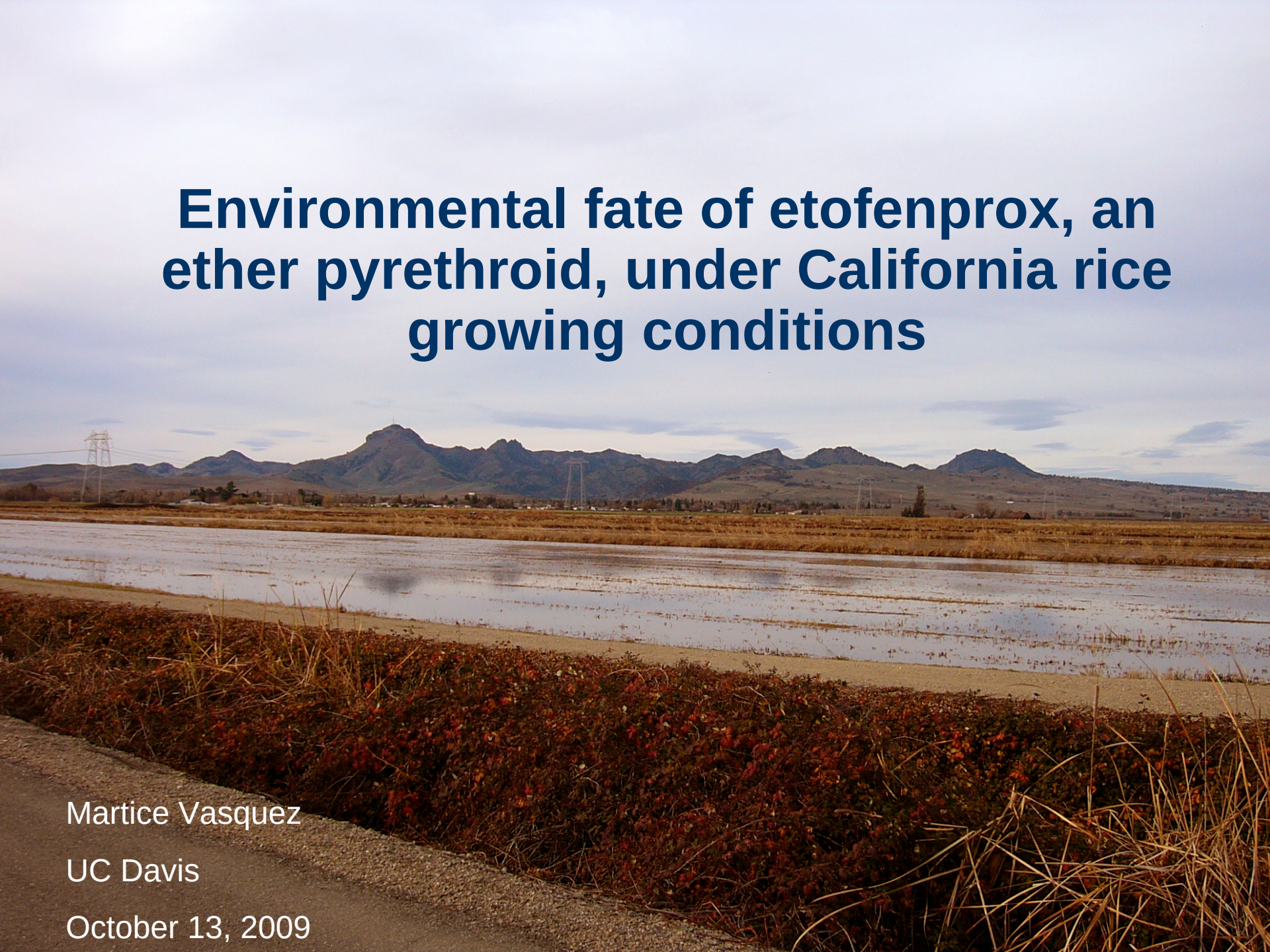
Environmental fate of etofenprox, an ether pyrethroid, under California rice growing conditions



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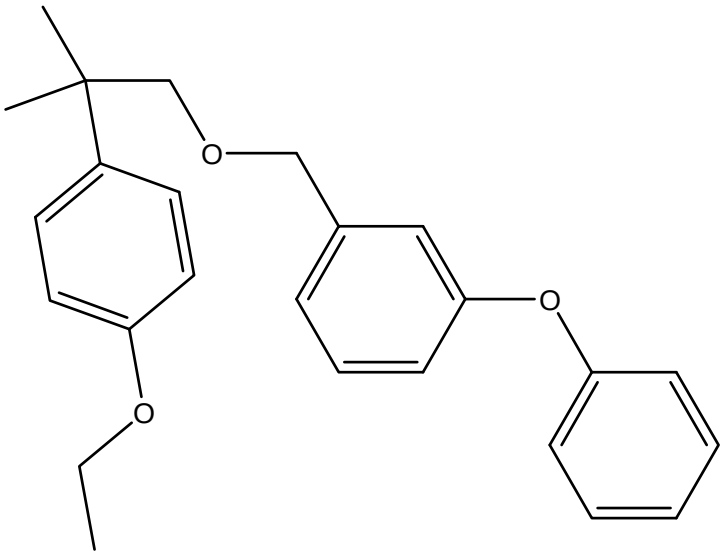
Structure of Presentation

- Etofenprox Introduction and Background
- Why a unique pyrethroid?
- Etofenprox in rice culture – environmental fate
- Partitioning between air, water and soil
- Microbial and photolytic degradation
- Conclusion

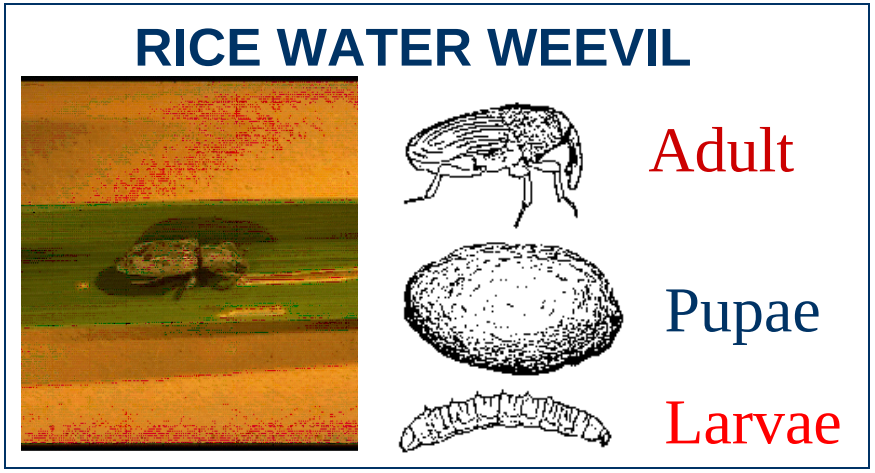
Etofenprox – A Synthetic Ether Pyrethroid

Physical/Chemical Properties:



- MW = 376 g/mol
- [1]VP = 8.3 x 10^{-7} Pa @ 25°C
- [1]C_{sat} = 22.5 ug/L @ 20°C
- [1]Log K_{ow} = 7.05
- [2]Log K_{oc} = 6.0-6.4

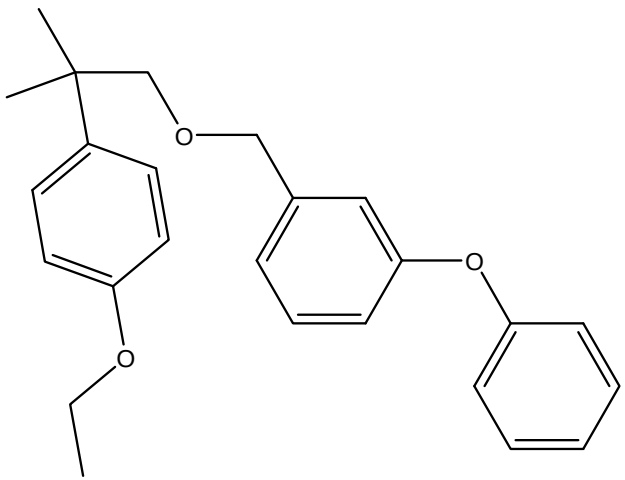
Etofenprox Target in Rice Culture



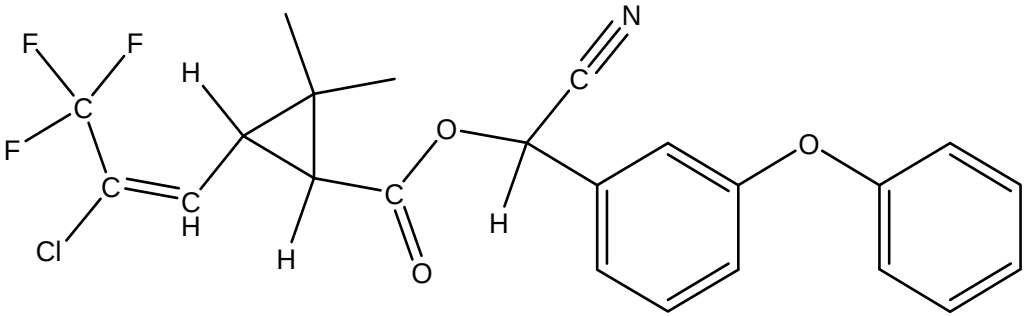
- Scarring of blades; destroy roots
- Targets Na Channel of insects
- Both adult and larvae susceptible

Etofenprox – A Unique Pyrethroid

- Ether not ester bond is central linkage
- Non-halogenated



ETOFENPROX



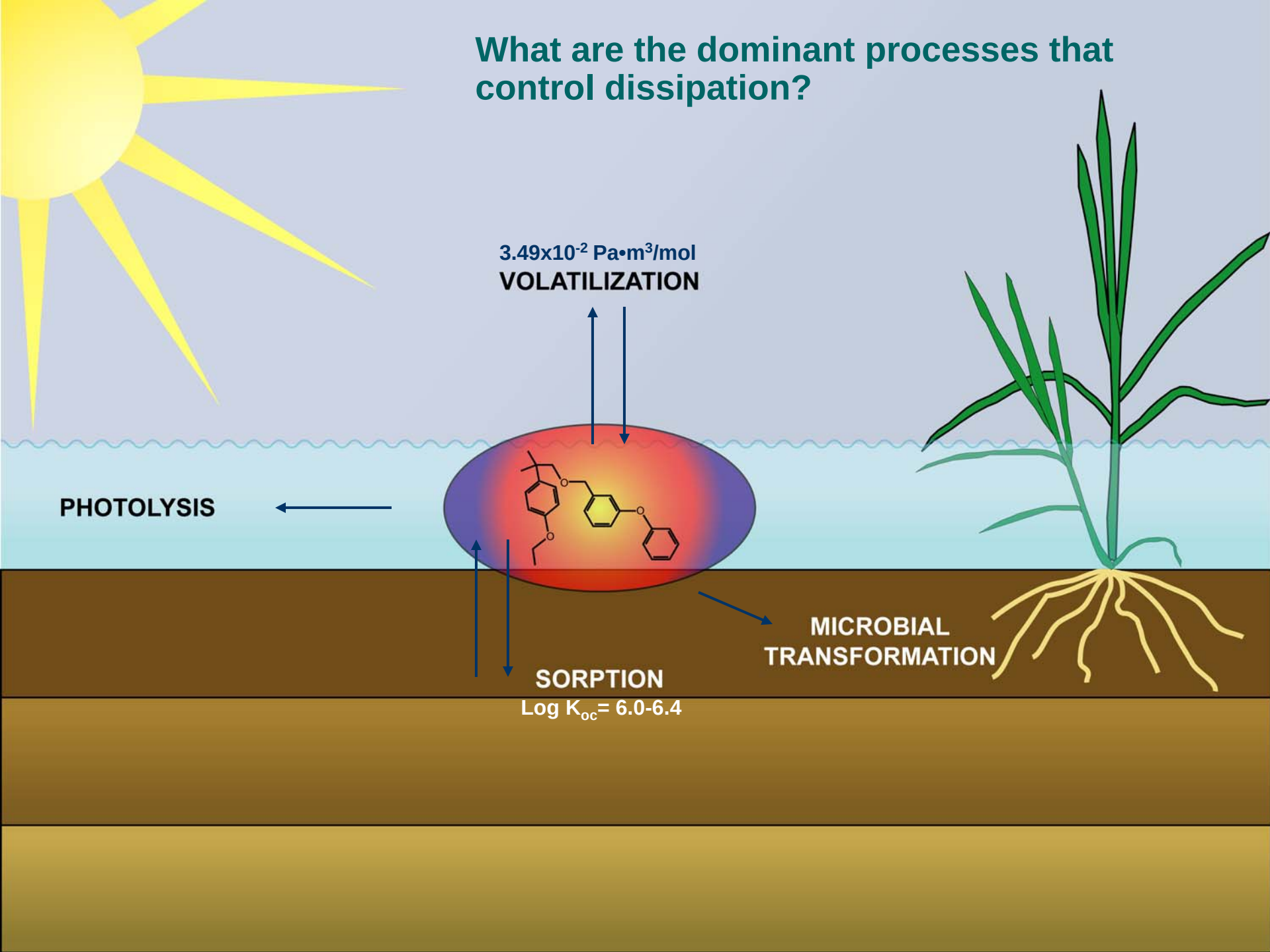
λ-CYHALOTHRIN[3]

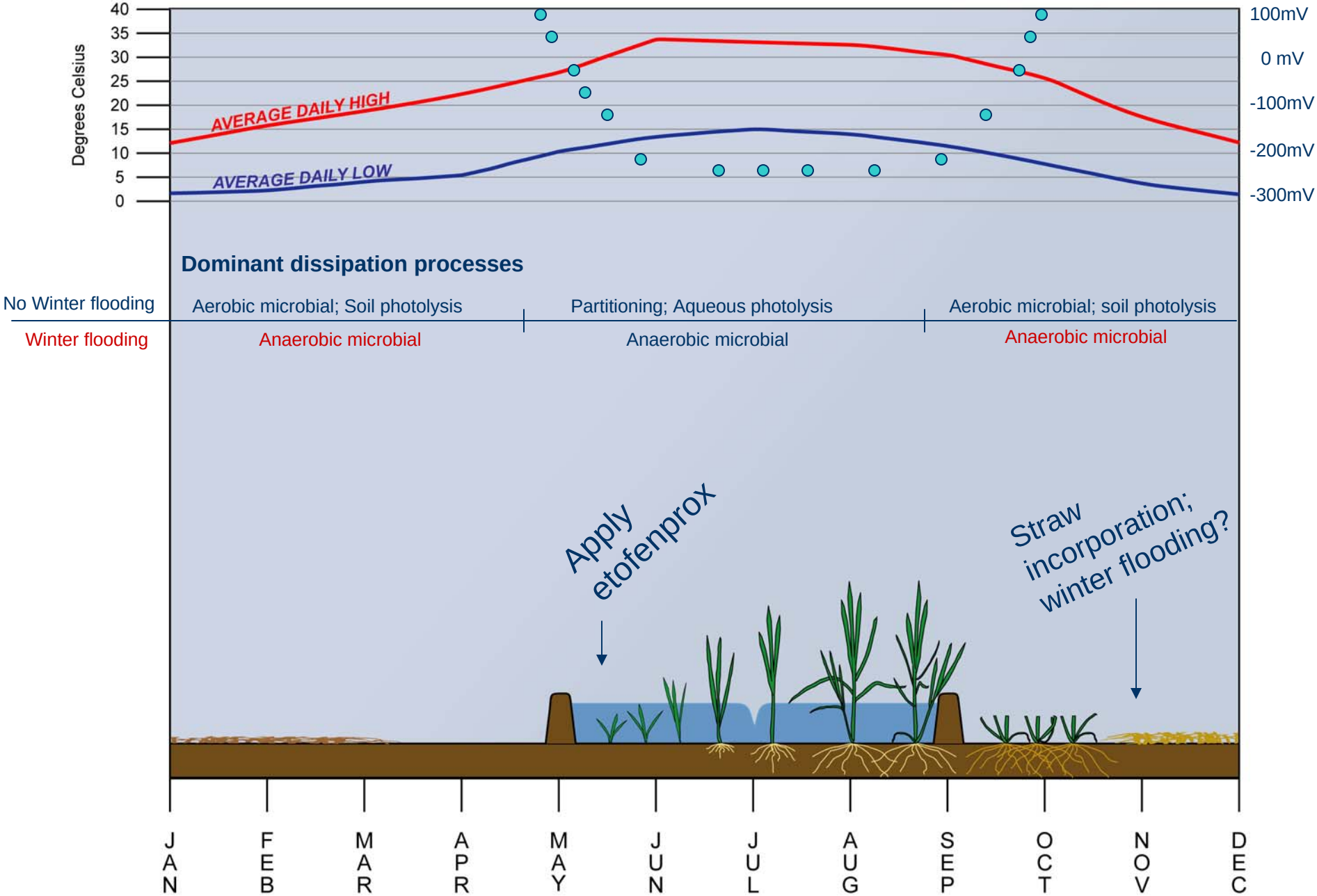
VP = 1 x 10^{-6} Pa @ 25°C
C_{sat} = 5 ug/L @ 20°C
Log Kow = 6.8
MW = 450 g/mol

Pyrethroid Issues

- Acute toxicity to aquatic species
  - Rainbow trout LC_{50} = 2.5-32 ppb eto[4]; 0.54ppb cyhalothrin[5], 5.4ppb permethrin[6]
  - Aquatic invertebrates vulnerable
- Toxicity events associated with pyrethroids in urban and agricultural waterways[7,8]
- Re-registration in California

What are the dominant processes that control dissipation?




Degrees Celsius
40
35
30
25
20
15
10
5
0
100mV
0 mV
-100mV
-200mV
-300mV
AVERAGE DAILY HIGH
AVERAGE DAILY LOW
Dominant dissipation processes
No Winter flooding
Winter flooding
Aerobic microbial; Soil photolysis
Anaerobic microbial
Partitioning; Aqueous photolysis
Anaerobic microbial
Aerobic microbial; soil photolysis
Anaerobic microbial
Apply etofenprox
Straw incorporation; winter flooding?
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC

Air-Water and Soil-Water Partitioning

Compare volatilization and soil sorption processes to determine respective contribution to overall dissipation of etofenprox under California rice growing conditions.

Hypothesis: Sorption will contribute greater to the overall dissipation of etofenprox from water than volatilization.

Air-Water Partitioning

Henry's constant:

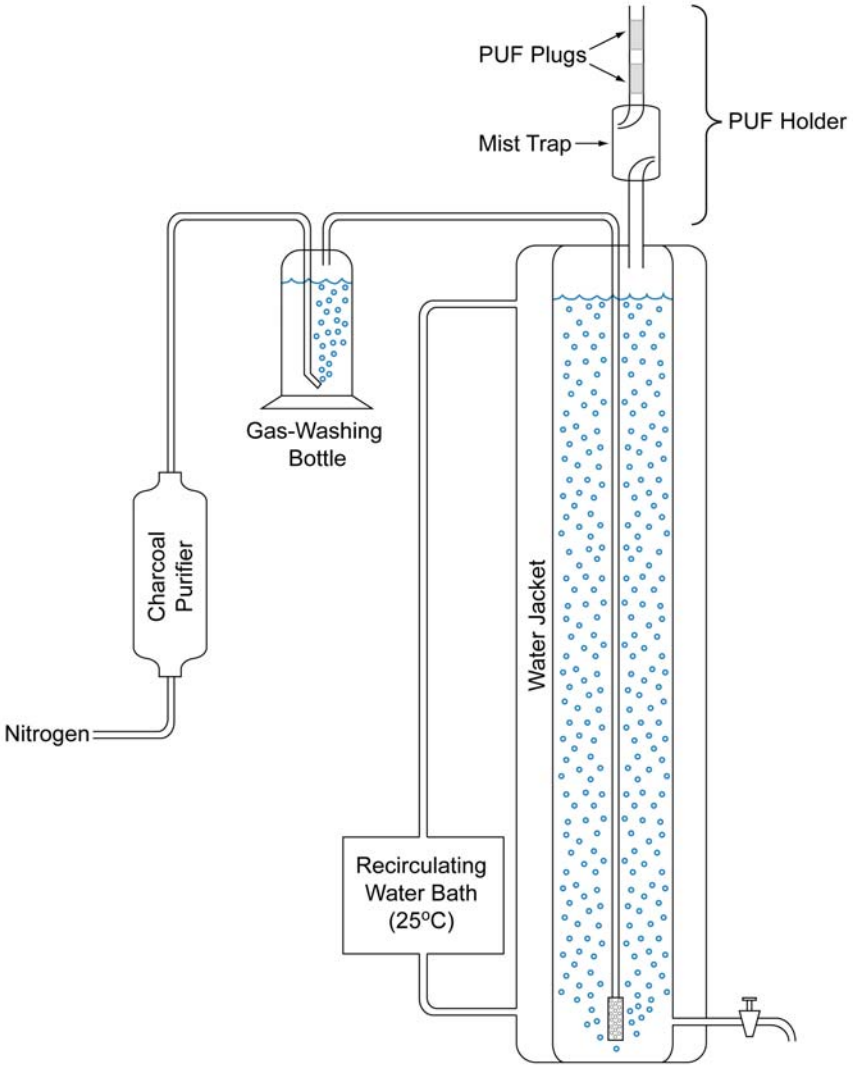
a measure of volatilization

$$K_H = p_g / C_w$$

P_g = vapor pressure

C_w = water solubility

(At defined Temp)



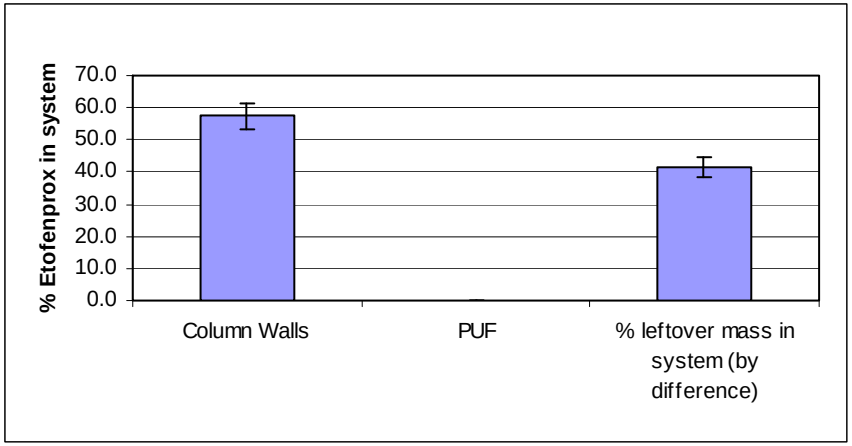
Gas stripping apparatus[9]

Air-Water Partitioning: Temperature effects

ETOFENPROX PHYSICAL/CHEMICAL PROPERTY	ESTIMATED VALUE	MANUFACTURER REPORTED VALUE
BOILING POINT	461°C	NA
VAPOR PRESSURE (Pa)		
5°C	4.11×10^{-06}	
15°C	1.85×10^{-05}	
20°C	3.75×10^{-05}	
25°C	7.43×10^{-05}	8.13×10^{-7} (exp)
35°C	2.71×10^{-04}	
40°C	4.99×10^{-04}	
AQUEOUS SOLUBILITY (mg/L)		
5°C	2.75×10^{-01}	
15°C	3.57×10^{-01}	
20°C	4.05×10^{-01}	2.25×10^{-02} (exp)
25°C	4.57×10^{-01}	
35°C	5.75×10^{-01}	
40°C	6.41×10^{-01}	
HENRY'S CONSTANT ($Pa \cdot m^3/mol$)		
5°C	5.62×10^{-03}	
15°C	1.94×10^{-02}	
20°C	3.49×10^{-02}	1.36×10^{-02}
25°C	1.22×10^{-02}	
35°C	1.77×10^{-01}	

Table from Vasquez, et al 2009.

Aqueous phase decrease due to sorption, not volatilization; temperature showed little effect



Mass distribution of etofenprox in apparatus during experimental determination of Henry's constant.

Soil-Water Partitioning of Etofenprox

Determine Soil-Water distribution coefficient (K_d) using representative rice soils at 25°C and 35°C.

$$K_d = C_s / C_w$$

C_s = equilibrium soil concentration

C_w = equilibrium aqueous concentration

Soil property	Soil (0-10 cm)	
	Princeton	Richvale
Straw removal practice	Burned	Incorporate
Sand (%)	14	23
Silt (%)	49	26
Clay (%)	37	51
Organic matter (%)	3.10	2.18
Total available nitrogen (μg/g)	0.175	0.142
Nitrate (NO_3) nitrogen (μg/g)	8.6	0.3
Exchangeable K (μg/g)	157	178
Exchangeable S (SO_4^{2-}; μg/g)	23	41
Phosphorus (μg/g)	6.2	2.4

Table from Vasquez, et al 2009.

Experimental Approach: Three Phase Model

5 – 15 ppb initial C_w

Soil (0.1g) + Aqueous Solution (125mL NH_4HCO_3 + NaN_3)

↓

Mix on Shaker in Dark @ °C

↓

Centrifuge

↓

Hexane extract aqueous phase; rinse bottles

↓

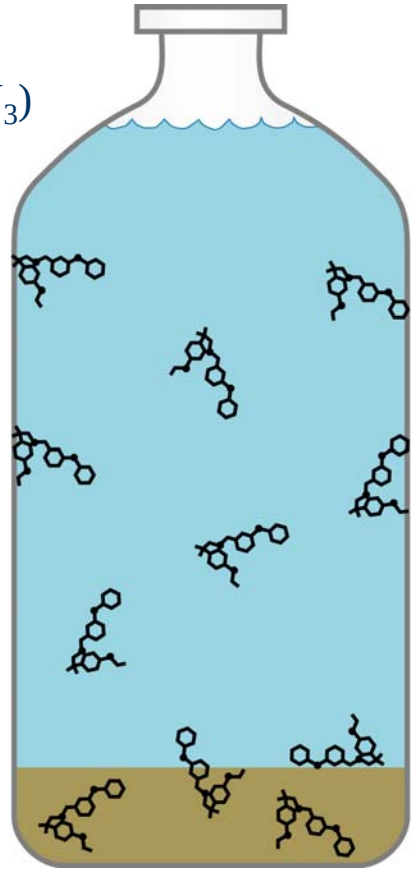
GC/MS SIM mode

↓

Calculate Mass Distribution

↓

Construct Isotherm

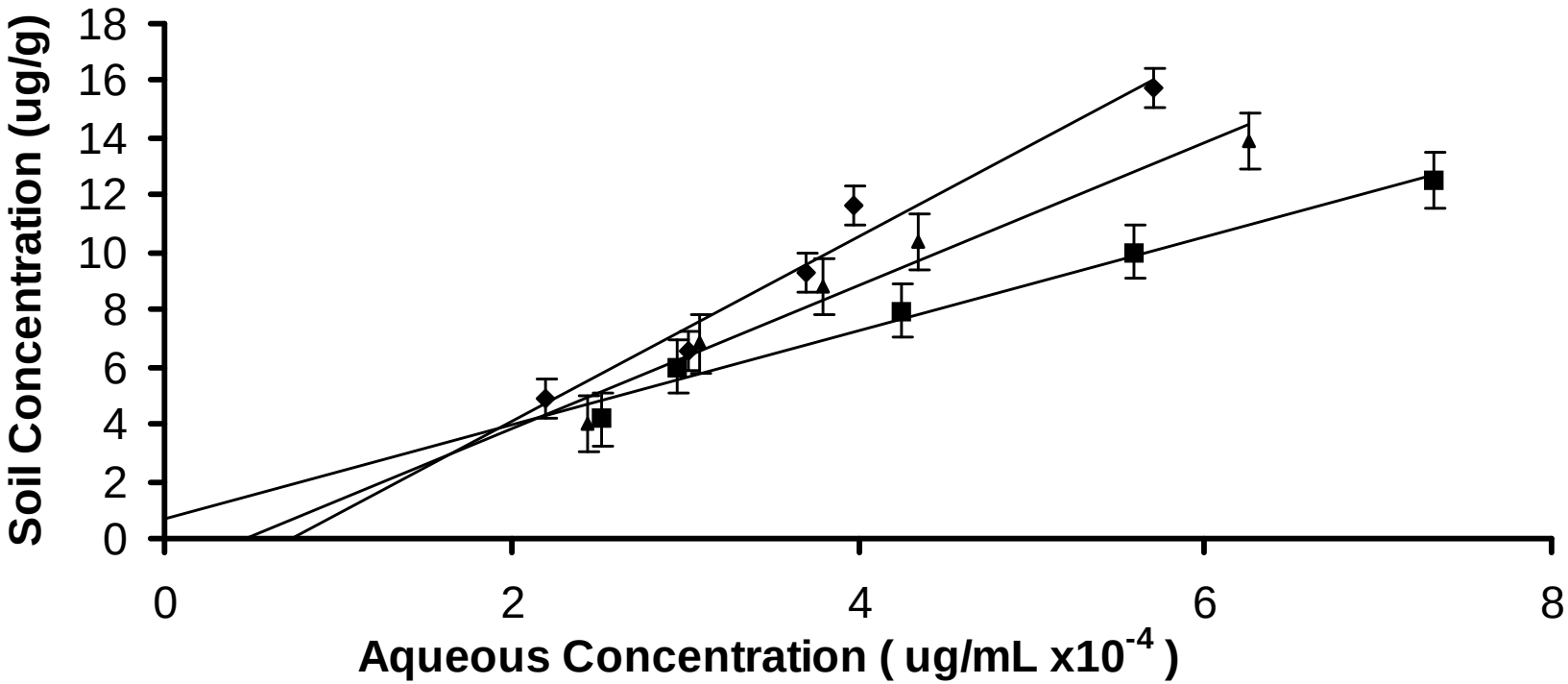


[Soil = Initial – (aqueous + bottle)]

Triplicate samples and control(no soil) at each conccentration level

(1st determine soil to solution ratio and time to equilibrium)

Soil-Water Partitioning: Temperature and soil type effects[2]



	Temp (°C)	Soil	*K*d (mL/g)	foc	*K*oc	log *K*oc (mL/g)	r^2
■	25	Princeton	16500	1.8	916667	6.0	0.9826
▲	35	Princeton	25074	1.8	1393000	6.1	0.9646
♦	25	Richvale	32304	1.3	2484923	6.4	0.9697

Microbial Degradation

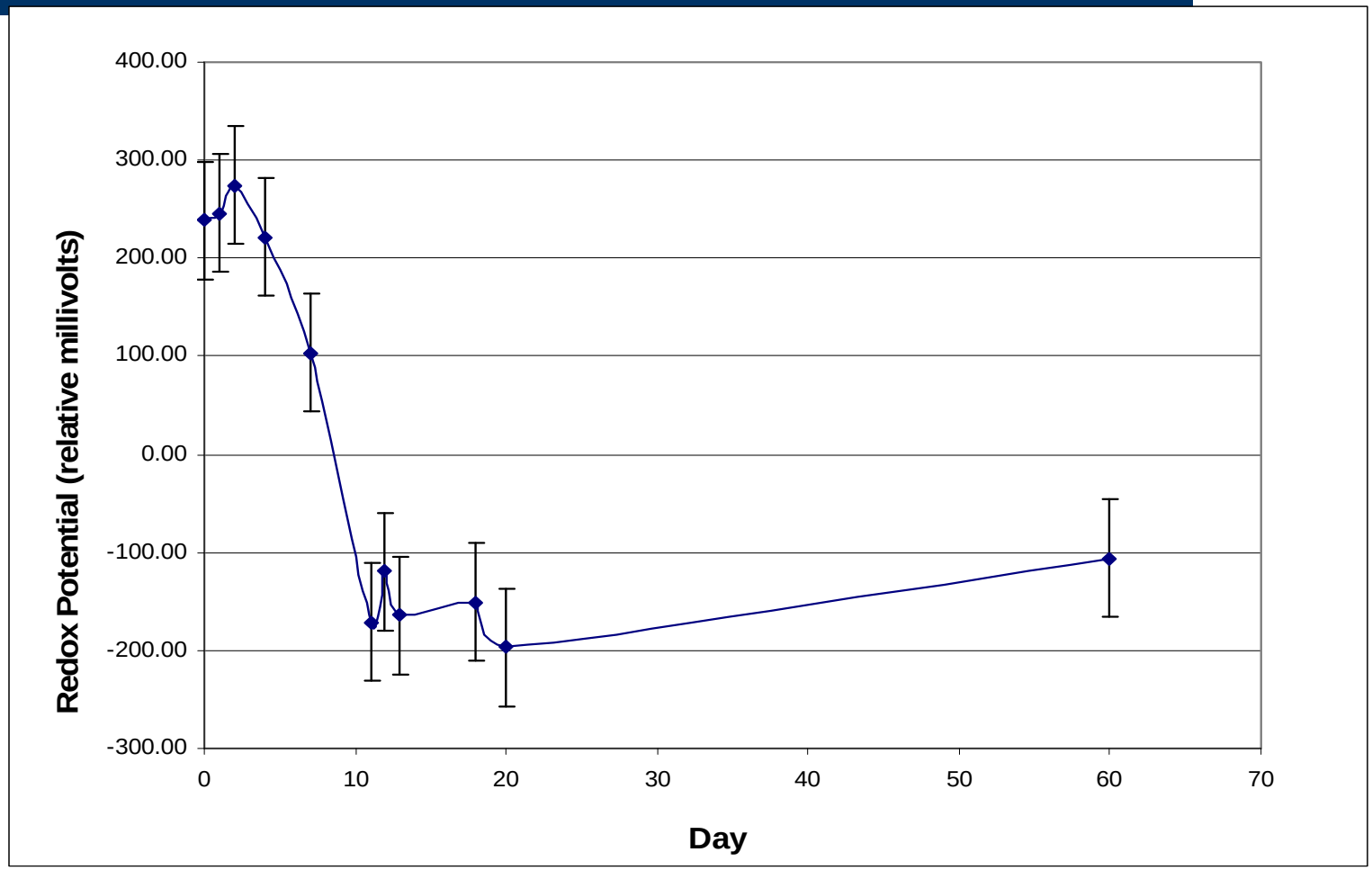
Compare anaerobic (flooded) and aerobic (drained) soil degradation to determine the effect of water regime on the overall dissipation of etofenprox in California rice culture.

Anaerobic Experimental Approach

- Soil Collected from Rice Experiment Station May 2008 – characterization by DANR lab
- Irrigation Water collected from campus outfall of Berryessa irrigation district; pH 7.5
- Soil: Aqueous Solution (50g:60mL)
- Application rate of 3 mg/kg (+150 ug etofenprox per bottle)
- Etofenprox added once system anaerobic (after 14 days of flooding)
- Incubate in Dark @ RT over 126 days
- Triplicate Samples and Controls t=0,1,3,7,14,21,28,35,42,56,126 day

Controls: (sterilized-autoclaved; azide/dark)

Redox potential of soil water system over time: anoxic conditions by day 10



Extraction

Add 60 mL acetone to system and shake at 135 rpm overnight

↓

Filter, blow off acetone, liquid/liquid extract water with hexane; dry hexane extract with Na_2SO_4

↓

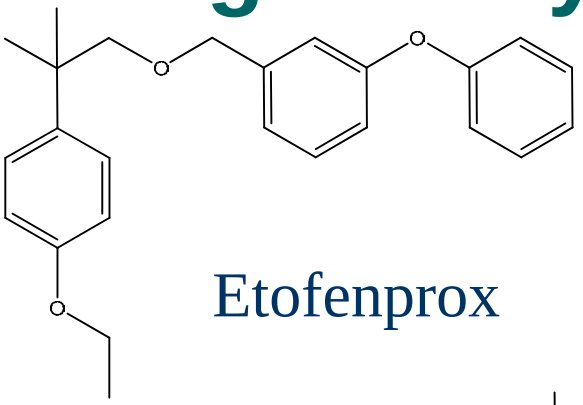
Blown down and dissolve in 40:60 ACN:H2O (~2mL); filter

↓

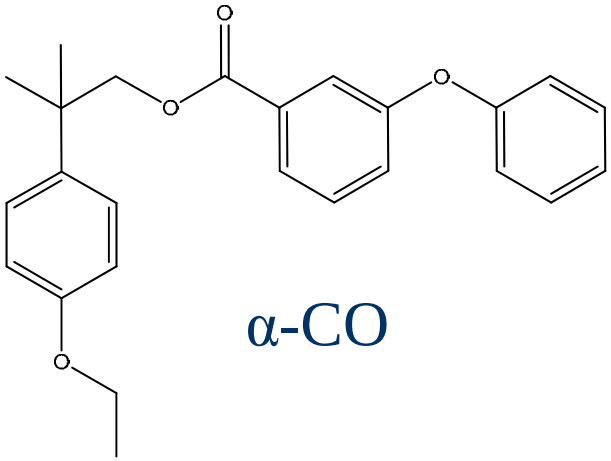
LC/MS-MS

Triplicate controls at each sampling interval: (sterilized/dark)

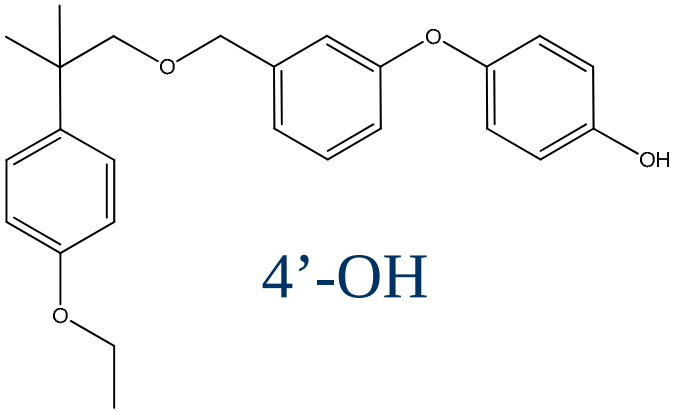
Products targeted by LC/MS/MS



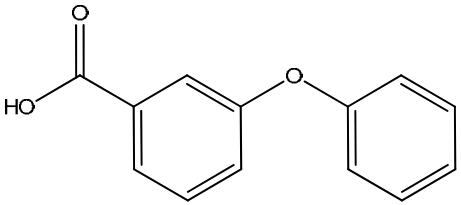
Etofenprox



α-CO

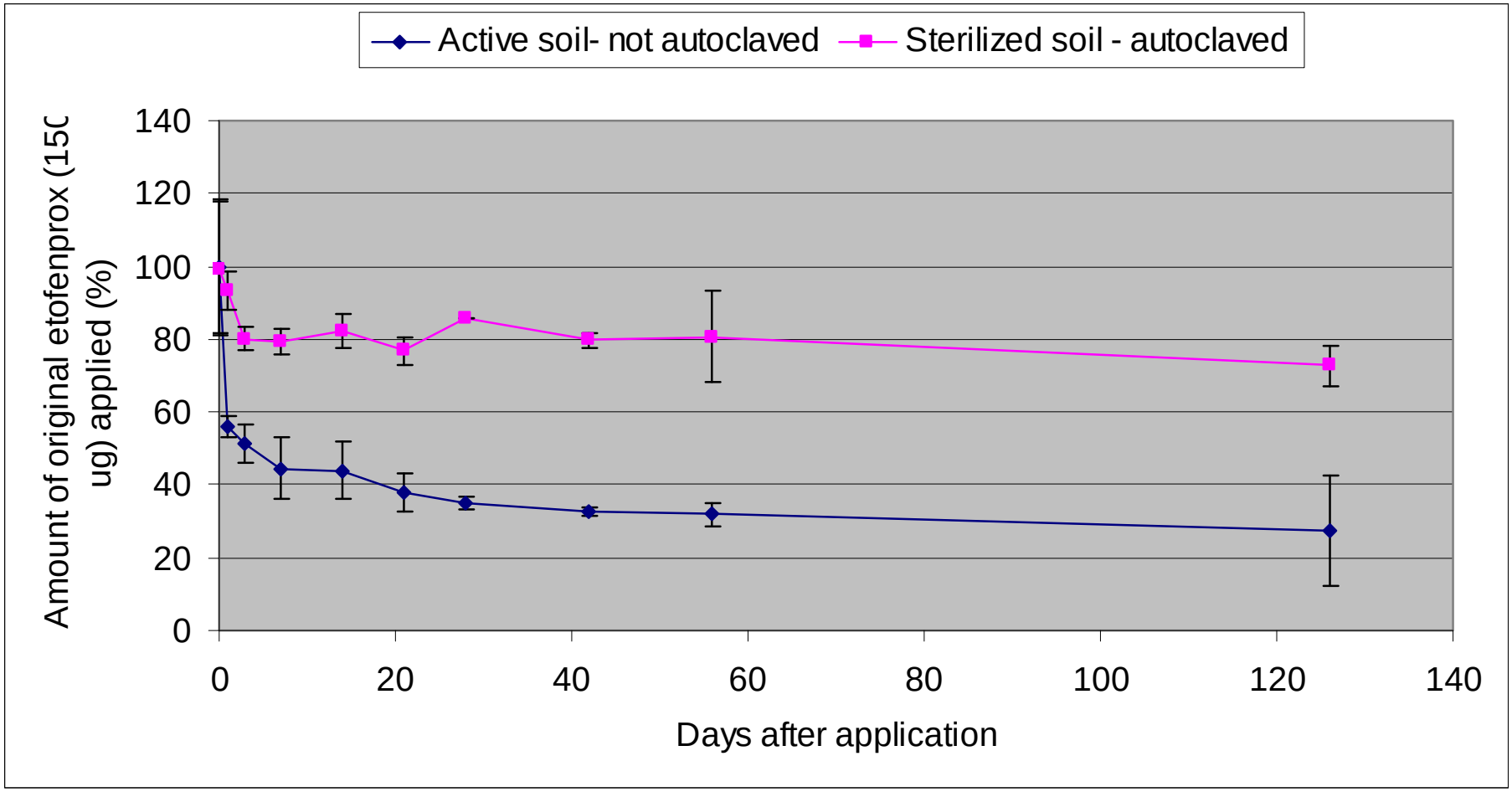


4’-OH



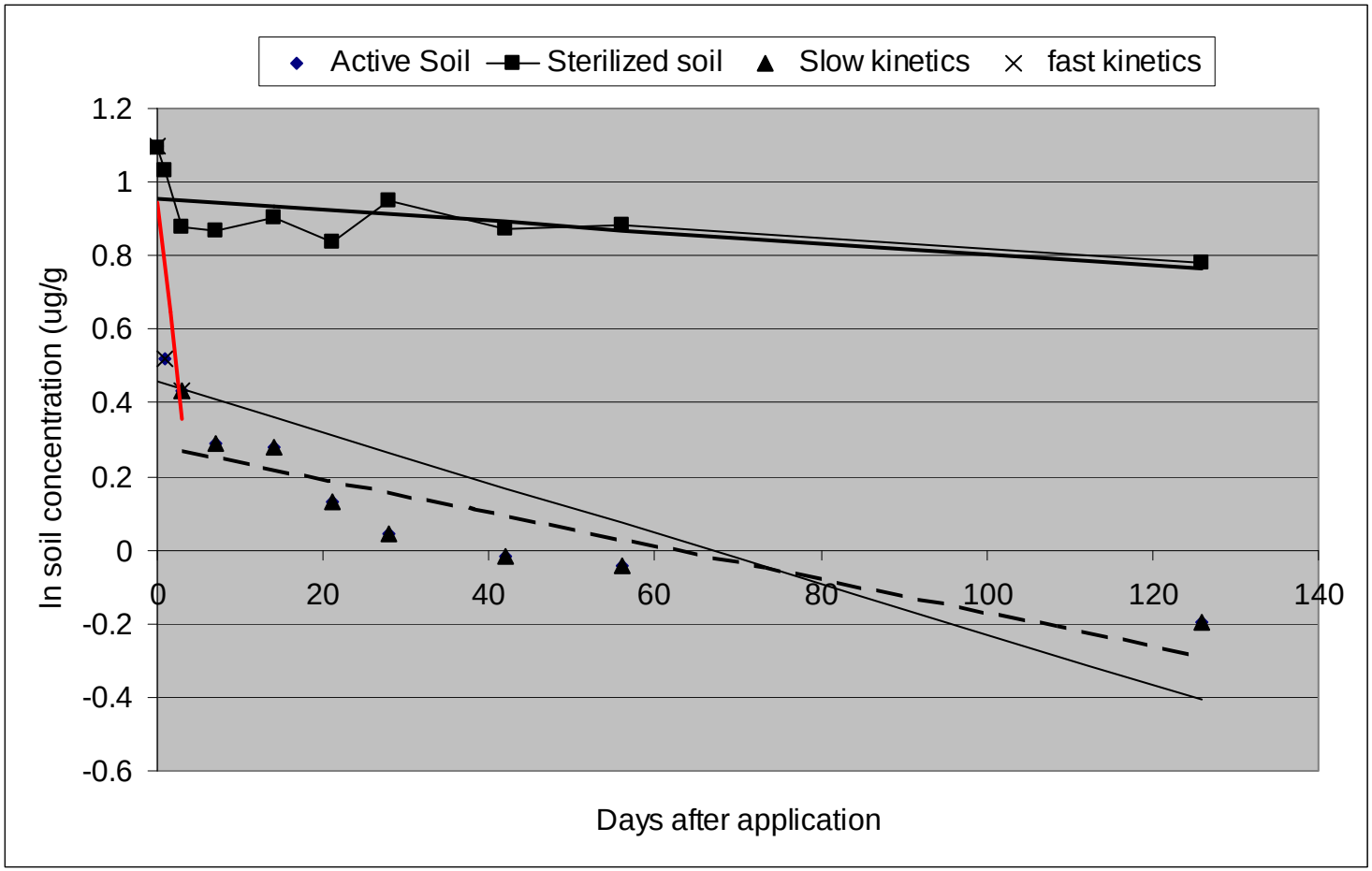
3-PBA

Dissipation of etofenprox in flooded rice soil



Points represent the mean ± SD (n = 3).

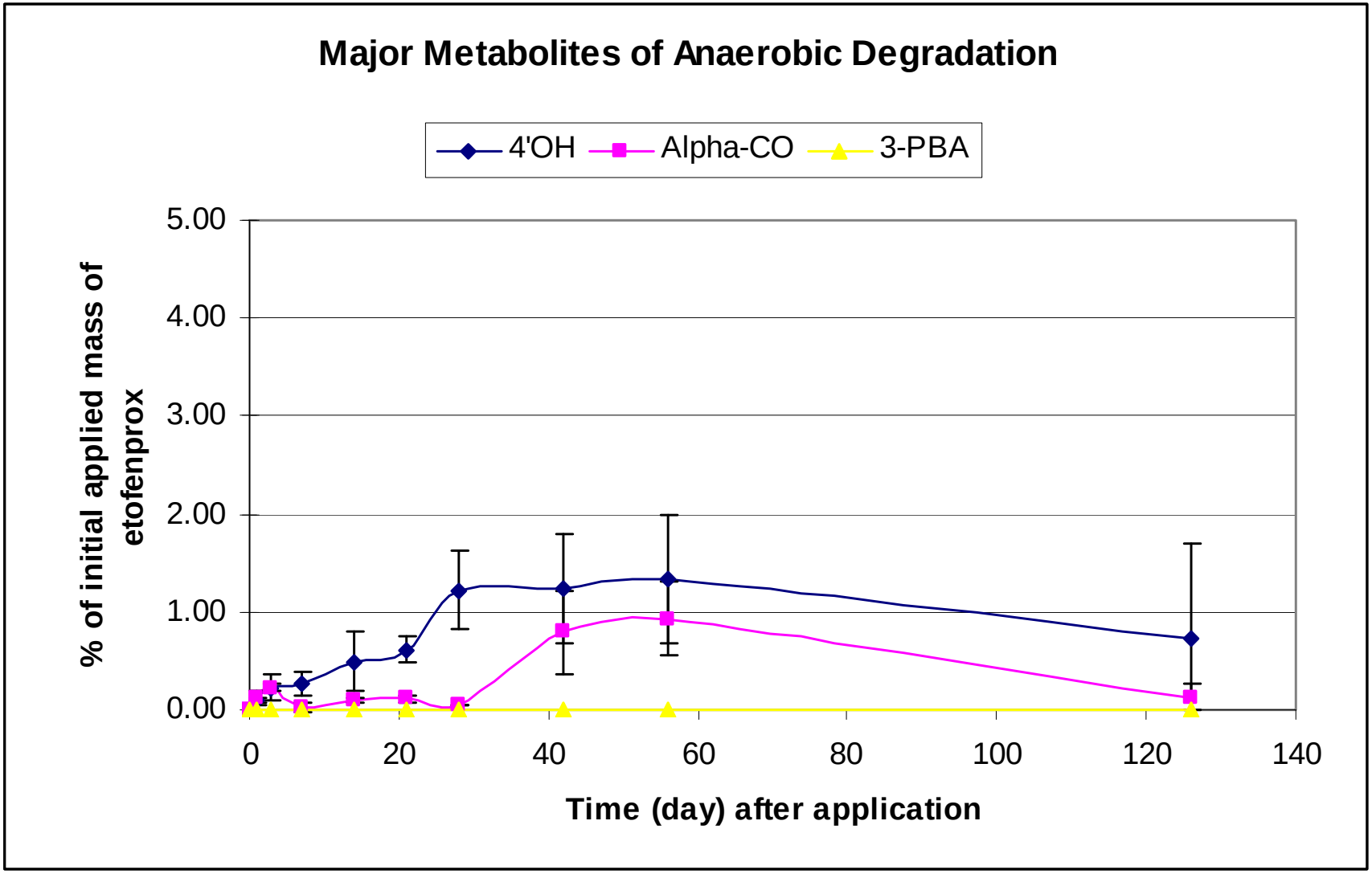
1st order kinetics of anaerobic rice soil microbial degradation of etofenprox

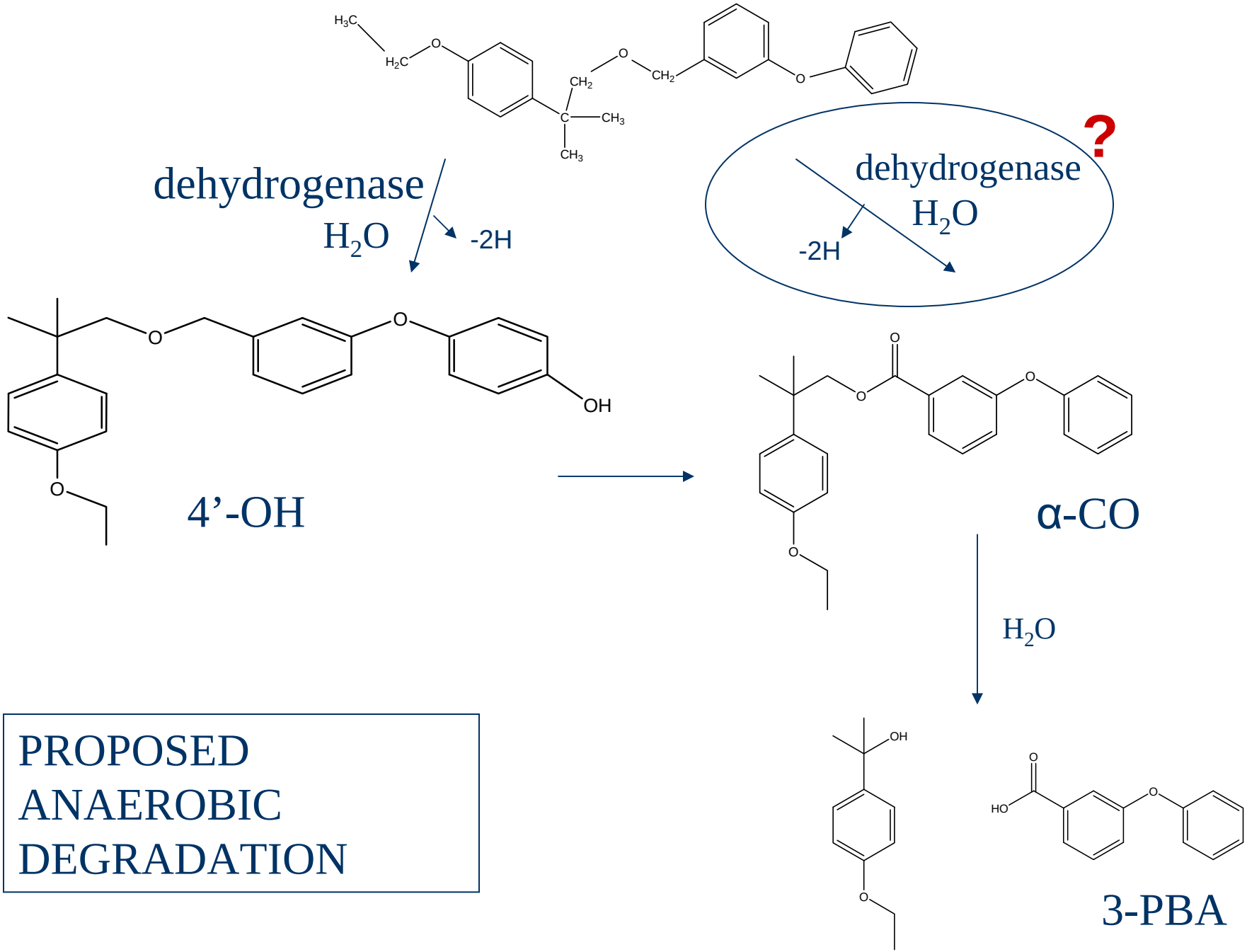


Model	Rate Constant (1/day)	t1/2 (days)	Correlation
fast kinetics	-0.1967	3.5	0.6873
slow kinetics k	-0.0045	154	0.7629
linear 1st order	-0.0069	100	0.5081
Control (linear)	-0.0023	462	0.3868

Mitsui half-life = 174 days (1st order; 0.9705)[1]

Anaerobic Metabolite Formation





PROPOSED ANAEROBIC DEGRADATION

Anaerobic Summary

- Dissipation rates and half-lives calculated
- 4’OH was major metabolite; alpha-CO produced
- Other unknowns in low abundance?
  - Didn’t detect 3-PBA
- Aerobic degradation experiments in progress
- Aerobic and Anaerobic Experiments at 40°

Photolysis

Compare aqueous and soil surface photolytic degradation to determine respective contribution to overall dissipation of etofenprox under California rice growing conditions.

Photolysis of etofenprox in literature

- Photolysis study[10] in mixture of 2:3 ACN:H2O
  - Not representative of environmental conditions
  - Solubility poses issues
- Etofenprox capable of photolytic transformation[10]

Concluding remarks

- Analytical Challenges
  - Extremely low water solubility
  - Significant sorption the glassware
- Offsite movement unlikely unless in bound state
- Preliminary microbial work suggests transformation possible by endemic microbes
- Kinetics are messy but residues detectable at 126 days after application

THANK YOU

References

1. Mitsui Chemicals, Inc. *Etofenprox Data Sheet MSDS # 62141E.* Tokyo, Japan (2005).
2. Vasquez, M; Gunasekara, A; Cahill, T; Tjeerdema, R. Partitioning of etofenprox under smulated Califonia rice growing conditions. (2009) *Pest Man Sci.*((www.interscience.wiley.com) DOI 10.1002/ps.1826.
3. Laskowski DA, Physical and Chemical Properties of Pyrethroids. (2002) *Rev. Environ. Contam. Toxicol*. 174**:**49-170
4. *Report of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment. World Health Organization*, Geneva, Switzerland, September *20-29*: 357-381 (1993).
5. Tomlin, C.D.S. (ed.). The Pesticide Manual - World Compendium. 10th ed. Surrey, UK: The British Crop Protection Council, 1994., p. 253.
6. Tomlin, C.D.S. (ed.). The Pesticide Manual - World Compendium. 10th ed. Surrey, UK: The British Crop Protection Council, 1994., p. 785*.*
7. Weston, et al. Aquatic Effects of Aerial Spraying for Mosquito Control over an Urban Area. (2006) *Env Sci Tech* 40:5817-5822
8. Weston, et al. Distribution and toxicity of sediment-associated pesticides in agriculture-dominated water bodies of California's Central Valley. (2004) *Env Sci Tech* 38:2752-9.
9. Lau FK, Charles MJ, Cahill TM. (2006) Evaluation of gas-stripping methods for the determination of Henry's law constants for polybrominated diphenyl ethers and polychlorinated biphenyls. *J. Chem. Eng. Data.* 51**:**871-878.
10. Class, T., Casida, J., Ruzo, L. (1989) Photochemistry of ethofenprox and three related pyrethroids with ether, alkane, and alkene central linkages. *Journal of Agricultural and Food Chemistry* 37: 216-222.