Copper in antifouling

Past, present and future

Presentation on behalf of the Copper Antifouling Task Force
What should we expect from an antifouling (a.i.)?

• Safe, no handling hazards
• Effective against fouling organisms at the surface of the underwater hull
• No or minimal effect on non target organisms
Where would we look for such an antifouling (a.i.)?

Marine environment

- Natural antifoulants, e.g. sponges, seaweed etc.
- Major natural constituents of the seawater, nutrients or trace elements
11 major constituents of the oceans*

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>$2.5 \times 10^{16}$ tonnes</td>
</tr>
<tr>
<td>Sodium</td>
<td>$1.4 \times 10^{16}$ tonnes</td>
</tr>
<tr>
<td>Magnesium</td>
<td>$1.7 \times 10^{15}$ tonnes</td>
</tr>
<tr>
<td>Calcium</td>
<td>$5.4 \times 10^{14}$ tonnes</td>
</tr>
<tr>
<td>Potassium</td>
<td>$5.0 \times 10^{14}$ tonnes</td>
</tr>
<tr>
<td>Silicone</td>
<td>$2.6 \times 10^{12}$ tonnes</td>
</tr>
<tr>
<td>Zinc</td>
<td>$6.4 \times 10^{9}$ tonnes</td>
</tr>
<tr>
<td>Copper</td>
<td>$2.6 \times 10^{9}$ tonnes</td>
</tr>
<tr>
<td>Iron</td>
<td>$2.6 \times 10^{9}$ tonnes</td>
</tr>
<tr>
<td>Manganese</td>
<td>$2.6 \times 10^{8}$ tonnes</td>
</tr>
<tr>
<td>Cobalt</td>
<td>$6.6 \times 10^{7}$ tonnes</td>
</tr>
</tbody>
</table>

*CRC Practical Handbook of Marine Science 1994, p. 106*
Copper equilibrium in seawater

< 1%     > 99%

$\text{Cu}^{2+} \leftrightarrow \text{Copper compound}$
Forms of copper found in water

- Cu in organisms
- Cu(I) e.g. CuCl
- Cu(II) e.g. CuCl$_2$
- Adsorbed Cu
- Inorganic complexes e.g. CuOH$^+$, CuCO$_3$
- Organic complexes e.g. Cu-fulvic acid
- Particles
- Inorganic ligands
- Biological availability
- Reduction
What should we expect from an antifouling (a.i.)?

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What should we expect from an antifouling (a.i.)?

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Copper deficiency/essentiality/toxicity

From: Karman et al. 1998
Copper in antifouling

- Microlayer
- Hull
- Cu\textsuperscript{2+}
- Cl\textsuperscript{-}
- Cu-ligand
- CuOH\textsuperscript{+}
- Cu-adsorbed
- CuCO\textsubscript{3}

Inset graph: Percentage of population under deficiency vs. Toxicity. Natural background concentration range (NRA) and Lowest NOEC.
Copper equilibrium in seawater

Copper AF $\rightarrow$ Cu$^{2+}$ $\leftrightarrow$ Copper compound
Use of copper as an antifouling ingredient

• Copper has always been the backbone of antifouling
• Historically metal sheets were used
• Insoluble copper compounds have been used since around 1850
• Copper has been used alone or alongside other biocidal compounds such as mercurials, arsenics, TBTO and all booster biocides
• Copper(I)oxide is the most common AF copper compound. CuSCN and metallic are used in yacht antifoulings
Use of copper as an antifouling ingredient
Human exposure risk

- Copper is an essential element with a Recommended Daily Intake of 2 – 3 mg/day.
- Acute toxicity: "Copper is remarkably non toxic"*
- Chronic: "Studies of copper miners show normal liver and serum concentrations despite years of exposure to oxides and sulphides"*
- Copper does not accumulate in food chains.

*VCH, Metals and Their Compounds in the Environment, 1991
Risk assessment of copper, common pitfalls

• **Heavy metal**

Heavy metal refers to all elements with a density higher than 5. This encompasses about 60 elements from Periodic Table of Elements with vast differences in properties; e.g. Arsenic, Gold, Iron and Thallium.
Risk assessment of copper, common pitfalls

- **Persistent**: Elements do not degrade, they get deactivated through other mechanisms
- **Bioaccumulative**: Bioaccumulation cannot be defined for a micronutrient
- **Toxic**: Toxicity is only seen when concentrations are above the optimum range (Paracelsus: "the dose makes the poison")
Risk assessment of copper, common pitfalls

- Risk assessment according to OECD guidelines
  - Method is developed for organic chemicals. Results in PNECs well below natural background levels.
  - Statistical or other more advanced methods must be used e.g. Probabilistic method.
Anthropogenic release of naturally occurring substances

The CO\textsubscript{2} case

• Atmospheric concentration of CO\textsubscript{2} has increased with 25% since 1750
• Atmospheric concentration will be doubled within 50 – 100 years if we do not achieve substantial reductions in emissions
"Back of the envelope calculation”

The "copper case”

- Volume of ocean: $1,35 \times 10^9$ km$^3$
- Average copper content: 1,9 µg/l
- Copper content in ocean: 2,6 billion tons
- Doubling of copper content based on current use in AF will take 100,000 years

No global effects
Where does the copper in nature come from?

Equilibrium
Main natural sources are:

- Atmospheric
- Rivers
- Weathering of rocks
- Subsea volcanoes
Subsea vulcanoes
Subsea volcanoes
Environmental risk assessment
Copper from antifouling

- Copper is a naturally occurring substance
- No difference between "natural" and anthropogenic copper
- Speciation, this leads to limited bioavailability
- Site specific characteristics
- Can be based on monitoring rather than modelling
- Should not use "assessment factor methods"
Dissolved copper vs. ionic copper

From: Practical Handbook of Marine Science, CRC 1994
Deterministic risk assessment for copper
(Hall et. al. MPB, Vol. 38)
A deterministic risk assessment for copper Monitoring data
Deterministic Risk Assessment for Copper

Conclusion

PNEC/OEC < 1 at 98 out of 101 sites.

"Based on copper chemistry and the Hazard Quotients described in this assessment, the probability of ecological risk from acute dissolved water column copper exposures in European saltwater environments is generally low”*

Fate and toxicity of copper in sediments

- Copper has a high tendency to bind to sulfides and/or organic material in sediments
- AVS (Acid Volatile Sulphide)
- SEM (Simultaneously Extracted Metals)
- No toxicity if SEM/AVS < 1 (Does not consider additional binding to organic material)
Monitoring of sediments from Holland (Hoop et. al.)

Sampling locations of Dutch marine and freshwater sediments
## Monitoring of sediments in Holland

<table>
<thead>
<tr>
<th>Sample (number/site)</th>
<th>AVS</th>
<th>Cd</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>SEM</th>
<th>SEM/AVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schoonrewoerdse wiel</td>
<td>52.0</td>
<td>0.018</td>
<td>0.33</td>
<td>0.46</td>
<td>0.44</td>
<td>2.42</td>
<td>3.67</td>
<td>0.07</td>
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<td>Botlek</td>
<td>22.6</td>
<td>0.055</td>
<td>0.78</td>
<td>0.39</td>
<td>0.62</td>
<td>7.50</td>
<td>9.35</td>
<td>0.41</td>
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<tr>
<td>Appelzak</td>
<td>22.6</td>
<td>0.004</td>
<td>0.04</td>
<td>0.04</td>
<td>0.12</td>
<td>0.88</td>
<td>1.08</td>
<td>0.05</td>
</tr>
<tr>
<td>Geul Zandvliet /Berendrechtssluis</td>
<td>21.2</td>
<td>0.066</td>
<td>0.42</td>
<td>0.23</td>
<td>0.61</td>
<td>6.97</td>
<td>8.30</td>
<td>0.39</td>
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<tr>
<td>Geul Boudewijn v Cauwelaertsluis</td>
<td>20.0</td>
<td>0.063</td>
<td>0.34</td>
<td>0.22</td>
<td>0.62</td>
<td>8.52</td>
<td>9.76</td>
<td>0.49</td>
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<tr>
<td>Oostvaarders Plassen</td>
<td>19.9</td>
<td>0.006</td>
<td>0.17</td>
<td>0.21</td>
<td>0.25</td>
<td>1.88</td>
<td>2.52</td>
<td>0.13</td>
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<tr>
<td>Nieuwersluis</td>
<td>19.8</td>
<td>0.004</td>
<td>0.10</td>
<td>0.16</td>
<td>0.36</td>
<td>2.32</td>
<td>2.94</td>
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<tr>
<td>Geul Kallosluis</td>
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<tr>
<td>Ketelmeer</td>
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<td>1.13</td>
<td>0.46</td>
<td>0.63</td>
<td>11.91</td>
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<td>Leegwaterplas</td>
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<td>0.003</td>
<td>0.02</td>
<td>0.13</td>
<td>0.06</td>
<td>0.35</td>
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<td>Schouwen-Duiveland 1a</td>
<td>8.0</td>
<td>0.001</td>
<td>0.02</td>
<td>0.02</td>
<td>0.04</td>
<td>0.32</td>
<td>0.40</td>
<td>0.05</td>
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<tr>
<td>Schouwen-Duiveland 4a</td>
<td>7.4</td>
<td>0.001</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.26</td>
<td>0.32</td>
<td>0.04</td>
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<tr>
<td>Drempel van Liloo</td>
<td>4.7</td>
<td>0.021</td>
<td>0.35</td>
<td>0.09</td>
<td>0.24</td>
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<tr>
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<td>0.08</td>
<td>0.04</td>
<td>0.08</td>
<td>1.07</td>
<td>1.28</td>
<td>0.31</td>
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<tr>
<td>Ter Heijden 4a</td>
<td>2.9</td>
<td>0.001</td>
<td>0.04</td>
<td>0.02</td>
<td>0.06</td>
<td>0.47</td>
<td>0.59</td>
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<tr>
<td>Sluissche Hompels</td>
<td>1.3</td>
<td>0.001</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
<td>0.39</td>
<td>0.47</td>
<td>0.36</td>
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<tr>
<td>Terschelling 100a</td>
<td>0.6</td>
<td>&lt;0.001</td>
<td>0.02</td>
<td>0.02</td>
<td>0.04</td>
<td>0.24</td>
<td>0.32</td>
<td>0.53</td>
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<tr>
<td>Vlieland 70a</td>
<td>0.5</td>
<td>&lt;0.001</td>
<td>0.02</td>
<td>0.02</td>
<td>0.05</td>
<td>0.40</td>
<td>0.49</td>
<td>0.98</td>
</tr>
<tr>
<td>Vlieland 4a</td>
<td>0.4</td>
<td>&lt;0.001</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.13</td>
<td>0.16</td>
<td>0.40</td>
</tr>
<tr>
<td>Terschelling 70a</td>
<td>0.2</td>
<td>&lt;0.001</td>
<td>0.02</td>
<td>0.02</td>
<td>0.05</td>
<td>0.40</td>
<td>0.49</td>
<td>2.45</td>
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<tr>
<td>Ter Heijden 2a</td>
<td>&lt;0.1</td>
<td>&lt;0.001</td>
<td>0.02</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>0.26</td>
<td>0.31</td>
<td>&gt;3.1</td>
</tr>
</tbody>
</table>
### Monitoring of sediments in Holland

#### Solubility of copper in sediments

<table>
<thead>
<tr>
<th>Metal sulphide</th>
<th>Log K</th>
<th>Metal sulphide</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnS</td>
<td>-13.33</td>
<td>PbS</td>
<td>-28.04</td>
</tr>
<tr>
<td>FeS</td>
<td>-18.80</td>
<td>CdS</td>
<td>-28.85</td>
</tr>
<tr>
<td>NiS</td>
<td>-20.97</td>
<td>CuS</td>
<td>-35.90</td>
</tr>
<tr>
<td>ZnS</td>
<td>-24.53</td>
<td>Ag₂S</td>
<td>-49.17</td>
</tr>
<tr>
<td>SnS</td>
<td>-27.49</td>
<td>HgS</td>
<td>-52.19</td>
</tr>
</tbody>
</table>
Monitoring of sediments in Holland (Hoop et. al. 1997)

Sampling locations of Dutch marine and freshwater sediments
Pleasure craft marina monitoring*
Copper content in harbour sediments
TBT content in harbour sediments
Summary on the use of copper as AF a.i.

- Micronutrient
- Natural and necessary component in the ocean
- High tendency to bind to organic matter biological activity
- Rapid deactivation due to binding both in the water column and in sediments
- Lower leaching rate in low salinity waters
- Environmental exposure has been assessed through monitoring not modelling with positive results
- No risk to operators or DIYs
- No risk for bioaccumulation in marine foodchains
What does copper offer as an antifouling (a.i.)?

- Safe, no handling hazards
- Effective against fouling organisms at the surface of the underwater hull
- No or minimal effect on non target organisms