Exposure along the Value Chain of Nano Products

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INTERFAces & Transfer @ CEREGE
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
- Nanoclay
Commercialized nanomaterials/nanoproducts are complex

- UV absorbers
- Stronger and lighter materials
- Faster electronic circuit
- Medical Applications
- Water treatment
- Antimicrobial
- Self-cleaning surfaces
- TiO$_2$
- SiO$_2$
- CNT, SiC…
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

- Nanomaterial manufacture
- Air exposure
- Accidental release
- Workers
- Plants

Nanomaterial use

- Self cleaning glasses, paints, Sunscreens...
- Aging, use
- Sunscreen

Release of nanoresidues and nanoparticles

Transfer in environmental compartments
Reactivity with pollutants or organic compounds

Aquifer transfer?

Surface water

Pollutants

Organic compounds

Sol

Aquifer
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$_2$ + AIOOH + 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: NanoCeO₂-composite in outdoor paint

Example: Self-cleaning cement

Example: Sunscreens

From Hansen et al, 2007©
Self-cleaning Cement

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-TiO$_2$ 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% + 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-$\text{TiO}_2$ 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 7 days 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 CaCO₃, 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

Volume size: 778 x 524 x 958 px

Nano-CT
Resolution = 150 nm

Non altered cement core
Porosity = 17%
Connectivity = 0.92

Percolating pore
Isolated pores
2-altered cements
Example 2: nano-TiO$_2$ formulations used in sunscreens

- 4 sunscreens with SPF $>50$

- Nano TiO$_2$ used in sunscreen: Fate and behavior of a nanomaterial in contact with «surface» water

Botta et al., Env. Poll., 2011 ©
Example 3: nano-TiO₂ formulations used in sunscreens

TiO₂ nanoparticles  v.s  TiO₂ nanocomposite used in sunscreen

TiO₂ core  AIOOH or SiO₂

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

Hydrophobic
No ROS generation

UVA and UVB absorption by TiO₂
TiO$_2$ nanocomposite Dispersion in water

Size distribution: Mass distribution after 48 h

Colloidal fraction increases with time

Unaltered Nms

Si-29 NMR

Unaltered PDMS

C-13 NMR

Strongly altered organic layer

Degradation of PDMS

Loss of C signal

X 32

Si-29 NMR

C-13 NMR

Al-27 NMR

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

TiO2

AlIV-O-Si

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

TiO2

Quasi intact Al layer

Auffan et al., Environ.Sci.Technol. 2010
One consequence: different production of ROS

Superoxide Production $O_2^{-}$ from altered nano $\ll$ 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

Band Gap Calculations (eV)

<table>
<thead>
<tr>
<th>Material</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$(P25)</td>
<td>3.42</td>
</tr>
<tr>
<td>TiO$_2$(P25)-SiO$_2$(2.5%)</td>
<td>3.43</td>
</tr>
<tr>
<td>TiO$_2$(P25)-SiO$_2$(10%)</td>
<td>3.45</td>
</tr>
<tr>
<td>TiO$_2$(P25)-SiO$_2$(20%)</td>
<td>3.47</td>
</tr>
</tbody>
</table>

Inactivation virus

$A$ Barron, ES and T. 2011,
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

<table>
<thead>
<tr>
<th></th>
<th>Europe</th>
<th>U.S.</th>
<th>Switzerland</th>
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</thead>
<tbody>
<tr>
<td>nano TiO2</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>surface water</td>
<td>0.015</td>
<td>0.002</td>
<td>0.02</td>
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<tr>
<td>STP effluent</td>
<td>3.5</td>
<td>1.8</td>
<td>4.3</td>
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<tr>
<td>Air</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
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<tr>
<td>soil</td>
<td>0.004</td>
<td>0.002</td>
<td>0.002</td>
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<tr>
<td>nano-ZnO</td>
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<td></td>
<td></td>
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<tr>
<td>surface water</td>
<td>0.25</td>
<td>0.02</td>
<td>0.32</td>
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<tr>
<td>STP effluent</td>
<td>10.8</td>
<td>7.7</td>
<td>11</td>
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<tr>
<td>nano-Ag</td>
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<tr>
<td>surface water</td>
<td>1.1</td>
<td>0.17</td>
<td>1.03</td>
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<tr>
<td>STP effluent</td>
<td>61.1</td>
<td>30.1</td>
<td>55.6</td>
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<td>CNT</td>
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<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
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<tr>
<td>STP effluent</td>
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<td>&lt;0.0005</td>
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<td>sediment</td>
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<td>air</td>
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<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
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<tr>
<td>Soil</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>sludge treated soil</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
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<tr>
<td>Fullerenes</td>
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<tr>
<td>surface water</td>
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<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
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<tr>
<td>STP effluent</td>
<td>0.026</td>
<td>0.023</td>
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<td>Soil</td>
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<tr>
<td>Sludge treated soil</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
</tr>
</tbody>
</table>
Ex of Ag\(^{+}\), the coating with PVP, GA... does not impact the dissolution, which follows the modified Kelvin equation i.e the ratio

\[ S_r = S_{bulk} \times \exp \left( \frac{2\gamma Vm}{RT} \times r \right) \]

\[ \frac{S_r}{S_{bulk}} \text{ only depends on the size} \]

Initial Np size \( \sim \) 5 to 80 nm
And coating by PVP, GA

Ma, R et al. ENVIRONMENTAL SCIENCE & TECHNOLOGY Volume: 46 Issue: 2 2012
Evolution of the silver Speciation in the bio-sludge through XANES experiments

More than 90% of Ag Nps are Transformed in Ag2S

Ex: Silver coated and uncoated Nps in a WWTP pilot

R Kaegi et al, ES and T 2011
Ce speciation through XANES spectra after 5 weeks in the bioreactors contaminated with pristine and citrate-functionalized CeO₂ ENMs:

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

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

Retention of Ce by biosolids $\geq 90\%$

Kinetic of reduction of CeO₄ 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.
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).
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)

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

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

USA CEINT:

CANADA:
Univ. of Montreal

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

AUTRALIA
Univ. New South Wales

Synthesis and properties
Ecotoxicity/toxicity
Life cycle assessment and Risk modeling
Thank you
Merci !
Ecotoxicity of bare TiO$_2$

- Ecotoxic Effect of Photocatalytic Active Nanoparticles (TiO$_2$) on Algae and Daphnids

![Graph showing immobilization of daphnids by TiO$_2$.](image)

Fig. 5: Immobilization of daphnids by TiO$_2$; significance: * $0.1 > p \leq 0.5$

Light increases effects