Exposure along the Value Chain of Nano Products

Jean-Yves BOTTERO
Research Director at CNRS
CEREGE - France
CNRS - Aix-Marseille Univ.
Adjunct Professor
DUKE Univ.

bottero@cerege.fr

http://www.i-ceint.org
http://ceint.duke.edu

INTERFAces & Transfer @ CEREGE

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Lab. of Excellence network

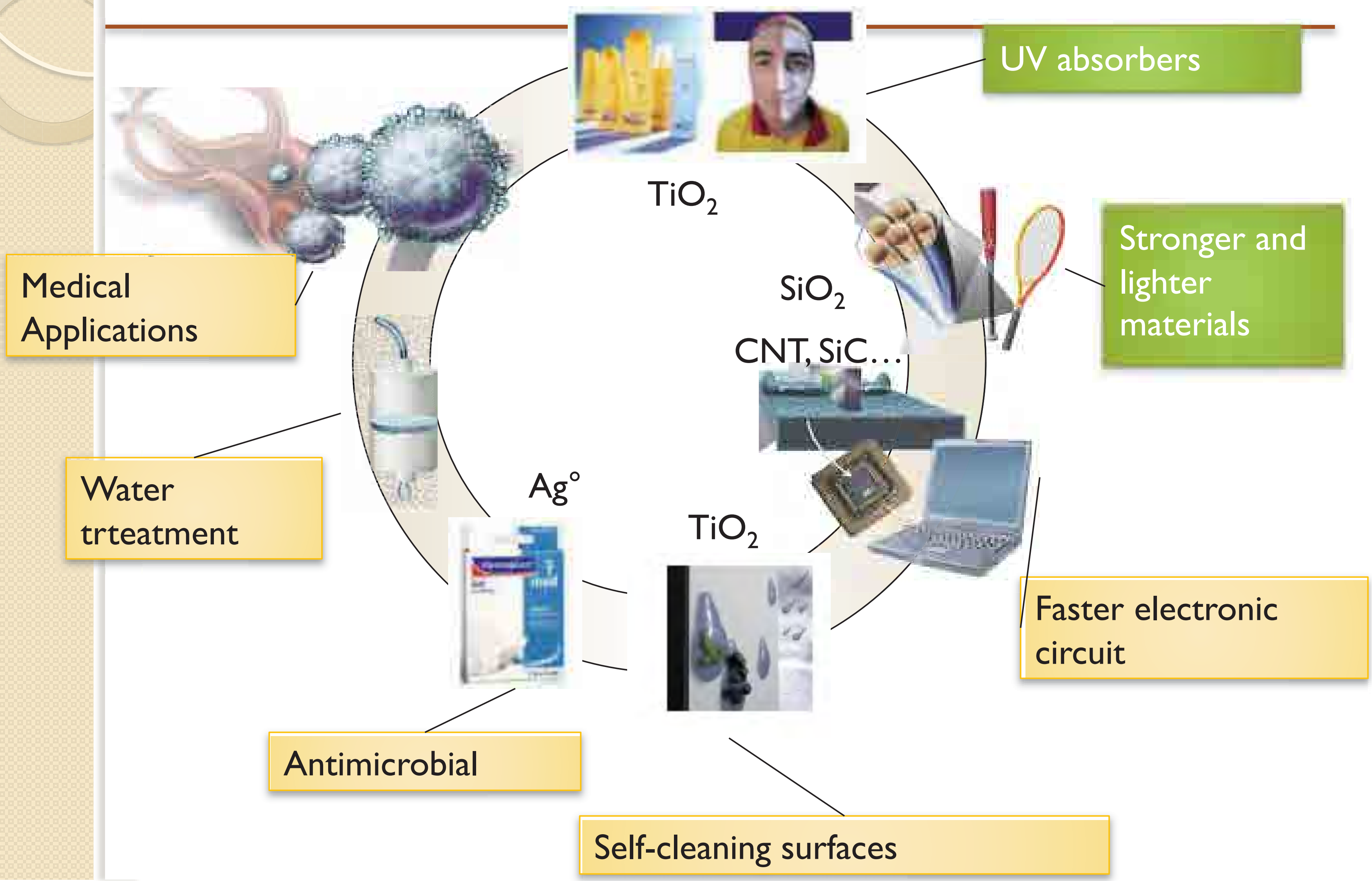
A focus on 'exposure along the value chain'

- Flashback few years ago : what was the priority list of NM to be studied?

OECD priority list of Nps

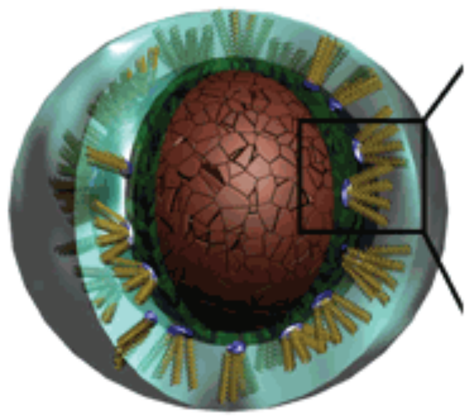
- Fullerenes (C60)
- Single-walled carbon nanotubes (SWCNTs)
- Multi-walled carbon nanotubes (MWCNTs)
- Silver nanoparticles
- Iron nanoparticles
- Carbon black
- Titanium dioxide
- Aluminum oxide
- Cerium oxide
- Zinc oxide
- Silicon dioxide
- Polystyrene
- Dendrimers
- Nanoclays

Commercialized nanomaterials/ nanoproducts are complex



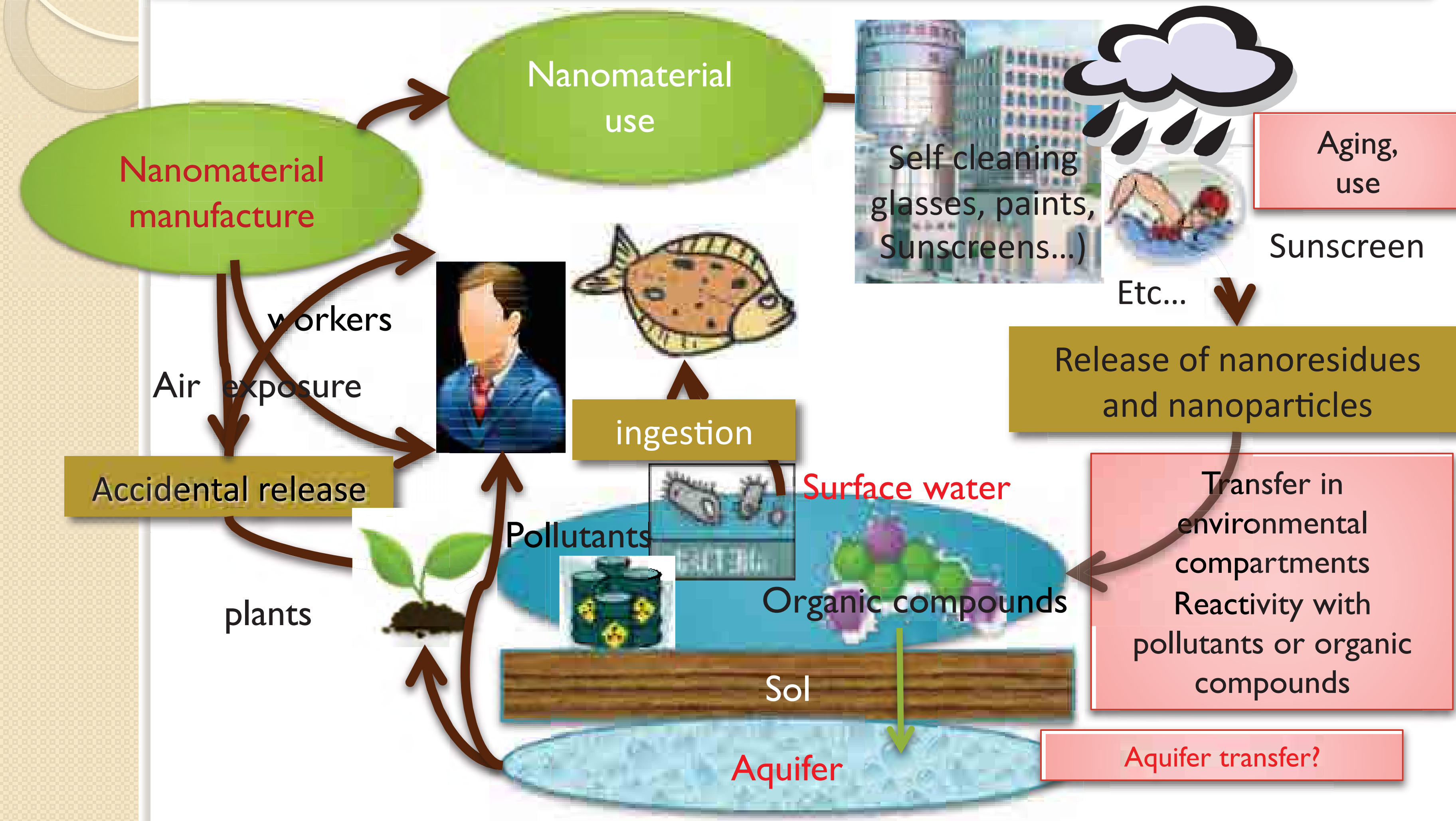
Commercial products

- In many cases nanomaterials are (surface) modified to be incorporated into products



- Priority: Bare nanomaterials? Coated? Extrapolation of results obtained with bare to coated?.

Exposure to Nanoproducts

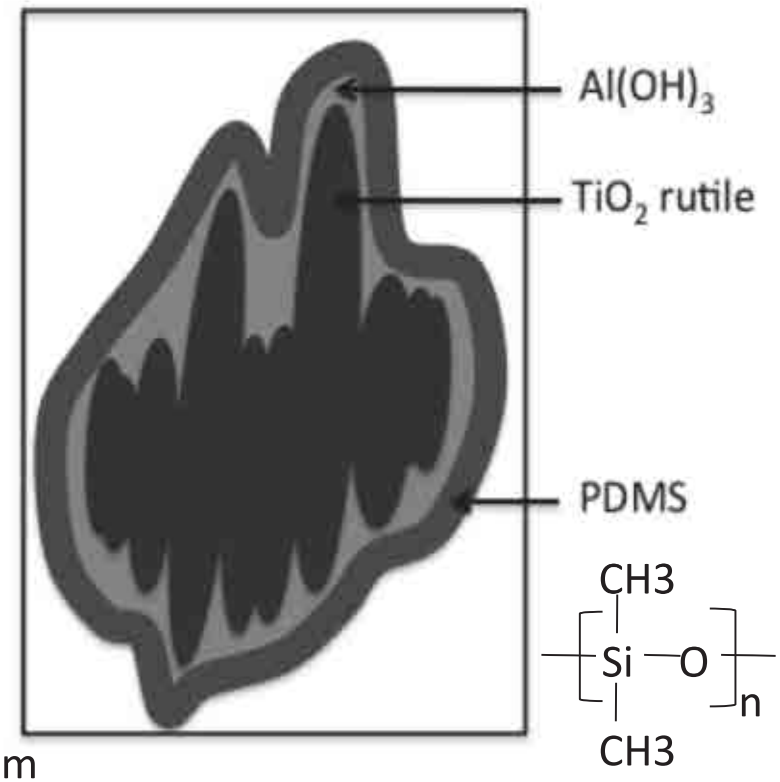


From products: the Nps are obtained from the alteration of materials as plastics, cosmetics, paints, …… These Nanomaterials are complex and may be they do not reveal the same properties as the pristine Nps

Ex: TiO_2 in sunscreens =

TiO_2 + AlOOH + PDMS or TiO_2 + SiO_2 + PDMS

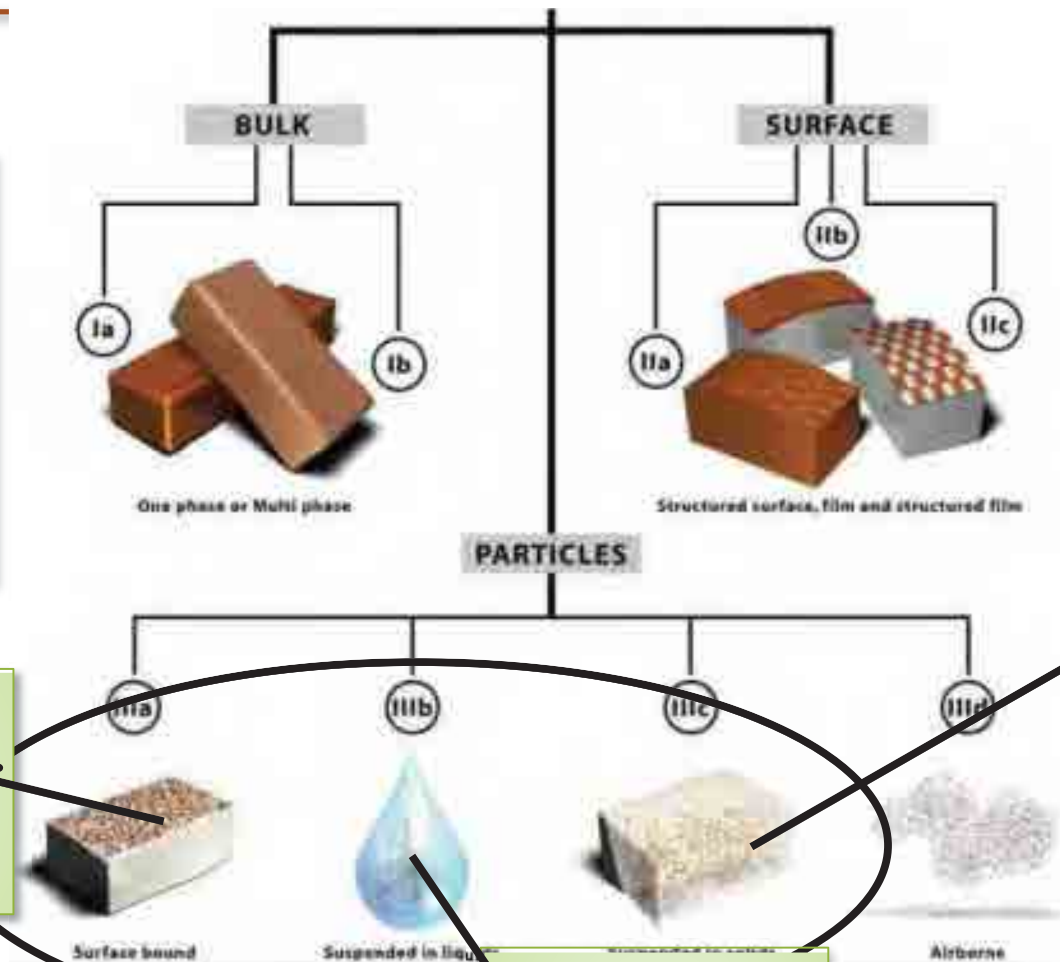
Size of particles: 10x50 nm



Nanoproducts v.s nanomaterials different case studies

- Nanomaterials: one dimension
  < 100nm
- Nanoproducts: 9 categories:

From Hansen, 2007



Example: NanoCeO$_2$-composite in outdoor paint

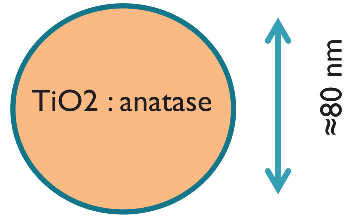
Example: Self-cleaning cement

Example : Sunscreens

From Hansen et al, 2007©

Self-cleaning Cement

+



- Self-cleaned surface
- Depolluted area

Aging during its use : effect of water exposure with time

Release process of nanoparticles

-Dissolution of matrixes around nano-TiO_2

-Transport into cement pores

Hypothesis: release of nano-TiO2 can be controlled by CEMENT POROSITY and MINERALOGY of hydrated cement phases at the
water-cement interface

http://www.ciments-calcia.fr/FR/Nos+produits/TX+Active/

Preparation of cement with different porosity

mixing

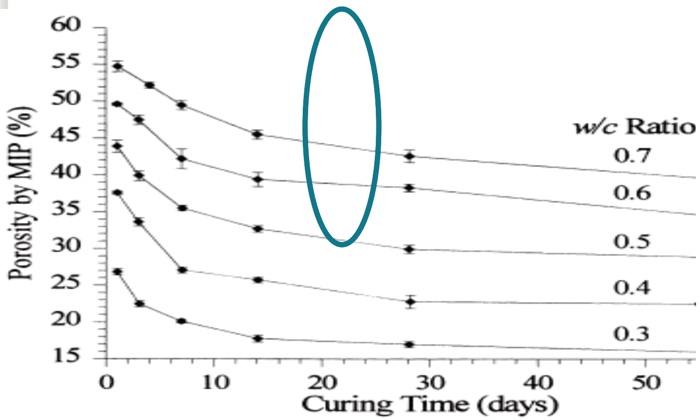
30%

40%

50%

Hydration :

28 days in dessicator at constant humidity

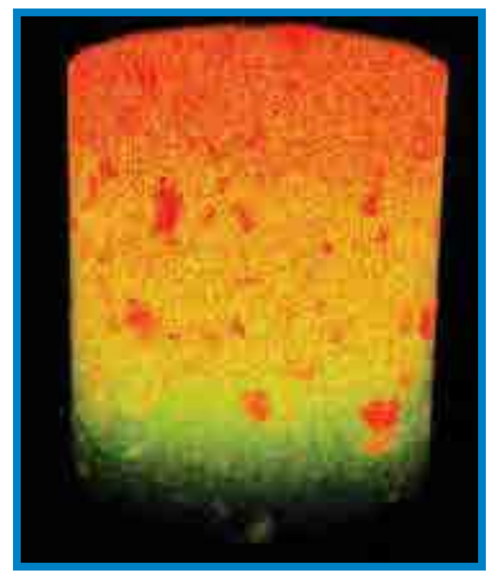


Raymond A. Cook, 1999©

Ti X-ray microtomography

Core

Surface

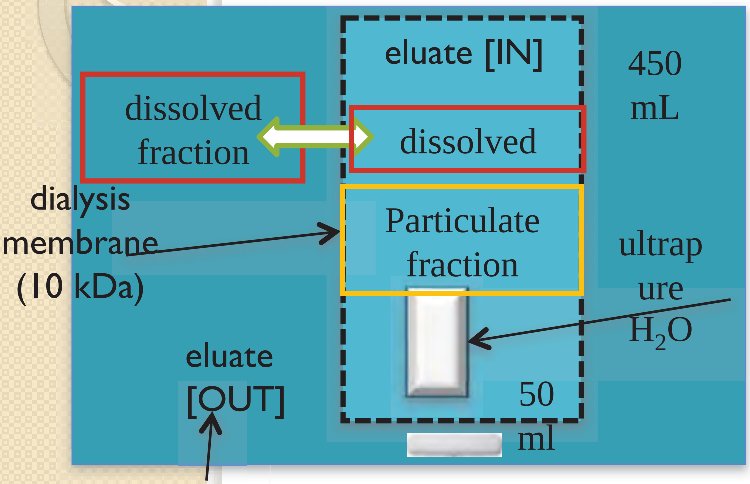


512 *512 px, 1px = 10µm

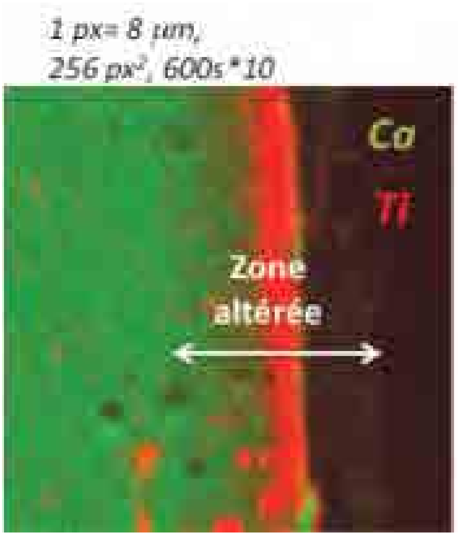
Image Ti µXRF intensity, core cement : L/S= 0.6

Dialysis test

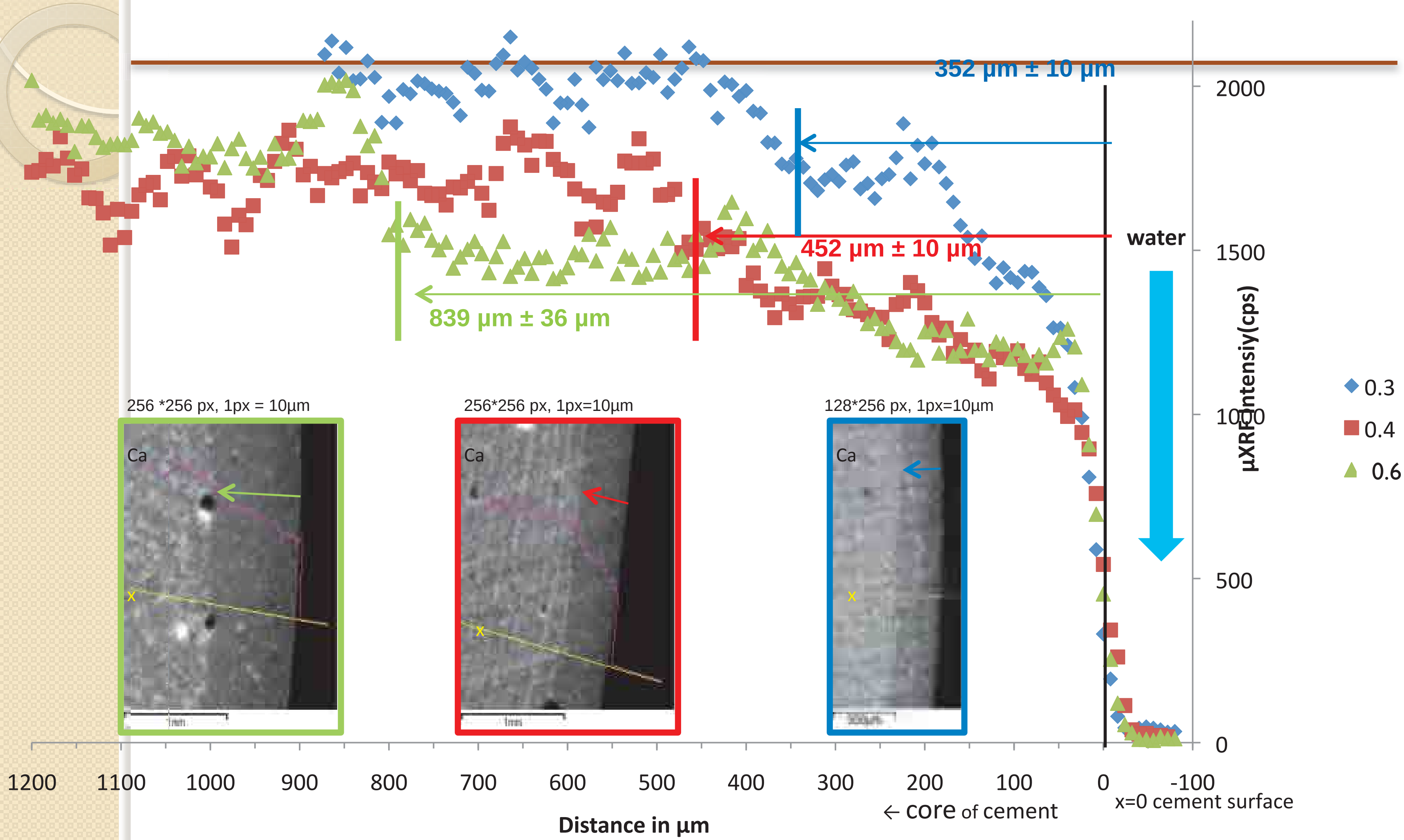
Different initial porosity: effect on nano-TiO_2 release

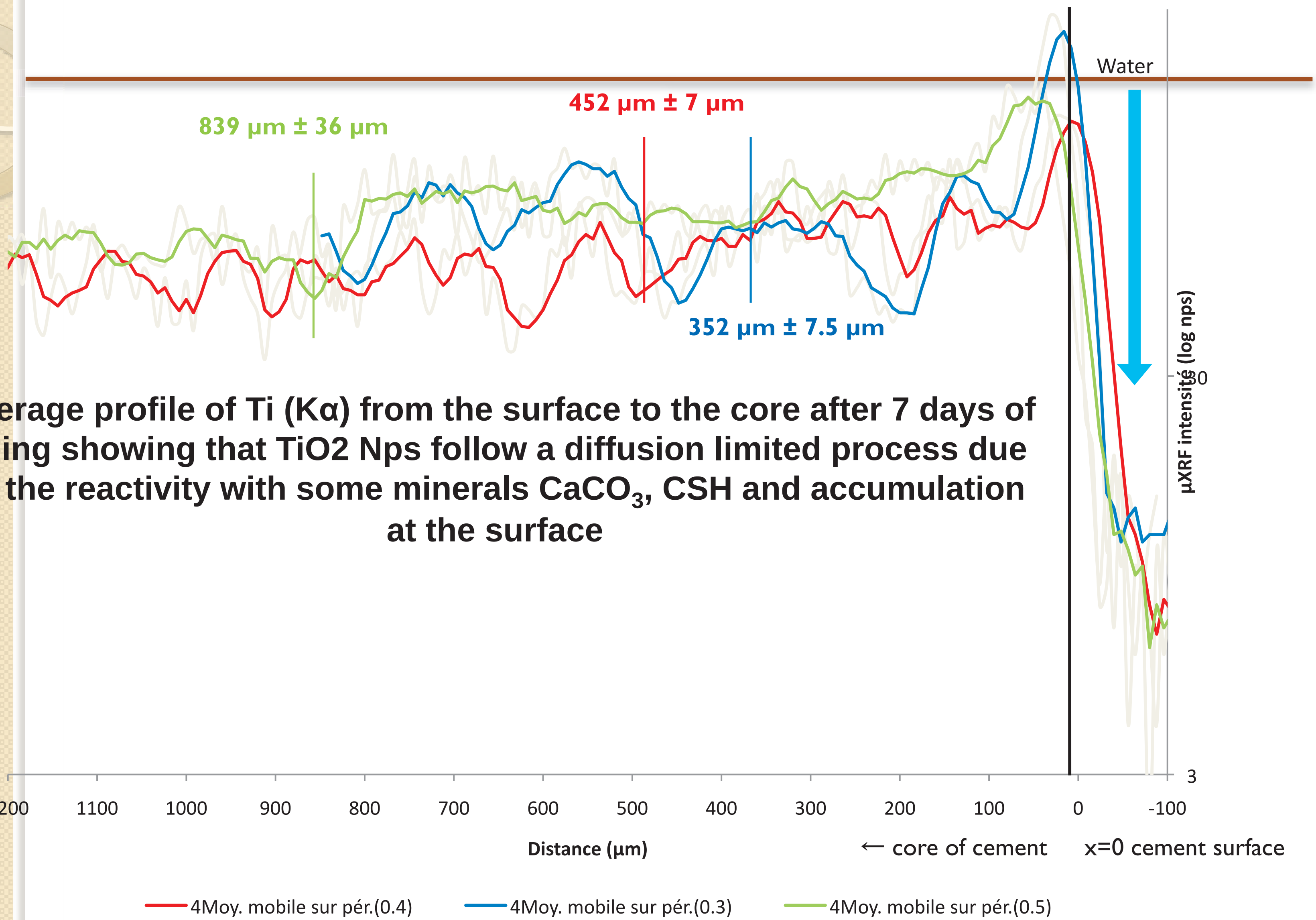


Hydrated cement paste (with various initial porosity)
0,3 – 0,4 – 0,5, w/w
4 replicates



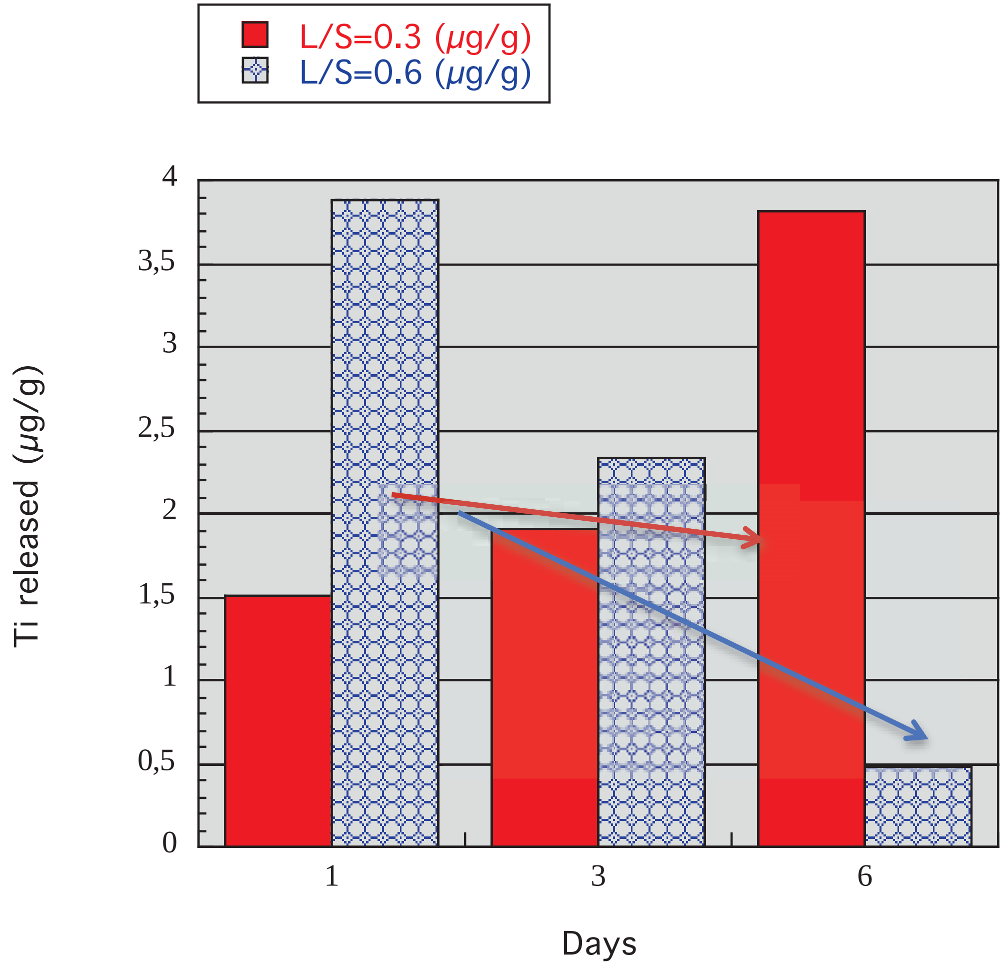
Profil of Ca (Kα) from the surface to the core of sections of cement after 7days of aging showing the increasing of the altered zone with L/S ratio



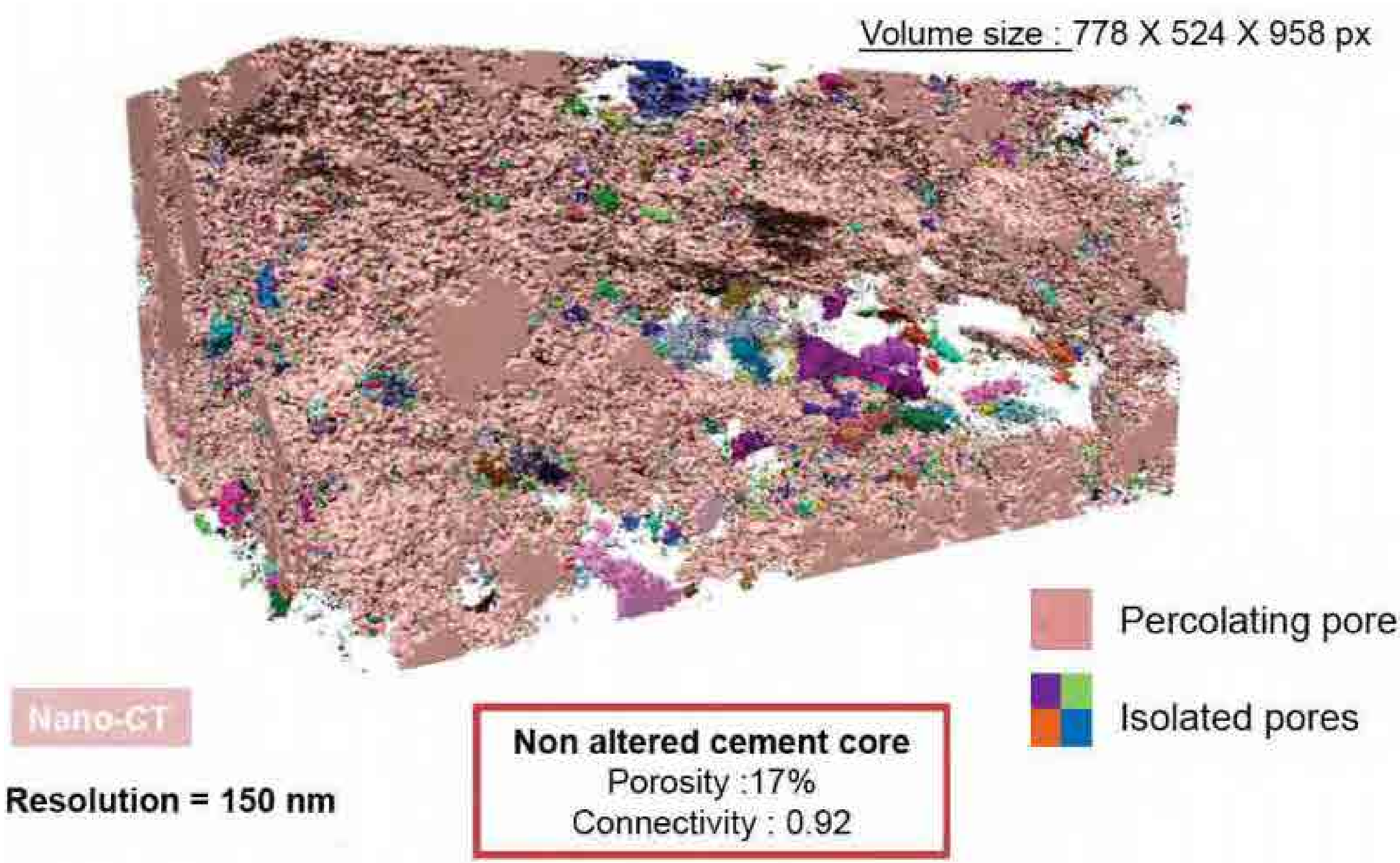


Average profile of Ti (Kα) from the surface to the core after 7 days of aging showing that TiO2 Nps follow a diffusion limited process due to the reactivity with some minerals $CaCO_3$, CSH and accumulation at the surface

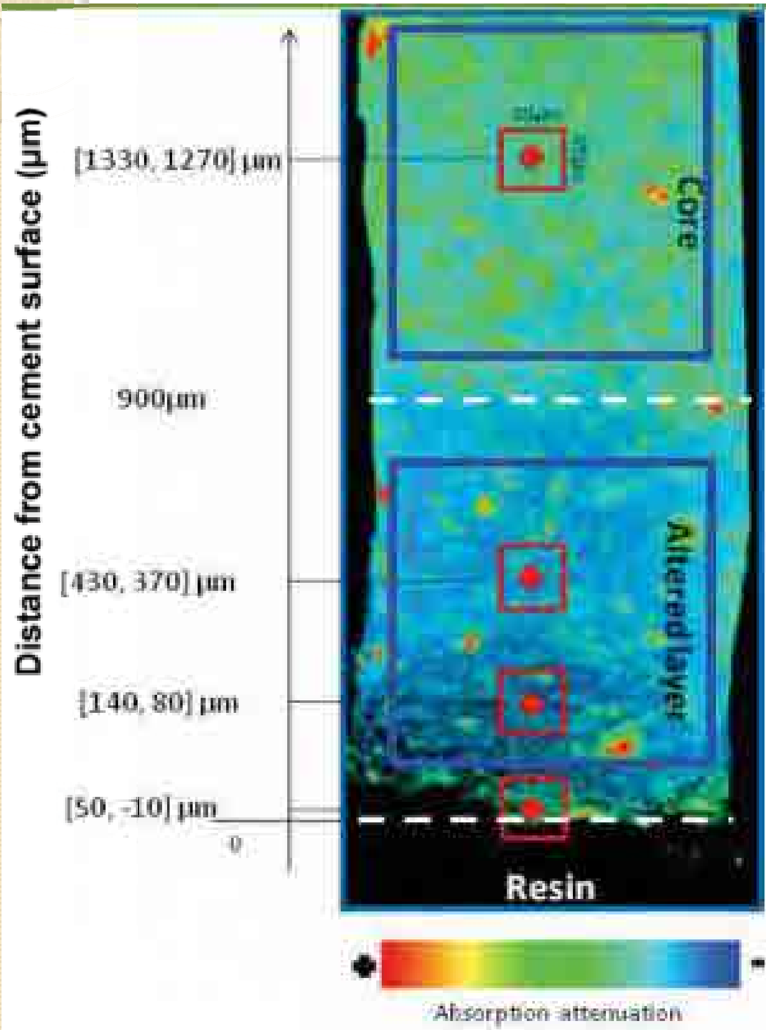
The release is controlled by the porosity and the minerals constituting the pore walls



3D pore volume using X-Ray micro and Nano Tomography
I- non-altered cement pores



2-altered cements



Micro-CT

Resolution 3 µm

Core
Porosity :10 %
Connectivity : 0.55

Altered layer

Porosity :18 %
Connectivity : 0.83

Nano CT

Resolution 150 nm

Core
Porosity :17%
Connectivity : 0.92

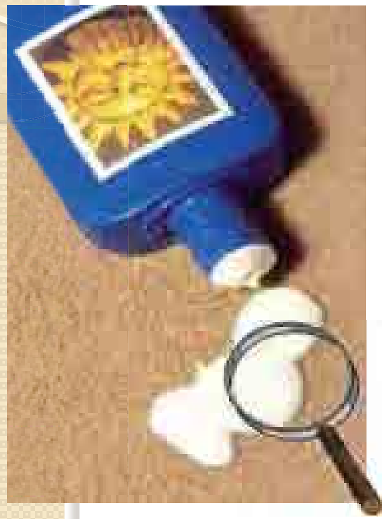
Altered layer

370-430 µm
Porosity : 32%
Connectivity : 0.97

80-140 µm
Porosity : 31%
Connectivity : 0.98

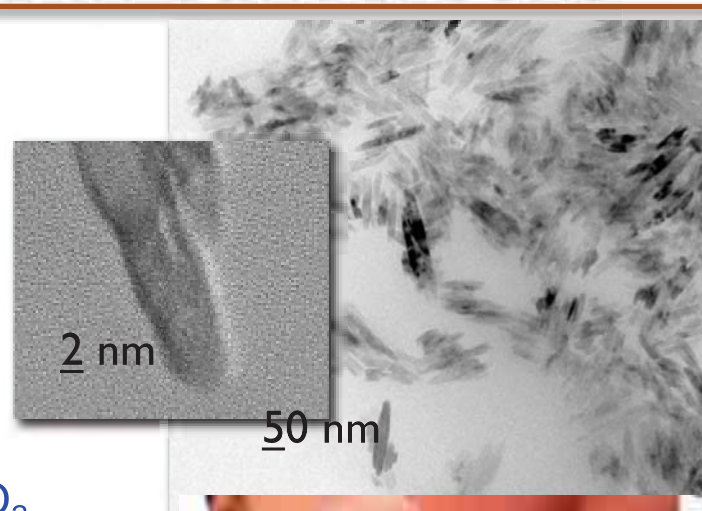
0-10 µm
Porosity : 58%
Connectivity : 0.99

Example 2: nano-TiO2 formulations used in sunscreens



4 sunscreens with SPF >50

≈ 4.6% per weight of TiO_2



- Nano TiO_2 used in sunscreen : Fate and behavior of a nanomaterial in contact with « surface » water

Botta et al., Env. Poll., 2011 ©

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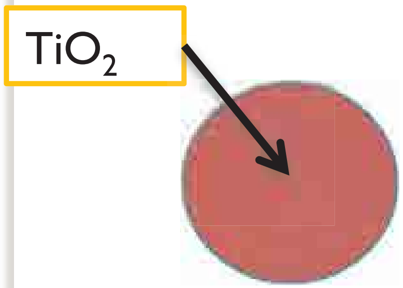
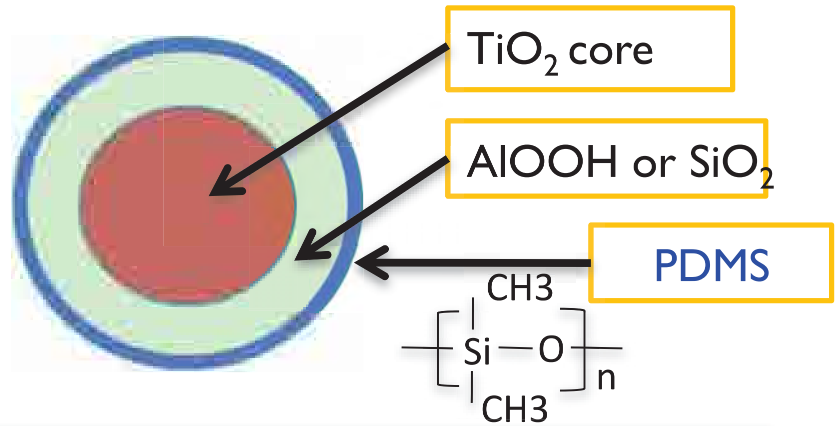
Example 3: nano-TiO_2 formulations used in sunscreens

TiO_2 nanoparticles v.s TiO_2 nanocomposite used in sunscreen

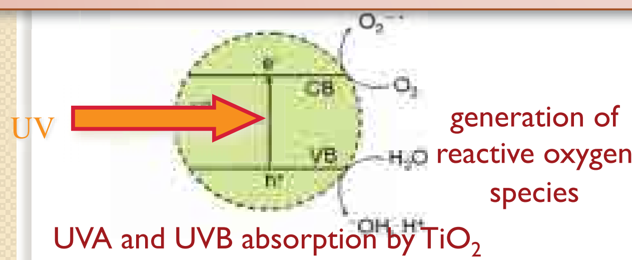




Initially

Hydrophilic
ROS Generation under light
(Photocatalytic properties)
Ecotoxicity (e.g daphnia mortality)

Hydrophobic
No ROS generation



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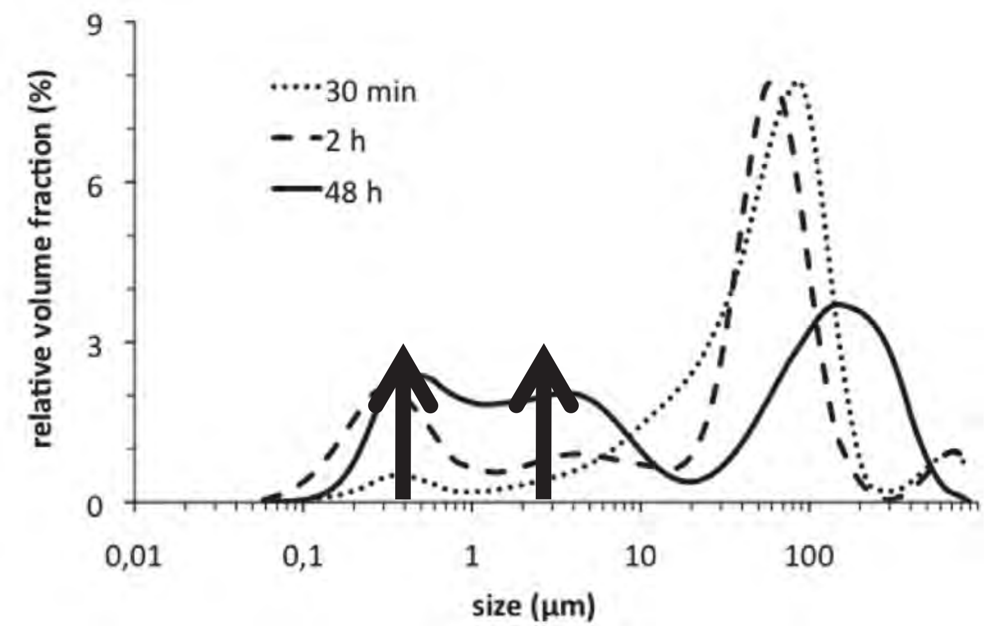
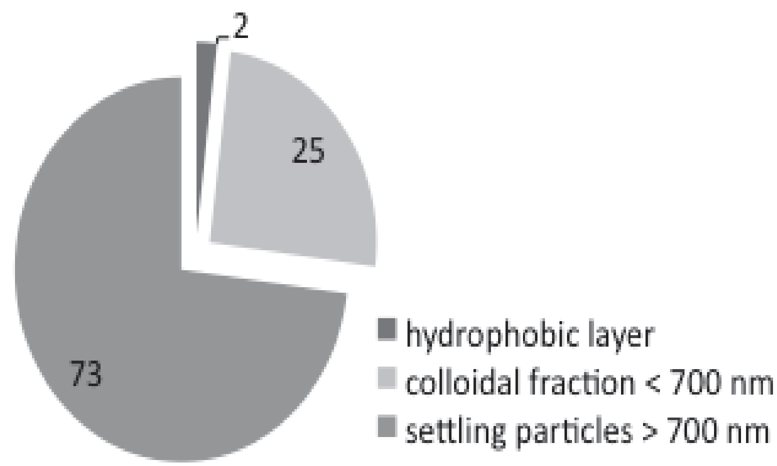
TiO_2 nanocomposite Dispersion in water

Size distribution:

Mass distribution after 48 h

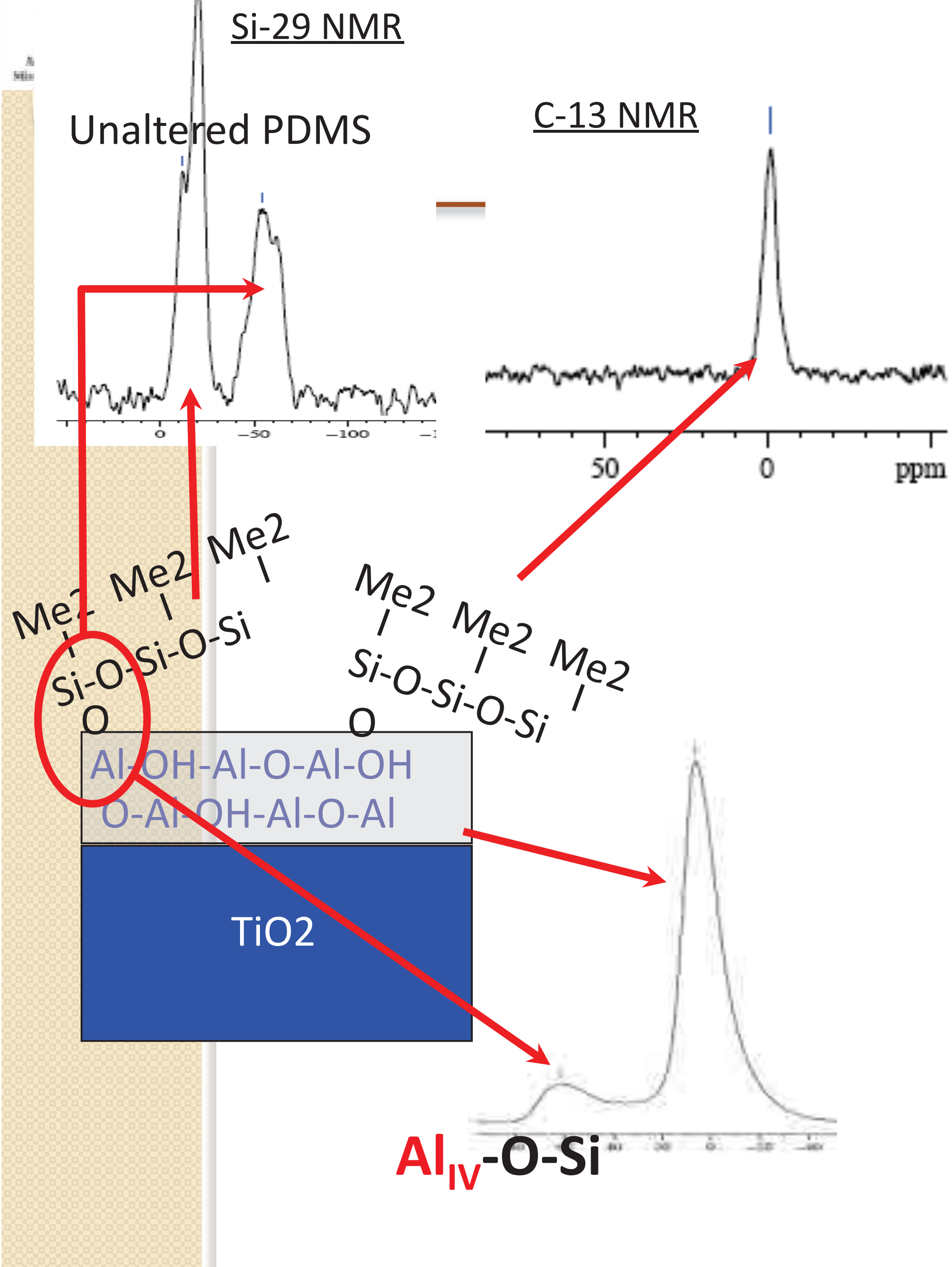




Colloidal fraction increases with time

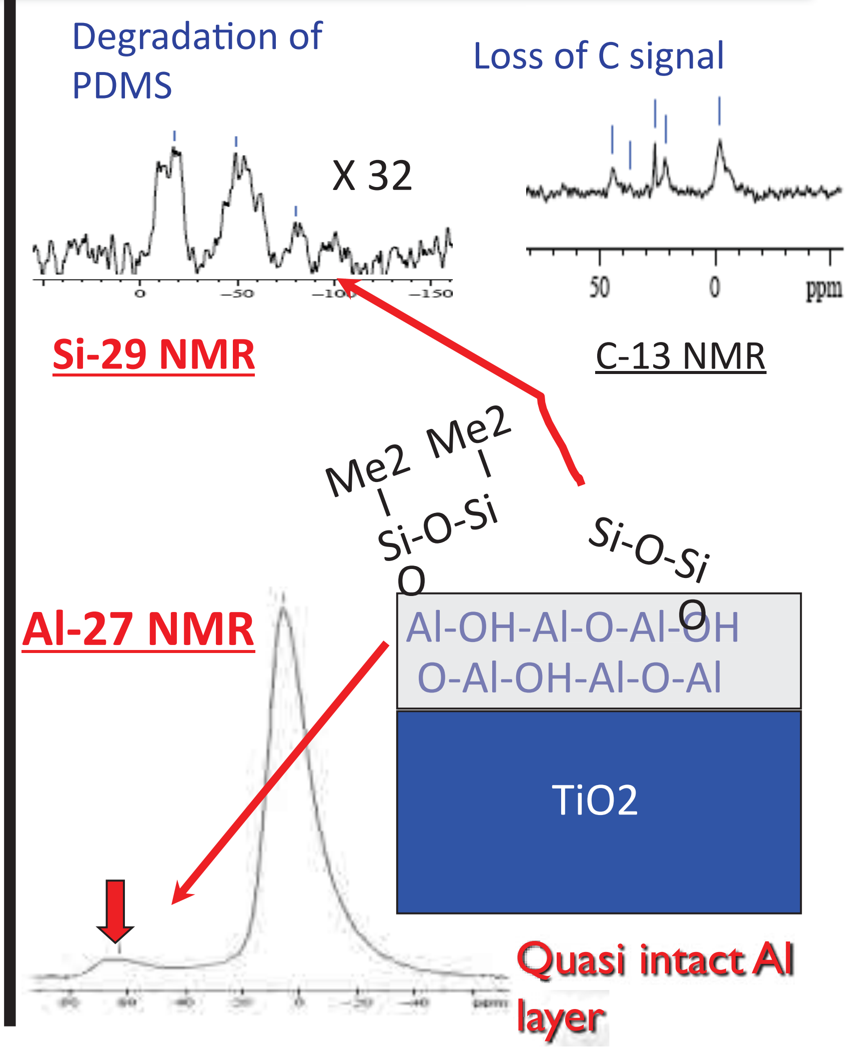
Labille et al, 2010, Environ. Poll., 2011

Unaltered Nms



Altered nanocomposite

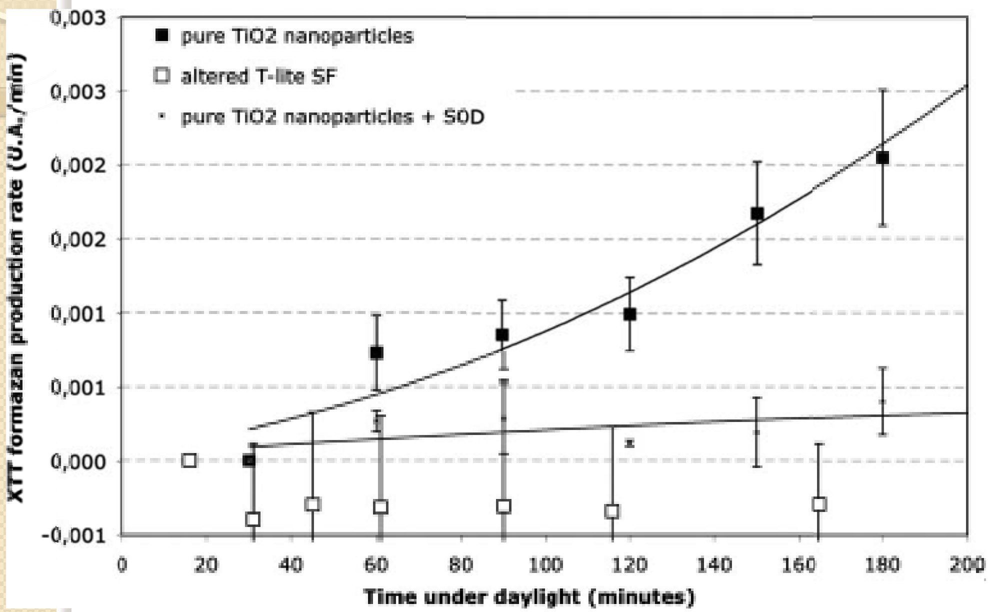
Strongly altered organic layer



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

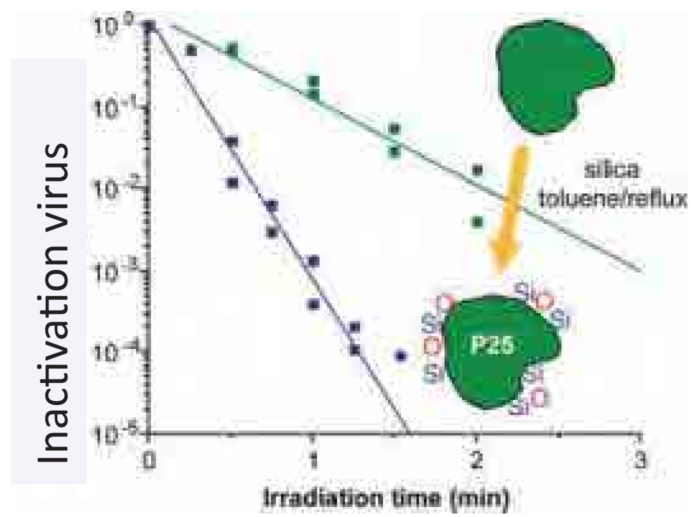
One consequence: different production of ROS

Super oxide Production $O_2^{-°}$ from altered nano << pristine rutile TiO_2
the layer of $Al(OH)_3$ strongly limits the production of ROS $O_2^{-°}$



M Auffan et al, ES and T 2010
J Labille et al Env Pollution, 2011

It is not the case for P25 coated by silica



A Barron, ES and T. 2011,

Band Gap Calculations (eV)	
TiO2(P25)	3.42
TiO2(P25)-SiO2(2.5%)	3.43
TiO2(P25)-SiO2(10%)	3.45
TiO2(P25)-SiO2(20%)	3.47

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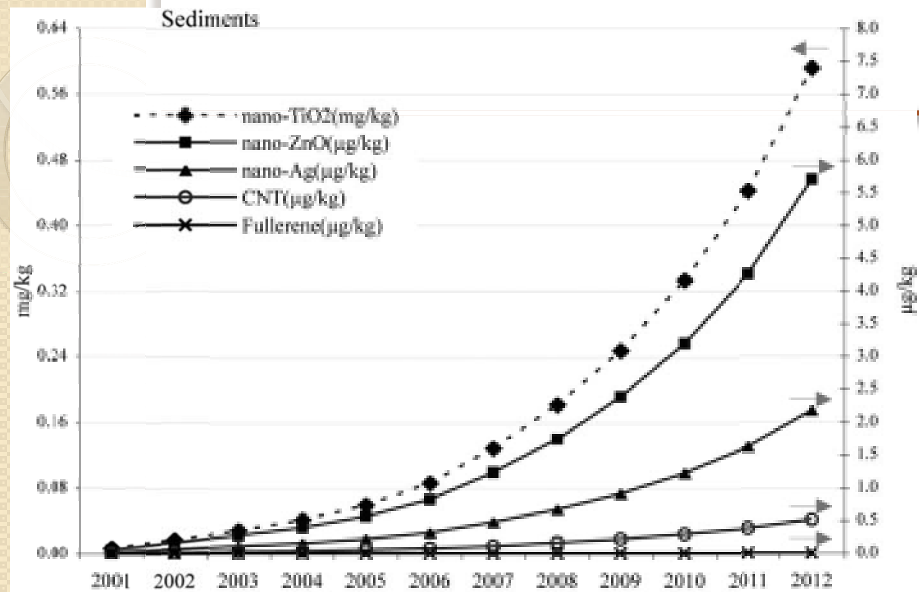
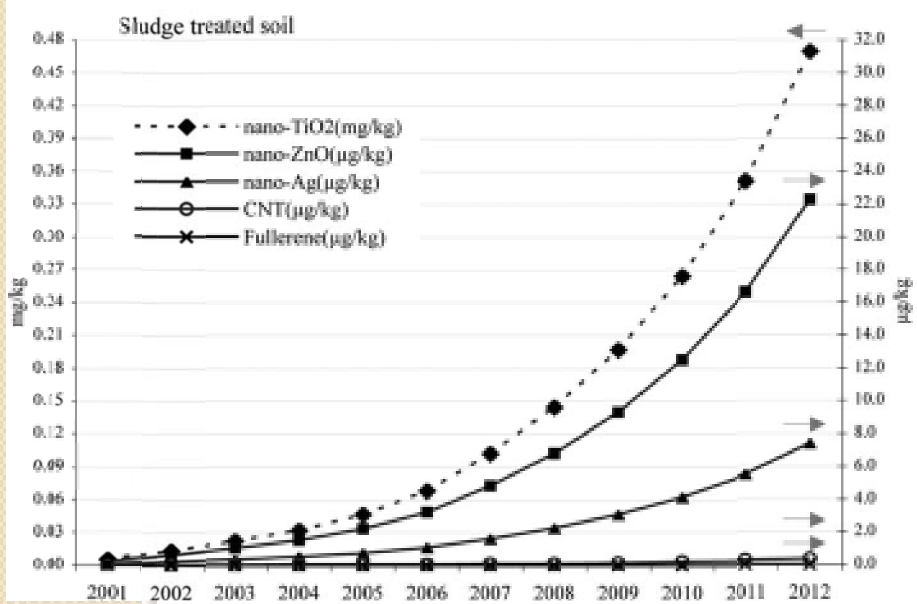
End of Life: the influence of bio-sludge in the Waste Water Treatment Plant on the transformation and exposure

Predicted nanomaterial concentrations (U.S.) in sediment and sludge treated soil for nano-TiO2 nano-ZnO, Ag°, CNT, C60: Importance of STP effluent ?

From F Gottschalk et al, ES and T 2009





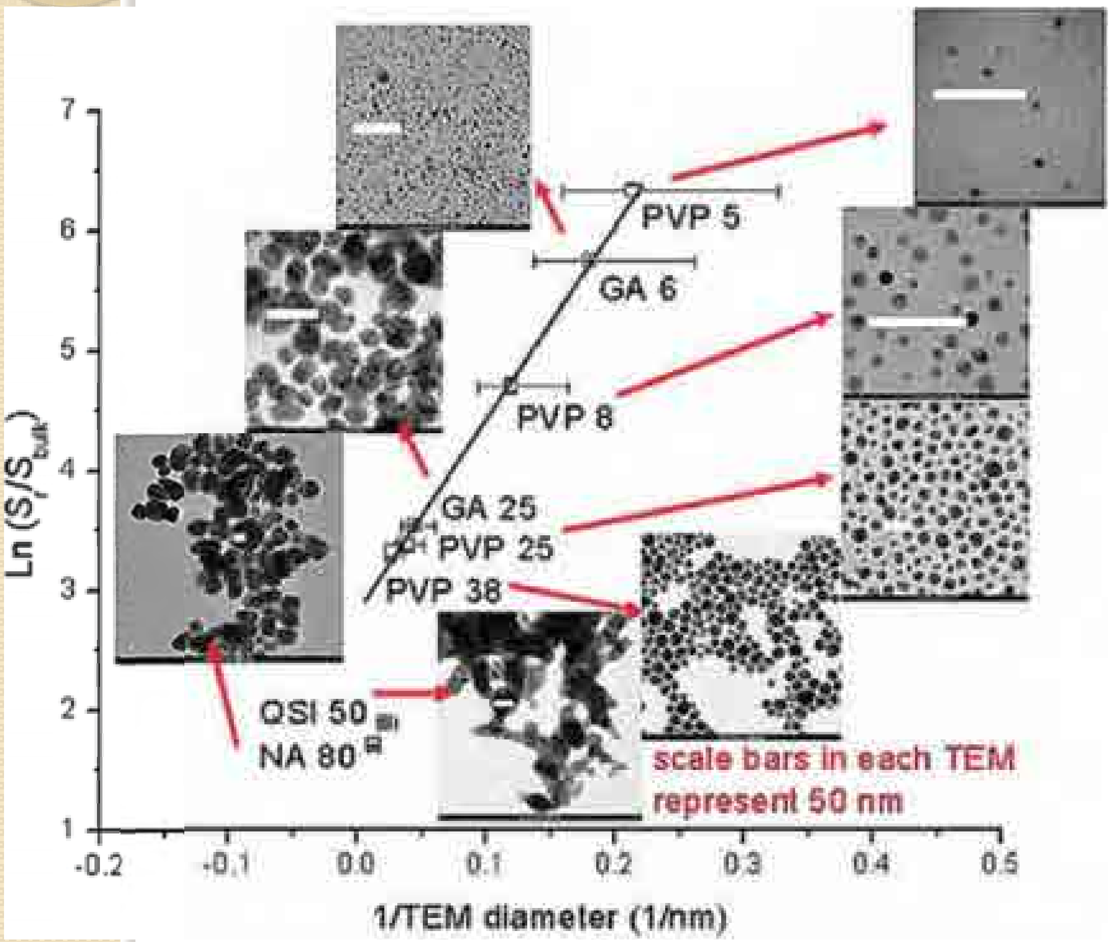
Risk Quotients (PEC/PNEC) for all ENM and Regions

compartment	Europe	U.S.	Switzerland
nano TiO2			
surface water	0.015	0.002	0.02
STP effluent	3.5	1.8	4.3
Air	<0.0005	<0.0005	<0.0005
soil	0.004	0.002	0.002
nano-ZnO			
surface water	0.25	0.02	0.32
STP effluent	10.8	7.7	11
nano-Ag			
surface water	1.1	0.17	1.03
STP effluent	61.1	30.1	55.6
air	<0.0005	<0.0005	<0.0005
CNT			
surface water	<0.0005	<0.0005	<0.0005
STP effluent	<0.0005	<0.0005	<0.0005
sediment	<0.0005	<0.0005	<0.0005
air	<0.0005	<0.0005	<0.0005
Soil	<0.0005	<0.0005	<0.0005
sludge treated soil	<0.0005	<0.0005	
Fullerenes			
surface water	<0.0005	<0.0005	<0.0005
STP effluent	0.026	0.023	0.019
Soil	<0.0005	<0.0005	<0.0005
Sludge treated soil	<0.0005	<0.0005	

Ex of Ag° ,the coating with PVP, GA….does not impact the dissolution, which follows the modified Kelvin equation i.e the ratio

$$S_r = S_{bulk} \times \exp(2\gamma Vm/RT \times r)$$

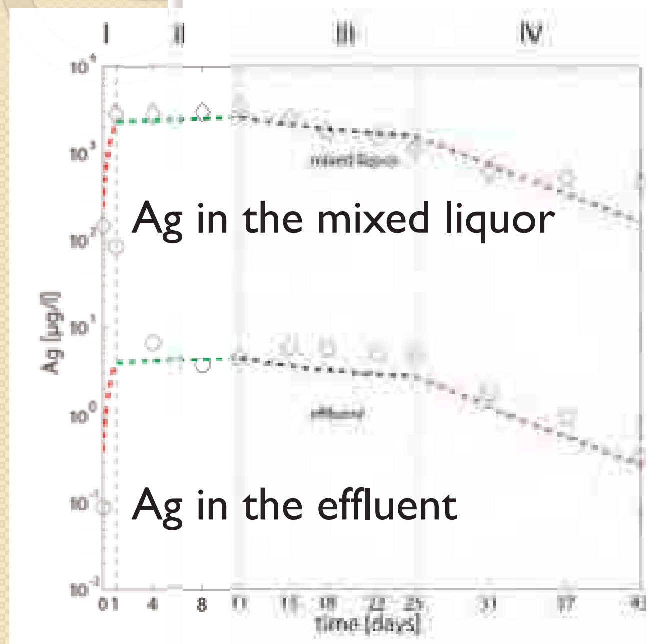
S_r / S_{bulk} only depends on the size



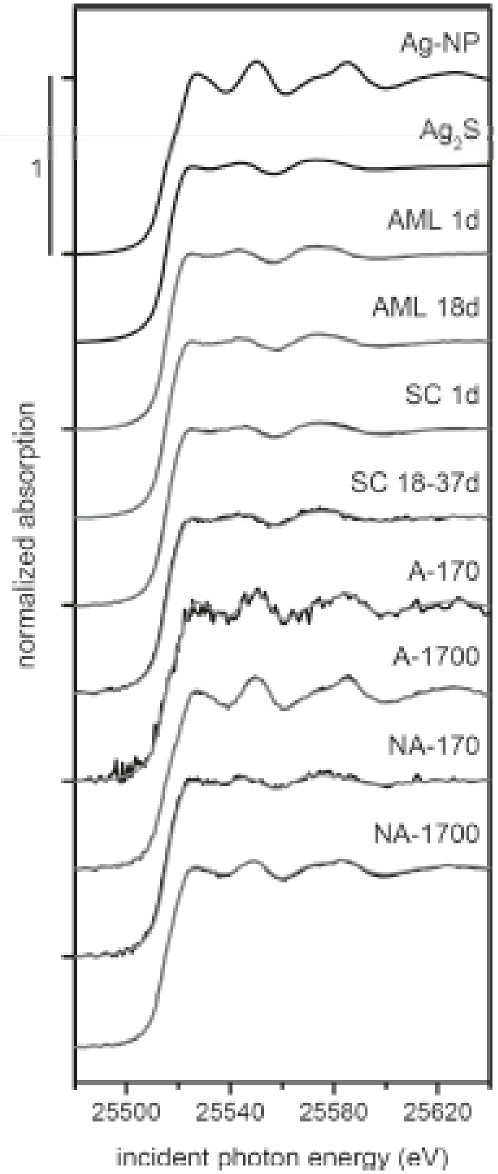
Initial Np size ~ 5 to 80 nm
And coating by PVP, GA

Ma, R et al. *ENVIRONMENTAL SCIENCE & TECHNOLOGY Volume: 46 Issue: 2 2012*

Ex: Silver coated and uncoated Nps in a WWTP pilot



Less than 10% of Ag are in the effluent



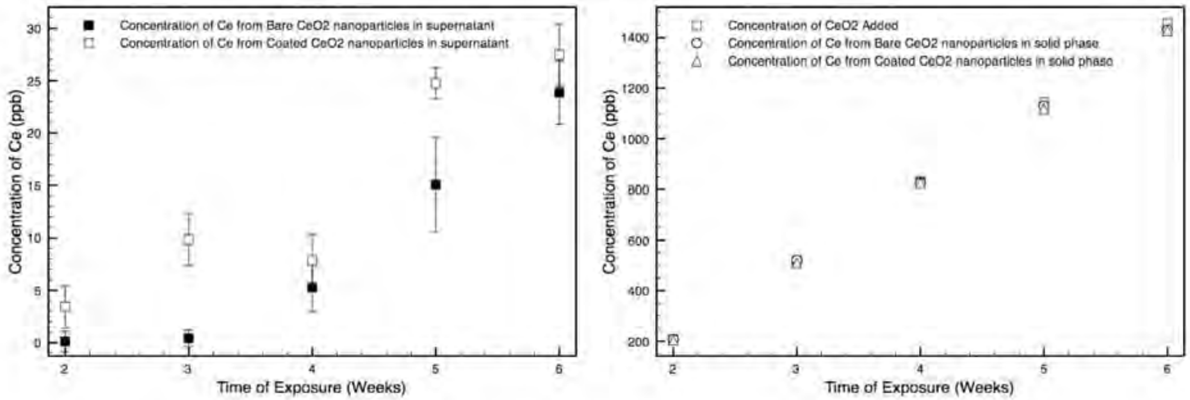
Evolution of the silver Speciation in the bio-sludge through XANES experiments

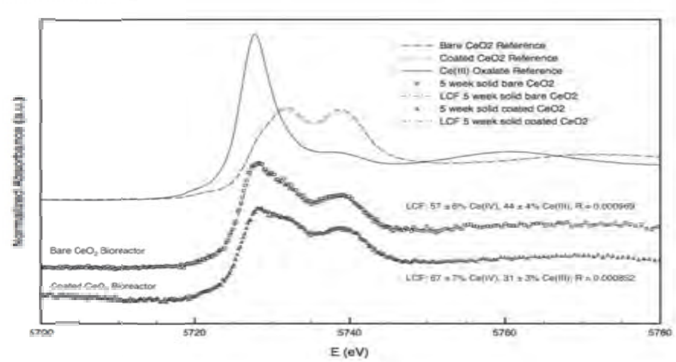
More than 90% of Ag Nps are Transformed in Ag2S

R Kaegi et al, ES and T 2011

Case of coated and uncoated industrial CeO2

Retention of Ce by biosolids ≥ 90%





Ce speciation through XANES spectra after 5 weeks in the bioreactors contaminated with pristine and citrate-functionalized CeO_2 ENMs :

More than 90% of Ce(IV) is reduced in Ce(III)

L. Barton et al, ES and T submitted (2013)

SAMPLE	% Ce(IV)	% Ce(III)	R factor	SAMPLE	% Ce(IV)	% Ce(III)	R factor
1 hour solid spike Pristine CeO_2	73	27	0.000270				
8 hour solid spike Pristine CeO_2	67	33	0.000281	8 hour solid spike Functionalized CeO_2	89	11	0.000249
1 day solid spike Pristine CeO_2	68	33	0.000317	1 day solid spike Functionalized CeO_2	89	12	0.000139
1 hour liquid spike Pristine CeO_2	> 90	< 10	0.000123				
8 hour liquid spike Pristine CeO_2	> 90	< 10	0.000106	8 hour liquid spike Functionalized CeO_2	> 90	< 10	0.000268
1 day liquid spike Pristine CeO_2	> 90	< 10	0.000067	1 day liquid spike Functionalized CeO_2	> 90	< 10	0.000149

Kinetic of reduction of CeO_4 showing the necessity to contact the bio-solids

Conclusion - Perspective

- Nanosafety context: It is important to study ENM containing products and their residues
  - different stages of life products, aging, … = Alteration of the substrate, release , chemistry and structure of the released particles…
  - Implementation of aging/alteration experiments … per products: cements, glasses, paints, cosmetics, plastics
  - Normal use v.s. accidental release (e.g. crash test, …)
- More realistic scenario evolution: from lab to mesocosms, And… natural systems.

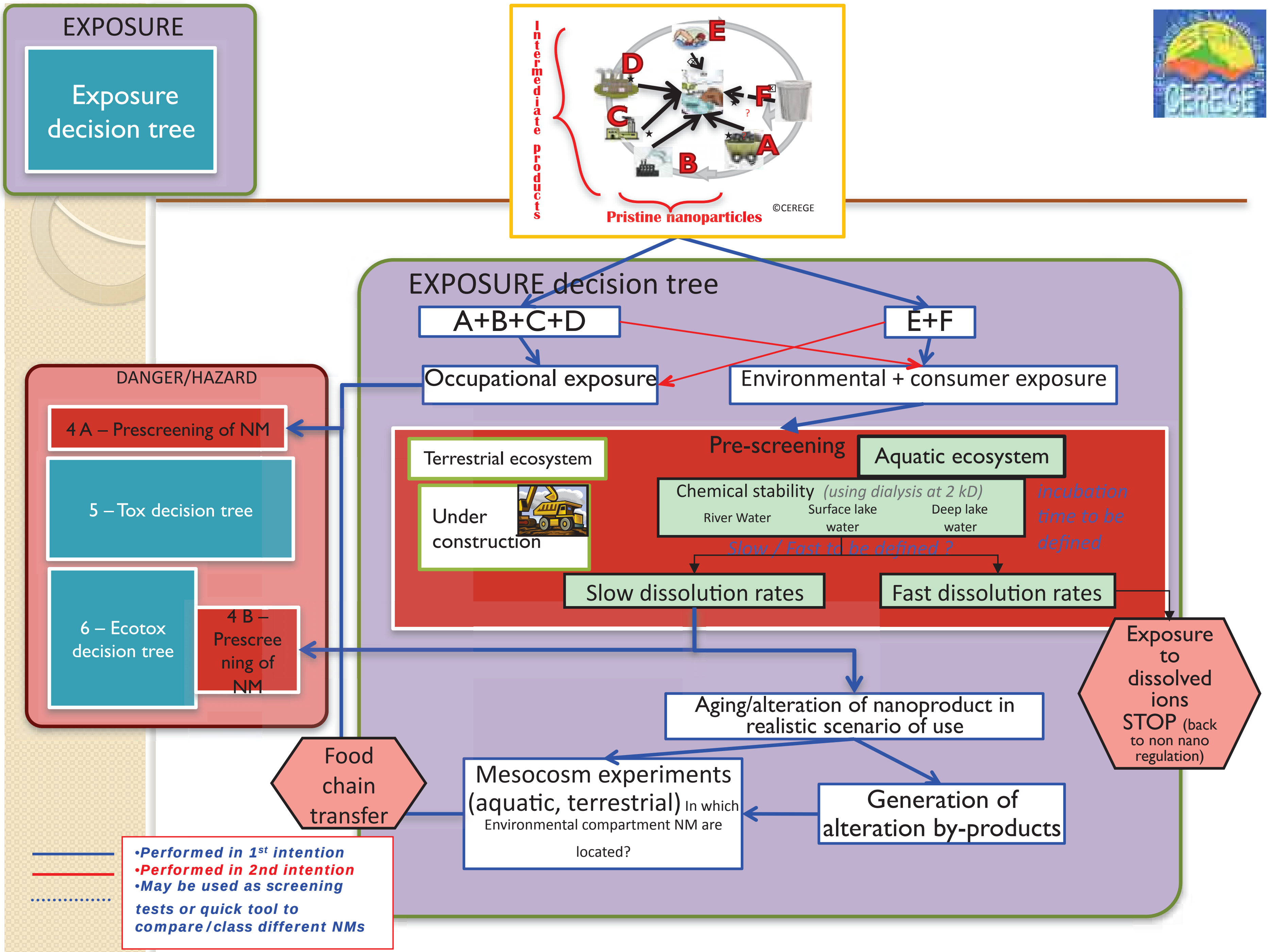
European 'conclusion'

- Nano-REG project (4 years, 66 partners)

« A common European approach to the regulatory testing of nanomaterials »

WP 3: Exposure through life cycle analysis

1) Characterise and quantify real exposures to humans and the environment (in terms of NM characteristic (metrics, size distribution, aggregation, composition, surface characterisation, with determination of uncertainty on the measurement etc), levels, time dependency, evolution, dispersion numbers exposed using modeling techniques rather than new measurements))
2) Develop "early warning signal" to exposure (monitoring, sensors…)
3) Identify critical life cycle stage (in terms of exposure)
4) **Develop an exposure decision tree and an exposure "categorization" procedure. (not case by case).**


EXPOSURE
Exposure decision tree
Intermediate products
D
E
F
C
A
B
Pristine nanoparticles
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EXPOSURE decision tree
A+B+C+D
E+F
Occupational exposure
Environmental + consumer exposure
DANGER/HAZARD
4 A – Prescreening of NM
5 – Tox decision tree
6 – Ecotox decision tree
4 B – Prescreening of NM
Pre-screening
Terrestrial ecosystem
Aquatic ecosystem
Under construction
Chemical stability (using dialysis at 2 kD)
River Water
Surface lake water
Deep lake water
incubation time to be defined
Slow / Fast to be defined ?
Slow dissolution rates
Fast dissolution rates
Exposure to dissolved ions STOP (back to non nano regulation)
Aging/alteration of nanoproduct in realistic scenario of use
Food chain transfer
Mesocosm experiments (aquatic, terrestrial) In which Environmental compartment NM are located?
Generation of alteration by-products
•Performed in 1st intention
•Performed in 2nd intention
•May be used as screening tests or quick tool to compare/class different NMs

Labex

An EU-US network from SERENADE
Toward safer and eco-designed innovative nanomaterials

"The new generation of materials safer by design"

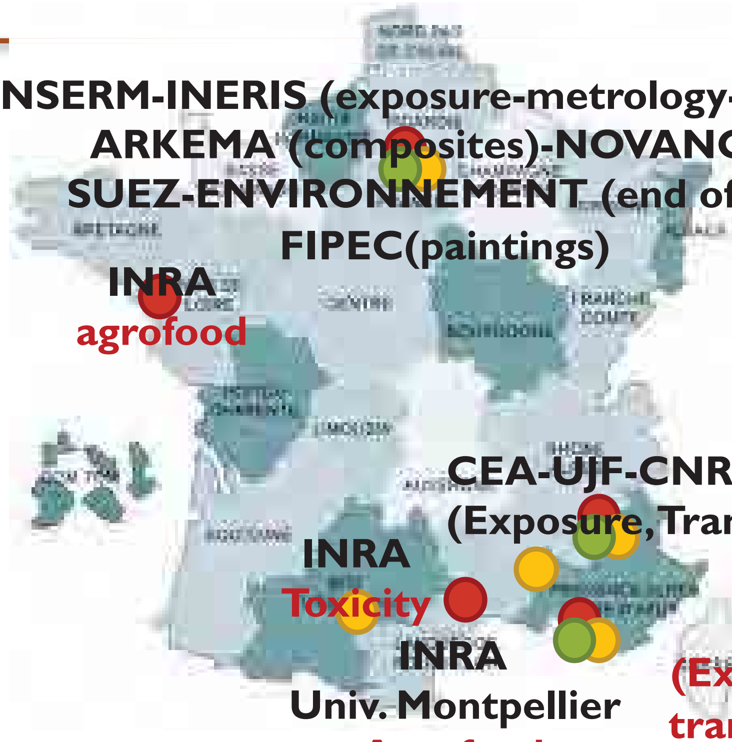
Coordination CEREGE:
Director : JY Bottero
Executive Director: J Rose

Programme Coordinator: Sophie Bonifay

Safer and Ecodesign Research and Education applied to NAnomaterial DEvelopment

CEREGE Nano Team: M Auffan; P Chaurand; Cl Levard: E Doelsch; A Masion; D Borschneck; B Angeletti; J Perrin; J Labille; Ch Pailles;
PhD and Post docs: A Avellan; N Bossa; L Wei; C Layet; M Tella; N Kumar; Cl Layet

French Partners



INSERM-INERIS (exposure-metrology-toxicity)
ARKEMA (composites)-NOVANCIA
SUEZ-ENVIRONNEMENT (end of life)
FIPEC(paintings)

INRA
agrofood

CEA-UJF-CNRS
(Exposure, Transformation)

INRA
Toxicity

INRA
Univ. Montpellier
Agrofood
Packaging

AMU-CNRS
CEA; INERIS
(Exposure, Life cycle, transformation, (eco) toxicity)
ALLIOS (paintings)

- Synthesis and properties
- Ecotoxicity/toxicity
- Life cycle assessment

Support letters:
Ital Cementi
Union des Industries de la Chimie
Danone

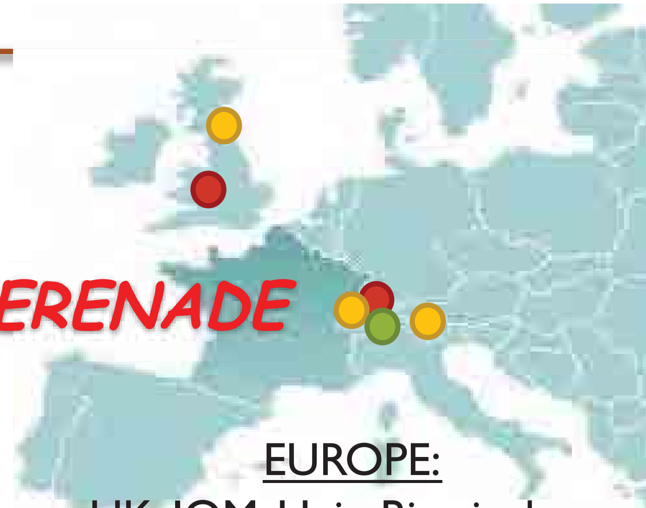
INTERNATIONAL NETWORKING

USA CEINT :

Duke Univ., Univ. of Kentuky, Virginia Tech, Stanford Univ. Carnegie Melon, Baylor

CANADA:

Univ. of Montreal



EUROPE:

UK: IOM, Univ. Birmingham,
SZ: EPFL, **EAWAG**, **EMPA**
AT : Universität Wien

- Synthesis and properties
- Ecotoxicity/toxicity
- Life cycle assessment and Risk modeling

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Thank you

Merci !

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http://Se3d.cerege.fr & http://nano.cerege.fr

Ecotoxicity of bare TiO_2

- Ecotoxic Effect of Photocatalytic Active Nanoparticles (TiO_2) on Algae and

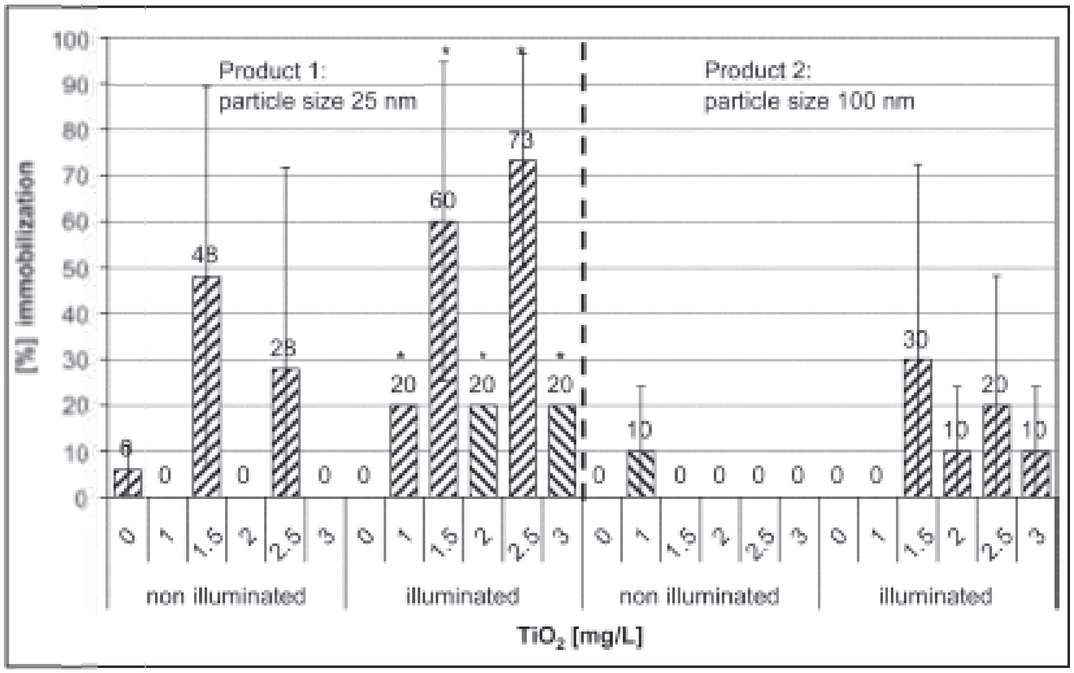

Fig. 5: Immobilization of daphnids by TiO_2; significance: * $0.1 > p \leq 0.5$

Light increases effects

Hund-Rinke and Simon Environ Sci & Pollut Res 2006: 1 – 8