Session: Improvements in environmental exposure assessment: Development and application of tools across industry sectors, regulatory agencies, and international boundaries
Platform Presentation
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Consideration of the bioavailability of metals and metal´compounds in freshwaters in regulatory frameworks

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Recent research has demonstrated that both total and dissolved metal concentrations are not the most appropriate parameters for the risk assessment of metals in aquatic systems. There is an increasing awareness by leading regulatory bodies in the USA, Europe and other countries that the bioavailable fractions of metals could be better descriptors of their risks. The principal concept of metal bioavailability is the Biotic Ligand Model (BLM) which allows site-specific assessments of metals' risks by considering the environmental factors which determine the bioavailability of dissolved metals in the aquatic environment. For many metals bioavailability in freshwaters is modulated by dissolved organic carbon (DOC) concentrations, water hardness, the pH of the water and other factors such as temperature, concentrations of further ions and suspended solids as well as metal speciation. Metal-specific BLMs were proposed for different biological species and both, acute and chronic exposures. The BLM approach has been described extensively in the scientific literature, and BLMs have been applied for the risk assessment of metals and metal compounds (e.g., for copper and zinc in the EU).

In the past, the broader use of the BLM approach for the site-specific evaluation of surface water monitoring data was hampered by the huge data requirements of the original BLMs (several site-specific water parameters). But the recent development of user-friendly BLM-based bioavailability tools (e.g., www.Bio-met.net, www.PNEC-pro.com) now allows the consideration of bioavailability for the evaluation of freshwater monitoring data of relevant metals. Such tools, which only need a basic set of easily available water parameters as input (mostly pH, Ca concentration, DOC, and dissolved metal concentration), are currently available for metals such as lead, nickel, copper and zinc. The new EU WFD environmental quality standards for lead and nickel according to Directive 2013/39/EU now consider the bioavailable fractions of these metals.

In this contribution, the advantages and possible drawbacks of BLM-based bioavailability tools are presented highlighting feasibility, ranges of validity, and comparability between tools. Finally, recommendations for the regulatory implementation are given. This contribution is based on the outcome of the IUPACsupported project "Consideration of bioavailability of metals/metal compounds in the aquatic environment" (#2011-060-1-600).

Consideration of the bioavailability approach for metals and metal compounds in freshwaters in regulatory frameworks

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IUPAC project #2011-060-1-600

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Background metal bioavailability

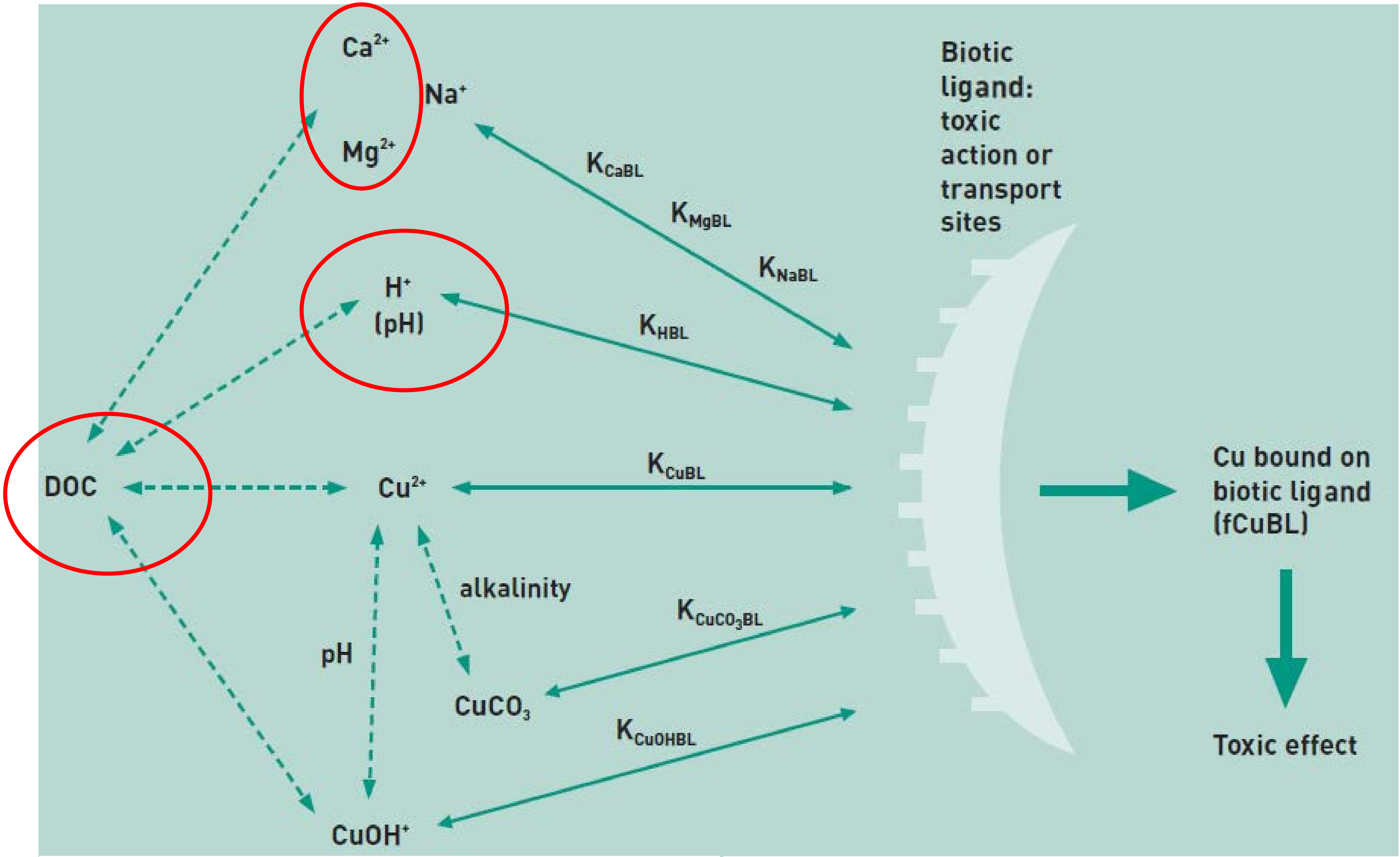
- **Recent research has demonstrated that both total and dissolved metal concentrations are not appropriate parameters for the risk assessment of metals in aquatic systems**

- **There is an increasing awareness by leading regulatory bodies that the bioavailable fractions of metals could be better descriptors of their risks**

- **For many metals bioavailability in freshwaters is modulated by the dissolved organic carbon (DOC) concentration, water hardness, the pH of the water and other factors such as temperature, concentrations of further ions and suspended solids as well as metal speciation**

Scheme: biotic ligand model (BLM)

http://bit.ly/2nsuNHF **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…

Application of the bioavailability approach in regulations

European Union

- Water Framework Directive (WFD, 2000/60/EC): bioavailability-based environmental quality standards (EQS) for Ni, Pb (Directive 2013/39/EU)
- UK national regulation: use of BLM-based tool for Cu, Zn, Mn (2014)
- European Chemicals' Management: risk assessment reports for certain metals (e.g., Cu, Zn, Pb) are based on the bioavailability concept

United States of America

- US EPA (2007): the aquatic life freshwater quality criteria for copper are based on bioavailability considerations (use of BLM required)

Canada

- Option to use BLM for deriving trigger values for metals by incorporation of exposure and toxicity-modifying factors (2007)

Australia and New Zealand

- Option on using site-specific bioavailable metal concentrations in the decision tree for compliance testing against trigger values (2000)

Application of bioavailability in regulations

OECD Document (2016)

Guidance on the Incorporation of Bioavailability Concepts for Assessing the Chemical Ecological Risk and/or Environmental Threshold Values of Metals and Inorganic Metal Compounds

Series on Testing & Assessment No. 259

ENV/JM/MONO(2016)66
Unclassified

Unclassified **ENV/JM/MONO(2016)66**

Organisation de Coopération et de Développement Économiques
Organisation for Economic Co-operation and Development **19-Dec-2016**

English - Or. English

ENVIRONMENT DIRECTORATE
JOINT MEETING OF THE CHEMICALS COMMITTEE AND
THE WORKING PARTY ON CHEMICALS, PESTICIDES AND BIOTECHNOLOGY

GUIDANCE ON THE INCORPORATION OF BIOAVAILABILITY CONCEPTS FOR ASSESSING THE CHEMICAL ECOLOGICAL RISK AND/OR ENVIRONMENTAL THRESHOLD VALUES OF METALS AND INORGANIC METAL COMPOUNDS

Series on Testing & Assessment
No. 259

Case study: European Water Framework Directive (EQS-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

Compliance monitoring of metals (EQS-Directive 2013/39/EU):

….. 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:

- **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**
- **natural background concentrations for metals and their compounds where such concentrations prevent compliance with the relevant EQS**

Case study: European Water Framework Directive (EQS-Directive 2013/39/EU)

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

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

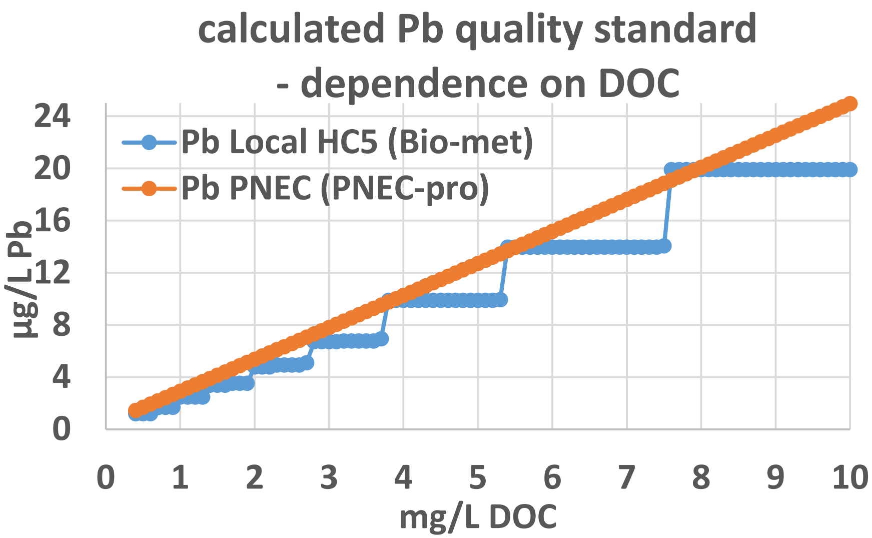
(1)	(2)	(3)	(4)	(5)	(6)	(7)
No	Name of substance	CAS number (1)	AA-EQS (2) Inland surface waters (3)	AA-EQS (2) Other surface waters	MAC-EQS (4) Inland surface waters (3)	MAC-EQS (4) Other surface waters
Pb Lead 82 207.2	Lead and its compounds	7439-92-1	1,2 (13)	1,3	14	14
Ni Nickel 28 58.693	Nickel and its compounds	7440-02-0	4 (13)	8,6	34	34

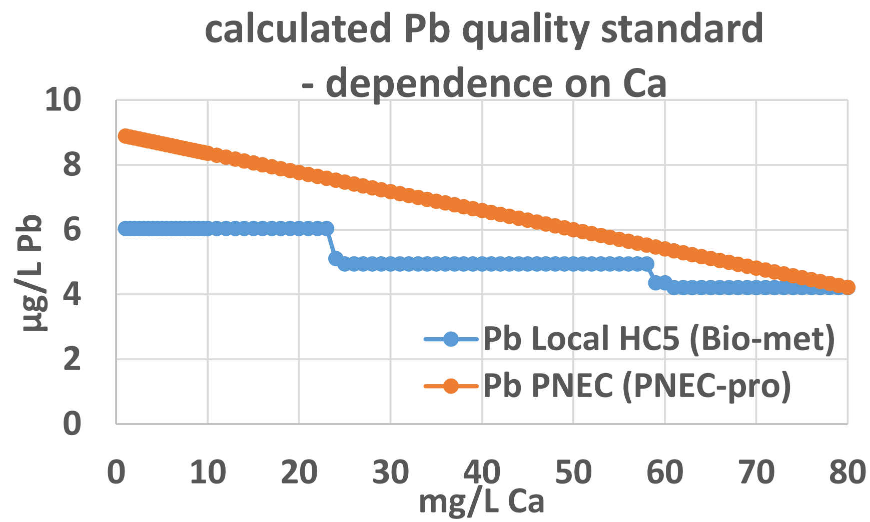
(13) These EQS refer to bioavailable concentrations of the substances

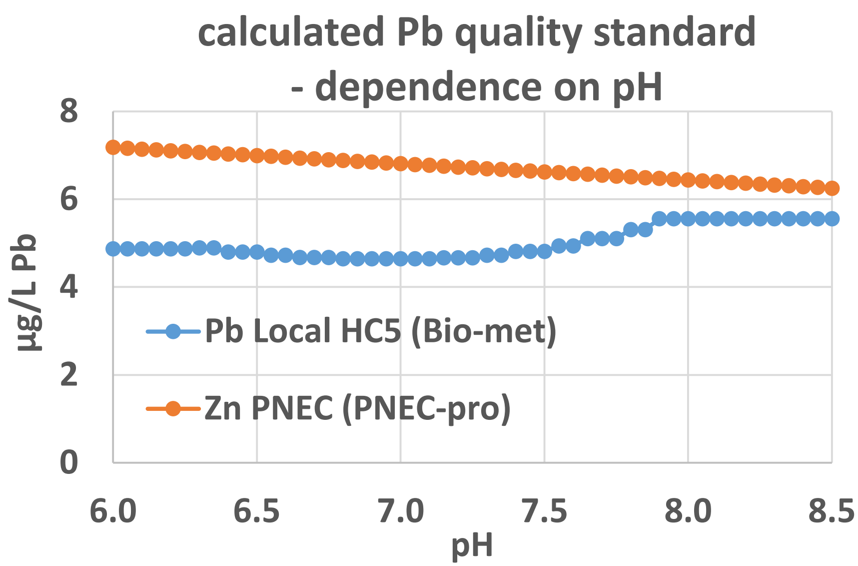
WFD: Application of user-friendly bioavailability-based software applications

- The most sensitive protection objective of the WFD EQS for metals is the pelagic community (chronic effects)
- To describe the ecotoxicity of metals towards water organisms in dependence on water parameters specific BLM are available
- The original BLM need more then ten water quality parameters; these are often not available from surface water monitoring
- Dedicated user-friendly BLM software tools basically require DOC, pH and hardness (Ca concentration), and the measured dissolved metal concentrations
- User-friendly tools allow the calculation of local quality standards (QS; as HC5 or PNEC) as dissolved Cu, Ni, Zn, Pb concentrations
- Tools compared here:
  Bio-met tool, Arche (BE) / wca (UK), version 4.0, 2017
  PNEC-pro tool, Deltares (NL), version 6, 2017
- Question: Are the assessment outcomes (local QS) similar?
  Standard scenario applied here: hardness (as Ca) 40 mg/L; dissolved organic carbon (DOC) 2.5 mg/L; pH 7.6

Comparison PNEC-pro / Bio-met for lead: influence of DOC, pH, hardness

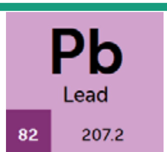




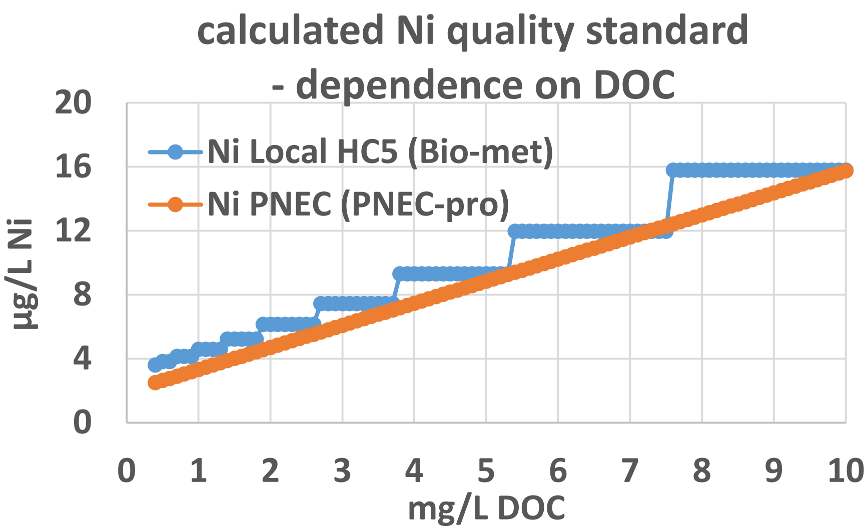


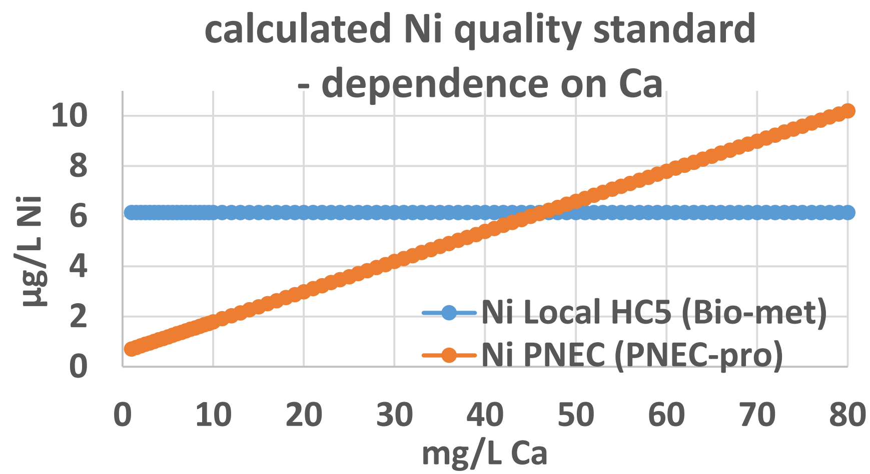
- **DOC: both tools show higher Pb-QS at increasing DOC levels**
- **Ca: Pb-QS decreases with increasing Ca levels, only slight Pb-QS range for Bio-met**
- **pH: slight decrease of Pb-QS with increasing pH for PNEC-pro, slight increase of Pb-QS at high pH values for Bio-met**

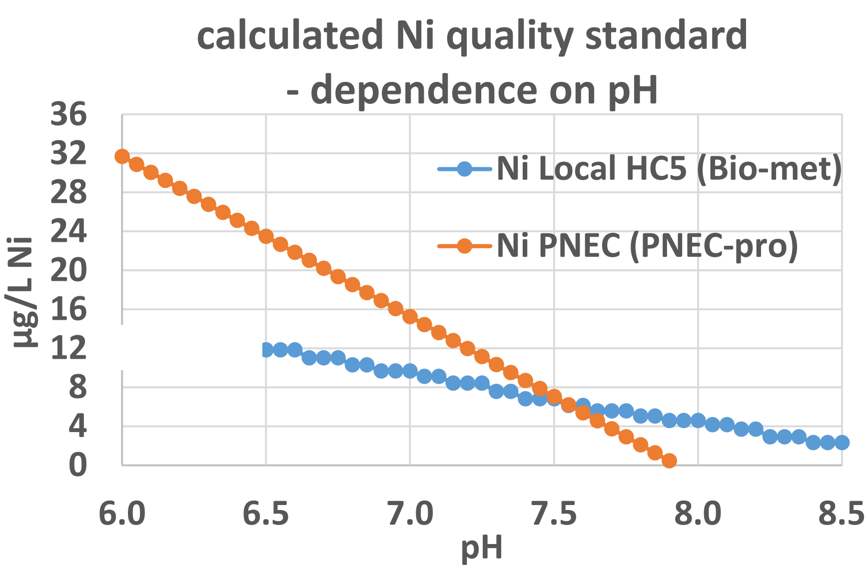
Standard conditions:
40 mg/L Ca, 2.5 mg/L DOC, pH 7.6



Comparison PNEC-pro / Bio-met for nickel: influence of DOC, pH, hardness







- **DOC:** both tools show higher QS at increasing DOC levels
- **Ca:** Ni-QS increases proportional to Ca for PNEC-pro, constant Ni-QS for Bio-met
- **pH: steep decrease** of QS with increasing pH for PNEC-pro, only slight decrease of Ni-QS over pH range for Bio-met

Standard conditions:
40 mg/L Ca, 2.5 mg/L DOC, pH 7.6

IUPAC project #2011-060-1-600

Conclusions

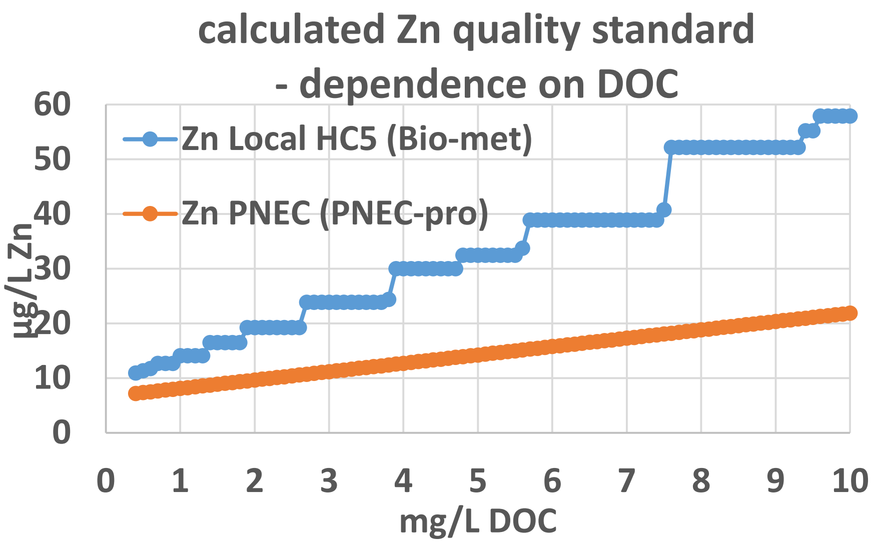
- The original BLM are scientifically recognized tools for assessing the bioavailability of metals – however, for use in routine water monitoring user-friendly applications of the original BLM are required (BLM-based tools such as PNEC-pro or Bio-met) since often only a few water quality parameters are available
- In the range of common water characteristics (pH, Ca, DOC), both tools show an agreement within factors of about 2; at the upper/ lower boundaries, larger differences occur (factors of 3 or larger)
- To allow a regulatory use a transparent documentation of the algorithms of the BLM-based tools is required
- The step changes of the quality standards observed for the Bio-met tool are impractical: small variations in the range of the measurement uncertainty of water parameters can result in large changes of calculated quality standard - continuous functions would be more practicable

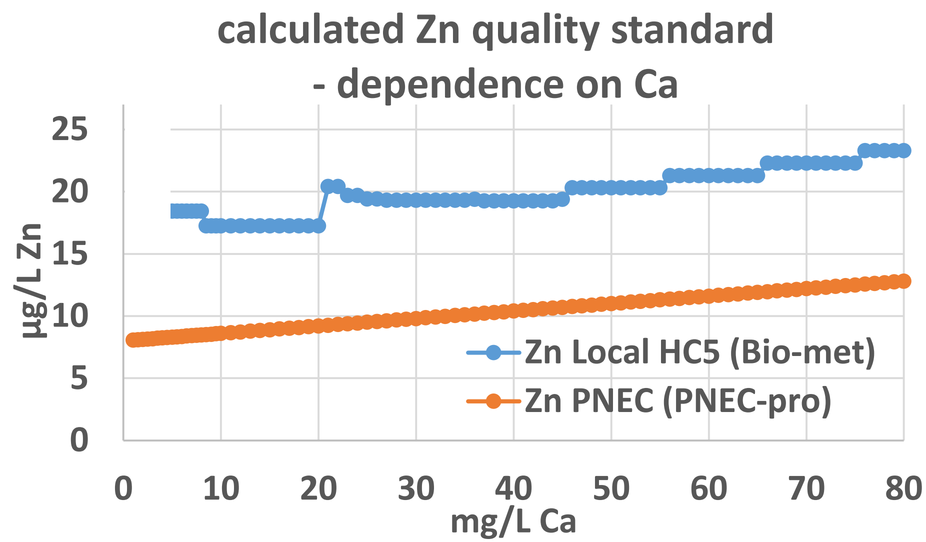
Recommendations for the regulatory implementation

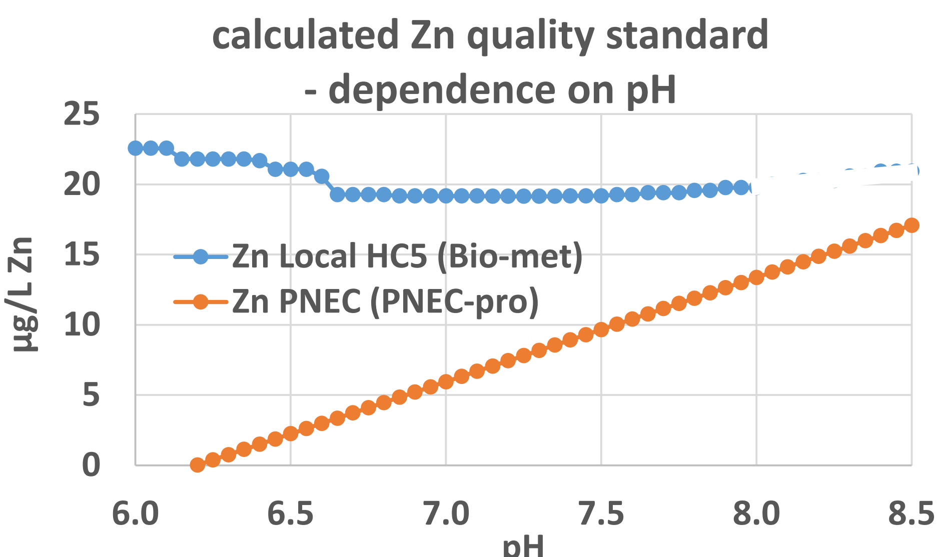
- BLM-based bioavailability tools should allow the assessment of all relevant metals (e.g., hardness-classes regulated Cd for EU WFD)
- Diverging outcomes of the assessments with different tools for the same scenarios probably will reduce acceptance of the BLM-based tools => inter-calibration studies should be initiated to demonstrate performance of the tools for test datasets
- If tools are specific to certain conditions, certain regions and/or countries, the validity range should be clearly stated
- For a broad implementation of BLM-based bioavailability tools into regulatory assessments, more guidance from competent authorities is required: e.g., support by webinars, workshops, and (online) tutorials - to ensure application of similar principles in all countries
- Important aspects of guidance are:
  - how to proceed if certain water quality data are missing
  - how to proceed if water criteria are outside the validity range
  - how to deal with sites with high natural metal background levels

Additional slides

Comparison PNEC-pro / Bio-met for zinc: influence of DOC, pH, hardness







- **DOC: higher Zn-QS at increasing DOC levels; Bio-met shows steeper increase**
- **Ca: Zn-QS increases slightly with increasing Ca levels, about factor 2 higher QS for Bio-met**
- **pH: continuous increase of Zn-QS with increasing pH for PNEC-pro, slight decrease of Zn-QS at high pH values for Bio-met**

Standard conditions:
40 mg/L Ca, 2.5 mg/L DOC, pH 7.6

Zn
Zinc
30 65.38

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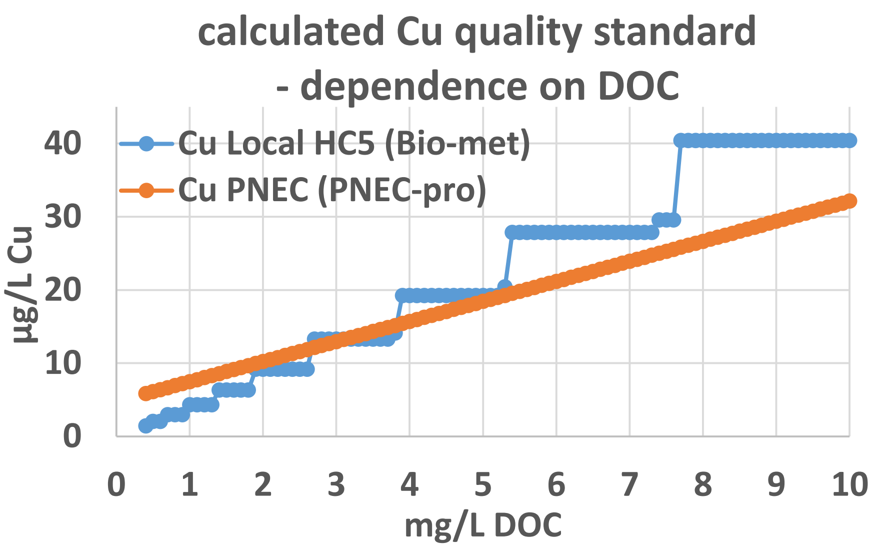
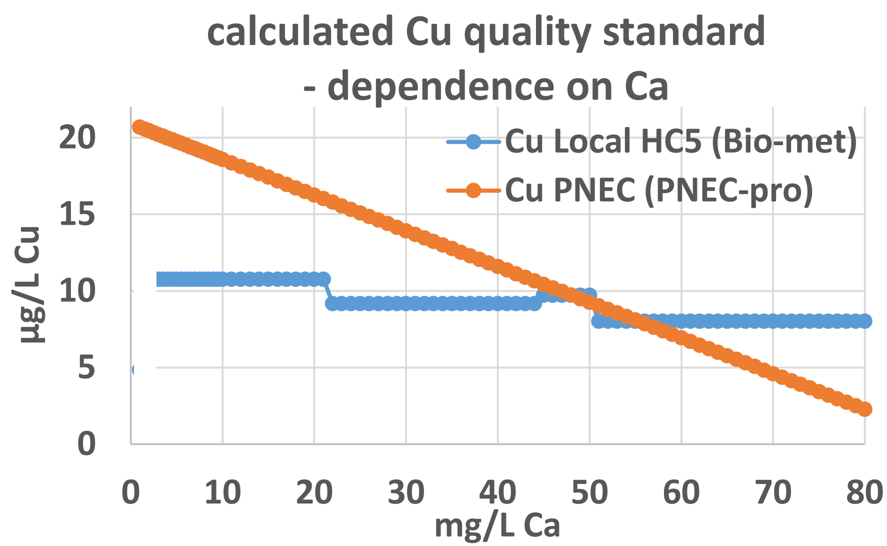
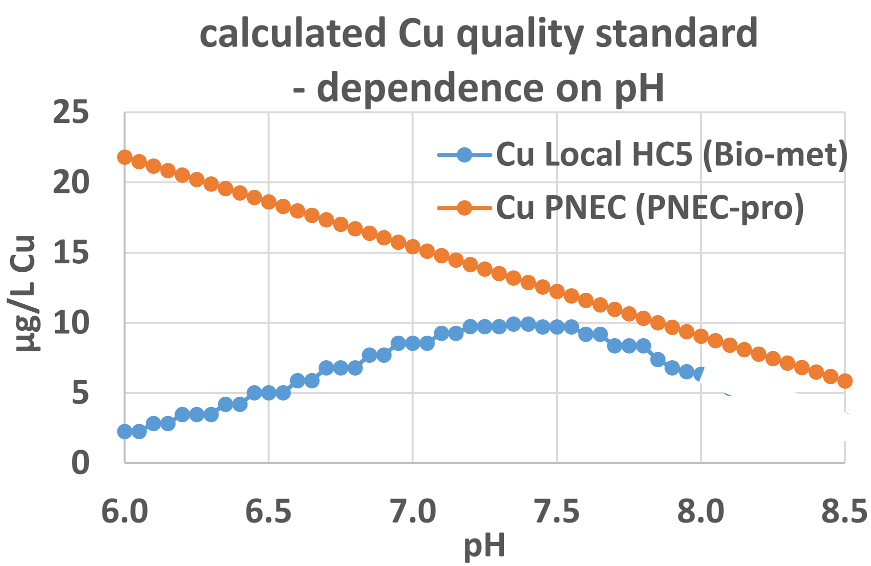
Comparison PNEC-pro / Bio-met for copper: influence of DOC, pH, hardness







- **DOC: higher Cu-QS at increasing DOC; steeper increase for Bio-met**
- **Ca: for PNEC-pro Cu-QS decreases sharply with increasing Ca levels; only slight decrease of Cu-QS for Bio-met**
- **pH: clear decrease of Cu-QS with increasing pH for PNEC-pro, increasing Cu-QS up to a maximum at about pH 7.3 for Bio-met**

Standard conditions:
40 mg/L Ca, 2.5 mg/L DOC, pH 7.6

Cu
Copper
29 63.546

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