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Metal Mitigation:
Nature based solutions for freshwater management

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Outline

1. Background; copper and zinc
2. Aim
3. Methods
4. Results
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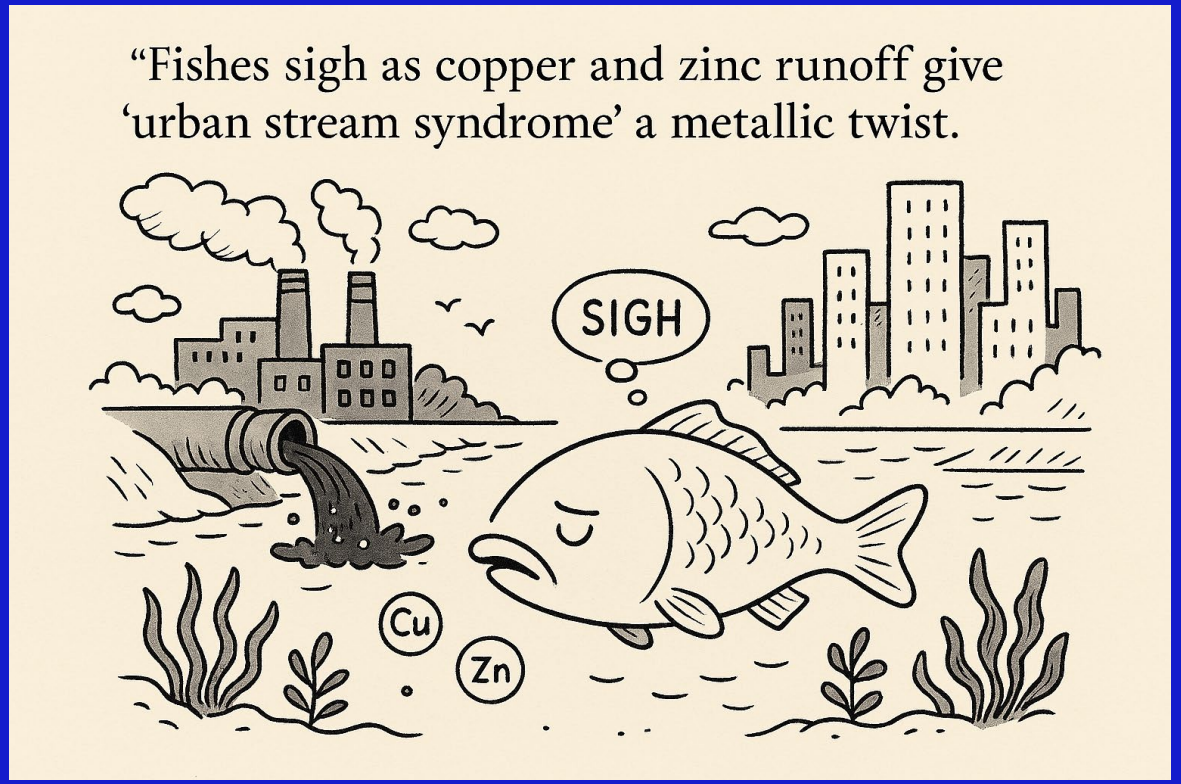
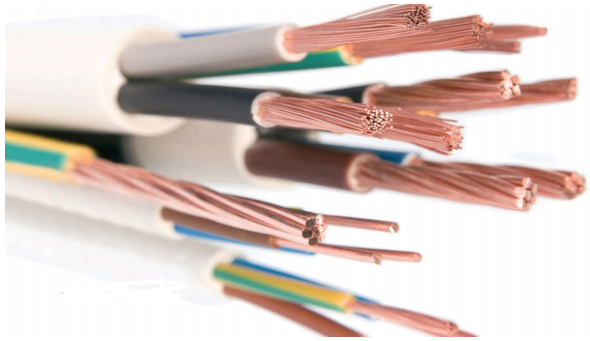


- Copper and zinc are essential metals for life - naturally present
- High concentrations lead to adverse effects
- Toxicity affected by:
  - Dissolved Organic Carbon (DOC)
  - Hardness
  - pH
- Concentrations during storm events often exceed ANZG values contributing to poor ecological health in urban areas

	Copper	Zinc
Main source	Wastewater discharge, brake linings, piping, roofing	Tyres and galvanised roofing
NZ pristine lake	0.04-0.5 µg/L	0.4-1.6 µg/L
Urban stream	<1-25 µg/L, higher in storm events	5-550 µg/L



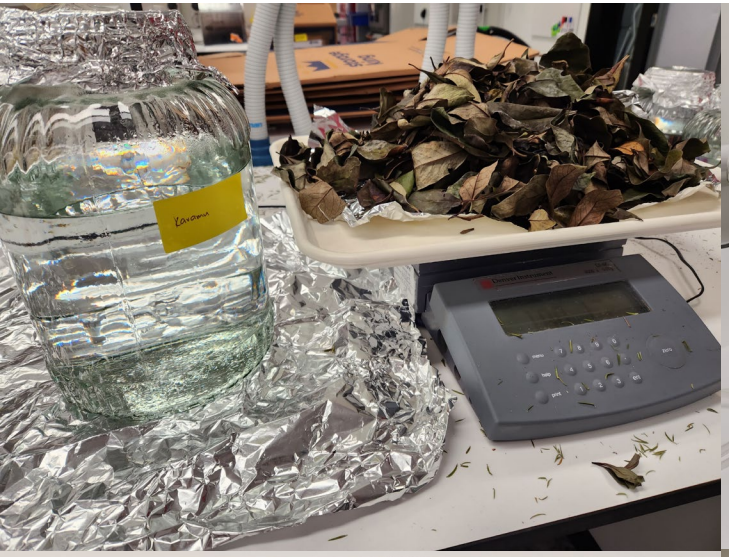



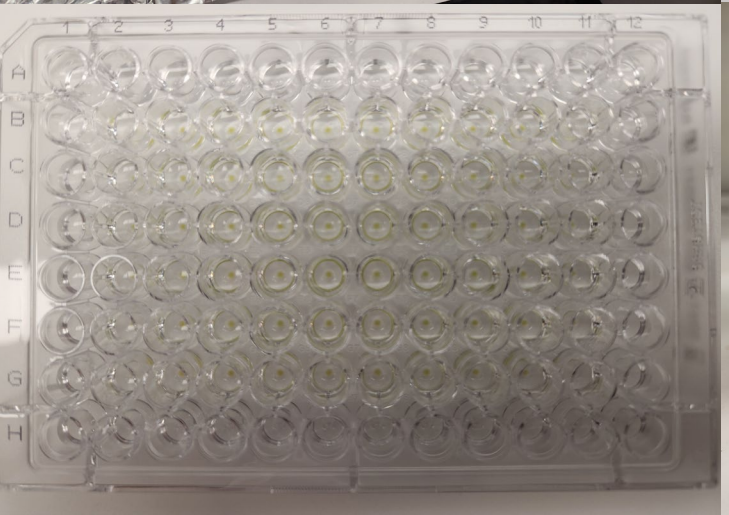

Aim

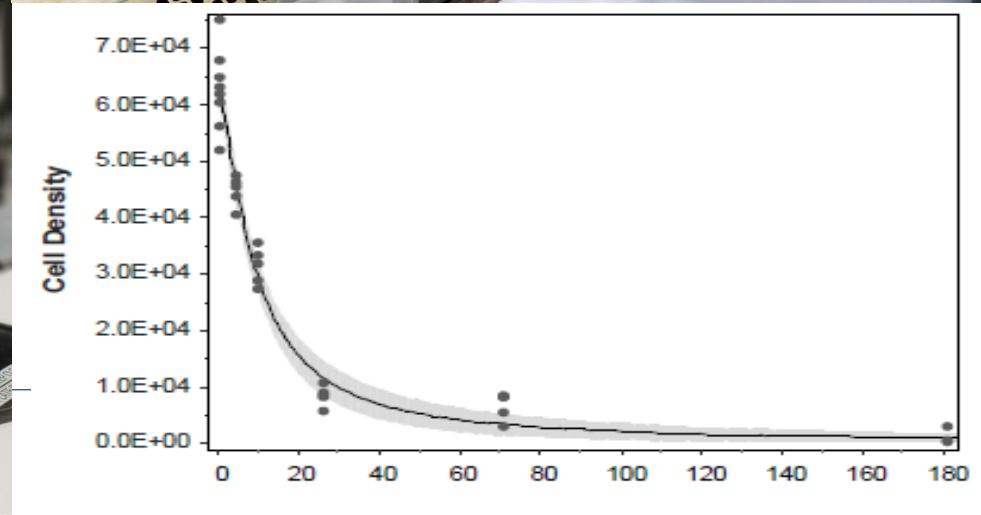
‘How do native super-producers of organic matter mitigate aquatic metal mixture toxicity?’

- Determine how DOM derived from NZ native plants can be optimally applied in nature-based solutions to reduce metal toxicity (Cu and Zn)
- Assist management of peak metal concentrations in NZ urban surface waters with DOM ‘super-producers’ in the right place

Toxicity testing with microalgae to determine metal mitigation potential of 5 NZ native plants







Methods – Plant leachates

5 Plants selected

- Mānuka, *Leptospermum scoparium*
- Karamū, *Coprosma robusta*
- Koromiko, *Hebe stricta*
- Kowhai, *Sophora molloyi*
- Pōhutukawa, *Metrosideros excelsa*

Leachates prepared

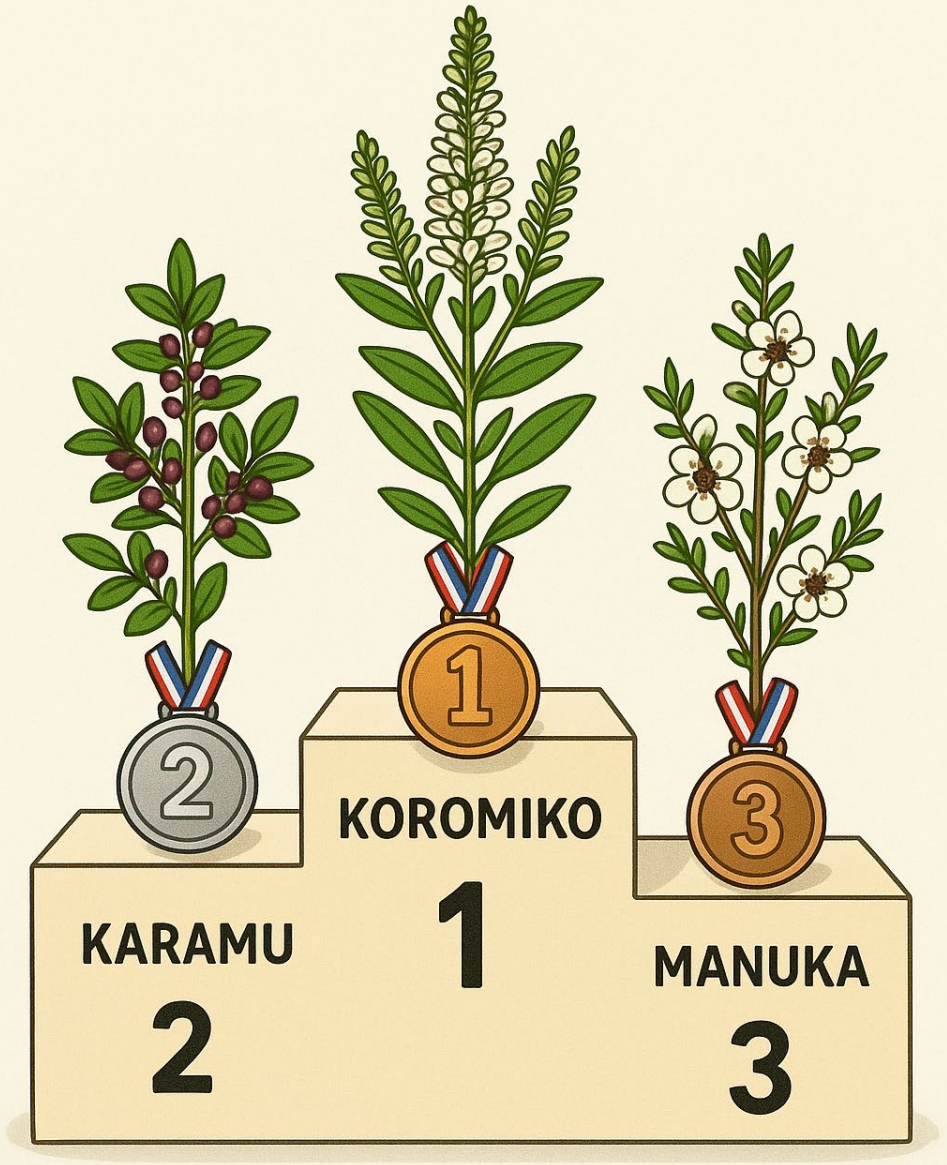
- 100 g dried leaves into 4 L MilliQ
- Brew for 1 week with aeration
- Sieve 2mm, centrifuged 15 min @3,000 RPM, and filtered GF/C
- Analysed for DOC concentration/yield
- Characterised (see Holland et al. presentation)

Methods – Toxicity testing

- Standard toxicity tests 72-hour EC_{50}
- Metals: Cu, Zn, and Cu: Zn mixture (1: 6)
- Test species: green alga *Raphidocelis subcapitata*
- DOC concentrations: 0 (-ve control), 5, 10 mg/L
- DOC sources: 5 plant leachates, reference SRFA standard
- Hardness: 18-26 mg/L $CaCO_3$
- Initial - final pH: 7.5±0.2 - 7.5±0.7
- *Daphnia thomsoni* also tested see Shepherd et al. poster

Results

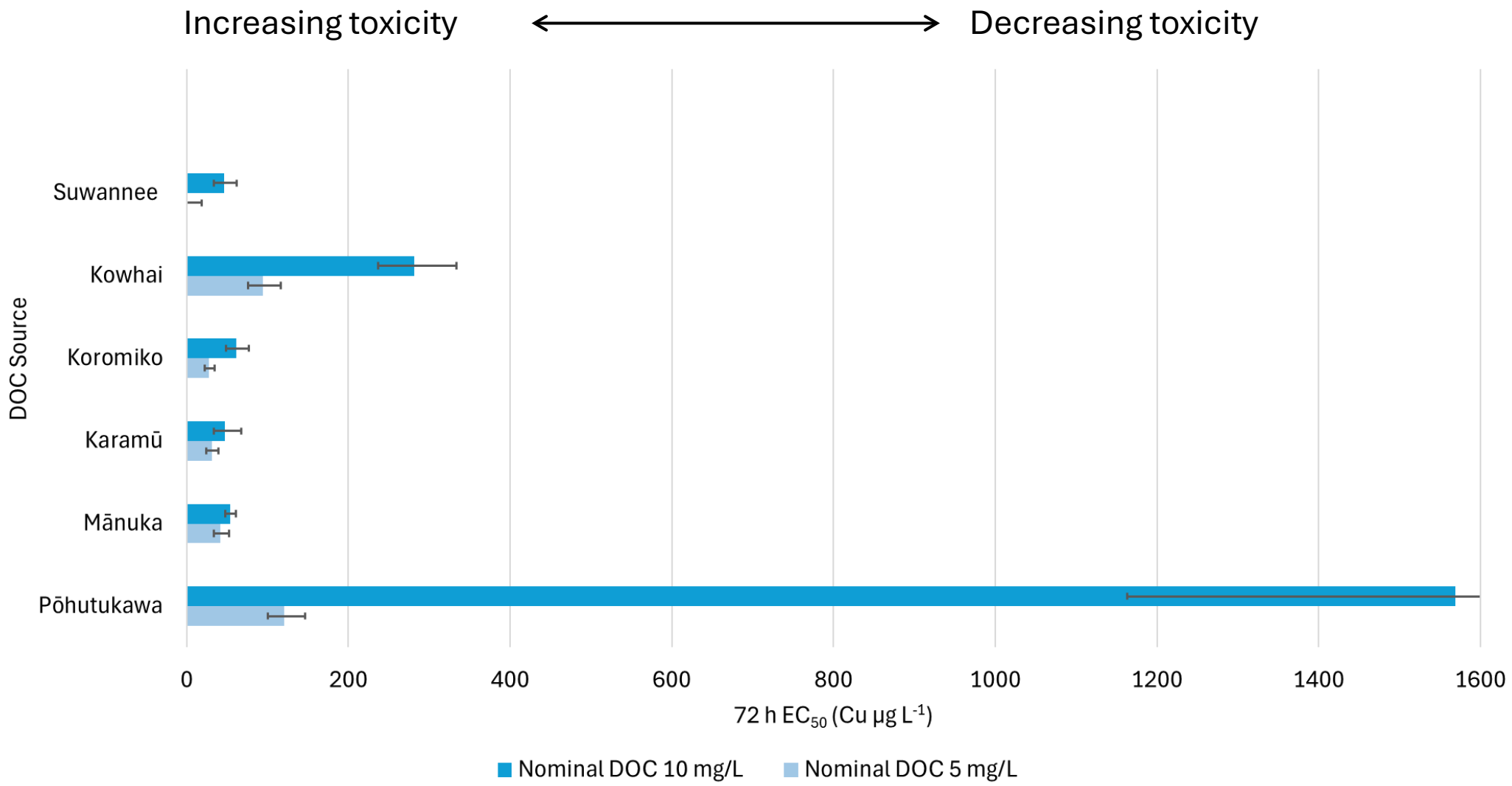
Plant	DOC mg/L	DOC yield mg/g	Rank
Mānuka	1120	45	3
Karamū	1300	52	2
Koromiko	1650	66	1
Kowhai	720	29	4
Pōhutukawa	630	25	5



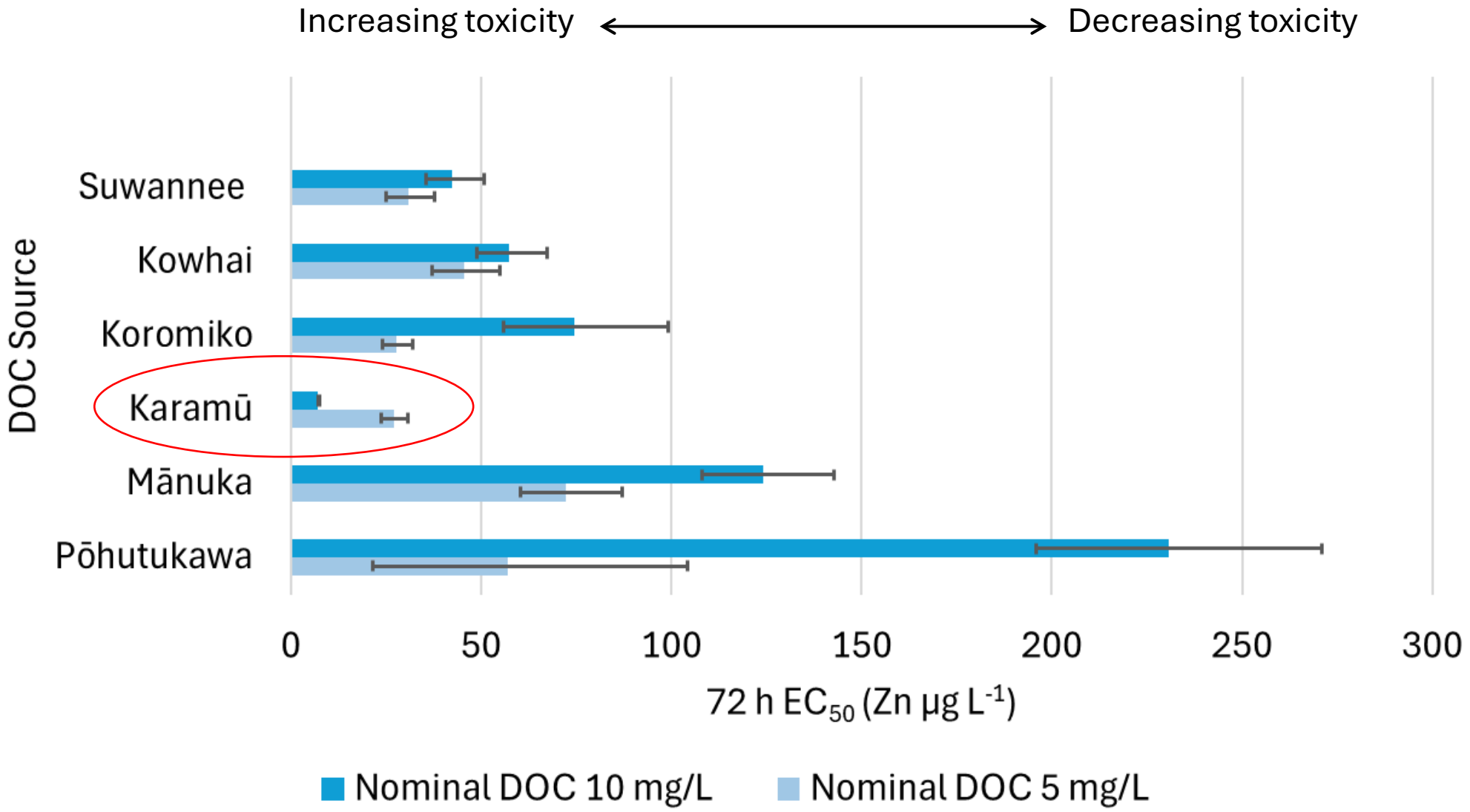
Treatments and Control Growth

Treatment	Nominal DOC mg/L	Actual DOC mg/L	Mean control growth 000's cells	Growth compared to negative DOC
Negative DOC	0	0.5	639 (n=3)	-
Suwannee River FA Standard	5 10	5.8 11.0	454 (n=3) 763 (n=2)	0.71 1.19
Mānuka	5 10	6.2 11.0	82 (n=3) 65 (n=3)	0.13 0.10
Karamū	5 10	5.3 11.3	123 (n=3) 109 (n=2)	0.19 0.17
Koromiko	5 10	5.5 10.8	129 (n=3) 102 (n=2)	0.20 0.16
Kowhai	5 10	4.4 11.0	104 (n=3) 101 (n=3)	0.16 0.16
Pōhutukawa	5 10	5.6 11.2	62 (n=3) 67 (n=3)	0.10 0.10

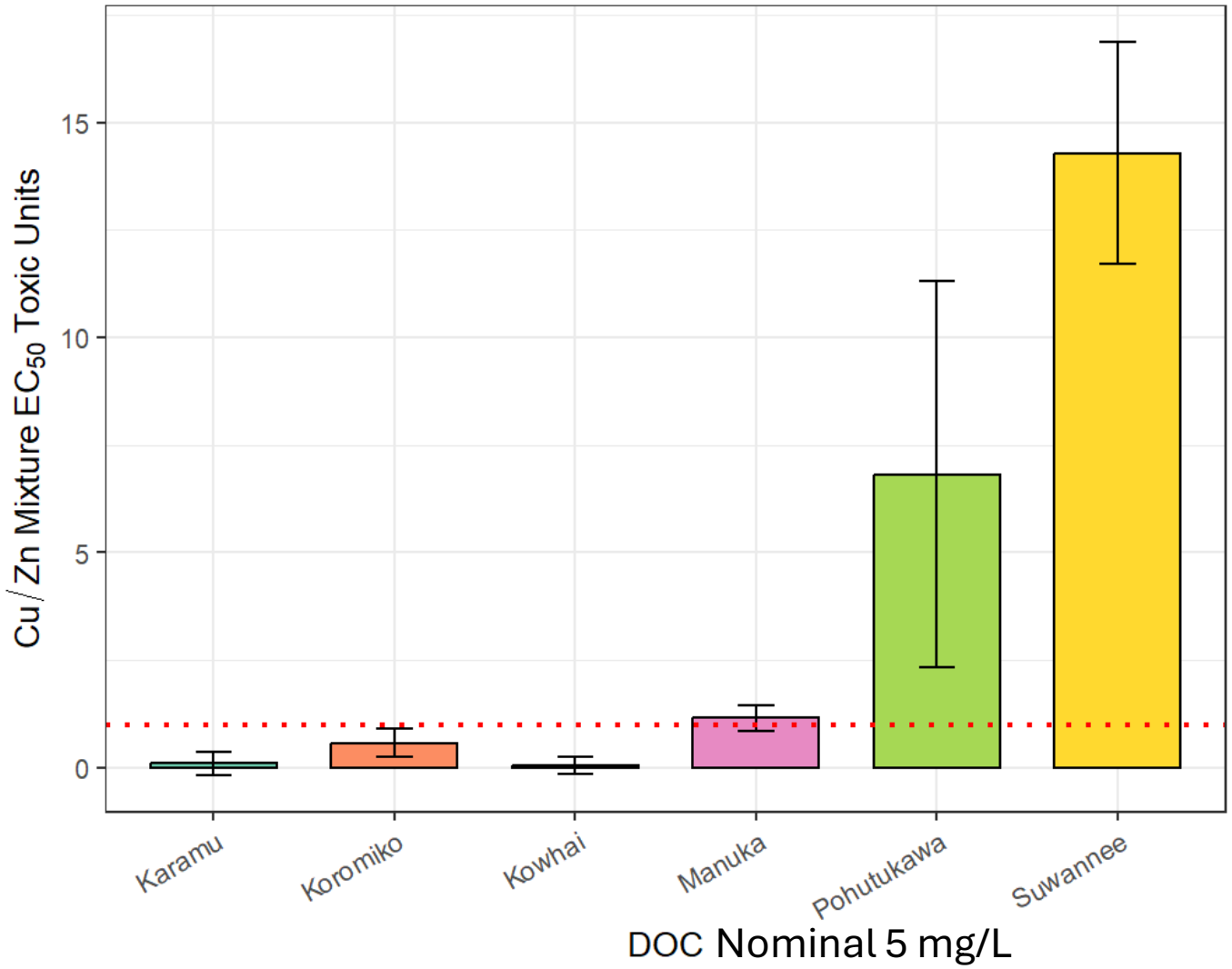
Copper


Increasing toxicity
Decreasing toxicity
DOC Source
Suwannee
Kowhai
Koromiko
Karamū
Mānuka
Pōhutukawa
0
200
400
600
800
1000
1200
1400
1600
72 h EC50 (Cu µg L-1)
Nominal DOC 10 mg/L
Nominal DOC 5 mg/L

Zinc


Increasing toxicity
Decreasing toxicity
DOC Source
Suwannee
Kowhai
Koromiko
Karamū
Mānuka
Pōhutukawa
0
50
100
150
200
250
300
72 h EC50 (Zn µg L-1)
Nominal DOC 10 mg/L
Nominal DOC 5 mg/L

1: 6 Cu: Zn mixture



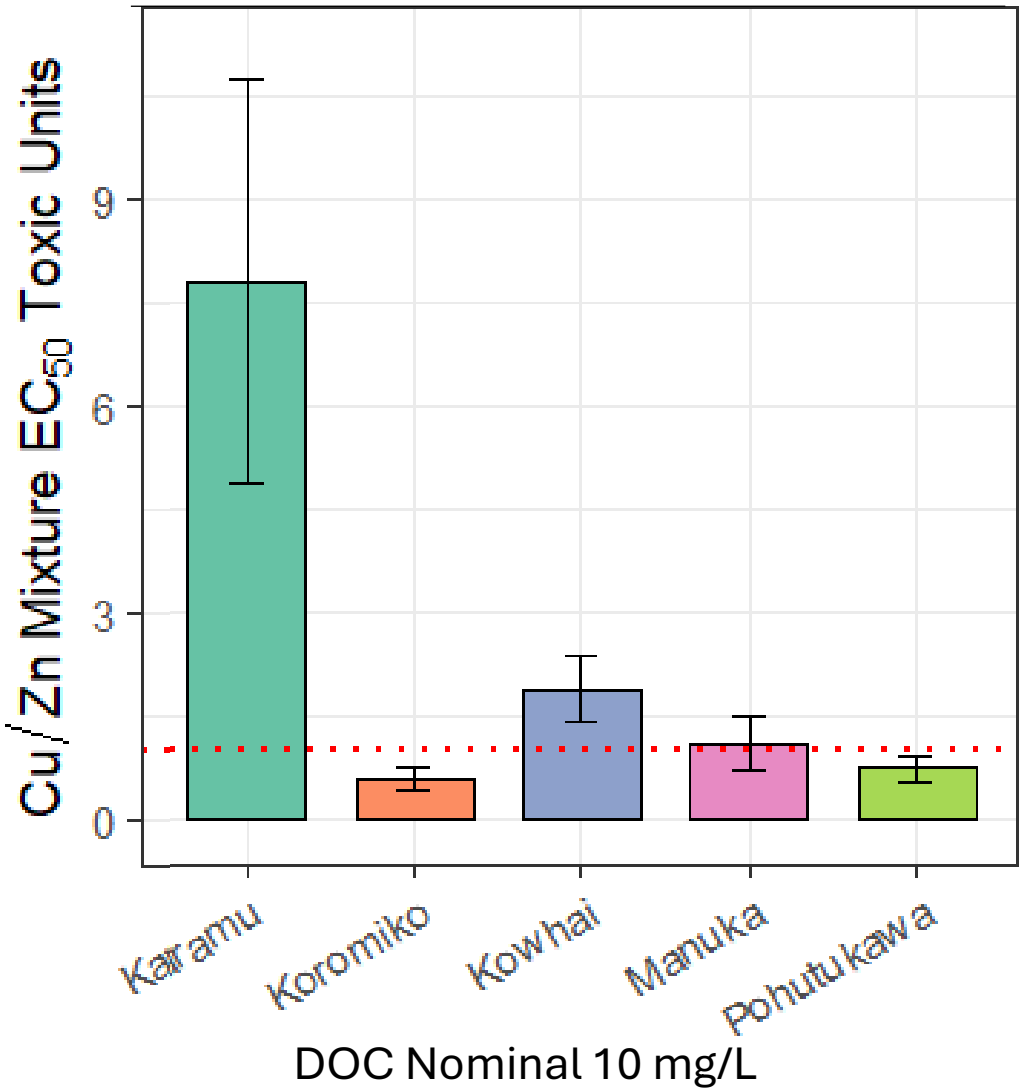
TU = 1 → **Additive** mixture toxicity matches prediction if effects were simply additive

TU < 1 → **Synergistic** mixture *more toxic* than expected

TU > 1 → **Antagonistic** mixture *less toxic* than expected

DOM Source	Estimate	Interaction
Karamū	0.091	Synergistic
Koromiko	0.566	Synergistic
Kōwhai	0.053	Synergistic
Mānuka	1.14	Additive
Pōhutukawa	6.81	Antagonistic
Suwannee	14.3	Antagonistic

1: 6 Cu: Zn mixture



DOM Source	Estimate	Interaction
Karamū	7.82	Antagonistic
Koromiko	0.581	Synergistic
Kōwhai	1.90	Antagonistic
Mānuka	1.11	Additive
Pōhutukawa	0.751	Synergistic
Suwannee	No data	No data

Summary

DOM Source	DOC yield	Control algal growth	Reduce Cu toxicity	Reduce Zn toxicity	Mixture Interaction at 5 mg/L	Mixture Interaction at 10 mg/L	DOM 'super producer' rank
Mānuka	✓	✗	✗	✓	✓	✓	2
Karamū	✓	✗	✗	✗	✗	✓✓	3
Koromiko	✓	✗	✗	✗	✗	✗	5
Kowhai	✗	✗	✓	✗	✗	✓	4
Pōhutukawa	✗	✗	✓✓	✓	✓✓	✗	1

Conclusions

- Complex
- DOM source strongly influences quantity, quality, and effects
- Effects are species-specific i.e. toxic to microalgae but not other species
- DOM reduces metal bioavailability
- Effects depend on DOM composition
- Mixture interactions vary with DOM source and concentration
- So complex….

Next steps

Model Development

→ Integrate DOM character metrics into bioavailability model

→ Account for metal-metal interactions and DOM variability

Model Validation

→ Use DOM from additional native plants

→ Conduct chronic toxicity tests on taonga species

Implementation Guidance

→ Translate model outputs into practical design recommendations for nature-based solutions e.g. riparian and roadside planting, green roofs, infiltration basins/strips, tree pits and raingardens.

→ Co-develop guidance with Engineering Advisory Group and iwi partners

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