

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



AQUEOUS SPECIATION

SORPTION

ON-GOING RESEARCH

FOCUS: EFFECT OF ORGANIC MATTER

Environmental Speciation of actinides (An)

- 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 that result in the production of relatively short-lived ^{231}Pa , $^{230,234}\text{Th}$, and $^{227,228}\text{Ac}$ daughter isotopes
- Other actinides (Np, Pu, Am, Cm) 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

Naturally abundant					Primarily anthropogenic				
Natural and anthropogenic					Anthropogenic & short lived				
☆ fissile isotope(s)									
☆ 89 Ac	90 Th	91 Pa	☆ 92 U	☆ 93 Np	☆ 94 Pu	95 Am	96 Cm	97 Bk	103 Lr
—	—	5f ²	5f ³	5f ⁴	5f ⁶	5f ⁷	5f ⁷	5f ⁹	5f ¹⁴
6d 7s ²	6d ² 7s ²	6d 7s ²	6d 7s ²	6d 7s ²	— 7s ²	— 7s ²	6d 7s ²	— 7s ²	6d 7s ²
Valence electrons:									
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 VII?		
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 et al. (eds))

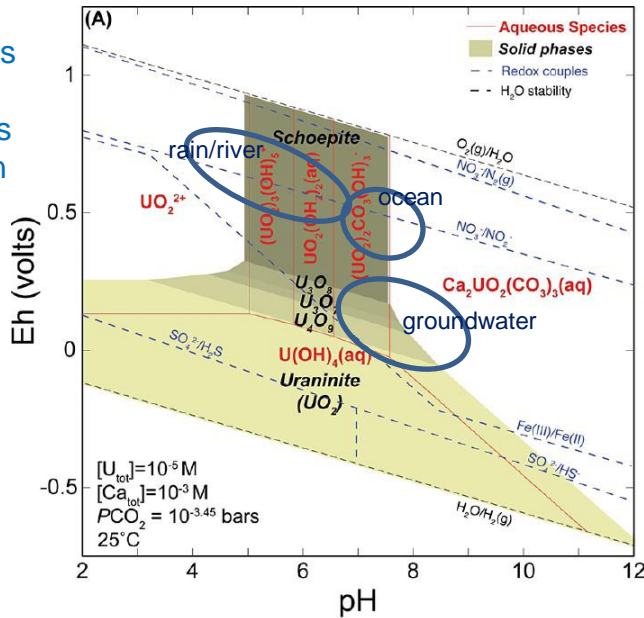
(after Maher et al. Inorg. Chem., 2013)

Environmental Speciation of actinides

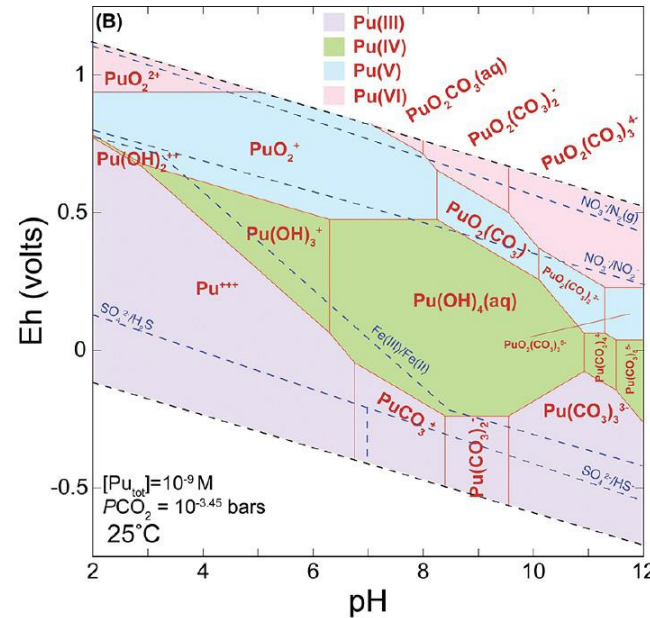
(An) – Aqueous species

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

U(IV) largely controlled by poorly-soluble uraninite



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



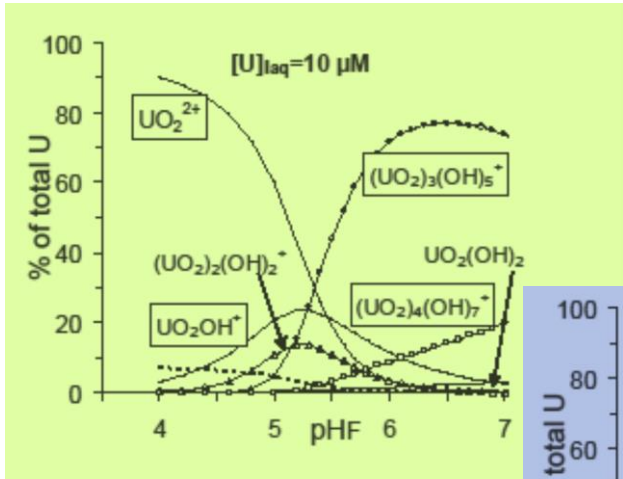
Pu(IV) stable at near-neutral pH and in mildly reducing conditions

Pu(OH)₄(s) at low [CO₂] (solubility 10⁻⁹ M) but hydroxo-bridged polymers at high [CO₂]: colloids

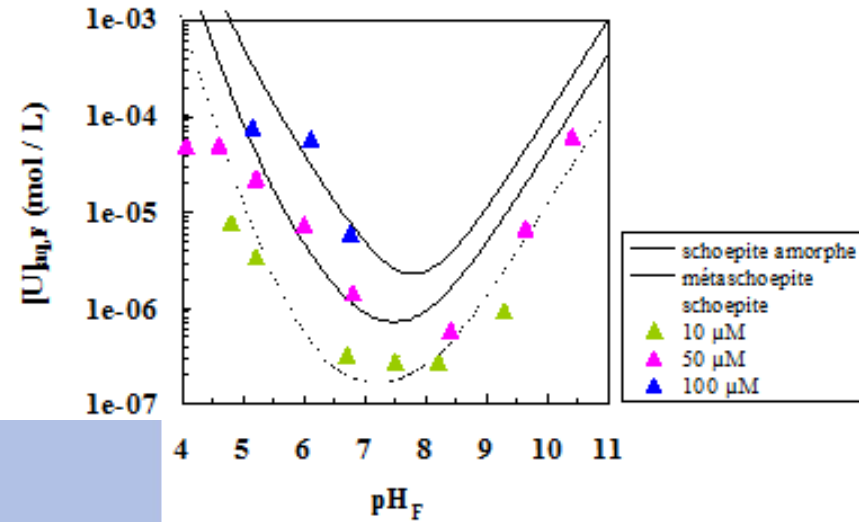
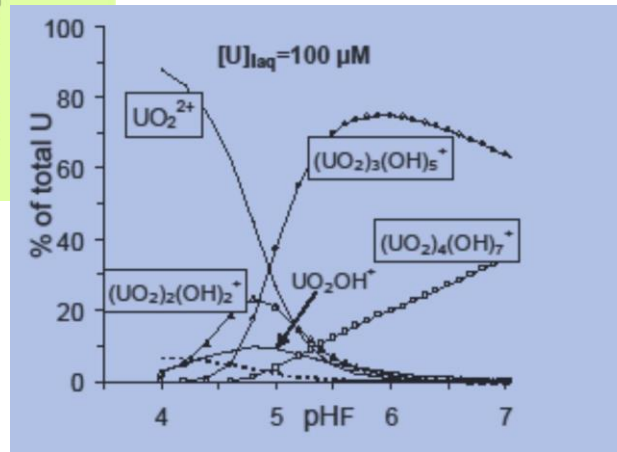
Pu(III), (IV), (V) forms stable complexes with many organic ligands, limiting Pu(IV) colloids



Environmental Speciation of actinides (An) – Aqueous species



Speciation of U(VI) in aqueous solutions under N₂-atmosphere



Final concentrations of U(VI) aqueous solutions after 3-days ageing under N₂-atmosphere and solubility curves of schoepitic minerals

(from Froideval et al. GCA, 2008)

**Tendency of An to form complexes : OH⁻ > F⁻ > NO₃⁻ > Cl⁻ >>> ClO₄⁻
CO₃²⁻ > SO₃²⁻ > C₂O₄²⁻ > SO₄²⁻**

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

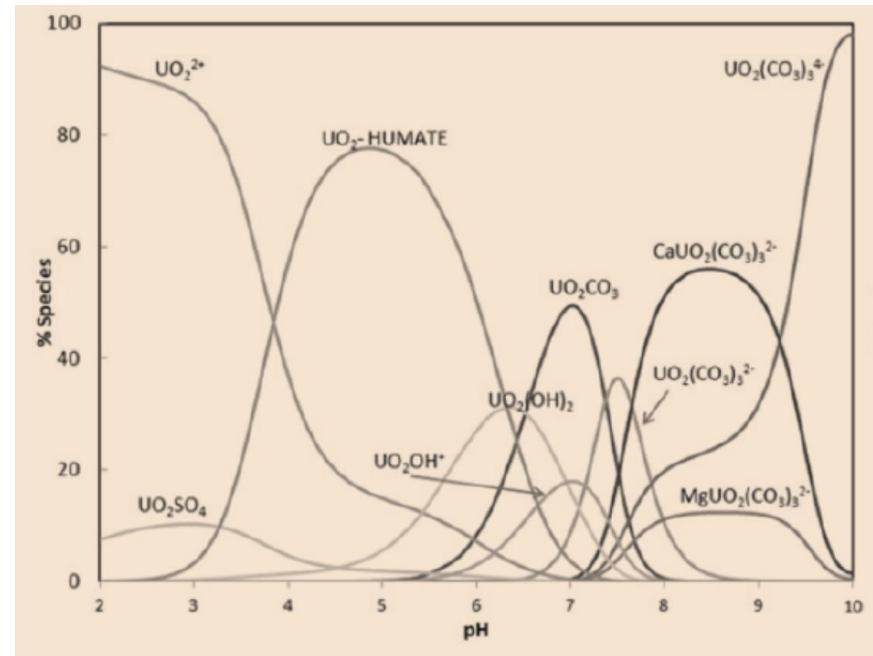
Uranyl forms stable organic complexes with a variety of organic ligands, from simple di- tri-carboxylic acids (10-100 ppm in surface and groundwaters) to humic / fulvic acids.

When small chelate rings with the equatorial oxygen atoms of UO_2^{2+} are formed, the uranyl chelates have exceptionally 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 (*Schild et al., Radiochim. Acta, 2000*)



Speciation diagram of uranyl calculated using PHREEQC $U = 1 \mu\text{M}$; Humate as a bidentate ligand; Atmospheric CO_2 .

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

Environmental Speciation of actinides (An) – Aqueous species

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	

One approach for modeling purpose has been to classify OM according to a series of functional groups for each type of OM, as a surrogate for their reactivity towards U

Complexity of OM ?

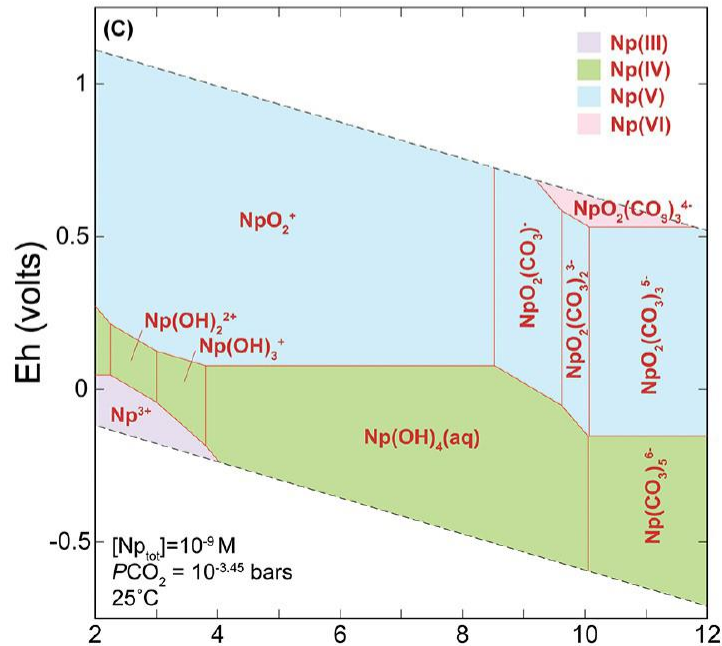
Occurrence of U colloids formation within OM ?

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 crystalline
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) $\text{An}^{4+} > \text{AnO}_2^{2+} \geq \text{An}^{3+} > \text{AnO}_2^+$

AQUEOUS CHEMISTRY

SORPTION

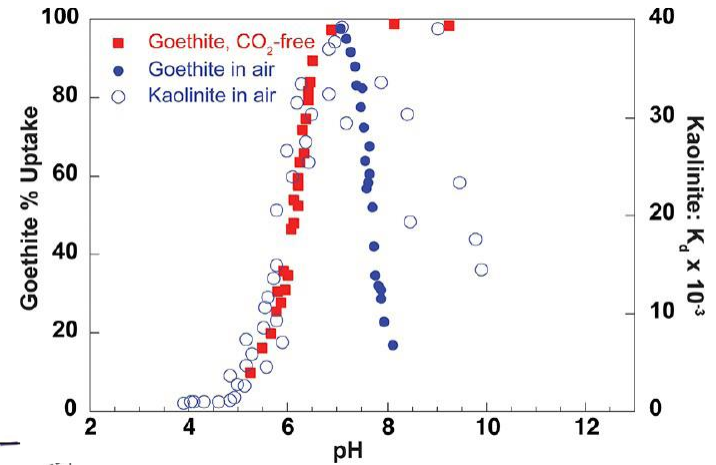
ON-GOING RESEARCH

FOCUS: EFFECT OF ORGANIC MATTER

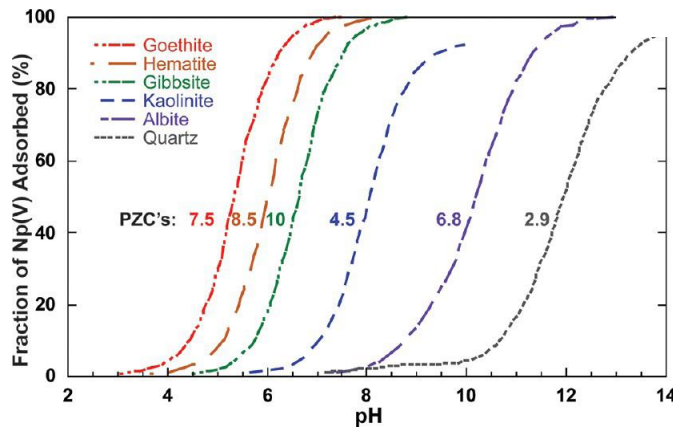
Environmental Speciation of actinides (An) – Sorption species

Presence of
(in)organic ligands
influence macroscopic
sorption

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



(after Thompson et al. 1998)



(from Kohler et al. 1992)

General order of actinide sorption : $\text{An}^{4+} > \text{An}^{3+} > \text{AnO}_2^{2+} > \text{AnO}_2^+$

Environmental Speciation of actinides (An) – Sorption species

Many molecular scale investigations

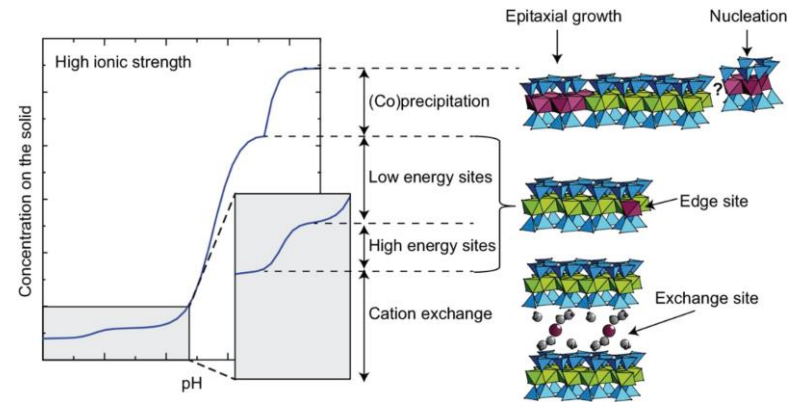
Critical for understanding and modelling fate of An

EXAFS spectroscopy

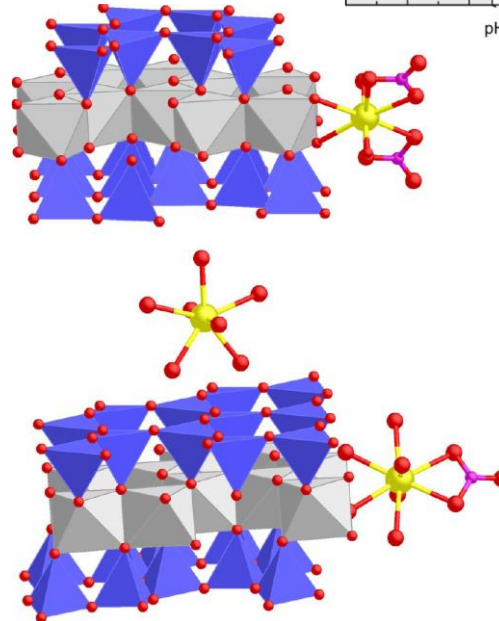
TRLF spectroscopy

ATR-FTIR spectroscopy

- ❑ 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)



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.

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

Environmental Speciation of actinides Mechanisms of U and P (co)sorption (An) – Sorption species



- ❑ Phosphate ligands (noted here: P) affect the retention behavior of uranium in oxic systems where U occurs in the hexavalent state, UO_2^{2+}

- ❑ Uranyl phosphates: important phases for controlling U mobility
 - at high [U],
 - at near-neutral pH where the solubility of uranyl phosphates is low

- ❑ (Co) sorption processes: important processes for controlling U mobility, at low [U] and at low pH, in P-rich soils containing Fe or Al oxihydroxides

- ❑ Postulated mechanisms of (co)sorption : formation of
 - surface complexes or surface precipitates of U(VI)-phosphate onto (hydr)oxides*
 - (surface) precipitates of Fe^{3+} -phosphate** or Al-phosphate* incorporating or adsorbing U.

•e.g. in soils developed over the Core Hill deposit, Virginia. Jerden J.L. and Sinha A.K., J. Chem. Explor. 91 (2006) 56.

**e.g. in weathering layers overlying the Bagombé reactor zone, Oklo Del Nero et al., Radiochim. Acta 87 (1999) 135.

Full identification of the mechanisms of U and P (co)sorption on Al-oxides requires in-situ investigations, during sorption, of the surface speciation

- Coordination environments of both P and U at the interface:
 - P-O stretching vibration of P → **ATR - FTIR spectroscopy**
 - Fluorescence emission characteristics of U → **TRLF spectroscopy**

- Mechanisms of sorption of U (trace concentration) at low pH on α -Al₂O₃ colloids, in presence of phosphate ligands
 - undersaturation / uranyl phosphate minerals
 - in absence of U: P is sorbed on α -Al₂O₃ via formation of phosphate surface complexes and of surface precipitates of Al-phosphate, whose relative contributions depend on time and P coverage*

**Del Nero M., Galindo C., Barillon R., Halter E. and Madé B., J. Colloid Interf. Sci. 342 (2010) 337.*

Identity of the uranyl surface species as function (i) of the transformation rate of the Al_2O_3 surface into Al-phosphates, (ii) of the aqueous uranyl species

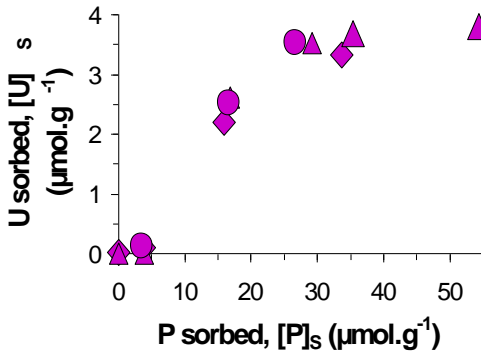
Sorption in alumina suspensions (2.5 g.L^{-1}) containing P

$\alpha\text{-Al}_2\text{O}_3$ ($380 \pm 20 \text{ nm}$) $\text{PIE} \sim 9$,
 $S = 7 \text{ m}^2.\text{g}^{-1}$. In NaCl
 (NaClO_4) solutions, pH 3.3

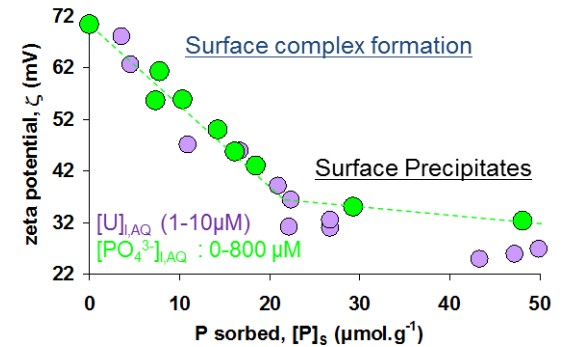
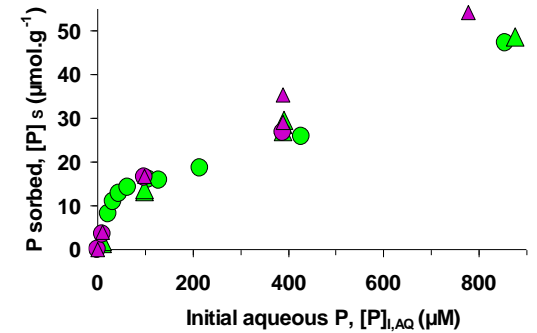
Aqueous phosphate added,
 H_2PO_4^-

Aqueous uranyl added **at trace
 concentration** ($1\text{-}10 \mu\text{M}$)

Reaction time: 3 hours (◆) or 3 (●) or 14 (▲) days



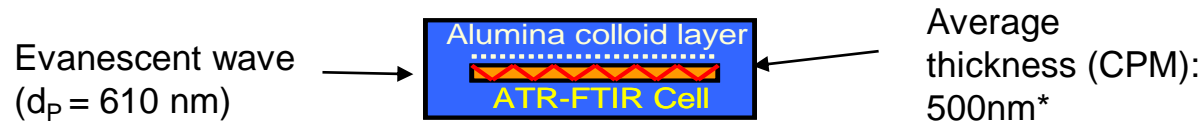
After Galindo et al. (2010)



Sorption of U(VI) at pH 3.3 on Al_2O_3 is promoted by presence of P ligands

Investigations of the P-O stretching vibrations at alumina / solution interface during (co)sorption of U and P

ATR-FTIR spectroscopy -Low r value ($\sim 0.1 \text{ g.L}^{-1}$)



Alumina layer coated on the ATR crystal (Ge) and brought in contact with solution*

→ In-situ IR analysis of the interface

2000 scans / spectrum, resolution 4 cm^{-1}

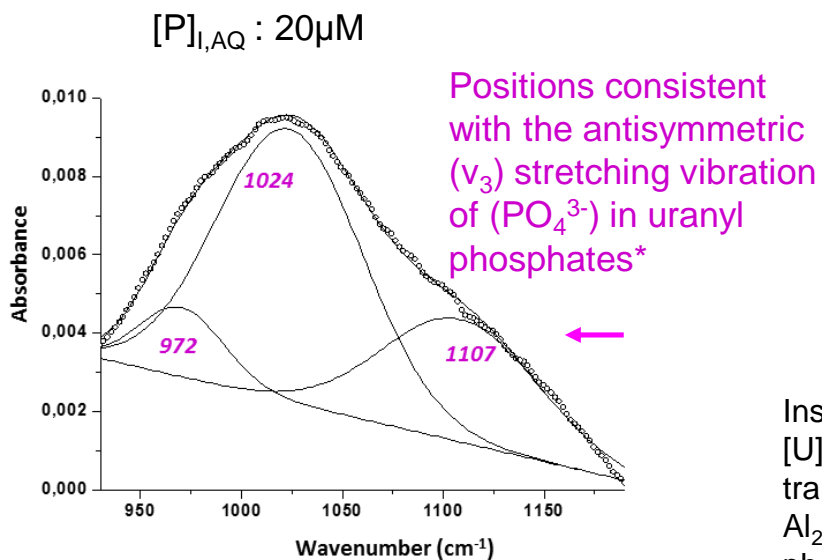
Cut-off of MCT detector: $\sim 900 \text{ cm}^{-1}$

High absorbance of Al_2O_3 below 1000 cm^{-1}

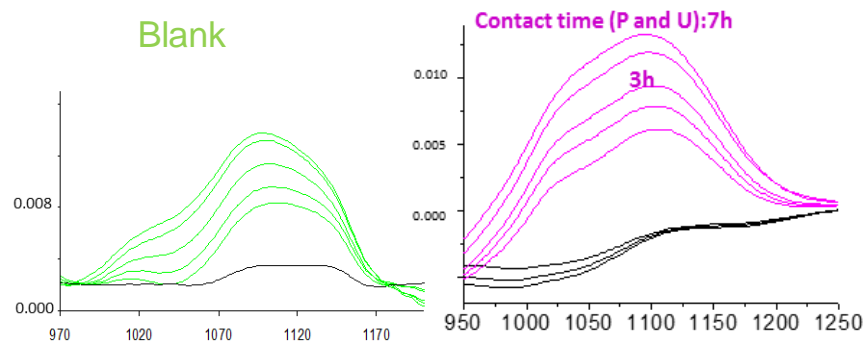
*cf. Montgomery P., Halter E., Montaner D., Barillon R., Del Nero M., Galindo C. and Georg S., *Applied Surf. Sci.* 256 (2010) 6144.

In-situ ATR-FTIR spectroscopy : coordination environment of P at the interface

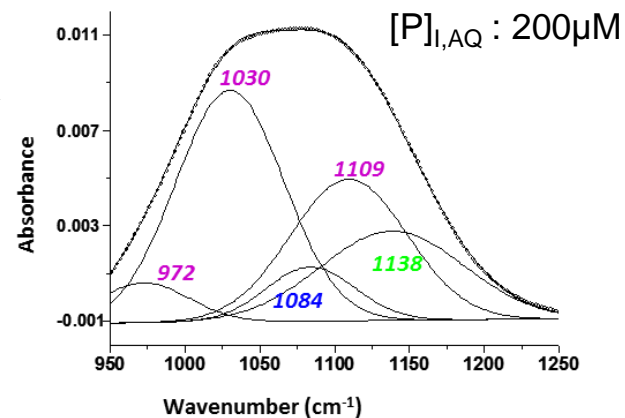
ATR-FTIR experiments of sorption of P and U



*Frost R.L., *Spectrochimica Acta part A* 60 (2004) 469



Insensitive to $[P]_{I,AQ}$,
 $[U]_{I,AQ}$, rate of
transformation of the
 Al_2O_3 surface into Al-
phosphate



Formation of surface precipitates of uranyl phosphates

TRLFS spectroscopy : coordination environment of U in suspension

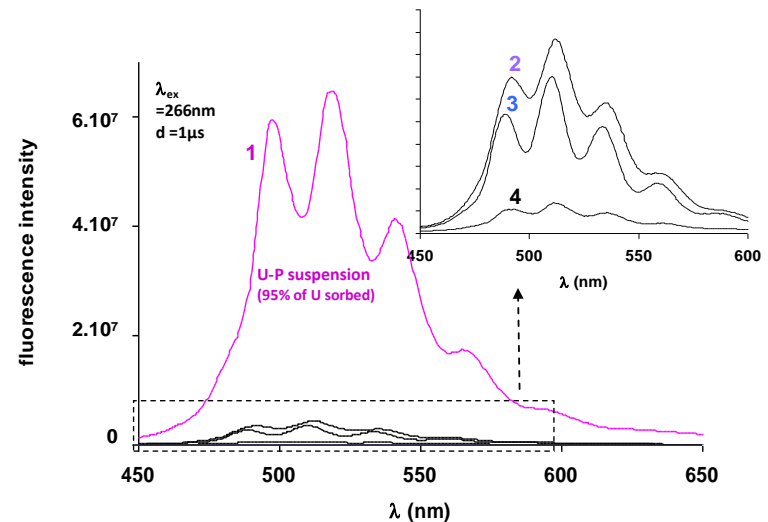
- In situ analysis of suspensions containing U at low concentration
- Position of emission peaks sensitive to c.

e. of U

$$I(t) = I_0 + \sum_i A_i e^{-t/\tau_i}$$

- Fluorescence decay and lifetimes sensitive to quenchers around U
- Emission spectra of U emitting components (varying gate delay, d)

1. Suspension: (2.5g.L⁻¹) Al₂O₃, [P]_{I,AQ}: 400μM, [U]_{I,AQ}: 10μM
2. Solution: [P]_{I,AQ}: 400μM, [U]_{I,AQ}: 10μM
3. Suspension: (2.5g.L⁻¹) Al₂O₃, [U]_{I,AQ}: 10μM
4. Supernatant of suspension 1



Formation of uranyl surface species of high quantum yield

- In situ analysis of suspensions containing U
- Position of emission peaks sensitive to c. e. U

Shift / $\text{UO}_2^{2+}(\text{aq})$ and U-P solutions

Consistent with U sorbed on alumina* and U(VI)-phosphate minerals**

Strong binding in equatorial plane of UO_2

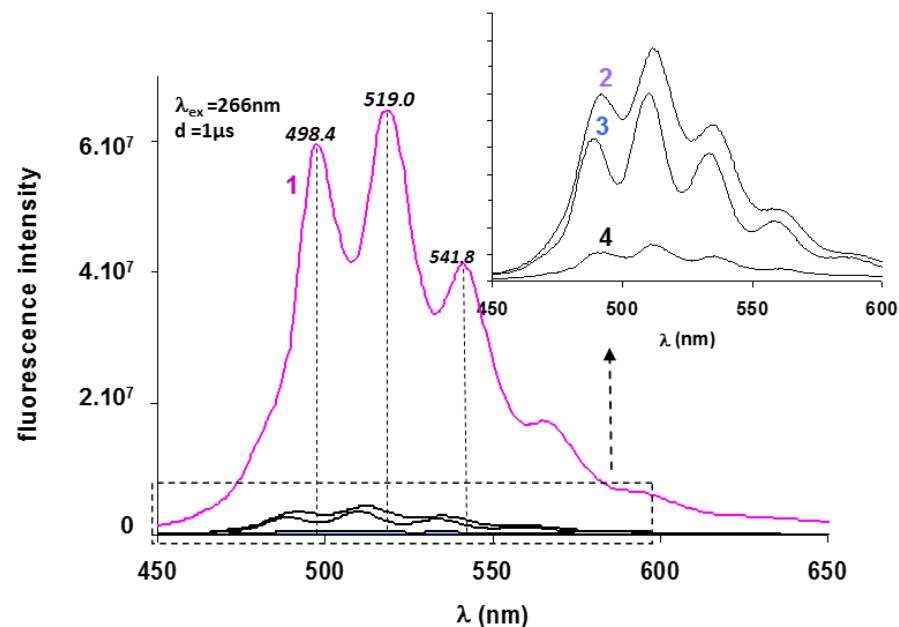
- Fluorescence decay and lifetimes sensitive to quenchers around U

ζ_i : 3-5, 15-20, 33-40, 140-170 μs

ρ_i : 30, 35, 25, 10

- Emission spectra of U emitting components (varying delay time, d)

1. Suspension: $(2.5\text{g.L}^{-1}) \text{Al}_2\text{O}_3$, $[\text{P}]_{\text{I,AQ}}: 400\mu\text{M}$, $[\text{U}]_{\text{I,AQ}}: 10\mu\text{M}$
2. Solution: $[\text{P}]_{\text{I,AQ}}: 400\mu\text{M}$, $[\text{U}]_{\text{I,AQ}}: 10\mu\text{M}$
3. Suspension: $(2.5\text{g.L}^{-1}) \text{Al}_2\text{O}_3$, $[\text{U}]_{\text{I,AQ}}: 10\mu\text{M}$
4. Supernatant of suspension 1



Formation of **uranyl phosphate** surface species

* Froideval et al. *Geochim. Cosmochim. Acta* 70 (2006) 5270.

** Geipel et al. *Radiochim. Acta* 88 (2000) 757.

- In situ analysis of suspensions containing U at low concentration

No variation with conditions, [P], [U], r

- Position of emission peaks sensitive to c. e. of U

Shift / $\text{UO}_2^{2+}(\text{aq})$ and U-P solutions

Consistent with U sorbed on alumina* and U(VI)-phosphate minerals**

Strong binding in equatorial plane of UO_2

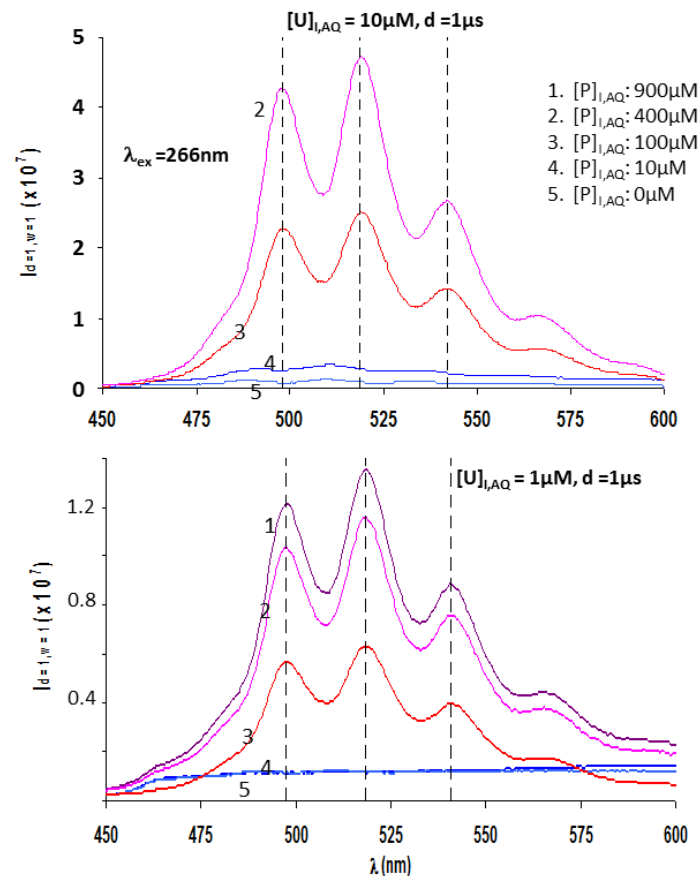
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** Geipel et al. *Radiochim. Acta* 88 (2000) 757.



TRLFS spectroscopy : coordination environment of U in suspension

Varying spectroscopic sample conditions

Striking feature:

Same surface species of uranyl phosphate

- over ranges of U coverage,

- irrespective of characteristics

- of initial solution:

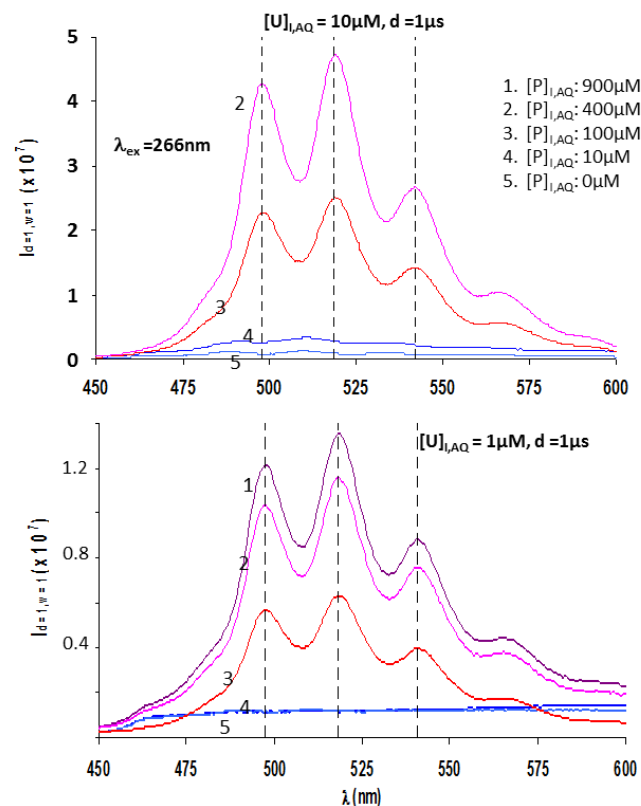
speciation, saturation state / uranyl

phosphates

- of alumina surface:

P loading, transformation rate into Al-

phosphate

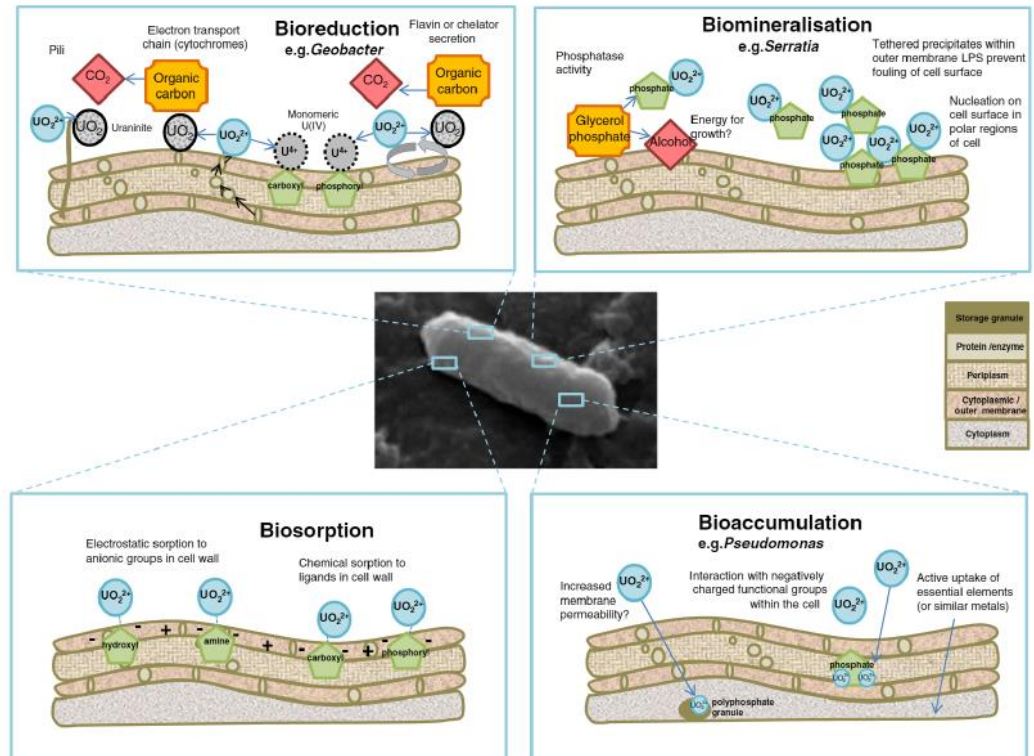


Formation of surface precipitates of U(VI) phosphate : long-term retention of U(VI)

On-going research

- Chemistry of Po, Ra, T...
- Formation of RN solid-solutions, surface precipitates
- Effect of colloids
- Effect of organic ligands, bioligands, complex natural organic matter on RN speciation
- Actions – retroactions between RNµorganisms
- Interactions RN-minerals-plants-microorganisms ...

Schematic representation of some mechanisms of U-microbe interactions



Taken from Newsome et al., *Chem. Geol.* 2014 (review paper)

AQUEOUS CHEMISTRY

SORPTION

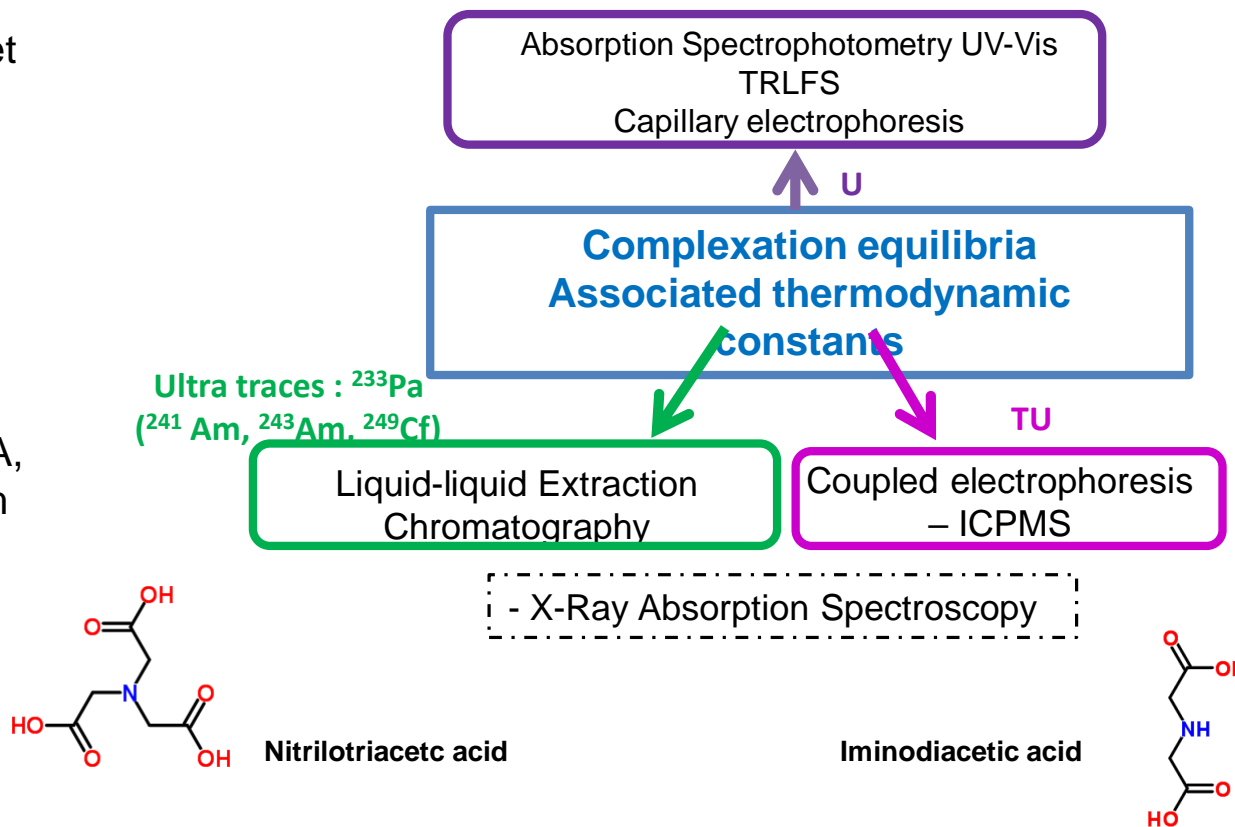
ON-GOING RESEARCH

FOCUS: EFFECT OF ORGANIC MATTER

On-going research

Complexation of actinides by organic ligands

- **Interactions** Pa(V), U(IV et VI) and transuranians with organic ligands
- **Model compounds** OM: carboxyl acids, polycarboxylics (oxalic, succinic) et polyaminocarboxylics (NTA, IDA, MIDA), derivatives from hydroxamic acid

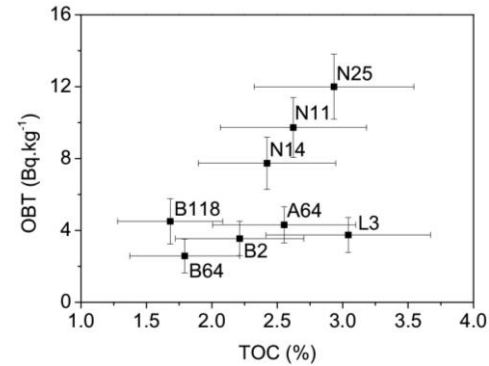
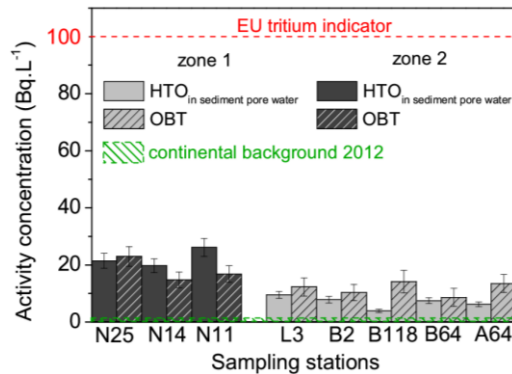
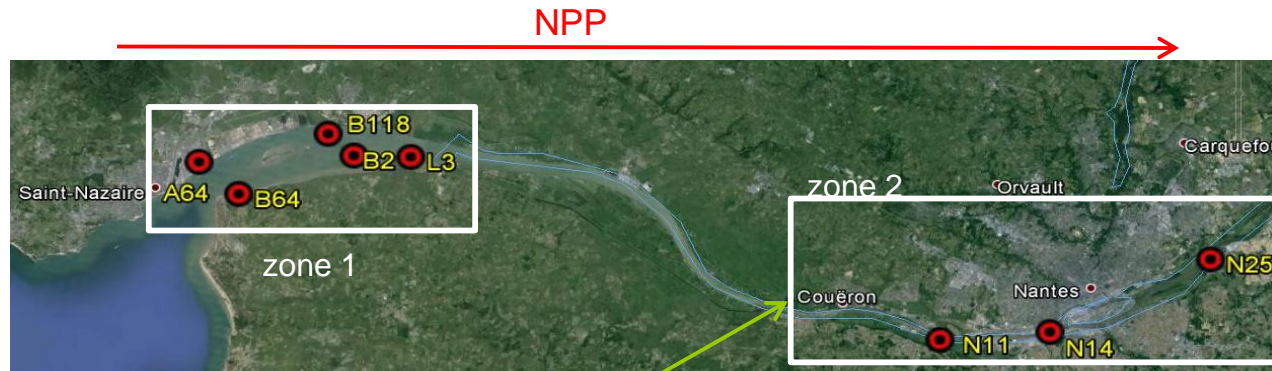


On-going research

Anthropic Tritium in the Loire Estuary



- HTO highly mobile
- Organically bound Tritium potentially ecotoxic due to its high biological half-life



O. Péron et. al, "Anthropogenic tritium in the Loire River estuary, France", *Journal of Sea Research* (2016)



On-going research

Phytoextraction and biomagnification of Cs in soils

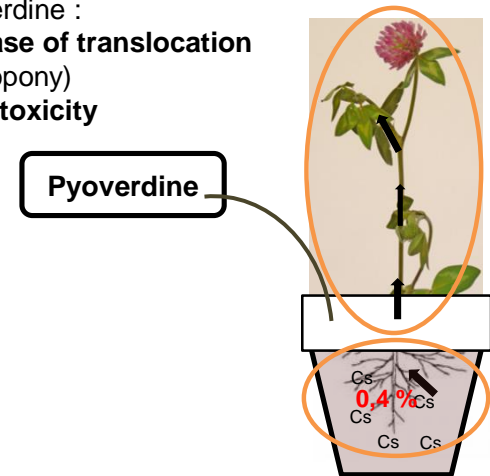
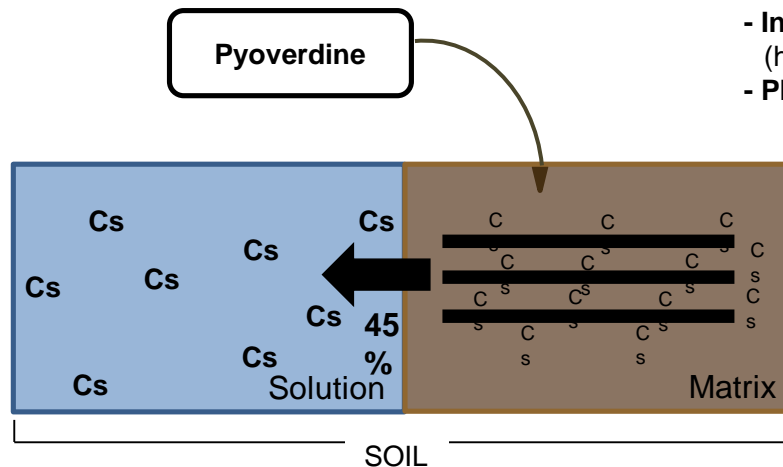
Mobilisation of Cs from illite

- 10 % **mobilisation of Cs** from illite by org. acids
- 21 % when *Pseudomonas fluorescens* added
- 45 % when **pyoverdine (250 $\mu\text{mol.L}^{-1}$)** added

Phytoextraction of Cs

- **75 % Cs taken** by plant in hydroponie (Cs bioavailable as **CsCl**)
- **Accumulation of Cs** sorbed on **illite** is poor (0,85 %)
- **Accumulation of Cs from soil is poor (0,4 %)**
- Pyoverdine :
 - **Increase of translocation** (hydropony)
 - **Phytotoxicity**

- Cs tightly bound to illite (replaces in interlayer space)
- Effect of presence of microbes (bioligand complexation) on mobilisation and phytoextraction



Hazotte A.A., Péron O., Abdelouas A., Montavon G., Lebeau T.
 "Microbial mobilization of cesium from illite: the role of organic acids and siderophores", *Chemical Geology*, 428, 8-14 (2016)

- **Application to Chernobyl accident:**

- Sampling of contaminated soils for bacterial inventory (cultural and molecular approaches)
- Strain culture collections elaborated from soil contaminated with ^{137}Cs
- Studies of interaction mechanisms using some of the strains

