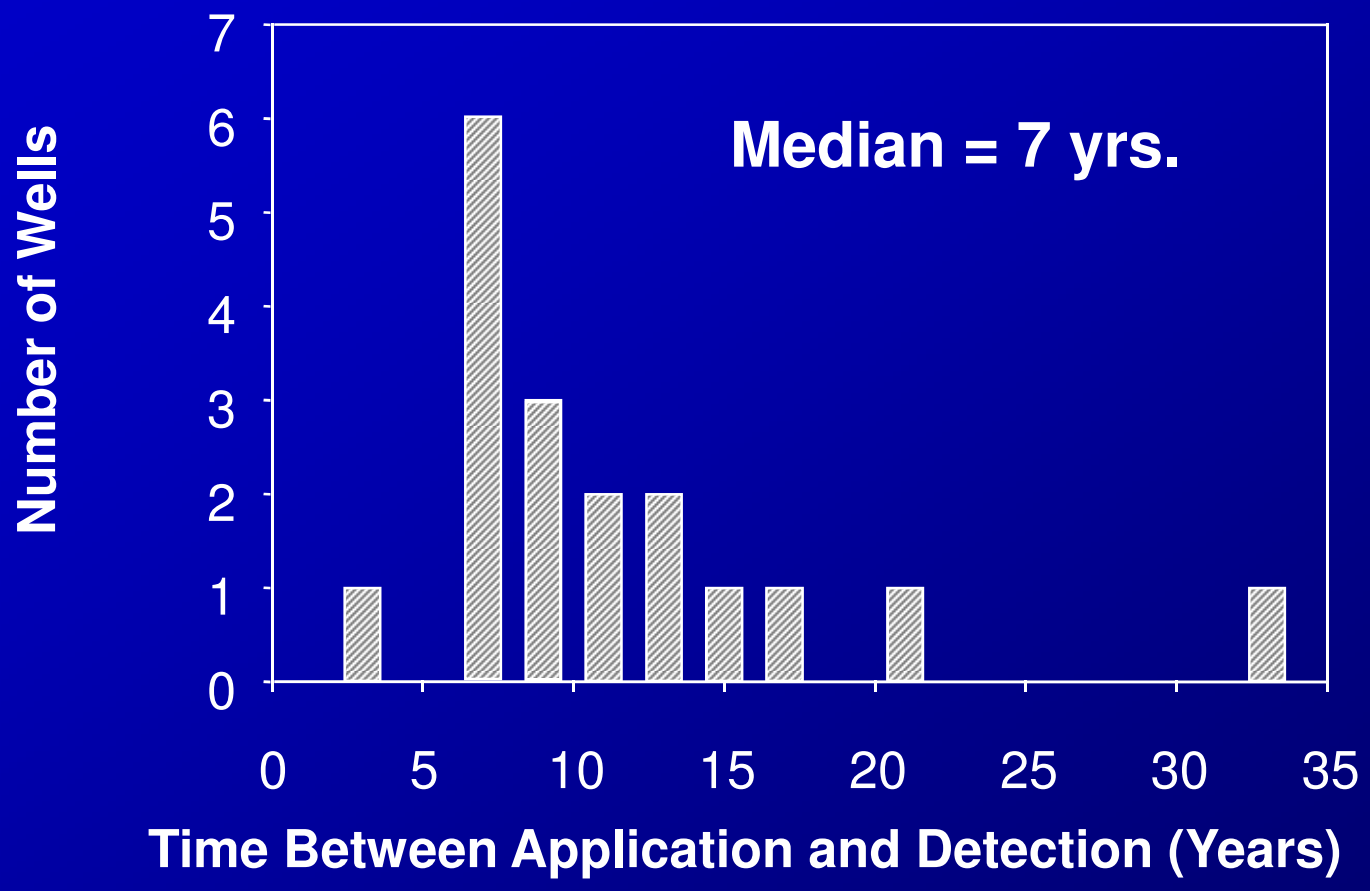
3. calculate $[CFC]_{air}$, obtain recharge year from graph

Depth below Water Table vs. Recharge Age



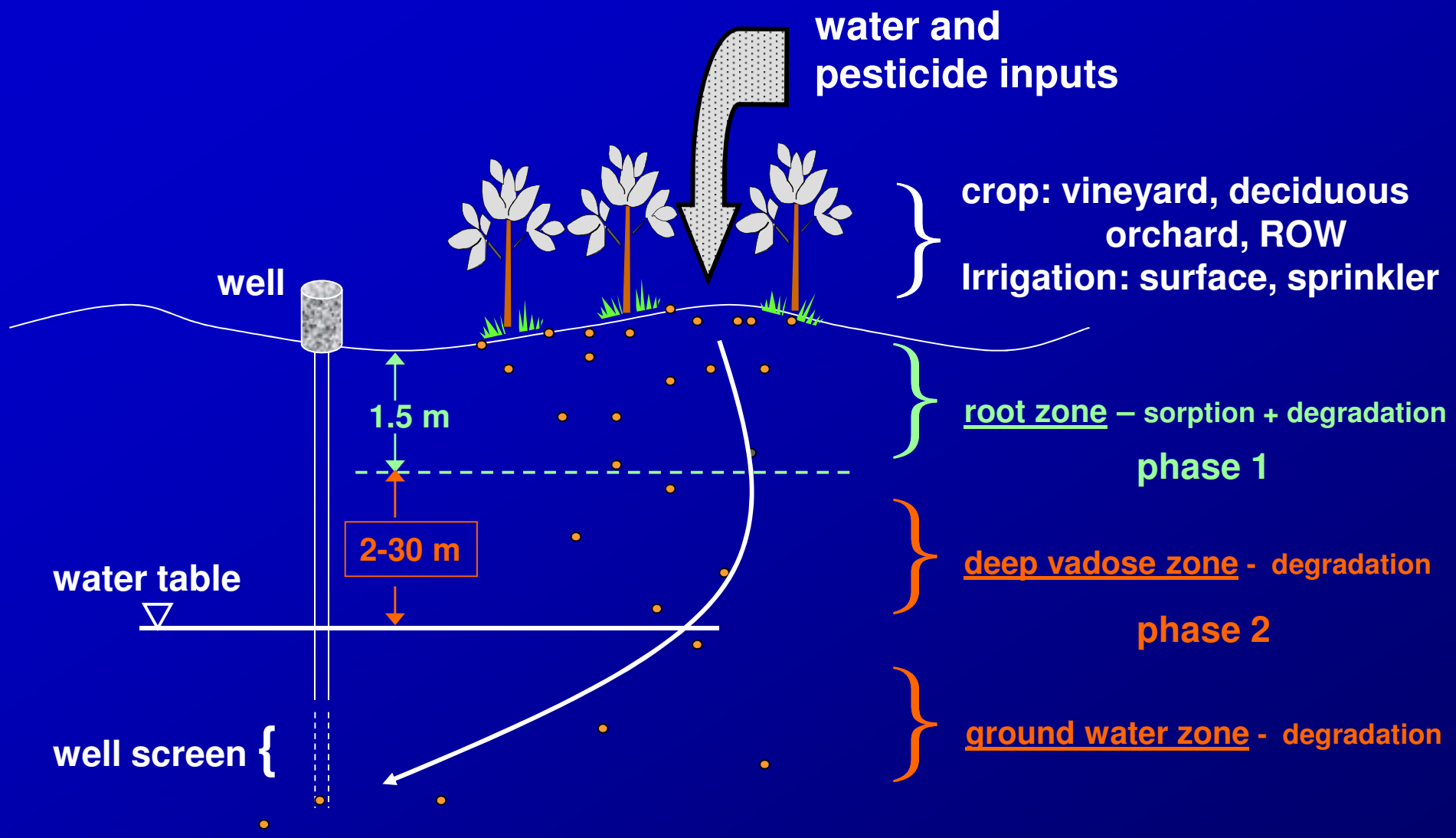
Estimated Time Between Herbicide Application and Subsequent Detection in 18 Wells

CFC-11, CFC-12, CFC-113



Spurlock, F., K. Burow, and N. Dubrovsky. 2000. Chlorofluorocarbon Dating of Herbicide-Containing Well Waters in Fresno and Tulare Counties, California. J. Environ. Qual. 29:474-483.

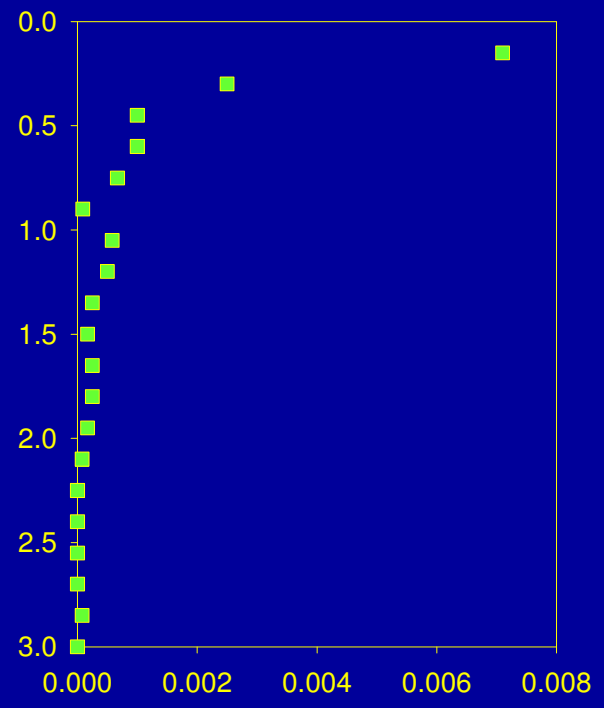
fig. 1



Random variables: K_{OC}, TFD, application rate, DGW, recharge age

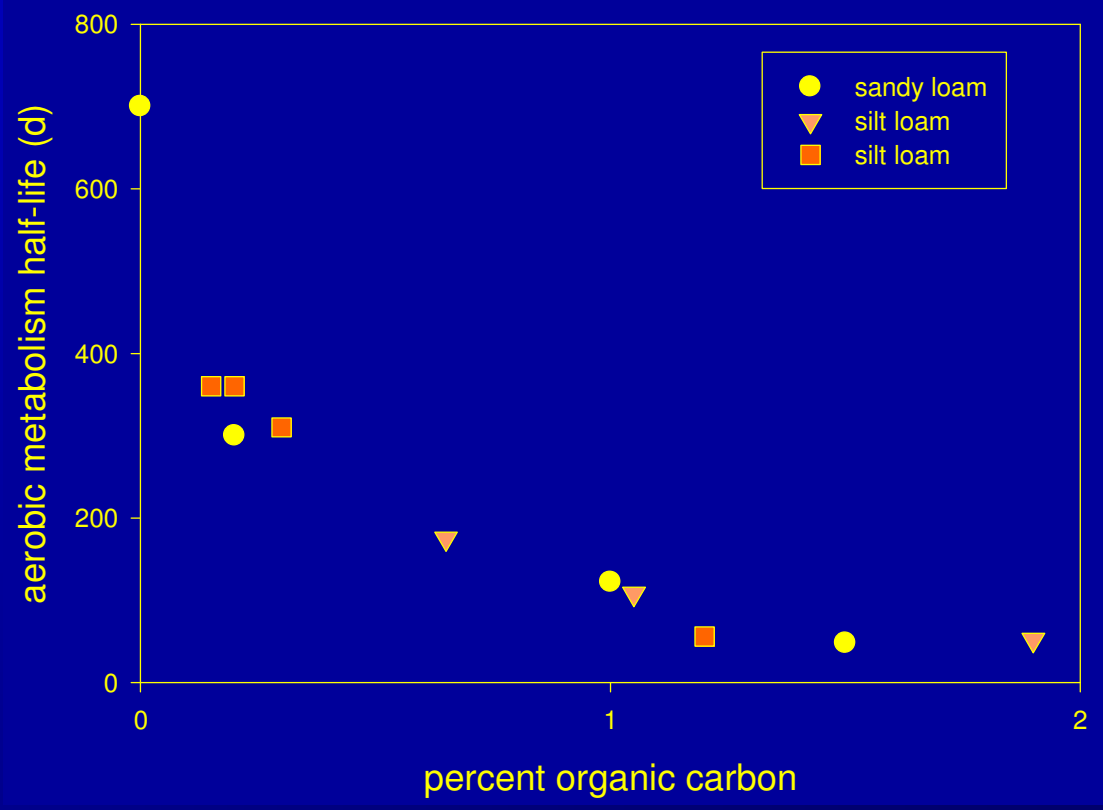
Environmental Fate in the Deep Vadose Zone – Degradation Rates?

"typical" organic carbon profile



degradation of simazine vs. OC in 3 german soils

Kordel et al., degradation capacities of chlorotoluron and simazine in subsoil horizons. Sci. Tot. Environ. 171:43, 1995



OC a surrogate for biological activity??

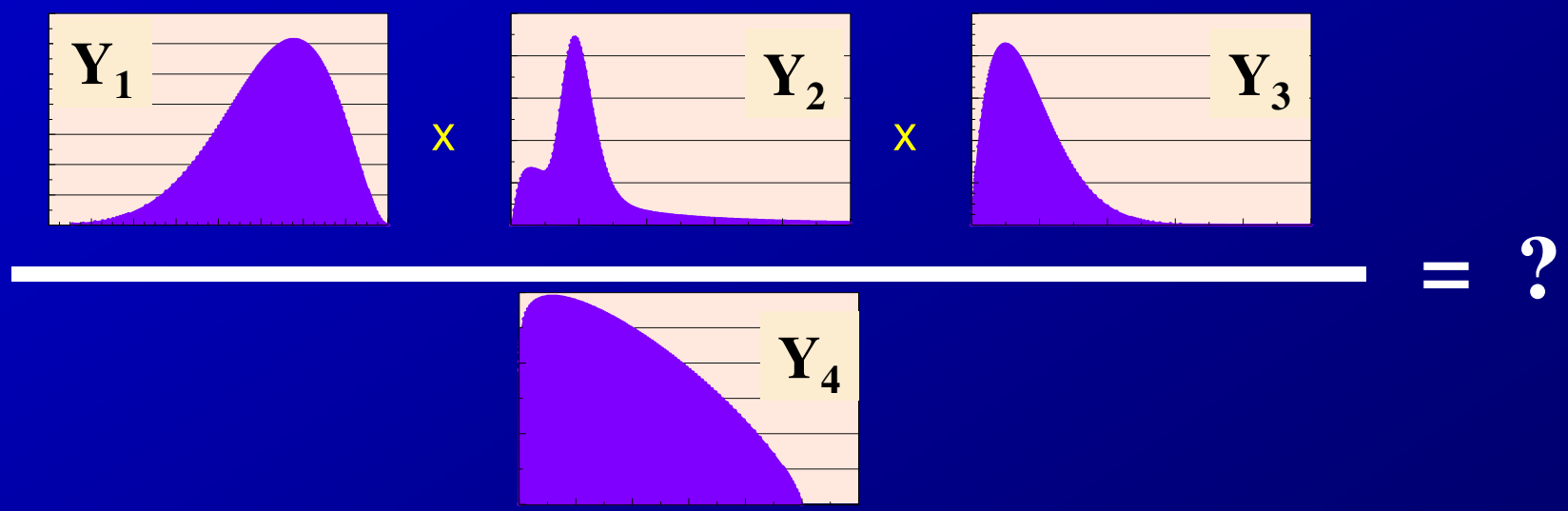
Monte Carlo Analysis

Given a mathematical model with uncertain or variable inputs, used to estimate the output distribution and statistics

$$Z = \frac{Y_1 \times Y_2 \times Y_3}{Y_4}$$

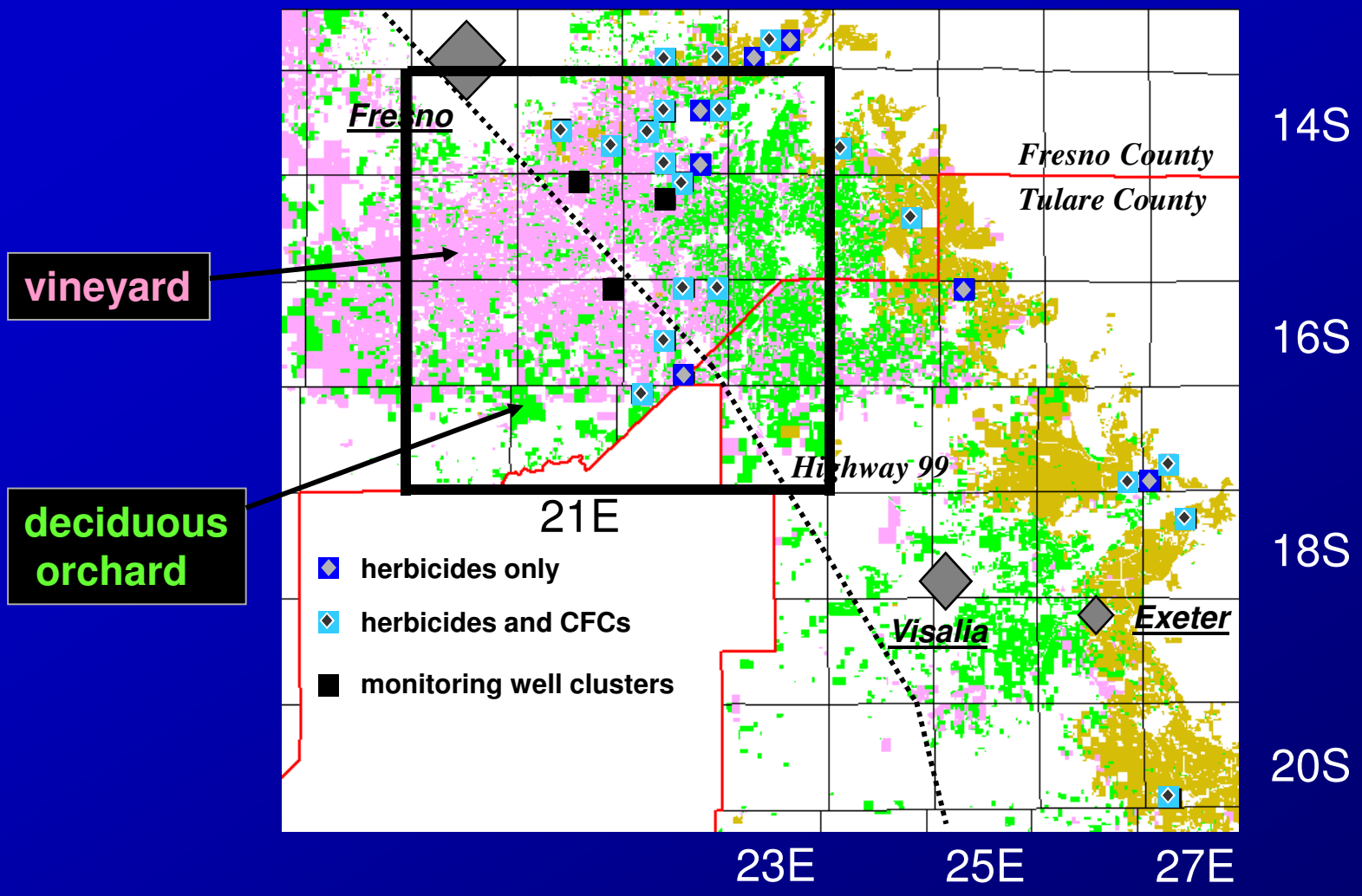
mathematical model ..... variable inputs
Monte Carlo analysis .....
output distribution and statistics

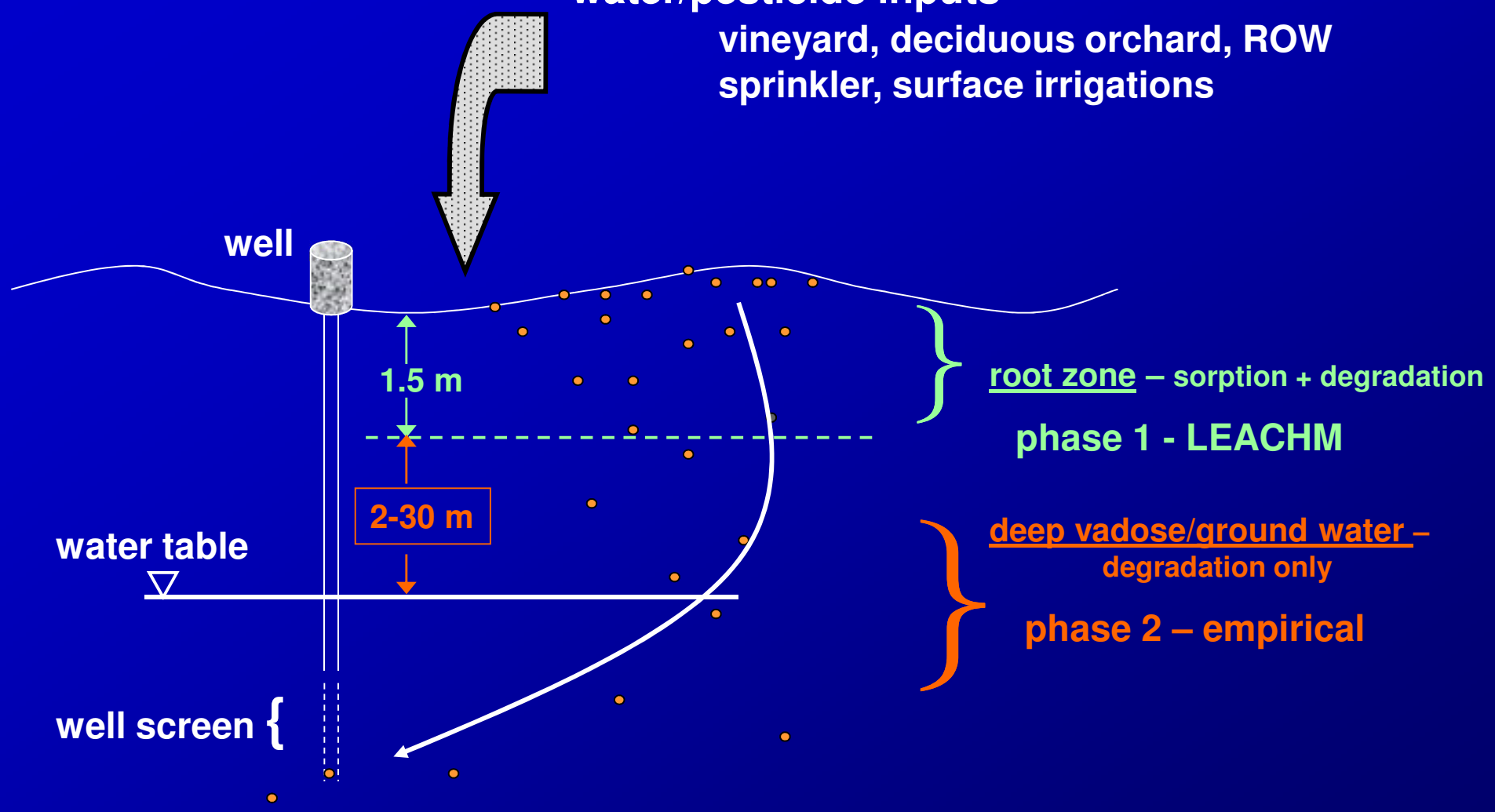
$$Z = \frac{Y_1 \times Y_2 \times Y_3}{Y_4}$$



SJV "Dune Sand" area

~ 330 wells sampled for simazine (df = 41%) and diuron (df=18%)





Random variables: K_{OC}, root zone degradation rates, application rate, DGW, recharge age

Random variables

simazine K_{OC}, L kg OC^{-1}

simazine TFD, d

diuron K_{OC}, L kg OC^{-1}

diuron TFD, d

simazine grape applic. rate, kg ha^{-1}

simazine orchard applic. rate, kg ha^{-1}

diuron grape applic. rate, kg ha^{-1}

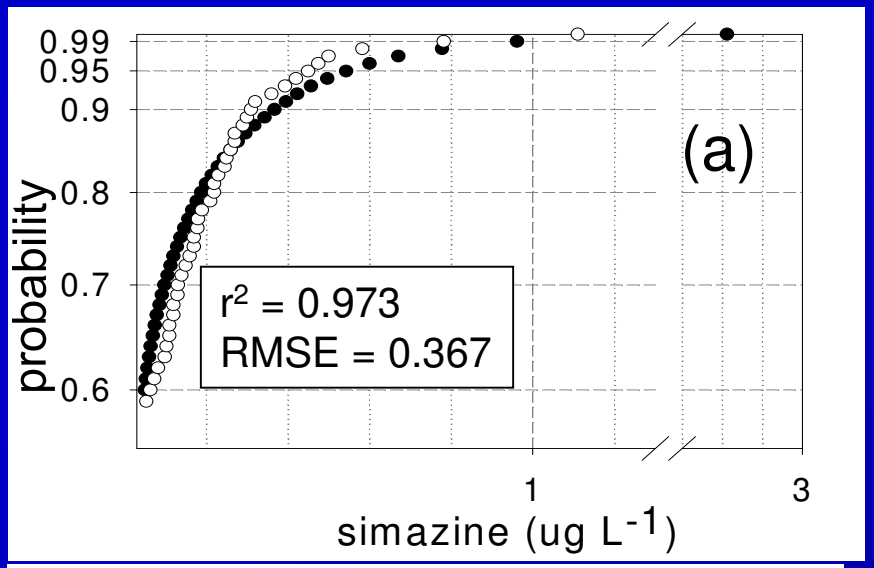
diuron orchard applic. rate, kg ha^{-1}

diuron right of way applic. rate, kg ha^{-1}

depth to ground water, m

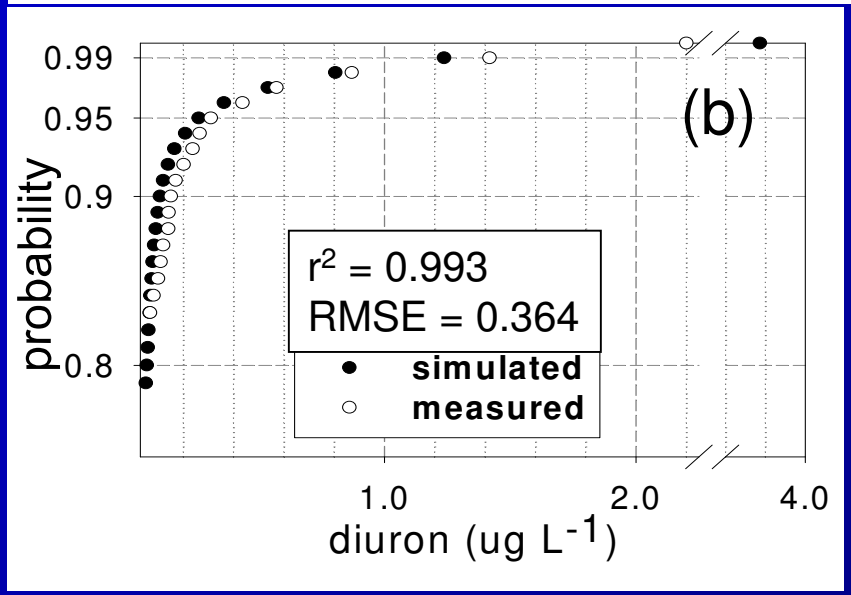
ground water recharge age, y

Calibration results



simazine

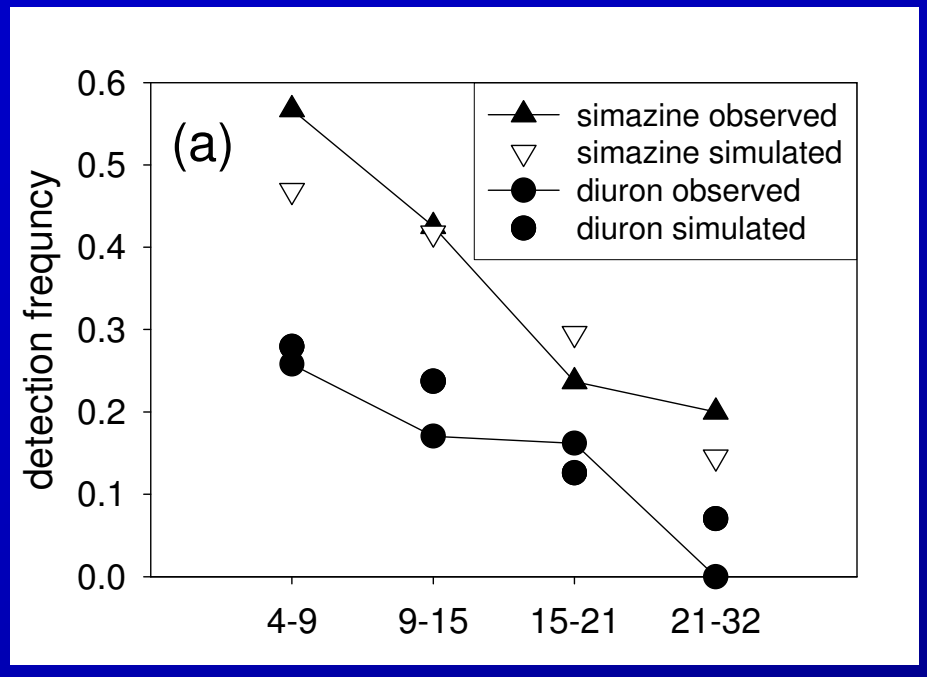
deep vadose/GW half-life:	330d
Kordel et al.:	175-700d
median TFD:	87d

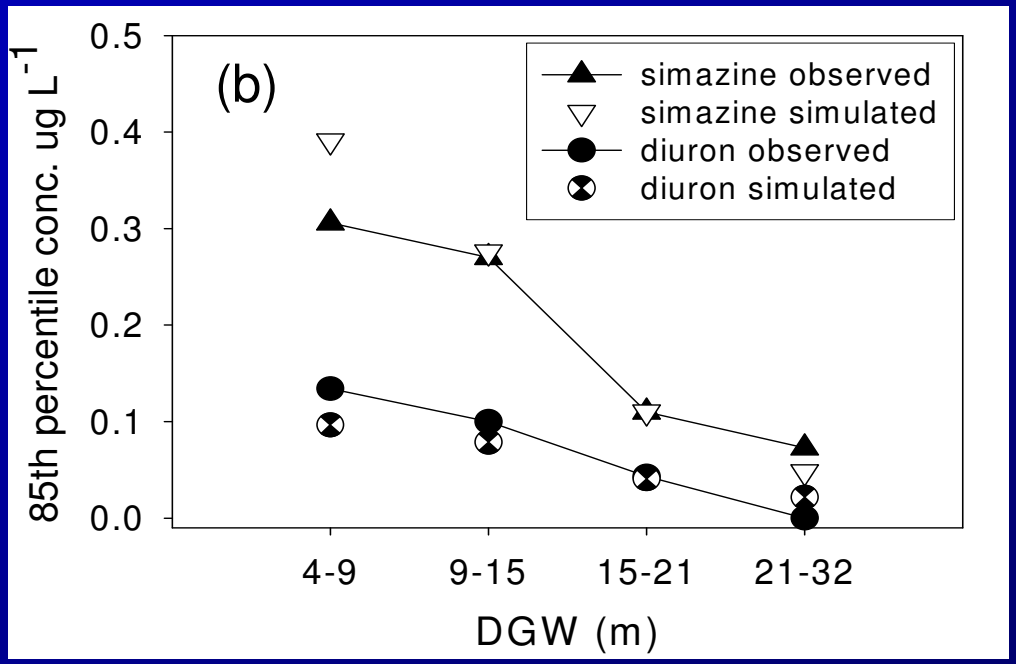


diuron

deep vadose/GW half-life:	455d
Kordel et al. (chlortoluron)	493d
median TFD:	102d

Spurlock, F., M. Clayton,and J. Troiano. 2006. Modeling Herbicide Movement to Ground Water in Irrigated Sandy Soils of the San Joaquin Valley, California. Water, Air, & Soil Pollution 176: 93-111


(a)
detection frequncy
0.6
0.5
0.4
0.3
0.2
0.1
0.0
4-9
9-15
15-21
21-32
simazine observed
simazine simulated
diuron observed
diuron simulated

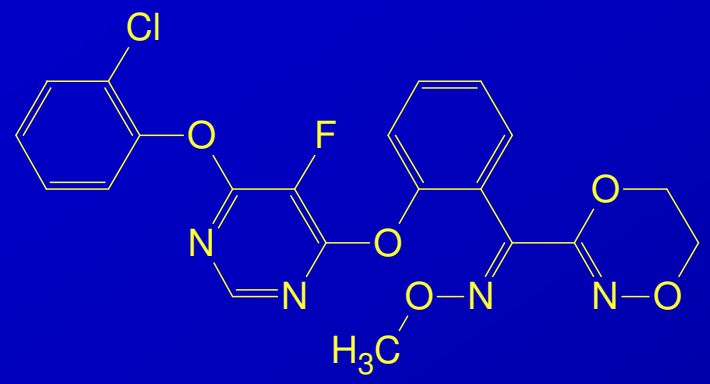

(b)
85th percentile conc. ug L-1
0.5
0.4
0.3
0.2
0.1
0.0
4-9
9-15
15-21
21-32
DGW (m)
simazine observed
simazine simulated
diuron observed
diuron simulated

Simulated mass balance budgets

fate process	simulation percentiles 50th	90th
simazine		
volatilization from soil surface	< 0.001	< 0.001
degradation in root zone	0.710	0.909
carry-over in root zone	0.003	0.031
leached out of root zone	0.288	0.544
degradation in vadose zone	0.193	0.376
degradation in ground water	0.079	0.196
measured in well water sample	0.001	0.010
diuron		
volatilization from soil surface	0.002	0.002
degradation in root zone	0.906	0.974
carry-over in root zone	0.144	0.218
leached out of root zone	0.089	0.159
degradation in vadose zone	0.049	0.093
degradation in ground water	0.033	0.070
measured in well water sample	0.001	0.008

fraction of application

New Chemistries – many systemic, surprisingly persistent, and low application rates (i.e. high biological activity)

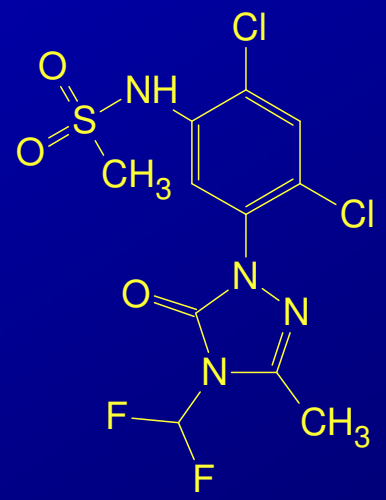


fluoxastrobin – fungicide *strobilurin*

FD – 97d
aerobic – 184d
0.20 kg ha^{-1}

imidacloprid – insecticide *neonicotinoid*

FD – 27-229d
aerobic – 997d
0.14 kg ha^{-1}



sulfentrazone – herbicide *neonicotinoid*

FD – 57-710d
aerobic – 81-541d
0.42 kg ha^{-1}

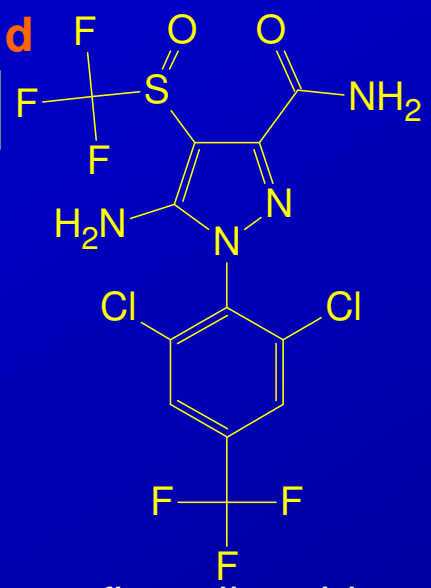
Fipronil and degradates

aerobic soil DT50s

Oncorhynchus mykiss LC50 (ug/L)

181d

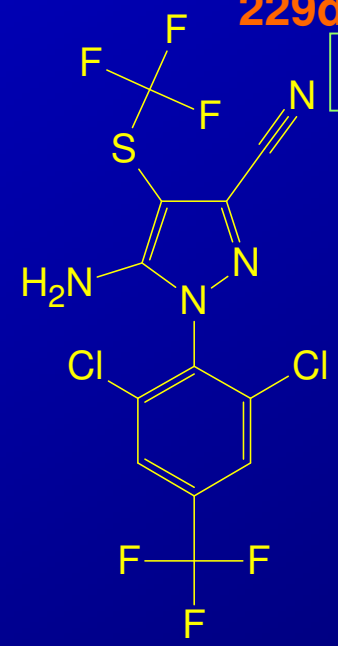
17



fipronil-amide

229d

0.030



fipronil-sulfide

0.039

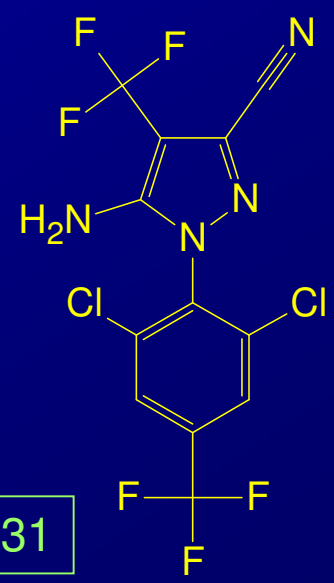
347d

fipronil-sulfone

142d

0.25

fipronil



0.031

fipronil-desulfinyl

QUESTIONS?