

Antifouling Presentation to California Marine Group

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How harmful is Copper?

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Risk Assessment

Risk assessment is relatively simple if there is likely to be more toxic substance in the water than is known to affect animals then alarm bells ring

$$\frac{\text{Predicted Environment Concentration (PEC)}}{\text{Predicted No Effect Concentration (PNEC)}} = >1 \text{ (harm)}$$

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Copper the problem

- For some harbours and marinas monitoring data based measuring total copper dissolved in the water shows higher concentrations than lab studies show effects on mussels. So there must be harm.
- *What is wrong with the assessment?*

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Copper the Problem

“but this [harm] cannot be firmly concluded because an unknown proportion of each [copper and zinc] was probably complexed with dissolved organic matter, and therefore less bioavailable”

Nearly all testing of copper has been done in clean seawater without natural complexing agents

*P. Matthiessen, J. Reed and M. Johnson, 1999. Sources and potential effects of copper and zinc concentrations in the estuarine waters of Essex and Suffolk, UK. Marine Pollution Bulletin 38(10):908-920

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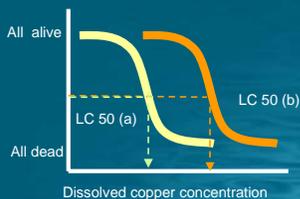
Copper testing the uncertainty

If the form (species) of copper present in the environment dictates toxicity

- We need to measure these forms
- Need to test the toxic effects of these forms on animals
- Need to compare toxic values with concentrations of copper in the real world

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Copper species toxicity



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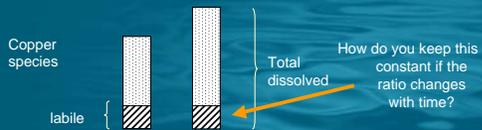
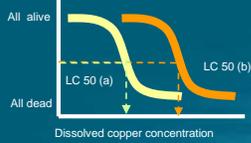
Measuring Copper – analytical methods



- Range of techniques used previously, many have complicated steps
- Our target - simple robust speciation of dissolved copper into labile (toxic ions and salts) and non-labile (less toxic complexed organic forms)

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Testing in experimental systems



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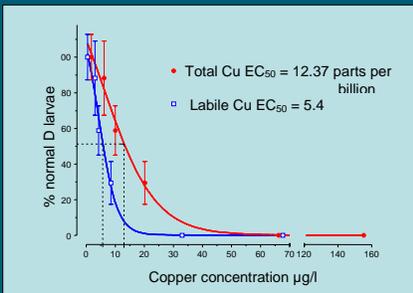


Flow-through copper dosing system

- Filtered seawater input in to system to reduce background DOC.
- CuCl_2 stock solution
- Dissolved organic carbon source as humic acid (HA).
- Cu aged (>32h) prior to exposure to test animals

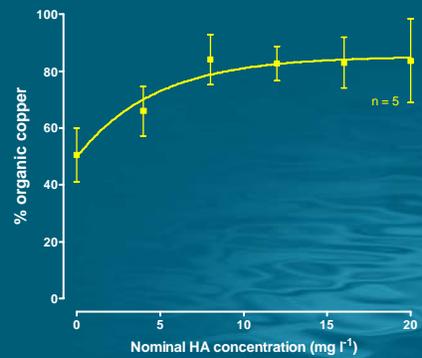
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Mussel Larvae



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Cu speciation with Humic Acid



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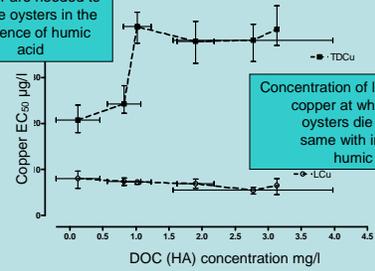
Oyster Embryo Bioassay



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Copper Toxicity to Oyster Embryos

High levels of dissolved copper are needed to kill the oysters in the presence of humic acid



Concentration of labile (toxic) copper at which half the oysters die stays the same with increasing humic acid

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Copper toxicity to Oysters



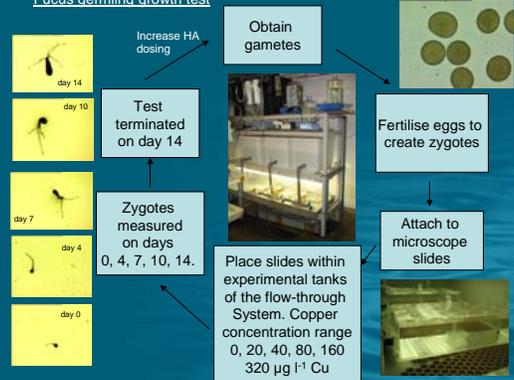
- The EC₅₀ for dissolved copper to oyster embryos doubles from 20 to 40 parts per billion (µg/l) in the presence of humic acid
- The EC₅₀ for labile copper is around 7 µg/l and unchanged as humic acid increases



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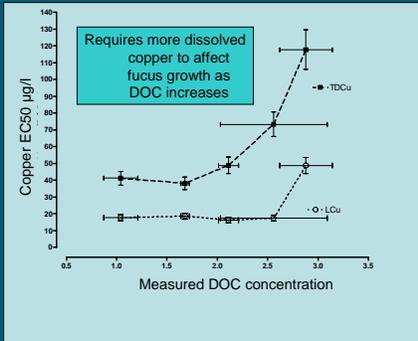
Copper Toxicity to Fucus

Fucus germling growth test



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Copper toxicity to Fucus



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Copper Toxicity to Fucus

- It takes 70 µg/l of dissolved copper to halve the growth rate of fucus if there is 2.5 mg/l of DOC in the water
- The EC₅₀ for labile (toxic) copper is around 20µg/l.

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How much toxic copper is out there?

- Previous Monitoring biased to discharges
- Our strategy examined:
 - Different types of sites – harbour/open marina/estuary
 - Different levels of humics in the water
 - Different levels of suspended sediment
 - Different seasons
 - Different depths
 - Different countries

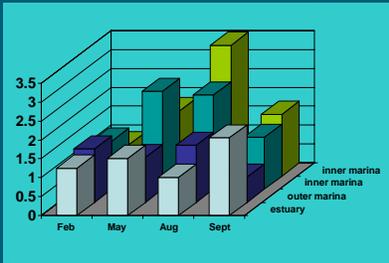
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How much toxic copper is out there?



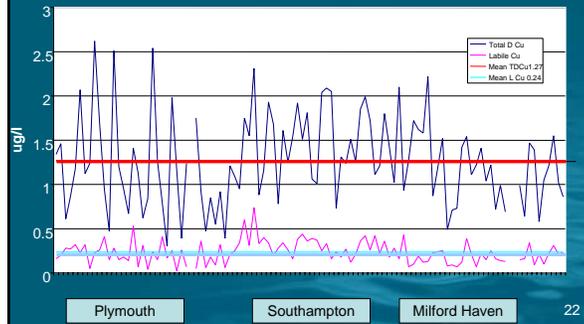
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Total Dissolved Copper $\mu\text{g/l}$ at Ocean Village Marina, 1m depth



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Estuary Total Dissolved and Labile Copper



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Copper in the real world

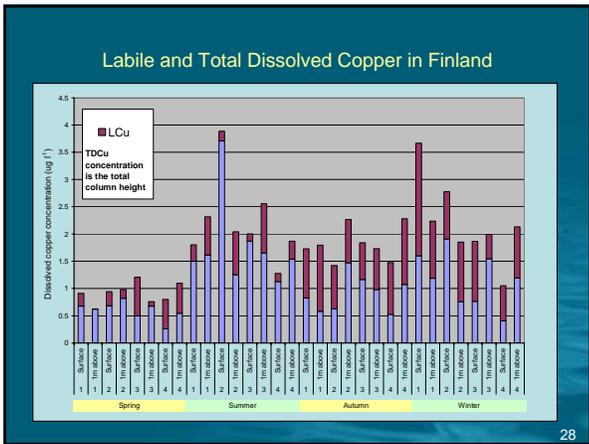
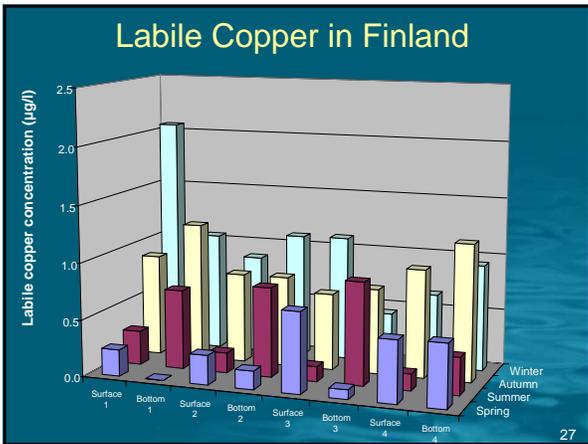
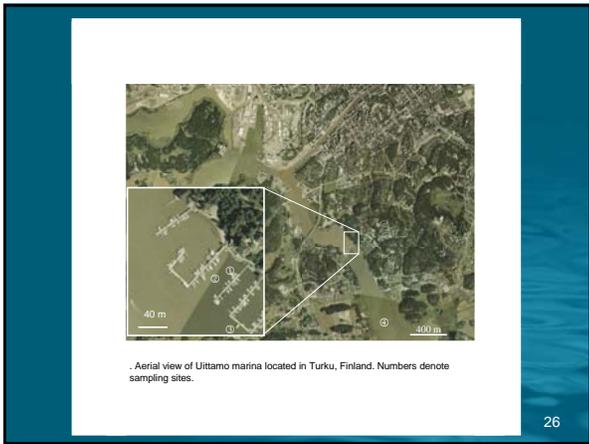
- Around 20% in toxic forms, higher proportions of toxic forms close to inputs and lower levels as samples age (further from point sources)
- Only one sample of 324 measurements exceeded the EQS (harmful level)

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Finland



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Risk Quotients

Total Dissolved Copper: **worst case**

$\frac{PEC}{PNEC} \Rightarrow 1$ (harm)

$\mu\text{g/l}$	Total DCu	Labile
No. Samples	108	108
Mean	1.68	0.38
95%ile	4.18	0.71
Max	6.68	2.69

Measured Total Dissolved Copper 6.68 (3.60)		In marina	Outside marina
Predicted No Effect Concentration 5	=	1.34	0.72
Measured labile copper 2.69 (0.38)		In marina	Outside marina
Predicted No Effect Concentration 5	=	0.54	0.08

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Conclusions

- Labile copper controls toxicity in the environment not total dissolved copper
- Bivalves and seaweed are tolerant to higher copper concentrations in the real world than previously thought
- We need to look at labile copper and actual measured toxicity in harbours, marinas and estuaries
- We do however need to control inputs of waste paint to stop the build up of copper in sediments – sensible use

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