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The Crest

Current Issues in Coastal Ocean and Estuarine Science

TBT or not TBT: Collaborators Search for a Solution to Pollution

By Dave Malmquist

Just how little is one part per trillion? "That's a single drop in 1 million 55-gallon drums," says VIMS researcher Dr. Mike Unger.

That might not seem like much, but for a substance like tributyl tin, or TBT, a concentration of 1 part per trillion (ppt) can significantly affect the health of marine organisms.

Unger is collaborating with Dr. Gary Schafran of Old Dominion University to help lessen TBT's environmental impacts by developing a mobile treatment plant to keep the compound from entering seawater.

TBT is used in boat paint to prevent fouling by marine organisms. It enters seawater through leaching and when a ship's hull is washed or its old paint removed. The compound remains toxic to marine organisms even at extremely low concentrations.

"Most environmental contaminants are toxic at parts per million, sometimes parts per billion," says Unger. "What's dramatic about TBT is that we see fairly significant environmental effects at concentrations as low as 1-10 parts per trillion."

The TBT treatment plant resides on a barge that can be moved between dry docks as needed.

Exposure to TBT at these concentrations has been linked to molting problems in copepods and to imposex in marine snails, a condition in which females develop male sex organs. At higher concentrations, say 100 ppt, experiments show that exposure to TBT will kill half a group of exposed organisms within a few days. Affected species include oysters, clams, and mussels.

Concern over these environmental effects has driven regulation of TBT worldwide. Virginia has enacted some of the world's most stringent TBT legislation. In 1987, the Commonwealth set a TBT water quality standard of 1 ppt, and, based on research showing

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Switch to Circle Hooks Would Benefit White Marlin

On-going studies by VIMS researchers suggest that a minor change in hook type could significantly improve the survival rate of white marlin released by recreational anglers.

Voluntary catch and release efforts by U.S. recreational anglers are one small part of an international effort to help conserve white marlin stocks. Scientists consider white marlin the most depleted billfish species in the Atlantic, with a population at less than 10% of its original level. Most white marlin mortality occurs as incidental catch on longline gear set for tuna and swordfish.

The VIMS studies, conducted by Dr. John Graves and his graduate student Andrij Horodysky, found that white marlin caught on traditional straight-shank "J" hooks were far less likely to survive a catch-and-release episode than those caught on circle hooks (see sidebar on page 2).

"There's a greater incidence of deep-hooking and tissue trauma associated with "J" hooks," say Graves. "Fish caught on circle hooks are more likely to be hooked in the jaw and less likely to incur serious injury."

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the highest TBT levels in recreational boating areas, banned its use on vessels shorter than 25 meters. The Virginia ban mirrored similar regulations passed earlier in France, the U.K. and by the U.S. federal government.

But TBT use continues on larger vessels, and for good reason. Application of TBT helps save fuel by reducing the drag generated when organisms like barnacles, mussels, and algae attach to a ship's hull. "The cost savings are phenomenal," says Unger. "Fouling organisms on a hull translates to fuel and pollution. That's why commercial ships, cruise ships, love it. They want their ships to be as fast as possible. Everybody does."

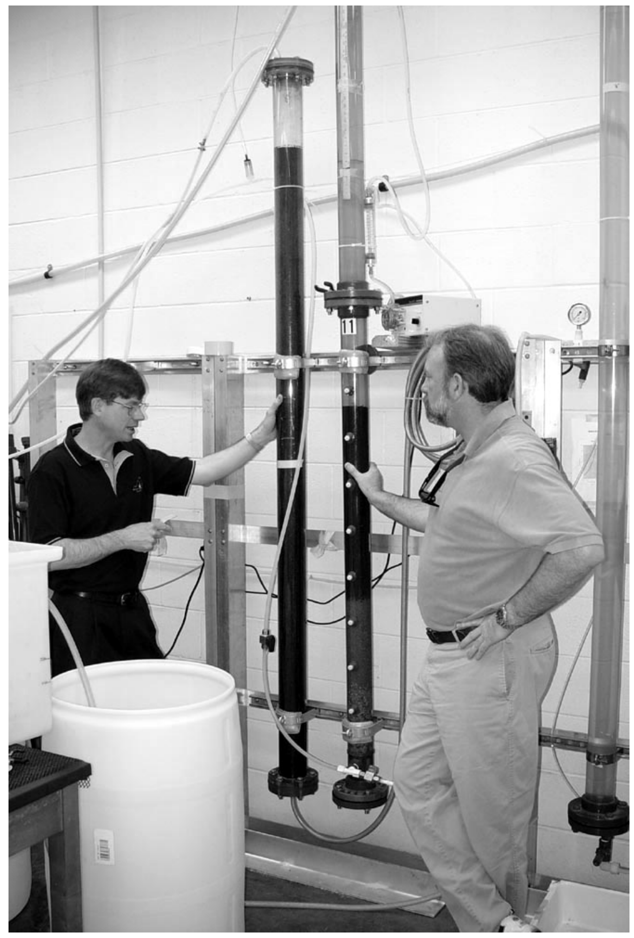
The advantages of TBT help explain why 70% of ocean-going vessels still use TBT paints. But continued widespread use of TBT, coupled with increasingly strict regulations (including a proposal by the U.N.'s International Maritime Organization to ban the release of TBT from any size vessel by 2008), has put local shipyards between a rock and a hard place.

"Therein lies the problem," says Unger. "You've got a water quality standard of 1 ppt, you've got shipyards that are in the business of servicing vessels, and you've got 70% of the merchant marine painted with TBT paint. Even if you're not going to paint with TBT again, you still have to get the old paint off."

Repainting a 900-foot long ship can produce up to 400,000 gallons of wastewater, with TBT concentrations a million times higher than the 1-ppt water quality standard allowed in Virginia.

Schafran began searching for a solution to the wastewater dilemma in 1998, when approached by representatives from the Center for Advanced Ship Repair and Maintenance, a Hampton Roads non-profit set up to encourage collaboration between Virginia's shipyards and universities.

The Center had begun with a literature search to see what had previously been done with TBT. "There were hundreds of papers on TBT's biological effects," Schafran says, "but only a handful dealt with treatment issues, and really none of them were relevant to shipyards, their wash waters, and their situations. There wasn't a single paper that addressed getting TBT out of waters where it was at a million ppt."



Drs. Gary Schafran (L) and Mike Unger inspect columns of activated carbon like those used to remove TBT from shipyard wastewaters.

To do that, Schafran spent the next few years developing a system of mechanical and chemical filters in collaboration with local shipyards. A key part of the system is a series of long tubes filled with activated carbon, the same material used to filter drinking water and home aquariums. Mounted on a barge, the mobile treatment plant can be towed to an active dry dock, where it helps removes TBT from wastewaters before they are released to the environment.

Early trials showed that the treatment plant could remove 99.8% of TBT from shipyard wastewaters. "From an engineering standpoint, that's phenomenal," says Unger. "But when you're starting with a part per million and you've got to get down to a few parts per trillion, you're not even close. That kind of puts the magnitude of the problem in perspective."

Treatment success was also inconsistent and difficult to predict. It depended not only on the initial concentration of TBT in the wastewater, but on the water's salinity, pH, and the presence of dissolved organic carbon. Effluent from the treatment plant might contain 20 ppt of TBT for half an hour, then suddenly spike up to 200 ppt. It achieved the 50 ppt level necessary for permits only 25% of the time.

To consistently achieve the additional removal needed to meet water quality standards, Schafran realized he had to better understand the intricacies of the treatment process. "Our focus was on the engineered system," he says. "We pretty regularly got 99.8% removal, but that's not good enough. So we wanted to know, 'Why isn't it good enough? Why does it sometimes work and sometimes not?' We needed a mechanistic understanding of what was going on."

That's when Schafran approached Unger. Unger studies the behavior of TBT in the environment, and thus has the expertise, methods, and instruments needed to identify and track TBT and related compounds at exceedingly low concentrations.

Schafran suspected that TBT-laden particles of activated carbon might occasionally break free to produce the TBT spikes he saw. Unger is testing this idea by using X-rays to analyze wastewater samples under a scanning electron microscope. Early results suggest that the water does indeed contain carbon particles, but that the tin is not associated with the particles. Instead, it appears to be dissolved in the wastewater itself.

Related experiments suggest that increasing the acidity of the wastewater increases the carbon's removal efficiency. They also show that dissolved organic carbon, which forms in wastewater when fouling organisms are washed or scraped off a ship's hull, may compete with the activated carbon to absorb TBT, thus decreasing its effectiveness.

Determining the chemical form of the dissolved tin is another crucial step in the analysis. "There's an orders of magnitude difference in toxicity between TBT and its breakdown products," says Unger. Thus the treatment process could reduce the environmental impacts of TBT even if it did not completely remove all the tin-bearing compounds. Degrading the original TBT to a less toxic form would also have value.

Unger uses a device called a gas chromatograph to determine the composition of the dissolved tin compounds in wastewater. This allows him to test the effectiveness of various methods for degrading TBT.

To date, two methods appear particularly promising. One is to expose wastewater to ultraviolet light after adding hydrogen peroxide. UV treatment has the added benefit of destroying many other organic contaminants that occur in the wastewater. Schafran plans to add a full-scale UV device to the end of the existing treatment plant at shipyards this July.

Schafran and Unger discovered the second option, treatment with bacteria, through a mixture of hard work and serendipity. One thing Schafran needed to know when designing his original treatment plant was how long the activated carbon would absorb TBT before it became saturated. Based on previous work, he thought it would take a few weeks. Instead, like the Energizer bunny the carbon just kept working. "We kept running it and running it and getting 99^{+}% removal continually, for 9 months," says Schafran.

Puzzled, Schafran invited Unger to his lab. During the visit, the pair noticed a pink coating inside the tube leading from the carbon filter. "I think you have bacteria growing in there," said Unger. "It was like, wow!" says Schafran. "I guess the TBT isn't too harmful for this bacteria! Somebody's eating it." An ODU biologist later confirmed that two species of bacteria were living in the tube.

Unger is now analyzing the bacteria to confirm that they are indeed accumulating or absorbing tin. "This is pretty wild stuff," says Unger. "Although we don't think it's a viable technique to treat the water, it may have other applications in terms of treatments of solids. What are you going to do with TBT-contaminated dredge spoils, things like that? We're hoping that it may be another avenue for research."

"To me, the really zippy part of the project is to use things that we've learned about here at VIMS to try answer an applied engineering question," he says. "I think the public perception is often that scientists are good at finding problems, but not so good at finding solutions. I think we have a responsibility to apply the techniques we use to answer basic science questions to help solve problems. Here's a case where we've been successful at that."

Funding for the pair's collaborative research comes from NOAA's Sea Grant program. To read an enhanced version of this article, visit www.vims.edu/newsmedia/topstories