# How harmful is Copper?

***Mike Waldock,***
***Centre for Environment Fisheries and Aquaculture***

***Science, UK***

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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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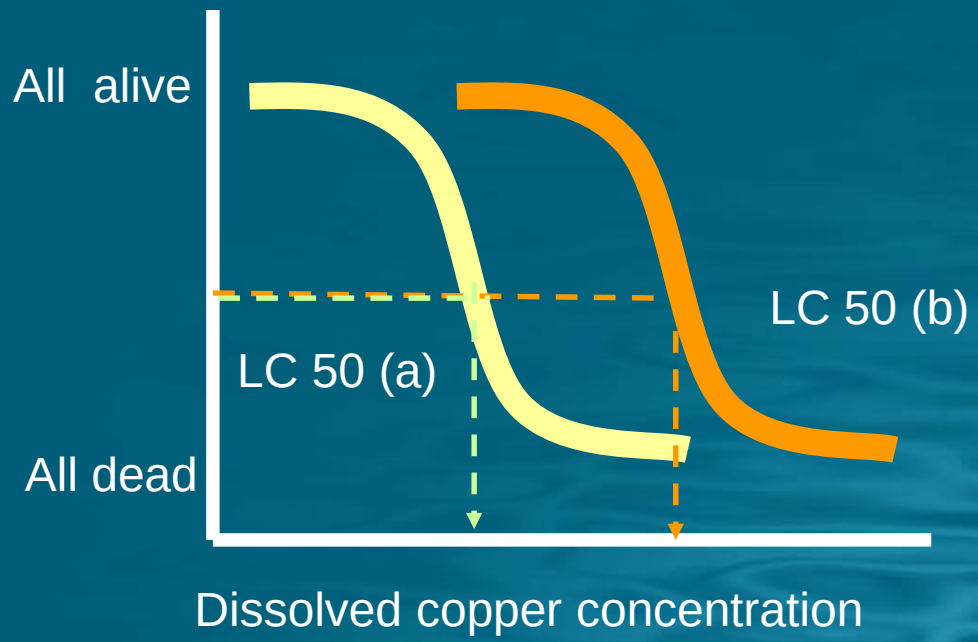
# Copper species toxicity

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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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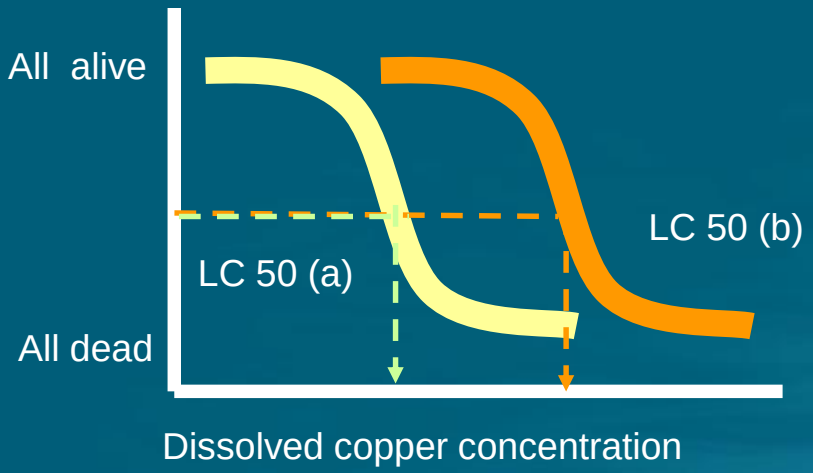
# Testing in experimental systems




Copper species

labile

Total dissolved

How do you keep this constant if the ratio changes with time?

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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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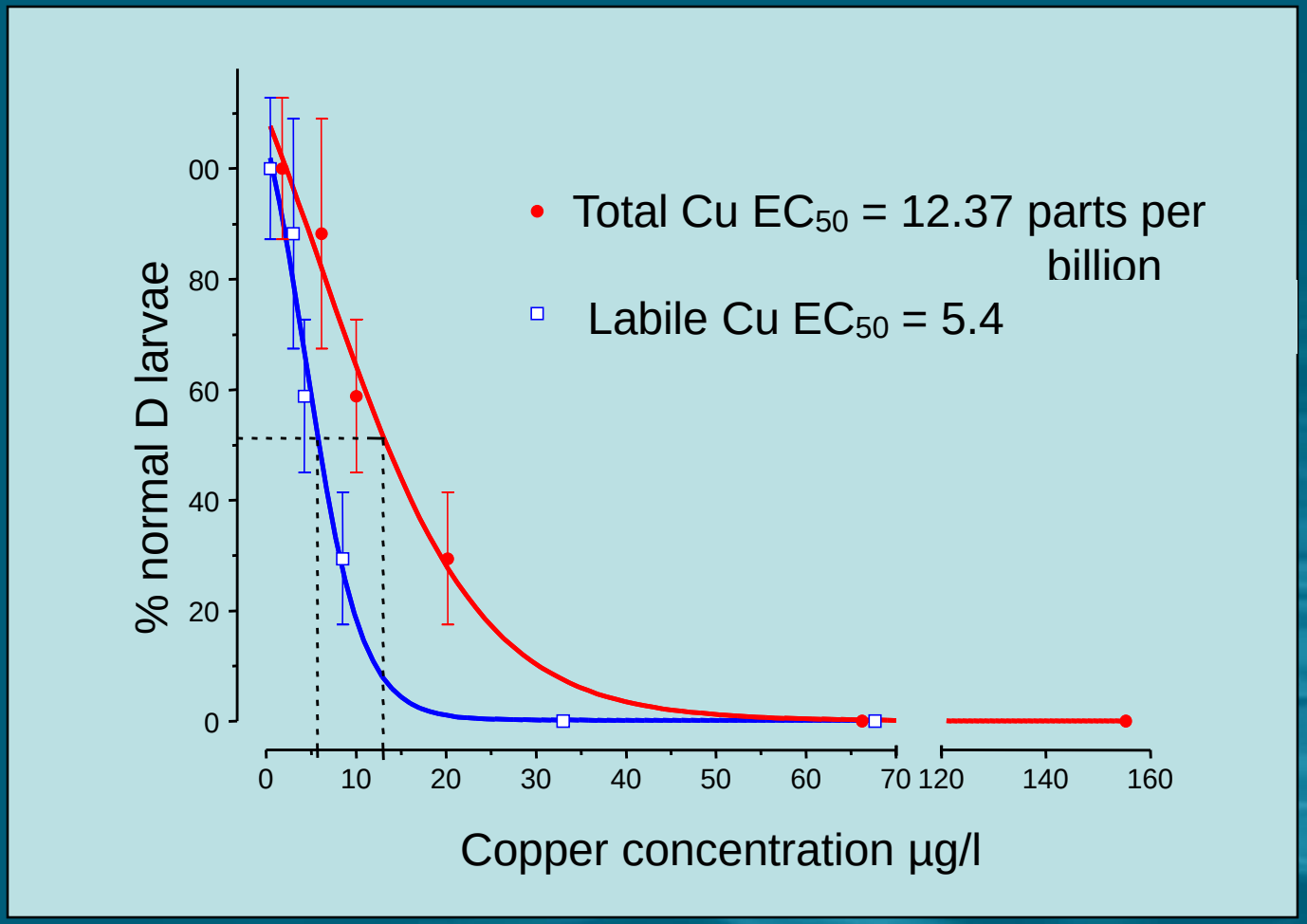
# Mussel Larvae

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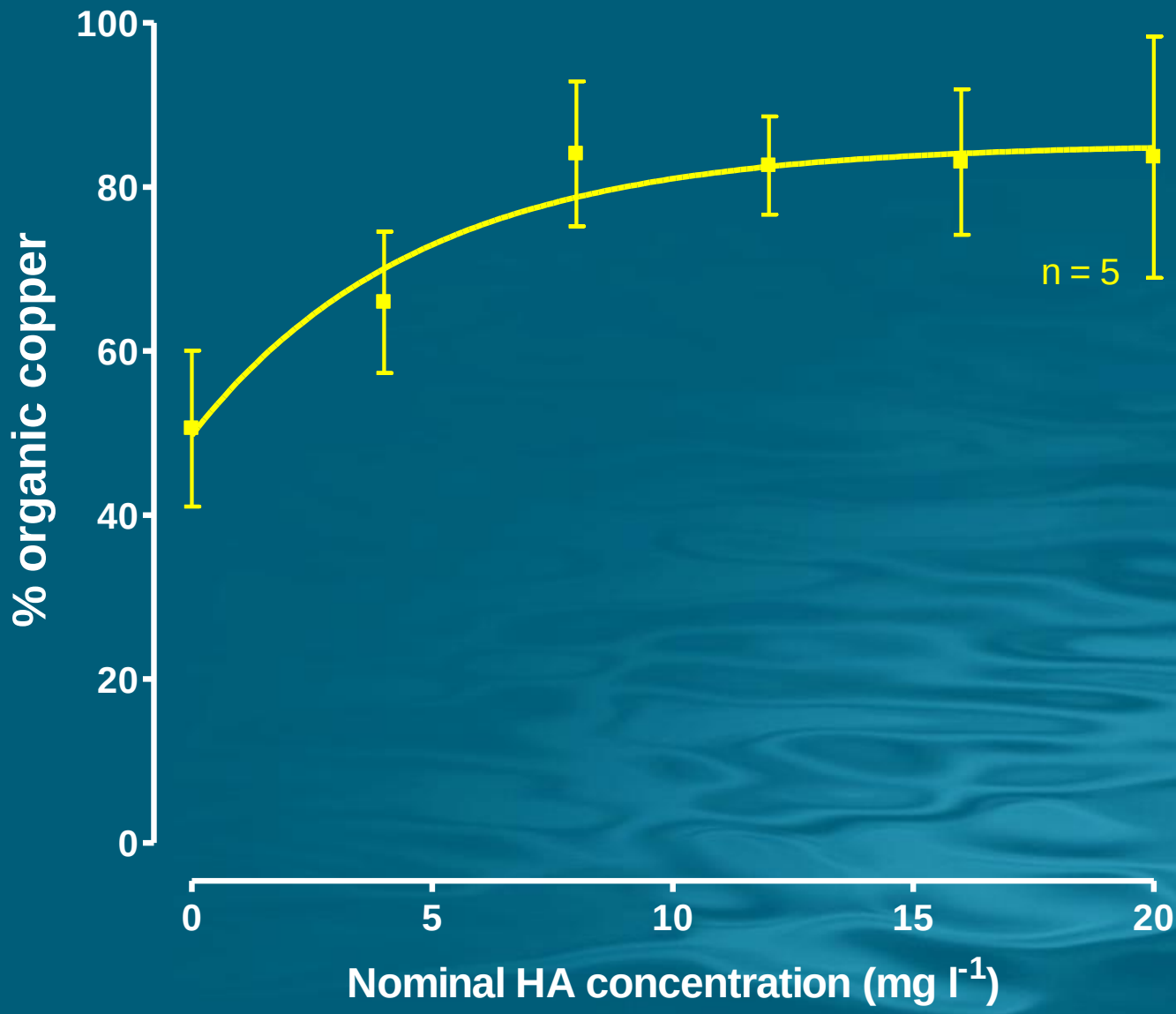
# Cu speciation with Humic Acid

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# Oyster Embryo Bioassay

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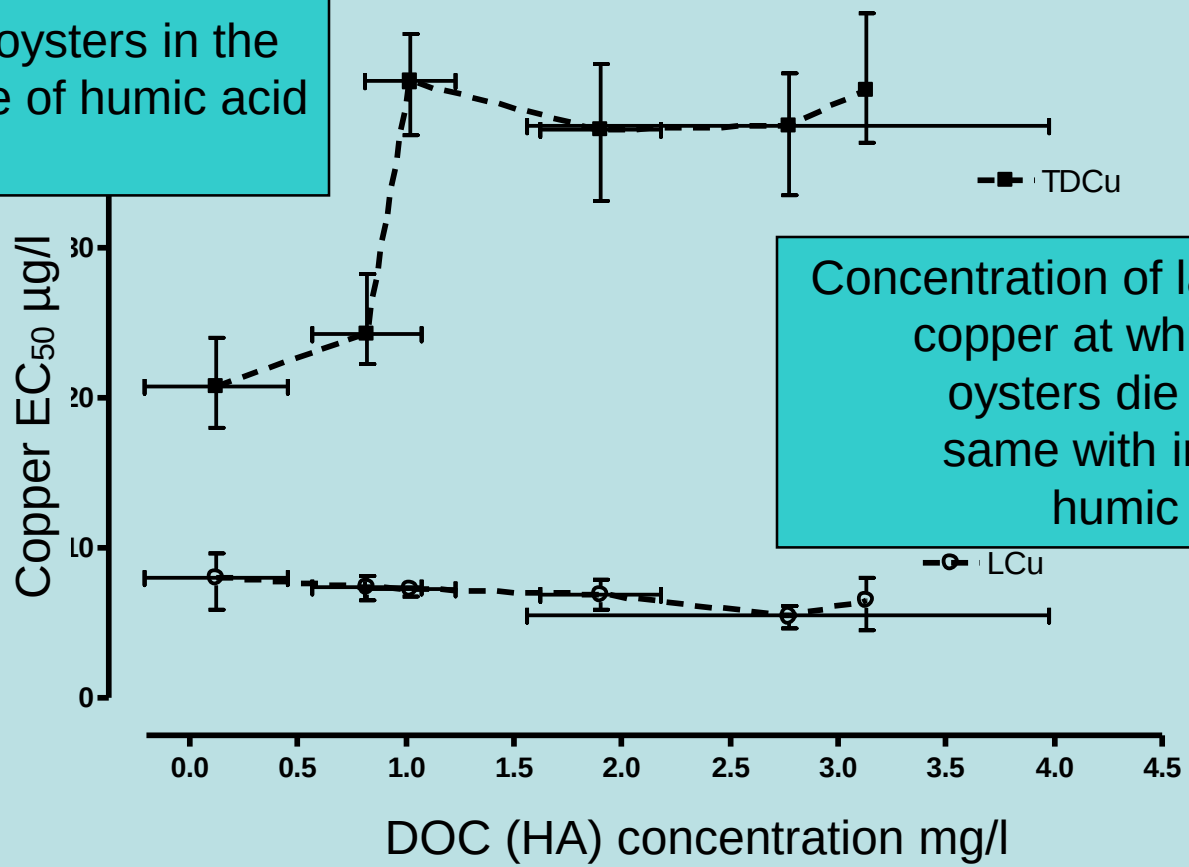
# Copper Toxicity to Oyster Embryos

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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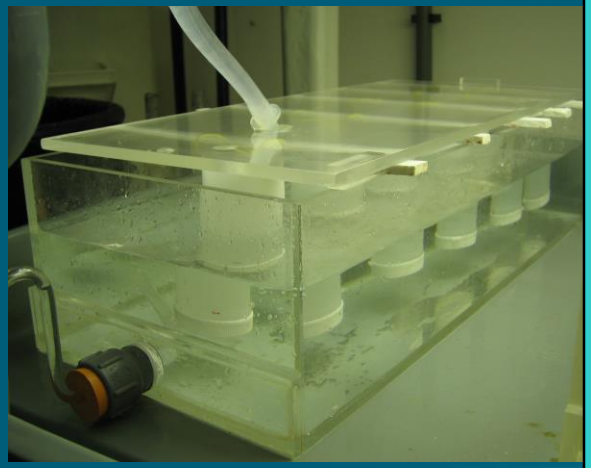
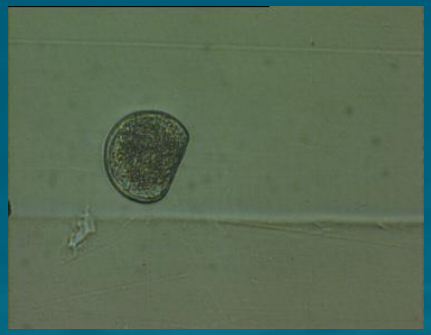
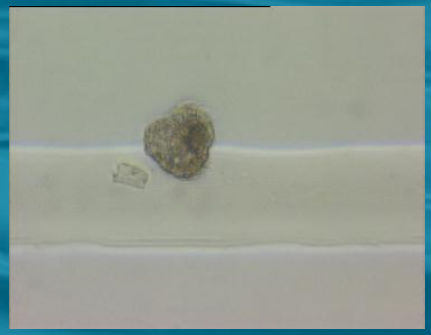
# Copper toxicity to Oysters



- The $EC_{50}$ for dissoved copper to oyster embryos doubles from 20 to 40 parts per billion (µg/l) in the presence of humic acid
- The $EC_{50}$ for labile copper is around 7µg/l and unchanged as humic acid increases





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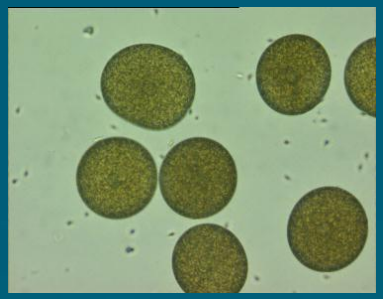
# Copper Toxicity to Fucus

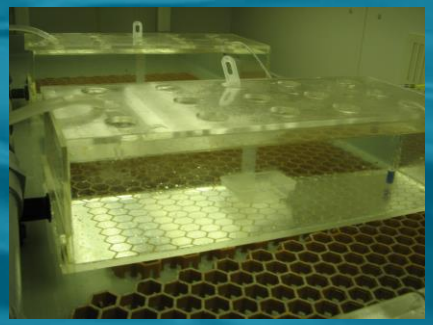
## Fucus germling growth test

Obtain gametes



Fertilise eggs to create zygotes

Attach to microscope slides



Place slides within experimental tanks of the flow-through System. Copper concentration range 0, 20, 40, 80, 160 320 µg $l^{-1}$ Cu

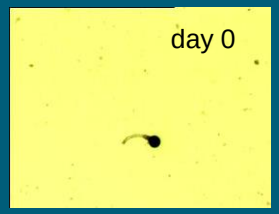
Zygotes measured on days 0, 4, 7, 10, 14.

Test terminated on day 14

Increase HA dosing





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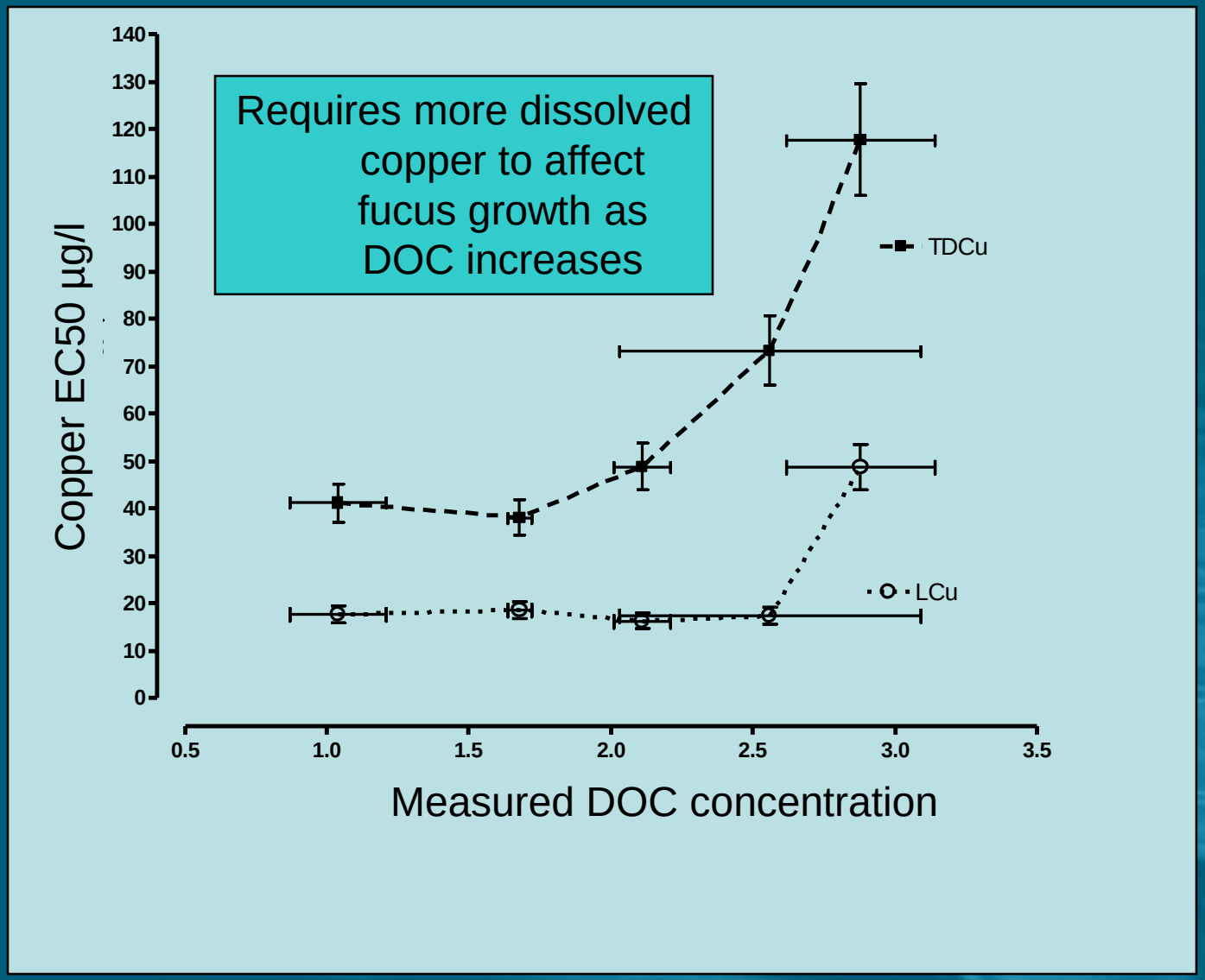
# Copper toxicity to Fucus

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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 $EC_{50}$ 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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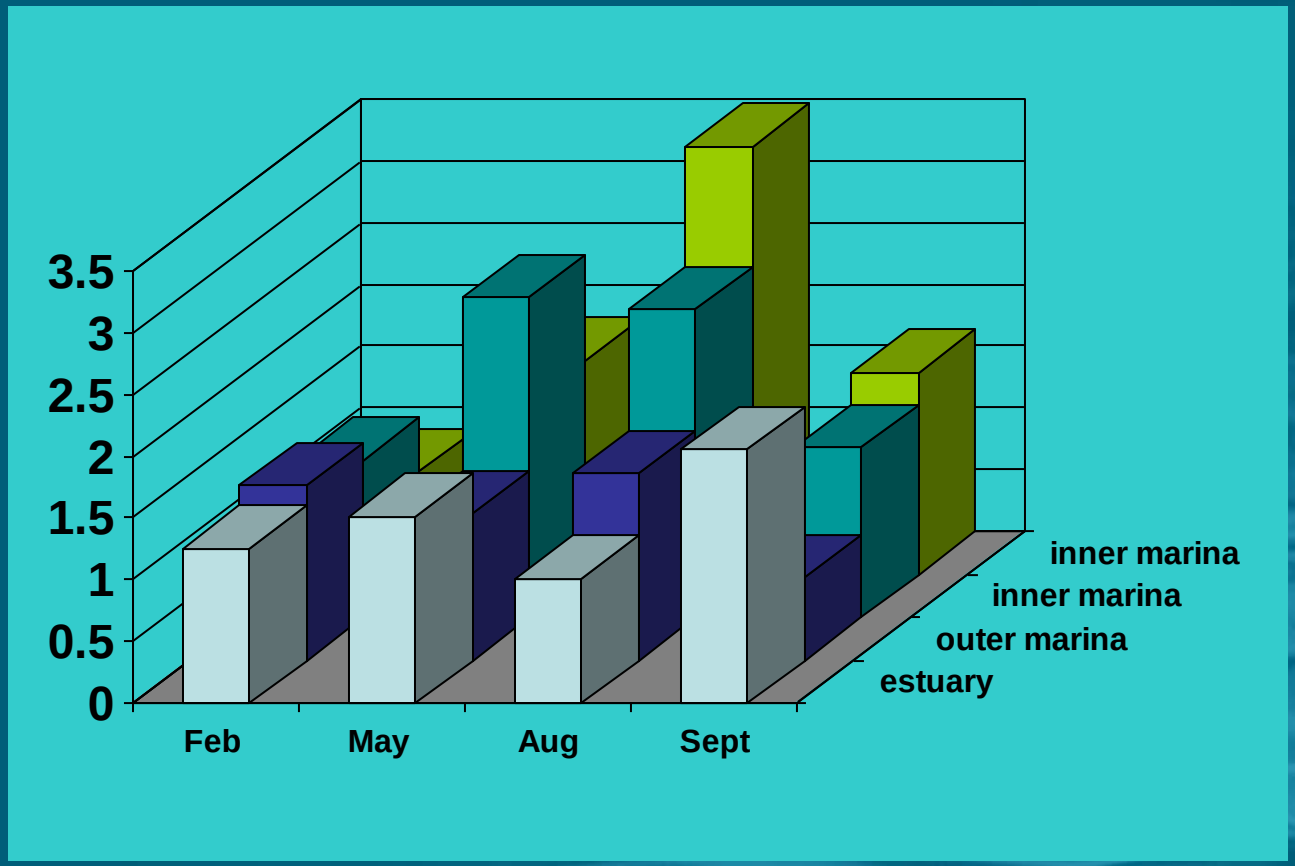
# Total Dissolved Copper µg/l at Ocean Village Marina, 1m depth

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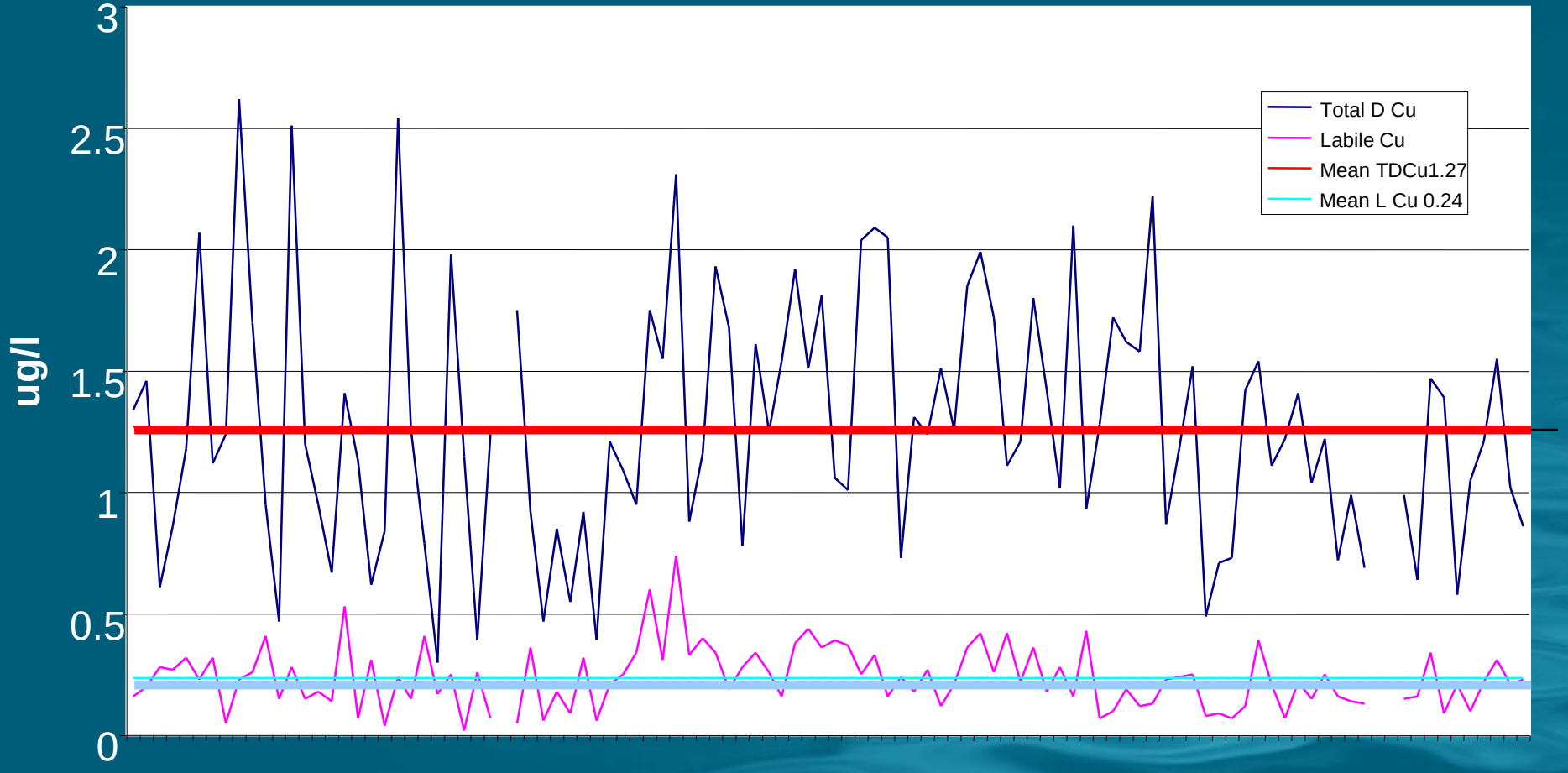
# Estuary Total Dissolved and Labile Copper




Plymouth

Southampton

Milford Haven

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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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Ylane
Loimaa
Forssa
ikaupunki
Mynämäki
Aura
Somero
Raisio
Turku
(Åbo)
Paimio
Naantali
(Nådendal)
Kaarina
Salo
Pargas
Lohjanjärvi
Korpo
Kimito
Dragsfjärd
Kirkko
Ekenäs
© Collins Bartholomew Ltd 2004
100 Km

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. Aerial view of Uittamo marina located in Turku, Finland. Numbers denote sampling sites.

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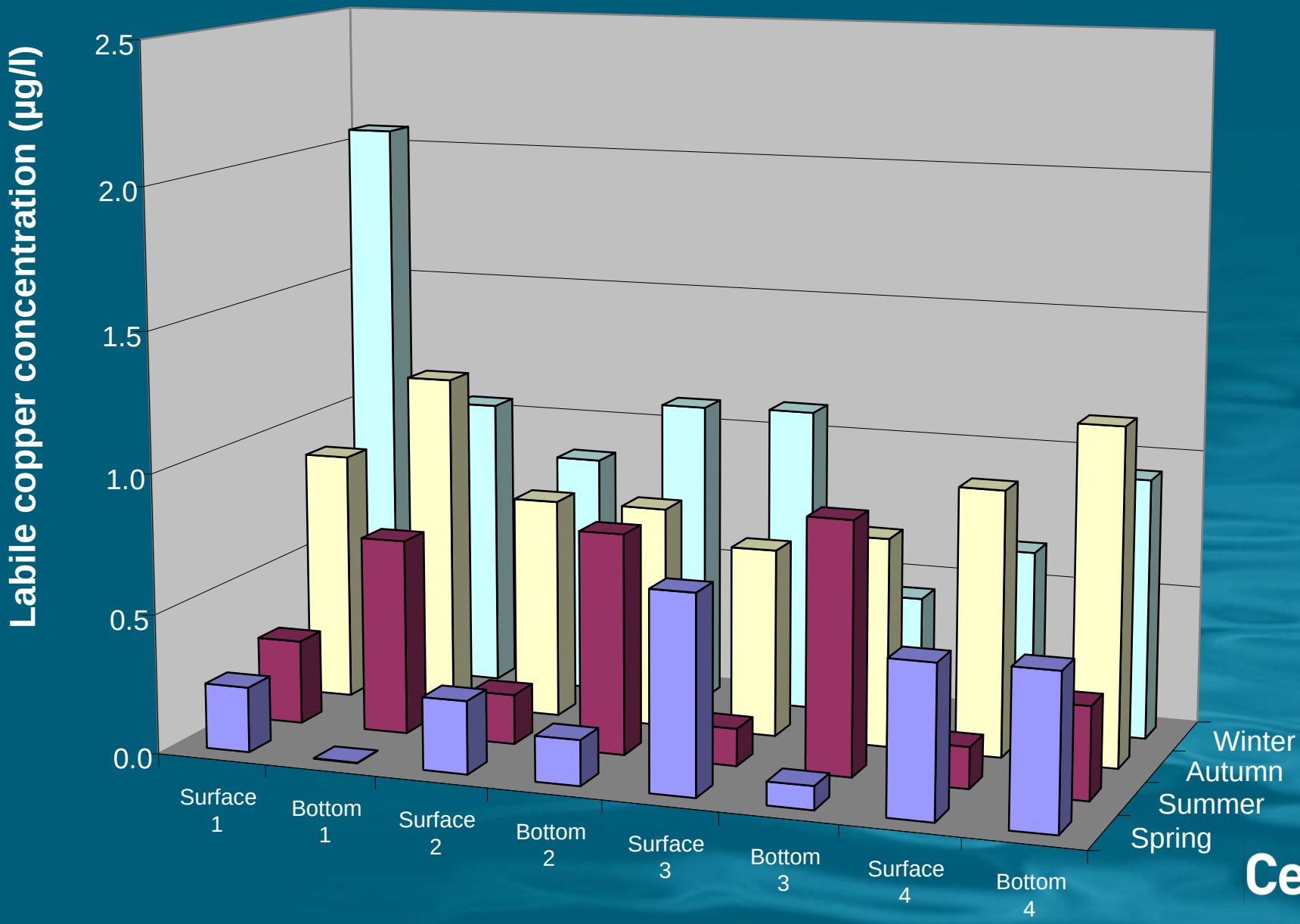
# Labile Copper in Finland

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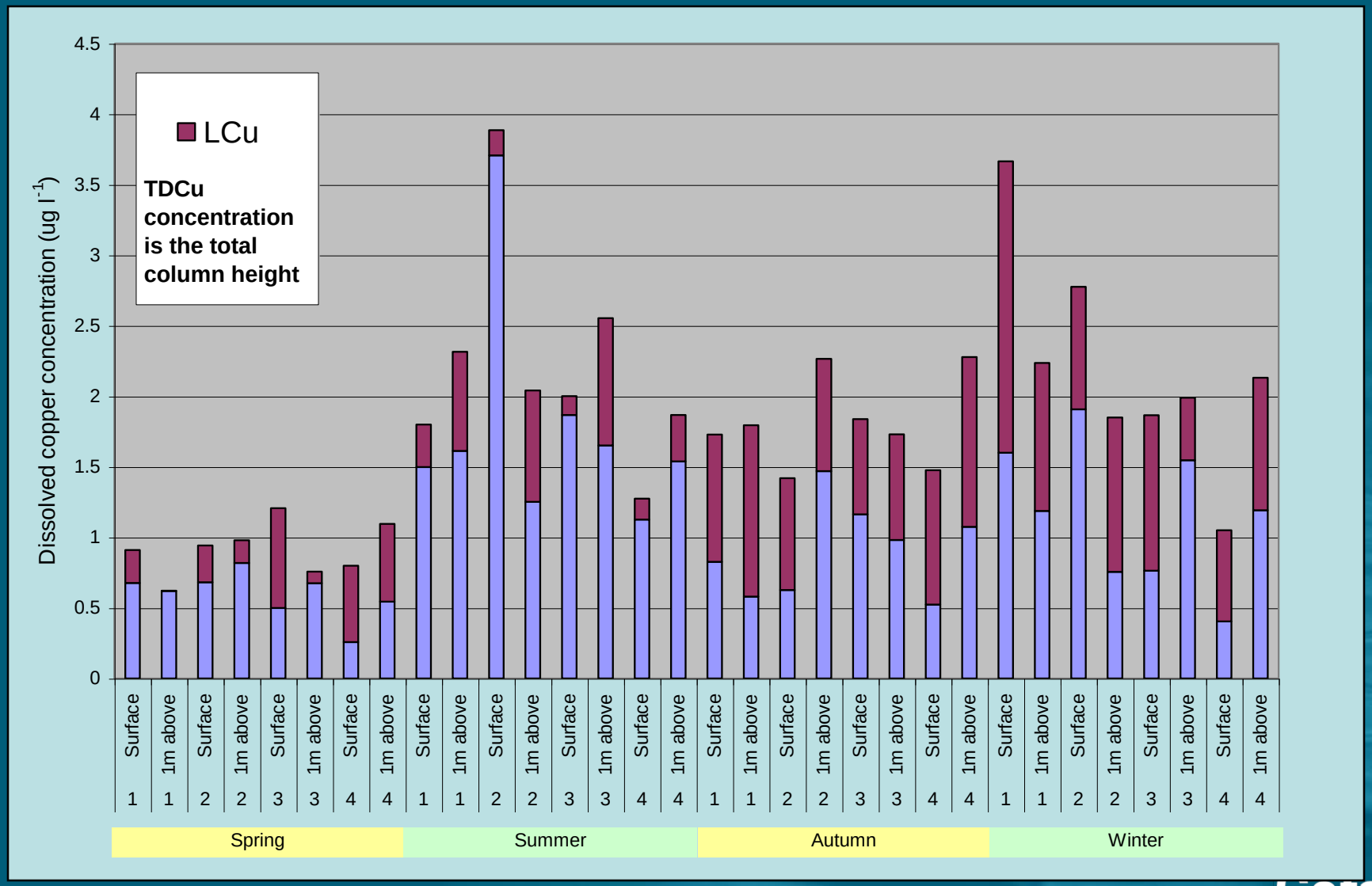
# Labile and Total Dissolved Copper in Finland



# Risk Quotients

Total Dissolved Copper: **worst case**

| µg/l | Total DCu | Labile |
|---|---|---|
| No. Samples | 108 | 108 |
| Mean | 1.68 | 0.38 |
| 95%ile | 4.18 | 0.71 |
| Max | 6.68 | 2.69 |

$$\frac{\text{PEC}}{\text{PNEC}} \quad => 1 \text{ (harm)}$$

$$\frac{\text{Measured Total Dissolved Copper 6.68 (3.60)}}{\text{Predicted No Effect Concentration 5}} =$$

| In marina | Outside marina |
|---|---|
| 1.34 | 0.72 |

$$\frac{\text{Measured labile copper 2.69 (0.38)}}{\text{Predicted No Effect Concentration 5}} =$$

| In marina | Outside marina |
|---|---|
| 0.54 | 0.08 |

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# Conclusions

- Labile copper controls toxicity in the environment not total dissolved copper
- As binding ligands (DOM, SPM) increase less copper is present in the labile (toxic) form
- Bivalves and seaweed are tolerant to copper in the real world – we have underestimated tolerance
- We have also overestimated concentrations in the real world
- There is little risk to marine species at current concentrations 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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# Conclusions

- Labile copper controls toxicity in the environment not total dissolved copper
- As binding ligands (DOM, SPM) increase less copper is present in the labile (toxic) form
- 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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