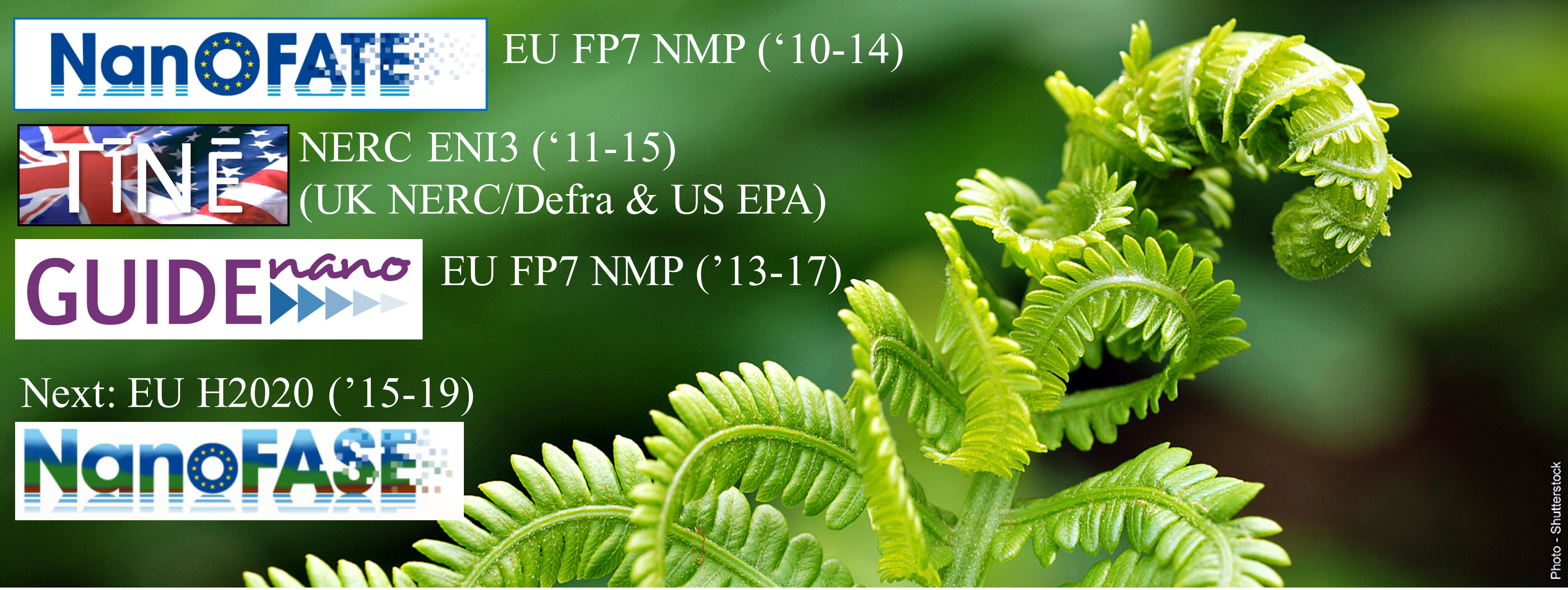


Modelling Environmental release and Nano Exposure

Claus Svendsen[1], Richard Williams[1], Ralf Kägi[2]

[1]NERC-CEH, Wallingford, United Kingdom
[2]Eawag, Zurich, Switzerland

Fate and Exposure models for you - www.nanofase.eu

Consortium
41 partners (incl. 4 Swiss partners and 7 Non European Collaborative Partners), 11 work packages, 17 countries

Budget
11,3 M€ – EC contribution: 10 M€

Duration
Sept. 2015 – Aug. 2019

Website
www.nanofase.eu

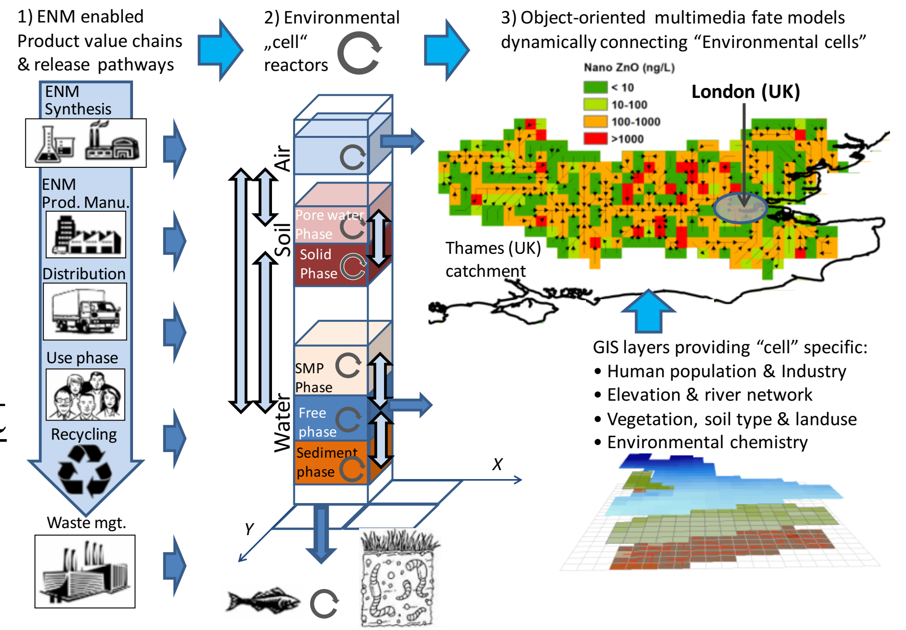
Project coordinator
Dr. Claus Svendsen, NERC, Wallingford, UK.
Email: nanofase@ceh.ac.uk
Tel: +44 (0)1491 692676

All about NM in the Environment

Where do they go?

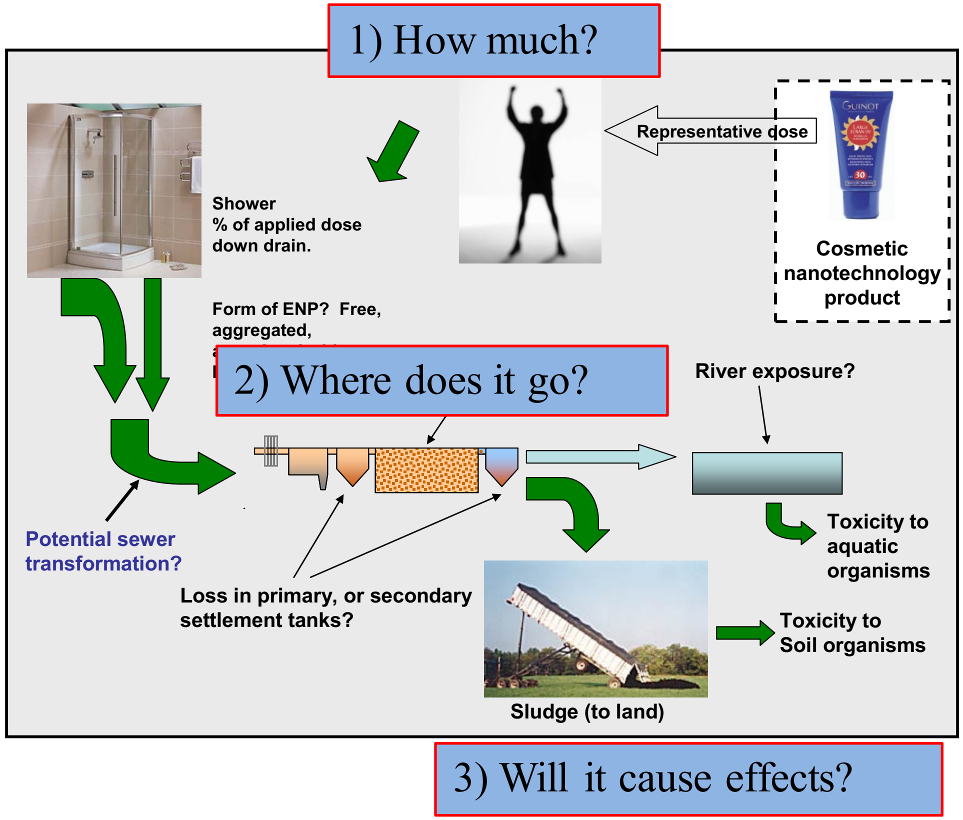
What do they turn in to?

How long does it take?



Conceptual workflow for a framework to deliver dynamic multimedia fate prediction both in a generalised model environment and GIS enabled mode.

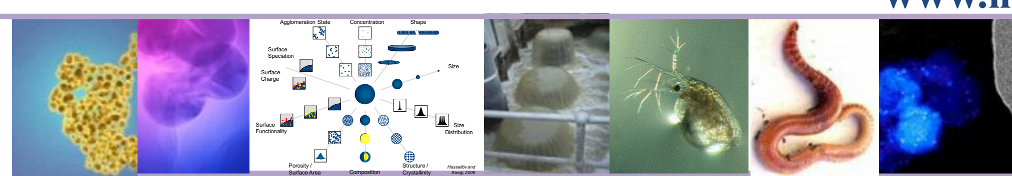
NanoFATE European scale framework



"Tools for mapping environmental risk across Europe from commercial nanoparticles used in consumer products"

www.nanofate.eu

NanOFATE

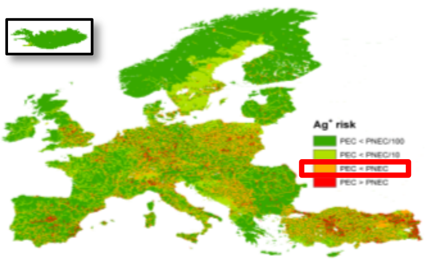


SEVENTH FRAMEWORK PROGRAMME

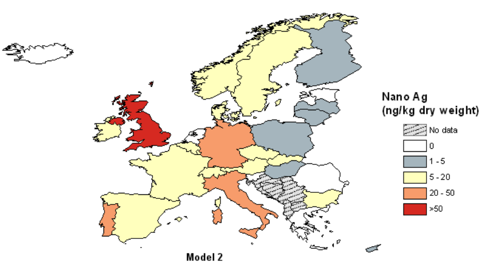
NanoFATE European scale framework

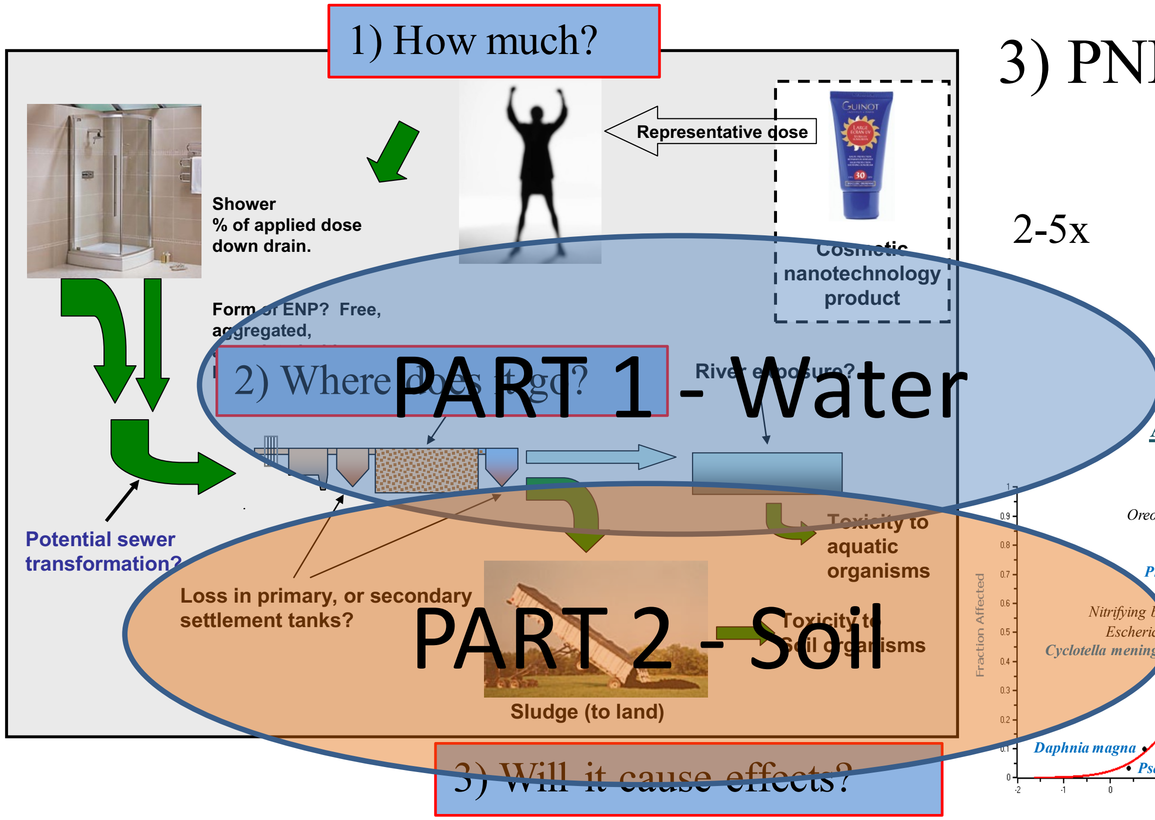
1) & 2) PECs:

Water:



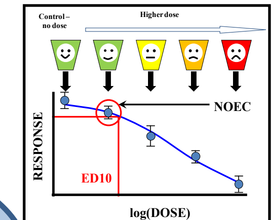
Soil:

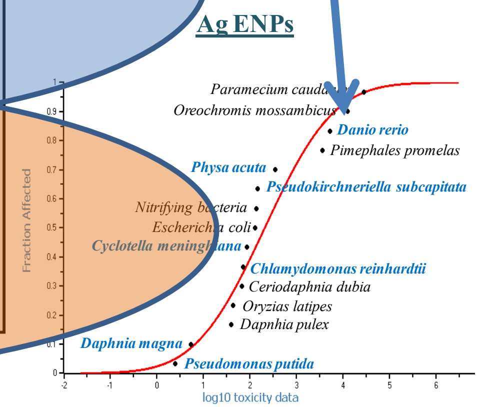




3) PNECs:

2-5x





"Tools for mapping environmental risk across Europe from commercial nanoparticles used in consumer products"

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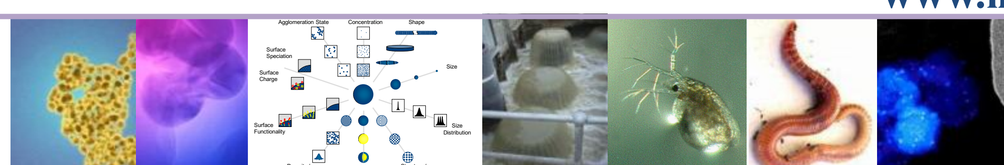
NanoFATE



SEVENTH FRAMEWORK PROGRAMME

WATER

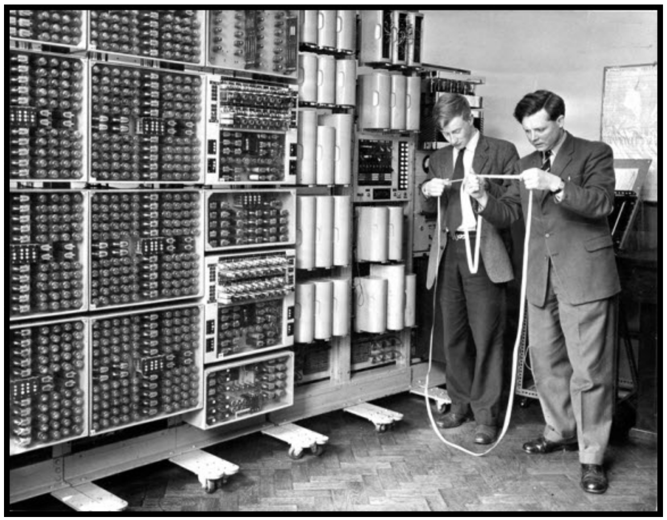
WATER: Standard worst case RA – 1) Exposure

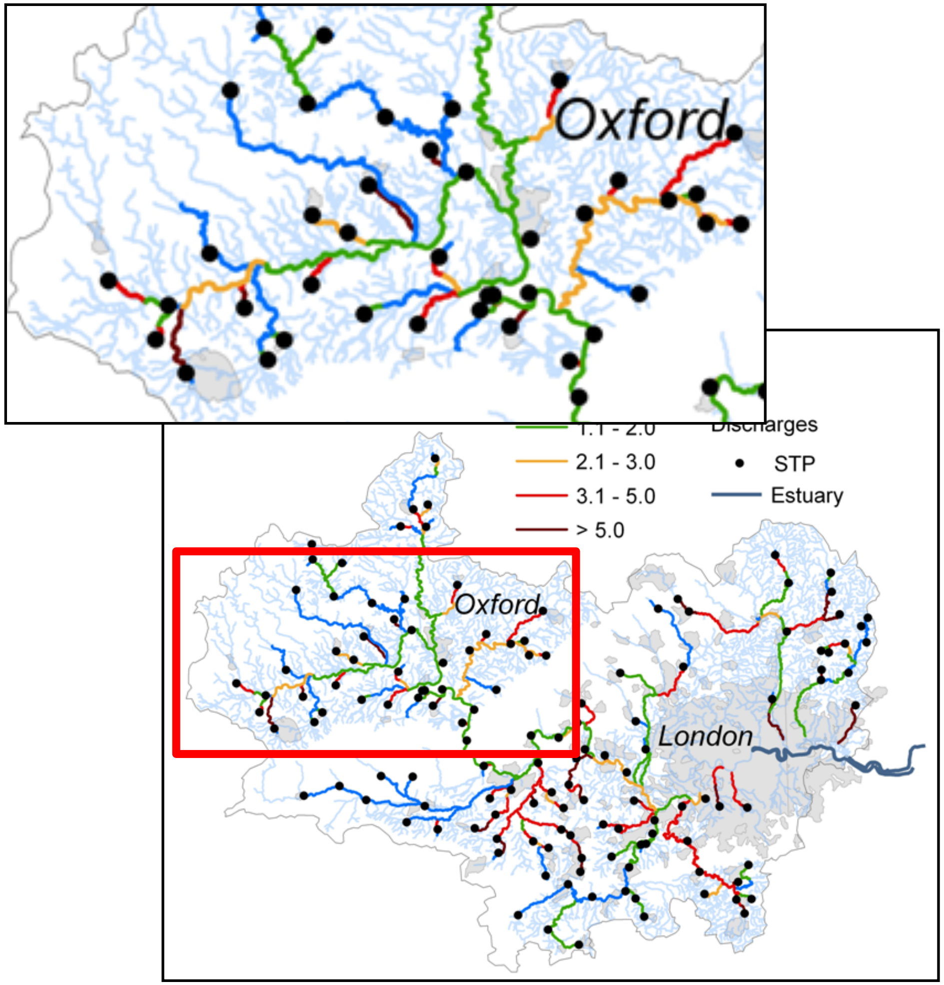
PEC derivation:

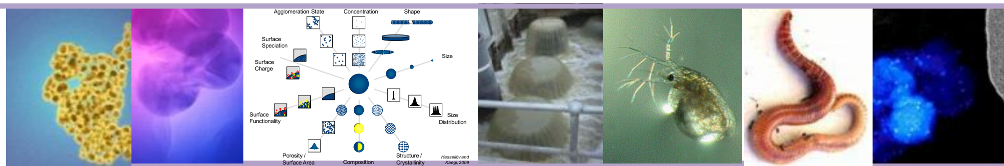
Along 1.2 million km of EU rivers

Assumptions:

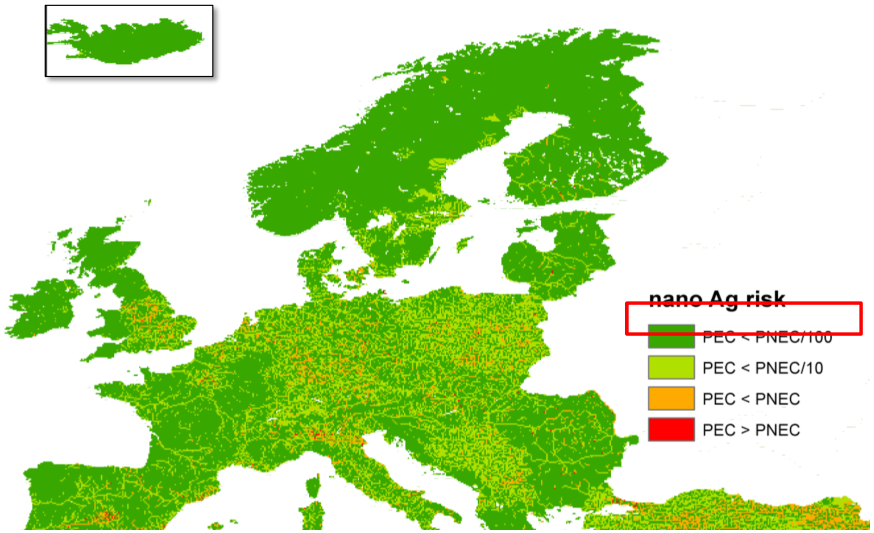
- *Estimated actual production volumes for EU27*
  (Piccino et al., 2012 J Nanopart Res 14:1109-1120)
- *Even use EU wide (also NO point sources)*
- ***No WWTP removal** or "in river sedimentation"*

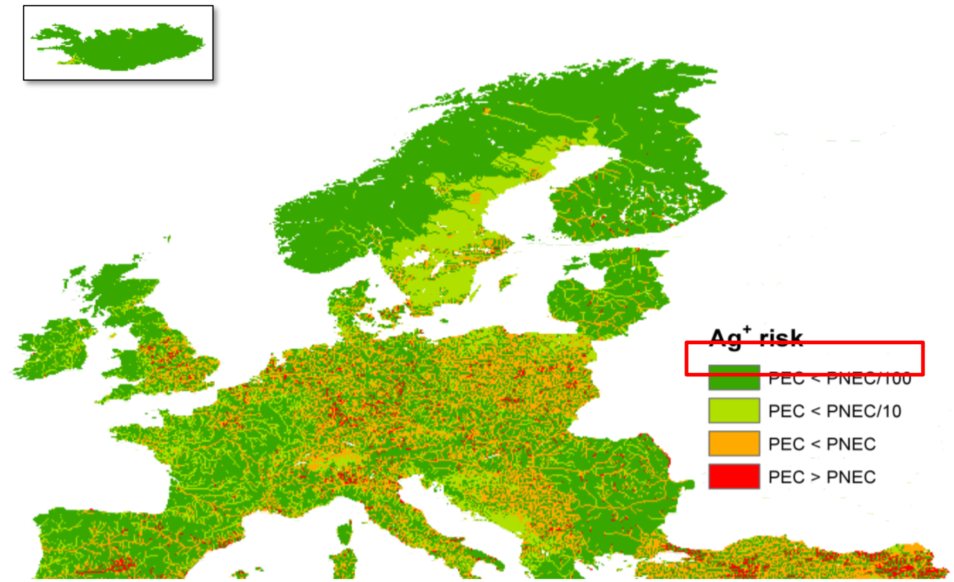






European Ag NP vs. Ionic risk map (PEC/PNEC)





Ag NP PNEC = 168 ng/L ***Ag+ PNEC = 26 ng/L***

Combining worst case 90%ile (no WWTP loss and no in-stream loss) PEC with *HC5 (safety factor of 5)*

- So as Ag^+ ions are more toxic than NPs, then either:

1. There will be a nano Ag problem in EU waters, or
2. Using "standard worst case" is to simple! ***What else to include?***

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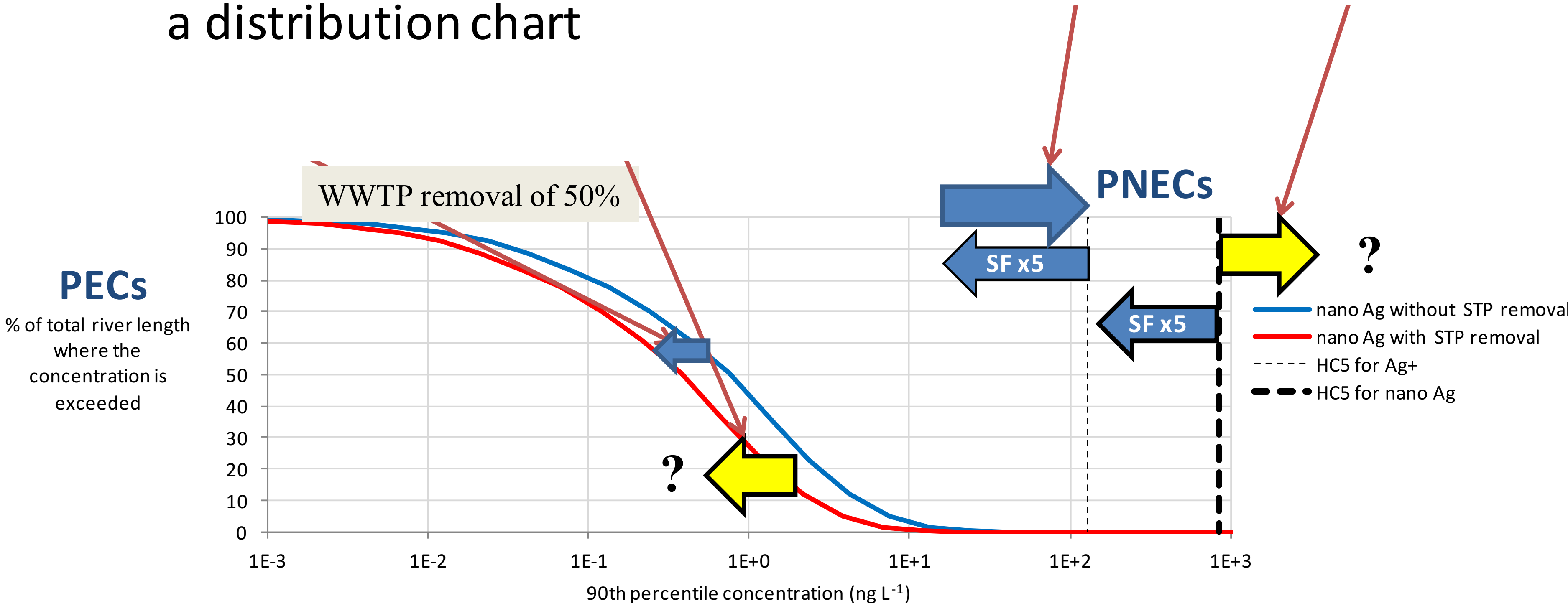
SEVENTH FRAMEWORK PROGRAMME

Water: Nano improvements for worst case RA

PEC derivation:

PNEC derivation:

Turn the map into
a distribution chart



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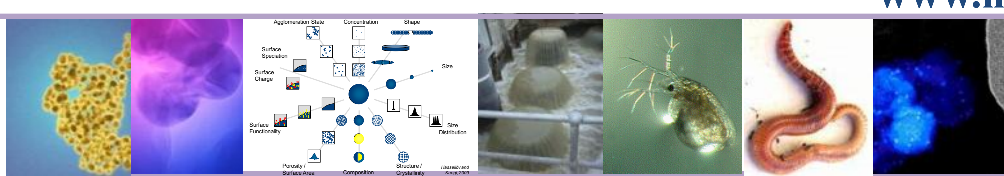


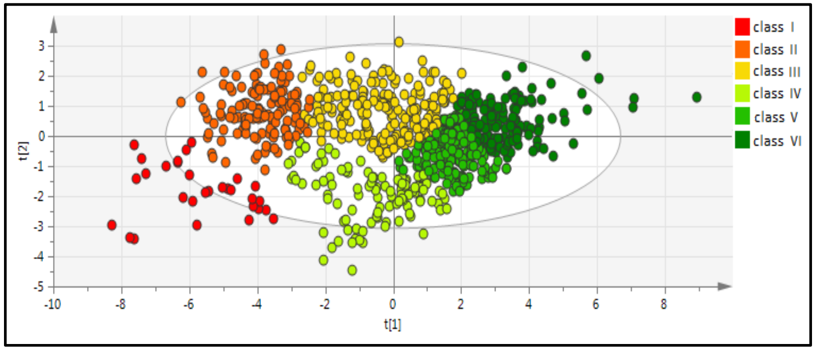
SEVENTH FRAMEWORK PROGRAMME

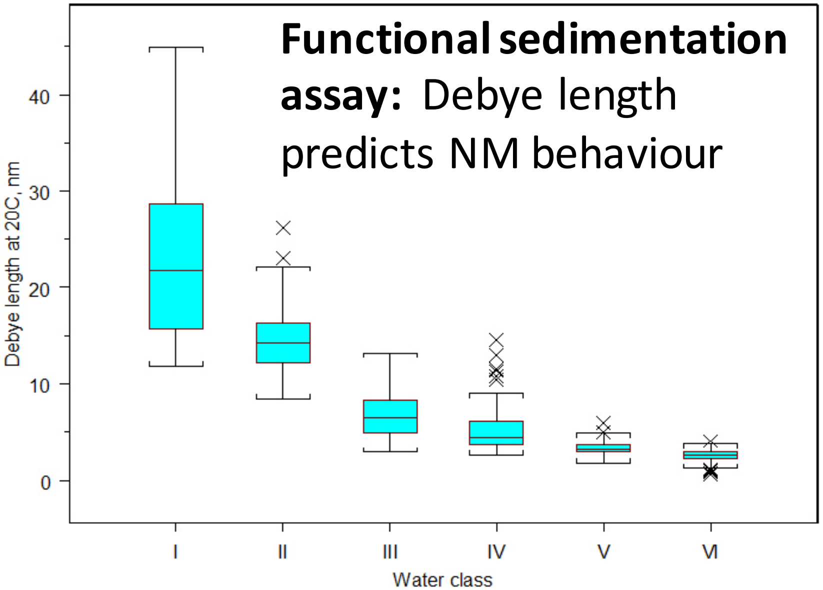
Modelling “availability” across EU Water types

PEC improved by addressing NM “fate” & “functional behaviour” across “media” in detail (equally PNEC studies needs to be linked to “media effects” on hazard potential).

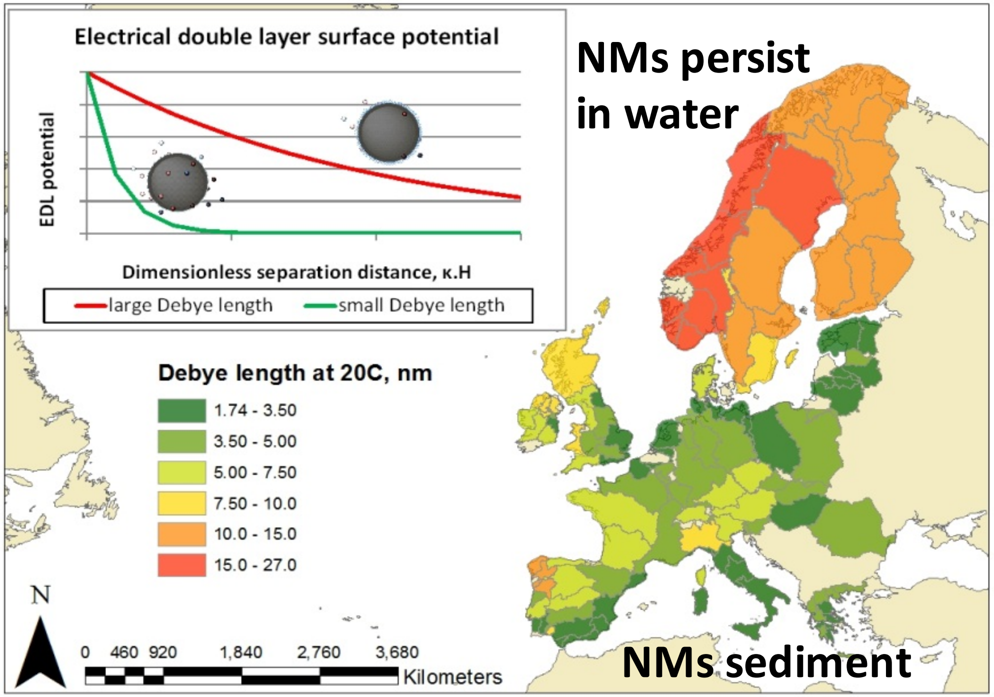
STANDARDISATION IS NOT ALL!

- Analysed EU water properties relevant for NP fate (e.g. ionic strength, pH, CEC, DOC,....)





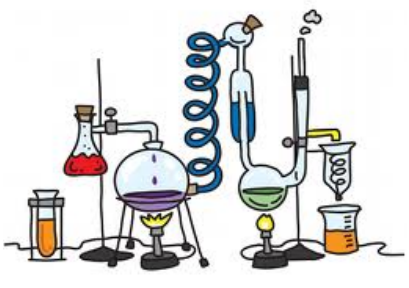
Debye length calculations
(electrostatic screening, modified by ionic strength)



Julia Hammes, Julian Gallego and Martin Hassellöv Water Research, 2013.

Effect of aging transformations on particle Tox

- **Particles artificially aged to mimic post WWTP speciation**



Standard C elegans test:

- In moderately hard reconstituted water
- 24h Mortality test with / without food

Treatments:

- Control
- Ionic control Ag^+ Pristine PVP Ag NP
- Artificially "Aged" sulfurdised Ag NP

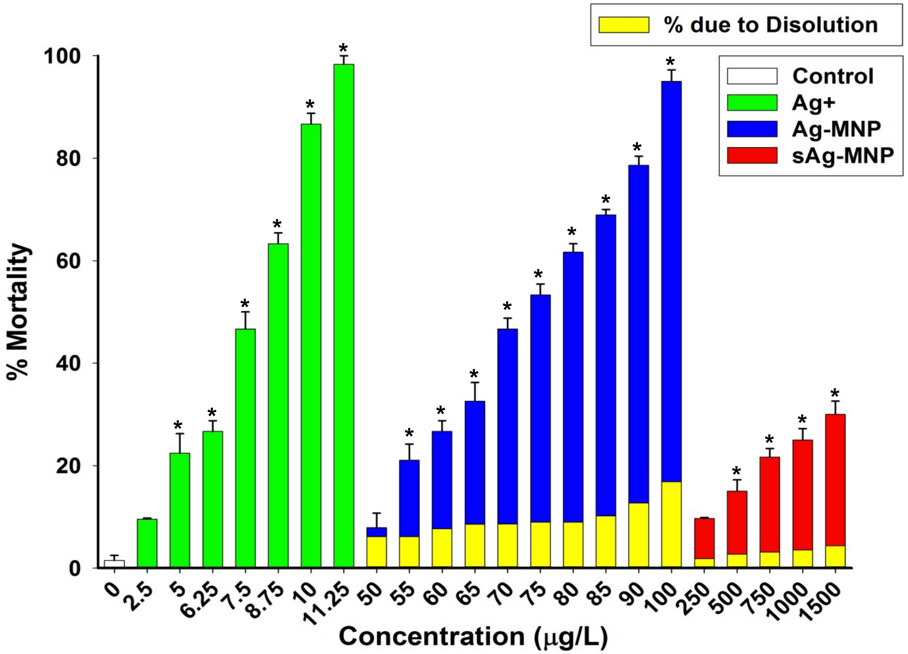
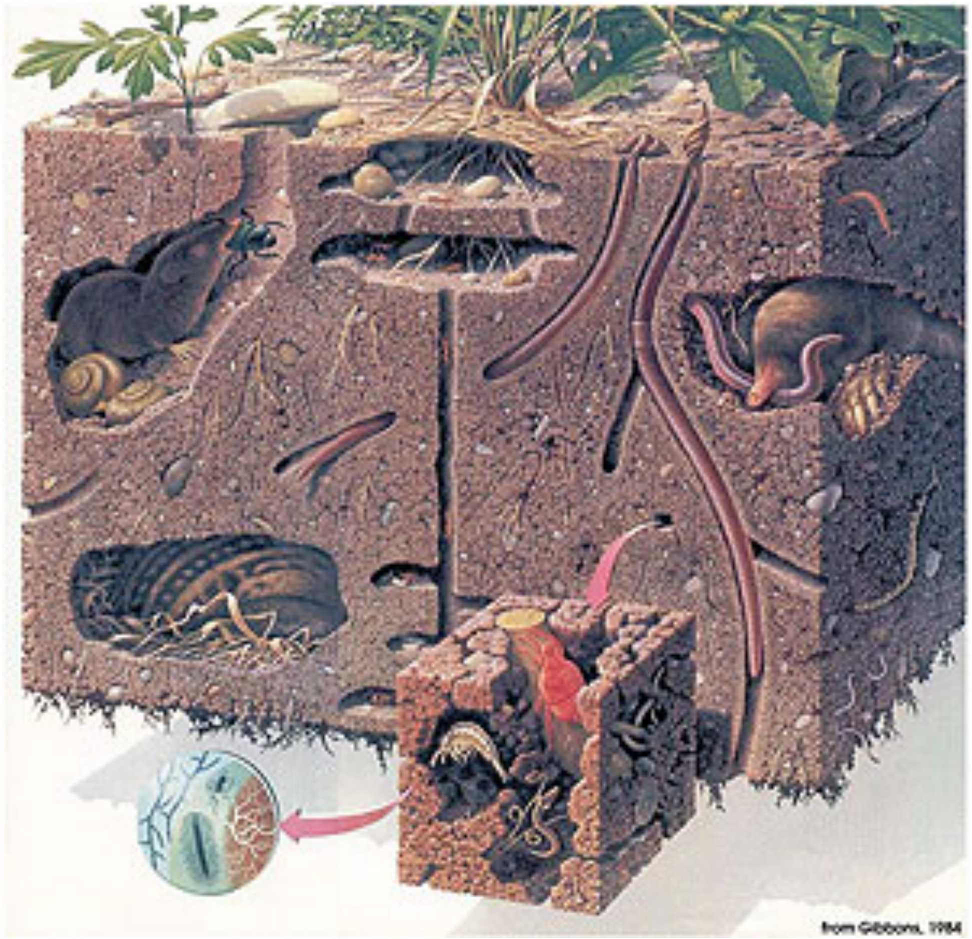


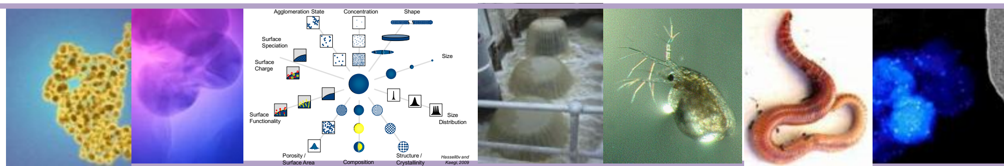
Figure 1. ***C. elegans*** **mortality after their exposure to Ag^+, Ag-MNPs and sAg-MNPs in Recon for 24h without feeding. Yellow area represents amount of mortality due to dissolution of Ag^+. * indicates significantly different than control ($p < 0.001$)**

- < 20% of mortality attributed to free Ag^+ in experiments without feeding
- Genes expression in Ag-MNP and sAg-MNP had more in common than either did with Ag^+

Daniel Starnes: "Sliver Nanoparticles get better with age"

SOIL





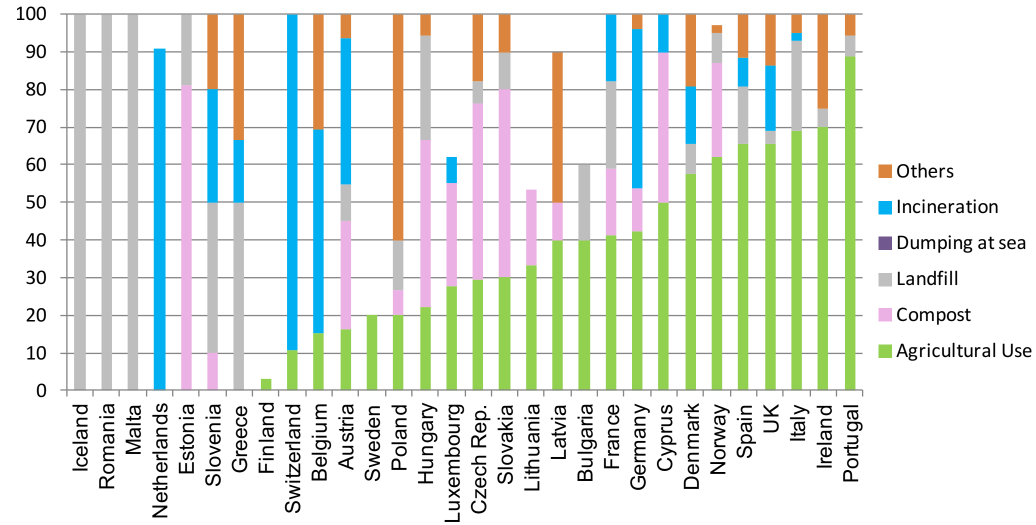
SOILS: Standard worst case RA

PEC derivation:

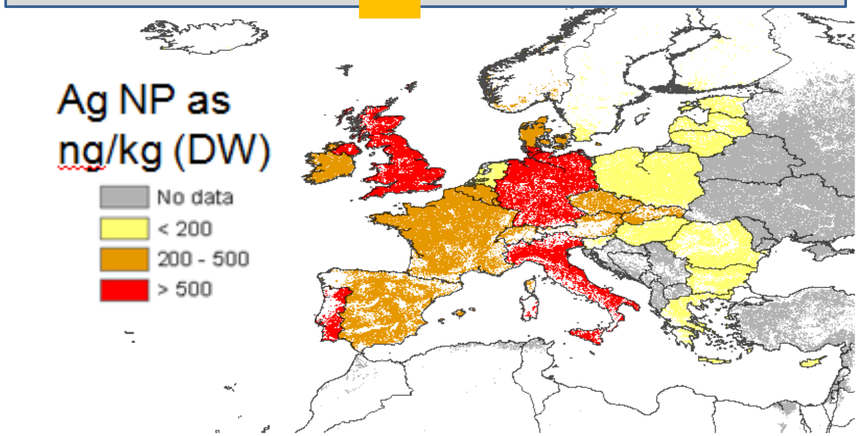
Where does the WWTP sludge go

Assumptions:

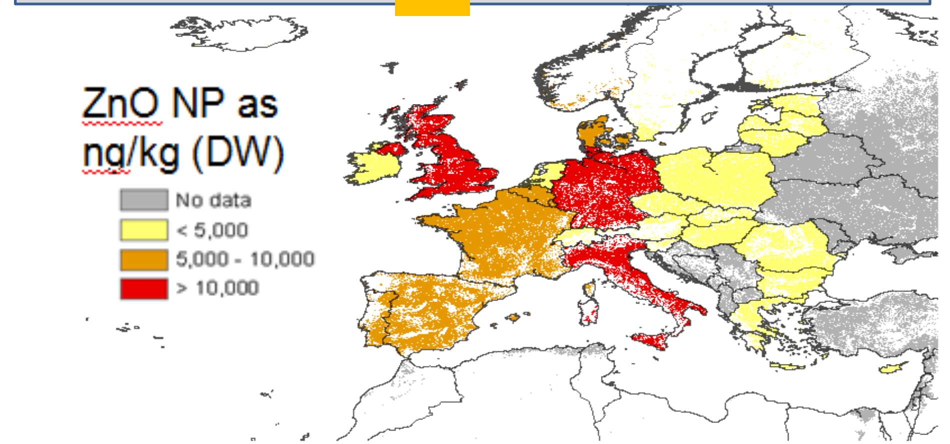
- *Estimated actual production volumes for EU27 (Piccino et al., 2012)*
- *Even use EU wide (NO point sources)*
- ***NOW: <u>Full</u> WWTP removal to sludge***



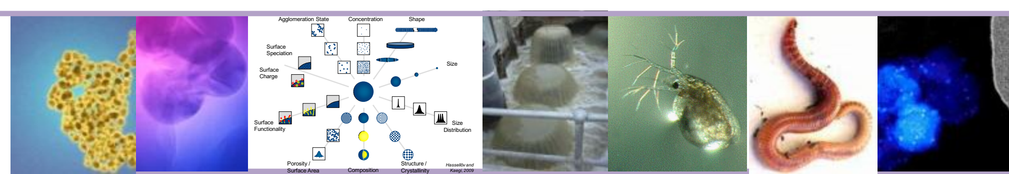
Ag NP – Max PEC = ? µg/kg (single app, UK)



ZnO NP – Max PEC = ? µg/kg (single app, UK)



NanOFATE



SEVENTH FRAMEWORK PROGRAMME

TINE – "real world" and long term in the field

The Transatlantic Initiative for Nanotechnology and the Environment

Sludge production at Cranfield University, UK

Three sewage sludge streams

Control	Ionic	NP
	Zn + Ag	Zn + Ag

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**

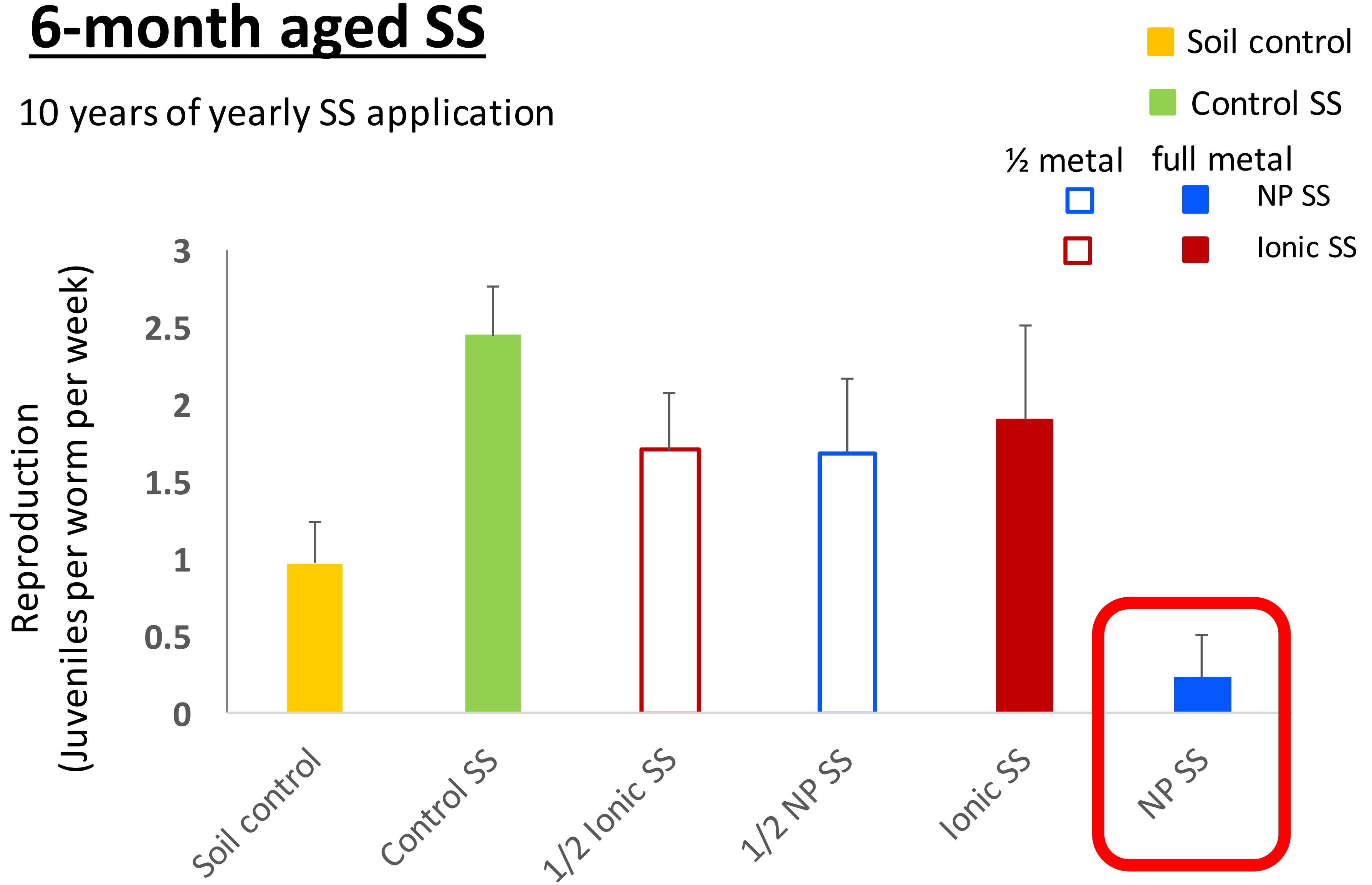
Zn limit:
2800 mg/kg
↓
Equivalent Ag:
250 mg/kg

US EPA Guideline (CFR 40 part 503)

Effects on earthworm reproduction

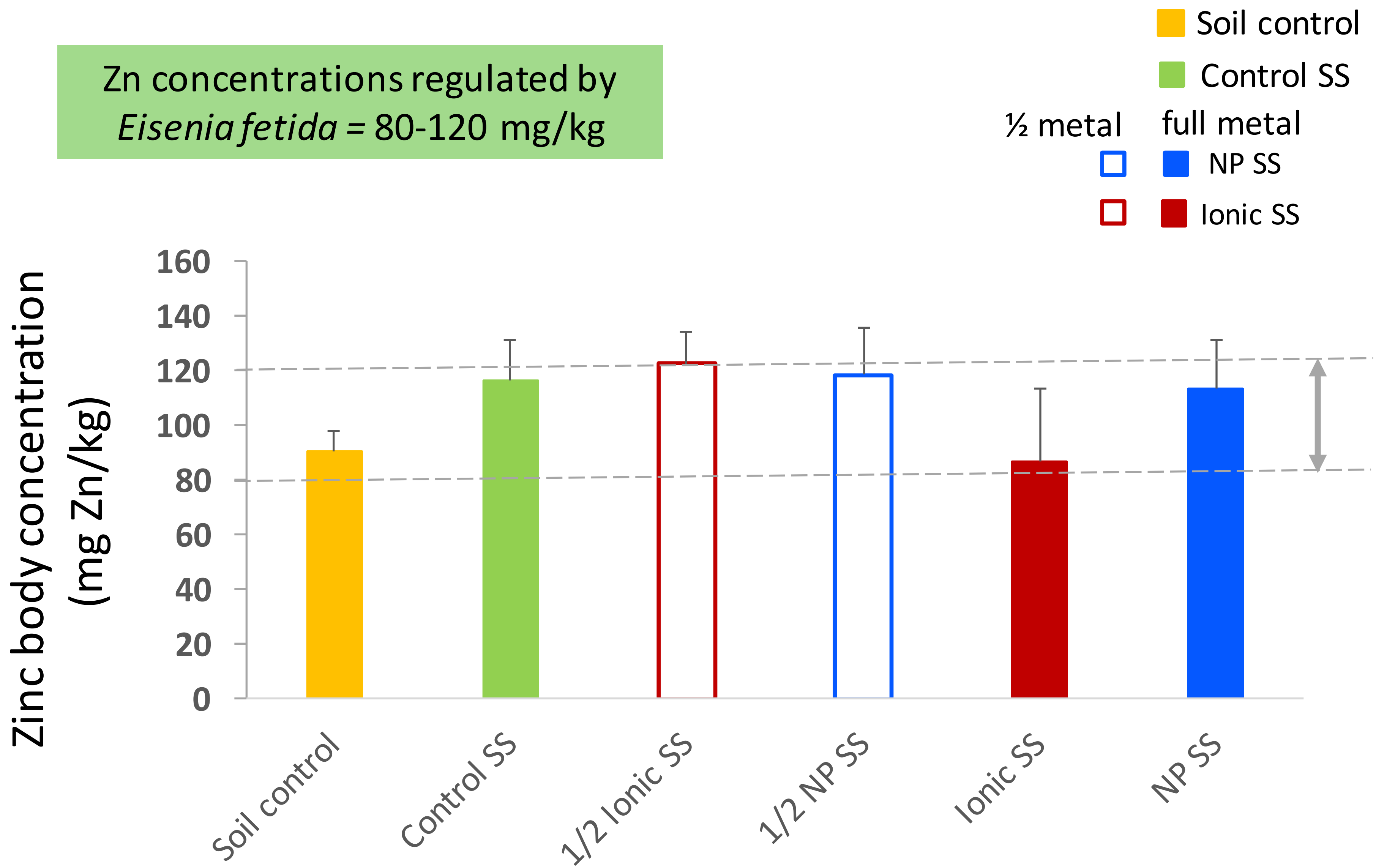
6-month aged SS

10 years of yearly SS application

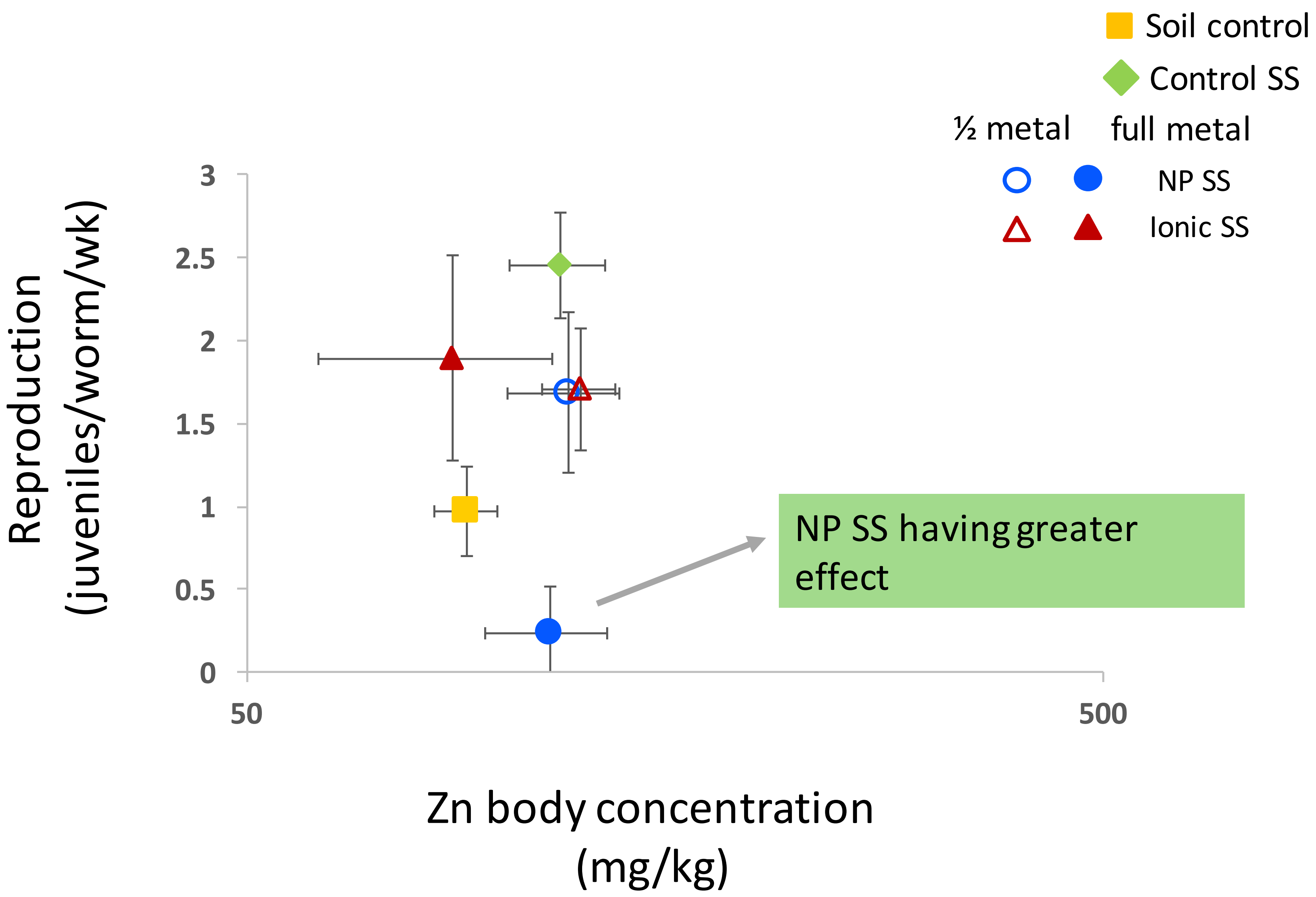


Earthworm body concentration

Zn concentrations regulated by *Eisenia fetida* = 80-120 mg/kg

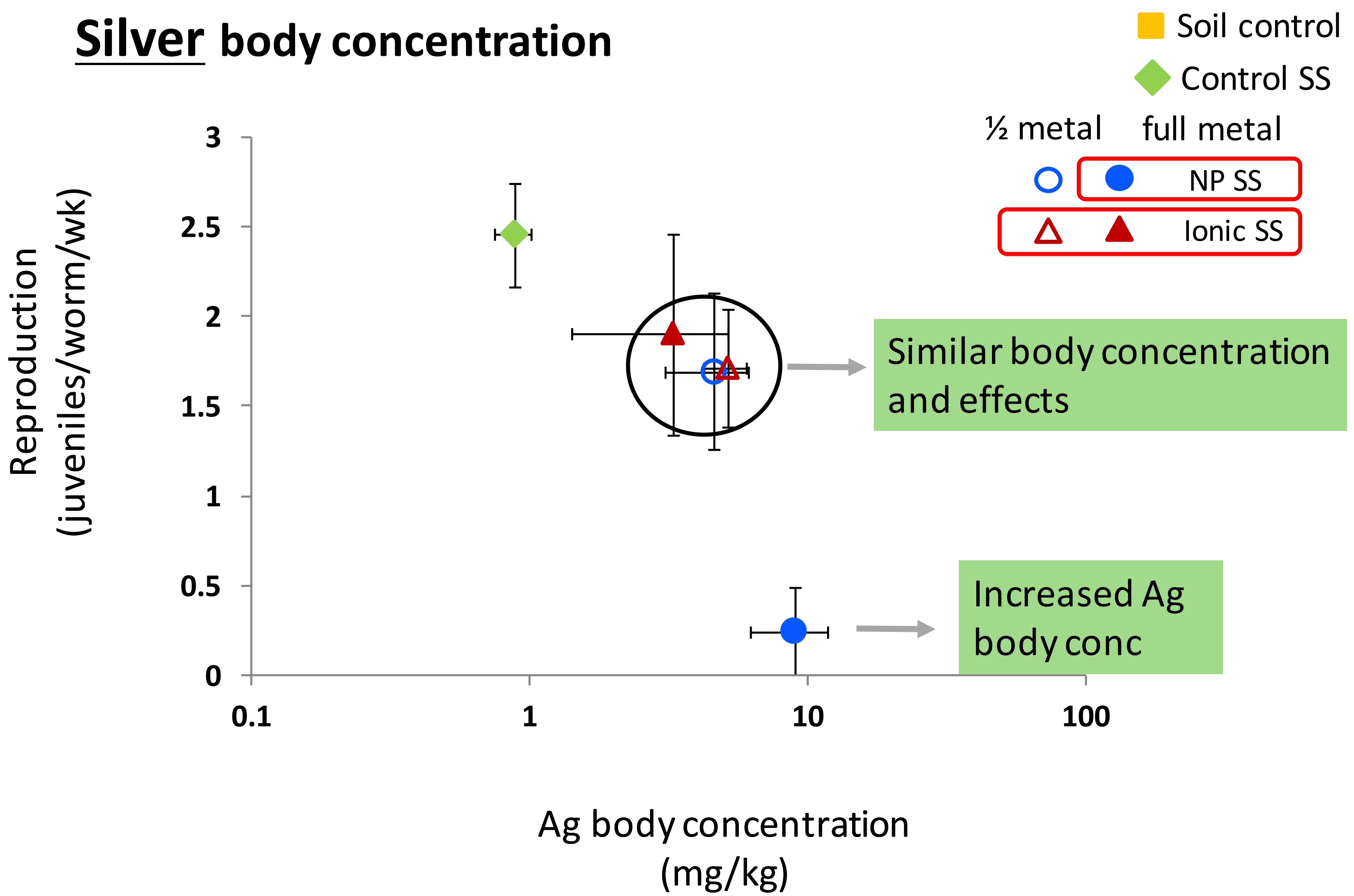


Reproduction + Earthworm body concentration

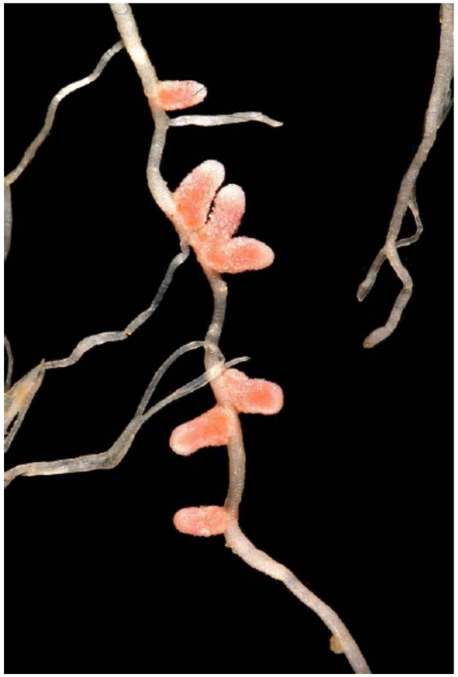


Earthworm body concentration

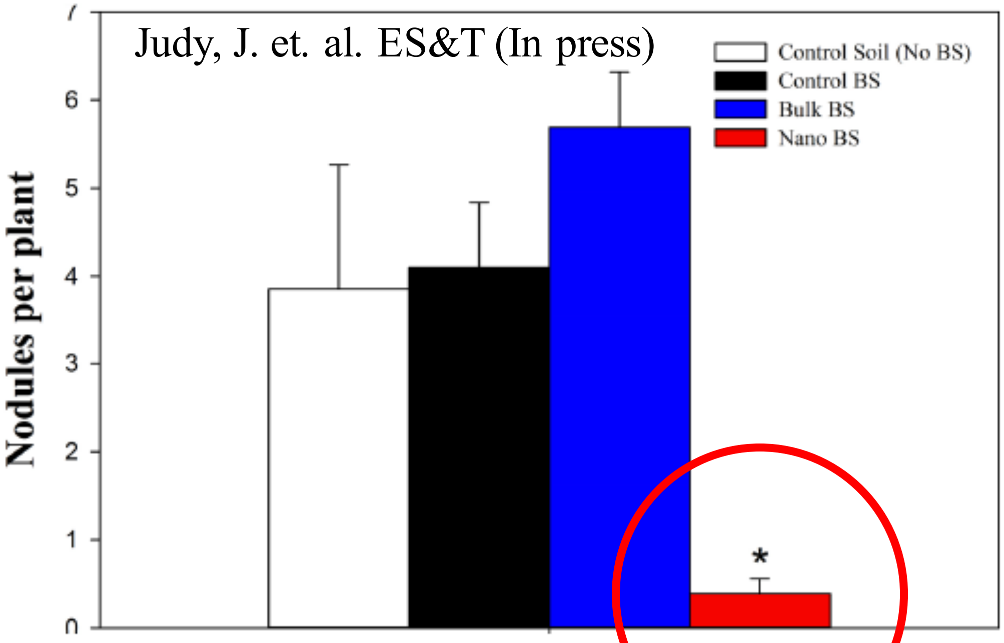
Silver body concentration

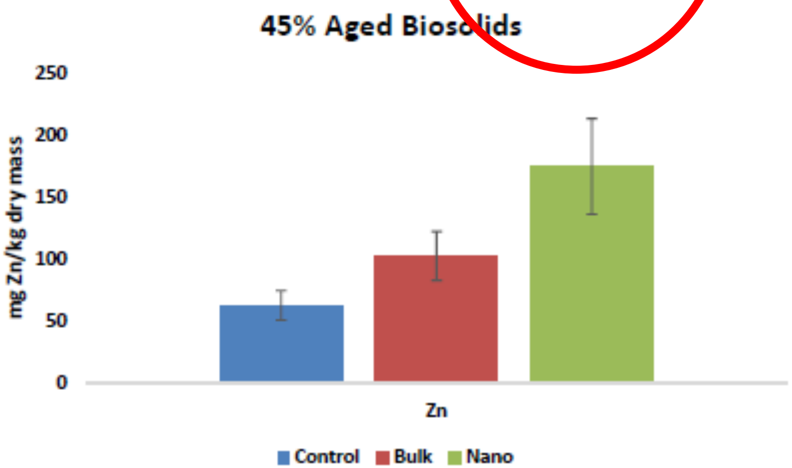


Effects on Medicago Nodulation



Medicago Nodulation (Legume N-acquisition)





So what is different about the metal from NP?

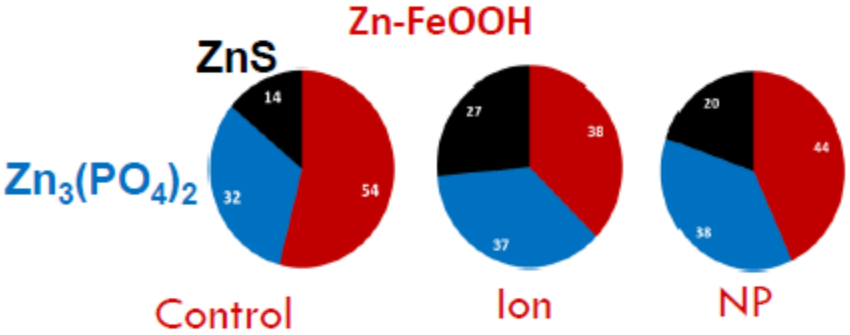
Question: What "difference" caused the SS metals to be more toxic?

Synchrotron speciation work by Greg Lowry and Jason Unrine's groups:

Pilot WWTP:

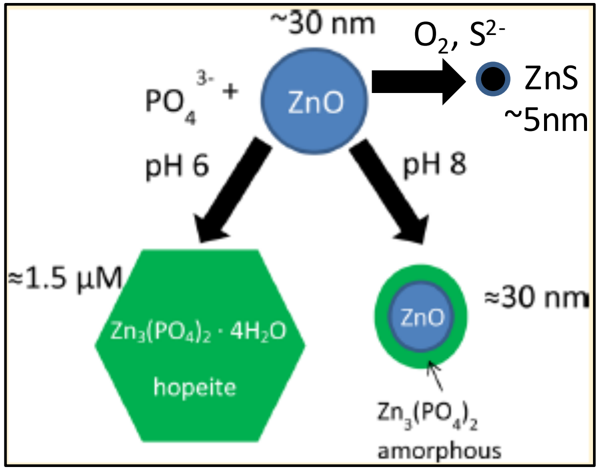
No ZnO left and

no overall Zn Speciation difference



Lab reactions:

Big differences in the detail



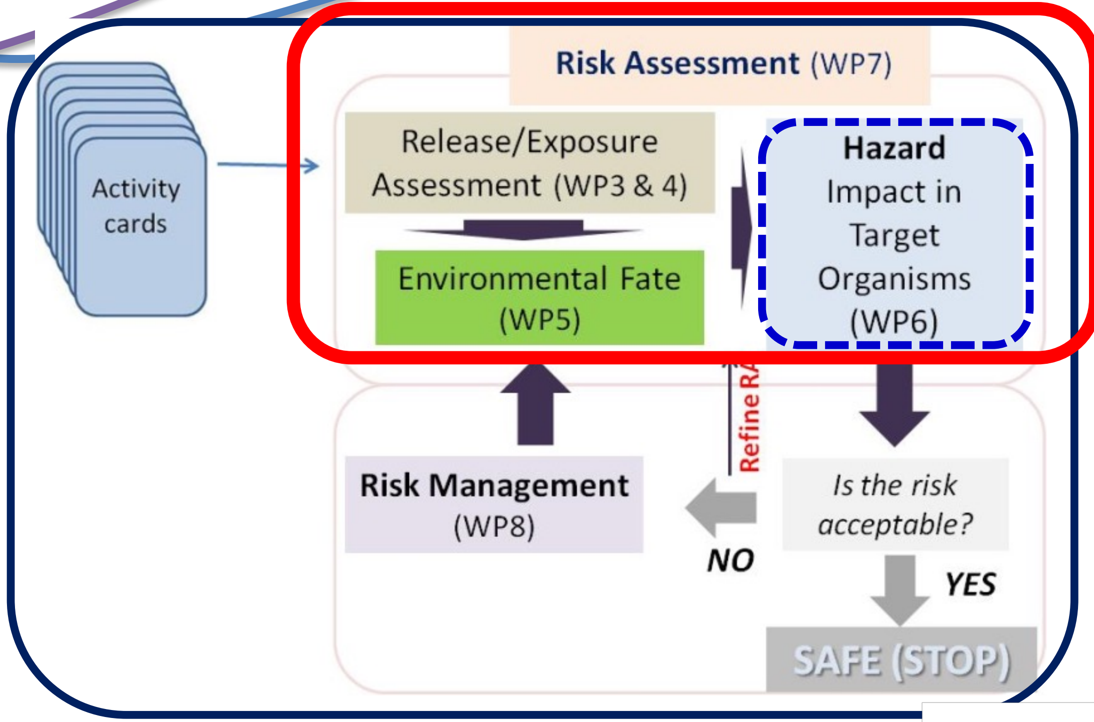
Characterisation in soilds:

Zn: no overall difference / Ag: <LOD

Mechanistic Lab experiments:

Understand reactions and rates

-> effects on fate and tox



Aim: to generate Exposure and Hazard estimates using as much of existing data and methods as possible.

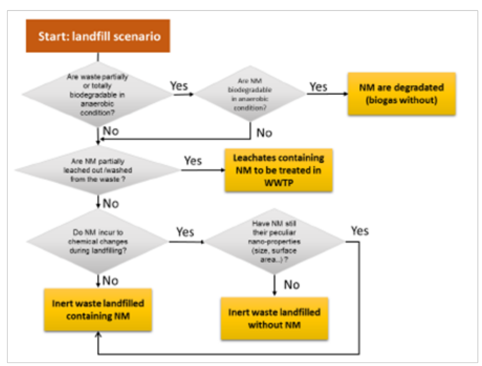
Predictive models, data & assumptions

$Ag^{+}_{tox} > Ag^{PVP}NP_{tox} > AgSNP_{tox}$

High dissolution => high ion tox

etc, etc

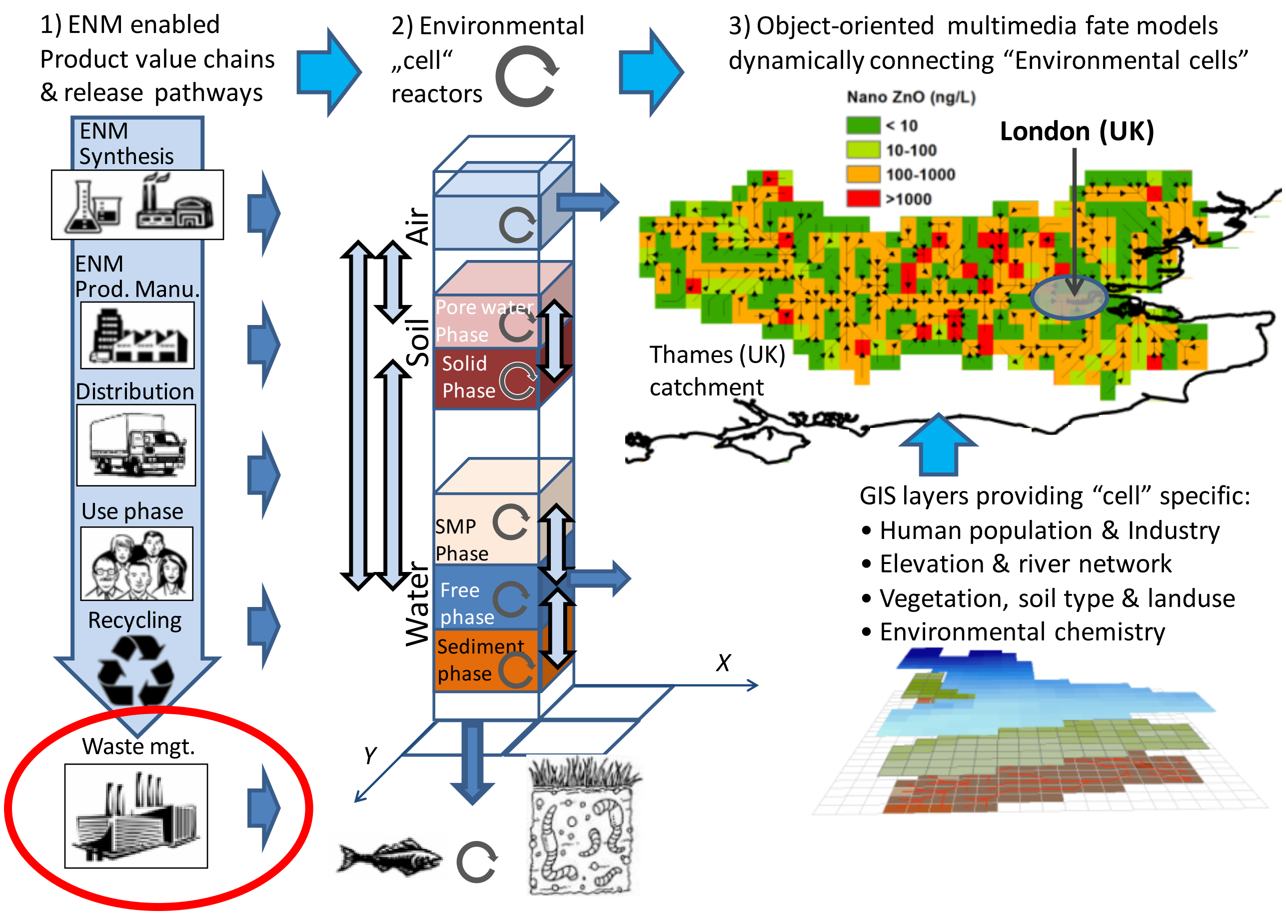
Decision-trees



Decision tables

	Data entry question or decision table	Answer	Action	DNEL	Uncertainty
1	Are there regulatory binding or provisional OELs/DNELs for the exposure relevant test material?	Yes	go to 2		
		No	go to 3		
2	Which is the OELs/DNELs value:	DNEL_VALUE	DNEL is defined. Finish.	Is DNELinh, long-term	llow
3	Are there valid inhalation studies with the exposure relevant test material or a similar one?	Yes	go to 4		
		No	go to 7		
4	Launches decision tree on relevance of test	Valid inhalation study	go to 5	defined in test relevance table	defined in test relevance table
		Not valid inhalation study	go to 7		

NM behaviour and fate is key, but hard to measure.
Build better models for: Where, in what form and for how long?



Conceptual workflow for a framework to deliver dynamic multimedia fate prediction both in a generalised model environment and GIS enabled mode.

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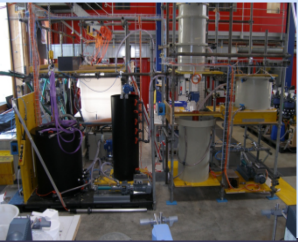
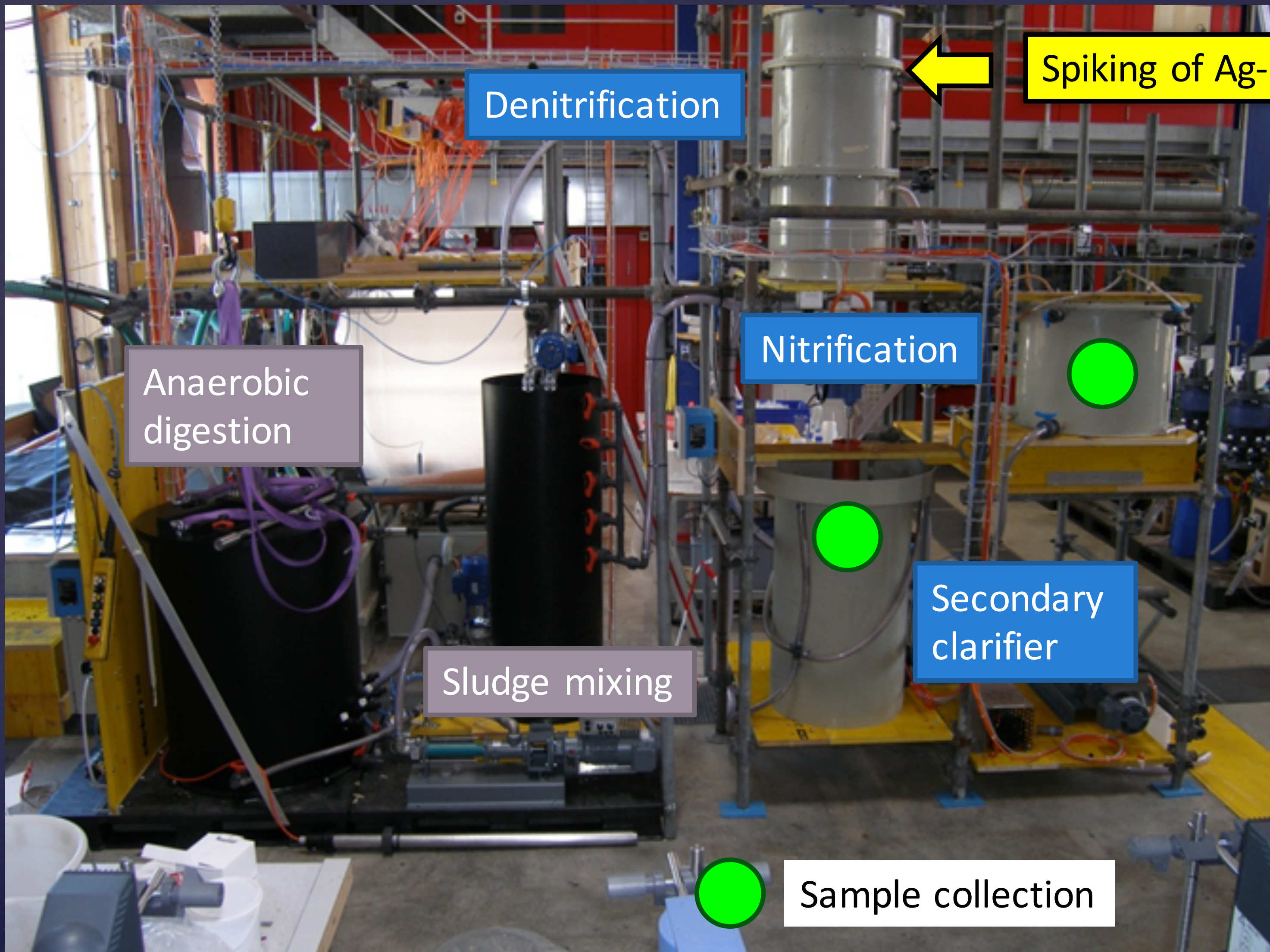
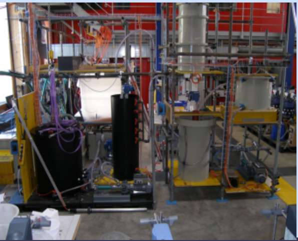


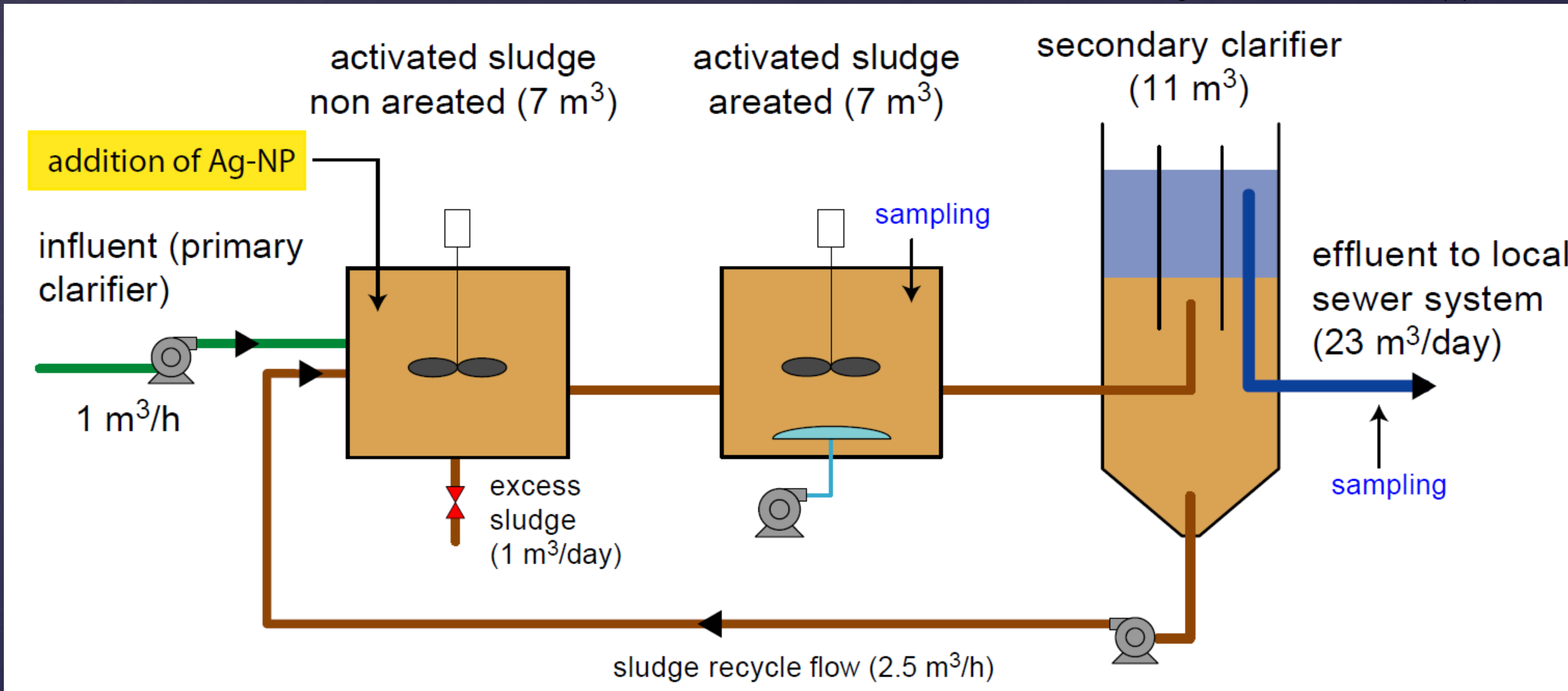
The WWTP: 'dynamic' experiments





Schematic WWTP

Kaegi et al, ES&T, 2011, 45(9):3902-8



Hydraulic retention time	Sluge age	pH	T	O2	TSS (ML)	TSS (effluent)
1 days	14 day	7.4 – 7.5	21 °C	3 mg/L	3g/L	5mg/L

Setting up a mass balance

V

Ag_{in}

Ag_{out}^{eff}

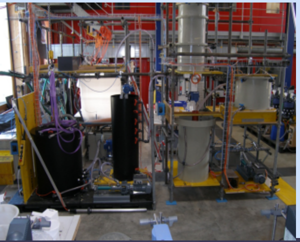
Ag_{out}^{sludge}

$$\frac{\Delta m_{Ag}}{\Delta t} = \frac{m_{Ag}^{in}}{\Delta t} - \frac{m_{Ag}^{out}}{\Delta t}$$

$$= c_{Ag}^{in} \cdot Q^{in} - c_{Ag}^{out} \cdot Q^{out} \quad ; \; c_{Ag}^{out} = \frac{m_{Ag}(t)}{V} \cdot Q^{out}$$

$$\frac{dm_{Ag}}{dt} = A + B \cdot m_{Ag}(t)$$

→ Differential equation



Ag-NP in a WWTP

eawag aquatic research

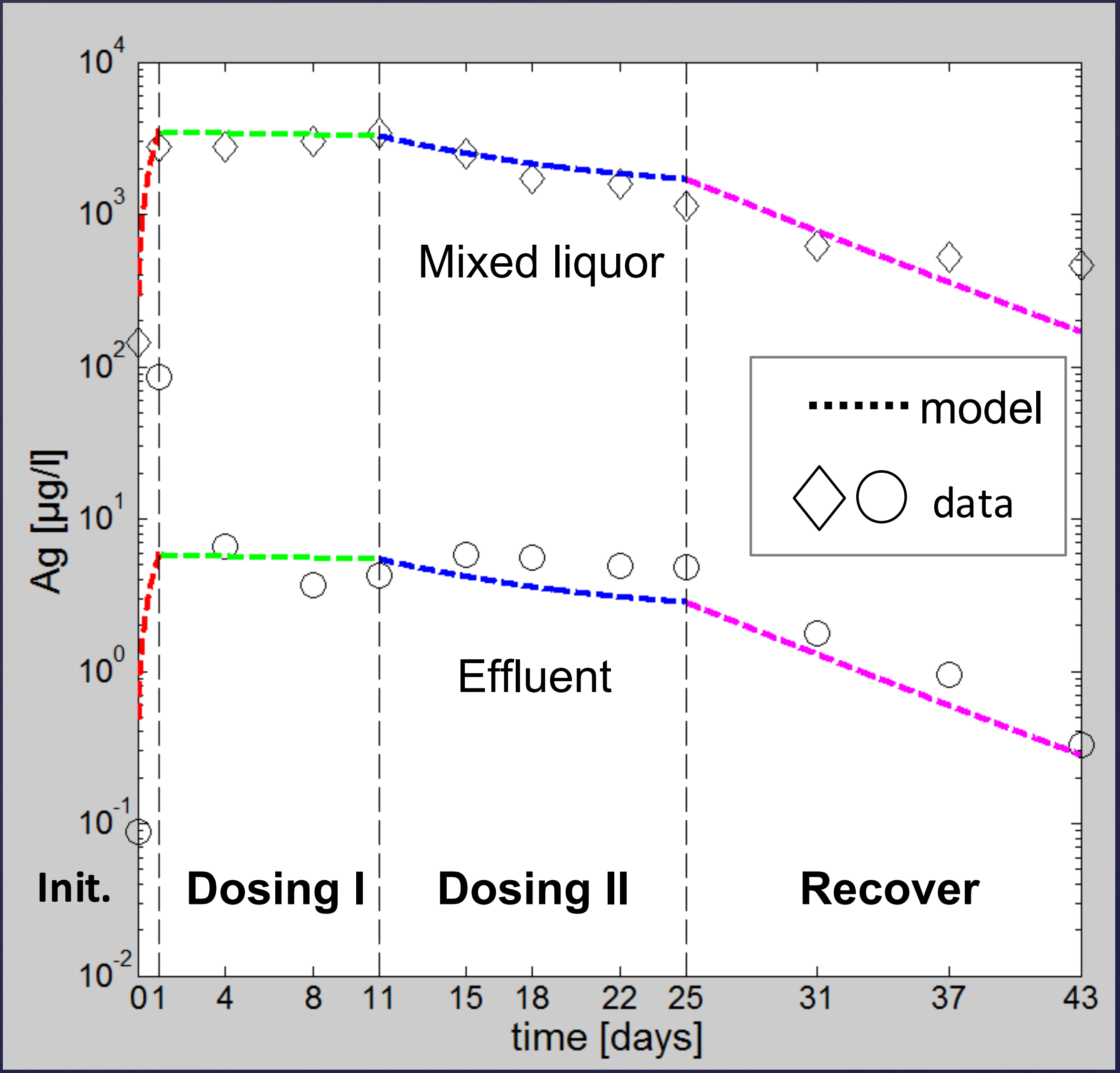
NanoFASE

Initial spike
(1day, 2400µg/l)

Dosing I
10days, 130µg/l, 1m3/d

Dosing II
10days, 130µg/l, 2.2m3/d

Recover
24days, no Ag added

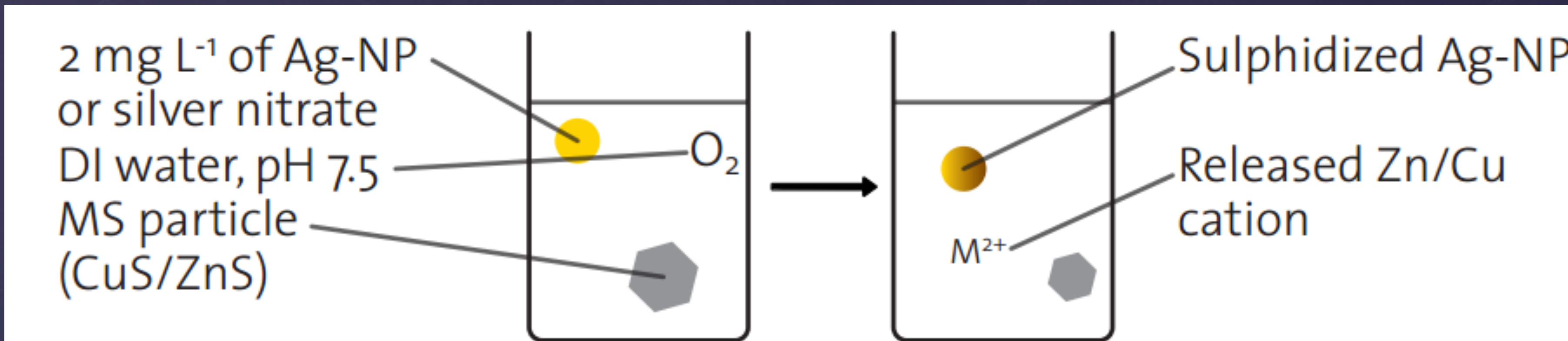


Kaegi et al, 2011, EST, 49/9, pp. 3902 - 3908

Experimental setup

eawag aquatic research

NanoFASE



$$2Ag_{(s)} + \frac{1}{2}O_{2(aq)} + 2H^{+}_{(aq)} + MS_{(s)} \rightarrow Ag_2S_{(S)} + H_2O_{(l)} + M^{2+}_{(aq)}$$

$$MS + 2O_{2(aq)} \rightarrow SO_4^{2-} + M^{2+}_{(aq)}$$

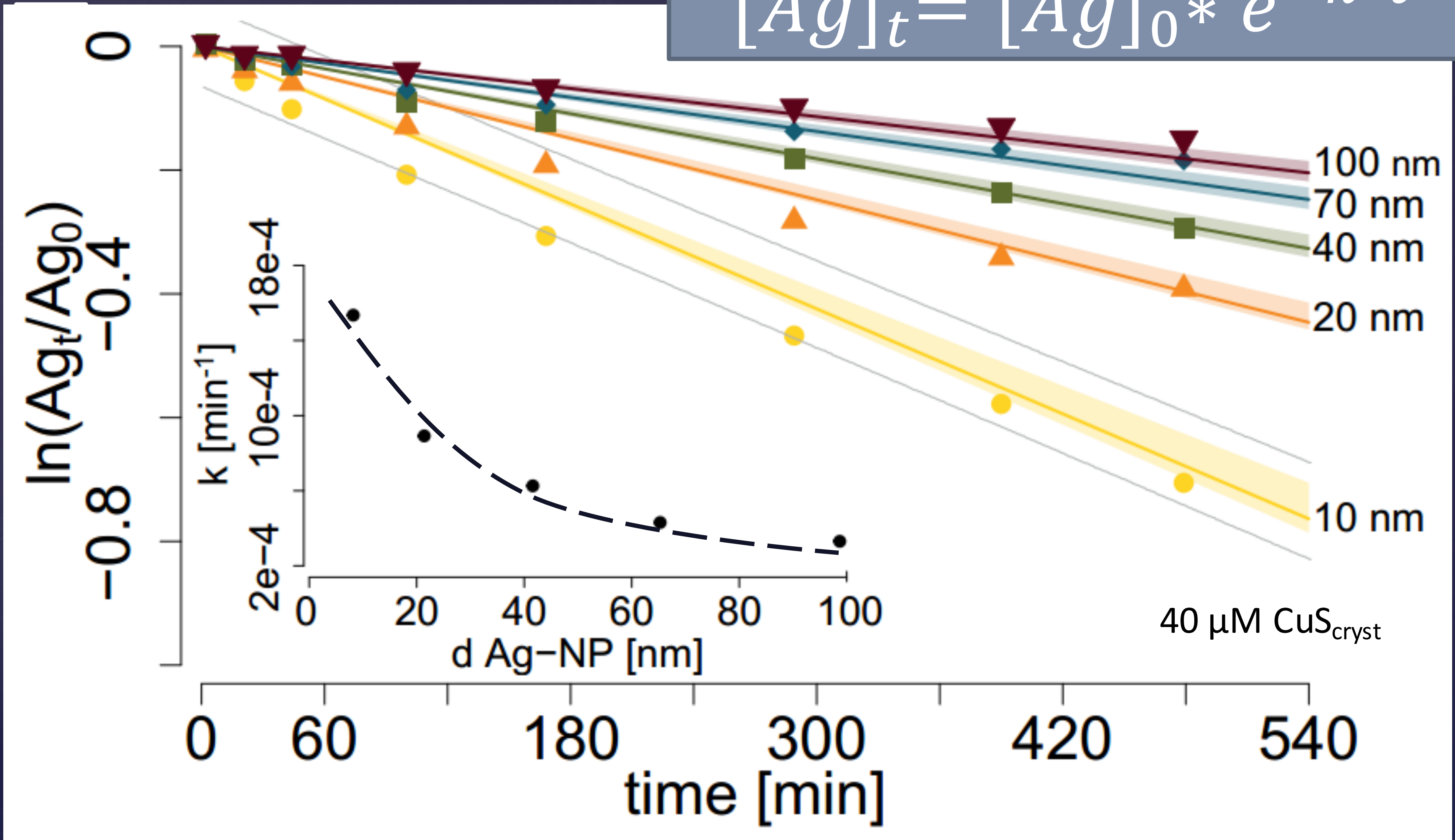
Ag –NP of different **sizes** (10, 20, 40, 70, 100 nm) were reacted with different **types** (CuS, ZnS) of different **crystallinities** (weakly crystalline, well crystalline) at different **concentrations** (40, 80, 130, 200 µM)

Reacting Ag-NP with CuS-cryst: Effect of the Ag-NP size

eawag aquatic research

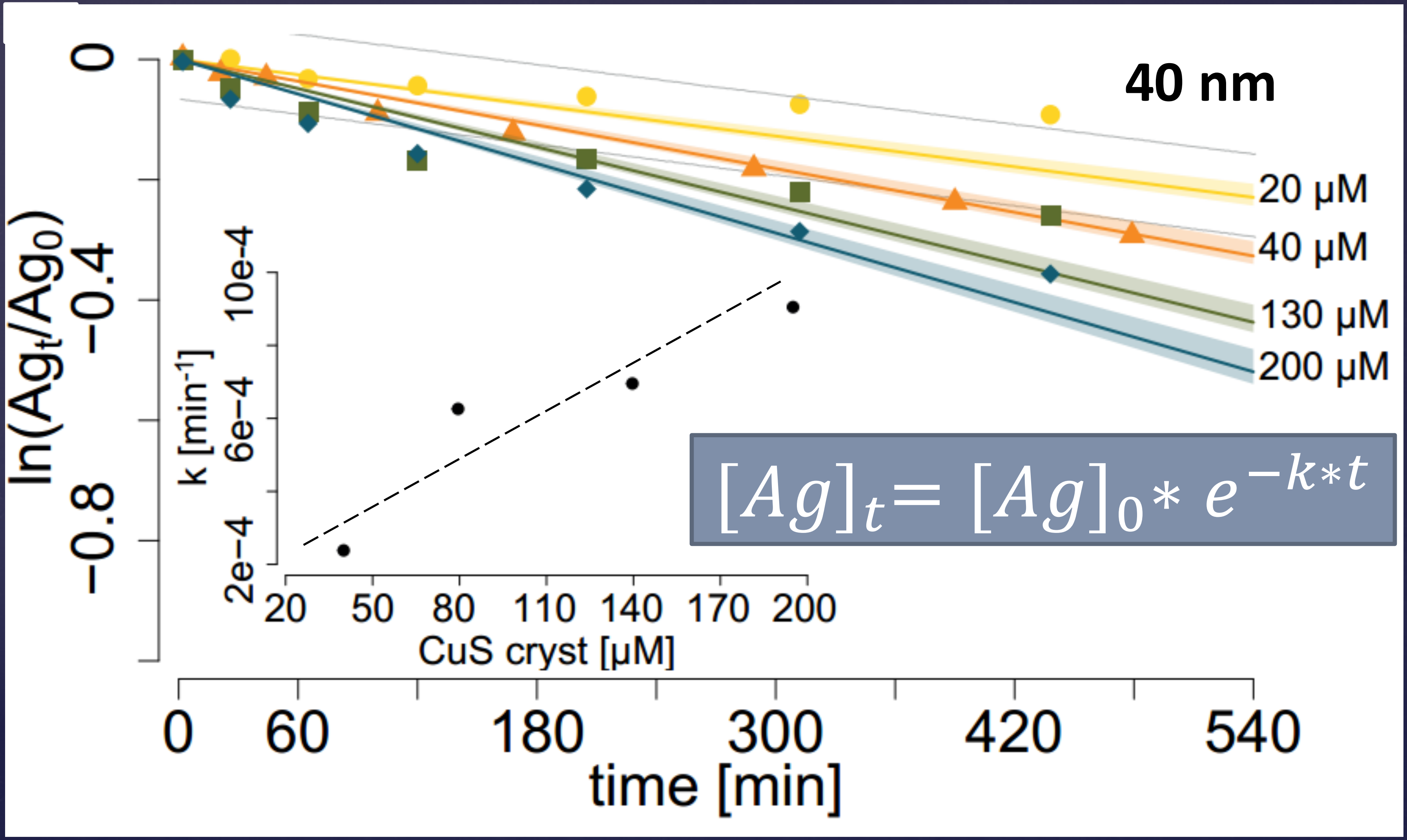
NanoFASE

$$[Ag]_t = [Ag]_0 * e^{-k*t}$$



Thalmann et al, EST, 2014

Reacting Ag-NP with CuS_{cryst}: Effect of the CuS concentration



$$[Ag]_t = [Ag]_0 * e^{-k*t}$$

Thalmann et al, EST, 2014

Sulfidation kinetics

eawag aquatic research

NanoFASE

$$[Ag]_t = [Ag]_0 * e^{-k*t}$$

$$k = k' * [MS]_{initial}{}^{a} * \left(\frac{1}{d_{Ag-NP}}\right)^{b}$$

	ZnS_{ppt}	CuS_{cryst}
a	0.78(3)	0.52(3)
b	0.53(2)	0.60(2)

a: Material property
b: NP-property (coating)

Thalmann et al, EST, 2014

Thank you & enjoy the exercise

Acknowledgements: **UK (NERC)/US (EPA)**

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

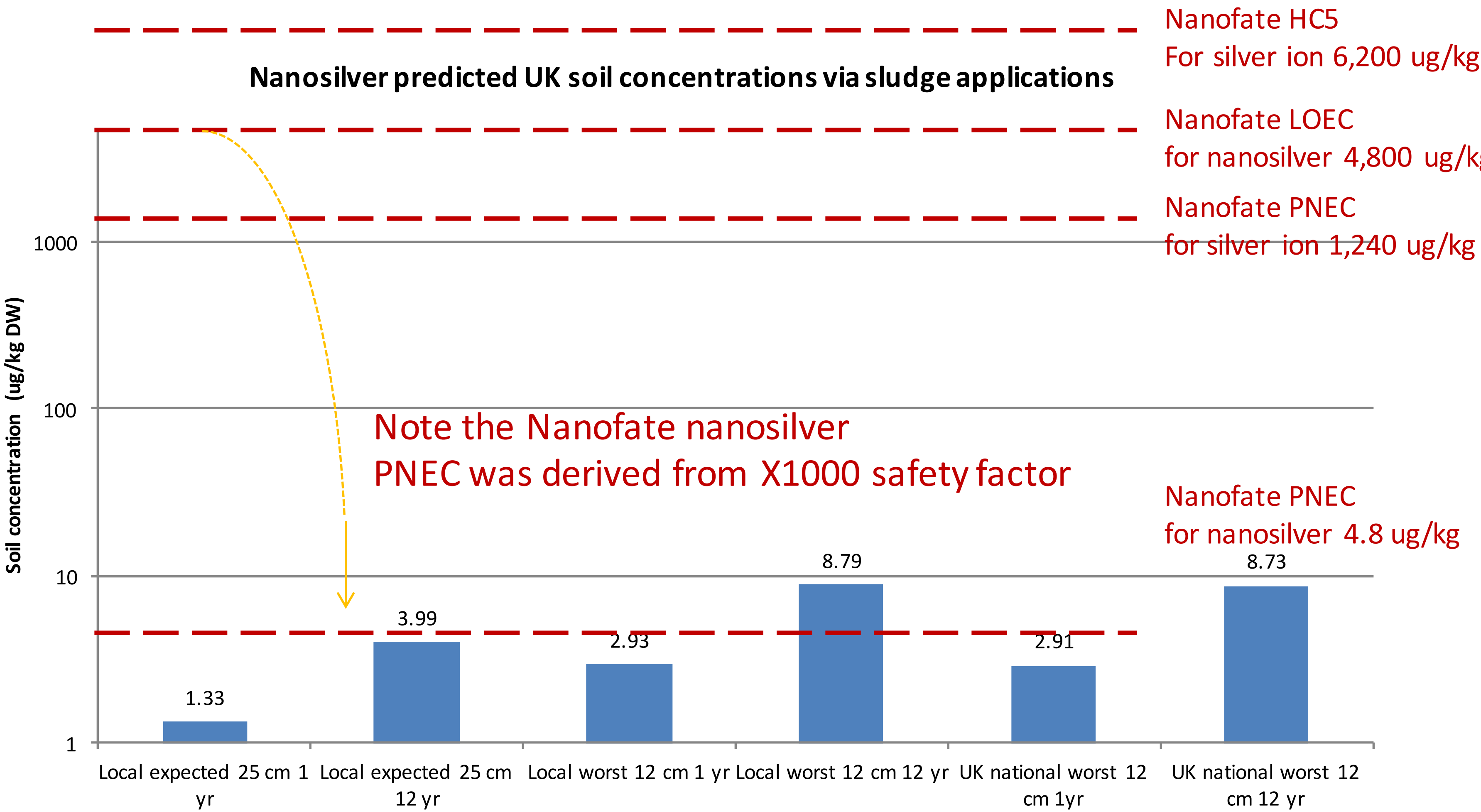
www.guideNANO.eu (EU CP-FP7 604387)

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

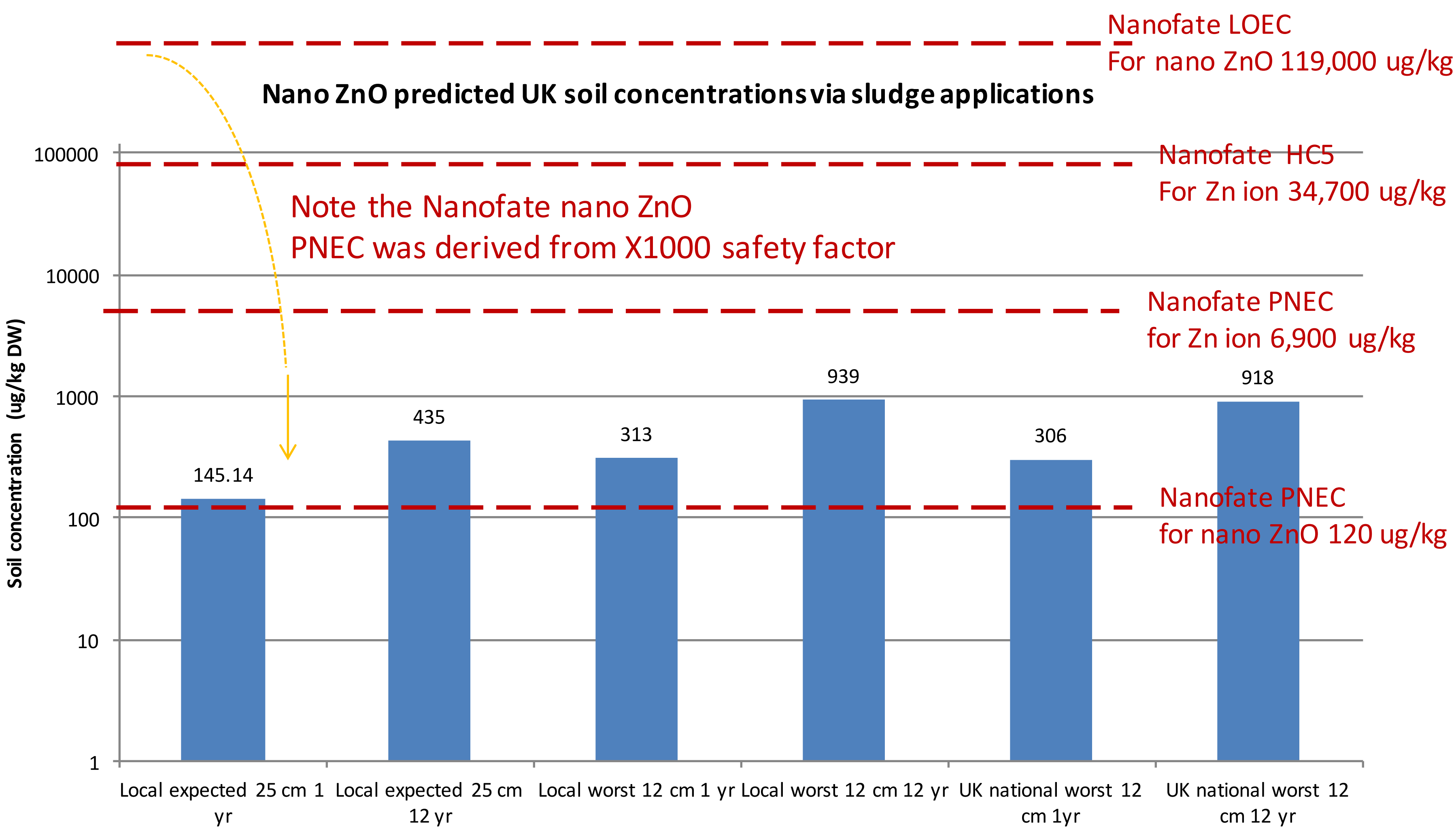
Centre for Ecology & Hydrology
NATURAL ENVIRONMENT RESEARCH COUNCIL

NERC SCIENCE OF THE ENVIRONMENT

Predicted nanosilver in UK soils and risks



Predicted nano ZnO in UK soils and risks



Thank you

Acknowledgements: UK (NERC)/US (EPA) TINE

NanoFATE

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

GUIDEnano

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

NanoFASE

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