Radionuclide speciation and transfers in the environment: recent research in radiochemistry and new perspectives from multidisciplinary approaches

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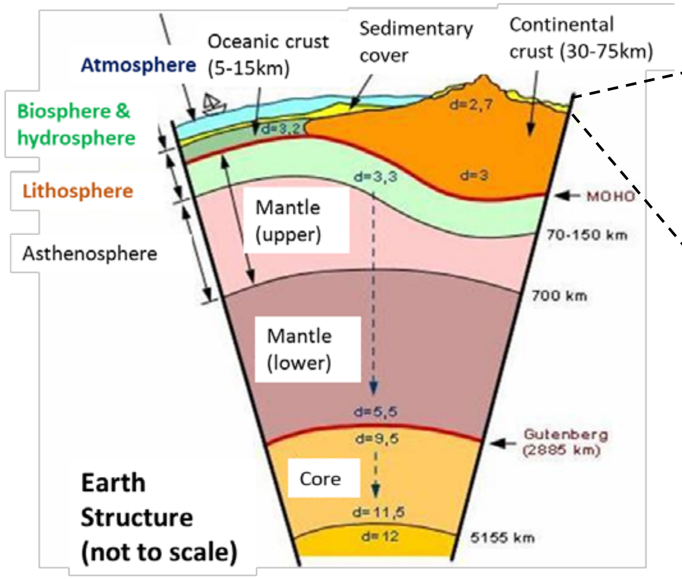
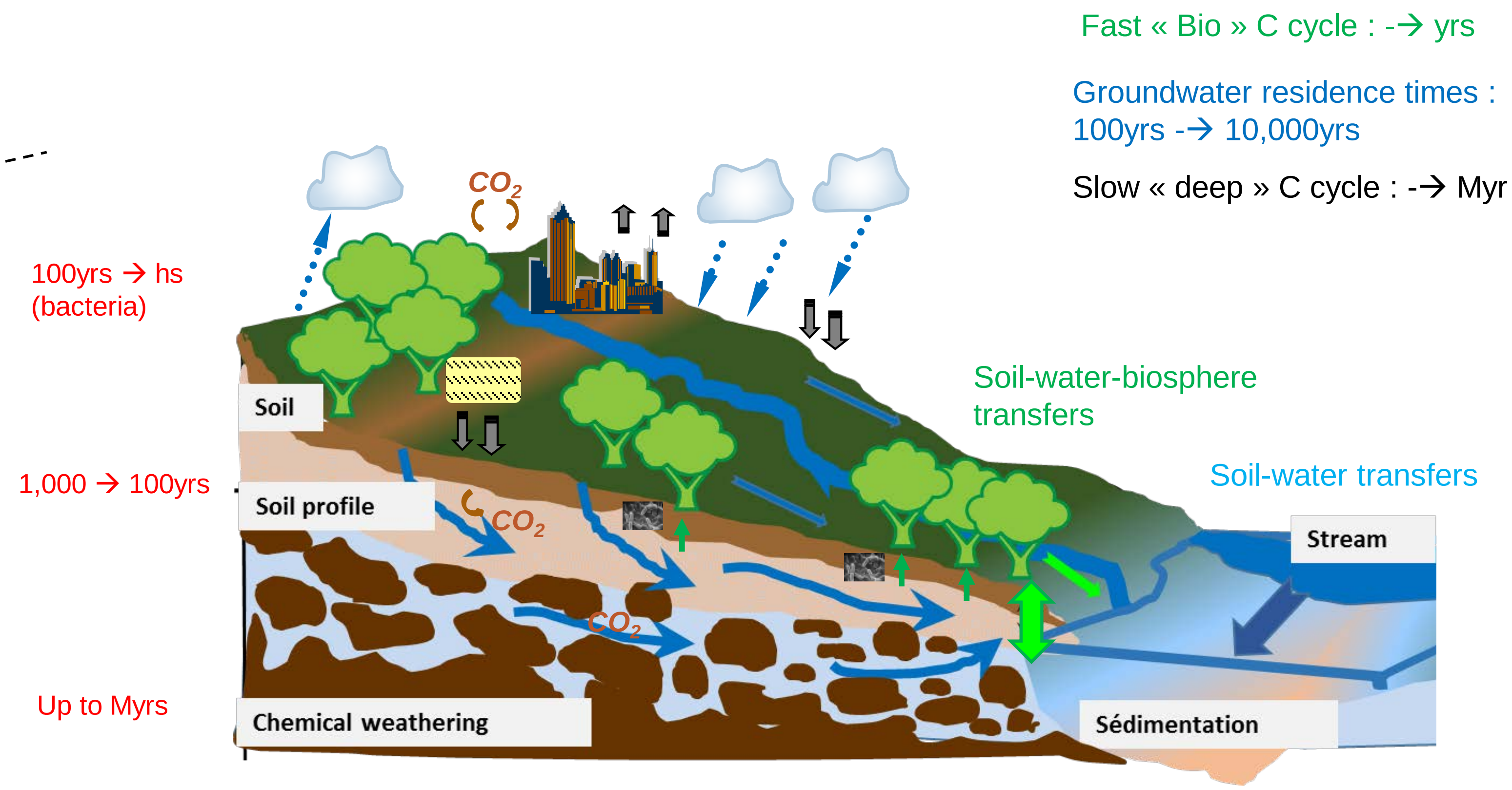
The “environment”

- A very thin pellicle at Earth’s surface
- Characterized by interfaces between atmosphere, hydro-, geo-& bio-sphere
- Interactions, transformations and element exchanges: rock alteration, soil formation, life growth, water / C / biogeochemical cycling
- Different time scales, spatial variations





The "environment"

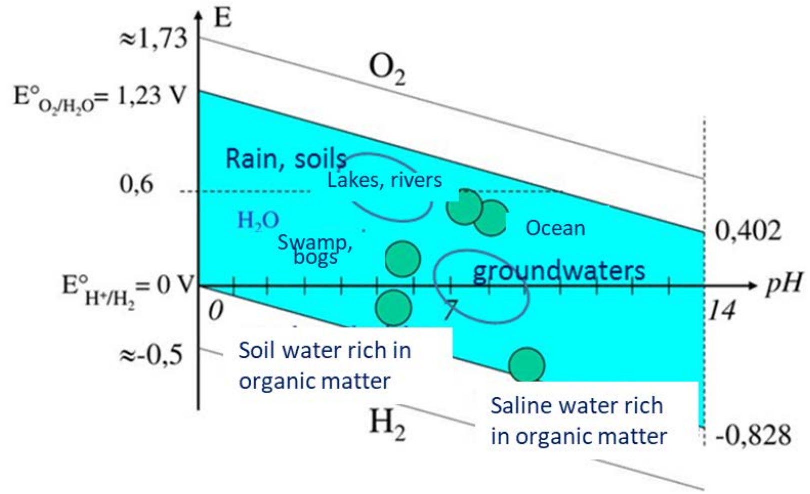
- Chemical parameters variations (time/space)
- Interactions, transformations and element exchanges: rock alteration, soil formation, life growth, water / C / biogeochemical cycling
- Different time scales, spatial variations

→ different sources & ecodynamics & chemical behavior of elements including radionuclides

Fast « Bio » C cycle : -→ yrs

Groundwater residence times : 100yrs -→ 10,000yrs

Slow « deep » C cycle : -→ Myr



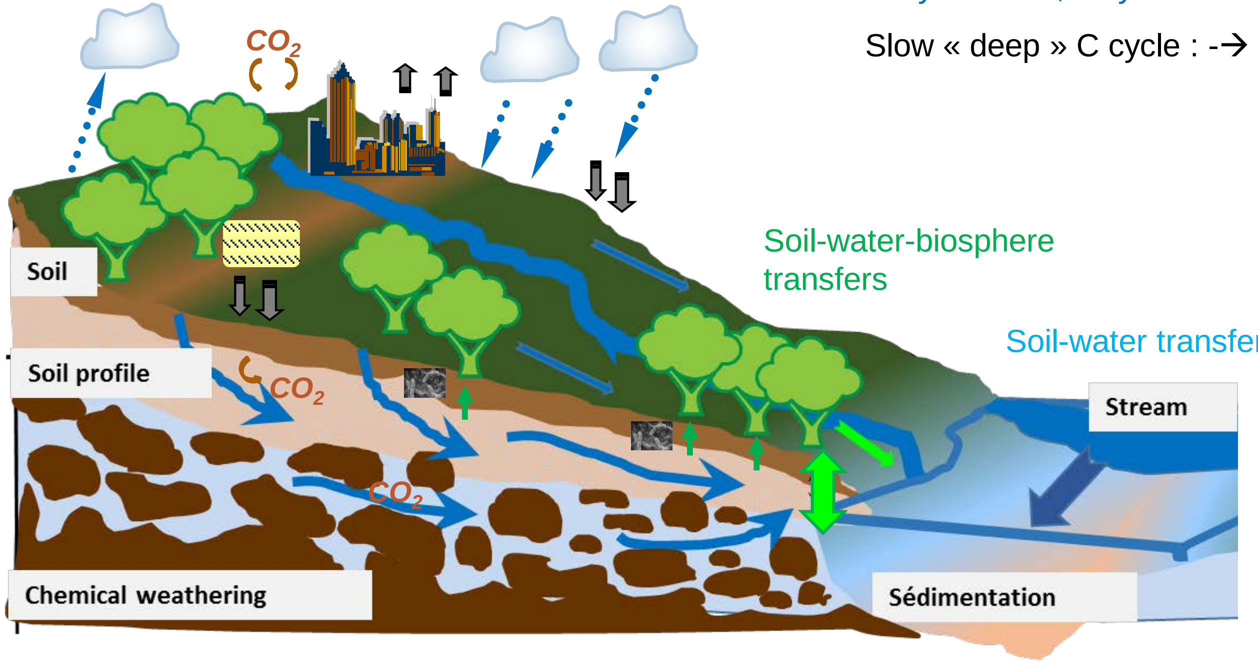
100yrs → hs (bacteria)

pH : 4-7;
DOC > 10mg.L^{-1}
pCO_2 : $10^{-3.5}$

1,000 → 100yrs

pH > 7
DOC : few mg.L^{-1}
pCO_2 : $10^{-2.5}$

Up to Myrs



Soil-water-biosphere transfers

Soil-water transfers

Radionuclides as a main issue of the environment

- Main source of radioactivity : NORM
- Naturally Occuring Radioactive Materials

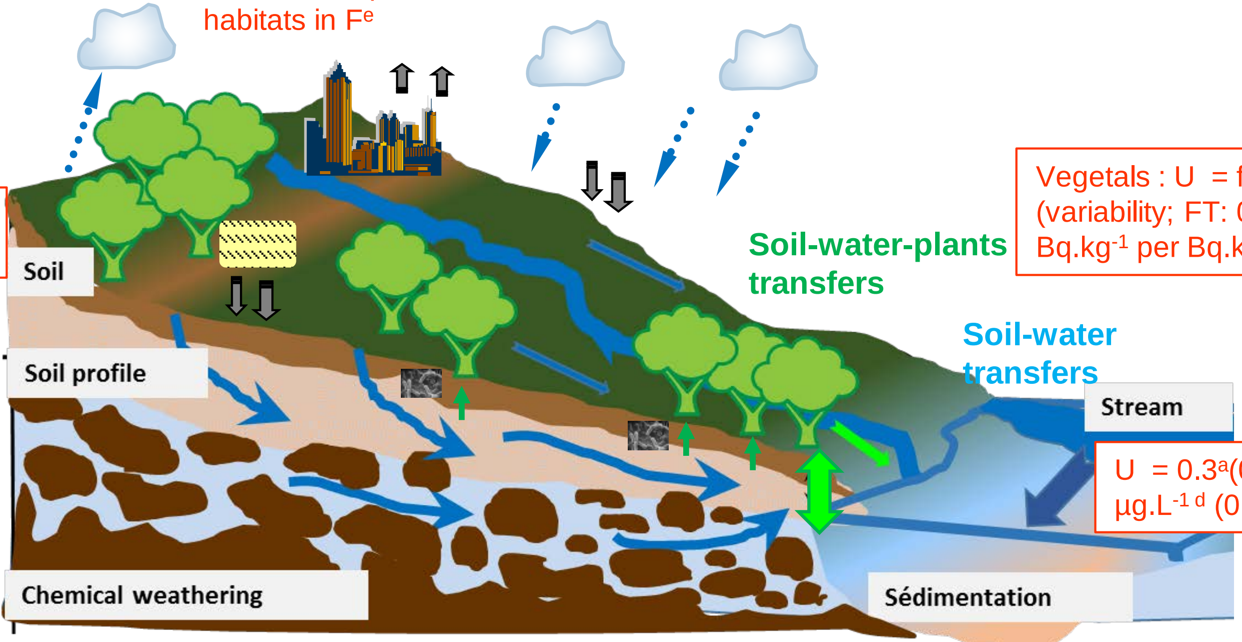
- Ubiquitous in all compartments

- Cosmogenic Radionucléides: ^{3}H, ^{14}C, ^{85}Kr
- Air Radionucléides : ^{219}Rn, ^{220}Rn, ^{222}Rn
- Telluric radionuclides: ^{40}K and decay series of ^{238}U, ^{235}U, ^{232}Th

Rn: 0-150 Bq/m^{3} in habitats in F[e]

Soils : U : 2(0.1-50)[a] mg.kg^{-1} (40 Bq.kg^{-1} [b])

Black shales, granites U : 300-5 mg.kg^{-1}

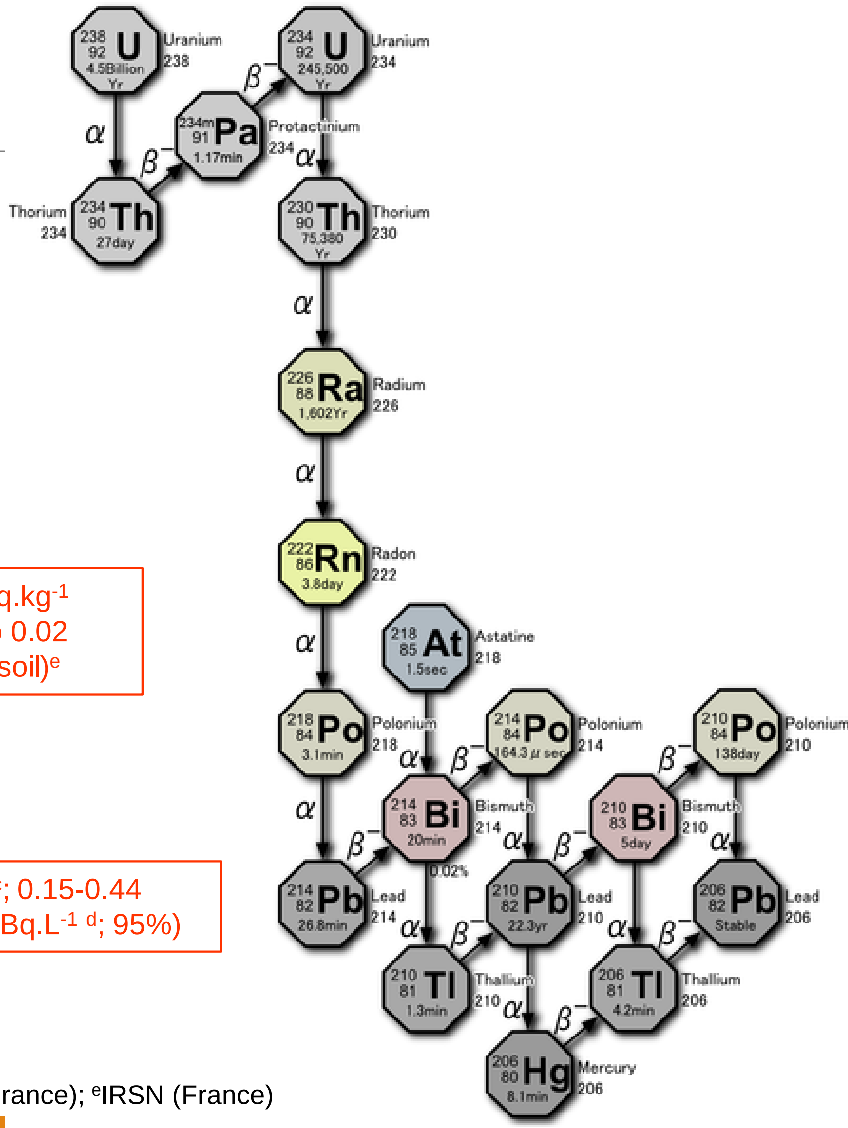


Soil-water-plants transfers

Soil-water transfers

Vegetals : U = few mBq.kg^{-1} (variability; FT: 0.001 to 0.02 Bq.kg^{-1} per Bq.kg^{-1} dry soil)[e]

U = 0.3[a](0.02-6)[c]; 0.15-0.44 µg.L^{-1} [d] (0.01-0.1 Bq.L^{-1} [d]; 95%)



[a]De Vos & Tarvainen, 2006 (Europe); [b]Le Roux (France); [c]Bonin & Blanc, 2001 (Europe); [d]Salpeteur & Angel, 2010 (France); [e]IRSN (France)

1. Introduction & background

Radionuclides as a main issue of the environment

- increasing variety of trace levels RNs in aquatic and terrestrial media,
- numerous pathways of introduction or exposure
- potential radio-/chemical toxicity (chronic, cocktail effects)

- TE-NORM Technologically Enhanced NORM (U-mines & mill tailings, coal,…)

Vue de la laverie chimique de Rophin en août 1950 (fond Orcel, MNHN)

- Artificial Radionucleides

Radionucléide	Half life	Emissions	Descendant	Origin
^{3}H	12.32 yr	β	^{3}He	Cosmic, Nuclear tests, releases of nuclear and clock industry
^{14}C	5 730 yr	β	^{14}N	Cosmic, Nuclear tests, Nuclear and research industry
^{60}Co	5.27 yr	Β, γ	^{60}Ni	Nuclear industry
^{90}Sr	28.78 yr	β	^{90}Y	Nuclear tests, Nuclear industry
^{131}I	8 d	β, γ	^{131}Xe	Medicine
^{137}Cs	30.07 yr	β, γ	^{137}Ba	Nuclear tests, Chernobyl, Nuclear industry
^{238}Pu	87.7 yr	α	^{234}U	Nuclear tests, Nuclear industry
$^{239+240}Pu$	24 100 & 6 560 yr	α	$^{235+236}U$	Nuclear tests, Nuclear industry

From Skipperud&Salbu, 2018 (sources of artificial RN in environment) ; cf also: Maher et al., Inorg. Chem, 2013 (USA); Thakur et al., STOTEN, 2013 (RN in northern hemisphere, Fukushima)

Radionuclides as a main issue of the environment

- NORM - TE-NORM
- Artificial Radionucleides

- Complexity of the bio-physicochemical mechanisms controlling their fate/eco-toxicity

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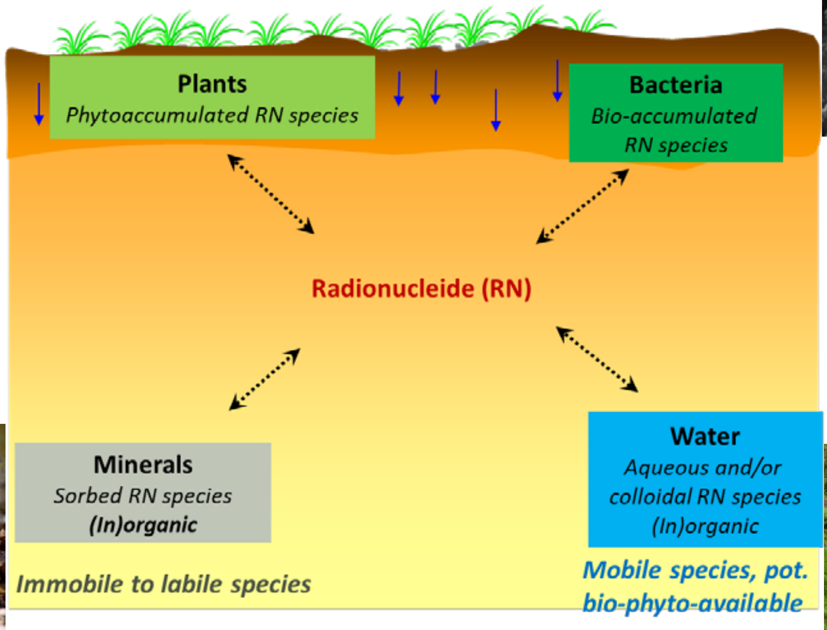
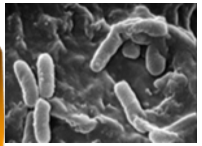
- Soil-water-plants transfers of a radionuclide depend on physico-chemical conditions (pH, Eh, C…) and on radionuclide interactions…

- For ex., Soil-water distribution coefficients measured in lab are highly variable : not predictive.

→ Supply to plants & organisms





→ Storage in soils (humic)

→ Supply to waters

Distribution coefficients soil-water Kd (Bq.kg^{-1} dry soil / Bq.L^{-1})

	^{238}U	^{241}Am	^{137}Cs
Sandy soil	33	2000 (11 – 2.6 10^5)	270
Clayey soil	1500	8100 (45 – 1.5 10^6)	1800
Silty soil	12	990 (600 – 1.6 10^5)	4400
Organic soil (> 30% organic matter)	400	1.1 10^5 (3.6 10^3 – 3.3 10^6)	270

IAEA, 1994

➢ **Need to rationalize knowledge…**

Radionuclides as a main issue of the environment

- NORM - TE-NORM
- Artificial Radionucleides

- A group of radioactive metallic elements with atomic numbers between 89 and 103 with sequentially filled 5f atomic subshells
- The isotopes ^{232}Th, ^{235}U, and ^{238}U are each progenitors of long α- and β-decay chains Other actinides (Np, Pu, Am, Cu) are primarily anthropogenic
- Primary factor governing the mobility and fate of An in environment is **oxidation state**
- **An^{3+}, An^{4+}, AnO_2^{+}, or AnO_2^{2+}**

LOWER SOLUBILITY, HIGHER TENDENCY TO SORB

- Environmental speciation of actinides : aqueous species

☆ fissile isotope(s)

	89 Ac ☆	90 Th	91 Pa	92 U ☆	93 Np ☆	94 Pu ☆	95 Am	96 Cm	97 Bk	103 Lr	
Valence electrons:	— 6d 7s²	— 6d² 7s²	5f² 6d 7s²	5f³ 6d 7s²	5f⁴ 6d 7s²	5f⁶ — 7s²	5f⁷ — 7s²	5f⁷ 6d 7s²	5f⁹ — 7s²	5f¹⁴ 6d 7s²	
Oxidation States: (all conditions)	III	(III) IV	(III) IV V	III IV V VI	III IV V VI VII	III IV V VI (VII)	III IV V VI VII?	III IV V? VI?			
Oxic zone: (groundwater)	III	IV	V	VI	V	IV VI	III (V)	III			
Suboxic zone: (microbially active)	III	IV	IV	IV VI	IV V	III IV	III	III			NO_3^- reduction, MnO_2 reduction, Fe(III)oxide reduction
Anaerobic zone: (microbially active)	III	IV	IV	IV	(III) IV	III IV	III	III			Fermentation, SO_4^{2-} reduction, Methanogenesis

(after Reed et al. 2010 In : the Chemistry of Actinides and Transactinide elements, Morss el al. (eds))
(after Maher et al. Inorg. Chem., 2013)

Tendency of An to form complexes : $OH^- > F^- > NO_3^- > Cl^- >>> ClO_4^-$

$CO_3^{2-} > SO_3^{2-} > C_2O_4^{2-} > SO_4^{2-}$

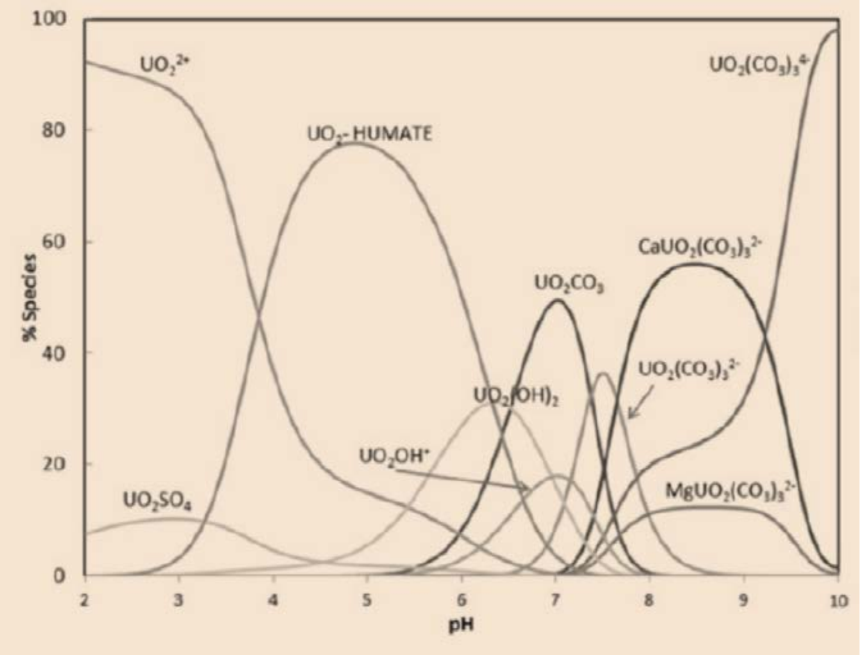
Strength of An complex (for a ligand) $An^{4+} > AnO_2^{2+} \geq An^{3+} > AnO_2^{+}$

Radionuclides as a main issue of the environment

- NORM - TE-NORM
- Artificial Radionucleides

- Environmental speciation of actinides : aqueous species

- Because of their ubiquity in natural waters, hydroxide and carbonate ligands are most important inorganic ligands for An
- Uranyle ions forms stable organic complexes with a variety of organic ligands, from simple di- tri-carboxylic acids (10-100 ppm in surface and groundwaters) to humic / fulvic acids.
- When small chelate rings with the equatorial oxygen atoms of UO_2^{2+} are formed, the uranyl chelates have exceptionnally high stability; Organic – chelated uranyl species can be highly mobile
- Natural and synthetic humic acids strongly complex U(VI) and also Pu(VI) *(Pompe et al., Radiochim. Acta, 2000)*
- Th(IV) humate complexes have also been reported *(Schield et al., Radiochim. Acta, 2000)*



Speciation diagram of U(VI) calculated using PHREEQC U= 1µM; Humate as a bidendate ligand; Atmospheric CO_2. (From Cumberland et al., Earth Science Review, 2016)

Radionuclides as a main issue of the environment

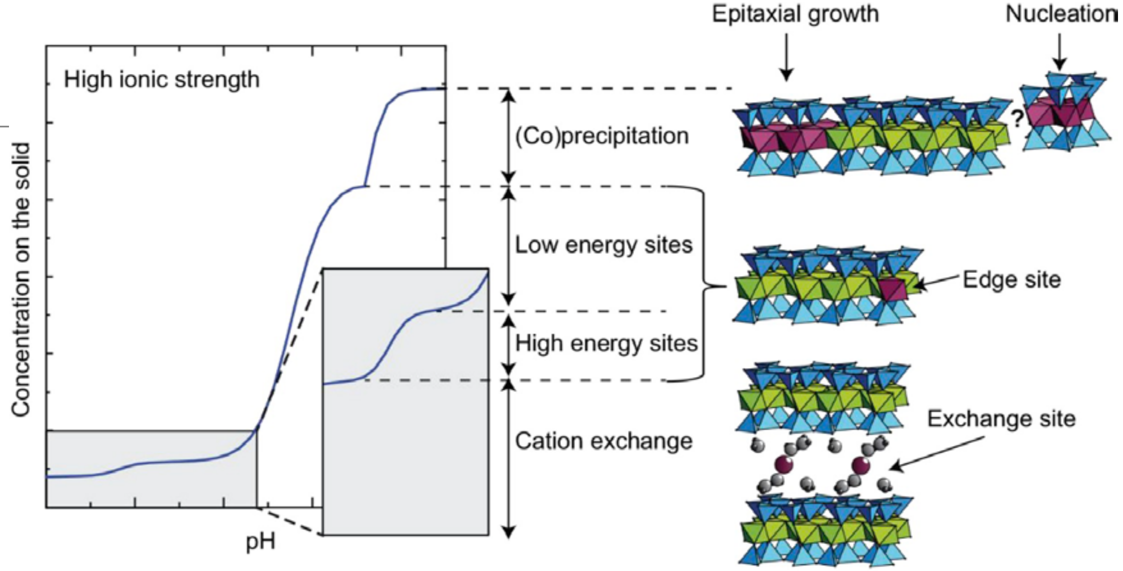
- Environmental speciation of actinides – Sorption species

- NORM - TE-NORM
- Artificial Radionucleides

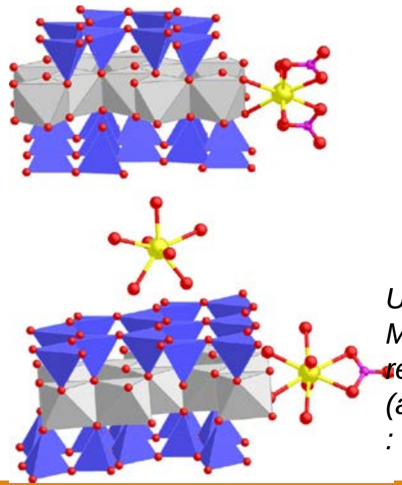
Many molecular scale investigations : EXAFS spectroscopy, TRLF spectroscopy ; ATR-FTIR spectroscopy

- ❑ Np(V) forms strong chemical bonds on goethite, hematite, gibbsite *(Combes et al., EST, 1992)*
- ❑ U(VI) forms several types of surface complexes on clays *(Catalano and Brown, GCA, 2005)* and stable U(VI) carbonato complexes on Fe oxihydroxides *(Bargar et al. GCA, 2000)*
- ❑ Pu associates with Mn oxides and smectites in Yucca tuf (Pu(V) → Pu(VI)), *(Duff et al. EST, 1999)*

General order of actinide sorption : $An^{4+} > An^{3+} > AnO_2^{2+} > AnO_2^{+}$



Schematic diagram of relative importance of identified sorption processes on montmorillonite as a function of pH (Tournassat et al., Am.J.Sci, 2013)



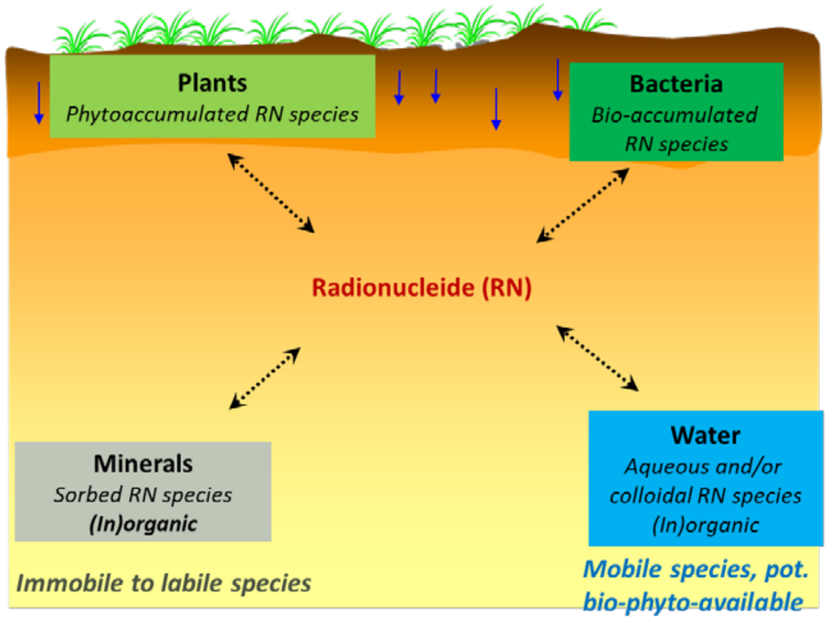
Uranyl and uranyl carbonato sorption complexes at Montmorillonite / water interfaces and in interlayer regions revealed by U LIII-edge XAFS spectroscopy (after Catalano and Brown, GCA, 2005). Yellow balls : U, red balls : O.

Radionuclides as a main issue of the environment

- NORM - TE-NORM
- Artificial Radionucleides

- Complexity of the bio-physicochemical mechanisms controlling their fate/eco-toxicity

- Soil-water-plants transfers of a radionuclide depend on physico-chemical conditions (pH, Eh, C…) and on radionuclide interactions…



- U(VI) – organic matter complexation data

System studied	ratio	Log β	pH	Group	Reference
UO_2-Humic acid	1:1	4.75 ± 0.08	4, I=0.1	carb	Lenhardt et al. 2000
UO_2-Humic acid	1:1	5.38 ± 0.08	5, I=0.1	carb	
UO_2-Fulvic acid	1:1	4.23	4, I=0.1	carb	
UO_2-Fulvic acid	1:1	4.54	5, I=0.1	carb	
UO_2-Humic acid	1:2	8.39	4, I=0.1	carb	
UO_2-Humic acid	1:2	9.59	5, I=0.1	carb	
UO_2-Fulvic acid	1:2	7.31	4, I=0.1	carb	
UO_2-Fulvic acid	1:2	7.54 ± 0.06	5, I=0.1	carb	
UO_2-Humic acid	1:1	7.8 ± 0.4	5-7.1 I=0.1	carb+phe	Knebk (1980)
UO_2-Humate	1:1	5.11 ± 0.02	4	carb	Shanbahg and Choppin, 1981
UO_2-Humate	1:2	8.94 ± 0.10	4	carb	
U(VI) Aldrich HA	1:1	9.13	8.4	phe	Warwick et al., 2005
U(VI) Boom Clay HA	1:1	4.42 to 8	5.9-8.1	phe	
U(IV) Aldrich HA	1:1	21.1 to 29.7	6-9	phe	
U(IV) Boom Clay HA	1:1	26.2 to 31.2	6.9-8.9	phe	

➢ **Further work: complexity of OM; Organic colloids; Co-sorption on minerals …**

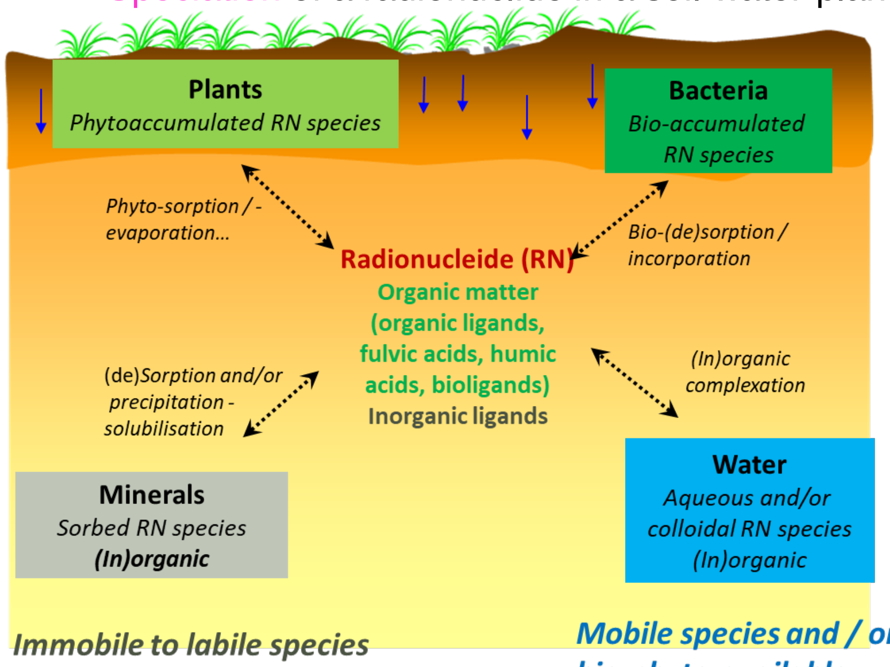
Challenges in environmental radiochemistry

- NORM - TE-NORM
- Artificial Radionucleides

The keys to develop robust models of a radionuclide's behavior in the environment :

- Establish the links between its transfers (lability, mobility and availability) and speciation
- Elucidating its speciation in relevant "model" systems (structure, stability, composition)

- Speciation of a radionuclide in a soil-water-plant system determines its degree of retention, lability, mobility and, partly bioavailability and ecotoxicity



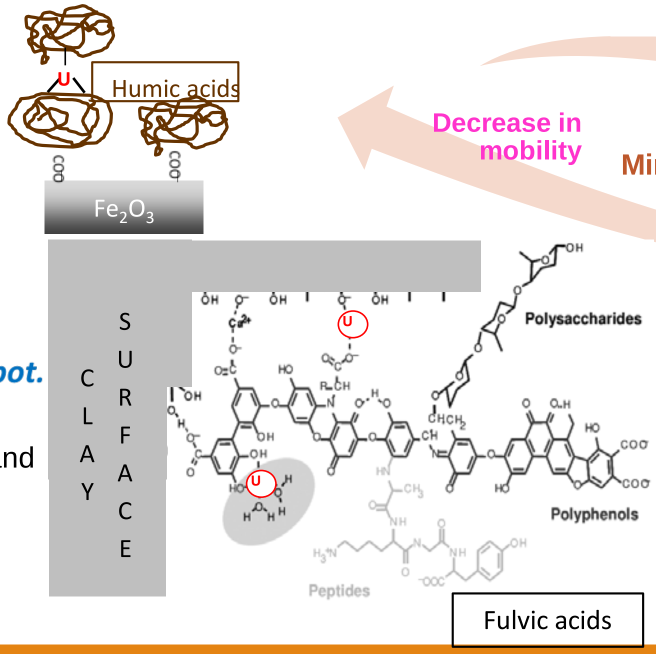
Mobile species and / or pot. bio-phyto-available

Reed et al., 2010 In : the Chemistry of Actinides and Transactinide elements, Morss el al. (eds)

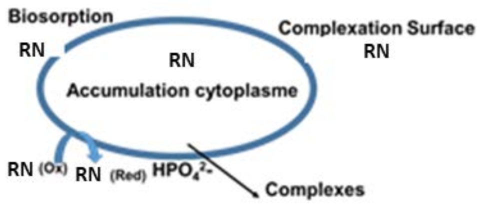
Maher et al. Inorg. Chem., 2013

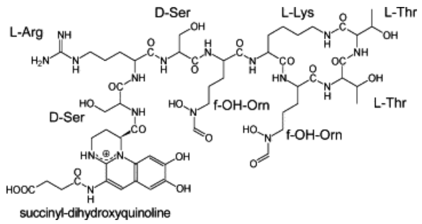
Cumberland et al., Earth Science Review, 2016

(Co)sorbed RN species on minerals



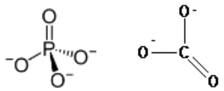
RN-bacteria interactions



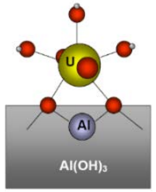


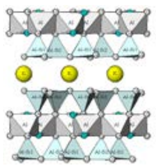
Mineral- organic Colloids ?

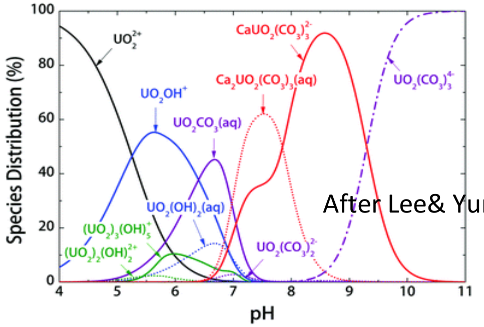
Hydrolysis products &(in)organic aqueous complexes of RN



Exchangeable RN on clays



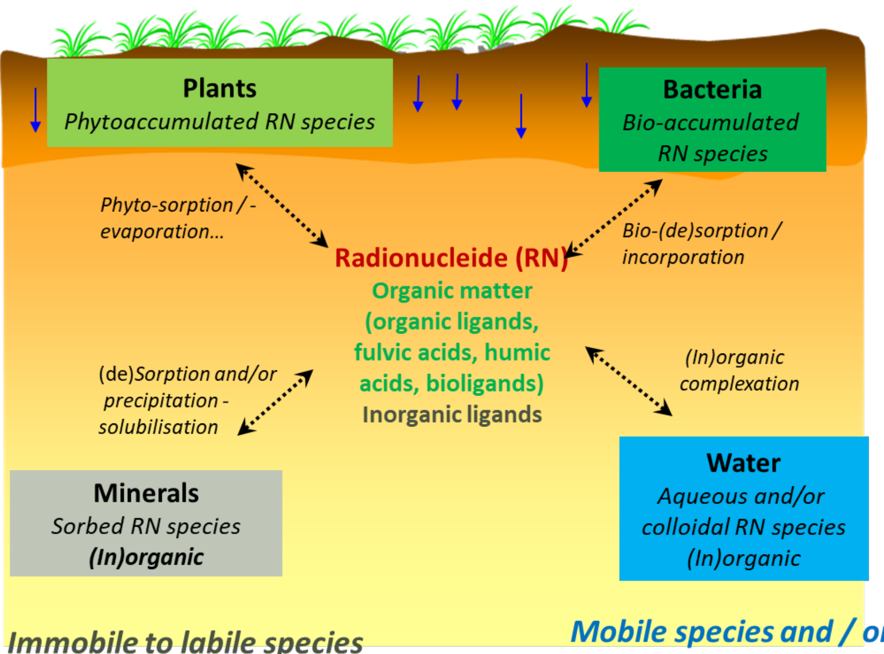




After Lee& Yun, 2013

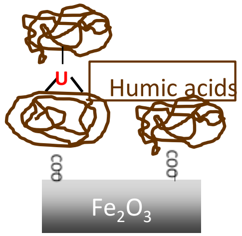
- NORM - TE-NORM
- Artificial Radionucleides

Work is still needed to elucidate :

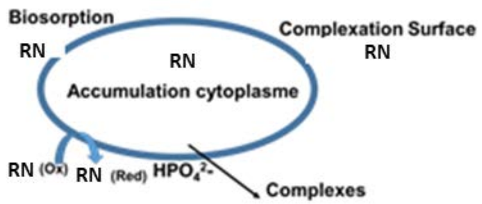


Mobile species and / or pot. bio-phyto-available

RN – organic matter – (mineral) interactions



RN-bacteria interactions



RN - Mineral – organic colloids ?

Vector of RN mobility ?
Effect on bioavailability ?

2. Linking transfers & speciation of radionucleides

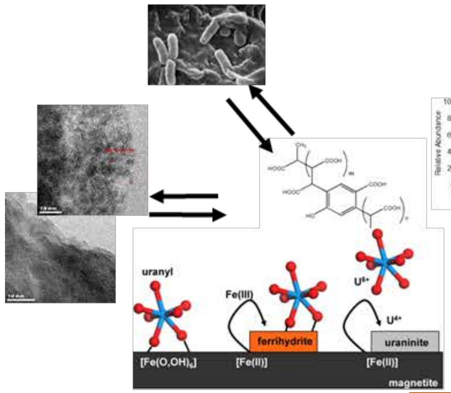
« INSPECT » : INteractions, SPeciation and Effets of natural radionuCleides (U, Th, ^{226}Ra, ^{210}Po…) of a wetland (Rophin)

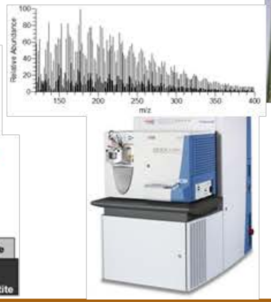
https://zatu.org/

Zones Ateliers TERRITOIRES URANIFERES

(CNRS, INEE), LTSER network

- A mechanistic and integrated approach of theTransfers of RN and effects in the water-soil-plants continuum
- From field study to the molecular level
- At the interface between chemistry and (micro)biology





NEEDS

NEEDS: Nucléaire : Energie, Environnement, Déchets, Société (CNRS, IRSN, CEA, IRSN, EDF, ORANO, ANDRA)

2. Linking transfers & speciation of radionucleides

2.1 Presentation of the Rophin site

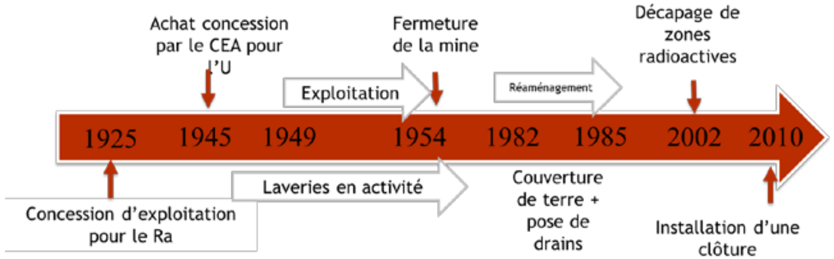
Granitic parent rock
Parsonsite ore (2PbO, UO_3,P_2O_5,H_2O)
Mixed forested area
Stream Le Gourgeat
Wetland

Vue de la laverie chimique de Rophin en août 1950 (fond Orcel, MNHN)

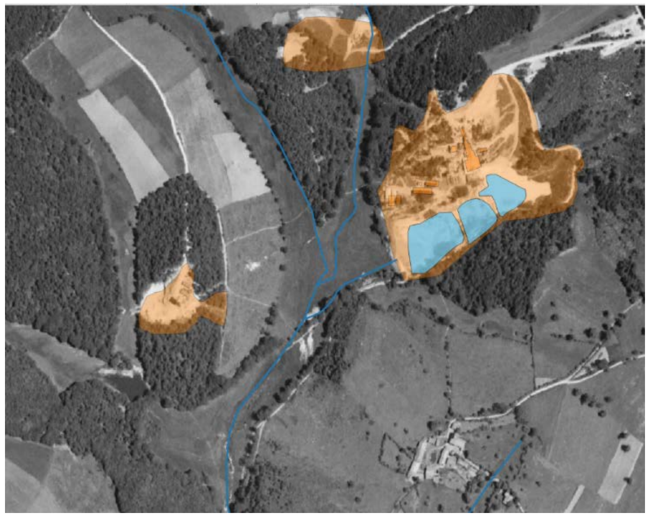
Vue générale de la laverie mécanique de Rophin en 1953 (photo CEA)

- Ponds rejected downstream white and contaminated argilaceous residues during floadings events

Martin et al. 2020, STOTEN

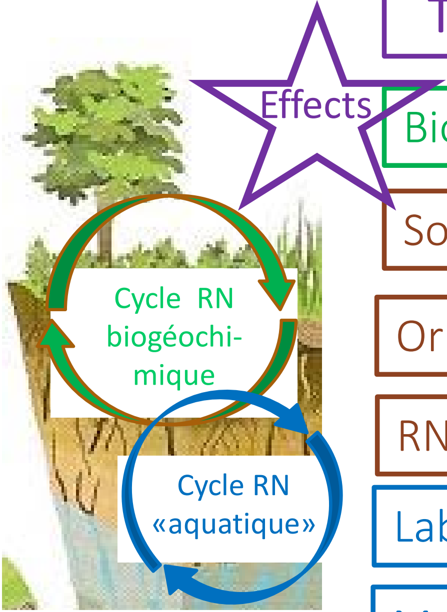


Since storage, the vegetation is left to grow on the storage site, potentially recycling radionuclides and heavy metals



During exploitation

In 2015



TRANSFERS RN

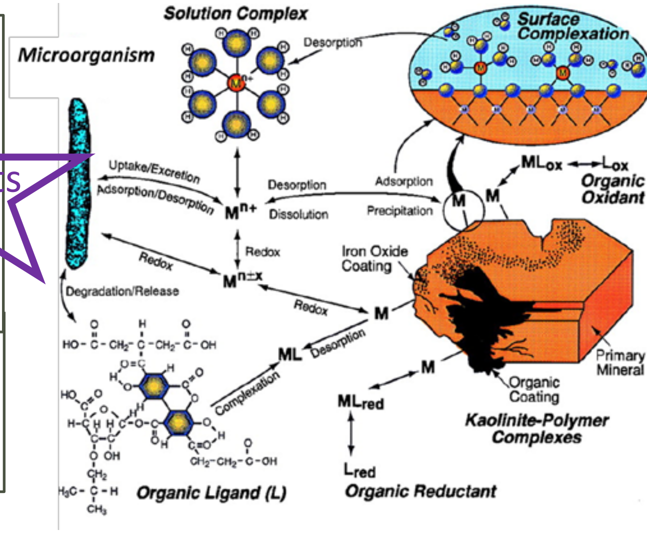
- Bioavailability of RN
- Soil characteristics
- Origins of RN
- RN (re)Distributions
- Lability of RN (pore water)
- Mobility of RN (stream)

- Interactions
- A specific bio geochimical functioning ?

MECHANISMS & SPECIATION

- Interactions RN - MO
  Variability, reactivity, sorption
- Interactions MI -RN
  Structures, fonctionnalities
- Sorption RN at interfaces,
  Redox – Sec. RN Minerals
- Complexation / colloïds RN

Effects



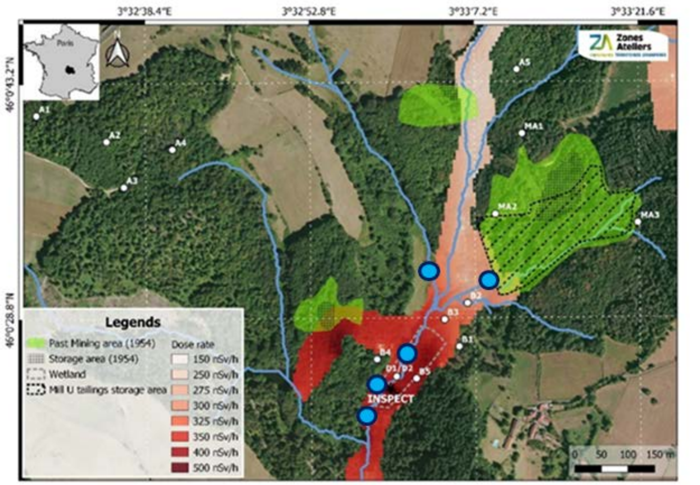
Radiological measurements
In-situ measurements
Sampling, chemical, mineralogical, isotopic analyses

Experiments Mesocosms - batch : (desorption, lability, dynamics : columns, rhizotests)

Molecular & spectroscopic analyses, Model systems, Microbiology : metagenomic and proteomic analyses...

2. Linking transfers & speciation of radionucleides

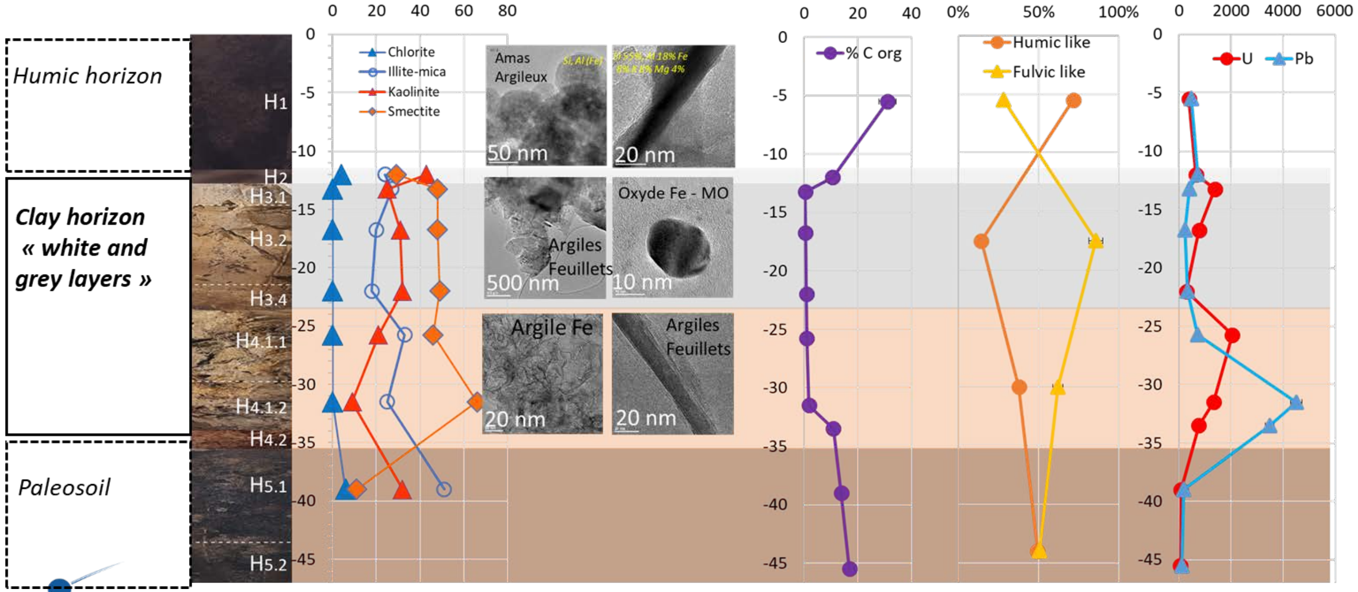
2.3 METHODOLOGIES



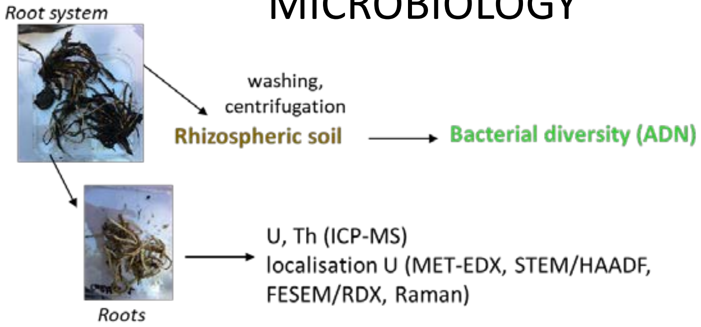
SOILS & CORES

DET-DGT

WATER



MICROBIOLOGY



PLANTS

Scirpus sylvaticus

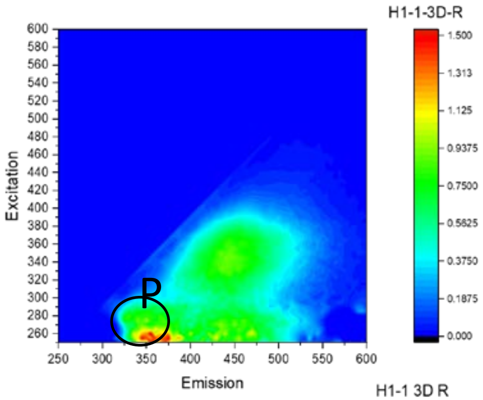
Caltha palustris

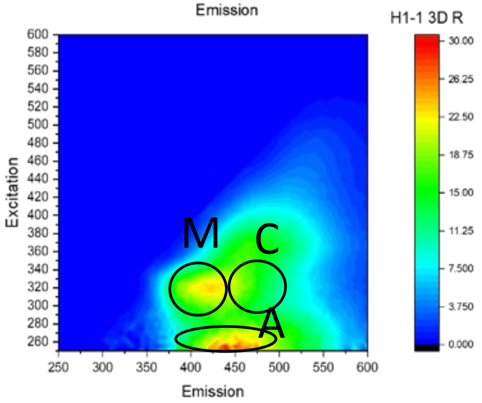
2 plants
- Scirpe
- Caltha

- SOIL DESORPTION EXPERIMENTS
- EXTRACTION ORGANIC MATTER
- CHEMICAL, SPECTROSCOPIC, MOLECULAR ANALYSES
- BACTERIAL DIVERSITY
- TRANSFER FACTORS TO PLANTS

2.3 METHODOLOGIES

Excitation / Emission fluorescence matrix : components

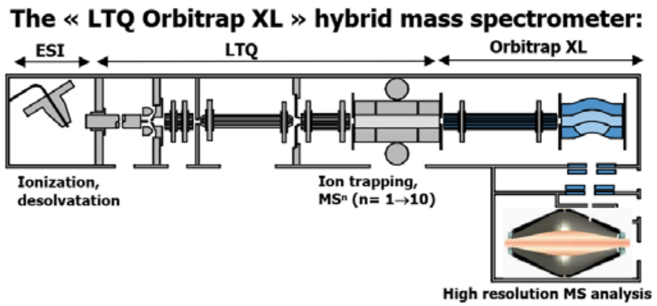




EEFM of MO *extracted (1st acid and basic extractions) from humic horizon*

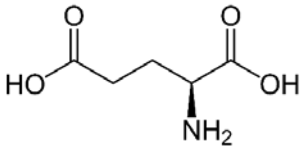
P : « protein -like » (tryptophane + tyrosine like)
A : condensed aromatics
C : more aliphatic molecules
M: biologically-derived

High – Resolution Electrospray ionisation mass spectrometry : molecules' identity in the supra-molecular assembly (OM)

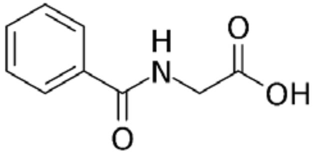


High resolving power, high mass accuracy
(100 000 at 400m/z, <3ppm with external calibration)

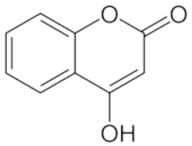
Glutamic acid



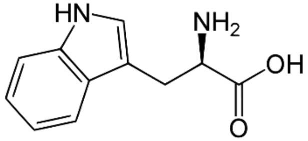
Hippuric acid

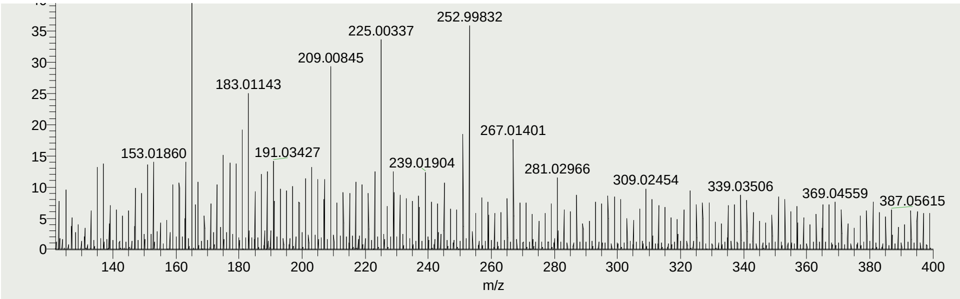


Hydroxy coumarin



Tryptophane



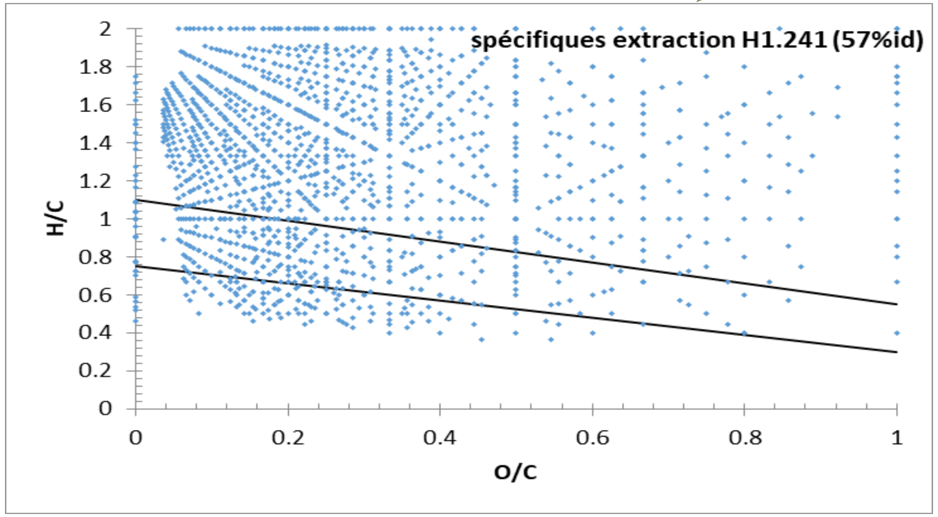


ESI(-)MS of MO *extracted (1ère basic extraction) from humic horizon*

Rough formula from precise mass - MSn

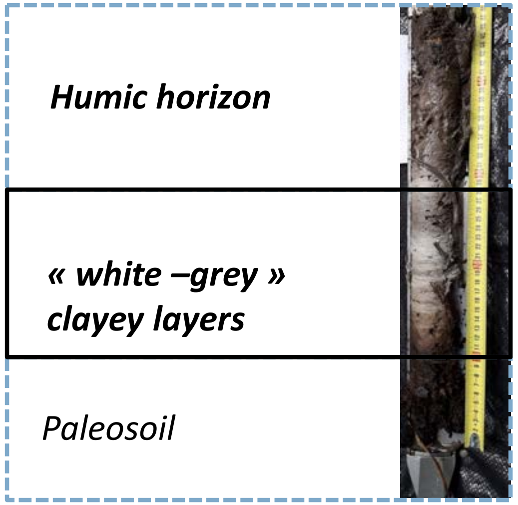
Determination of chemical formula

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



Van Krevelen of MO *extracted (1ère basic extraction) from humic horizon (1 point = 1 molecule)*

2.4 RESULTS : LABILE FRACTION OF U IN WETLAND SOILS



- ***In laboratory :***

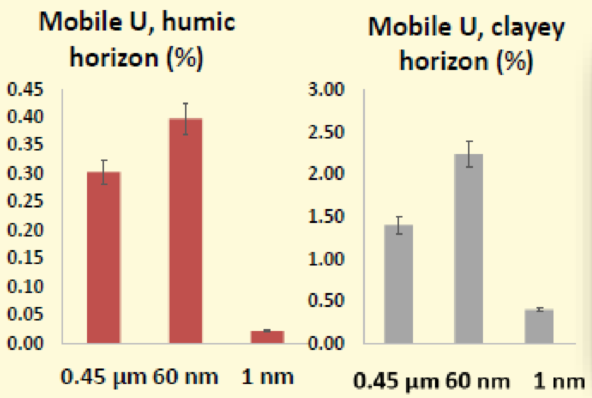
Desorptions :
Ratios [m/V] (Subatech) OR
Successives (IRSN LR2T) OR
Filtrations (IPHC)

[Sol / Water synth.]

Equilibrium ~24h ; pH ~ 5

Chemical / spectroscopic analyses of supernatants / filtrates

Desorbed Uranium



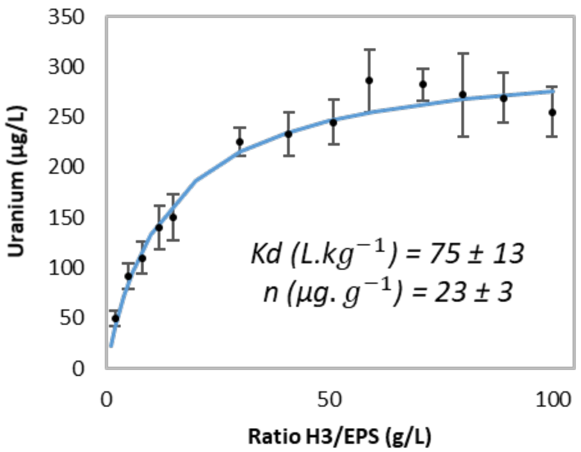
Uranium contained in both horizons is not very mobile at pH 5. U mobility is linked to the colloidal fraction. But with which part of this fraction is U linked ?
Is it :

- **With nano-minerals, as iron oxydes or clays ?**
- **With OM sorbed onto those nano-minerals ?**
- **With purely organic colloids ?**

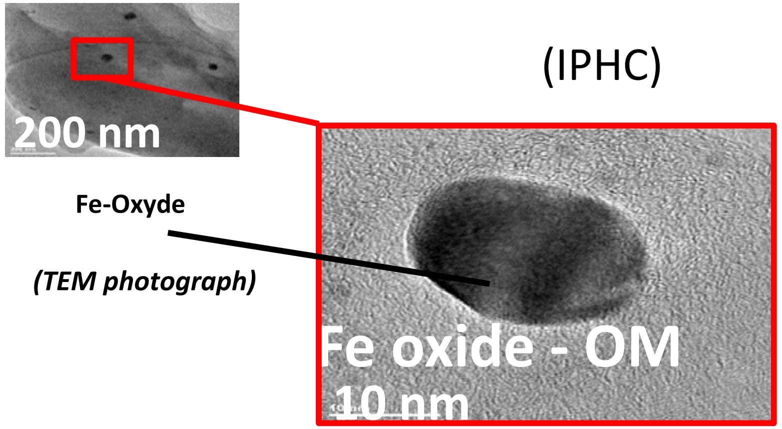
	Subatech	IRSN LR2T
Fraction labile (%) Humic	***0,3 ± 1,5 %***	***0 %*** *(avec $T_{1/2}$=50j)*

	Subatech	IRSN LR2T
Fraction labile (%) Clay horizon	***3,1 ± 2,2 %***	***2,4 ± 0,2 %***

Desorptions [m/V] (Subatech)



(IPHC)



Fe-Oxyde

(TEM photograph)

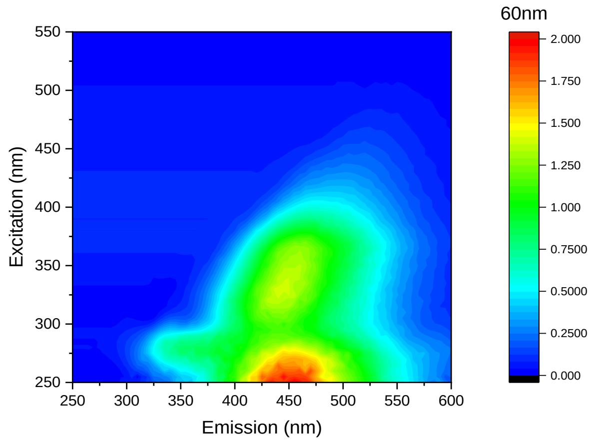
U poorly labile
Desorbed as pseudo-colloid

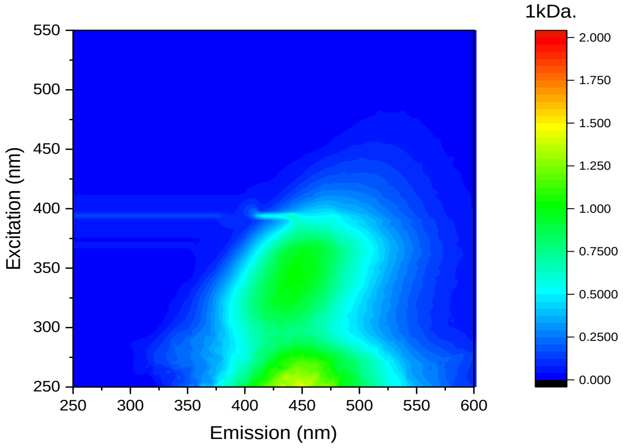
2.4 RESULTS: LABILE FRACTION OF ORGANIC MATTER

(Thesis S. Ferrères, IPHC)

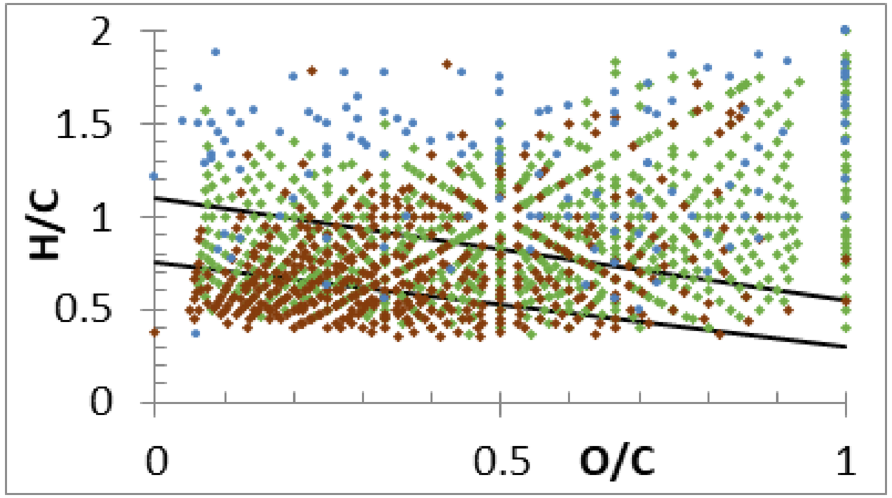
Molecular fractionation of OM between colloids<60 nm and true dissolved phase :
a chemical fractionation : molecules with different reactivity

-→ U is mainly associated to (mineral)organic colloids (condensed aromatics and biologically-derived organic molecules)





Organic Matter in desorption experiments at pH 5 using humic soil. Left : OM desorbed in Colloidal fraction (associated with U); right : OM desorbed in Dissolved fraction

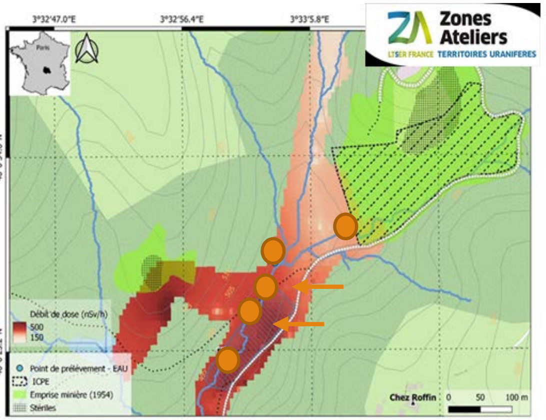


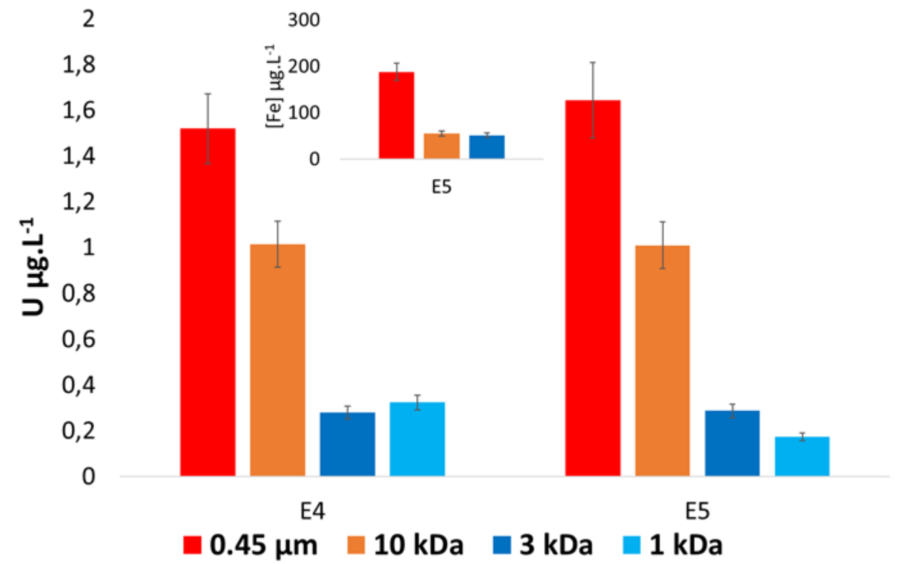
VK diagram of organic matter in desorption experiments at pH 5 : brown : molecules in colloidal fraction; blue : molecules in dissolved fraction, green : in both fractions

2. Linking transfers & speciation of radionucleides

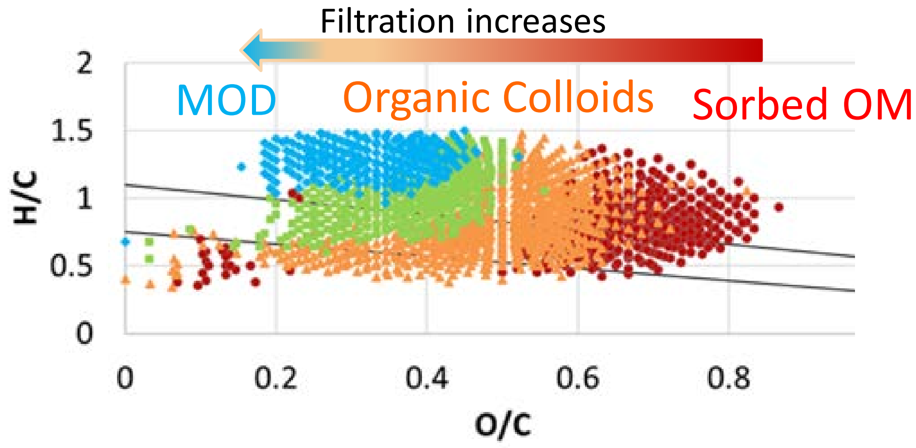
2.4 RESULTS : MOBILE FRACTION OF U (STREAM)

(Thesis S. Georg, IPHC)

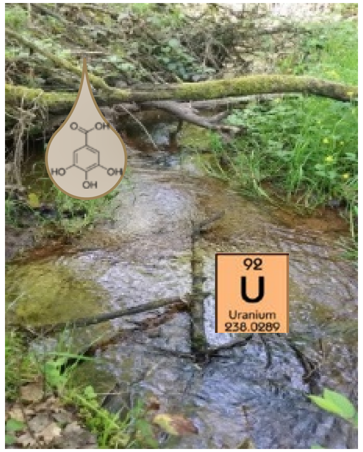




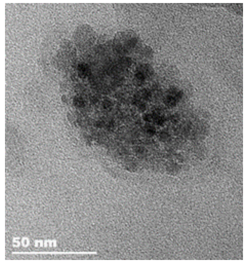
Concentration U (Fe in insert) in water as a function of water filtration



Organic molecule composition (atomic ratios H/C vs. O/C) of wetland waters analysed by ESI-FTMS and constitutive of the OC, SOM, MOD fractions.



- Importance of pseudo-colloid formation in the transport of U in water :
- U-OC (2-5 nm) : Complexes of U with molecules of organic colloids
- U-Mineral-organic colloids (5-450 nm) : Surface complexes of U and sorbed organic matter onto hematite

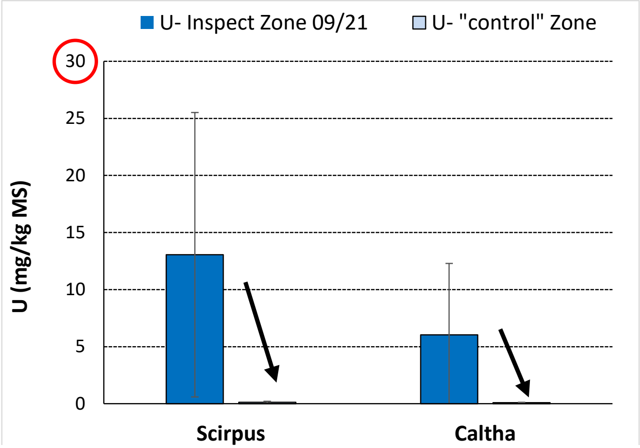


Fe-Oxydes (5-10nm) in an organic gangue (TEM)

2.5 RESULTS: BIOAVAILABILITY OF U - MICROORGANISMS

(IRSN, BIAM, IP2iB, LMGE, LPC)

- Low factor of transfers of U
- U is mainly associated to the roots in the rhizosphere, associated to Fe-oxides and clays sticking on the roots and / or to bacteria
- Rhizospheric microbiota are specific to each plant species
- In the U-rich horizon, presence of groups of bacteria, archaea and fungi specific to and potentially capable of influencing U speciation (redox cycle, organic matter degradation).



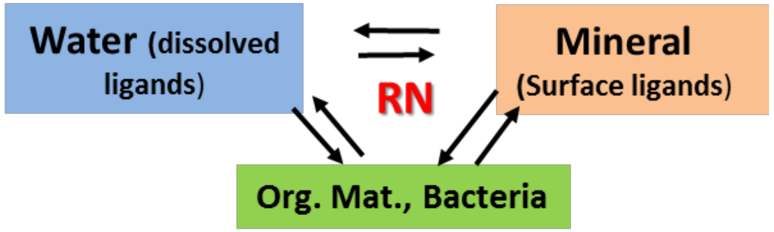
Scirpus sylvaticus

Caltha palustris

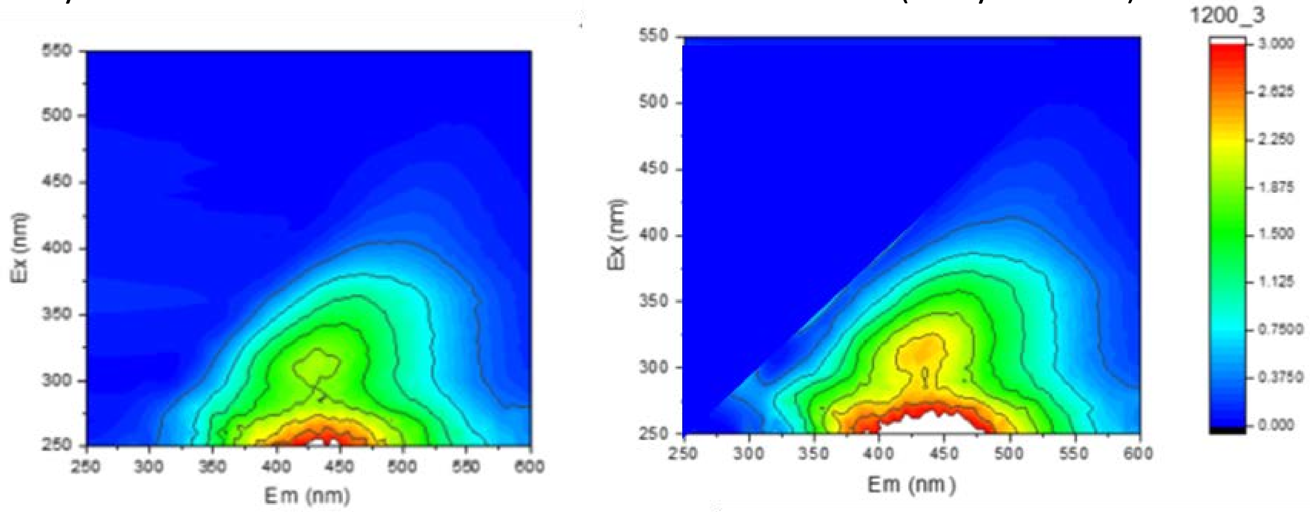
Importance of U-mineral-organic matter - bacteria interactions

Importance of U-mineral-organic matter - bacteria interactions:→ Model systems

Direct and indirect effects of bacteria (Microbacter) on the interactions of U with organic matter (and mineral)



Systèm : OM without bacteria | OM + bacteria (2 days contact)



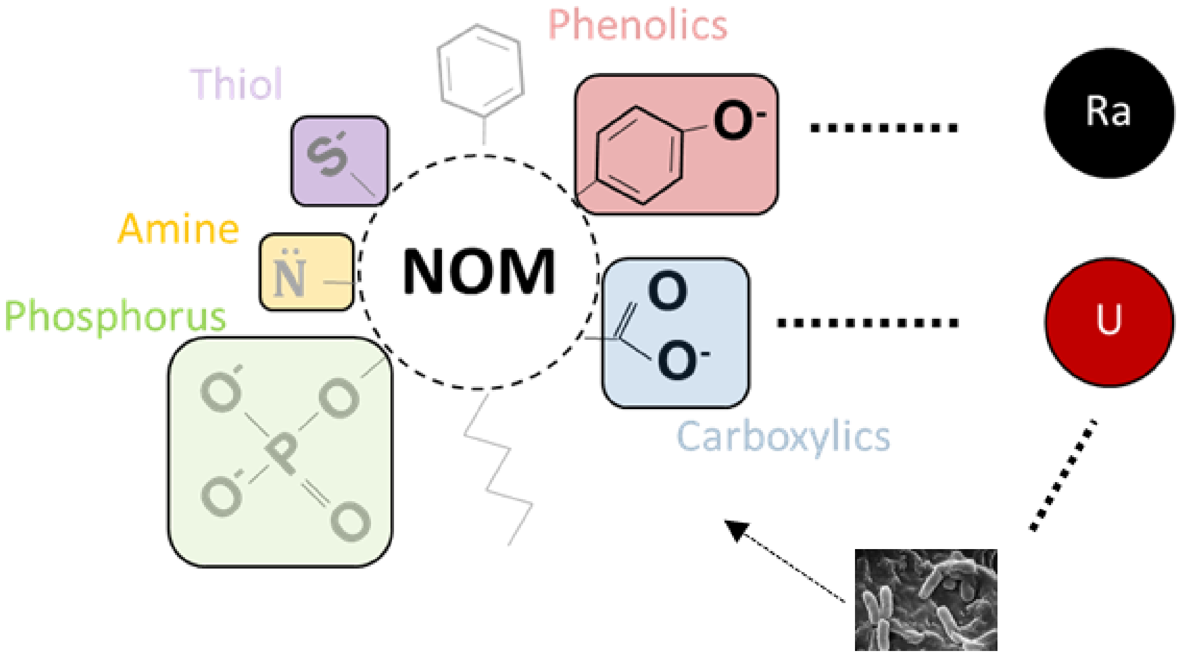
An important change in OM composition due to Microbacter

IPHC – BIAM - IRSN

Importance of U-mineral-organic matter - bacteria interactions:→ Model systems

Determinations of structures and stability (constants) of organic complexes of U and Ra formed with « building blocks » of natural organic matter (different model molecules of different structures and functional groups)

Data to simulate the complexation of the radionucleides with (colloidal) natural organic matter



IPHC – BIAM - SUBATECH

Thanks to

- NEEDS PROGRAM & ZATU (LTSER)

- Participants to the INSPECT project

SUBATECH : G. Montavon, C. Landesman, O. Perron, D. Karine , A.L. Nivesse
IPHC : O. Courson, S. Georg, S. Ferreres, R. Barillon
LPC : D. Sarramia, V. Breton, P. Chardon
IP2i : C. Sergeant, M.H. Vesvres, C. Holub
LMGE : C. Mallet, D. Biron
Geolab : A. Beauger
BIAM : V. Chapon, C. Berthomieu
LPCV: J. Bourguignon, S. Ravanel
LR2T : F. Coppin, P. Henner, L. Février
LELI : A. Gourgiotis, T. Geng, L. Darricau, J. Gorny, A. Mangeret, A. Courtin, C. Cazala

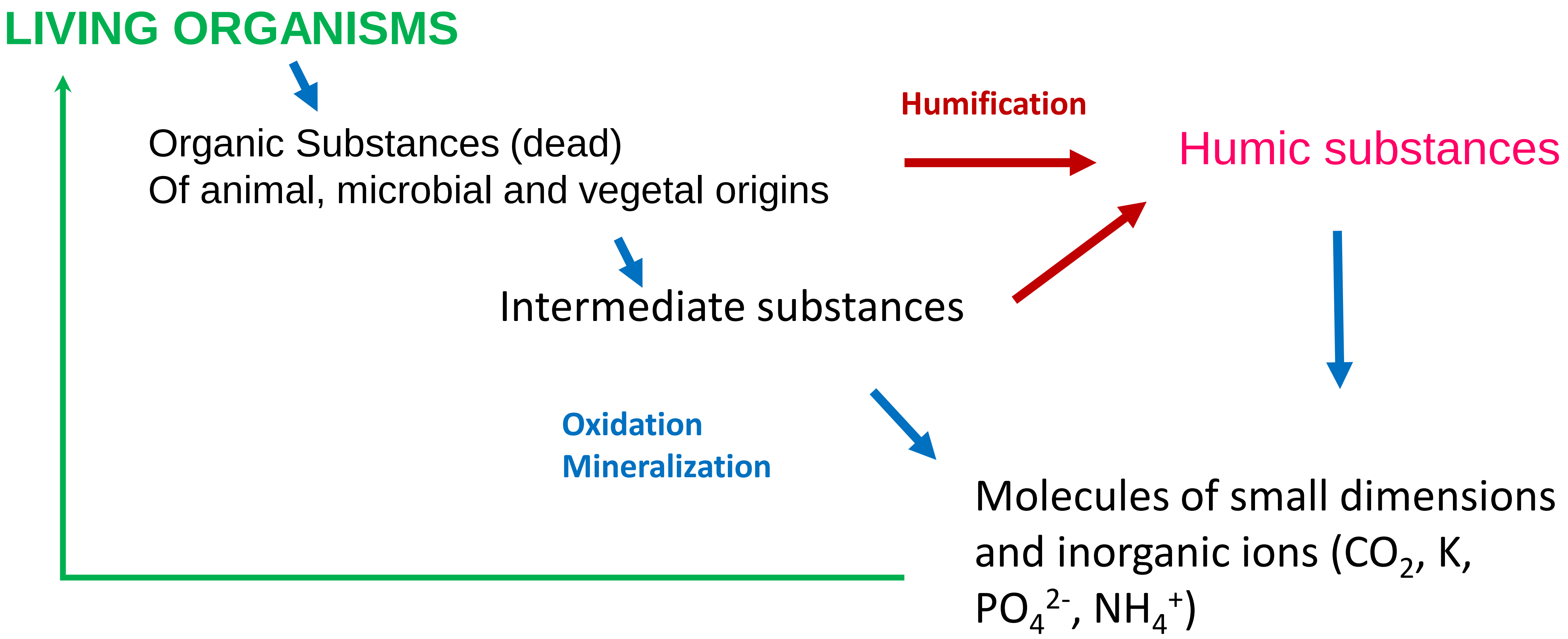
KIT-INE : M. Bouby

Thank you for your attention !

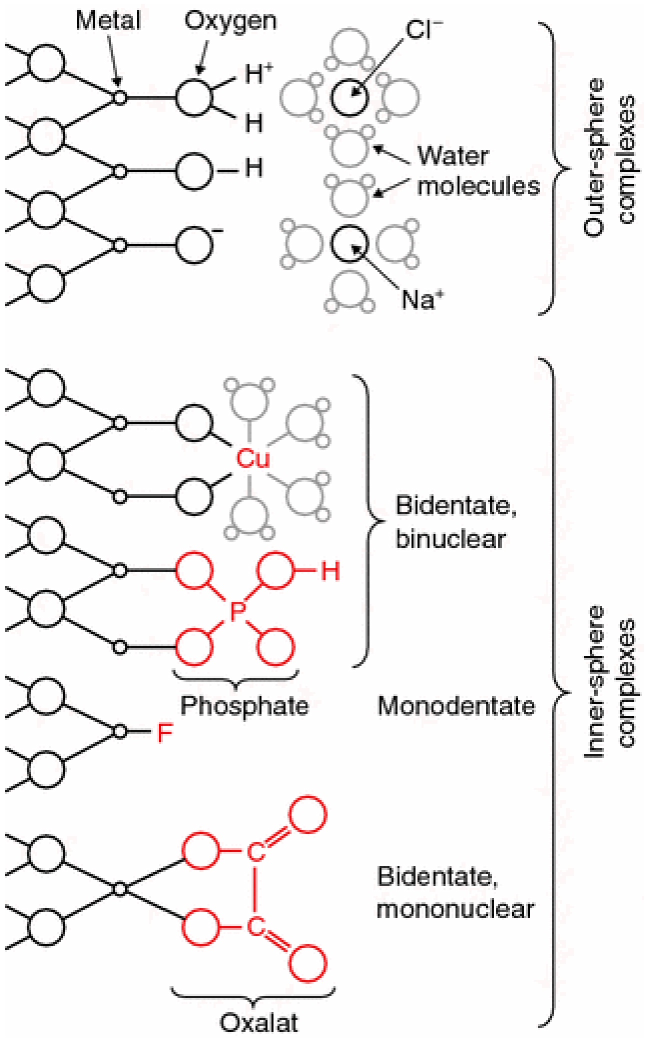
ANNEX

Biological and organic matter

1 g of soil contains 100,000 to 1 M bacteria



Sorption processes



Reactions at mineral-solution interfaces

Acid-base equilibria

$$S\text{–}OH + H^+ \rightleftharpoons S\text{–}OH_2^+$$

$$S\text{–}OH\ (+\ OH^-) \rightleftharpoons S\text{–}O^-\ (+\ H_2O)$$

Metal binding

$$S\text{–}OH + M^{z+} \rightleftharpoons S\text{–}OM^{(z-1)+} + H^+$$

$$2\ S\text{–}OH + M^{z+} \rightleftharpoons (S\text{–}O)_2M^{(z-2)+} + 2\ H^+$$

$$S\text{–}OH + M^{z+} + H_2O \rightleftharpoons S\text{–}OMOH^{(z-2)+} + 2\ H^+$$

Ligand exchange (L^- = ligand)

$$S\text{–}OH + L^- \rightleftharpoons S\text{–}L + OH^-$$

$$2\ S\text{–}OH + L^- \rightleftharpoons S_2\text{–}L^+ + 2\ OH^-$$

Ternary surface complex formation

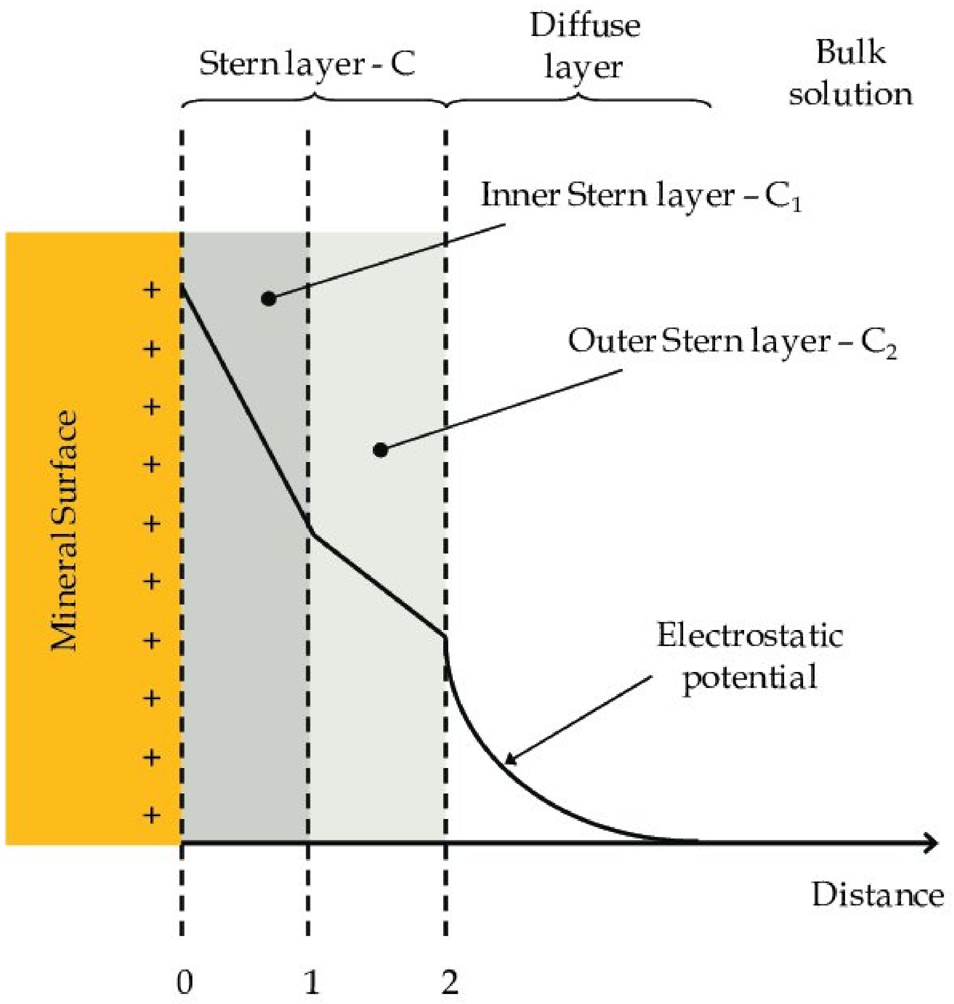
$$S\text{–}OH + L^- + M^{z+} \rightleftharpoons S\text{–}L\text{–}M^{z+} + OH^-$$

$$S\text{–}OH + L^- + M^{z+} \rightleftharpoons S\text{–}OM\text{–}L^{(z-2)+} + H^+$$

Secondary retention of Me, (in)organic ligands…

Sorption processes

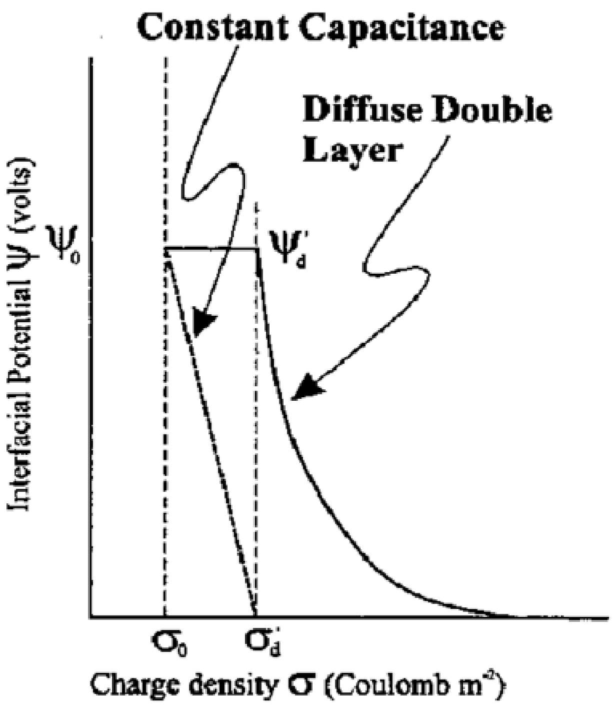
Reactions at mineral-solution interfaces



- Sorption takes place at specific coordination sites
- Sorption reactions can be described by mass law equations
- Surface charge results from the sorption (surface complex formation) itself
- The effect of surface charge on sorption can be taken into account by applying to the mass law constants for surface reactions a correction factor derived from the electric double-layer theory

Sorption processes

SCM



Reactions protonation / deprotonation of surface hydroxyls

$$S-OH + H^+ \overset{K_+^{int}}{\longleftrightarrow} S-OH_2^+$$

$$S-OH \overset{K_-^{int}}{\longleftrightarrow} S-O^- + H^+$$

Relation intrinsic constants and conditional constants

$$K_+^{int} = K_+^c \exp(+F\Psi_0/RT) = ([S-OH_2^+]/([S-OH]\{H^+\}))\exp(+F\Psi_0/RT)$$

$$K_-^{int} = K_-^c \exp(-F\Psi_0/RT) = (([S-O^-]\{H^+\})/[S-OH])\exp(-F\Psi_0/RT)$$

Relation Charge – potential (DLM)

$$-\sigma_0 = \sigma_d = -0.1174\sqrt{I}\sinh(zF\Psi_0/2RT)$$

$$\Psi_0 = \Psi_d$$

Environmental Speciation of actinides (An) – Aqueous species

Because of their ubiquity in natural waters, hydroxide and carbonate ligands are most important inorganic ligands for An

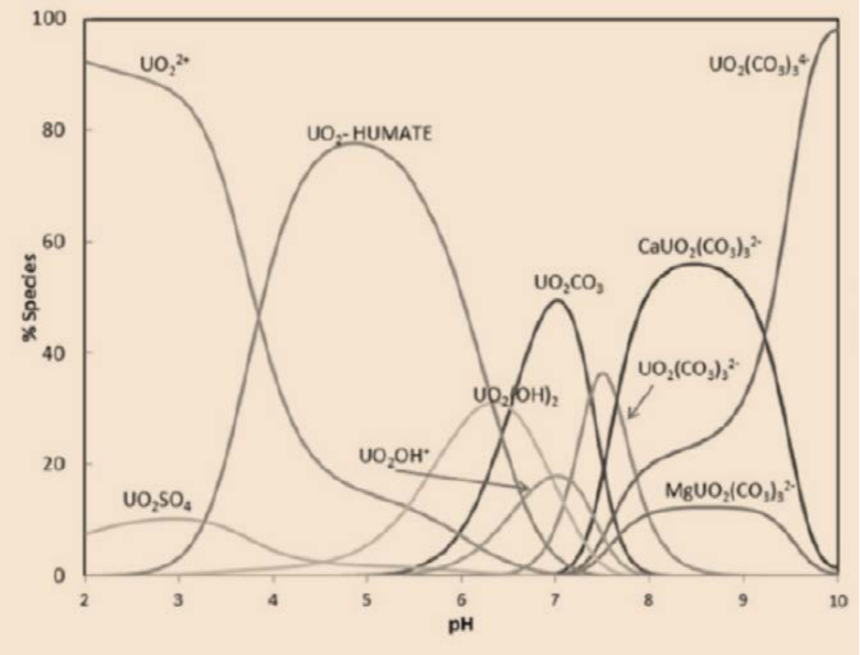
Uranyle forms stable organic complexes with a variety of organic ligands, from simple di- tri-carboxylic acids (10-100 ppm in surface and groundwaters) to humic / fulvic acids.

When small chelate rings with the equatorial oxygen atoms of UO_2^{2+} are formed, the uranyl chelates have exceptionnally high stability

Organic –chelated uranyl species can be highly mobile

Natural and synthetic humic acids strongly complex U(VI) and also Pu(VI) *(Pompe et al., Radiochim. Acta, 2000)*

Th(IV) humate complexes have also been reported *(Schield et al., Radiochim. Acta, 2000)*



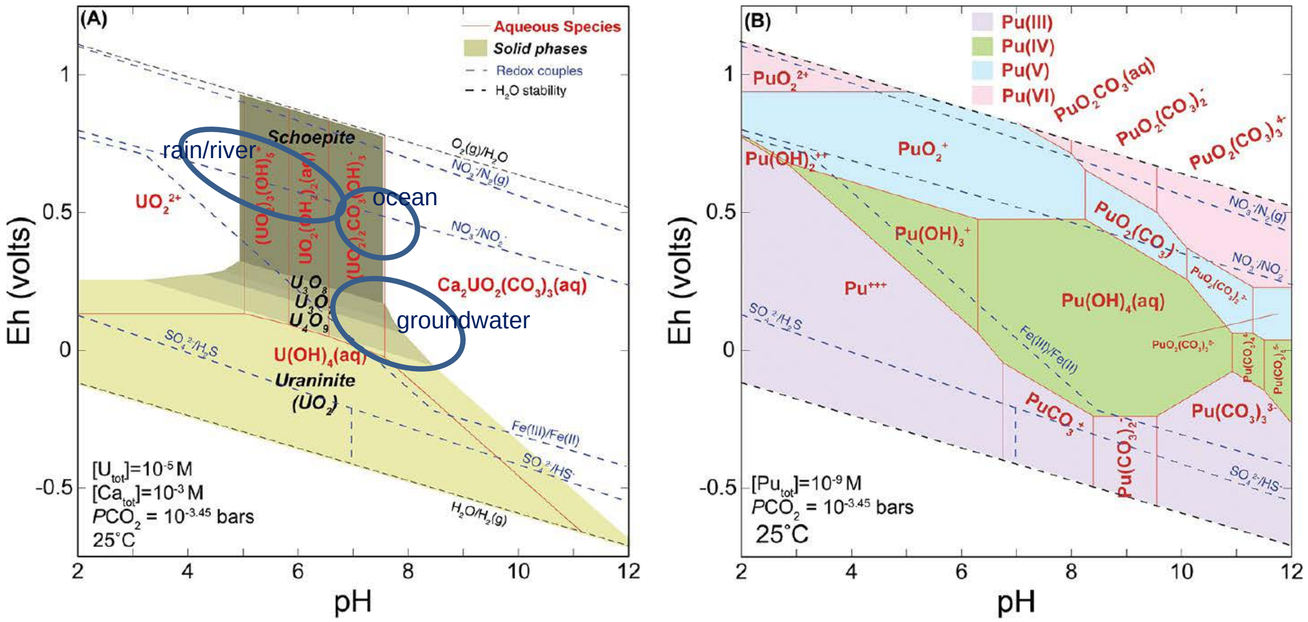
Speciation diagram of uranyle calculated using PHREEQC U= 1µM; Humate as a bidendate ligand; Atmospheric CO_2.

(From Cumberland et al., Earth Science Review, 2016)

Environmental Speciation of actinides (An) – Aqueous species

U(VI) forms a series of anionic and polynuclear species influencing sorption and inhibting biotic reduction

U(IV) largely controlled by poorly-soluble uraninite



(from Maher et al. Inorg. Chem., 2013)

Pu(IV) stable at near-neutral pH and in midly reducing conditions

$Pu(OH)_4$(s) at low [] (solubility 10^{-9} M) but hydroxo-bridged polymers at high [] : colloids

Pu(III), (IV), (V) forms stable complexes with many organic ligands, limiting Pu(IV) colloids

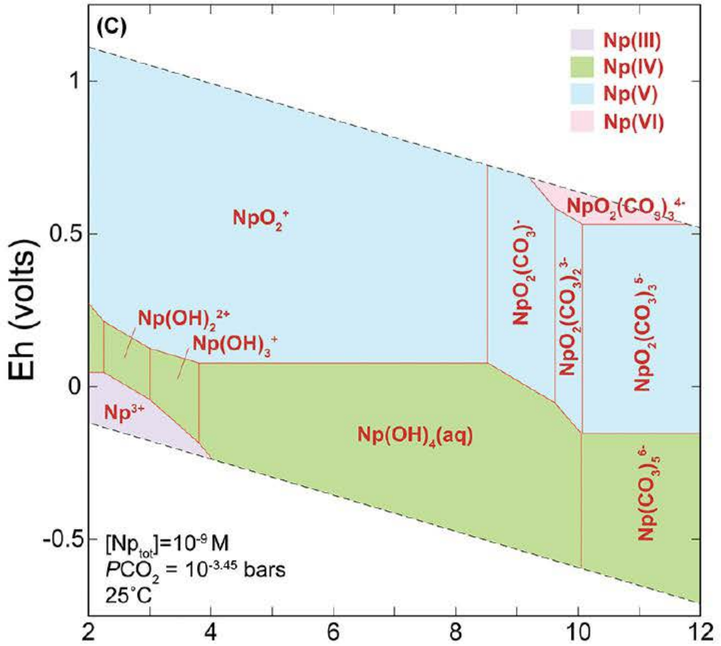
Strength of An complex (for a ligand) $An^{4+} > AnO_2^{2+} \geq An^{3+} > AnO_2^{+}$

Environmental Speciation of actinides (An) – Aqueous species

Pentavalent Np is stable under oxic to moderately suboxic conditions as dioxoneptunyl cation or neptunyl carbonate species : highly mobile

Tetravalent Np is incorporated into sparingly soluble $Np(OH)_4$

Depending on its oxidation state, solubility of Np are likely controlled by poorly cristalline oxihydroxides at 10^{-8} ($Np(OH)_4$) to 10^{-4}M (Np_2O_5)

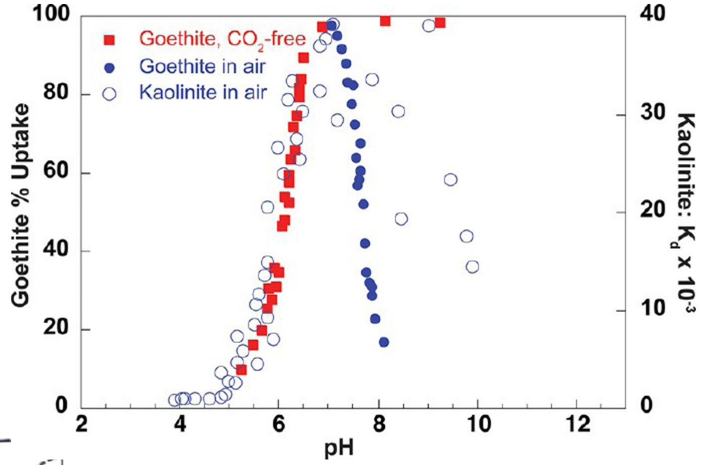


(from Maher et al. Inorg. Chem., 2013)

Strength of An complex (for a ligand) $An^{4+} > AnO_2^{2+} \geq An^{3+} > AnO_2^{+}$

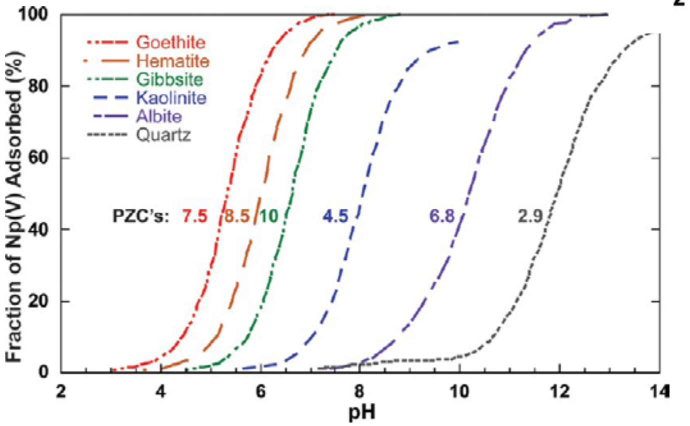
Environmental Speciation of actinides (An) – Sorption species

Presence of (in)organic ligands influence macroscopic sorption



(after Thompson et al. 1998)

Mineral surface influences macroscopic sorption : adsorption of NpO_2^+ on minerals having distinct pH of point –of –zero charge values suggests formation of inner sphere surface complexes at surfaces of Al / Fe oxihydroxides



(from Kohler et al. 1992)

General order of actinide sorption : $An^{4+} > An^{3+} > AnO_2^{2+} > AnO_2^{+}$

Environmental Speciation of actinides (An) – Sorption species

Many molecular scale investigations

Critical for understanding and modelling fate of An : EXAFS spectroscopy, TRLF spectroscopy ATR-FTIR spectroscopy…

- U(VI) forms dominantly inner-sphere complexes with oxygen based minerals, predominantly bidentate linkages to oxo surface groups
- ThIV, NpV, and AmIII have also been found to form inner- sphere complexes on various mineral surfaces
- UO_2^{2+} can also be sequestered through the incorporation into or physical association with iron (oxyhydr)oxides such as ferrihydrite and their transformation products
- Review papers : Brown and Sturchio, Rev. Min. Geoch., 2002; Denecke, Coordination Chem. Rev., 2006; Geckeis and Rabung, J. Cont. Hyd., 2008; 88 Antonio and Soderholm, in the Chemistry of Actinide and Transuranic Elements, 2010; Tan et al. Molecules, 2010; Maher et al., Inorg. Chem., 2013