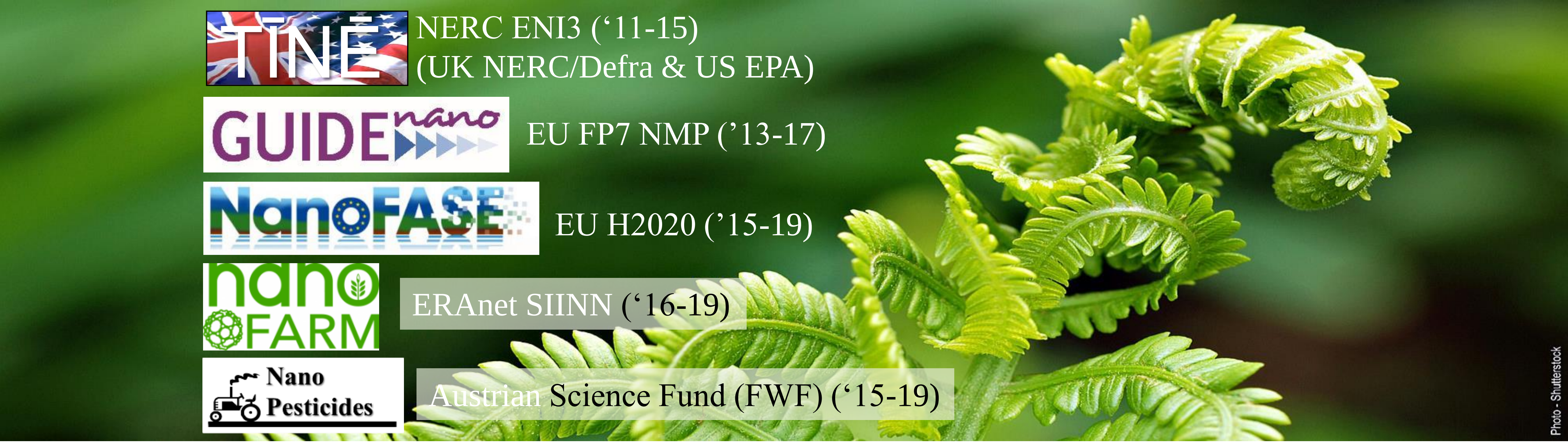

Current scientific developments in the environmental risk assessment of nanomaterials

Claus Svendsen[1], Elma Lahive[1], Marianne Matzke[1], Geert Cornelis[2], Jason White[3], Melanie Kah[4], Frank von den Kammer[4], Susana Loureiro[5], David Spurgeon[1] and Steve Lofts[6]

[1]**NERC-CEH, Wallingford, United Kingdom**
[2]Swedish University of Agricultural Sciences (SLU), dept. Soil and Environment, Sweden
[3]The Connecticut Agricultural Experiment Station, New Haven CT, USA
[4]University of Vienna, Austria
[5]University of Aveiro, Portugal
[6]NERC-CEH, Lancaster, United Kingdom

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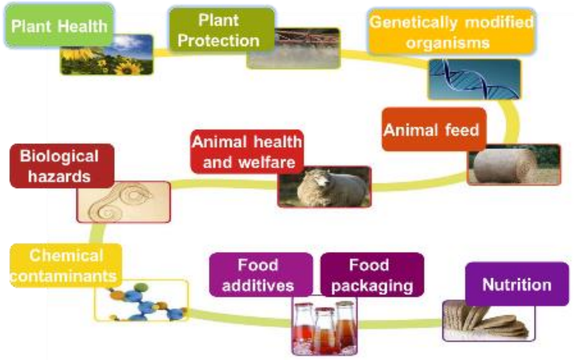
Overview

Introduction

- Introduction - What and where is nanotechnology?
- Where is Nano relevant across the EFSA “Farm to Fork” continuum
- Why is RA & ERA of nanoforms different to “classical chemicals”

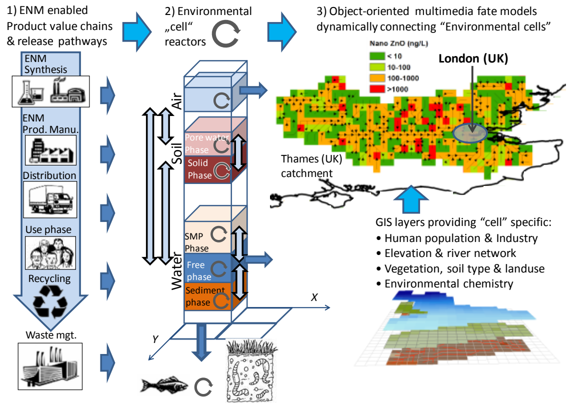
How nanomaterials may benefit or impact things we value?

- Direct application examples
    - Food and Feed
    - Plant disease control & health
- Unintended exposures – contamination & pathways to harm
    - Routes and forms of exposure
    - Comparison to Classical chemical Exposure and Hazard Assessment



Implications for ERA considerations, approaches and tools

- New hazards or exposure routes?
- Environmental fate
- Biodegradation/ accumulation/ biomagnification
- Technical / Analytical needs + Test Guidance



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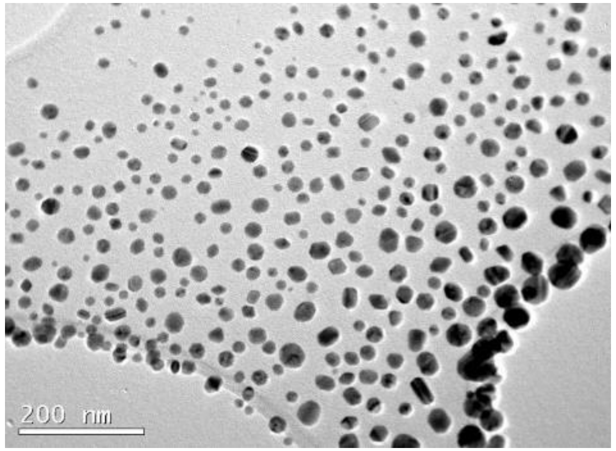
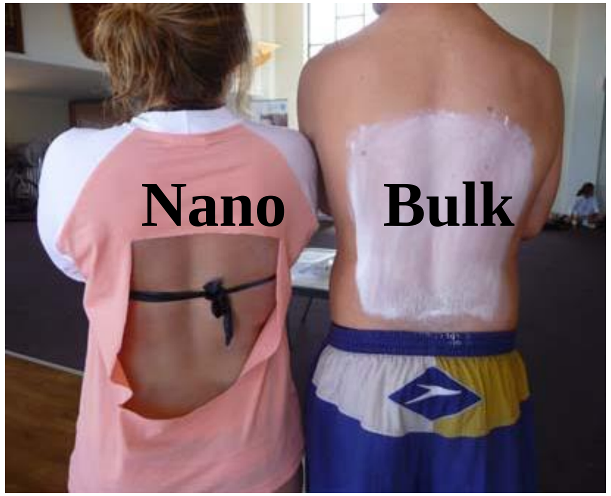
What and where is nanotechnology?

Clear Sunscreen
(ZnO or TiO_2)





They have wide application and it is a fast growing market.

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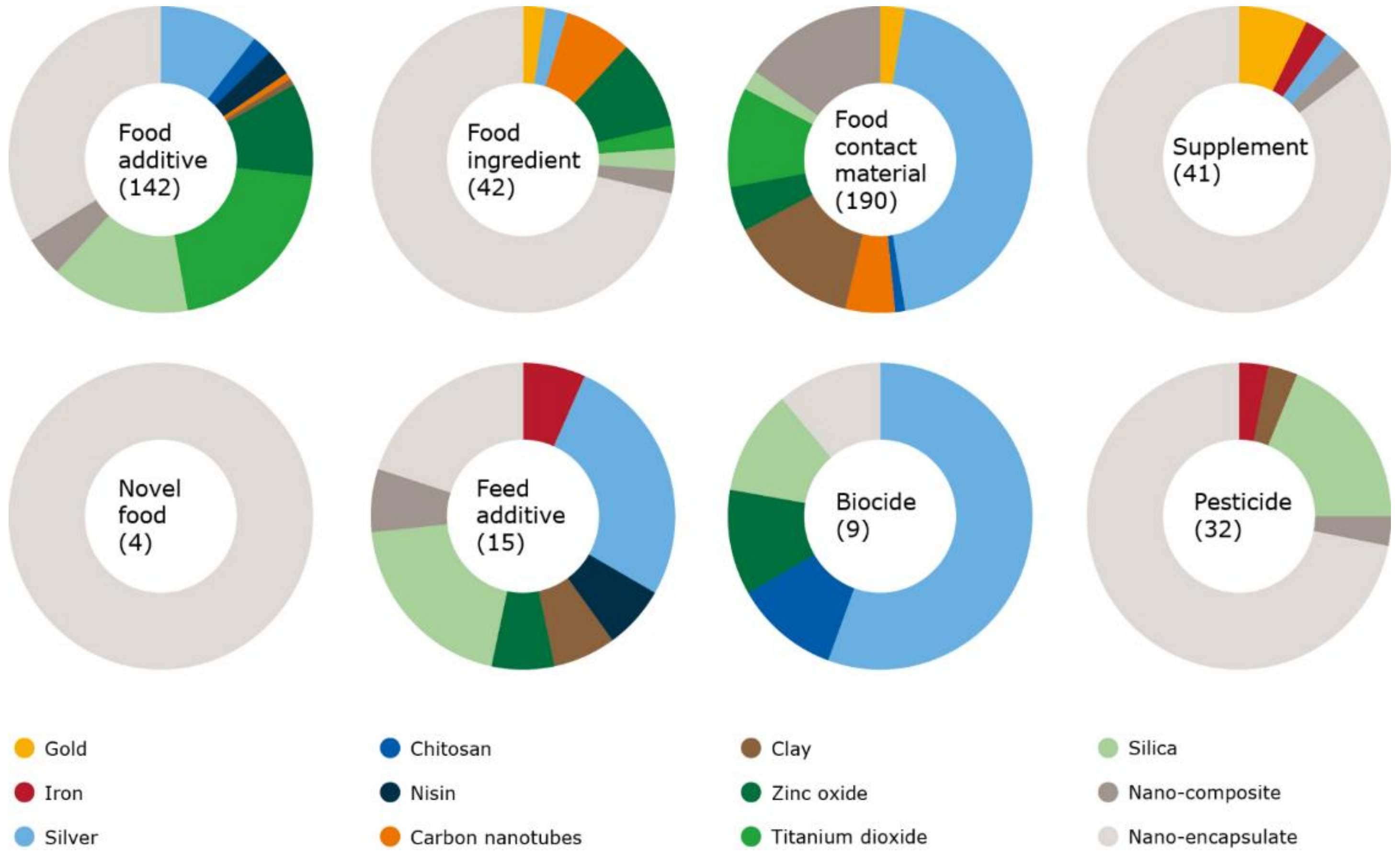
What and where is nanotechnology for EFSA?



Peters, R.J.B. et al (2016), Nanomaterials for products and application in agriculture, feed and food, Trends in Food Science & Technology 54 (2016) 155-164

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What defines “NanoMaterials”?

EC (short) Definition: ..*material with 50% or more of the particles in the number size distribution having one (or more dimensions) <100nm*

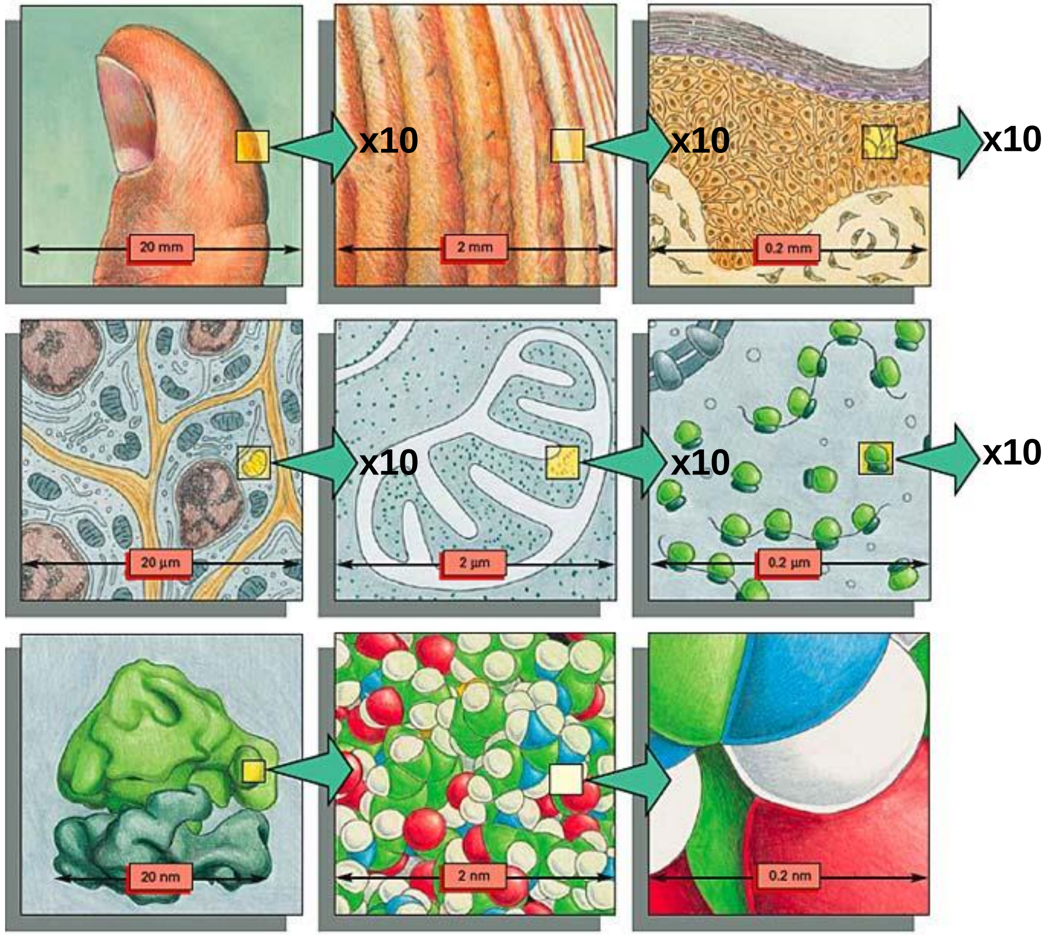
Small stone

X 1000

PM10

X 1000

Nano



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"Classical chemicals" vs Nanoforms

The main (E)RA difference: Dissolved vs Suspended behave different

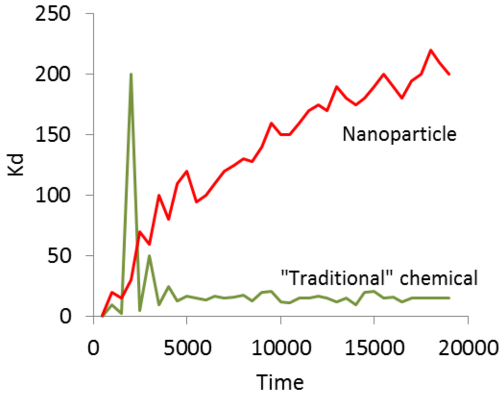
Ions:

K_d = $[A]_{solid}/[A]_{aqueous}$

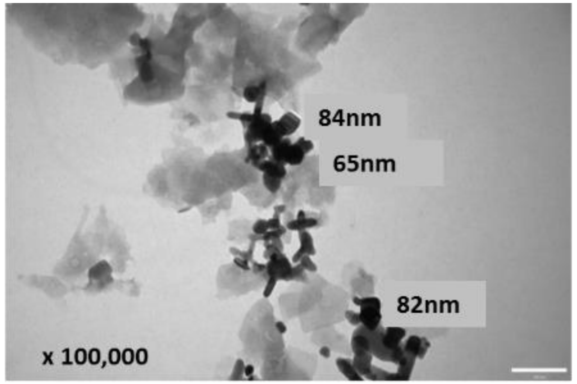
Particles:

K_d = $[NP]_{solid}/[NP]_{aqueous}$

Kinetic fate descriptor for particles



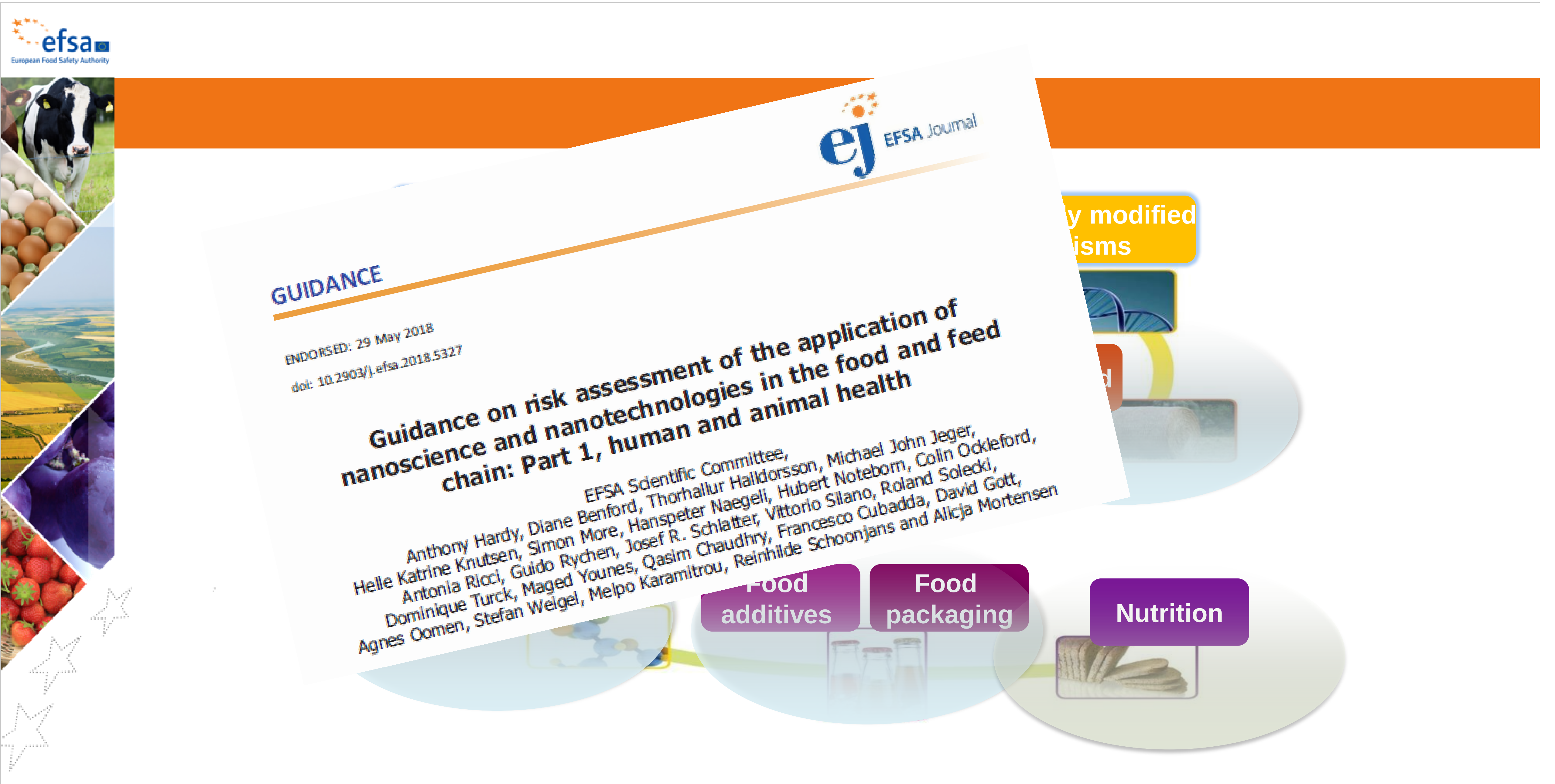
Concentrations
vs
Fluxes and co-transport



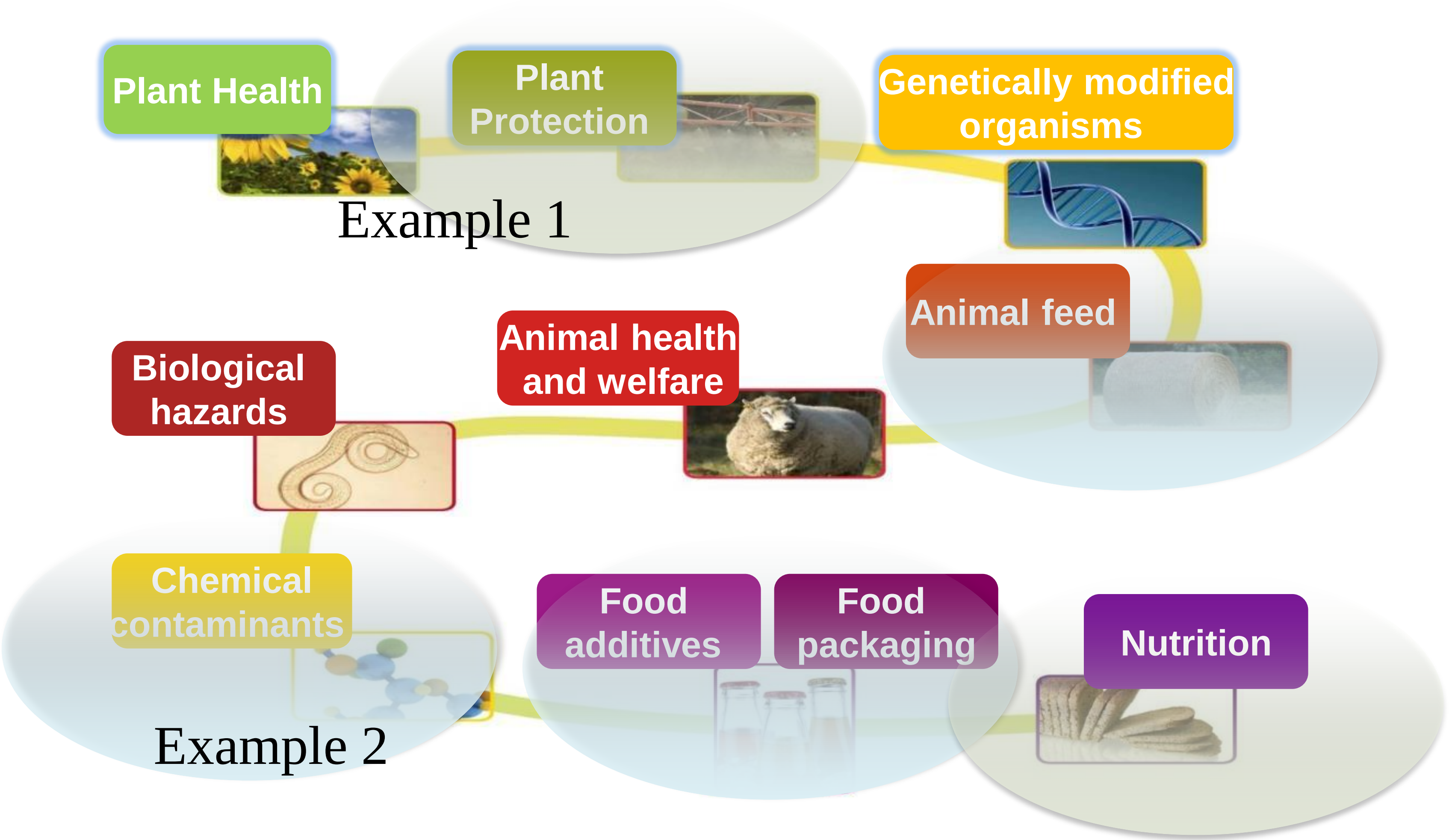
SEM of ZnO NPs attached to soil pore water DOM, by PL Waalewijn-Kool & CAM van Gestel, VU Amsterdam

Slide from Geert Cornelis

Where is nanotechnology for EFSA?



Where is nanotechnology for EFSA?



Plant disease and nutrition

Nanoscale Nutrients and Root Disease

- Fungal pathogens reduce annual crop yield by 20% and economic return by $200 million, in spite of $600 million spent on control
- Many micronutrients (Cu, Mn, Zn, Mg, B, Si…) stimulate or are part of plant defense systems
- However, these nutrients have limited availability to roots when delivered in soil
- Can they be added via topical leaf application and translocated to roots?

Nanoscale micronutrients (Cu, Zn, B, Si…) applied to leaf in greenhouse → **Transplanted into infested soils** → **Monitored yield, disease and root content**

Slide from Jason White (Elmer and White (2016) Environ. Sci.: Nano. 3:1072-1079.)

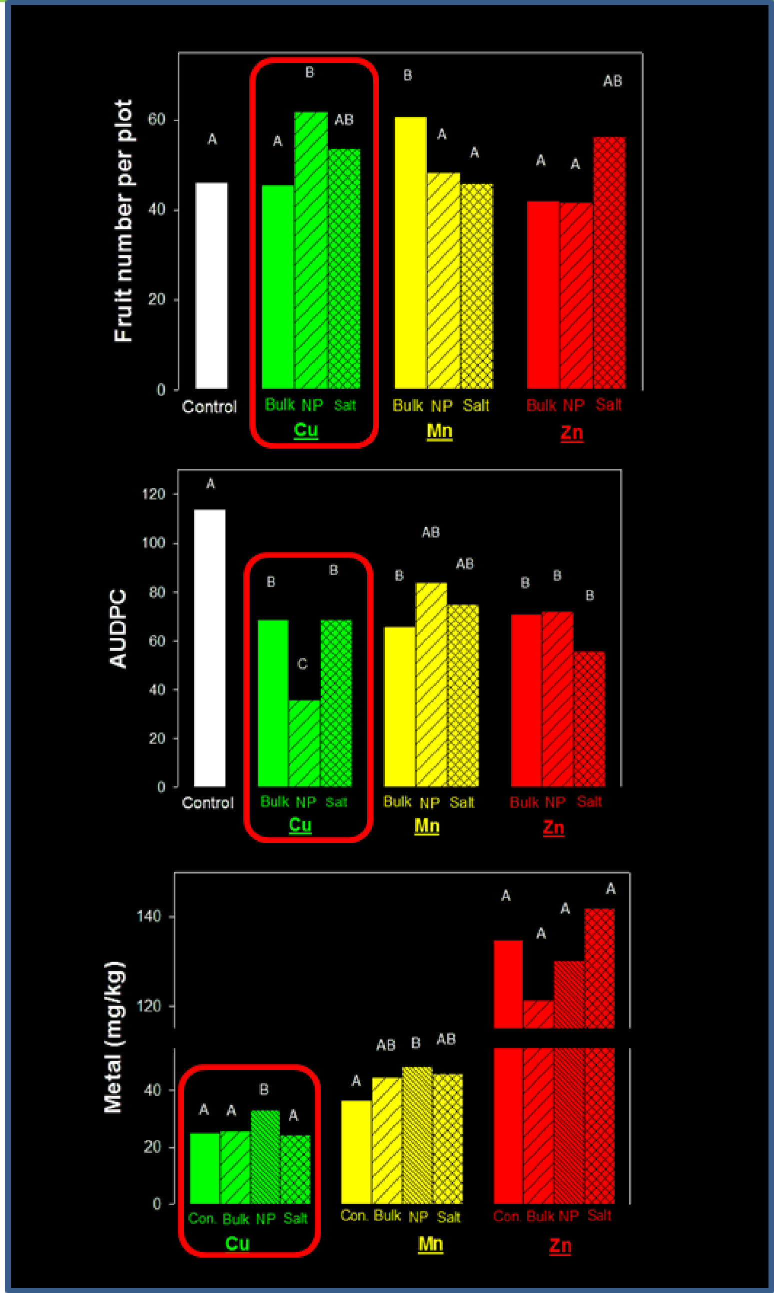
Plant disease and nutrition

Nanoscale Nutrients and Root Disease

- Single foliar application of NP (bulk, salt) CuO, MnO, or ZnO (100 mg/L) to seedling; transplant to infested soil worked.

- <u>NP CuO treated plants had:</u>
  - Increased yield,
  - greater disease suppression (AUDPC),
  - and higher Cu root content.

- <u>Bottom line:</u>
  - A $44/acre cost for NP CuO suppressed a root pathogen of eggplant,
  - increasing yield from $17,500/acre to $27,650/acre



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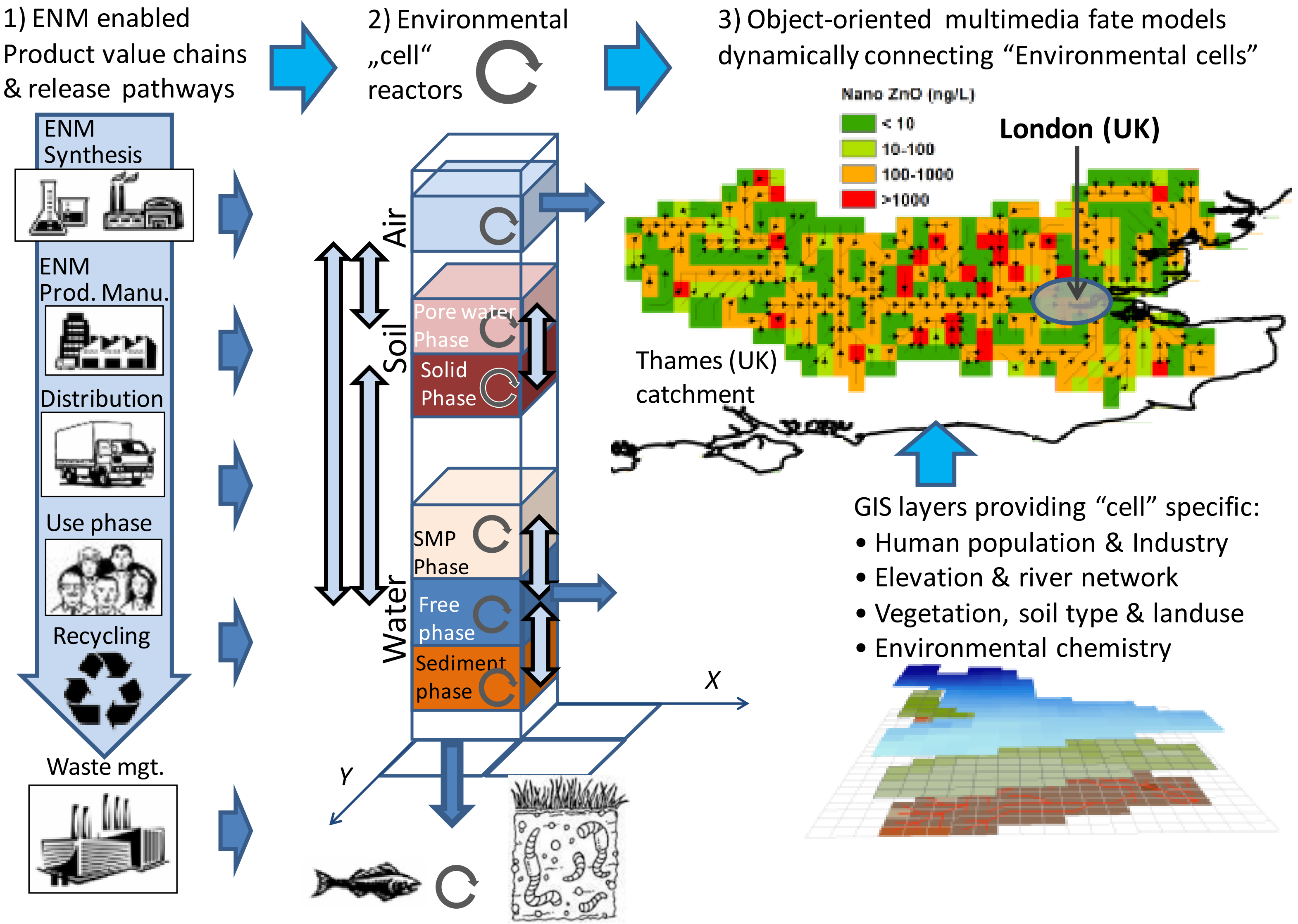
Release & Exposure - Nanomaterial fate in the environment:

Where, what and for how long?



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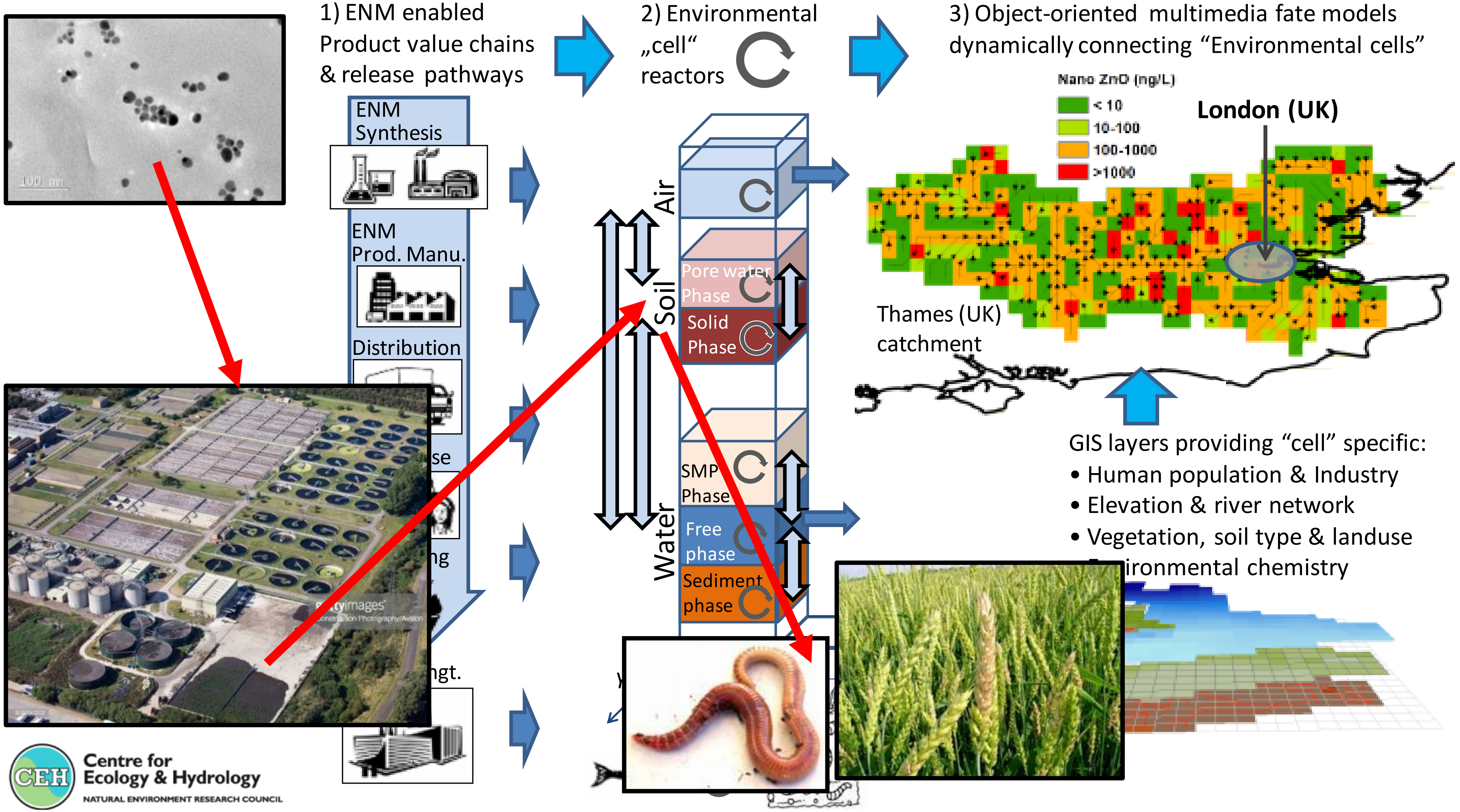
Release & Exposure - Nanomaterial fate in the environment:

Where, what and for how long?



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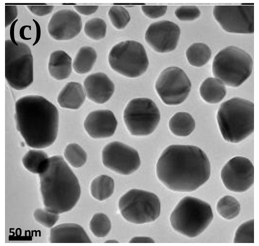
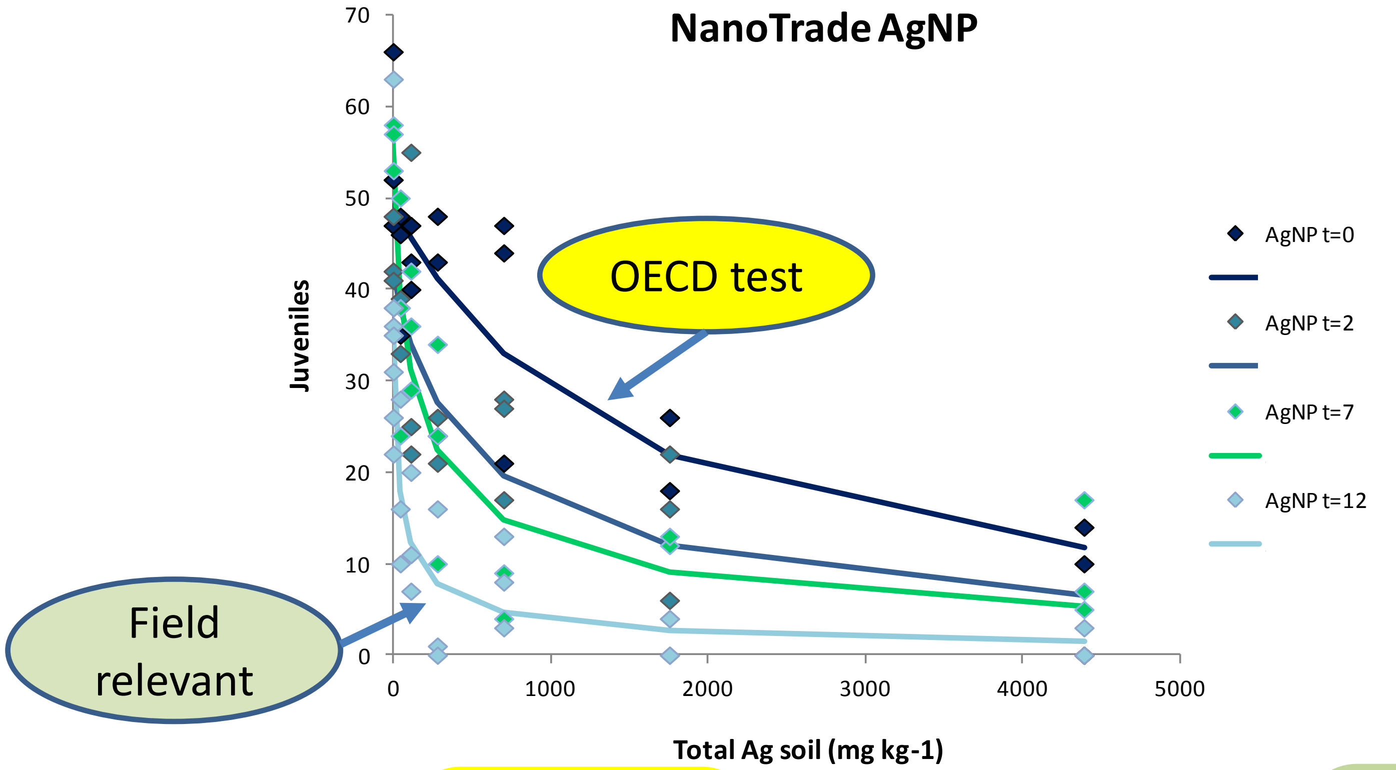
Standard test vs. Field exposure (Pristine NP)

50nm AgNPs (uncoated)





Ageing dosed soil for 0, 2, 7 & 12 months

- In dark at 20 ± 1°C
- Continuously aerated
- Moisture loss adjusted

Soil EC50 (mg/kg dry soil)	**T=0**	**T=2mth**	**T=7mth**	**T=12mth**
AgNP	1420 (407-2432)	588 (65-1110)	142 (5-278)	34 (-117)
$AgNO_3$	49 (46-51)	30 (16-43)	90 (29-151)	104 (63-144)

Diez-Ortiz, M *et. al.* Environmental Pollution, 203, 191–198 (2015)

Testing pristine vs exposure relevant NPs

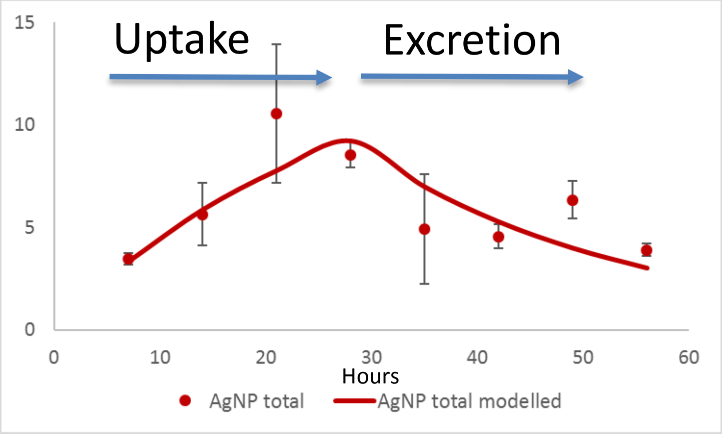
Kinetics of whole organismal uptake of Ag-NPs in Earthworms

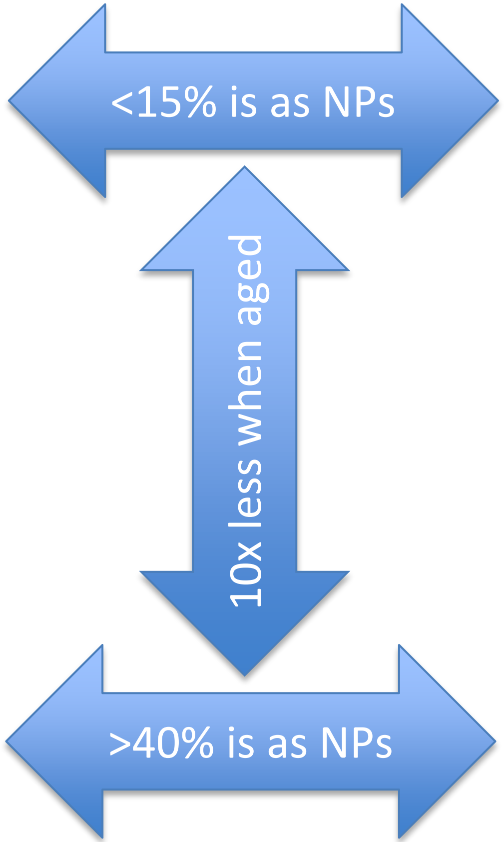
Marta Baccaro

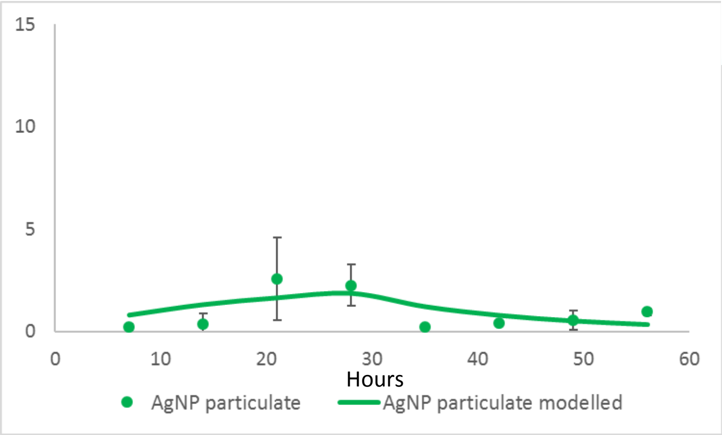
Total Ag (ICP-MS)

Particulate Ag (spICP-MS)

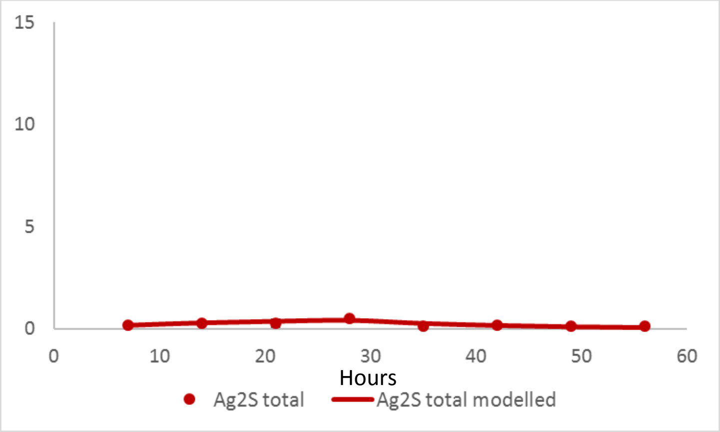
Pristine Ag-NPs (mg/kg)

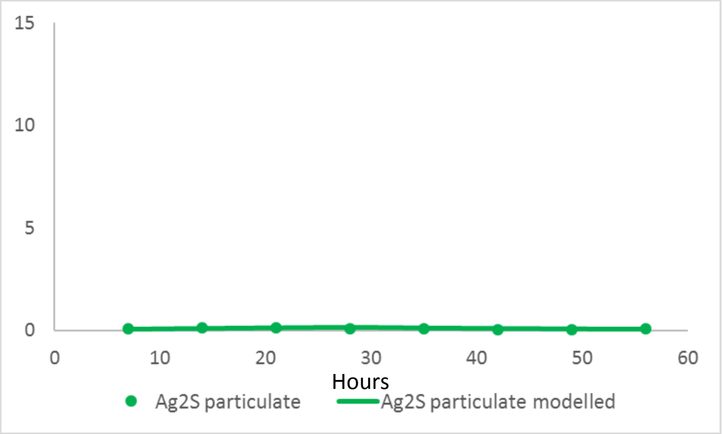






Ag_2S-NPs (mg/kg)





WAGENINGEN UR For quality of life

Baccaro, M. et al, Environ. Sci.: Nano, 2018, 5, 1107

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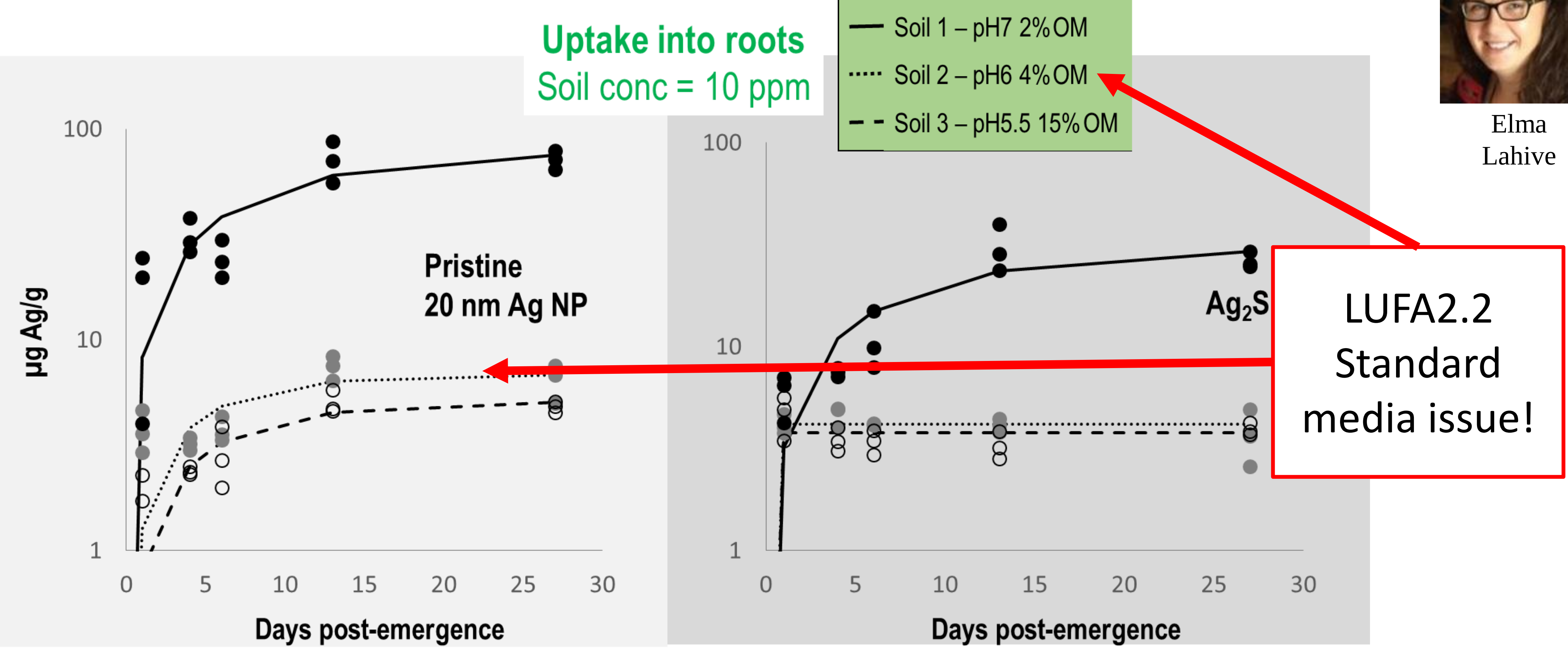
Testing pristine vs exposure relevant NPs

Kinetics of uptake of Ag and Ag_2S-NPs by wheat in different soils



Elma Lahive

- Uptake from Ag_2S was only about 2.5 times less compared to pristine Ag
- Accumulation was higher in soil with high pH and low organic matter content

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Implications for ERA considerations, approaches and tools

New hazards or exposure routes?

- Hazard: For current forms only really photo-reactivity and ROS generation
- Routes: No new routes, but rates and internal transport vary between forms

Environmental fate

- Very different - rules if and where there may be possible Nano Exposures => should inform what Nano-form(s) are “exposure relevant”
- Long time scales => Current standard hazard tests may not be “worst case”
  => Pre-aging of test media?

Biodegradation/ accumulation/ biomagnification

- Tested exposure forms must be the relevant ones
- Form (size and speciation) of internalised material ideally identified

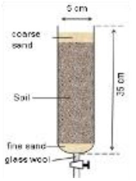
Technical / Analytical needs + Test Guidance

- New analytical and testing techniques needed (kept simple and repeatable)
- Move from “Solute based” to “kinetic” tests

Sorption
OECD 106

Degradation
OECD 307

Leaching
OECD 312



ICPMS to spICPMS

New analytics for organic NMs

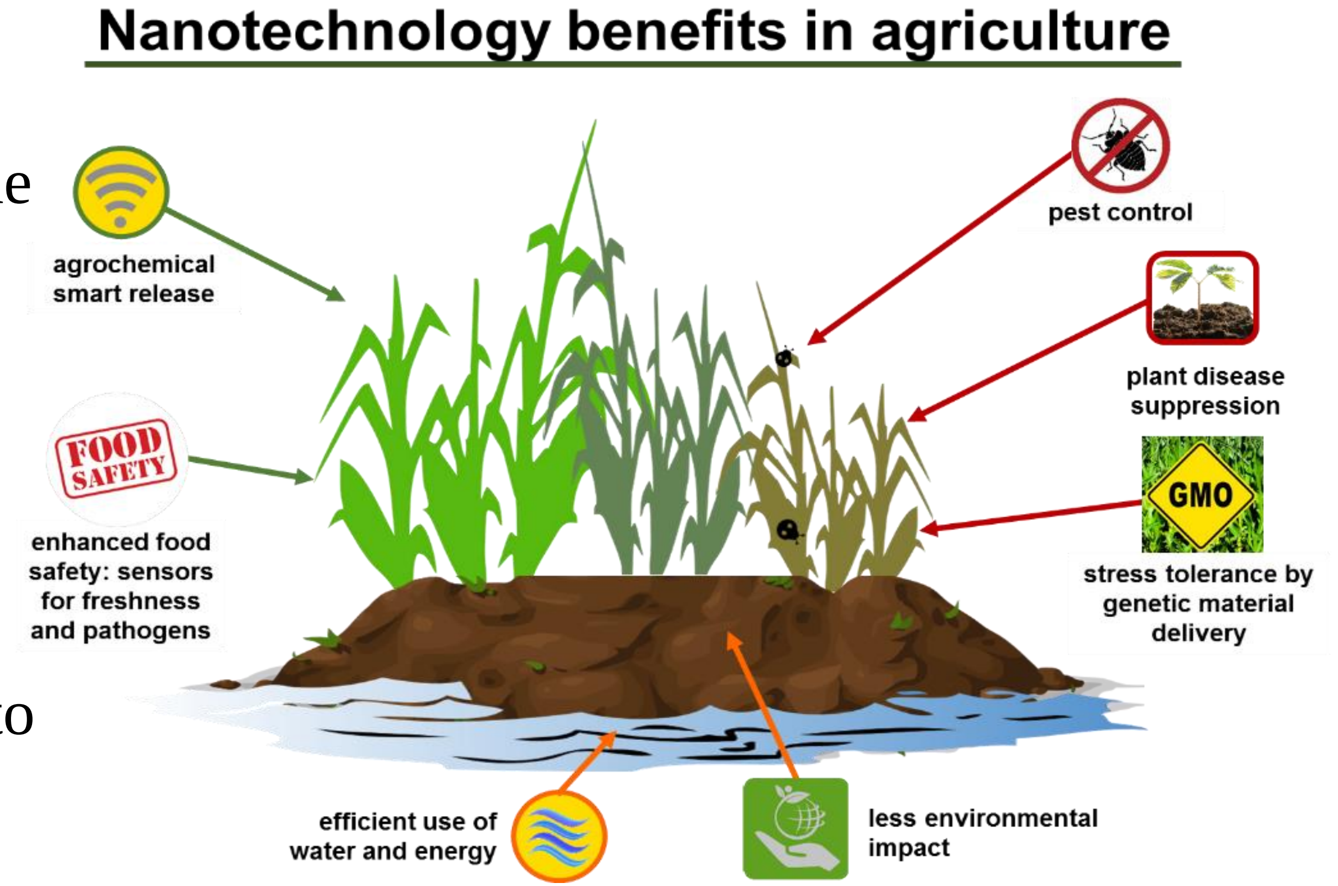
X-ray based for speciation

ECHA EUROPEAN CHEMICALS AGENCY

OECD

Overall conclusions

- Be aware that the "nano specific elements" will differ between interned uses and the materials involved – must be addressed in the problem formulation stage.
- Because of this and widespread use of nanomaterials in other sectors, exposure in the food supply may become significant
- An understanding of fate processes, mechanisms of action/interaction is needed to enable accurate ERA.
- Nanotechnology has the potential to improve agriculture, and trade-offs against safety and uncertainty should be discussed



White and Gardea-Torresdey, 2018 *Nature Nanotech.* 13:627-629.

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We are learning, but with good guidance an direction we can make it through the “rough stuff”!

Acknowledgements: UK (NERC)/US (EPA)

TINE

NanoFATE
www.NanoFATE.eu (EU CP-FP7 247739)

GUIDEnano
www.guideNANO.eu (EU CP-FP7 604387)

nano FARM

SIINN
2015-2018

Nano Pesticides

FWF 2015-2019

NanoFASE
www.NanoFASE.eu (EU H2020 Proj. 646002)

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NERC SCIENCE OF THE ENVIRONMENT

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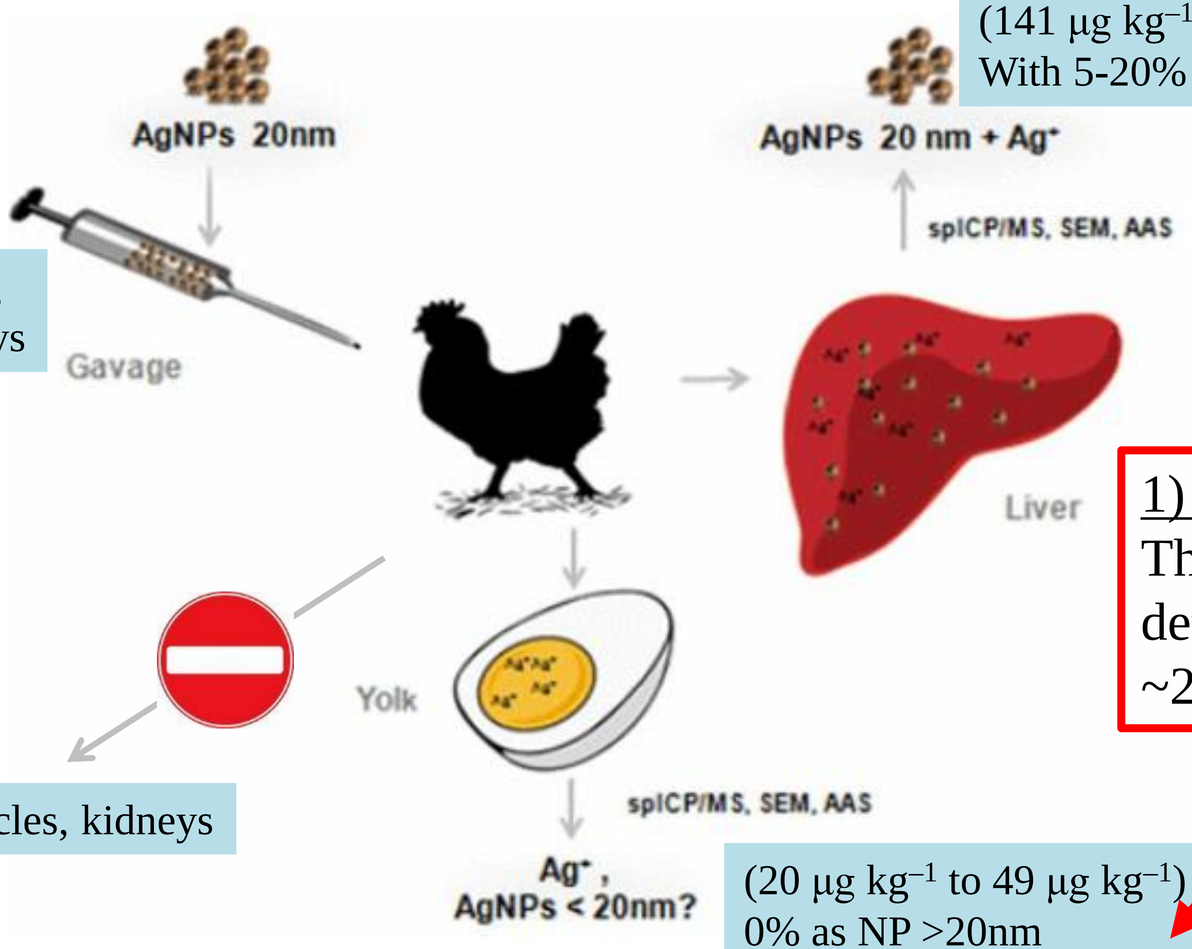
Feed and Food - Animal feed to animal products

Transfer Study of Silver Nanoparticles in Poultry Production
Gallochio, F et al, 2017, *J. Agric. Food Chem.*, *65* (18), pp 3767–3774

(141 µg kg^{-1} to 269 µg kg^{-1})
With 5-20% as NP ~20nm

6x 1mg/kg
over 22days



muscles, kidneys

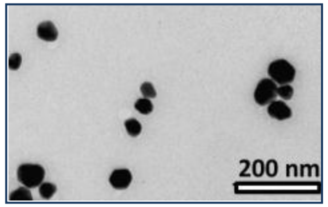
1) Technical issue:
The size limit for detection is ~20nm

(20 µg kg^{-1} to 49 µg kg^{-1})
0% as NP >20nm

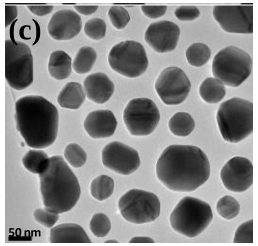
2) ERA issue: The mass balance says “most” left the chicken, but in what form?

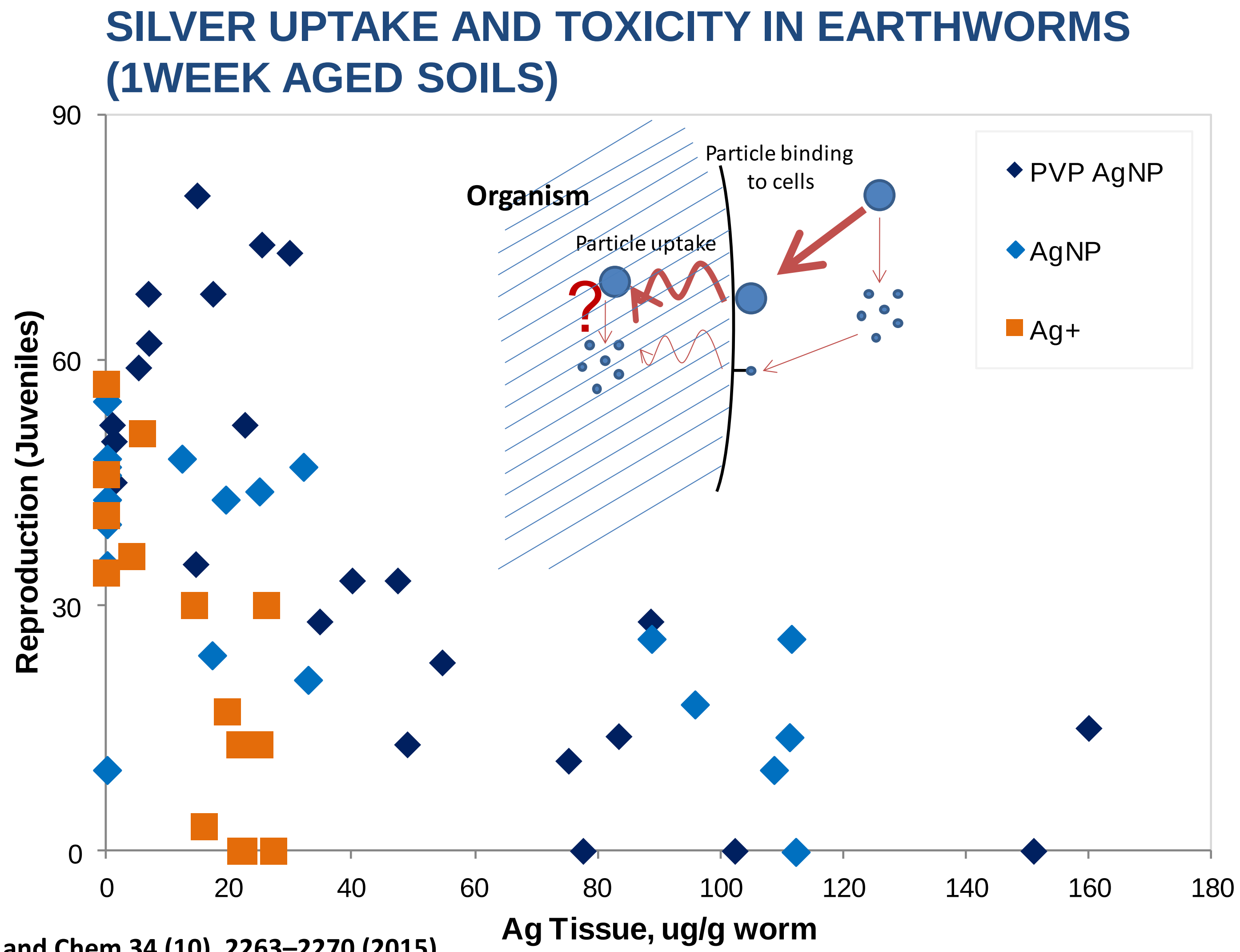
Bioaccomulation: Does “the dose make the poison”?

50nm AgNPs (PVP coated)



50nm AgNPs (uncoated)



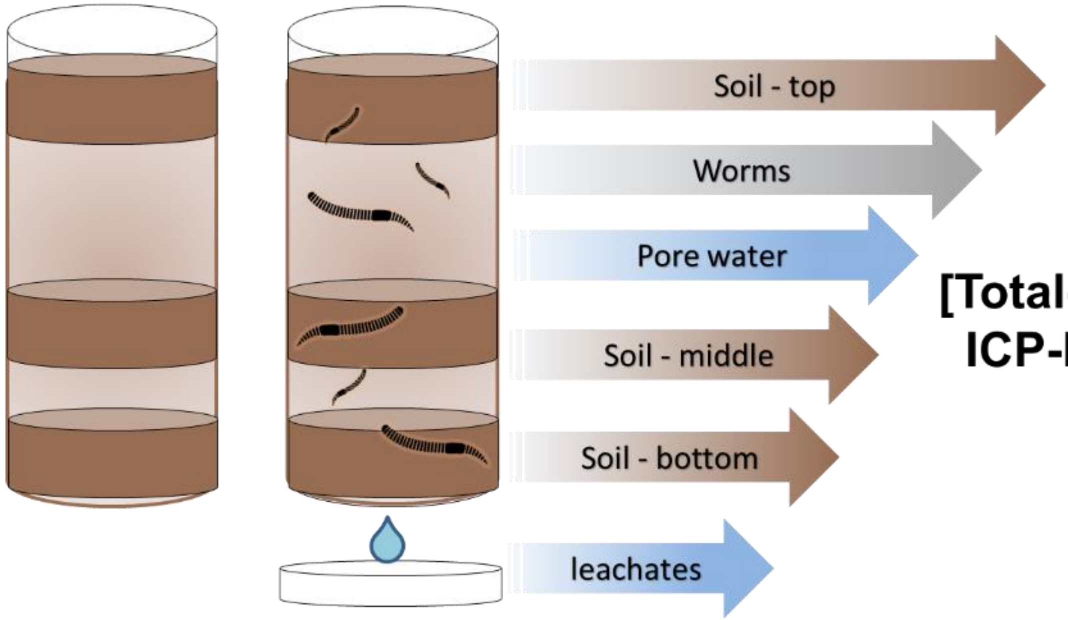


Diez-Ortiz, M *et. al.* Environ Tox and Chem 34 (10), 2263–2270 (2015)

NP mobility in Soil vs Earthworm driven bioturbation

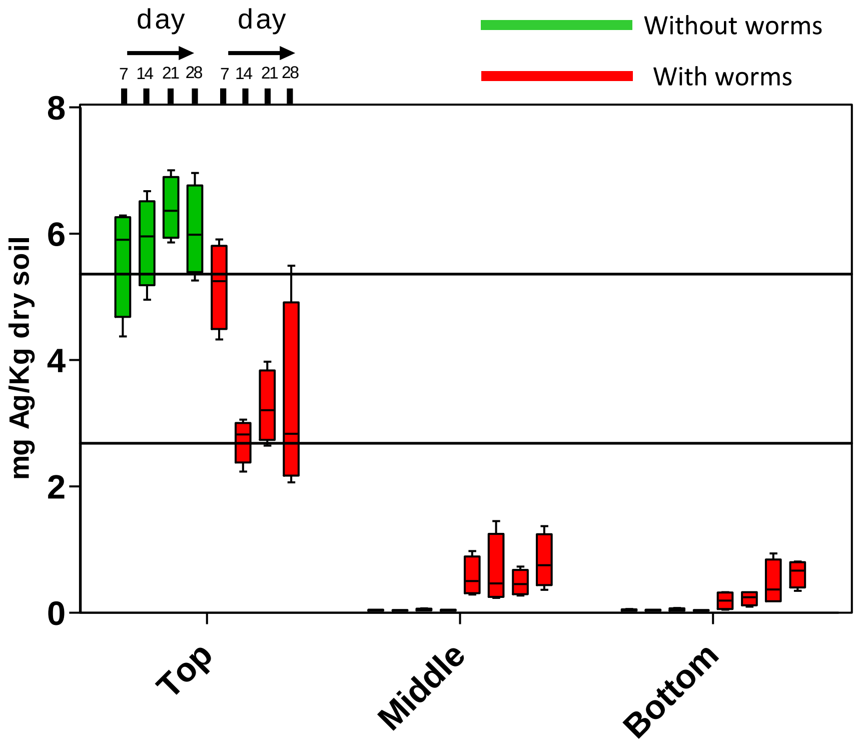
Sampling strategy

Analysis



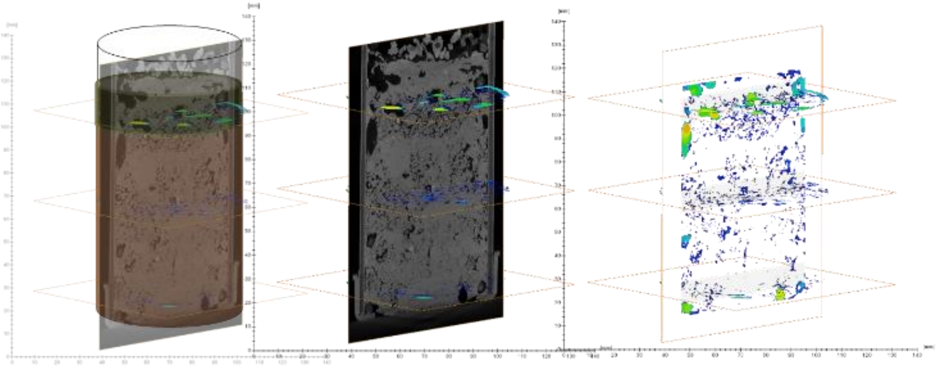
[Total-Ag]
ICP-MS

Results



Marta Baccaro

x ray computed tomography



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Baccaro, M. et al, submitted 2018

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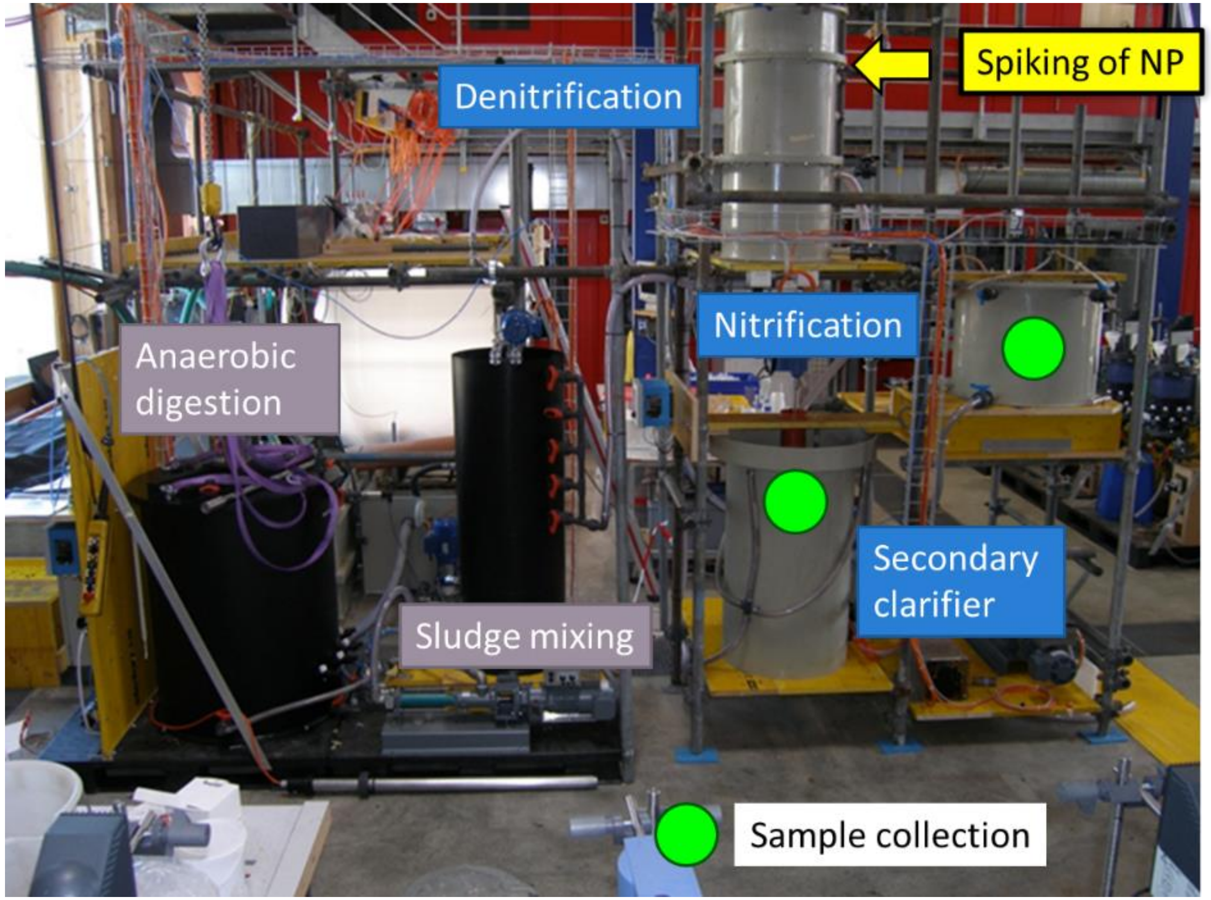
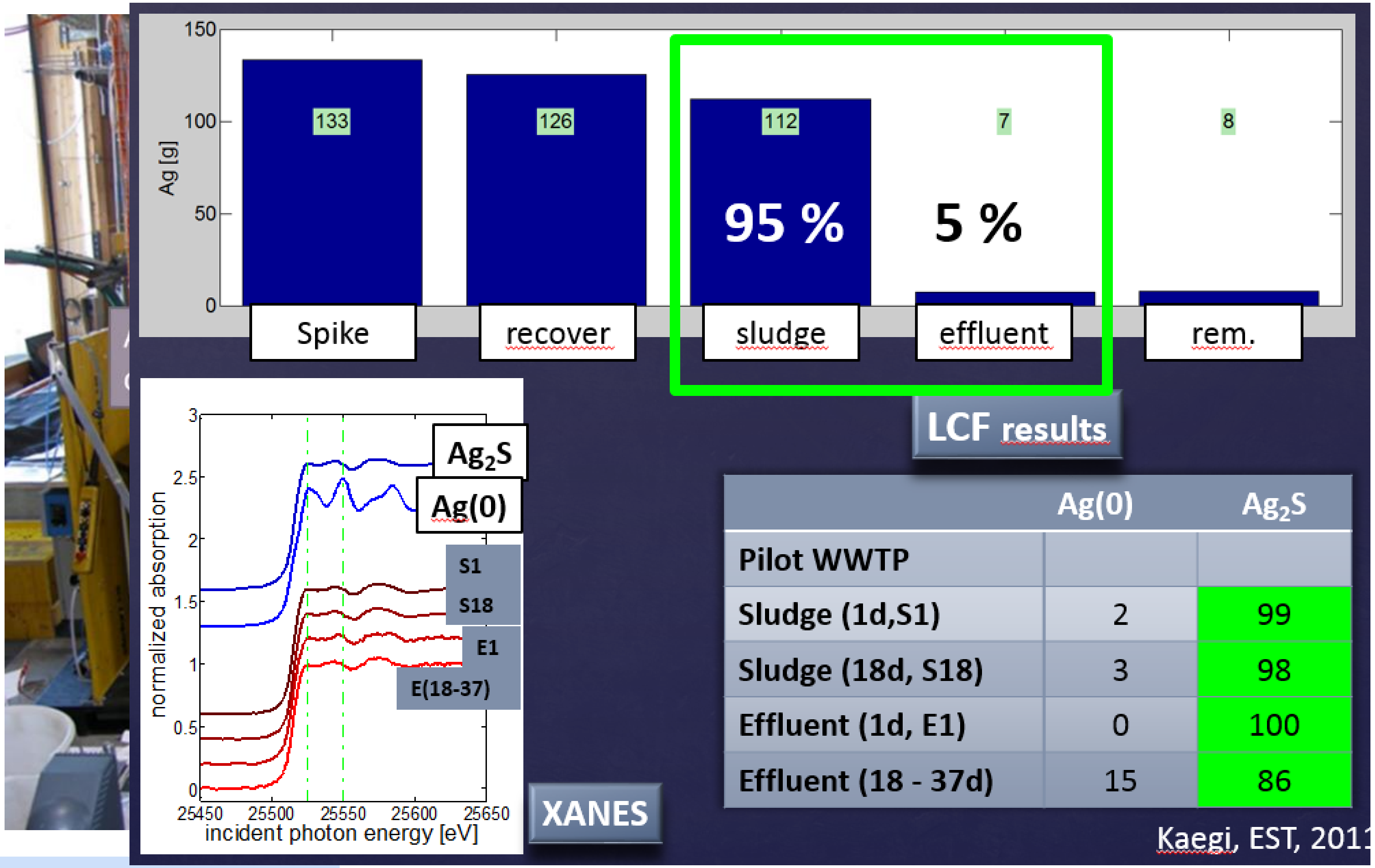
Exposure assessment what is released to environment?

Waste Water Treatment Plant



Exposure assessment what is released to environment?

Waste Water Treatment Plant – Ag and CuO NPs



	Ag(0)	Ag_2S
Pilot WWTP		
Sludge (1d,S1)	2	99
Sludge (18d, S18)	3	98
Effluent (1d, E1)	0	100
Effluent (18 - 37d)	15	86

eawag aquatic research

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Real world "Aged" sewage sludge NPs trials

Three sewage sludge streams

Control	Ionic	NP
	Zn + Ag	Zn + Ag

Zn limit:
2800 mg/kg

Equivalent Ag:
250 mg/kg

US EPA Guideline (CFR 40 part 503)

Sludge

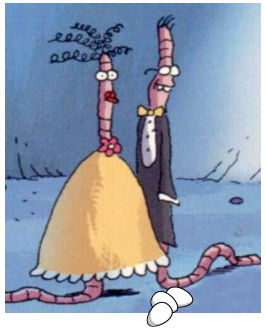
Control SS | Ionic SS | NP SS

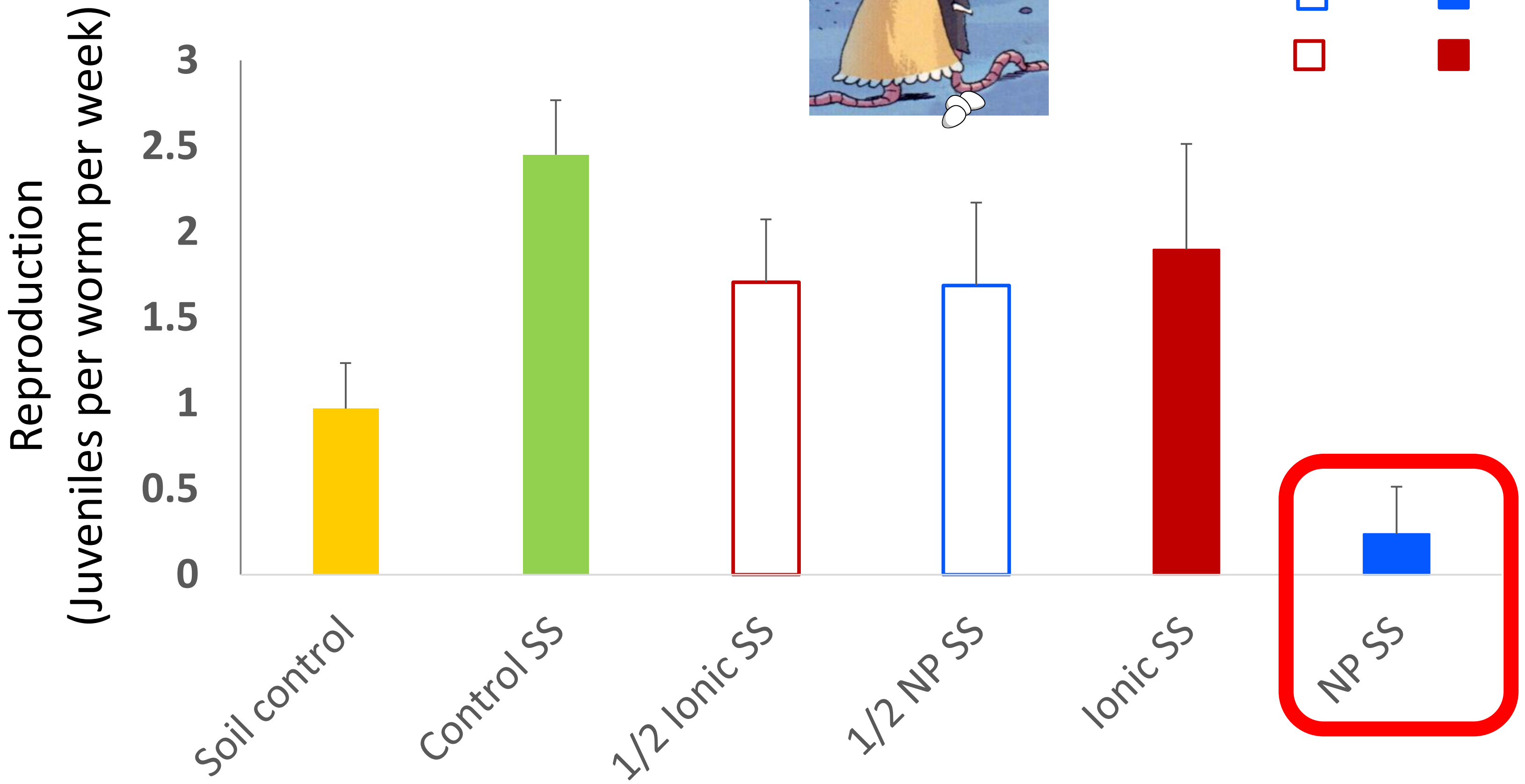
- Mixed with soil to Max. Zn loading from sewage sludges in US soils = **1400 mg Zn/kg**
- **Aged 6months in outdoor mesocosms**

Effects on earthworm reproduction

6-month aged SS

10 years of yearly SS application



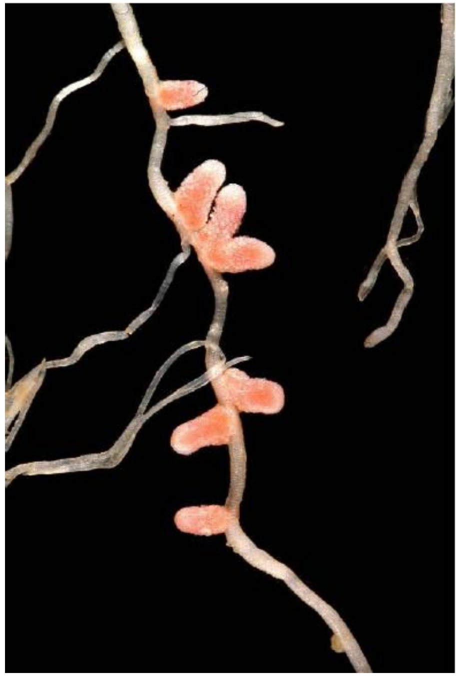


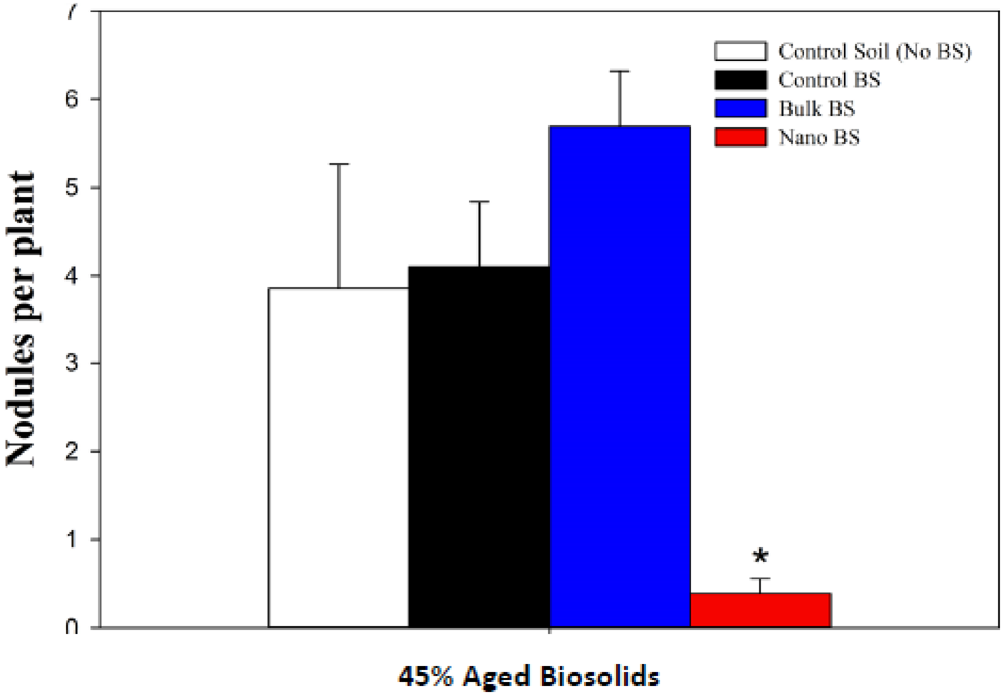
NOTE: US collaborators found the same effect pattern for plants!

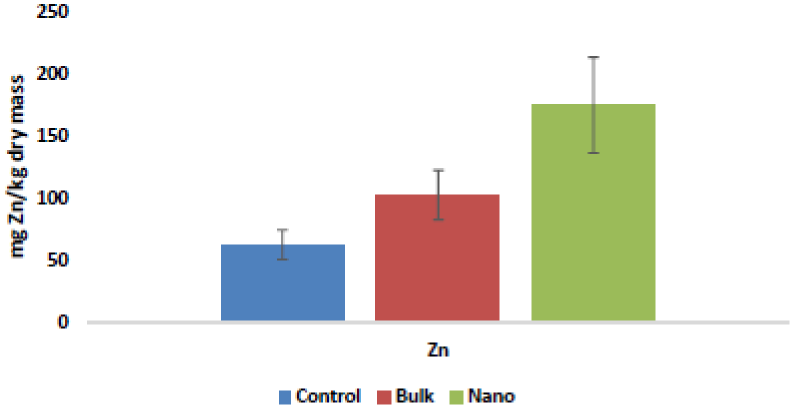
Elma Lahive

Effects on Clover nodulation

Medicago Nodulation (Legume N-acquisition)



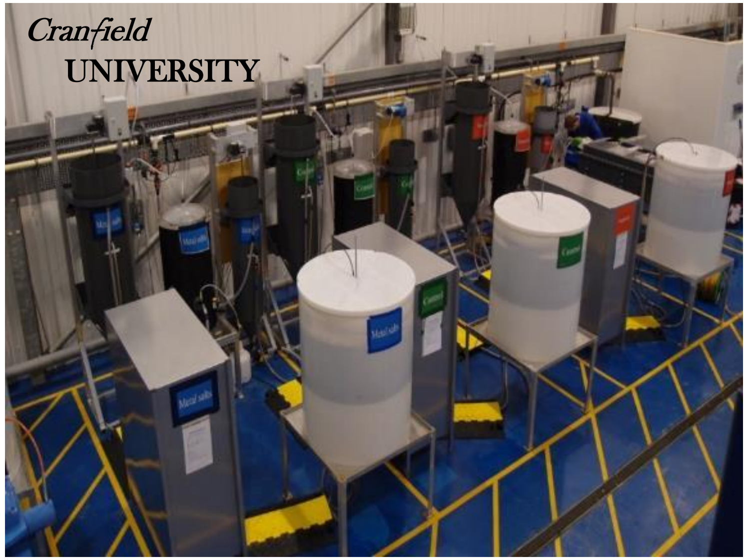




Judy, J. et. al. (2015) ES&T 49 (14)

Real world “Aged” sewage sludge NPs trials

Question: What is different when metals arrive as NP vs. ions?



- **Three sewage sludge streams:** Control, Ionic and NP
- No Zn Speciation difference and no ZnO left