Waste management and fate of nanomaterials : identify releases of nanomaterials during waste treatment .

New Evidence Towards the Release of Airborne nanomaterials when Burning Nanocomposite Polymers

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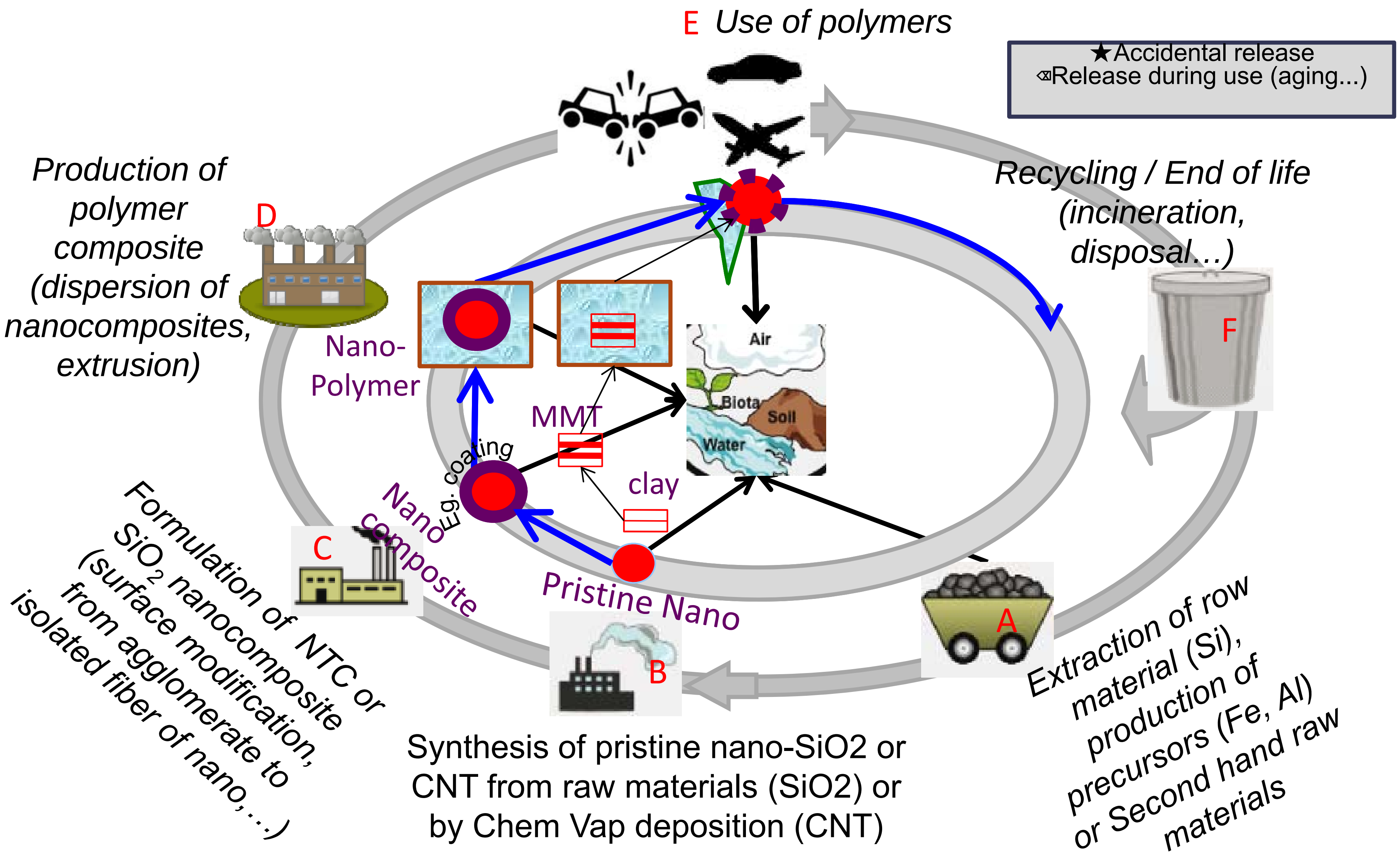
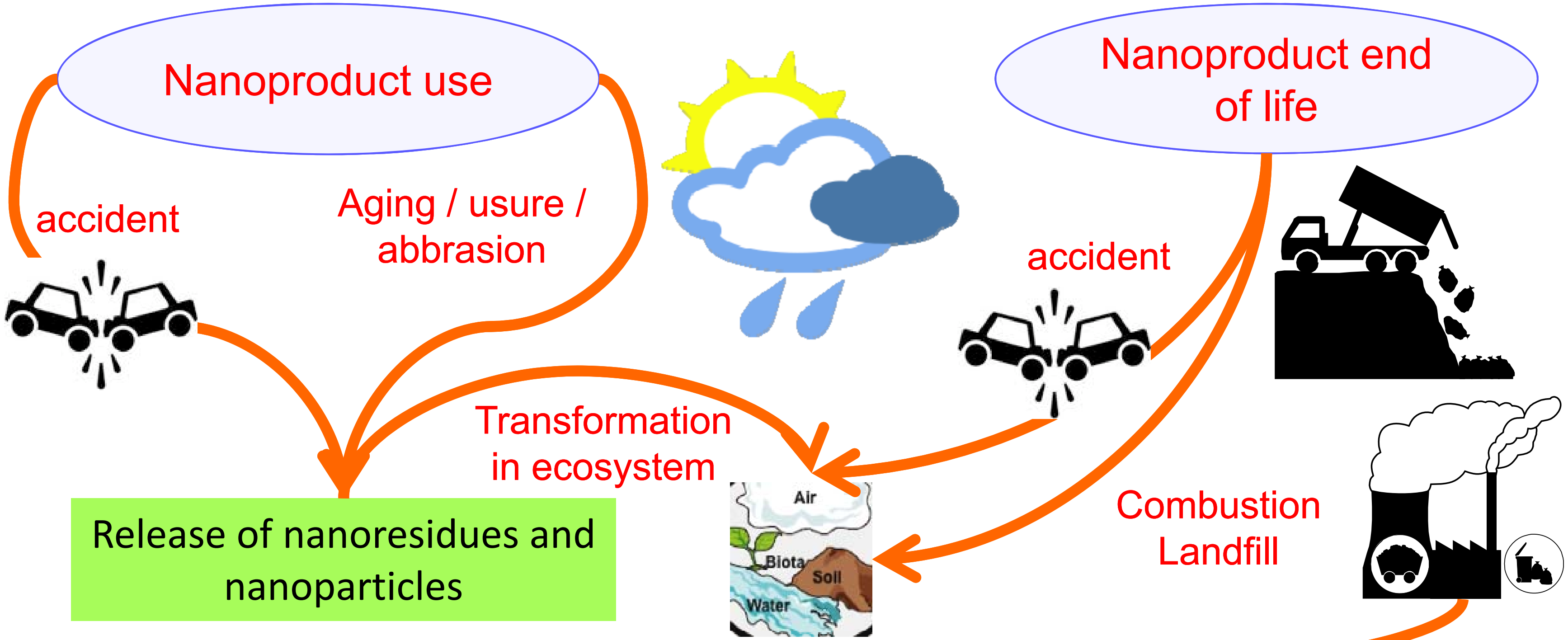
Introduction
Polymer nanocomposites



Introduction
Polymer nanocomposites

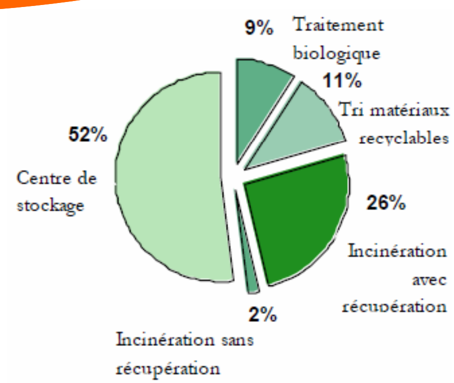
- Common polymeric materials reinforced with nanofillers or nanosilica to prepare enhanced materials: weight reduction, electrical conductivity, improved mechanical strength…
- The plastics industry is considered to be one of the main field in which the new nanotechnologies can play a key role

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



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)**



“New Evidence Towards the Release of Airborne nanomaterials when Burning Nanocomposite Polymers”
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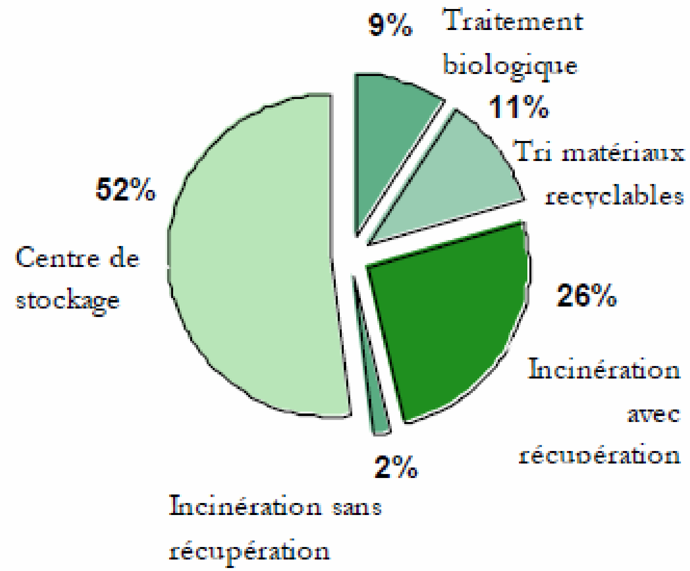
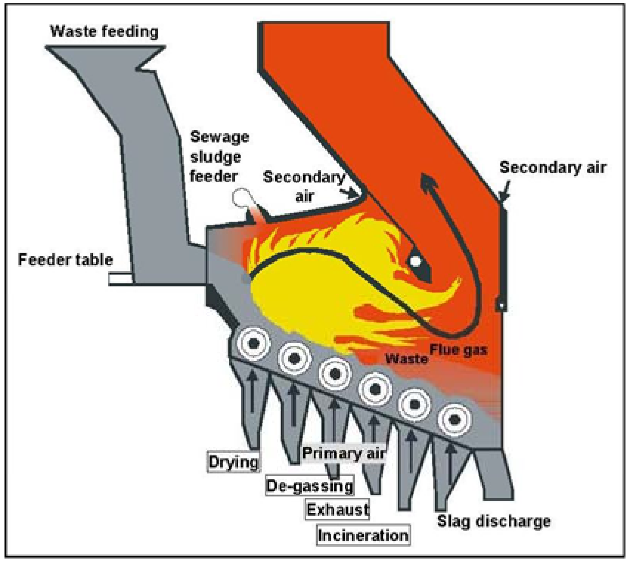
NANOFlueGas



Case study of a waste incineration facility

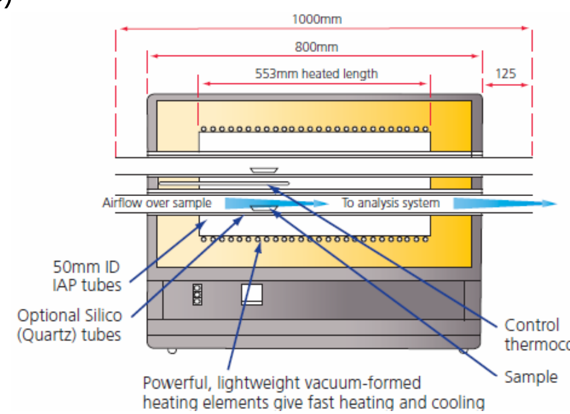


IncinerationTechnique:

> 90% the facilities in Europe / Grid type incineration

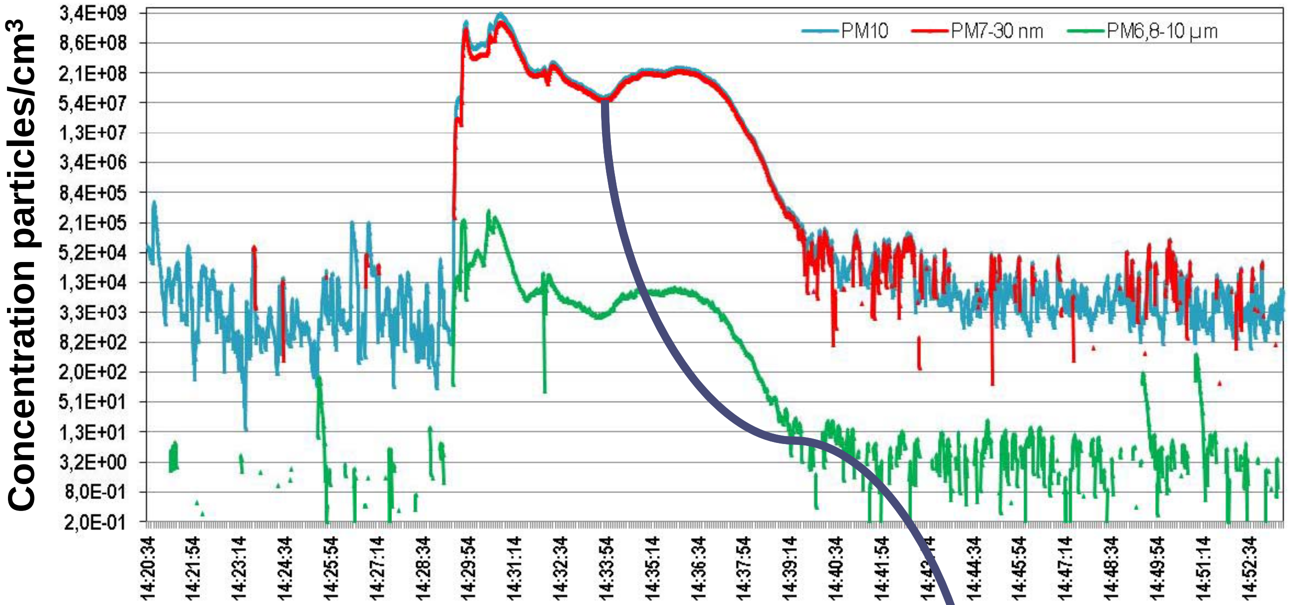
(Best techniques of incineration, 2006)

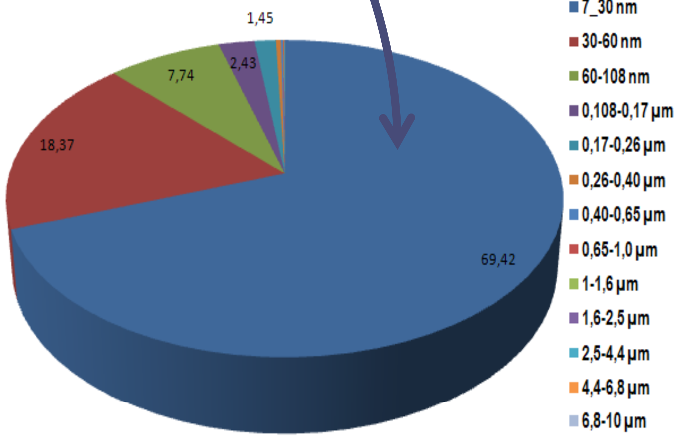
Preliminary lab scale test



Lab scale tests

NANOFlueGas





Number concentration
7 nm – 10 µm : $2{,}9.10^{8}$ particles/cm^3

Question: can we have nanomaterials ?

Introduction
State of the art: CNT release

- Nyden *et al.* (NIST),“Characterizing Particle Emissions From Burning Polymer Nanocomposites”, Nanotech 2010 conference
  - Tested material: Polyurethane Foam (PUF) + CNTs
  - Test setup: smoke chamber
  - No CNT in the smoke / High level of nanoparticle (inc. CNT) in the chars
- Motzkus *et al.* (LNE), “Characterization of airborne particles released by the combustion of nanocomposites”, Nanotech 2011 conference
  - Tested materials: CNT-PMMA and CNT-PA6 nanocomposites
  - Test setup: cascade impactor coupled with a cone calorimeter
  - Small rods/pieces of CNT identified into the fumes (AFM analysis).

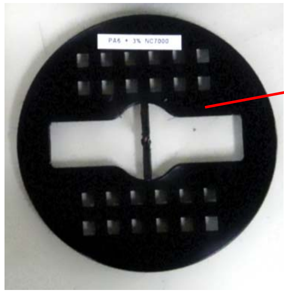
- Only a few publications focusing on the release of CNT or SiO2 during fire or combustion processes
- No clear proof of CNT fibers or SiO2 release during the combustion of those types of polymer nanocomposites

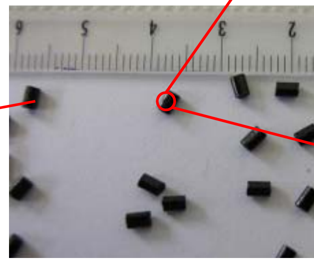
THE EXPERIMENTS

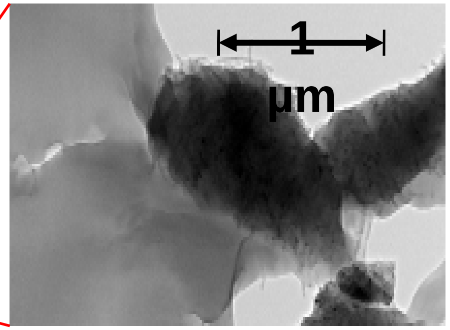
Experiment

Tested materials (CNT polymers)

- Injection-moulded nanocomposite polymers:
  - **Matrix:** ABS (Acrylonitrile butadiene styrene) polymer matrix, a special grade for high temperature processes
  - **Nanofiller (3%w.):** Multiwall carbon nanotubes
    - Length: 0.1-10 µm
    - Diameter: 10-15 nm,
    - **Agglomerated in bundles**







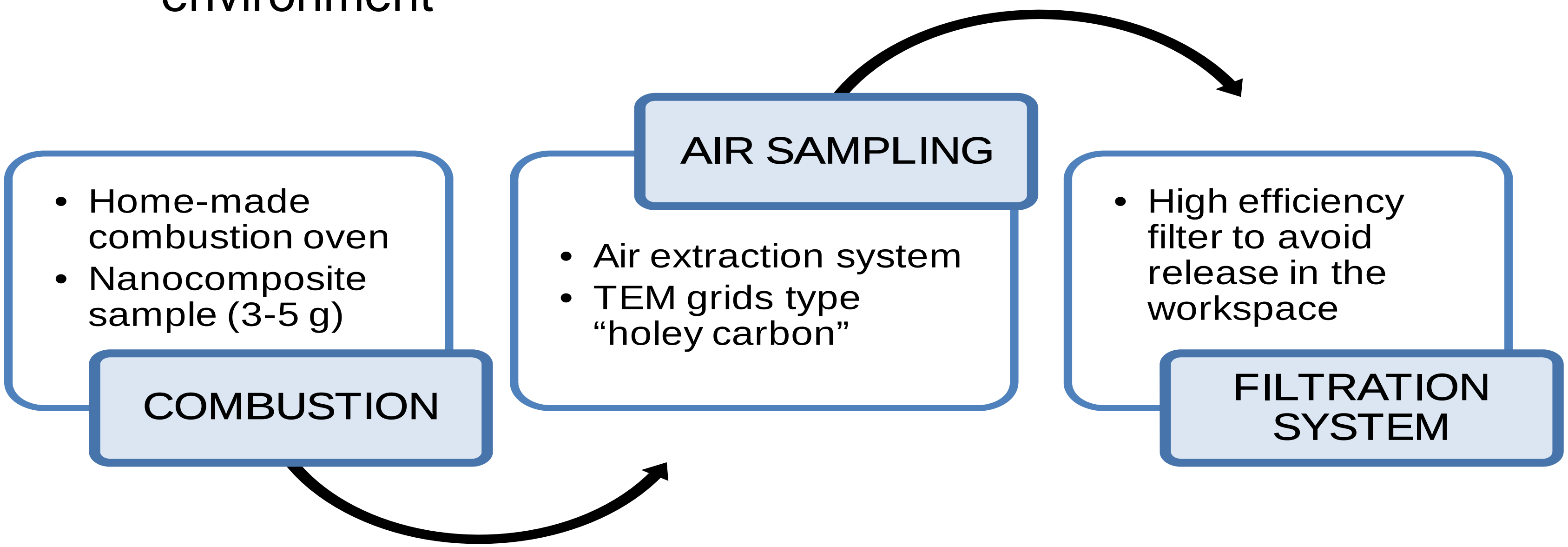
Masterbatch granules used to produce nanocomposite plates via the melt-mixing routes process

Experiment

Test setup (CNT polymers) : INERIS demonstrator

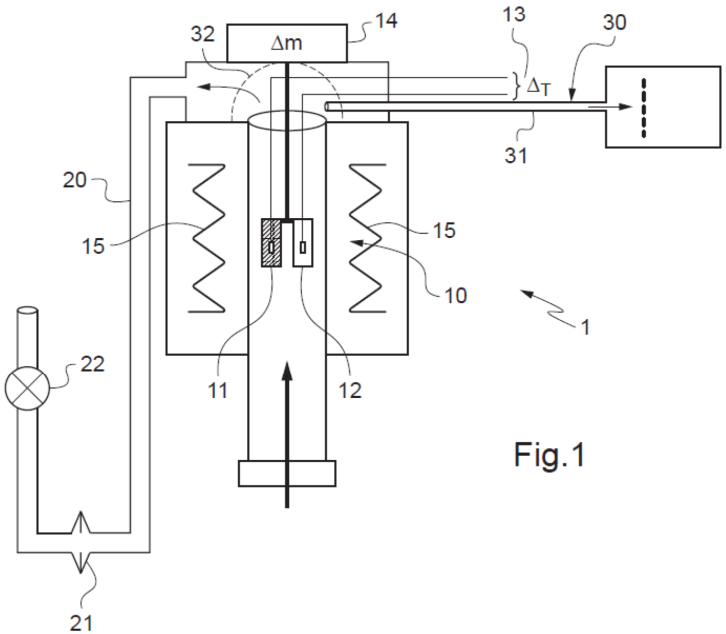
INERIS demonstrator is composed by 3 modules:

- **Combustion:** a home-made oven is used to burn the sample, monitor the loss of weight and the temperature
- **Air sampling:** airflow is sample in order to identify the presence of released nanofillers
- **Filtration system:** avoid any hazardous release into the environment

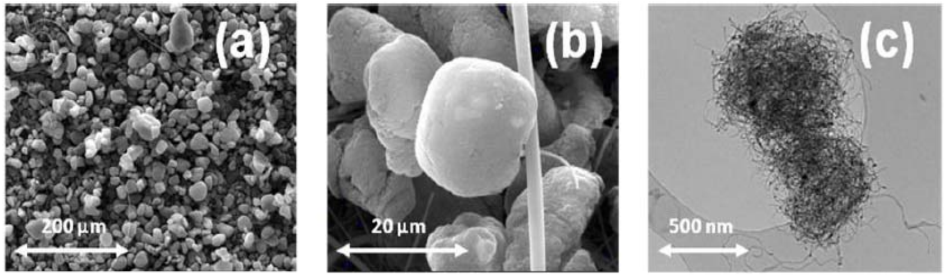


Nanowaste key issue
Dedicated metrology for characterization

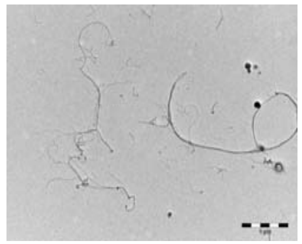
Airborne nanoparticle sampling and characterization
→ Fast and reliable technique for fume characterization



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

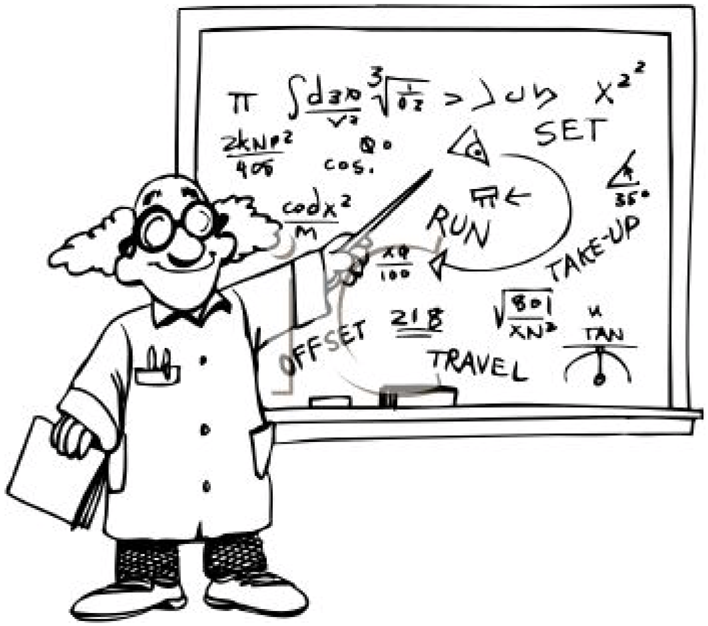


Quartz filter surface SEM image | SEM image of CNT bundles | TEM image of CNT bundle



Bouillard et al, Nanosafe 2011

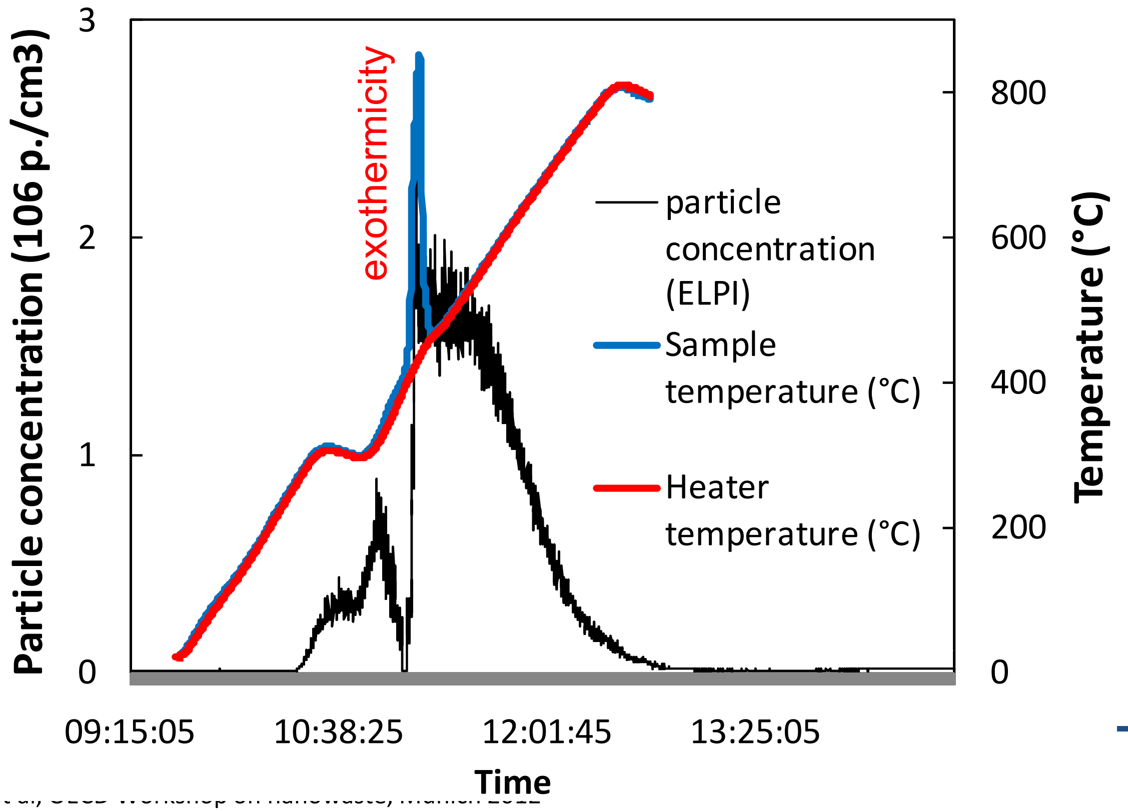
THE RESULTS



Results

combustion kinetics & particle concentration measurements (ELPI)

- Strong correlation between the particle concentration and the temperature increase
- **Blank test performed:** same behaviour (part. concentration & temperature) for both samples.

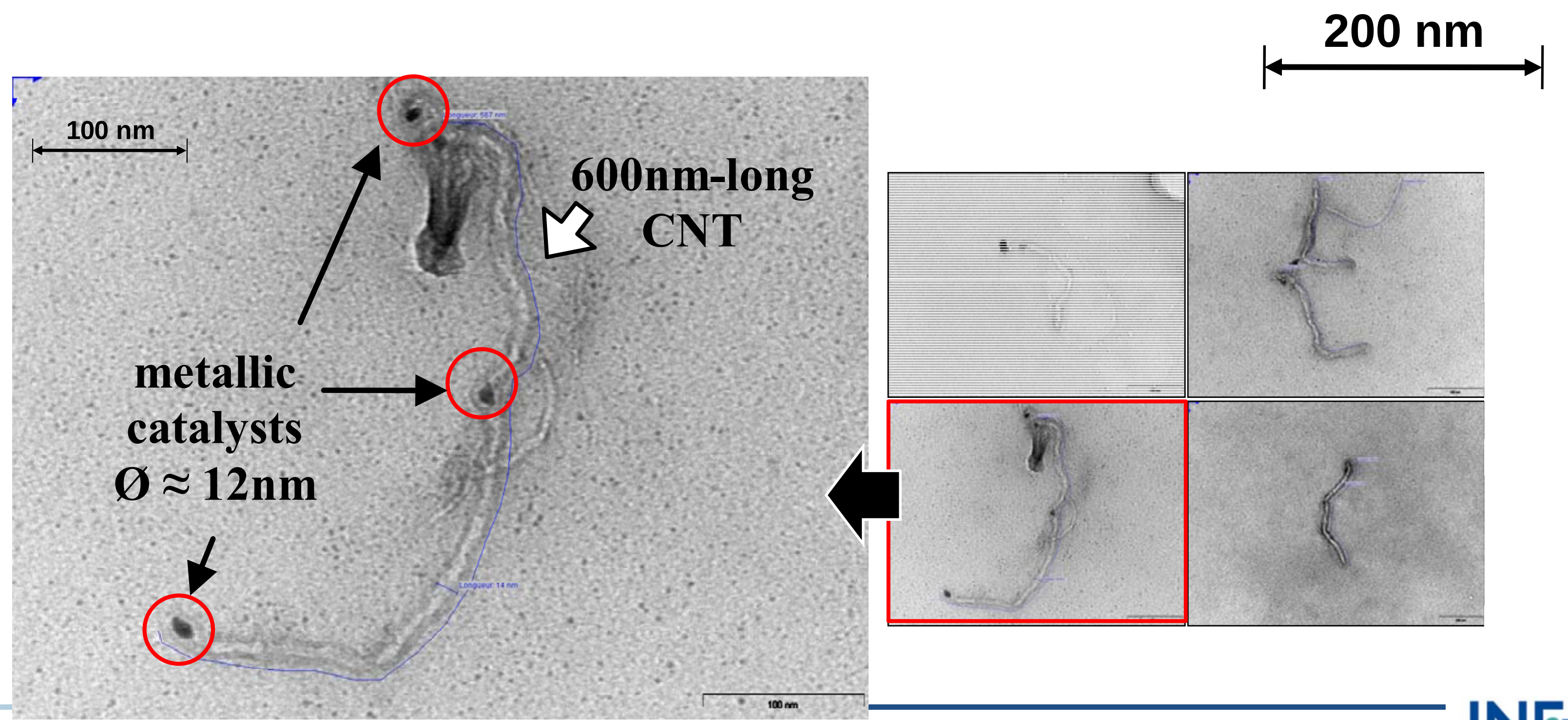


The peak of combustion (exothermicity) traduces the combustion of the polymer

Results

Fumes analysis (TEM sampling)

- **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



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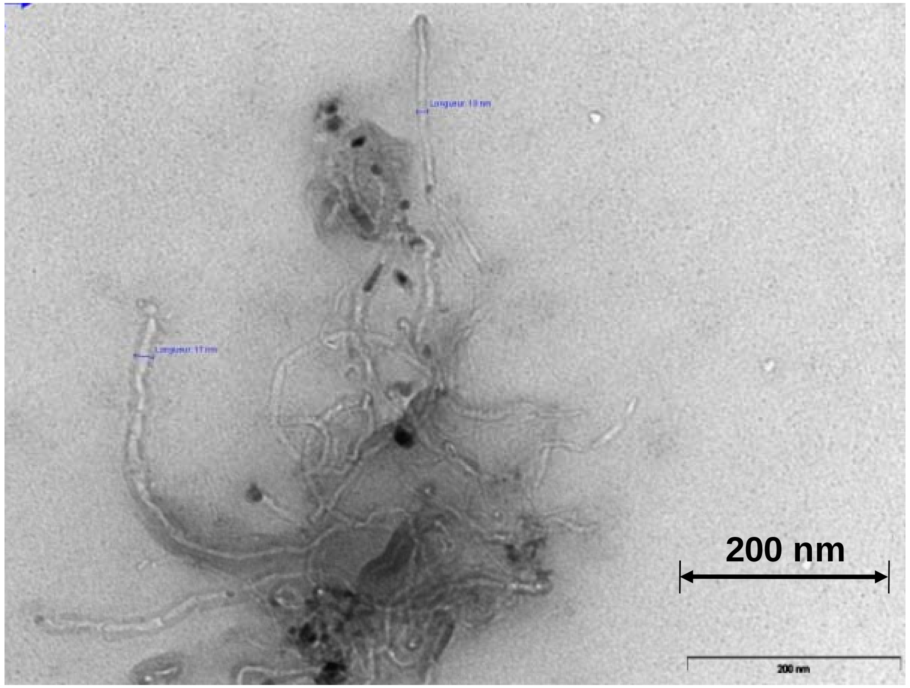
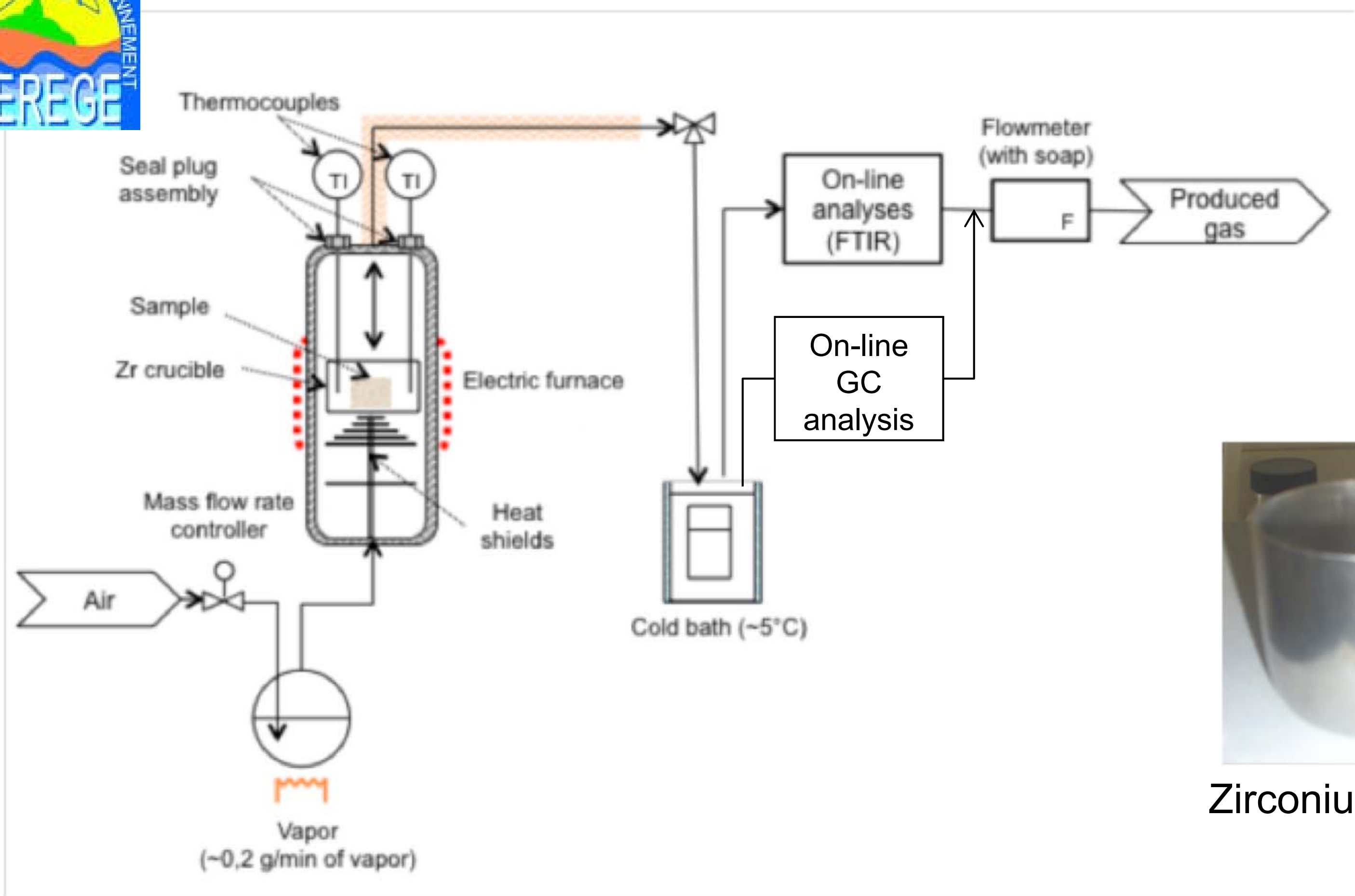
Results
Fumes analysis (TEM sampling)

- The fume analysis also reveals some agglomerated CNT whose catalysts are still attached
- No piece of polymeric matrix is found in the fumes, it may have burned and transformed into carbonaceous materials (soot)



Case study : polymers reinforced with SiO2

Materials and method



Sample (m_0)

Zirconium crucible

Furnace temp: 950°C, temperature ramp: 120°C, 190°C, 950°C

Duration: about 2.5 hours (based on CO_2 emission)

Case study : polymers reinforced with SiO2

Preliminary results

NP_LO_SiO2+PP

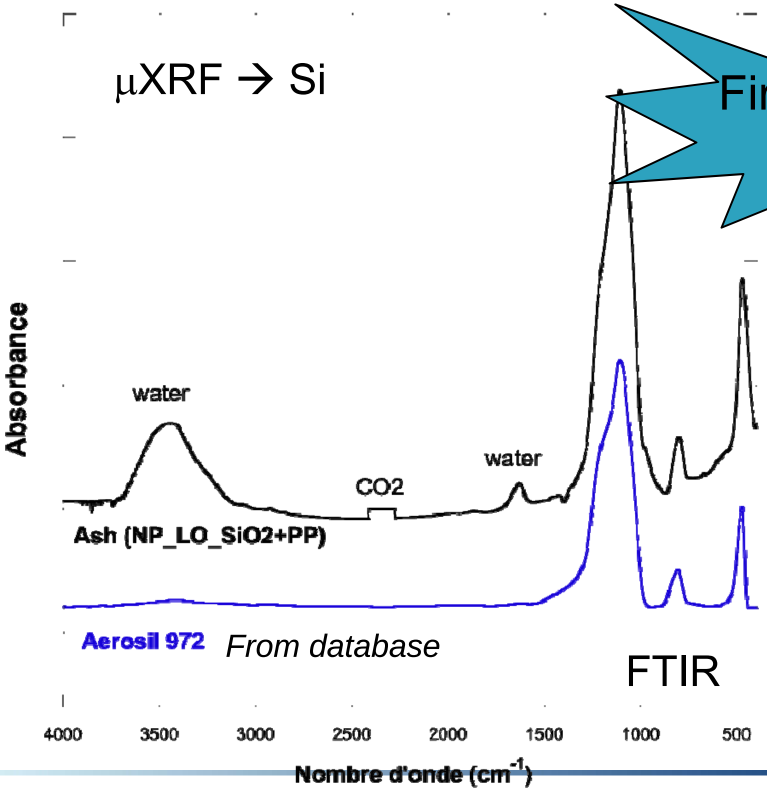
Solid residue characterization
(XRD, FTIR, µXRF)

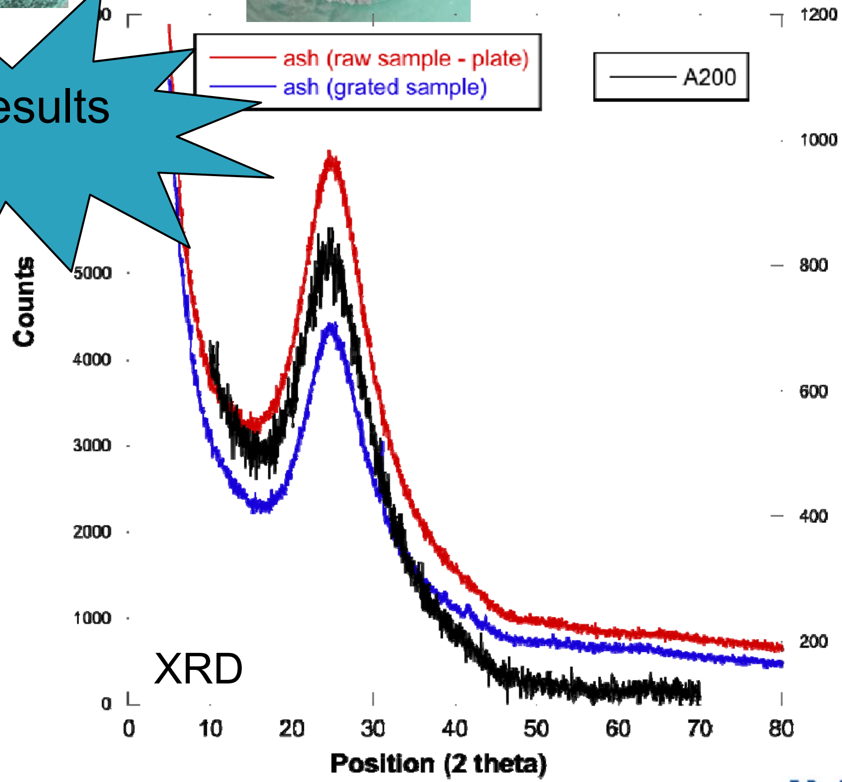
Raw sample

Grated sample

µXRF → Si

First results





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Case study : polymers reinforced with SiO2

Preliminary result

NP_LO_SiO2+PP

Gaz & particles emission ?

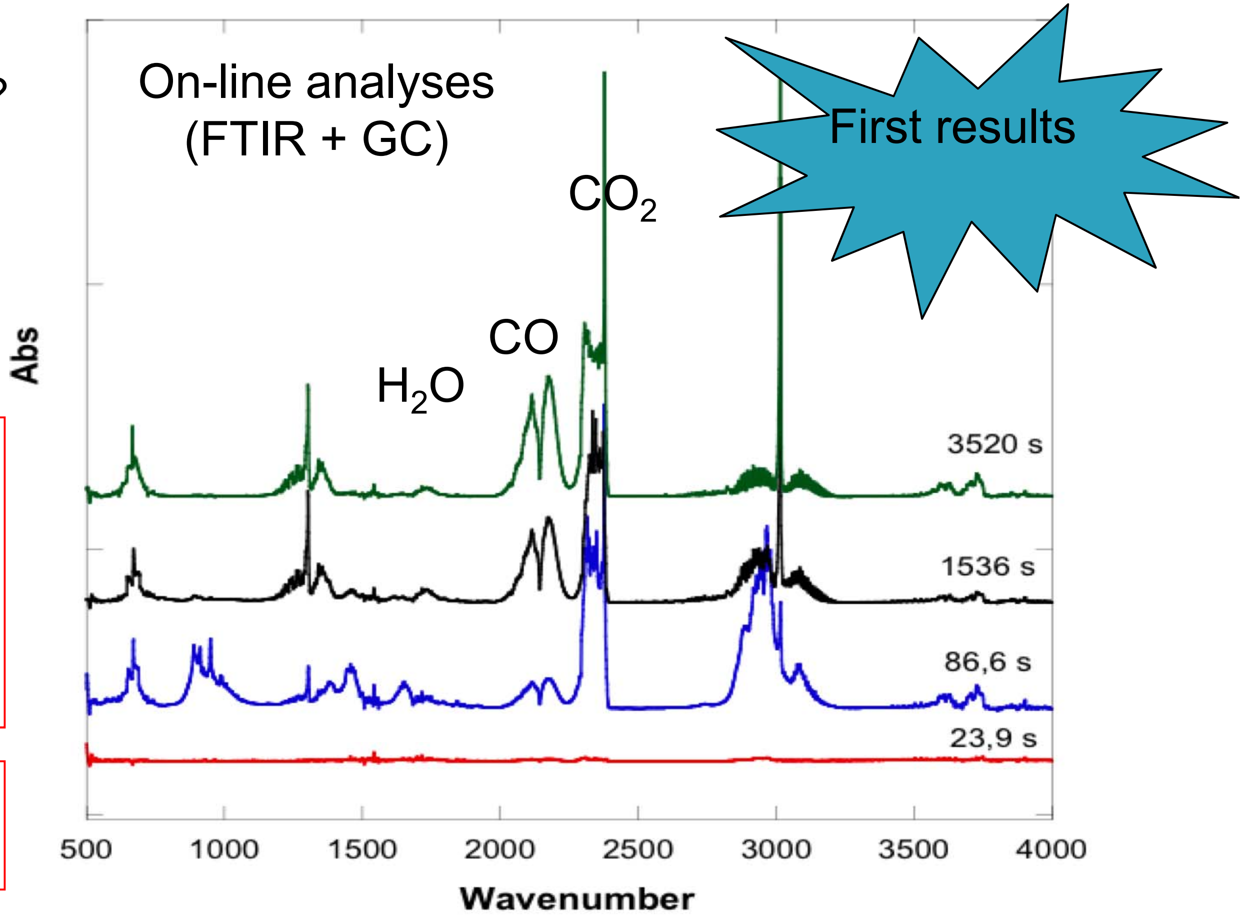
to be compared to

3. Emission from NP_LO+PP

Data treatment in progress

"Si" mass seems to remain constant in the combustion solid residues, ash : no emission in fume

Production of combustible gas ?



Discussion

A first evidence ?

- 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.*

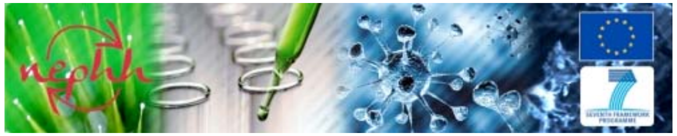
Must be continued → understanding of the release mechanisms

(eg. does nanomaterial affect nanoproduct combustion Temp and thus gaz/particulate emissions associated)

Economic viability of a nanoproduct relies also on its recycling capbilities

NANOFlueGas

Acknowledgements



These studies were or are performed within :

- *The European Project "FP6-SAPHIR"*
- *The European Project "FP7-NEPHH"*
- *The French ADEME Project "NanoFlueGas"*

Thank you !

Environmental Exposure to Nanomaterials – The Example of Silver

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Munich, 10th May 2012

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UNIVERSITY OF APPLIED SCIENCES

UMTEC
Institute for Environmental and Process Engineering

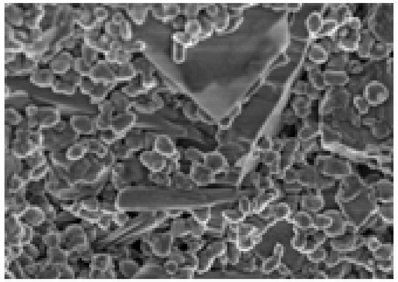
Institute of Environmental and Process Engineering (UMTEC)

- HSR University: 1500 students / staff
- UMTEC: 15 engineers, technicians, and 4 professors
- Mission: Source control measures and end-of-pipe technology

Waste
Processing and Recycling

Odor
Measurements and Modelling

Wastewater
Emission control and Treatment



Nanomaterials
Application and Environmental Exposure

Structure

1. Transfer Pathways

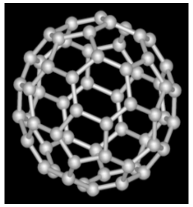
2. Analytical Methods

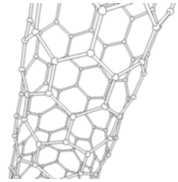
3. Case Study “Silver”

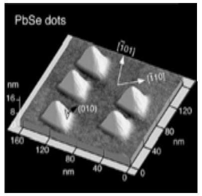
4. Conclusions

Anthropogenic vs. Natural Nanomaterials

Engineered (ENM)
Carbon-based NTs, Fullerenes
Metal Oxides
Quantum Dots
Nanotubes
Nanowires
Dendrimers



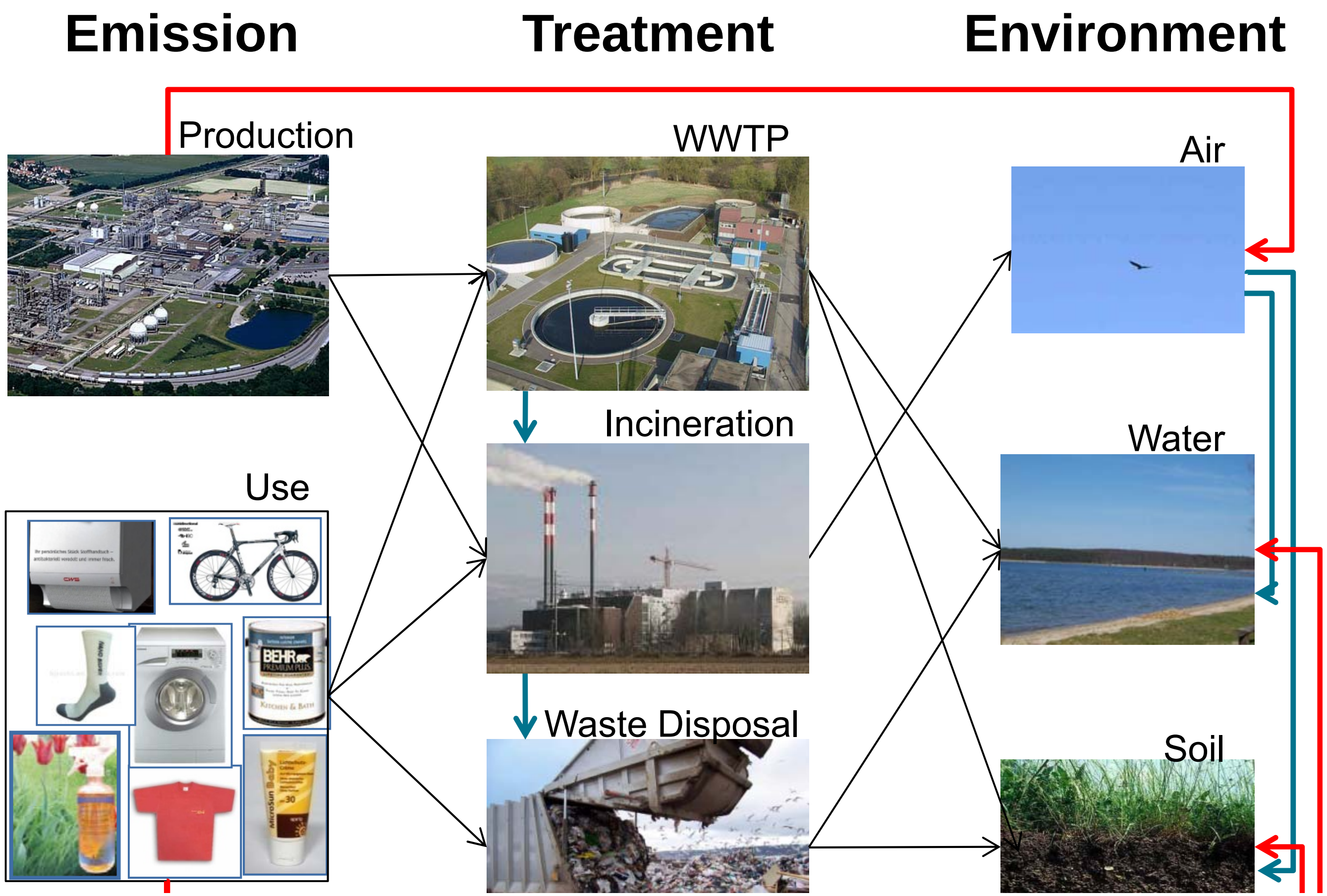




Incidential	Natural
Combustion	Plants, Trees
Industrial Processes	Oceans, other water bodies
Vehicles	Erosion
Construction	Dust

➡ **Which ENM should we focus?**

Environmental Exposure Pathways

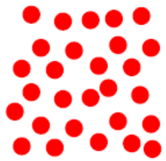
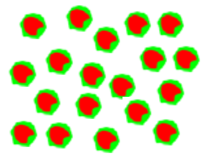
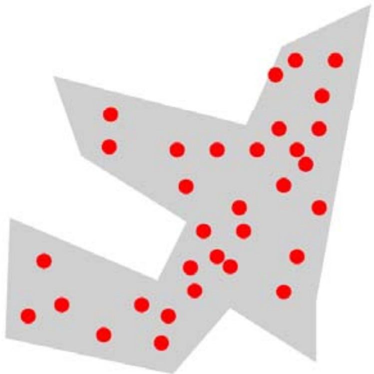
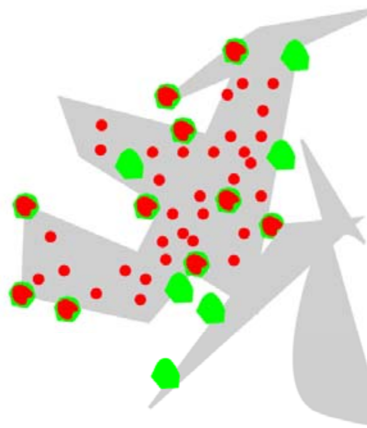


Which pathways are most relevant (due to free nanoparticles present and exposure risk)?

Structure

1. Transfer Pathways
2. **Analytical Methods**
3. Case Study "Silver"
4. Conclusions

Conditions of Laboratory vs Environment (Sludge, Waste)

	Non-Reactive (“inert”)	Reactive (“aging”)
Laboratory (nm-scale, individuals)		
Environment (µm-scale, aggregates)		

Which methods are appropriate for environmental issues?

Methods for Characterization of ENM

Method	Size (nm) 1 10 100 1000	PSD capability	Shape[A] capability	Agglomeration state capability[B]	Concentr. range	Surface Chemistry / Charge / Area	Structure / Crystallinity	Single part./ population	Dynamics capability[C]	Level of perturbation
AFM					ppb – ppm			sp		medium
BET					powder	SSA		pp		high
Centrifugation					det. dep.			pp		low
Dialysis					det. dep.			pp		low
DLS					ppm			pp		minimum
Electrophor.					ppm			pp		minimum
EELS/EDX					ppm in sp			sp		high
ESEM					ppb – ppm			sp		medium
Filtration					det dep			pp		low-medium
Flow FFF Sed FFF					UV: ppm, ICPMS: ppb			pp		low
HDC					det. dep.			pp		low
ICP-MS					ppt – ppb			pp		N/A
LIBD					ppt			sp		minimum
NTA					ppb-ppm			sp		minimum
SEC					det dep			pp		medium
SEM					ppb – ppm			sp		high
SLS					ppm			pp		minimum
SAED								sp		high
Spectrometry					ppb – ppm			pp		minimum
TEM					ppb – ppm		(HR)	sp		high
Turbidimetry					ppb – ppm			pp		minimum
Ultrafiltration					det. dep.			pp		medium
XPS					powder			pp		
XRD					powder			pp		high

M. Hassellov, R. Kägi, in *Nanoscience and Nanotechnology, 2008*

Methods for Environmental Samples

Conventional methods

- Chemical analysis (ICP-OES, -MS) – quantitative
- Electron microscopy (SEM, TEM) – qualitative / semi-quantitative

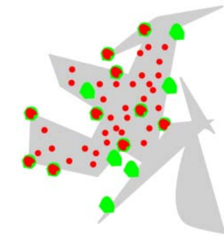
… including time consuming sample preparation

- Chemical extraction (nitric acid, aqua regia, hydrofluoric acid)
- Centrifugation (stepwise separation, enrichment)

Nice-to-Have

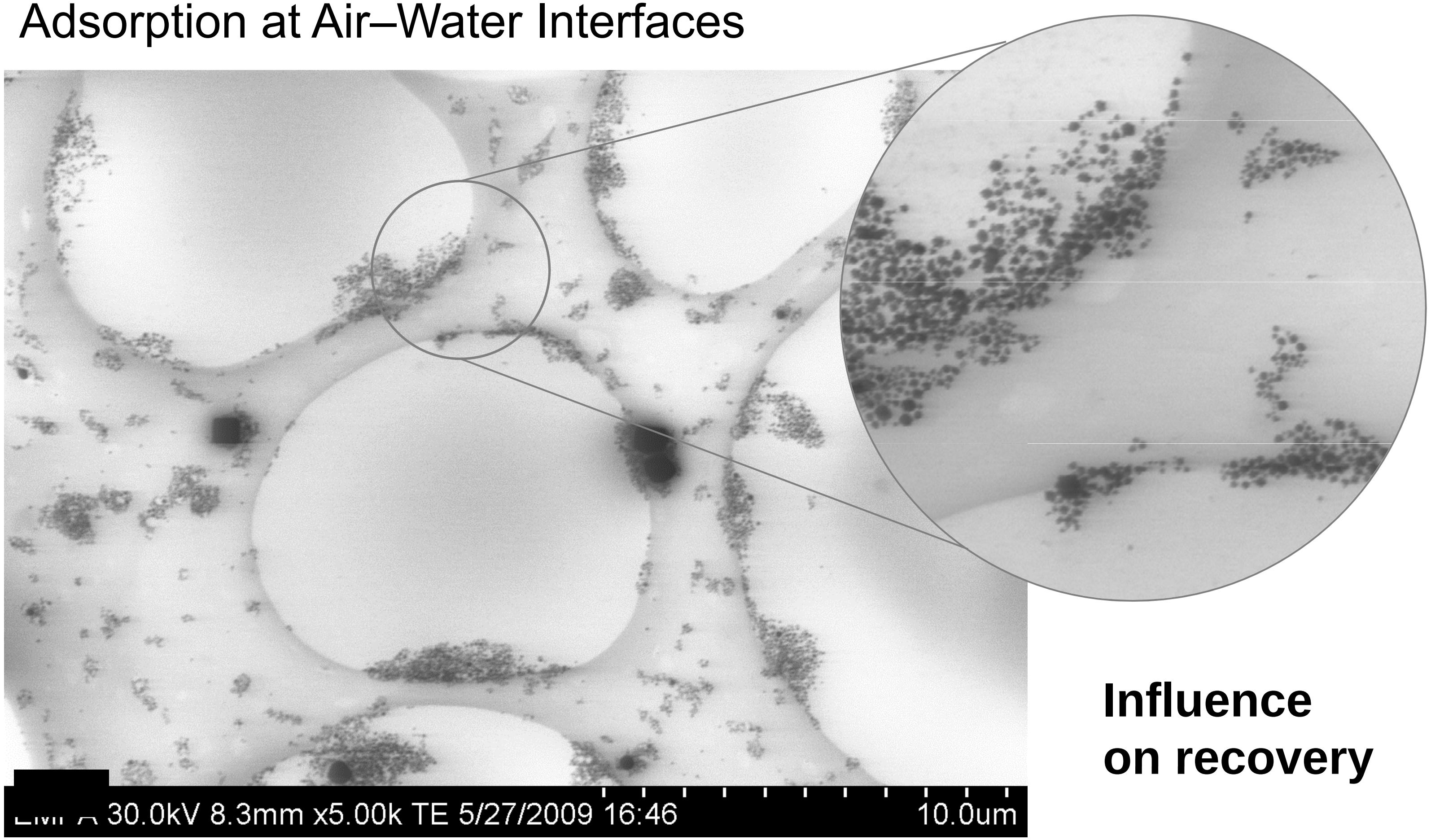
- Rapid non-invasive routine analysis of individual nanoparticles is lacking (e.g. non-invasive single particle XRF for metals …)

→ **Even combination of conventional methods hard to manage (regulation without control?)**



Attention: Artefacts in Sample Preparation

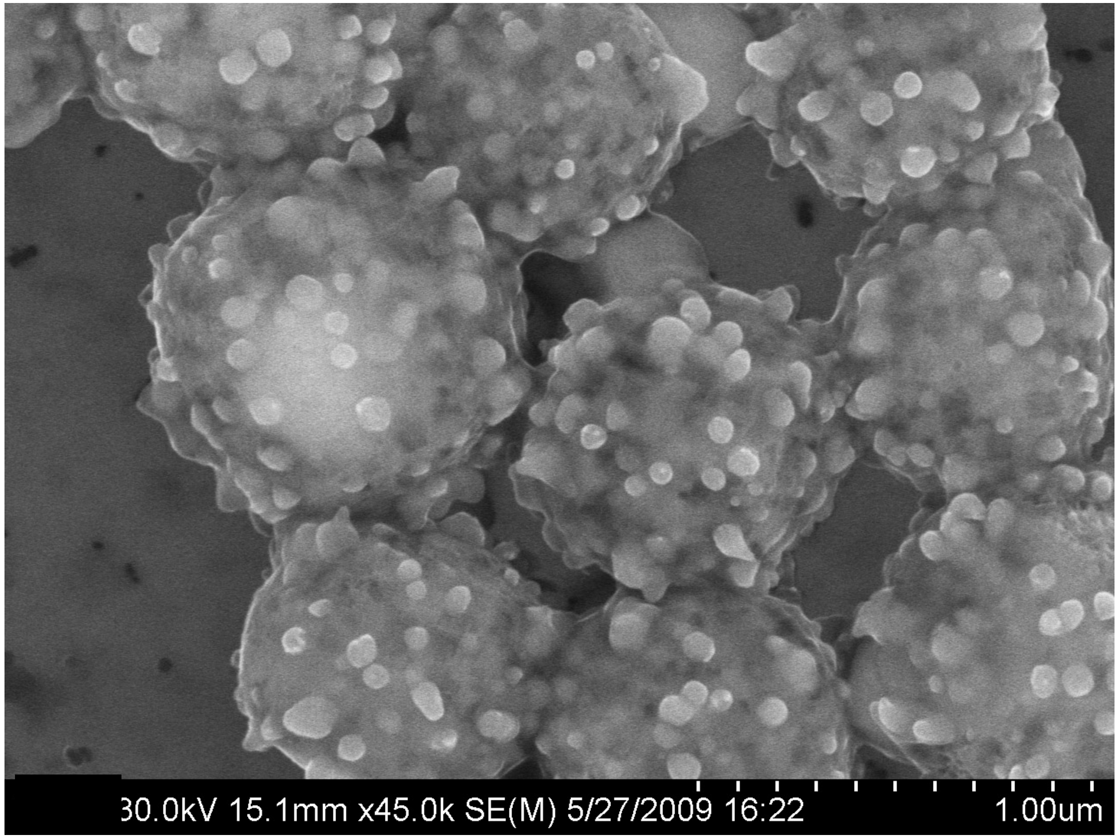
Adsorption at Air–Water Interfaces



Influence on recovery

… Generation of Secondary Nanoparticles

Reduction of AgCl to nano-Ag^0 by Electron Beam



Artefacts by sample analysis

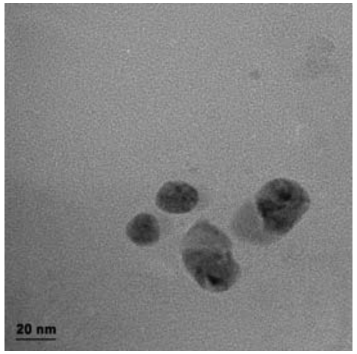
Structure

1. Transfer Pathways
2. Analytical Methods
3. **Case Study "Silver"**
4. Conclusions

(Nano)Silver Emissions from Textiles Industry (Case Study)

Analysis of mass flow and transfer pathways

- Emission from production processes
  - Assessment of waste flow from supply chain
  - Discharge to wastewater from washing process (laundry)
- Treatment in WWTP
  - Fate in wastewater of WWTP

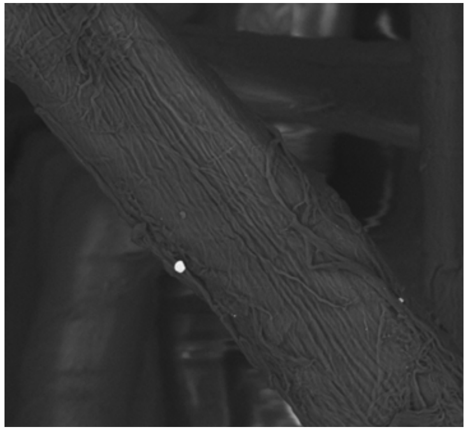


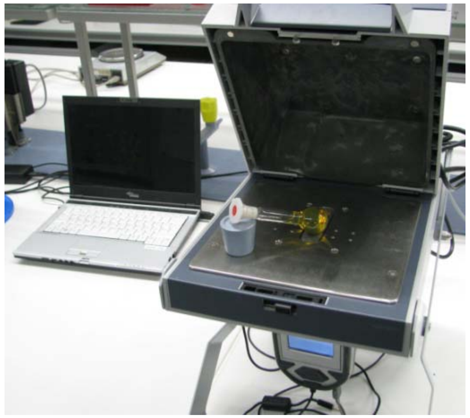
➡ **Focus on experimental investigation of silver**

1. Assessment of Waste Flow in Supply Chain

Goal

- Silver mass flow analysis of entire supply chain (production of silver, yarn, fabrics, etc.)
- Evaluation of silver detection methods and technologies to extract nanosilver



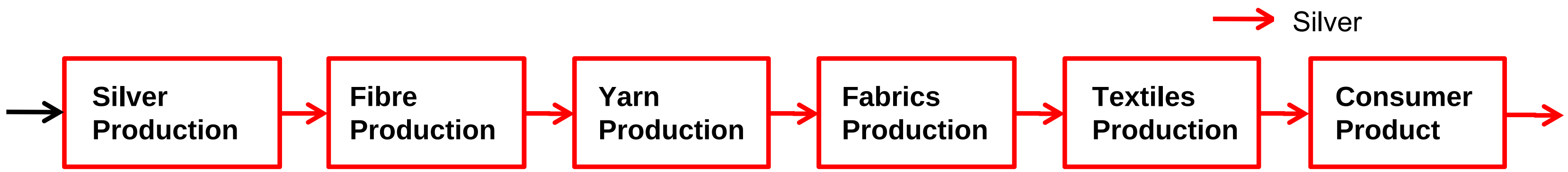


Industrial collaborators

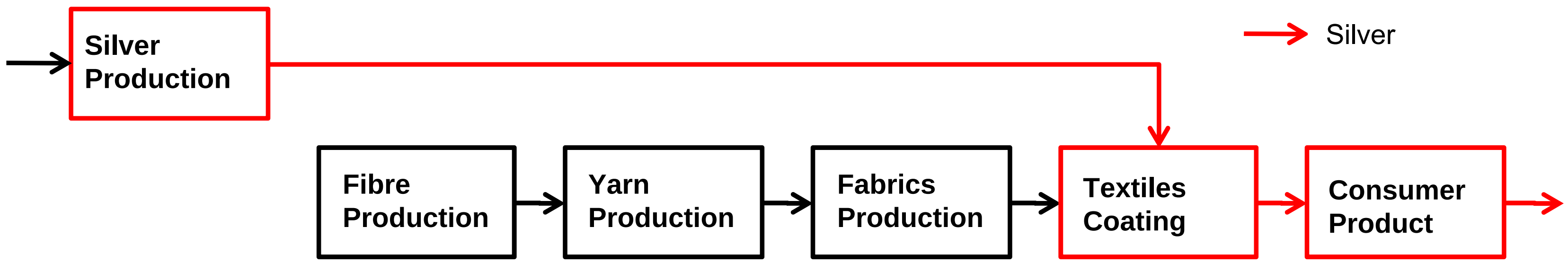
- CHT Bezema, HeiQ, RAS, Noyfil, Nanosys etc.
- ENCROS, Terraconsult

Flow Analysis of Production Processes (Examples)

1. Fibre integration process using masterbatch



2. Addition of silver in washing process



Silver containing waste reviewed for supply chain

Management of Silver containing Waste

Silver production (waste from procution)

- High silver concentration (1.0-2.5%), small amounts (<0.5 t/a)
- Liquid (suspension) or solid (masterbatch)
- <1% silver in waste (to WWTP, incineration plant, or recycling <5 kg/a per site)

Fibre integration process (waste from processing)

- Low silver concentration <150 ppm (0.0125%)
- Solid (masterbatch)
- 4% silver in waste (negligible flow to WWTP, 4% to incineration plant)

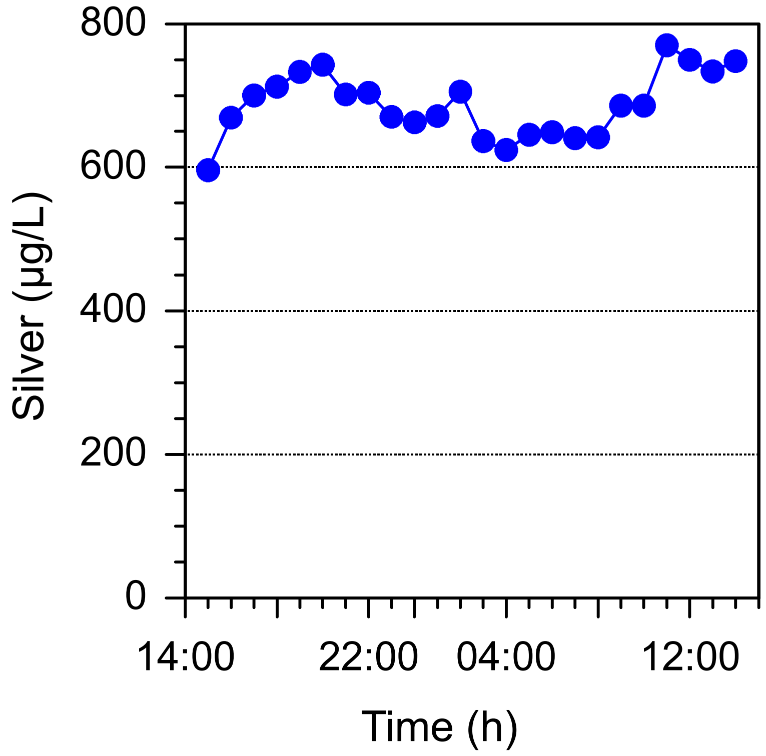
Washing process (waste from processing)

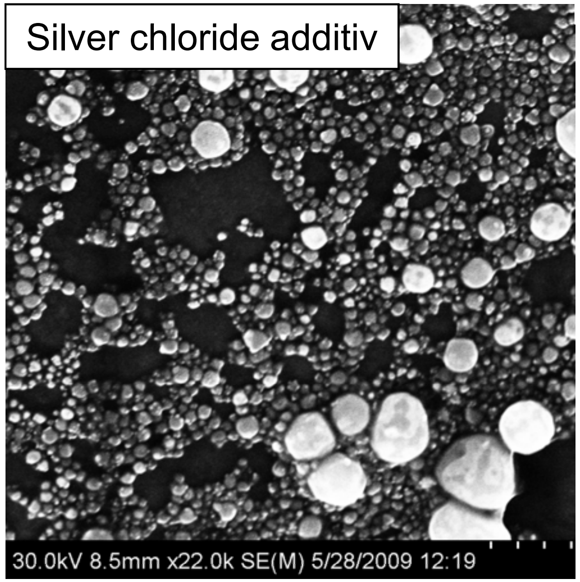
- Low silver concentration <10 ppm
- Liquid (wastewater) and solid (sludge)
- 70% of silver in waste (60% to WWTP, 10% to incineration plant)

→ **If required, how to control these end-of-life mass flow?**

* Burkhardt et al. (2011): Entsorgung nanosilberhaltiger Abfälle in der Textilindustrie - Massenflüsse und Behandlungsverfahren. BAFU, Bern.

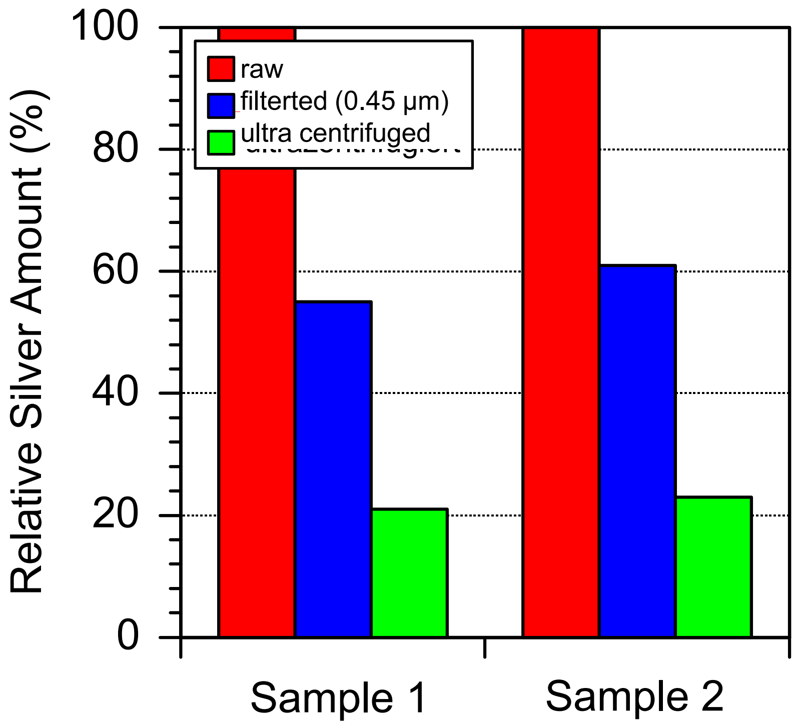
Silver flow to WWTP from industrial laundry

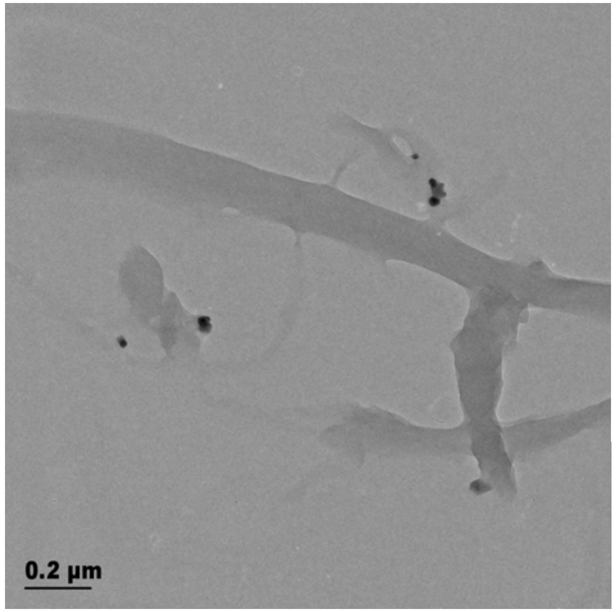




→ Silver emissions to WWTP significant (but stopped)

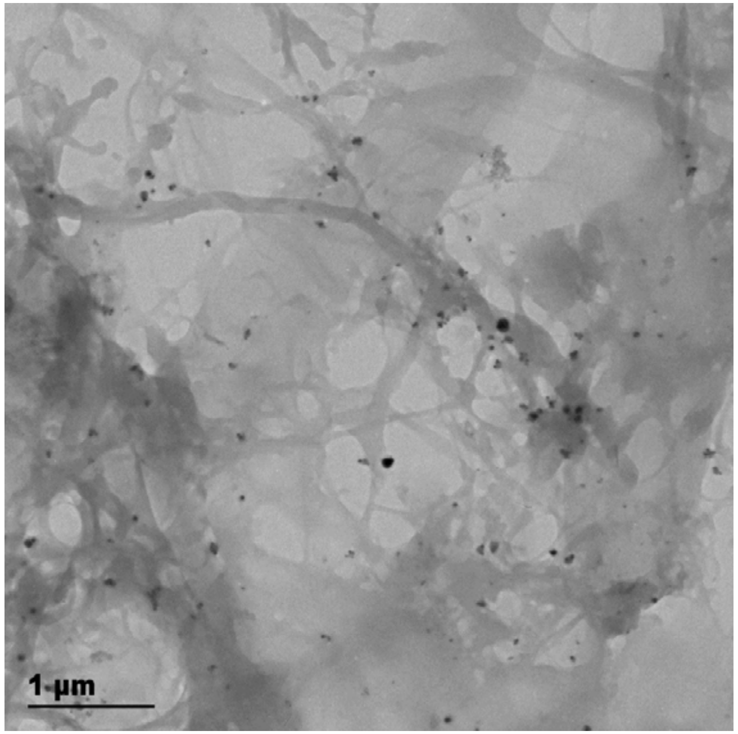
Occurrence in Wastewater

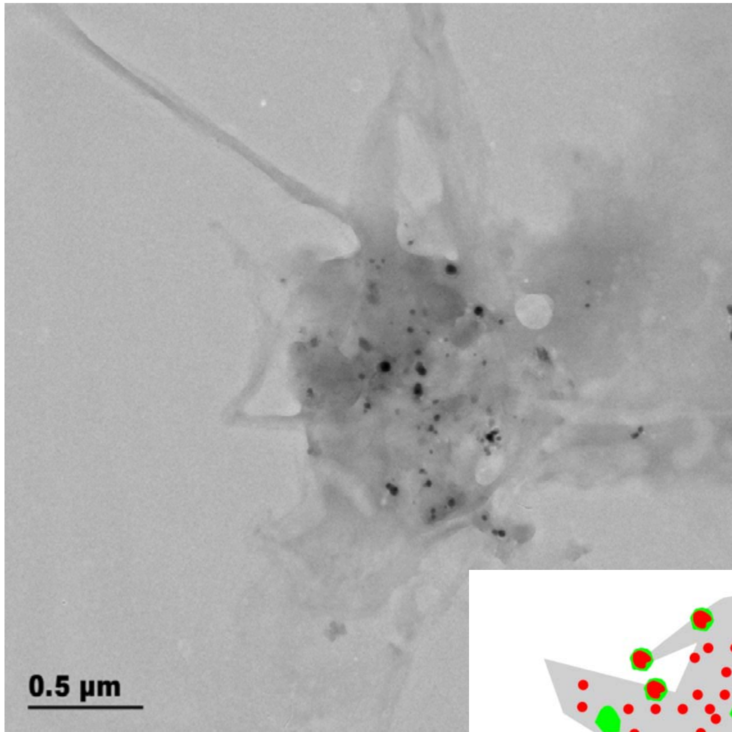


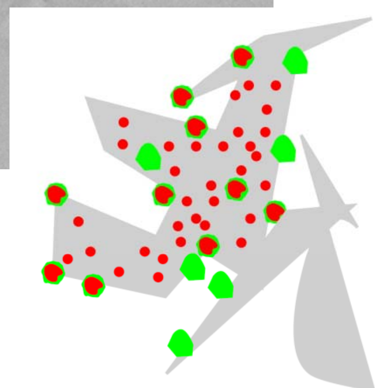


Sample preparation and TEM give insight to particles fate

Particulate Silver adsorbed to Cotton Fibres



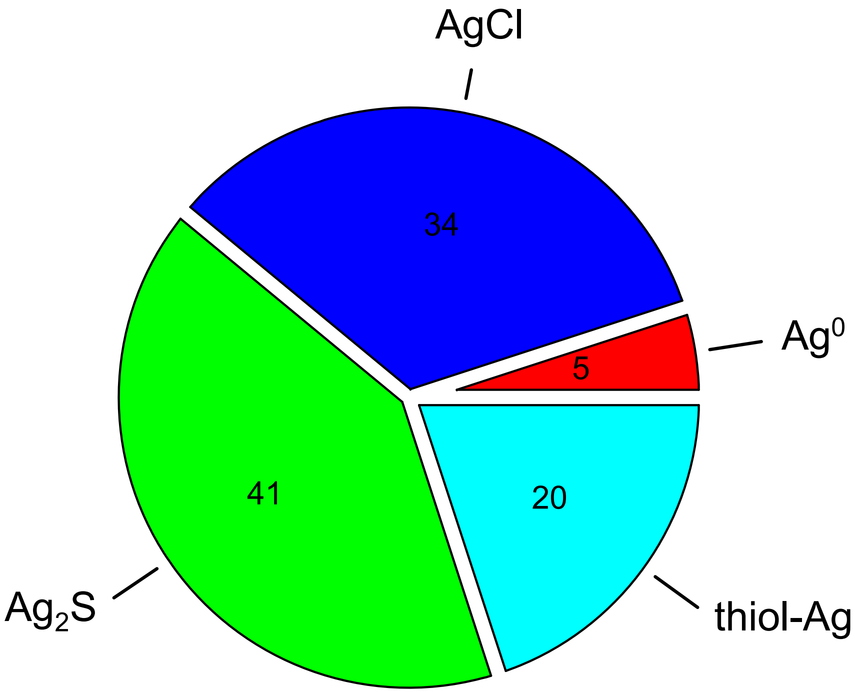




Silver in sludge – incineration plant

Silver-Transformation determined by Sophisticated Method

EXAFS: Extended X-ray Absorption Fine Structure (Swiss Light Source, SLS)

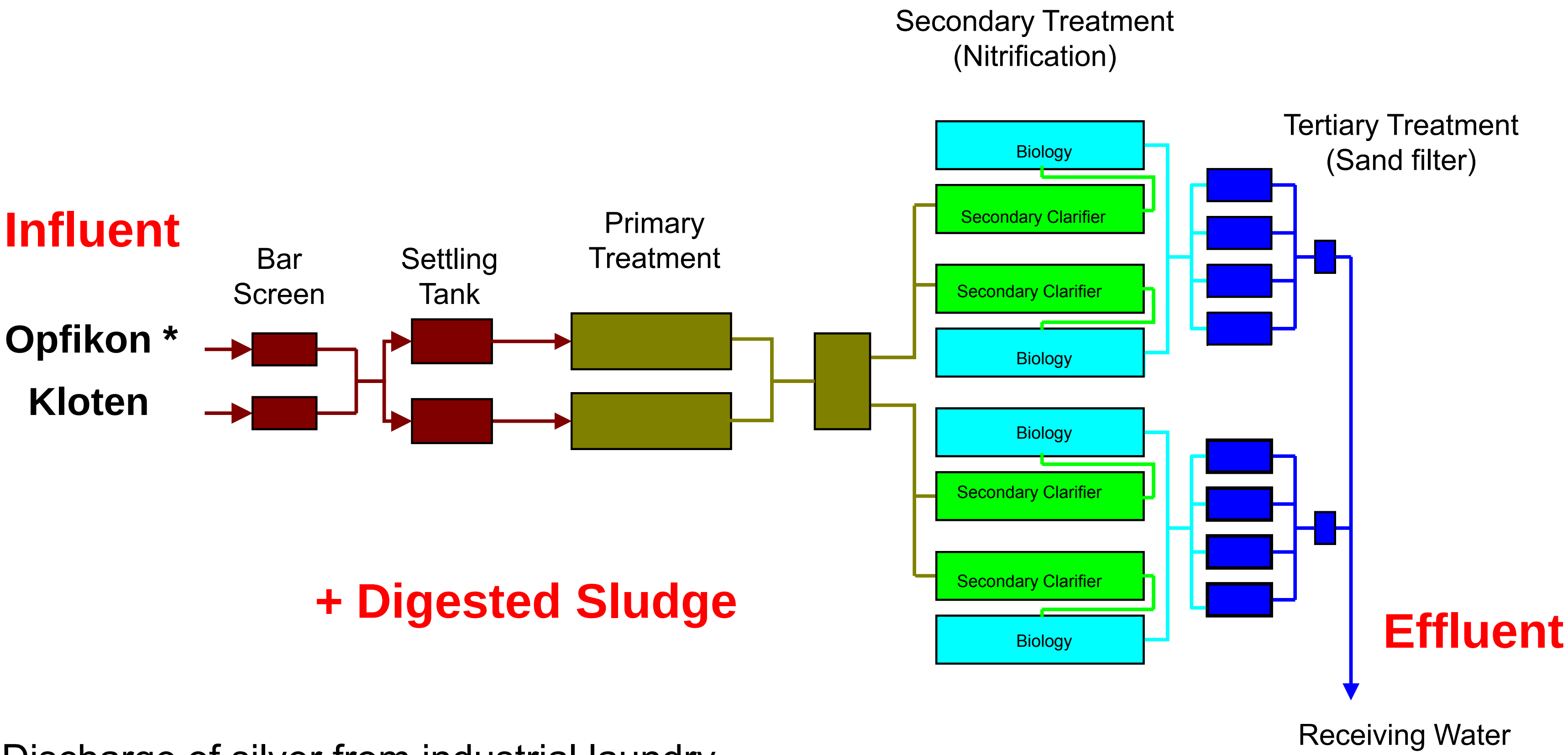


Limited number of labs able to measure with EXAFS (application required for concise risk management)

3. Fate in Wastewater of WWTP

Kloten/Opfikon for 60'000 inhabitant equivalent

Appropriate Sampling Scheme in WWTP



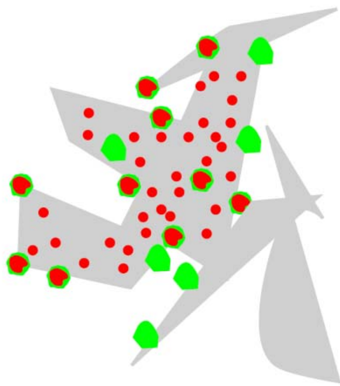
* Discharge of silver from industrial laundry.
Application stopped completely 2010.

Elimination of Silver in WWTP

Daily composite samples of dry weather flow

Sample	**In** (µg Ag /L)		**Out** (µg Ag /L)		**Elimination**
	Opfikon*	Kloten**	Effluent	Sludge	(%)
1	14.0	1.9	0.54	870	94
2	18.4	1.6	0.19	860	98
3	12.3	5.3	0.08	740	99
4	12.3	2.5	0.07	580	99

Similar elimination of CeO and TiO_2 in OECD-plant

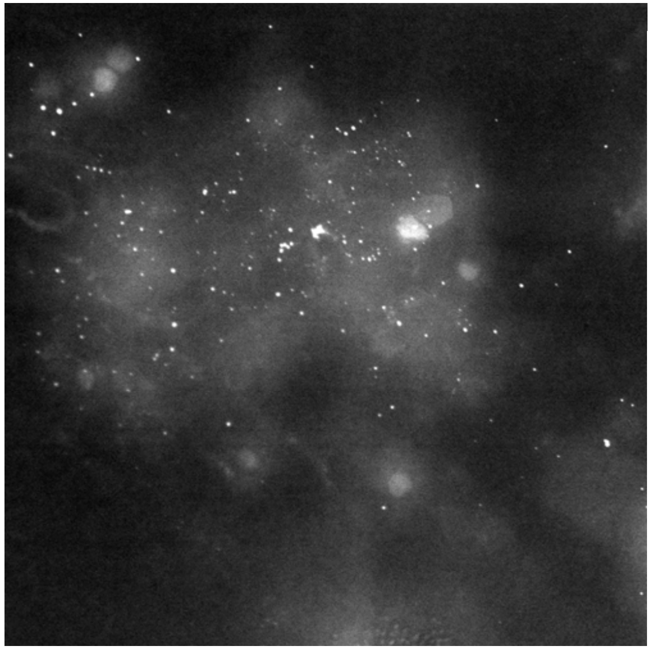


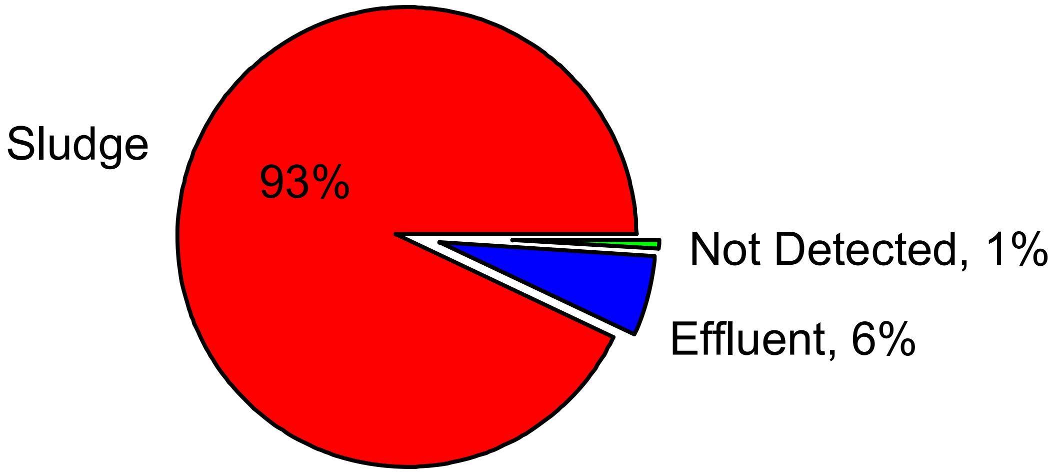
➡ **Aquatic exposure negligible, sludge is "sink"**

* Limbach et al. 2008; Kuhlbusch et al. 2011

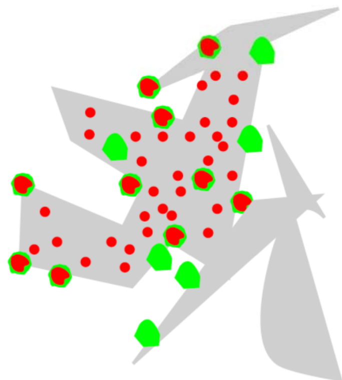
Pilot Plant WWTP Study with Silver

Addition of metallic nanosilver (OECD NM-K 300) and silver chloride





Transformation
to silver sulfide



→ **Confirmation of results from full scale WWTP**

Structure

1. Transfer Pathways
2. Analytical Methods
3. Case Study “Silver”
4. **Conclusions**

Conclusions specifically for Nanosilver / Particulate Silver

- Problems of terminology – typical for nanoparticles discussions (size matters – but who cares about size …?)
- Nanosilver is handled as liquid in production process
- Silver amounts release to the environment are small (e.g. from facades, laundry)
- Loss of functionality (rapid transformation to insoluble Ag_2S)
- Not present as single nanoparticles (95-99% elimination by attachment to micrometer biosolids and sludge)
- Sludge is the Nano-"sink" (Incineration in Switzerland or Application in agriculture)

→ **Is (nano)silver the ENM of concern?**

What did we learn from these studies in general?

- Laboratory tests give limited insight to environmental exposure
  = Testing under “artificial” conditions (matrix, concentration) without matrix components is misleading
- Analytical methods for routine monitoring in waste and wastewater are lacking
  = Without chemical and morphological characterization results do not represent “state of the art” in ENM-research
- Main waste stream of ENM enter recycling and/or incineration plants and waste disposals (“end-of-life”)
- Limited resources (personnel, finances) for exposure / risk research need to be spend on a concise evaluation procedure

→ **Any move forward regarding ENM in waste need to address analytical control mechanisms (toolbox)**

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Thank you for Attention !

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