Fate and uptake of nanoparticles in aquatic systems: what are the implications for environmental risk assessment

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Uses of nanomaterials

- New nano-scale materials with novel properties
- Fast growing sector, already multibillion US$ industry, likely to exceed 1 trillion US$ mark by 2015
- Already in many consumer products

Applications

Application	Nanomaterial	Concentration (%)
Personal care products (sunscreens, toothpaste, soap, shampoo, face creams	TiO_2 Hydroxyapetite Ag Fullerene C_{60}	5 15 0.02 0.05 – 0.25
Paints and coatings	TiO_2 SiO_2 ZnO Alumina Silica/Alumina	5 15 1-10 0.5-5 7-10
Medical	Ag API	5 1-20
Food and packaging	nanoclay	5
Fuel catalysts	CeO2	5-10

Potential environmental levels

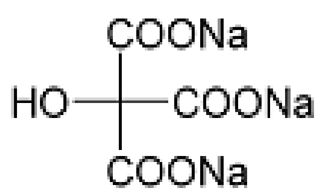
	Water (μg/l)	Soil (μg/kg)	Air (mg/m^3)	Aggregate size (nm)
Ag	0.010	0.43	-	-
AlO_3	0.0002	0.01	-	-
Au	0.14	5.99	-	-
CeO_2	<0.0001	<0.01	6×10^{-7}	-
fullerenes	0.31	13.1	-	75 (25-500)
hydroxyapatite	10.1	422	-	-
latex	103	4307	-	-
organo-silica	0.0005	0.02	-	-
SiO_2	0.0007	0.03	-	205 (135-510)
TiO_2	24.5	1030	7	330 (175-810)
ZnO	76	3194	-	480 (420 – 640)

Objectives

- Establish a set of well characterized engineered nanoparticles covering a range of properties
- Explore the those factors and processes affecting the fate of engineered nanoparticles in aquatic systems
- Determine the uptake of engineered nanoparticles into aquatic organisms from a range of taxonomic groups and with different feeding traits (e.g. detritovores, filter feeders)
- Develop guidance on the design and interpretation of environmental fate and effect studies for environmental risk assessment of engineered nanoparticles

Model particles

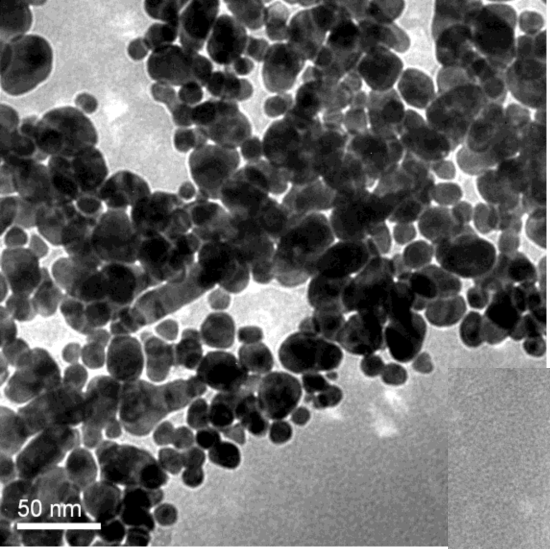
- Model particles - Au
  - easy to synthesise
  - different sizes and surface coatings
  - manufactured in large quantities
  - high purity
  - easily characterised
  - traceable by numerous methods



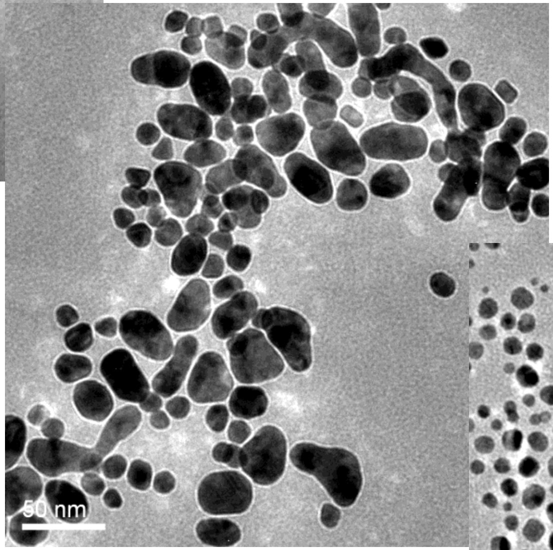
Sodium Citrate tribasic Dihydrate

11-Mercaptoundecanoic Acid

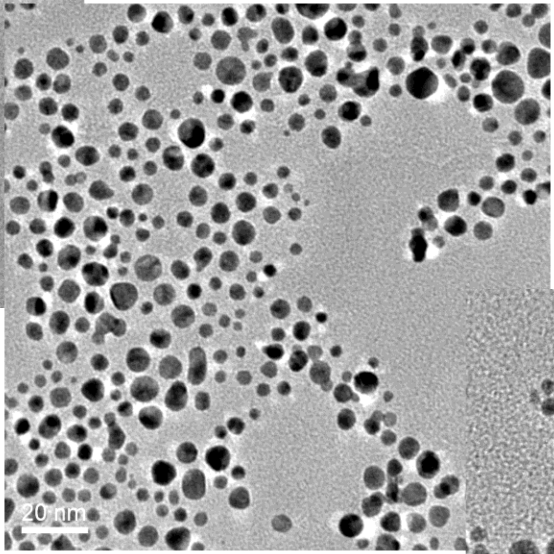
Model Au particles



30 nm, Citric



30 nm
SH(CH2)10COOH



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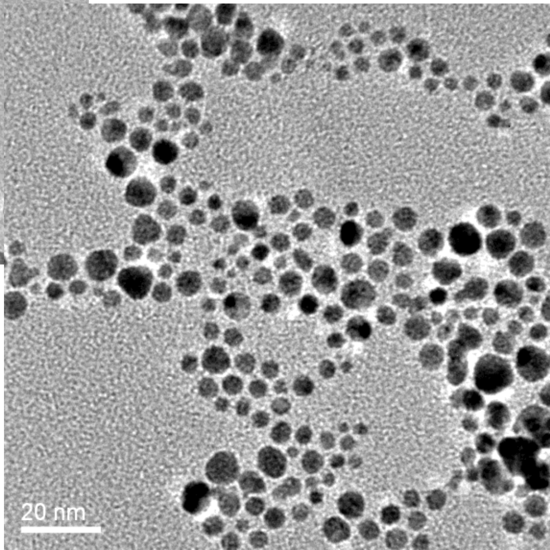


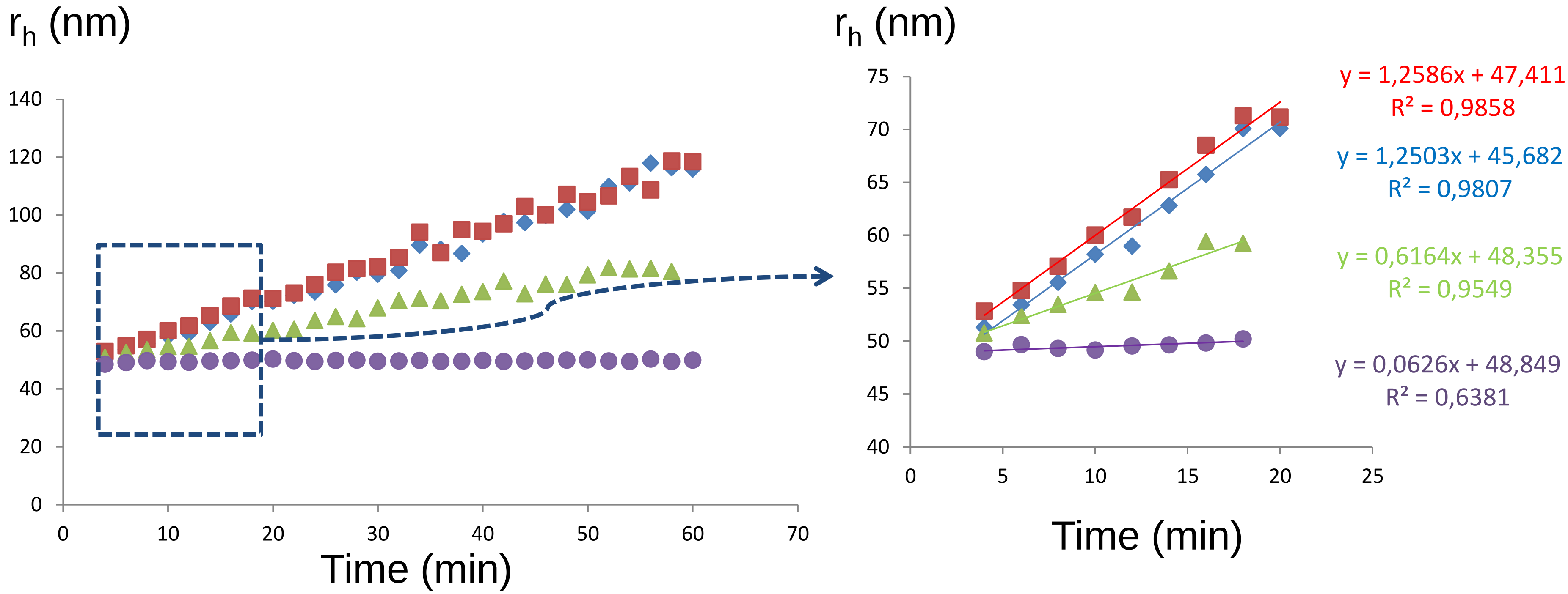
Characterization of NPs

Core	Coating	Mass Con, mg L^{-1}		No. Con, 10^{11}	Mean Size, nm	
		ICP-MS	NTA	No. CNTA	DNTA	DTEM
Au	Citrate_10 nm	42.8	-	-	-	6.16±6.45
Au	Citrate_30 nm	30.9	136.4	1.13±0.07	49.3	32.6±15.1
Au	M11_10 nm	45.7	-	-	-	5.88±6.45
Au	M11_30 nm	42.7	144.6	1.33±0.07	47.6	27.5±14.5
Au	BSA_30 nm	34.7	20.35	0.03±0.00	87.56	8.7±2.5
NOTE : "-" not applied						

Fate of ENPs

- Effects of environmental parameters
- Single parameter studies
  - Kinetic studies
  - Particle concentration
  - NOM
  - pH
- Multi-parameter studies
  - stability studies
  - pH, NOM, monvalent and divalent cations

Aggregation rate studies



$$\left(\frac{dr_h}{dt}\right)_{t\to 0} \propto kC$$

Coagulation rate (nm/sec)

$$\alpha = \frac{1}{W} = \frac{k}{k^f}$$

Attachment efficiency

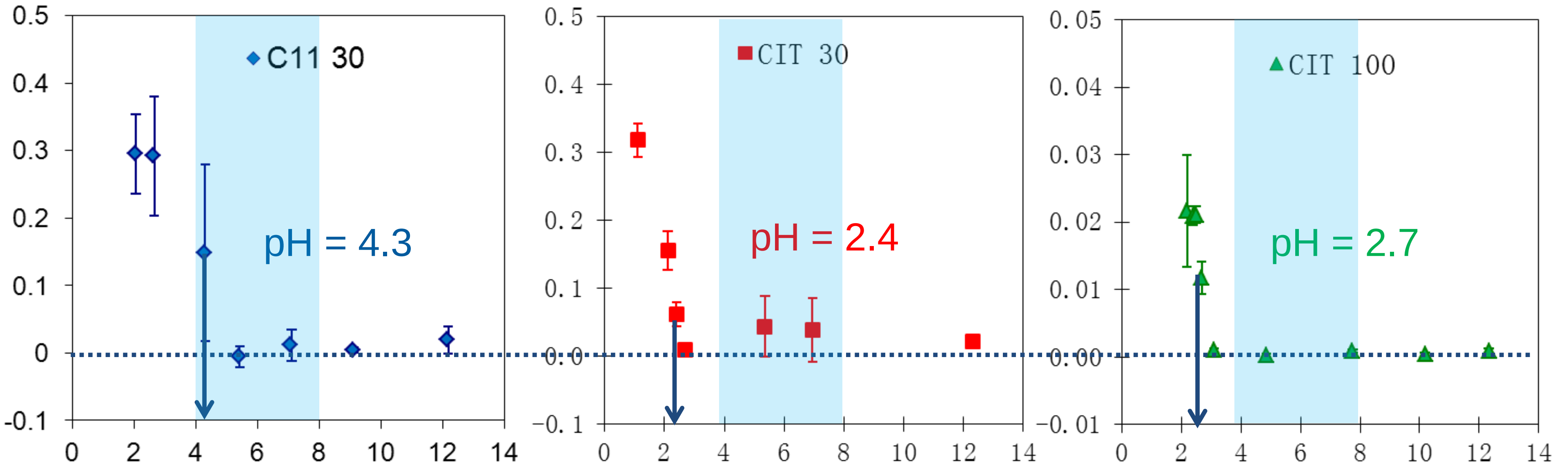
Stability ratio

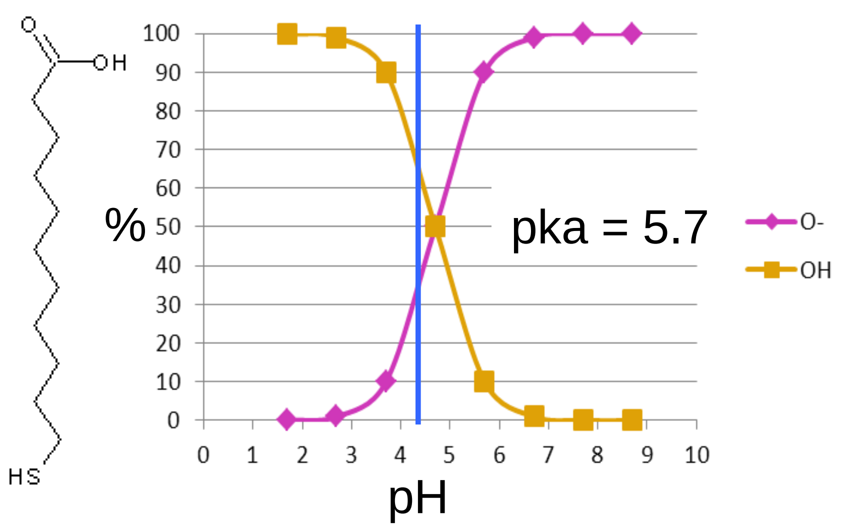
Kretzschmar et al., J. Col. Inter. Sci. 1999

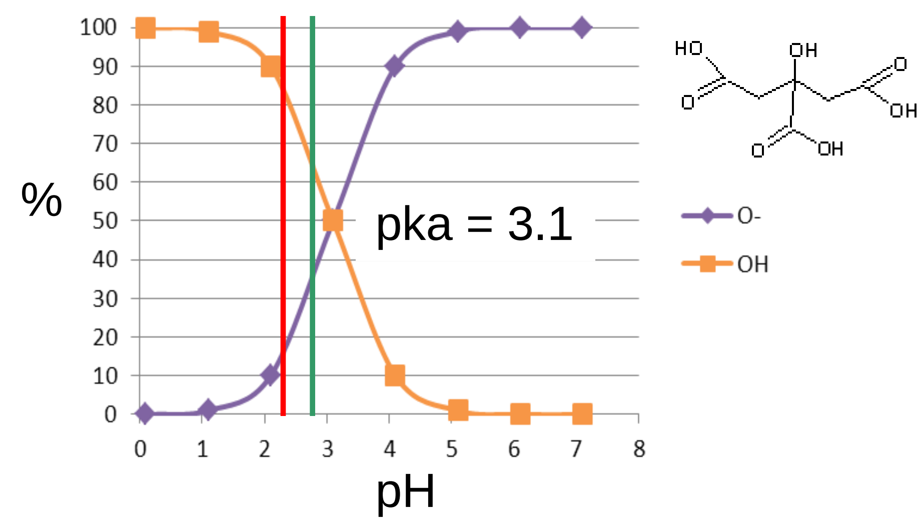
Effect of pH

k (nm/sec)

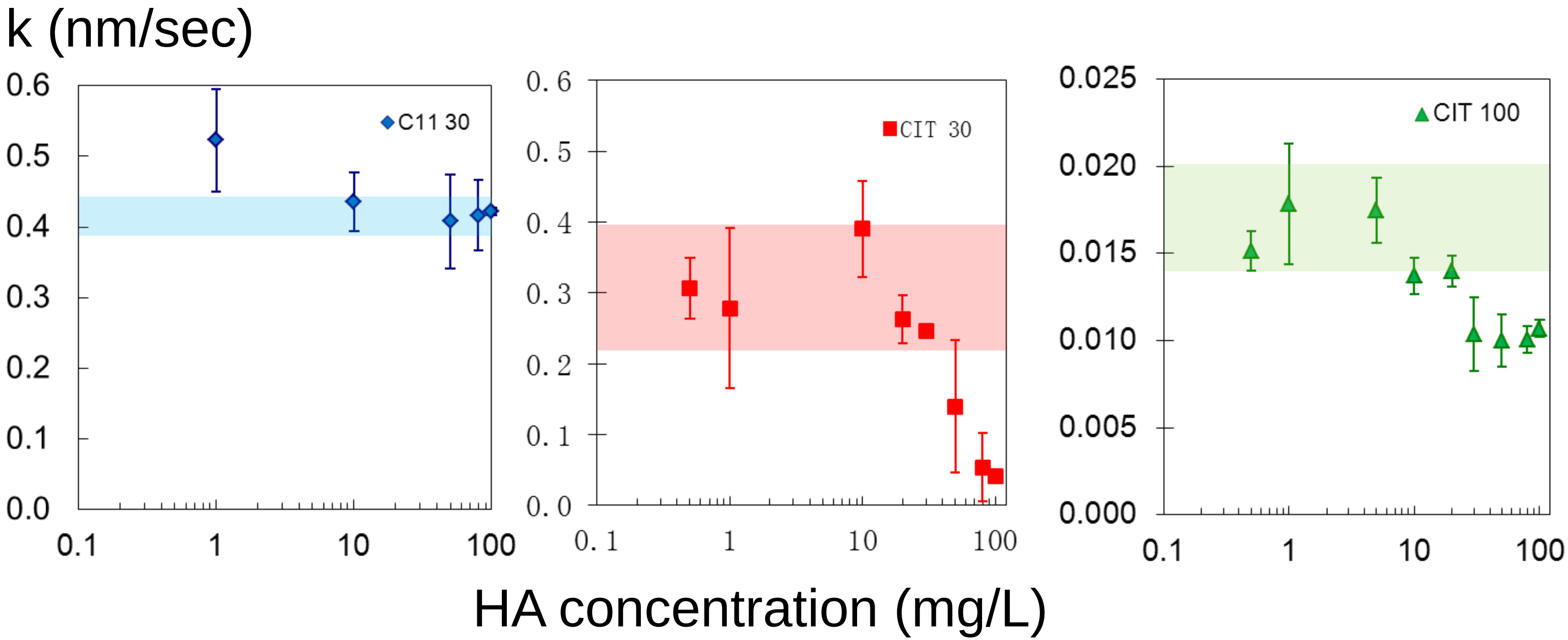
pH ≤ pka then k ↑







Humic acids

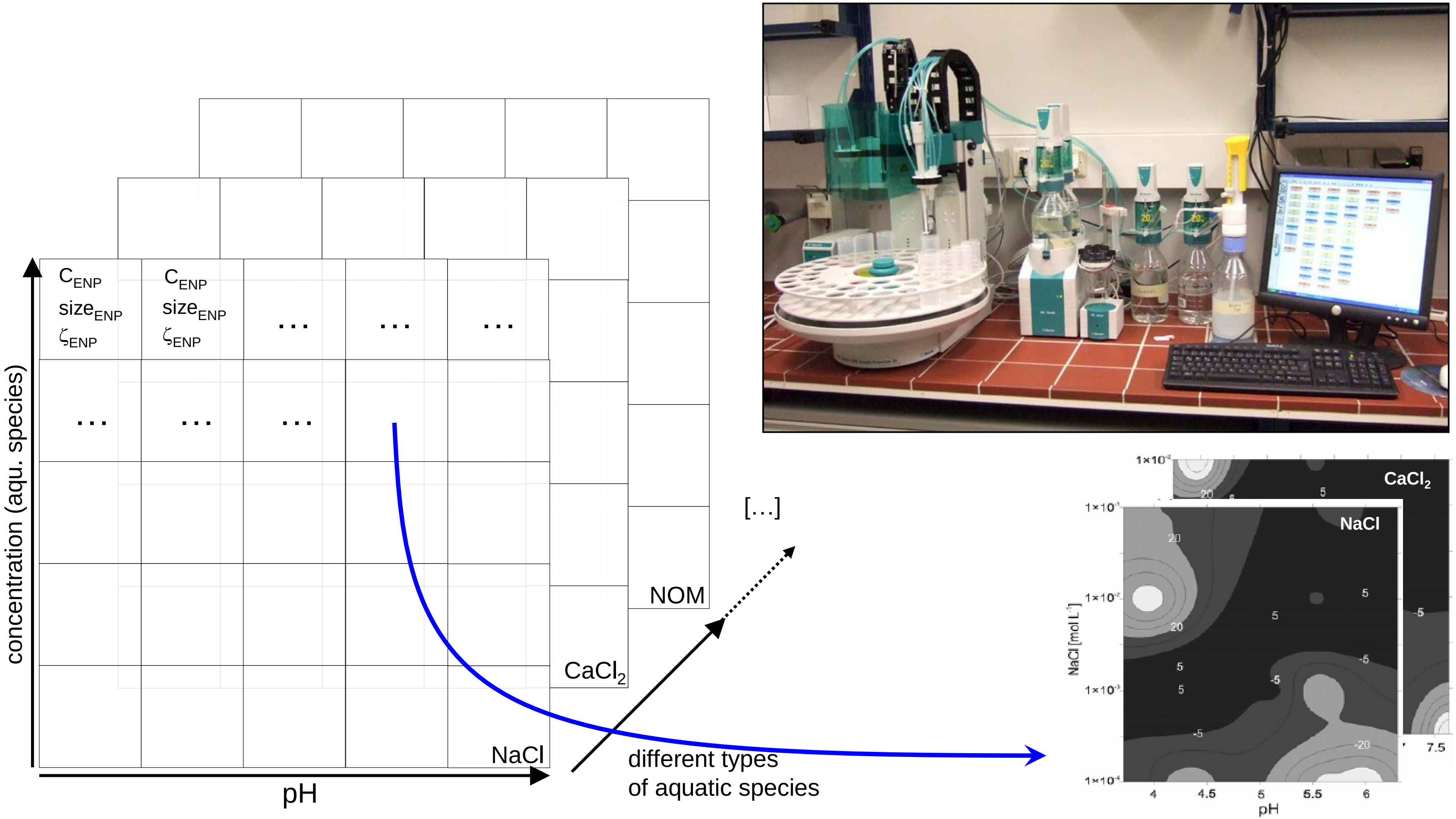


For citrate GNPs, addition of the SRNOM reduced the coagulation rate more significantly for CIT 30 (from 0.39 to 0.041) comparing with CIT 100 (from 0.018 to 0.010).

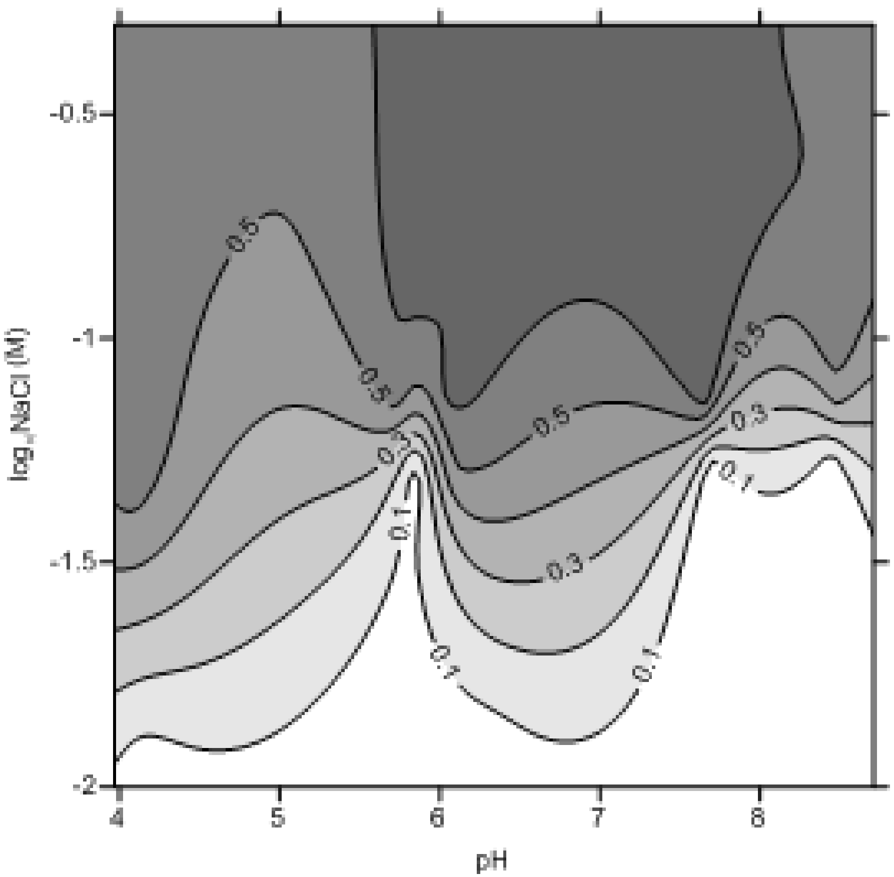
Addition of the SRNOM did not reduce coagulation rate for C11 30. The regression of the coagulation constant did not exist for the C11 30.

Diegoli et al., Sci. tot. Env. 2008

Multi-parameter effects



Monovalent cation electrolytes vs pH



- Citrate particles
- MUDA particles
- pH
- With and without NOM
- Na salts
- Ca salts
- Mg salts

Main messages

- Important drivers of aggregation vs stability
  - Particle number concentration
  - pH
  - NOM
  - Divalent cations
- Behaviour makes sense
- Ultimately need a model covering particle properties and important environmental parameters

Uptake NPs into organisms

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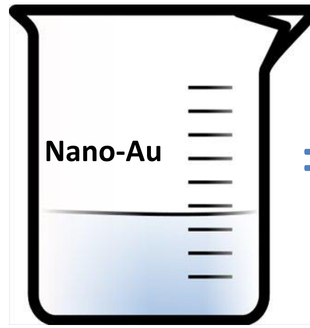

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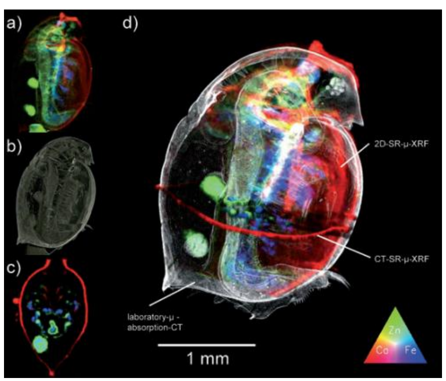
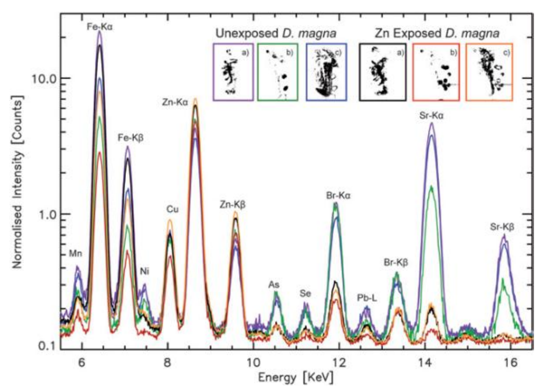
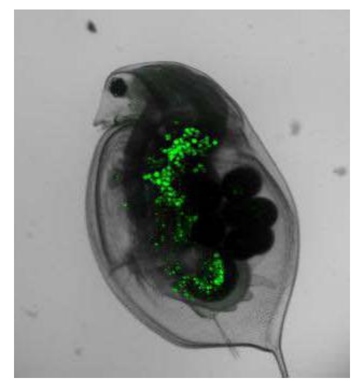
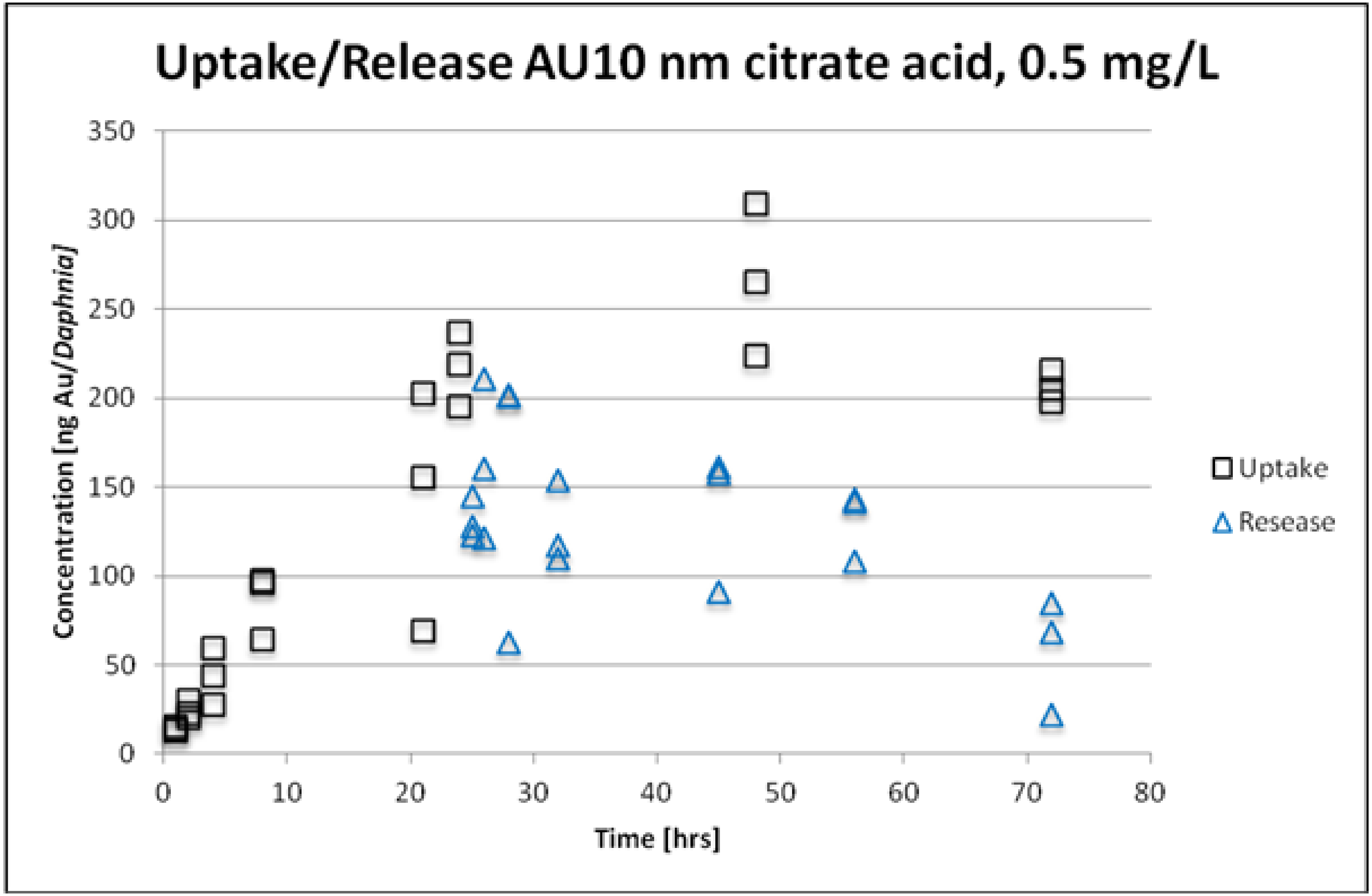
X-ray Synchrotron **ICP-MS** **TEM/SEM/WetSEM**







Uptake into *Daphnia*

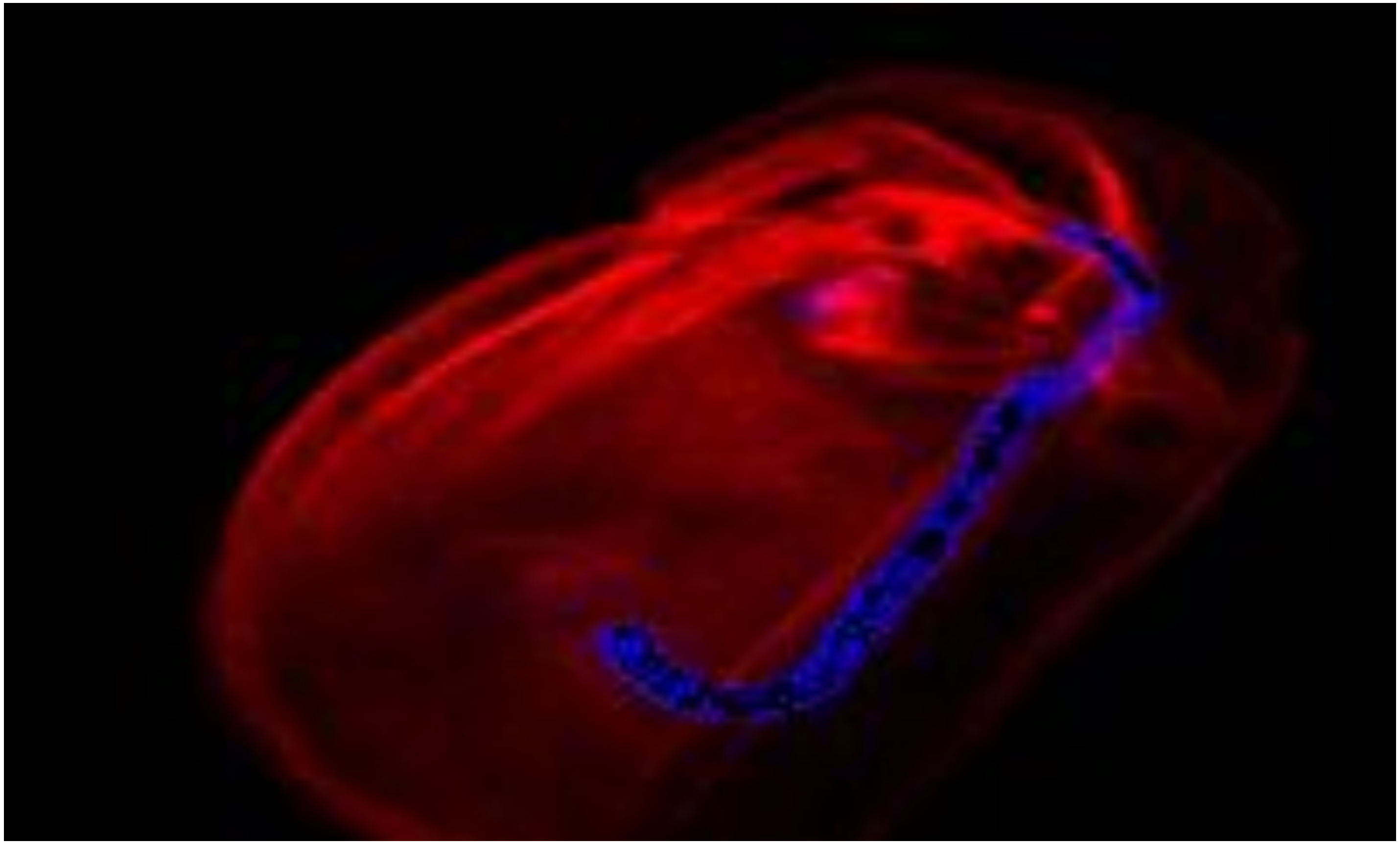


BCF values

Test ID	Rate of Uptake [h^{-1}]	Rate of Release [h^{-1}]	BCF [l/kg]
10 MUDA	1.69	0.01	130
30 MUDA	0.49	0.03	19
10 CITRATE	1.14	1.56	0.7

Where are the particles?

Synchotron X-ray fluorescence characterisation



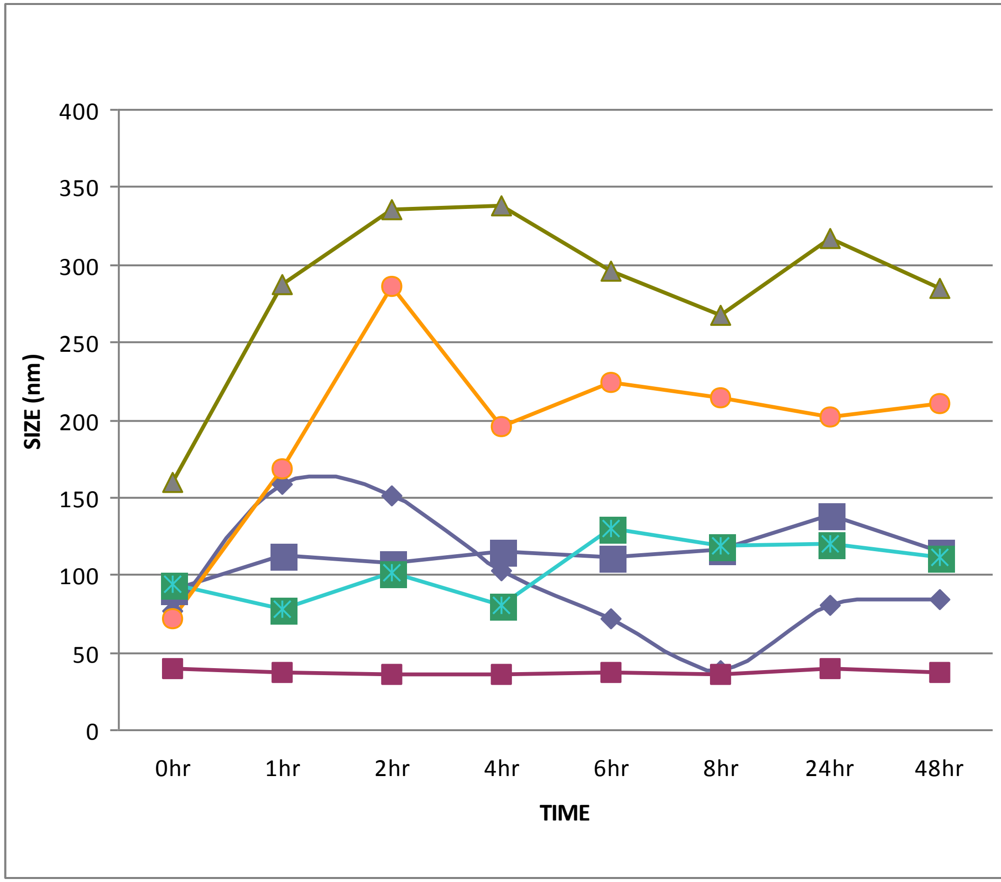
- TEM and SEM characterisation indicated no internalisation

Uptake conclusions

- Size and surface effects seen
  - 10 nm > 30 nm
  - MUDA > Citrate
- BCFs low so particles would not be an issue in current risk and hazard assessment schemes (low uptake also seen in Lumbriculus)
- ENPs appear to accumulate in the gut
- Can we rule out greater uptake in natural systems?

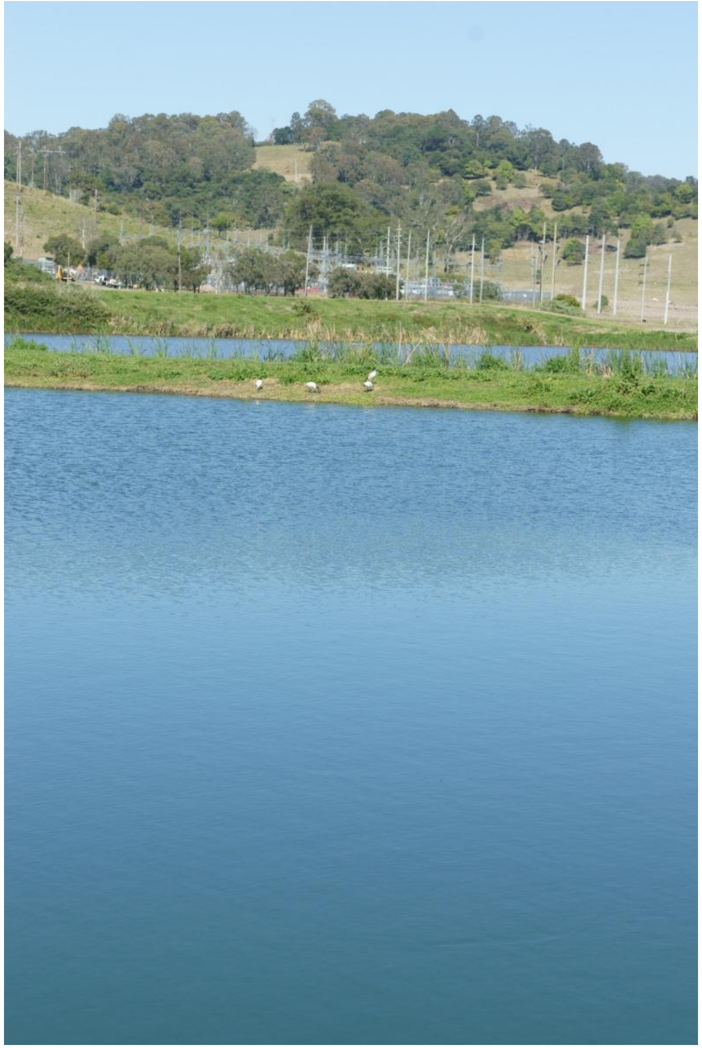
Understanding behaviour in ecotoxicity media

- Short (1 h) and long-term (48 – 96 h) kinetic studies
- Wide range of standard media
  - marine, freshwater
  - Algae, invertebrates, macrophytes, fish
- With and without test species
- 30 nm Citrate data presented



Test media	Media only (nm)	With organisms (nm)
DI water		-
APW		
M4 media		
Algae media		-
Lemna media		
ASW		-
HW		-
SW		-

Do these tests mimic natural systems?



- 23 water samples from N.E England
- Range in pH (3 – 7)
- Fully characterised
  - Cations
  - Anions
  - DOC
  - pH
- Kinetic studies

Behaviour in natural waters

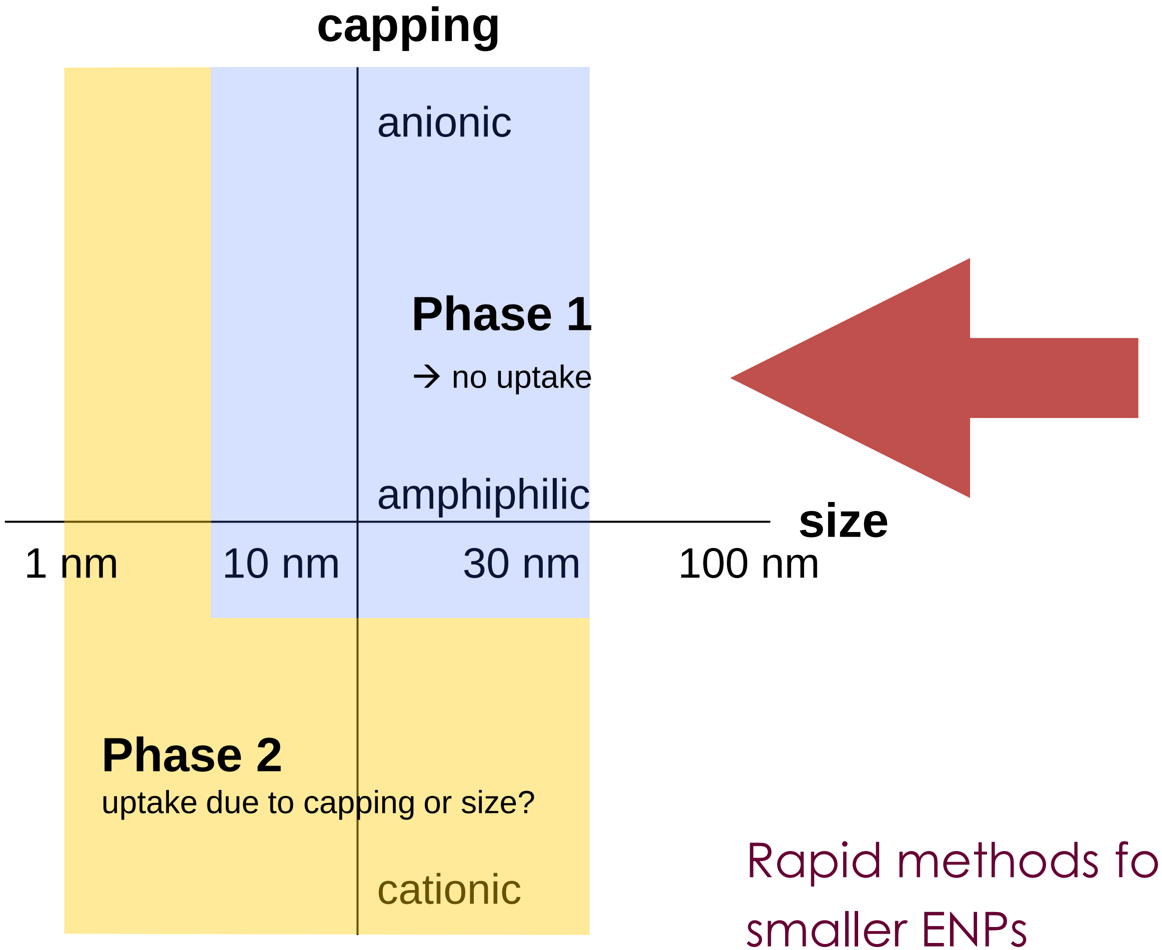
Natural water		
'pH3' (n = 6)		
'pH4' (n = 6)		
'pH6' (n = 4)		
'pH7' (n = 7)		

Speciation in laboratory studies shows limited relationship to natural systems

Implications for environmental risk assessment

ERA component	Adaptations
Fate assessment	Aggregation must be considered New speciation models
Bioconcentration/accumulation assessment	May need to rethink test matrices Need to consider where the particles go
Effects assessment	Test endpoints appropriate Need to rethink test matrices

Next steps



Environmental conditions

Rapid methods for characterising smaller ENPs

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