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Inorganic Pollutants – Introduction

Environmental Behavior of Trace Metals

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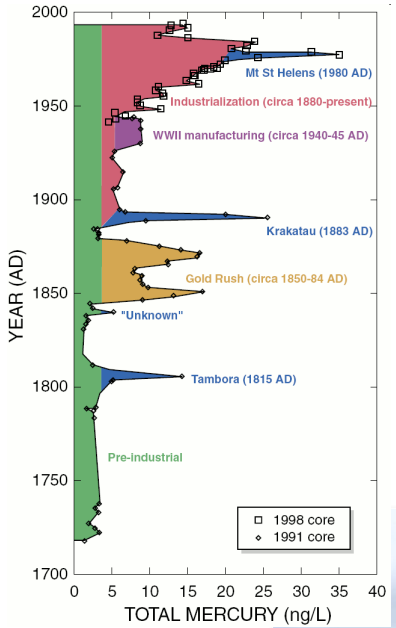


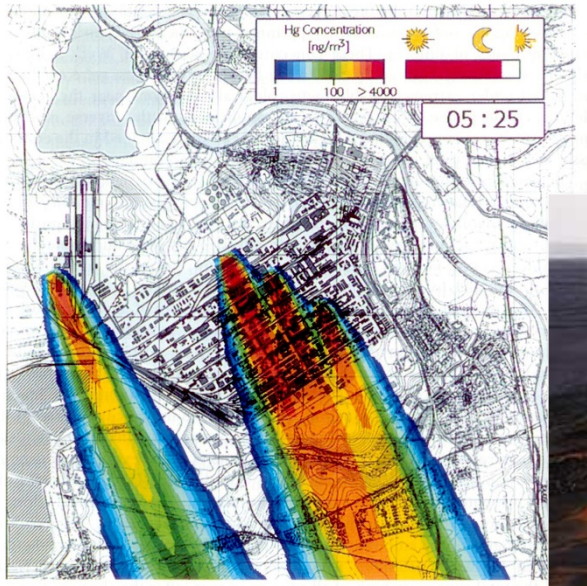
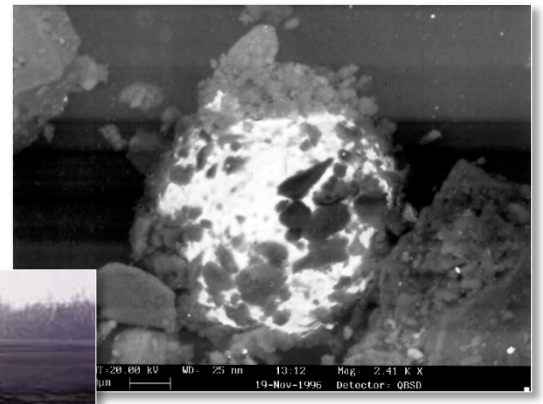


Fig. 6. Dispersion of gaseous mercury at BSL Werk Schkopau near Halle/Saale in the early mo
June 14, 1995, at 5:25 UTC



MES 2 – Course Environmental Chemistry

- **Introduction to general environmental processes including metals**
  - pH
  - dissolution/precipitation
  - complexation
  - redox
  - (sorption)
  - metals in the environment
  - some analytical techniques

MES 2 – General Behavior of Trace Metals in the environment

- They appear as hydrated or complexed cations (Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, …)
- Some metals/metalloids appear as oxo-anions (AsO_3^{3-}, AsO_4^{3-}, CrO_4^{2-}, SbO_3^{-},…)
- Some metals form metal-organic compounds (Hg, As, Sb…) as methyl mercury
- The pH is a controlling factor for speciation, dissolution and adsorption
    - Cations: low pH increases solubility and decreases adsorption
    - Oxo-anions: more complex but lower pH tends to favor adsorption
- They tend to adsorb to mineral surfaces and organic carbon
- Dissolved organic matter plays a role as ligand to enhance dissolved concentration and mobility
- The “free” hydrated metal ion is relevant for plant uptake and toxicity
- Complexation by natural organic matter or sorption to soil organic matter and mineral surfaces reduces plant uptake and toxicity

MES 3 – Inorganic Pollutants

- They appear as hydrated or complexed cations (**Pb^{2+}**, Cd^{2+}, Zn^{2+}, Cu^{2+}, …)
- Some metals/metalloids appear as oxo-anions (**AsO_3^{3-}, AsO_4^{3-}**, CrO_4^{2-}, SbO_3^-,…)
- Some metals form metal-organic compounds (Hg, **As**, Sb…) as methyl mercury
- The pH is a controlling factor for speciation, dissolution and **adsorption**
    - **Cations: low pH increases solubility and decreases adsorption**
    - **Oxo-anions: more complex but lower pH tends to favor adsorption**
- They tend to adsorb to mineral surfaces and organic carbon
- Dissolved organic matter plays a role as ligand to enhance dissolved concentration and mobility
- **The “free” hydrated metal ion is relevant for plant uptake and toxicity**
- Complexation by natural organic matter or sorption to soil organic matter and mineral surfaces reduces plant uptake and toxicity

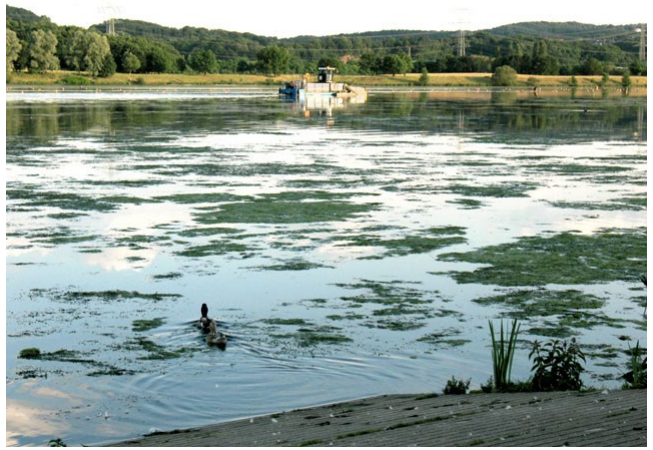
Trace (heavy) metals – why do we care?

- **Heavy metal pollution and toxicity is still a very prominent issue today**
  - 8 of the 10 most polluted sites in the world have a major problem with trace metals or radionuclides
- **Heavy metals appear naturally in varying concentrations**
  - Natural background (what is normal and what is anthropogenic?)
- **Heavy metals are persistent – they can‘t be degraded or destroyed**
  - Emission leads to immision and increase of concentration in their respective sinks
- **Some trace (heavy) metals can be both detrimental/toxic at elevated concentrations and beneficial as nutrients**
- **Take up, distribution and accumulation along the food chain from food, water and air**

Inorganic Pollutants – other than metals

nutrients e.g.

nitrate, phosphate (NO_3^-, PO_4^{3-})



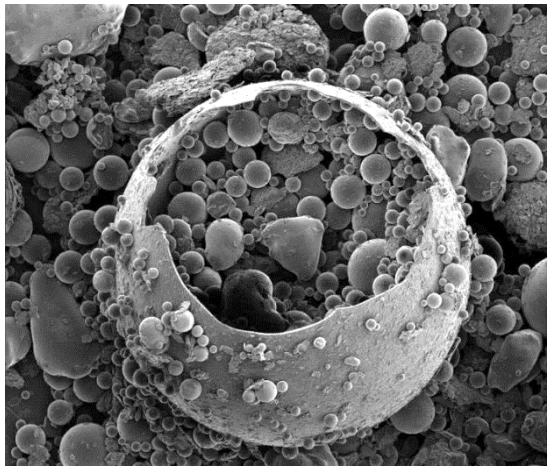
keywords:

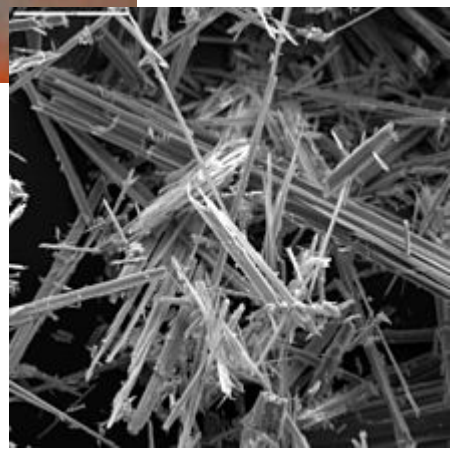
- **P & N cycles**
- **limiting nutrient**
- **eutrophication**
- **phosphate binding**
- **redox conditions**
  - **NO_3^- → NH_4^+**
  - **FeOx dissolution**

Inorganic Pollutants – other than metals

dust & fibres e.g.

„fine dust“ as automotive exhaust
asbestos
silicate dust
dust & soot particles from combustion
welding fumes





keywords:

- **aerosol**
- **inhalation**
- **removal in resp. tract**
- **particle toxicity**
- **particle contamination**
- **uptake**
- **air transport**

Inorganic Pollutants – other than metals

radionuclides e.g.

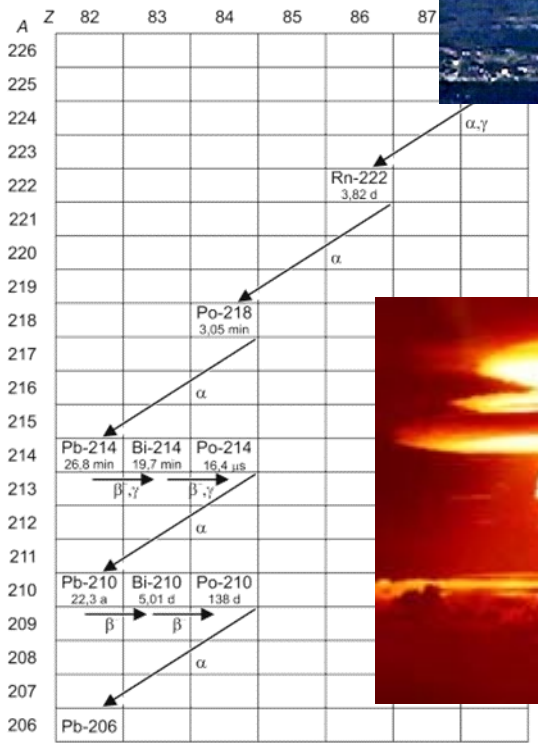
Radon , ^{222}Rn (α) → ^{218}Po (α) → ^{214}Pb (β)

Iodine ^{131}I (β), Cesium ^{137}Cs (β, γ)

Plutonium ^{238}Pu (α)

Uranium

…



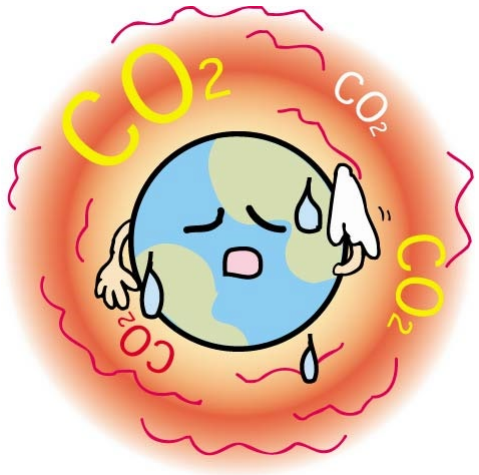
keywords:

- **type of radiation (α,β,γ, N)**
- **intensity versus dose**
- **low level effects**
- **intake / uptake**
- **chemical toxicity (e.g. Pu)**
- **long range transport**

Inorganic Pollutants – other than metals

gaseous oxides e.g.

NO_x – SO_2 – CO_2



keywords:

- **acid rain (SO_2 NO_x)**
- **climate change (CO_2, CH_4, NH_3)**
- **smog (SO_2)**
- **acidification (CO_2, soil, oceans)**
- **effective pollution control (SO_2)**
  gypsum cardboard…
- **(fake) reduction (NO_x)**
- **hopeless (?) situation (CO_2)**

Inorganic Pollutants - metals

some Trace Elements with high toxicity „heavy metals“

PERIODIC TABLE OF THE ELEMENTS

Metals
Nonmetals
Metalloids

	IA 1	IIA 2	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	VIIIB 8	VIIIB 9	VIIIB 10	IB 11	IIB 12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	0 18
1	1 H 1.008																1 H 1.008	2 He 4.0026
2	3 Li 6.941	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.9984	10 Ne 20.1797
3	11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815	14 Si 28.085	15 P 30.9738	16 S 32.06	17 Cl 35.453	18 Ar 39.948
4	19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.845	27 Co 58.9332	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.798
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.9058	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.96	43 Tc (98)	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.9045	54 Xe 131.293
6	55 Cs 132.9055	56 Ba 137.327	57 La 138.9055 *	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.084	79 Au 196.9666	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.9804	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227) **	104 Rf (265)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Uut (284)	114 Fl (289)	115 Uup (288)	116 Lv (293)	117 Uus (294)	118 Uuo (294)

*Lanthanide Series

58 Ce 140.116	59 Pr 140.9076	60 Nd 144.242	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.500	67 Ho 164.9303	68 Er 167.259	69 Tm 168.9342	70 Yb 173.054	71 Lu 174.9668

** Actinide Series

90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Note: Atomic masses are 2009 IUPAC values (up to four decimal places). More accurate values for some elements are given in the table inside the back cover.

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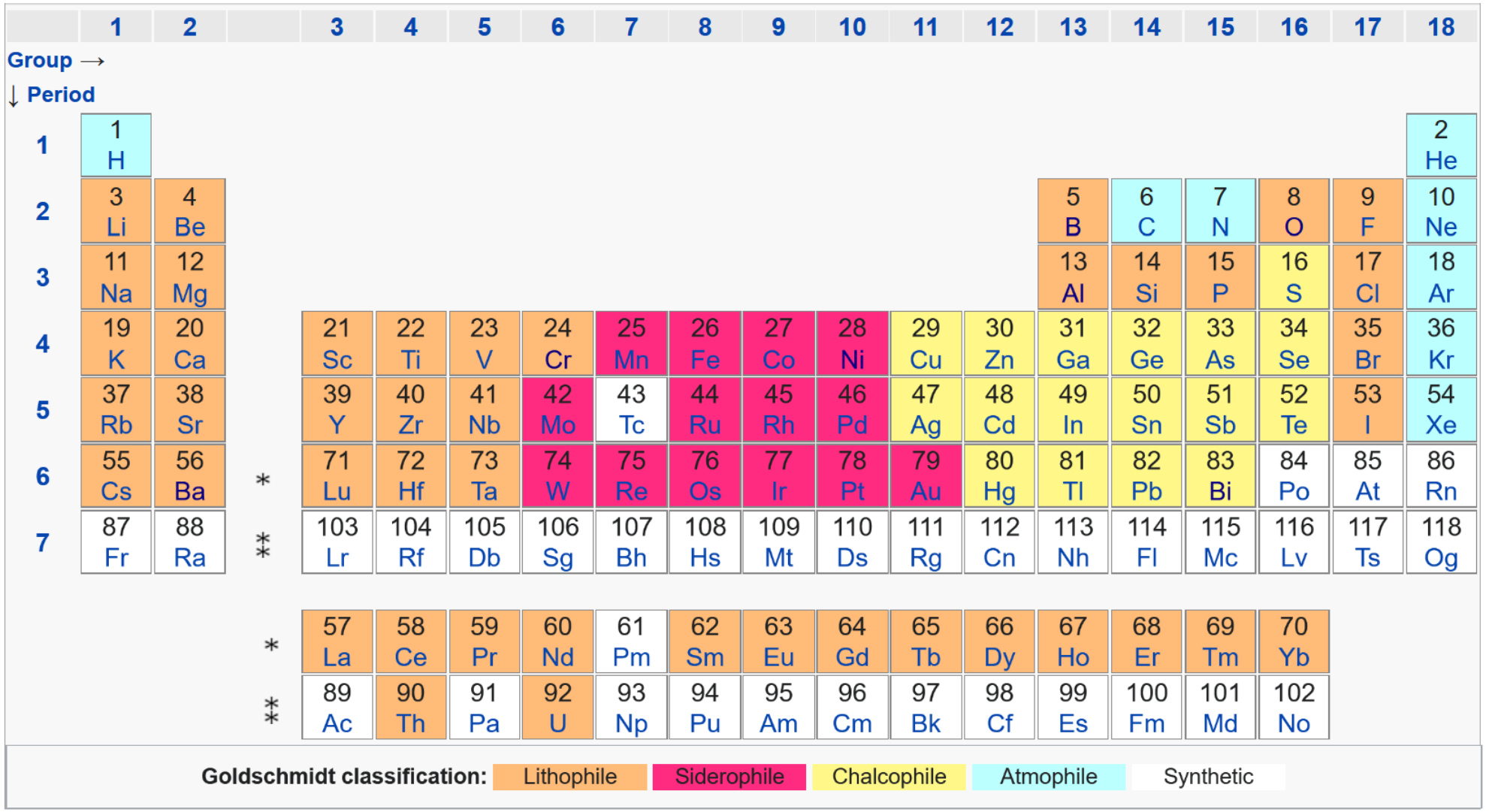
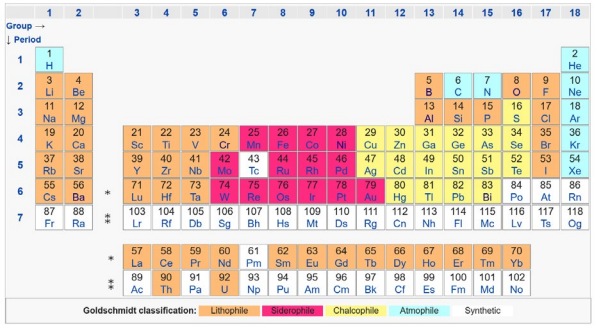
The Goldschmidt classification of elements



developed by Victor Goldschmidt (1888–1947)

The Goldschmidt classification of elements



Classification stems from the behavior of the metals during the formation of Earth. But still usable to get an idea of their general behavior

Lithophile elements are those that combine readily with oxygen

Due to their strong affinity for oxygen, lithophile metals, were never available as free metals before the development of energy-intensive electrolysis

Chalcophile elements are those that remain on or close to the surface because they combine readily with sulfur

They can easily be extracted by the reduction with coke (not without relevant emissions of SO_2)

Siderophile elements tend to concentrate in (molten) iron.
Although not directly relevant for their current behavior, this means that they are seldom (even precious metals) and do very little associate with oxygen. They rather take sulfur or carbon, but not to an extent that they would classify as chalcophile.
…well… that is of course not the case for Fe and Mn…

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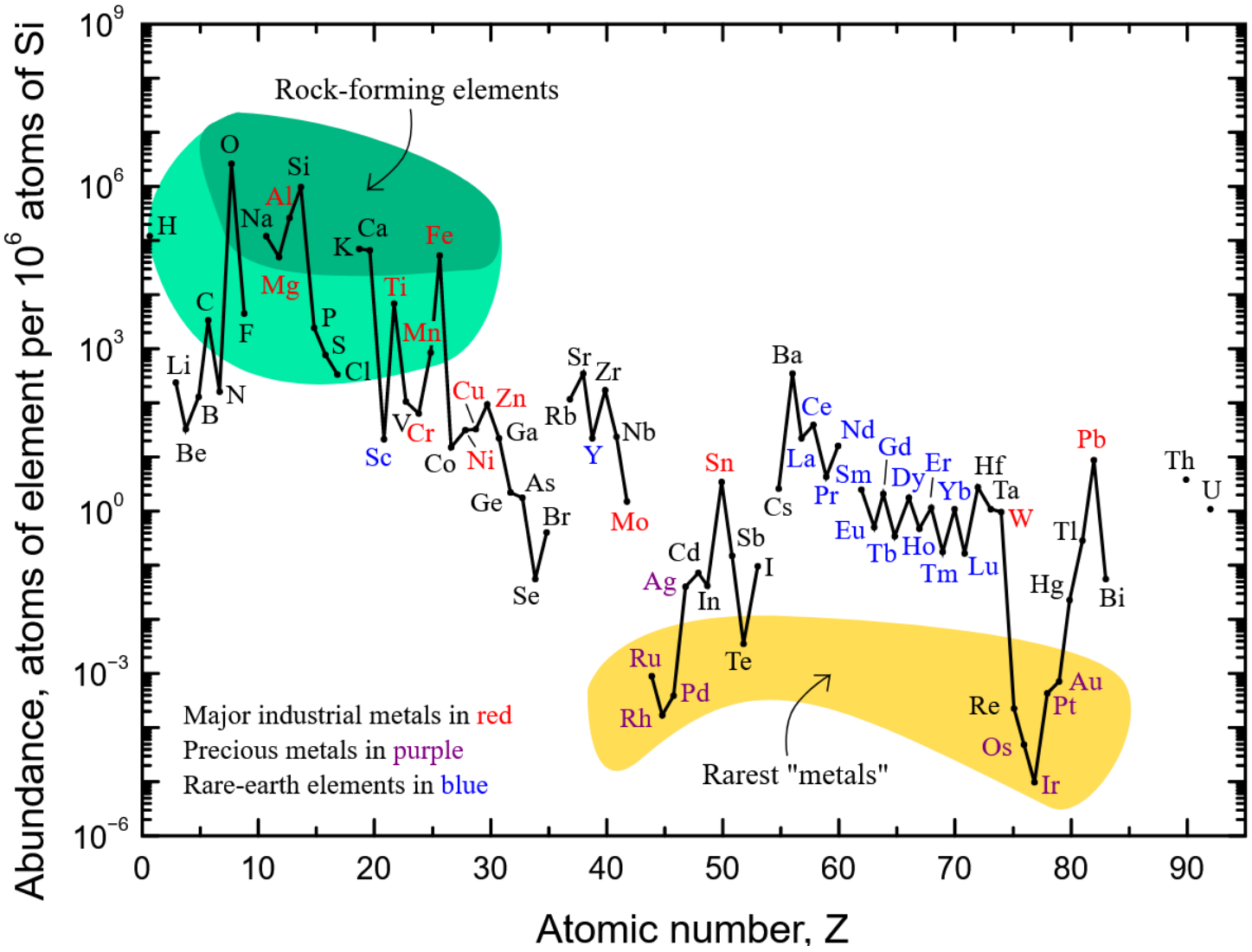
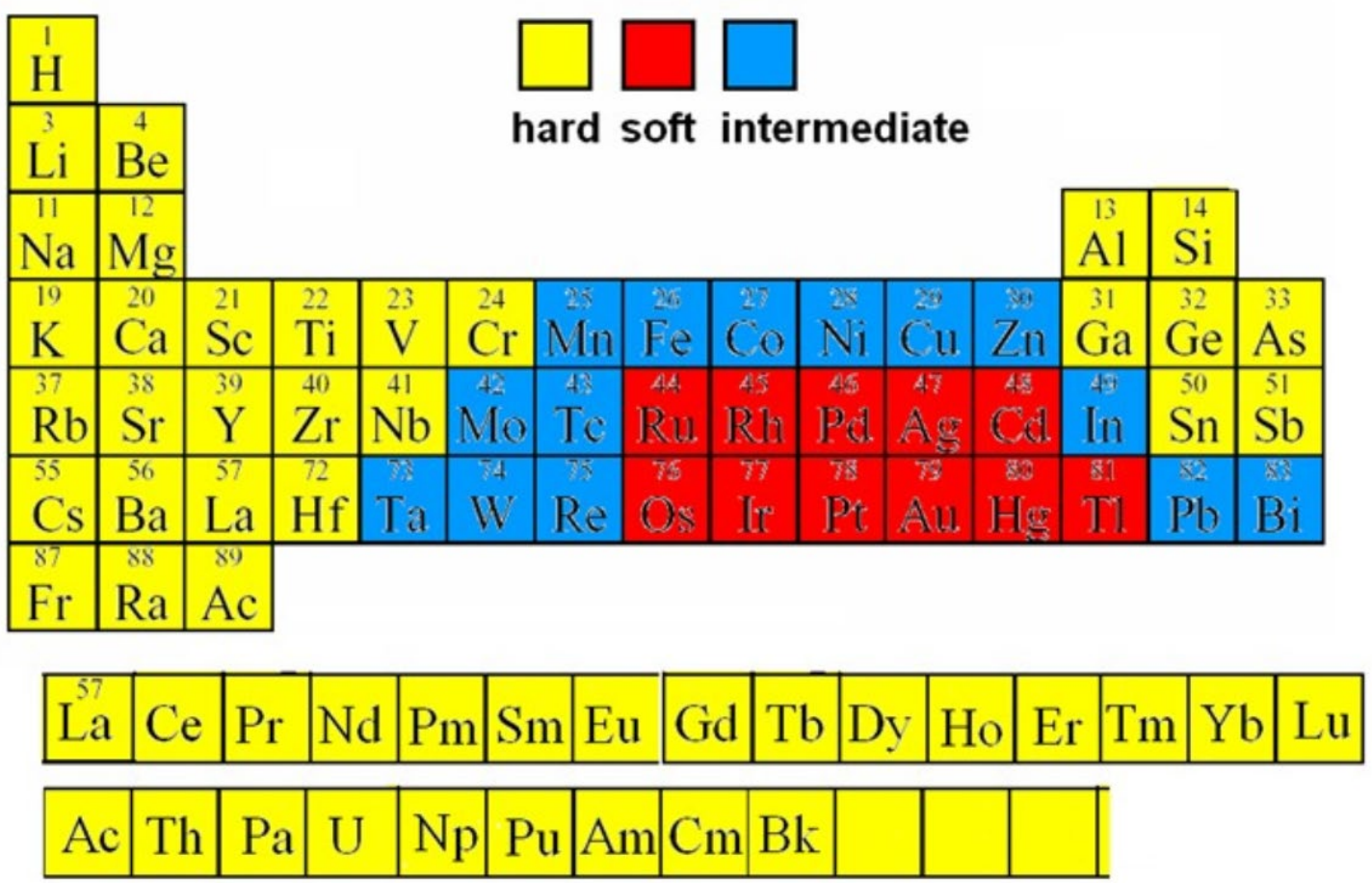
Abundance in crust relative to silicon



Another concept: hard and soft acids and bases



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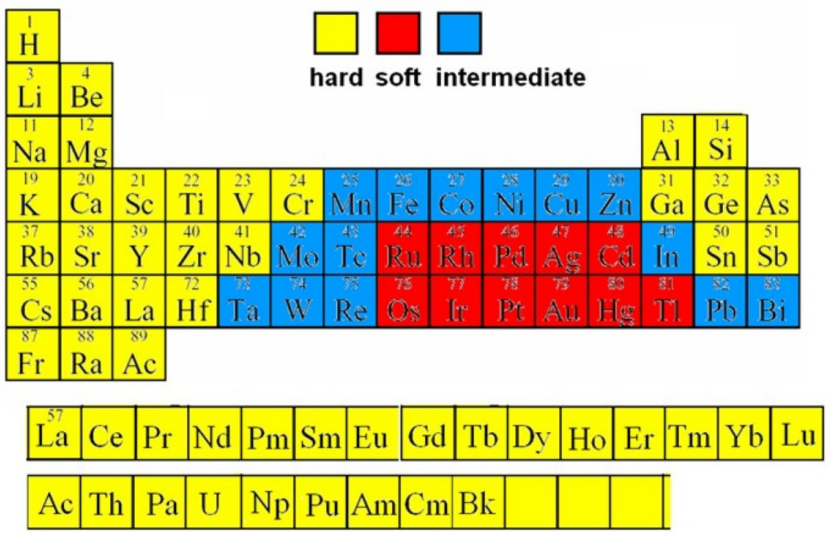


hard acids and hard bases tend to have certain properties:

- small atomic/ionic radius
- high oxidation state
- low polarizability
- high electronegativity (bases)

Some hard acids are:

H^+, Li^+, Na^+, K^+
Ti^{4+}, Cr^{3+}, Cr^{6+}, As^{3+}, Se^{3+}, Si^{4+}

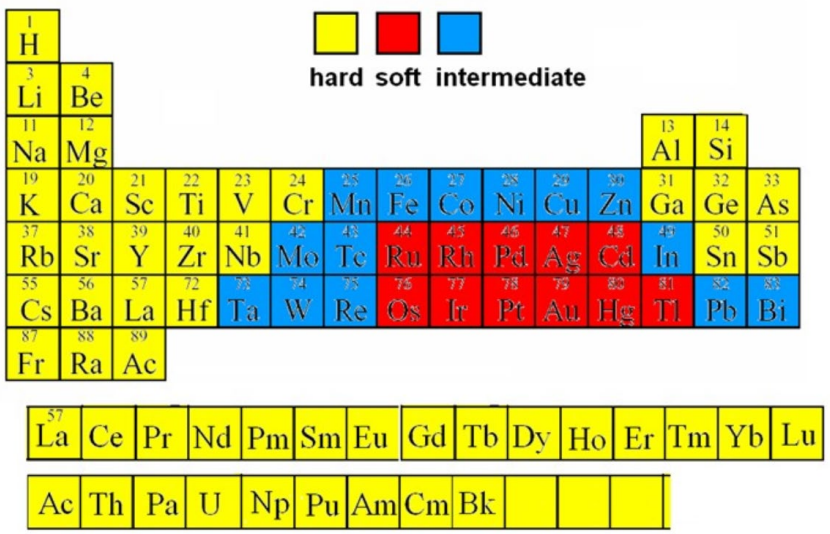
Some hard bases are:

ClO_4^-, CO_3^{2-}, F^-, H_2O, NCS^-, NH_3, NO_3^-, O_2^-, OH^-, PO_4^{3-}, R-CO_2^-, SO_4^{2-}

R-: alkyl groups

The bonding between hard acids and hard bases is mainly ionic in nature.

Another concept: hard and soft acids and bases



soft acids and soft bases tend to have certain properties:

- large atomic/ionic radius
- low or zero oxidation state bonding
- high polarizability
- low electronegativity

Some soft acids are:

Ag^{+}, Au^{+}, Cd^{2+}, CdR^{+}, $Co(CN)_5^{3-}$,, Hg^{+}, Hg_2^{2+}, Hg^{2+}, $Hg\text{-}R^{+}$, $InCl_3$, Pd^{2+}, Pt^{2+}, Pt^{4+}, Tl^{+}, Tl^{3+}

R-: alkyl groups

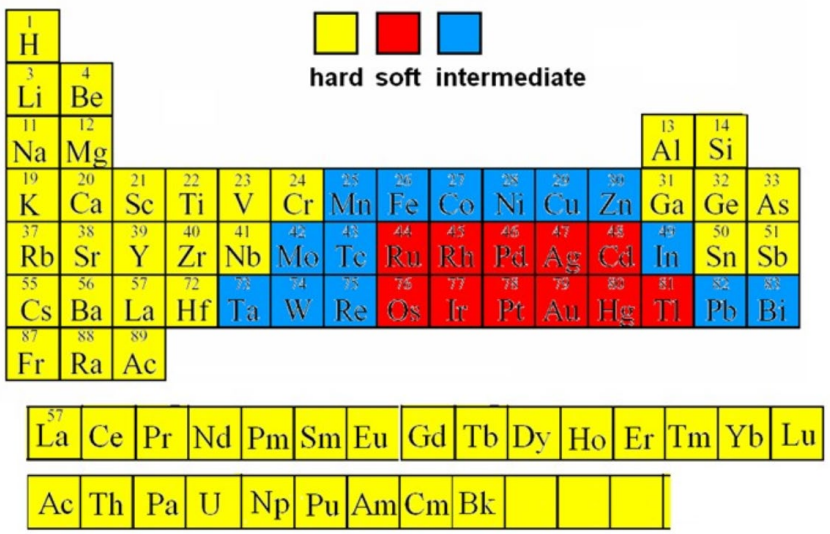
Some soft bases are:

$As\text{-}R_3$, BH_4^{-}, CN^{-}, CO, I^{-}, $P(OR)_3$, $R\text{-}Se^{-}$, R-SH, S^{2-}, SCN^{-}

R-: alkyl groups

The bonding between hard acids and hard bases is mainly <u>covalent</u> in nature.

Another concept: hard and soft acids and bases



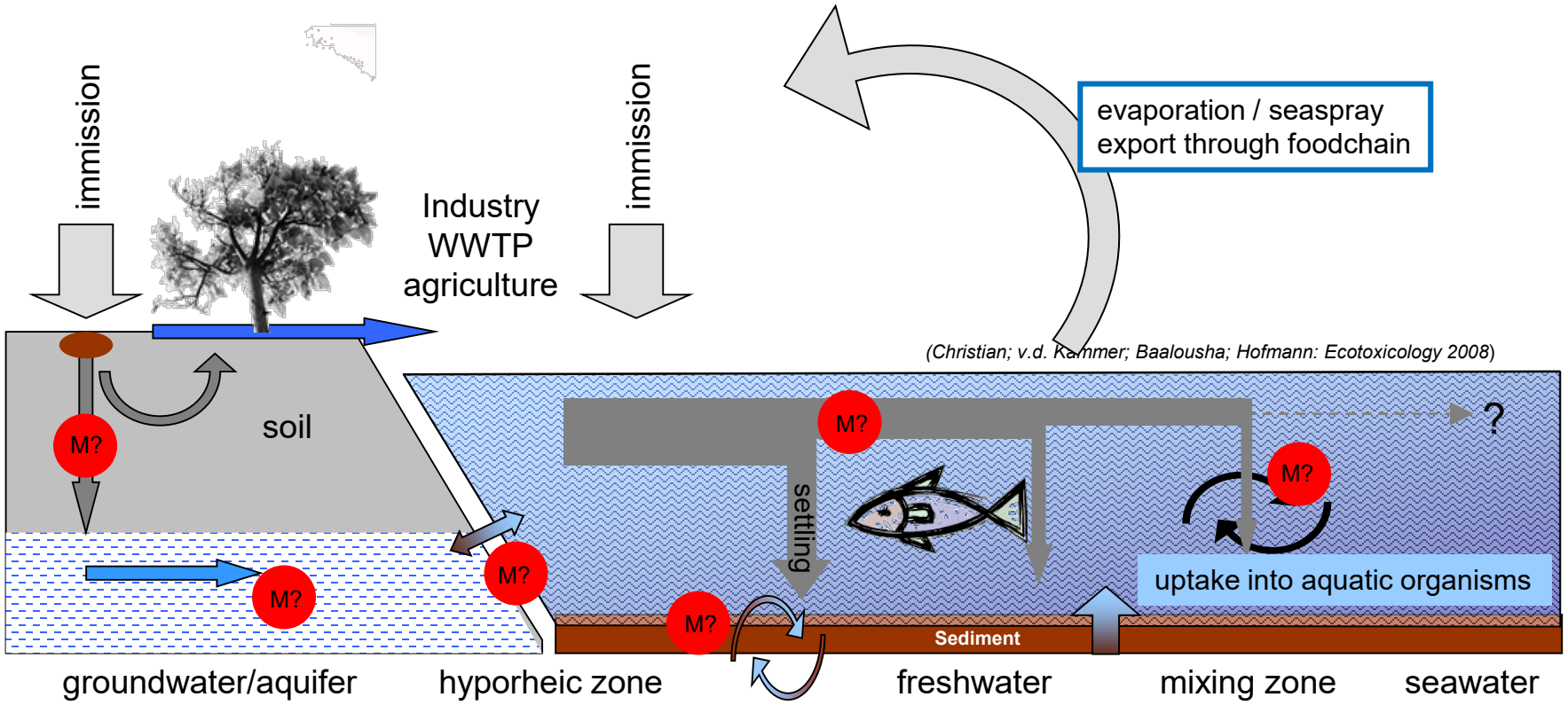
From a qualitative approach we could deduce that

- Ti, Si and Al would rather react with oxygen to form TiO_2, SiO_2 and Al_2O_3
- Hg would rather react with sulfur or R-SH (sulfhydryl groups)

- But! Also Cu and Zn “love” to form sulfides

- Check https://www.chemicool.com/examples/hard-soft-acids-bases.html for more, especially organic molecules and metal-organic compounds

Reactions, transport and fate in the environment



deposition / surface runoff
transport in soil &
in groundwater
root/plant uptake

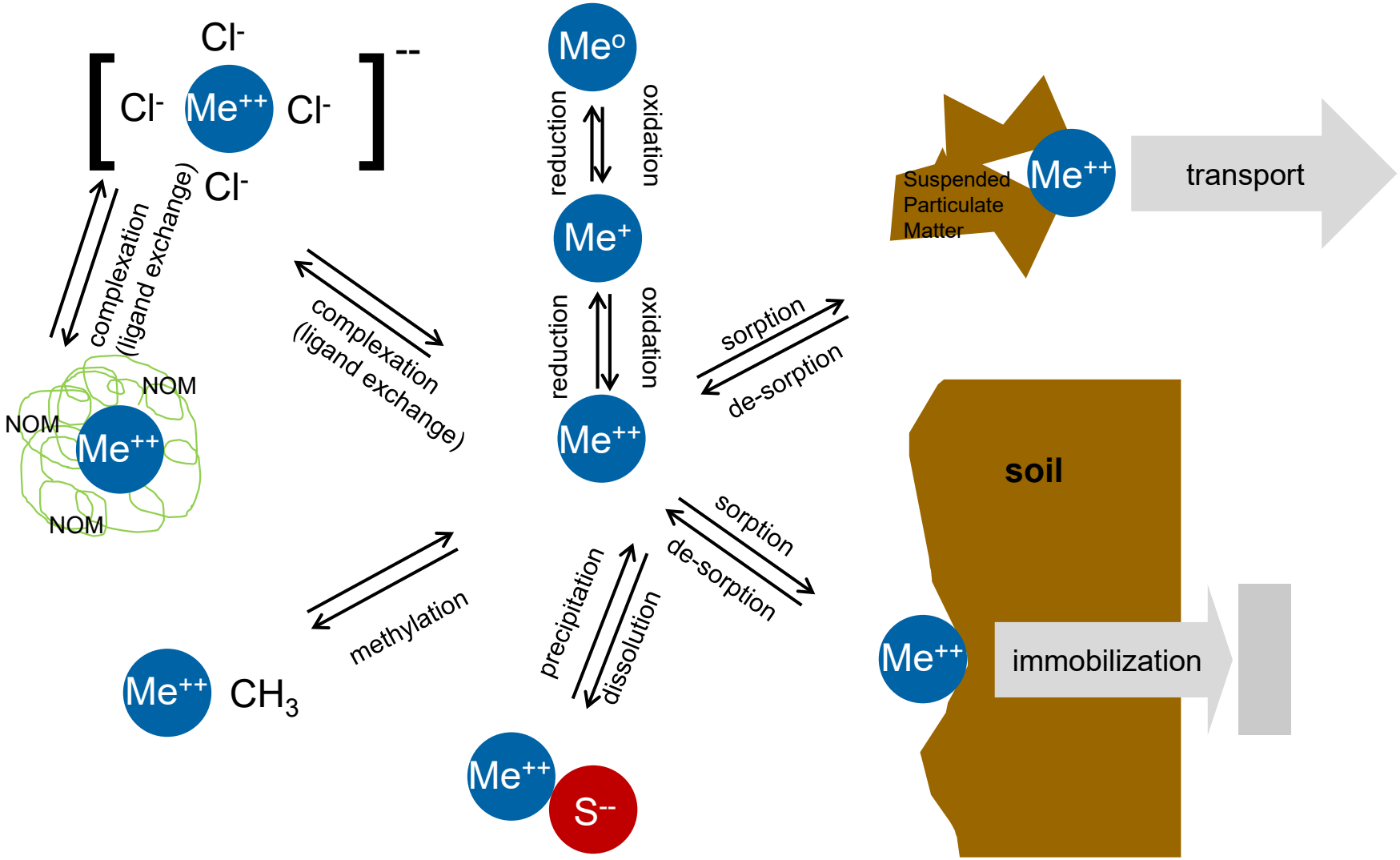
Interaction with suspended particulate matter

sediment/porewater transformations

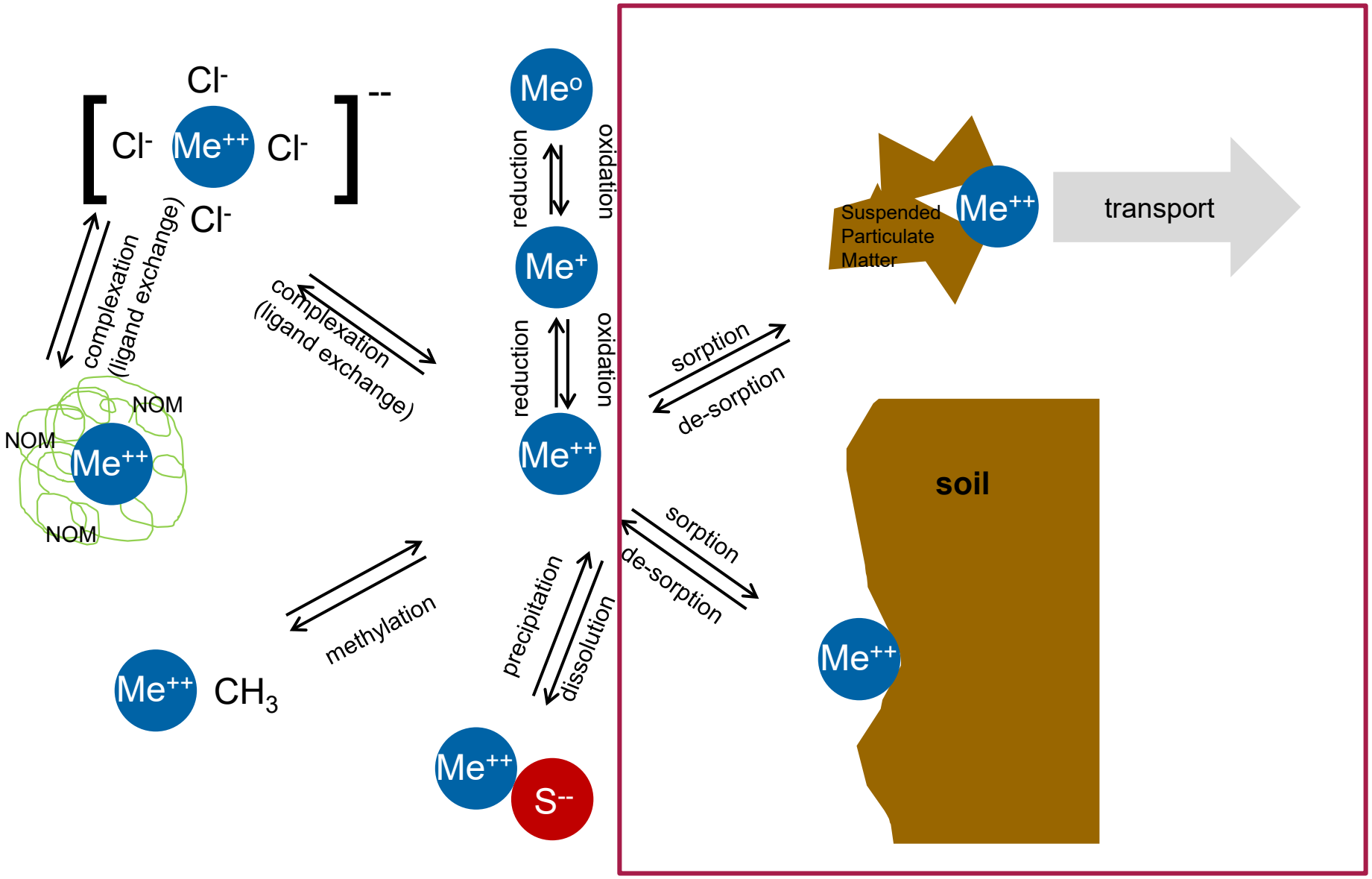
remobilisation from or with sediment

→ process understanding & system knowledge

Pivotal processes involving trace metals



Sorption!


Cl-
Cl-
Me++
Cl-
Cl-
--
complexation (ligand exchange)
complexation (ligand exchange)
NOM
NOM
Me++
NOM
methylation
Me++
CH3
Meo
reduction
oxidation
Me+
reduction
oxidation
Me++
precipitation
dissolution
Me++
S--
sorption
de-sorption
sorption
de-sorption
Suspended Particulate Matter
Me++
transport
soil
Me++

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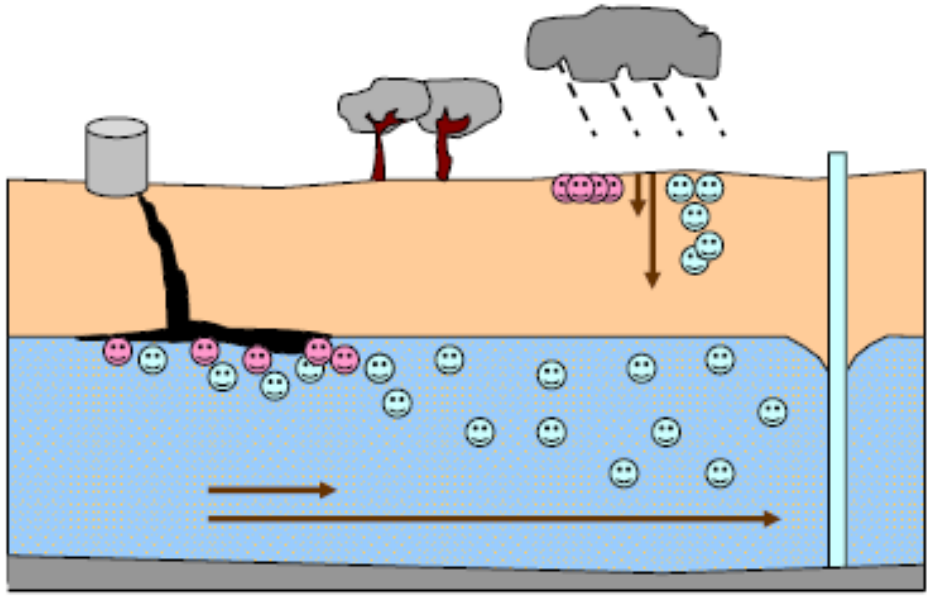
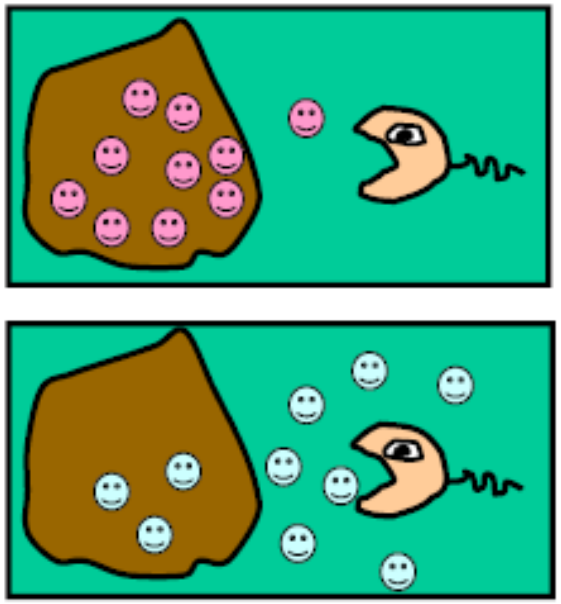
To understand contaminant fate and transport, we need to first understand sorption in the environment

Solute Transport



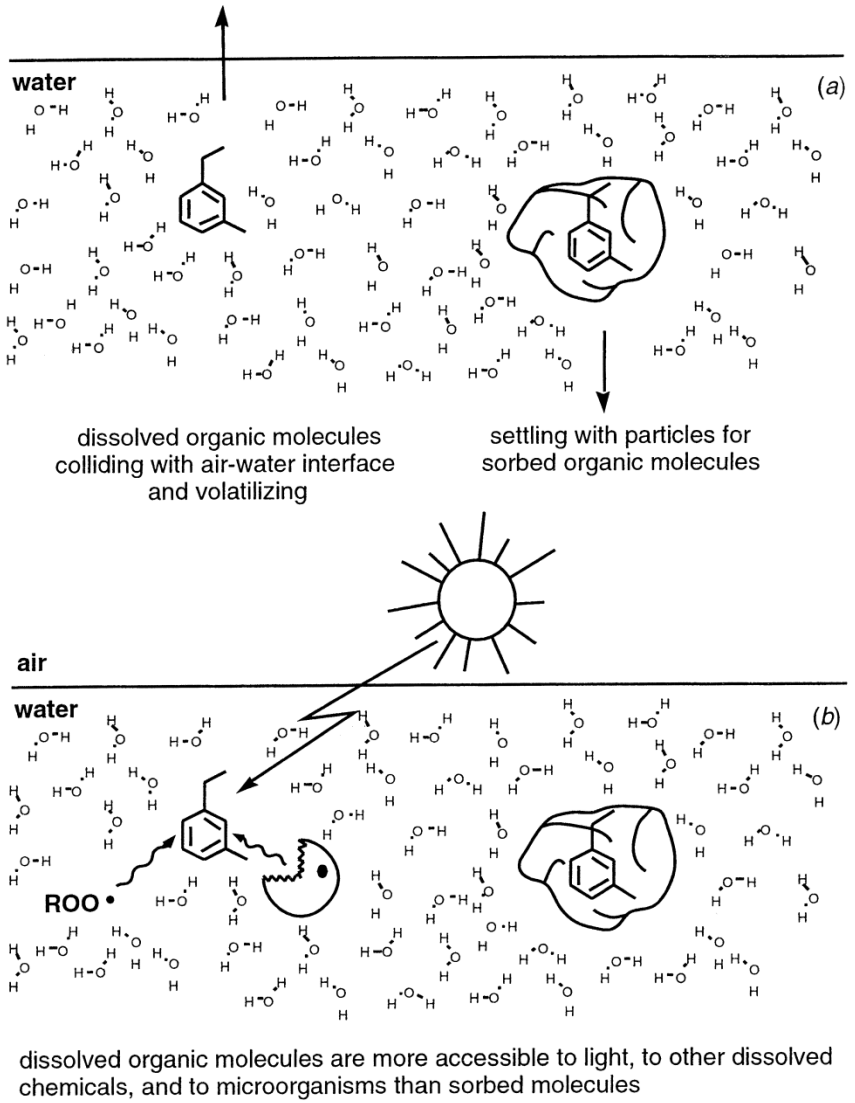
Bioavailability



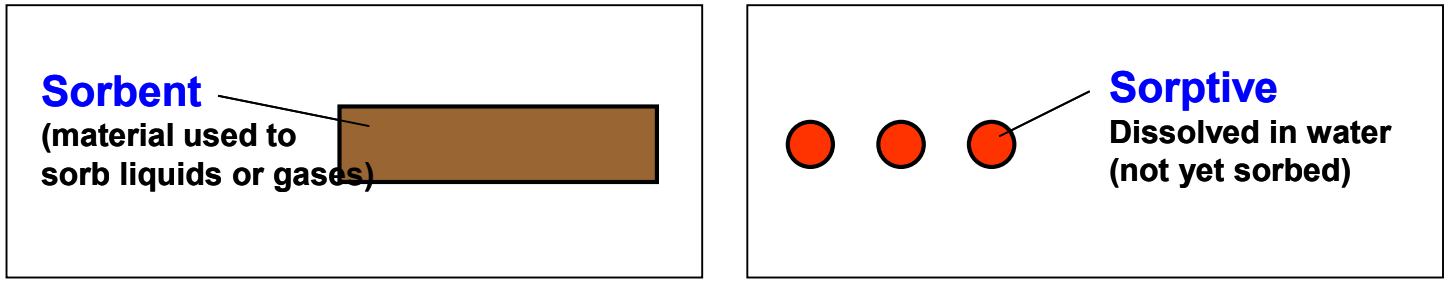
Sorption from water to particulate matter strongly influences the fate compounds

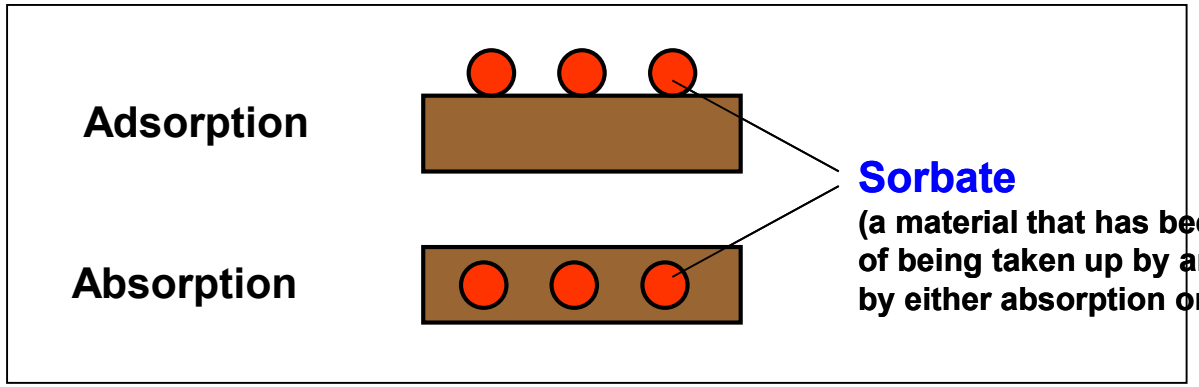
Sorption controls:

- Transport in surface and subsurface water
- (Phase transfer)
- Bioavailability and, thus, (bio-degradation) and toxicology
- (Direct photolysis)
- (Radical oxidation)
- Chemical reactions

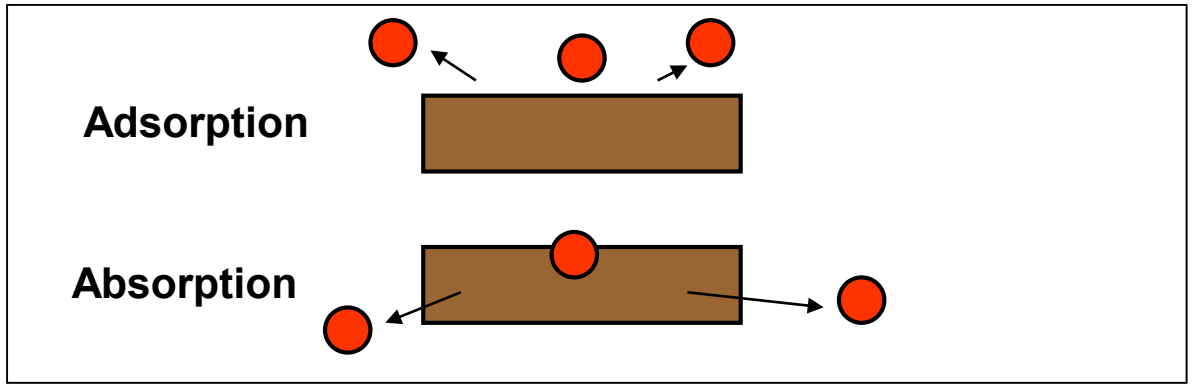


Schwarzenbach et al. 2003.





Sorption



Desorption

- Absorption
  - precipitation, co-precipitation, inclusion
  - matrix-sorption

- adsorption
  - physisorption

    weak, reversible

    Van der Waals & electrostatic interactions

    ➡ ion exchange

  - chemiesorption

    strong, not always reversible

    hydrogen bonding, covalent bonding

    ➡ surface complexation

Absorption

Adsorption

ion exchange – capacity and selectivity

- requires a charged surface terminated by exchangeable ions
- exchange of ions against others of the same polarity (+ for +)

  mainly from immobile ions that are associated with a surface

  against those that are dissolved in a solute

  e.g.:

  2 X-SO_3Na + Ca^{2+} → $(X\text{-}SO_3)_2Ca$ + 2 Na^+

- cation exchangers (+) anion exchangers (-) amphiphilic exchangers (+/-)

- with industrial exchange resins the selectivity of the exchange increases with valence of the ion and hydrated ion radius

  weakly bound ← Na < Ca < Fe(II) < Cd < Ni < Pb < Cu < Hg → strongly bound

selectivity increases by about 1000 to 10,000 times in this sequence

influencing factors are the nature of the exchange groups, pH, concentration and composition of the liquid phase

ion exchange – capacity and selectivity

- cation exchange capacity (CEC) calculated:

CEC_{Corg} (meq/100g) ~ 51 pH – 59 (*Scheffer & Schachtschabel 1970*)

CEC_{tot} (meq/100g) ~ 0.7 (% clay) + 3,5 (% C_{org})

$CEC = 3{,}97 \times (1 - 0{,}183 \times (8{,}2 - pH)) \times C_{oc} + 0{,}57 \times (1 - 0{,}102 \times (8{,}2 - pH)) \times C_{clay}$

- selectivity of some natural phases:

montmorillonite	Ca > Pb > Cu > Cd > Zn >> Na
ferrihydrite	Pb > Cu > Zn > Ni > Cd >> Na
peat (org. carbon)	Pb > Cu > Cd = Zn > Ca

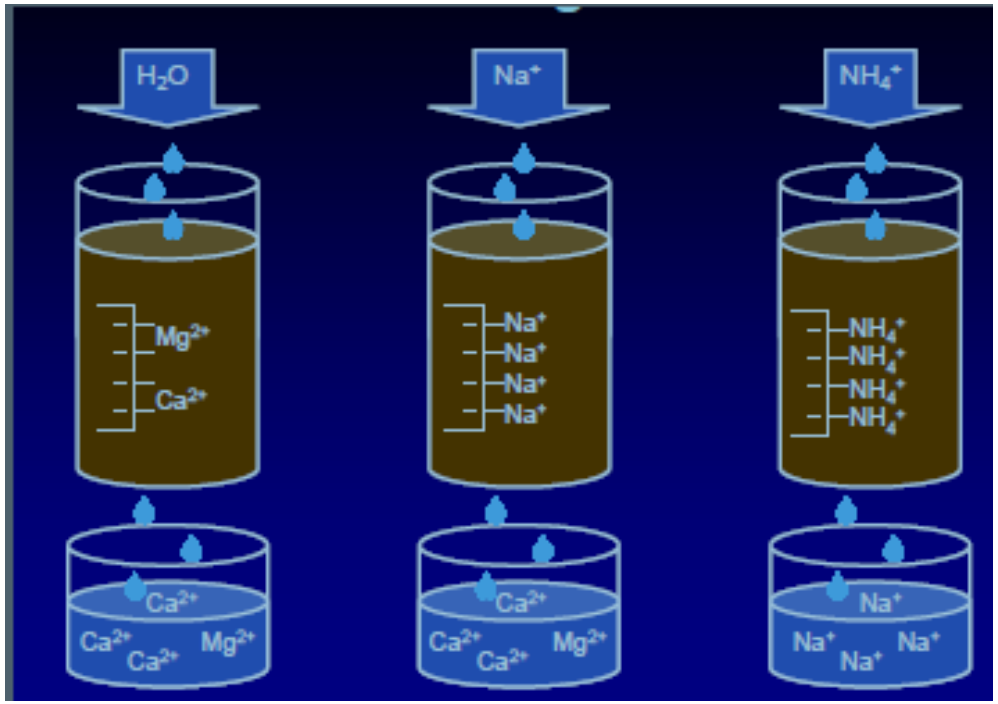
ion exchange – capacity

determining the CEC:

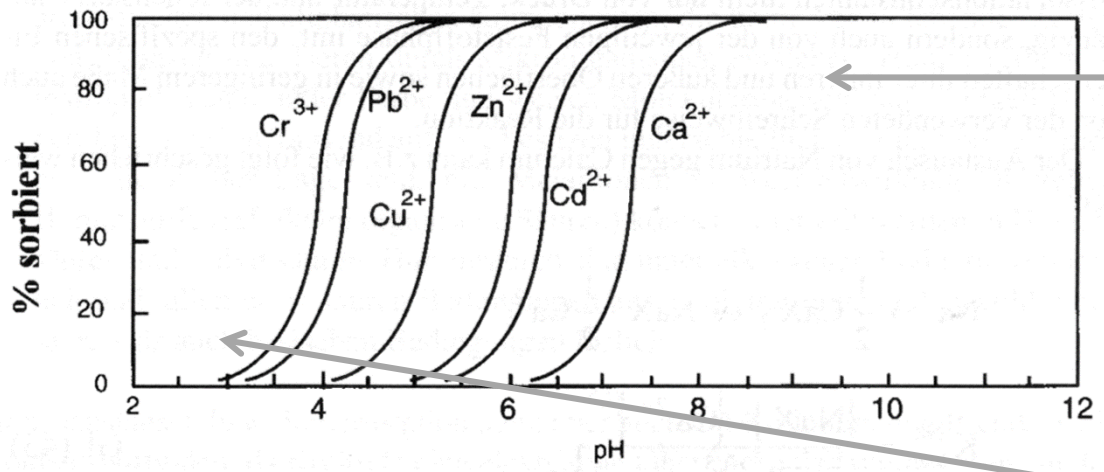
we know that a large concentration of a cation can replace all exchangeable cations

1) wash the material (soil) with an electrolyte of high concentration (NaCl, $BaCl_2$) >1 mol/L
2) keep the wash solution if you wish to determine the exchanged (formerly bound) components
3) exchange the cation against e.g. $MgCl_2$ or NH_4Cl
4) determine the amount of the back-exchanged cation (Ba or Na)

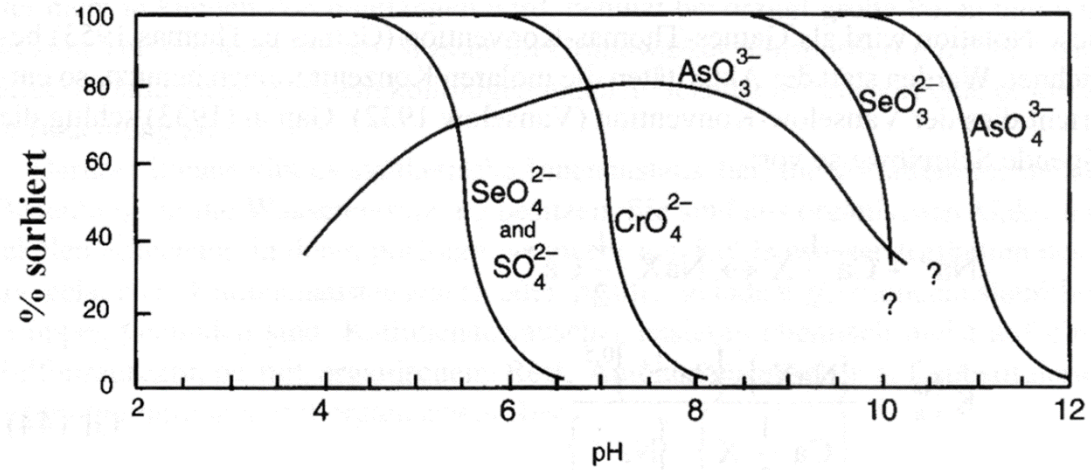
For Na you can use a flame photometer (~ € 4000) for Ba you would need an ICP-OES (€ 50,000)



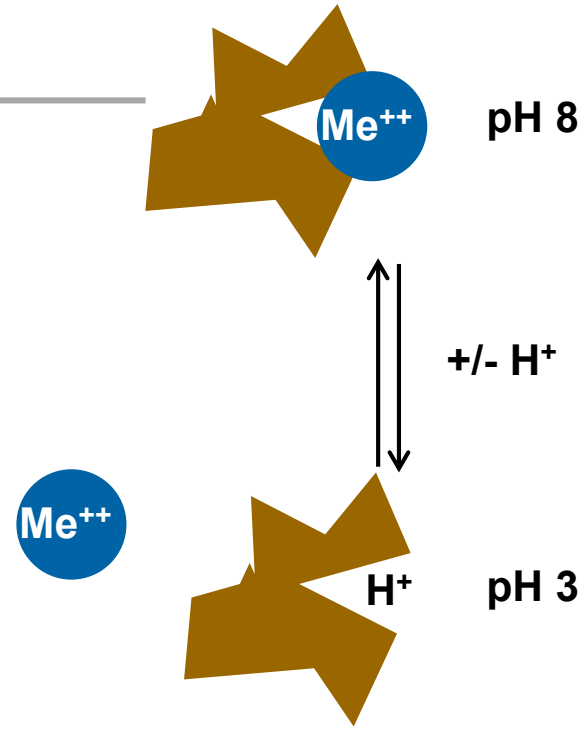
Adsorption is pH and species dependent



pH abhängige Sorption von Metallkationen an Eisenhydroxid (n. Drever 1997)

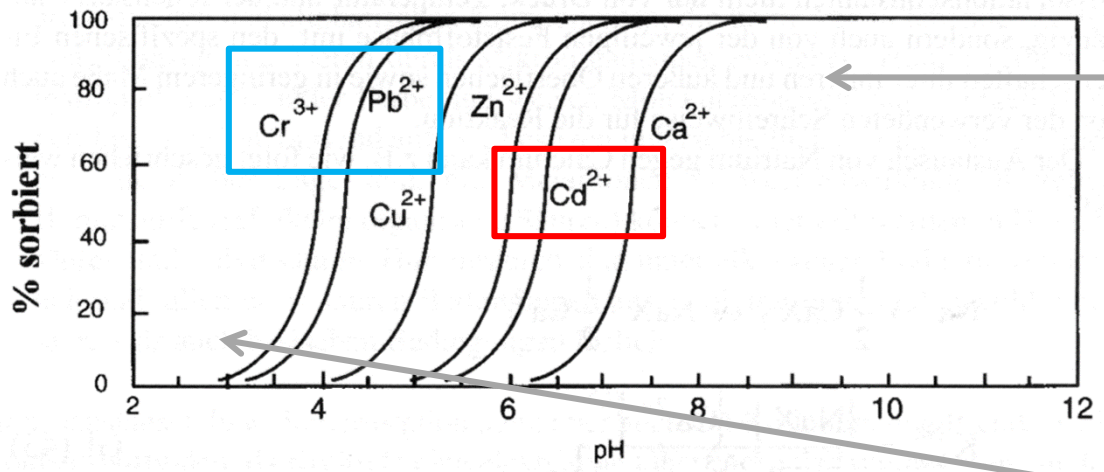


pH abhängige Sorption von Anionen an Eisenhydroxid (nach Drever 1997)

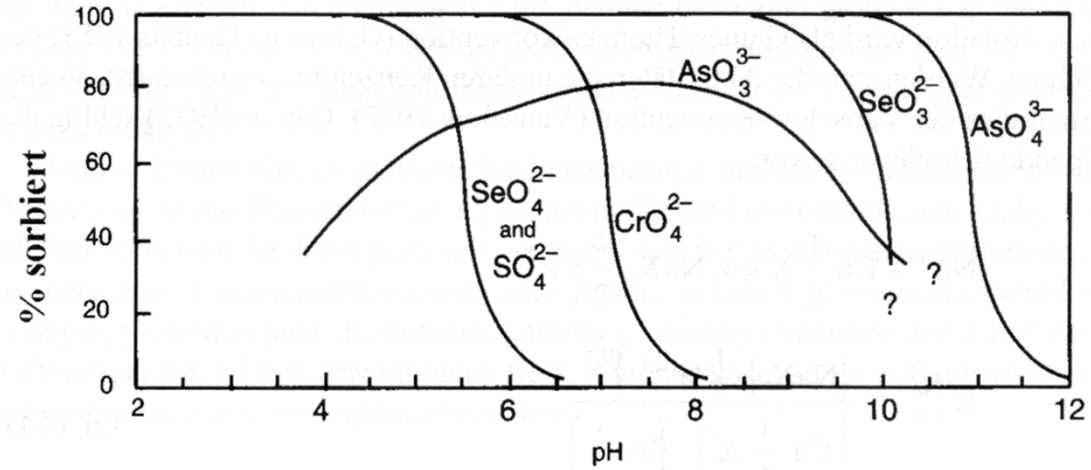


Merkel & Planer-Friedrich 2002

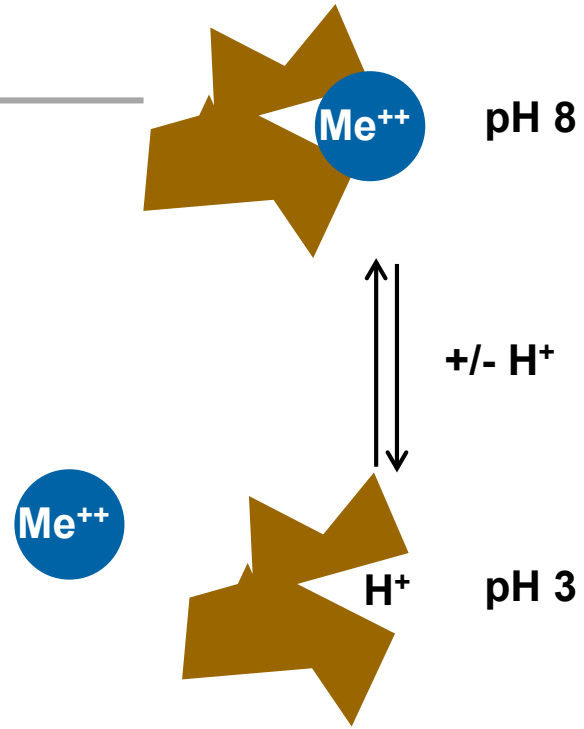
Adsorption is pH and species dependent



pH abhängige Sorption von Metallkationen an Eisenhydroxid (n. Drever 1997)



pH abhängige Sorption von Anionen an Eisenhydroxid (nach Drever 1997)



Merkel & Planer-Friedrich 2002

How does the metal distribute between solution and solid? Concept of Kd

Distribution coefficient (Kd):

Kd [L/kg] = Msorb [mg/kg] / Mdiss [mg/L]

Sorbed portion **Dissolved portion**

M = any substance

How does the metal distribute between solution and solid? Concept of Kd

Distribution coefficient (Kd):

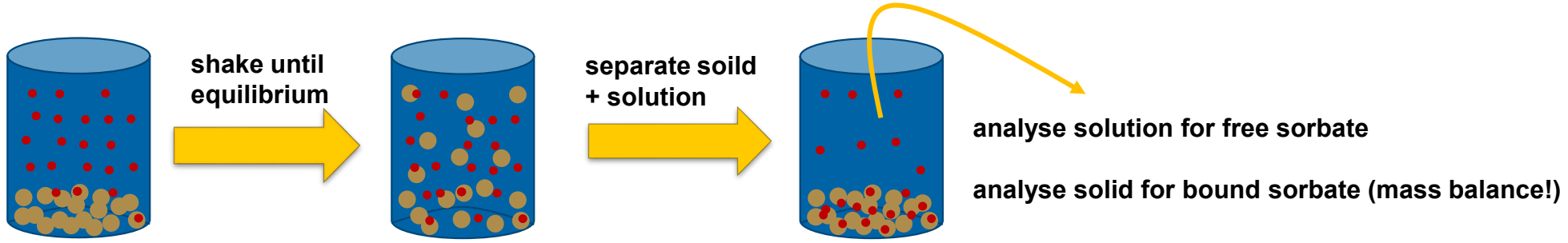
Kd [L/kg] = Msorb [mg/kg] / Mdiss [mg/L]

Sorbed portion | **Dissolved portion**

M in soil =
- **soil organic matter**
- **oxides**
- **clays**
- **quartz**

dissolved species
- **free metal ion**
- **inorganic complexes**
- **NOM complexes**

How to determine the distribution coefficient Kd



several experiments will be conducted with different amounts of dissolved metal and sorbent!

the ratio of adsorbed metal ion to free metal ion (distribution) is determined by

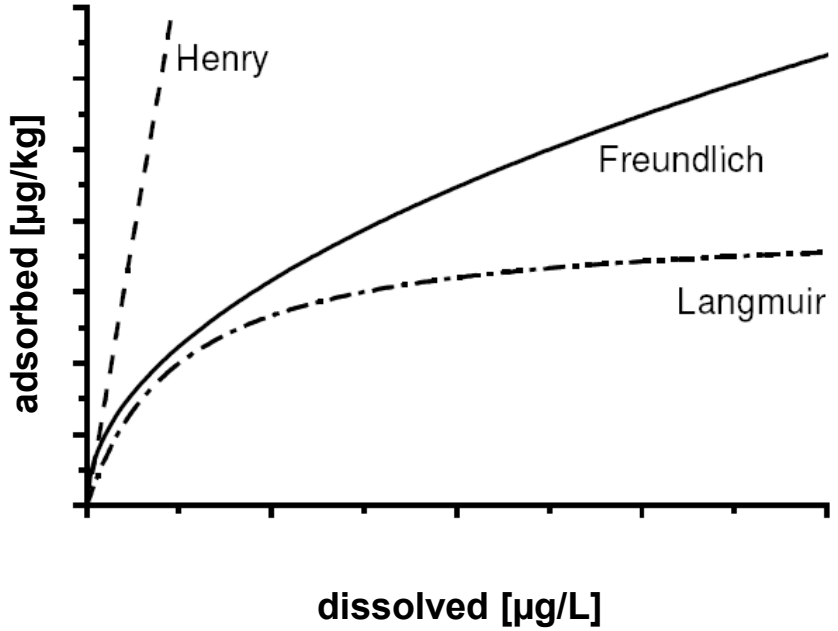
- **type of the sorbent**
- **pH**
- **speciation of metal**

- **temperature (sorption might be exothermic or endothermic)**
- **other competing ions**
- **substances that reduce the activity of the sorbate (complexation)**
- **concentration of the sorbent**

The 3 standard types of sorption isotherms

$$C_{solid} = K_D \cdot C_{dissolved}$$

With a series of experiments you can draw the dependency of adsorbed metal concentration to dissolved metal concentration and gain a sorption isotherm (means: at constant temperature)



$$C_{solid} = K_f \cdot C_{dissolved}^{\ n}$$

$$C_{solid} = \frac{K_L \cdot C_{\max} \cdot C_{dissolved}}{1 + K_L \cdot C_{dissolved}}$$

Abb. 2: Sorptionsisothermen zur quantitativen Beschreibung der Wechselwirkung von Schadstoffen mit der Bodenmatrix.

The 3 standard types of sorption isotherms

- Henry isotherm (K_D-approach) :

  linear unlimited

$$C_{solid} = K_D \cdot C_{dissolved}$$

- Freundlich Isotherm

  non-linear and unlimited

$$C_{solid} = K_f \cdot C_{dissolved}^{\ n}$$

n = 1: Henry; n < 1: decrease of sorption sites

n > 1: double layers

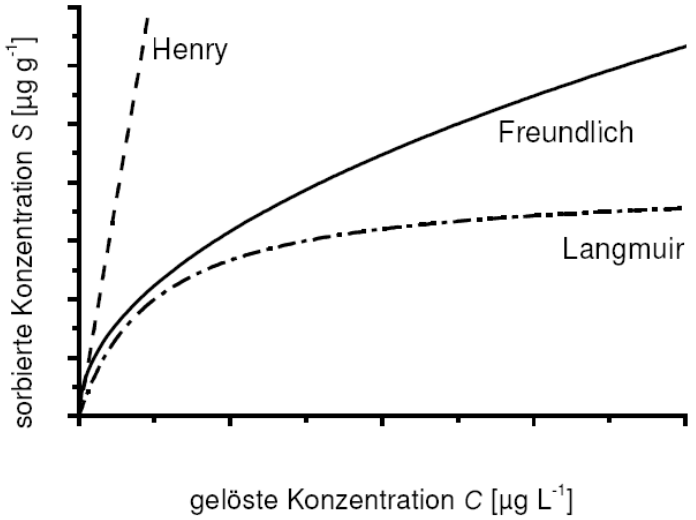


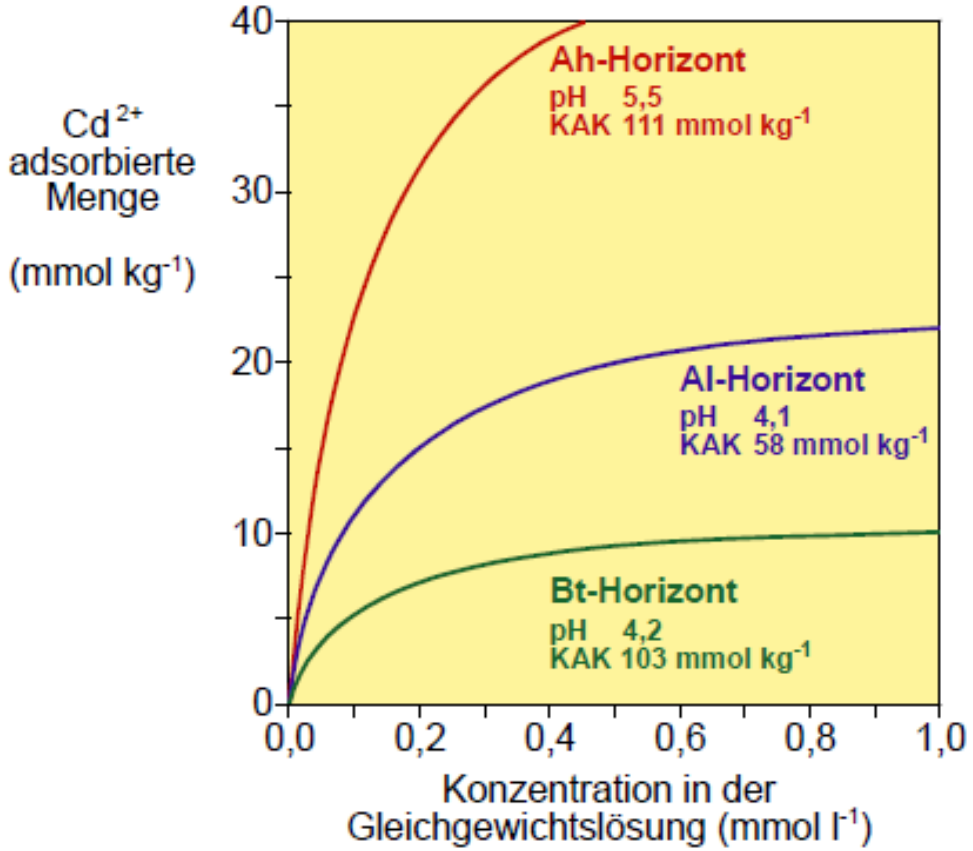
Abb. 2: Sorptionsisothermen zur quantitativen Beschreibung der Wechselwirkung von Schadstoffen mit der Bodenmatrix.

- Langmuir Isotherm

  non-linear and limited

$$C_{solid} = \frac{K_L \cdot C_{\max} \cdot C_{dissolved}}{1 + K_L \cdot C_{dissolved}}$$

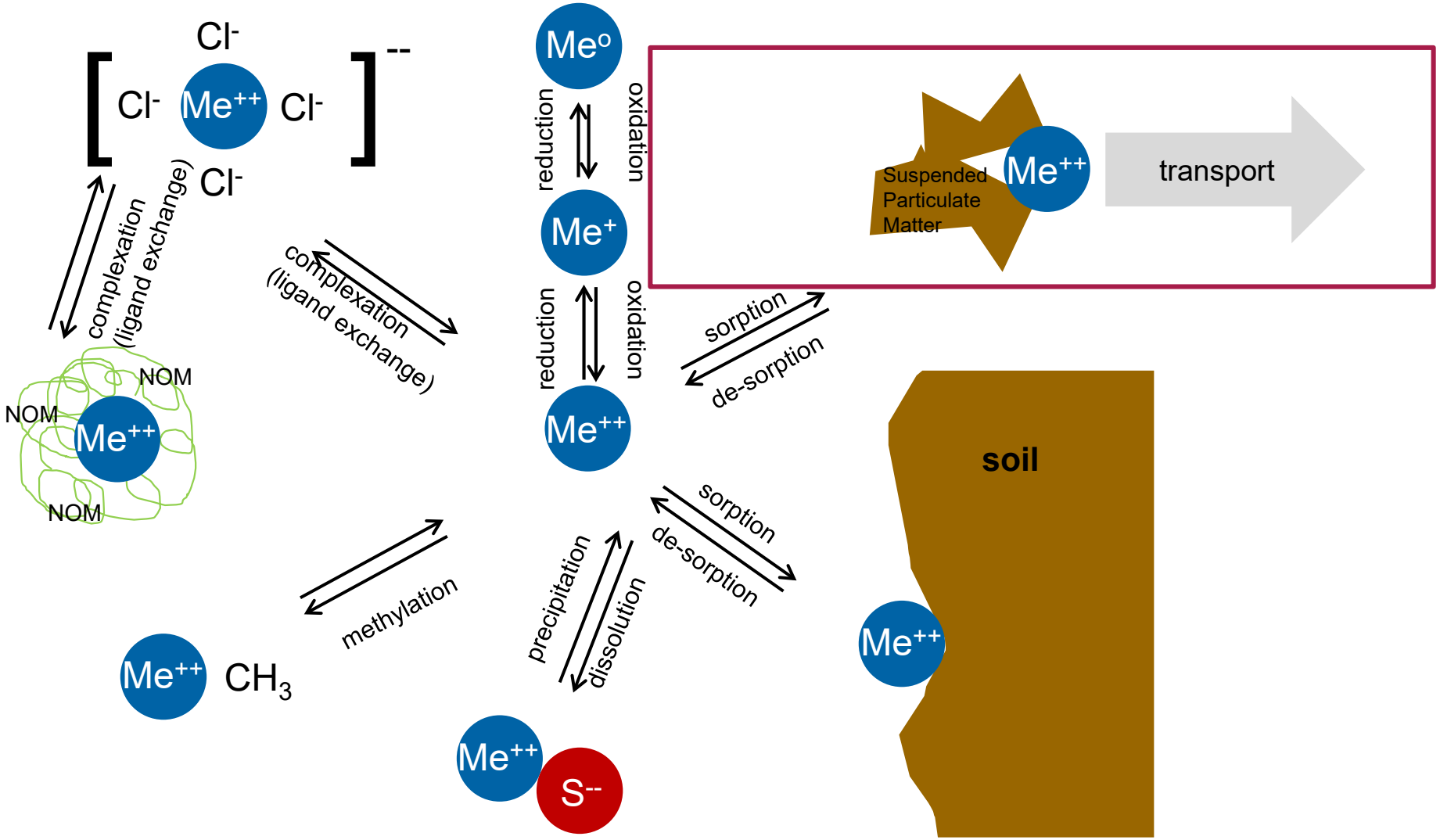
But soil is a complex environment… and the isotherms are empiric!



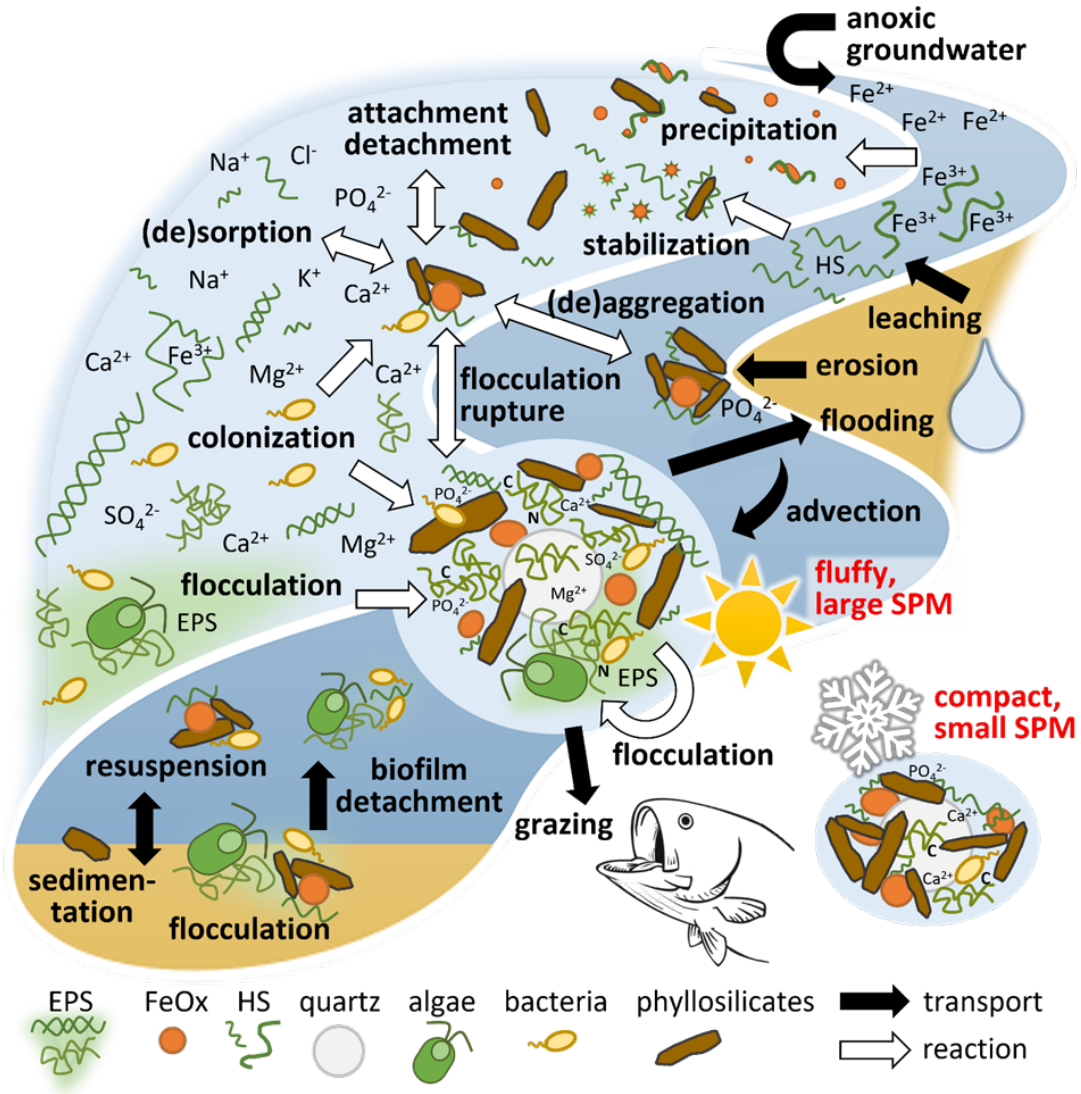
Adsorptionsisothermen von Cadmium für 3 Horizonte einer Parabraunerde
Bodenökologie, Gisi, 1997

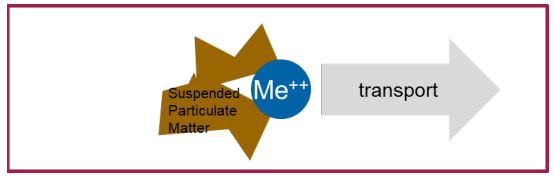
So, the determined Kd value only holds true for the sorbent (soil, sediment) determined

Sorption to SPM or small particles (colloids/nanoparticles)!



Sorption to SPM or small particles (colloids/nanoparticles)!





Riverine Suspended Particulate Matter (SPM)

About 10^9-10^{13} tons of SPM are discharged into the oceans every year

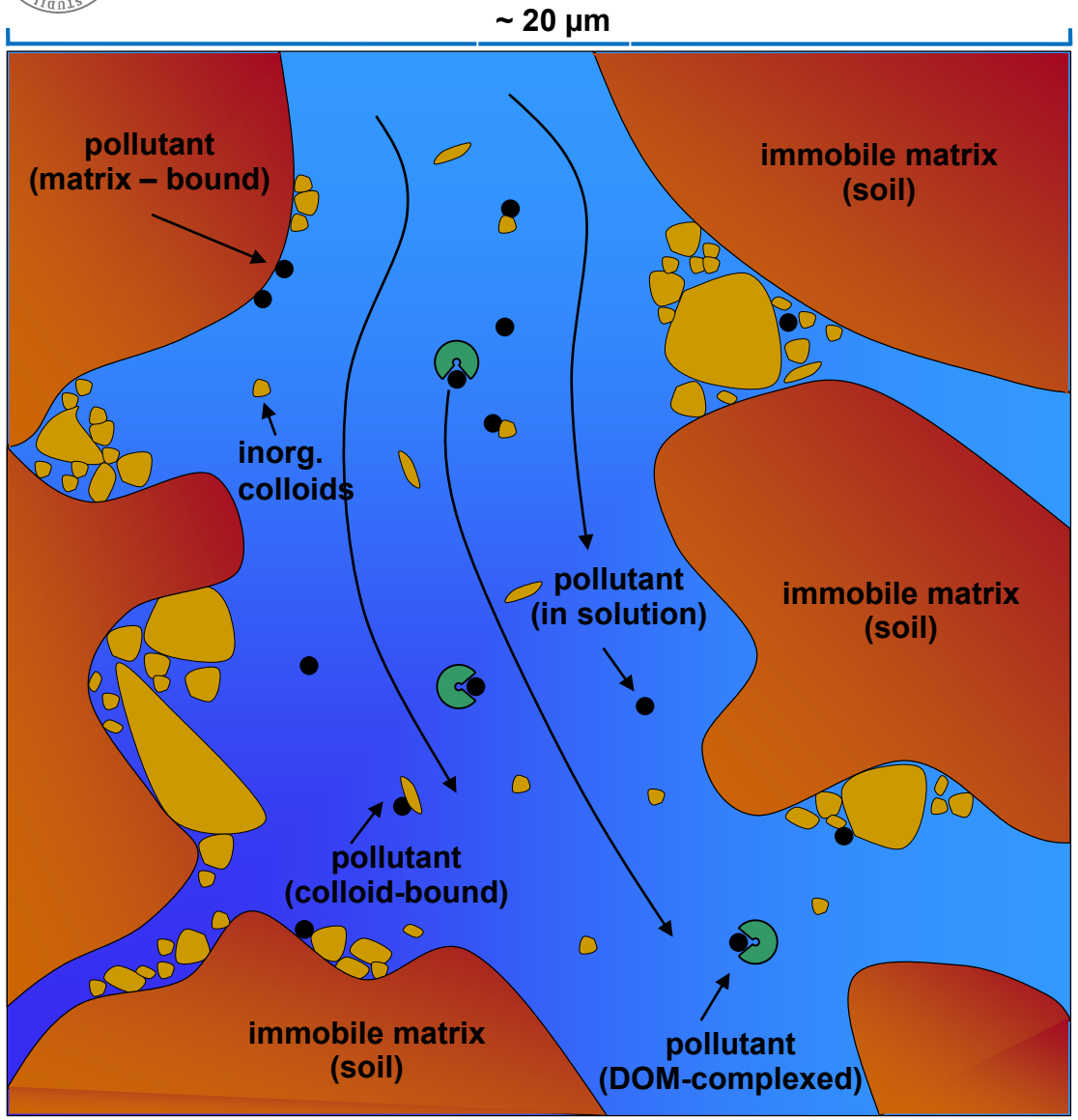
A large proportion of trace metals is bound to SPM

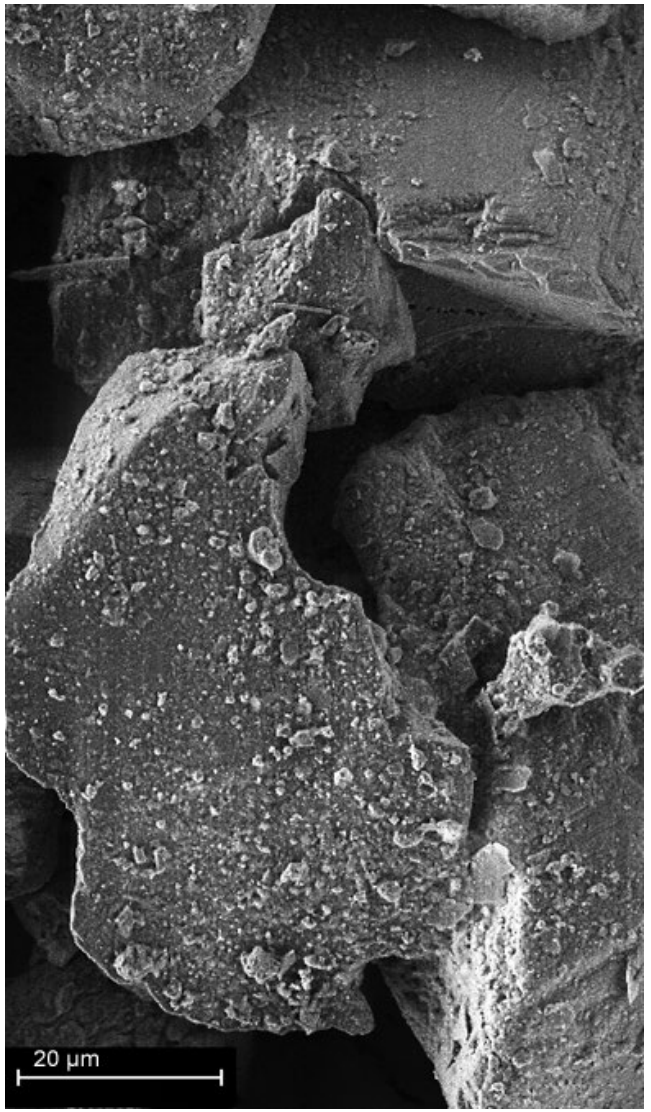
Pb ~ 95 – 99%
As, Cd, Zn ~ 30 – 80 %

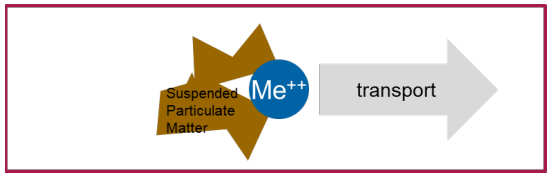
Concentrations on SPM typically in the mg/kg, in water in the µg/L region (particulate/dissolved)

Walch, von der Kammer, Hofmann 2022: https://eartharxiv.org/repository/view/3113/

Sorption to SPM or small particles (colloids/nanoparticles)!

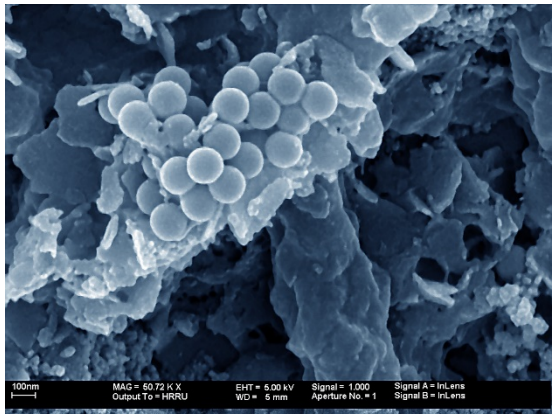




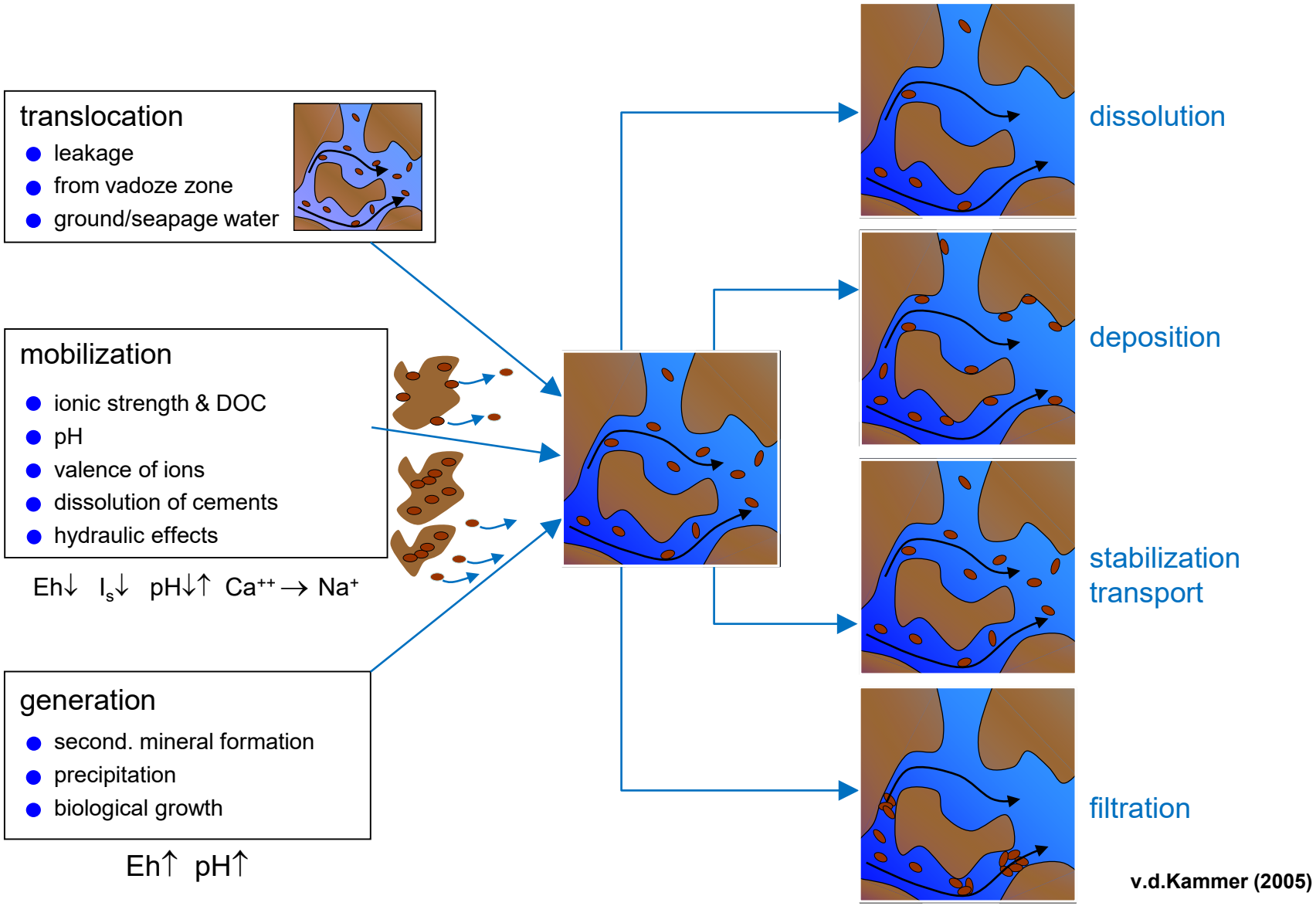


The pollutant can be

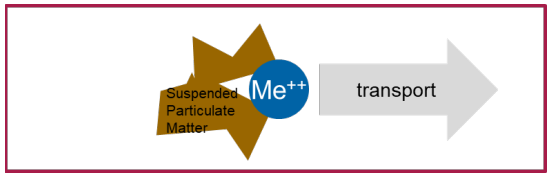
- **In solution (free ion or NOM-complexed)**
- **Sorbed to the stationary matrix**
- **Sorbed to mobile particles**



Sorption to SPM or small particles (colloids/nanoparticles)!

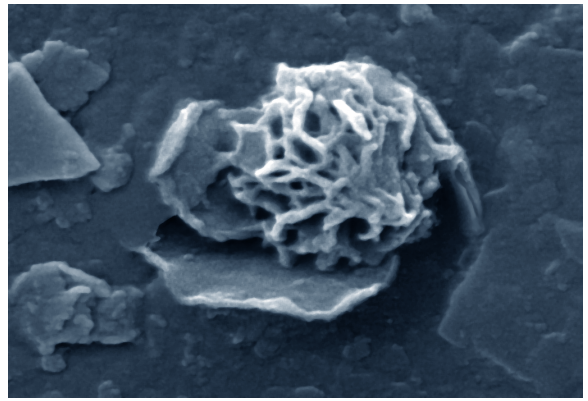


v.d.Kammer (2005)

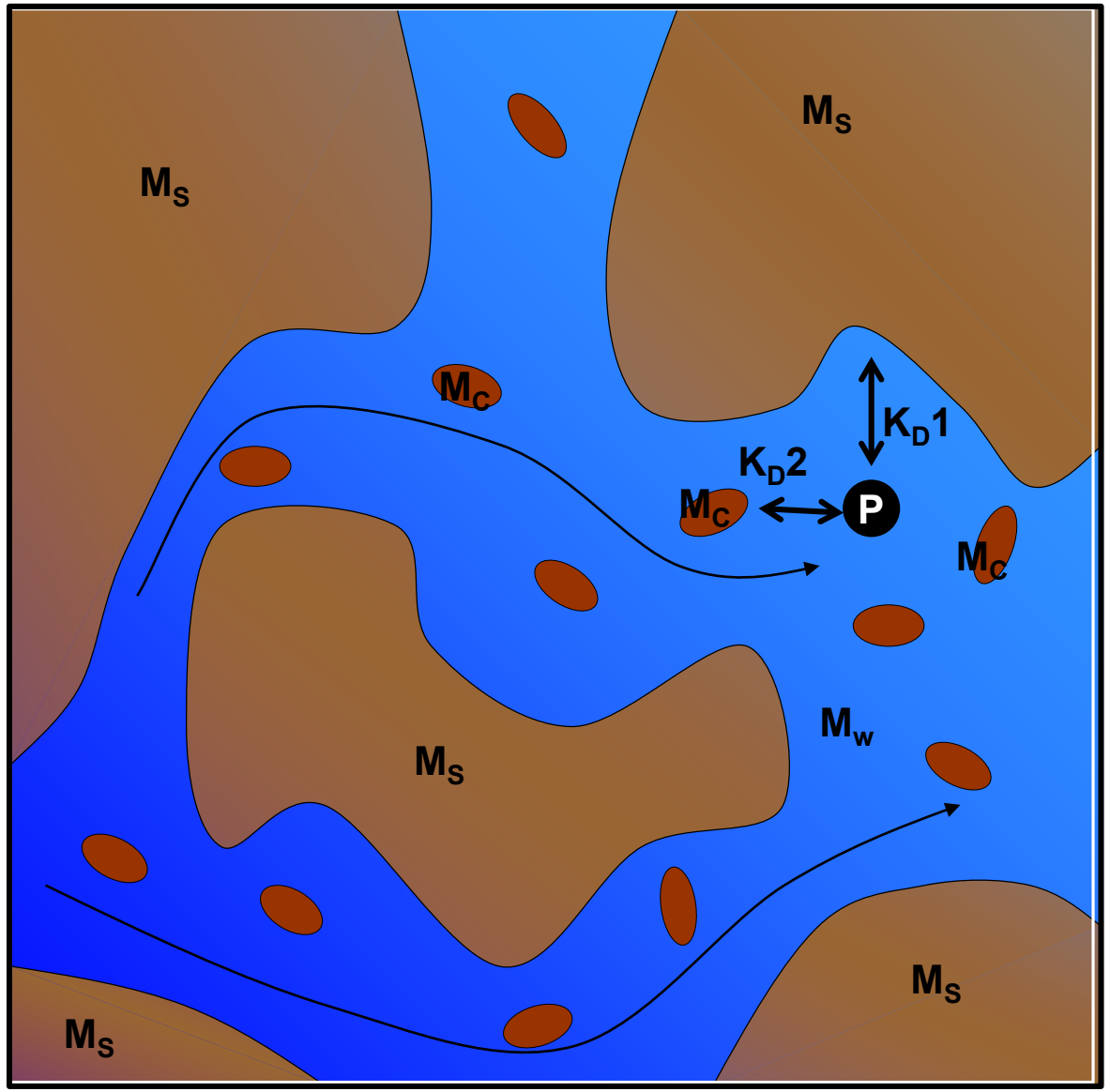


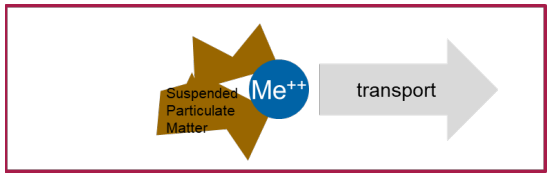
The mobile particles

- Need to be „there“ – concentration
- Need to be mobile
- Need to be stable
- Need to be „attractive“ for pollutant



Sorption to SPM or small particles (colloids/nanoparticles)!

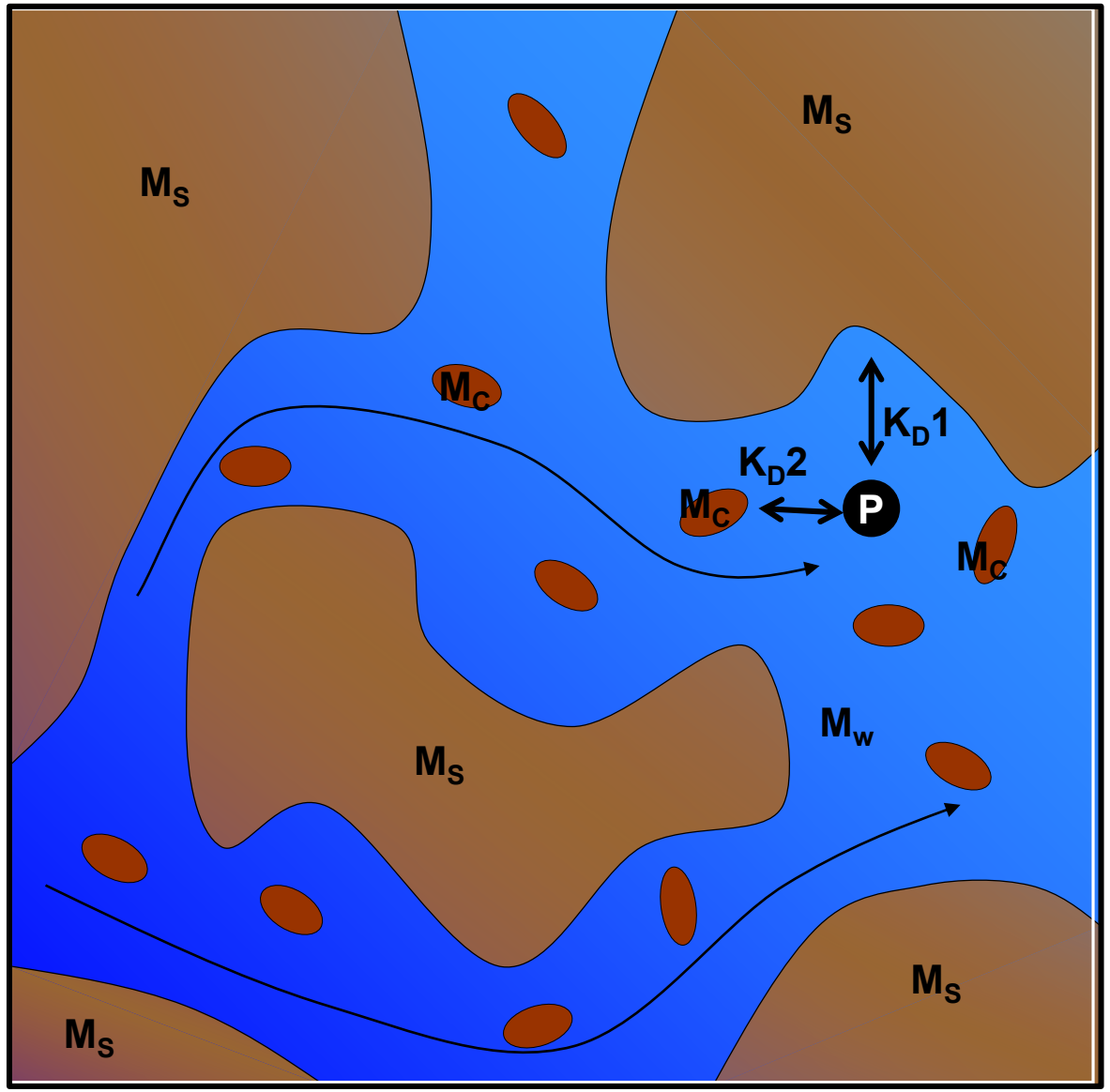


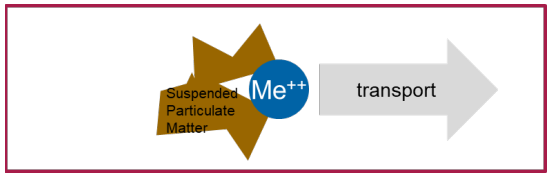


M_S ~ 2.000 g/L
M_W ~ 350 g/L
M_C ~ 10 mg/L

What does that mean for K_D1 and K_D2?
How can M_C become important?

Sorption to SPM or small particles (colloids/nanoparticles)!





M_S ~ 2.000 g/L
M_W ~ 350 g/L
M_C ~ 10 mg/L

What does that mean for K_D1 and K_D2?
How can M_C become important?

1) **The colloids/particles must be mobile and persistent**
2) **The concentration must be high**
3) **The pollutant must strongly sorb/bind to colloids**
4) **The sorption must be (almost) irreversible**

Castan et al. 2020: Microplastics and nanoplastics barely enhance contaminant mobility in agricultural soils. Nature Communications Earth & Environment

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More next…