

Environmental Colloids and Nanoparticles: Occurrence, Behaviour and Relevance for Engineered Particles

FRANK VON DER KAMMER*

THILO HOFMANN*

KELLY PLATHE*,¹

MIKE HOHELLA¹

SAMUEL LEGROS*

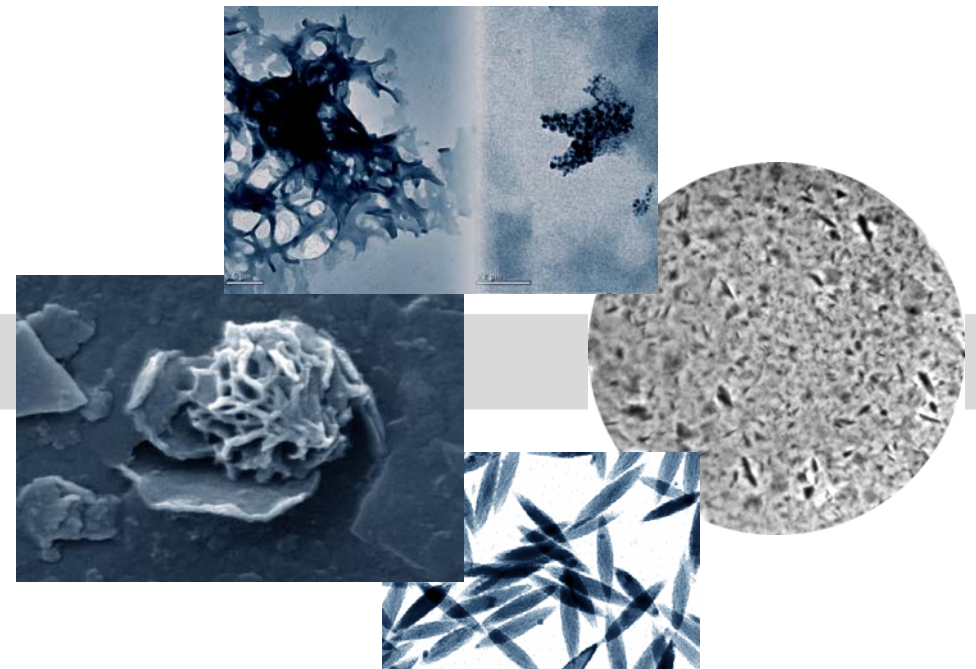
ELISABETH NEUBAUER*

PHILIPPE LE COUSTOMER²

* University of Vienna

¹ Virginia Tech

² University of Bordeaux



Introduction

Trace metal associations with mineral colloids

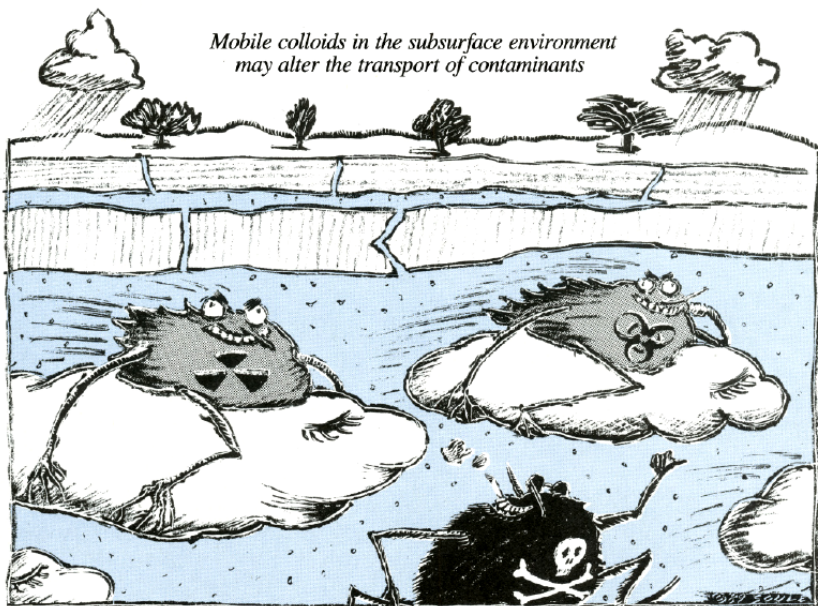
Trace metal associations with mineral colloids & natural organic matter

Contaminant transport with natural and engineered nanoparticles

ES&T
FEATURES

Subsurface transport of contaminants

Mobile colloids in the subsurface environment may alter the transport of contaminants



John F. McCarthy
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6036

John M. Zachara
Battelle Pacific Northwest Laboratory
Richland, WA 99352

1989

Research | Article

Manufactured Nanomaterials (Fullerenes, C₆₀) Induce Oxidative Stress in the Brain of Juvenile Largemouth Bass

Eva Oberdörster

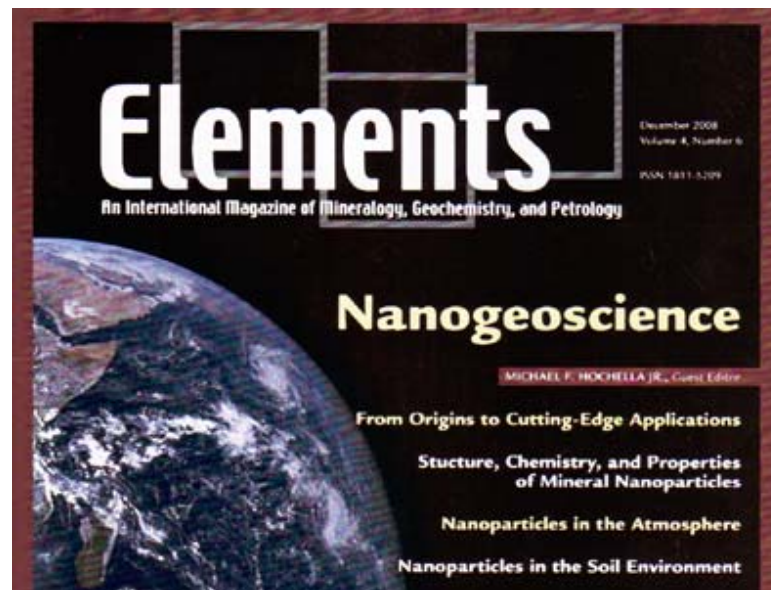
Duke University Marine Laboratory, Beaufort, North Carolina, USA; Department of Biology, Southern Methodist University, Dallas, Texas, USA

Although nanotechnology has vast potential in uses such as fuel cells, microreactors, drug delivery devices, and personal care products, it is prudent to determine possible toxicity of nanotechnology-derived products before widespread use. It is likely that nanomaterials can affect wildlife if they are accidentally released into the environment. The fullerenes are one type of manufactured nanoparticle that is being produced by tons each year, and initially uncoated fullerenes can be

bulb (Bodian and Howe 1941; DeLorenzo 1970; Howe and Bodian 1941; Oberdörster et al. 2004). This pathway also exists in rodents and fish for soluble metals (Tjälve and Henriksson 1999; Tjälve et al. 1995).

I hypothesized that this neuronal trans-

2004



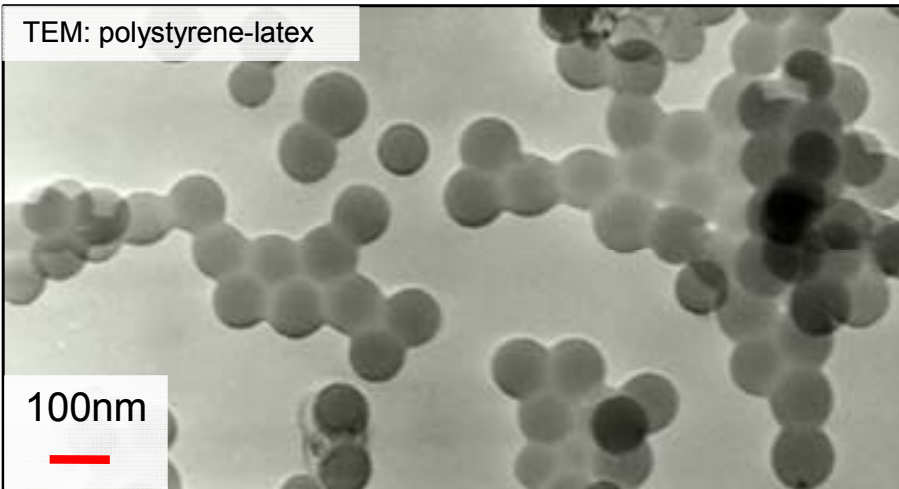
2008

environmental aquatic colloids		
natural colloids	anthropogenic colloids	engineered nanoparticles
<u>inorganic colloids</u> <ul style="list-style-type: none"> - silicates (e.g. clays) <ul style="list-style-type: none"> smectites montmorillonite nontronite hectorite chlorites mica kaolinite - oxides / hydroxides <ul style="list-style-type: none"> Fe-oxohydroxides Mn-oxides - carbonates - phosphates - metal sulfides - polym. silicic acid 	<u>organic colloids</u> <ul style="list-style-type: none"> - macromolecules <ul style="list-style-type: none"> humic acids fulvic acids polysaccharides proteins peptides exo-polymers, EPS - bio-colloids <ul style="list-style-type: none"> bacteria viruses fungi - coal/soot/black carbon - cellular debris 	<u>wear & corrosion products</u> <ul style="list-style-type: none"> - from tire & brakes - from catalysts (e.g. Pt, Pd) - metals (wear in bearings) - metal oxides (roof run-off) - additives to lubricants <u>waste & combustion products</u> <ul style="list-style-type: none"> - soot - "anthropogenic" humic acids <ul style="list-style-type: none"> from e.g. waste dumps - tar leachates in plumes - fly ash - fine dust (inorganic & organic)
		<u>standard industrial products</u> <ul style="list-style-type: none"> - polymers - surfactants - dyes & pigments - metal oxides <u>NP metals & metal oxides</u> <ul style="list-style-type: none"> - metals (Au, Ag, Fe) - metal oxides (of Ti, Zn, Zr, Ce...) - metal tubes and wires <u>carbon based</u> <ul style="list-style-type: none"> - fullerenes - single & multi walled nanotubes <u>hybride structures</u> <ul style="list-style-type: none"> - quantum dots - functionalized materials - core-shell structures

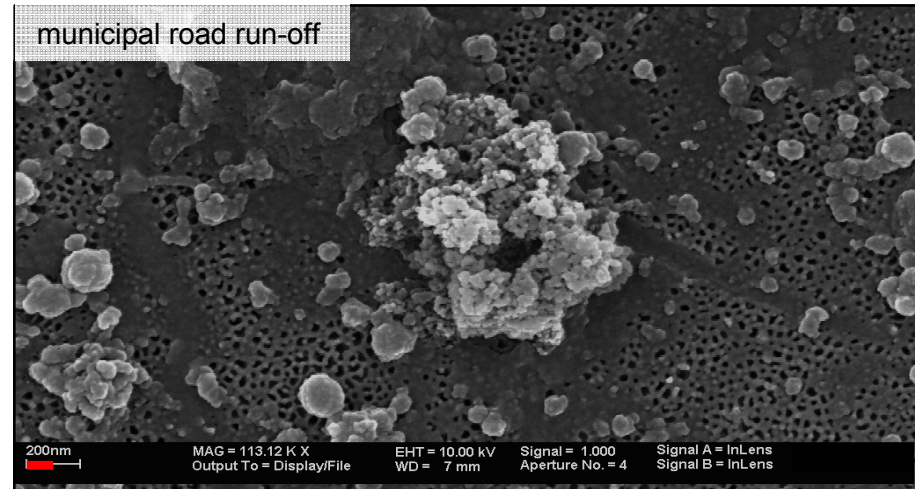
origin

composition

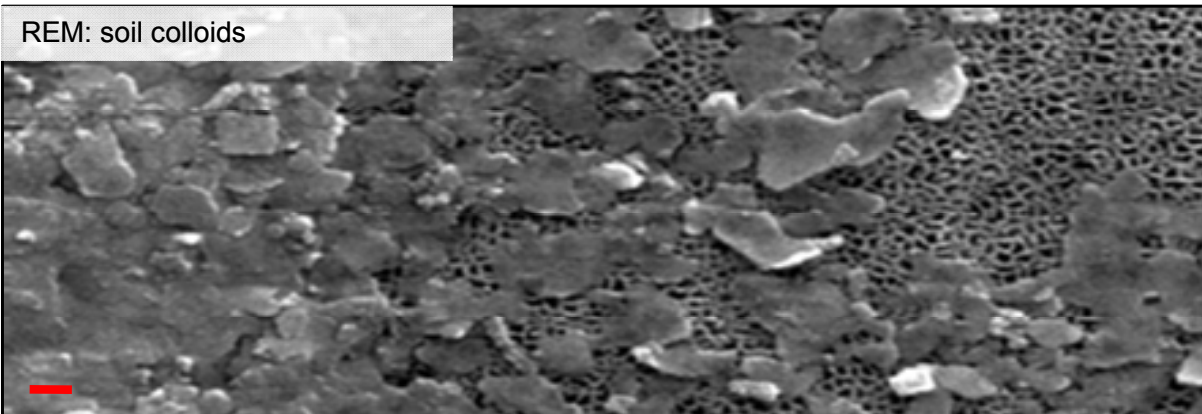
TEM: polystyrene-latex



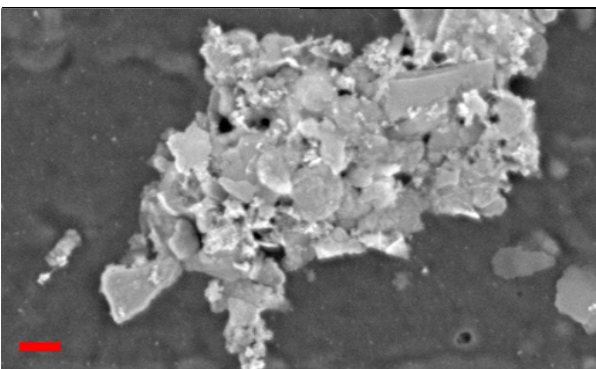
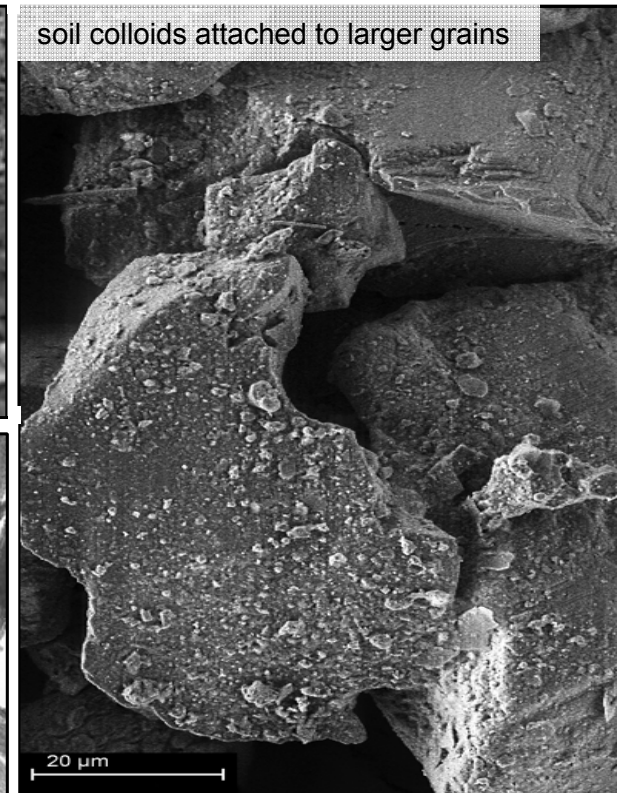
municipal road run-off



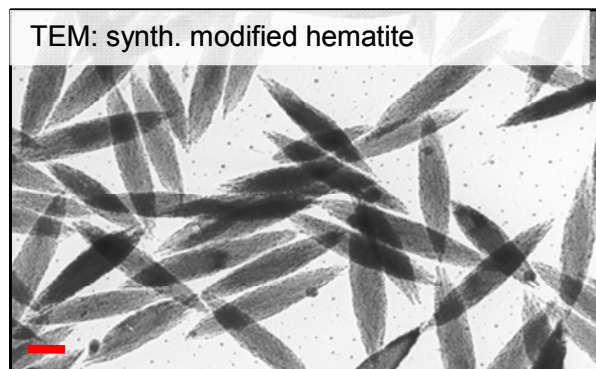
REM: soil colloids



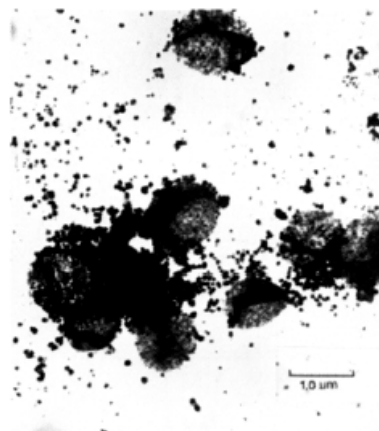
soil colloids attached to larger grains



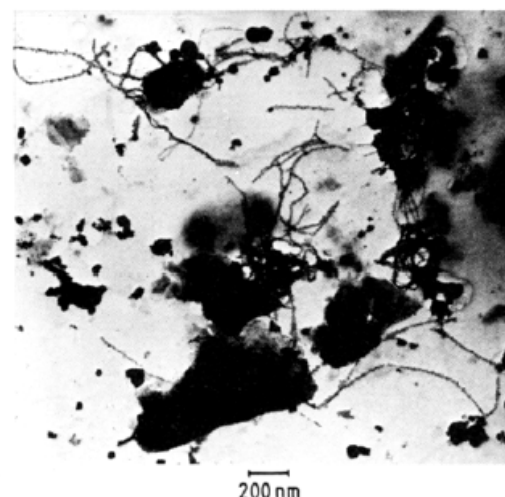
TEM: synth. modified hematite



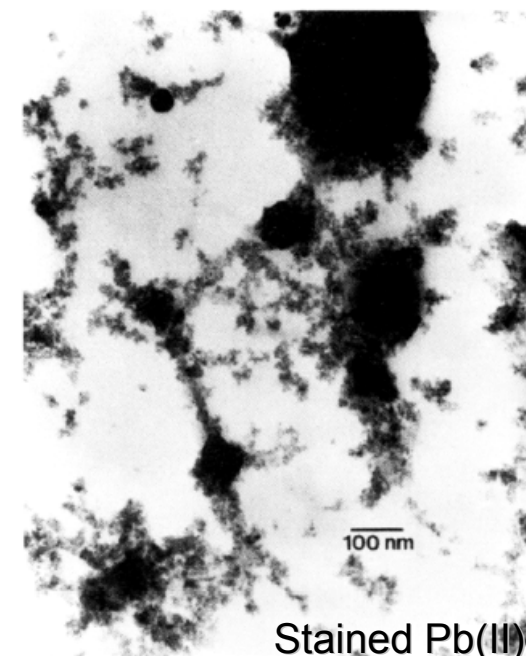
A) Spores covered and glued together by iron oxyhydroxide globules



B) Clay and iron oxyhydroxide globules, aggregated by a mesh of organic filaments

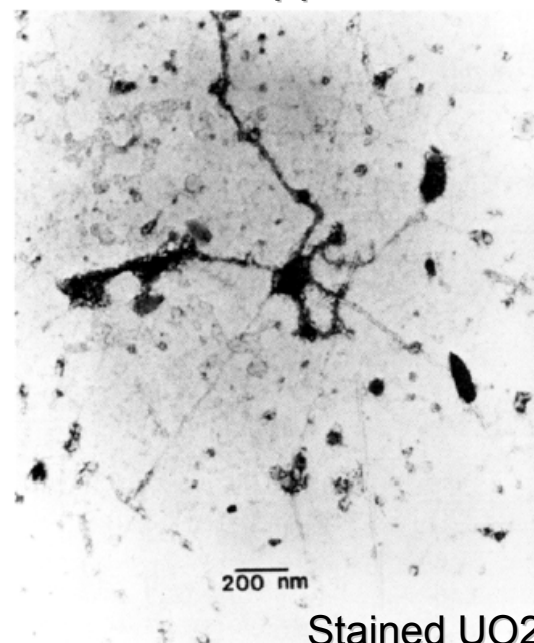


C) Si-rich colloids aggregated in looser matrix of organic material



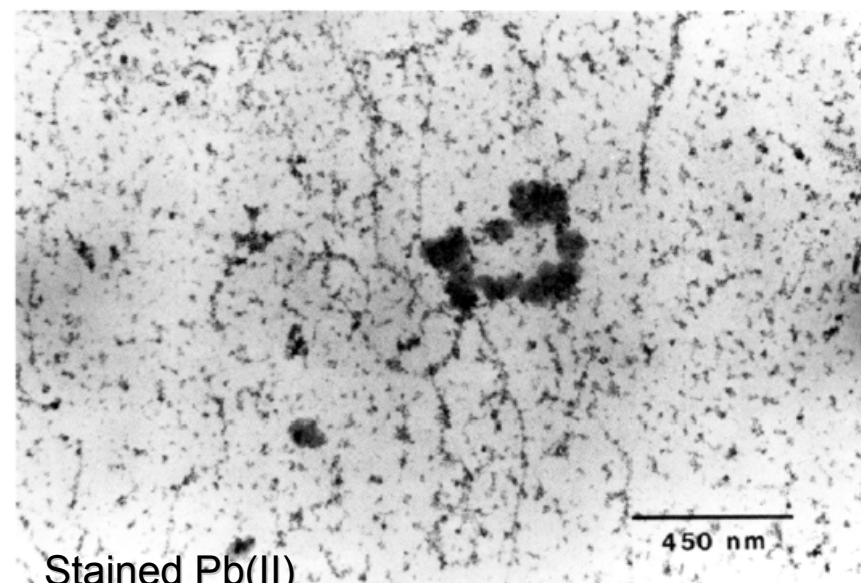
Stained Pb(II)

D) Inorganic colloids bound by fibrillar material



Stained UO₂⁺

E) Soil-derived fulvic compounds aggregated in slightly larger entities



Stained Pb(II)

Buffle & Leppard 1995 EST

Important reactions of environmental nanoparticles

- transport (mobilization – attachment)
- formation, transformation and dissolution
- growth, aggregation – segregation
- interaction with contaminants, nutrients and NOM (co-transport)
- electron transfer

colloid dynamics in groundwater

translocation

- leakage
- from vadoze zone
- ground/seepage water

mobilization

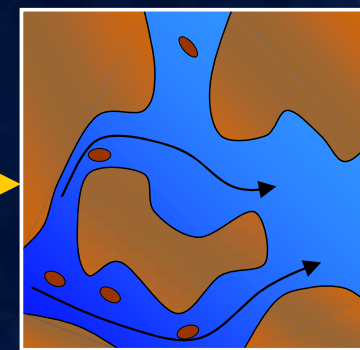
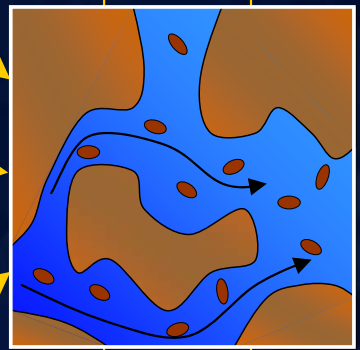
- ionic strength
- pH
- valence of ions
- dissolution of cements
- hydraulic effects / diffusion

$Eh \downarrow$ $I_s \downarrow$ $pH \downarrow \uparrow$ $Ca^{++} \rightarrow Na^+$

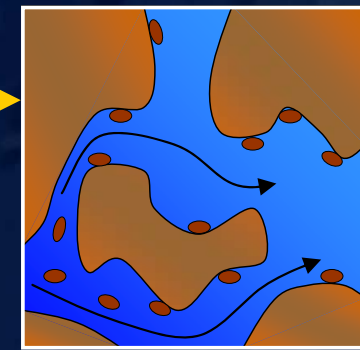
generation

- second. mineral formation
- precipitation
- biological growth

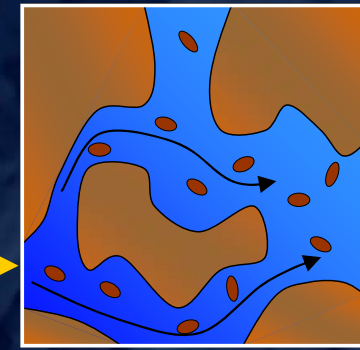
$Eh \uparrow$ $pH \uparrow$



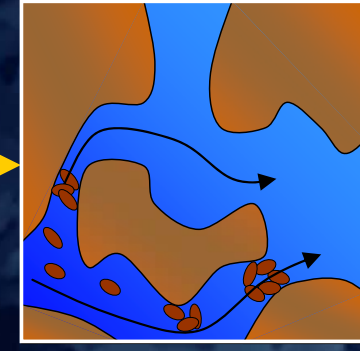
dissolution



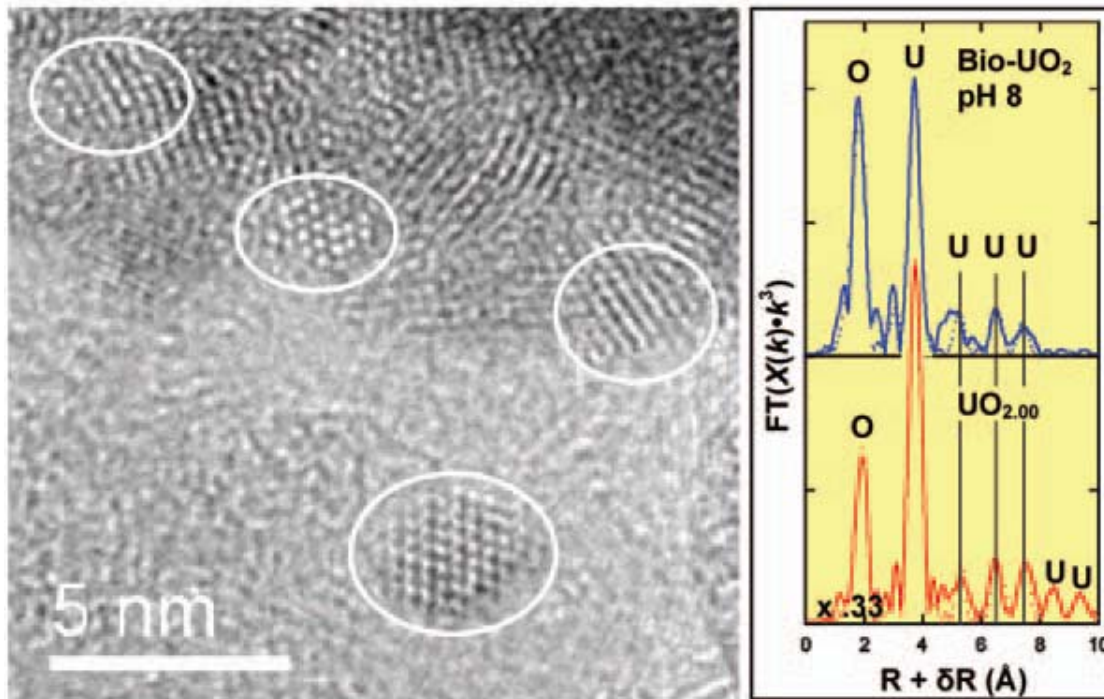
deposition



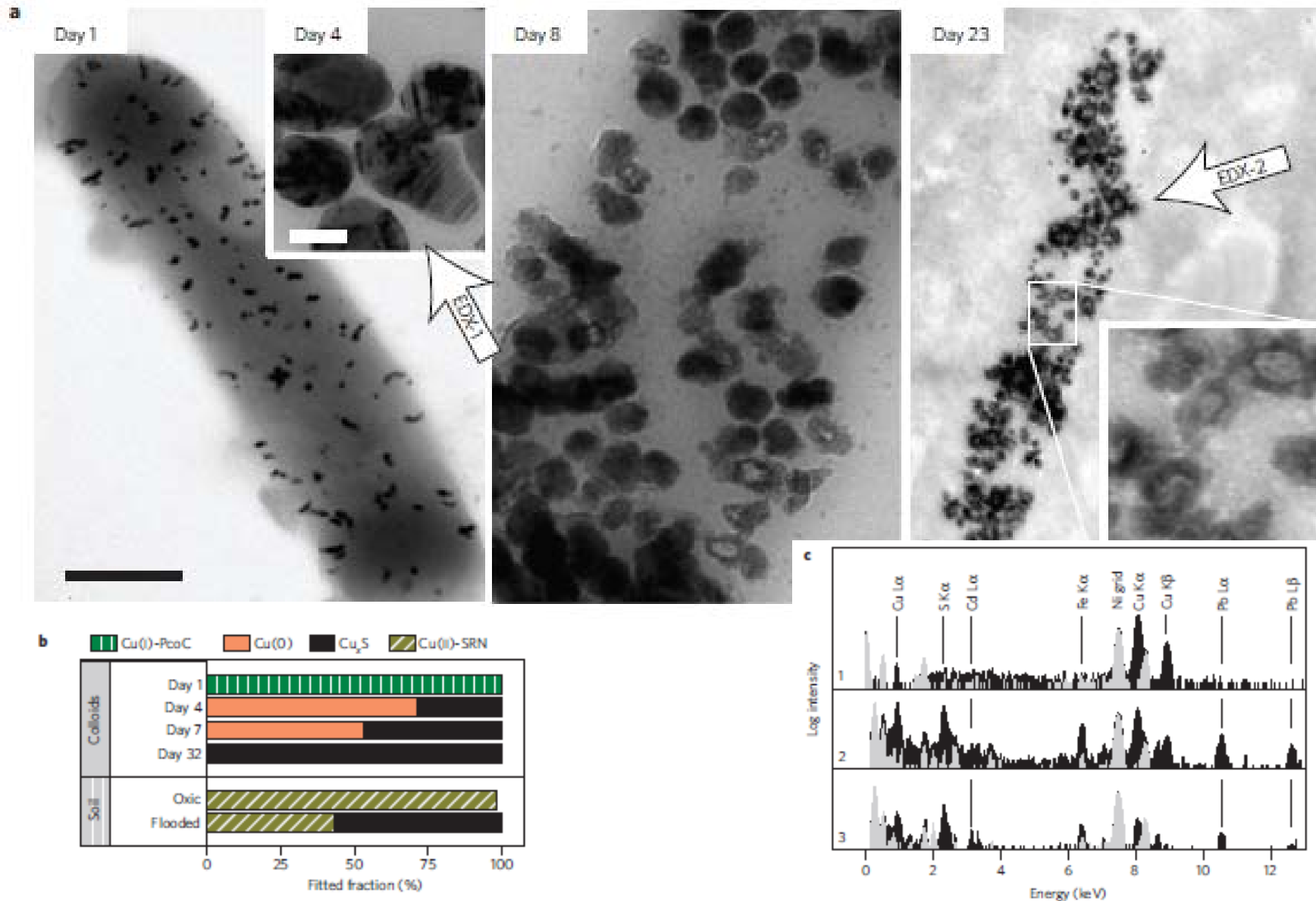
stabilization
transport



filtration



Biogenic Uraninite nanoparticles formed under anoxic conditions by *Shewanella oneidensis* strain MR-1, showing UO_2 lattice fringes.



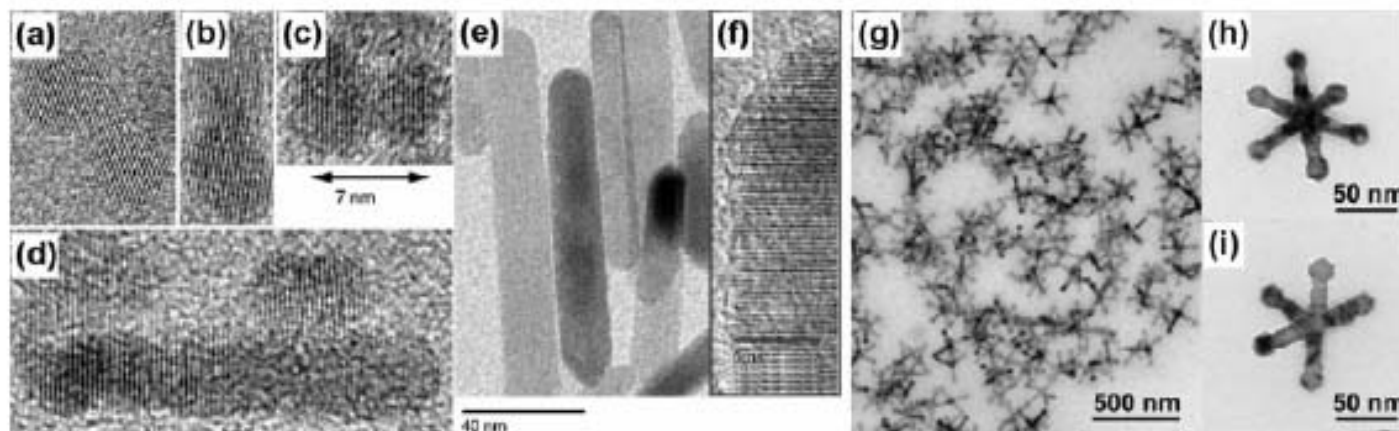
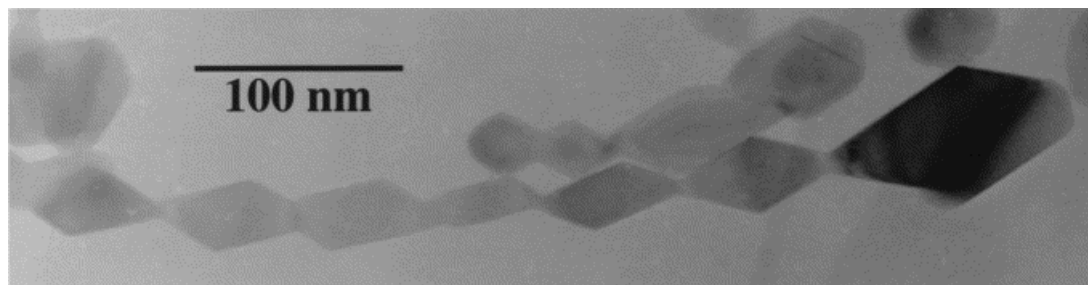
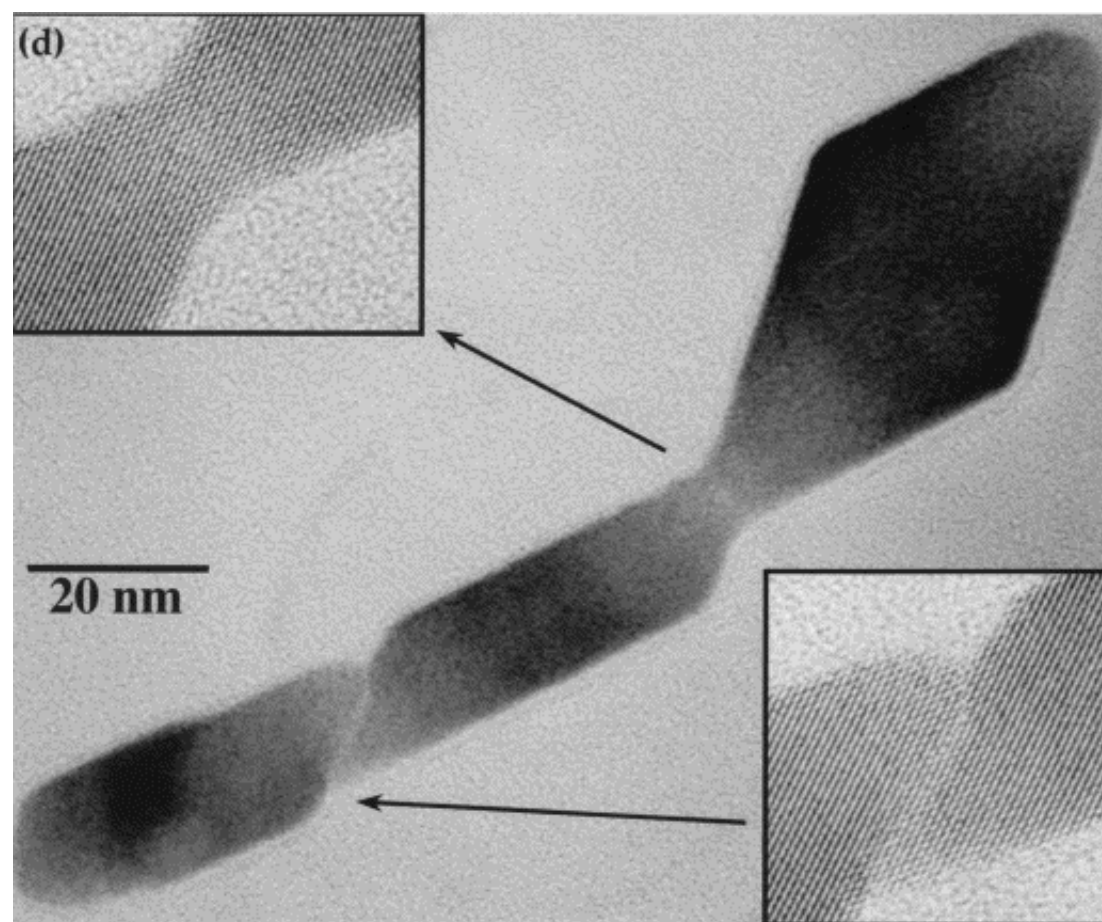
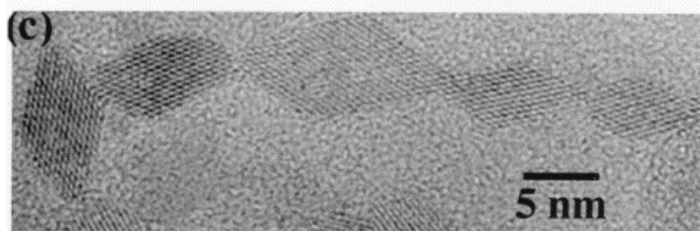
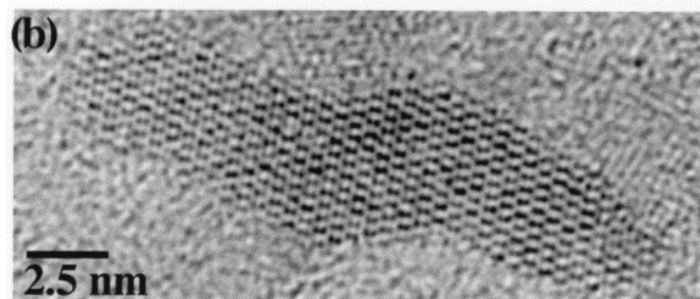
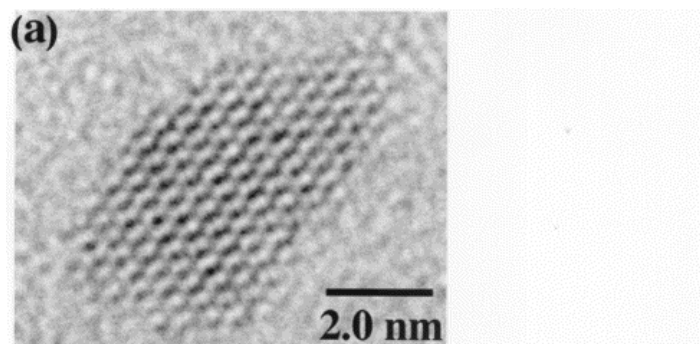


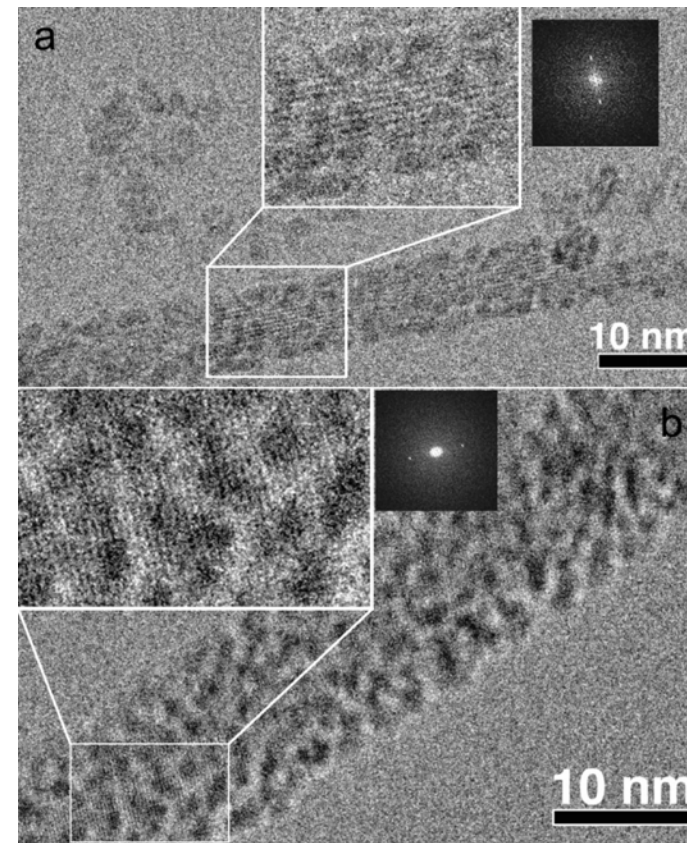
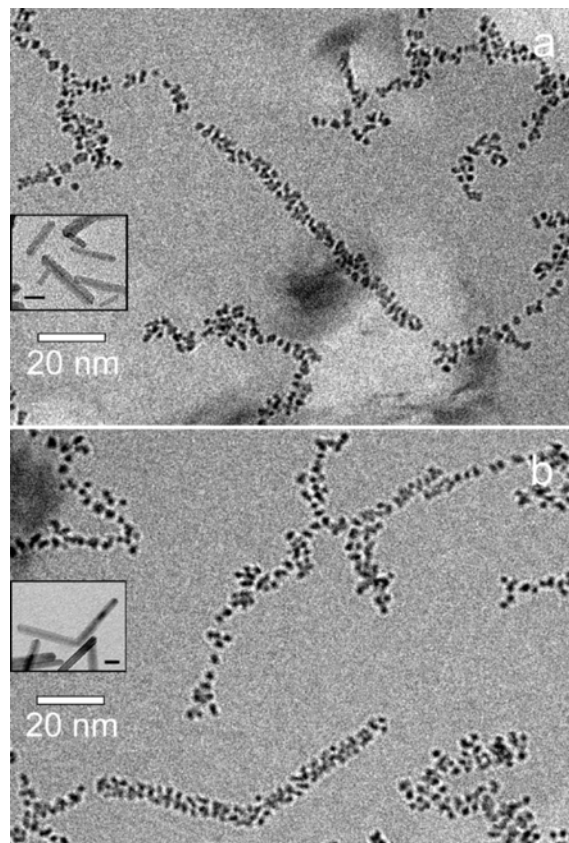
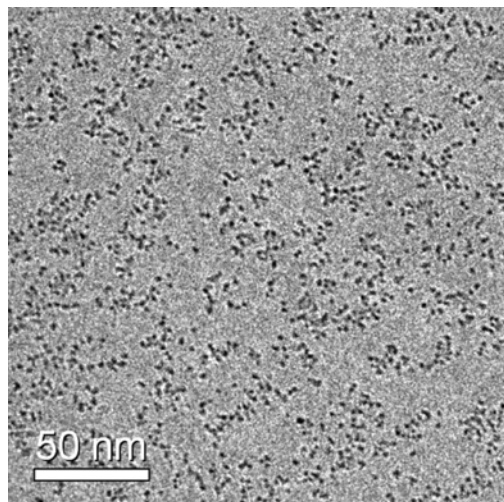
Fig. 4 (a)–(d) HRTEM images of ZnO nanoparticle assemblies, (e) TEM image of ZnO nanorods, (f) HRTEM image of a part of such a rod, (g) TEM overview image of MnO multipods, (h) TEM image of a MnO hexapod, (i) TEM image of a MnO pentapod. Images (a)–(f) reprinted from C. Pacholski, A. Kornowski and H. Weller, *Angew. Chem., Int. Ed.*, 2002, **41**, 1188, with permission from Wiley-VCH.⁸¹ Images (g)–(i) reprinted with permission from D. Zitoun, N. Pinna, N. Frolet and C. Belin, *J. Am. Chem. Soc.*, 2005, **127**, 15034. Copyright 2005 American Chemical Society.⁸²



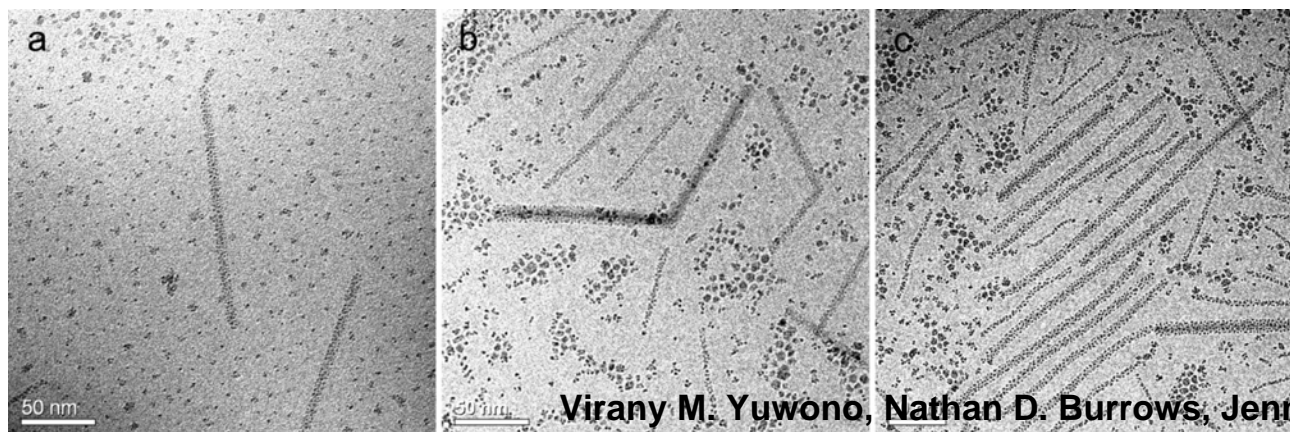
R. LEE PENN and JILLIAN F. BANFIELD (GCA 1999)

how to distinguish
aggregate (strong bonds)
and
agglomerate (weak bonds)





how to distinguish
aggregate (strong bonds)
 and
agglomerate (weak bonds)



Virany M. Yuwono, Nathan D. Burrows, Jennifer A. Soltis and R. Lee Penn (JACS 2010)



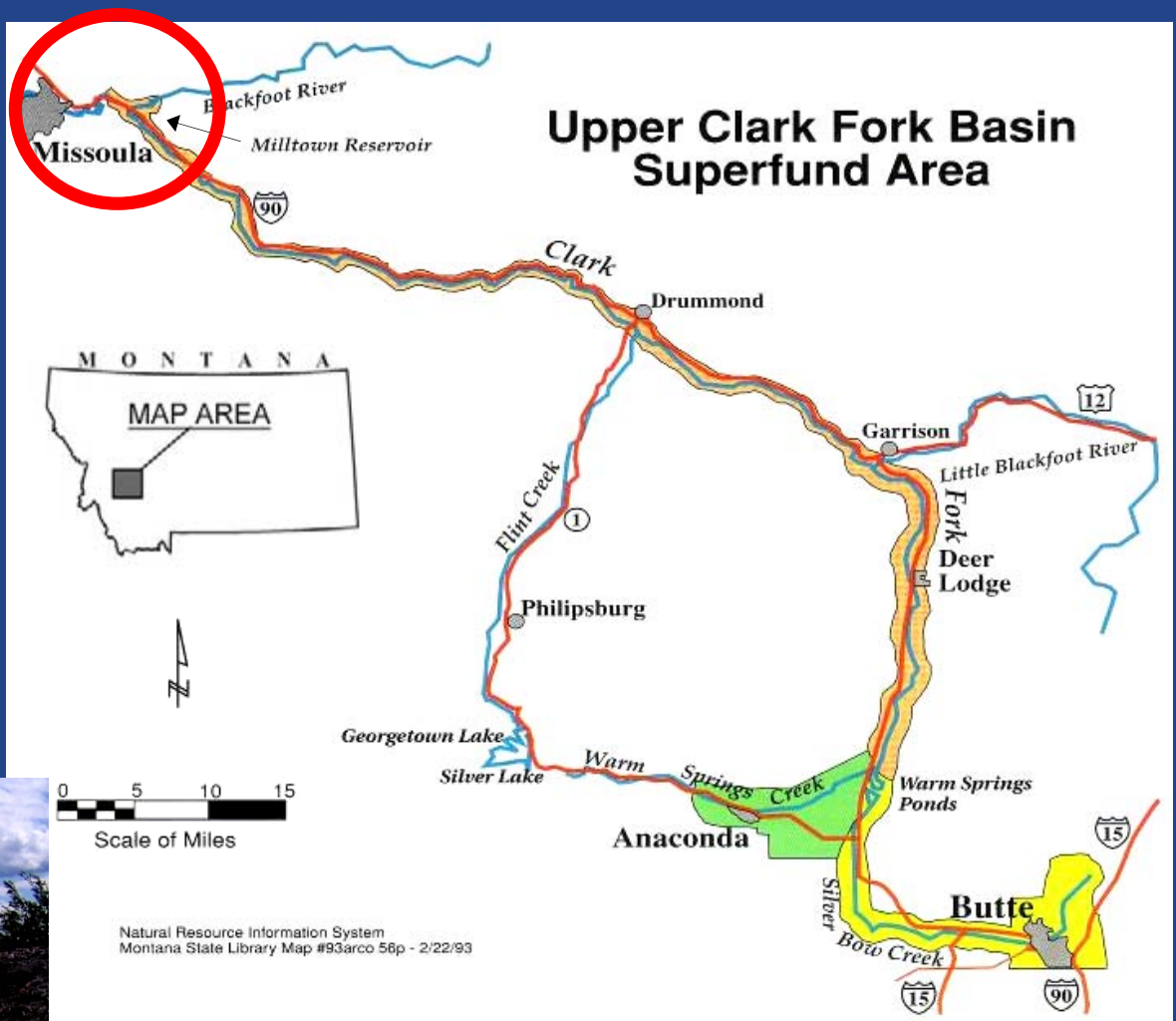
Trace metal associations with mineral colloids



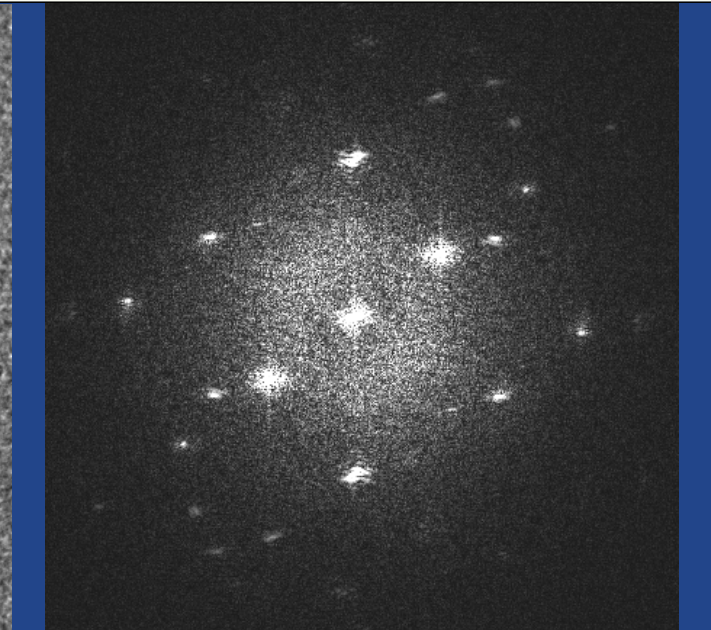
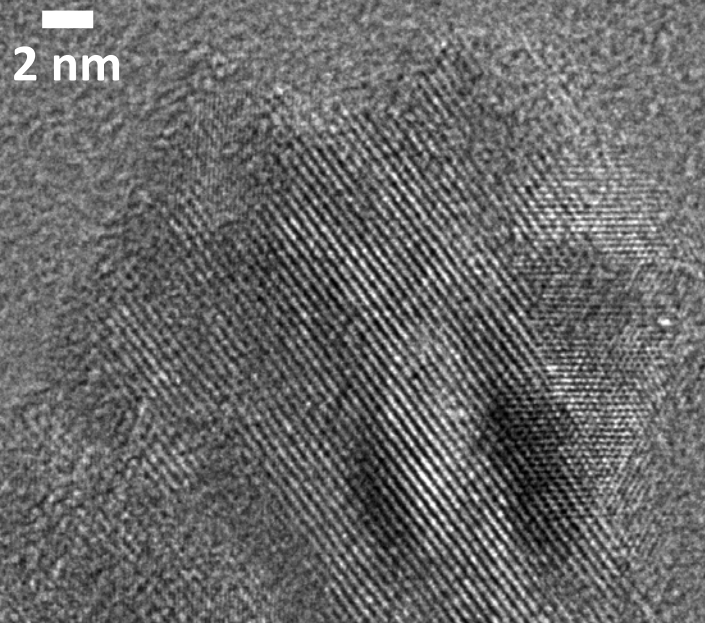
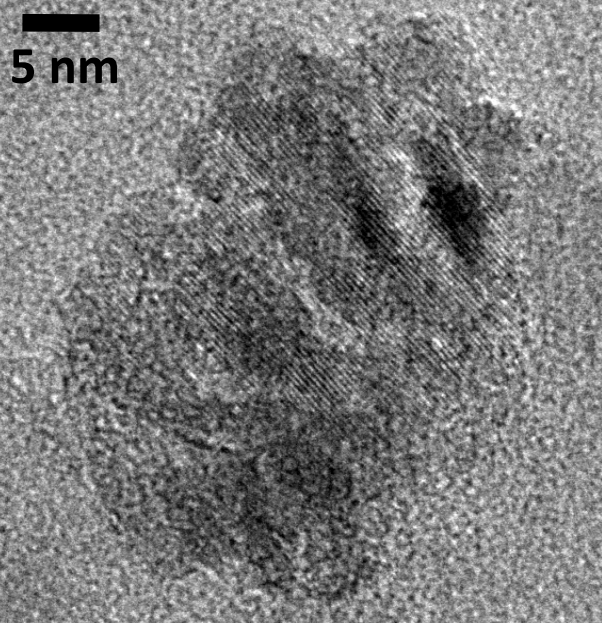
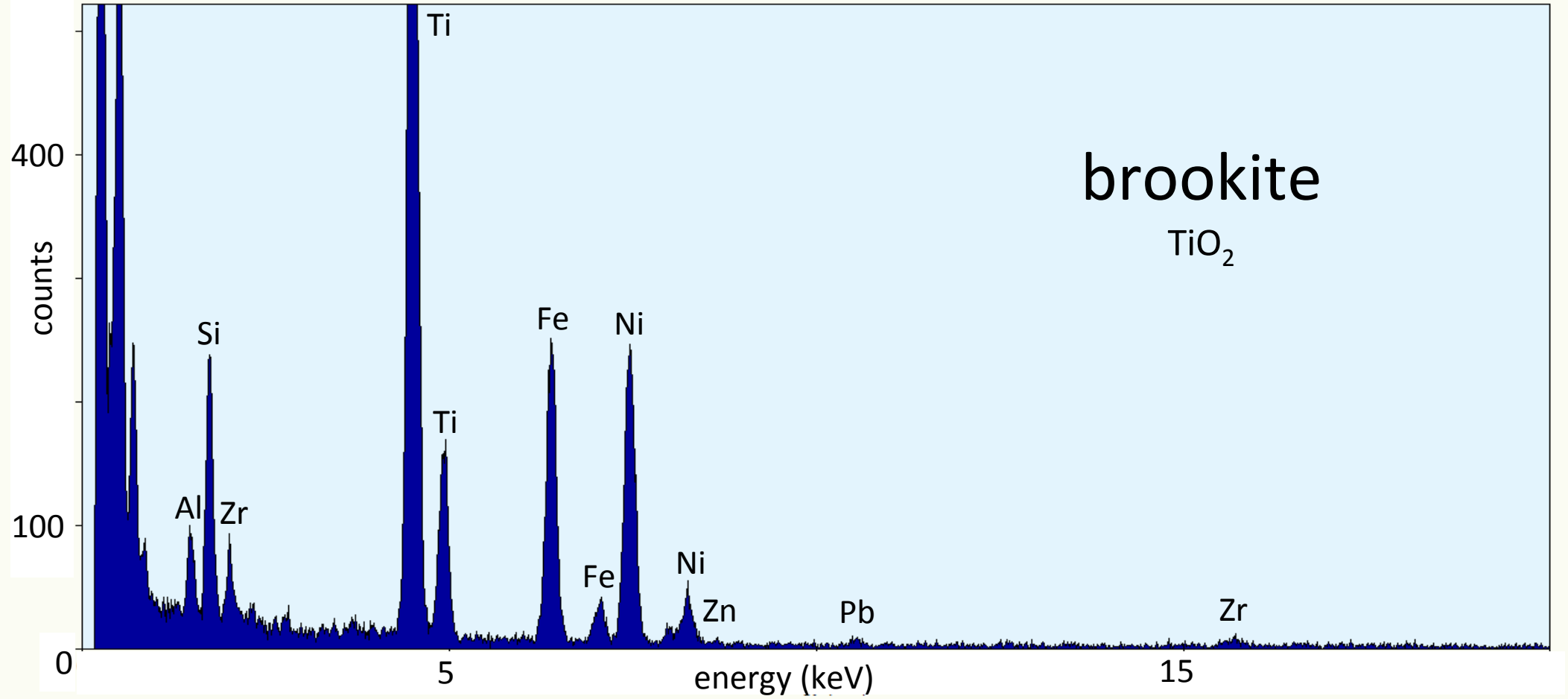
Trace metal associations with mineral colloids & natural organic matter

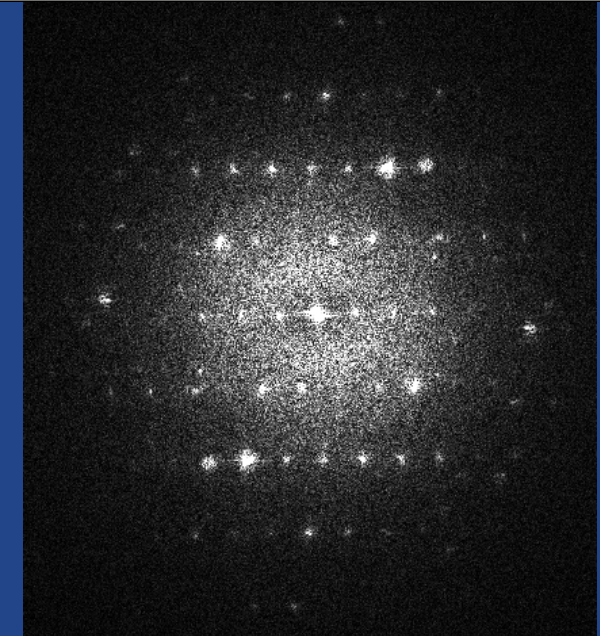
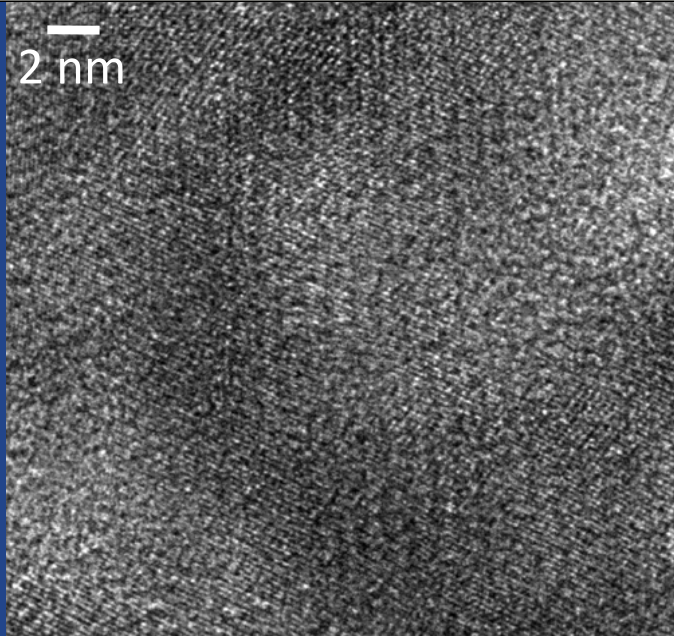
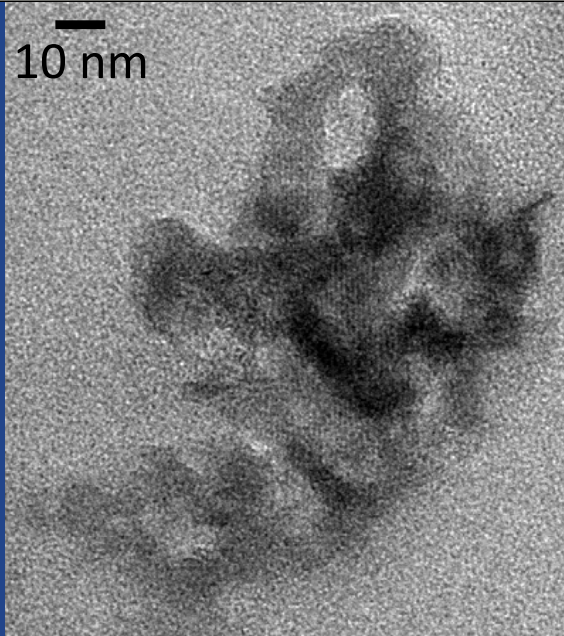
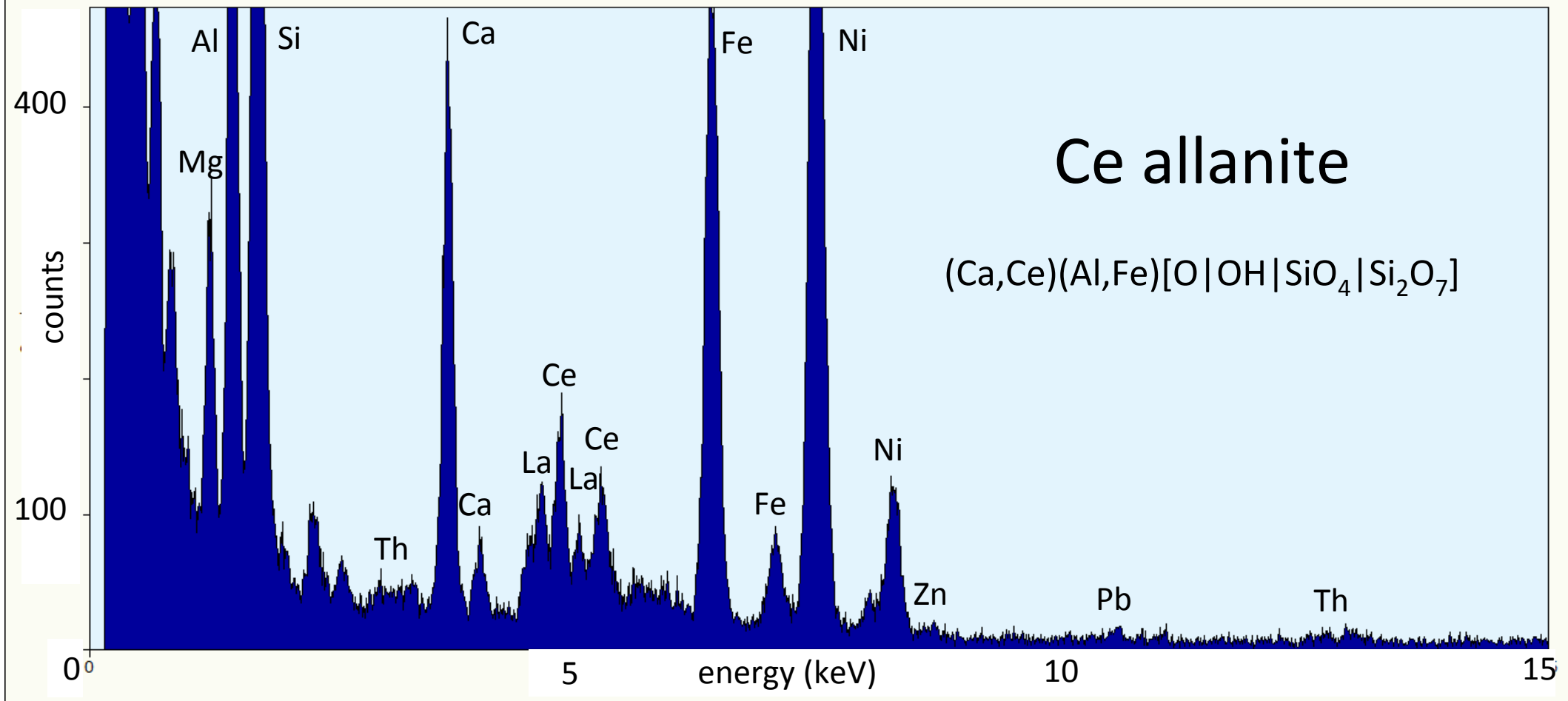


Contaminant transport with natural and engineered nanoparticles



Plathe; von der Kammer; Hochella et al. 2010 (Environmental Chemistry)



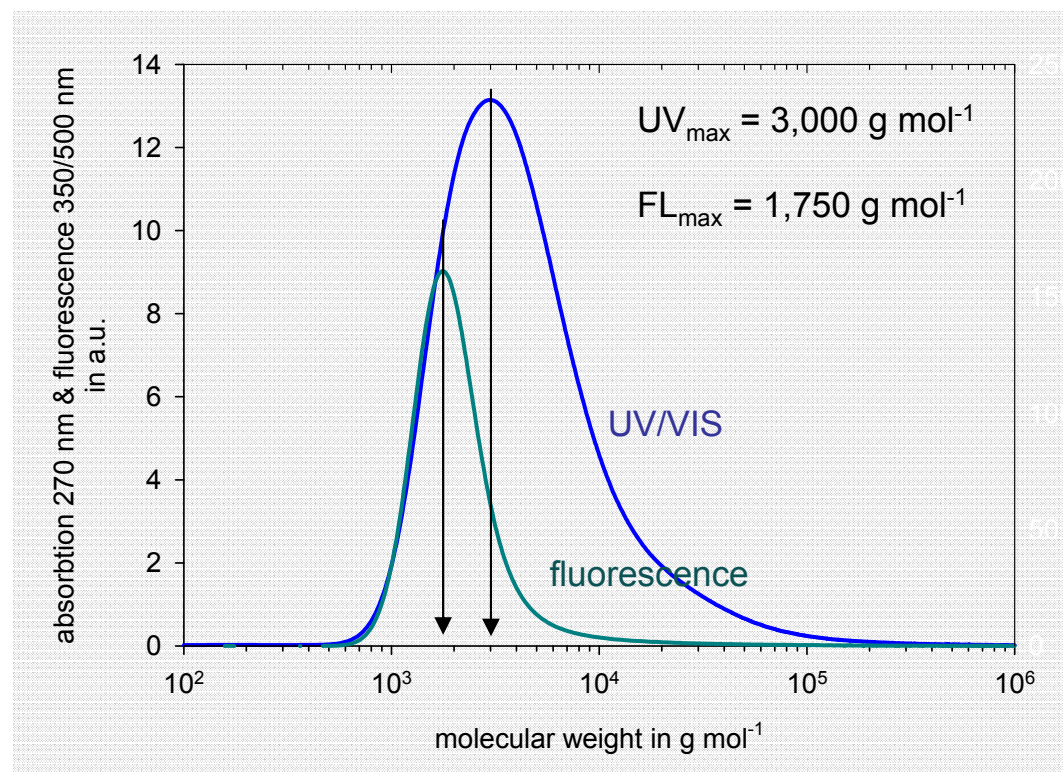
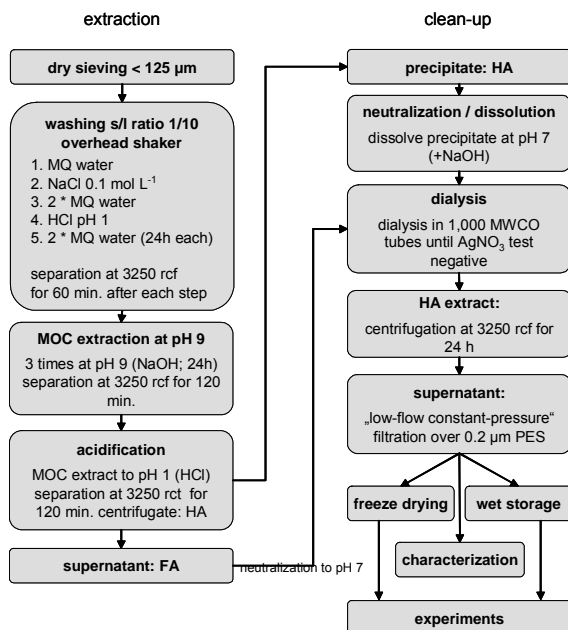


Trace metal associations with mineral colloids

Trace metal associations with mineral colloids & natural organic matter

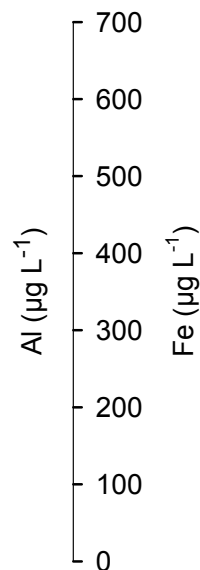
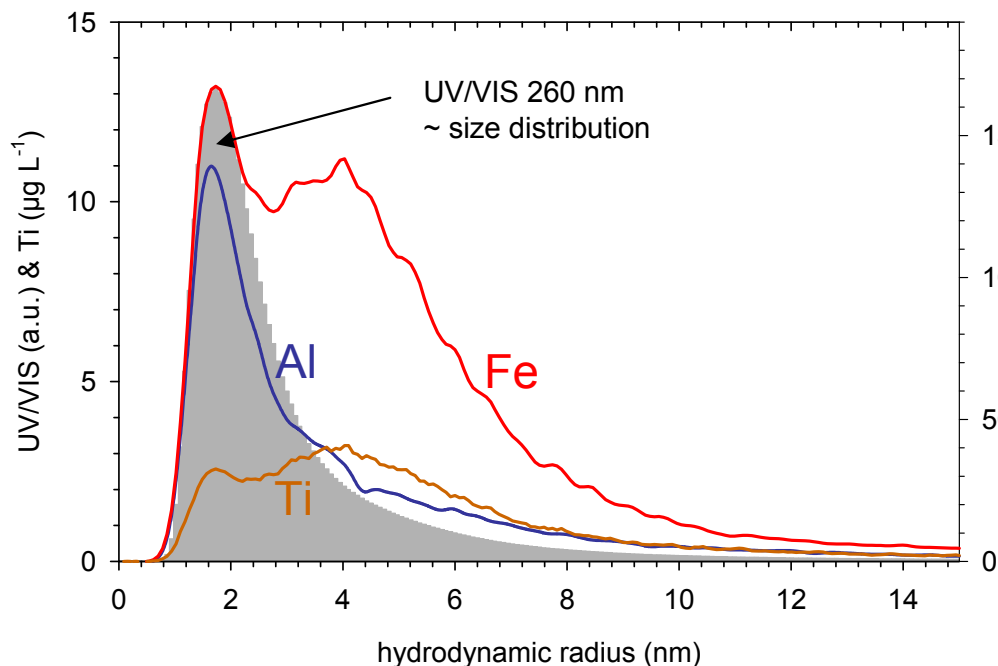
Contaminant transport with natural and engineered nanoparticles

pH9 - organic rich top-soil extraction



Composition of the aqueous soil extract:

Cd	Cu	Pb	Zn	Fe	Al	Na	Ca	Mg	Mn		
μg/L	μg/L	μg/L	μg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		
0.64	262	454	161	138	10.5	163	2.61	< 0,15	0.35		
DOC	C	H	N	S	O	RES	PO ₄ ³⁻	F ⁻	NO ₃ ⁻	NO ₂ ⁻	Cl ⁻
mg/L	%	%	%	%	%	%	mg/L	mg/L	mg/L	mg/L	mg/L
1159	43	5	3	0.6	36	12.4	1,3	< 0,5	< 0,3	< 0,2	1,3



3 domains

fluorescing NOM (~ 1 nm)
 UV absorbing NOM (1.5 – 4 nm)
 particulates (from 3 nm)

selective or predominant metal binding to a domain

domain 1+2:

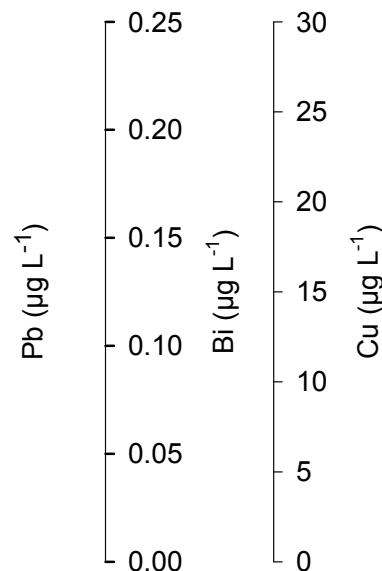
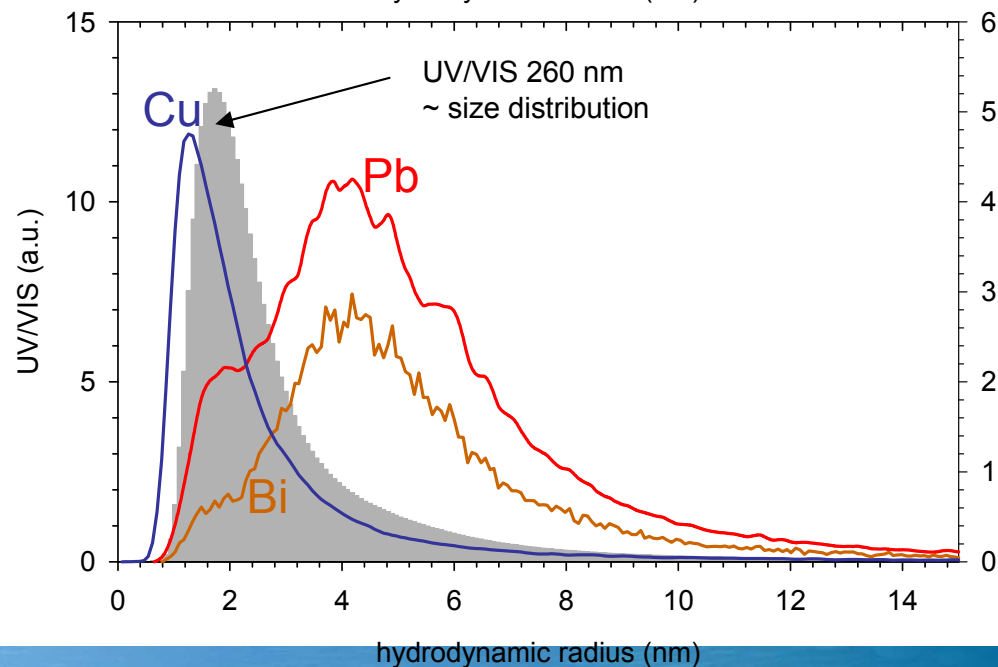
Cu, Sb

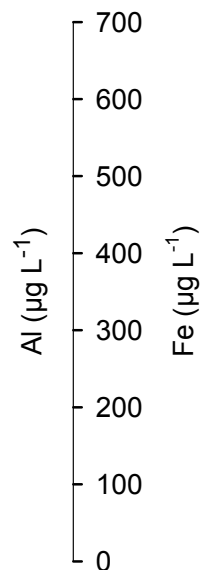
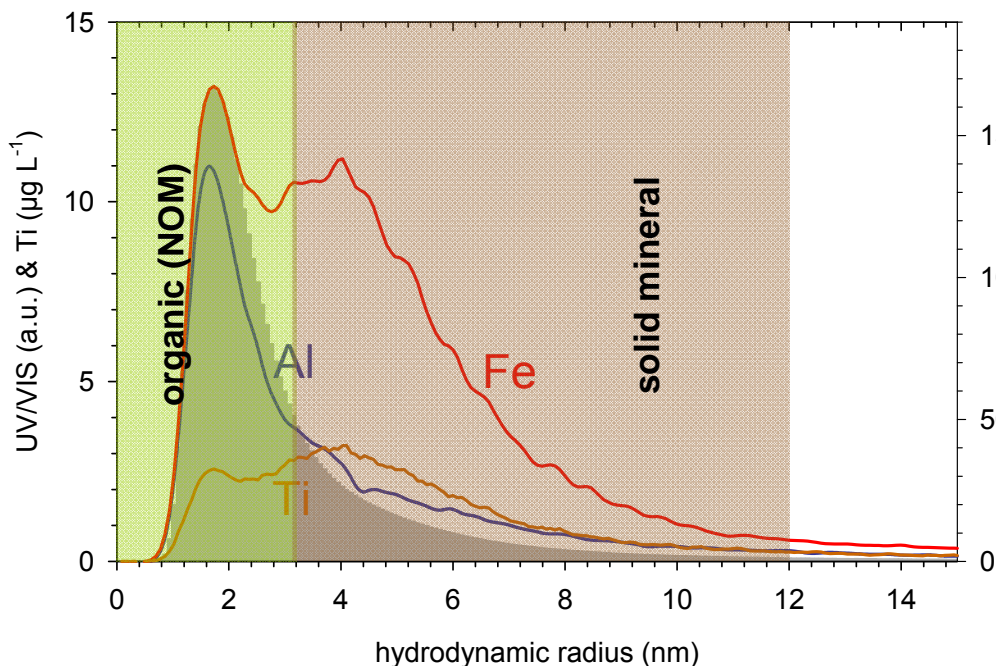
domain 2:

Al, Ca,
 Zn, Ni, U, Pt, Cd, Cr, Co

domain 2 & 3:

Fe, Mn, P
 Pb, Ti, Bi, Sn, V





3 domains

fluorescing NOM (~ 1 nm)
 UV absorbing NOM (1.5 – 4 nm)
 particulates (from 3 nm)

selective or predominant metal binding to a domain

domain 1+2:

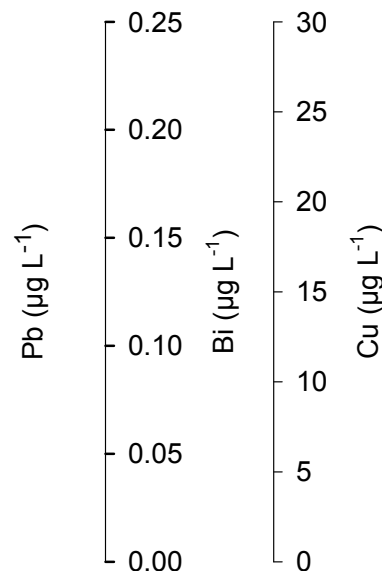
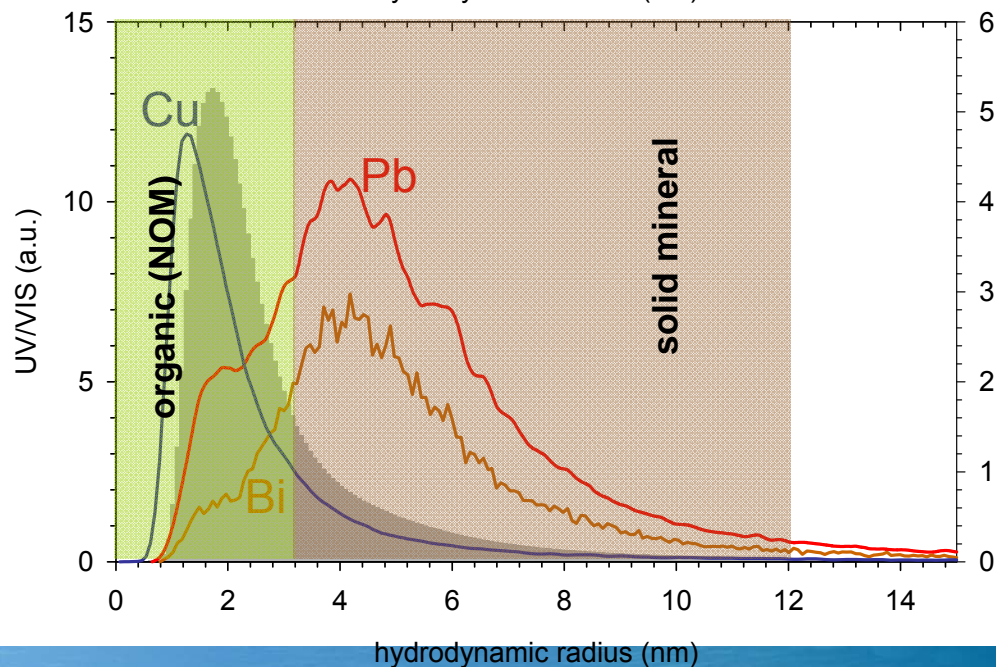
Cu, Sb

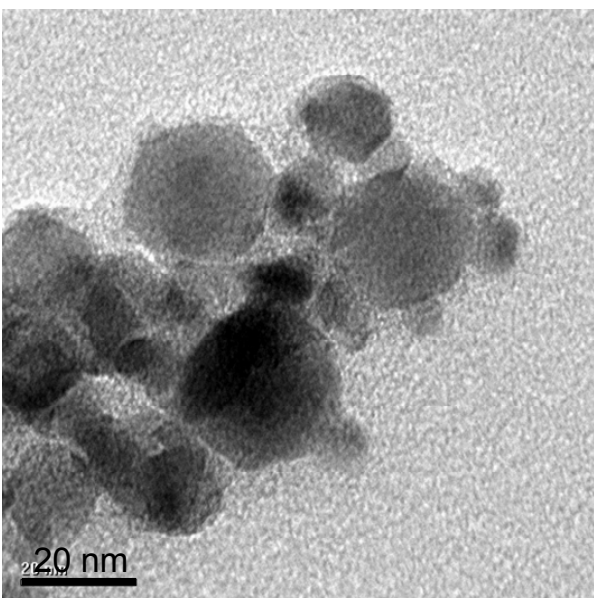
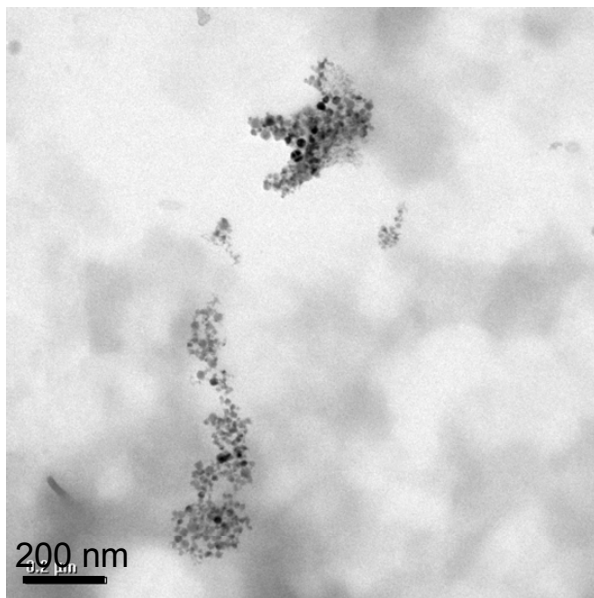
domain 2:

Al, Ca,
 Zn, Ni, U, Pt, Cd, Cr, Co

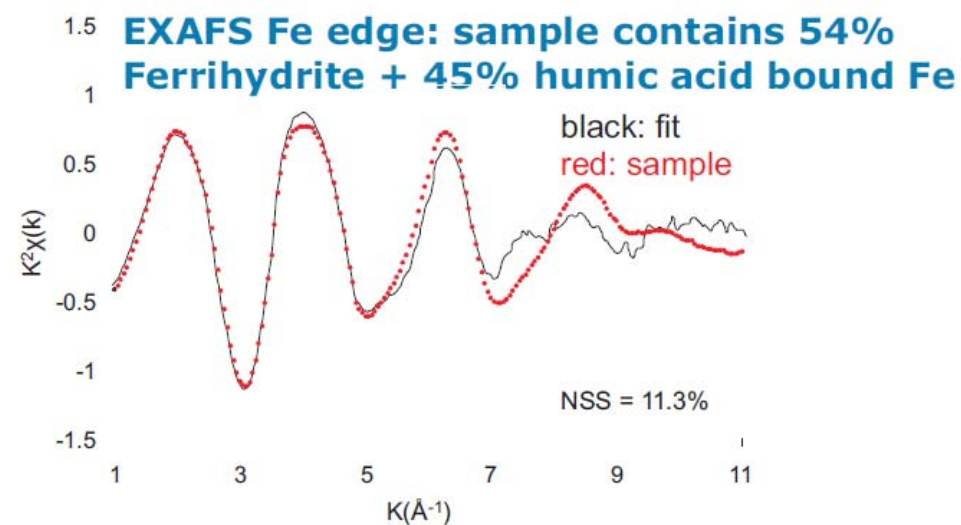
domain 2 & 3:

Fe, Mn, P
 Pb, Ti, Bi, Sn, V

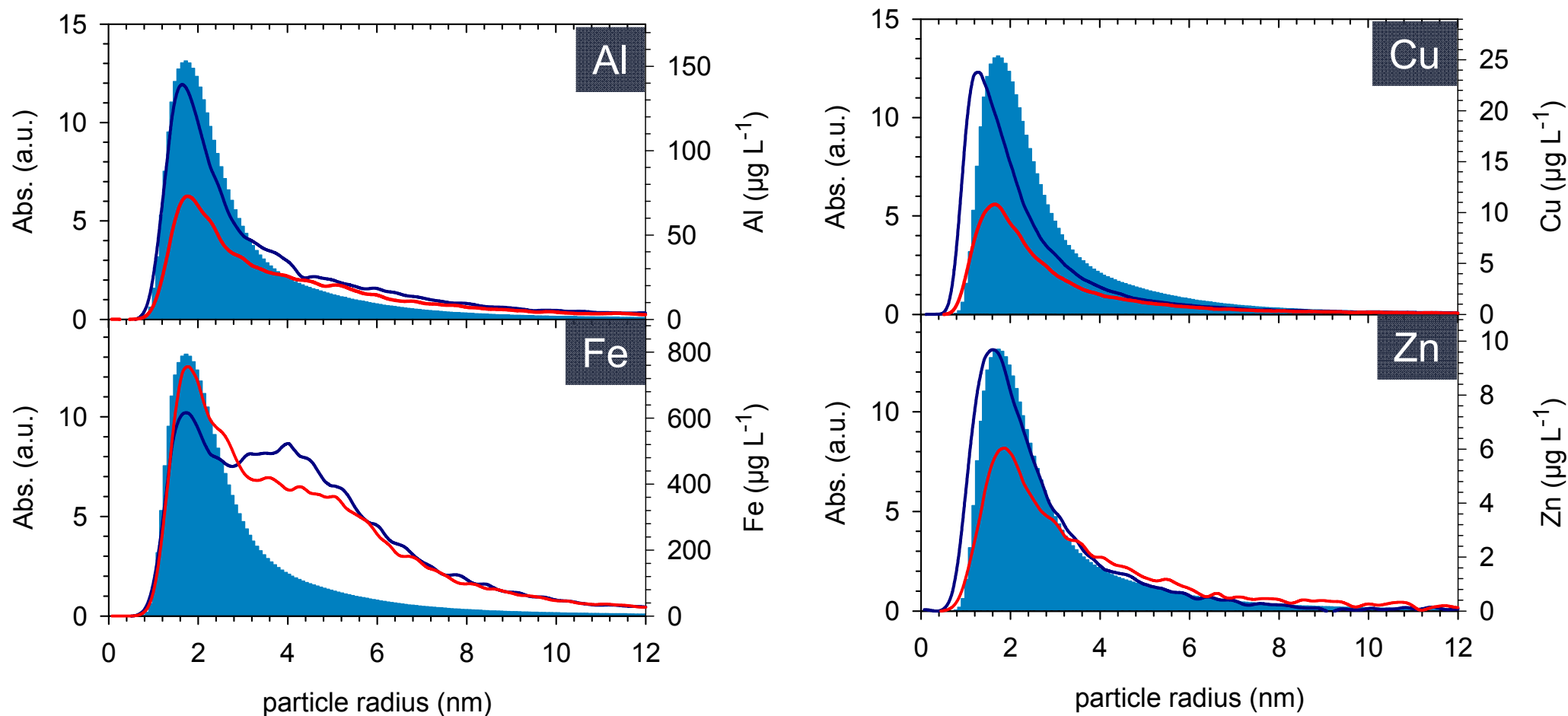




Identified by EDX: Fe, Cu, Ti, Al, Mg, Na

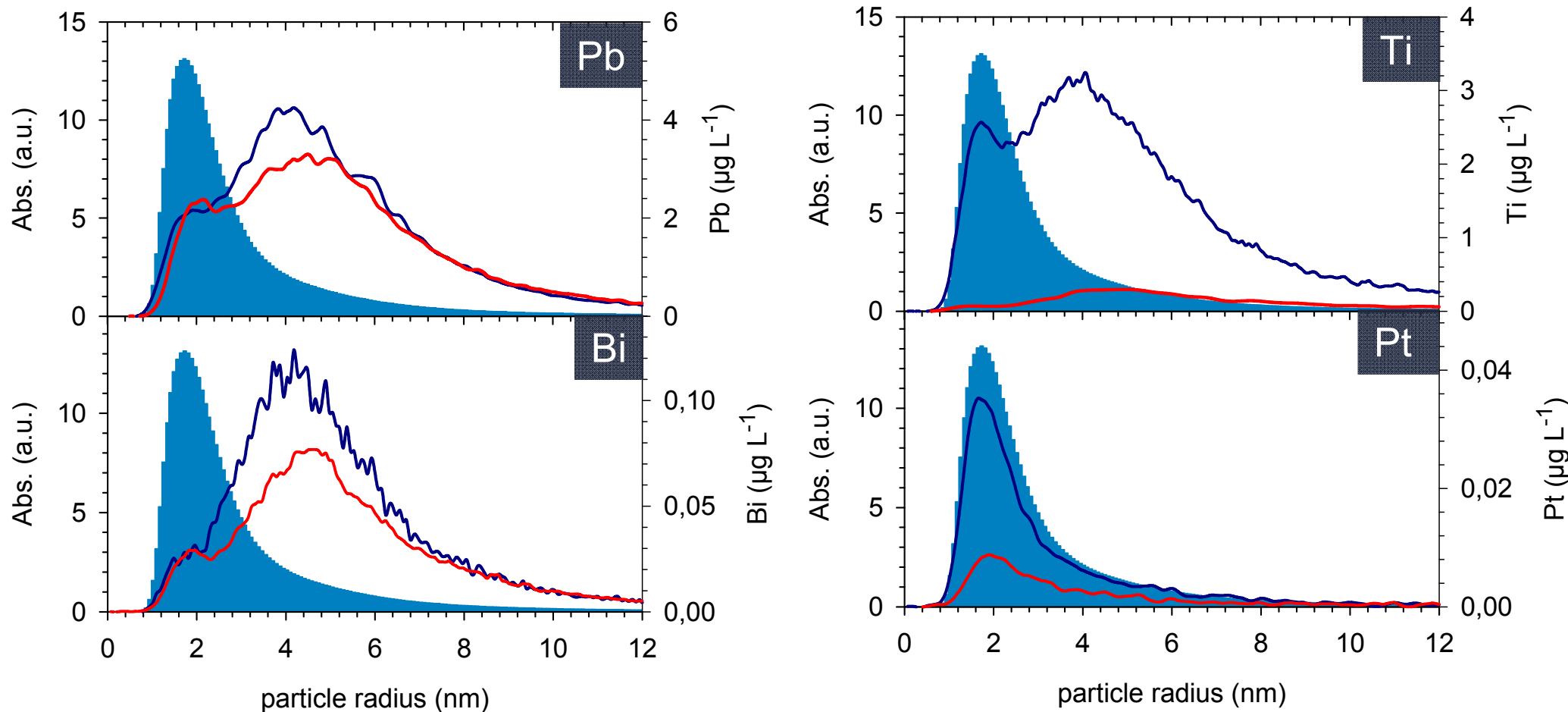


Extended X-ray absorption fine-structure spectroscopy (**EXAFS**):
distances, coordination number, and nature of the neighbours of the
absorbing atom



Original sample: shaking 60 days as is

Chelex sample: shaking 60 days with 2 g Chelex /250mL of sample



Original sample: shaking 60 days as is

Chelex sample: shaking 60 days with 2 g Chelex /250mL of sample

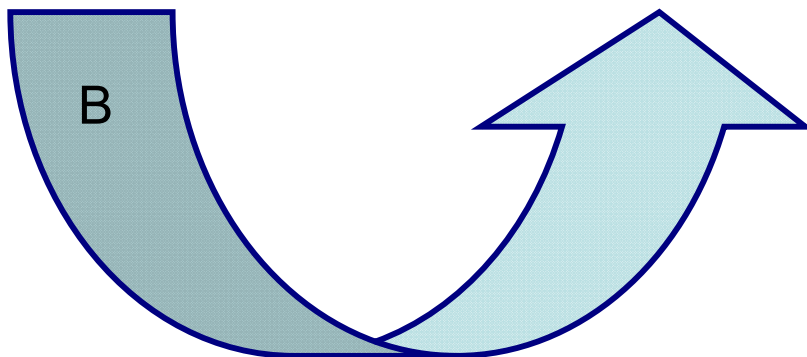
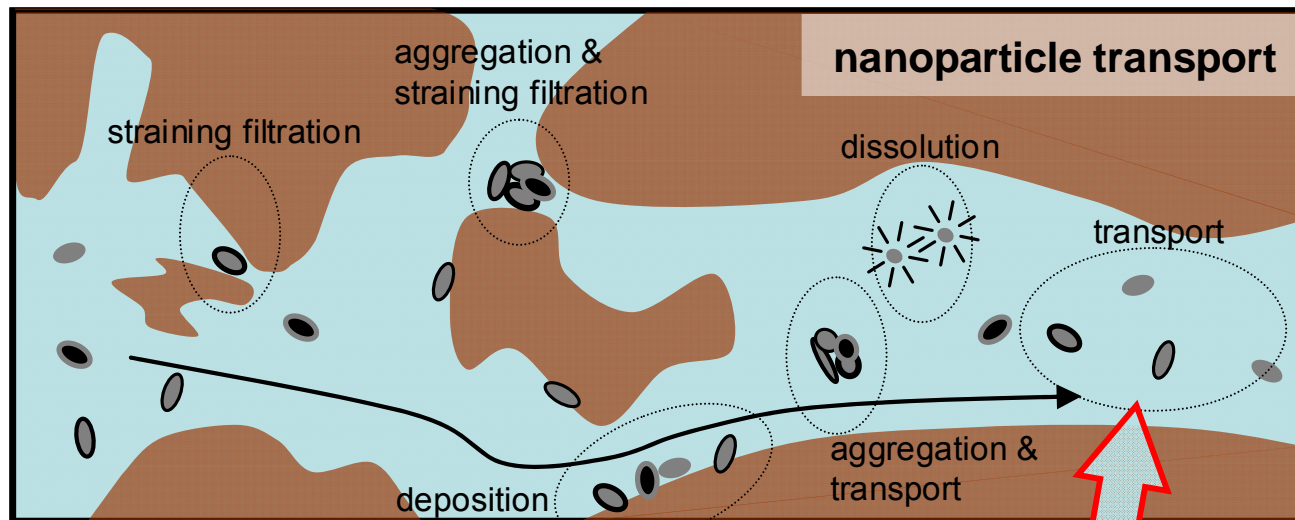
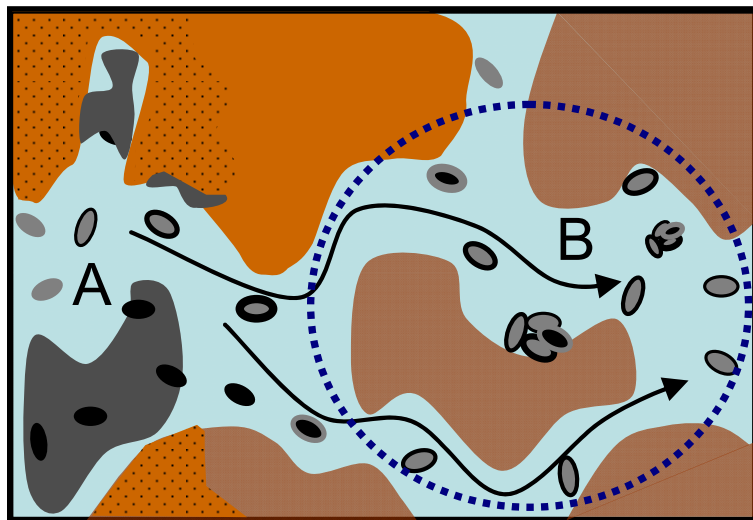
Trace metal associations with mineral colloids

Trace metal associations with mineral colloids & natural organic matter

Contaminant transport with natural and engineered nanoparticles

particle
loading

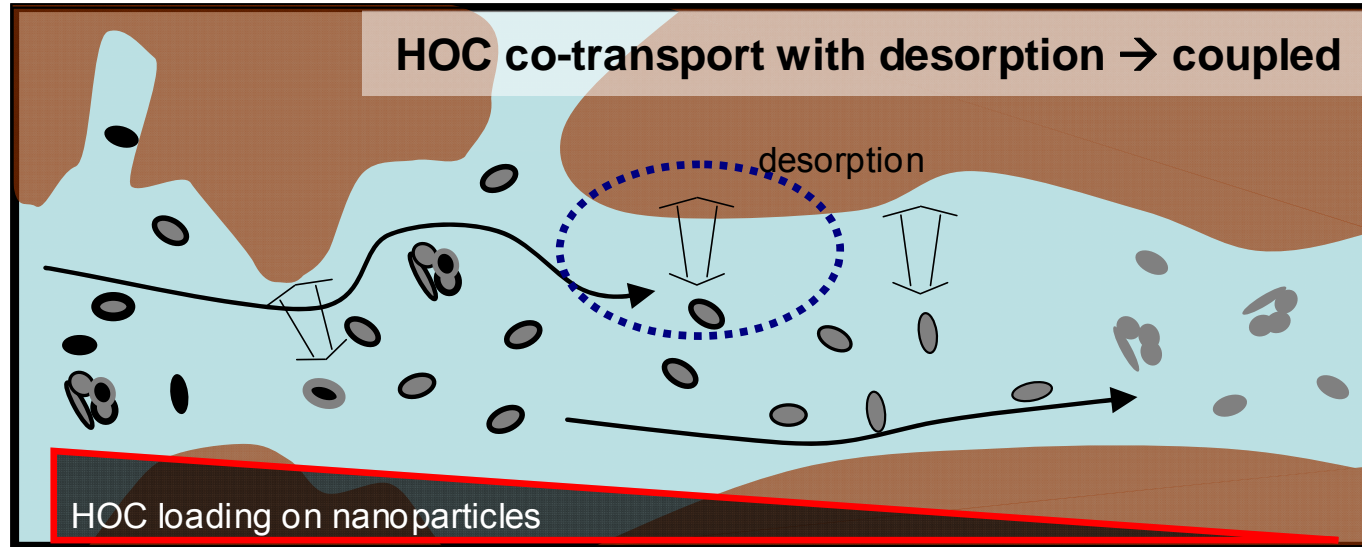
transport & desorption



100 % transport

- no deposition
- no filtration
- no dissolution

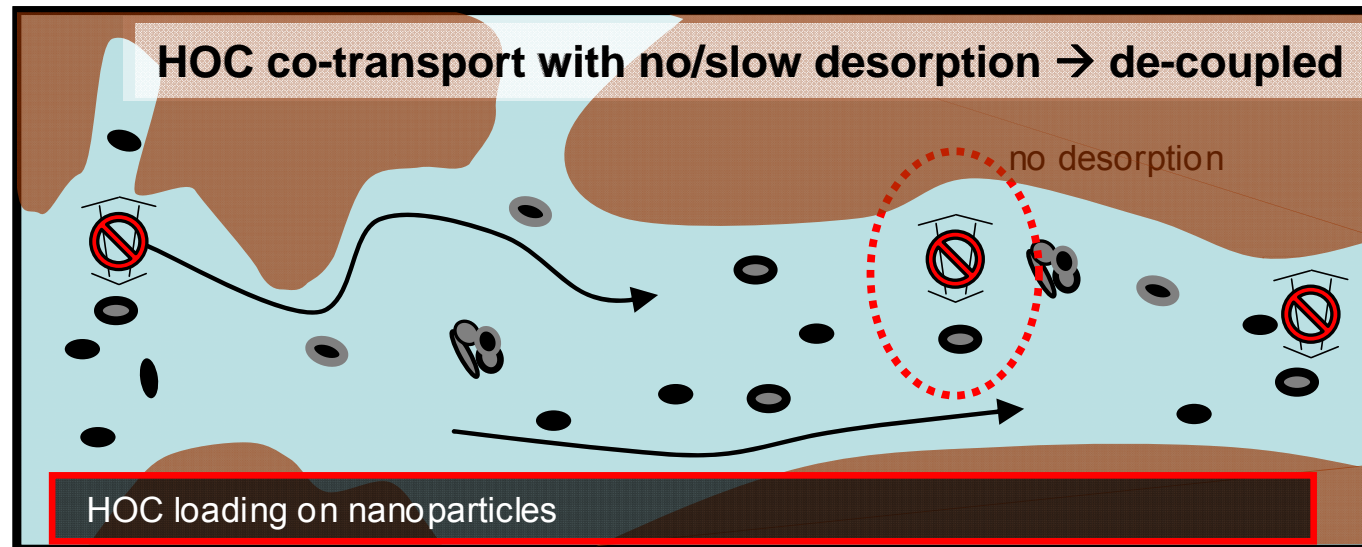
worst case scenario



Equilibrium:

HOC desorption is fast compared to the transport time scale

HOC will partition to matrix



De-coupled:

HOC desorption is slow compared to the transport time scale

HOC will be relocated with nanoparticles

Conditions:

avg. particle size 250 μm

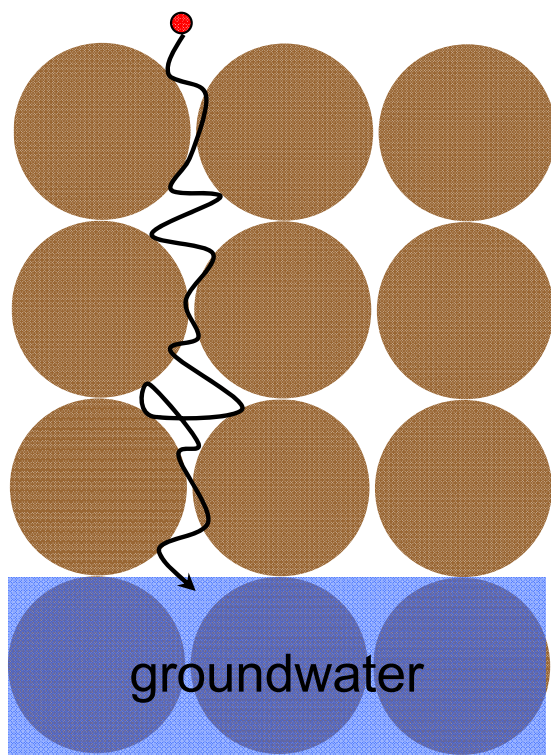
avg. pore size 100 μm

porosity 35%

GW renewal 350 mm/h

attachment efficiency = 10^{-4}

Kd of contaminant = ∞



radius	diffusion coefficient	Brownian displacement	settling rate (D2.6)
10^{-8} m (10 nm)	2.1×10^{-11} m ² s ⁻¹	390 $\mu\text{m h}^{-1}$	0.8 $\mu\text{m h}^{-1}$
10^{-7} m (100 nm)	2.1×10^{-12} m ² s ⁻¹	1.23 $\mu\text{m h}^{-1}$	80 $\mu\text{m h}^{-1}$

steady state, saturated, non-transient conditions

10 nm diameter particles

travel time: ~1 year

collisions through diffusion: ~4/h \rightarrow 35000 per year

\rightarrow attachment through diffusional movement

\rightarrow particles will be „lost“ 3.5 times during transport

100 nm particles

travel time: ~1 year

\rightarrow diffusion negligible (100 collisions / year)

\rightarrow sedimentation accounts for ~ 10.000 collisions / year

Conditions:

avg. particle size 250 μm

avg. pore size 100 μm

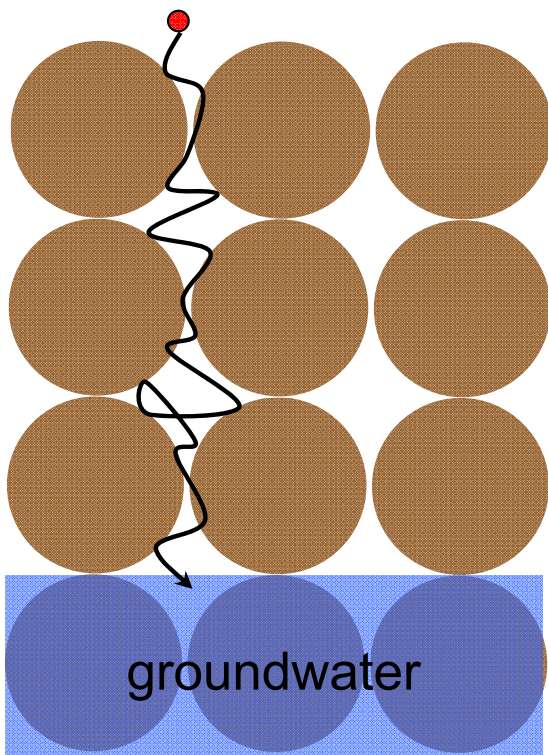
porosity 35%

GW renewal 350 mm/h

attachment efficiency = 0

Kd of contaminant = 10^{-5}

radius	diffusion coefficient	Brownian displacement	settling rate (D2.6)
10^{-8} m (10 nm)	2.1×10^{-11} m ² s ⁻¹	390 $\mu\text{m h}^{-1}$	0.8 $\mu\text{m h}^{-1}$
10^{-7} m (100 nm)	2.1×10^{-12} m ² s ⁻¹	1.23 $\mu\text{m h}^{-1}$	80 $\mu\text{m h}^{-1}$



1 m

steady state, saturated, non-transient conditions

concentration ENP in soil: ~ 10 mg/L

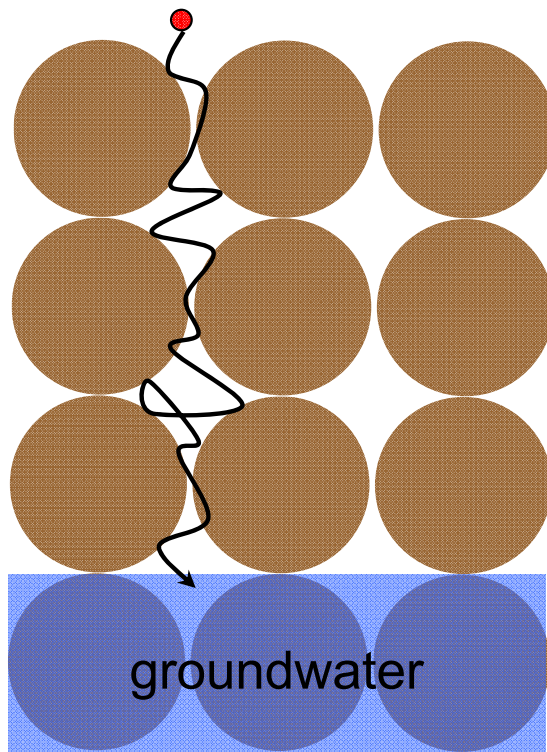
concentration of matrix: 1.820 g/L

ratio of ENP to matrix: 5.6×10^{-6}

equilibration of contaminant in source: $\sim 50:50$

→ transported for 1 year through clean soil

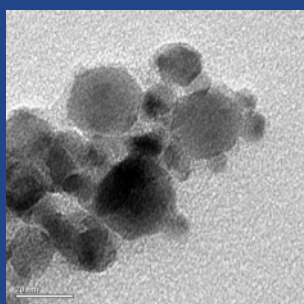
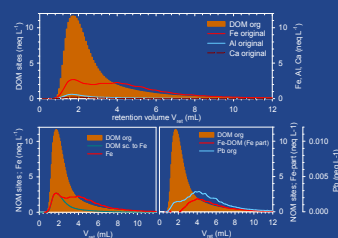
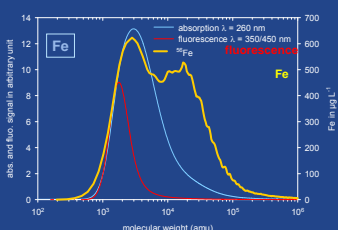
radius	diffusion coefficient	Brownian displacement	settling rate (D2.6)
10^{-8} m (10 nm)	$2.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$	$390 \text{ } \mu\text{m h}^{-1}$	$0.8 \text{ } \mu\text{m h}^{-1}$
10^{-7} m (100 nm)	$2.1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$	$1.23 \text{ } \mu\text{m h}^{-1}$	$80 \text{ } \mu\text{m h}^{-1}$



1 m

what are the critical parameters?

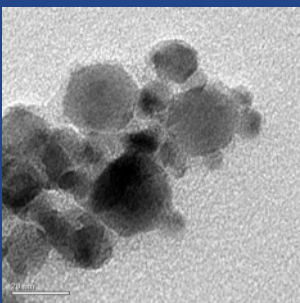
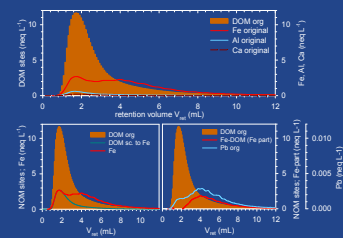
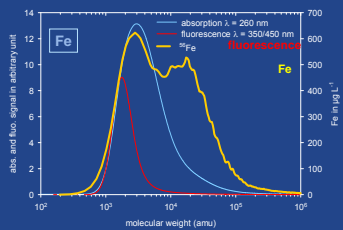
- preferential transport of particles (not much information)
- very large K_d values for the contaminant/ENP (unlikely)
- very low desorption kinetic (not much information)



- natural nanoparticles are complex and heterogeneous systems
 - they are still poorly understood
 - in natural complexity they are seldom described quantitatively
 - NPs are mobile, but mobility and appearance of “free” NP seems limited
 - contaminants as Pb seem to be predominantly bound to Fe / Mn / Ti phases
 - presence of well defined & stable mineral phases ~ 10 nm
 - trace elements distribute specifically between different NP phases (& sizes)
-
- aggregates and agglomerates: more clarification or confusion?
 - co-transport of contaminants with ENP is limited but possible
 - important to look at the important controlling processes!
 - are those ENPs (which we look at currently) really so different from natural ones?

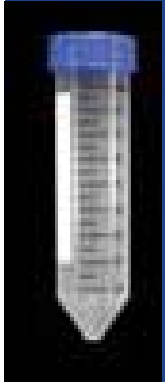
Thank you !

With support from: Elisabeth Neubauer, Samuel Legros, Martin Hasselov, Philippe Le Coustumer, Lei Shi....



- Trace elements are associated with smaller non-clay type NPs and the NOM
- Pb seems to be predominantly bound to Fe / (Mn) / Ti phases
- trace elements distribute specifically between different NP phases (& sizes)
- Redox processes lead to continuing re-formation and re-distribution
- size-separation alone is not sufficient to explain the processes
- chemical speciation at the nanoscale is required (spatial resolution, sensitivity)

NANOPARTICLE SEPARATION: AQUEOUS EXTRACTION METHODOLOGY

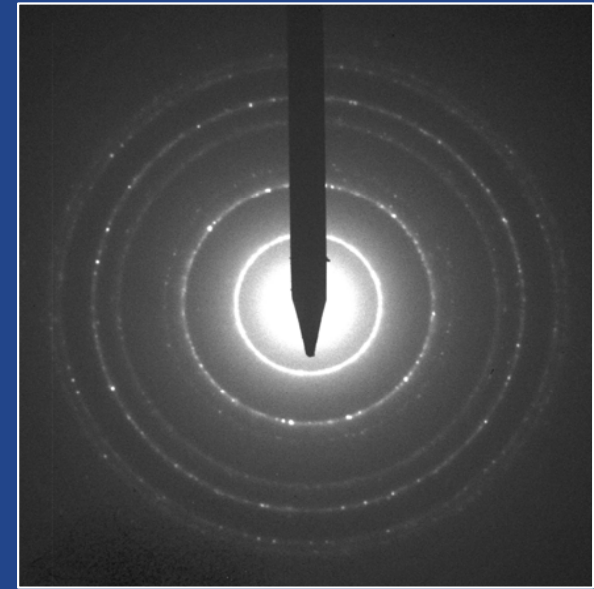
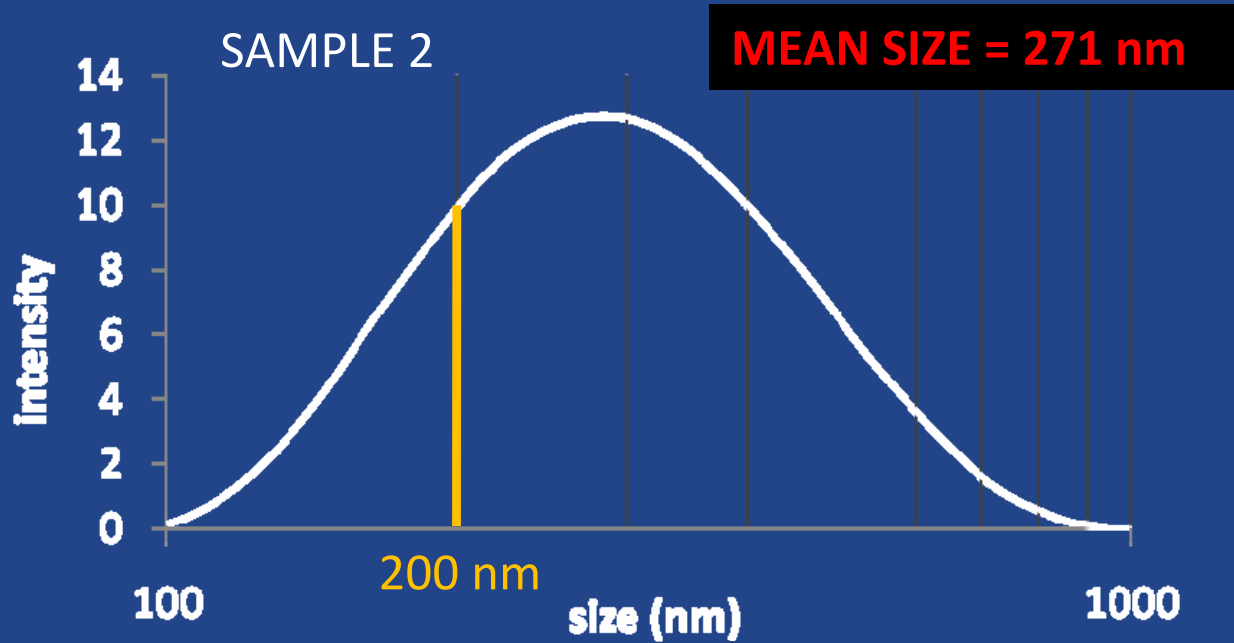


1. 4 g sediment +
40 mL 0.1 M NaCl
2. centrifuged at 4500rpm, 90 min
3. supernatant drained, sediment
washed multiple times with MQ
water
4. when supernatant returns turbid:
→ 200nm cutoff
→ collect supernatant



$$t_s = \ln\left(\frac{r_{out}}{r_{in}}\right) \frac{18\eta}{4\pi^2 \Delta\rho d^2 (rpm / 60)^2}$$

LIGHT SCATTERING



quartz
albite

mica-montmorillonite

orthoclase

illite

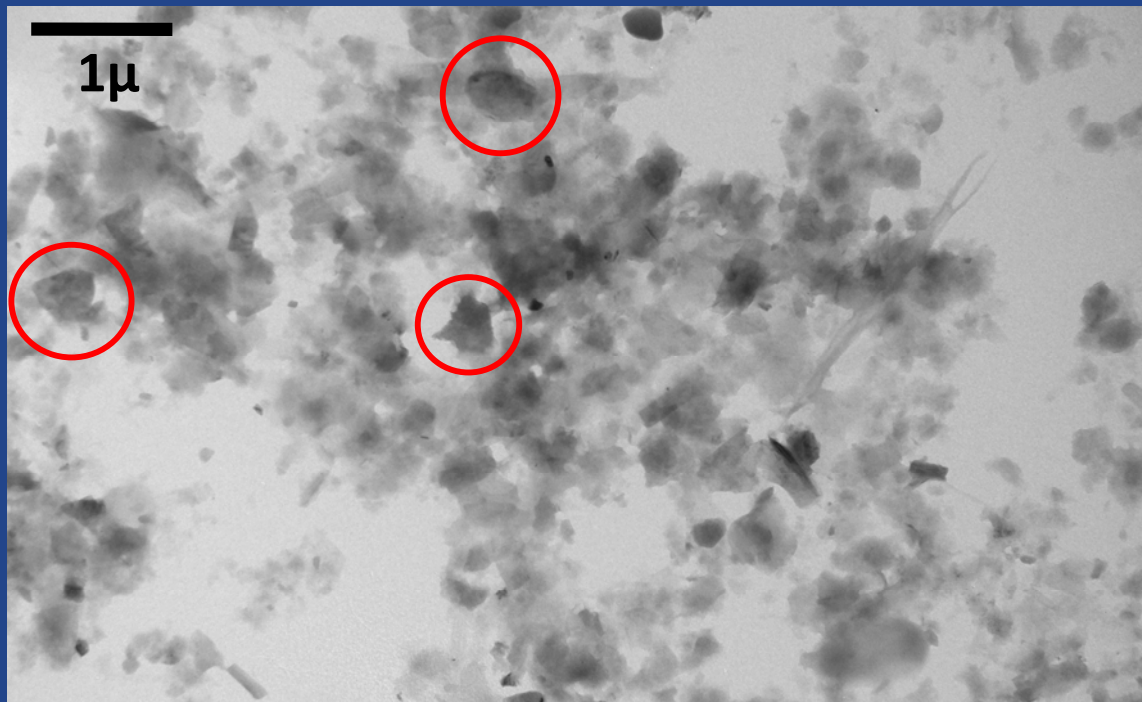
nontronite

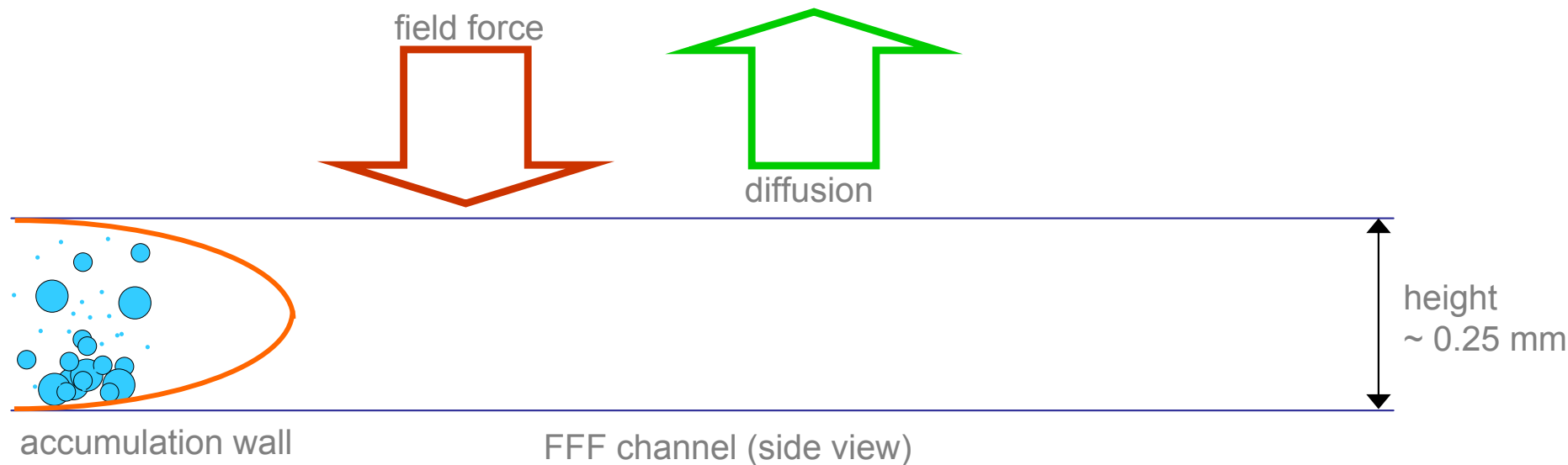
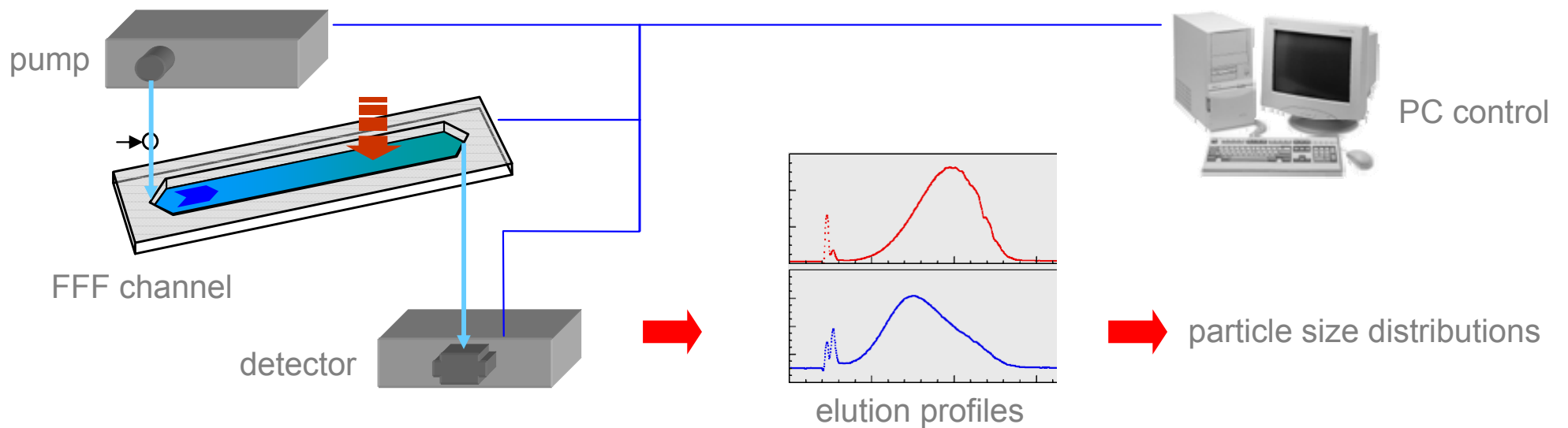
microcline

paragonite

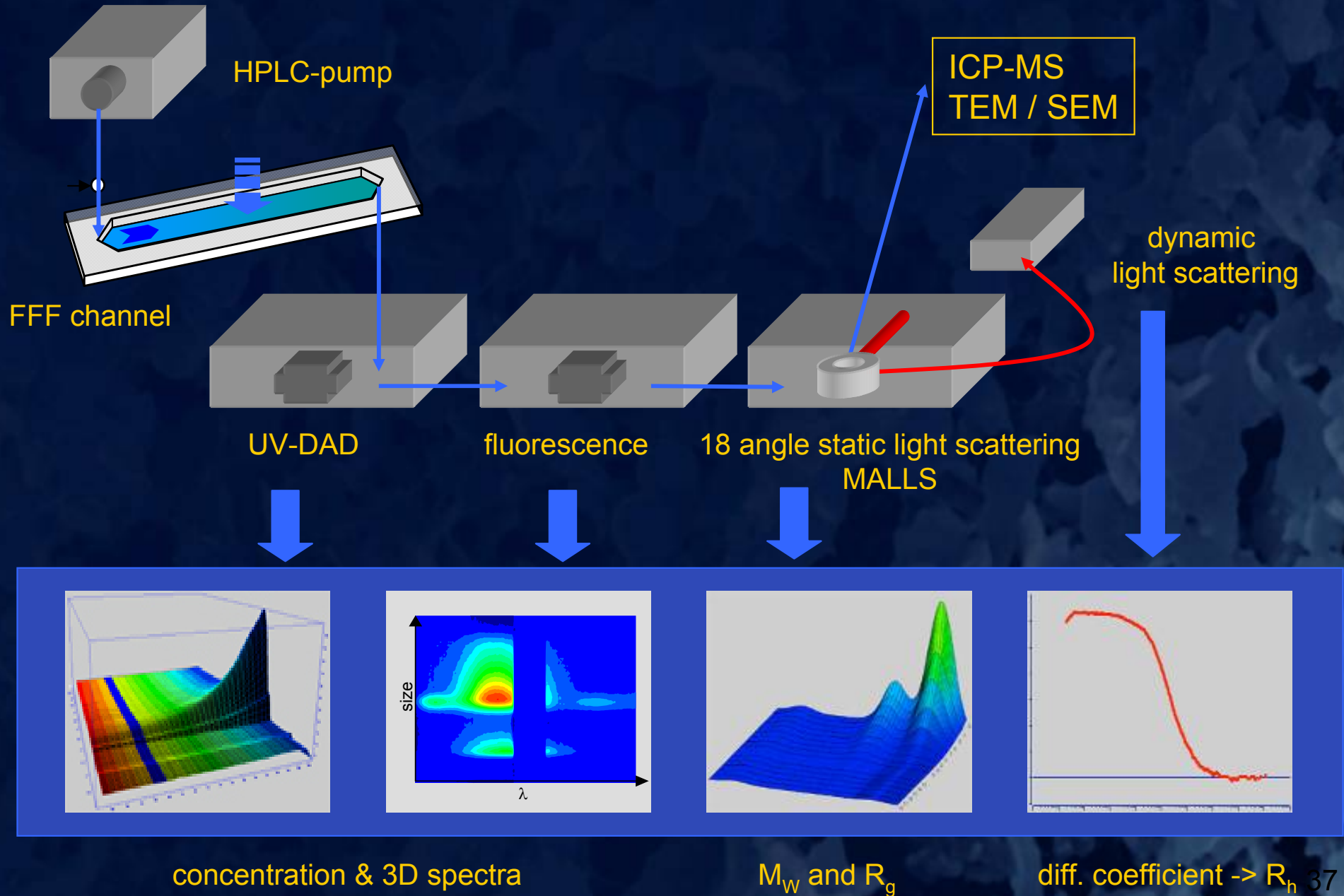
pyrophyllite

muscovite



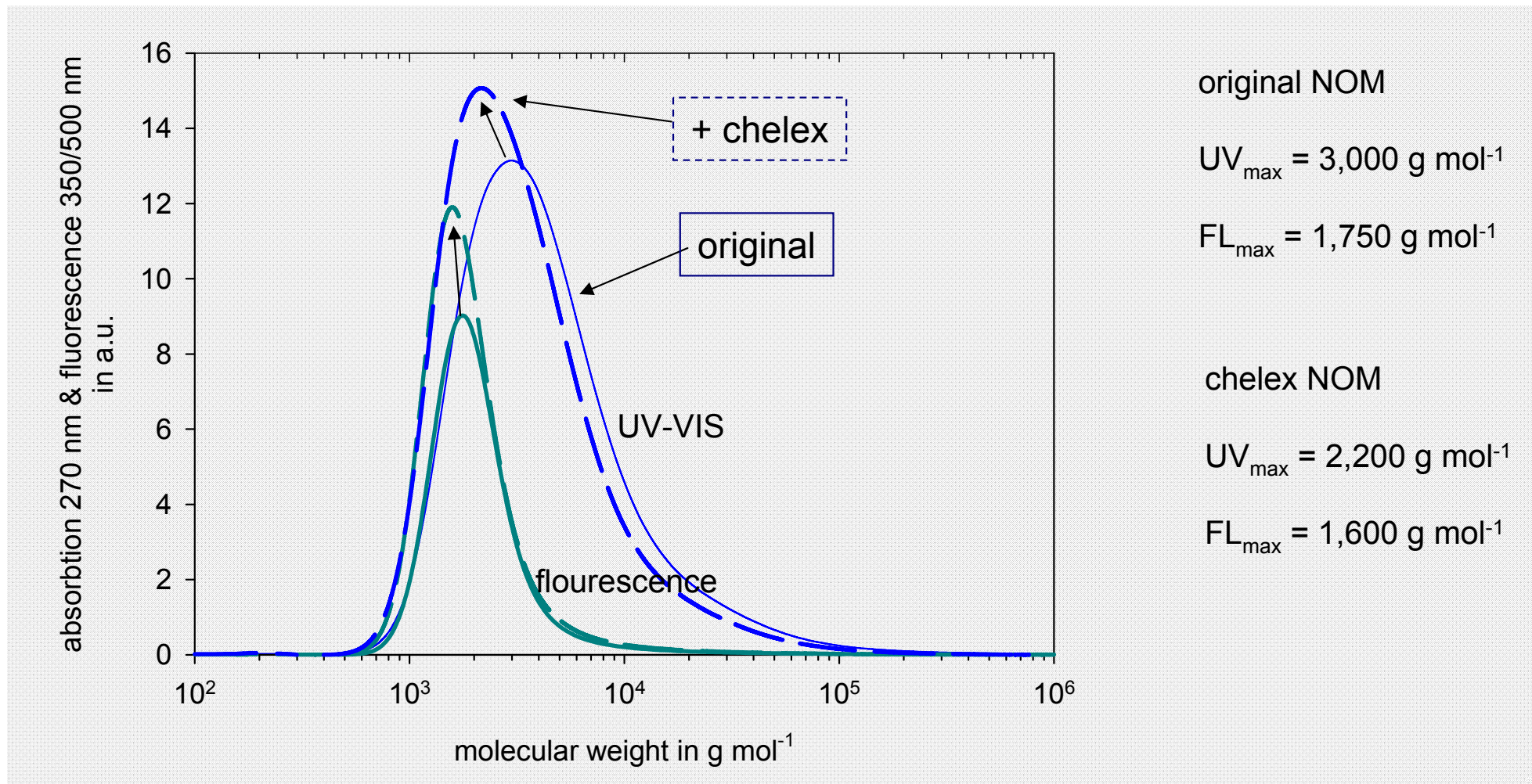


Flow-Field Flow Fractionation – analytical separation of NPs according to diffusion coefficient



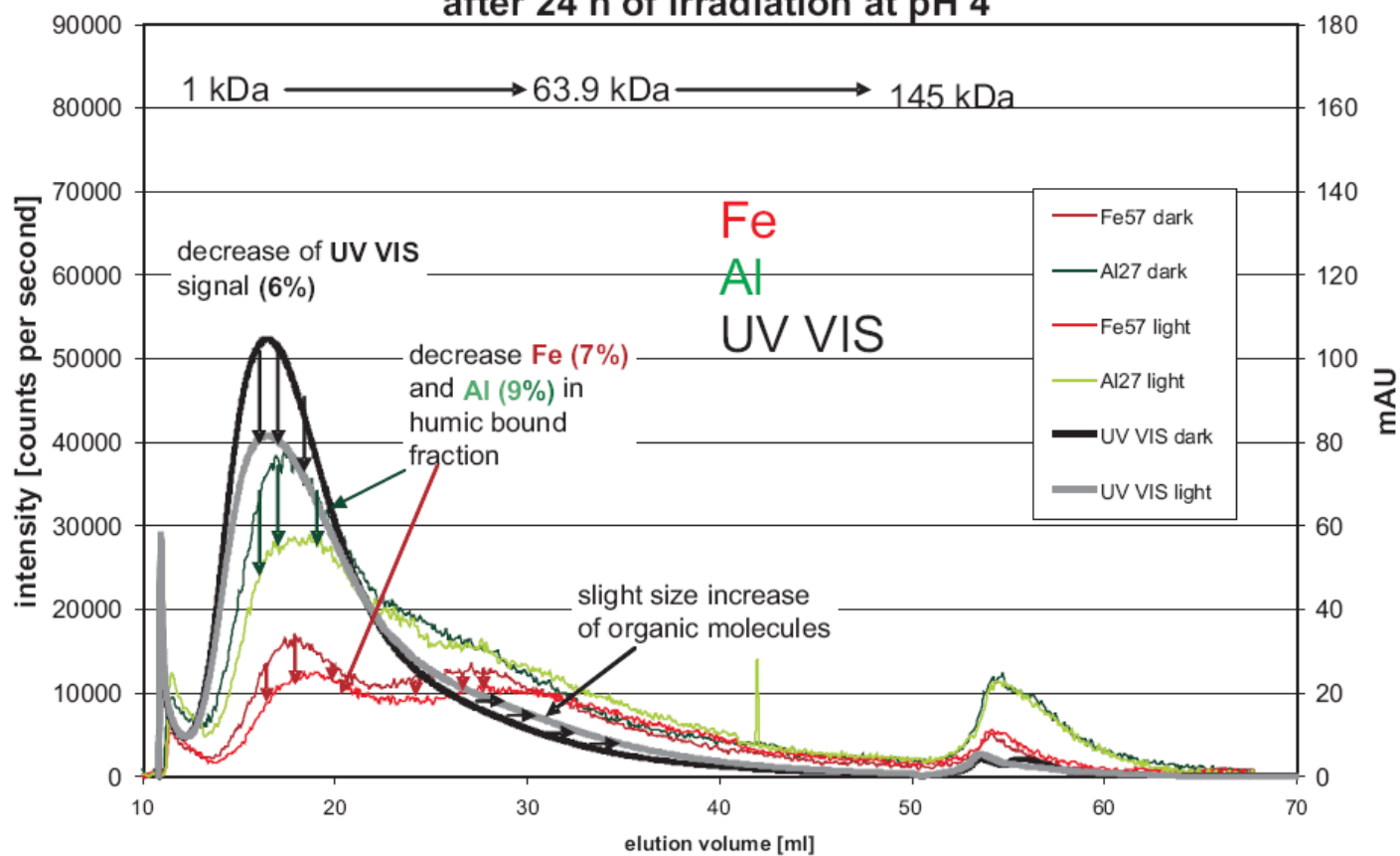
Original sample: shaking 60 days as is

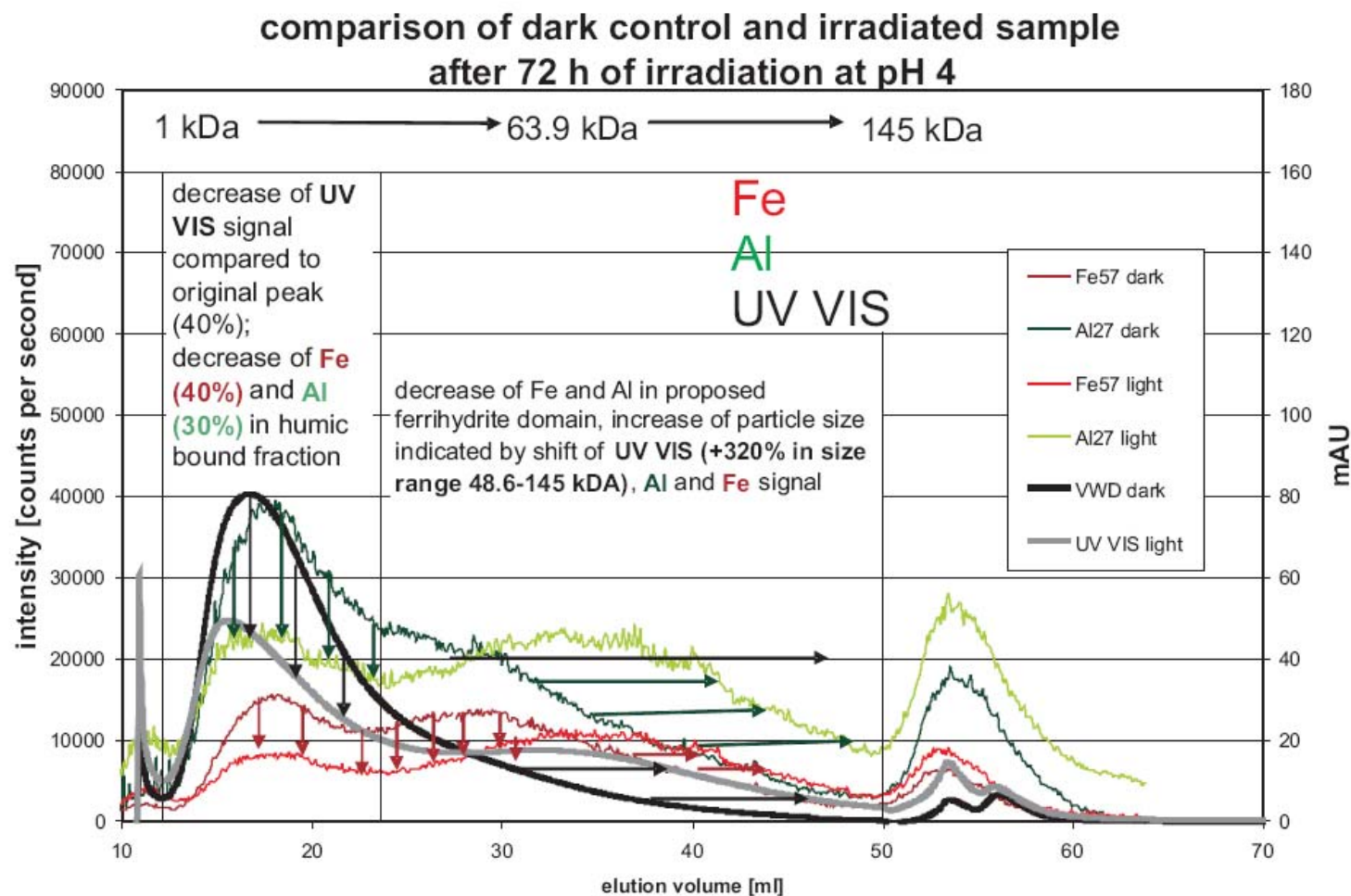
Chelex sample: shaking 60 days with 2 g Chelex /250mL of sample

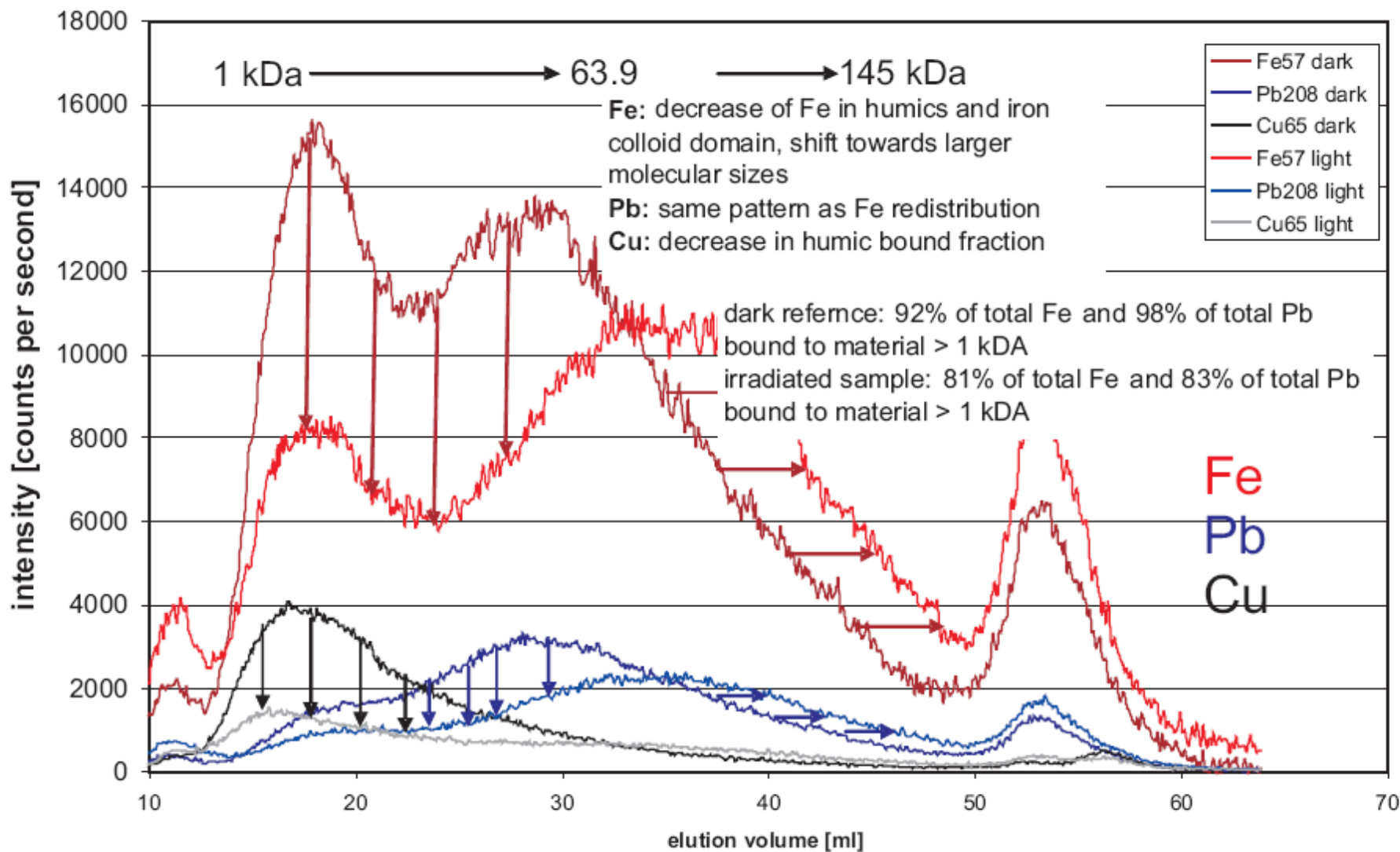


Irradiation experiment at pH 4

comparison of dark control and irradiated sample
after 24 h of irradiation at pH 4







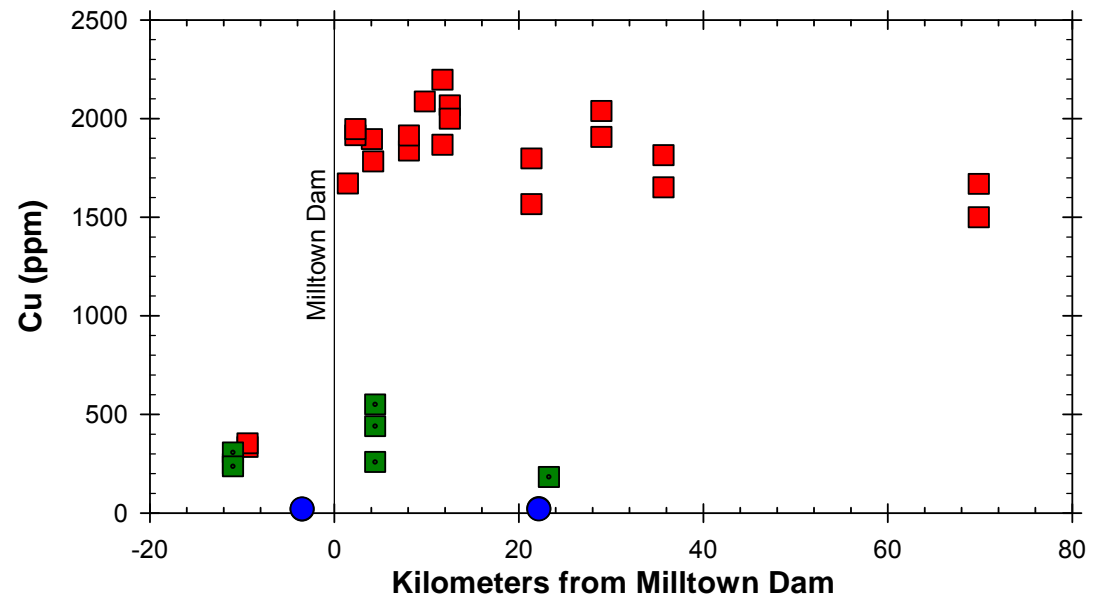
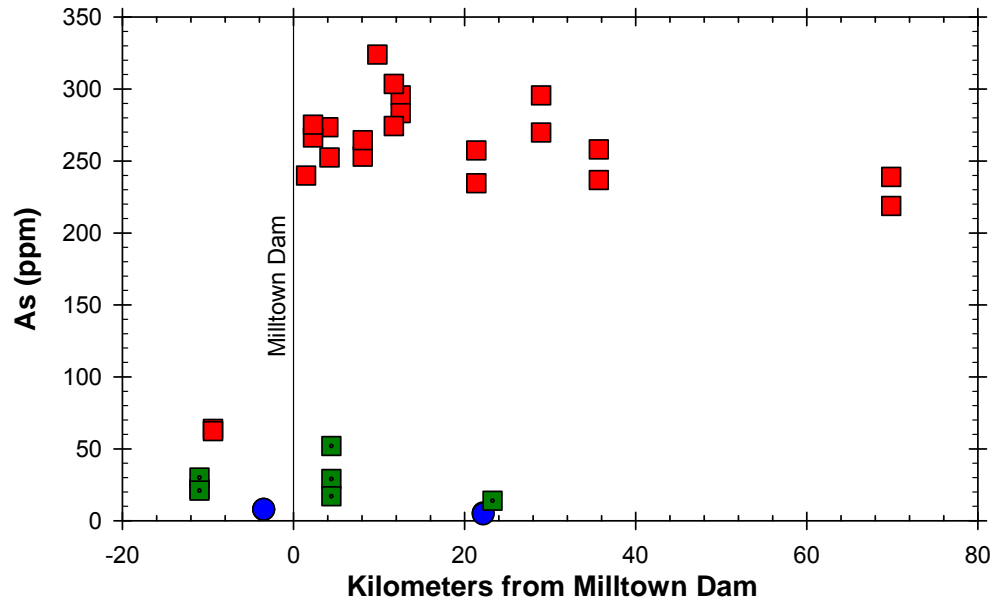
Milltown Sediment Release

As

Cu

Milltown Sediment Release Arsenic Concentrations

Milltown Sediment Release Copper Concentrations



upstream

downstream



Clark Fork riverbed mud: post dam breaching



tributaries (used for background levels at time of sampling)



USGS data from 2004, 2005 and 2006 (pre dam breaching)

Milltown Dam Removal



1,600 t As

1,600 t Pb

13,000 t Cu

25,000 t Zn