

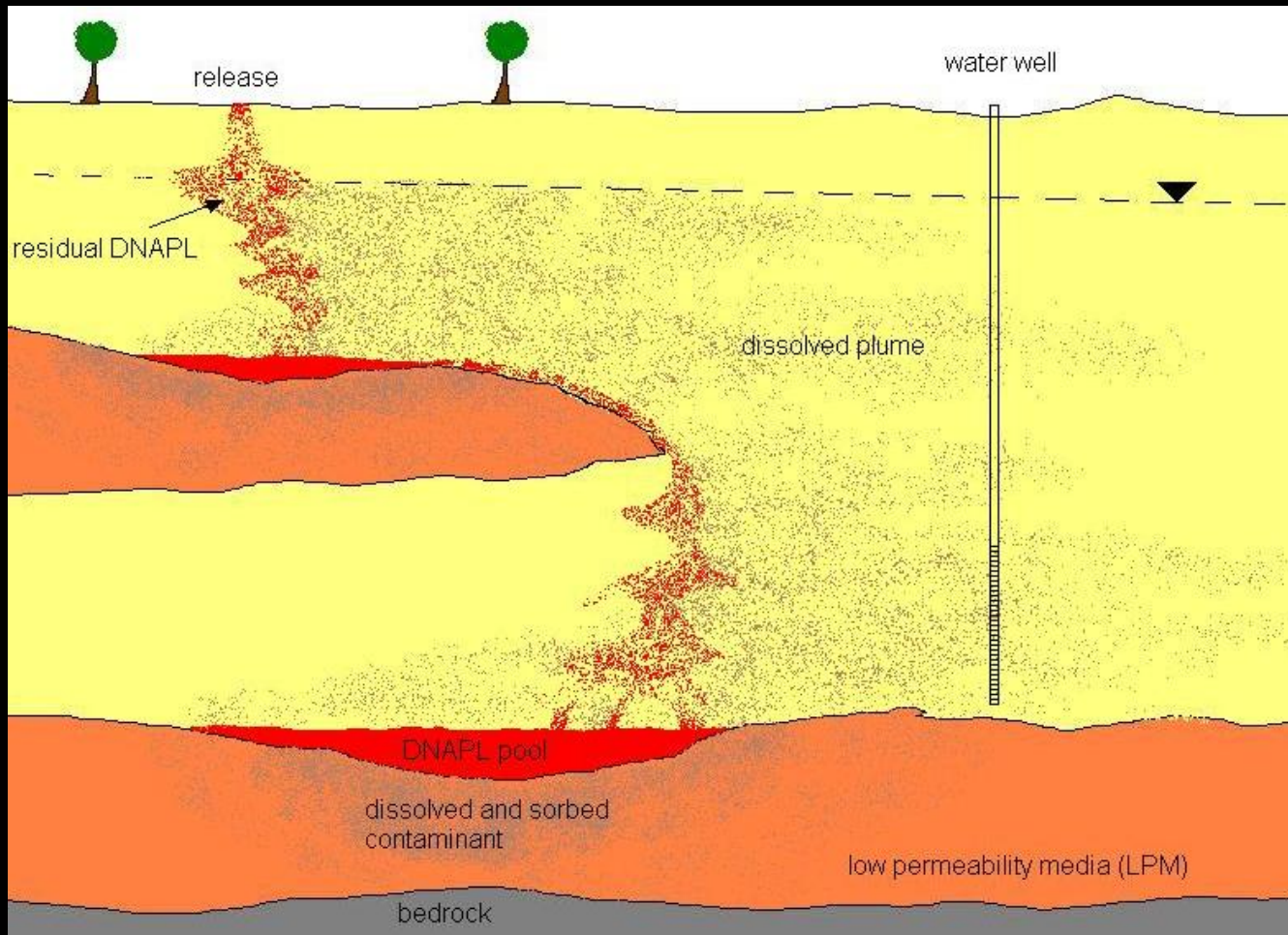
# **Nanoiron in the Subsurface: How far will it go and how does it change?**

G. Lowry, Y. Liu, N. Saleh, T. Phenrat, B. Dufour, R. Tilton,  
K. Matyjaszewski  
Carnegie Mellon University

T. Long and B. Veronesi

National Health and Environmental Effects Research Laboratory, US EPA

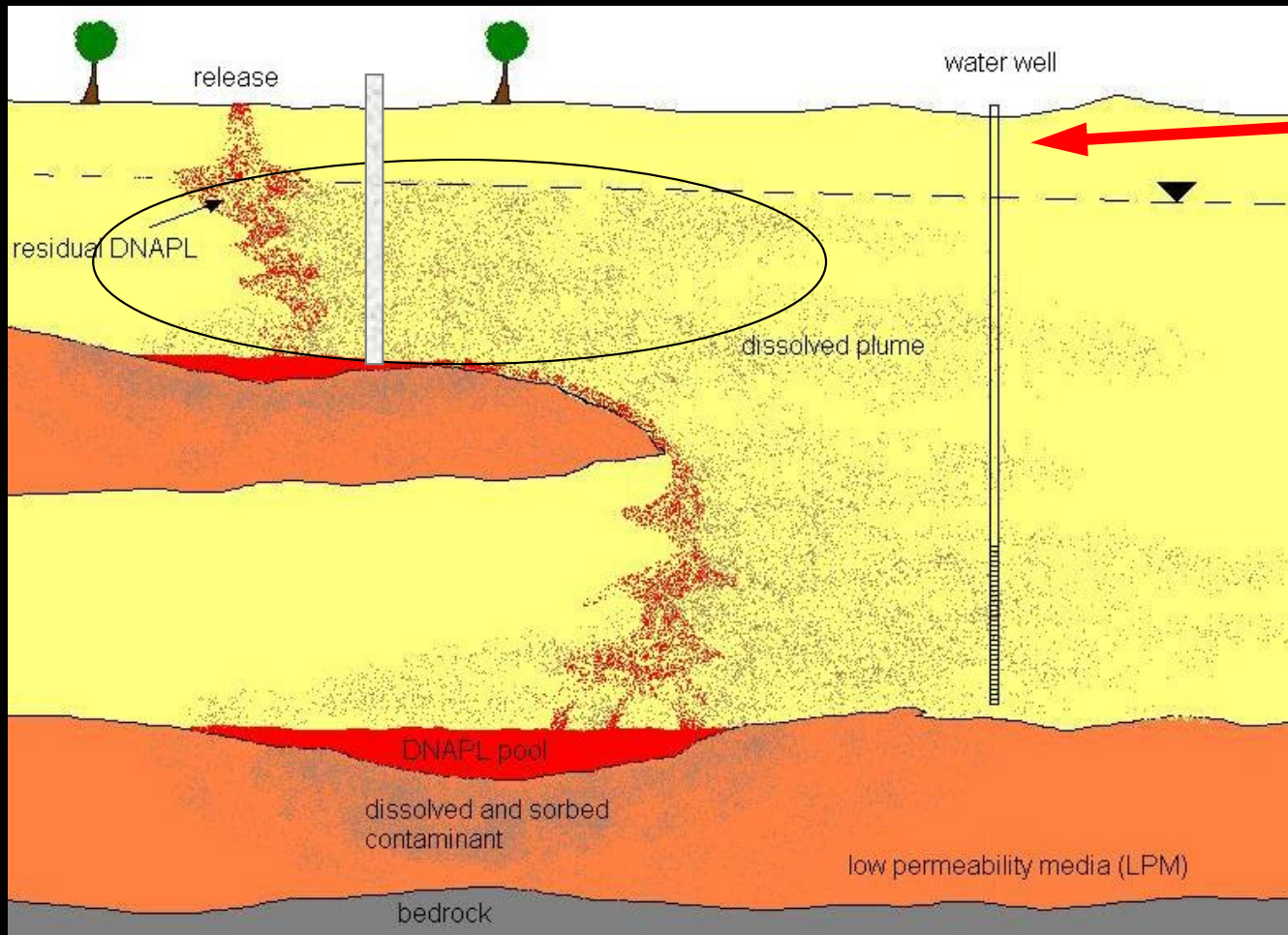
# Conceptual Model



Nanoiron treatment of source or plume is possible



# 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

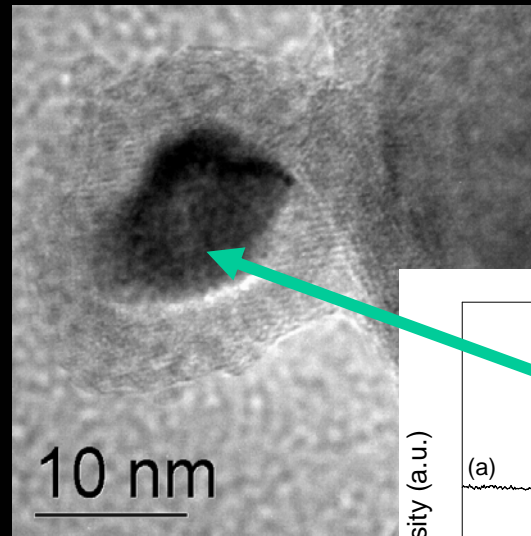
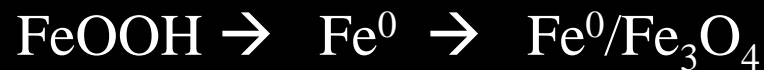
# Does Nanoiron Pose a Risk?

- 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?

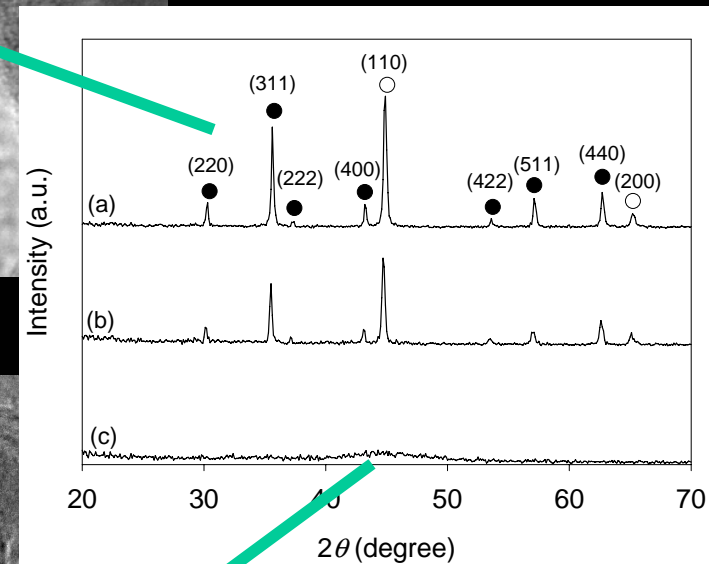
# Types of Nanoiron

## RNIP

**Fe<sup>0</sup> core  
Fe<sub>3</sub>O<sub>4</sub> shell**

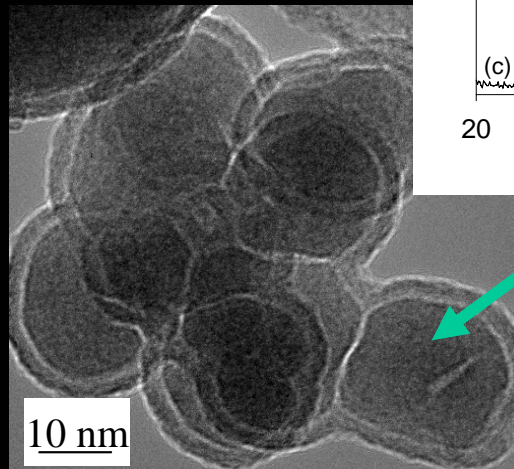


**Crystalline**



## Fe(B)

**Fe<sup>0</sup> core  
Borate shell**

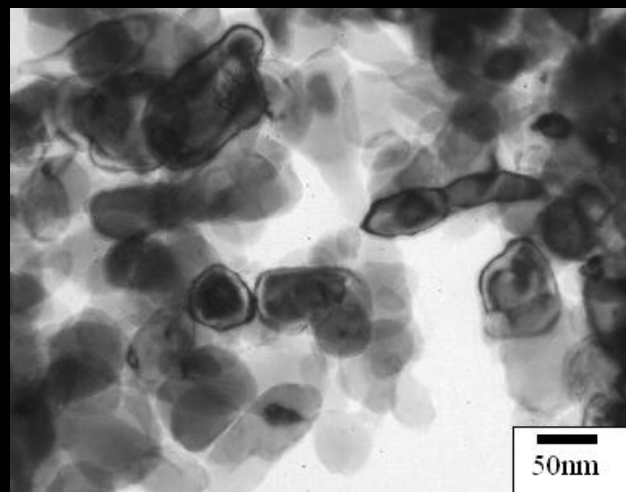


**Amorphous**

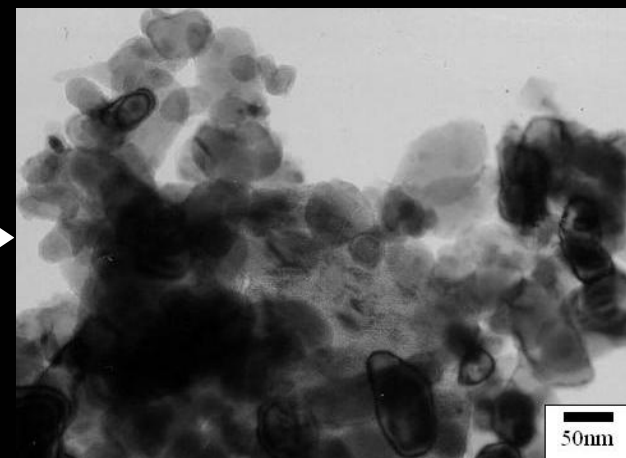
Liu et al, (2005) *ES&T* 39, 1338; Liu et al, (2005) *Chem. Mat.* 17(21); 5315-5322;  
Nurmi et al. (2005) *ES&T* 39, 1221.

# Nanoiron After Reaction with TCE in Water

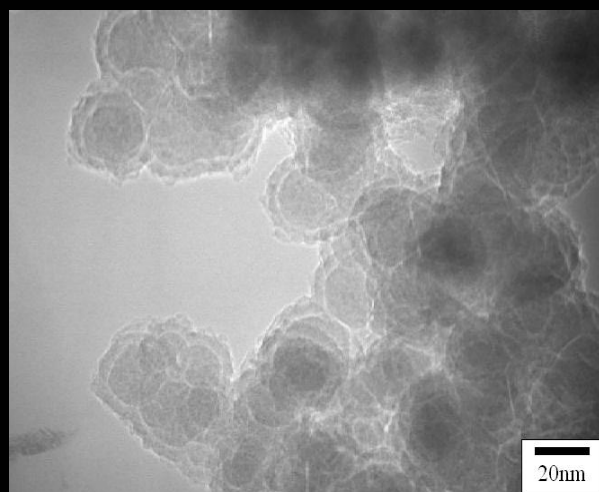
## RNIP



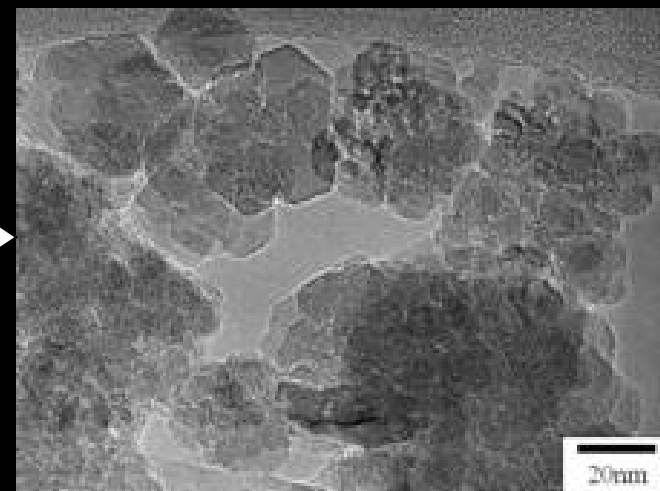
+ TCE/H<sub>2</sub>O



## Fe(B)

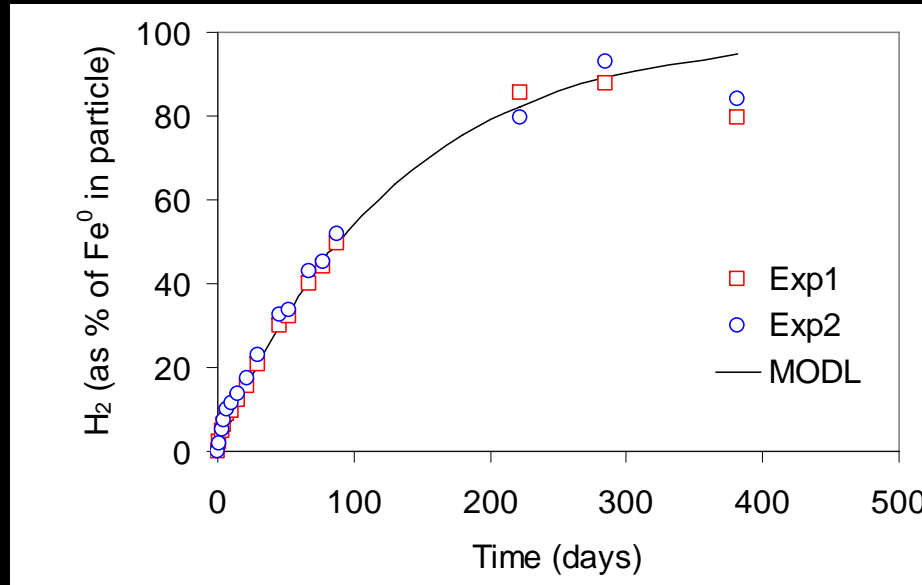


+ TCE/H<sub>2</sub>O



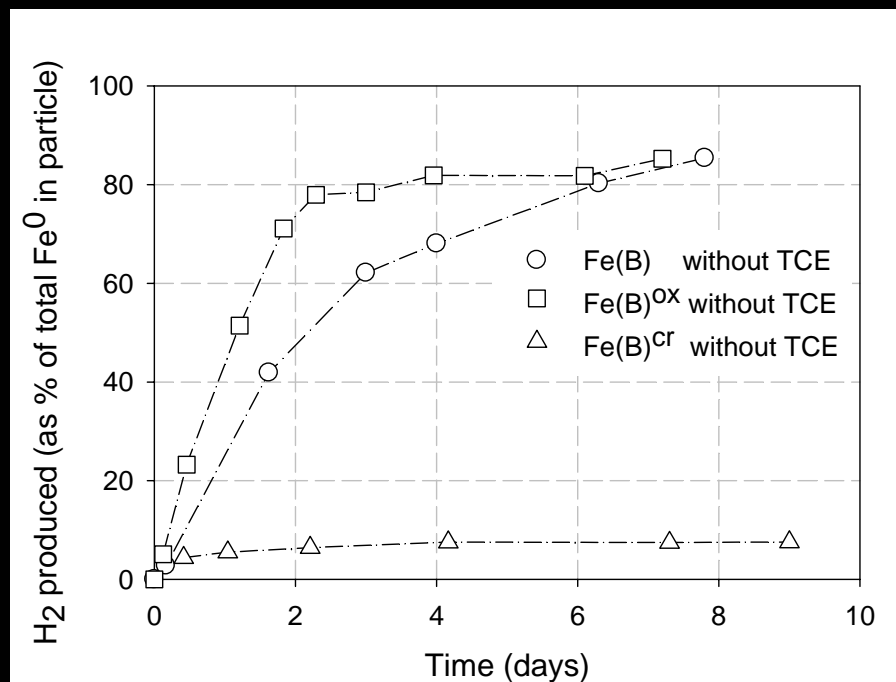
# Fe<sup>0</sup> Corrosion Rate (pH=8-9)

## RNIP



~1 year

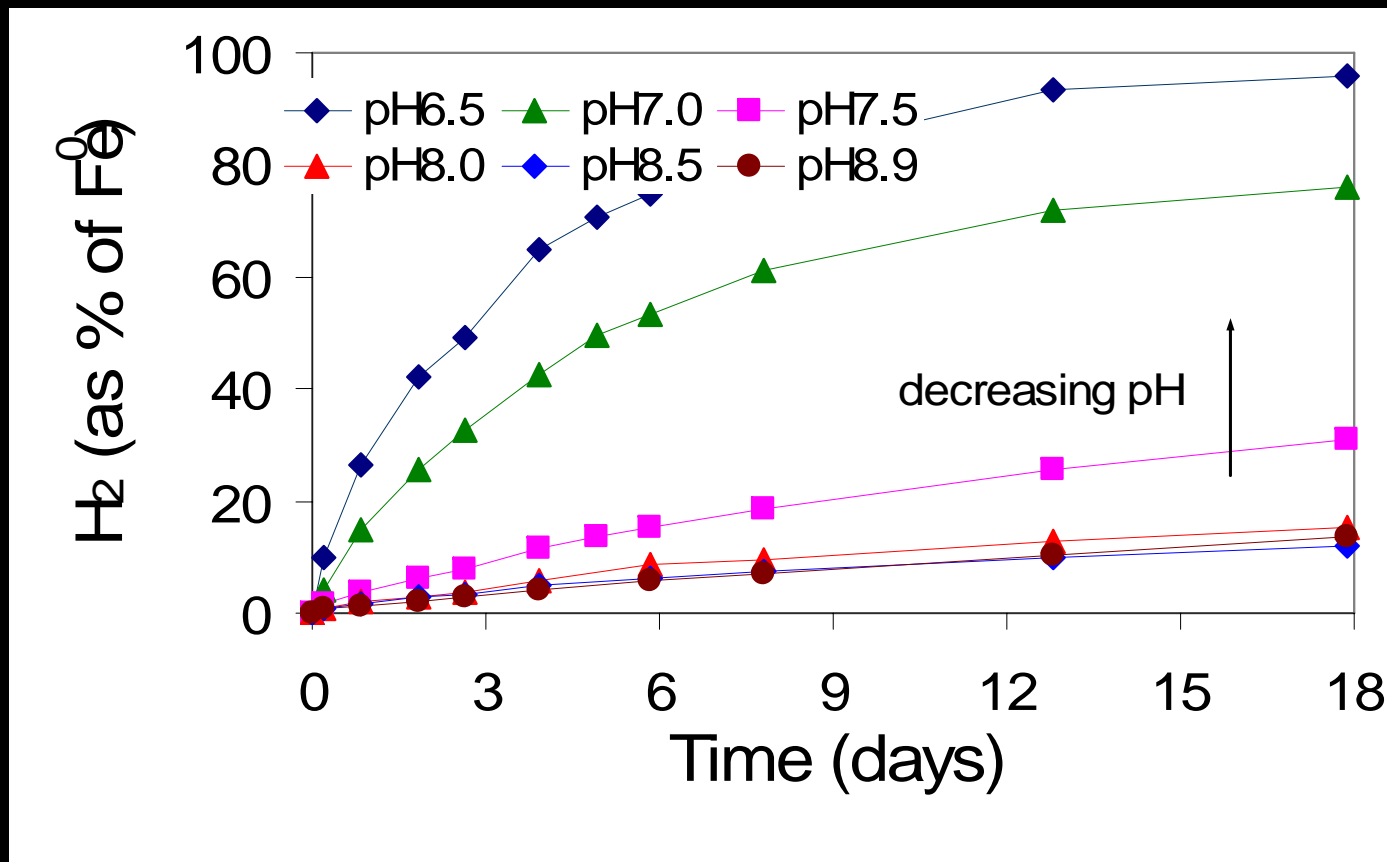
## Fe(B)



~1-2 weeks

# Fe<sup>0</sup> Corrosion Rate Depends on pH

## RNIP

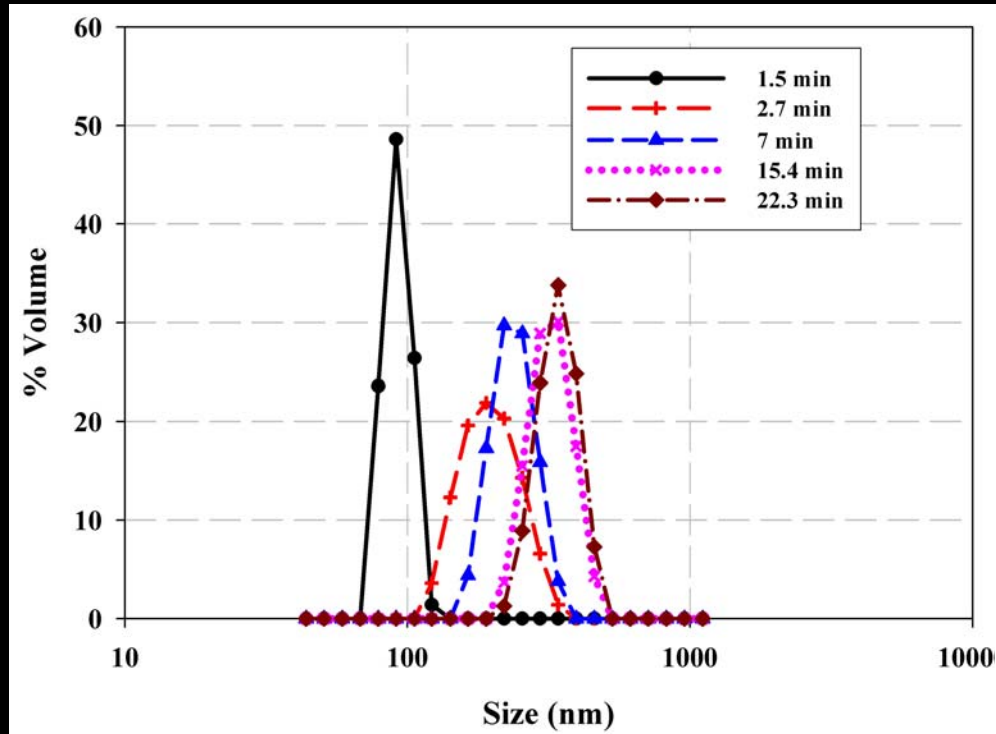


~2 weeks  
pH=6.5

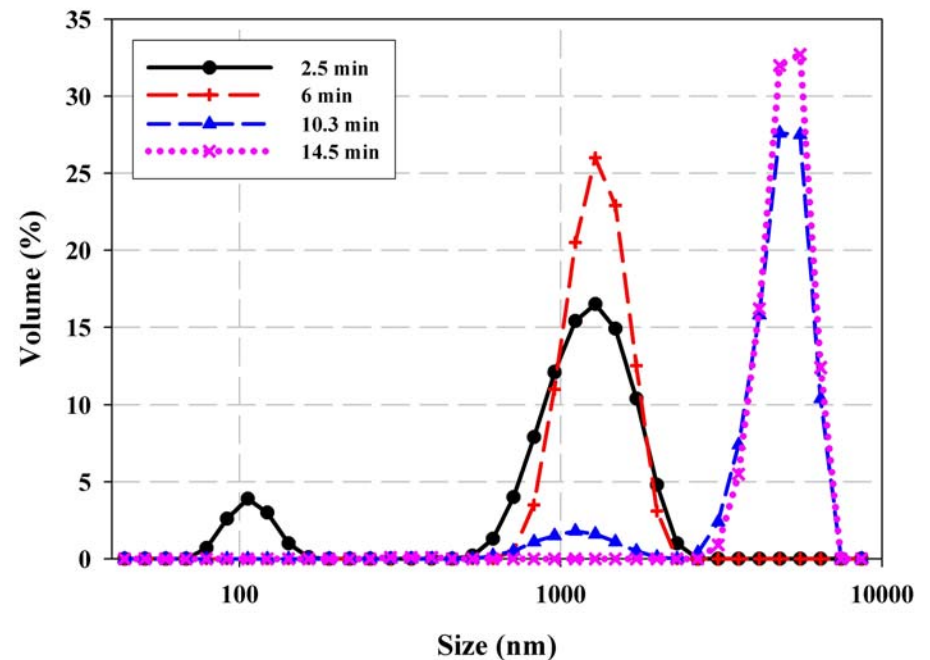
~1 year  
pH=8.9



# How long is Nanoiron Nano?

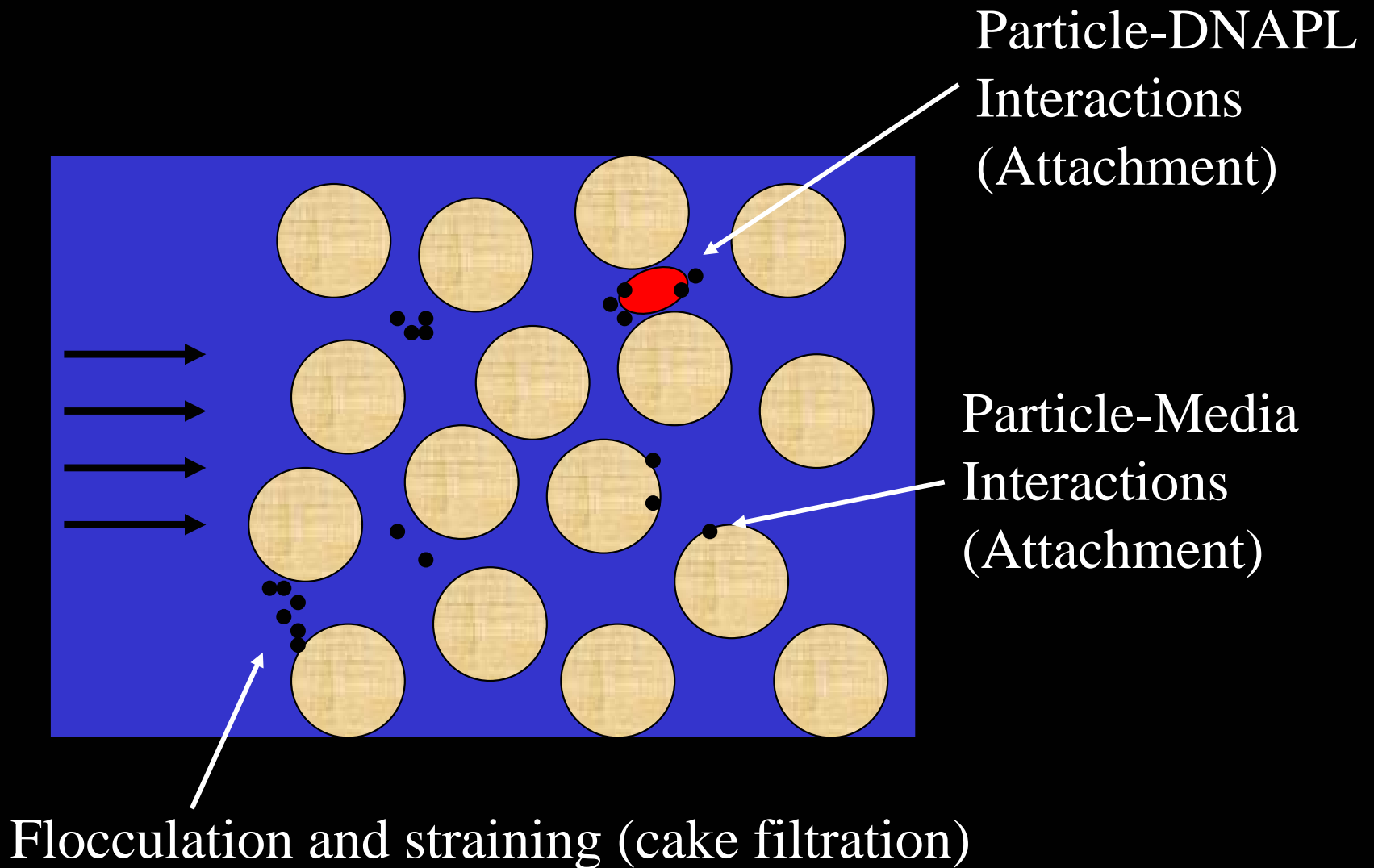


Concentration=79 mg/L  
Stable size= $\sim$ 5000 nm  
Time=10 minutes



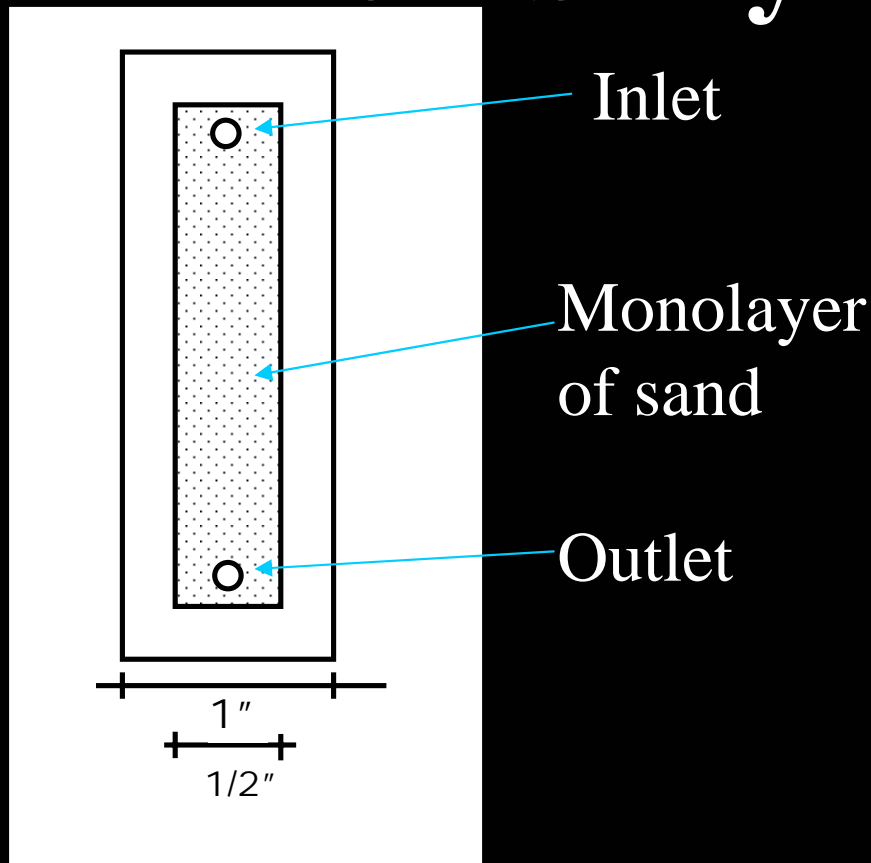
Concentration=1.9 mg/L  
Stable size= $\sim$ 400 nm  
Time=15 minutes

# Nanoiron Transport is a Filtration Problem



Uniqueness- High particle concentration and flow velocity

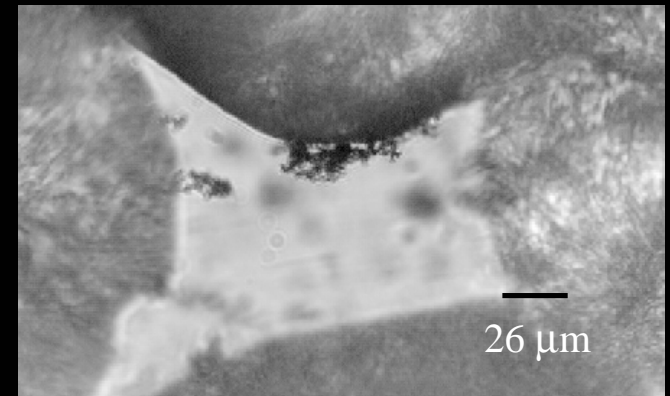
# Nanoiron Aggregation Affects the Ability to Transport



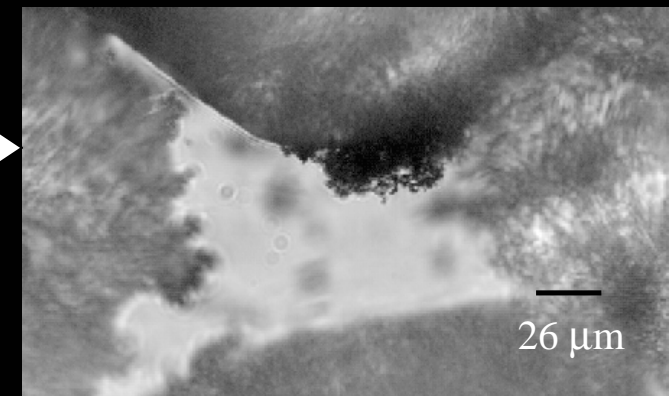
Micro-fluidic  
PDMS cell

Nanoiron  
aggregates are  
filtered

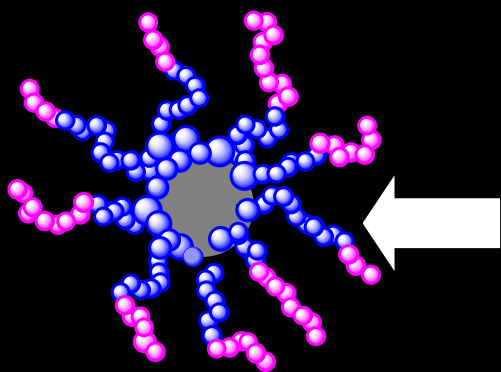
Time=1 min



Time=10 min



# Surface Modifiers Increase Transportability

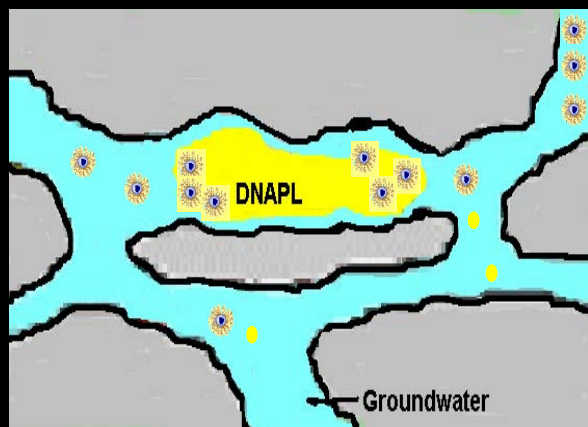
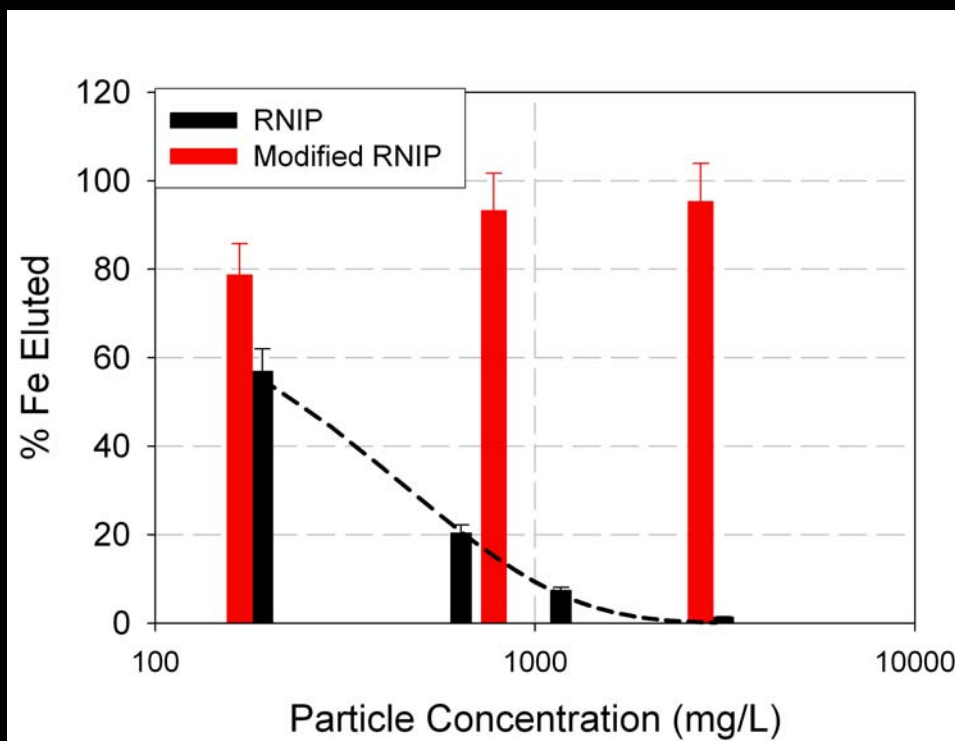


## 1. Potential Surface Coatings

- ✓ Polyelectrolyte
- ✓ Surfactants
- ✓ Cellulose/polysaccharides

## 2. Enhanced transport

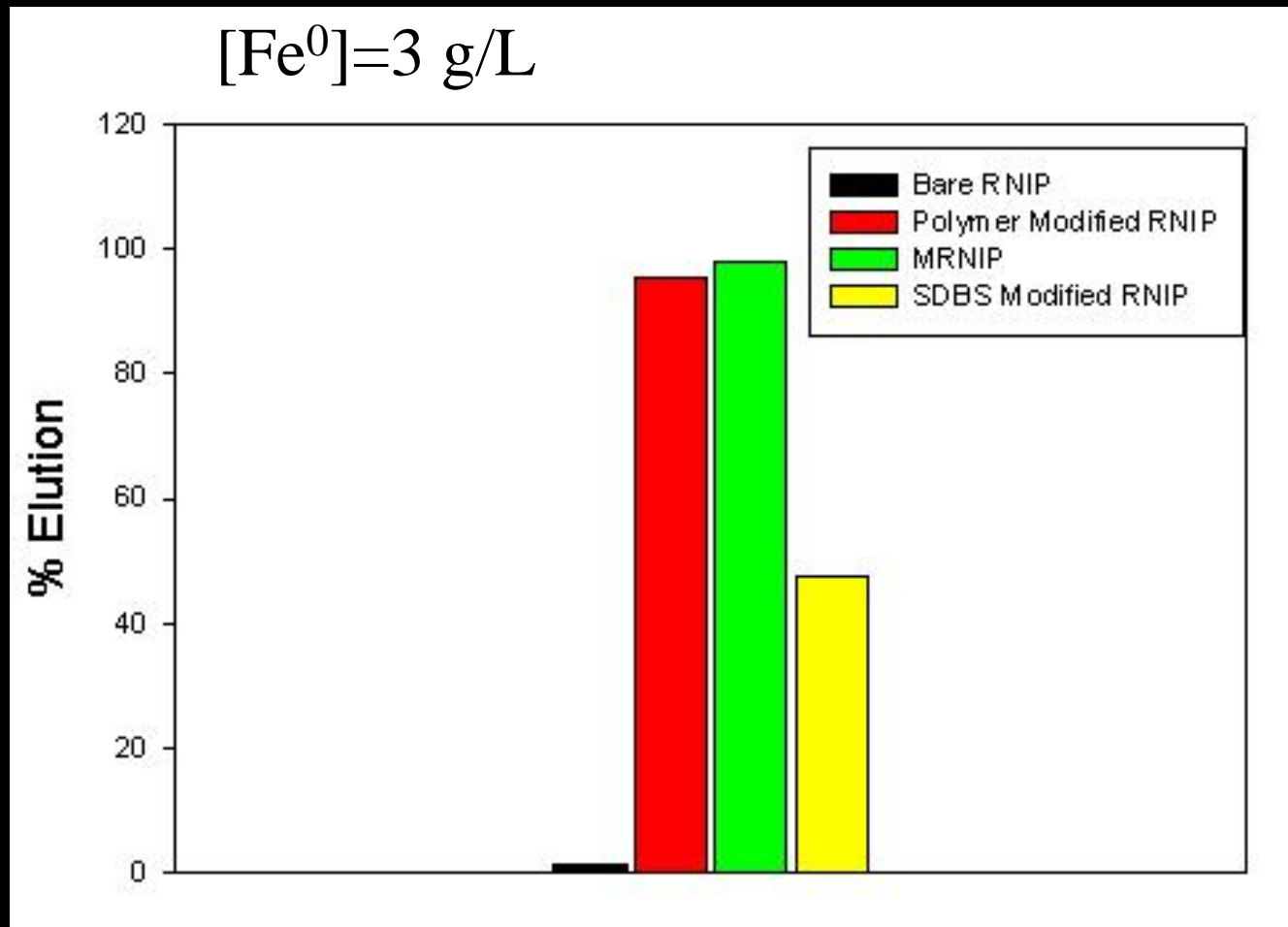
Charge and steric stabilization minimize particle-particle and particle-media interactions



## 3. Affinity for DNAPL

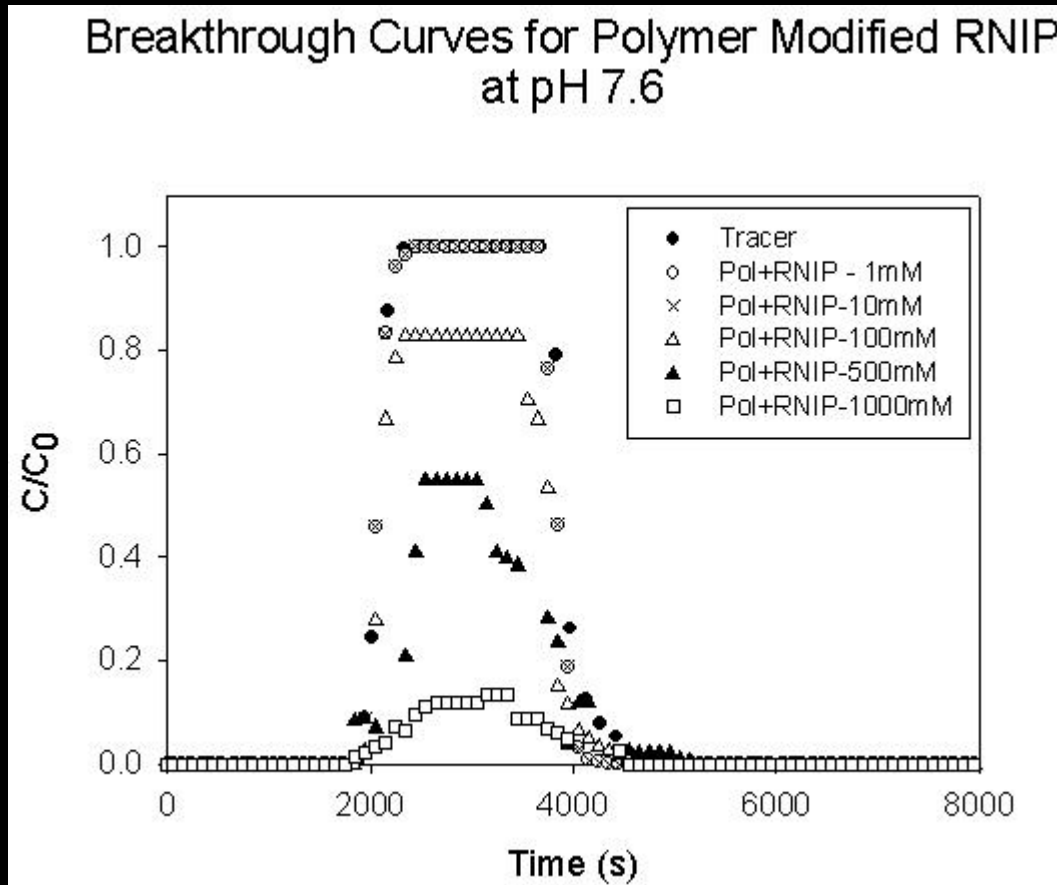
Surface coatings provide affinity for NAPL

# Effect of Different Modifiers



Potential to select transport distance

# Hydrogeochemical Effects on Nanoiron Transport



- ✓ Transportability is a strong function of site hydrogeochemistry.
- ✓ Systematic evaluation of hydrogeochemical effects is needed

# Nanoiron Toxicity?

Why suspect that ZVI causes OS?

- Surface chemistry
- Reactive oxygen species
- Literature-daphne, fish ..... glutathione depletion

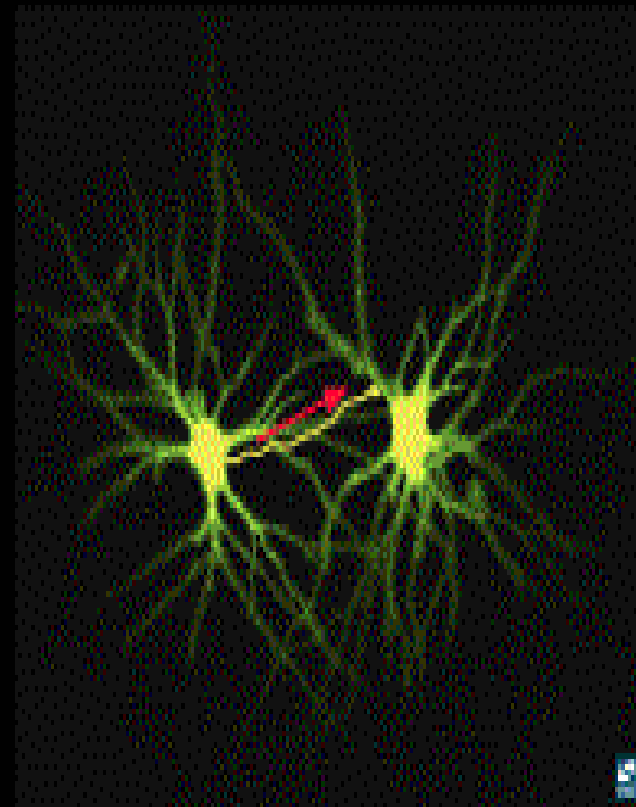
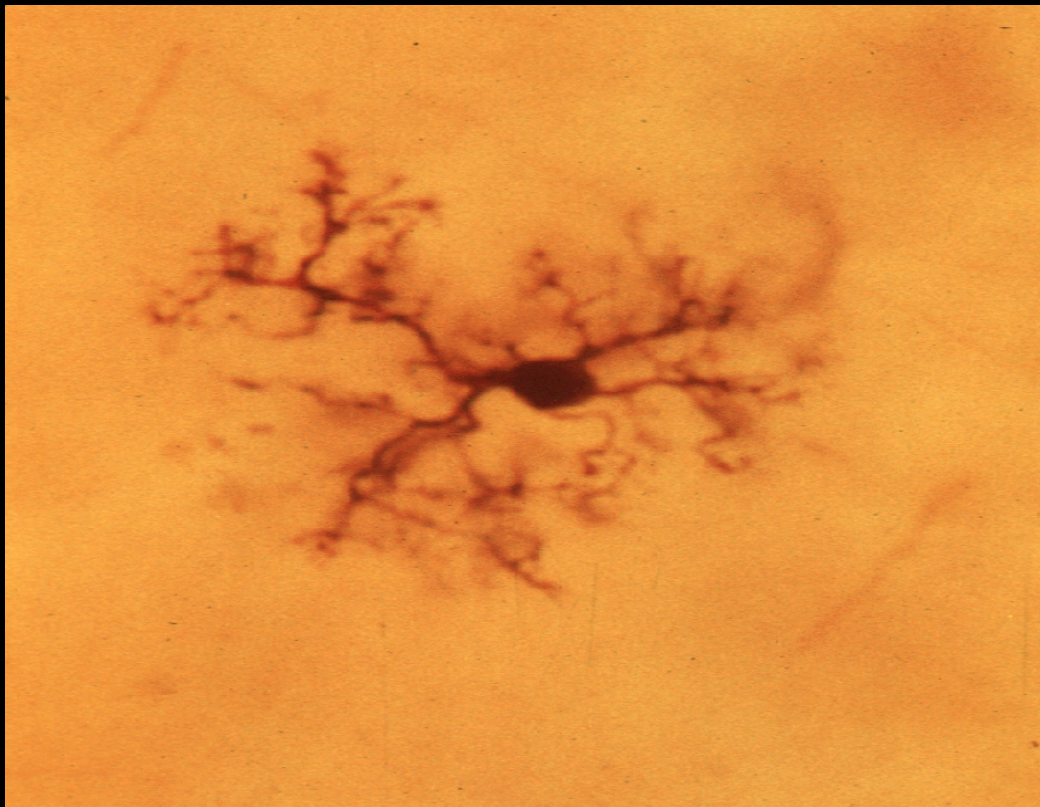
Why the brain?

- Serious consequences from damage
- Target of OS-lipid content...high energy use

# Nanoiron Toxicity

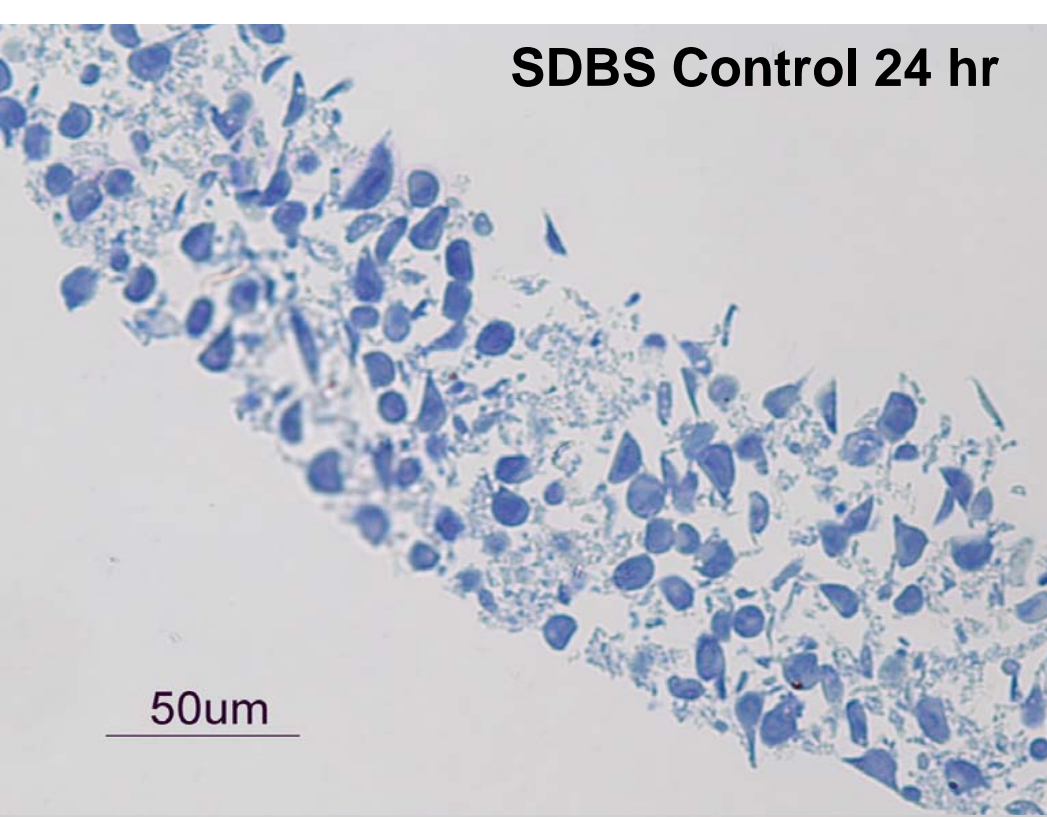
## Mammalian brain macrophage (microglia)

- ✓ Fe<sup>0</sup> and modified-Fe<sup>0</sup> (1-30 ppm)
- ✓ Whole-cell and genomic responses
  - ✓ OS-specific endpoints
- ✓ TEM, confocal microscopy

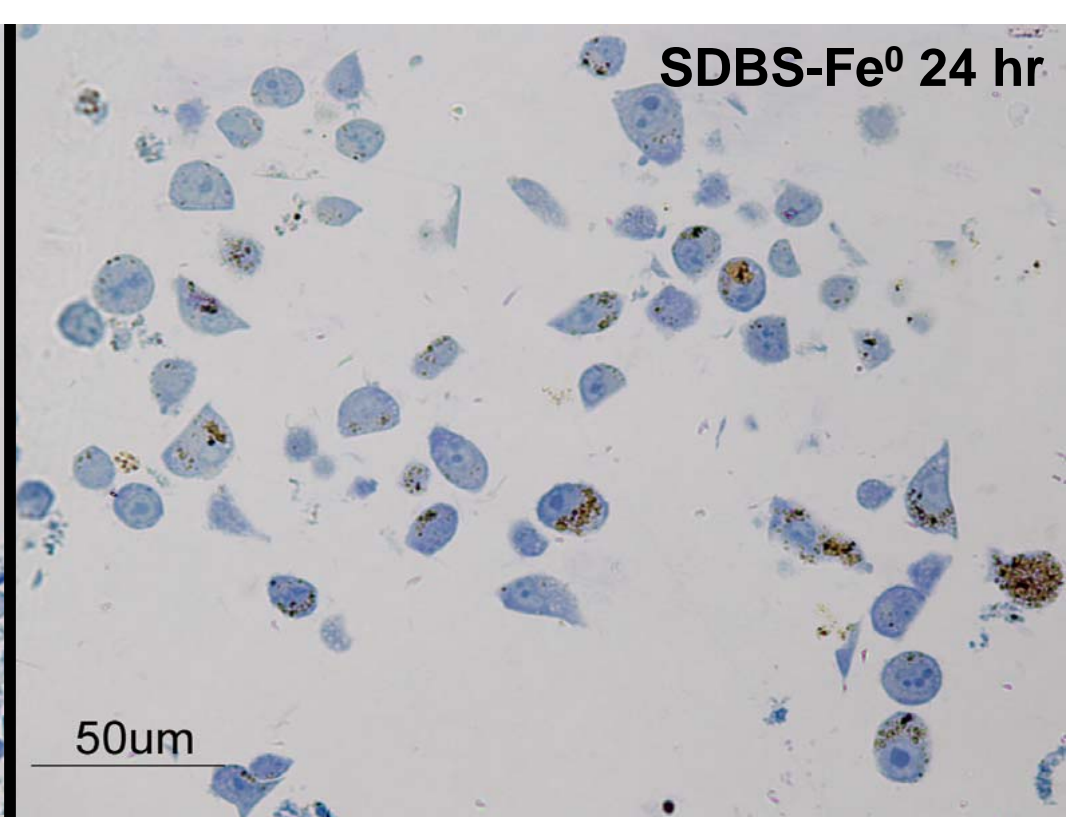




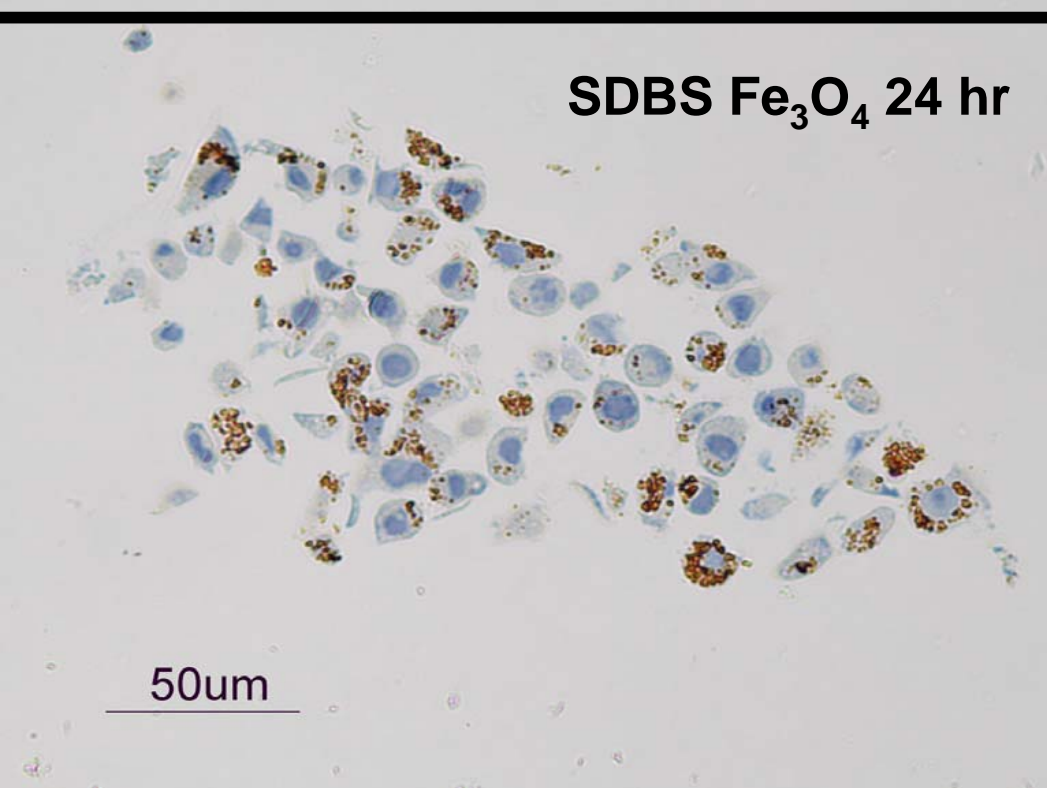
**SDBS Control 24 hr**



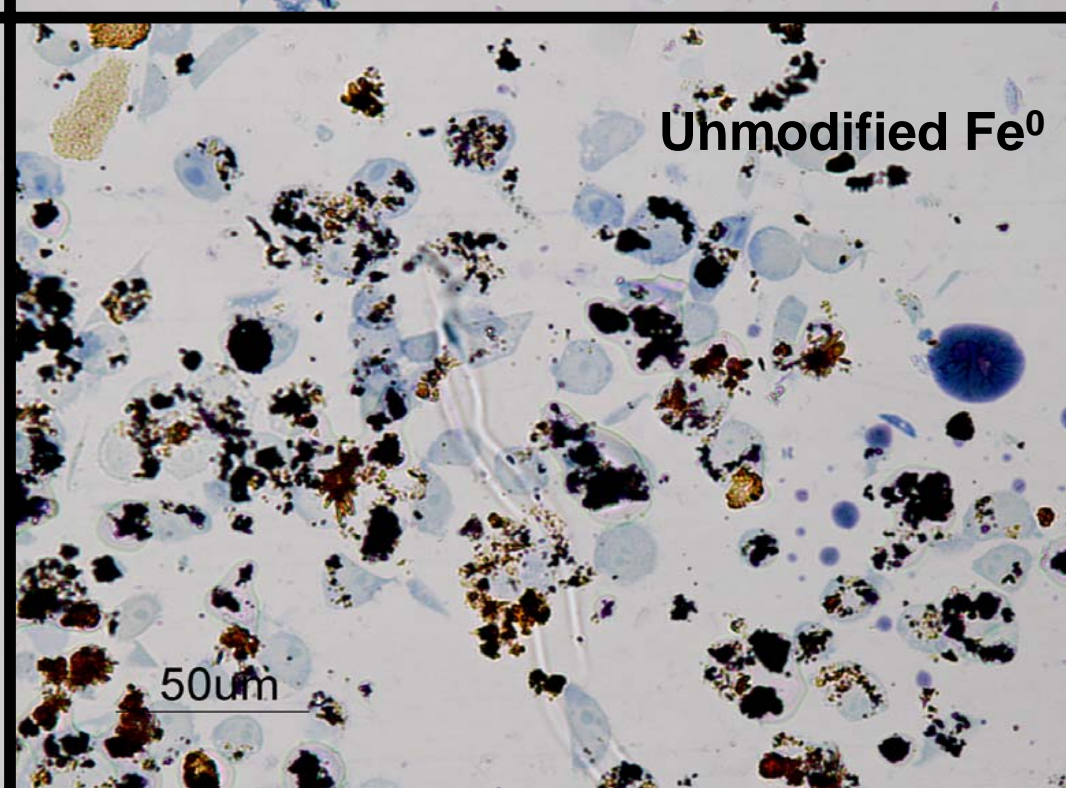
**SDBS-Fe<sup>0</sup> 24 hr**

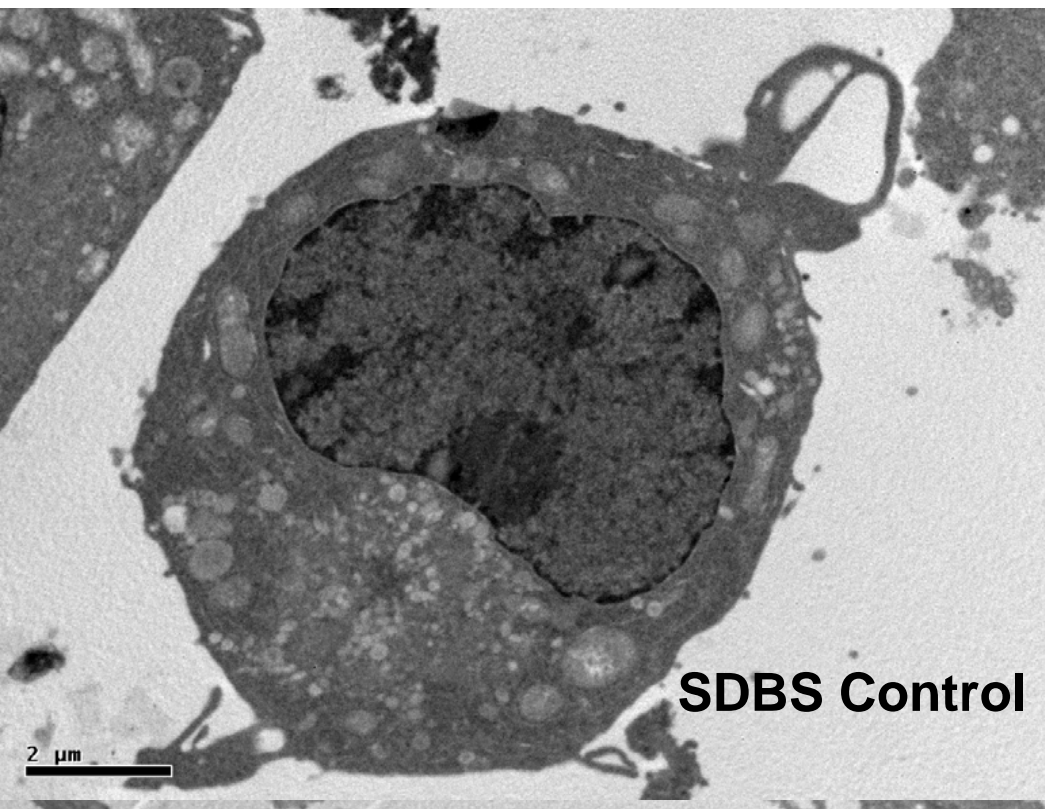


**SDBS Fe<sub>3</sub>O<sub>4</sub> 24 hr**

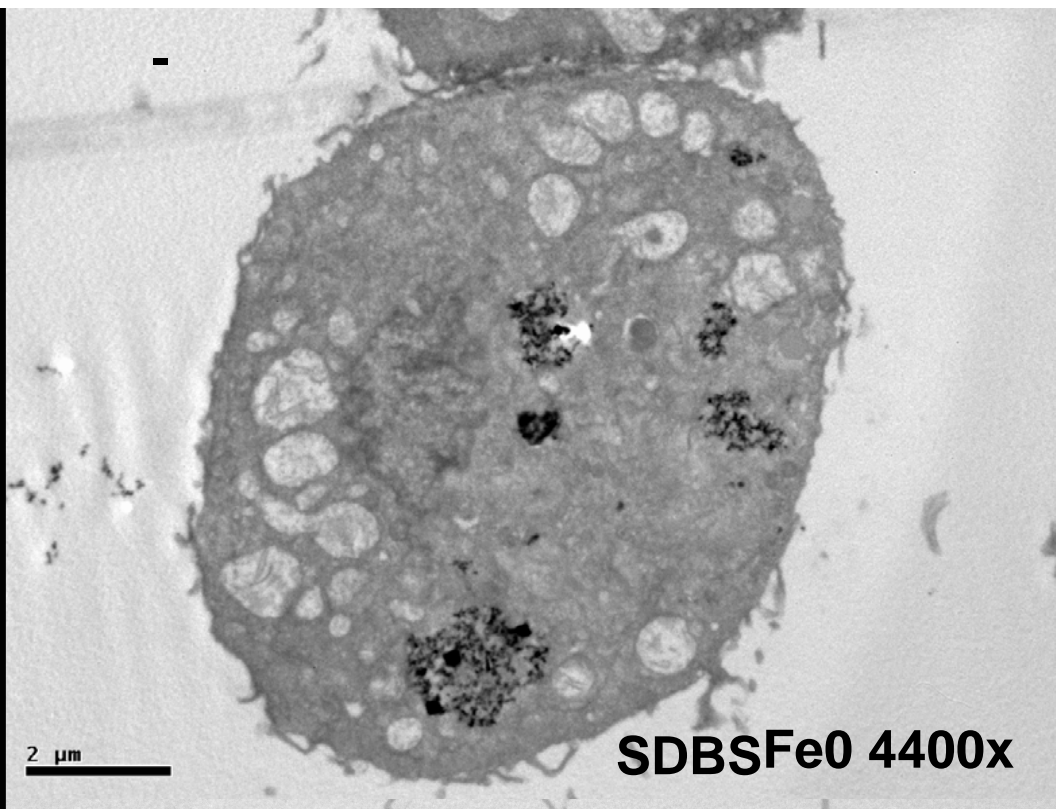


**Unmodified Fe<sup>0</sup>**

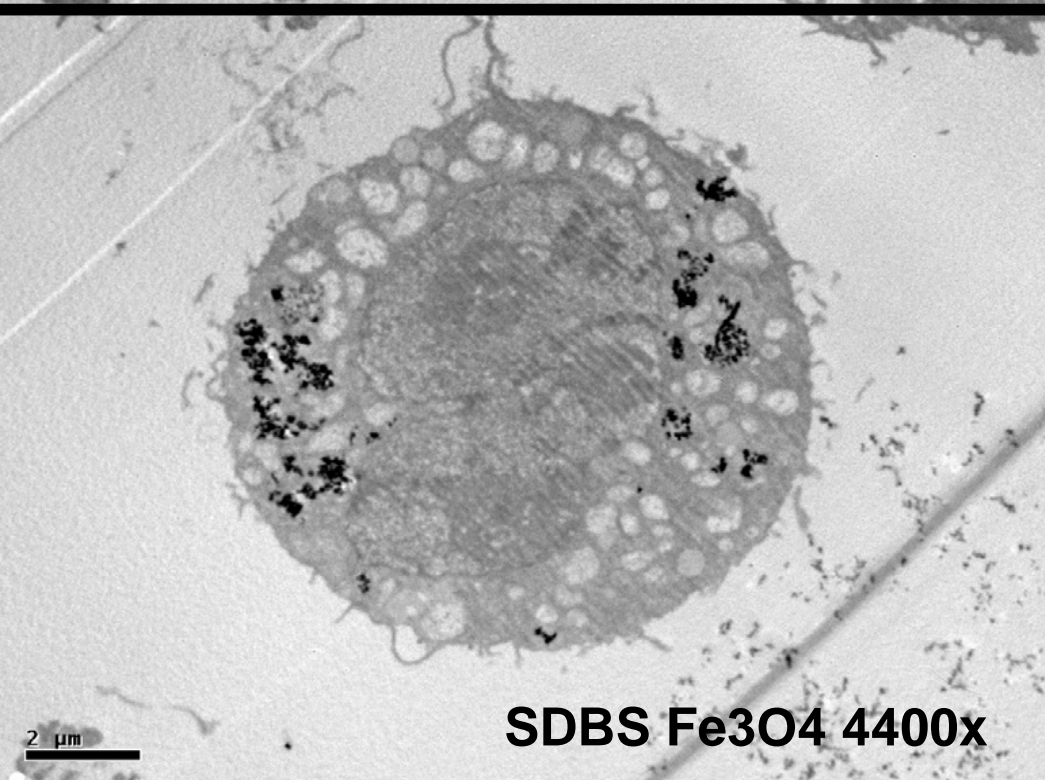




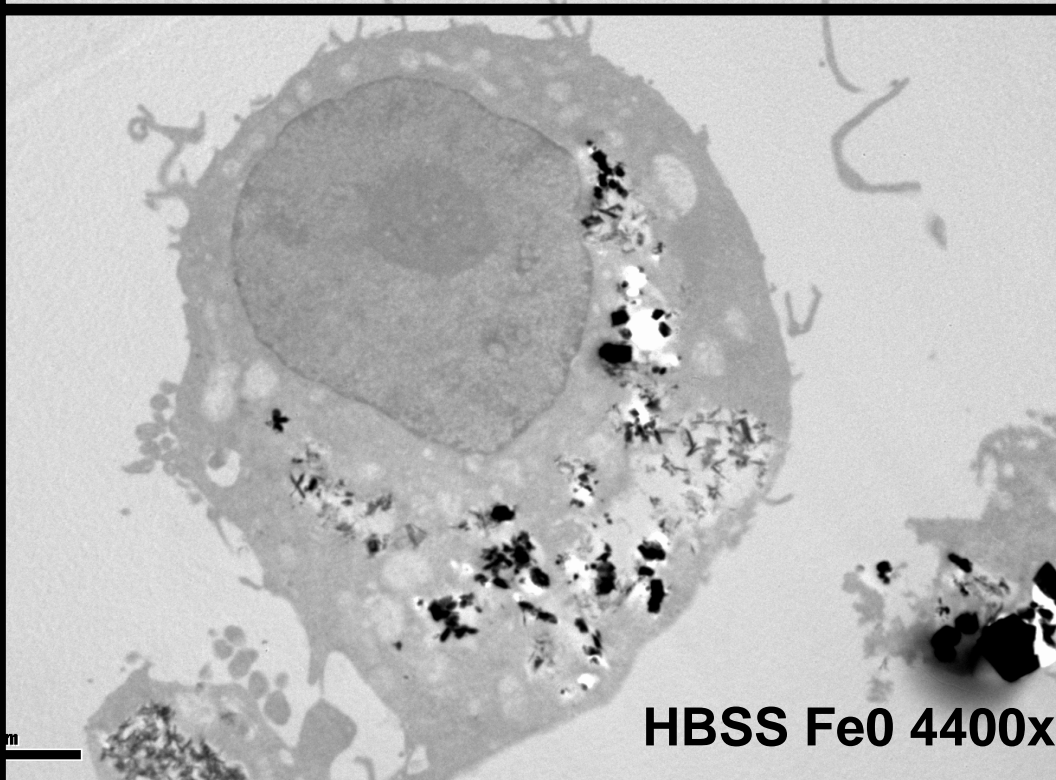
**SDBS Control**



**SDBSFe0 4400x**



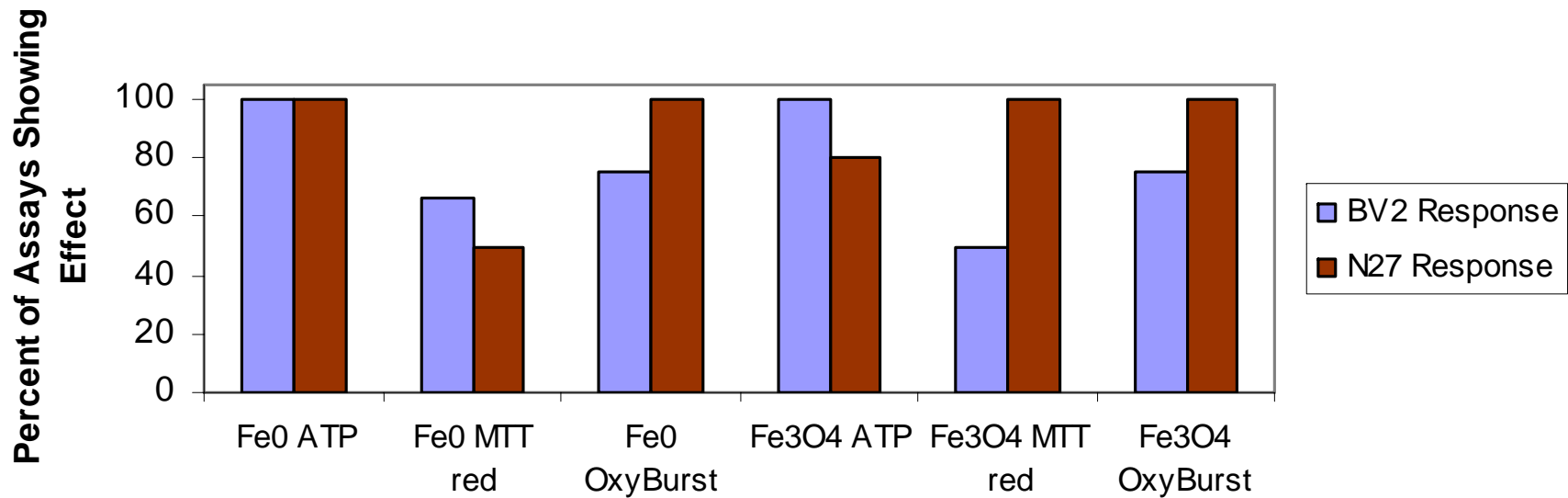
**SDBS Fe<sub>3</sub>O<sub>4</sub> 4400x**



**HBSS Fe0 4400x**

# Fe<sup>0</sup>-induced Oxidative Stress in CNS Cells

Response of Microglia (BV2) and Mesencephalic Neurons (N27) to Iron Nanoparticles (1-30 ppm)



Future Studies:  
Apo E Mice and Medaka Fish

# Conclusions

- Potential toxicity risk warrants careful evaluation
- $\text{Fe}^0$  fairly rapidly oxidizes to Fe-oxides
  - $\text{Fe}^0$  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

# 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

# Acknowledgement

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- CMU project team