Use of iron nanoparticles in soil and groundwater remediation

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A Risk/Benefit Approach to the Application of Iron Nanoparticles for the Remediation of Contaminated Sites in the Environment

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Defra Research Project Final Report

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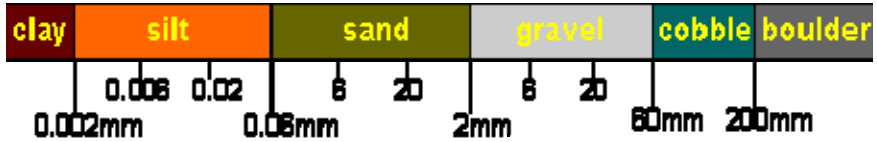
What are nano particles (NP)?

- Micro particles 1um = 10^{-6} m
- Nano particles 1nm = 10^{-9} m

- Sand 0.06 – 2mm = ca 1mm = 10^{-3} m
- Silt 0.002 – 0.006mm = ca 10^{-6} m
- Clay <0.002 mm = < 10^{-6} m



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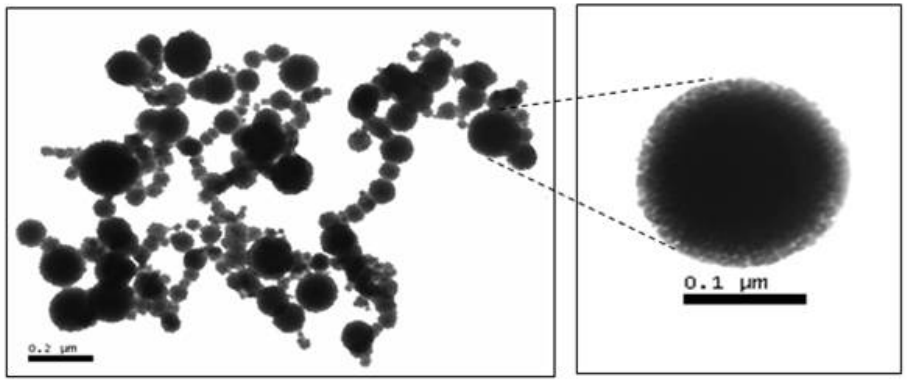
- Manufactured NPs 60-100 nm



Why are NPs a hot topic?

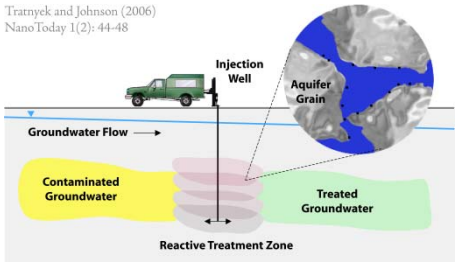
- Potential efficiency improvement
- Claims of step change – complex organics *???*
- Contested properties
- High uncertainty
- Precautionary principle
- Public fear of new technologies
  - genetically modified organisms (GMO);
  - nuclear magnetic resonance, NMR
    (aka Magnetic Resonance Imaging, MRI)

Where and how is ZVI being used?

Granular ZVI

- Iron (Fe0):
  - Zero valent iron (ZVI)
  - dechlorinates chlorinated solvents such as PCE & TCE
  - Used in reaction chambers and

injected to form permeable reactive barriers (PRB)



Where and how are NP being used

- Instead of ZVI use nZVI (nano zero valent iron)
- Field scale applications
  - USA, Canada
  - Germany, Spain (research)
- Research interest
  - FP7-NMP-2012-LARGE-6

Treatable contaminants (based on field scale applications)

Table 4 Treatable Contaminants and Matrices for Zero-Valent Iron NPs based on Field Scale Applications.

APPLICABLE Contaminants and materials – *Outcome: destruction or stabilisation*								
Organic	Halogenated volatile	✓✓	Organic	PCBs	✓	Inorganic	Cyanides	?
	Halogenated semivolatile	✓✓		Pesticides/herbicides	?		Corrosives	?
	Non-halogenated volatile	?		Dioxins/furans	?			
	Non-halogenated semivolatile	?	Inorganic	Volatile metals	?	Misc	Asbestos	*x*
	Organic corrosives	?		Non-volatile metals	✓		Oxidisers	✓
	Organic cyanides	?		Radionuclides	?		Reducers	?

Gravel – >2mm	Sand – 0.06 to 2mm	Silt – 2 – 60µm	Clay – < 2µm	Peat
✓✓	✓✓	?	?	?

Key: ✓✓ Usually applicable; ✓ Likely applicable; ? May be applicable; *x* not treatable; *x x* may worsen situation.

Notes

PRB configurations, or possibly introduction in fracture zones may be applicable for low permeability aquifers

Laboratory based studies indicate that potentially the range of contaminant types is wider than currently achieved in the field (see Table 5)

Bardos et al. 2011, p 20

Why are NPs NOT being used?

DoD News Briefing - Secretary Rumsfeld and Gen. Myers 12 February 2002

- Known knowns
  - things we know that we know.
- Known unknowns
  - That is to say there are things that we now know we don't know.
- unknown unknowns.
  - There are things we do not know we don't know
- Unknown knowns
  - Things that we don’t know but someone else does

Why are NPs NOT being used?

- Epistemic uncertainty
  (poor knowledge)
  - Reliability of information
  - Scarcity of information
  - Conflicting information
  - Uneven distribution of information
- Aleatory uncertainty
  (natural random variation)
  - Formation penetration
  - Durability
  - Reactivity

Precautionary principle

- free release of nanomaterials for environmental applications, such as **remediation of groundwater**, be prohibited until appropriate research has been undertaken to demonstrate that the benefits outweigh the potential risks

  Royal Society and Royal Academy of Engineering (2004)

“UK Nanotechnologies Strategy”
(HM Government 2010)

- recognised the role of government in encouraging a “cohesive and flourishing industry” while
- “also acknowledging and addressing the implications for health, safety and the environment”.

Caught between a rock and hard place

Why are NPs NOT being used?

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  (poor knowledge)
  - Reliability of information
  - Scarcity of information
  - Conflicting information
  - Uneven distribution of information
- Aleatory uncertainty
  (natural random variation)
  - Formation penetration
  - Durability/ aggregation
  - Reactivity

Reduced effectiveness

- Aggregation
  - NPs ‘clump’ together to form larger, micro-scale particles,
  - which in almost all cases reduces their mobility in water and their effective surface area
- Passivation
  - oxidation of iron NPs before reaching the contaminants they are intended to react with, through reaction with water, groundwater constituents such as nitrate and dissolved organic matter and the subsurface matrix
  - Micro organism mediated *abiotic redox processes ???*

NB field evidence is tending to show an overall synergistic effect between injected nZVI and the microbial consortia responsible for anaerobic biodegradation. (Elliott 2010)

NOT all Nano ZVI particles are equal

- Uncoated
- Coated
  - biodegradable organic and inorganic stabilizer to aid dispersion.
  - non-crystalline carbon layer of approximately 2.5 nm; ‘air stable’
  - *Noble metal (palladium, silver, copper) to aid stability/ hinder aggregation*

Coated and uncoated ZVI NPs have different properties;
Coated nZVI toxicity is significantly different and probably greater than uncoated nZVI

Risk assessment

- Source – pathway – receptor
- Function of
  - Fate: will the substance survive in the environment
  - Transport: will the substance be able to reach the receptor
  - Toxicity: how will the substance harm the receptor

Fate

will the substance survive in the environment

- Aggregation
- Dissolved oxygen rapidly oxidises SVI
- Rapid reaction in sub surface to form hydroxides
- nano particles larger than 30nm essentially behaved and should be regulated as their bulk counterparts, while nano particles smaller than 30nm "*have a size-dependent crystallinity that gives them properties drastically different from the bulk material*". Auffan *et al.* (2009)
- Life span: 3 – 4 weeks, up to 6 months?
  NB Poor tracking technology

Transport/ mobility

will the substance be able to reach the receptor

- Can flow >20m in groundwater
- Aggregation is a limiting factor
- Mobility is enhanced at but reduces reactivity

Toxicity

how will the substance harm the receptor

- Macro scale Iron is not particularly toxic (cf SGV Taskforce)
- "*our knowledge of the potential environmental and health hazards posed by these nanomaterials is* [acknowledged to be] *in its infancy*". Karn *et al.* (2009)
- *"Toxicity, human hazard, and environmental fate and effects data available from potential suppliers are highly variable in both quality and completeness. In many cases, it is not clear from the information provided whether the EHS data is based on the nZVI or on larger sized simple iron powder."* Du Pont (2007)

Conclusions

- The jury is out!
- nZVI may offer efficiency improvements
- nZVI could offer step change in terms of substances treated
- BUT toxicity of especially coated forms is likely to be great
- Short life spans and limited penetration are constraints

Thank you!

- Questions?

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