PILOT TEST OF ISCO TECHNOLOGIES LEADS TO IMPROVED UNDERSTANDING OF IMMEDIATE AND MID-TERM GEOCHEMICAL RESPONSE AND CONTAMINANT DESTRUCTION WITHIN PETROLEUM HYDROCARBON PLUME

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REMTECH 2008 at Banff, Alberta

Presentation Goal

Report on ISCO pilot test involving activated sodium persulfate and petroleum hydrocarbons (PHC) that was designed to gather critical information on:

1) Spatial distribution of components of injected fluids and chemical and biological reaction by-products within 7 and 20 days of start of chemical application; and

2) Magnitude of sediment and groundwater contaminant concentration reduction in the presence of non-aqueous phase liquid (NAPL).

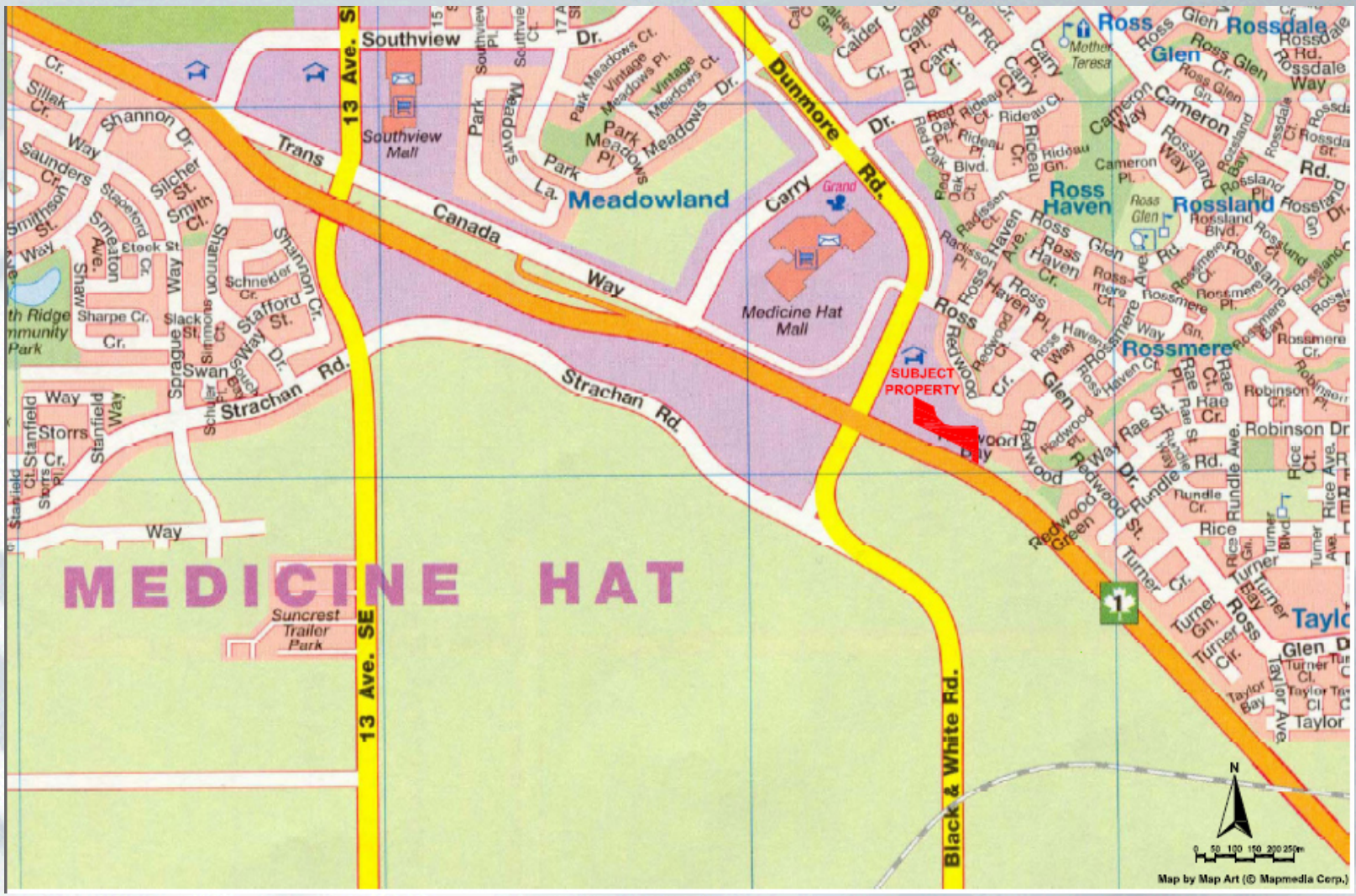
Presentation Outline

- Chemical Oxidation and Injection Overview
- Pilot Test Background and Program
- Results - Immediate (7 Day) Injectate Distribution
- Results - Distribution of Treatment Chemicals and Reaction Byproducts within Mid-Term (20 Days)
- Results - PHC Reductions in GW and Soil at Day 20
- Summary and Implications

Project History and Site Features

- Former retail service station in Southern Alberta
- Operated for 30 years - multiple fuel releases
- Decommissioned in 1989 - site assessment followed
- Underlain by a sandy unconfined aquifer (6 m-bg)
- PHC plume including smear zone and groundwater
- Area of impact ~ 5000 m^2 (high impact area ~1000 m^2)
- Plume stable or growing slowly as of 2007
- Requirement for remedial action and developer interest in property led to feasibility study and pilot test in 2007

Site Location



Chemical Oxidation Overview

- In Situ Chemical Oxidation involves the injection of a dilute oxidant (and potentially an activator) into the subsurface to transform organic contaminants into by-products of carbon dioxide, water, and other benign compounds

- "Low temperature combustion" of organic chemicals (e.g., fuels, herbicides/pesticides, PCE, TCE, high explosives)

- Success depends on effective chemical and hydrogeologic engineering

Chemical Oxidation Overview

The chemical oxidation technology area currently includes four unique classes:

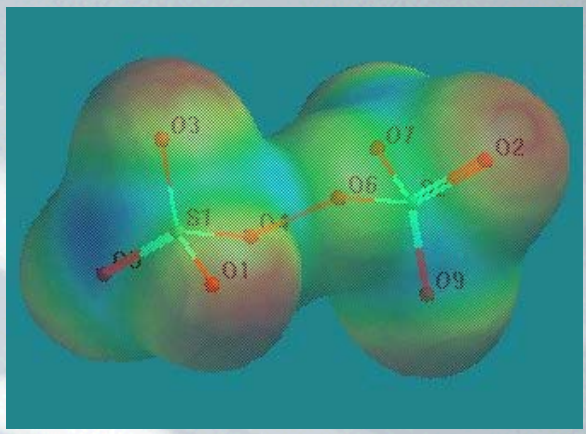
- Ozonation (O_3 and radicals)
- Permanganate (MnO_4)
- Catalyzed Hydrogen Peroxide (H_2O_2 and radicals)
- **Activated Persulfate (S_2O_8 and radicals)**

Chemical Oxidation Overview

Klozur® Persulfate

$S_2O_8^{-2}$

Strong Oxidizer



Persulfate anion:

$E^0 = 2.12$ v

$$15S_2O_8^{-2} + 30H^+ + 30e^- \rightarrow 30HSO_4^{-1}$$

Example of direct oxidation of benzene (C_6H_6)

$$C_6H_6 + 12H_2O \longrightarrow 6\,CO_2 + 30\,H^+ + 30e^-$$

Need 15 mole $S_2O_8^{-2}$ per mole of C_6H_6 mineralized

Chemical Oxidation Overview

In general, direct oxidation by persulfate anion is *kinetically slow…..*

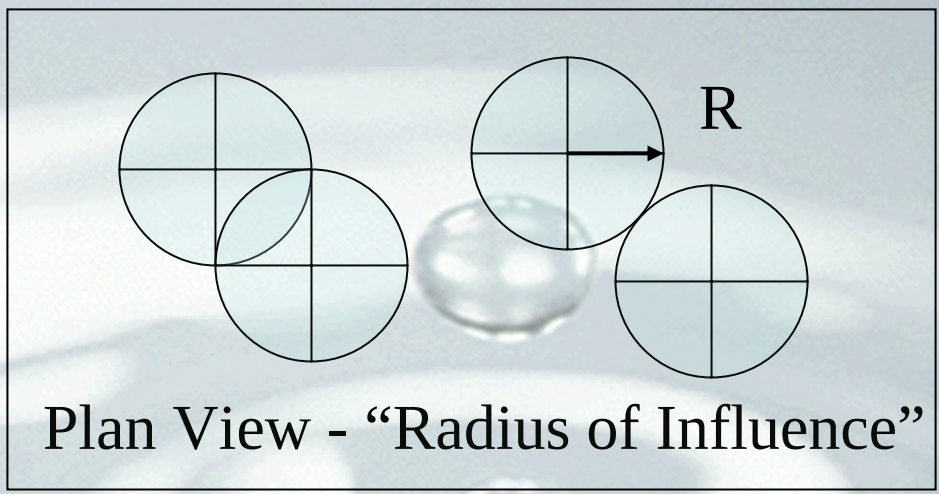
….activation of the anion produces a very strong and kinetically fast acting oxidizer in the Sulfate Free Radical

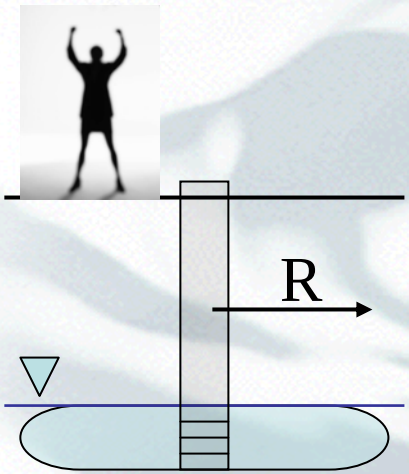
$$SO_4^{\bullet -} + e^- \rightarrow SO_4^{-2} \qquad E^0 = \sim 2.6\ v$$

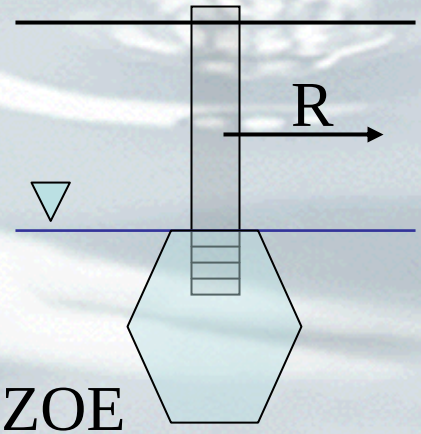
$$S_2O_8^{-2} \rightarrow 2\ SO_4^{\bullet -} \quad \text{or} \quad (SO_4^{\bullet -} + SO_4^{-2})$$

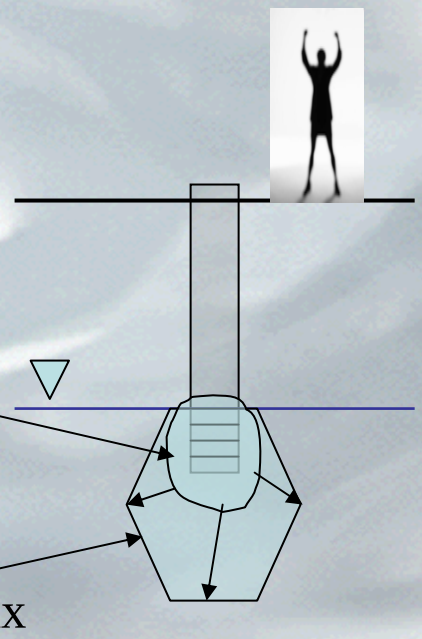
Initiation, propagation, and termination reactions are complex and may involve many types of radicals

Conceptualization of Injection & Placement



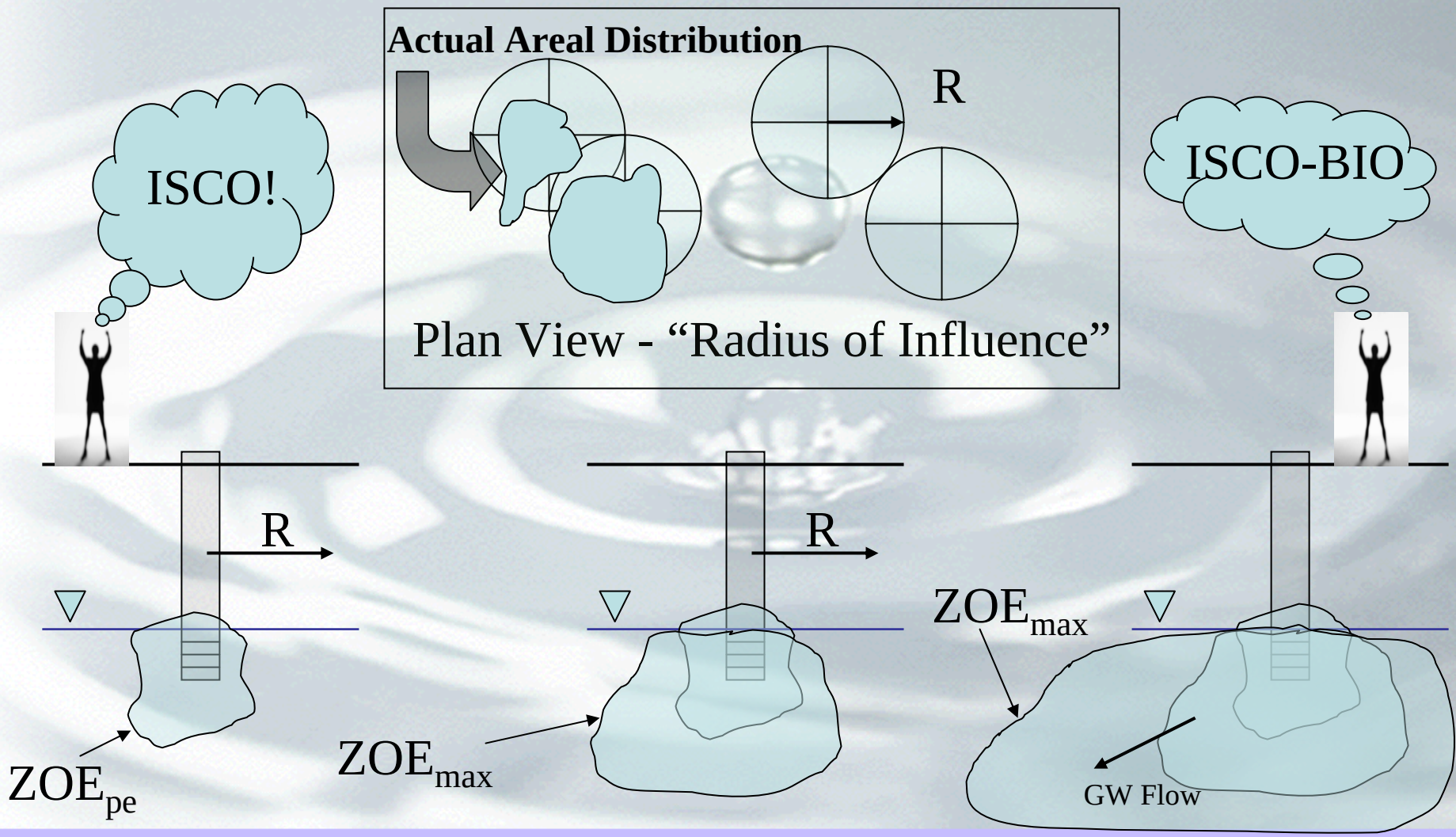




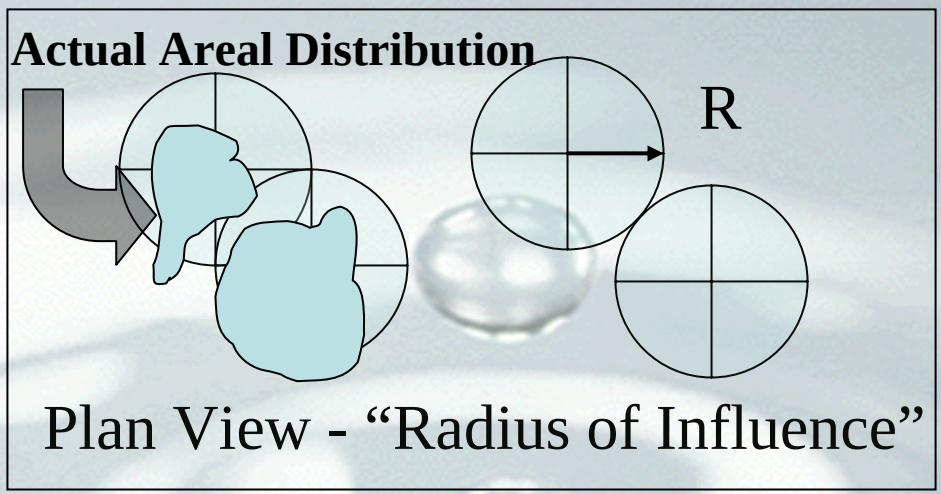


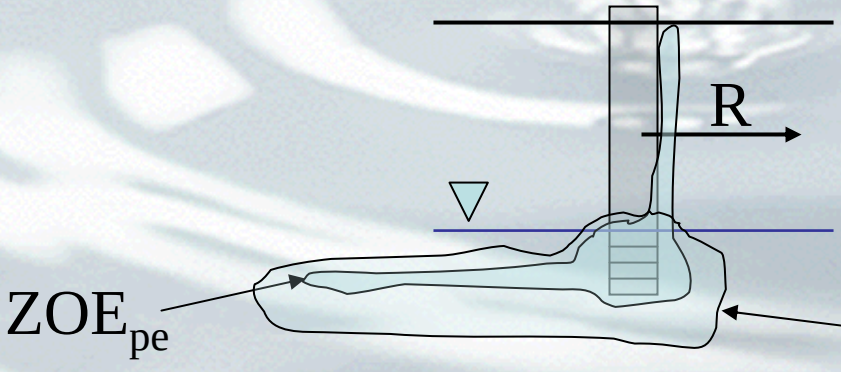
ZOE = Zone of Effect at times of physical displacement and max dev

Conceptualization of Injection & Placement



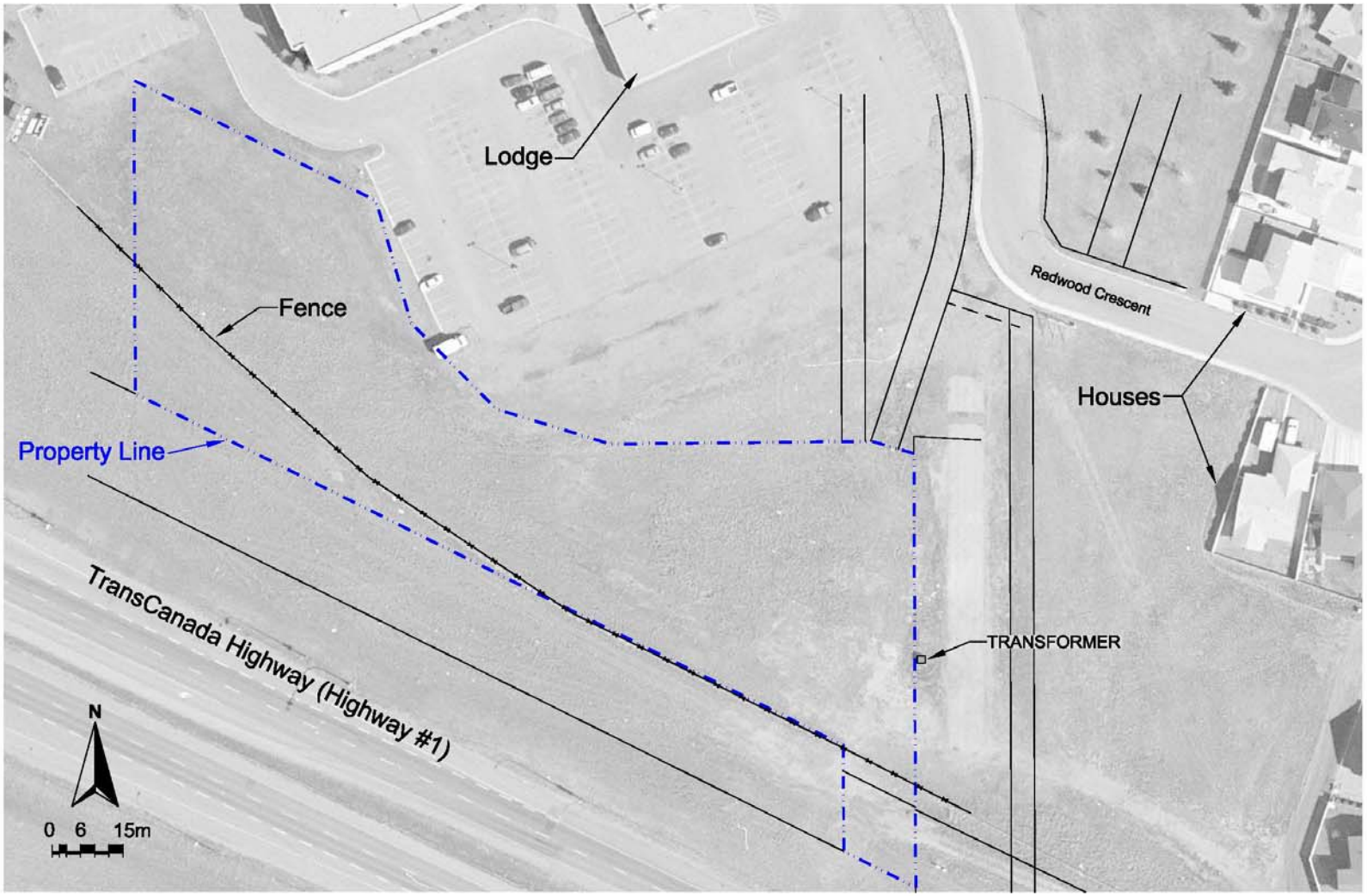
Conceptualization of Injection & Placement





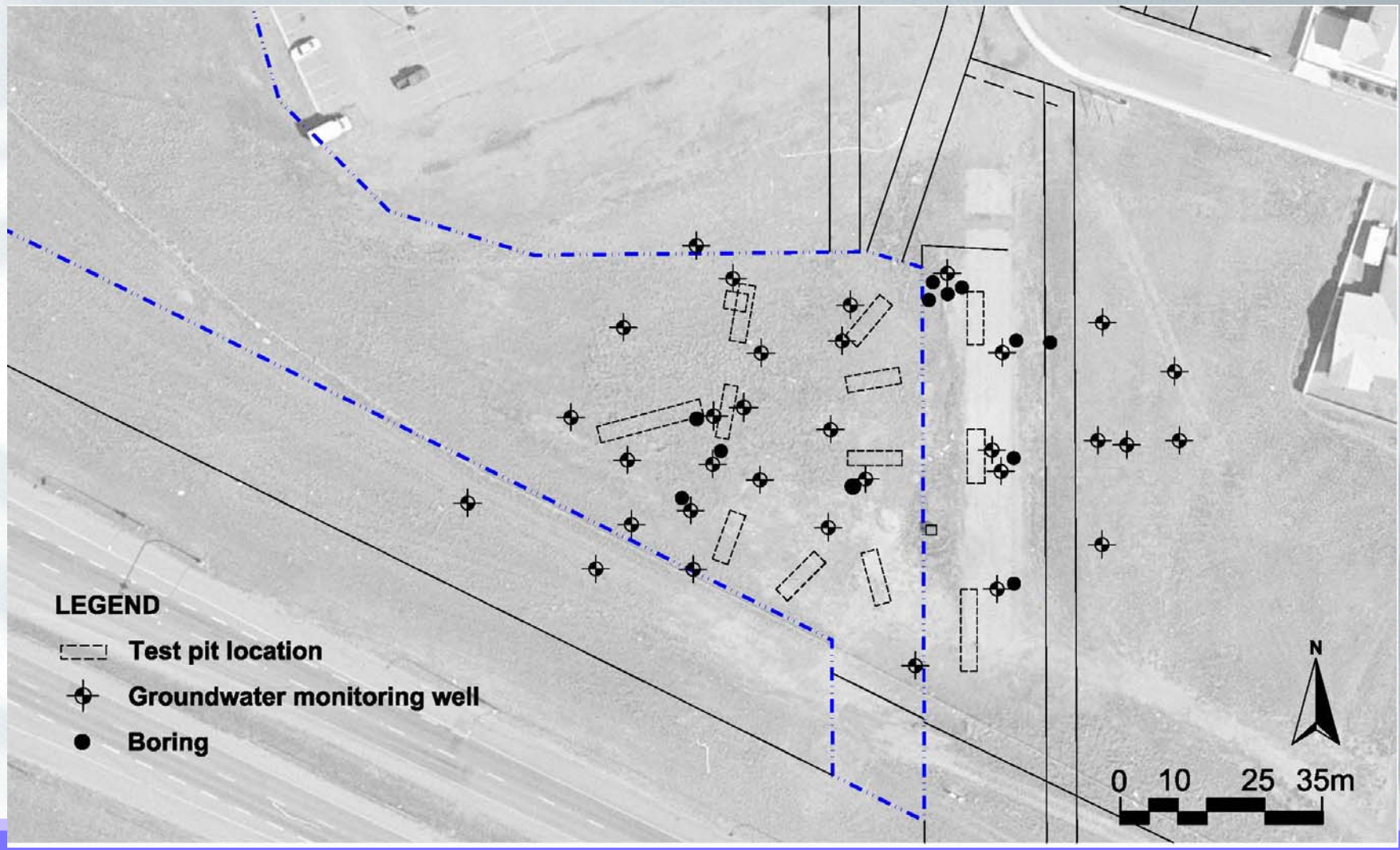
Reality Bites!

Site and Vicinity

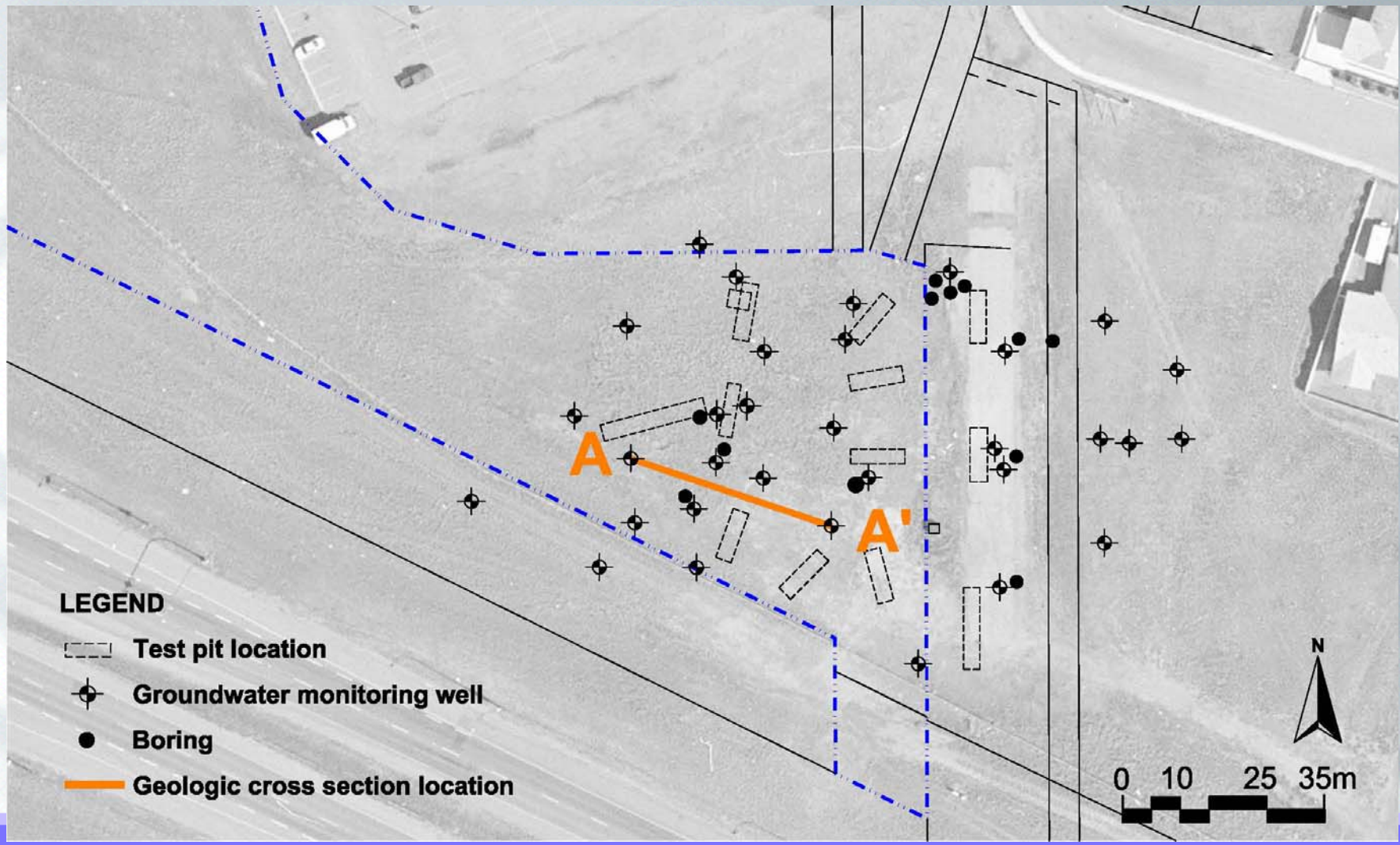


Looking West

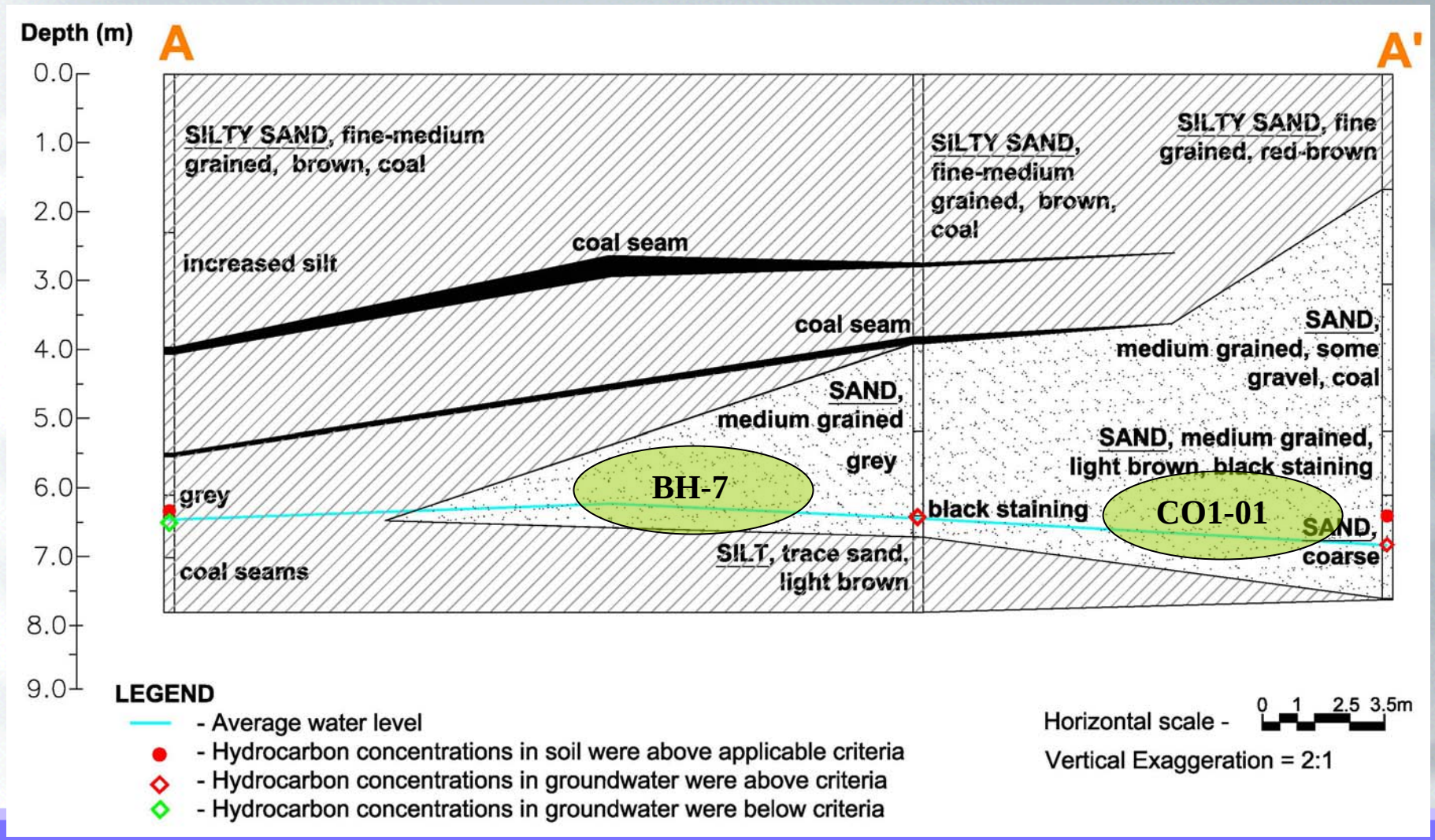
Test Pits, Borings and Wells (2006)



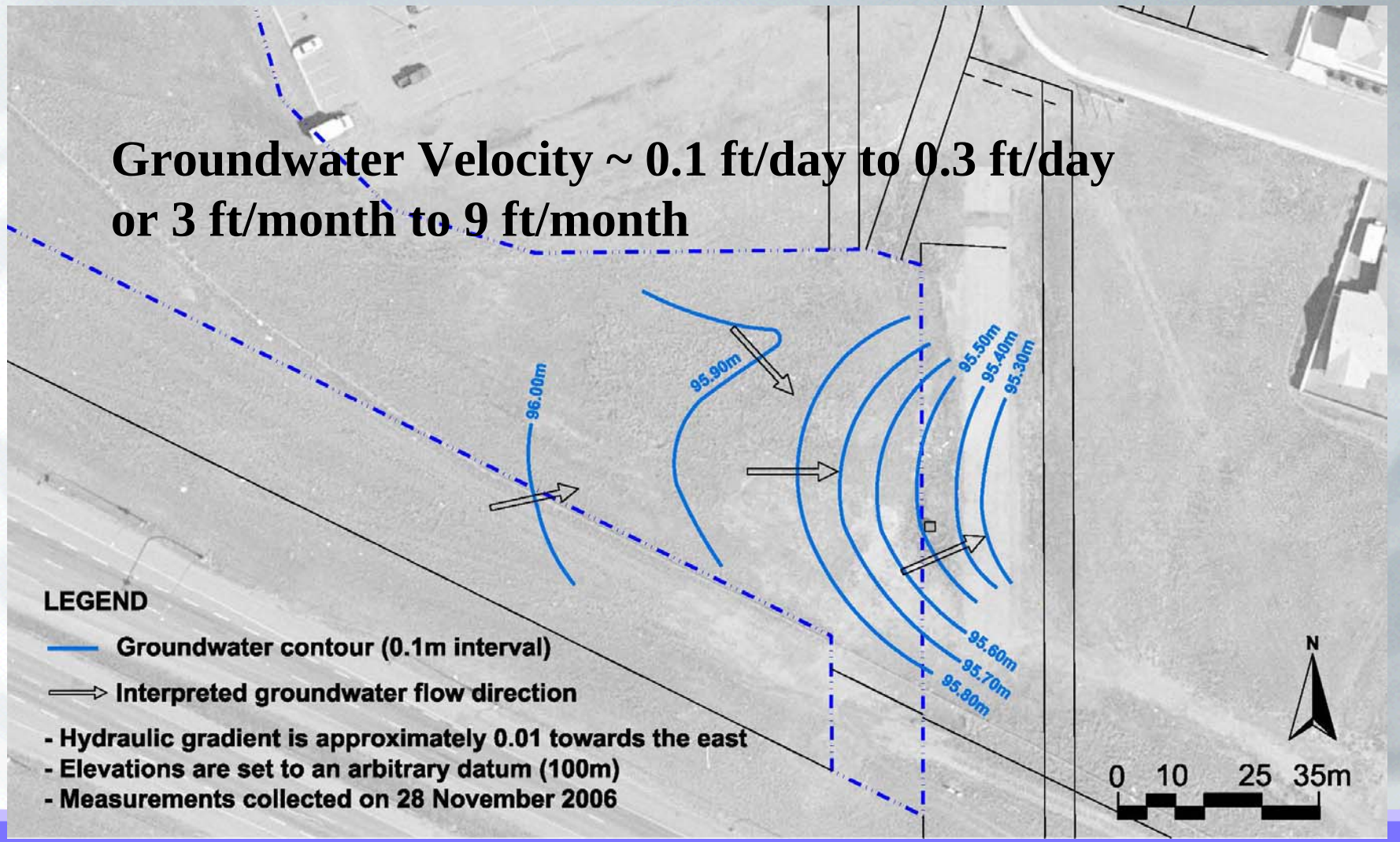
Geologic Profile A-A’



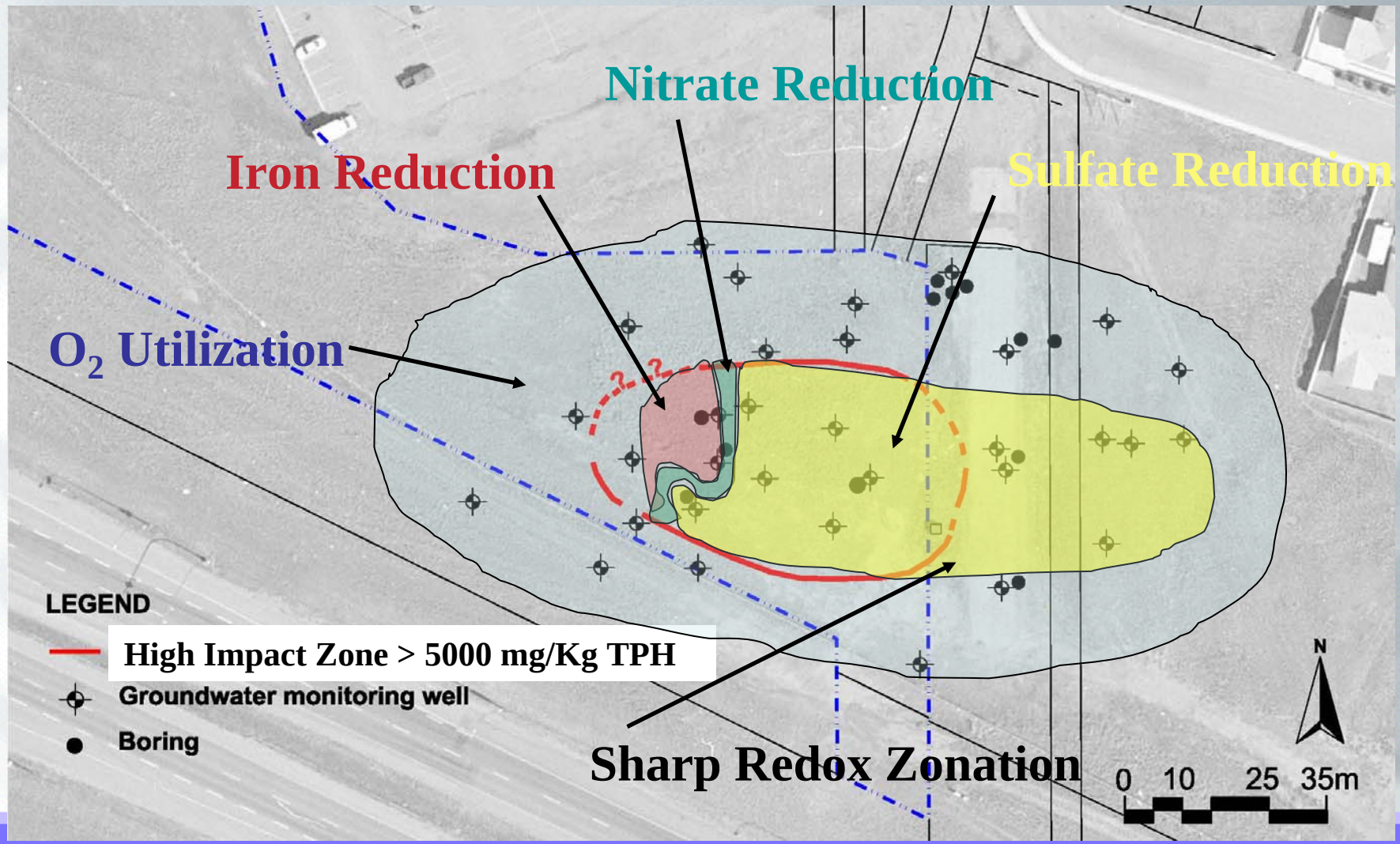
Geologic Profile A-A'(2006)



Potentiometric Surface (2006)



Hydrocarbon Plume (pre-test)



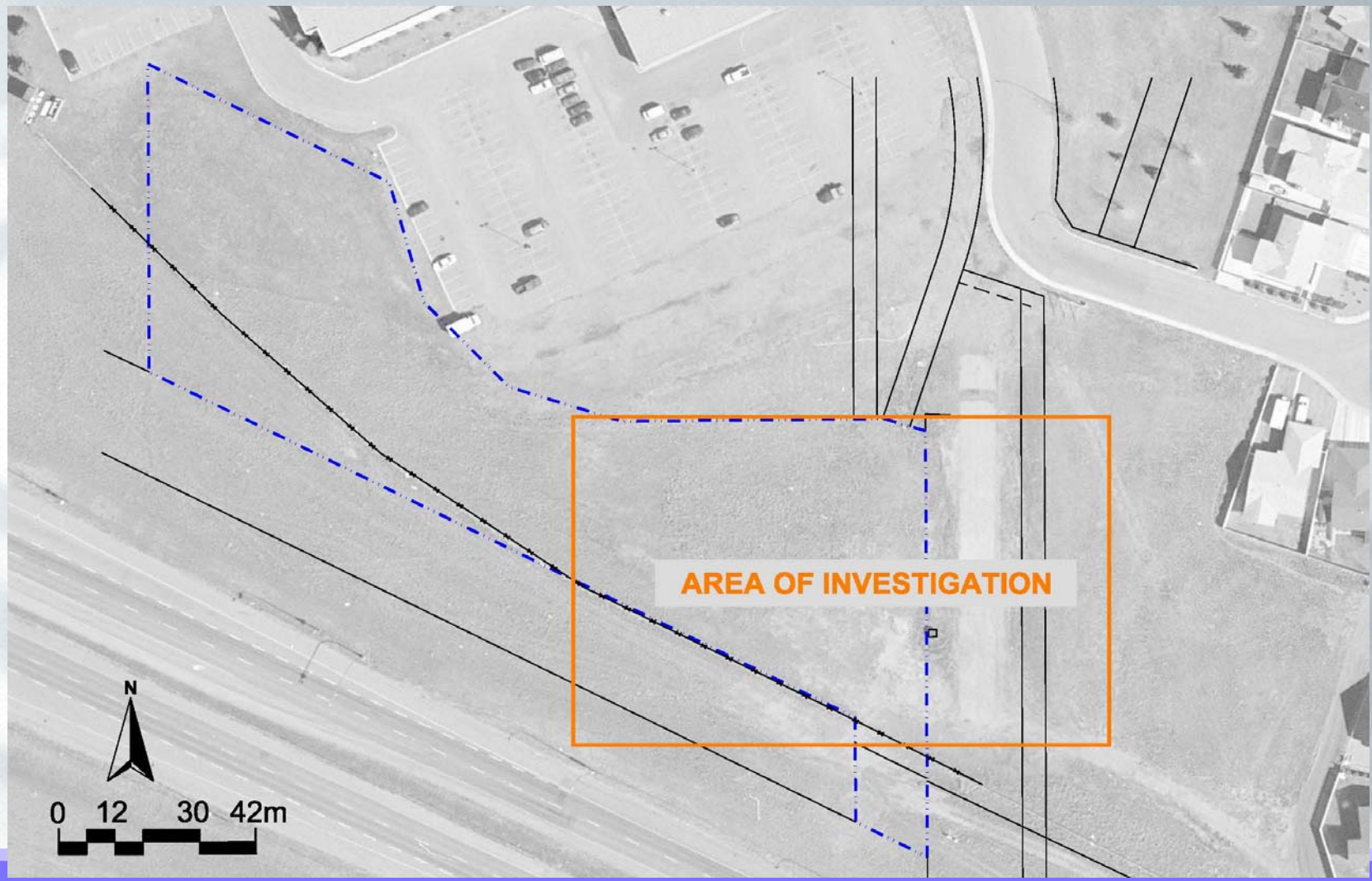
Pilot Test Program

- Pilot Test Program
  - Design Data Collection (DDC)
  - Treatability Study
    - Klozur® $Na_2S_2O_8$ and iron-EDTA
    - Klozur® CR (base activated chemox-bio)
    - H_2O_2
  - Field Pilot Test (Klozur® CR, Klozur and Dissolvine)

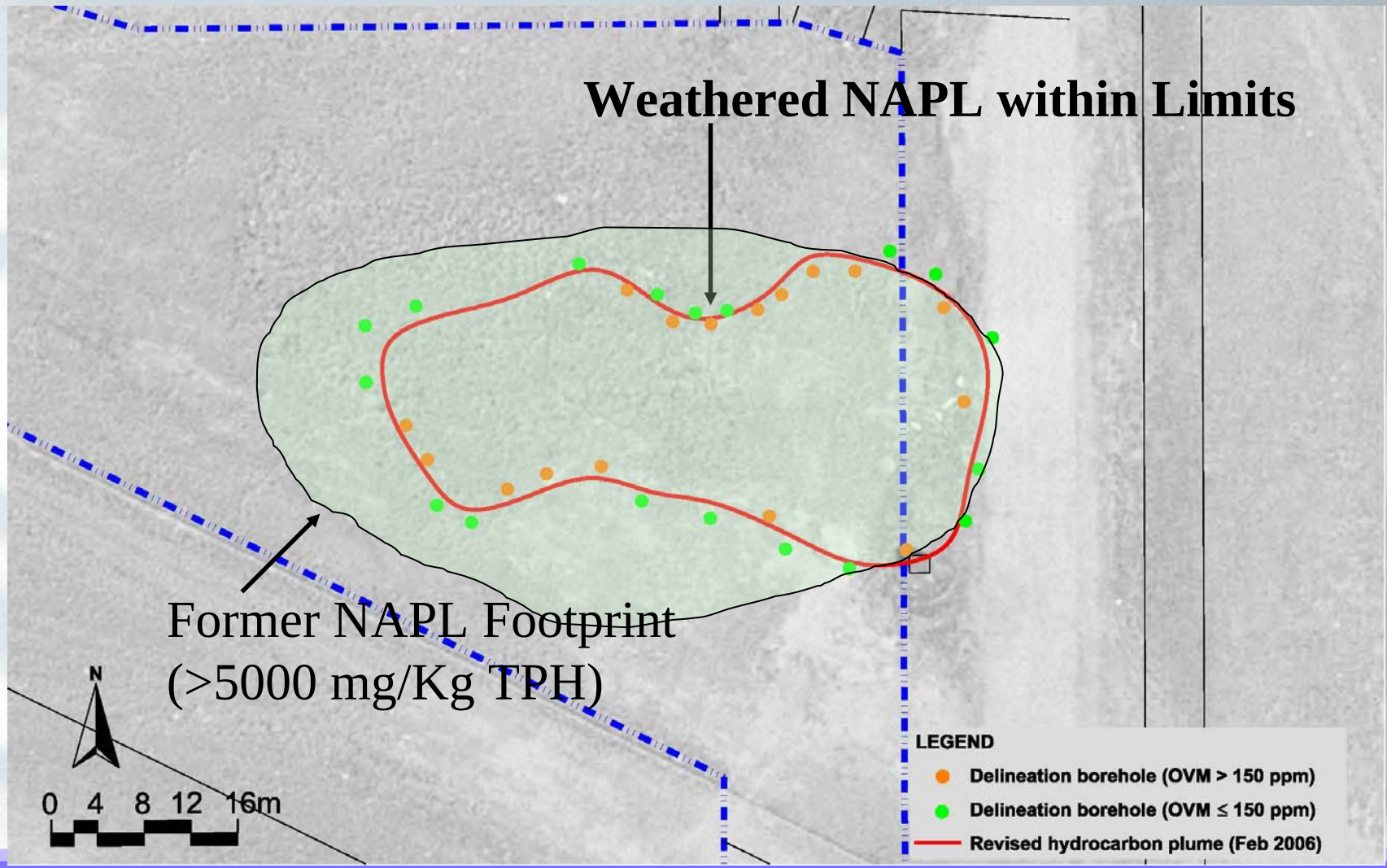
DDC Scope:

1. Direct push continuous sampling
2. Collection of sediment core and samples for:
   1. OVA screening, NAPL detection, TOC, TPH
   2. Geologic description
3. Install pilot test array - test out field protocols
4. Baseline groundwater sampling and analysis (TOC + DOC)

Pilot Test Area



Hydrocarbon Plume (DDC 2/08)



DDC Plume Delineation

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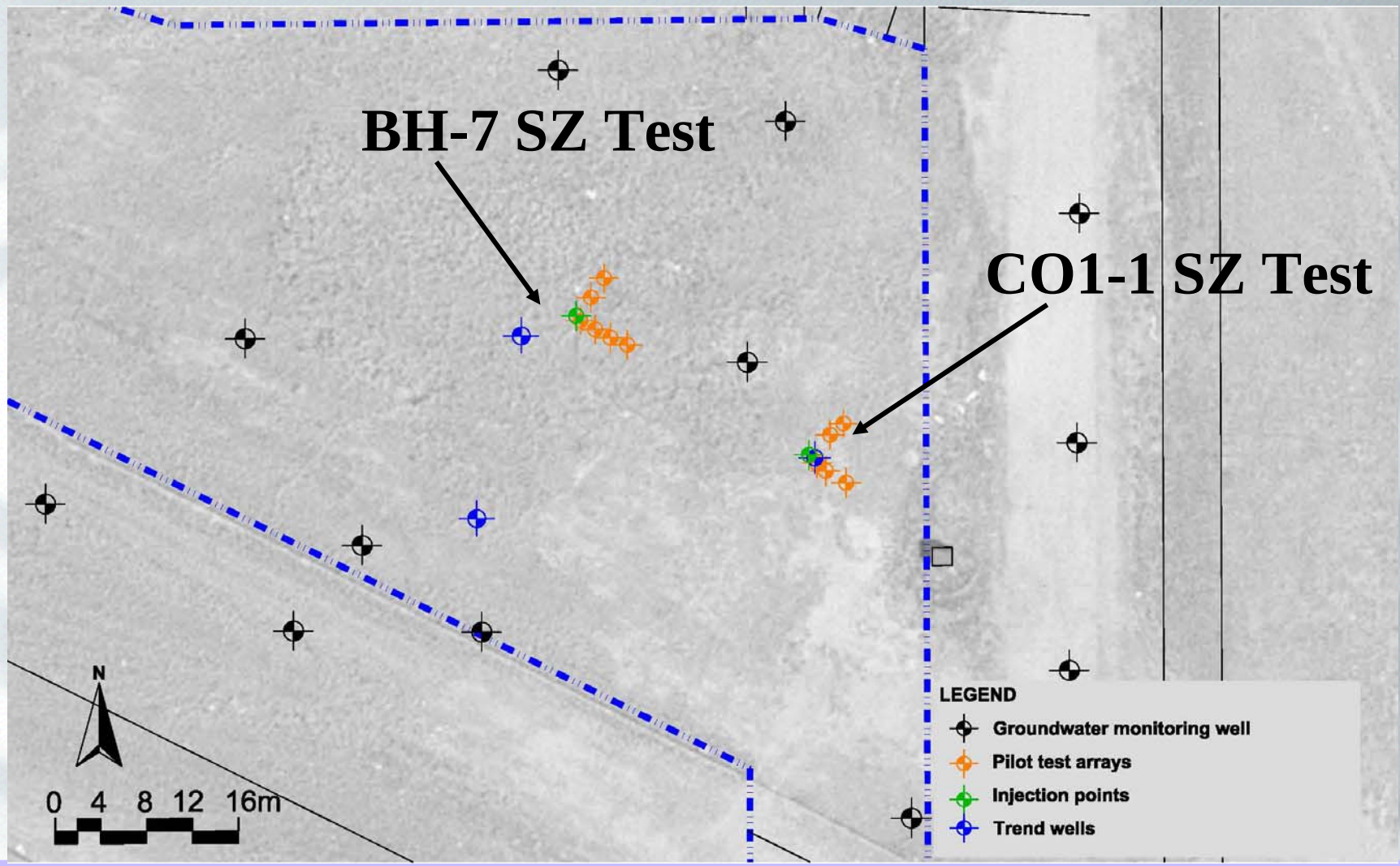
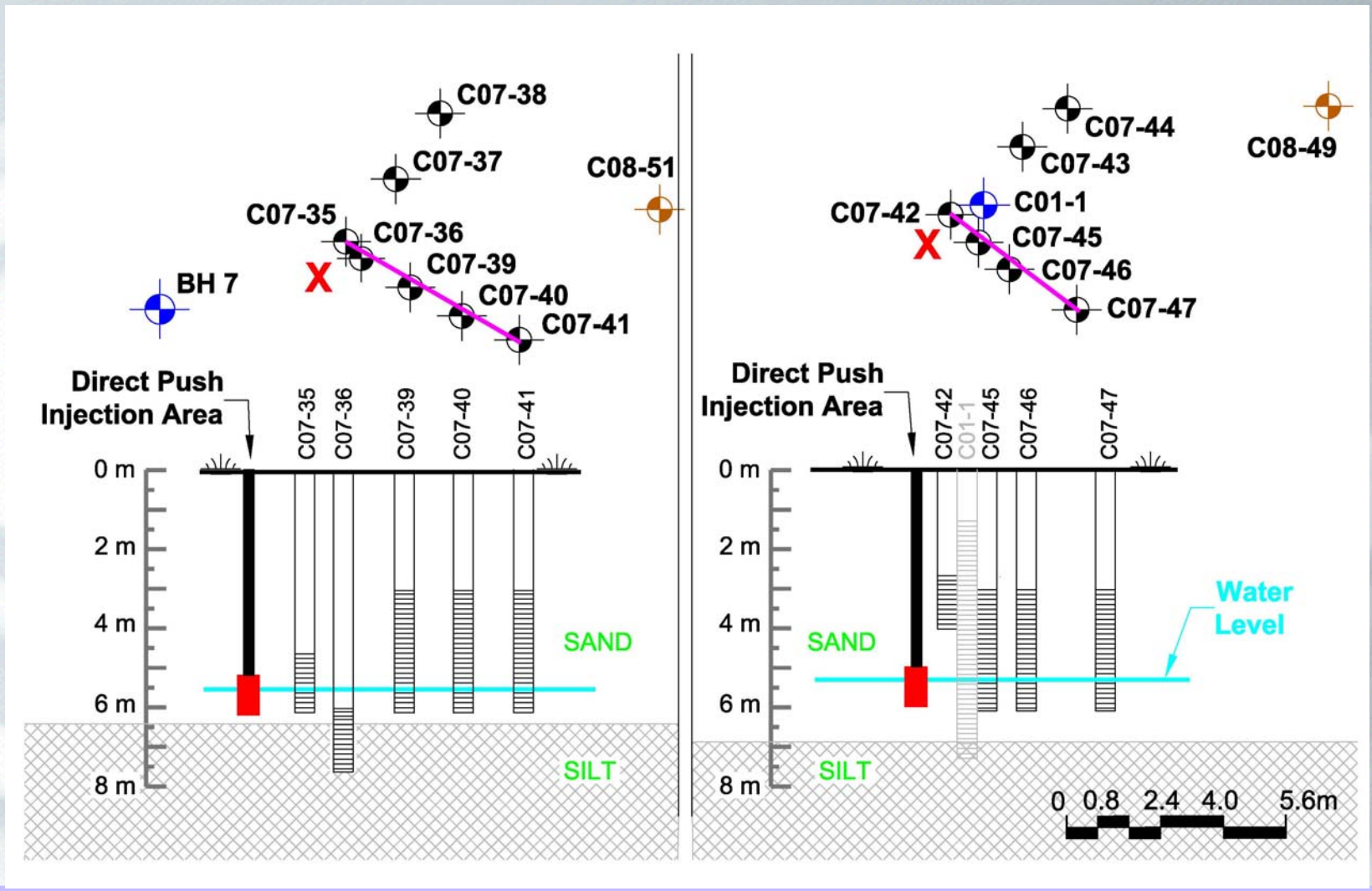
Pilot Test Arrays and Injection Pts



Pilot Test Array Detail



Pilot Test Implementation Detail

Injectate Summary for BH07 (Klozur+Fe-EDTA)

Date	Batch No.	Klozur	Fe-EDTA	Water	% w/w
2/22/12	1	25	0.1	37.5	15
2/22/12	2	25	0.1	37.5	15
2/26/12	3	25	0.1	37.5	15
2/26/12	4	25	0.1	37.5	15

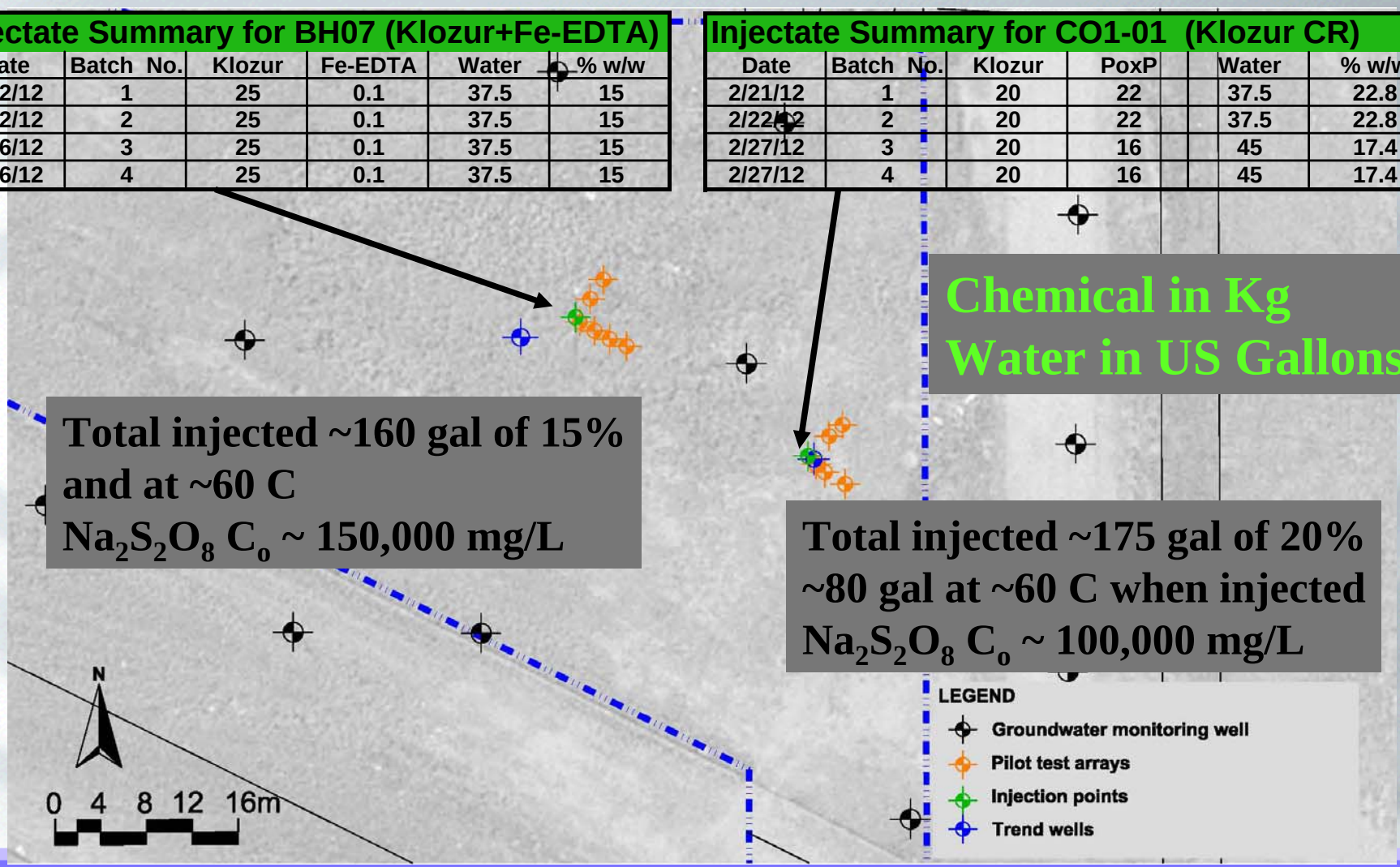
Injectate Summary for CO1-01 (Klozur CR)

Date	Batch No.	Klozur	PoxP	Water	% w/w
2/21/12	1	20	22	37.5	22.8
2/22/12	2	20	22	37.5	22.8
2/27/12	3	20	16	45	17.4
2/27/12	4	20	16	45	17.4

Chemical in Kg
Water in US Gallons

Total injected ~160 gal of 15% and at ~60 C
$Na_2S_2O_8$ C_o ~ 150,000 mg/L

Total injected ~175 gal of 20% ~80 gal at ~60 C when injected
$Na_2S_2O_8$ C_o ~ 100,000 mg/L



Pilot Test Implementation Detail

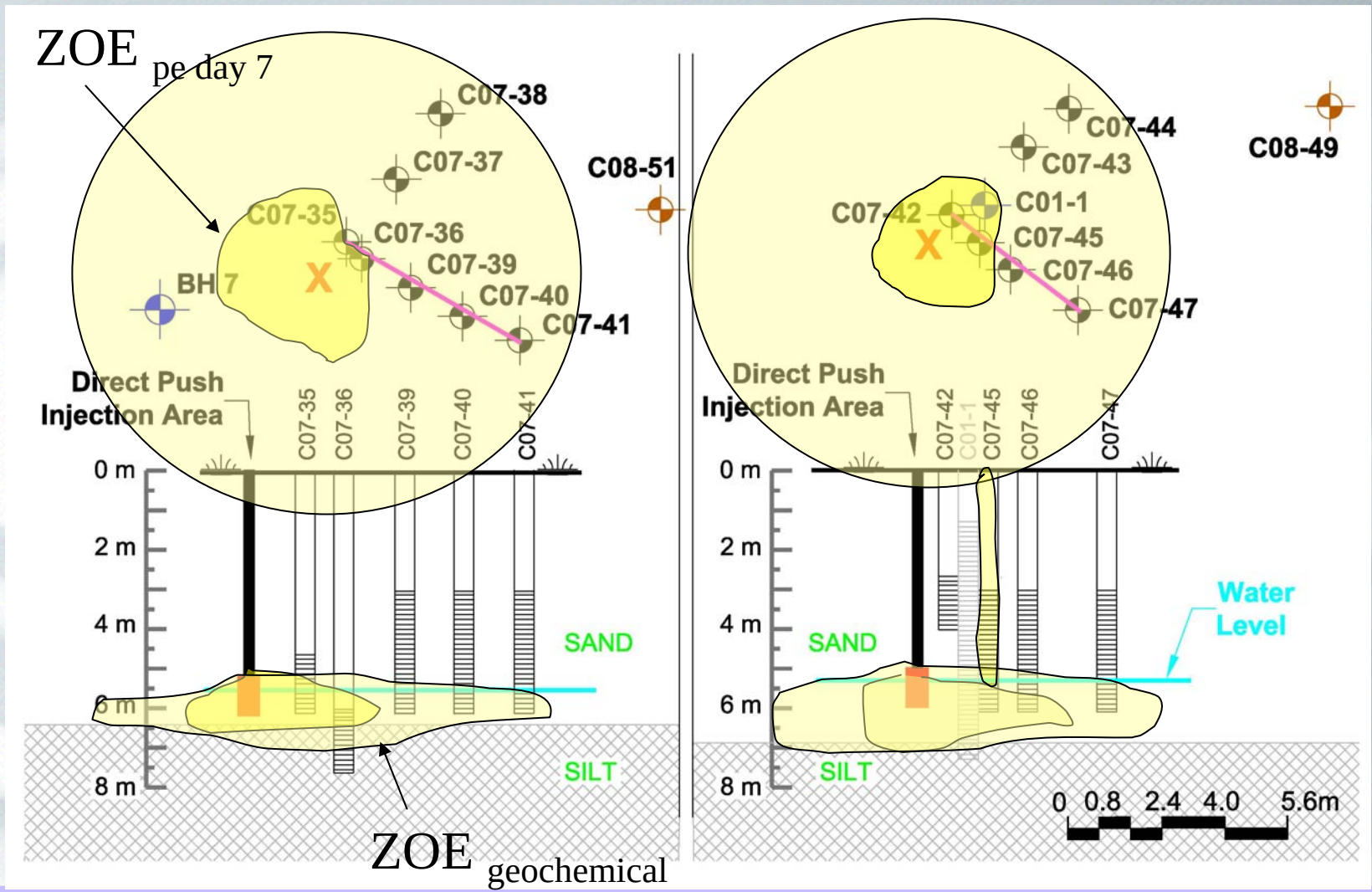
Process Monitoring

- Visual Observations at monitoring wells / ground surface
- Electrical Conductivity
- Sulfate
- pH
- Temperature (heated water used)
- ORP (strong function of pH)
- Dissolved Oxygen

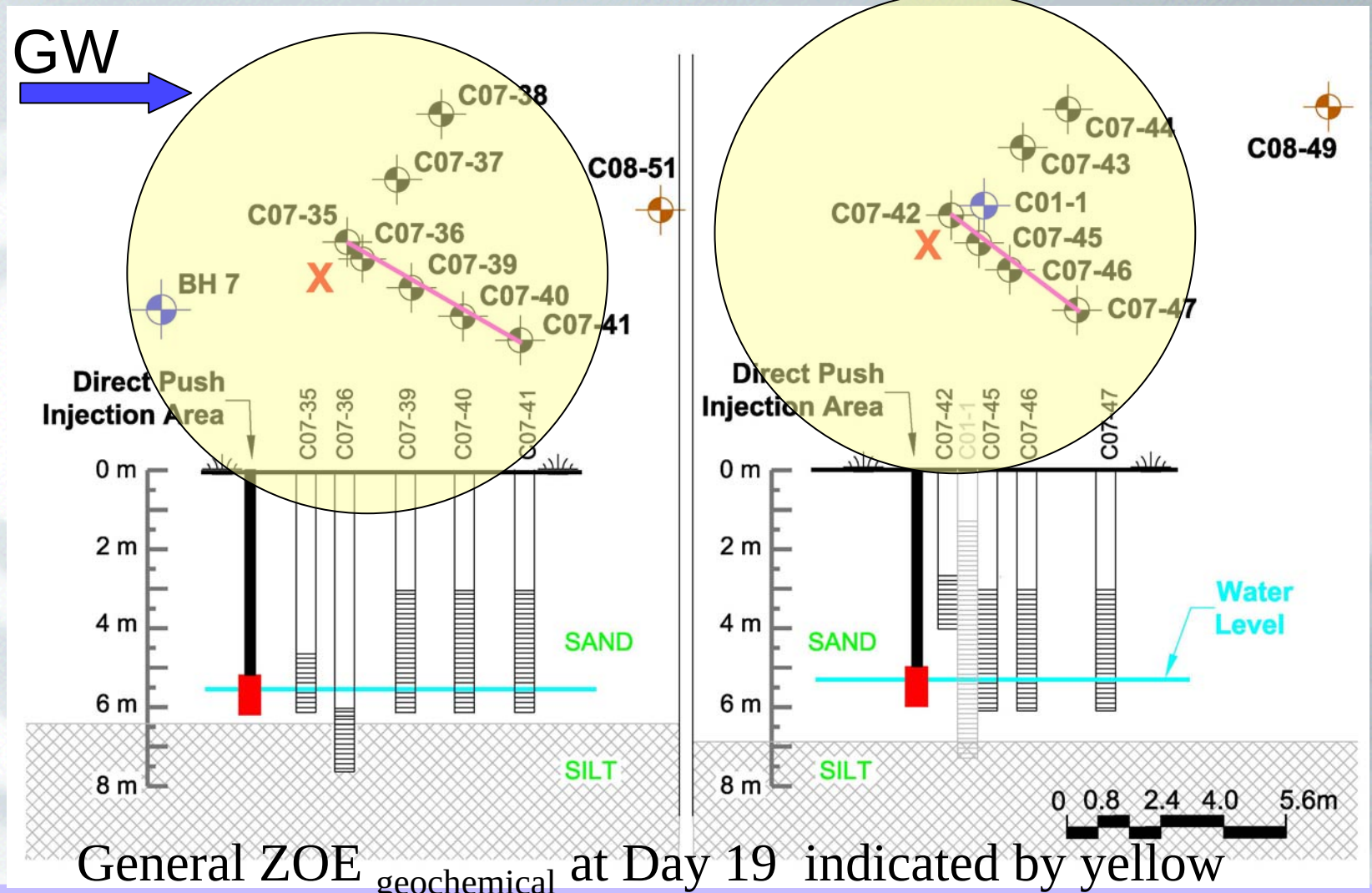
Performance Assessment

- Soil and groundwater sampling and analysis for TOC/DOC and BTEX F1 F2 F3 F4 (F3 and F4 for soil only)

Immediate Distribution (Day 7)



Mid-term Distribution (Day 19)



General ZOE $_{\text{geochemical}}$ at Day 19 indicated by yellow

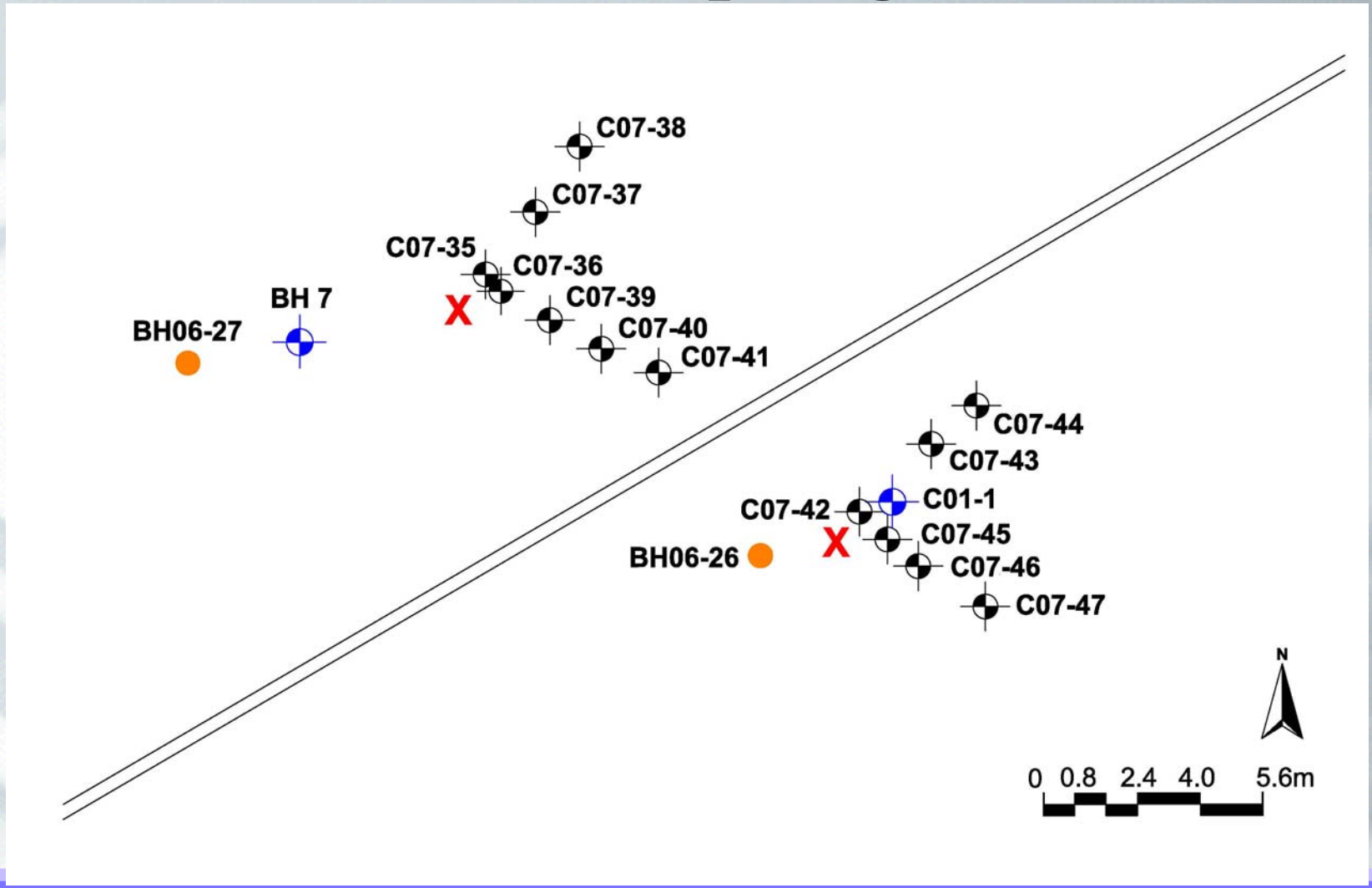
Groundwater PHC Concentrations (Baseline to Klozur® CR Day 20)

Well		Benzene	Toluene	E-benzene	Xylenes	F1	F2
CO1-01	Baseline	ND	ND	0.511	1.16	4.3	2.71
1 m NE	Day 20	ND	ND	0.554	1.78	4	3
CO7-43	Baseline	ND	ND	0.938	0.0453	2.2	31.5
2.5 m NE	Day 20	ND	ND	0.345	0.009	1.9	5.2
CO7-44	Baseline	ND	0.009	1.29	0.0107	3.5	21
4.0 m NNW	Day 20	ND	ND	1.71	0.0083	2.9	6.4
CO7-47	Baseline	ND	ND	0.205	0.258	14.3	22.5
4.0 m E	Day 20	ND	ND	0.174	0.0939	3.3	9.4

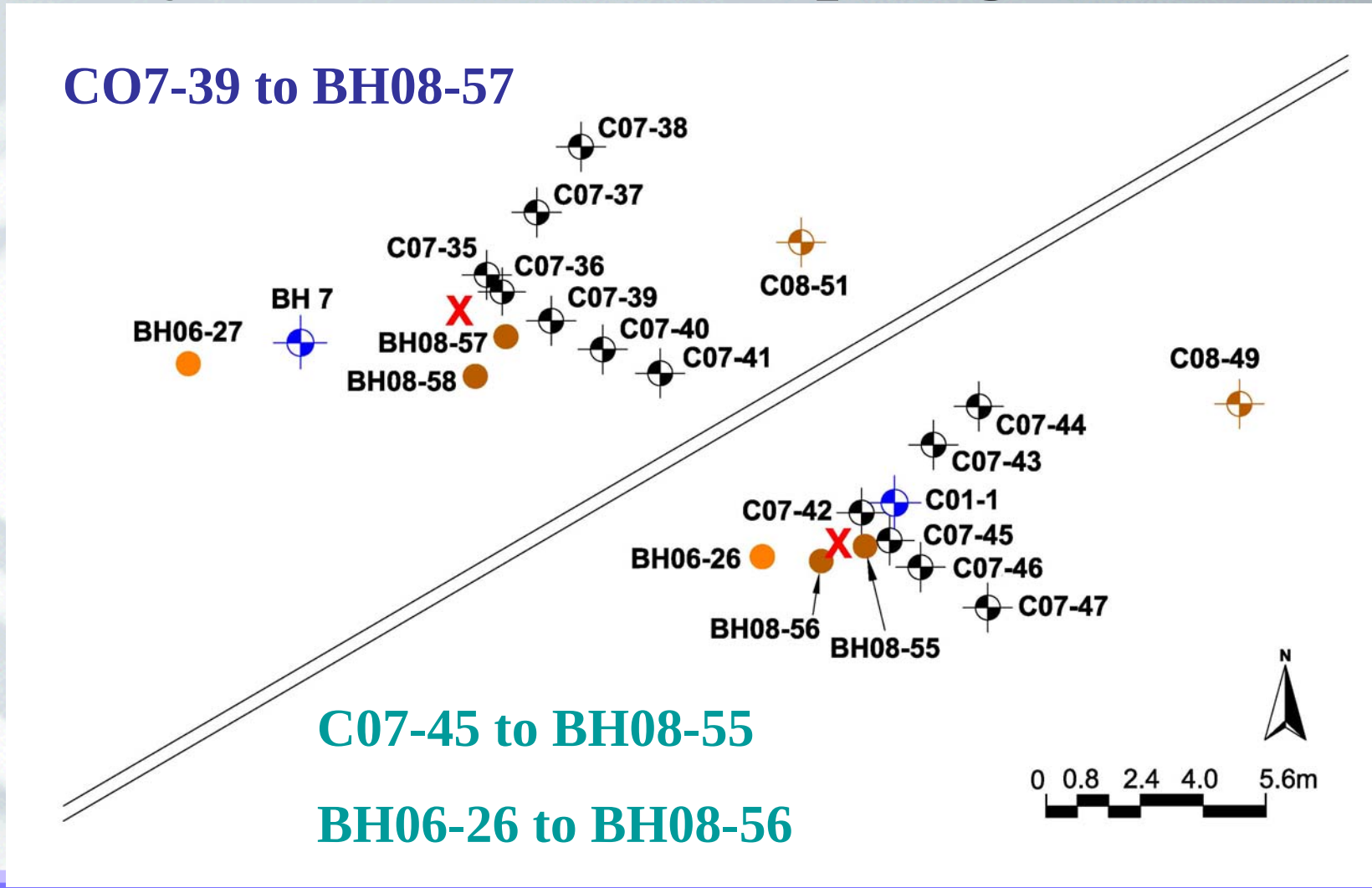
Groundwater PHC Concentrations (Baseline to Klozur® Iron-EDTA Day 19)

Well		Benzene	Toluene	E-benzene	Xylenes	F1	F2
C07-35	Baseline	ND	ND	0.0185	0.0016	0.5	3.3
1 m NNE	Day 20	ND	ND	0.0038	ND	0.1	0.7
C07-36	Baseline	ND	ND	0.121	ND	0.7	2
1 m NNE	Day 20	ND	ND	0.0282	ND	0.3	0.9
C07-38	Baseline	ND	ND	0.0016	0.0029	0.2	1.4
4 m NNE	Day 20	ND	ND	ND	0.005	ND	0.3
C07-41	Baseline	ND	ND	0.0062	0.0027	6.4	5.7
5 m ESE	Day 20	ND	ND	ND	ND	0.3	0.7

Baseline Soil Sampling Locations



Post-Injection Soil Sampling Locations



Soil PHC Concentration Changes (Day 20 after First Klozur® CR Batch Injection)

Comparison of CO7-45 to BH08-55 (Before and After)

Analyte	CO07-45, mg/Kg	BH08-55, mg/Kg
Benzene	<0.005	<0.005
Toluene	<0.05	<0.05
Ethyl Benzene	**14.2**	**1.35**
Xylenes	**56.4**	6.61
F1 -BTEX	**800**	40
F2	**1980**	39
F3	473	60
F4	12	<10

Note: Value in bold indicates the soil remediation guideline is exceeded.

Soil PHC Concentration Changes (Day 20 after First Klozur® CR Batch Injection

Comparison of BH06-26 to BH08-56 (Before and After)

Analyte	BH06-26, mg/Kg	BH08-56, mg/Kg
Benzene	0.11	<0.005
Toluene	0.11	<0.05
Ethyl Benzene	**84**	<0.01
Xylenes	**315**	<0.05
F1 -BTEX	**3630**	<10
F2	**4710**	51
F3	1020	34
F4	<10	<10

Note: Value in bold indicates the soil remediation guideline is exceeded.

Soil PHC Concentration Changes (Day 19 after First Klozur and Iron-EDTA Injection)

Comparison of CO07-39 to BH08-57 (Before and After)

Analyte	CO07-39, mg/Kg	BH08-57, mg/Kg
Benzene	<0.005	0.057
Toluene	<0.05	<0.05
Ethyl Benzene	**7.1**	**0.95**
Xylenes	<0.05	1.14
F1 -BTEX	**810**	**460**
F2	**906**	**2360**
F3	258	844
F4	<10	16

Note: Value in bold indicates the soil remediation guideline is exceeded.

Summary and Implications

- Idealized injection ROI rarely occurs and is even more rarely observed - the ZOE_{pe} and ZOE_{max} (or ZOE_{time}) concept is more applicable
- Few empirical studies of short and mid-term injectate and by-product distribution (need more and better studies)
- ISCO and ISCO-Bio phases of action are highly dynamic in four dimensions - what is your ROI???

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Summary and Implications

- Distribution and migration tracked using visual presence of injectate, heat, sulfate, EC, pH, ORP, DO, TOC/DOC as well as BTEX F1-F4
- Short term ZOEpe non-uniform and variable but geochemical response more uniform-widespread
- Significant mid-term expansion observed that exceeds groundwater advection rate

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Summary and Implications

•Klozur CR performed better then iron-EDTA activated Klozur persulfate

• NAPL presence was not a show stopper

• ZOE_{max} for CR is best determined at later times (e.g., six month to year) and future studies should encompass larger area, more depth, and more discrete intervals

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