

Comparison of bioavailability & effects of Cu in two lentic freshwater microcosm studies

**Christoph Schäfers,
Heinz Rüdel, Udo Hommen**

Fraunhofer Institute
for Molecular Biology
and Applied Ecology (IME)
Schmallenberg, Germany



The compared studies - objectives

Study objective

Higher tier risk assessment study
for a copper based fungicide:

- Community level effects
after worst case use (wine)
- Time until and extent of recovery

Setting water quality objectives
for copper:

- Community level effects of a
continuous copper exposure
- Adaptation? Active Cu species?

Applied copper salt

WP-formulated Cu-hydroxide

Cu-sulphate

Dosing

spraying on the water surface
6 applications every 10 days

Continuously (3 x weekly) adding
a solution equilibrated for 24 h

Nominal concentration (μg total Cu/L)

2.5, 12, 24, 120, 240

5, 10, 20, 40, 80, 160

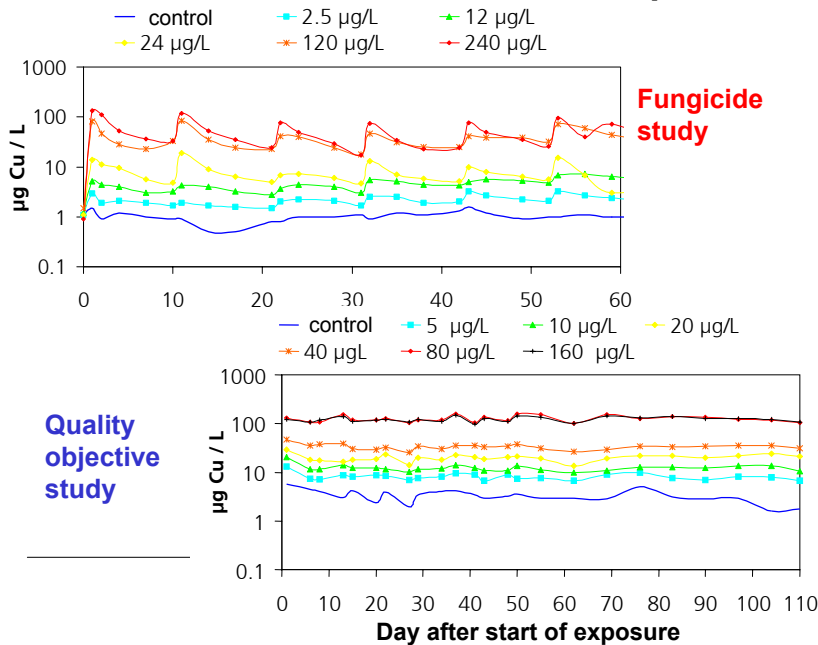
Total amount of Cu applied (g)

0.01, 0.05, 0.11, 0.54, 1.08

0.04, 0.08, 0.18, 0.40, 0.76, 1.56

Dosing: 50 d; observation: 385 d **study duration** 112 d

Concentration of dissolved Cu (0.45 µm filtered)



The compared studies – common aspects

- Indoor systems with additional illumination (1 KW metal halid lamps)
- Volume of the microcosms: approx. 1m x 1m X 1m
- Sediment layer of 20 cm
- Design (2 replicates/concentration, 4 controls) and statistics
- Water and included planktonic community of the same source
- Observed endpoints
abundances of phyto- and zooplanktonic species
and of benthic macroinvertebrates,
production of macrophytes (*Elodea densa*),
water parameters
- Simulated seasons during application (early to late summer)

The compared studies – nutrient state

Water from the same source („pristine“ reference site)

sediment

Fungicide study

fish pond

TOC: 4.5 %

resulting microcosm water at study start

8 mg/L

0.5 mg/L

4-5 mg/L

< 0.1 mg/L

DOC

total phosphate

nitrate

ammonium

Quality objective study

„pristine“ reference site
(small lake)

TOC: 2 %

4 mg/L

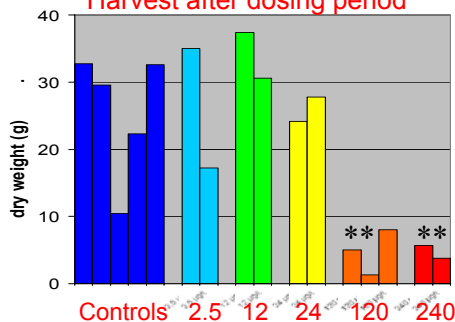
< 0.1 mg/L

4-5 mg/L

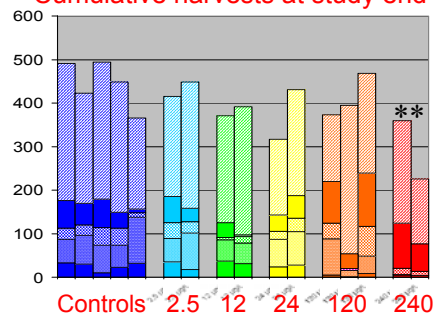
< 0.1 mg/L

Biomass production of macrophytes (*E. densa*)

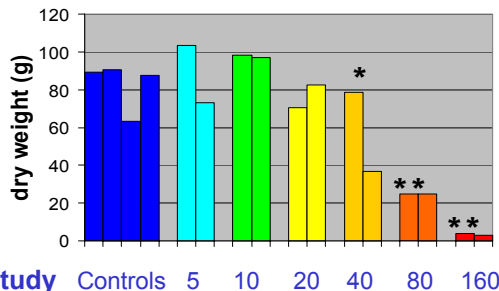
Harvest after dosing period



Cumulative harvests at study end

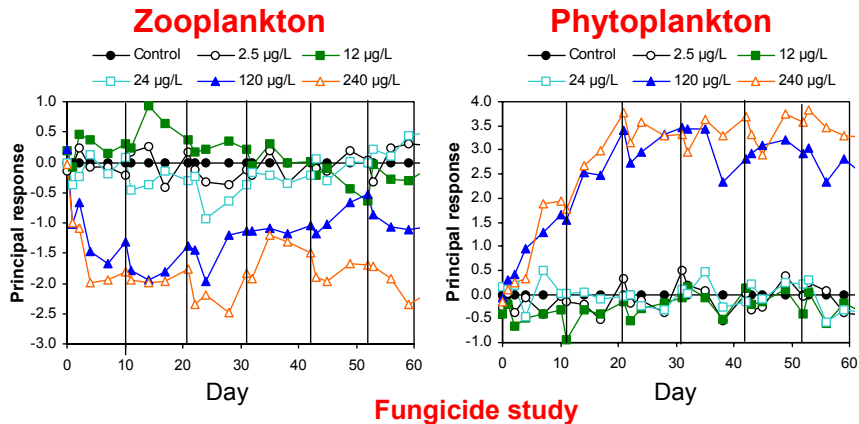


Fungicide study



Quality objective study

Plankton community PRCs

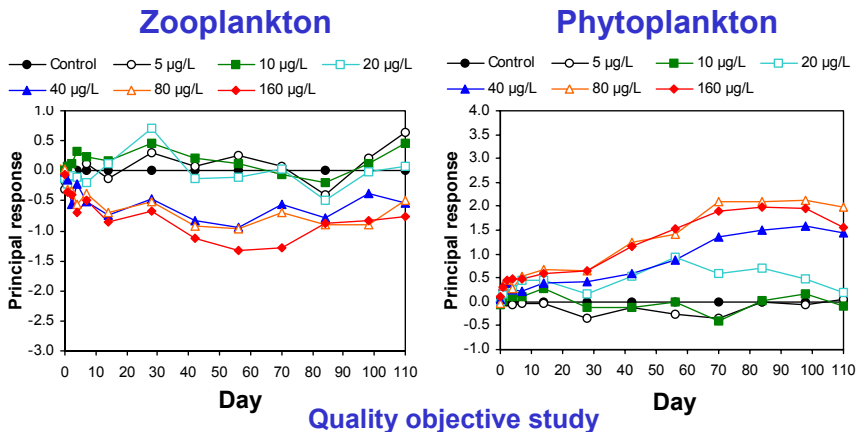


Fungicide study

Slight temporary zooplankton effect at 24 µg/L caused by *Chydorus sphaericus*

After the dosing period:
NOEC = 24 µg/L
LOEC = 120 µg/L

Plankton community PRCs



Quality objective study

Temporary phytoplankton effect at 20 µg/L mainly caused by Picoplankton

At study termination:
NOEC = 20 µg/L
LOEC = 40 µg/L

Summary: population and community effects

Nominal concentration [$\mu\text{g/L}$]					Endpoint	Nominal concentration [$\mu\text{g/L}$]					
2.5	12	24	120	240		5	10	20	40	80	160
			indirect	indirect	Zooplankton PRCs	not sufficient					
					Diversity, Similarity						
					Phyllopoda <i>Daphnia</i>						
					<i>Chydorus sphaericus</i>						
					Rotatoria <i>Keratella</i>						
			indirect	indirect	Copepoda <i>Cyclops</i>	not sufficient					
					Ostracoda						
					Phytoplankton PRCs						
					Diversity, Similarity						
					Chlorophyta						
			indirect	indirect	Cyanobacteria	indirect					
					Picoplankton						
					Diatomea						
					Cryptophyta						
					Macroinvertebrates						
			indirect	indirect	Macrophyte prod.						
					Water parameters						

No effect	transient slight effects	transient strong effects	permanent slight effects	permanent strong effects
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Angeordnete Ökologie

Additional information: Recovery

Fungicide study:

After day 50, no further application was performed until the end of the study (early summer if the following year).

All endpoints observed showed full recovery up to nominally 120 $\mu\text{g/L}$.

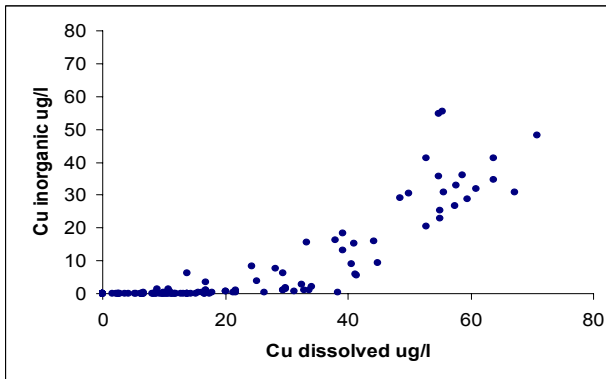
At 240 $\mu\text{g/L}$, only macrophyte biomass production was not able to catch up with the controls.

The study was sponsored by the European Copper Task Force, and monitored by



Additional information: speciation/complexation

Quality objective study



The study was sponsored by the ICA, represented by the European Copper Institute (ECI),



and performed in cooperation with WRC-NSF, UK

The copper complexation capacity of the microcosm water was determined to be 20 to 30 µg Cu/L.

Discussion

Similar results (despite dosing regimen and applied copper salt):

- No observed effect on sediment organisms
=> no bioavailable active copper species in sediment
- Comparable effects on plankton and macrophytes
=> formulation seems to compensate for solubility
- Threshold concentration for effects around 20 µg/L
=> copper complexation capacity of oligotrophic lentic systems is able to eliminate bioavailable active copper species up to 20 µg/L

Differences:

Fungicide study

high plankton density

effects more pronounced

higher complexation capacity?

WQ objective study

low plankton density

effects more sensitive

less compensatory potential

Conclusions

High dynamics (high nutrient levels, spring conditions)

- effects on growth and reproduction amplified
- indirect effects dominant
- suited for outdoor studies

Low dynamics (low nutrient levels, summer conditions)

- communities exploiting habitat capacity
- effects less amplified
- direct effects more sensitive
- suited for managed indoor studies

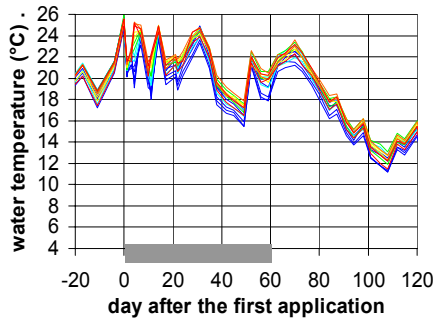
Differentiated Taxa (69)

Zooplankton (13 taxa)	Copepoda (adults, nauplii)	2	Macro- phytes (1 taxon)	<i>Elodea densa</i>	
	Ostracoda	1			
	Cladocera	5	Filamentous Algae (1)	Chlorophyta	
	Rotatoria	5			
Benthic macro- Invertebrates (11 taxa)	Odonata	2	Phyto- Plankton (29 taxa)	Cyanophyta	4
	Coleoptera	1		Crypto- phyceae	3
	Trichoptera	1		Chlorophyta	14
	Chironomidae	1		Conjugato- phyceae	3
	Brachycera	2		Diatomea	2
	Megaloptera	1		Eugleno- phyceae	1
	Bivalvia	1		Picoplank- ton < 5µm	1
	Tubificidae	1		Unknown	1
	Hirudinea	1			
Benthic Meiofauna (14 taxa)	Nematoda	14			

Temperature in the microcosms

Simulation of early summer to early autumn

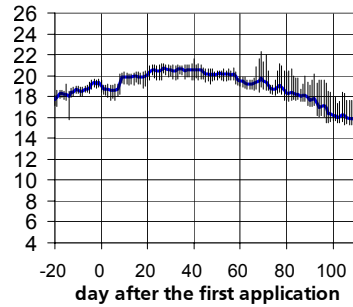
Fungicide study



By adjusting room temperature
to the outdoor temperature

grey: compared dosing period

Quality objective study



By temperating
the water

vertical lines: daily max, min