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

Re-painted

After one-year voyage

Kobe Univ. Training ship
FUKAE-MARU,
Photo by Captain YANO
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\textsubscript{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\textsubscript{2}O)
   - 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

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

<table>
<thead>
<tr>
<th></th>
<th>02/2005</th>
<th></th>
<th>03/2017</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>paint products</td>
<td>biocide</td>
<td>paint products</td>
</tr>
<tr>
<td>Biocide-free</td>
<td>16</td>
<td>0</td>
<td>17</td>
</tr>
<tr>
<td>Biocide</td>
<td>325</td>
<td>16</td>
<td>356</td>
</tr>
<tr>
<td>total</td>
<td>341</td>
<td></td>
<td>374</td>
</tr>
</tbody>
</table>
# 17 A/F biocides in commercial paints in Japanese market.

<table>
<thead>
<tr>
<th>CAS RN</th>
<th>Trivial name</th>
<th>Frequency</th>
<th>Ratio</th>
<th>Approved by BPR</th>
<th>Approved by USEPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1317-39-1</td>
<td>Dicopper oxide (Cu2O)</td>
<td>246</td>
<td>0.69</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>14915-37-8</td>
<td>Copper pyrithione (CuPT)</td>
<td>124</td>
<td>0.35</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>13463-41-7</td>
<td>Zinc pyrithione (ZnPT)</td>
<td>84</td>
<td>0.24</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>971-66-4</td>
<td>Pyridine triphenylborane (TPBP)</td>
<td>58</td>
<td>0.16</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>64359-81-5</td>
<td>DCOIT (Sea Nine 211)</td>
<td>54</td>
<td>0.15</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>330-54-1</td>
<td>Diuron</td>
<td>32</td>
<td>0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28159-98-0</td>
<td>Cybutryne (Irgarol 1051)</td>
<td>25</td>
<td>0.07</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>122454-29-9</td>
<td>Tralopyril (ECONEA)</td>
<td>19</td>
<td>0.05</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>12122-67-7</td>
<td>Zineb</td>
<td>19</td>
<td>0.05</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>731-27-1</td>
<td>Tolyfluanid</td>
<td>9</td>
<td>0.03</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>1111-67-7</td>
<td>Copper thiocyanate (CuSCN)</td>
<td>8</td>
<td>0.02</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>1897-45-6</td>
<td>2,4,5,6-Tetrachloroisophthalonitrile</td>
<td>5</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13167-25-4</td>
<td>N-(2,4,6-Trichlorophenyl)maleimide</td>
<td>4</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>137-30-4</td>
<td>Ziram</td>
<td>4</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13108-52-6</td>
<td>2,3,5,6-Tetrachloro-4-(methylsulphonyl)pyridine</td>
<td>1</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>117659-55-9</td>
<td>2,3-Dichloro-N-(2-ethyl-6-methylphenyl)maleimide</td>
<td>1</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>56746-18-0</td>
<td>2,3-Dichloro-N-(2,6-diethylphenyl)maleimide</td>
<td>1</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>86347-14-0</td>
<td>Medetomidine</td>
<td>0</td>
<td>0</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>7440-50-8</td>
<td>Copper flake</td>
<td>0</td>
<td>0</td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>

*Total 374 products including 356 biocide-type and 18 foul-release type from 12 companies are registered under the auspices 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)

Degradation pathway

No data at 1996, I had Cybutryne from Dr. Liu, NWRI, Canada.
- Residues in seawater, Japan?
- Environmental fate?
- Degradation?

M1
Cybutryne residues in 1999 survey, Japan

Detection frequency: 84/143 = 60%

260 ng /l

Pacific ocean

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
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.

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

HC5 = 0.17 μg/l = 170 ng/l
Environmental Risk of Cybutryne by the highest toxicity value

RQ = PEC/PNEC

Residue concentrations reported (n=327)

Cybutryne PNEC from the toxicity values

<table>
<thead>
<tr>
<th>genera</th>
<th>Freshwater species</th>
<th>time</th>
<th>µg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algae</td>
<td>Navicula pelliculosa</td>
<td>120-h</td>
<td>0.096</td>
</tr>
<tr>
<td>Crustacean</td>
<td>Daphnia magna</td>
<td>48-h</td>
<td>2400</td>
</tr>
<tr>
<td>Fish</td>
<td>Oncorhynchus mykiss</td>
<td>96-h</td>
<td>860</td>
</tr>
<tr>
<td>others</td>
<td>Seawater species</td>
<td>µg/l</td>
<td></td>
</tr>
<tr>
<td>Algae</td>
<td>Tetraselmis sp.</td>
<td>3-d</td>
<td>0.116</td>
</tr>
<tr>
<td>Crustacean</td>
<td>Mysisipolis bahia</td>
<td>96-h</td>
<td>480</td>
</tr>
<tr>
<td>Fish</td>
<td>Menidia beryllina</td>
<td>96-h</td>
<td>1760</td>
</tr>
<tr>
<td>others</td>
<td>Seriatophora hystricx</td>
<td>10-h</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Assessment Factor = 100

PNEC = 0.096 µg/l /100 = 0.96 ng/l

PNEC = 0.017 µg/l /10 = 1.7 ng/l

PNEC 0.96 ng/l. All seawater exceeded PNEC

Acute Toxicity by EC50/LC50

Chronic Toxicity by NOEC

Freshwater species | time  | µg/l  |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Navicula pelliculosa</td>
<td>72-h</td>
<td>0.02</td>
</tr>
<tr>
<td>Chironomus riparius</td>
<td>28-d</td>
<td>30.3</td>
</tr>
<tr>
<td>Oncorhynchus mykiss</td>
<td>95-d</td>
<td>4</td>
</tr>
<tr>
<td>Potamopyrgus antipodaru</td>
<td>56-d</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Seawater species µg/l

Tetraselmis sp. | 3-d | 0.017 |
Mysisipolis bahia | 28-d | 110  |
Cyprinodon variegatus | 33-d | 170  |
Llyanassa obsoleta | 4-d | 1500  |

Assessment Factor = 10

RQ = PEC/PNEC

16/24
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.

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

Dissolved Cu species in seawater
TD-Cu > D-Cu > L_{DGT}-Cu
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
   - $L_{\text{DGT}}$-Cu by 24-h deployment of DGT,
   - and TD-Cu & D-Cu by 3 replicated spot samplings within the 24-h deployment.

Deployed at 1 m depth
**Dissolved copper residues in seawater 2015-2016**

### Summary

<table>
<thead>
<tr>
<th>Area</th>
<th>Sample no.</th>
<th>TD-Cu (μg/L)</th>
<th>D-Cu (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>SD</td>
<td>90%tile</td>
</tr>
<tr>
<td>Marine Harbor Port</td>
<td>10</td>
<td>2.96</td>
<td>2.45</td>
</tr>
<tr>
<td>Inland sea</td>
<td>54</td>
<td>1.17</td>
<td>0.63</td>
</tr>
<tr>
<td>Coastal area</td>
<td>15</td>
<td>1.26</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Five samples (D-Cu) exceeded CCC.
Dissolved copper concentrations in seawater at the University Pier 2014-2016

- 90th percentile TD-Cu: 3.2 µg/l (n=45)
- 90th percentile D-Cu: 2.5 µg/l (n=45)
- 90th percentile LDGT-Cu: 1.5 µg/l (n=15)
- 90th percentile DOC: 10.4 mg/l (n=45)

Two seawater samples exceeded CCC.

TD-Cu > D-Cu > LDGT-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!

Acknowledgements

Dr. Liu, D., NWRI, Canada
Mr. Li, Kitano, and Lin, Graduate students

okamurah@maritime.kobe-u.ac.jp