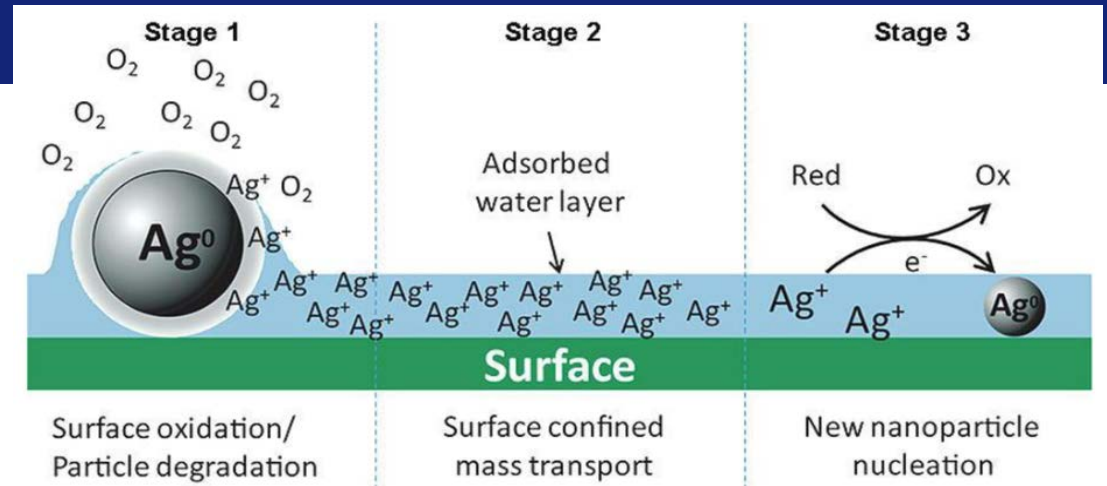
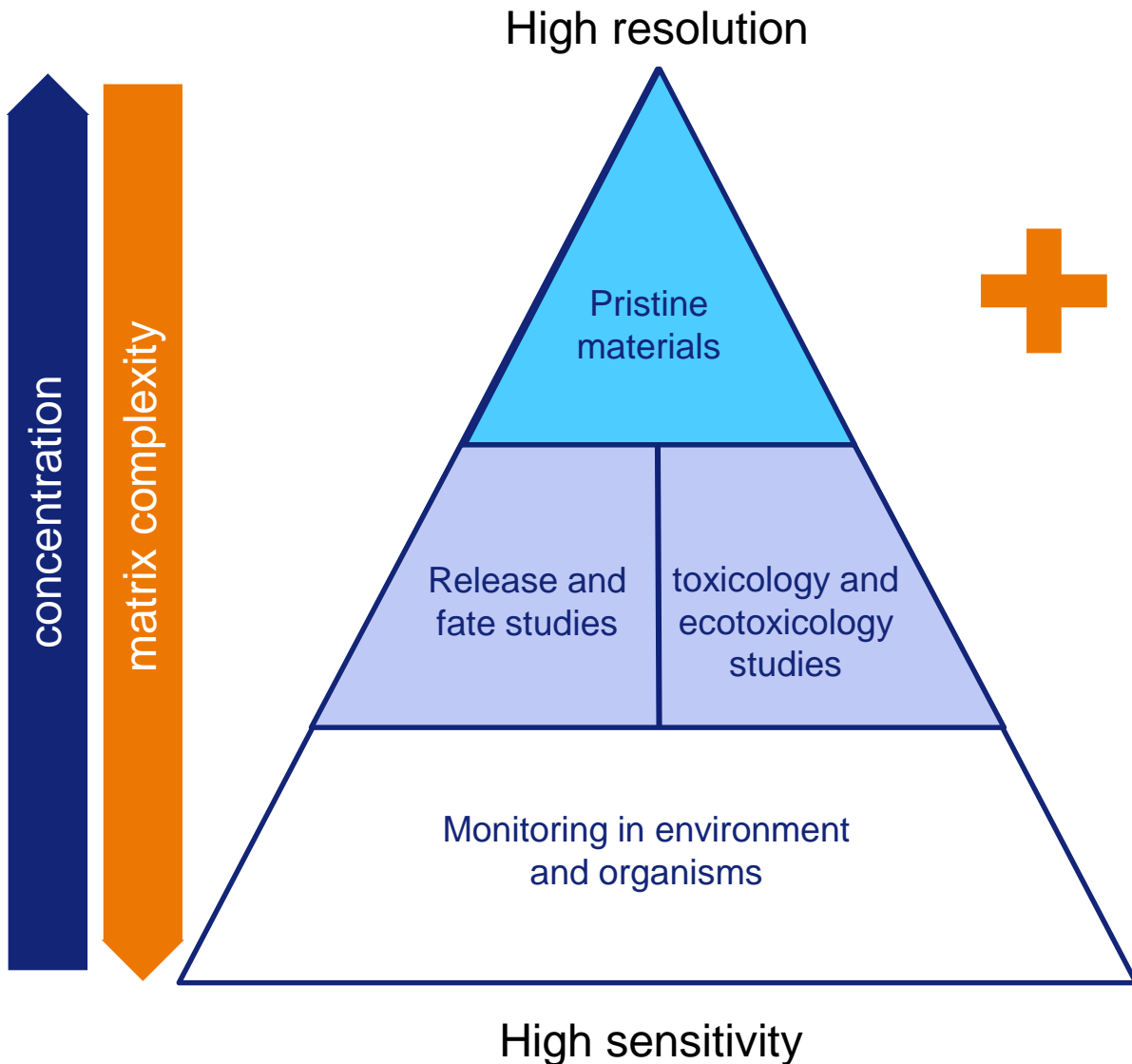


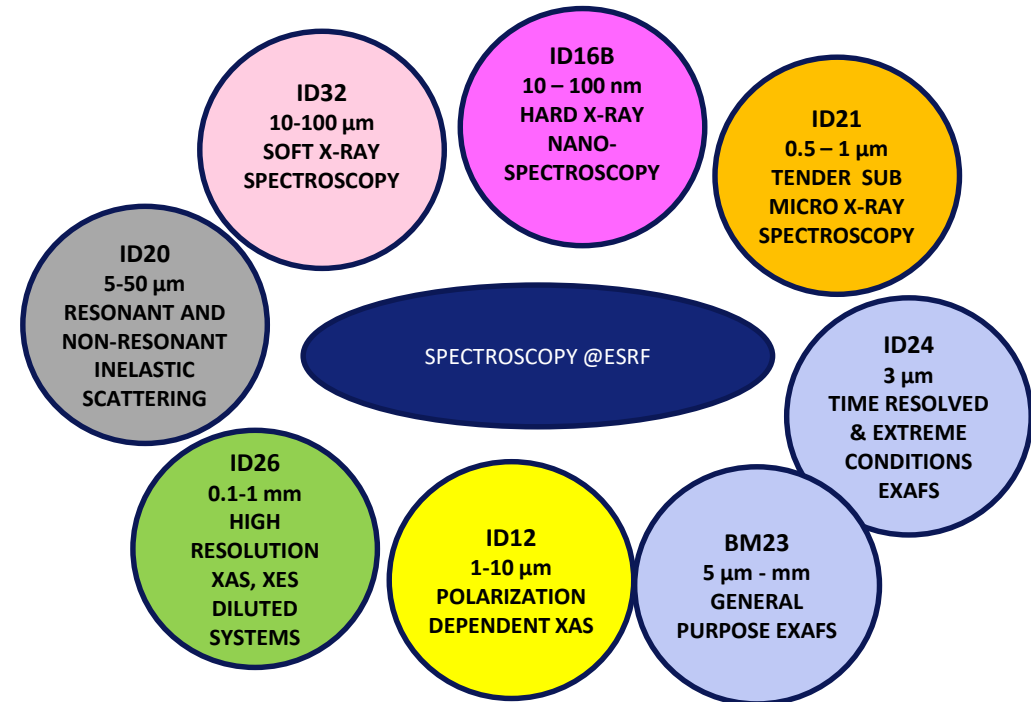


X-ray microspectroscopy for life and environmental nanotoxicology

Hiram Castillo-Michel
ID21 beamline scientist
castillo@esrf.fr

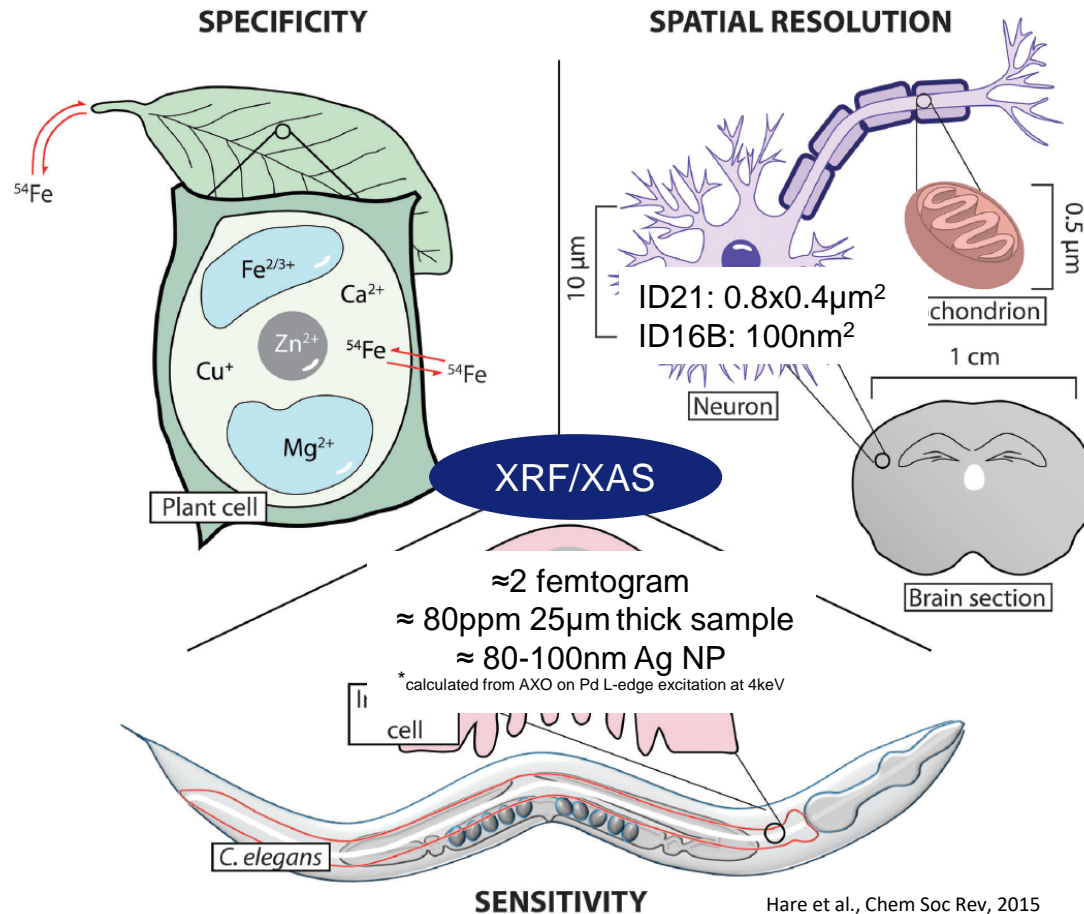


High specificity



“Inorganic engineered nanomaterials are considered a new sort of analytes”

- Imaging of metals and ENMs in biology is a balance of sensitivity, selectivity and spatial resolution.
- Disruption of the native chemical environment, through both sample preparation and during analysis, should be minimised.



Hare et al., Chem Soc Rev, 2015

ID21 Scanning X-ray microscope

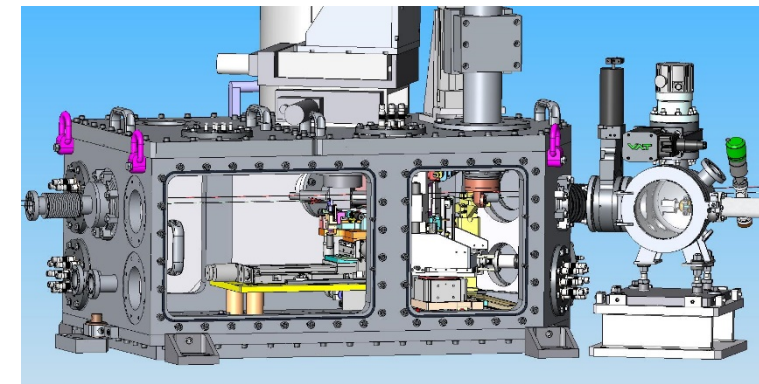
2-9keV

Under vacuum

$0.2(\text{V}) \times 0.7(\text{H}) \mu\text{m}^2$

Micro X-ray fluorescence

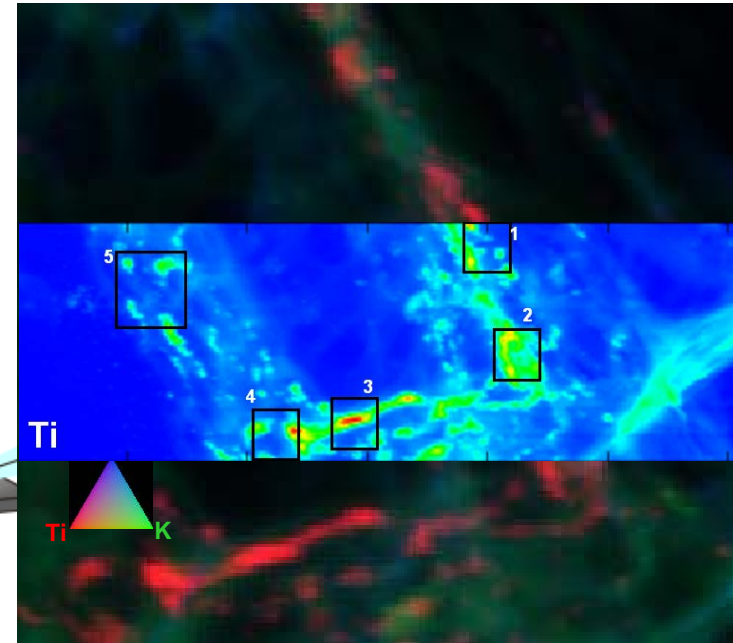
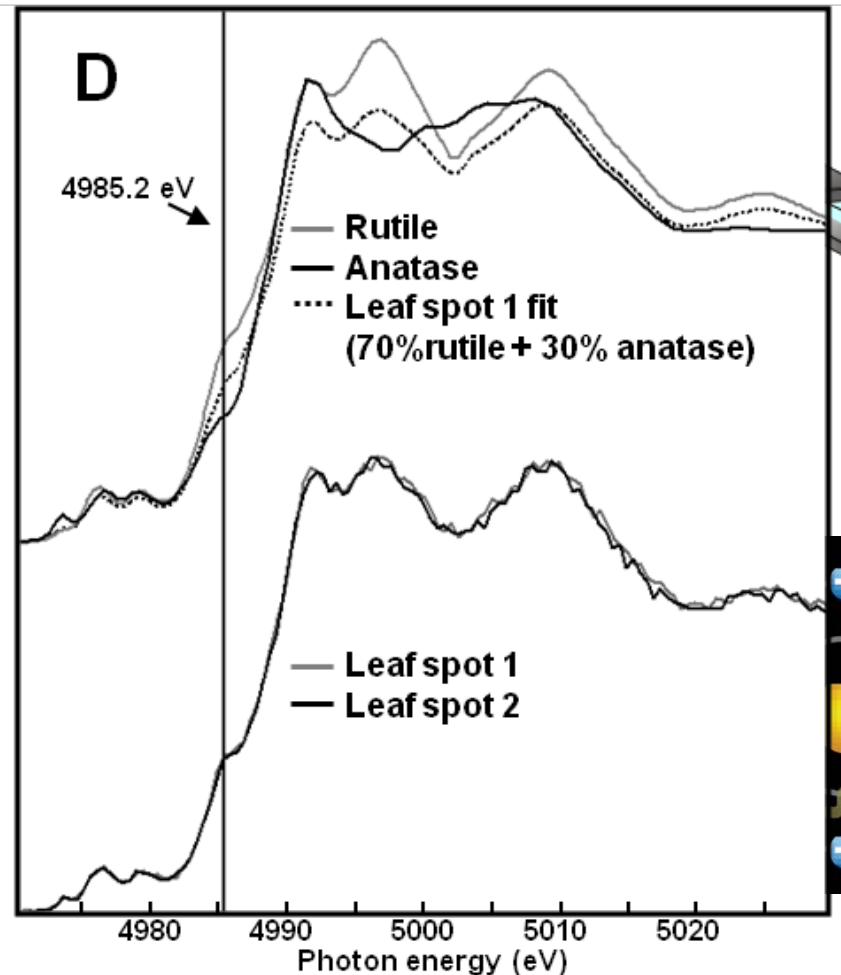
Micro X-ray Absorption Spectroscopy



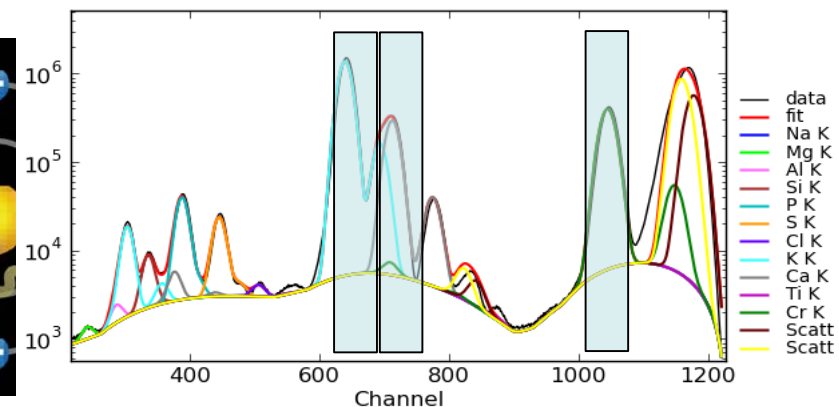
Scanning X-ray microscope

-Multielemental detection by X-ray Fluorescence

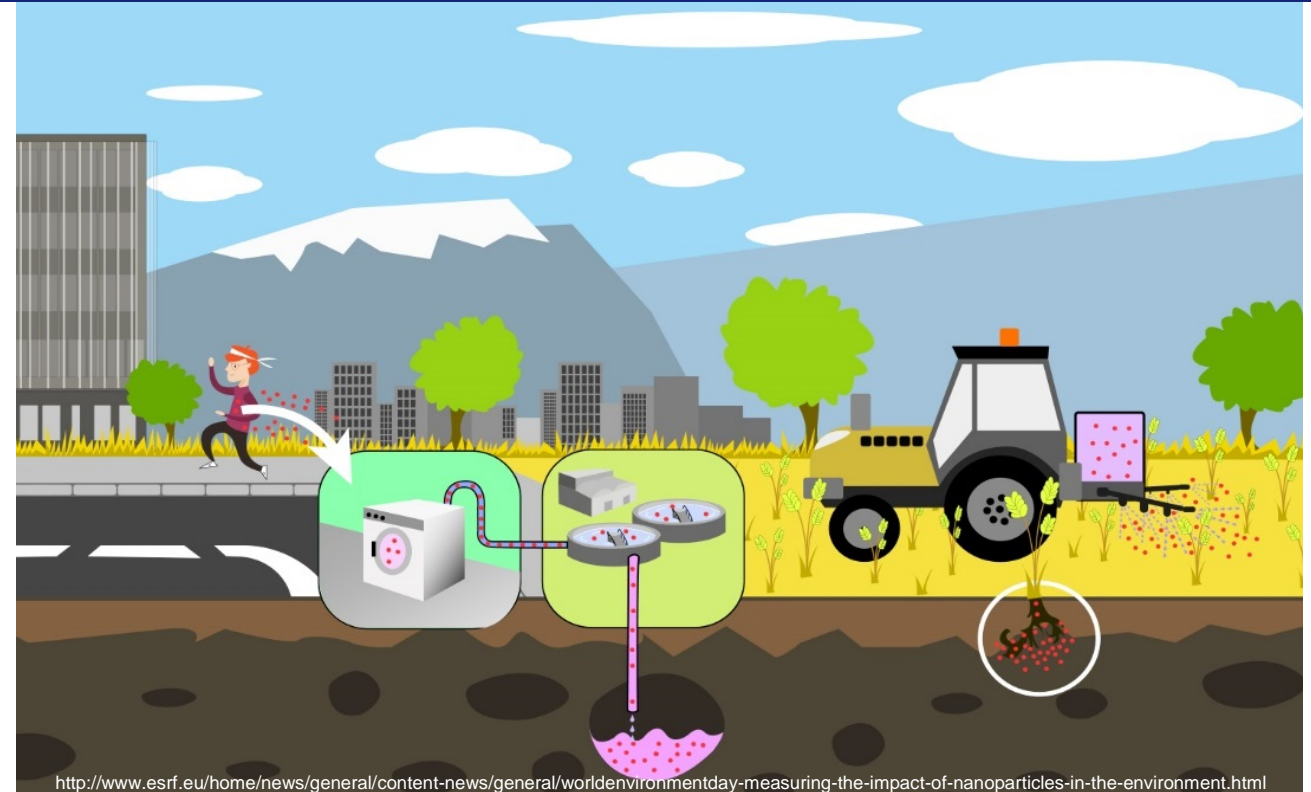
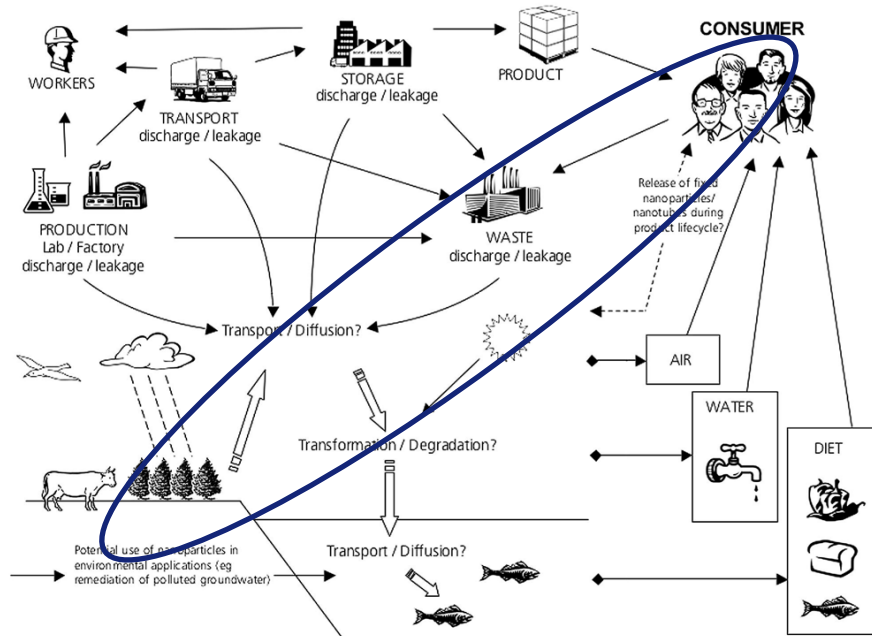
-Access to chemical state information using X-ray Absorption spectroscopy



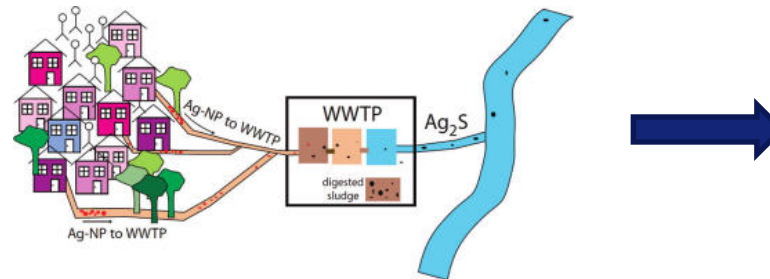
μXRF



Ag NPs: Environmental Fate and Impacts



Ag NPs Release from consumer products



90% retained in the sludge most likely as Ag_2S



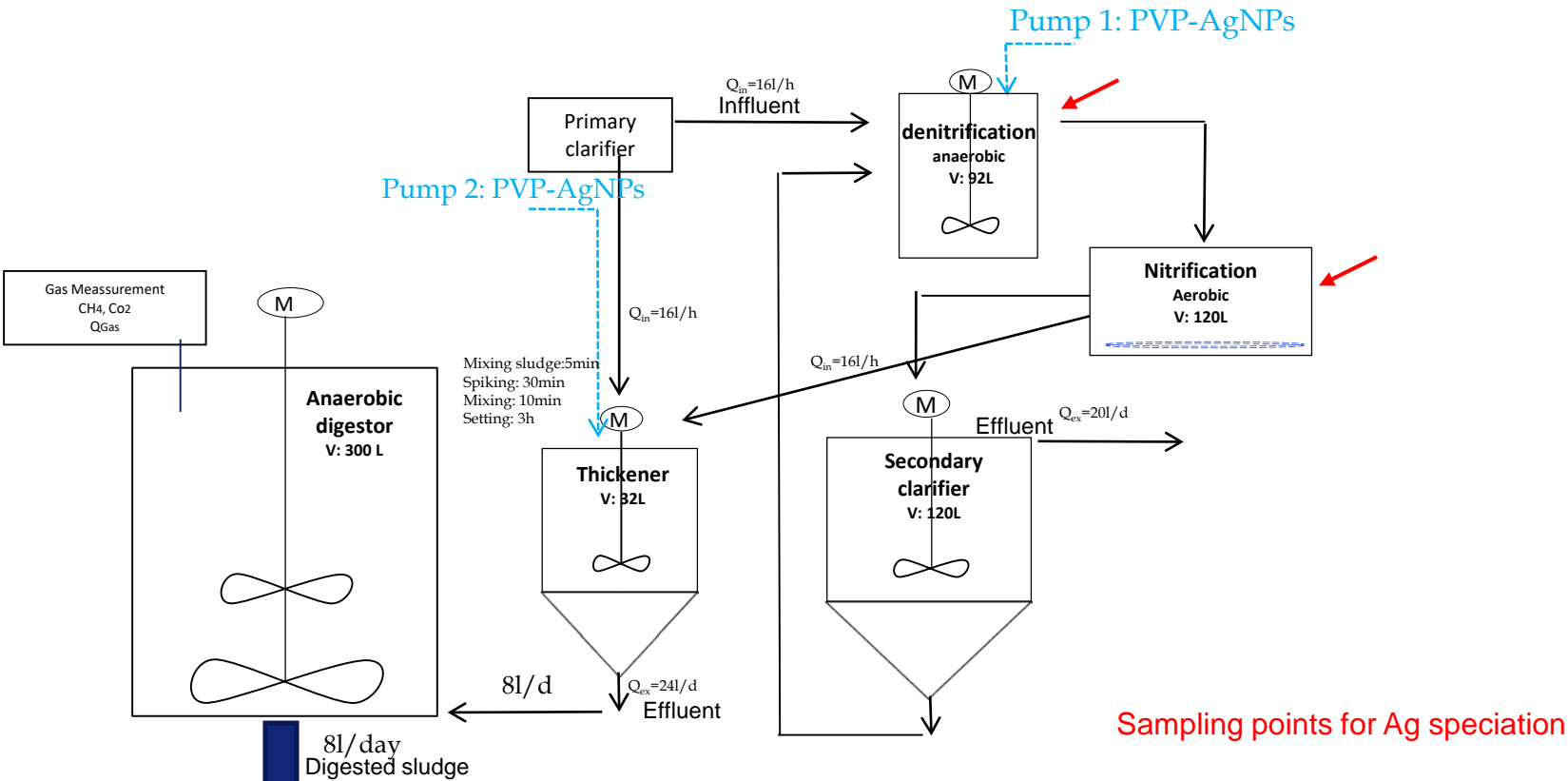
In Europe 55% of this sewage sludge is applied on agricultural soils as a fertilizer

Ag NPs: Speciation in waste water treatment plant sludges

PVP coated AgNPs were continuously injected during 4 weeks into a pilot WWTP at **EAWAG (Dübendorf, Switzerland)**



G. Sarret and A. Pradas del Real

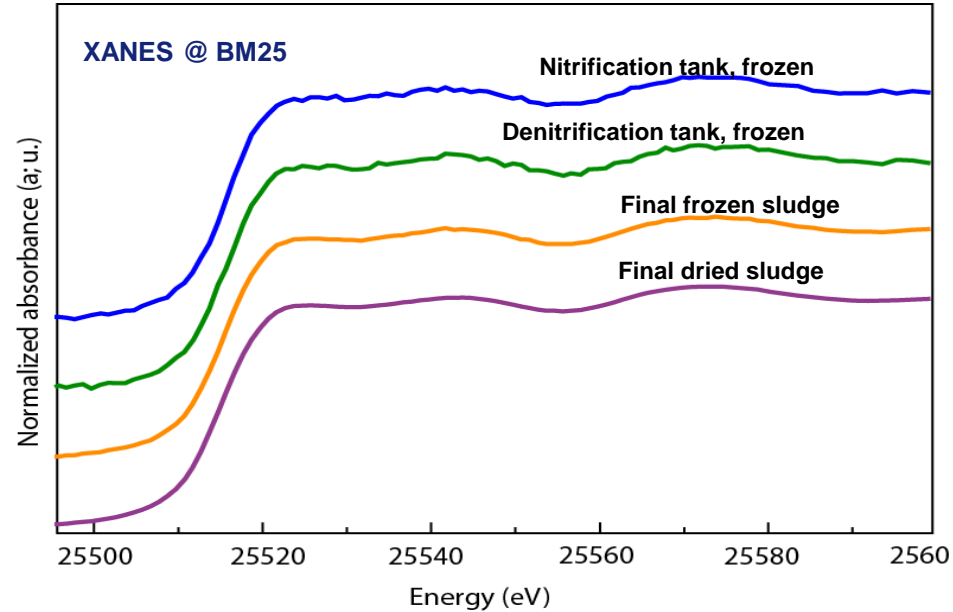
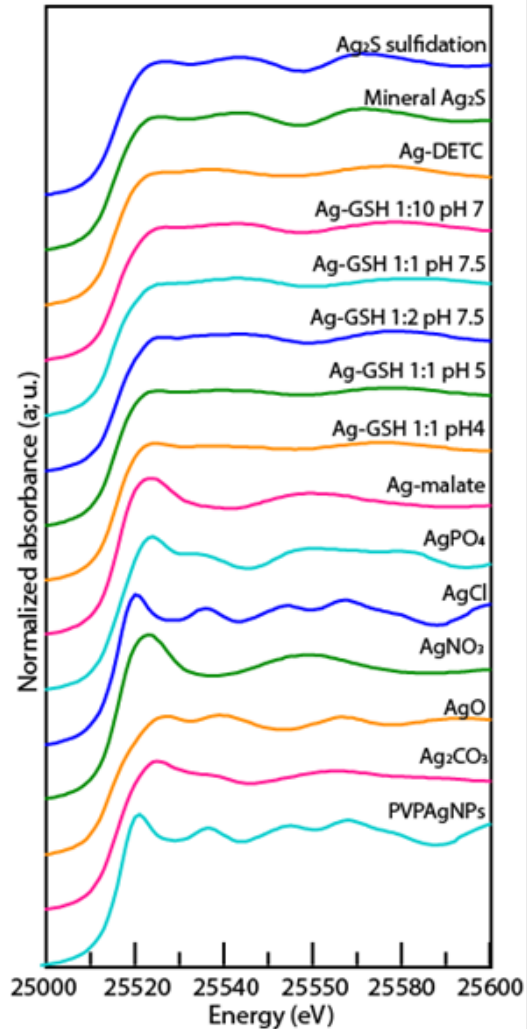


Sampling points for Ag speciation

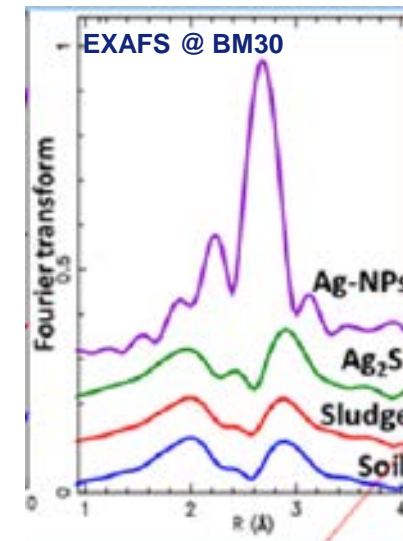


- Control: 14 mg Ag·Kg⁻¹
- Low dose: 18 mg Ag·Kg⁻¹
- High dose: 400 mg Ag·Kg⁻¹

Ag K-edge XAS analysis



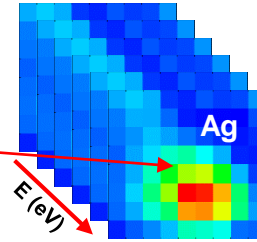
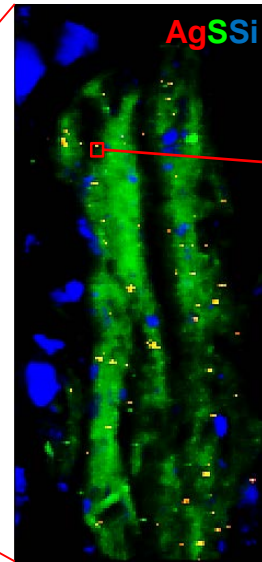
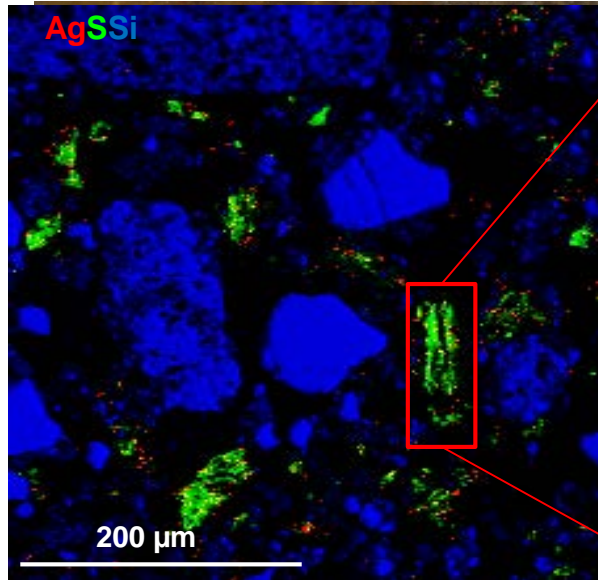
Ag metallic NPs transformed to Ag_2S (NPs?)



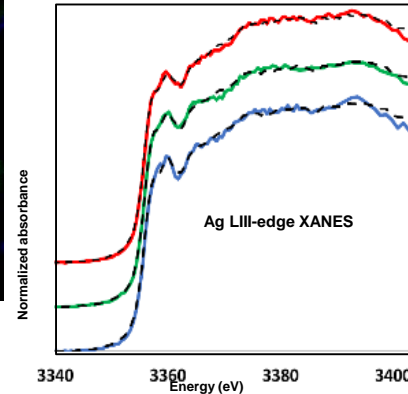
Ag NPs: Application of sludge in agricultural soils

- Sludge obtained from a pilot waste water treatment
- Sludge mix with soil and used to grow plants
- Mix prepared as polished thin section analyzed at **ID21** and **ID16b**

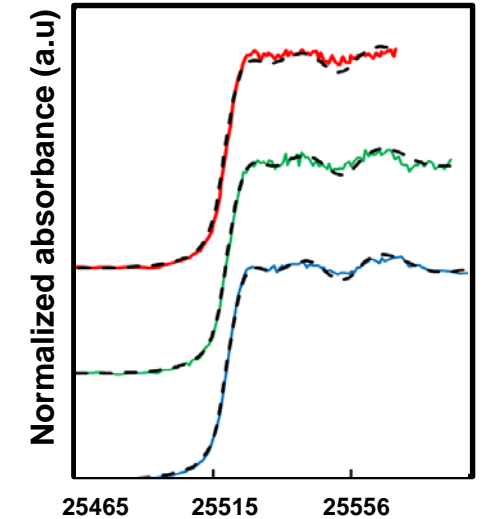
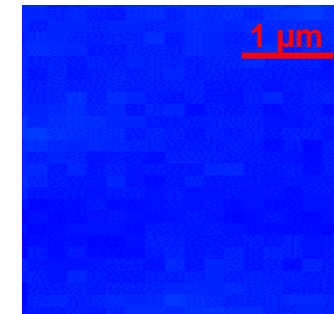
Ag₂S NPs seem stable in wheat cultivated soils



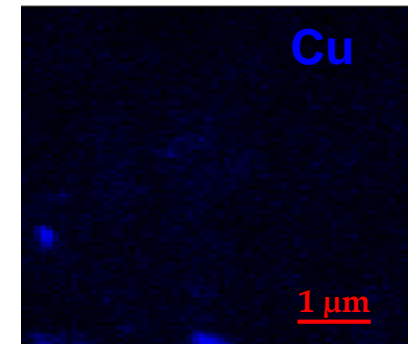
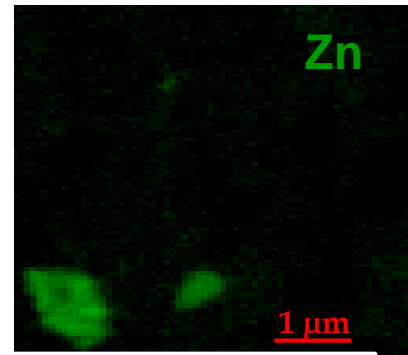
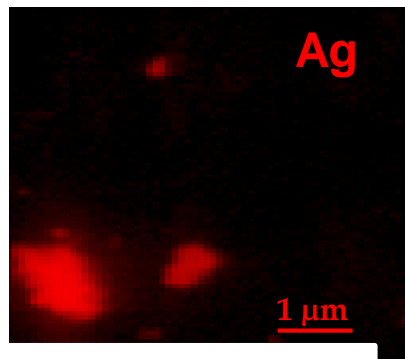
microXANES
ID21



nanoXANES
ID16b



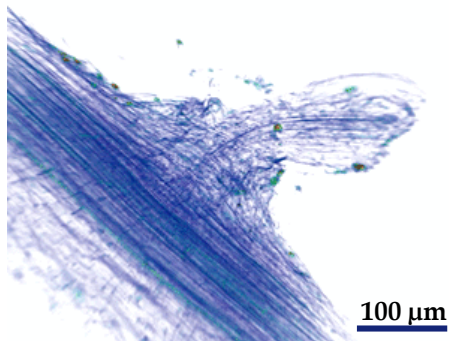
ID16b @ 29.6 keV



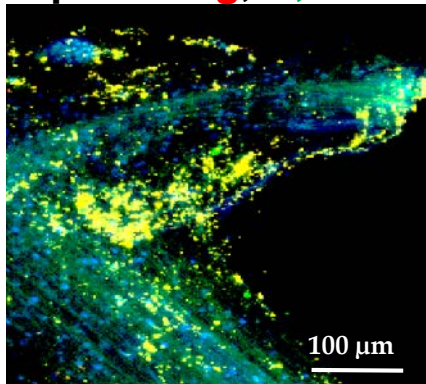
Pradas et al. 2016, ES&T

Wheat plants exposed to Ag_2S NPs

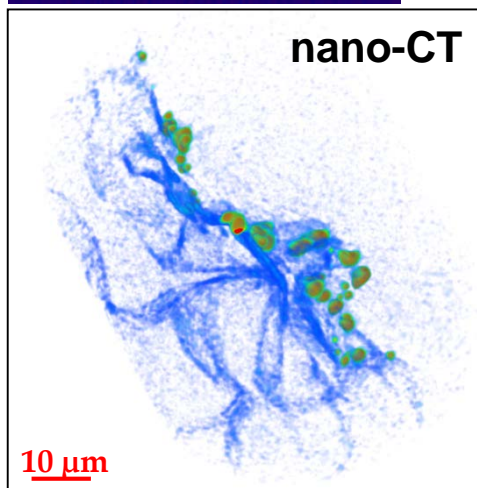
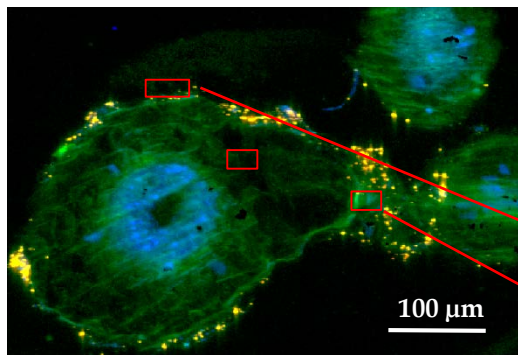
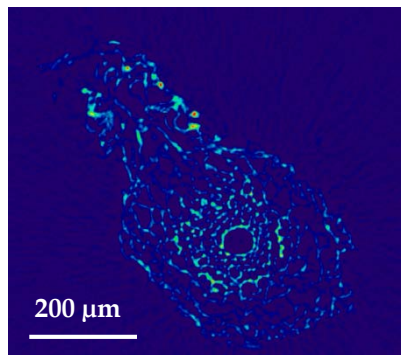
μ -CT



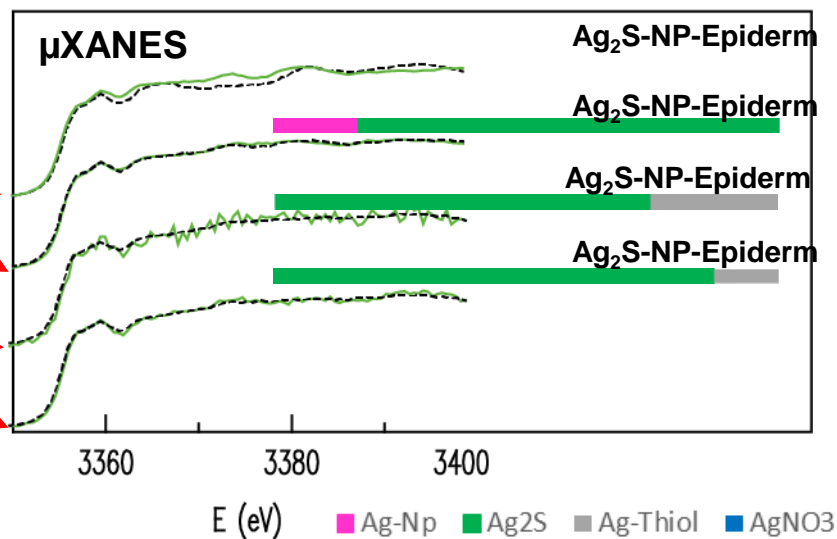
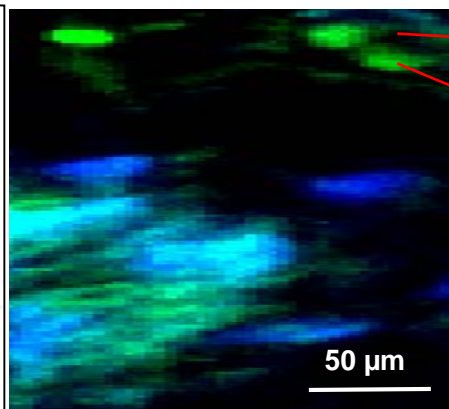
μ XRF: Ag, S, P



Evidence of Ag_2S dissolution
No evidence of direct NPs uptake

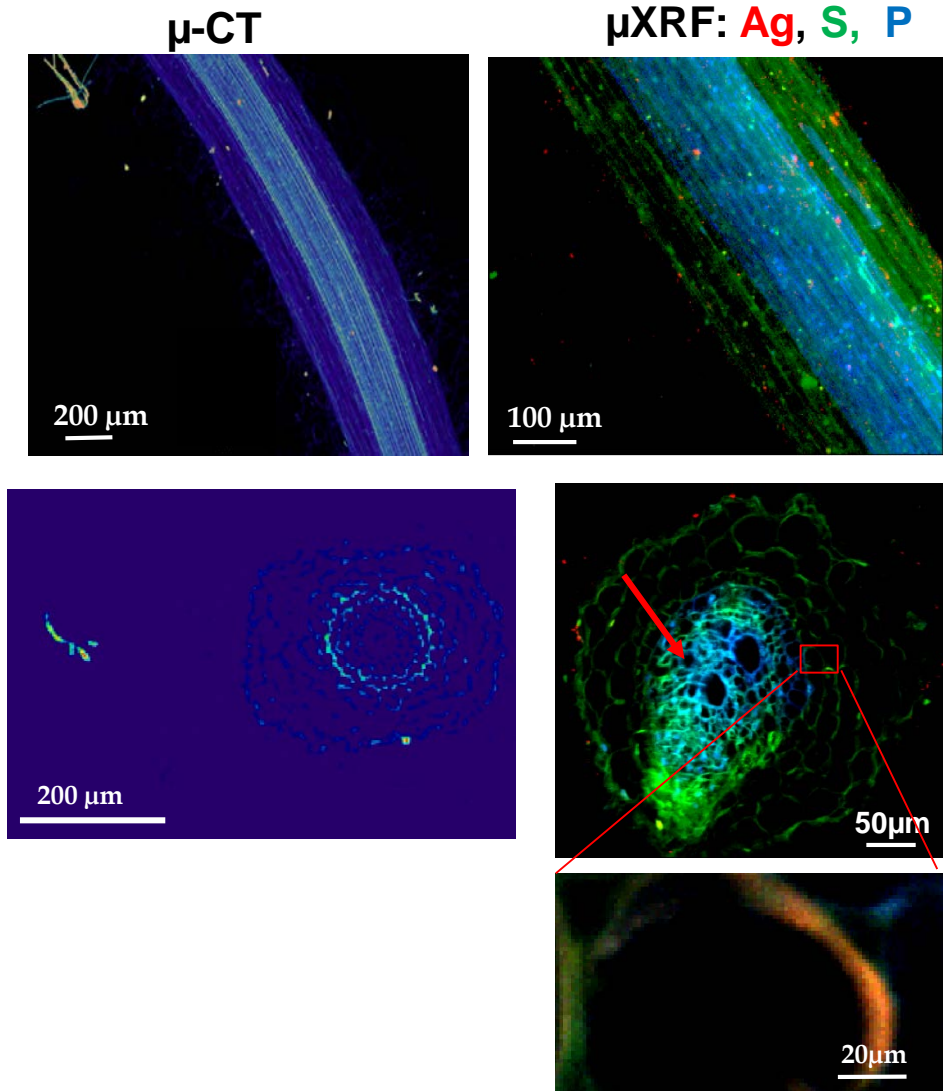


nano-CT



Pradas et al. 2017, ES&T

Wheat plants exposed to Ag NPs



-Ag=>aggregates in the epidermis and in root hairs

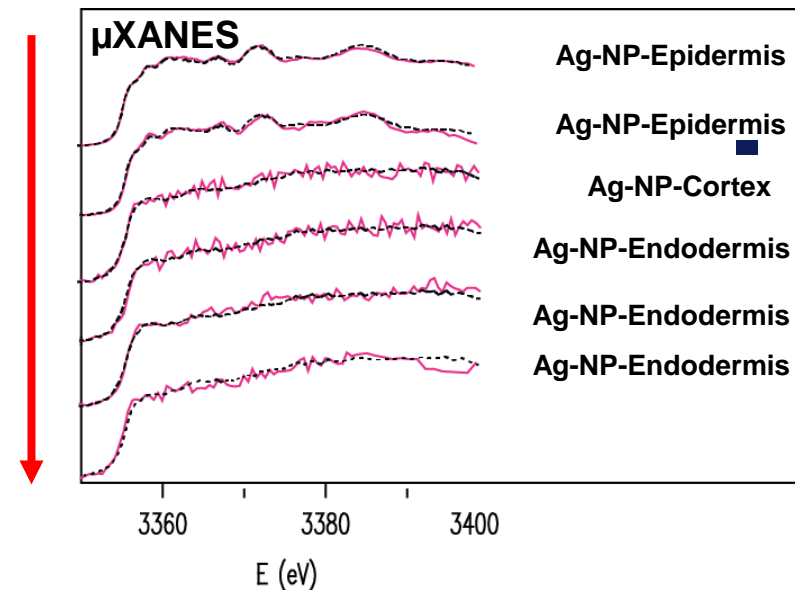
-Impact on root architecture

No Secondary roots

↑↑ root hairs

Toxicity symptom ↑

↑Ag uptake



-**Gradient:** Oxidation/Dissolution in the epidermis=> chelation
-No evidence of direct NPs uptake

Ti nanoparticles in sewage sludge

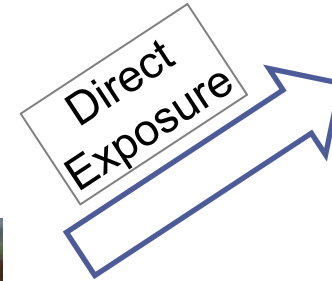
- Sludge from waste water treatment plants (WWTPs)
- Excellent source of organic matter, N and P to crops
- Is this a safe practice?



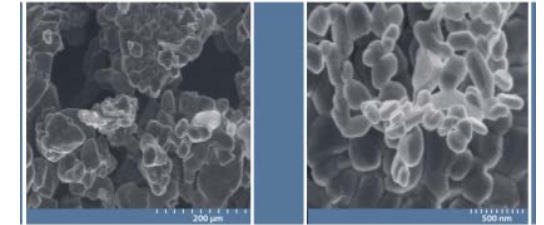
Sludge



Amend to soil
Waste=food



Occupational Exposure to Titanium Dioxide



Potentially Carcinogenic
breathing exposure

DEPARTMENT OF HEALTH AND HUMAN SERVICES
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health



Crops

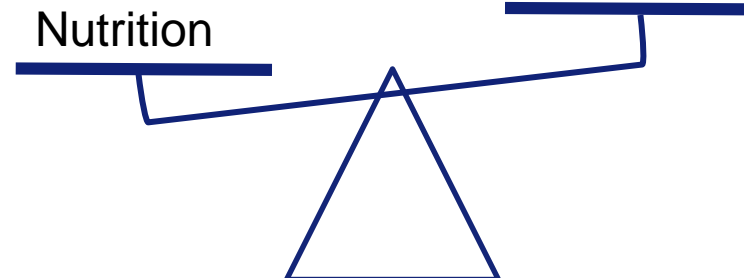


Soil
microorganisms



NPs toxicity

Nutrition



Paints & Coatings



Plastics



Cosmetics

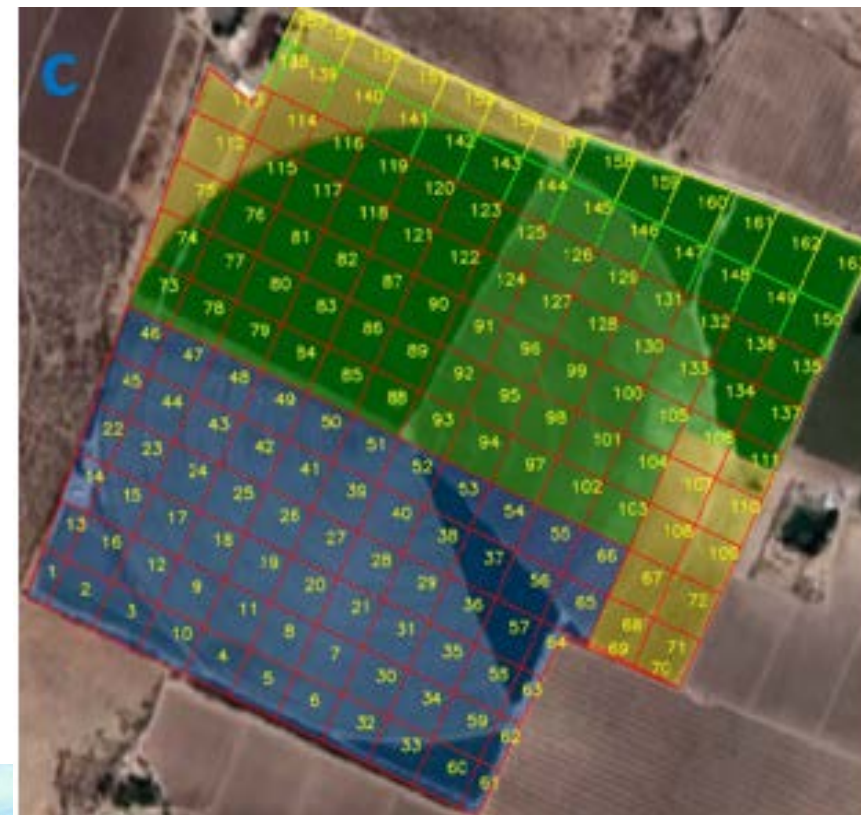
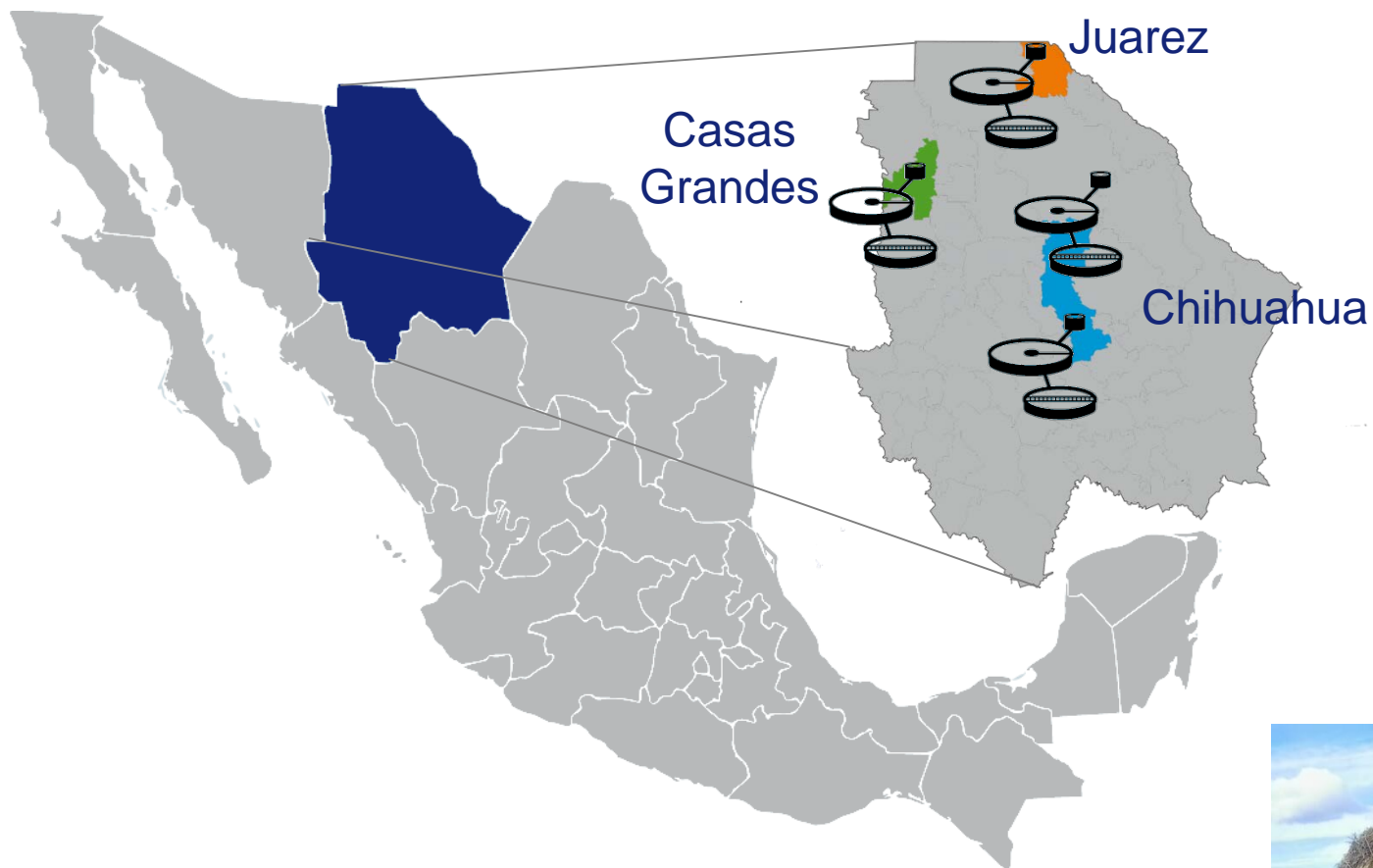


Toothpaste &
Sunscreen

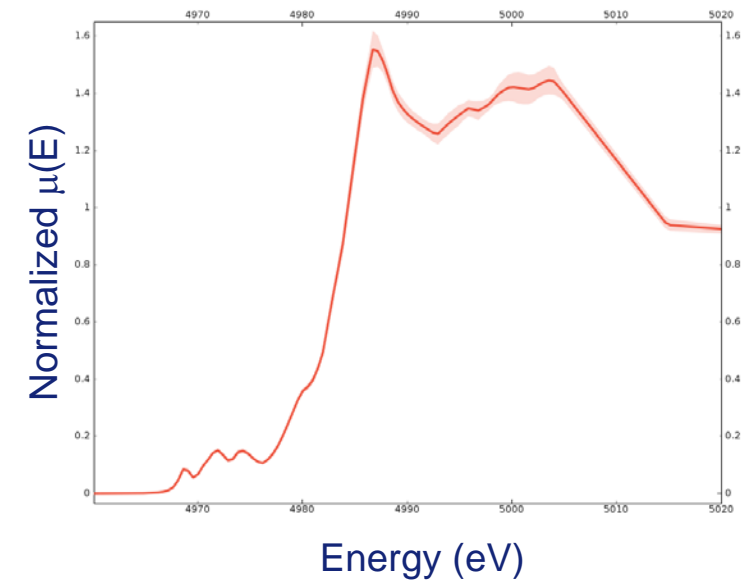
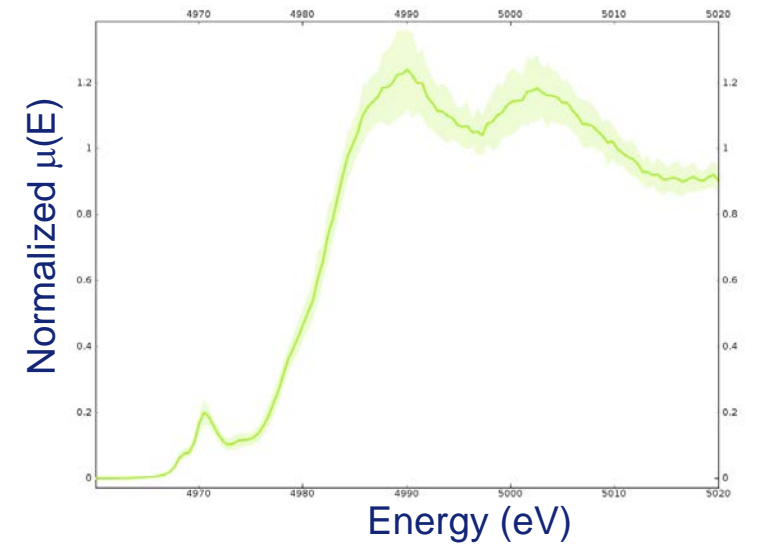
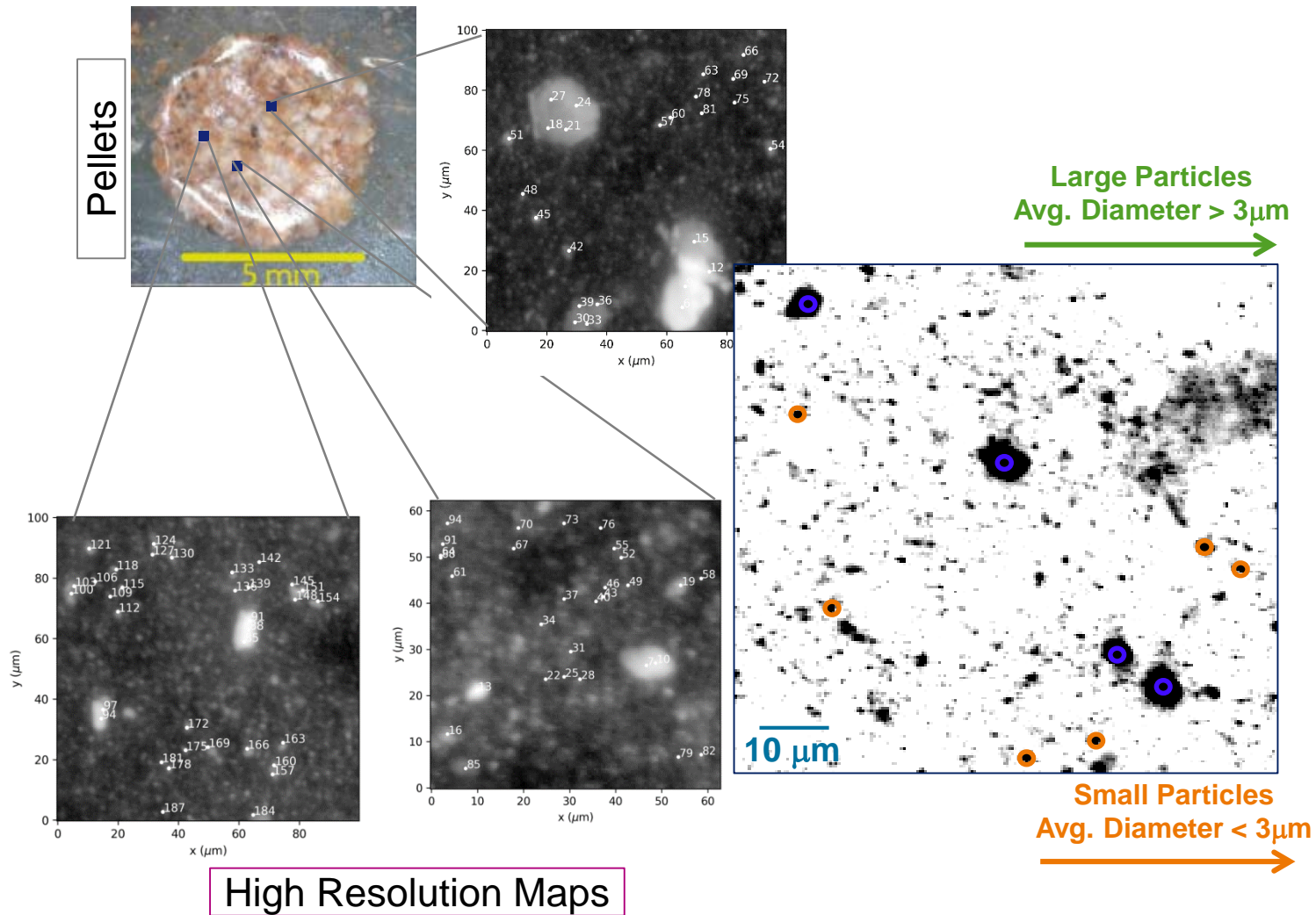


Food Industry

Governed by EU Council Directive No. 86/278/EEC:
It prescribes prior testing of sludge and soil not to exceed critical concentrations of pollutants (Cd, Pb, Cr, Hg, As,...) but not for Ti or nanomaterials.

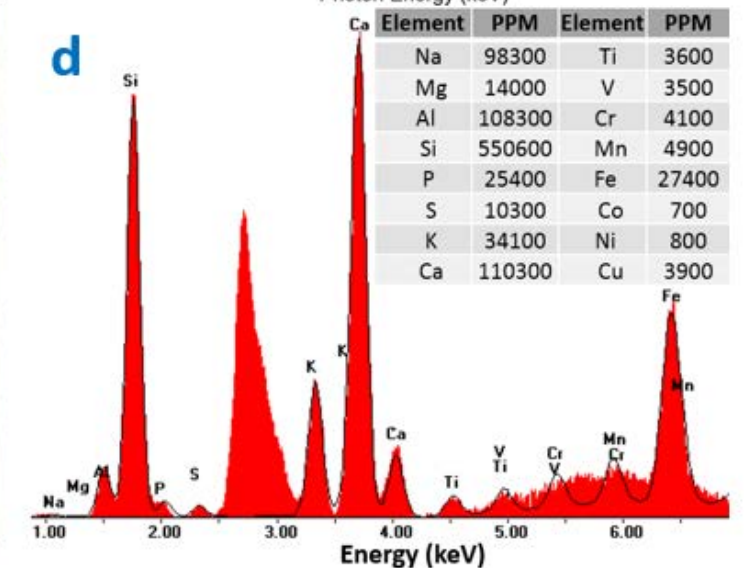
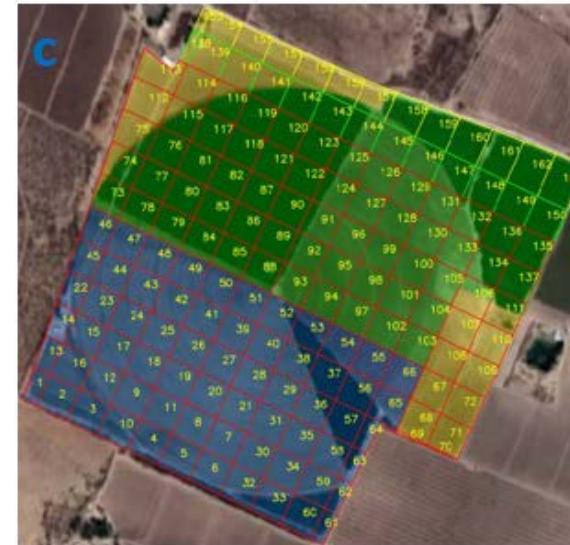
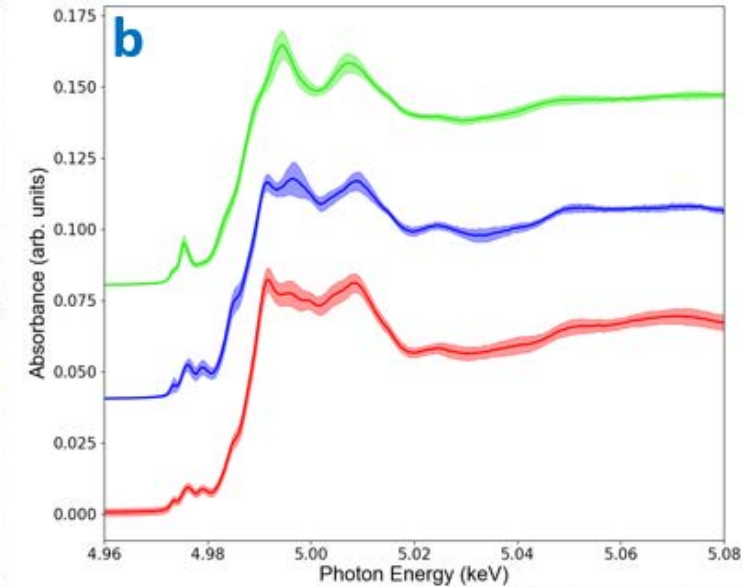
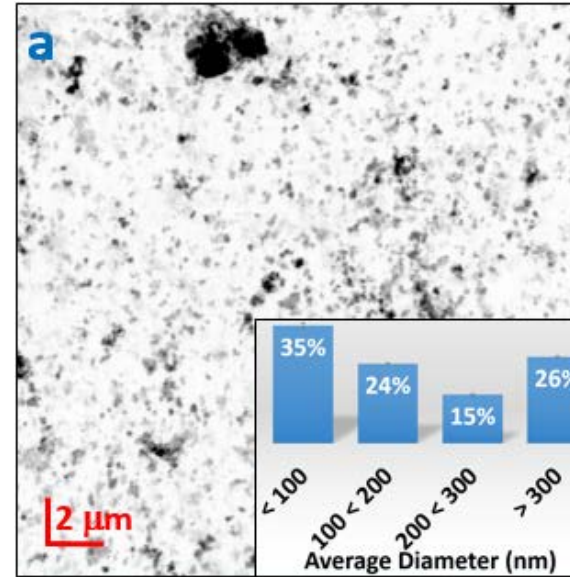


- WWTPs from Chihuahua state in Mexico
- 168 sampling points from Agricultural field amended with sewage sludge from Chihuahua WWTPs
- 2 Alfalfa plant samples (root, stem, leaf) from this site (pilot study)



Ti nanoparticles in sewage sludge summary

- ❑ Clear evidence of nanoscale Ti material was found in the sludge (including Cu and Zn).
- ❑ Three chemical species of titanium oxides have been found:
 - Anatase
 - Rutile
 - Ilmenite
- ❑ Investigate the impact on agricultural soils
 - ❑ 1-3 consecutive years of application
 - ❑ Ti transfer to Alfalfa plants



H. Castillo-Michel
J. Reyes-Herrera

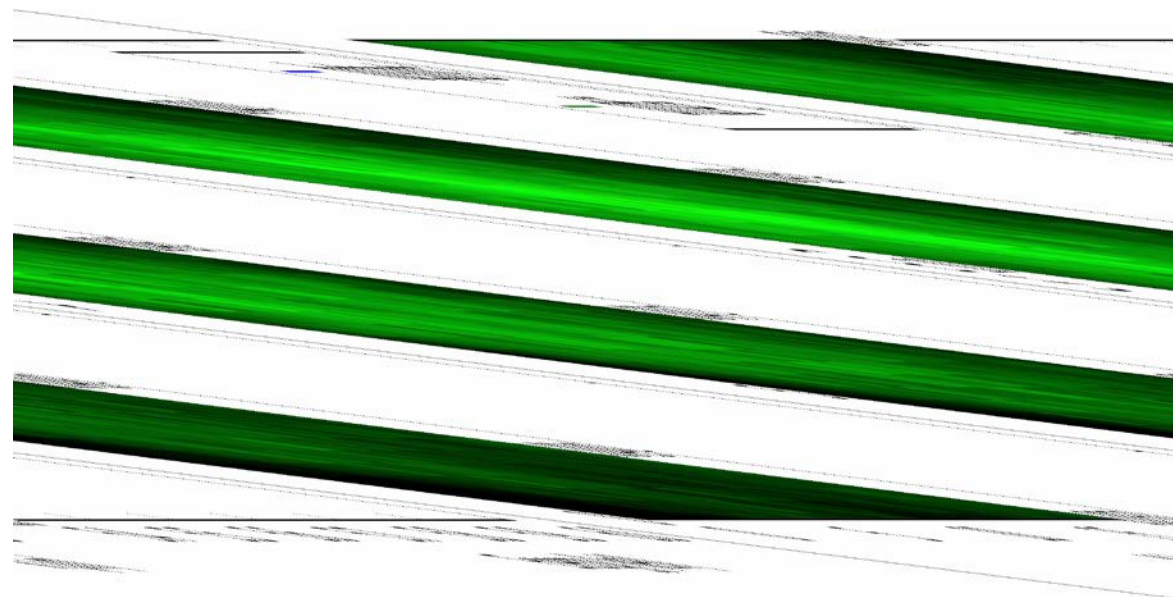
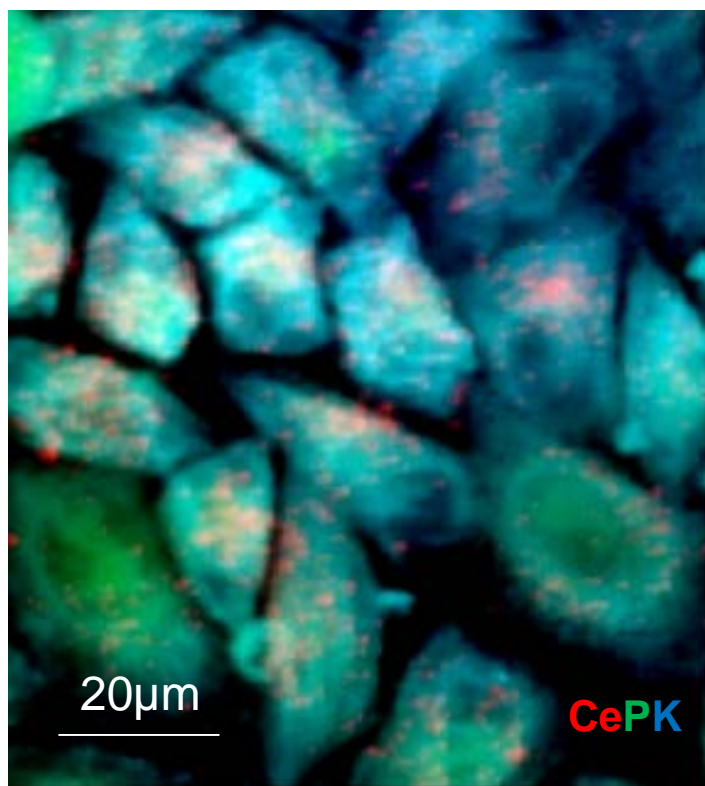


C. Valles
M. Roman

Dependence of the Ce(III)/Ce(IV) ratio on intracellular localization in ceria nanoparticles internalized by human (HeLa) cells

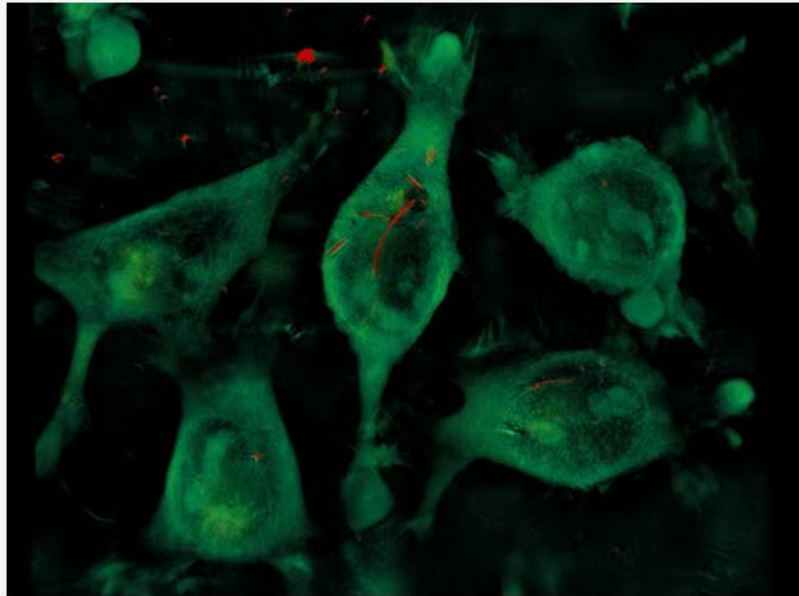
Ferraro et al., Nanoscale 2017

Dr. Sommi
Dr. U. Anselmi
Dr. P. Ghigna



CNPs incubated for 24 h showed a significant increase in Ce(III).
Internalized CNPs accumulate in endolysosomes that promote the oxidation state change.

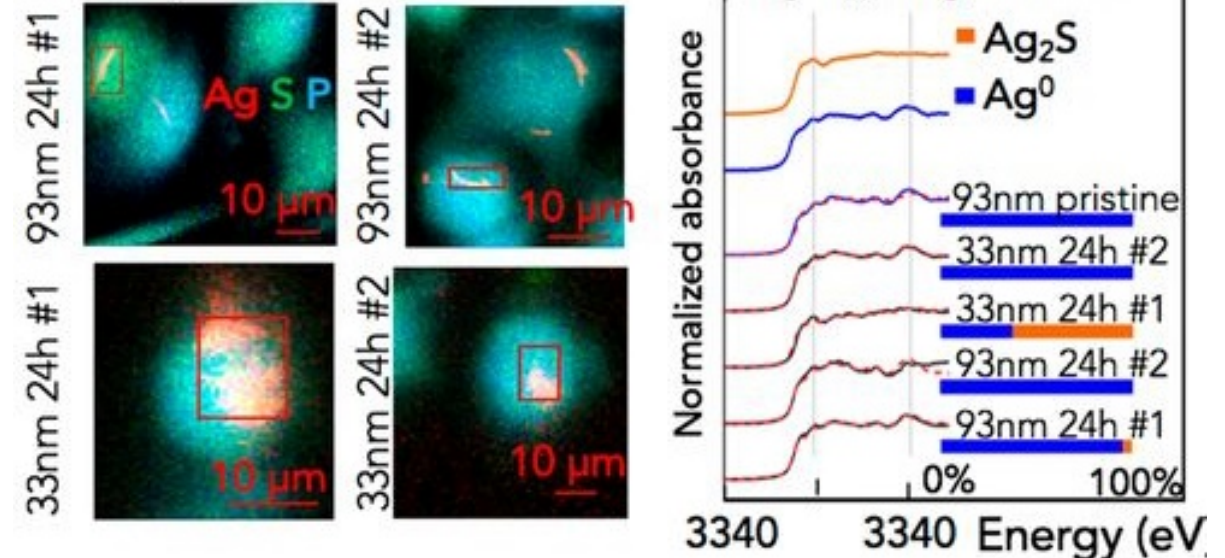
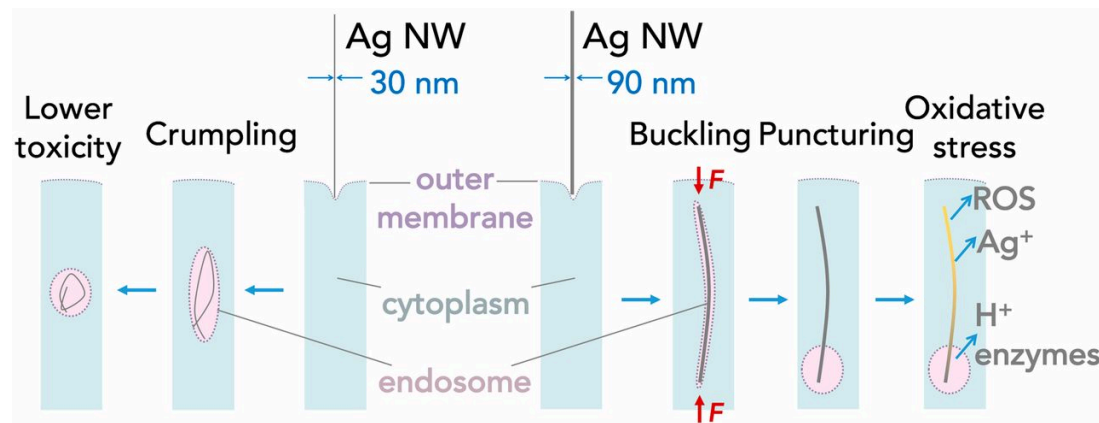
Sylvia G. Lehmann, Djadidi Toybou, Ana-Elena Pradas del Real, Devrah Arndt, Abderrahmane Tagmount, Muriel Viau, Malak Safi, Alexandra Pacureanu, Peter Cloetens, Sylvain Bohic, Murielle Salomé, Hiram Castillo-Michel, Brenda Omaña-Sanz, Annette Hofmann, Christopher Vulpe, Jean-Pierre Simonato, Caroline Celle, Laurent Charlet, and Benjamin Gilbert

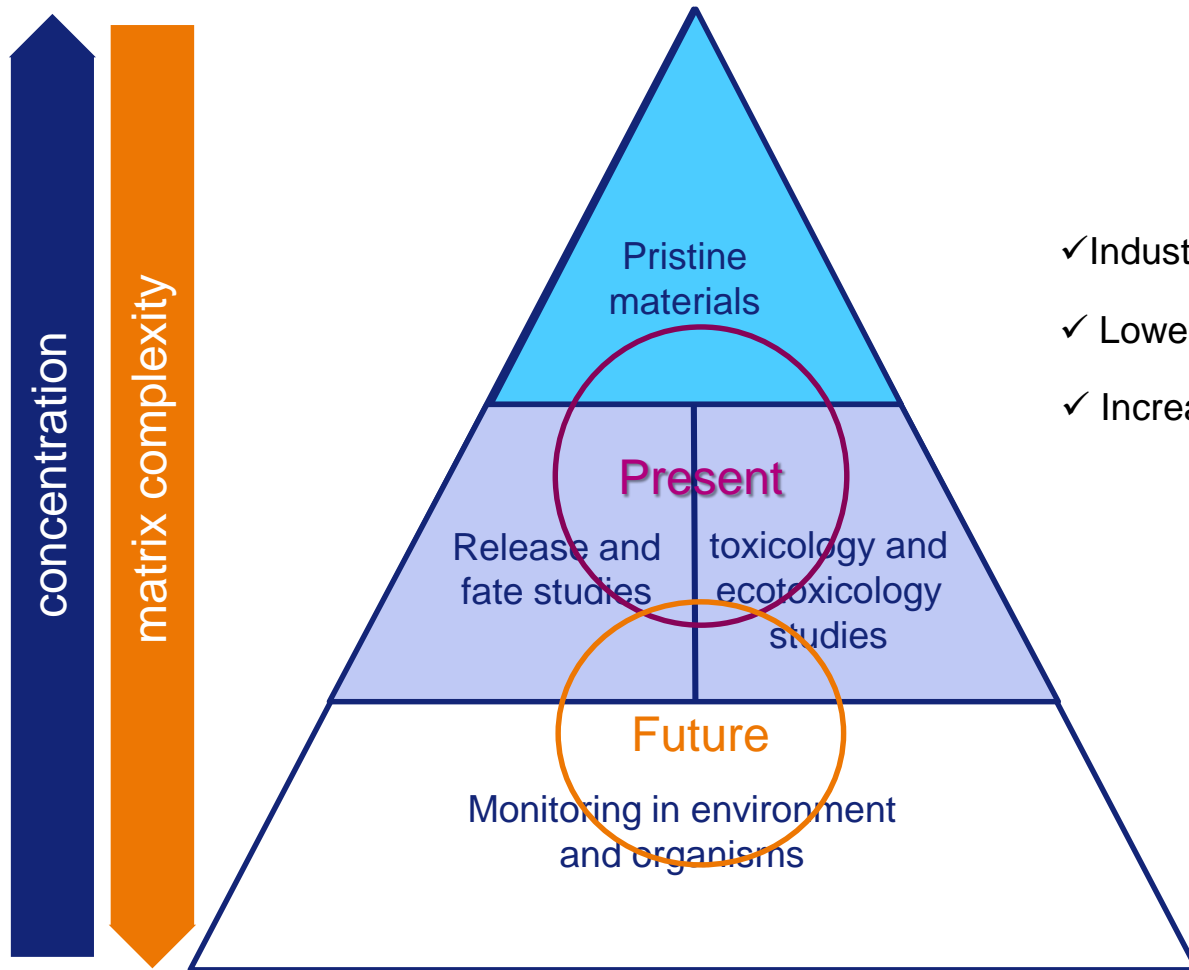


10-07-2019

One of the weaknesses of smartphones is their rigid screen, which can easily crack when the phone drops on the floor. An international, interdisciplinary team of scientist have shown that very thin silver nanowires may be the safe solution to manufacturing flexible screens without losing properties. They publish their results in PNAS.

Share   





THE ID21 STAFF



Thanks for your attention!



Collaborators: M. Gonzalez-Guerrero, G. Sarret, C. Larue, M. Roman, K. Vogel-Mikus, A. Servin, J. Villanova, I. Schreiber, and many others

Support teams: B. Baker, R. Barrett, G. Berruyer, C. Cohen, C. Cornu, E. Gagliardini, R. Hino, J. Keiffer, J. Morse, M. Papillon, V. A. Solé, A. Vivo, L. Zang, and many others