

# Chlorinated Solvent Source Area Remediation: Combining Biotic and Abiotic Enhanced Reduction Approaches

**Fernanda P. Wilson, PhD** [fpwilson@ftch.com](mailto:fpwilson@ftch.com)

Michael S. Apgar [msapgar@ftch.com](mailto:msapgar@ftch.com)

Bruce E. Gillett, CPG [begillett@ftch.com](mailto:begillett@ftch.com)


Daniel Leigh [daniel.leigh@peroxychem.com](mailto:daniel.leigh@peroxychem.com)

John Valkenburg [john.valkenburg@peroxychem.com](mailto:john.valkenburg@peroxychem.com)



# Outline

- Background
- Site Hydrogeology
- Biotic Remedial History
- Abiotic Remedial Implementation
- Performance Monitoring Results
- Lessons Learned



# Background & Site Hydrogeology

Middleville, Mich.

# Background

- Site is located inside a **manufacturing plant in southwestern Michigan.**
- Contamination was discovered in **soil and groundwater.**
- **Chemicals of concern: Trichloroethylene** and its daughter products.

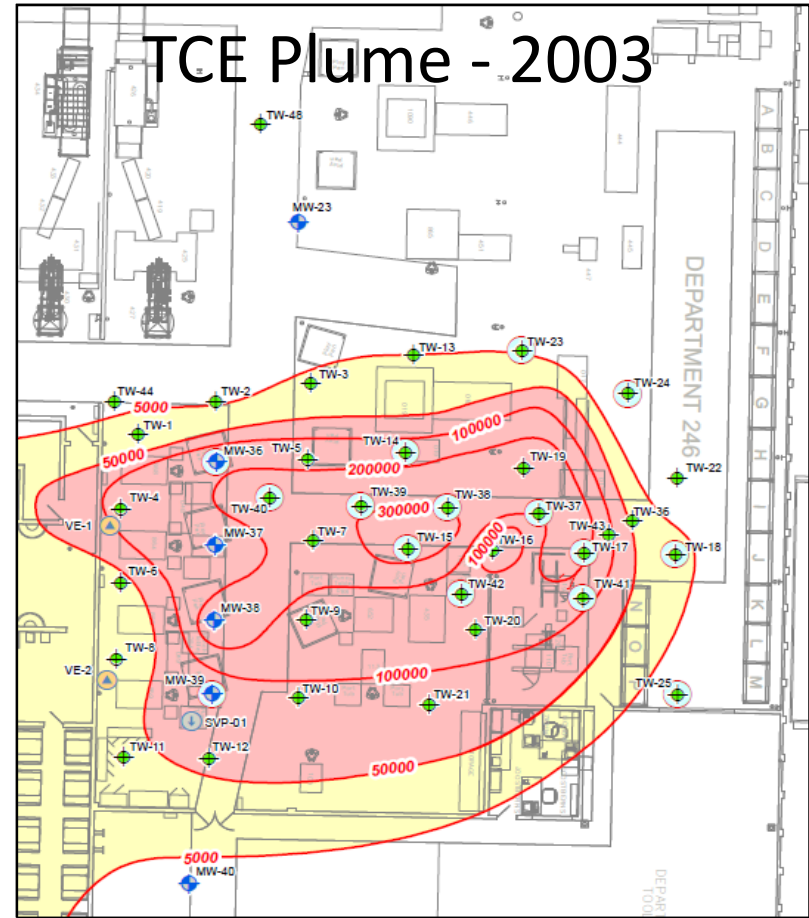
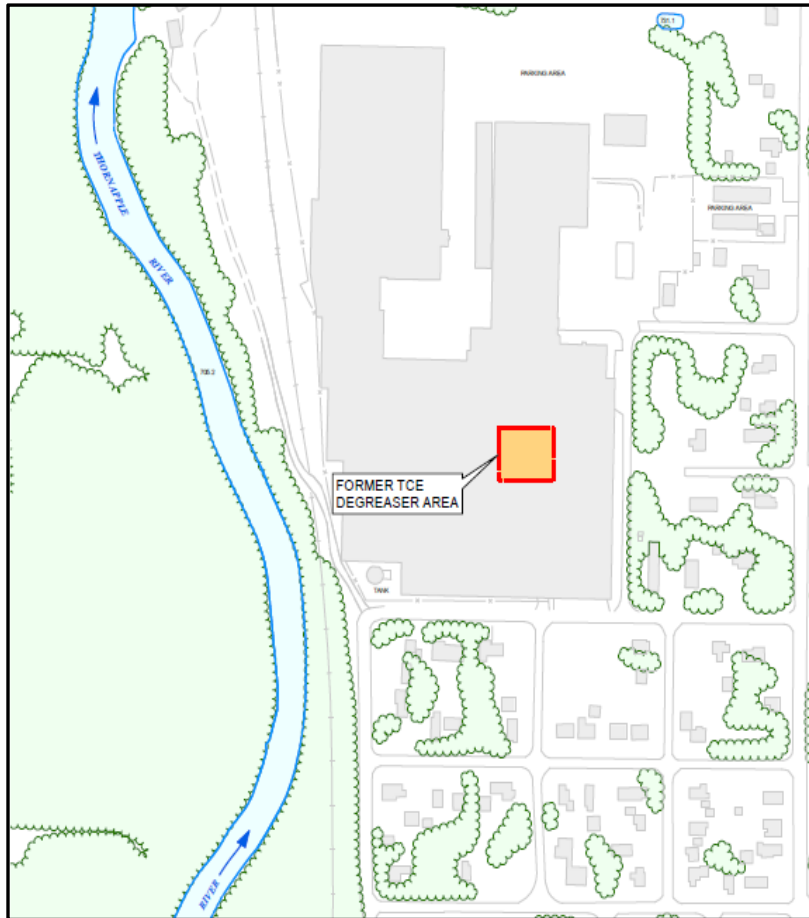


# Background

- Studied area located **beneath the active plant**, at the former locations of two degreasers.
- **Chlorinated solvents** were used to degrease equipment and products as part of the manufacturing.
- Employee-owned **water heater** manufacturer with over **1,500 employees**.

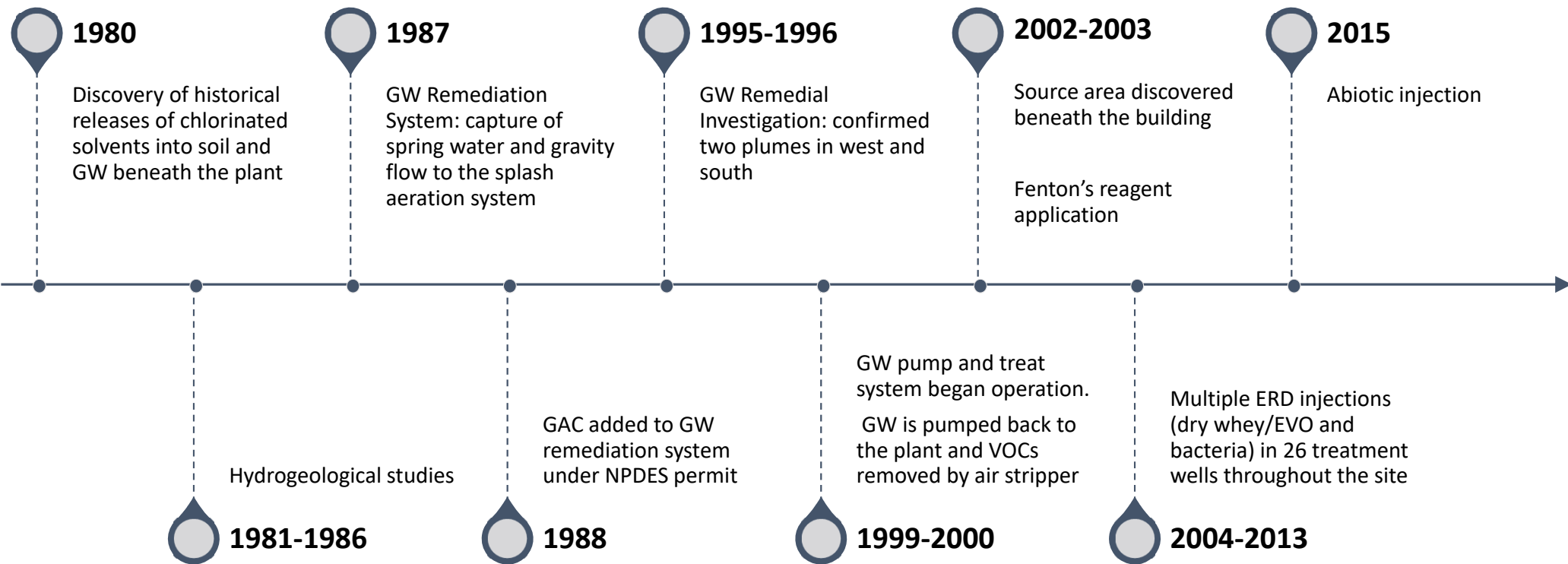


# Site Map



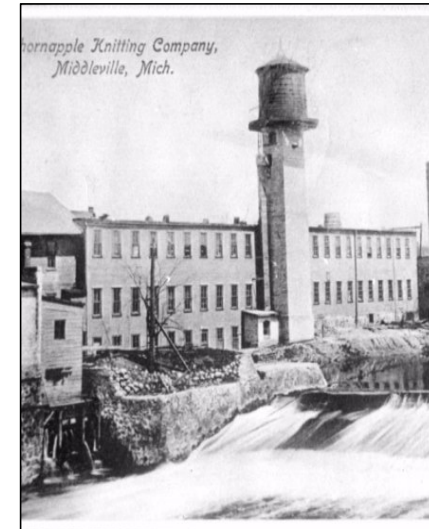
Middleville, MI

# Site Timeline



# Background

- **Chlorinated solvents** which are no longer used, leaked from two degreasing pit locations beneath the plant floor.
- Soil: Limited info, but likely greatly reduced by the operation of an **SVE system** since 2007 (CVOCs and methane).
- GW: The **impacted aquifer** from ~15 to 30 feet below floor level (bfl).



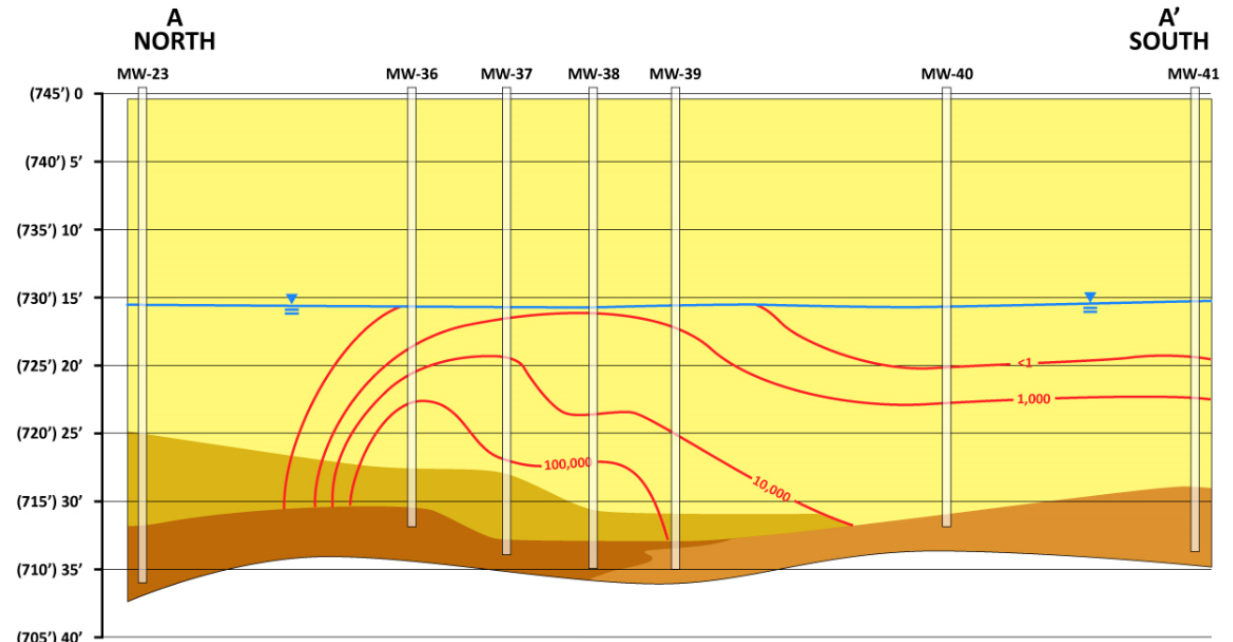
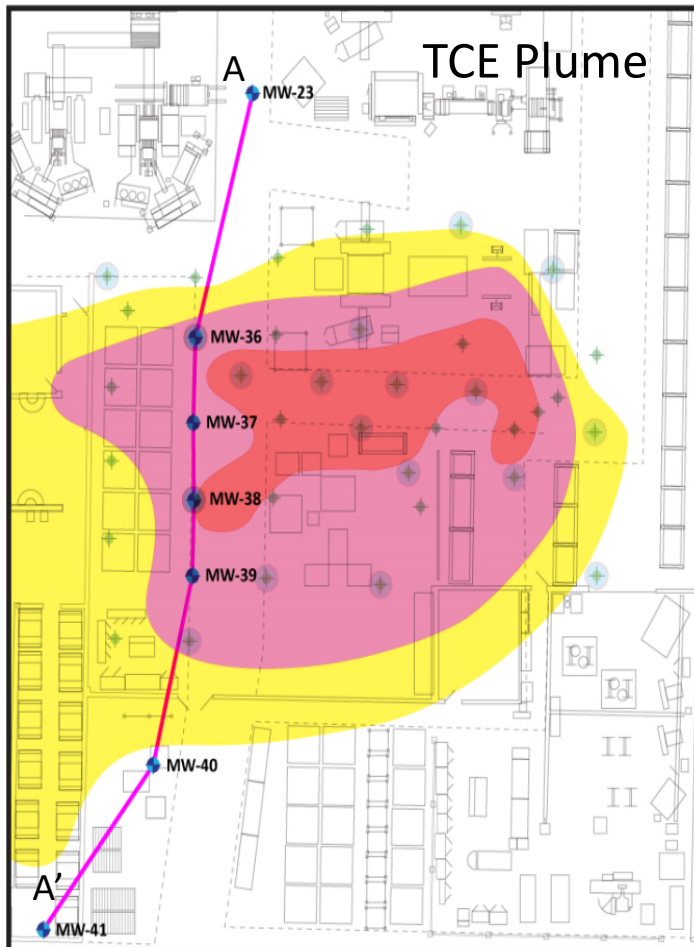


# Existing Capture System

- 1999-Present
- **Former TCE degreasing Area** to be discussed in this presentation
- **Concentrations downgradient** of Capture system are low and **meet site-specific GIS** criteria



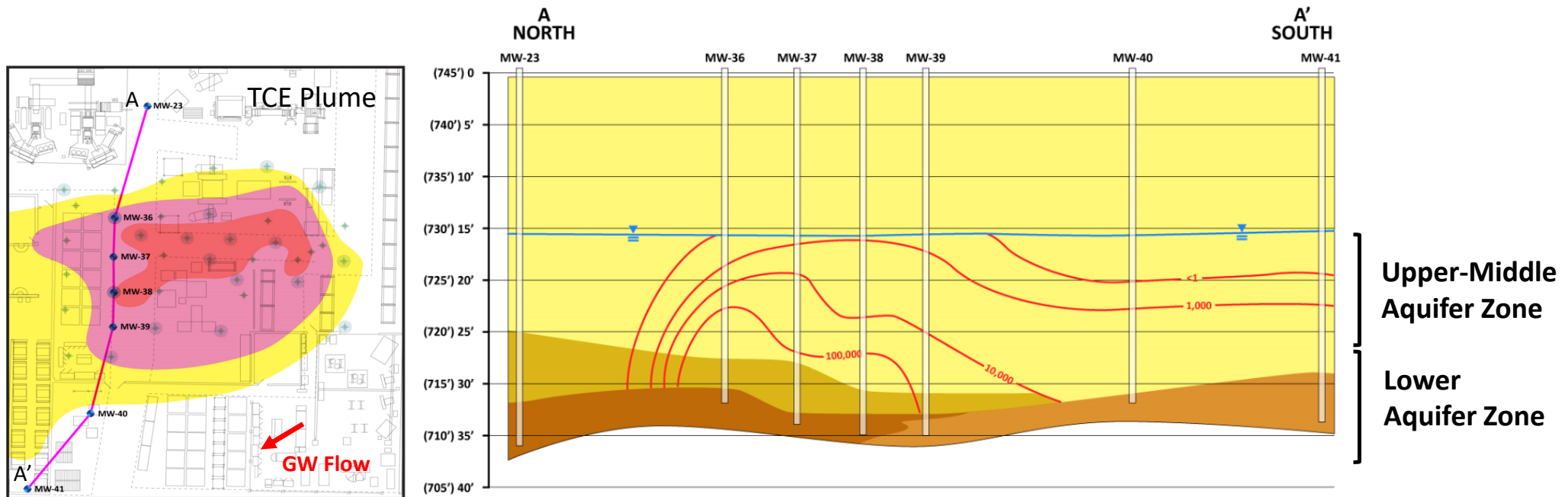
# Hydrogeology



- **Fine to medium sand:** below the plant floor to approximately 28 feet bfl.
- **Silty, fine to medium sand:** thickness ranges from 2-3 feet below the fine to medium sand.
- **Dry, clay unit:** under the silty, fine to medium sand.

# Hydrogeology

Groundwater flows to the Southwest and it is encountered at approximately 15 feet bfl



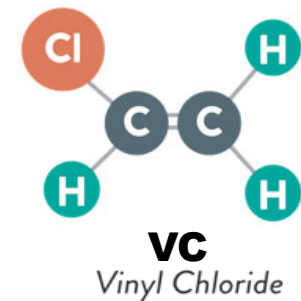
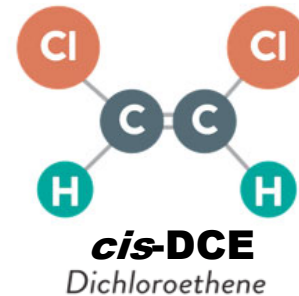
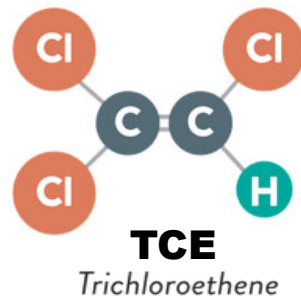
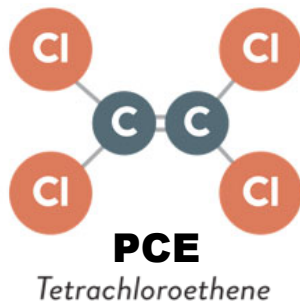
Most chlorinated volatile organic compound (**CVOC**) mass is in the **lower aquifer zone**



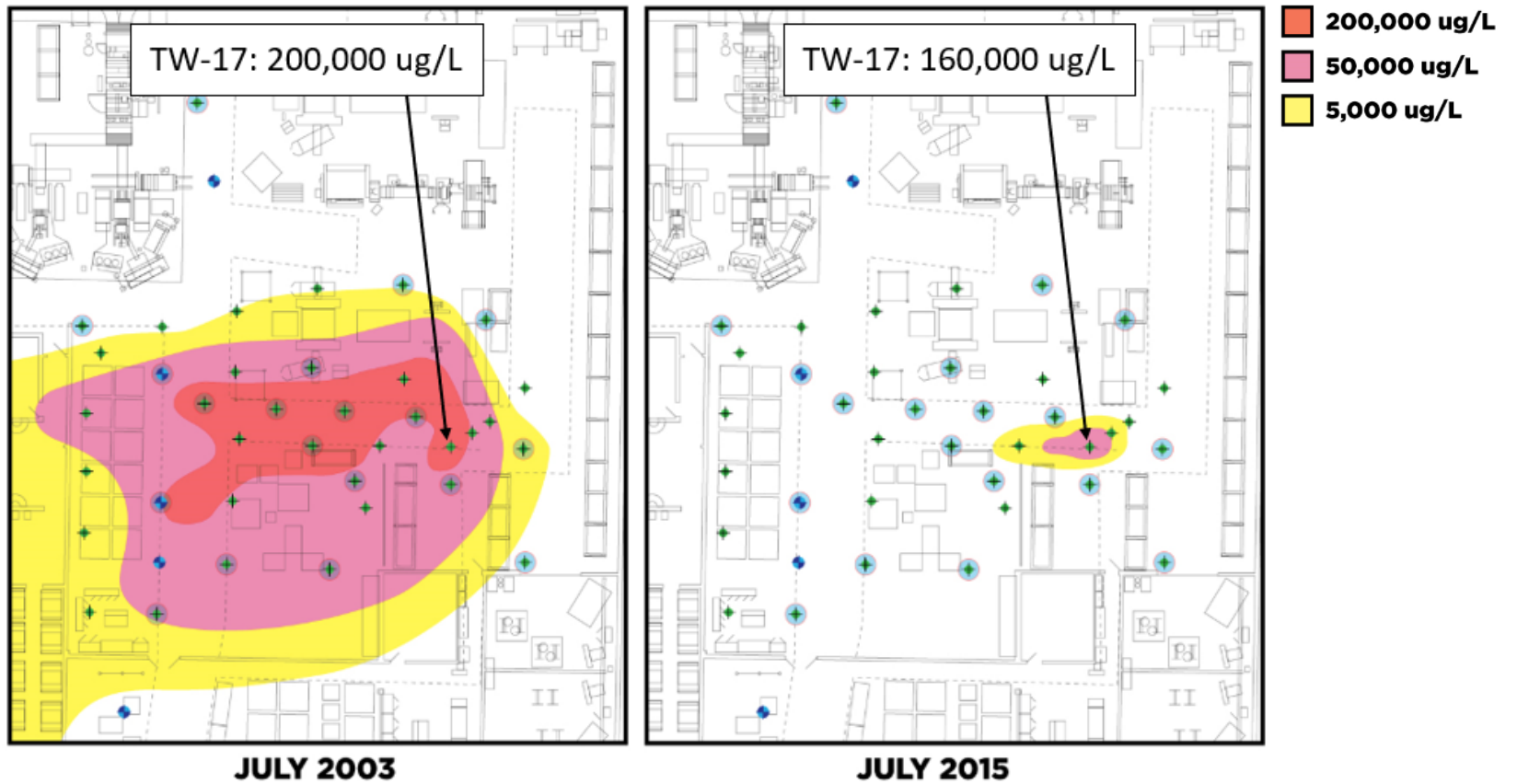
# Biotic Remedial History

# Biotic Remedial History: ERD injections 2004-2013

- Both aquifer zones were initially remediated with enhanced reductive dechlorination (ERD) utilizing **EVO** injections followed by inoculation with *Dehalococcoides*.
- GW monitoring over 10 years showed dramatic **reduction (over 98%) of DNAPL mass**; but **one hot spot persisted** in the source area.
- **Suspected toxicity limitation for ERD warranted a new strategy** for the hot spot in the source area.



# Hot Spot in the Source area - TCE Plume



Need to Address the hot spot in the source area...

## Main Objective

Promote **remediation of the Hot Spot in the Source Area** by augmenting the existing biotic treatment with injections to **establish abiotic pathways for CVOC reduction.**

# Abiotic Remedial Implementation

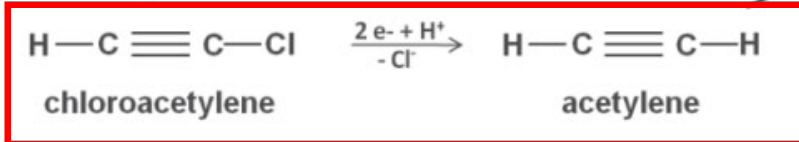
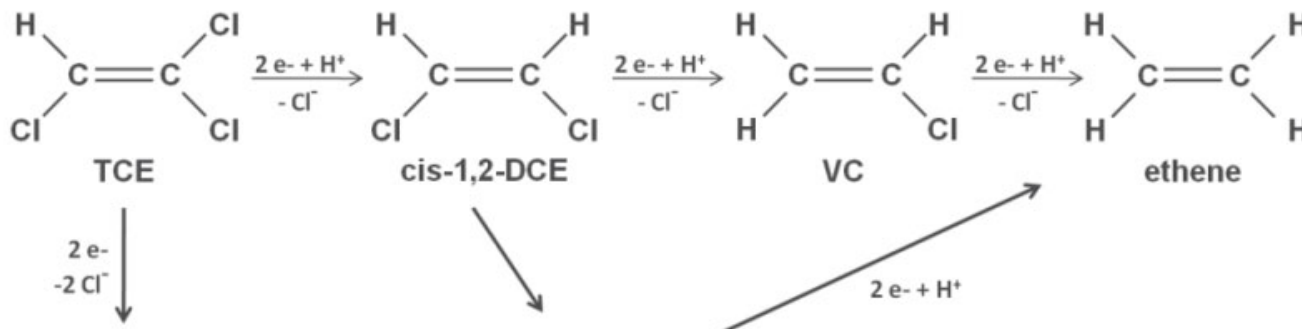




# Abiotic Remedial Implementation

- **July 2015:** abiotic direct injection event
- **Product selected:** EHC-L reagent

## Biotic Pathway (Step-Wise Reductive Dechlorination)

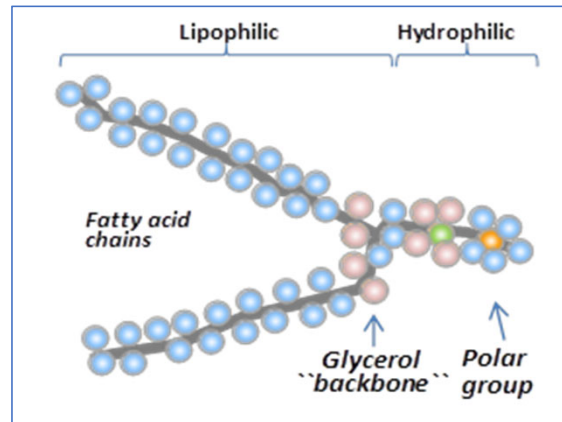


## Main Abiotic Pathway ( $\beta$ -Elimination)



# Abiotic Remedial Implementation

ELS 25% microemulsion



Structure of Lecithin

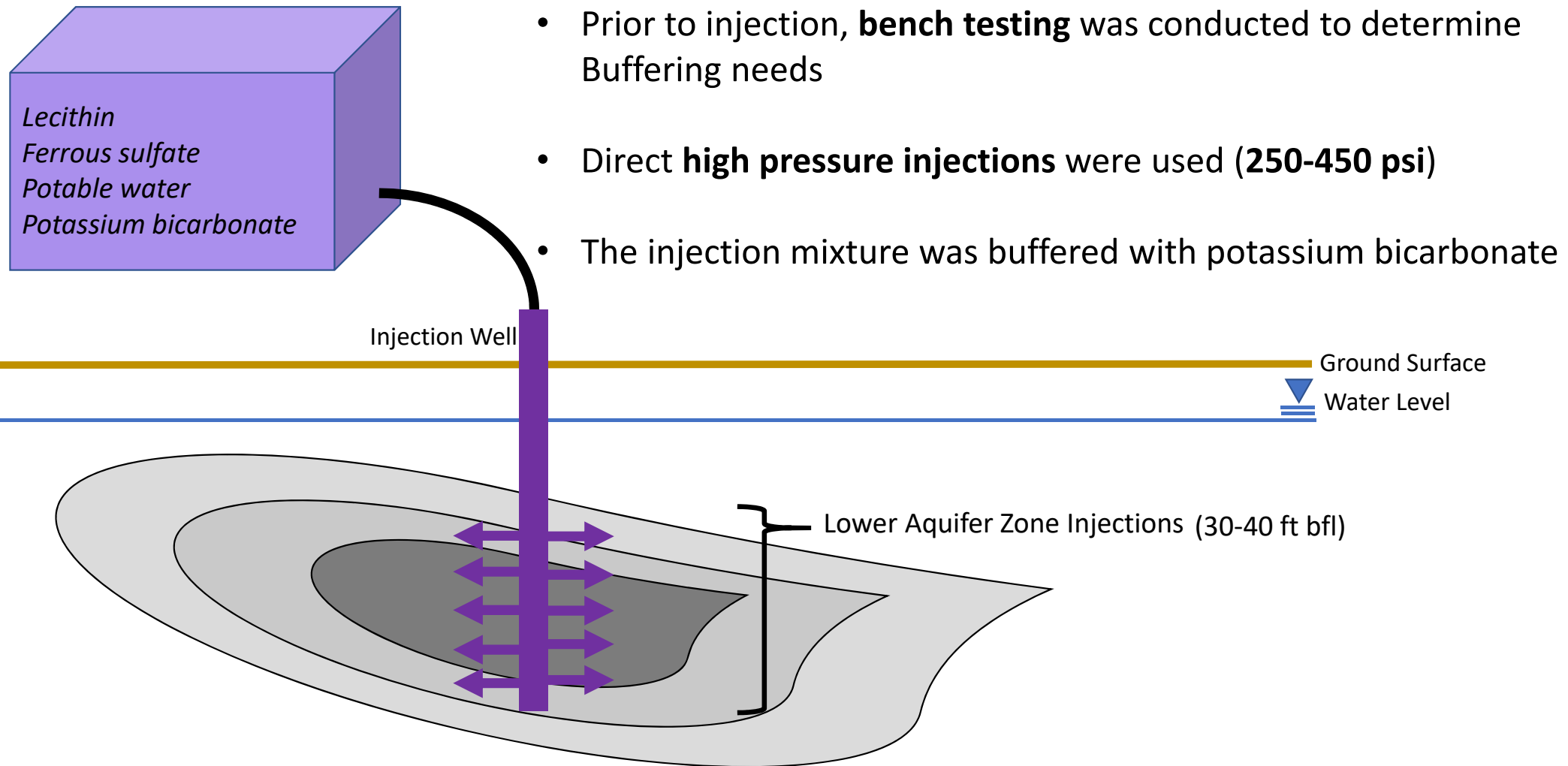
Injection Mix: lecithin, ferrous sulfate, and potable water solution, buffered with potassium bicarbonate

- **Lecithin**: organic carbon to support biodegradation and deepen the reducing environment
- **Ferrous sulfate**: form iron sulfide minerals to establish an abiotic reductive pathway

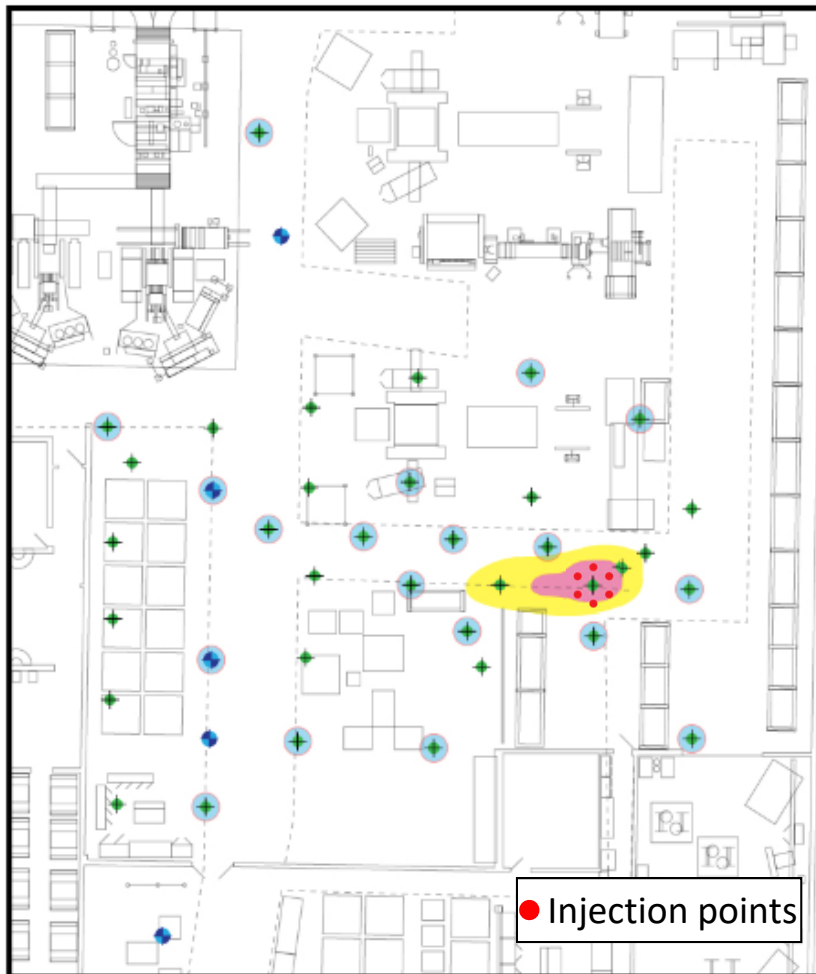


EHC- Liquid two parts

# Abiotic Injection

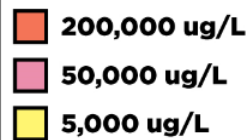


# Abiotic Injection

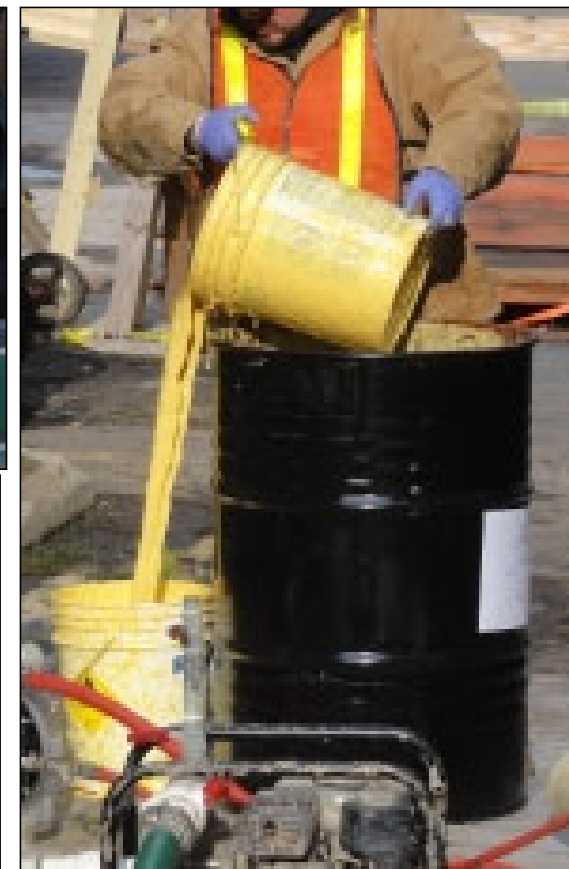


**JULY 2015**

- **226 gallons** of the injection mixture was used
- **6 direct-push locations** surrounding TW-17 (Hot Spot)



# Abiotic Remedial Implementation



Preparation of the Injection Mixture

# Abiotic Remedial Implementation



Direct High Pressure Injection



**Performance Monitoring  
Results and  
Lessons Learned**

# Performance Monitoring Results

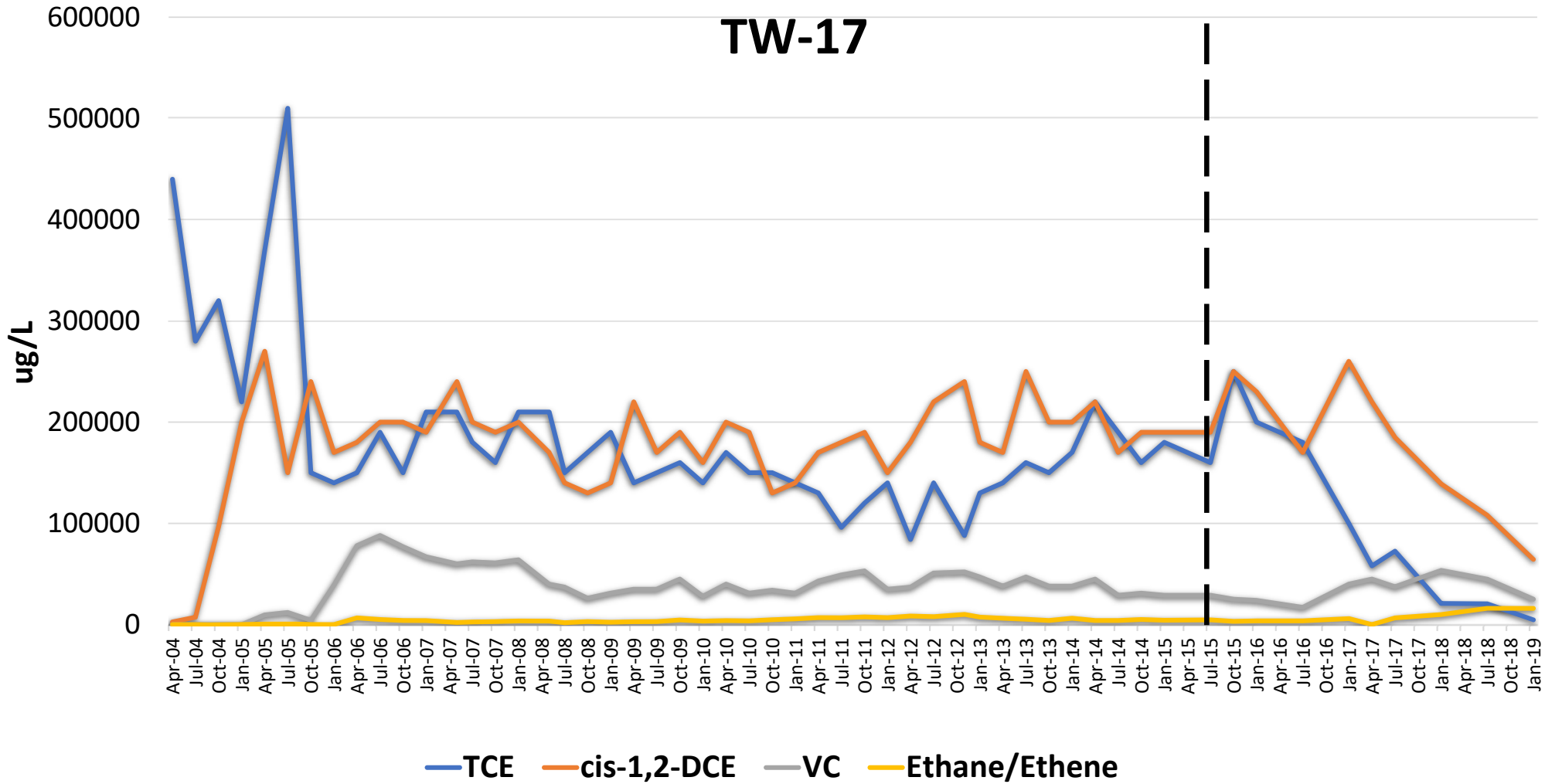
ERD conditions over the years of the treatment

## TW-17

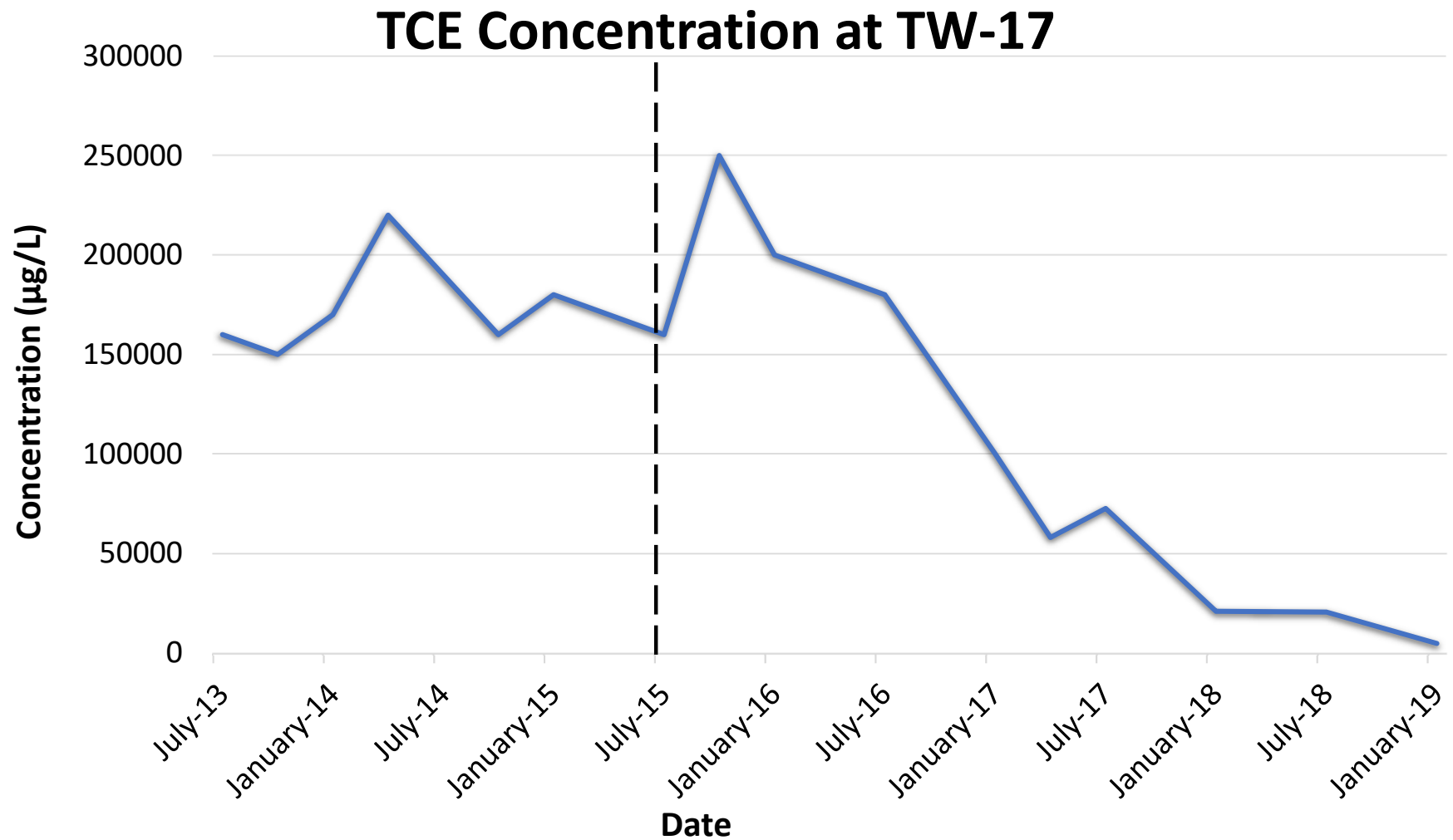
| Collection Date | TOC (mg/L) | Alkalinity, Total (mg/L) | Chloride (mg/L) | N, Nitrate (mg/L) | Phosphorus, T. (mg/L) | Sulfate (mg/L) | Ferrous Iron (mg/L) | Diss. Oxygen (mg/L) | Eh (mV) | pH (s.u.) | Temperature (°C) |
|-----------------|------------|--------------------------|-----------------|-------------------|-----------------------|----------------|---------------------|---------------------|---------|-----------|------------------|
| 08/18/15        | --         | --                       | --              | --                | --                    | --             | --                  | 1.3                 | 110     | 6.4       | 20.4             |
| 10/29/15        | 110        | --                       | --              | --                | --                    | 440            | --                  | 0.1                 | 91      | 6.4       | 17.7             |
| 01/19/16        | 56         | --                       | --              | --                | --                    | 85             | --                  | 0.2                 | 84      | 6.4       | 17.4             |
| 07/18/16        | 27         | 440                      | 270             | 0.05 U            | 0.05 U                | 27             | --                  | 0.2                 | 63      | 6.5       | 17.8             |
| 01/03/17        | 49         | --                       | --              | --                | --                    | 6.0            | --                  | 0.2                 | 36      | 6.2       | 17.2             |
| 04/26/17        | 43         | --                       | --              | --                | --                    | --             | 3.0                 | 0.2                 | -98     | 6.2       | 17.8             |
| 07/18/17        | 27.4       | 370                      | 263             | 0.05 U            | --                    | 16.1           | --                  | 0.2                 | 140     | 6.4       | 17.3             |
| 01/23/18        | 42.7       | --                       | --              | --                | --                    | 10.5           | --                  | 0.2                 | 170     | 6.3       | 17.0             |
| 04/18/18        | 73.8       | --                       | --              | --                | --                    | --             | --                  | 0.3                 | 140     | 6.2       | 16.7             |
| 07/18/18        | 84.5       | 344                      | 303             | 0.05 U            | --                    | 11.5           | --                  | 0.1                 | 100     | 6.5       | 17.0             |
| 10/18/18        | 49.2       | --                       | --              | --                | --                    | --             | --                  | 0.3                 | 110     | 6.3       | 16.0             |
| 01/28/19        | 47.6       | --                       | --              | --                | --                    | 12.1           | --                  | 0.2                 | 120     | 6.3       | 17.6             |



# Performance Monitoring Results

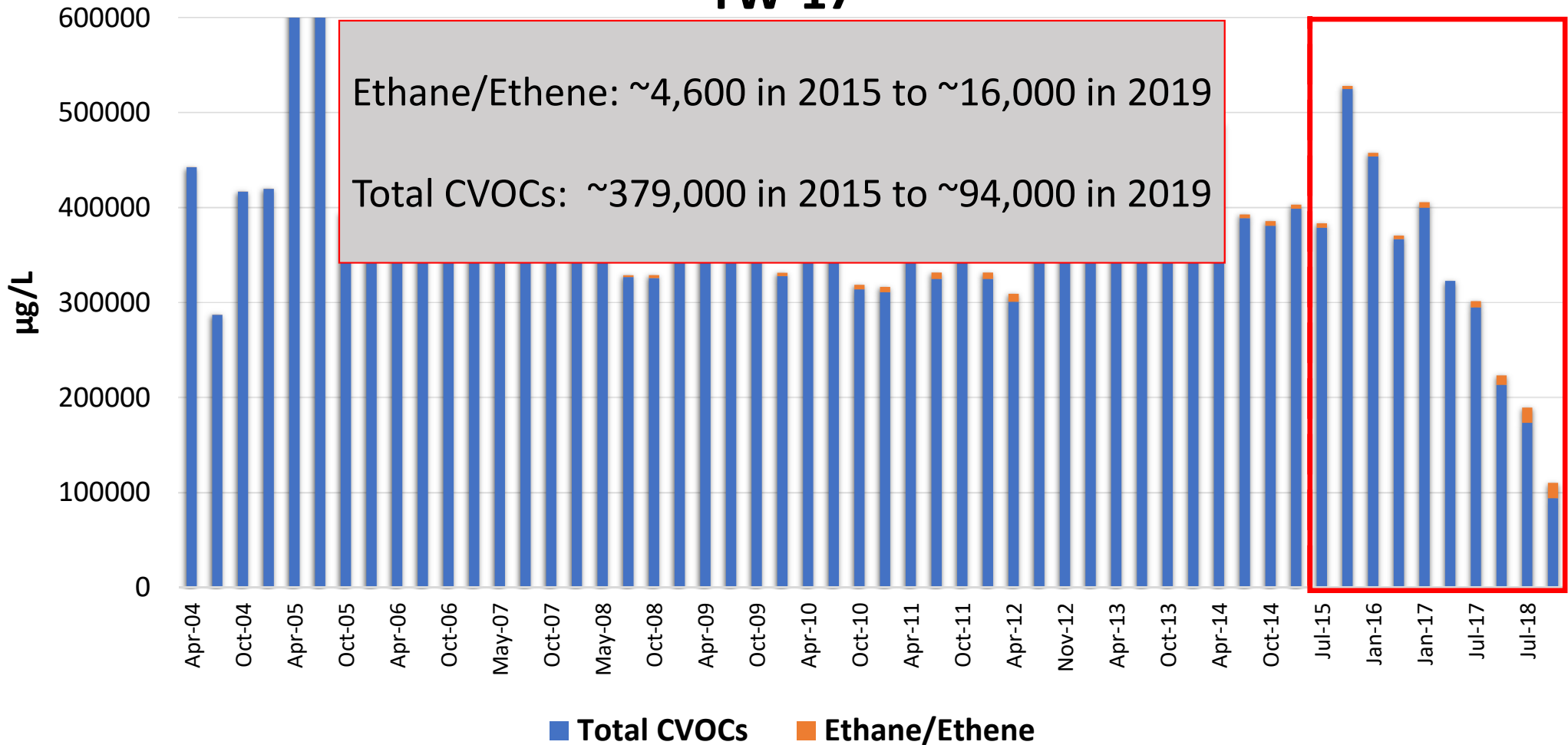


# Performance Monitoring Results



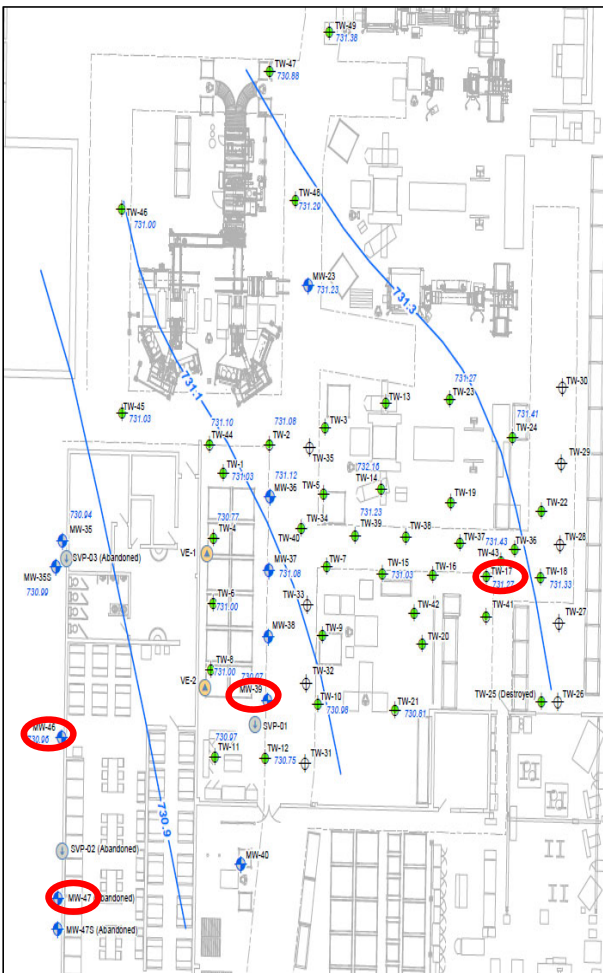
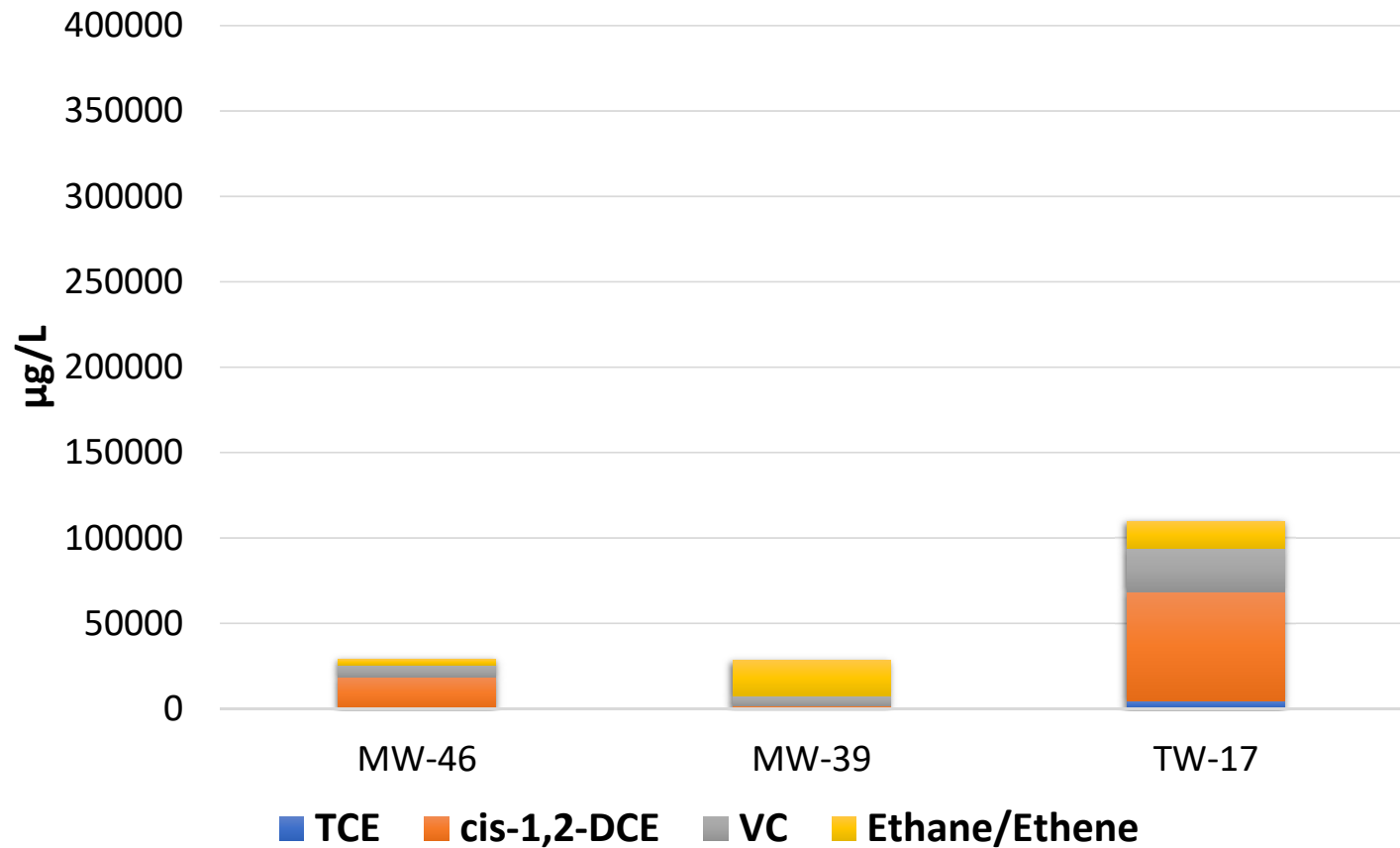
# Performance Monitoring Results

## TW-17



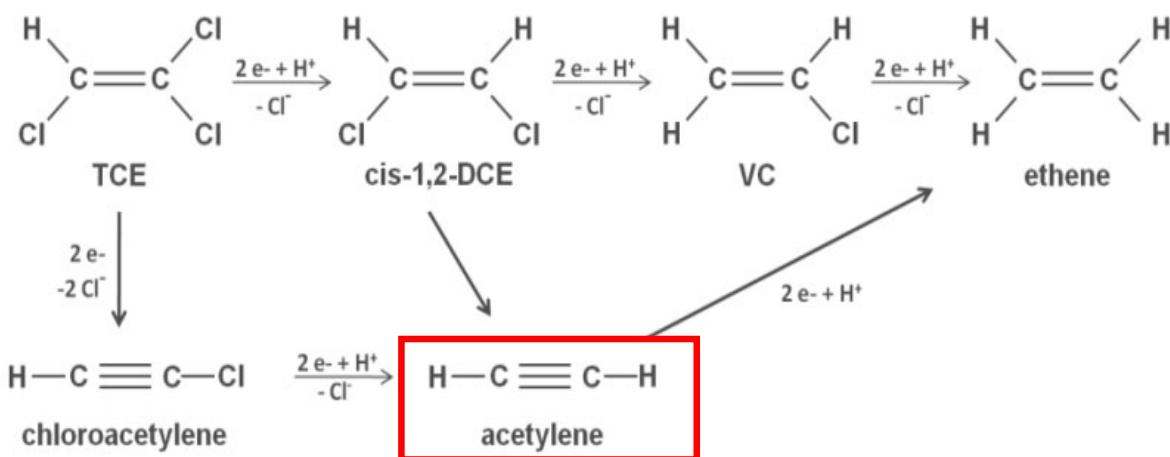
# Performance Monitoring Results

## Profile of Concentrations - January 2019



# Proof of Abiotic Pathway?

## Biotic Pathway (Step-Wise Reductive Dechlorination)

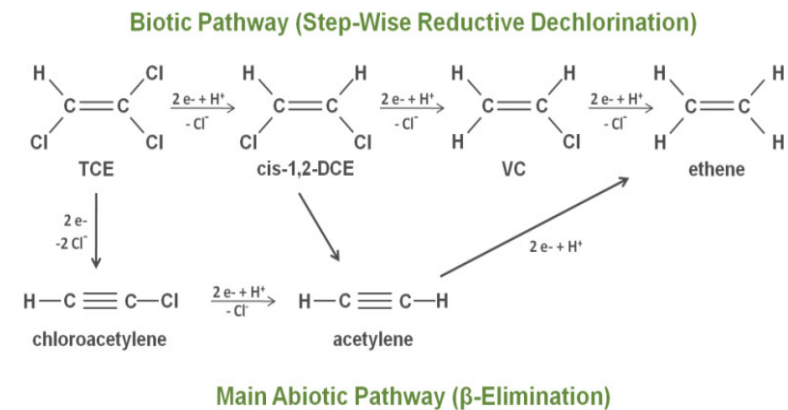
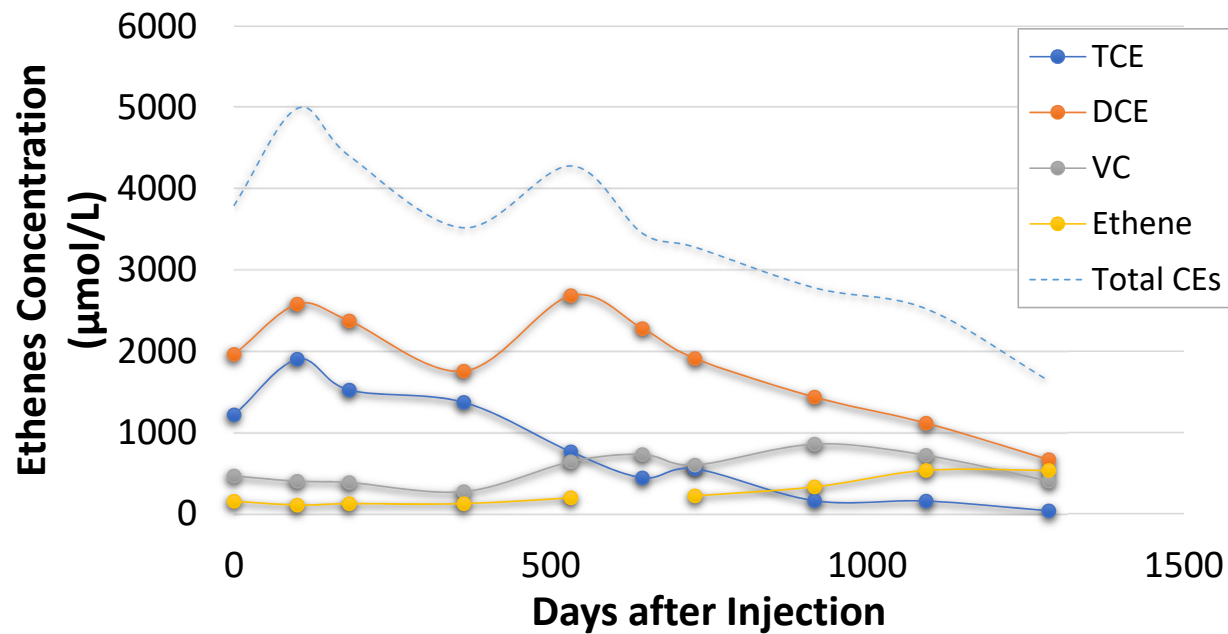


## Main Abiotic Pathway ( $\beta$ -Elimination)



- Acetylene was first measured and detected in 2017, but concentrations were low thereafter – **very labile or too late?**
- Magnetic Susceptibility and X-Ray Diffraction analyses in 2018: Iron sulfides and oxides (Magnetite, Mackinawite, Pyrite and Green Rust) were not detected/different than background – **looking in the wrong place?**

# Proof of Abiotic Pathway?



- TCE  $\rightarrow$  cDCE : primarily biological;
- cDCE  $\rightarrow$  VC : Some VC is produced but not the stoichiometric equivalent of DCE reduced. Some other process (assumed to be abiotic degradation\*) is occurring.

\*dilution and dispersion or rapid degradation of the VC

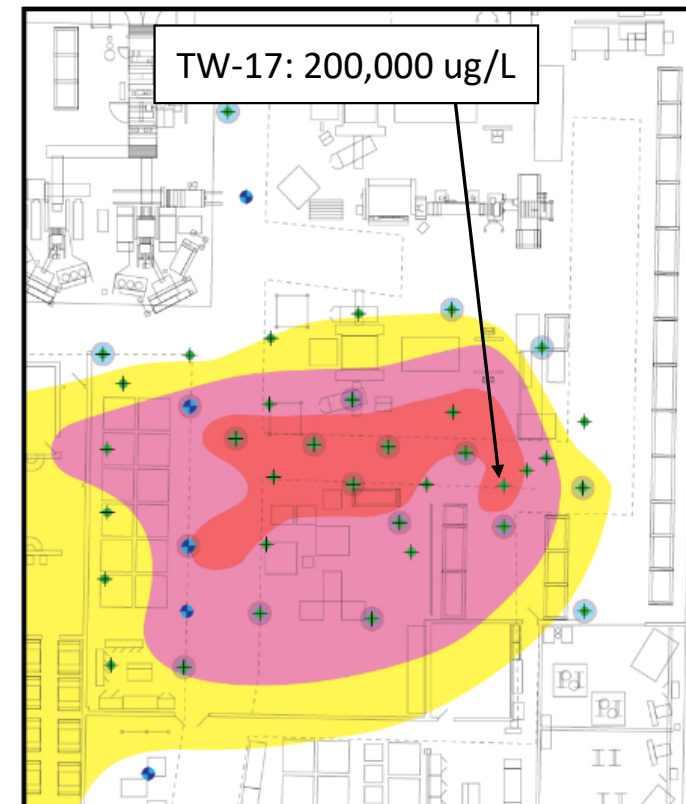
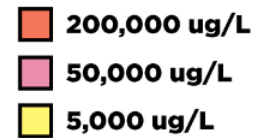
# Summary of Results

- Abiotic **injections from July 2015** addressed the stagnant high concentration of TCE at the Source Area.
- Detection of acetylene in 2017 and current detections of cDCE and VC, indicate that **both abiotic and biotic reductive pathways were/are relevant** for TCE degradation in the Hot Spot Source Area.
- Reduction of **TCE** in the Hot Spot Source Area (**160,000 to 4,500 µg/L**) has occurred since 2015 with no significant alteration of pH.

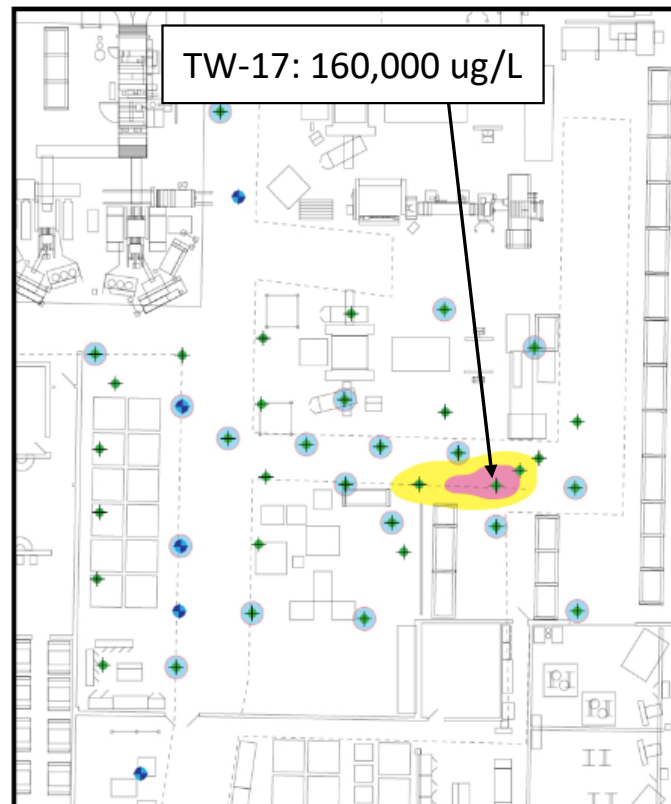


# Summary of Results

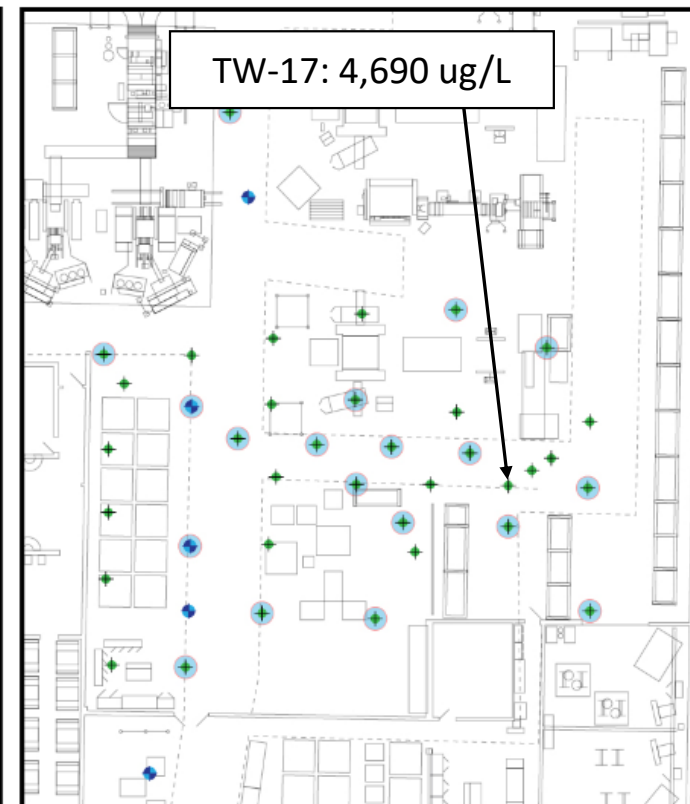
## SOURCE AREA REMEDIATION PRESS ROOM - TCE



**JULY 2003**



**JULY 2015**



**JANUARY 2019**



# Final Thoughts – Why it Worked?

- Extremely high concentrations at source area might have been inhibiting biological ERD
- Efforts to enhance both biotic and abiotic reductive pathways were relevant for TCE degradation in the Hot Spot Source Area.
- Mechanical “pushing” (flushing) during injection may have helped promote ERD degradation



# Final Thoughts – Lessons Learned

- Doing the same thing over and over won't give you different results
- Brainstorm with people from different areas of expertise
- Take advantage of your resources/vendors
- Every site is unique



# Acknowledgments



Michael S. Apgar [msapgar@ftch.com](mailto:msapgar@ftch.com)

Bruce E. Gillett, CPG [begillett@ftch.com](mailto:begillett@ftch.com)

Steve Macdonald, PE

Mike Colvin, CPG

Mike Ingersoll



Daniel Leigh [daniel.leigh@peroxychem.com](mailto:daniel.leigh@peroxychem.com)

John Valkenburg [john.valkenburg@peroxychem.com](mailto:john.valkenburg@peroxychem.com)

# Thank you

Fernanda P. Wilson, PhD [fpwilson@ftch.com](mailto:fpwilson@ftch.com)

