

Etudes environnement et radiochimie sur synchrotron

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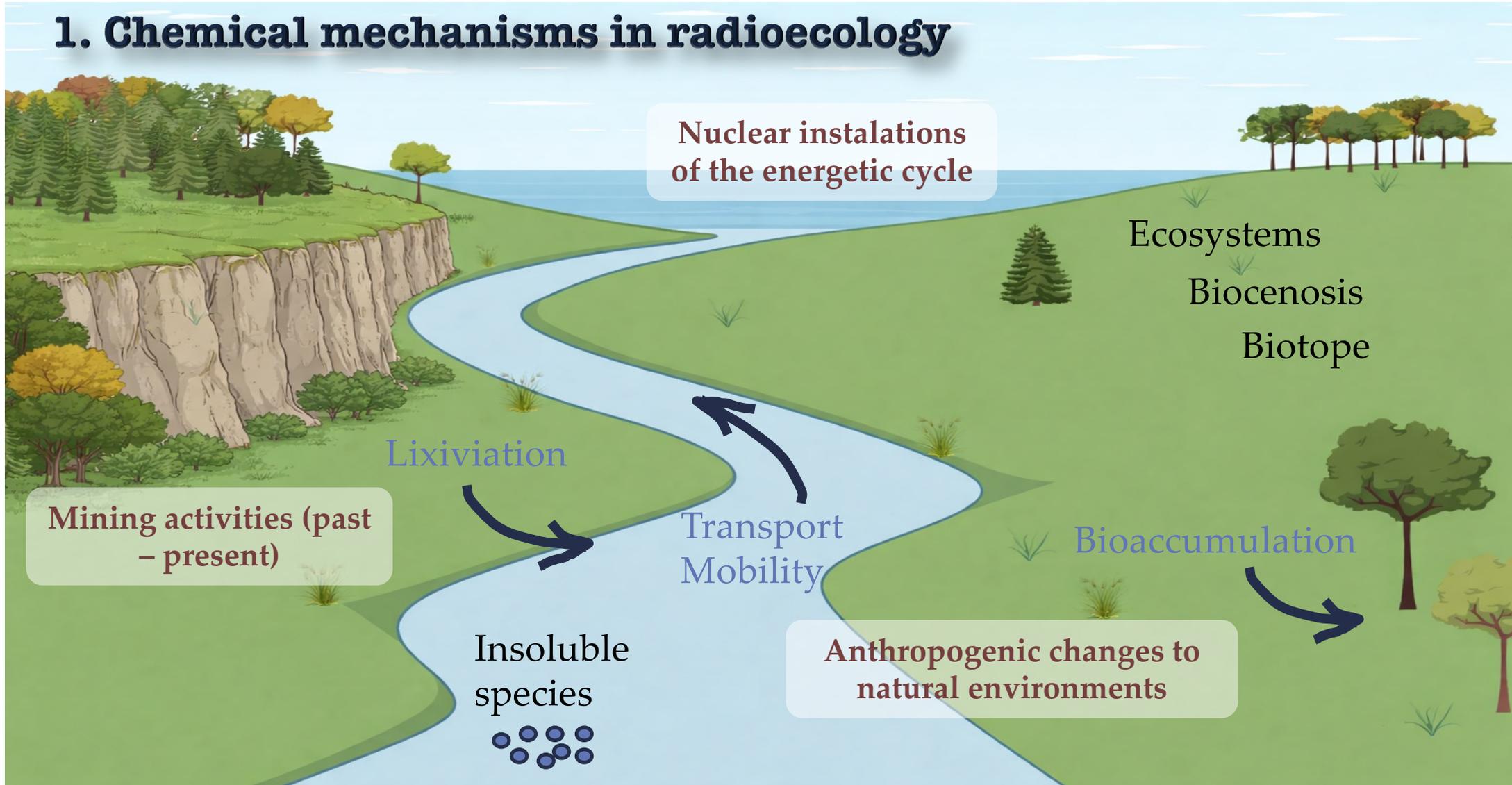
Radioecology became recognized as a branch of ecology in response to the radioactive fallout associated with the proliferation of atmospheric nuclear weapons testing at the onset of the Cold War period in the 1950s (1)

Alongside radioecology, **environmental radiochemistry** emerged in the 70's in response to the larger use of nuclear energy (2)

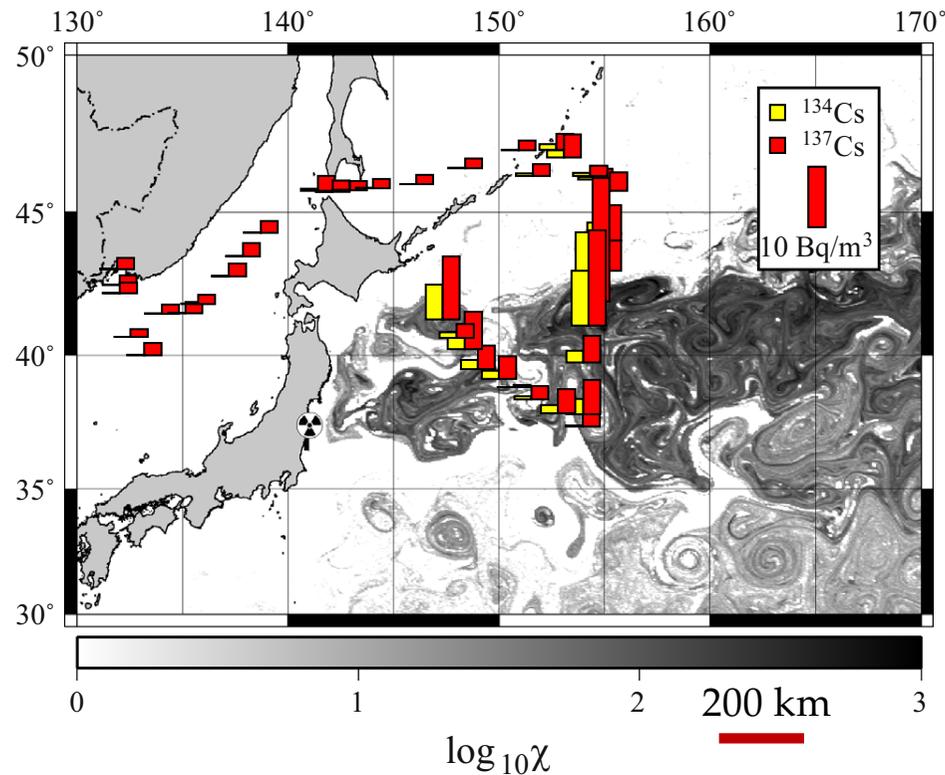
(1) Kangas, P.C., 2022. A History of Radioecology. Routledge Ed, USA.

(2) J. Aupias *et al.* STOTEN, 2024, 935, 173247.

1. Chemical mechanisms in radioecology



From global inventories (macro-scale)

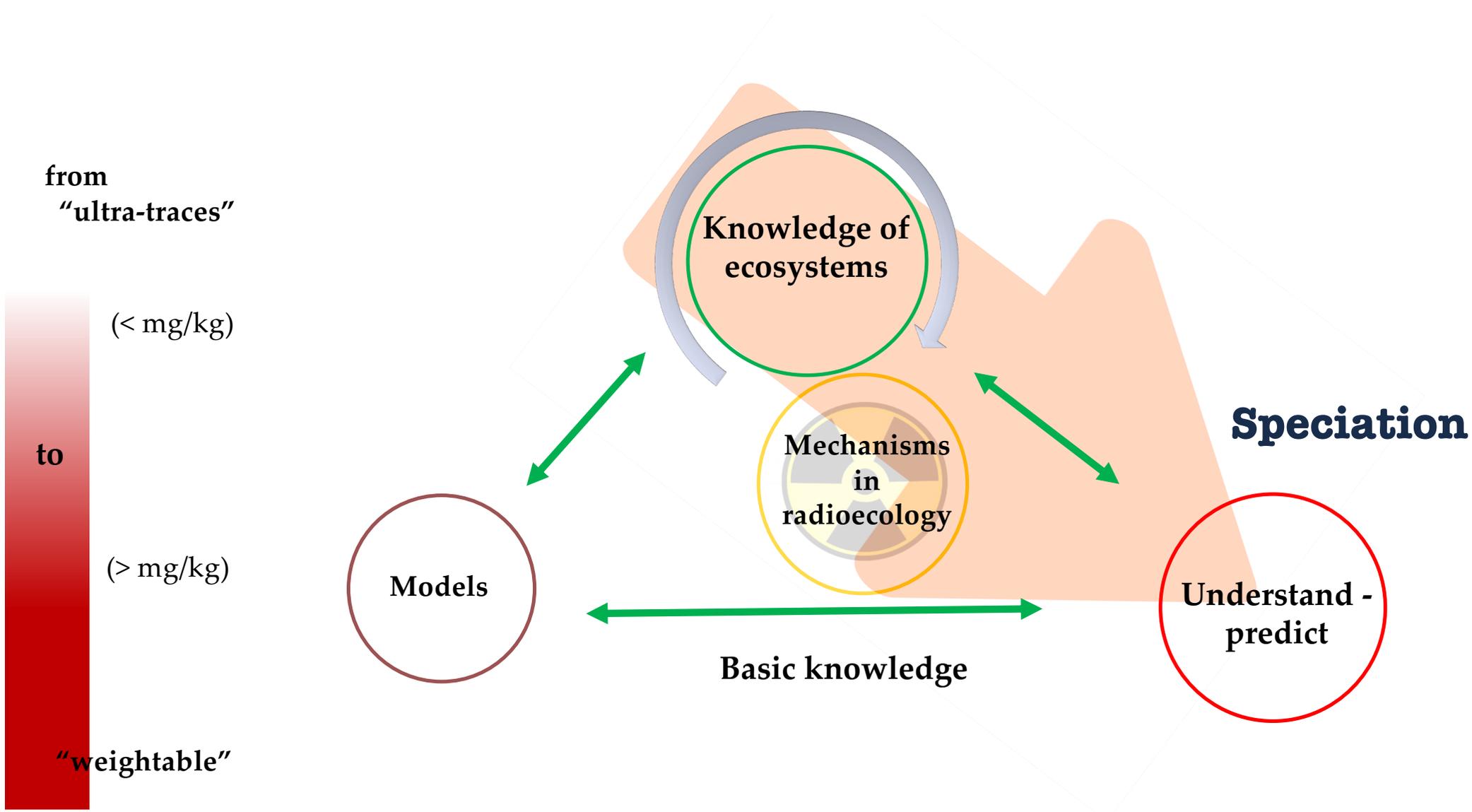


Fukushima accident : 11 March 2011

Simulated distribution of radionuclides concentration in the Northwest Pacific to the end of June 2012 with measured concentrations of ^{134}Cs and ^{137}Cs in Bq.m⁻³.⁽¹⁾

....to molecular speciation (micro-scale)

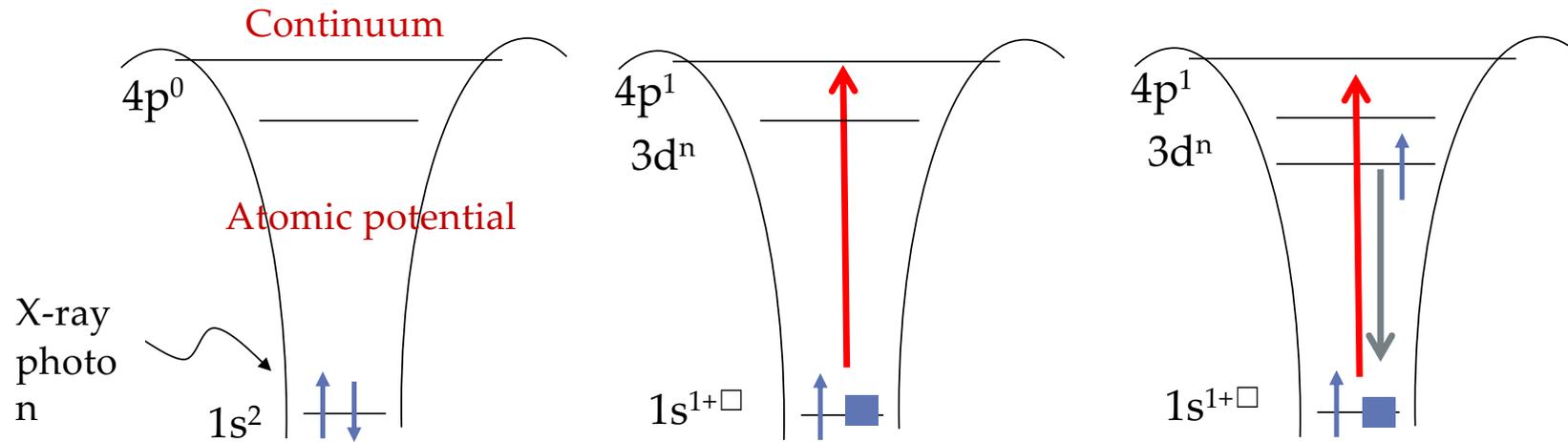
(1) M. V. Budyansky, Deep-Sea Research I 96 (2015) 15–27



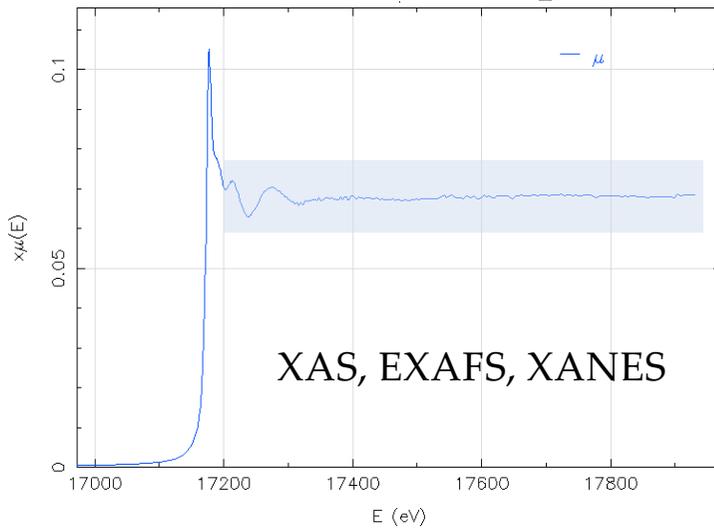
J. Aupiais et al. STOTEN (2024), 935, 173247
M. R. Beccia et al. ChemPlusChem (2022), 87, e202200108



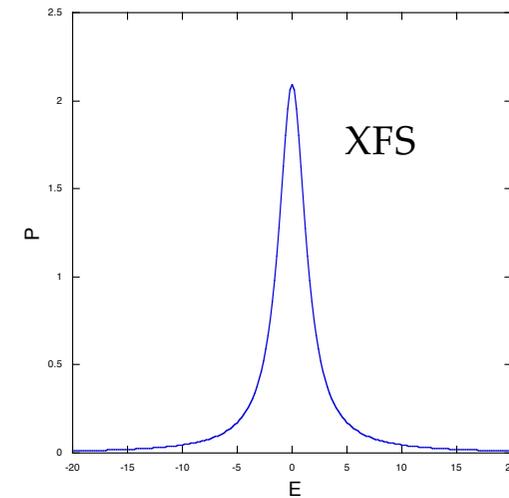
2. Speciation, core electrons spectroscopy at the synchrotron



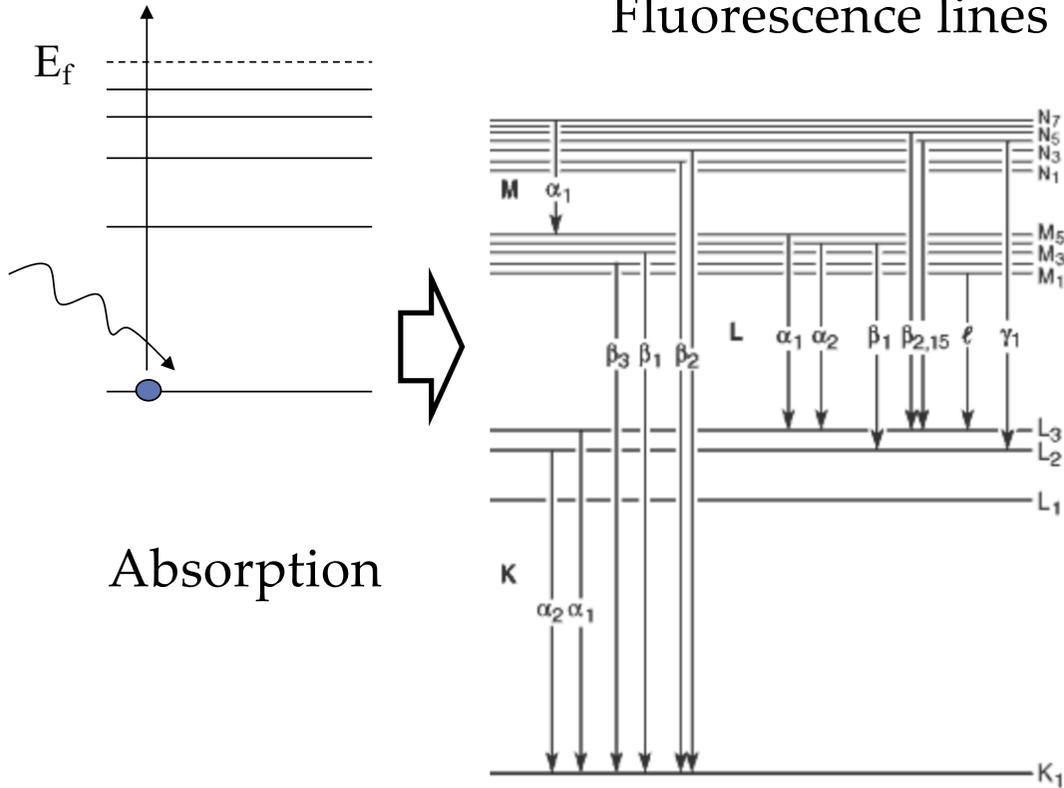
Absorption



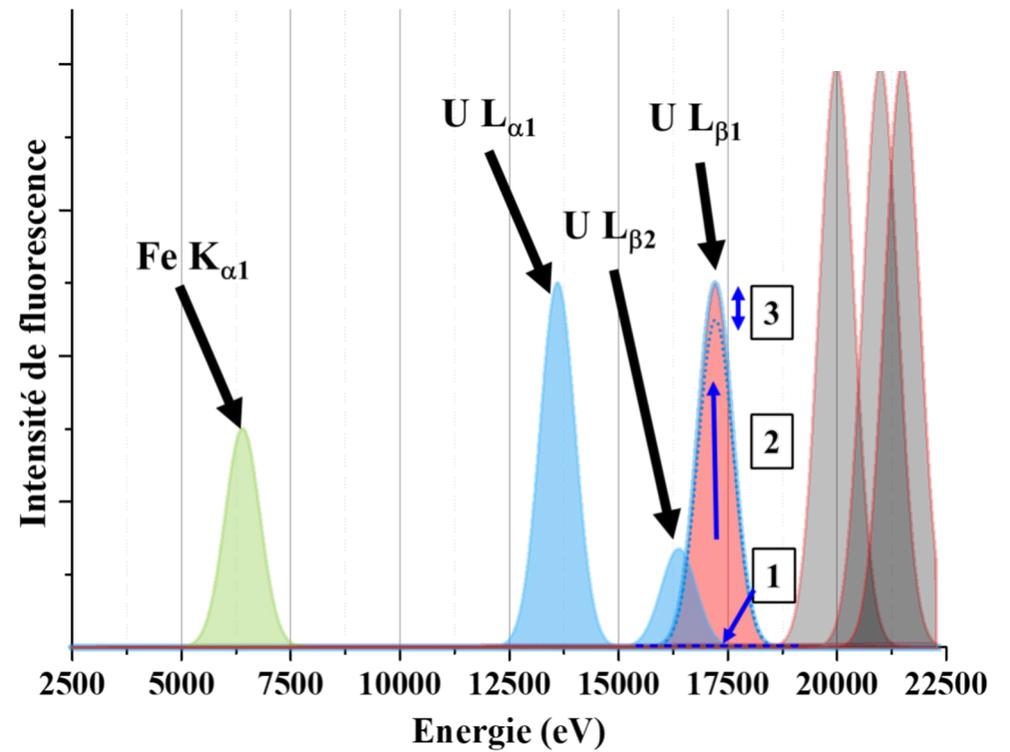
Relaxation



Relaxation Fluorescence lines

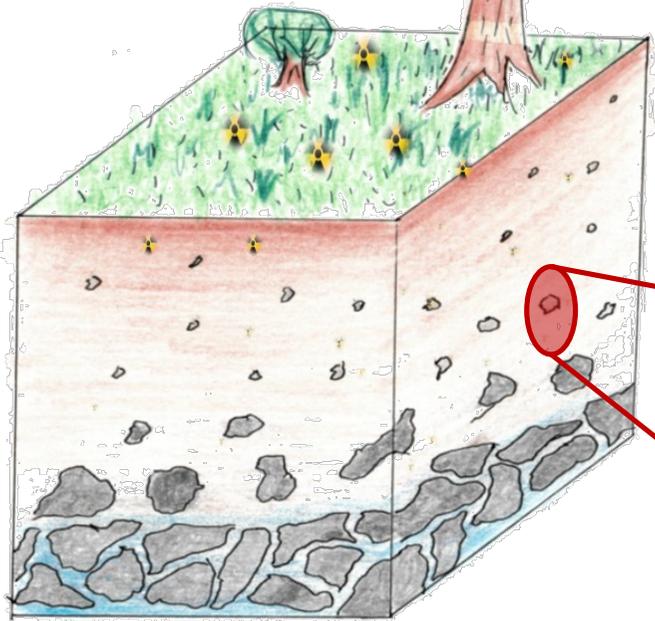


Sample : fluorescence emission lines

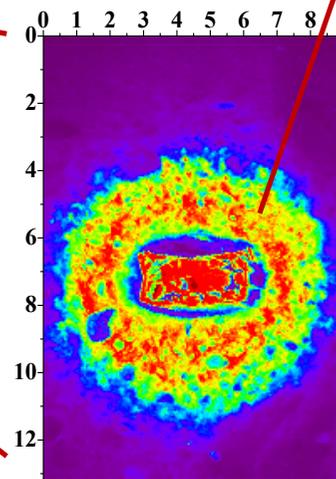
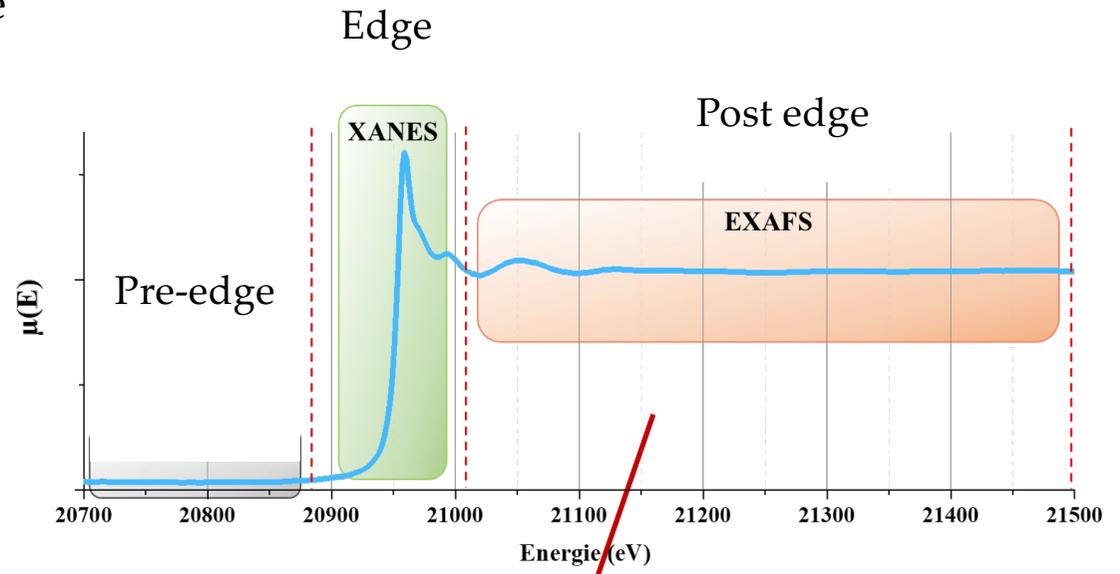




For a natural sample



X ray beam



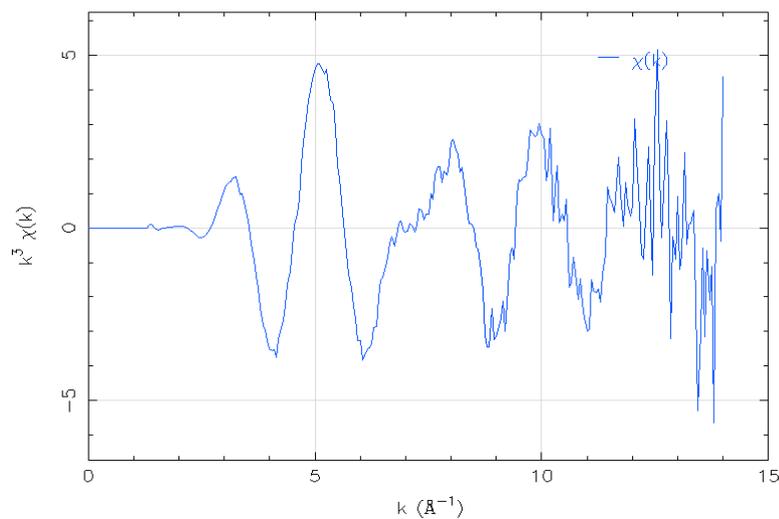
**Localization
+
Speciation**



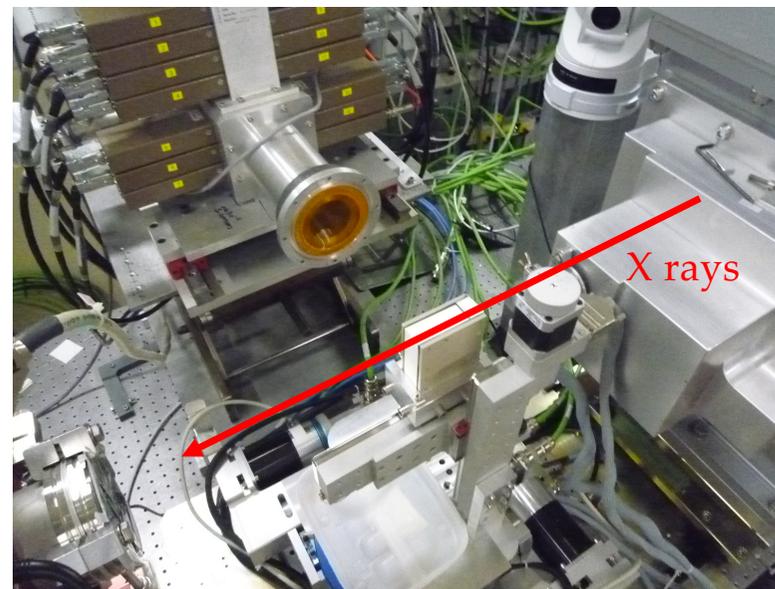
@ SOLEIL

XAS : X-ray Absorption Spectroscopy

L_{III} edge of heavy elements



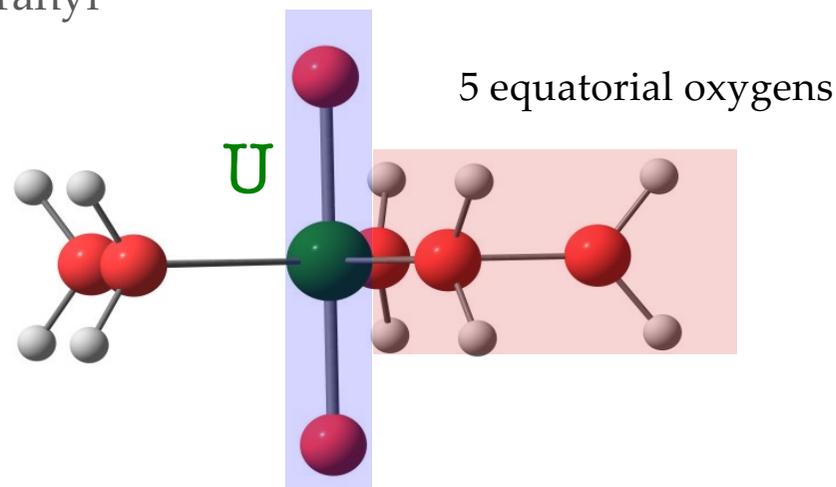
Fingerprint of the metal coordination sphere



Dedicated beam line, MARS, SOLEIL

2 yl oxygens

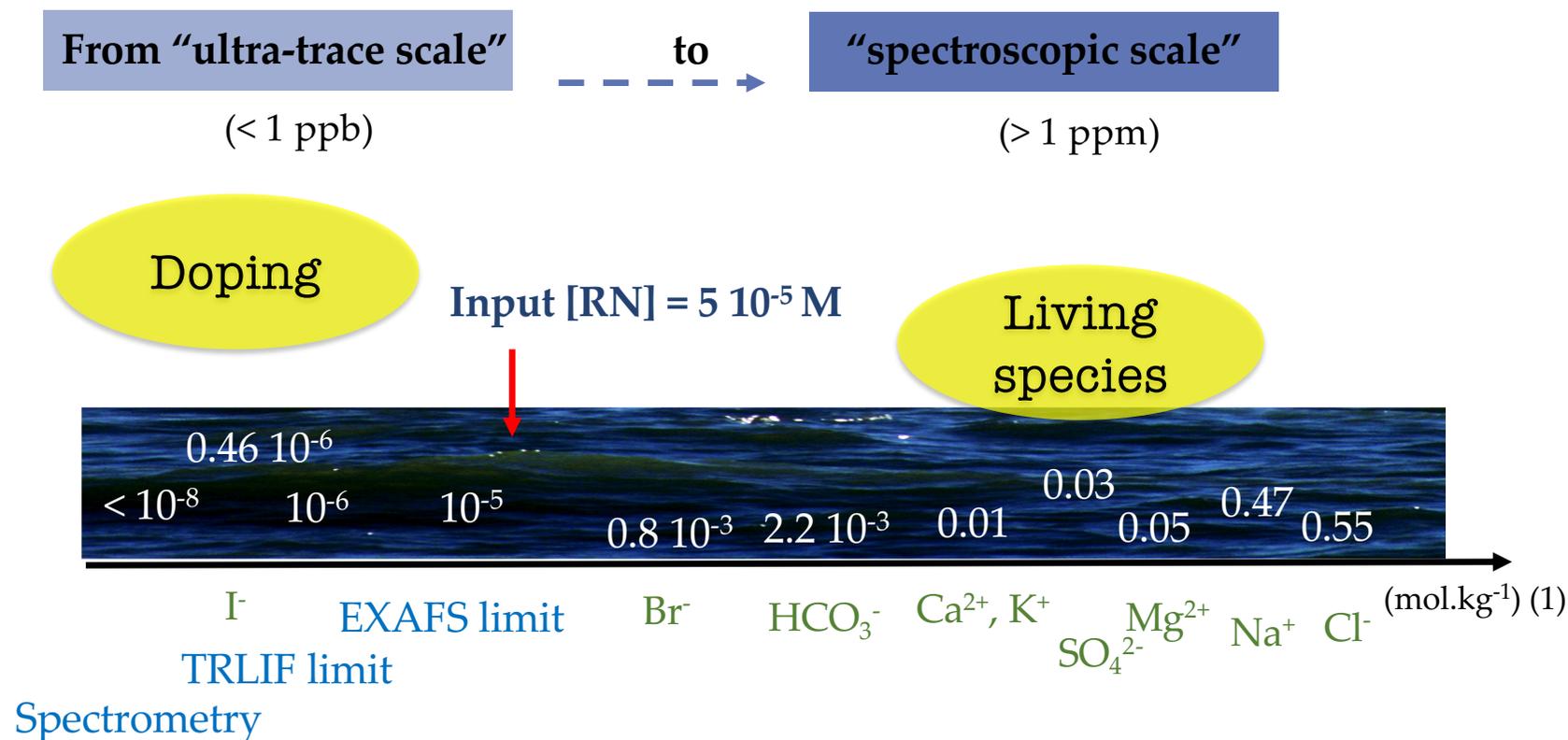
Uranyl



5 equatorial oxygens

3. A methodology based on model ecosystems

Multi-technique approach combining analytical tools with spectroscopic tools and modeling



Which species of interest ?

~ **Sentinels** demonstrate the presence of bioavailable contaminants and the extent of exposure

~ **Surrogates** indicate potential human exposure and effects

~ **Predictors** assess long-term effects on the health of populations or the integrity of the ecosystem (1)

A sentinel and sedentary species

- Sea Mussle *Mytilus Galloprovincialis*

Aquaculture, 94 (1991) 225-243
Elsevier Science Publishers B.V., Amsterdam

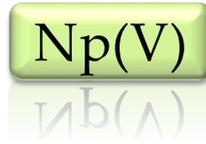
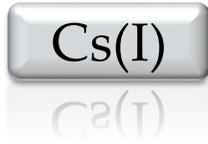
Mussels as biological indicators of pollution

A. Viarengo and L. Canesi

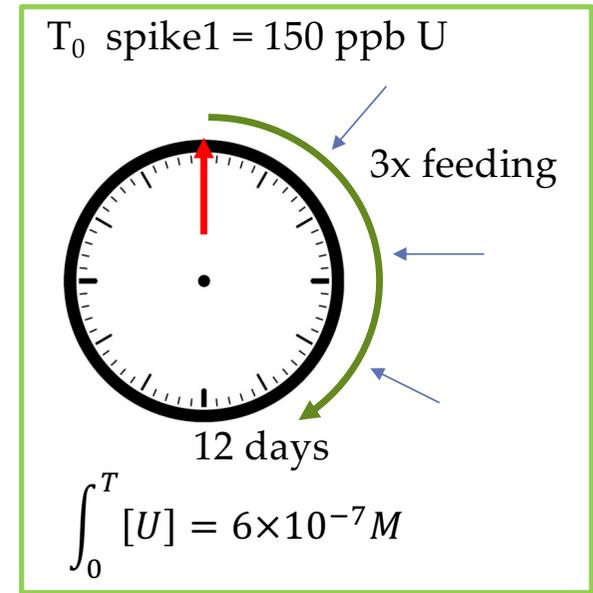
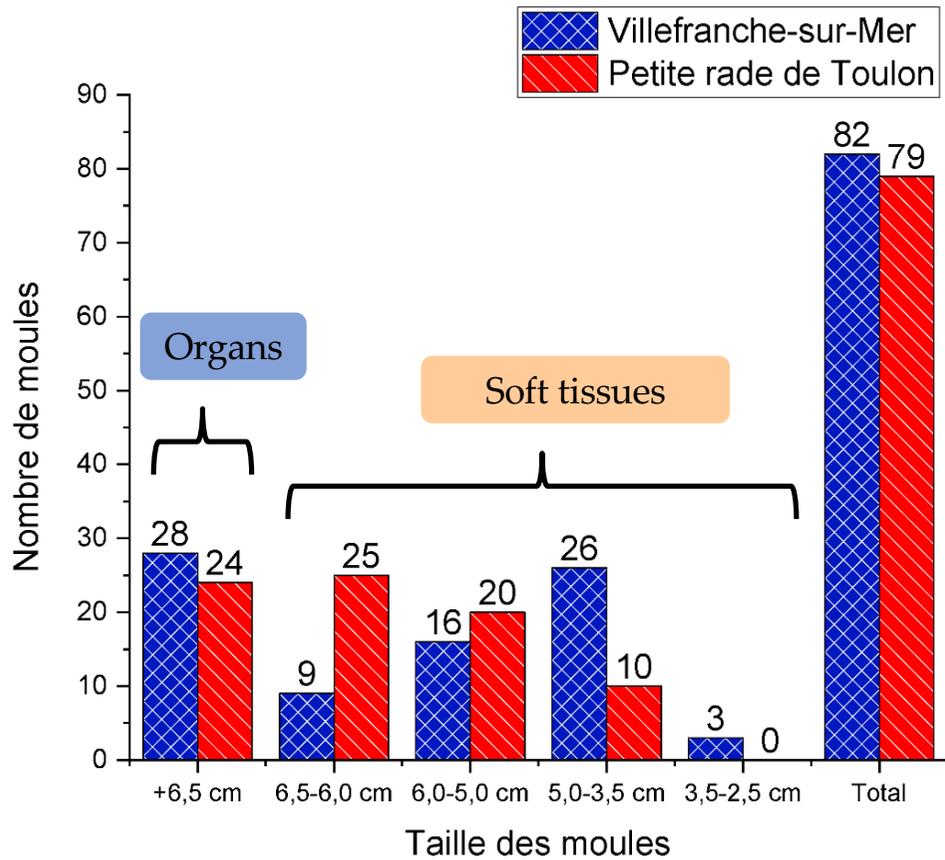
Istituto di Fisiologia Generale, Università di Genova, Corso Europa 26, 16132 Genova, Italy

(1) J. F. McCarthy, L. R. Shugart, *Biomarkers of Environmental Contamination*, CRC Press, 2018

Methodology

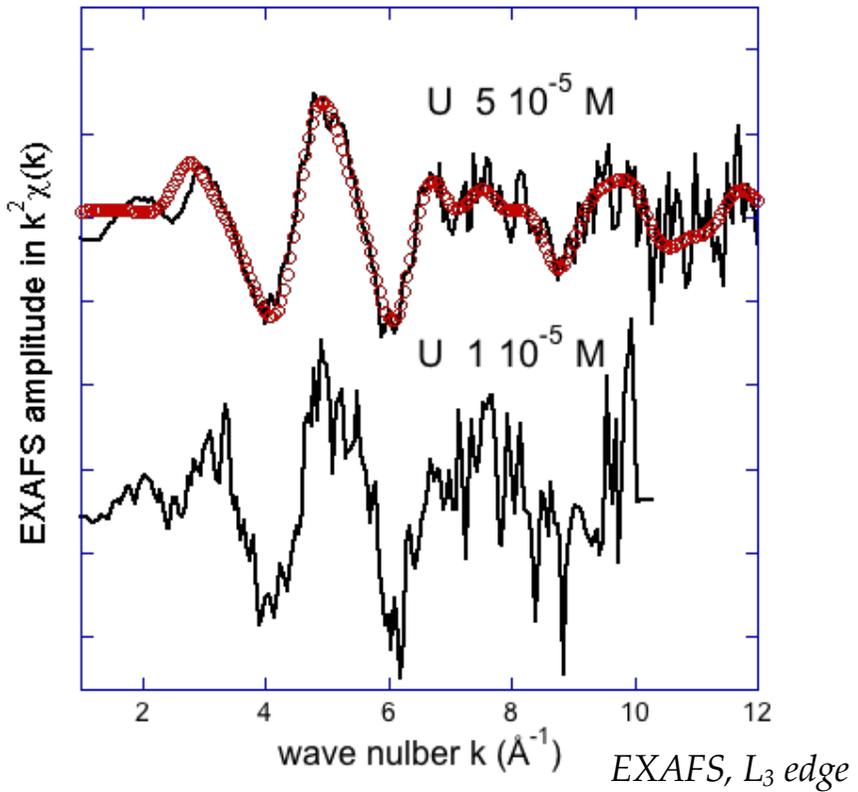
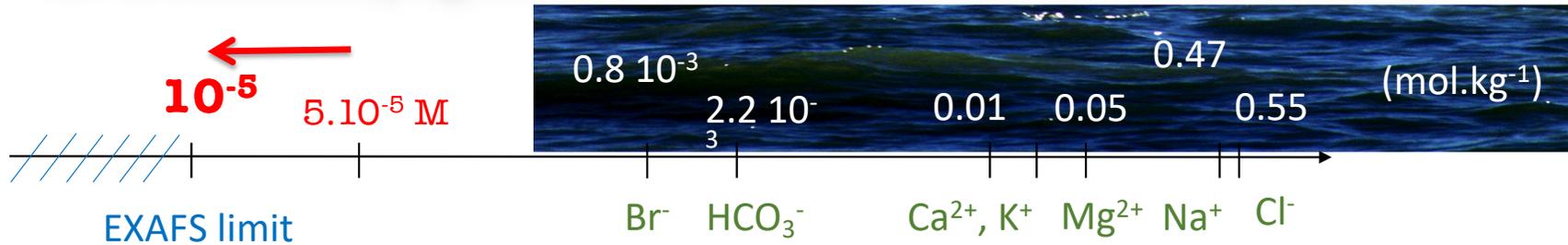


Cohorte of *ca.* 80 mussels, Villefranche sur mer / Toulon harbor

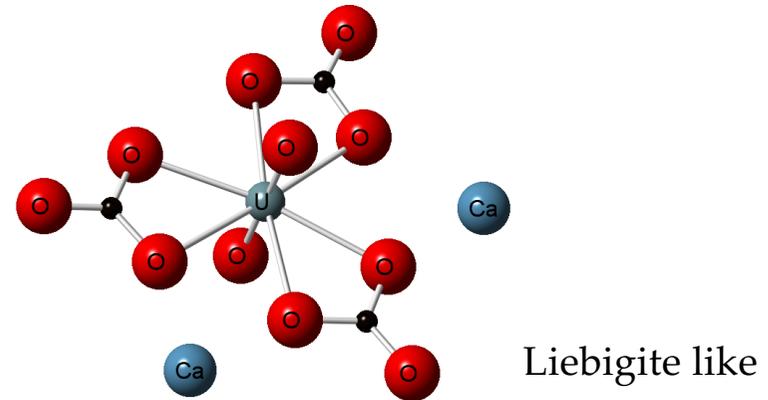


U(VI)

4. Uranium, speciation and transfer in seawater



No difference in speciation (1)
 $A_2UO_2(CO_3)_3 \cdot nH_2O$



(1) M. Maloubier et al., Dalton Trans (2015), 44, 5417

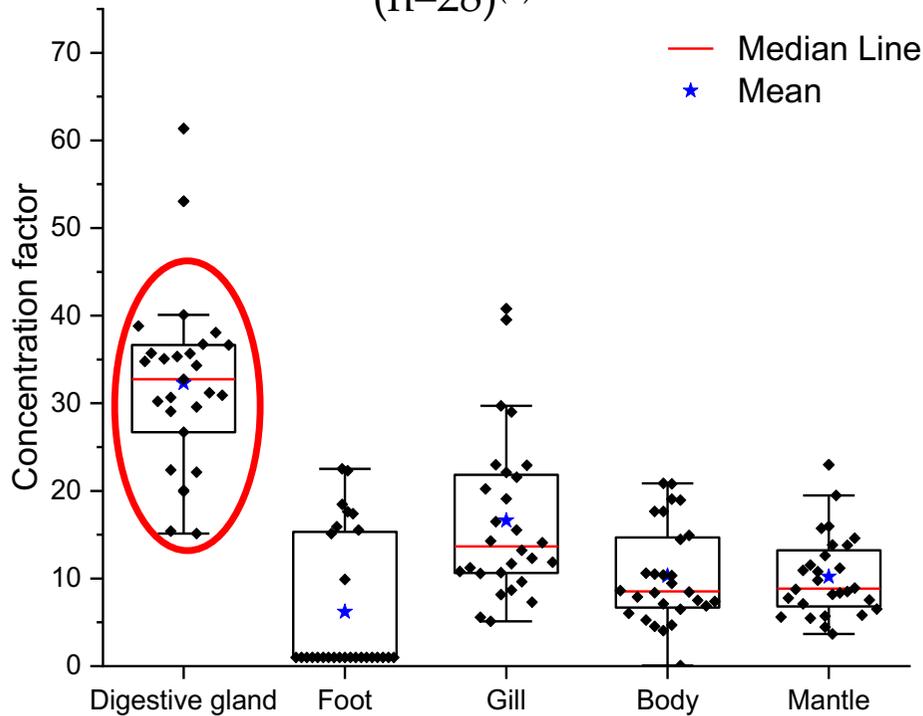
Conditions : 82-79 mussels
12 L NatU : 6×10^{-7} M
12 days
Villefranche-sur-Mer
Petite rade de Toulon



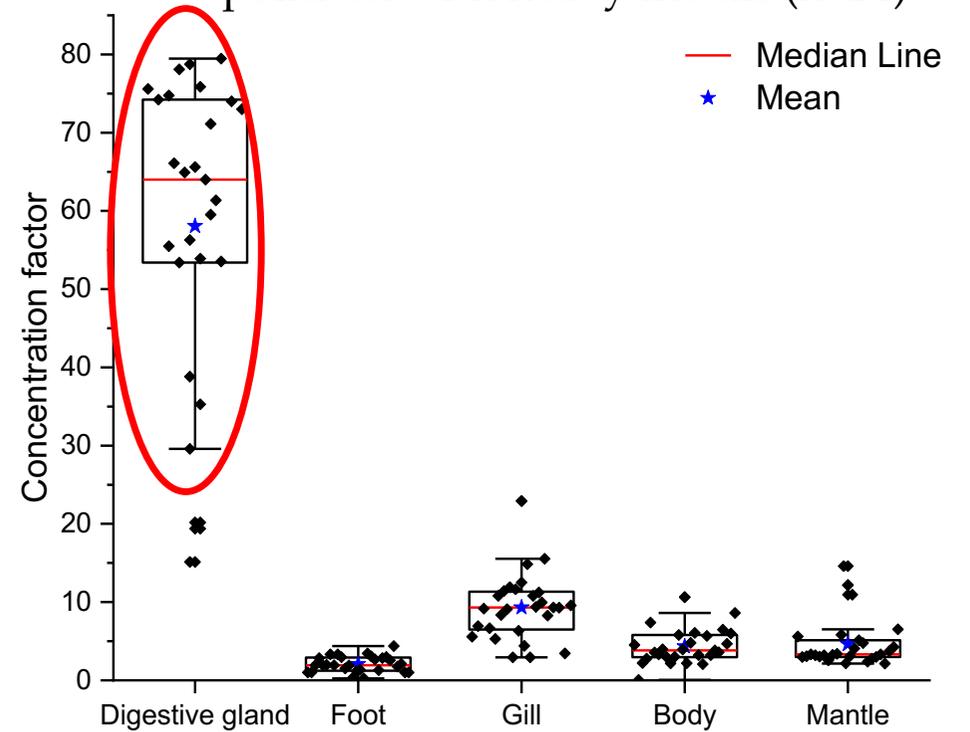
Adaptation to HM pollution ⁽²⁾
Detoxification mechanism ?

Concentration Factor (CF)

Mussels from the Villefranche area
(n=28)⁽¹⁾



Mussels from Toulon harbor highly
polluted with heavy metals (n=24)⁽¹⁾



(1) R. Stefanelli et al. Environ. Res, 252 (2024) 118877

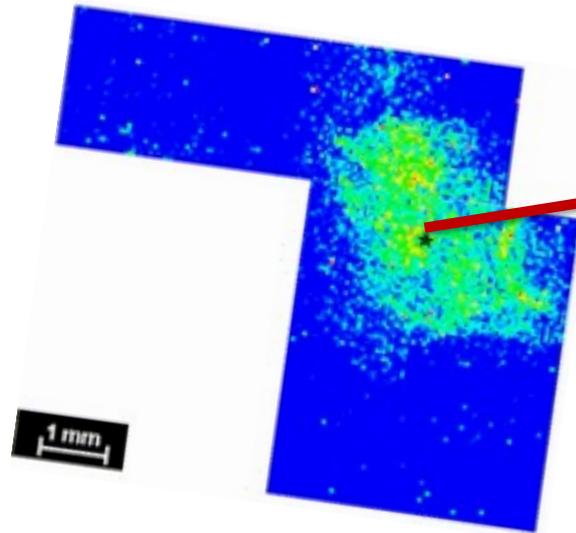
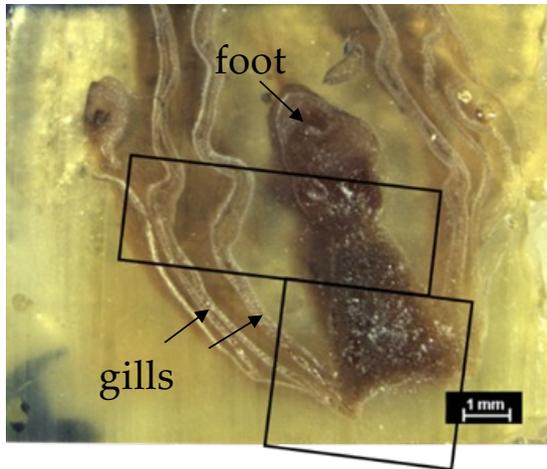
(2) S. Nicholson et al. Marine Pollution Bul. (2003), 46, 1040

Digestive gland

μ -XRF \rightarrow U L_{II} edge at 20 948 eV

$L_{\beta 1}$ 17 220 eV

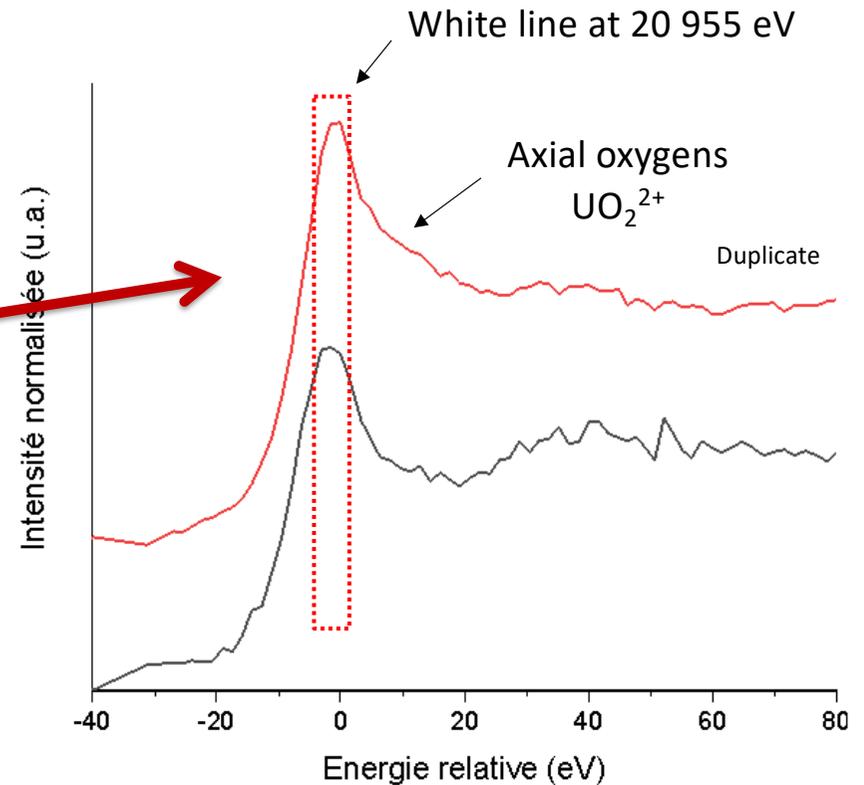
$L_{\alpha 1}$ 13 614 eV (interference with Sr- K_{β})



Beam size $29 \times 24 \mu\text{m}$
Steps of $50 \mu\text{m}$, int time 500 ms

Imaging of uranium distribution

Conditions : 2 moules – 4 réplikas
2 L NatU : 5×10^{-5} M
12 jours
Villefranche-sur-Mer



Diffuse distribution, no condensed form

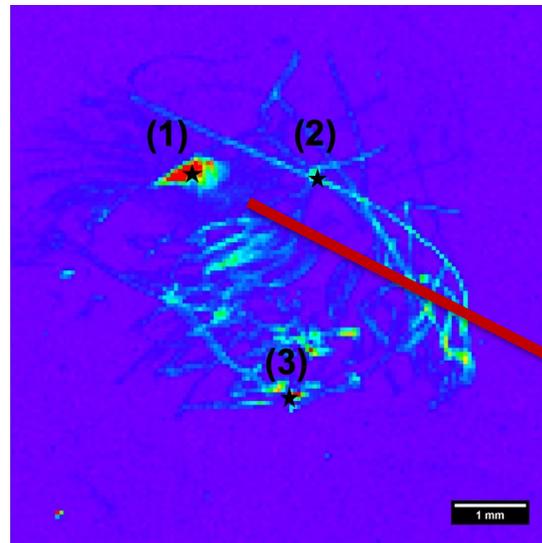
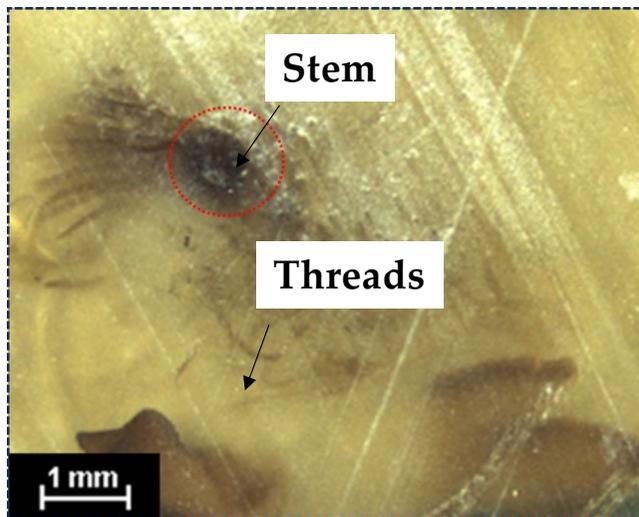
Byssus

μ -XRF \rightarrow U L_{II} edge at 20 948 eV

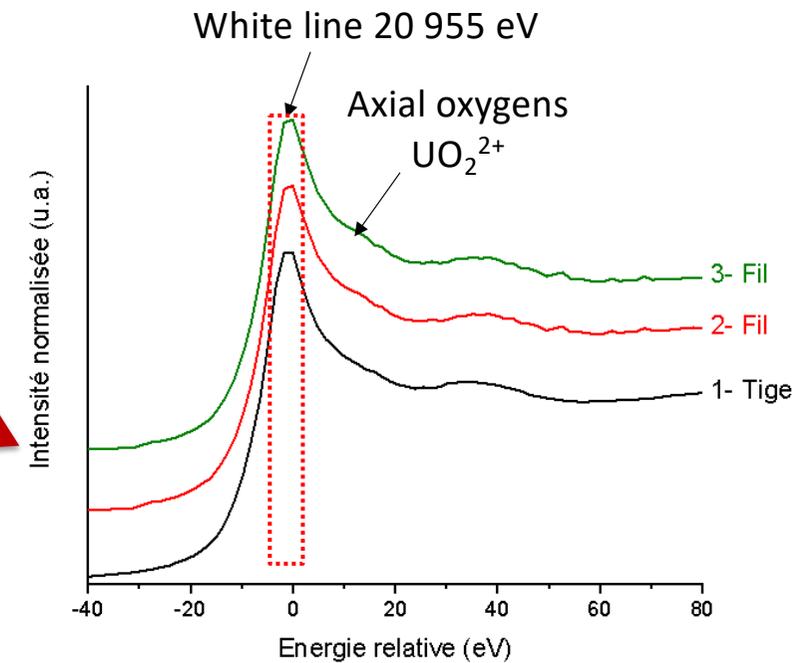
$L_{\beta 1}$ 17 220 eV

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Conditions : 2 moules – 4 répliques
2 L NatU : 5×10^{-5} M
12 jours
Villefranche-sur-Mer



Beam size $29 \times 24 \mu\text{m}$
Steps of $50 \mu\text{m}$, int. time 500 ms



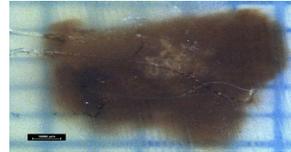
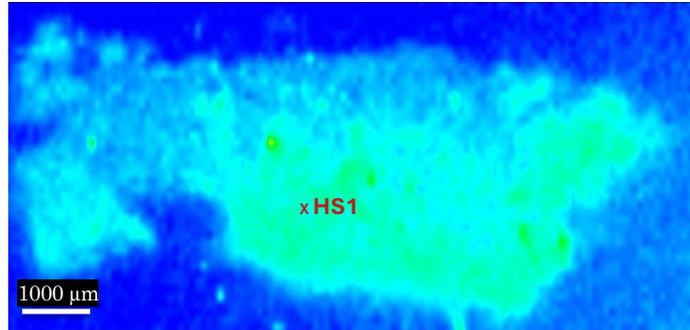
Distribution along the threads

Cs(I)
Cs(I)

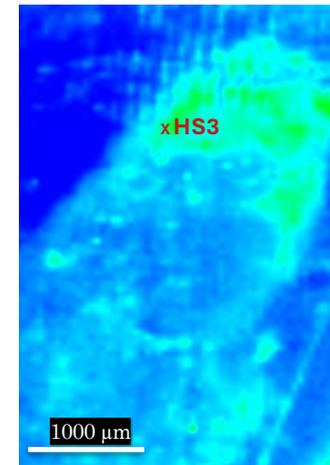
5. Cesium, speciation and transfer in seawater

μ -XRF analysis of ^{133}Cs at
 Cs-L_{III} edge (5012 eV)

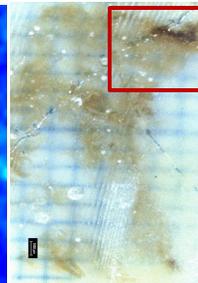
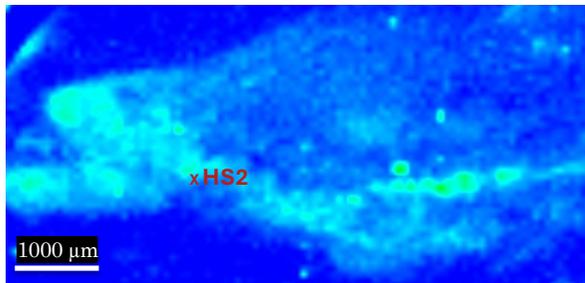
Digestive gland



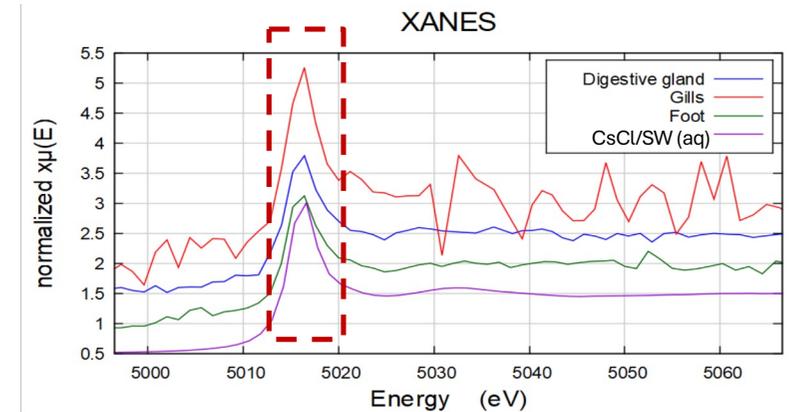
Foot



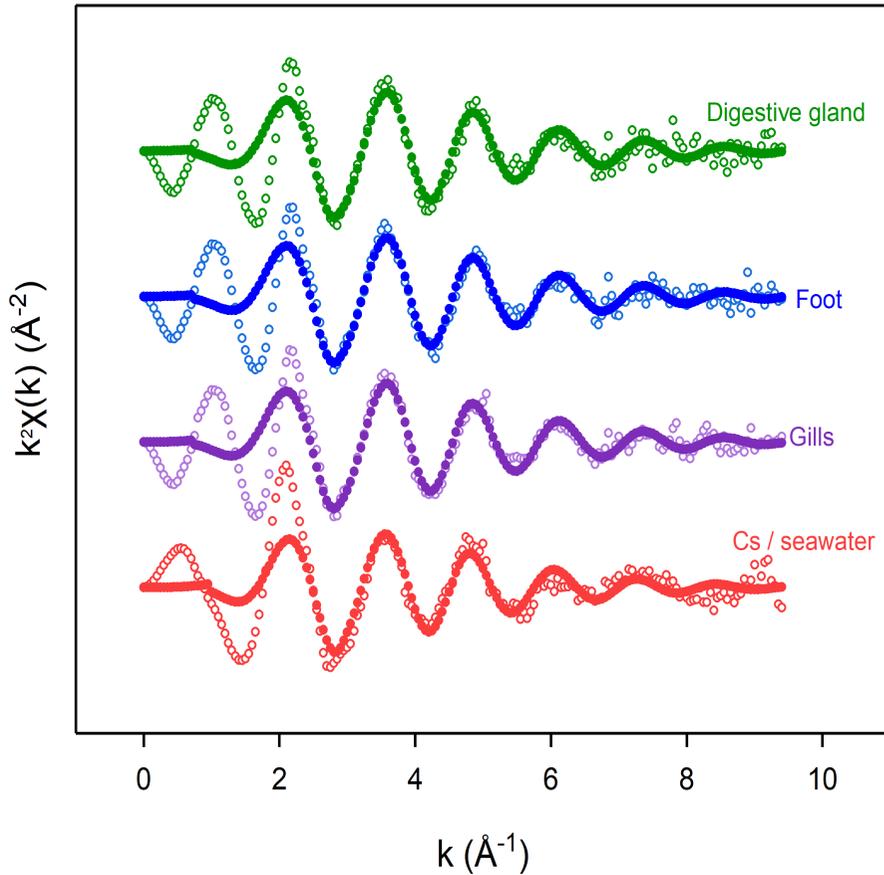
Gills



The presence of Cs was confirmed from
XANES spectra carried out on the hot
spots (**HS**) of mapped samples.



EXAFS analysis at Cs-L_{III} edge (5012 eV)



➔ Cs has the same speciation as in seawater.

- Same speciation in organs in first coordination sphere
- Coordination environment characterized by a single type of oxygen

• Cs in organs

Neighbour	CN	R
Cs-O	8	3.05 (1) Å

• Cs in seawater

Neighbour	CN	R
Cs-O	8	3.02 (3) Å

- Prediction of interaction with organisms, accumulation and toxicity.

6. Summary

From "tracer scale"

to

"spectroscopic scale"

Example from a soil column

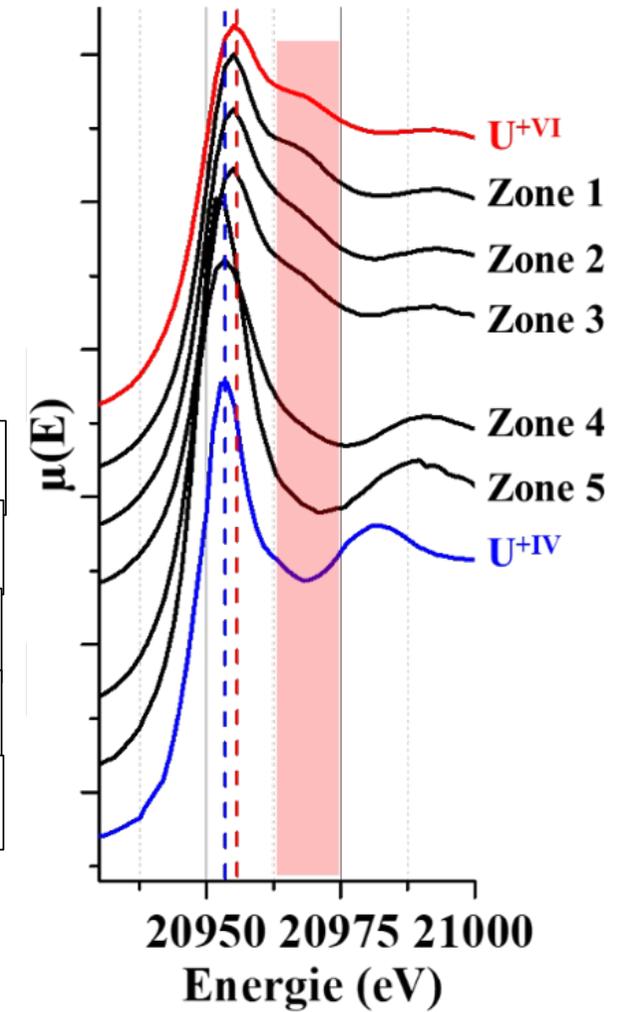
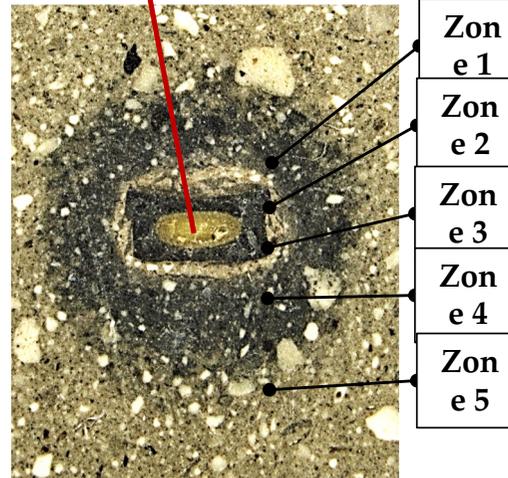
1) Isotropic diffusion around the U source

2) Presence of a depletion zone around the source

3) Migration of U further away from the source

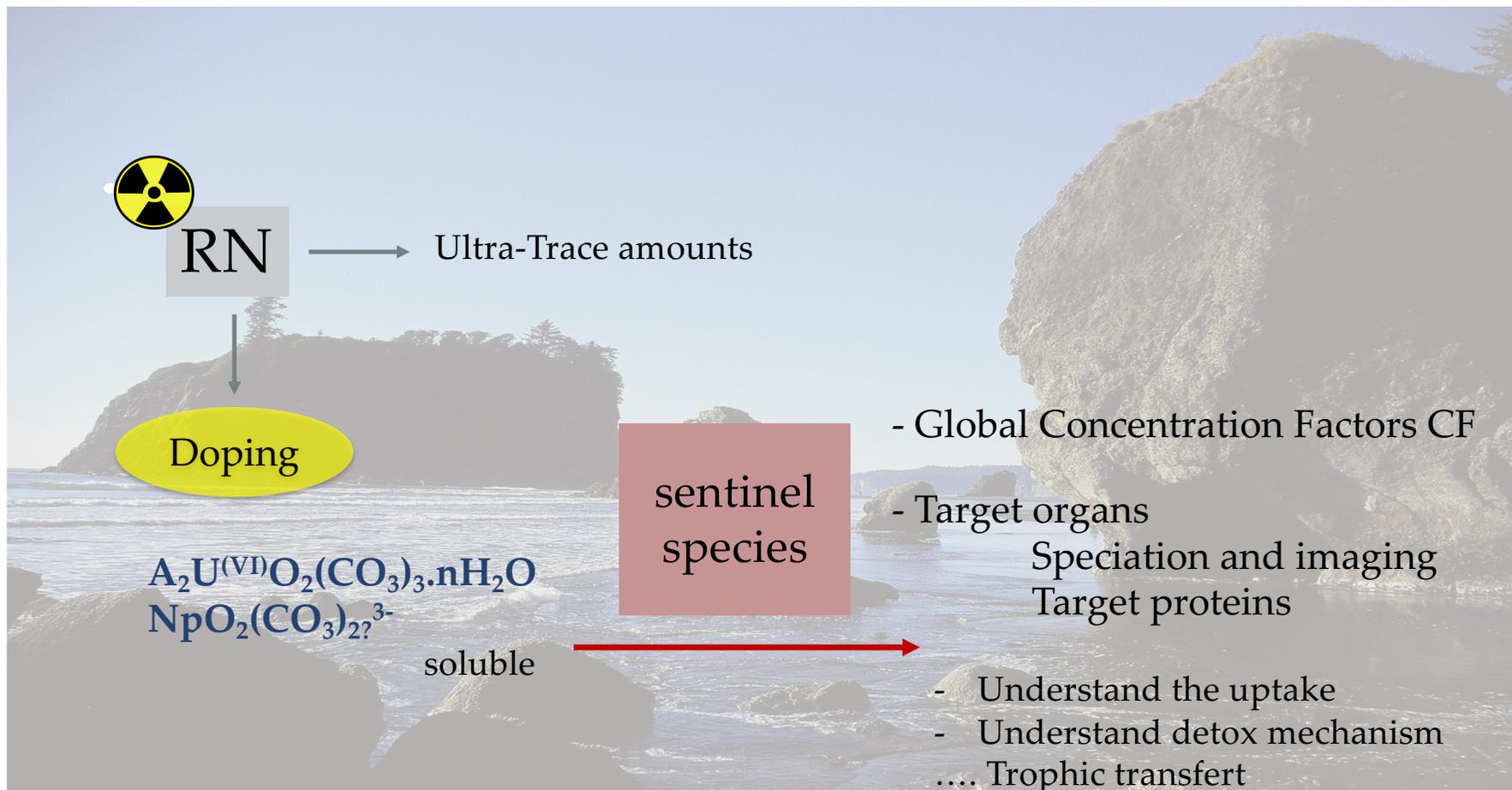
Natural soil

Metaschoepite
 $UO_2(OH)_2$



Réduction of uranium to U(IV)

Shift from global approaches to “mechanistic radioecology”^(1,2)



(1) M. R. Beccia et al. ChemPlusChem (2022), 87, e202200108

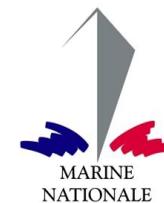
(2) J. Aupiais et al. STOTEN (2024), 935, 173247



Damien Prieur
Kristina Kvashnina



Pier-Lorenzo Solari



LASEM

Françoise Vernier



N. Belkessa [1], Ana Plasajec [1], R. Stefanelli [1], S. Bayle [1,2], M. Maloubier [1,3], B. Reeves [1], M. R. Beccia [1], A. Jeanson [1], Anne-Laure Faure [4], J. Aupiais [4], M. Monfort [4]

[1] Université Côte d'Azur, CNRS, ICN, Nice, Fr

[2] now Commissariat à l'Energie Atomique, DES Marcoule, Fr

[3] now IJCLab, Orsay, Fr

[4] Commissariat à l'Energie Atomique, DAM DIF, Fr



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