Overview of the recommendations of the WG-EG-EQS (ISPRA) concerning environmental quality standards for metals in sediment

SedNet, May 2008

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On behalf of the WG-EG-EQS – metals subgroup and Eurometaux water working group
Content

- Can we set triggers on the need for sediment QC?
- Sediment PNEC setting -MERAG and EU RAs
- Incorporation of bioavailability
- Compliance checking
- Conclusions and future needs
Triggers for setting sediment QC

Principles:

Sediment Metal quality criteria are relevant, in addition to the setting of water quality criteria IF the QC set for the water would not protect benthic organisms appropriately. The following aspect are therefore relevant to assess the need for sediment QC:

- What is the mode of action – gill binding?
- What is the most relevant toxicity route (water and/or food)?
- Is there evidence of toxicity from dietary exposure beyond what is observed from water exposure?
- What integrated toxicity can be expected?
Sediment PNEC setting
Weight of evidence approach

1. Direct sediment ecotoxicity

2. Equilibrium partitioning

3. Mesocosm
   Field data
Derivation of a PNEC sediment

1. Whole sediment toxicity tests-

Q1 data set (# NOECs = 95), 6 species

- **Surface deposit feeders**
  - crustaceans
    - Hyallela azteca
  - Gammarus pulex

- **Sub-surface feeders**
  - oligochaetes
    - Tubifex tubifex

- **Burrowing & surface/sub-surface feeding**
  - insects
    - Chironomus riparius
  - Lumbriculus variegatus
  - Hexagenia

Representativeness
Issues in sediment ecotoxicity: Intra-species variability in NOECs (mg Me/kg dry weight)

Sediments have large variation in characteristics: e.g., OC and sulphide content

Ensure appropriate pre-equilibration and evaluate water column metal toxicity

<table>
<thead>
<tr>
<th>Species</th>
<th>Max/Min ratio growth</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>T. tubifex</em></td>
<td>101</td>
</tr>
<tr>
<td><em>H. azteca</em></td>
<td>70</td>
</tr>
<tr>
<td><em>C. riparius</em></td>
<td>26</td>
</tr>
</tbody>
</table>

Ensure appropriate pre-equilibration and evaluate water column metal toxicity
Metal bioavailability
a. Principle of MeS binding

Different metal species

Water phase

Oxic Layer

Me2+

Me- OC

Sediment phase

Anoxic Layer

MeS

1M HCl extraction

SEM (Simultaneously Extracted Metals) + AVS (Acid Volatile Sulfide)

\[ \Sigma SEM = SEM_{Cu} + SEM_{Pb} + SEM_{Cd} + SEM_{Zn} + SEM_{Ni} \] (AVS affinity Hg > Cu > Pb > Cd > Zn > Ni)

Excess SEM\textsubscript{Cu} = SEM\textsubscript{Cu} - (AVS total - SEM\textsubscript{Hg}) \rightarrow potentially bioavailable

MnO, FeO...
Effectiveness of Me- binding to AVS

Basic concept

“Me++ bound to sulphides are not available”

= accepted under MERAG & RAs (Zn, Cd, Cu, Ni, Pb)

Di Toro et al, 2002
Metal bioavailability
b. Importance of to OC

Different metal species

Water phase

<table>
<thead>
<tr>
<th>Sediment phase</th>
<th>Oxic Layer</th>
<th>Me$^{2+}$</th>
<th>Me- OC</th>
<th>Mineral bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anoxic Layer</td>
<td>MeS</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Metal bound
Effectiveness of OC binding

Influence OC on ecotoxicity

Variability in EC-50 values, obtained from benthic ecotox tests in different sediments

<table>
<thead>
<tr>
<th>Species</th>
<th>Total Cu (mg/kg)</th>
<th>OC-normalized Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EC₅₀ ratio</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mean</td>
<td>range</td>
</tr>
<tr>
<td>Tubifex</td>
<td>2.4</td>
<td>2.2-2.8</td>
</tr>
<tr>
<td>Hyalella</td>
<td>3.3</td>
<td>-</td>
</tr>
<tr>
<td>Chironomus</td>
<td>6.2</td>
<td>4.7-7.7</td>
</tr>
<tr>
<td>Overall</td>
<td>4</td>
<td>2.2-7.7</td>
</tr>
</tbody>
</table>

De Schamphelaere et al, 2004

\[ \text{NOEC}_{OC, \text{normalized}} = \frac{\text{NOEC}_{\text{total}}}{fOC} \]

Suggested under MERAG and accepted for the Cu RA
Metal bioavailability

c. Importance of MnO, FeO...

Different metal species

Water phase

Me^2+

Me- OC

Mineral bound

Sediment phase

Oxic Layer

Me^2+

MeS

Anoxic Layer

MnO, FeO... = future research needs
Derivation of a PNEC sediment
Whole sediment toxicity tests

- NOEC total – mg/kd dry weight
  ➔ NOEC-AVS corrected - mg/kd dry weight
  ➔ NOEC/OC – mg/kg OC
  ➔ PNEC – mg/kg OC
    Based on lowest NOEC/SSD and AF

EU Natl Local

Bioavailability
Derivation of a PNEC sediment
Whole sed tests- Data-rich metals

Log normal HC5-50 sed (benthic SSD)
= 1741 (1112-2071) mg Cu/kg OC
Sediment PNEC setting
Weight of evidence approach

- Equilibrium partitioning
- Direct sediment ecotoxicity
- Mesocosm
  Field data
Derivation of a PNEC sediment

2. Equilibrium partitioning method

Basic Principle

\[ PNEC_{\text{sed}} (\text{mg kg}^{-1}) = PNEC_{\text{fw}} (\text{mg l}^{-1}) \times Kd (\text{l kg}^{-1}) \]

PNEC total – mg/kd dry weight

\[ PNEC_{\text{EqP/OC}} (\text{mg/kg OC}) \]

PNEC total – mg/kd dry weight

\[ PNEC_{\text{sed}} (\text{mg kg}^{-1}) = PNEC_{\text{fw}} (\text{mg l}^{-1}) \times Kd (\text{l kg}^{-1}) \]

\[ Kd (\text{l kg}^{-1}) : \text{Wham defined} \]
Derivation of a PNEC sediment
3. Field data and WOE

- PNEC - Equilibrium partitioning
- PNEC- Direct sediment ecotoxicity
- Mesocosm studies
  Field data

Background
AF need
Metal compliance checking

\[ RCR = \frac{PEC_{AVS\text{OC}}}{PNEC_{AVS\text{OC}}} \]

- \( T_{OX_{\text{total}}} \)
- \( C_{\text{SED}} \)
- \( T_{OX_{AVS\text{OC}}} \text{ normalized} \)
- \( C_{AVS\text{OC}} \text{ normalized} \)
- \( PNEC_{AVS\text{OC}} \text{ normalized} \)
- \( PEC_{AVS\text{OC}} \text{ normalized} \)

Metal compliance checking includes EU, Natl, and Local regulations.
Conclusions and Future needs

Metals SQC may be needed for metals, passing the trigger criteria

Draft proposal metal EQS is based on metal RARs and MERAG and includes
- A weight of evidence approach
- Bioavailability corrections - AVS and OC

Further discussion of the proposal by the WG-EF-EQS

Further research on metal binding to FeO, MnO... and its influence on ecotoxicity

Refined monitoring: including measurements of AVS, OC...

Possibility for integrated field assessment