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


Nanaimo, Canada
PICES 2013

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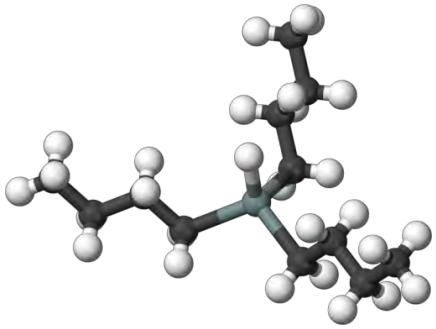
Butyltin compounds



- **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

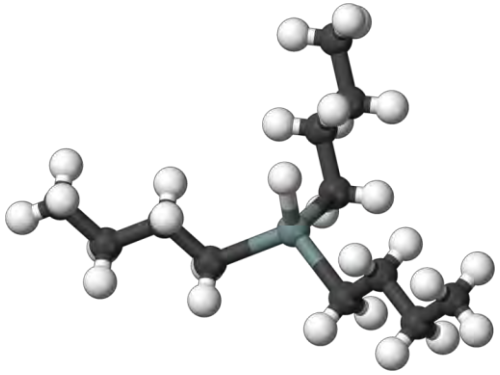
$$\mathbf{R_3SnX} \longrightarrow \mathbf{R_2SnX_2} \longrightarrow \mathbf{RSnX_3} \longrightarrow \mathbf{SnX_4}$$

  - Photolysis, biological degradation, and chemical cleavage

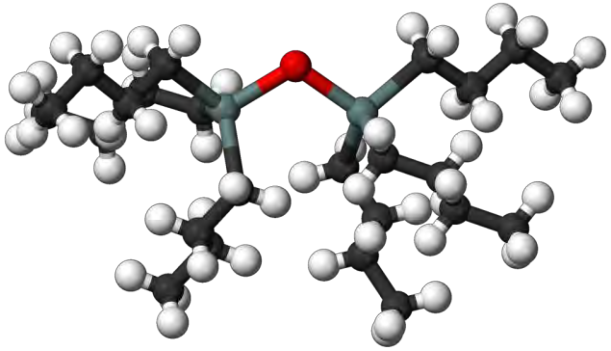
Tributyltin compounds

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

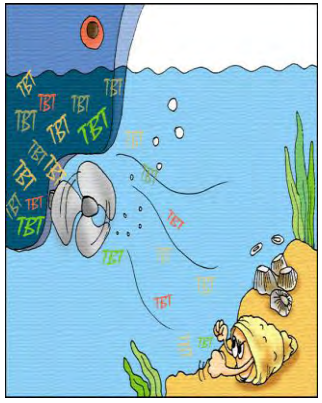
Tributyltin hydride



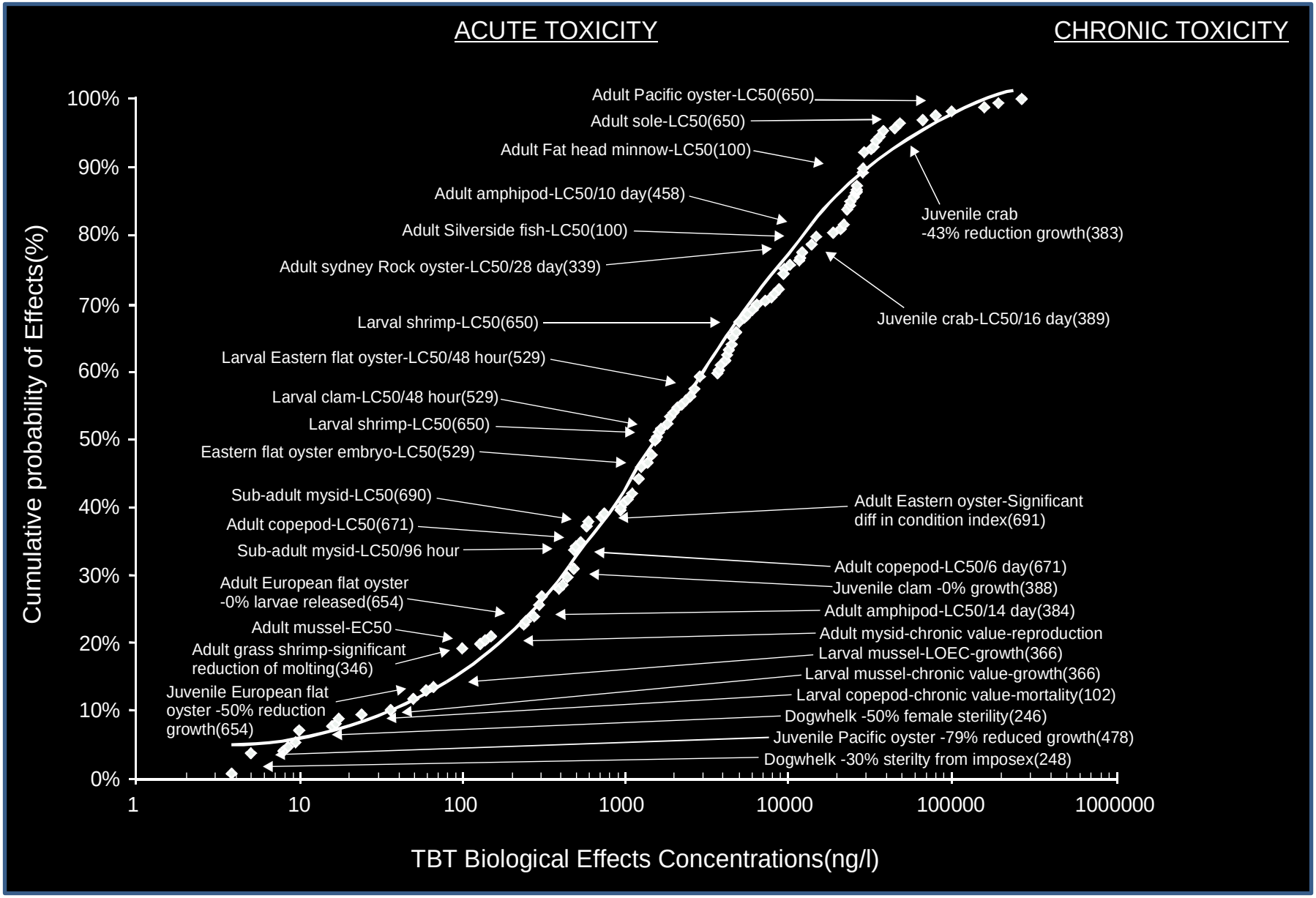
Bis-tributyltin oxide



Effects on non-target organisms



Species sensitivity distribution of TBT



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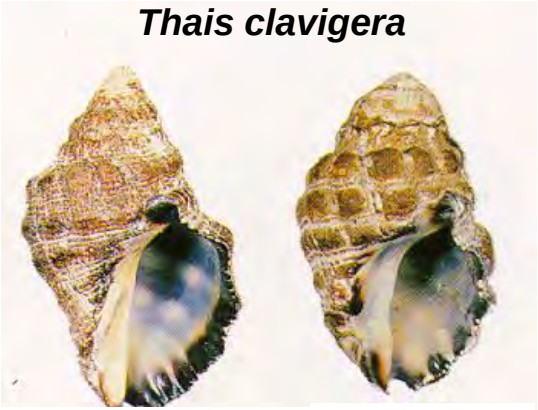
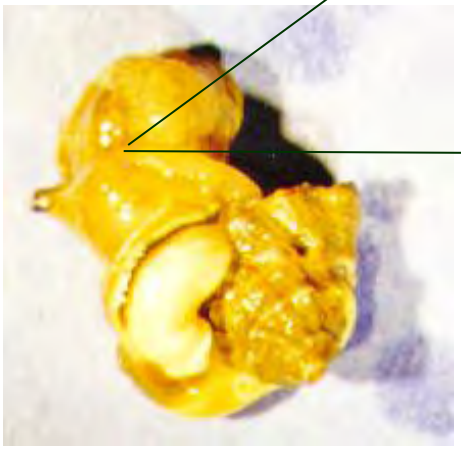
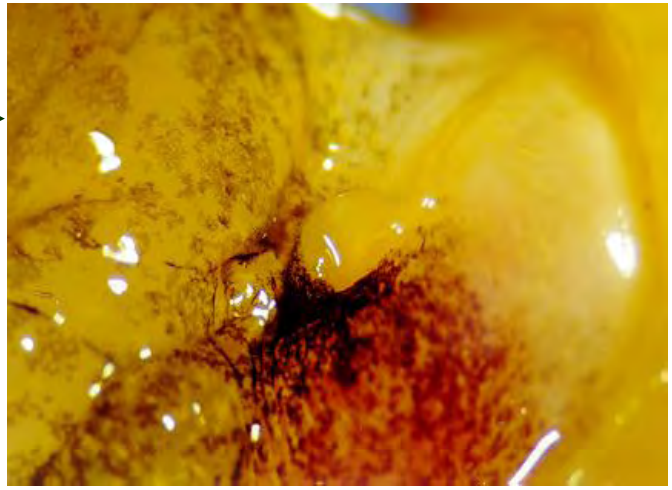
Imposex in *Thais clavigera* (Neogastropod)



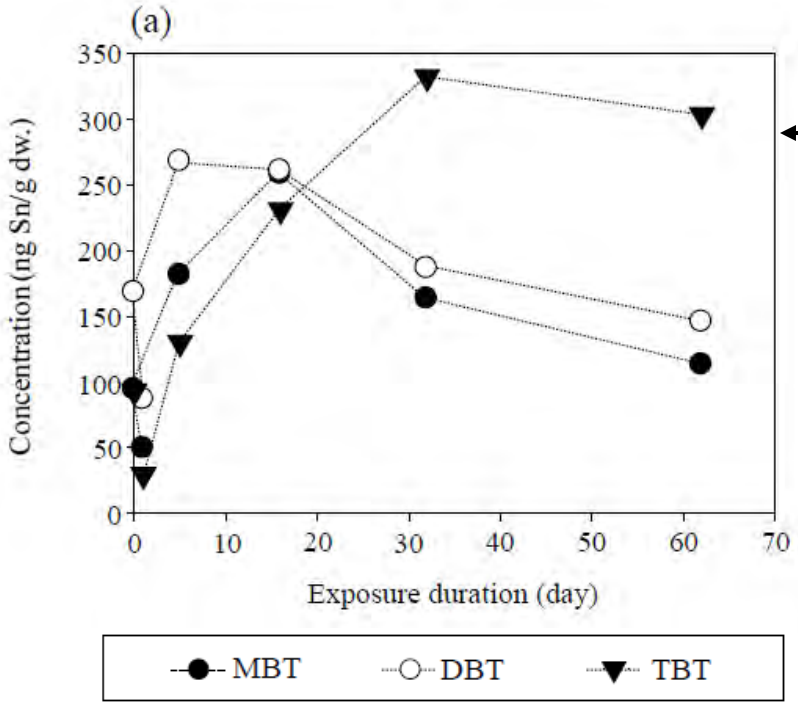
Normal penis in male *T. clavigera*

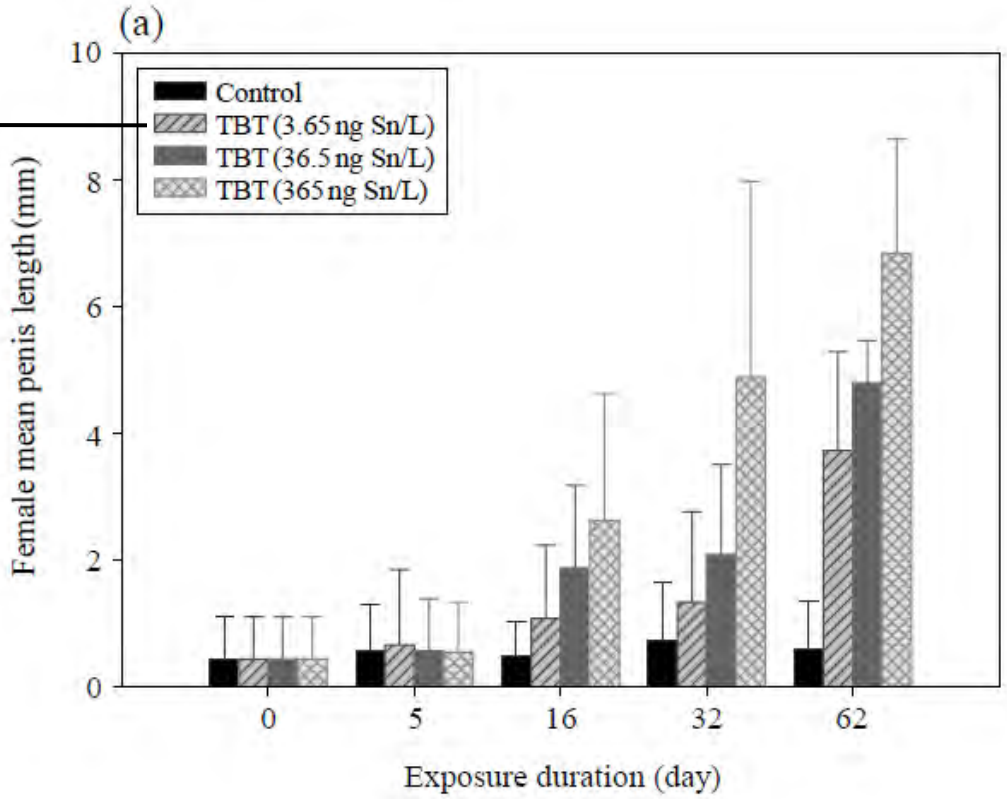




abnormal pseudo-penis in female *T. clavigera* (imposex)

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

Step	Date	Regulation	Remark
1	9 Mar 2000	Fishing and pleasure boasts, fishing gear, and submerged structures	> 90,000 ships
2	29 Jun 2001	Domestic ferry boats	161 ships
3	1 July 2002	Domestic cargo vessel	1,279 ships
4	1 Nov 2003	Ocean going vessels*	424 ships

***Ships with Korean flag**

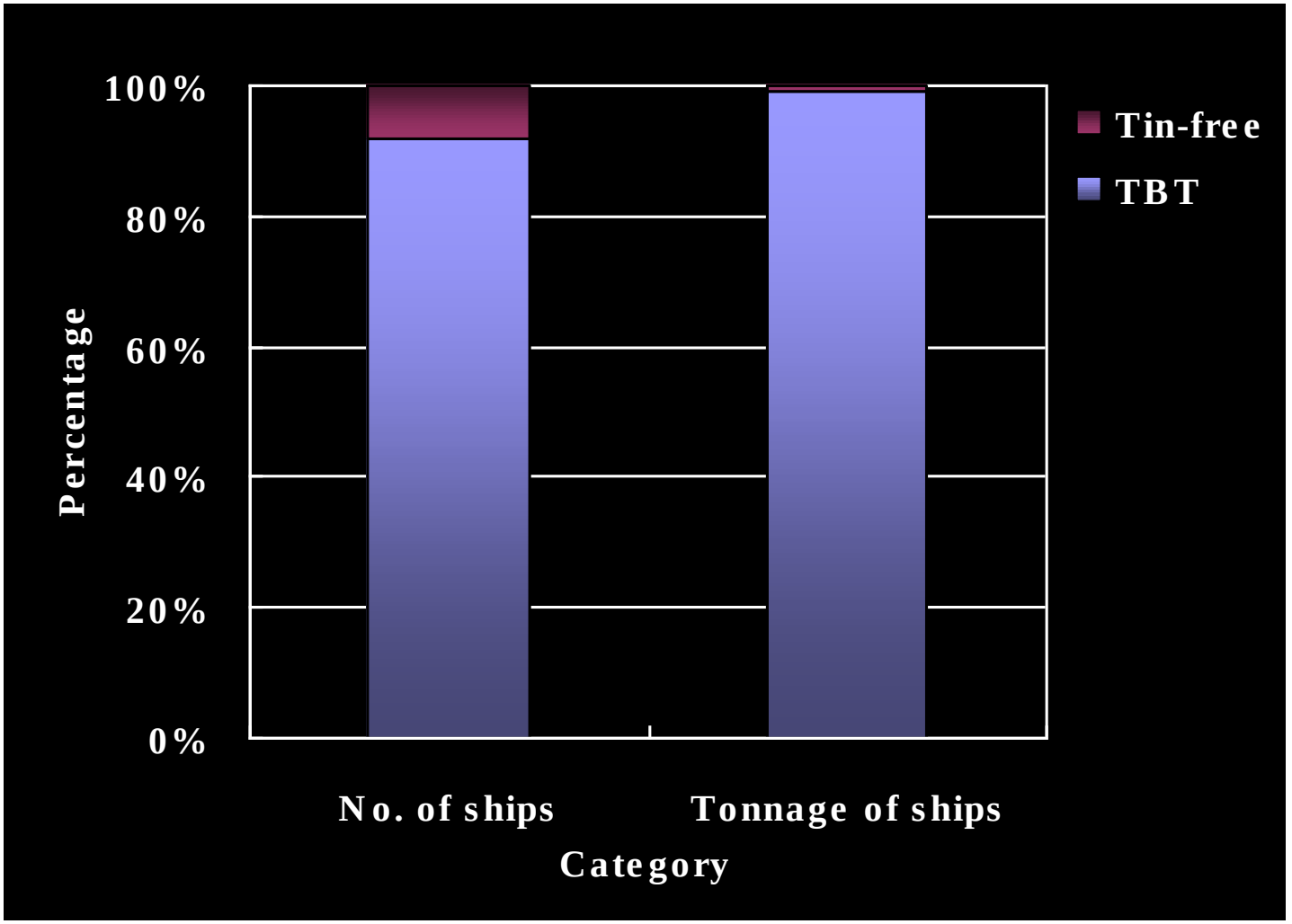
IMO – AFS Treaty

Step	Regulation*
1	Global prohibition of the application of organotin compounds which act as biocides in antifouling systems on ships by 1/Jan/2003
2	Complete prohibition on the presence of organotin compounds which act as biocides in antifouling systems on ships be in place by 1/Jan/2008

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

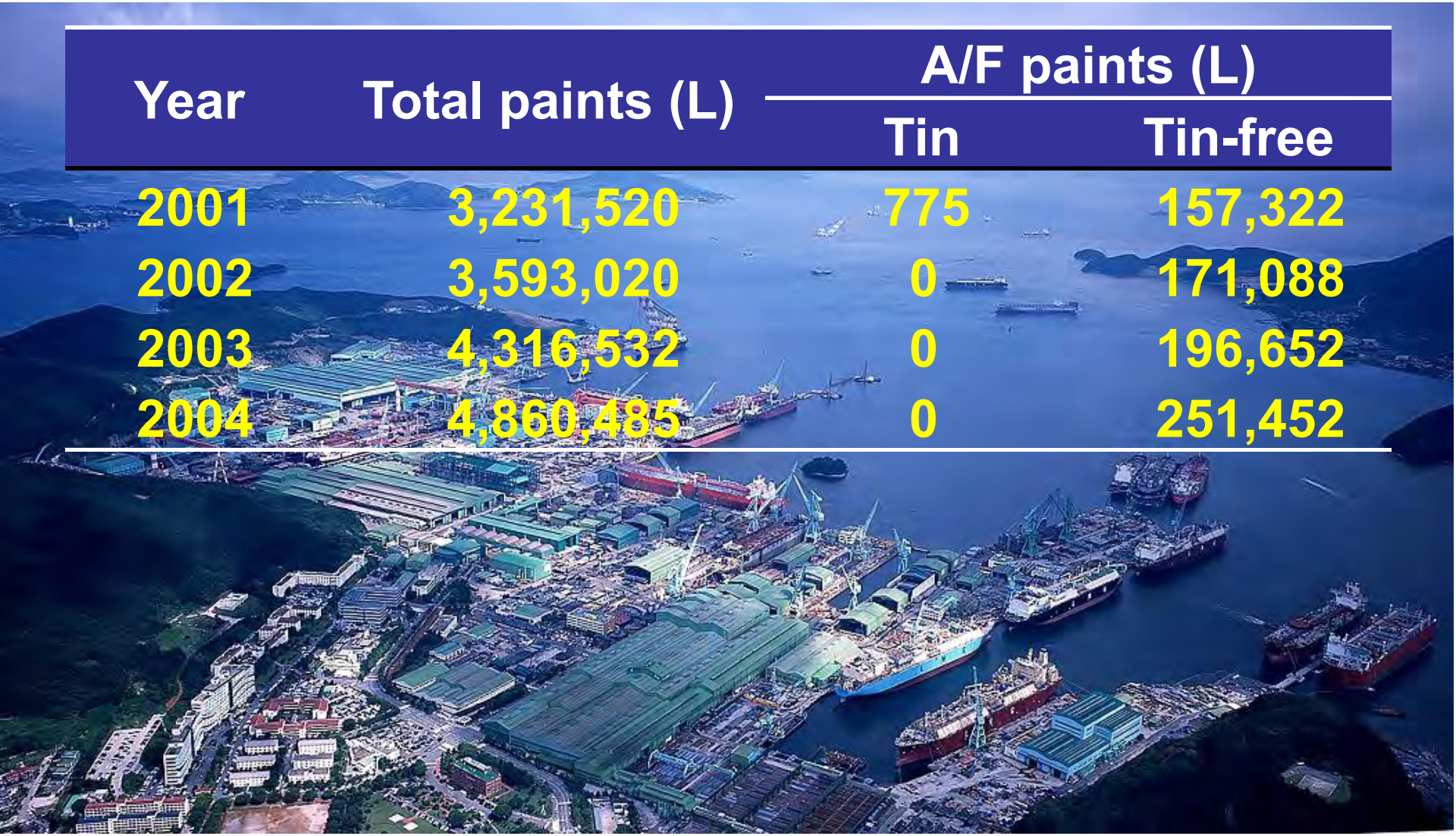
: AFS has entered into force on 17 Sep 2008

Usage history of TBT based and tin-free A/F paints on domestic ocean going vessels in 2002 (before total ban), Korea

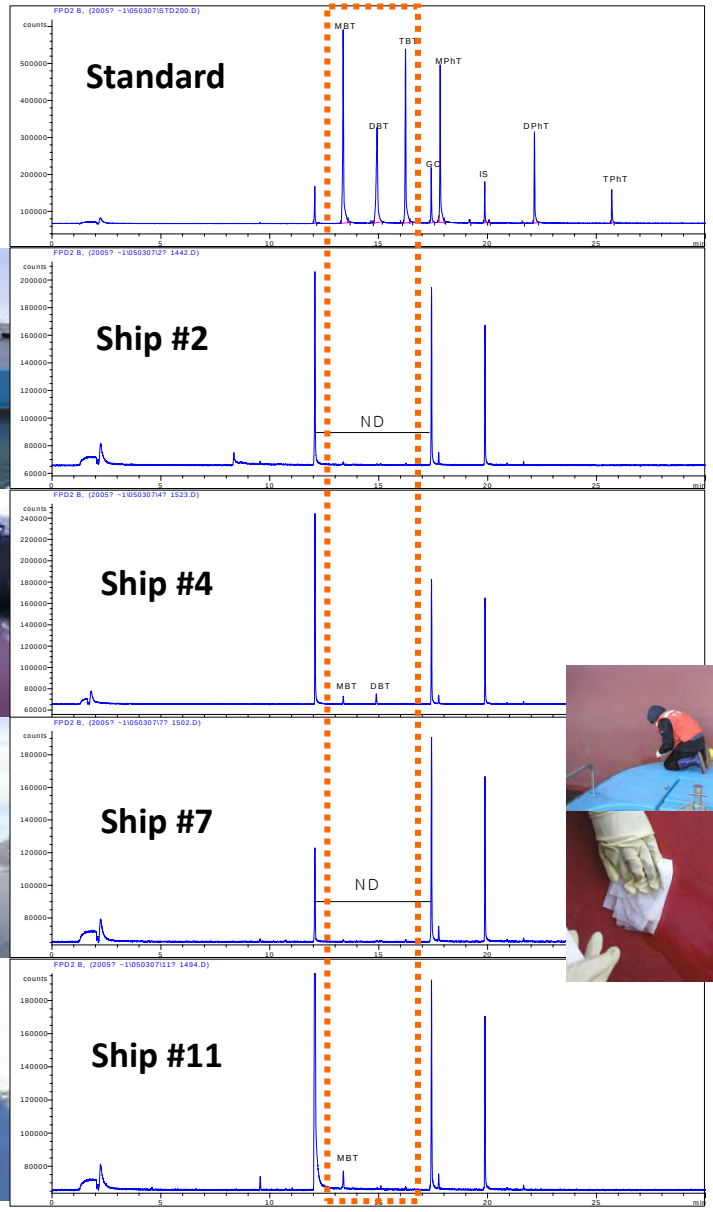


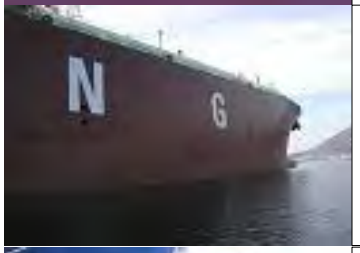
A/F paints consumed in a ship building company

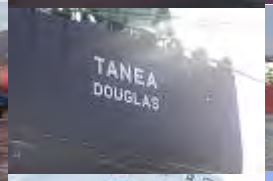
Year	Total paints (L)	A/F paints (L)	
		Tin	Tin-free
2001	3,231,520	775	157,322
2002	3,593,020	0	171,088
2003	4,316,532	0	196,652
2004	4,860,485	0	251,452

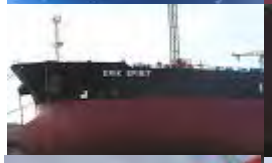


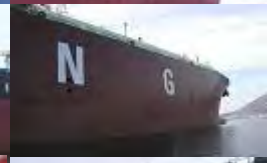
Investigation of new ships for TBT application after the total ban

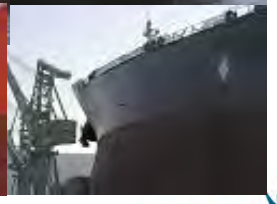


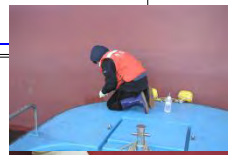


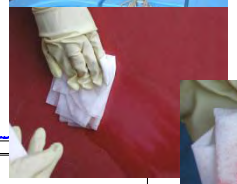












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TBT regulation is effective enough?

- 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

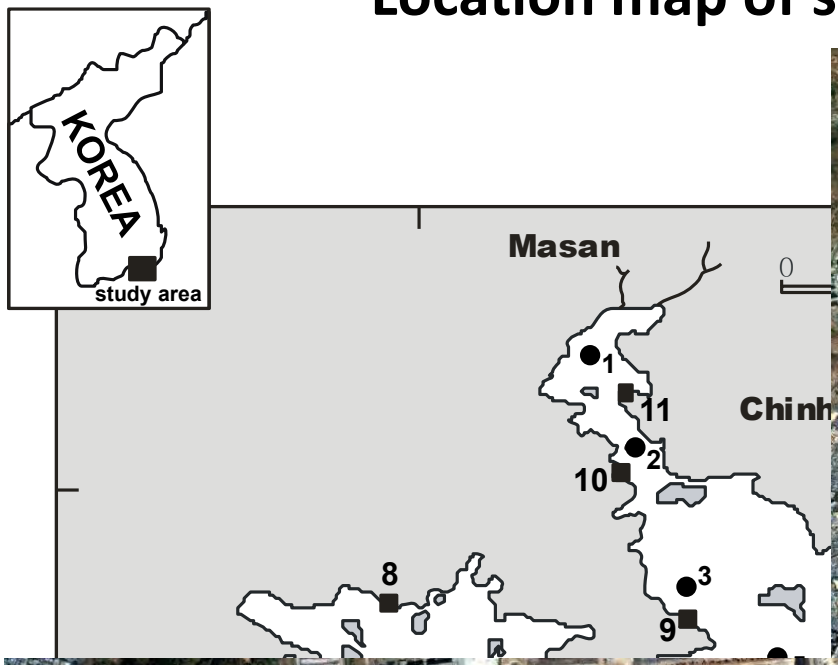
- Unclear regulatory effectiveness in big commercial harbors and shipyards where ocean going vessels are moored and built

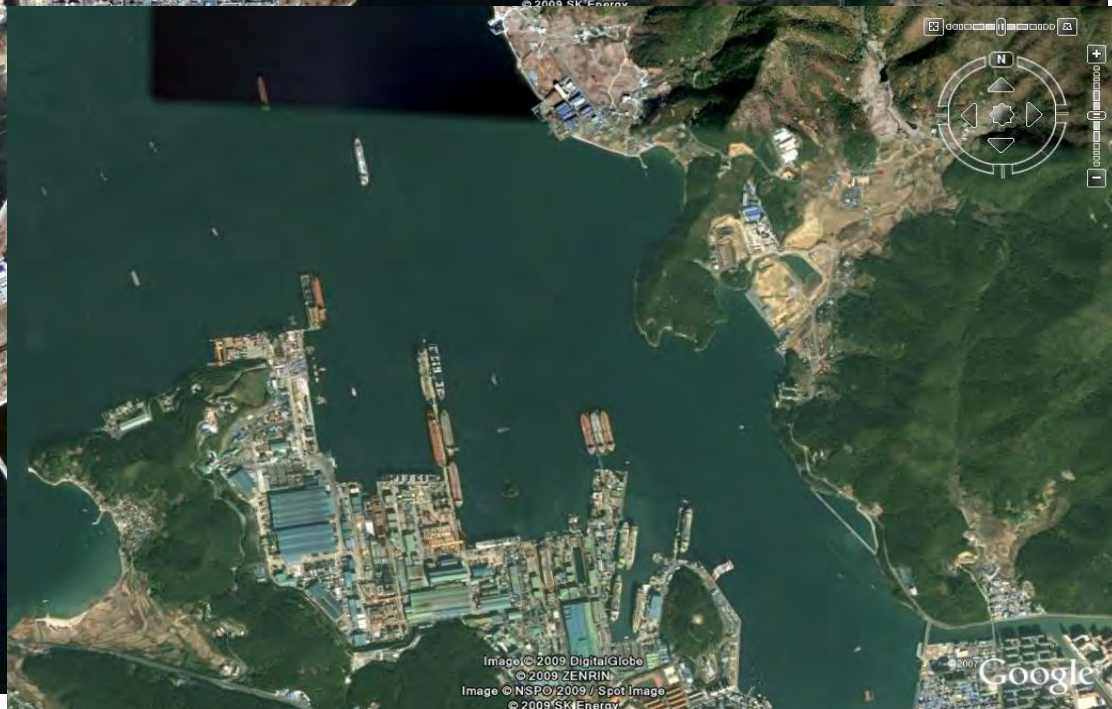
Before

Soccer in lunch time

After

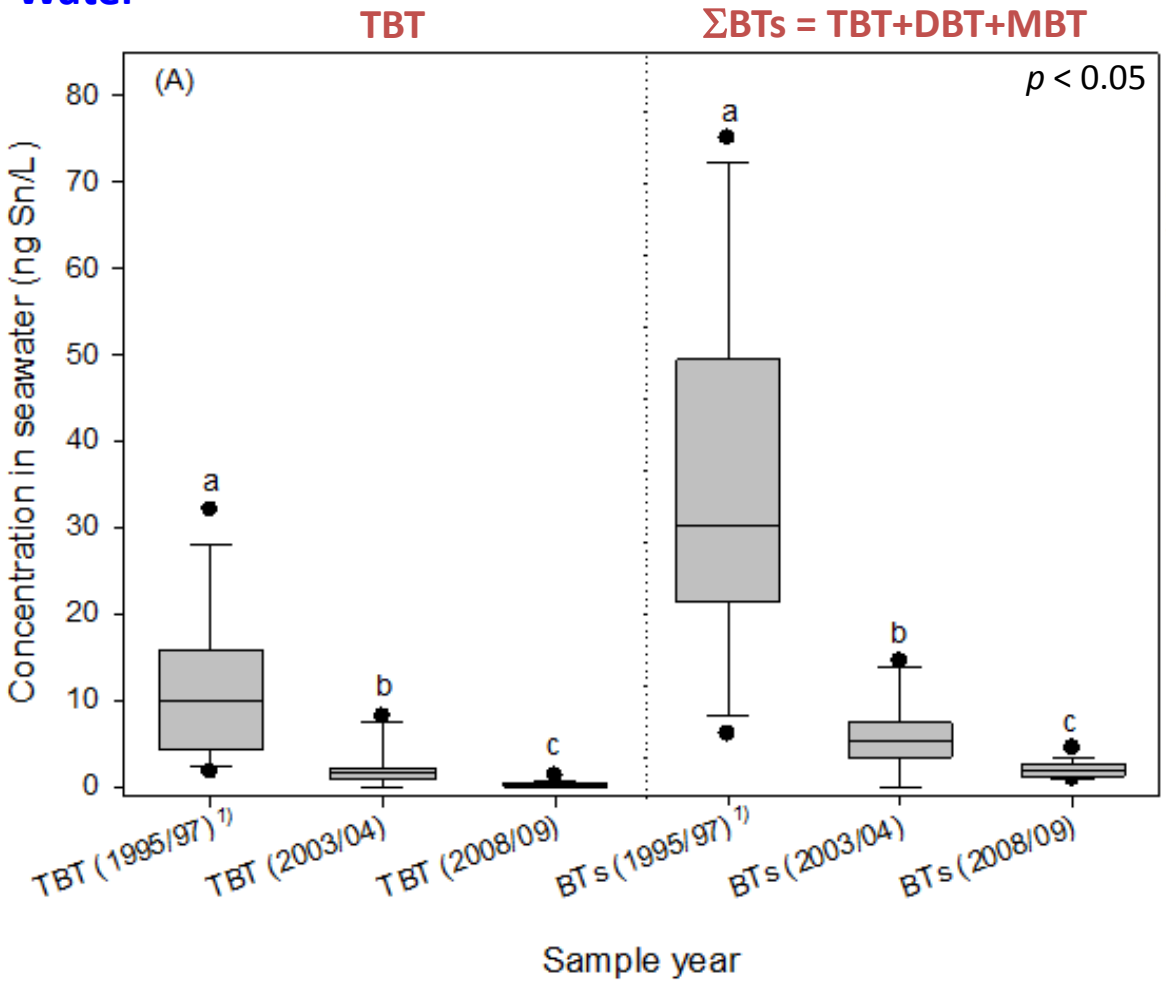
Location map of sampling sites in Jinhae Bay

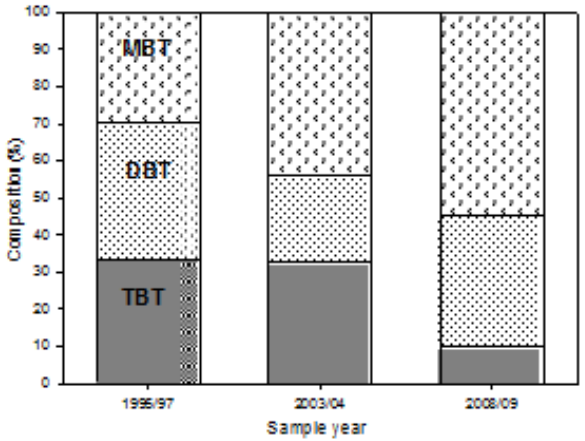




Comparison of water TBT and ΣBTs concentrations in Jinhae Bay before and after the total ban in Korea

Water





[1)]Shim et al. (1998) *Arch. Environ. Contam. Toxicol*.

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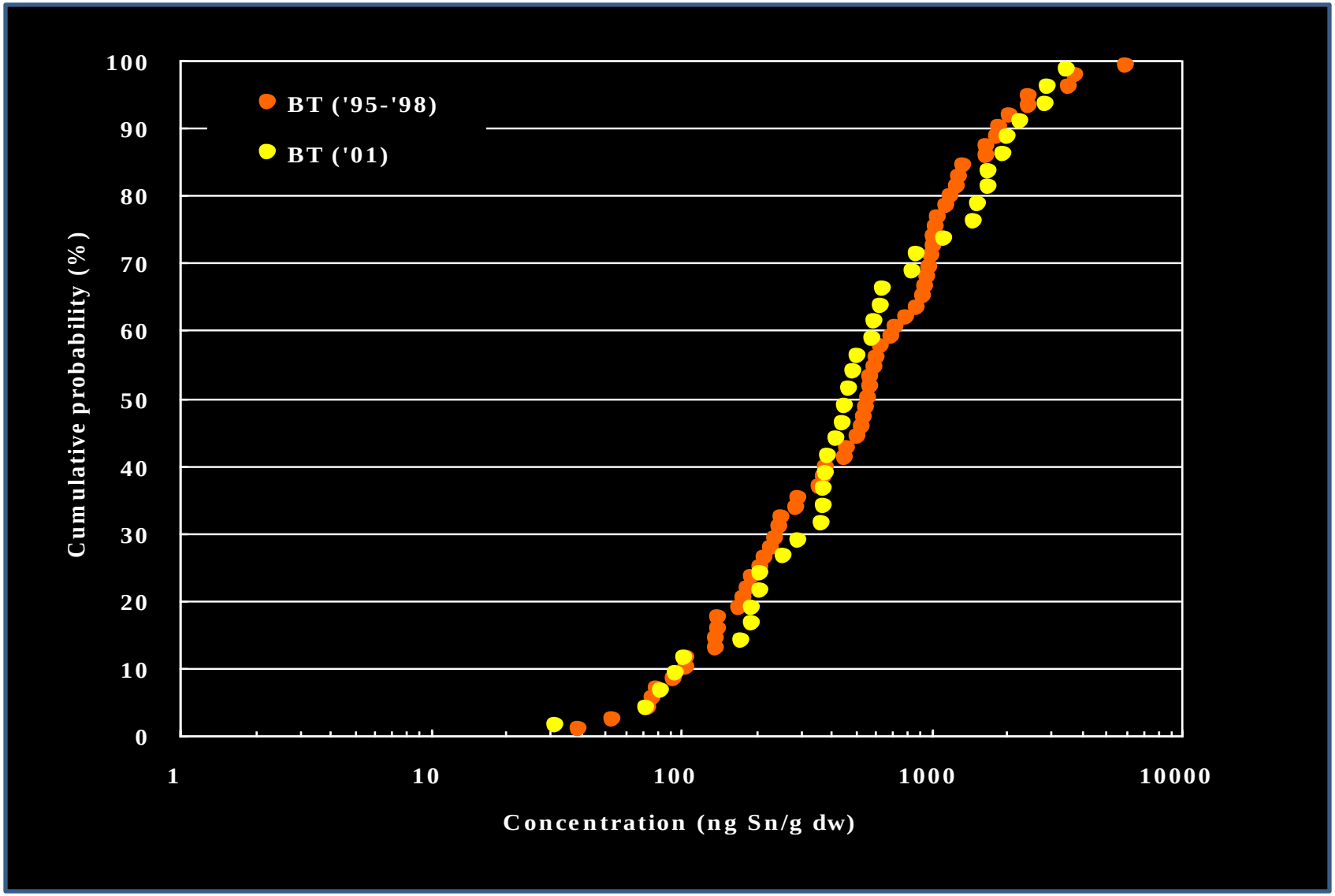
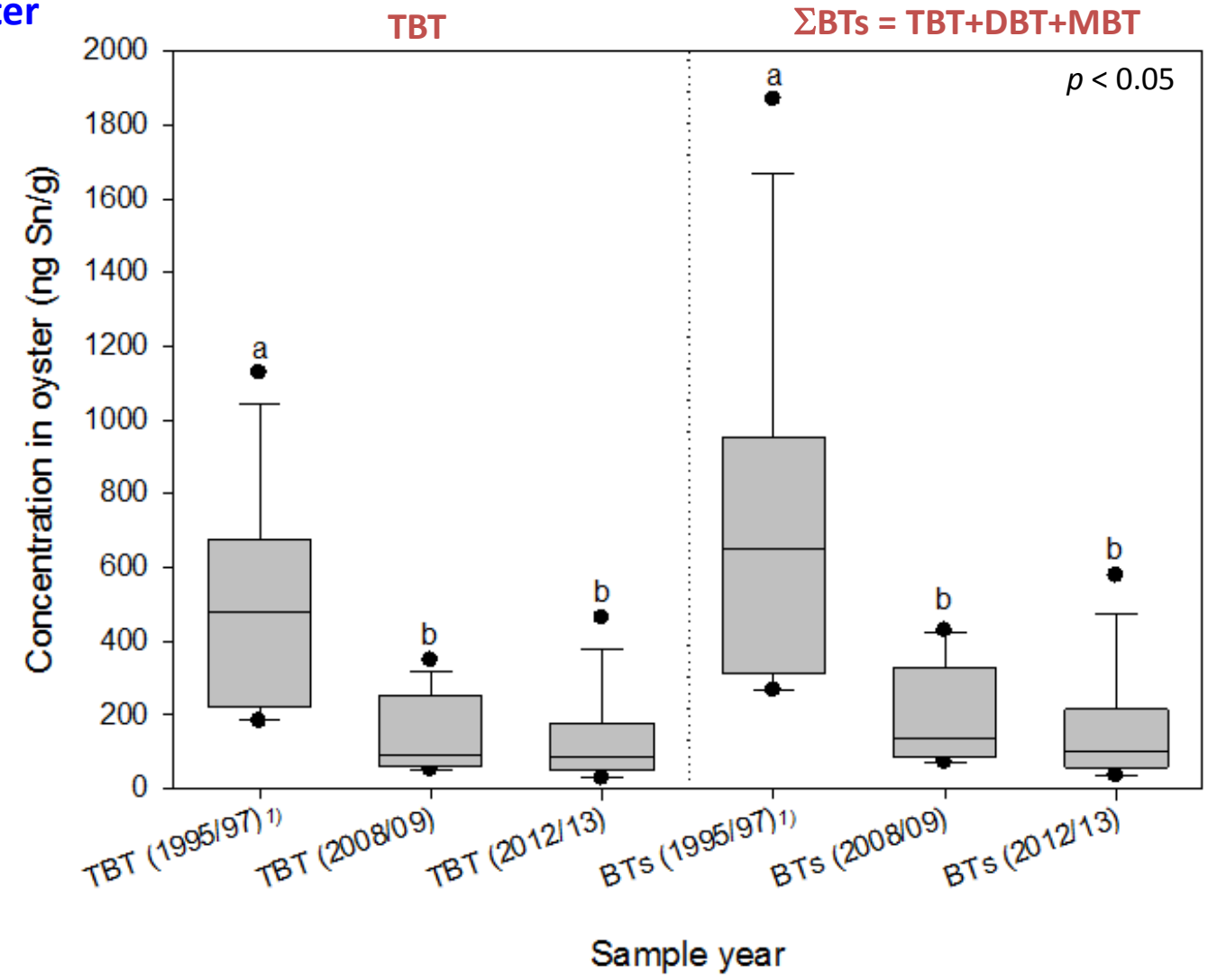
Cumulative distribution of ΣBT concentrations in oyster and mussel in 1995–1998 and 2001 along the Korean coast



Shim et al. (2005) *Mar. Pollut. Bull.*

Comparison of oyster TBT and ΣBTs concentrations in Jinhae Bay before and after the total ban in Korea

Oyster



[1)]Shim et al. (1998) *Arch. Environ. Contam. Toxicol*.

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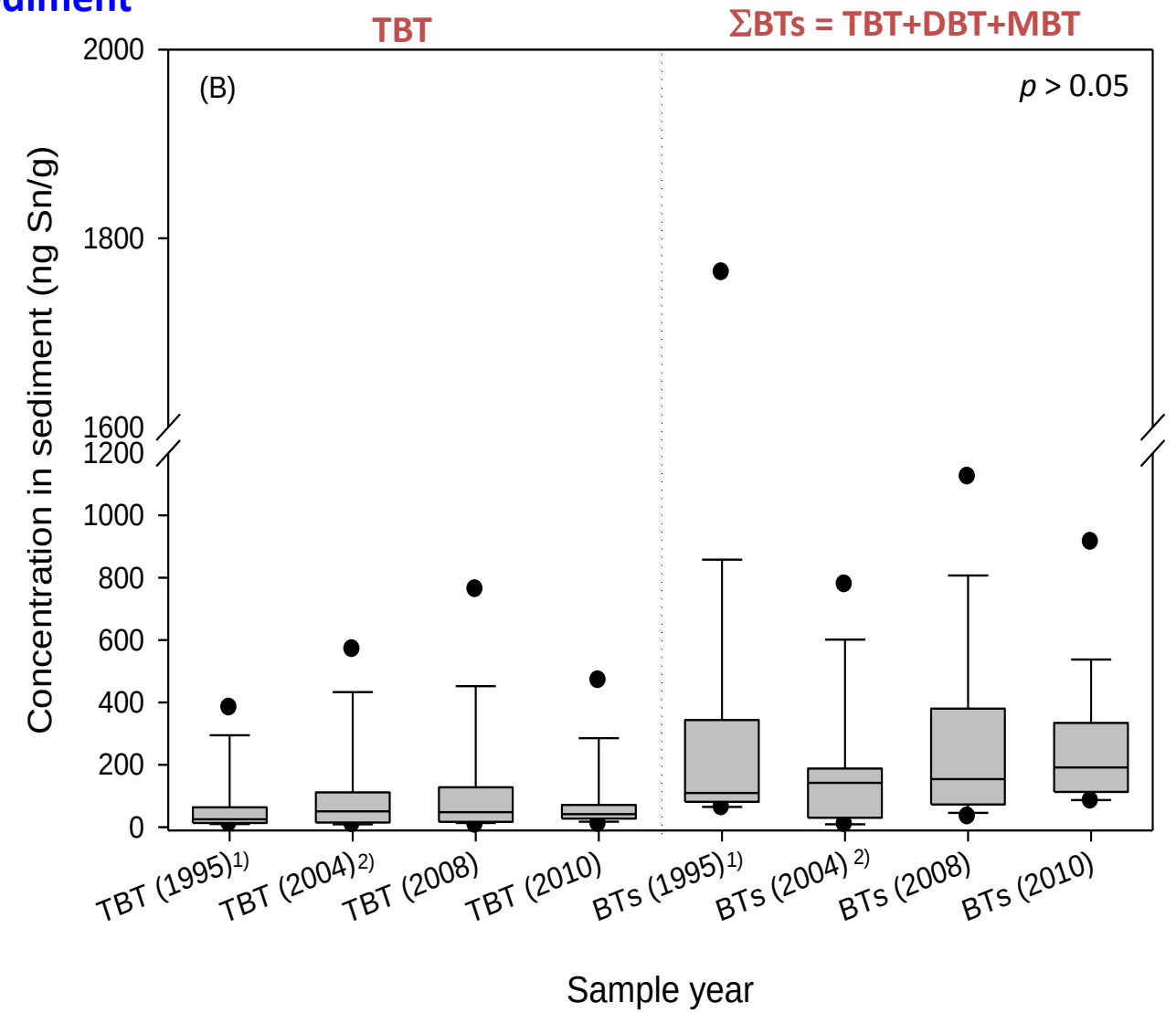
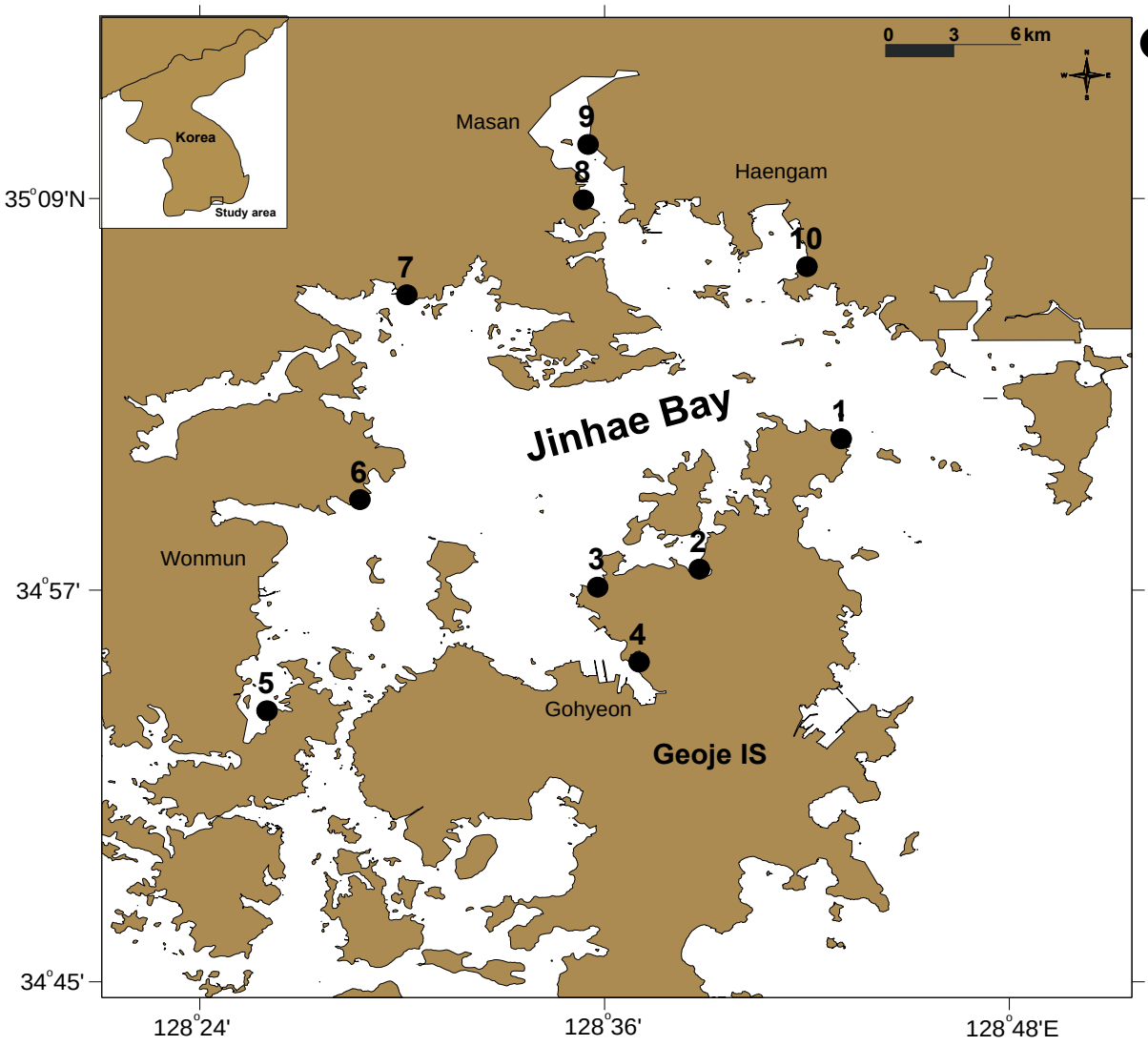
Comparison of sediment TBT and ΣBTs concentrations in Jinhae Bay before and after the total ban in Korea

Sediment



[1)]Shim et al. (1999) *Environ. Pollut.*

Location map of sampling sites for rock shell in Jinhae Bay



● : Rock shell (*Thais clavigera*)
(1995/1997, 2008, 2013)

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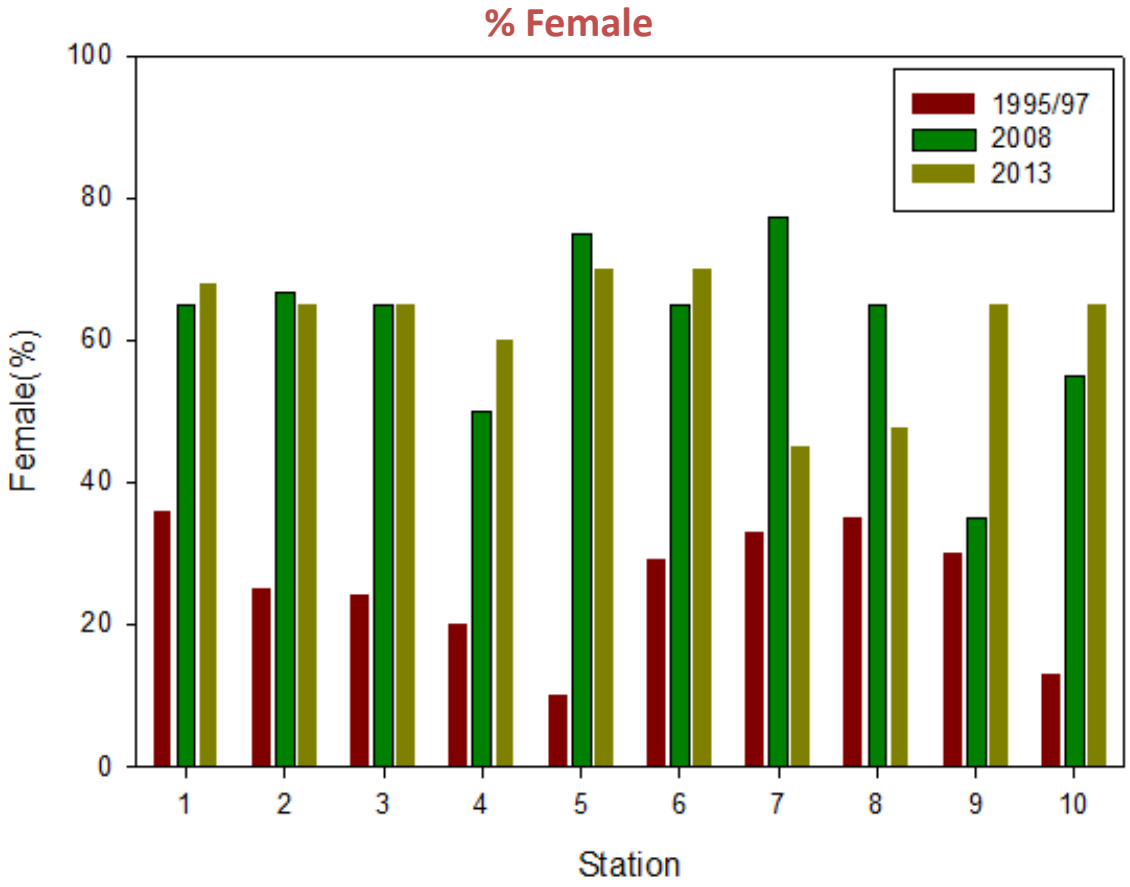
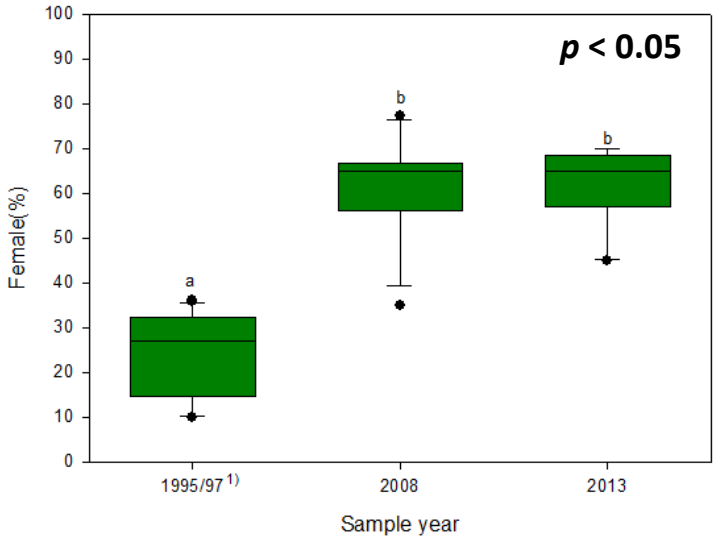
Temporal change of % female in rock shell from Jinhae Bay before and after the total ban in Korea

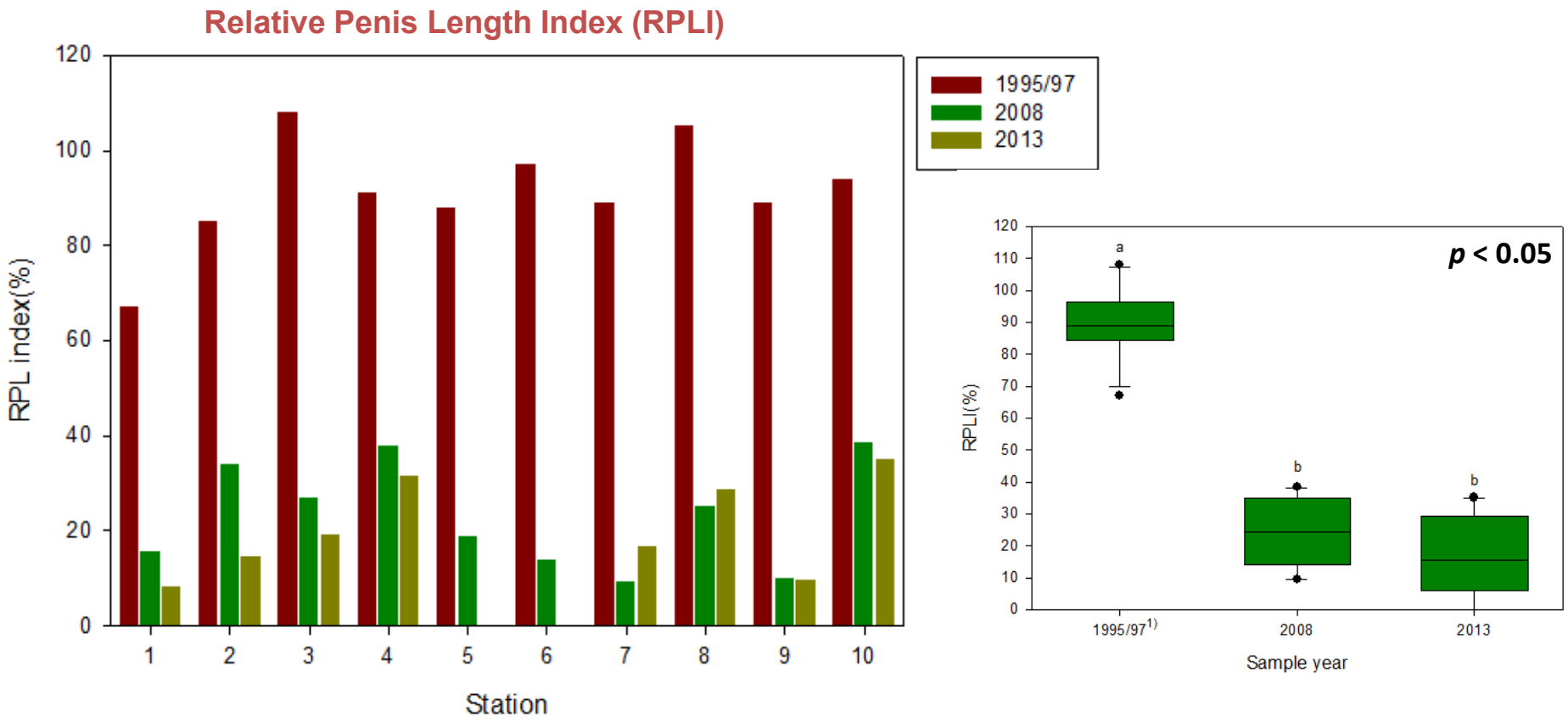




[1)]Shim et al. (2000) *Mar. Environ. Res.*

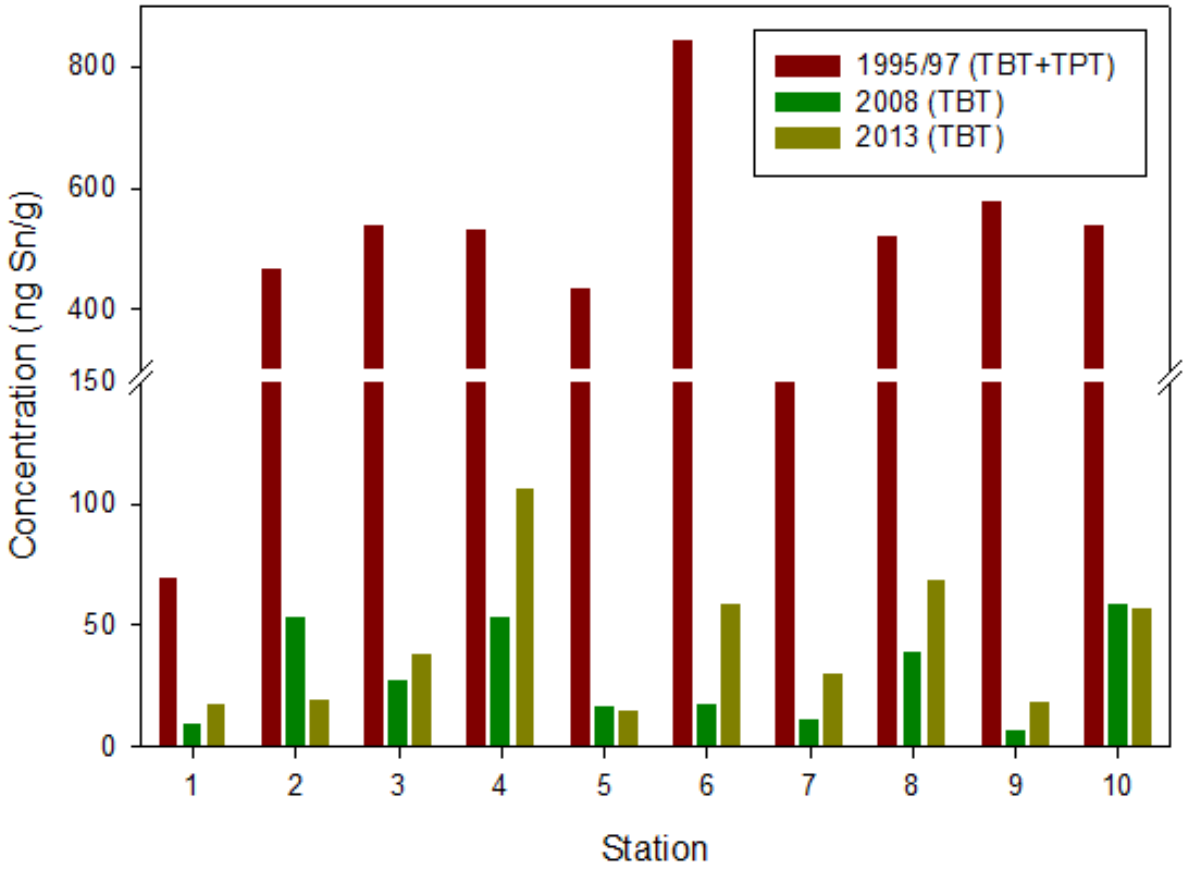
Temporal change of RPLI in rock shell from Jinhae Bay before and after the total ban in Korea

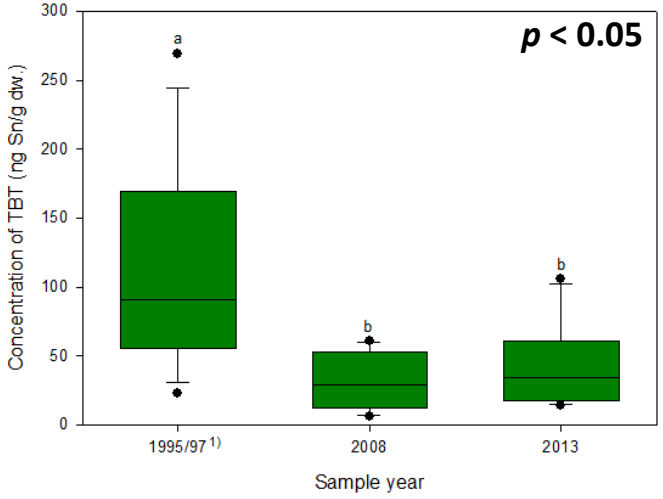
RPLI (%) = [mean female pseudo-penis length] / [male penis length]



Temporal change of TBT concentrations in rock shell from Jinhae Bay before and after the total ban in Korea

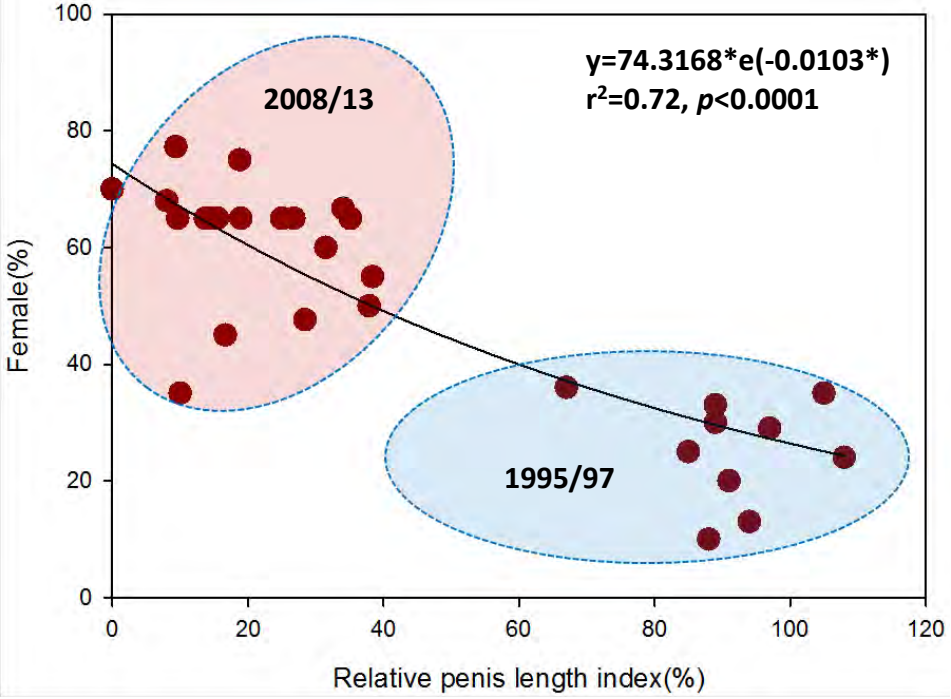
TBT and TPT concentrations



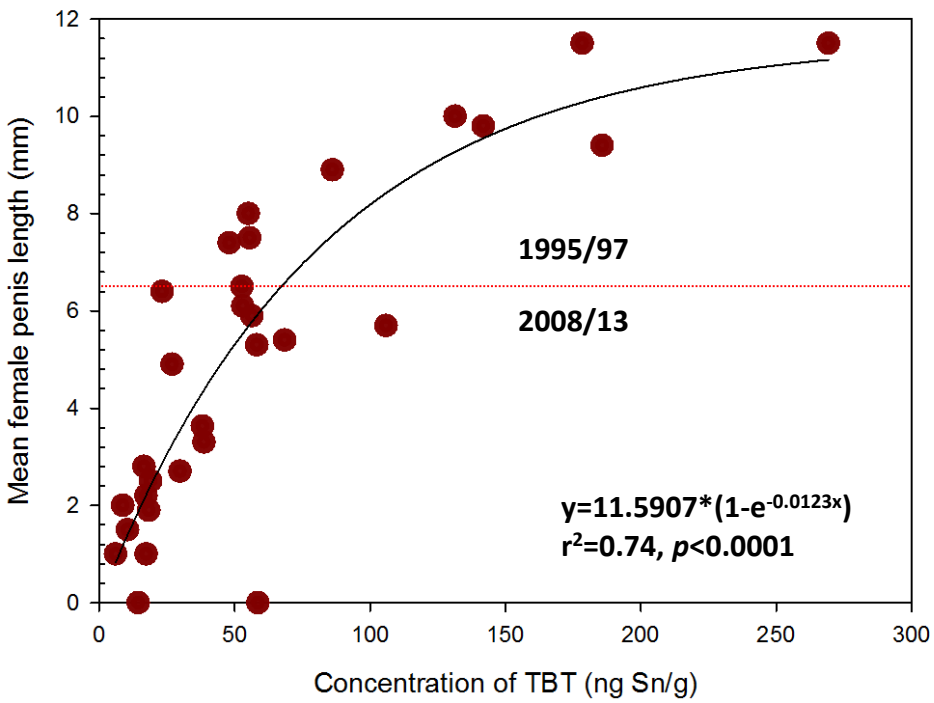


Relationship between RPL index *vs* % female and TBT concentrations *vs* mean female pseudo-penis length in rock shell from Jinhae Bay

RPL index *vs* % female



TBT *vs* mean female pseudo-penis length



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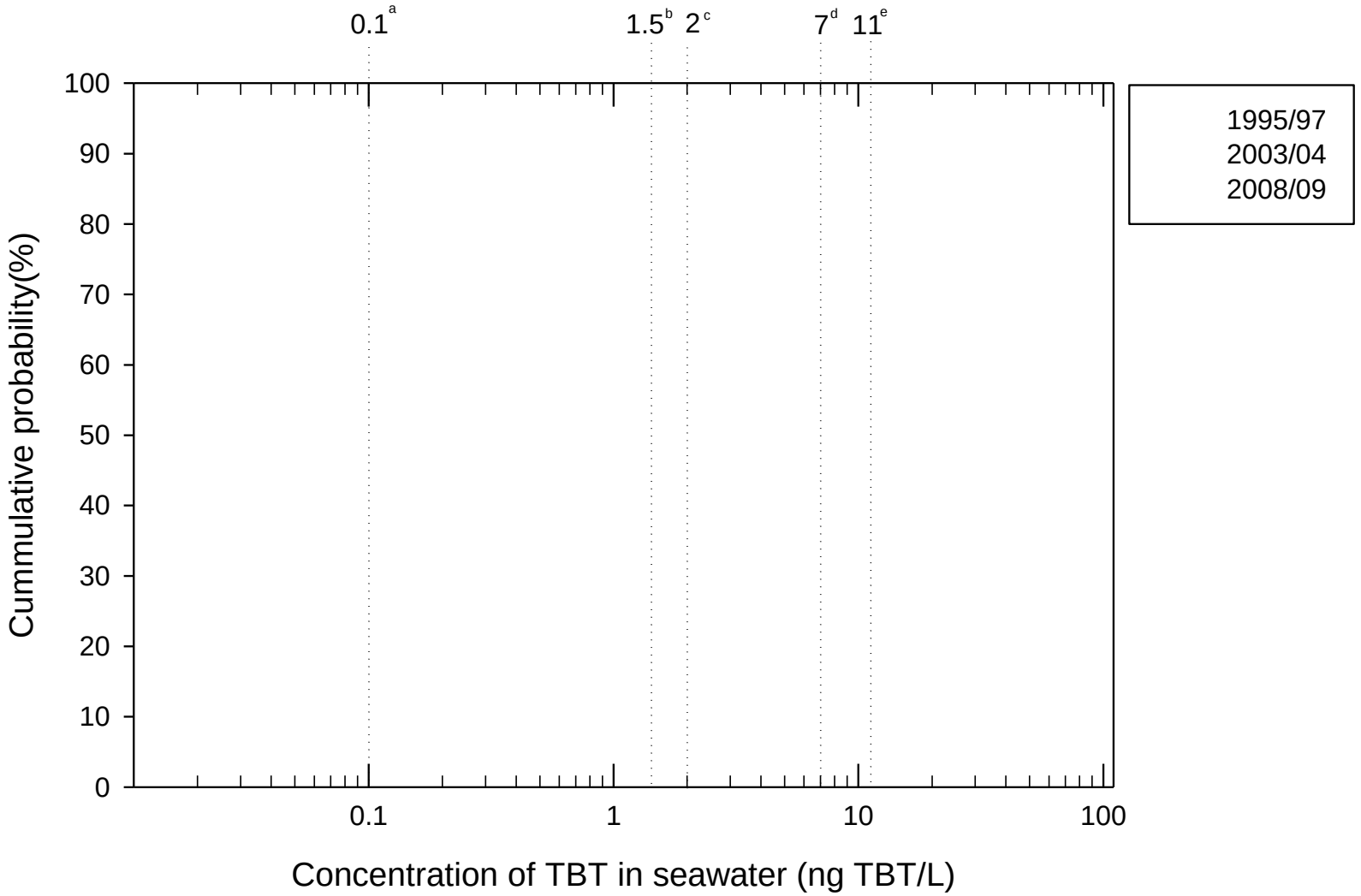
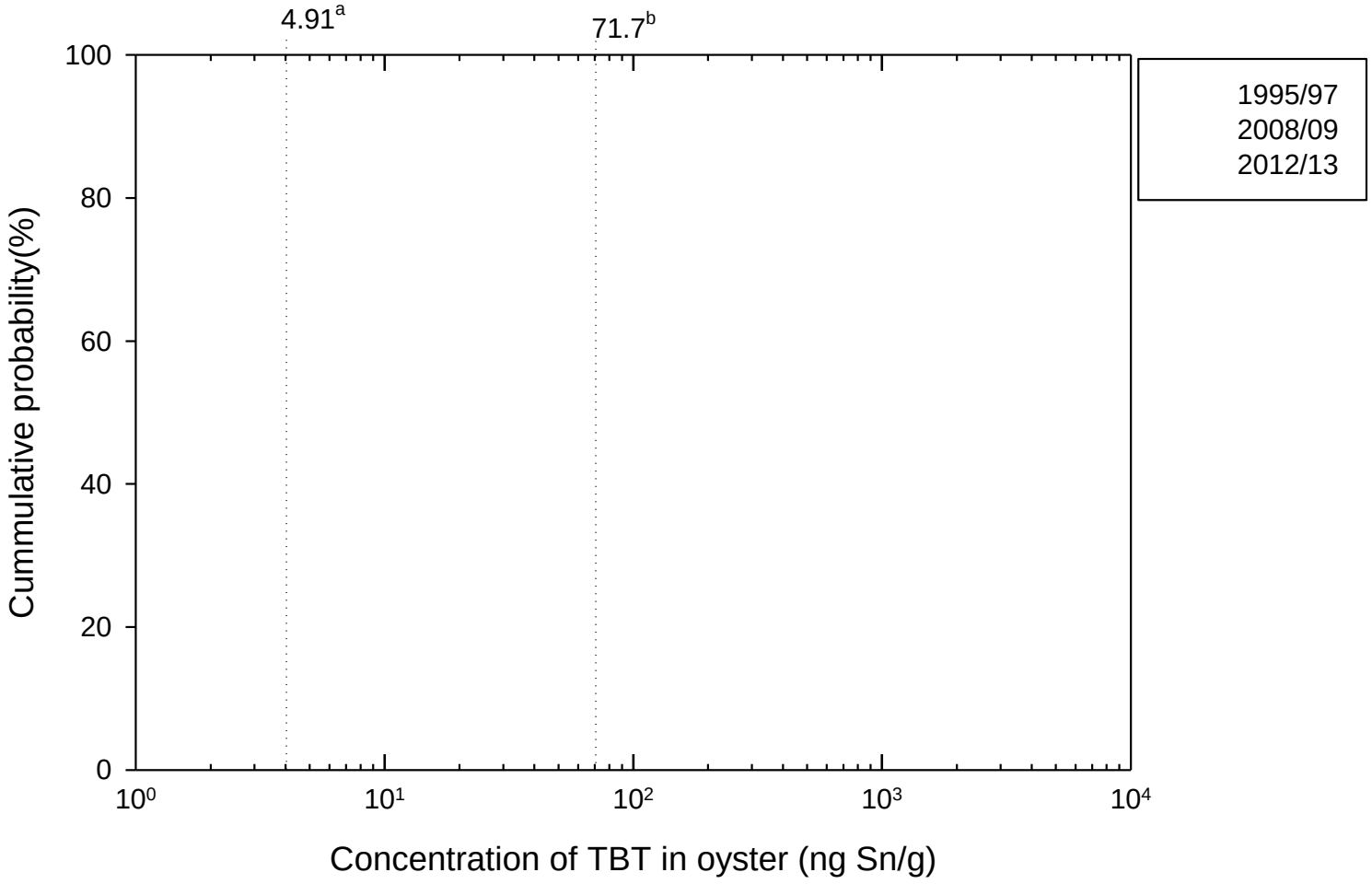
Ecological concern of current TBT concentrations in seawater



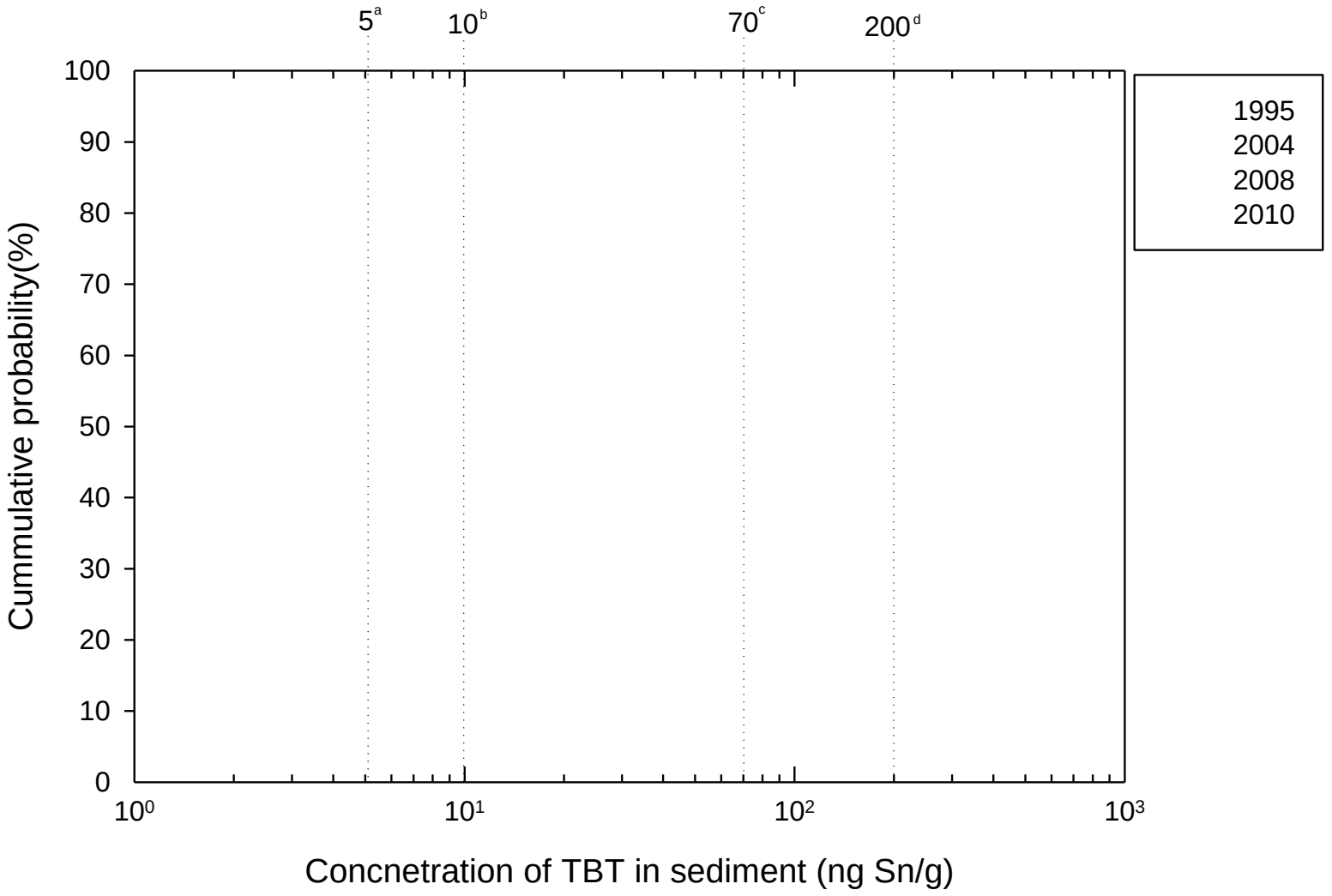
[a],[b] Lower and upper ecotoxicological assessment criteria (EAC) values by the OSPAR Commission (OSPAR, 2004)
[c] UK environment quality target (EQT) (UK, 1989)
[d] Chronic Criterion by US EPA (US EPA, 2004)
[e] Dutch government environmental quality limit (converted ion to chloride) (Rajendran et al., 2001)

Ecological concern of current TBT concentrations in oyster



[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



[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

KIOST 한국해양과학기술원
Oil & POPs RESEARCH GROUP
해양수산부 MINISTRY OF OCEANS AND FISHERIES
mev 환경부 MINISTRY OF ENVIRONMENT

Nam Sook Kim
Sang Hee Hong
Gi Myung Han
Sung Yong Ha

Thank you!