Antimethanogenic ISCR Approaches for Urban Dry Cleaner Sites: Source Mass Destruction and Dissolved Phase Dehalogenation

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Fifth International Symposium on Bioremediation and Sustainable Environmental Technologies; April, 15-18, 2019; Baltimore, Maryland

PRESENTATION OUTLINE

- History/Background
- Technology Description
- Implementation
- Case Studies

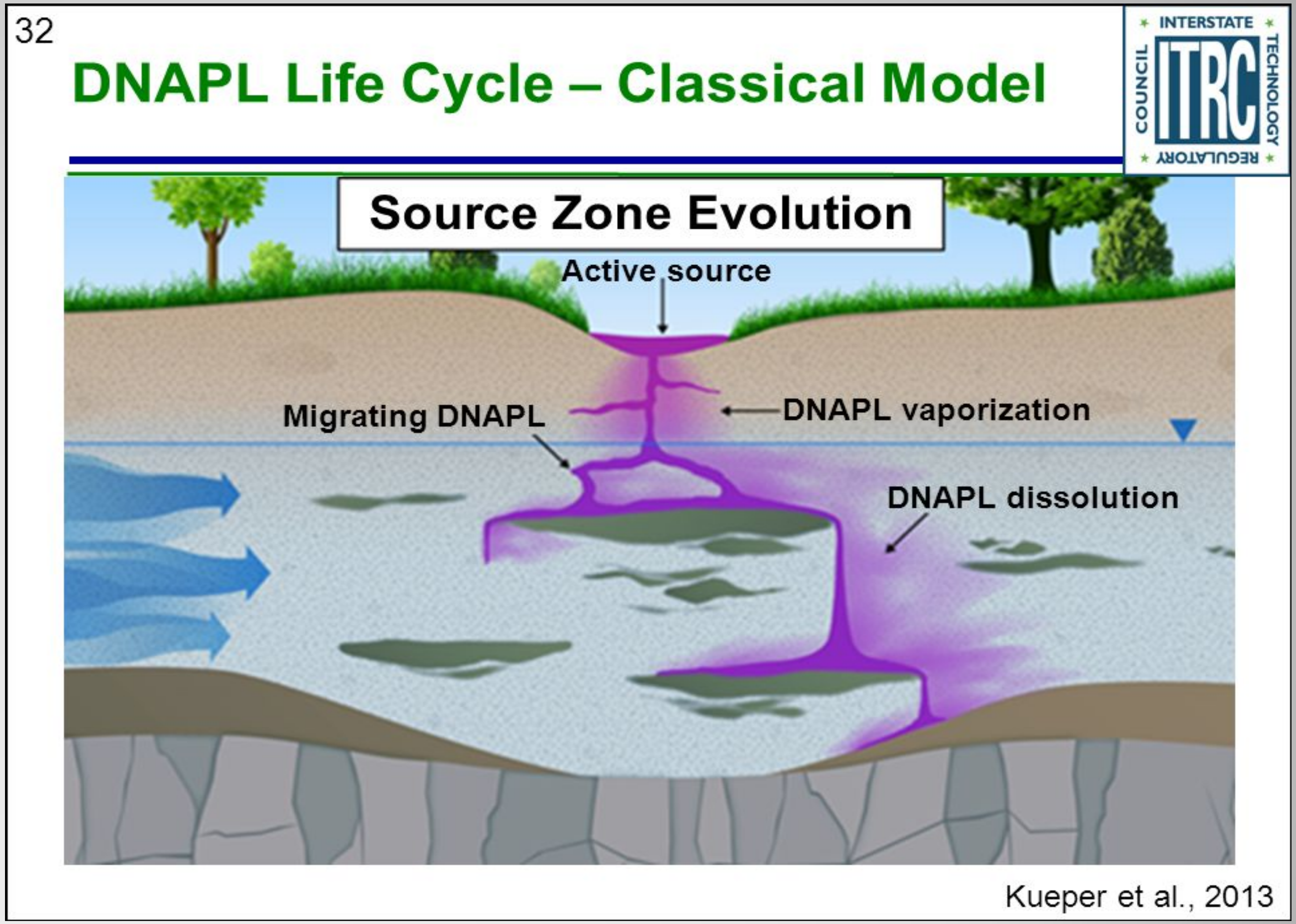
Presentation Goal:

To present what the antimethanogenic EZVI technology is (and isn't), how to utilize the benefits of this substrate and when to use it in difficult urban settings to both perform ERD/ISCR at a high level as well as manage methane for both scientific and regulatory reasons.

HISTORY/BACKGROUND

History – DNAPL Remediation Issues – Why is this difficult?

- Physical Chemistry
  - Hydrophobic
  - Dense & low viscosity
  - Low water solubility
- Location
  - Precision
- Treatment
  - Contact
- Site Use
  - Past and Future



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The curious case of the urban dry cleaner:
Why is this so hard?

Physics and Chemistry

- Must be understood well to design remediation – see site use.

Site Use

- Dry cleaners
  - Strip malls
  - Very tight areas
  - Residential areas
  - Large process plants
  - Historical handling practices
  - Sensitive human receptors (VI)
  - Sensitive environmental receptors
  - Many have historical uses such as gas stations that complicate remediation

Invention of EZVI

Scientists at UCF and NASA (KSC) invented EZVI to address chlorinated solvent DNAPL contamination at the Kennedy Space Center in Cape Canaveral, FL.

NASA utilized TCE as a degreaser for rocket engine parts throughout the 1960's.

DEVELOPMENTS TO DATE

- 1997 – 1998: Conceptualization/Development
- 1999 – 2002: Proof of Concept R&D at UCF/KSC
- 2003 – 2004: Pilot studies – EPA SITE Evaluation
- **2005 – 1st FULL SCALE implementation**
- 2005 – Present: Various Applications across USA, Canada, EU
- 2015 – Technology Enhancement – new product **EZVI-CH4™**
- 2015 – Present: Continued Optimization of the EZVI product
- 2016, 2017 – Remediation events with results presented here
- 2019 – Most Recent Research Article (shown on right)

Hindawi
Journal of Chemistry
Volume 2019, Article ID 7565464, 8 pages
https://doi.org/10.1155/2019/7565464

Research Article

Remediation of Chlorinated Alkanes by Vitamin B_{12} and Zero-Valent Iron

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Received 27 November 2018; Revised 15 January 2019; Accepted 29 January 2019; Published 25 March 2019

Academic Editor: Bryan M. Wong

Chlorinated alkanes were heavily used in a wide range of industrial applications including as degreasers, paint strippers, chemical intermediates, and soil fumigants. These compounds are an environmental concern due to the adverse health effects associated with them and have been detected in environmental matrices including soils and groundwater. Chlorinated alkanes are recalcitrant, and current remediation methods that employ zero-valent iron (ZVI) are unable to directly dehalogenate these compounds, limiting the available approaches for *in situ* remediation of these widely utilized chemicals. This study employed a novel approach for the remediation of 1,2,3-trichloropropane (TCP), 1,2-dichloropropane (1,2-DCP), 1,3-dichloropropane (1,3-DCP), 1-chloropropane (1-CP), and 1,2-dichloroethane (1,2-DCA) in the presence of ZVI and vitamin B_{12}, a naturally occurring electron mediator. Batch reactions were performed in order to determine a kinetic model for the associated degradation mechanisms. Dechlorination byproducts were confirmed through gas chromatography-mass spectrometry (GC-MS) coupled to a purge and trap. Free chloride was quantified by ion chromatography (IC) utilizing suppressed conductivity detection. In the absence of vitamin B_{12}, reductive dechlorination of chlorinated alkanes was observed to not occur when exposed to only reactive ZVI particles (<5 μm). However, in the presence of ZVI combined with vitamin B_{12}, complete reductive dechlorination was observed and followed a pseudo-first-order reaction.

1. Introduction

Chlorinated volatile organic compounds (Cl-VOCs) were heavily used until the mid-1980s as solvents in industrial applications such as dry cleaning, pharmaceutical synthesis, adhesive manufacturing, metal component cleaning, and many others [1, 2]. These compounds have been inadvertently released into the environment through various activities including spills, leaks, and improper disposal, or intentionally released [3]. Chlorinated solvents have been detected at roughly 80% of US Superfund sites and at over 3,000 US Department of Defense sites [4]. Common physical properties of Cl-VOCs include higher densities and lower viscosities than water, high volatility and low water solubility. Due to these characteristics, these compounds are able to migrate vertically beneath the water table and persist as dense nonaqueous phase liquids (DNAPLs). In subsurface environments, after penetrating the saturated zone, DNAPL contamination can exist as free phase, in pools, or in a residual phase, that is sorbed onto soils. Any of these forms can then act as long-term sources of groundwater contamination and are also known as contaminant "source areas" in the environmental remediation industry. Remediation of Cl-VOCs such as 1,2,3-trichloropropane (TCP), 1,2-dichloropropane (1,2-DCP), and 1,2-dichloroethane (1,2-DCA) is of great concern due to their environmental persistence. These substances pose serious health risks to humans and are all currently classified as anticipated human carcinogens [5–7]. More information on these compounds is shown in Table 1. Chlorinated

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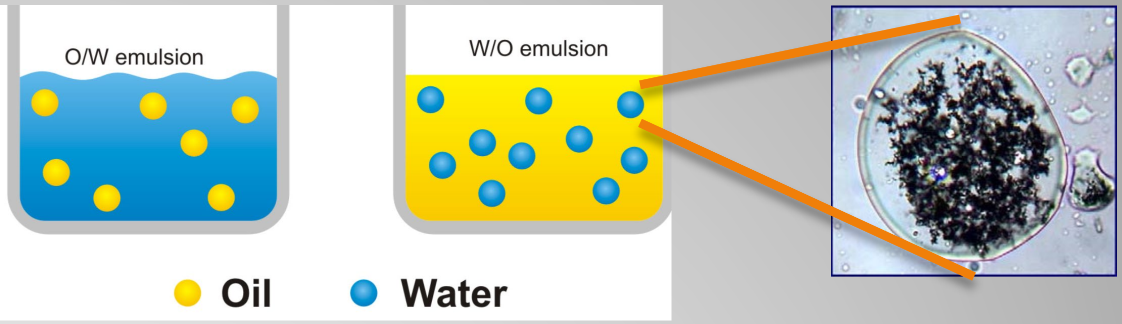
TECHNOLOGY DESCRIPTION

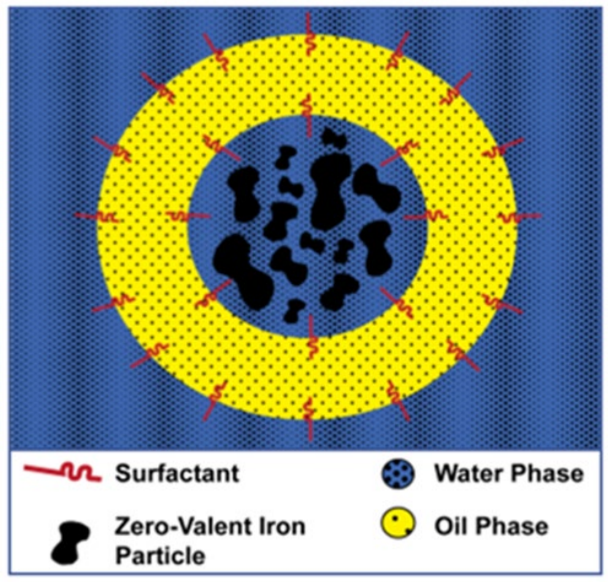
What is EZVI?

- Surfactant stabilized, water-in-oil emulsification with small micron (< 5 mm) ZVI particles suspended in the water drops.
- EZVI is a DNAPL (hydrophobic, sinker)

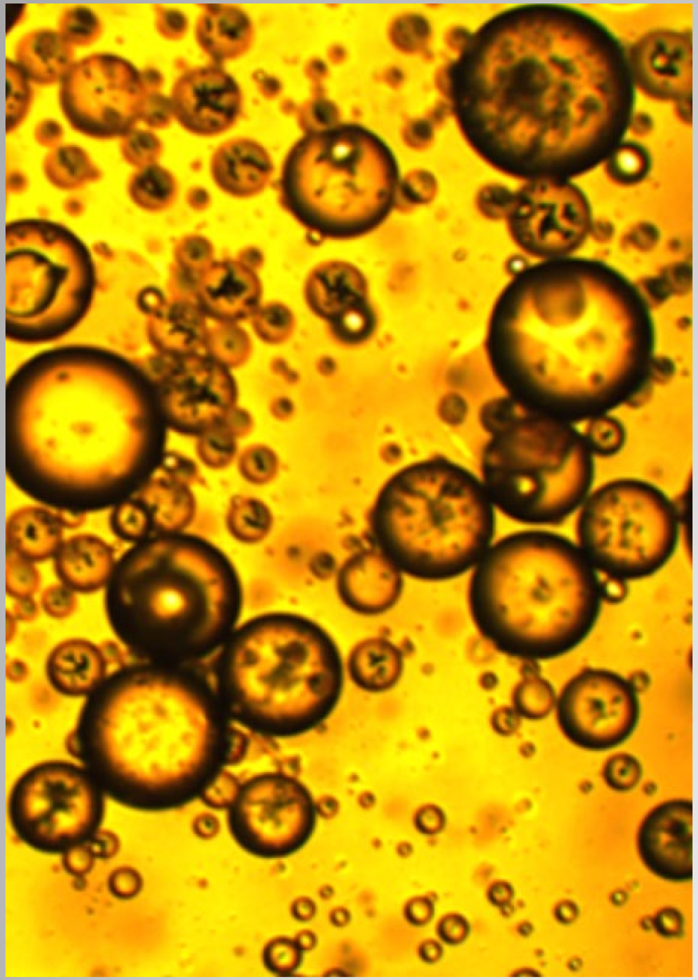


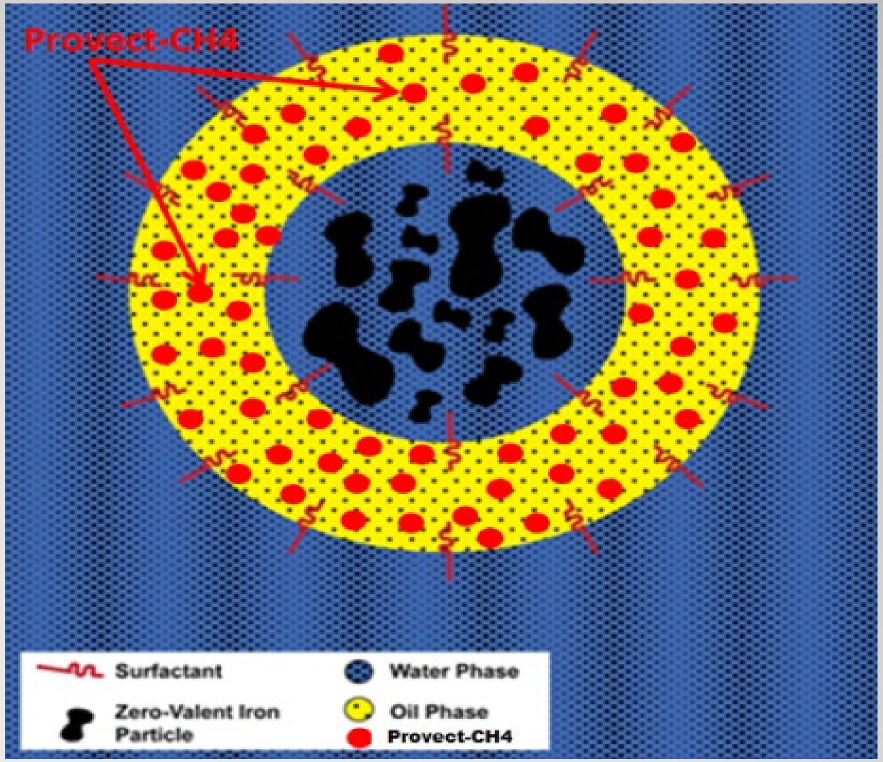
What is the innovation?

- Miscibility with DNAPLs
- Combination Technology utilizing abiotic & biotic processes AND physical chemistry
- Viscosity is lower than slurry applications
- Emulsion structure is key



In-situ DNAPL Destruction <u>with</u> Controlled Methanogenesis
*The EZVI is made with or without AMR as needed





EZVI-CH4™

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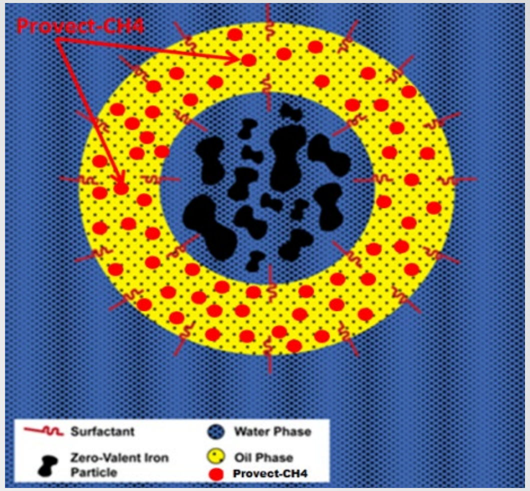
How Do We Control Methanogens?

RED RICE EXTRACT

ESSENTIAL OILS/SAPONINS

- Methanogens are genetically unique – Archaea
- Utilizing naturally occurring statins (RYR Extract) and select essential oils/saponins to disrupt enzyme and coenzyme processes unique to methanogens



IMPLEMENTATION

EZVI-CH4™

- Engineered as an *in situ* source area destruction technology
- Emplaced directly into source area soils
- Effective in vadose and saturated soils under certain conditions

- EZVI usually delivered via:
  - Direct Push
  - Hydraulic & Pneumatic Fracturing
  - Soil Mixing

When is EZVI an option?

- DNAPL is likely present:
  - COC(s) in GW ≥ 10% of water solubility (EPA approach)
  - The site is conducive to a reductive, *in situ* approach

How much do I need?

- Dosing is based on soil pore volume (not stoichiometry)
- Typical approach utilizes ~ 10% of available pore space

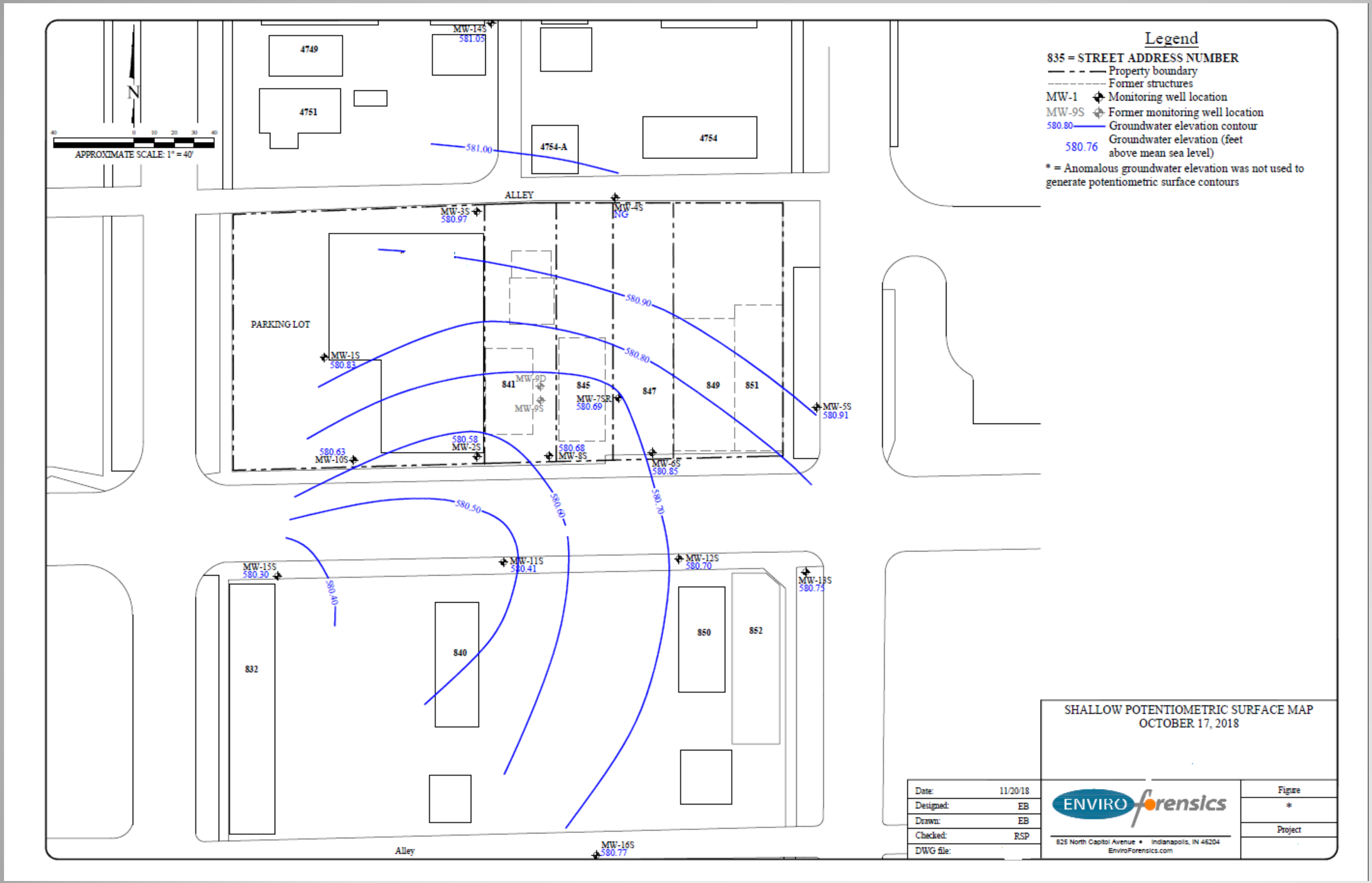
Can EZVI be injected through well screens?

- Not typically recommended
- This approach minimizes technology efficacy, but is adaptable for certain situations

CASE STUDIES

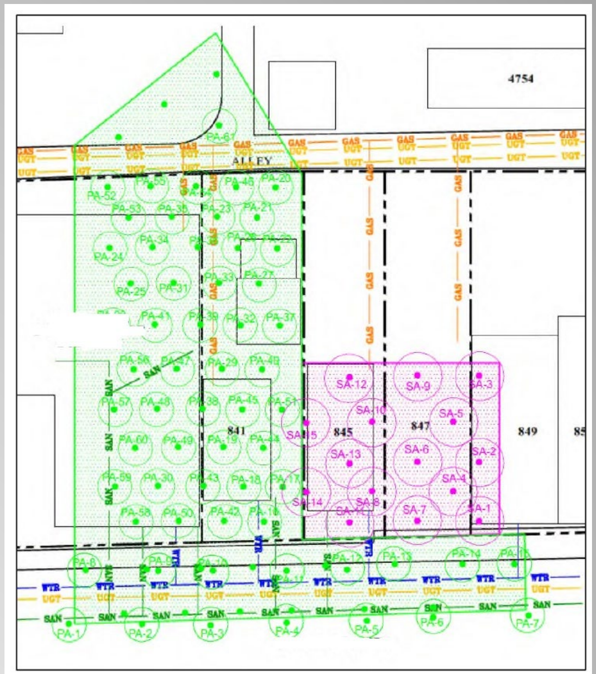
Urban Dry Cleaner Northwest Indiana

- Stand alone structure surrounded closely by residential structures on two sides and mixed residential/commercial structures on two
- Drycleaning operations have ceased; future site use unclear
- DNAPL concentrations of PCE in soil and groundwater
- DNAPL was observed during sampling
- Methane control must be utilized to protect surrounding structures and site structure
- Municipality denied the use of thermal remediation for source treatment due to proximity to utility corridors
- EZVI-CH4 was selected for source treatment and antimethanogenic Provect-IR for lower concentration plume mass
- It was assumed that multiple treatments would be required
- Currently monitoring initial treatment



General Site Layout

- Site Use
- Groundwater Flow
- Geology 0-23’
- Contaminant Distribution

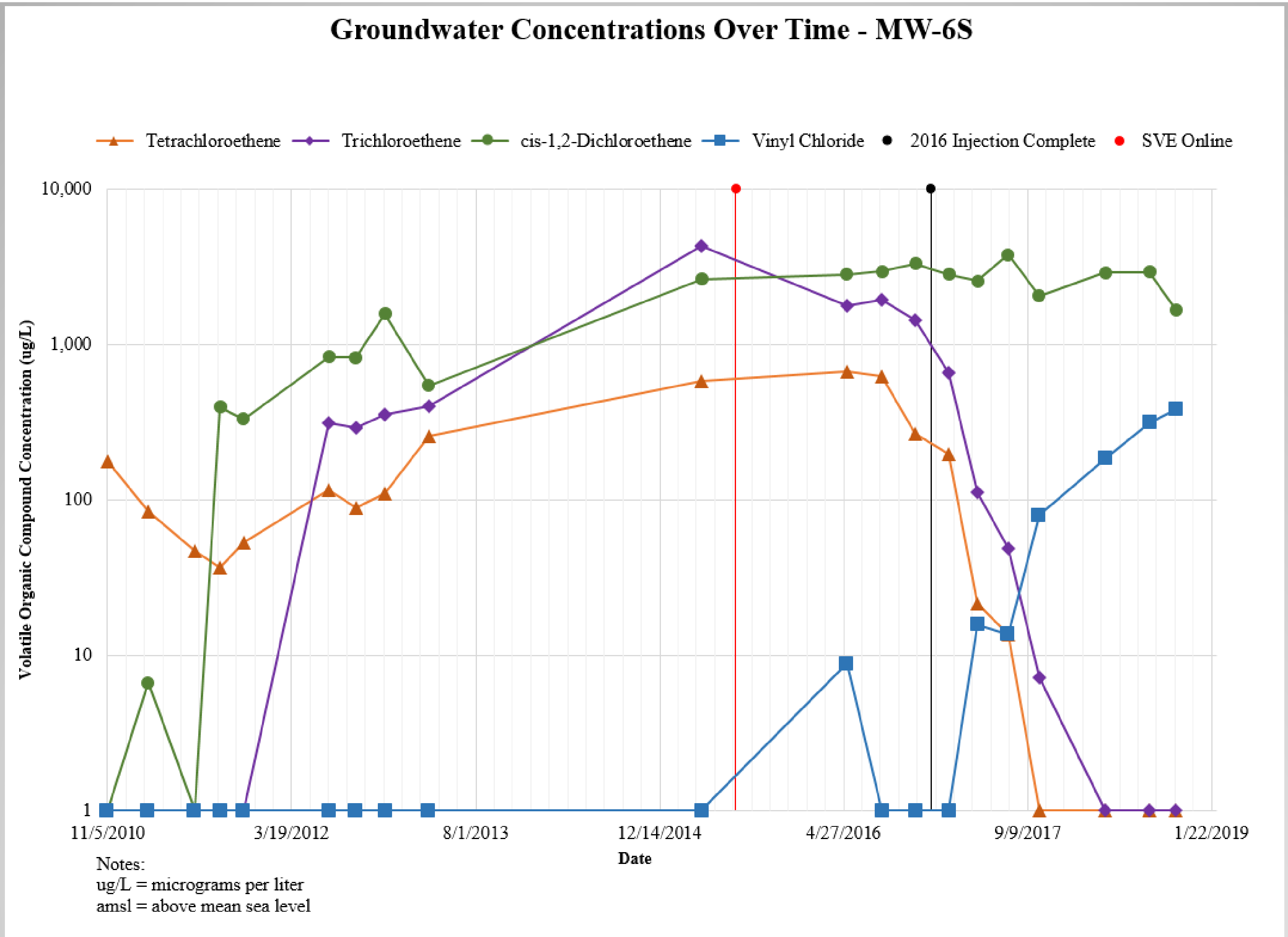


December 2016:

9,000 gallons of EZVI-CH4 in the pink source area (above)

14,000 gallons antimethanogenic Provect-IR in the green plume area (above)

Following graphs show wells within the EZVI-CH4 injection area.



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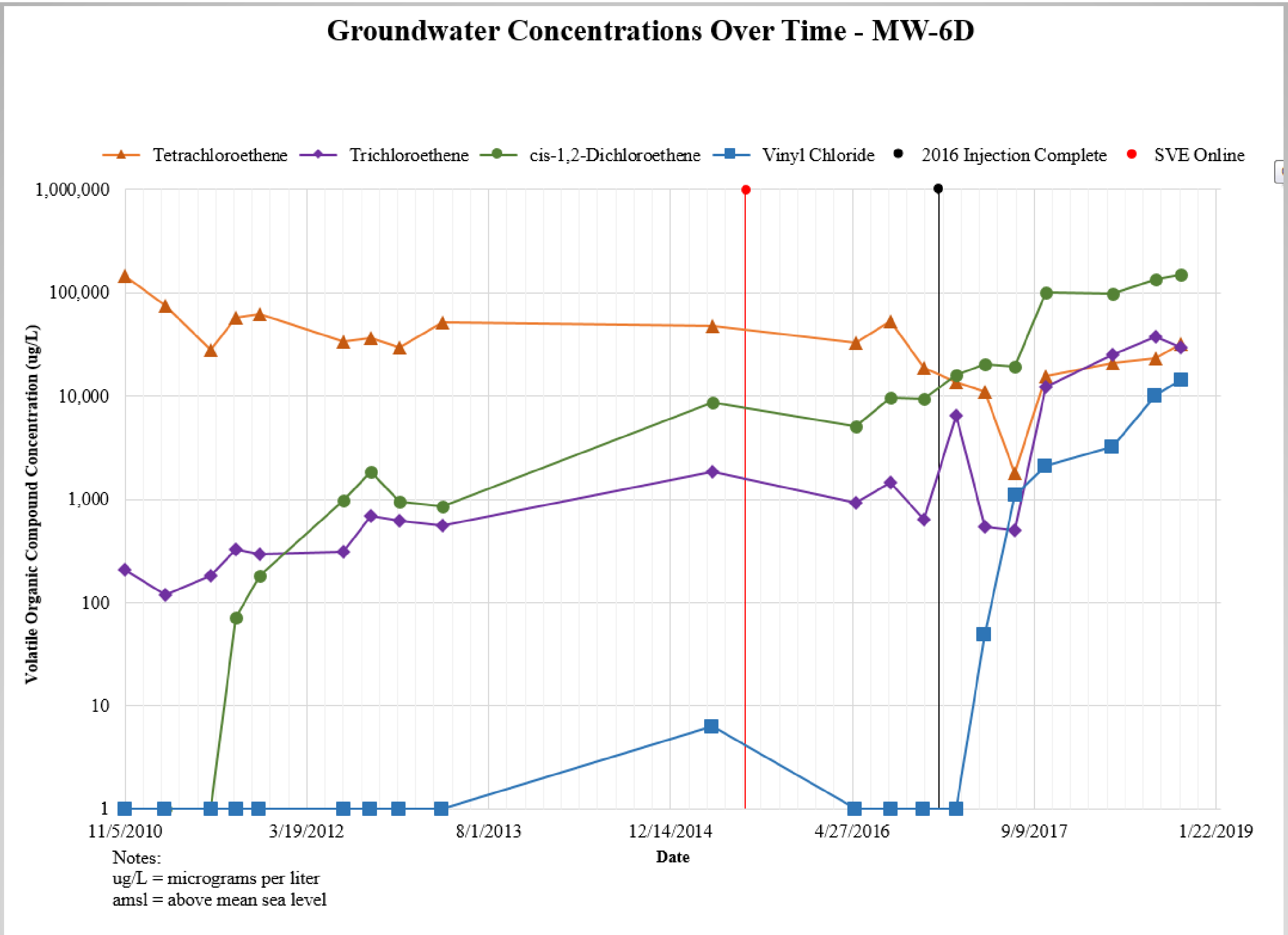

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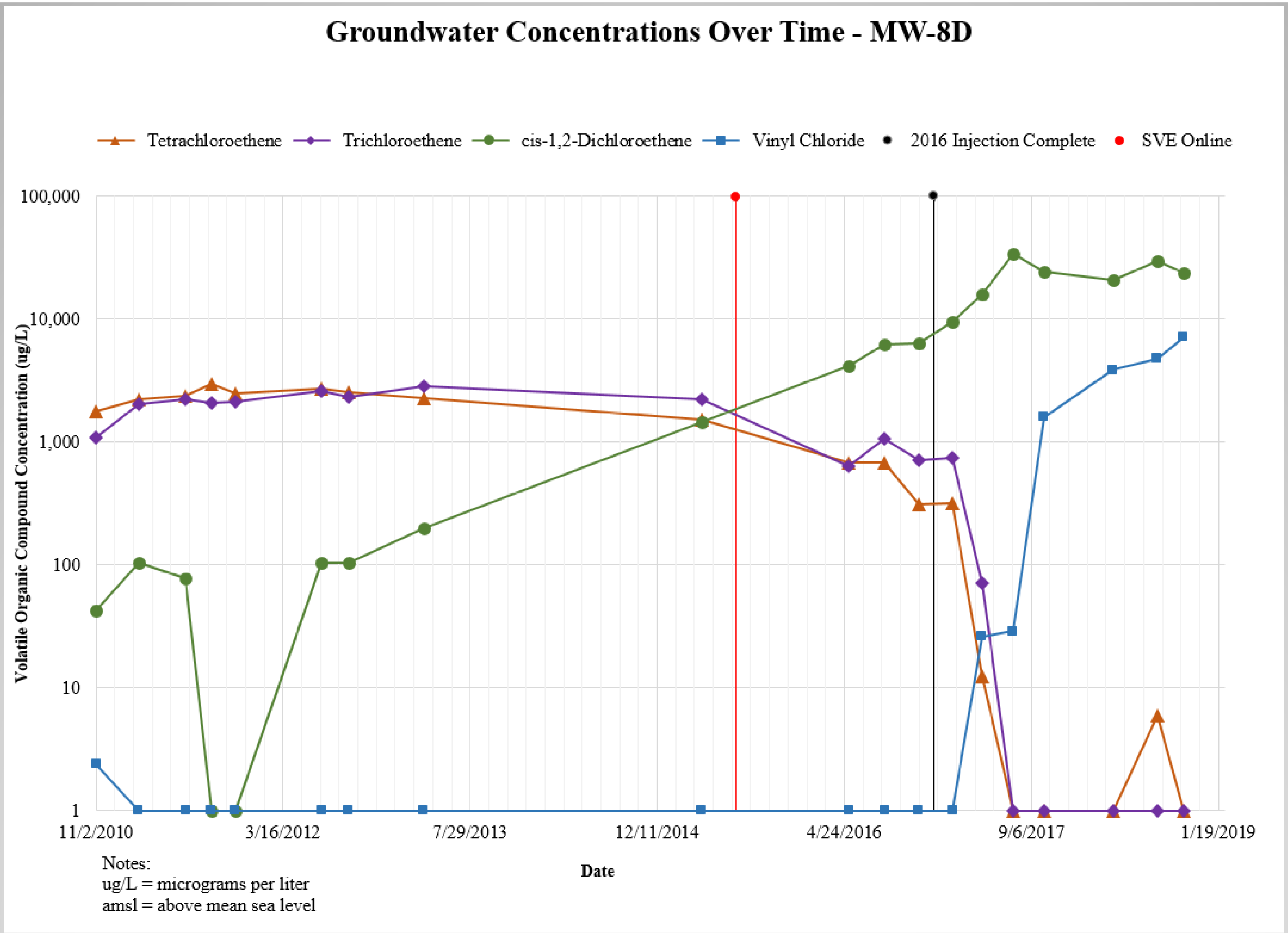
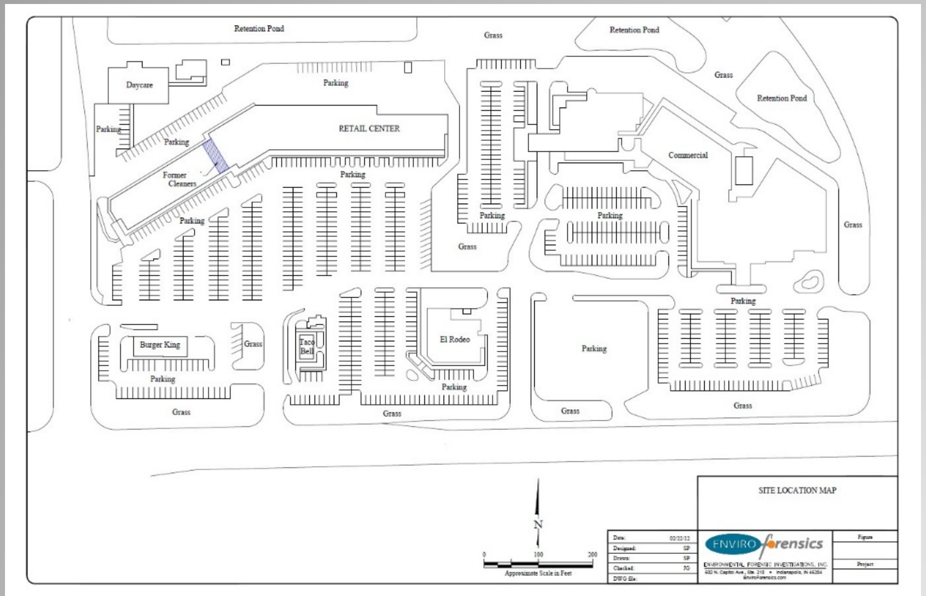

Groundwater Concentrations Over Time - MW-8D
Tetrachloroethene
Trichloroethene
cis-1,2-Dichloroethene
Vinyl Chloride
2016 Injection Complete
SVE Online
100,000
10,000
1,000
100
10
1
Volatile Organic Compound Concentration (ug/L)
11/2/2010
3/16/2012
7/29/2013
12/11/2014
4/24/2016
9/6/2017
1/19/2019
Date
Notes:
ug/L = micrograms per liter
amsl = above mean sea level

Methane Meter Readings from Late 2016 to Present

- Subslab port 1
  - 31 samples
  - 6% LEL Max concentration, 19 samples 0%
- Subslab port 2
  - 31 samples
  - 11% LEL Max concentration, 20 samples 0%
- Subslab port 3
  - 31 samples
  - 10% LEL Max concentration, 20 samples 0%
- Subslab port 4
  - 31 samples
  - 5% LEL Max concentration, 17 samples 0%
- Soil gas ports at 5 residences never exceeded 2% LEL
- Onsite indoor air did not exceed 0% LEL

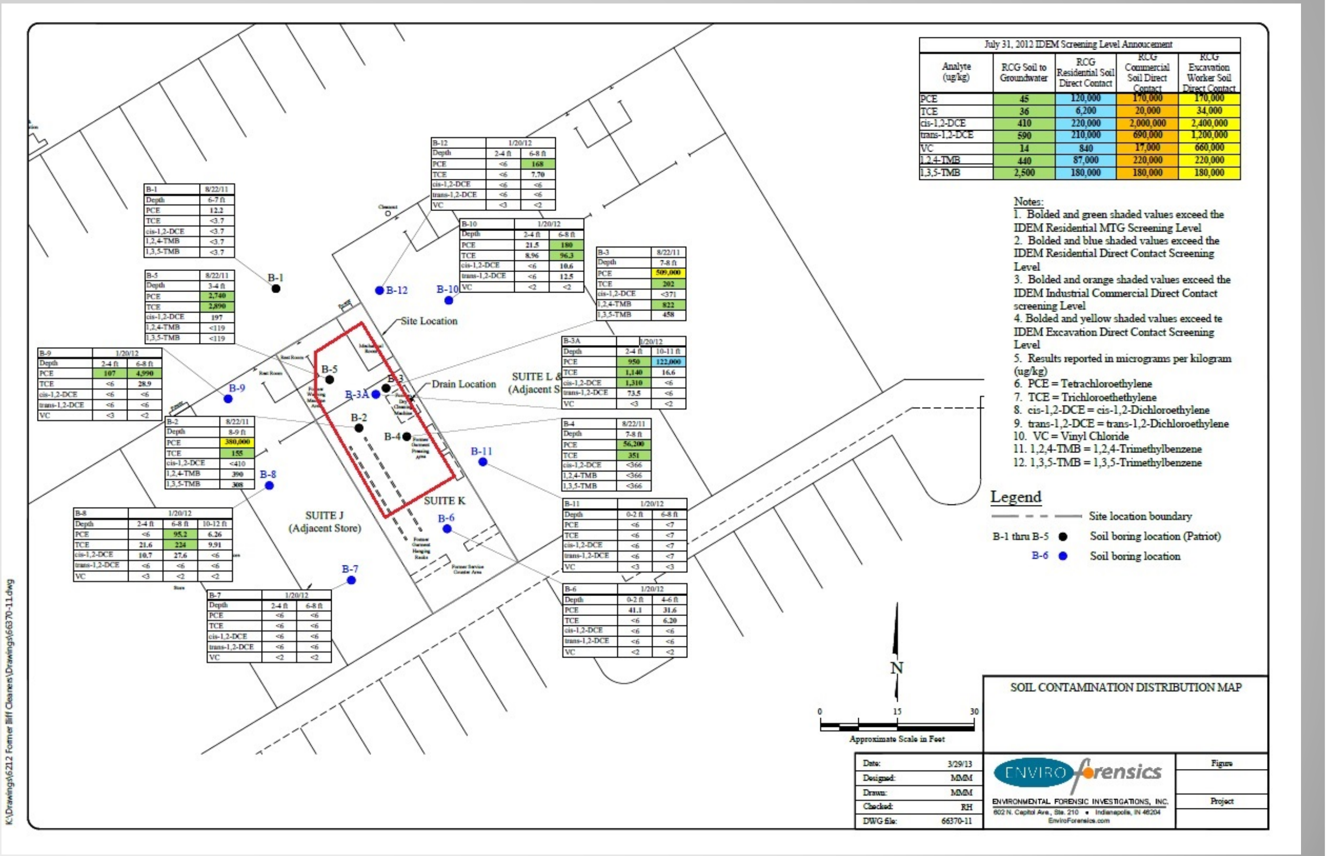
Urban Dry Cleaner Central Indiana

- Site is tenant space in the middle of a strip mall
- Dry cleaning operations ceased, currently a doughnut shop
- Surgical excavation was completed but tight space did not allow all impact to be removed
- High concentrations remained in soil and “bathtub” groundwater
- PVC structures emplaced for either venting or injection of substrate
- Groundwater was exhibiting high concentrations and no downward trend
- EZVI-CH4 was selected for treatment by injecting into and filling the excavation scar (backfilled with pea gravel)
- Idea was to aggressively treat back diffusion from the excavation walls where impact was left in place
- Currently monitoring initial treatment

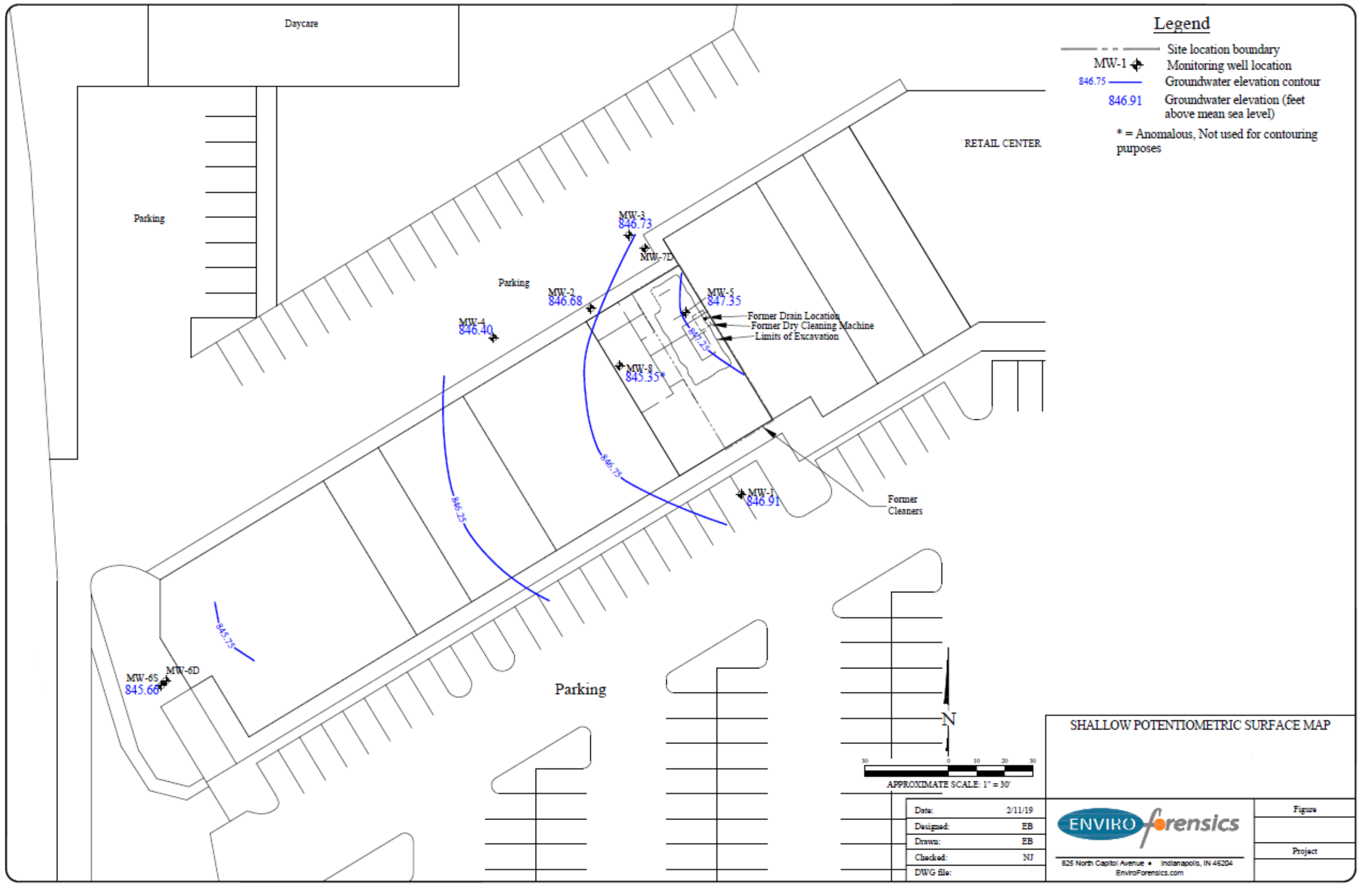


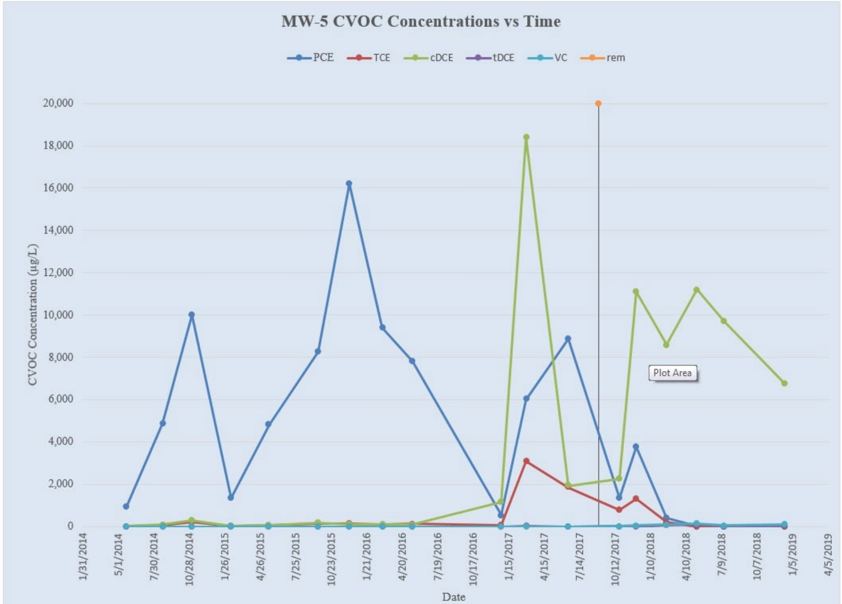
Dry cleaner location and sensitive receptors

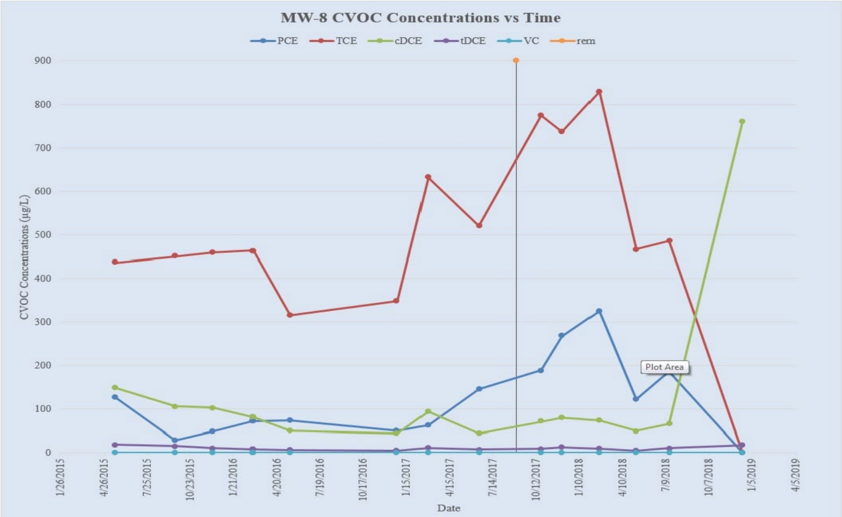
Excavation location and soil sampling results



Injected 600 gallons of non-diluted EZVI-CH4 into PVC piping into the former excavation fill







Note significant results in PCE and TCE at both MW-5 and later at MW-8 after the remediation front reached that point.

Methane Meter Readings from Late 2017 to Present

- Subslab port 1
  - 17 Samples
  - 3% LEL Max concentration, 11 samples 0%
- Subslab port 2
  - 17 samples
  - 3% LEL Max concentration, 16 samples 0%
- Subslab port 3
  - 17 samples
  - 4% LEL Max concentration, 11 samples 0%
- Subslab port 4
  - 17 samples
  - 3% LEL Max concentration, 14 samples 0%
- Onsite indoor air had one detection of 3% LEL and 8 of 9 samples did not exceed 0% LEL
- Offsite locations did not exceed 0% LEL

Questions?

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