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Incorporation of Metal Bioavailability into the EU Risk Assessment Framework and Significance of Sediments

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Science, policy, and trends of metals risk assessment at EPA: How understanding metals bioavailability has changed metals risk assessment at US EPA

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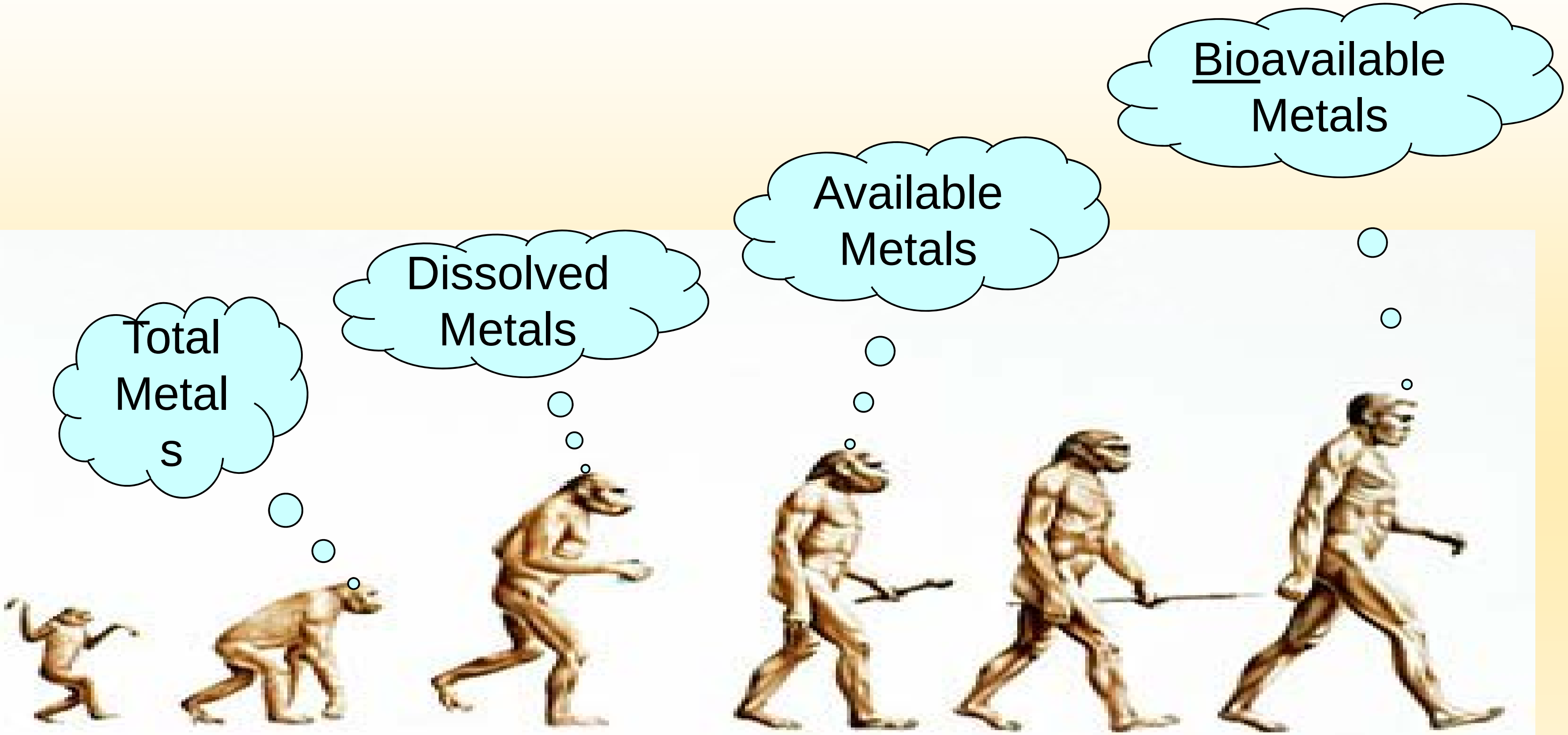
Evolution of Metal Risk Assessment



Bioavailability is key to understand the possible ecological impact!

Metal speciation

Accumulation of lead by freshwater algae 201

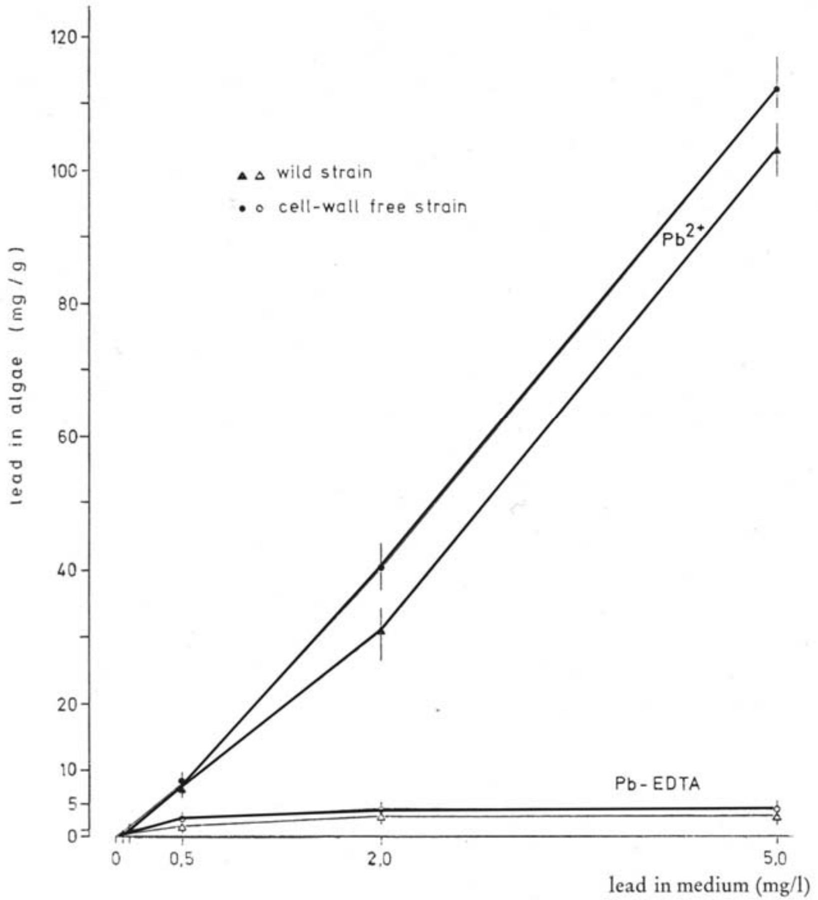


Fig. 2: Relation between lead concentration in the medium (added as Pb^{2+} or Pb-EDTA) and accumulation by *Chlamydomonas reinhardii* after 24 h incubation, pH = 6,6.

The presence of the hydrophilic complexing agent EDTA in water reduces the equilibrium of free Pb2+ ions, with a corresponding decrease in the metal uptake rate.

Chemical activity is a property of the pollutant rather than of the sorbent

Ahlf, Irmer & Weber, 1980

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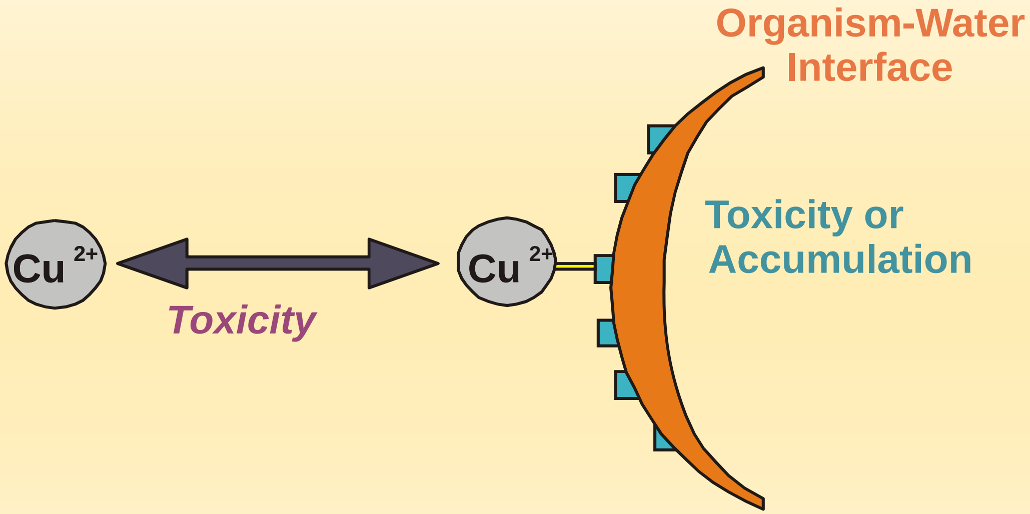
Model: FIAM (free ion activity model)



Gill Site Interaction Model (Pagenkopf, 1983)

Katrien Delbeke, ECI

New equilibria in estuaries

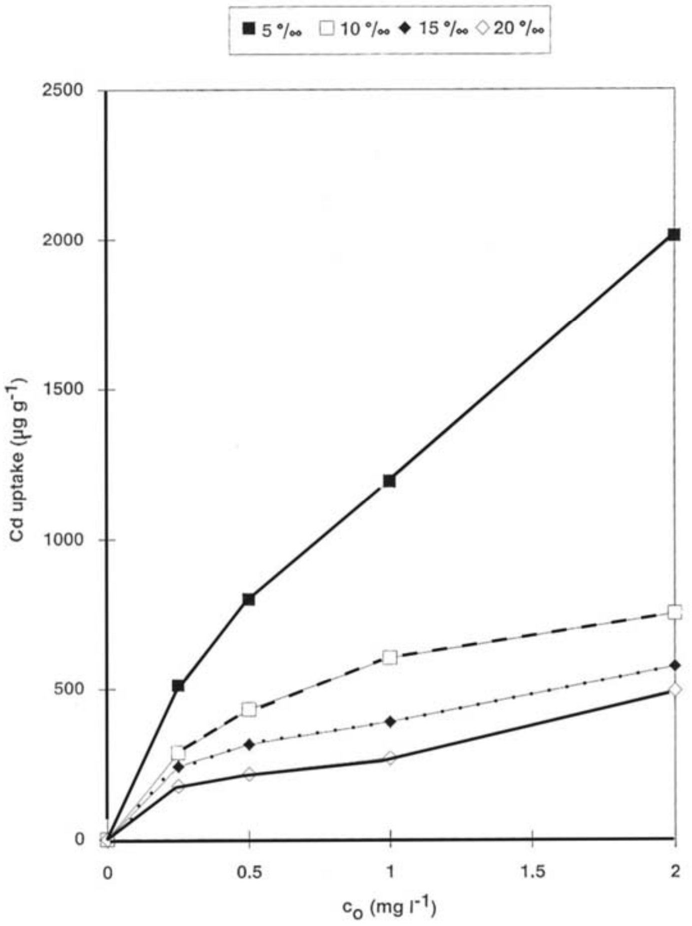


Fig. 6. Sorption of Cd^{2+} on *Brachiomonas submarina* at different salinities.

Table 2. Calculated Cd-species distribution [%] at different salinities.

Cd^{2+}	19.63	11.43	7.65	5.41
$[CdCl]^{+}$	65.46	61.97	55.95	49.71
$[CdCl_2]$	13.74	22.15	29.40	33.44
$[CdCl_3]^{-}$	0.72	2.37	4.42	6.56
$[CdCl_4]^{2-}$	0.12	0.84	2.39	4.72
[CdCl(OH)]	0.21	0.19	0.17	0.15
Positively charged species	85.1	73.4	63.6	55.1
Neutral or negatively charged species	14.9	26.6	36.4	44.9

Calmano, Ahlf, Bening, 1992

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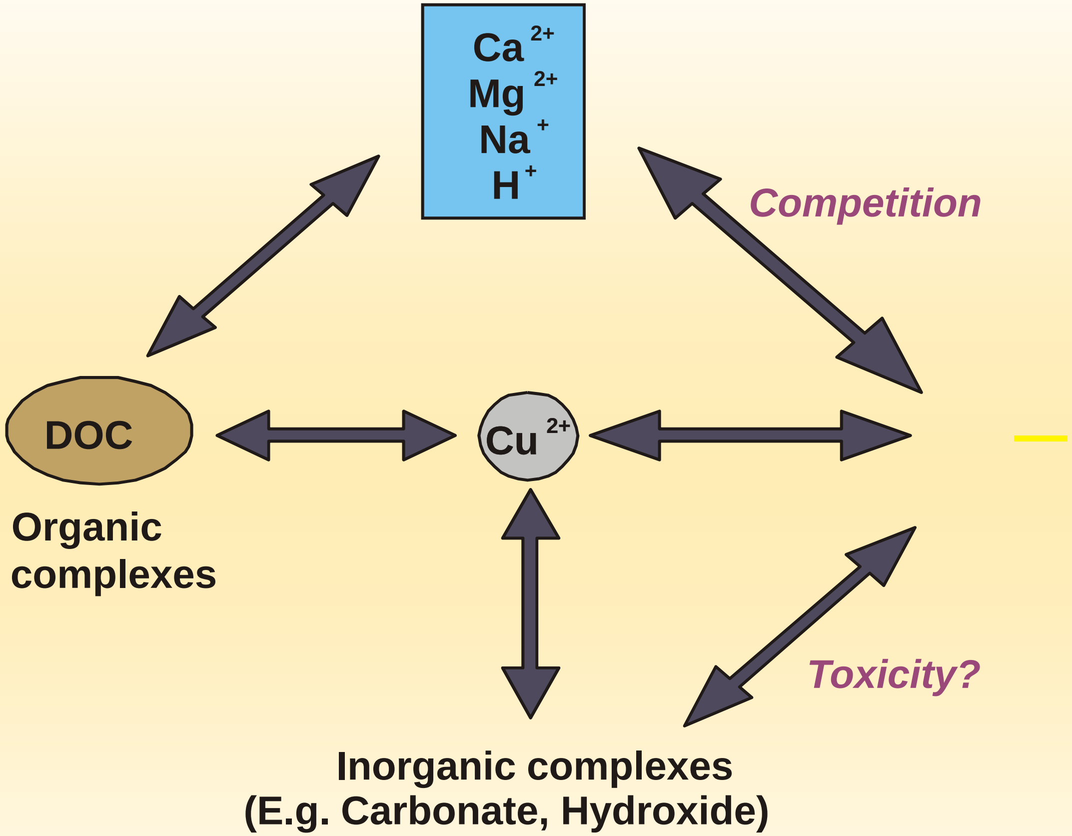
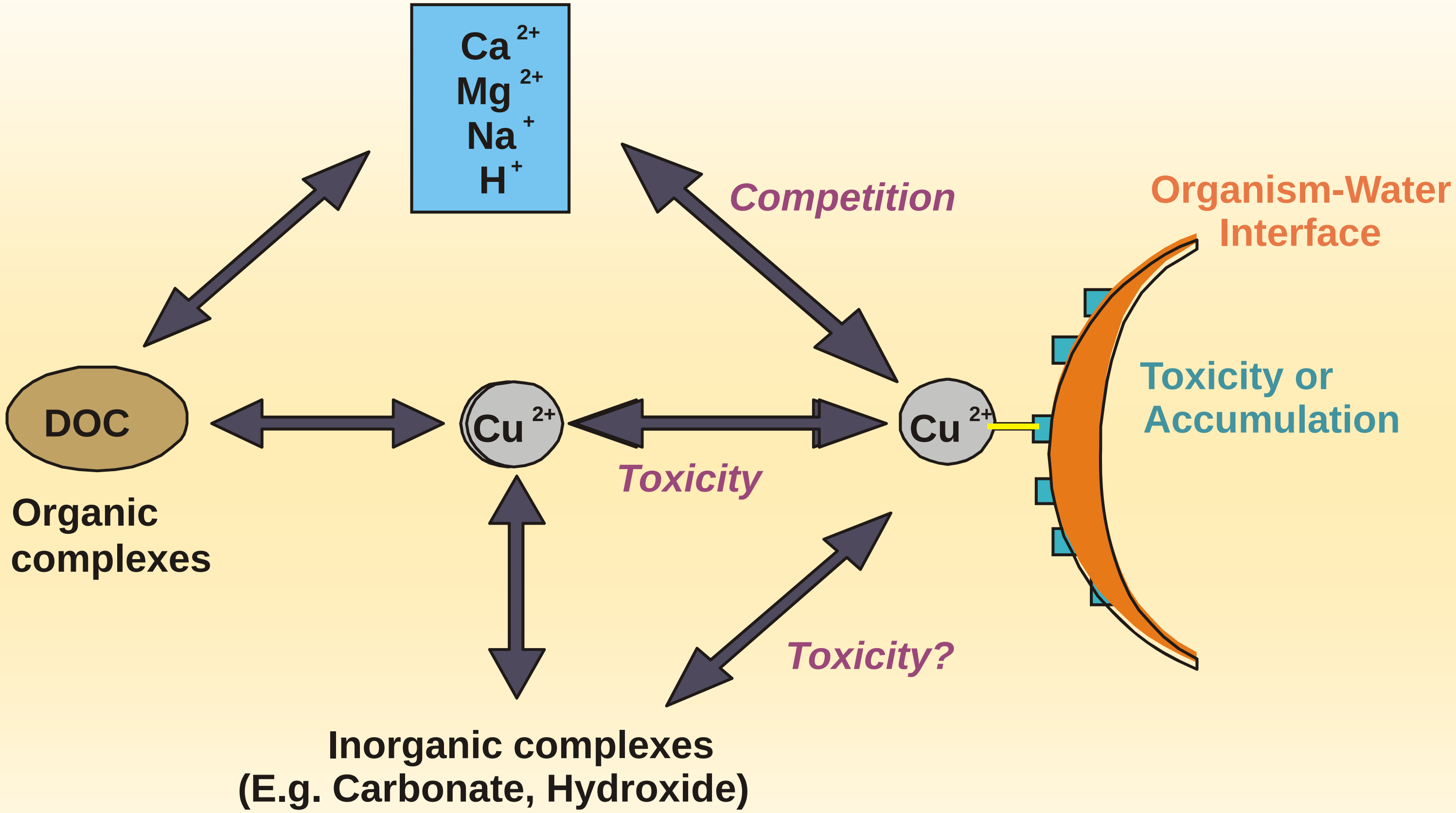
Model: WHAM (Windermere humic aqueous model)



WHAM
(Tipping, 1994)

Model: WHAM (Windermere humic aqueous model)



WHAM
(Tipping, 1994)

Gill Site Interaction Model
(Pagenkopf, 1983)

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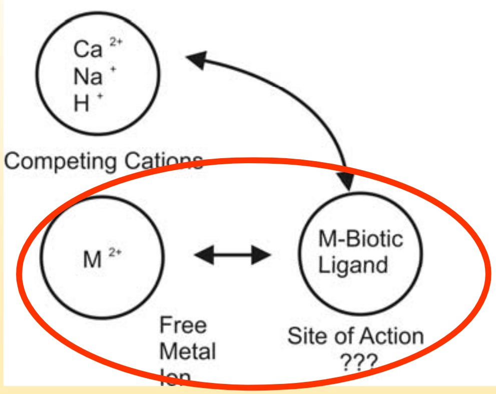
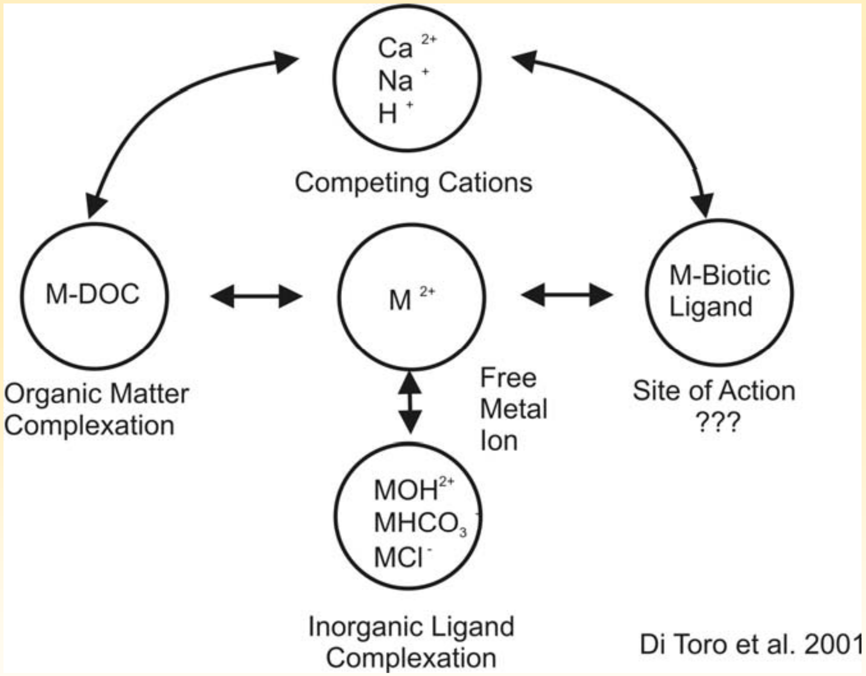
BLM - Biotic Ligand Model

The bioavailable form of metals is the free ion



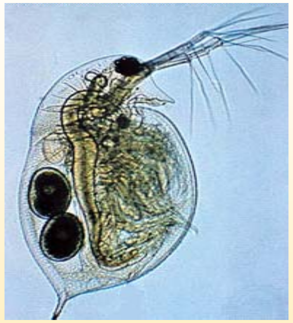
Equilibrium exists between the free metal ions in solution and the metal ions bound to transport "ligands"

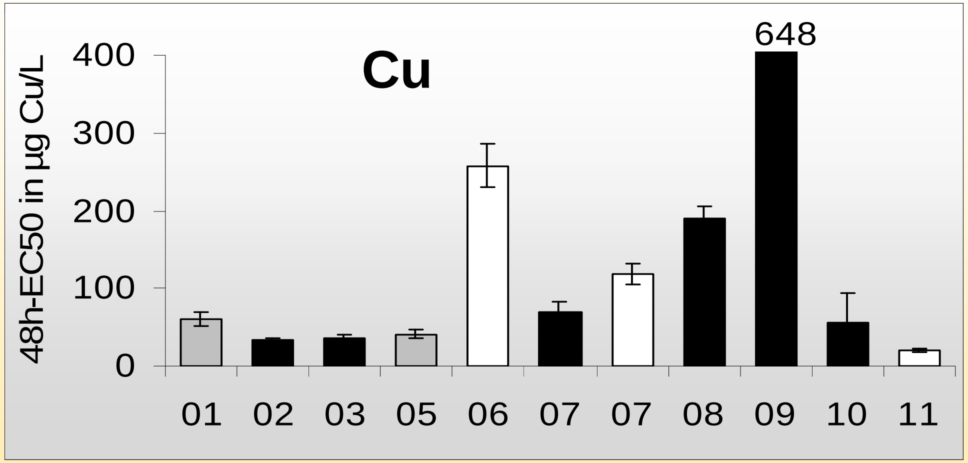
The only role of ligands in solution is to complex metals and decreasing the equilibrium concentration of surface-bound metal

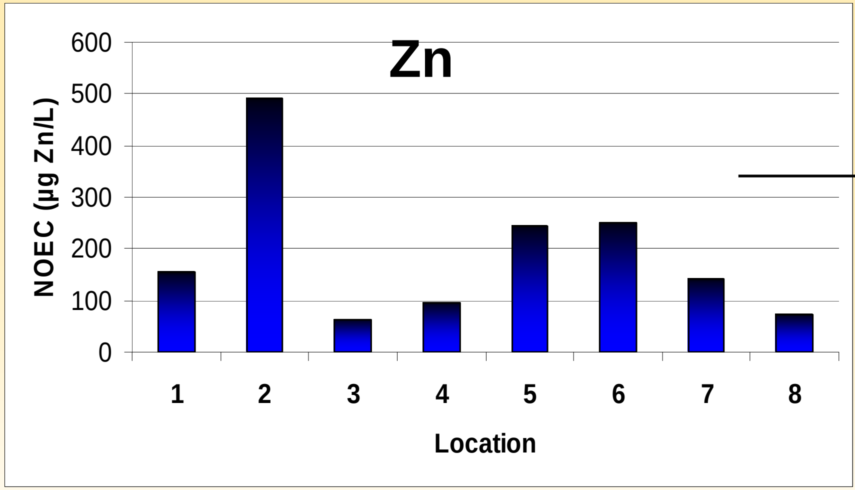


The model predicts that the formation of complexes in solution will reduce trace metal uptake and thus reduce metal bioavailability!

Why it is useful to consider bioavailabilty in metal RA?







Site-specific toxicity for Cu and Zn varies up to a factor of 50

Toxicity of metals ~ water chemistry & biology

Katrien Delbeke, ECI, Frank Van Assche ,IZA- Europe

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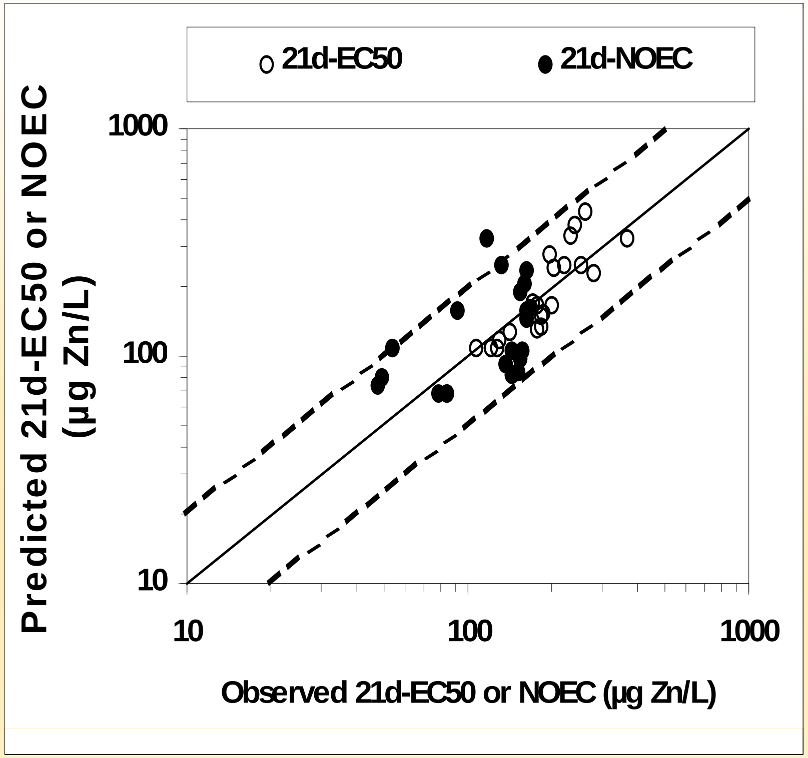
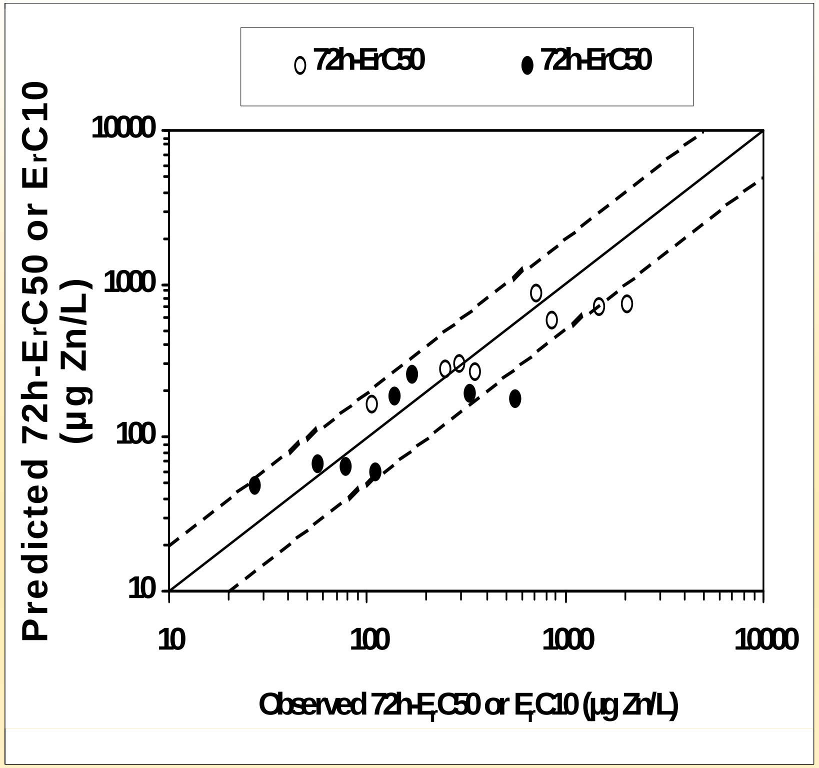
BLM toxicity prediction from water characteristics





Daphnids

toxicity predicted within factor 2

Algae

toxicity predicted within factor 2

Normalisation = reduction of the variability

Katrien Delbeke, ECI

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Use of bioavailability in EU regulations

- **For several metals, EU risk assessments have been made**
  - Approved data sets are available
  - RA data sets checked for quality and relevancy

⇨ Corrections for metal bioavailability have been applied for

- Cd : Hardness correction on dissolved metal concentrations

- Zn, Ni, Cu : BLM correction on dissolved metal concentrations

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European Regulation

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sediment

EU-Waterframework Directive:

- ecological approach
- water catchment areas
- aim: good status of waterbodies until 2015
- quality criteria for priority substances for waterphase, sediment and biota

REACH:

- Existing Substances Risk Assessment for the compartment sediment

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New equilibria in estuaries with suspended matter

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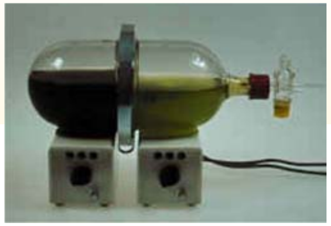

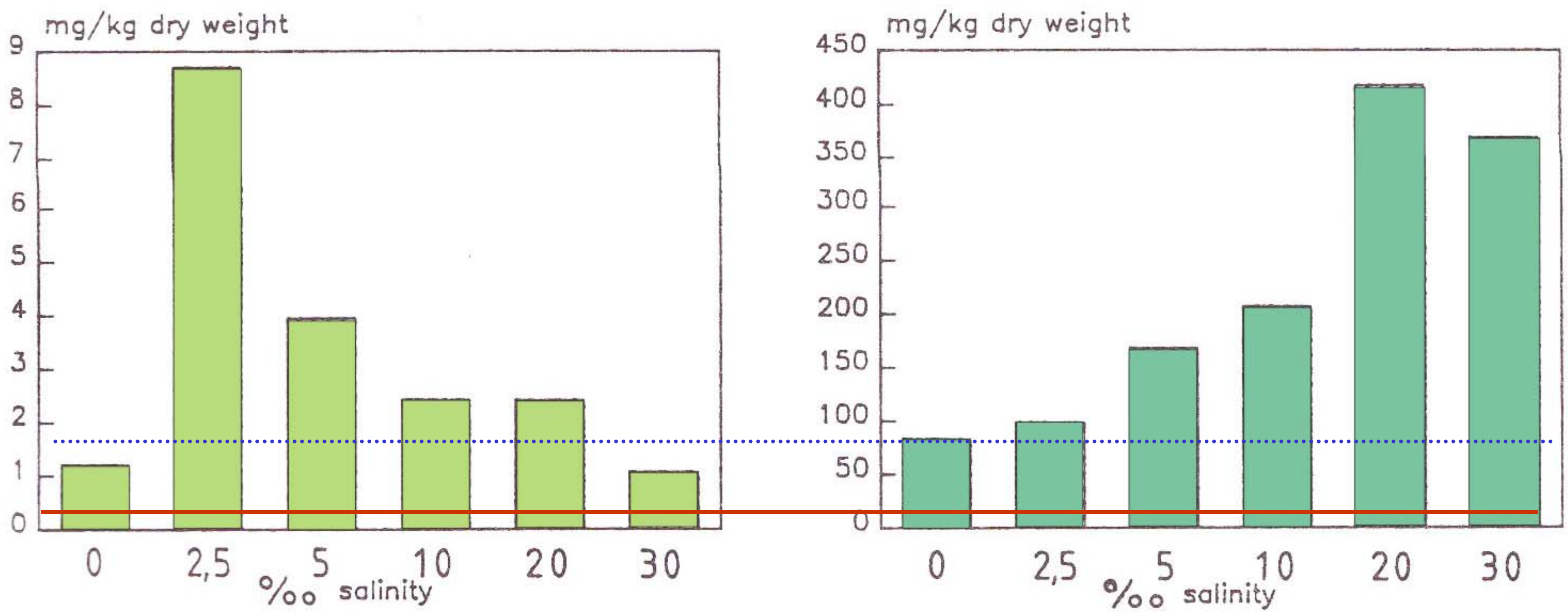

Fig. 7. Effect of salinity on metal contents in *Stichococcus bacillaris* grown for 96 h with resuspended sediment (Ahlf, 1987).

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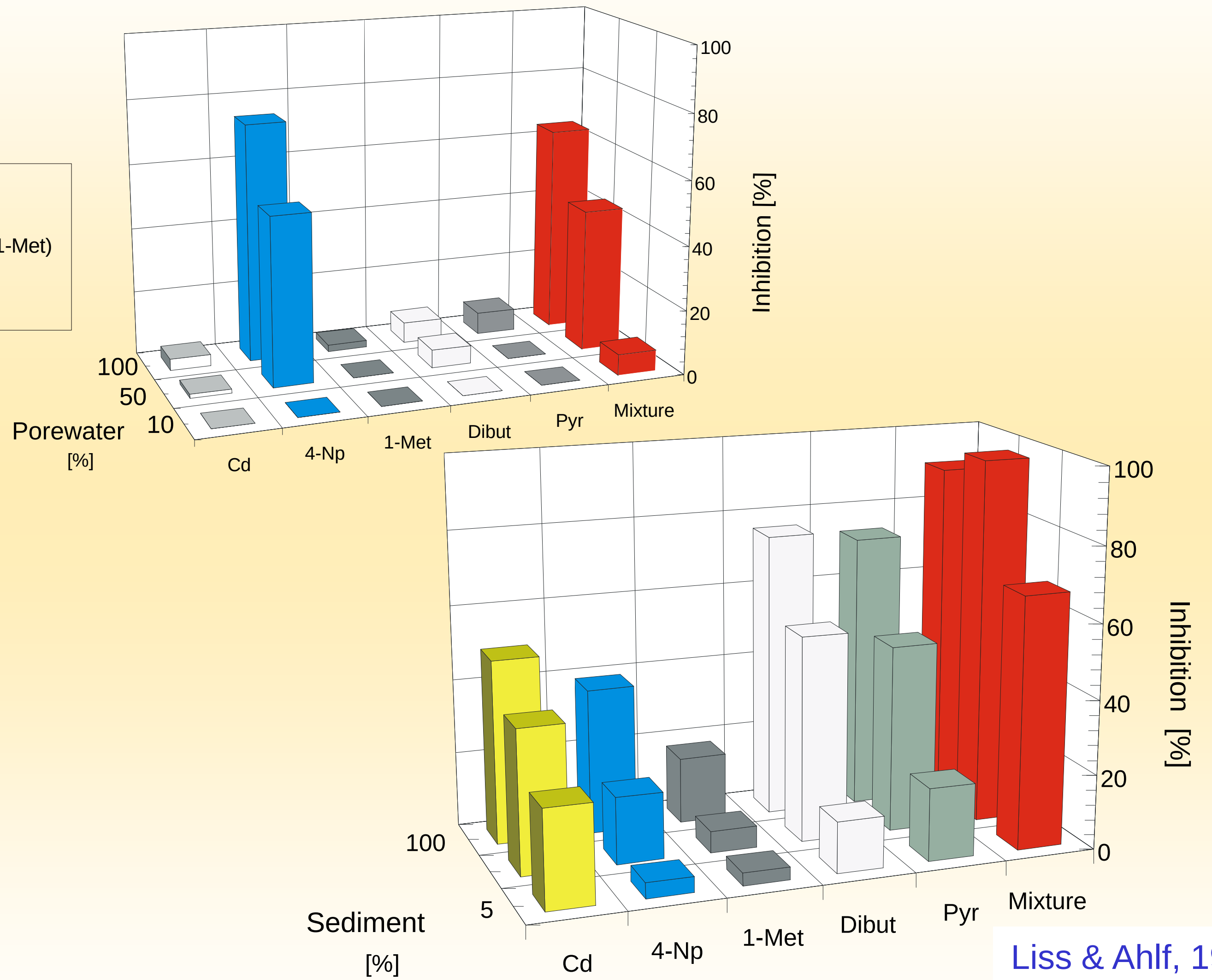
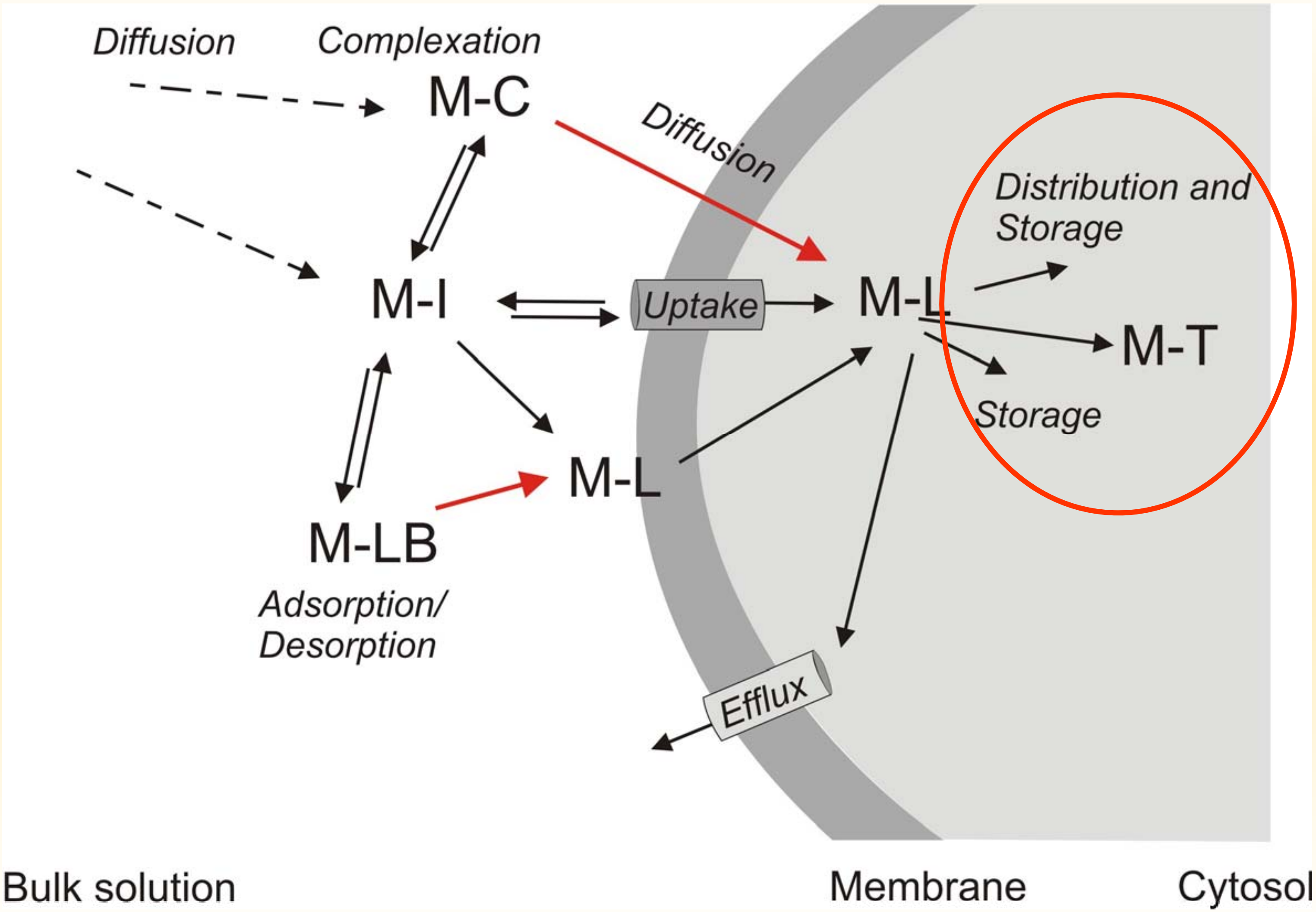
Effects of porewater and suspended sediment

Cadmiumnitrate (CD)
4-Nitrophenole (4-NP)
1-Methylnaphtalene (1-Met)
Dibutylphtalate(Dibut)
Pyrene (Pyr)

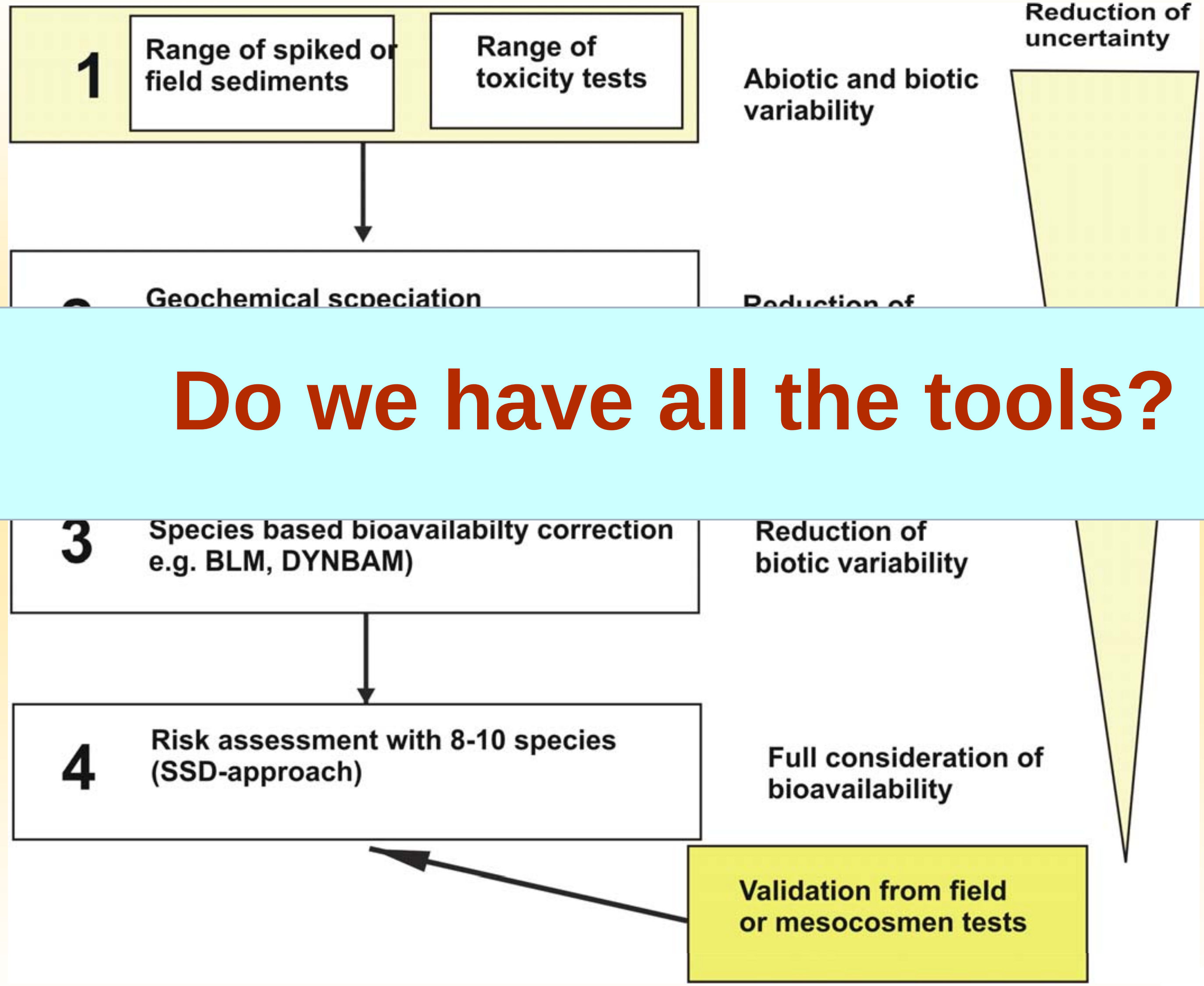


Liss & Ahlf, 1996

Uptake, retention and efflux of metals



Derivation of a PNEC$_{sediment}$



Do we have all the tools?

Do we have the tools? - spiking

Percentage of Cd- accumulation in *Macoma balthica* via sediment exposure

Sediment (µg/g)	Pore water (µg/L)	Kd (Kg/L)	% Cd
16 (dotiert)	2000	8	**0,8**
72 (dotiert)	1620	44,4	**4,3**
62,4 (dotiert)	2500	25	**2,4**
65,5 (dotiert)	800	81,9	**7,2**
10 (field test)	1	10.000	**90,9**

Schlekat & Luoma, 2000

SOP for a spiking procedure is lacking

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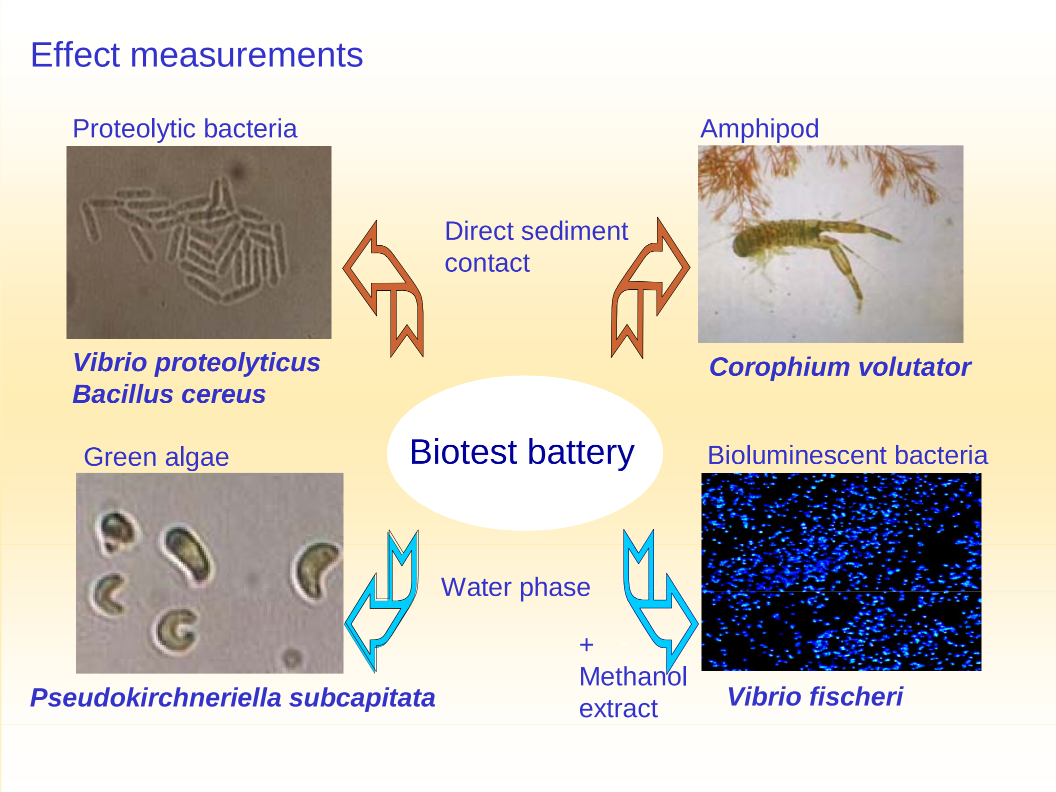
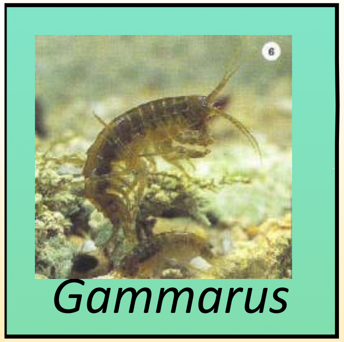
Do we have the tools? – standardized toxicity tests





Caenorhabditis elegans

The number of whole sediment tests is low!

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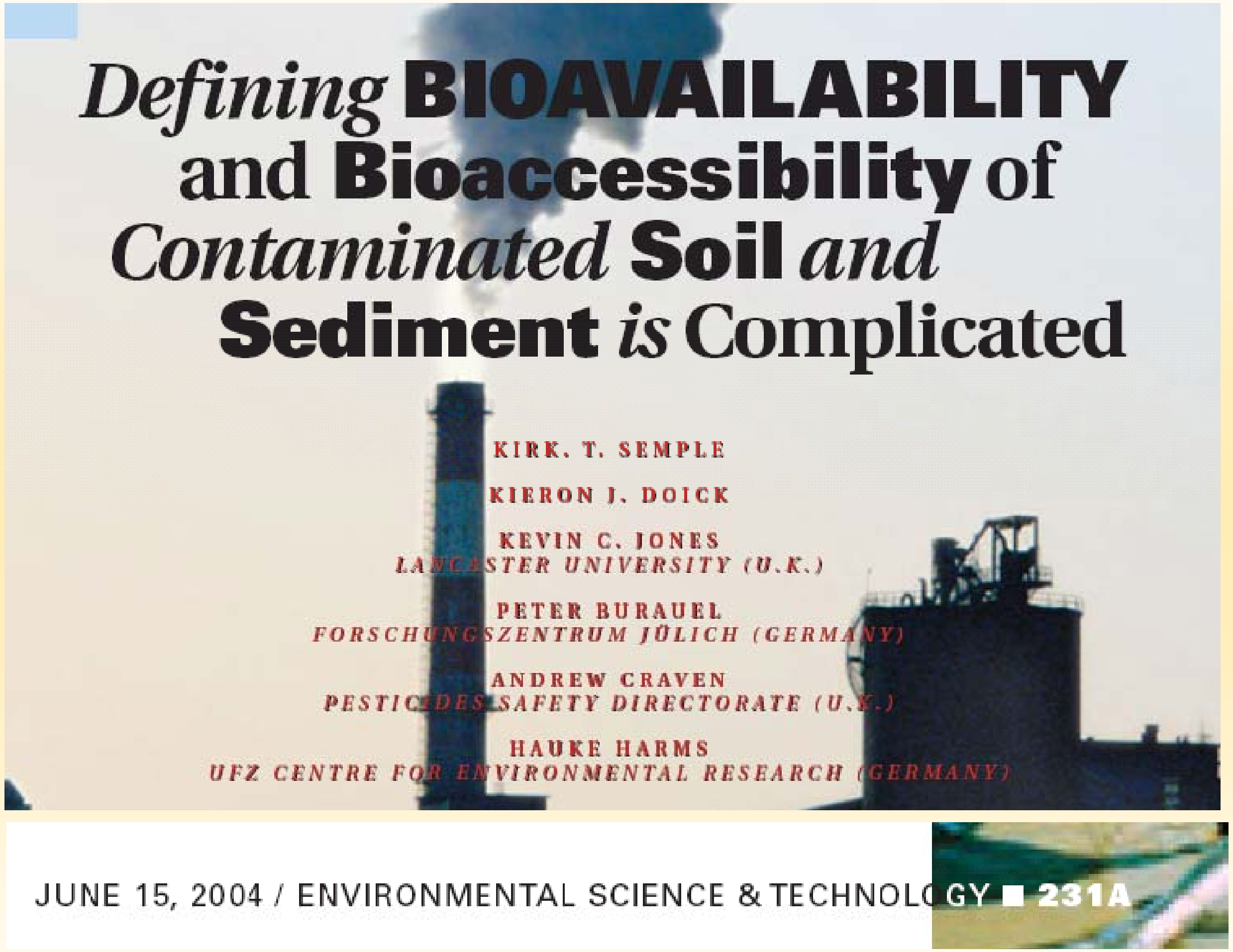
Conclusions

1. Bioavailability of metals is the key for understanding environmental impact, importance of toxicity tests has increased
2. Uncertainties of exposure predictions are reduced by geochemical analyis
3. Geochemical models are refined by (eco) toxicological studies
4. Tools have to be customized for the bioavailability concept

Thank you for attention!


Defining **BIOAVAILABILITY** and **Bioaccessibility** of *Contaminated* **Soil** *and* **Sediment** *is* Complicated

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