Fundamentals and Application of Environmental Isotopes in Chlorinated Solvent Investigations

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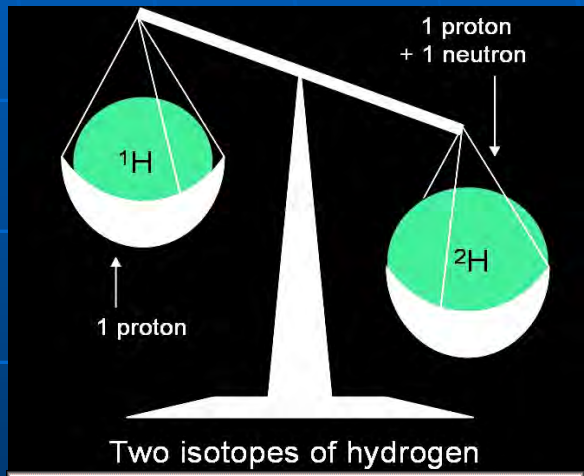
Outline

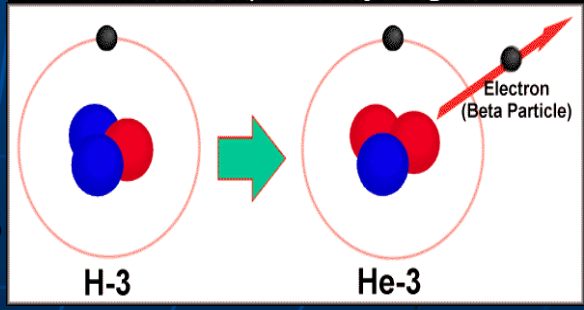
- Fundamentals of Environmental Isotopes and Compound-Specific Isotope Analysis (CSIA)
- Collection, Preservation and Storage of Samples for CSIA of Chlorinated Solvents
- CSIA Data Can Distinguish Between Different Chlorinated Solvent Sources
- CSIA Data Can Guide Remediation Decision and Help Achieve Site Closure

Part I. Environmental Isotopes

- Definition: atoms of an element with the same number of protons but different number of neutrons
- Some isotopes are stable
  - ^{1}H (1p0n), ^{2}H or D (1p1n, 0.015%)
  - ^{12}C (6p6n), ^{13}C (6p7n, 1.1%)
  - ^{35}Cl (17p18n), ^{37}Cl (17p20n, 24.23%)
- Some isotopes are unstable
  - ^{3}H or Tritium (1p2n): $T_{1/2}$ ~12.4 years
  - ^{14}C (6p8n): $T_{1/2}$ ~5730 years



Two isotopes of hydrogen



Clark and Fritz, 1997

Isotope Ratios

- **Definition: Ratio of the two most abundant isotopes in a sample compared to the same ratio in an international standard, using the 'delta' (δ) notation.**
- **Because the differences in ratios between the sample and standard are very small, they are expressed as parts per thousand (‰) deviation from the standard. For carbon:**

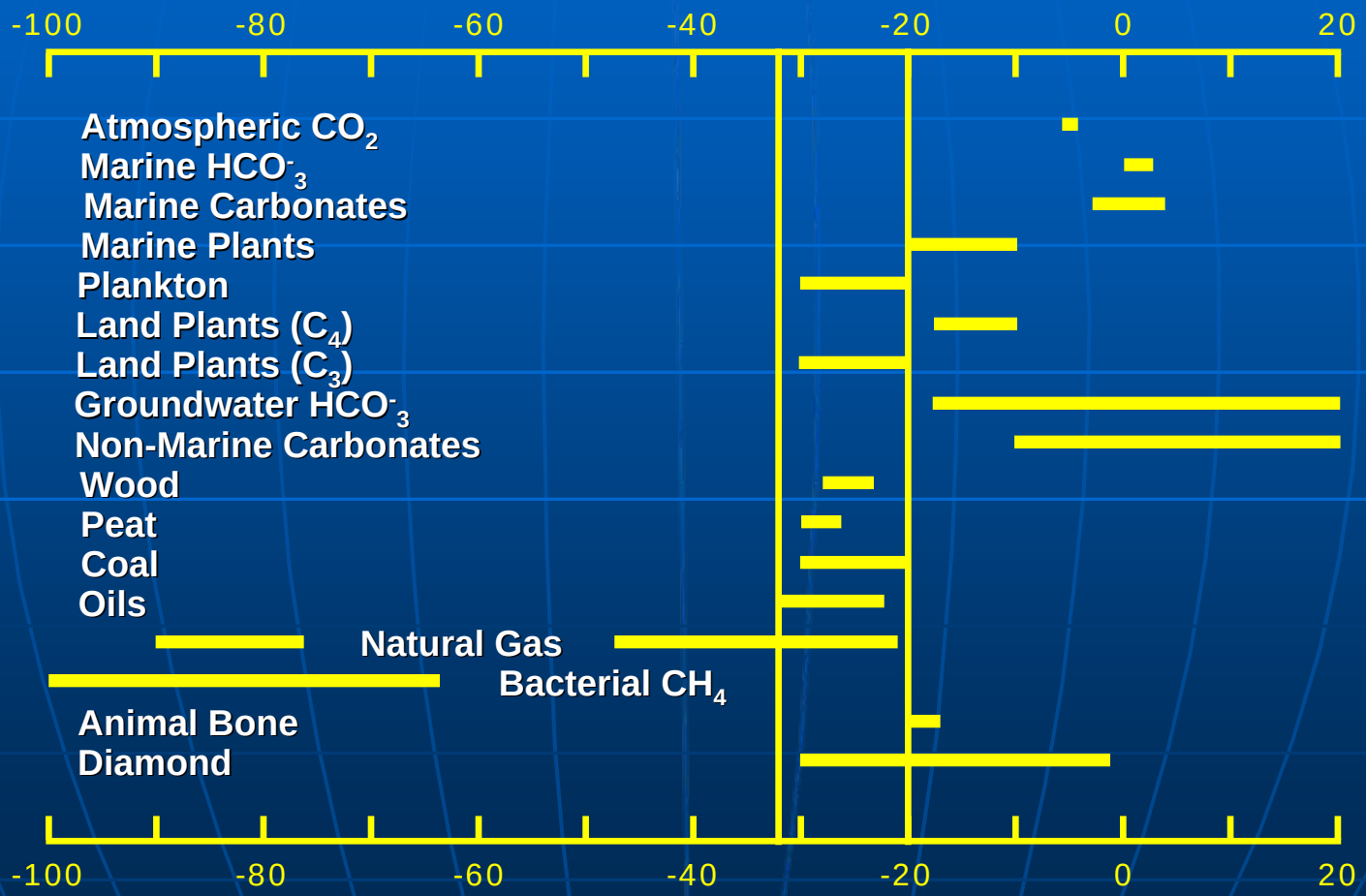
$$\delta^{13}C_{sample} = [(^{13}C/^{12}C_{sample})/(^{13}C/^{12}C_{standard})\text{-}1]x1000 \text{ PDB}$$

Clark and Fritz, 1997

δ Values: Positive or Negative

- International standard for carbon is Pee Dee Belemnite (PDB, a carbonate formation)
- PDB's absolute ratio of $^{13}C/^{12}C$ is 0.0112372.
- PDB standard is defined as 0‰.
- Samples with ratios of $^{13}C/^{12}C$ > 0.0112372 have **positive** δ values, and those with ratios < 0.0112372 have **negative** δ values.

Natural Variations in the Carbon Isotopic Compositions



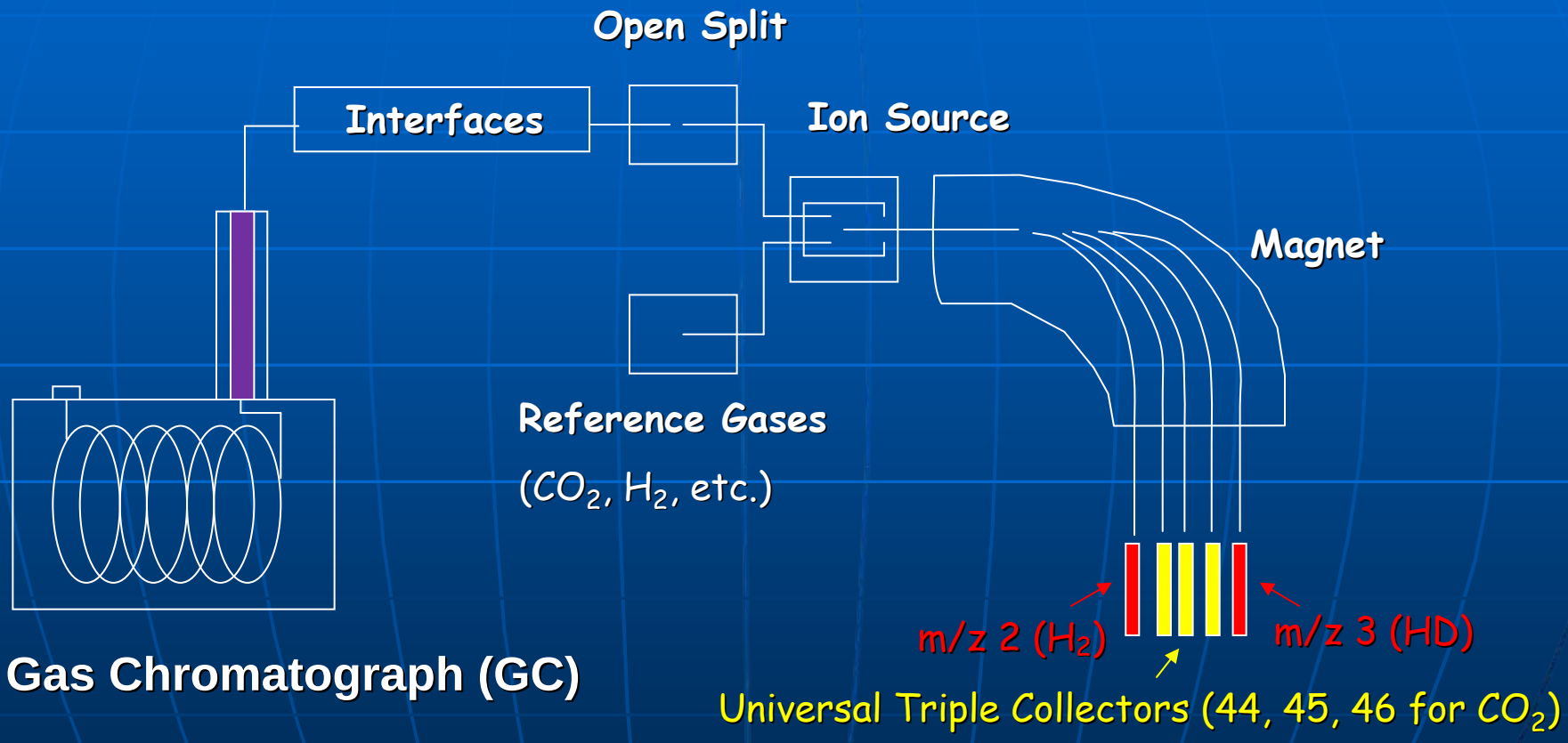
From multiple publications

Isotope Fractionation

- Definition: Any process that changes the relative abundances of stable isotopes of an element.
- Isotope fractionation can occur during chemical, physical and biological processes.
- Elements with low atomic numbers always incur greater isotope fractionation due to greater mass difference between isotopes.
- Small molecules always incur greater isotope fractionation.

Clark and Fritz, 1997

Compound-Specific Isotope Analysis



Gas Chromatograph (GC)

Isotope Ratio Mass Spectrometer (IRMS)

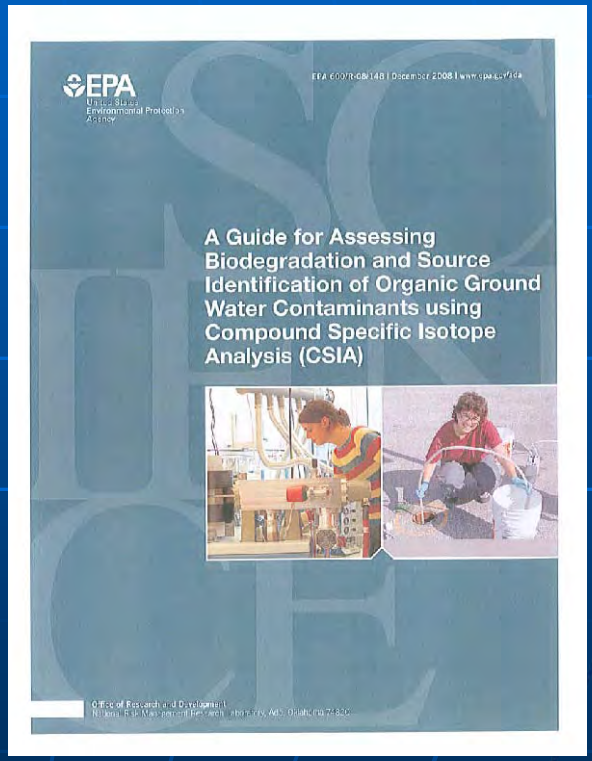
Freeman et al., 1990

A Stable Isotope Laboratory

Wang et al., 2004

US EPA Guidance Document for CSIA Emphasizes Regulatory

- A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA), US EPA, December 2008



To download this guide, go to http://www.epa.gov/ada/pubs/reports/600r08148/600r08148.pdf

Hunkeler et al., 2008

Part II. Collection, Preservation and Storage of Samples for CSIA

- Sample Types: soil/water (s/w)
- Container (s): 4 oz wide mouth glass jar w/ Teflon-lined closure
- Container (w): 40mL HCl pre-preserved glass VOA vials
- Pre-cleaned sample containers are provided free of charge

Collect Samples for CSIA

- Collect site information such as history, plume shape/size, concentrations, ground water flow direction, aquifers, etc.
- Based on the present composition data, if it seems to be a homogenous plume, collect 5-8 samples, including 4-6 samples from the edges of all directions, and 1-2 samples from the center.
- Otherwise add 3-4 samples to assess any plumes of different sources

Murphy and Morrison, 2002

Collection, Storage and Shipping of Chlorinated Solvent Samples

- Soil Collection: Fill up 1-2 jars for each sample, avoid loss of volatiles
- Water Collection: Fill up 6-8 VOA vials for each sample, pH<2 to preserve
- Storage and Shipping: keep <4ºC in the dark and ship overnight on ice to lab

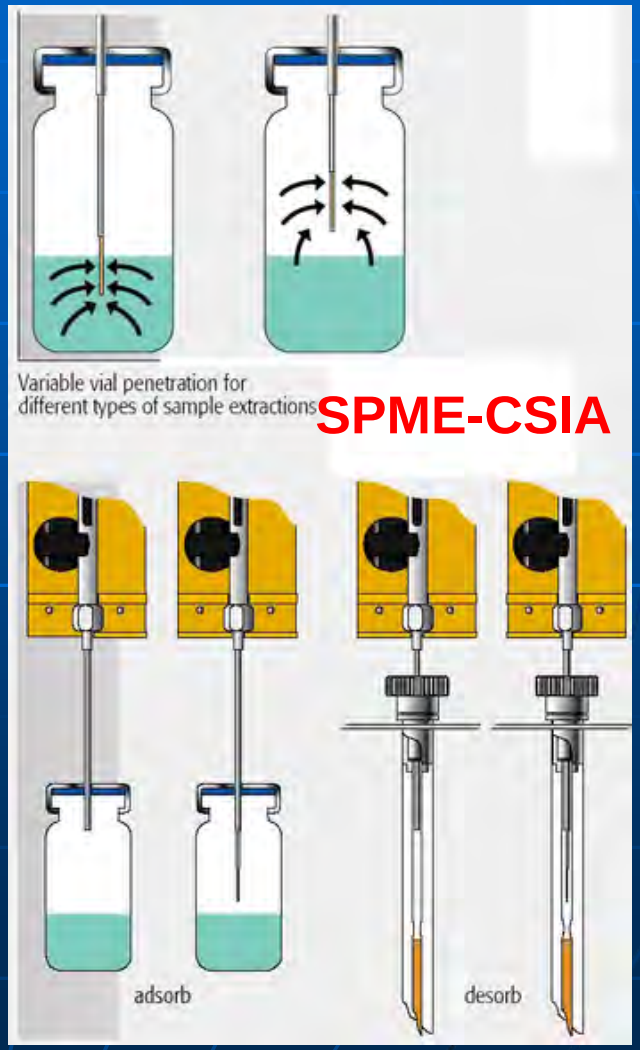
Hunkeler et al., 2008

Holding Time, Turn-Around-Time and Analytical Cost for CSIA

- **Holding Time of Samples:**
  - 14 days for Composition Test
  - 30 days for CSIA
- **Turn-Around-Time:**
  - 30 days, or rush upon request
- **Costs Per Sample:**
  - $300/CSIA
  - (Optional) Composition Test
  - (Optional) Interpreting & Forensics

CSIA of Chlorinated Solvents

- Volatiles adsorbed from sample by Solid Phase Micro-Extraction (SPME)
- Volatiles desorbed in GC inlet at high temperature for isotope analysis (CSIA)
- CSIA for $\delta^{13}C$ (‰, PDB); CSIA for δD (‰, SMOW); CSIA for $\delta^{37}Cl$ (‰, SMOC)



Hunkeler et al., 2008

CSIA for Chlorine Isotope

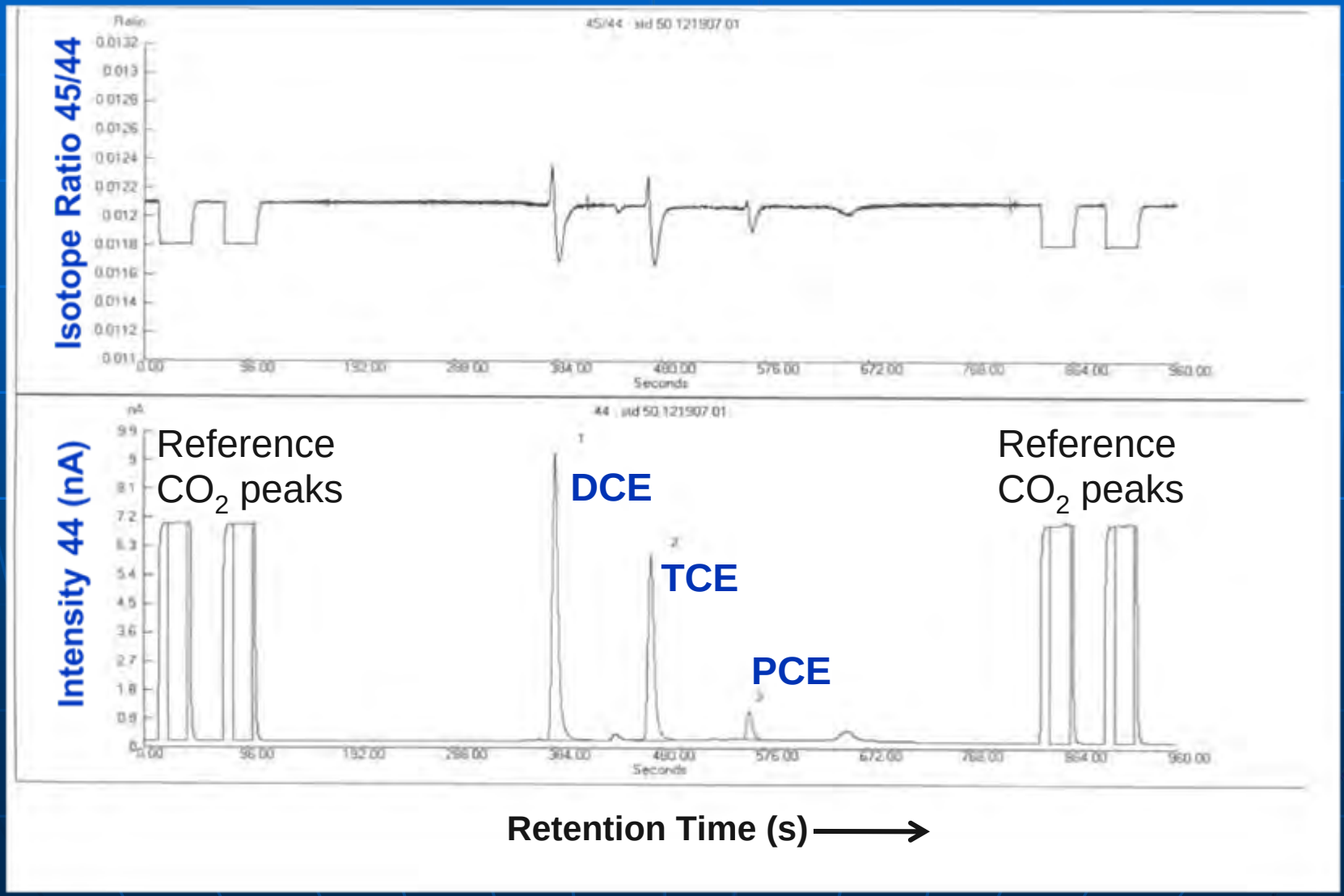
- Traditional methods involve labor-intensive offline pretreatments and comprehensive dual inlet-IRMS operations for ^{37}Cl measurement
- Recently $\delta^{37}Cl$ for chlorinated solvents can be determined precisely by two online methods:

Methods	Requirement	Precision	Cost	TAT
GC-IRMS UW, Canada	9-Collector Configuration	+/-0.3‰	$550/each compound	Not Promised Academic lab
GC-MS ZymaX, USA	Standard Configuration	+/-0.5‰	$300/each sample	30 days Promised TAT

- $\delta^{37}Cl$ by GC-MS analyzing peak intensities of molecular and fragment ions of chlorinated compound: a great "Fast-Screening Tool"

Sakaguchi-Soder et al. 2007

CSIA Chromatogram for $\delta^{13}C$

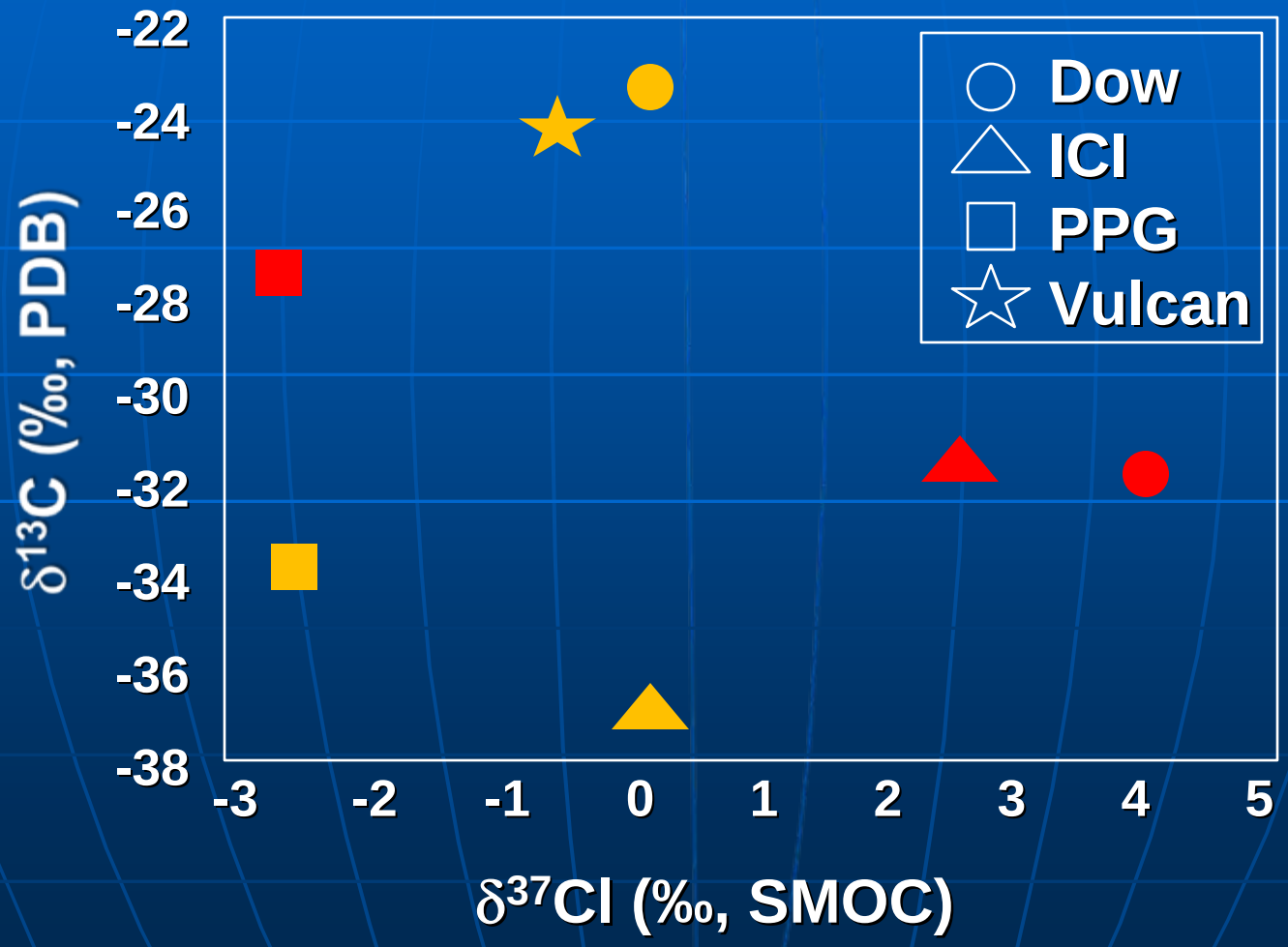


Part III. CSIA Data Distinguish Different Chlorinated Solvent Sources

- Is PCE or TCE in one plume from one or more sources?
  - $\delta^{13}C$ and $\delta^{37}Cl$ recommended
- Is PCE or TCE in separate plumes from the same source or different sources?
  - $\delta^{13}C$ and $\delta^{37}Cl$ recommended
- Is TCE in a PCE plume from degradation of PCE or from a separate TCE source?
  - $\delta^{13}C$, $\delta^{37}Cl$, and δD recommended

Morrison 1999

$\delta^{13}C$ and $\delta^{37}Cl$ values for PCE and TCE from Different Manufacturers



van Warmerdam et al. 1995

Allocation Two Sources by TCE $\delta^{13}C$ and $\delta^{37}Cl$

Source A:

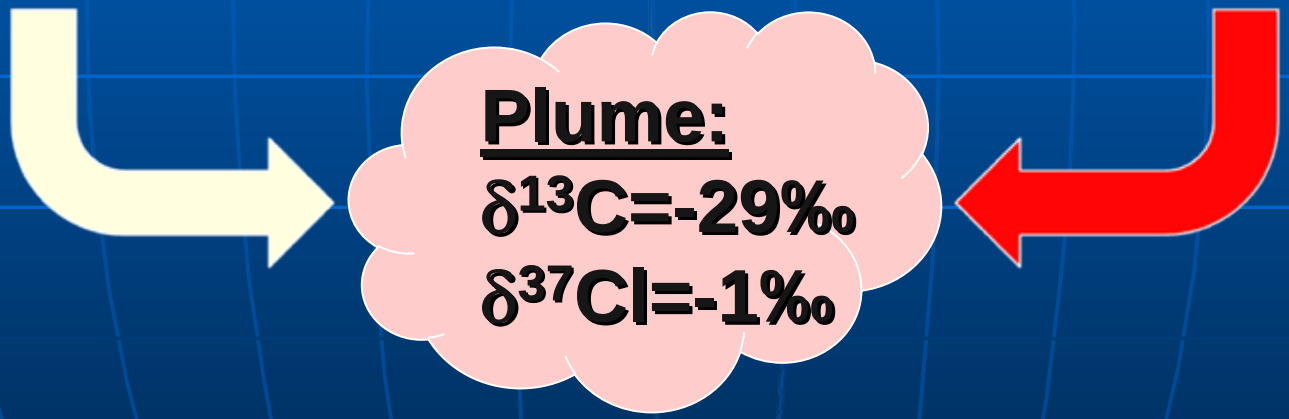
$\delta^{13}C = -30‰$

$\delta^{37}Cl = -2‰$

Source B:

$\delta^{13}C = -25‰$

$\delta^{37}Cl = +3‰$



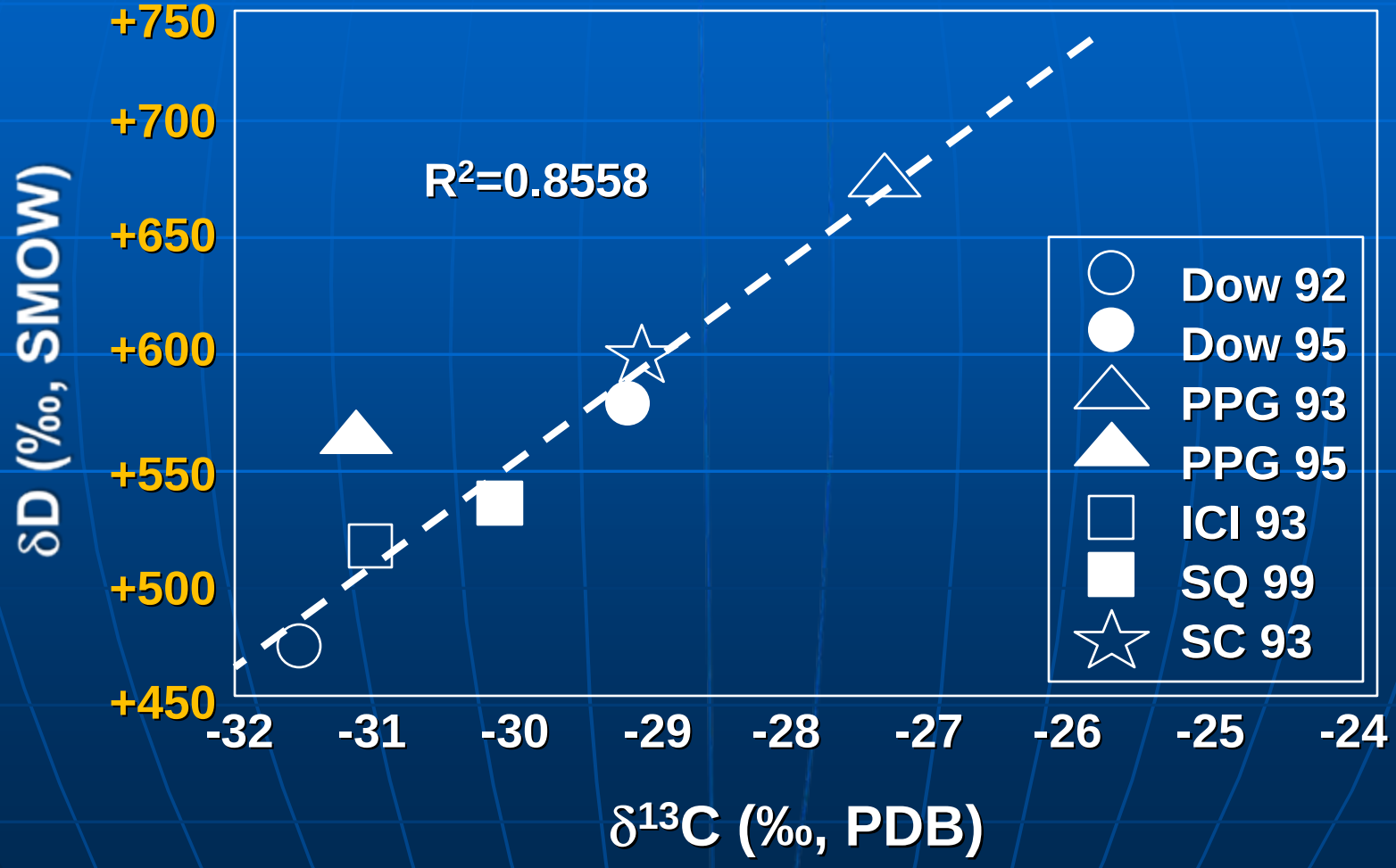
Plume = 80% Source A, 20% Source B

by $\delta^{13}C$: $-29*1 = -30*x + (-25)*(1-x)$ $x=0.8$

by $\delta^{37}Cl$: $-1*1 = -2*x + 3*(1-x)$ $x=0.8$

Sueker, 2003

δD and $\delta^{13}C$ values for TCE from Different Manufacturers and Different Years



Poulson S. R. and Drever J. I., 1999; Shouakar-Stash et al. 2003

Manufactured TCE

- The range of δD measured for manufactured TCE: **+467 to +682‰**
- **Extremely Heavy** H isotope composition is a function of isotope fractionation associated with synthesis reactions used to produce TCE:

$$C_2H_2 + 2Cl_2 \rightarrow CHCl_2CHCl_2$$
$$CHCl_2CHCl_2 \rightarrow C_2HCl_3 + HCl$$

- Here the HCl removed is **extremely light**, hence the produced TCE is **extremely heavy**

Shouakar-Stash et al. 2003

TCE Degraded from PCE

- The range of δD measured for TCE degraded from PCE by iron dechlorination: **-352 to -320‰**
- TCE gains its **H** atom from surrounding water (δD=-206‰) during dechlorination of PCE:

$$C_2Cl_4 \xrightarrow{-Cl + H} C_2HCl_3$$

- **Extremely light H** isotope composition of TCE is a function of isotope fractionation during the reaction that involves freeing more of the **light** H isotope from the surrounding water

Shouakar-Stash et al. 2003

Manufactured TCE or TCE degraded from PCE?

- Manufactured TCEs have completely different δD signatures from TCEs produced through PCE dechlorination.
- Strong implications for distinguishing dechlorination products (PCE to TCE) from manufactured TCE by using a combination of $\delta^{13}C$, $\delta^{37}Cl$ and δD.

Part IV. CSIA Data Can Guide Remediation Decision and Help Achieve Site Closure

1. CSIA can provide valuable insights on degradation of chlorinated solvents:

- Degradation Mechanisms
- Degradation vs Dilution
- Extent and Rate of Degradation

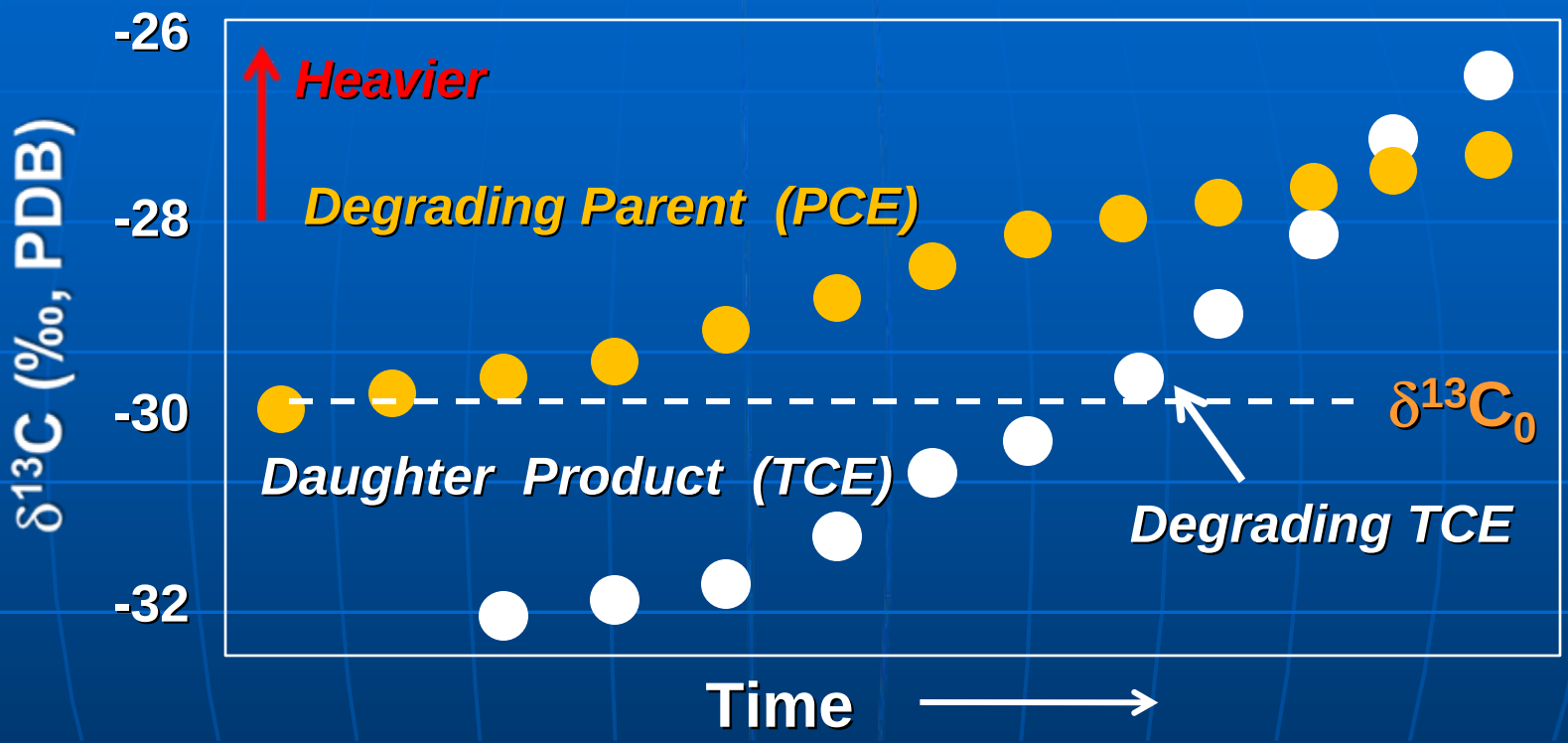
2. CSIA Monitoring Can Help Achieve Remediation Site Closure by:

- Identifying cost reduction opportunities
- Assessing effectiveness of existing remediation strategies
- Providing new kind of data to avoid unnecessary or redundant monitoring and remediation costs

Degradation vs Dilution

- Both degradation and dilution could lead to decreased concentrations…
- Concentration measures the number of molecules that make up a compound.
- CSIA measures the type of those molecules and provide new information independent of concentration.

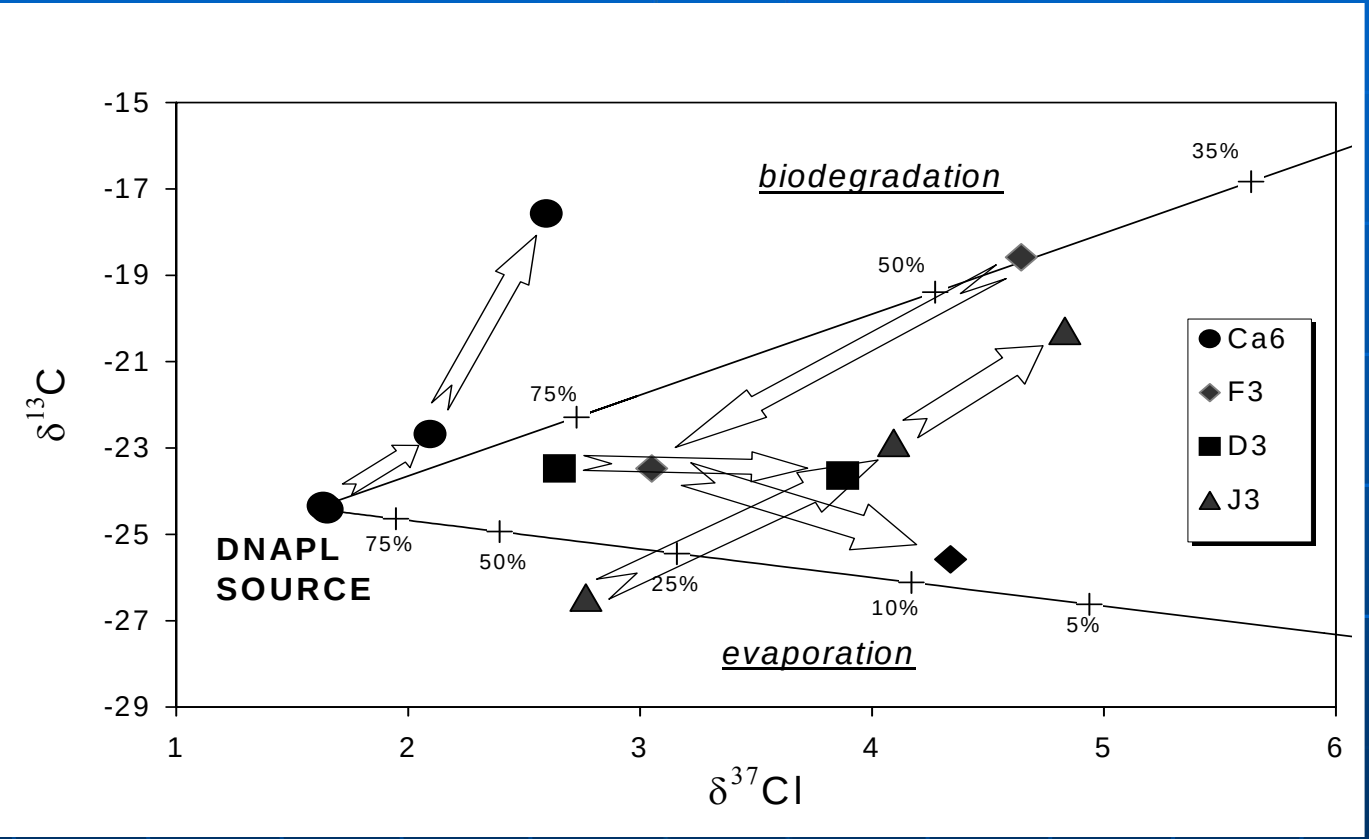
CSIA Forensics Assessing Degradation



- PCE's degradation confirmed by its ratios getting heavier
- TCE's degradation is not confirmed by its ratios getting heavier as its parent PCE's ratios are getting heavier too
- TCE's degradation is not confirmed until its ratios become heavier than its parent PCE's original ratio $\delta^{13}C_0$

Pirkle, 2006

CSIA Forensics during in situ Electrical Resistance Heating (ERH) Remediation



Carbon vs. chlorine isotope ratios of TCE extracted from groundwater from 4 wells at a Chicago site during ERH remedial activities in a year. Evaporation and biodegradation theoretical trends are shown, with residual TCE% indicated. Arrows indicate time sequence.

Smith, 2009

Warning! Stable isotope data may cause severe stomach upset if taken alone. Take it with a healthy dose of other hydrological, geological, and geochemical information, you will find stable isotope data very beneficial.

-Marvin O. Fretwell, 1983

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Thank you!
Any questions?