Assessment of surface water monitoring data: Application of biotic ligand model-based software tools to address the bioavailability of metals

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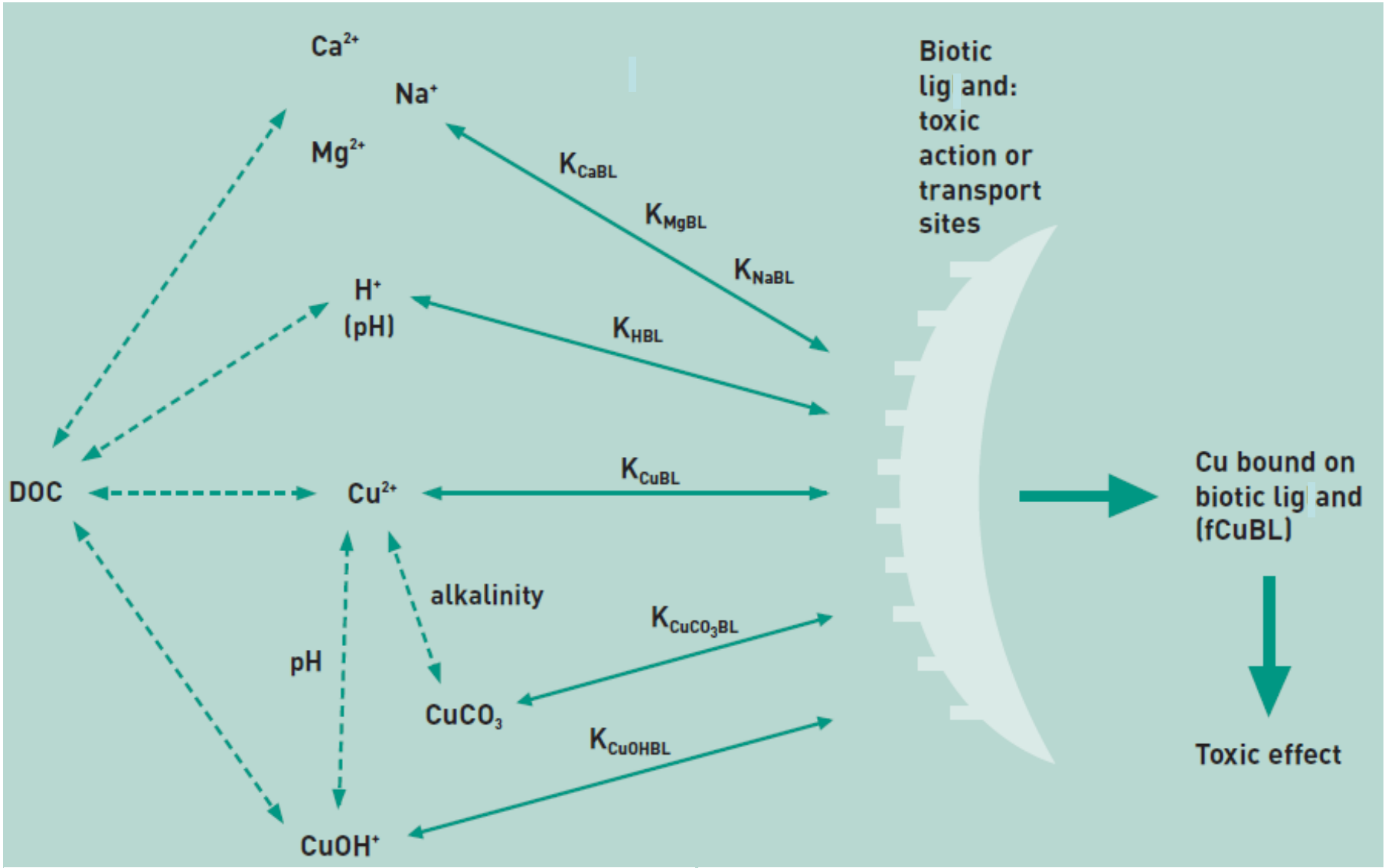
Heinz Rüdel

Fraunhofer Institute for Molecular Biology and Applied Ecology

Overview

- Background of the investigation
- Testing of biotic ligand model (BLM) software tools in dependence of the parameters pH, water hardness, dissolved organic carbon (DOC) for site specific assessments
- Influence of measurement uncertainty on the results
- Results for a representative surface water data set
- Conclusions

Background BLM www.icmm.com/document/15 **MERAG project**



Calculation of the speciation: WHAM (Windermere Humic-Aqueous Model)
Tipping, Comp. Geosci. 1994

In total about 10 water parameters are required: concentrations of anions and cations, DOC, temperature…

Current reference – Directive 2013/39/EU

DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 12 August 2013

amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy

(Text with EEA relevance)

Reference to the compliance monitoring of metals:

By way of derogation from the first subparagraph, in the case of cadmium, lead, mercury and nickel (hereinafter "metals"), the water environmental quality standards (EQS) refer to the dissolved concentration, i.e. the dissolved phase of a water sample obtained by filtration through a 0,45 µm filter or any equivalent pre-treatment, or, where specifically indicated, to the bioavailable concentration.

Member States may, when assessing the monitoring results against the relevant EQS, take into account:

(a) natural background concentrations for metals and their compounds where such concentrations prevent compliance with the relevant EQS;

(b) hardness, pH, dissolved organic carbon or other water quality parameters that affect the bioavailability of metals, the bioavailable concentrations being determined using appropriate bioavailability modelling.

Current reference – Directive 2013/39/EU

AA: annual average **EQS: environmental quality standard**

MAC: maximum allowable concentration **[µgL]**

(1)	(2)	(3)	(4)	(5)	(6)	(7)
No	Name of substance	CAS number (1)	AA-EQS (2) Inland surface waters (3)	AA-EQS (2) Other surface waters	MAC-EQS (4) Inland surface waters (3)	MAC-EQS (4) Other surface waters
(20)	Lead and its compounds	7439-92-1	1,2 (13)	1,3	14	14
(23)	Nickel and its compounds	7440-02-0	4 (13)	8,6	34	34

(13) These EQS refer to bioavailable concentrations of the substances

Applied biotic ligand model-based software applications

- **Bio-met tool, Arche (BE) / wca (UK), version 2.3, 2013**
  PNEC.Pro tool, Deltares (NL), version 5, 2013
  M-BAT tool, UK EPA, version 30.0, Nov. 2013
- **BLM tools use DOC, pH and Ca (and partly other available water quality data, which are not covered here), to calculate site specific local quality standards (QS or PNEC) as dissolved Cu, Ni, and Zn concentrations - to be compared with measured metal concentrations in water**
- **The calculated quality standards are here interpreted as $QS_{fw,eco}$ (QS for freshwater pelagic community), since for the overall WFD environmental quality standard (EQS) also other protection goals have to be covered (e.g., secondary poisoning)**
- **For the Bio-met and M-BAT tools, the local quality standards (local QS) can be related to the generic or bioavailable QS, which correspond to the full bioavailability of the dissolved metals (BioF – bioavailable fraction)**

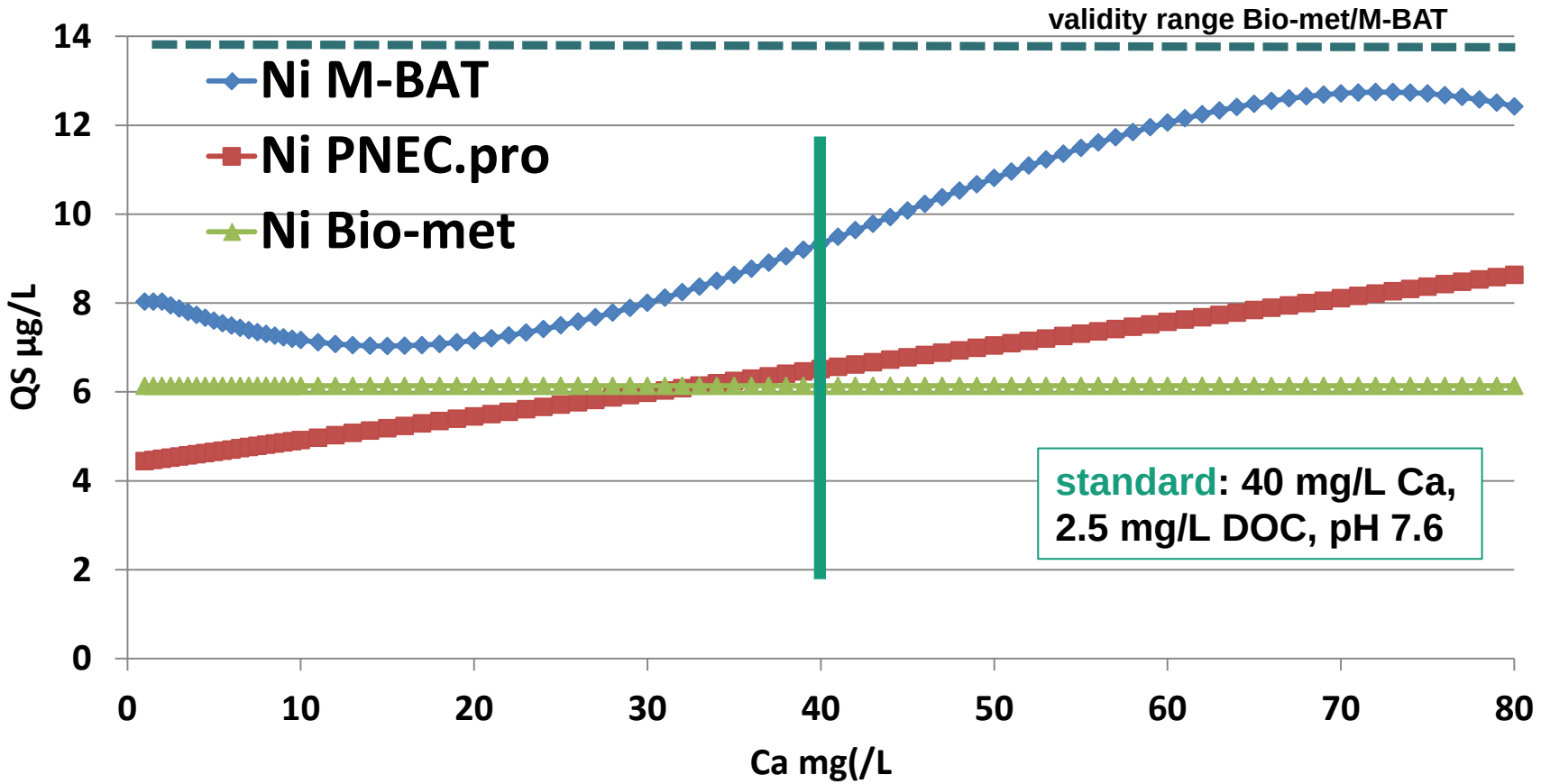
Standard scenario

- hardness (as Ca): 40 mg/L
- dissolved organic carbon (DOC): 2.5 mg/L
- pH 7.6

Comparison with a data set from a German federal state (NRW, LANUV 2011):

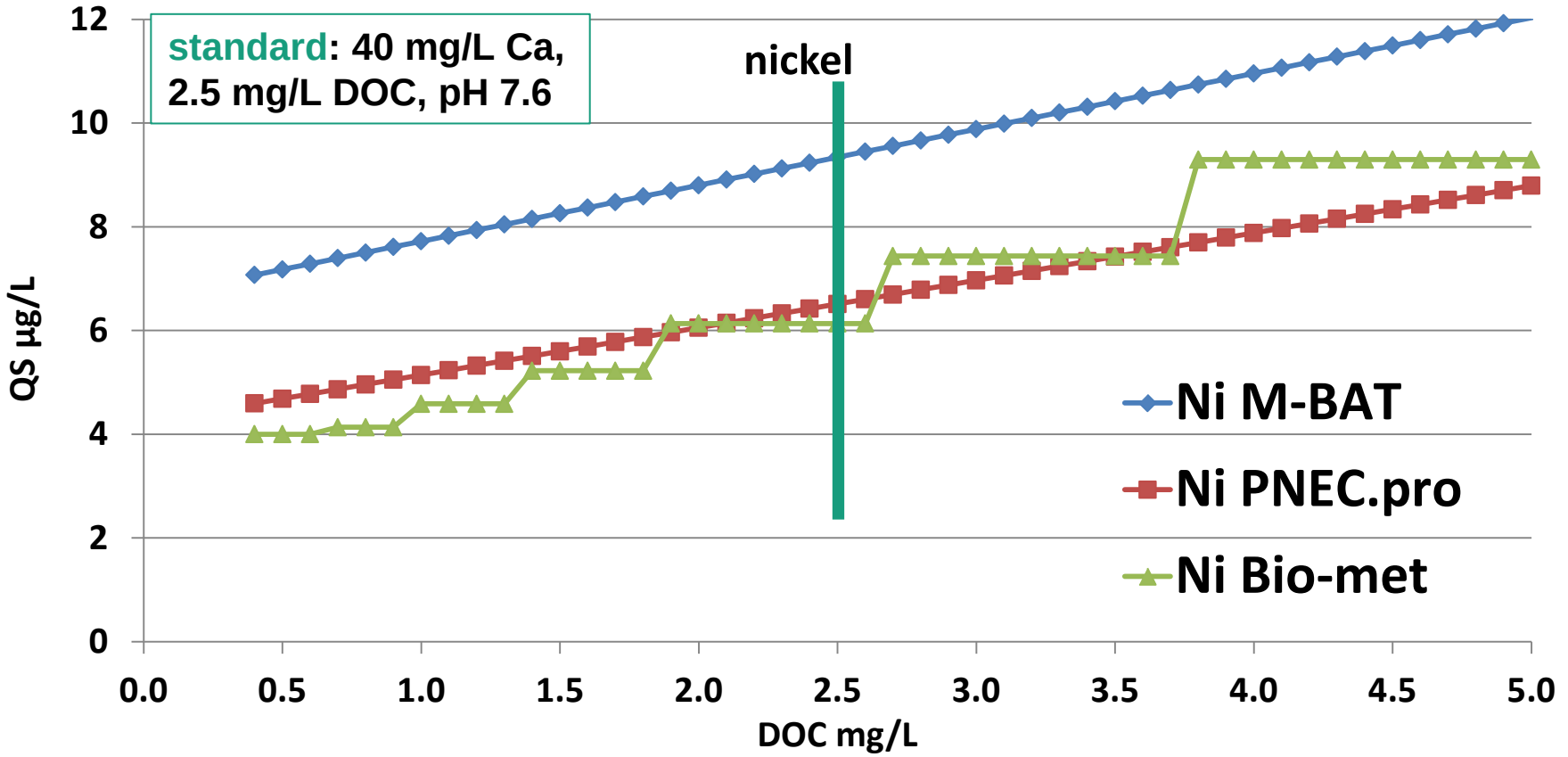
Parameter	pH	Ca [mg/L]	DOC [mg/L]
Minimum	4.6	1	0.4
Maximum	10.3	610	55.0
Mean	7.7	50	3.6
Median	7.8	43	2.9
Number	10,635	10,277	10,549

Variation of parameters - Ca: comparison PNEC.pro / Bio-met / M-BAT for Ni



- local Ni quality standard increases proportional to Ca for PNEC.pro
- local Ni quality standard is independent of the Ca level for Bio-met
- complex dependence of Ni quality standard on Ca levels for M-BAT

Variation of parameters - DOC: comparison PNEC.pro / Bio-met / M-BAT for Ni

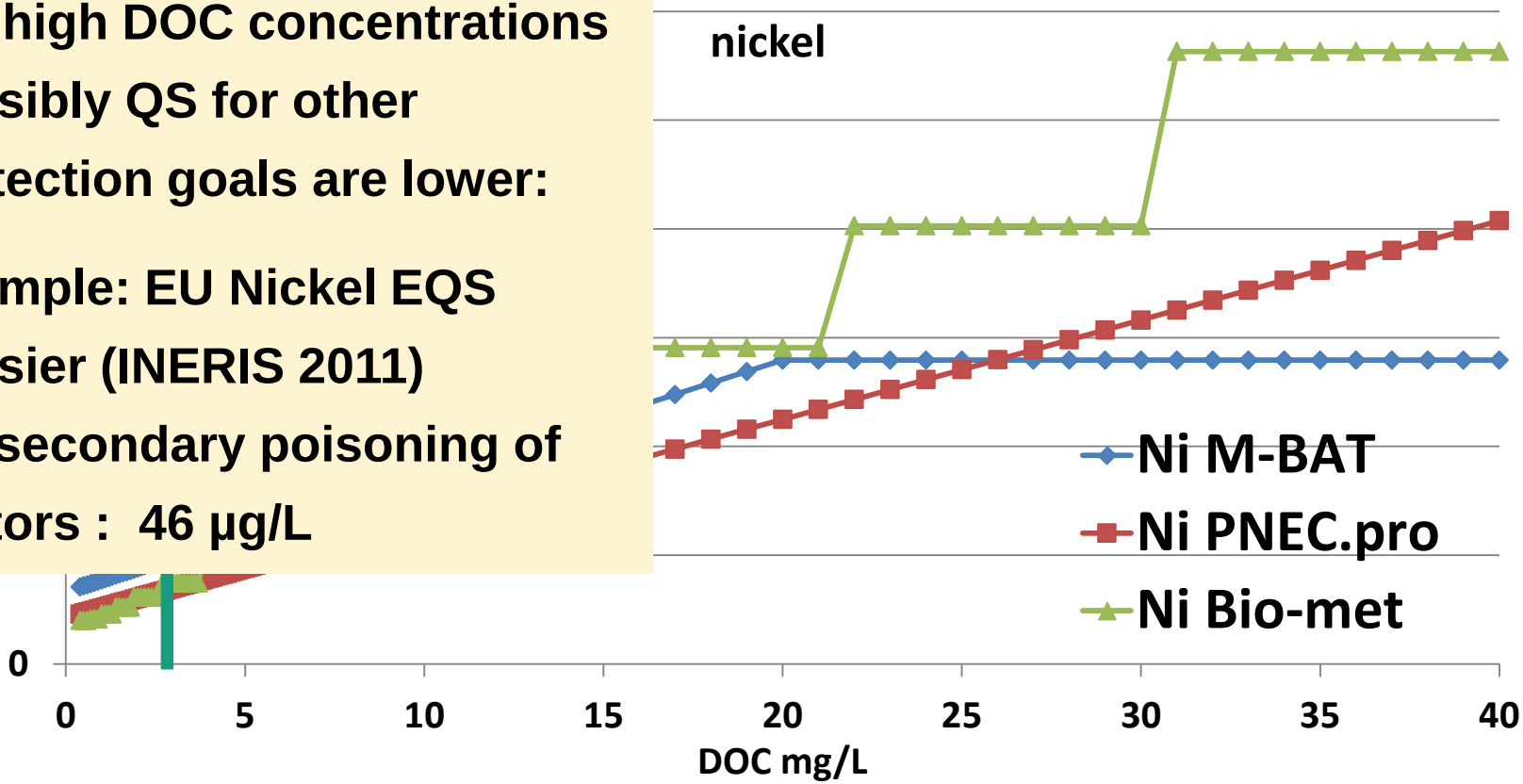


- local Ni quality standard increases proportional to DOC for all tools
- stepwise increase by Bio-met, QS similar to PNEC.pro
- highest Ni QS calculated for M-BAT at DOC levels up to 5 mg/L

Variation of parameters - DOC: comparison PNEC.pro / Bio-met / M-BAT for Ni

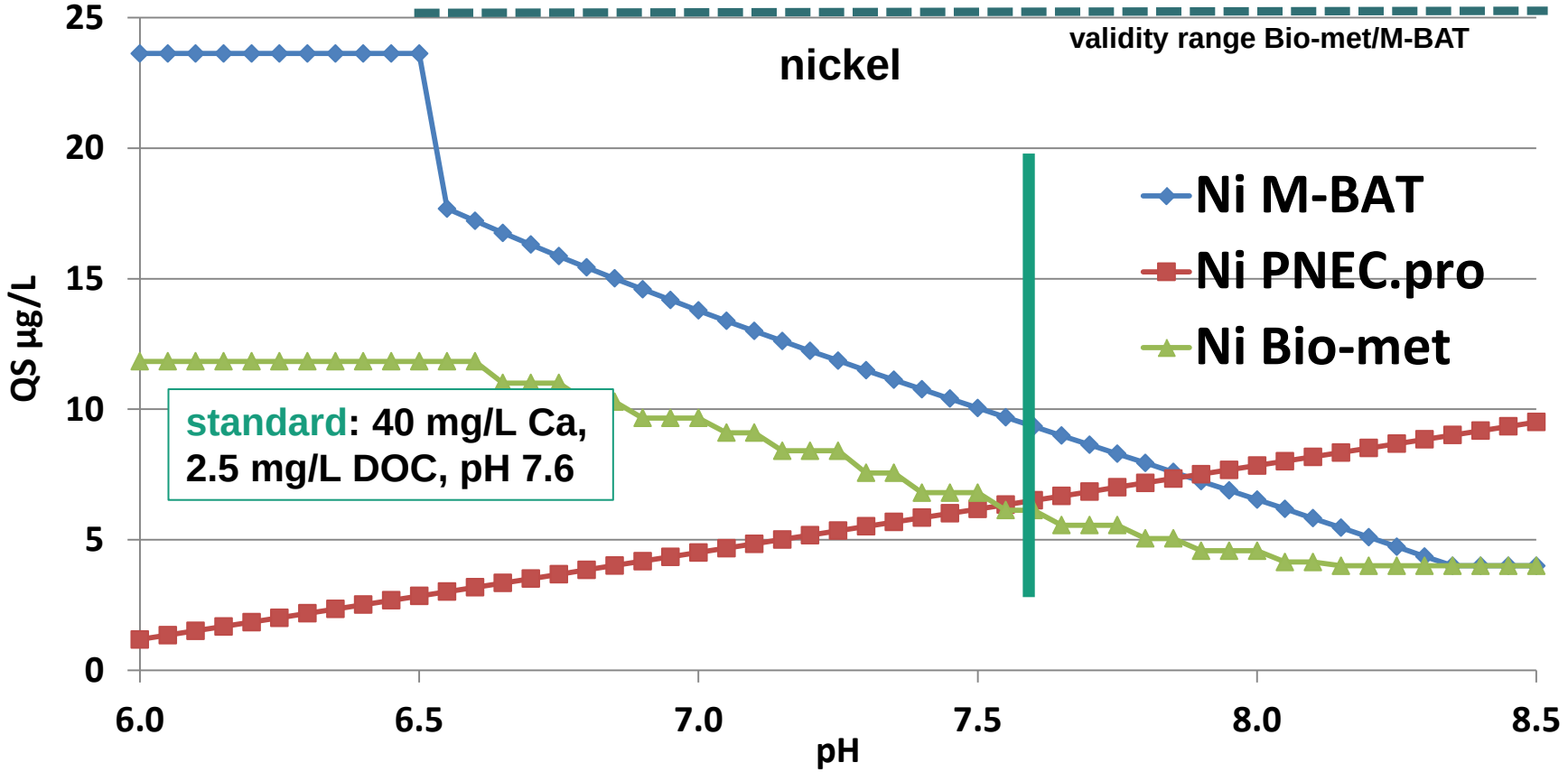
For high DOC concentrations possibly QS for other protection goals are lower:

Example: EU Nickel EQS dossier (INERIS 2011)
QS secondary poisoning of raptors : 46 µg/L



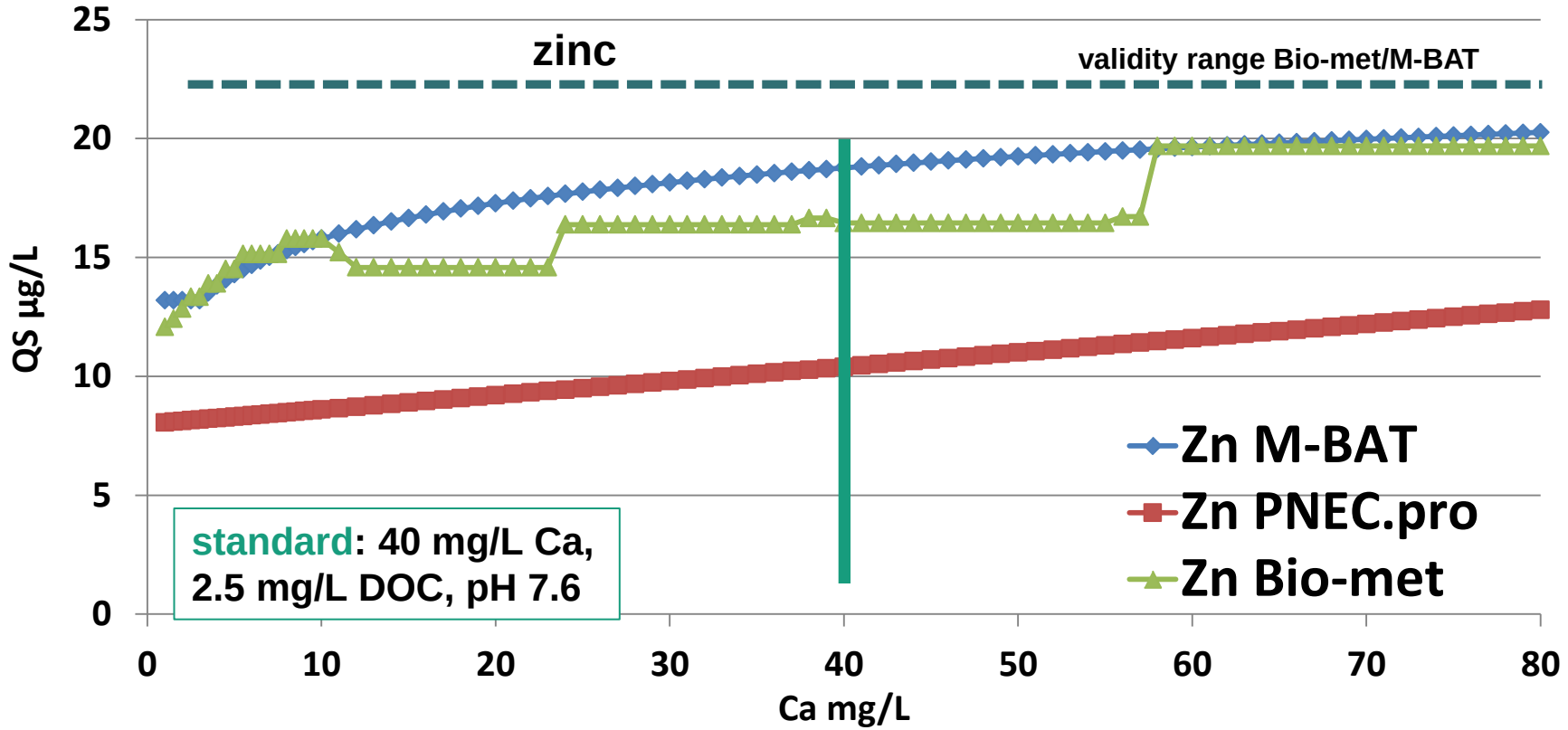
- local Ni quality standard increases proportional to DOC (limited for M-BAT)
- stepwise increase of Ni QS for the Bio-met tool
- highest QS calculated for Bio-met at high DOC levels

Variation of parameters - pH: comparison PNEC.pro / Bio-met / M-BAT for Ni



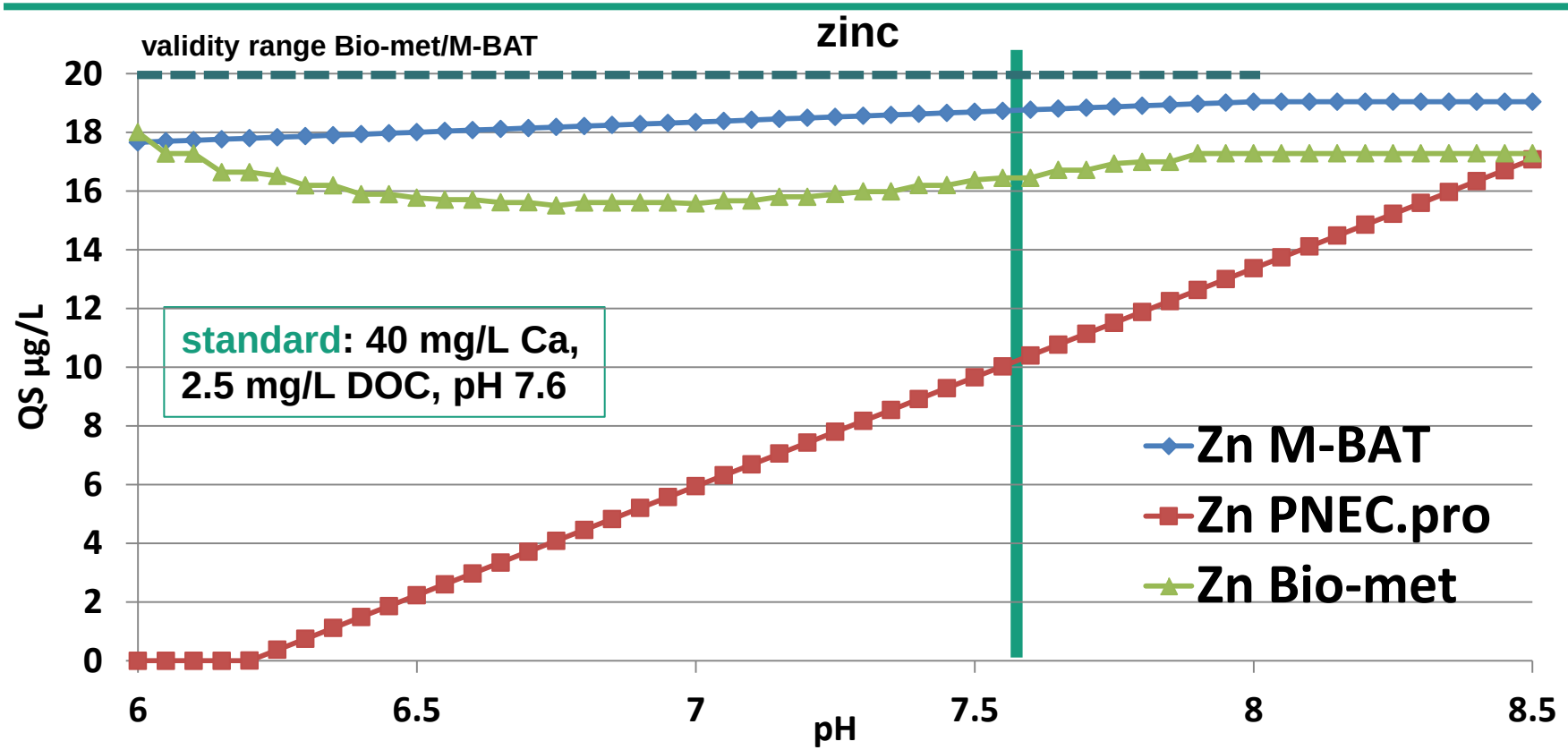
- local Ni quality standard decreases proportional to pH for M-BAT, Bio-met
- local Ni quality standard increases proportional to pH for PNEC-Pro
- large difference between Ni QS calculated by all tools at lower pH values

Variation of parameters - Ca: comparison PNEC.pro / Bio-met / M-BAT for Zn



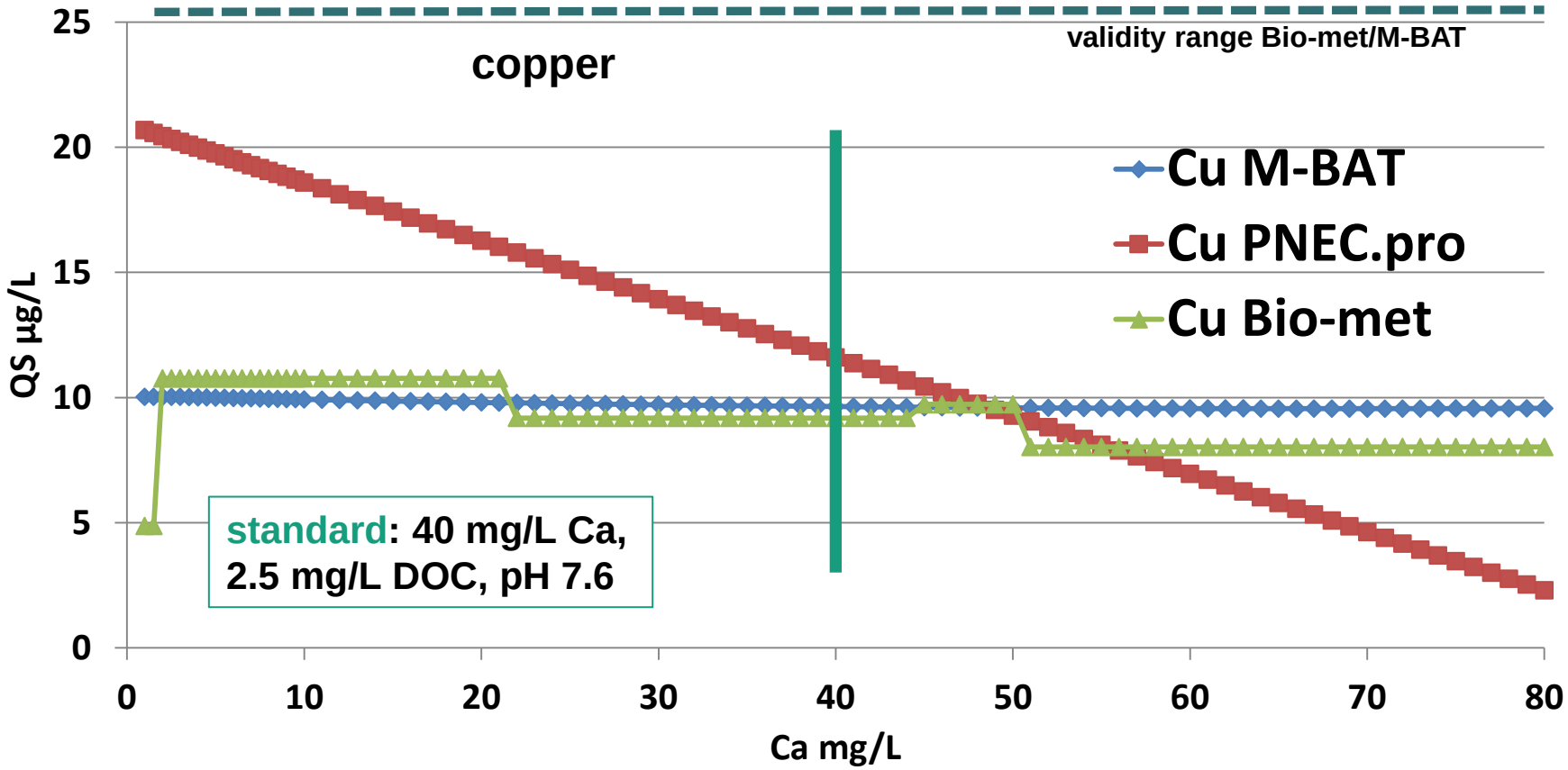
- local Zn quality standard increases proportional to Ca concentration for M-BAT and PNEC-Pro
- non-linear, stepped change for the Bio-met tool output
- large difference between Zn QS calculated by PNEC-Pro and M-BAT/Bio-met

Variation of parameters - pH: comparison PNEC.pro / Bio-met / M-BAT for Zn



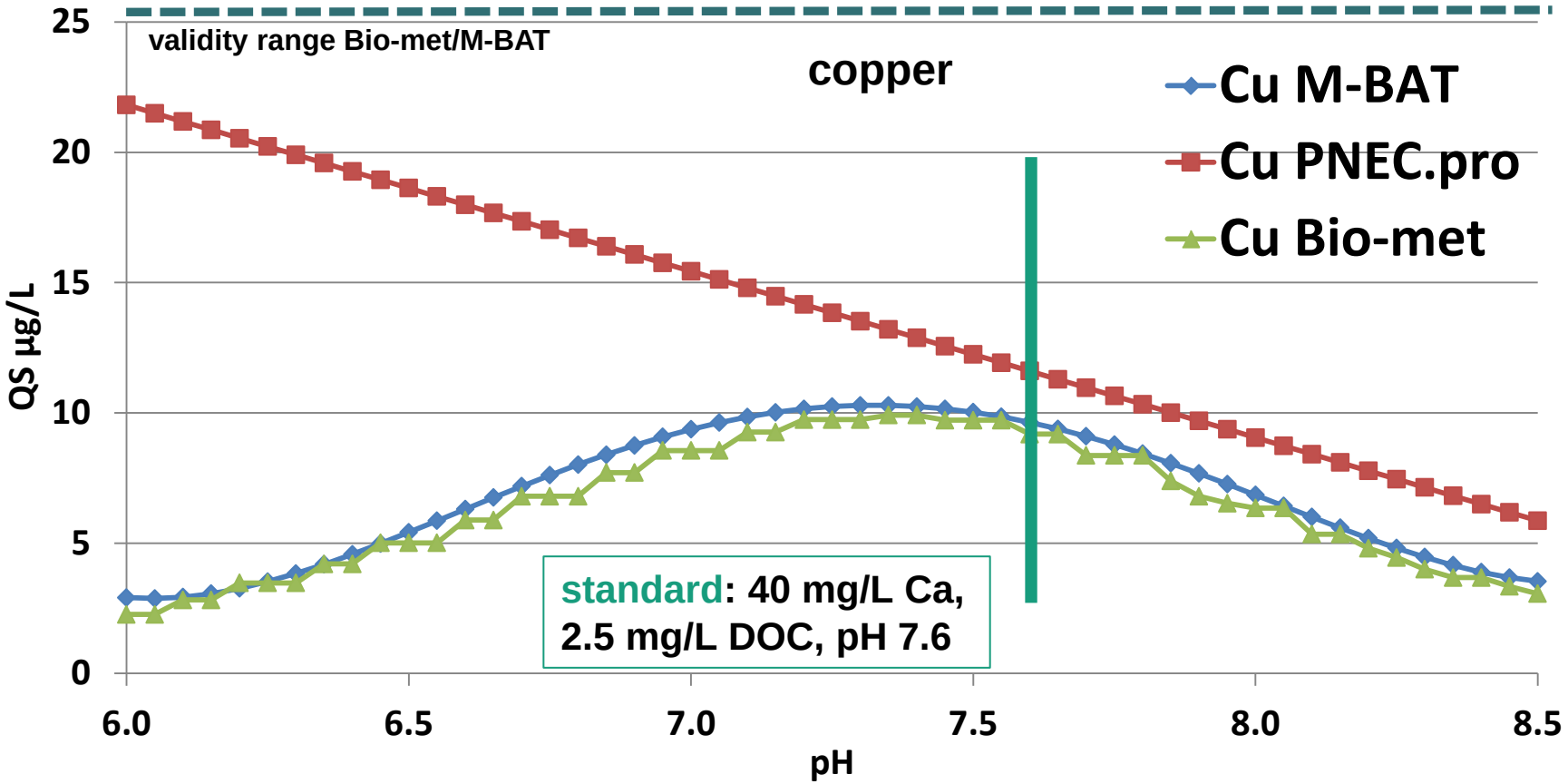
- local Zn quality standard increases proportional to pH for PNEC-Pro
- only slight changes in the whole pH range for M-BAT and Bio-met outputs
- large difference between Zn QS calculated by PNEC-Pro and M-BAT/Bio-met especially at lower pH values

Variation of parameters - Ca: comparison PNEC.pro / Bio-met / M-BAT for Cu



- local Cu quality standard decreases proportional to Ca for PNEC.pro
- local Cu quality standard is independent of the Ca level for M-BAT
- complex dependence of quality standard on Ca levels for Bio-met

Variation of parameters - pH: comparison PNEC.pro / Bio-met / M-BAT for Cu



- local Cu quality standard decreases proportional to pH for PNEC.pro
- local Cu quality standard has a maximum at about pH 7.3 for M-BAT/Bio-met
- large difference of calculated Cu quality standard at low pH

Consideration of the expanded measurement uncertainty

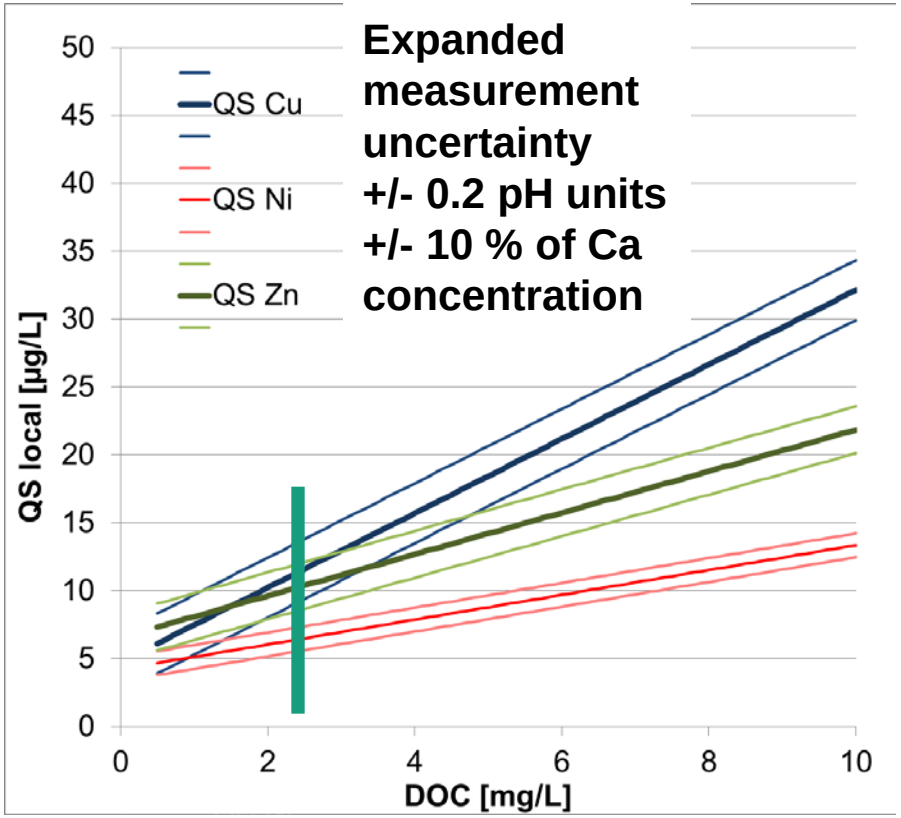
- **hardness** **+/- 10 % of the Ca concentration**
- **DOC** **+/- 30 % of the DOC concentration**
- **pH** **+/- 0,2 pH units**

- **metals:** **+/- 10 % of the dissolved concentrations**

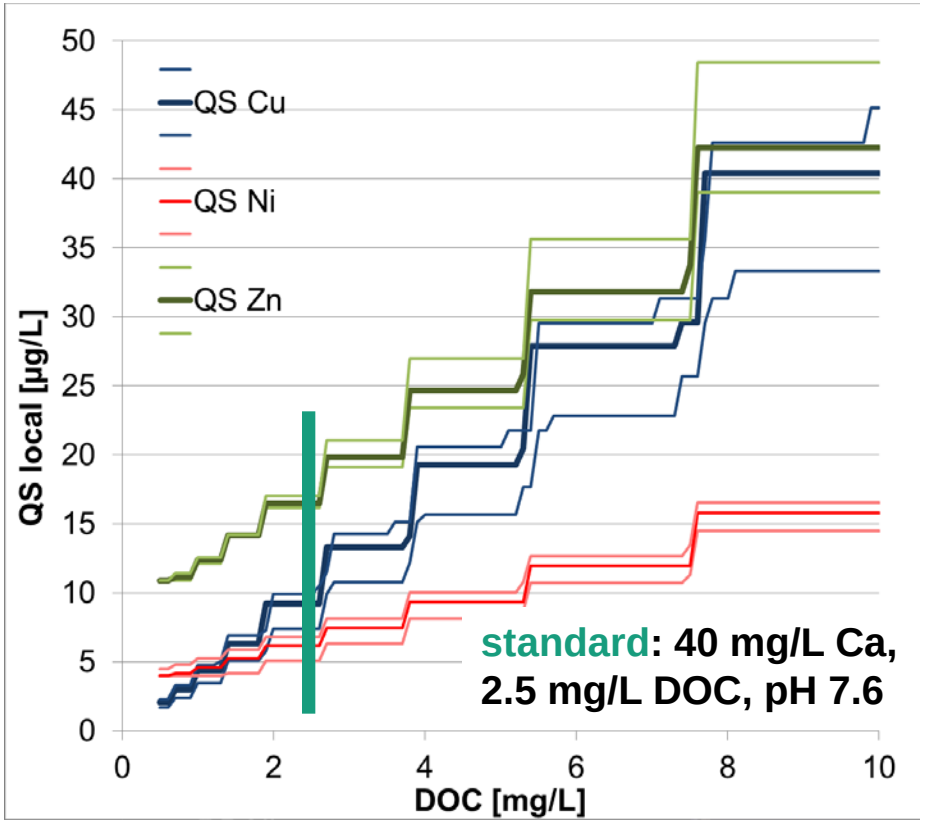
Specified on basis of discussions with representatives of water monitoring authorities of several German federal states for a former project for the German Environmental Agency (Umweltbundesamt)

Influence of measurement uncertainty: comparison PNEC.pro / Bio-met

PNEC.pro



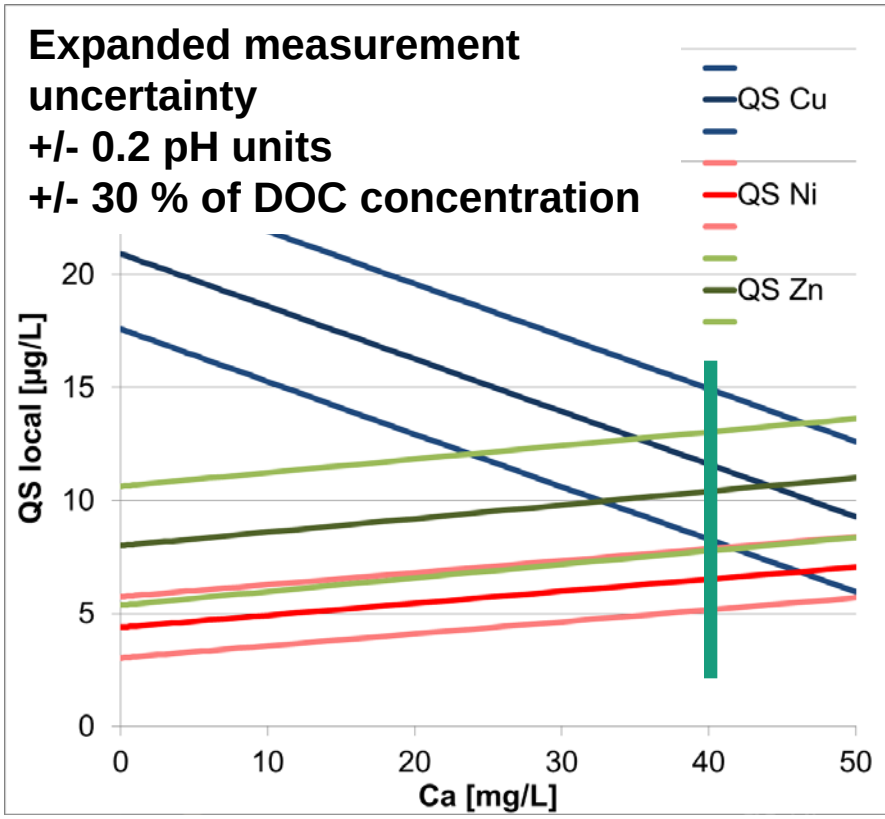
Bio-met



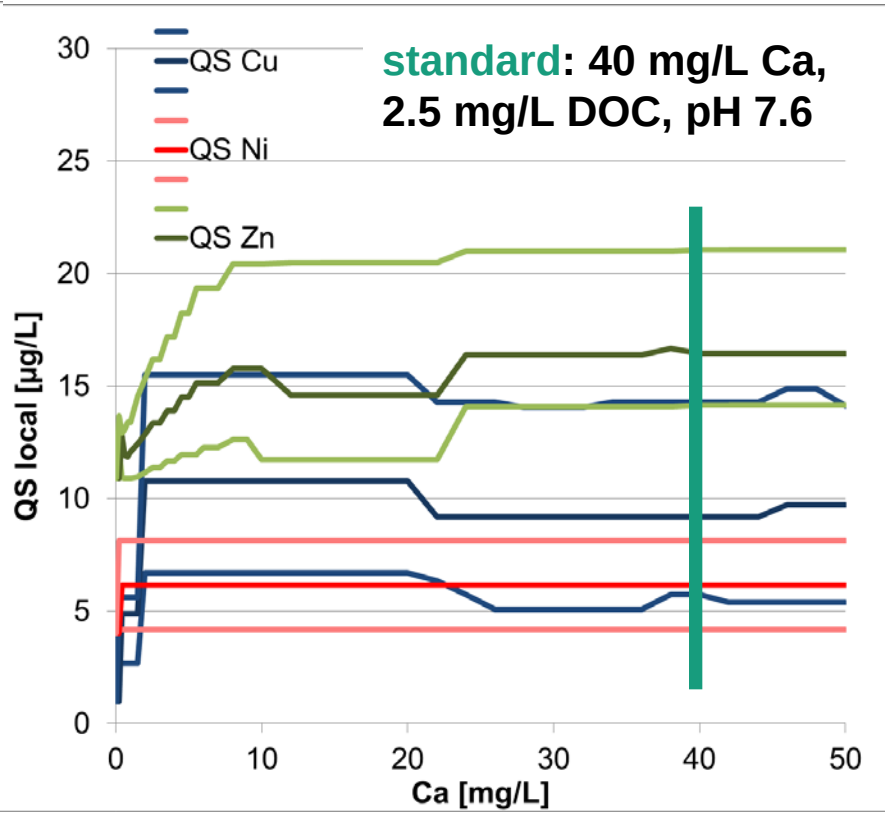
- Confidence interval of QS local is relatively constant for PNEC.pro
- Bio-met tool: especially at higher DOC levels a larger influence of the measurement uncertainty on the QS local is observed (Cu, Zn)

Influence of measurement uncertainty: comparison PNEC.pro / Bio-met

PNEC.pro



Bio-met



- Confidence interval of QS local is constant for the PNEC.pro tool
- Bio-met tool: variations at low Ca concentrations, relatively constant at high Ca levels; however, the confidence interval is larger (Cu, Zn)

Evaluation of a representative surface water data set (LANUV NRW 2011)

From a former project conducted for the German Environment Agency (Umweltbundesamt) a data set from the federal state of North Rhine Westphalia which was kindly provided by LANUV NRW

data in total		Cu (4281)	Ni (4281)	Zn (4281)
incl. metal conc.		3260	2662	3205
minimum		0.01	0.00	0.01
maximum		98.0	690.0	1100
mean	µg/L	1.5	5.4	10.0
stand. dev. (sd)		2.7	27.5	53.1
relative sd	%	184	512	531
median	µg/L	1.1	1.5	0.02
5th percentil		0.01	0.1	0.01
10th percentil		0.01	0.5	0.01
50th percentil		1.1	1.5	0.02
90th percentil		2.9	5.5	18.0
95th percentil		3.7	11.0	31.0

Evaluation of a representative surface water data set (LANUV NRW 2011)

	Cu			Ni			Zn		
	PNEC	p	RCR	PNEC	p	RCR	PNEC	p	RCR
no.	3876	3876	3876	4182	4182	4182	4154	4110	4110
min	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0	0.0
max	45.8	1.0	74.4	49.8	1.0	105.1	64.5	1.0	285.1
mean	**14.0**	**0.1**	**0.2**	**7.5**	**0.1**	**0.4**	**12.3**	**0.1**	**0.9**
sd	7.1	0.1	1.5	3.6	0.2	2.7	5.6	0.3	6.7
rel sd %	50.5	139.9	771.4	48.0	277.7	643.6	45.3	262.4	750.9
median	**13.96**	**0.03**	**0.05**	**6.93**	**0.00**	**0.10**	**11.56**	**0.00**	**0.00**
factor max/min									
min	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.1**	**0.0**	**0.0**
5er percentil	2.6	0.0	0.0	2.8	0.0	0.0	4.3	0.0	0.0
10er percentil	4.6	0.0	0.0	3.6	0.0	0.0	5.8	0.0	0.0
50er percentil	14.0	0.0	0.1	6.9	0.0	0.1	11.6	0.0	0.0
90er percentil	22.9	0.3	0.3	11.9	0.2	0.6	19.4	0.6	1.0
95er percentil	26.4	0.4	0.6	13.3	0.5	1.0	21.3	1.0	2.8
max	**46**	**1**	**74**	**50**	**1**	**105**	**65**	**1**	**285**

results of PNEC.pro tool

331	**n**		**18**	**n**		**109**	**n**	
OD			**OD**			**OD**		
10.2	**%**		**0.7**	**%**		**3.4**	**%**	
97	**n**		**217**	**n**		**423**	**n**	
RCR >=1			**RCR >=1**			**RCR >=1**		
3.0	**%**		**8.2**	**%**		**13.2**	**%**	

- **Out of domain („OD“): about Cu 10 %, Ni 0.7 %, Zn 3 %**
- **Exceedance (RCR ≥ 1): about Cu 3 %, Ni 8 %, Zn 13 %**

RCR - risk characterization ratio:
ratio dissolved metal concentration / calculated QS local

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Evaluation of a representative surface water data set (LANUV NRW 2011)

	Measured Copper Conc (dissolved) [µg/L]	Measured Nickel Conc (dissolved) [µg/L]	Measured Zinc Conc (dissolved) [µg/L]	Local EQS (dissolved) [µg/L]	BioF	RCR	Local EQS (dissolved) [µg/L]	BioF	RCR	Local EQS_{add} (dissolved) [µg/L]	BioF	RCR
no.	3260	2662	3205	4281	4281	3260	4281	4281	2662	4281	4281	3205
min	0.01	0.00	0.01	1.00	0.01	0.00	4.00	0.13	0.00	10.90	0.15	0.00
max	98.0	690.0	1100.0	79.0	1.0	5.9	31.8	1.0	139.6	74.4	1.0	87.3
mean	**1.5**	**5.4**	**10.0**	**10.0**	**0.2**	**0.2**	**6.9**	**0.7**	**0.9**	**19.6**	**0.6**	**0.6**
sd	2.7	27.5	53.1	7.3	0.1	0.3	2.9	0.2	5.4	7.8	0.2	3.2
rel sd %	183.5	512.0	530.7	73.4	82.1	144.8	41.8	33.4	566.3	39.8	32.6	542.8
median	**1.11**	**1.50**	**0.02**	**8.29**	**0.12**	**0.14**	**6.14**	**0.65**	**0.24**	**17.26**	**0.63**	**0.00**
factor max/m	19600	276000	220000									
min	**0.01**	**0.00**	**0.01**	**1.00**	**0.01**	**0.00**	**4.00**	**0.13**	**0.00**	**10.90**	**0.15**	**0.00**
5er percentil	0.01	0.09	0.01	2.54	0.04	0.00	4.00	0.33	0.01	10.90	0.30	0.00
10er percentil	0.01	0.50	0.01	3.29	0.06	0.00	4.00	0.37	0.09	11.73	0.37	0.00
50er percentil	1.1	1.5	0.0	8.3	0.1	0.1	6.1	0.7	0.2	17.3	0.6	0.0
90er percentil	2.9	5.5	18.0	18.0	0.3	0.4	10.7	1.0	0.8	29.6	0.9	1.0
95er percentil	3.7	11.0	31.0	22.9	0.4	0.6	12.1	1.0	1.6	36.9	1.0	2.2
max	**98.0**	**690.0**	**1100.0**	**79.0**	**1.0**	**5.9**	**31.8**	**1.0**	**139.6**	**74.4**	**1.0**	**87.3**
				446 n			**18 n**			**1013 n**		
				OD			**OD**			**OD**		
				13.7 %			**0.7 %**			**31.6 %**		
				35 n			**212 n**			**319 n**		
				RCR >=1			**RCR >=1**			**RCR >=1**		
				1.1 %			**8.0 %**			**10.0 %**		

results of the Bio-met tool

- **Out of domain:** about **Cu 14 %, Ni 0.7 %, Zn 32 %**
- **Exceedances (RCR ≥ 1):** about **Cu 1 %, Ni 8 %, Zn 10 %**

RCR - risk characterization ratio:
ratio dissolved metal concentration / calculated QS local

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comparison of Bio-met / PNEC.pro results:

	out of domain Bio-met	out of domain PNEC.pro	match
➢ Cu	n = 446	n = 331	n = 188
➢ Ni	n = 18	n = 18	n = 16
➢ Zn	n = 1013	n = 109	n = 103

	RCR > 1 Bio-met	RCR > 1 PNEC.pro	match
➢ Cu	n = 35	n = 97	n = 6
➢ Ni	n = 212	n = 217	n = 166
➢ Zn	n = 319	n = 423	n = 238

Conclusions

- The available original BLM are scientifically recognized tools for assessing the bioavailability of metals – however, for use in routine water monitoring user-friendly applications of the original BLM are required (BLM-based tools)
- The differences between the results of the here tested software applications Bio-met, M-BAT and PNEC.pro are very large - both the dependencies of the parameters and the calculated quality standards
- An analysis of the causes as well as a transparent documentation of the algo-rithms is required - including the derivation of the applied QS (if not regulated); to increase the BLM tool acceptance, a harmonization seems necessary
- The step changes of the quality standards observed for the Bio-met tool are impractical: variations caused by the measurement uncertainty can result in large changes - continuous functions would be more practicable
- BLM tools should not give out data out of their validity range
- Clear hints are needed how to proceed in case of QS exceedances: use of complex BLM, consideration of background values (added risk approach), ...
- At high DOC and Ca concentrations sometimes high QS are calculated; here it has to be checked whether the QS for other protection goals are exceeded (e.g. secondary poisoning of predators in case of nickel)