

Spéciation de l'uranium dans les écosystèmes marins : du modèle à la réalité

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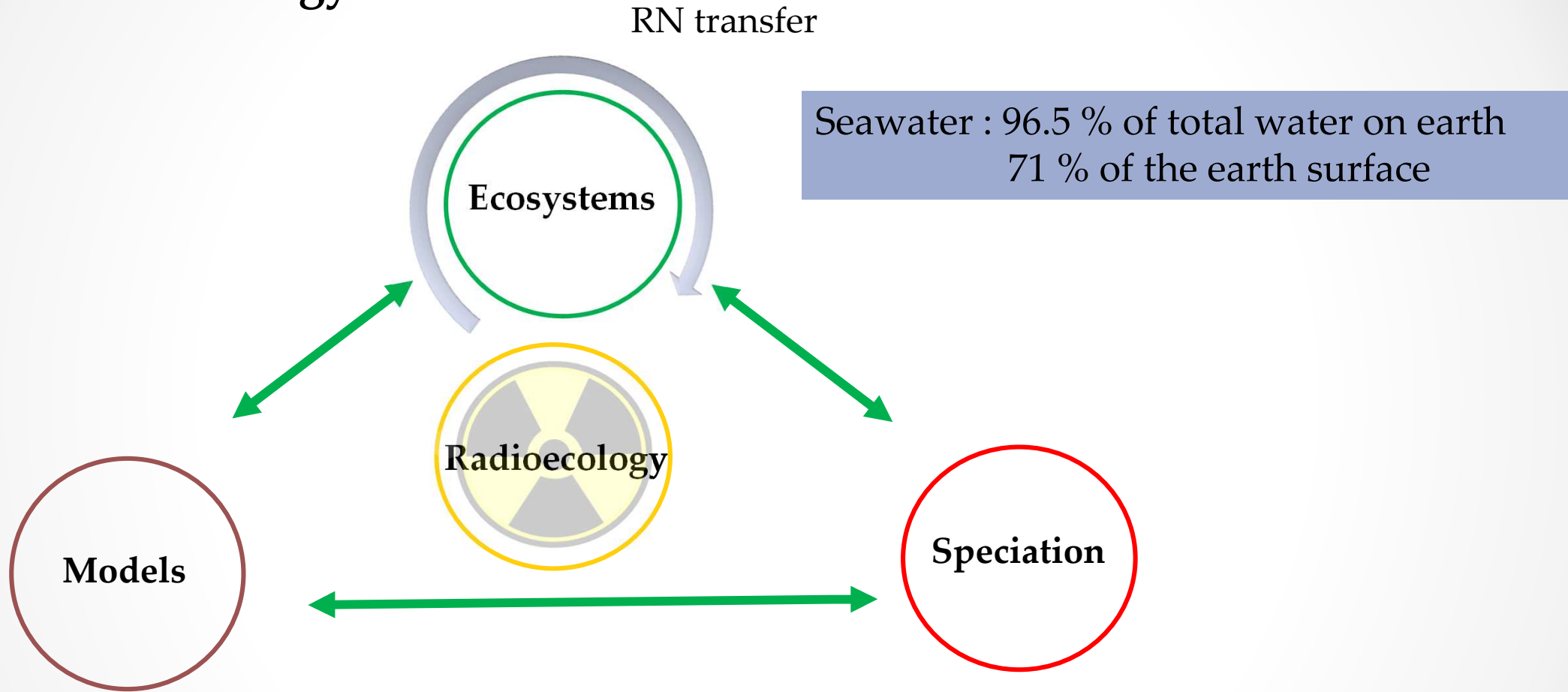
[6] Lawrence Berkeley National Laboratory, Chemical Sciences Division, Berkeley, CA94720, USA

\$ secondment at SGDSN, Paris, France

[7] Synchrotron SOLEIL, MARS beam line, 91047 Gif sur Yvette, France

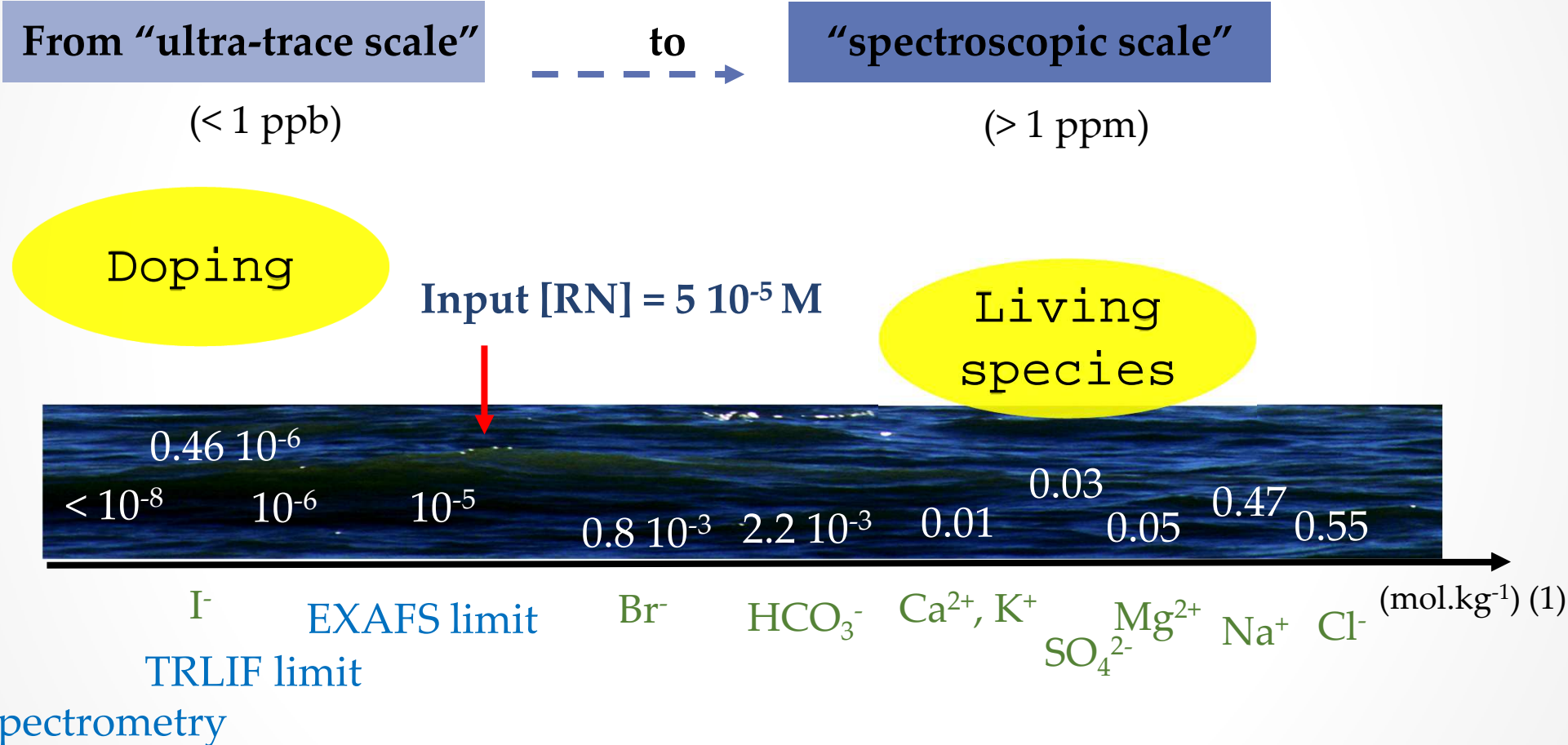
financial support : CEA DAM- DIF, DPN, ESPERAME project

Questioning chemical mechanisms in radioecology



Radioecology : A branch of ecology concerned with the problems of irradiation, radioactivity and contamination due to radioactive dispersion.

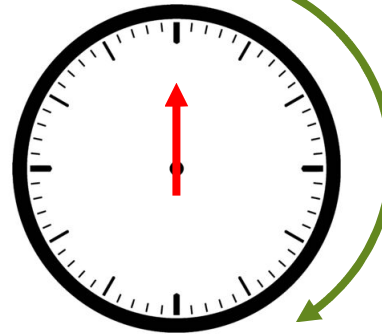
ulti-technique approach combining analytical
ols with spectroscopic tools and modeling



ps://www.mbari.org/science/uppe-ocean-systems/chemical-sensor-
/periodi-table-of-elements-in-the-ocean/

Sentinals species : demonstrate the presence of bioavailable contaminants and the extent of exposure⁽¹⁾

Spike at day 1



Duration of the experiment

Doping

RN

Semi-natural systems

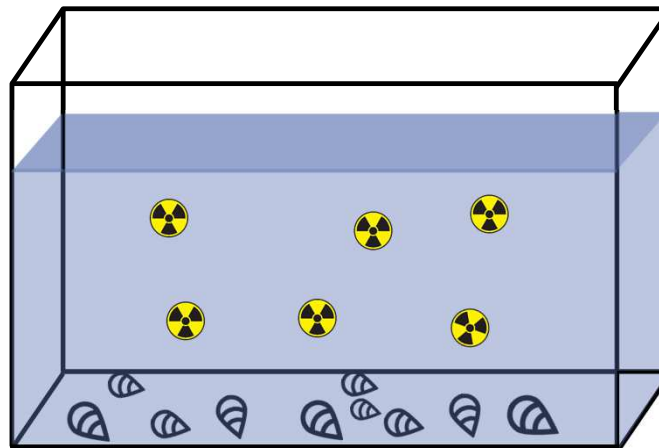
Water samples

Species

Monitoring the uptake

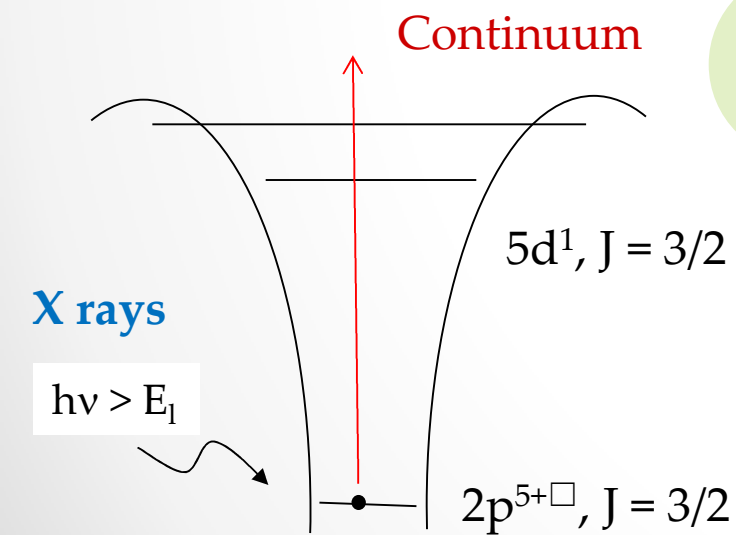
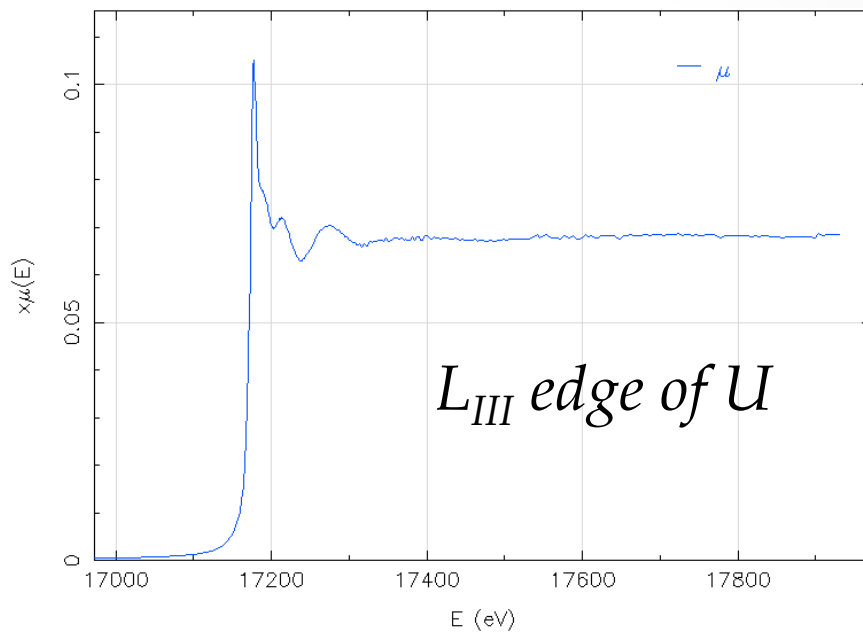
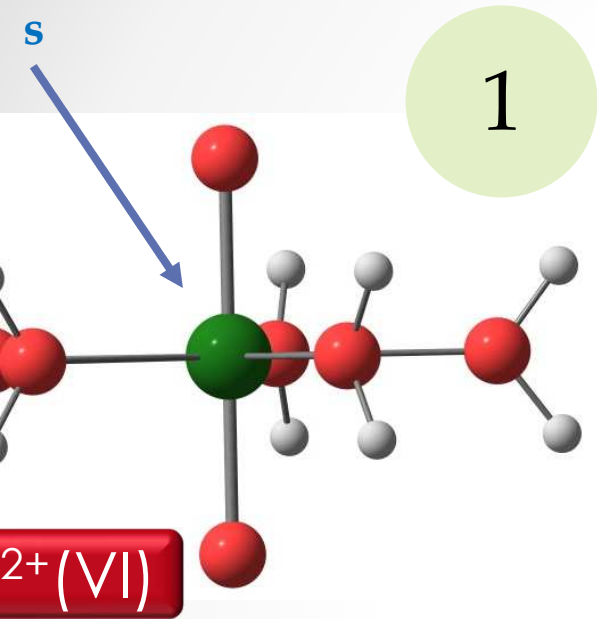
Living species
Concentration of RN
in the organs
Speciation
Imaging

Concentration of RN in
seawater
ICP-MS
 γ spectrometry



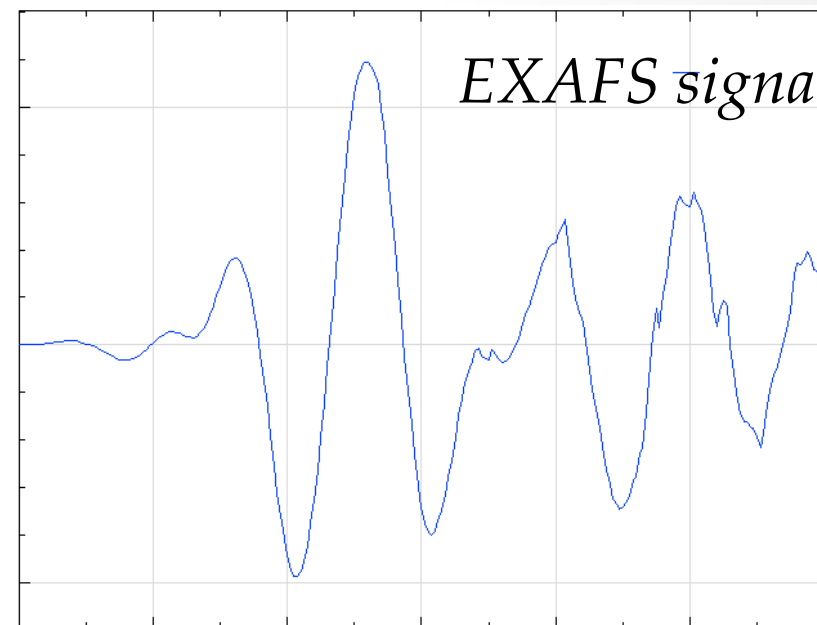
Concentration Factor $CF = \frac{\text{concentration in organism (mg.kg}^{-1}, dw)}{\text{concentration in seawater (mg.kg}^{-1})}$

hrotron based X-ray Spectroscopy



L_{III} edge

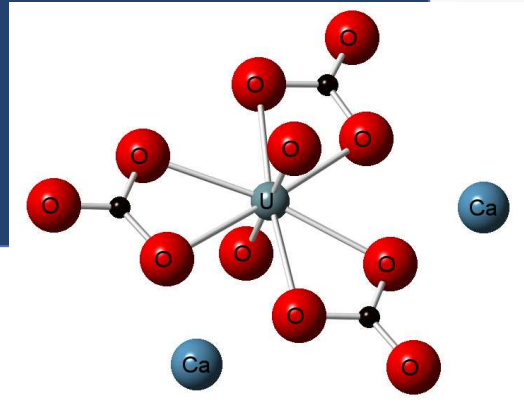
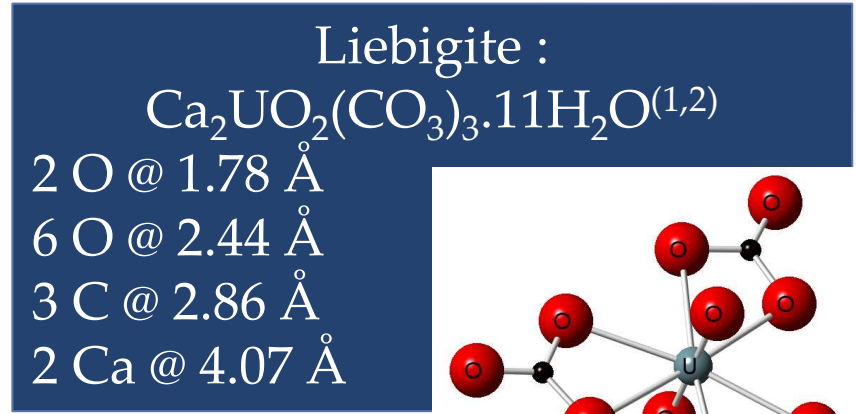
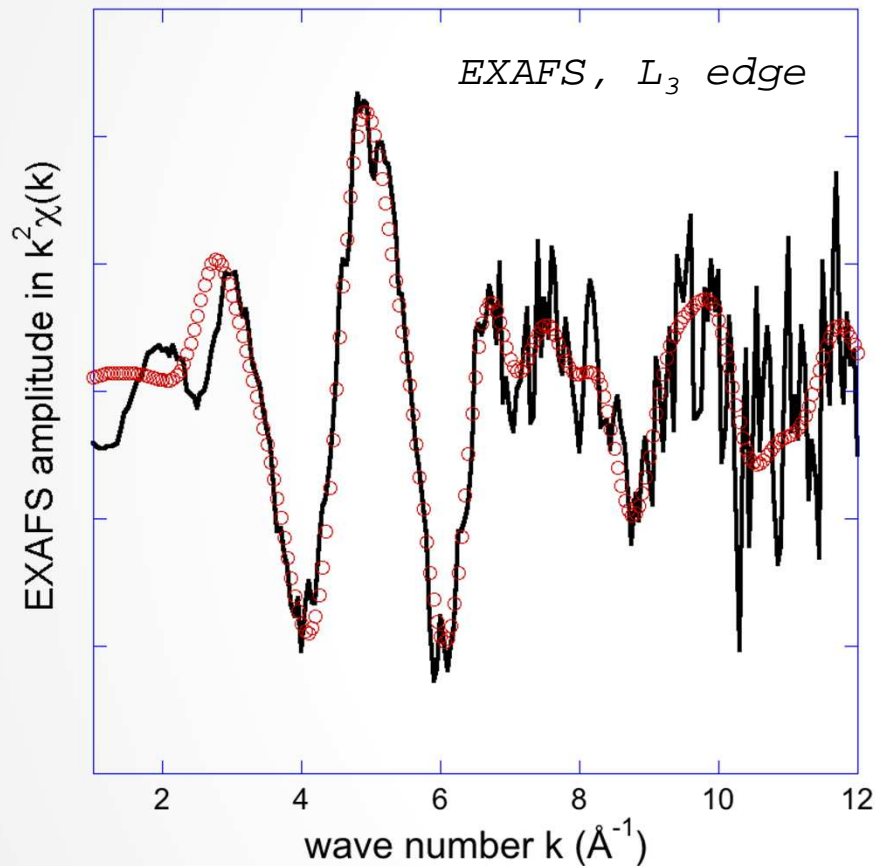
Fingerprint of the uranium coordination sphere



Uranyl(VI) speciation in seawater

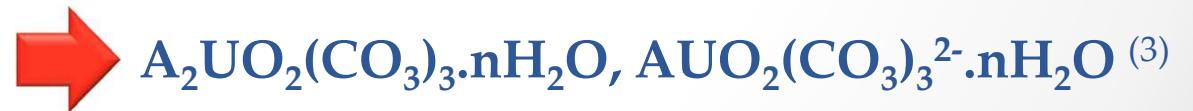
$\text{UO}_2^{2+}(\text{VI})$

Sea water, input $[\text{U}] = 5 \cdot 10^{-5} \text{ M}$



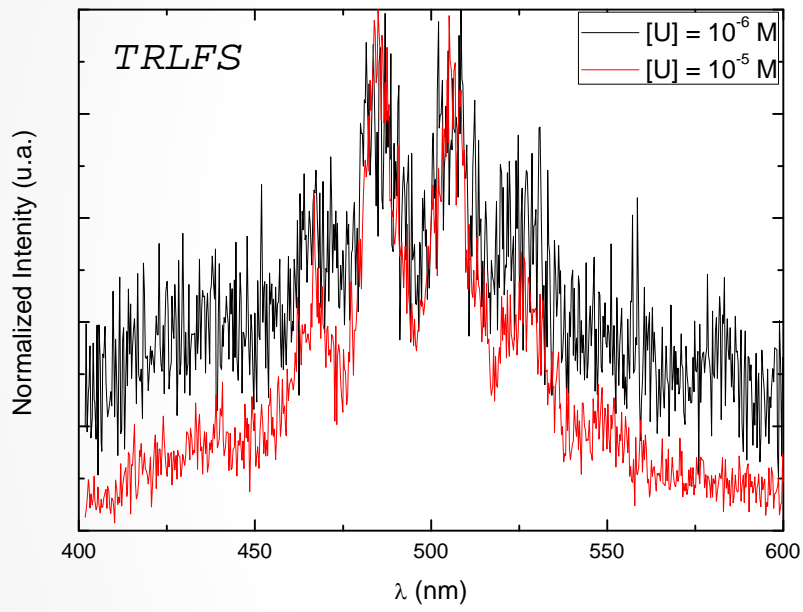
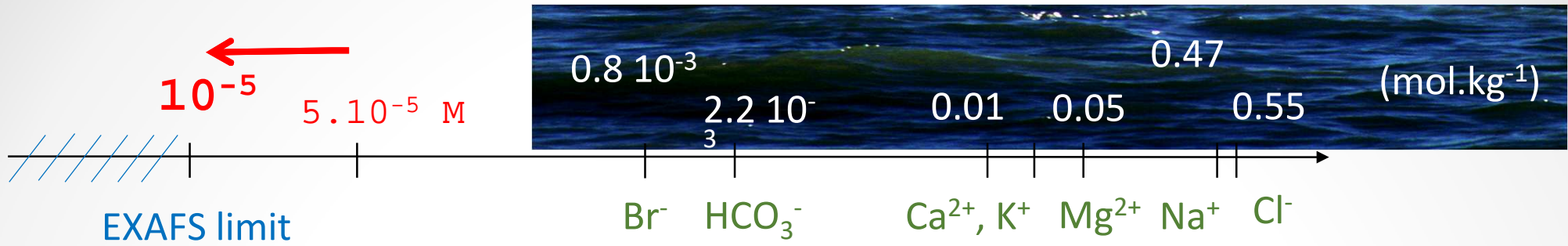
2 U - O_{ax} at 1.80(1) Å, $\sigma^2=0.0013 \text{ \AA}^2$
 5.8(5) U - O_{eq} at 2.43(1) Å, $\sigma^2=0.095 \text{ \AA}^2$
 2.9(3) U...C at 2.90(1) Å, $\sigma^2=0.0060 \text{ \AA}^2$

$S_0^2 = 1.0$, $e_0 = -1.70 \text{ eV}$, R-factor = 1.5%

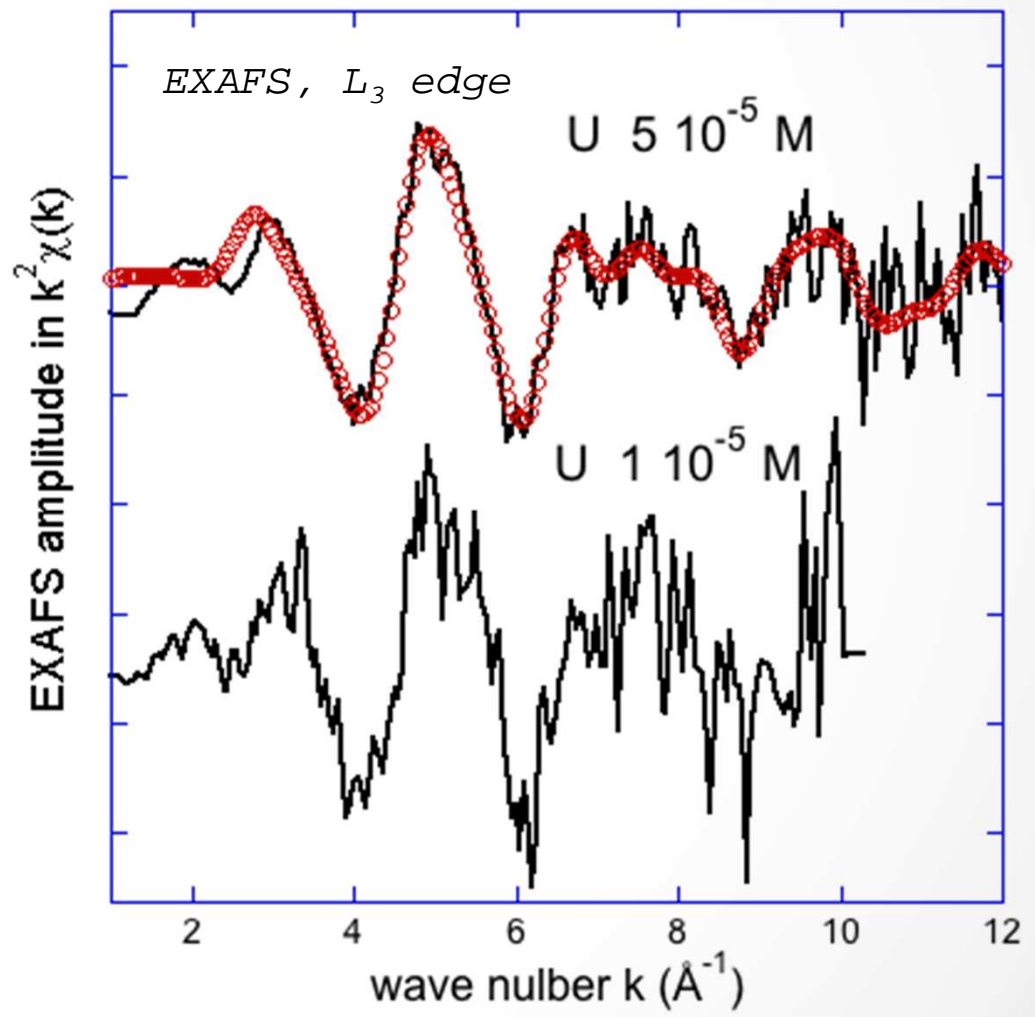


A = Ca^{2+} , Mg^{2+} etc..... (probed with A EXAFS)⁽⁴⁾

ard et al. Radiochimica Acta 74, 87 (2001)
 et al. Geochim. Cosmo. 71, 821 (2007)
 aloubie et al., Dalton Trans (2015), 44, 5417
 Beccia et al. J. Env. Rad. 2017), 178-179, 343



➔ No difference in speciation



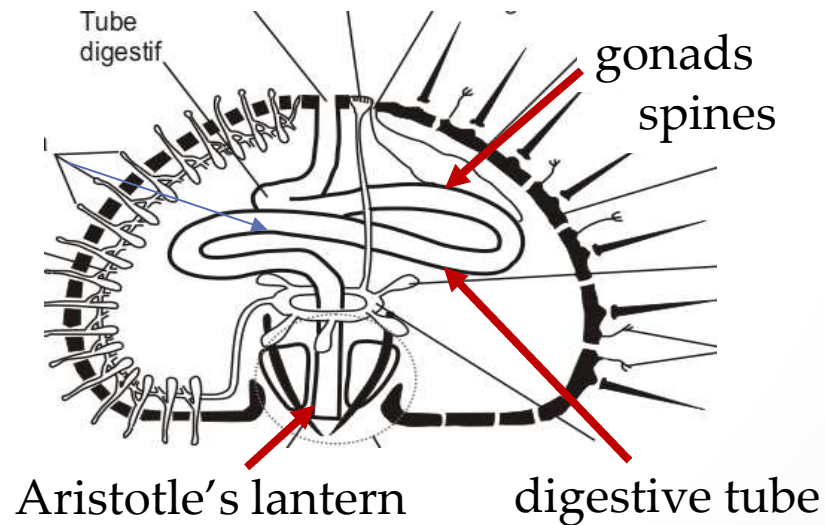
Echinoderms

UO₂²⁺ (V)



Sea urchin *Paracentrotus Lividus*

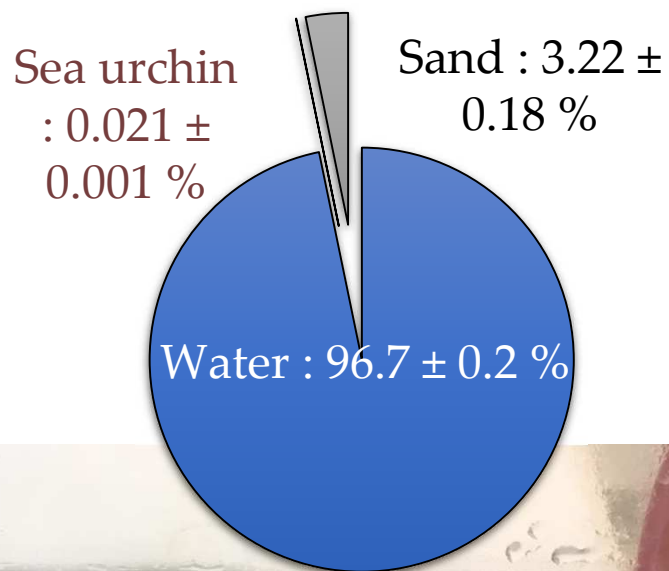
- ~ An ideal biological model
- ~ Have sedentary habits and well-known sensitivity to pollutants (2,3)



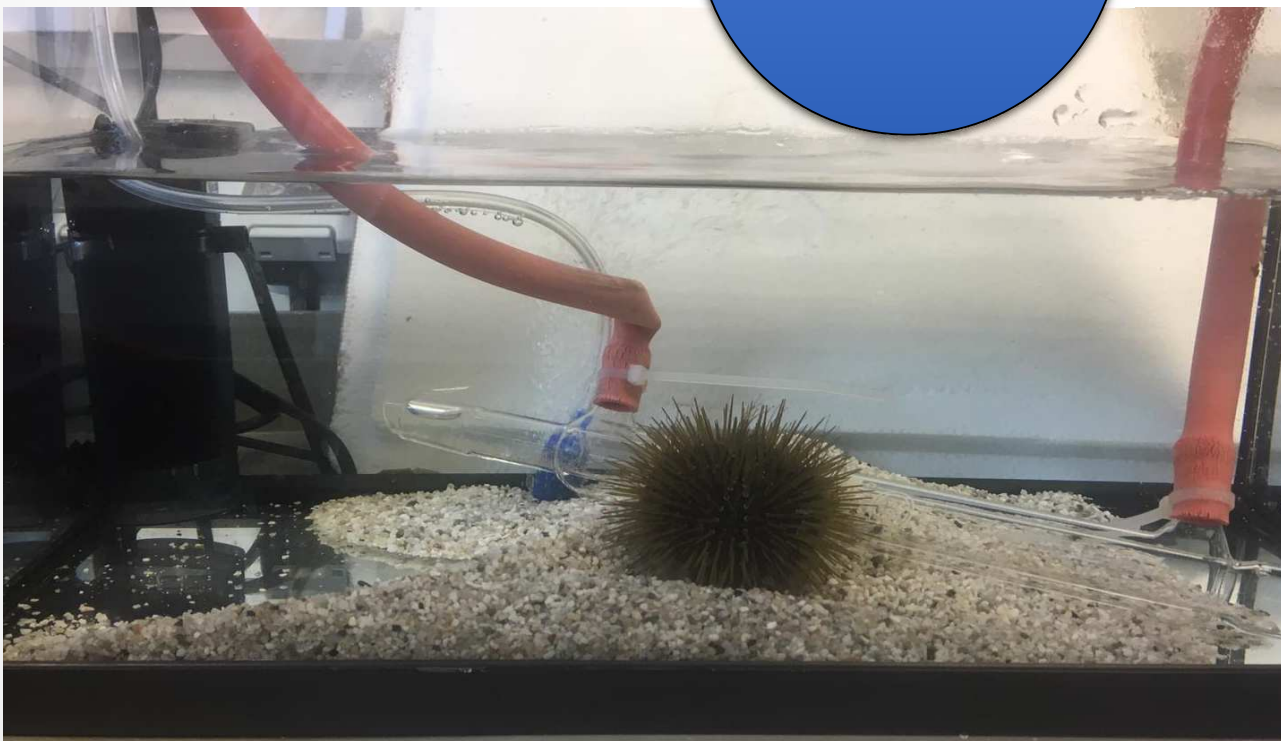
Tree of Life project <http://tolweb.org>
ualili et al. J Mar Sci 2008), 65, 132.
arnau et al Journal of Sea Research (1998), 39, 267.

Methodology

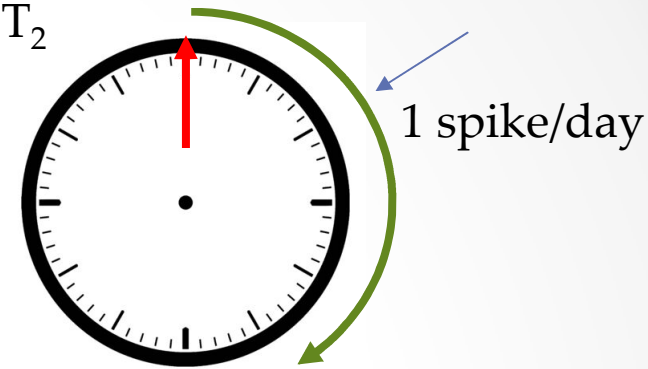
U distribution (mass)



Total = 10 L, 750g of sand
T = 16 °C

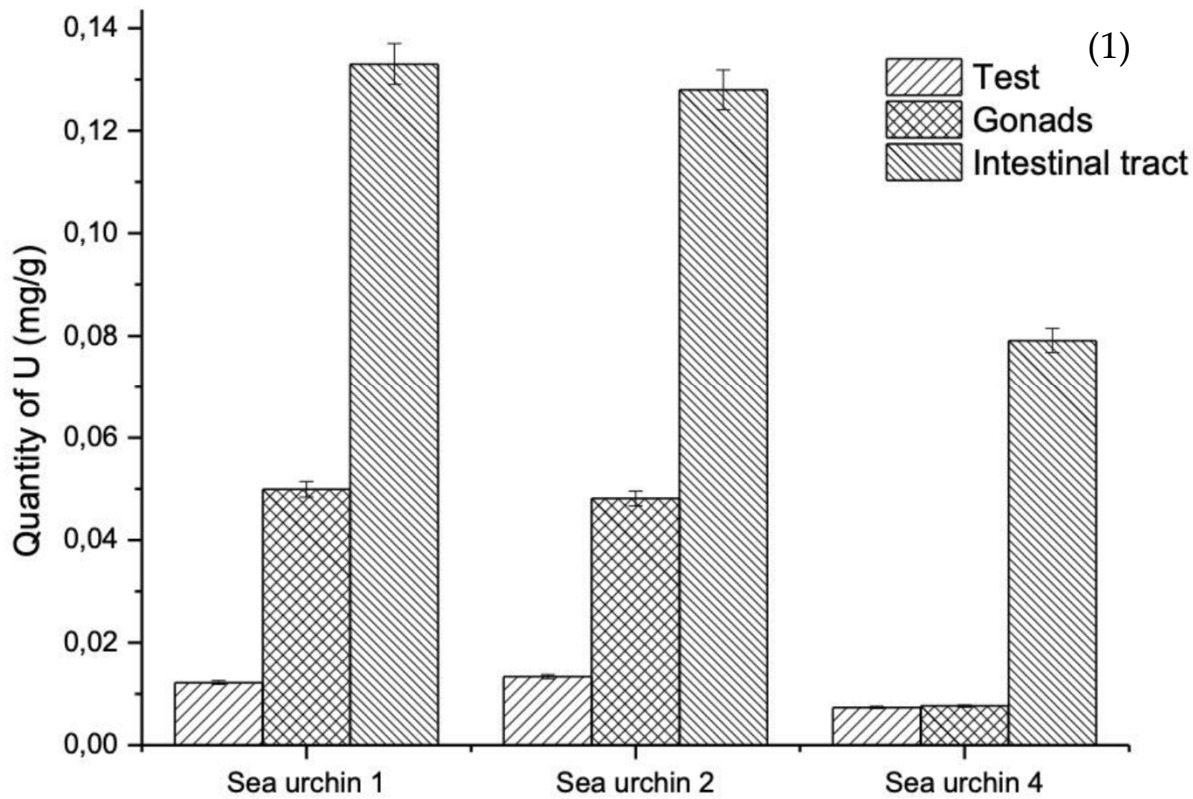


T_0 spike1 = 47.6 mg d'U
 T_1 24h spike2 = 47.6 mg d'U
 T_2



10 days

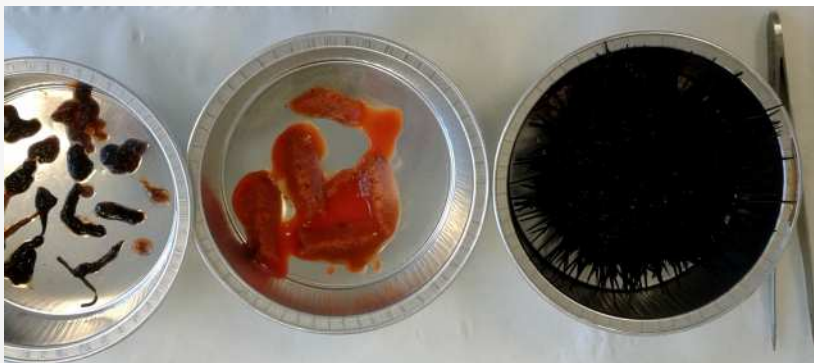
$$\int_0^{10T} [U] = 1.9 \times 10^{-4} M$$



Intestin >> gonads >> test

U in mg.g⁻¹, dry weight

Comparison : *Paracentrotus lividus*, Calvi⁽²⁾

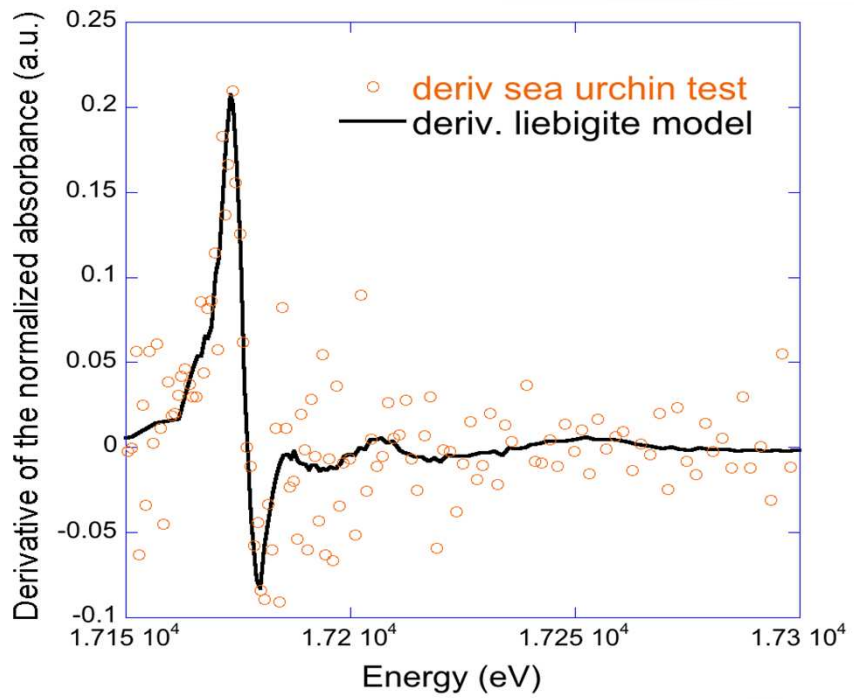
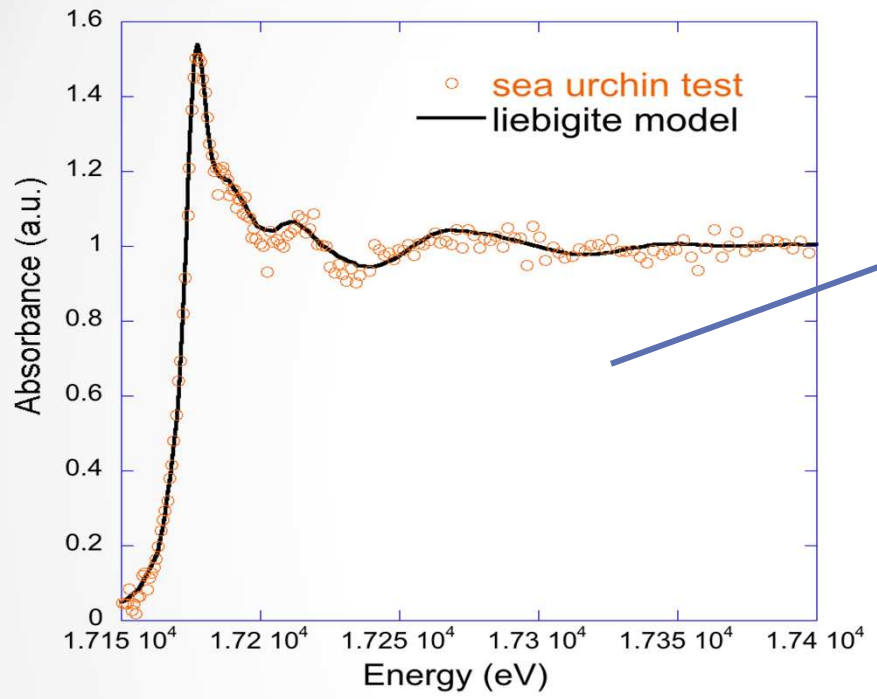


	Fe	Zn
Test	4.4 µg/g	3.8 µg/g
Gonads	47 µg/g	161 µg/g
Digestive tubes	139 µg/g	70 µg/g

Reeves et al. ES&T, 2019), 53, 7974-7983

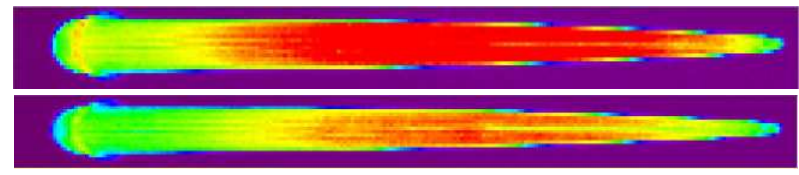
. Warnau et al. The Sci. Total Environ. 1995), 171, 95

Test, about 10 ppm of U



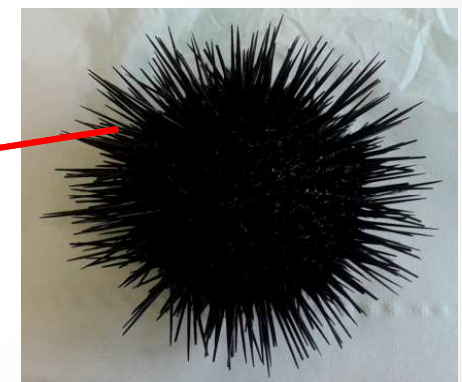
XANES, L_{III} edge

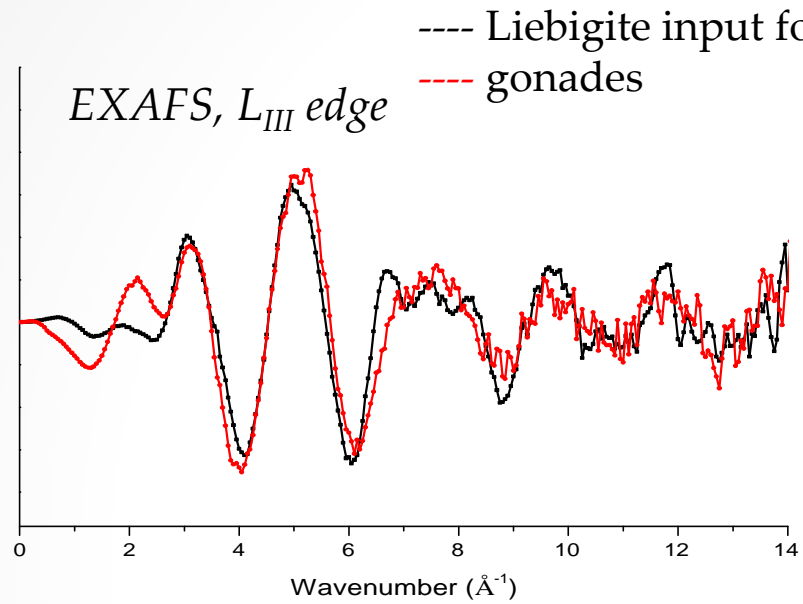
XRFmap



1 pixel = 50 μ m

XRFmap, $K\alpha$ of Sr (17100 eV)
before and after U edge (17166 eV)



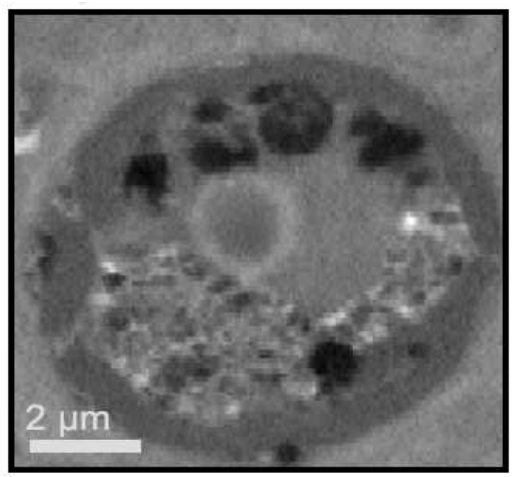


About 50 ppm of U

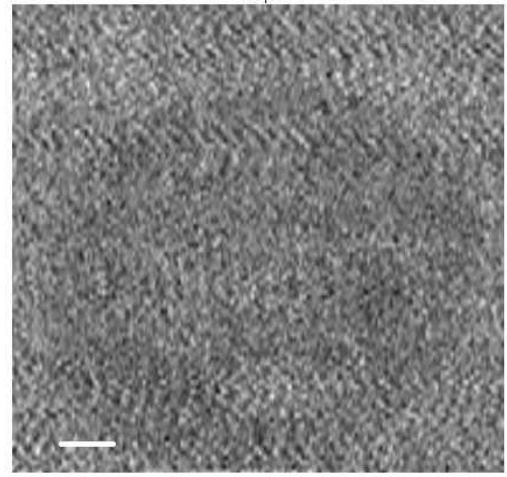


Change of speciation.
 Complexation by major protein ?

STXM, N_{IV} edge



Low contrast in the cell wall

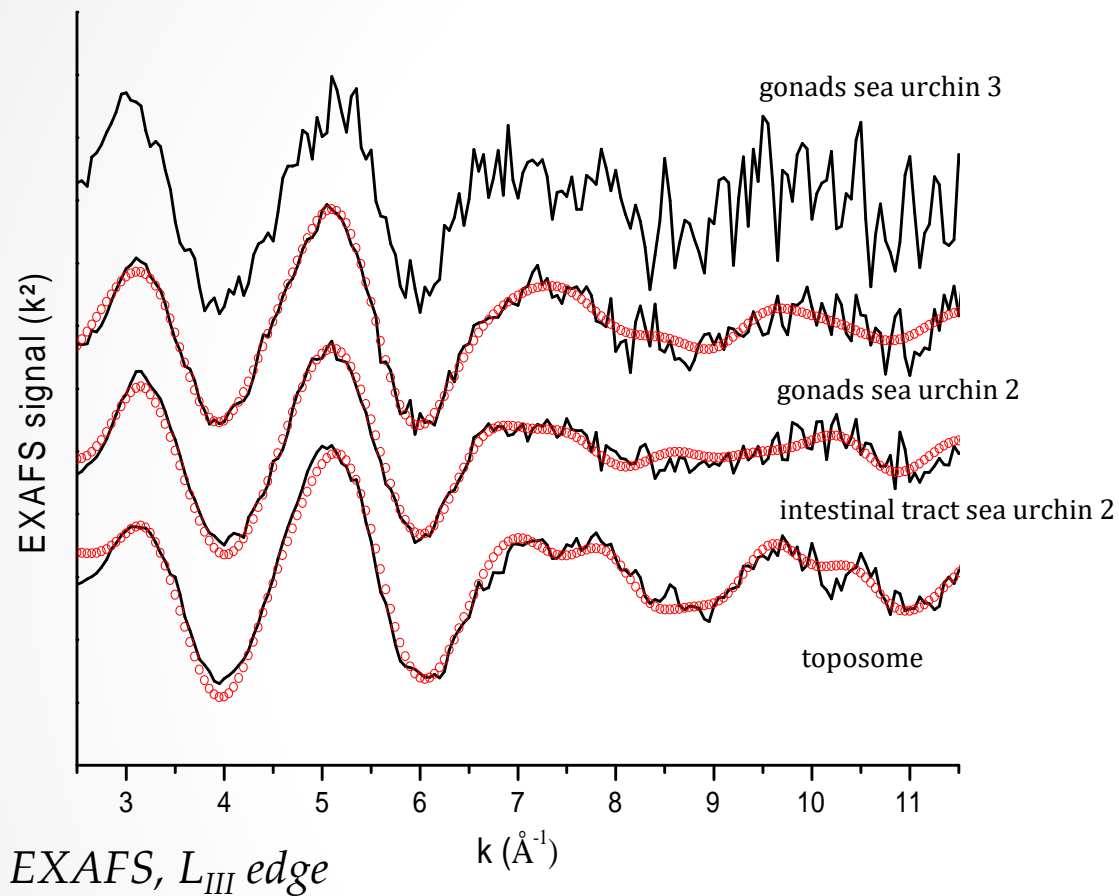


Contrast image before and after the edge N_{IV} of uranium ($E = 725 \text{ eV}$ et 738 eV respectively)

Toposome

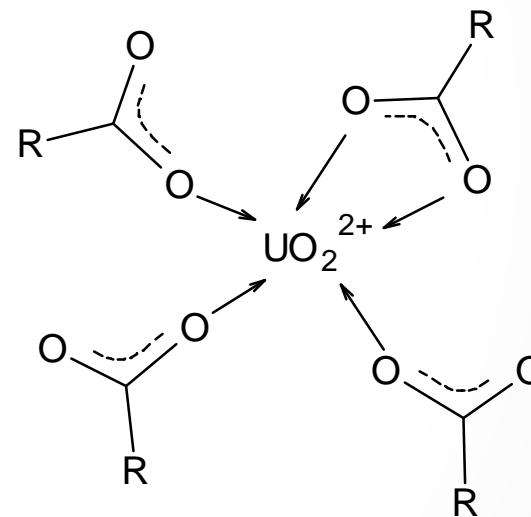
→ Over 30% of the amino acids of the protein are carboxylic-based⁽¹⁾

Comparison, gonads, intestinal tract, toposome⁽¹⁾



2 U – O_{ax} at **1.79(1)** \AA , $\sigma^2=0.003 \text{\AA}^2$
 5.1(3) U-O_{eq} at **2.37(1)** \AA , $\sigma^2=0.008 \text{\AA}^2$
 3.3(9) U...C at **2.94(3)** \AA , $\sigma^2=0.007 \text{\AA}^2$

$S_0^2 = 1.0$, $e_0 = 1.56 \text{ eV}$, R-factor = 1.6%



- Comparable chemical environment in gonads, intestinal tract and toposome
- On the average, presence of monodentate carboxylate groups

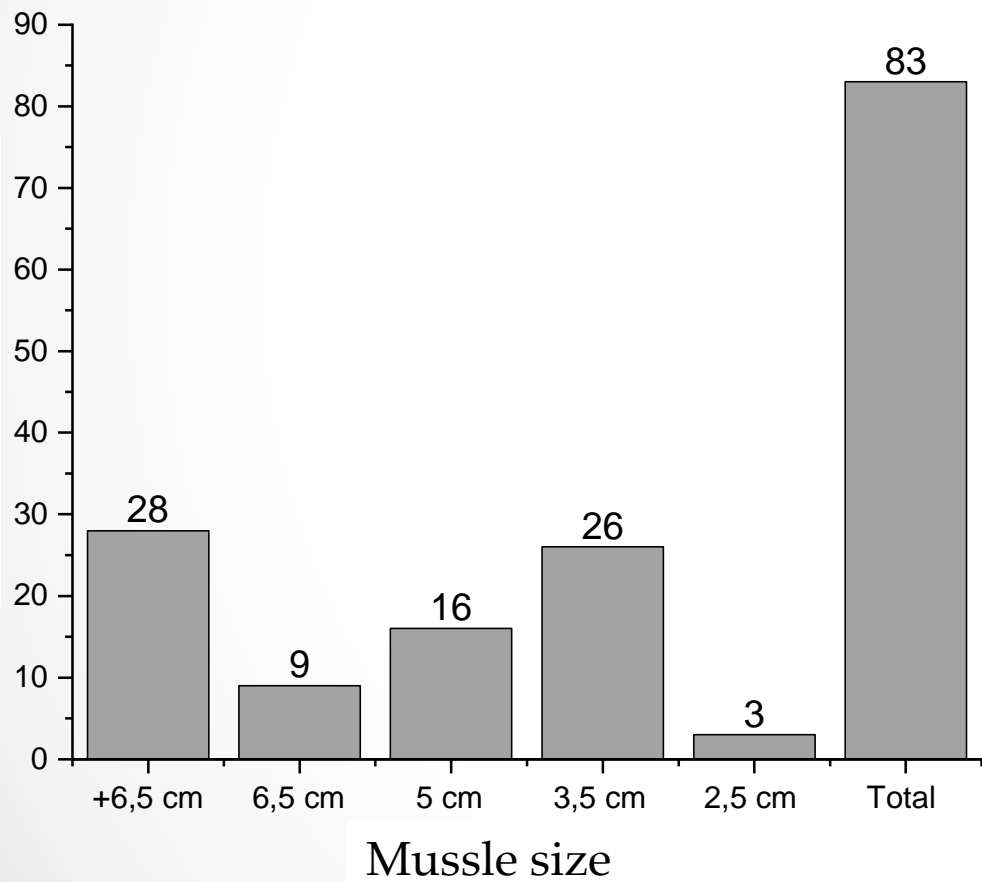


Mytilus Galloprovincialis

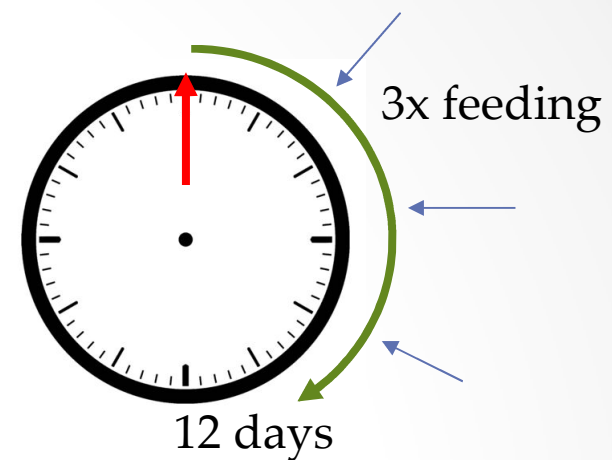
~ Widely used as a bioindicator for monitoring of coastal water pollution : mussel watch programs⁽¹⁾

Methodology

Cohorte of 83 mussels

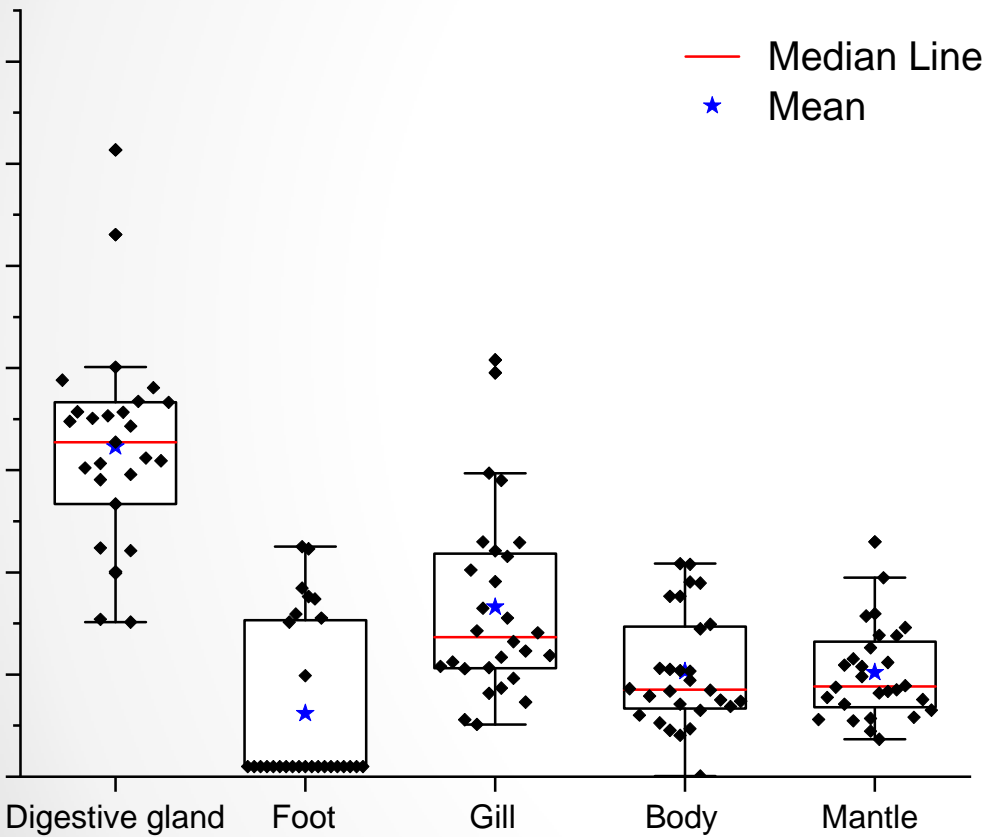


T_0 spike1 = 150 ppb U

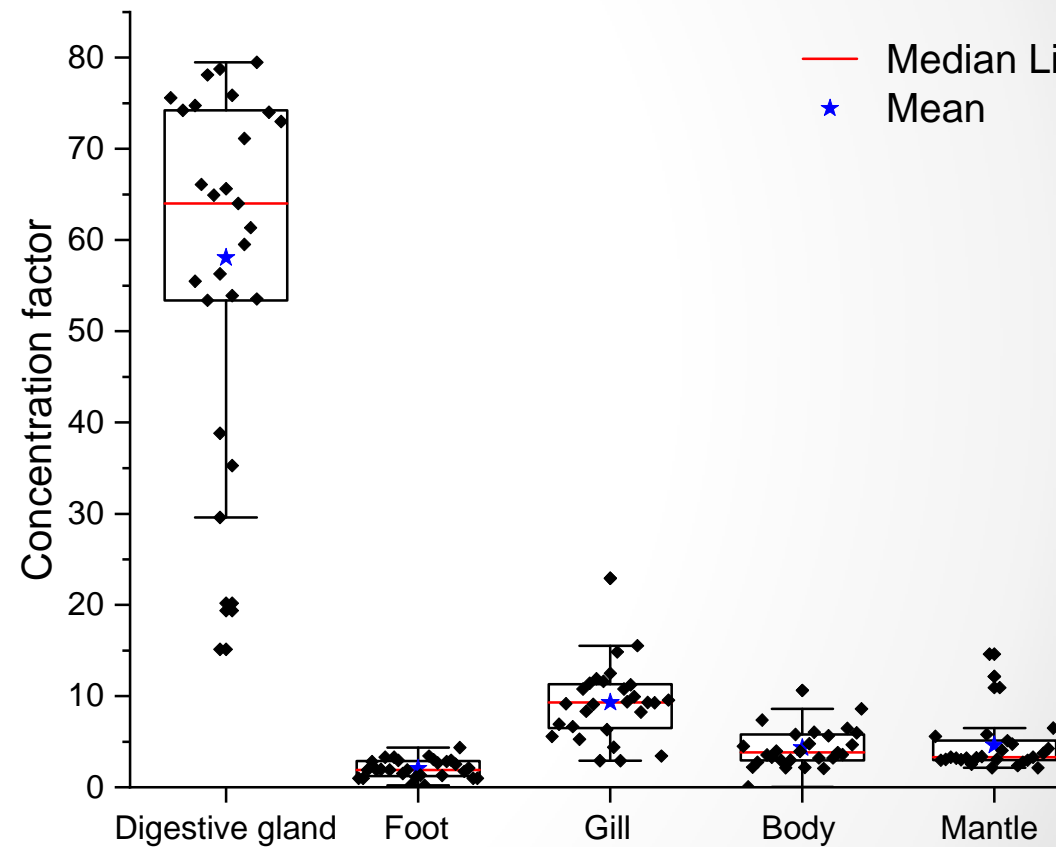


$$\int_0^T [U] = 6 \times 10^{-7} M$$

Mussels from the Villefranche area
(n=28)



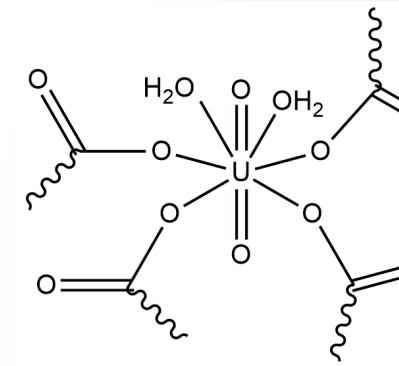
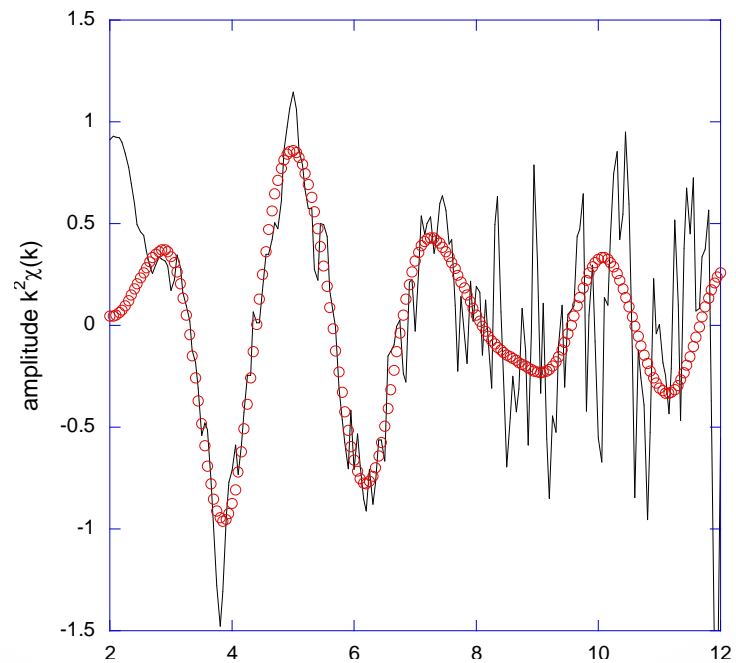
Mussels from Toulon naval base highly
polluted with heavy metals (n=24)



Byssus

- O_{ax} at $1.75(2) \text{ \AA}$, $\sigma^2=0.0001 \text{ \AA}^2$
- 2) $U-O_{eq}$ at $2.30(2) \text{ \AA}$, $\sigma^2=0.0015 \text{ \AA}^2$
- 3) $U-O_{eq}$ at $2.54(1) \text{ \AA}$, $\sigma^2=0.0019 \text{ \AA}^2$
- ...C at $3.19(16) \text{ \AA}$, $\sigma^2=0.0021 \text{ \AA}^2$

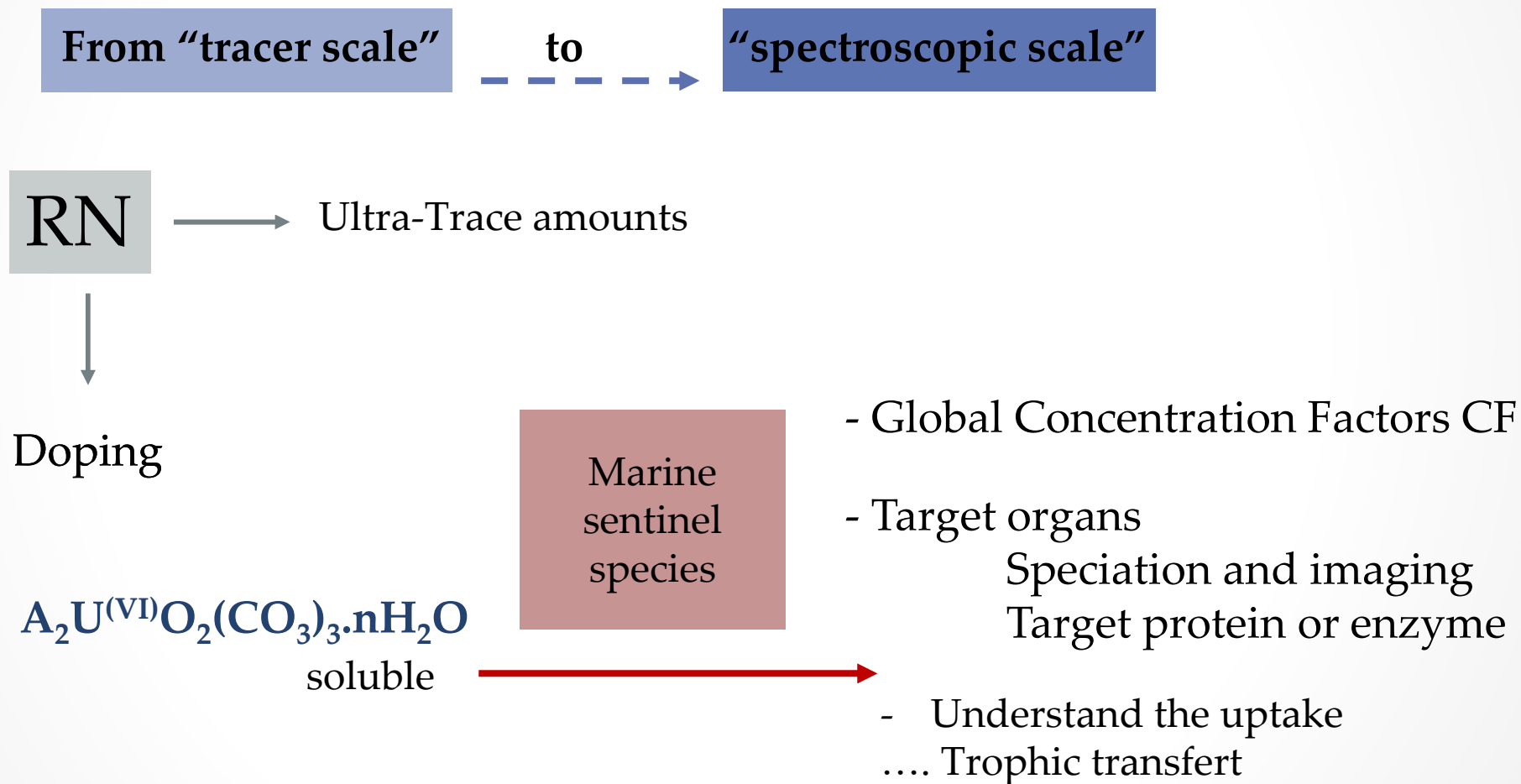
.0, $e_0 = -4.23 \text{ eV}$, R-factor = 2.9%



U-protein interaction with mainly monodentate carboxylates

Summary

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



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