

# Aquatic Refugia: Relevance and Significance in Ecological Risk Assessment

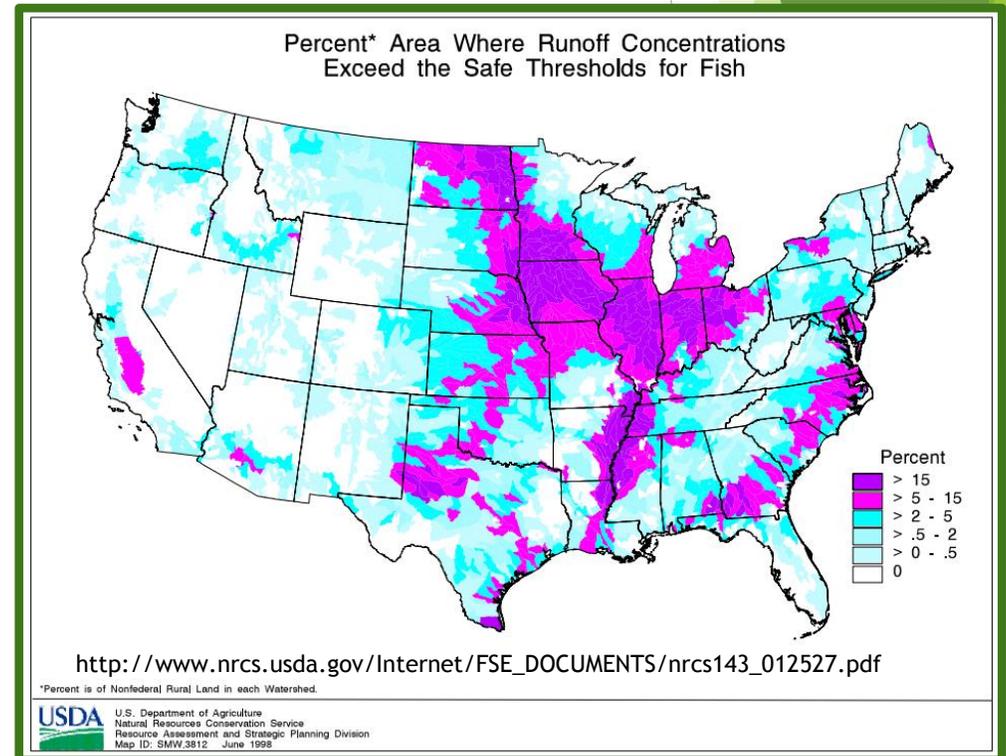
Kayla Campasino, Jeffrey Giddings, David Campana



**COMPLIANCE SERVICES INTERNATIONAL**

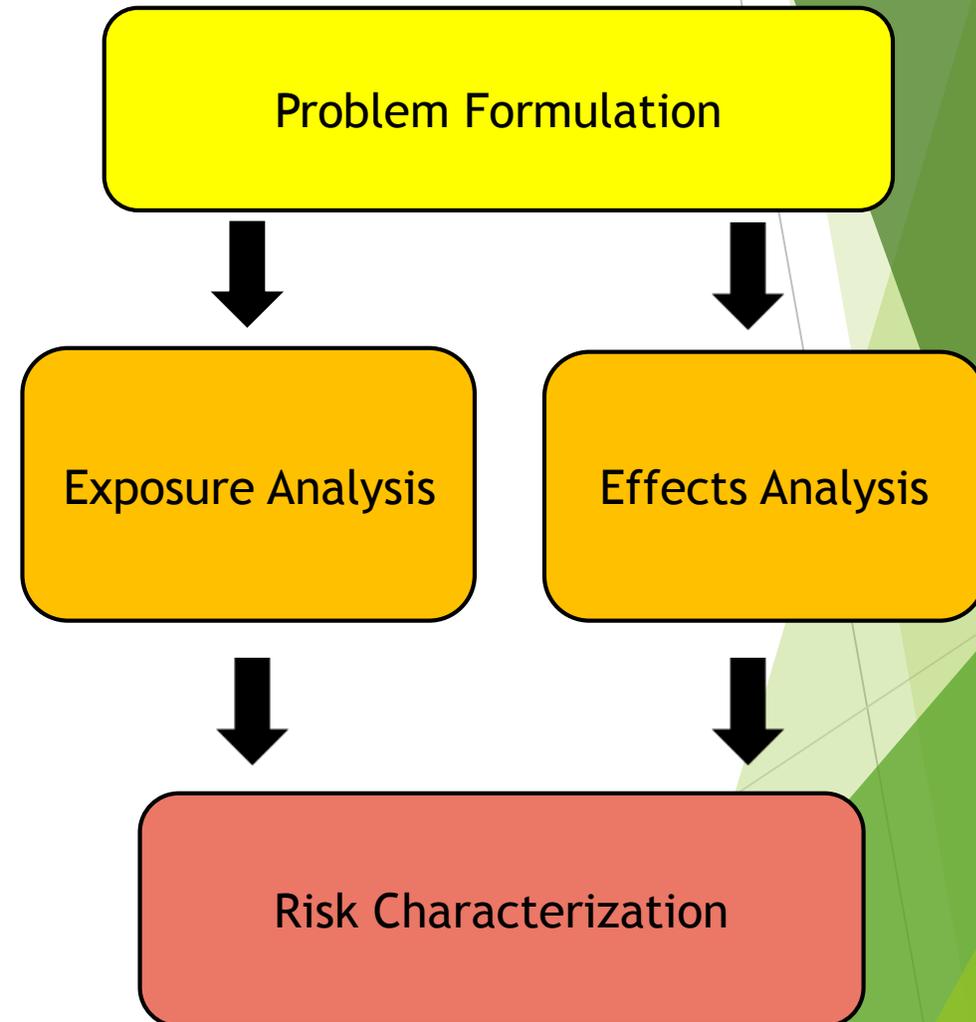
# Introduction

- ▶ Pesticides may enter aquatic environments via spray drift, runoff, erosion, etc.<sup>1, 2, 3</sup>
  - ▶ National Pesticide Loss database indicates runoff concentrations exceed toxicity thresholds for fish in numerous areas
  - ▶ Pyrethroids detected in 73% of sediment samples collected from water bodies adjacent to agricultural fields in CA Central Valley<sup>4</sup>
- ▶ Pyrethroids
  - ▶ Synthetic insecticides (bifenthrin, cypermethrin, permethrin, etc.)
  - ▶ Hydrophobic ( $\log K_{ow}$  6.40 - 7.48)<sup>5</sup>
  - ▶ Ecological risk assessment part of registration review process



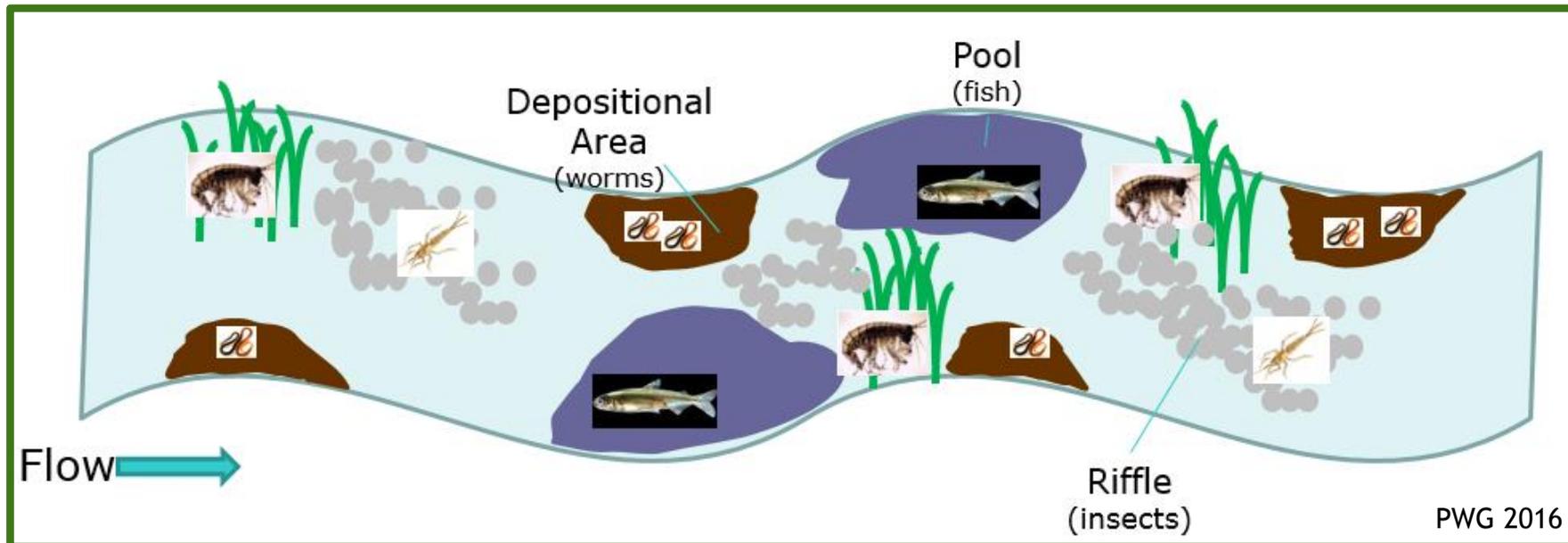
# Ecological Risk Assessment (ERA)

- ▶ Estimating the likelihood that adverse effects will occur from exposure
- ▶ EPA framework
  - ▶ Problem formulation: product use and assessment endpoints
  - ▶ Exposure analysis: modeling to estimate exposure concentrations
  - ▶ Effects analysis: derived from ecotoxicology studies
  - ▶ Risk characterization
- ▶ Current models assume a homogeneous distribution of the chemical within the water body



# Refugia

- ▶ Places or times where the negative effects of disturbance are lower than in affected areas or times<sup>6</sup>
- ▶ Variables that influence refugia
  - ▶ Environmental heterogeneity: vegetated sections, sediment organic carbon gradients
  - ▶ Physicochemical properties: hydrophobicity → sorption to organic matter
  - ▶ Environmental fate: degradation, transport



# Environmental heterogeneity creates spatial and temporal refugia

- ▶ Runoff simulation in a vegetated 650 m drainage ditch<sup>7</sup>
- ▶ Sorption of bifenthrin and lambda-cyhalothrin to aquatic macrophytes reduced downstream water concentrations
  - ▶ Aquatic vegetation acts as a sink
  - ▶ Rapid aqueous dissipation

Table 4. Estimated mass (g) of bifenthrin and lambda-cyhalothrin in the water, sediment, and plant compartments relative to each sampling time (\*total active ingredient amended to ditch at time zero). E-02, E-03, and E-04 represent  $10^{-2}$ ,  $10^{-3}$ , and  $10^{-4}$ , respectively, for significant digit purposes

Bifenthrin (g)					Lambda-cyhalothrin (g)				
Time	Water	Plants	Sediment	Total	Time	Water	Plants	Sediment	Total
0 h	—	—	—	*11.4	0 h	—	—	—	*5.70
3 h	5.78	6.29	3.85E-02	12.1	3 h	3.10	6.13	6.24E-02	9.29
12 h	0.718	7.22	3.30E-02	7.97	12 h	0.353	3.76	1.12E-02	4.13
24 h	0.191	4.03	1.13E-02	4.24	24 h	0.106	1.59	3.68E-03	1.70
7 d	0.134	1.93	6.31E-02	2.13	7 d	4.05E-02	6.74E-02	1.79E-02	0.126
14 d	4.48E-02	3.00	5.25E-02	3.10	14 d	6.90E-03	2.09E-01	129E-02	0.229
30 d	4.37E-03	0.199	1.93E-03	0.206	30 d	1.05E-03	3.41E-02	4.24E-02	7.75E-02
44 d	8.82E-04	4.89E-02	8.31E-04	5.07E-02	44 d	6.22E-03	9.10E-02	5.04E-02	0.148

# Environmental heterogeneity creates spatial refugia

- ▶ Pyrethroid runoff from nursery application into a sedimentation pond and 260 m drainage channel<sup>8</sup>
- ▶ Sorption of bifenthrin and permethrin to sediment resulted in increasing sediment concentrations with increasing distance from sedimentation pond
  - ▶ Offsite transport
  - ▶ Lower bioavailability in water column

**Table 2. Concentrations of bifenthrin and permethrin in sediments along a runoff path.**

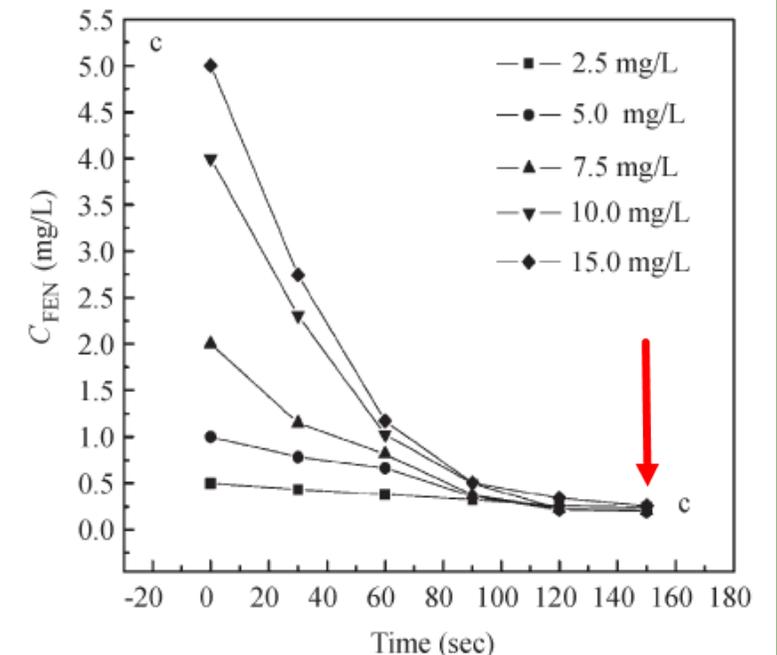
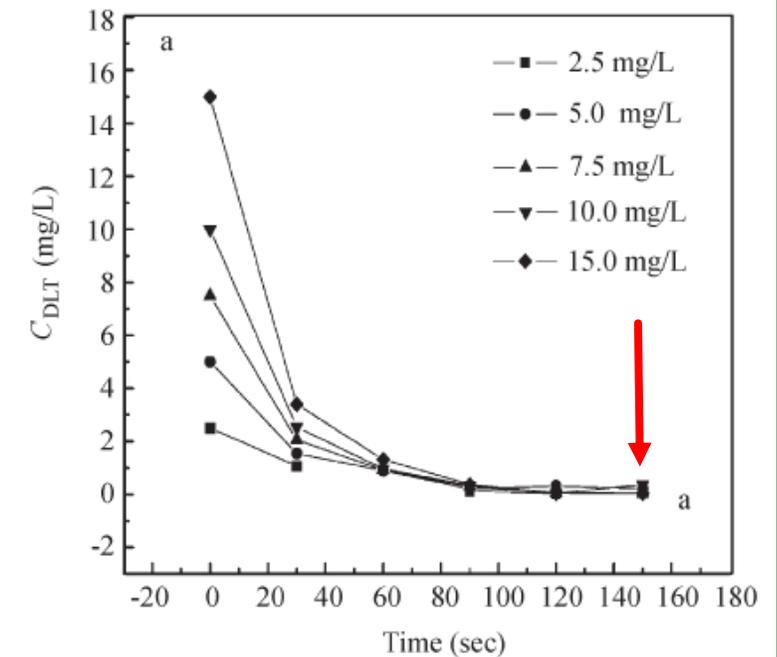
Distance from the sedimentation pond m	Concentration			OC <sup>†</sup> %	Clay
	Bifenthrin	<i>cis</i> -Permethrin	<i>trans</i> -Permethrin		
	mg kg <sup>-1</sup>				
0	0.33 ± 0.01 (1.0) <sup>‡</sup>	0.77 ± 0.07 (1.0)	0.20 ± 0.03 (1.0)	0.65 (1.0)	5 (1.0)
104	2.27 ± 0.09 (6.9)	1.10 ± 0.03 (1.4)	0.28 ± 0.05 (1.4)	2.35 (3.6)	5 (1.0)
145	10.64 ± 2.82 (32.2)	4.45 ± 0.03 (5.8)	0.92 ± 0.22 (4.6)	6.37 (9.8)	23 (4.6)
166	10.06 ± 0.18 (30.5)	2.73 ± 0.12 (3.5)	0.82 ± 0.09 (4.1)	5.80 (8.9)	19 (3.8)
210	8.47 ± 1.10 (25.7)	6.10 ± 0.26 (7.9)	1.26 ± 0.20 (6.3)	4.58 (7.0)	19 (3.8)

<sup>†</sup> Organic carbon content.

<sup>‡</sup> Numbers in parentheses are relative enrichment ratios.

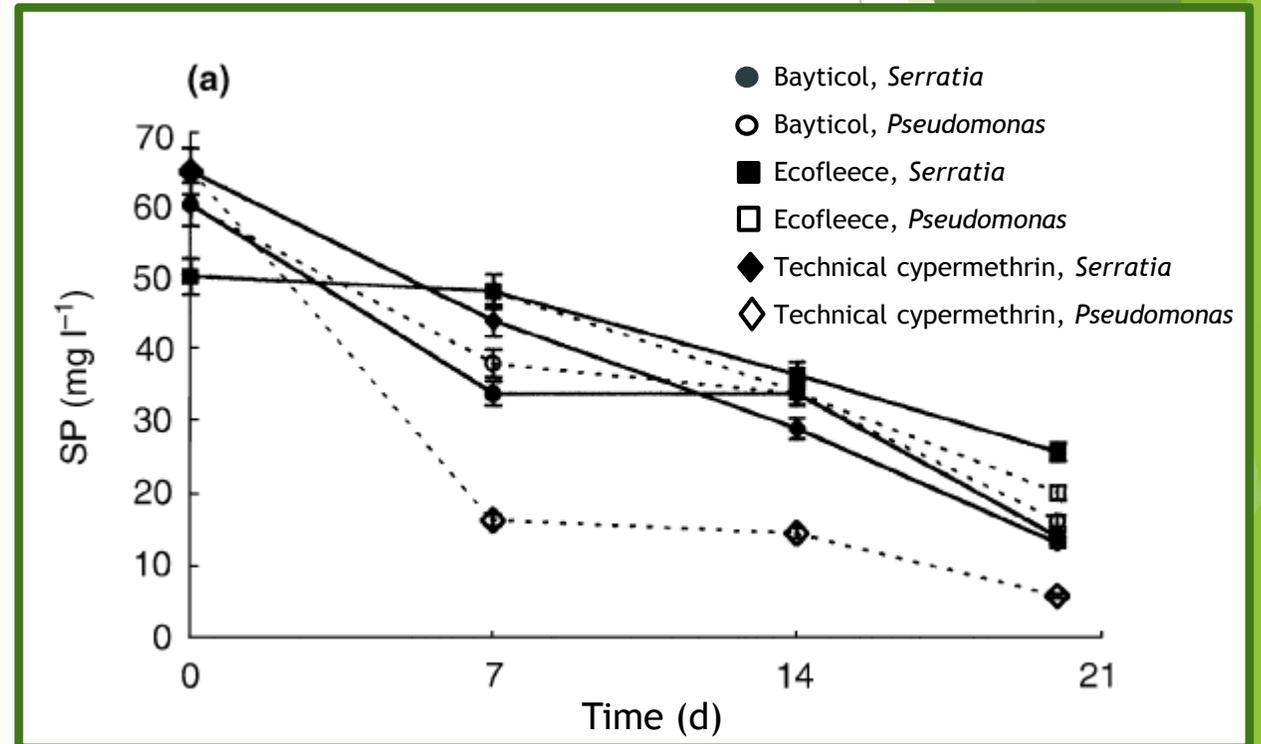
# Environmental processes create spatial and temporal refugia

- ▶ Degradation of deltamethrin and fenvalerate exposed to UV light<sup>9</sup>
- ▶ > 95% degradation after 160 seconds
- ▶ Photoproducts (3-phenoxy benzaldehyde and 3-phenoxybenzoic acid) suggest photo-oxidation is the primary reaction
- ▶ Limited light penetration in water body → more rapid degradation at water surface



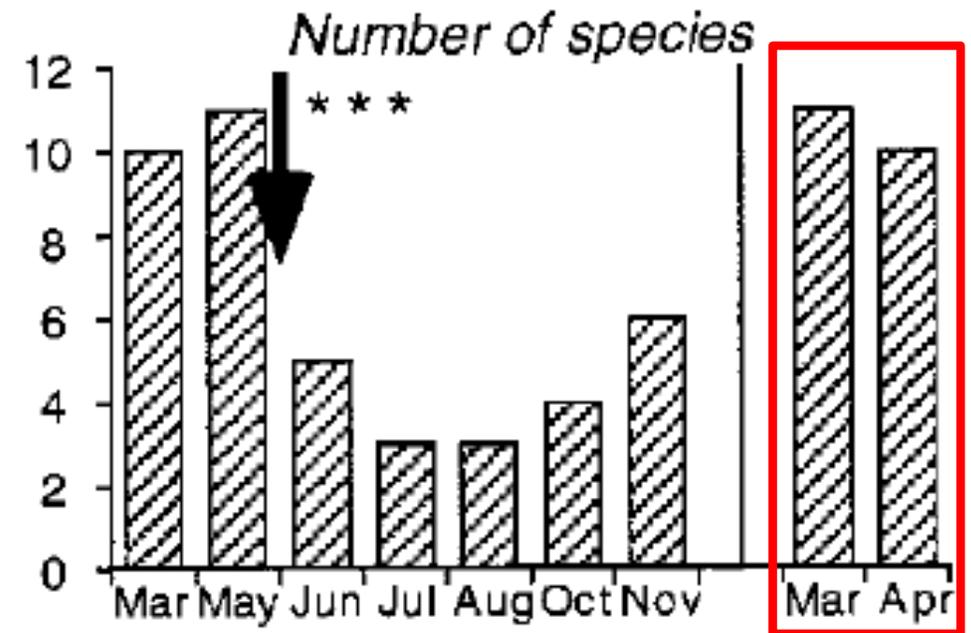
# Environmental processes create spatial and temporal refugia

- ▶ Microorganisms (*Pseudomonas* and *Serratia* spp.) were cultured with cypermethrin or flumethrin<sup>10</sup>
- ▶  $\geq 50\%$  of the pyrethroids were degraded after 20 days
- ▶ Average pyrethroid concentration in cultures after 20 days
  - ▶ With microorganisms:  $\sim 15\text{mg/L}$
  - ▶ Without microorganisms:  $\sim 34\text{ mg/L}$
- ▶ Pyrethroid degradation may be more rapid in sediments harboring abundant microbial communities compared to environments with less microbial biodiversity

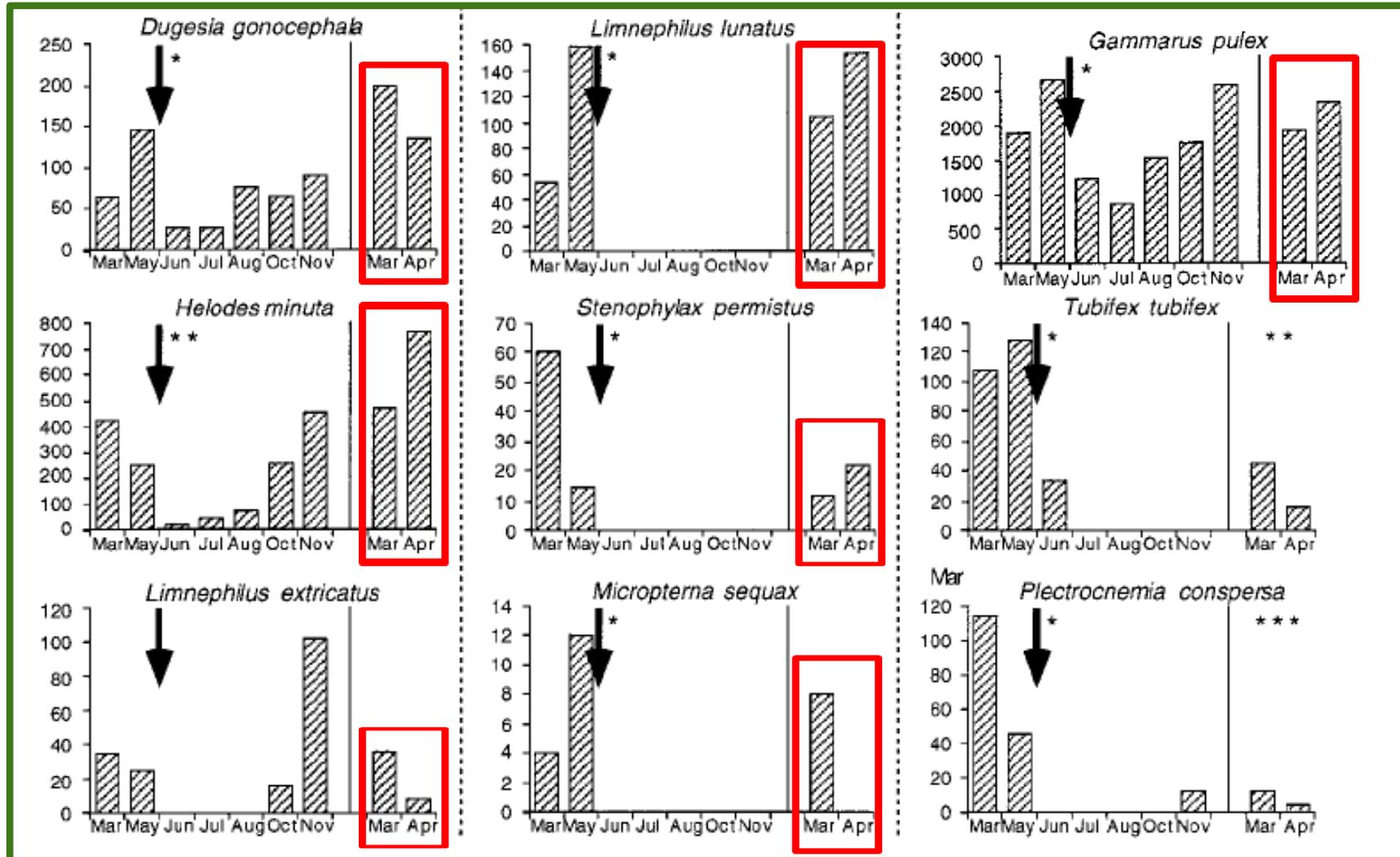


# Habitat refugia contribute to ecosystem recovery after pesticide contamination

- ▶ Rainfall-induced parathion-ethyl and fenvalerate runoff into a headwater stream on agricultural land<sup>11</sup>
- ▶ Eight out of 11 macroinvertebrate species eliminated after three high contamination runoff events
- ▶ 9 out of 11 populations recovered within 11 months despite no observed in stream emergence
- ▶ No observed in stream emergence; uncontaminated stream located 500 m from study site
- ▶ Population recovery likely due to recolonization from less affected sites

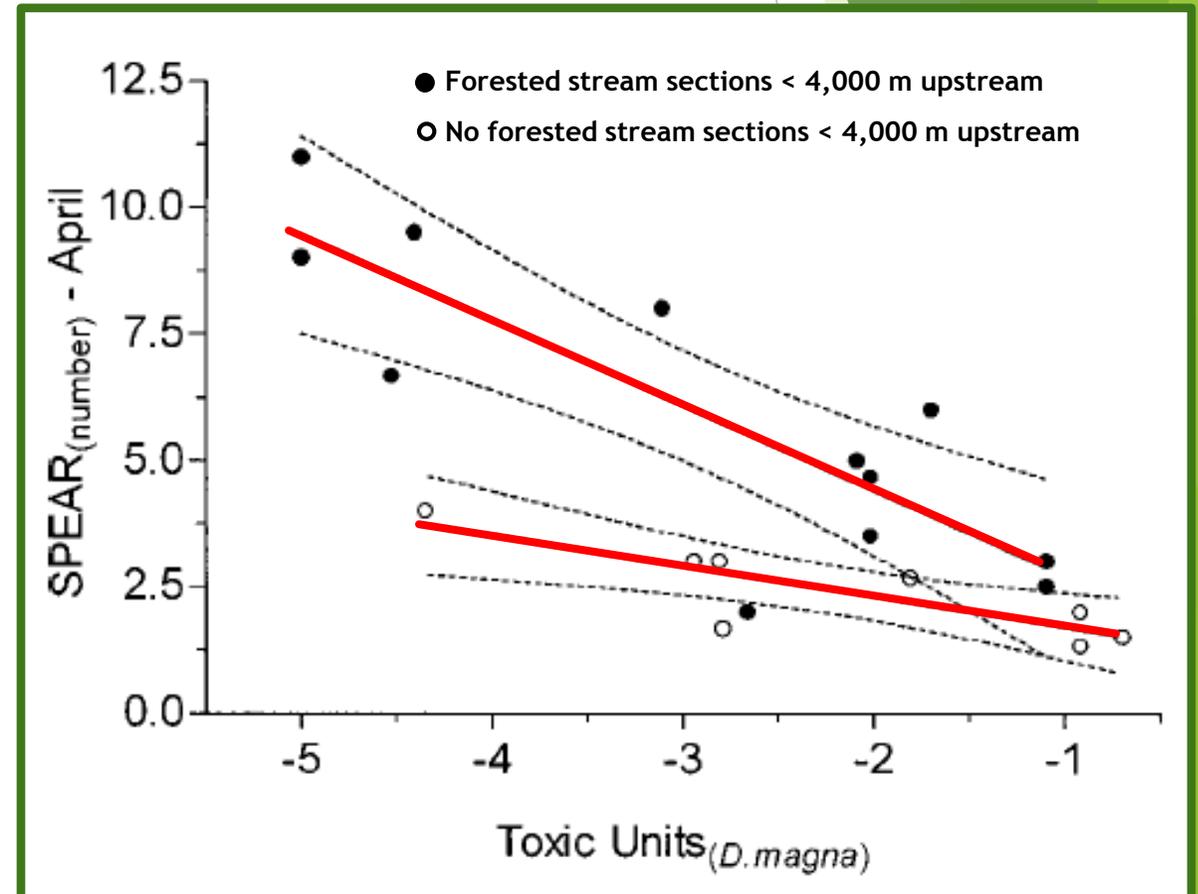


# Habitat refugia contribute to ecosystem recovery after pesticide contamination



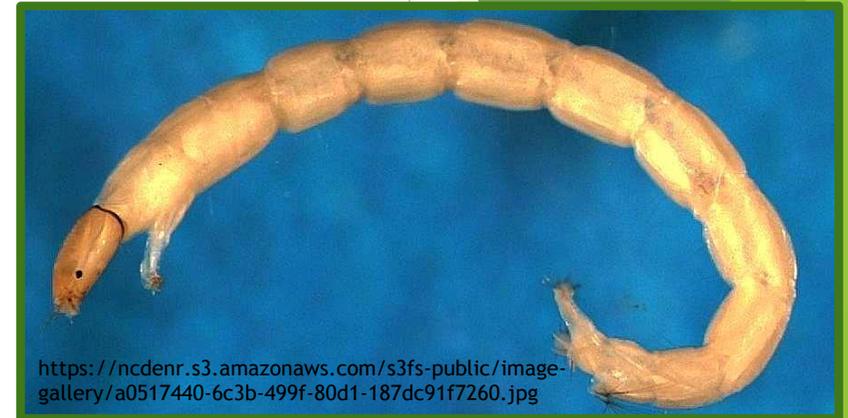
# Habitat refugia contribute to ecosystem recovery after pesticide contamination

- ▶ Macroinvertebrate abundance measured in streams subjected to agricultural runoff<sup>12</sup>
- ▶ SPEAR = Species At Risk
  - ▶ Sensitivity to pesticides
  - ▶ Life history traits influencing recovery
- ▶ Ten months after the peak pesticide concentrations, SPEAR were more abundant in affected stream sites when forested sections were less than 4,000 m from study sites and greater than 200 m in length
- ▶ Upstream forested sections allowed in-stream recolonization



# Effect of refugia on aquatic recovery after exposure to pesticides may vary with species

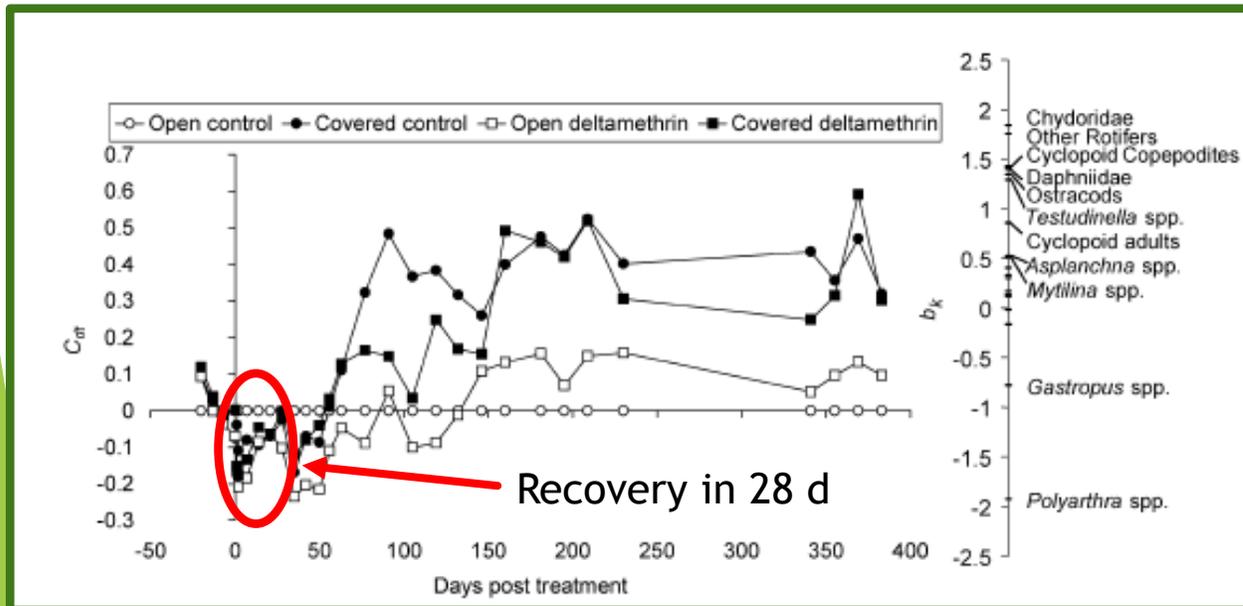
- ▶ Invertebrate recovery in covered vs. open pond mesocosms after deltamethrin treatment<sup>13, 14</sup>
- ▶ Caquet et al. (2007)
  - ▶ Open mesocosms → faster benthic macroinvertebrate recovery
  - ▶ Aerial recolonization probably had a significant influence on recovery
- ▶ Hanson et al. (2007)
  - ▶ Closed mesocosms → faster zooplankton recovery
  - ▶ Recovery likely due to sediment egg bank and predation release
- ▶ Internal vs. external recovery mechanisms in different species groups



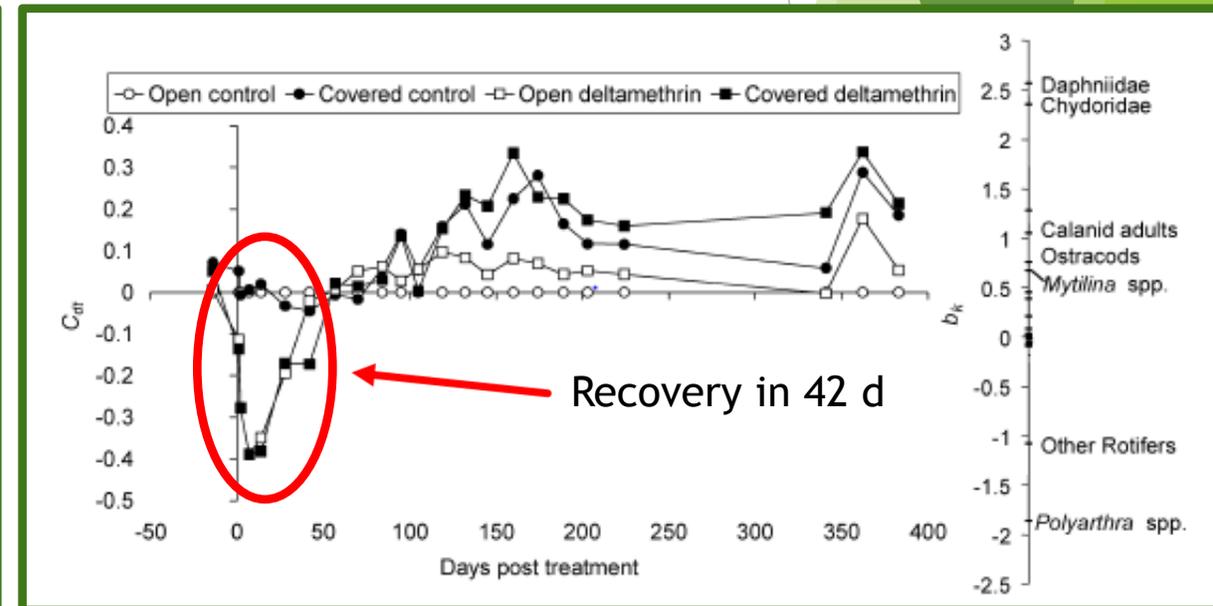
# Effect of refugia on aquatic recovery after exposure to pesticides may vary with species

- ▶ Benthic vs. water column zooplankton recovery in covered vs. open pond mesocosms after deltamethrin treatment<sup>14</sup>
- ▶ Recovery of benthic organisms was slower than recovery of organisms found in the water column
- ▶ Different species groups utilize refugia differently with a water body

Water column

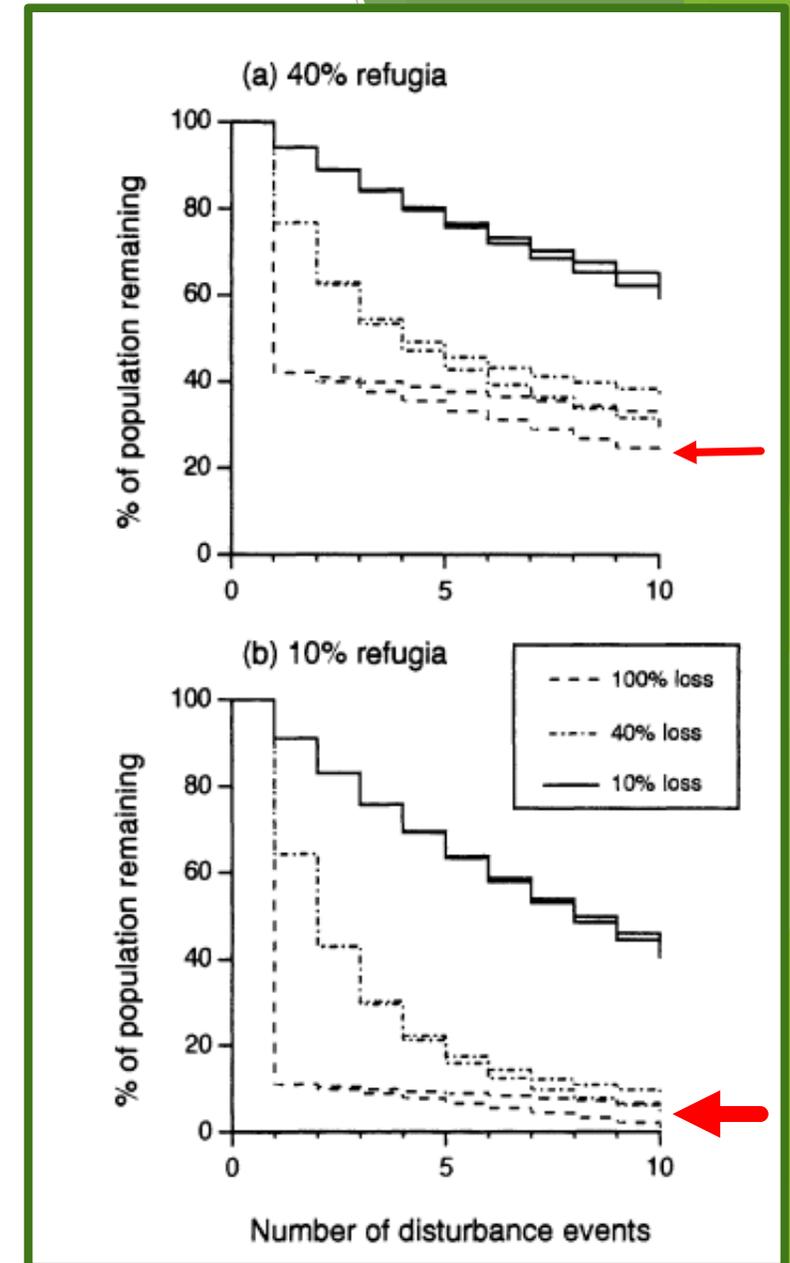


Sediment surface



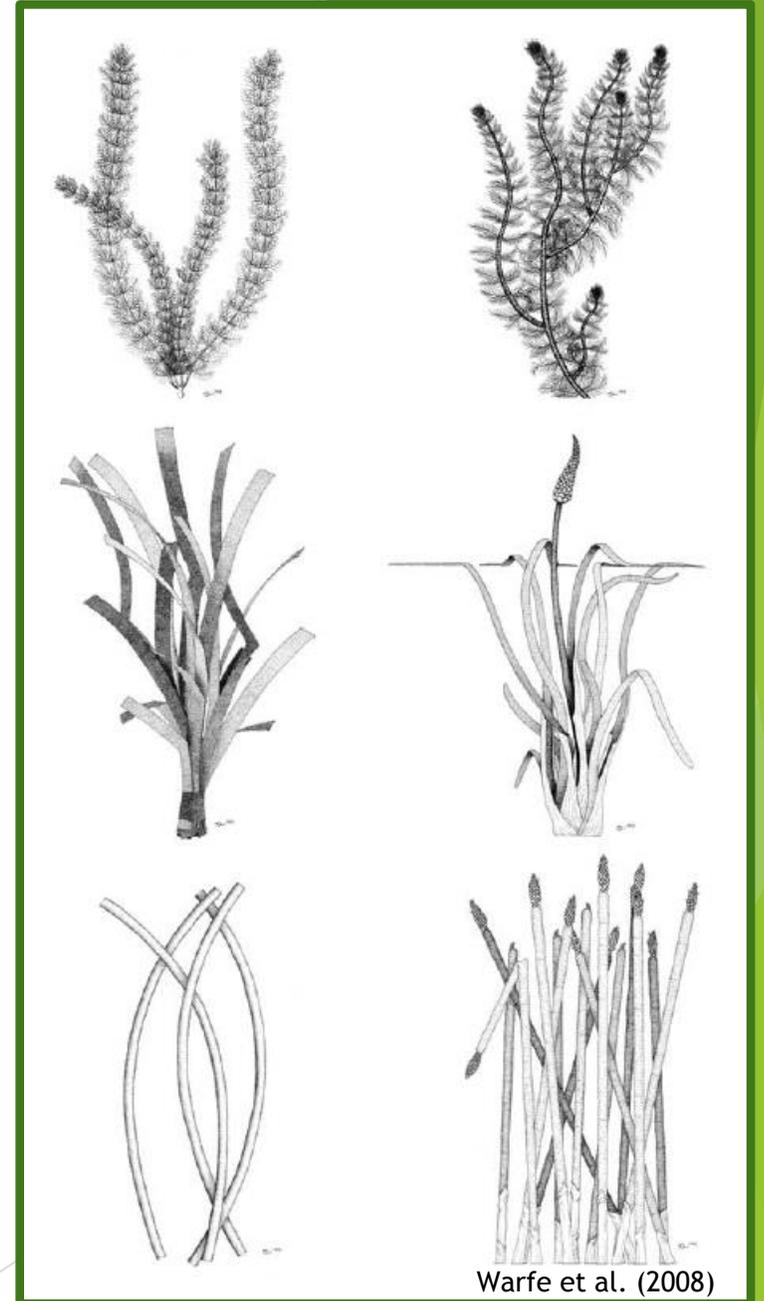
# Refugia in ERA

- ▶ Mathematical models supported by empirical evidence<sup>6</sup>
  - ▶ Simulated population changes after disturbance events
  - ▶ Refugium size, proportion of individuals lost, time between disturbances
- ▶ Simulated short term movements of individuals into and out of refugia
  - ▶ Population persistence with 10% vs. 40% refugia
  - ▶ Total area of refugia had a greater impact on population persistence than proportional loss or disturbance frequency



# Refugia in ERA

- ▶ Quantifying refugia<sup>15</sup>
  - ▶ Relationship of macrophyte structure and macroinvertebrate abundance and species richness
  - ▶ Surface convolution and refuge space correlated to macroinvertebrate distribution
- ▶ Population modeling<sup>16</sup>
  - ▶ Comparison of ecological models applicable to risk assessment
  - ▶ Suitable aquatic ecosystem models
    - ▶ AQUATOX
    - ▶ IFEM
    - ▶ CASM



# Conclusions

- ▶ Models assume homogeneous distribution
- ▶ Sorption to sediment, vegetation, and other organic matter reduces aqueous concentrations
- ▶ Pyrethroid concentrations are highly dynamic within a water body across small temporal and spatial scales
- ▶ Invertebrate populations exhibit faster recovery when refugia are present; may be variable depending on internal vs. external refugia
- ▶ Refugia may have a smaller effect on species without dispersal capabilities
- ▶ Development of methods to incorporate quantifying refugia and population modeling into ERA should lead to more realistic estimates of exposure and effects



# References

- ▶ <sup>1</sup>Schulz, R. (2004). Field studies on exposure, effects, and risk mitigation of aquatic nonpoint-source insecticide pollution: A review. *Journal of Environmental Quality*, 33(2), 419-448.
- ▶ <sup>2</sup>Werner, I., Deanovic, L. A., Hinton, D. E., Henderson, J. D., De Oliveira, G. H., Wilson, B. W., . . . Zalom, F. G. (2002). Toxicity of stormwater runoff after dormant spray application of diazinon and esfenvalerate (asana®) in a french prune orchard, glenn county, california, USA. *Bulletin of Environmental Contamination and Toxicology*, 68(1), 29-36.
- ▶ <sup>4</sup>Weston, D. P., You, J., & Lydy, M. J. (2004). Distribution and toxicity of sediment-associated pesticides in agriculture-dominated water bodies of california's central valley. *Environmental Science and Technology*, 38(10), 2752-2759.
- ▶ <sup>5</sup>Dix M. 2014. Determining the partitioning coefficient (n-octanol/water) of nine pyrethroids by the slow-stirring method following OECD guideline 123. PWG Report - PWG-ERA-04a. MRID 49314702. Smithers Viscient. Wareham, MA.
- ▶ <sup>6</sup>Lancaster, J., & Belyea, L. R. (1997). Nested hierarchies and scale-dependence of mechanisms of flow refugium use. *Journal of the North American Benthological Society*, 16(1), 221-238.
- ▶ <sup>7</sup>Bennett, E. R., Moore, M. T., Cooper, C. M., Smith Jr., S., Shields Jr., F. D., Drouillard, K. G., & Schulz, R. (2005). Vegetated agricultural drainage ditches for the mitigation of pyrethroid-associated runoff. *Environmental Toxicology and Chemistry*, 24(9), 2121-2127.
- ▶ <sup>8</sup>Gan, J., Lee, S. J., Liu, W. P., Haver, D. L., & Kabashima, J. N. (2005). Distribution and persistence of pyrethroids in runoff sediments. *Journal of Environmental Quality*, 34(3), 836-841.
- ▶ <sup>9</sup>Liu, P., Liu, Y., Liu, Q., & Liu, J. (2010). Photodegradation mechanism of deltamethrin and fenvalerate. *Journal of Environmental Sciences*, 22(7), 1123-1128.
- ▶ <sup>10</sup>Grant, R. J., Daniell, T. J., & Betts, W. B. (2002). Isolation and identification of synthetic pyrethroid-degrading bacteria. *Journal of Applied Microbiology*, 92(3), 534-540.
- ▶ <sup>11</sup>Liess, M., & Schulz, R. (1999). Linking insecticide contamination and population response in an agricultural stream. *Environmental Toxicology and Chemistry*, 18(9), 1948-1955.
- ▶ <sup>12</sup>Liess, M., & Von Der Ohe, P. C. (2005). Analyzing effects of pesticides on invertebrate communities in streams. *Environmental Toxicology and Chemistry*, 24(4), 954-965.
- ▶ <sup>13</sup>Caquet, T., Hanson, M. L., Roucaute, M., Graham, D. W., & Lagadic, L. (2007). Influence of isolation on the recovery of pond mesocosms from the application of an insecticide. II. benthic macroinvertebrate responses. *Environmental Toxicology and Chemistry*, 26(6), 1280-1290.
- ▶ <sup>14</sup>Hanson, M. L., Graham, D. W., Babin, E., Azam, D., Coutellec, M. -, Knapp, C. W., . . . Caquet, T. (2007). Influence of isolation on the recovery of pond mesocosms from the application of an insecticide. I. study design and planktonic community responses. *Environmental Toxicology and Chemistry*, 26(6), 1265-1279.
- ▶ <sup>15</sup>Warfe, D. M., Barmuta, L. A., & Wotherspoon, S. (2008). Quantifying habitat structure: Surface convolution and living space for species in complex environments. *Oikos*, 117(12), 1764-1773.
- ▶ <sup>16</sup>Pastorok, R. A., Akçakaya, H. R., Regan, H., Ferson, S., & Bartell, S. M. (2003). Role of ecological modeling in risk assessment. *Human and Ecological Risk Assessment*, 9(4), 939-972.
- ▶ Pyrethroid Working Group (PWG). (2016). "Overview of lines of evidence relevant to pyrethroid aquatic risk assessments". Meeting with US EPA, 27 April, 2016.