

# 3D-CSIA Forensics to Support Green Remediation

What we are measuring and why it works

Yi Wang, Ph.D.

ZyMaX Forensics Isotope

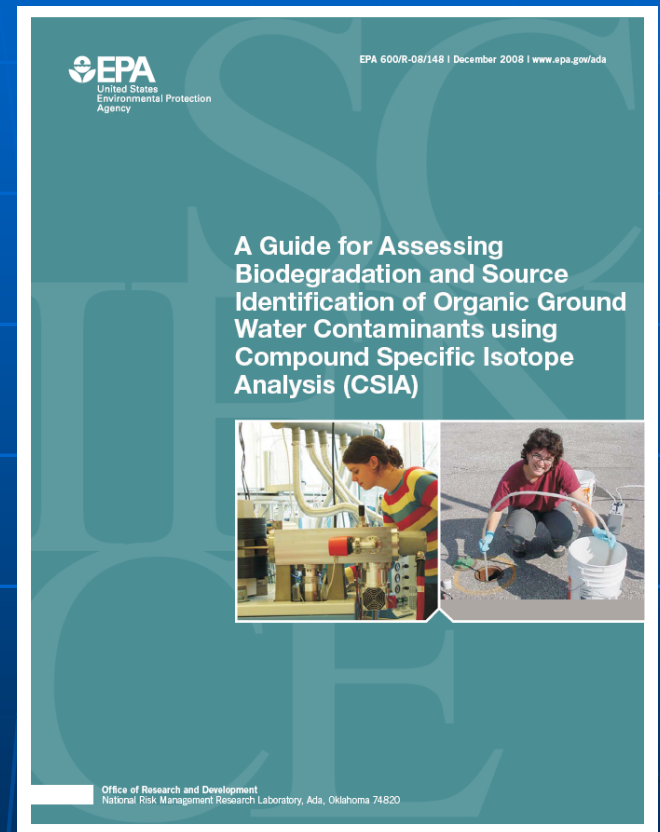
Escondido, California

yi.wang@zymaxUSA.com



# EPA's Guide to CSIA Forensics

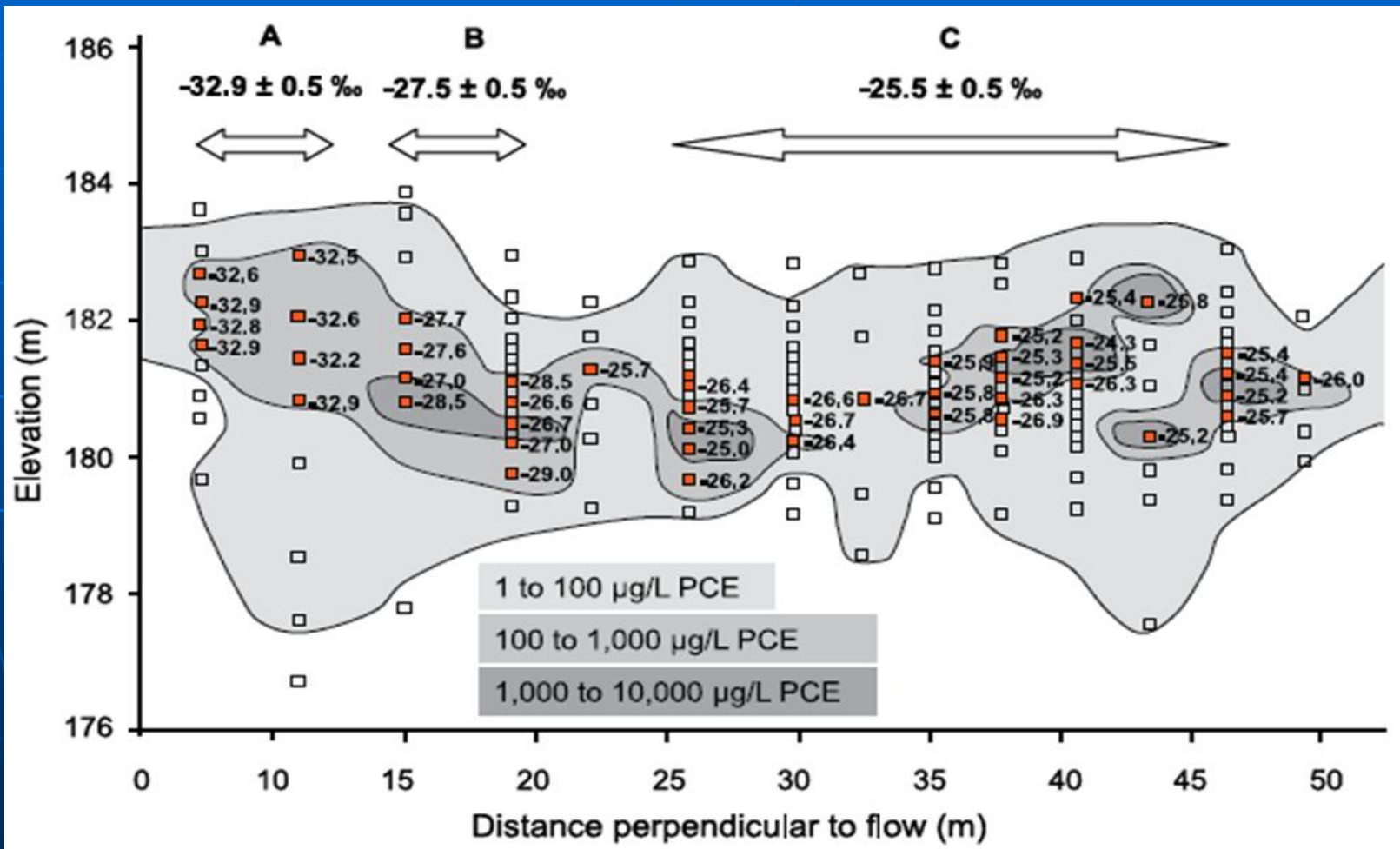
- **A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA), U.S. EPA, Dec 2008**



<http://www.epa.gov/ada/pubs/reports/600r08148/600r08148.pdf>

# 3 PCE Sources Identified by $^{13}\text{C}$ Isotope

“Mission Impossible” if [conc.] used alone!



# Outline

- **Fundamentals** of 3D-CSIA Forensics
- **Remediation** Optimized by 3D-CSIA
- **Strategy** for Successful 3D-CSIA

# Part I. Stable Isotope Ratio ( $\delta$ )

## What we're measuring

- **Ratio of the two most abundant stable isotopes** (for carbon,  $^{13}\text{C}/^{12}\text{C}$ ) in a sample compared to the same ratio in an international standard, 'delta' ( $\delta$ ) notation
- Because the differences in ratios are very small, they are expressed as **parts per thousand** or **per mil (‰)** deviation from the standard. For carbon,

$$\delta^{13}\text{C}_{\text{sample}} = [(\text{^{13}C/^{12}C}_{\text{sample}})/(\text{^{13}C/^{12}C}_{\text{standard}})-1]\times 1000$$

- Commonly observed **negative  $\delta^{13}\text{C}_{\text{sample}}$**  mean **less  $^{13}\text{C}$**  in samples than in the standard PDB ( $\delta^{13}\text{C}_{\text{PDB}} = 0\text{‰}$ )

# 3D-CSIA Forensics

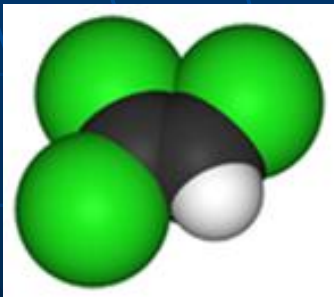
- Up to three isotopes or three dimensional (3D-CSIA) Forensics of Organics, such as **Chlorinated Solvents**, **MTBE**, **Petroleum Hydrocarbons (BTEX)**, and **PAH**, etc.

Carbon:  $\delta^{13}\text{C}$  (‰, PDB)

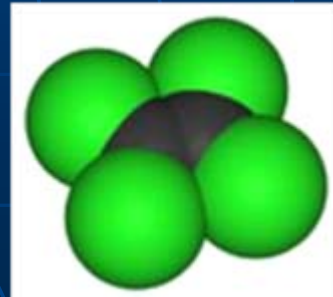
Hydrogen:  $\delta^2\text{H}$  (‰, SMOW)

Chlorine:  $\delta^{37}\text{Cl}$  (‰, SMOC)

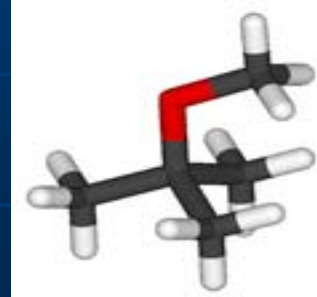
**TCE**



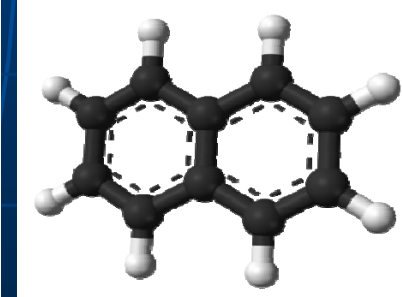
**PCE**



**MTBE**



**Naphthalene**

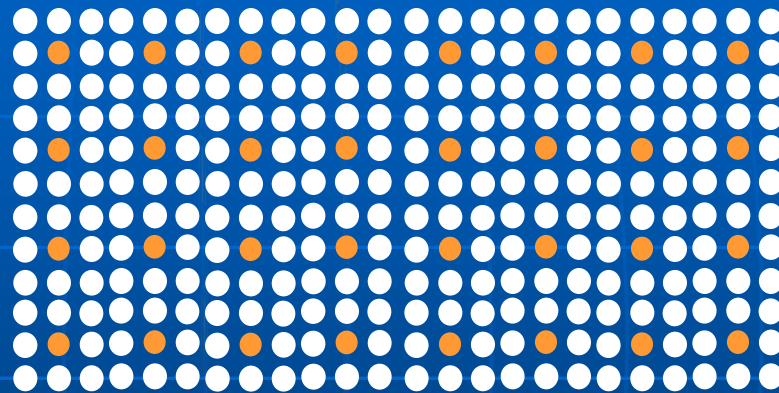
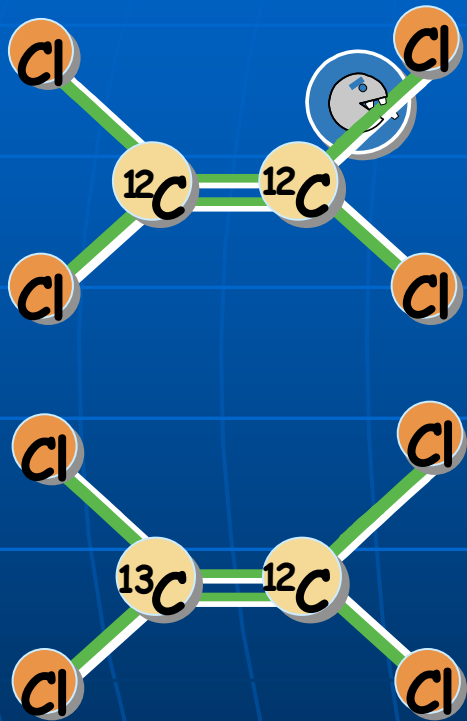


# Isotope Fractionation

## What we're measuring

- **Change in the isotope ratio** during a process
  - ❖ **Physical** (volatilization, diffusion, sorption...)
  - ❖ **Chemical** (abiotic transformations...)
  - ❖ **Biological** (aerobic & anaerobic biodegradation)
- **Controls for extent of isotope fractionation**
  - ❖ **Reaction mechanism – Dominant Control**  
e.g. if broken bonds involved? Yes > No
  - ❖ **Mass difference** for different elements - **Potential**  
e.g.  ${}^2\text{H}/{}^1\text{H}$  (100%) >  ${}^{13}\text{C}/{}^{12}\text{C}$  (8%) >  ${}^{37}\text{Cl}/{}^{35}\text{Cl}$  (5%)

# Example: PCE Getting Enriched in $^{13}\text{C}$ ( ) During Biodegradation



If Original  
Ratio is  $1/9$

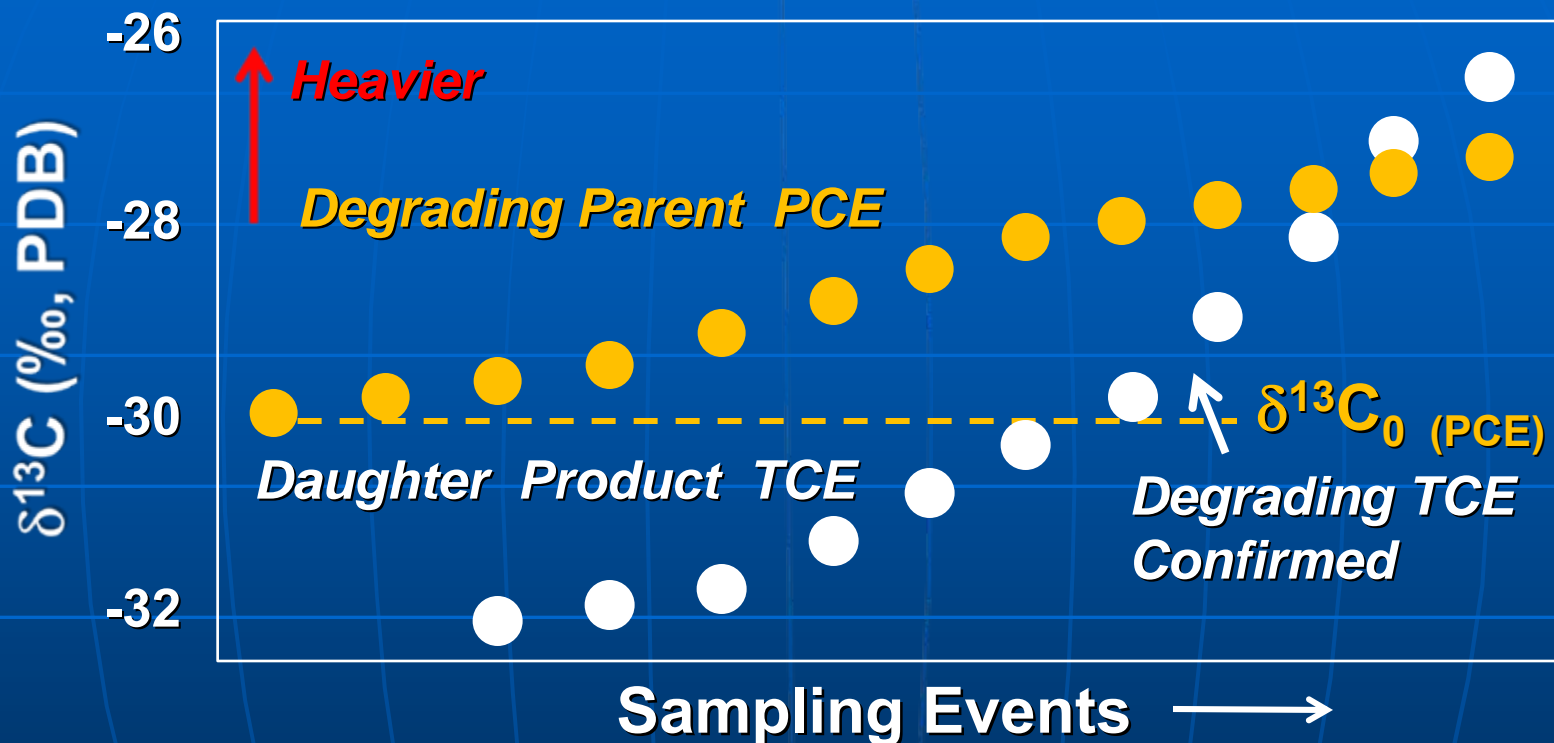
Enrichment in  
the heavy isotope



12.5% Remaining  
Ratio is  $1/3$

In this example, ratio enhanced from  $1/9$  to  $1/3$ ,  
when the rate of removal of heavy isotope is  
75% of the rate of removal of light isotope

# Enhanced $^{13}\text{C}$ ratios: Direct Evidence of Effective PCE/TCE Degradation



- PCE's degradation **confirmed** by its ratios getting **heavier**
- Daughter product TCE's degradation **NOT confirmed** by its ratios getting **heavier** as its parent PCE's ratios are getting **heavier** too
- TCE's degradation **confirmed** when  $\delta^{13}\text{C}_{\text{TCE}}$  greater than  $\delta^{13}\text{C}_0$  (PCE)

# Part II. Remediation Optimized by 3D-CSIA Forensics

- A Plume Well Defined by 3D-CSIA Tools, etc. Allows for Focused, Aggressive Treatments
- **Direct Evidence** for Effective Remediation!
  - ❖ Decreased Concentration – Indirect, Uncertain
  - ❖ Enhanced  $\delta^{13}\text{C}$  – **Broken Bond Evidence**
  - ❖ Mechanism, extent, rate – **Bonus from CSIA**
    - ✓ **1D-CSIA of  $\delta^{13}\text{C}$  Required**
- **Optimized Remediation – Cost Effective**
  - ❖ Assess current or new Treatment – **Save \$\$**
  - ❖ Avoid redundant monitoring & treatment – **Save \$\$**
  - ❖ Use focused treatment & achieve site closure faster for Monitored Natural Attenuation – **Go Green!**
    - ✓ **1D-CSIA or 2D-CSIA Required**

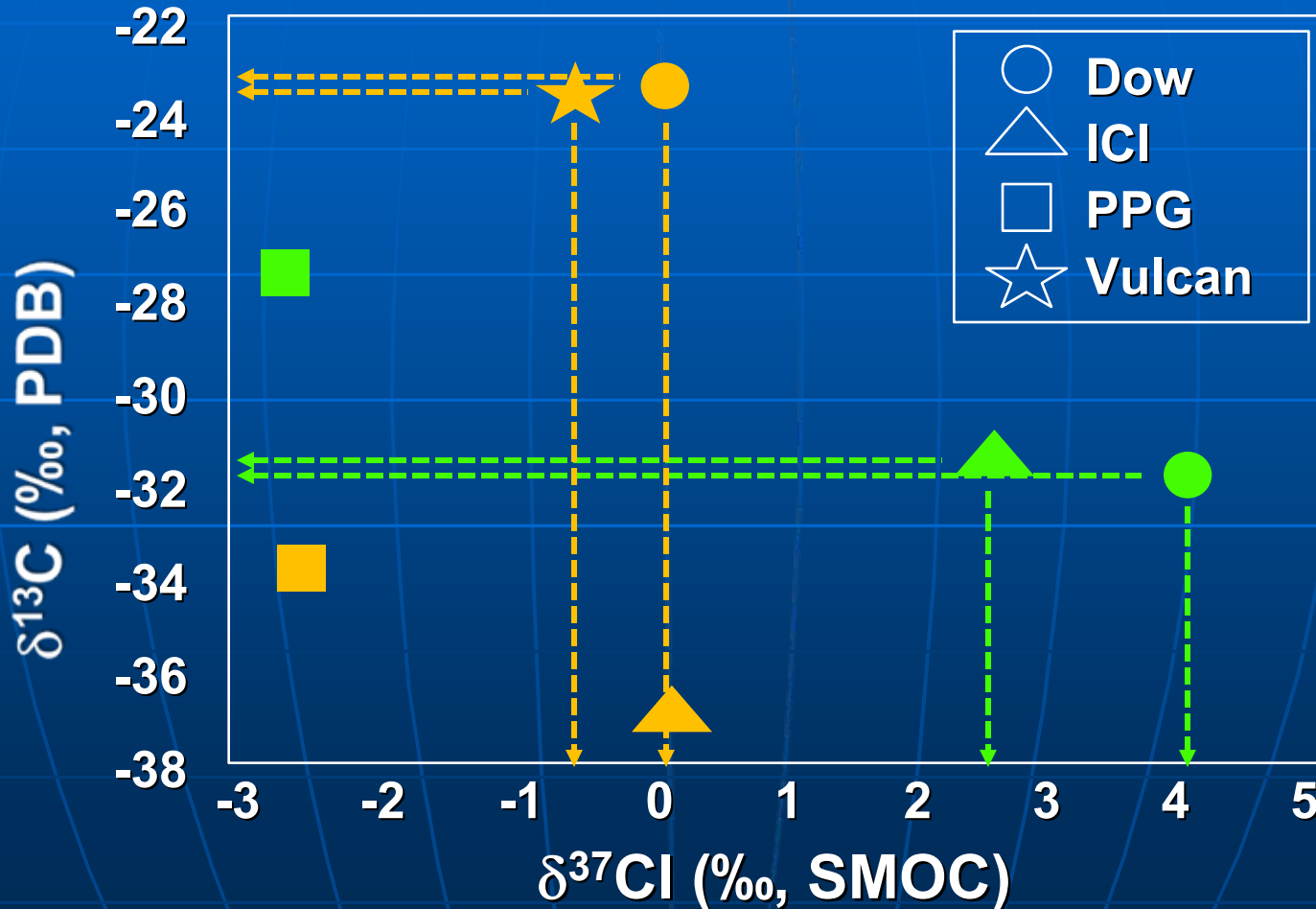
# A Plume Defined by 3D-CSIA Forensics Has Less Uncertainty

## Frequently Asked Questions, e.g. for Solvents:

- Is PCE or TCE in one plume from one or more sources (co-mingled plume)?
  - ✓ **2D-CSIA** of  $\delta^{13}\text{C}$  and  $\delta^{37}\text{Cl}$  required
- Is PCE or TCE in separate plumes from the same source or different sources?
  - ✓ **2D-CSIA** of  $\delta^{13}\text{C}$  and  $\delta^{37}\text{Cl}$  required
- Is TCE in a PCE plume from degradation of PCE or from a separate TCE source?
  - ✓ **3D-CSIA** of  $\delta^{13}\text{C}$ ,  $\delta^{37}\text{Cl}$ , and  $\delta^2\text{H}$  required

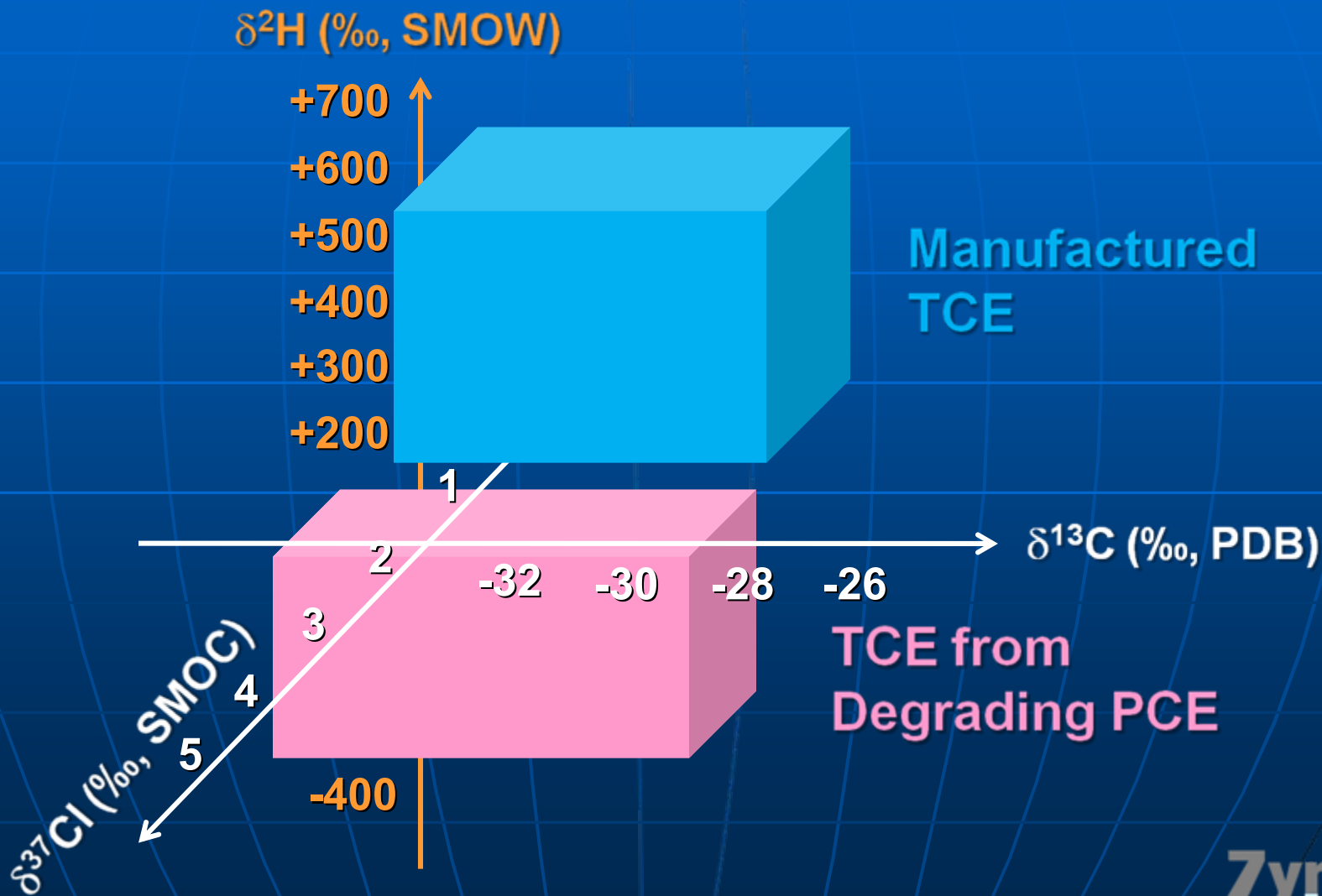
# Why 2D-CSIA Forensics

PCE or TCE from 4 Manufactures

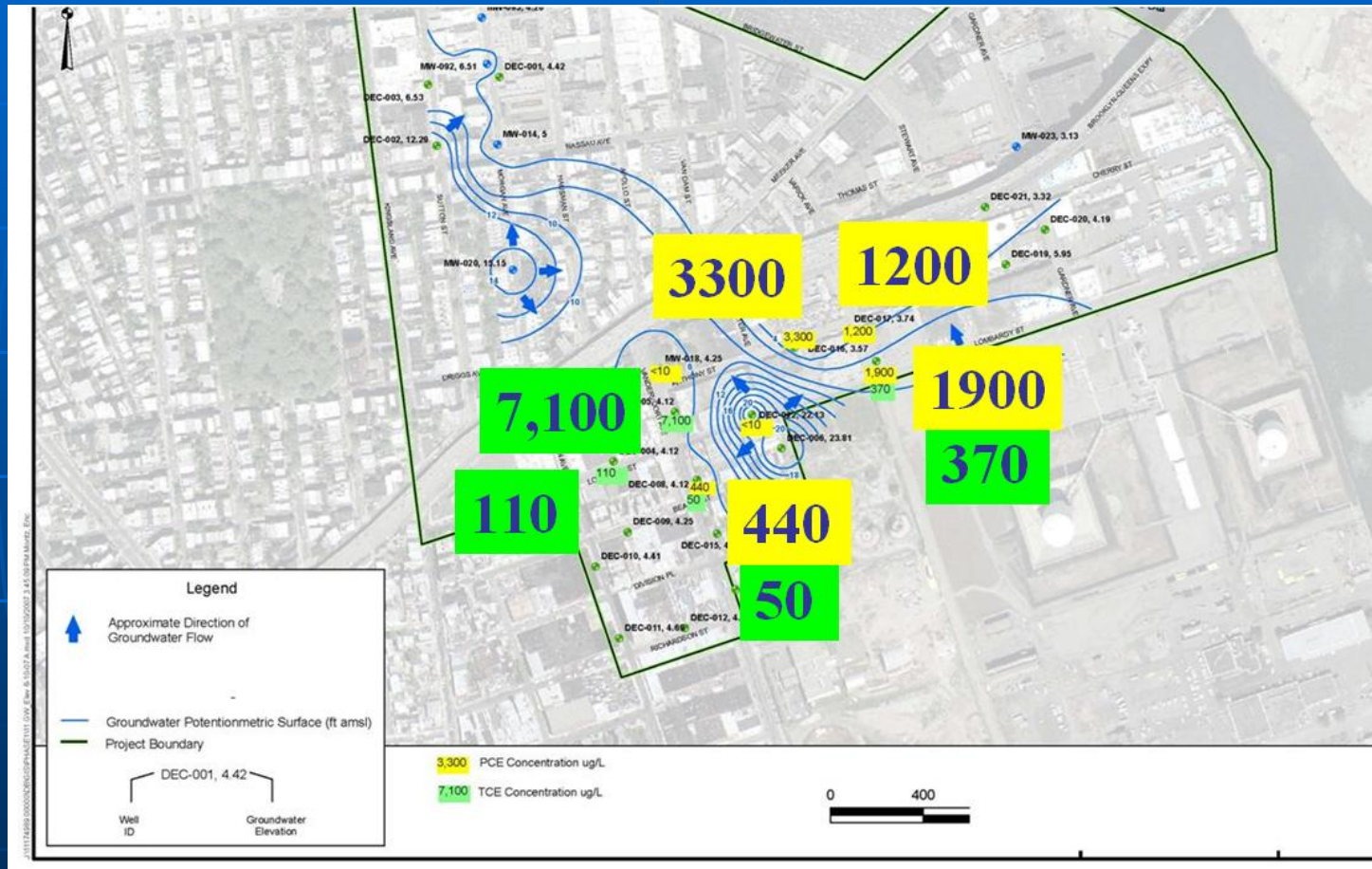


# Why 3D-CSIA Forensics

3D-Plot determines TCE's origin



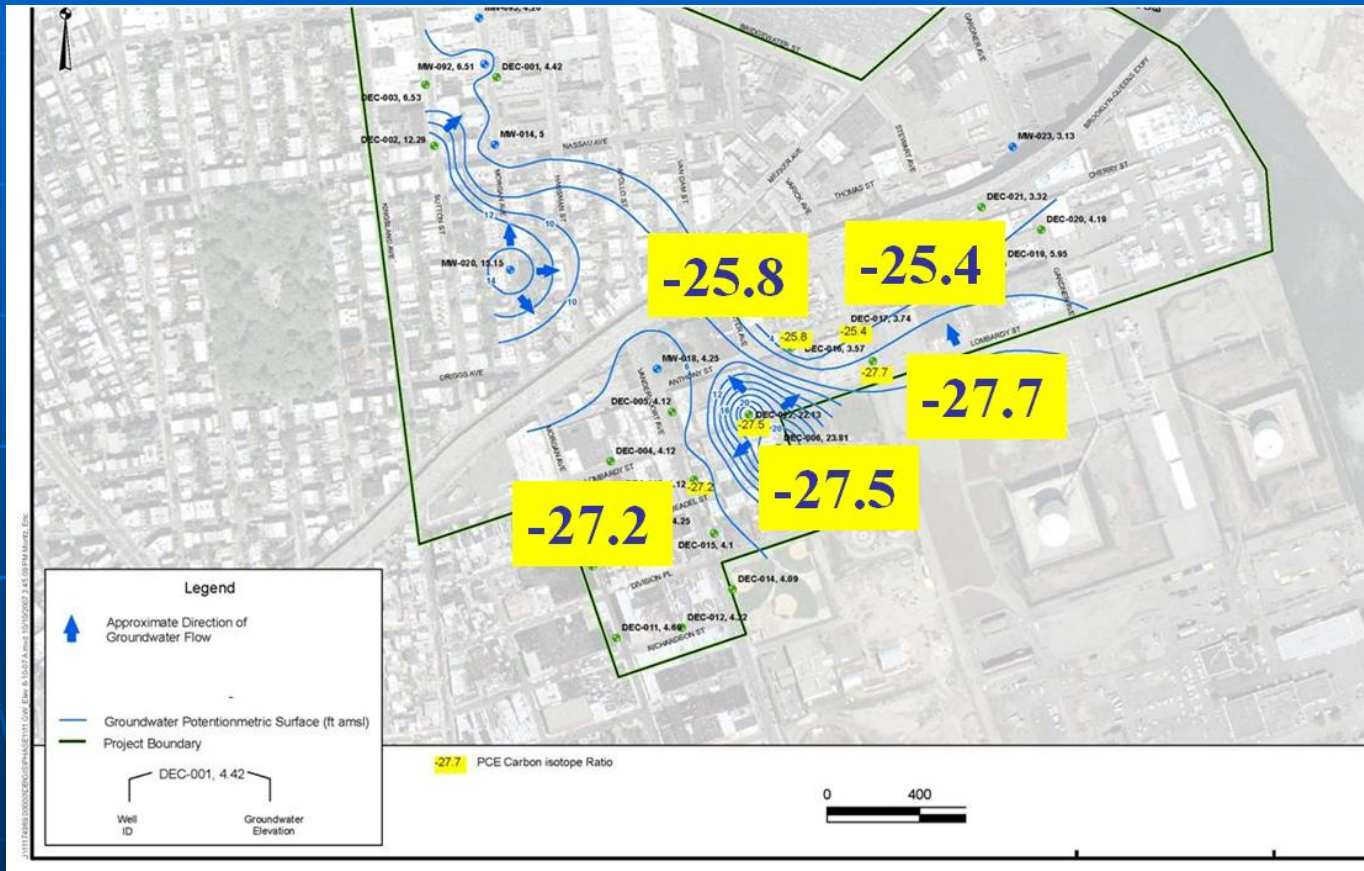
# Case Study: PCE/TCE Plumes



- PCE and TCE Concentrations ( $\mu\text{g/L}$ )

# PCE/TCE Plumes

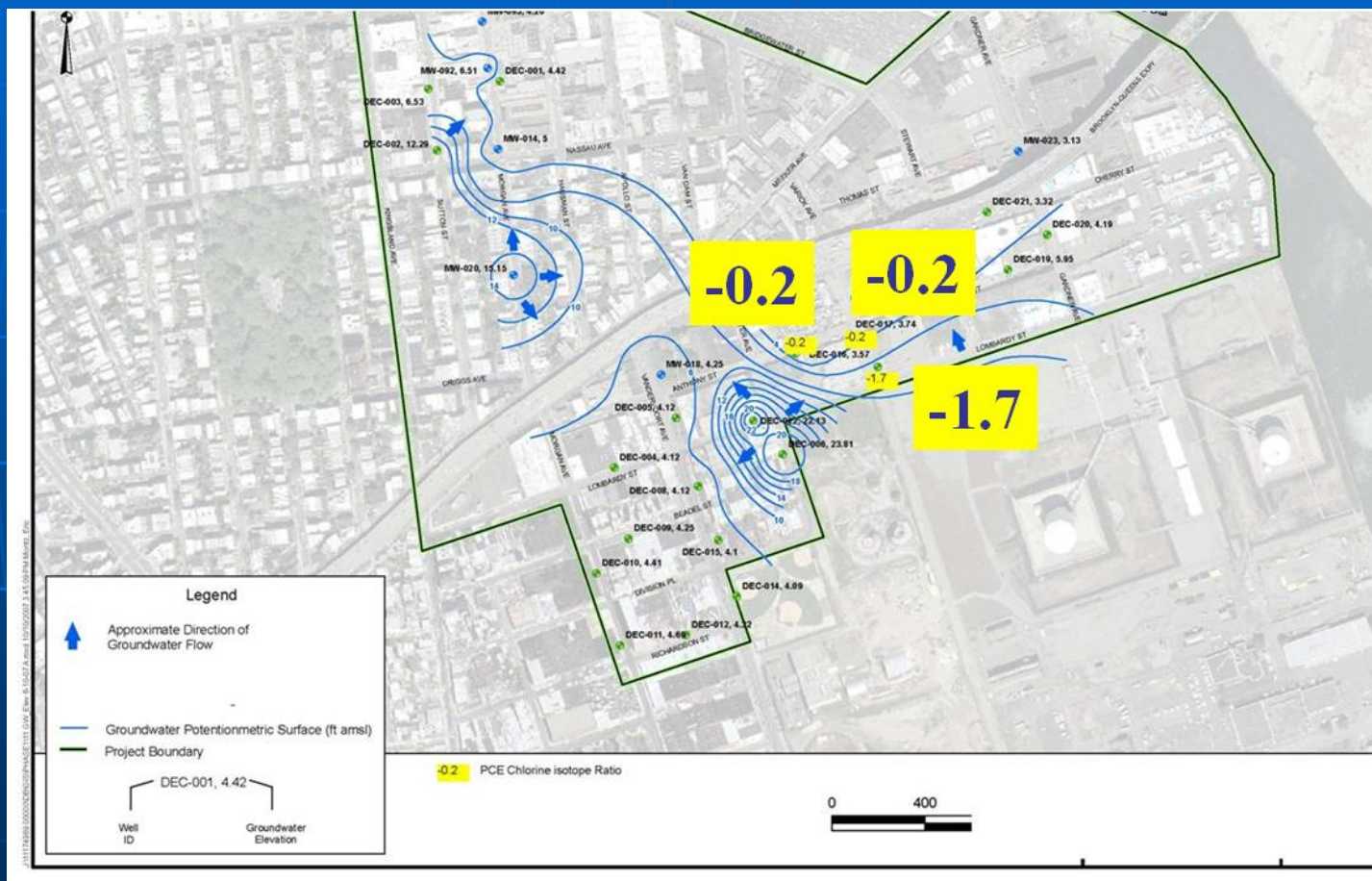
## 1D-CSIA: $\delta^{13}\text{C}$ of PCE



- One or more than one **PCE** plumes?

# PCE/TCE Plumes

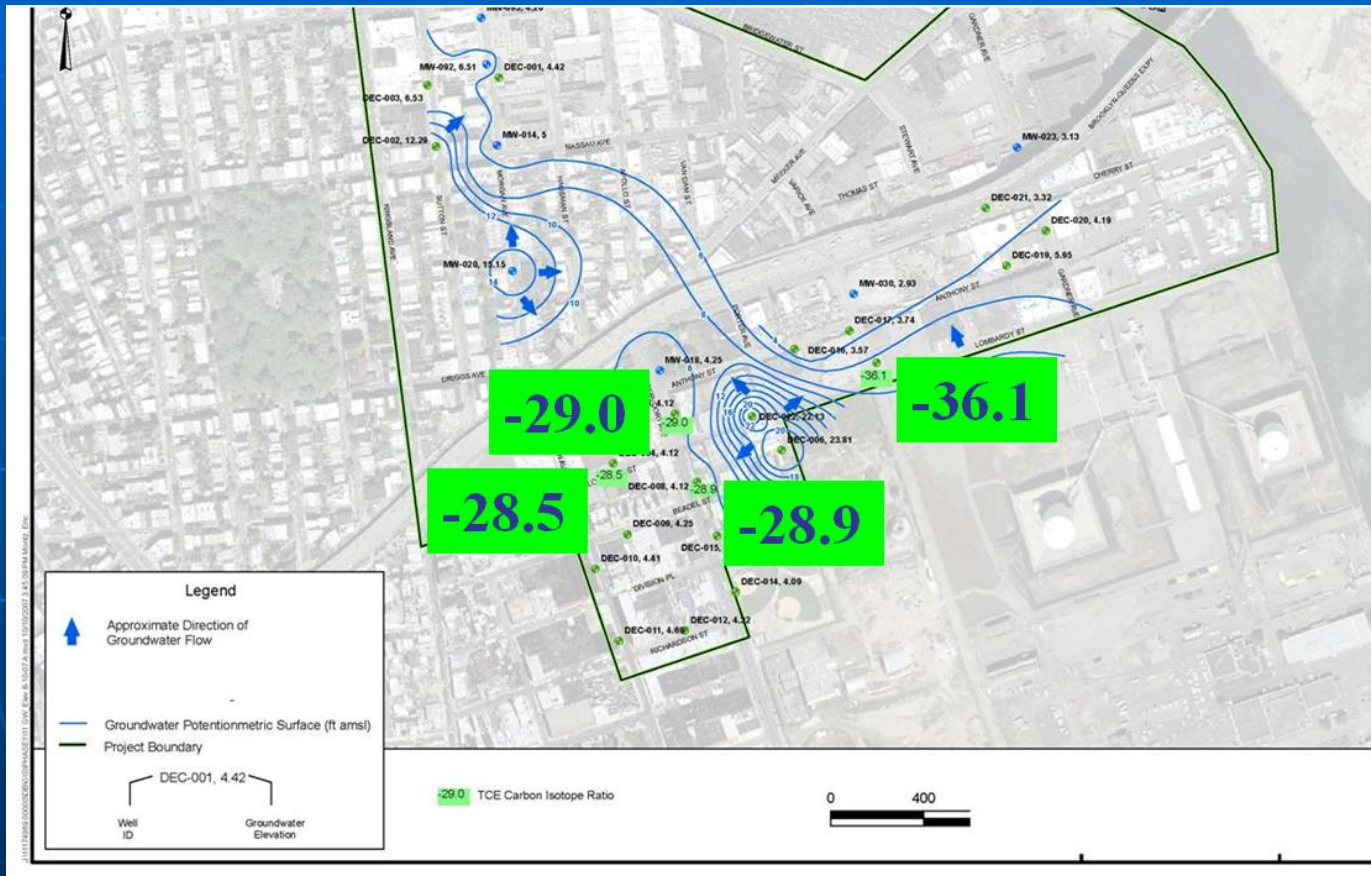
## 2D-CSIA: $\delta^{37}\text{Cl}$ of PCE



- Two **PCE** Plumes Confirmed

# PCE/TCE Plumes

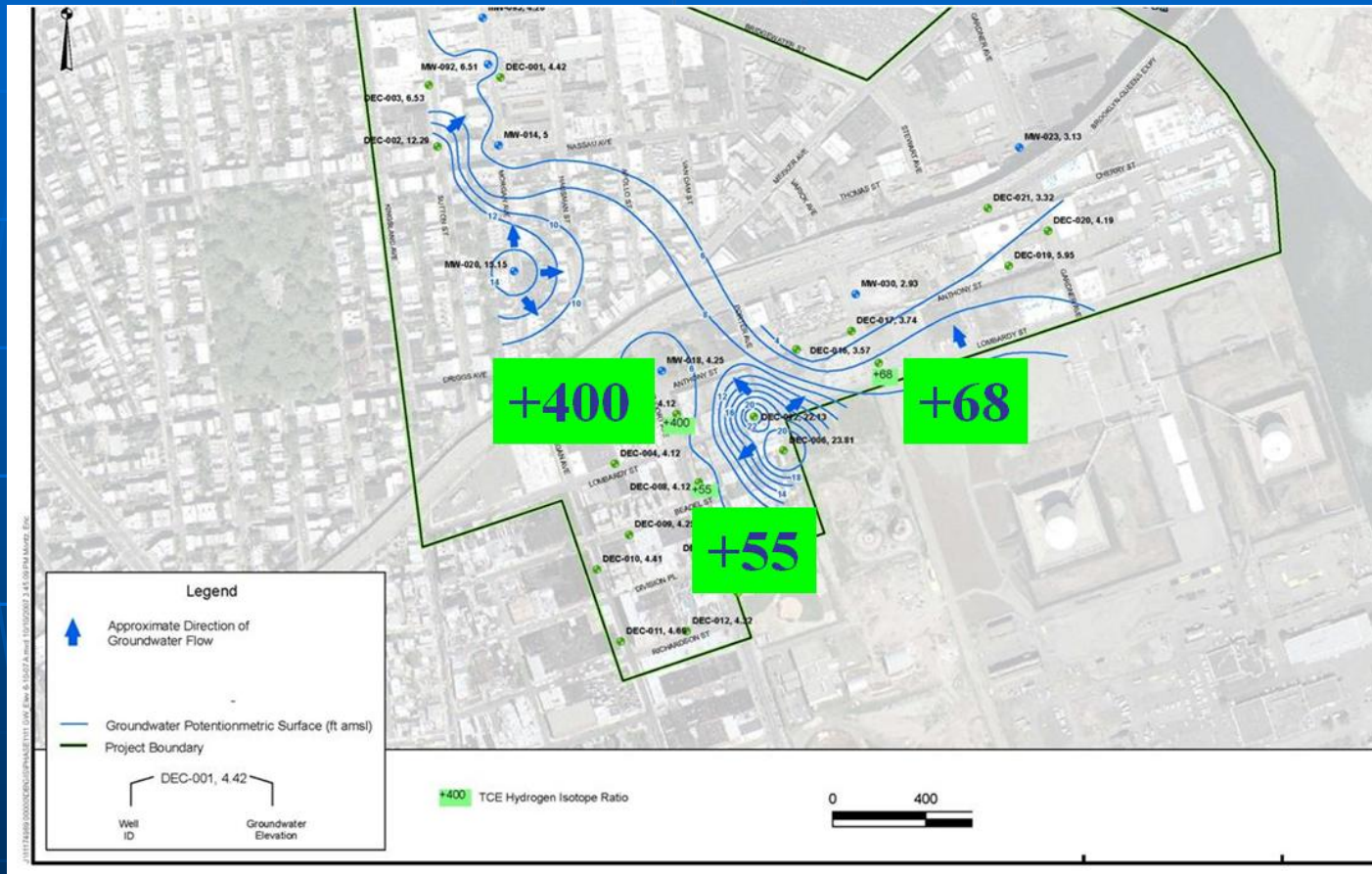
## 1D-CSIA: $\delta^{13}\text{C}$ of TCE



- **TCE** plume: has it affected adjacent wells?

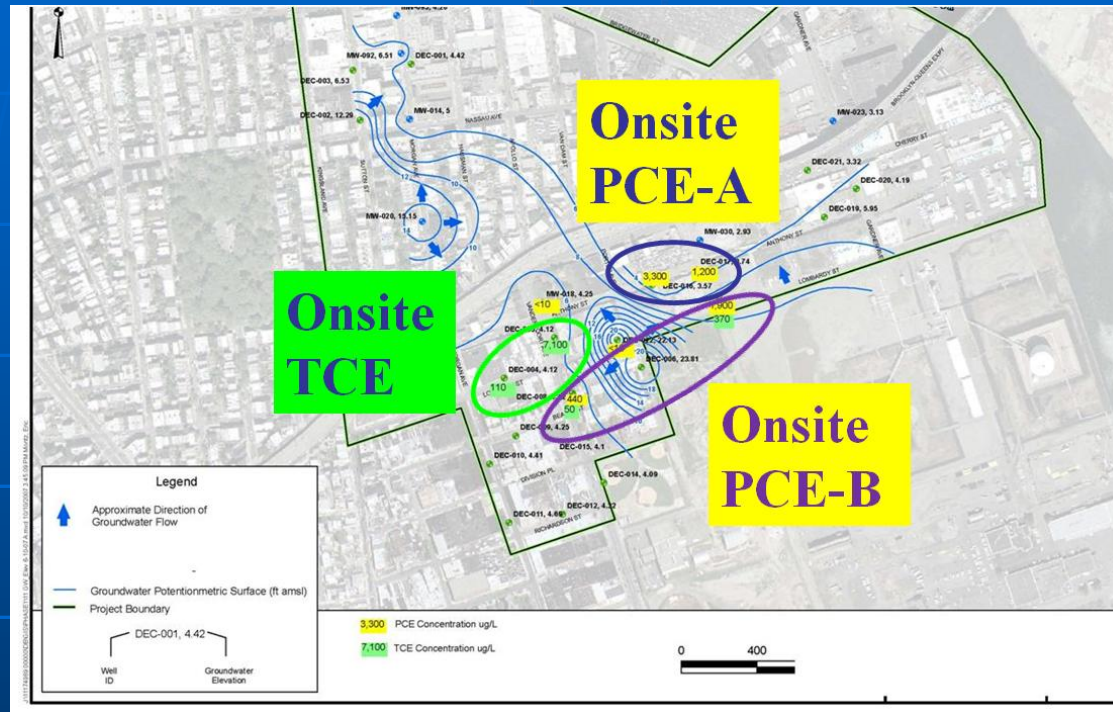
# PCE/TCE Plumes

## 3D-CSIA: $\delta^2\text{H}$ of TCE



- Onsite **TCE** release, limited migration

# PCE/TCE Plumes Defined by 3D-CSIA Forensics



- Two **PCE** plumes – confirmed by  $^{13}\text{C}$  and  $^{37}\text{Cl}$  ratios
- Possible migration pathway for **PCE**
- **TCE** plume – limited migration; other **TCE** from **PCE** degradation – confirmed by  $^2\text{H}$  ratios of **TCE**

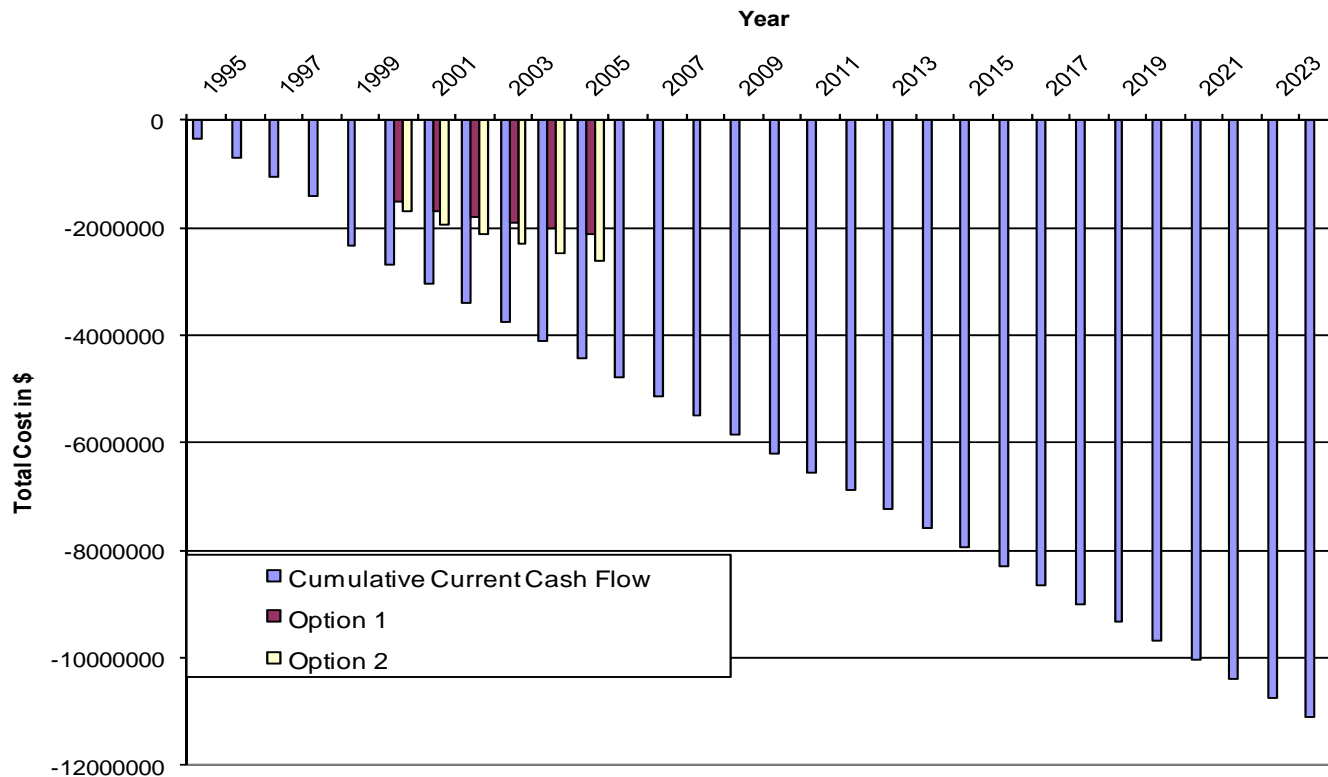
# New Options Reduce Cost by 50%

## PCE/TCE Site in Salt Lake City

- Existing **Pump & Treat** to remediate PCE/TCE in groundwater, plume migrated off site
- Two suspected source locations, with great **uncertainty** as to **location** and **definition**
- DNAPL believed present, unfortunately, it was **not investigated** by existing consultant!
- Options (1) Electrical Resistance Heating (ERH) (2) Permeable Reactive Barrier (PRB)
- **Cost dependent on plume characterization!**

# How Much You May Save

## Long-Term vs. Short-Term Treatment

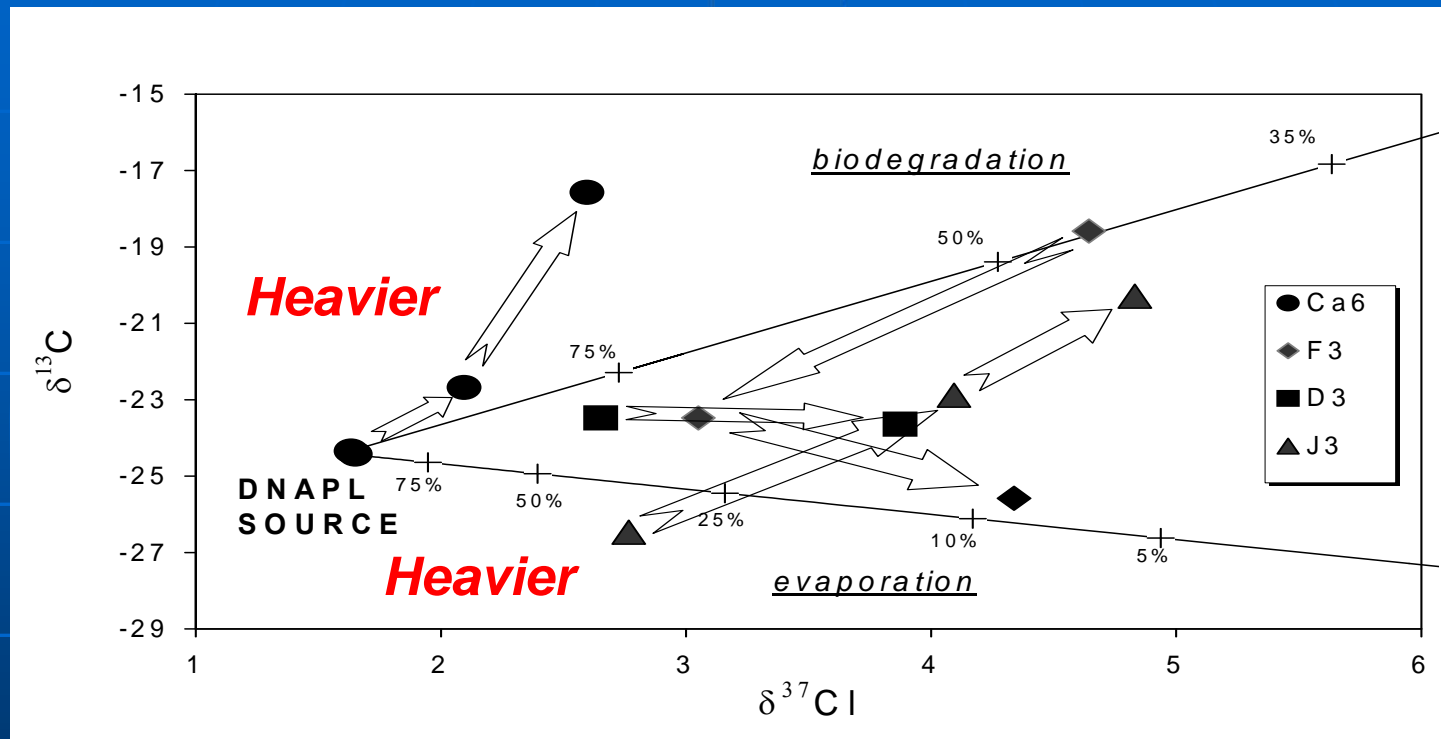


# Cost Comparison

## Long-Term vs. Short-Term Treatment

- Existing **Pump and Treat**, started at ~\$0.5M, will last **>30 years**, total cost **>\$10M**
- Option 1: **ERH**, starts at ~\$1.5M, gets closure within 6-8 years, total cost **<\$3.5M**
- Option 2: **PRB**, starts at ~\$1.6M, gets closure within 6-8 years, total cost **<\$4.0M**
- Source/plume characterization allows for focused, more aggressive treatment, achieving site closure faster, **reducing cost by >50%**

# Remediation Optimized by Isotope Tracers



$\delta^{13}\text{C}$  vs.  $\delta^{37}\text{Cl}$  of solvent extracted from 4 wells during remedial activities (Vapor Extraction, Steam Injection, and Electrical Resistance Heating) over a year. Evaporation and biodegradation theoretical trends are shown, with residual solvent% indicated. Arrows in white indicate time sequence.

# Mechanisms Indicated by Isotope Tracers

- Well J3: evaporation then biodegradation. Well used for steam injection ~6 years then stopped
- Well D3: biodegradation then evaporation. DNAPL into this location. Heated with steam, then electrical resistance heating applied
- Well F3: **biodegradation**, **dissolution**, then **evaporation**. Perimeter on site, biodegradation occurred. Steam injection and ERH used later
- Well Ca6: heating was sufficient to stimulate biodegradation, but not for evaporation

# Part III. Strategy to Achieve Successful 3D-CSIA Forensics

## Job Done Right with Limited Budget

### ■ Critical Steps 1-2-3 to Success

- ❖ Appropriate Sampling Strategy
- ❖ Reliable & Prompt 3D-CSIA
- ❖ Defensible and Understandable Data Interpretation

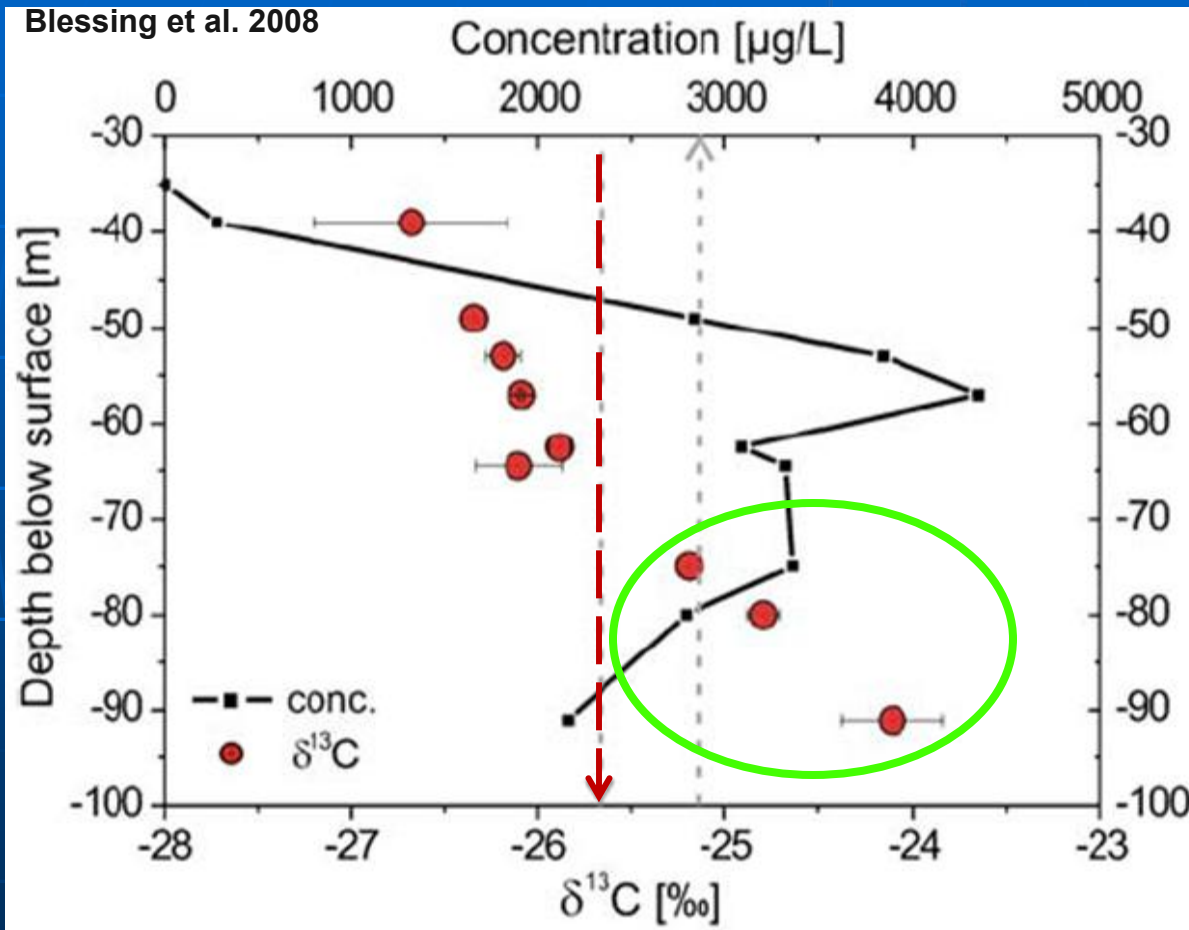
### ■ CSIA Sampling Strategy

- ❖ **Source identification** - Take NAPL; if N/A, take  $\geq 3$  samples in high concentration zone
- ❖ **Plume characterization** - Take  $\geq 3$  samples in each plume or plume segment. **Consider** the following:
- ❖ Vertical; Preliminary survey; Analytical limits

# CSIA Sampling Strategy

<b>Purposes – Locations</b>	<b>Samples</b>
<b>Preliminary Survey to Justify Comprehensive Study</b>	<b>4 to 6 Wells</b>
<b>Comprehensive Survey or Monitoring Natural Attenuation</b>	<b>12 to 24 wells</b>
<b>Up gradient of source</b>	<b>1 to 2 wells</b>
<b>Source zone</b>	<b>3 to 5 wells</b>
<b>Center flow line</b>	<b>4 to 5 wells</b>
<b>Boundary of plume</b>	<b>4 to 8 wells</b>
<b>Vertical extent</b>	<b>1 to 4 wells</b>
<b>Plume Stability: Monthly to Yearly</b>	<b>6 to 15 wells</b>

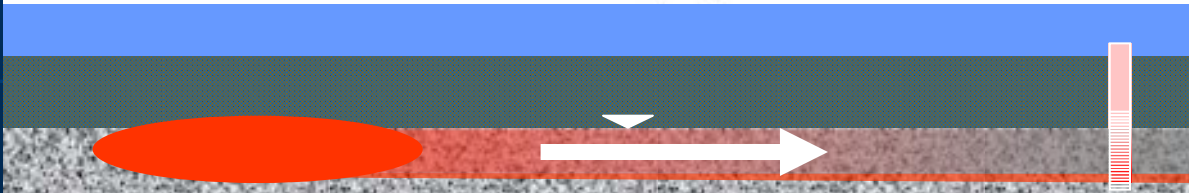
# Vertical vs. Point-Scale Sampling



Mean [Conc.] of 2,900  $\mu\text{g/L}$  would have been obtained by a point-scale sampling



Weight-averaged  $\delta^{13}\text{C}$  of -25.7‰ would have been obtained by a **point-scale sampling**, which **missed critical information on the effective degradation process**



# How to Collect, Store and Ship Samples for 3D-CSIA Forensics

- **Container (soil):** 4 oz wide mouth glass jar w/ Teflon-lined closure, fill up 2 replicate jars for each sample, avoid loss of volatiles
- **Container (water):** 40mL HCl pre-preserved glass VOA vials, ensure  $\text{pH} < 2$ , take  $\geq 8$  replicate vials from each well, leave zero headspace
- **Storage and Shipping:** keep  $\sim 4^{\circ}\text{C}$  in the dark and ship overnight on ice to lab for VOCs ( $n=2$ ) and CSIA ( $n \geq 6$ )



# Forensics Package, HT and TAT

- **One Stop Shopping for Isotope Forensics**
  - ✓ Sampling Strategy Advice
  - ✓ Concentration and Isotope Analysis
  - ✓ Data Interpretive and Forensics Report
  - ✓ Expert Witness Testimony – Litigation Support
  - ✓ Optimized Remediation
- **Holding Time (HT)**
  - ❖ Concentration Test (VOCs, etc.): 14 days
  - ❖ CSIA: N/A – use 14 days if litigation is the focus\*
- **Turn-Around-Time (TAT)**
  - ❖ Concentration Test (VOCs, etc.): **5 days**
  - ❖ 3D-CSIA: **30 days**, or rush upon request

# **Thank you!**

## **Questions and Comments?**

**Contact Info: [yi.wang@zymaxUSA.com](mailto:yi.wang@zymaxUSA.com)**

**ZymaX Forensics Isotope  
600 South Andreasen Drive, Suite B  
Escondido, CA 92029  
Phone: 760.781.3338 ext 43**