Aquatic Systems & Environmental Health

Aquatic Toxicology of Pesticides

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Pesticides

- 1000 B.C. sulfur used in China
- 1500 arsenic
- 1700 tobacco extract
- 1850 rotenone, chrysanthemum extract
- 1900 arsenates in common use
- 1930s DDT, 2,4-D, dithiocarbamate fungicides
- 1944 parathion
- 1960 carbamate insecticides, synthetic pyrethrins

Types of Pesticides

- Insecticides
- Herbicides
- Fungicides
- Avicides
- Molluscicides
- Rodenticides

Pesticide Usage

- billions of pounds made in US each year
- Over 300 pesticides in use in US
- >50% of use is non-commercial
- many benefits, including higher crop yields and better health (malaria, West Nile virus). Nobel prize awarded for DDT in 1948.

Insecticide aquatic ecotoxicity

- Insects are arthropods (Class Insecta). Many Arthropods share similar neurochemical or xenobiotic metabolism pathways.
- Result is that pesticides tend to affect non-target arthropods (crustaceans) at very low concentrations.
- Arthropods are not highly visible, but are very important in aquatic ecosystems (carbon cycling, sediment bioturbation, energy trophic transfer).

Insecticide classes

- Organochlorines
- Antiesterases
  - Organophosphates and carbamates
- Pyrethroids
  - similar to the natural chemical pyrethrins produced by the flowers of pyrethrums (Chrysanthemums)
- Fipronil
- Insect Growth Regulators

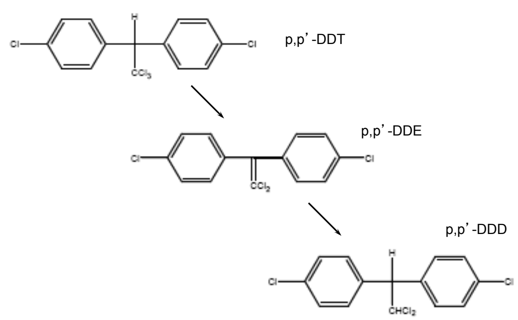
Organochlorines

- DDT,aldrin, dieldrin, chlordane, toxaphene, endosulfan
- Very heavily used from the 1940s to the 1970s
- Mostly phased out in developed countries
- Still used in developing countries
- Environmentally persistent
- All OCPs are lipophillic and highly bioaccumulated

DDT toxicity

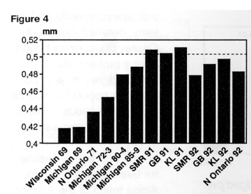
- DDT causes toxicity by blocking Na+ channels in neurons, leading to hyperpolarization of the membrane and persistent excitatory activity
- DDT is relatively non-toxic in birds, with LC50s ranging from 800 -2,000 mg/kg
- DDT is very toxic to aquatic invertebrates, with 96hour LC50s ranging from 0.18 to 7 ug/L
- DDT is also toxic to fish, with LC50s generally below 10ug/L
- Very low solubility in water; most is bound to sediment
- DDT has BCFs ranging from 1000 to 1000000

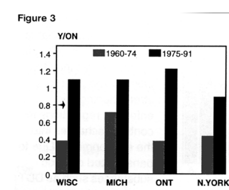
DDT metabolism



Chronic toxicity of OCPs

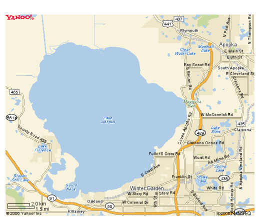
- DDE appears to be an endocrine disruptor, leading to eggshell thinning in birds, potentially by actions on PTH or PG synthase

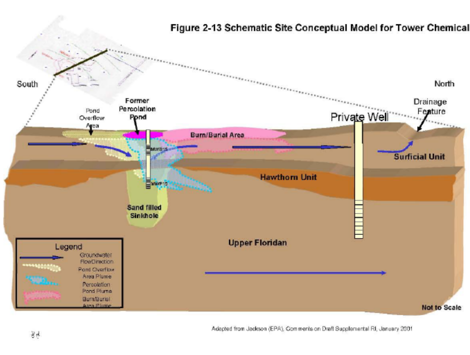


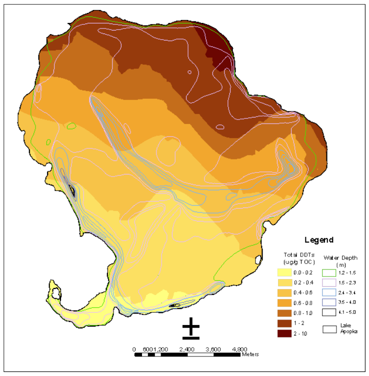


Lake Apopka

- One of the largest lakes in FL
- In 1980, the Tower Chemical Co. which manufactured DDT and dicofol, spilled large amounts of DDT into Lake Apopka
- Subsequent decline in alligator population attributed to pesticides
  - Females had elevated E2 in plasma and abnormal ovaries
  - Males had decreased T and abnormal testes and reduced penis size
  - 80+% of eggs failed to hatch with resulting high mortality rates



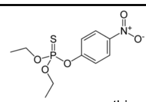




NSRA of Apopka

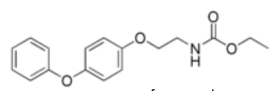
- Muck farms on the North Shore of Apopka encompassed approximately 14,000 acres
- Largely vegetable farms growing corn, radishes, carrots, greens, and cabbage
- In 1967, typical crop of sweet corn used 0.4lbs of chlordane, 13.3 lbs of toxaphene, 68 lbs of DDT and 11lbs of parathion/acre
- 40+ years of pesticide application resulted in very high levels of pesticides in soil
- In 1998, St. John's WMD purchased the land and reflooded portions. Resulted in large bird kill due to bioconcentration of pesticides
- Similar sites along the Ocklawaha river chain have had serious problems with fish reproduction
  - Little or no juvenile recruitment
  - Altered steroid levels

Organophosphates


parathion

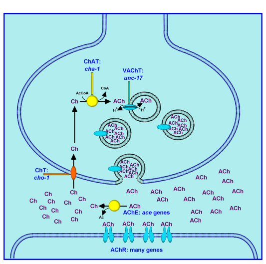
- Parathion, Malathion, Methyl parathion, Chlorpyrifos, Diazinon
- Designed to replace OCPs
- Breakdown relatively quickly in environment
- Acetylcholinesterase inhibitors
- Must be metabolized to active form
- Produce irreversible AChE inhibition after aging

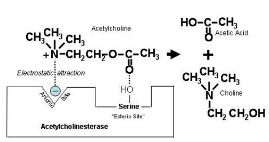
Carbamates


fenoxycarb

- Also AChE inhibitors
- Reversible AChE inhibition
- Aldicarb, Carbofuran, Furadan, Fenoxycarb, Carbaryl, Sevin,

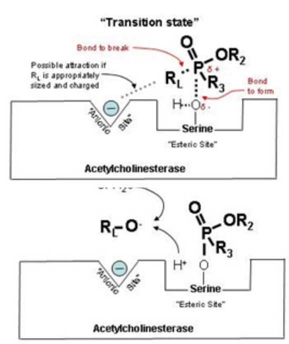
Cholinergic neurotransmission



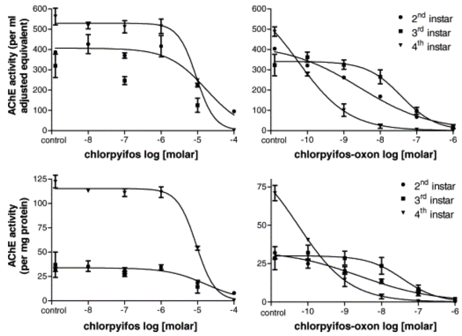


Cholinesterase Inhibition

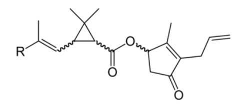
- •Organophosphate and carbamate insecticides bind to AChE and inhibit the enzyme
- •Allows ACh to buildup, leading to overstimulation of receptors with ensuing SLUD symptoms



Stage specific AChE sensitivity



Pyrethroids



permethrin

- Na^+ channel agonists
- Low toxicity to mammals, low environmental persistence (UV irradiation).
- Often combined with piperonyl butoxide (potent cytochrome P450 inhibitor)
- Sumithrin, Resmethrin, Bifenthrin, Cypermethrin, Deltamethrin, Permethrin

Case study 1– pyrethroid toxicity

- Pyrethroid insecticides now fill most of the residential needs previously met by organophosphates.
- Landscape irrigation or stormwater runoff could play similar roles in transporting residentially used pyrethroids into urban water bodies.
- Does residential use of pyrethroids result in sediment concentrations that cause mortality in sediment toxicity tests?
- *Hyallela azteca* (sediment ingesting amphipod) 10 day sediment toxicity assay.

Table 2. Reported Pyrethroid Use (kg/year) in Placer County, California in 2003 (Reported Data Include Only Commercial Applications, Not Use by Homeowners)

pyrethroid	agricultural use	structural pest control	landscape maintenance
bifenthrin	0.01	141.4	6.2
cyfluthrin	0	275.1	3.9
cypermethrin	0	3337.9	0.05
deltamethrin	0	32.1	0.83
esfenvalerate	17.8	0.02	0
lambda-cyhalothrin	22.6	2.3	0
permethrin	0	673.5	157.5
other	0	1.2	0

Figure 1 Map of study area with sampling sites shown. Inset map shows location of study area within California. Areas of housing development can be inferred from density of roads. Water flow in all creeks shown is from east to west. Stations 5, 6, and 7 are in Pleasant Grove Creek off the left side of the map, approximately 7, 10, and 13 km downstream of station 4, respectively. They are not shown because doing so would substantially reduce the detail visible in the map.

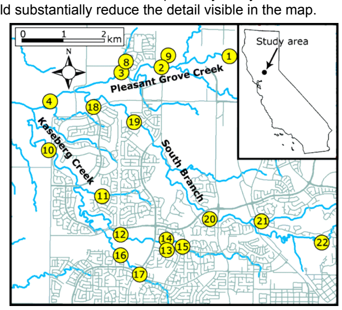
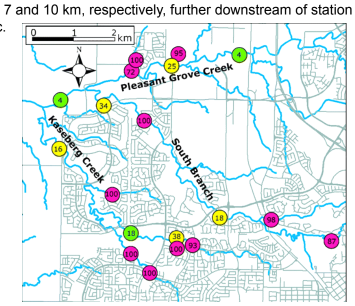


Figure 2 Distribution of sediment toxicity among the study sites. The numerical values at each site indicate the percent mortality of *H. azteca* in 10-d toxicity tests. Results are also illustrated by color coding (red = high toxicity with >70% mortality; yellow = moderate toxicity with mortality significantly greater than control but <70%; green = nontoxic with mortality not significantly different than control). Two stations (sites 5 and 6) not shown, but located on Pleasant Grove Creek 7 and 10 km, respectively, further downstream of station 4 were also nontoxic.



Case study 1 – pyrethroid toxicity

- Pyrethroids can have a devastating impact on aquatic crustacean communities.
- Majority of input from homeowner/ residential applications, rather than from agricultural runoff.

Fipronil

- Fairly new pesticide (1990's)
- GABA antagonist
- Very toxic to non-target arthropods
- Also highly toxic to other aquatic organisms (fish, shrimp).
- Has serious effects beyond GABA
- Implicated in many reproductive and neurodevelopmental abnormalities in aquatic organisms
- Enantiomers have differential toxicity

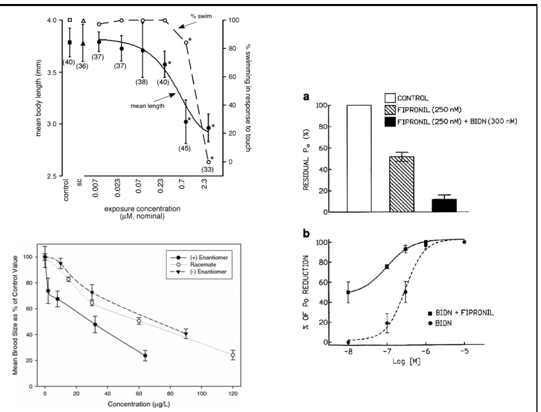
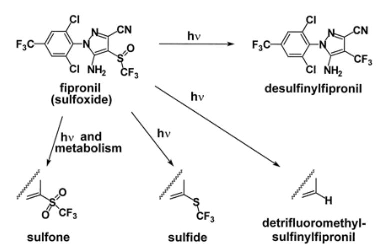
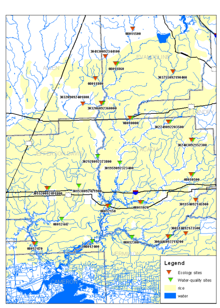


Figure 1. Fipronil degrades photochemically (h) under environmental conditions to the desulfinyl derivative as the major photoproduct and the detrifluoromethylsulfinyl, sulfone, and sulfide compounds as minor products. Metabolism of fipronil in mice yields the sulfone but not the other derivatives.



Case study 2: Fipronil toxicity

- Mermentau River basin
  - 400,000 acres for rice cultivation
  - Ricefields are periodically flooded and drained
- Crayfish are double-cropped in flooded fields.
  - Economically very important, especially when droughts make rice farming impractical
- Starting in 1990's, dramatic increase in crayfish mortality was observed
- Attention turned to Fipronil, a new GABA agonist pesticide



FP-treated rice seeds

Rice seeds treated with FP (Icon) had very high levels of FP and FP-degradates. No FP was found in untreated seeds.

Table 1. Average (± SD) concentration (μg/g) of fipronil and its degradation products in Icon 6.2FS™-treated and untreated rice seeds

Seed Type	Fipronil	Sulfone	Sulfide	Desulfinyl
Fipronil treated	249 ± 9	7.02 ± 0.21	0.41 ± 0.06	3.4 ± 0.12
Untreated seed	N/D	N/D	N/D	N/D

N/D = no detection.

FP and FP degradates were present at high concentrations in water/sediment from Icon treated rice, absent from control fields.

Table 4. Toxicity and average concentration of fipronil and its degradation products in water and sediment from fields receiving water from ricefields planted with Icon 6.2FS™ and untreated rice seed

Exposure Type	Fipronil[a]	Sulfone[a]	Sulfide[a]	Desulfinyl[a]	Survival (%)[b]
Thibideaux (Icon 6.2 FS™)					
Water	9.1	6.9	3.4	16.5	40 ± 17*
Sediment	5.5	ND[c]	1.8	ND[c]	
Wild (untreated)					
Water	1.2	ND[c]	1.4	2.4	83 ± 21
Sediment	ND[c]	ND[c]	ND[c]	ND[c]	

[a] Units of concentration in sediment samples were μg/kg, while in water samples concentrations were μg/L.
[b] Percent survival ± SD of *Procambarus clarkii*.
[c] No detection: sediment—1 μg/kg—all compounds; aqueous—fipronil (0.5 μg/L); sulfide (1.0 μg/L); desulfinyl (0.5 μg/L); sulfone (2.0 μg/L).
* $p \leq 0.05$ ($n = 3$).

Crayfish survival was decreased by ~ 50% in Icon-treated fields

Water from treated commercial rice farms had concentrations of FP degradates as high as 60 times a LC50 dose of desulfinyl fipronil (HQ = 122)

Table 5. Hazard quotient analyses (measured water concentrations/ $0.5 \times LC_{50}$) of Thibodeaux farm (Icon 6.2FS™-treated) and the effects of water filtration of suspended sediment

Collection Date	Fipronil	Sulfone	Sulfide	Desulfinyl
April 23	9*	6.9*	3.4	16.5
	7	5.6	7.75	34.3
March 23	3–48*	64–455*	8–23*	122–175*
	7	5.6	7.75	34.3
March 23	6–9*	19–163*	2–13*	27–36*
0.45 μm Filtered	7	5.6	7.75	34.3

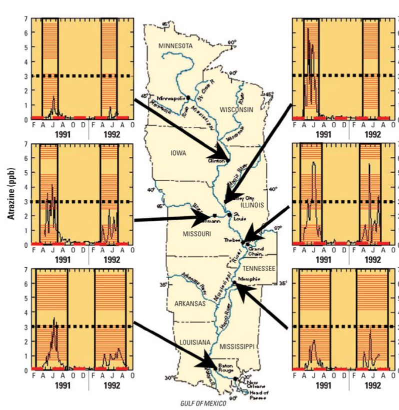
* Contains samples > 1.

Fipronil toxicity

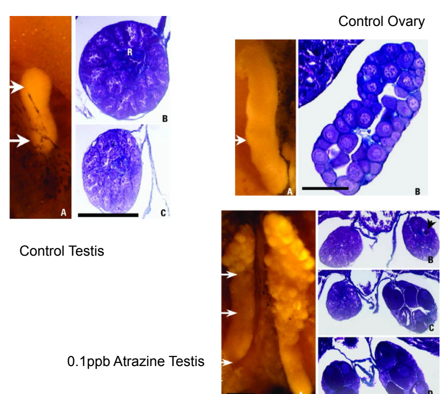
- High affinity of FP for organic matter (log Kow = 4) implies sediment associated FP can be transported downstream
- High concentrations of FP were observed several miles downstream of the application area (***4.07 ug/L***)
- Photo degradates of FP are longer-lived, and at least as toxic to aquatic crustaceans as parent compound

Atrazine

- One of the most widely used herbicides in the world
- Produced by Syngenta Crop Protection
- Market is over $400M/year
- Sprayed on ~70% of corn acreage in US (62M acres)
- Measurable in nearly all US surface waters, though typically below 3ppb level established by EPA
- Nearly non-toxic to birds, fish and mammals
- Raging debate over its effect on frogs



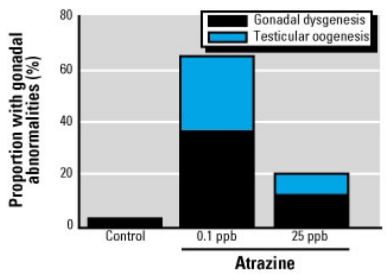
Control Ovary



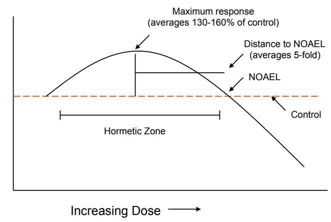
Control Testis

0.1ppb Atrazine Testis

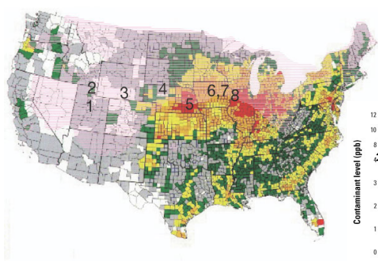
From Hayes et al., 2003

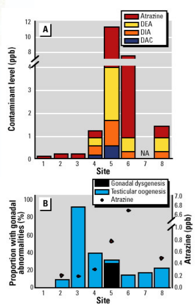


Hormesis



Dose-response curve depicting the quantitative features of hormesis





Hayes et al., 2003

Debate about atrazine

- Lack of typical dose-response raises issues
- Other scientists unable to replicate Hayes' results. They are funded by Syngenta, which raises questions about conflict of interest
- In December 2007, EPA concluded that atrazine does not affect amphibian gonadal development, based on results of 19 studies
- Use of atrazine has been restricted in Europe since 1998

Final thoughts on pesticides

- Pesticide metabolites may have toxicity
- Binding to sediment can increase environmental persistence
- Aquatic invertebrates are very susceptible to many insecticides
- Non-standard toxicological findings cause a lot of debate. Really question what is ecologically significant.
- If it doesn't affect population levels, is it a problem?