



*Using Stable Isotopes in a Multiple-Lines-of-Evidence Approach to Evaluating Sources and Degradation of Trichloroethylene*



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## Using Stable Isotopes in a Multiple-Lines-of-Evidence Approach to Evaluating Sources and Degradation of Trichloroethylene

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SMART Remediation 2017

## Outline

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- Context
- Assignment – Problem Formulation
- Site History
- Assessment Strategy
  - Hydrogeology
  - Groundwater Quality
  - CVOC Ratios
  - CSIA
- CVOC Degradation
- Conclusions



# Context

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## Legal action between adjacent property owners

- Diminution of property value
- Business interruption: delay of property sale
- Nuisance: alleging diminishment of the enjoyment, value, and beneficial use of the property



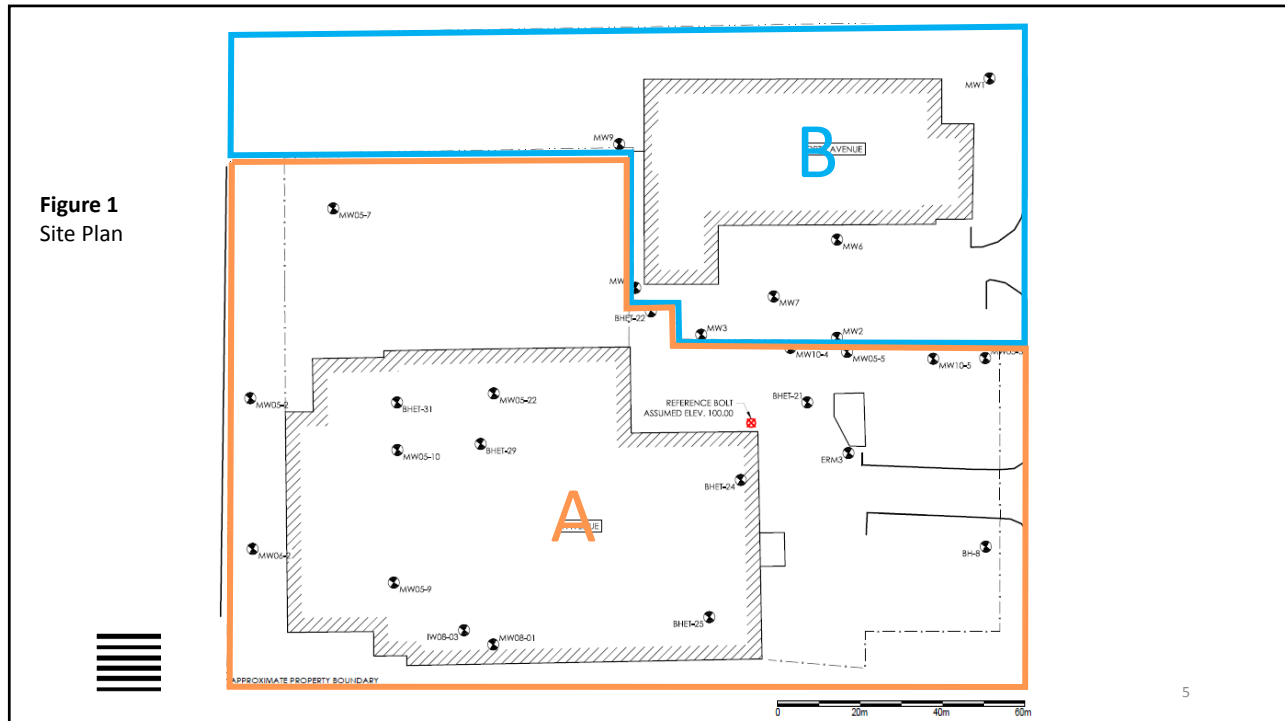
# Assignment – Problem Formulation

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- Property A is the alleged source of cVOC impacts to Property B.
- Assess whether impacts at Property B are attributable to the alleged source at Property A.
- Is it possible that this allegation is unfounded?
- How many lines of evidence are required on the balance of probabilities to prove or disprove the allegation?



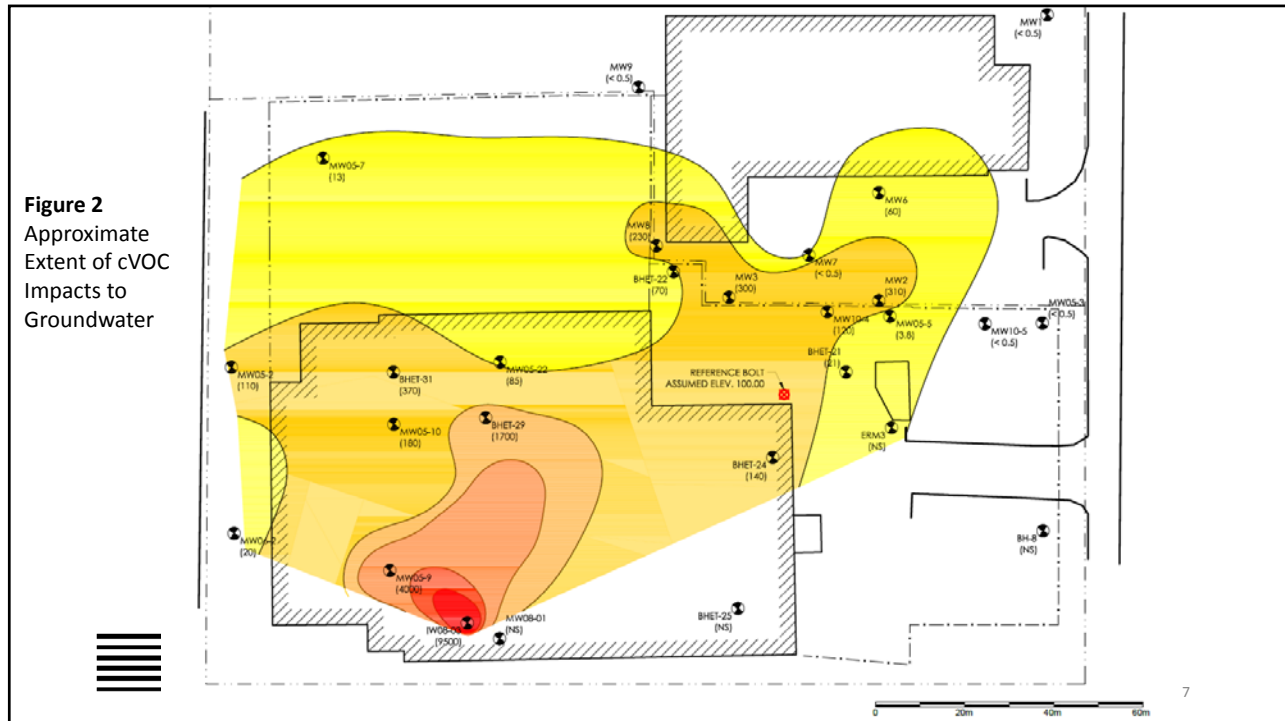
Figure 1  
Site Plan



## Site History

- Industrial operations since 1940s
- Manufacturer of automotive and aircraft parts
- Solvents and cutting oil used and stored at the Property (A)
- Adjacent property (Property B) initially used for warehousing then later sold to an automotive part distributor

**Figure 2**  
Approximate  
Extent of cVOC  
Impacts to  
Groundwater



## Assessment Strategy

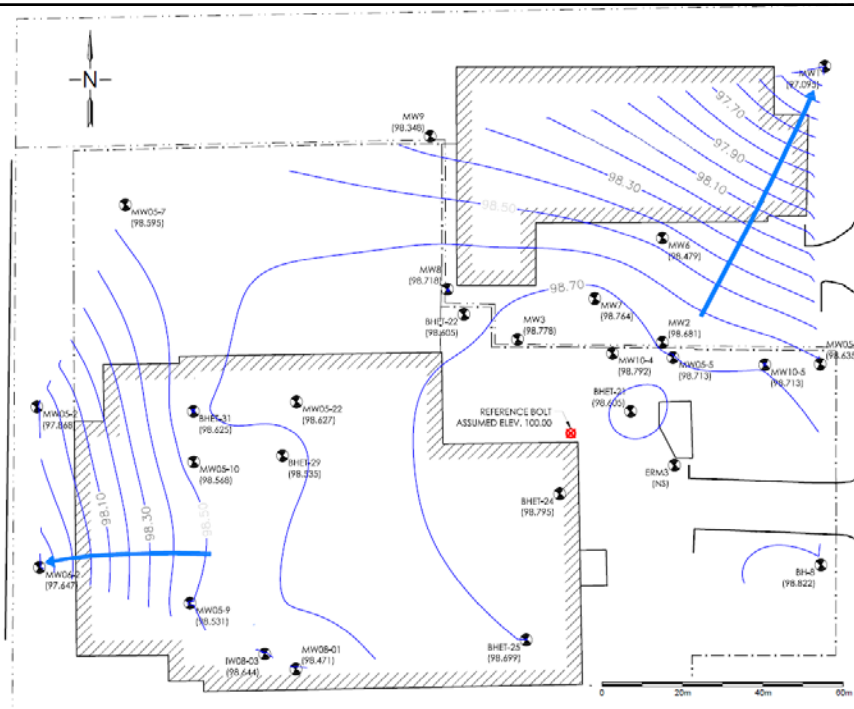
- 1) Hydrogeology:
  - Water level measurements
  - Survey both properties to common datum
  - Slug tests
- 2) Groundwater Quality:
  - 23 groundwater samples
  - Concentration profiles at Property A and Property B
- 3) cVOC ratios:
  - 15 sets of analyses
  - Comparison from Property A and Property B along the groundwater flow path
  - Ratios of TCE to daughter products
- 4) Stable Isotopes:
  - 15 sets of analyses
  - Variable enrichment/depletion of  $^{13}\text{C}$  the flow path

# Hydrogeology

- Two components of shallow groundwater flow direction; northeast and west.
- Principal direction of flow is toward Property B.
- Slug tests were conducted at several monitoring wells to estimate hydraulic conductivity.
- Groundwater flow velocities estimated to be 2 to 4 m/year.
- Estimated velocities are within expected range considering plume dimensions.



**Figure 3**  
Interpreted  
Groundwater  
Flow Direction



## Hydrogeology

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- Two components of shallow groundwater flow direction; northeast and west.
- Principal direction of flow is toward Property B.
- Slug tests were conducted at several monitoring wells to estimate hydraulic conductivity.
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## Groundwater Quality

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- Groundwater samples collected at Property A (16 wells) and at Property B (7 wells).
- The nature, extent, and character of the cVOCs in groundwater were evaluated.
- The same cVOCs were documented at Property A and at Property B.
- Larger concentrations of TCE and cis-1,2-DCE were measured in groundwater at Property A compared to those measured in groundwater at Property B.

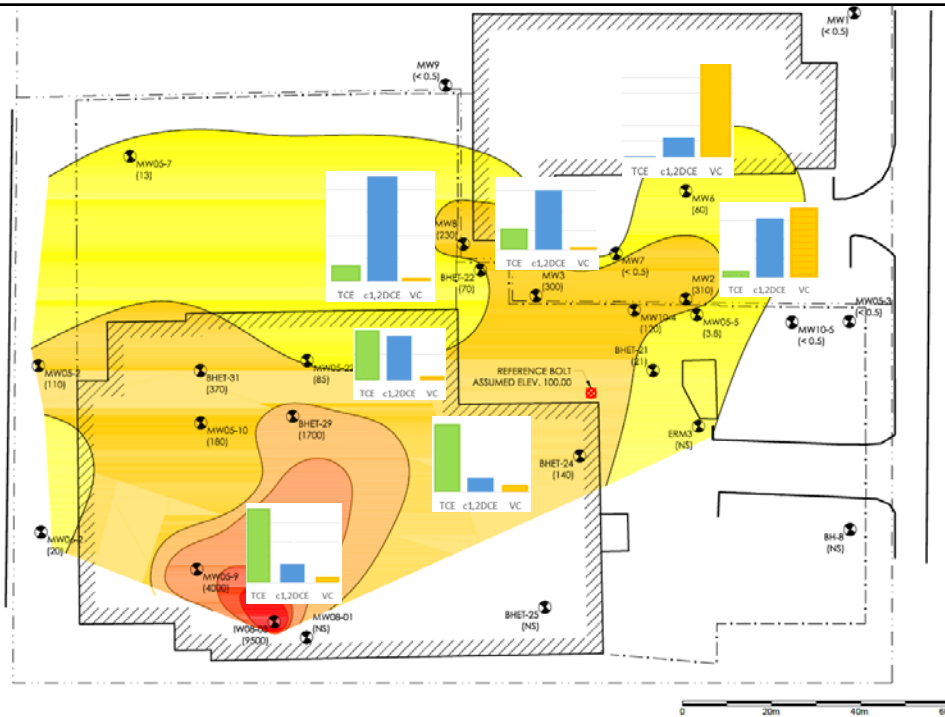


# TCE: Degradation Compound Ratios

- The presence or absence of parent compounds and their breakdown compounds can provide evidence for source area identification.
- Parent-compound to daughter-compound concentration ratios of chlorinated ethenes are frequently stable within source zones, but will decrease as a result of natural attenuation along the groundwater flow path.
- Abrupt increases in parent-compound to daughter-compound ratios indicate a contribution from additional sources of chlorinated ethenes.

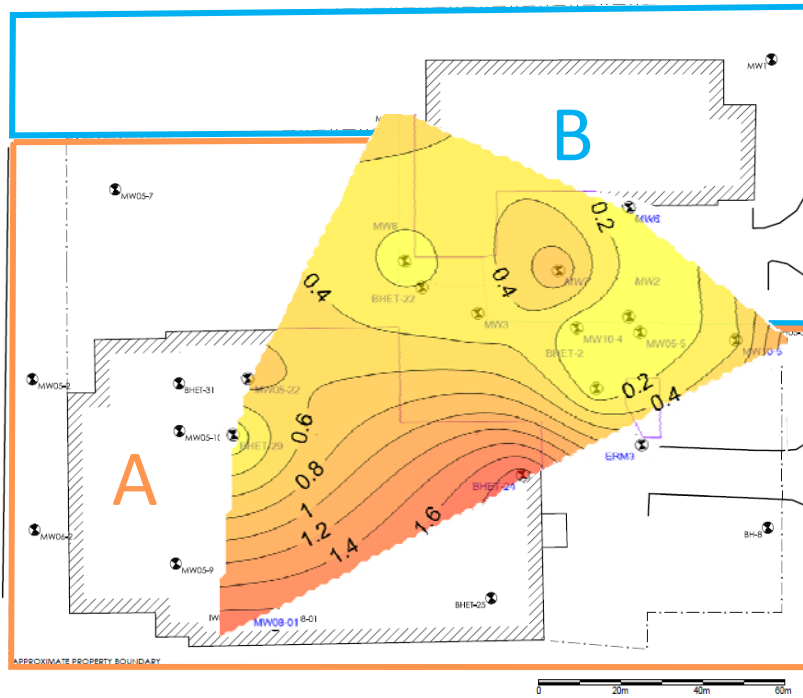


**Figure 4**  
Select cVOC ratios: TCE to Degradation Compounds





**Figure 5**  
TCE – Daughter  
Compound  
Ratio Contours



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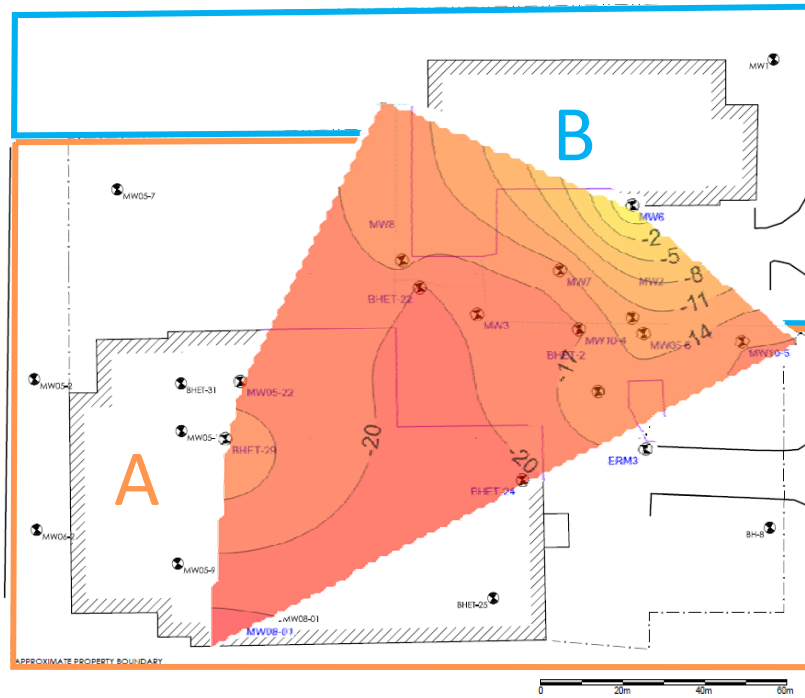
## Stable Isotopes

### CSIA Basics

- Carbon exists in stable form as  $^{12}\text{C}$  and  $^{13}\text{C}$  (radioactive  $^{14}\text{C}$  not applicable in this study).
- With respect to its molecular weight,  $^{12}\text{C}$  is lighter than  $^{13}\text{C}$ .
- $^{12}\text{C}$  preferentially degraded: less energy to break the bond
- Over time, the isotopic ratio of  $^{13}\text{C}$  to  $^{12}\text{C}$  will change.
- Enrichment in the heavier isotope ( $^{13}\text{C}$ ) is expressed as  $\delta^{13}\text{C}$  in per mil notation (‰, parts per thousand), relative to a standard.
- Typical range of manufactured/un-degraded TCE  $\delta^{13}\text{C}$  is -31.9‰ to -27.4‰.



**Figure 6**  
 $^{13}\text{C}$  Enrichment  
Contours



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## Stable Isotopes

- Lower (more negative)  $\delta^{13}\text{C}$  values in the suspected source areas.
- Enrichment in the  $\delta^{13}\text{C}$  along the groundwater flow path.
- Results indicated that it was unlikely that a source of TCE impacts to groundwater was at Property B.
- $\delta^{13}\text{C}$  values from TCE in samples from Property B were consistent with TCE degradation along the groundwater flow path from Property A.

# TCE Degradation

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- Mass reduction or dilution?
- Non-degradative processes do not fractionate
- TCE in groundwater from locations further down-gradient of the source areas may be expected to show increasing enrichment of  $^{13}\text{C}$  and increasing  $\delta^{13}\text{C}$  values in TCE, consistent with the increasing degradation of TCE to other cVOCs.
- Pattern can be masked or altered in situations where active remediation has degraded the parent compound TCE by chemical oxidation or reductive de-chlorination.
- Some degradation in the source area.



# Conclusions

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- 1) Plume extent consistent with groundwater flow direction and velocity.
- 2) Pattern of TCE and daughter products consistent with source area at Property A and migration along flow path to Property B.
- 3) Ratio of TCE to daughter products did not indicate secondary source at Property B.
- 4) Results of Isotope analysis did not indicate a secondary source at Property B.

Each line of evidence indicated that cVOC impacts to groundwater at Property A were the likely source of cVOC impacts at Property B.

