Metal Bioavailability
Critical Aspects

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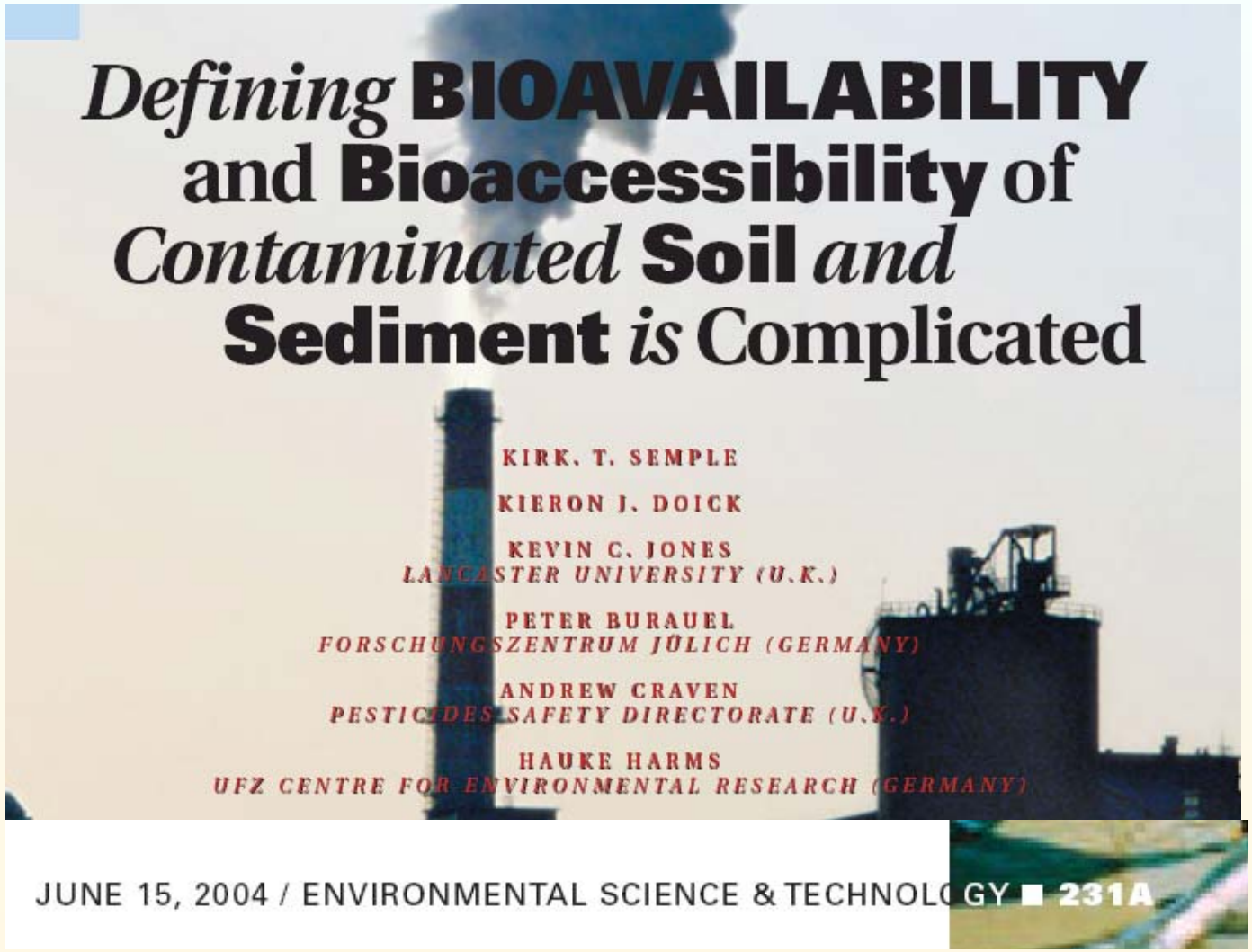
Introduction



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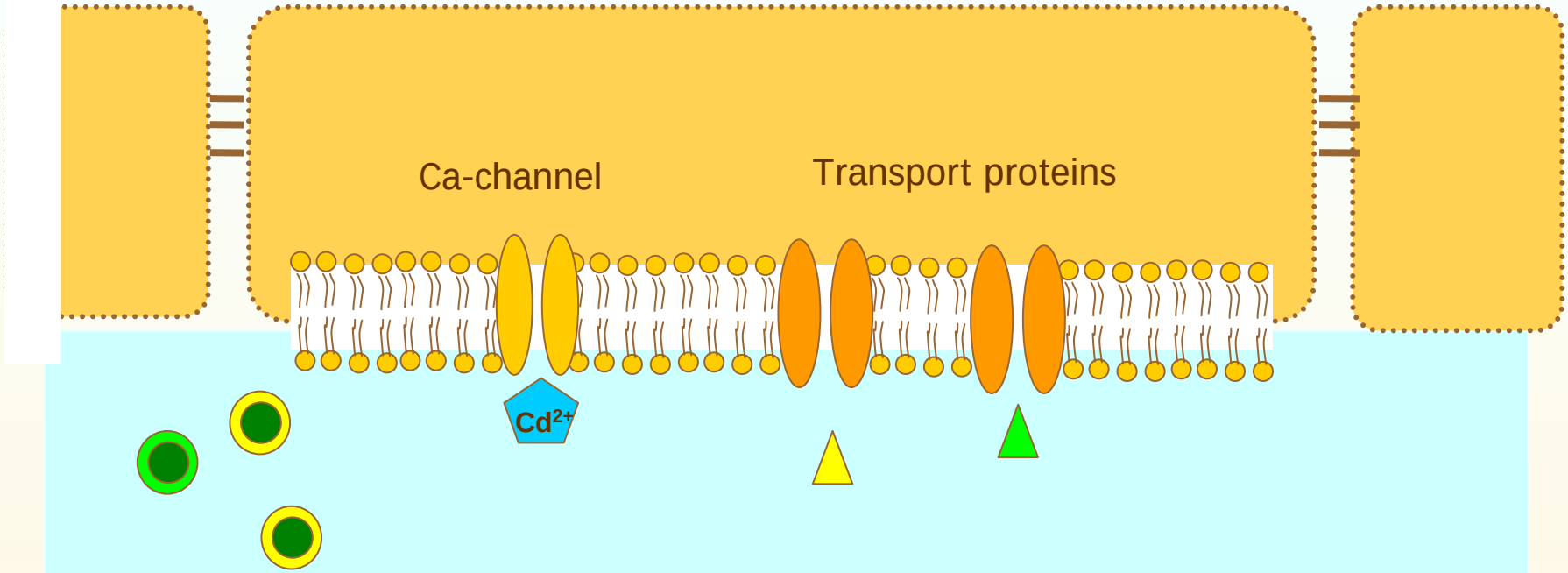
Uptake – membrane as barrier



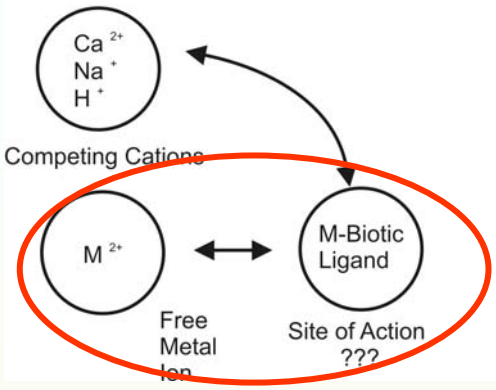
Water layer as diffusion barrier

1) Transport through protein channels down a concentration gradient

2) Carrier-mediated transport

BLM - assumptions

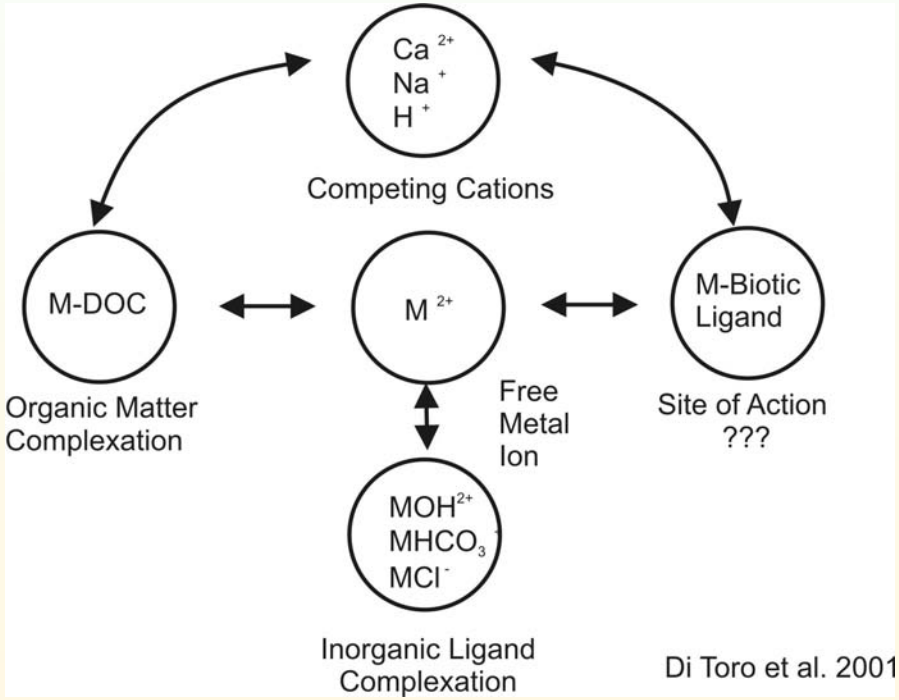
The bioavailable form of metals is the free ion



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



Di Toro et al. 2001

BLM - prediction

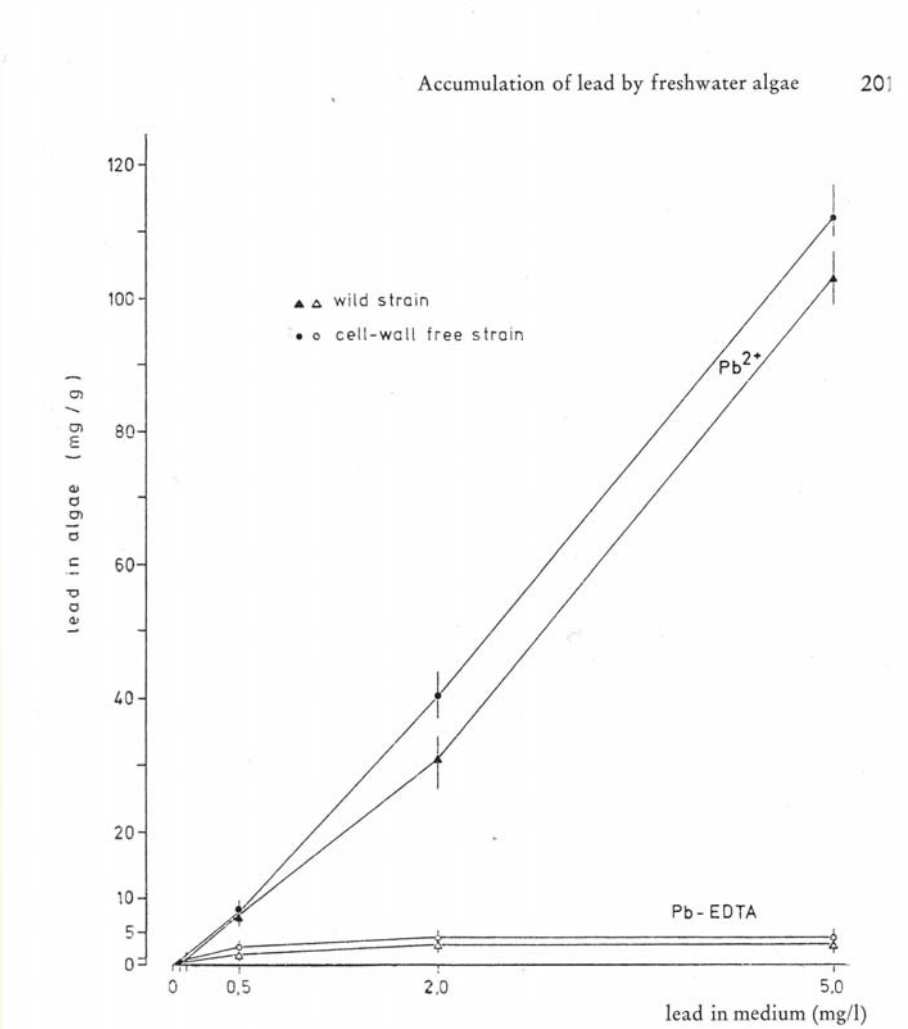


Fig. 2: Relation between lead concentration in the medium (added as Pb^{2+} or Pb-EDTA) and accumulation by *Chlamydomonas reinhardii* after 24 h incubation, pH = 6,6.

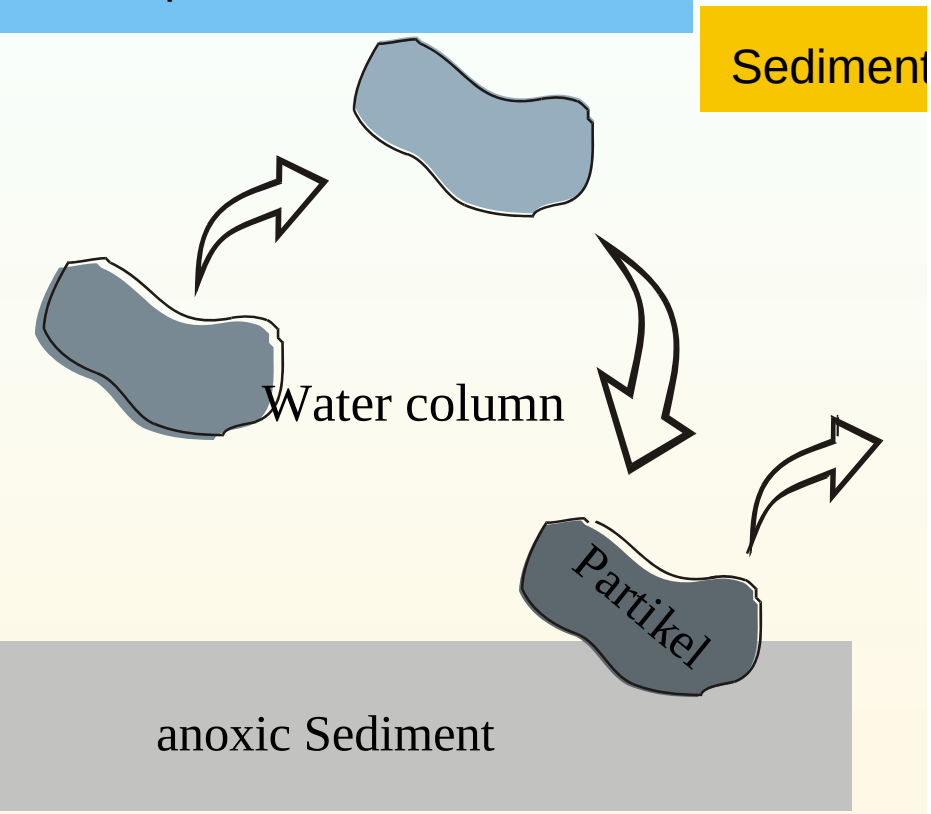
The presence of the hydrophilic complexing agent EDTA in water reduces the equilibrium of free Pb2+ ions, with a corresponding decrease in the metal uptake rate.

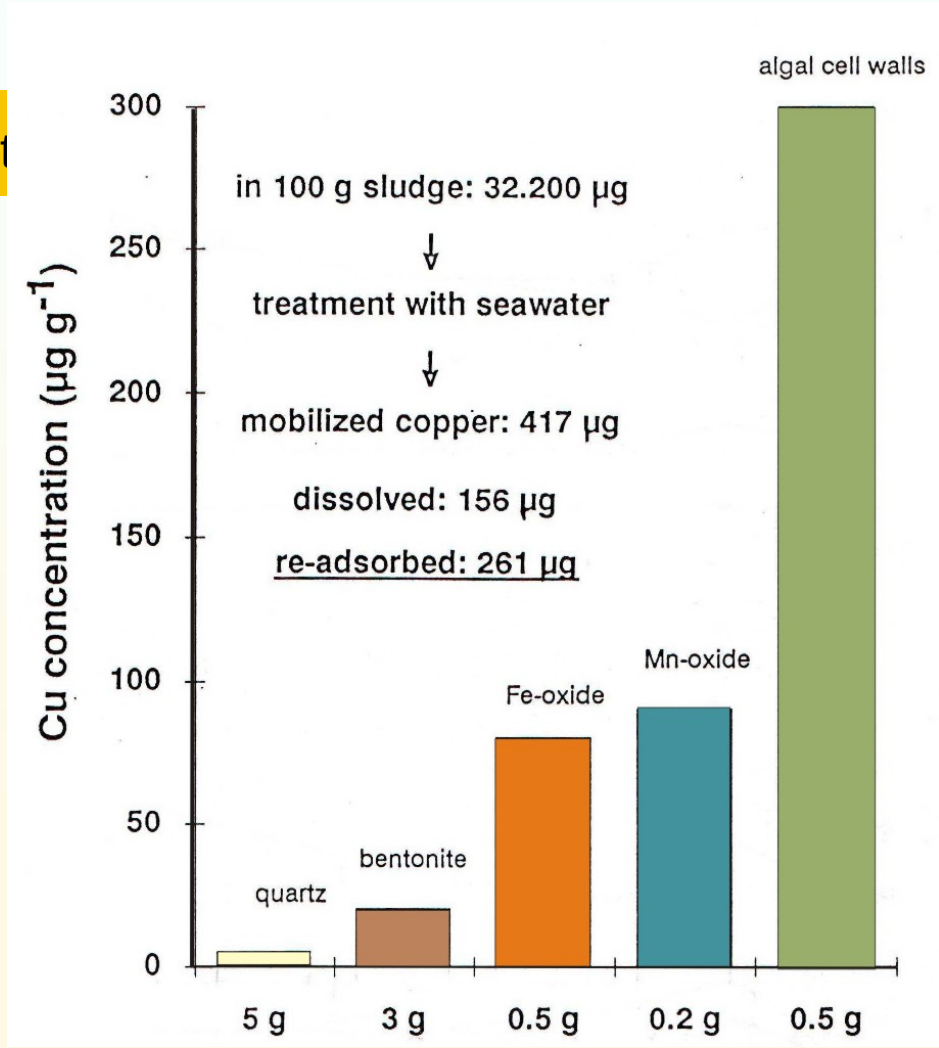
Chemical activity is a property of the pollutant rather than of the sorbent

Ahlf, Irmer & Weber, 1980

Transport and sorption processes

Resuspension und Oxidation:





Förstner, Ahlf, Calmano, 1989

New equilibria in an estuary

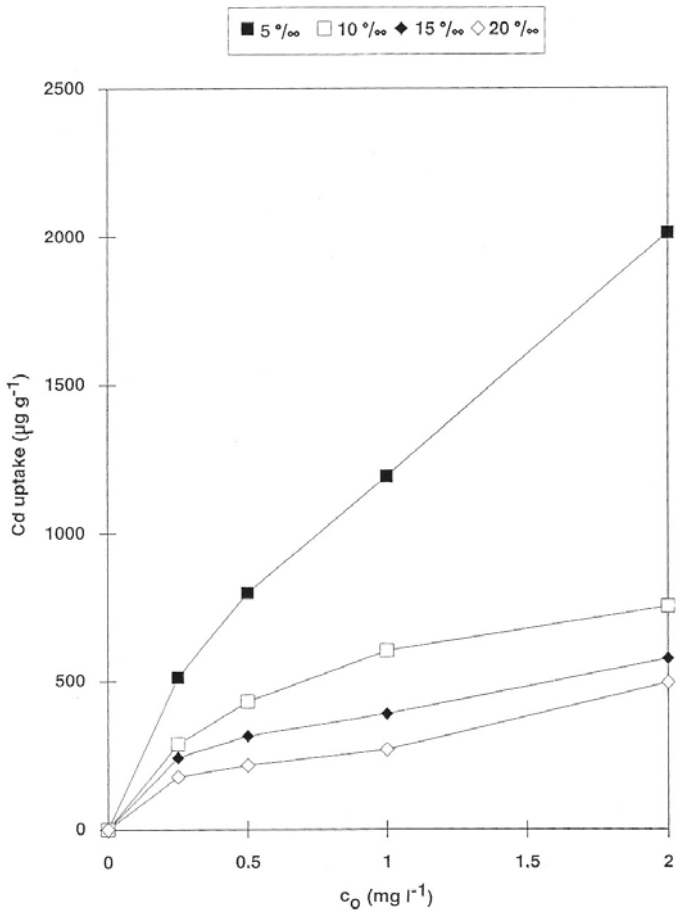


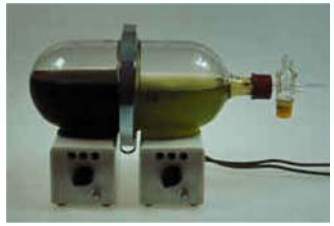
Fig. 6. Sorption of Cd^{2+} on *Brachiomonas submarina* at different salinities.

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

New equilibria in an estuary



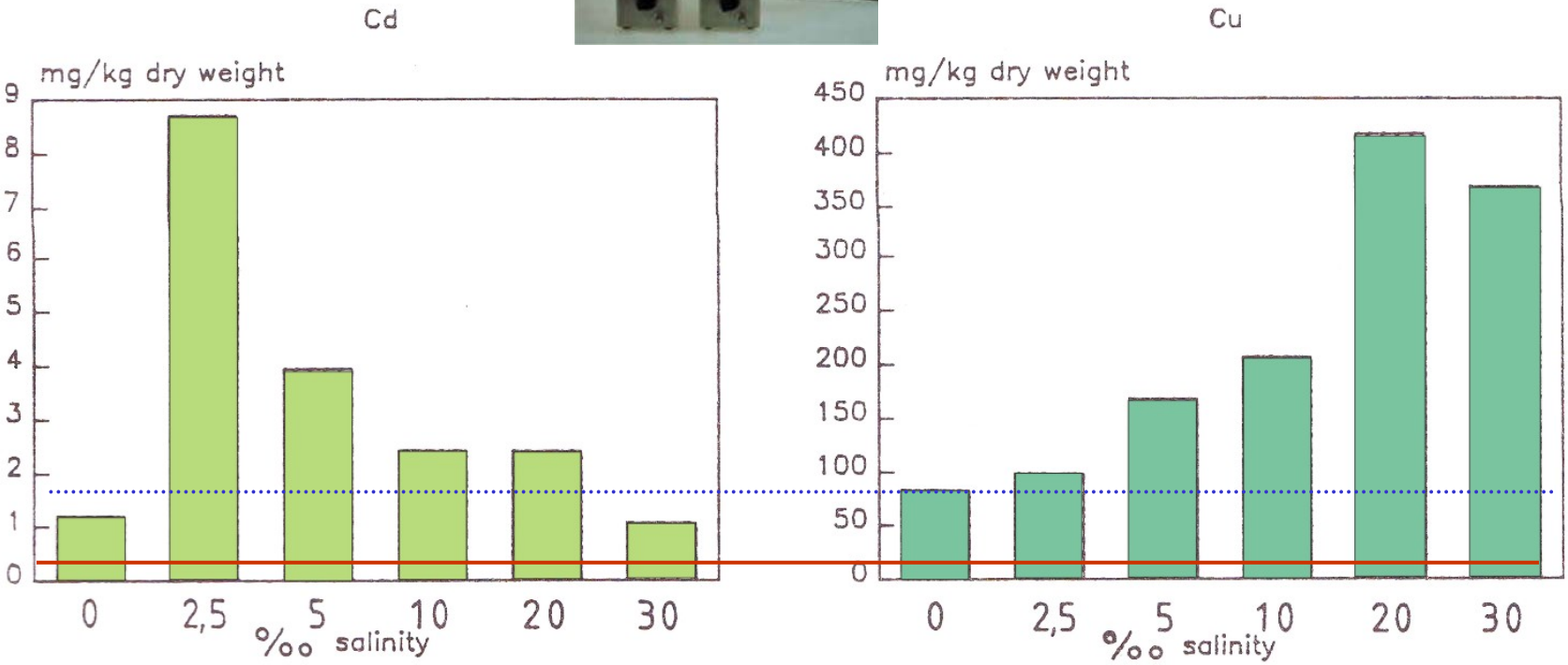
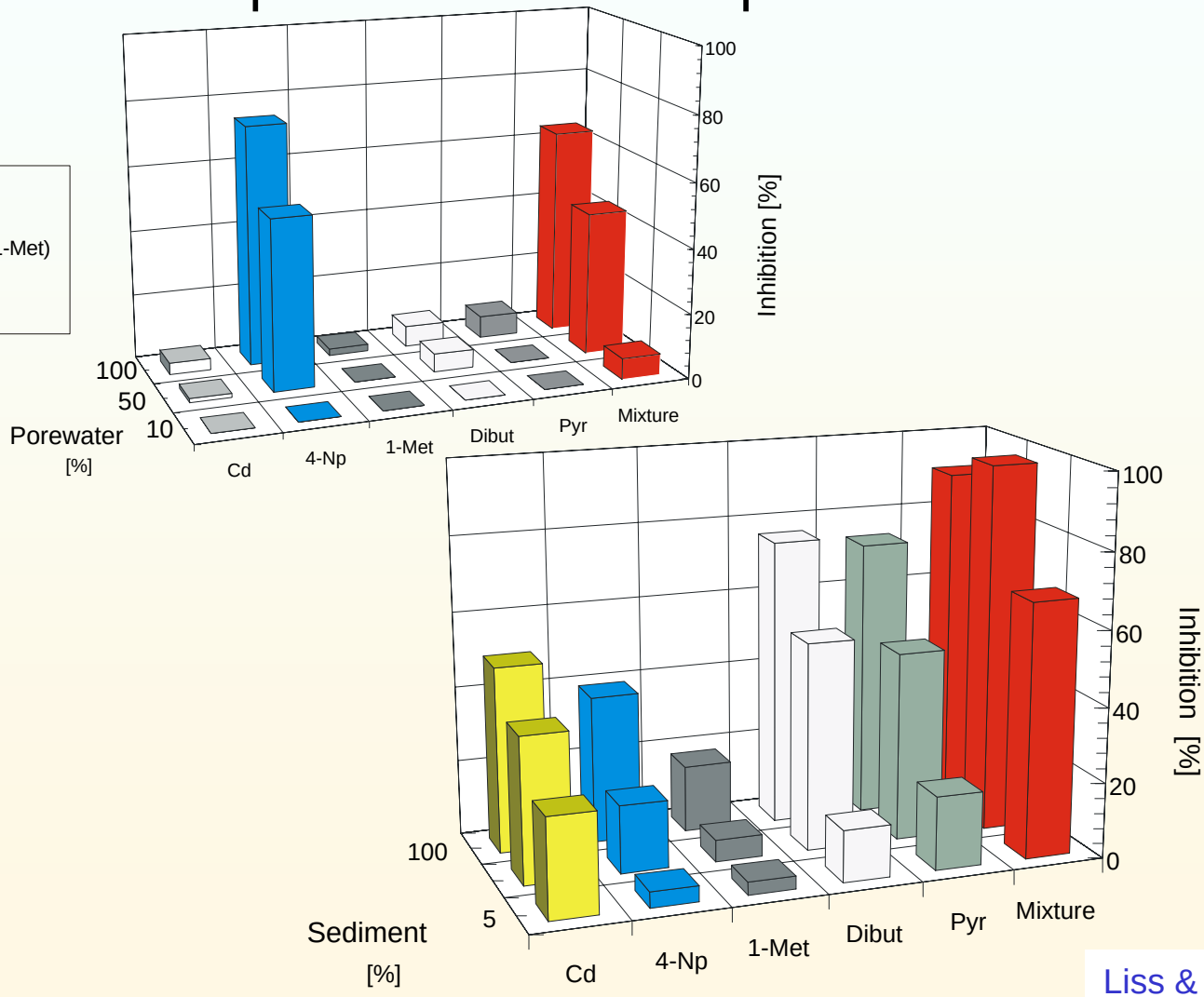


Fig. 7. Effect of salinity on metal contents in *Stichococcus bacillaris* grown for 96 h with resuspended sediment (Ahlf, 1987).

Particle associated impact on bacteria

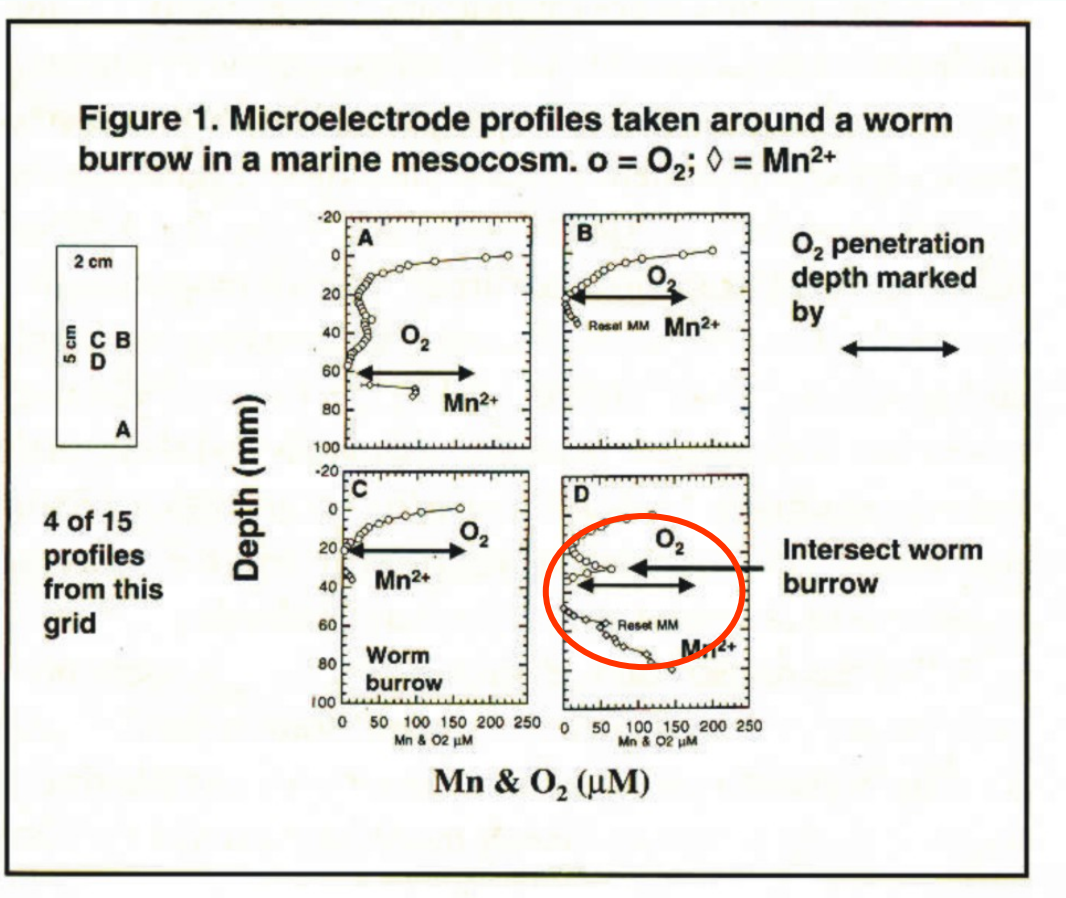
Effects of porewater and suspended sediment

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



Liss & Ahlf, 1996

Bound or complexed metals are bioavailable!

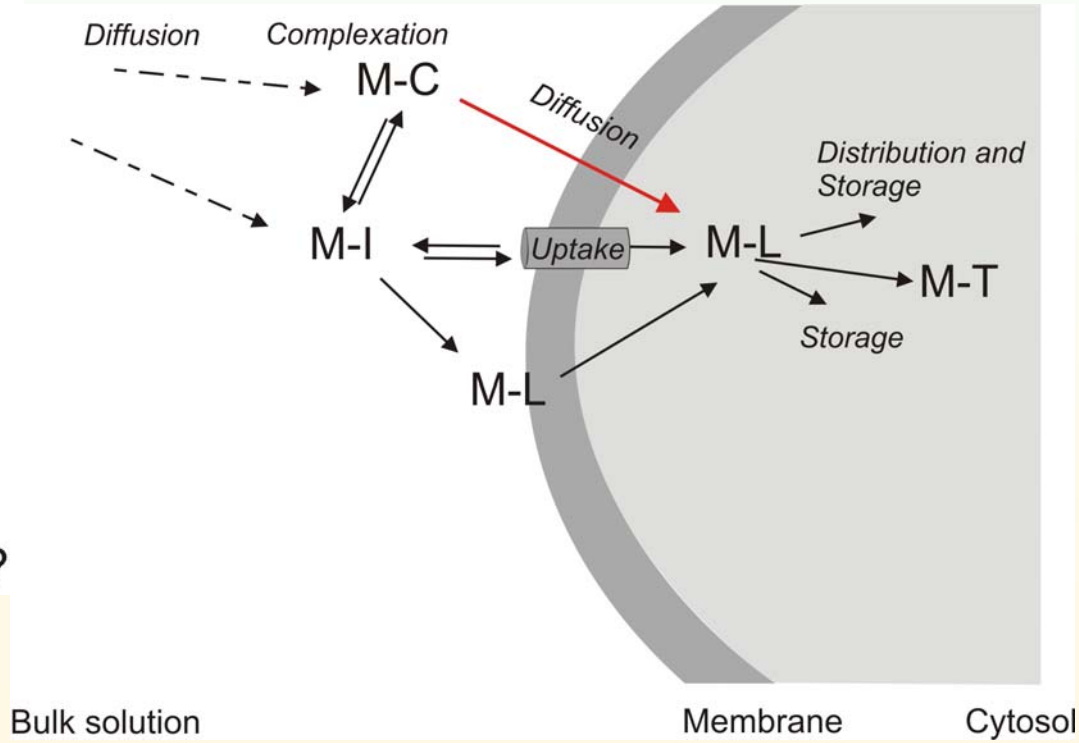


Heavy metals bound to oxides or precipitated as sulfides are (partly) bioavailable for organisms. (Lee et al. 2002, Science, 287, 282-284.)

Biological view: what are the main uptake routes?

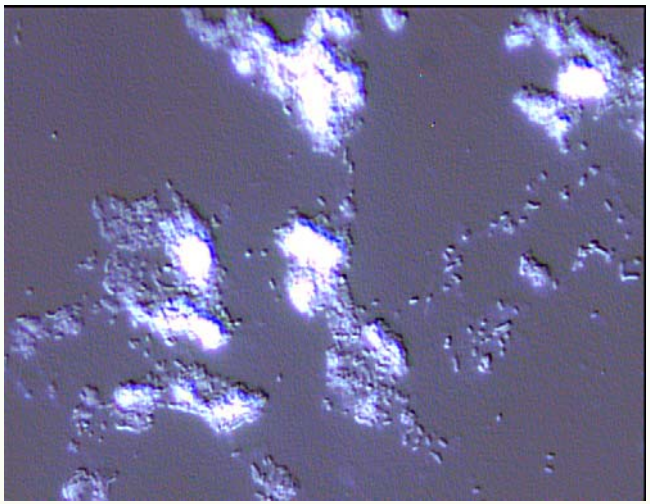
"are there any other ifs and buts?

Small lipophilic metal complexes can cross a biological membrane by diffusion.

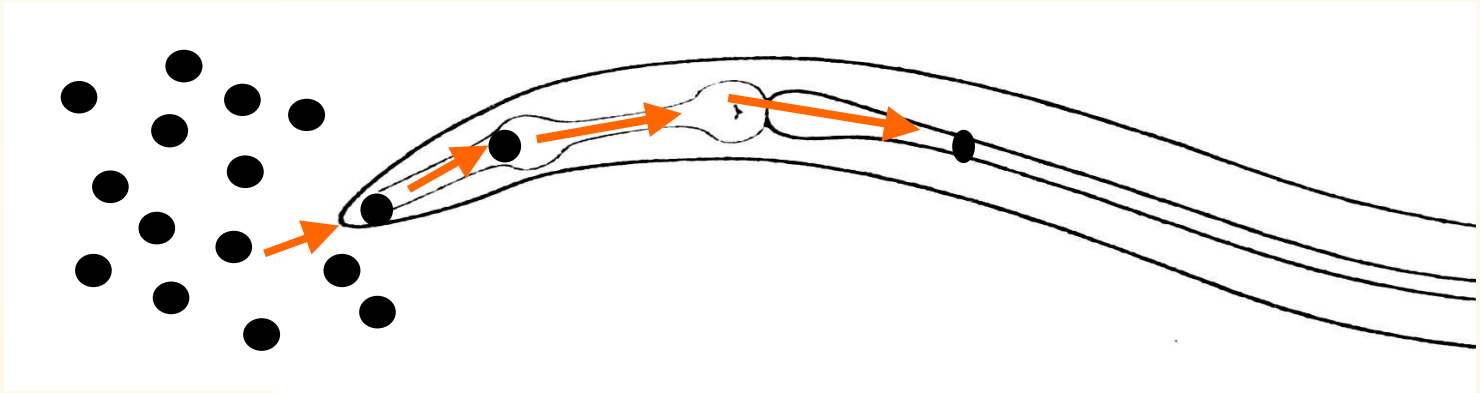


Passive uptake of neutral, lipophilic metal complexes is a nonequilibrium effect

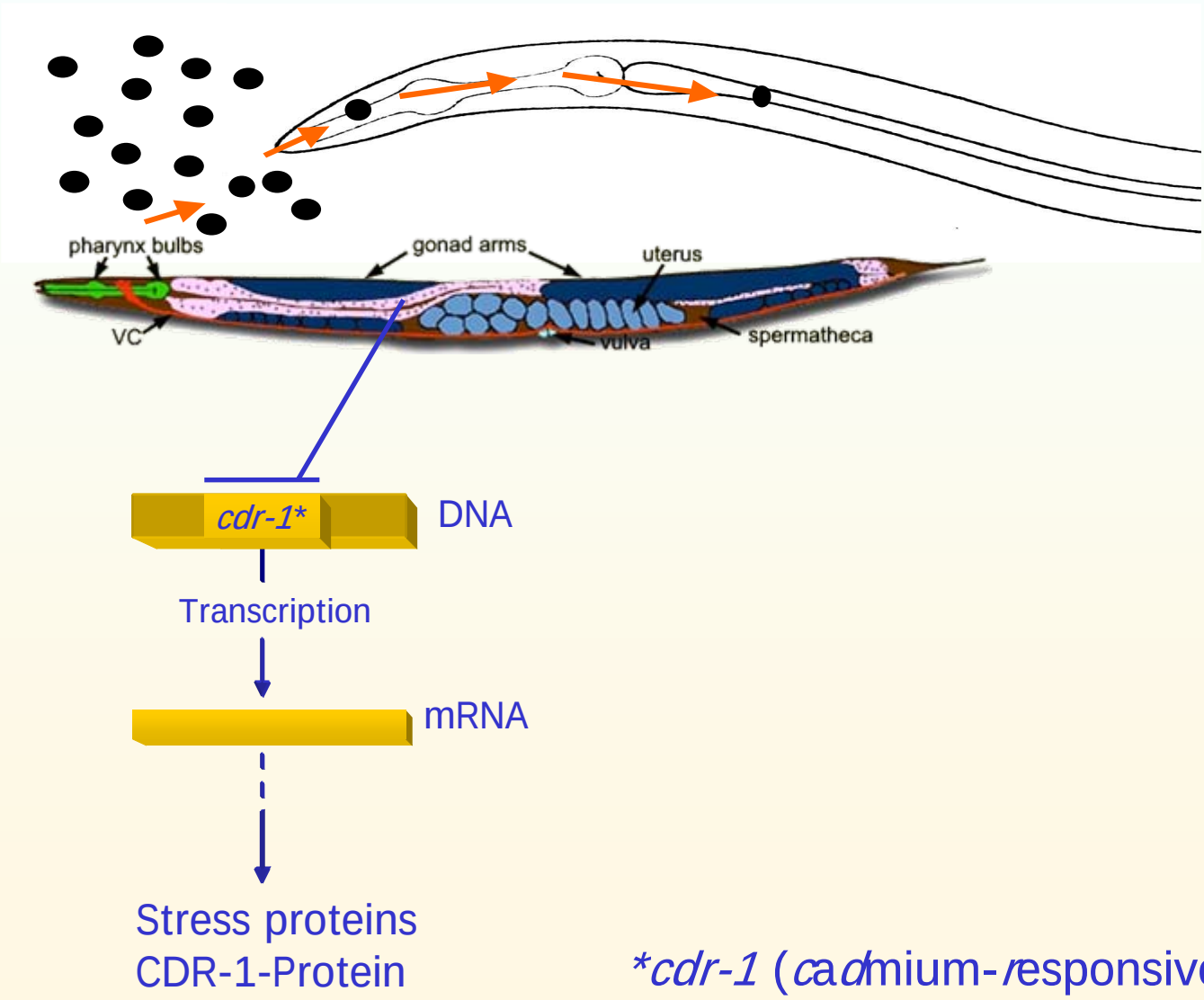
Food and inorganic particles



Caenorhabditis elegans

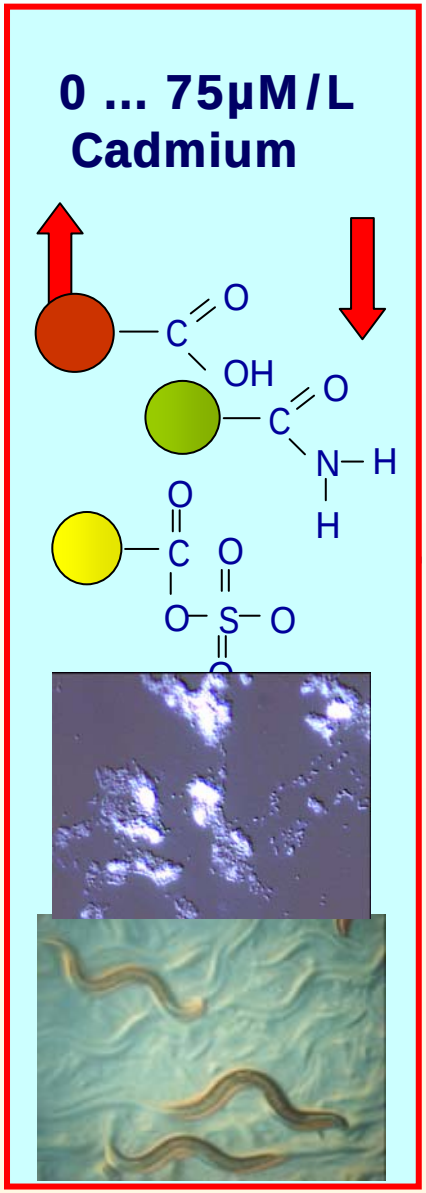


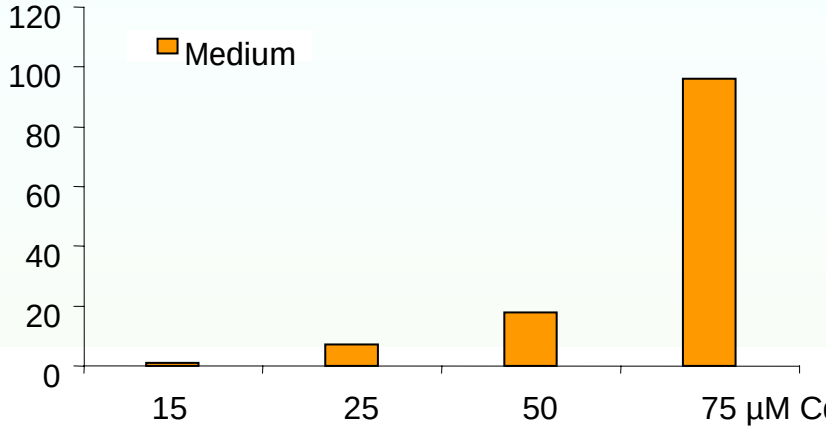
Trophic transfer – effects

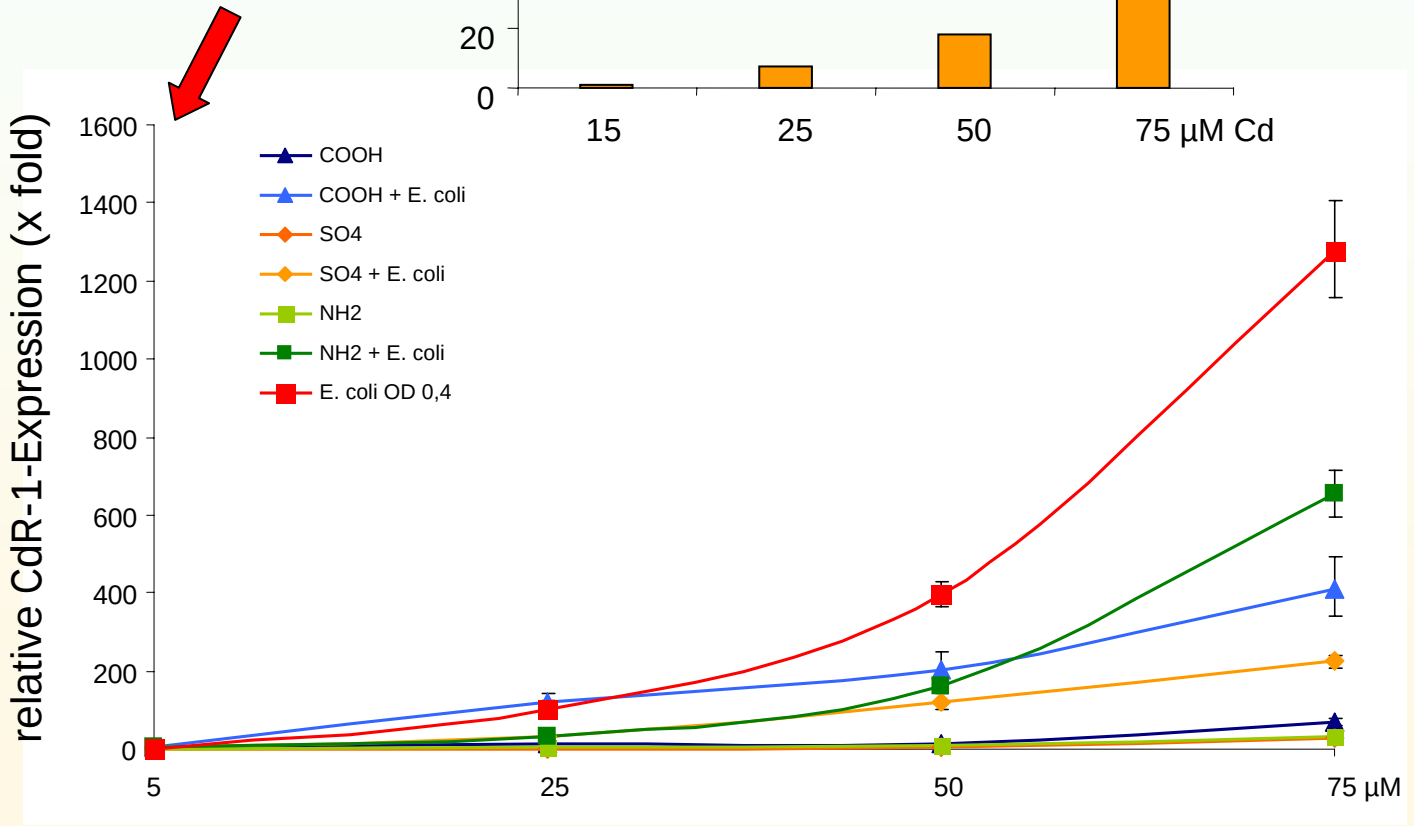


cdr-1 (*c*a*d*mium-*r*esponsive gene-*1*)

Particle quality

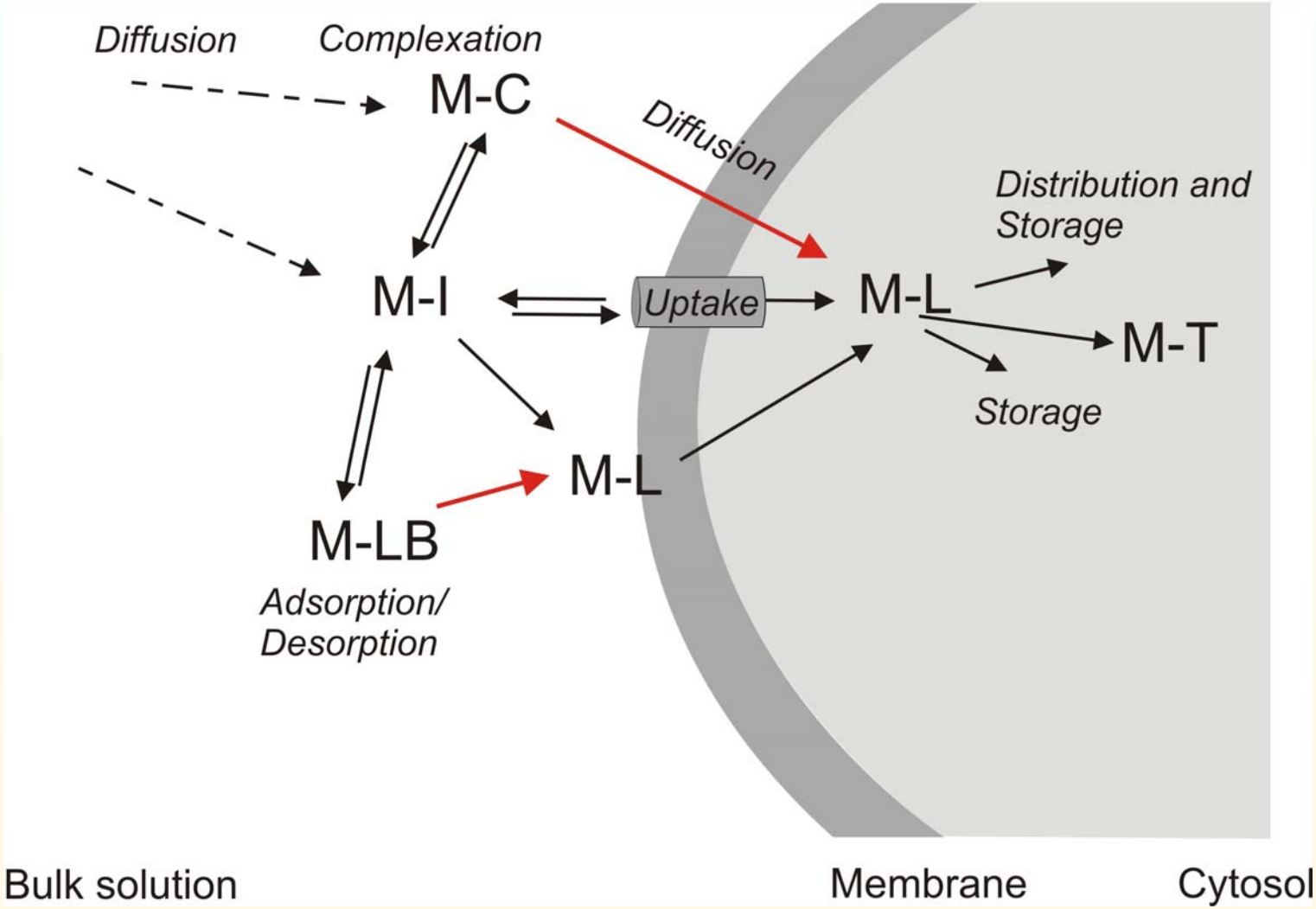




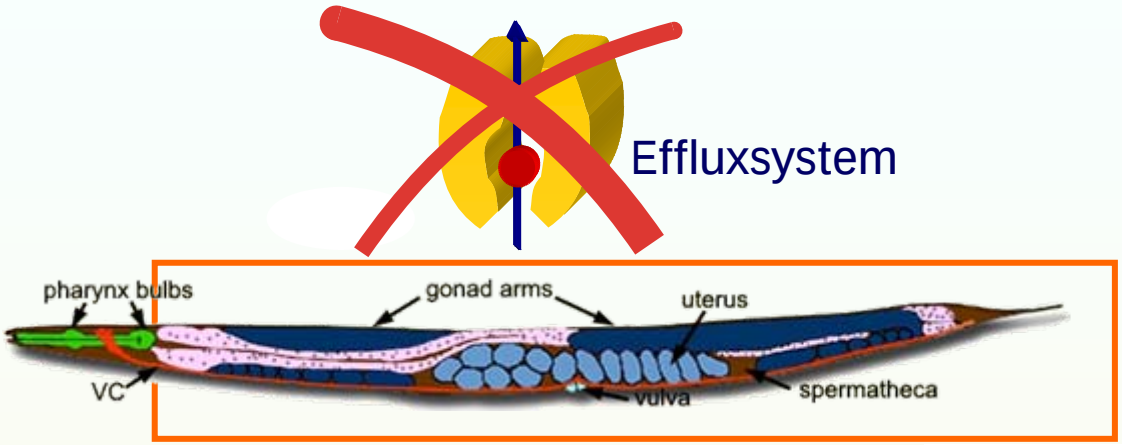


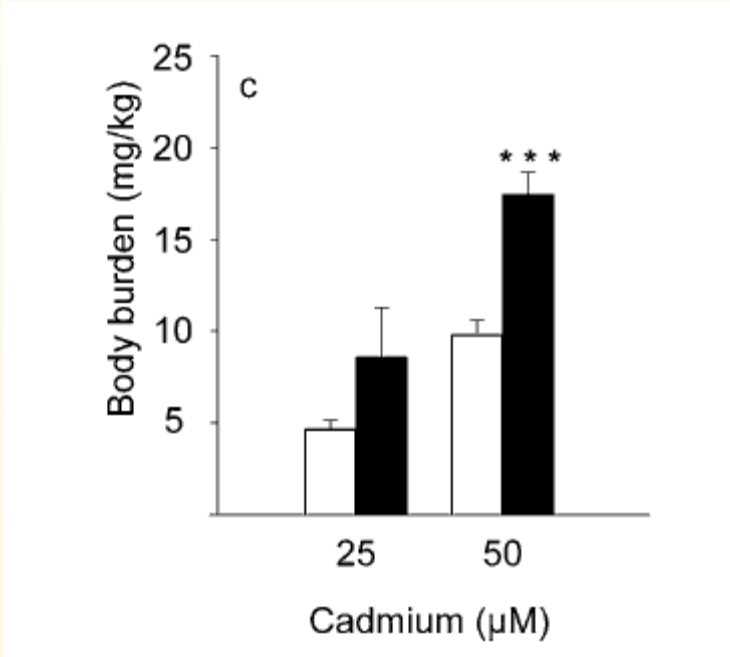
Offermann et al., ETC, in press (2009)

Main uptake routes



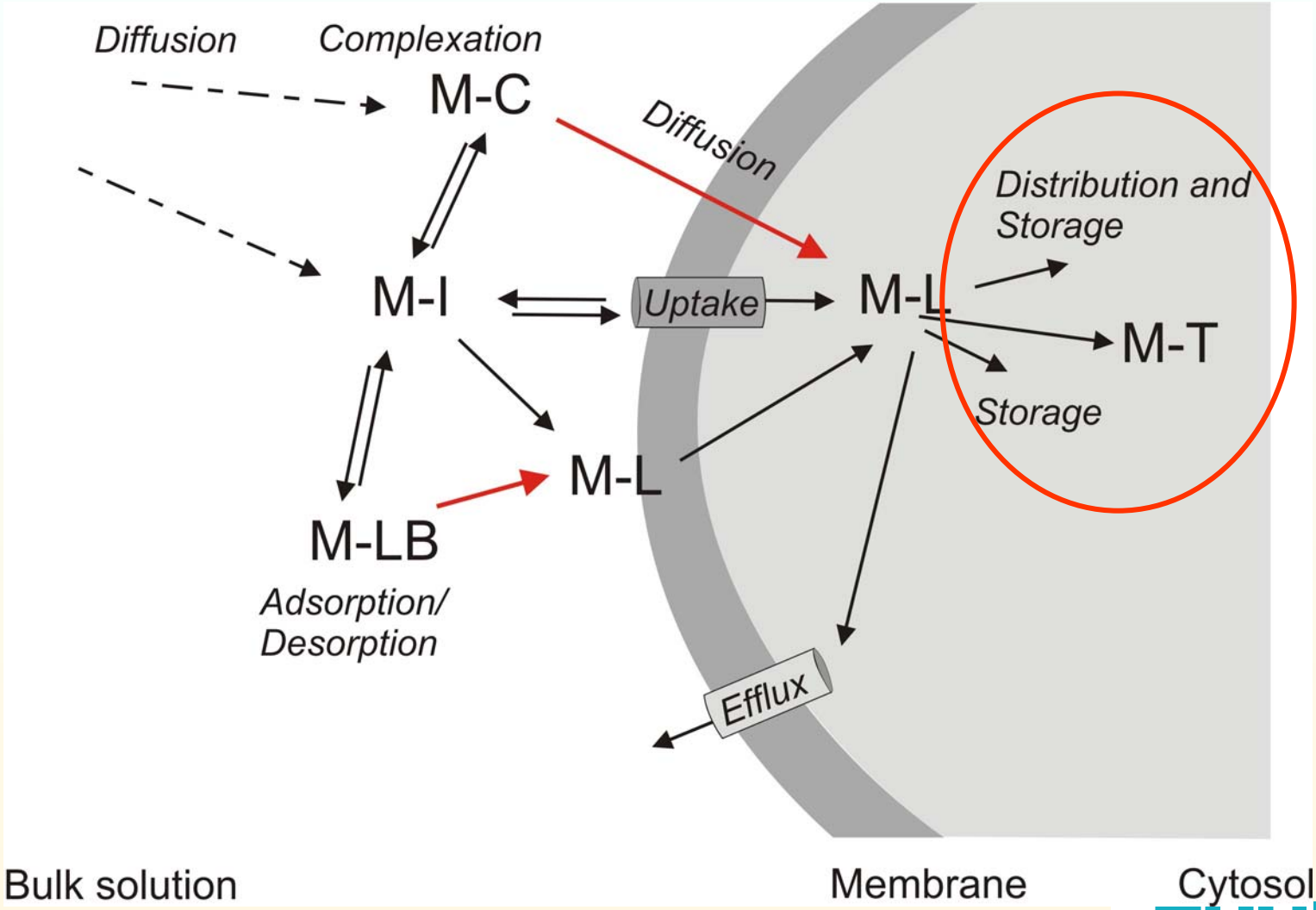
Is metal uptake by organisms under thermodynamic or kinetic control?





Offermann et al., 2009

Uptake, retention and efflux of metals



Conclusions

Asking for the relevant exposure pathways for inorganic metals to organisms, we have to consider:

1. **In addition to freely dissolved concentrations, metal complexes, dietary and particle-bound metals**
2. **Nonequilibrium and kinetic factors for metal uptake**

Thank you for your attention!

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