

Hydrogen Isotope Exchange Between Trichloroethene and Water:

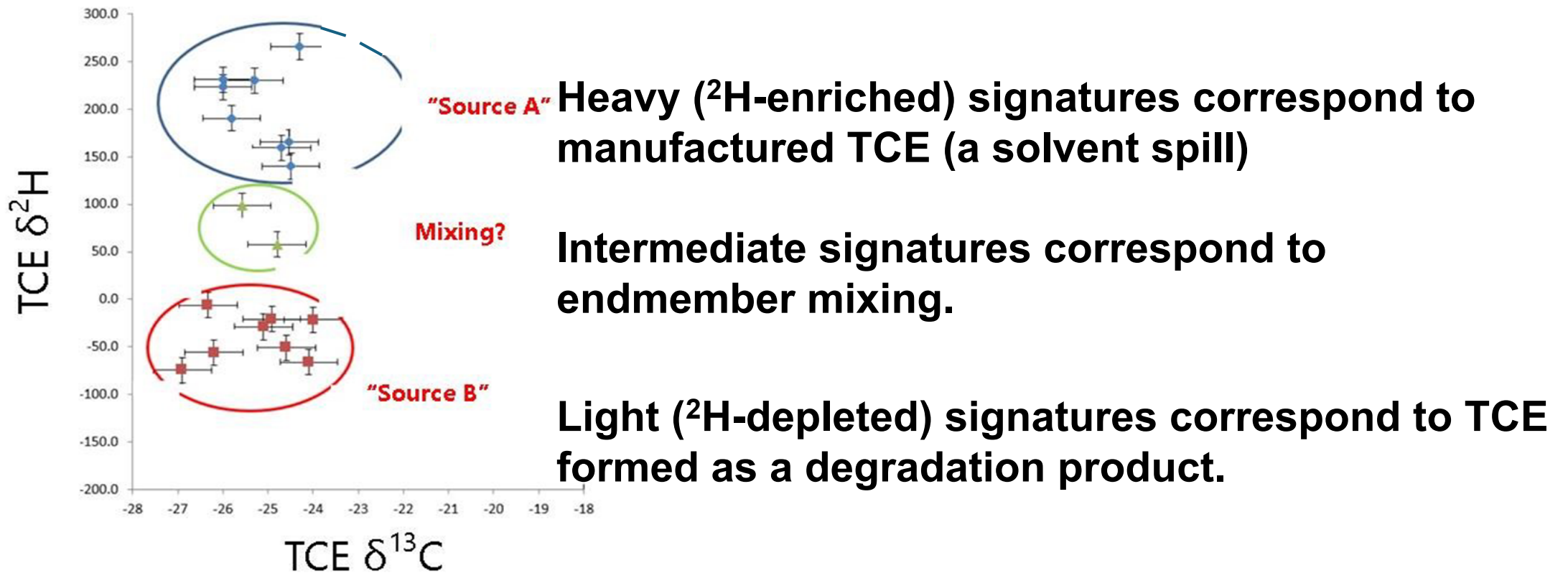
A Disadvantage for the Use of Hydrogen CSIA for TCE Source Apportionment and an Opportunity for Developing Contaminant Dating Applications.

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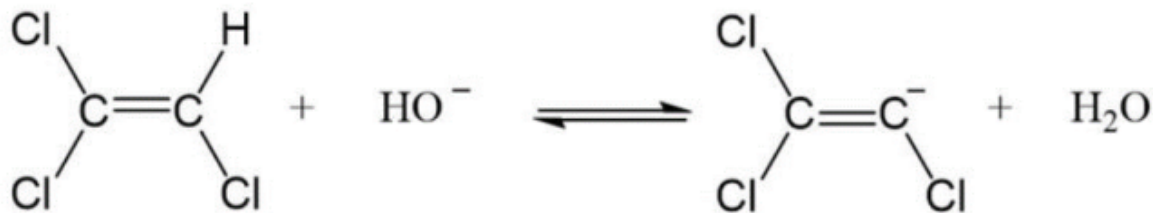
³ Auburn University, Auburn, AL

Hydrogen CSIA of TCE is Most Commonly Applied as a Line of Evidence for TCE Source Apportionment



Is Carbon-Bound Hydrogen Subject to Exchange in Water?

- ❖ Certain hydrogen functional groups are readily exchangeable with water (-OH groups). Exchangeable hydrogen does not preserve contaminant source signatures.
- ❖ Carbon-bound hydrogen is generally perceived as inert under normal environmental conditions.
- ❖ For certain halocarbons, H exchange is facilitated by the presence of strong electron-withdrawing groups (Cl, Br) adjacent to the C-H. Examples of such reactions in **strongly alkaline solutions** have been reported previously in chemistry literature, including for TCE.



- ❖ The reaction is a simple acid-base proton exchange catalyzed by HO^- , with TCE acting as a Brønsted acid.

Experimental Verification of the Reaction Rates at Lower pH



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Article

Hydrogen Isotope Exchange between Trichloroethene and Water under Mild Environmental Conditions—Implications for the Use of Hydrogen CSIA in Contaminated Site Assessment

Tomasz Kuder* and Ann Sullivan Ojeda



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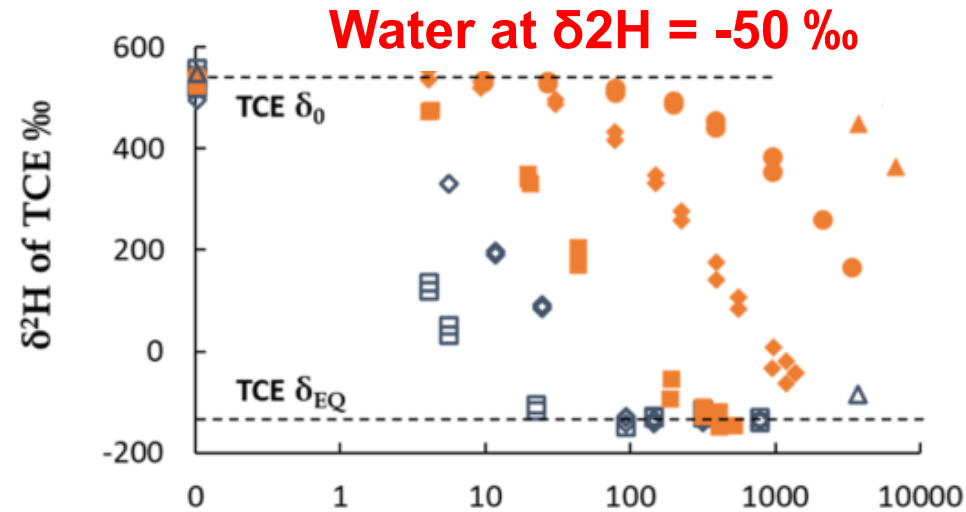


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- ❖ TCE was incubated in buffered solutions at above-neutral pH (7.2-8.5), to determine the effect of hydroxide concentration on the reaction rate.
- ❖ The experiments were replicates at different temperatures (20-80°C) to determine the temperature effect on the reaction rate.
- ❖ $^2\text{H}/^1\text{H}$ determined by CSIA provided a direct measure for the fraction of hydrogen exchange.

Partial funding provided by SERDP project ER-2623

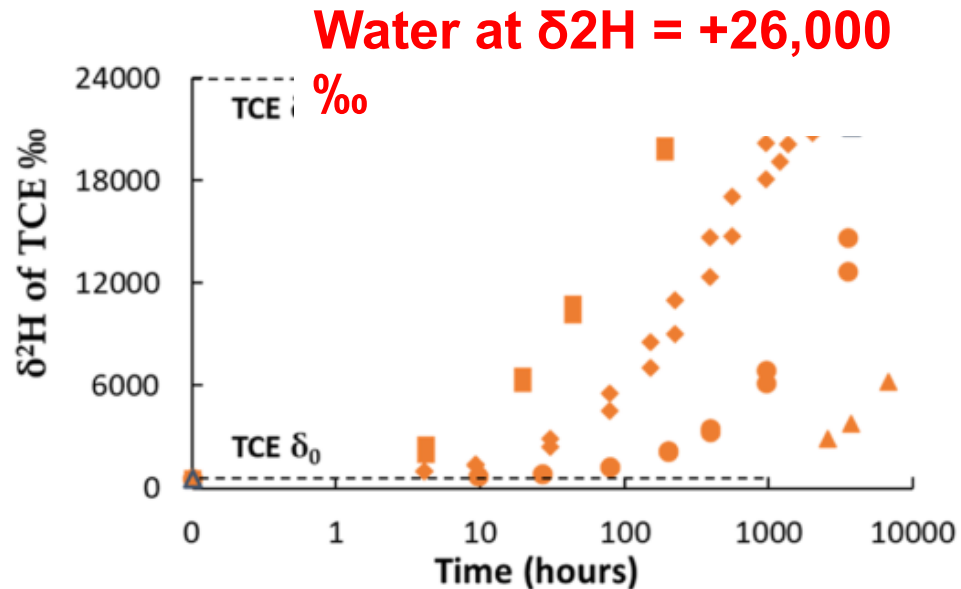
Evolution of $^2\text{H}/^1\text{H}$ of TCE over Time



Initial TCE at $\delta^2\text{H} = +550 \text{ ‰}$



Equilibrated TCE at $\delta^2\text{H} = -140 \text{ ‰}$

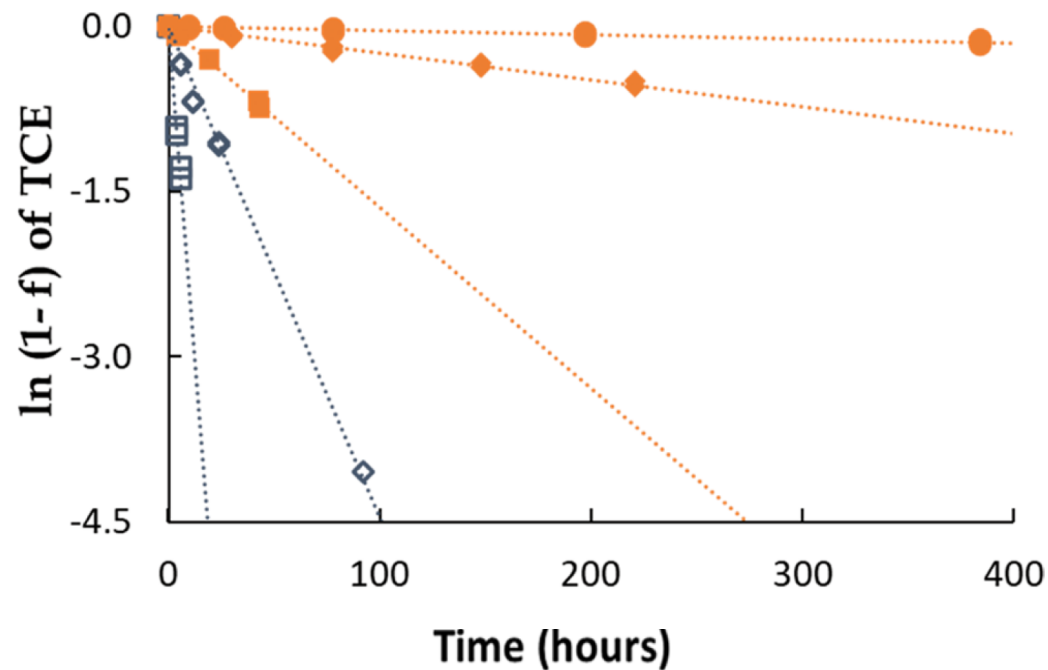


Equilibrated TCE at $\delta^2\text{H} = +24,000 \text{ ‰}$



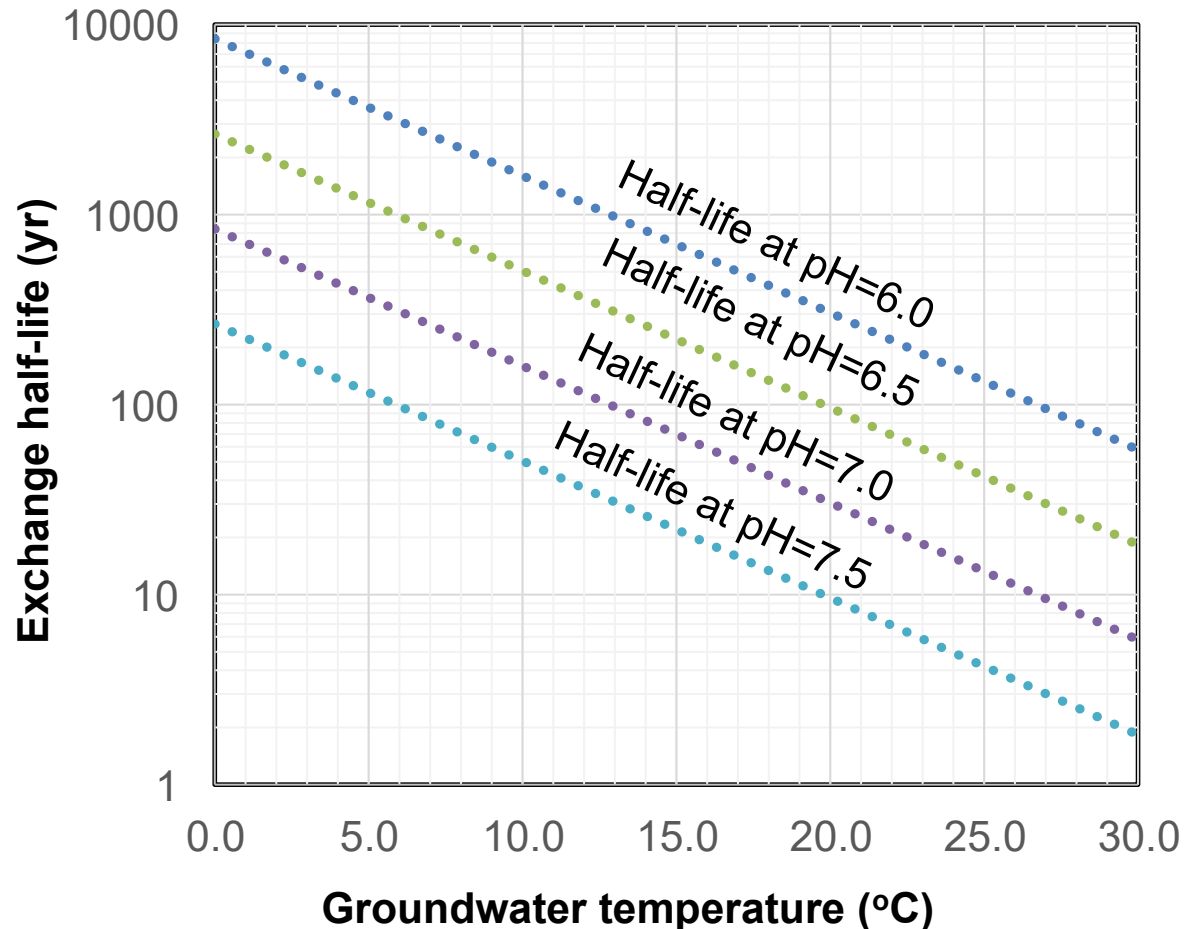
Initial TCE at $\delta^2\text{H} = +550 \text{ ‰}$

TCE-Water Exchange Kinetics



- ❖ At given pH and temperature, the reaction kinetics is first-order.
- ❖ Rates increased proportionally to concentration of hydroxide. One pH unit corresponds to a 10-fold rate effect.
- ❖ The effect of temperature followed the standard Arrhenius model. At given pH, the rates were 10-fold faster with water temp. increasing by 14°C.
- ❖ Robust kinetic parameters over the experimental range of pH and T justifies extrapolation of the results to a wider pH and T range.

Exchange Half-Life is a Function of pH and Temperature

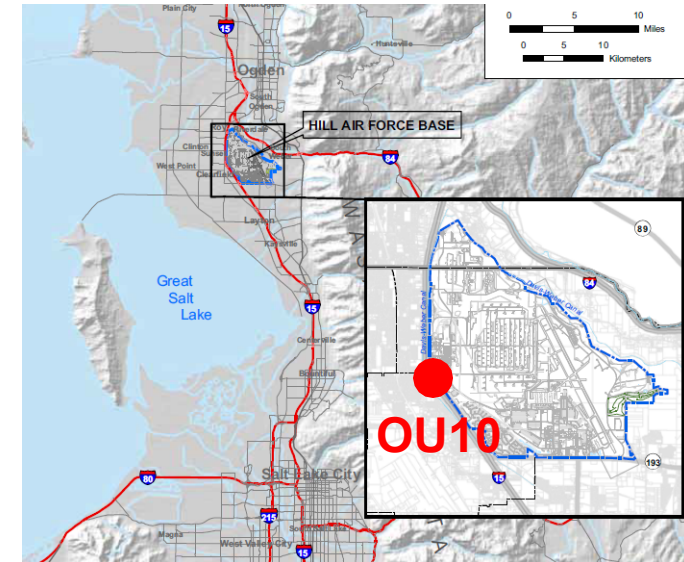
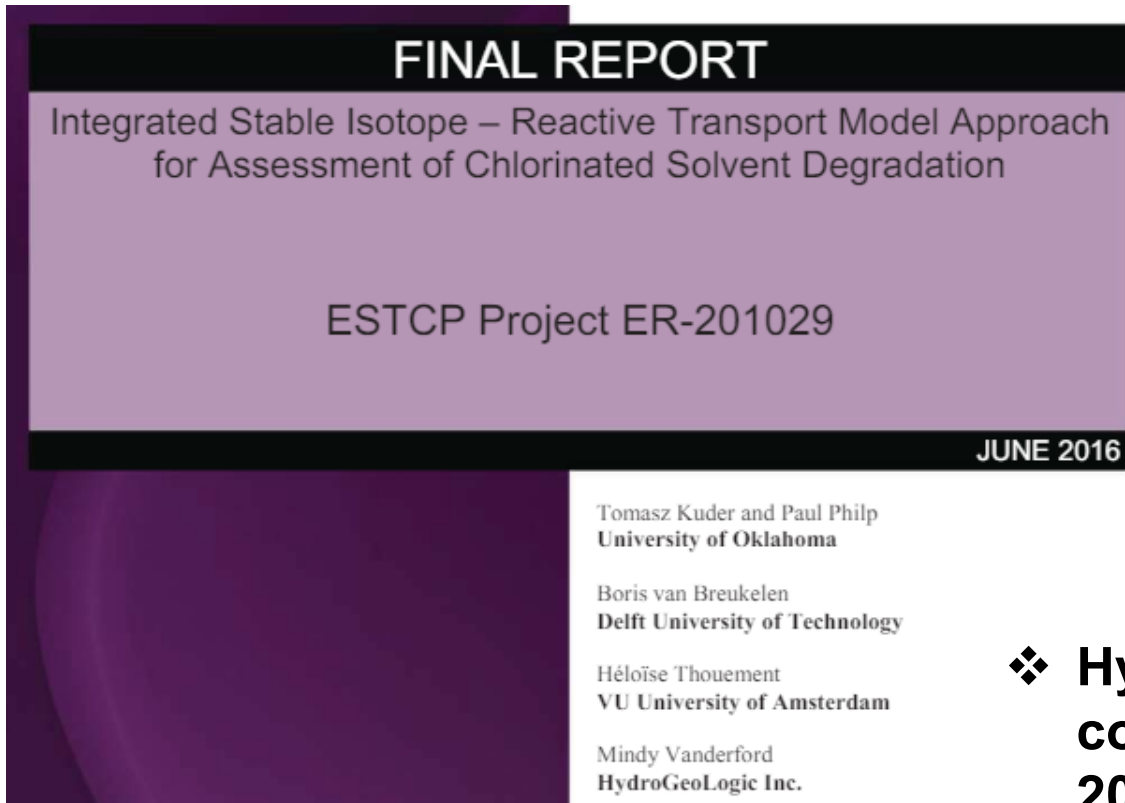


- ❖ Half-life ($t_{1/2}$) defines the potential impact of the hydrogen exchange on the original TCE isotope signature.
- ❖ No measurable effect on $\delta^2\text{H}$ with $t_{1/2}$ of ~3000 yrs.
- ❖ Change of $\delta^2\text{H}$ by several tens of permil with $t_{1/2}$ of ~500 yrs.
- ❖ Change of $\delta^2\text{H}$ by several hundreds of permil with $t_{1/2}$ of ~100 yrs.

TCE-Water Exchange: Implications to TCE Site Assessment

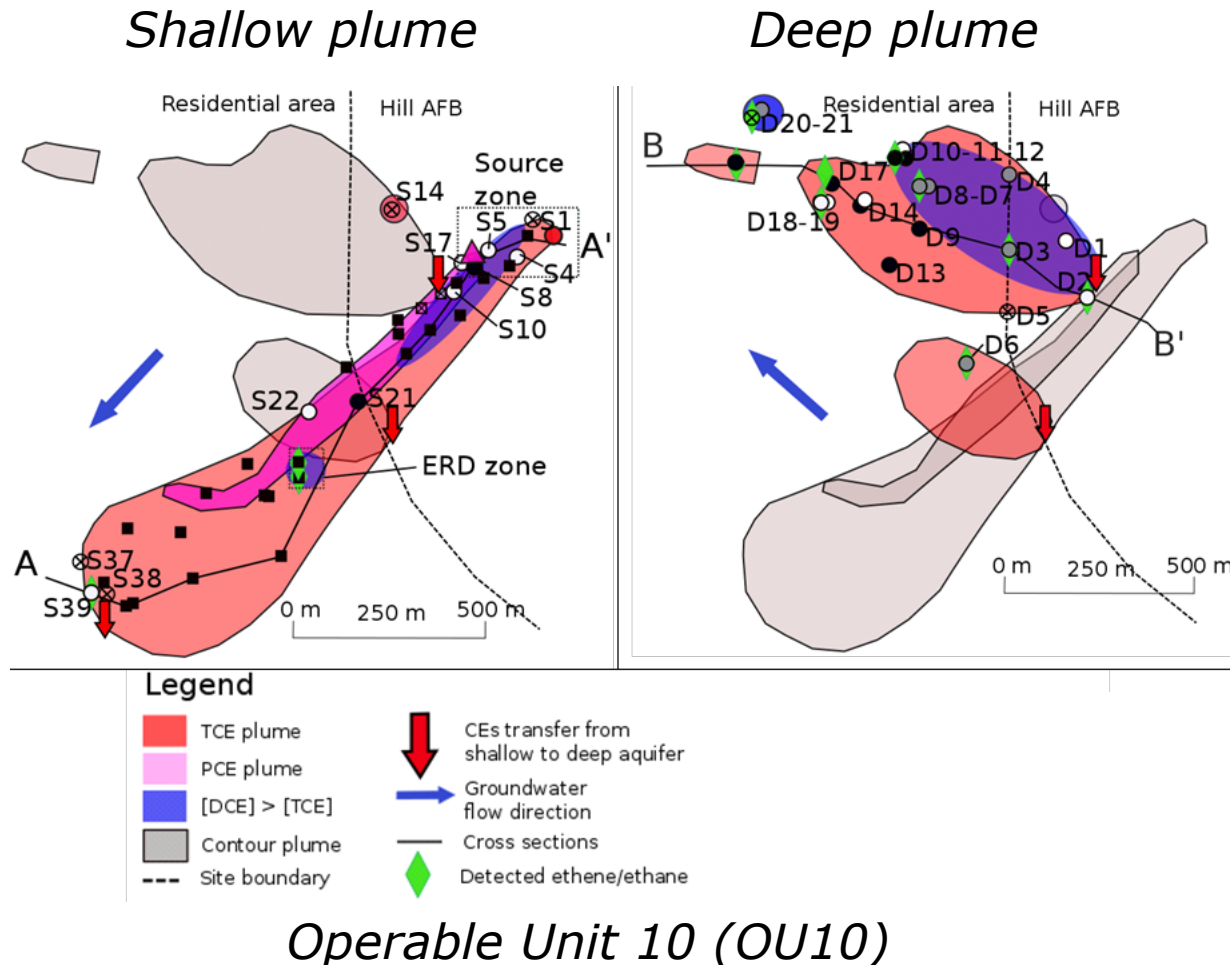
- ❖ **Changes of $\delta^2\text{H}$ driven the hydrogen exchange with water complicate the use of H CSIA data for TCE source apportionment. Water temperature and pH data should be considered carefully to decide if the conditions are appropriate for the type of application and to estimate the added uncertainty.**
- ❖ **On the other hand, the $t_{1/2}$ calculated for a specific location can be used for TCE dating purposes. Isotope composition of TCE combined with $t_{1/2}$ can help to estimate the length of TCE residence in aqueous phase.**

Case Study: OU10 Hill AFB, UT



- ❖ Hydrogen CSIA was part of the scope of ER-201029 completed in 2016 (samples were analyzed in 2011 and 2014)
- ❖ Tabulated results are available in the Final Report. The present discussion used the same data after correction to address the revision of the TCE reference material

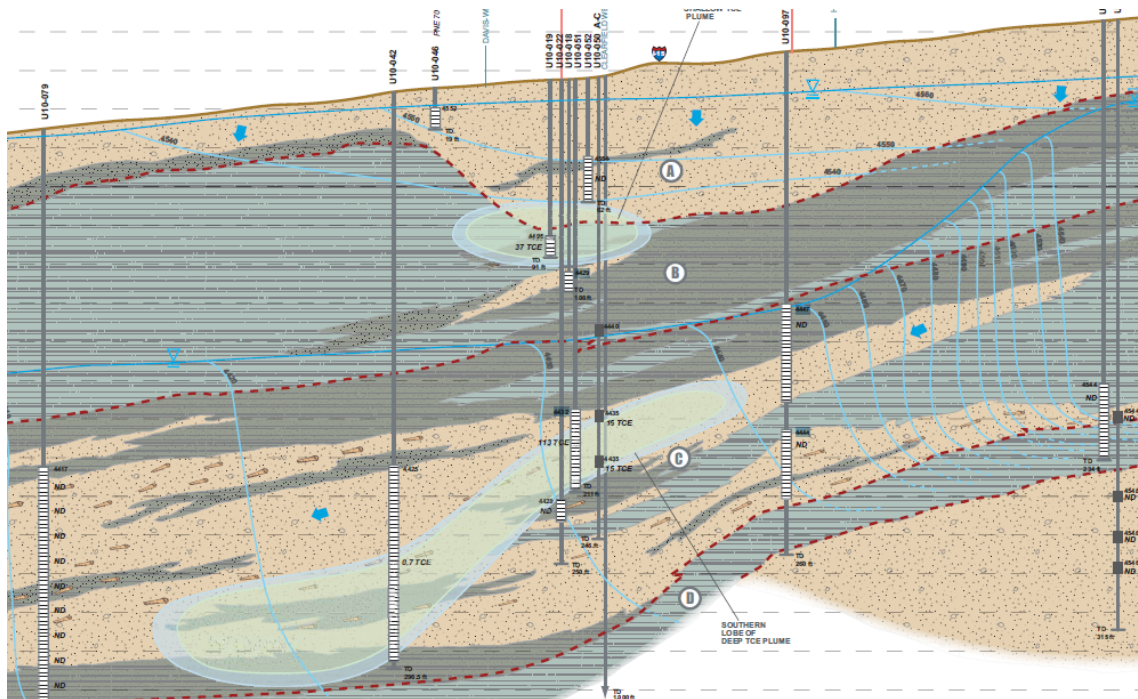
Case Study: OU10 Hill AFB, UT



- ❖ The primary release into the Shallow Unit occurred at an Oil-Water Separator (since 1940s, site decommissioned in 2003). The same release eventually impacted the Deep Unit.
- ❖ TCE was the main contaminant at the site. PCE was present at smaller scale only in the Shallow Plume.

Case Study: OU10 Hill AFB, UT

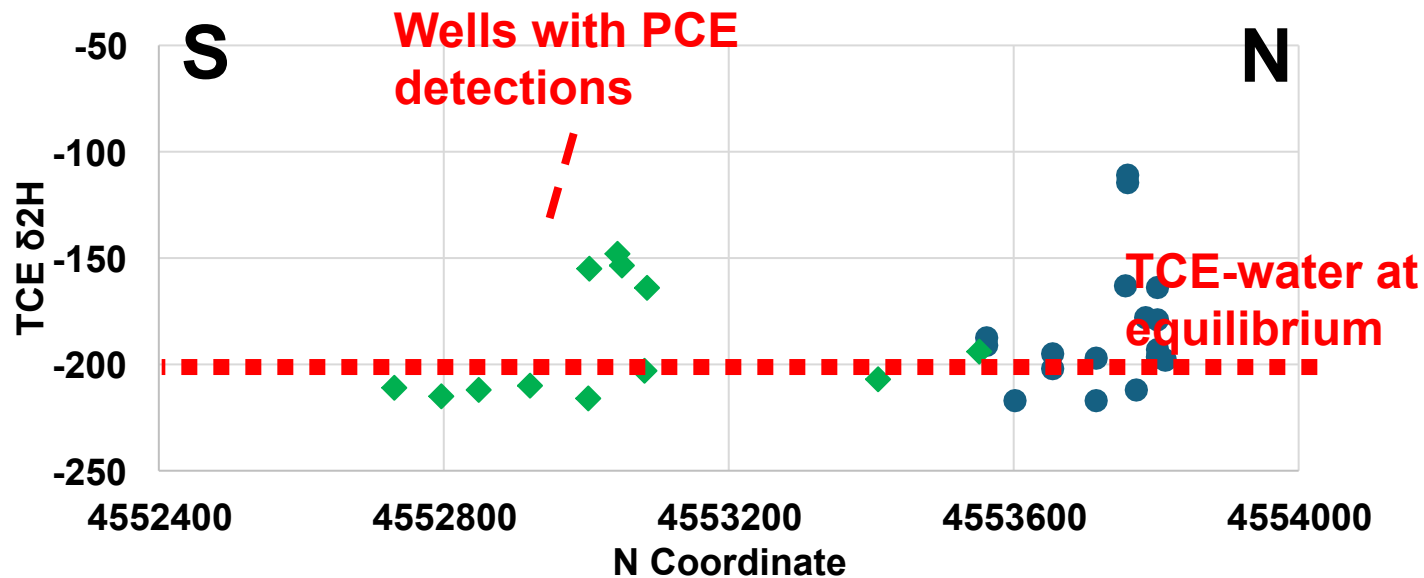
The site has complex lithology, with sand interbedded with silt and clay. The confining layer between the Upper and Lower units is partially eroded which permitted TCE impact on the Lower unit.



LEGEND

- SM/SW/SP (SILTY SAND AND SAND)
- CL/SM/ML (INTERBEDDED SAND, SILT AND CLAY)
- ML/CL (SILTY CLAY AND CLAYEY SILT)
- WOOD / PLANT DETRITUS / DECAYING PLANT MATTER
- POTENTIOMETRIC SURFACE
- GROUNDWATER FLOW DIRECTION

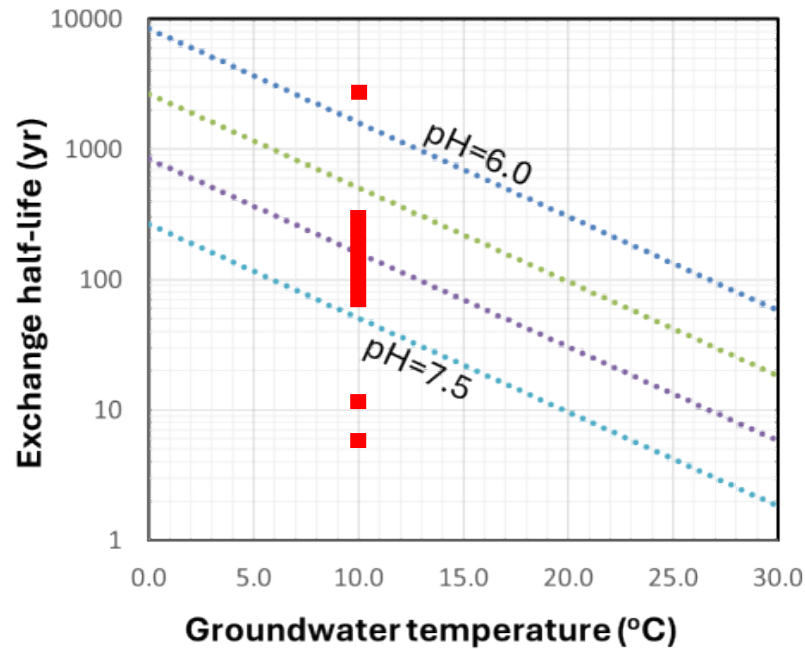
Case Study: OU10 Hill AFB, UT



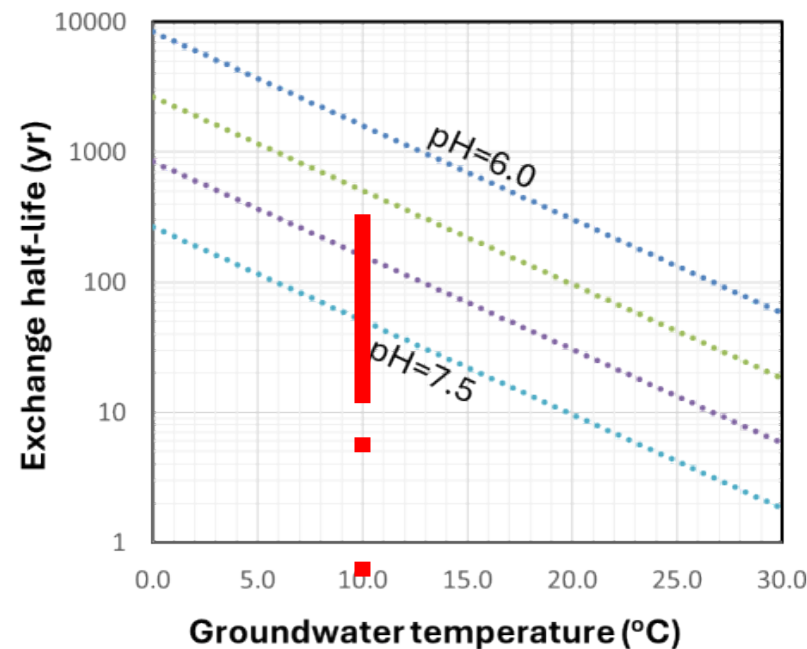
- ◆ Shallow Plume
- Deep Plume

- ❖ All results fall in the “depleted” range, well below the $\delta^2\text{H}$ of modern TCE from N American producers (+400 to +700) and below the range of any TCE products reported to date (-85 to +170).
- ❖ In most wells, TCE $\delta^2\text{H}$ is reasonably close to the TCE-water equilibrium.
- ❖ A cluster of four wells in the Shallow Plume shows elevated $\delta^2\text{H}$ (all from the area with commingled PCE).
- ❖ Several wells in the Deep Plume show elevated $\delta^2\text{H}$ with no known relationship to PCE.

Case Study: OU10 Hill AFB, UT



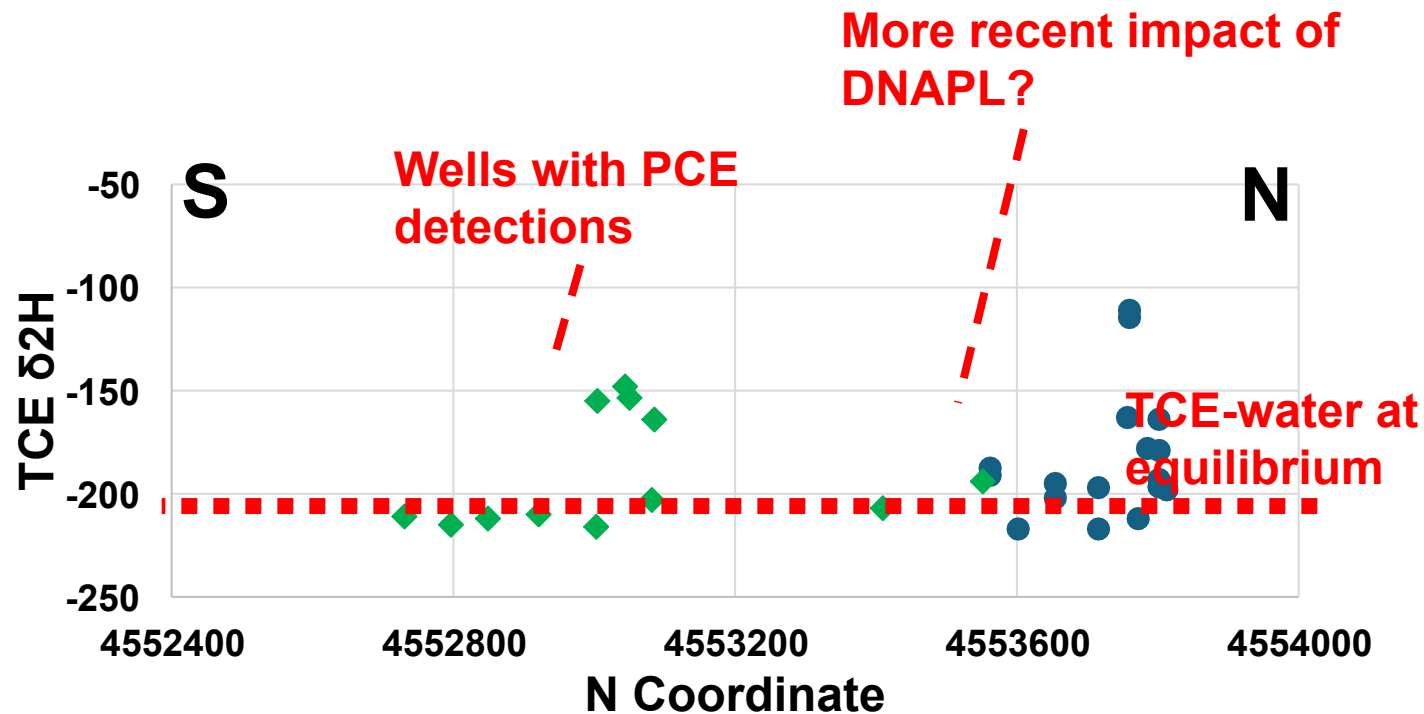
Shallow Plume: $t_{1/2}$ 60-300 years



Shallow Plume: $t_{1/2}$ 15-300 years

- ❖ Predominant $t_{1/2}$ was estimated at 30-110 years using water pH and average annual temperature.
- ❖ The calculated $t_{1/2}$ appears too high to explain the apparent TCE-water equilibrium.

Case Study: OU10 Hill AFB, UT



- ◆ Shallow Plume
- Deep Plume

- ❖ The high fraction of H exchange above that predicted by well water pH suggests that the plumes are fed by flux from low-permeability sediment (with pH above that in sandy layers due to dampened impact of surface recharge).
- ❖ The less-depleted signatures can be rationalized by relatively more recent input of less-depleted degradation product TCE within the footprint of the PCE plume, or by a separate and more recent primary source of TCE.

Case Study: Oak Grove, MO

**FINAL
DATA EVALUATION REPORT
OAK GROVE VILLAGE WELL SITE
OPERABLE UNIT 1
FRANKLIN COUNTY, MISSOURI**

Prepared for:



U.S. Environmental Protection Agency Region 7
11201 Renner Boulevard
Lenexa, Kansas 66219

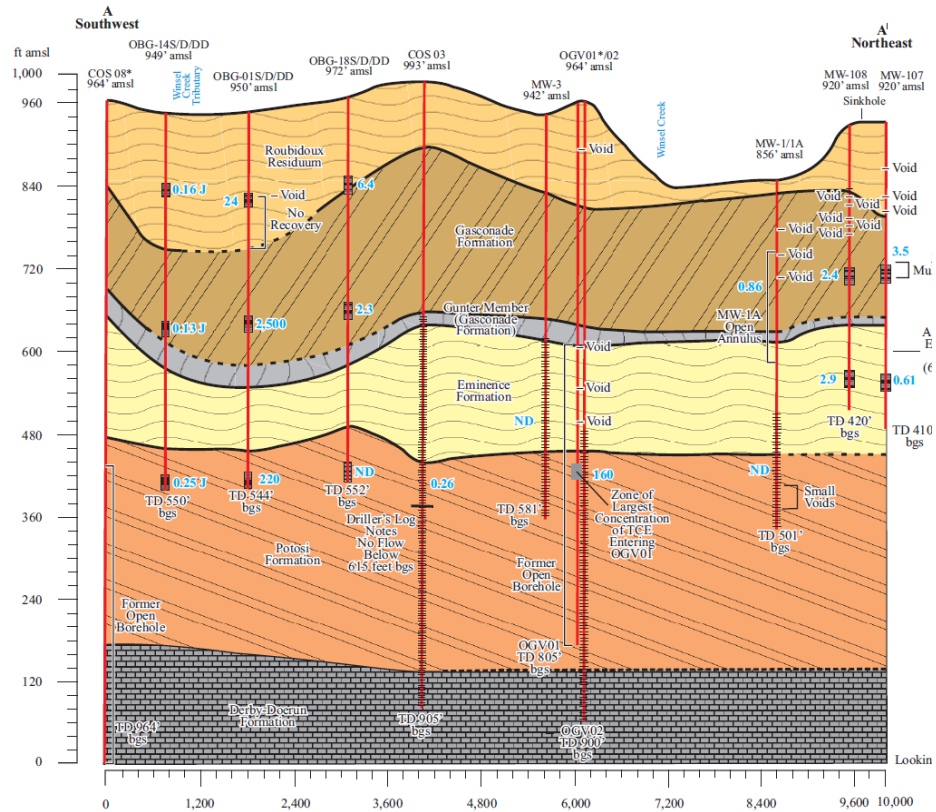
Architect and Engineering Services Contract EP-S7-05-05
Task Order: 0049

January 2020

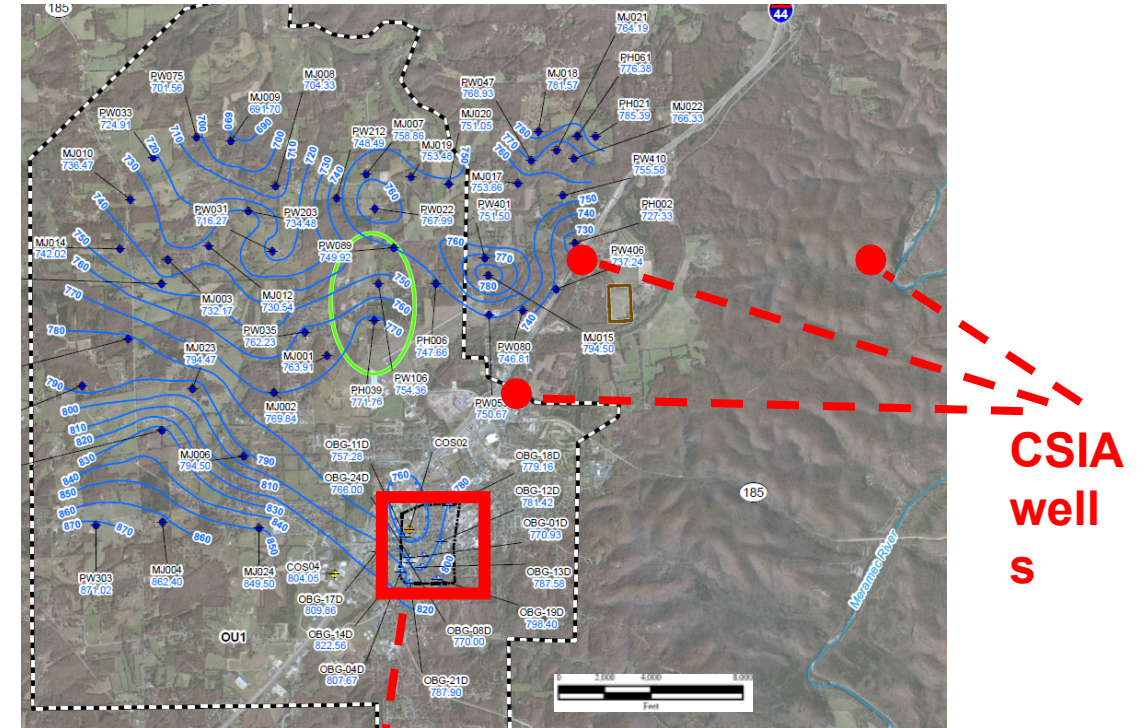


The following discussion uses figures adopted from the US EPA Report prepared by HGL (the CSIA section was authored by John Schumacher, U.S. Geological Survey). CSIA data for that project were produced by the present author, in 2014.

Case Study: Oak Grove, MO

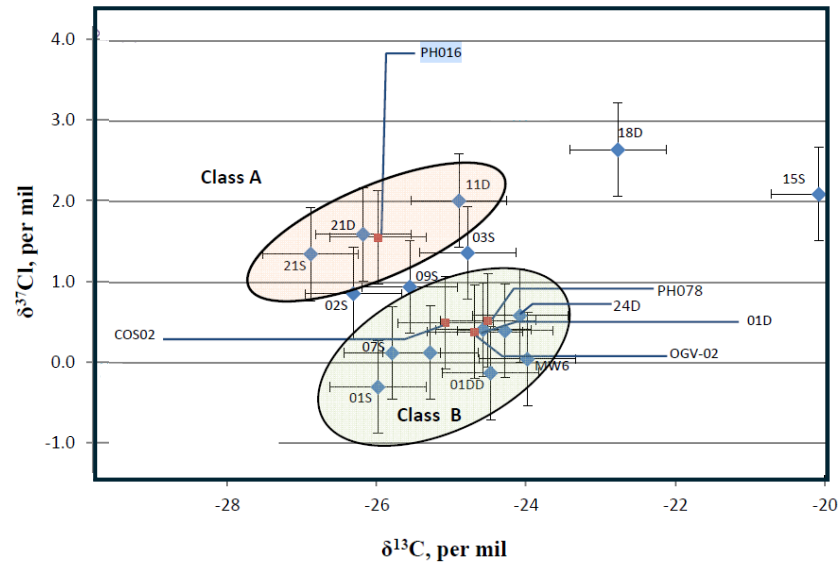


The site is located within the Ozark aquifer: deeper sections are fractured carbonate with karst features. The top unit hosting shallow wells consists of unconsolidated and predominantly sandy weathered residue.

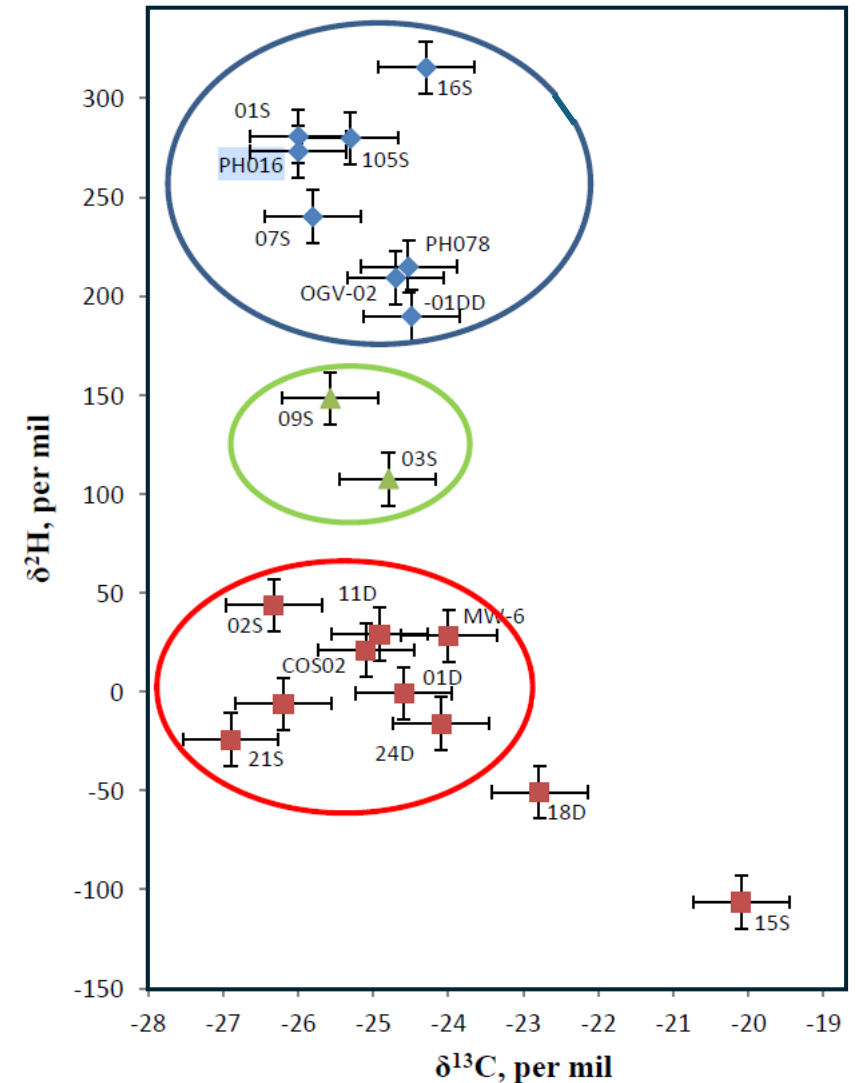


CSIA wells at former TRW/Ramsey facility (active 1940s-1980s)

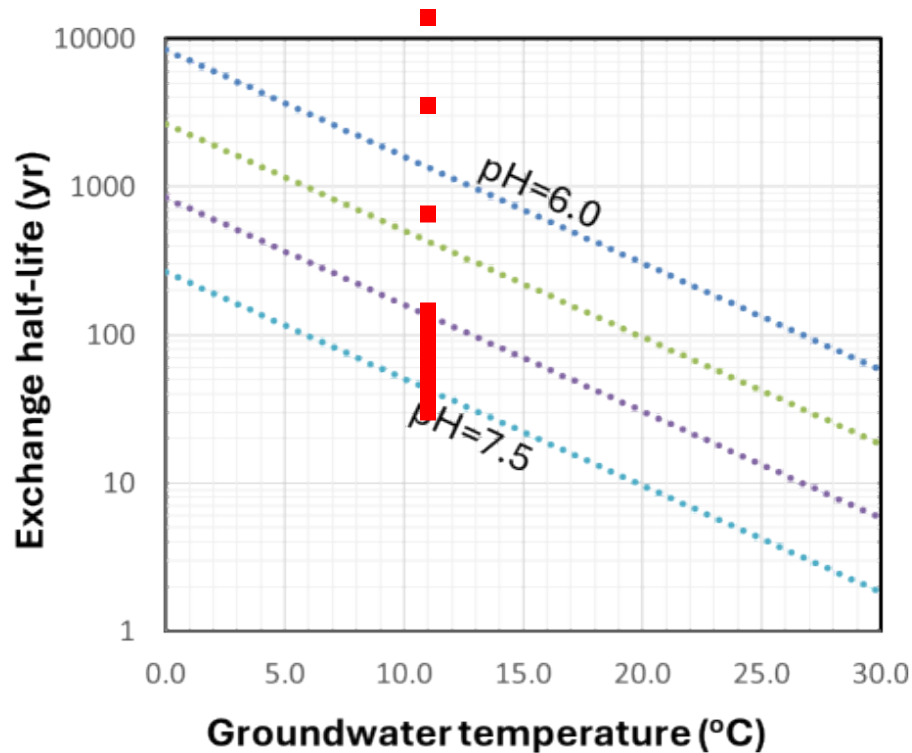
Case Study: Oak Grove, MO: CSIA Summary



- ❖ Well grouping based on C-Cl plot shown relatively minor differences among the TRW and downgradient wells.
- ❖ Two distinct clusters of wells with a couple of “mixed signature” intermediates were apparent in the C-H plot.
- ❖ At the site, the “light” cluster is not readily

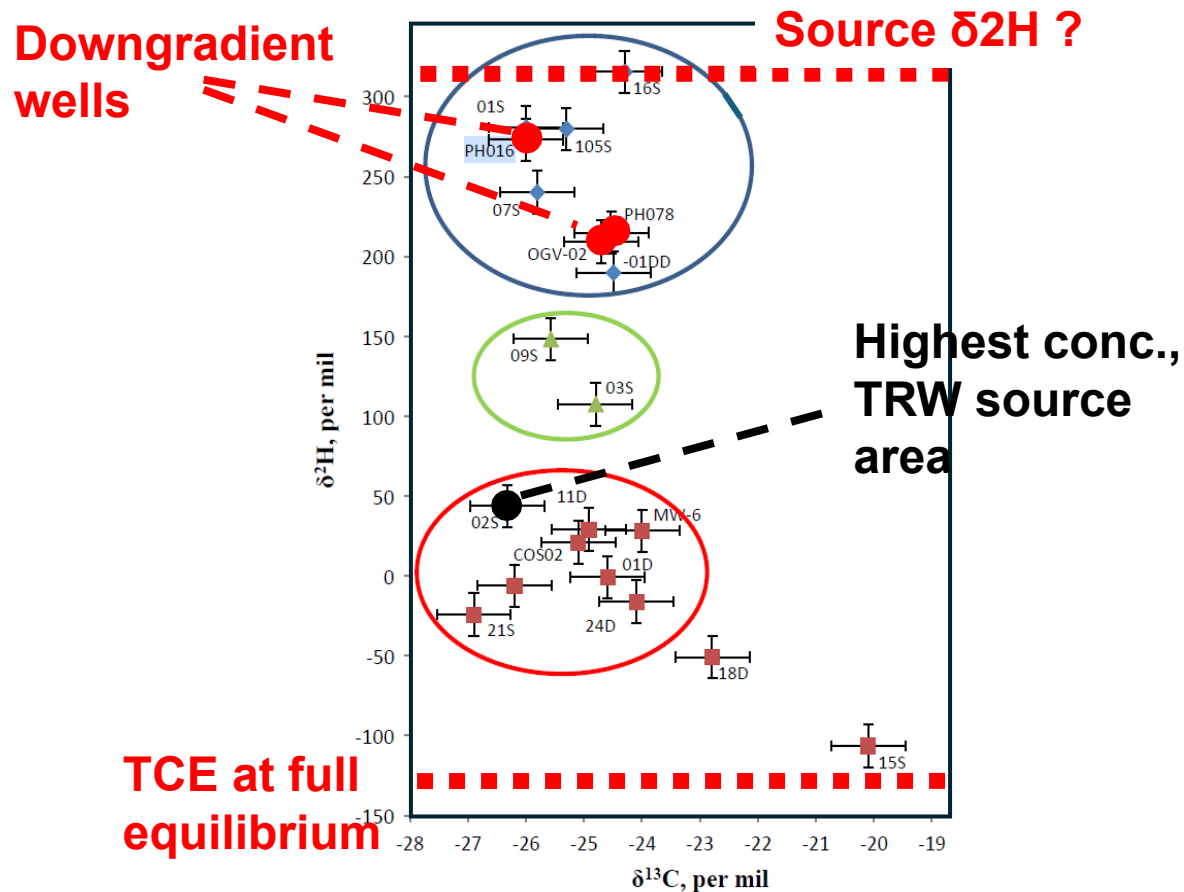


Case Study: Oak Grove, MO



- ❖ $T_{1/2}$ was estimated at 30-110 years using water pH and average annual temperature.
- ❖ Site use indicates that TCE age at the time of sampling was 30-70 years, allowing for ~1 exchange half-life.
- ❖ Assuming the heaviest TCE readings from the site are close to the original source $\delta^2\text{H}$ signature (+300), the exchange over the time interval puts the final $\delta^2\text{H}$ between +100 and 0 permil, which matches the signature of well OBG-2S (a shallow well in the TRW source area with the maximum TCE concentration).

Case Study: Oak Grove, MO



- ❖ The TRW source area shows variable H isotope ratios. The heavy ones may reflect ongoing partitioning of TCE from DNAPL (i.e., TCE with short residence time in water).
- ❖ All three downgradient wells show limited impact of the exchange. This would suggest: (i) short residence time in aqueous phase; (ii) no connection to the high-concentration TCE in the shallow unconsolidated sediment in the TRW area, and (iii) contribution of TCE actively dissolving from DNAPL, likely in the deeper carbonate bedrock.

Concluding Remarks

- ❖ The understanding of TCE-water hydrogen exchange will help to identify the candidate sites for traditional TCE source apportionment applications.
- ❖ Similarly, it will help avoiding errors of attribution of isotope effects resulting from H exchange to degradation or to physical attenuation.
- ❖ On a different level, H CSIA of TCE from sites conducive to the TCE-water exchange can be informative for the purpose of CSM development.
- ❖ Research gaps remain, including on the behavior of TCE in low permeability sediment (does sorption of TCE exert steric protection from contact with HO^- ?), the reactivity of TCE with other Brønsted bases, inorganic, such as HS^- (HS^- is a weaker base, but can be locally present at significant concentrations), or biological, in the form of enzymatic catalysis of the exchange.