

OECD WORKSHOP

SAFE MANAGEMENT OF NANOWASTE

**Hosted by the Federal Ministry of Environment,
Nature Conservation and Nuclear Safety (BMU) of
Germany**

Munich, 9-11 May 2012

DRAFT AGENDA 27 April

DRAFT AGENDA (27 April 2012)

The main objectives of the workshop are:

- to get a better understanding of the potential risks posed by nanowaste and waste containing nanomaterials
- to exchange information about existing initiatives/approaches addressing nanowaste management
- to identify what OECD and member country governments can do to ensure safe management of such materials.

The workshop will take place in Room 03 of the International Congress Center of Munich, Messe Munich International – MMI

WEDNESDAY 9 MAY

15:00: Workshop participants are invited for an introduction meeting in Room 03 followed by a visit of the IFAT ENTSORGA fair [<http://www.ifat.de/en/Home>]

Ms. Jutta Struwe, from Prognos AG, will give a welcome address on:

Nanomaterials and Possible Recycling Opportunities

THURSDAY 10 MAY

1) Welcome and introduction: objectives of the workshop

10:00 - 10:10 *by Andreas Jaron (BMU) and Peter Börkey (OECD Secretariat).*

10:10 – 10:30: *Prof. Heidi Foth, Professor of Environmental Toxicology and Director of the Institute of Environmental Toxicology at the Martin Luther University Halle-Wittenberg (Germany),*

will set the scene by addressing the following issues

- ✓ What is meant by “nanowaste”?
- ✓ Why is nanowaste an issue?
- ✓ What do we know about the risks that may result from the different management options for waste containing nanomaterials (landfilling, incineration, recycling)?
- ✓ What can presently be undertaken by OECD and governments to tackle the issue?

2) Potential risks of products containing nanomaterials and of released nanomaterials:

- 10:30 – 11:15 (30 minutes presentation and 15 minutes discussion)

Certain materials or goods contain nanomaterials that may be released into the environment during their production, consumption or disposal/recovery phase. There are circumstances where these operations may release nanomaterials and pose some risks for human health and the environment. The objective of this session is to identify the types of products as well as the circumstances or actions which may lead to such risks, and what types of risks have been identified so far.

Speaker: Ms. Lori Sheremeta (National Institute of Nano-Technology in Canada)

- 11:15 – 11:45 (20 minutes presentation and 10 minutes discussion)

Presentation of the work programme of the OECD Working Party on Manufactured Nanomaterials (WPMN): reasons for tackling the issue of manufactured nanomaterials, objective of the work, relationship with nanowaste.

Speaker: Ms. Mar Gonzalez (OECD Secretariat to the WPMN)

3) Waste management and fate of nanomaterials contained in waste:

3.1 Review of existing waste treatments and their related processes: landfilling, sewage sludge treatment, incineration, recycling.

11:45 – 12:30 (30 min presentation and 15 min discussion)

During this session the existing techniques for managing waste will be examined, with the perspective of possible releases of nanomaterials originally enshrined in waste.

Speaker: Mr. Emeric Fréjafon (INERIS, France)

12:30 – 14:00 Lunch break

3.2 Waste management and fate of nanomaterials:

14:00 – 15:10 (40 min presentation followed by 30 min discussion):

The objective of this session is to identify releases of nanomaterials during the waste treatment operations and the possible pathways to the different environmental media (e.g. emissions from incineration of wastes containing nanomaterials, shredding for recycling, leachates from sewage sludge used in agriculture, etc.).

Speakers:

- **Dr. André Hauser (Office fédéral suisse de l'environnement)**
- **Mr. Emeric Fréjafon (INERIS, France)**

4) Measurement of environmental exposure to nanomaterials, including nanowastes

15:10 – 15:55 (30 min presentation followed by 15 min discussion):

This session will discuss the current technologies for measurement of exposure to nanomaterials and nanowastes and the results of actual studies.

Speaker: Dr. Michael Burkhardt UMTEC (Institut für Umwelt und Verfahrenstechnik, Institute for Environment and Process Technology, Switzerland)

15:55 – 16:30 Coffee break

5) Illustration of issues raised by nanowastes:

16:30 – 17:15 (30 min presentation followed by 15 min discussion)

Case study on end-of-life tyres including nanomaterials

Speaker: Francis Peters (Michelin, France).

19:00 : Dinner offered by the German Ministry of Environment, Nature Conservation and Nuclear Safety at Hackerhaus, in Munich Center.

FRIDAY 11 MAY

6) What is currently undertaken on nanowaste within OECD countries and international bodies?

09:00 – 09:45 (30 min presentation followed by 15 min discussion)

An overview of initiatives/approaches and activities on nanowaste management which exist or are under development, domestically and internationally, has been carried out by *Dr. Mathias Tellenbach (Terra Consult, Switzerland)* on behalf of OECD.

Dr. Tellenbach will present the findings of this survey and lessons revealed by this survey.

7) What's next?

09:45 – 10:45 (general discussion led by the Chair)

The Chair will summarise what has been learnt and heard during the previous sessions of the workshop.

On this basis, participants will discuss how can international cooperation help to move the nanowaste agenda forward (e.g. by sharing experience and knowledge, or coordinating research activities, by examining to which extent existing guidelines or

policy approaches might fulfil the needs of nanowaste management, by developing guidance for producers using nanomaterials, for waste managers, etc.).

After the Munich workshop, a report on the discussions and conclusions of the workshop will be produced by the OECD Secretariat, for submission to the next meeting of the WPRPW in November 2012. The report will include proposals for further work and potential role of OECD in this area.

Participants list

Belgium/Belgique

Ms. Kathleen DIERICK

OVAM

Canada

Miss Veronic PICHARD

*Program Scientist
Waste Reduction and Management Branch
Environment Canada*

Ms. Lori SHEREMETA

*Faculty of Engineering
National Institute for Nanotechnology*

Denmark/Danemark

Ms. Trine LETH KØLBY

*Environmental Protection Agency
Danish Ministry of the Environment*

Estonia/Estonie

Mr. Peeter EEK

*Director General Waste Department
Ministry of the Environment*

Finland/Finlande

Mr. Ari SEPPÄNEN

*Environmental Protection
Ministry of the Environment*

France

M. Emeric FREJAFON

*L'Institut National de l'Environnement Industriel et
des Risques
INERIS - French National Institute for Industrial
Environment and Risks*

Germany/Allemagne

Mr. Andreas JARON

*Head of Division
WA II 1 - General Matters of Waste Management,
Transboundary Movement of Waste
Federal Ministry for the Environment, Nature
Conservation and Nuclear Safety (BMU)*

Dr. Wolfgang DUBBERT

Federal Environment Agency (Umweltbundesamt)

Professor Heidi FOTH

*Director
the Institute of Environmental Toxicology at the
Martin Luther University
Institute of Environmental Toxicology*

Ms. Susann KRAUSE

*Deputy Head of Section
Municipal Waste Management Hazardous Waste,
Focal Point to the Basel Convention
Federal Environmental Agency*

Mrs. Jutta STRUWE

*Waste Management and Secondary Raw Materials
Prognos AG*

Mr. Volker WEISS

Federal Environmental Agency

Mr. Benjamin WIECHMANN

*Researcher
Federal Environmental Agency*

Ireland/Irlande

Mr. Brendan O'NEILL

*Senior Adviser (Environment)
Department of the Environment, Community and
Local Government*

Poland/Pologne

Ms. Kinga MROZIEWICZ

*Specialist
Bureau for Chemical Substances and Preparations*

Slovak Republic/République slovaque

Mr. Marian STRYCEK

*Waste Management Departement
Ministry of Environment of the Slovak Republic*

Switzerland/Suisse

Dr. Michael BURKHARDT

UMTEC

Mr. Andreas HAUSER

Office fédéral de l'environnement (OFEV)

EU/UE

Mr. Henrik LAURSEN

*Policy Officer
DG ENV
European Union*

Russian Federation/Fédération de Russie

Mr. Konstantin KUSHNIR

*Chief specialist
Department of state policy and regulation
Ministry of natural resources and environment of
the Russian Federation*

Chinese Taipei/Taipei chinois

Dr. Harvey HOUNG

Environmental Protection Agency

Business and Industry Advisory Committee (BIAC)/Comité consultatif économique et industriel (BIAC)

Dr. Steffi FRIEDRICHS

*Director General
Nanotechnology Industries Association*

Mme Jenny HOLMQVIST

*Global Product Stewardship Manager
European Chemical Industry Council*

Mr. Francis PETERS

*Worldwide Materials Projects Director
Industry Standard & Government Regulation
BIAC*

Dr. Martin REUTER

VCI

Mr. Unico VAN KOOTEN

Dutch Waste Management Association - DWMA

Trade Union Advisory Committee (TUAC)/Commission syndicale consultative (TUAC)

Ms. Aida PONCE

*researcher
European Trade Union Institute*

Environmental NGO

Ms. Dania CRISTOFARO

*Pollution Control Officer
ECOS European Environmental Citizens'
Organisation for Standardisation*

OECD/OCDE

Mr. Peter BORKEY

*Principal Administrator
ENV/EEI
OECD*

Mme Soizick DE TILLY

*Administrator
ENV
OECD*

Ms. Mar GONZALEZ

*Administrator, Nanosafety
ENV/EHS
OECD*

Tecnalia Research & Innovation

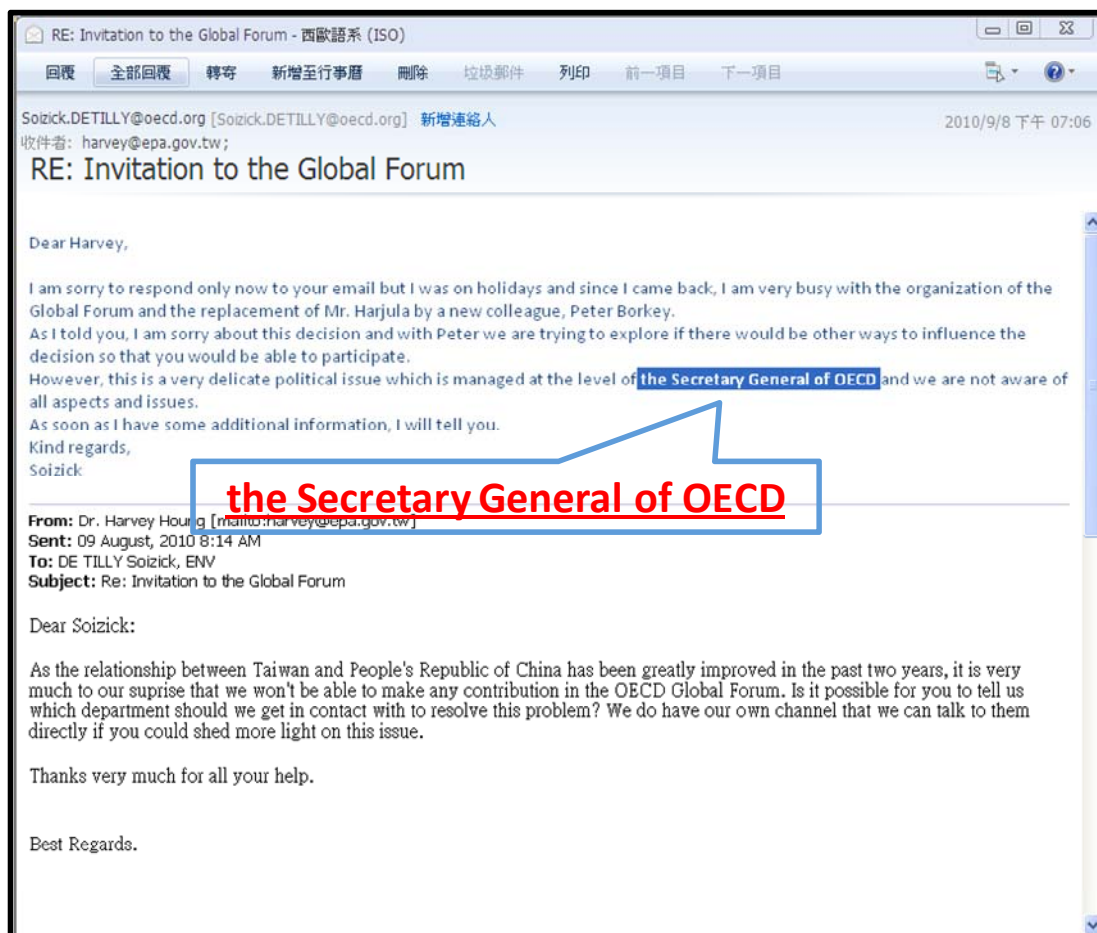
Mr. Pablo BENGURIA

*Head of Tecnalia's Nano and Water Group
Tecnalia Research & Innovation*

Terra Consult Bern

Dr. Mathias TELLENBACH

*Consultant
Terra Consult Bern*



在中國大陸壓力下，OECD 秘書長辦公室在大會前 2 個月表示無法邀請我國與會



奈米廢棄物研討會中場休息時間・與 OECD 總監及主講人聯誼



奈米廢棄物研討會・晚宴



奈米廢棄物研討會現場

中共施壓 吳釗燮吃閉門羹

五名前美國國務卿 拒與吳釗燮同桌 OECD中共也運作簽署諒解備忘錄 對我「七不」

【華盛頓特派員張宗智／十八日電】駐美代表吳釗燮十八日透露，五位前美國國務卿在中國施壓下，拒絕與他在亞特蘭大一場政論會中同桌，讓他決定被迫缺席；此外，中共正運作透過與經濟合作暨發展組織（OECD）簽署諒解備忘錄（MOU）的方式，全面打壓台灣的國際參與空間。

吳釗燮說，目前台灣與友好國家協助化解中共在OECD的打壓，但台灣憂心中共在總統選後及總統就職前，對台灣外交瘋狂打壓已經成真，對照中共國家主席胡錦濤及總理溫家寶近來對台灣的軟調話，反差極大。

吳釗燮也批評中共打壓台灣的作法，指出中共對台灣「講一套，做一套；軟的用講的，硬的用做的。」

吳釗燮在駐美代表處與媒體茶敘時表示，總部設在亞特蘭大的智庫南方國際研究中心，原本邀他出席三月下旬的一場美國卸任國務卿的政論會，但上週主辦單位卻告訴他，五位計畫出席的前美國國務卿聯名寫信給該中心，強調如果吳釗燮在場，他們就

不出席。

這場政論會是由南方研究中心的年度重頭戲，過去也會邀請台灣的駐美代表參加，台灣外交部也例往例出資二萬五千元贊助該中心活動。

不過，今年錢捐出去了，主辦單位卻臨時告知台灣駐亞特蘭大辦事處，五位前國務卿杯葛吳釗燮出席這個棘手的情況。

吳釗燮表示，中共駐休士頓總領事就此事分別向南方中心及計畫出席的前國務卿施壓，吳釗燮為了顧全與該中心的友誼，最後決定不出席。

這五位聯名寫信的前國務卿是季辛吉、貝克、克里多福、歐布萊特及鮑爾。即使吳釗燮決定不出席，最後還是只剩克里多福出席。

此外，吳釗燮也表示，中共正與世界衛生組織（WHO）簽署諒解備忘錄（MOU），讓台灣與WHO接觸必須轉透過中共授權的方式，也和台灣可參與的經濟合作暨發展組織（OECD）簽署MOU，要求OECD承諾「對台七不」。

「七不」包括OECD不接受台灣為會員、不接受台灣成為OECD附屬機構的會員或觀察員、不接受台灣人員成為OECD的官員、不接受OECD在台灣召開會議或活動、不接受OECD與台灣共同召開會議與活動、不接受OECD高層官員訪問台灣、不接受台灣官員訪問OECD。

中共要求 OECD 承諾對台「七不」

- ◆ OECD 不接受台灣為會員
- ◆ 不接受台灣為觀察員
- ◆ 不接受台灣人員成為 OECD 官員
- ◆ 不在台灣召開會議或活動
- ◆ 不與台灣共同召開會議與活動
- ◆ 不接受 OECD 官員訪臺
- ◆ 不接受台灣官員訪問 OECD

中國大陸得悉我國應邀參加 OECD 大會，發出聲明要求 OECD 承諾對台「七不」

Precautionary strategies for management of Nanomaterials Nanowaste

**Prof. Dr. Heidi Foth
Deputy Chair
German Advisory Council on the Environment
Institute of Environmental Toxicology
Martin Luther University Halle-Wittenberg**

About us

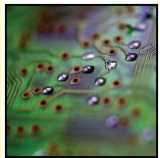
- ❑ independent academic advisory body since 1971, appointed by the German government for a four-year period
- ❑ seven university professors from a range of different environment-related disciplines
- ❑ mission is to describe and assess environmental conditions, problems, and political trends and to point out solutions and preventive measures



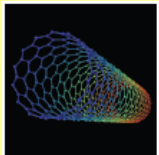
Set the scene



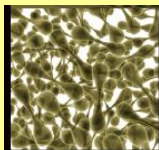
What is meant by nanowaste ?



Why is nanowaste an issue ?



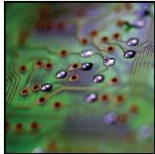
Risks from handling nanowaste ?



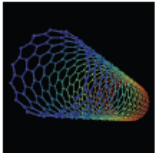
Options to tackle the issue ?



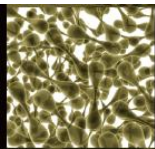
New dimensions for medical devices, probes, diagnostics



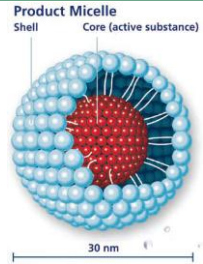
Microelectronics, Conductors, Storage, . . .



New materials, Carriers,



Dyes, new functionalities, lip sticks,



Established	Fe	Pigment, dye, iron supplementation
	Fe	(MR) contrast agent
	air	Ultra sonic contrast agent
	Au	Biological Labeling
	HA	„Biodynamic“ Systems
Visions	Lipids	Drug delivery systems
	C60	
	Zn Al HA	Bioceramics



	since	Nano Objects	Nano structured M
Aluminium Oxide	1955	NO	YES
Ceroxide	1995	NO	YES
Silicon Dioxide	1944	YES	NO
Silicon Dioxide	1944	NO	YES
Titanium Dioxide	1970	NO	YES
Zinc Oxide	1970	NO	YES
Silver	1995	NO	YES
Carbon Black	1900	NO	YES
CNTs (SWCNT)	2002	NO	YES
CNTs (MWCNT)	2000	NO	YES

Nano Object: Particle, Fibre, Plate

Source CEFIC

Silica	Concrete polishing agent	hardening, durability production of waver
Titanium dioxide	Surface coating UV Protection	cleaning, photocatalyst transparent sunblocker
Aluminium oxide	Polymer composites ceramics, dyes Cosmetics	reinforcement of material anti hyperhidrosis
Zinc oxide	UV light absorption precursors for pigments dirt repelling textiles ceramics	UV protection colour surface protection
Carbon black Clay mineral	Filler PET bottles	improved properties of material gas impermeability flame retardancy, improved material performance
Ceroxium Oxide	Electronics Diesel	 improved efficiency
Iron oxide(s)	pigments, magnetic recording electronics	

Researchers	freedom for basic research, but the boundaries between Physics – Chemistry – Biology are vague
Producer	Innovation is urgently needed freedom to produce and trade within accepted boundaries of hazards, safety measures and risk management
Regulator	established rules are valid, but data sets have gaps some test methods are technically questionable
Social Scientists	More participation needed, sustainability questionable
Stake holders	Consumers need informed choice and information
Lawer	regulatory gap, precautionary principle instead of hazard control



Research	Instruments Technologies Materials	no specific regulation except hazard
Development	” ” ”	
Production Processing	Chemicals	REACH, (hazard identification, classification, safe handling)
Marketing	Chemicals non-food products food & packaging material cosmetics Biocides/Pesticides Pharmaceuticals	REACH (.....) (Novel) <i>Food directive</i> <i>Cosmetic directive</i> <i>Pesticides Directive</i> <i>Pharmaceuticals Directive</i>

How to deal with the regulatory gap dilemma?

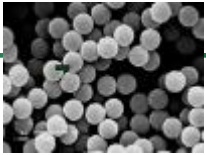


Nanomaterials → Functionality → Product → Properties

? A simple monolithic process ?

Metals	Quantum effects	Storage	Electron transport & binding
Metal-oxides		Material	
Minerals		Indicator	
Metal-Polymer	Catalytic effects	Inert surface	Emission & absorption of light
Composition		Separation	
Co-polymers	Separation/ coating	Protection	
Carbon		Carrier	
Carbohydrates			Chemical reactivity
Lipoproteins	Vehicle		
Lipids			

- No overarching nanospecific hazard identified
- Almost no characteristics in common between nanoforms
- Life time of „nanostatus“ is very diverse
- Conditions of production and application are very different
- Possible damage is strictly linked to uptake and biological (re)activity



Nano- specific properties

amorphous SiO₂
mechanical hardness
interaction with water

Applications

high precision polishing agent
filler, as gel in cosmetics, impregnants
viscosity control agents, excipients

Needs for legal regulation

medicinal use, additive in food,
inhalation on workplaces,
carrier

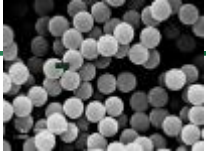
Effects relevant for Safety

biopersistent, inflammation,
irritant

Open Tasks

granulomas in lung ?
relevant carcinogenic risk?
oral uptake?

Source: Supplier



Nano Zinc oxide, ZnO



Nano- specific properties

absorption of UV light, transparent
low water solubility

Applications

UV protection in sun screens,
cosmetics, on textiles, paint,
spectacles glass

Needs for legal regulation

use in cosmetics, feed additive
mobility in soil,

Effects relevant for Safety

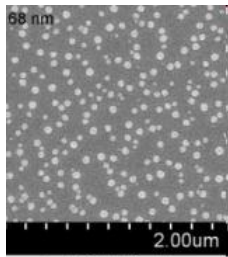
active species zinc ion, irritant,
reactive oxygen species
ecotoxic, persistent in soil

Open Tasks

uptake through skin?
transplacental transfer?
access into brain?

Source: Supplier

Nano Silver, Ag



Ag/a-C:H:N Coating

Nano-specific properties

antimicrobial (traditional knowledge),

Applications

treatment of surfaces (skin, textile,
consumer articles, bath cleaner)
biocide

Needs for legal regulation

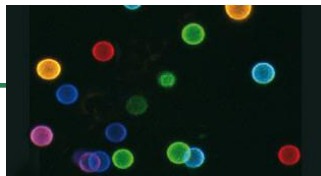
medicinal use (bandage)
inhalation from aerosols,
wide spread distribution in environment

Effects relevant for Safety

active species Ag ion, biopersistent ?
bacterial resistance

Open Tasks

risk by bacterial resistance?
Chronic organ toxicity, access into brain?
ecotoxicity? fate in waste treatment



Nano Gold, Au



Nano-specific properties

catalytic, polychrome

Applications

air refresher, solid catalyst,
in biological labeling (quantum dots),

Needs for legal regulation

wide spread use in technology and
in/on consumer articles,
(ex vivo) indicator test

Effects relevant for Safety

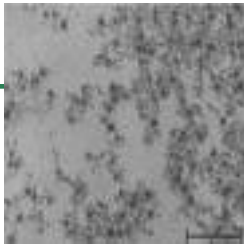
DNA-binding of Au₅₅ cluster,
coatings are decisive, (bio)persistent

Open Tasks

use in cosmetics and food supplements?
absorption and subcellular distribution?
ecotoxicity? fate in waste treatment



Lycurgus Cup, British Museum, 4th century BC Source: RCEP-Report 2008



Nano Iron, Fe, Fe-Oxide



Nano- specific properties

supra magnetic
catalytic (oxidative)

Applications

remediation of contamination sites
(MR) contrast agent
supplement in anaemia

Needs for legal regulation

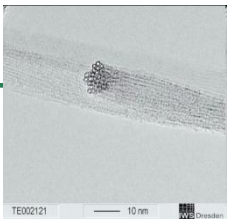
medicinal use (intravenous, oral)
mobility in soil,

Effects relevant for Safety

explosive (specific circumstances),
irritant, reactive oxygen species ↑

Open Tasks

transplacental transfer?
access into brain?
contamination of ground water ?



Nano- specific properties

low weight,
high mechanical strength

Applications

new material
conductive storage,
composites, electronics,

Needs for legal regulation

work places standards, abrasion
and weathering during use,

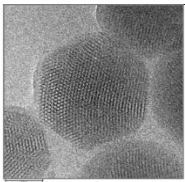
Effects relevant for Safety

inflammation and carcinogenic
(under specific circumstances),

Open Tasks

overload phenomena?
form and shape?
behaviour in environment?

Fullerene (C60)



50 nm

Nano- specific properties

heat resistant
semi conductor (at low temperature)
scavenger (particle form),
antibacterial

Applications

calatyst, lubricant
semi conductor,
antioxidant

Needs for legal regulation

use in cosmetics
uptake by inhalation,

Effects relevant for Safety

variant absorption, coatings
watersoluble forms: inflammation,
reactive oxygen species

Open Tasks

transplacental transfer?
access into brain?



Safety at Working places

- the discussion is focussed on free particles

Production / Packaging / Transport / Processing

Silica, Al(OH), ZnO, Fe, Carbon-Nanotubes, Carbon Black

Similarity to „WHO fibres“ and „GBS“ dusts

Challenges

Monitoring (technology, modelling)

overload phenomena in testing

systemic available fraction and form

Cosmetics

- before marketing testing is obligatory within certain limits

the discussion is focussed on safety tests

animal free test systems

endpoints

phototoxicity

sensitization

immunotoxicity

exclusion of genotoxicity

Challenges

standardisation of parameters for exposure

definition of nano sized forms

Food and Food packaging

- the discussion is focussed on free particles

unintended „contamination“ by abrasion

lifetime of nanostatus (minerals, titanium nitrid, clay)

absorption rate,

degradation and products thereof

ADME

genotoxicity

Challenges

monitoring systems (technology, modelling)

abrasion from package material

systemic available fraction and form

Environment

- the discussion is focussed on

behaviour and fate of engineered nanomaterials in water and soil (metals, carbon allotropes, rare elements)
waste treatment and secondary products of combustion
life cycle analysis

Challenges

balance between natural and intentionally produced nanomaterials

management of resources

waste treatment and risk assessment

What is nanowaste ?



Topics to address

- Waste from production **and a valuable resource**
 - ? Nano-specific issues
 - ? (im)purity
 - ? Differences to natural sources
- Waste from processing
 - ? Secondary reactions, coating
 - ? Mixed nano sized material
- Waste from products
 - ? Life time of nano sized material
 - ? (re)active surfaces
 - ? Release by weathering
 - ? Rare elements with unknown toxicity

Why is nanowaste an issue ?



Because the discussion has raised issues which need to be answered

? Is it safe not to cause damage to humans and environment

? Are the criteria to define dangerous properties valuable for nanowaste

Nanowaste may be something special

? unnaturally pure composition on nano sized material

? unusual shape and coating and by thus behaviour

? unusual mobility, reactivity, persistence

? contains rare elements with widely unknown toxicity

It is a discussion of uncertainty because low knowledge/experience

However, the discussion has its own risk to cause damage

misperception of risks by wrong labeling

need to recycle

valuable resource of the future

Wide distribution of nanomaterial / particles / fibres

Unknown secondary particles by incineration

Existing rules may miss the target

Recycling may be blocked

Future „urban mining“ need conceptual support

Definitions may have an unwanted impact in the outcome

Definitions are needed for practical work

Approve whether the common criteria for dangerous properties are valid

In general, production and use needs to avoid, recycle and store the rest safely

For „nanowaste“

- Define aims to achieve and prioritize them

- keep nanowaste from production and separation separated

- define robust criteria when the life time of nanomaterial has ended

- identify parameter, data needed for regulatory decision

Progress may be blocked by overstretched expectations and unintended consequences
follow up plus tiered approach ?

National Institute for Nanotechnology • Institut national de nanotechnologie

Nanotechnology & Waste Issues

Lori Sheremeta, LL.M.
Counsel, Strategy & Stakeholder Relations
National Institute for Nanotechnology,
Edmonton, Alberta, CANADA

A JOINT INITIATIVE OF
HEALTH CANADA / LEANNEAUVE S.S. | National Research Council Canada / Conseil national de recherches Canada | UNIVERSITY OF ALBERTA | Government of Alberta | Canada

Overview

- Definitional Issues
 - Nanotechnology
 - Nanomaterials
 - Nanoparticles
 - Nanowaste
- Materials and Products of Interest
- Current efforts
- Challenges
 - Scientific Uncertainty
 - Regulatory Coherence across jurisdictions leading to industrial certainty
- Next steps

Nanotechnology

Not "nano by accident"

"The purposeful engineering of matter at scales of less than 100 nanometers (nm) to achieve size-dependent properties and functions."

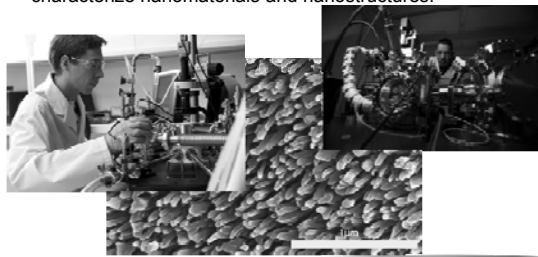
Really small

Not just "small," "small and different"

Lux Research Inc., Nanomaterials State of the Market Q3 2008: Stealth Success, Broad Impact, July 2008 at p 13


Nanotechnology Includes

- The technologies used to make, manipulate and characterize nanomaterials and nanostructures.









Nanomaterial

- A material having one or more external dimensions in the nanoscale or a material that is nanostructured.
- Nanoscale materials have always existed.
- BUT, we have only recently been able to intentionally manufacture, observe and manipulate materials at that scale.



Nanoparticle

- A nanomaterial with size $\leq 100\text{nm}$ in 3 dimensions

		Typical visible diameter 100 nm	100 nm (0.1 μm)	
Graphene sheets		Carbon nanotubes Diameter 10 nm	10 nm (0.01 μm)	"Transition Zone Between Atomic and Bulk-like State"
Semi-conductor nano-crystals		Quantum dots Diameter 5 nm	5 nm (0.005 μm)	
C60		Fullerene Diameter 1 nm	1 nm (0.001 μm)	
		DNA strand Diameter 1 nm	1 nm (0.001 μm)	
		Carbon atom Diameter 0.07 nm	0.1 nm (0.0001 μm)	

Royal Commission on Envir. Pollution, 2008

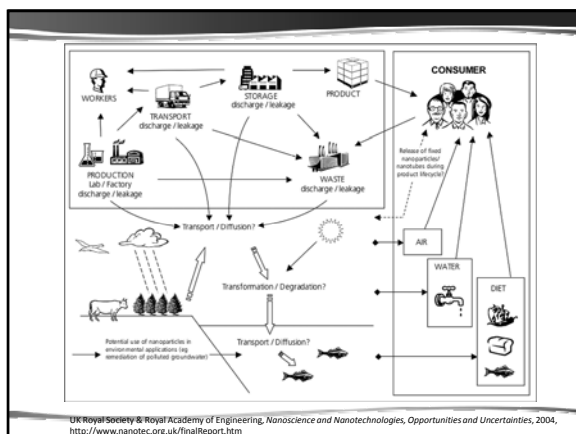
What is important about the nanoscale?

- Materials, known to us in their bulk form, can behave differently at the nanoscale
- Physico-chemical properties are mutable as size changes
 - Size leads to ↑ Surface Area
 - Potential for increased chemical and biological reactivity and a loss of predictability
- Small particles can go where larger particles cannot
 - Translocation across cell membranes is increased as particle size decreases
 - Potential for some nanoparticles to cross the blood brain barrier in animals and humans has raised concern
 - Longer fibres have longer persistence than shorter filaments

Nanoscience and Nanotechnologies: Opportunities and Challenges, July 2004

- Important report published in response to public action group's call for moratorium on the commercial production of new nanomaterials (ETC Group, January 2003).
- Moratorium not feasible; exposure to NMs should be limited insofar as possible; treat as hazardous and seek to remove them from waste streams.
- The use of free manufactured nanoparticles in environmental applications such as remediation should be prohibited until appropriate research has been undertaken to ascertain that the benefits > risks.
- Relevant regulatory bodies should consider whether existing regulations are appropriate to protect humans and the environment from NMs/NPs.
- Life Cycle Assessment should be used to examine exposure risk from cradle to grave.

<http://www.nanotec.org.uk/finalReport.htm>



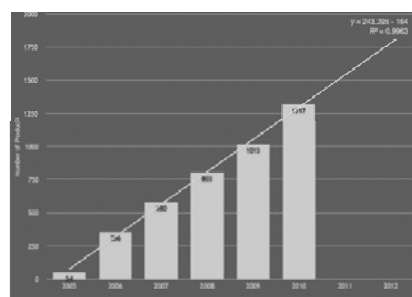
Definition: "Nanowaste"

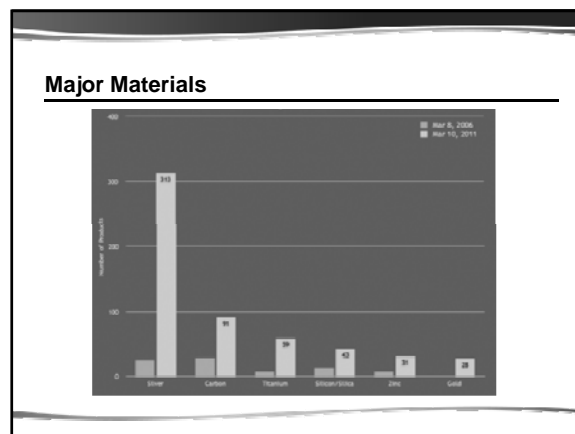
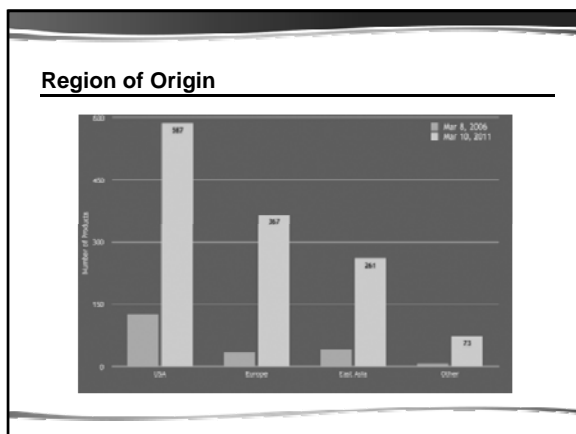
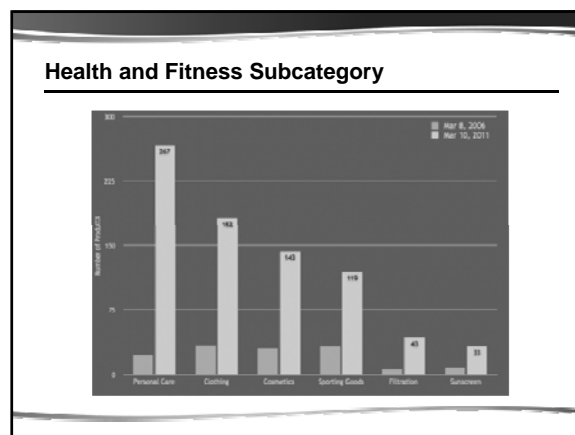
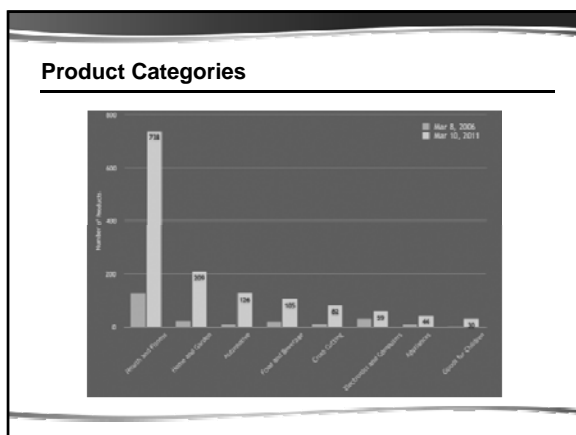
- A term used to describe "by-products, emissions, fugitive emissions, contaminants and debris associated with nanomanufacturing processes, nanoproduct wear and tear, as well as end of lifecycle products and components containing nanostructured materials and nano-objects."

Points to Consider

- Nomenclature is important.
- Do we care if waste is **nanoscale or not**?
- What about nanoscale contaminants, debris and byproducts associated with manufacturing generally?*
- How do we define the following terms?
 - "nanomanufacturing processes"
 - "nanoproducts"?
 - "nanostructured materials" and "nano-objects"?
- A clear working definition of "nanowaste" is needed.

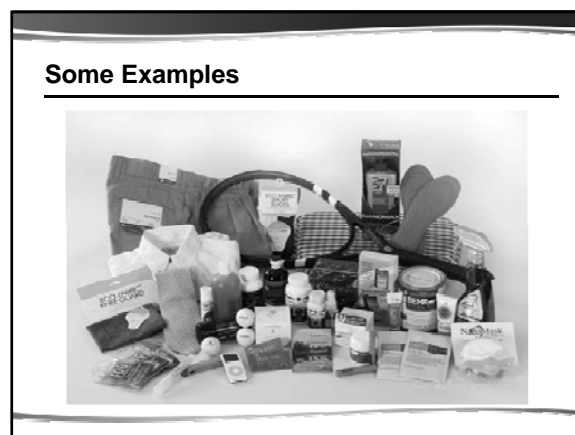
Total Products Listed





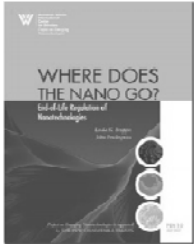
Nanotechnology Across Sectors

Auto Industry *Lightweight composites *Paint & exterior coatings *Catalysts *Tires *Sensors *Coatings	Chemical Industry *Paint fillers *Composites *Adhesives *Magnetic fluids *Separations *Pesticides & herbicides	Engineering *Protective coatings for tools and machines *Lubricant free bearings *Machine ceramics
Electronics *Semiconductors *Displays *Data memory *Laser diodes *Fibre optics *Conductive, anti-static coatings	Construction *Lightweight materials *Insulation *Flame retardants *Surface coatings *Mortars, cements	Recreation *Tennis rackets/balls *Golf clubs *Anti-mildew coatings *Anti-fog coatings *Anti-bacterial materials *Ski wax
Textiles *Surface coatings *"Smart" textiles and paper *Anti-bacterials	Energy *Fuel cells *Solar cells *Batteries *Capacitors *Fuel additives	Household *Ceramic coatings for irons *Odor removers *Cleaning products
Food & Beverages *Packaging *Sensors *Additives *Nutrition delivery systems	Medicine *Biomimetic materials *Drug delivery systems *Sensors	Cosmetics *Sunscreens *Lipsticks *Skin creams *Toothpastes



Where Does the Nano Go? July 2007

- Express focus on end-of-life issues.
- Are existing practices for handling, treating, storing and disposing of bulk forms of solid wastes appropriate for nanoscale wastes of the same chemicals.



<http://www.nanotechproject.org>

Materials of Particular Interest

Fullerenes (C60)	Aluminum Oxide
Single Walled Carbon Nanotubes	Cerium Oxide
Multi Walled Carbon Nanotubes	Zinc Oxide
Silver Nanoparticles	Silicon Dioxide
Iron Nanoparticles	Polystyrene
Carbon black	Dendrimers
Titanium Dioxide	Nanoclays
	(Crystalline Nanocellulose)

OECD Working Party on Manufactured Nanomaterials
Priority Testing List

Current Activities (from OECD Survey)

Activity	CA	DK	FR	FRG	SL	UK	US	EU
Basic EHS research	✓	✓	?	?	✓	✓	✓	?
Waste specific research	✓	?	?	?	✓	✓	✓	?
Survey of academic use of NMs	✗	✗	?	?	?	?	?	?
Survey of industrial use of NMs	✗	✗	✓	?	?	?	✓	?
"Nano" contemplated in current risk assessment and management	✓	?	?	?	?	?	?	✓
Life Cycle Analysis/Nano Release	✓	?	✓	?	?	✓	✓	?
Industry Guidance (by and for industry)	✗	?	?	✓	?	✓	✓	?
Policy Framework Assessment	✗	?	?	✓	✓	✓	✓	?
Applicability of existing laws/regs	✓	?	?	✓	?	✓	✓	✓
Government/agency guidance for industry or academia	✗	?	?	?	✓	✓	✓	✓
Legal/Regulatory Framework Development	✓	?	?	?	✓	?	✓	?
Nano-specific laws/regs	✗	?	?	✗	✗	?	✓	?

Proposed Criteria for Selection of Priority Materials for Nanowaste Risk Assessment

- Current industrial use
 - Need to balance:
 - Method of production
 - Mass quantity produced
 - Perceived potential toxic effect(s) of process and product
 - Degree to which the material is free or bound in final product(s)
 - Anticipated life cycle of products into which the materials are expected to be incorporated
- Current research focus + high potential for widespread industrial use
- Expert opinion will be of great value in selecting materials/products of interest.

Environ. Sci. Technol. 2008, 42, 887-893

Early Evaluation of Potential Environmental Impacts of Carbon Nanotube Synthesis by Chemical Vapor Deposition

DESIREE L. PLATA,^{1,2,3} JOHN HART,¹ CHRISTOPHER M. SWIFT,¹ AND PHILIP M. GARDNER¹
¹Department of Civil and Environmental Engineering, Johns Hopkins University, Baltimore, Maryland, USA
²Cambridge Environmental Laboratory and Laboratory Materials, 1000 Lincoln St., Cambridge, Massachusetts, USA
³Department of Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland, USA

designed to maximize material performance and minimize production costs, but little attention has been devoted to a global environmental impact evaluation. This paper has focused on selected environmental and ecological environmental effects, and at an advanced stage of industrial development, after industrial processes are in very different stages. In some cases, the residual impacts, as exemplified by other industrially large-scale metal tube-related technologies of comparable environmental impacts, have not been fully evaluated. This paper reports on the results of a preliminary environmental impact assessment of carbon nanotube synthesis and manufacturing efforts (e.g., polyfunctionalized acid from tubule manufacturing) and ultimately resulted in a practical basis and development of specific technologies (e.g., many industrial chemical processes) to minimize the impact of this process.

ScienceDaily
 Web address: <http://www.sciencedaily.com/releases/2007/06/070621091446.htm>

Received June 21, 2009
September 15, 2009, 12:00

Toxic Byproducts of Carbon Nanotube Manufacturing: Are There Green Alternatives?

ScienceDaily (Aug. 31, 2007) — A new analysis of by-products discharged to the environment during production of carbon nanotubes (CNTs) — expected to become the basis of multibillion-dollar industries in the 21st Century — has identified carbon-containing compounds, air pollutants, and other substances of




Where the Chips Fall:

Chemicals of concern in the semiconductor industry:

- Acetone
- Arsenic
- Benzene
- Cadmium
- Hydrochloric Acid
- Lead
- Methyl Chloroform
- Toluene
- Trichloroethylene

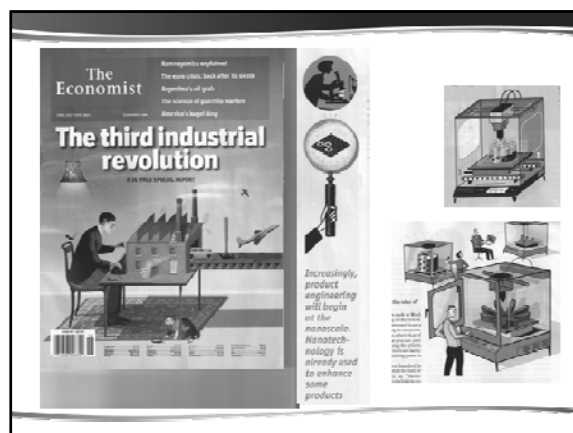
Environmental Health
in the Semiconductor Industry



R Chespeuk, EHP, 107:9 Sept 1999

Nanotechnology holds promise in key areas relevant to waste issues

- **Precision manufacturing** – next industrial revolution – ICT, novel materials, better robots, new processes (notably 3D printing) and range of web-based services.
- **Environmental remediation** - tailored nanoscale materials) can be mounted on a solid matrix such as activated carbon and used to treat wastewater or gaseous process streams. Effective transformation and detoxification of chlorinated organic solvents, pesticides and PCBs in soil.
- Through fundamental understanding of chemical and material interactions NT may ultimately provide many solutions to chemical waste management issues.



Risk Assessment Paradigm Applied Across the Nanomaterial Lifecycle

Product Lifecycle Stages	Raw Materials	R&D	Production	Commercialisation Consumer Use	Disposal/Recycling
Exposure Assessment	Air	Water	Soil	Wastewater	Landfills
• Concentration		Aquatic	Terrestrial		
• Transformation					
Hazard ID	Initialiation		Ingestion		Dermal Absorption
• Dose					
• Response					
Effects		Ecosystems		Humans	
EVIDENCE BASE					
Predictive Modeling					
Research Planning					
Strategic Risk Management & Risk Communication					
Regulatory Decision-Making					

Nanoparticles health impacts?

By David S. Veitch

LETTERS

Nanoparticles – known and unknown health risks
Peter HM Hoet¹, Inese Binkis-Hohledd² and Oleg V Sulau³*

Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study

CHRIST A. POLAND, ROBERT CUPP, DAN KILGUS, JACQUES MARAND, WILLIAM A. H. INGLIS, MICHAEL SUTTON, YONG STORE, SIMON SPERRY, WILLIAM BARNETT FOR NANOPARTICLES

ehp Environmental Health Perspectives

Manufactured Nanomaterials (Hullmes, 400) Induce Oxidative Stress in Brain of Juvenile Largemouth Bass

For **OVERSIGHT** doi:10.1289/ehp.1021 (available at <http://dx.doi.org/>) Online 7 April 2012

Exposure to nanoparticles is related to pleural effusion, pulmonary fibrosis and granuloma

A. Hoet, I. Binkis-Hohledd, O. Sulau

Challenges: Regulatory Coherence

Environment Canada Canadian Environmental Protection Act •New Substances Notification Regs •Persistence and Bioaccumulation Regs Canadian Environmental Assessment Act
Fisheries Act, Oceans Act
Agricultural Products, Pest Control and Fertilizers Acts
Health Canada Food & Drugs Act •Food & Drugs Regs •Medical Devices Regs •Cosmetics Regs •Natural Health Products Regulations Hazardous Products Act •Controlled Products Regulations •Work Hazardous Materials Information System

Main Policy Challenge

- Maintaining public trust
- Expect that something will go wrong
- Public trust is not unconditional
- Strive to ensure that societal benefits are maximized and risks minimized in accordance with societal values .
- To do this, education, engagement and communication strategies around nanotechnology and responsible (nano-)waste management are needed.

Conclusions

- Major gaps exist in our understanding of the health, safety and environmental impacts of nanomaterials and nanoparticles.
- Coordinated, strategic research is essential to develop the foundational knowledge that will empower the responsible development of key technologies.
- Public trust in the scientific enterprise depends on a coherent and rational approach to stewardship.
- National and international dialogue, cooperation and coordination is necessary to ensure that: risks are mitigated and all nations have the opportunity to implement appropriate strategies to deal with the challenges.

Future Efforts

- Identify who is doing what, where (what materials, what quantities, what processes)
- Prioritize materials/products based on expert opinion
- Understand manufacturing processes and identify improvement strategies
- Expand efforts on "nano-release" based on expert opinion of priorities (e.g. abrasion, incineration, weathering, release from washing)
- Expand efforts to understand impact of NMs on landfills and aquatic systems (seek to interest researchers and funders)
- Strategic risk communication – researchers, small companies, publics (benefits/risks)

Acknowledgements

- National Institute for Nanotechnology/University of Alberta
- Alberta Innovates – Technology Futures
- Environment Canada
- Health Canada
- OECD



OECD's work on the Safety of Manufactured Nanomaterials

May 2012

Environment, Health and Safety Division (EHS)
OECD Environment Directorate



Contents

- Overview of the OECD work on Chemicals
- Establishment of a Programme on Manufactured Nanomaterials
- Scope of the WPMN
- Projects

OECD Chemicals Safety

The main **objectives** of OECD's programme on Environment, Health and Safety are:

- To protect humans and the environment;
- gain efficiencies in chemicals management; and
- avoid non-tariff trade barriers.

This is **achieved** through:

- The development of quality tools for testing, assessment and management of chemicals
- Optimising use of resources for member countries
- Co-operation with non-members
- Assisting member countries in implementing UN Strategic Approach to Chemicals Management (SAICM)

Mutual Acceptance of Data (MAD)

Meet regulatory needs
of member countries
Reflect scientific
progress
Address animal
welfare aspects
Improve cost-
effectiveness of test
methods

Test Guidelines

**Good Laboratory
Practice**

A single
quality
standard for
test facilities
throughout
OECD and
applied for
testing of all
chemical
substances

Mutual Acceptance of Data

Legally binding on OECD Member countries
MAD Council Decision open to selected non-members

- **Avoids duplication of testing: around Euros 150 million saved each year**
- **Reduces use of animals**
- **Reduces trade barriers**

Nanotechnologies

- **Nanotechnologies will/are having a major impact across a range of economic sector:**
(e.g.) energy production, health industry, cosmetics, information technology, textiles
- **Global Market of Nanotechnologies has increased over time**
 - By 2015, 2 million jobs & \$1 trillion production (National Nanotechnology Initiative(NNI))

Programme on the Safety of Manufactured Nanomaterials

To ensure that the approach to hazard, exposure and risk assessment is of a high, science-based, and internationally harmonised standard.

- The Programme is implemented by the Working Party on Manufactured Nanomaterials (WPMN), which was established in 2006
- Subsidiary body of the Chemicals Committee
- The WPMN meets every 8/9 months

Current areas of work

- Safety Testing of MN: “Sponsorship Programme for Testing Manufactured Nanomaterials”
- Manufactured Nanomaterials and Test Guidelines
- Alternative Methods in Nanotoxicology

- Database on Manufactured Nanomaterials to Inform and Analyse EHS Research Activities
- Voluntary Schemes and Regulatory Programmes
- Risk Assessment
- Environmentally Sustainable Use of Nanotechnology
- Exposure Measurement and Mitigation: Occupational, Consumers & General Population, and Environmental

OECD Database on Research into the Safety of Manufactured Nanomaterials

Human Health and Environmental Safety Research



Search this database

Search ICON

Search NIOSH

[Advanced Search](#)

[List all projects](#)

- Launched , 1 April 2009
- Completed, Current and Planned research on human health and environmental safety
- List of Test Guidelines are included to search projects which includes testing of MNs by using OECD Test Guidelines.
- www.oecd.org/env/nanosafety/database

OECD Database on Research into the Safety of Manufactured Nanomaterials

Human Health and Environmental Safety Research

[Simple Search](#)

▼ [Advanced Search Criteria](#) :

Keywords include:

Principal Investigator name contains:

Include additional investigators in the search

From the country:
Afghanistan
Albania
Algeria
American Samoa
Andorra
Angola

From the organisation:
Academy of Corporate Governance
African Capacity Building Foundation (ACB)
African Development Bank (ADB)
African Seed Trade Association (AFSTA)
African Union
African, Caribbean, and Pacific Group of S

Project active in year: and
 Include a summary of funding data for all matches

With a funding source including:

Categorisation:

Research Themes: [i](#)

Material Name: [i](#)

Test Method: [i](#)

All Any Research Theme

All Any Material Name

All Any Test Method

- | | | |
|--|---|--|
| <input type="checkbox"/> 1. Characterisation and measurement of | <input type="checkbox"/> Nano Carbon | <input type="checkbox"/> SECTION 1 - PHYSICAL-CHEMICAL PROPI |
| <input type="checkbox"/> 2. Exposure assessment for humans and t | <input type="checkbox"/> Polymers specifically synthesized to explo | <input type="checkbox"/> SECTION 2 - EFFECTS ON BIOTIC SYSTEM |
| <input type="checkbox"/> 3. Interaction of nanomaterials with biolog | <input type="checkbox"/> Dendrimers [WPMN] | <input type="checkbox"/> SECTION 3 - DEGRADATION AND ACCUM |
| <input type="checkbox"/> 4. Human Health | <input type="checkbox"/> Components of Quantum Dots | <input type="checkbox"/> SECTION 4 - HEALTH EFFECTS |
| <input type="checkbox"/> 5. Ecotoxicology | <input type="checkbox"/> Inorganic Nanomaterials (in Alphabetical | <input type="checkbox"/> Other test methods (indicated below) |
| <input type="checkbox"/> 6. Control measures at workplace | <input type="checkbox"/> Inorganic Nanomaterials (in Alphabetical | <input type="checkbox"/> Not relevant (the project does not addres |

Both Manufactured Non-Manufactured [i](#)

Relevance to the Safety of Manufactured Nanomaterials:

Project status:

Project Ref.:

Search this database
with these criteria

Reset fields

[List all projects](#)



Search this database

Search ICON

Search NIOSH

Advanced Search

[List all projects](#)

Testing and Assessment of MN

Testing MN

Testing

Programme: International effort to share the testing of an agreed set of MN selected by WPMN

- Fullerenes (C60)
- SWCNTs
- MWCNTs
- Silver nanoparticles
- Iron nanoparticles
- Titanium dioxide
- Aluminium oxide
- Cerium oxide
- Zinc oxide
- Silicon dioxide
- Dendrimers
- Nanoclays
- Gold nanoparticles



Test Guidelines

To review existing OECD TGs for adequacy

- Phys-chem
- biotic systems
- degradation and accumulation
- health effects

Guidance documents:

- Guidance Manual for the Testing Programme
- Sample Preparation and Dosimetry (GNSPD).



	Lead sponsor(s)	Co-sponsor(s)	Contributors
Fullerenes(C60)	Japan, US		Denmark, China
SWCNTs	Japan, US		Canada, France, Germany, EC, China, BIAC
MWCNTs	Japan, US	Korea, BIAC	Canada, France, Germany EC, China, BIAC
Silver nanoparticles	Korea, US	Australia, Canada, Germany, Nordic Council of Ministers	France, Netherlands, EC, China, BIAC
Iron nanoparticles	China	BIAC	Canada, US, Nordic Council of Ministers
Titanium dioxide	France, Germany	Austria, Canada, Korea, Spain, US, EC, BIAC	Denmark, Japan, UK, China
Aluminium oxide			Germany, Japan, US
Cerium oxide	US, UK/BIAC	Australia, Netherlands, Spain	Denmark, Germany, Japan Switzerland, EC
Zinc oxide	UK/BIAC	Australia, US, BIAC	Canada, Denmark, Germany, Japan, Netherlands, Spain, EC
Silicon dioxide	France, EC	Belgium, BIAC	Denmark, Japan, Korea
Dendrimers		Spain, US	Austria, Korea
Nanoclays	BIAC		Denmark, US, EC
Gold nanoparticles	South Africa	US	Korea, EC

List of endpoints

- ▶ **Nanomaterial Information/Identification** (9 endpoints), e.g. substance name, chemical identity, uses, coating
- ▶ **Physico-chemical Properties and Material Characterization** (17 endpoints), e.g. water solubility, particle size, surface characteristics, agglomeration / aggregation
- ▶ **Environmental Fate** (15 endpoints), e.g. biodegradability, adsorption, accumulation
- ▶ **Environmental Toxicology** (6 endpoints), e.g. effects on aquatic and terrestrial organisms
- ▶ **Mammalian Toxicology** (9 endpoints), e.g. inhalative toxicity, reproductive toxicity, genotoxicity, toxicogenetics
- ▶ **Material Safety** (3 endpoints), e.g. flammability



	PRINCIPAL MATERIAL(S)	ALTERNATE MATERIAL(S)	PROPERTIES	COMMERCIAL USES
FULLERENES (C60)	Fullerene (C60) Nanom Purple	TBD	Spherical molecule structure consists of 12 five-membered rings and 10 six-membered ring of carbon	Sporting tool and cosmetics. In the future, fuel cell, optical parts, gas sensor, etc.
SINGLE-WALLED CARBON NANOTUBES (SWCNTS)	Nikkiso SWCNT	SWCNT (CVD method), SWCNT (Arc method), SWCNT (HiPCO method)	A honeycomb carbon lattice rolled into a cylinder	Super-capacitors, high speed transistor, fuel cell, super high strength wire etc.
MULTI-WALLED CARBON NANOTUBES (MWCNTS)	Nikkiso MWCNT	Graphistrength C100 Mitsui MWNT-7 Baytubes® NANOCYL™ NC7000	A honeycomb carbon lattices rolled into multi-layer tubular shape	Super-capacitors, batteries, sporting equipments, conductive sheet, medical use, etc.
SILVER NANOPARTICLES	10-15 nm (citrate), 10-20 nm (PVP), 50-100 nm (citrate), 50-100 nm (PVP)	Silver nanoparticles: 20 nm, 15 nm, 18 nm (Daedeok Science), 10-15 nm (NanoSys GmbH), etc. various sizes and manufactures		Biocides,
IRON NANOPARTICLES	TBP			
TITANIUM DIOXIDE	Aeroxide® P25	PC105, Tiona AT-1, Hombikat UV 100, UV TITAN M212, UV TITAN M262	TiO ₂ , Basically spherical morphology Neither coated nor modified Alumina and glycerin (hydrophilic) Alumina dimethicone (hydrophobic)	Semiconductor catalyst for photocatalytic processes, sunscreen products, pigment of multiple uses: for paint, paper, ceramics
ALUMINIUM OXIDE	TBD			
CERIUM OXIDE	Cerium (IV) Oxide, Cerium Oxide (Nanograin Ceria)	TBD	CeO ₂ , Cubic, Nanostructured powder	Catalysts and chemomechanical polishing
ZINC OXIDE	Z-COTE®, Z-COTE HP 1®	Nanosun Zinc Oxide P99/30	ZnO, White powder, spherical morphology	UV- protection for the use in sunscreens
SILICON DIOXIDE	NM-200	TBD	SiO ₂ , strong, directional covalent bonds, and has a well-defined local structure	HPV chemical, car tires, printing inks, pharmaceuticals, cosmetics, animal feed, etc.
DENDRIMERS	G3-PAMAM-(NH ₂) ₃₂ , G4-PAMAM-(NH ₂) ₆₄	G3-PAMAM-50% C ₁₂ , G4-PAMAM-50% C ₁₂	C ₃₀₂ H ₆₀₈ N ₁₂₂ O ₆₀ , C ₆₂₂ H ₁₂₄₈ N ₂₅₀ O ₁₂₄ for principal materials. Highly viscous oils	<i>In Vitro</i> diagnostics, additives, controlled drug delivery, etc.
NANOCLAYS	TBP			
GOLD NANOPARTICLES	TBP			Catalysis; Diagnostics & therapeutics; water monitoring & remediation . <i>In vitro</i> work: interference assays; Bacterial reverse mutation test; Cytotoxicity to BEAS-2B cells; iptake by BEAS-2B cells

Exposure

The overall objective is to exchange information on guidance for exposure measurement (including sampling techniques and protocols) and exposure mitigation for manufactured nanomaterials and to develop suggestions for further steps to be undertaken by the WPMN.

Exposure Measurement and Exposure Mitigation

- **Publications**
 - Compilation and Comparison of Guidelines Related to Exposure to Nanomaterials in Laboratories
 - OECD Workshop on Exposure Assessment and Exposure Mitigation: Manufactured Nanomaterials
 - Comparison of Guidance on Selection of Skin Protective Equipment and Respirators for Use in the Workplace: Manufactured Nanomaterials
 - Emission Assessment for Identification of Sources and Release of Airborne Manufactured Nanomaterials in the Workplace: Compilation of Existing Guidance
 - Identification, Compilation and Analysis of Guidance Information for Exposure Measurement and Exposure Mitigation: Manufactured Nanomaterials
 - Preliminary Analysis of Exposure Measurement and Exposure Mitigation in Occupational Settings: Manufactured Nanomaterials



Project “Disposal and Treatment Technologies of Manufactured Nanomaterials”

*This project aims to develop an **inventory of available information, including publications and research activities, on disposal and treatment technologies for nanomaterials**, which is needed to fully characterize the life-cycle impact of nanomaterials.*

A survey has been developed. Delegations are currently responding to this survey (so far three countries).

OECD’s Working Party on Resource Productivity and Waste (WPRPW) developed an overview.



Safety of Manufactured Nanomaterials

www.oecd.org/env/nanosafety

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INERIS – Expert in Risk Prevention

Waste management and fate of nanomaterials

Review of existing waste treatments and issues addressed by nanomaterials : landfilling, incineration, recycling...

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Introduction

About INERIS

Ineris, an assessment based on the experimental approach, the modelling and the knowledge of the industry

- Long-time experience of the industrial world (> 60 years)
- under the trusteeship of the Ministry in charge of Ecology
- Multidisciplinary teams : chemistry, physics, life science, economy, sociology, medicine...
- An annual budget of 70 M€ :
 - support public bodies (60%),
 - private and public research (20%),
 - support industries/expertise & training (20%)
- A staff of 600, including 350 engineers and researchers
- Full scale tests facilities (animal facilities, mesocosm, physics, chemistry and biology labs, pyrotechnic zone, hazard bench...
- Headquarters extend to 50 ha
- 25 000 m² of laboratories
- More than 1 000 French and international customers per year
- 50 PhD students & 15 post-doctoral fellowships



A synergy between services for private customers, research activities and technical support for regulators

Introduction

About INERIS

Expertise



Prevention of industrial and technological risks.



Prevention of risks associated with chemical substances.



Participation in the development, dissemination and sharing of best technologies and best practices.



Introduction

About INERIS

Our goal:
supporting you in risk assessment and reduction

related to your substances, processes and installations

- Chemical substances, **nanoparticles**, ...
- Equipments, ATEX products, ...
- Industrial processes and workplaces
- Industrial installations
- Hazardous materials transport
- Underground storages, quarries, mines, dumps
- Polluted sites and soils

for the human health, workers and the environment



Introduction

About INERIS / Nanotechnology risk assessment

PROCESS SAFETY

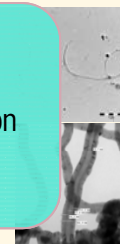
- Fire, explosion hazards
- Loss of containment
- Safety parameters
- Molecular modeling



Battery before and after fire test

METROLOGY

- On-line monitoring
- Sampling & characterization
- Instrumental calibration
- Nano generation tools



Online CNT detection unit

PRODUCTS CHARACTERIZATION NANOBENCH

- Physico-chemical properties
- Use and aging (mechanic stress...)
- End of life (recycling, burning)



Calorimeter Tewarson
ASTM E 2058 – NFPA 287

TOXICOLOGY

- Experimental (stress, inflam., genotox..)
- In vitro & In-silico (QSARs, TK, PBPK...)
- Inhalation exposure system (nanomaterials)

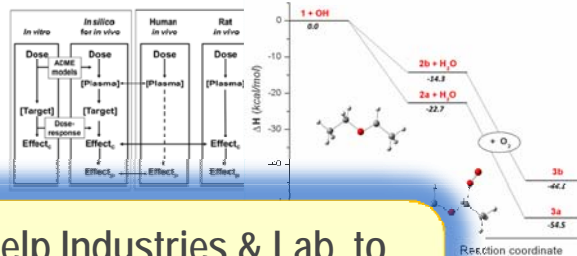


ECOTOXICOLOGY

- Experimental (Ageing, OECD)
- Large scale (mesocosm)

GLP facilities

Nano-Safety Lab



MODELISATION

- nucleation, agglomeration
- Reactivity-Transport
- QSARS, QSPRs, Q. Meca.

Help Industries & Lab. to
develop safer nanotech.
Processes & products

RSIK ANALYSIS

- "Control banding" tools
- Semi-quantitative risk assessment
- Safety barriers management
- Intrinsic safety

EXPOSURE ASSESSMENT

- Occupational exposure
- Accidental exposure scenarios
- Environmental exposure

STANDARDIZATION

- nanoREACH, ANSES
- ISO, CEN & AFNOR
- OECD – WPNM

SOCIO-ECONOMIC ANALYSIS

- Integration of LCA and LCC results
- Cost/benefit /efficiency (CBA, CEA)
- Multi-criteria analysis (MCA)

TRAINING

- Workers, H&S dept.
- nanosafety /workplace
- risk assessment

CERTIFICATION

- Workers, H&S, products
- NanoCert
- ElliCert Batteries



INERIS

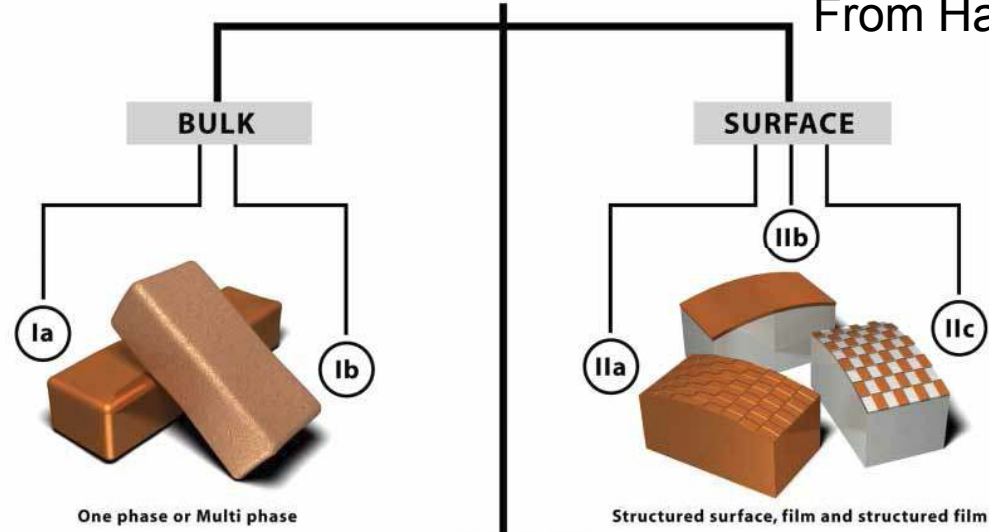
maîtriser le risque
pour un développement durable

Context

Waste management of nano and nanomaterialsb

NANOMATERIALS

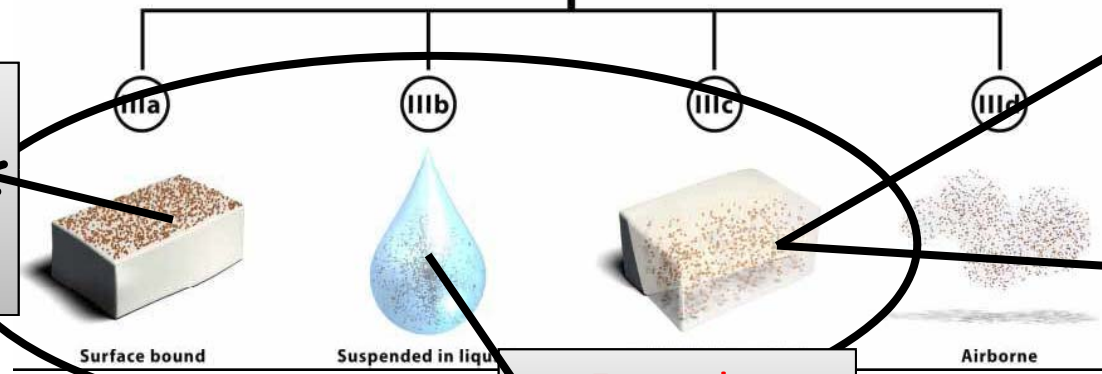
From Hansen et al, 2007©



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

From Hansen, 2007

PARTICLES



Example: Self-cleaning cement

Example: Nano-composites

Example : NanoCeO₂- composite in outdoor paint

Example: Sunscreens

"NanoWaste : review on waste management and key issue on nanotechnology Frejafon et al, OECD Workshop on nanowaste, Munich 10th May 2011

Context

Waste management / approach

Waste management and fate of nanomaterials

Review of existing waste treatments and issues addressed by nanomaterials

Case by case study of nanomaterials and nanoproducts → that gives step by step milestones thus guidelines

- Landfilling or recycling (eg. Cement),
- Sewage (eg. TiO₂, CeO₂)
- Incineration (eg. Polymers)

Both Nanomaterial and Nanoproducts

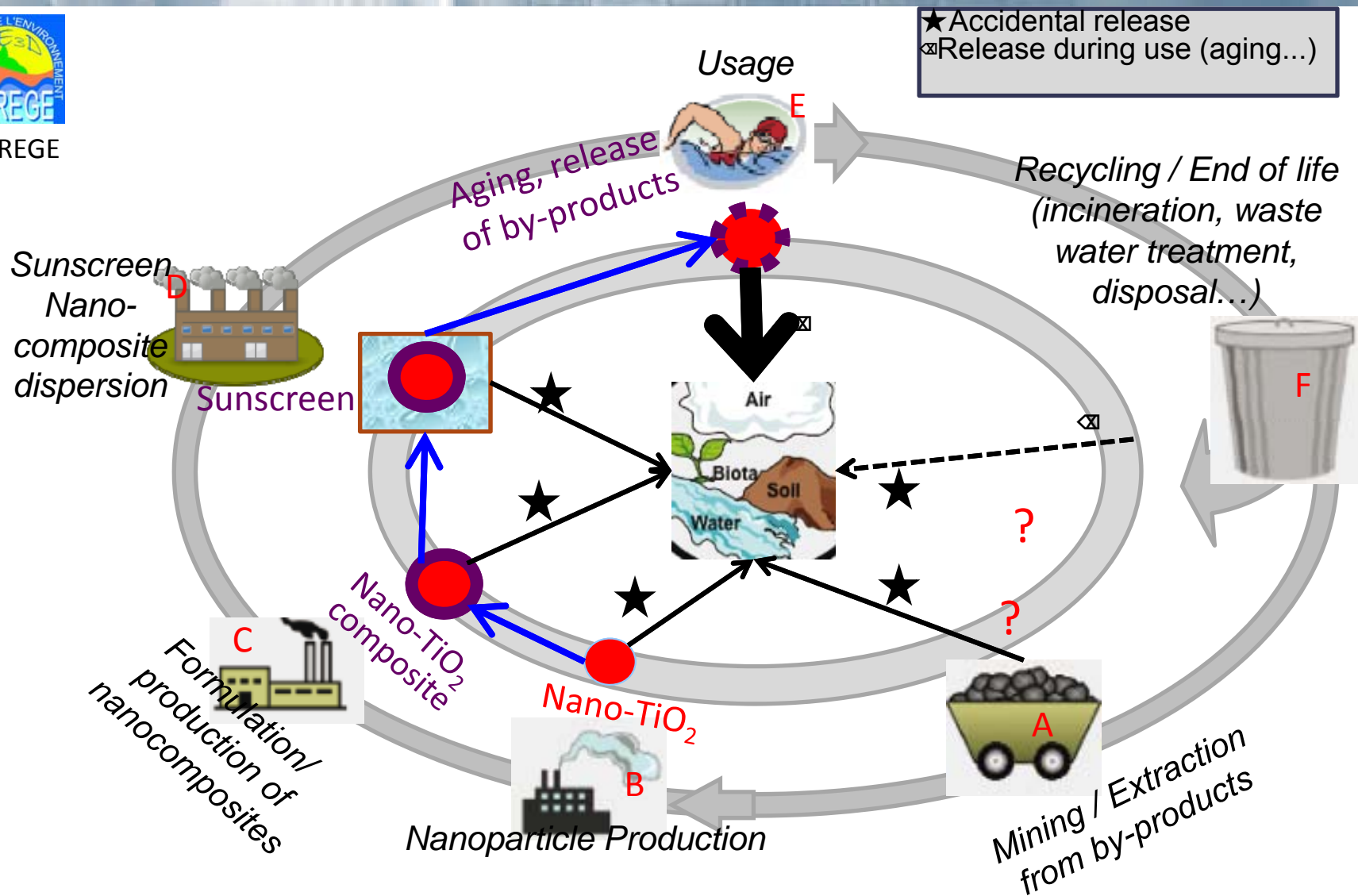
→ As nanoproduct can liberate initial or modified nanomaterials
→ Safer by design production as hazard and risk was evaluated during live cycle up to waste product → key inputs in production strategy

Sewage treatment plant

Case study : nano-TiO₂ formulation sunscreens



© CEREGE

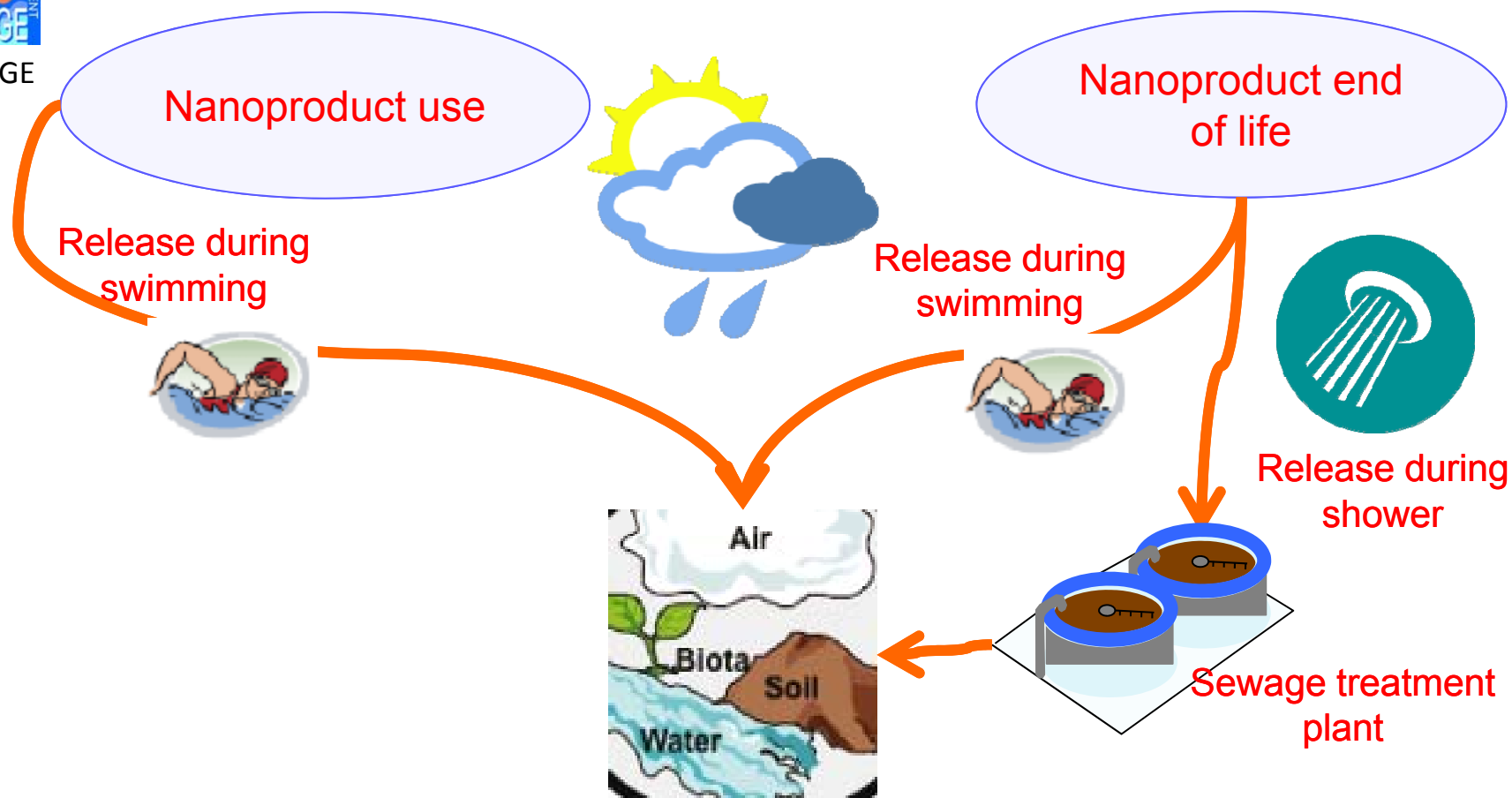


Sewage treatment plant

Case study : nano-TiO₂ formulation sunscreens



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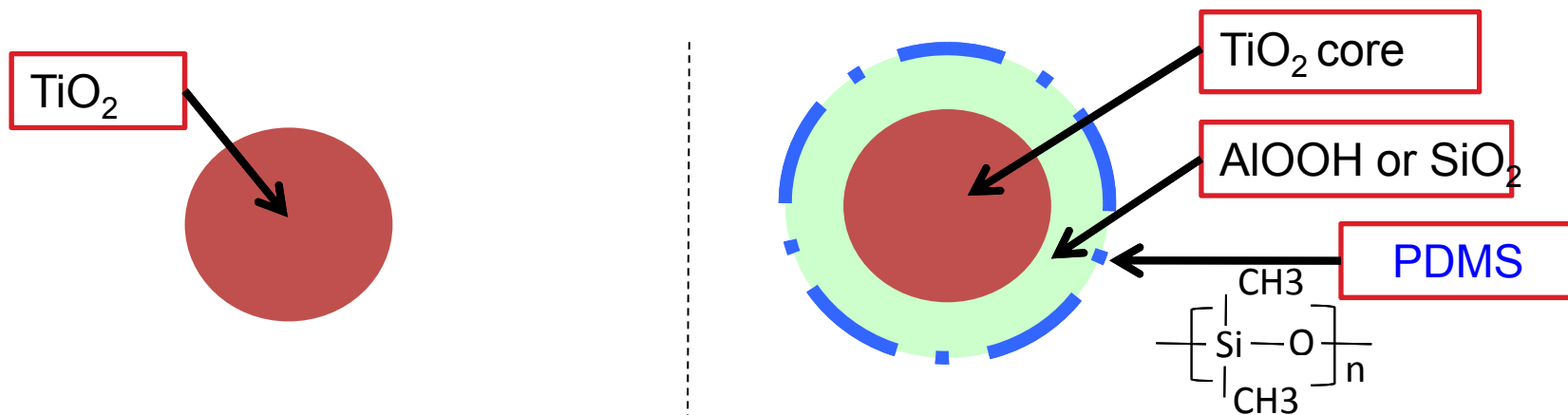
Sewage treatment plant

Case study : nano-TiO₂ formulation sunscreens

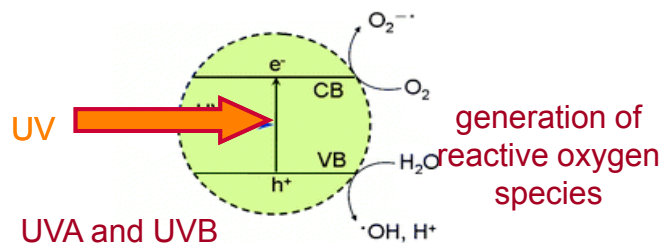


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TiO₂ nanoparticles v.s TiO₂ nanocomposite used in sunscreen



<p>Initially Hydrophilic ROS Generation under light (Photocatalytic properties) Ecotoxicity (e.g daphnia mortality)</p>	<p>Hydrophobic No ROS generation</p>
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≈ 4.6% per weight of TiO₂

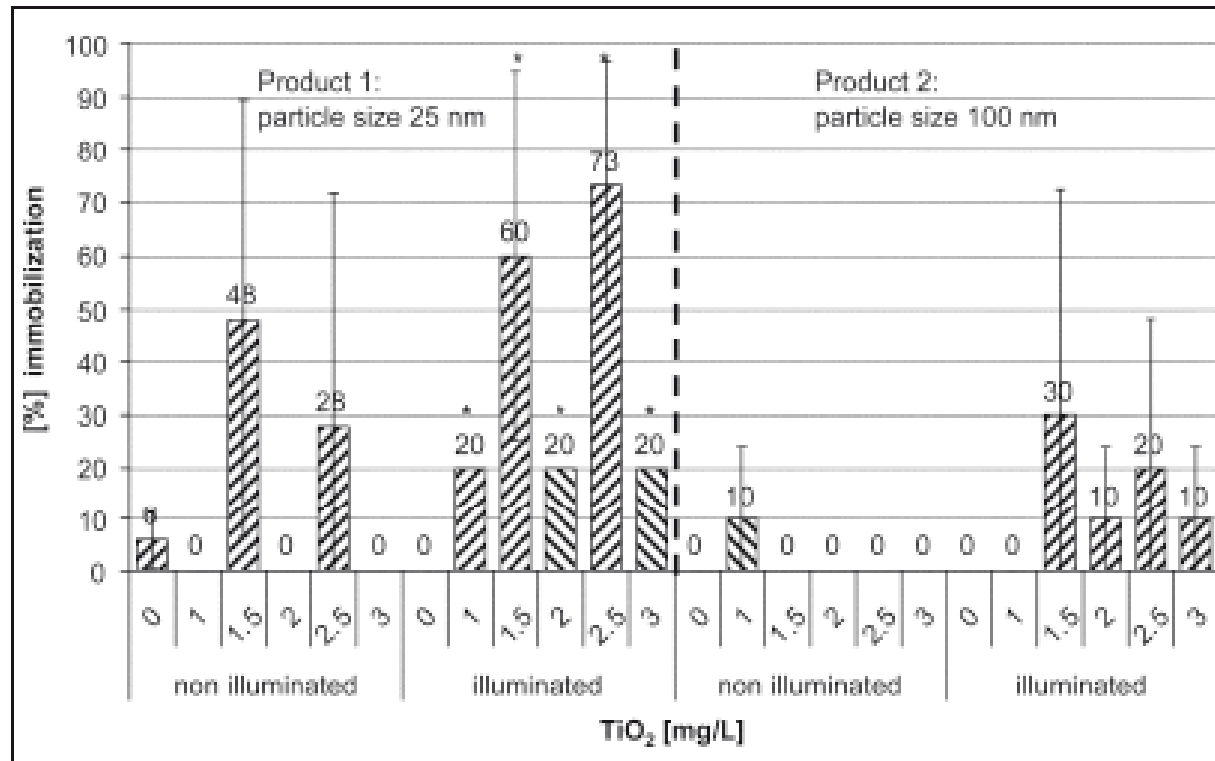
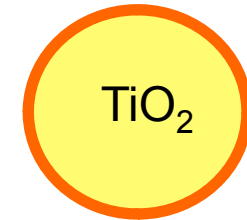
“NanoWaste : review on waste management and key issue on nanotechnologies”
Frejafon et al, OECD Workshop on nanowaste, Munich 10th May 2011

Sewage treatment plant

Case study : nano-TiO₂ formulation sunscreens

©CEREGE

Ecotoxic Effect of Photocatalytic Active Nanoparticles (TiO₂) on Algae and **Daphnids**



Light
→ increases effects



Fig. 5: Immobilization of daphnids by TiO₂; significance: * 0.1 > p ≤ 0.5

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

“NanoWaste : review on waste management and key issue on nanotechnologies”
Frejafon et al, OECD Workshop on nanowaste, Munich 10th May 2011

Slide 11

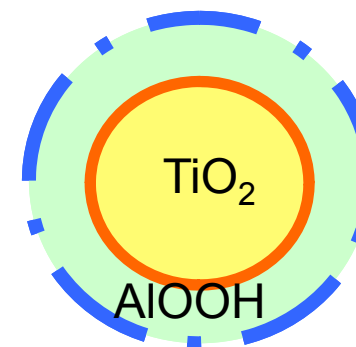
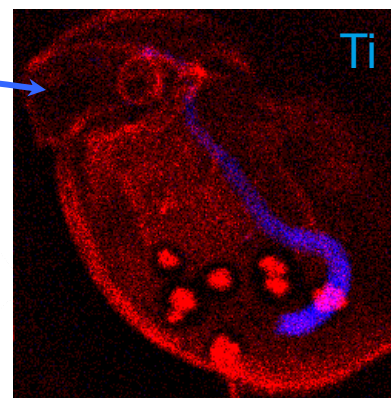
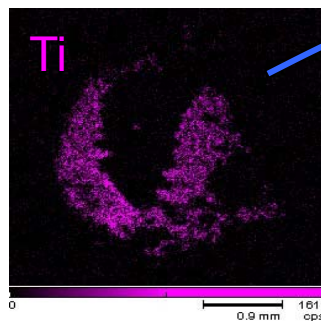
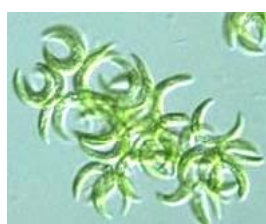
Sewage treatment plant

Case study : nano-TiO₂ formulation sunscreens



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Bio-assimilation of the altered-formulation



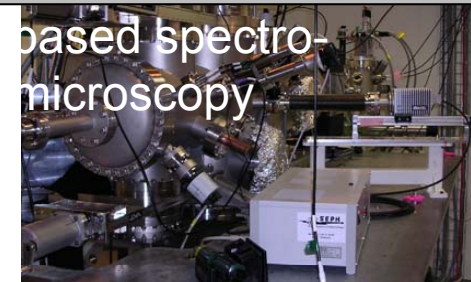
(1) Adsorption onto micro-algae

(2) Ingestion by Daphnia

No mortality
Early eclosion rate
Decrease of the reproduction rate

Fouqueray, M., et al (2012), "Effects of aged TiO₂ nanomaterial from sunscreen on Daphnia magna exposed by dietary route". *Env. Poll.* 163 55-61.

Importance of aging procedures to test the coating stability



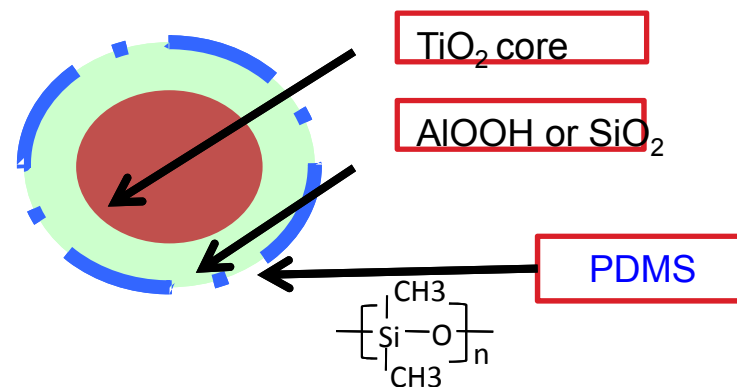
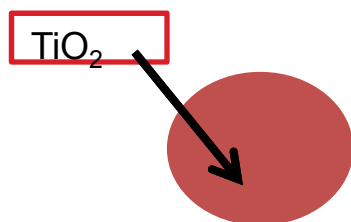
Sewage treatment plant

Case study : nano-TiO₂ formulation sunscreens



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TiO₂ nanoparticles v.s TiO₂ nanocomposite used in sunscreen



Initially	Hydrophilic ROS Generation under light Ecotoxicity (e.g daphnia mortality)	Hydrophobic No ROS generation
After aging In water (and UV)	Hydrophilic ROS Generation under light Ecotoxicity (e.g daphnia mortality)	Hydrophilic No ROS generation (except ¹ O ₂) Low Ecotox (no daphnia mortality)



Ecotox effect depends on core composition, size and morphology, surface properties and its time evolution (eg. Organic coating aging) BUT also on e protocols used to evaluate the effect !

End of life

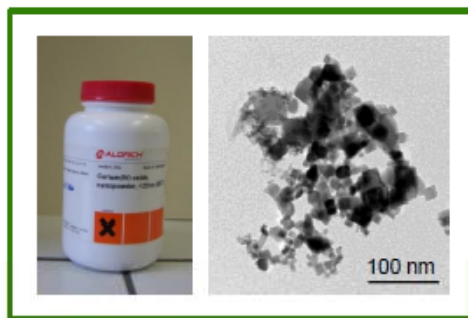
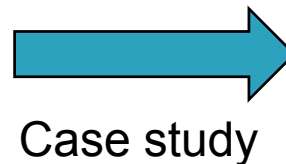
Ecotoxicity : limitations of ISO and OECD methods, case study on nano-ceria

Ecotoxicity of nanomaterials towards aquatic micro-invertebrates and algae

CONTEXT

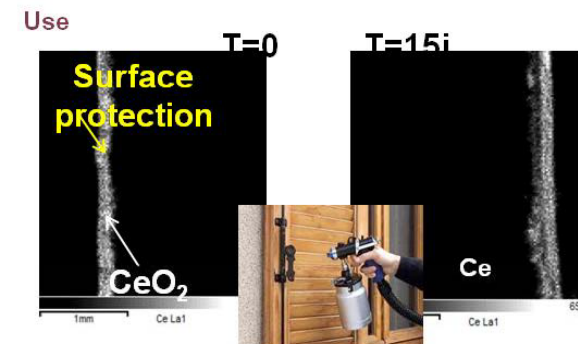
- Environmental impact of nanomaterials are unknown
- Questions rise concerning the relevance of the existing methods (SCENIHR, OECD)
- Sample preparation for lab testing is a key issue when considering physico-chemical properties of nano (OECD 2010)

→ Determine whether the use of different ecotoxicological media and different methods to suspend a ceria nanopowder can influence its behavior and its ecotoxicity towards aquatic organisms



Commercially available $n\text{CeO}_2$ (Sigma Aldrich)

Diameter of the primary particles < 25 nm (sup data)



Release of Ceria in environment ?

End of life

Ecotoxicity : limitations of ISO and OECD methods, case study on nano-ceria

Ecotoxicity of ceria ENM towards aquatic micro-invertebrates and algae

Methods of dispersion	Organisms	Medium	EC ₅₀
			(mg/L)
24h-stirring	<i>D. magna</i>	ISO	> 100
		ISO+HA	> 100
		MHW	> 100
		MHW+HA	> 100
	<i>C. dubia</i>	MHW	> 100
		MHW+HA	> 100
Probe sonication 1 minute	<i>D. magna</i>	MHW	> 100
		MHW+HA	> 100
	<i>C. dubia</i>	MHW	13.6 (11.2 - 14.6)
		MHW+HA	25.3 (18 - 33.1)
		MHW	16.8 (15 - 17.8)
		MHW+HA	11.9 (9.5 - 15)

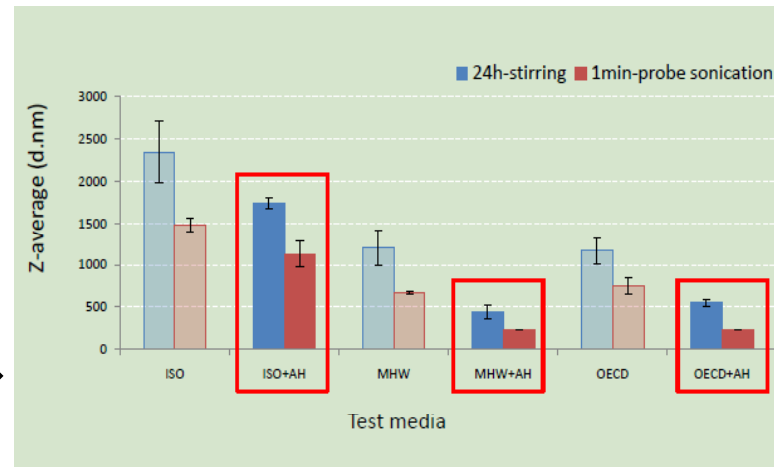
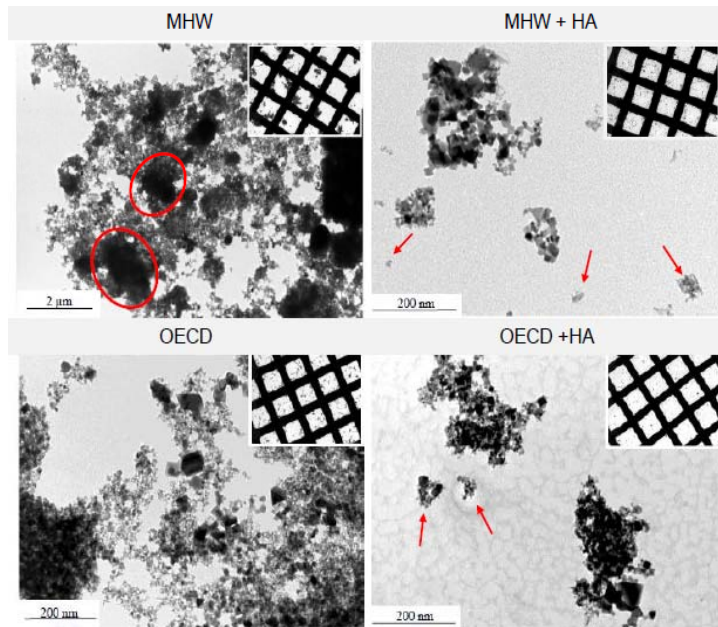


- No effect on *D. magna* and *C. dubia* exposed to the 24h-stirring suspensions
- Increase of the mobility inhibition of *C. dubia* exposed to the probe-sonicated suspensions
- The addition of HA did not influence the toxic effect in those experiments

End of life

Ecotoxicity : case study of ENM ceria (paintings) applying OECD method

Ecotoxicity of ceria ENM towards aquatic micro-invertebrates and algae



Behavior of nanoparticles can differ greatly considering :
The ecotoxicological media used for aquatic ecotoxicity test
The dispersal protocol used to suspend the $nCeO_2$ in the medium
Addition of Humic Acids limits the agglomeration
Surface activity have also temporal evolution

OECD Methods → Limitations for the case of nanomaterials

→ Need to optimized existing methods or to develop new ones

Manier N, Garaud M, Delalain P, Aguerre-Chariol O, Pandard P . 2011. Behaviour of ceria nanoparticles in standardized test media – influence on the results of ecotoxicological tests. *Journal of Physics Conference Series*. **304:012058**

Storage or recycling in new materials

Case study : nano-TiO₂ formulation for self-cleaning materials



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NF EN 12457 Test: leaching + mechanical effects (mortar)

CTG-Leachcrate (cement paste)

Dialysis test (cement paste)

Climate chamber (mortar)



Cement + TiO₂ = photocatalytic cements

Storage or re-use (2nd hand material)

→ Addressing both Mobility capability of nanomaterials in complex matrix



Major concern as:

storage capabilities are low compare to building end of life management

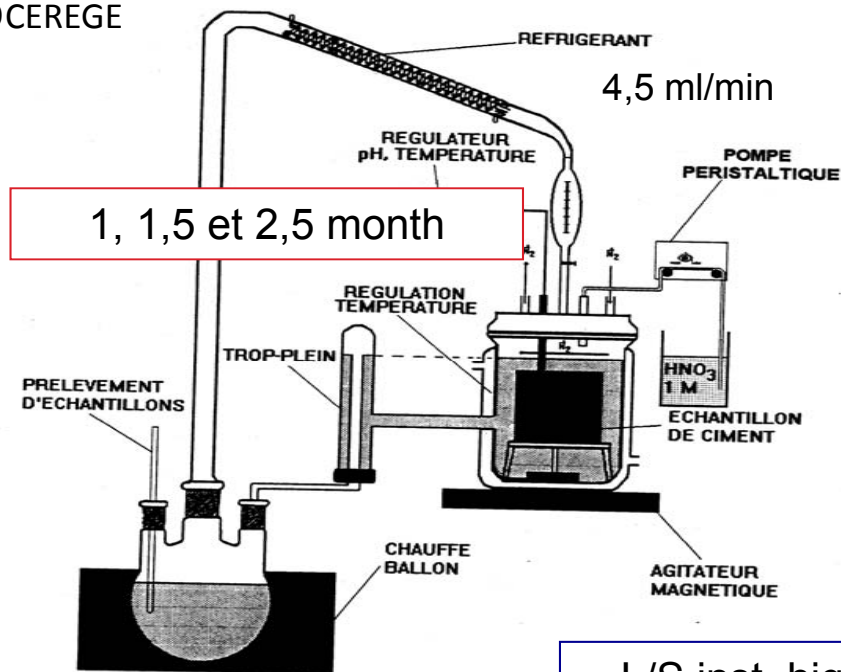
Re-use if possible → then product effect study is needed

Storage or recycling in new materials

Case study : nano-TiO₂ formulation for self-cleaning materials

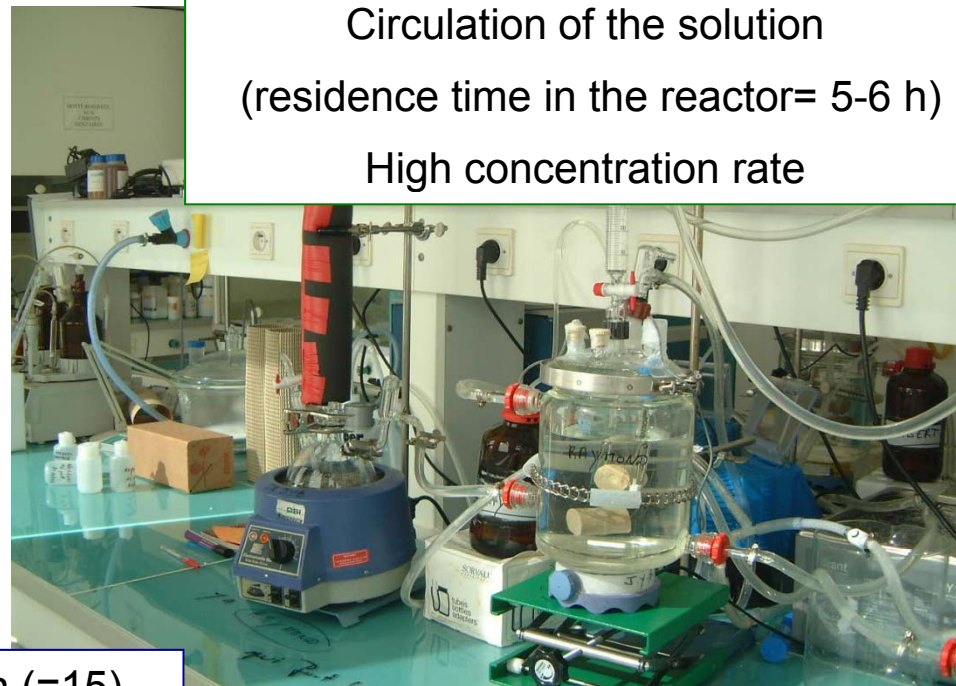


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Acidification + Filtration 0,2 µm

L/S inst. high (=15)
→ Saturated media

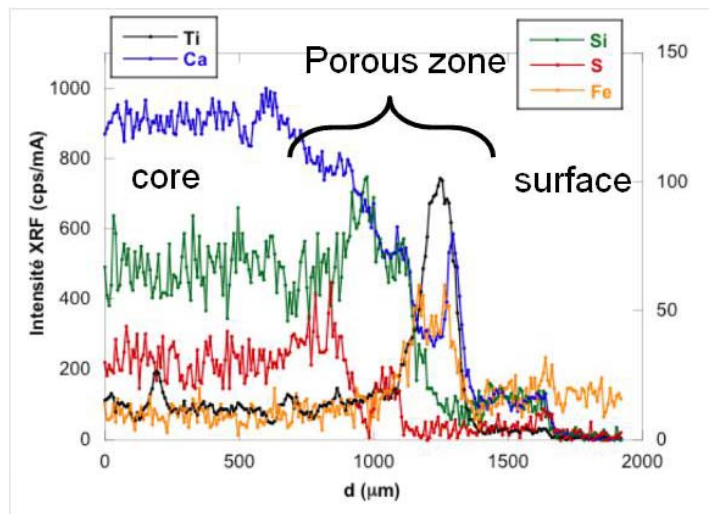


Storage or recycling in new materials

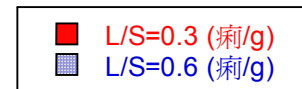
Case study : nano-TiO₂ formulation for self-cleaning materials



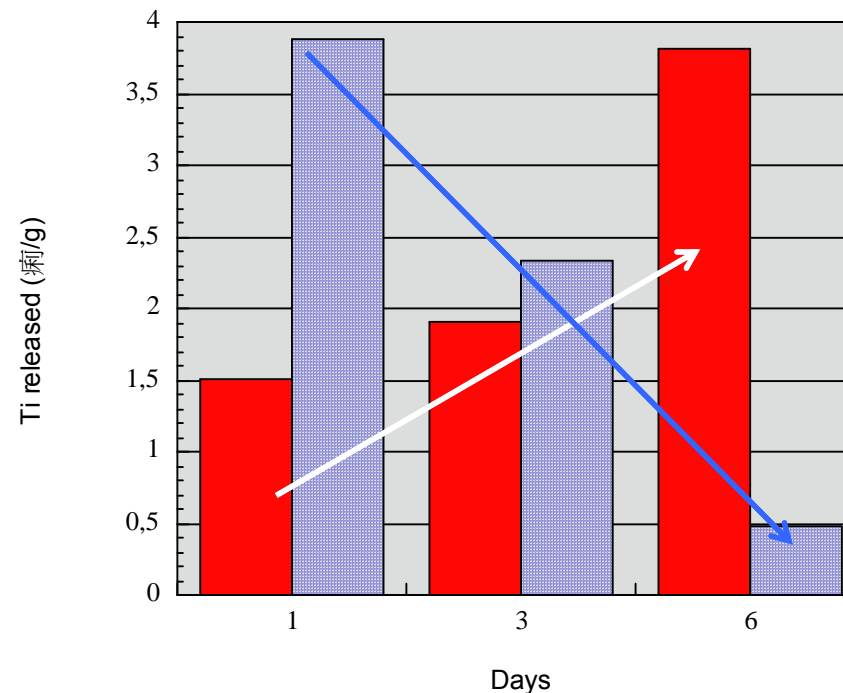
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Nano-TiO₂ released:
Function of the inclusion method
(near the surface or in the matrix)
→ case by case study



Low porosity
High porosity



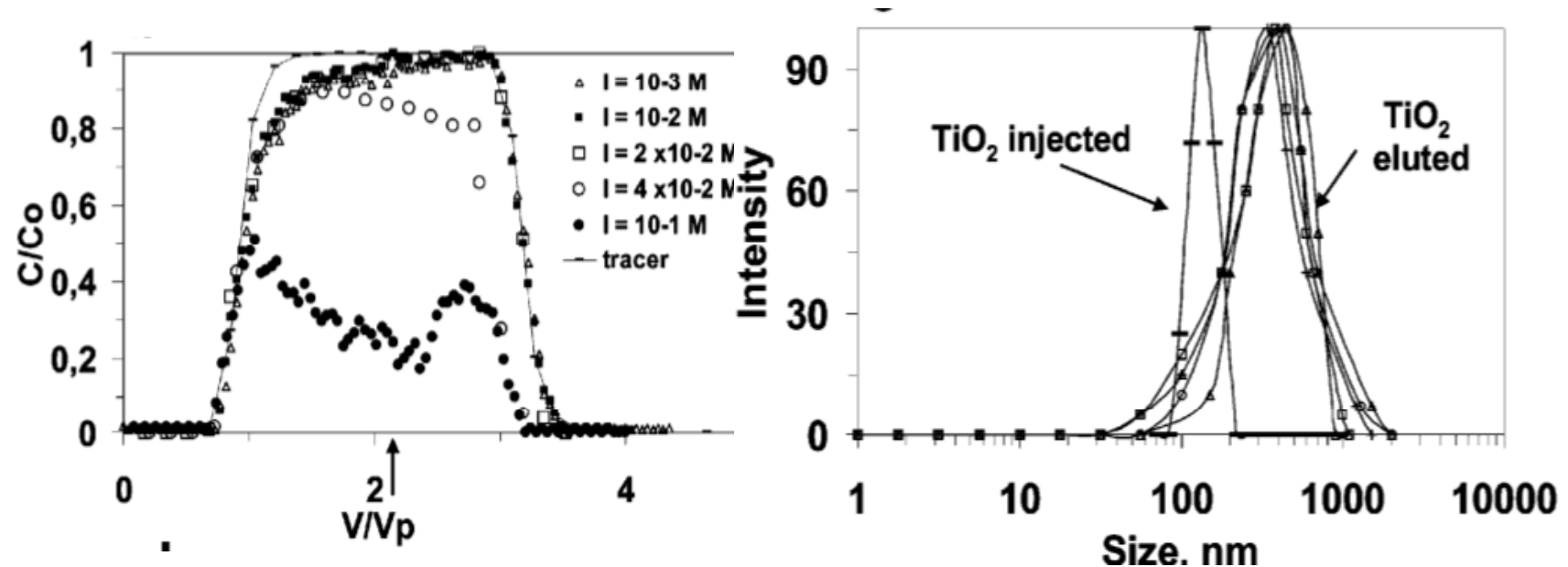
Nano-TiO₂ released:
Function of porosity → case by case study

Storage or recycling in new materials

Case study : nano-TiO₂ formulation for self-cleaning materials

Transfert of nanomaterials (TiO₂) in porous media

Case study: TiO₂ nanomaterials in small scale column (7 cm long./dia. 4,7 cm) filled with sand:



Résultats:

Possible aggregation in porous media but depend on surface fomrulation

Effect of the Organics compounds on transfert rate (same as Heavy metals)

Storage or recycling in new materials

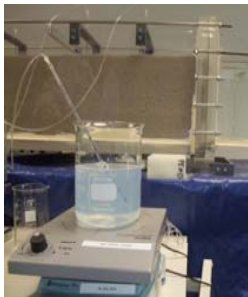
Case study : nano-TiO₂ formulation for self-cleaning materials

Middle scale pilot system including sampling tools



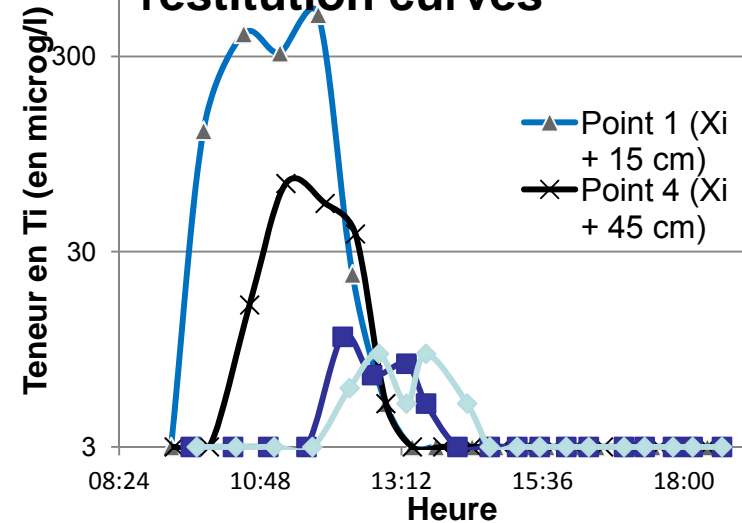
Dispositif de suivi d'une injection de nanoparticules de titane

- Using tracers (uranine) and the TiO₂ NP
- 11 sampling points, 20 times
- NP size distribution control before and after



Injection of TiO₂ NP

Comparison of NP restitution curves



Résultats :

- Fast decrease of TiO₂ concentration compare to tracer:
 - 1 order of magnitude after 45 cm
 - 2 orders of magnitude after 115 cm

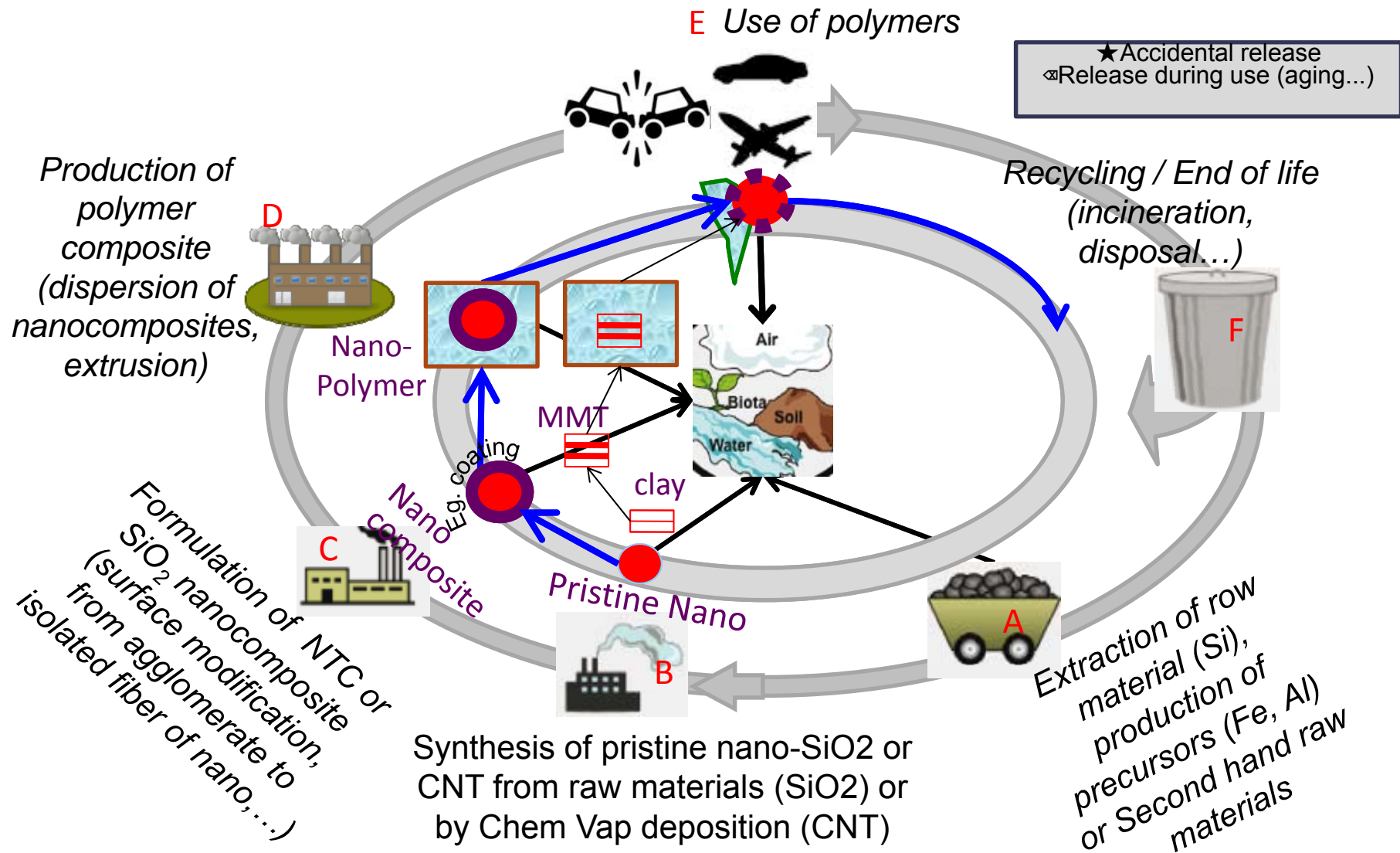
Transfer in porous media

→ Approaches used doesn't differ that much to standards methods used (eg. Used for heavy metals)

→ EXCEPT metrology tool which is dedicated

Incineration / recycling

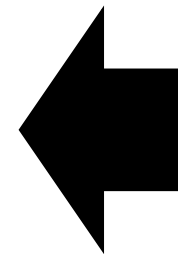
Polymer nanocomposites



Incineration /recycling

Polymer nanocomposites

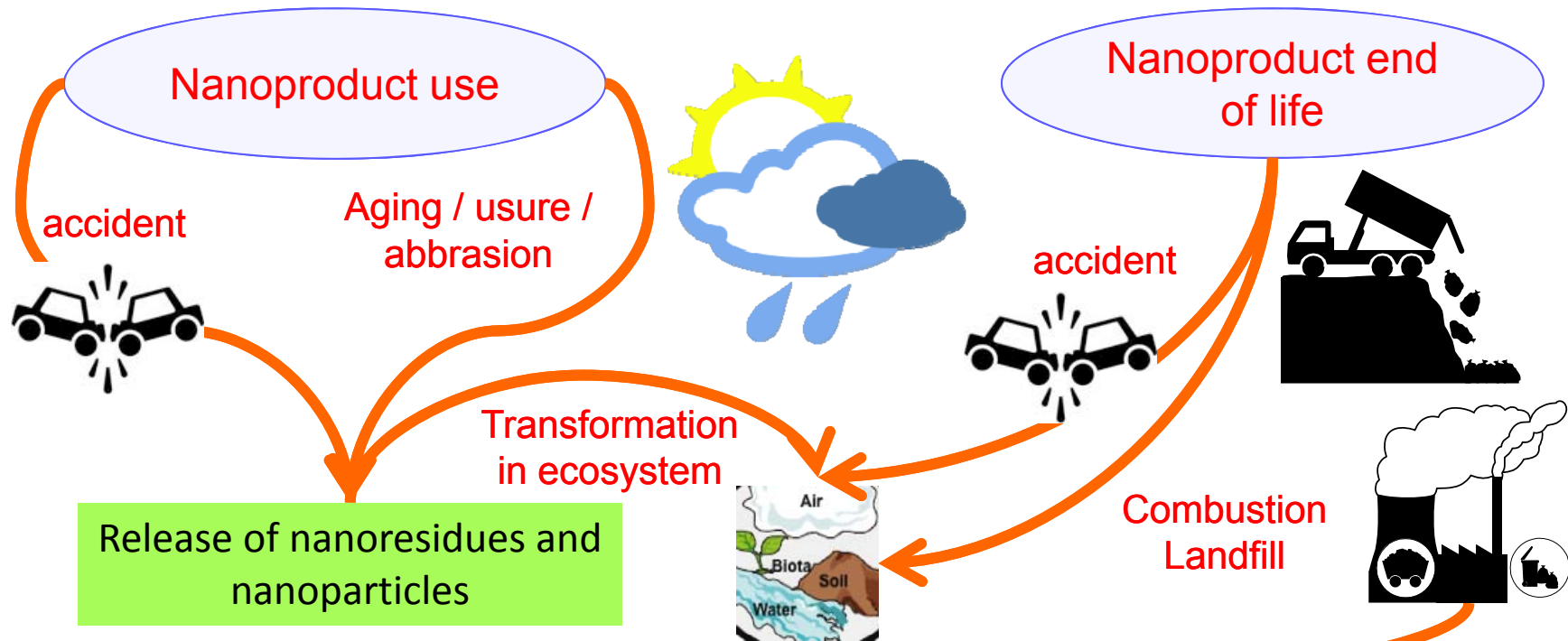
- Common polymeric materials **reinforced with nanofillers or nanosilica to prepare enhanced materials**: weight reduction, electrical conductivity, improved mechanical strength...
- The plastics industry is considered to be one of the main field in which the new nanotechnologies can play a key role



Example of application: lighter automotive lights (with high thermal conductive plastics based on polymeric material doped with carbon nanotubes)

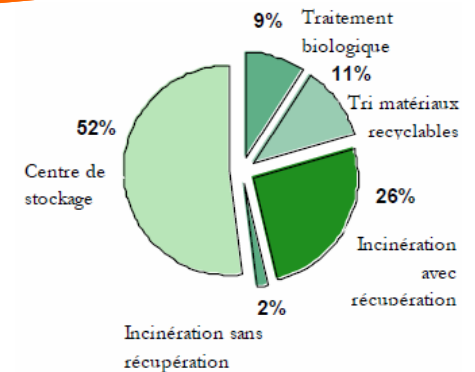
Incineration / recycling

Polymer nanocomposites



Question: can then nanomaterials be released from the matrix in case of thermal decomposition ?

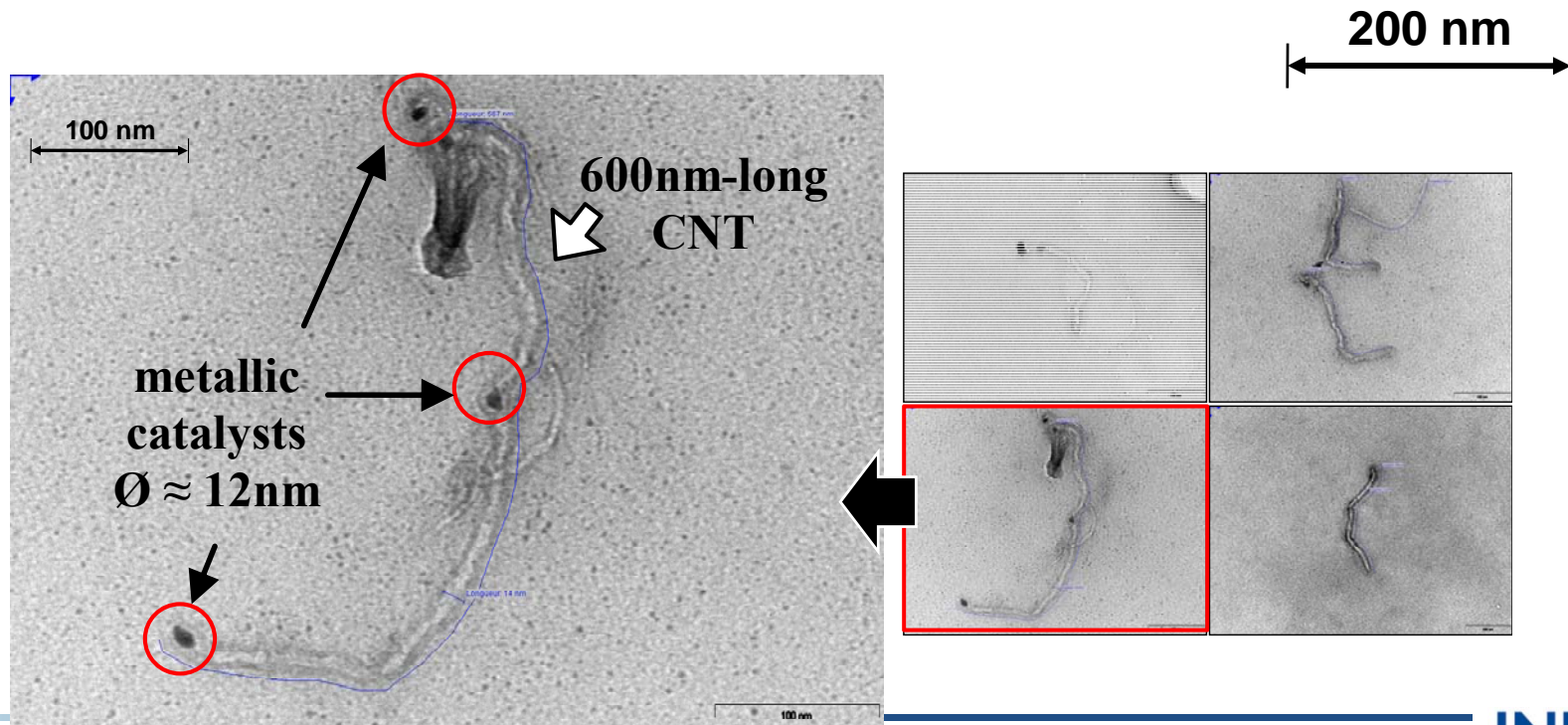
- Recycling (re-use) into valued materials
- **Energy valorisation by combustion/incineration**
- **Accidental burn (fire)**



Incineration / recycling

Fumes analysis (TEM sampling) of CNT-polymers during burning process

- TEM sample analysis reveals some **isolated** CNTs released through the combustion fumes
- no CNT on the blank test sampling (consistent)
- Some metallic catalysts are still attached to the nanotubes



Incineration / recycling

Fumes analysis (TEM sampling) of CNT-polymers during burning process

- Qualitative **experiment** (emission factor can not be devised)
- Success of the demonstration conditioned by a **careful adjustment of the test parameters** (sampling duration, oven aeraulics, temperature)
- Usefulness of the **TEM grid sampling** for such experiment: the direct particle concentration measurement (ELPI) is unable to show a difference between the blank sample and the nanocomposite !
- Evidence of CNT release in accordance with Chivas-Joly *et al.*

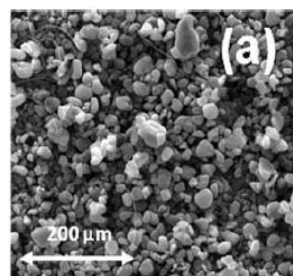
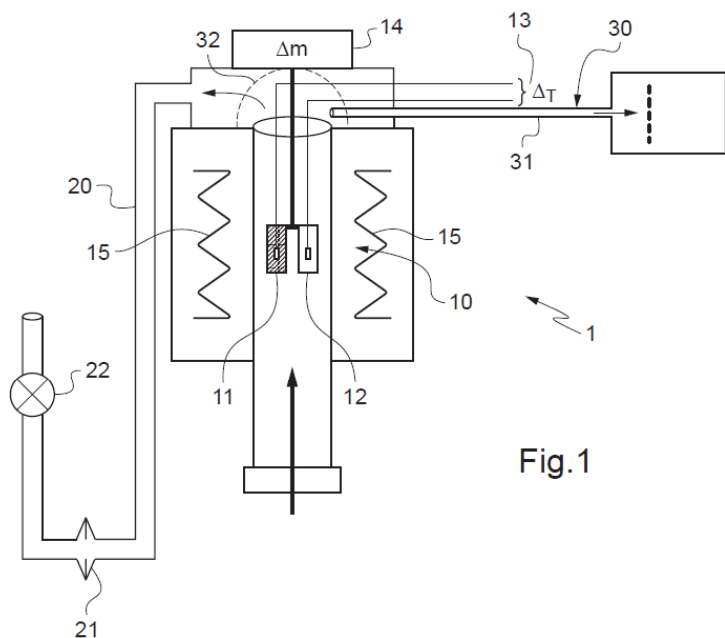


Must be continued → understanding of the release mechanisms

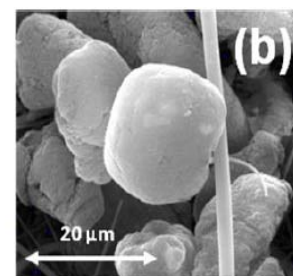
Nanowaste key issue

Dedicated metrology for detection & characterization

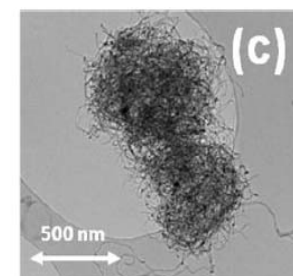
Airborne nanoparticle sampling and characterization
 → Fast and reliable technique for fume characterization



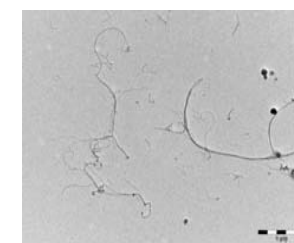
Quartz filter surface SEM image



SEM image of CNT bundles



TEM image of CNT bundle



Bouillard et al, Nanosafe 2011

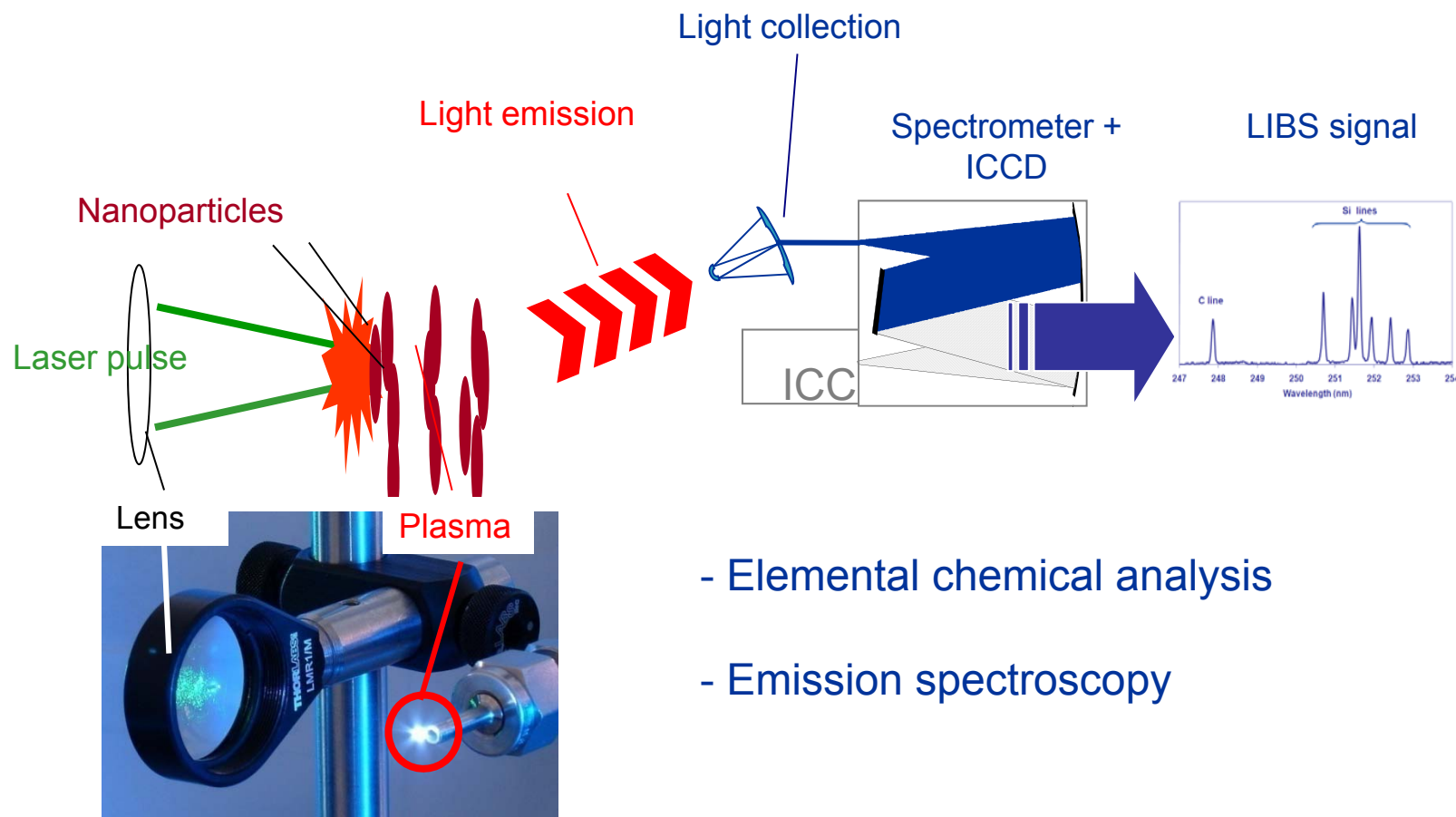
Patented-2011-INERIS, N° 1154795
 (Bouillard, J., E. Frejafon, B. Rmili, et D. Fleury)

Nanowaste key issue

Dedicated metrology for detection & characterization

LIBS : On-line detection & speciation of nanoparticles

Application to detection of nanoparticles in air media



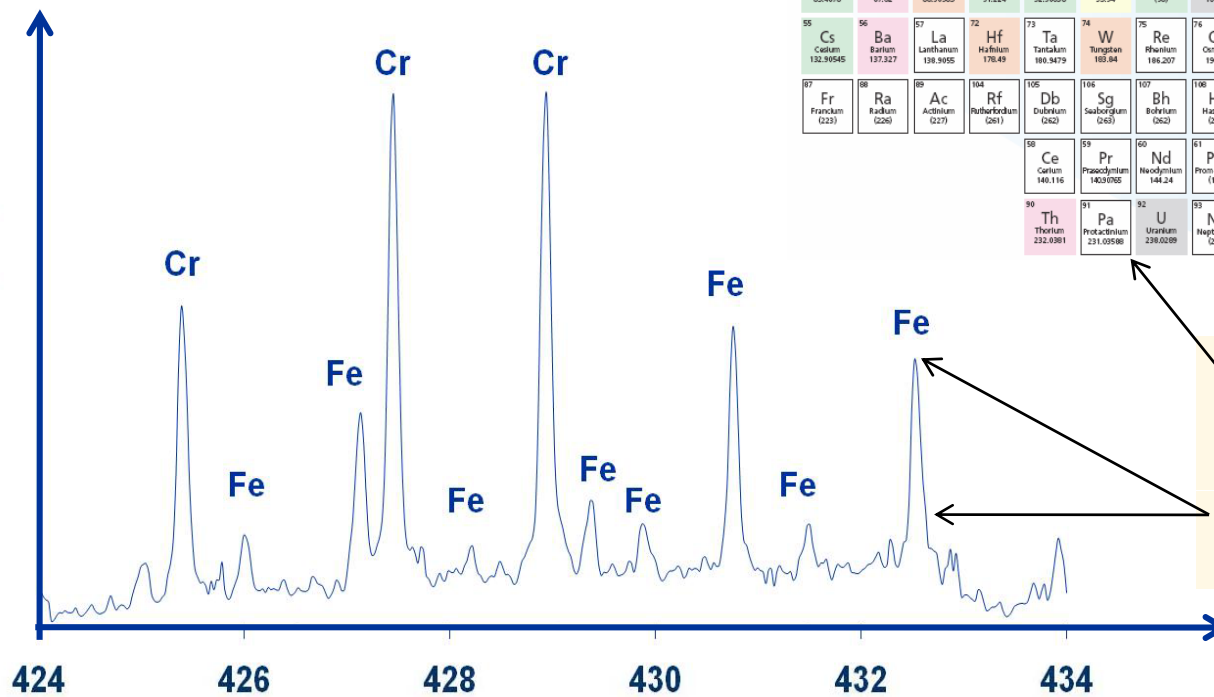
Nanowaste key issue

Dedicated metrology for detection & characterization

LIBS (Laser-Induced Breakdown Spectroscopy)

Information obtained

Intensity = mass concentration



Periodic table of the elements

1 H Hydrogen 1.00784																	5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994													
3 Li Lithium 6.941	4 Be Beryllium 9.012182																	13 Al Aluminium 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulphur 32.066												
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050																	19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938045	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60																		
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.2217	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)																		
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (268)	111 (272)	112 (277)	113	114																				
		58 Ce Cerium 140.116	59 Pr Praseodymium 140.90768	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421																				
		90 Th Thorium 232.0381	91 Pa Protactinium 231.03688	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)																				

- X axis : chemical identification
- Y axis: Quantification

Wavelength = chemical identification (Multi elemental analysis)

“NanoWaste : review on waste management and key issue on nanotechnologies”
 Frejafon et al, OECD Workshop on nanowaste, Munich 10th May 2011

Nanowaste key issue

Dedicated metrology for detection & characterization



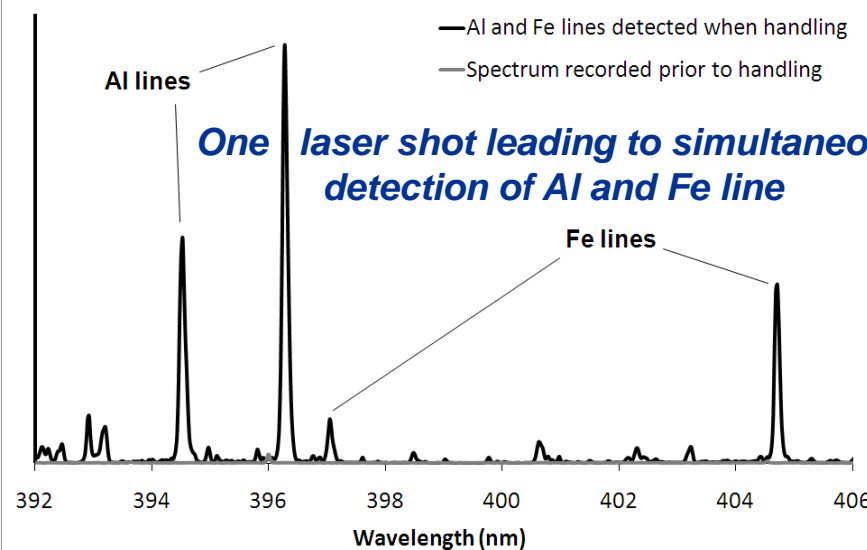
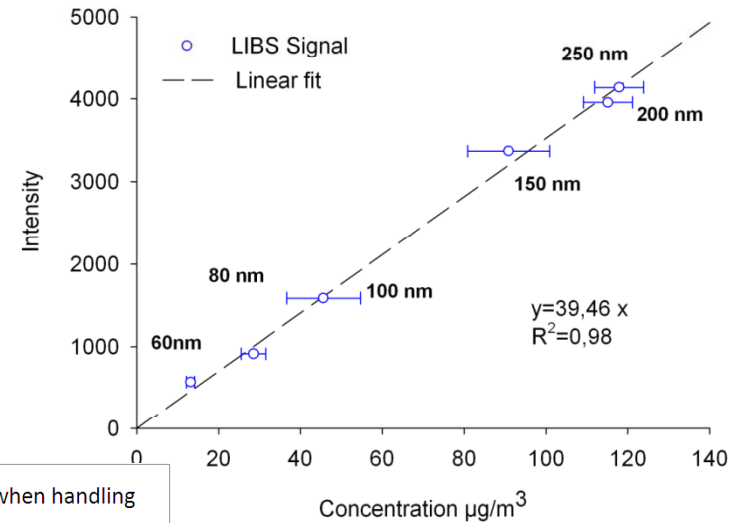
INERIS Prototype



Real time concentration
With low detection limit
($\mu\text{g}/\text{m}^3$ range in air, $\mu\text{g}/\text{l}$ in liquid)

Differentiate nanomaterials from
others nanoparticles
(on-line elemental composition)

12 ISI publications, 1 patent
2012 French Research award



Amodeo et al, Nanotech 2011
R,Mili et al Carbon Nanotube 2012

Conclusion

Waste management and fate of nanomaterials

- involve expertise in chronic risk, accidental risk, metrology, soil management....
- To evaluate if new properties is associated with new potential hazards
- To determine if we can use conventional approaches or new methods, approaches

Review of existing waste treatments and issues addressed by nanomaterials, based on a case by case approach, gives step by step milestones thus guidelines

- Some effect studies are not disconnected to that of chemical substances, but limitations appears.
- Aging have to be taken into consideration (eg. coated nanomaterials)

Nanomaterial and nanoproducs need both to be studied

- Safer by design production might be reached when hazard and risk are evaluated during live cycle up to waste product
- key inputs in production strategy

Acknowledgements

These studies were or are performed within :

- *The European Project “FP6-SAPHIR”*
- *The European Project “FP6-NanoSafe2”*
- *The European Project “FP7-NEPHH”*
- *The French ADEME Project “NanoFlueGas”*
- *The French Ministry of Environment programs*

Thank you !



Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Swiss Confederation

Federal Department of the Environment,
Transport, Energy and Communications DETEC

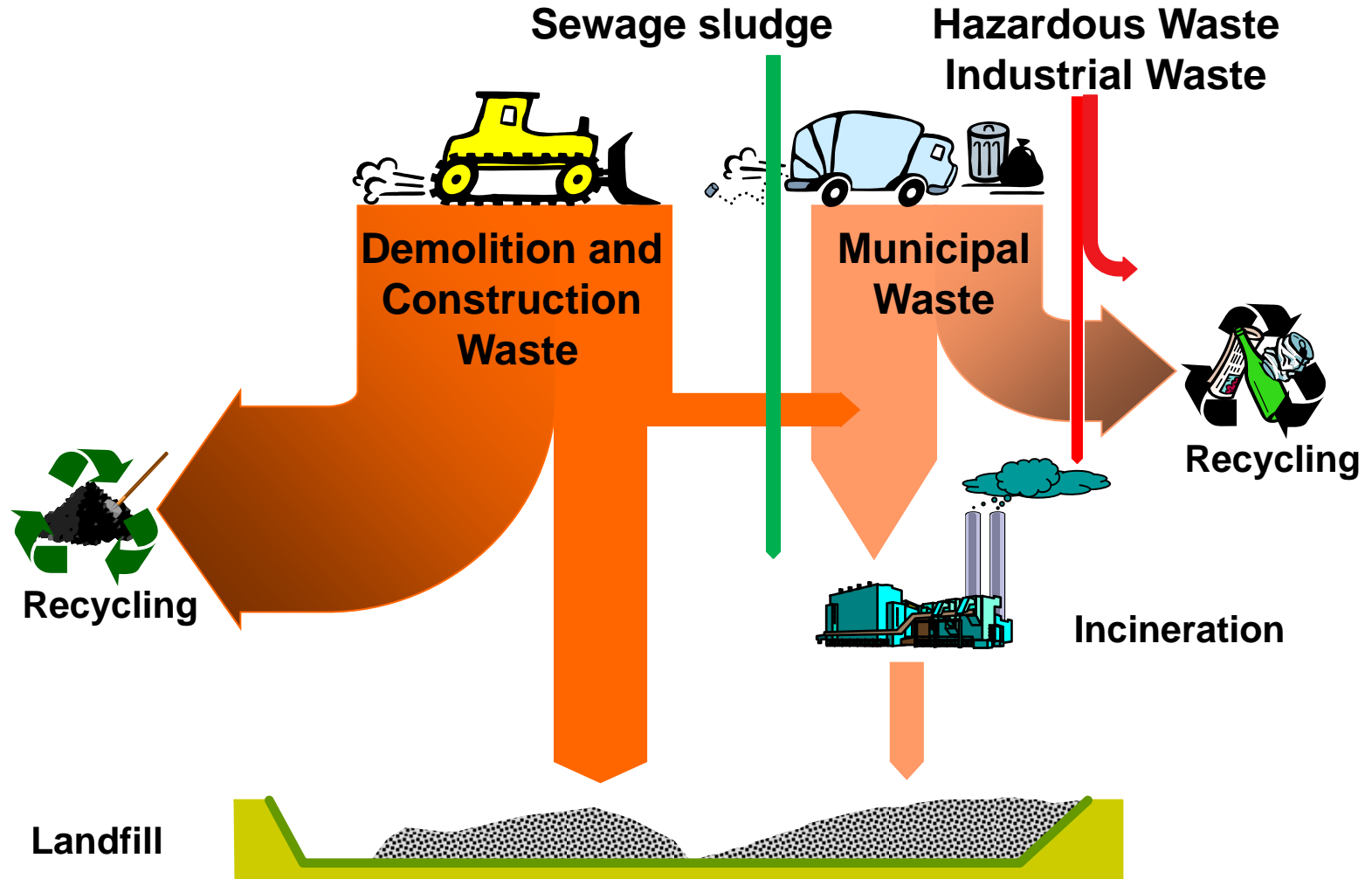
Federal Office for the Environment FOEN
Waste Management, Chemicals and Biotechnology Division

Treatment of waste containing nano materials

André Hauser

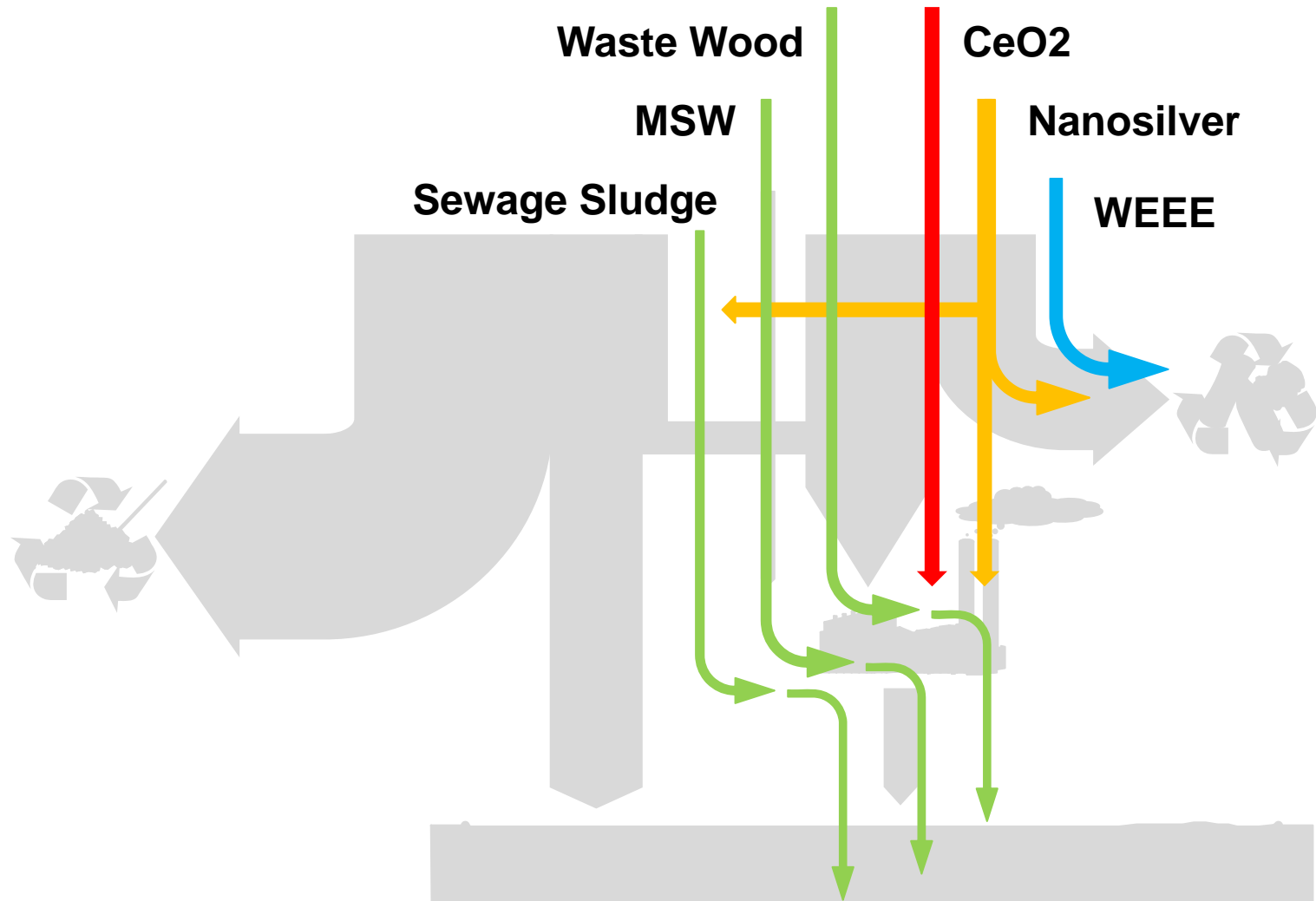


Waste Management in Switzerland





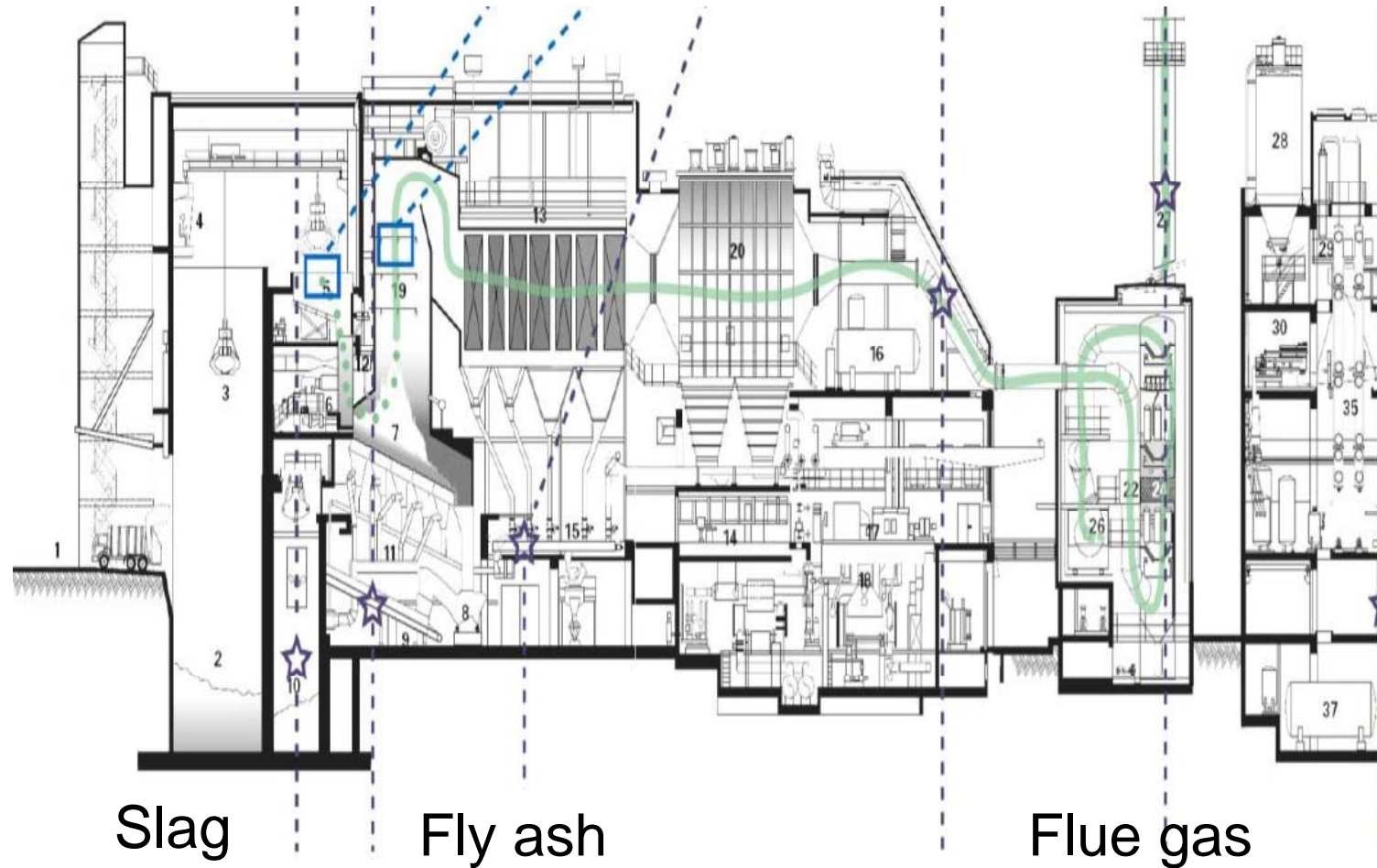
Investigated Waste streams





CeO₂ in a municipal solid waste incinerator

CeO₂ feed





Results

Paper submitted to Nature Nanotechnology



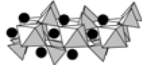

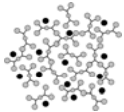


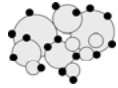
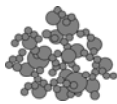
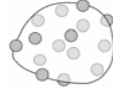
Nanosilver containing wastes from textile industries

- 140 t/a Ag for biocidal applications world wide (0.5%)
- 28 t/a in textiles world wide (0.2 t/a in Switzerland)
- 70% of Ag in textiles from Switzerland and Germany

- 79% silver salts (e.g. AgCl or AgCl composites)
- 13% metallic silver or metallic silver composites
- 8% ion exchanger (e.g. zeolites or polymers)



Applied silver particles

	Silver Ion Exchanger				Silver Salt		Metallic Silver	
Silver Species	Silver zirconium phosphate	Silver zeolithe	Silver glass	Silver polymer	Microcomposite Silver chloride	Silver chloride	Metallic Nanosilver	Metallic Microcomposit Silver
Size (nm)	Ion	Ion	Ion	Ion	20 - 500	20 - 2000	5 - 25	5 - 25
Matrix	Exchange Resin	Alumo Silicate	Phosphate Glass	Polymer	Titanum Dioxide, Zeolith	-	-	Amorph Silicate
Size (nm)	>1000	>1000	>1000	>1000	>1000	-	-	>1000
Amount (%)	1 - 5	1 - 5	1 - 5	3	10 - 20	1 - 5	99	5 - 30
Structure								



Wastes

- Wastes from the production of silver particles
 - Sewage water (1% of Ag as waste)
 - Masterbatch (solid) (1% of Ag as waste)
 - Hazardous waste treatment
- Wastes from textile finishing
 - Surface applications (90%)
 - Washing (70% Ag as waste)
 - Foulard process (1.2% Ag as waste)
 - Masterbatch integration (10%)



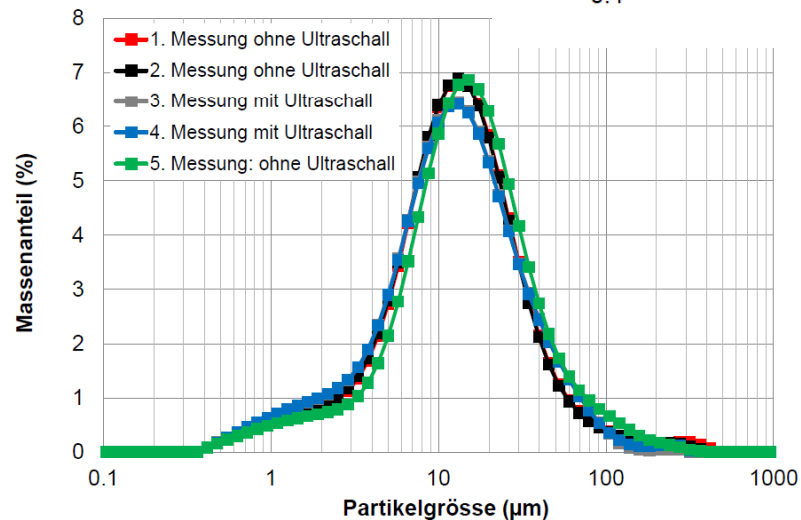
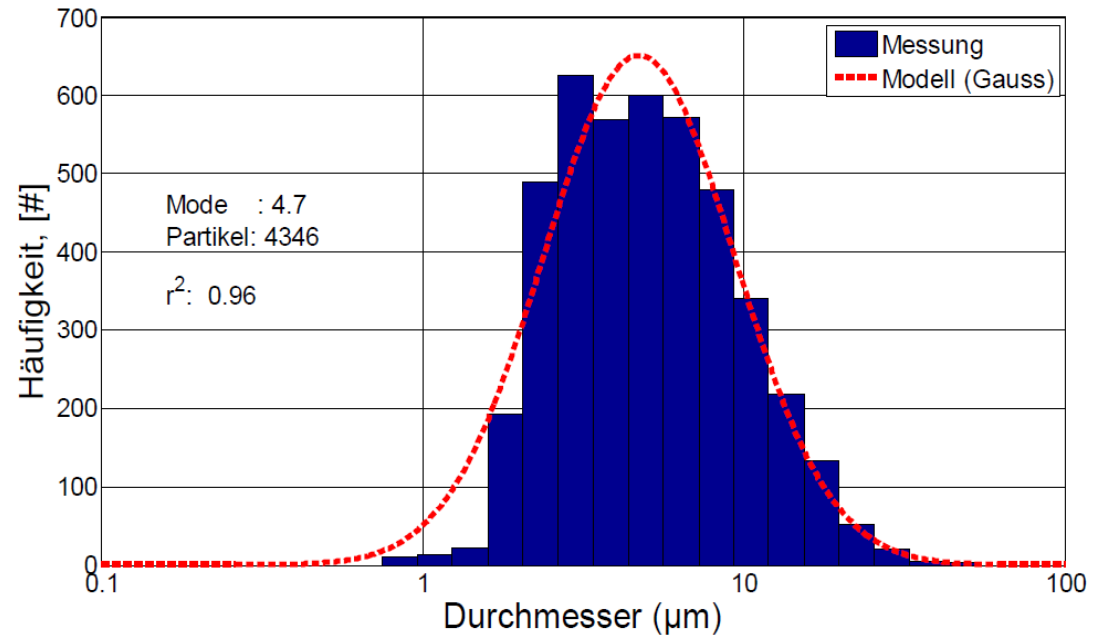
Waste treatment

- Sewage water (CH: 10 kg Ag / year)
 - Sewage water treatment
 - Transfer of Ag to sewage sludge (95%)
 - Incineration of sewage sludge
- Masterbatch (CH: 10 kg Ag / year)
 - MSW incineration
- Hazardous waste treatment
- Recycling options
 - Low concentrations in textiles
 - Detections and extraction not feasible



Filter dust from WEEE shredder

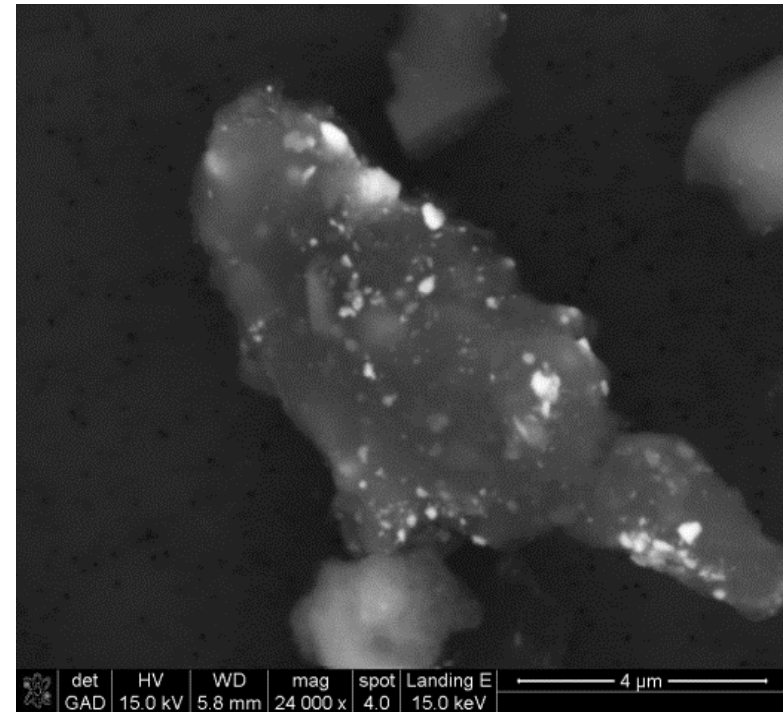
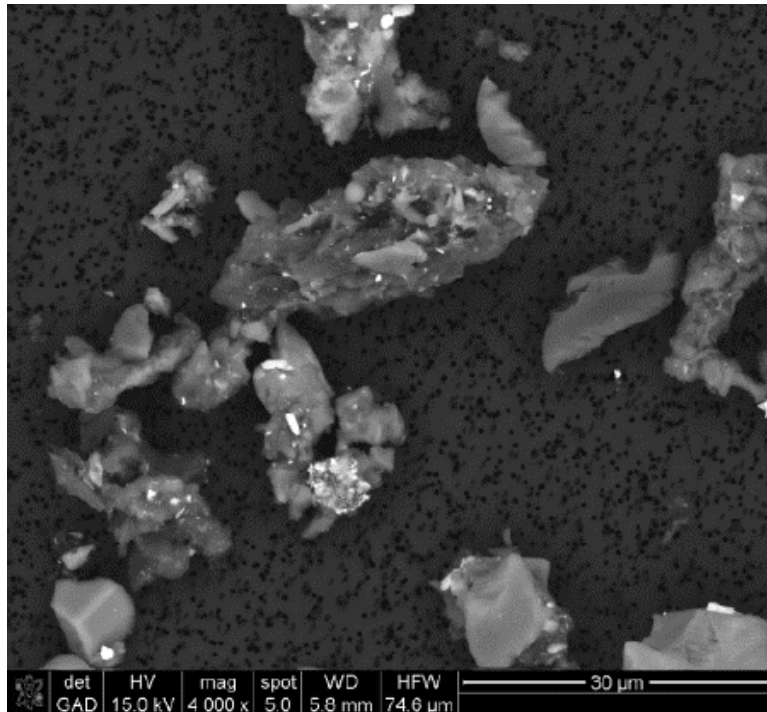
Grain-size distribution by SEM



Grain-size distribution by LDS:
Before and after ultrasonic treatment



Particle analysis



Metal particles < 100 nm embedded in larger plastic particles



Input of nanomaterials into landfill (1)

- Literature study
 - Characterisation of incineration residues i.e. particles < 100 nm
 - Characterisation of powder products e.g. TiO₂, SiO₂, ZnO and carbon black i.e. particles < 100 nm
 - Characterisation of leachates from landfills with regard to metallic particles < 0.45 µm



Input of nanomaterials into landfill (2)

- Grain size distribution incl. < 100 nm of
 - TiO₂ and ZnO pigments
 - Fly ash from the incineration of
 - Municipal solid waste
 - Sewage sludge
 - Wood waste
- Modelling of the input of nano materials to landfills



References

- CeO₂ in a municipal solid waste incinerator
Nature Nanotechnology (submitted)
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http://www.umtec.ch/fileadmin/user_upload/umtec.hsr.ch/120310_Studie_NanAgTex_Abschlussbericht_BAFU_Final.pdf
- Burkhardt, M., et al. (2010): Verhalten von Nanosilber in Kläranlagen und dessen Einfluss auf die Nitrifikationsleistung in Belebtschlamm. Umweltwissenschaften und Schadstoff-Forschung (UWSF) 22, 529–540.
- Kägi, R., et al. (2011): Behavior of metallic silver nanoparticles in a pilot wastewater treatment plant.
Environmental Science & Technology 45, 3902-3908
- Filter dust from WEEE shredder
(internal report FOEN, not available to public)
- Input of nano materials into landfills (in progress)