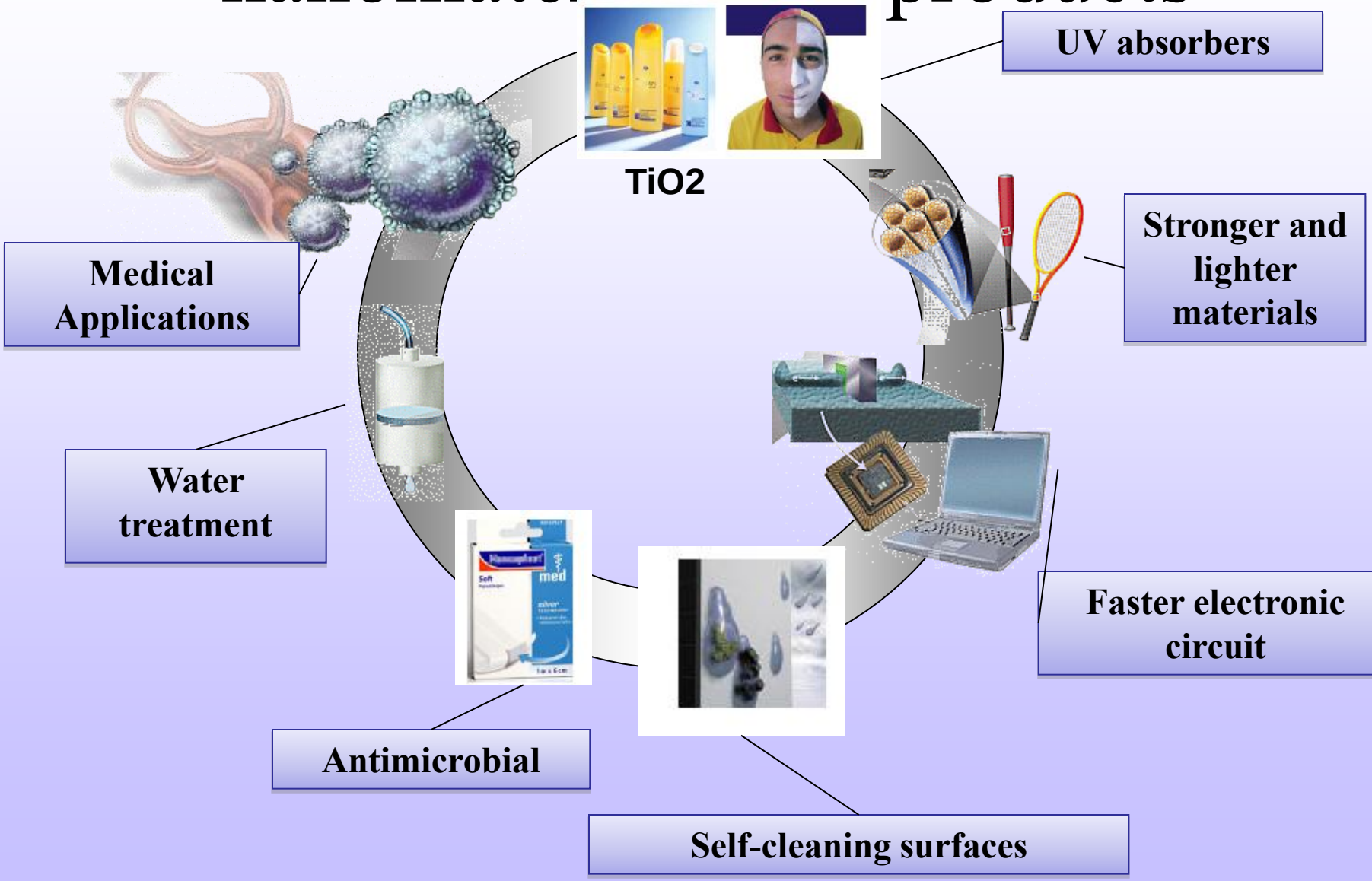
Nanomaterials: from cradle to grave or the need to study the life-cycle

J.Y. Bottero*$, A. Masion*$, C. Levard*$, N. Solovitch*$, M.A. Diot*$, M. Auffan*$, A. Thill$,& C. Botta*$, J. Labille*$, J. Rose*$, P. Chaurand*$, D. Borschneck*$, E. Doelsch*$, F. Ziarelli°; O Proux°°$, J.L Hazeman°°$

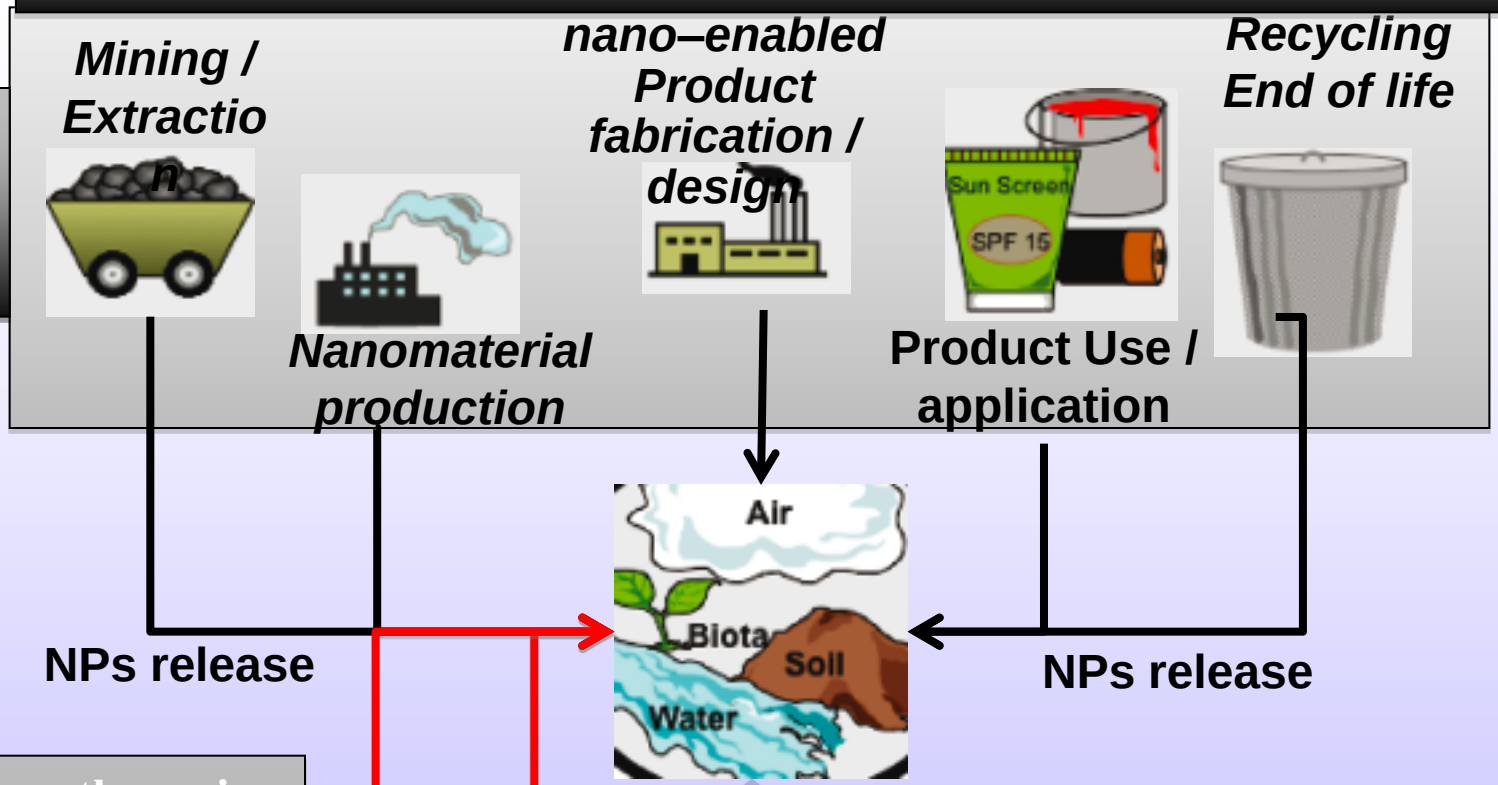
*** CEREGE UMR 6635 CNRS-Aix-Marseille Univ**
° Spectropole Aix-Marseille Univ
& LIONS-IRAMIS-CEA
°° ESRF-Fame
$ I-CEINT GDRI CNRS-CEA

Comercialized nanomaterial/nanoproducts



Perspectives: a complex approach

Life cycle



The water as the main agent of the alteration of the materials: several examples: C60, TiO_2, CeO_2

Hazard Identification

Exposure Assessment

Hazard Characterisation

Risk assessment

From Robichaud et al, 2009, ES&t

Nanos in the environment

- Mobility of the NPs

- **Surface chemistry**
- **Size and shape**

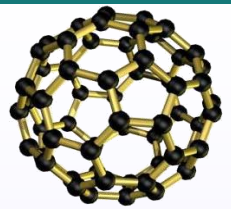
Speciation and reactivity ==➔ toxicity ?

Minor changes in physico-chemical conditions may alter significantly the mobility (e.g. aggregation)

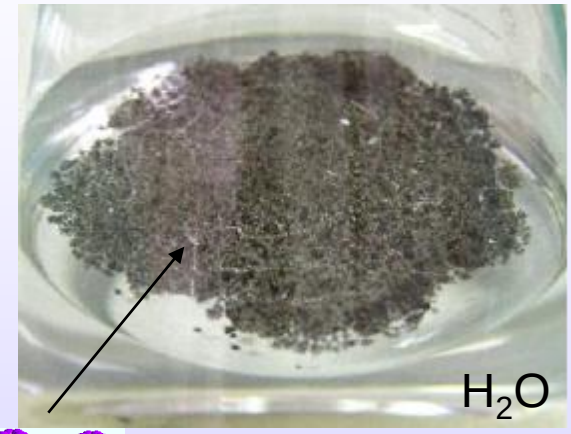
==> intrinsincally toxic NP may represent a moderate risk due to poor mobility .

CHARACTERIZATION of alteration mechanisms and chemical and physical properties of altered nanomaterials are a necessity for a RISK ASSESSMENT based on LIFE CYCLE

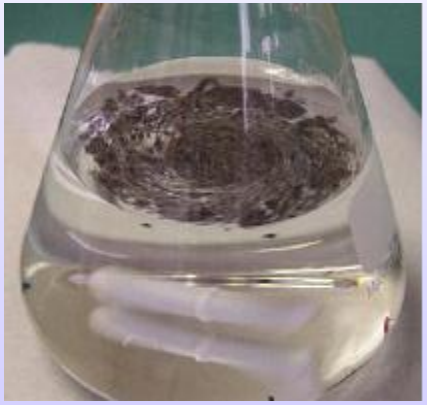
Fate of C60 fullerenes in water

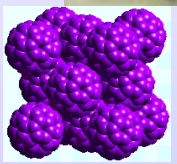


1 nm soccer ball, production of ROS $^1O_2$, $O_2^{\bullet -}$, $OH^{\bullet}$



stirring & patience

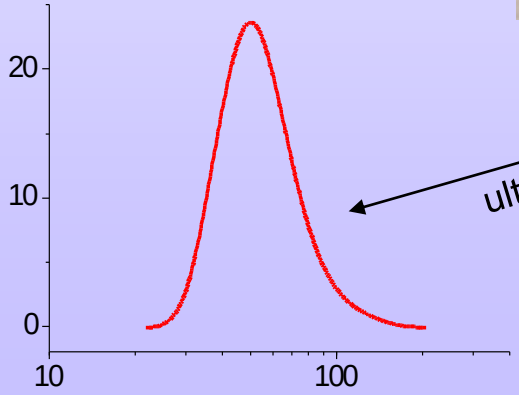




C60 fullerite

Hydrophobic

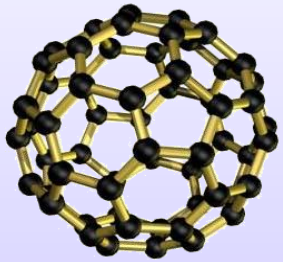
ultracentrifugation



stable suspension of nanosized crystallites (nC60)
40 nm

Fullerenes Hydroxylation under mild conditions

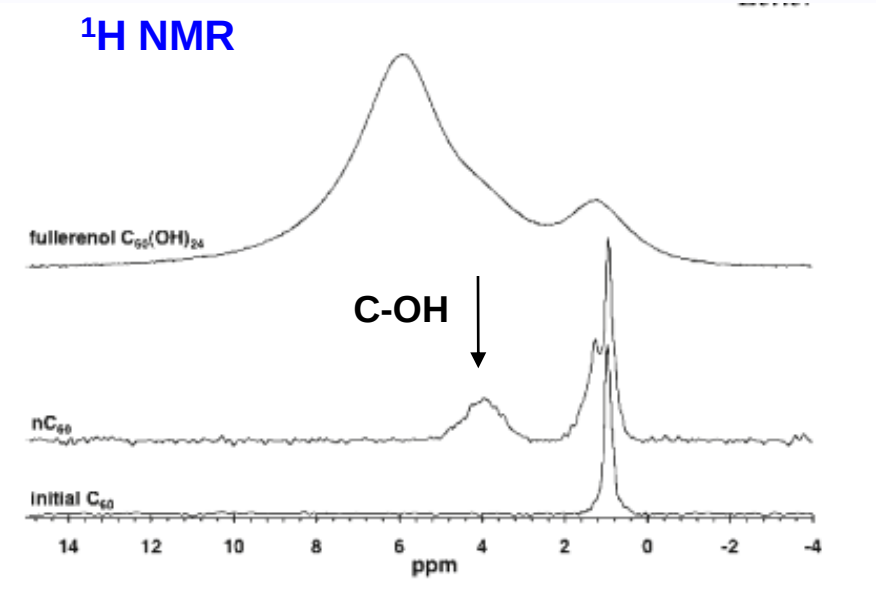
Fullerene

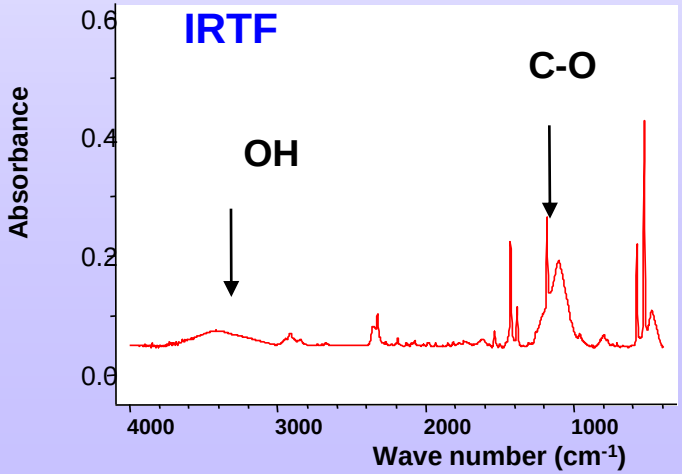


C_{60}

$+ H_2O$ →

Fullerol

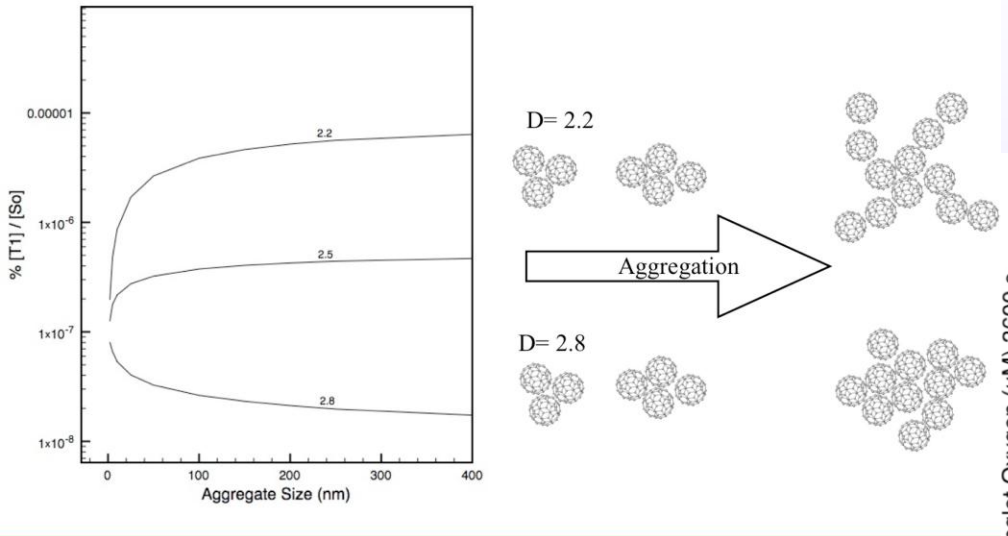




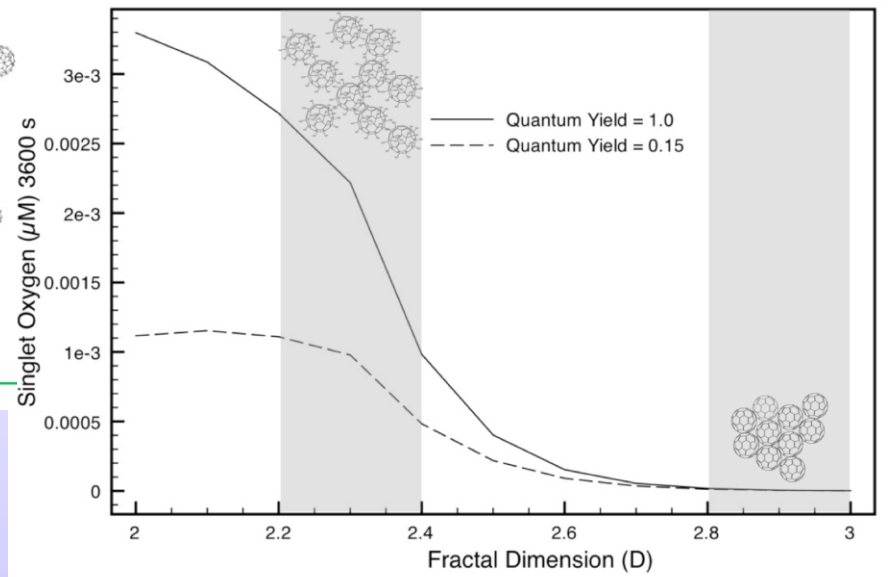
Hydrophilic C60
Mobile, bioavailable

Labille et al. Langmuir 2009

Effec of the aggregation on the singlet oxygen for fullerol and hydrated nC60



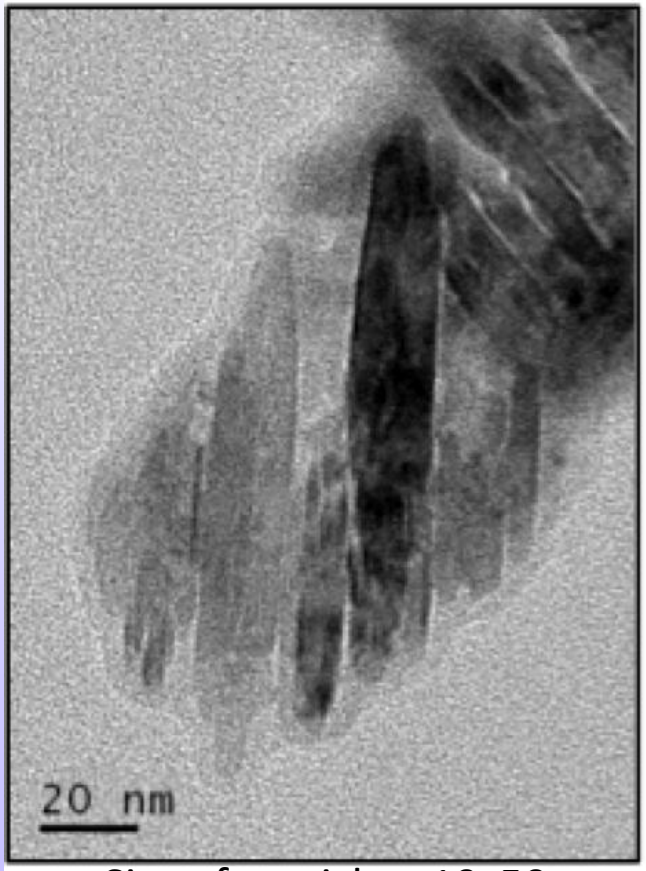
% triplet state of the C60 Nps vs fractal dimension D_f and number of C60 in the aggregates



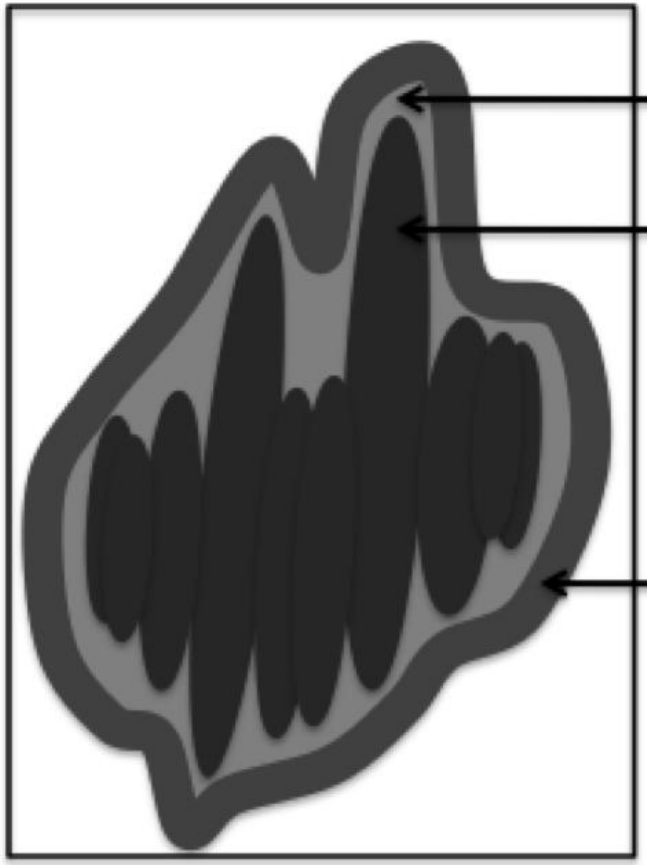
Production of singlet O for Fullerol and nC_{60} aggregates vs D_f

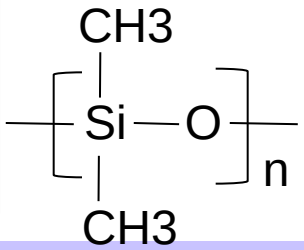
M Hotze et al, Langmuir Vol 26 issue 13 pp11170-11175

Fate of Titanium dioxide-based nanocomposite

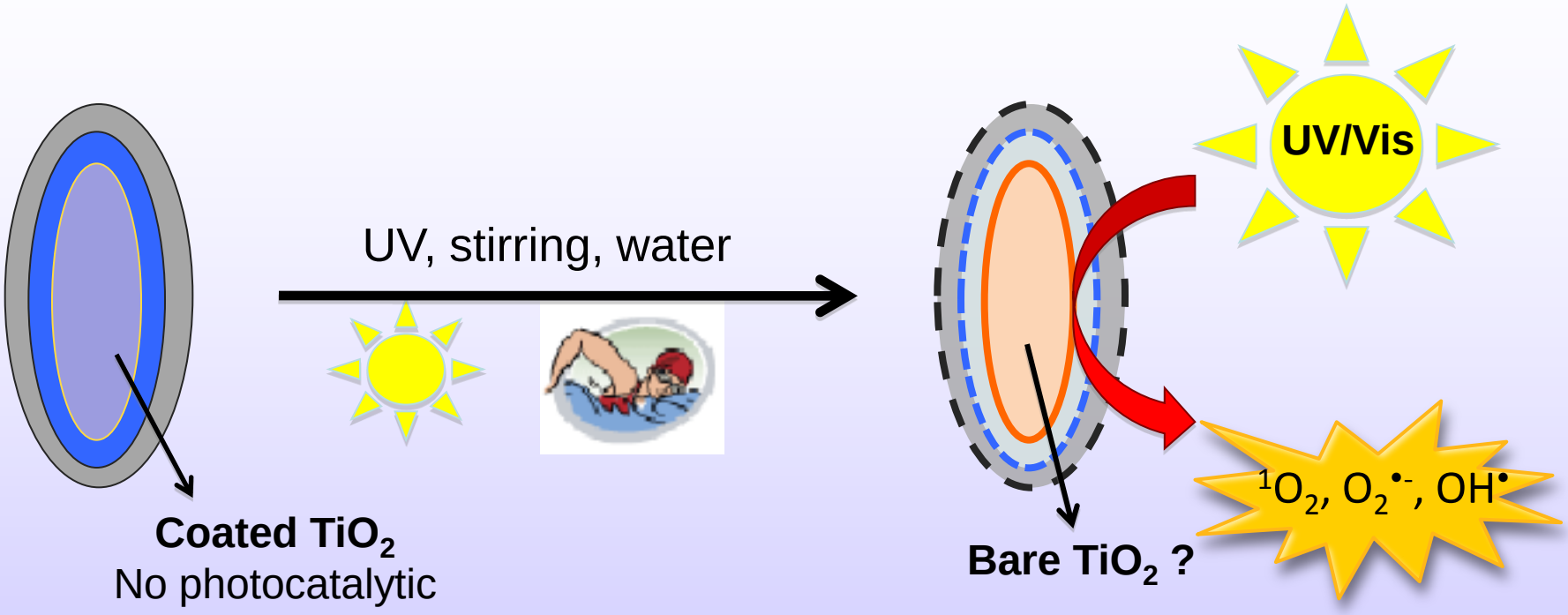


Size of particles: 10x50 nm

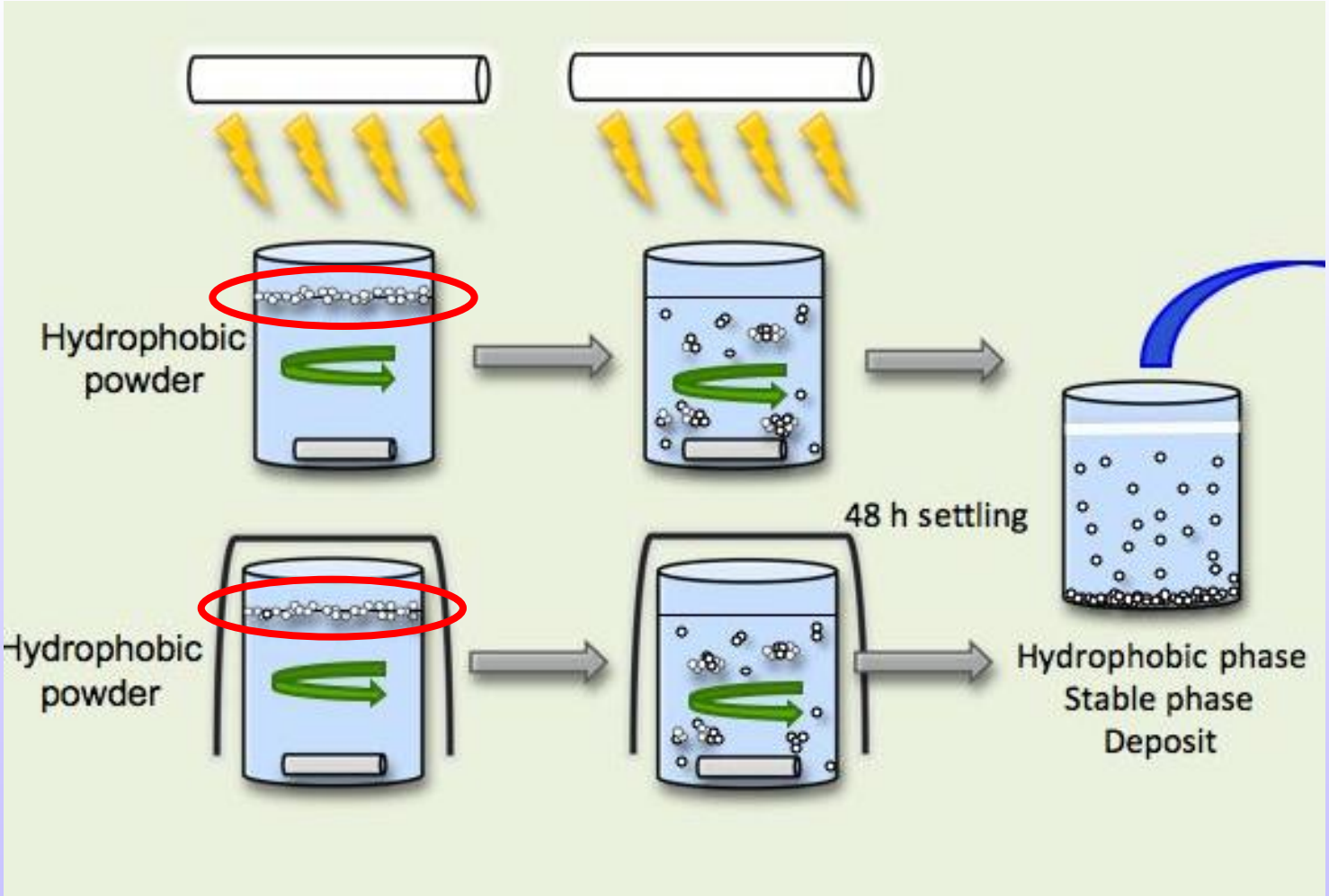


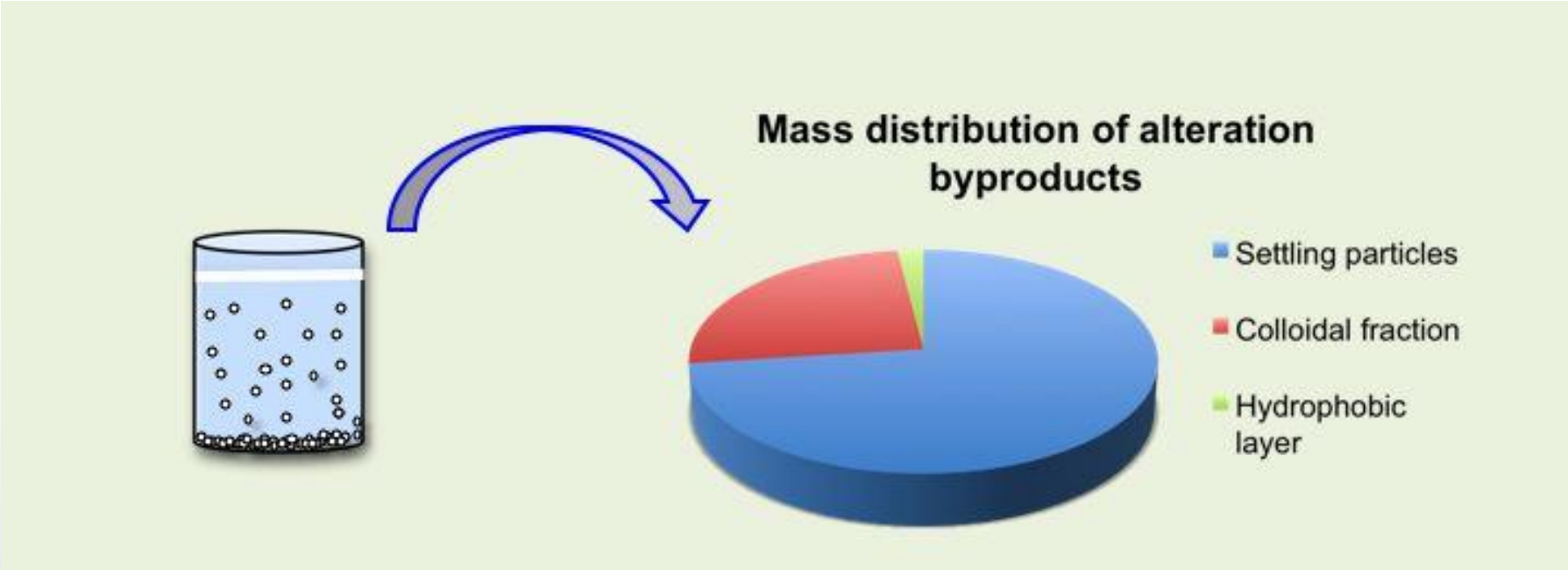


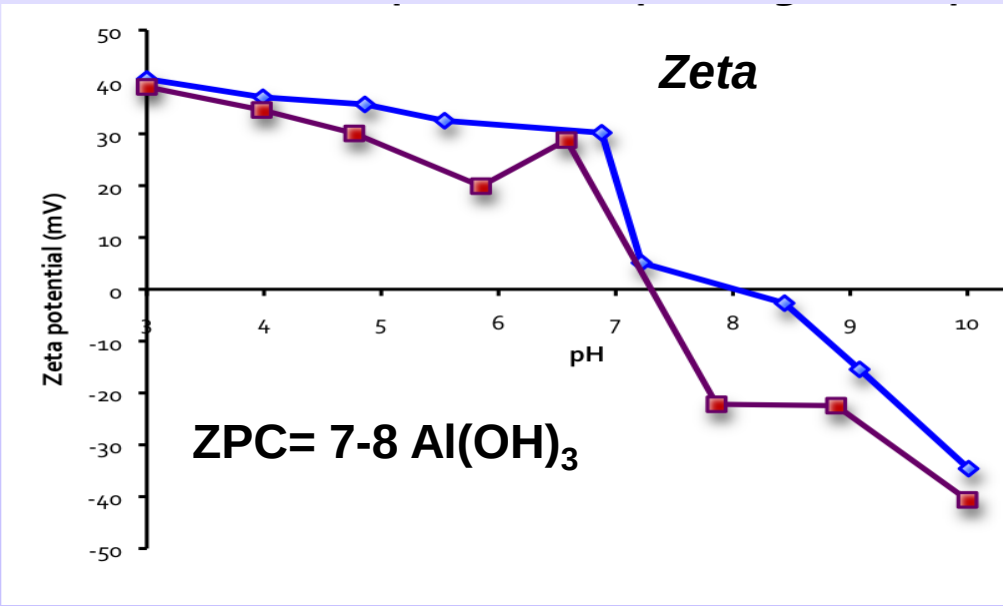
What happens to the NP during/after use ?

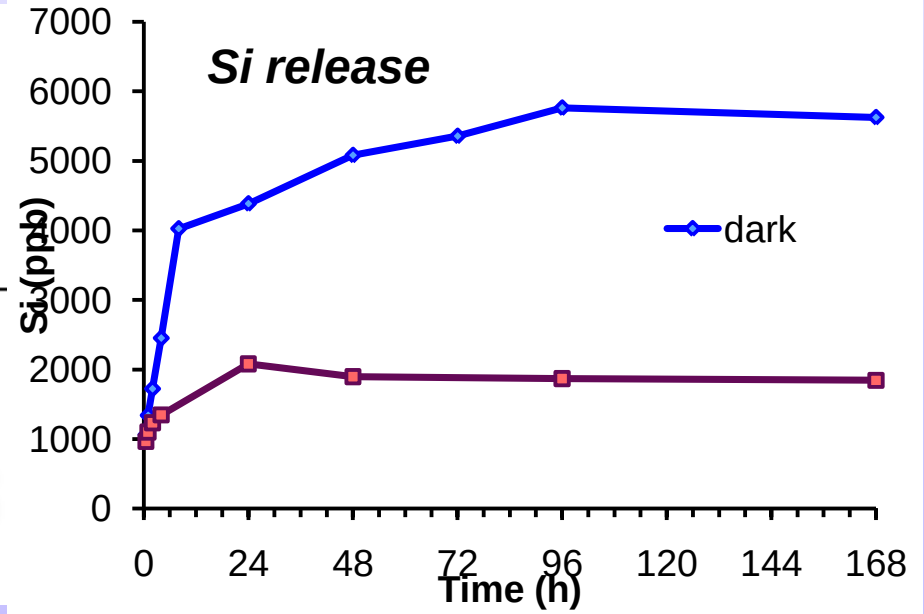


Alteration protocol



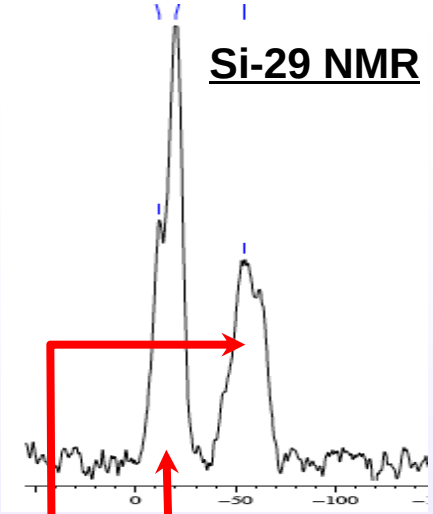

Mass distribution of alteration byproducts
Settling particles
Colloidal fraction
Hydrophobic layer


Zeta
Zeta potential (mV)
pH
ZPC= 7-8 Al(OH)3

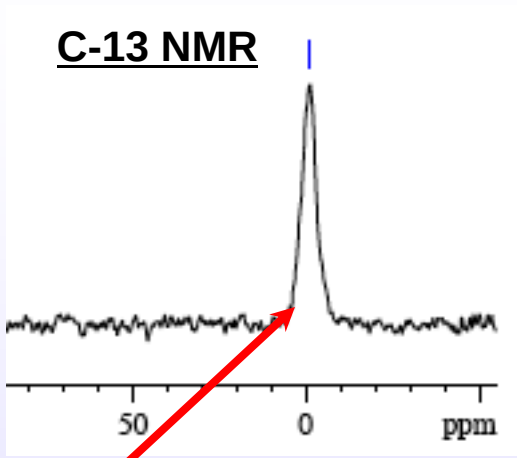

Si release
Si (ppb)
Time (h)
dark

Initial particle

Si-29 NMR



C-13 NMR

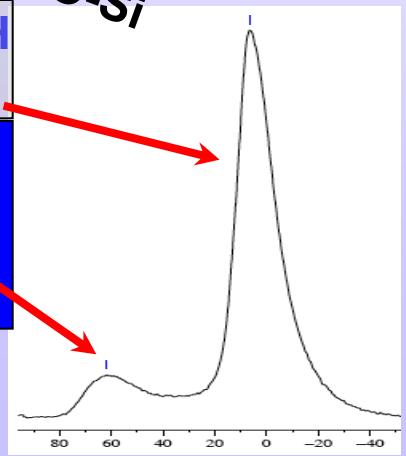


Me2 Me2 Me2
Si-O-Si-O-Si
O

Me2 Me2 Me2
Si-O-Si-O-Si
O

Al-OH-Al-O-Al-OH
O-Al-OH-Al-O-Al

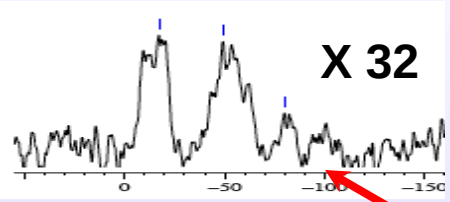
TiO2



Aged particle

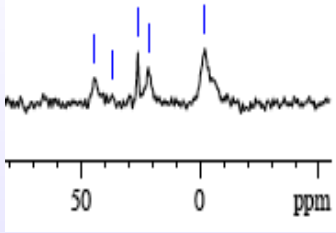
Strongly altered organic layer

Degradation of PDMS



Si-29 NMR

Loss of C signal

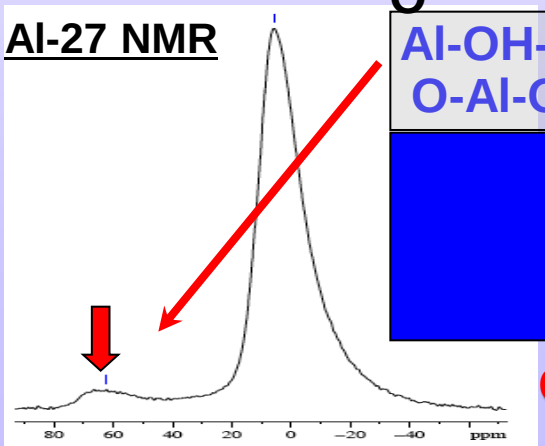


C-13 NMR

Me2 Me2
Si-O-Si
O

Si-O2-Si
O

Al-27 NMR



Al-OH-Al-O-Al-OH
O-Al-OH-Al-O-Al

TiO2

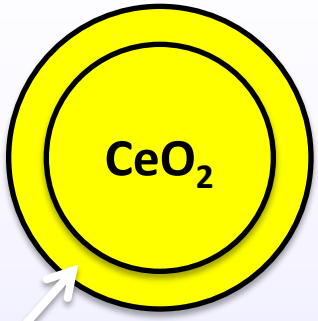
Quasi intact Al layer

Auffan et al., Environ.Sci.Technol. 2010

Fate of Cerium dioxide-based nanocomposite

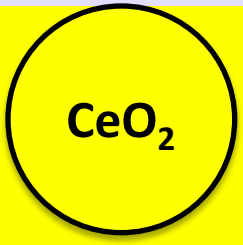
NANOMATERIAL (OUT-DOOR WOOD PAINT ADJUVENT)

- Core : nanoparticles of CeO_2
- Coating : $C_6H_{17}N_3O_7$ (triammonium citrate)
- Size : 8 nm



$C_6H_5O_4(NH_4^+)_3$

NANOPARTICLE OF CERIA : CeO_2



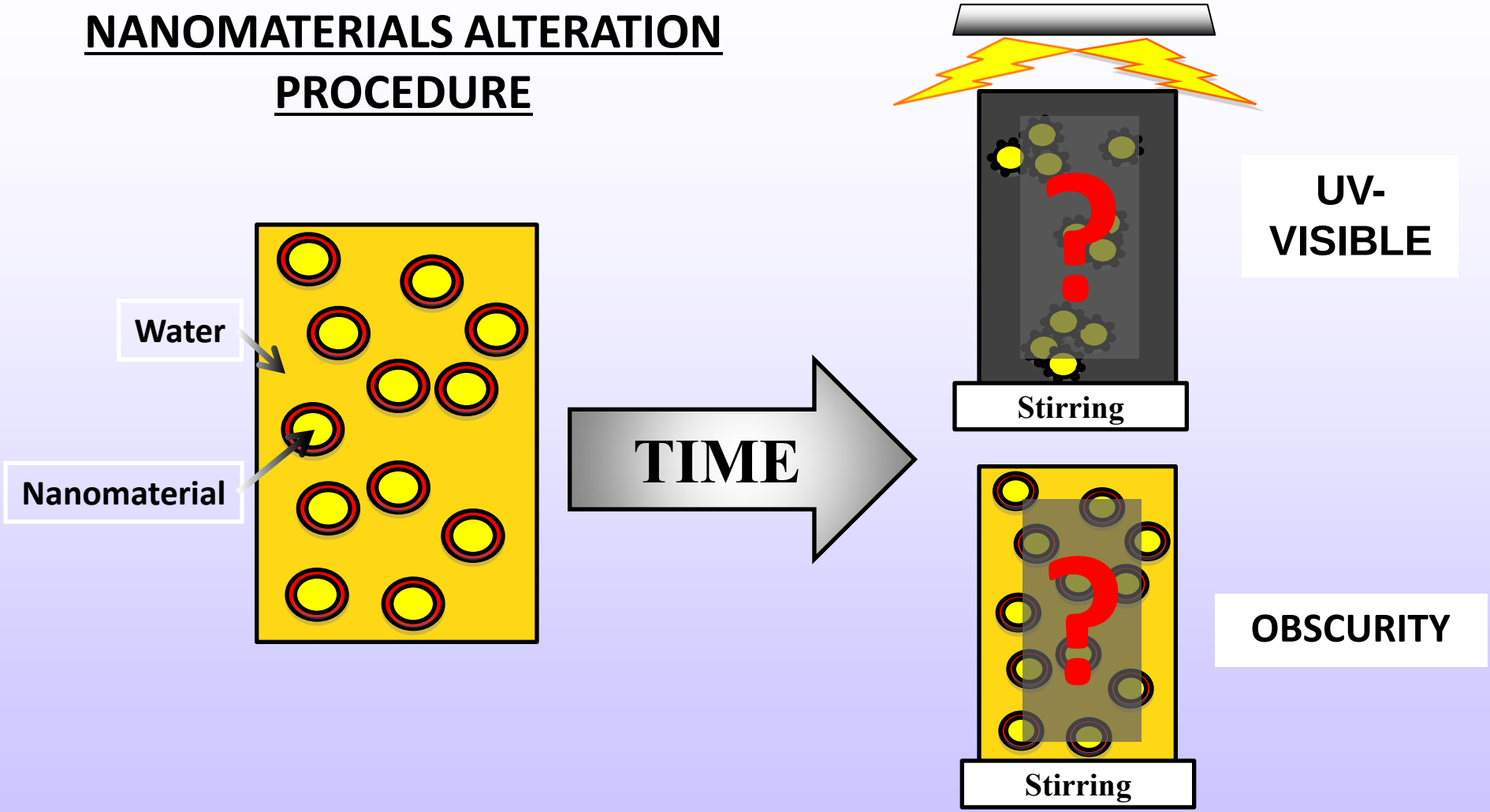
- Size : 8 nm

2 oxidation states : Ce(III) and Ce(IV)

Redox cycle at the surface of nano-CeO_2

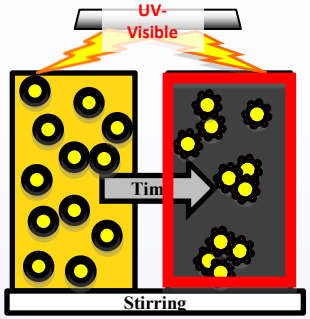
Auffan et al., Nanotoxicology, 2009

NANOMATERIALS ALTERATION PROCEDURE

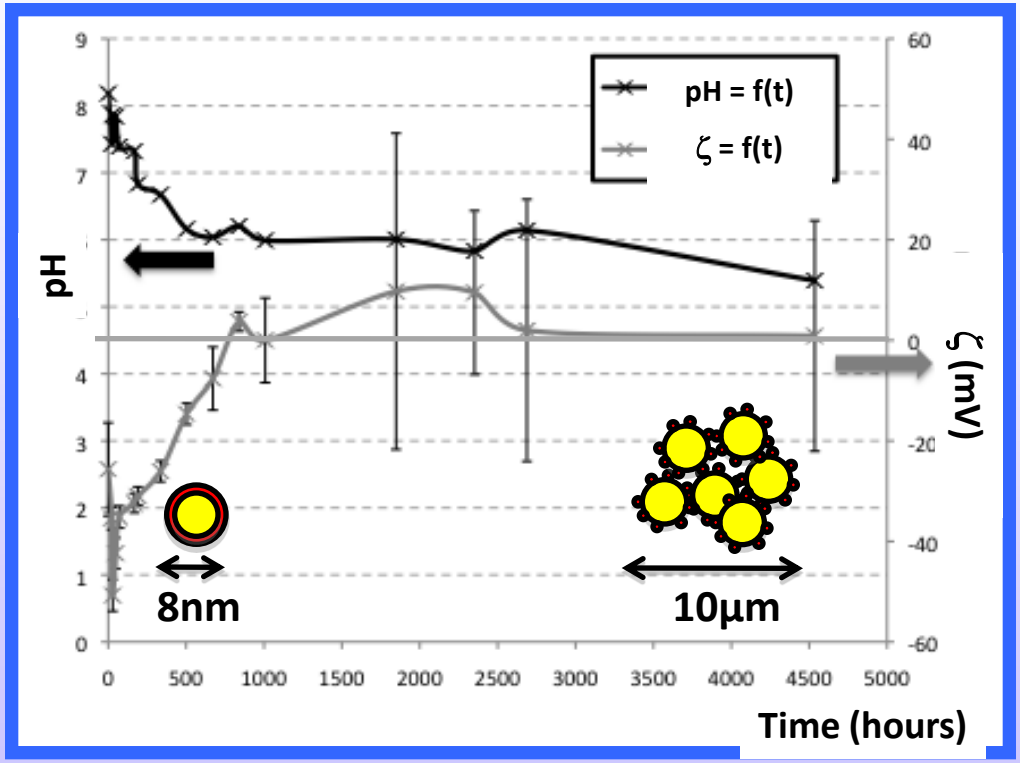


How coating controls the fate of the nanoparticles?

Results



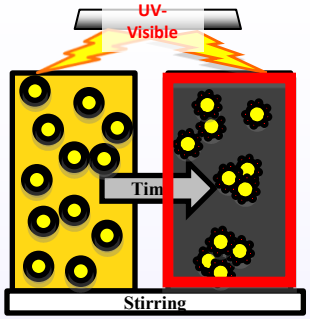
PH AND ZETA POTENTIAL (ζ) = F(TIME)
LONG-TERM (4 MONTHS)



- ⊙ pH : regular and slow decrease of two pH units
- ⊙ ζ : Inversion of the surface charge at 1500h (2 months) → favor aggregation

In the dark, no evolution of the pH, the ζ and the size…

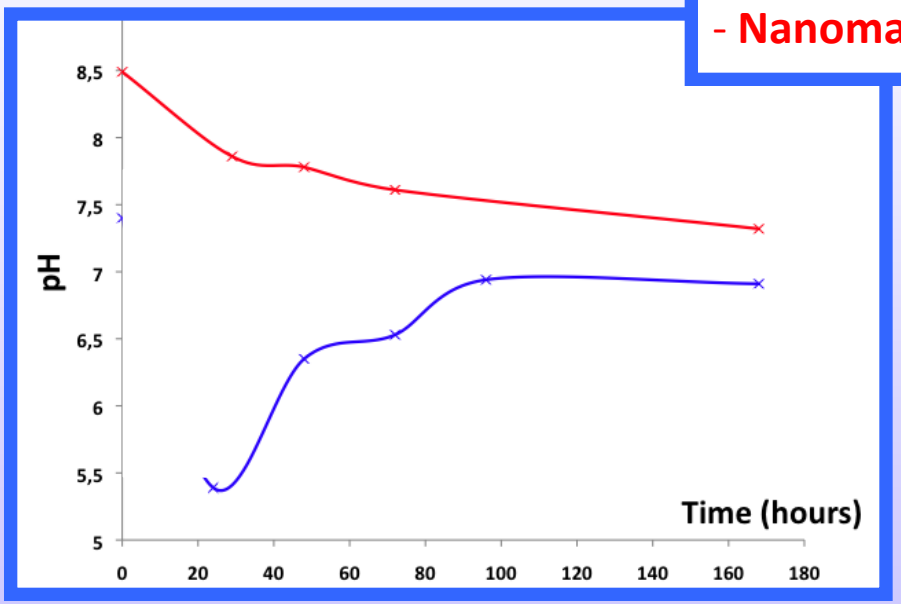
Results

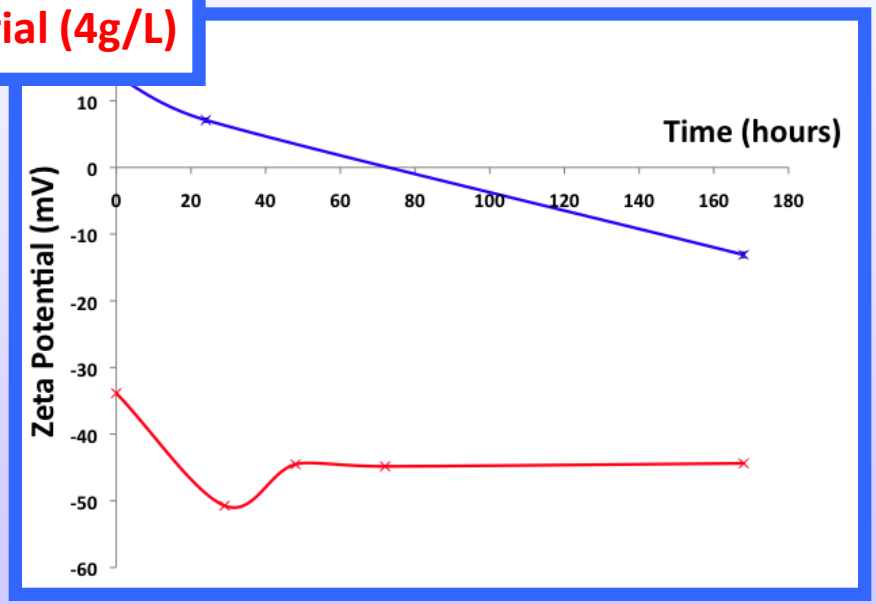


PH & ZETA POTENTIAL = F(TIME)

SHORT-TERM (1 WEEK)

- Nano CeO_2 (1g/L)
- Nanomaterial (4g/L)



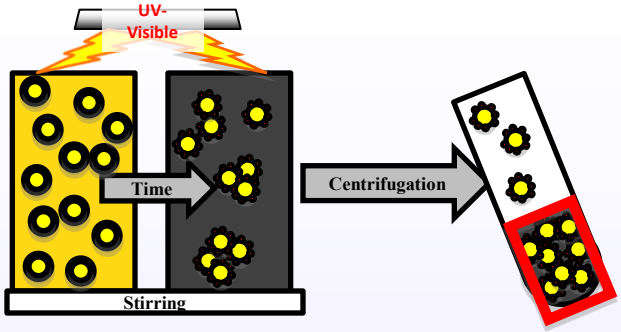


- Fast increase of the pH and stabilization at 7 : probable reaction of reduction ($CeO_2 + 2e^- + 2H^+ \rightarrow Ce_2O_3 + H_2O$)
- Regular and slow decrease of the pH : 8,5 → 7

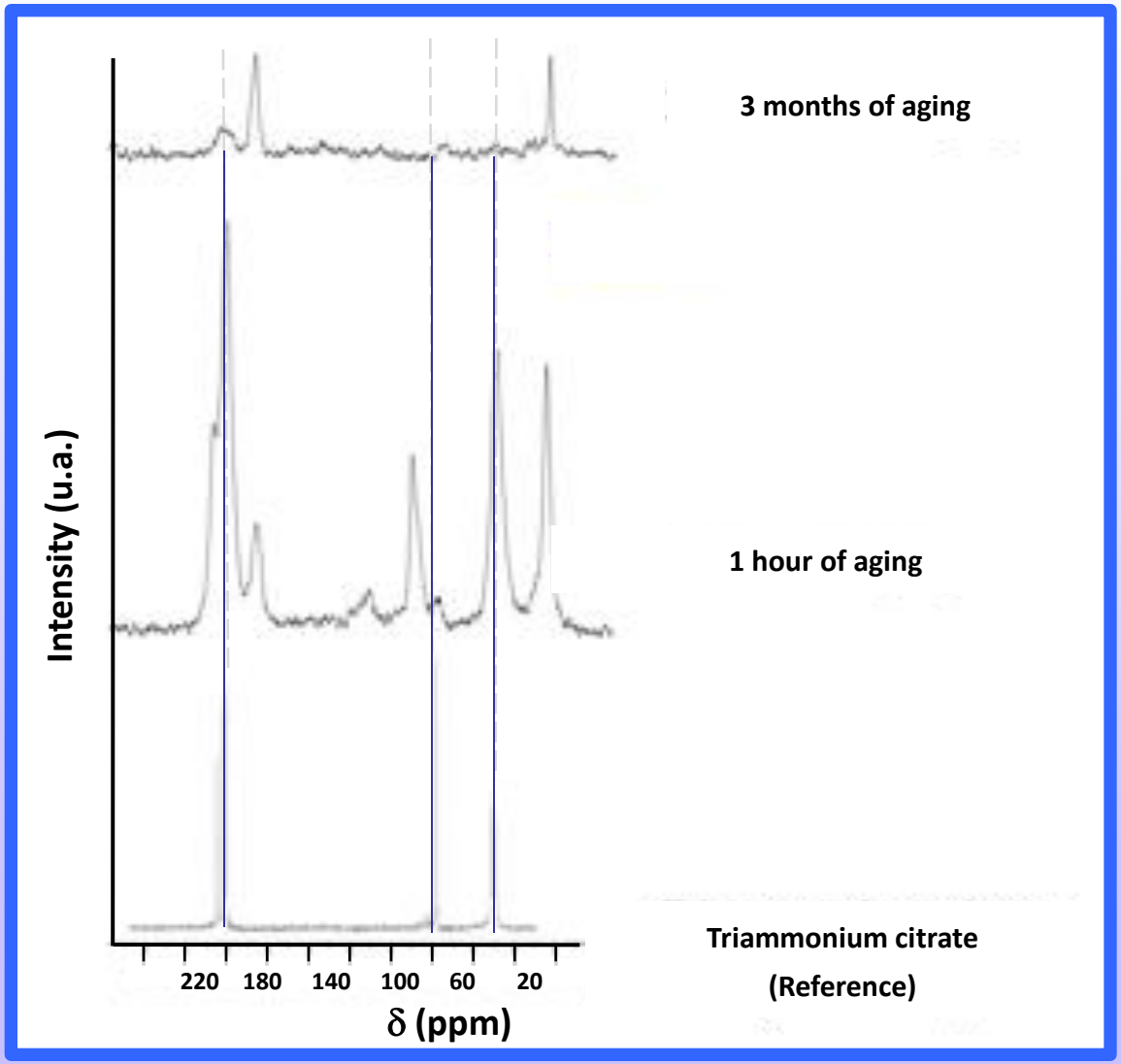
- Inversion of the surface charge → aggregation
- ζ = -40/-50 mV : stability of the suspension

Results

COATING DEGRADATION

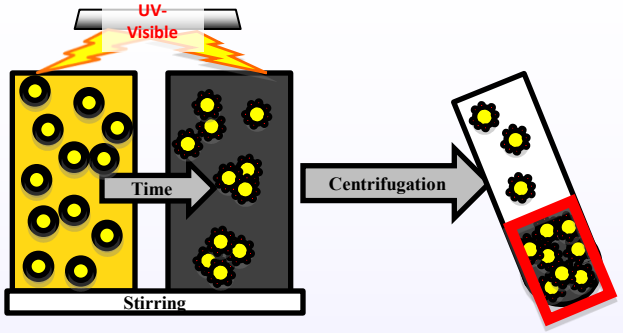


NMR ^{13}C



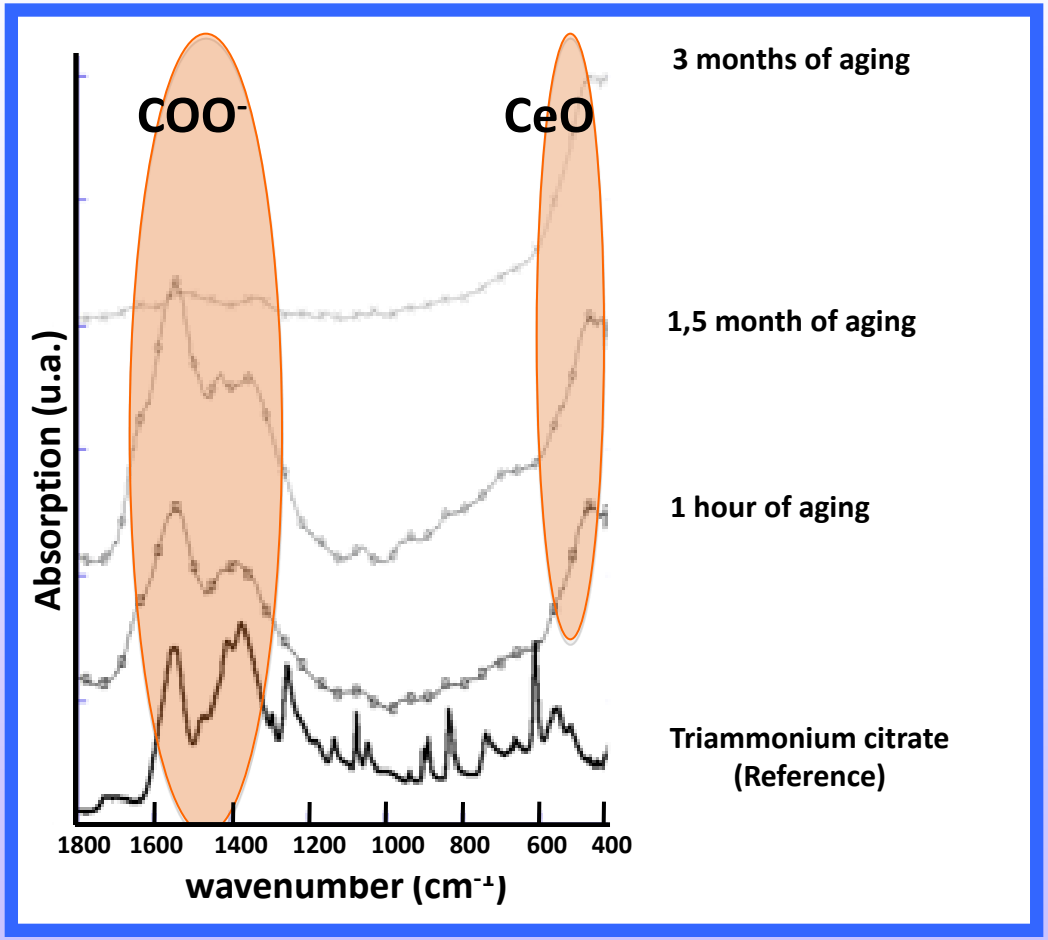
- Decrease of the coating contribution , disappearance of triammonium citrate peaks

Results



COATING DEGRADATION :

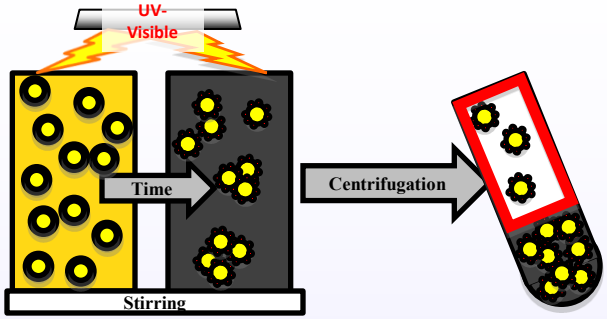
FTIR



- Decrease of the coating contribution, low intensity of the FTIR peaks in the 1400-1600 cm^{-1} range

Can Li et al., 1990 - A. Siokou et al., 1999

Results



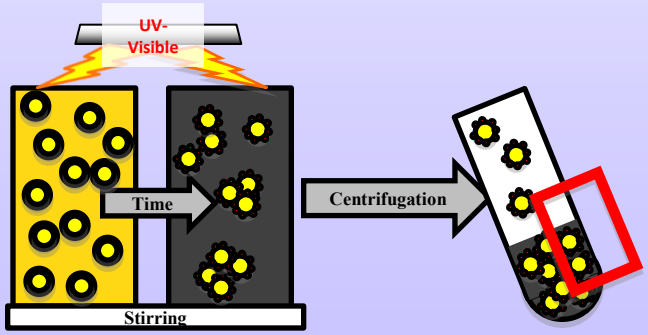
CERIA DISSOLUTION

ICP- MS

⊙ very weak dissolution of the CeO_2

Initial CeO_2 concentration : 4000 mg/L

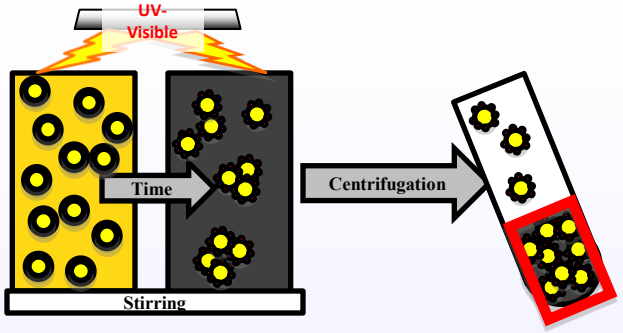
Ce release : 1 mg/L

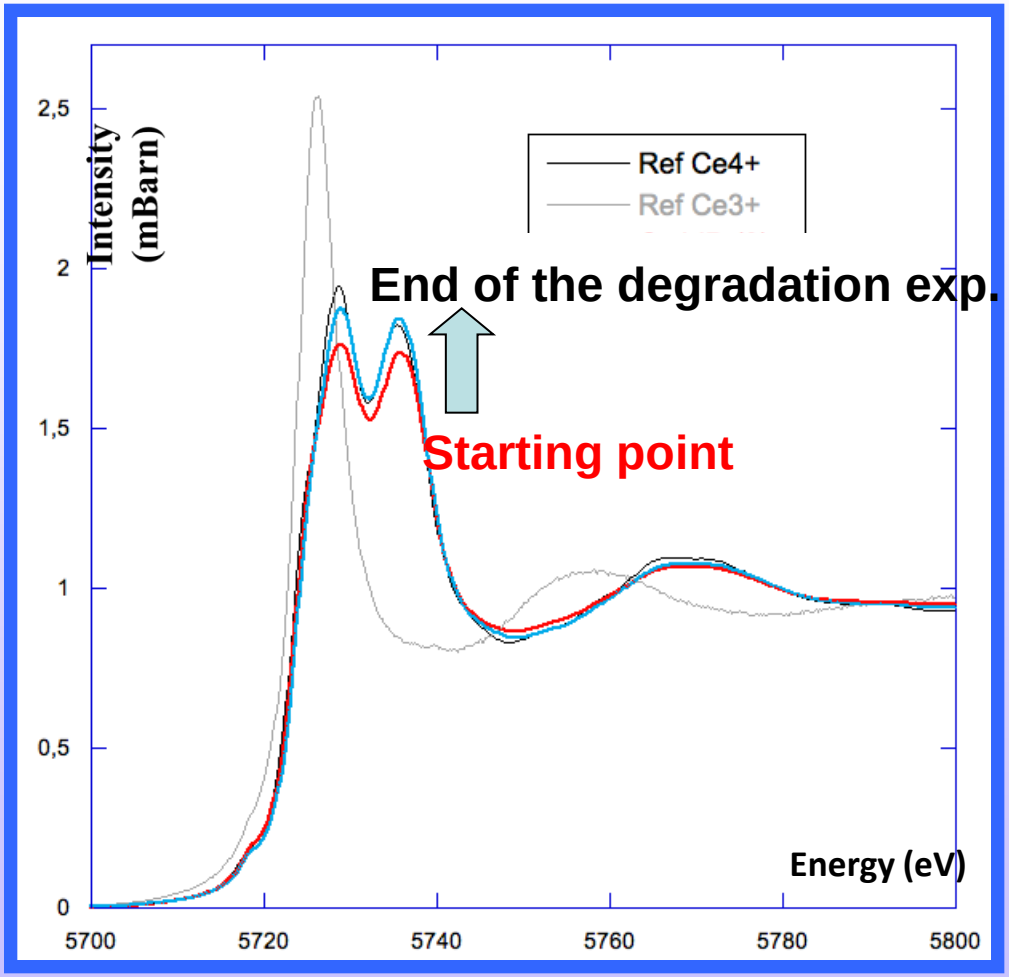


CHANGE IN THE CRYSTAL STRUCTURE

XAS and XRD

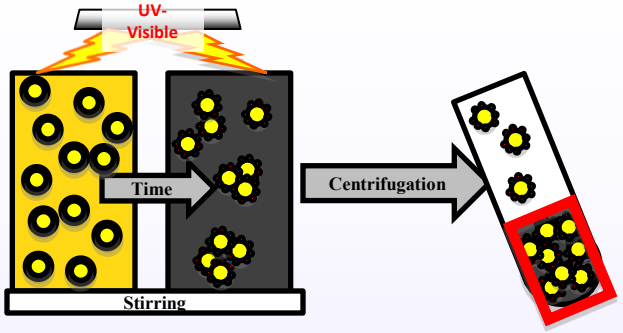
Results

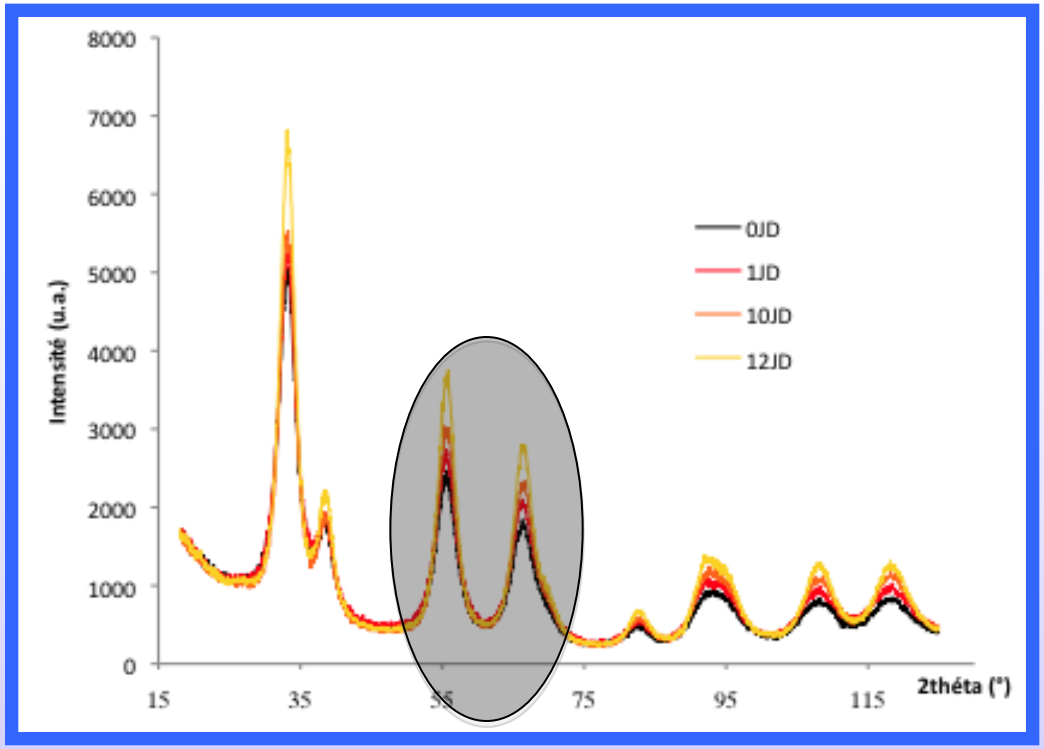




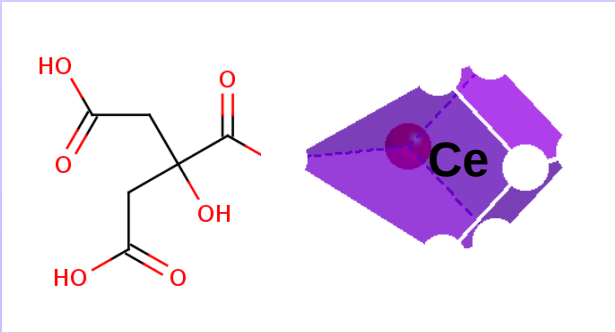
- ⊙ No Ce^{3+} contribution
- ⊙ Increase of the XANES peaks over time :
  - Increase of the nanoparticles size ?
  - Better crystallinity ?

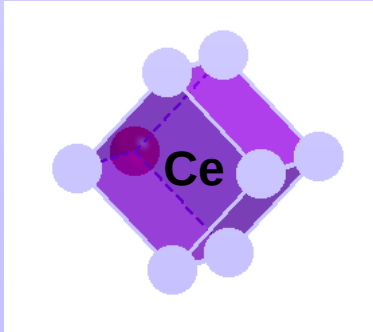
Results



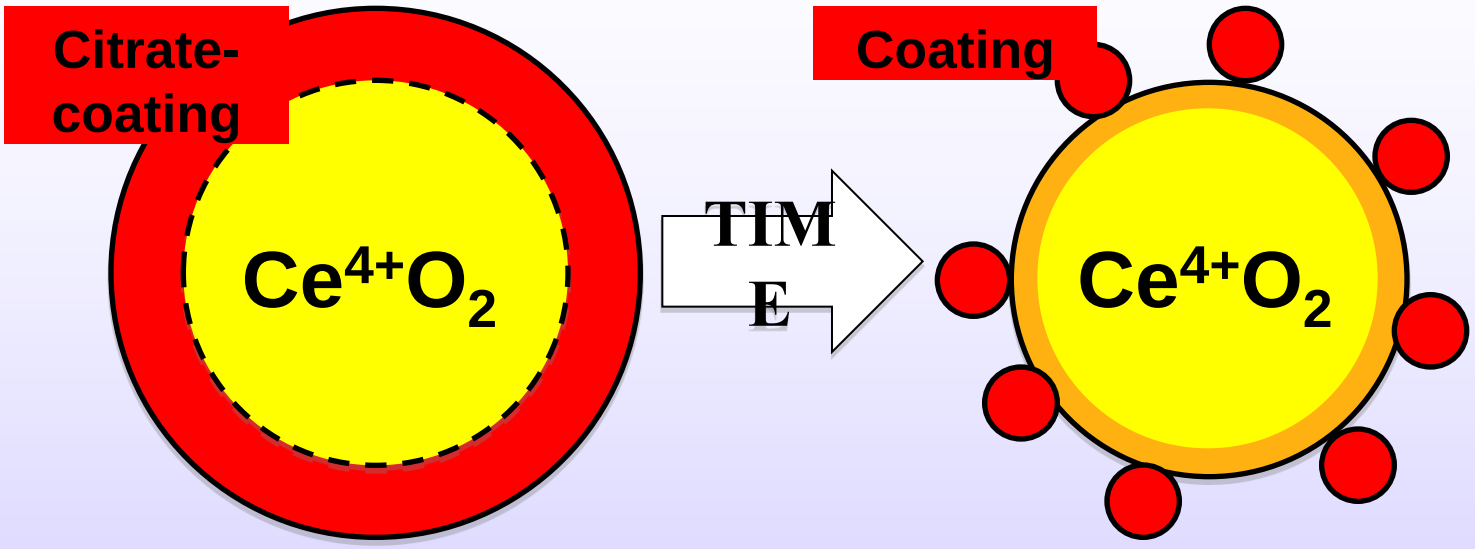


- Decrease of FWHM with time :
  - Increase of the coherent diameter
  - Better crystallinity





MECHANISM HYPOTHESIS

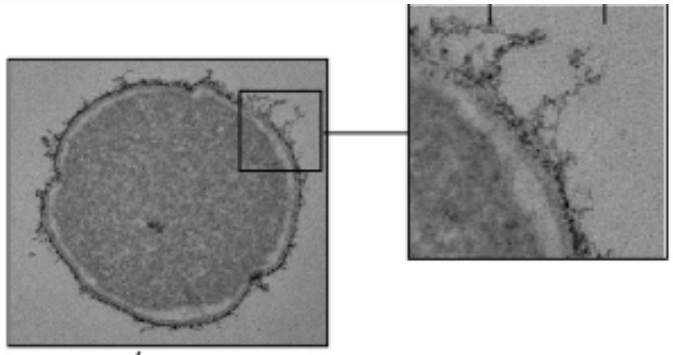


4 month of degradation under UV light :

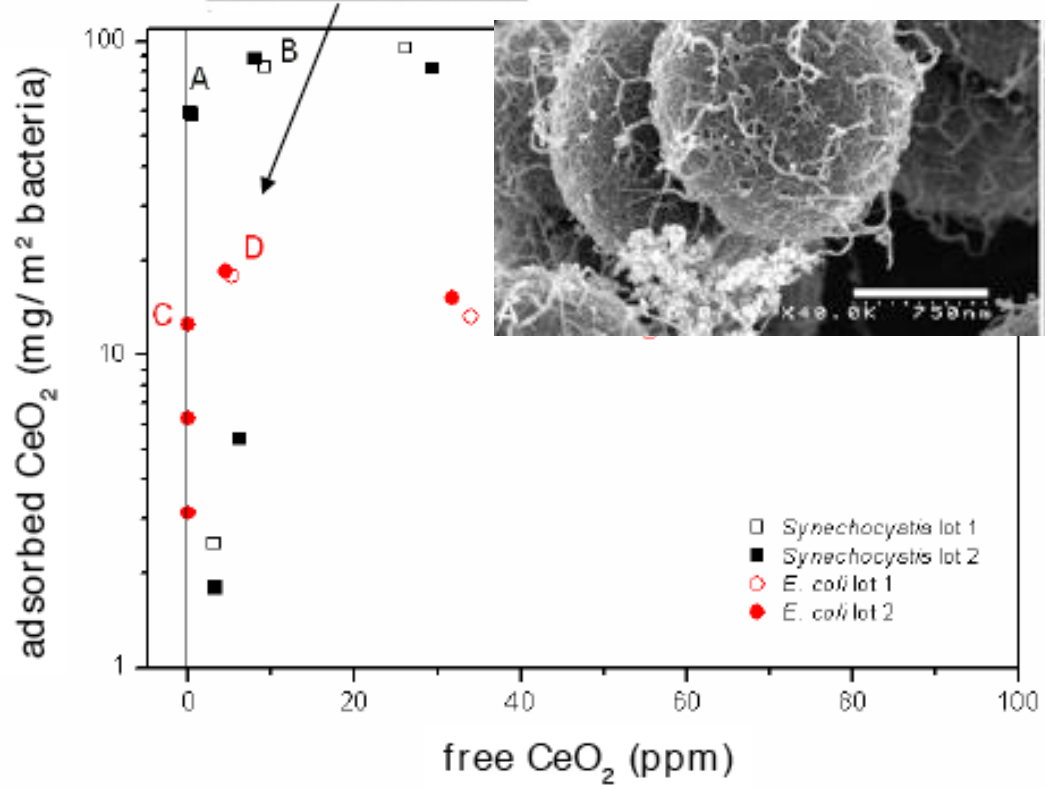
- ✓ **Aggregation after 2 months of aging**
- ✓ **After 3 month, coating disappearance**
- ✓ **No dissolution equilibrium and weak release of Ce^{3+}**
- ✓ **Increase of the cristallinity**

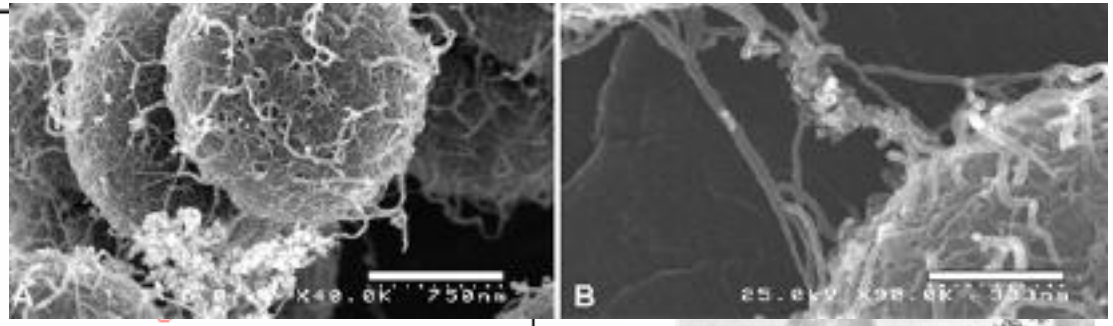
After the total alteration of the coating, is there a difference between bare nanoparticles and altered nanomaterial?

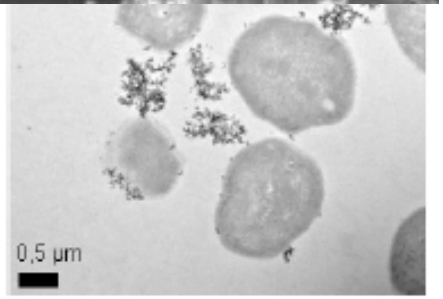
III- Methodology for evaluating the environmental biological impacts:
- the toxicity is associated to a strong affinity for cells



$S_{NP} / S_{coli} \sim 1$







$S_{NP} / S_{synecho} \sim 7.5$

Zeyon, Thill et a ES and T 2008 et Langmuir 2009

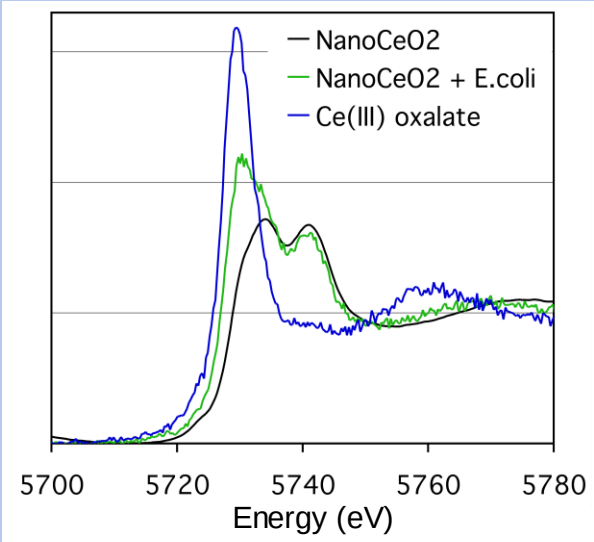
-The toxicity is also associated to ROS or RNS production via electron transfer

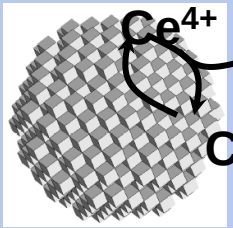
Exemple : CeO_2 (7 nm)

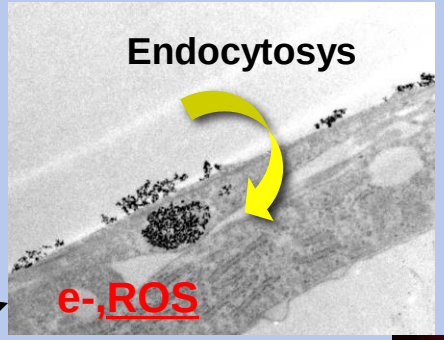
30% of surface atoms are reduced

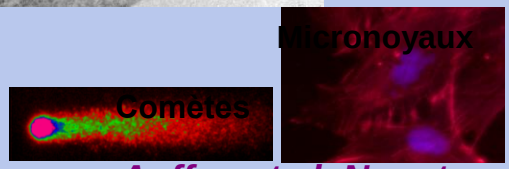
No cytotoxicity BUT
Genotoxicity for > 0,06 mg/L

XANES
Ce L-edge







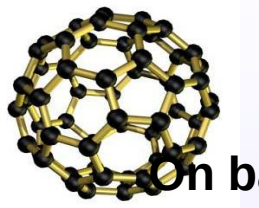


Auffan et al. Nanotox, 2009

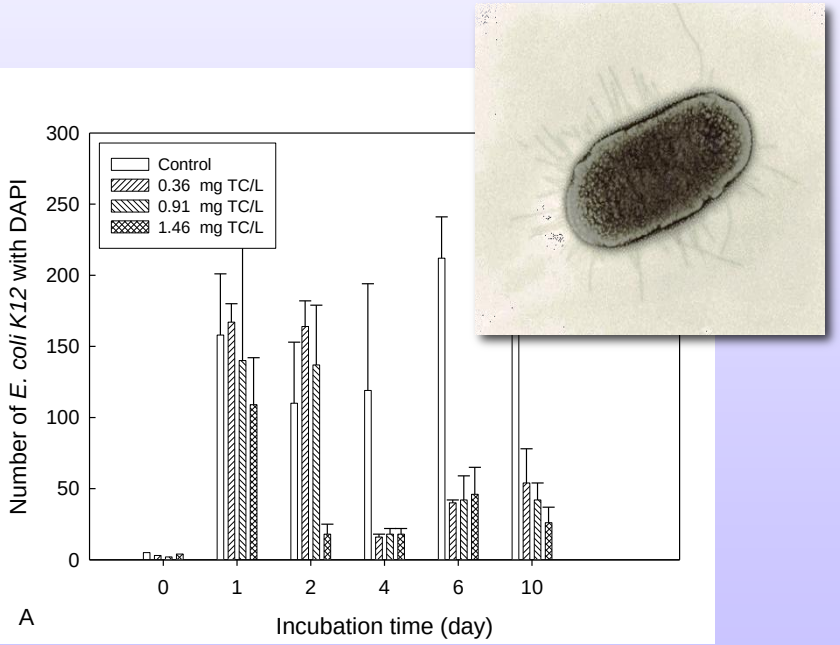
Redox cycles Ce^{3+}/Ce^{4+} $\xrightarrow{\text{ROS}}$ genotoxicity, Oxidant stress

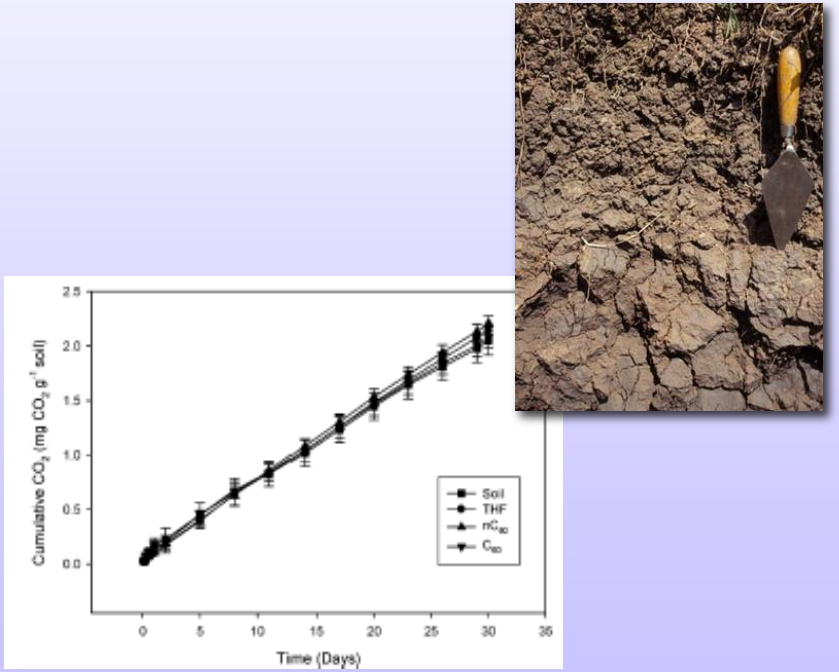
But there is a necessity for changing the scale from a laboratory scale i.e 1 cell and 1 Np to a natural and complex ecosystem

Toxic
On bacteria



Non Toxic
On bacteria community when mixed with a soil

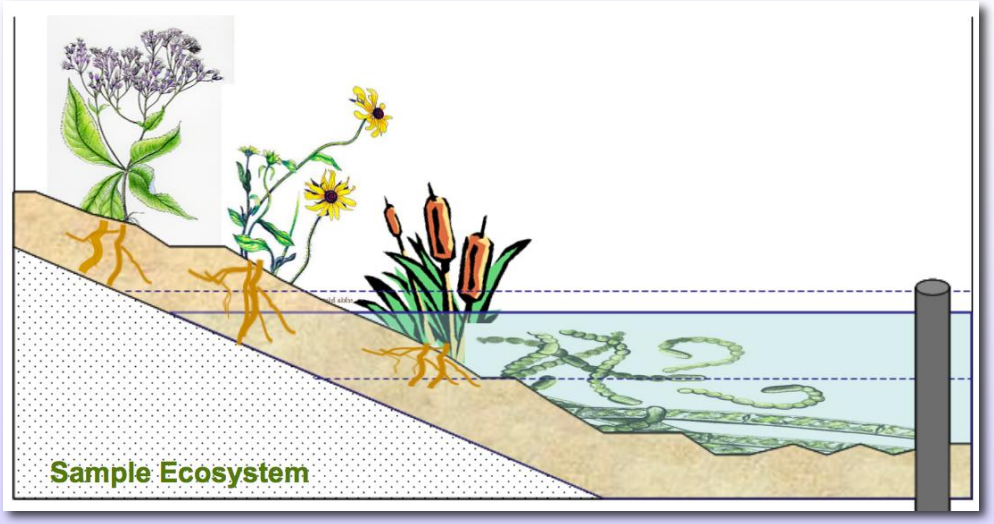


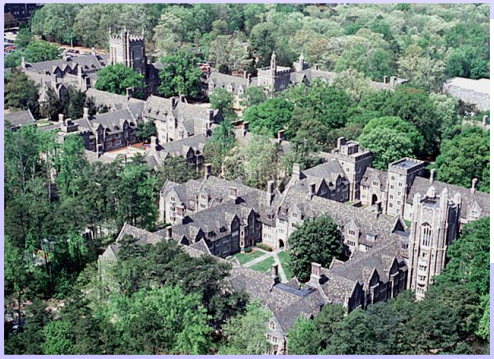


Lab culture – Chae et al. In prep

Real World – Tong et al. 2007 ES&T

Mesocosms= low concentrations, long time for experiments …..
-Modelization of aggregation, settling, transfer to compartments ….
-Impacts on community, populations…inter-generations
- genotoxicity, growth…biomarkers





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DUKE university
www.ceint.duke.edu

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