



Accounting for bioavailability in the aquatic risk assessment of metals

Graham Merrington



- Introduction
 - Challenges assessing metal environmental risks
 - What is bioavailability and why account for it in risk assessment?
 - Biotic ligand models.....
 - User-friendly tools
 - What do you need?
 - Some examples.....
-
- **Queries and questions: common problems and issues...**



Challenges assessing metal environmental risks

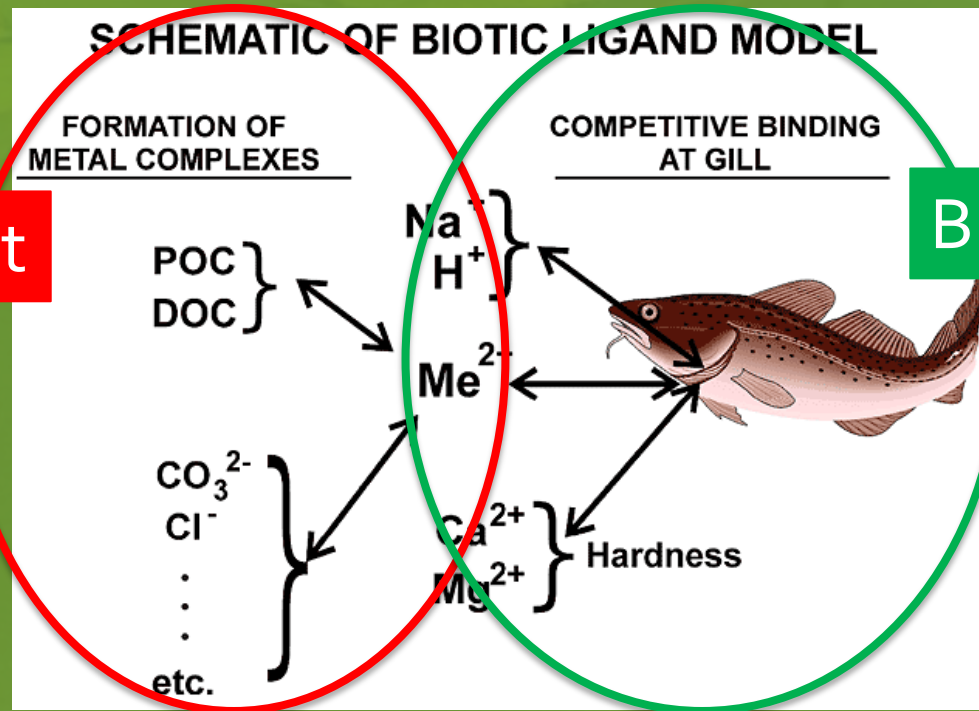
- Metals are ubiquitous
- Can change chemical form in response to water chemistry
- The form of the metal influences the ecotoxicity to aquatic organisms
- Some metals are essential for the functioning of biological systems
- One limit value doesn't fit all situations



What is bioavailability?



-combination of the physico-chemical factors in the water column governing metal behaviour and the biological receptor - its specific pathophysiological characteristics (?)



Chemistry bit

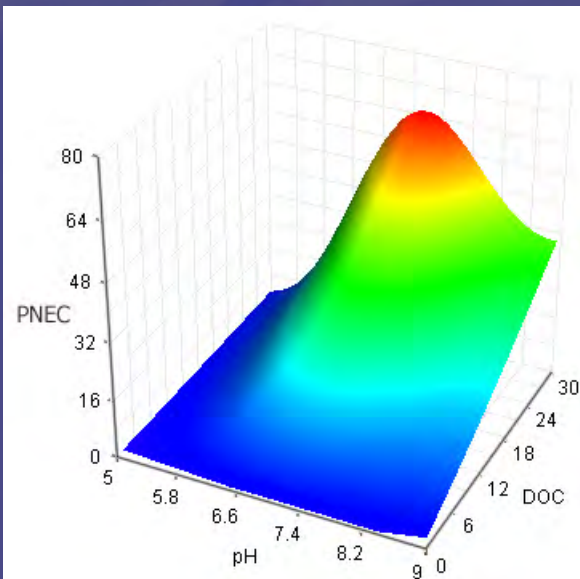
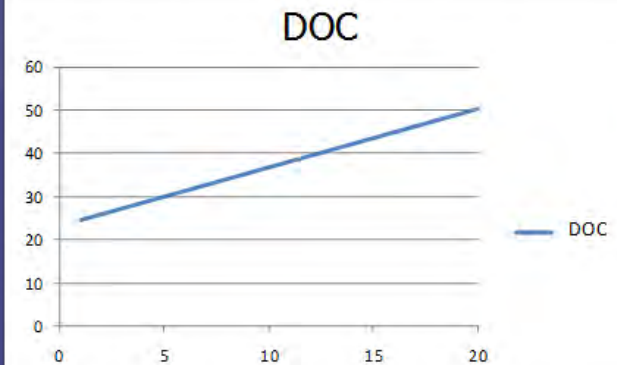
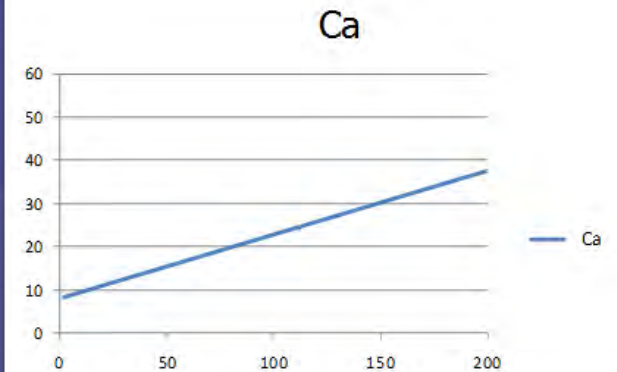
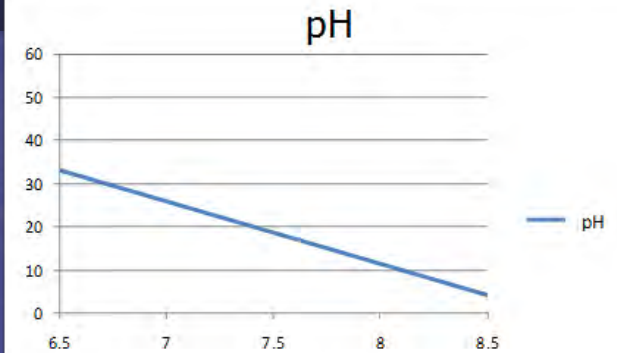
Biological bit

Why account for bioavailability in environmental risk assessment?



Predicted 'stylised' changes in the ecotoxicity of nickel, expressed as an HC₅, for pH, Ca (mg l⁻¹) and DOC (mg l⁻¹). Individual parameters were varied while the other two parameters remained constant (pH 7, Ca 120 mg l⁻¹, DOC 2 mg l⁻¹).

Hazardous Concentrations $\mu\text{g Ni l}^{-1}$



Predicted variation in copper toxicity (HC₅) $\mu\text{g Cu l}^{-1}$ as a function of pH and DOC in soft water.

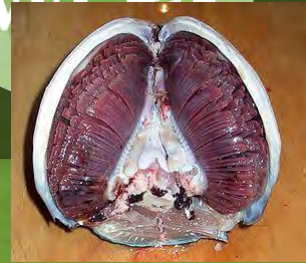
Why account for bioavailability in environmental risk assessment?



System	Canadian Shield Lake	Lake Ontario	Desjardin Canal
Characteristics	Hardness: 4 mg CaCO ₃	Hardness: 124 mg CaCO ₃	Hardness: 318 mg CaCO ₃
	DOC: 6 mg/L	DOC: 1.1 mg/L	DOC: 5.8 mg/L
	pH: 6.5	pH: 8.2	pH: 7.7
Hardness-based WQG (Current approach)	25 µg Ni/L	112 µg Ni/L	150 µg Ni/L
Hardness-based Rank Order	1	2	3
Bioavailability-based EQS (direct application of EU approach to Canadian waters)	16.3 µg Ni/L	4 µg Ni/L	11.3 µg Ni/L
Bioavailability-based Rank Order	3	1	2

- Hardness based approaches may not be reaching the appropriate conclusions

Biotic ligand models



- Gill Surface Interaction Model – Pagenkopf 1983
 - » Describes interaction of metals with fish gills (the sites of toxic action) and competition from other ions
- Humic Ion Binding Model V – Tipping 1992
 - » Describes binding of metals with natural organic matter and competition from other ions
- Biotic Ligand Model – Di Toro 2001
 - » Combines both of these models to describe toxicity as a function of water chemistry
- **Competition and complexation effects are critical in being able to describe the effect of a metal as a function of water quality.**

Biotic ligand models (continued)



- These BLM describes competitive interactions for binding by DOC and the biotic ligand.
- Can quantitatively relate binding to chronic toxicity (fractional occupancy at EC10)
- But.....these models are quite complex, require in-depth understanding to use
- Data input requirement (> 10 physico-chemical water parameters)
- They are very robust tools to make predictions, but complex andbeautiful



User-friendly tools



- Need a way to mimic the BLM outputs
- Using a reduced number of inputs
- In a package the runs on routine office software
- With loss of accuracy likely to lead to a precautionary assessment
- The output needs to be....understandable and useable!
- Back in 2007, the Environment Agency of England and Wales commissioned wca to develop user-friendly tools for copper and zinc....

What do you need?



- Two tools are available M-BAT (the UK Environment Agency's) and Bio-met.
- Both are based on chronic ecotoxicity data and the outputs of the different BLMs for Cu, Ni, Zn (and Mn in the case of M-BAT)
- Key input parameters are for matched (taken from the same sample at the same time) dissolved **organic carbon (DOC), pH and calcium/hardness**
- All three are needed

Some examples using bio-met



Copy of Bio-met_bioavailability_tool_v3.03_04-01-2016 - Excel

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"User-friendly" Biotic Ligand Model Version 3.0 - December 2015

Please register at www.bio-met.net to ensure you're using the most recent version of the tool

bio met

Start

Help

Glossary

Generic EQS Bioavailable

Login

About this tool

This software tool estimates the potential risk to the aquatic environment posed by **copper, nickel and zinc** after considering **bioavailability**. The tool will calculate Local EQS values and Bioavailable Metal Concentrations based on information on local water physicochemistry. This tool has been developed as part of the *bio-met* project and has been designed to operate in Microsoft Excel 2007 and 2010. A **web-based** version of this tool, together with a fuller description of the science underpinning the tool, a description of the tool's operation and validation, case studies and comprehensive guidance on its use are available at www.bio-met.net.

This software tool is based on calculations from Biotic Ligand Models. It is currently only applicable for use in European freshwaters and is intended to be used as part of tiered risk assessment or as an early tier in compliance assessment.

How to use this tool

Please read these instructions carefully before you start. Further guidance on using this tool can be obtained by visiting www.bio-met.net

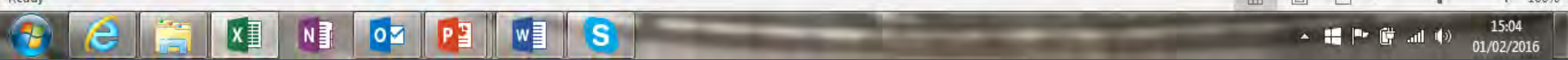
Hints and Tips

You can enter data for up to 2000 samples. Make sure that each

Introduction Sheet1

Ready

15:02



Some examples using bio-met



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D11

Calculate

Clear Data

Back

Samples Processed
0

INPUT (MONITORING) DATA											RESULTS (Copper)		
ID	Optional Sample Name	Optional Sample Number	Optional Date	Optional Measured Copper Conc (dissolved) [µg/L]	Optional Measured Nickel Conc (dissolved) [µg/L]	Optional Measured Zinc Conc (dissolved) [µg/L]	Required pH	Required DOC [mg/L]	Required Ca [mg/L]	Optional Zinc ABC Conc (dissolved) [µg/L]	Local EQS (dissolved) [µg/L]	BioF	Bioavailable Copper Conc [µg/L]
	ohb. Silbertal			0.7	1.1	1.4	7.8	0.3	8.2				
	Nickelsdorf			1	1.3	4	8	1.7	65.6				
	Riezern			3	2.4	3	8.5	0.8	42.2				
	Lule älv Luleå			0.52	0.35	2.11	6.81	1.1	8.157172				
	Kvistforsen			0.55	0.17	3.32	7.05	3.9	11.81038				
	Gide älv Gideåbacka			0.41	0.68	2.85	6.61	9.5	5.955236				
	Gavleån Gävle			1.7	1.02	4.11	6.85	13.3	18.51628				
	Maltby, u/s STW (opposite Muglet Lane)			7.02	2.1	25.5	7.89	3.15	68.8				
	Maltby d/s STW (Gypsy Lane Bridge)			5.08	1.5	19.9	7.67	5.21	75.1				
	North West Region, England			0.8	0.4	2	6.681429	0.51	3.026875				
	North West Region, England			0.6	0.3	1.2	6.4625	0.45	2.436111				
	North West Region, England			0.7	0.5	3.2	6.2825	0.44	2.033529				
	North West Region, England			0.2	0.8	2.1	7.59375	0.33	10.32294				
	River Hamble @ Durley			3.22	1.22	24.7	7.965946	3.165	86.419				
	EAGLEY BK D/S BELMONT STW			3.74	4.45	16.8	7.64	7.82	7.7				
	RIVER LEE, Thames			4.8	0.85	49	7.13	0.39	86.6				

Sheet1 Results

Select destination and press ENTER or choose Paste

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Some examples using bio-met



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MONITORING DATA

Optional Measured Copper Conc (dissolved) [µg/L]	Optional Measured Nickel Conc (dissolved) [µg/L]	Optional Measured Zinc Conc (dissolved) [µg/L]	Required pH	Required DOC [mg/L]	Required Ca [mg/L]	Optional Zinc ABC Conc (dissolved) [µg/L]	Local EQS (dissolved) [µg/L]	BioF	Bioavailable Copper Conc [µg/L]	RCR	Notes	Local EQS (dissolved) [µg/L]	BioF	Bioavailable Nickel Conc [µg/L]	RCR	Notes	Local EQS (dissolved) [µg/L]	BioF	Bioavailable Zinc Conc [µg/L]	RCR	Notes
0.7	1.1	1.4	7.8	0.3	8.2	1	1.07	0.94	0.65	0.65		4.00	1.00	1.10	0.28	Y	11.90	0.92	1.28	0.12	
1	1.3	4	8	1.7	65.6	1	3.70	0.27	0.27	0.27		4.00	1.00	1.30	0.33	Y	20.06	0.54	2.17	0.20	
3	2.4	3	8.5	0.8	42.2	1	1.13	0.89	2.66	2.66		4.00	1.00	2.40	0.60	Y	12.87	0.85	2.54	0.23	
0.52	0.35	2.11	6.81	1.1	8.15717	1	3.82	0.26	0.14	0.14		8.90	0.45	0.16	0.04		11.90	0.92	1.93	0.18	
0.55	0.17	3.32	7.05	3.9	11.8104	1	20.87	0.05	0.03	0.03		12.23	0.33	0.06	0.01		23.89	0.46	1.51	0.14	
0.41	0.68	2.85	6.61	9.5	5.95524	1	28.22	0.04	0.01	0.01		19.22	0.21	0.14	0.04		33.45	0.33	0.93	0.09	
1.7	1.02	4.11	6.85	13.3	18.5163	1	55.23	0.02	0.03	0.03		23.57	0.17	0.17	0.04		44.10	0.25	1.02	0.09	
7.02	2.1	25.5	7.89	3.15	68.8	1	7.90	0.13	0.89	0.89		5.82	0.69	1.44	0.36		28.45	0.38	9.77	0.90	
5.08	1.5	19.9	7.67	5.21	75.1	1	16.94	0.06	0.30	0.30		8.69	0.46	0.69	0.17		37.48	0.29	5.79	0.53	
0.8	0.4	2	6.68143	0.51	3.02688	1	1.59	0.63	0.50	0.50	Y	9.06	0.44	0.18	0.04	Y	11.90	0.92	1.83	0.17	Y
0.6	0.3	1.2	6.4625	0.45	2.43611	1	1.00	1.00	0.60	0.60	Y	9.86	0.41	0.12	0.03	Y	11.90	0.92	1.10	0.10	Y
0.7	0.5	3.2	6.2825	0.44	2.03353	1	1.00	1.00	0.70	0.70	Y	9.86	0.41	0.20	0.05	Y	11.90	0.92	2.93	0.27	Y
0.2	0.8	2.1	7.59375	0.33	10.3229	1	1.17	0.86	0.17	0.17		4.00	1.00	0.80	0.20	Y	11.90	0.92	1.92	0.18	
3.22	1.22	24.7	7.96595	3.165	86.419	1	7.90	0.13	0.41	0.41		5.82	0.69	0.84	0.21		29.27	0.37	9.20	0.84	
3.74	4.45	16.8	7.64	7.82	7.7	1	35.48	0.03	0.11	0.11		15.12	0.26	1.18	0.29		74.89	0.15	2.45	0.22	

Sheet1 Results

Ready 95%

Some examples using bio-met



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MONITORING DATA

Optional Measured Copper Conc (dissolved) [µg/L]	Optional Measured Nickel Conc (dissolved) [µg/L]	Optional Measured Zinc Conc (dissolved) [µg/L]	Required pH	Required DOC [mg/L]	Required Ca [mg/L]	Optional Zinc ABC Conc (dissolved) [µg/L]	Local EQS (dissolved) [µg/L]	BioF	Bioavailable Copper Conc [µg/L]	RCR	Notes	Local EQS (dissolved) [µg/L]	BioF	Bioavailable Nickel Conc [µg/L]	RCR	Notes	Local EQS (dissolved) [µg/L]	BioF	Bioavailable Zinc Conc [µg/L]	RCR	Notes
0.7	1.1	1.4	7.8	0.3	8.2	1	1.07	0.94	0.65	0.65		4.00	1.00	1.10	0.28	Y	11.90	0.92	1.28	0.12	
1	1.3	4	8	1.7	65.6	1	3.70	0.27	0.27	0.27		4.00	1.00	1.30	0.33	Y	20.06	0.54	2.17	0.20	
3	2.4	3	8.5	0.8	42.2	1	1.13	0.89	2.66	2.66		4.00	1.00	2.40	0.60	Y	12.87	0.85	2.54	0.23	
0.52	0.35	2.11	6.81	1.1	8.15717	1	3.82	0.26	0.14	0.14		8.90	0.45	0.16	0.04		11.90	0.92	1.93	0.18	
0.55	0.17	3.32	7.05	3.9	11.8104	1	20.87	0.05	0.03	0.03		12.23	0.22	0.06	0.01		23.89	0.46	1.51	0.14	
0.41	0.68	2.85	6.61	9.5	5.95524	1	28.22	0.04	0.01	0.01		19.22	0.21	0.14	0.04		33.45	0.33	0.93	0.09	
1.7	1.02	4.11	6.85	13.3	18.5163	1	55.23	0.02	0.03	0.03		23.57	0.17	0.17	0.04		44.10	0.25	1.02	0.09	
7.02	2.1	25.5	7.89	3.15	68.8	1	7.90	0.13	0.89	0.89		5.82	0.69	1.44	0.36		28.45	0.38	9.77	0.90	
5.08	1.5	19.9	7.67	5.21	75.1	1	16.94	0.06	0.30	0.30		8.69	0.46	0.69	0.17		37.48	0.29	5.79	0.53	
0.8	0.4	2	6.68143	0.51	3.02688	1	1.59	0.63	0.50	0.50	Y	9.06	0.44	0.18	0.04	Y	11.90	0.92	1.83	0.17	Y
0.6	0.3	1.2	6.4625	0.45	2.43611	1	1.00	1.00	0.60	0.60	Y	9.86	0.41	0.12	0.03	Y	11.90	0.92	1.10	0.10	Y
0.7	0.5	3.2	6.2825	0.44	2.03353	1	1.00	1.00	0.70	0.70	Y	9.86	0.41	0.20	0.05	Y	11.90	0.92	2.93	0.27	Y
0.2	0.8	2.1	7.59375	0.33	10.3229	1	1.17	0.86	0.17	0.17		4.00	1.00	0.80	0.20	Y	11.90	0.92	1.92	0.18	
3.22	1.22	24.7	7.96595	3.165	86.419	1	7.90	0.13	0.41	0.41		5.82	0.69	0.84	0.21		29.27	0.37	9.20	0.84	
3.74	4.45	16.8	7.64	7.82	7.7	1	35.48	0.03	0.11	0.11		15.12	0.26	1.18	0.29		74.89	0.15	2.45	0.22	

Sheet1 Results

Ready

Some examples using bio-met



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Page Layout

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Gridlines

Headings

Zoom 100%

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Freeze Panes

Split

Hide

Unhide

View Side by Side

Synchronous Scrolling

Reset Window Position

Switch Windows

Macros

Workbook Views

Show

Zoom

Window

fx

Sign inShare

MONITORING DATA

RESULTS (Copper)

RESULTS (Nickel)

RESULTS (Zinc)

Optional Measured Copper Conc (dissolved) [µg/L]	Optional Measured Nickel Conc (dissolved) [µg/L]	Optional Measured Zinc Conc (dissolved) [µg/L]	Required pH	Required DOC [mg/L]	Required Ca [mg/L]	Optional Zinc ABC Conc (dissolved) [µg/L]	Local EQS (dissolved) [µg/L]	BioF	Bioavailable Copper Conc [µg/L]	RCR	Notes	Local EQS (dissolved) [µg/L]	BioF	Bioavailable Nickel Conc (µg/L)	RCR	Notes	Local EQS (dissolved) [µg/L]	BioF	Bioavailable Zinc Conc (µg/L)	RCR	Notes
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1	1.3	4	8	1.7	65.6	1	3.70	0.27	0.27	0.27		4.00	1.00	1.30	0.33	Y	20.06	0.54	2.17	0.20	
3	2.4	3	8.5	0.8	42.2	1	1.13	0.89	2.66	2.66		4.00	1.00	2.40	0.60	Y	12.87	0.85	2.54	0.23	
0.52	0.35	2.11	6.81	1.1	8.15717	1	3.82	0.26	0.14	0.14		8.90	0.45	0.16	0.04		11.90	0.92	1.93	0.18	
0.55	0.17	3.32	7.05	3.9	11.8104	1	20.87	0.05	0.03	0.03		12.23	0.33	0.06	0.01		23.89	0.46	1.51	0.14	
0.41	0.68	2.85	6.61	9.5	9.95524	1	28.22	0.04	0.01	0.01		19.22	0.21	0.14	0.04		33.45	0.33	0.93	0.09	
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Sheet1Results

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Some examples using bio-met



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MONITORING DATA

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1	1.3	4	8	1.7	65.6	1	3.70	0.27	0.27	0.27		4.00	1.00	1.30	0.33	Y	20.06	0.54	2.17	0.20	
3	2.4	3	8.5	0.8	42.2	1	1.13	0.89	2.66	2.66		4.00	1.00	2.40	0.60	Y	12.87	0.85	2.54	0.23	
0.52	0.35	2.11	6.81	1.1	8.15717	1	3.82	0.26	0.14	0.14		8.90	0.45	0.16	0.04		11.90	0.92	1.93	0.18	
0.55	0.17	3.32	7.05	3.9	11.8104	1	20.87	0.05	0.03	0.03		12.23	0.33	0.06	0.01		23.89	0.46	1.51	0.14	
0.41	0.68	2.85	6.61	9.5	5.95524	1	28.22	0.04	0.01	0.01		19.22	0.21	0.14	0.04		33.45	0.33	0.93	0.09	
1.7	1.02	4.11	6.85	13.3	18.5163	1	55.23	0.02	0.03	0.03		23.57	0.17	0.17	0.04		44.10	0.25	1.02	0.09	
7.02	2.1	25.5	7.89	3.15	68.8	1	7.90	0.13	0.89	0.89		5.82	0.69	1.44	0.36		28.45	0.38	9.77	0.90	
5.08	1.5	19.9	7.67	5.21	75.1	1	16.94	0.06	0.30	0.30		8.69	0.46	0.69	0.17		37.48	0.29	5.79	0.53	
0.8	0.4	2	6.68143	0.51	3.02688	1	1.59	0.63	0.50	0.50	Y	9.06	0.44	0.18	0.04	Y	11.90	0.92	1.83	0.17	Y
0.6	0.3	1.2	6.4625	0.45	2.43611	1	1.00	1.00	0.60	0.60	Y	9.86	0.41	0.12	0.03	Y	11.90	0.92	1.10	0.10	Y
0.7	0.5	2	6.2825	0.44	2.03353	1	1.00	1.00	0.70	0.70	Y	9.86	0.41	0.20	0.05	Y	11.90	0.92	2.93	0.27	Y
0.2	0.8	2.1	7.59375	0.33	10.3229	1	1.17	0.86	0.17	0.17		4.00	1.00	0.80	0.20	Y	11.90	0.92	1.92	0.18	
3.22	1.22	24.7	7.96595	3.165	86.419	1	7.90	0.13	0.41	0.41		5.82	0.69	0.84	0.21		29.27	0.37	9.20	0.84	
3.74	4.45	16.8	7.64	7.82	7.7	1	35.48	0.03	0.11	0.11		15.12	0.26	1.18	0.29		74.89	0.15	2.45	0.22	

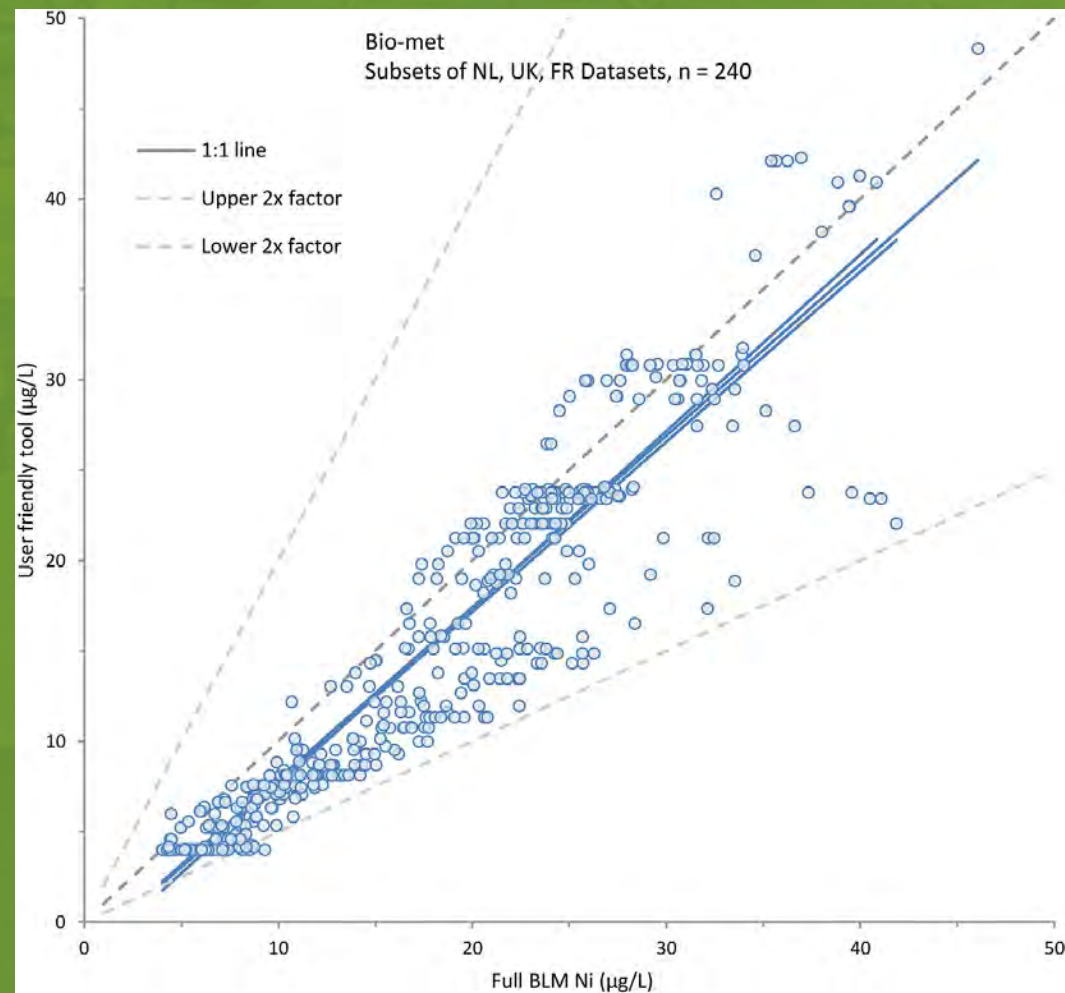
Sheet1 Results

Ready 95%

Queries and questions....



- Only covers freshwaters (at the moment!)
- Built in EQS (WQG) for long-term exposures
- Regulatory tool NOT a replacement for the BLMs



Validated boundaries



- Validation ranges.....

Metal	pH	Ca, mg L ⁻¹	DOC, mg L ⁻¹
Cu	6.0-8.5	3.1-93	Unlimited
Ni	6.5-8.2	2.0-88*	Unlimited
Zn	6.0-8.(2)	2.0-160	Unlimited

- Determined by the ranges over which the ecotoxicity tests have been performed.
- Validated in the field too!

Summary



- Accounting for bioavailability of trace elements reflects what the aquatic organism actually “experiences”.
- Simplified tools allows local assessment of potential metal risks
- These tools are already being used by regulators – well validated
- Provides an evidence-base for decision making
- As with soils though – be wary of using WQG or EQS from other jurisdictions!



- Questions?

Some useful (?) material.



- <http://bio-met.net>
- <http://www.wfduk.org/search/Bioavailability>
- <https://www.nickelinstitute.org/en/MediaCentre/News/CurrentYear/20160205-Bioavailability.aspx>
- <http://bio-met.net/wp-content/uploads/FINAL-TECHNICAL-GUIDANCE-TO-IMPLEMENT-BIOAVAILABILITYNovember-20142.pdf>

A composite image featuring a family of four (a man, a woman, and two children) walking along a path in a park. The path is bordered by a stream on the right and a field of red poppies on the left. In the background, there is a lake and a line of trees. Overlaid on the center of the image is a large, semi-transparent green circle containing the white text 'wca'. The overall scene is bright and sunny, suggesting a pleasant day outdoors.

wca