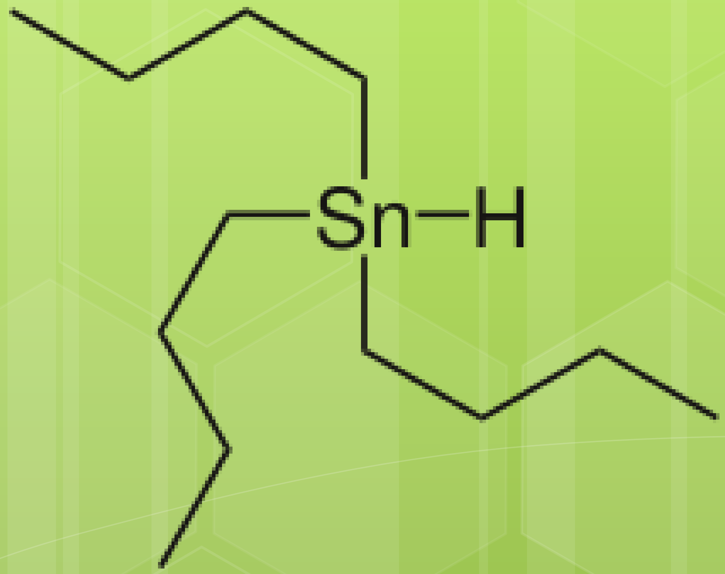

Innovative Chemical Treatment of TBT (Tributyltin)-Impacted Marine Sediments: A Bench Scale Study

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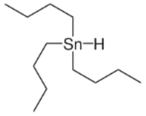
OVERVIEW

This presentation will focus on a novel chemical REDOX (reduction/oxidation) approach for the treatment of Tributyltin (TBT), and its anlogs present in contaminated marine sediments.

TBT has been used globally since the 1950's as an inexpensive biocide and antifouling agent in marine paints to minimize aquatic organisms, such as barnacles and algae, from adhering to the hulls of ships.



Fouling = Increased Fuel Consumption

- In order *to compensate for over a one knot speed loss due to hull fouling*, the crew had to *apply more throttle to achieve its normal mission spee*d, resulting in additional power and fuel consumption.
- *Fuel was being wasted due to the 35% extra power required to maintain the ship's operating speed* with a fouled hull.
- This was estimated to cost around *$136,000 per month of unnecessary fuel consumption by one Navy ship*.

A 1% Increase in Drag ≥ 10%

Increase in Fuel Consumption

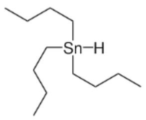
BENCH SCALE OVERVIEW

The bench scale study described in this presentation uses a unique approach for the REDOX chemical degradation treatment (I-ROX®) of TBT to achieve trace to non-detectable concentrations in the treated marine sediments.

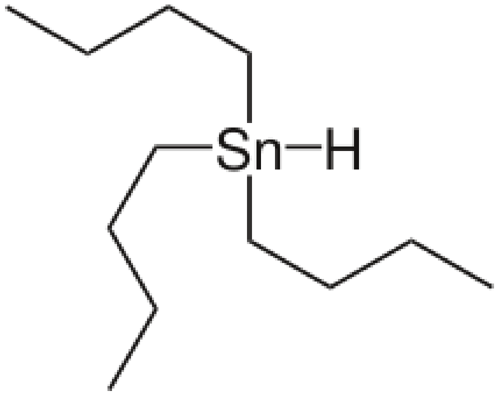
This paper will also include the degradation of associated chemical compounds; Dibutyltin (DBT) and Monobutyltin (MBT), with similar results.

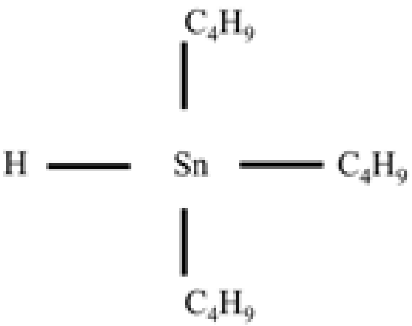
DBT and MBT are also toxic to aquatic life, and may be omitted from regulatory enforcement in some jurisdictions.

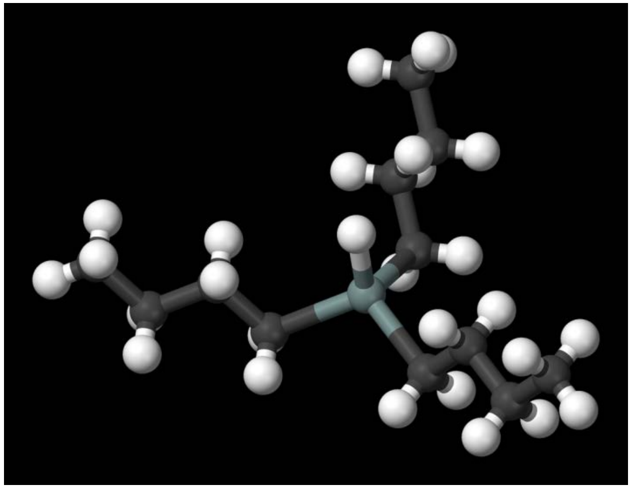
But some background on TBT first…



Tributyltin (TBT)





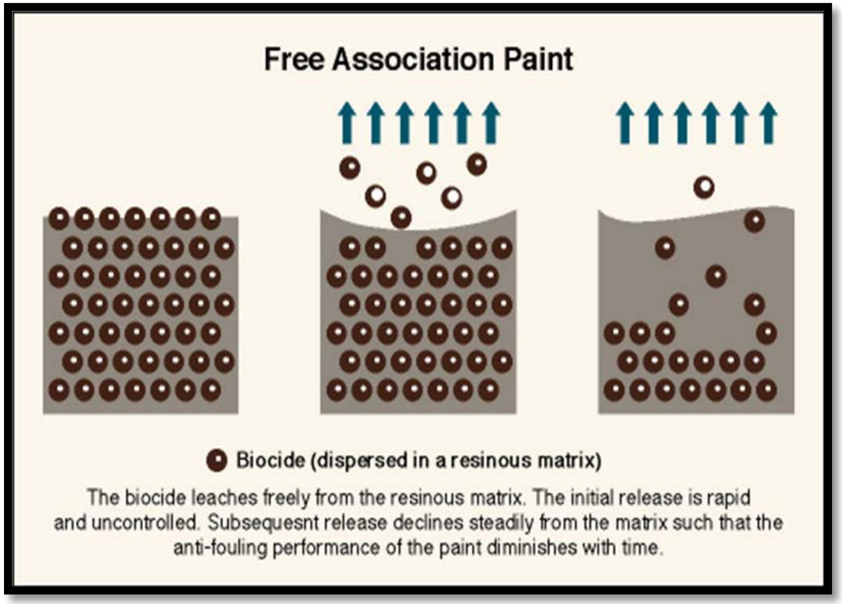


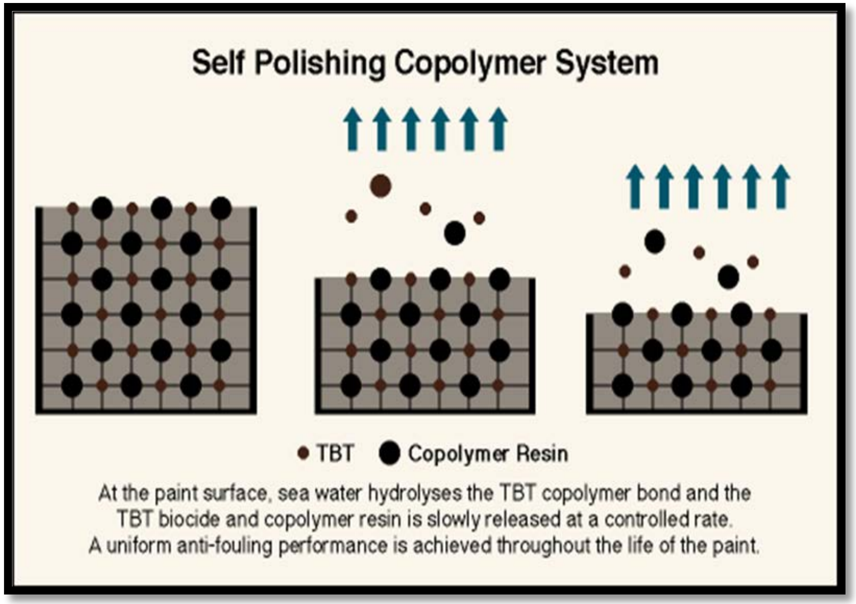
SOURCES OF HUMAN AND ENVIRONMENTAL EXPOSURE

- Tributyltin compounds have been registered
  - as molluscicides;
  - as antifoulants on boats, ships, quays, buoys, crab pots, fish nets, and cages;
  - as wood preservatives;
  - as slimicides on masonry;
  - as disinfectants; and as biocides for cooling systems, power station cooling towers, pulp and paper mills, breweries, and leather processing and textile mills.
- *Tributyltin in antifouling paints was first marketed in a form that allowed free release of the compound.*
- *More recently, controlled-release paints, in which the Tributyltin is incorporated in a copolymer matrix, have become available.*

Without Verses With TBT

TBT Release Mechanisms To Water

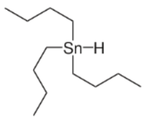




1 PPB

TBT has since been determined to be very harmful to invertebrates and vertebrates, including humans, with toxic effects occurring at concentrations as low as
1 nano-gram per litre (1 ppb) of water for some species.

Although TBT has been banned from use globally since the 1980’s and 1990’s, the presence and persistence of TBT in marine sediments is ubiquitous and poses an ongoing health risk due to the recalcitrant nature of TBT.



ENVIRONMENTAL TRANSPORT, DISTRIBUTION, & TRANSFORMATION

As a result of its low water solubility and lipophilic character, Tributyltin (TBT) *adsorbs readily onto particles* (IPCS, 1990).

Environmental Levels

- Tributyltin compounds have been found in water, sediment, and biota in areas close to pleasure boating activity, especially in or near marinas, boat yards, and dry docks (IPCS, 1990).

- The degree of tidal flushing and the turbidity of the water influence Tributyltin concentrations.

- As reported in IPCS (1990), Tributyltin levels have been found to reach 1.58 µg/litre in seawater and estuaries; 7.1 µg/litre in fresh water; 26.3 mg/kg in coastal sediments; 3.7 mg/kg in freshwater sediments; 6.39 mg/kg in bivalves; 1.92 mg/kg in gastropods; and 11 mg/kg in fish.

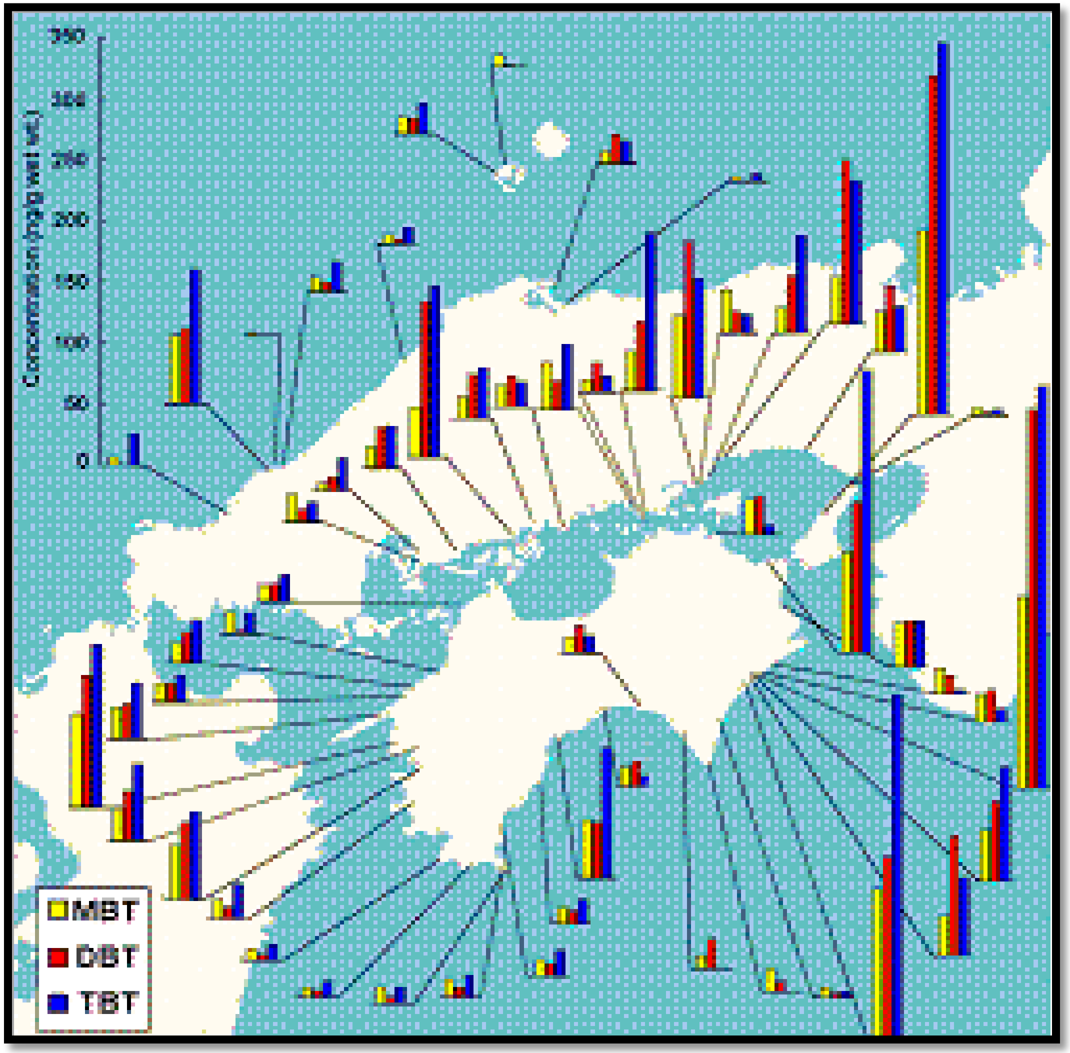
Environmental Levels (cont.)

- *More recent data (collected up to the mid-1990s) have documented a decline in Tributyltin levels in the environment, presumably due to the restrictions placed on the use of antifouling paints on vessels* (CEFIC, 1994; Ruiz et al., 1996; Stronkhorst, 1996; Tolosa et al., 1996; NIVA, 1997; dela Cruz & Molander, 1998).

- The range of concentrations reported in coastal waters and estuaries is 1-10 ng/litre; the *range reported for water in marinas and major ports is 20-460 ng/litre*.

- Most of the sediment samples analysed contained less than 100 µg/kg, although some samples exceeded 1000 µg/kg.

Sample Map TBT In Marine Sediments (Illustrative Example)



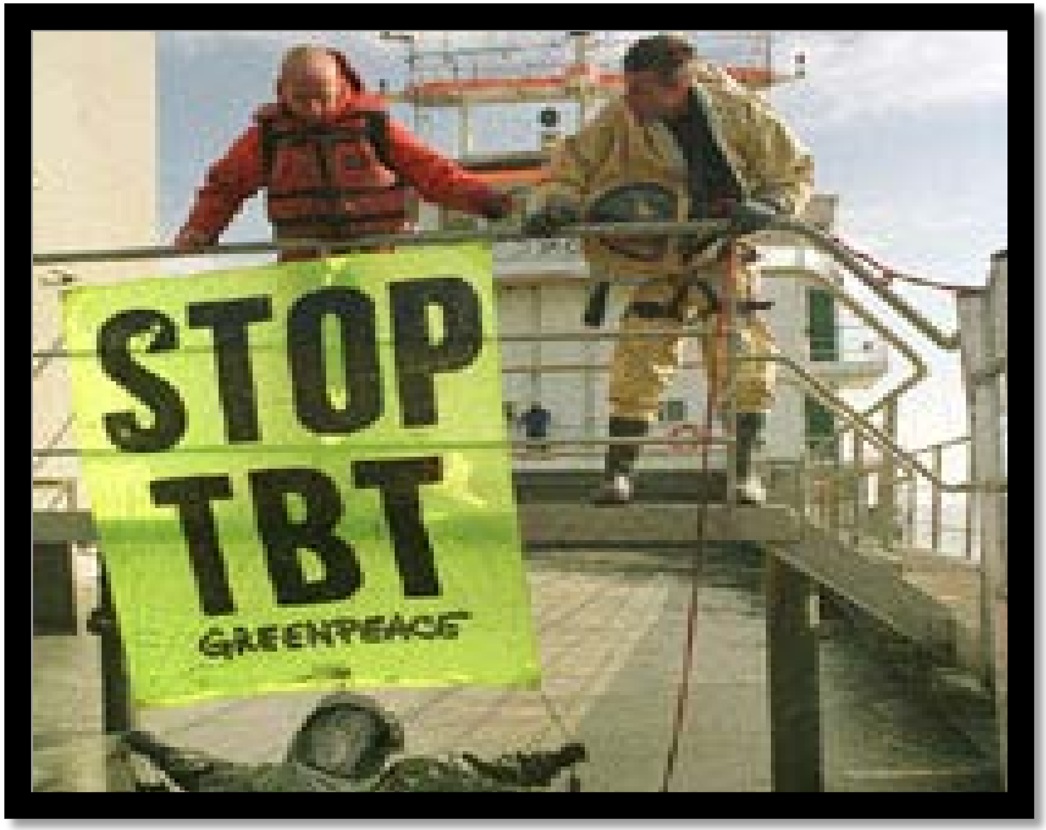
Neurotoxicity

- Triethyltin and trimethyltin compounds have been shown to cause severe neurotoxicity (for a summary, see Boyer, 1989).
- Triethyltin causes interstitial oedema throughout the white matter in the spinal cord and various regions of the brain; less marked damage occurs in the peripheral nervous system.
- Trimethyltin also causes severe and permanent damage to the central nervous system. In this case, however, the effect is neuronal necrosis, rather than oedema.

Oyster TBT Contamination

No Exposure

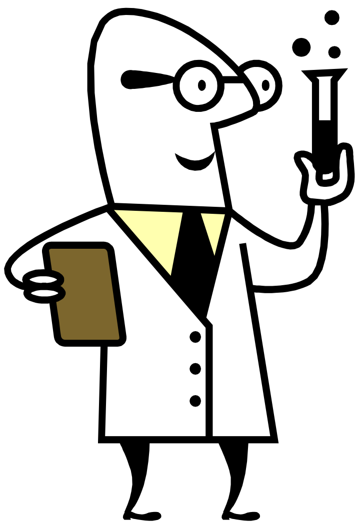
TBT Exposure


STOP
TBT
GREENPEACE

CURRENT REGULATIONS, GUIDELINES, AND STANDARDS

Many countries have restricted the use of TBTO. Information on national regulations, guidelines, and standards may be obtained from UNEP Chemicals (IRPTC), Geneva.

BENCHSCALE STUDY



Bench Scale I-ROX Treatability Test - TBT Contaminated Sediments

- IVEY was provided with a 3 kg sediment soil sample described as aquatic sediments, comprised of fine to coarse grain soil texture (poorly sorted), that was impacted with TBT (Tri-Butyl-Tin).

- IVEY completed a bench scale I-ROX treatability study to determine if the I-ROX (REDOX) technology could chemically degrade the TBT rendering the sediments remediated following treatment.

- The sediment sample was thoroughly mixed to homogenize the TBT concentration before the collection of a representative '*control*' sample (Not subjected to I-ROX treatment), and preparation of three test samples that would be subjected to different % by weight I-ROX applications (i.e., 5%, 10% and 20%).

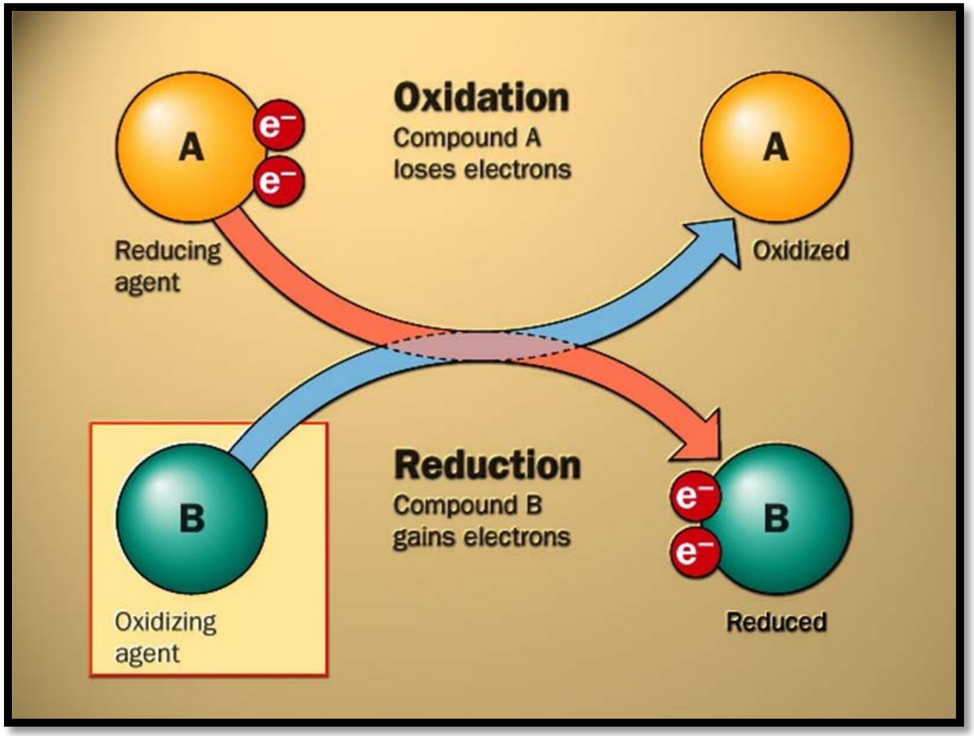
- The control and all I-ROX treated samples we gently mixed for 3 minutes (by hand) using a scoopula in glass sample jars. Each sample was prepared to rest at room temperature (20 to 22 ^{o}C) for seven (7) days before laboratory analysis.

  Note: What was not known at the time the samples were provided to the laboratory, three (3) days post treatment; was that the laboratory unintentionally stored the subject samples at 4^{o}C for the last four (4) days of the holding period before sample extraction and analysis.

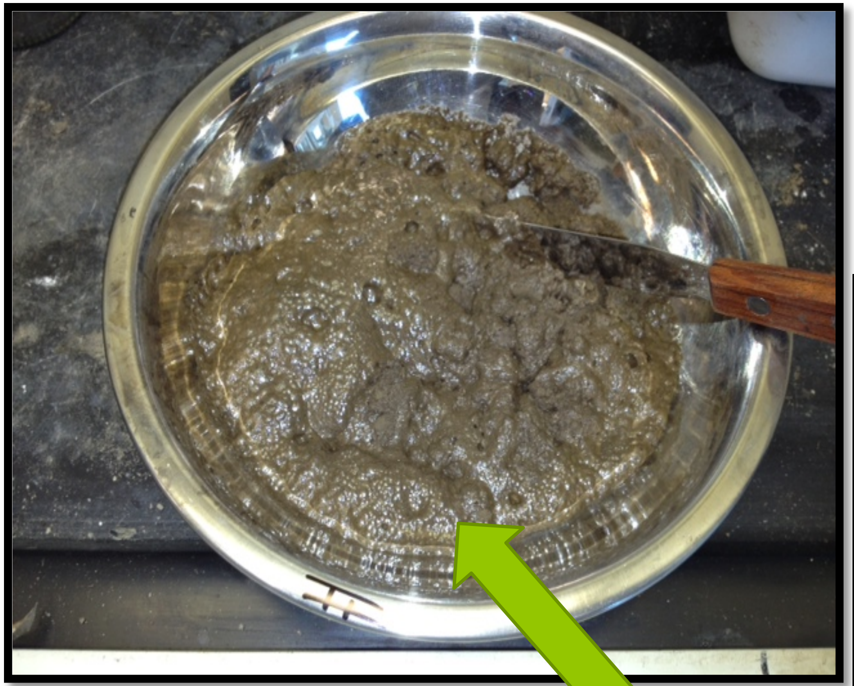
I-ROX (REDOX) Treatment

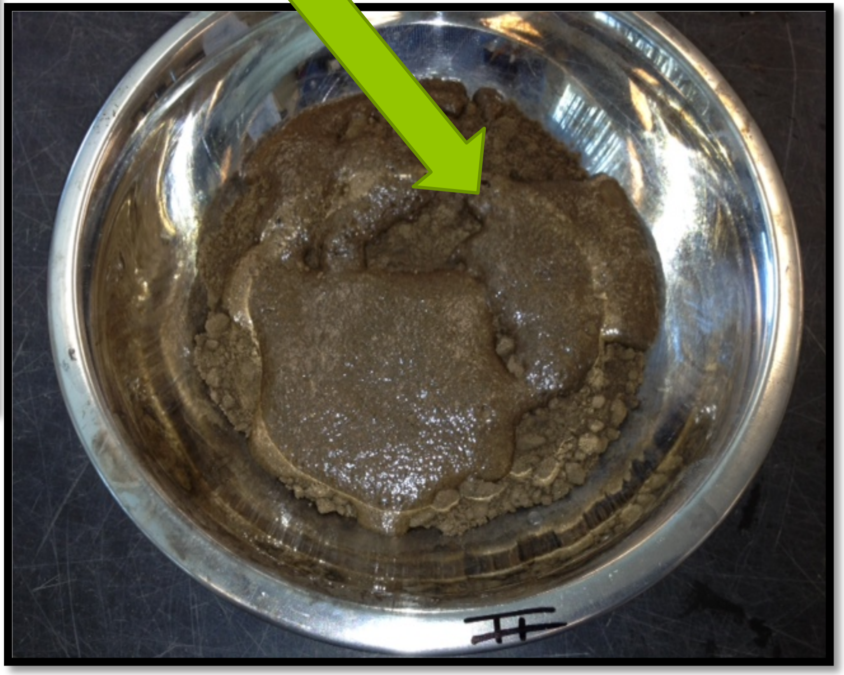
I-ROX
(Reduction/Oxidation)

POP or COC → Oxidized and Reduced Degradation Products



I-ROX Chemical REDOX Sediment Treatment





- The chemical breakdown of TBT follows a Reductive Elimination mechanism, whereby the I-ROX reagent facilitates the mechanistic removal of the butyl groups (C4H9) successively until all three organic constituents have been eliminated.

$$\mathbf{Sn\ (C_4H_9)3 \xrightarrow{\text{I-ROX}} Sn\ +\ 3(C_4H_9)}$$

- The butyl group will most likely be in a butane or butane form following the subject reaction, while the tin will be in an inorganic non TBT form.

- The reaction will be slightly shifted to resemble a more oxidative/reductive reaction mechanism and could resemble, in part, a *Grignard type organometallic reaction*, but the ability of metals to be somewhat labile, regarding their electron density, during de-alkylation can make precise determinations of the actual single or multi-step reaction mechanism *more* challenging to state.

Analysis & Results

- All samples (control and treated) were analyzed for TBT, DBT (Dibutyltin) and MBT (Monobutyltin) to ensure the degradation of the TBT did not generate DBT and MBT as incomplete by product treatments, and the DBT and MBT present in the sediments was also getting effectively degraded.

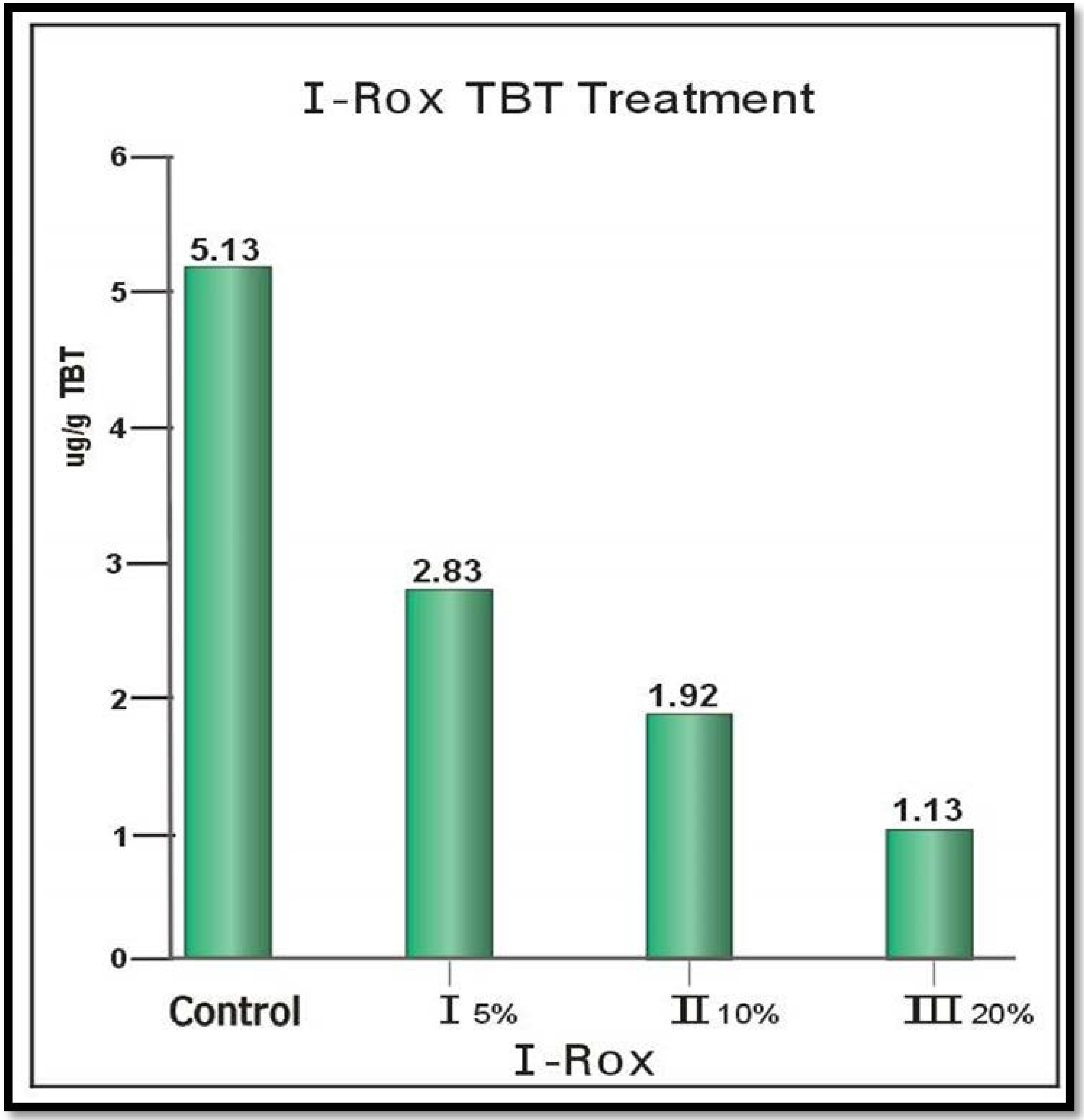
- The analytical method employed was HRGC/LRMS (high resolution gas chromatography - low resolution mass spectrometry) 1,8 for Tributyltin with a detection limit of 0.001 ug/g (1 ppb). The results are provided in Table and graph TBT, Table DBT, and Table MBT.

TBT Results

I-ROX % by Weight Vs. TBT Concentration[1]

SAMPLE	I-ROX 0%	I-ROX 5%	I-ROX 10%	I-ROX 20%	% TBT Reduction
Control	**5.13**				**0.00**
1		**2.52**			**50.8**
2			**1.71**		**66.7**
3				**1.00**	**80.5**

Note: *Analytical Method: HRGC/LRMS[8] analysis for TBT. Units ug/g. Detection limit 0.001 ug/g (1 ppb). 0% = Control*



I-Rox TBT Treatment
ug/g TBT
6
5
4
3
2
1
0
5.13
2.83
1.92
1.13
Control
I 5%
II 10%
III 20%
I-Rox

I-ROX TBT Treatment Conclusion

Based on the Table TBT results, the I-ROX was very effective for chemically degrading the TBT by 50% to 80%, which increased as a function of the % by weight of I-ROX (Graph).

DBT and MBT Results

I-ROX % by Weight Vs. DBT Concentration[1]

SAMPLE	I-ROX 0 %	I-ROX 5%	I-ROX 10%	I-ROX 20%	% DBT Reduction
Control	**0.114**				**0.00**
1		**0.009**			**92.1**
2			**0.033**		**71.1**
3				**0.011**	**90.4**

Note: ***Analytical Method: HRGC/LRMS[8] analysis for DBT. Units ug/g. Detection limit 0.001 ug/g (1 ppb). 0% = Control***

I-ROX % by Weight Vs. MBT Concentration[1]

SAMPLE	I-ROX 0 %	I-ROX 5%	I-ROX 10%	I-ROX 20%	% MBT Reduction
Control	**0.299**				**0.00**
1		**ND**			**100**
2			**0.005**		**98.3**
3				**ND**	**100**

Note: ***Analytical Method: HRGC/LRMS[8] analysis for MBT. Units ug/g. Detection limit 0.001 ug/g (1 ppb). 0% = Control. ND = Non Detectable.***

I-ROX DBT and MBT Treatment Conclusions

- Based on the Table DBT results, the I-ROX was very effective for chemically degrading the DBT by 71 % to 92%.
- Based on the Table MBT results, the I-ROX was very effective for chemically degrading the MBT by 98 to 100%.
- If the degradation of the TBT and or DBT by I-ROX generated by-products, including DBT and/or MBT, this was effectively degraded with no apparent physical accumulation from the subject I-ROX treatment.

CONCLUSION

Based on the findings of this study, the I-ROX (REDOX) approach could be used as an effective methodology for the treatment of dredge marine sediments to reduce the TBT, DBT, and MBT concentrations.

In addition, it could allow for the ‘sustainable’ reuse of the post-treated sediments in the environment.

Question & Answer Period

Come Visit Us At Our Booth

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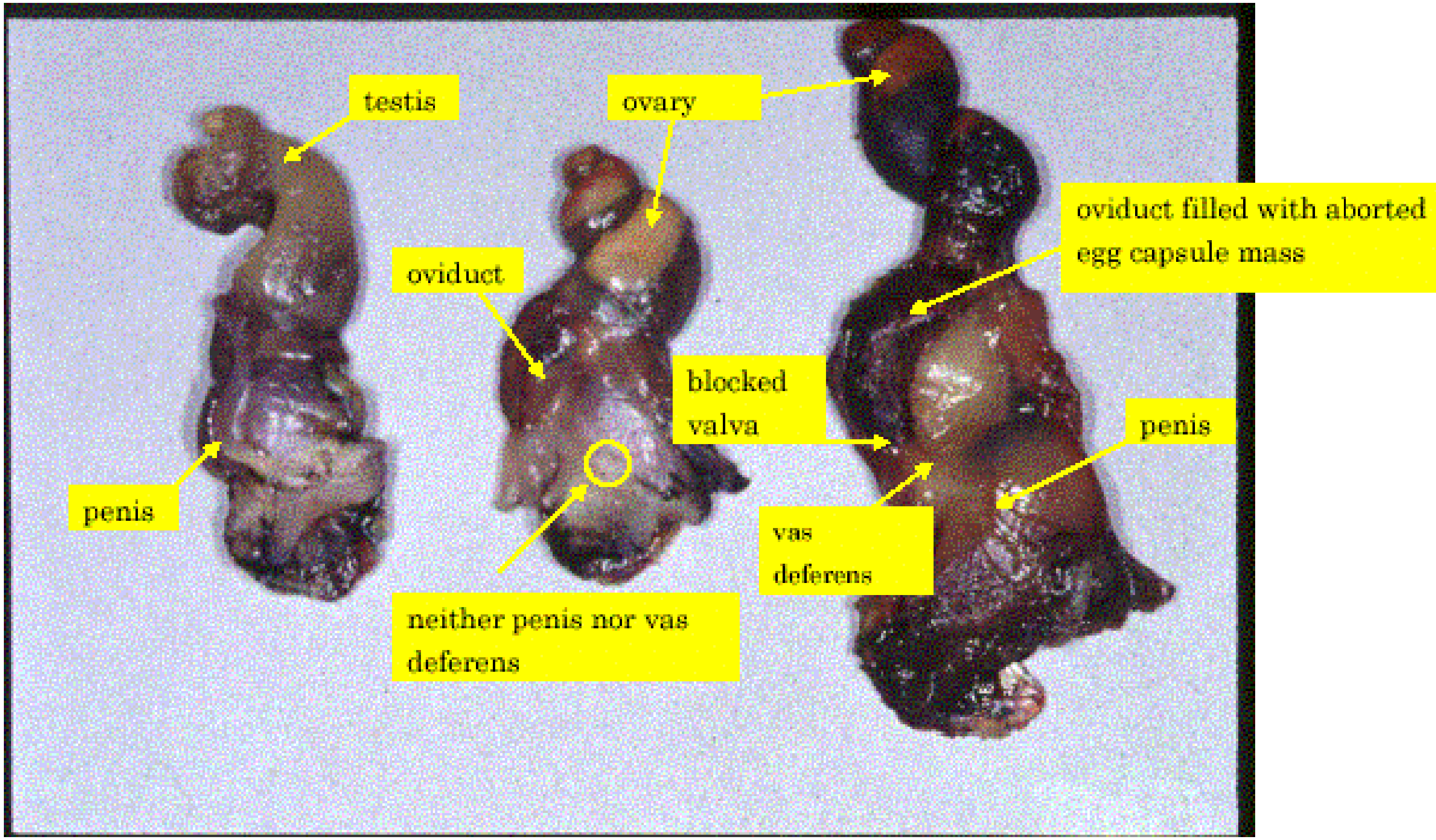
testis
ovary
oviduct filled with aborted egg capsule mass
oviduct
blocked valva
penis
penis
vas deferens
neither penis nor vas deferens