An overview of aqueous speciation of metals for geochemical and toxicity modelling.

by

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Outline

- **Background**
  - The need for “speciation”
  - What is speciation anyways?
  - Metal-water and metal-ion interactions (equilibrium constant ***K***)
  - … for geochemical modelling
- **Case studies (2002-07)**
  - Pre-assessment of “speciation” of radioactive contaminants
  - Recent developments – multi response fluorescence

The need for “speciation”

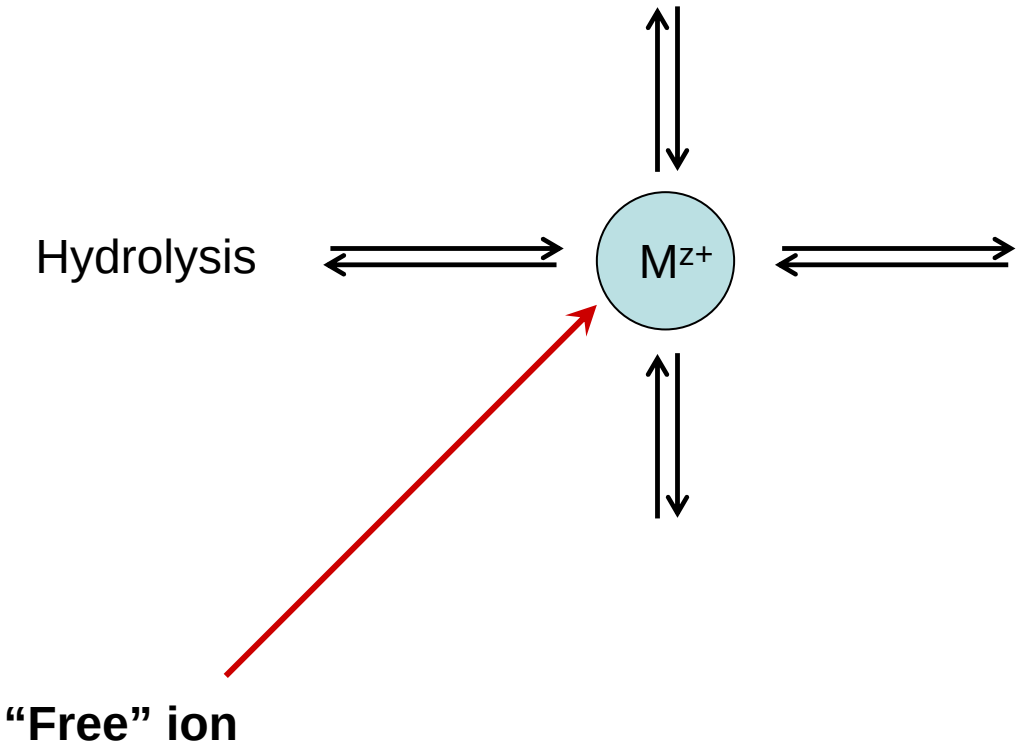
- The need for “speciation” depends upon the end use of the information:
  - Thermodynamic speciation (theoretic approach)
  - Toxicity studies – kinetically limited
  - **Mobility, remediation of contaminated soils** – “stable” species

- There is no unified scheme to determine the “speciation” of an element.

- In environmental samples, “speciation” has to be tailored to the need:
  - ***Operationally-defined “speciation”*** is often used but not chemically rigorous.
  - This “speciation”, however, remains *useful* if the interpretation is limited to the conditions in which measurements are made.

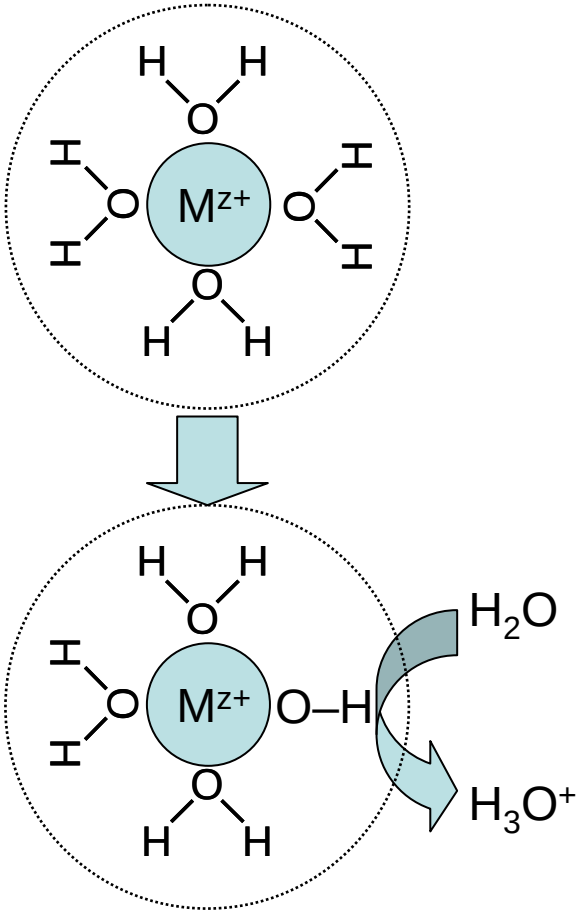
What is speciation anyways?

Suppose a cationic element M^{z+} :



What is speciation anyways?

$M^{z+} + 6\ H_2O \rightarrow \quad M(H_2O)_6^{z+}$ (assume C.N. = 6)
"Free" ion

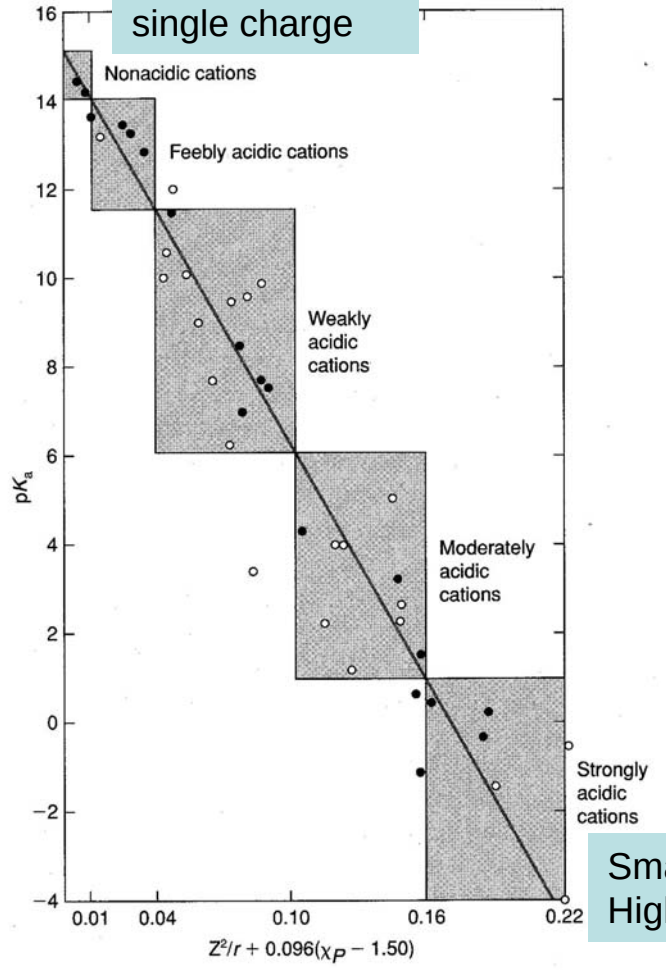


First hydrolysis:
$M(H_2O)_6^{z+} \rightarrow \quad M(H_2O)_5(OH)^{(z-1)+} + H^+$

$$K_{eq} = \frac{M(H_2O)_5(OH)^{(z-1)+} \times H^+}{M(H_2O)_6^{z+}}$$

What is speciation anyways?

Large cations, single charge



Small cations, High charge

Hydrolysis of cations:
Latimer relationship
(G. Wulfsberg, University Science books, Sausalito, CA, 2000)

Line: $pK_a = 15.14 - 88.16(Z^2/r)$
(first hydrolysis)

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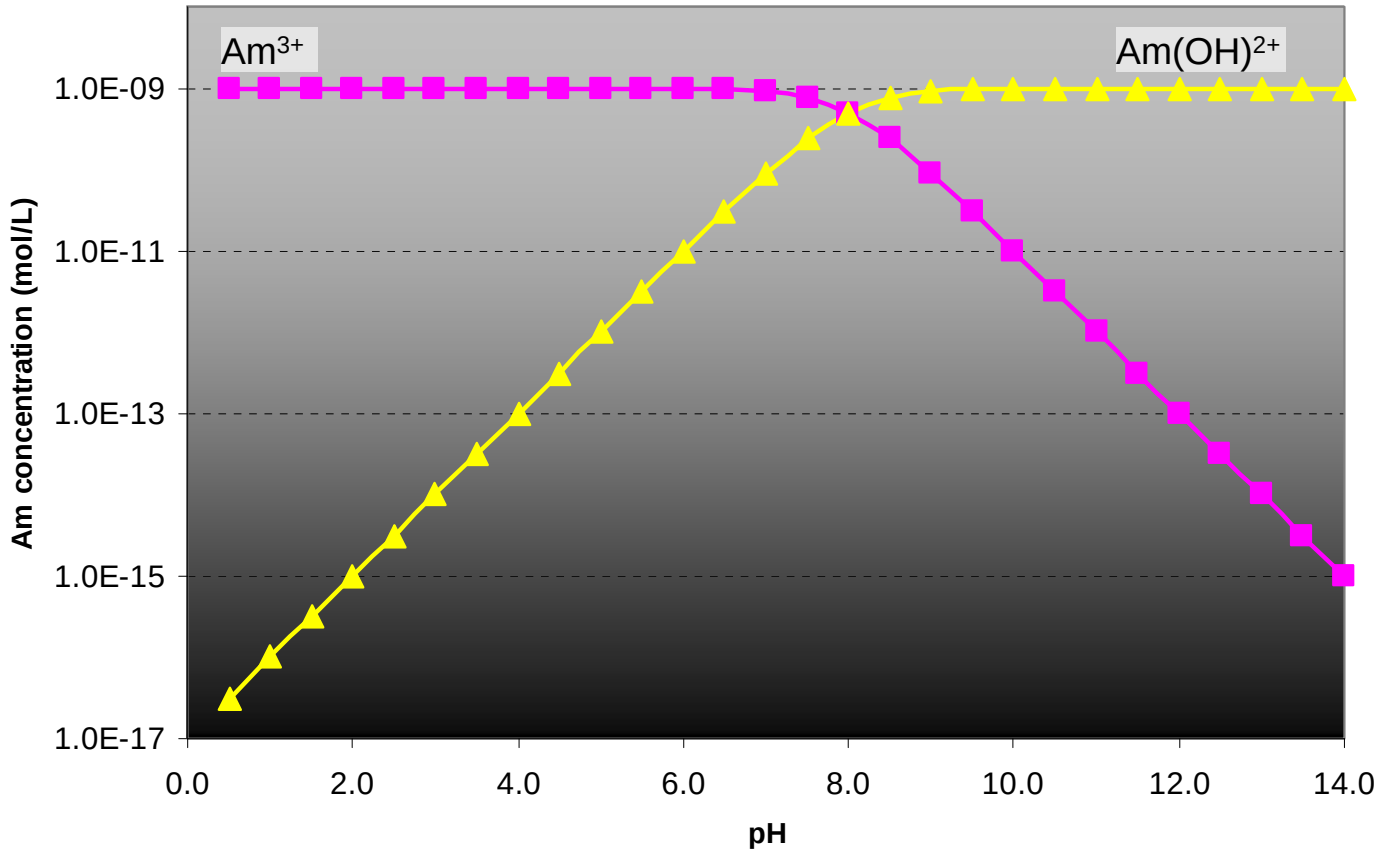
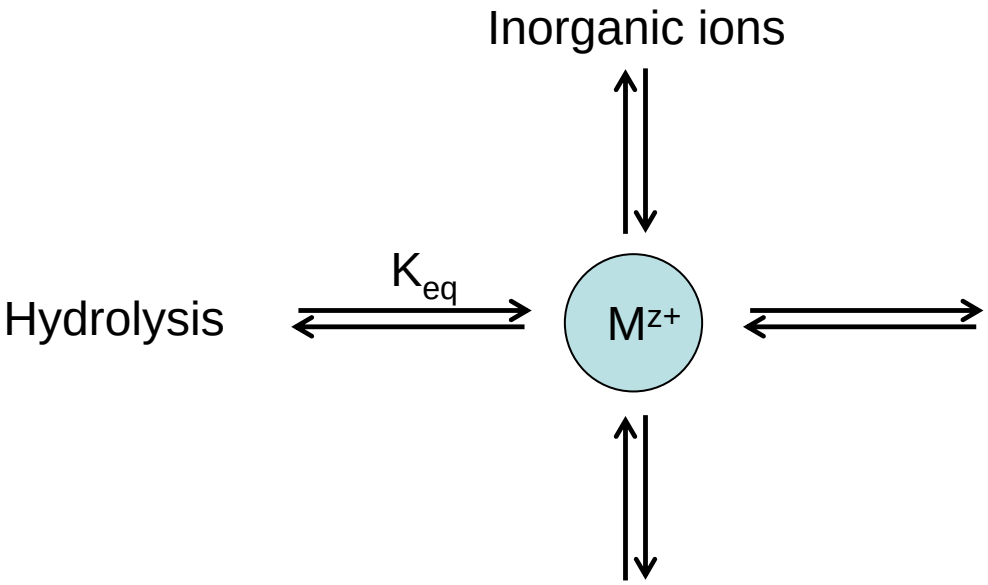
What is speciation anyways?

First hydrolysis plot for Americium ($Am_T = 10^{-9}$ mol/L), pK_{a1} = 8.0 (**calculated**)



What is speciation anyways?



What is speciation anyways?

Reactions with other inorganic ligands (L):

$M^{z+} + L^{-} \rightarrow M(L)^{(z-1)+}$

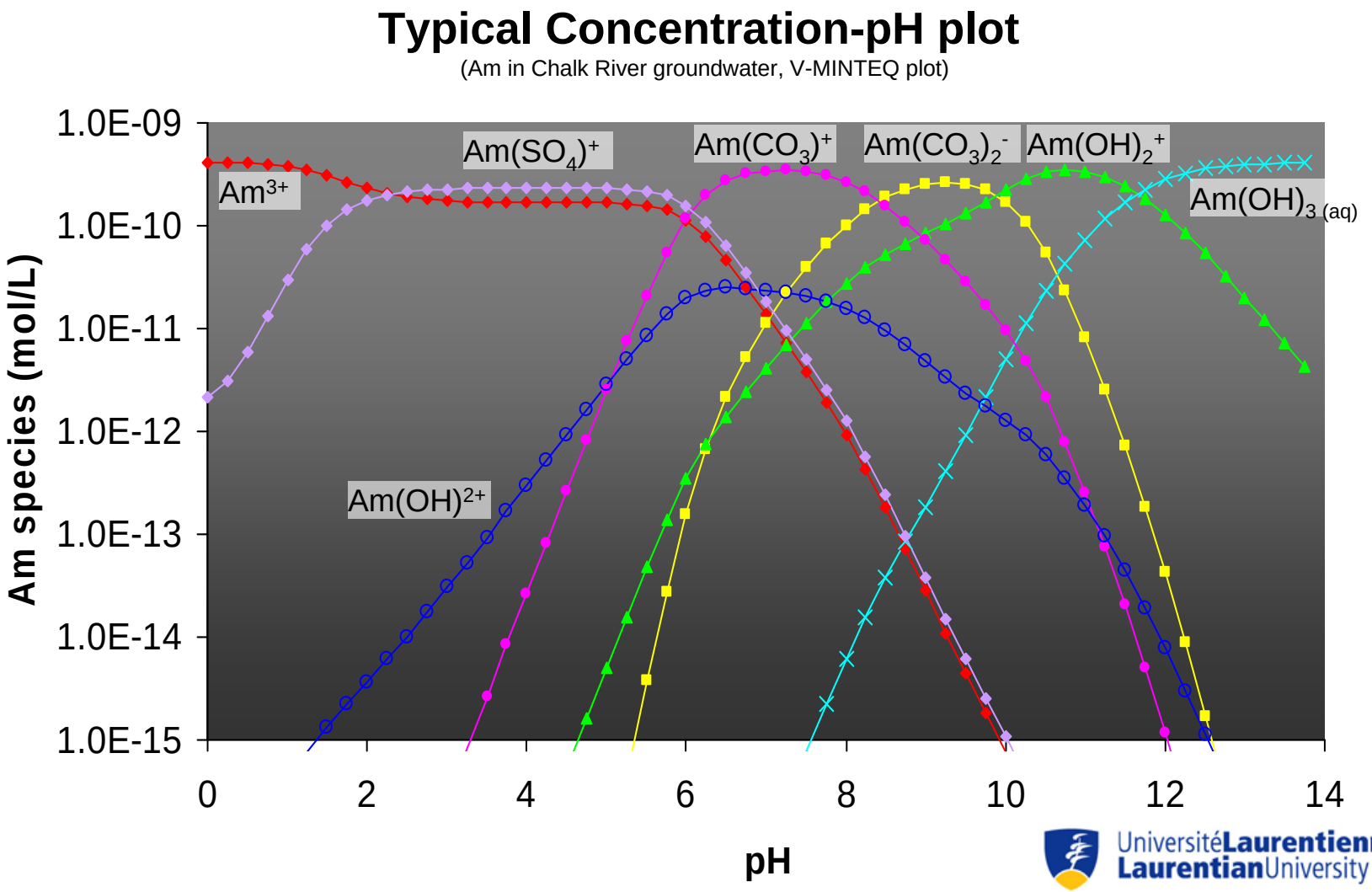
K_{eq} = … with all ligands or ions present in solution

$$M^{z+} + L^{n-} \overset{\beta}{\longleftrightarrow} ML^{(z-n)+}$$

$$\beta = \frac{[M\ L^{(z-n)+}]}{[M^{z+}][L^{n-}]}$$

Example with Am^{3+}: $Am^{3+} + CO_3^{2-} \rightarrow Am(CO_3)^{+}$

What is speciation anyways?



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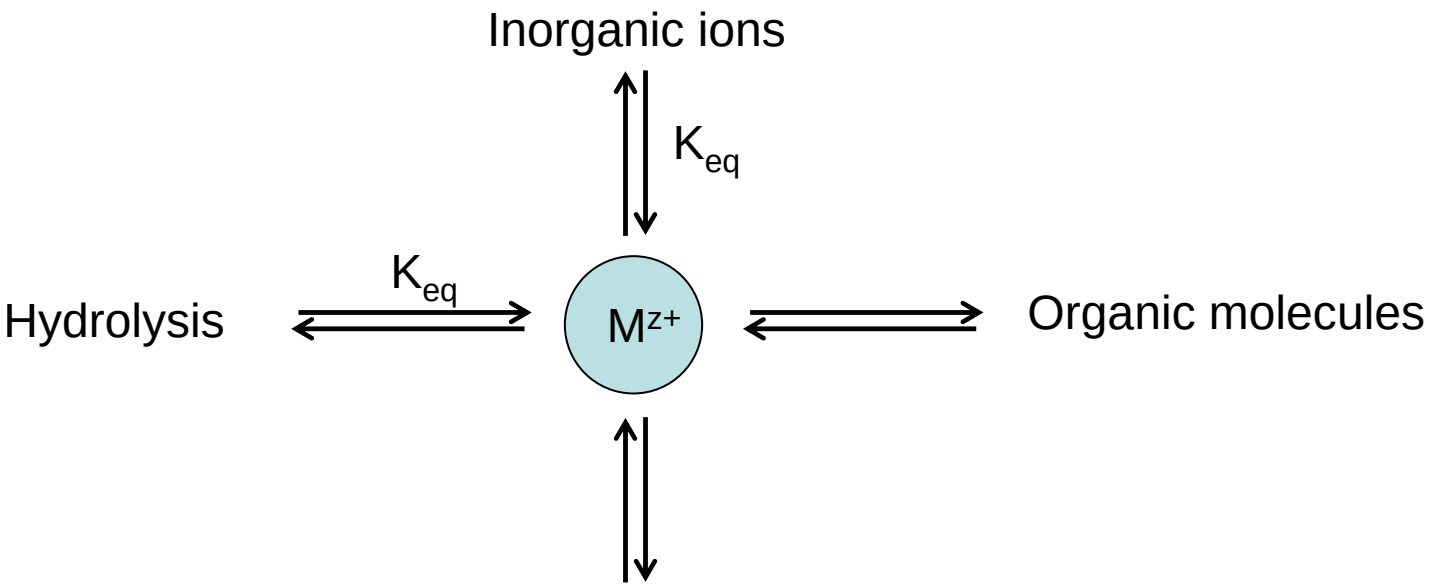
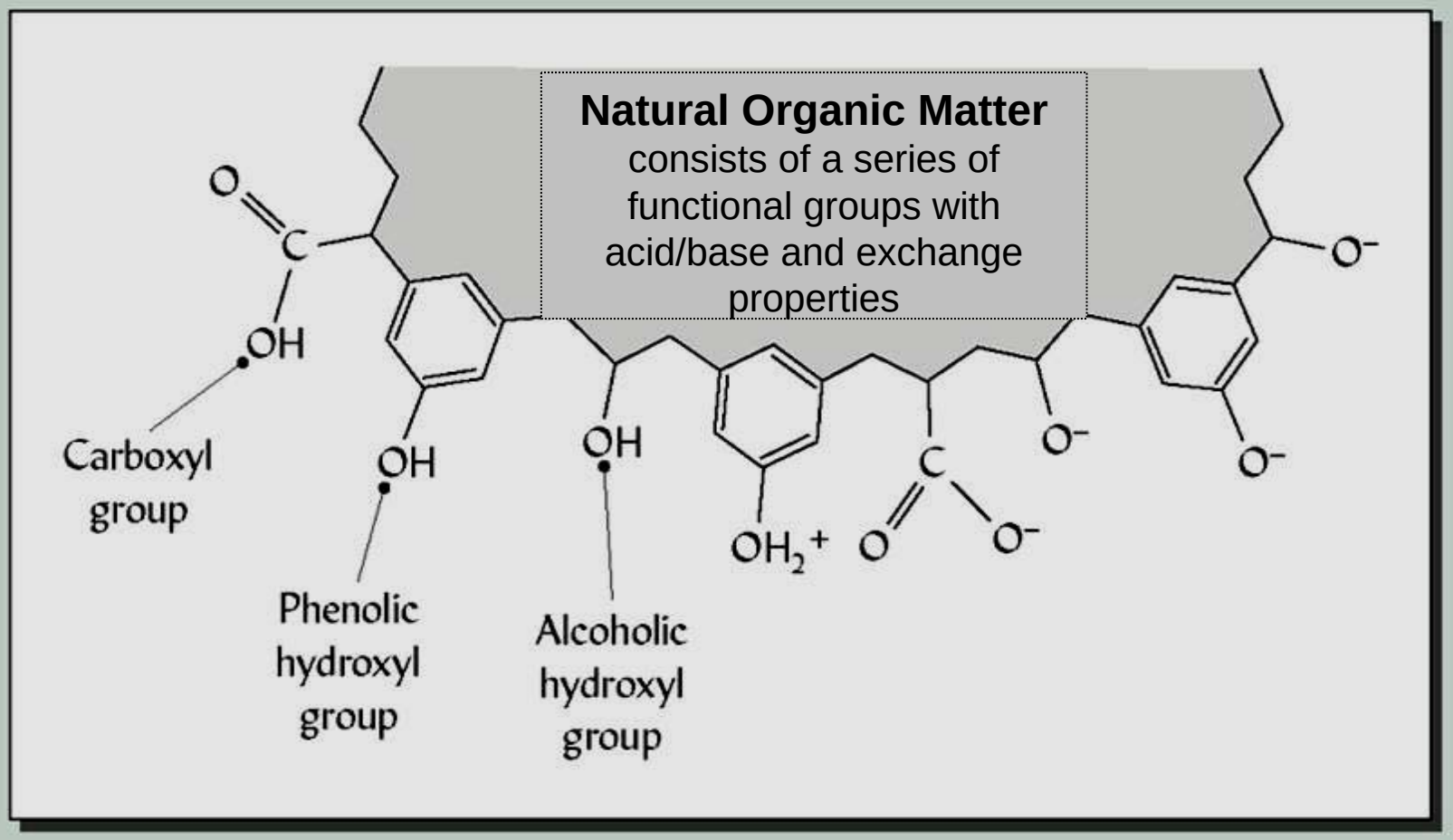
What is speciation anyways?



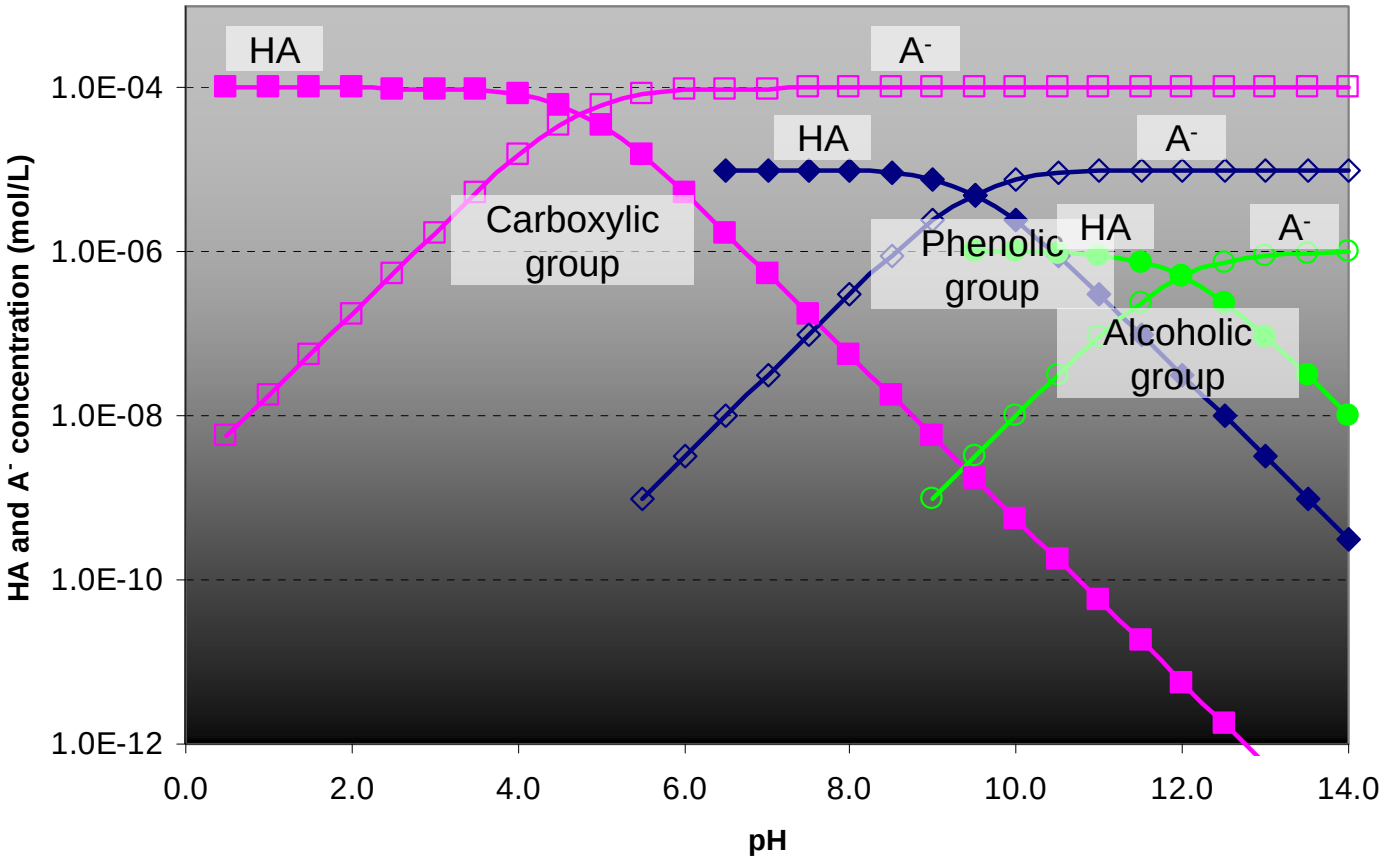
Speciation with organic “molecules”



Modified from http://www.enst.umd.edu/enst411

Speciation with organic “molecules”

Hypothetical polyprotic acid containing 10^{-4} M carboxylic, 10^{-5} M phenolic, 10^{-6} M alcoholic groups



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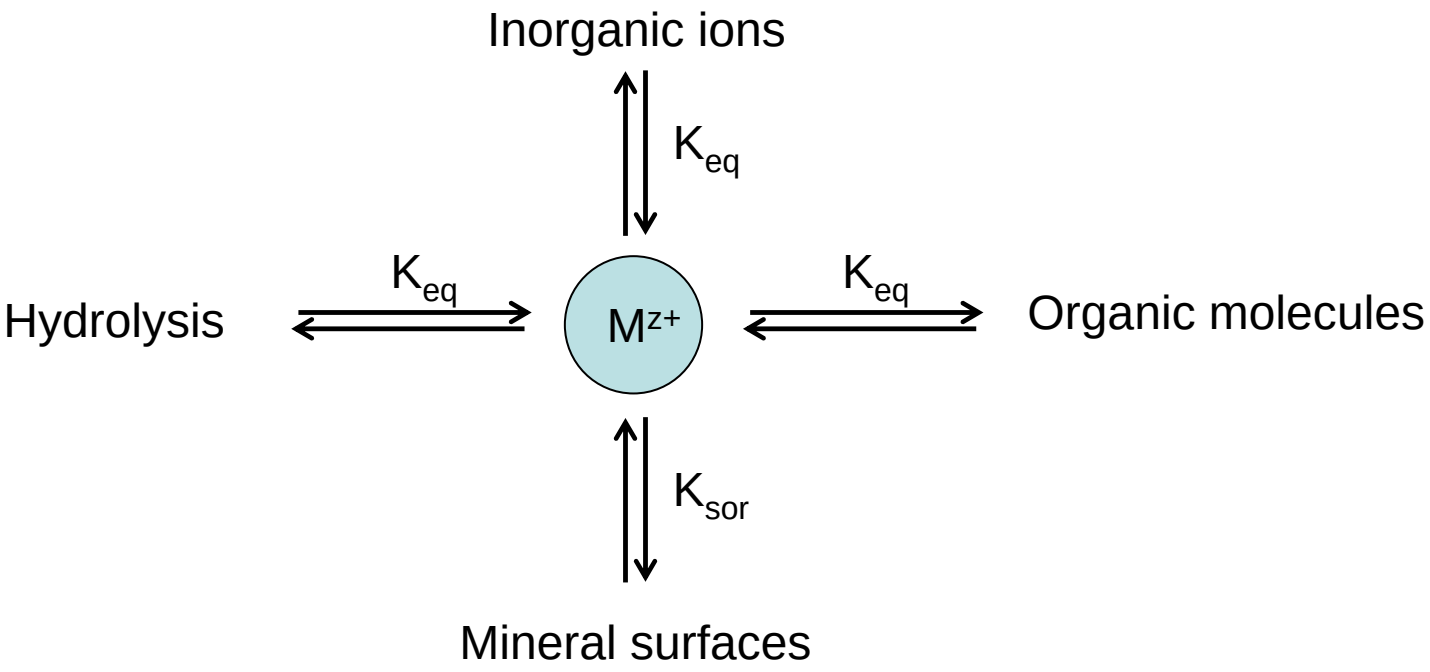
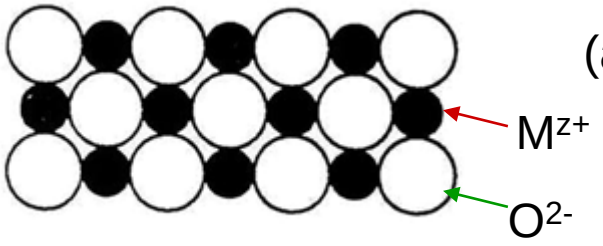


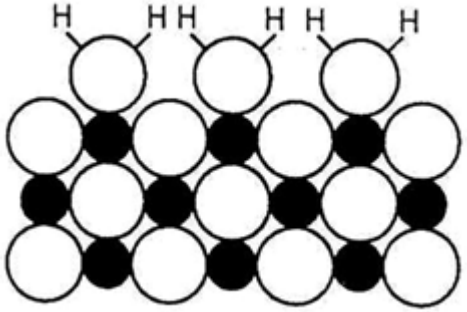
Some reactions of inorganic surfaces

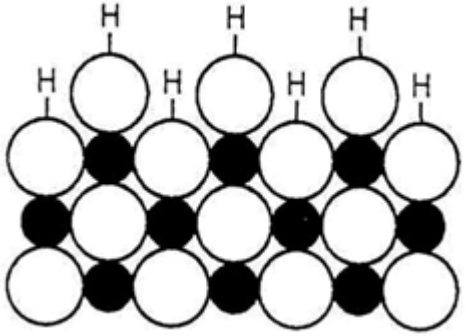
Surface charges induced by changes in pH



(a) Metal oxide surface, assumed dry.

(b) Metal oxide surface, with monolayer of water molecules. Each metal ion at the surface will tend to attract water molecules;





(c) De-protonated surface at high pH.

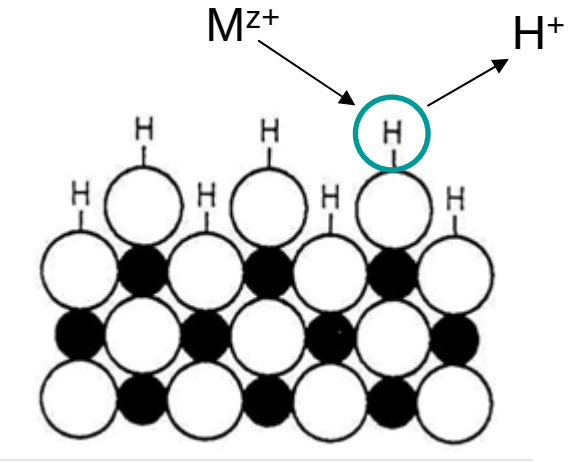
Some reactions of inorganic surfaces

M^{z+} + Surface-H → Surface-$M^{(z-1)+}$ + H^+

(sorption by surface complexation)

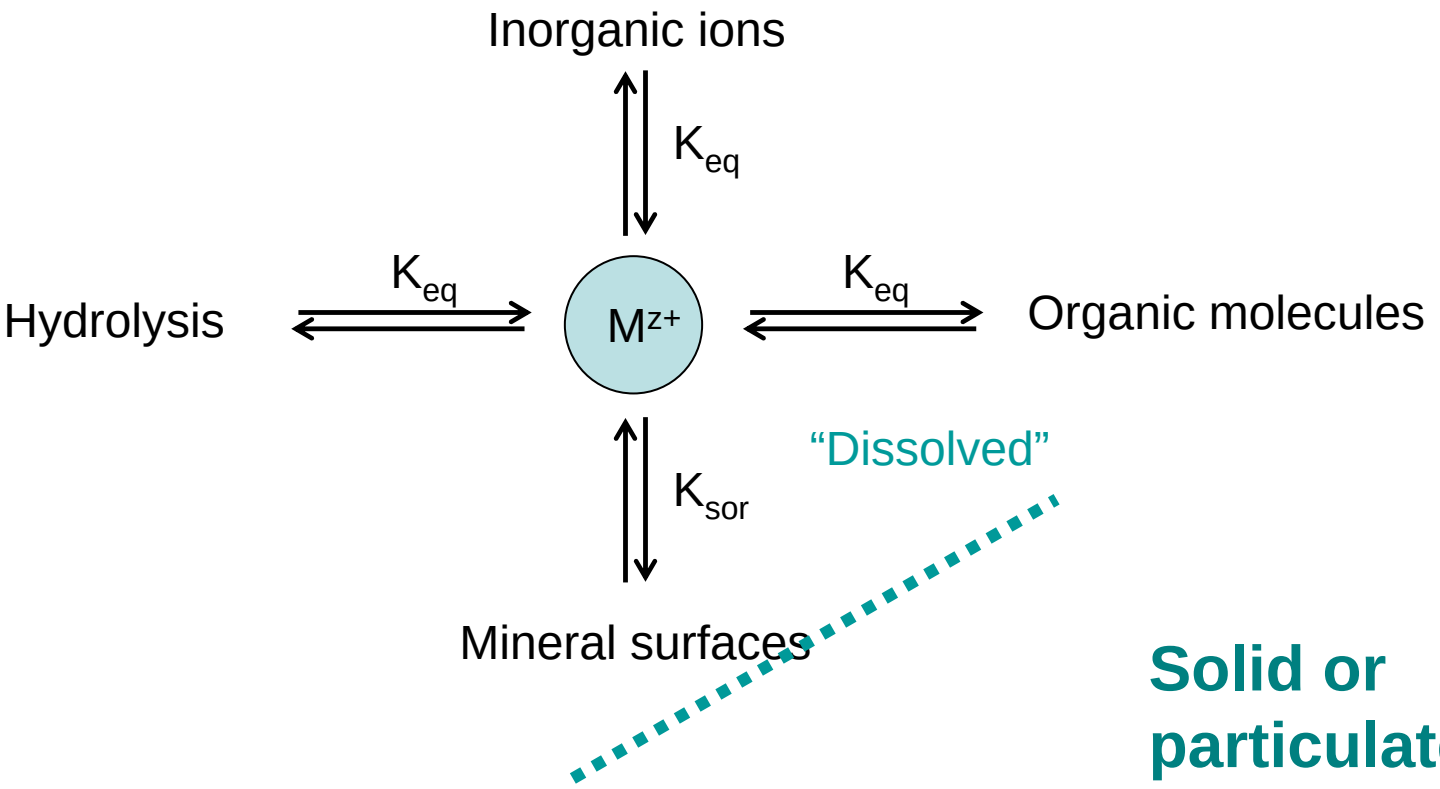
$$K_{sor} = \frac{Surface - M^{(z-1)+} \times H^+}{M^{z+} \times Surface - H}$$

This type of mechanism is very sensitive to pH (hydrolysis, surface charge)



A well-characterized surface can behave like other chemical constituents in water

What is speciation anyways?



“Dissolved” vs Colloidal vs particulate

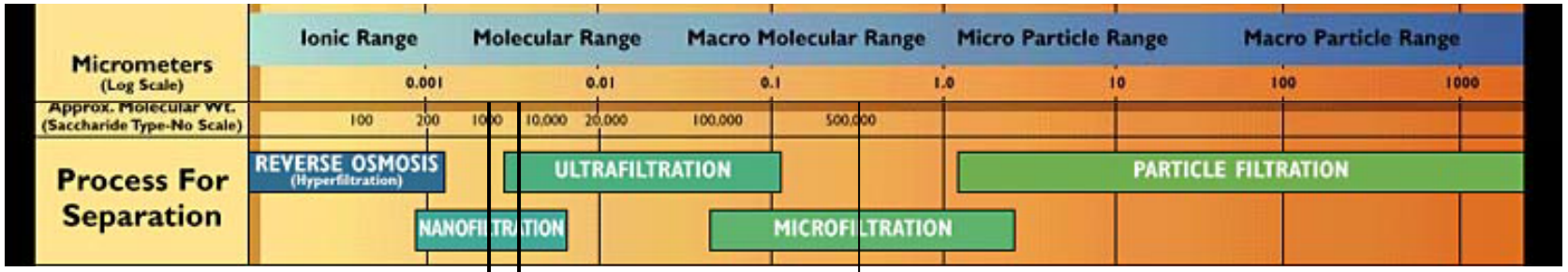


Figure modified from Osmonics.com

<1000 Da MWCO
<~0.003 µm

>500 000 Da MWCO
>0.45 µm pore size

<5000 Da MWCO
<~0.005 µm

“Colloidal” – sized particles

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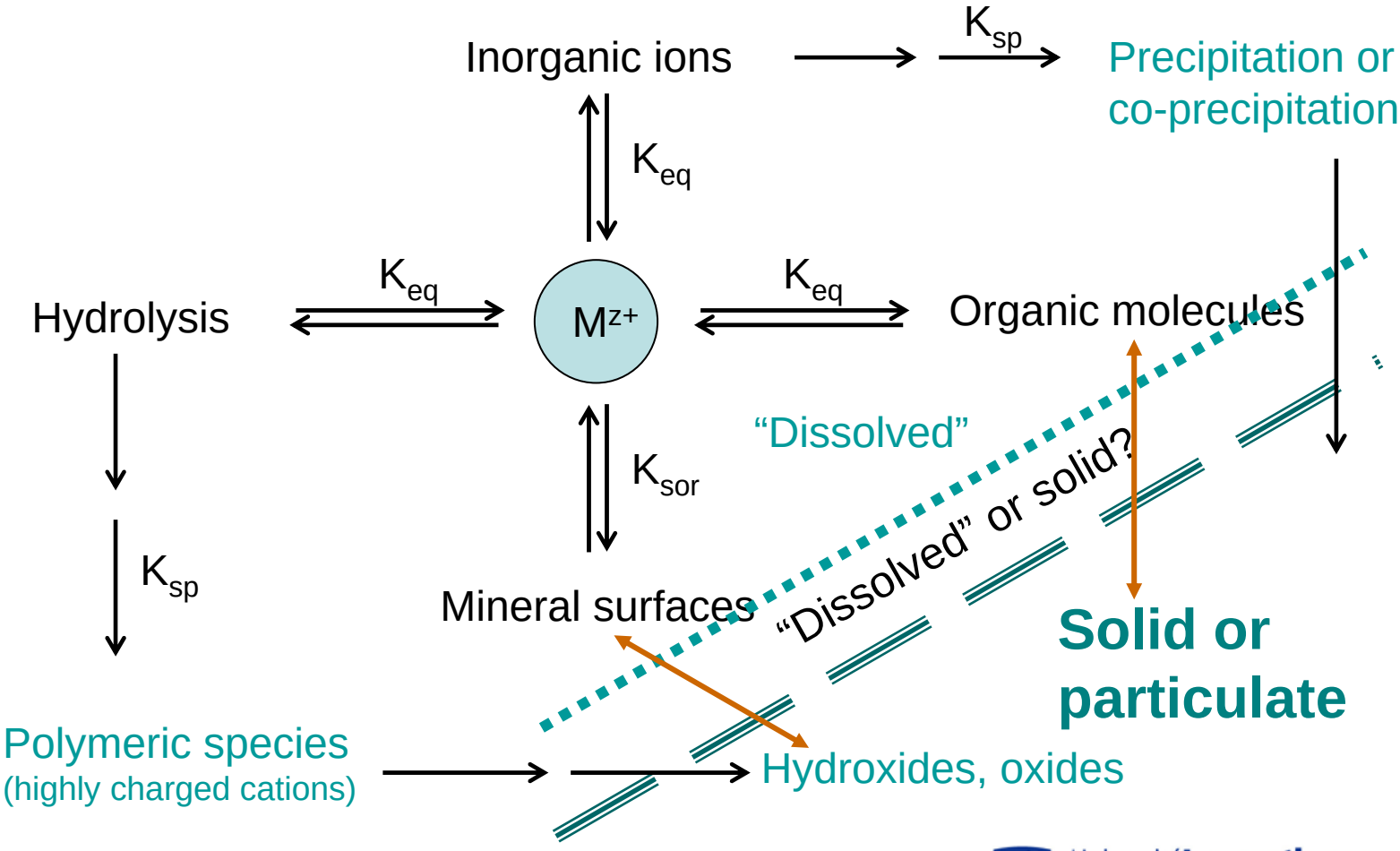
What is speciation anyways?



The need for “speciation”

- In environmental samples, “speciation” has to be tailored to the need:
  - Environmental speciation is often dominated by just a few processes – we just need to find the right one!
  - *Operationally-defined “speciation”* is used, which can closely represent the key interaction in the sample;
  - Representativity: the ideal analysis should be non-invasive.

Equilibrium constant and “true” species

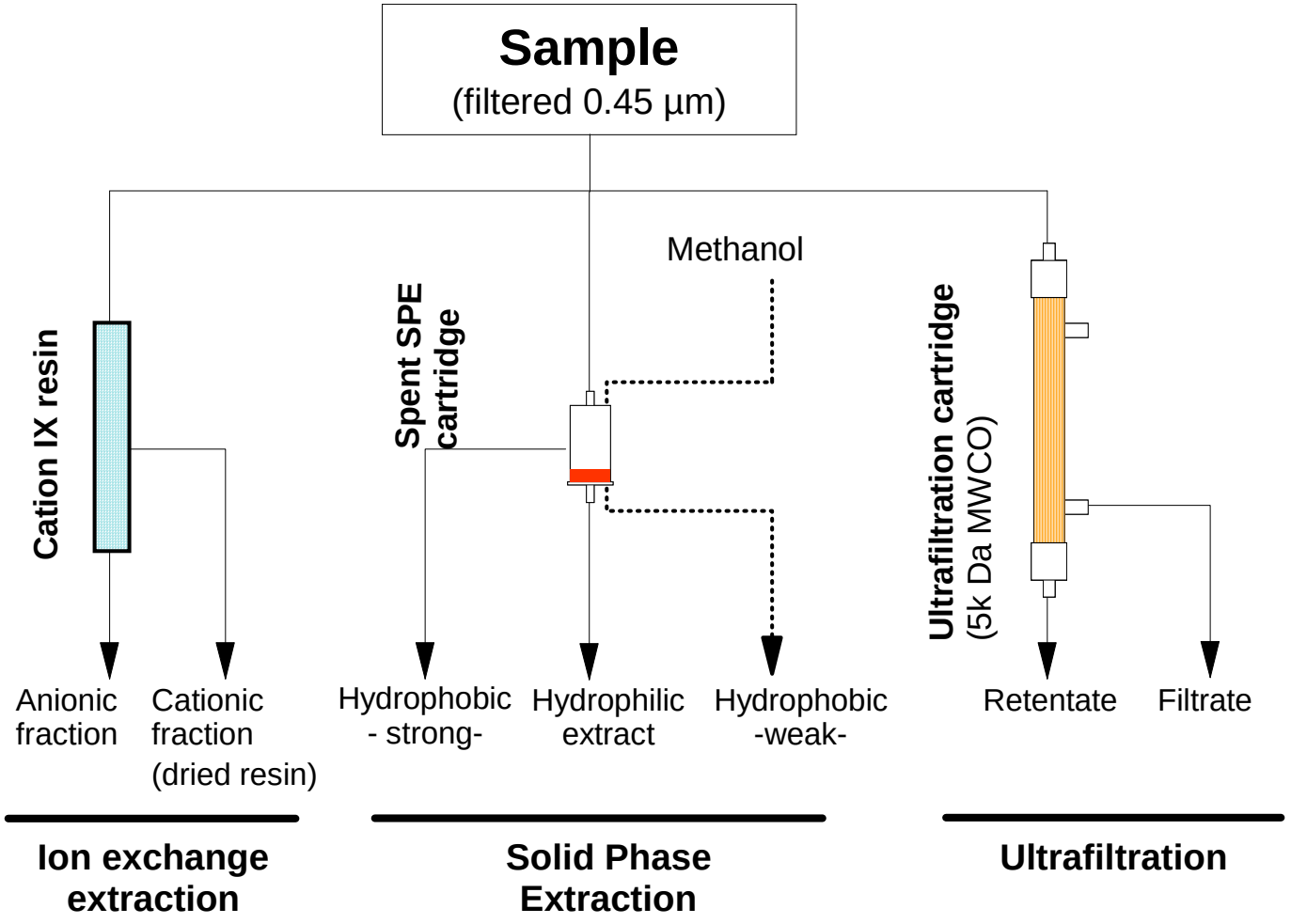
$$M^{z+} + L^{n-} \xleftrightarrow{K_{eq}} ML^{(z-n)+}$$

$$K_{eq} = \frac{[M\ L^{(z-n)+}]}{[M^{z+}_{free}][L^{n-}_{free}]}$$

- Independent methods are needed for the “true” species:
  - Free metal;
  - Free ligand – binding site analysis/titration;
  - Metal bound to organics:
    - Separation, isolation, concentration methods ?? – This should be representative of the Metal-NOM association in the sample –
    - Equilibrium conditions??

Modified (layered) sampling scheme

Actual contaminated site (Chalk River)



Caron and Mankarios, ***J. Environ. Rad.,*** 77: 29-46 (2004)

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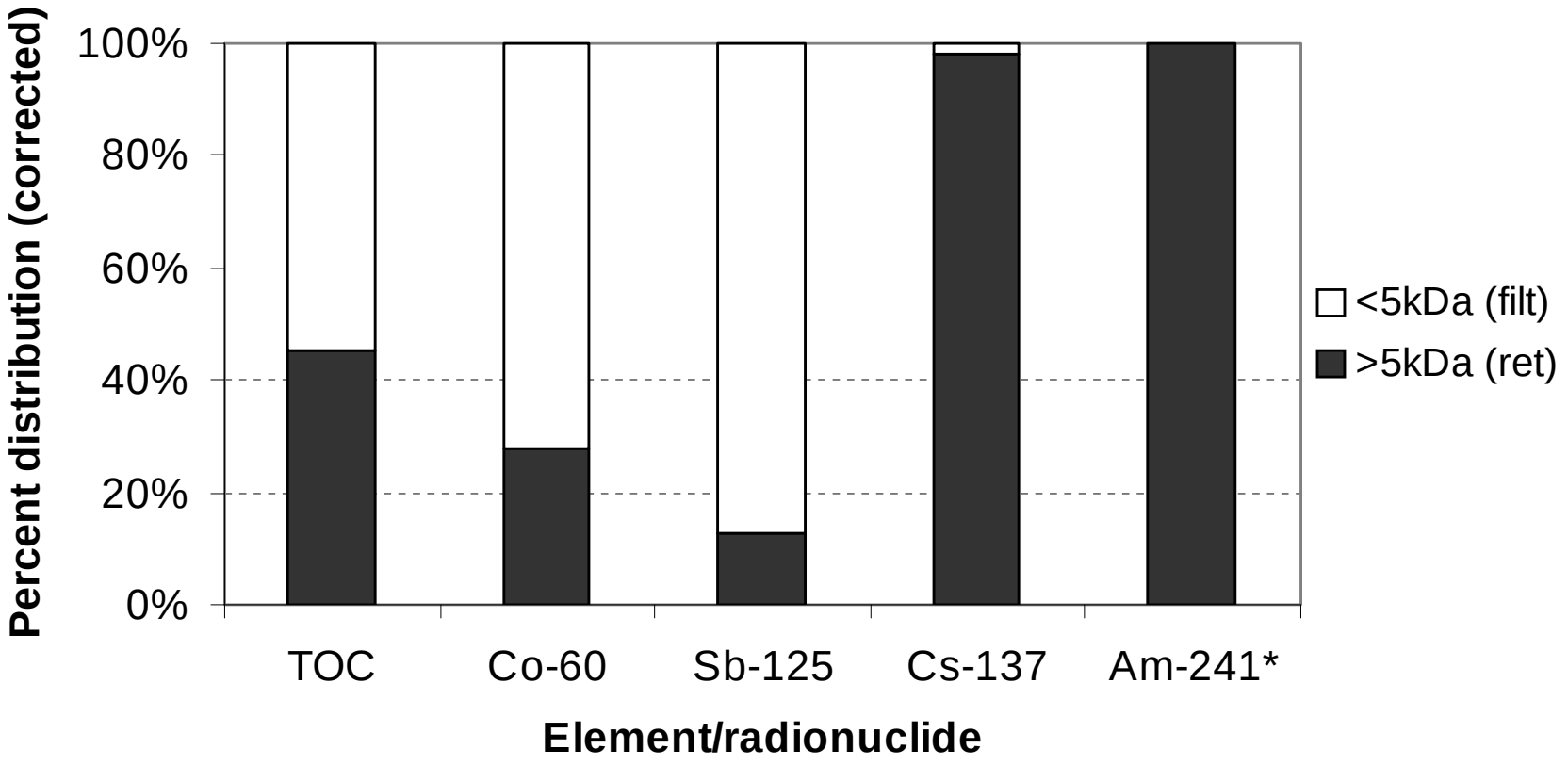
Summary of ultrafiltration

Actual contaminated site (Chalk River)

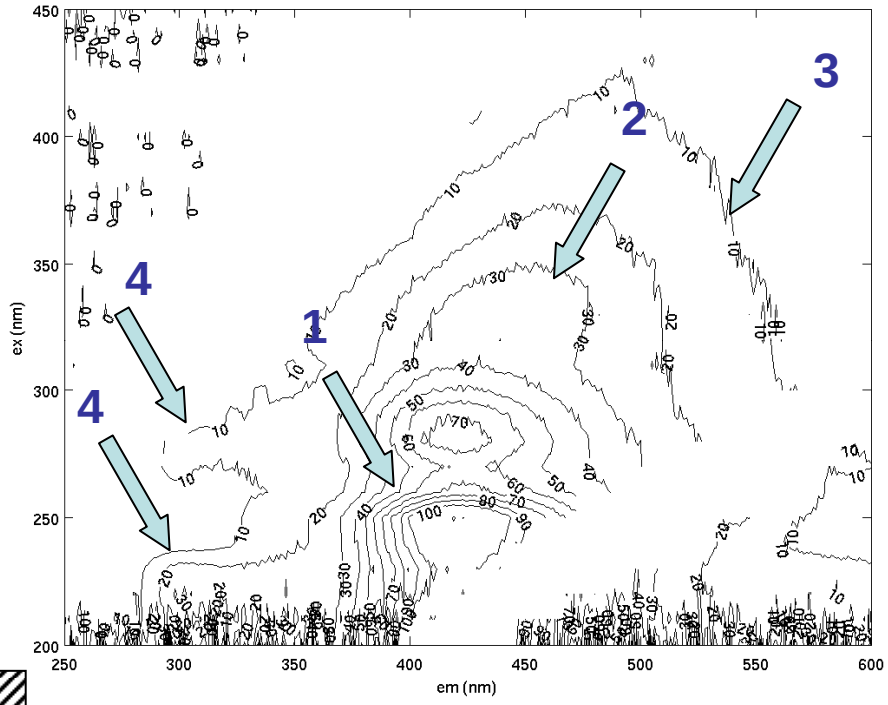


Caron et al., *Water, Air, Soil Pollution* 178: 121 (2007)

Cs-organics association: a myth?

- Cs is usually bound to clays or as free ionic species in water;
- Our work has shown the closest evidence that ^{137}Cs is chemically bound to natural organic matter (NOM):
  - Ultrafiltration: ^{137}Cs is associated with NOM-dominated fractions;
  - SPE: ^{137}Cs is co-extracted with NOM;
  - Charge character: association of ^{137}Cs with negative species;
  - Targeted sampling: no known clay minerals in site, absence of inorganic colloids & clays (SEM, XRD, elemental analysis, etc.);
  - **Direct chemical bond Cs-organics (fluorescence) – this project**

Cs-organics association: a myth?



- Component 1 is fulvic-like
- Component 2 appears humic-like; it is strongly influenced by pH at 9-10
- Component 3 is humic-like
- Component 4 is protein-like

Caron et al., Poster presentation, MIGRATION 2007, Munich, Ger., Aug 26-31, 2007

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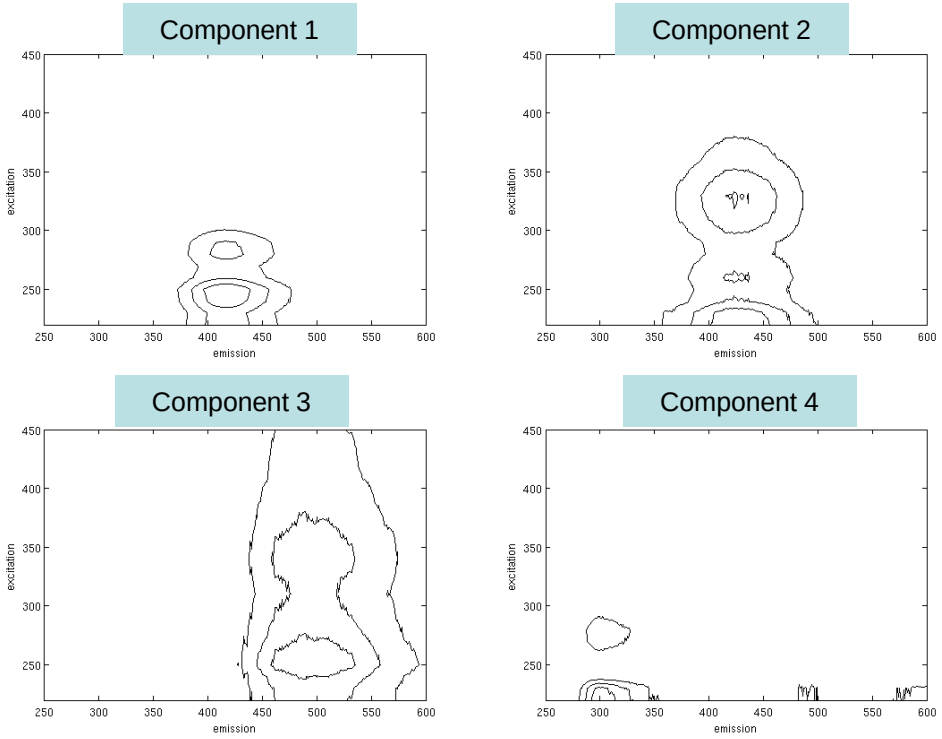

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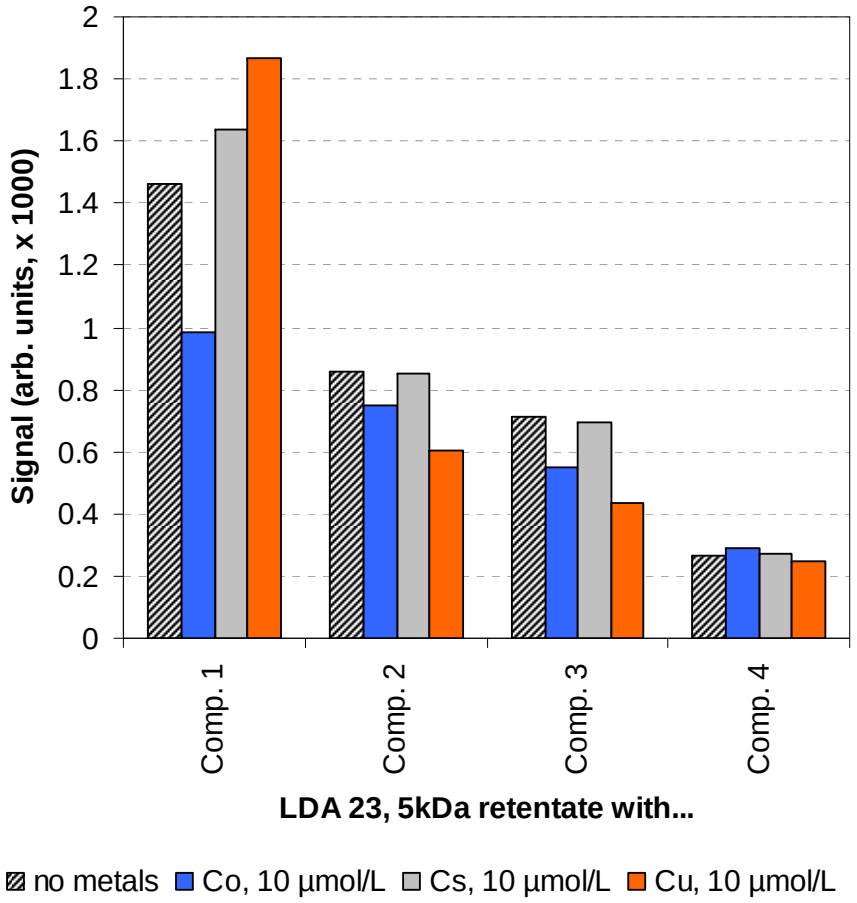

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Conclusions

- What is speciation, anyways?
- “Speciation” has to be tied to the need:
  - Most environmental work focus on migration or toxicity;
- Sampling and analysis have to be tied to the need
- Ideally, analysis should be non-intrusive and non-invasive, with samples representative of field conditions.

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