Challenging today.
Reinventing tomorrow.

Low-Temperature Haloalkane Treatment Using In-situ Thermal Hydrolysis

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Thirteenth International Conference on Remediation of Chlorinated and Recalcitrant Compounds

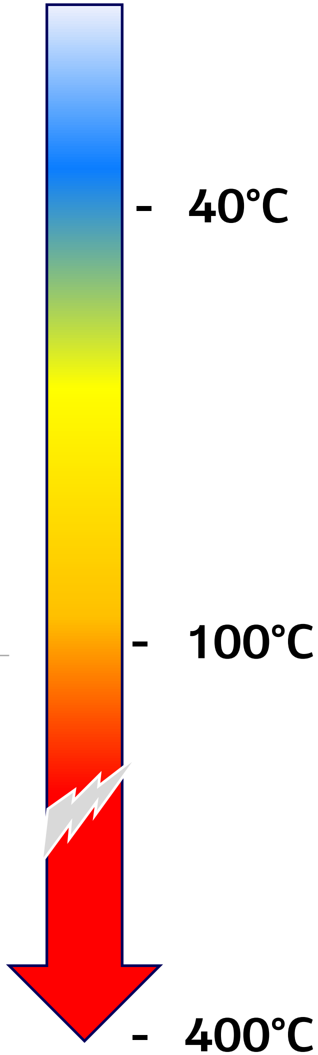
Acknowledgements

Joel Krueger (Jacobs, Chicago, IL)
Gary Dyke   (Jacobs, Detroit, MI)
McMillan-McGee Corporation (Calgary, AB)
TerraTherm, Inc (Gardner, MA)

Treatment Temperature Standards Lack Industry Definition

Electrical Resistance Heating
Thermal Conduction Heating
Steam Enhanced Extraction

Thermal Conduction Heating

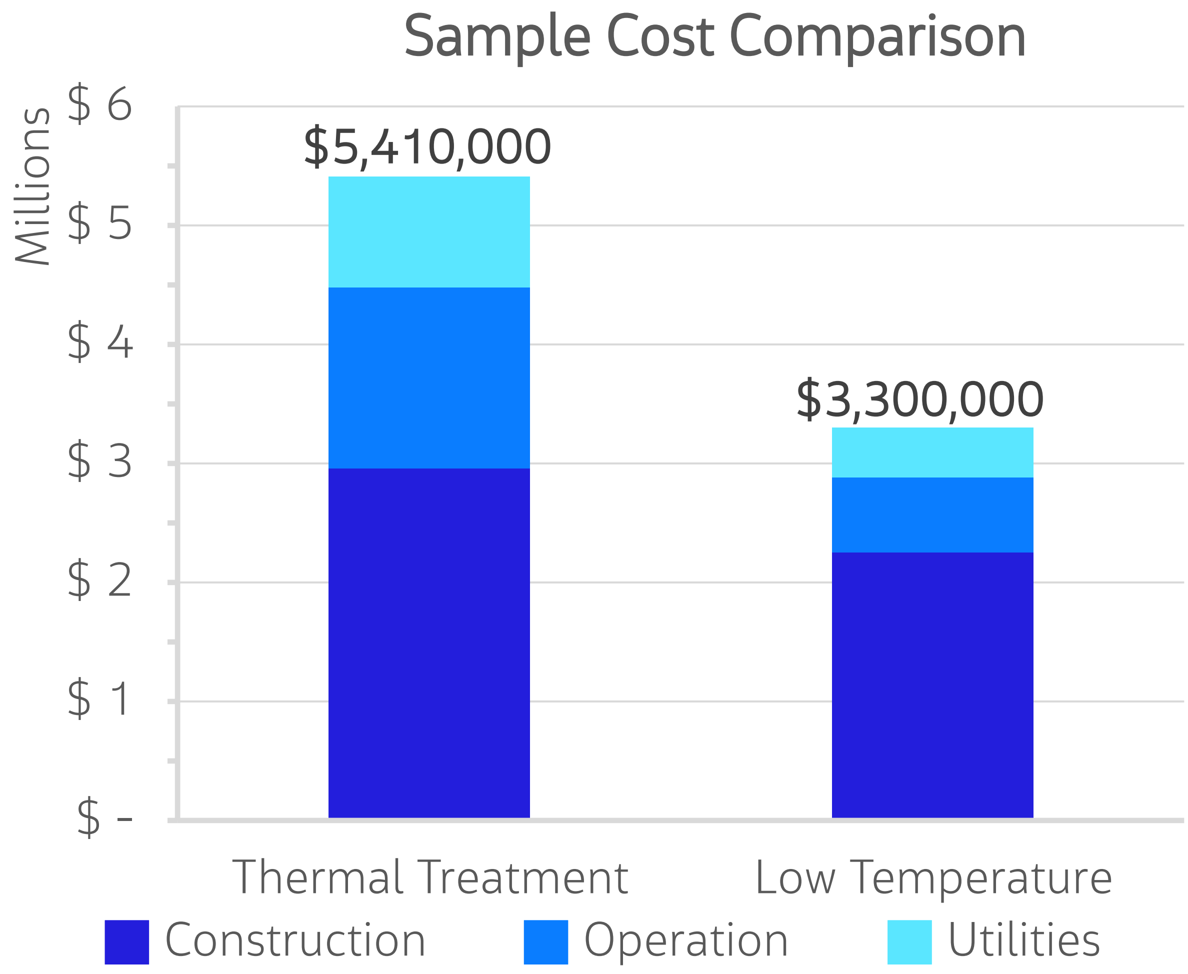


- Thermal Enhancement
  - Biological treatment
  - Target below 40°C
- Low Temperature
  - Chemical or physical treatment
  - Below boiling or co-boiling conditions
- Thermal Treatment
  - Achieve boiling under local conditions
- High Temperature Treatment
  - Exceed boiling temperatures

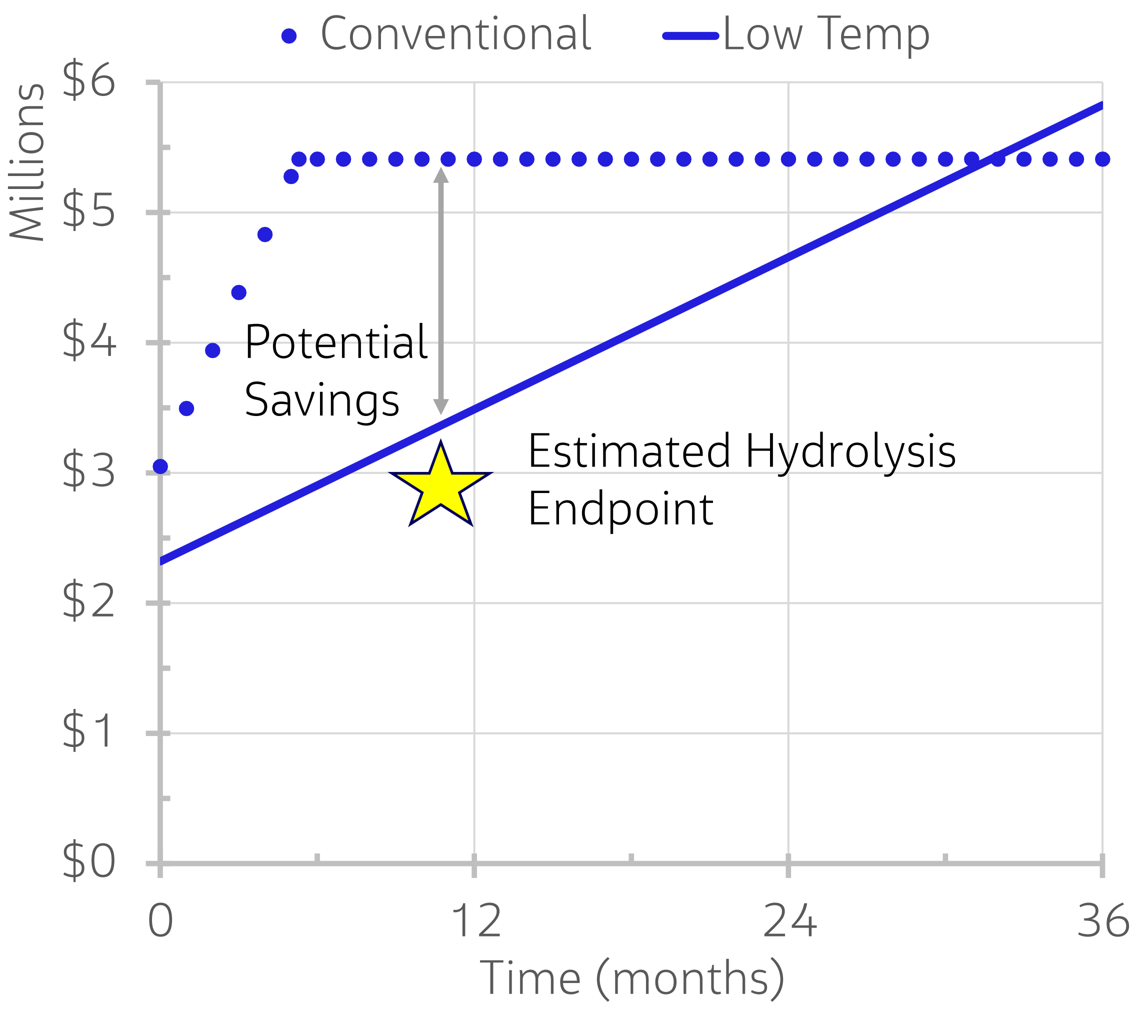
Low Temperature Heating Benefits

- Vapor extraction and treatment adds significant complexity and cost to any thermal remediation process
  - Supplemental equipment needs
  - Sampling, permitting and reporting
  - Operations labor
  - Waste disposal

- Subsurface heating processes are comparatively simple and much less expensive to operate



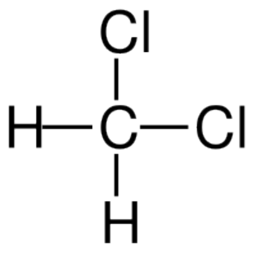
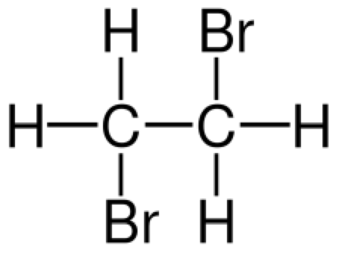
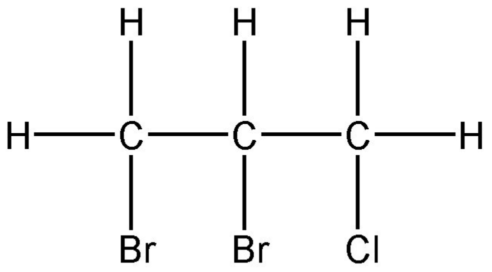
Low Temperature Applicability Considerations



- Contaminant Removal Mechanism
  - Biodegradation
  - Hydrolysis
  - Oxidation
- Site Contaminant(s)
  - The removal mechanism must be viable
  - All contaminants must be susceptible

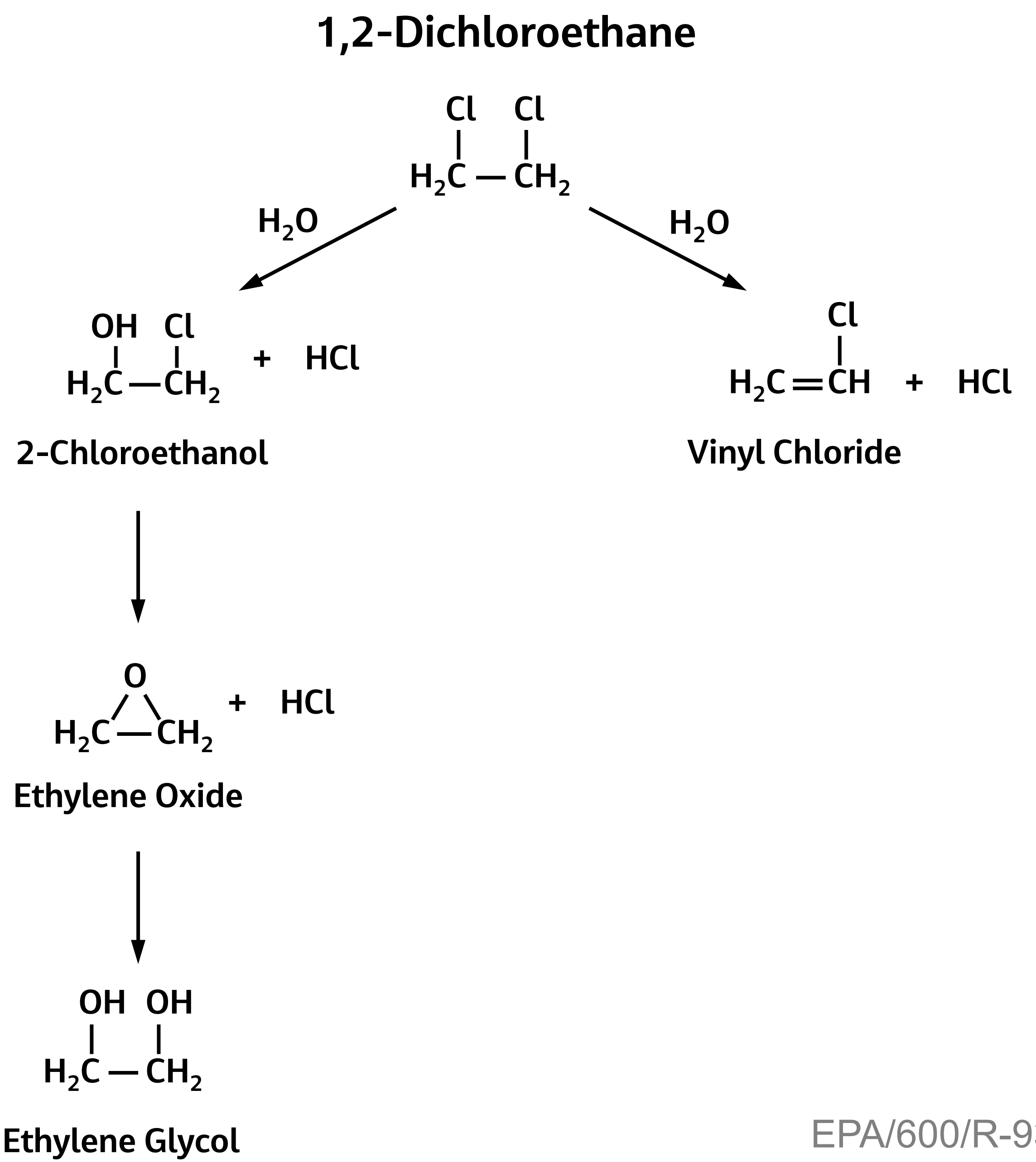
Halogenated Alkanes

- Common class of chemical compounds with diverse uses in manufacturing, agriculture, pharmaceuticals, refrigeration and fire protection
- Identifiable where one or more of the hydrogen atoms in an alkane are substituted by halogen atoms (fluorine, chlorine, bromine or iodine); examples include

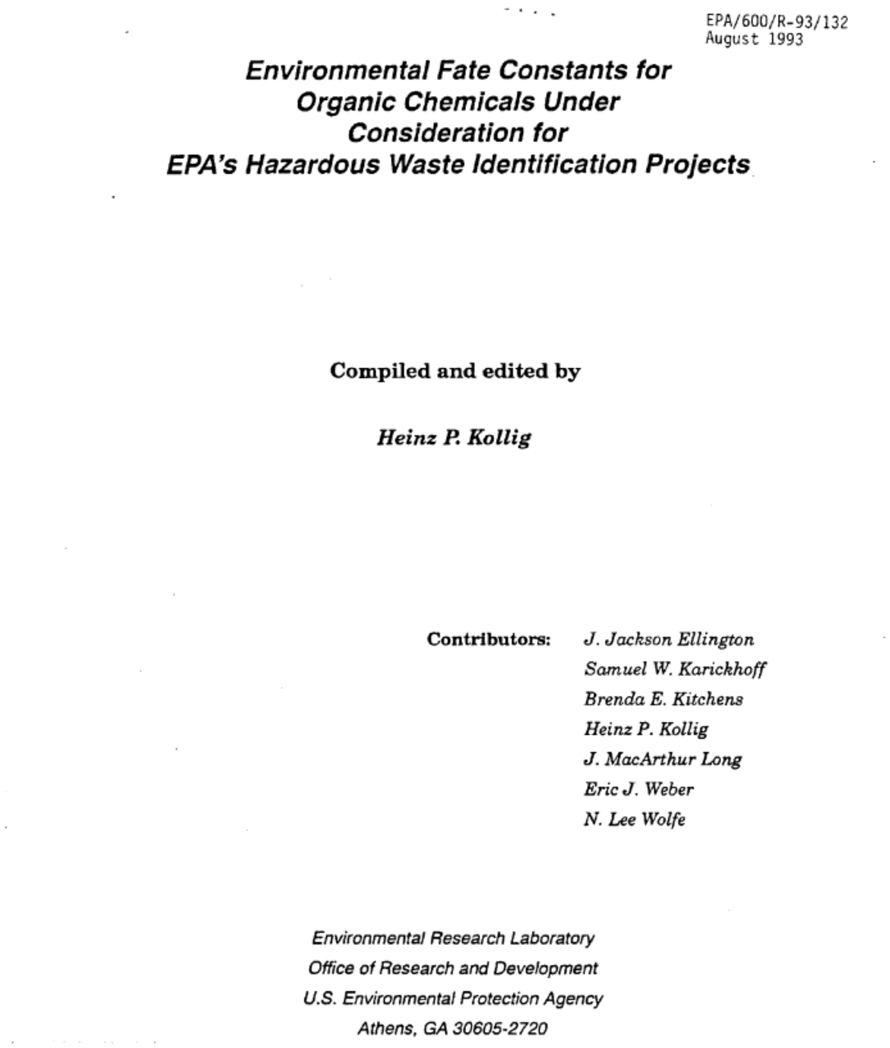
Methane	Ethane	Propane
		
Dichloromethane	1,2-Dibromoethane	1,2-Dibromo-3-chloropropane

- Nearly every compound within this functional chemical class are persistent and recalcitrant environmental contaminants.

Revisiting History



EPA/600/R-93/132
August 1993



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Environmental Fate Constants for Organic Chemicals Under Consideration for EPA's Hazardous Waste Identification Projects

Compiled and edited by

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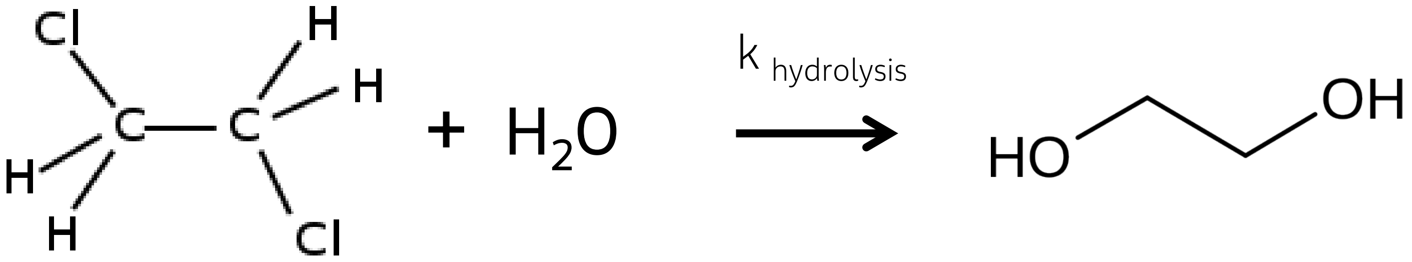
Athens, GA 30605-2720

What is Hydrolysis

- Decomposition of a dissolved compound by reaction with water



1,2-Dichloroethane (EDC) Ethylene Glycol

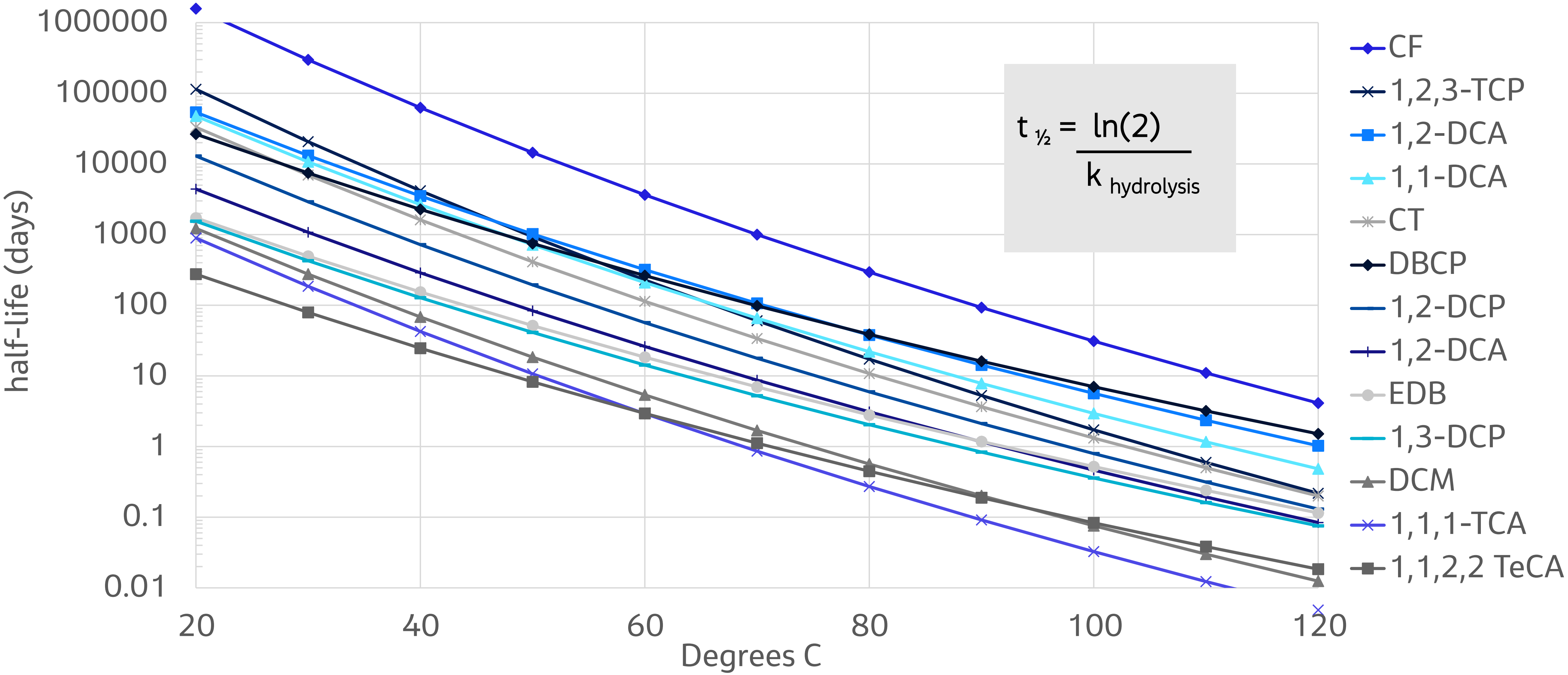
$C_2H_4Cl_2$ (EDC) + H^+ + $2OH^-$ → $C_2H_6O_2$ (ethylene glycol) + H^+ + $2Cl^-$

Every mole of EDC degraded
consumes two moles of $[OH^-]$

Increasing $[H^+]$

Decreasing pH

Haloalkane Hydrolysis Temperature Dependence



(after data compiled from Jeffers, et. al, 1989 & Washington, 1995)

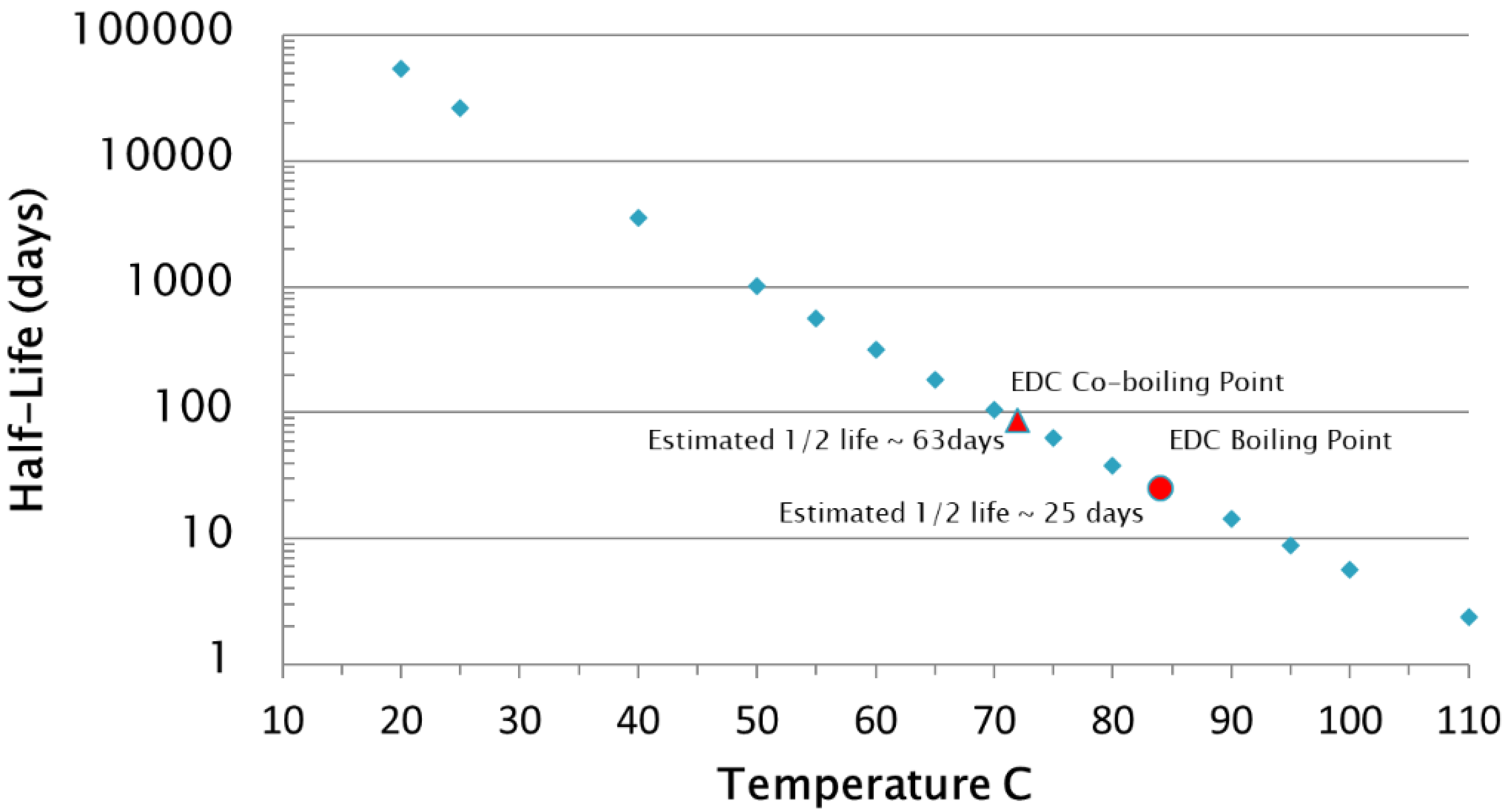
EDC Thermal Hydrolysis

Proof of Concept

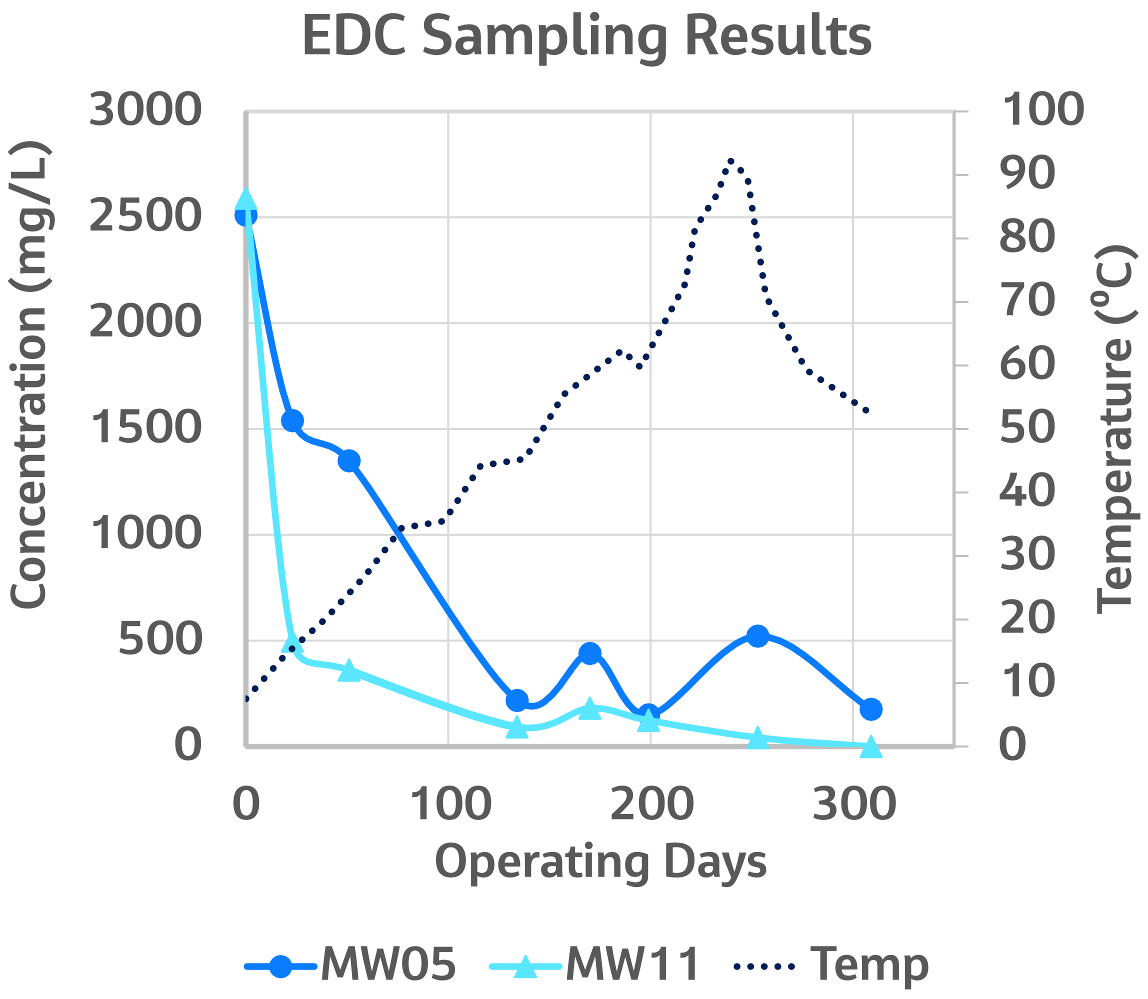
Thermal Hydrolysis Pilot Test

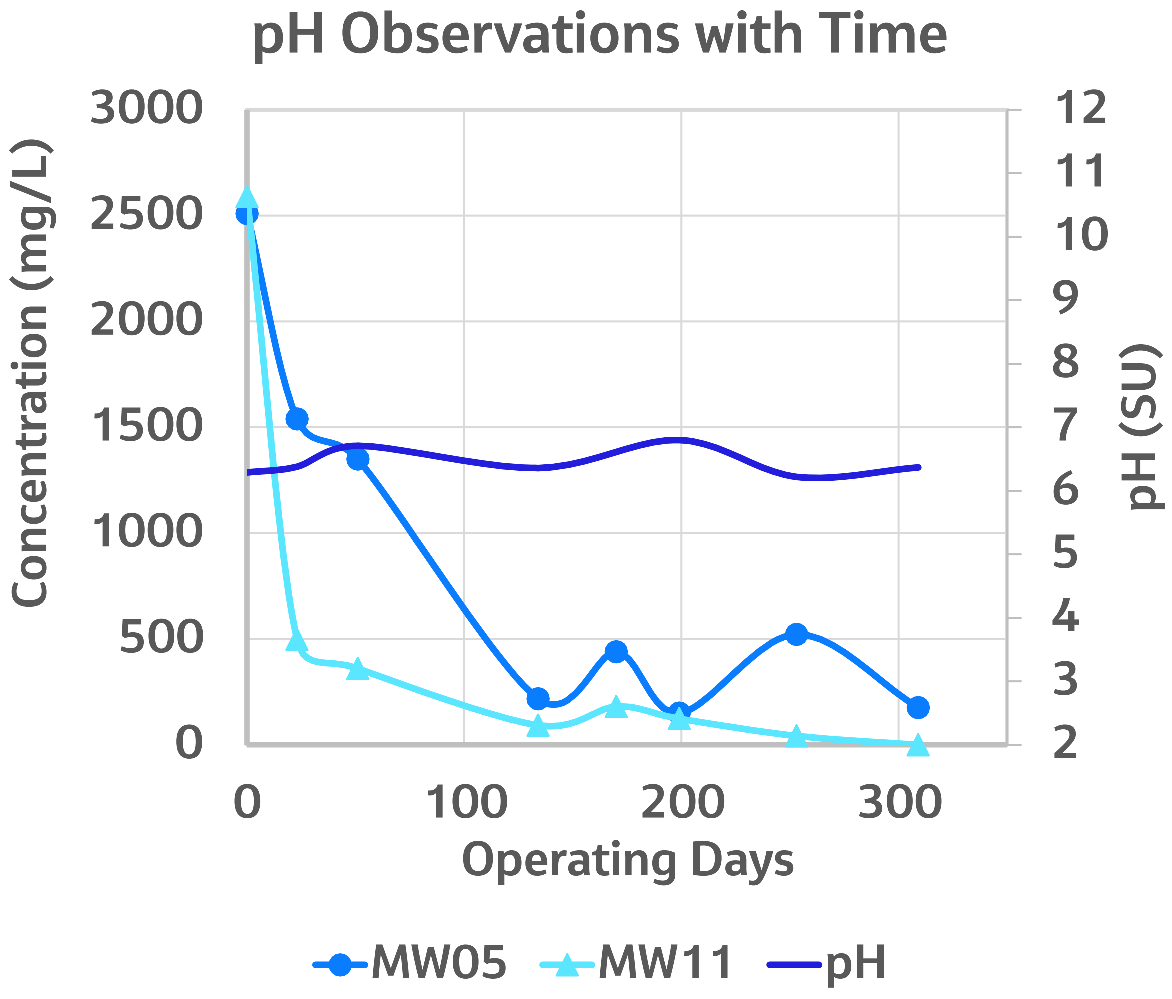
- Electrical Resistance Heating
  - 24 Electrodes
  - 15 Monitoring locations
  - No vapor extraction applied
- Target Treatment Zone
  - Area ~ 4,500 square feet
  - Depth: 6-23 feet below grade
  - Volume: 2,800 cubic yards
- Target Temperature: 60°C

Treatment Temperature Selection

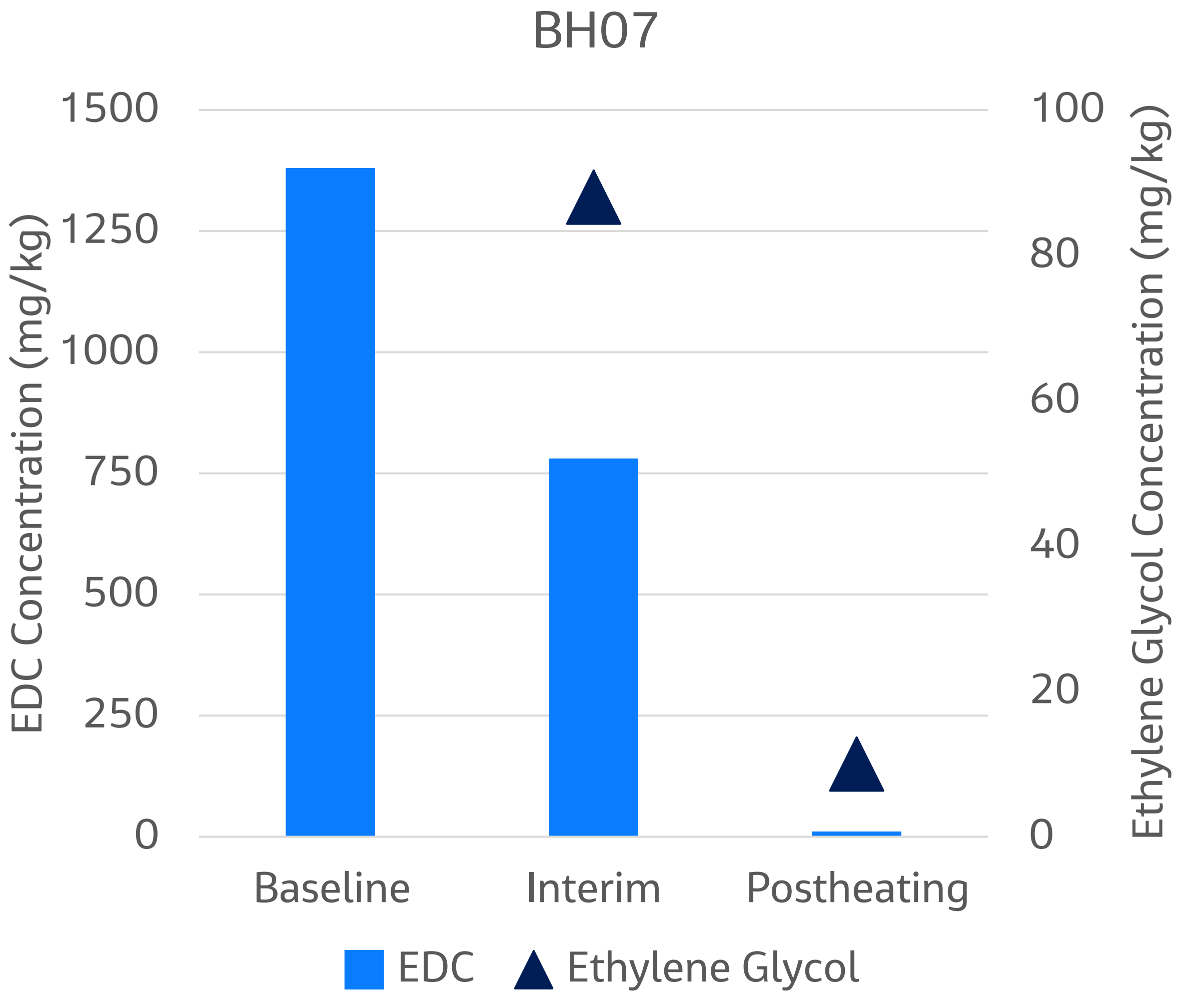


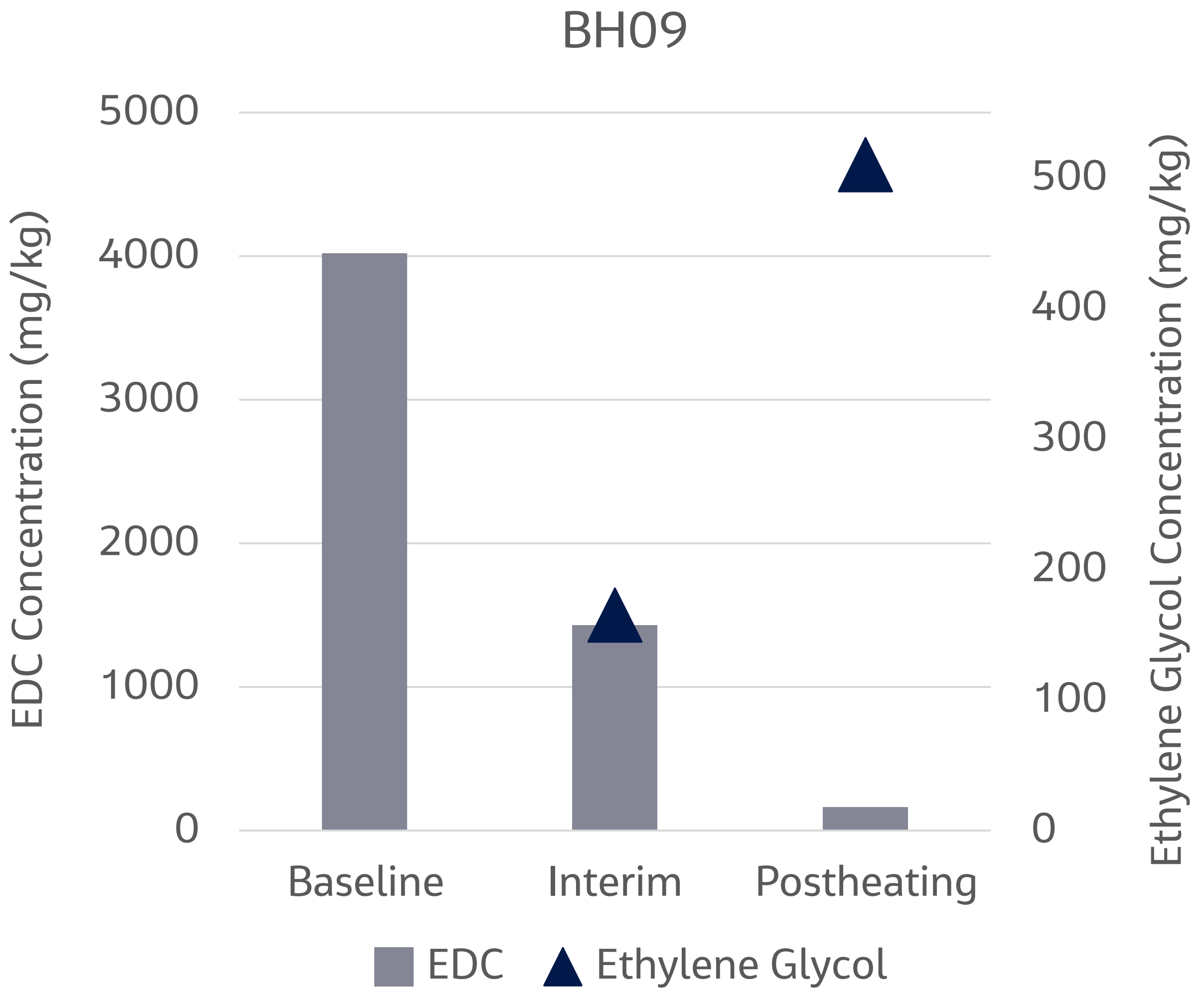
Groundwater Performance





Soil Sampling Observations





Pilot Conclusions

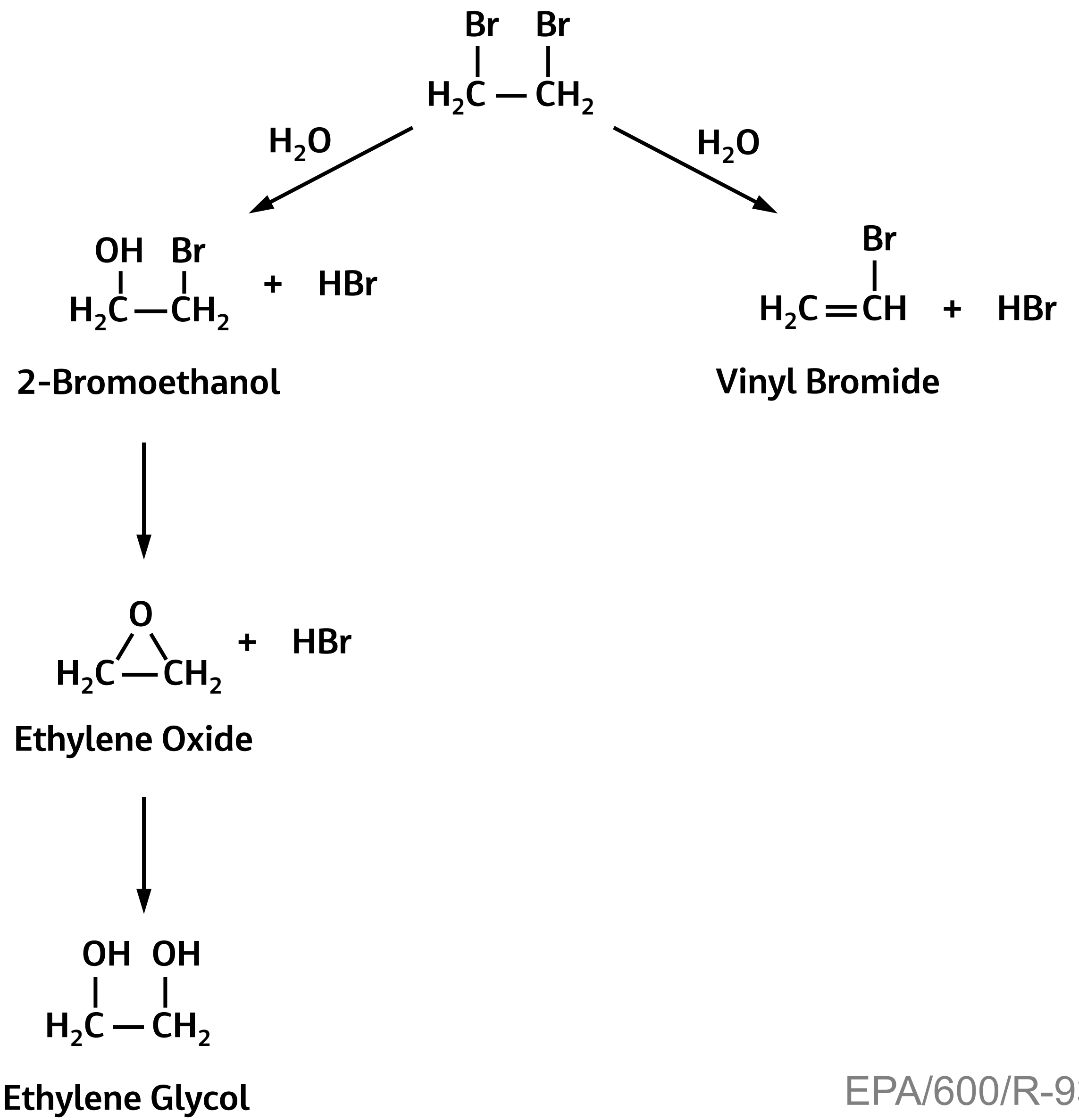
- EDC was quickly reduced in soil and groundwater
- Sampling results indicate hydrolysis occurred; vinyl chloride was not detected in soil or water samples
- Treatment zone pH remained stable during heating and unaffected by EDC breakdown

- Viable remediation technology when:
  - Contaminants are susceptible
  - Site factors may preclude other approaches
  - Accelerated in-situ treatment is desired

EDB Thermal Hydrolysis

Field Treatability Evaluation

1,2-Dibromoethane



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History Repeats

EPA/600/R-93/132
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Thermal Treatment Facilitates Treatability Testing

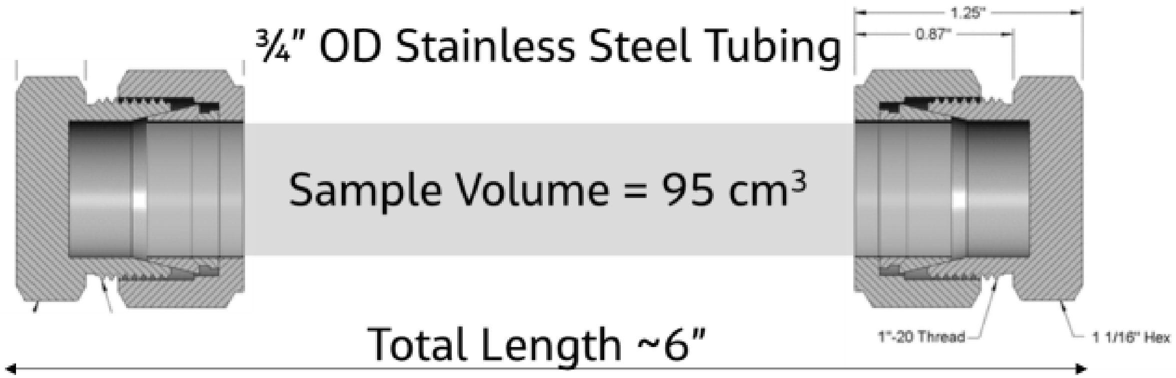
- Ethylene dibromide (EDB) thermal hydrolysis was evaluated <u>below neutral pH</u> during thermal treatment of a multi-contaminant source zone

- The presence of 1,2-dibromo-3-chloropropane eliminated potential for lab testing

- A novel approach was developed to assess hydrolysis under field conditions

Hydrolysis Testing Approach

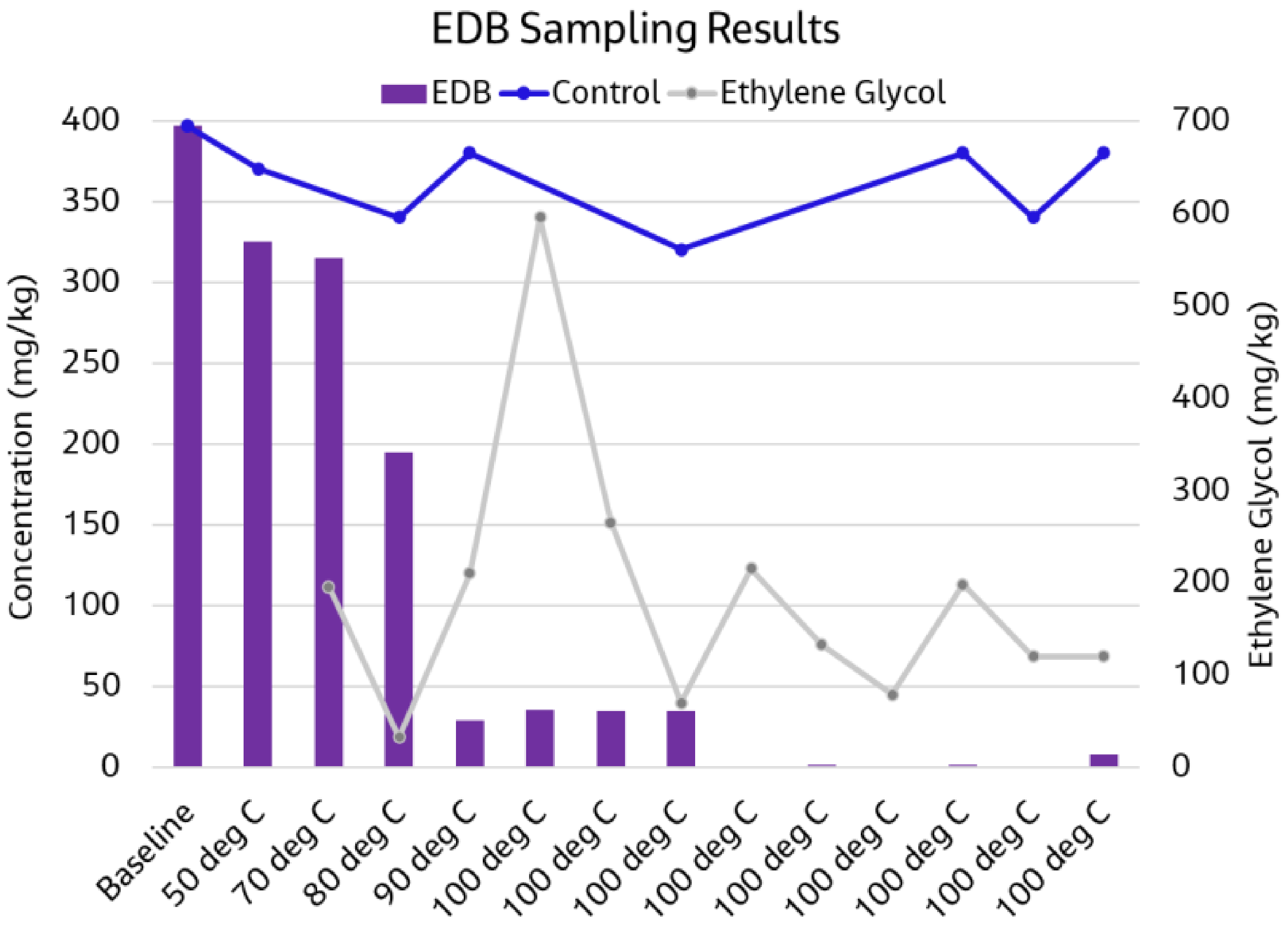
- Sealed chambers containing source area soil and groundwater were developed to evaluate the effects of temperature on contaminant transformation



- Filled chambers were submerged in a heated water bath in the center of the heated area; chambers submerged in a monitor well outside the heated zone served as experimental controls

Test Results

- Select chambers were removed at set temperatures during site treatment and submitted for sacrificial analyses
- EDB fully removed before reaching 90 ° C; detection of ethylene glycol confirms mineralization by hydrolysis mechanism
- Contaminants persisted in unheated control samples
- Hydrolysis occurred despite acidic groundwater (~ pH 5)



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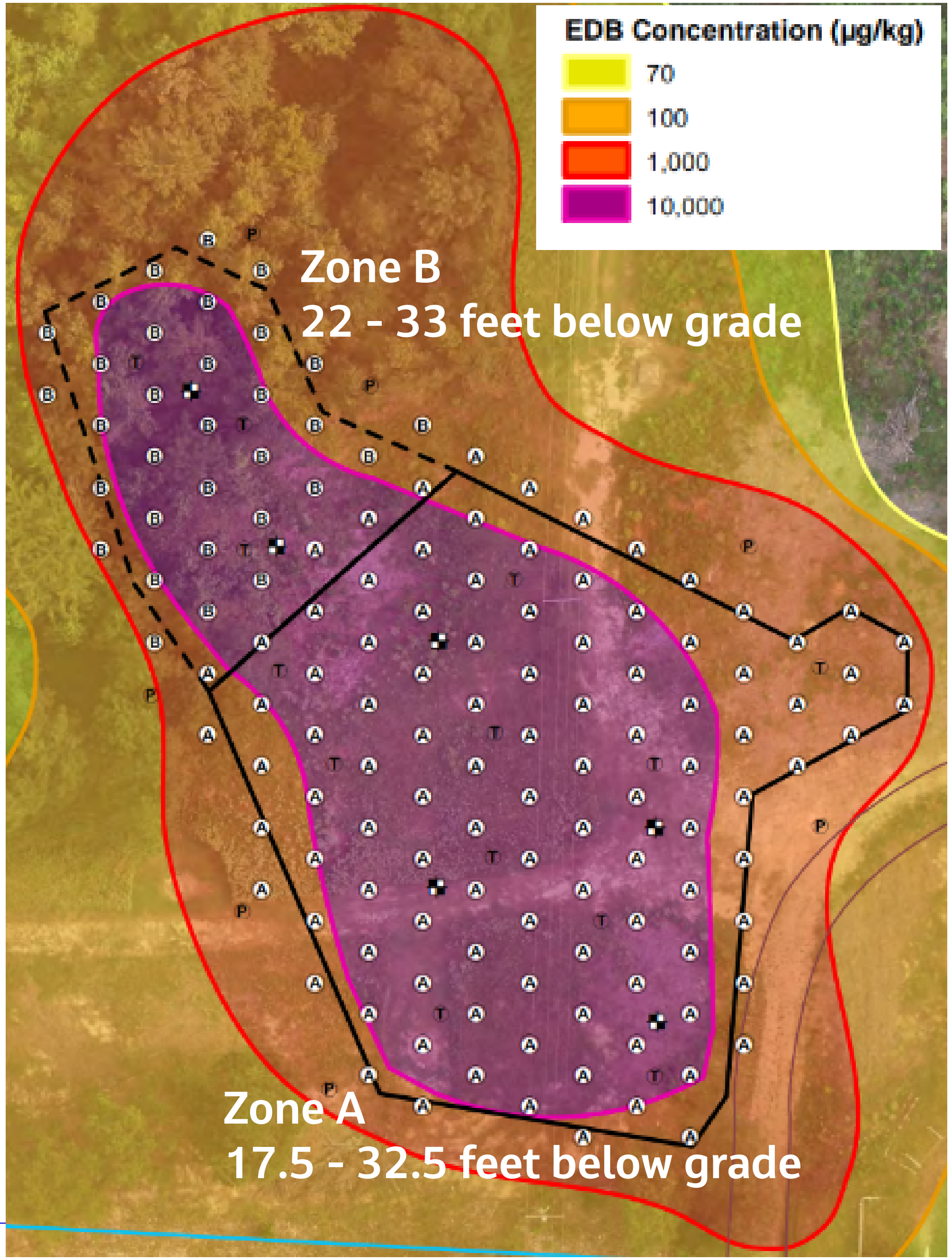
Full-Scale Thermal Hydrolysis

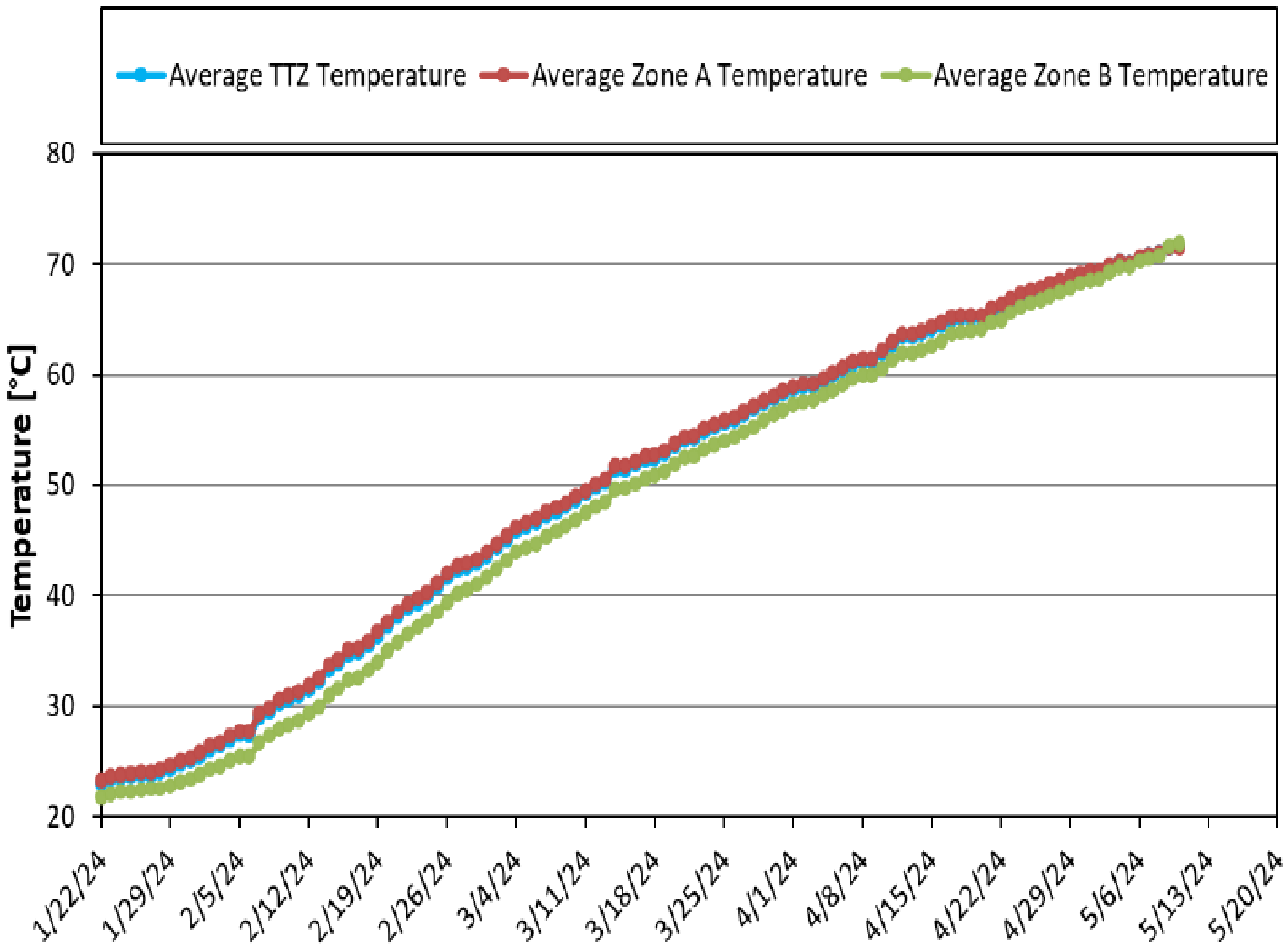
Two sites – Two contaminants – Two sets of challenges

EDB Treatment Under Low pH Conditions

- Low temperature hydrolysis selected for site contaminant mass reduction
- Electrical Resistance Heating Only
  - 137 Electrodes
  - No vapor extraction applied
- Two Target Treatment Zones
  - Total Area: ~31,500 square feet
  - Total Volume: ~14,600 cubic yards
  - Target Temperature: 70°C
- Subsurface Conditions
  - Low groundwater pH (3-4 Standard Units)
  - Elevated electrical conductivity

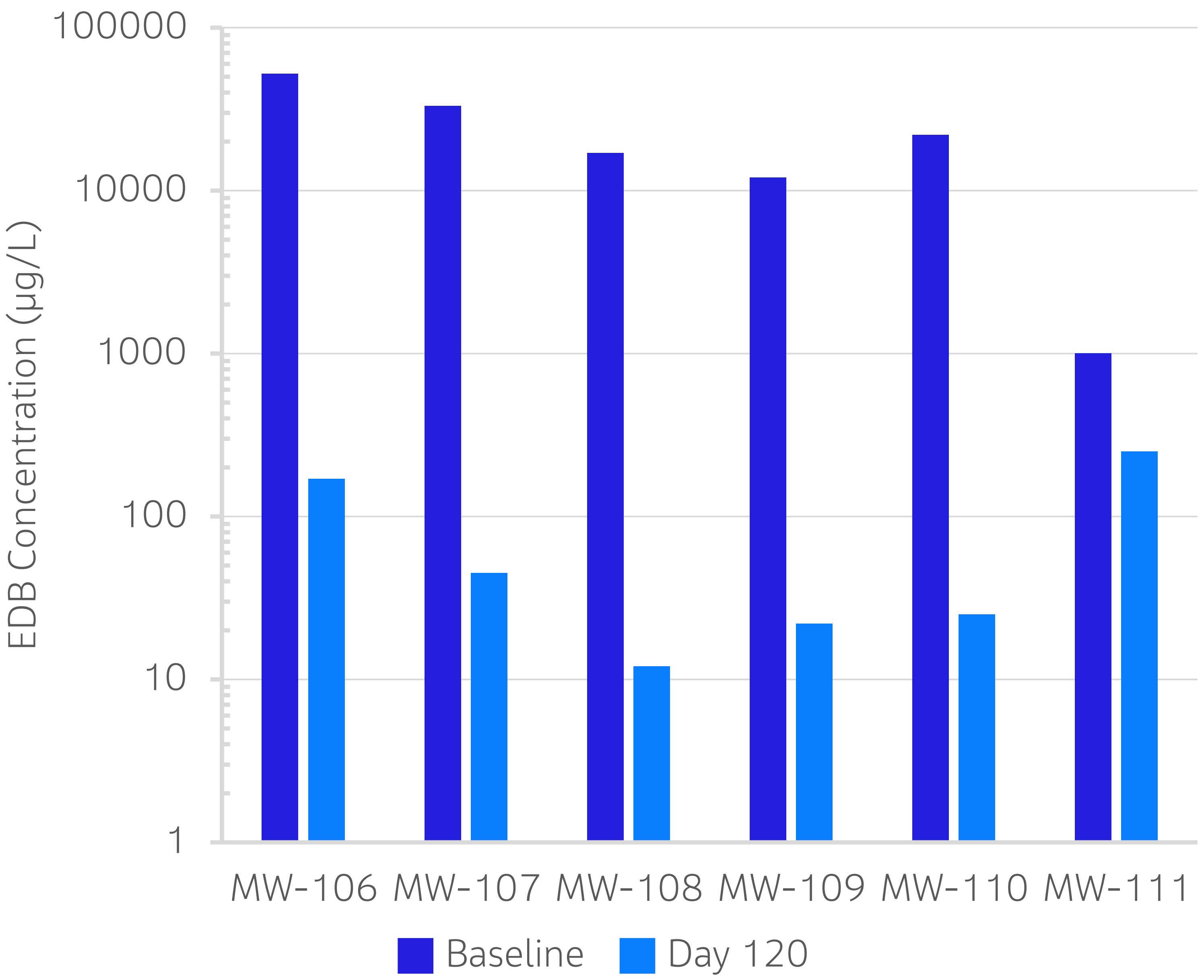


Design Temperature Achieved



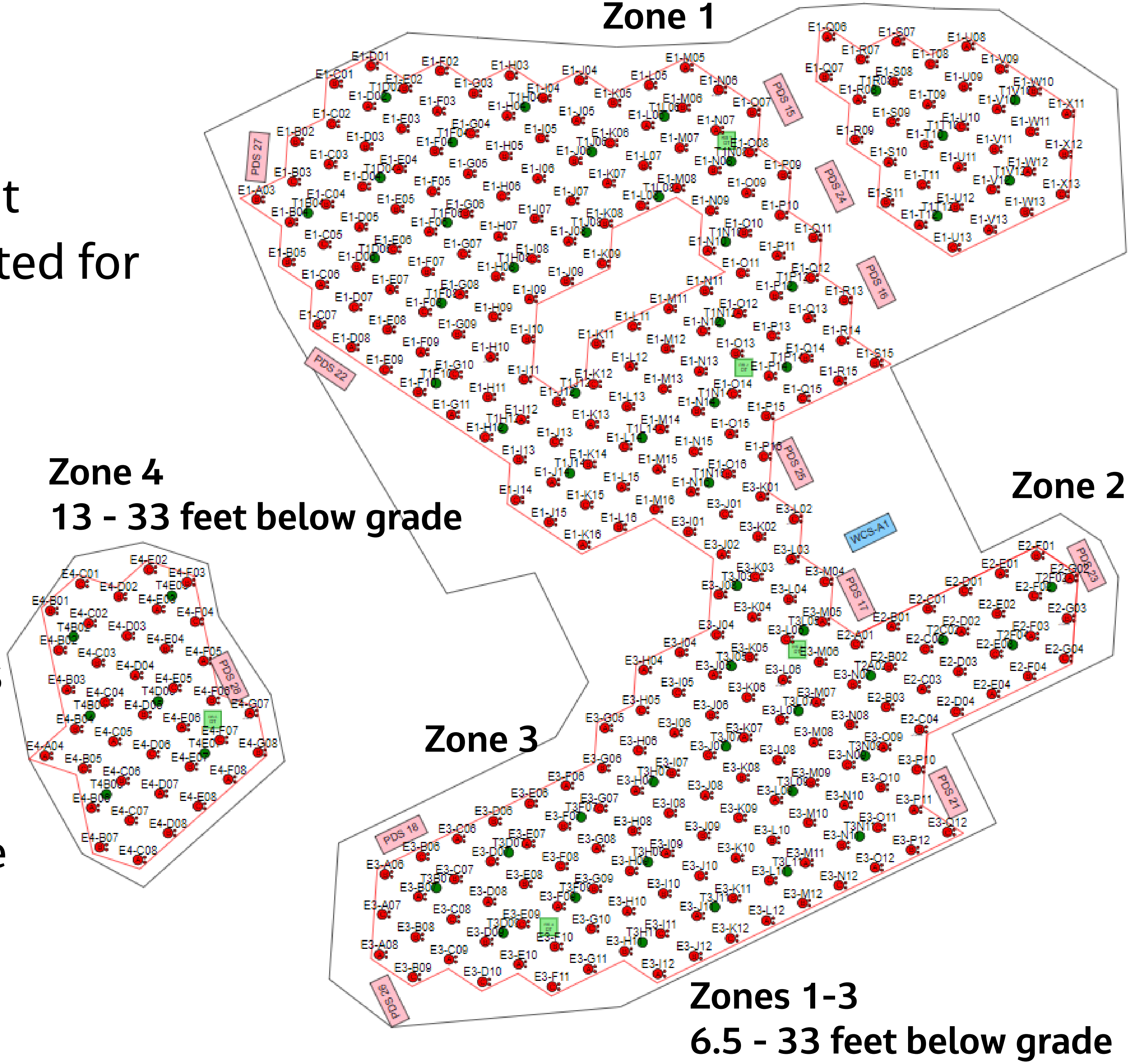
EDB Groundwater Observations

- Groundwater sampling performed at target temperature achievement
- Measurable changes in ethylene glycol concentration were not observed
- pH consistent with historical monitoring results
  - (~3 to 4 SU)

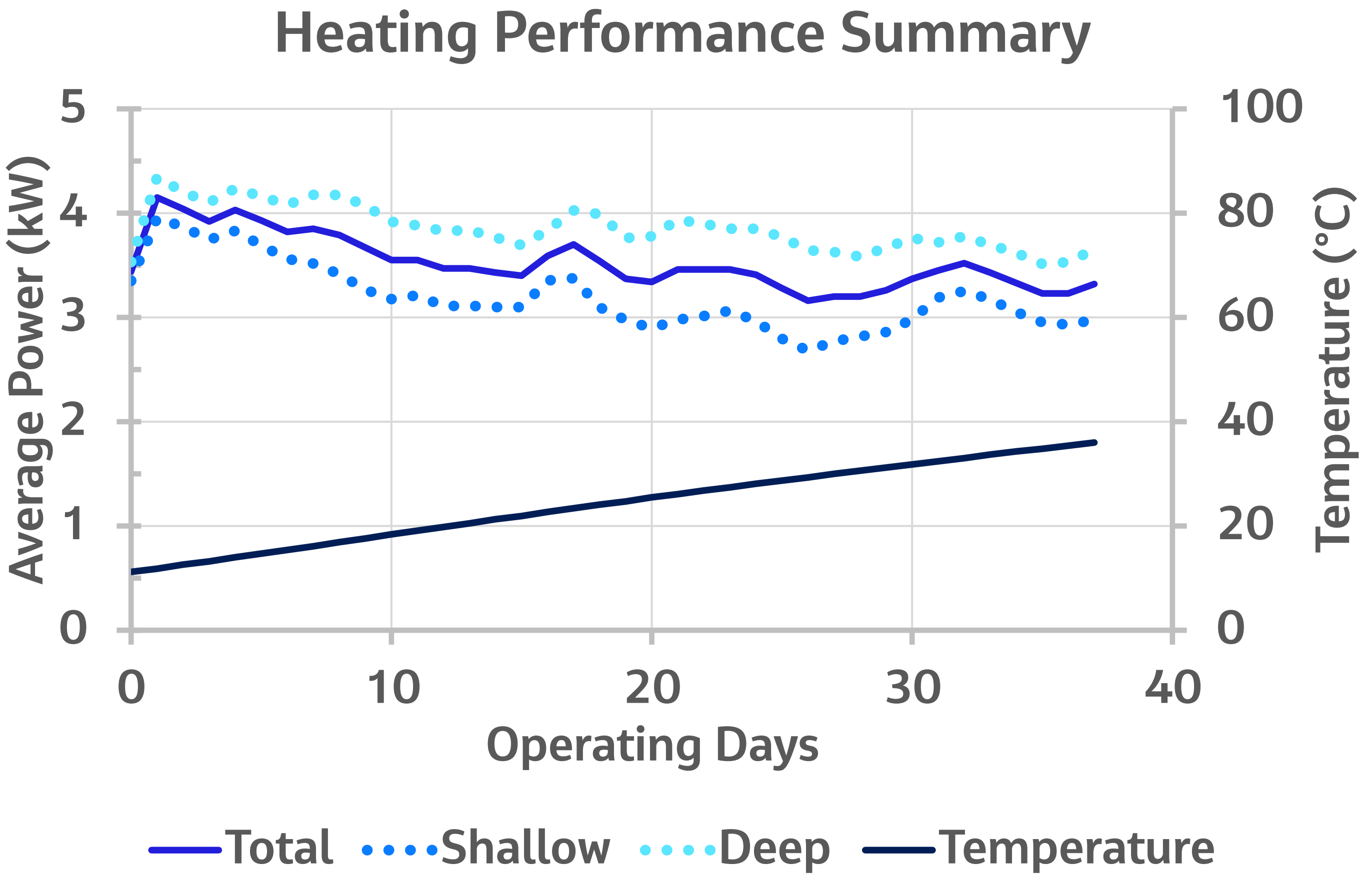


Accelerated EDC Treatment

- Industrial property redevelopment
- Low temperature hydrolysis selected for mass reduction
- Electrical Resistance Heating
  - 350 borings; 700 electrodes
  - No vapor extraction applied
- Four Target Treatment Zones
  - Total Area: ~61,200 square feet
  - Total Volume: ~59,500 cubic yards
- Target Temperature: 72°C
  - Target energy density 135 kWh/cy
  - Increase temperature to accelerate reaction rate in absence of fugitive emissions



Current Conditions



- Heating underway in all zones
- Groundwater sampling – Early July
- Late May - Vadose zone vapor sampling

Closing Remarks

- Low temperature heating can be an effective in-situ solution for treating haloalkanes
  - Preliminary EDB observations appear promising
- Hydrolysis reactions are contaminant specific and may not be suitable for every site
- Eliminating contaminant extraction and treatment provides significant cost savings over applications which favor boiling conditions

Thank You

Jason Cole

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