Measurements of transport and fate of emerging contaminants in soil and aquifer environments

Ishai Dror

WEIZMANN INSTITUTE OF SCIENCE

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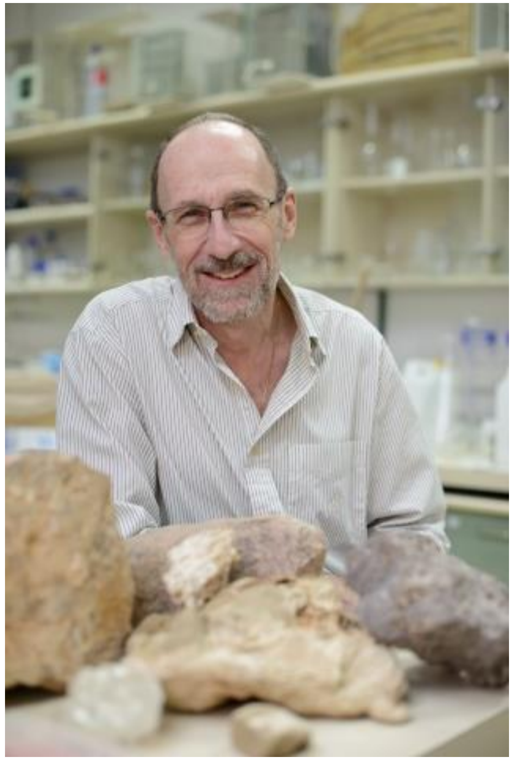
We –Need Final Conference

Jayashree Nath



Natalia Goykhman

Yinon Yecheskel

Brian Berkowitz

Objectives based on the project WPs and last meetings

Transport experiments with emerging contaminants:

Pharmaceuticals:

- **Roxarsone + Gd (data already available, sent to UPC)**
- **Azithromycin (AZT, shared with Aveiro)**

  Perfluorooctanesulfonic acid **(PFOS, shared with Aveiro)**

  Perfluorooctanoic acid (**PFOA, shared with Aveiro)**
- **Pt-based pharmaceuticals (partially presented previously)**

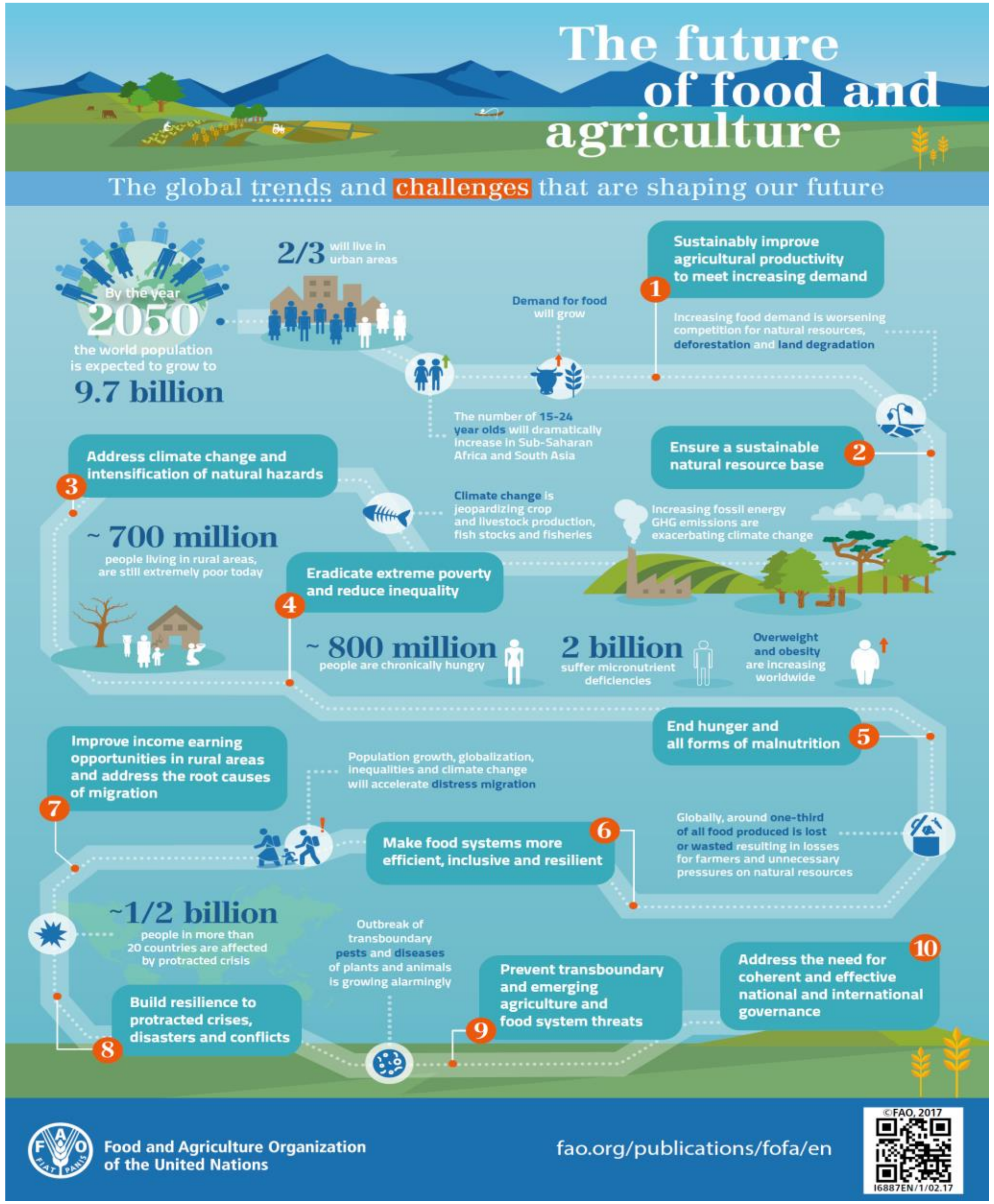
Nanoparticles: **(partially presented previously)**

- AgNPs + silver sulfide NPs
- AuNPs
- ZnO NPs
- CuO NPs

To meet demand, agriculture in 2050 will need to produce almost 50 % more food, feed and biofuel than it did in 2012

"The UN updated predication are that world's population would reach 9.73 billion by this year….In sub-Saharan Africa and South Asia, agricultural output would need to more than double by 2050 to meet increased demand, while in the rest of the world the projected increase would be about one-third above current levels"

FAO. 2017. The future of food and agriculture – Trends and challenges. Rome



It can be done –
it has been done in the past ….

But , *We have to overcome -*
Climate change
Pollution of resources (soil, water)

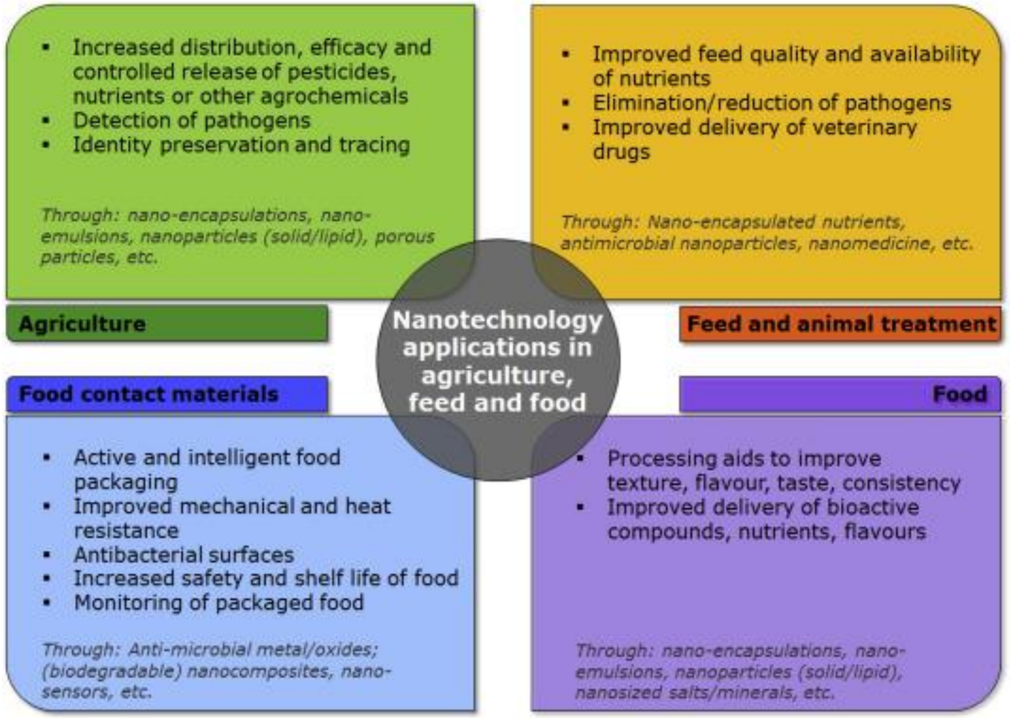
For this we will have to develop much more efficient Agriculture practices.

Nanotechnology

Nanotechnology is being strongly advocated for improving agricultural productivity and sustainability through promoting plant and animal health and production, effective, sustained delivery of agrochemicals (e.g., pesticides), and intelligent surveillance via nanosensors.

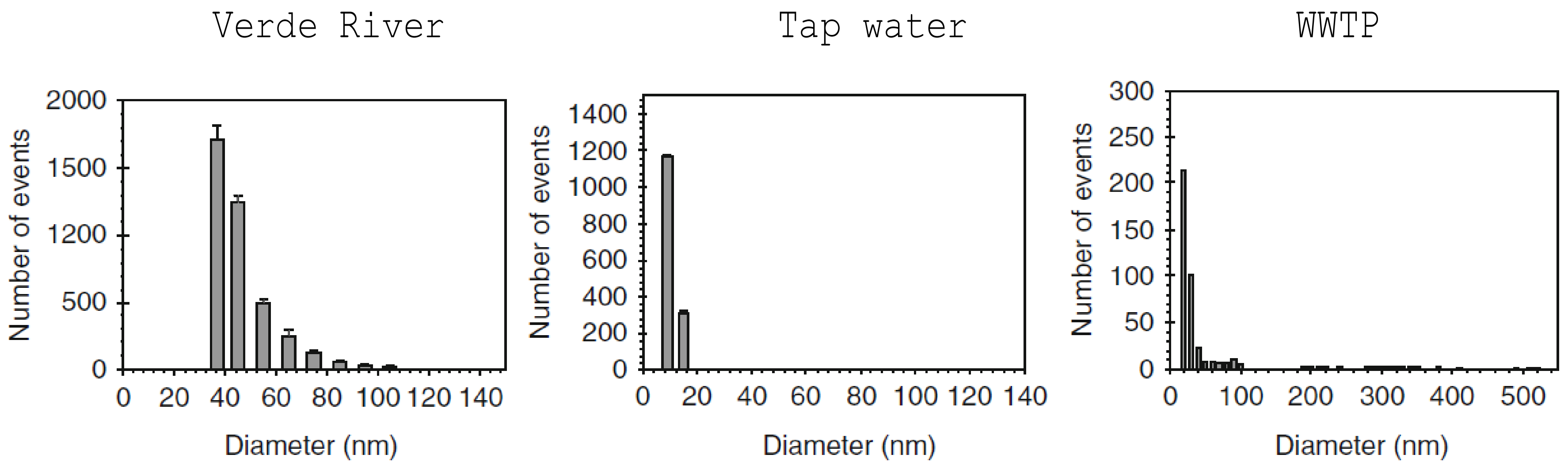
The development of pesticides using nanotechnology (i.e., nanopesticides) has drawn immense attention from scientific and industrial communities. Over 3000 patents of nanopesticides were registered within the last decade and some nanopesticides are already in the market.

Kah, et al. Crit. Rev. Environ. Sci. Technol. 2013, 43, 1823-1867.



Amenta et al. Toxicol. Pharmacol., 2015, 73, 463-476

Size distribution of CeO_2 particles in environmental samples

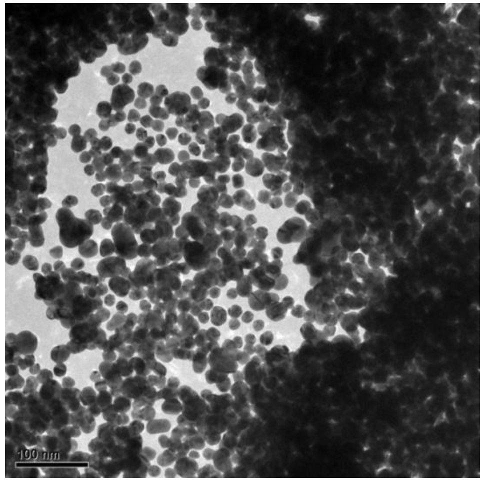


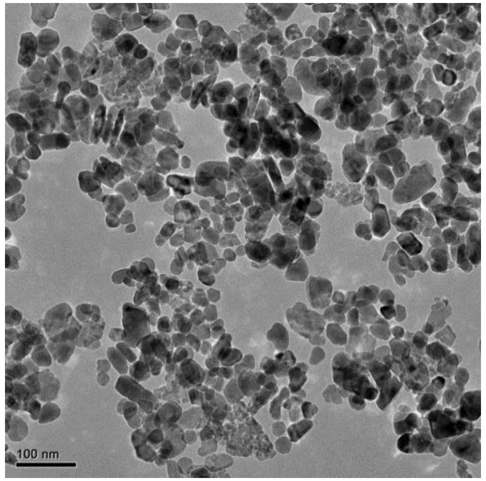
	Verde River	Tap water	WWTP
Number conc. (ml^{-1})	4.83×10^4	1.76×10^4	5.56×10^3
Particle mass conc. (ng/L) as Ce	18	0.1	42
Dissolved conc. (ng/L) as Ce	45	0.1	5.4
Total conc. (ng/L) as Ce	63	0.2	47
% nanoparticles of total Ce	28.5	50	88

Yang and Westerhoff 2014, DOI 10.1007/978-94-017-8739-0_1

Nanoparticles (NPs) Studied

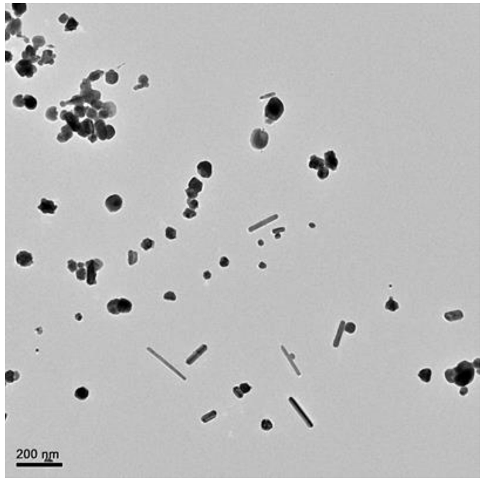
Au-NPs
Suspension color: red
Shape: round
ζ potential = -43.8
d = 49 nm (DLS)

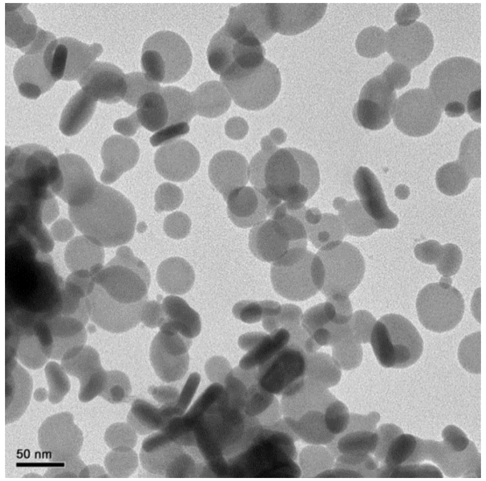




ZnO-NPs
Suspension color: transparent
Shape: mixed
ζ potential = 10.9
d = 70 nm (DLS)

Ag-NPs
Suspension color: green gray
Shape: hexagonal
ζ potential = -55.5
d = 79 nm (DLS)

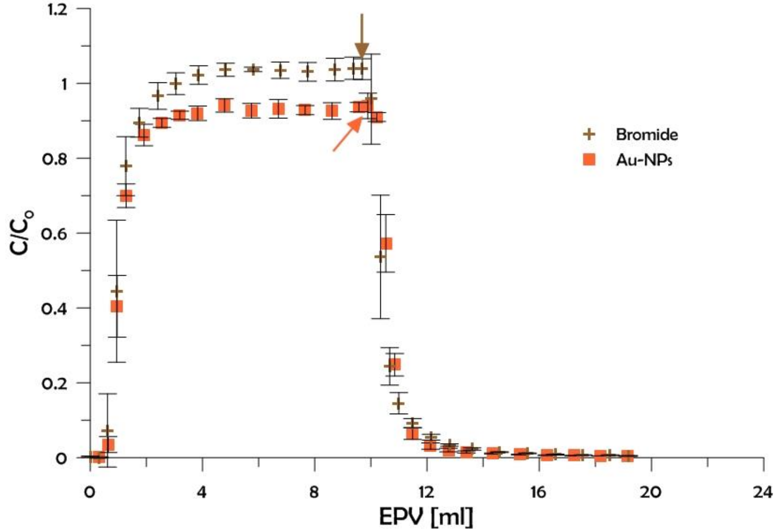


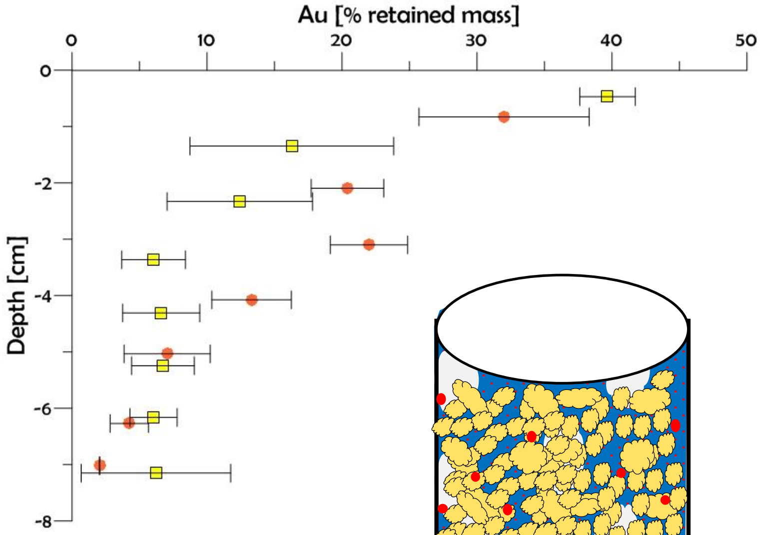


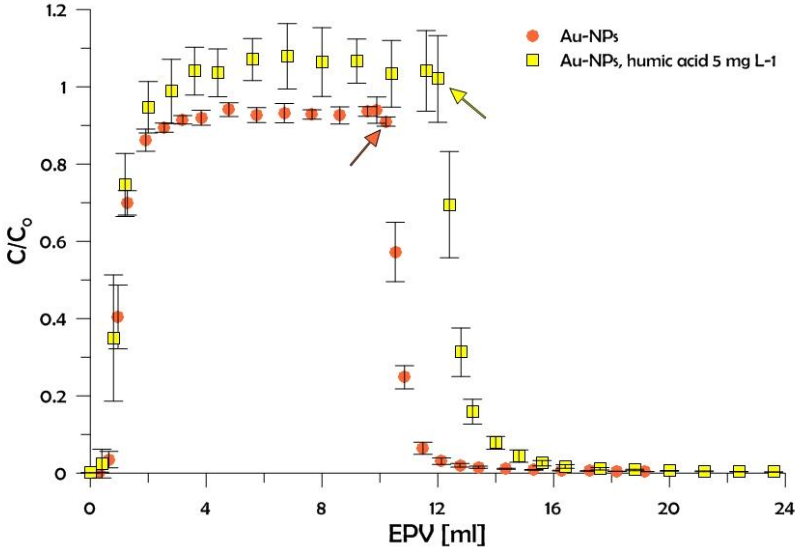
Ag_2S-NPs
Suspension color: brown
Shape: round
ζ potential = -51.3
d = 84 nm (DLS)

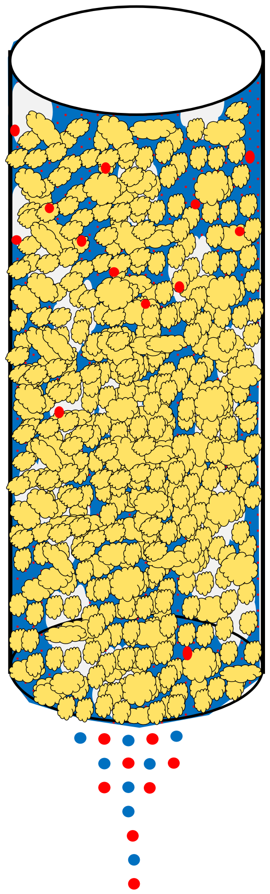
Bromide Tracer & Gold (Au)-NP transport in partially saturated sand column

Arrows indicate end of NP injection step and start of column washing with background solution.









Br^- / Au-NP conc. 1000 μg L^{-1} column saturation ~40%

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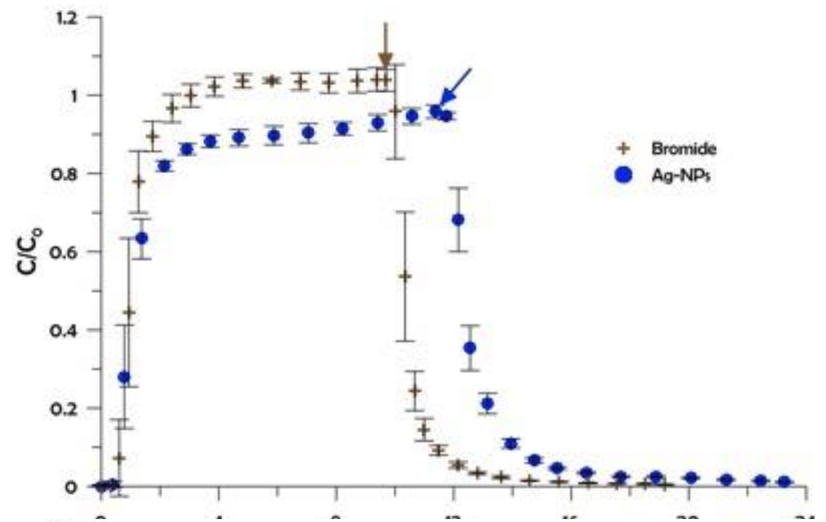
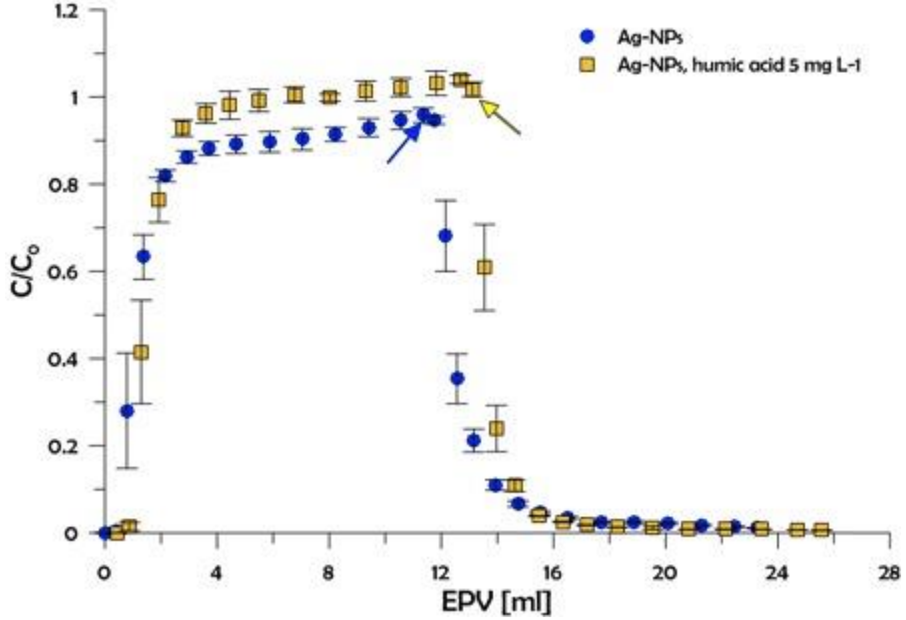
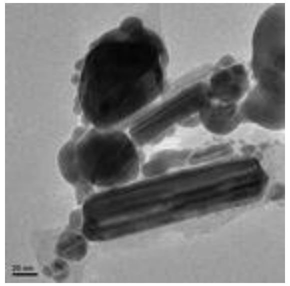
Silver (Ag) -NPs transport in Partially saturated column

Br^- / Au-NP conc. 1000/500 µg L^{-1} column saturation ~35%







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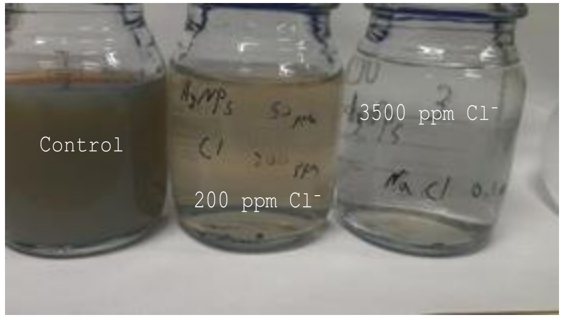
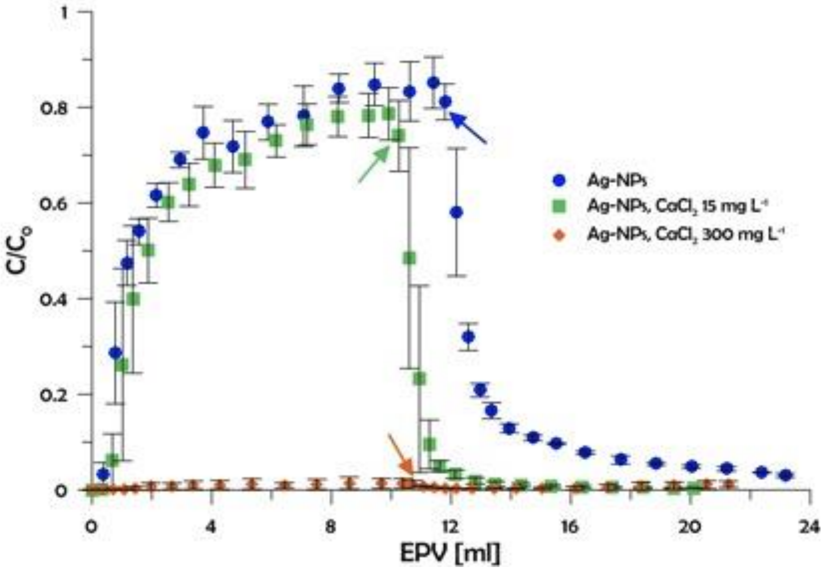
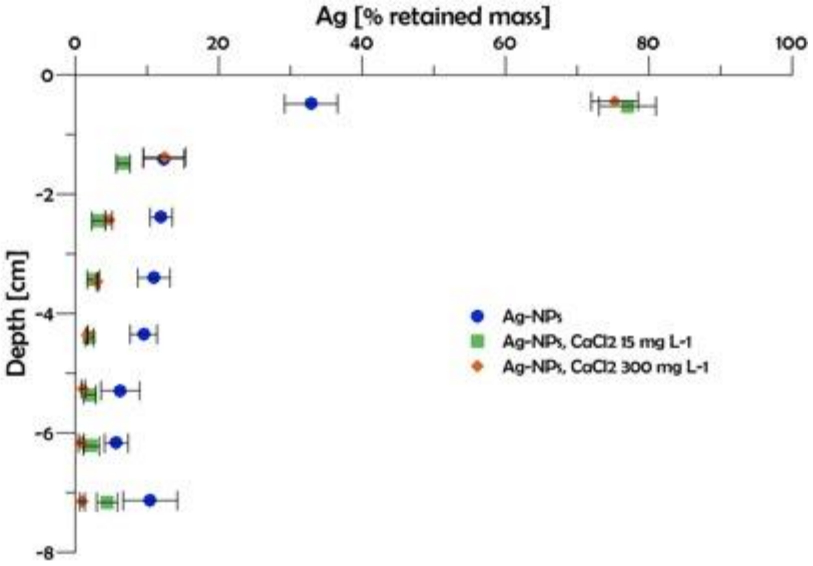
Silver (Ag)-NPs transport in Partially saturated column
Reaction with solution components.



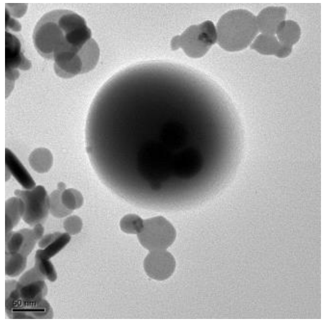
$Ca(NO_3)_2$
diameter- 1556nm
zeta Potential -1.5

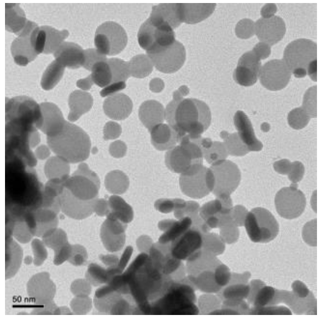




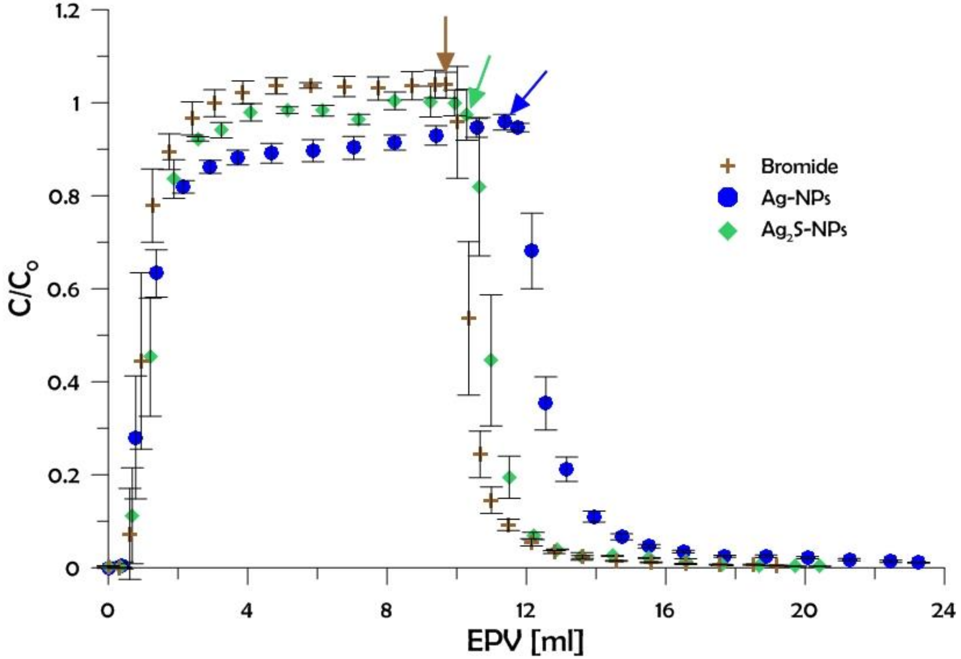
Ag-NP conc. 500 µg L^{-1} column saturation ~40%

Silver Sulfide (Ag_2S)-NP transport in partially saturated column

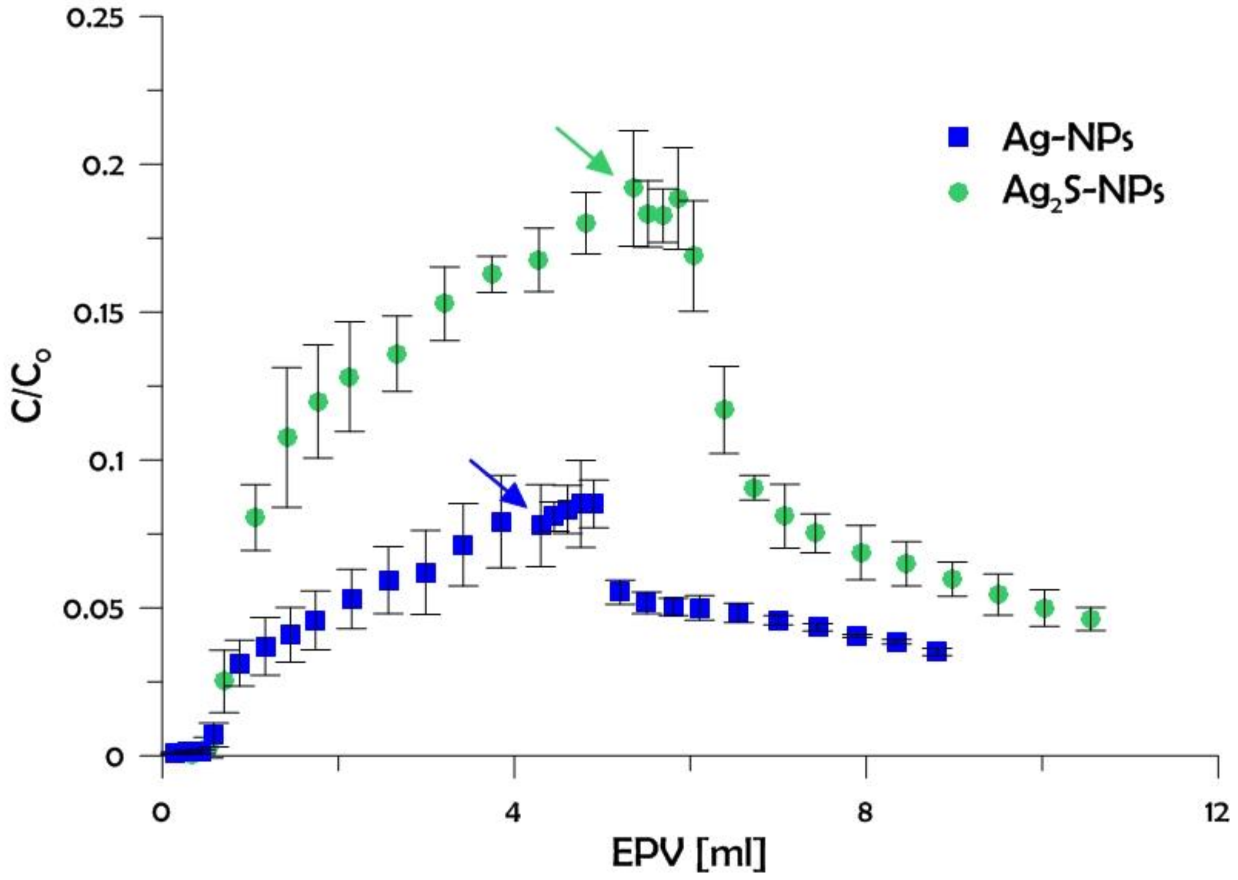




Br^- / Ag_2S-NP conc. 1000 µg L^{-1} column saturation ~40%

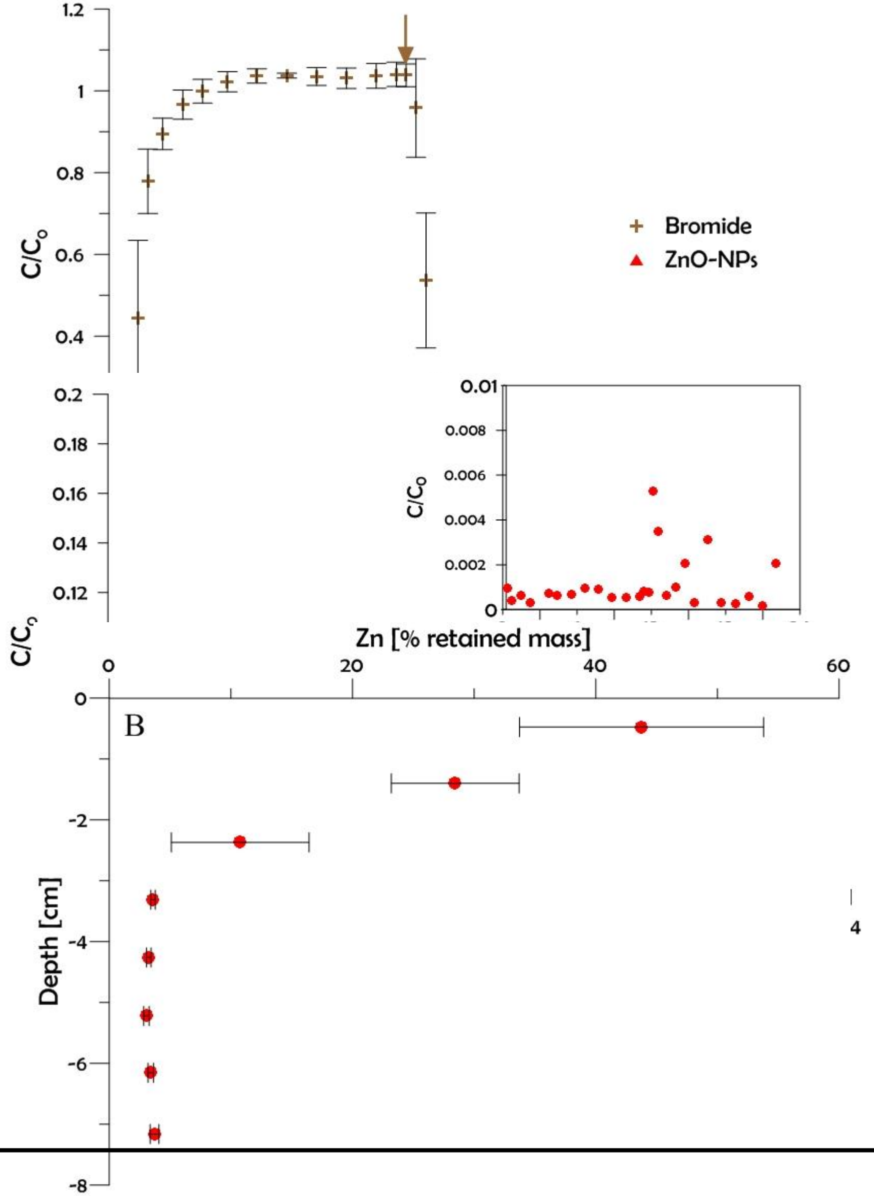


Breakthrough curve comparison: Ag-NPs and Ag_2S-NPs in partially saturated soil column



Arrows indicate end of NP injection step and start of column washing with background solution.

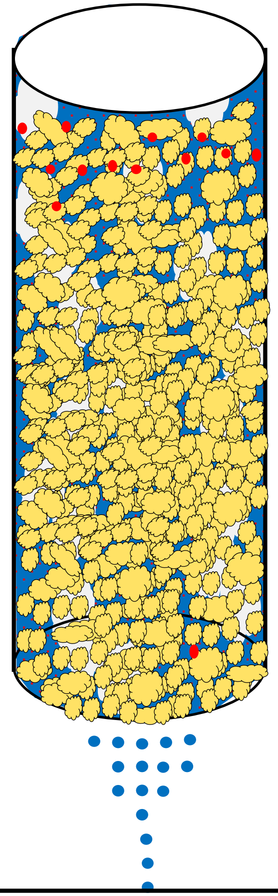
ZnO-NP transport in partially saturated column



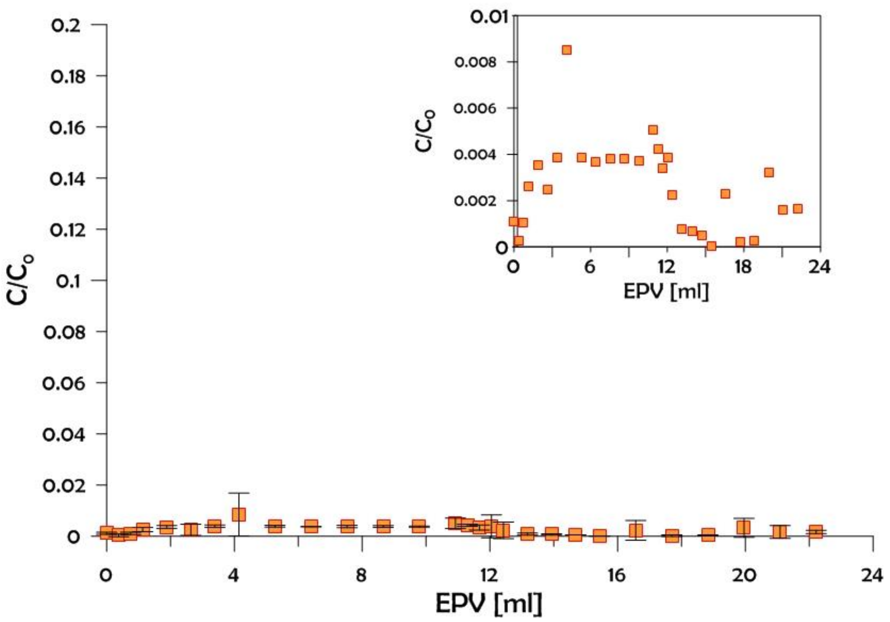
Saturation 37%

Zeta potential 10.9 (1.45)

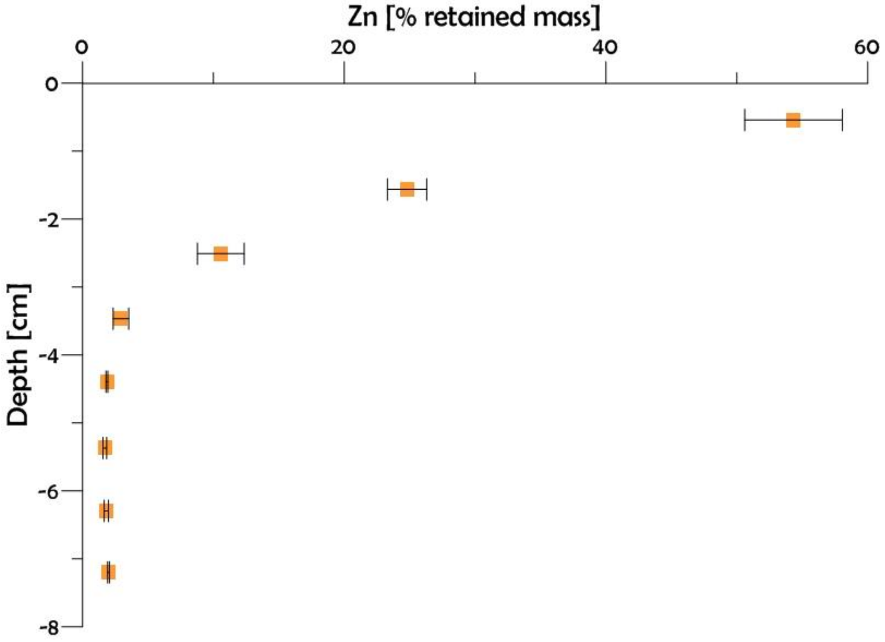
Average diameter DLS 66.6 (1.76)



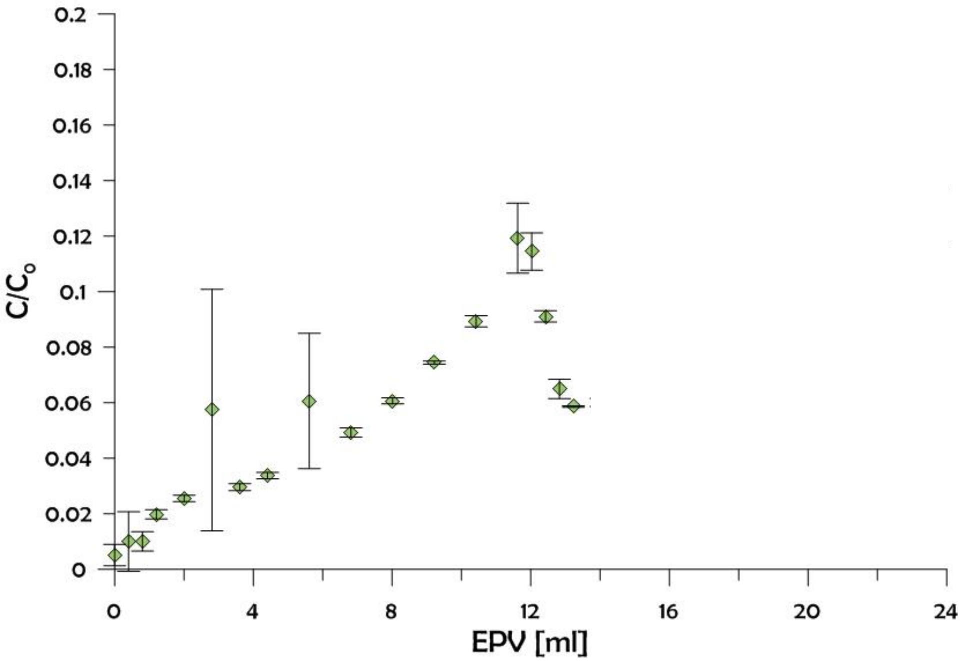
ZnO-NP transport in partially saturated column, in the presence of humic acid

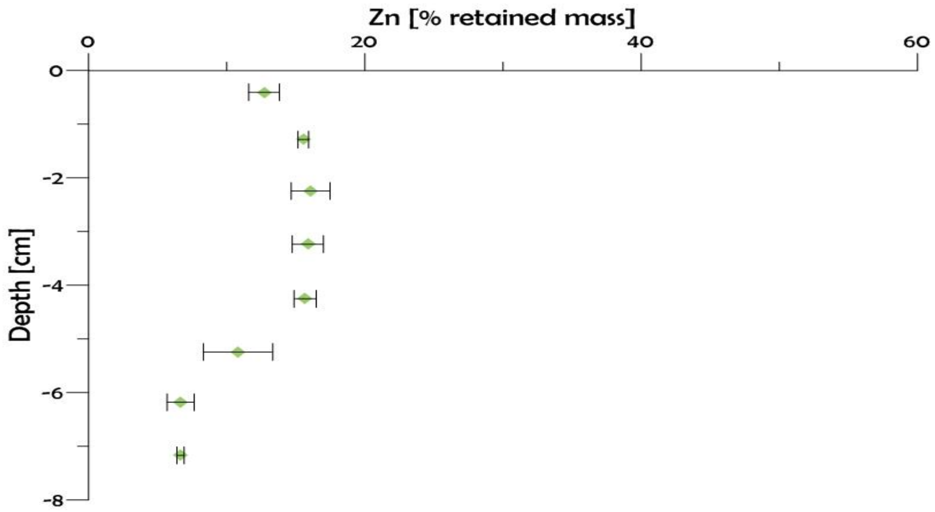


Saturation 36%
Humic acid conc. 5 ppm
Zeta potential -23.7 (0.66)
Average diameter DLS 204.9 (2.91)

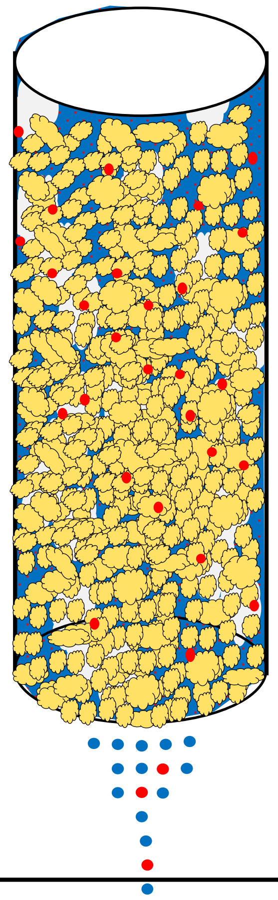


ZnO-NP transport in partially saturated column, in the presence of humic acid





Saturation 34%
Humic acid conc. 50 ppm
Zeta potential -26.8 (0.66)
Average diameter DLS 124.7 (2.91)



Nanotechnology --- an ever increasing field

NPs

- **Medicine** — Imaging and drug delivery
- **Cosmetics** — Sunscreens, shampoo etc.
- **Agriculture** — Food products
- **Industry** — Automobile, lubricants, circuitry, chemicals
- **Biosensors**

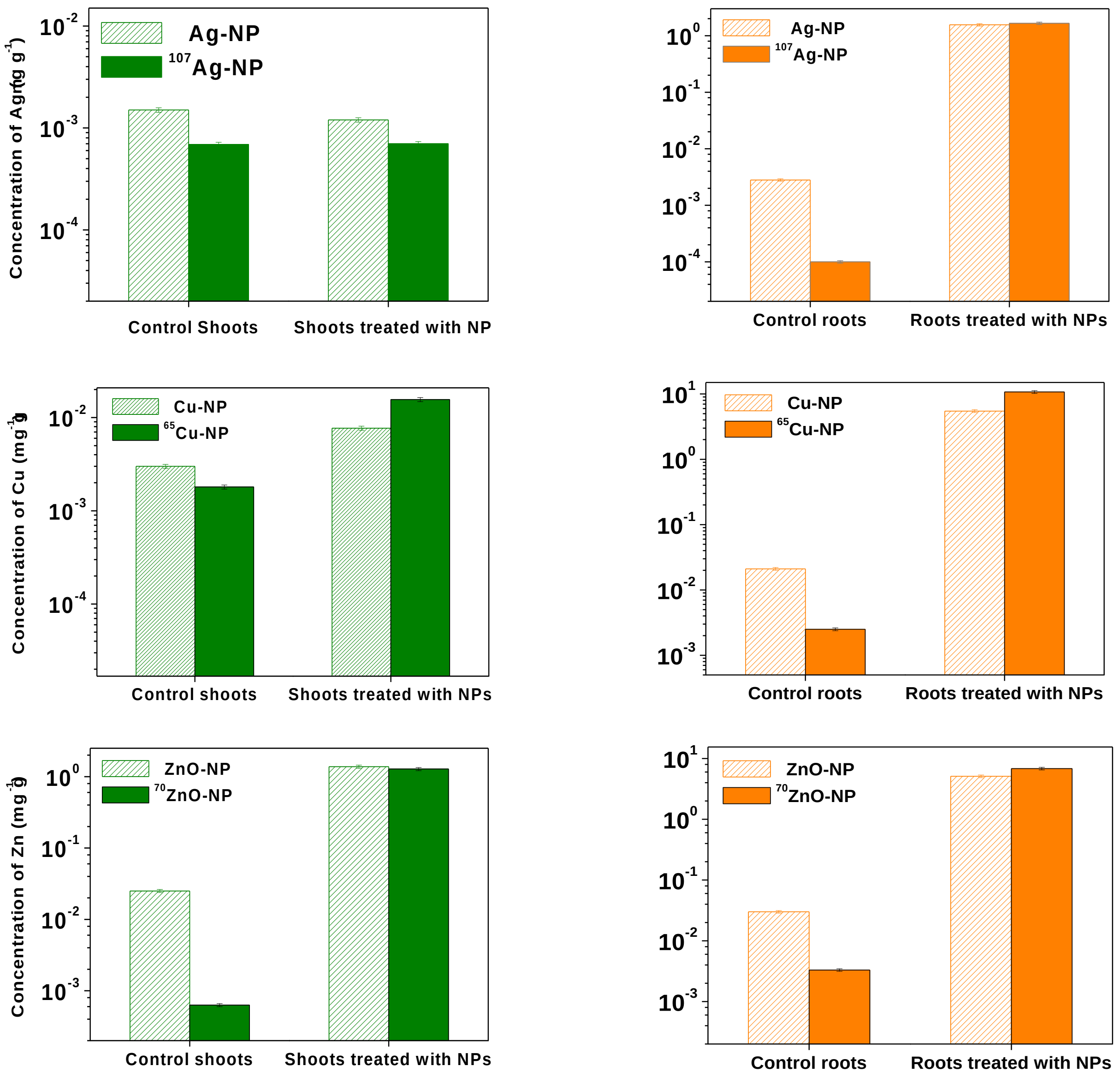
PLANTS - environmental matrix

Rising concern

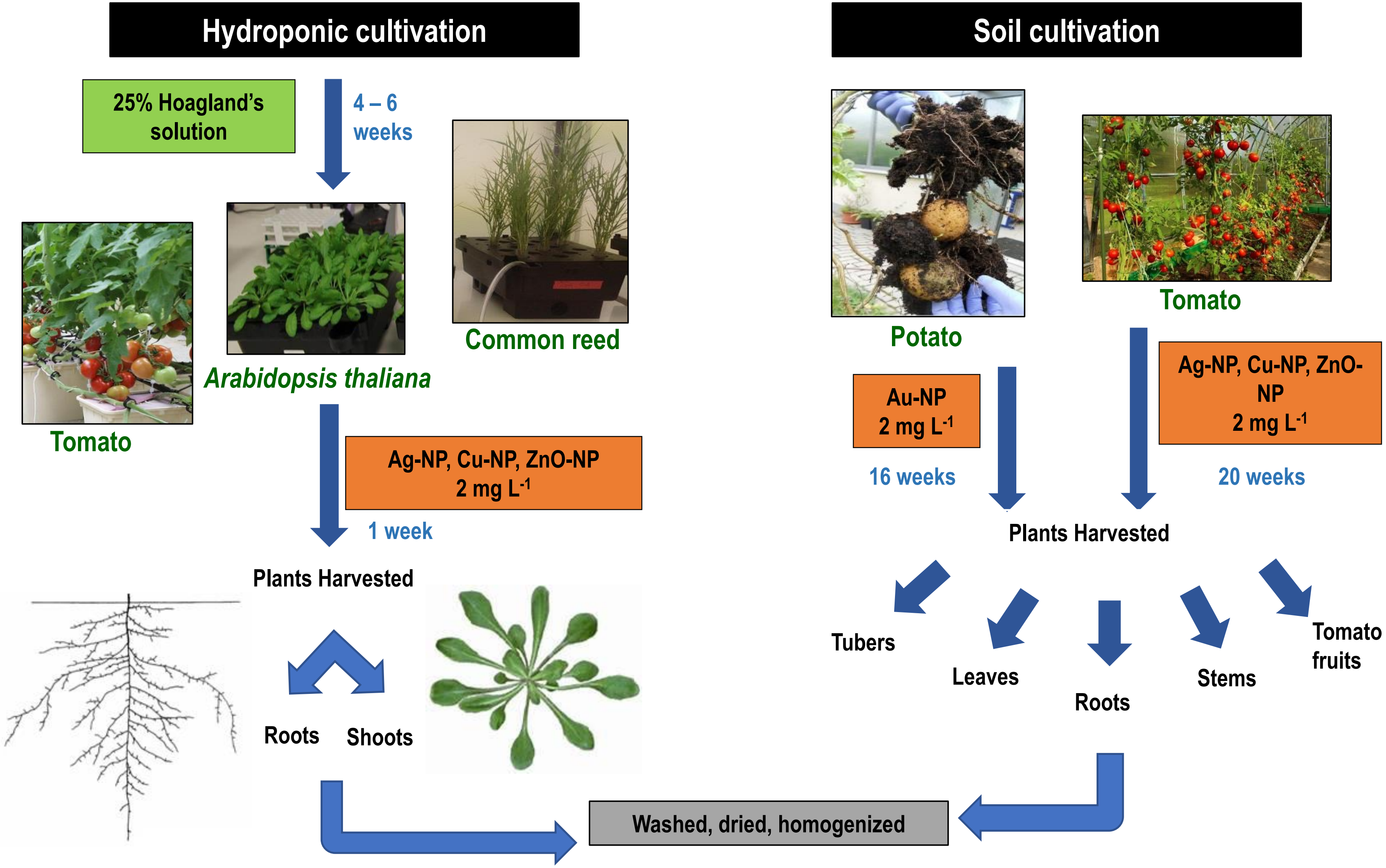
Inevitably released into soil-water environments

Eco-toxicity of the NPs

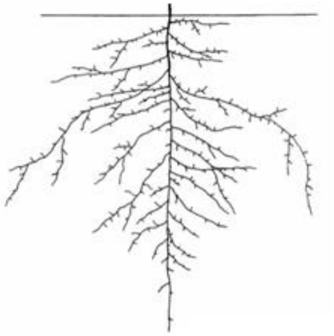
Isotopically-labeled NPs provide lower background in controls and similar levels of metal concentration when exposed to NPs. Isotopic labelling improves the detection sensitivity by enabling a larger detection range.

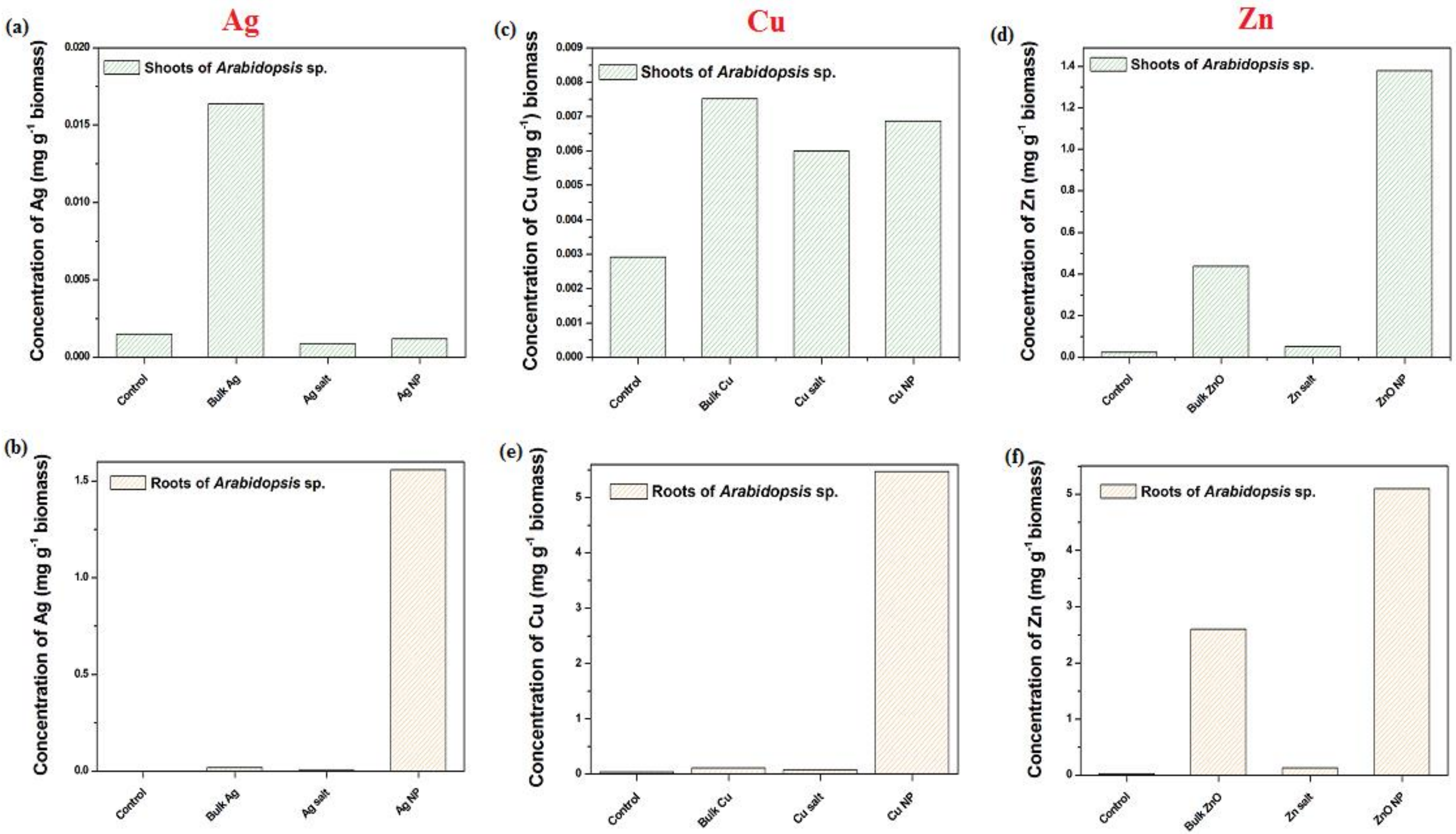


Tracing experiments with different plants under hydroponic conditions and in soil



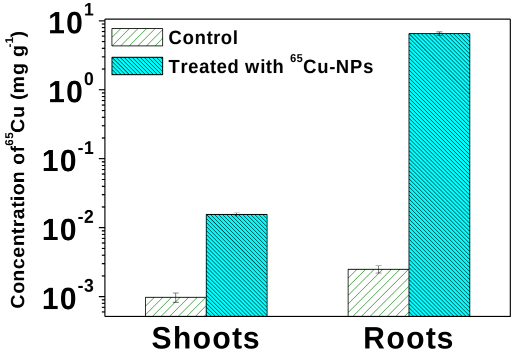
Uptake of metals by *A. thaliana* from different states (bulk, ionic and nanoparticle)

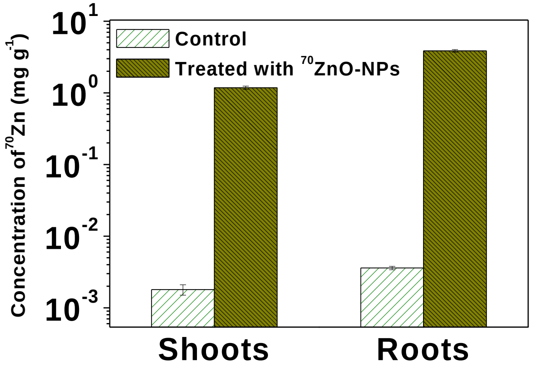


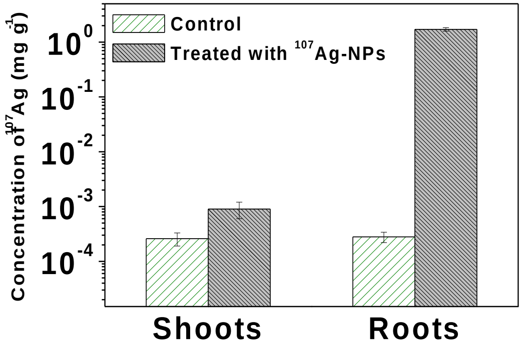


Total concentrations of metals (mg/g biomass) in shoots and roots of different plants exposed to isotopically-labeled nanoparticles under hydroponic conditions.

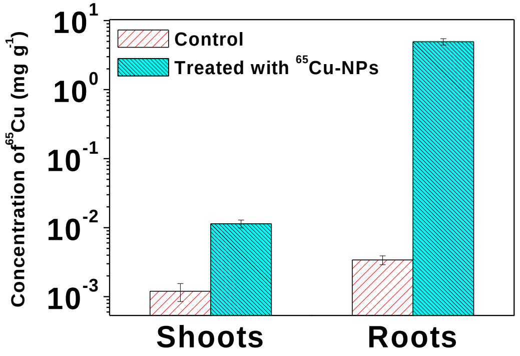
Arabidopsis thaliana

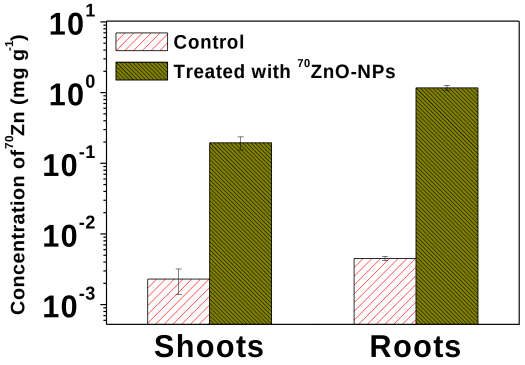


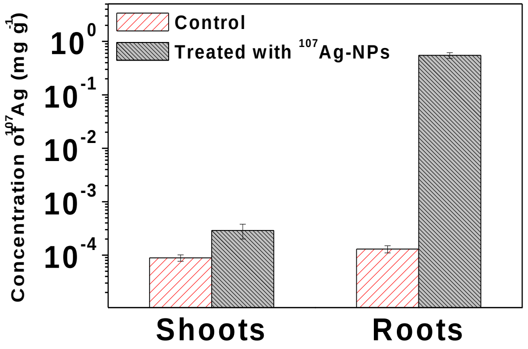




Tomato







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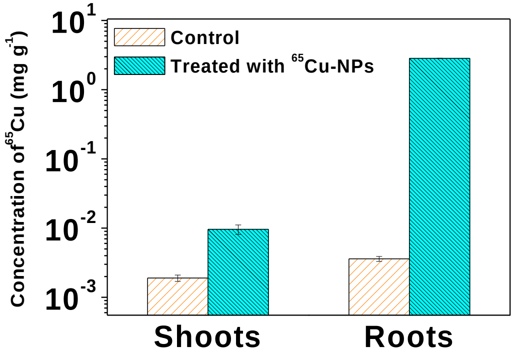
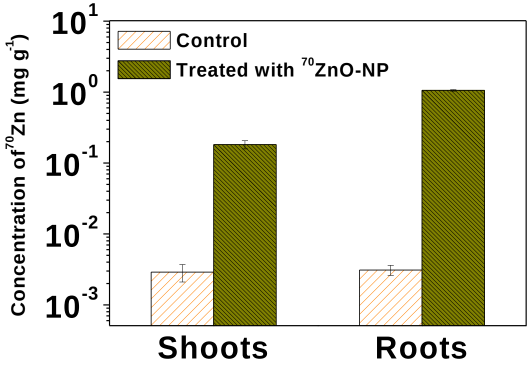
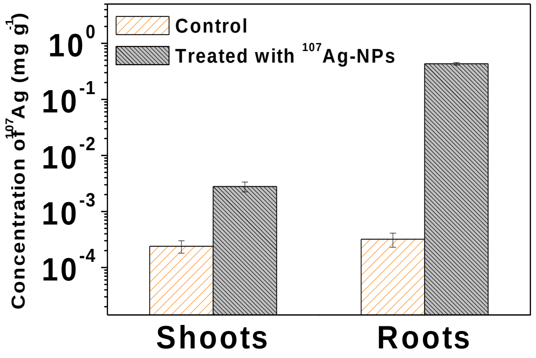


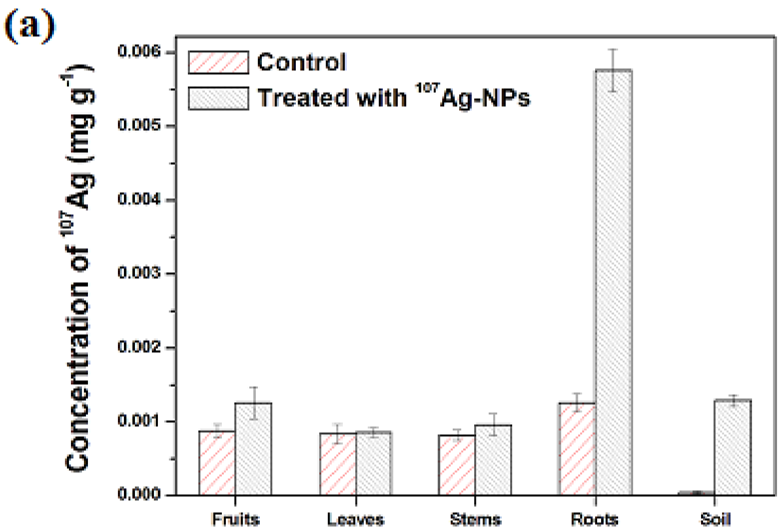


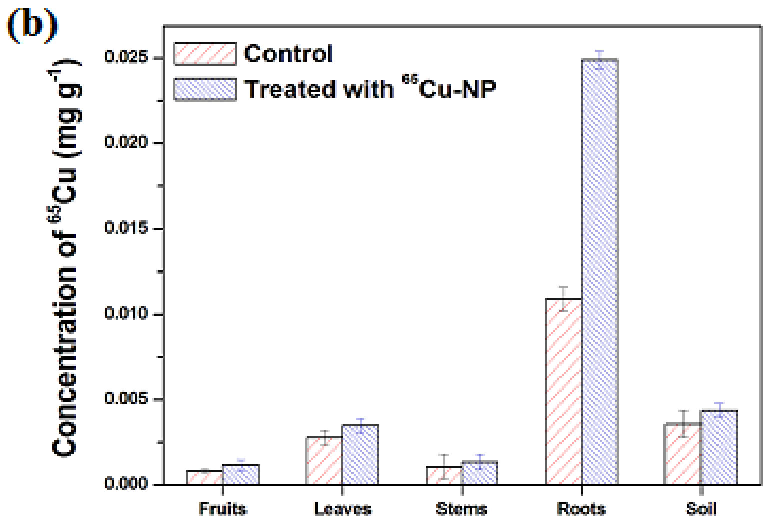


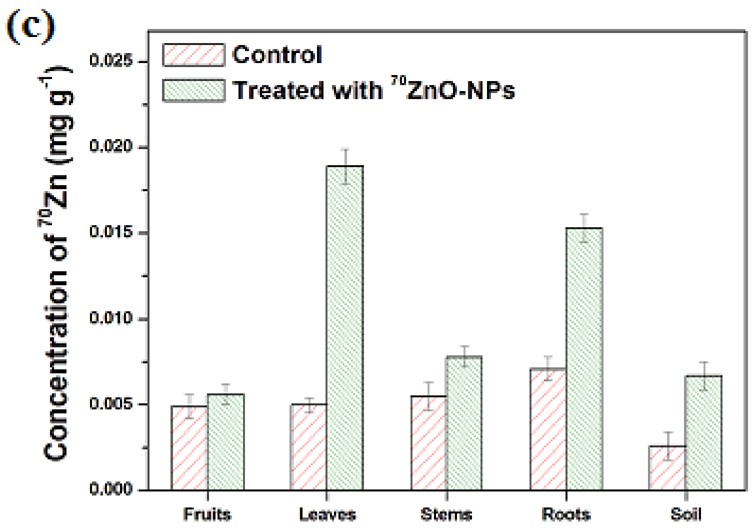
Tomato plants treated with isotopically labeled Ag-NPs, Cu-NPs & ZnO-NPs in soil (2 mg L^{-1})

Tomato plants
(*Solunum lycopersicum*)

Grown in soil
Greenhouse conditions

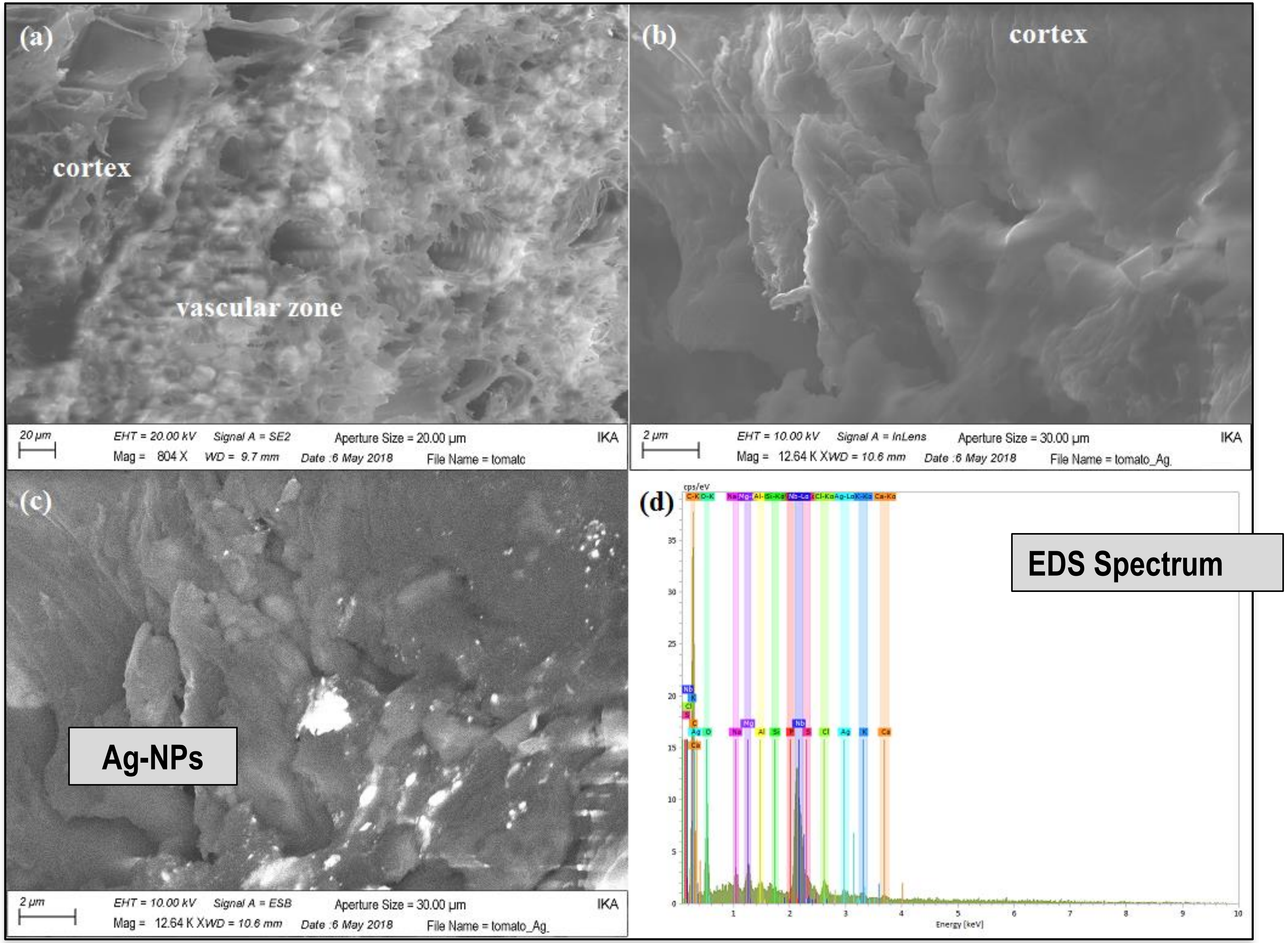






Parts of *Solunum lycopersicum* plants and soil for cultivation

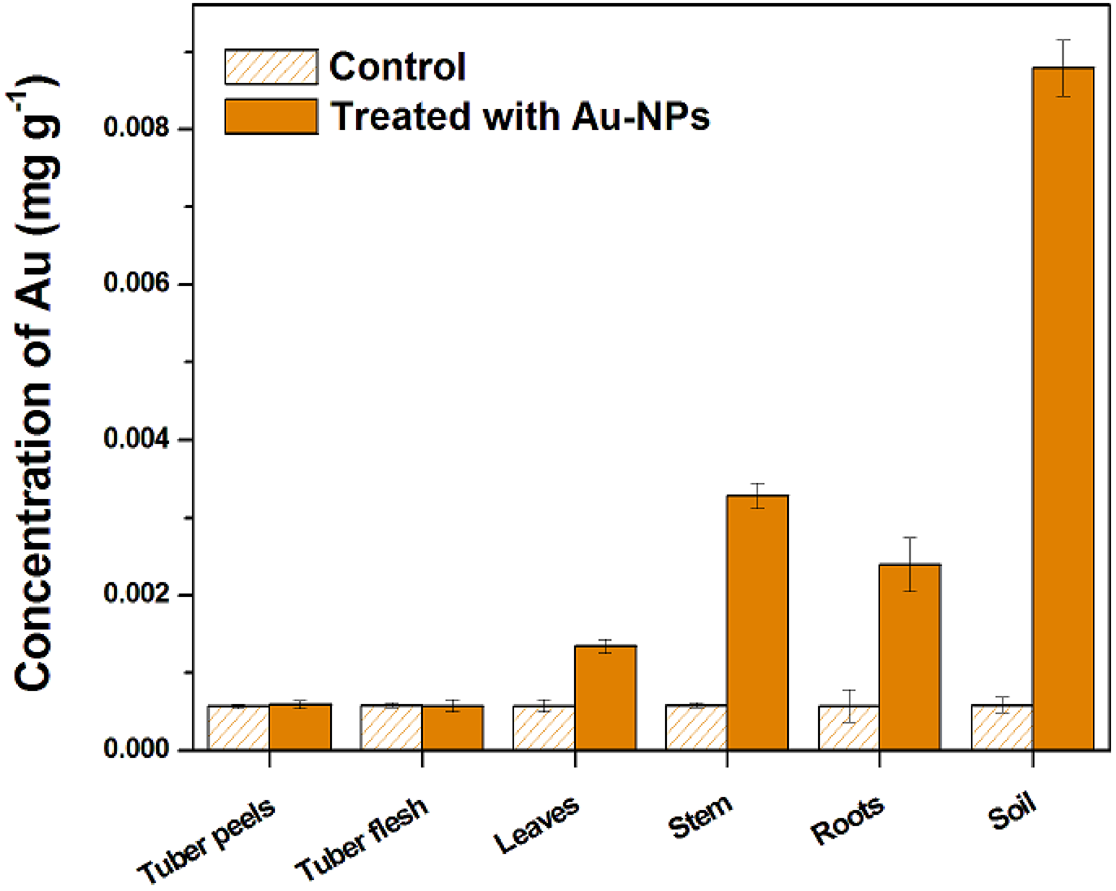
SEM and EDS of Tomato plant roots exposed to ^{107}Ag-NPs



Tracing experiments with Potato plants in soil under real environmental conditions with Au-NPs (2 mg L^{-1})

Potato plants
(*Solunum tuberosum*)

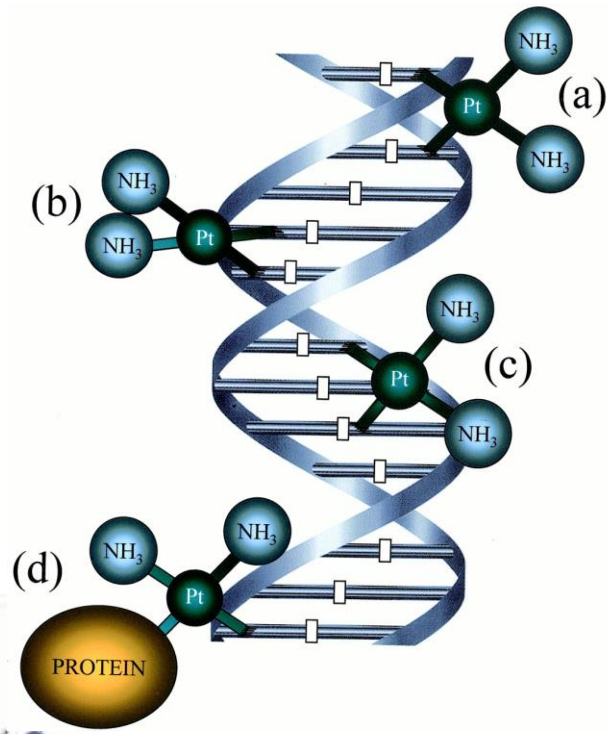
Grown in soil
Real environment conditions

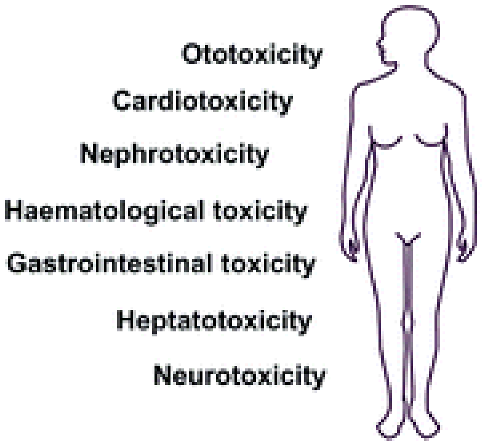


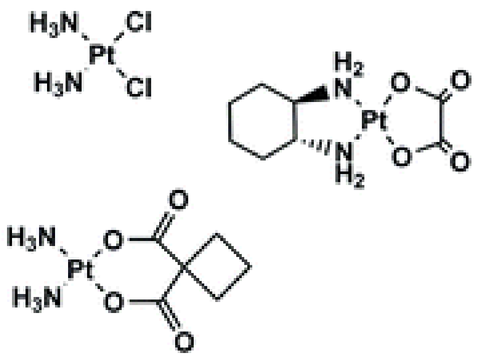
Parts of *Solunum tuberosum* plants and soil for cultivation

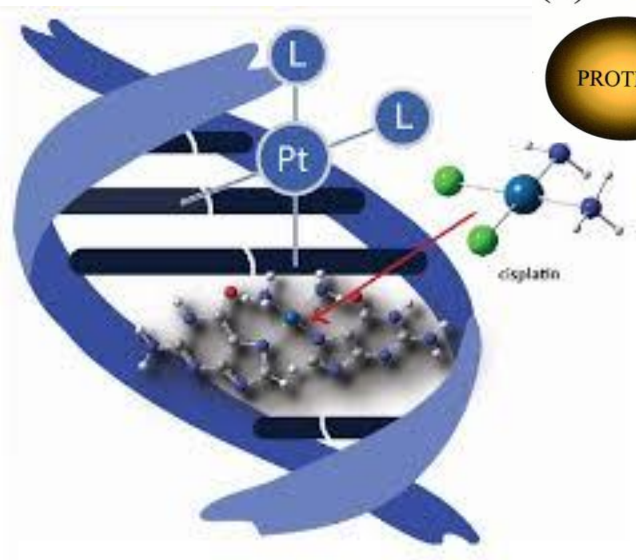
Pt-based Pharmaceuticals

- Widely used in chemotherapy
- Attach to DNA and inhibit cell growth
- Non-selective and toxic
- Detected in wastewater around the world: 4 ng/L[a] – 150 µg/L[b]
- Environmental fate: several sorption studied with conflicting results

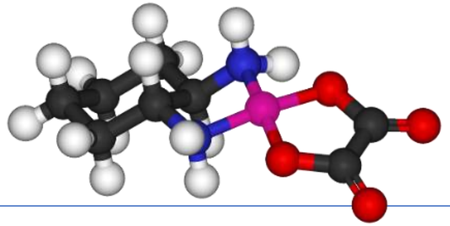
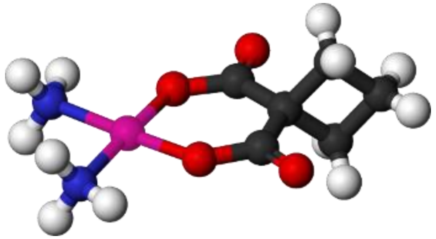
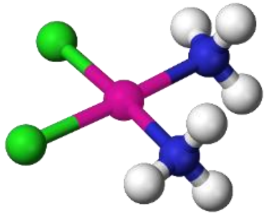






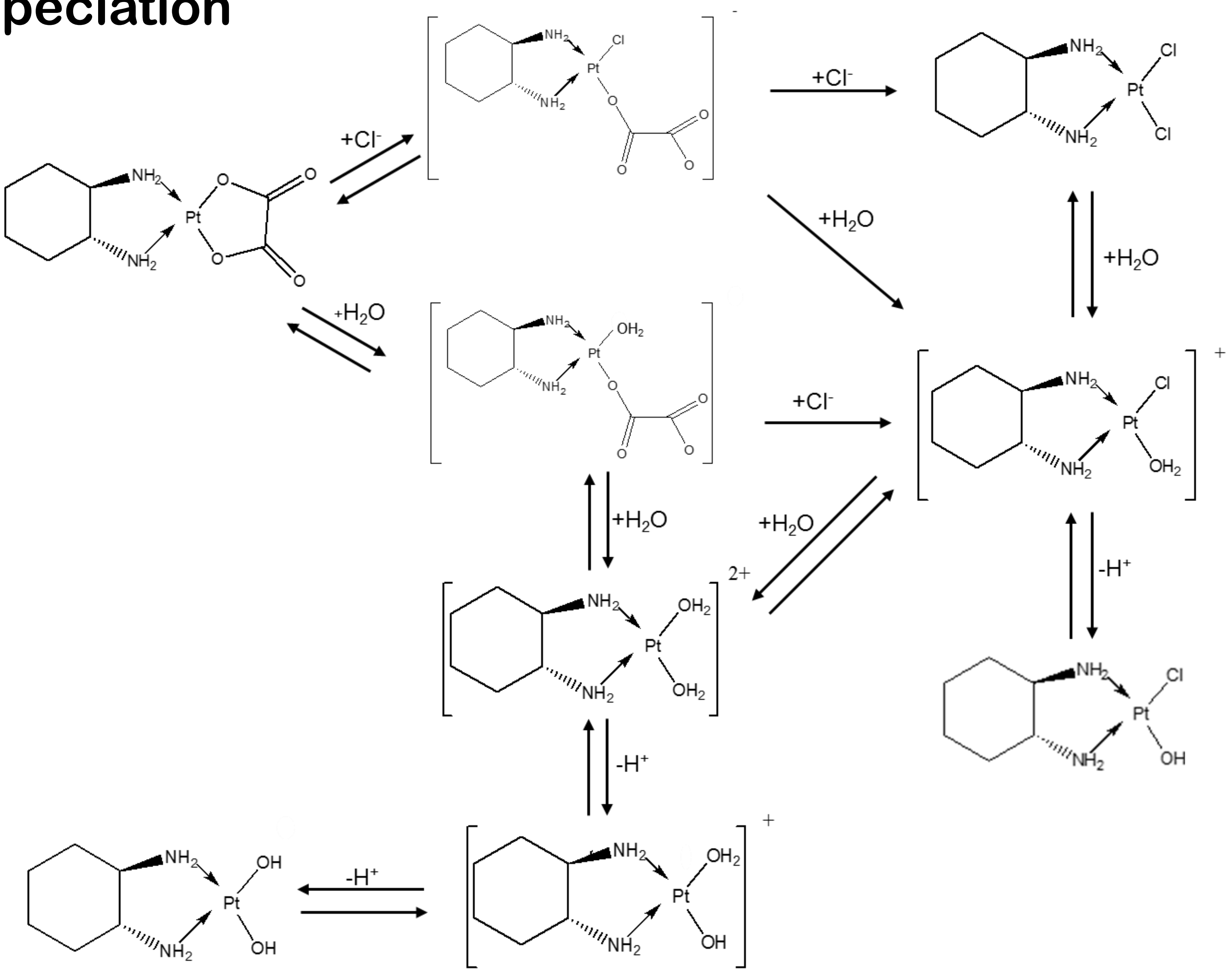


a. Kummerer, 2001. *Chemosphere* 45, 957-969. b. Lenz et al., 2007. *Chemosphere* 69, 1765-1774.

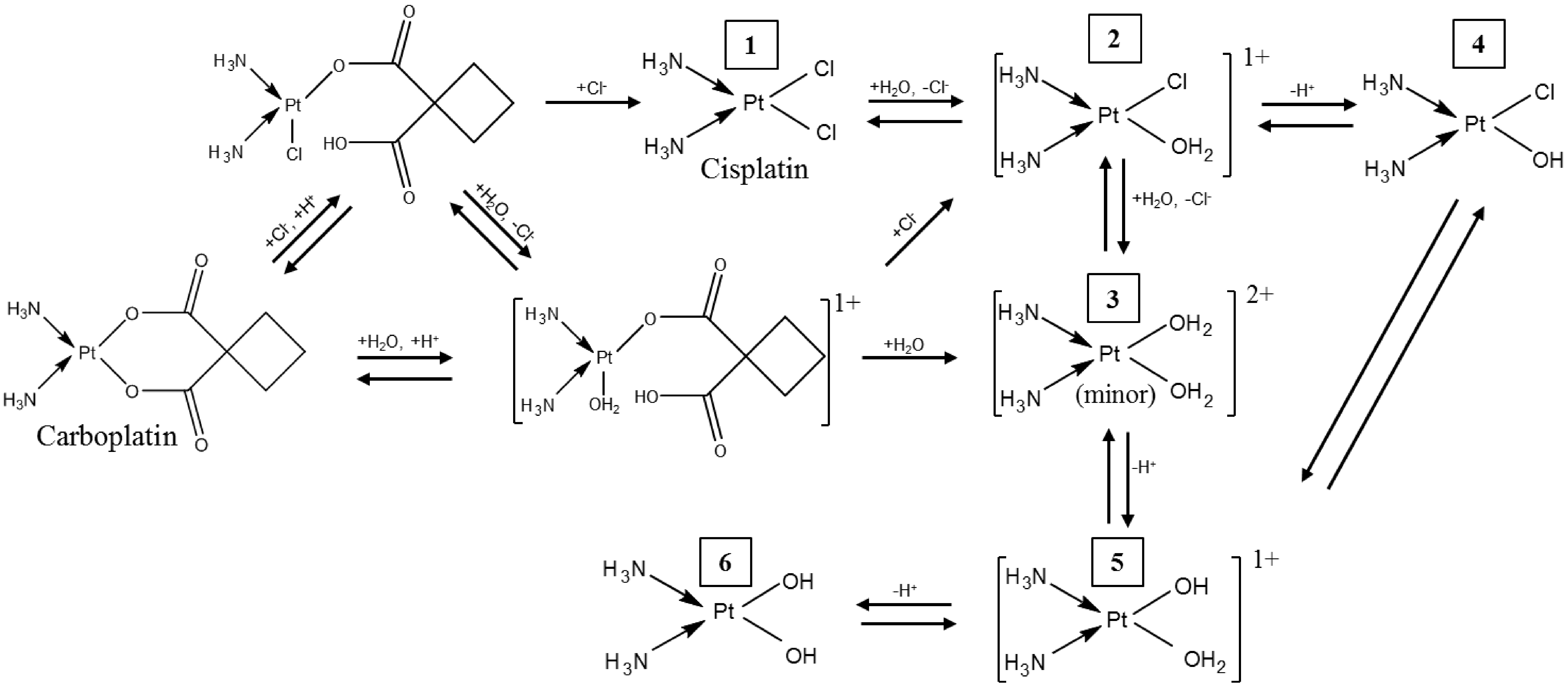
Structure	Formula	MW [g/mol]	Solubility [g/L] 25 ℃	Log K_{OW}	Compound
Oxaliplatin	$C_8H_{12}N_2O_4Pt$	397.29	7.9	1.65 ± 0.21	
Carboplatin	$C_6H_{12}N_2O_4Pt$	371.25	17	2.30 ± 0.10	
Cisplatin	$N_2H_6Cl_2Pt$	300.05	2.53	2.19	

- **Cisplatin is the most reactive pharmaceutical in aqueous solutions**
- **Carboplatin is the least reactive pharmaceutical in aqueous solutions**

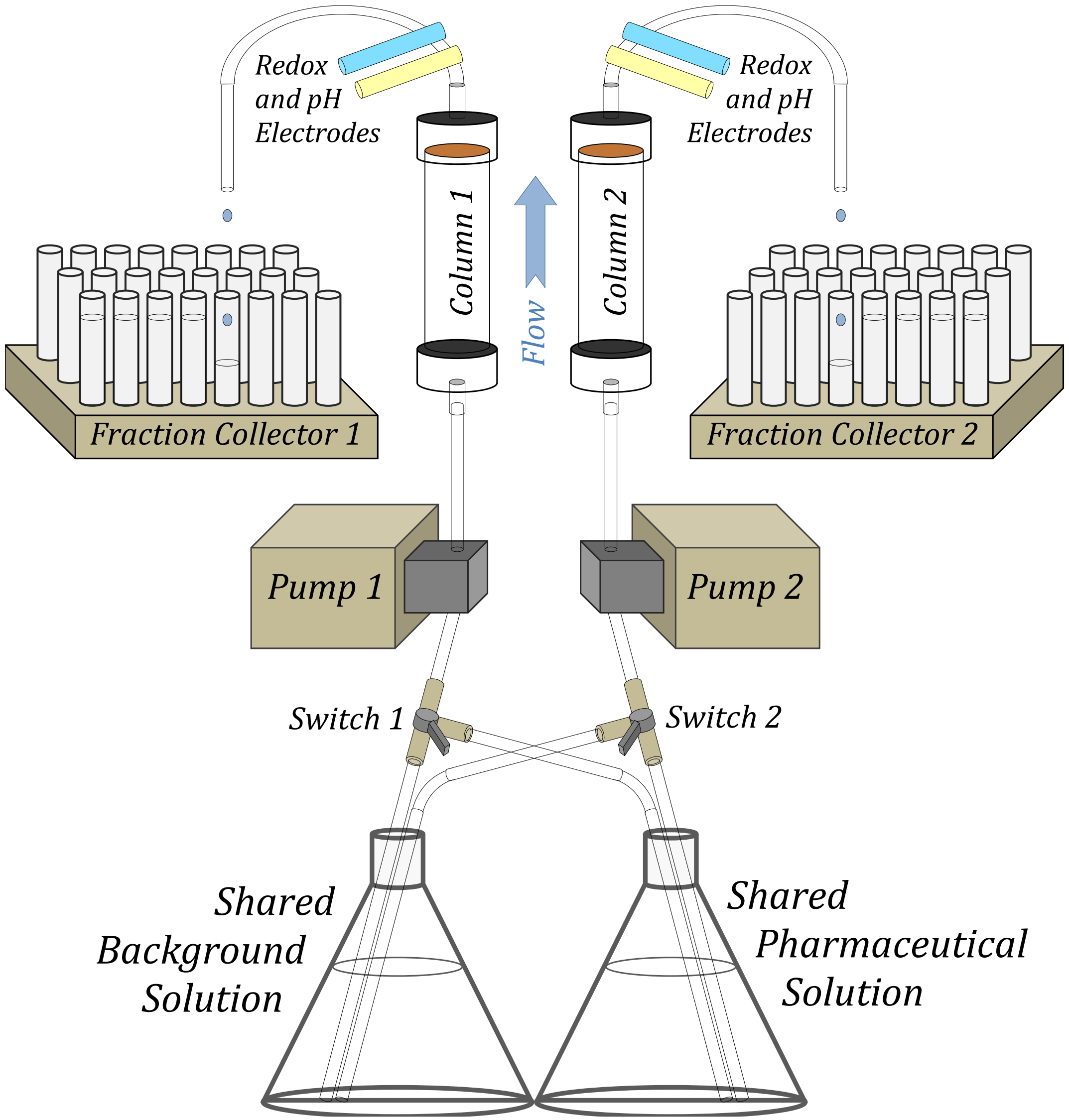
Oxaliplatin Speciation



Speciation – Carboplatin and Cisplatin



Experimental set-ups column experiments for fully saturated conditions



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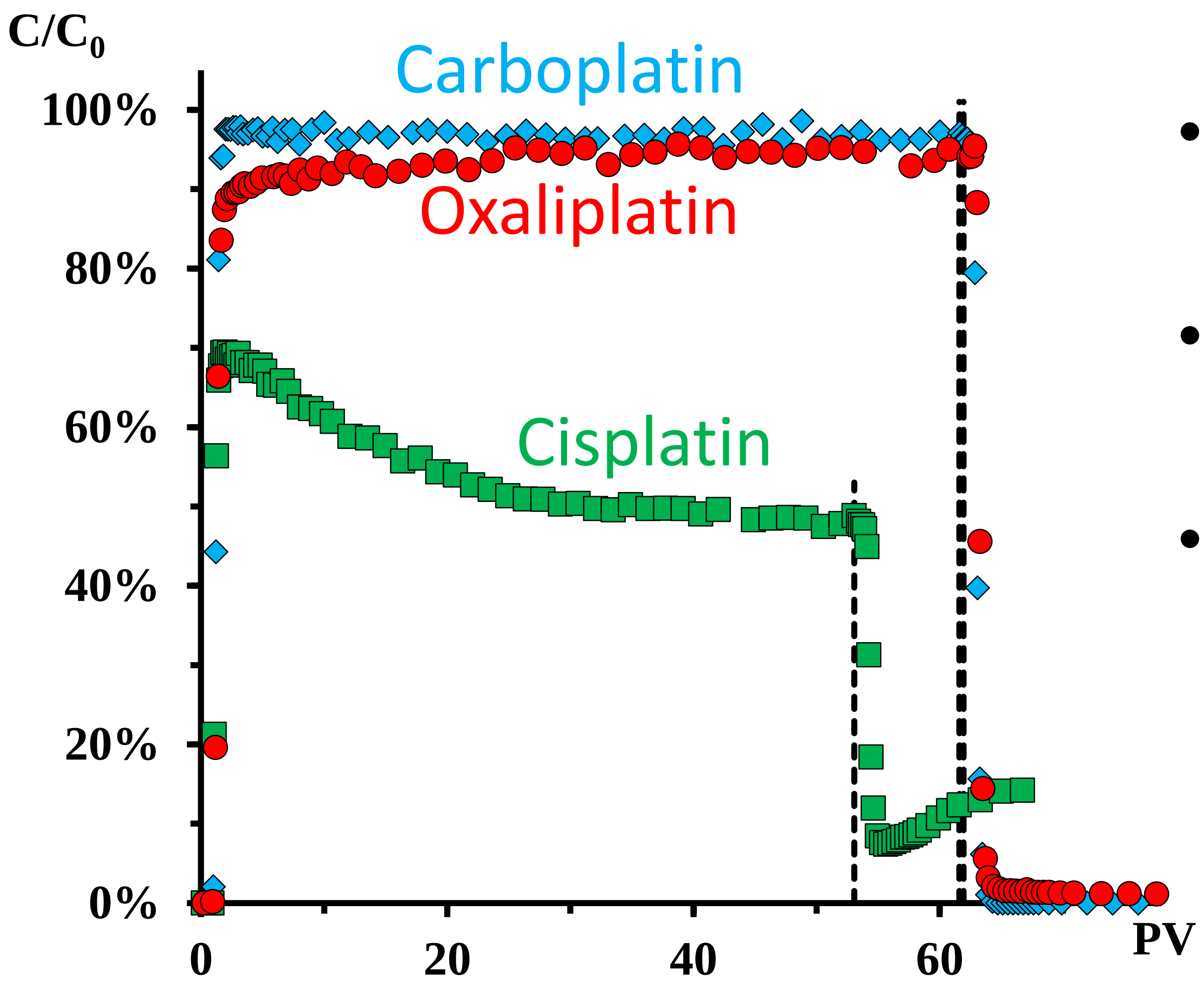
Sand – Benchmark – Overview

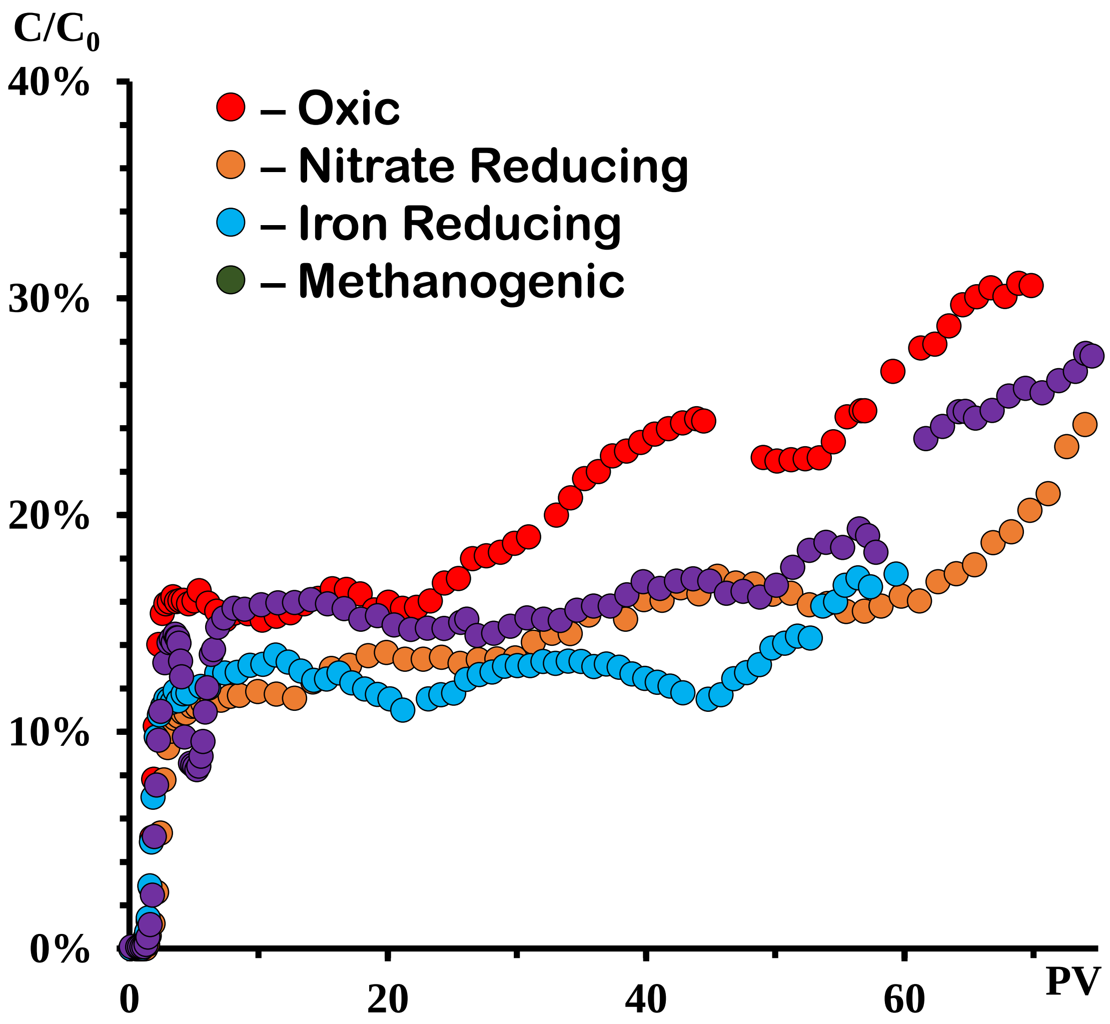


- Different behavior for each pharmaceutical
- Ligand lability dictates fate in the sand-water environment
- Carboplatin and oxaliplatin exhibit very low reactivity

	Oxaliplatin	Carboplatin	Cisplatin
Retained	7%	3%	45%

Goykhman et al. *Chemosphere 2019*.

Oxaliplatin in Soil – Overview

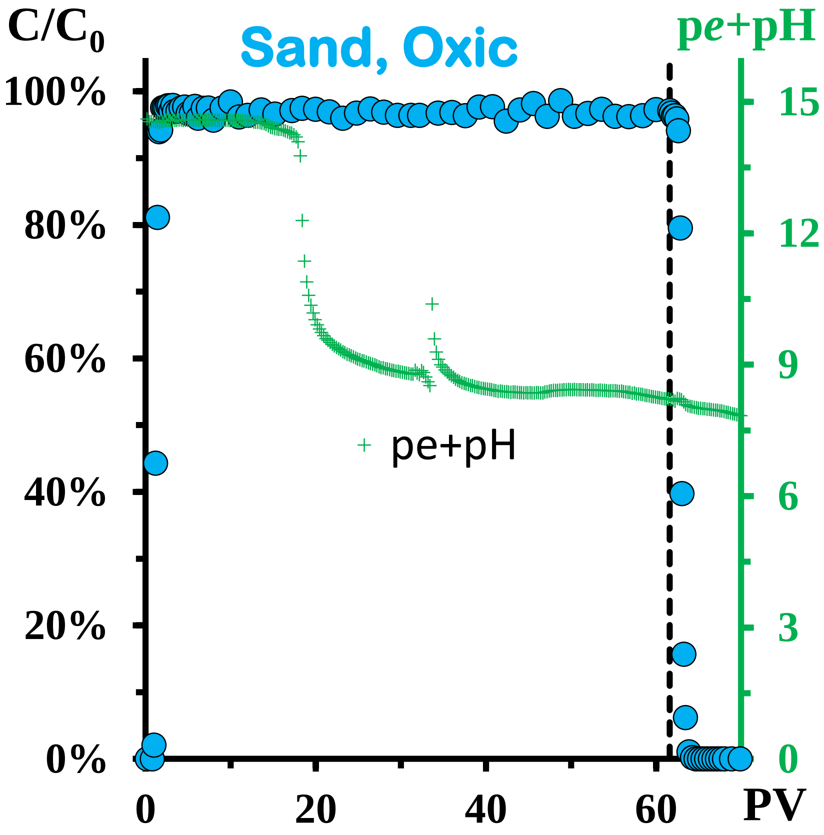


Nitrate Reducing		Methanogenic	Iron	Oxic
Retained	85%	84%	87%	79%
Released (of Retained)	0.6%	1.5%	0.1%	0.4%
K_d [mL/g]	138	191	642	118
R_f	2.3	1.7	1.7	2.1

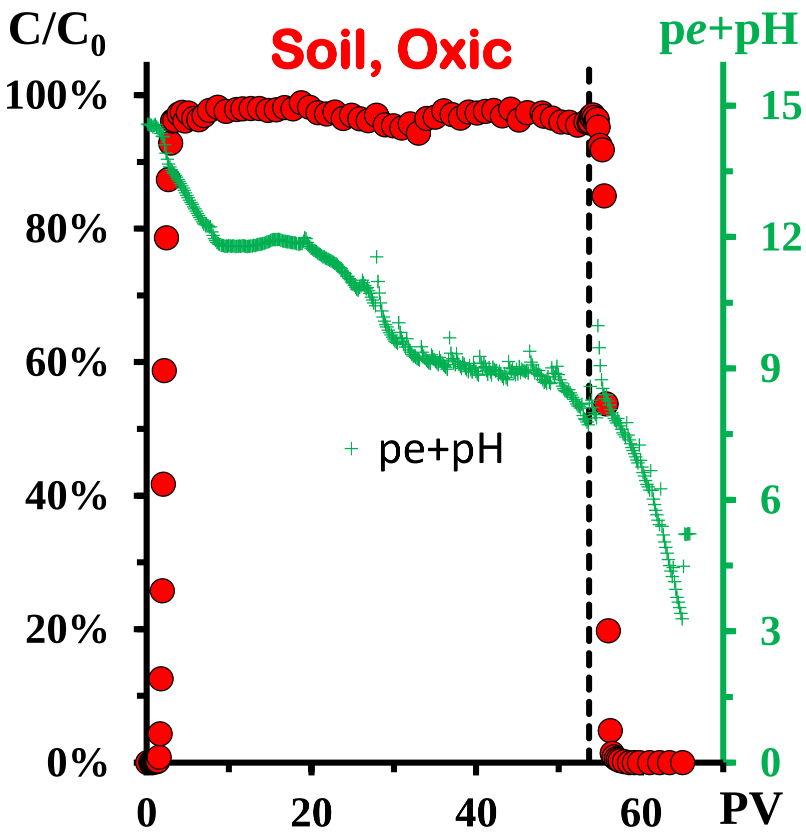
- Similar retention under all redox conditions
- Continuous increase in recovery due to the filling of preferential sorption sites

Carboplatin – Practically Inert in Both Sand and Soil

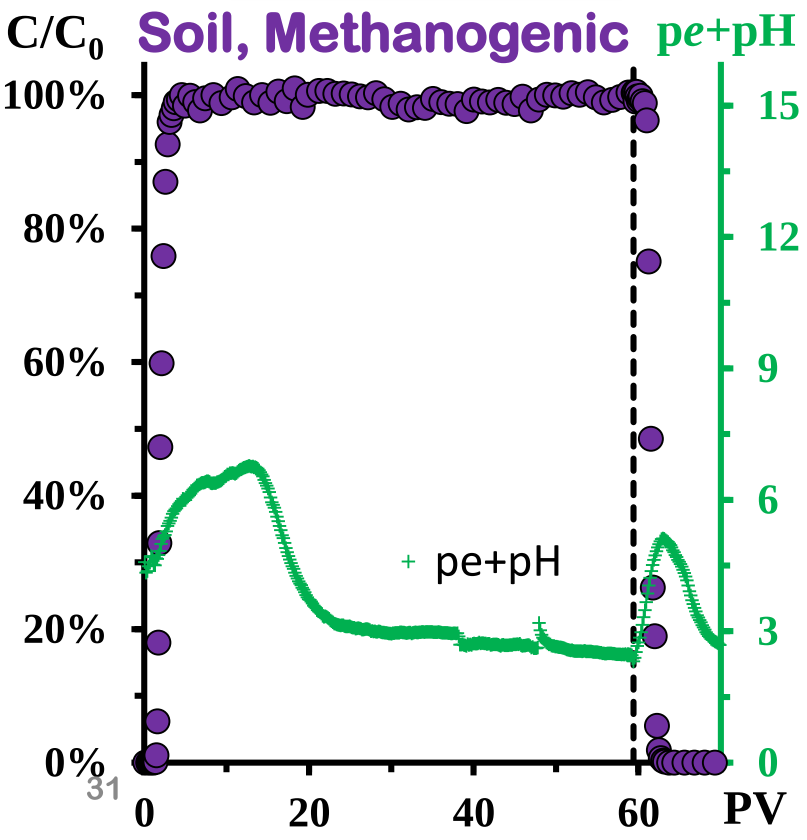
Retained	3%
Released (of Retained)	19%
K_d [mL/g]	---
R_f	1.0



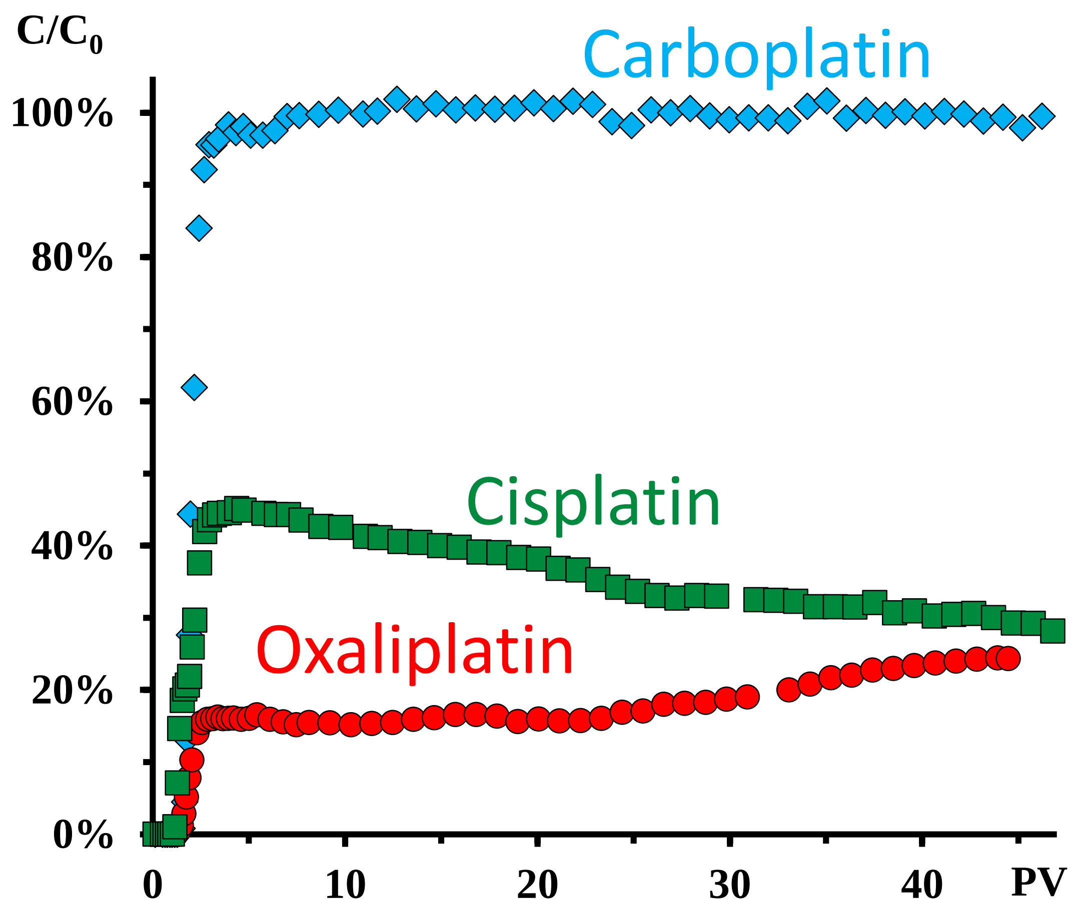
Retained	<6%
Released (of Retained)	---
K_d [mL/g]	0.26
R_f	2.2



Retained	<4%
Released (of Retained)	---
K_d [mL/g]	0.27
R_f	1.9



Soil – Overview (Oxic Redox Conditions)



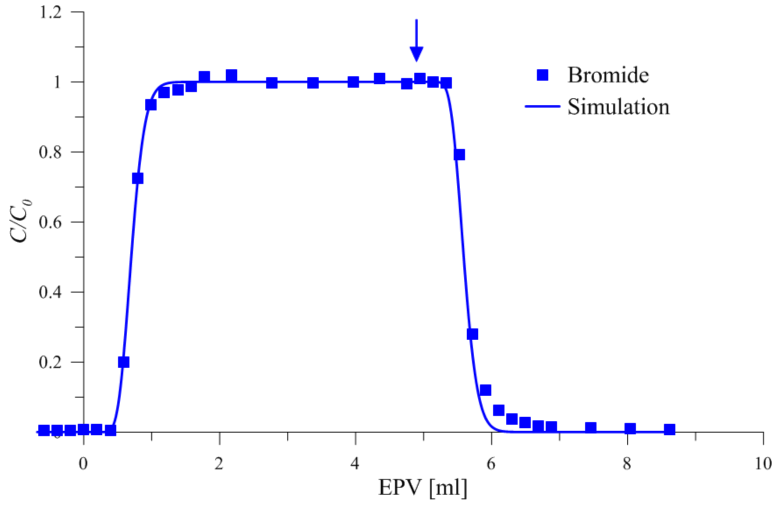
- **Ligand lability dictates fate in the soil-water environment**
- **Behavior ranges from tracer-like to pronounced sorption**

	Oxaliplatin	Carboplatin	Cisplatin
Retained	79%	< 6%	64 %

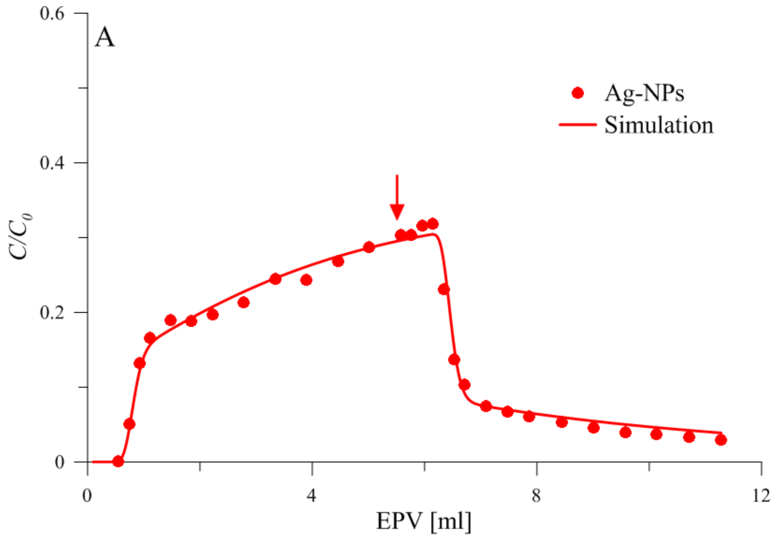
Conclusions

- ENPs are mobile in partially saturated conditions (in both soil and sand columns).
- ENP mobility is strongly affected by environmental conditions: Physical and chemical interactions influence NP transport.
- Transformed ENPs can remain in solution and be transported
- Retained ENPs can be remobilized if suitable aqueous solutions are applied.
- ENPs are source of metals for plants that can either transform them to ions or uptake them as particles.
- Pt-based pharmaceuticals are relatively mobile in the soil-water environment.
- Similar pharmaceuticals may exhibit very different transport characteristics under similar conditions (e.g. porous medium, solution chemistry and redox conditions).
- Caution should be taken when prescribing a certain behavior to a pharmaceutical without a direct investigation.

Bromide Tracer & Ag-NP transport in partially saturated soil column



Tracer simulated using the Advection – Dispersion Equation (ADE) without retention.



Two kinetic sites model.
Langmuirian: time-dependent blocking and depth-dependent straining.