Endocrine Disruptors* in Florida Keys Waters

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What are Endocrine Disruptors anyway?

Where are they? I can't see them.

* Also termed Hormone Disruptors

1. Pictorial perspective, from 1980 to 2005

What happened?

2. Environmental Changes, not for the good

Disease, primarily coral, but also *Diadema* Loss of herbivory and biodiversity Climate change; temperature, acidification Overfishing, overuse Presence of human generated pollutants Endocrine disruptors (Stealth Pollution) Effects and possible effects of EDs

3. What can we do about it?





































The question is----

What happened?



Coral cover in the Keys declined from 50% to less than 10% in the last 35 years.



Coral disease and bleaching



¹⁹⁸⁰ Loss of herbivory



The Great Plague of 1983





Climate change; bleaching, acidification



Overfishing, overuse





Pollution! (You know it when you see it.)

But sometimes you can't see it.... or smell it, or taste it, and the damage it does can be hidden for years.



Endocrine Disruptors – (Stealth Pollution)

What are Endocrine Disruptors?

An endocrine disruptor is an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism or its progeny or (sub)populations.

A chemical that prevents the normal activity of reproductive and developmental hormones, to a greater or lesser extent, in plants and animals.

A potential endocrine disruptor is an exogenous substance or mixture that possesses properties that might be expected to lead to endocrine disruption in an intact organism, or its progeny, or (sub)populations.

A chemical that could be, probably is, an endocrine disruptor with the affects attributed to endocrine disruptors.

Over 800 chemicals have been identified as endocrine disruptors.

There are very few studies on the effects of endocrine disruptors on marine aquatic organisms, especially invertebrates.

Sources of endocrine disruptors in marine environments

Stormwater runoff, septic systems, ocean outfalls, boat discharge, construction waste, agricultural runoff, industrial discharge, industrial spills, oil spills, rivers, basically any effluent from our affluent society.

Endocrine disruptors come from chemicals and their derivatives found in:

Herbicides (Roundup!), pesticides, some fertilizers, insect repellents, sunscreens, fragrances, household chemicals, human and veterinary pharmaceuticals, heavy metal compounds including mercury, anti-fouling paints and compounds, anti-inflammatory drugs, antibiotics, birth control hormones, and many other drugs, Beta-Estradiol and Estrone, components of human estrogen hormones, and plasticizers like Bisphenol-A, PCBs Alkylphenols, phthalates, PVC products, atrazine, and many other chemicals

Endocrine disruptors are biologically active at PPM, PPB, PPT, even PPQ.

The theory that EDs could be disrupting hormone activity in aquatic and terrestrial animals was first published in 1992.

It is an absolute certainty that endocrine disruptors are present in Florida Bay, our canals, and the near shore waters of the Florida Keys, as well as in all other aquatic ecosystems of our planet. What is not known is what chemicals are present, in what concentrations, and at what times, and most important, what effects, if any, do these chemicals have on the presence and development of aquatic life in our waters. (Moe, CORAL magazine, Jan/Feb 2012)

Why am I so sure that there are endocrine disruptors in the waters of the Florida Keys?

How could endocrine disrupting chemicals get into the waters of the Florida Keys?

Gulf Coast Rivers

Mississippi **Alabama River** Escambia Chipola Apapachicola **Ochlockonee** Suwanee Withlacoohee Crystal Weeki Wachee **Kissimmee** Hillsborough Alafia Manatee Peace **Caloosahatchee** Shark

Miami River and ocean sewer outfall about 195 million gallons per day

Caribbean water flow

The big picture

ED contributions can come from middle America, West and South Florida, and even as far away as the Amazon River. Atrazine was banned in the European Union (EU) in 2004 because of its persistent groundwater contamination. In the United States, however, atrazine is one of the most widely used herbicides, with 76 million pounds of it applied each year, in spite of the restriction that used to be imposed. Its endocrine disruptor effects, possible carcinogenic effect, and epidemiological connection to low sperm levels in men has led several researchers to call for banning it in the US.



How could endocrine disrupting chemicals get into the waters of the Florida Keys?

Everglades and South Miami/Dade agricultural and urban runoff

Keys sewer and land runoff Canal sediment accumulation Upwelling from groundwater?

ants

The local picture

South Florida, agricultural runoff, Keys wastewater and land runoff

Lower Matecumbe Key, 2007

The Gulf of Mexico receives much of the waste of the United States, Mexico, and the Caribbean, and much of this journeys by and through the Florida Keys.

Florida Bay is a sink for nutrients, toxic chemicals, and endocrine disrupting chemicals.





Endocrine disrupting chemicals eventually bind to organic and inorganic molecules and become part of the benthic sediments. There they can impact organisms that live in and feed on sediments. But do they stay in these sediments?



But when the winds blow, as they often do, the waters become murky with sediments lifted off the shallow bottoms.

The Keys are known for their calm. clear inshore waters.



You said this on slide 26, so is there any evidence or indications that there are endocrine disrupting chemicals in our waters?

What is not known is what chemicals are present, in what concentrations, and at what times, and most important, what effects, if any, do these chemicals have on the presence and development of aquatic life in our waters.

Ahh, you're paying attention. I'm glad you asked.

We can't find what we don't look for!

I'll run through a few reasons that are compelling to me.

Chemical Studies

Ogden, et. al., 1974. Significant levels of DDT, arsenic , and methylmercury were found in the tissues of Everglades fish, invertebrates and birds.

Scott, et. al., 2002. The waters of the C-111 canal and north Florida Bay were tested for pesticides. The pesticide endosulfan (an endocrine disruptor) was found in 100% of the samples.

Gardinali, 2011. Peiro Gardinali (UM) found insect repellents, sunscreens, fragrances, plasticizers, human and veterinary pharmaceuticals, anti-inflammatory drugs, antibiotics, birth control hormones and many other drugs. Endocrine distuptors in this witch's brew include Beta-Estradiol and Estrone, components of human estrogen hormones, and Bisphenol-A, a plasticizer, among others. Many microconstituent endocrine disruptors can survive existing waste water treatments and move through underground waters into freshwater and marine environments. They are present in the Miami River and in the Port Largo Canal on Key Largo. Working with the African clawed frog, Hayes and his colleagues showed in 2002 that tadpoles raised in atrazinecontaminated water become hermaphrodites -- they develop both female (ovaries) and male (testes) gonads. This occurred at atrazine levels as low as 0.1 parts per billion (ppb), 30 times lower than levels allowed in drinking water by the EPA (3 ppb).

On Wednesday, Oct. 11, 2007 the U.S. Fish and Wildlife Service announced that it would not protect the northern leopard frog under the Endangered Species Act. Hidden in that announcement was the admission, however, that pesticides (particularly atrazine) "has likely contributed to northern leopard frog population extirpations throughout their range." Atrazine, the most frequently detected pesticide overall, was detected in about 90 percent of all samples. The other most frequently detected pesticides overall were metachlor, simazine, tebuthiuron, norflurazon, bromacil, and diuron.

Southern Florida surface waters U.S. Geological Survey Circular 1207

Todd J. Janzen, Partner, Plews Shadley Racher & Braun LLP 01/31/2013 12:12:57 PM EST A class action lawsuit alleging that the herbicide Atrazine contaminated various Midwestern water supplies has been settled. As part of the settlement, Syngenta Crop Protection, Inc. (Syngenta), the maker of Atrazine, has agreed to pay \$105 million to over 1100 class members, consisting of water utilities across the Midwest.

Mercury as methylmercurcy

The Perfect Environmental Storm!

Mercury from aerial deposits and sulfate (reduces to sulfide) from agricultural runoff combine in the sediments to form methylmercury.



PERCENTAGE OF METAL EXCEEDANCES OF BACKGROUND COMPARISON LEVELS AT WATER CONSERVATION AREA

| Monitoring Sites | LOX8 | LOX10 | WCA2F1 | CA215 | CA33 | CA315 |
|------------------|------|-------|--------|-------|------|-------|
| Arsenic | 33 | 25 | 100 | 100 | 17 | 100 |
| Cadmium | 10 | 10 | 10 | 10 | 0 | 0 |
| Chromium | 8 | 17 | 17 | 17 | 0 | 0 |
| Copper | 100 | 100 | 82 | 82 | 36 | 91 |
| Lead | 100 | 100 | 83 | 92 | 50 | 92 |
| Mercury | 100 | 100 | 100 | 100 | 100 | 100 |
| Nickel | 83 | 92 | 83 | 83 | 0 | 92 |
| Silver | 27 | 30 | 18 | 33 | 0 | 25 |
| Zinc | 92 | 67 | 69 | 50 | 0 | 92 |

Note: Monitoring Sites: LOX8 and LOX10 are in WCA-1/Arthur R. Marshall Loxahatchee National Wildlife Refuge (LNWR); WCA2F1 and CA215 are in WCA-2A; and CA33 and CA315 are in WCA-3A

Florida Department of Environmental Regulation. 2002. Development of an Interpretive Tool for Assessment of Metal Enrichment in Florida Freshwater Sediment. Tallahassee Fl. Peter Frederick, an ecologist at the University of Florida, Gainesville, and his colleagues collected 160 white ibis nestlings from breeding colonies in south Florida in 2005, and split them into four groups, each composed of 20 males and 20 females. Once the birds were 90 days old, the researchers began adding methylmercury to their feed. Three of the groups were given low, medium or high doses of mercury based on levels ranging from 0.05–0.3 parts per million recorded in the wild, while the fourth group were given no mercury.

The team found that the levels of mercury built up in the birds over time, and that exposure resulted in roughly 13–15% more nests failing to produce any offspring. A high proportion of these failed nests were found to be male-male pairings.



Boring worms, tube worms, barnacles, algae, corals, bacterial slime, bryozoans, oysters, other mollusks, polychaete and other tube worms, are among the 1700 species of organisms responsible for fouling the bottoms of boats large and small. This is not good for boats and boaters.

So we paint the bottoms of boats with highly toxic antifouling paint (new methods for controlling bottom fouling are being developed).

We spend more then 5.7 billion \$ each year to prevent and control biofouling on ships and boats. Problem solved, or at least contained.

Most current antifouling paints contain copper or zinc. Tributyltin (TBT), highly toxic, removed from common use in 1988, but is still used on commercial and naval vessels, and widely used in India and China.







Pseudo Persistence (temporal accumulation)

Sunscreen and bottom paint

UV filters in chemical sunscreens (found in urine and breast milk)

benzophenone-3 (BP-3) 3-benzylidene camphor (3-BC) 3-(4-methyl-benzylidene) camphor (4-MBC) 2-ethylhexyl 4-methoxy cinnamate (OMC) Homosalate (HMS) 2-ethylhexyl 4-dimethylaminobenzoate (OD-PABA) and 4-aminobenzoic acid (PABA)

Bottom Paint (active ingredients commonly copper and zinc)

Tributyltin (not legal) copper and zinc compounds chemical biocides Econea (Tralopyril -- 2-(p-chlorophenyl)-3-cyano -4-bromo-5-trifluoromethyl pyrrole) pesticide, molluscicide

Macro and micro plastic pollution





Nurdles

Macro

Micro



Dr. Charles Manire of the Mote Marine Laboratory and colleagues studied the reproductive abnormalities in this small species of shark in 1998 through 2001. Because of their persistence in marine environments, organochlorine compounds from pesticides are persistent in marine environments and pose significant health risks to marine organisms.

Quantifiable levels of PCBs and 22 organochlorine pesticides were detected in livers of 95 bonnethead sharks from Apalachicola Bay, Tampa Bay, and Florida Bay.

Unfertilized ova were found 75 percent of pregnant females. Low sperm viability was also found.



Bonnethead shark, Sphyrna tiburo,



Possible effect of ED pollution in Caribbean corals



Near ready Acropora coral eggs from Ken Nedimyer's farmed corals

The iconic Queen Conch, Strombus gigas

Extensive research by Robert Glazer, and Gabriel Delgado of the FWRI laboratory and eight other scientists resulted in a study that implicated zinc and possibly copper in the reproductive failure of near shore queen conch.

"This study supports the hypothesis that heavy metals may contribute to the reproductive failure of NS conchs. Zn and possibly Cu are elevated in the NS conch digestive gland, and Zn may be elevated in the testis. Given that Zn and Cu are known to reduce gastropod fecundity, the possibility that these same metals may also inhibit gametogenesis in both males and females merits further consideration."

Queen Conch (*Strombus gigas*) Testis Regresses during the Reproductive Season at Nearshore Sites in the Florida Keys Daniel J. Spade¹, et. al. PLoS ONE 5(9): e12737. doi:10.1371 Published: September 15, 2010

But, it's complicated...



From the published queen conch studies...

Estradiol and ethynylestradiol (EE2) were found in measurable quantities both offshore and nearshore. This implies that sewage enters the offshore zone because EE2 is a synthetic estrogenic prescribed for birth control in humans.

Because a component of reproduction in marine gastropods appears to be neurologically controlled by the gonads, estrogen or estrogen-like compounds in the environment may have no effect on their reproduction. However, the estrogenic compounds that we found should be considered a warning flag for the overall health of the Florida Keys ecosystem. Many species other than marine gastropods, including fish and other invertebrates (e.g., scallops) do respond directly to exogenous sources of estrogen and phenolic compounds by producing Vtg, and are likely to be sensitive to these contaminants (Castro et al., 2007; Bannister et al., 2007; Iguchi et al., 2007; Köhler et al., 2007). This has implications for the healthy function of the Florida Keys marine ecosystem.

Diadema antillarum, the long spined sea urchin of the coral reefs



Spawning is not a problem, well... not a big problem.

Larval development, settlement, metamorphosis and juvenile survival All stages are susceptible to developmental endocrine disruption

















Also of note and worthy of wonder:

Stone crabs: "Worst season we've ever seen," said Candice Jolly, manager of City Seafood in Everglades City, Stone Crab Harvest Down, Prices Up, CBS 4, Miami, March 24, 2013 2:03 PM

Shrimp: Shrimpers enduring abysmal season in Biscayne Bay, Susan Cocking, Miami Herald, March 24, 2013

Lobster: "It was one of the worst seasons I have ever seen." Gary Nichols, Keys fisherman, Lousy lobster season comes to an end, Free Press, April 3, 2013

Sea Urchins: In January and February, 2013, the crafty ladies of Lower Matecumbe collected many intact sea urchin tests in the weed wrack on Sea Oats beach. The tests were intact so predation could not be the cause of the mortality. In this one basket there are three species, one *Diadema*, and then many *Tripneustes* and *Lytechinus*.



Solutions to the problem of endocrine disturbers in our waters Research (Identifying the problem(s) comes before solution)

What is in our waters, when is it there, what does it do?

How does it get in our waters, how can we keep it out of our waters?

Education (Knowledge is necessary before action)

Local education for residents and visitors commensurate with the urgency of the problem.

National education, not just for human developmental concern but also for environmental concern.

Legal

It should not be legal to release endocrine disrupters into our environment.

The biggest problem is not what we have already put into our waters, but what we continue to pour into them at an ever increasing rate.

THE REEF & MARINE AQUARIUM MAGAZINE

Coral Culture

- Keeping Rhinopias
 Biopellet Guide
- Reefs of the Maldives

JAN/FEB 2012 U.S. \$7.99

VIEW POINT

by MARTIN A. MOE, JR.

Endocrine disruptors: on finding invisible pollution in my backyard

Mother Earth went to the doctor for her 50,000-year checkup. The doctor sat her down in his office afterward and said, "Well, I have some bad news. You have an unnatural cancer in all your oceans and waters. I know you feel good now, at least reasonably good, considering everything, but if we don't take care of this very soon you will become crippled and much of the life you have created may even disappear. Your cancer is the unchecked accumulation of endocrine disruptors."

> "Oh, my God, Doc, I bet that's the cause of the nausea I feel in my plankton," responded Mother Earth. "Most likely so," said the doctor. "This is a root-of-life problem, and its effects are spreading up your food chains. Unless we get this under control soon, there is the real possibility that your ecosystems will change drastically, and your intelligent life, unique in your solar system, will decline and regress into famines and wars." Mother Earth got up to leave and said, "I'll do my best, Doc, but those dumb humans had better get their act together. What they have done to me in the last 100 years is criminal, even if they didn't know what they were doing."

> e can see and smell what we know is pollution and the results of pollution, including oil, sludge, black water, hydrogen sulfide, plastic and other debris, dead fish, sick birds, algae blooms, and trash on our beaches and reefs. But there is a great load of chemicals, natural and manmade, created by our advanced civilization that have been accumulating in our environment, most in extremely small concentrations, for many years. These invisible chemicals are dissolved in water in very low concentrations and escape our notice—and usually our concern. Some are considered harmless, some beneficial (especially the natural ones), but many of them are suspected or known to be endocrine disruptors.

WHAT ARE ENDOCRINE DISRUPTORS?

Endocrine disruptors are substances that can interact with all the normal biological processes of life that depend on hormone activity. However, those that affect the hormone receptor

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CORAL magazine, January/February issue, page 30



broodstock in his home breeding lab on Lower Matecumbe Key, Florida.

The author

with sea urchin

Questions and Discussion

In the Florida Keys alone, tourism generates over \$1.2 billion annually with coral reefs being the primary attraction." (Mote Marine Laboratory) So how much do we invest in protection and restoration of our coral reefs and near shore marine environments?

At this point, all things considered, not enough.....