Emerging Opportunities of Nanotechnology to Address Groundwater Remediation Challenges and Enhance Bioremediation

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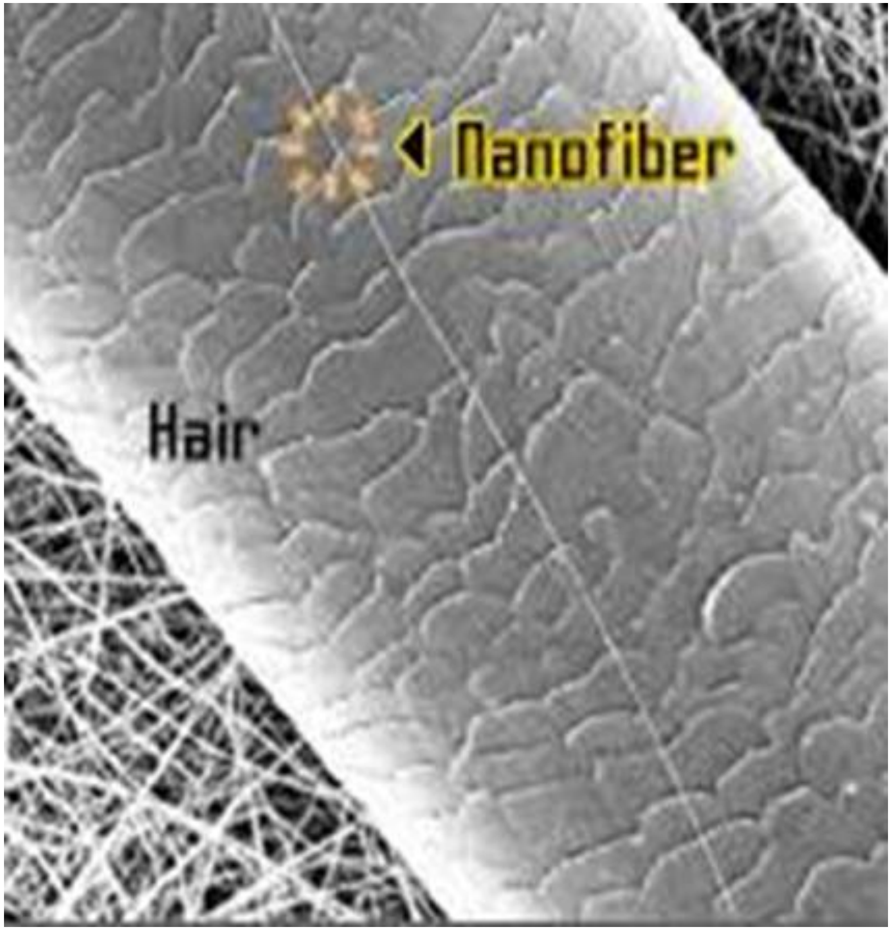
Nano = Dwarf (Greek) = 10^{-9}

"Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications."

-National Nanotechnology Initiative



Opportunities for Engineered Nanomaterials (ENMs) in Hazardous Waste Treatment
(mainly above-ground applications)

ENM Properties	***Examples of Enabled Technologies***
Large surface area to volume ratio	Superior sorbents (e.g., nanomagnetite or graphene oxides to remove heavy metals and radionuclides)
Enhanced catalytic properties	Hypercatalysts for advanced oxidation & reduction processes
Antimicrobial properties	Disinfection and biofouling/biocorrosion control without harmful byproducts
Multi-functionality (antibiotic, catalytic)	Fouling-resistant (self-cleaning & self-repairing) membranes that operate with less energy; trap & zap sorbents
High conductivity	Novel electrodes for selective electro-sorption and energy-efficient electrocatalytic treatment

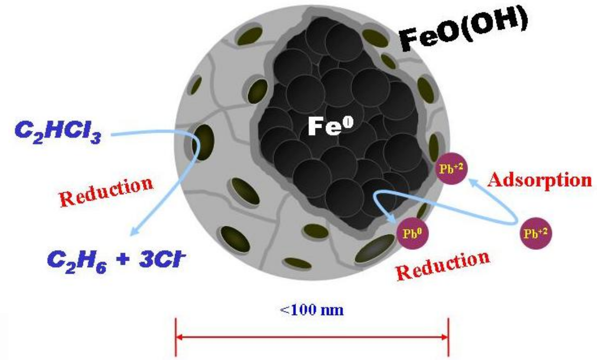
When Does Nano Make Sense?

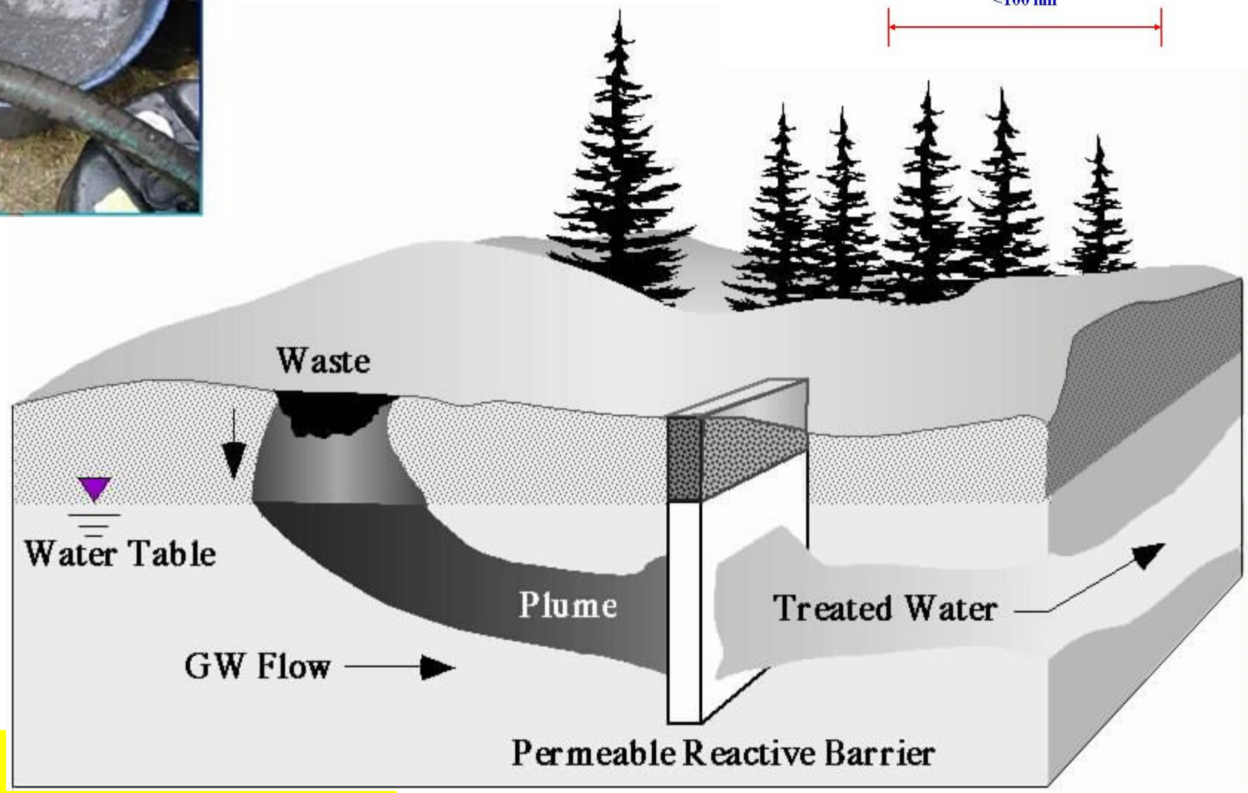
- Where current technologies **do not meet** current or upcoming **regulations**;
- When it **enhances cost-effectiveness** (e.g., faster, less energy, and less materials)
- When one needs easy-to-deploy modular systems with small footprint (remote locations?)

Opportunities in Remediation

- Degradation of recalcitrant compounds (when biodegradation alone is ineffective)
- Higher selectivity towards target contaminants to efficiently utilize the available treatment capacity
- Multifunctionality to address mixed contamination.
- Lower energy requirements for thermal treatment
- Improve source zone remediation (AOPs, ARPs)
- Improve monitoring of remediation progress.

Example 1. Nano-Scale Zerovalent Iron (NZVI)

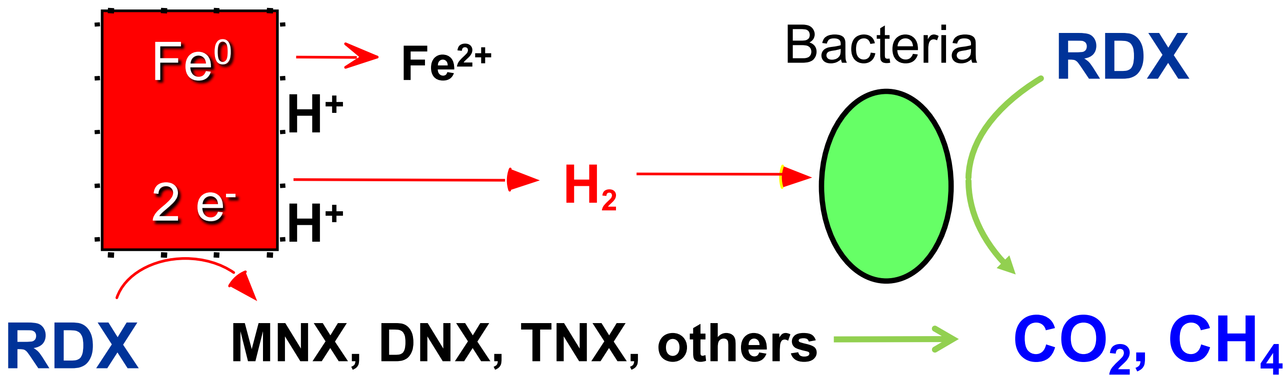




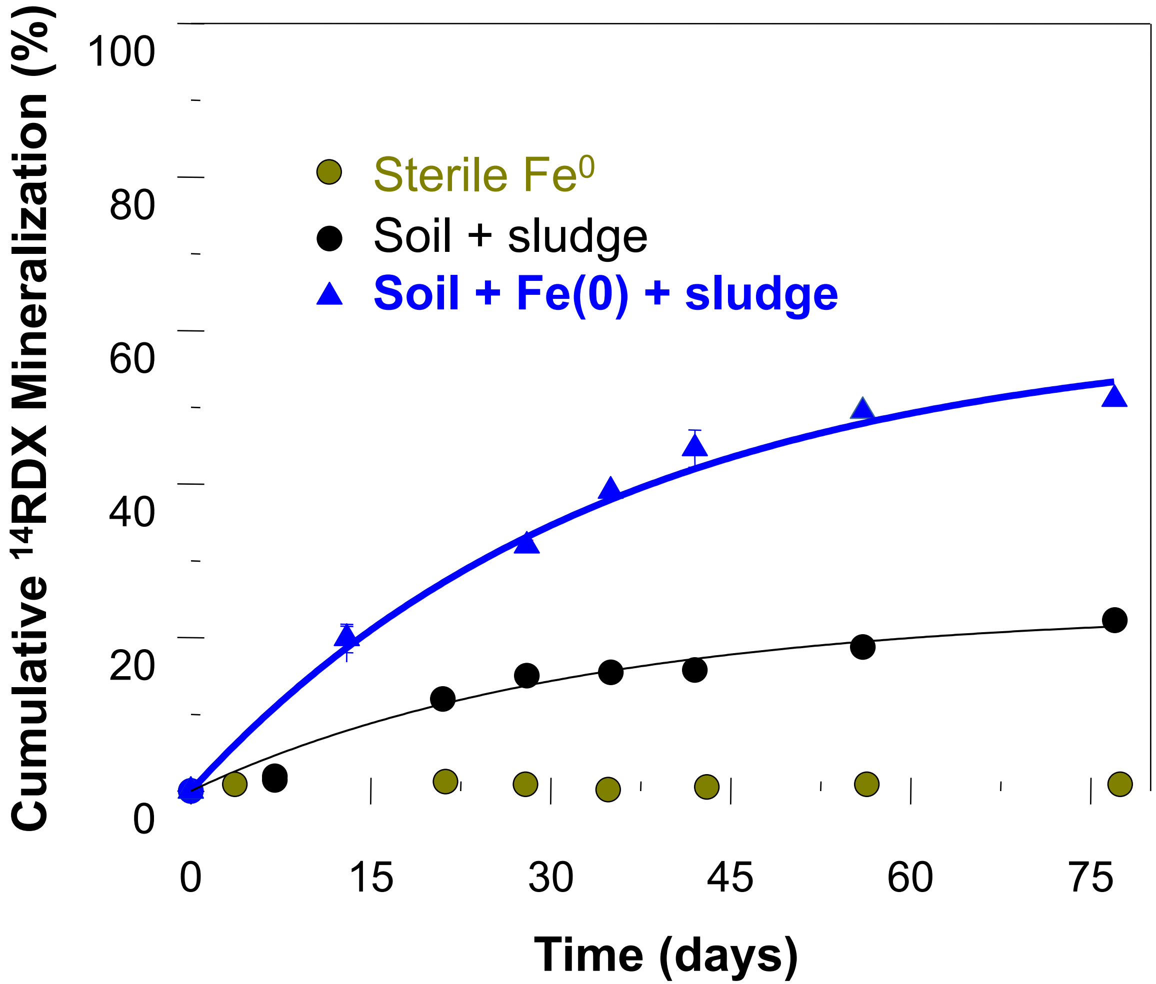
First used in 2000
70 full scale or pilot tests by 2013

Synergistic Biogeochemical Interactions

H_2 produced by iron corrosion stimulates RDX mineralization: $Fe^0 + 2H_2O \rightarrow Fe^{+2} + H_2 + 2OH^-$

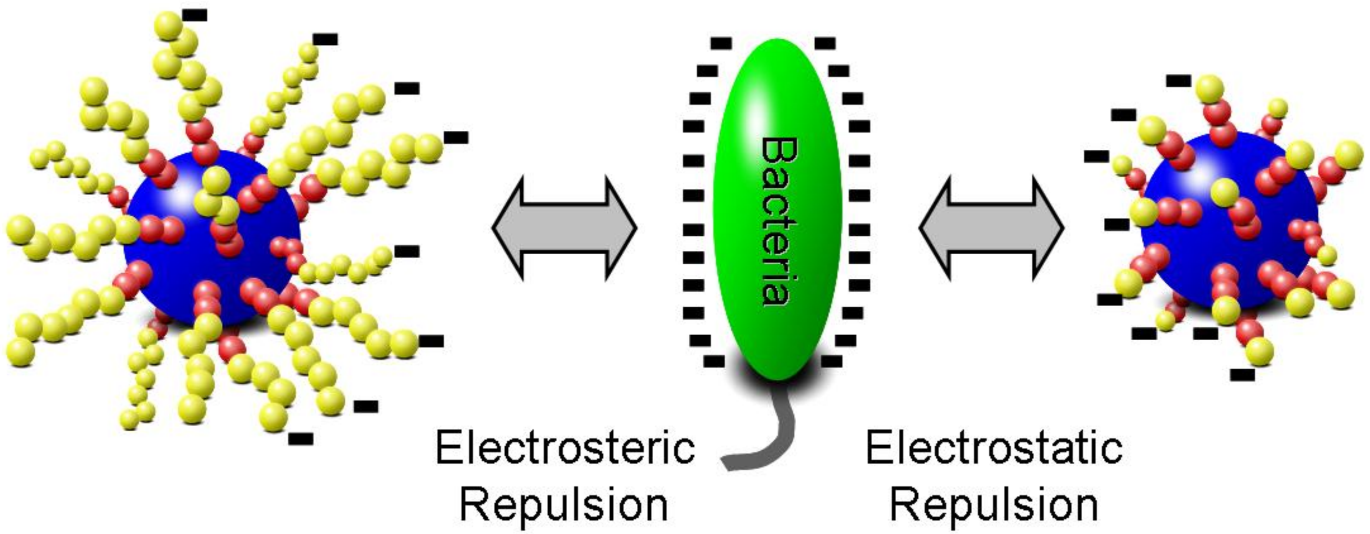


RDX Mineralization ($^{14}CO_2$) is mediated by bacteria, and Fe^0 has a stimulatory effect



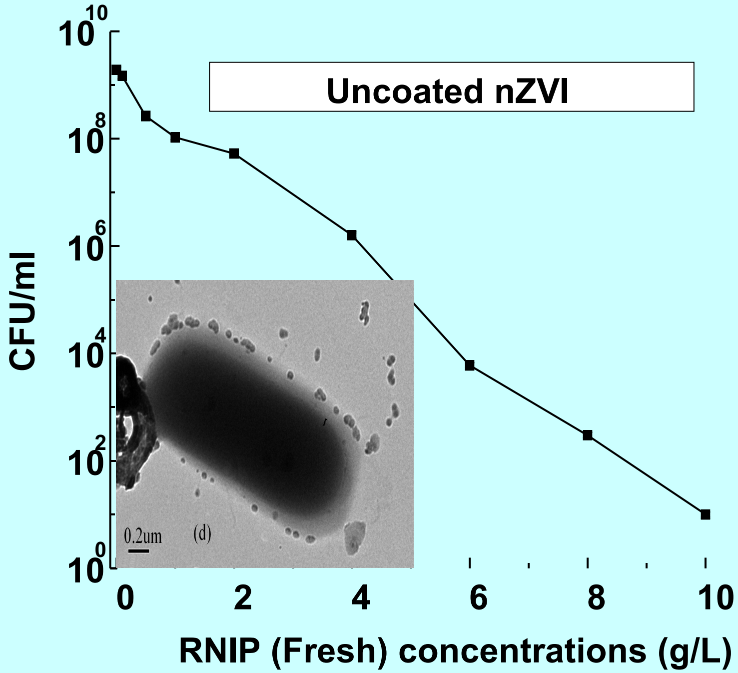
Oh, Just, and Alvarez (2001). *Environ. Sci. Technol.* 35(21):4341-4346

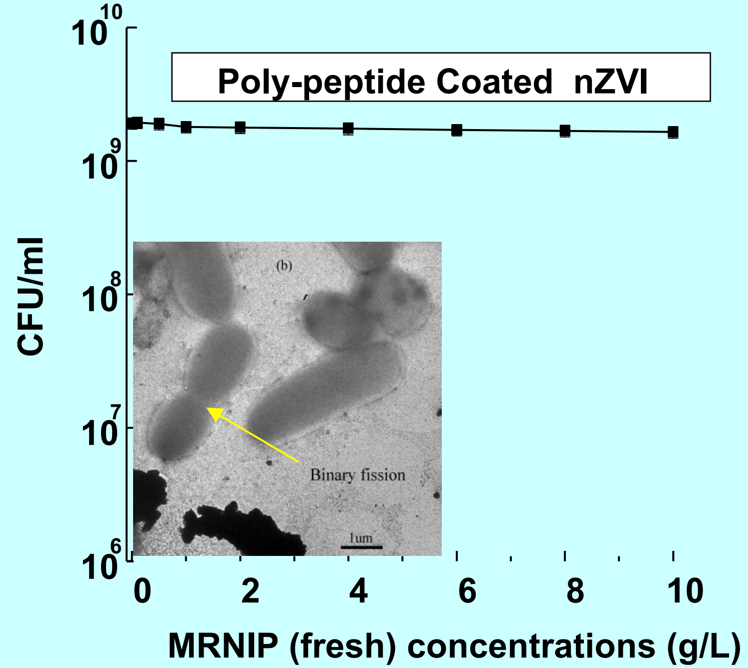
Polymer Coatings Mitigate NZVI Aggregation and Toxicity to Bacteria



Li Z., K. Greden, P.J.J. Alvarez, K.Gregory, and G.V. Lowry. Environ. Sci. Technol. 44 (9):3462–3467

Dose response of *E. coli* exposed to nZVI

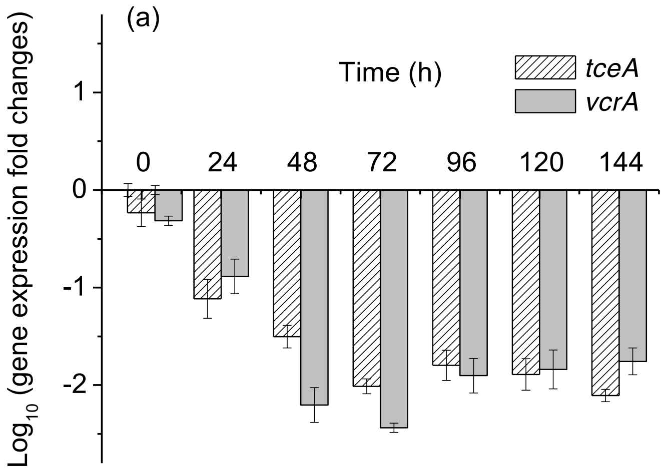




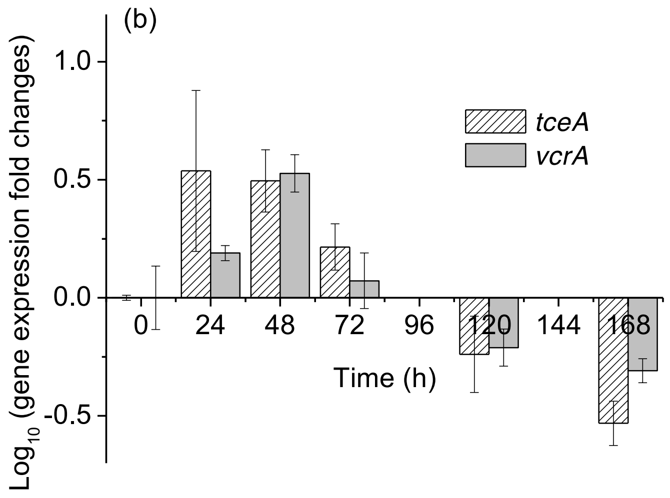
Xiu Z-M, Z-H Jin, T-L Li, S. Mahendra, G.V. Lowry, and P.J.J Alvarez. Bioresource Technology 101: 1141–1146

Coating the NZVI Enables Expression of Dehalogenase Genes as it Mitigates Toxicity *(Enables Microbial Reductive Dechlorination)*

Uncoated nZVI: downregulated

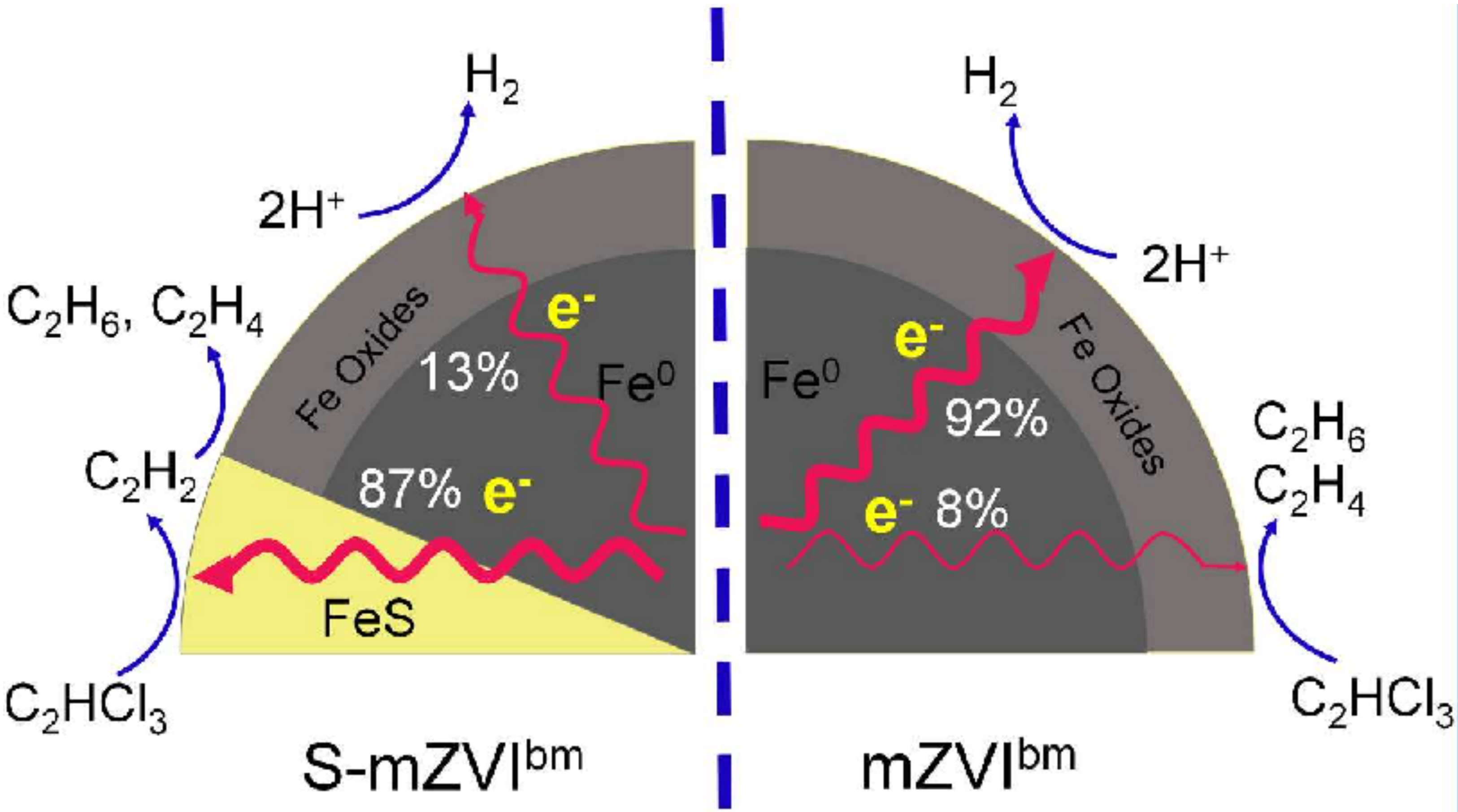


Poly-peptide Coated nZVI: upregulated



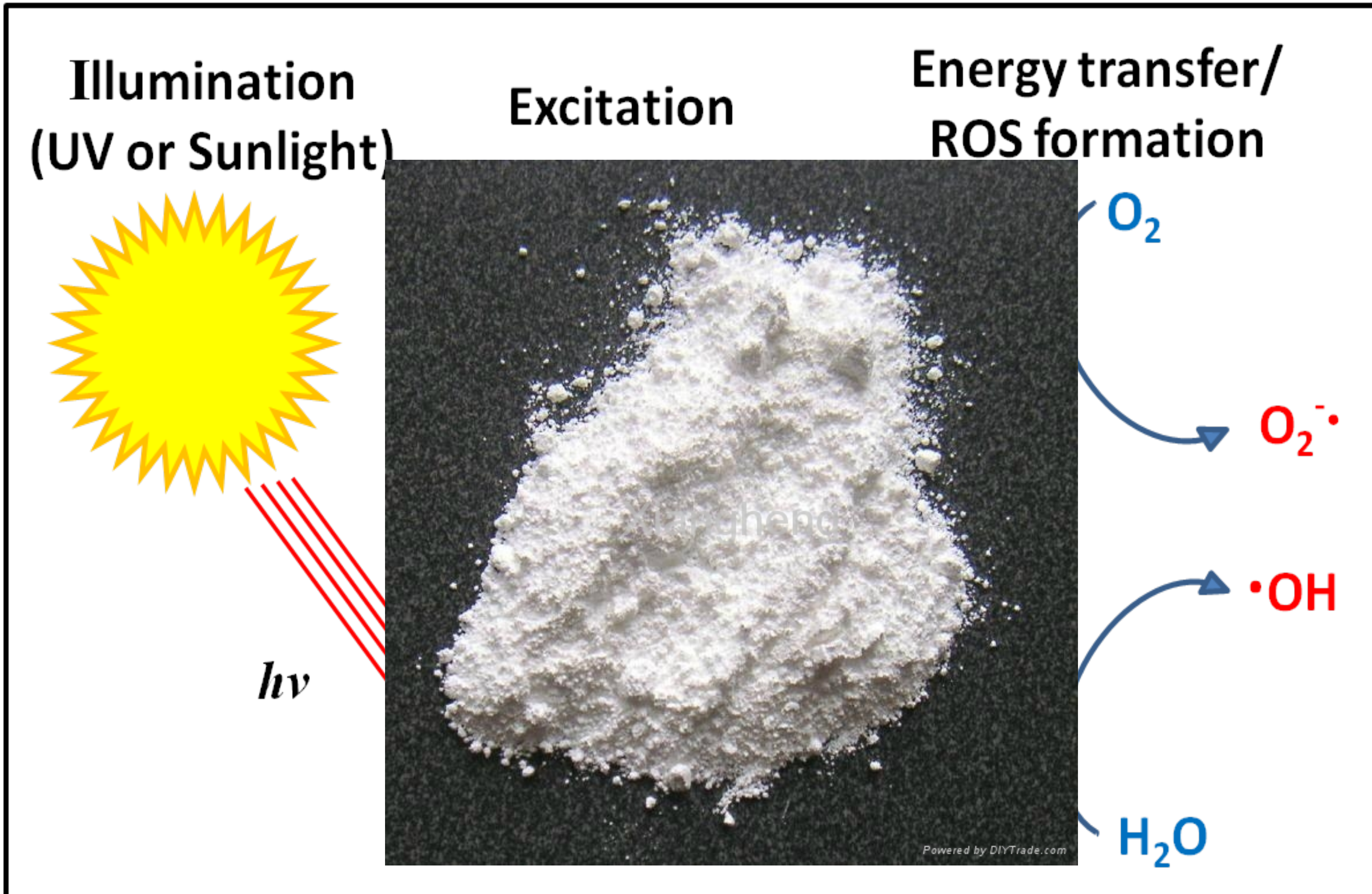
Xiu Z-M, K.B. Gregory, G.V. Lowry, and P.J.J. Alvarez. Environ. Sci. Technol. 44: 7647–7651

Sulfidation overcomes preferential reaction of nZVI with Water

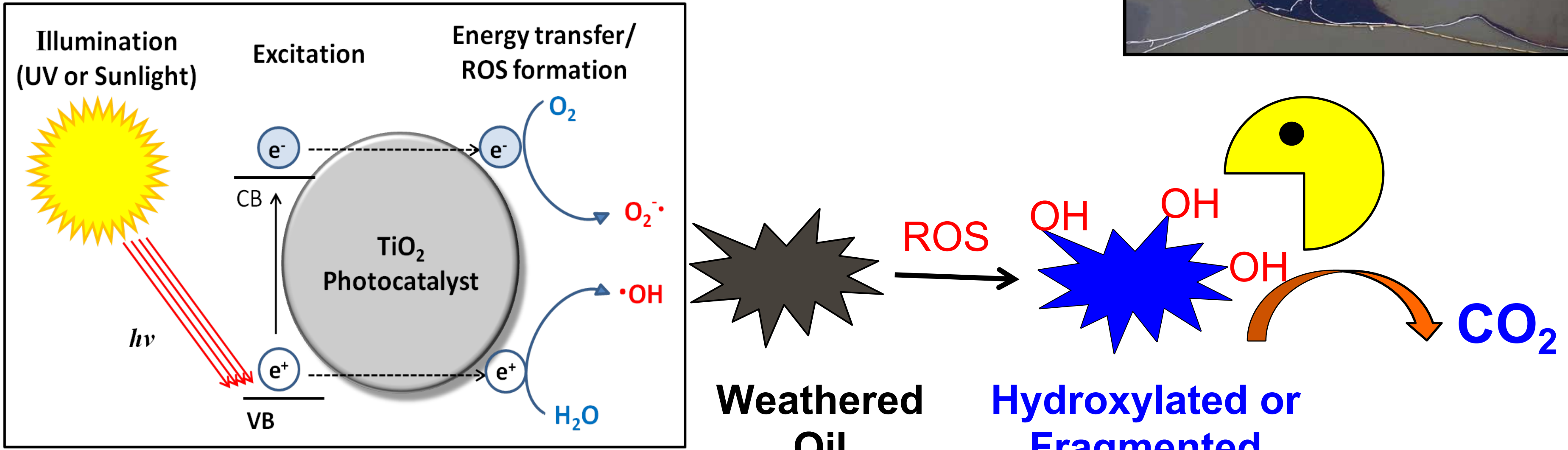


Gu. Wang and Tratnyek, ES&T 2017; DOI:10.1021/acs.est.7b03604

Example 2: Photocatalysis with $nTiO_2$



Photocatalytic Hydroxylation of Weathered Oil to Enhance Bioavailability and Bioremediation

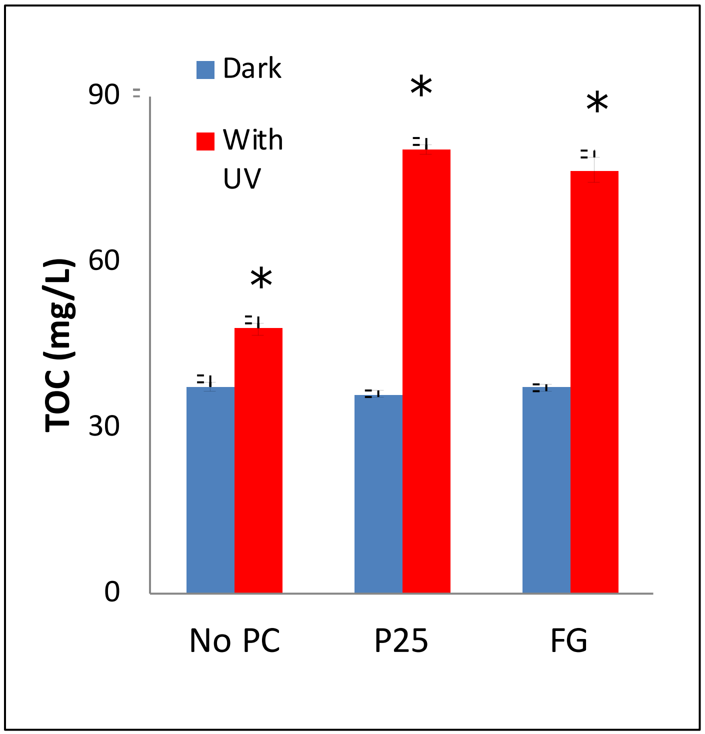


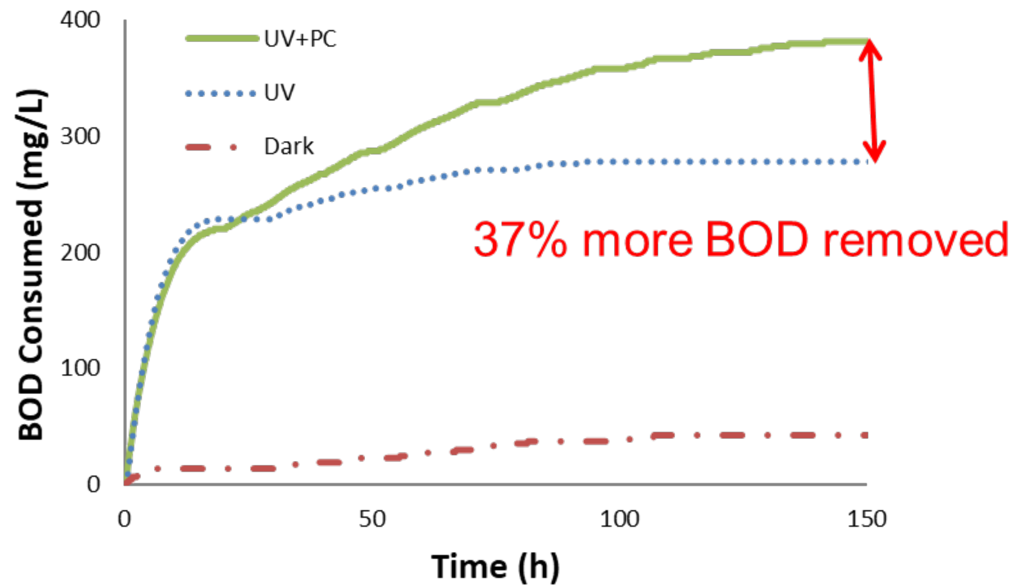
Photocatalyst

Weathered Oil (Recalcitrant)

Hydroxylated or Fragmented Residue (Bioavailable)

Photocatalysis Increased Solubilization and Biodegradation of Weathered Oil

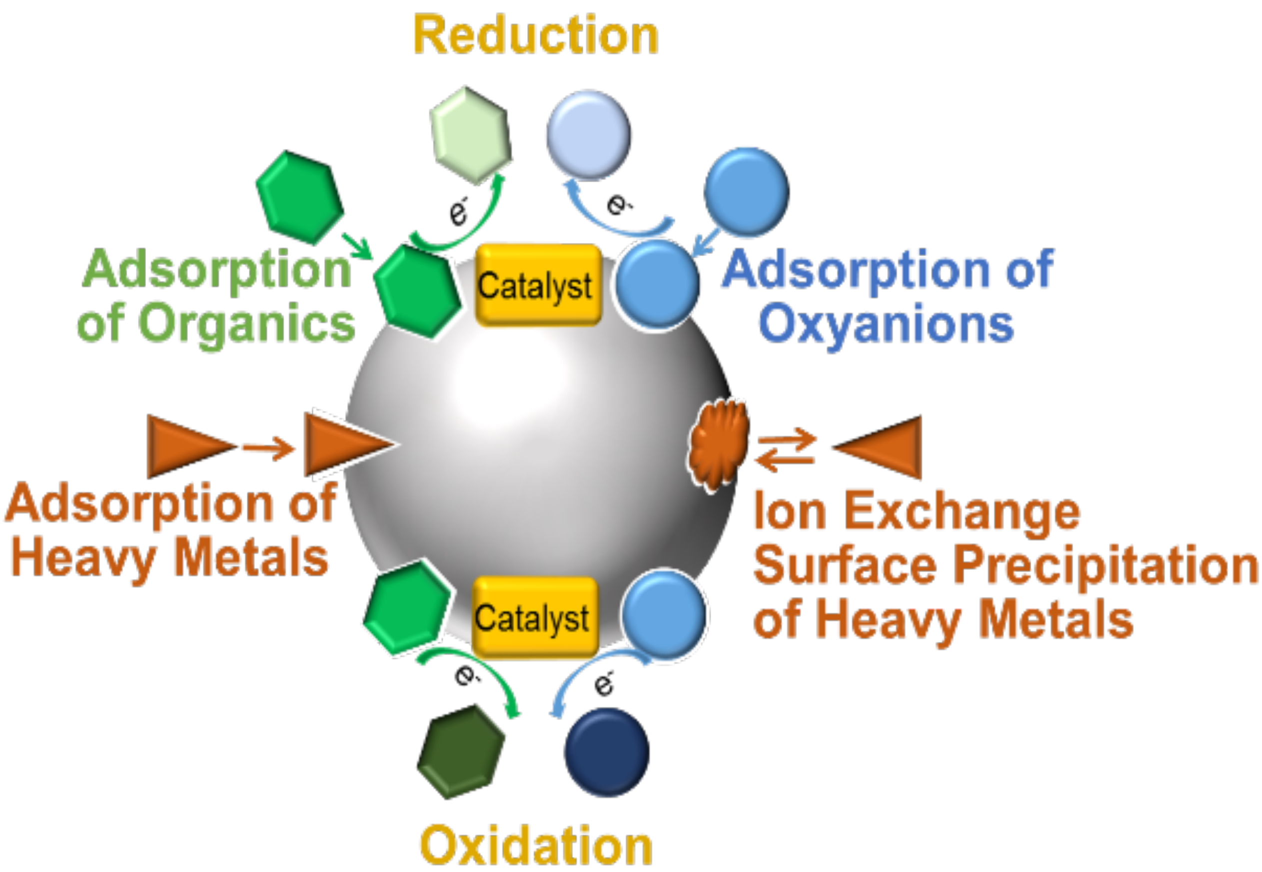




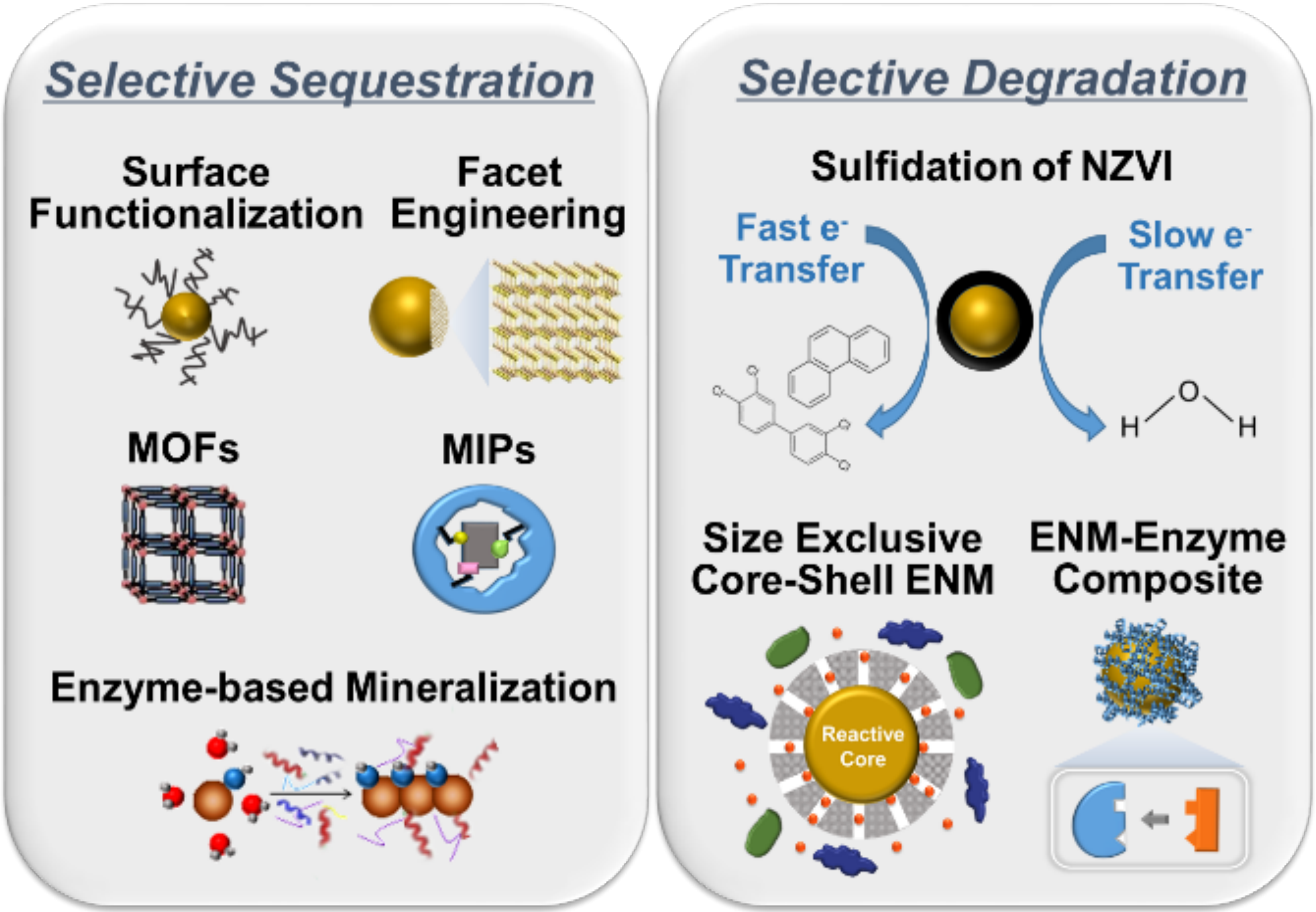
* statistically significant (*p* <0.05) after 1-day exposure

Brame J., S.W. Hong, J. Lee and P.J.J. Alvarez . *Chemosphere* 90: 2315–2319.

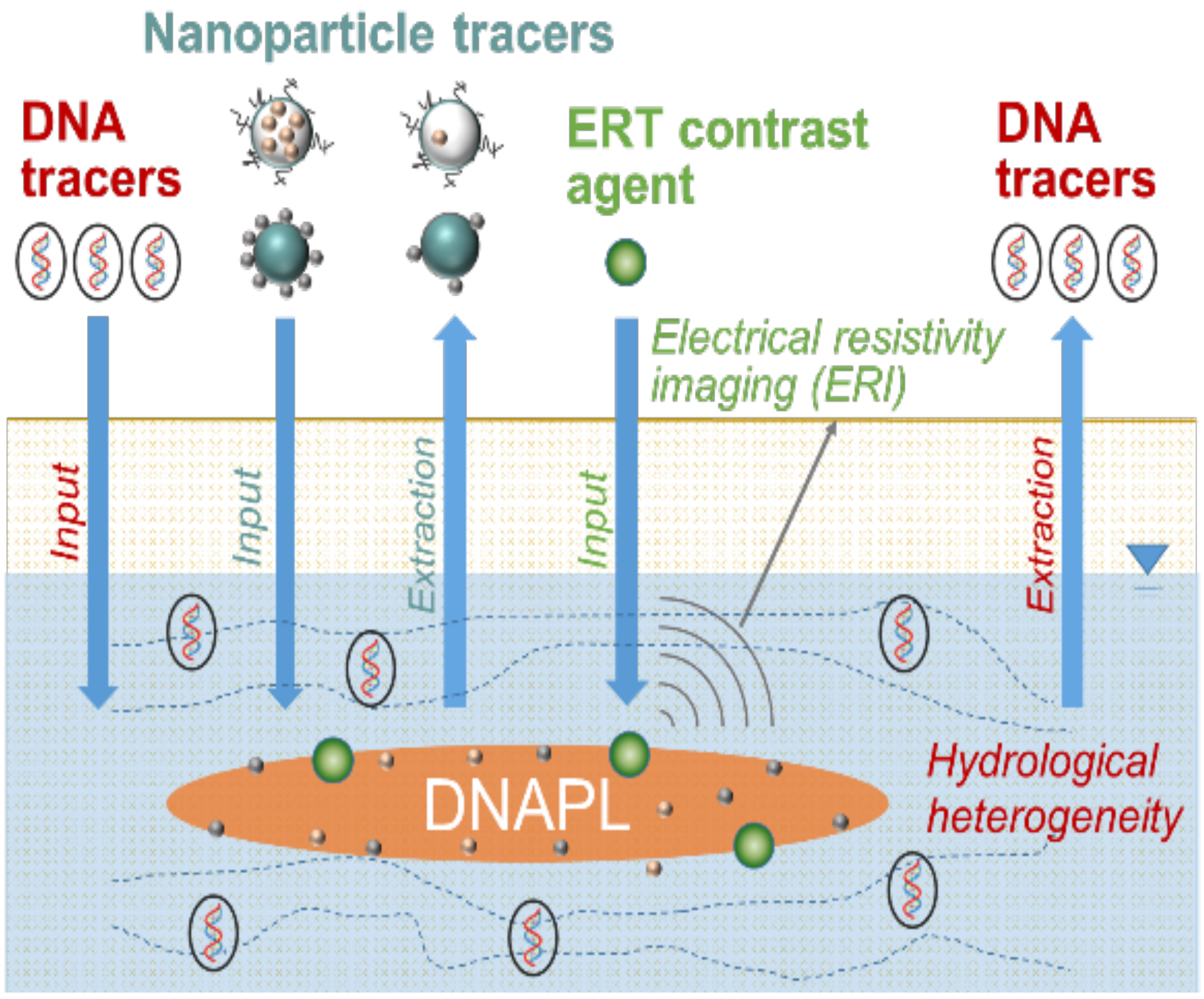
Looking Forward: ENMs with multifunctionality could target complex contaminant mixtures



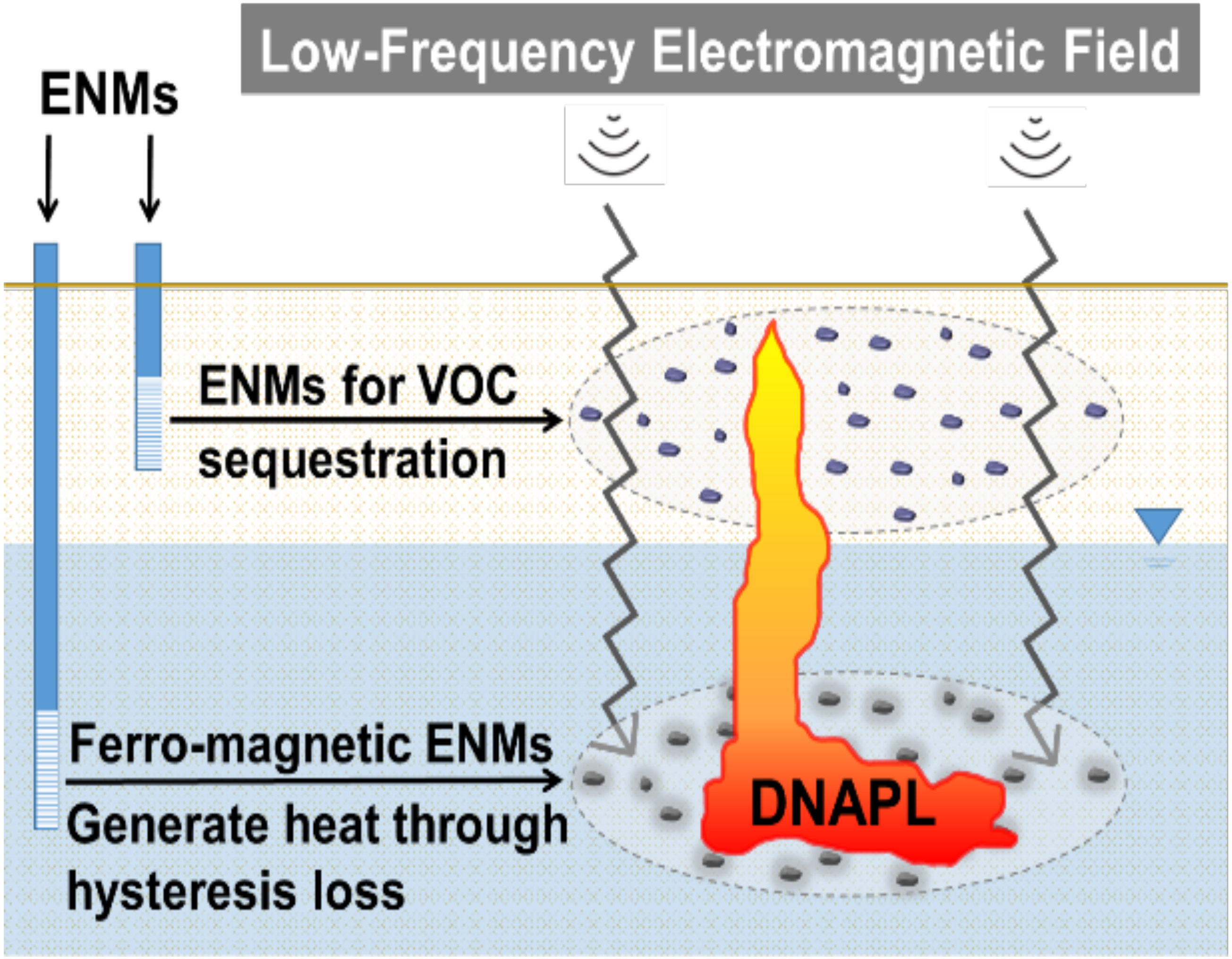
ENMs with high selectivity for contaminants could improve performance and reactive lifetime



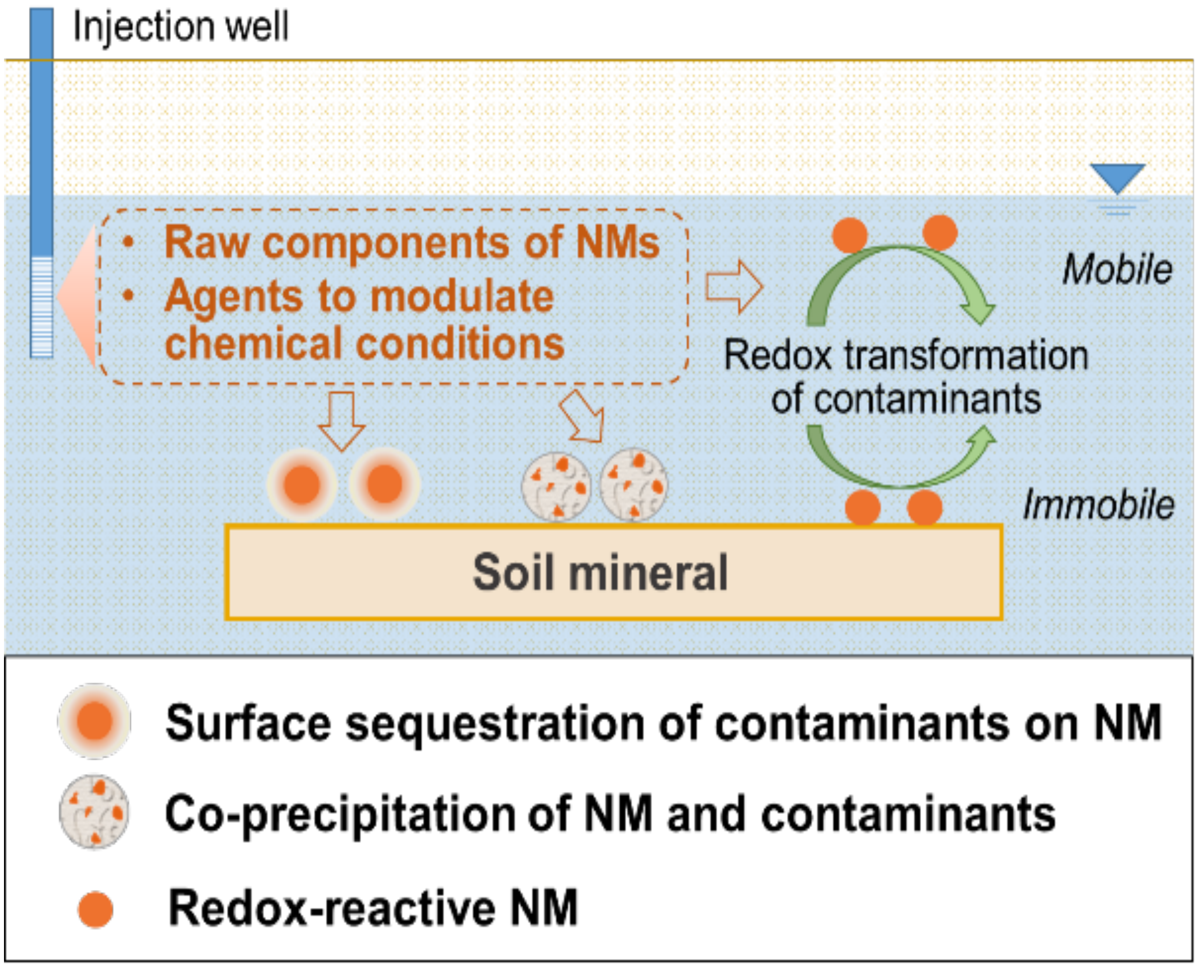
Nano-tracers to delineate distribution of contaminants in the subsurface



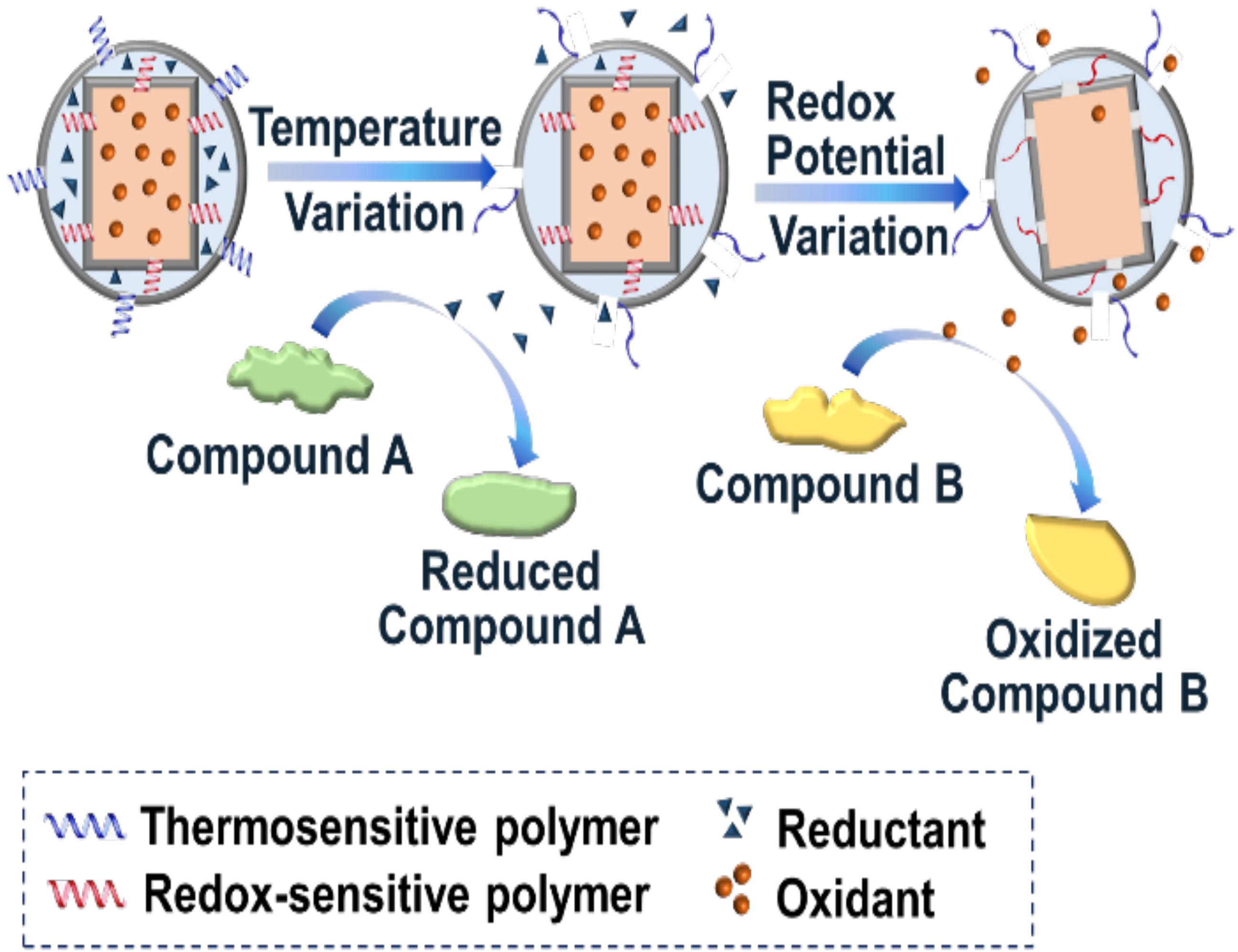
ENMs to enhance thermal treatment and decrease energy requirements?



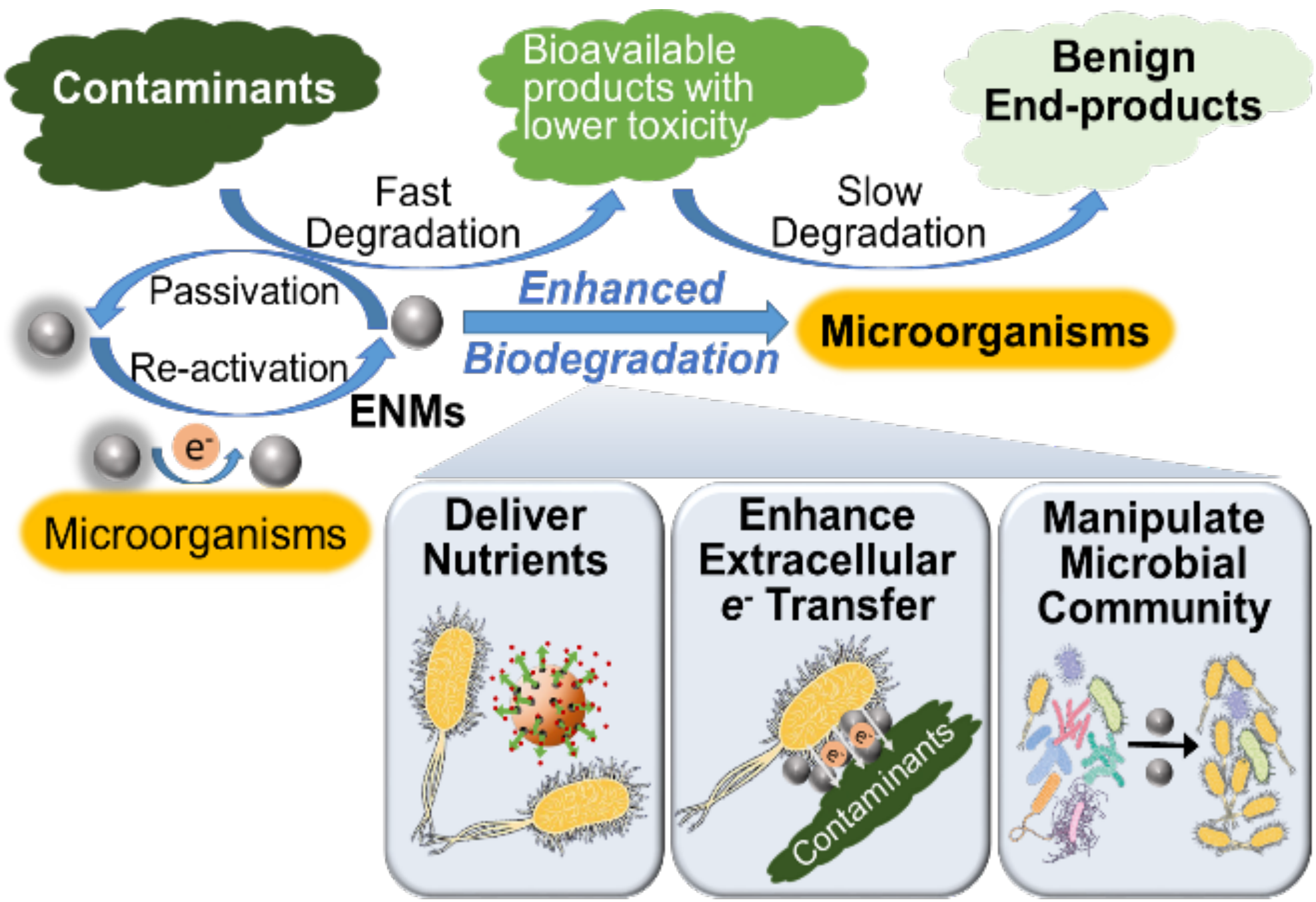
In situ generation of NMs to provide NMs in low-conductivity regions to sequester or degrade contaminants?



Stimuli-responsive ENM that release reactants/biostimulants only when needed

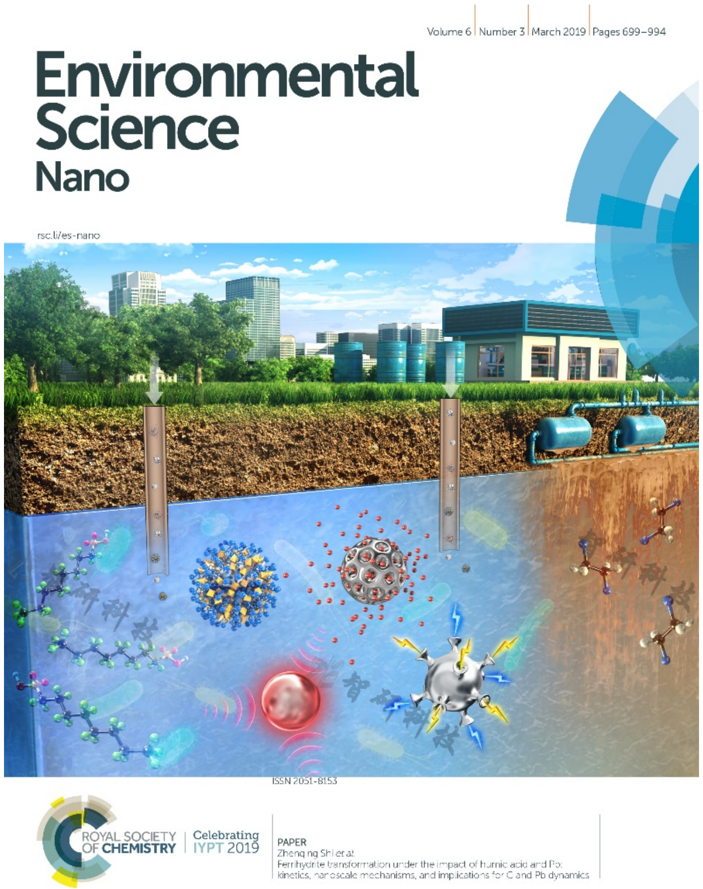


ENMs to enhance rates and performance of bioremediation



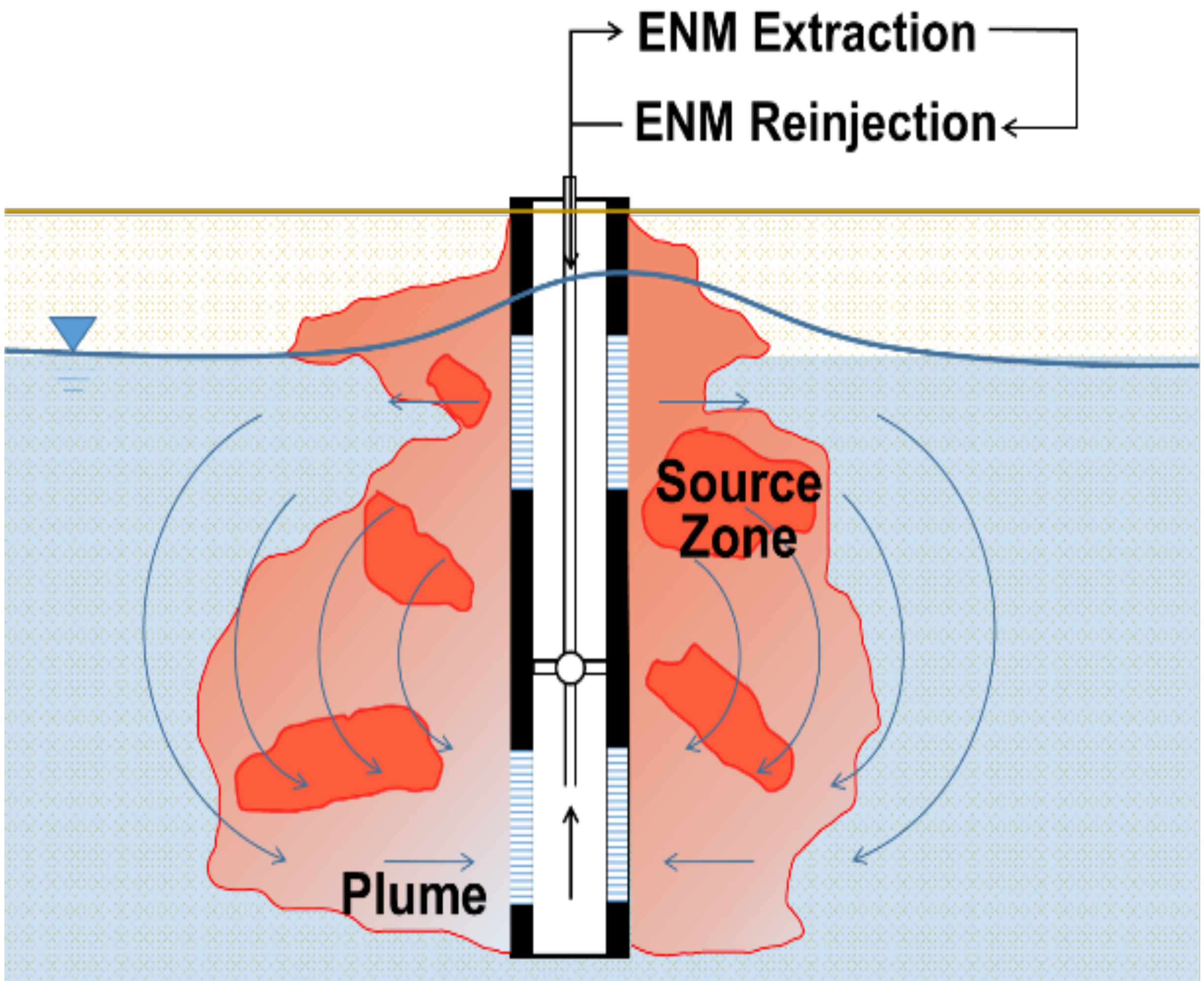
CONCLUSIONS

- Some ENMs offer high-performance remediation opportunities as hypercatalysts, oxidants, reductants, and improved separation processes.
- Mainly for above-ground treatment (higher selectivity, lower EEO) but also as pretreatment or biostimulants for enhanced *in situ* bioremediation
- Need pilot studies to delineate practical applicability and limitations

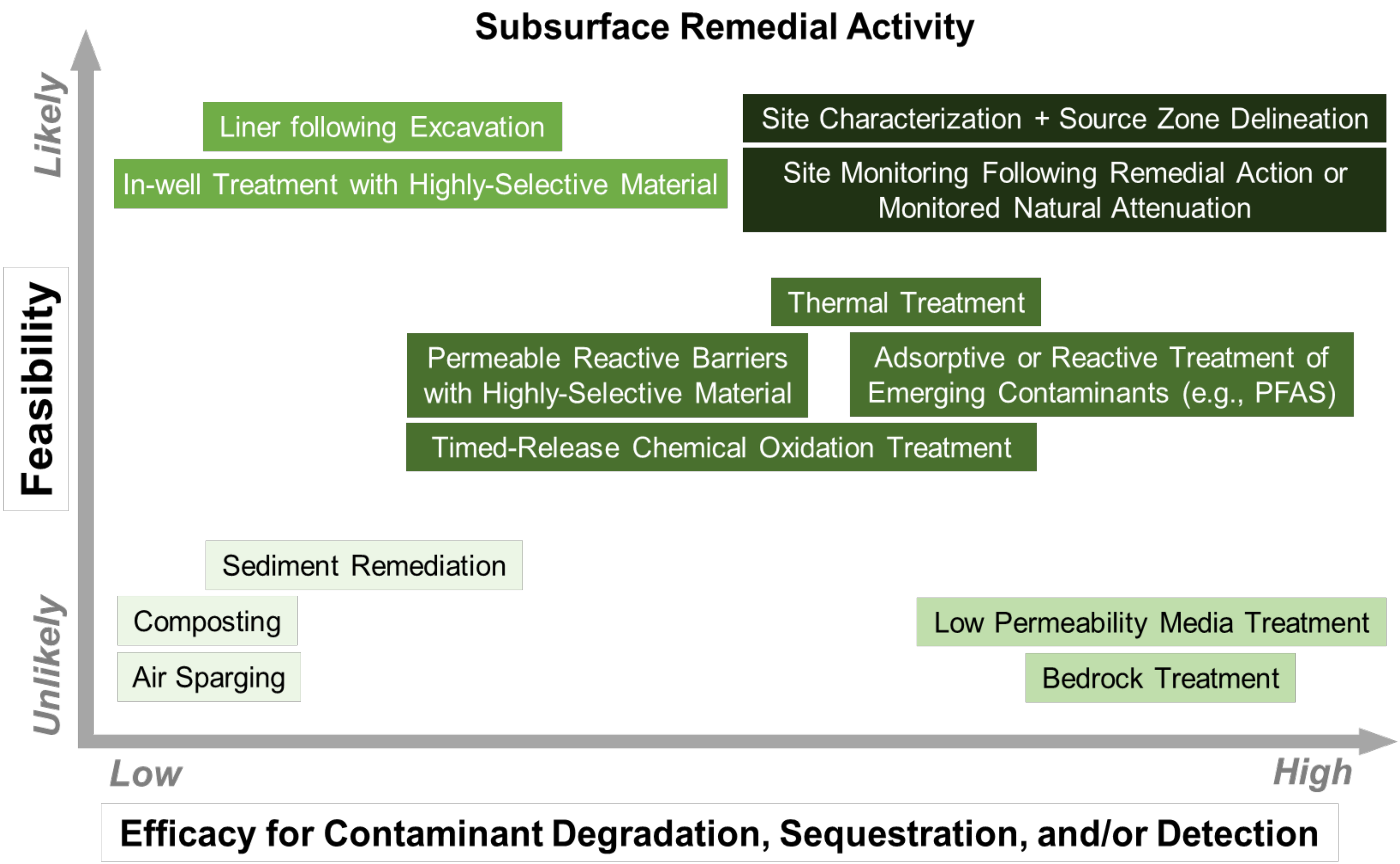


Backup Slides

Groundwater circulating wells to emplace ENMs over larger areas?



Feasibility of ENMs to improve specific remediation niches

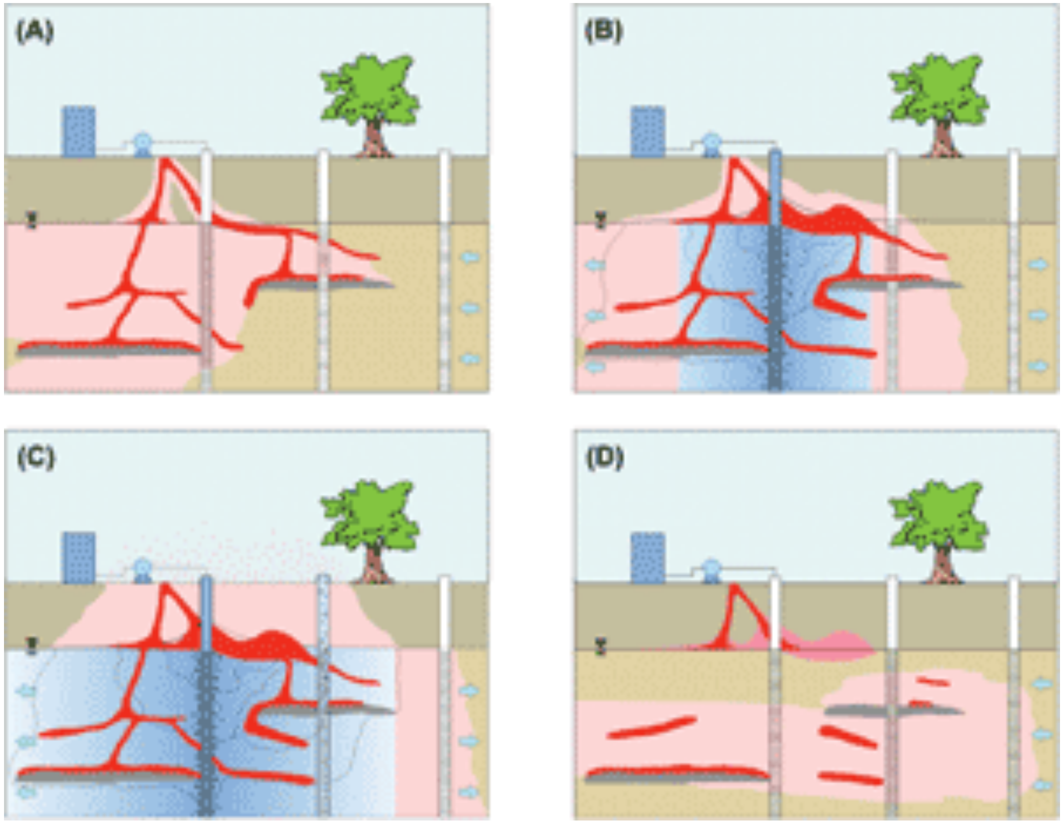


In Situ Chemical Oxidation Using NZVI (Fenton's Reaction)

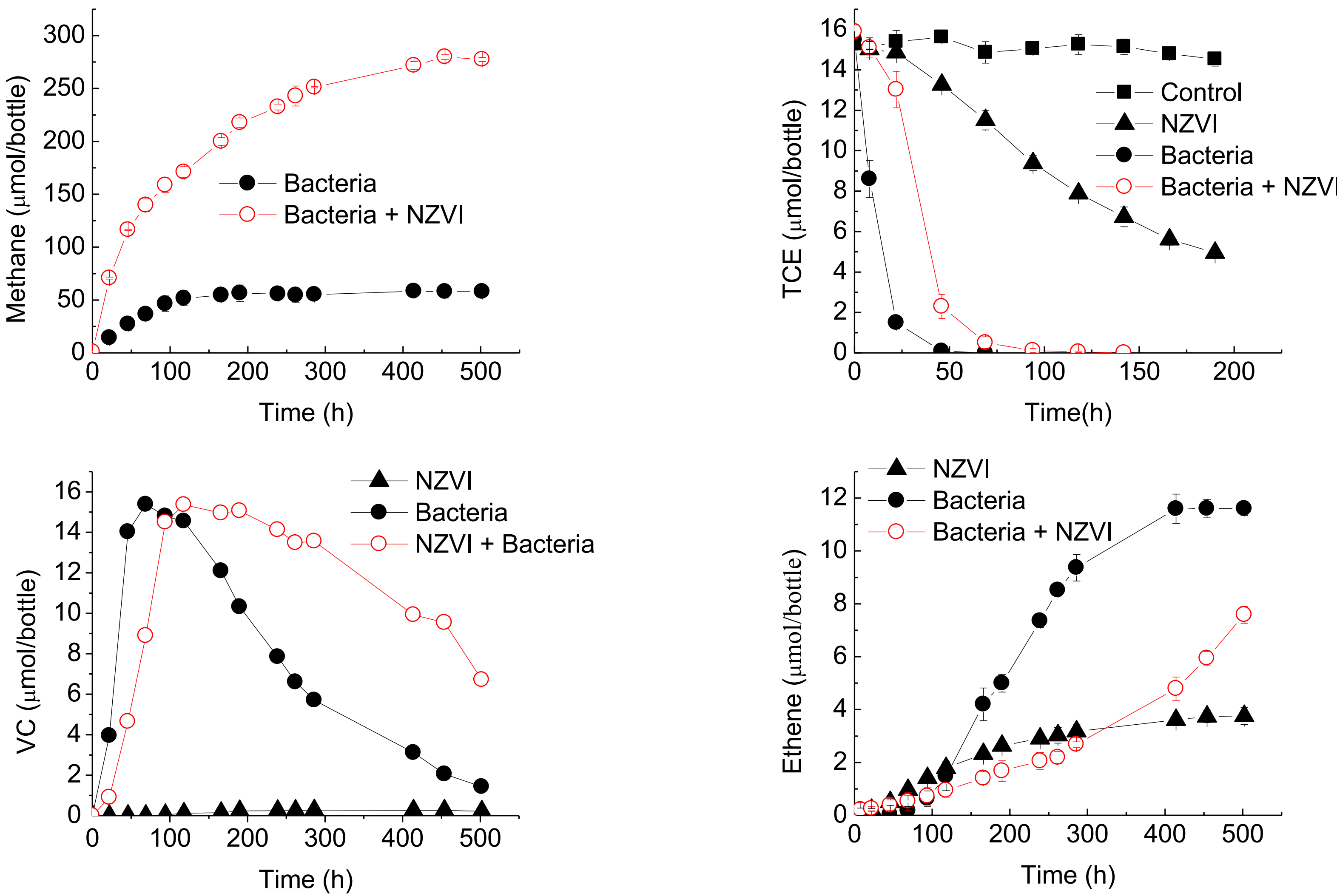
$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2$$

$$Fe^0 + H_2O_2 \rightarrow Fe^{2+} + 2\,OH^-$$

$$Fe(II) + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^-$$



NZVI (1g/L) Preferentially Biostimulated Methanogens, also Dechlorinators after Inhibitory Period



Xiu Z-M, Z-H Jin, T-L Li, S. Mahendra, G.V. Lowry, and P.J.J Alvarez (2010). Bioresource Technology 101: 1141–1146

Enhancing Land Farming ?

- Contaminated soil is spread as a thin layer (< 0.3 m) on a prepared surface
- Indigenous microorganisms (bacteria and fungi) remove hydrocarbons
- Bioremediation is stimulated by aeration and addition of nutrients and moisture.
- Can be slow (6-month cycles)
- ***TiO_2 pre-treatment could increases number of cycles per year per pit***

1 Spray dissolved TiO_2 photocatalyst

2 Bioremediation (Landfarming)

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Other Potential Applications (TRL 1-4)

- Nanoparticles that enhance in situ (microwave) heating to enable thermal desorption/smoldering
- Nano-sorbents that selectively bind priority pollutants (higher capacity, faster kinetics)
- Nano-catalysts for faster (pump and treat) advanced oxidation or reductive dehalogenation
- Porous nanocarriers with antimicrobial agents that minimize membrane biofouling

Oxidized GW Pollutants Degraded by NZVI

- Organics:
  - Chlorinated solvents (PCE, TCE)
  - Munitions Wastes (TNT, HMX, RDX)
  - PFCs
- Inorganics:
  - Nitrate
  - U(VI)
  - Cr(VI)

- The Dirty Dozen:
- Dioxins
  - Furans
  - PCBs
  - HCB
  - DDT
  - Chlordane
  - Toxaphene
  - Dieldrin
  - Aldrin
  - Endrin
  - Heptachlor
  - Mirex