Nanoiron in the Subsurface: How far will it go and how does it change?

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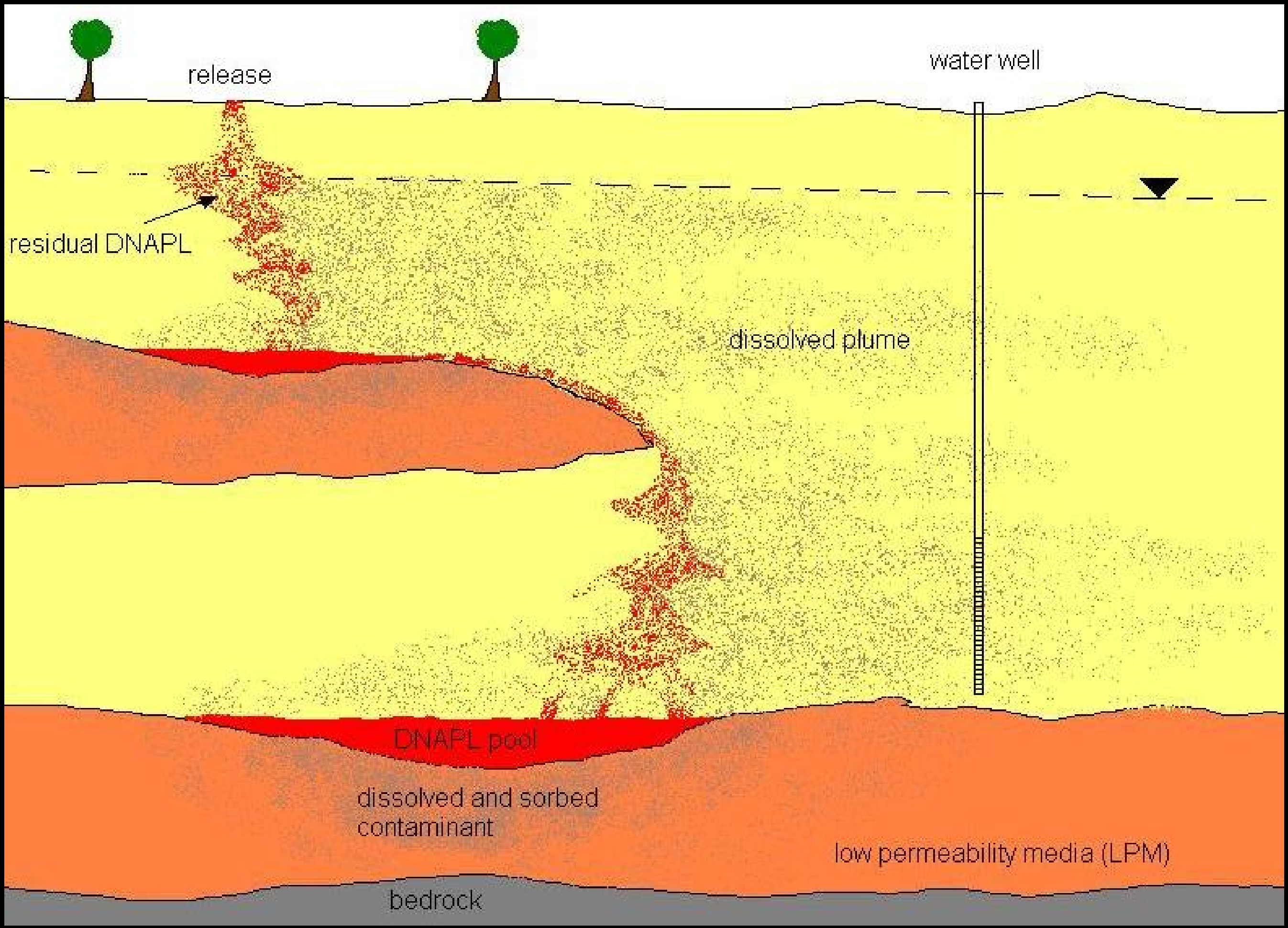
Conceptual Model



Nanoiron treatment of source or plume is possible

TCE + Fe^0 → HC Products + Cl^- + Fe^{2+}/Fe^{3+}

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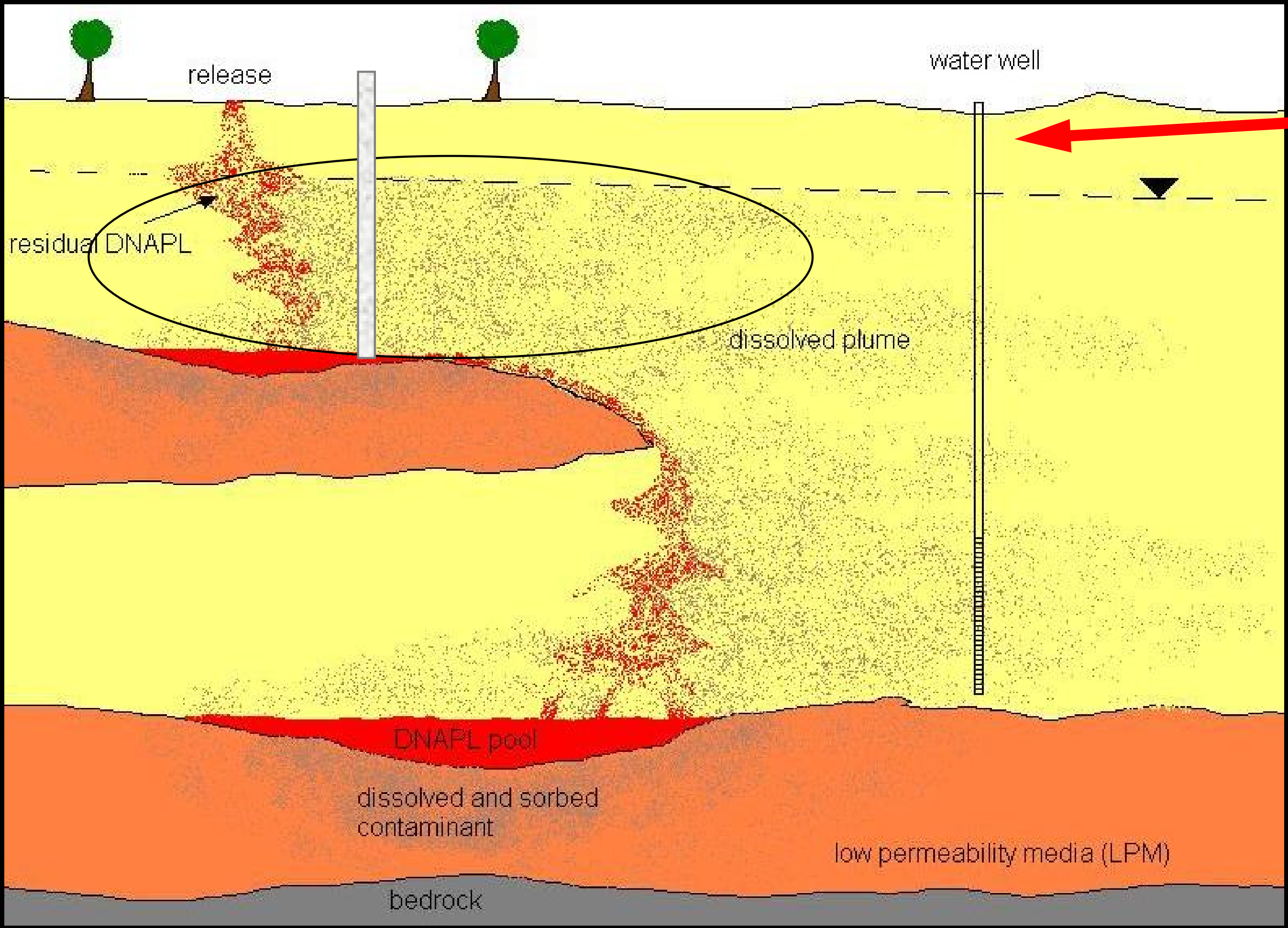
Conceptual Model



Potential human exposure

Goal:
Maximize treatment, and minimize unwanted exposures

Need to understand transport and fate of nanoiron to optimize treatment and understand potential risks

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Does Nanoiron Pose a Risk?

- Exposure
  - What are we potentially exposed to?
    - What Fe phases and nanoparticle sizes?
    - Does nanoiron change over time?
    - How quickly does it change?
  - How much are we exposed to?
    - Nanoiron transport distance?
    - What hydrogeochemical factors control it?
- Toxicity
  - Is there toxicity or ecotoxicity?
    - What conditions lead to toxicity?

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Types of Nanoiron

RNIP

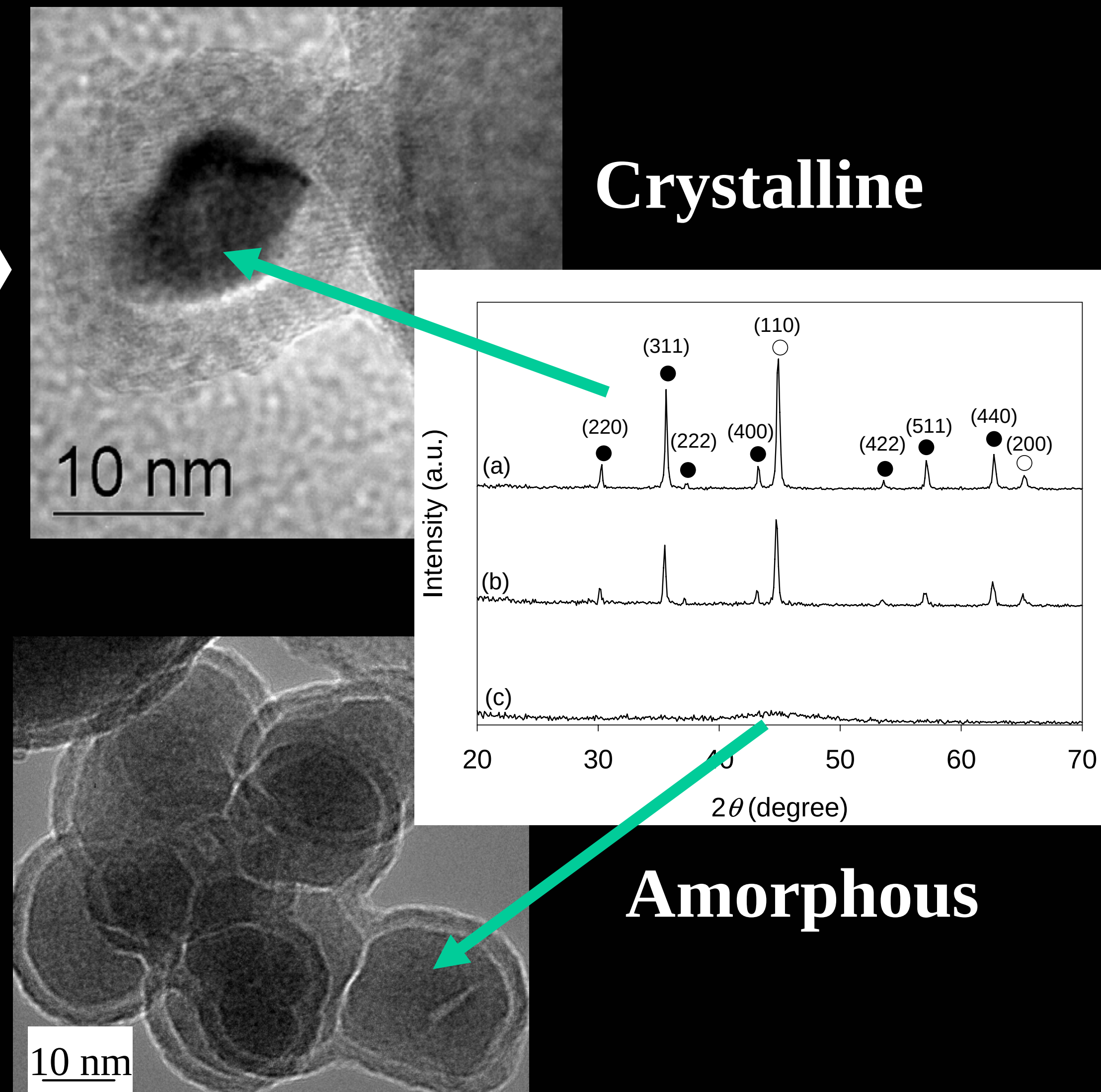
Fe^0 core
Fe_3O_4 shell

$FeOOH \rightarrow Fe^0 \rightarrow Fe^0/Fe_3O_4$

Fe(B)

Fe^0 core
Borate shell

$Fe^{2+} + BH_4^- \rightarrow Fe^0/FeB_x/Na_2B_4O_7$



Liu et al, (2005) *ES&T 39, 1338*; Liu et al, (2005) *Chem. Mat. 17(21); 5315-5322;* Nurmi et al. (2005) *ES&T 39, 1221*.

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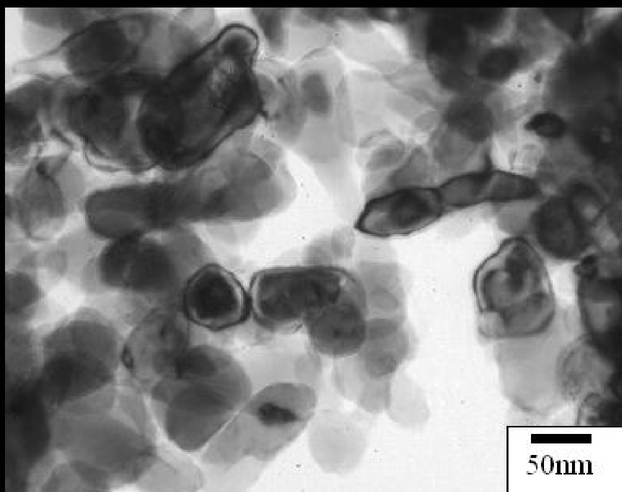
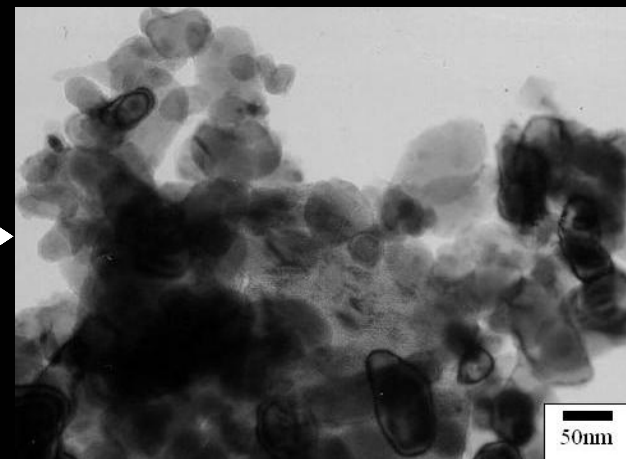
Nanoiron After Reaction with TCE in Water

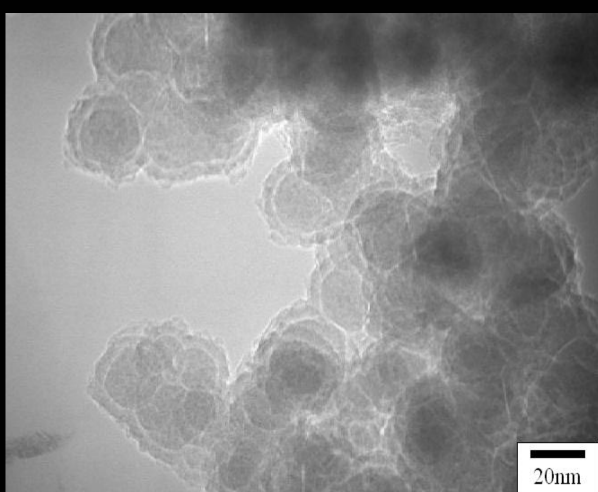
RNIP



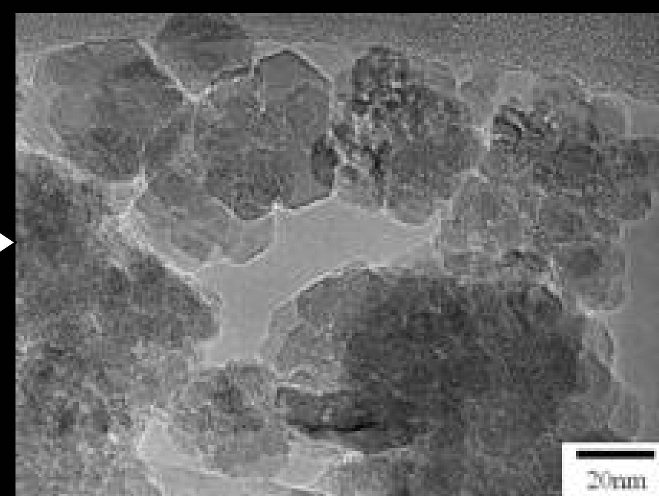
+ TCE/H_2O



Fe(B)



+ TCE/H_2O

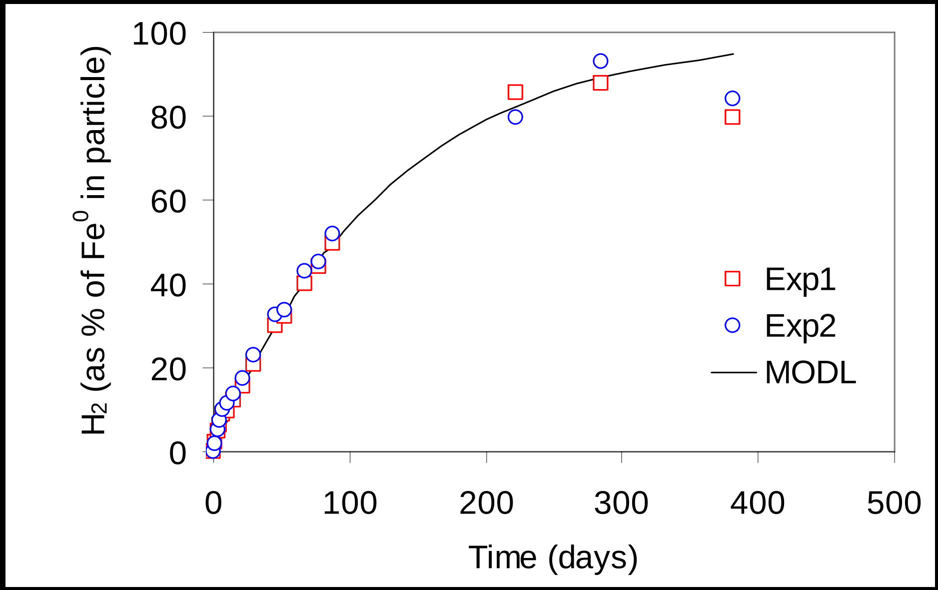


Fe^0 Corrosion Rate (pH=8-9)

RNIP

$Fe^0/Fe_3O_4 + H_2O$

$\rightarrow Fe_3O_4 + H_2$



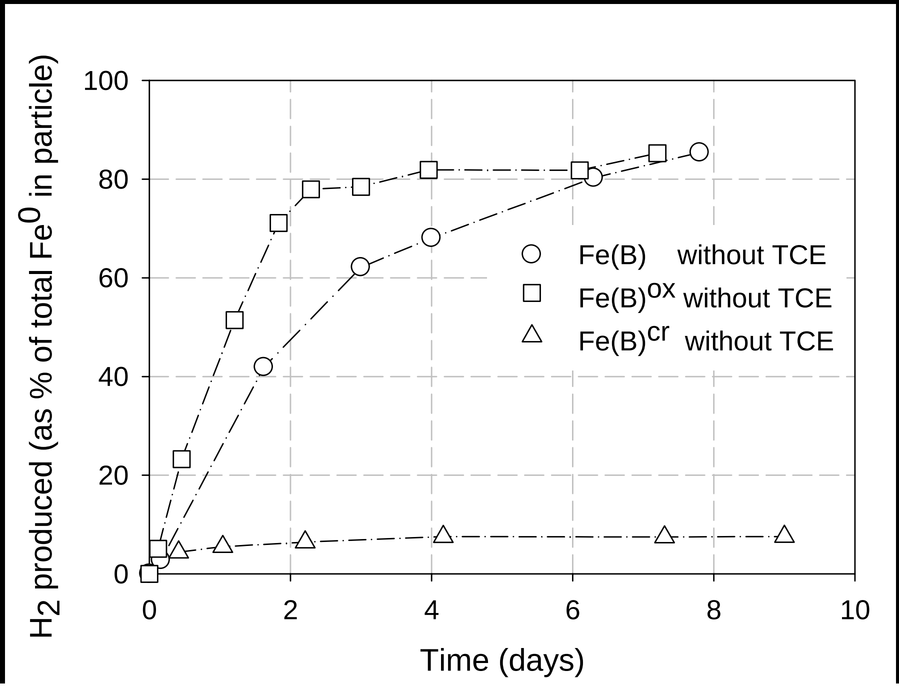
~1 year

Fe(B)

$Fe^0/FeB_x/Na_2B_4O_7 + H_2O$

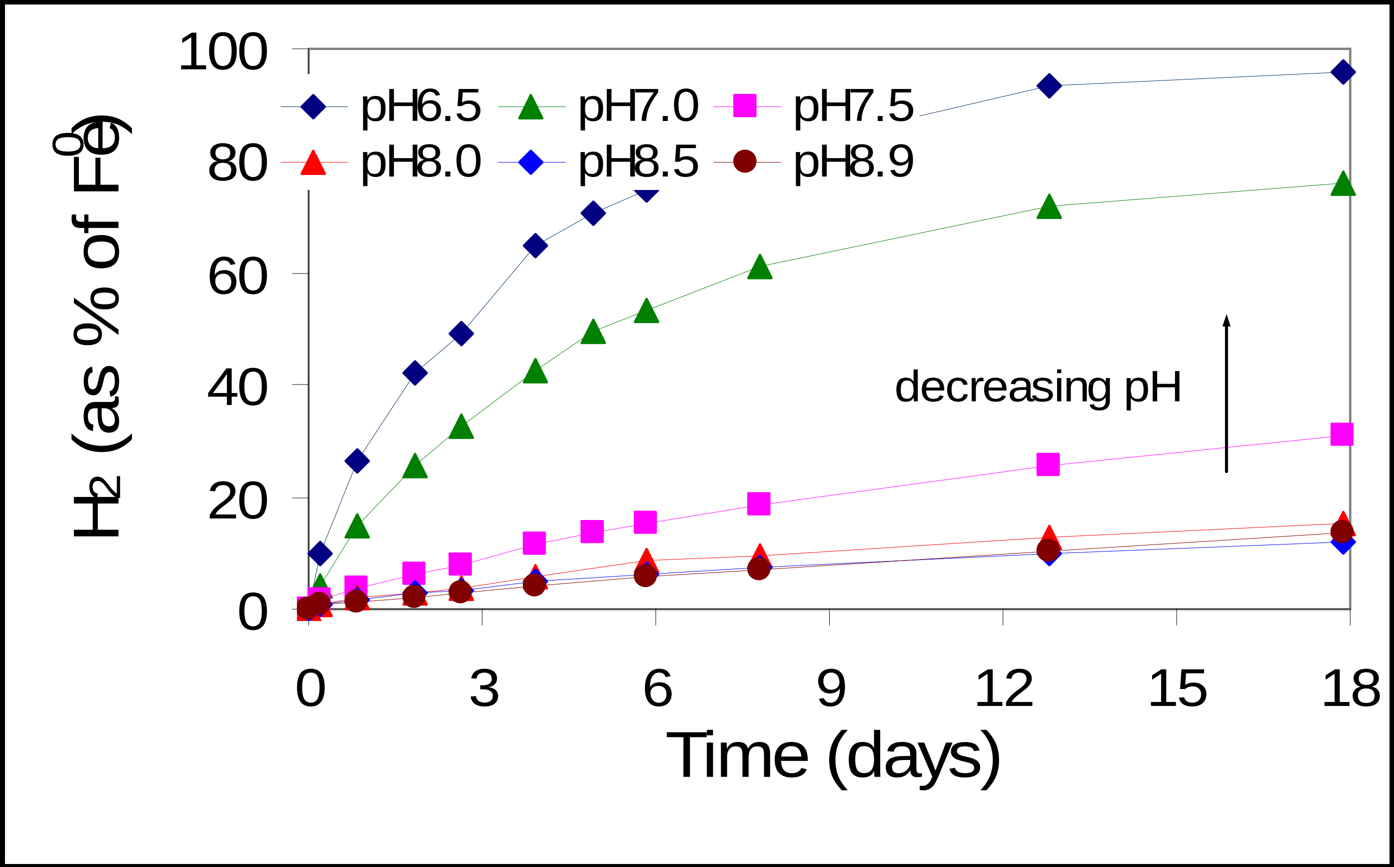
$\rightarrow$ Fe-oxide + $H_2 + B_4O_7^{2-}$

~1-2 weeks



Fe^0 Corrosion Rate Depends on pH

RNIP



~2 weeks pH=6.5

~1 year pH=8.9

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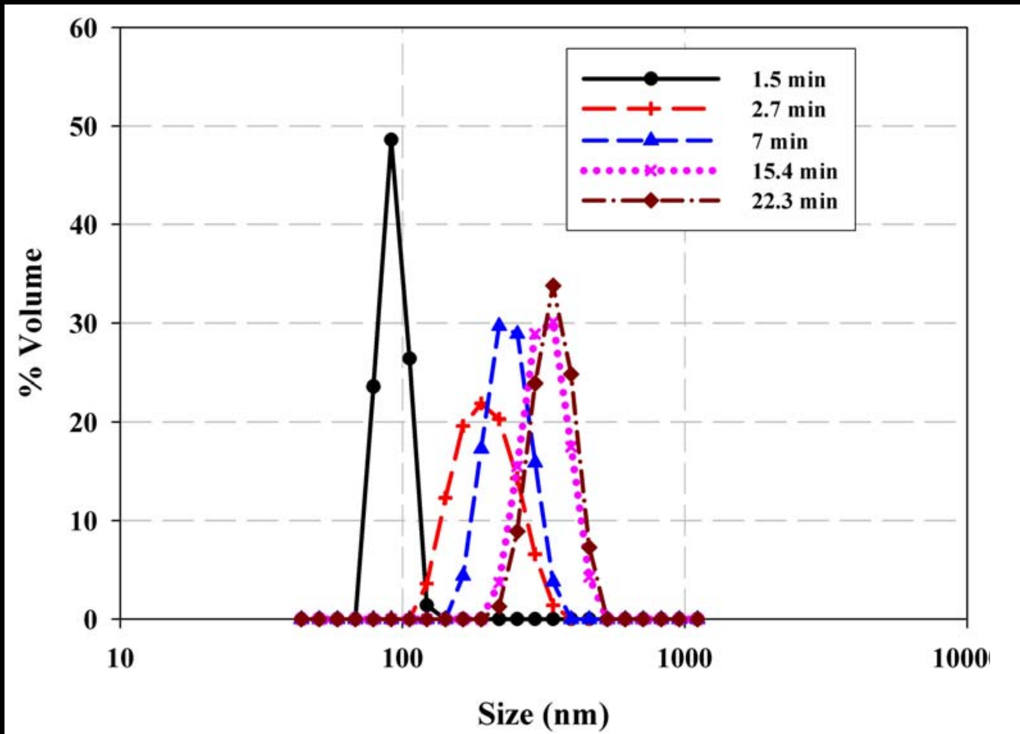
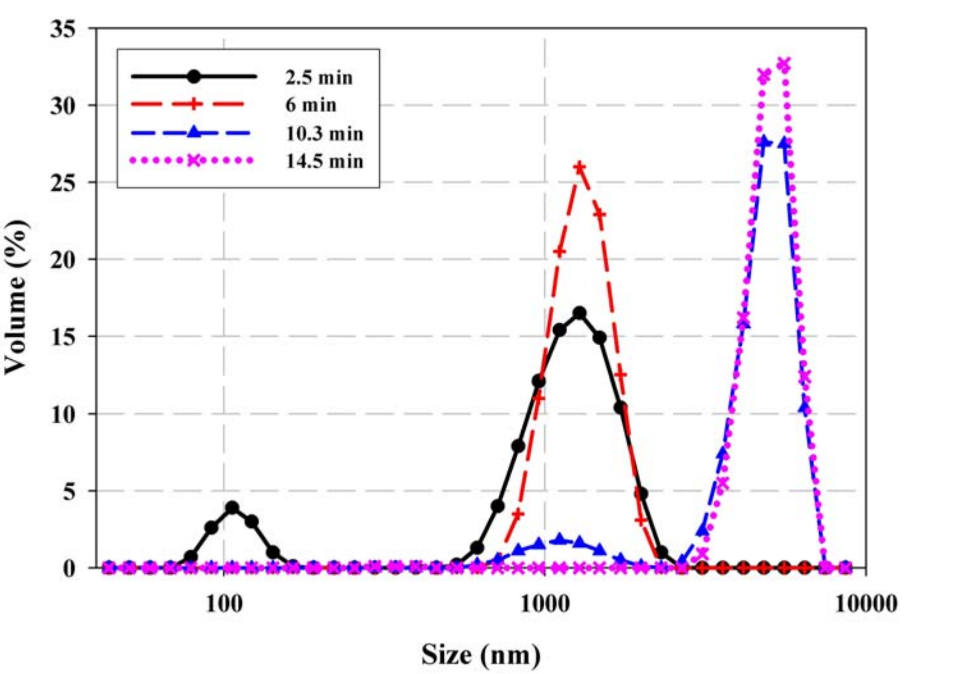
How long is Nanoiron Nano?

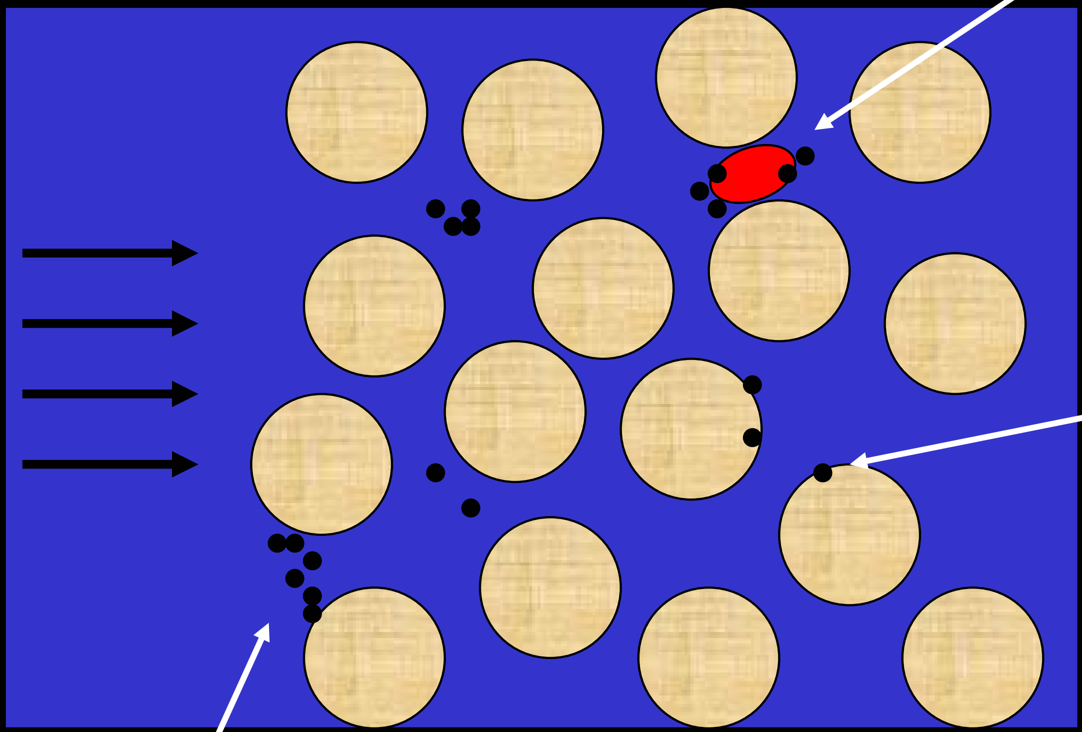


Concentration=79 mg/L
Stable size=~5000 nm
Time=10 minutes



Concentration=1.9 mg/L
Stable size=~400 nm
Time=15 minutes

Nanoiron Transport is a Filtration Problem



Particle-DNAPL Interactions (Attachment)

Particle-Media Interactions (Attachment)

Flocculation and straining (cake filtration)

Uniqueness- High particle concentration and flow velocity

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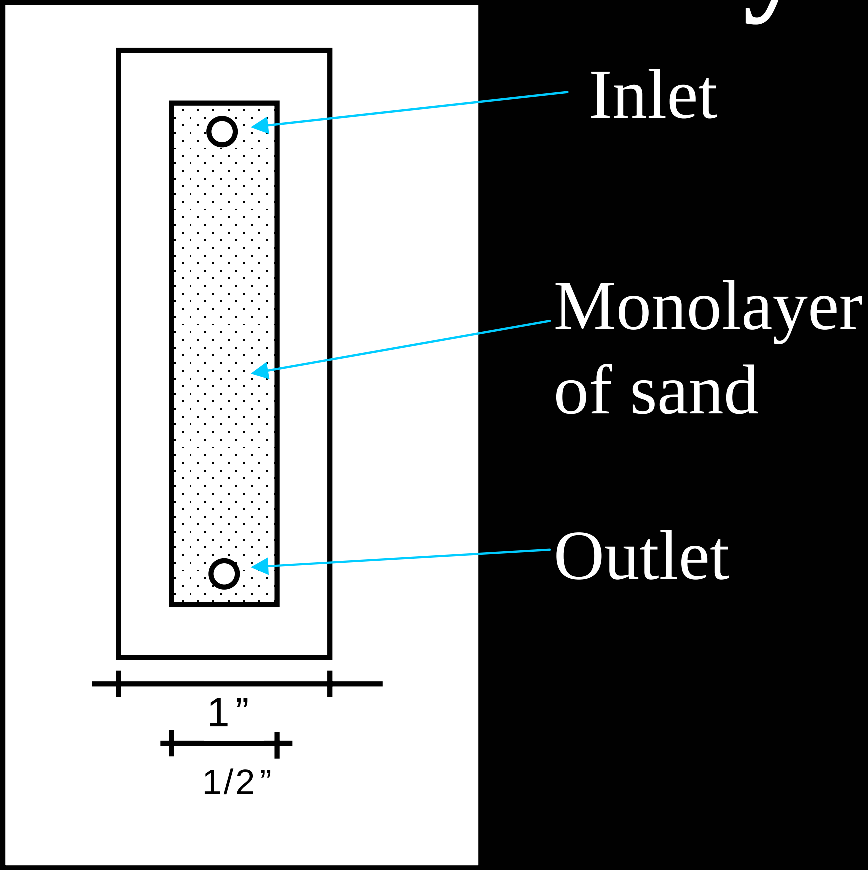
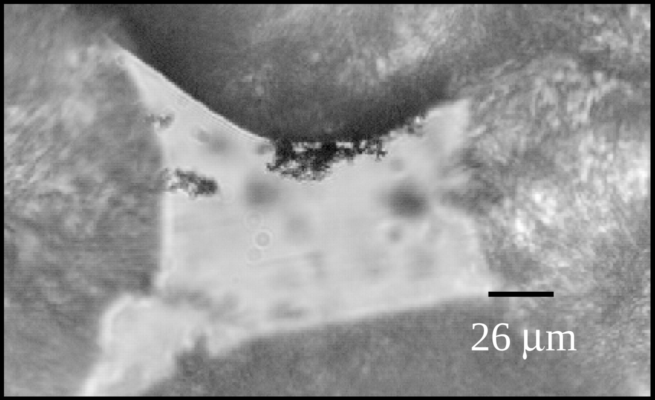
Nanoiron Aggregation Affects the Ability to Transport



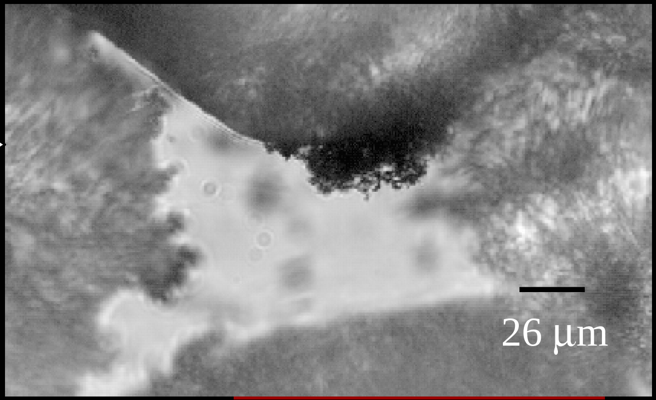
Micro-fluidic PDMS cell

Time=1 min

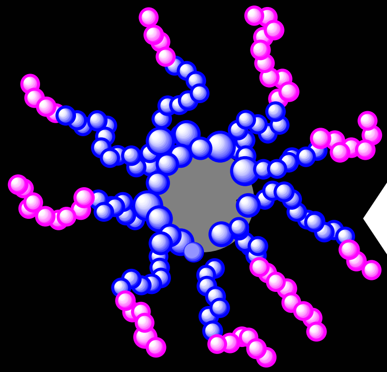


Time=10 min

Nanoiron aggregates are filtered



Surface Modifiers Increase Transportability

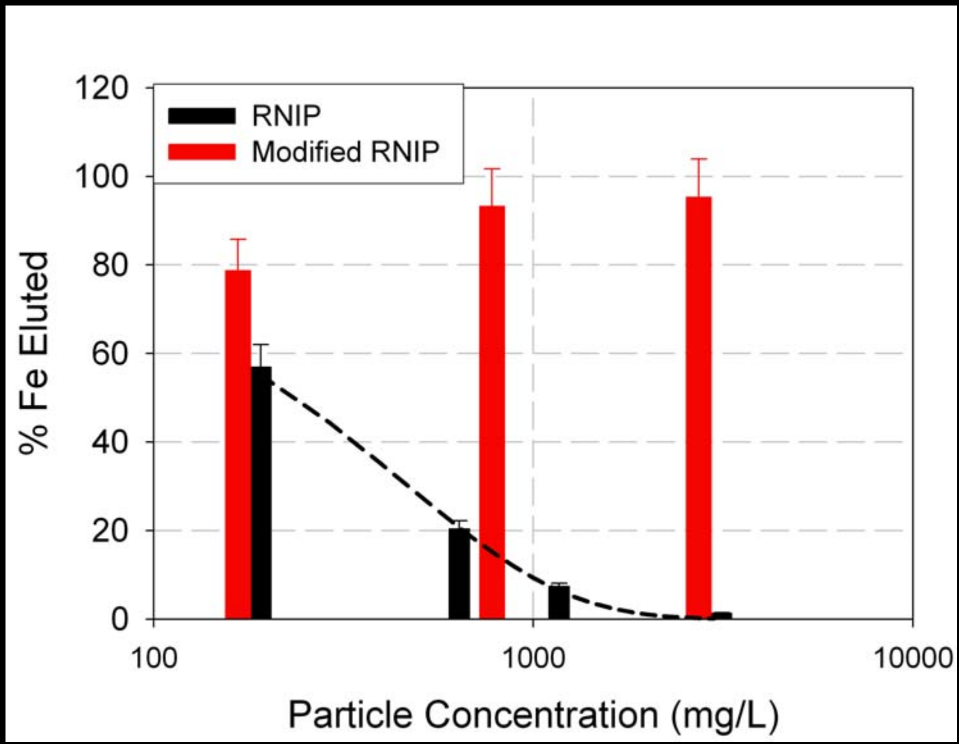


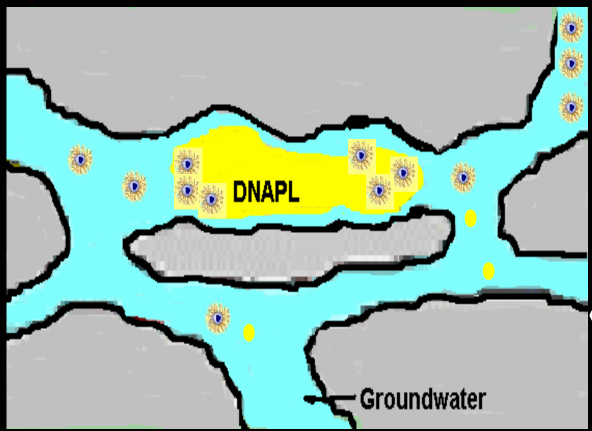
1. Potential Surface Coatings

- ✓ Polyelectrolyte
- ✓ Surfactants
- ✓ Cellulose/polysaccharides

2. Enhanced transport

Charge and steric stabilization minimize particle-particle and particle-media interactions





3. Affinity for DNAPL

Surface coatings provide affinity for NAPL

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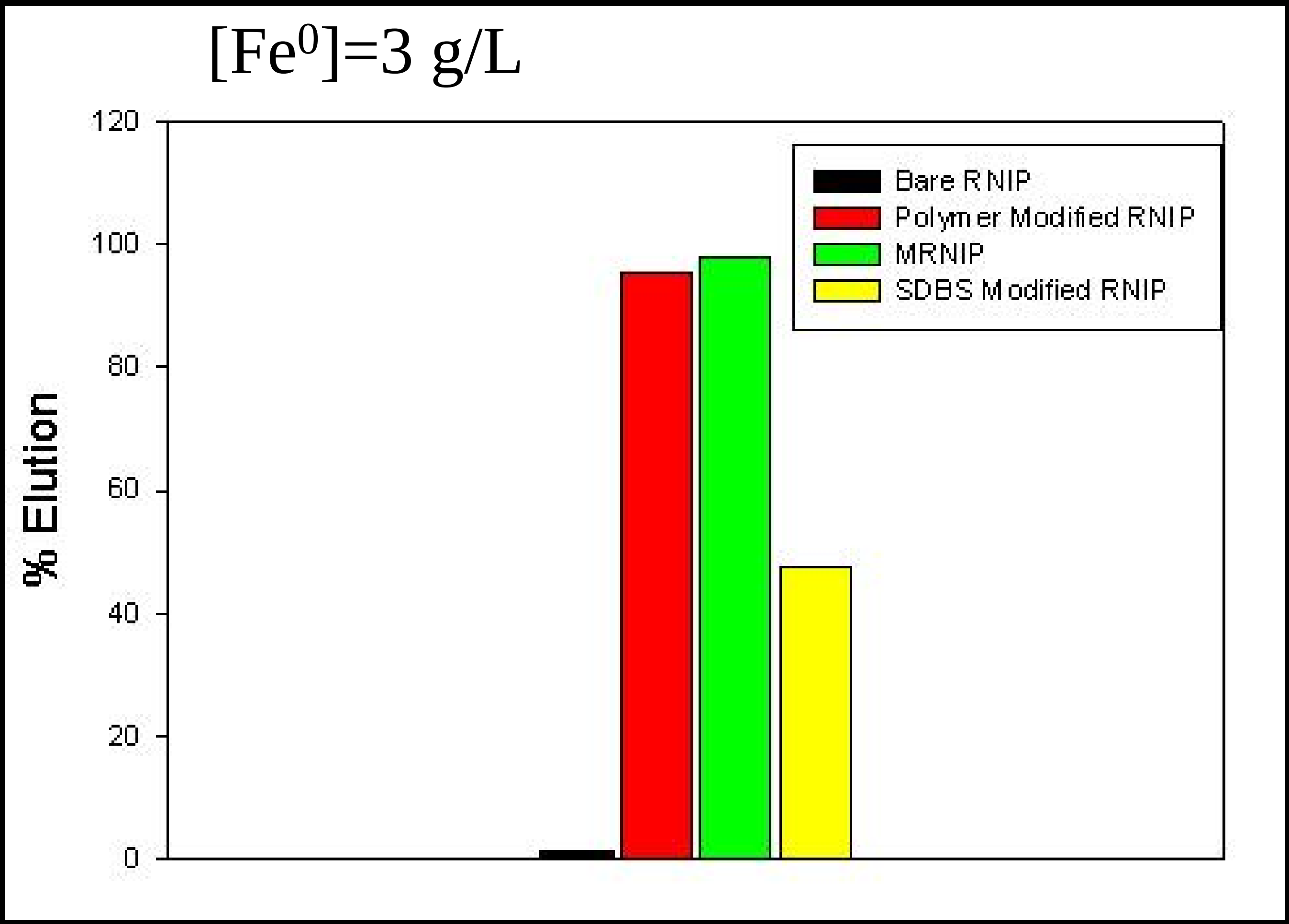
Effect of Different Modifiers



Potential to select transport distance

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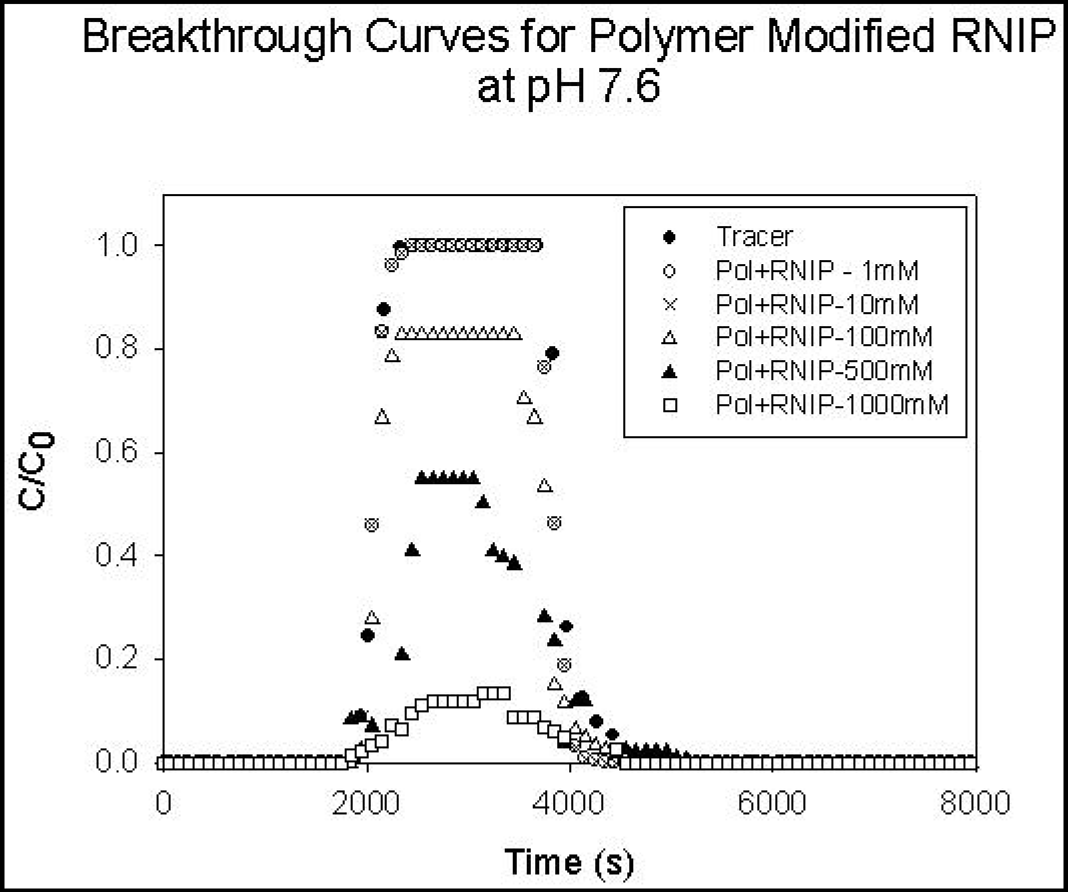
Hydrogeochemical Effects on Nanoiron Transport



✓Transportability is a strong function of site hydrogeochemistry.

✓Systematic evaluation of hydrogeochemical effects is needed

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Nanoiron Toxicity?

Why suspect that ZVI causes OS?

•Surface chemistry

•Reactive oxygen species

•Literature-daphne, fish ….. glutathione depletion

Why the brain?

• Serious consequences from damage

•Target of OS-lipid content…high energy use

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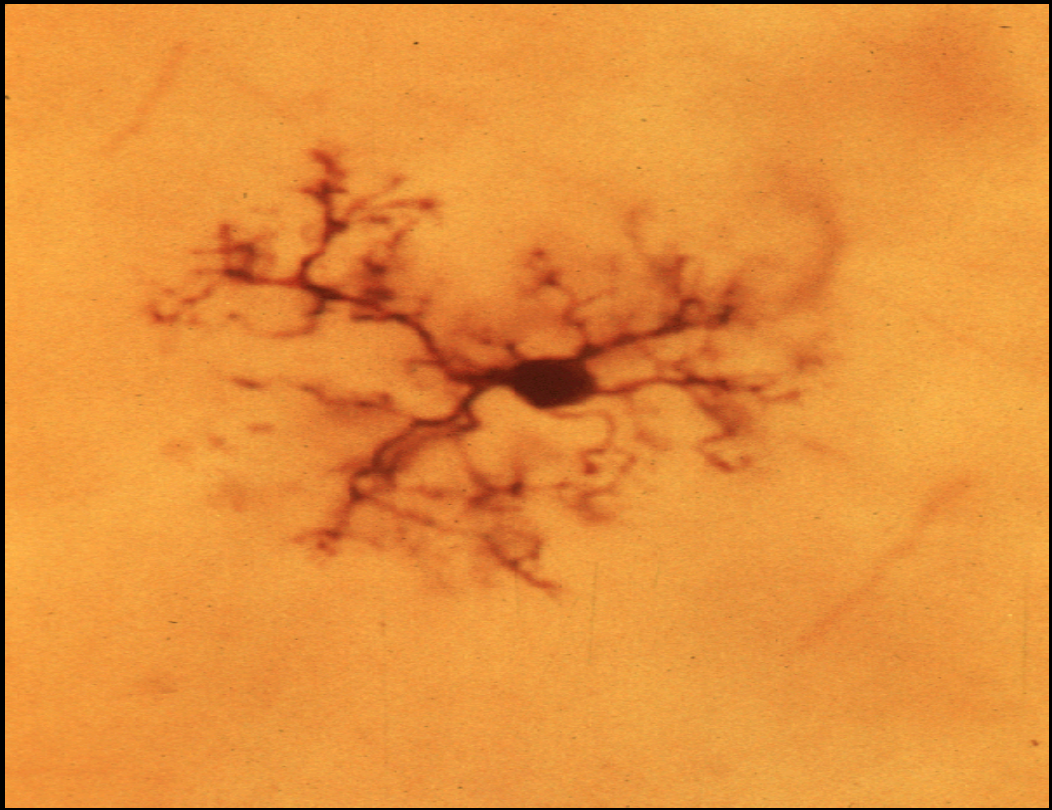
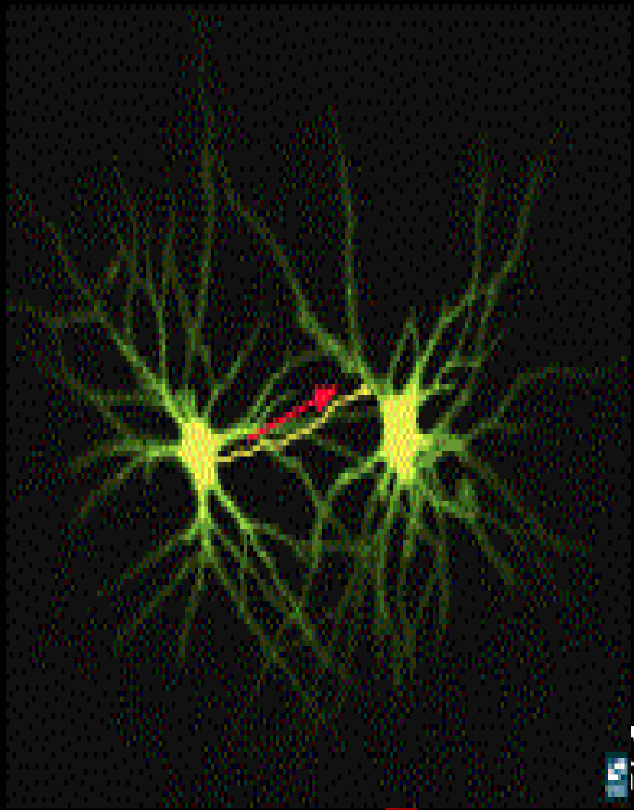
Nanoiron Toxicity

Mammalian brain macrophage (microglia)
✓Fe^0 and modified-Fe^0 (1-30 ppm)
✓Whole-cell and genomic responses
✓OS-specific endpoints
✓TEM, confocal microscopy





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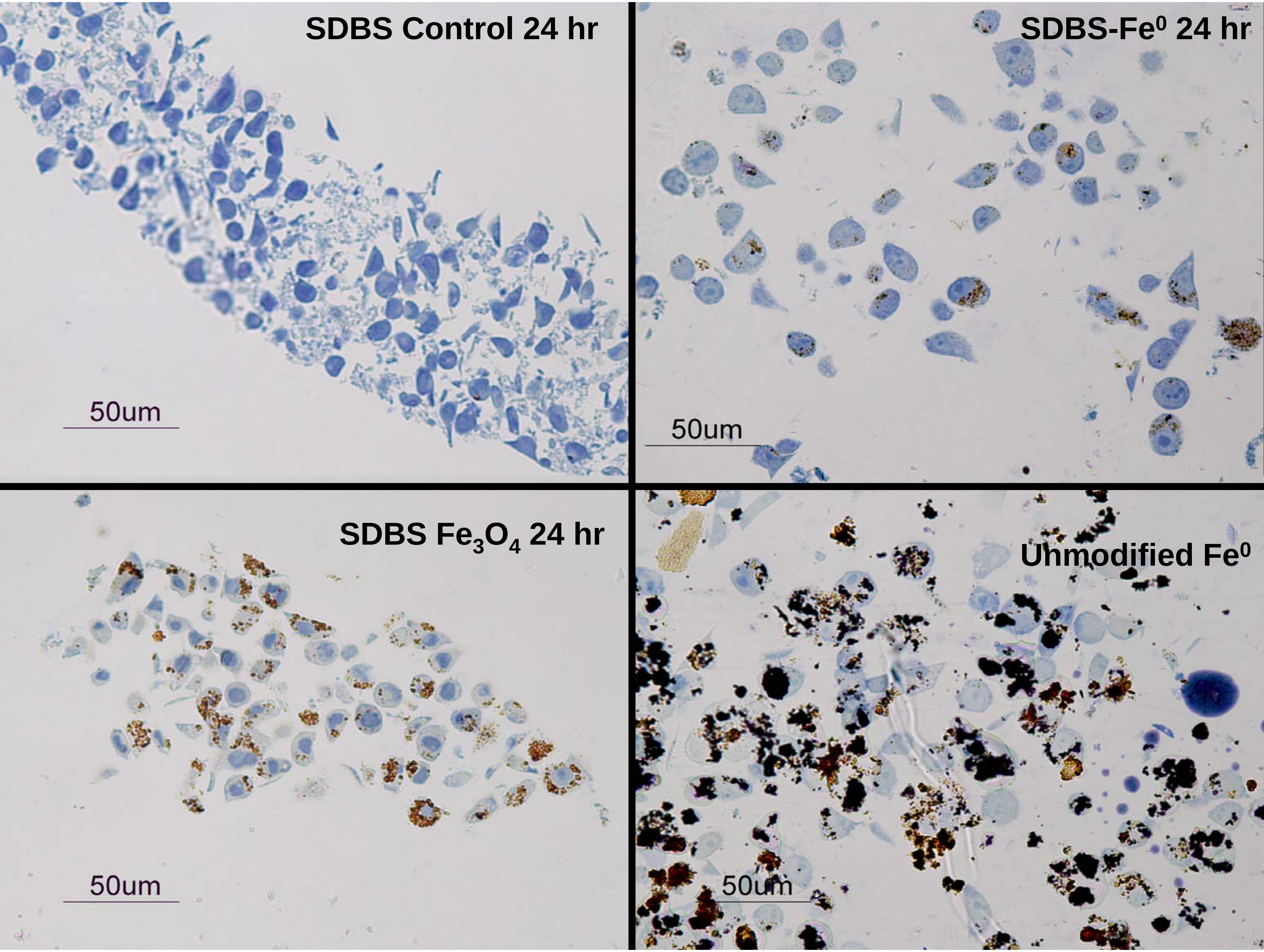
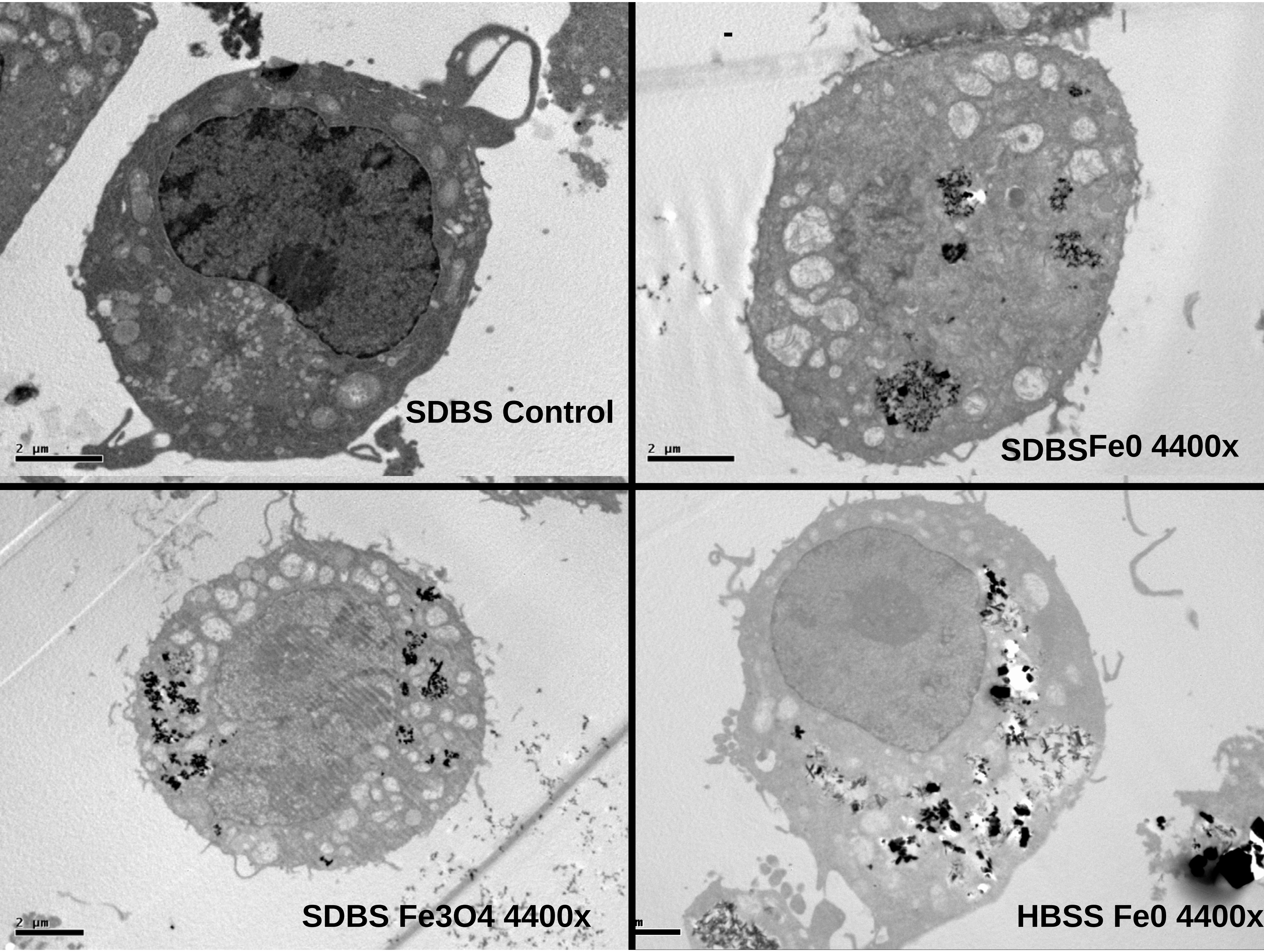
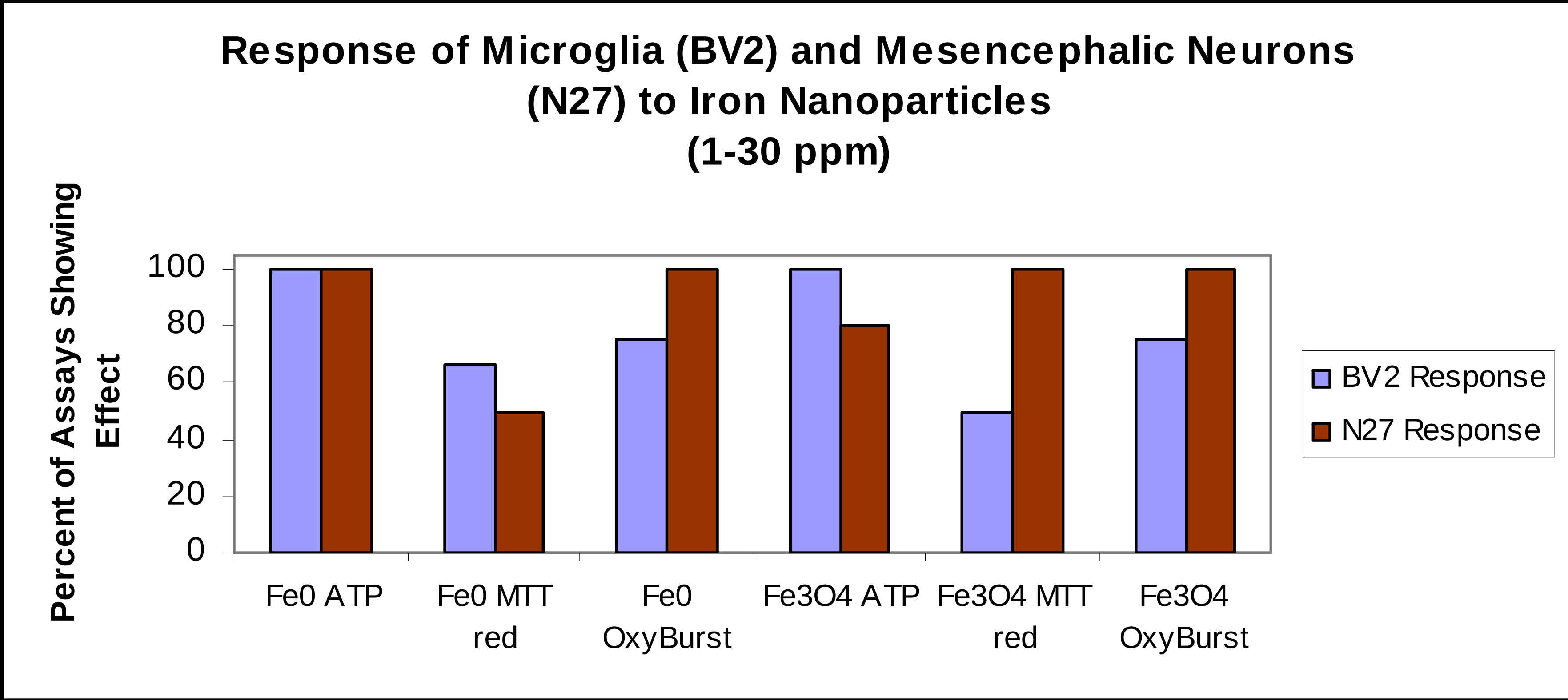


SDBS Control 24 hr
50um
SDBS-Fe0 24 hr
50um
SDBS Fe3O4 24 hr
50um
Unmodified Fe0
50um


SDBS Control
2 µm
-
SDBSFe0 4400x
2 µm
SDBS Fe3O4 4400x
2 µm
HBSS Fe0 4400x

Fe^0-induced Oxidative Stress in CNS Cells



Future Studies:

Apo E Mice and Medaka Fish

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Conclusions

- Potential toxicity risk warrants careful evaluation
- Fe^0 fairly rapidly oxidizes to Fe-oxides
  - Fe^0 lifetime ranges from weeks to a year
  - Lifetime depends on nanoiron properties and geochemical conditions (e.g. pH)
  - Unmodified nanoiron rapidly aggregates, size is concentration dependent

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Conclusions

- Transport of unmodified nanoiron in porous media is limited.
- Particle surface chemistry strongly influences transportability
  - function of modifier type and geochemical conditions
  - May be predictable from filtration/colloid transport theory
  - Matching surface modifications to site geochemistry offers the potential for well-controlled placement

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