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

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National Park Service – Cooperative Science

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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
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.

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
  - $\alpha$ Endosulfan is volatile
  - $\beta$ 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
GEER 2008: Endosulfan in Organisms FIU-ENP (Fish) and NOAA MW (Oysters)

Map provided by Max Feken
What criteria is available for management?

<table>
<thead>
<tr>
<th></th>
<th>Class I</th>
<th>Class II</th>
<th>Class III Freshwater</th>
<th>Class III Marine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Florida</td>
<td>≤0.056 µg/L</td>
<td>≤ 0.0087 µg/L</td>
<td>≤ 0.056 µg/L</td>
<td>≤ 0.0087 µg/L</td>
</tr>
<tr>
<td>Hawaii (1999)</td>
<td>Freshwater</td>
<td>Wildlife</td>
<td>Acute 0.22 µg/L</td>
<td>Chronic 0.056 µg/L</td>
</tr>
<tr>
<td>Hawaii (1999)</td>
<td>Saltwater</td>
<td>Wildlife</td>
<td>Acute 0.034 µg/L</td>
<td>Chronic 0.0087 µg/L</td>
</tr>
<tr>
<td>Colorado (1999)</td>
<td>Freshwater</td>
<td>Wildlife</td>
<td>Acute 0.11 µg/L</td>
<td>Chronic 0.056 µg/L</td>
</tr>
</tbody>
</table>

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

“Not all species behave the same way”

SSD 10th Centile = 0.11 µg/L

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?

**Bluegill sunfish**

LC$_{50}$ 3.8 µg/L (EPA 2007)

**Fathead Minnow**

LC$_{50}$ 3.4 µg/L (FIU)

**Mosquitofish**

LC$_{50}$ 4.7 µg/L (FIU)

- 10% Mortality
- 77 - 96 hours
- S-178
- 1.35ug/L

*Data generated at FIU

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

- Schimmel et al 1977
- Mullet (25 mm) *Mugil cephalus*
- Uptake and depuration from water at 0.0350μg/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

T½ = 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?

[Graph showing endosulfan concentrations from Nov(08) to May(09) with data points for endosulfan sulfate, endosulfan II, and endosulfan I.]
Residues in whole fish: Endosulfan sulfate ONLY

2001-2004

2005-2009
Distribution of fish concentrations
Other organisms?

NOAA's Mussel Watch Joe Bay (FBJB)

Concentration (ng/g dry weight)


S-178 CLAM

S-178 MUSS

NOAA's Mussel Watch Joe Bay (FBJB)

Concentration (ng/g dry weight)


S-178 CLAM

S-178 MUSS
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-fs.html
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.
But we have to be patient…

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