Influence of solution parameters on Europium(III), α-Al2O3 and humic acid interactions

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Context

Interactions between Natural Organic Matter (NOM) and minerals modify mobility and bioavailability of trace elements. A better description of these ternary metal/NOM/mineral surface systems is needed to improve the understanding of radionuclides transfer from a repository site to the geosphere. This study is focused on Europium(III) speciation in presence of aluminum oxide α-Al_2O_3 and Purified Aldrich Humic Acid (PAHA) as a surrogate of NOM. In case of lanthanides, one way to obtain both macroscopic and spectroscopic information on metal sorption onto mineral surfaces is through Time-Resolved Laser-induced Luminescence Spectroscopy (TRLS), which allows to have a direct insight on speciation of ions in solution at relevant environmental metal concentration. Macroscopic and spectroscopic experiments have been carried out to see the influence of solution parameters (pH, ionic strength, humic concentration) on the evolution of the different binary Eu(III)/α-Al_2O_3 and Eu(III)/PAHA and ternary Eu(III)/PAHA/α-Al_2O_3 systems.

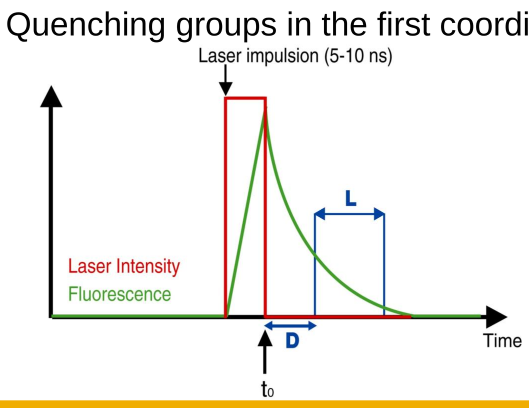
Methodology

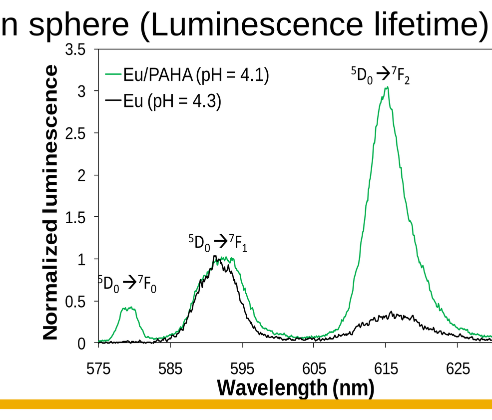
▪ Description of experiments

- Contact time: 3 days
- Ultracentrifugation: 2h, 60000 rpm
- PAHA concentration: DOC, UV
- [Eu(III)] = 10^{-6} mol/L
- [α-Al_2O_3] = 1 g/L
- [PAHA] = 28 mg_{HA}/L
- I = 0.01 or 0.1M $NaClO_4$

▪ Time-Resolved Laser Induced Luminescence Spectroscopy

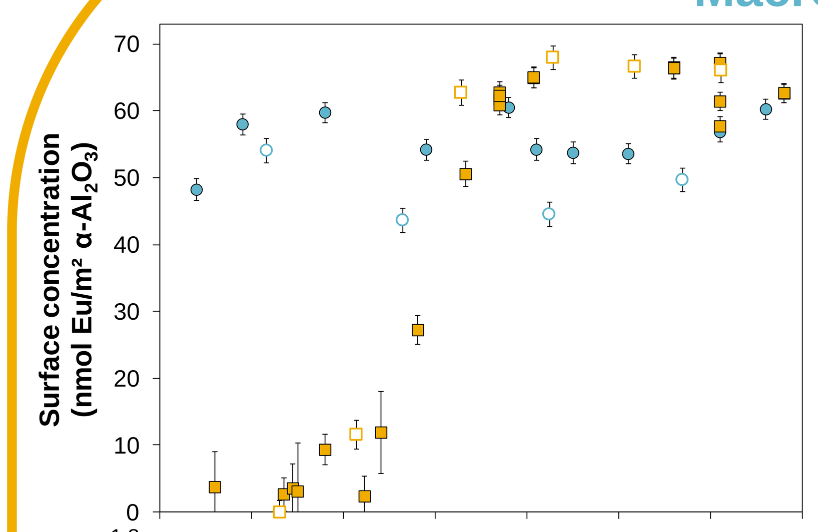
- Eu(III) complexation (asymmetry ratio $^7F_2/^7F_1$)
- Symmetry of Eu(III) environment ($^7F_0$)
- Quenching groups in the first coordination sphere (Luminescence lifetime)

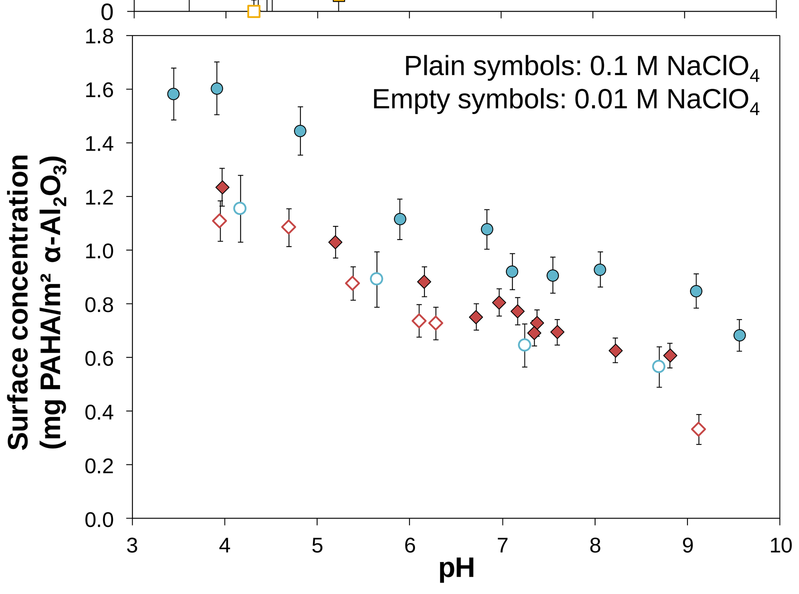




Influence of pH and ionic strength on Eu(III) speciation in the ternary system(1,2)

Macroscopic results





▪ Evolution of Eu(III) retention onto the surface

In the binary system:

- Sorption-edge observed at pH 7 (expected)
- Low dependence to ionic strength

In the ternary system:

- Eu(III) behavior shows high dependence to PAHA retention onto the mineral
- At high pH, increase due to direct sorption of Eu(III) onto the mineral

▪ Evolution of PAHA retention in the surface

- Sorption decreases with increasing pH
- Sorption decreases with ionic strength (electrostatic repulsion)
- Presence of Eu(III) increases the humic sorption in the whole pH range (from 88 to 38%)
- Less effect of Eu(III) addition at lower ionic strength

Figures legend:
ternary **Eu/α-Al_2O_3/PAHA** system
binary **Eu/PAHA** system
binary **Eu/α-Al_2O_3** system
binary **PAHA/α-Al_2O_3** system

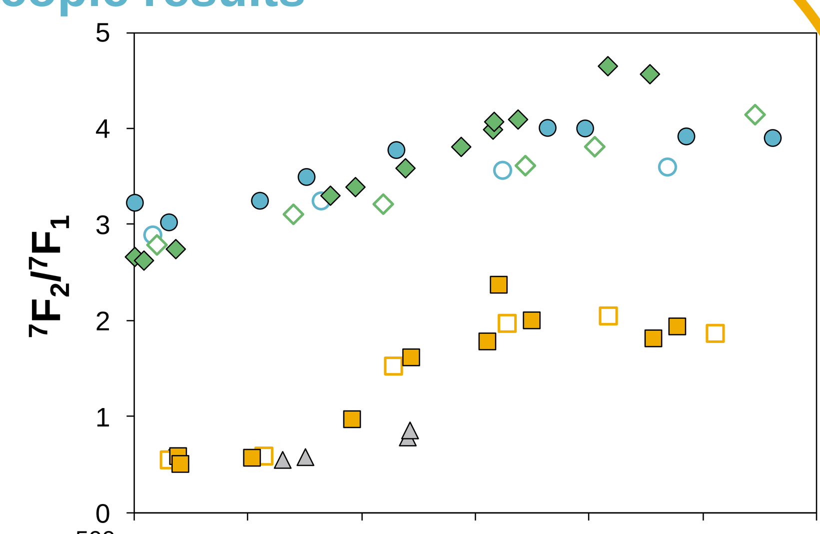
Spectroscopic results

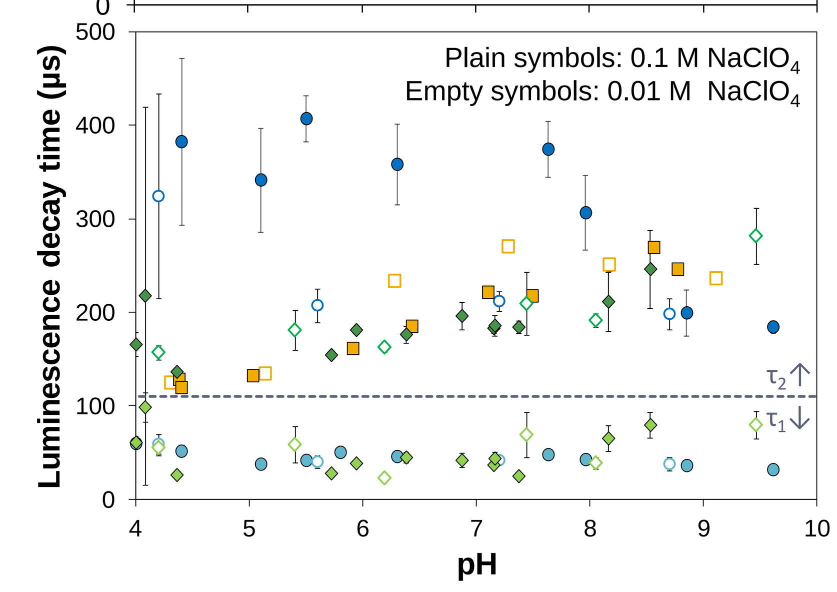
▪ Evolution of Eu(III) environment symmetry

- In the ternary system, at pH < 7 : similar to Eu(III)/PAHA
- At high pH, shift of maxima and change of peaks shapes. Eu(III) on the surface but bound to HA
- Influence of ionic strength on humic molecules conformation, and on humic-bound Eu(III) environment

▪ Evolution of luminescence lifetimes

- τ_1 presence: Eu(III) always bound to PAHA
- Higher τ_2 in the ternary system: more constrained environment, but of the same symmetry than in binary Eu(III)/PAHA system (comparable spectra)
- τ_2 decreases when pH increases: Eu(III) more exposed to quenching groups; progressive change in structure of Eu(III)/PAHA complexes onto the surface





Influence of humic concentration on Eu(III) speciation(2)

▪ Evolution of Eu(III) retention onto the surface

Below pH edge:

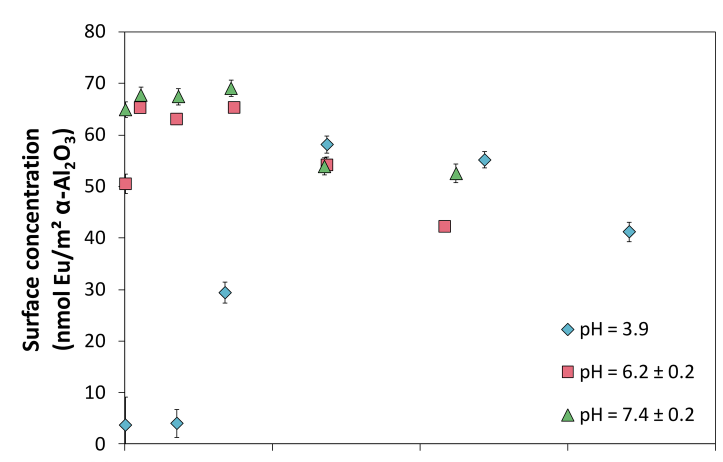
- Presence of HA increases Eu(III) adsorption

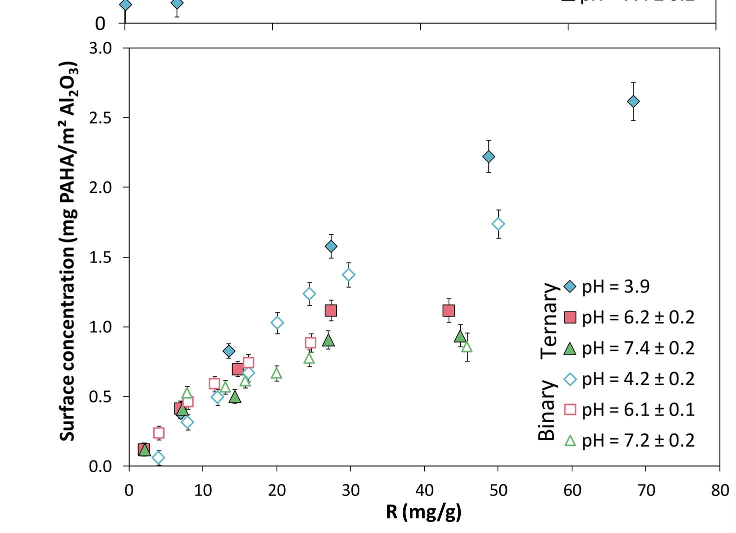
Around the pH edge:

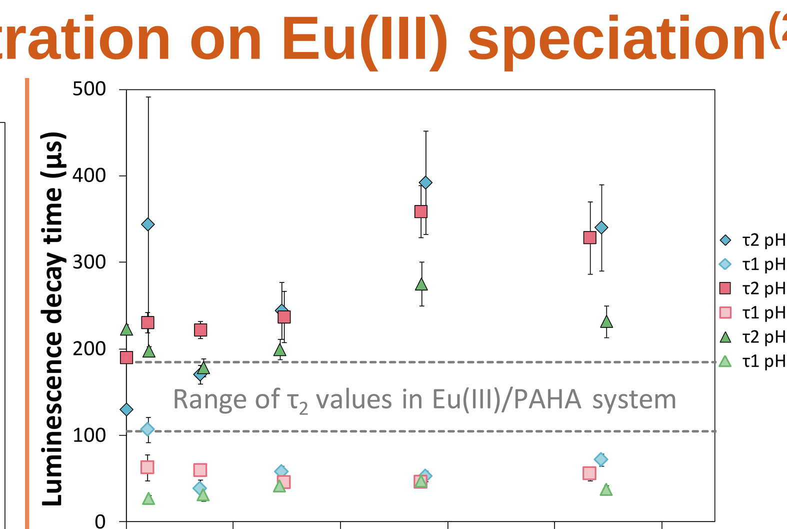
- Eu(III) retention increases at low HA concentration
- After saturation of the surface, competition with non-sorbed HA fractions

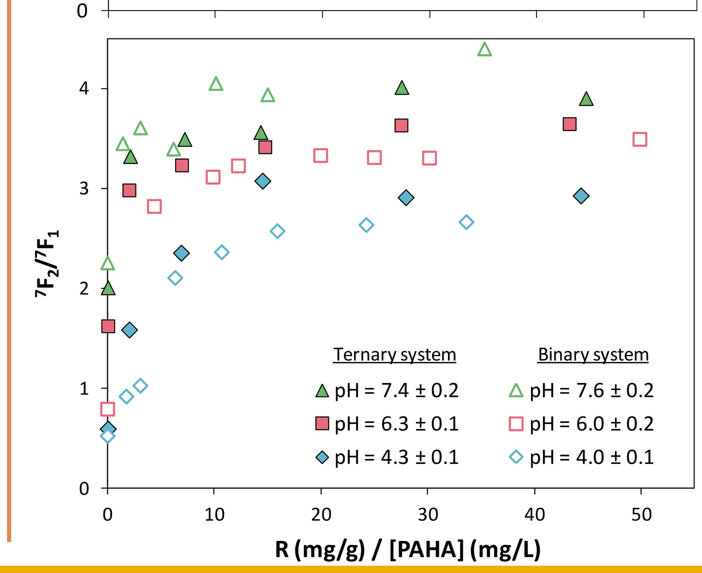
▪ Evolution of PAHA retention onto the surface

- No influence of Eu(III) presence at medium and high pH
- At low pH and high HA concentration, presence of HA increases HA retention
- No saturation of surface seen at low pH









▪ Evolution of luminescence lifetimes

- τ_1 presence: Eu(III) always bound to PAHA
- Increase of τ_2 with humic concentration, due to progressive complexation of Eu(III)
- In the ternary system, higher τ_2: more constrained environment of Eu(III) when it is bound to adsorbed PAHA moieties

▪ Evolution of Eu(III) environment symmetry

- At same PAHA concentration, no difference of asymmetry ratios between binary and ternary systems
- Presence of mineral surface has almost no influence on Eu(III) environment symmetry below pH 8
- Unlikely presence of europium-bridged humic-surface complexes

Modeling Europium(III) speciation in ternary systems

Binary Eu(III)/α-Al_2O_3 system

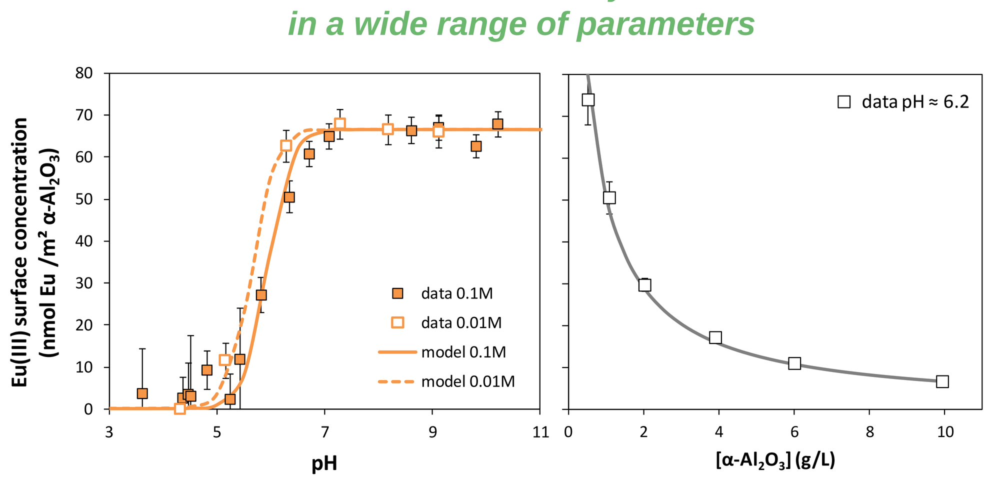
1-pK modeling:

$$\equiv AlOH^{-1/2} + Eu^{3+} \leftrightarrows \equiv AlOHEu^{+5/2} \quad \log K = 13.5$$

Repartition of Eu(III) charge in the Stern layer:

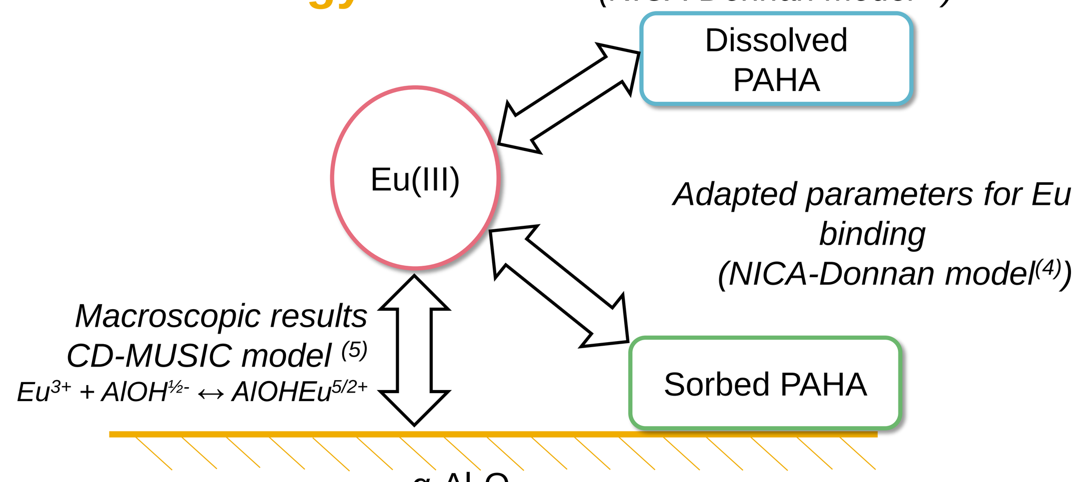
$\Delta z_0 = 1.93$
$\Delta z_1 = 1.07$

Good correlation with this study and literature data in a wide range of parameters



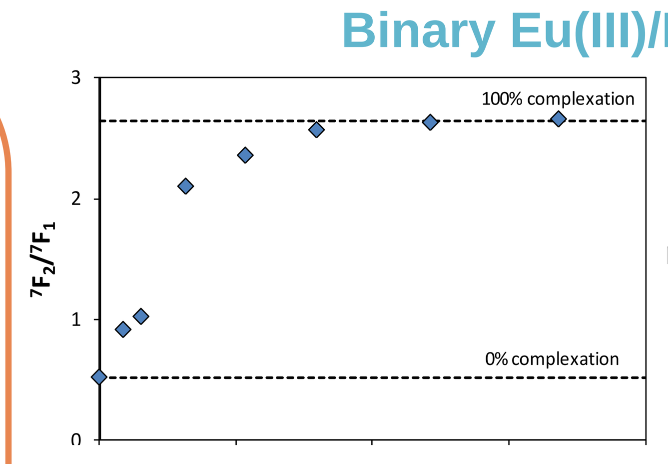
Methodology

Proton-binding parameters from spectro-photometric titrations of supernatant from retention experiments(3,6) (NICA-Donnan model(4))

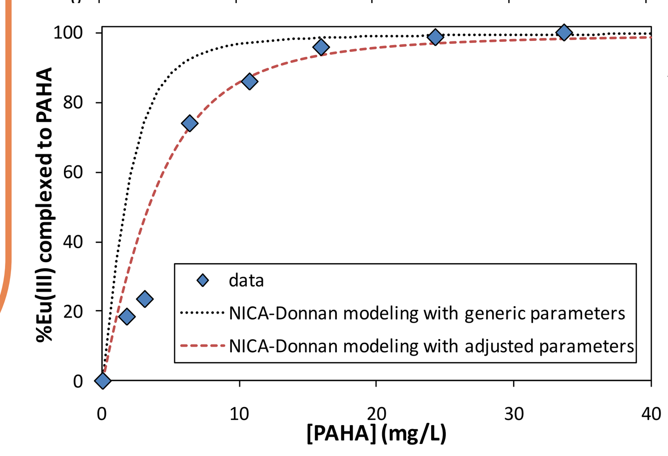


Potentiometric titrations: Description of surface reactivity (CD-MUSIC model (5))

Binary Eu(III)/PAHA system



Use of spectroscopic data (peak ratio) at pH 4 as a titration curve of Eu(III)-PAHA complexation



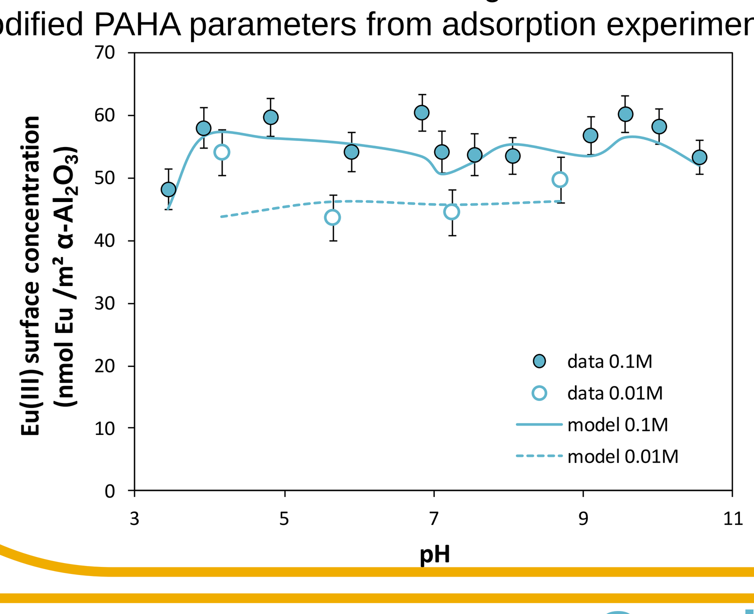
Adjustement of generic Eu(III)/HA binding parameters of the NICA-Donnan model(7) to fit our system:

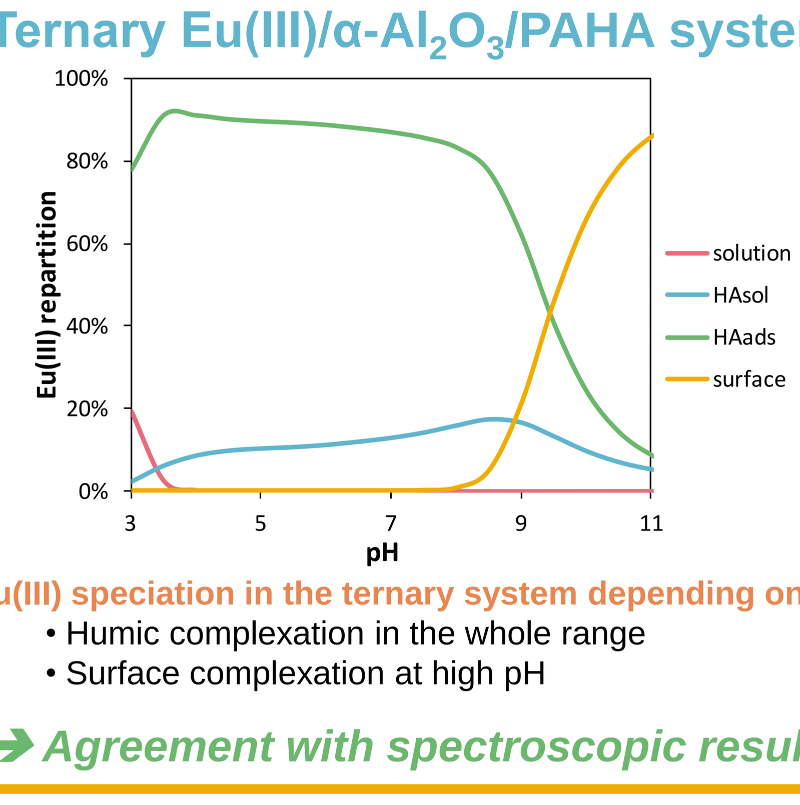
	$\log \tilde{K}$	n
S1-Eu	1.05	0.50
S2-Eu	3.43(7)	0.36(7)

Ternary Eu(III)/α-Al_2O_3/PAHA system

▪ pH and ionic strength dependence

- Good prediction of the model
- Variations due to initial concentration variation between batches
- Need more data at lower ionic strength
- Modified PAHA parameters from adsorption experiments at 0.1 M at pH 7(6)





▪ Eu(III) speciation in the ternary system depending on pH

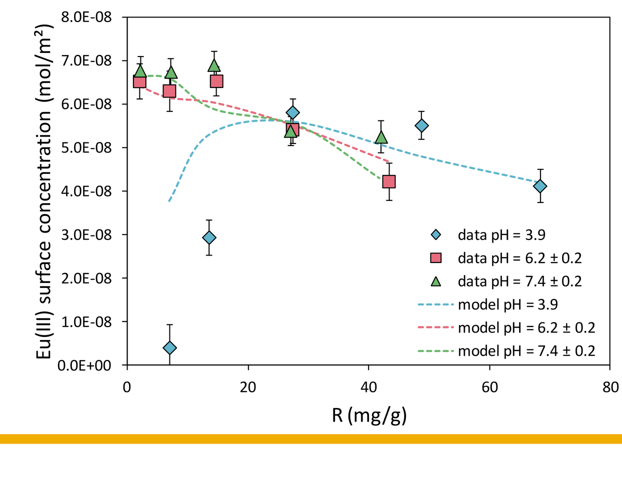
- Humic complexation in the whole range
- Surface complexation at high pH

➔ Agreement with spectroscopic results

▪ Humic concentration dependence

- Good prediction at high concentration
- Use of average parameters for humic protonation

➢ Need improvement at low ratio (high fractionation rate)
➢ Parameters from adsorption experiments at pH 7(6) (explains the poor description at low pH)



Conclusions

✓ Acquisition of data set in a various range of solution conditions
➢ Importance of humic concentration, ionic strength on contaminant mobility, not only pH

✓ Good description on Eu(III) repartition in a ternary system
➢ Need to take into account the modifications of PAHA reactivity with fractionation due to adsorption

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