

**INTRODUCTORY PART**  
**WEATHERING & SOIL CHEMISTRY**  
**ENVIRONMENTAL RN CHEMISTRY**  
**LL RADIOACTIVE WASTES & TENORM**  
**IN FRANCE**



**AQUEOUS CHEMISTRY**

**SORPTION**

**ON-GOING RESEARCH**

**FOCUS : EFFECT OF ORGANIC MATTER**

## Focus

## Effect of natural organic matter

- Lack of understanding specific interactions between RN and organic moieties of NOM : uncertainty in predicting fate (complexation, sorption, mobility) in surface environments
- Need to identify the organic compounds as carriers for radionuclides in soil and water environments
  - Examples of plutonium
- Need to understand effect of sorptive fractionation of complex organic acids (NOM-mineral interactions) on RN behaviour
  - Examples of humic substances – mineral – lanthanide interactions
- Use of advanced mass spectrometry techniques

## Focus

## Identification of NOM carriers of Pu

Four mechanisms for NOM influencing the environmental mobility of Pu have been suggested:

- 1) formation of ternary complexes (mineral phase- NOM- Pu) on immobile surfaces
- 2) formation of immobile binary complex (Pu sequestration to NOM intrinsic colloids / aggregates)
- 3) formation of mobile Pu-NOM complex
- 4) formation of ternary complexes on mobile inorganic colloids

A strategy to solve the issue : (*Santschi et al., J. Environ. Radioactivity, 2017*)

- Extract natural organic macromolecules that are complexing and immobilizing /remobilizing Pu
- Obtain detailed information on molecule characteristics using high resolution Fourier Transform Mass spectrometry

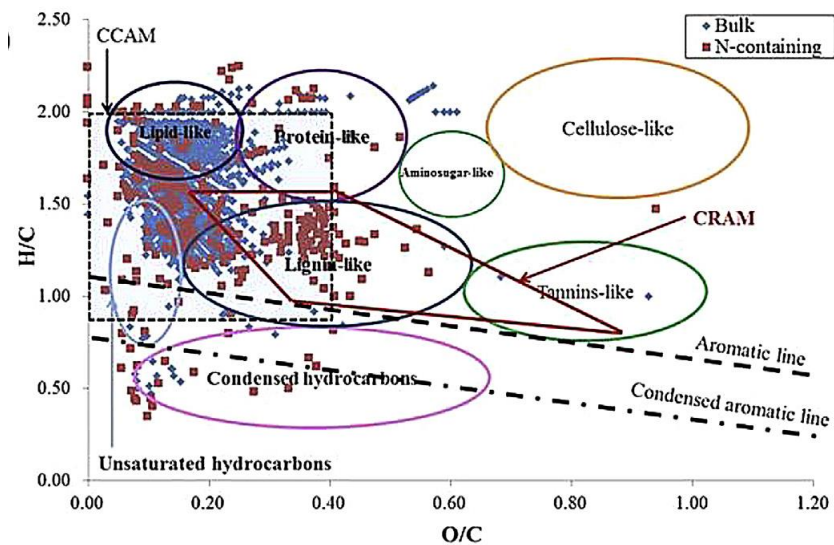
## Focus

## Identification of NOM carriers of Pu

Pu-rich NOM fraction extracted by a complex procedure of soils of the Savannah River Site\*

For further characterization, formulas assigned to the Pu-carrying NOM that originated from the bulk mobile colloidal fraction

\*Savannah River Site : Created in 50's for nuclear material processing (nuclear weapons). Today, environmental stewardship activities including the management, treatment, and disposal of radioactive, hazardous, and mixed wastes



van Krevelen diagram showing all 1259 formulas (blue) and the N-containing formulas (red) of the Pu enriched fraction purified via isoelectric focusing experiment (Santschi et al., 2002)

## Focus

## Identification of NOM carriers of Pu

Molecules mainly aliphatic with some minor fractions of aromatics - Many N-containing molecules

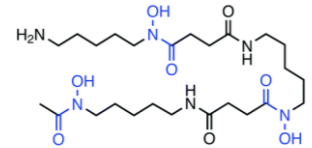
Molecules covered an overlapping region for lipid-like, protein like, lignine like and carboxyl containing alicyclic molecules (CCAM)

Comparison between the extract and a siderophore standard suggested presence of hydroxamate siderophore functionalities

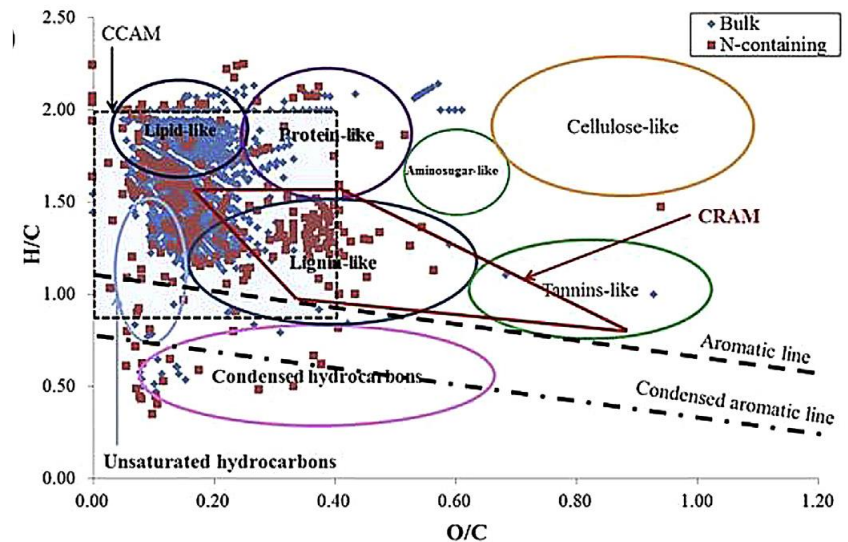
Moreover siderophore were detected in colloidal and particulate fractions

→ Pu chelated to hydroxamate compounds

### Hydroxamate



Desferrioxamine B



van Krevelen diagram showing all 1259 formulas (blue) and the N-containing formulas (red) of the Pu enriched fraction purified via isoelectric focusing experiment (Santschi et al., 2002)

# Effect of HS sorptive fractionation on Ln / TME behaviour

**M. Del Nero, G. Fleury, O. Courson, S. Meyer-Georg, R. Barillon**



## Effect of HS sorptive fractionation on Ln / TME behaviour

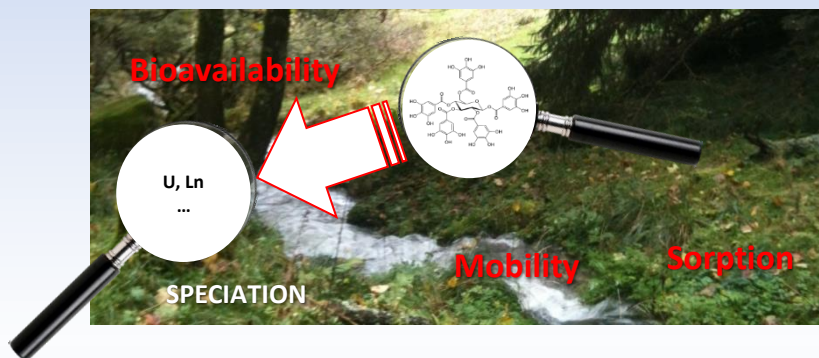
### Humic substances (HS) : Fulvic / Humic Acids (FA / HA)

- Ubiquitous in soil / water systems
- Sorb at mineral surfaces<sup>1</sup>
- Bind metals<sup>2</sup>

### RN & Trace metal elements (TME)

- Natural and anthropogenic origins
- Toxic at trace levels (U, Ln, Pb, Cd...) or at excess [ ] (Cu, Zn...)
- Speciation → sorption, mobility, bioavailability

### Ecotoxicological impacts



**Assessment of impacts of toxic RN / TME in soils requires knowledge of their speciation in presence of FA/HA<sup>3</sup> and on their bioavailability<sup>4</sup>**

**→ Identity of metallo-organic species in mineral-solution-FA systems ?**

<sup>1</sup>e.g. Ochs et al. (1994) GCA 58, 639; <sup>2</sup>e.g. Pandey et al. (2000) Ecotoxicol. Environ. Saf.. 47, 195;

<sup>3</sup>Elliott et al. (1986), J. Environ. Qual. 15, 214; <sup>4</sup>Gummuluru et al. (2002) ES&T 36 (12), 2645.



## Why studying fulvic acid – mineral surface interactions at the molecular scale ?

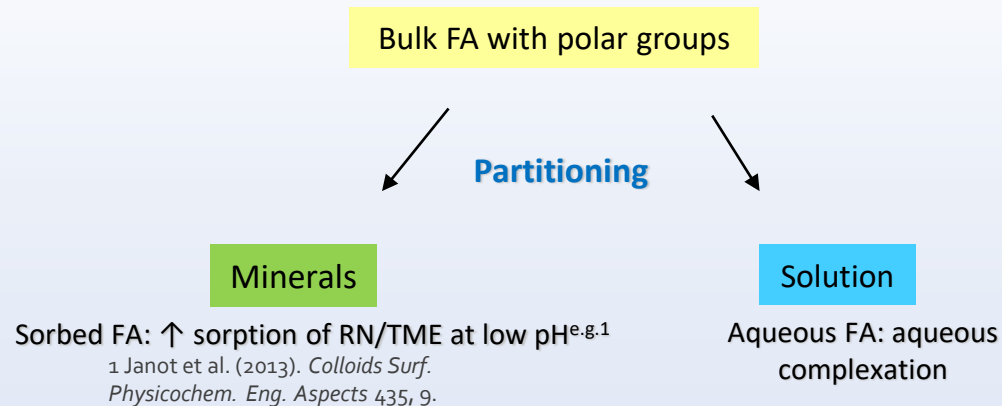
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**Fulvic Acids (FA)** : ubiquitous in all surface systems; mixtures of organic compounds from NOM degradation; chemically reactive : bind metals and sorb onto minerals

→ FA sorption of interest for understanding the fate of trace metals (TME)

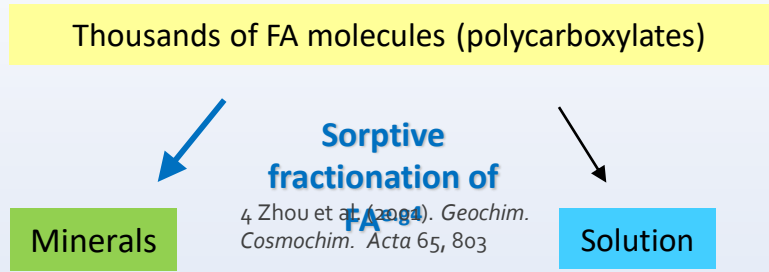
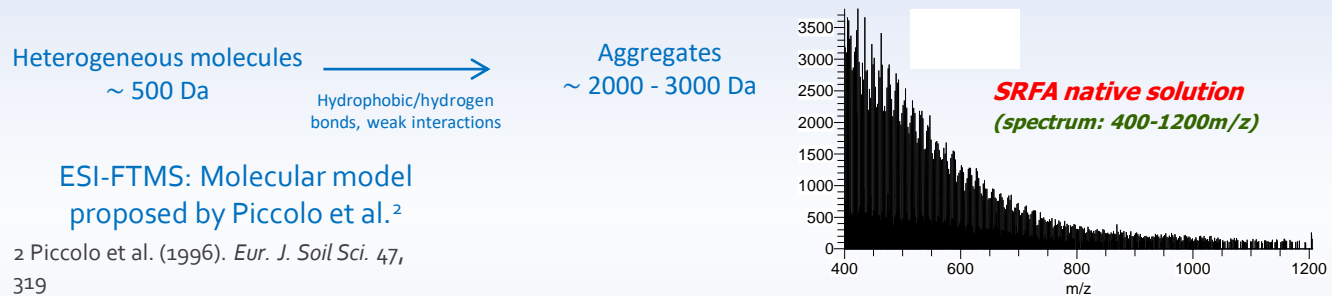
Macroscopic studies : average sorption properties of FA (functionalities, sorption constants)

→ vary from one FA to another !



# Why studying fulvic acid – mineral surface interactions at the molecular scale ?

**Fulvic Acid** : A complex mixture of thousands of molecules held together by weak bonds



<sup>2</sup> McKnight et al. (1992) *ES&T* 26, 1388. Kaiser (2003) *Org. Geochem.* 34(11),1569.

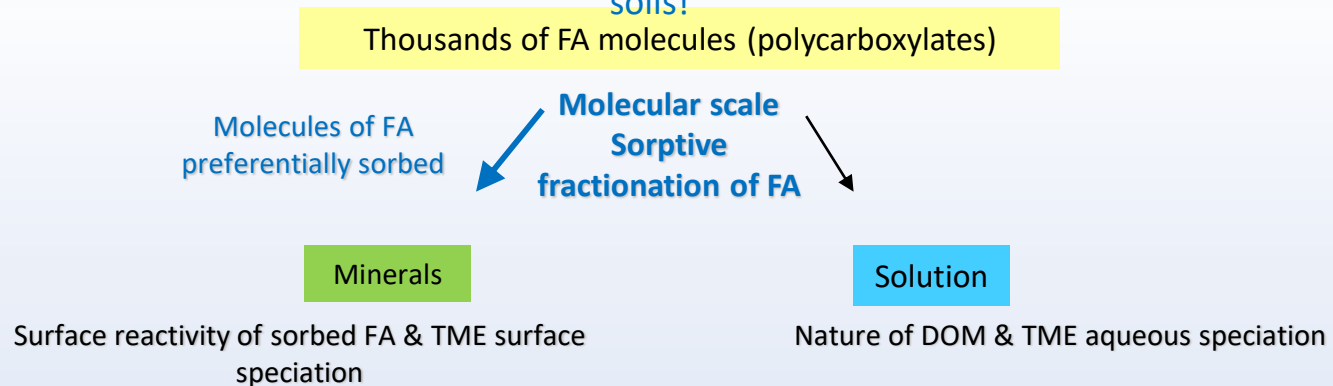
## Why studying fulvic acid – mineral surface interactions at the molecular scale ?

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**Fulvic Acid** : A complex mixture of thousands of organic molecules

**Molecular scale => each molecule has its own chemical characteristics (composition, structure, aromaticity, hydrophobicity, acidity)<sup>2</sup> and its own affinity for a mineral surface<sup>3</sup>**

**!**  
Information needed for building realistic models of coupled cycles of OM and TMEs in soils!



<sup>3</sup>Reiller et al. (2006) ES&T 40(7), 2235. Galindo and Del Nero (2014) ES&T 48, 7401; (2015) RSC Advances 5, 73058.

## Questions and objectives

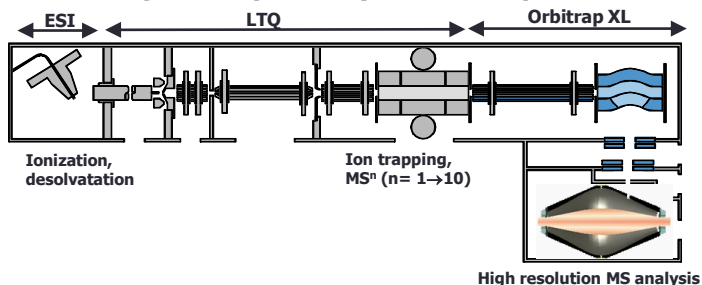
We addressed the sorptive fractionation of FA at the molecular level

1. Relations between the chemical characteristics of a FA molecule and its affinity for a mineral surface ?
    - Identity of the sorbed / not sorbed FA molecules  
(Composition, acidity, hydrophobicity, number of functionalities of a molecule)
  2. Influence of key mineral or solution parameters on FA fractionation ?
    - Mineral surface properties (Al / Fe oxides vs. clay), FA-to-mineral ratio, pH
  3. Effect of sorptive fractionation of FA on TME sorption ?
- 
1. Apply molecular data to TME transfers in a forested soil-water system

Molecular level : consider each FA molecule with its own characteristics (composition, structure, aromaticity, hydrophobicity, acidity) and affinity for a mineral surface

## Elucidation of the nature of compounds in a complex mixture

### The « LTQ Orbitrap XL » hybrid mass spectrometer:



High resolving power, high mass accuracy

(100 000 at 400m/z, <3ppm with external calibration)

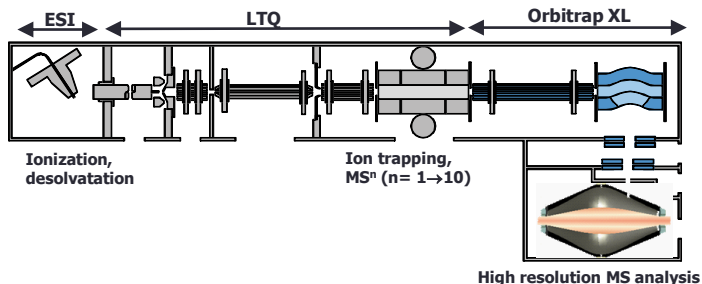
→ Determination of chemical formula

$C_xH_yO_zN_t$  with  $x \leq 200$ ,  $y \leq 600$ ,  $z \leq 50$ ,  $t \leq 1$

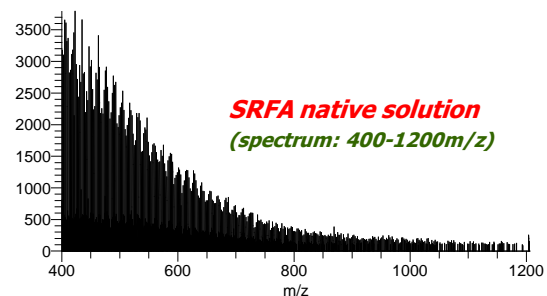
#### **ESI(-)FTMS analysis:**

- Aqueous solutions introduced directly in ESI probe (flow rate:  $10\mu\text{L}\cdot\text{min}^{-1}$ ).
- Temperature of the transfer tube:  $275^\circ\text{C}$ .
- Spray voltage: 3.7kV. Voltage applied to capillary, multi-poles, tube lens: automatically tuned to favour transmission of HMW ions

The « LTQ Orbitrap XL » hybrid mass spectrometer:



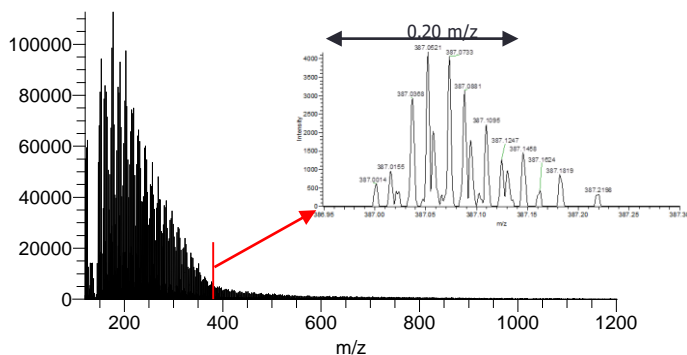
High resolving power, high mass accuracy  
(100 000 at 400m/z, <3ppm with external calibration)



→ Determination of chemical formula



ESI-FTMS spectra recorded using negative ionisation mode  
SRFA native solution (spectrum:120-1200m/z)

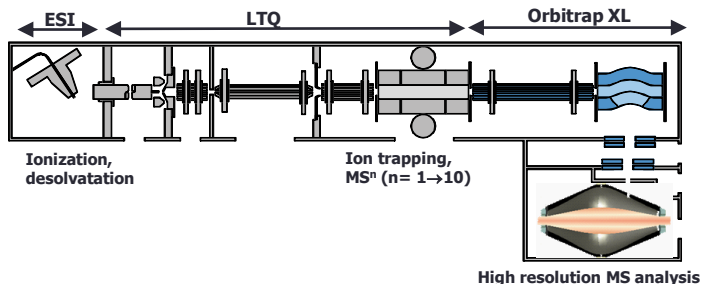


- **SRFA is a very complex mixture**; dozen of peaks at same nominal mass
- Spectra display typical patterns (intense peaks at odd m/z, peaks of lower intensity at even m/z)
- Formation in ESI of singly charged constituents only
- SRFA constituents do not exceed 980 Da in agreement of the **concept of supramolecular assemblies** of Piccolo et al. (1996)

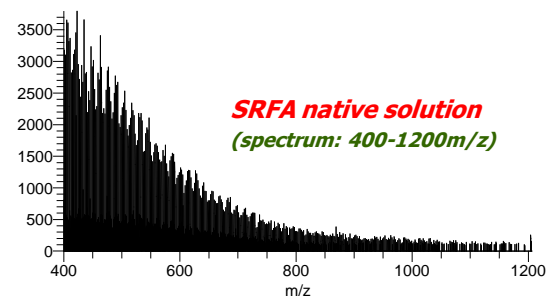
SRFA: ~ 8400 compounds detected (S/N>2); ~5700 elemental compositions identified

## Elucidation of the nature of compounds in a complex mixture: SRFA

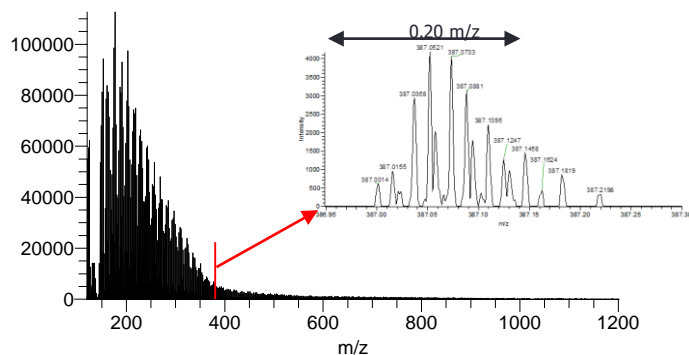
### The « LTQ Orbitrap XL » hybrid mass spectrometer:



High resolving power, high mass accuracy  
(100 000 at 400m/z, <3ppm with external calibration)



### ESI-FTMS spectra recorded using negative ionisation mode SRFA native solution (spectrum:120-1200m/z)



→ Determination of chemical formula

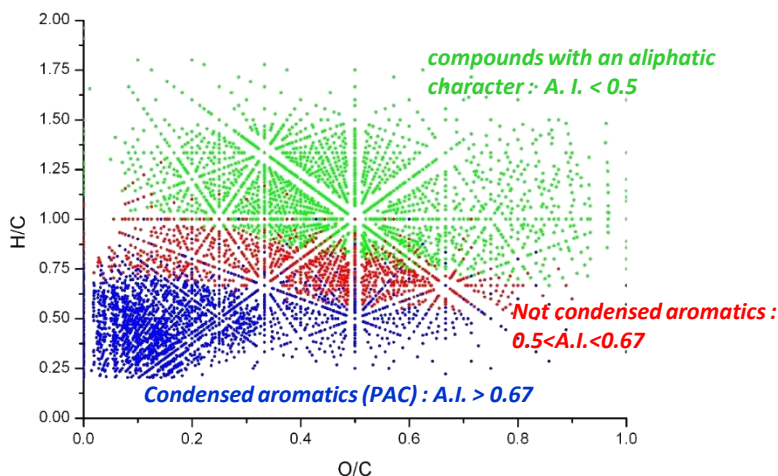


#### Chemical formula:

Automated assignment of chemical formulae carried out using Xcalibur software. All possible formulae attributable to a given m/z value calculated by considering  $^{12}C$ ,  $^1H$ ,  $^{16}O$ ,  $^{14}N$  and by rejecting all formulae whose theoretical mass differs from 3 ppm or more from measured mass.

## → Determination of chemical formula

→ Van Krevelen diagram of SRFA



*Elemental compositions of compounds constitutive of the Suwannee River fulvic acid (obtained after ESI-FTMS analysis of native solution)*

### Aromaticity index

defined by Koch and Dittmar (2006)

$$A. I. = \frac{1 + C - \frac{O}{2} - \frac{H}{2}}{C - \frac{O}{2} - N}$$

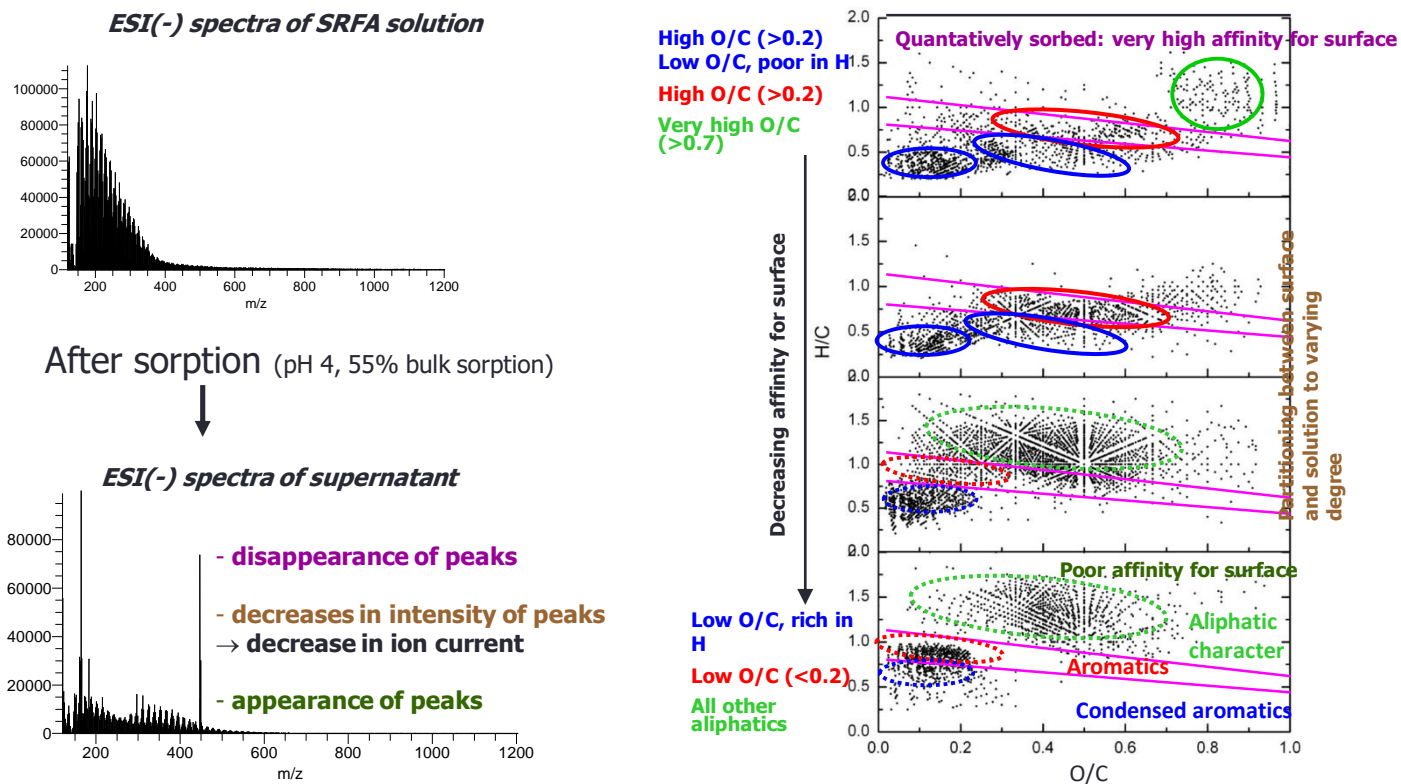
- Aliphatics: A.I. ≤ 0.5
- Not-Condensed Aromatics: 0.5 < A.I. ≤ 0.67
- Polycyclic Aromatics: 0.67 < A.I.

SRFA compounds occupy a wide region of the VK diagram extending from polycyclic aromatic compounds (PAC) with H/C > 0.23 and O/C > 0.02 (bottom left) to compounds of aliphatic character with H/C < 1.5 and O/C < 0.92 (top right).

SRFA: ~ 8400 compounds detected (S/N > 2); ~ 5700 compositions identified



## Results: molecular scale study of the sorption of SRFA onto alumina



**Strong sorptive fractionation of SRFA !**

Compounds showing the highest affinity for alumina surface:

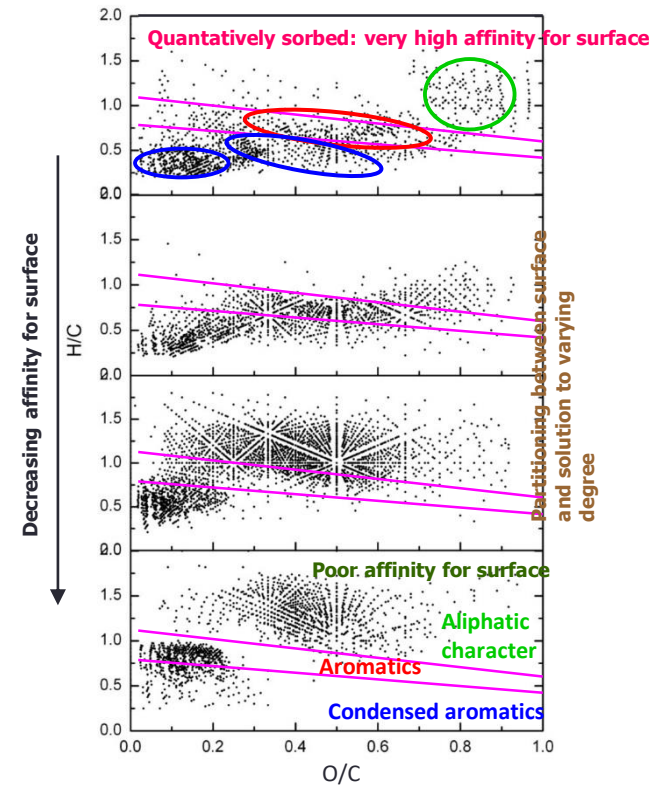
- PAC, aromatics > aliphatic compounds (except those with  $O/C > 0.7$ )

- PAC and aromatic compounds with multiple oxygenated functionalities

➤ chemical sorption via O-functionalities but **why multiple functionalities...**?

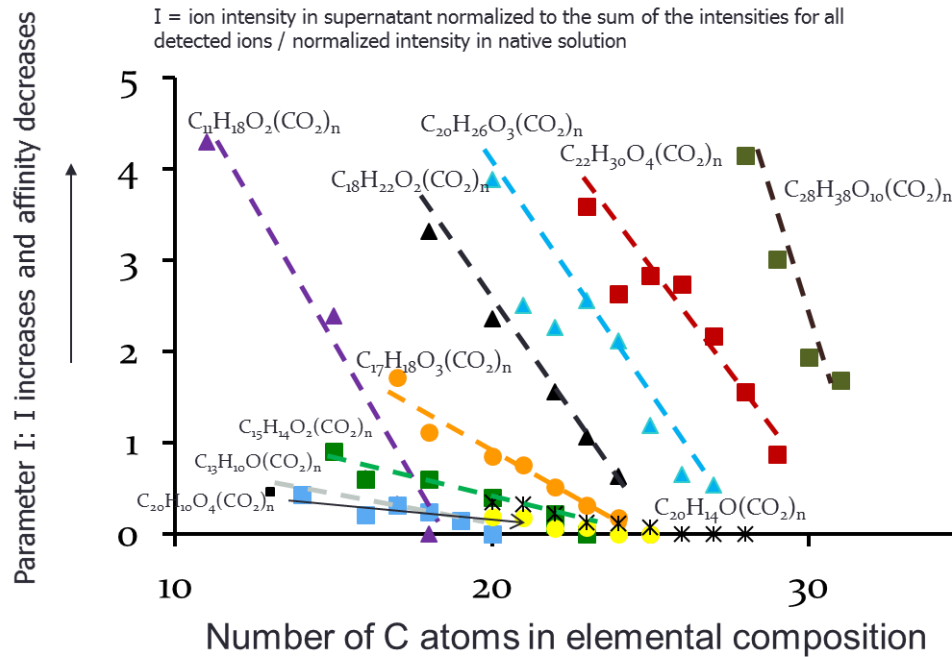
- PAC depleted in hydrogen and carrying few oxygenated groups :

➤ mechanisms ?



## Relations chemical characteristics of a SRFA compound and its surface affinity

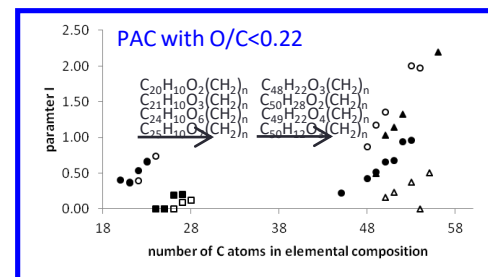
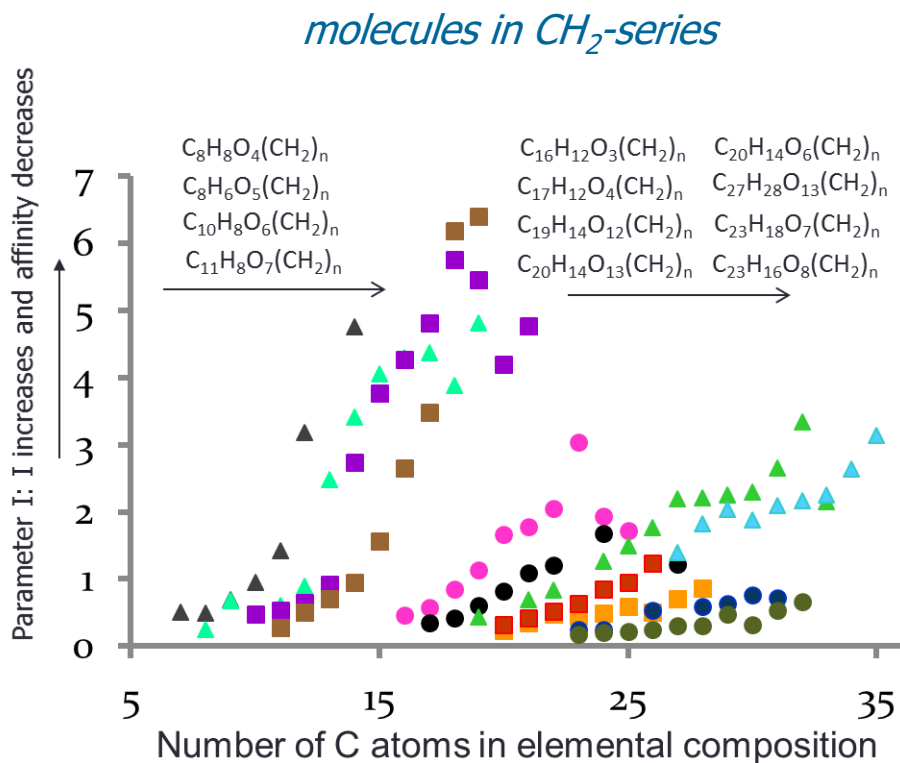
### *molecules in CO<sub>2</sub>-series*



**molecule acidity** is the main chemical parameter governing the sorptive fractionation of SRFA

Positive correlation between the sorption degree of a molecule within a CO<sub>2</sub>-series and its number of CO<sub>2</sub> groups.

# Relations chemical characteristics of a SRFA compound and its surface affinity



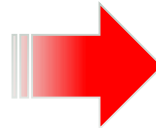
**molecule acidity** is the main chemical parameter governing the sorptive fractionation of SRFA

Inverse correlation between the sorption degree of a molecule within a CH<sub>2</sub>-series and its number of CH<sub>2</sub> groups.

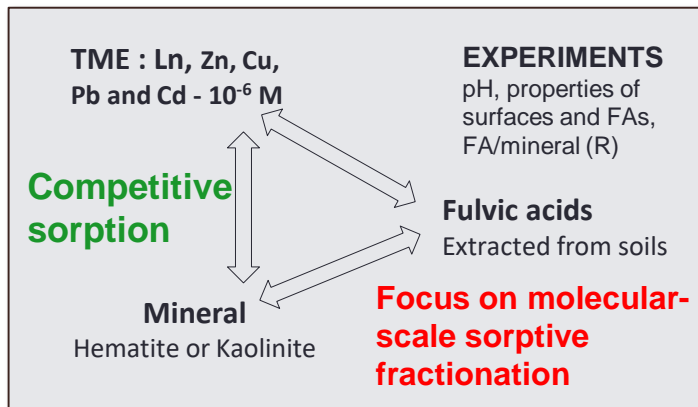
# OBJECTIVES : APPLICATION TO SOIL WATER STUDIES

Acquire knowledge on effect of sorptive fractionation of FA on the speciation and bioavailability of TMEs in soils

1. Study of model systems :  
TME speciation, FA  
fractionation



2. Study of TME availability in soils  
:  
Use new knowledge on speciation

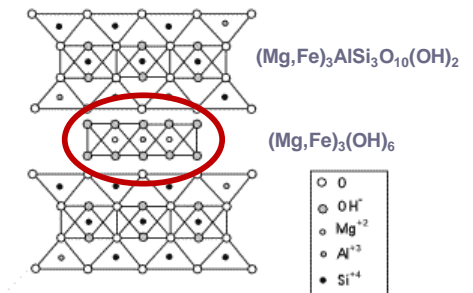
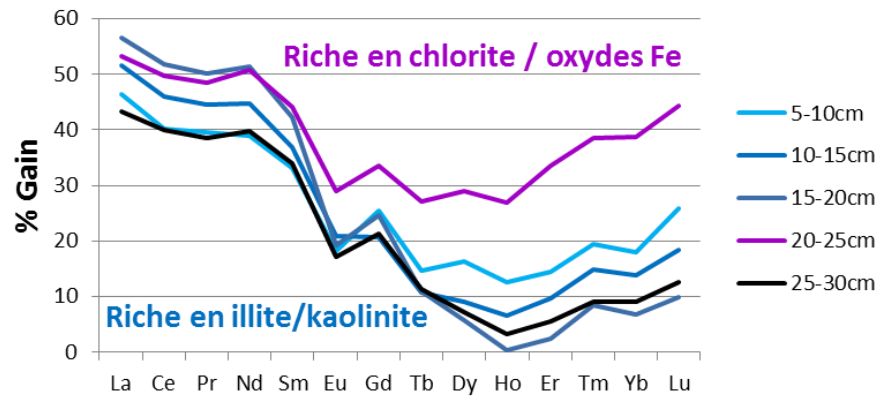


# STUDY OF SOIL – WATER TRANSFERS

## Behaviour of Ln elements in soil profiles

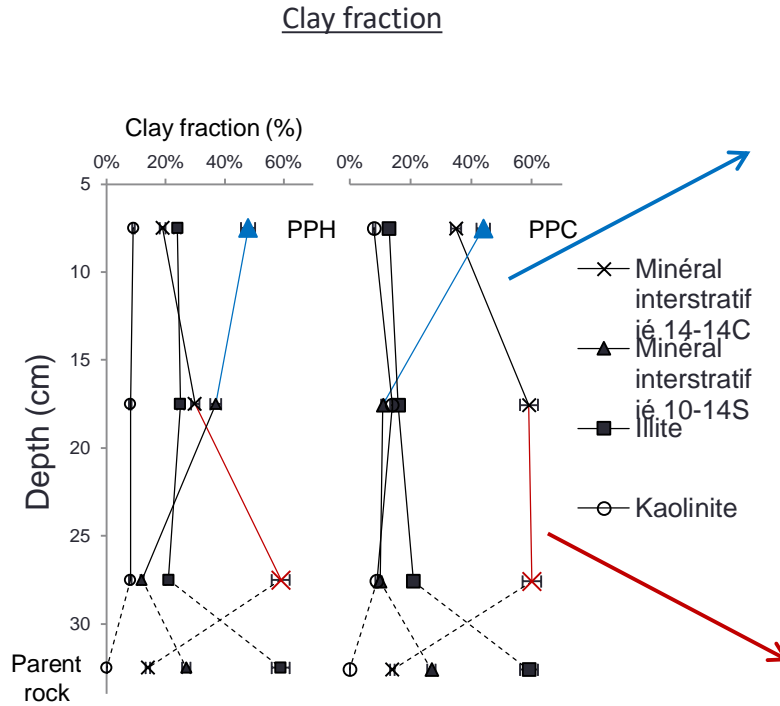
Mass balances / parent rock (Reference element : Th)

- Ln : absolute gains
- Relative gains Light Ln / Heavy Ln,  $\nearrow$  with depth
- Peculiar samples in depth

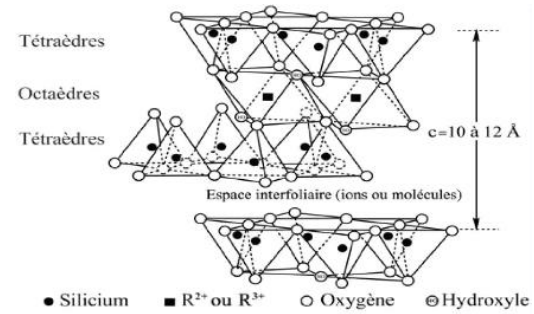


=> distribution of Ln linked to mineralogy changes

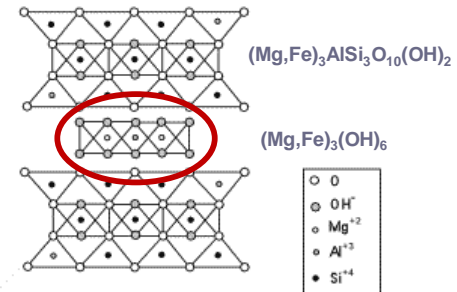
# Mineralogical composition of soils



## Smectitic minerals



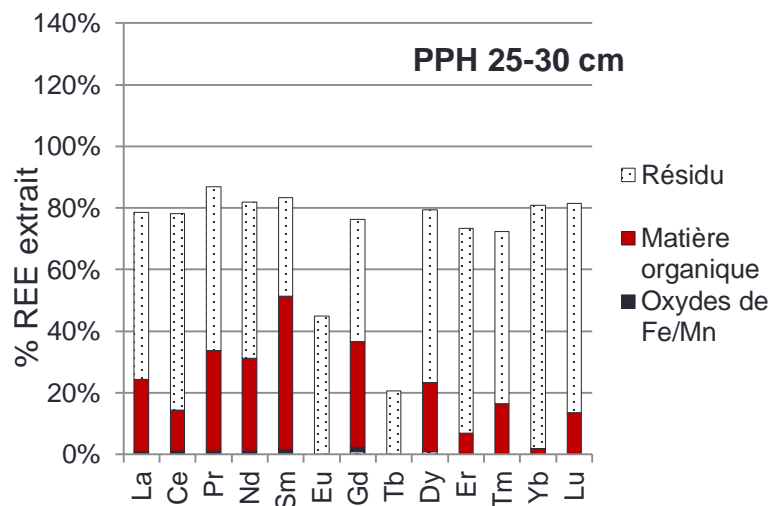
## Chloritic minerals



## Distribution of Ln elements between different phases of soils

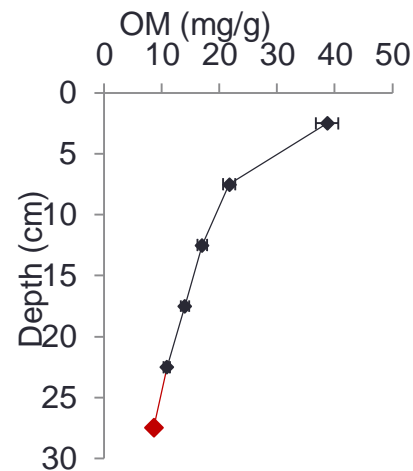
Mass balances / parent rock (Reference element : Th)

**Selective extractions\*** = distribution of REE between ≠ phases of soils



⇒ Some organic constituents are specifically involved in the REE retention ... which ones ?

A significant fraction associated to OM !

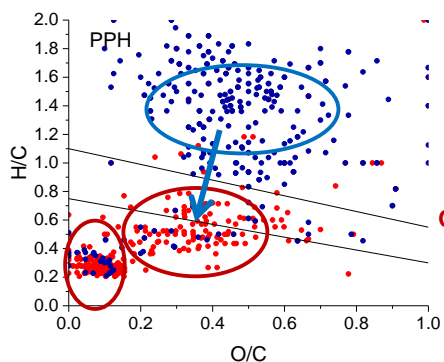


\*Tessier A., Campbell P. G. and Bisson M. (1979) *Anal. Chem.* 51, 844-851



# Dynamic of FA compounds in soils

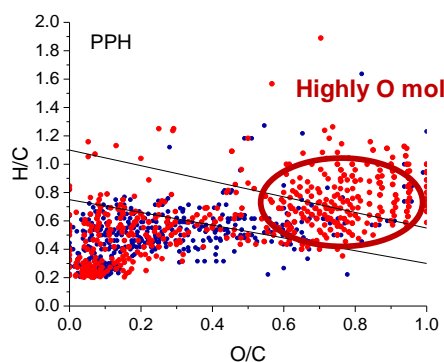
Specific compounds / 25-30 cm



aliphatics  
O/C intermédiaires

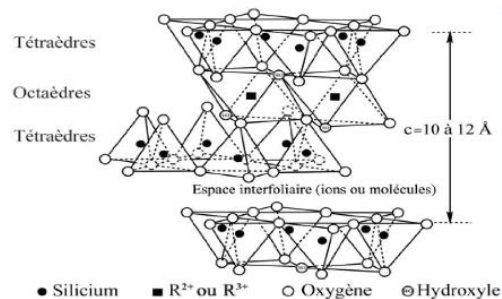
Oxygenated or  
hydrophobic  
PACs

Composés identifiés spécifiquement / 0-5 cm

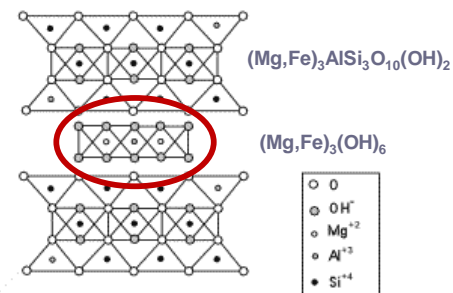


Highly O molecules

## Smectitic minerals



## Chloritic minerals



**High capacity for metal coordination**

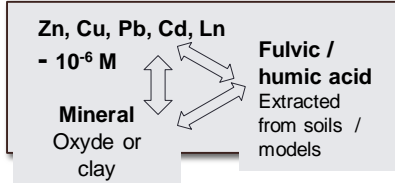
⇒ high accumulations of Ln in chlorite rich layers

# METHODOLOGY

## EXPERIMENTS

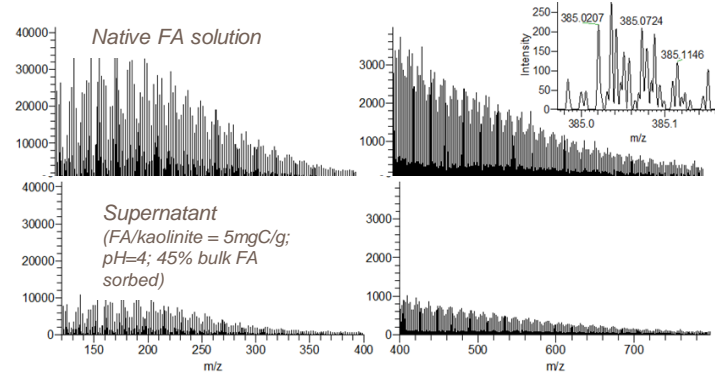
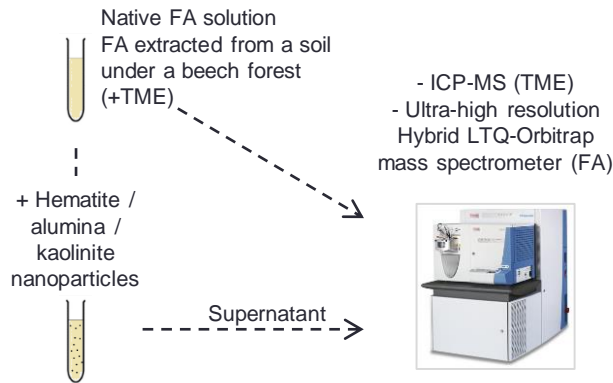
Innovative approach :

Batch experiments of FA (and TME) sorption  
ESI FTMS analysis of native FA solution and supernatants



→ ESI (-) MS SPECTRA

- FA : a very complex mixture
- Formation in ESI of singly charged ions
- FA constituents do not exceed 900 Da
- Variable ↓ in peak intensity after sorption



ESI-FTMS : identifying molecules in mixtures  
 - Soft ionization  
 - High resolving power, mass accuracy (100 000 at 400m/z, <3ppm ext. cal.)  
and elucidating sorptive fractionation

**Ca. 3, 000 compounds detected in FA**  
**Sorption induces a fractionation of FA !**

## → ROUGH CHEMICAL FORMULA

### Xcalibur™ software

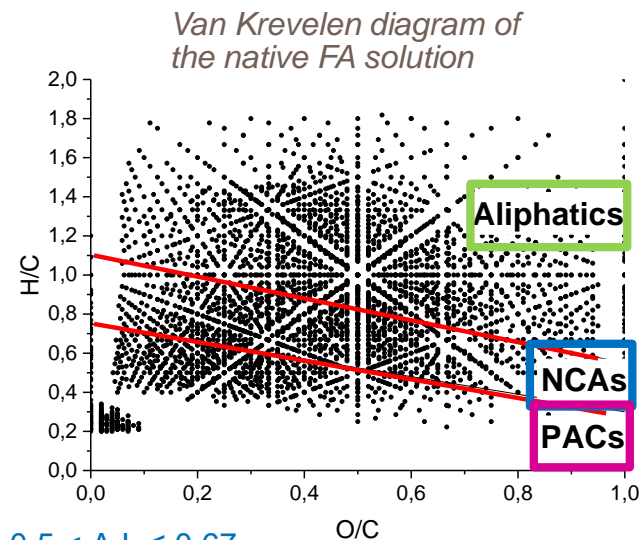
- S/N ratio > 4
  - $^{14}\text{N} \leq 1$  ;  $^{16}\text{O} \leq 50$  ;  $^{12}\text{C} \leq 200$  ;  $^1\text{H} \leq 600$
- 85% of the 3000 detected compounds in the native solution were identified

### Aromaticity index

defined by Koch and Dittmar (2006)

$$\text{A. I.} = \frac{1 + \text{C} - \frac{\text{O}}{2} - \frac{\text{H}}{2}}{\text{C} - \frac{\text{O}}{2} - \text{N}}$$

- Aliphatics:  $\text{A.I.} \leq 0.5$
- Not-Condensed Aromatics:  $0.5 < \text{A.I.} \leq 0.67$
- Polycyclic Aromatics:  $0.67 < \text{A.I.}$



Homologous  $-\text{CH}_2$  and  $-\text{CO}_2$  series (Kendrick mass analysis) : up to 14 and 8 molecules, respectively

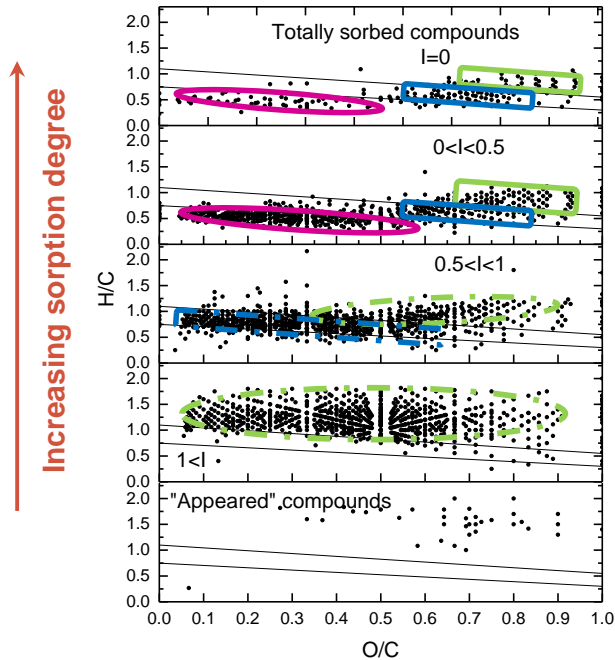
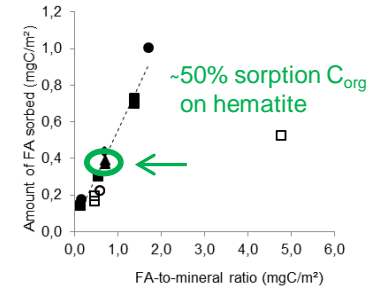
**FA molecules : a wide range of composition, degree of aromaticity, acidity, hydrophobicity, number of O-functionalities...**

# FA FRACTIONATION ON HEMATITE

## Van Krevelen diagrams

$I$  = intensity of an ion in the supernatant normalized to the total ion current / normalized intensity of this ion in native solution

$I \nearrow \Rightarrow$  Sorption degree  $\searrow$



Highly or well sorbed :

- Aliphatic compounds of O/C (> 0.6) and low H/C
- NC Aromatic compounds of high O/C
- Polycyclic aromatic compounds

Less or Poorly sorbed :

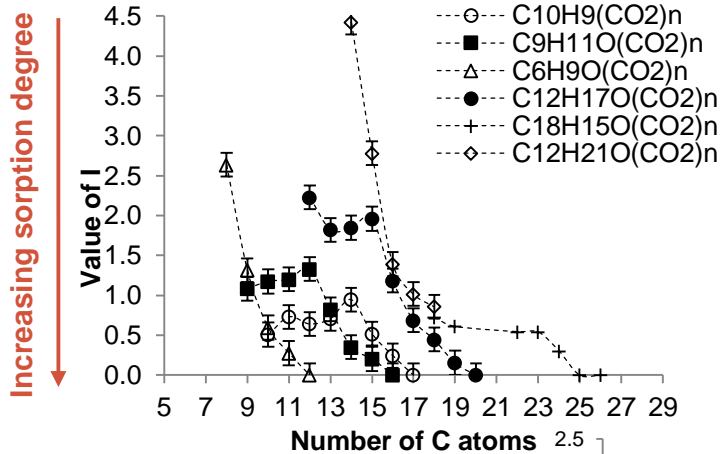
- All other Aliphatic compounds
- NC Aromatic compounds of O/C < 0.5

- Strong fractionation
- Aliphatics and NC aromatics : Chemical sorption via O-functionalities & multiple functionalities
- PAC: mechanisms ?

# FA FRACTIONATION ON HEMATITE

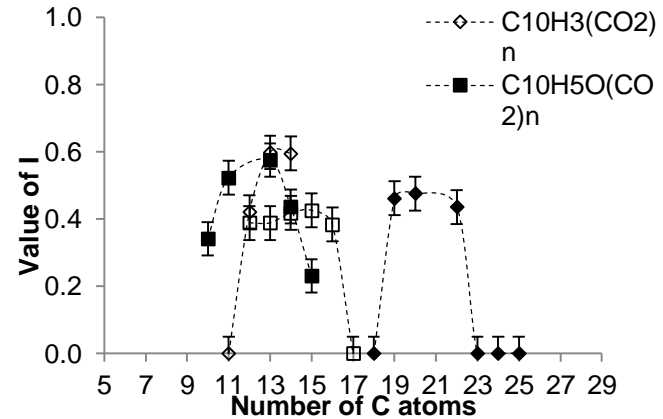
## CO<sub>2</sub> and CH<sub>2</sub> series

### Aliphatics and NC aromatics

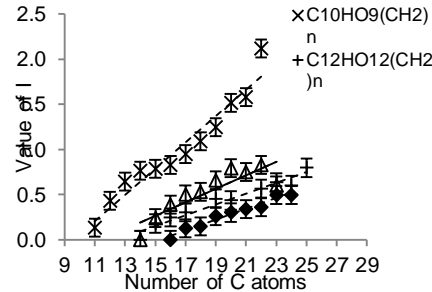


Positive correlation between the sorption degree of a molecule within a CO<sub>2</sub>-series and its number of CO<sub>2</sub> groups.

### Polycyclic aromatics



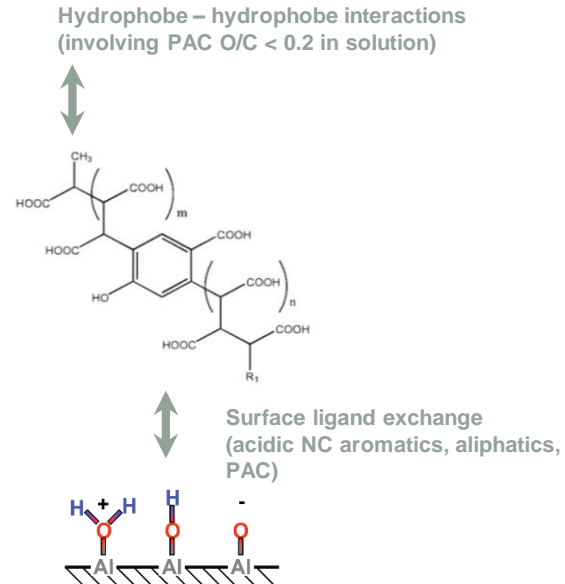
Sorption degree of a molecule within a CO<sub>2</sub>-series decreases then increases (O/C > 0.2) with its number of CO<sub>2</sub> groups



Inverse correlation between the sorption degree of a molecule within a CH<sub>2</sub>-series and its number of CH<sub>2</sub> groups.

# FA FRACTIONATION ON HEMATITE

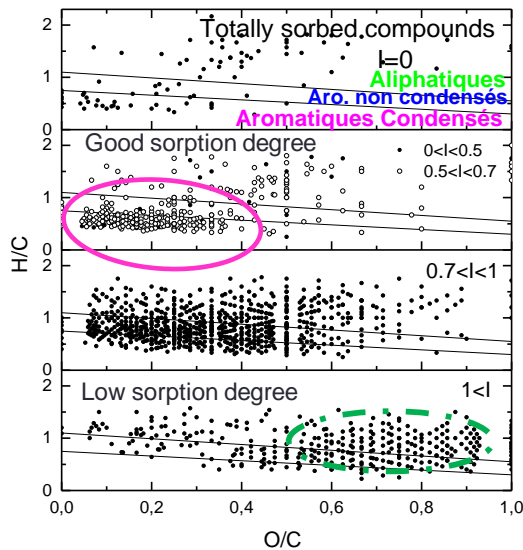
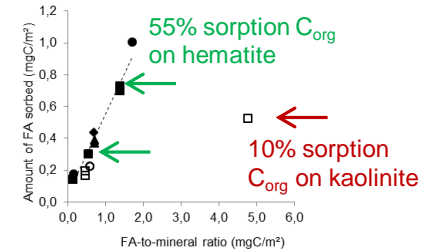
- **Molecular acidity** is the main chemical parameter governing the sorptive fractionation of FA (aliphatics and not-condensed aromatics) on Al/Fe oxides : surface ligand exchange
- Similar results for alumina and hematite (Fleury et al., 2017a,b), aquatic FA and soluble fraction of HA (Galindo and Del Nero, 2014, 2015)
- Both **molecular acidity** and **degree of hydrophobicity** control the degree of sorption of polycyclic aromatics : surface ligand exchange and hydrophobe - hydrophobe interactions for PAC with O/C < 0.2
- Similar results for alumina and hematite (Fleury et al., 2017a,b)



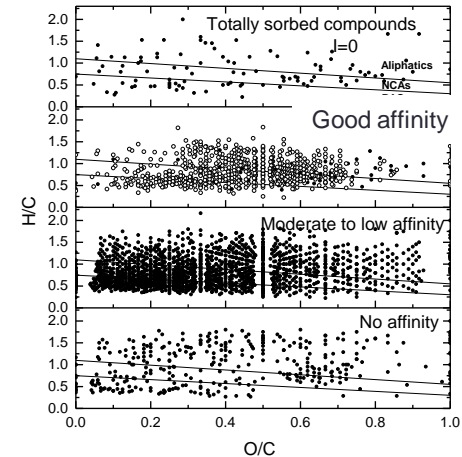
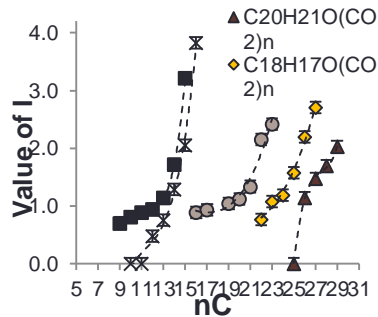
# KEY PARAMETERS

$I \nearrow \Rightarrow$  Sorption degree  $\searrow$

FA sorptive fractionation on hematite (at high R)



FA Sorptive fractionation on kaolinite : a low selectivity !



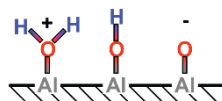
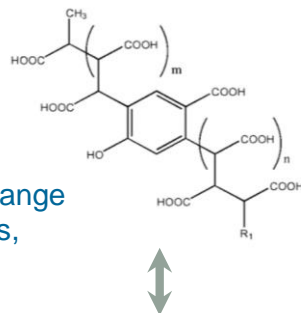
High FA-to-hematite ratios (and high pH) :  
 High sorption degree of PAC & Prevent sorption of  
 the most acidic and highly O aliphatics and NCA

Key parameters governing FA sorption : FA/mineral ratio & mineral properties

## Fe / Al oxides

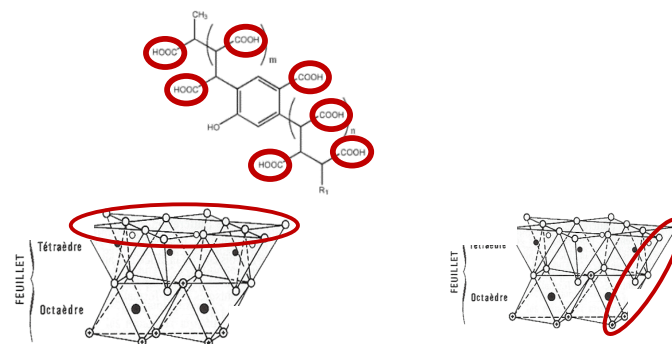
- **Molecule acidity** is the main chemical parameter governing the sorptive fractionation of FA (aliphatics and NC aromatics): surface ligand exchange
- Both **molecular acidity** and **degree of hydrophobicity** control the degree of sorption of polycyclic aromatics on Al/Fe oxides
- Increasing FA-to-hematite ratio favours preferential retention of most acidic PAC whereas aliphatics and NCA are left in solution

Surface ligand exchange  
(acidic NC aromatics,  
aliphatics, PAC)



## Kaolinite

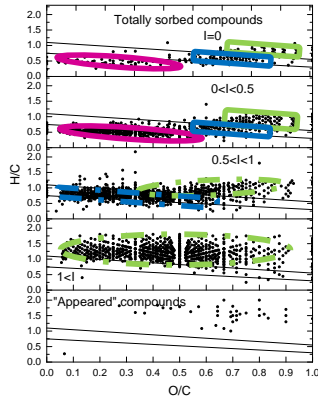
- **Weak selectivity** of the kaolinite surface towards FA molecules
- Poor sorption of PACs O/C < 0.2
- H-bonding of the FA molecules at weak sites (aluminol groups and silanol groups) on the basal plane of kaolinite is a good candidate



H-bonding at basal planes

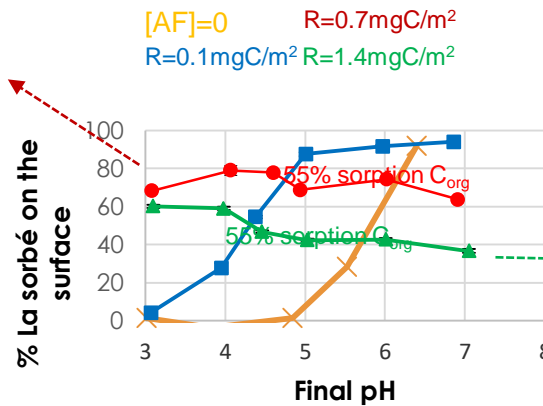


# LN SORPTION ON HEMATITE

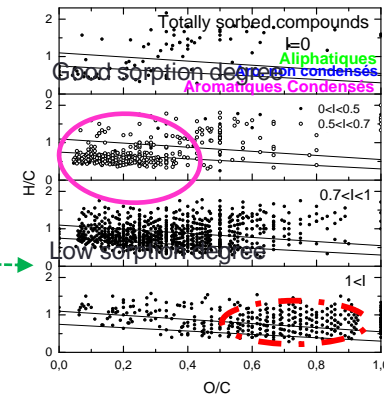
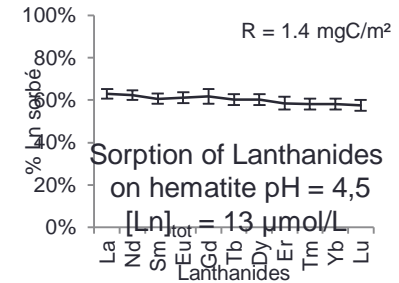


Formation of La-fulvate surface complexes favored

## Sorption of Lanthane onto hematite



Sorption order : Ln > Pb, Cu > Zn, Cd : sorption of strong Lewis acids favoured

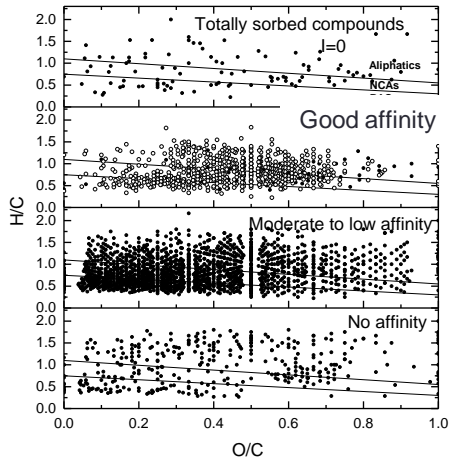
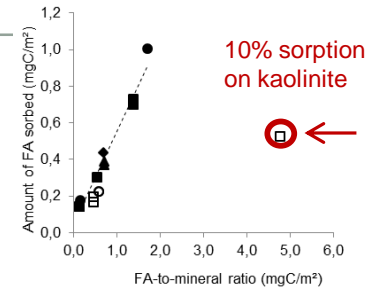


Formation of aqueous La-fulvate promoted

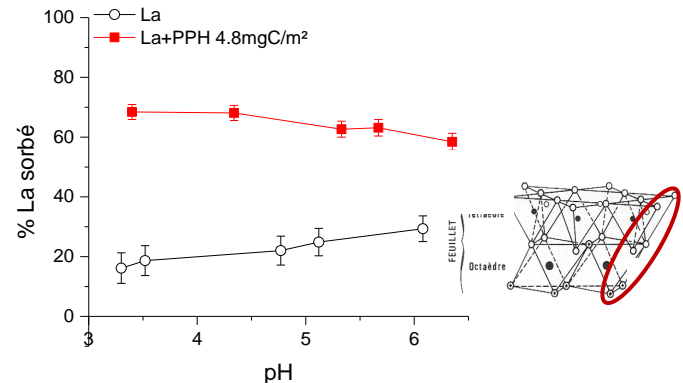
FA-to-hematite ratio and pH influences FA sorptive fractionation  
 Type of sorptive fractionation of FA influences Ln sorption

# FA & Ln SORPTION ON KAOLINITE

Sorptive fractionation : a low selectivity !



## La sorption



Promoted by FA whatever pH Possibly surface complexes with the most acidic and oxygenated molecules sorbed on high affinity sites

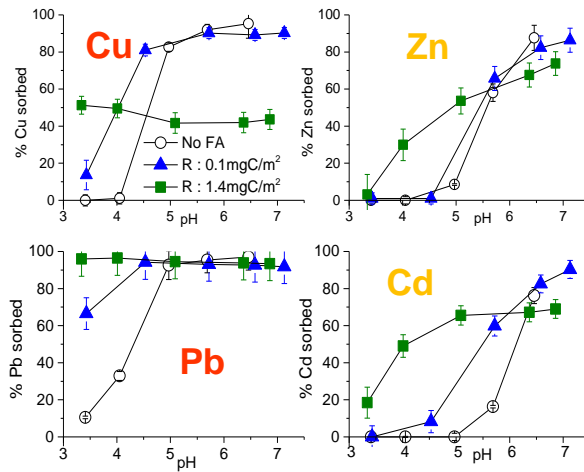
≈ 12 μmol sites/L (limited amount !)- [Ln]<sub>tot</sub> = 13 μmol/L

Further studies needed for Ln-HS-clays

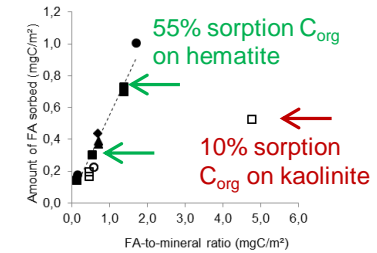
# KEY PARAMETERS FOR TME SORPTION

## Sorption of TME onto Hematite

[AF]=0      R=0.7mgC/m<sup>2</sup>  
 R=0.1mgC/m<sup>2</sup>   R=1.4mgC/m<sup>2</sup>

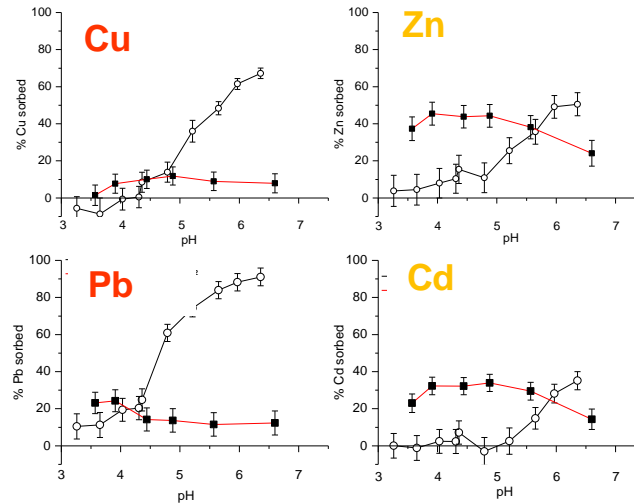


Sorption order : Ln > Pb > Cu > Cd, Zn  
 Sorption of strong Lewis acids favoured



## Sorption of TME onto Kaolinite

[AF]=0      R=4.8mgC/m<sup>2</sup>



Sorption order : Ln > Zn, Cd (low lewis acids) > Pb, Cu

Type of mineral influences FA sorptive fractionation and order of TME sorption

## Concluding remarks

- NOM Molecular-level studies using ESI-FTMS is a novative approach very useful to understand coupled cycling of RN or TME and OM in water - soil systems. 😊
- Valuable insights into the characteristics of OM molecules involved in the formation of aqueous / surface complexes but no structural information 😞
- Further fundamental and field studies required to gain a more comprehensive understanding of complex interactions of RN with abiotic and biotic soil / water components