



Rémi Marsac

**Modélisation de la spéciation des
contaminants dans l'environnement**

**UMR CNRS 6118 - Géosciences Rennes
Equipe Nano-BioGéochimie**

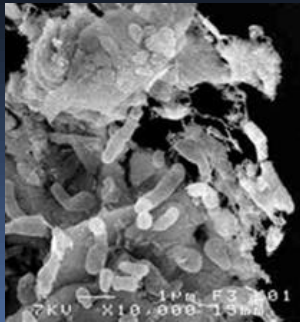
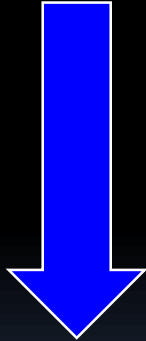
General context

Fate of trace contaminants:

- Metals and et metalloids: Cu, Pb, As...
- Radionuclides: Pu, Tc...
- Emerging organic contaminants...

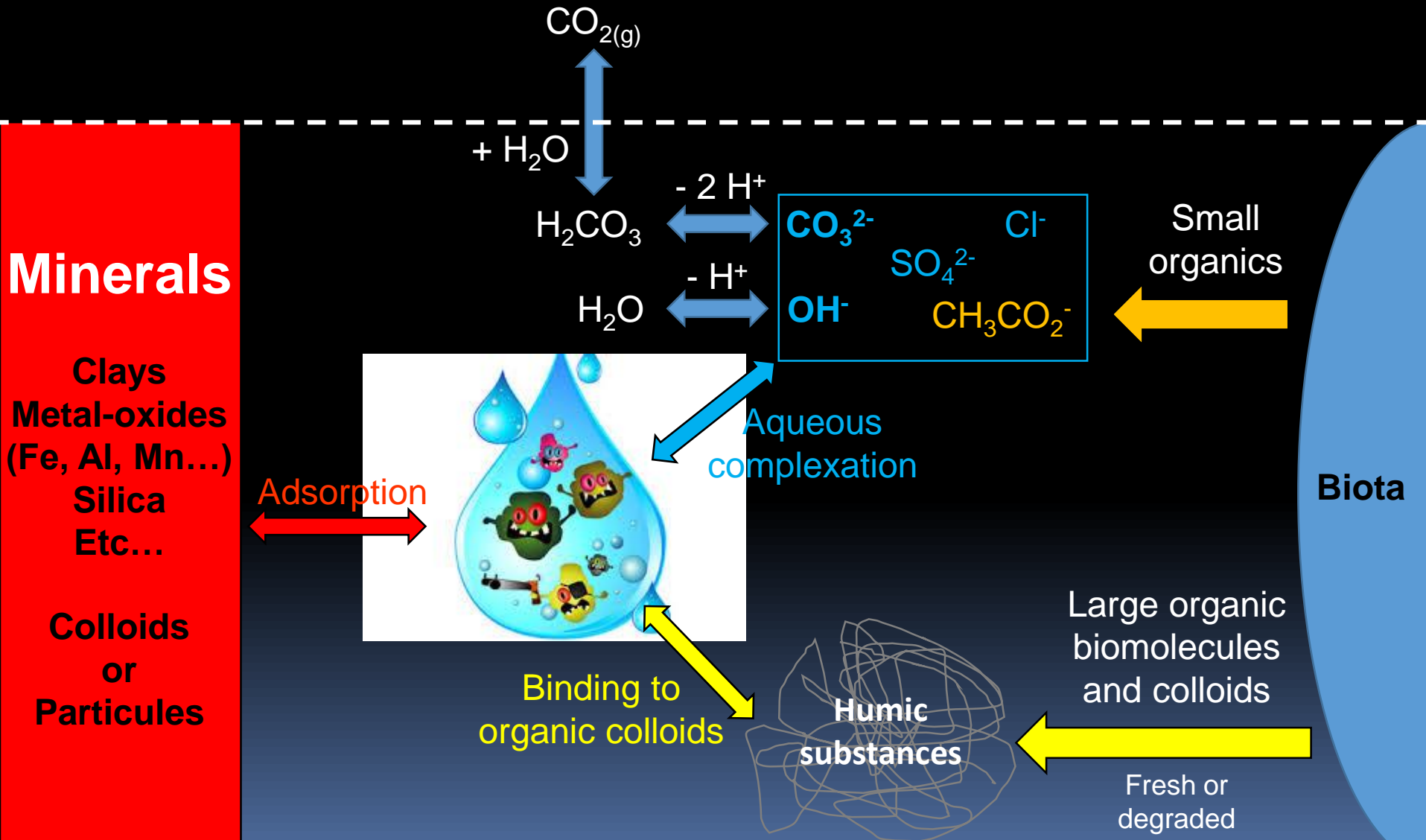


Threat for ecosystems and soil and water resource



Speciation of contaminants

For the same contaminant, various chemical species exist



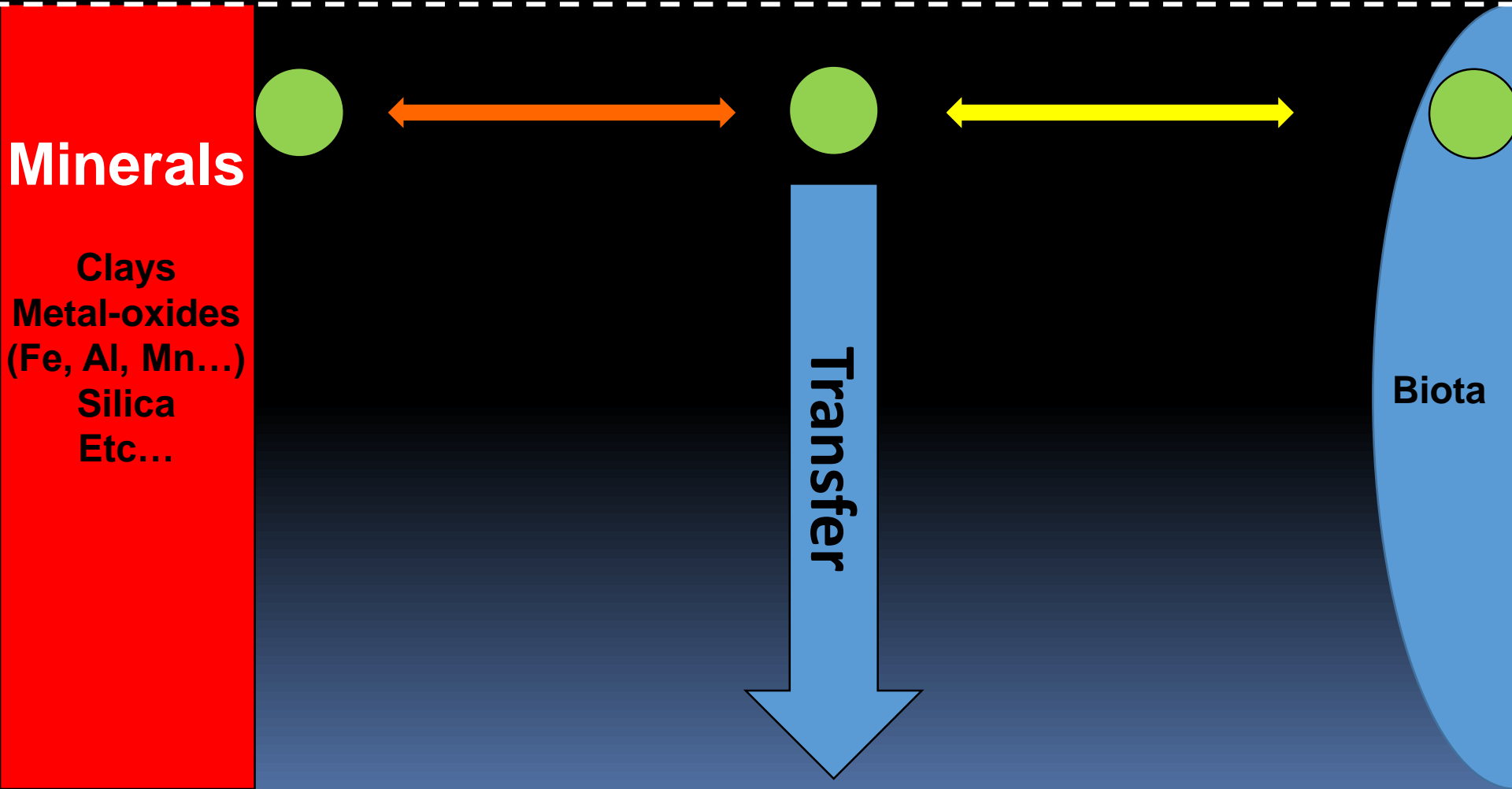
Speciation of contaminants

Total contaminant concentration is meaningless...

Contaminants **speciation** controls:

⇒ Their migration

⇒ Their bioavailability/toxicity



Minerals

Clays
Metal-oxides
(Fe, Al, Mn...)
Silica
Etc...

Transfer

Biota

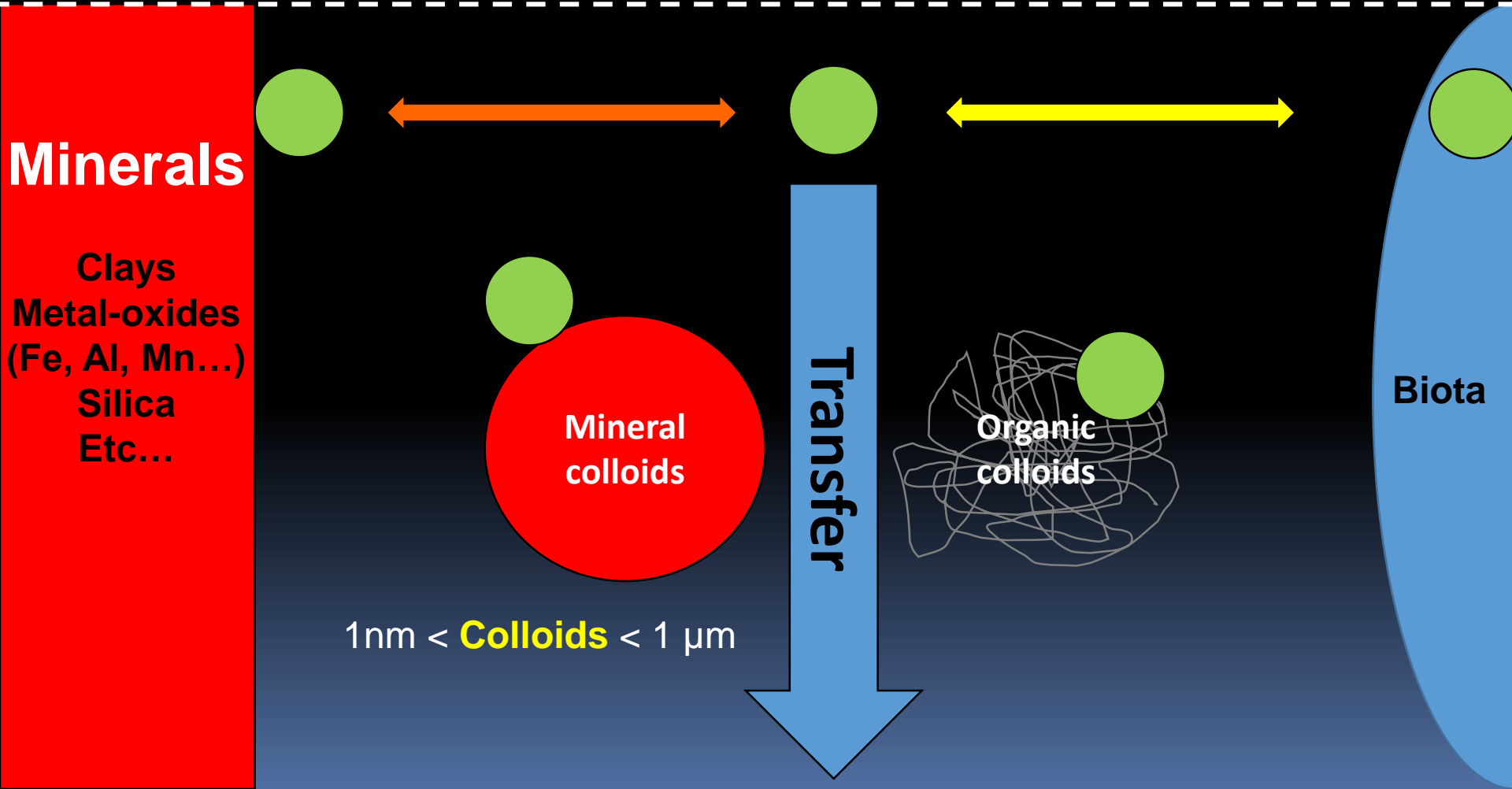
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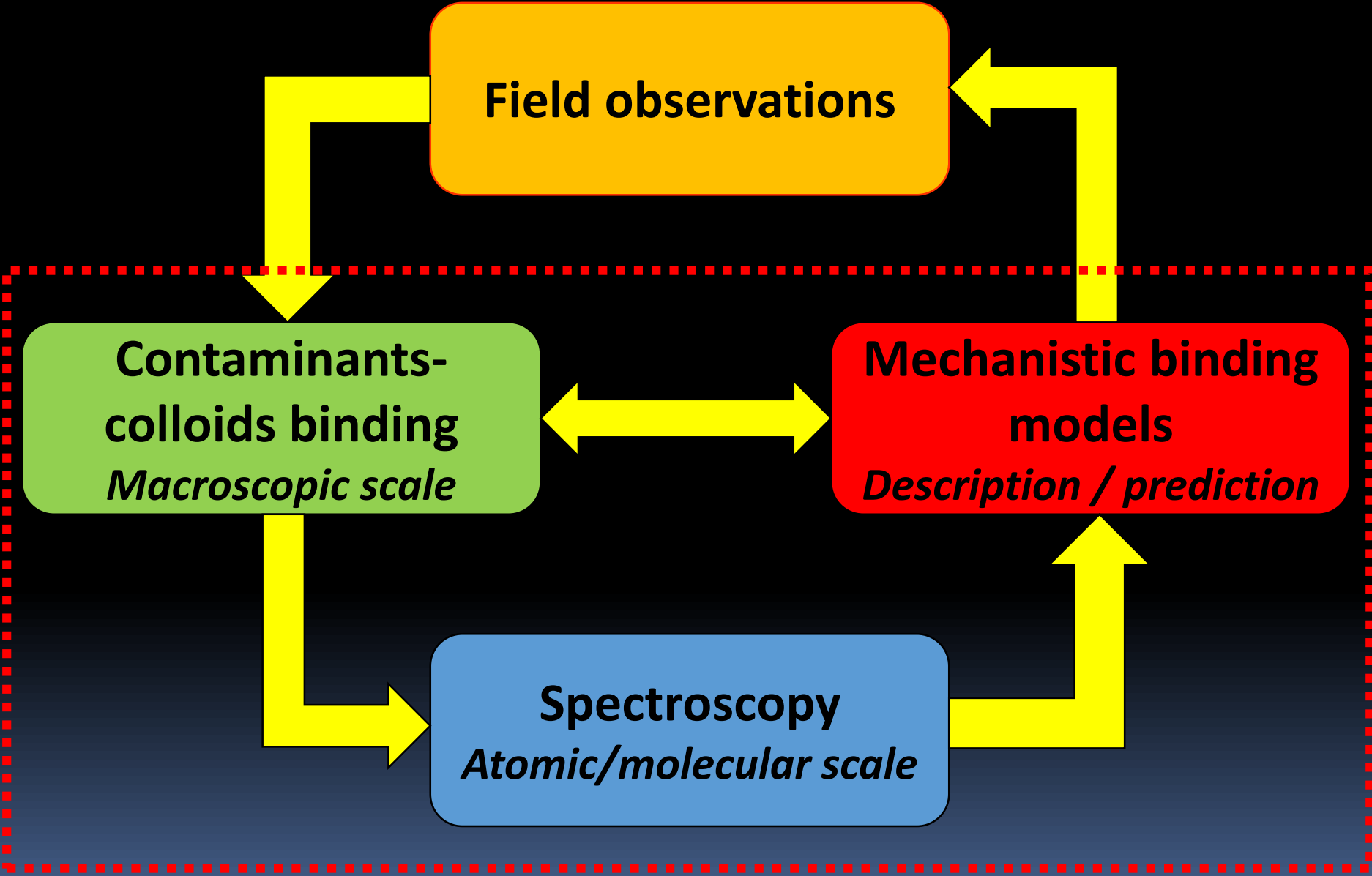
**Mineral
colloids**

**Organic
colloids**

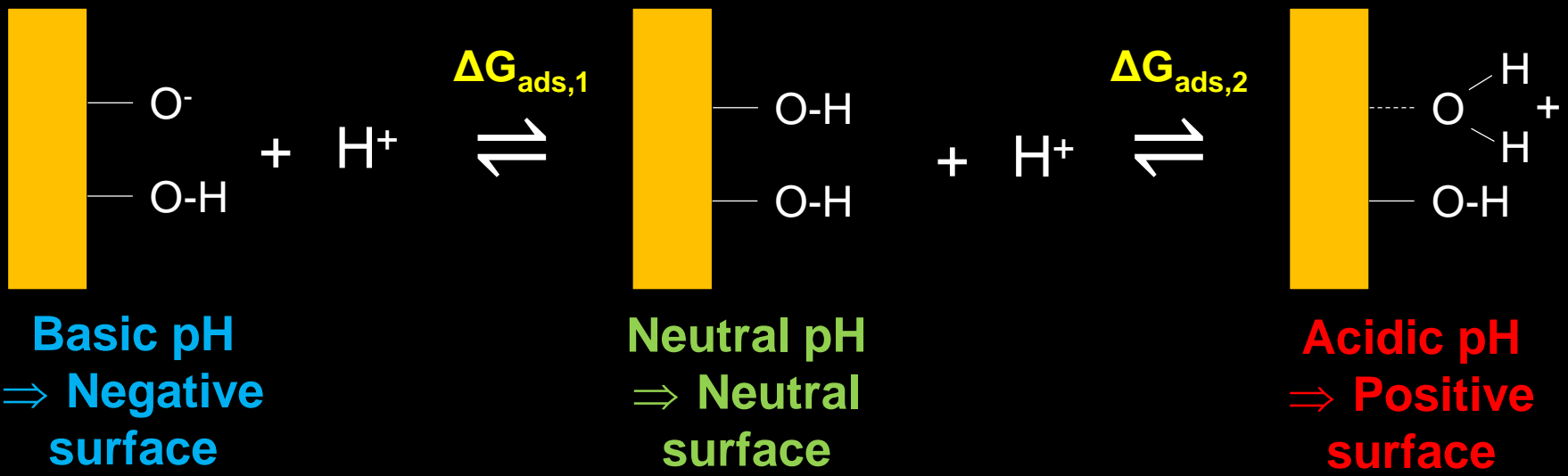
Transfer

$1\text{nm} < \text{Colloids} < 1\ \mu\text{m}$

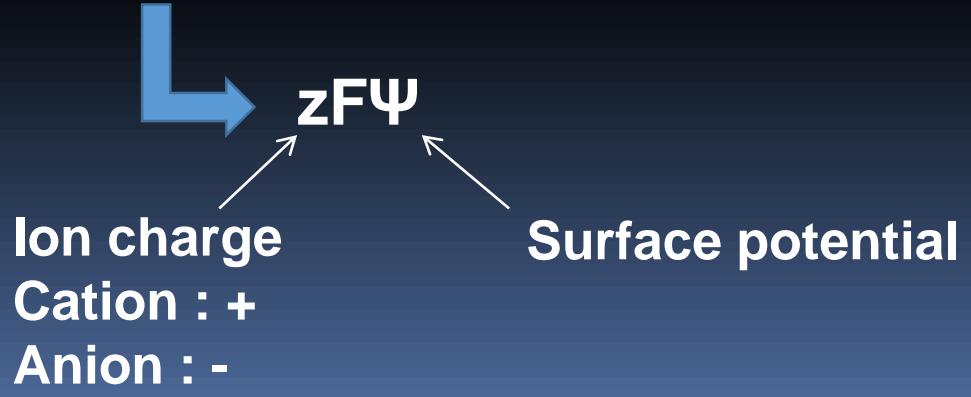
Approach



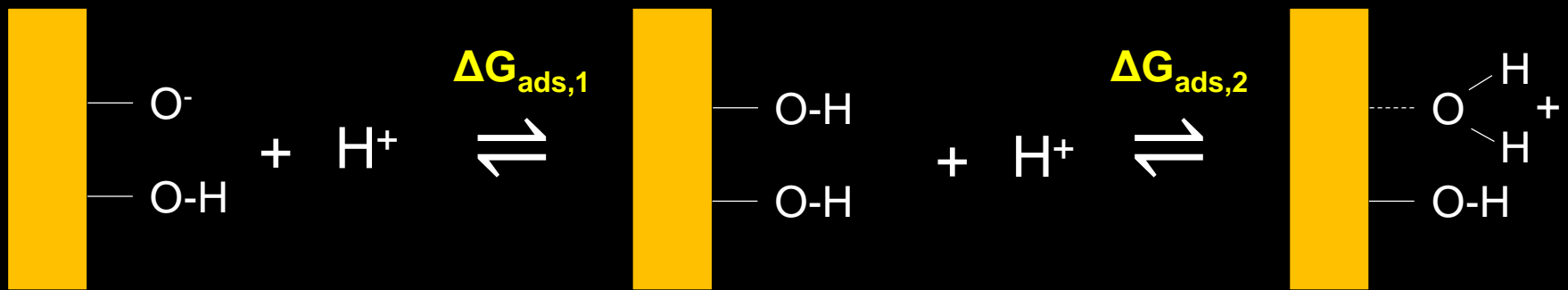
Modeling processes at colloids-solution interfaces



$$\Delta G_{ads,i} = \Delta G_{ch,i} + \Delta G_{elec,i}$$



Modeling processes at colloids-solution interfaces

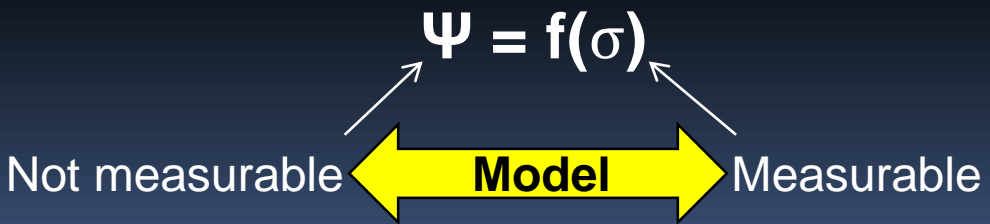


Basic pH
 \Rightarrow Negative surface

Neutral pH
 \Rightarrow Neutral surface

Acidic pH
 \Rightarrow Positive surface

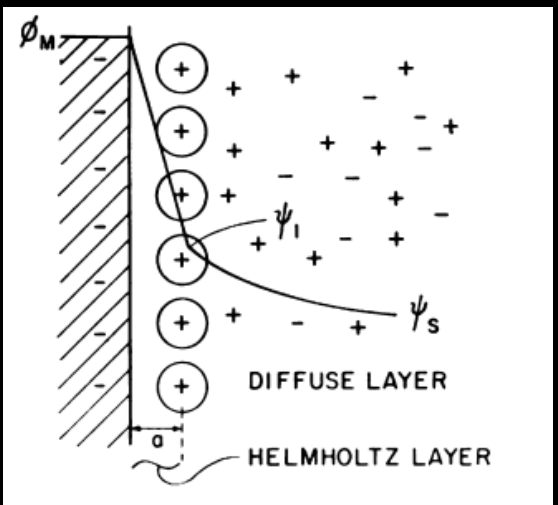
Surface charge (σ) \nearrow when pH \searrow



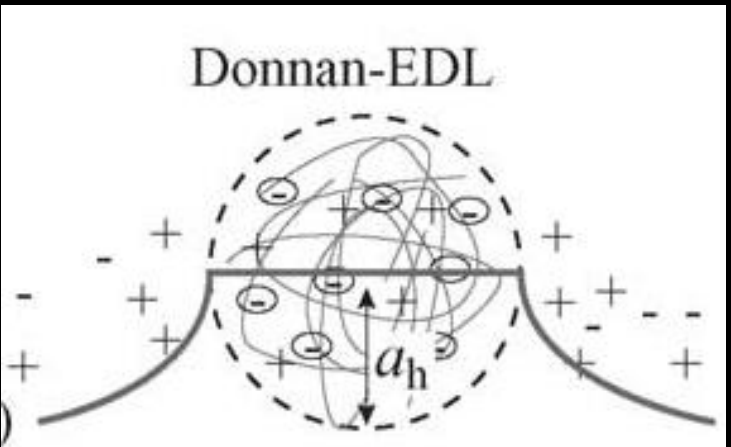
Hypothesis: charge distribution at the interface (geometry)

Modeling processes at colloids-solution interfaces

Hard particles



Soft particles



Powerful predictive tools for pure phases

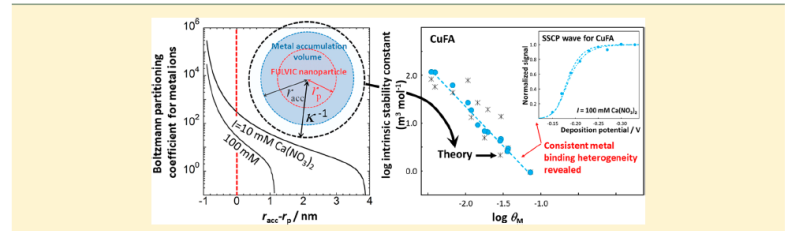
But limitations
⇒ Active research area

The Intrinsic Stability of Metal Ion Complexes with Nanoparticulate Fulvic Acids

Raewyn M. Town,^{†,‡,||} Jérôme F. L. Duval,^{‡,§} and Herman P. van Leeuwen^{||}

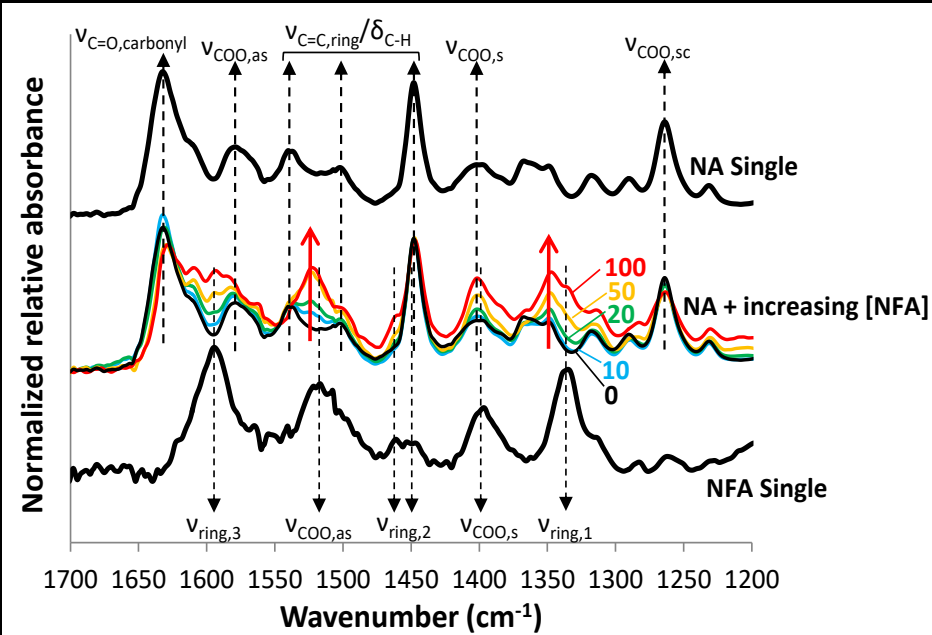
[†]Systemic Physiological and Ecotoxicological Research (SPHERE), Department of Biology, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium
[‡]CNRS, Laboratoire Interdisciplinaire des Environnements Continentaux (LIEC), UMR 7360, Vandoeuvre-lès-Nancy, F-54501 Nancy, France
[§]Université de Lorraine, LIEC, UMR 7360, Vandoeuvre-lès-Nancy, F-54501 Nancy, France
^{||}Physical Chemistry and Soft Matter, Wageningen University & Research, Stippeneng 4, 6708 WE Wageningen, The Netherlands

Supporting Information

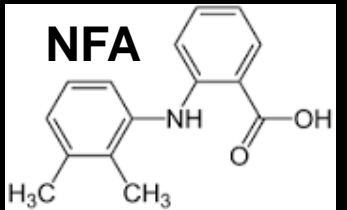
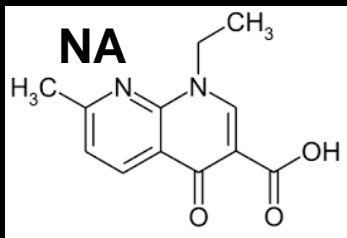


Example:

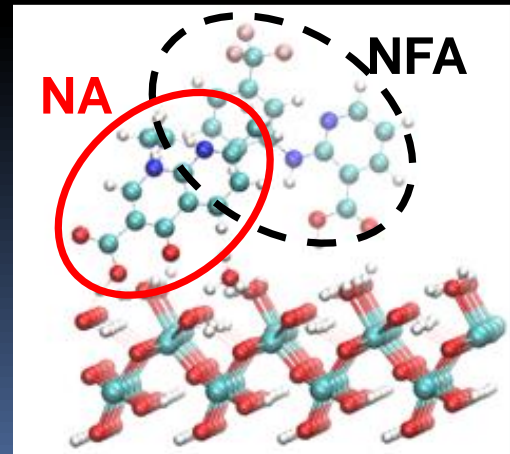
Small organic molecules + hard particle



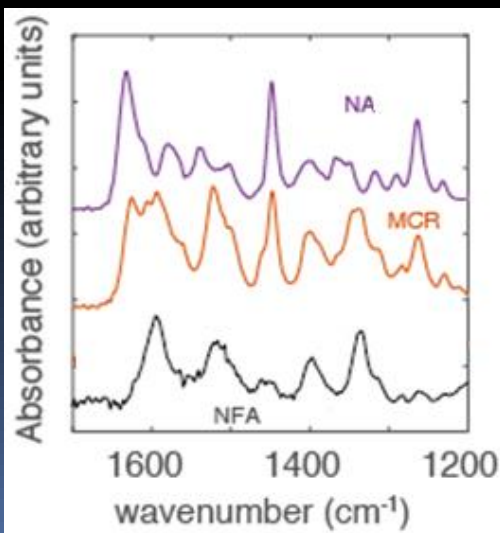
Characteristic bands of NA and NFA single
+
New bands with NA+NFA



Supported by quantum chemical calculations

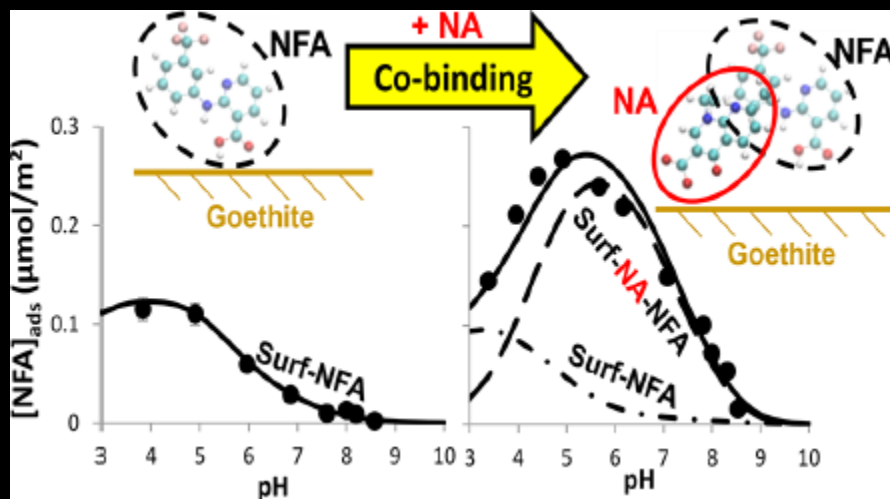


Multivariate curve resolution (MCR) analysis:
Evidence of a surface NA-NFA dimer



Example:

Small organic molecules + hard particle



Cobinding of Pharmaceutical Compounds at Mineral Surfaces: Mechanistic Modeling of Binding and Cobinding of Nalidixic Acid and Niflumic Acid at Goethite Surfaces

Jing Xu,^{†,‡} Rémi Marsac,^{‡,§,⊖} Cheng Wei,[‡] Feng Wu,^{||,⊖} Jean-François Boily,[⊖] and Khalil Hanna^{*,‡,⊖}

ANR: C-FACTOR

**Contaminants FAte is ConTrolled by
colloidal ORganic matter speciation**

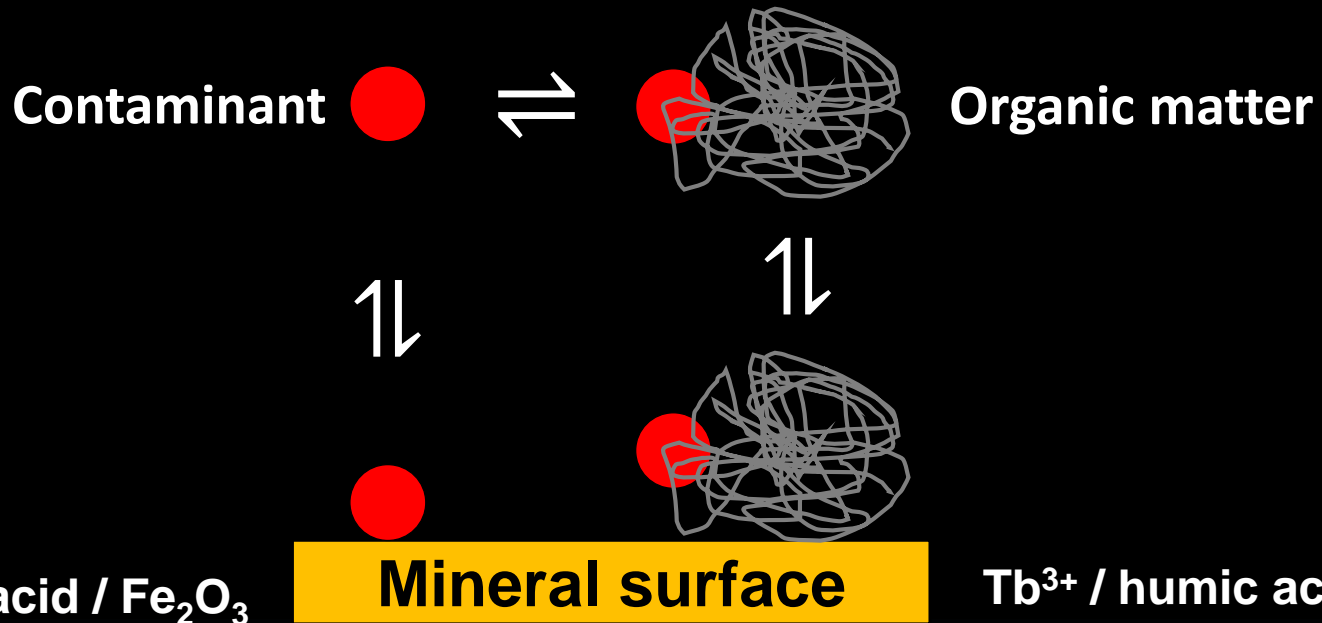
(01/10/2018 - 30/09/2022)

PI: R. Marsac

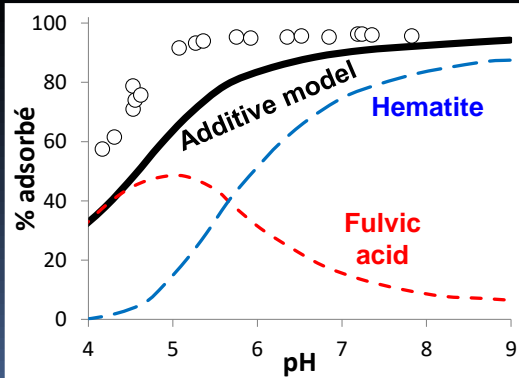
Observation

Natural colloids are not pure phases

↳ **Organo-mineral assemblages**

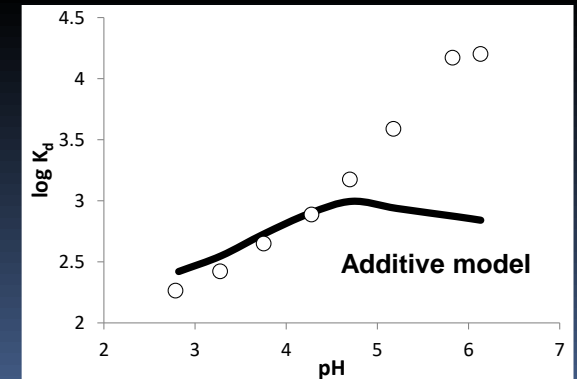


Cu²⁺ / fulvic acid / Fe₂O₃



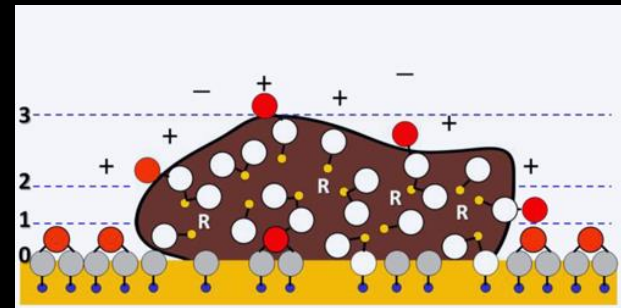
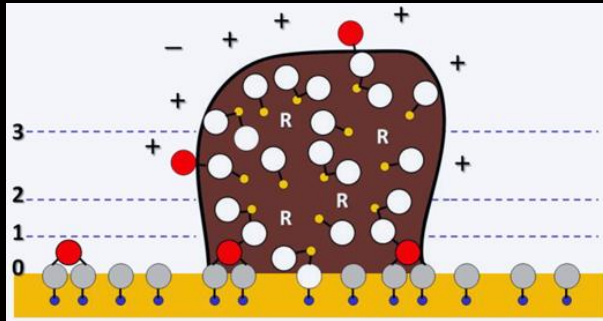
We cannot predict the interactions between contaminants and organo-mineral colloids!

Tb³⁺ / humic acid / clay



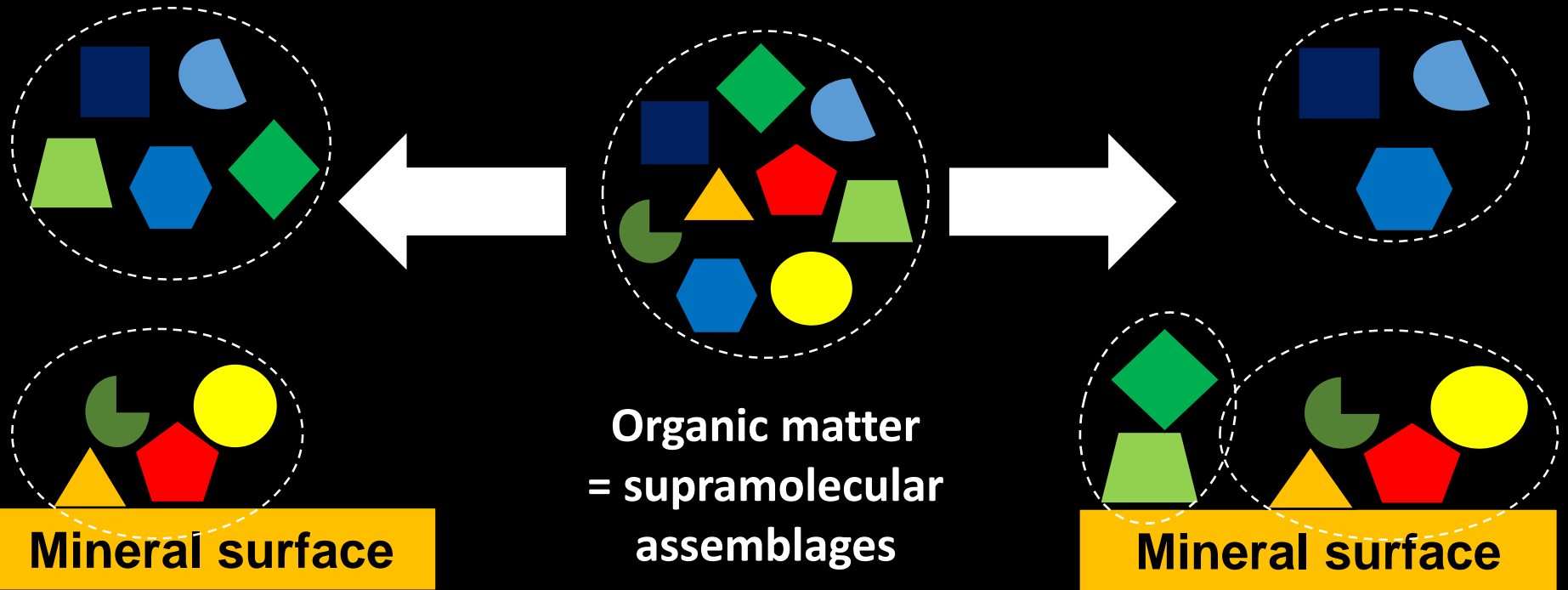
Modeling processes at heterogeneous surfaces

Surface charge development :



Conformation (geometry) of organic mater at mineral surface

Modeling processes at heterogeneous surfaces



Numerical model :

- Interaction between various molecules
- Fractionation of organic matter

Discrete molecules or distribution???

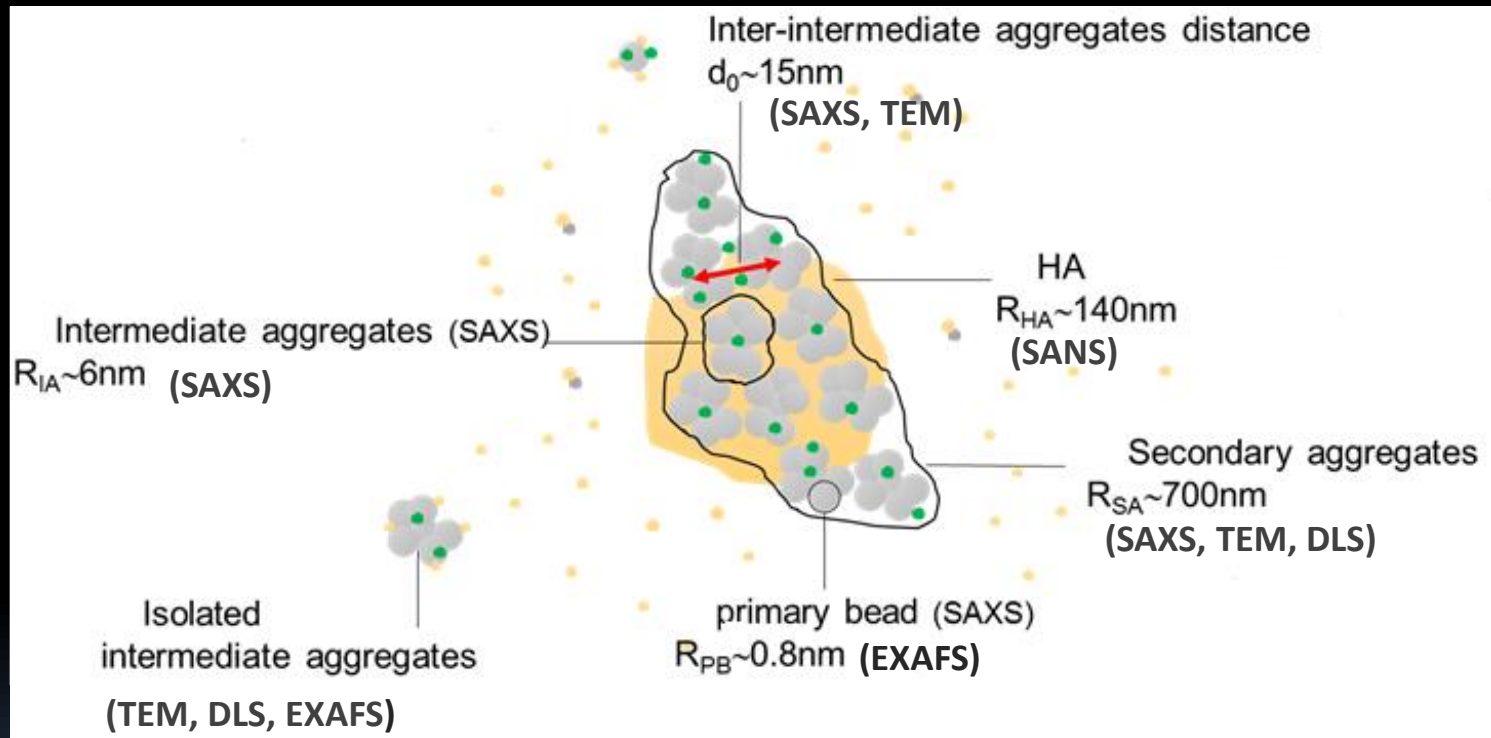
Organo-mineral colloids at larger scale

**PhD Thesis:
H. Guenet, A. Beauvois**

**ANR INCA (to be submitted)
D. Vantelon (SOLEIL)
M. Davranche (Géosciences Rennes)**

Organo-mineral colloids at larger scale

1nm  100nm / 1µm



Dynamic fractal organisation:

Reactive surface area?

Inter-aggregate distance = $f(\text{pH, salinity, Fe/OM, etc})$

Summary

- **Contaminants speciation** affects their biogeochemical cycles (transport, bioavailability/toxicity)
- Important role of **natural surfaces**: particles or colloids

 Physico-chemical phenomena at **"solid"-water interface**

- Active research field:
 - Geosciences, environmental chemistry...
 - Electrochemistry, Catalysis, nanomaterials...
- Advanced numerical models required

Mathematics inside:

- Geometry
- Chemometric analysis (stats)
- Spectroscopy (signal processing)
- Quantum chemistry

Programming issue...

Thank you for your attention!