An almost successful story of TBT regulation to protect the coastal environments of Korea

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Butyltin compounds

- **Molecular formula**
  - BTs: \((C_4H_9)_nSnX_{4-n}\)

- **Applications**
  - **TBT**: antifouling agent, bactericide, molluscide, fungicide, preservatives for wood and textile, etc.
  - **DBT/MBT**: PVC stabilizer, catalysts for silicone rubber and polyurethane, and etc.

- **Degradation**
  - Progressive removal of the organic groups from the tin atom
    \[ R_3SnX \rightarrow R_2SnX_2 \rightarrow RSnX_3 \rightarrow SnX_4 \]
  - Photolysis, biological degradation, and chemical cleavage
Tributyltin compounds

- Moderately to highly (in anoxic sediment) persistent
- Bioaccumulative (not likely biomagnified)
- Toxic to aquatic organisms
- Endocrine disrupting chemical

Tributyltin hydride

Bis-tributyltin oxide
Effects on non-target organisms
Species sensitivity distribution of TBT

**ACUTE TOXICITY**
- Adult Pacific oyster-LC50(650)
- Adult sole-LC50(650)
- Adult Fat head minnow-LC50(100)
- Adult amphipod-LC50/10 day(458)
- Adult Silverside fish-LC50(100)
- Adult sydney Rock oyster-LC50/28 day(339)
- Larval shrimp-LC50(650)
- Larval Eastern flat oyster-LC50/48 hour(529)
- Larval clam-LC50/48 hour(529)
- Eastern flat oyster embryo-LC50(529)
- Sub-adult mysid-LC50(690)
- Adult copepod-LC50(671)
- Sub-adult mysid-LC50/96 hour
- Adult European flat oyster -0% larvae released(654)
- Adult mussel-EC50
- Adult grass shrimp-significant reduction of molting(346)
- Juvenile European flat oyster -50% reduction growth(654)

**CHRONIC TOXICITY**
- Adult Eastern oyster-Significant diff in condition index(691)
- Adult copepod-LC50/6 day(671)
- Juvenile clam -0% growth(388)
- Adult amphipod-LC50/14 day(384)
- Adult mysid-chronic value-reproduction
- Larval mussel-LOEC-growth(366)
- Larval mussel-chronic value-growth(366)
- Larval copepod-chronic value-mortality(102)
- Dogwhelk -50% female sterility(246)
- Juvenile Pacific oyster -79% reduced growth(478)
- Dogwhelk -30% sterility from imposex(248)
- Juvenile crab-LC50/16 day(389)
- Juvenile crab -43% reduction growth(383)
Imposex in *Thais clavigera* (Neogastropod)

**Thais clavigera**

Normal penis in male *T. clavigera*

abnormal pseudo-penis in female *T. clavigera* (imposex)
Accumulation of TBT and Induction of imposex in female *Thais clavigera* exposed to TBT in the laboratory for 60 days.
### Regulation of TBT based A/F paint in Korea and IMO

#### Korea

<table>
<thead>
<tr>
<th>Step</th>
<th>Date</th>
<th>Regulation</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9 Mar 2000</td>
<td>Fishing and pleasure boasts, fishing gear, and submerged structures</td>
<td>&gt; 90,000 ships</td>
</tr>
<tr>
<td>2</td>
<td>29 Jun 2001</td>
<td>Domestic ferry boats</td>
<td>161 ships</td>
</tr>
<tr>
<td>3</td>
<td>1 July 2002</td>
<td>Domestic cargo vessel</td>
<td>1,279 ships</td>
</tr>
<tr>
<td>4</td>
<td>1 Nov 2003</td>
<td>Ocean going vessels*</td>
<td>424 ships</td>
</tr>
</tbody>
</table>

*Ships with Korean flag

#### IMO – AFS Treaty

<table>
<thead>
<tr>
<th>Step</th>
<th>Regulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Global <strong>prohibition of the application</strong> of organotin compounds which act as biocides in antifouling systems on ships by 1/Jan/2003</td>
</tr>
<tr>
<td>2</td>
<td>Complete <strong>prohibition on the presence</strong> of organotin compounds which act as biocides in antifouling systems on ships be in place by 1/Jan/2008</td>
</tr>
</tbody>
</table>

*Min. requirement: >50% ratification of member countries or >25% of registered ships

**AFS has entered into force on 17 Sep 2008**
Usage history of TBT based and tin-free A/F paints on domestic ocean going vessels in 2002 (before total ban), Korea
A/F paints consumed in a ship building company

<table>
<thead>
<tr>
<th>Year</th>
<th>Total paints (L)</th>
<th>A/F paints (L)</th>
<th>Tin</th>
<th>Tin-free</th>
</tr>
</thead>
<tbody>
<tr>
<td>2001</td>
<td>3,231,520</td>
<td></td>
<td>775</td>
<td>157,322</td>
</tr>
<tr>
<td>2002</td>
<td>3,593,020</td>
<td></td>
<td>0</td>
<td>171,088</td>
</tr>
<tr>
<td>2003</td>
<td>4,316,532</td>
<td></td>
<td>0</td>
<td>196,652</td>
</tr>
<tr>
<td>2004</td>
<td>4,860,485</td>
<td></td>
<td>0</td>
<td>251,452</td>
</tr>
</tbody>
</table>
Investigation of new ships for TBT application after the total ban

Standard

Ship #2

Ship #4

Ship #7

Ship #11

0/17
TBT regulation is effective enough?

- Reduction of TBT contamination in most of countries that placed partial TBT regulation for small ships (<25 m in length) in the 1980s and 1990s

- But questions on illegal use where TBT levels remain comparable long after the TBT regulation

- Presence of previous TBT application in ship hulls are questionable

- Unclear regulatory effectiveness in big commercial harbors and shipyards where ocean going vessels are moored and built
Before

Soccer in lunch time

After
Location map of sampling sites in Jinhae Bay

Comparison of water TBT and $\sum$BTs concentrations in Jinhae Bay before and after the total ban in Korea

Water

$\sum$BTs = TBT + DBT + MBT

$TBT < 0.05$

$P < 0.05$

Cumulative distribution of $\Sigma$BT concentrations in oyster and mussel in 1995–1998 and 2001 along the Korean coast

Comparison of oyster TBT and $\sum$BTs concentrations in Jinhae Bay before and after the total ban in Korea

$\sum$BTs = TBT + DBT + MBT

$TBT_p < 0.05$

Sample year

$1^{st}$ Shim et al. (1998) *Arch. Environ. Contam. Toxicol.*
Comparison of sediment TBT and $\Sigma$BTs concentrations in Jinhae Bay before and after the total ban in Korea

\[ \Sigma \text{BTs} = \text{TBT} + \text{DBT} + \text{MBT} \]

Location map of sampling sites for rock shell in Jinhae Bay

- Rock shell (*Thais clavigera*)
Temporal change of % female in rock shell from Jinhae Bay before and after the total ban in Korea

% Female

![Graph showing temporal change of % female in rock shell from Jinhae Bay before and after the total ban in Korea.](image)


p < 0.05
Temporal change of RPLI in rock shell from Jinhae Bay before and after the total ban in Korea

RPLI (%) = [mean female pseudo-penis length] / [male penis length]

Relative Penis Length Index (RPLI)

Graph showing the RPLI (%) for different stations and years.
Temporal change of TBT concentrations in rock shell from Jinhae Bay before and after the total ban in Korea

TBT and TPT concentrations

Concentration (ng Sn/g)

Station

1 2 3 4 5 6 7 8 9 10

1995/97 (TBT+TPT) 2008 (TBT) 2013 (TBT)

Concentration of TBT (ng Sn/g dw)

Sample year

1996/97 2008 2013

\( p < 0.05 \)
Relationship between RPL index vs % female and TBT concentrations vs mean female pseudo-penis length in rock shell from Jinhae Bay

y=74.3168*e(-0.0103*)

\[ r^2 = 0.72, \ p < 0.0001 \]

y=11.5907*(1-e^{-0.0123x})

\[ r^2 = 0.74, \ p < 0.0001 \]
Ecological concern of current TBT concentrations in seawater

Concentration of TBT in seawater (ng TBT/L)

Cumulative probability(%)

0.1\textsuperscript{a}  1.5\textsuperscript{b}  2\textsuperscript{c}  7\textsuperscript{d}  11\textsuperscript{e}

1995/97  2003/04  2008/09

\textsuperscript{a,b} Lower and upper ecotoxicological assessment criteria (EAC) values by the OSPAR Commission (OSPAR, 2004)
\textsuperscript{c} UK environment quality target (EQT) (UK, 1989)
\textsuperscript{d} Chronic Criterion by US EPA (US EPA, 2004)
\textsuperscript{e} Dutch government environmental quality limit (converted ion to chloride) (Rajendran et al., 2001)
Ecological concern of current TBT concentrations in oyster

Concentration of TBT in oyster (ng Sn/g)

Cumulative probability(%)

10^0 10^1 10^2 10^3 10^4

4.91^a

71.7^b

1995/97
2008/09
2012/13

^a Lower EAC value by the OSPAR Commission for mussel (OSPAR, 2004)
^b Upper EAC value by the OSPAR Commission for mussel (OSPAR, 2004)
Ecological concern of current TBT concentrations in sediment

\[\text{Concentration of TBT in sediment (ng Sn/g)}\]

Cumulative probability (°)

0

10

20

30

40

50

60

70

80

90

100

1995

2004

2008

2010

\[a,c\] Australian sediment quality guideline (SQG) low and high trigger values, respectively (Burton et al., 2005)

\[b,d\] SQG low and high trigger values by Spanish, respectively (Port of Helsinki, 2004)
Conclusions

- Question: Is the regulatory measure to control the TBT levels in Korea effective?
  - Yes, showing good sign of recovery in water, biota and imposex.
  - But, not enough yet for sediment.

- Question: Is the current level of TBT safe enough to protect the coastal environment of Korea?
  - No, it seems to require longer time scale to reach well down to the level.
Acknowledgements

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