Taking metal bioavailability into account
- The concepts of the tiered approach

Metals in the Environment

Incorporation of

Metal Bioavailability into Regulatory Frameworks

Wiebke Drost, Federal Environment Agency, Dessau, Germany

Overview

I. Metal properties

II. Fate of metals in the environment

III. Environmental risk assessment of metals

IV. Biotic Ligand Model

V. SEM/AVS

VI. Risk Characterisation

VII. Questioning/Uncertainties

VIII. Conclusion

Metal properties

- occur naturally
- have been used for a long time (natural background, historical emission)
- some are essential
- excess metal is allways toxic
- can occur in different oxidation states, i.e. different properties (e.g. Cr(III) and Cr(VI))

Metal properties

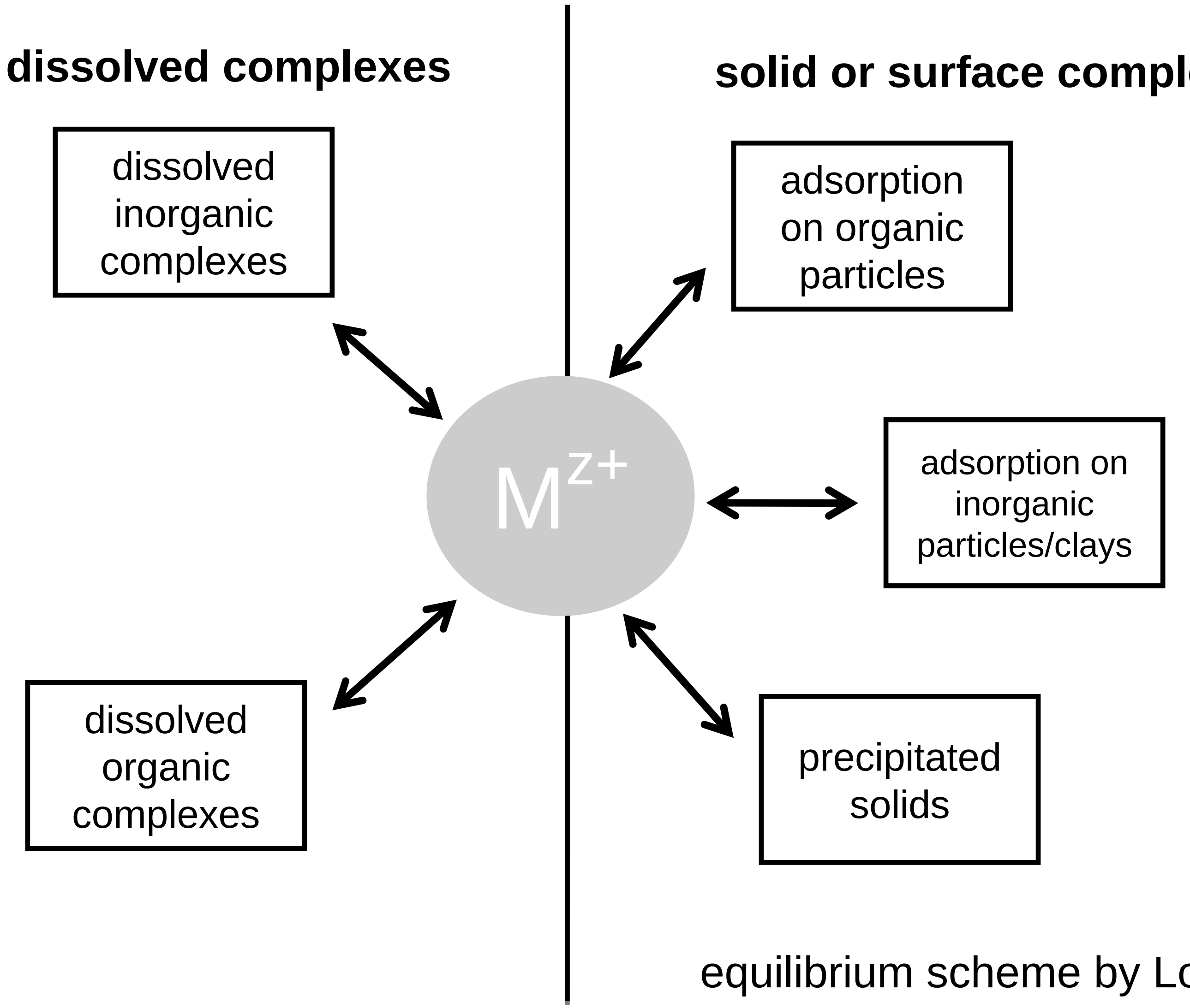
differences to organic compounds

- no abiotic or biotic degradation
- metals are persistent (some organic compounds are too)
- no vapour pressure
- no volatilisation
- No Log_{Kow} i.e. no lipophilie, no conclusions can be drawn on the bioaccumulation potential

Fate of metals in the environment

- can occur as dissolved free metal ions
- possible interaction with anions, cations, dissolved organic matter(DOM), minerals in soils and sediment
  - Precipitation
  - Complexation
  - Adsorption
- speciation of metals depends on environmental condition; pH, redox-condition, temperature, ionic strength, organic matter, clay content
- distribution of metals over solid and liquid phase, soil and sediment are metals sinks

Fate of metals in the environment



equilibrium scheme by Lofts and Tipping

Environmental risk assessment of metals

- due to their different properties there is a guidance document for metals
- R 7.13-2 Environmental risk assessment for metals and metal compounds

Environmental risk assessment of metals

- considers the bioavailbility
- risk assessment can be improved if there is knowledge on the uptake
- in order to be toxic a substance has to be taken up:

  nominal concentration

  bioavailable concentration

  internal concentration target

  site concentration

Environmental risk assessment of metals

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- guidance on metal risk assessment:
  - " only a fraction of the metal present in the environment may be available for biological uptake dependent on various biotic and abiotic parameters“
- Regarding the speciation of metals: what are the relevant bioavailable forms which can be taken up?

Problem concerning bioavailability

- What fraction? How large is this fraction? Which fraction is the most importent?
- What abiotic and biotic parameters are important in order to consider the bioavailability accuratly?

Biotic Ligand Model/ aquatic compartment

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- One approach given in the guidance is the Biotic Ligand Model (BLM).
- It is based on conceptual model similar to the gill surface interaction model by Pagenkopf.

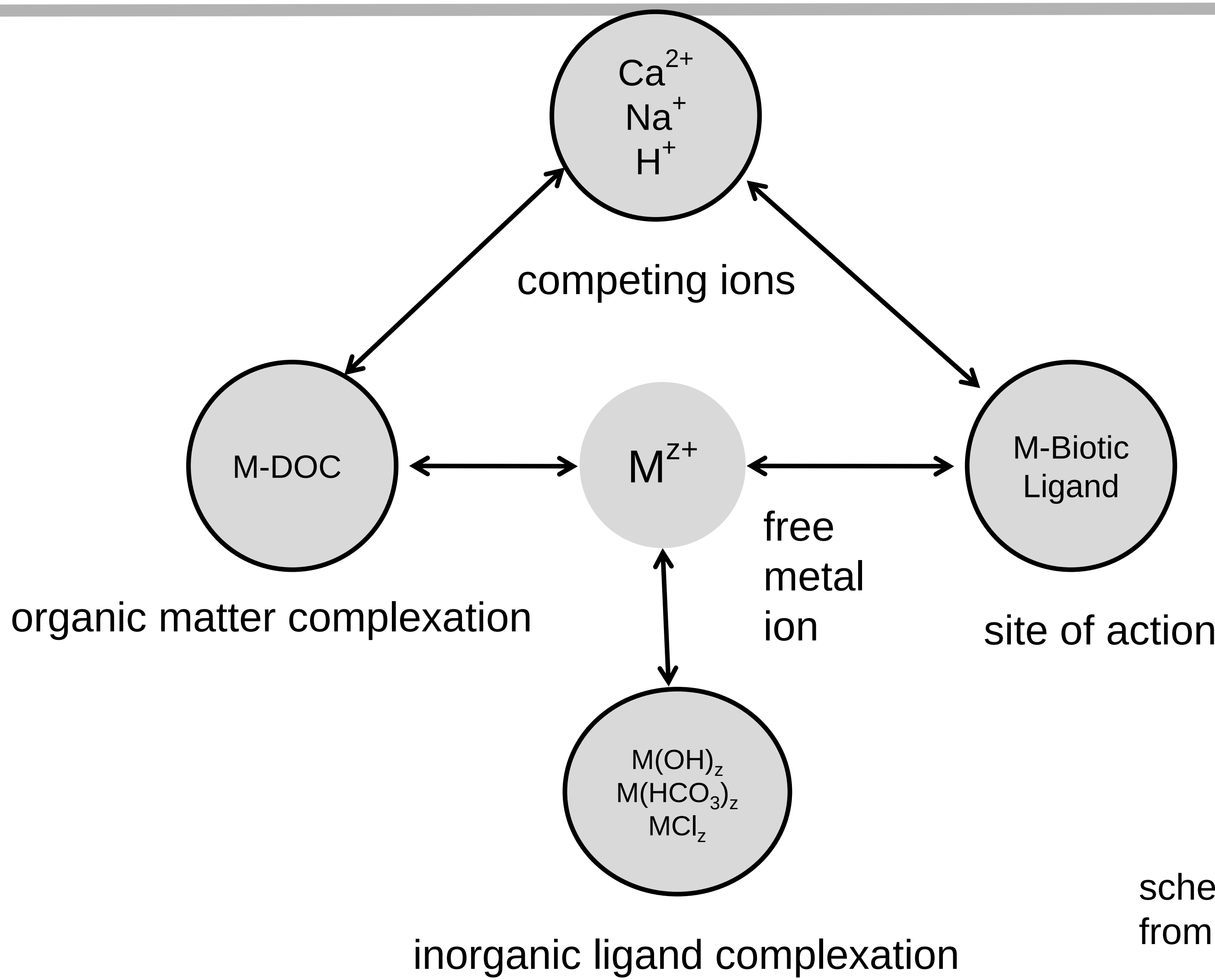
assumptions:

- free metal concentration is the most relevant for uptake
- competetive inhibition of binding to a ligand i.e. organism (fishgills) between metal and major cations
- binding to biotic ligand directly linked to toxic effect

development of a BLM

- has to be developed for each metal individually
- developed for different organisms; fish, daphnia, algea
- developed for different test durations; acute, chronic
- univariate testdesign, one ion at a time others constant
- combination of **speciation model** and **competition model**

Biotic Ligand Model



schematic diagram from Di Toro

normalization / sediment

- metals in sediments can interact with the clay, sulphide and organic matter
- organic carbon normalisation, if there is a linearity between toxicity and organic carbon content
- consideration of the fraction of metals which may bind to sulphides

SEM/AVS

- sulphides in anoxic sediment

assumptions

- activity of divalent metals (Zn, Cu, Pb, Cd…) is controlled by the binding as sulphides
- sulphur bound metals are not bioavailable i.e. not toxic

SEM/AVS

- AVS (acid volatile sulphides): sulphides which are extracted by cold extraction with 1 M HCl
- SEM (simultaneously extracted metals): those metals which are liberated under the conditions of the AVS analysis
- SEM/AVS= amount of excess metal which is not bound as sulphides

Aquatic compartment

- use of dissolved concentration
- use of physico-chemical speciation models
- use of a Biotic Ligand Model

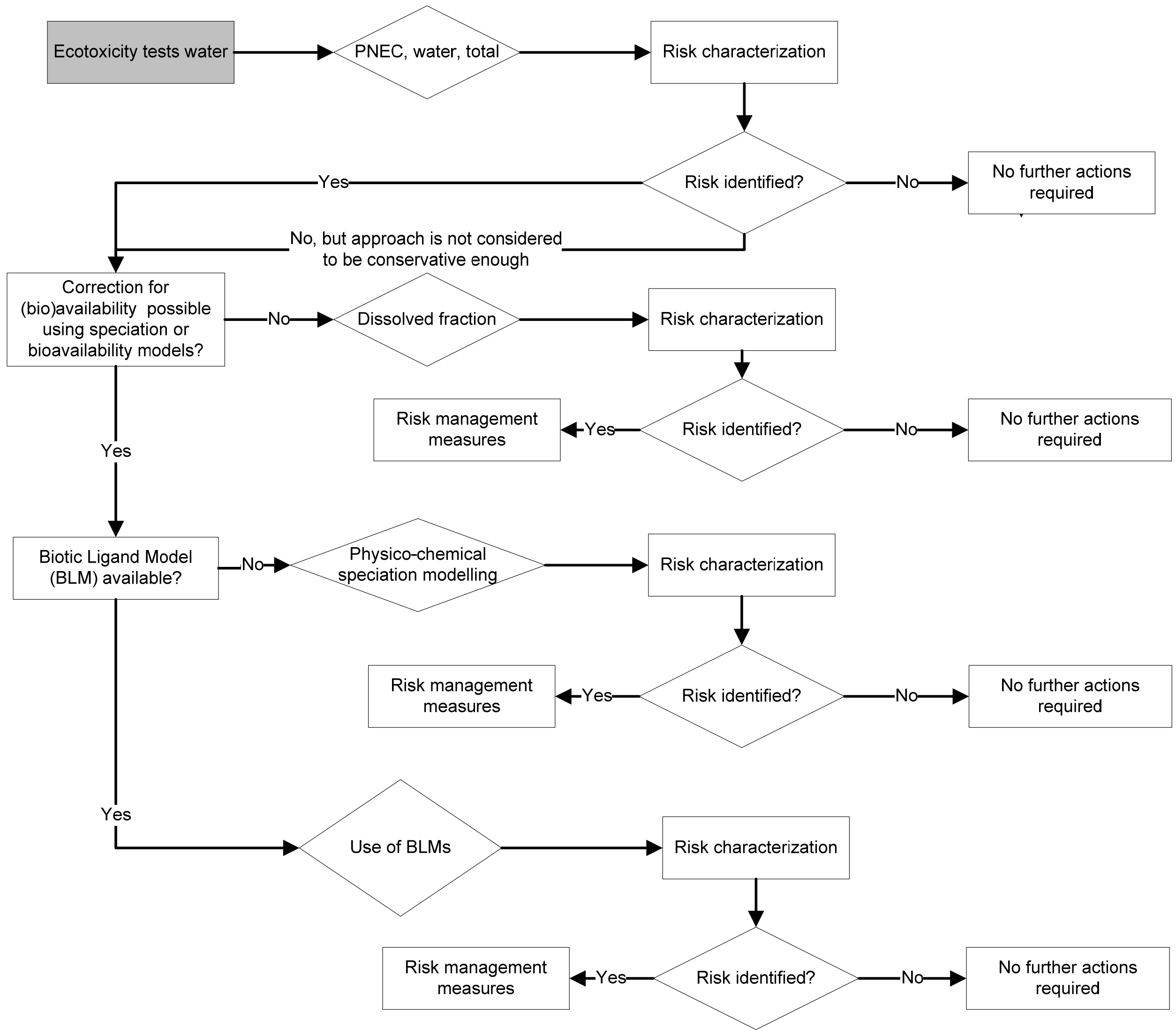
Sediment

- SEM/AVS and/or organic carbon

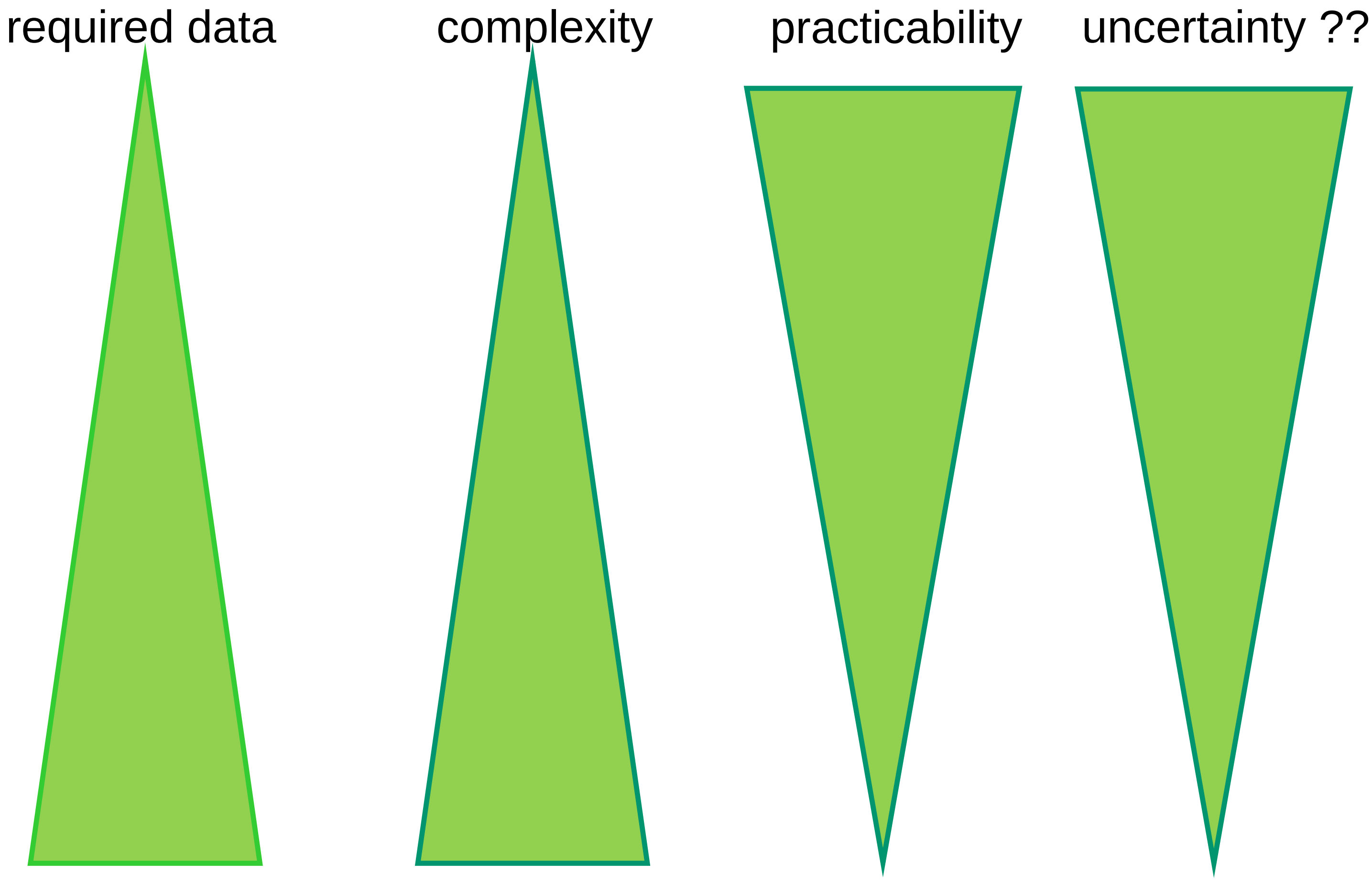
Risk characterization

- How many steps considering biotic and abiotic parameters taken into account depends on:
  - risk identification
  - availability of physico-chemical data
  - availability of a speciation or Biotic Ligand Model for the metal regarded

Risk characterisation



Questioning



Uncertainties

possible exposure pathways for metals

- dietary uptake of metals
- uptake of metals bound to particles
- uncertainty about waterborne versus dietary uptake, variability between different species

➡ free metal ion concentration is not allways the most important

Uncertainties

- aquatic systems are dynamic interaction between sediment, suspended matter with freshwater, porewater, non-equilibrium situation
- contaminant/particle interaction and can be superimposed by organisms' activity, like feeding or burrowing behaviour
- physico chemical parameters vary depending on time an site, can be influenced by organisms (pumping oxygene into anoxic sediment)

Uncertainties

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- What about metal mixtures? Influence on uptake?
- cation competition can also be anti-competitive, non competitive or mixed
- applicability of BLM to water with low ionic strength?

Conclusion

- The biovailability of metals is very complex.
- It depends on physico chemical parameters. How about feasability and reproducable monitoring?
- It depends on the biology e.g. feeding habits and behaviour.
- Considering the free metal ion concentration as the most important can be underestimative.

Thank you for your attention

Kontakt:

wiebke.drost@uba.de

Umweltbundesamt
Fachbereich IV Chemikaliensicherheit
Fachgebiet IV 2.3 Chemikalien
Wörlitzer Platz 1
06844 Dessau-Roßlau

Telefon: +49-340-2103-3112
Fax: +49-340-2104-3112