Korleis påverkar kopar og biocid groe og andre organismar?

Bjørn Einar Grøsvik

Environmental impact and animal welfare in fish farming

Genetic introgression
- Increased vulnerability in wild populations

Animal welfare

Bacteria, virus and parasites
- Infectious Salmon Anemia Virus
- Salmonid Alfa Virus
- Salmon lice

Use of wild caught wrasse for use in de-lousing of farmed salmon
- Pathogen transmission
- Genetic introgression
- Overfishing
- Bycatch

Anti-sea lice therapeutants
- Impact on non-target species
- Bath treatment
- In-feed treatment

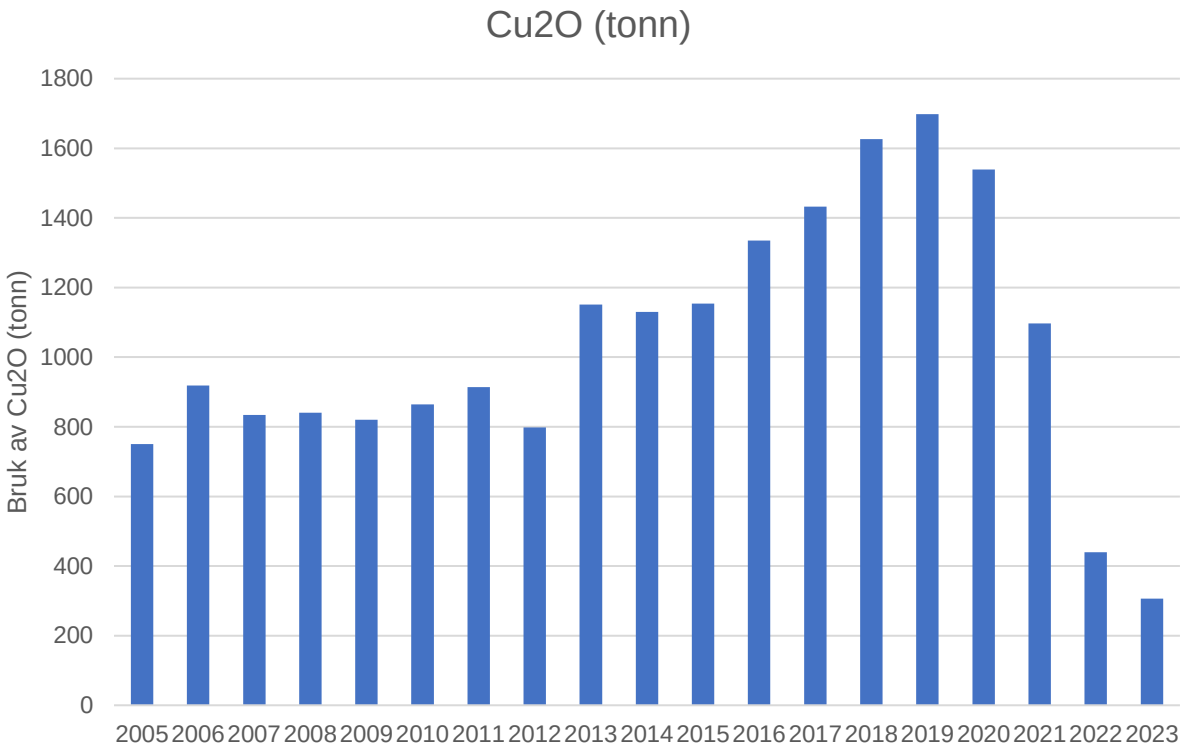
Environmental pollutants
- Anti-fouling agents
- Copper, Tralopyril and Zn/Cu pyrithion
- Pollutants from fish feed/waste

Particulate organic matter
- Impact on sediment chemistry and biodiversity

Dissolved nutrients
- Eutrophication
- Harmful algae bloom

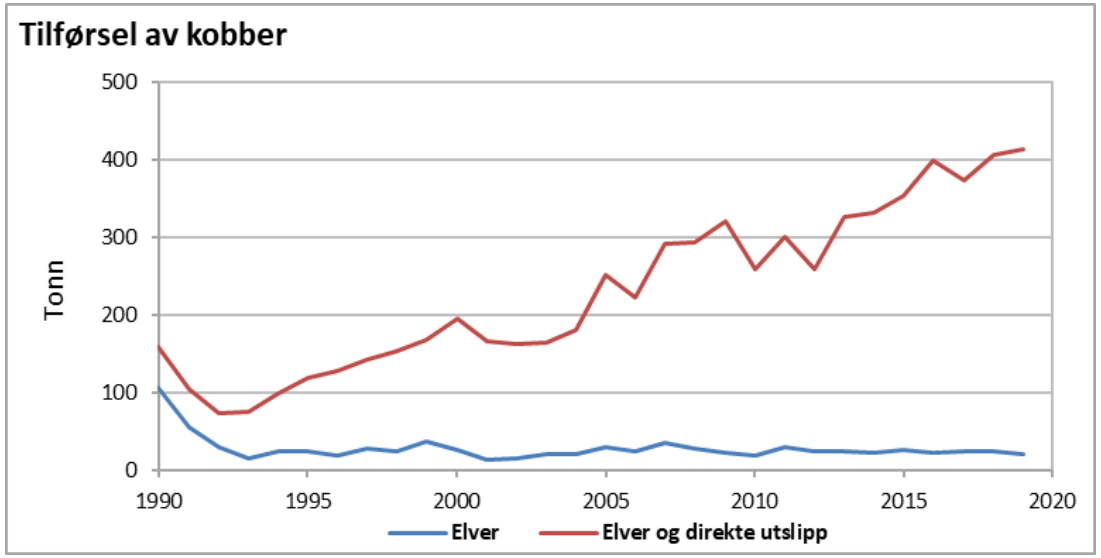
Ringstad Design

Store mengder Cu_2O brukt årleg i norsk akvakultur fram til nyleg



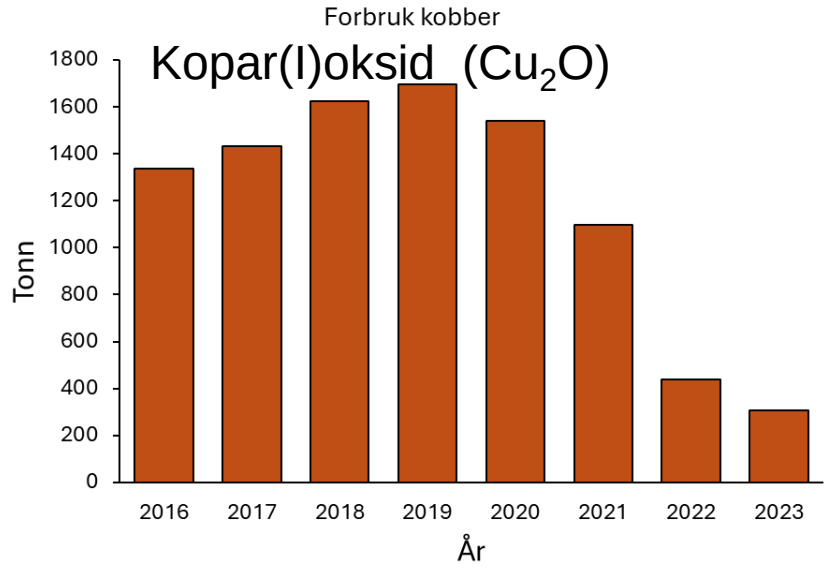
Miljødirektoratet

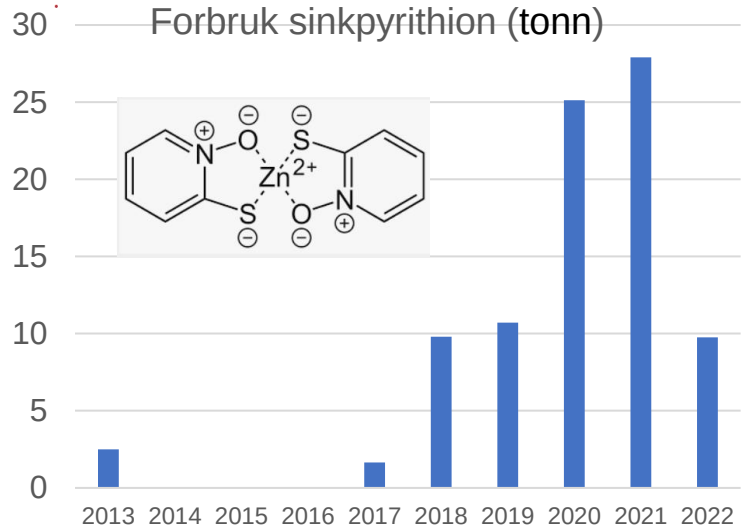
Tilførsel av kopar til Nordsjøen

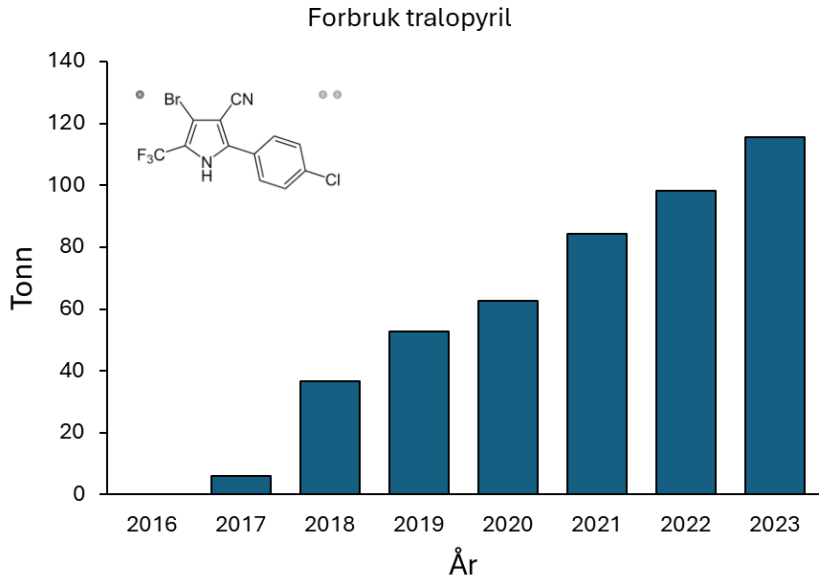


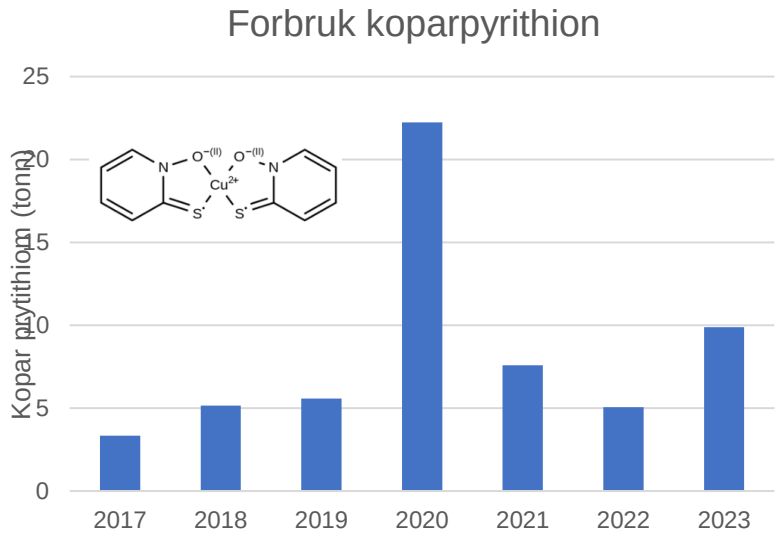
Miljøstatus.no

Forbruk av kopar og nye biocid (tralopyril , Zn- og Cu pyrithion)









Verknadsmekanismar for kopar:

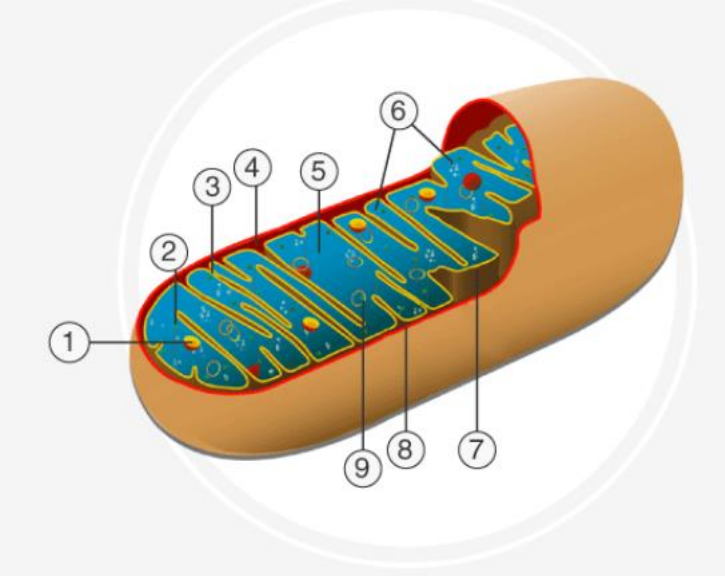
- Giftighet frå kopar kjem frå koppariona si evne til å skifte mellom oksidasjonstrinn, danne reaktive oksygen forbindelsar (ROS):

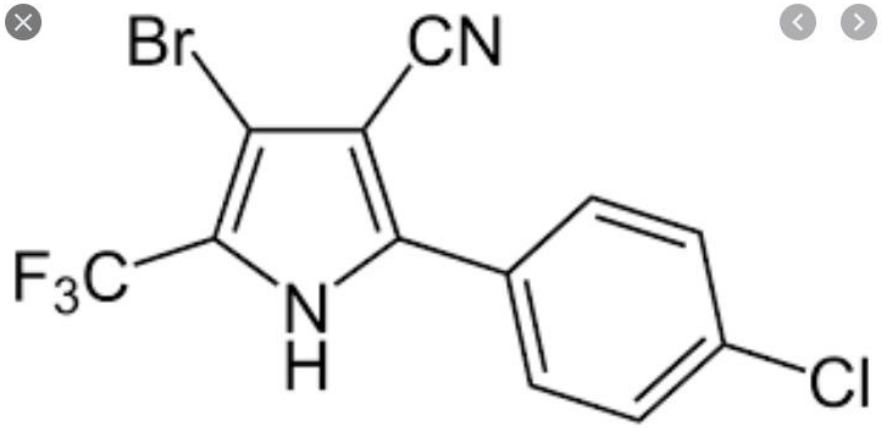
$$Cu^{+} + H2O2 \rightarrow Cu^{2+} + OH- + \cdot OH$$

- Kan binde og øydelegge protein, bryte SH-grupper, endre 3Dstruktur av protein
- For høge nivå av ROS kan føre til lipid peroksidering (membrane skade), trådbrudd på DNA som kan gi mutasjonar
- Stoppe elektrontransportkjeda (mitokondriefunksjon)
- Bytte ut essensielle metall
- Forårsake celledød (apoptose og nekrose)

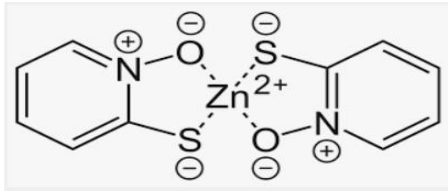
Tralopyril – verkar giftig ved å:

- Øydelegge protongradienten over den indre membranen i mitokondria slik at dei ikkje klarer å utføre oksidativ fosforylering
  - Dette hindrar danning av ATP og fører til rask mangel på energi i cellene
  - Organismen døyr på grunn av energimangel



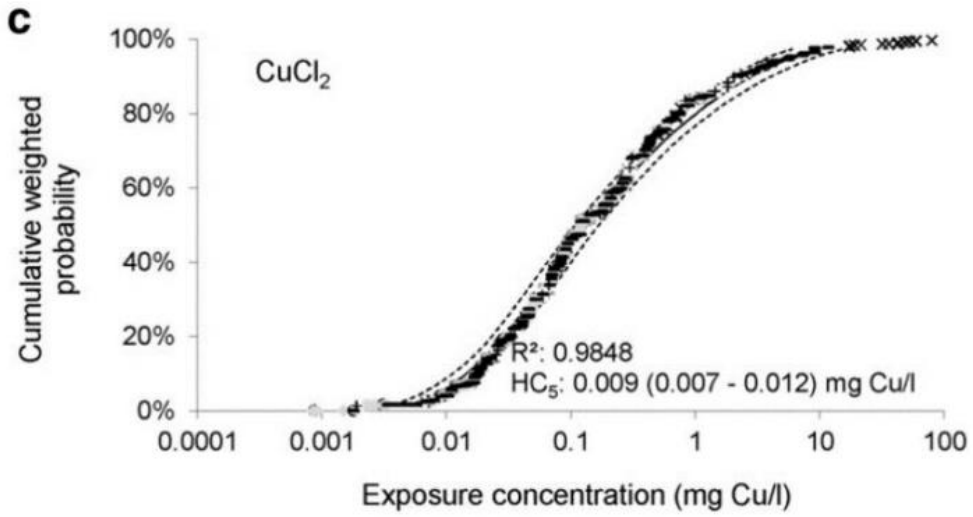


Zn-pyrithion verkar giftig ved å:

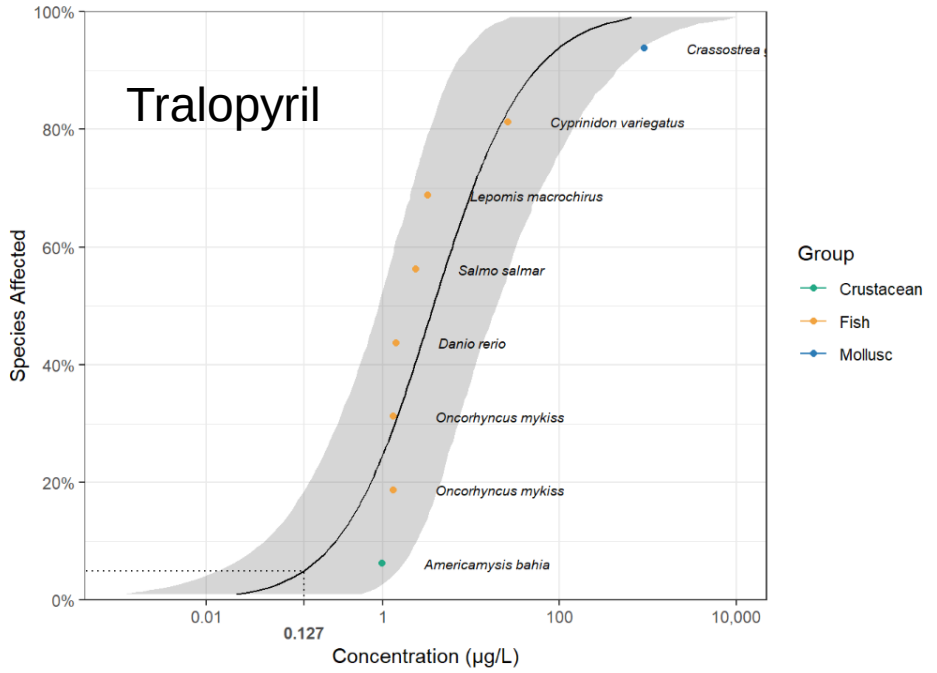


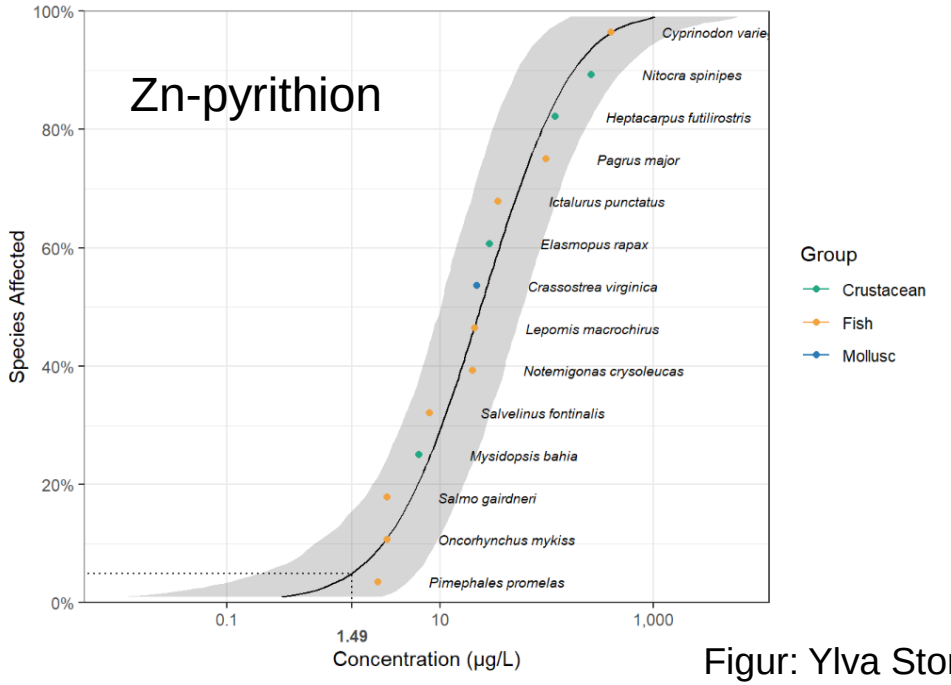
- Zn pyrithion er eit organometallkompleks som er brukt både som anti sopp- og antibakterie middel
- Øydelegg metallhomeostase, mitokondriefunksjon og redoks jamvekt
- Skader membran transport and metall opptak
- Gir oksidative stress - danning av reaktive oksygen radikal (ROS)
- Øydelegg mitokondrie funksjon som fører til for liten produksjon av ATP
- Kan føre til apoptose og nekrose (celledød)

Giftighet av antigroemiddel
SSD kurver og terskelverdiar



Cu: EQS Sjøvatn: 2,6 µg/l





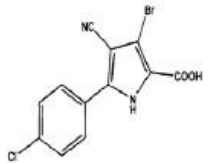
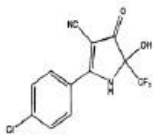
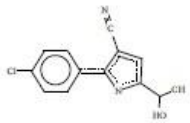
Tralopyril: Foreslått EQS ferskvatn: 0.002 ug/l

Foreslått EQS Zn-Pt: 0,014 µg/l
Foreslått EQS CuPt: = 0,19 µg/l
(Martins et al., 2018)

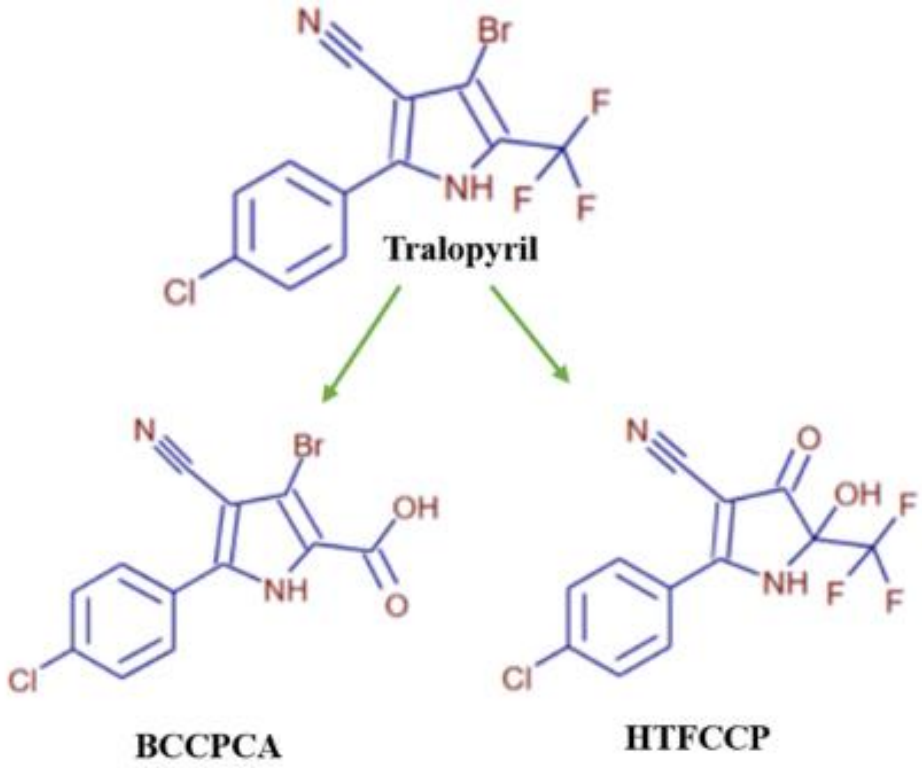
Figur: Ylva Storås

Tralopyril minus F3 minus Br minus F3 og Br

Table 1: Chemical and Physical Properties of Tralopyril Degradates

Property	Parent tralopyril	CL 322,250	CL 325,195	CL 322,248
PC Code	119093	N/A	N/A	N/A
Cas. No.	122454-29-9	N/A	N/A	N/A
Chemical Family	Halogenated Pyrrole Nitrile	Pyroles	Pyroles	Pyroles
Molecular Formula	$C_{12}H_5BrClF_3N_2$	$C_{12}H_6BrClN_2$	$C_{12}H_6F_3ClN_2O_2$	$C_{11}H_7ClN_2$
Smiles code	Brc2c(C(#N))c(c1ccc(CL)cc1)nc2C(F)(F)F	Brc2c(C(#N))c(c1ccc(CL)cc1)nc2C(=O)(O)	c2c(C(#N))c(c1ccc(CL)cc1)nc2C(F)(F)F	c1cnc(c2ccc(CL)cc2)c1(C(#N))
Molecular Weight g/ml	349.53	325.55	302.64	248.67
Molecular Structure				
Log P (Log Kow)	3.5	3.55	4.17[A]	1.68 [A]
Solubility in water mg/l	0.17 (pH 4.9) 0.16 (seawater)	5.63	17.95	476
Vapor pressure [B]	1.42×10^{-10} mm Hg (20 °C) 3.45×10^{-10} mm Hg (25 °C)	7.62×10^{-7}	3.45×10^{-9}	7.0×10^{-11}
Henry's Law (atm m^3 mol^{-1}) [C]	9.3×10^{-10} (25 °C)	8.29×10^{-8}	7.65×10^{-11}	4.8×10^{-14}

CL 322,250 = parent compound minus three fluorines forming a carboxylic acid by hydration
CL 325,195 = debrominated parent compound with hydration forming a ketone and an ortho hydroxylated trifluoromethyl group
CL 322,248 = (Debrominated CL 322,250)

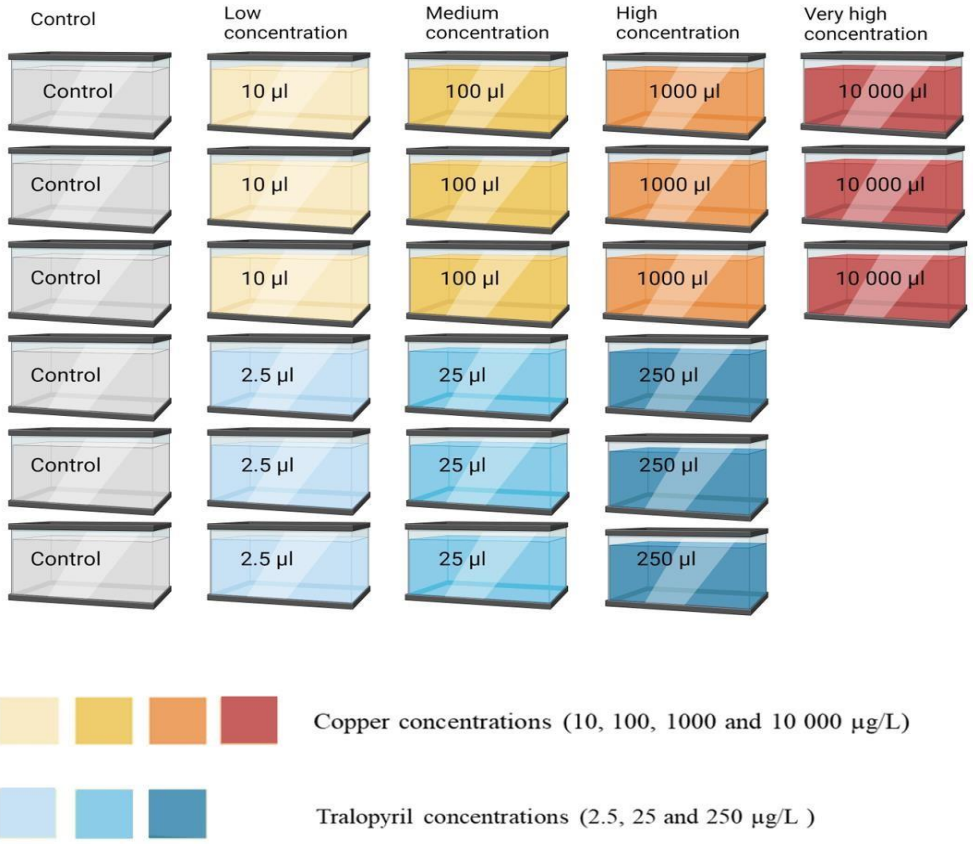


CL 325,250

CL 325,195

Eksponeringsstudie med blåskjell

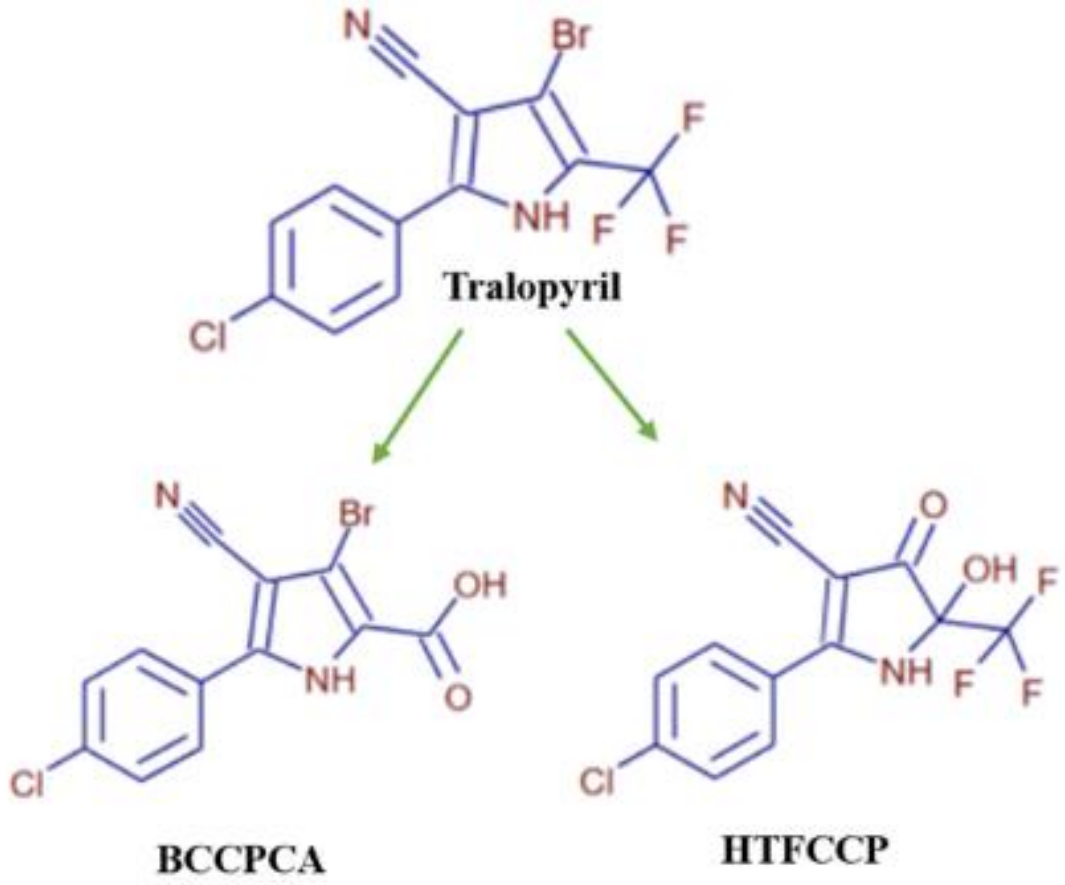
Målsetjing: Å studere bioaccumulering og effektar av Cu og tralopyril i ein dose-response eksponering



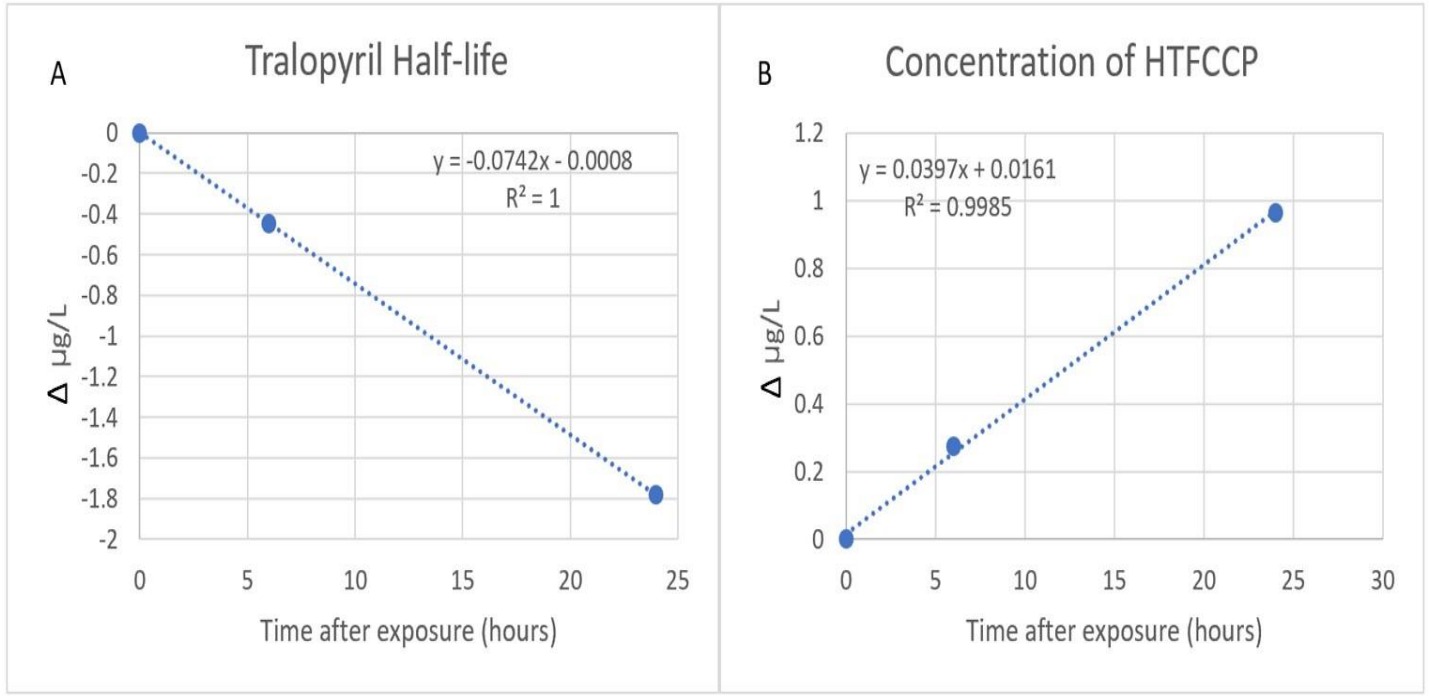
- Varighet: 1- and 24- timar
- 3 dagar med recovery

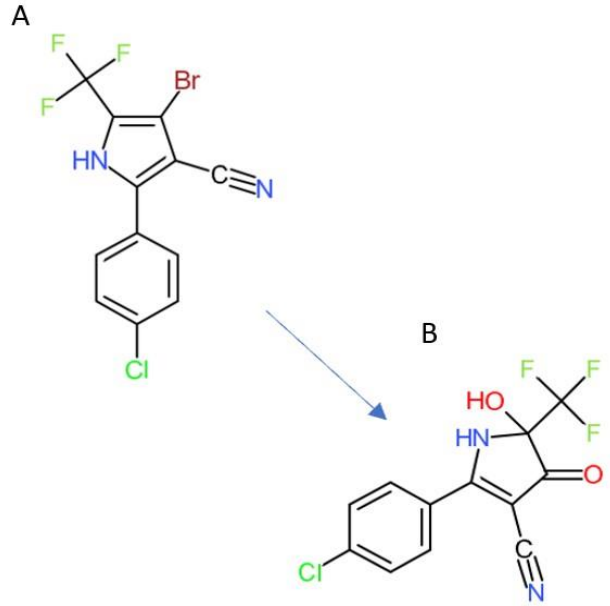
Nedbrytingsprodukt av tralopyril i sjøvatn

- 3-bromo-5-(4-chlorophenyl)-4-cyano-1*H*-pyrrole-2-carboxylic acid (BCCPCA)
- 2-(4-chlorophenyl)-5hydroxy-4-oxo-5-(trifluoromethyl)-4,5-dihydro-1H-pyrrole-3-carbonitrile (HTFCCP)



Tralopyril and the transformation product HTFCCP



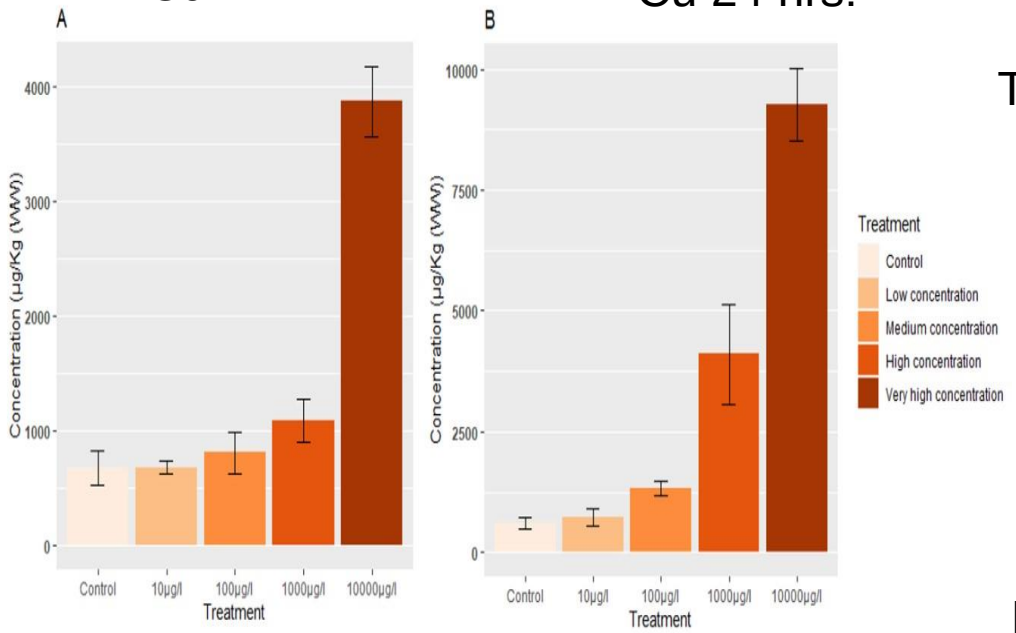


- 2-(4-chlorophenyl)-5hydroxy-4-oxo-5-(trifluoromethyl)-4,5-dihydro-1H-pyrrole-3-carbonitrile (HTFCCP)

Bioakkumulering i blåskjell

Cu 1 hr:

Cu 24 hrs:

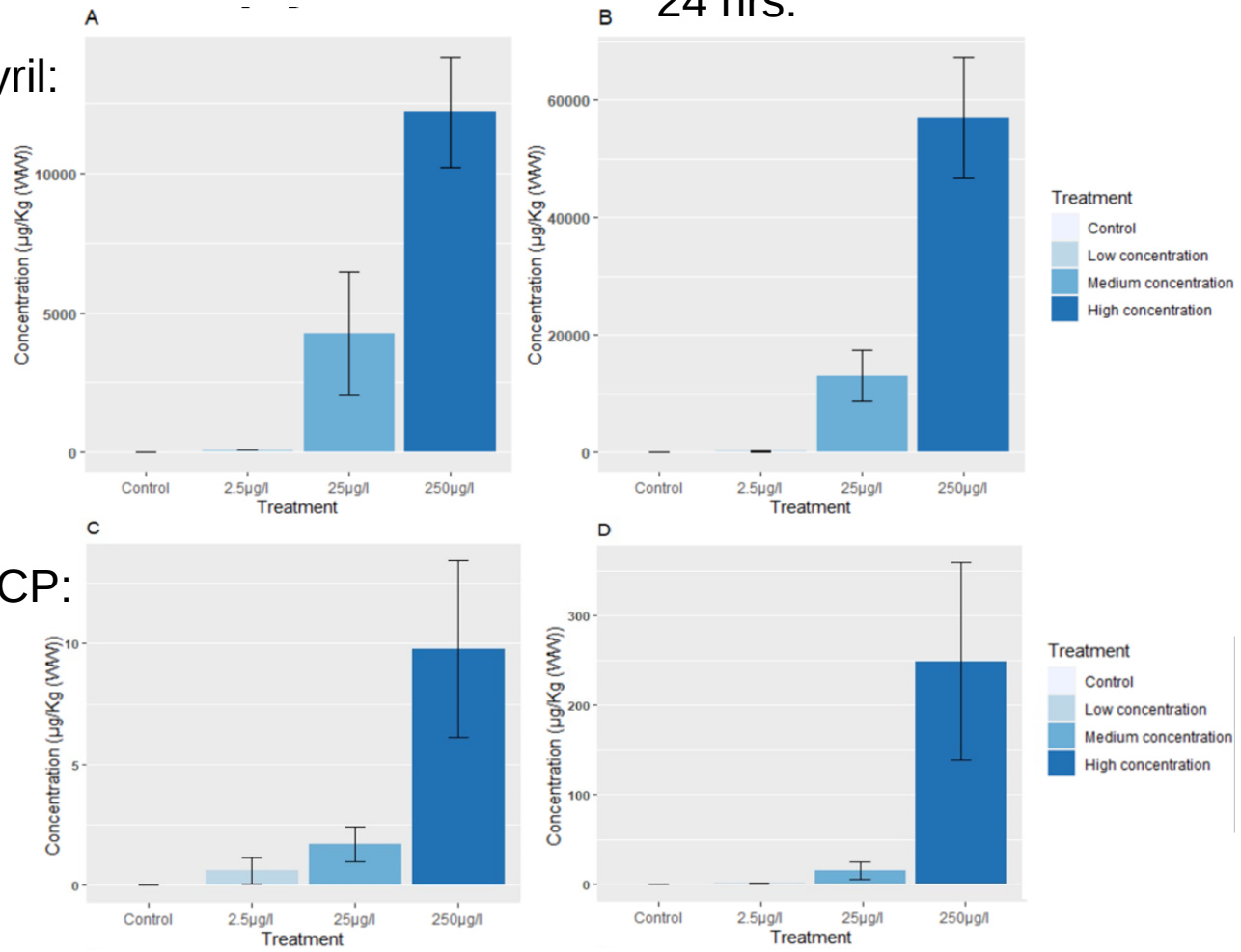


1 hr:

24 hrs:

Tralopyril:

HTFCCP:



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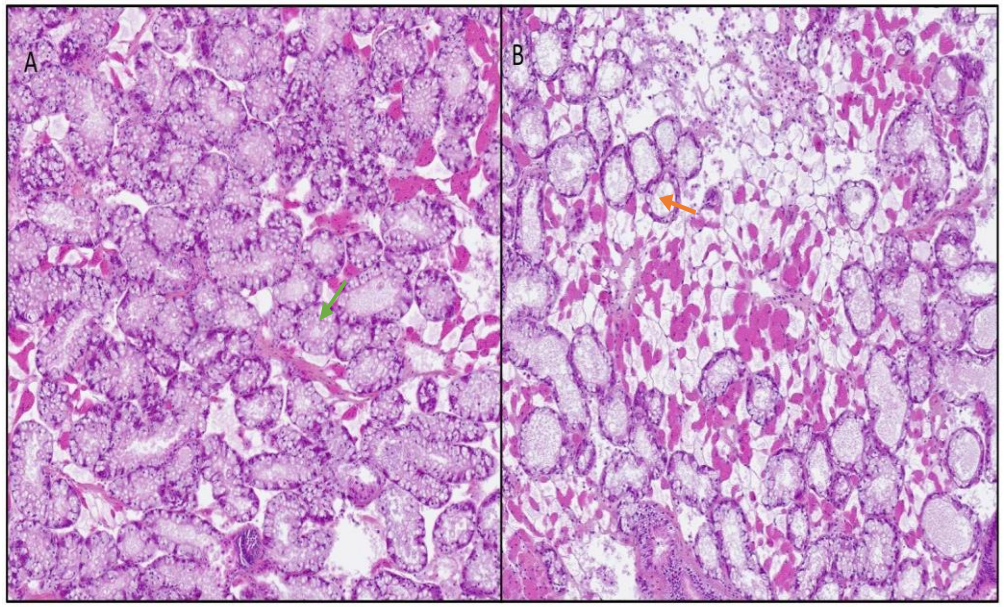
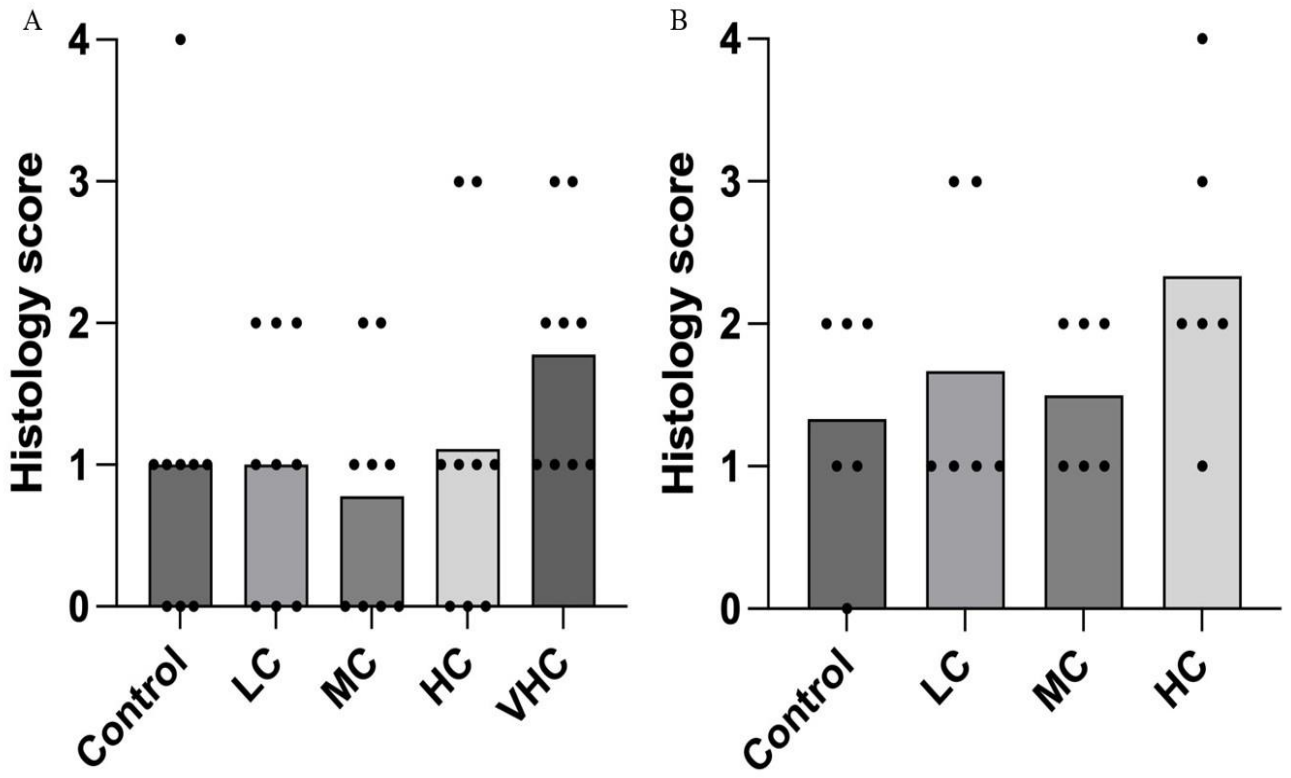
Vevsendring i fordøyelsesceller (atrofi)



Kontroll Eksponert



Kopar Tralopyril

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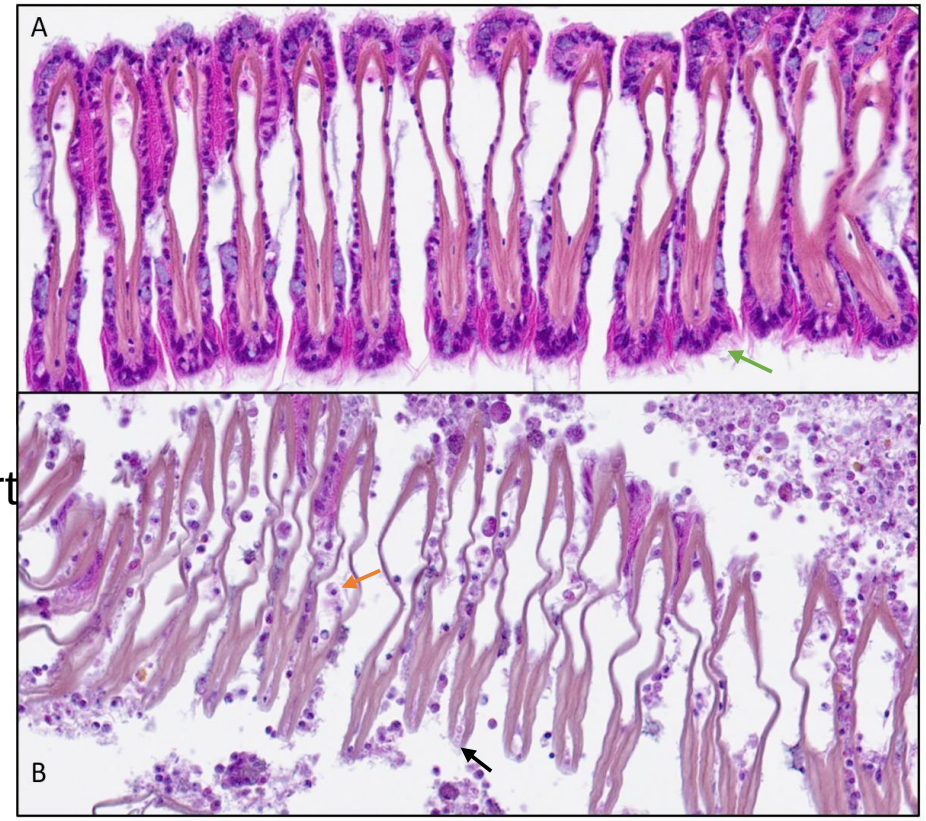
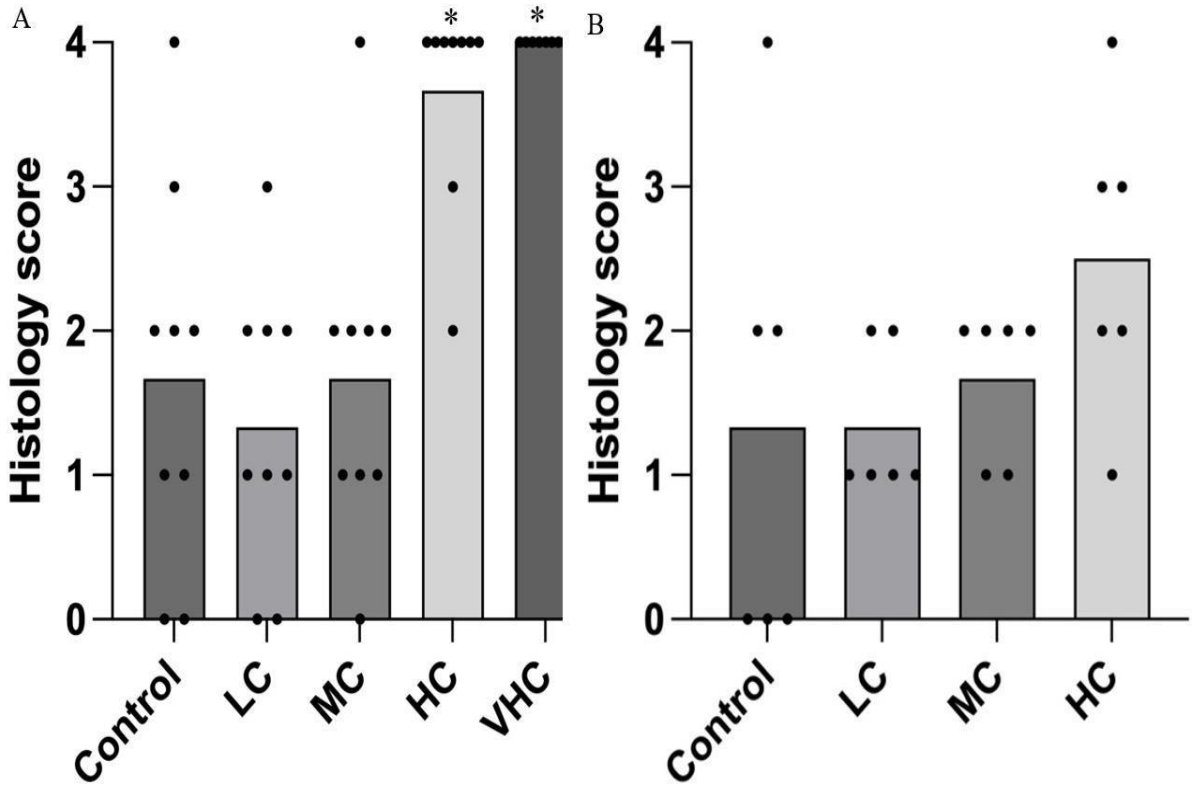
Vevsendring i gjeller (hemocytt infiltrasjon)

Kontroll

Eksponert





Kopar

Tralopyril

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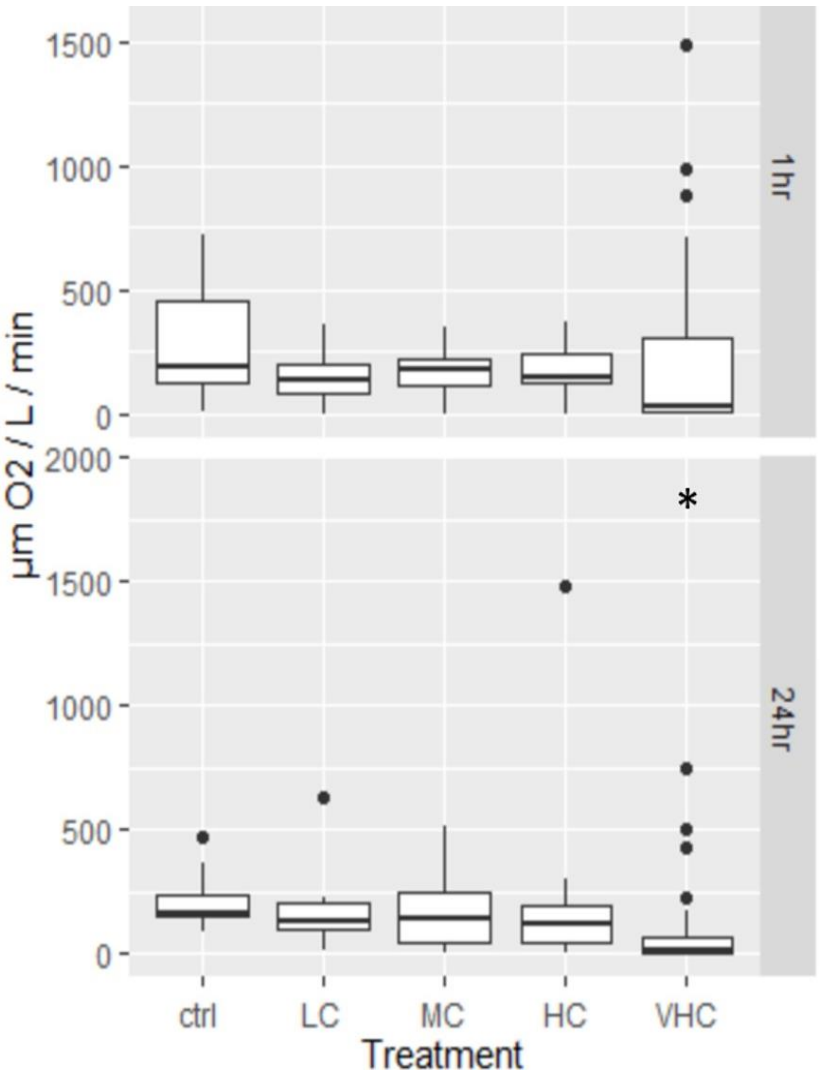
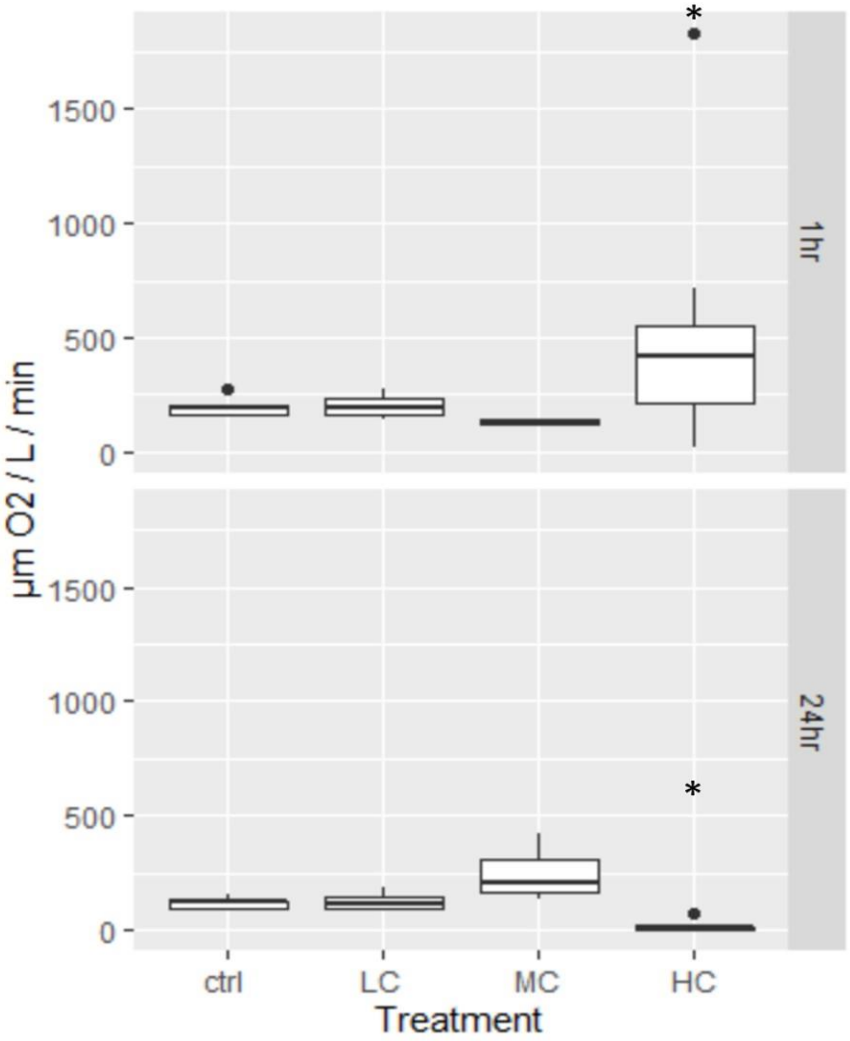
Effekt på oksygen metabolisme



Copper



Tralopyril

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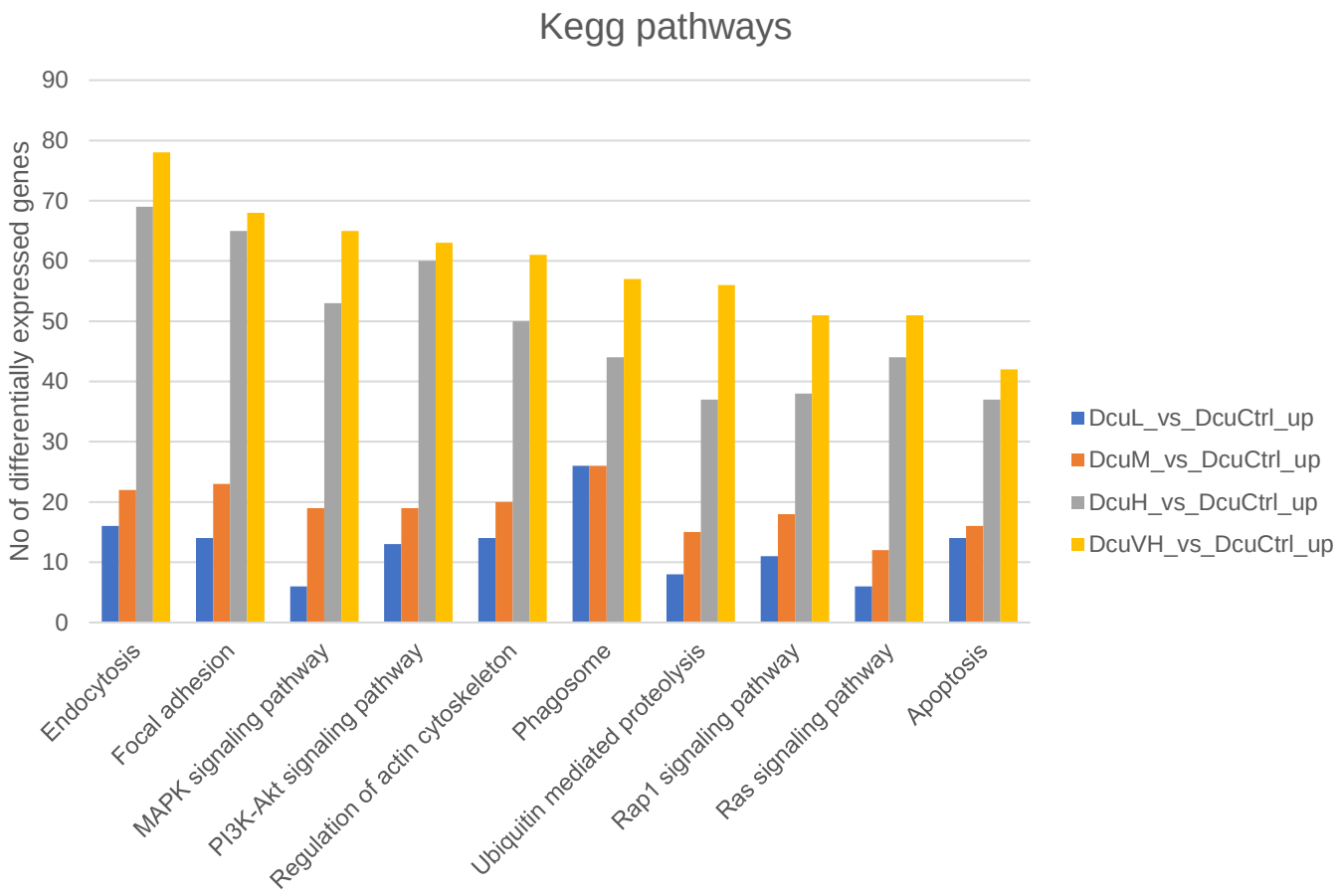
Endring i genutrykk i fordøyelseskjertel etter Cu eksponering



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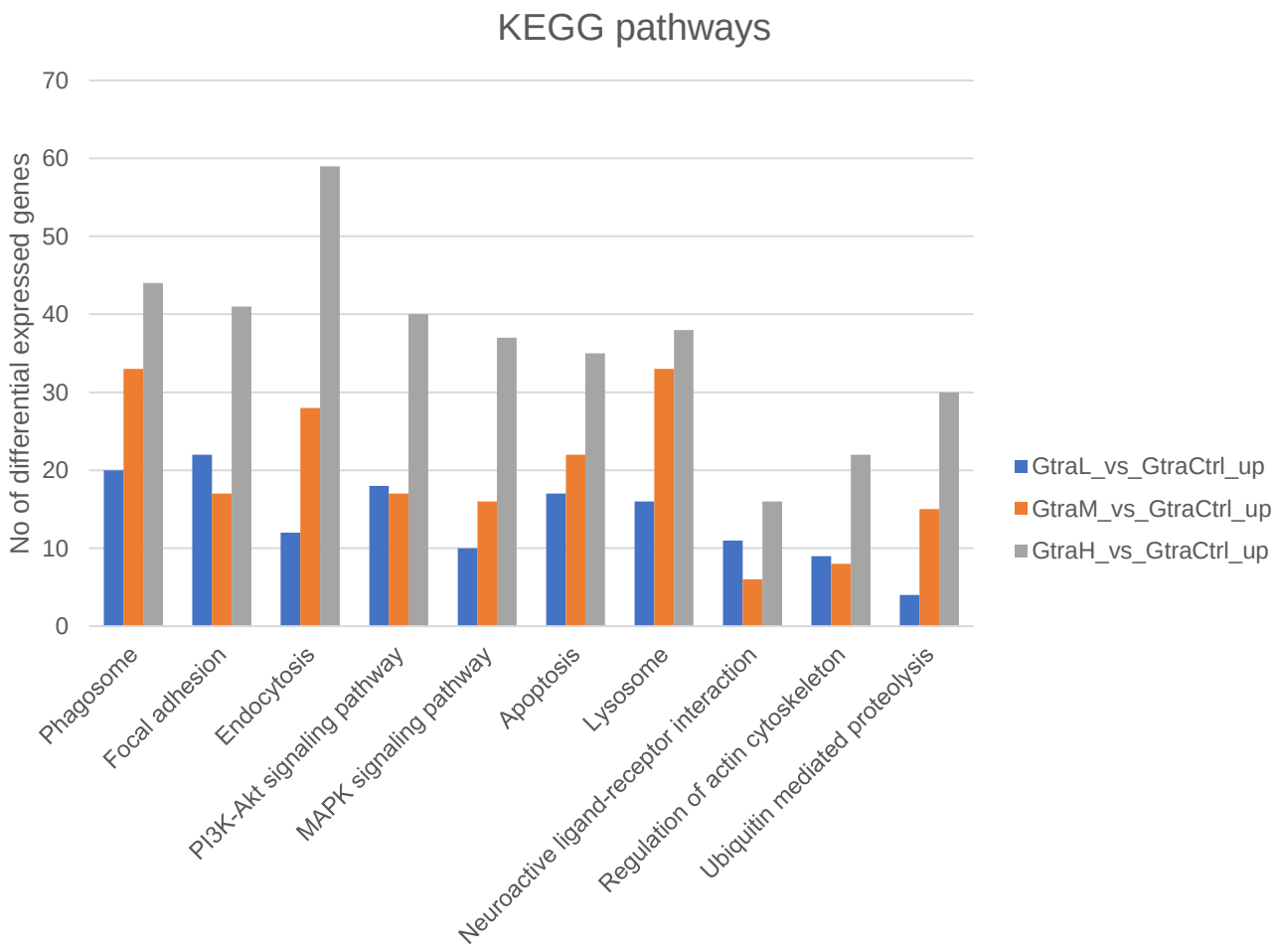
Endring i genutrykk i gjeller etter tralopyril eksponering



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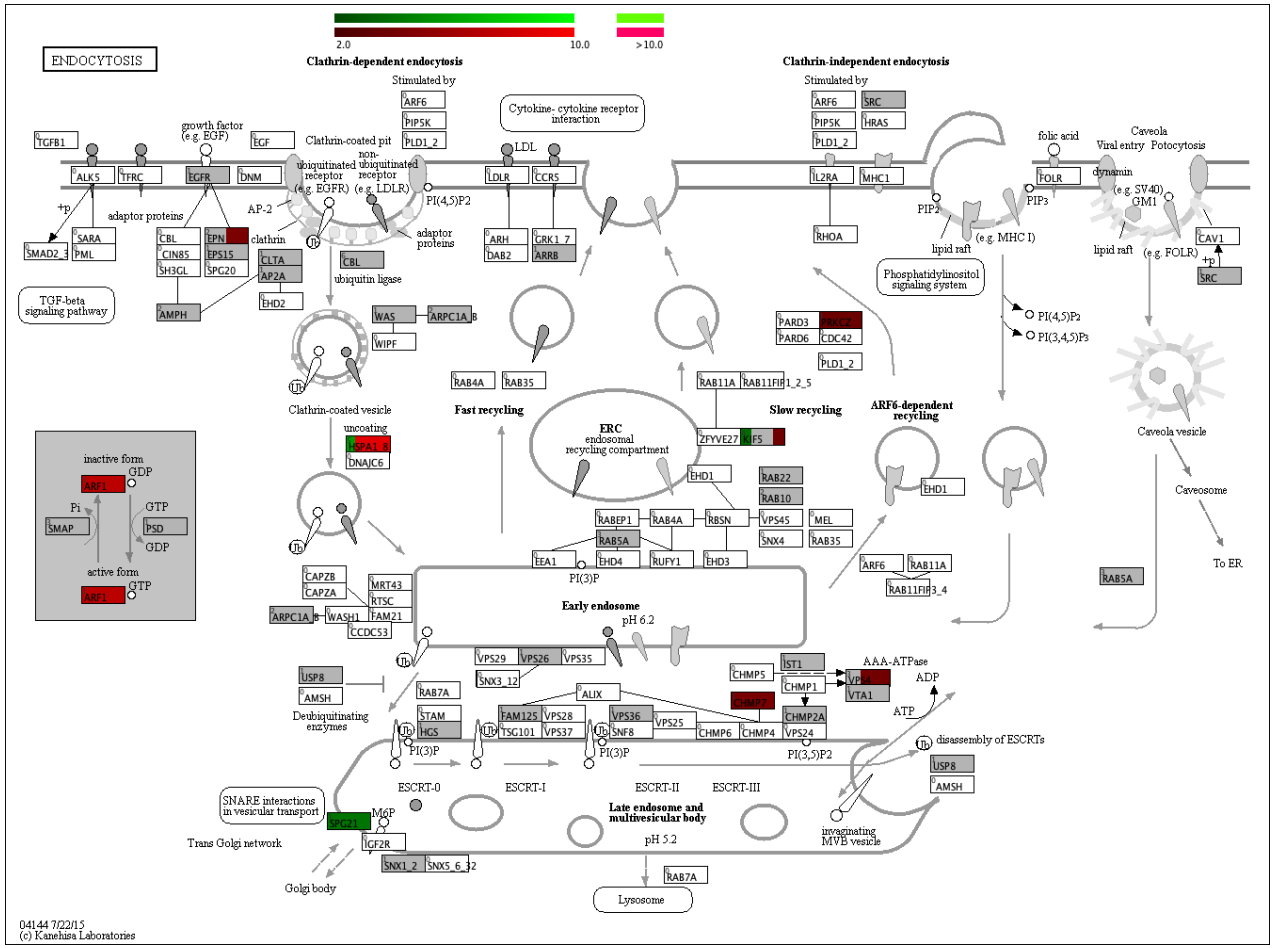
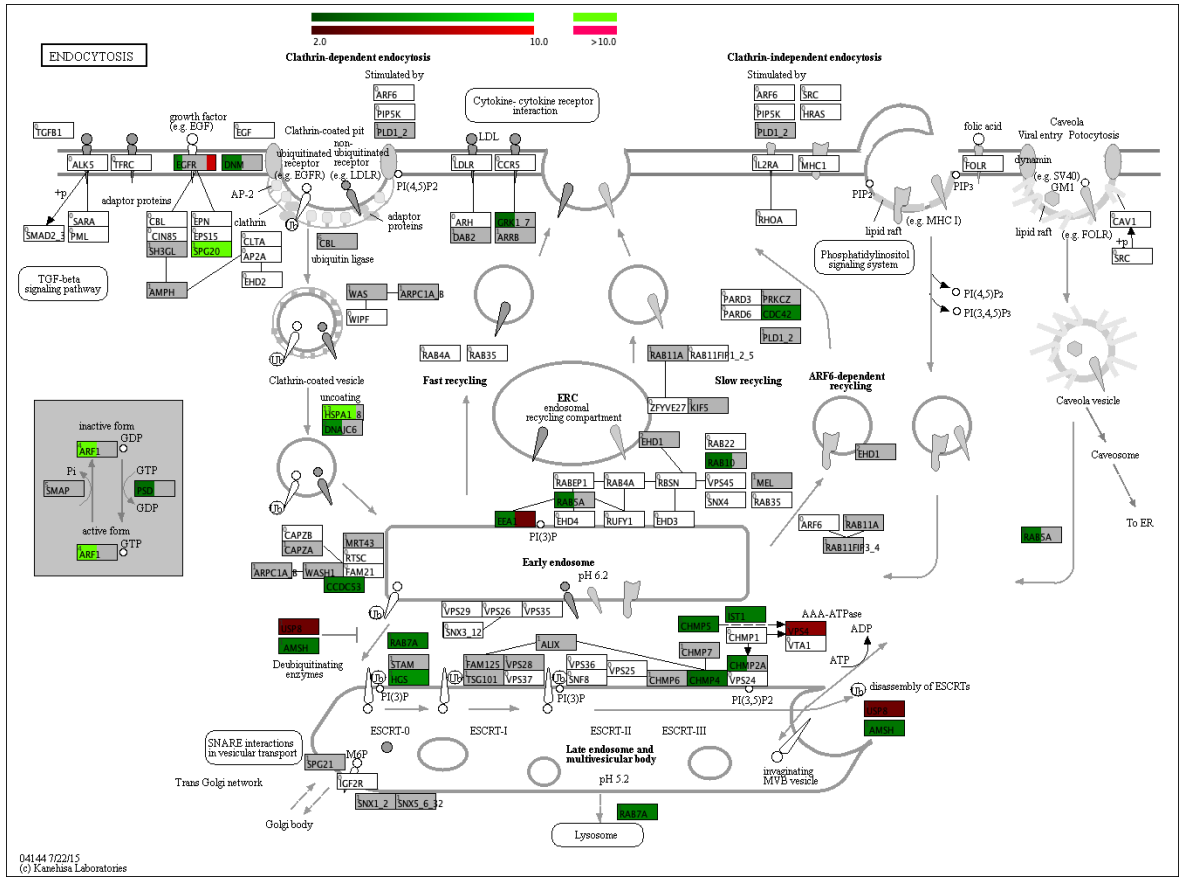
Kegg pathway: Endocytosis of gills of low vs high concentration tralopyril

Tralopyril: Low vs Control



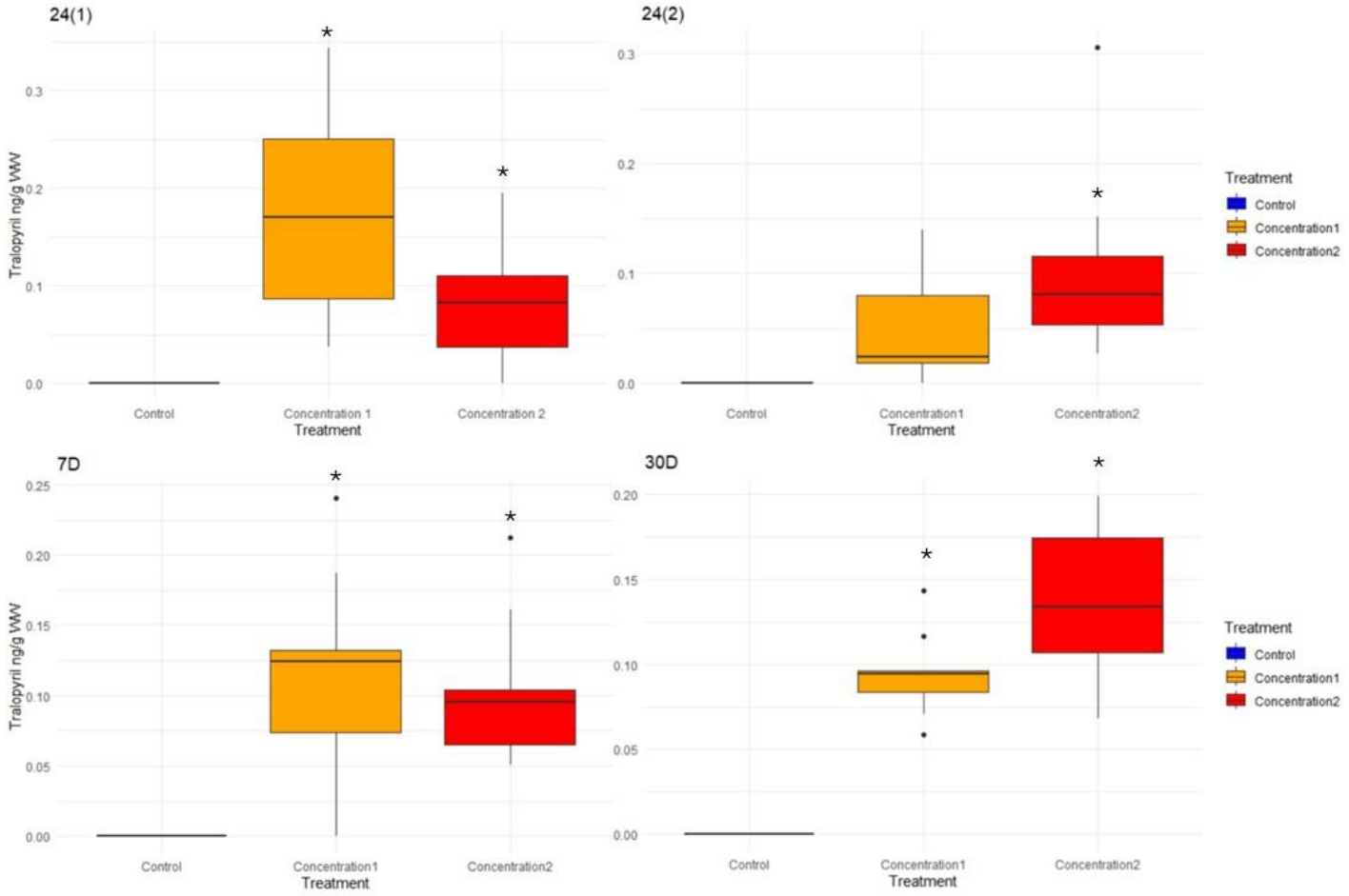
Tralopyril: High vs Control



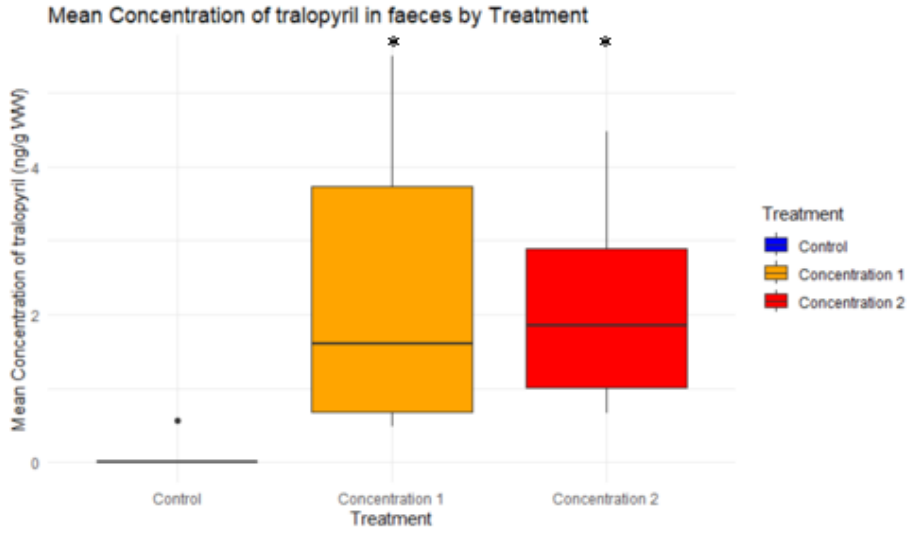
Tralopyril i laksemuskel og fekalier

- Laks (ca 200 g) i kar med notbit impregnert med 3 eller 4,5 % tralopyrili 30 dagar med gjennomstraumande vatn (3000 l per min)
- LOQ 0.061 ng/g
- Tralopyril > LOQ i laksemuskel: 90-100 %
  Tralopyril > LOQ i fekalier: 100 %

Tralopyril i laksemuskel



Tralopyril i fekalier



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Hending med laks i merd

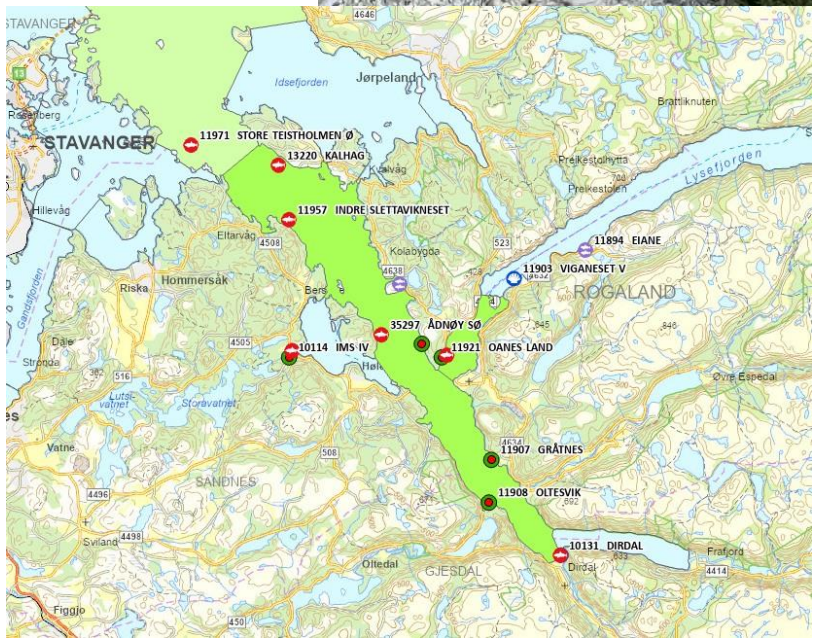
- Observert dødelighet (25 %) i eit forsøk med luseskjørt ved Matre 30. Mai 2024
- Nye nøter impregnert med Econea (tralopyril)
- LC50(96 t) for postsmolt i Atlantisk laks på 2.37 µg/l (Janssen PMP).
- Hendinga reiser bekymring ved bruk av tralopyril ved bruk av luseskjørt

Date	Sample and depth (m)	Comments	Consentration of tralopyril (µg/l)
03.06.2024	Reference, 1 m	100 m distance from the net pens	0
03.06.2024	Net pen no 3, 1 m	Net pen without skirt and MNR	0.328
03.06.2024	Net pen no 3, 9 m	Net pen without skirt and MNR	0.356
03.06.2024	Net pen no 4, 1 m	Before MNR	2.813
03.06.2024	Net pen no 4, 1 m	2 hours after MNR	3.311
03.06.2024	Merd 4, 9 m	2 hours after MNR	0.423

Unpublished results

Hending med døde krill og svarthå

- Frafjord 17. mars 2024
- Spyling Ådnøy 5. og 6. mars
- Observasjon av døde krill (1 m belte ca 100 m) og svarthå (ca 200 svarthå)
- Analysar av tralopyril:
  - Krill samleprøve: 5,7 ng/g
  - Svarthå muskel (N=5): 0
  - Svarthå mageinnhald (N=5): 22±23 ng/g vv
  - Svarthå lever 1 av 5 > LOQ (0,09 ng/g vv)



Unpublished results

Impacts of new aquaculture antifouling agents tralopyril and zinc pyrithione on the deep-water coral *Lophelia pertusa* (Linnaeus, 1758)

Gry Hunvik

Master of science in Biology – Aquaculture biology

Department of Biological Sciences, University of Bergen

Main supervisors: Tina Kutti, Ketil Hylland

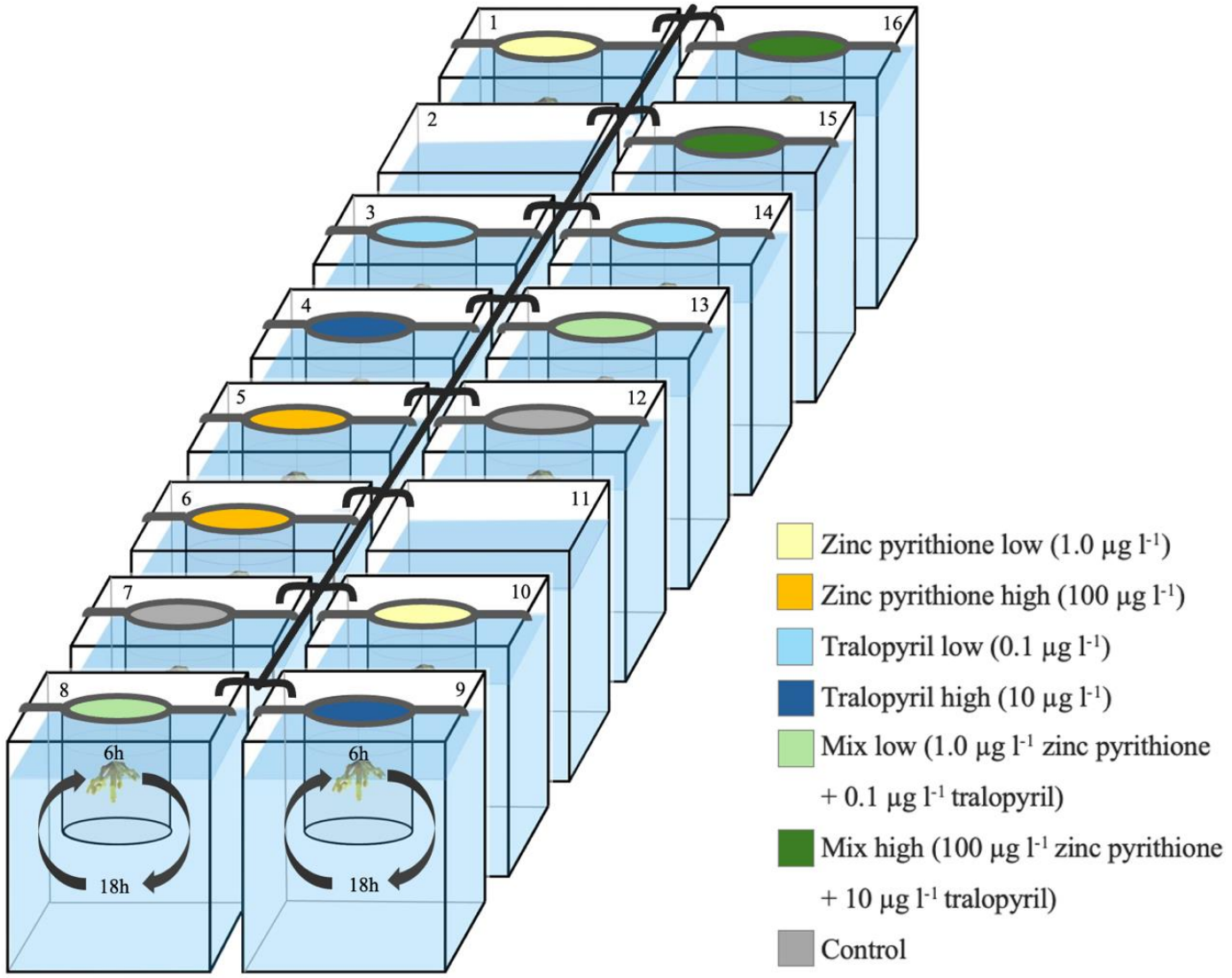
Objectives

- Assessing the behavioural response of *Lophelia pertusa* to individual and combined exposures of tralopyril and zinc pyrithione (ZnPT) at low and high concentrations, with focus on tentacle retraction and mucus production as early stress indicators.
- Evaluating the physiological impacts of exposure to tralopyril and ZnPT individually and combined at low and high concentrations on *L. pertusa* by measuring calcification-, excretion- and respiration rates.
- Determining the potential of bioaccumulation of tralopyril and ZnPT in corals tissues.
- Provide insight into the potential ecological risks associated with antifouling agents in marine environments where *L. pertusa* are present.

Master thesis Gry Hunvik, 2025

Exposure set-up

- Pilot study
- 6h exposure in static water
- Observation points prior to exposure, after 1h and 5h of daily exposure:
  - Tentacle retraction levels (1-4)
  - Mucus production
  - Drooping tentacles
  - Skeletal dissolution
- ~1 min ‘cleaning’ in clean seawater
- 18h recovery time in flow-though tanks
- 2 exposure rounds → 32 individual corals
- Water samples taken from exposure beakers to document the persistence of tralopyril and ZnPT.



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Conclusion

Behavioural responses	Physiological responses
No early signs of stress were detected by monitoring mucus production or tentacle retraction.	Ammonia excretion rates and calcification rates were not adjusted as a response to exposure.
ZnPT exposure seemed to trigger polyp-bail out.	Lower respiration rates in corals exposed to high concentrations of tralopyril and ZnPT was observed.
Drooping tentacles was observed in all treatment groups.	Tralopyril was found to accumulate in *L. pertusa*. ZnPT accumulation was not analysed.

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Konklusjon

- Det raske skiftet og den auka bruken av tralopyril ofte brukt saman med sink pyrithion eller kopar pyrithion er ikkje tilstrekkeleg utgreidd i forhold til påverknad på miljøet
- Spyling aller børsting av impregnert merd gir auka utslepp
- Vi finn at tralopyril blir spreidd og kan målast i marine organismar
- Vi bør jobbe for å få til alternative og giftfrie løysingar
- Td. kontinuerleg børsting på notmateriale som ikkje er impregnert med giftstoff og som reduserer utslepp av mikroplast så mykje som råd
- Vi treng meir kunnskap om:
  - Spredning til vannsøyla og betre input til modellering
  - nedbrytingsprodukt
  - tålegrenser for relevante artar

Takk for oppmerksomheten!

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