Ship antifouling biocides used in Japan and their environmental risk

1. Biofouling /Antifouling (A/F)
2. Ship A/F biocides in Japan
3. Environmental risk assessment
4. Cybutryne study
5. Copper study

Hideo OKAMURA and Hiroshi KAWAI

Kobe Univ. Research Center for Inland Seas (KURCIS)

Biofouling on boat

Countermeasure to prevent Biofouling

Anti-fouling (A/F) system is needed

to prevent biofouling on ship hulls, fishing nets, submerged structures, and water cooling pipes, and so on,

For ships

1) to improve fuel efficiency,

2) to improve ship operation (=ship maneuverability),

3) to suppress CO_2 and air pollutant emission via exhaust gas,

4) to suppress translocation of alien species via ship-hull.

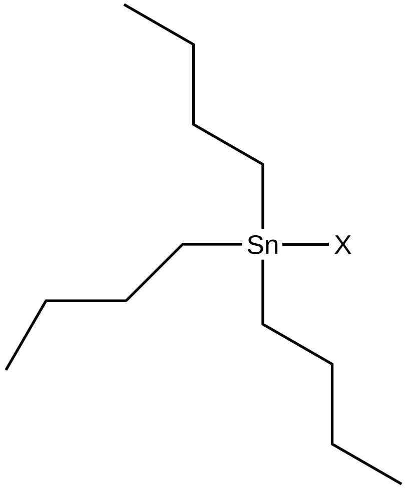
Two major A/F systems

1. Biocide A/F system = Toxic chemical type

- Copper and copper compound (Cu_2O)
- Booster organic compound

2. Non-biocide A/F system = Physical foul-release type

- Silicon, semi-silicon, Teflon, Fluoropolymer
- Fiber-flock system etc.



TBT banned due to PBT features+

Persistency: high

Bioaccumulation: moderate

Toxicity: high and

Imposex as endocrine disrupting activity

TBT on ship hull banned since 2008 by IMO (International Maritime Organization) - AFS (Anti-Fouling System) Convention

"International convention on the control of harmful antifouling systems on ships, 2001", entered into force on 17 September 2008.

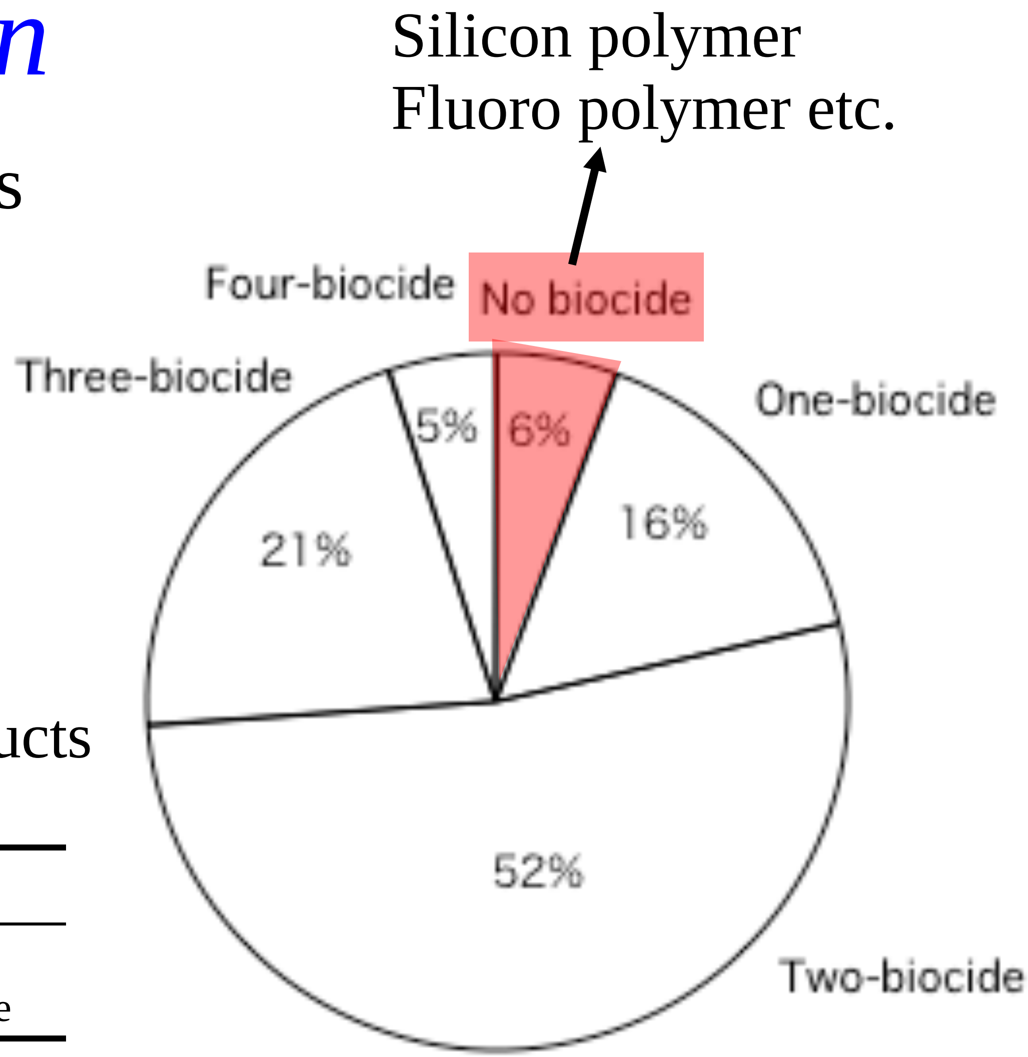
AFS Convention banned TBT and bans harmful compounds in the future.

A/F systems in Japan

JPMA (Japan Paint Manufacturers Association) has regulated A/F system used in Japan since 2004, based on environmental risk approach for A/F biocides.

Number of commercial A/F paint products in Japan

	02/2005		03/2017	
	paint products	biocide	paint products	biocide
Biocide-free	16	0	17	0
Biocide	325	16	356	17
total	341		374	



AF paint products at 2005

17 A/F biocides in commercial paints in Japanese market.

● persistent

Copper included

CAS RN		trivial name	in 356 biocide-type products* frequency	ratio	approved by BPR	USEPA
1317-39-1	●	Dicopper oxide (Cu_2O)	246	0.69	yes	yes
14915-37-8		Copper pyrithione (CuPT)	124	0.35	yes	yes
13463-41-7		Zinc pyrithione (ZnPT)	84	0.24		yes
971-66-4		Pyridine triphenylborane (TPBP)	58	0.16		
64359-81-5		DCOIT (Sea Nine 211)	54	0.15	yes	yes
330-54-1	●	Diuron	32	0.09		
28159-98-0	●	Cybutryne (Irgarol 1051)	25	0.07		yes
122454-29-9		Tralopyril (ECONEA)	19	0.05	yes	yes
12122-67-7		Zineb	19	0.05	yes	
731-27-1		Tolylfluanid	9	0.03	yes	yes
1111-67-7	●	Copper thiocyanate (CuSCN)	8	0.02	yes	yes
1897-45-6		2,4,5,6-Tetrachloroisophthalonitrile	5	0.01		
13167-25-4		N-(2,4,6-Trichlorophenyl)maleimide	4	0.01		
137-30-4		Ziram	4	0.01		
13108-52-6		2,3,5,6-Tetrachloro-4-(methylsulphonyl)pyridine	1	0.00		
117659-55-9		2,3-Dichloro-N-(2-ethyl-6-methylphenyl)maleimide	1	0.00		
56746-18-0		2,3-Dichloro-N-(2,6-diethylphenyl)maleimide	1	0.00		
86347-14-0		Medetomidine	0	0	yes	
7440-50-8	●	Copper flake	0	0	yes	yes

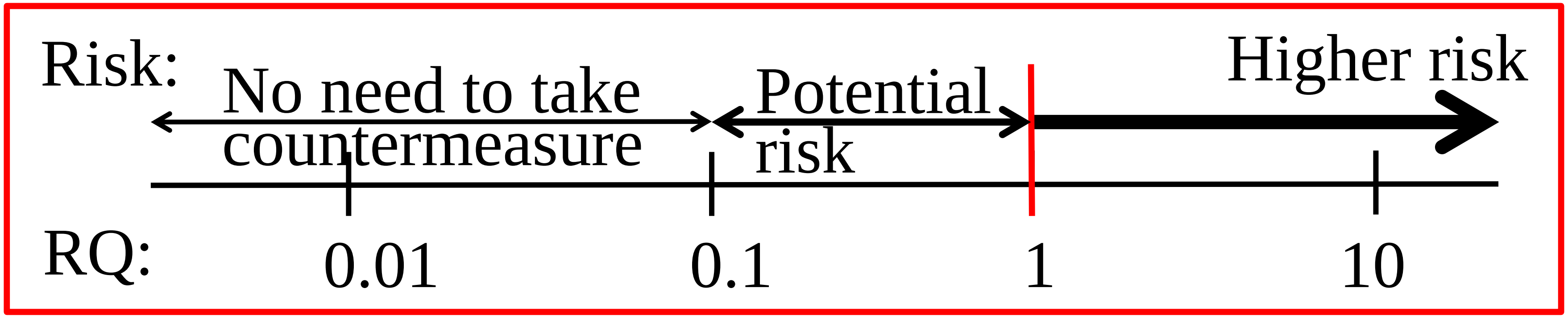
* Total 374 products including 356 biocide-type and 18 foul-release type from 12 companies are registered under the auspicies of JPMA (Japan Paint Manufacturers Association) investigation dated on March 2017.

Environmental Risk Assessment of Chemical

Risk Quotient (RQ) = PEC / PNEC > 1

PEC: Predicted Environmental Concentration

PNEC: Predicted No-observed Effect Concentration



As PEC, the concentrations calculated by model simulation or the ones reported in references (monitoring data)

As PNEC, the Hazard Concentration (HC5)* calculated from Species Sensitivity Distribution (SSD) analysis or the highest toxicity values (EC50/LC50 or NOEC)** to different genus organisms

*the HC5 be divided by assessment factor (1~10)

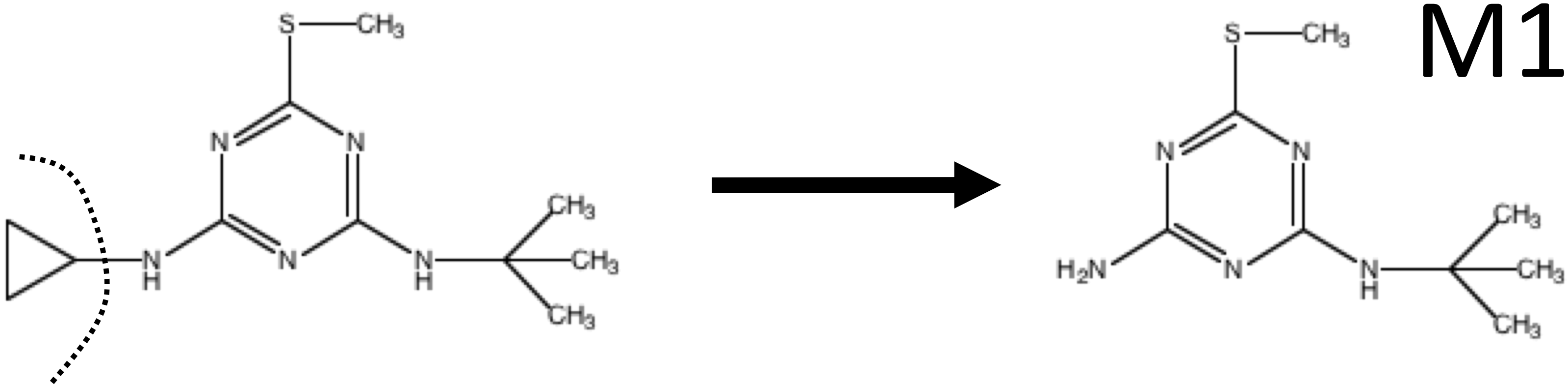
**the lowest toxicity values be divided by assessment factor (10, 100, or 1000)

Cybutryne= Irgarol 1051

- a *s*-triazine compound
- not used as herbicide anywhere
- Residues in seawater, Monaco
  (Readman et al., 1993)

No data at 1996, I had Cybutryne from Dr. Liu, NWRI, Canada.

- Residues in seawater, Japan ?
- Environmental fate?
- Degradation?



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Degradation pathway

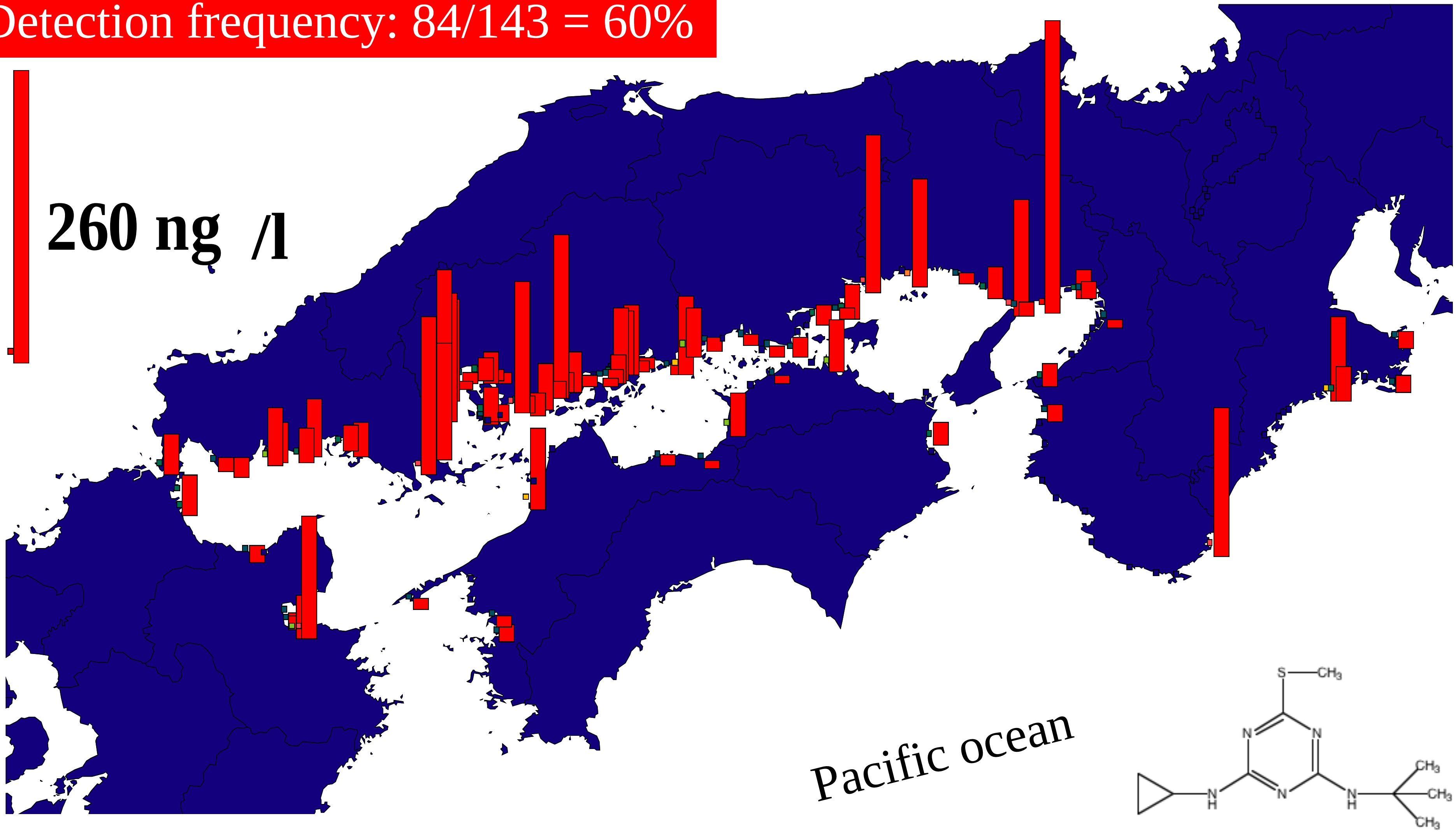
1) biodegradation by white rot fungi by Liu *et al* (1997) *Water Res* 31: 2363

2) hydrolysis catalysed by mercuric ion by Liu *et al* (1999) *Water Res* 33: 155

3) photodegradation by natural sunlight by Okamura *et al* (1999) *J Environ Sci Health* B34: 225

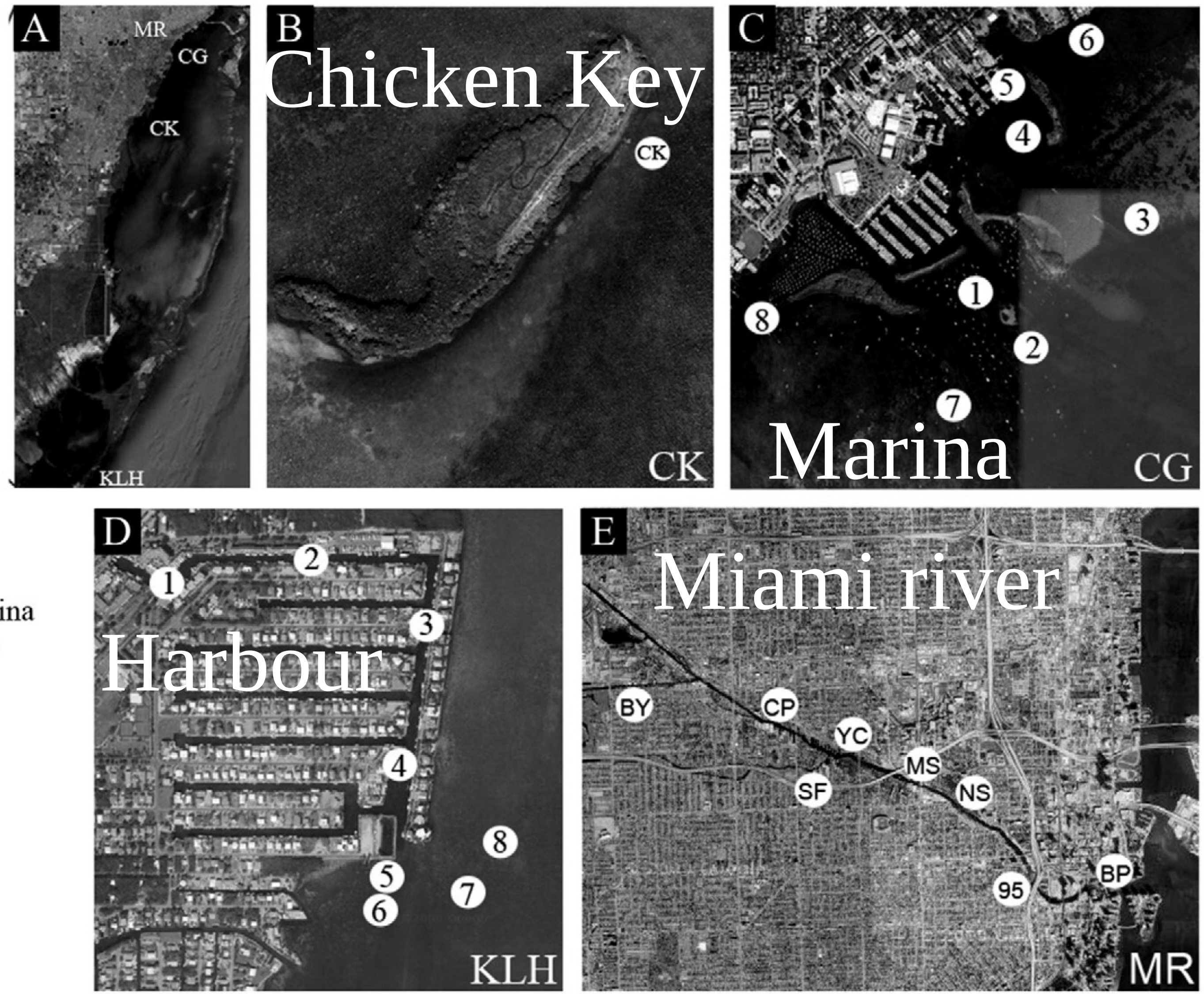
Cybutryne residues in 1999 survey, Japan

Detection frequency: 84/143 = 60%



Okamura et al. 2003. *Mar. Pollut. Bull*. 47: 59

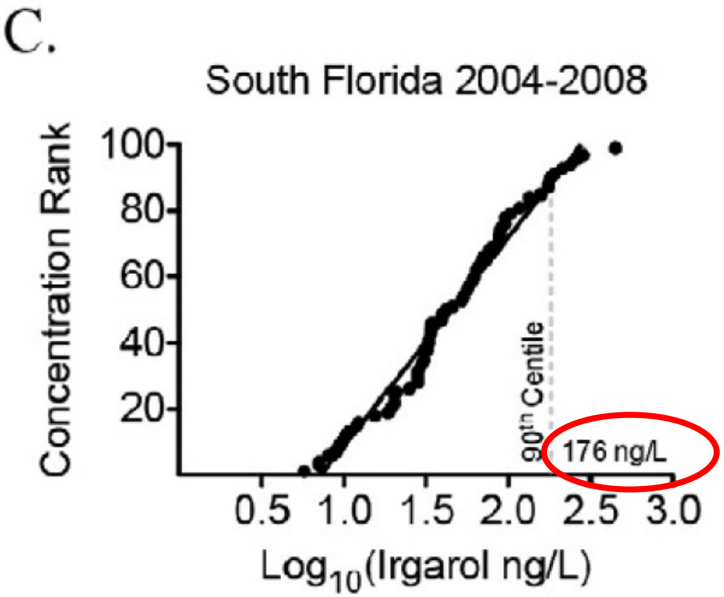
*Cybutryne residues in 2004-2008, the United States**



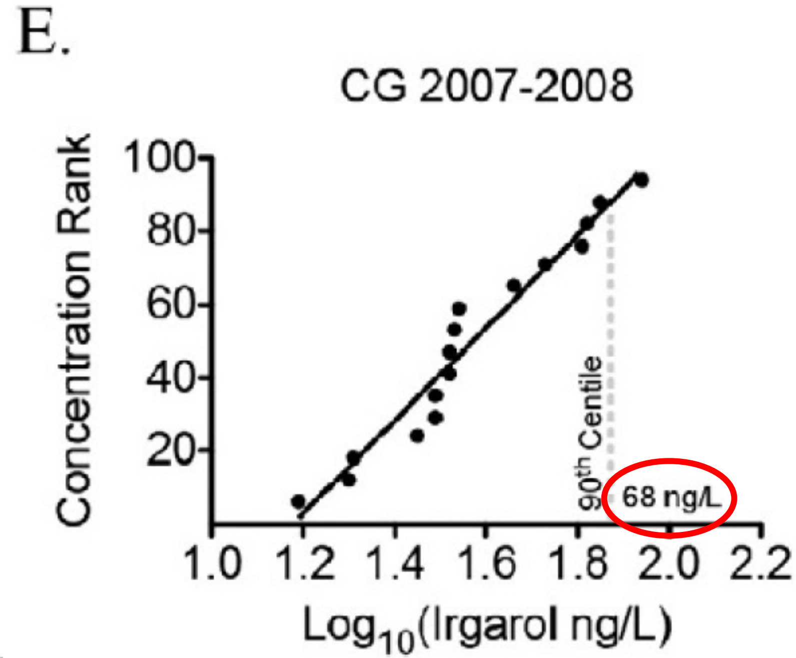
A. Southeast Florida
B. CK = Chicken Key
C. CG = Coconut Grove Marina
D. KLH = Key Largo Harbor
E. MR = Miami River

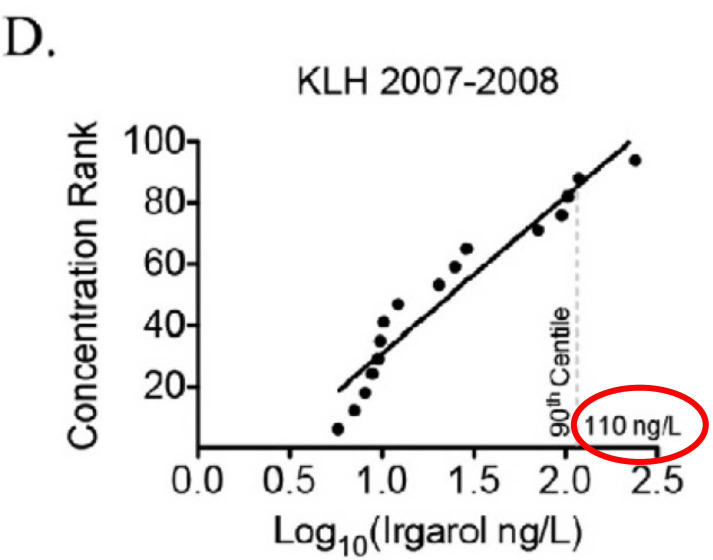
*Fernandez, M.V
& Gardinali, P.R. 2016.
Sci.Total Environ., 541:
1556-1571

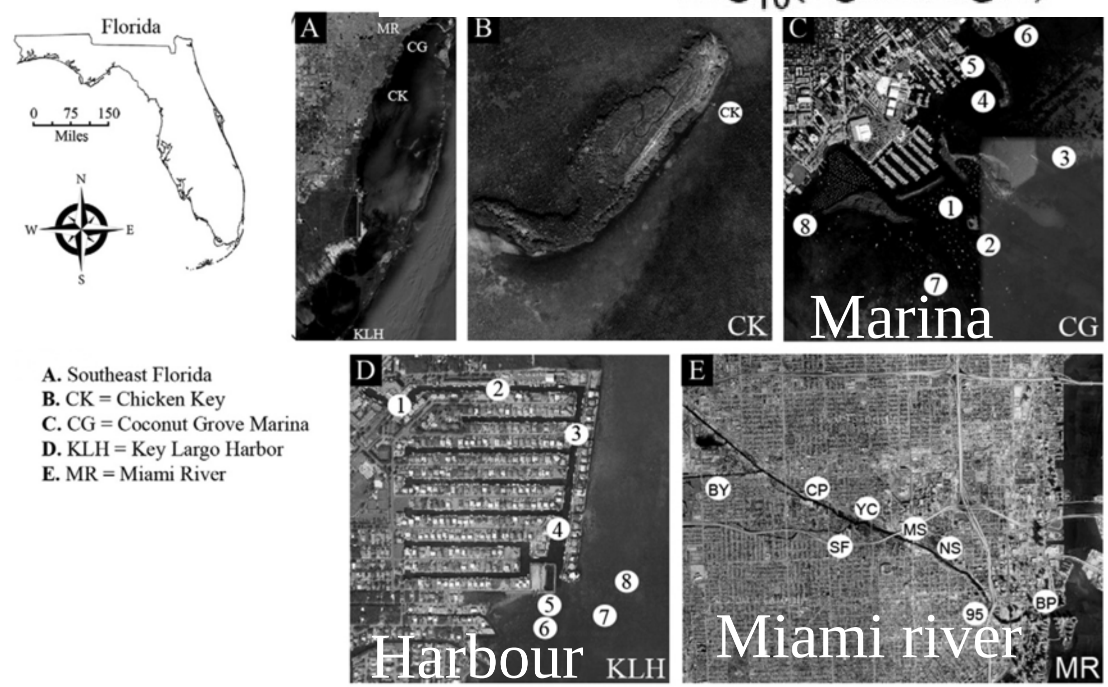
90th percentile of Cybutryne residues in seawater



Cybutryn
= Irgarol
= Irgarol 1051

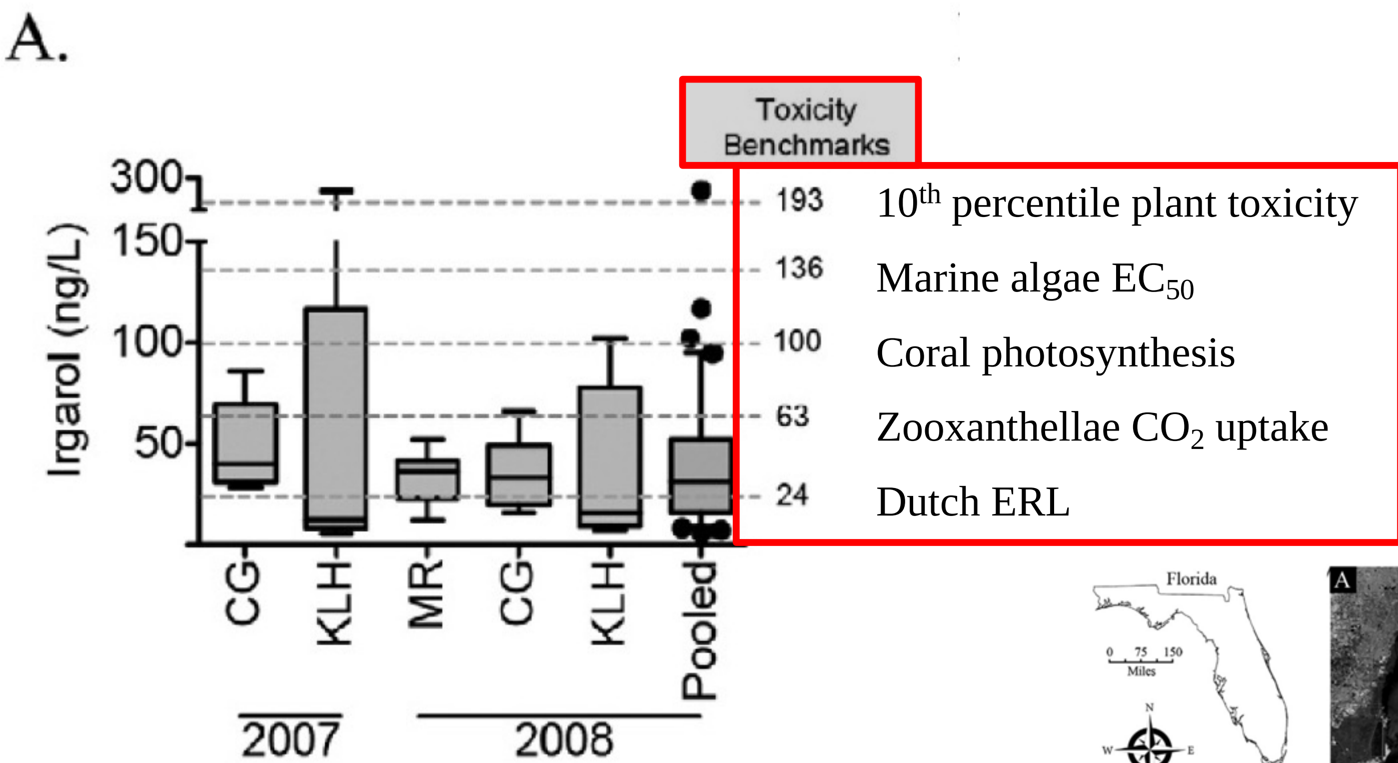




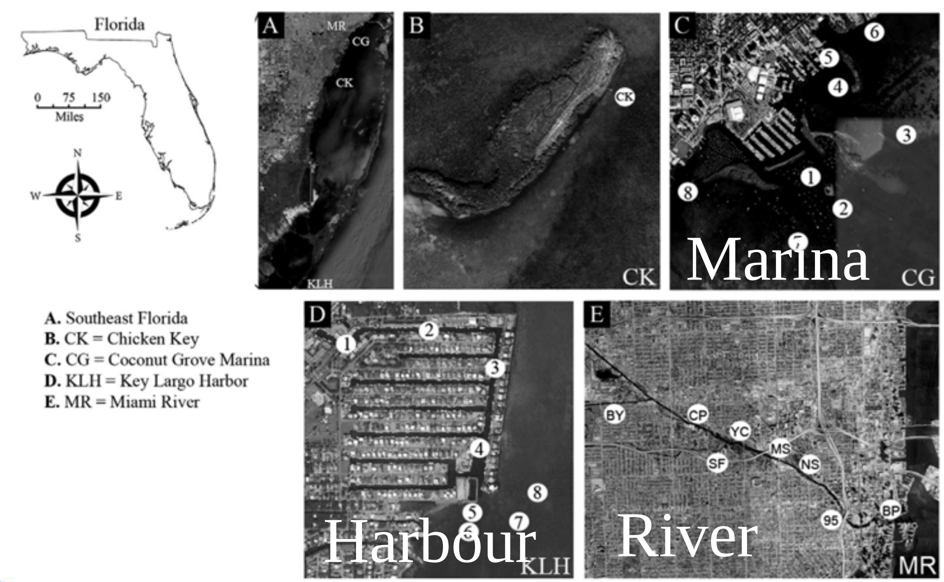


Cybutryne Residues with Toxicity Benchmark

*Fernandez, M.V & Gardinali, P.R. 2016. Sci.Total Environ., 541: 1556



Use of Cybutryne has been regulated within EU, already banned in Denmark, UK, Sweden, Netherlands, New Zealand, and Bermuda by 2016, and will be banned by IMO.



Cybutryne regulation by IMO

INTERNATIONAL MARITIME ORGANIZATION

E

Environmental Risk
RQ = PEC/PNEC > 1 ?

SUB-COMMITTEE ON POLLUTION PREVENTION AND RESPONSE
6th session
Agenda item 6

Cover page

PPR 6/INF.7
10 December 2018
ENGLISH ONLY

AMENDMENT OF ANNEX 1 TO THE AFS CONVENTION TO INCLUDE CONTROLS ON CYBUTRYNE, AND CONSEQUENTIAL REVISION OF RELEVANT GUIDELINES

Information presenting scientific evidence for the adverse effects of cybutryne to the environment

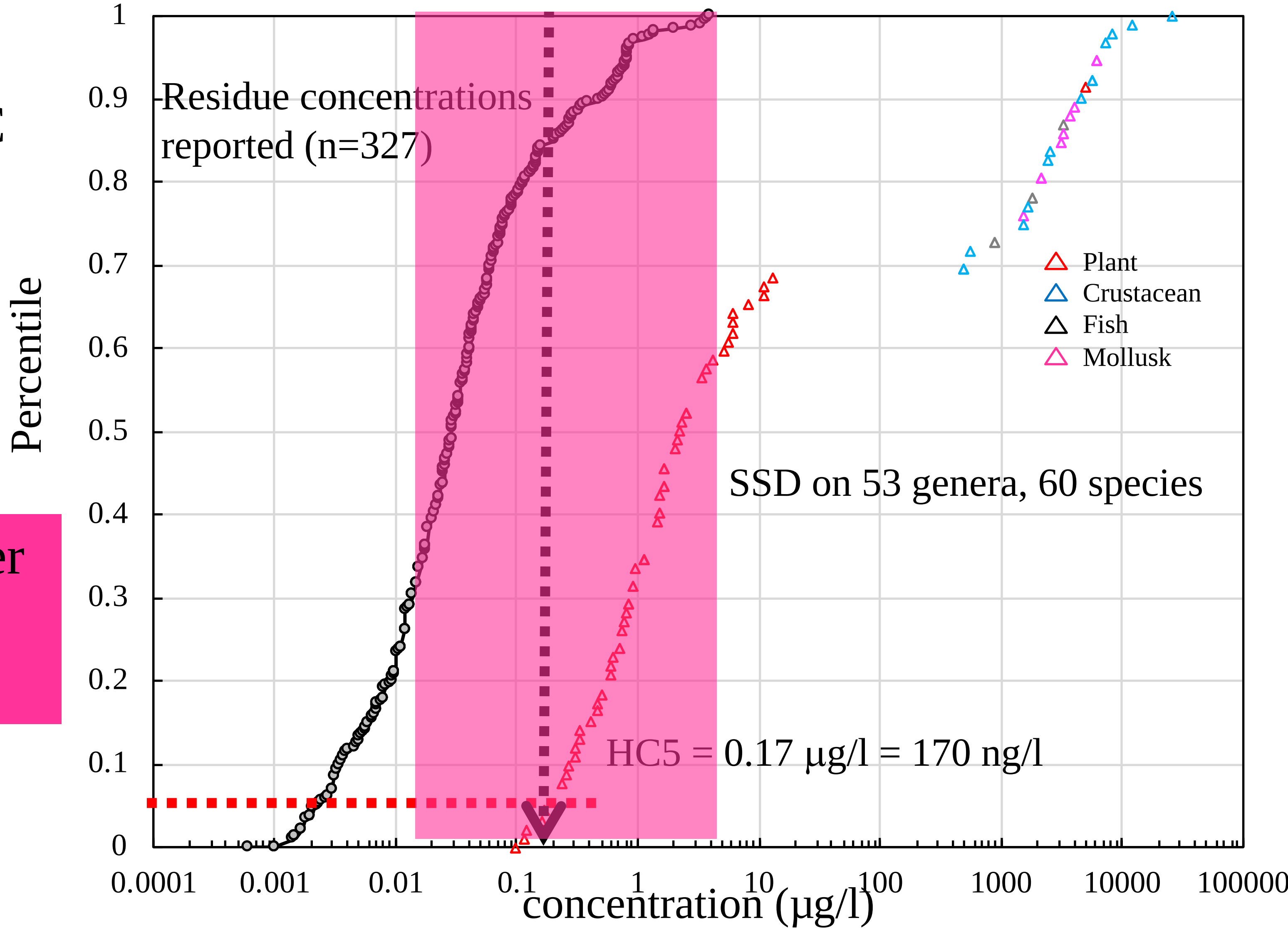
The document summarizes the data published on hazard as well as on exposure of Cybutryne.

Analysis of the data to estimate environmental risk of Cybutryne
For PEC, monitoring data worldwide (n=327) were made in graph.
PNEC was estimated by two method using hazard data.
1) the HC5 from SSD analysis
2) the highest toxicity value, adopted by Japan Ministry of the Environment.

Environmental Risk of Cybutryne by SSD

(Species Sensitivity Distribution)

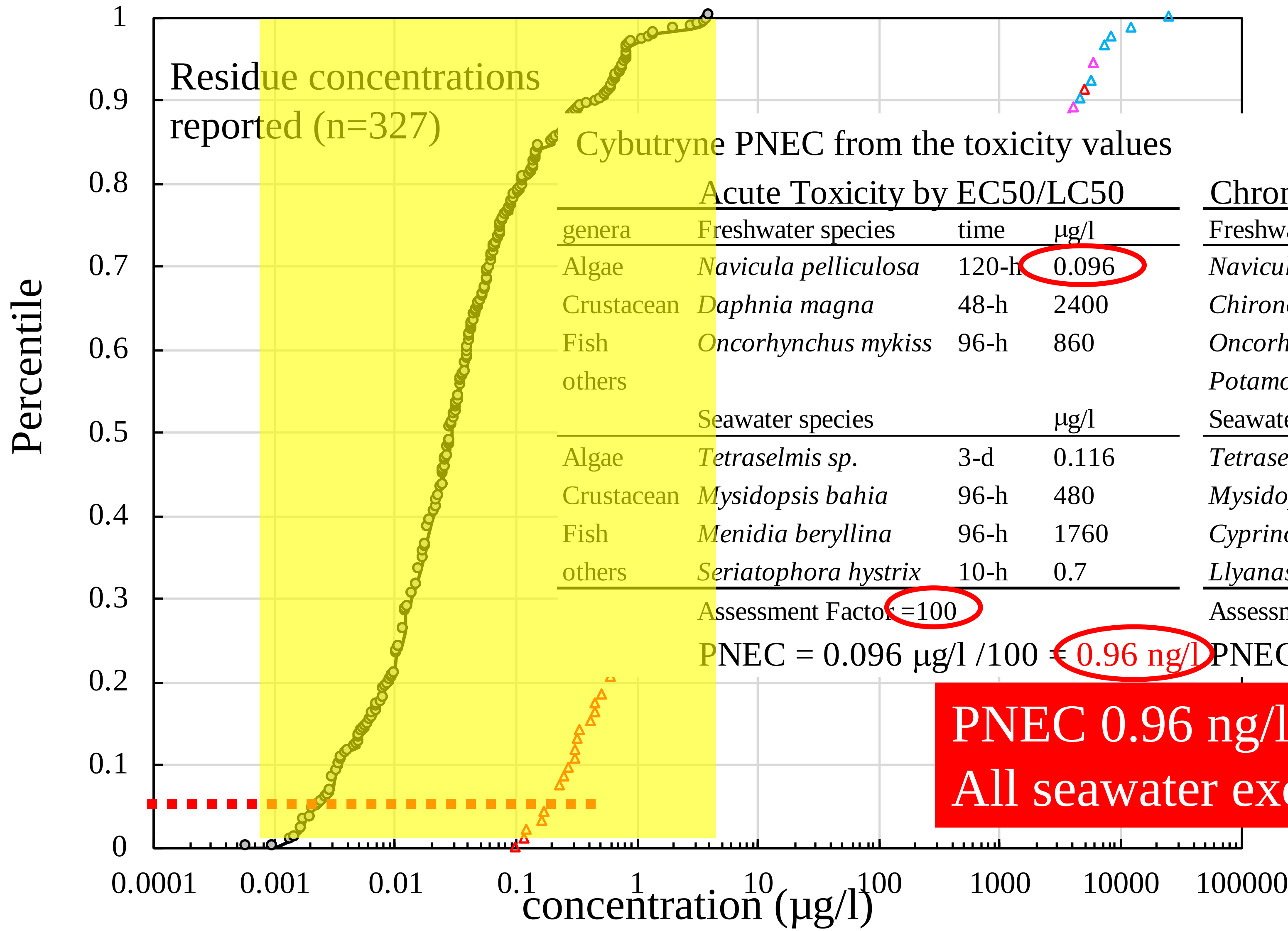
RQ = PEC/PNEC



About 70% seawater exceeds PNEC (HC5/10= 17 ng/l).

Environmental Risk of Cybutryne by the highest toxicity value

RQ = PEC/PNEC



Cybutryne PNEC from the toxicity values

Acute Toxicity by EC50/LC50

genera	Freshwater species	time	μg/l
Algae	*Navicula pelliculosa*	120-h	0.096
Crustacean	*Daphnia magna*	48-h	2400
Fish	*Oncorhynchus mykiss*	96-h	860
others			
	Seawater species		μg/l
Algae	*Tetraselmis sp.*	3-d	0.116
Crustacean	*Mysidopsis bahia*	96-h	480
Fish	*Menidia beryllina*	96-h	1760
others	*Seriatophora hystrix*	10-h	0.7

Assessment Factor =100

PNEC = 0.096 μg/l /100 = 0.96 ng/l

Chronic Toxicity by NOEC

Freshwater species	time	μg/l
Navicula pelliculosa	72-h	0.02
Chironomus riparius	28-d	30.3
Oncorhynchus mykiss	95-d	4
Potamopyrgus antipodaru	56-d	0.04
Seawater species		μg/l
Tetraselmis sp.	3-d	0.017
Mysidopsis bahia	28-d	110
Cyprinodon variegatus	33-d	170
Llyanassa obsoleta	4-d	1500

Assessment Factor = 10

PNEC = 0.017 μg/l /10 = 1.7 ng/l

PNEC 0.96 ng/l.
All seawater exceeded PNEC

Copper study

1. Copper is essential element and toxic heavy metal.
2. Copper toxicity is known to be influenced by water parameters such as organic matters, salinity, pH and water temperature.
3. No systematic data on dissolved Cu species in Japan coastal seawater.

We determined dissolved Cu species in Japan coastal seawater and compared the residue levels with Cu CCC (Criterion Continuous Concentration) calculated by a estuarine/marine BLM (Biotic Ligand Model) proposed by US-EPA, 2016.

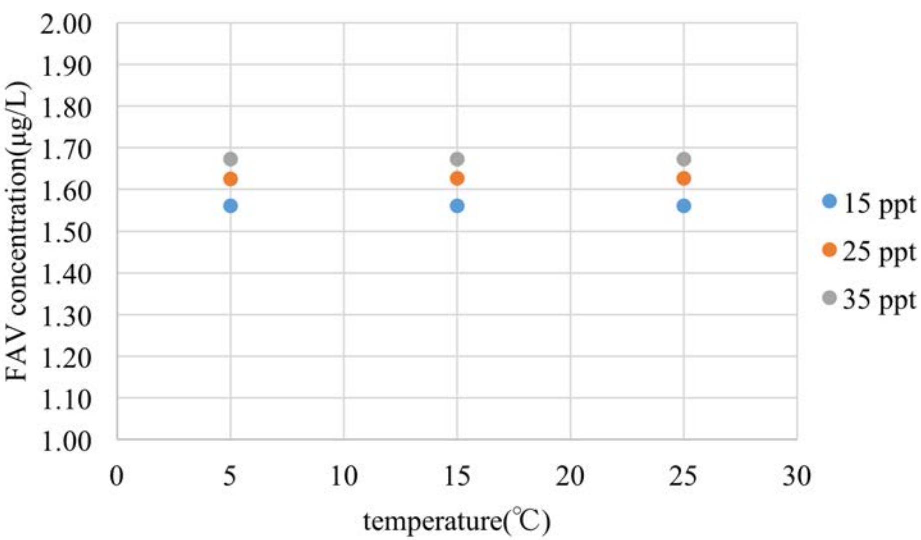
Estuarine/Marine Biotic Ligand Model (Marine BLM)

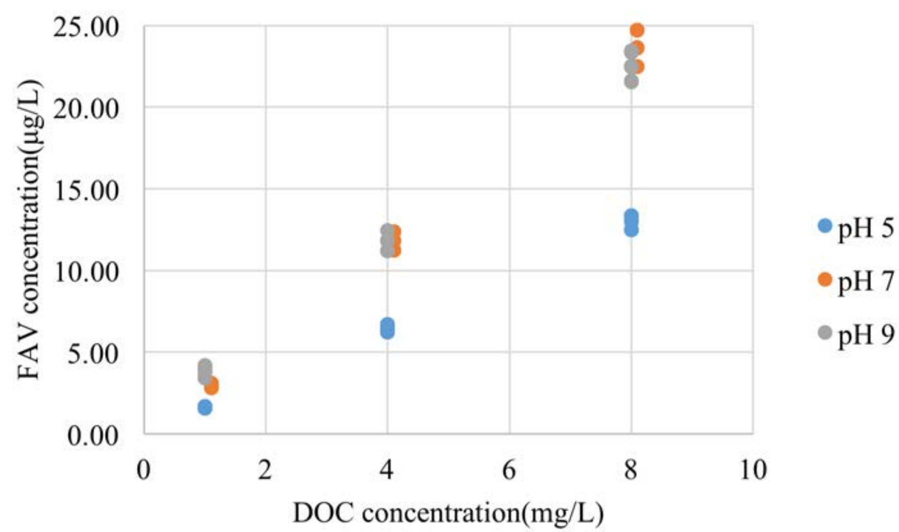
Draft aquatic life ambient estuarine/marine water quality criteria for copper-2016, using Draft estuarine/marine biotic ligand model for EPA estuarine/marine copper water quality criteria. Version 0.6.2.39:

Since the BLM includes inorganic and organic metal speciation and competitive complexation with biotic ligand, the amount of dissolved metal required to reach this threshold will vary, depending on the water chemistry.

Temperature, pH, Salinity, DOC (Dissolved Organic Carbon) →

FAV: Final Acute Value
→ CMC: Criterion Maximum Concentration
→ CCC : Criterion Continuous Concentration

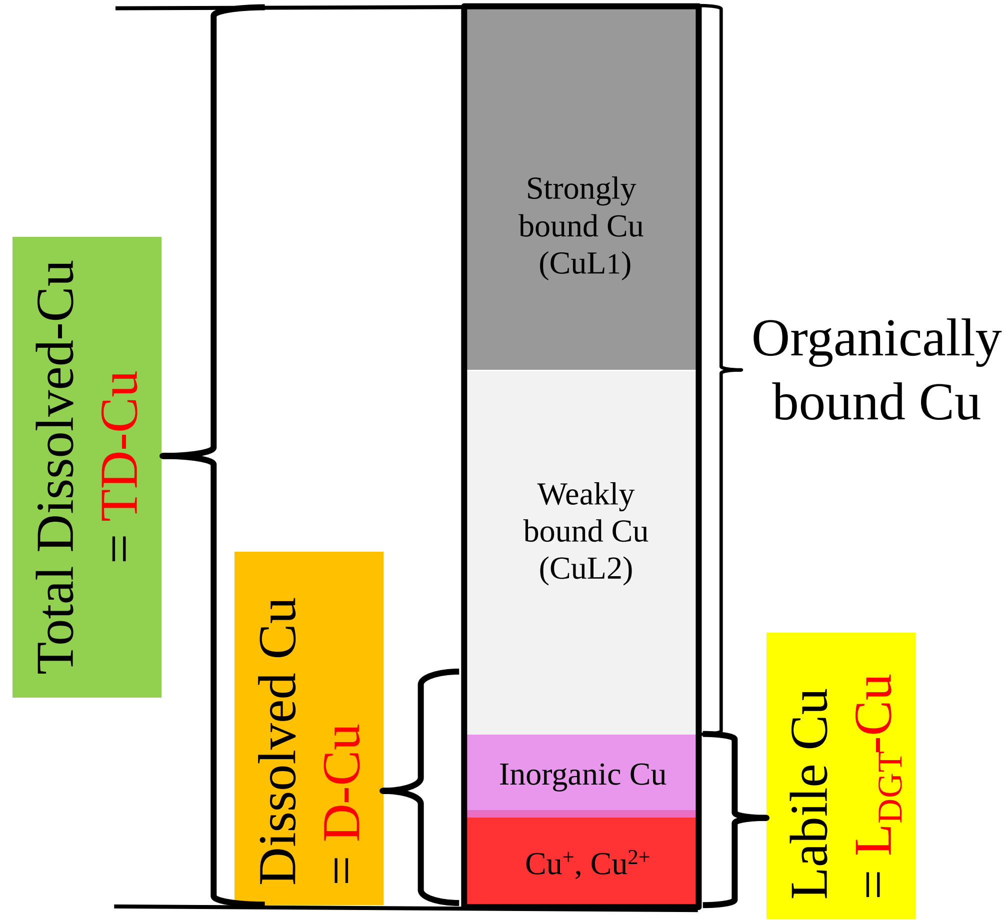




Dissolved copper species in coastal seawater

Seawater sampled (Spot sampling)
- filtrated and decomposed organic matters by UV lamp
- de-salted and concentrated by chelating resin

Determine Cu by FLAAS



1. Spot sampling

TD-Cu with DOC decomposition

D-Cu without decomposition

2. Passive sampling

DGT labile Cu (=L_{DGT}-Cu) determined after in situ deployment of DGT device for 24 hours, regarded as a time-average concentration.

Dissolved Cu species in seawater

TD-Cu > D-Cu > L_{DGT}-Cu

DGT: Diffusive Gradient in Thin-films to determine labile fraction.

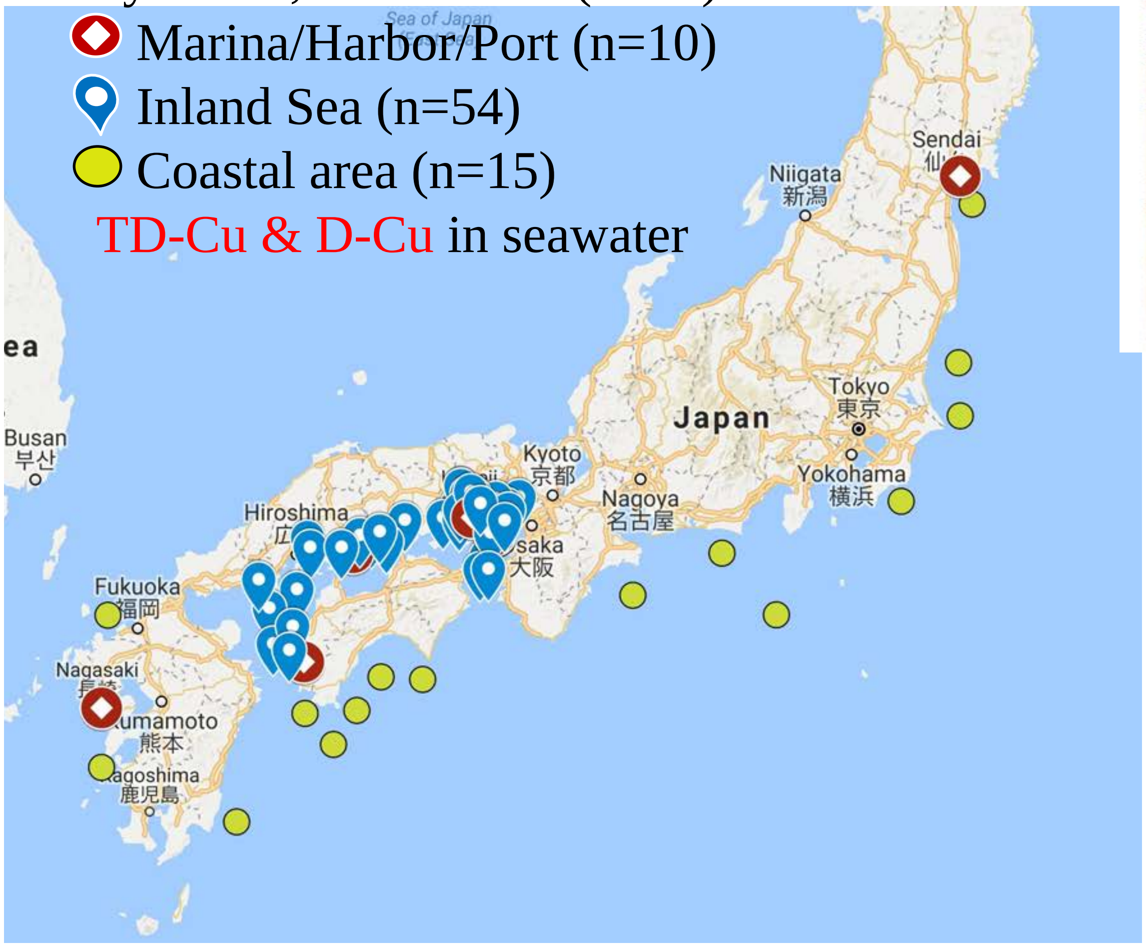
Two seawater samplings

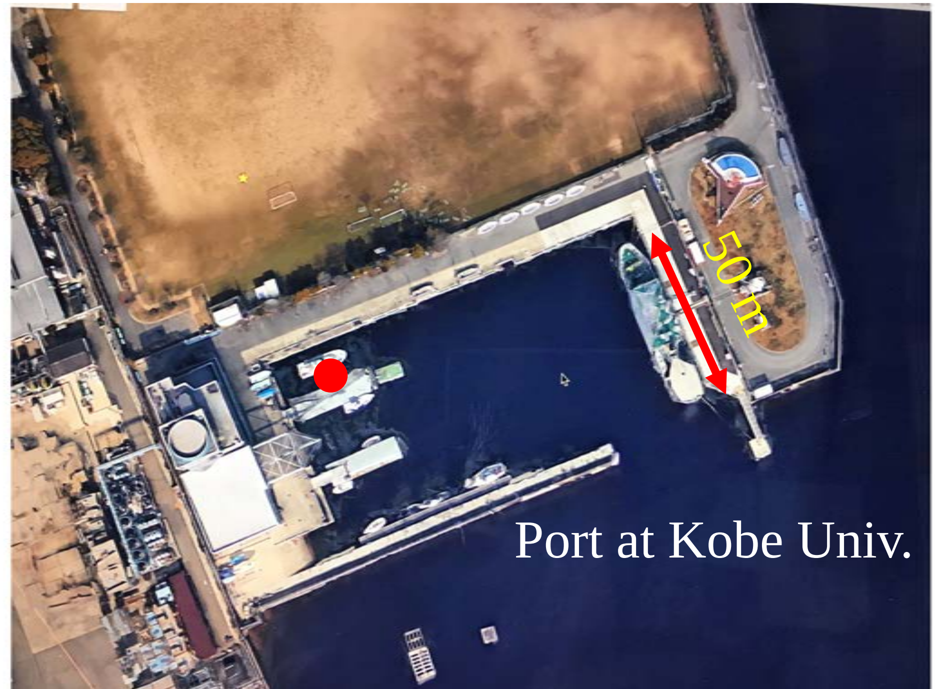
1. Spot sampling along the coast

by cruise, 2015-2016 (n=79)

- Marina/Harbor/Port (n=10)
- Inland Sea (n=54)
- Coastal area (n=15)

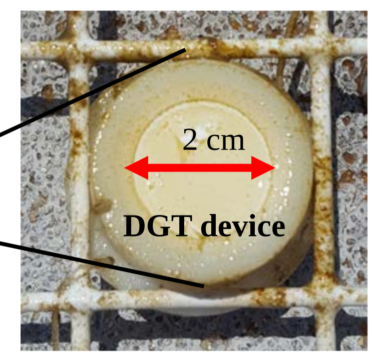
TD-Cu & D-Cu in seawater



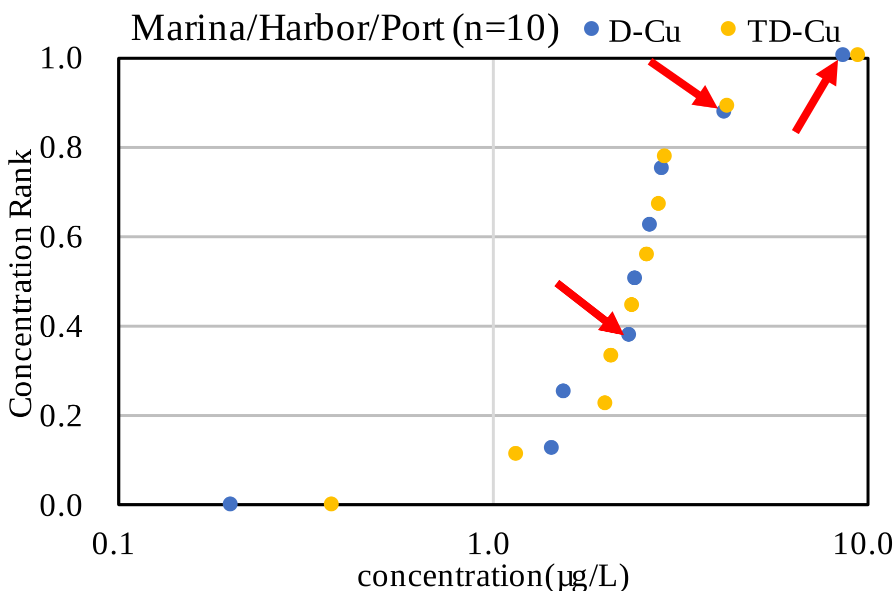


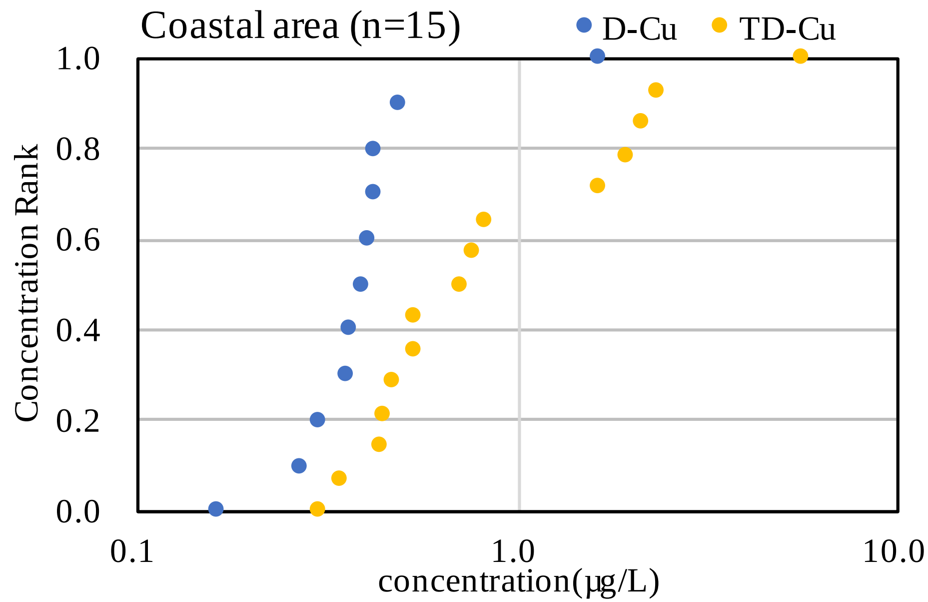
2. Passive sampling, 2015-2016

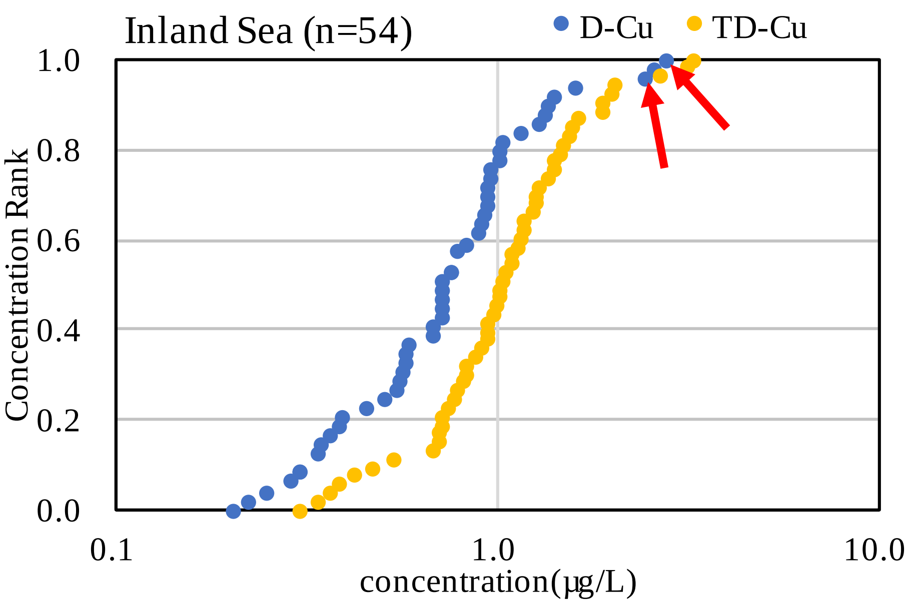
L_{DGT}-Cu by 24-h deployment of DGT, and TD-Cu & D-Cu by 3 replicated spot samplings within the 24-h deployment.



Dissolved copper residues in seawater 2015-2016







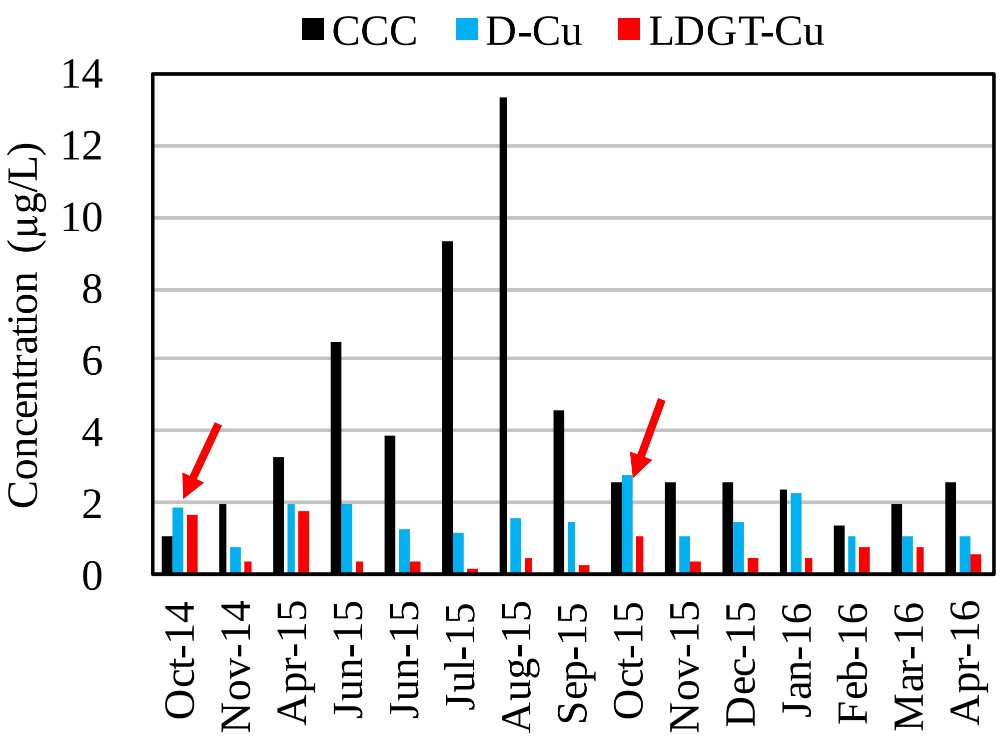
D-Cu compared with Cu CCC

Summary

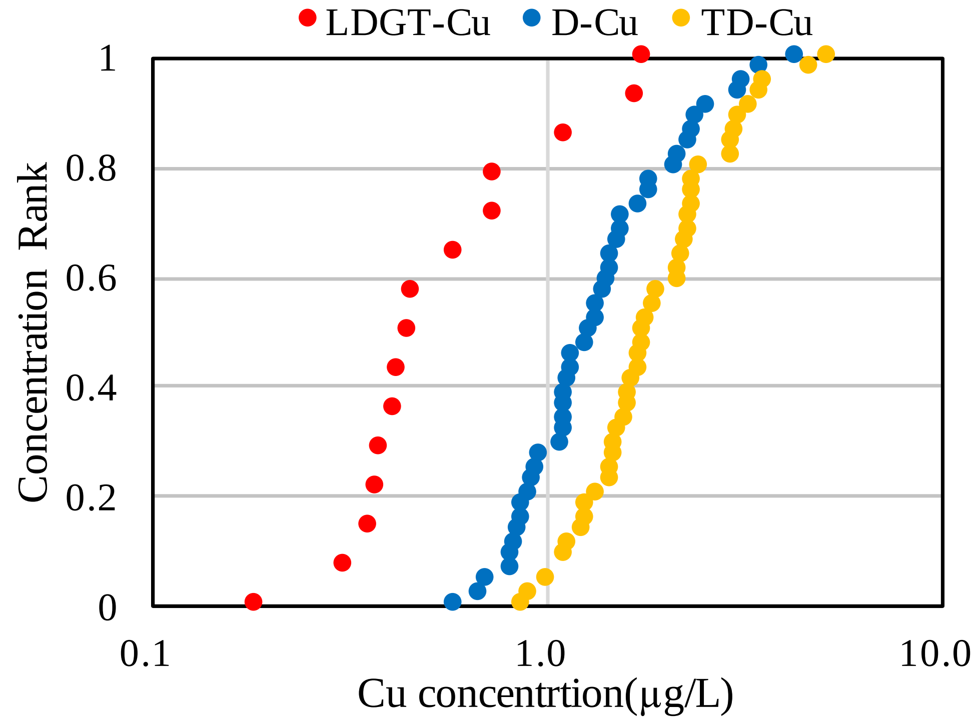
Area	Sample no.	TD-Cu (μg/L)			D-Cu (μg/L)		
		Average	SD	90%tile	Average	SD	90%tile
Marine Harbor Port	10	2.96	2.45	4.73	2.89	2.40	5.0
Inland sea	54	1.17	0.63	1.90	0.86	0.57	1.4
Coastal area	15	1.26	1.38	2.24	0.47	0.39	0.5

Five samples (D-Cu) exceeded CCC.

Dissolved copper concentrations in seawater at the University Pier 2014-2016



Two seawater samples exceeded CCC.



90th percentile TD-Cu ; 3.2 µg/l (n=45)

90th percentile D-Cu ; 2.5 µg/l (n=45)

90th percentile L_{DGT}-Cu ; 1.5 µg/l (n=15)

90th percentile DOC ; 10.4 mg/l (n=45)

TD-Cu > D-Cu > L_{DGT}-Cu

Summary

- Seventeen antifouling biocides are used for ship hull in Japan. Most of the biocides are degradable, but some are highly persistent.

- IMO will ban Cybutryne for ship AF biocide due to its environmental risk.

- A Cu Marine BLM proposed by USEPA revealed some of Japan coastal seawater at marina/inland sea had Cu environmental risk. But it was hard to conclude the copper toxicity was only due to a DGT labile copper concentration in seawater.

Thank you!

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okamurah@maritime.kobe-u.ac.jp