The art of monitoring metals: pitfalls and remedies

Frank Van Assche
Director, European Affairs
International Zinc Association
168, Avenue de Tervuren
B-1150 Brussels
Belgium
Zinc...essential for life

All starts with measuring metals (e.g. in water)
All starts with measuring metals (in water)

measured dissolved metal concentrations
pitfalls

• Sampling procedure
• Contamination of samples
• LOD/LOQ
1. Sampling for the dissolved metal concentration

- CIS for WFD, guidance doc 19:
  - « The EQS for metals refers to the dissolved concentration...obtained by filtration on a 0.45µm filter »
  - « The filtrate shall be acidified with nitric acid to ensure pH <2 »

  - Focus on avoiding adsorption to the container
    - Can be prevented by acidifying the sample
    - But solubilisation of (...metal) has to be avoided
    - Therefore « analyse asap »....
  - no clear guidance of conditions for sampling for dissolved metals
  - ⇒ first stabilisation, then filtration...?
Zinc...essential for life

Measured metal depends on sampling approach

- Conservation acid after filtration
- Conservation acid before filtration after 24h
- Total metal after destruction with Aqua regia

Filter first, then stabilise
Contamination of water samples

- Metals are naturally present in soil, dust, air...
- Labware may contain significant amounts of metals that can leach into the sample, e.g.:
  - filter material, rubber stoppers, tubes; plastic syringes, valves, beakers; lab gloves (talcum powder!)

- E.g.: % of cases where $[\text{Me}]_{\text{dissolved}} > [\text{Me}]_{\text{total}}$

<table>
<thead>
<tr>
<th>River province</th>
<th>Cu</th>
<th>Zn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dommel</td>
<td>26</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Regge &amp; Dinkel</td>
<td>14</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>Schieland</td>
<td>34</td>
<td>21</td>
<td>50</td>
</tr>
</tbody>
</table>

(after Zwolsman & De Schamphelaere 2007)
Attention points, e.g.:

- use of rigorously cleaned material
- field rinsing of equipment used to collect samples
- proper handling of equipment and samples,
- routine collection of samples for quality-control
- Field personnel trained in the implementation of good field practices.

 altijd include distilled water blancs
LOQ versus EQS

• LOQ vary strongly between countries/labs
  – can even vary within 1 country
• LOQ/2 can be >> EQS
• E.g.: country dataset 2012, 73 sampling points
  – Dissolved concentrations measured
  – EQS$_{Zn}$: 10.9 µg/l (+BG)
  – 35/73: PEC < EQS
  – 38/73: PEC > EQS
    • At 23 locations LOQ = 50 or 75 µg/l ⇒ LOQ/2 > EQS
    • 8 locations LOQ = 10 µg/l
• ⇒ Relevancy of data where LOQ/2 > EQS ??