

*The presence of Endosulfan Sulfate
Residues in Water, Sediment and
Biological Samples in South Florida:*

*Potential Environmental
Implications*

South Florida CARE

Contaminant Assessment & Risk Evaluation

**Piero Gardinali, Adolfo Fernandez, Gary Rand, John Carriger
Tham Hoang and Joffre Castro**



National Park Service – Cooperative Science



GEER – July 14, 2010

Contaminants in South Florida: the old picture



Publications

- Miles & Pfeuffer (1997)
- Miller & McPherson (2001)
- Scott et al. (2002)
- Key et al. (2003)
- Caccia et al. (2003)
- Fulton et al. (2004)

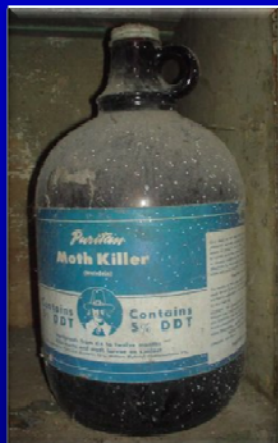
Monitoring Programs

- SFWMD
- USGS
- NOAA
- DERM
- USDA-ARS
- FIU

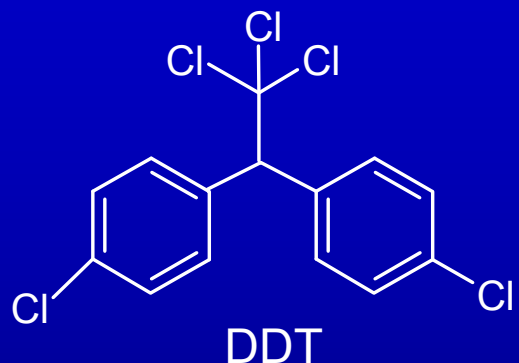


DDT, DDD and DDE: environmental legacy

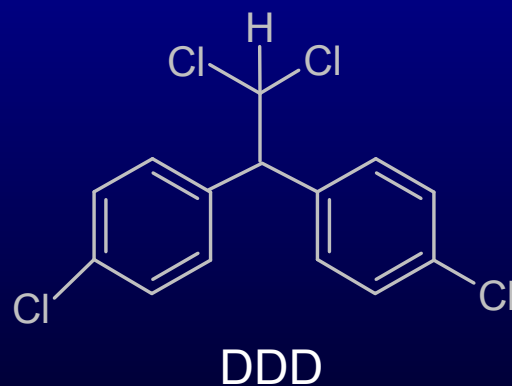
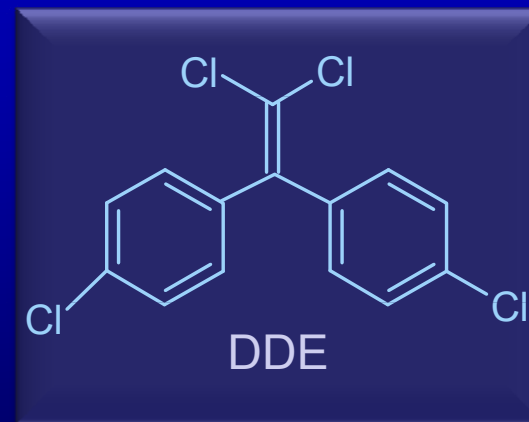
Paul Hermann Müller won the 1948 Nobel Prize in Physiology or Medicine for his 1939 discovery of DDT as an insecticide useful in the control of malaria, yellow fever and many other insect-vector diseases.



p,p'-DDT
+
o,p-DDT



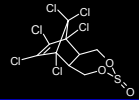
- SOIL
- SEDIMENT
- ORGANISMS



DDMU, DDA, DBP...

Rappolt, RT (1973). "Use of oral DDT in three human barbiturate intoxications: hepatic enzyme induction by reciprocal detoxicants". Clin Toxicol 6 (2): 147-51

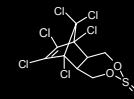
Endosulfan: The Last Chlorinated Pesticide?



- Endosulfan (**Thiodan**) is a commercial mixture of two active isomers
- Controls **wide range** of insect pests
- Residual effects
- Used on white flies, army worms and caterpillars in **South Florida tomato regions** (3 lb/acre)
- Used on non-food crops (cotton, tobacco, **ornamentals**) and food crops (vegetables, fruits, cereals)



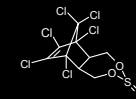
Endosulfan: The Last Chlorinated Pesticide?



- **Only** remaining organochlorine insecticide registered under USEPA FIFRA
- In use since 1950's but **not produced** in US since 1982
- Classified as a persistent organic pollutant (POP)
 - Persistence
 - Accumulation
 - Long-range transport
- Scheduled for inclusion in the Stockholm Convention
- Canada (2007) under consideration for phase-out
- Phased out in EU in 2007 (18 month grace period)



Endosulfan: The Last Chlorinated Pesticide?



- Will likely be replaced by organophosphates and pyrethroids
- Still clear advantages → will NOT develop pest resistant
 - α Endosulfan is volatile
 - β Endosulfan is more persistent
 - Endosulfan sulfate is the main metabolite
- Endosulfan sulfate is the only compound present in fish
- Fish are the most sensitive non-target organisms



What criteria is available for management?

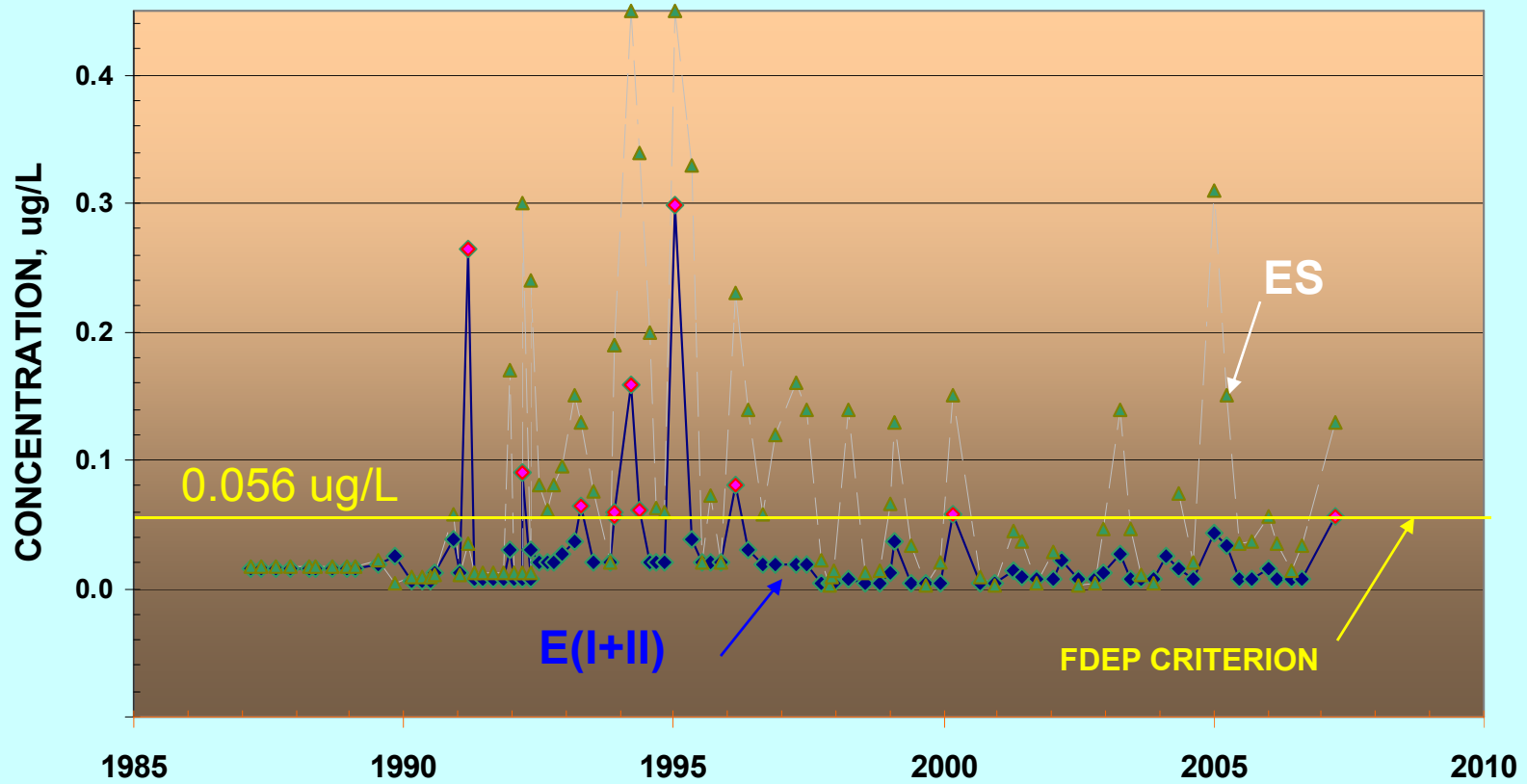
Available Environmental Criteria				
Florida	Section 62-302.530 - Table: Criteria for Surface Water Quality Classifications (Effective July 27, 2005)			
	Class I	Class II	Class III Freshwater	Class III Marine
	≤0.056 µg/L	≤ 0.0087µg/L	≤ 0.056 µg/L	≤ 0.0087 µg/L
Hawaii (1999)	Freshwater	Wildlife	Acute 0.22 µg/L	Chronic 0.056 µg/L
Hawaii (1999)	Saltwater	Wildlife	Acute 0.034 µg/L	Chronic 0.0087 µg/L
Colorado (1999)	Freshwater	Wildlife	Acute 0.11 µg/L	Chronic 0.056 µg/L

This guidelines apply only to Endosulfan α or β but not to Endosulfan Sulfate



Surface Waters: SFWMD Data

ENDOSULFAN AT S-178



What has changed since then:

The endosulfan *residues of toxicological concern* are: α -endosulfan, β -endosulfan , *and* endosulfan sulfate.

For purposes of conducting the endosulfan *risk assessment*, the Agency (EPA) assumed that the 3 residues of toxicological concern are *approximately equal in toxicity* due to their similar structures and physicochemical properties.

(EPA-HQ-OPP-2001-0262-0180)

What has changed since then:

The *chronic* toxicity of endosulfan to freshwater *fish* is estimated as low as **0.023 µg/L** (estimated NOAEC), which is about *half* of EPA's freshwater chronic water quality criterion of **0.056 µg/L**.

Chronic toxicity of freshwater *invertebrates* is estimated as low as **0.011 µg/L** (estimated NOAEC).

Chronic effects associated with NOAECs used to derive these toxicity reference values include impacts on survival, growth and reproduction.
(EPA-HQ-OPP-2001-0262-0162)

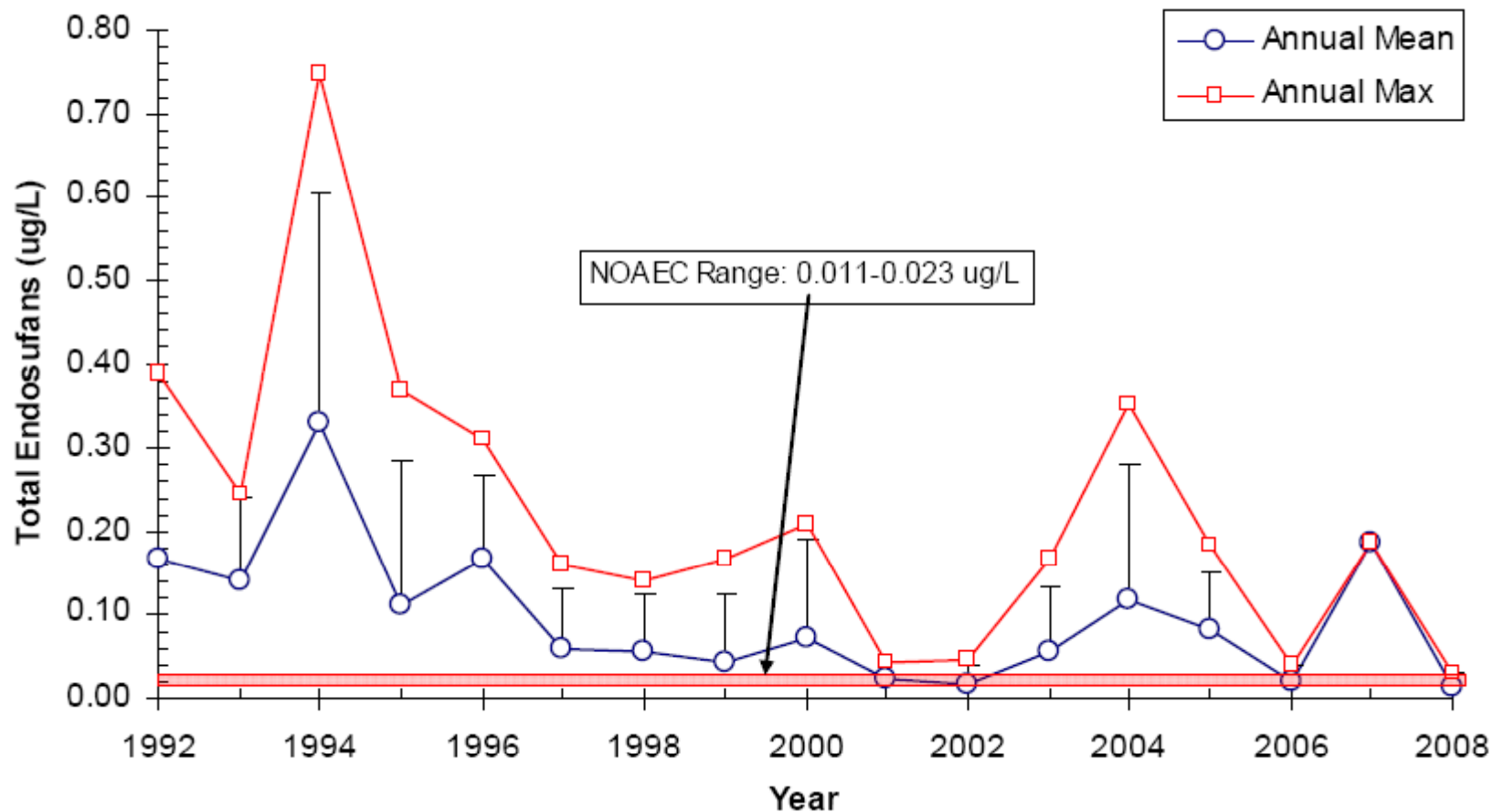


Figure 3.53. Average annual concentrations of total endosulfans in surface water samples from SFWMD site S178 (1992-2008, Source SFWMD, error bars = 1 standard deviation).

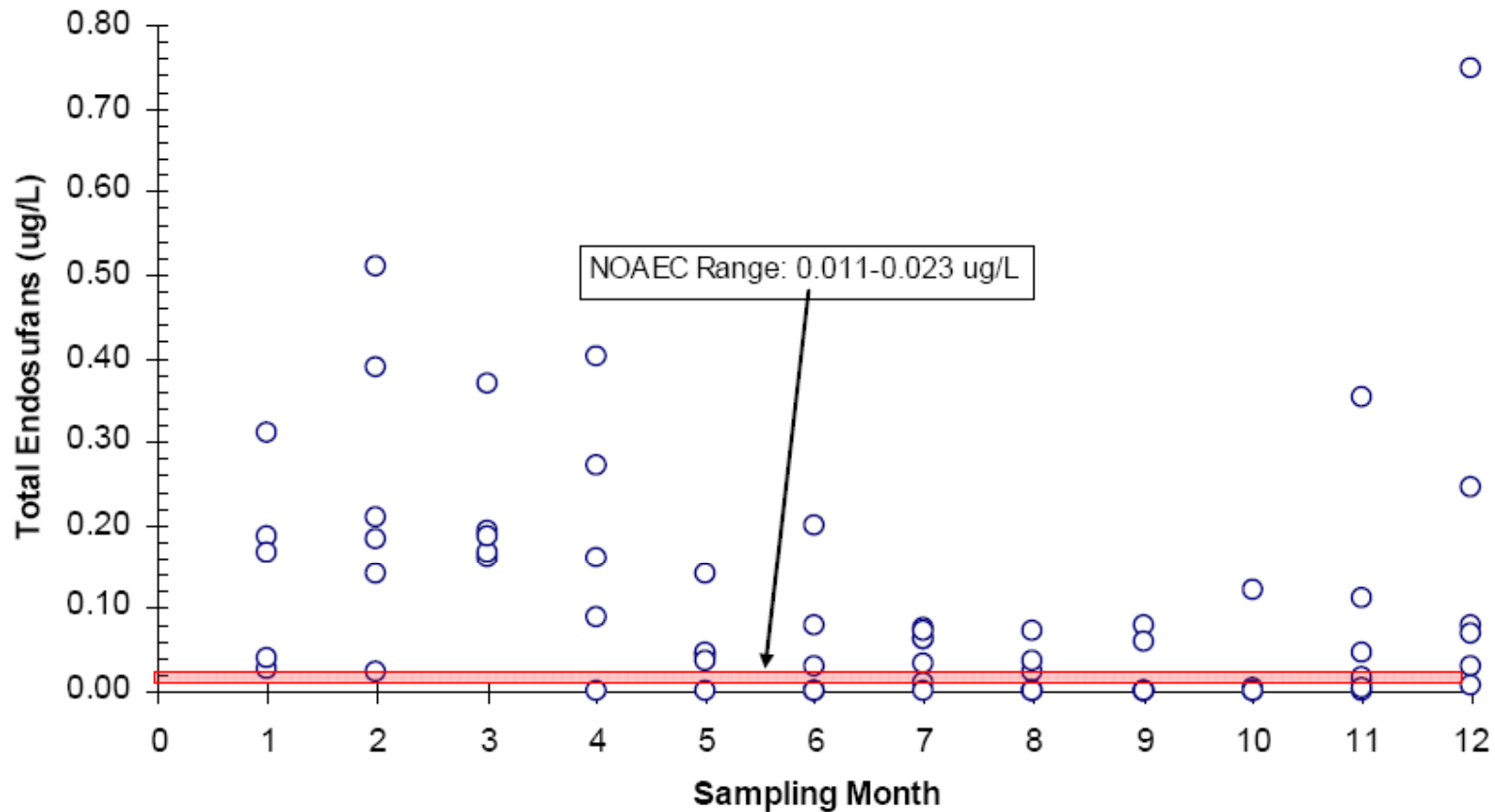


Figure 3.54. concentration of total endosulfan (alpha + beta + sulfate) by sampling month reported for the S178 station (data source: SFWMD)

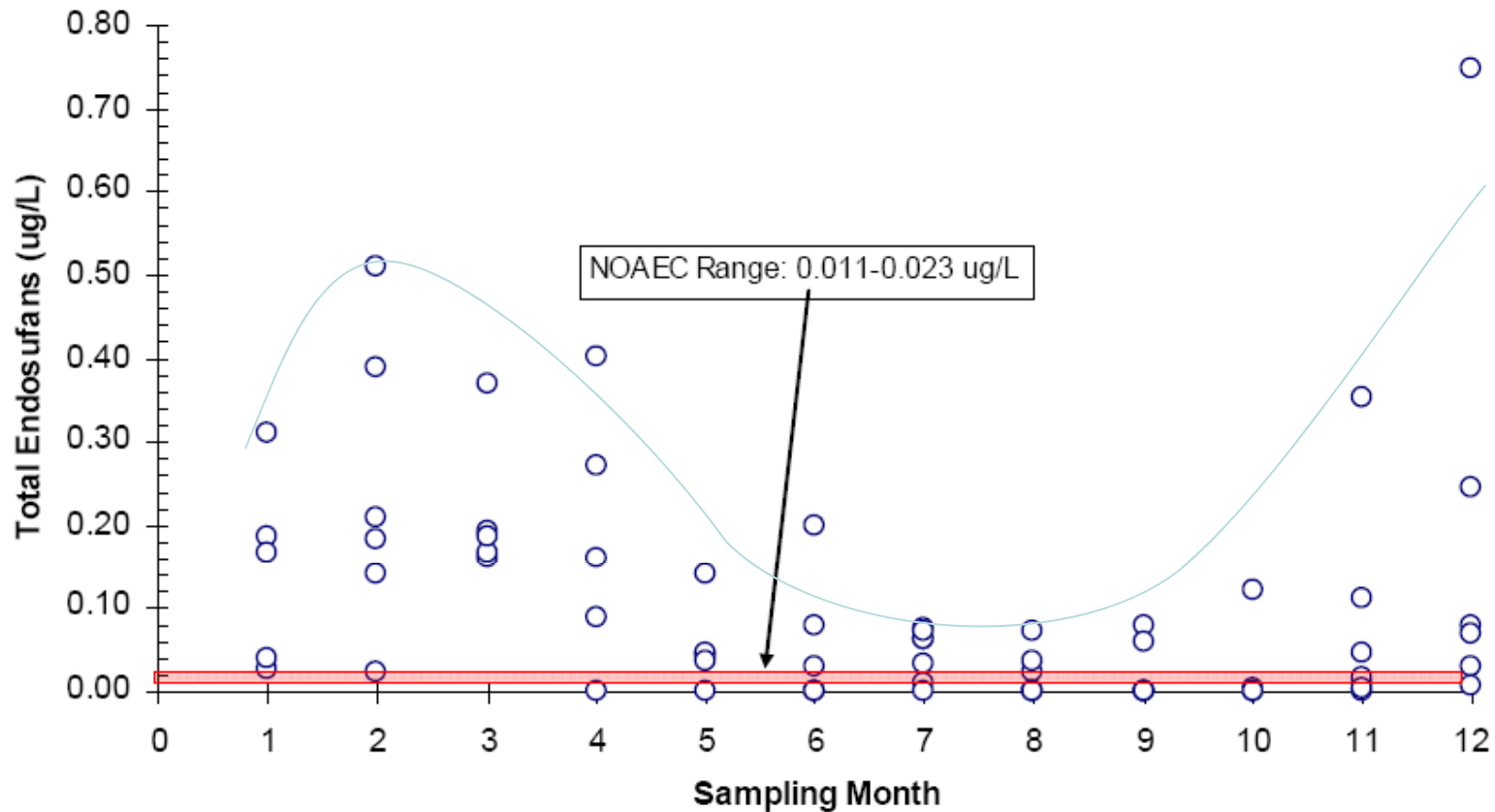
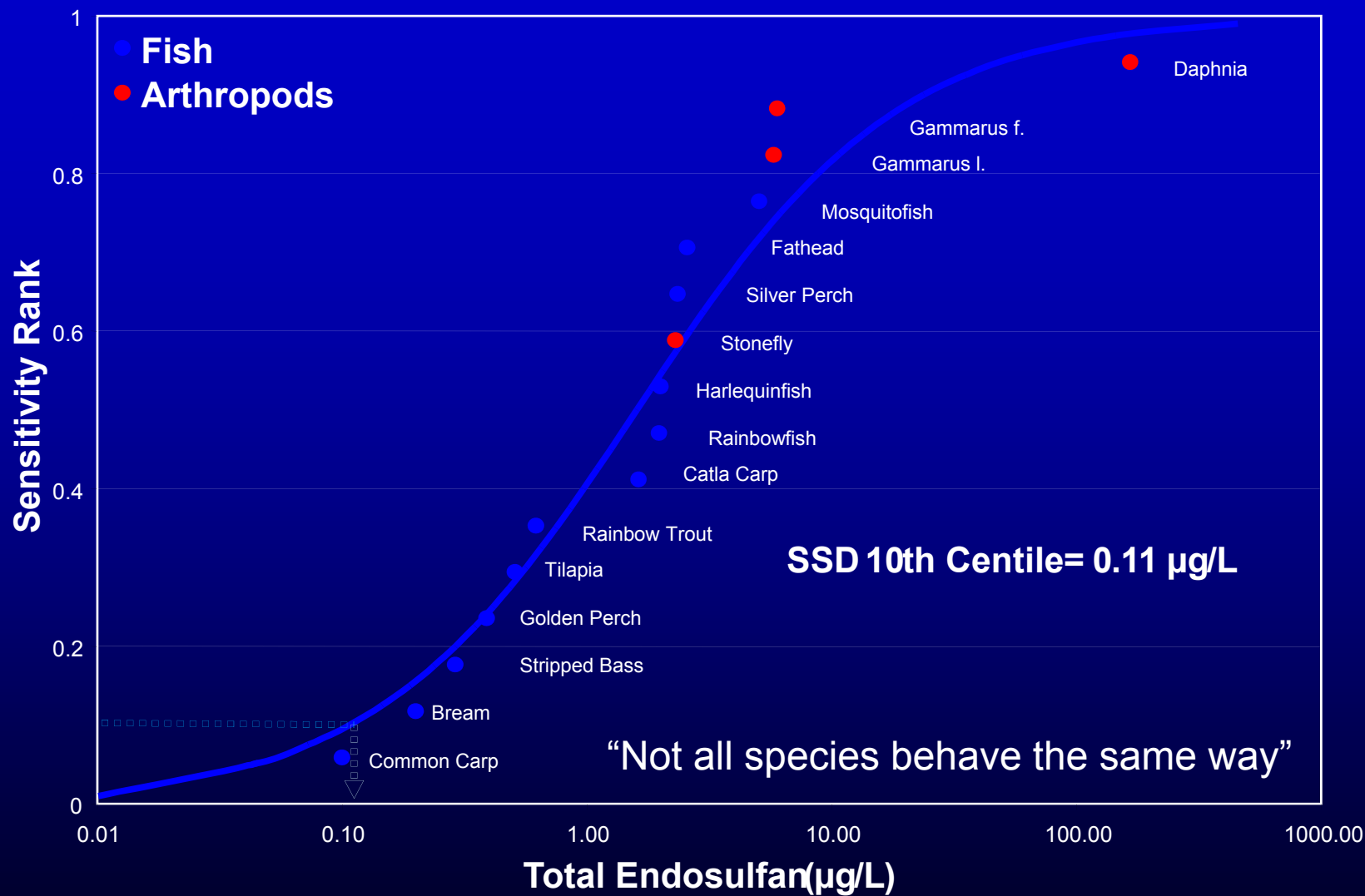


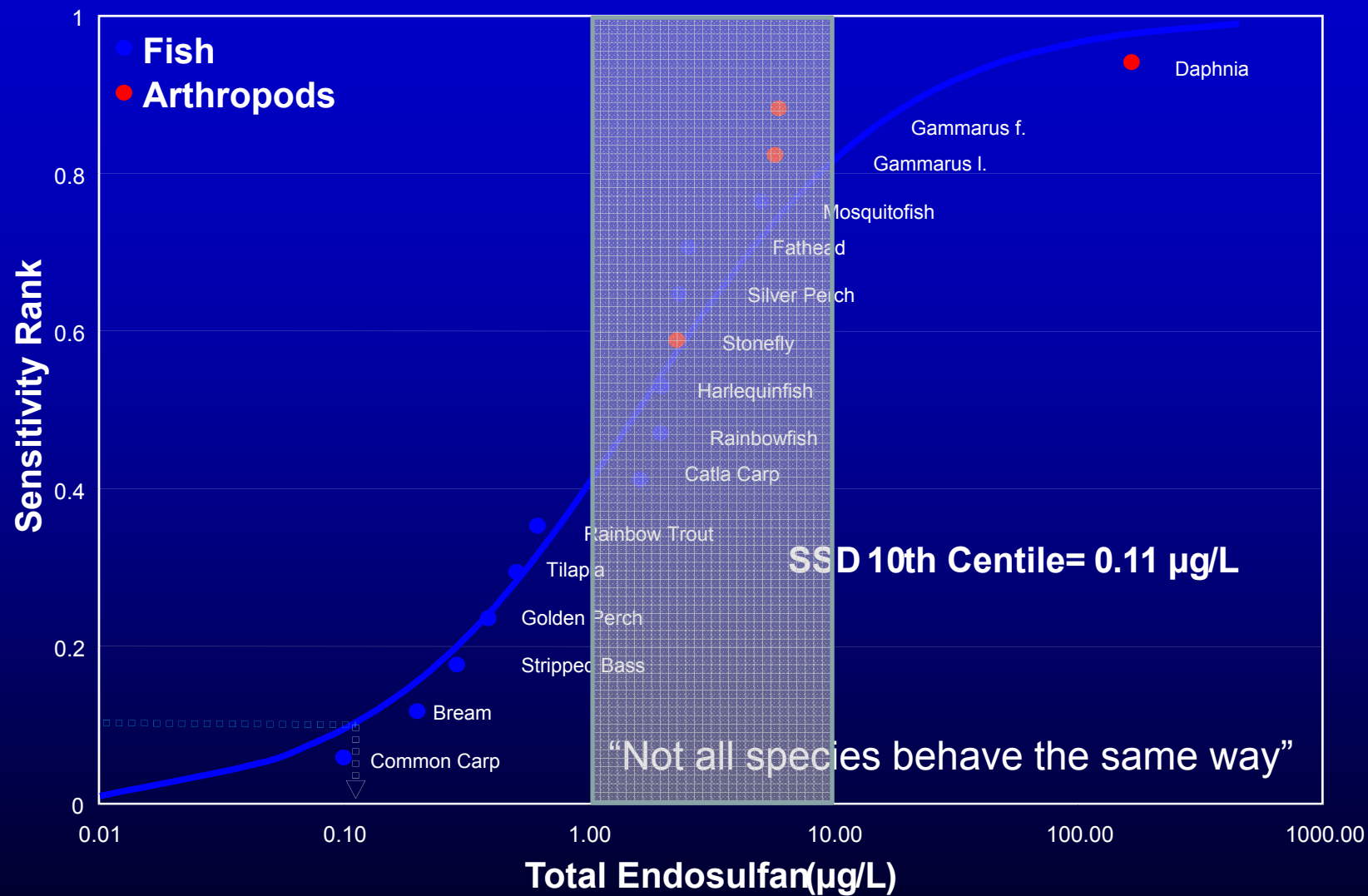
Figure 3.54. concentration of total endosulfan (alpha + beta + sulfate) by sampling month reported for the S178 station (data source: SFWMD)

How toxic is the metabolite?



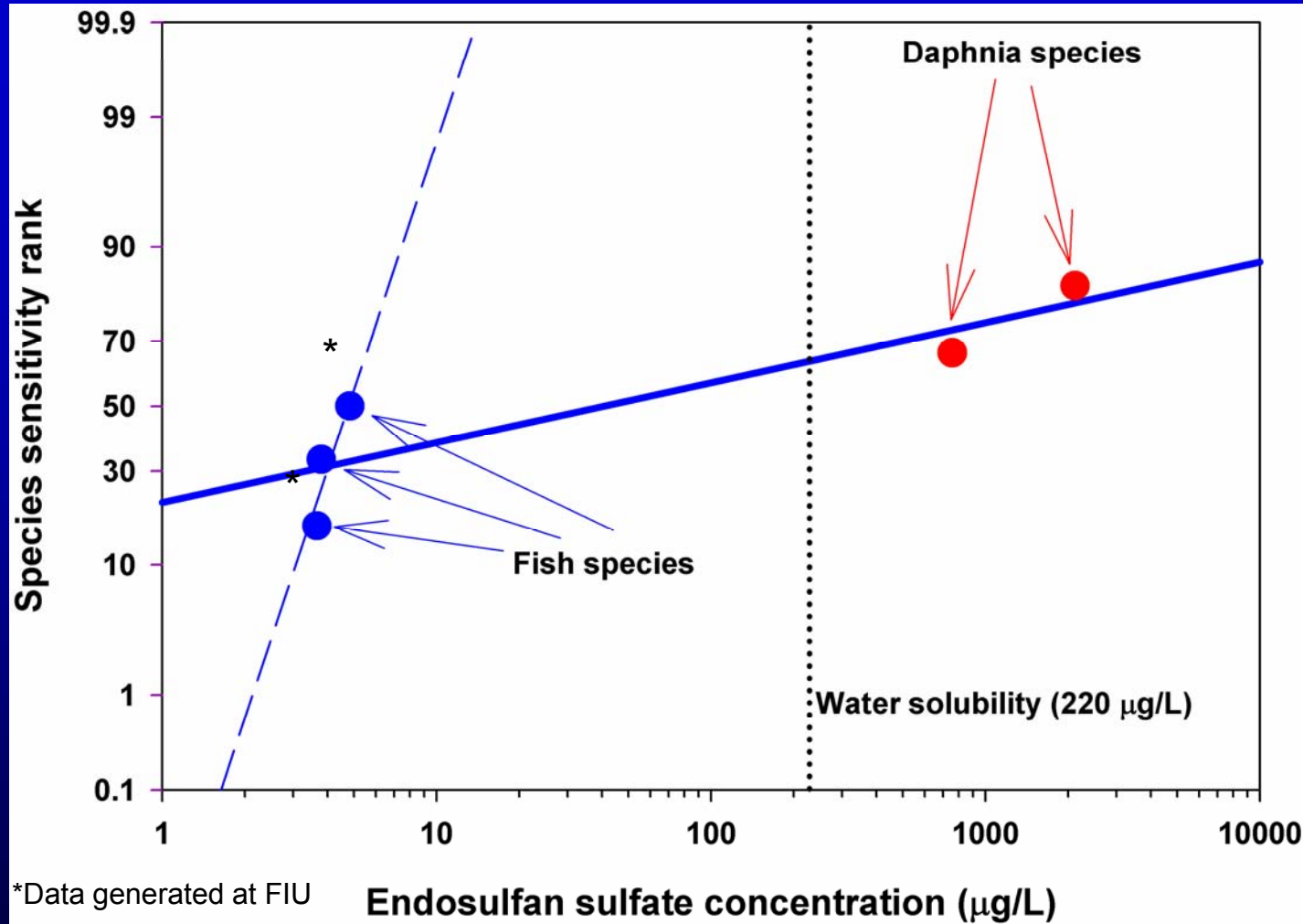
DATA ARE FOR ENDOSULFAN ONLY NOT THE METABOLITE

How toxic is the metabolite?



DATA ARE FOR ENDOSULFAN ONLY NOT THE METABOLITE

Is the metabolite as toxic and the parent compounds?

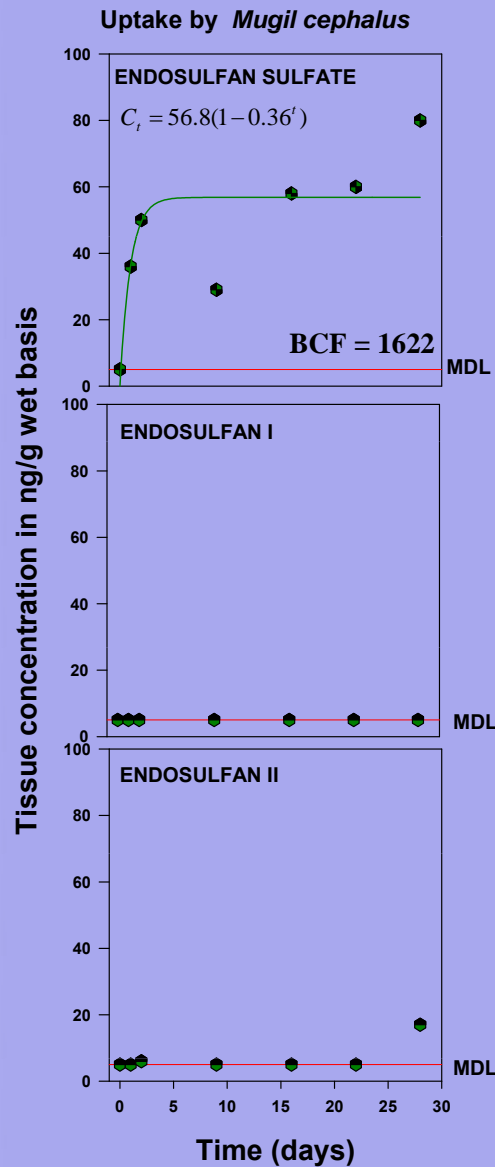


Carriger et al., (2010) Arch Environ Contam Toxicol 58:1015-1022

- Bluegill sunfish
LC₅₀ 3.8 $\mu\text{g/L}$
(EPA 2007)
- Fathead Minnow
LC₅₀ 3.4 $\mu\text{g/L}$
(FIU)
- Mosquitofish
LC₅₀ 4.7 $\mu\text{g/L}$
(FIU)
- 10% Mortality
- 77 - 96 hours
- S-178
- 1.35 $\mu\text{g/L}$

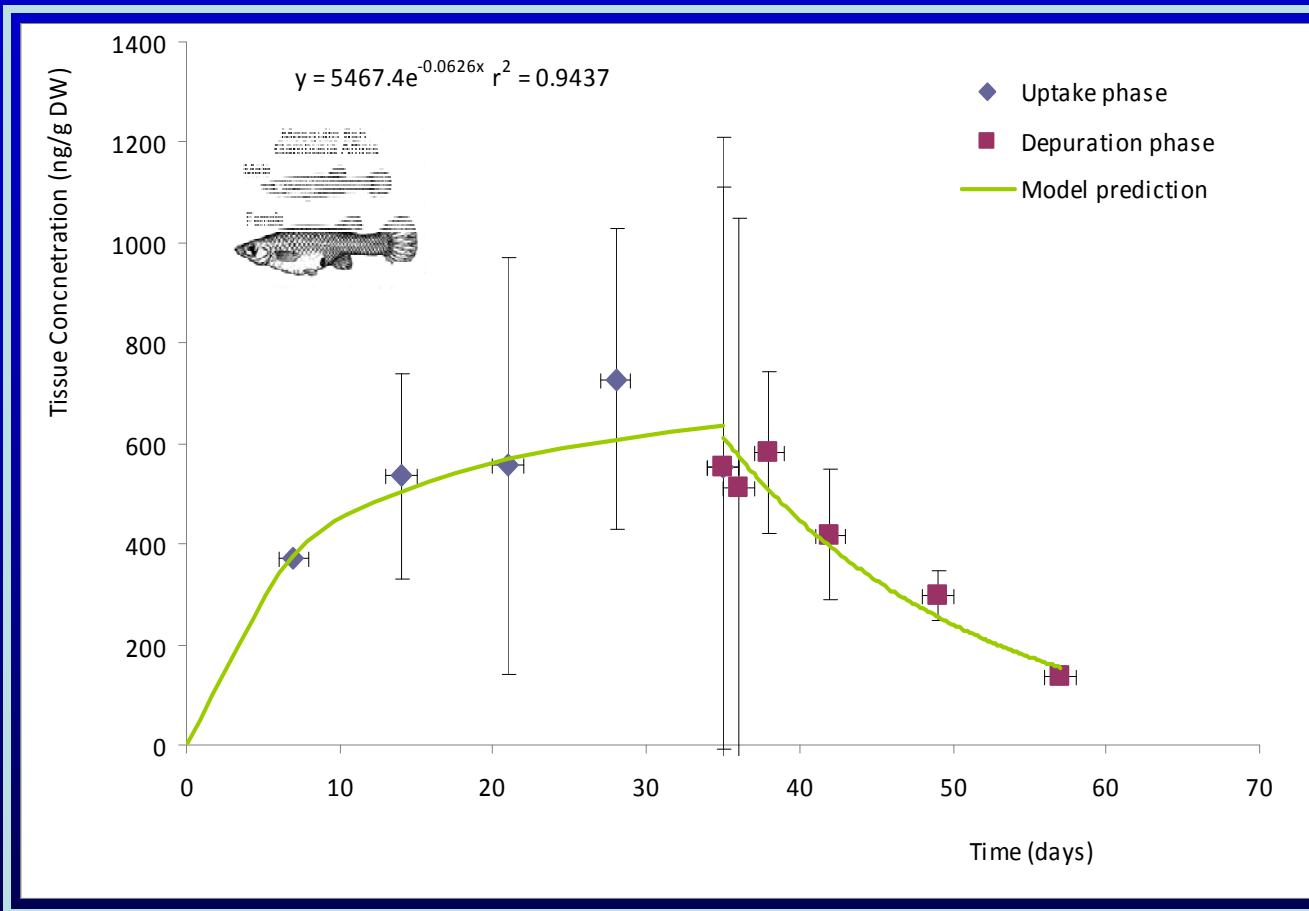


Bioconcentration in Fish? Only **ES** present in tissue



- Schimmel et al 1977
- Mullet (25 mm) *Mugil cephalus*
- Uptake and depuration from water at $0.0350\mu\text{g/L}$ for 28 days
- Commercial formulation (Thiodan)
- **Only ES accumulated**
- Edible ~Whole tissue
- Modeled **BCF 1622**
- Rapid elimination <48h

Depuration "fast" but data scarce...



- Sub-lethal exposure
- 90th centile
- 0.100 ug/L
- Endosulfan sulfate
- 35 days

$T_{1/2} = 11$ days

>>> 48 hours

Hoang et al., (2010) In preparation



Worst case scenario: Loveland Slough

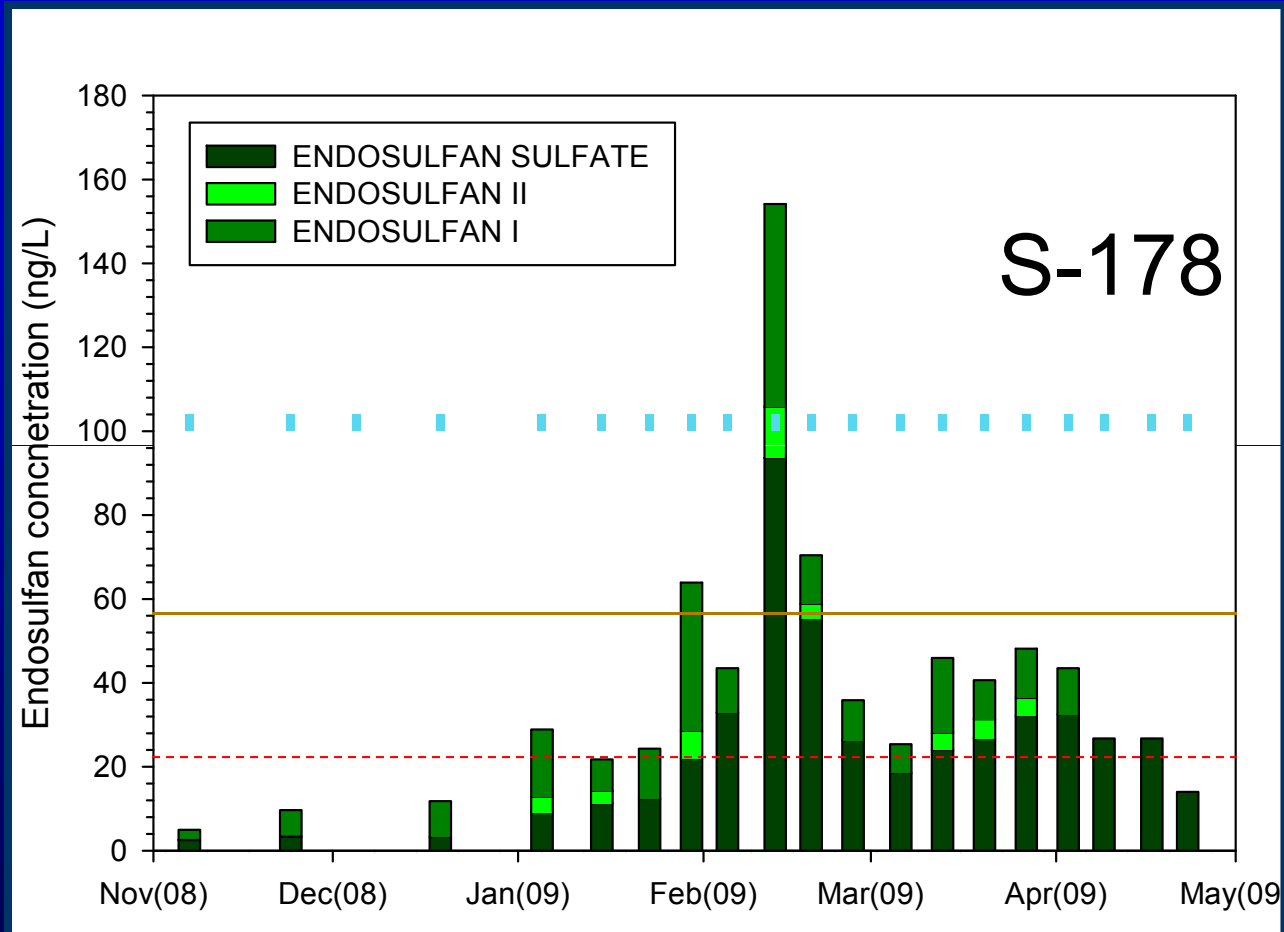


- Intensive
- Water
- Sediment
- Fish
- Benthic

- Endosulfan

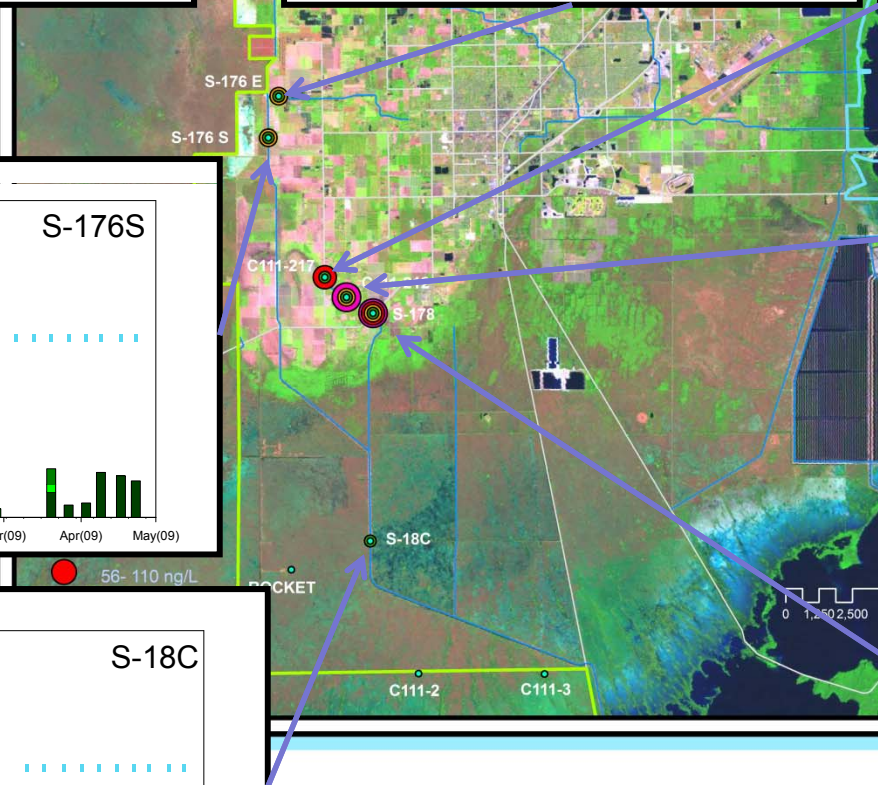
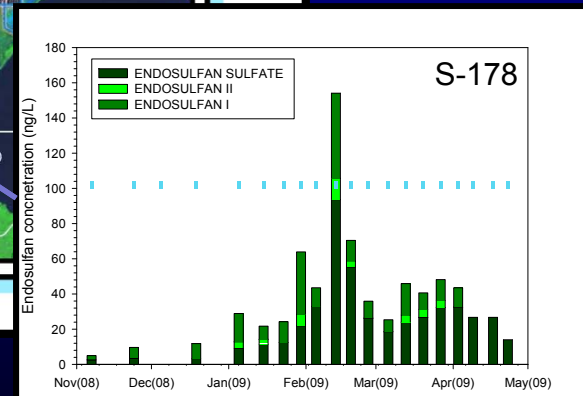
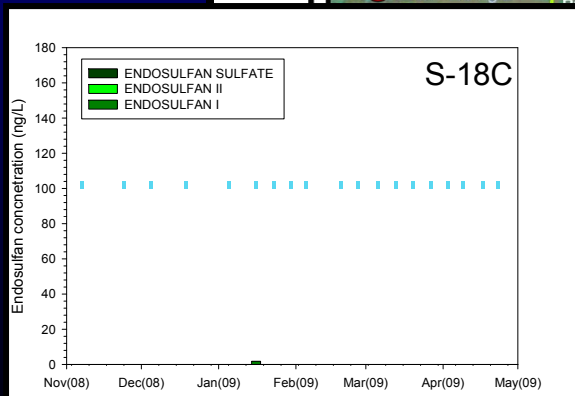
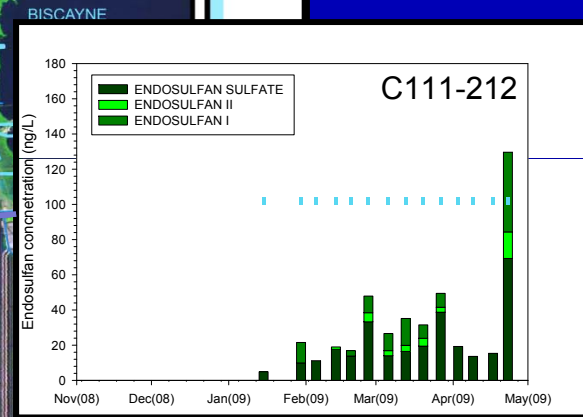
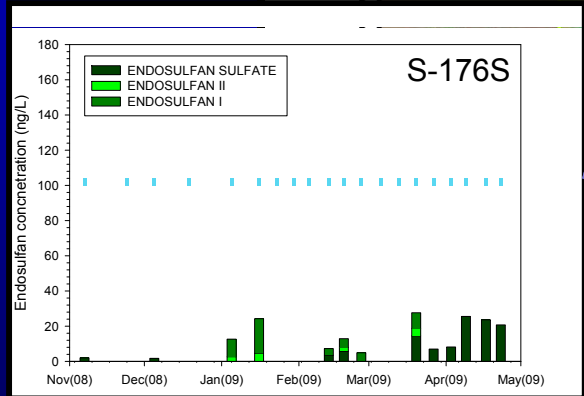
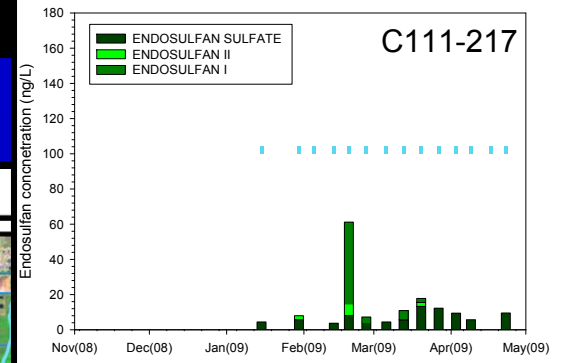
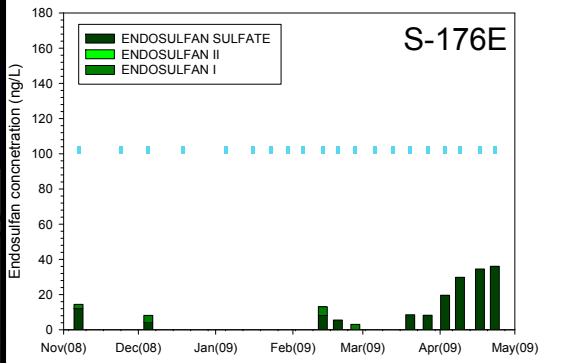
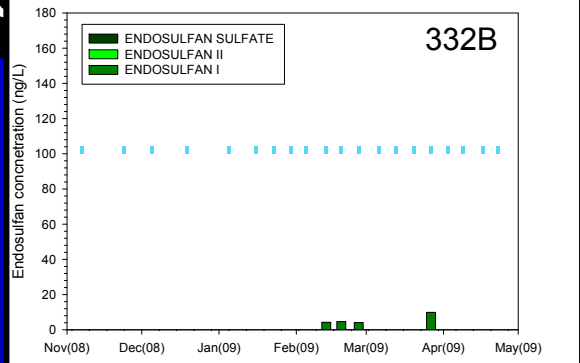


Surface water concentrations at S-178: Localized?



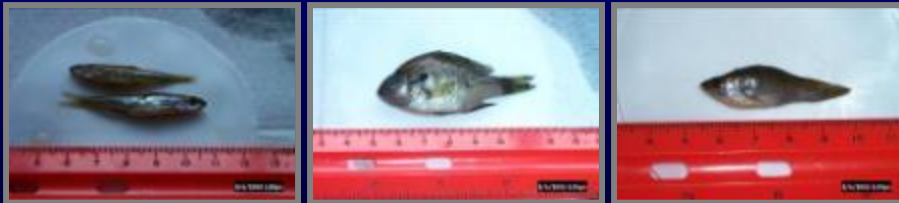
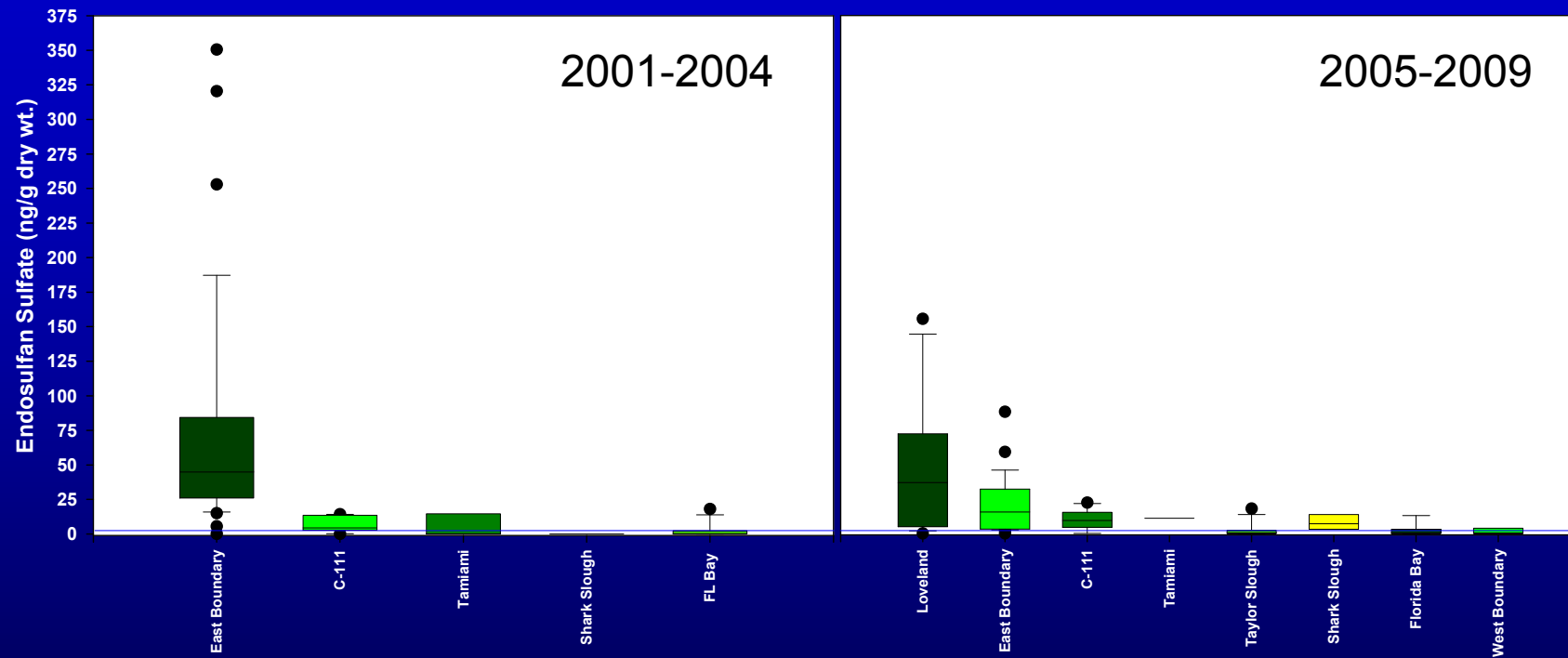
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BISCAYNE

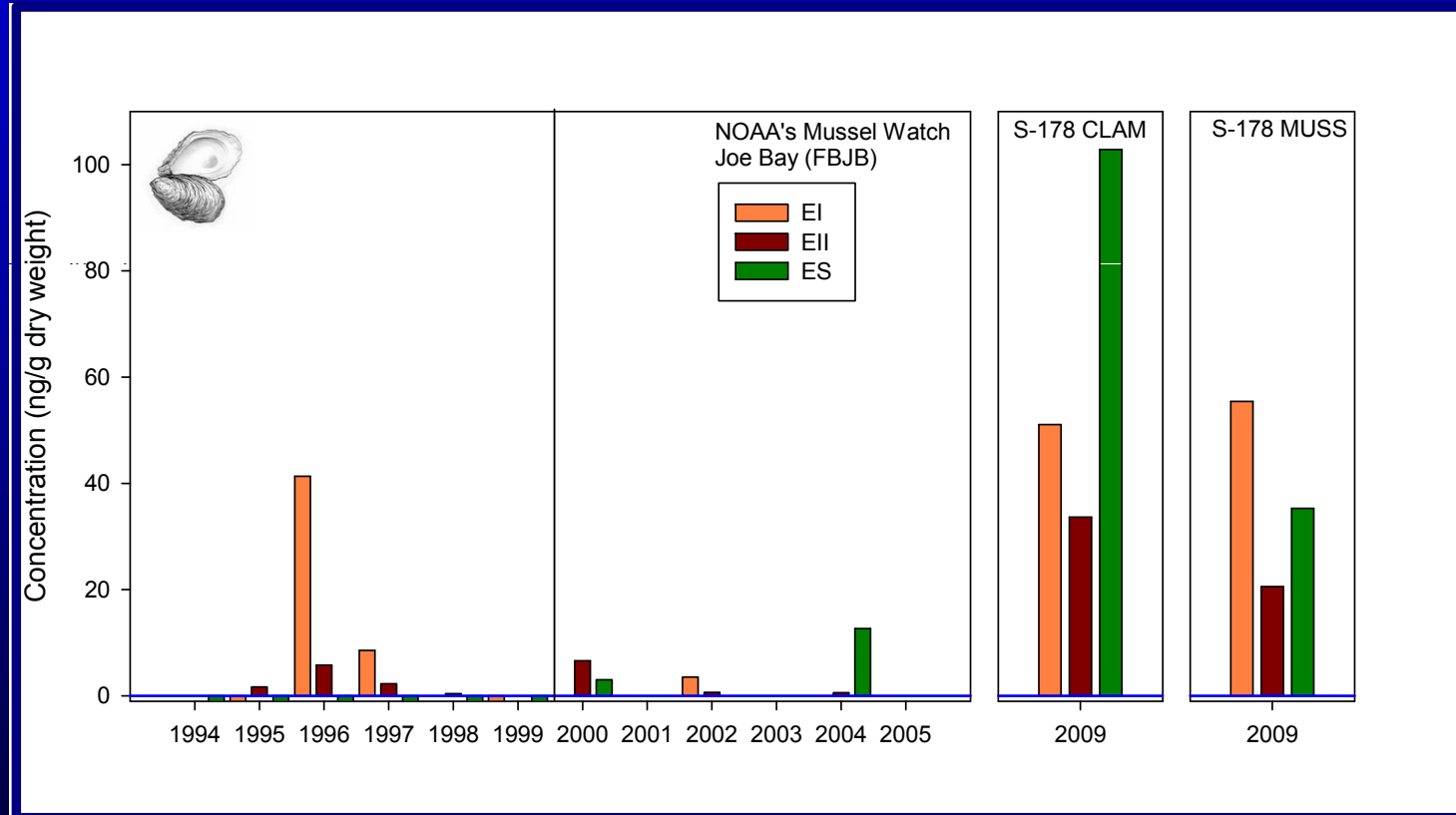
Residues in whole fish: Endosulfan sulfate ONLY



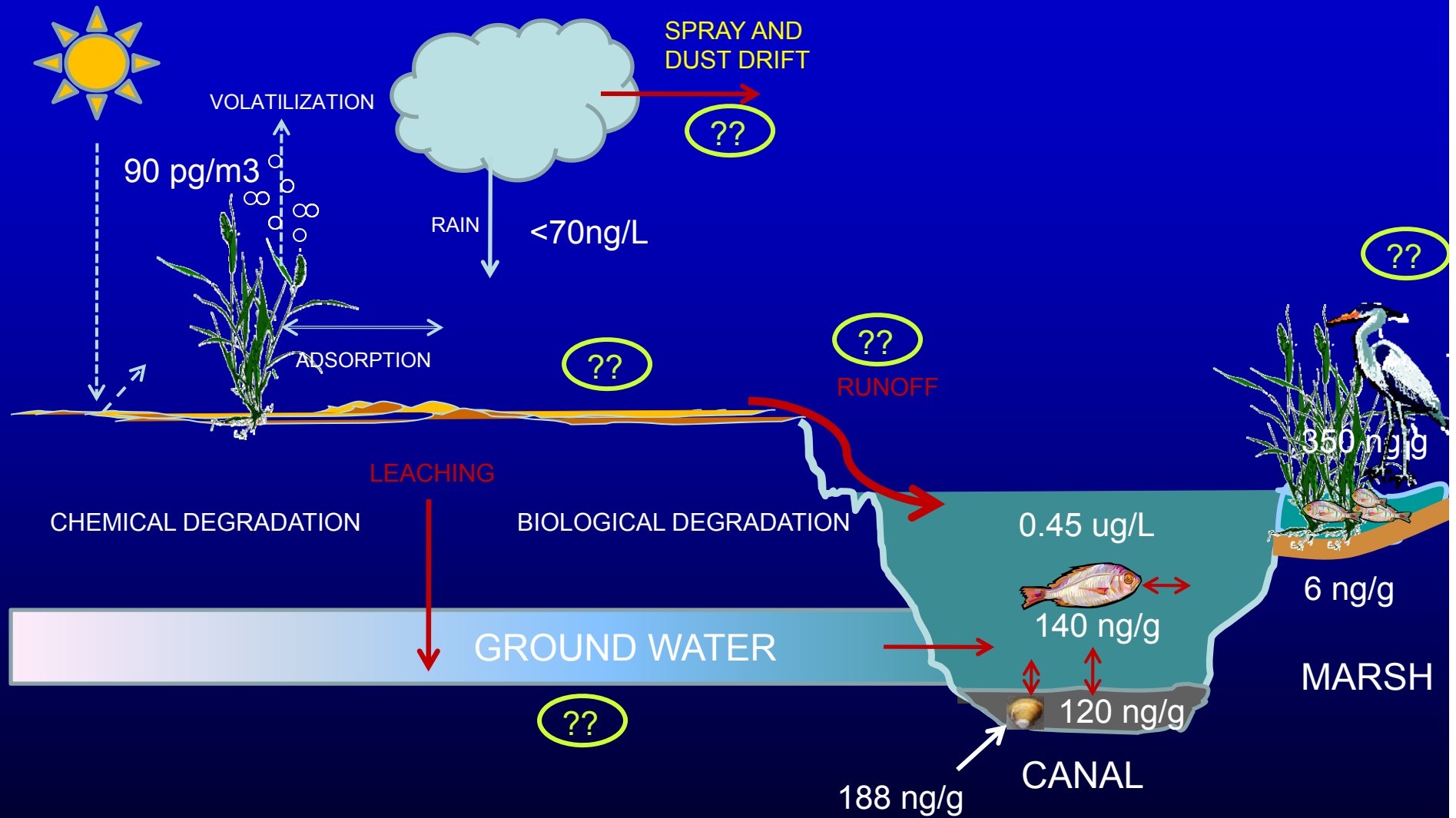
Distribution of fish concentrations



Other organisms?



Endosulfan Fate and Transport



A little conclusion slide...

EPA Moves to Terminate All Uses of Insecticide Endosulfan to Protect Health of Farmworkers and Wildlife

Release date: 06/09/2010

Contact Information: Dale Kemery kemery.dale@epa.gov 202-564-7839
202-564-4355

WASHINGTON – The U.S. Environmental Protection Agency (EPA) is taking action to end all uses of the insecticide endosulfan in the United States. Endosulfan, which is used on vegetables, fruits, and cotton, can pose unacceptable neurological and reproductive risks to farmworkers and wildlife and can persist in the environment...

For more information:

<http://www.epa.gov/pesticides/reregistration/endosulfan/endosulfan-cancel.html>



Another conclusion slide...

EDITION: U.S. | INTERNATIONAL | MÉXICO

CNN Health

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the chart

brain gallbladder stomach kidney small intestine

June 10th, 2010
10:57 AM ET

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EPA moves to ban DDT cousin



By David S. Martin
CNN Medical Senior Producer

Unacceptable neurological and reproductive risks to farm workers and wildlife have prompted the **Environmental Protection Agency** to move toward a ban of the insecticide endosulfan, the federal agency announced.

The United States would join the European Union and other countries already barring the use of endosulfan, a chemical cousin of DDT currently used on vegetables, fruits, cotton and ornamental shrubs, trees and vines.

Some 1.4 million pounds of **endosulfan** are used annually in the United States, according to the EPA.

Dr. Sanjay Gupta

f/u @candoorg pulled up a truck, filled it and took to orphanage. food was just sitting there - no distribution plan!

Updated: 11:44 pm UTC, July 12 2010

Twitter | Sanjay Gupta MD

Elizabeth Cohen

Whooping cough spreading in California - 5 babies die. What could have saved them? <http://bit.ly/cOgXai> #cnn

Updated: 1:58 pm UTC, June 28 2010

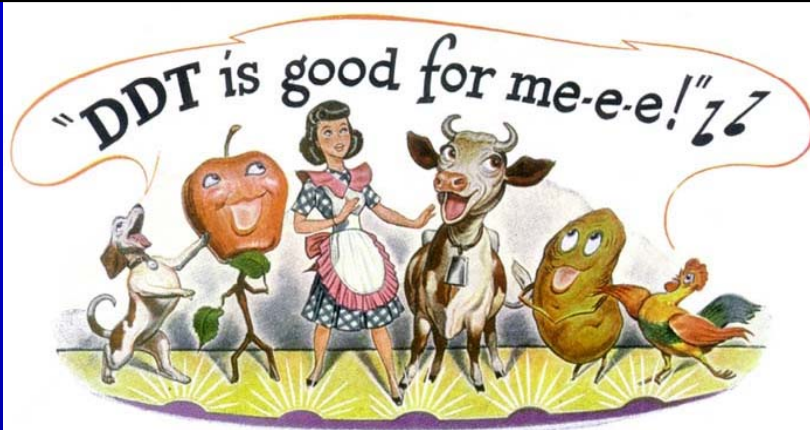
Twitter | Empowered Patient

About this blog

Get a behind-the-scenes look at the latest stories from CNN Chief Medical Correspondent, **Dr. Sanjay Gupta**, Senior Medical Correspondent **Elizabeth Cohen** and the CNN Medical Unit producers. They'll share news and views on health and medical trends - info that will help you take better care of yourself and the people you love.



But we have to be patient...



The great expectations held for DDT have been realized. During 1946, exhaustive scientific tests have shown that, when properly used, DDT kills a host of destructive insect pests, and is a benefactor of all humanity.

Pennsalt produces DDT and its products in all standard forms and is now

one of the country's largest producers of this amazing insecticide. Today, everyone can enjoy added comfort, health and safety through the insect-killing powers of Pennsalt DDT products . . . and DDT is only one of Pennsalt's many chemical products which benefit industry, farm and home.



GOOD FOR FRUITS—Bigger apples, juicier fruits that are free from unsightly worms . . . all benefits resulting from DDT dusts and sprays.



GOOD FOR STEERS—Beef grows meatier nowadays . . . for it's a scientific fact that—compared to untreated cattle—beef-steers gain up to 50 pounds extra when protected from horn flies and many other pests with DDT insecticides.



KNOX FOR THE HOME—helps to make healthier, more comfortable homes . . . protects your family from dangerous insect pests. Use Knox-Out DDT Powders and Sprays as directed . . . then watch the bugs "bite the dust"!



KNOX FOR DAIRIES—Up to 20% more milk . . . more butter . . . more cheese . . . tests prove greater milk production when dairy cows are protected from the annoyance of many insects with DDT insecticides like Knox-Out Stock and Barn Spray.

KILLING SALT
CHEMICALS

87 Years' Service to Industry • Farm • Home



GOOD FOR ROW CROPS—25 more barrels of potatoes per acre . . . actual DDT tests have shown crop increases like this! DDT dusts and sprays help truck farmers pass these gains along to you.



KNOX FOR INDUSTRY—Food processing plants—laundries, dry cleaning plants, hotels . . . dozens of industries gain effective bug control, more pleasant work conditions with Pennsalt DDT products.

Ban decree June 14, 1972

Enacted December 31, 1972

Last used in the US in June 1979

Produced until 1985 abroad

DDE still present in biota today

