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Developing test strategies to quickly assess fate and transport of metals and metal nanoparticles in soils: relevance for novel agrichemicals

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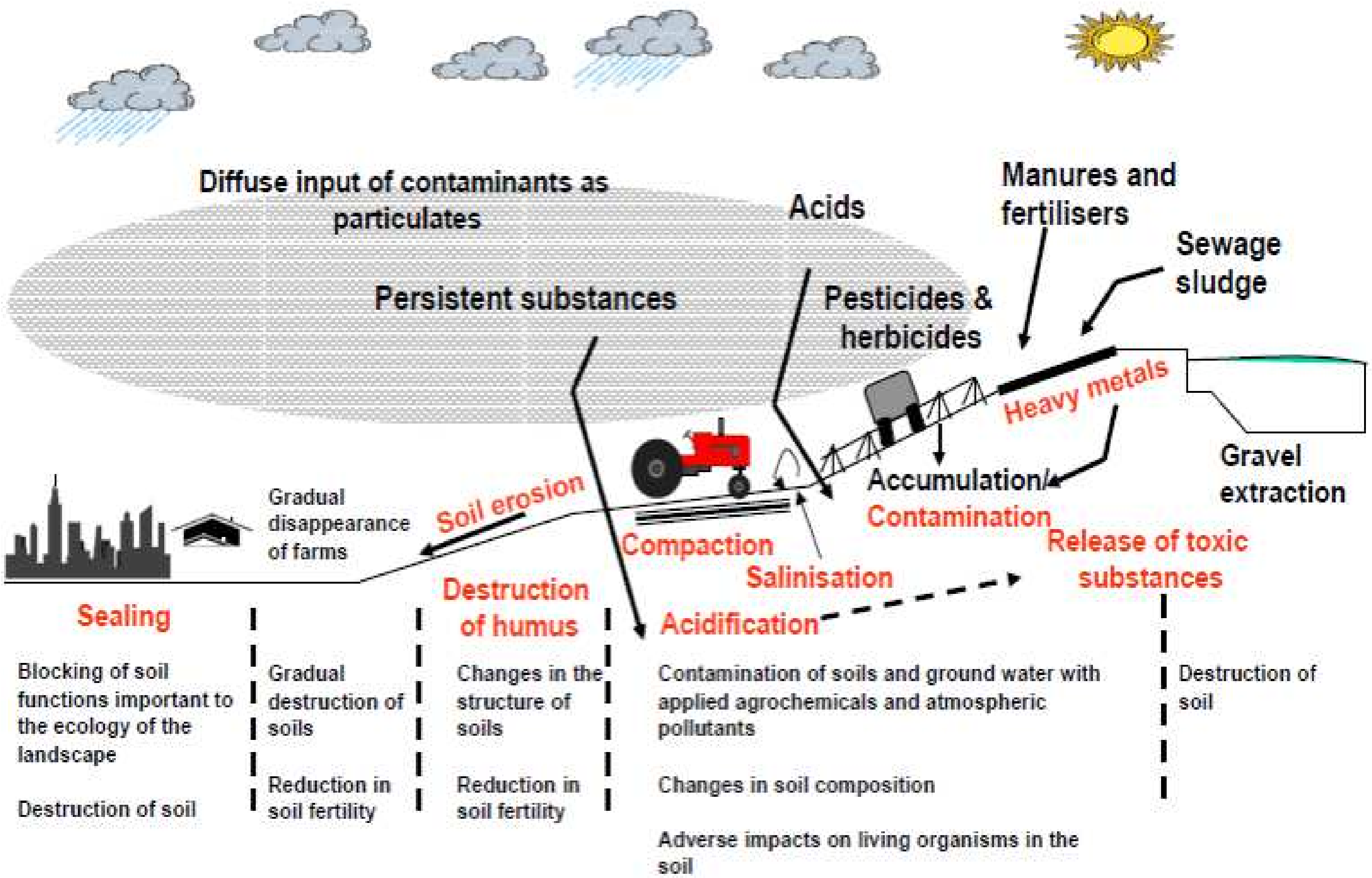
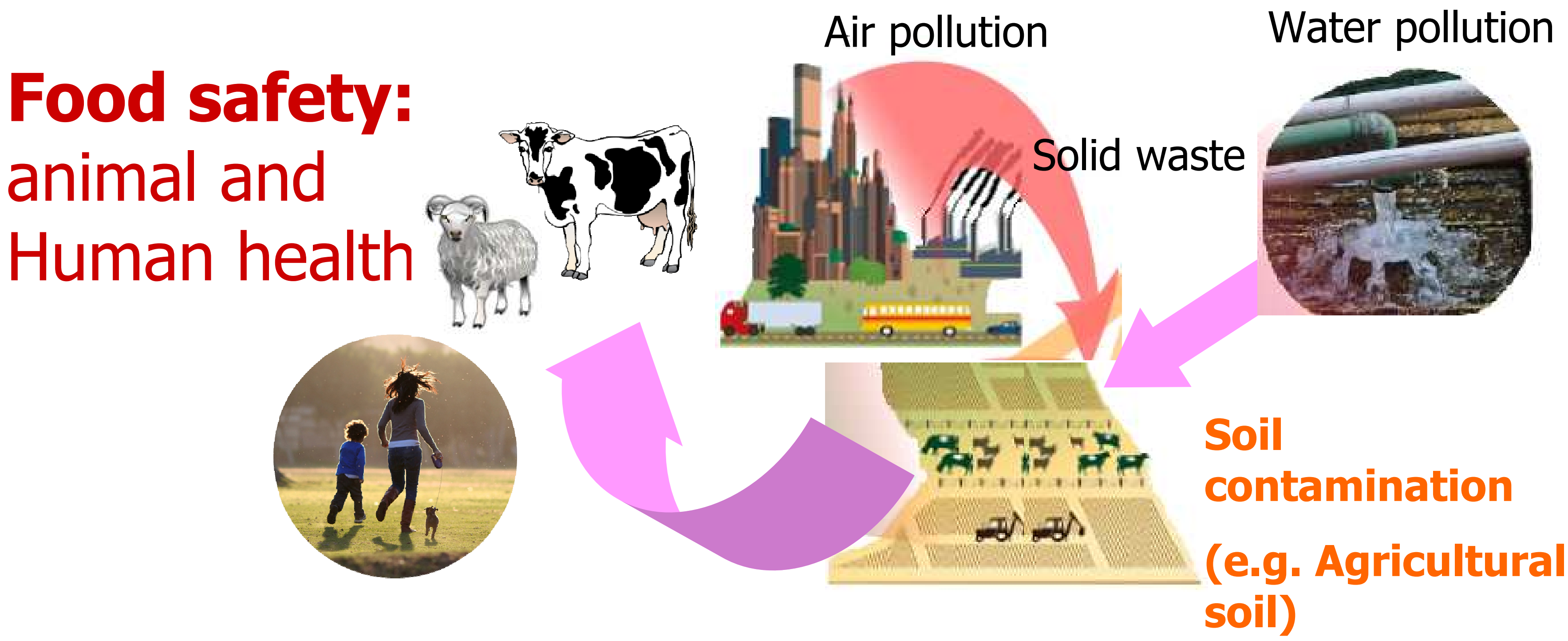
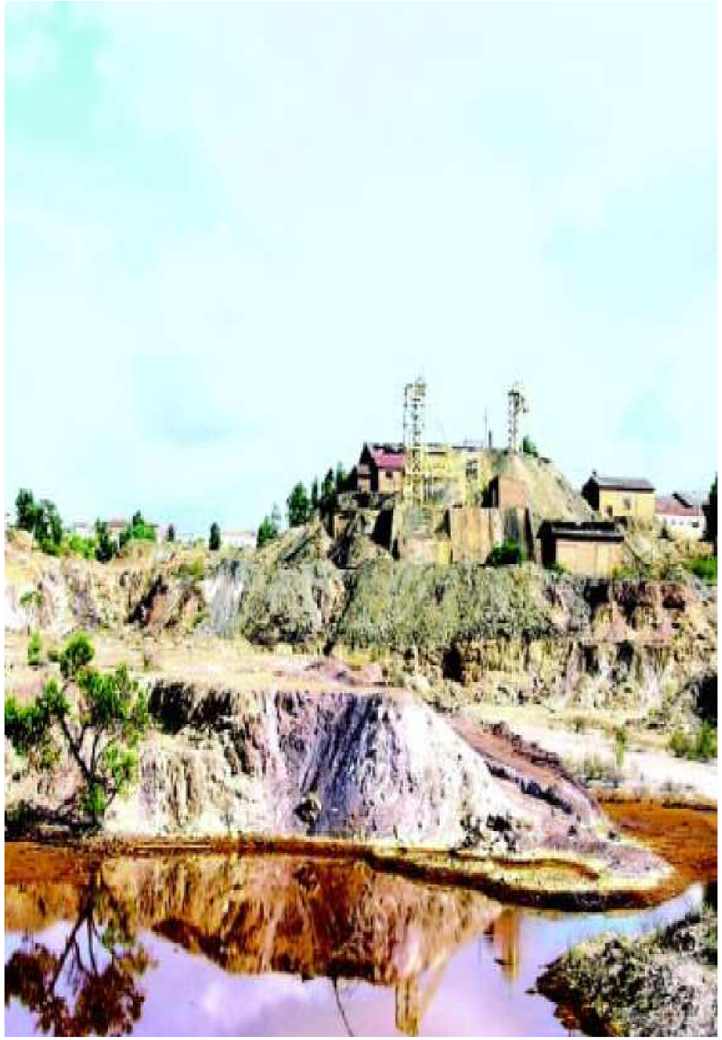
The impact of human activities on soil



Soil Threats

- **Deposition of solid waste; liquid effluents; atmospheric pollutants**
- **Competition between landuses: urbanization; industry; tourism; agriculture; etc**

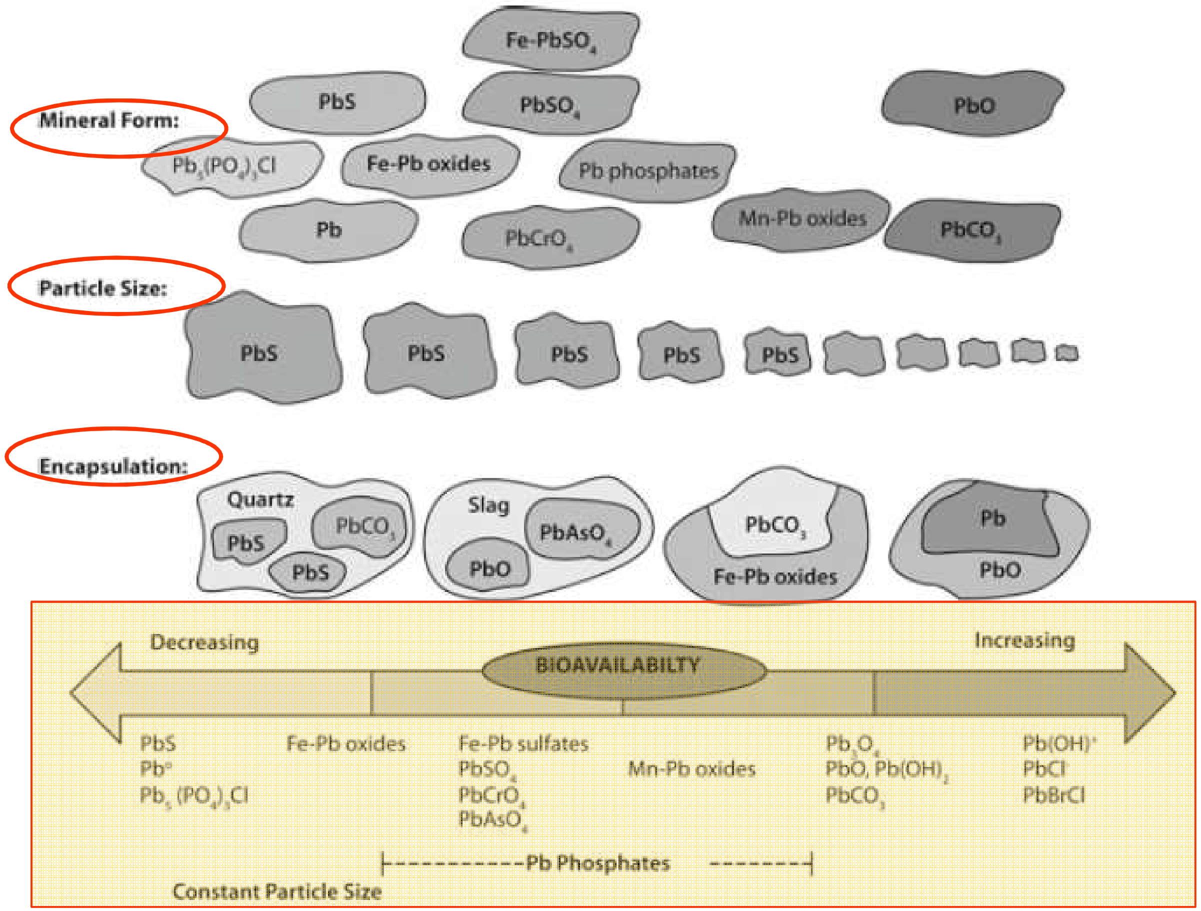




SOIL –

Soil Chemistry and Risk Assessment

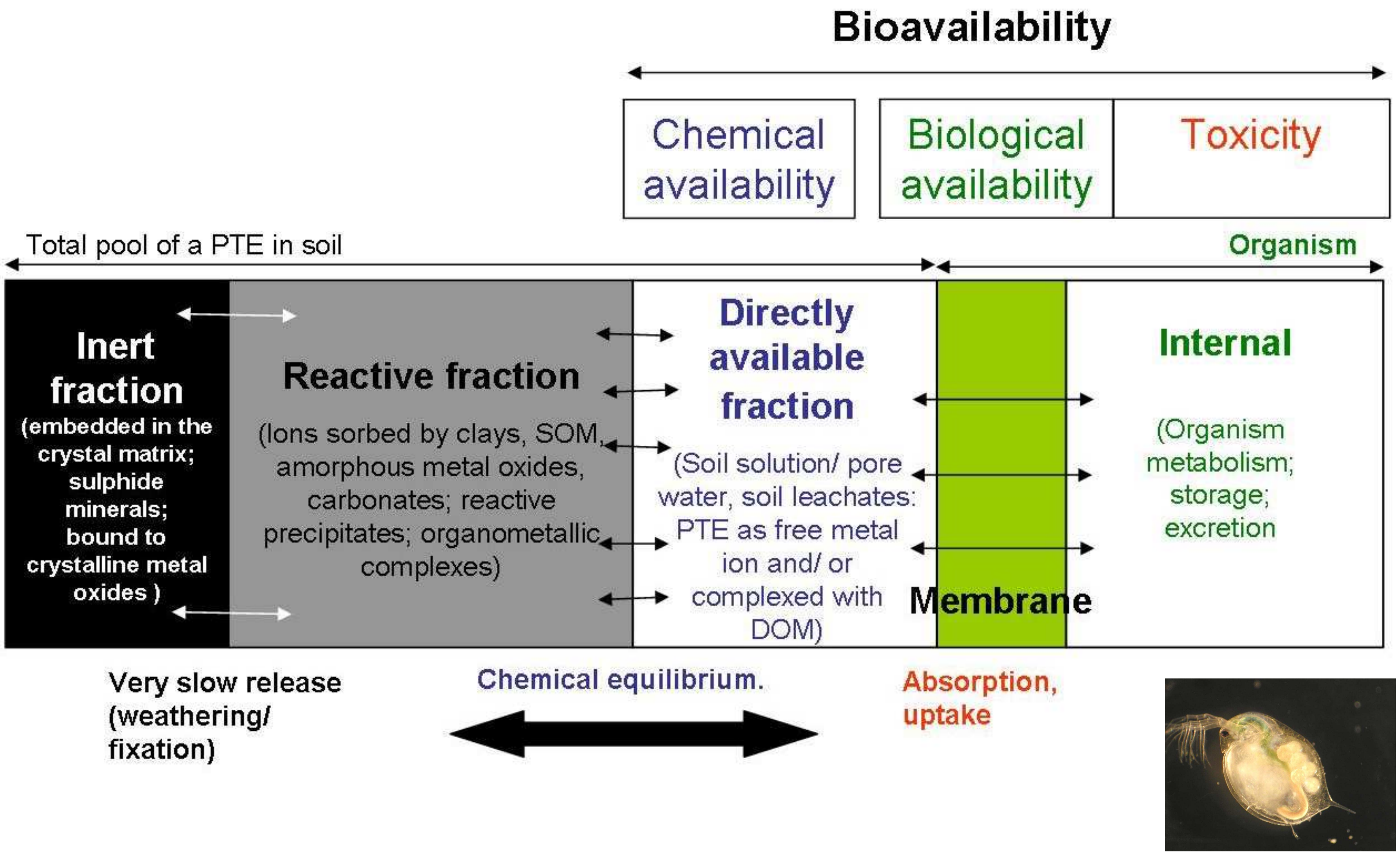
Key issue:
(geo)chemistry vs impact/effect



Schematic of how different lead species, particle sizes, and morphologies affect lead bioavailability.

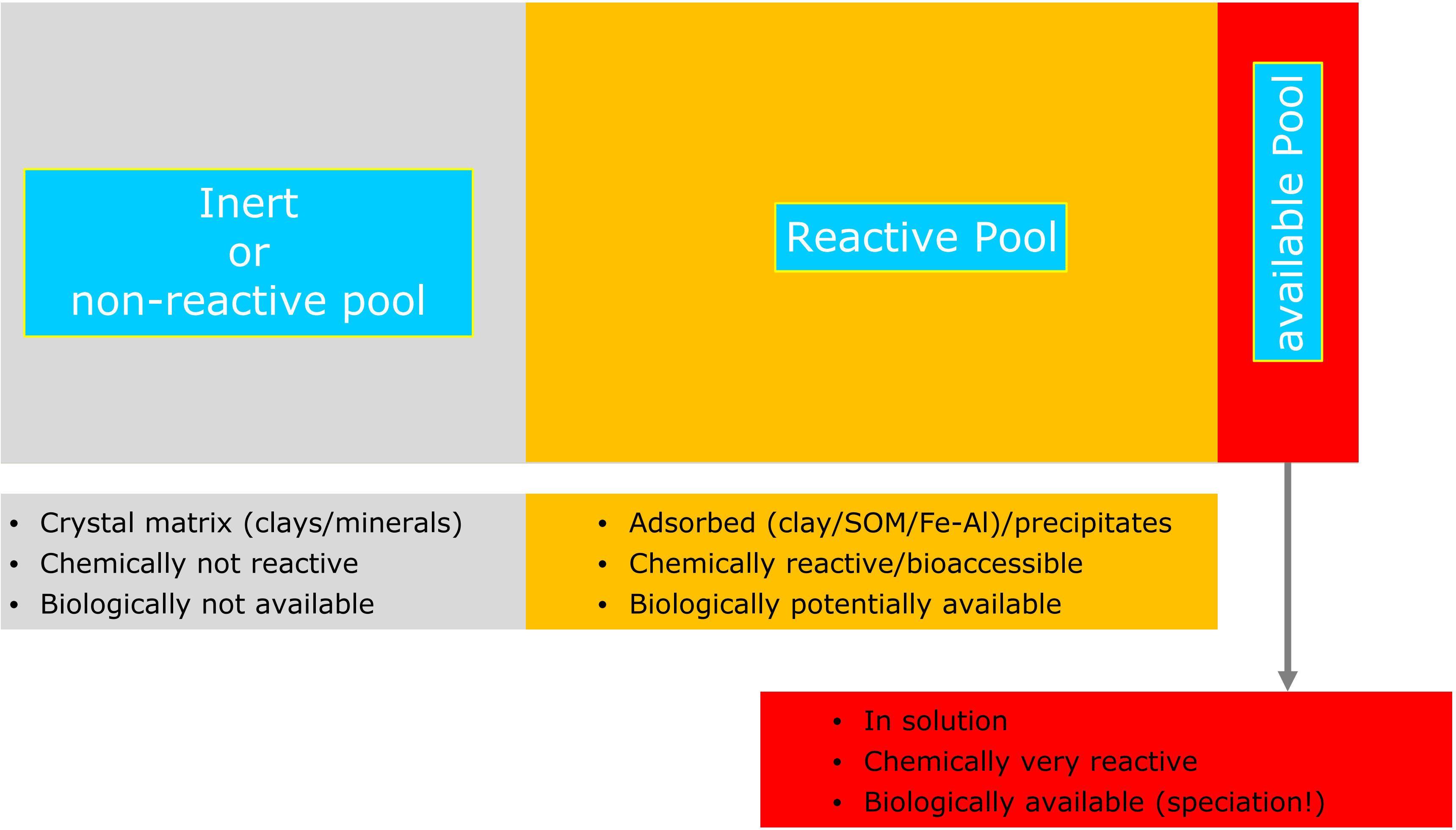
Fig. 7.7 Schematic diagram of how different lead species, particle size and morphologies affect lead bioavailability (after Ruby et al. 1996)

Reactivity: the concept



Rocha et al.,Chemosphere 2011

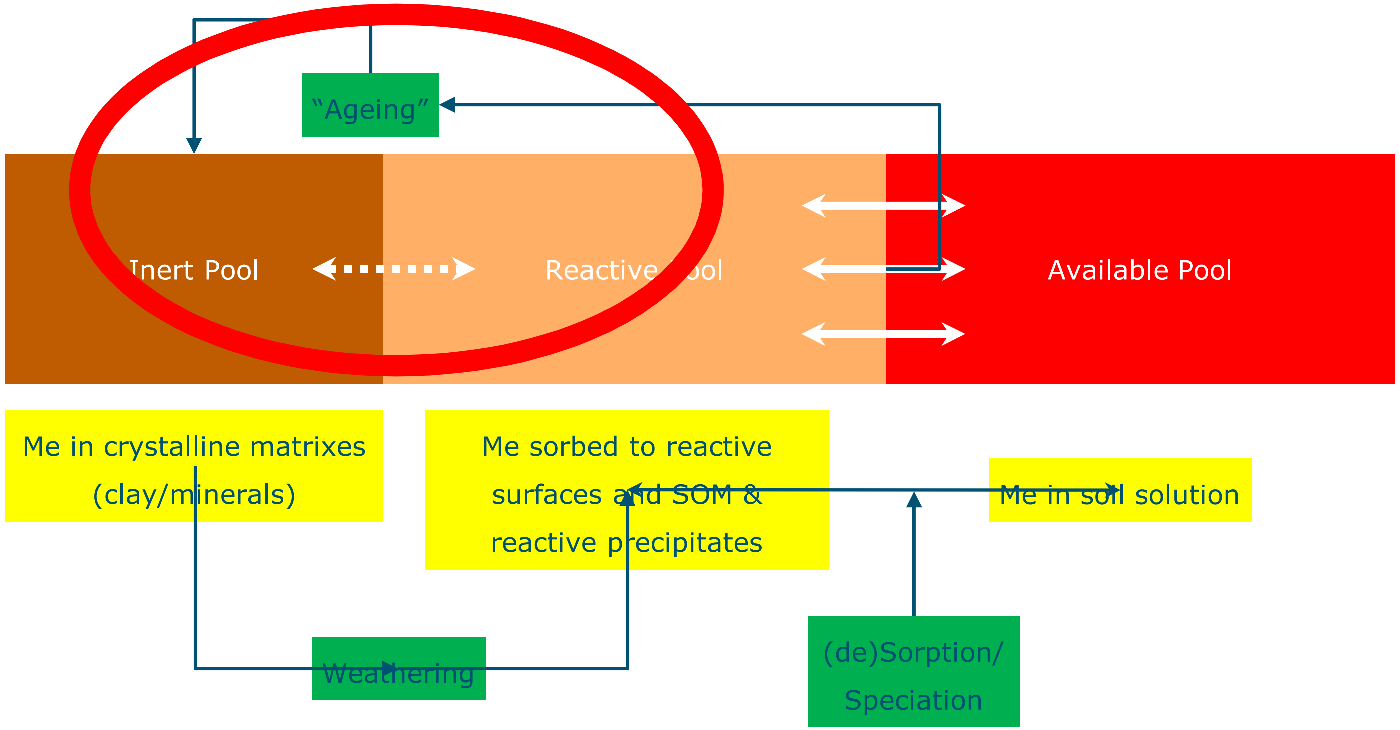
Reactivity: its meaning



Rodrigues et al., 2010; 2013

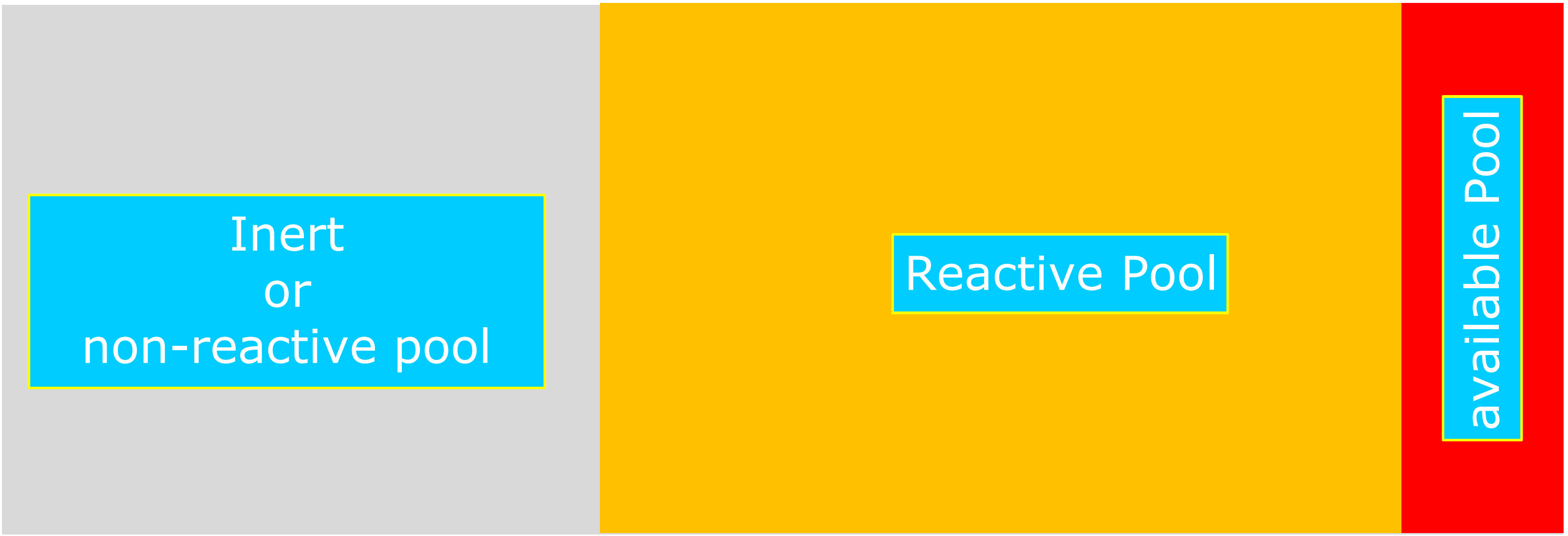
Reactivity: Effect of ageing

Ageing: slow transfer of metals from reactive to non-reactive pool



Reactivity: how to measure it?

Use of chemical extraction tests as proxies for geochemical reactivity



Strong acid:

HF
(Aqua Regia)

Dilute acid:

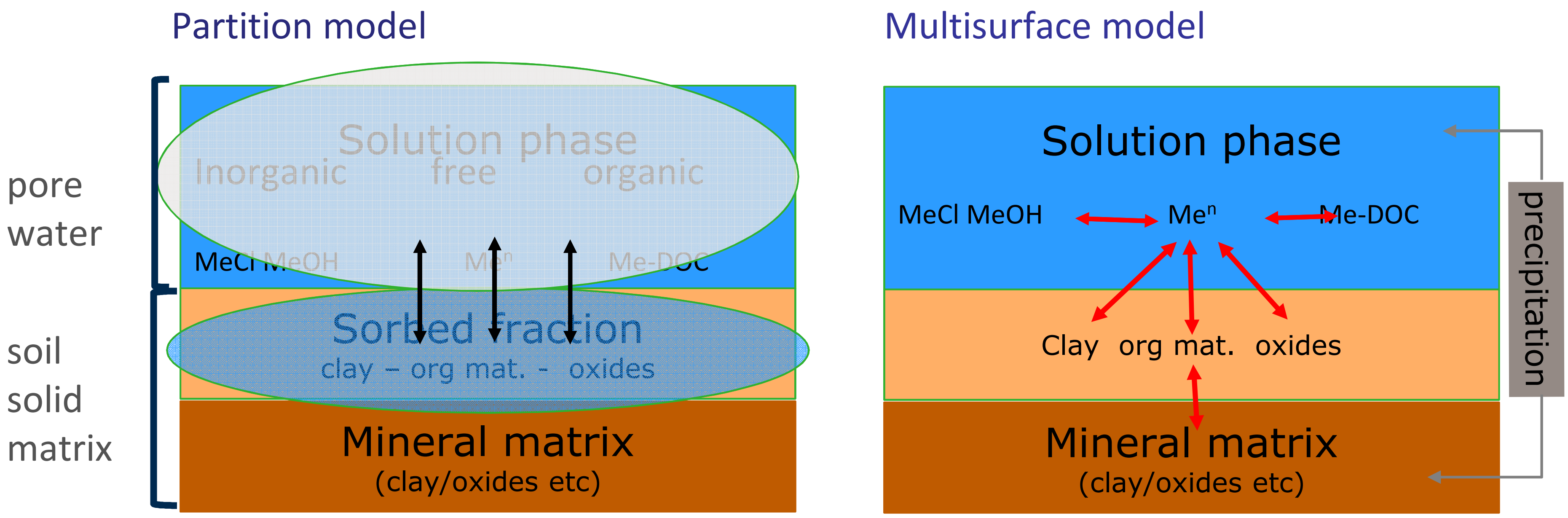
0.1 M HCl
0.43 M HNO_3

Salt:

0.01 M $CaCl_2$

Rodrigues et al., 2010; 2013

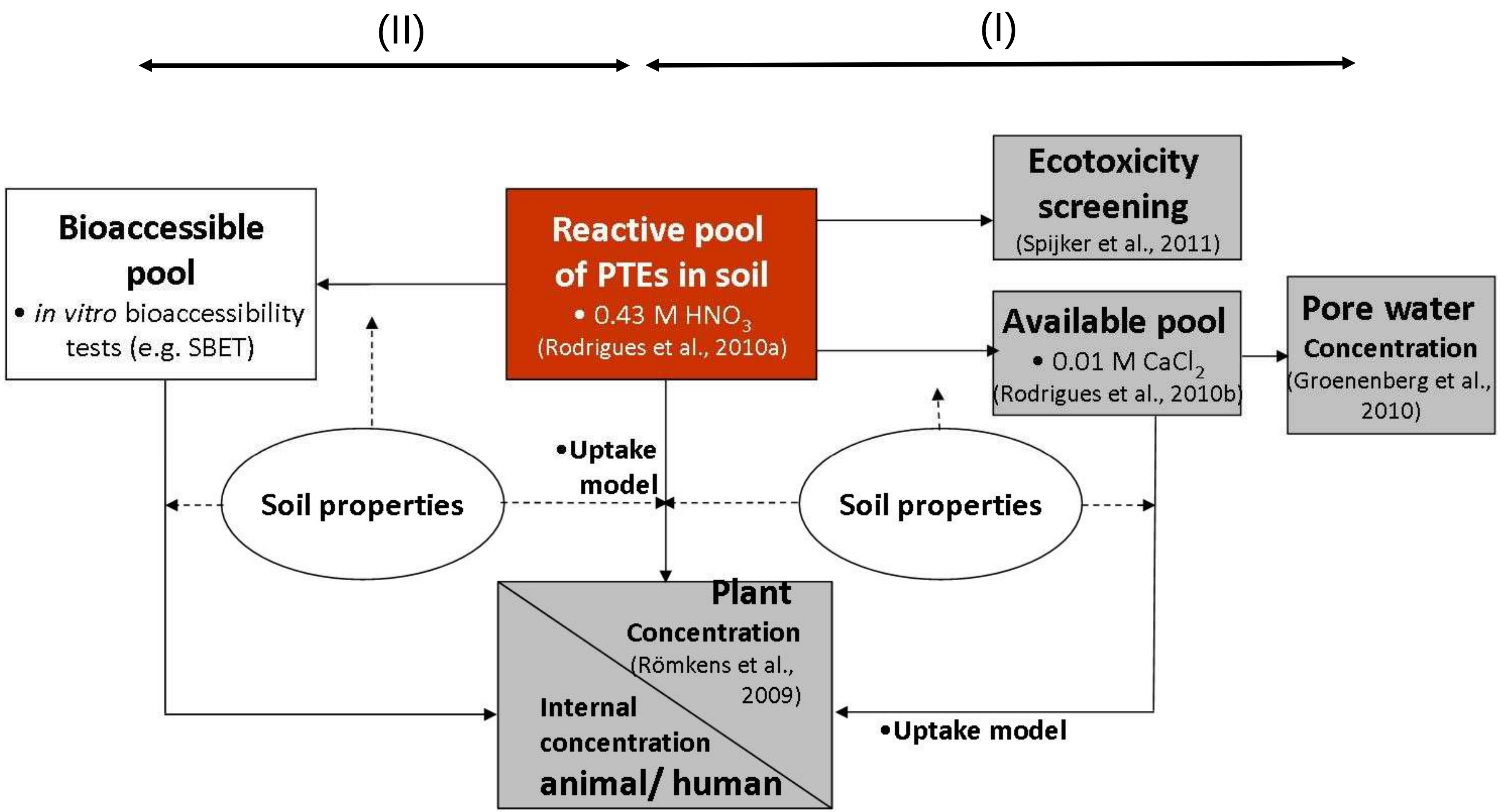
- From Partition Models to Mechanistic Modelling



Rodrigues et al., 2010; 2013

The concept of reactivity in risk assessment

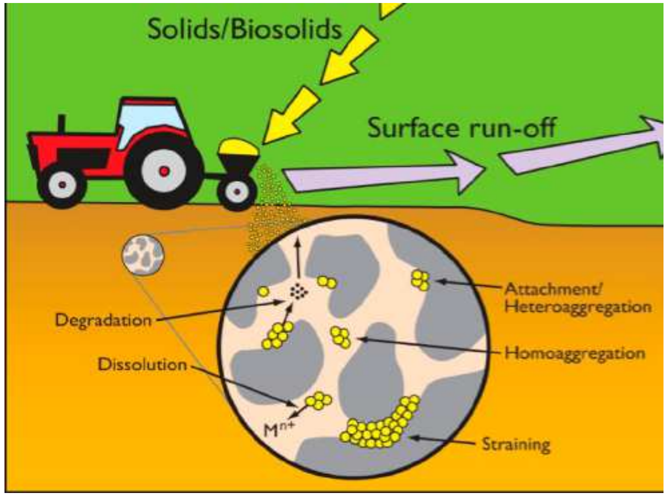
In relation to plant uptake and leaching (I) *vs.* the oral bioaccessibility (II)

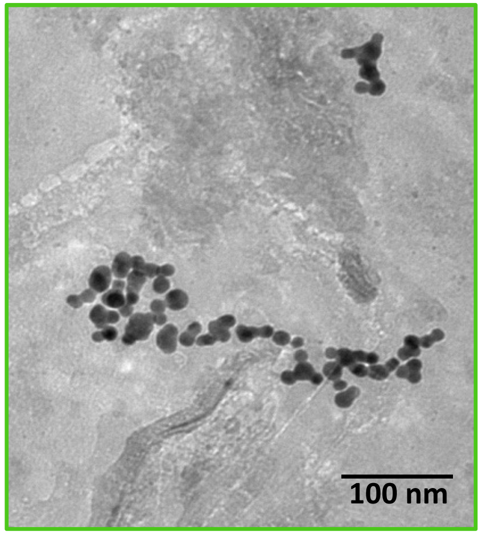


The concept of reactivity in risk assessment: metals

Risk Assessment based on “Reactivity” rather than total metal level yields reliable results (looking at risk)

Reduce analytical costs arising from risk assessment and increase analytical accuracy using fast and reproducible soil tests (e.g. 0.43 M HNO_3)





SOIL –

What about metallic nanoparticles?

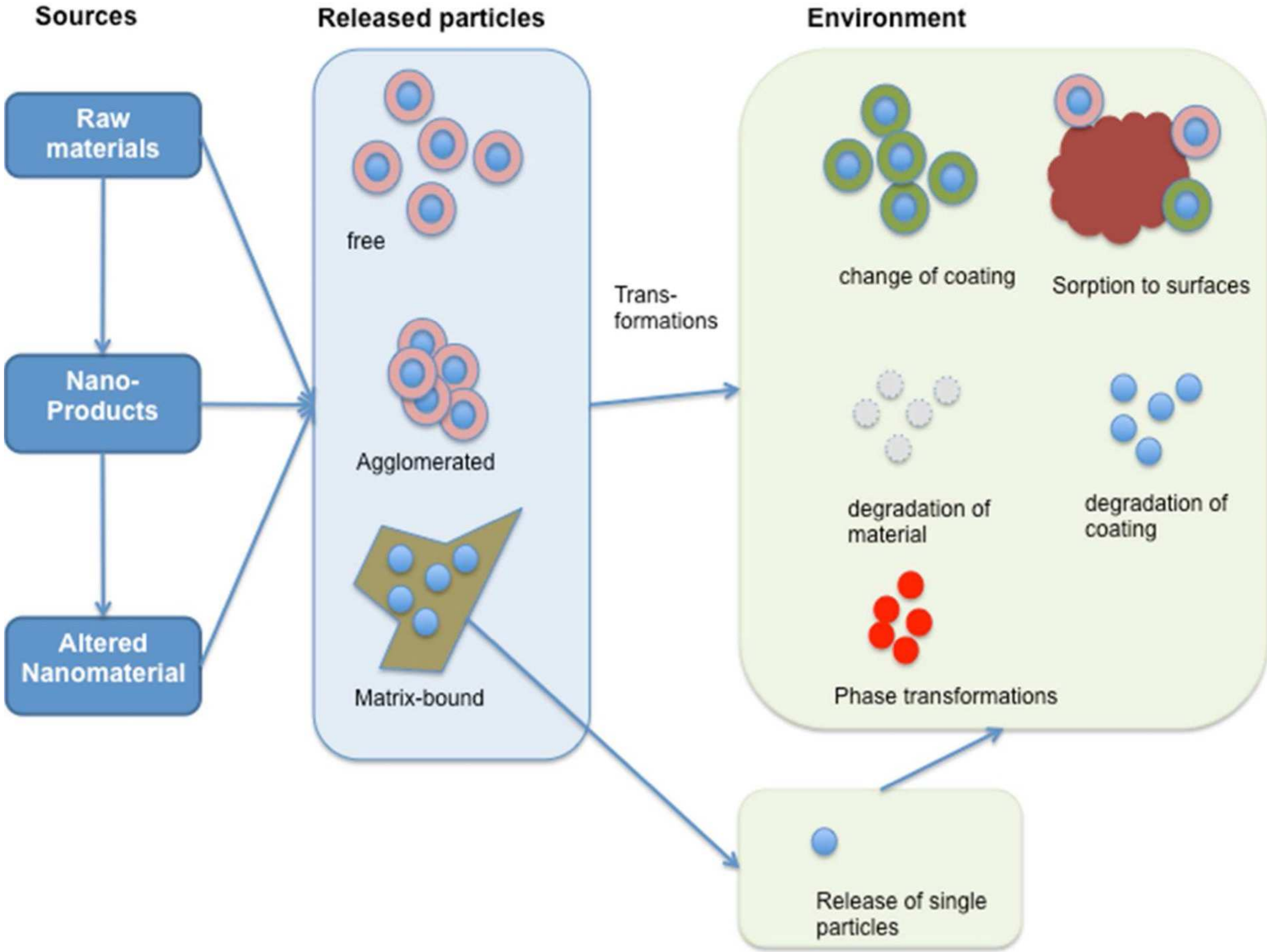
Soil components: From Macro- to Nanoscale

✈**Most of the surface area and electrostatic charge in soils resides in the <1 µm size fraction** (Borkovec *et al.,* 1993)

✈**Colloidal fraction controls almost all surface-controlled processes, including adsorption reactions and precipitation/dissolution -** colloidal clays, Fe and Mn hydrous oxides, and dissolved organic matter (fulvic and humic acids), exudates from microorganisms (polysaccharides and some proteins)

(Goldberg *et al.,* 2000)

Transformation of nanoparticles in natural media



Westerhoff and Nowack, *Acc Chem Res,* 2013

Fate of metallic nanoparticles in soil

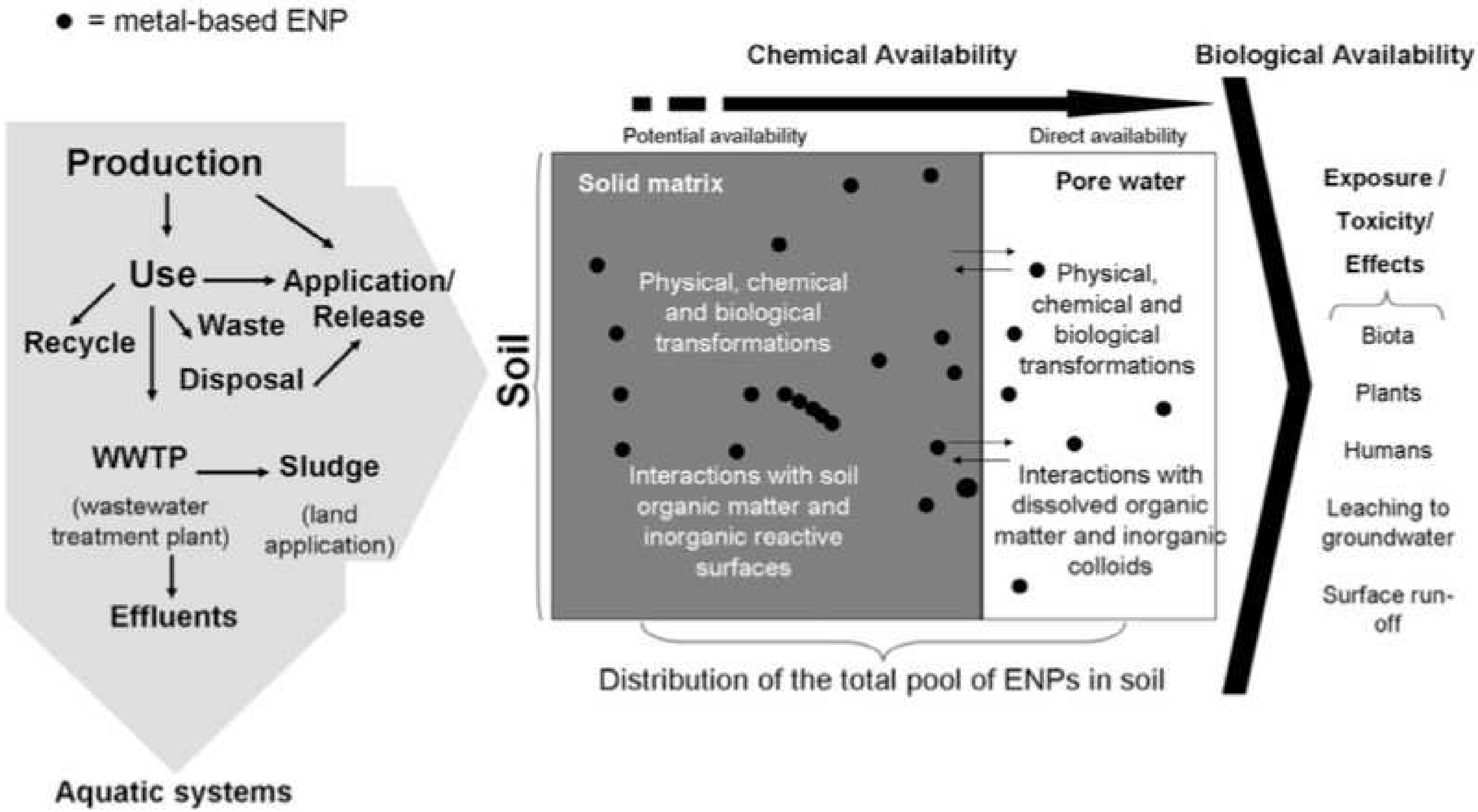
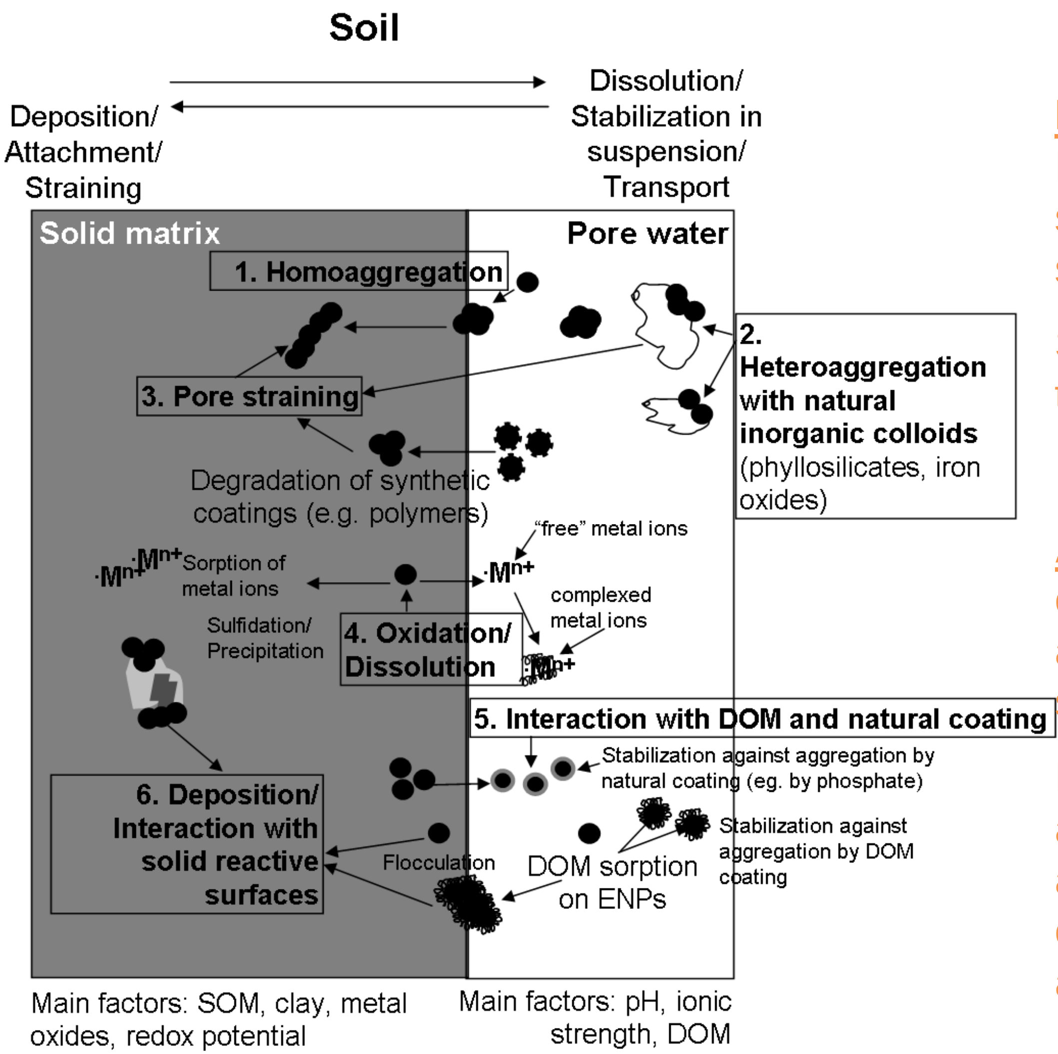


Fig. 1. Schematic overview of the distribution of the total pool of ENPs in soil.

Rodrigues et al., *TrAC,* 2016

Fate of metallic nanoparticles in soil



Dissolution: e.g. Dissolution of MeNPs involves the oxidation of surface elemental Me to Me^{n+} and subsequent desorptive dissolution.

Soluble ionic metal fraction is the most toxic to aquatic and terrestrial biota

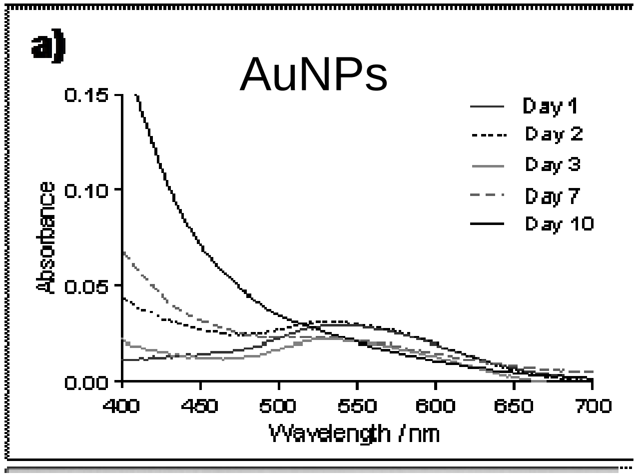
Aggregation: controlled by surface charge, particle size, ionic strength, pH and cation composition of the soil solution as well as NPs shape

Heteroaggregation with soil colloids and natural NPs: colloidal clays, Fe and Mn hydrous oxides, and dissolved organic matter (fulvic and humic acids), exudates from microorganisms

Rodrigues et al., *TrAC,* 2016

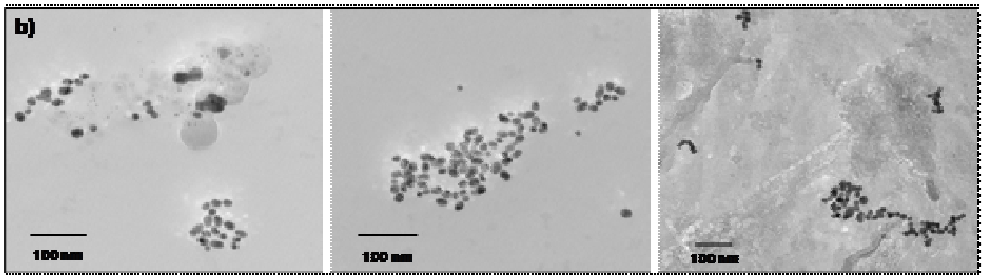
Fate of metallic nanoparticles in soil

Example 1: Presence of AuNPs in pore water

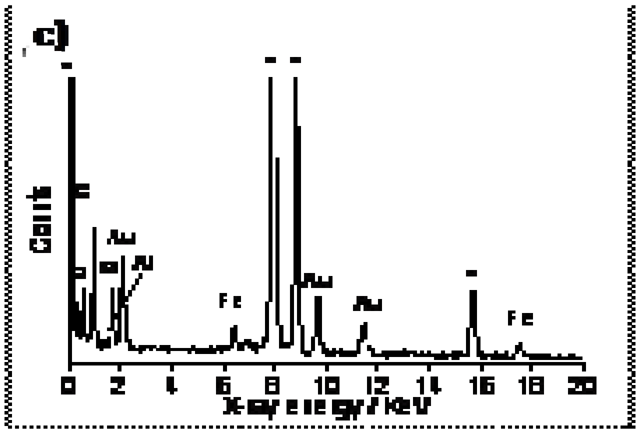


UV-Vis

1) AuNPs observed by UV-Vis in soil pore water samples collected until 7 days after amendment



TEM (24 h)

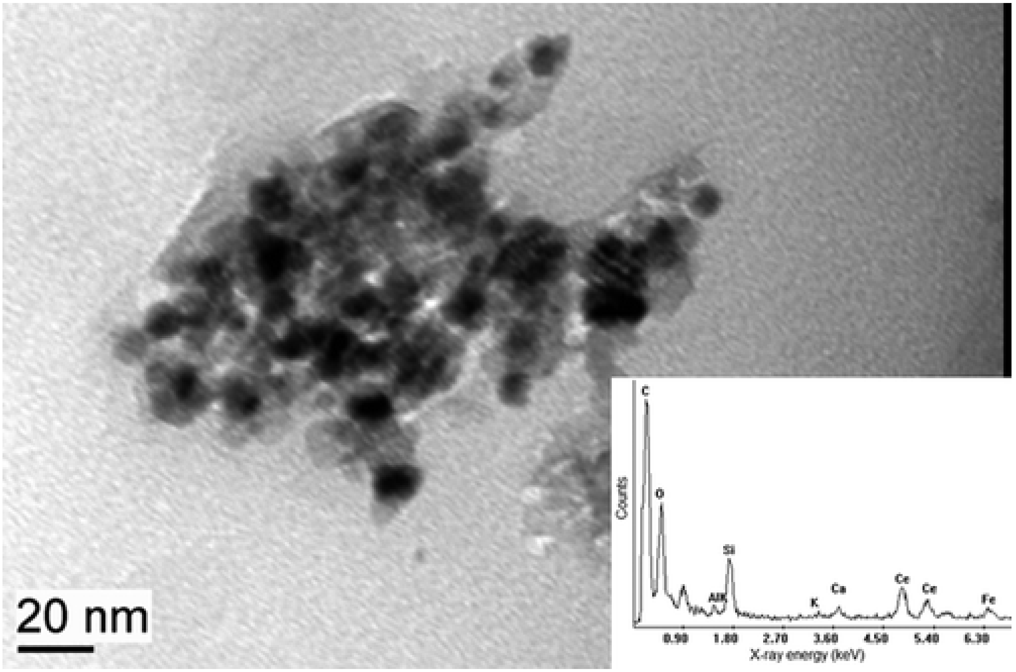


EDX (24 h)

Tavares et al., *Chemosphere,* 2015

Fate of metallic nanoparticles in soil

Example 2: Colloid-mediated detachment of CeO_2 nanoparticles in soil



1) No dissolved Ce detected in soils spiked with CeO_2 NPs

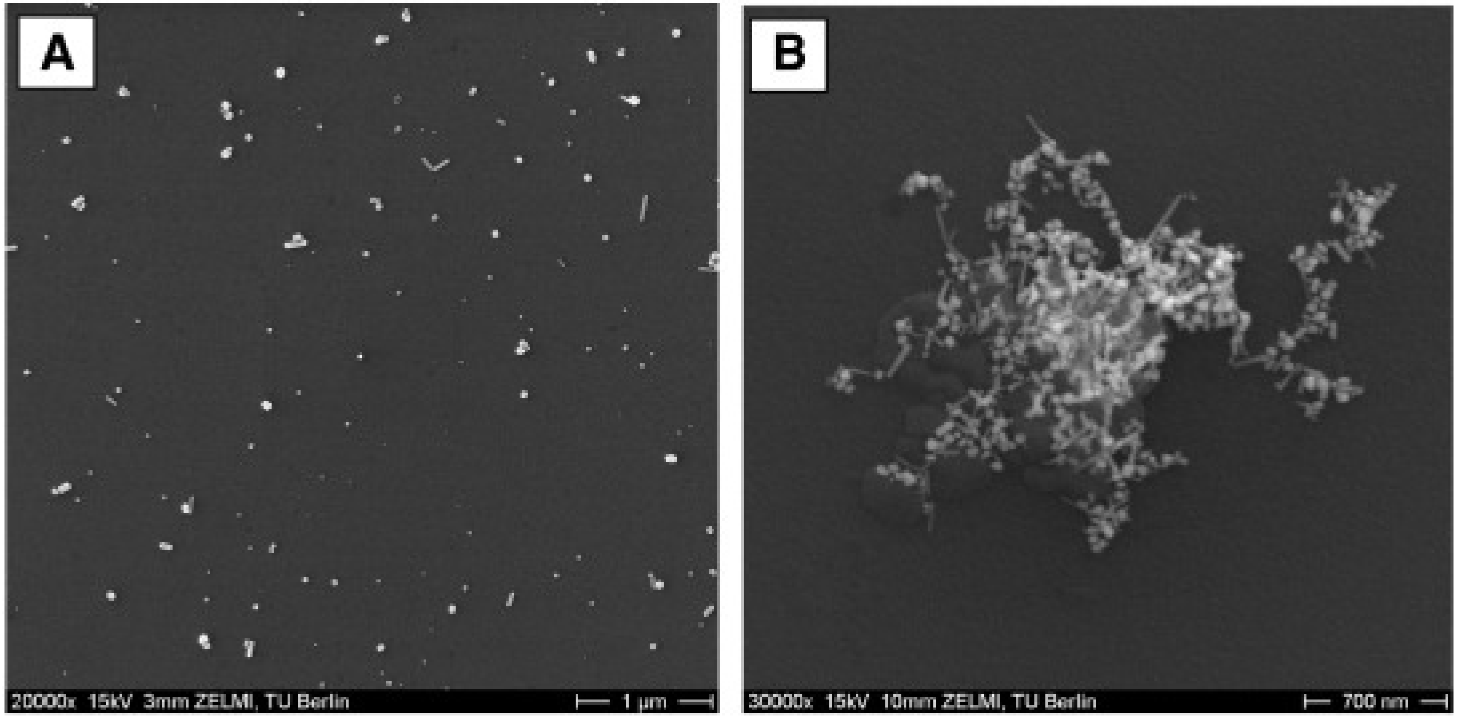
2) Low CeO_2 NPs retention in soil (nonequilibrium retention K_r=9.6 L kg^{-1})

3) Low retention explained by: surface adsorption of phosphate to NPs causing negative zeta potential and heteraggregation with natural inorganic colloids (clays)

Cornelis et al., *ES&T,* 2011

Fate of metallic nanoparticles in soil

Example 3: Stability of AgNPs in pore water



Scanning electron microscopy image of citrate-stabilized Ag NP following equilibration in (A) Millipore water and (B) soil solution.

1) Attributed to sorption of short-chained Dissolved Organic Matter (DOM)

Klitzke et al., *STOTEN,* 2015

Fate of metallic nanoparticles in soil

Example 4: Reactions of Ag in pore water

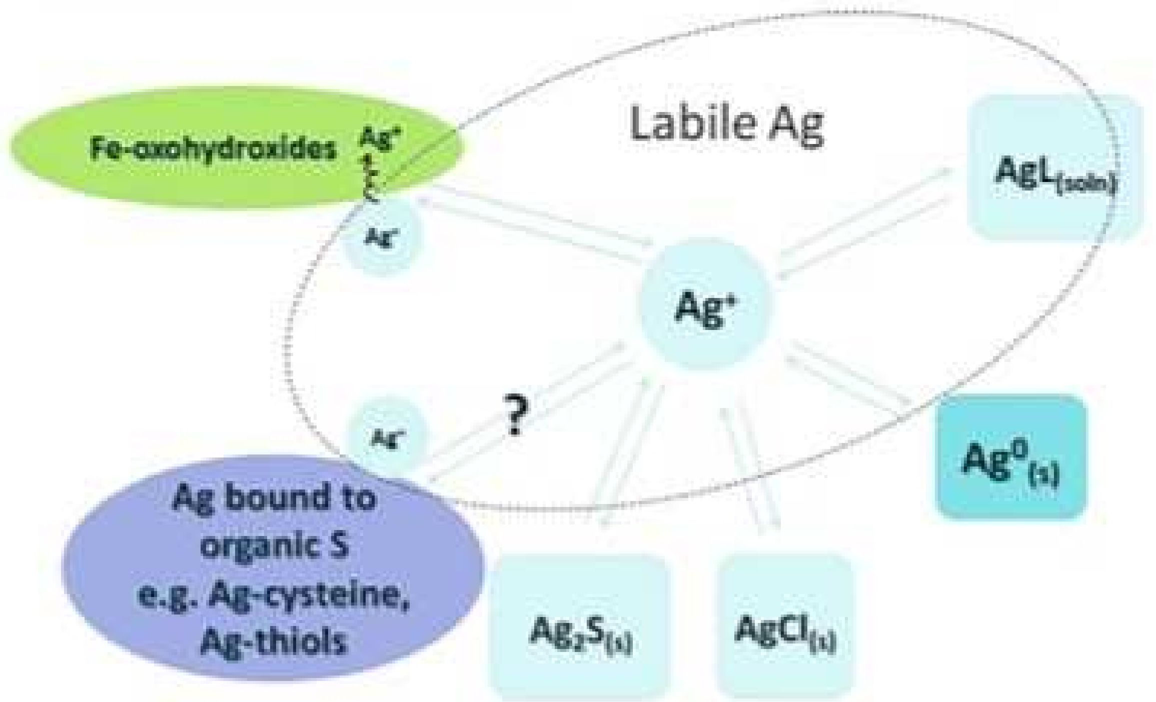


Fig. 5. Summary schematic of the possible transformations of labile Ag to non-labile Ag fractions in soils according to speciation data collected by XANES. The dotted oval represents all labile forms of Ag: Ag^+, reversibly sorbed Ag^+ to Fe-oxohydroxides and organic S of organic matter, Ag^+ weakly complexed with other soil solution ligands (L). Non-labile Ag is solids: metallic Ag, AgCl and Ag_2S and Ag irreversibly bound to organic S and Fe-oxohydroxides (surface precipitated or fixed within crystal lattices).

Settimio et al., *Environ. Pollut.,* 2014

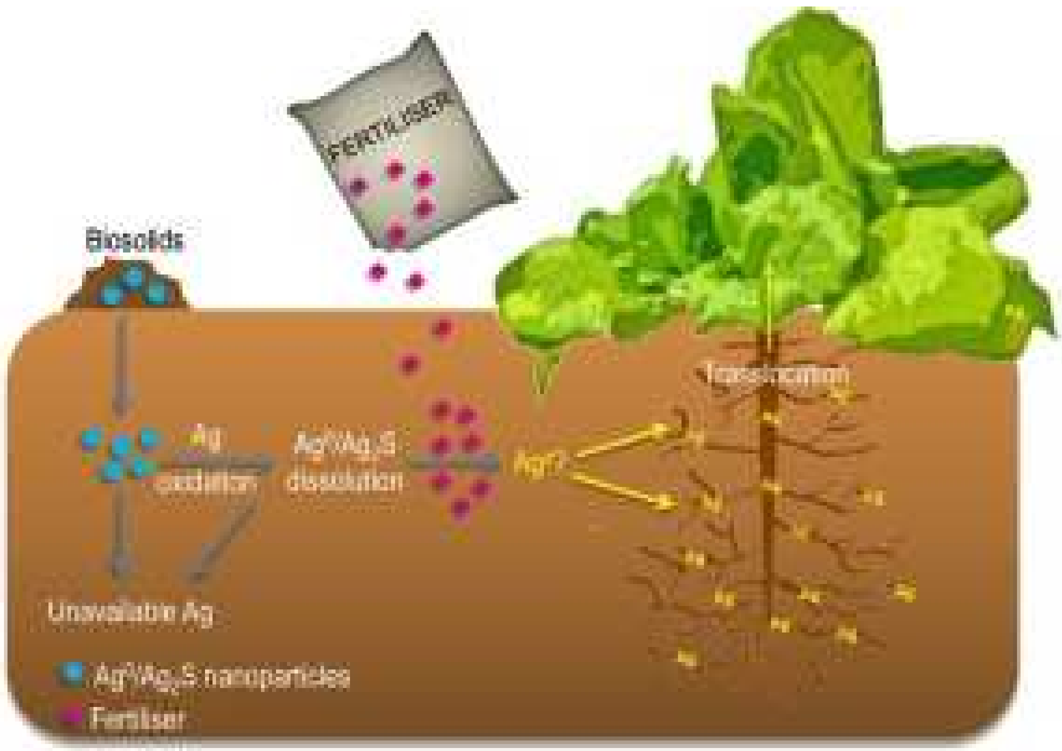
Fate of metallic nanoparticles in soil

Example 5: Bioavailability of AgNPs and Ag_2S NPs to lettuce

Plant uptake of Ag from AgNP and Ag_2S-NP dosed soil is dependent on NP dissolution.

Ammonium thiosulfate (fertiliser) increases bioavailability of Ag from AgNPs and Ag_2S-NPs.

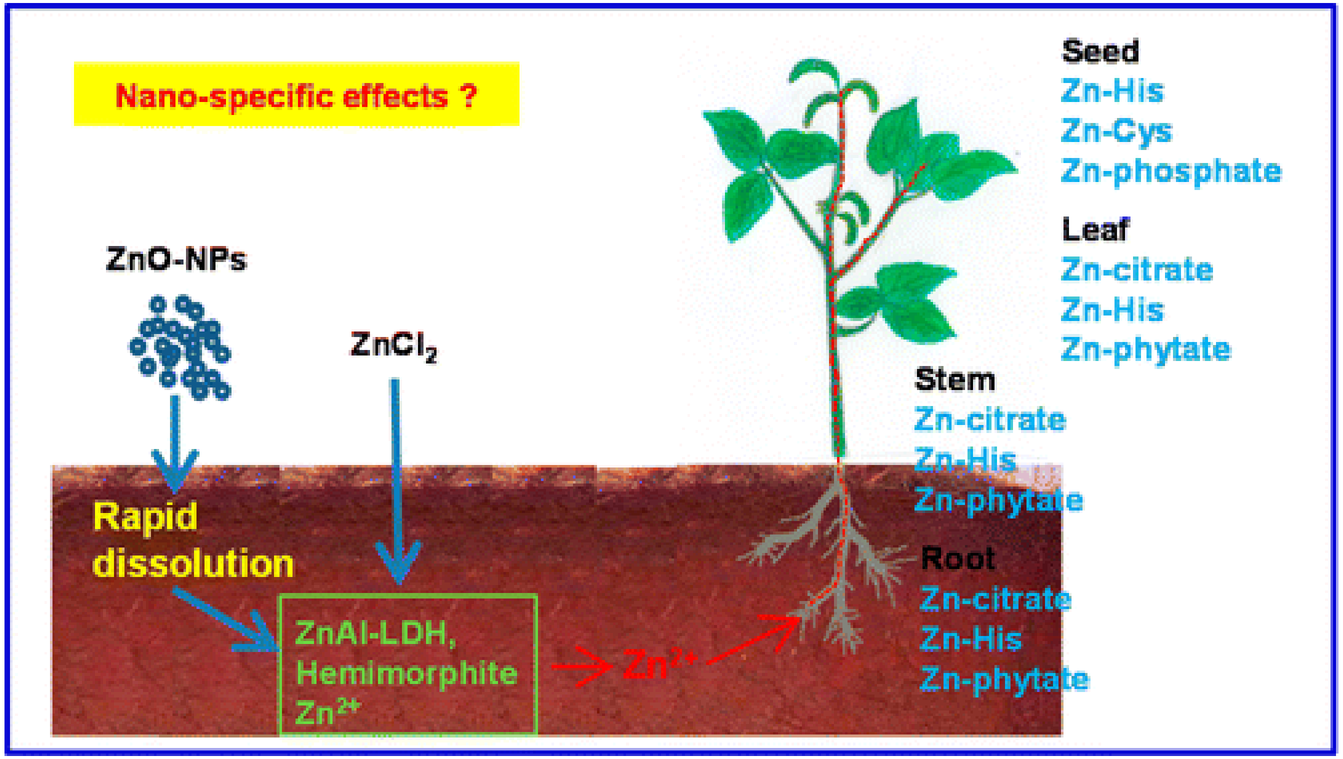
Soil application of phosphate and H_2O_2 decreases Ag shoot concentrations.



Doolette et al., *J. Hazard Mat.*, 2015

Fate of metallic nanoparticles in soil

Example 6: Fate of ZnO Nanoparticles in soils and Cowpea



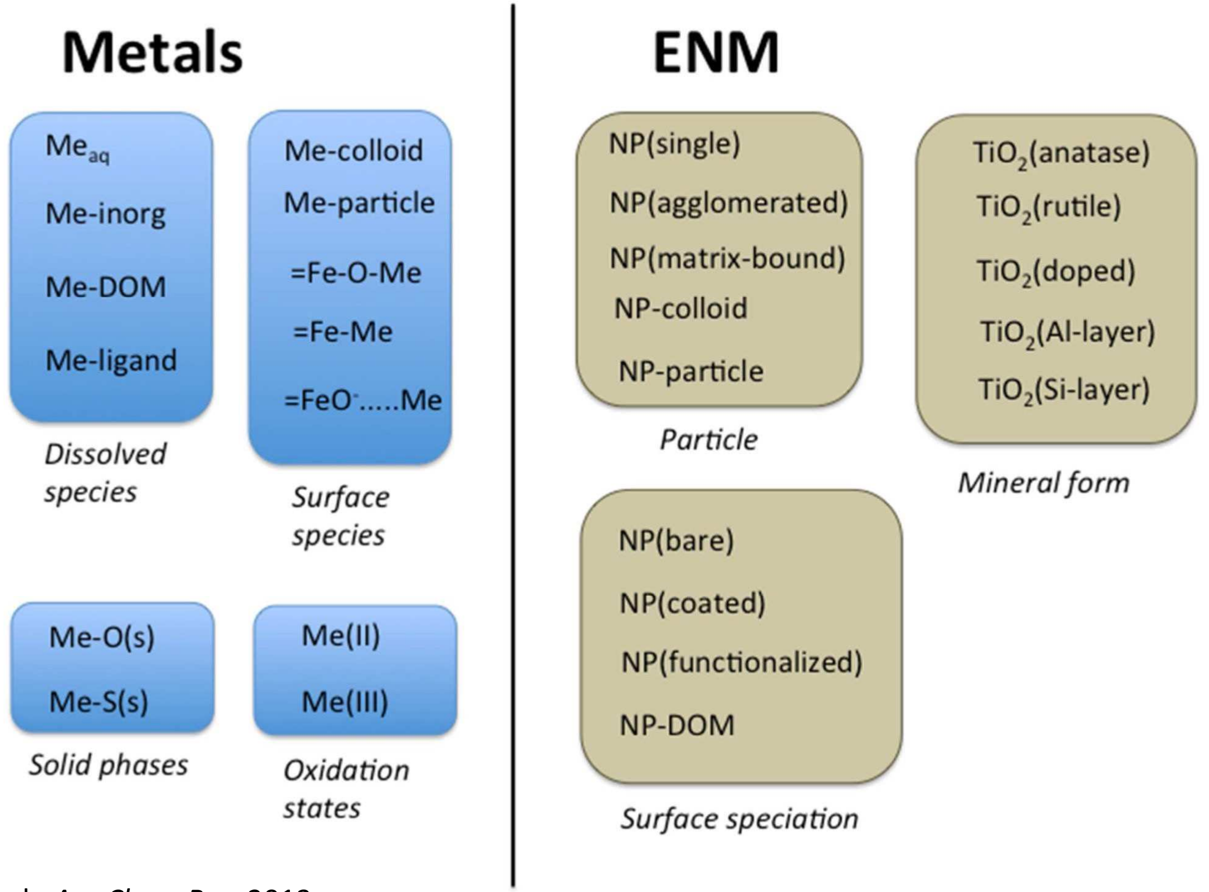
Added ZnO-NPs underwent rapid dissolution following their entry into the soil
No significant difference in plant growth and accumulation or speciation of Zn in plant tissues between soluble Zn and ZnO-NP treatments
No nanospecific effects observed in this study

Wang et al., *ES&T,* 2013

Fate of NPs in soil: how to model it?

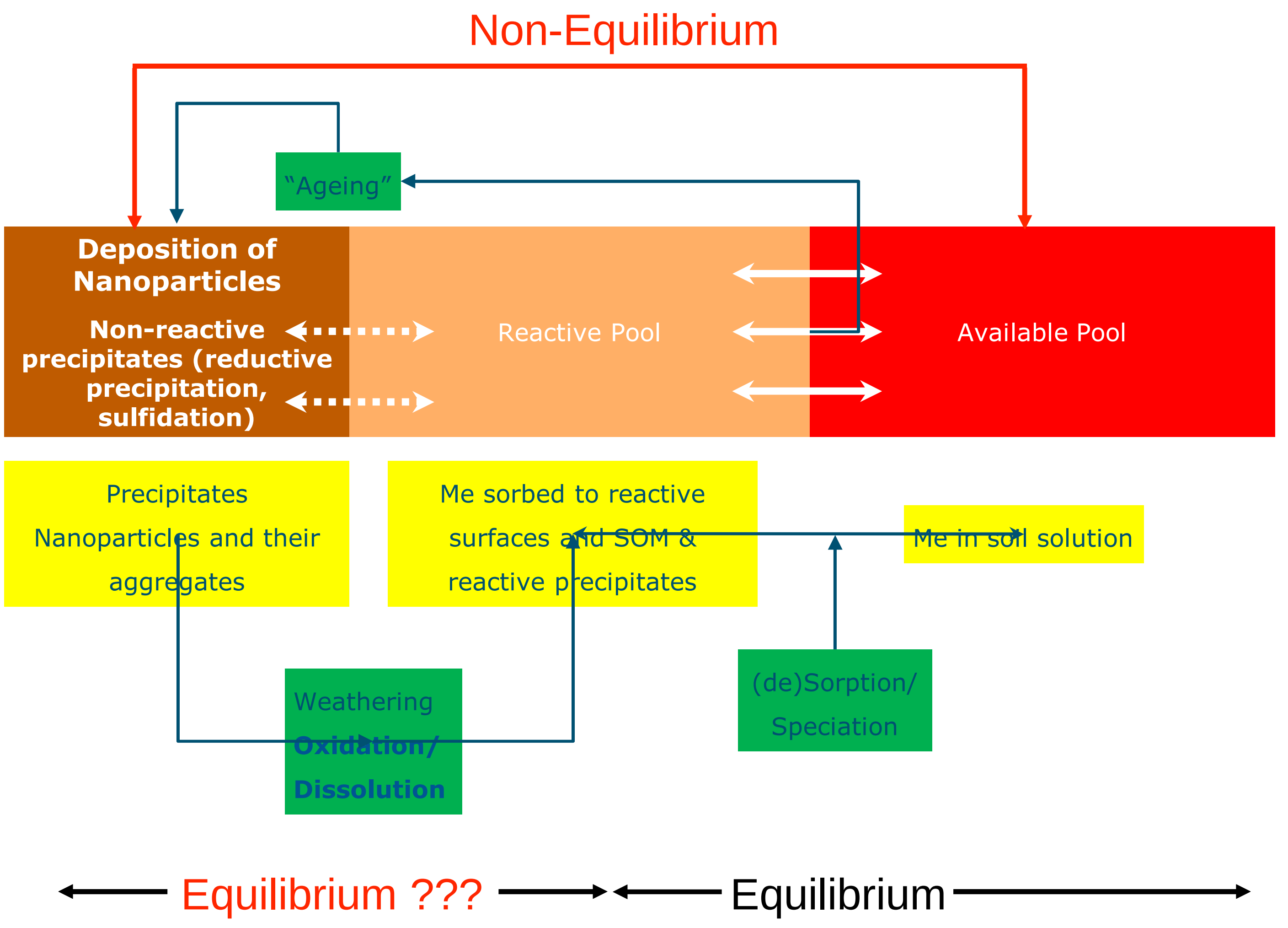
Environmental fate models for ENM need to incorporate the different reactivities of the different forms of a specific ENM

Similar for metals where it is necessary to understand speciation in order to predict the different reactivities of different forms



Westerhoff and Nowack, *Acc Chem Res,* 2013

Fate of metallic nanoparticles in soil



Non-equilibrium processes:

- Effects of coatings and artificial coating degradation

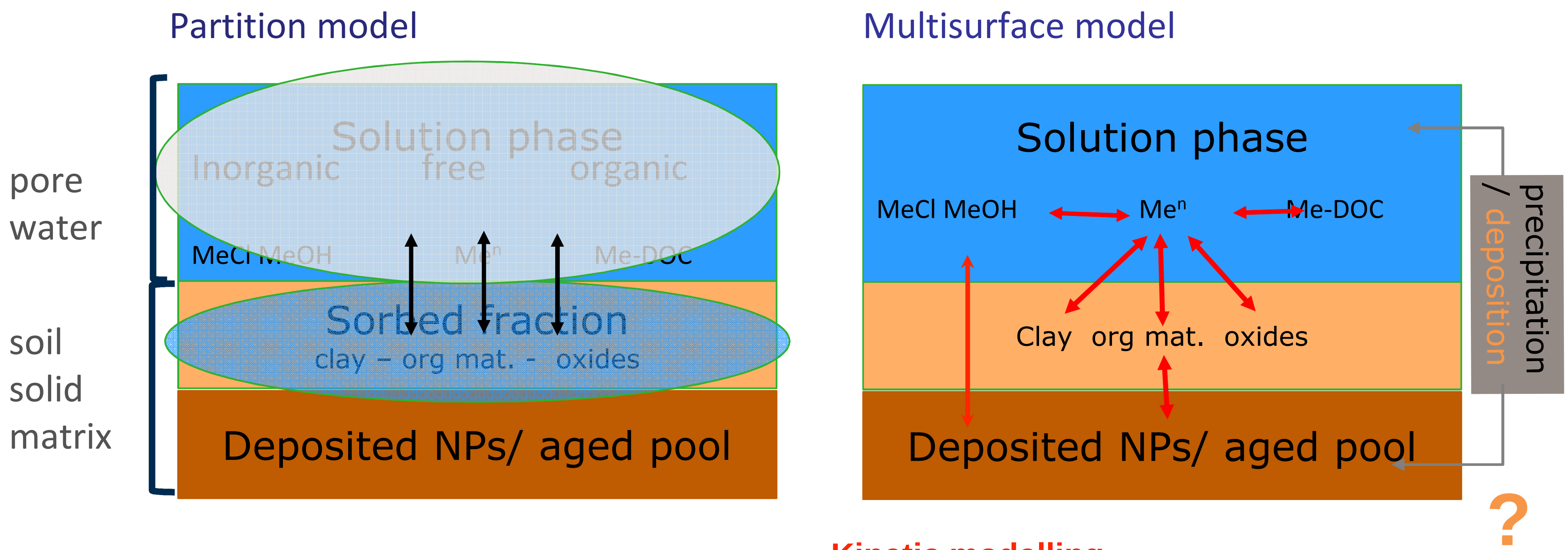
- Nanospecific properties (e.g. changes in surface structure leading to additional adsorption sites) **will affect:**

- **interaction of MeNPs with soil colloidal and solid constituents**
- **the ratio of free versus MeNPs-bound**

…which will determine dissolution rate, distribution between soil and pore water and availability of MeNPs in soil

Fate of NPs in soil: how to model it?

- From Partition Models to Mechanistic Modelling



Kinetic modelling

Account for dissolution and partitioning (K_d)
And for detachment of NPs from soils: e.g. nonequilibrium retention coefficient (K_r) by Cornelis *et al. ES&T*, 2011

e.g. DLVO theory underpredicted transport of MeNPs by failing to account for the “lubricant” effect of surfactants or DOM

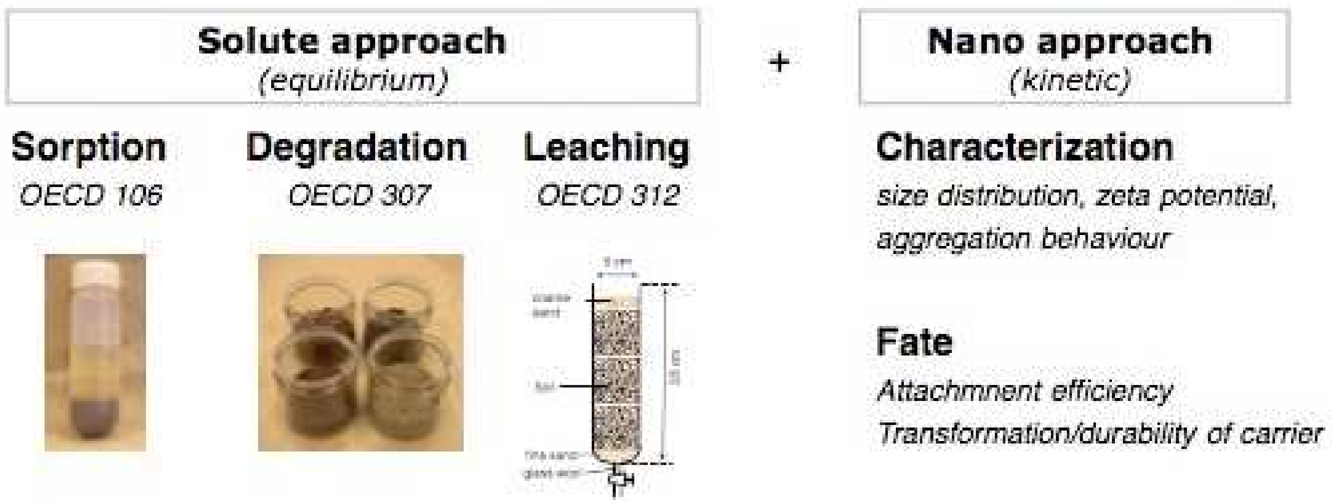
Additional metrics (e.g. number concentrations) related to MeNPs specific properties and transformations may be needed :

for improved understanding of the fate and effects associated with MeNPs in soil which are constantly changing size, composition, and distribution as they age in soils.

New nano-enabled agrichemicals: Examples of relevant processes to characterize

- Dissolution kinetics
- Transformation/ metal speciation in soil
- Surface affinity/ Aggregation/ Detachment/ Mobility/ Transport
- Uptake/ Bioaccessibility/ Bioaccumulation rate
- Effects/ Toxicity

Test schemes for measuring NPs bioavailability



- OECD (other examples OECD TG 222, 225, 308 315, 317): Revise guidelines available for applicability/ Revise and develop guidelines
- Harmonize testing conditions, media, parameters, methods
- Measuring bioavailability through the assessment of the geochemical available fraction: developing proxies, e.g. chemical extraction methods

Difficulties:

- Analysis and characterization of MeNPs in complex matrices (including soil and pore water)
- Sensitivity of methods required to measure very low concentrations of Me(NPs)

Challenges (I): Selection of methods that allow detection of NPs in soil

Total metal concentration: complex, careful digestion procedure?

- Bulk soil analysis: natural background concentration for some elements is high, so work with high concentration of MeNP is necessary (or the use radio or stable isotopic labelled MeNP)
- For some MeNP (e.g. Au), detection via SEM or ESEM is possible, EDX, EELS, also size distribution, number concentrations; time consuming!

Challenges (II): Selection of a standard method to quantify release of dissolved ions (real time kinetics) and to discriminate between ions and NPs associated with colloids in pore water

- Separation techniques: separation of pore water, more techniques available for pore water analysis, recovery for some elements low.
- FFF laborious, but advantages (e.g. low size limit, data treatment…).
- Single particle-ICP-MS: slightly higher size limit than FFF and TEM; method requires development, but very low number concentrations are possible and fast method.
- Combination of FFF and sp-ICP-MS possible.

Challenges (III): Account for the effect of variable soil properties and soil constituents

Examples: Although generalization is not possible, for most NPs:

- pH: affects dissolution, stability of NPs in suspension; influences aggregation through changes in surface charge and speciation
- Ionic strength: favours deposition, aggregation and pore straining, reducing mobility and bioavailability, although adsorption of soil anions may stabilise positively charged NPs
- DOM: stabilization in suspension, reduce aggregation and deposition afecting mobility and bioavailability
- Soil texture (clay): increase pore straining, deposition and/or heteroaggregation with soil colloids affecting mobility and bioavailability

Thank you for listening!!!!

Acknowledgements:

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