In Situ Hydrolysis and Thermal Treatment of 1,1,1-TCA during Electrical Resistance Heating

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April 9, 2018

Site Description

- 5 acre parcel in mixed zoned area; Site has vacant building and open/paved ground

- Formerly an automobile manufacturing plant and a publishing/printing business

- Contaminated due to historical site operations plus a chemical warehouse fire on adjacent uphill property

Site Plan
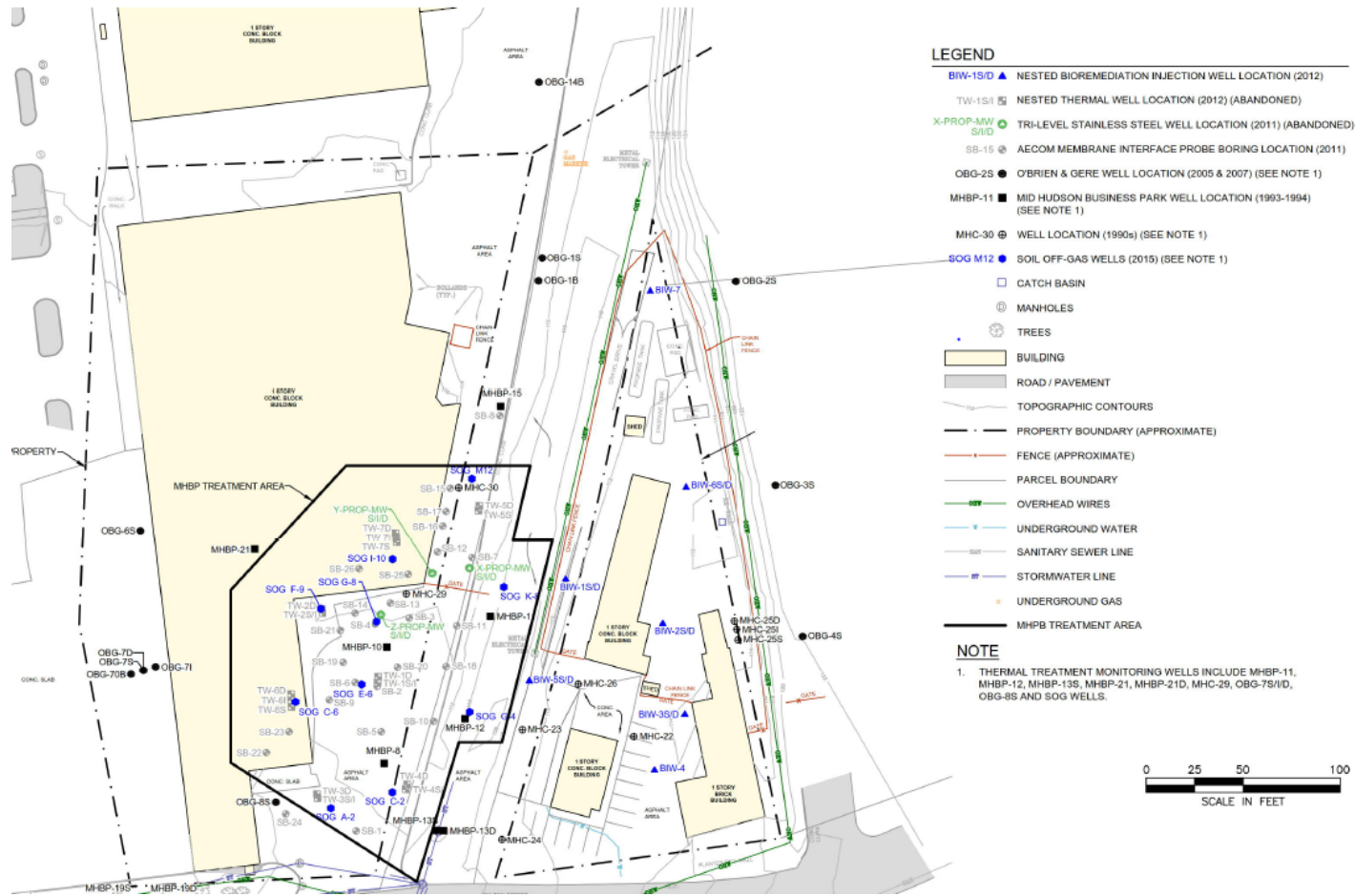
Site Description

- An unconsolidated soil aquifer underlain by a shallow bedrock aquifer; groundwater at 5 ft bgs

- Contaminants limited to unconsolidated aquifer from 5-50 ft; majority from 10-20 ft

- COC consist of 1,1,1-TCA, 1,1-DCA, 1,2-DCA, 1,1-DCE, plus other minor solvents

- Total CVOC impacts up to 1,342,000 µg/l or NAPL levels

- 1,1,1-TCA is the principal contaminant (max levels)
  - Soil – 480,000 mg/kg
  - GW – 1,000,000 µg/l

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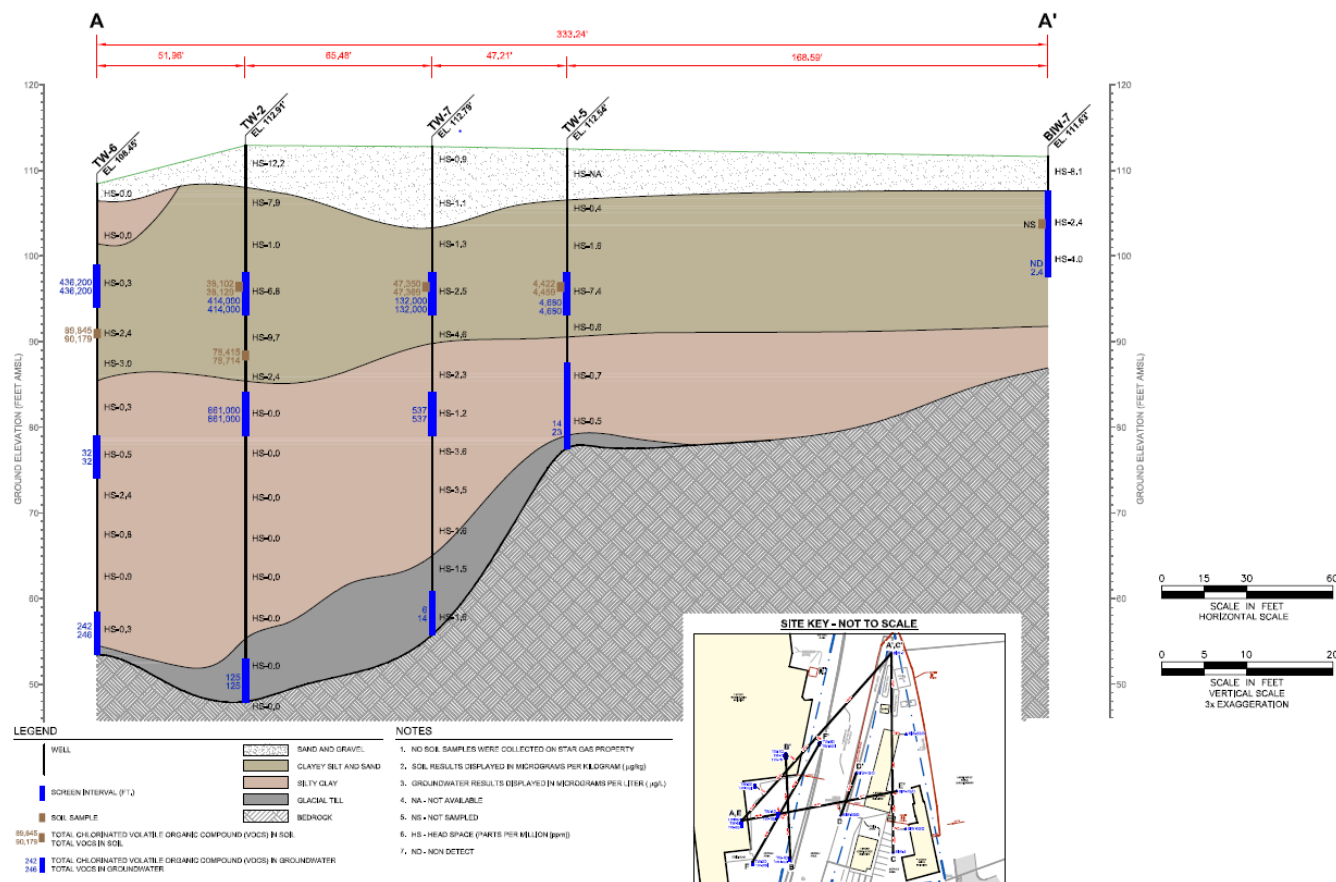
Natural Environmental Fate of 1,1,1-TCA

- Volatilization (1,1,1-TCA vapor pressure 122 mm Hg at 20 ° C)

- Dissolution and migration (solubility 1255-1500 mg/l; Henry's Law constant 1.76)

- Biological degradation (aerobic oxidation, co-metabolic, anaerobic)
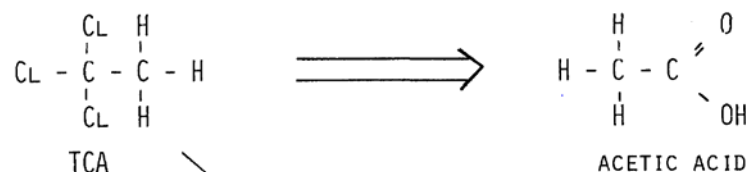
- Abiotic transformation
  - Hydrolysis

    o 70% Substitution (SN1 mechanism)
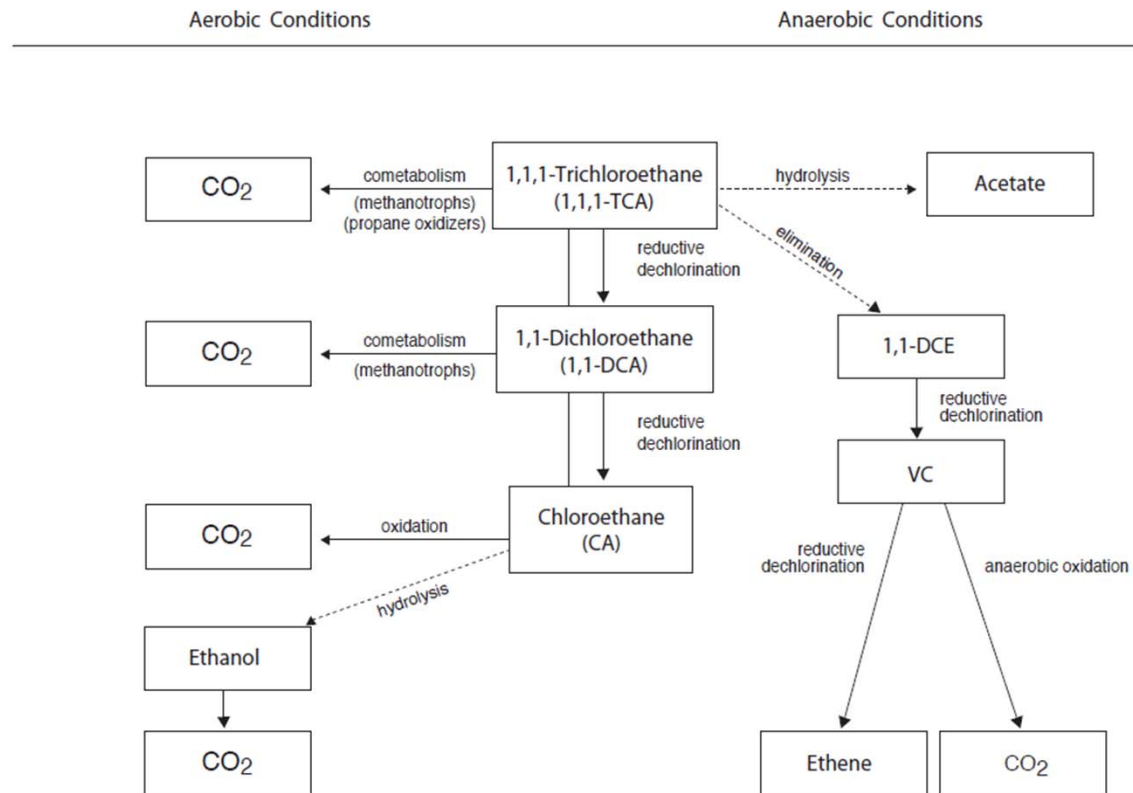   - major pathway; product is acetic acid
    o 30% Elimination (alternative less common pathway)
      - favored at higher pH; also increases at higher temperatures; product is 1,1-DCE
 - Geochemical reactions (iron reactive mineral process)

TCA Hydrolysis Kinetics

– Since water is freely available, only 1,1,1-TCA concentrations affect the rate and so the reaction can be considered first-order

– Rate of hydrolysis of 1,1,1-TCA is dependent on temperature but relatively independent of pH between 4 and 9

– The half-life (t ½) is the time needed for 50% of the reactant to be consumed by a reaction. For the TCA hydrolysis rate:

t ½ = ln 2/k   where the reaction rate constant k increases exponentially with a change in temperature and is described by the Arrhenius equation

– Half-life at 15 ° C is 6 years but at 100° C it is 0.03 days (Jeffers et al, 1989)

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Hydrolysis Rates of Selected Halogenated Alkanes

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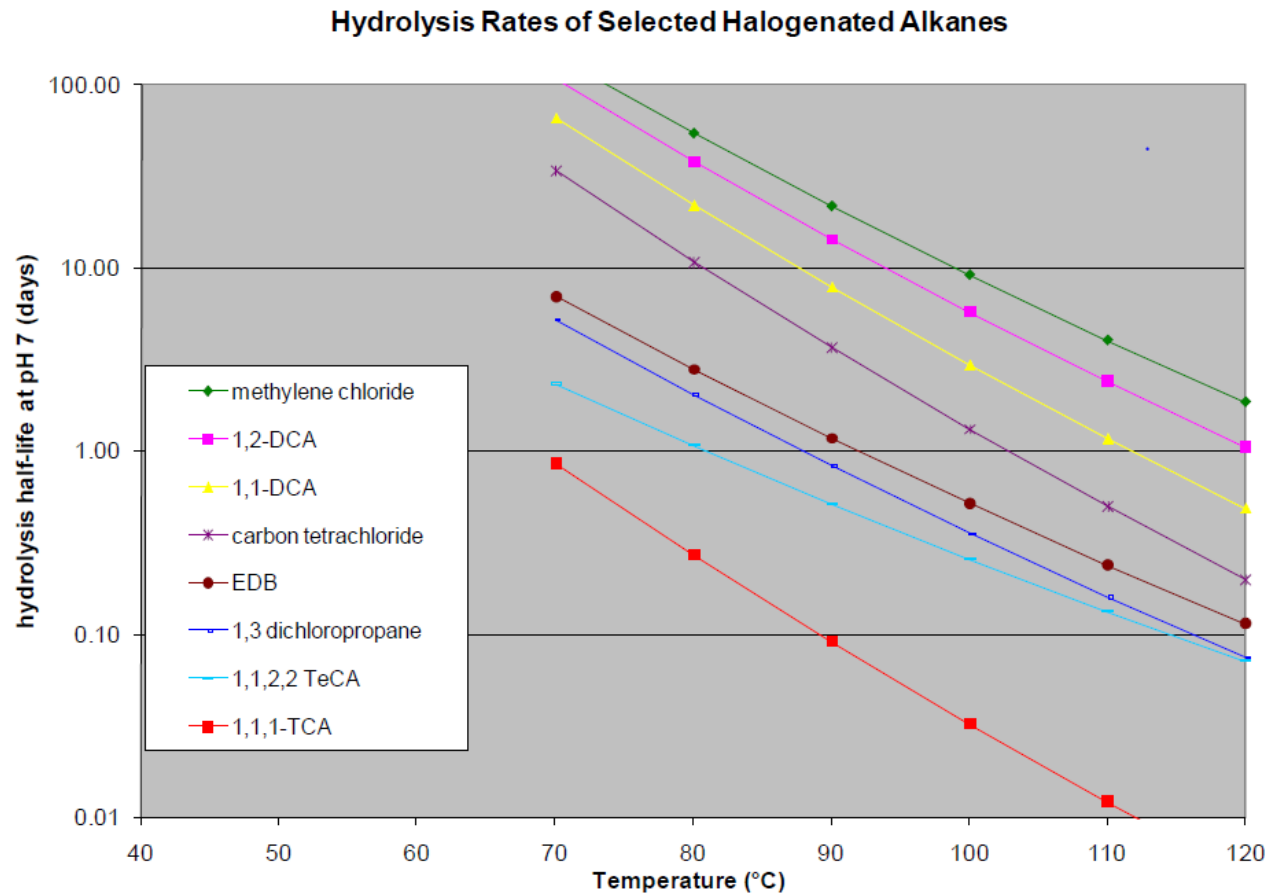
Design of Treatment - Temperature Objective

– Heating can increase the rate of remediation of compounds subject to hydrolysis.

– Hydrolysis only occurs when compound is dissolved in water; heating assists by desorption from soils, dissolution of NAPLs, etc.

– Faster half-lives decrease dissolved concentrations which further enhance dissolution

– In addition to hydrolysis, heating subsurface to the boiling point of water (100° C) will address other compounds that do not undergo hydrolysis, reducing treatment time

1,1,1 TCA Half Life, Days

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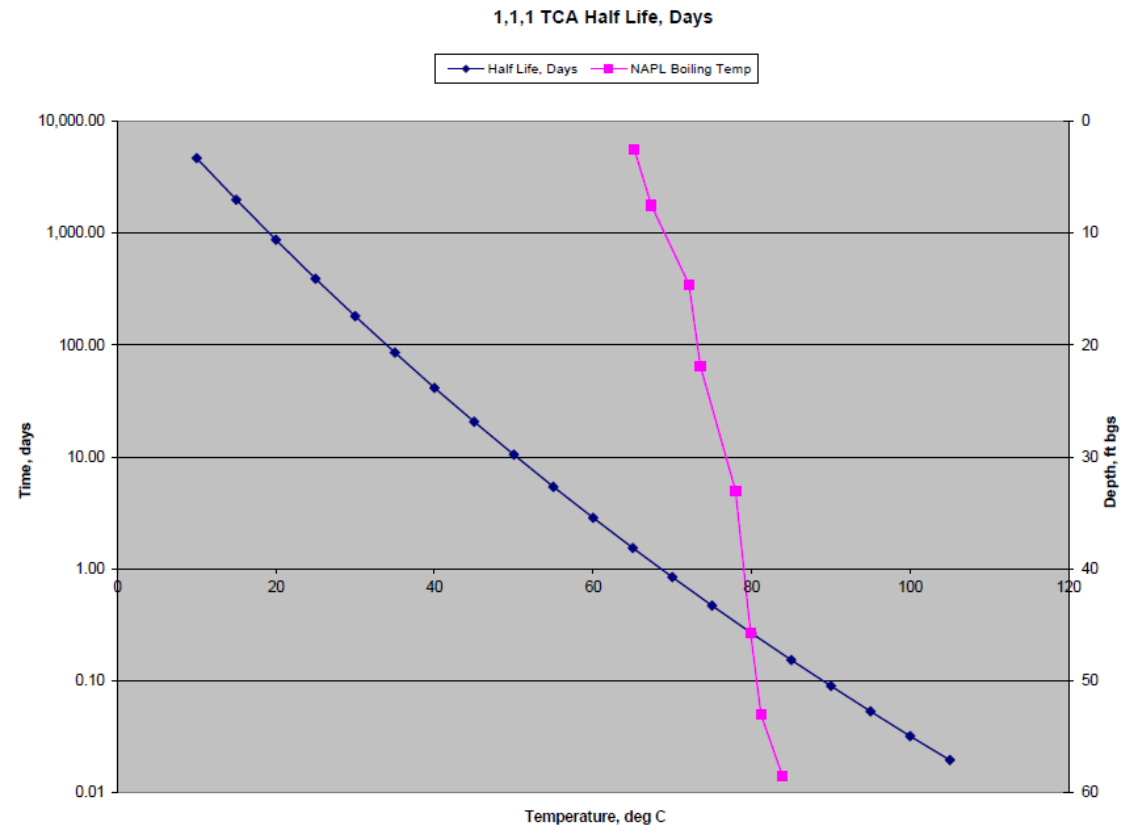
ERH Design

- ERH chosen for heating method

- Treated area 35,000 sq ft

- Three contiguous zones treated:
  - A: 5 to 25 ft;

  - B: 5 to 35 ft;

  - C: 5 to 50 ft

- Goal was to reach at least 75-80° C for 1,1,1-TCA but extended to 100° C for other COCs

- ~100 electrodes spaced 20 ft on center with co-located and shallow steam and vapor collection vents

ERH Design

– Vapors, steam, and water extracted/condensed and multi-phase separation

– Treatment of wastewater and recovered vapors and discharge of effluent

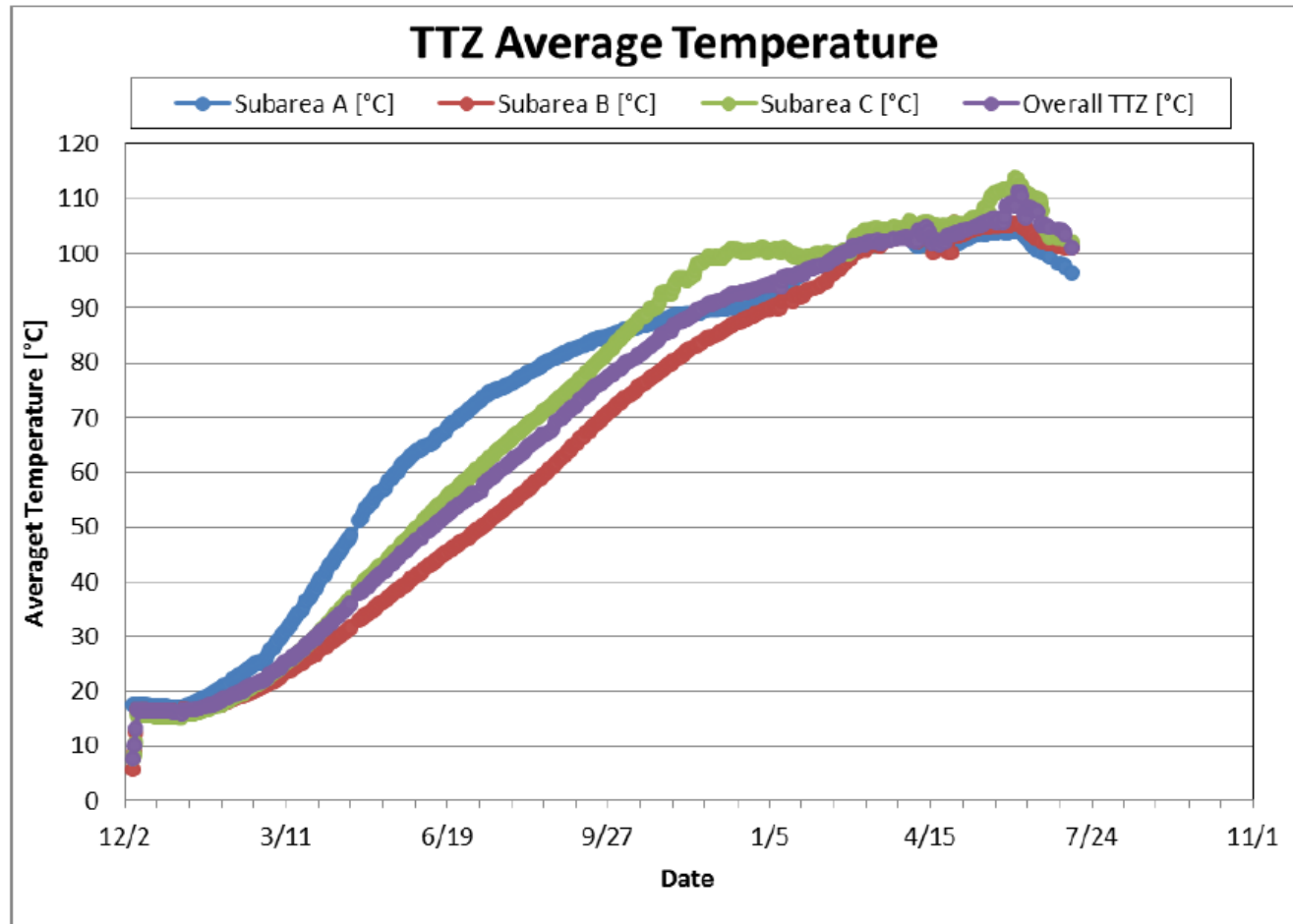# ERH Electrodes and Vapor Recovery – Inside Building

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Full ERH Treatment System and Surrounding Neighborhood

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Temperature Increases During ERH (2016)

MP4 Weekly Mass Removed from Subsurface (lbs)

Legend:
- Total VOCs
- 1,1,1-TCA (ug/m3)
- 1,1-DCA (ug/m3)
- 1,1-DCE (ug/m3)
- Other VOCs (includes 1,2-DCA) (ug/m3)
- Start of heating (12/7/15)

"Other VOCs" does not include chloroethane.

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Cumulative Mass Recovered from Subsurface Vapor with Time

MP4 Cumulative Mass Removed from Subsurface (lbs)

Legend:
- Total VOCs
- 1,1,1-TCA (ug/m3)
- 1,1-DCA (ug/m3)
- 1,1-DCE (ug/m3)
- Vinyl Chloride (ug/m3)
- Other VOCs (includes 1,2-DCA) (ug/m3)
- Start of heating (12/7/15)

"Other VOCs" does not include chloroethane.

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MHC-29 (10-20 ft bgs)
Area C
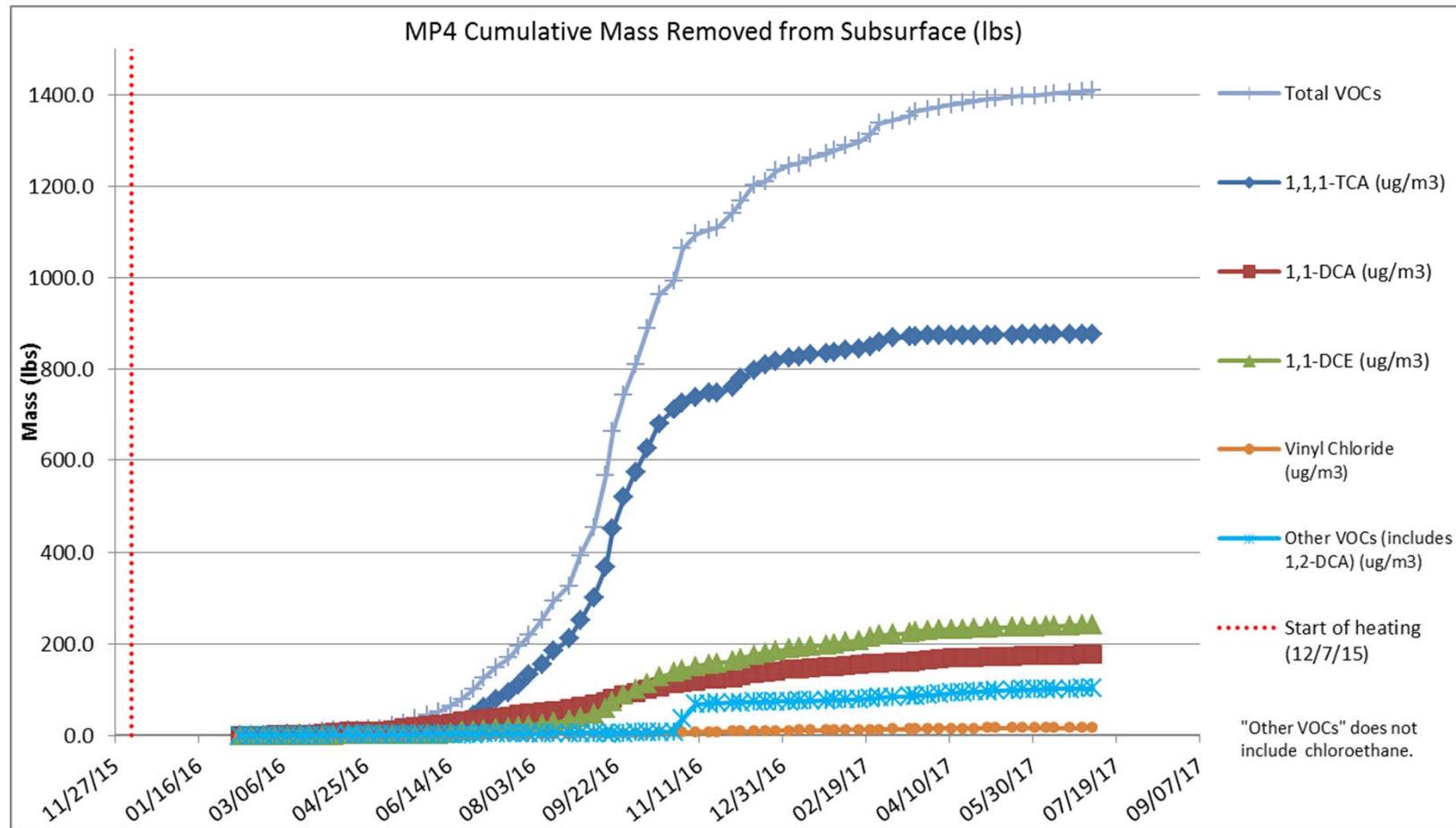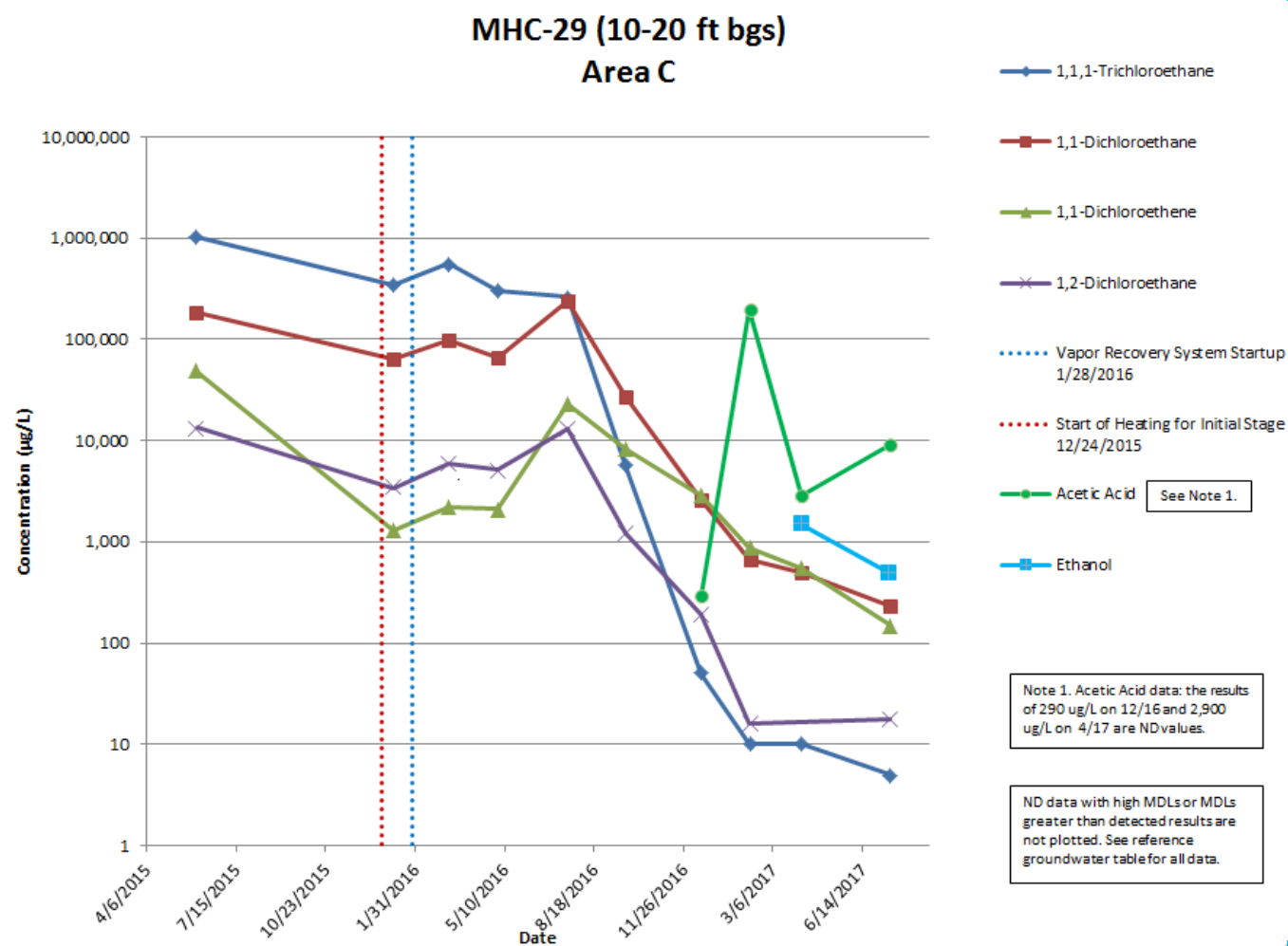
Acetic acid mass generation and amount of TCA transformed

- $C_2H_3Cl_3 + 2H_2O \rightarrow C_2H_4O_2 + 3\,HCl$

- 1 mole acetic acid is 45.5% of the mass of 1 mole of 1,1,1-TCA in hydrolysis. Therefore, 100 lb of acetic acid would be generated from 220 lbs of 1,1,1-TCA (factor of 2.2X).

- The mass of acetic acid at the site was estimated in the 10-20 ft depth interval using groundwater concentrations during thermal treatment.

- An estimated total mass of 735 lbs of acetic acid (aqueous) was calculated for the site which corresponds to **1,617 lbs** of 1,1,1-TCA hydrolyzed.

- The amount of 1,1,1-TCA hydrolyzed was most likely actually greater due to the transient nature of acetic acid (highly degradable, high solubility/migration, etc.)

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1,1,1-TCA Mass Balance

- Initial (pre-treatment 2012) sorbed and aqueous 1,1,1-TCA (from 10 to 50 ft bgs) = ~4,200 lbs

- 1,1,1-TCA recovered from subsurface (all depths) in vapor phase = ~875 lbs

- 1,1,1-TCA hydrolyzed (estimate) = ~1,620 lbs (from 10-20 ft bgs)

- 1,1,1-TCA remaining (post-treatment) = 0.024 lbs (negligible)

❖ 4,200 lbs – 875 lbs – 1,620 lbs = ~1,700 lbs unaccounted for
  - 1,1,1-TCA hydrolyzed is an underestimate due to short monitoring life of acetic acid,
  - Some 1,1,1-TCA underwent biodegradation during the initial thermal ramp up period,
  - Some 1,1,1-TCA was hydrolyzed at 20-50 ft bgs to acetic acid which was not estimated.

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pH and Conductivity Changes from Hydrolysis of 1,1,1-TCA

– During hydrolysis, free protons (H+) and chlorides are produced, which decrease pH and increase specific conductivity.

– pH decreases and conductivity increases were observed and corresponded to 1,1,1-TCA decreases in 2016 when temperatures reached approximately 70 °C and hydrolysis increased significantly.

pH
MHBP-12 and MHC-29

Specific Conductivity (µS/cm^c)
MHBP-12 and MHC-29

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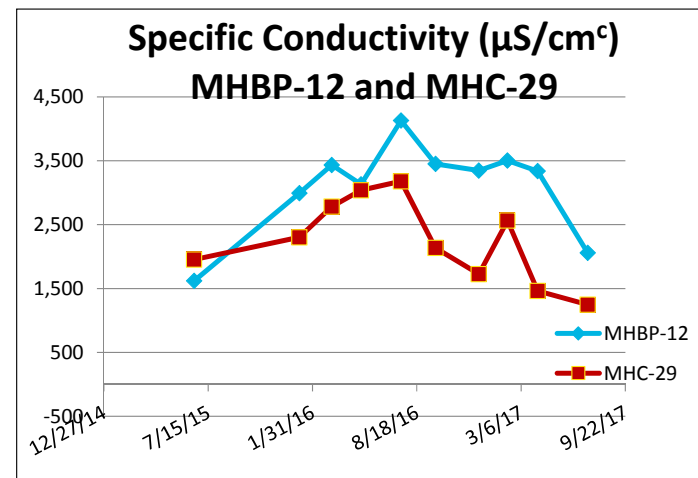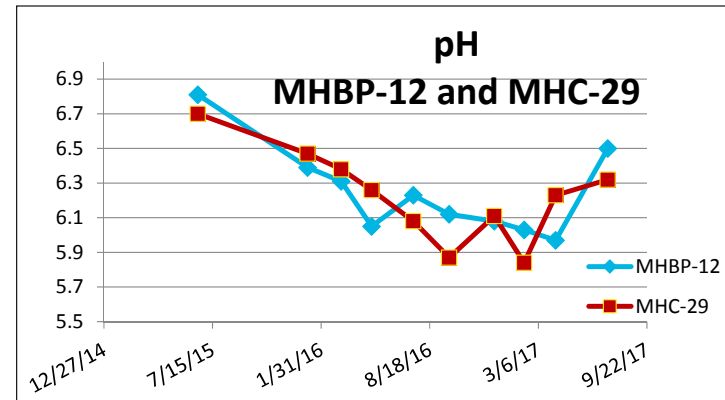
Treatment Results

- 550 days of heating

- 7 MM kWh input

- 184 kWh/cy treated

- Maximum concentration changes in select wells:
  - 1,1,1-TCA treated from 558,000 ug/l to 2 ug/l
  - 1,1-DCA treated from 306,000 ug/l to 230 ug/l
  - 1,1-DCE treated from 32,000 ug/l to 210 ug/l
  - 1,2-DCA treated from 43,000 ug/l to 82 ug/l

- Site will be monitored long term to determine if additional polishing of groundwater is necessary

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Conclusions

- ERH was effective in treating significant soil and groundwater impacts of several CVOCs to low levels

- Hydrolysis is a chemical process that normally occurs at low rates in the ambient environment but can become very useful at increased temperatures

- Use of in situ (or ex situ) thermal treatment processes as part of the design to create thermally enhanced hydrolysis of selected contaminants is an important strategy

- Through the hydrolysis reaction, the compounds of concern can then either be mineralized or converted to a less recalcitrant (and likely less toxic) compound

- Resultant process can ultimately decrease treatment duration and costs

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Acknowledgements

- NYSDEC

- Sealand Enviro, LLC

- Cascade/TerraTherm/Current Environmental Solutions

- Scott Underhill

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Thank You!

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