Remediation of Perchlorate, NDMA, and Chlorinated Solvents Using Nanoscale ZVI

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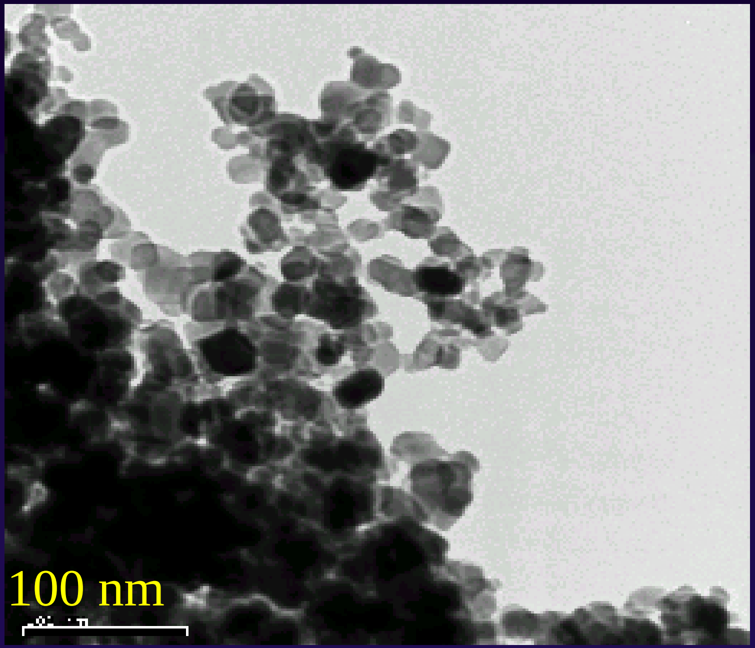
Presentation Outline

- Technology Overview
- Project Motivation
- Demonstration Project: California Site
  - Bench test approach
  - Bench test results
  - Pilot test plan
- R&D Needs

Nanoscale ZVI – Technology Overview



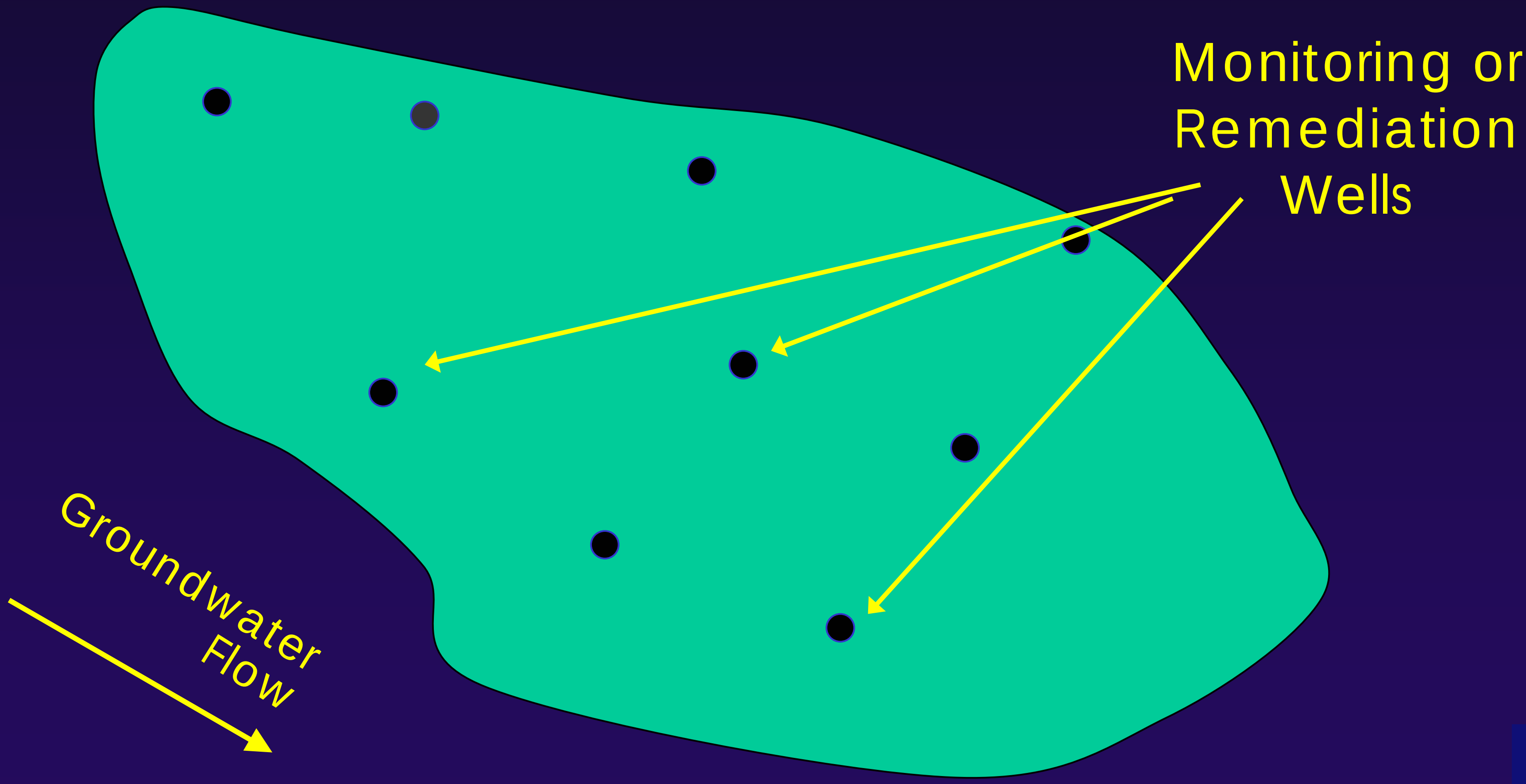
- Typical diameter < 100 nm
- Specific surface area: 33.5 m^2/g (vs. < 1 m^2/g for commercial Fe powder)
- Treatment rates 10 to 100 times faster than ZVI powder
- Addition of noble metal (< 1% wt.) dramatically increases treatment rates
- Ease of deployment:
  - Direct injection into wells
  - Ex situ slurry reactors (e.g., GAC, zeolite)
  - Fixed to membranes

Nanoscale ZVI: Compounds Treated

- Chloroethenes – PCE, TCE, cDCE, VC
- Chloromethanes – CTET, Chloroform
- Chlorobenzenes
- Organochlorine pesticides (e.g., Lindane)
- PCBs
- N-nitrosodimethylamine (NDMA)
- Cr^{VI}, As^{V}, Pb^{II}
- Perchlorate, NO_3^-
- *Everything else treated by granular ZVI, except > 10x faster*

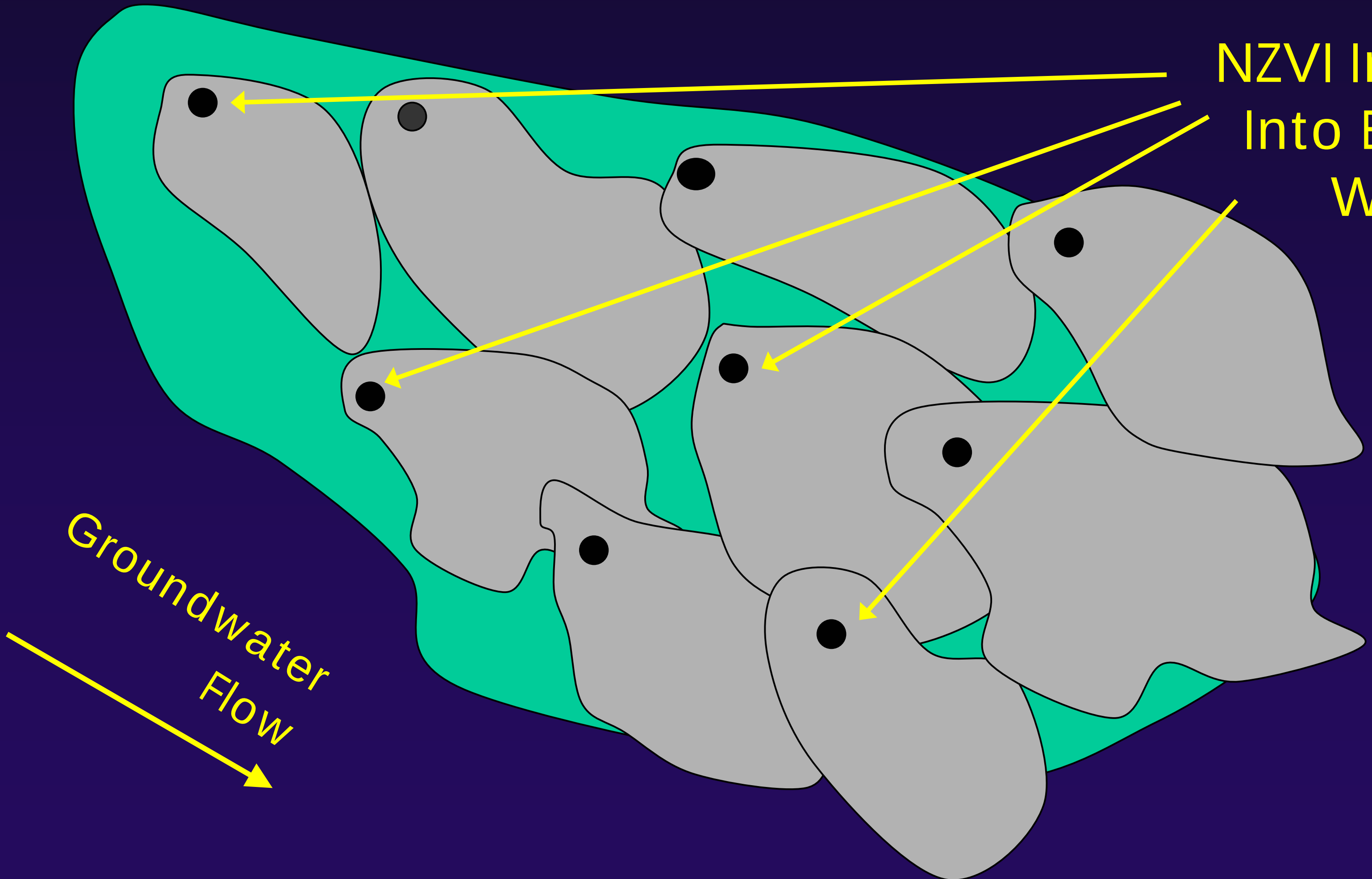
Nanoscale ZVI – In Situ Approaches

Plume-Wide Remediation



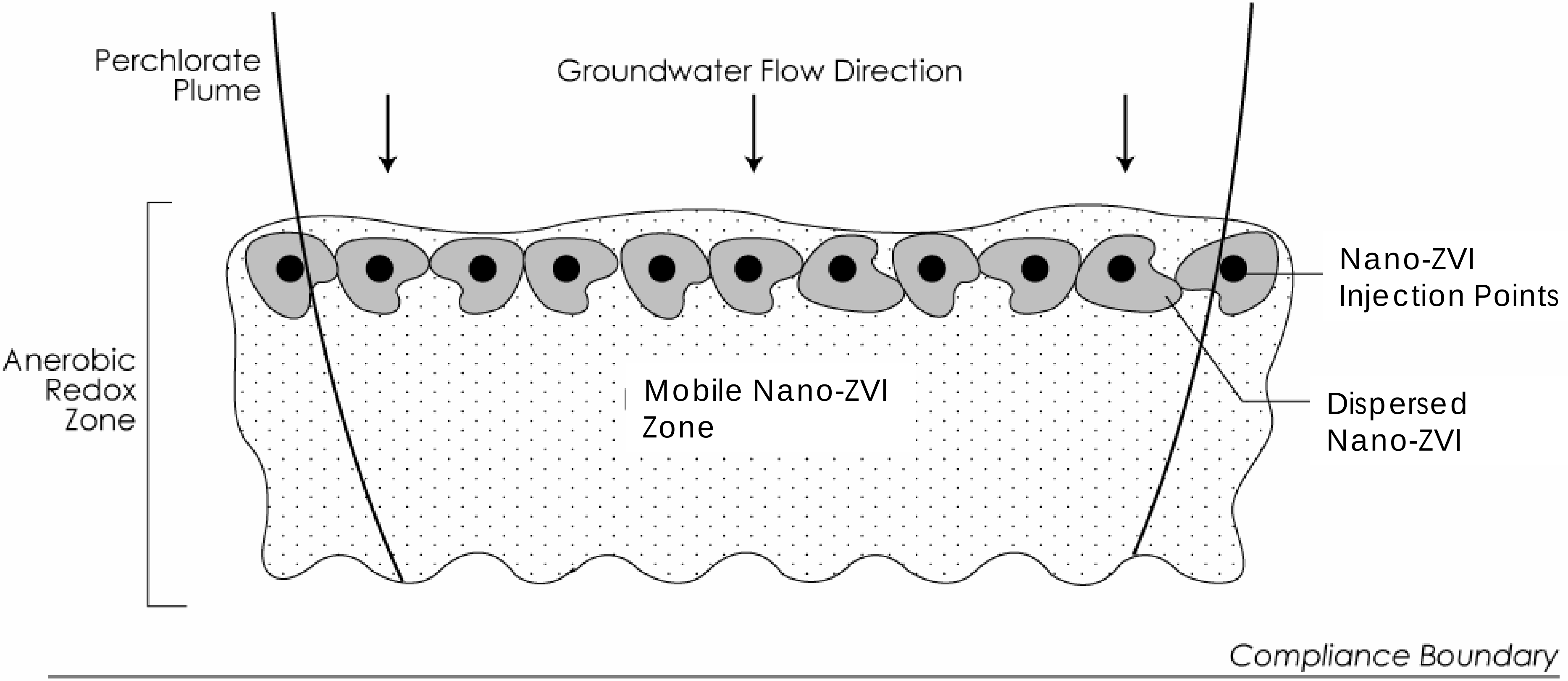
Nanoscale ZVI – In Situ Approaches

Plume-Wide Remediation



Nanoscale ZVI – In Situ Approaches

Plume Containment via PRB



Project Motivation

- Perchlorate (ClO_4) is a national threat to drinking water
  - Produced, handled, or used in at least 44 states
  - Present in groundwater supplies in $\geq$ 18 states
  - Detected in water supplies of > 15 M people in CA, AZ, NV
- Incidence of ClO_4 detection continues to increase
- ClO_4 is highly soluble and generally un-reactive in groundwater
- Plumes are frequently large and deep
- Conventional ex situ treatment technologies (e.g., ion exchange) carry high capital cost

Project Motivation

- ClO_4 plumes often contain *N*-nitrosodimethylamine (NDMA), and chlorinated solvents (especially at rocket test sites)
- Few (if any) conventional technologies can treat all these compounds at once
- Nanoscale ZVI has potential to treat these compounds simultaneously, in situ
- However, subsurface transport and longevity of NZVI poorly understood

Project Motivation

- Moore et al. (2003) demonstrated abiotic dechlorination of ClO_4 in presence of granular and powder ZVI, and
- Concluded that rates were too slow for application for site remediation…But,
- Did not examine nanoscale ZVI

Rate and Extent of Aqueous Perchlorate Removal by Iron Surfaces

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Environ. Sci. Technol. **2003**, *37*, 3189−3198

Project Motivation

- Gui et al. (2000) demonstrated effective abiotic dechlorination of NDMA in presence of granular ZVI, and Nickel-ZVI;
- Transformation rates have not been reported for Nano-ZVI

Reduction of *N*-Nitrosodimethylamine with Granular Iron and Nickel-Enhanced Iron. 1. Pathways and Kinetics

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Environ. Sci. Technol. 2000, *34*, 3489−3494

Technology Demonstration: Treatment of ClO_4, NDMA, Chloroethenes, and Nitrate at Aerospace Site

Sacramento, California

Demonstration Objectives

Phase I: Bench Test (On-going)

- Confirm treatability
- Determine site-specific Nano-ZVI loading requirements
- Estimate site-specific transformation rates
- Determine treatment capacity (reactive longevity) under site-specific conditions
- Measure retardation and transport of Nano-ZVI in aquifer columns

Phase II: Pilot Test (Planned)

- Nano-ZVI delivery and performance in active recirculation cell
- Nano-ZVI delivery and performance in passive PRB

Example Batch Reactors

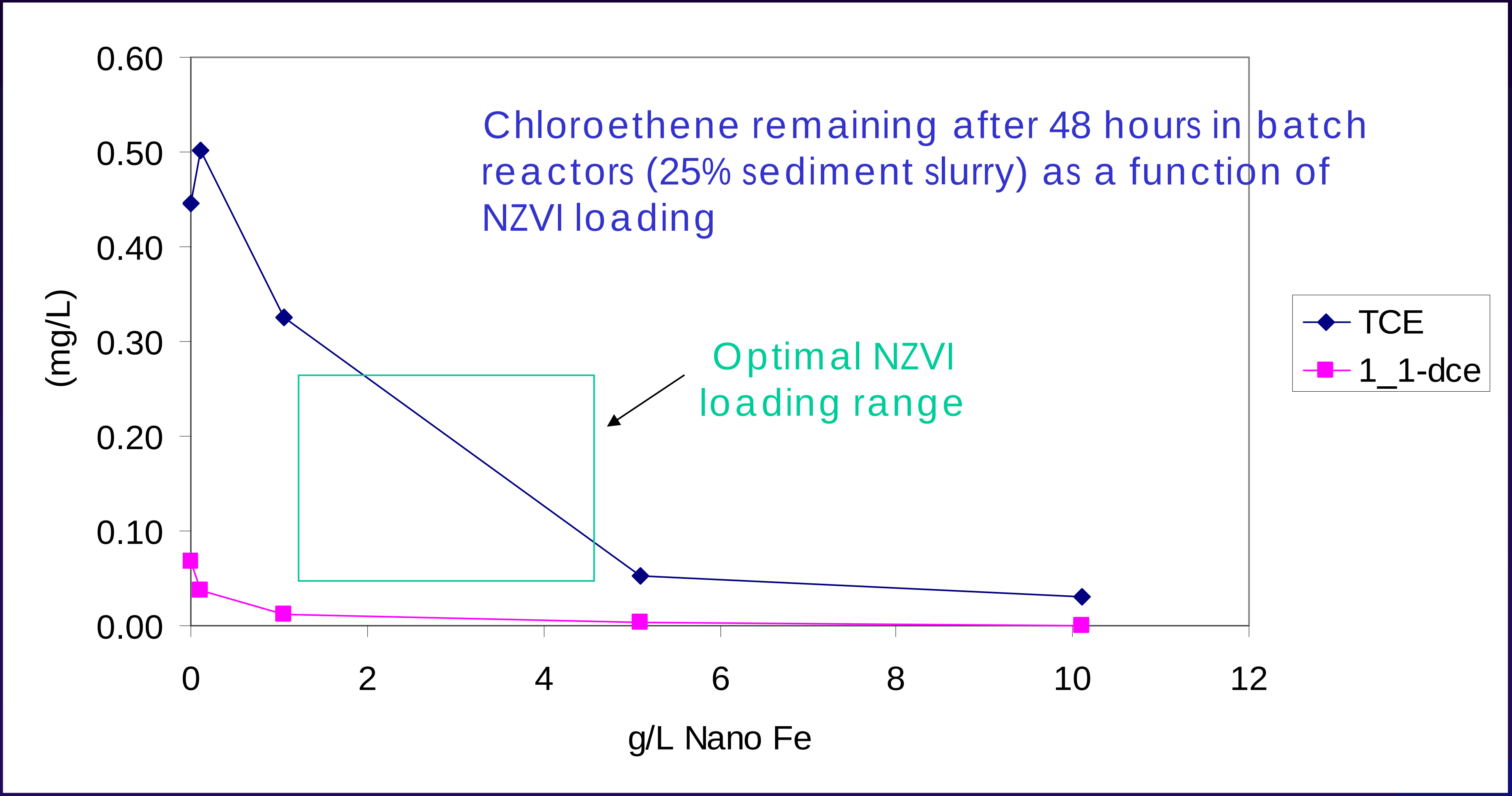
Optimal Loading Tests (ongoing)

Objective: estimate optimal range for NZVI loading concentration

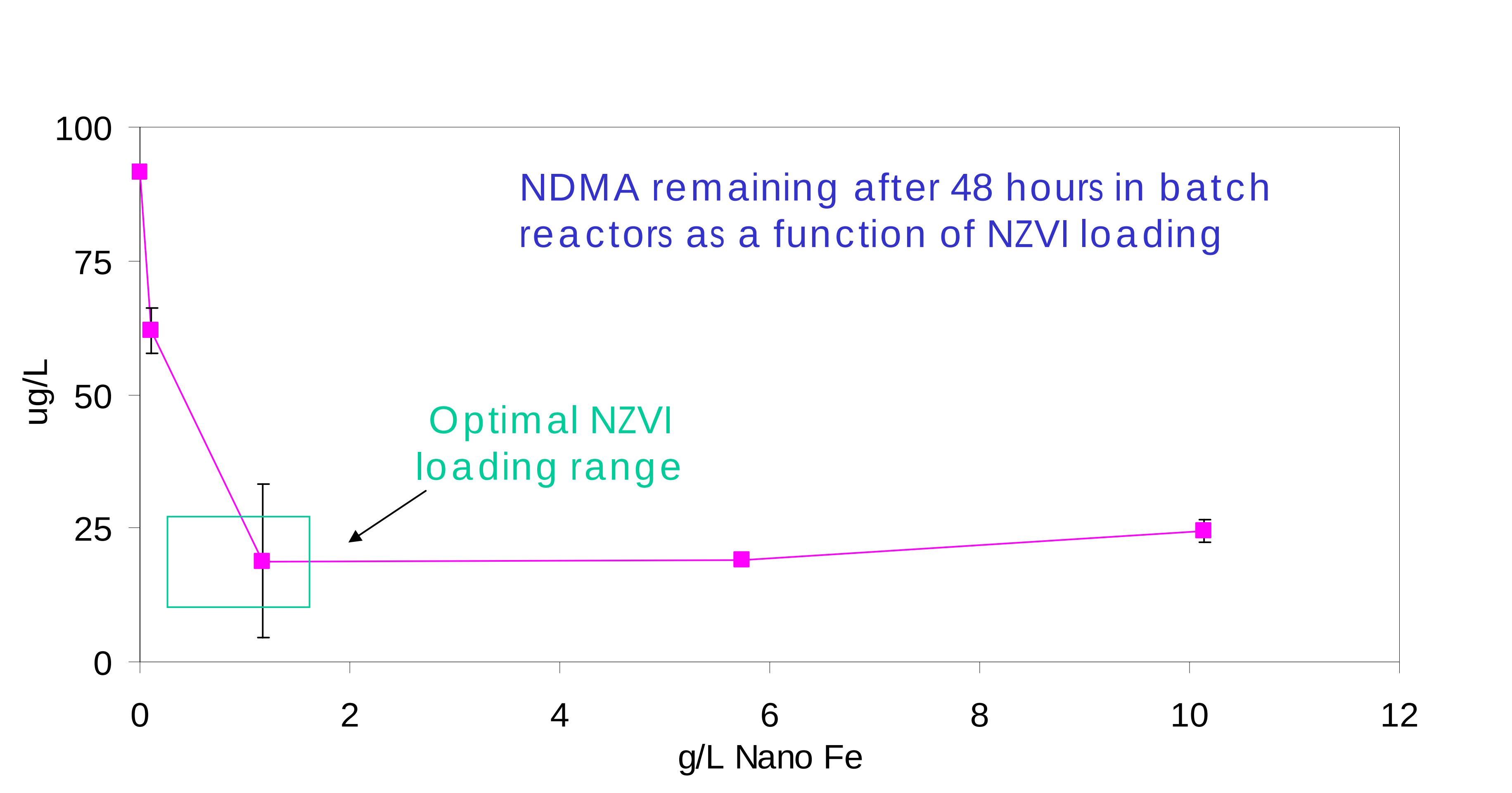
Set-up

- Separate batch reactors treated with either 0, 0.5, 1, 5, or 10 g/L Nano-ZVI
- 25% aquifer sediment slurry in site groundwater
- React for 48 hours
- Measure contaminant remaining
- Only tested chloroethenes and NDMA so far…

Preliminary Results
Determination of Optimal Loading for Chloroethene Treatment



Preliminary Results
Determination of Optimal NZVI Loading For NDMA Treatment



Optimal Loading Tests – Summary of Preliminary Results

- Nano-ZVI effective treatment agent for TCE, NDMA
- TCE and perchlorate are driver compounds (loading requirement for TCE >> NDMA)
- Optimal Nano-ZVI loading requirement: 2 to 5 g/L

Transformation Rate Tests

<u>Objectives</u>

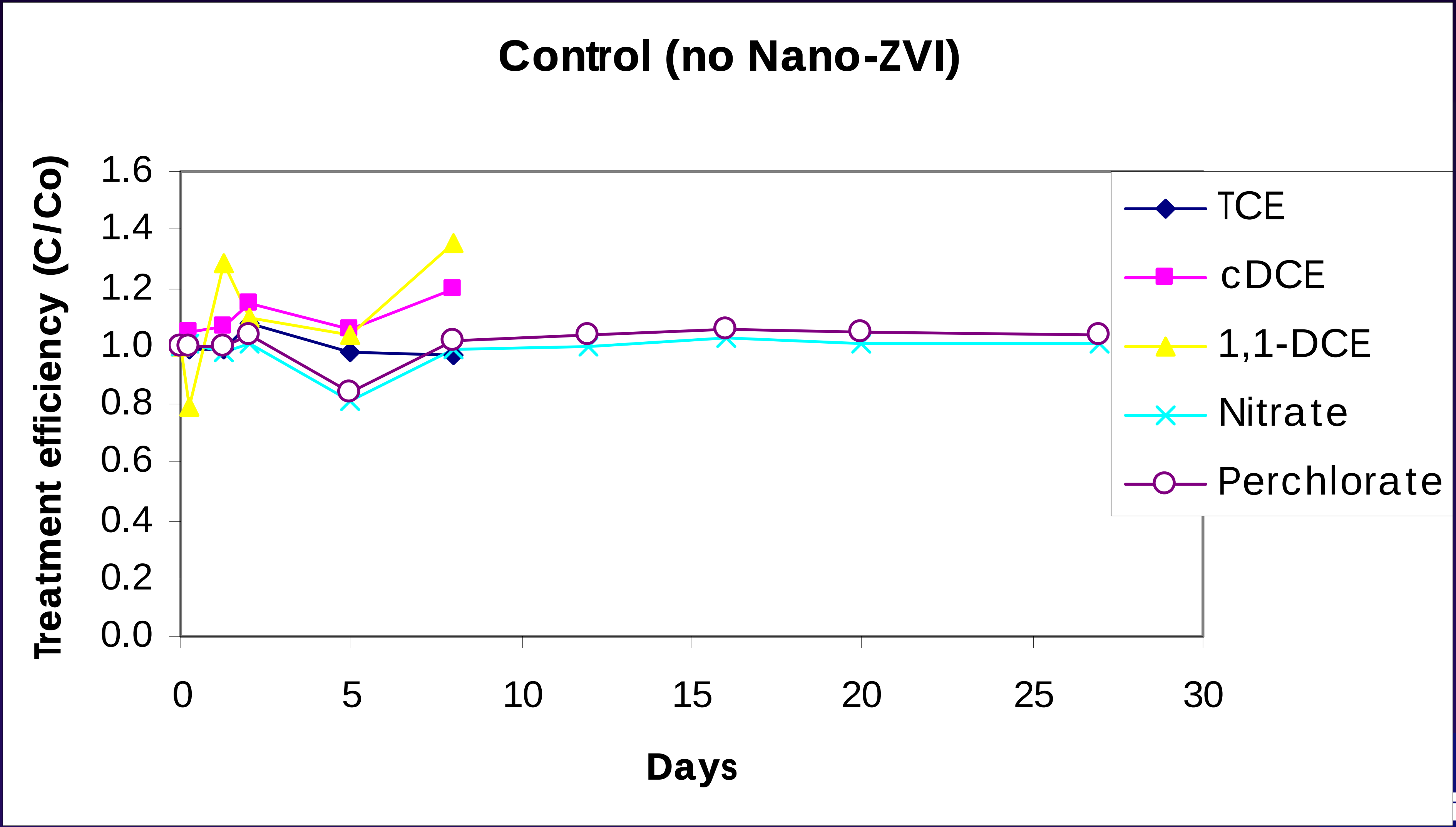
(1) estimate ClO_4, chloroethene, and nitrate transformation rates in the presence of 10 g/L Nano-ZVI

(2) compare rates for commercial and laboratory synthesized NZVI

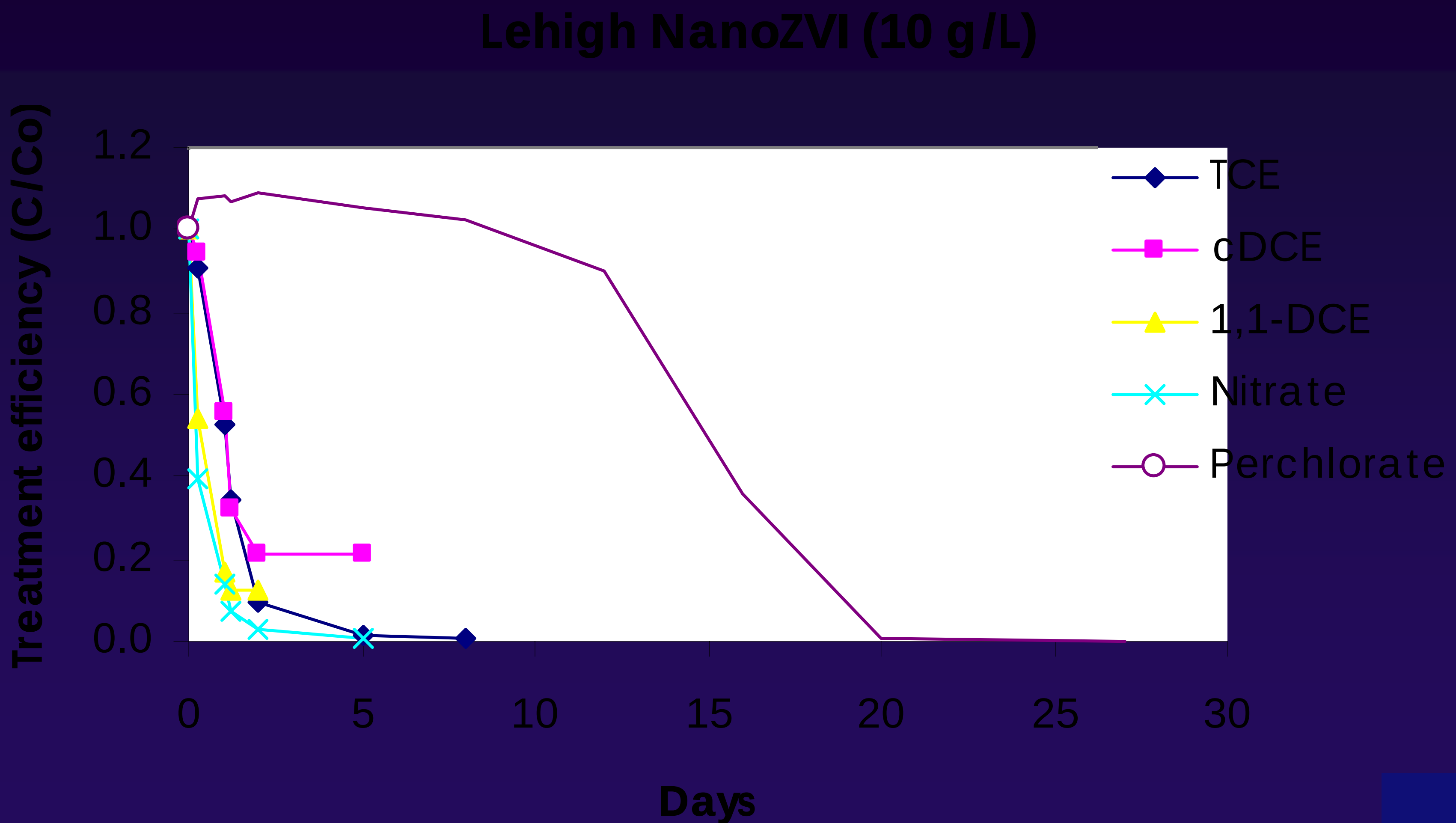
<u>Set-Up</u>

- Duplicate reactors, sampled at various intervals for 27 days
- 25% aquifer sediment slurry in site groundwater
- Included control reactors (sediment + water, w/o Nano-ZVI)
- Initial concentrations: ClO_4 = 14 ppm; TCE= 2 ppm; nitrate = 20 ppm

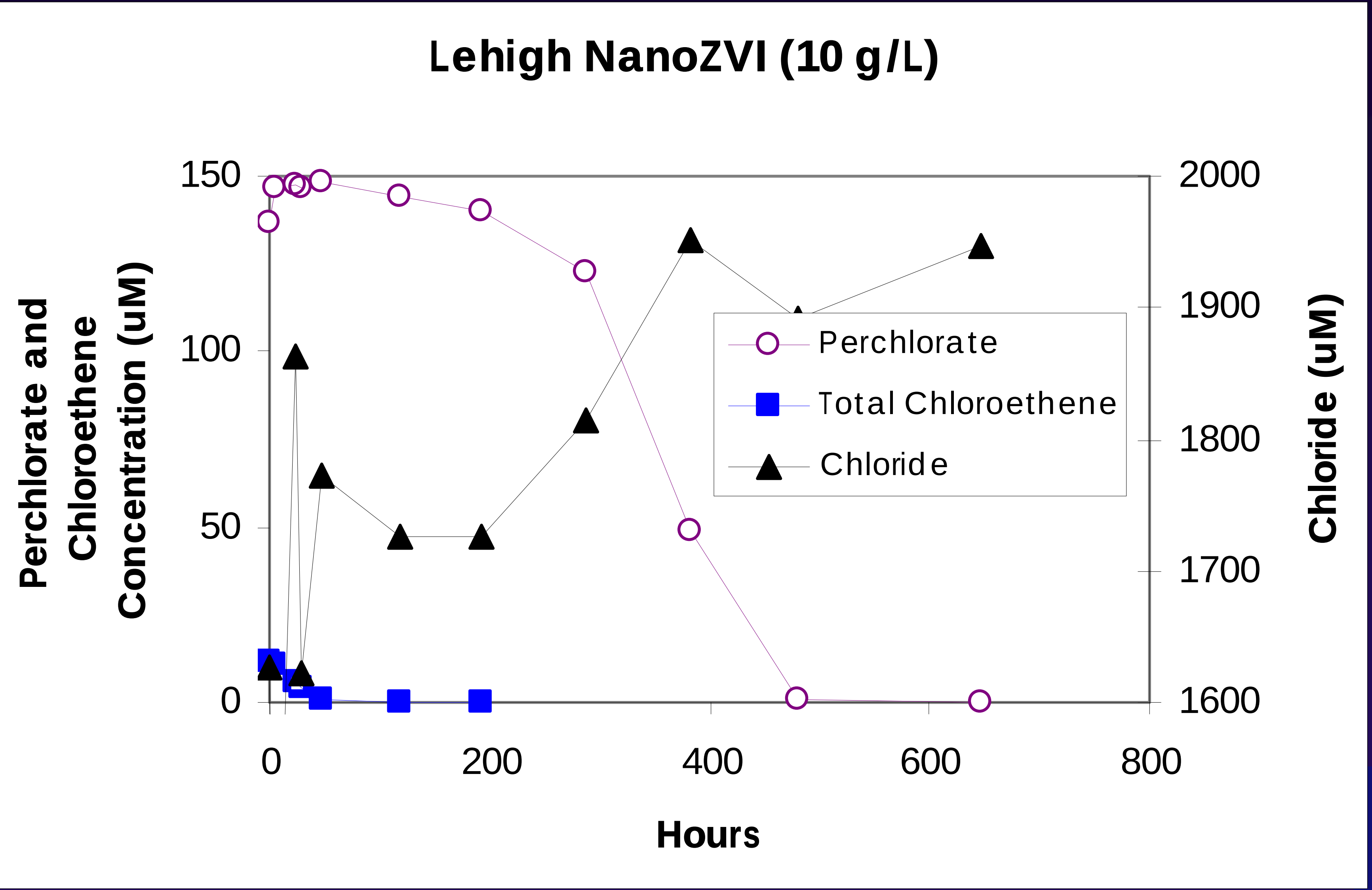
Transformation Rate Tests – Controls



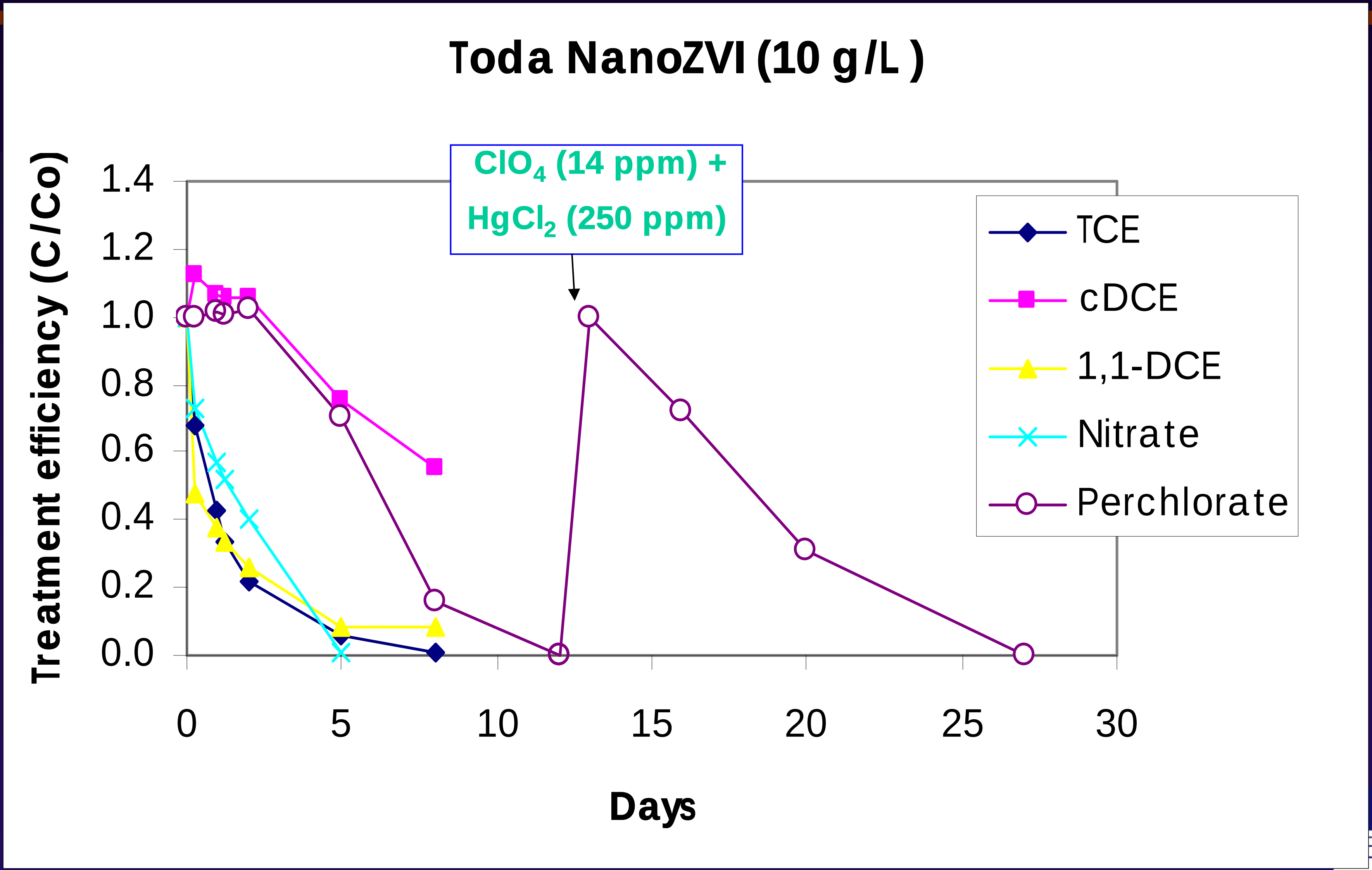
Transformation Rate Tests
Lehigh Nano-ZVI



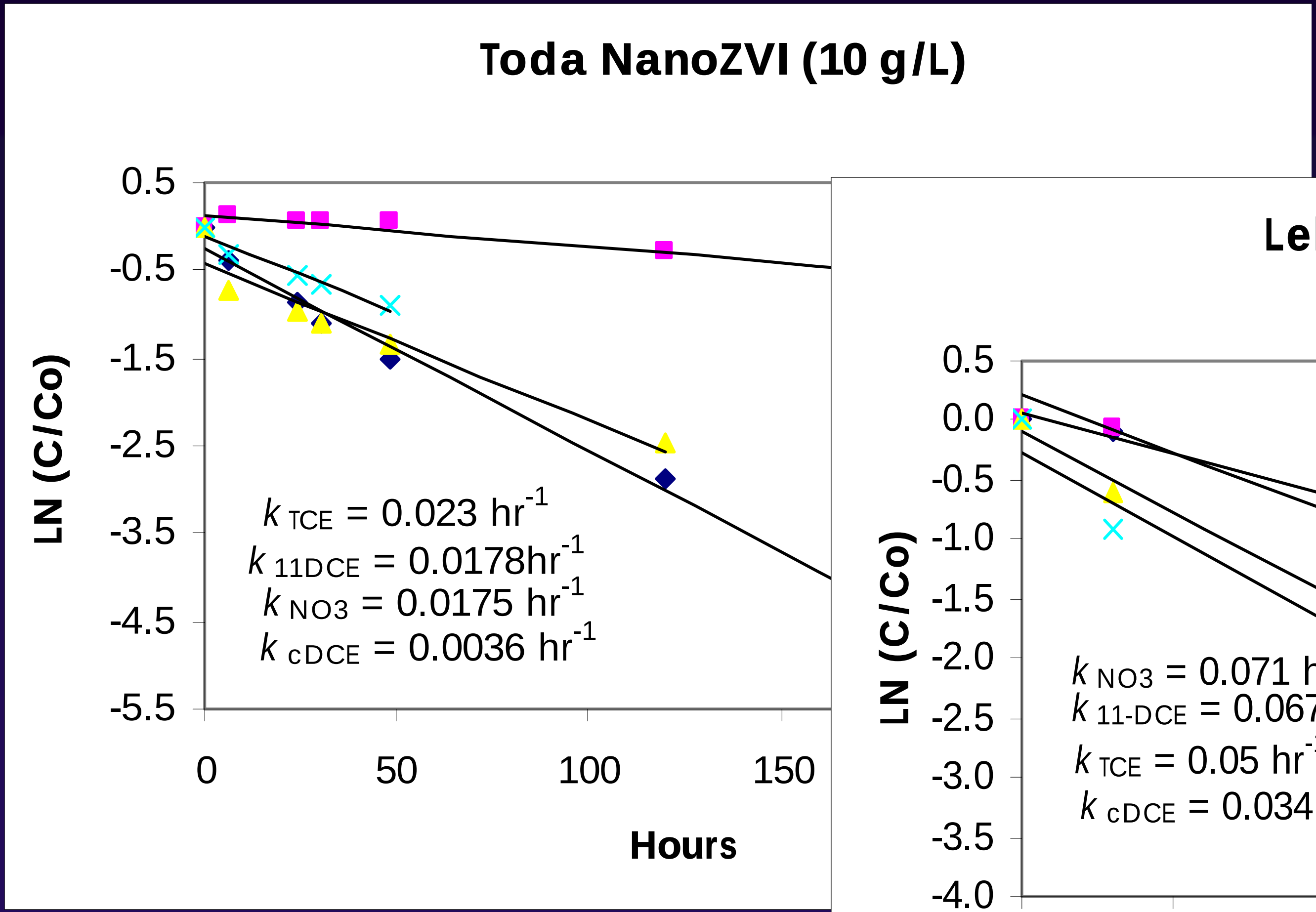
Transformation Rate Tests
Lehigh Nano-ZVI

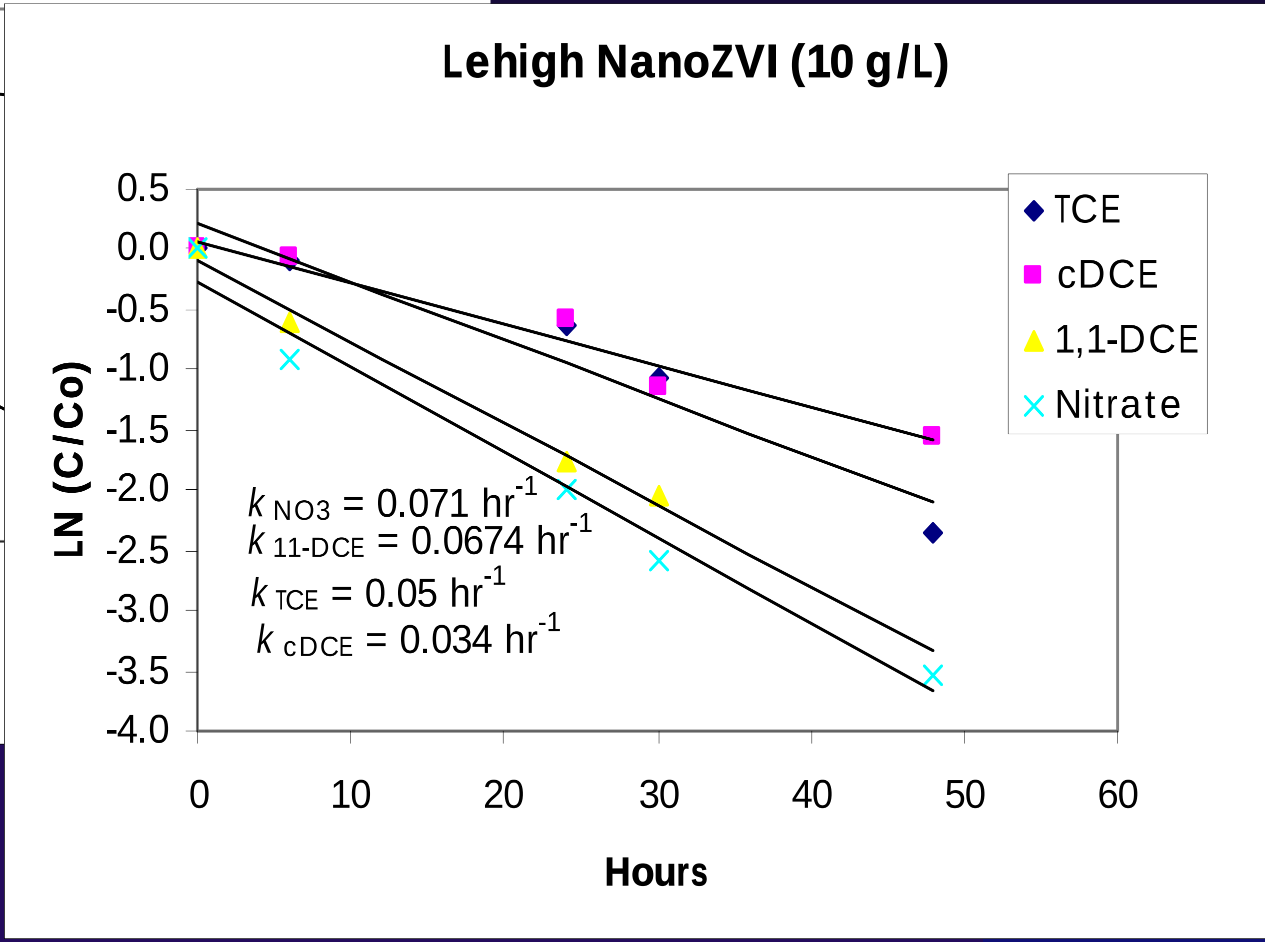


Transformation Rate Tests
Toda Nano-ZVI

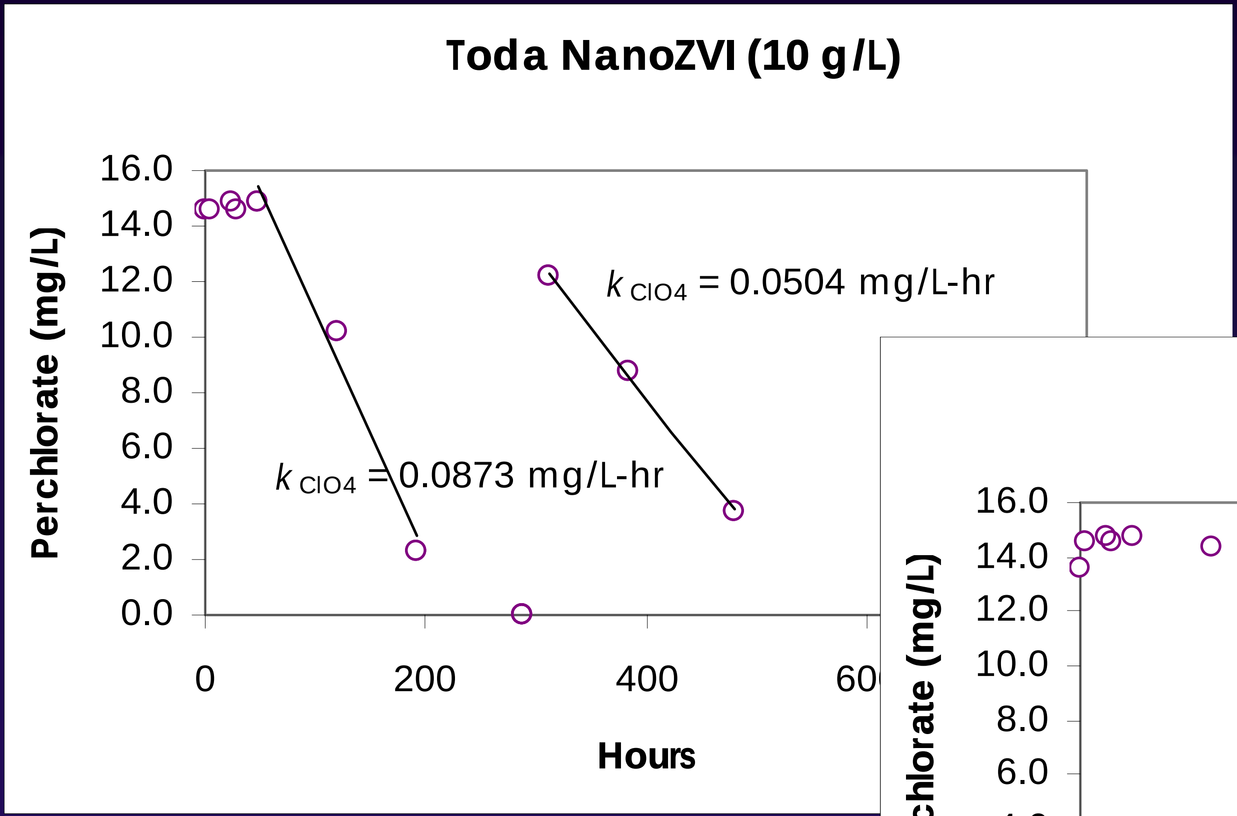


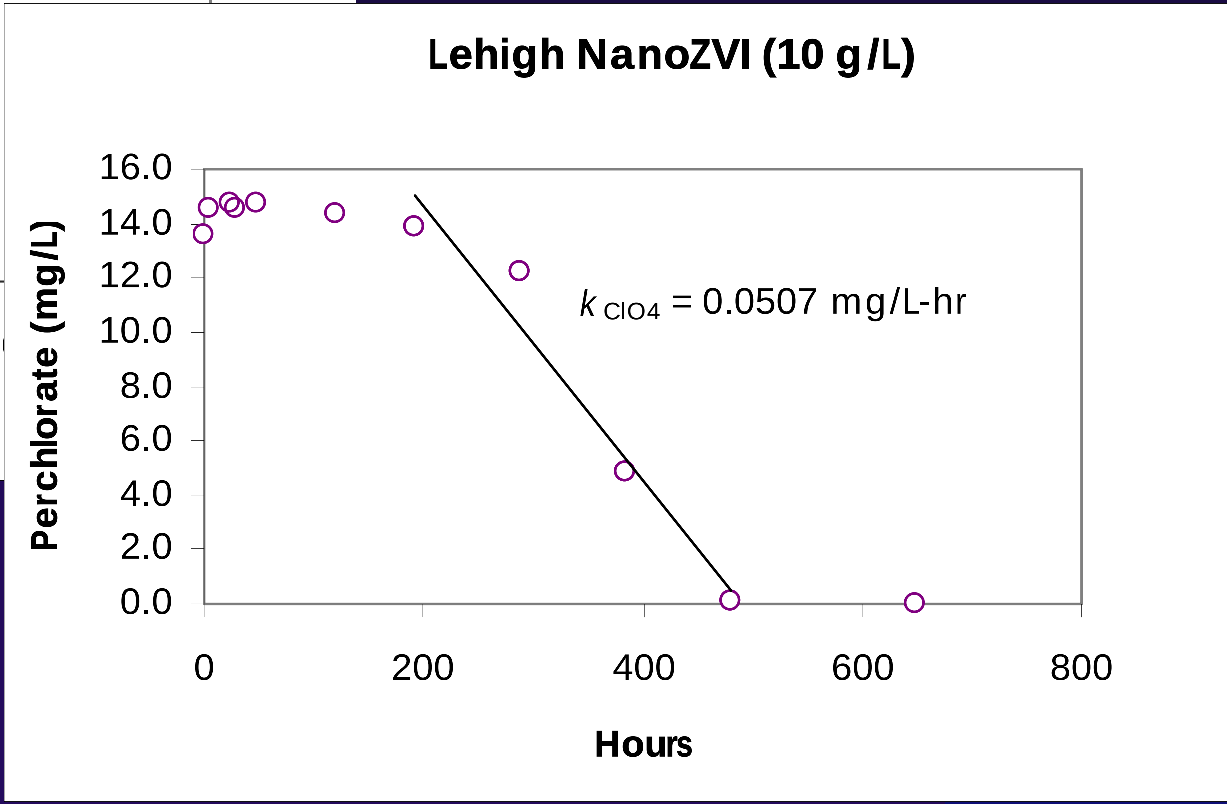
Transformation Rate Tests
Comparison of Nano-ZVI Performance for Chloroethenes





Transformation Rate Tests
Comparison of Nano-ZVI Performance for Perchlorate





Transformation Rate Test – Summary of Observed Transformation Rates

Constituent	Toda Nano-ZVI				Lehigh Nano-ZVI			
	Zero Order (mg/L-hr)	First Order (hr^{-1})	Half-Life (d)	Surface-Area Normalized Rate Coefficient ($L/hr/m^2$)	Zero Order (mg/L-hr)	First Order (hr^{-1})	Half-Life (d)	Surface-Area Normalized Rate Coefficient ($L/hr/m^2$)
Perchlorate	0.0504				0.0507			
TCE		0.023	1.3	6.57E-05		0.050	0.6	1.49E-04
1,1-DCE		0.018	1.6	5.09E-05		0.067	0.4	2.01E-04
c-DCE		0.004	8.0	1.03E-05		0.034	0.8	1.01E-04
Nitrate		0.018	1.7	5.00E-05		0.071	0.4	2.12E-04

Transformation Rate Test – Summary of Preliminary Findings

- Nano-ZVI treats chloroethenes, ClO_4, NDMA, and nitrate in Site groundwater; ClO_4 is rate-limiting step.
- Lehigh Nano-ZVI degraded chloroethenes 2 to 3 times faster than Toda Nano-ZVI.
  - Why? Lehigh material has fewer impurities (i.e., oxides)
- Degradation of ClO_4 was preceded by lag period for both for Toda NZVI and Lehigh NZVI
  - Why? Possible that anions competitively inhibited ClO_4 sorption to Nano-ZVI (this is a critical first step)

Transformation Rate Test – Summary of Preliminary Findings

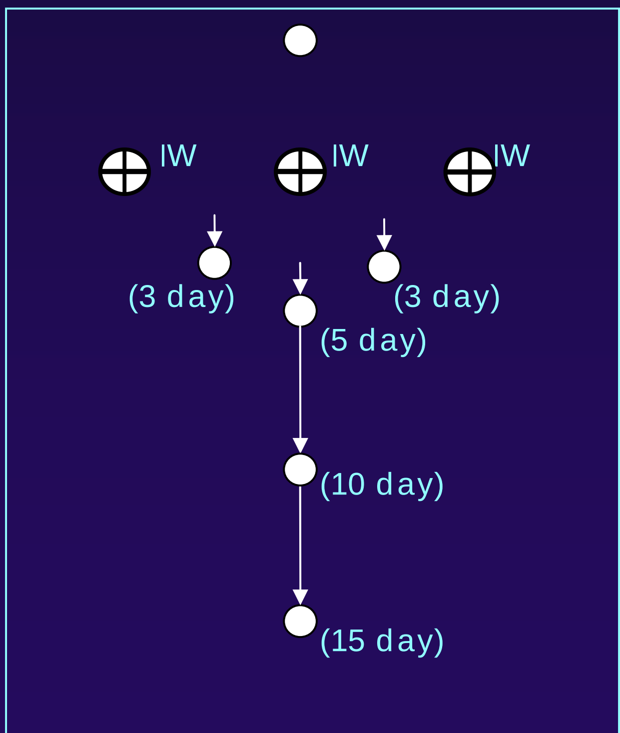
- Lag period to onset of ClO_4 degradation was shorter for Toda NZVI (2 to 5 days) than for Lehigh NZVI (5 to 8 days)

  - Why? Mixed oxide/ZVI content of Toda-NZVI is more favorable for dechlorination of perchlorate (Moore et al. 2003)

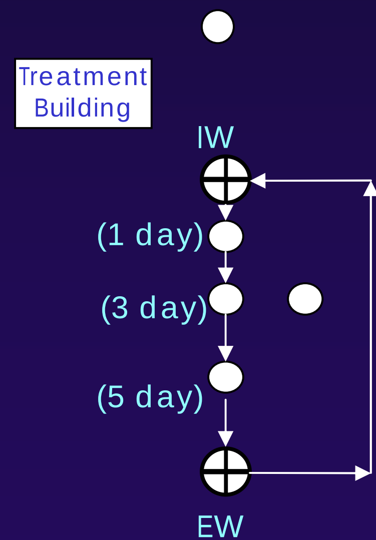
Aerospace Site – Pilot Test Plans

Direction of Groundwater Flow

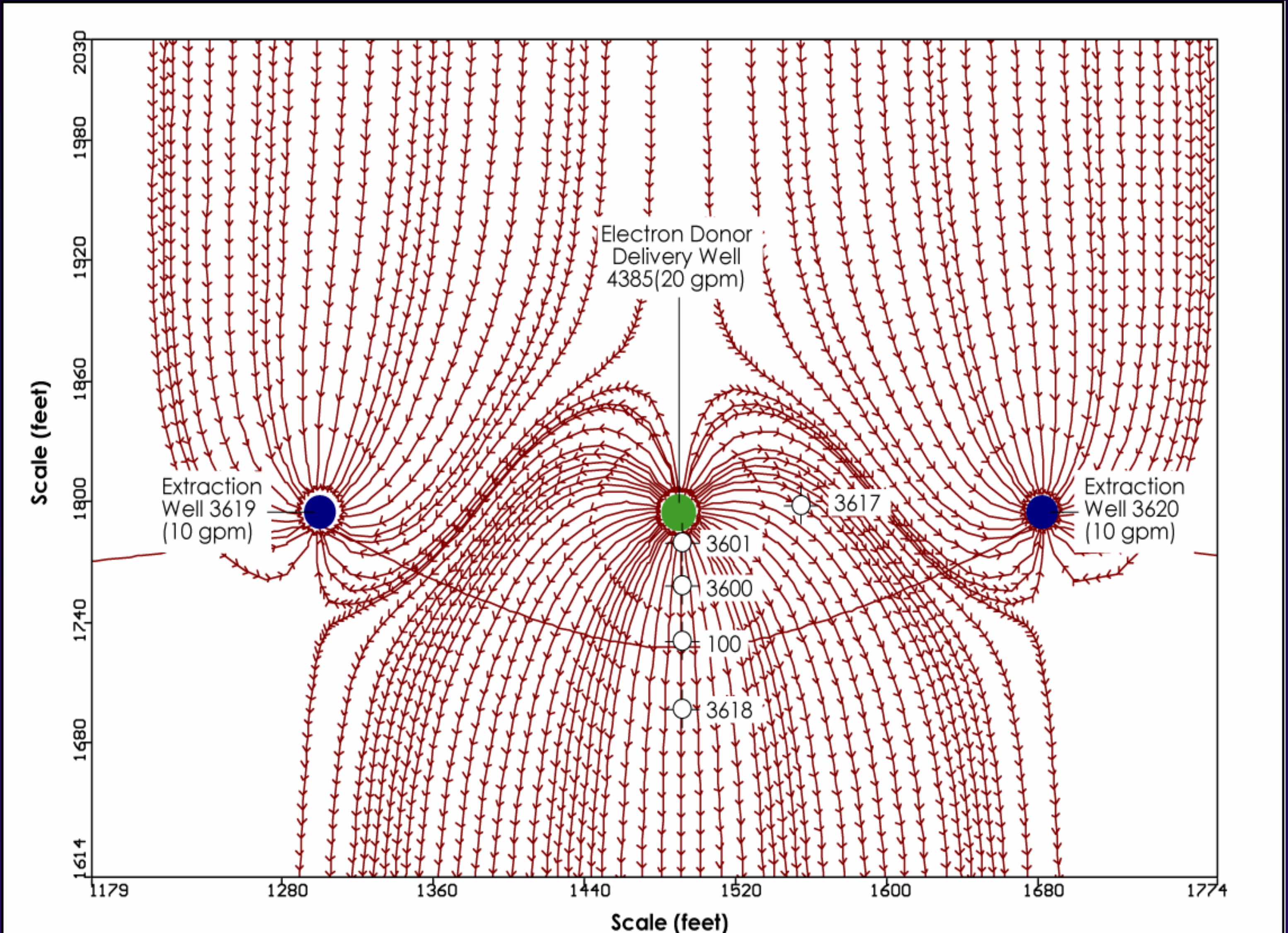
Passive Treatment Demo Layout



Active Treatment Demo Layout



Aerospace Site
Potential Approach for NZVI delivery



Research and Development Needs

- Cost effective approaches for particle synthesis/manufacture
- Field studies evaluating Nano-ZVI particle transport and reactive longevity
- Laboratory evaluation of relationship between particle shape and transport characteristics
- Evaluation of optimal modes for particle delivery
- Rigorous performance and cost comparison with in situ bioremediation (for perchlorate and chloroethenes)