Monitoring Subsurface Fluid Flow using Perfluorocarbon Tracers: another tool potentially available for subsurface fluid flow assessments

Presented by: Tommy J. Phelps

Oak Ridge National Laboratory

Phone: 865-574-7290 email: phelpstj@ornl.gov

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Collaborators on the DOE-FE Carbon Sequestration project include:

Barry Freifeld, Paul Cook and team at LBNL,

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Juske Horita, Texas Tech and Dave Cole now at The Ohio State University

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Candidate Tracers for Verification or Assessment

(complementing geophysics)

Brines: **Native non-conservative tracers that respond to changes**

pH, alkalinity, electrical conductivity

Cations: Na, K, Ca, Mg, ΣFe, Sr, Ba, Mn

Major anions: Cl, HCO_3, SO_4, F

Organics: DOC, acetate, methane, benzene, toluene

Gases: **Native conservative tracers or added conservative tracers**

Ions: Br, I (*Na, K*) **Gases: CO_2, N_2, H_2, CH_4, $C_2 – C_n$**

Noble gas tracers: Ar, Kr, Xe, Ne, He (and their isotopes)

Perfluorocarbon tracers (PFT's):

PMCP, PECH, PMCH, PDCH, PTCH (SF_6)

Isotopes: **D/H, $^{18}O/^{16}O$, $^{87}Sr/^{86}Sr$ in water, DIC, minerals**

$^{13}C/^{12}C$ in CH_4, CO_2, DIC, DOC, carbonate minerals

Perfluorocarbon Tracers (PFTs) Complement stable Isotopes and Geochemistry for Verifying, Assessing or Modeling Fluid Flow

PFTs areConservative, Non-reactive & Non- Hazardous tracers

PFT's sensitive at pg-fg, (versus stable isotopes at ppt)

PFT's easy and cheap as multiple combinations or suites for multiple breakthroughs

Complements geochemistry and geophysics providing multiple lines of evidence for flow path assessment

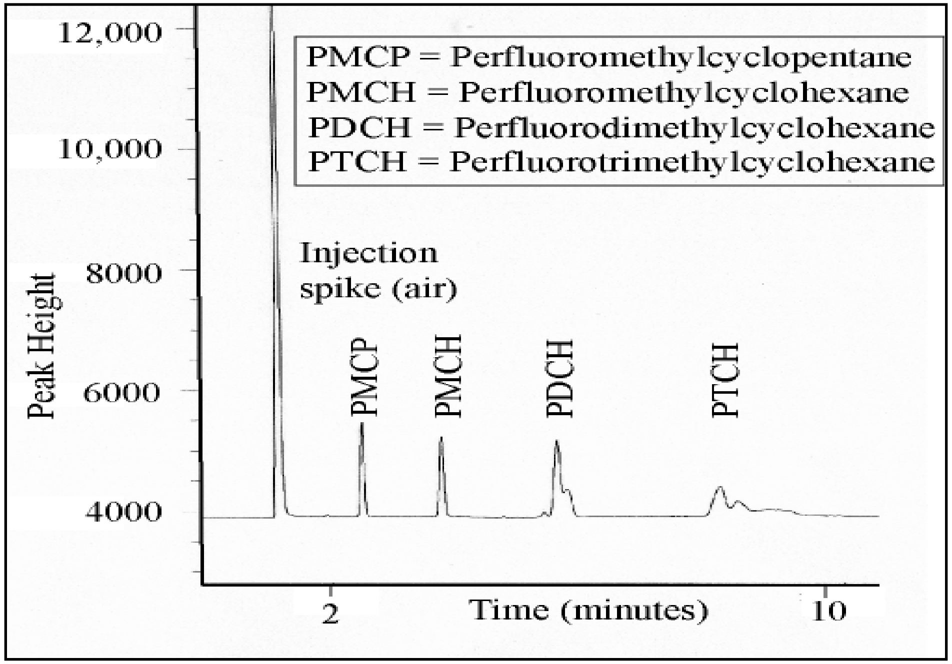
Applicable at near-surface or depth

Scalable to thousands of samples

Can be analyzed in field or preserved

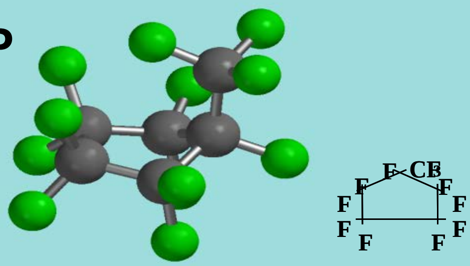
Analysis uses GC with electron capture detection

Proven established procedures

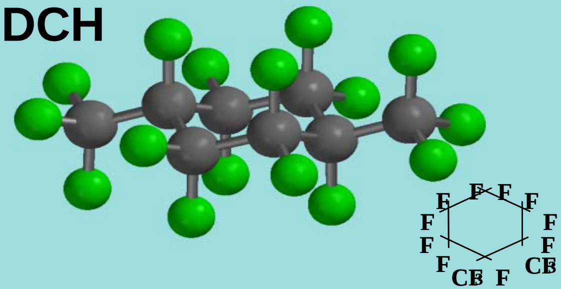


Example PFTs used and sample collection

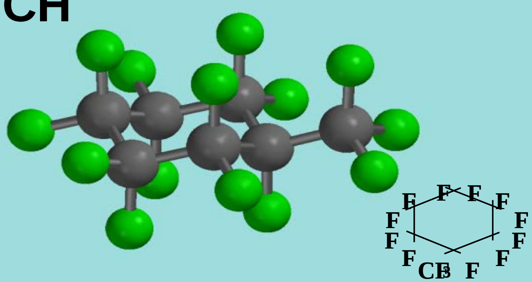
PMCP



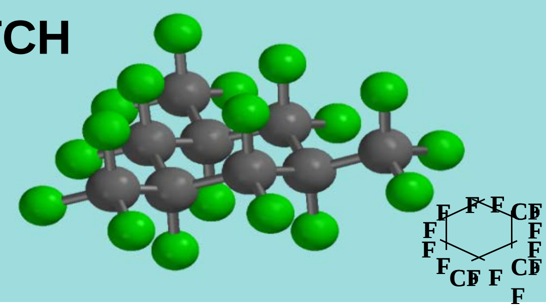
PDCH



PMCH



PTCH



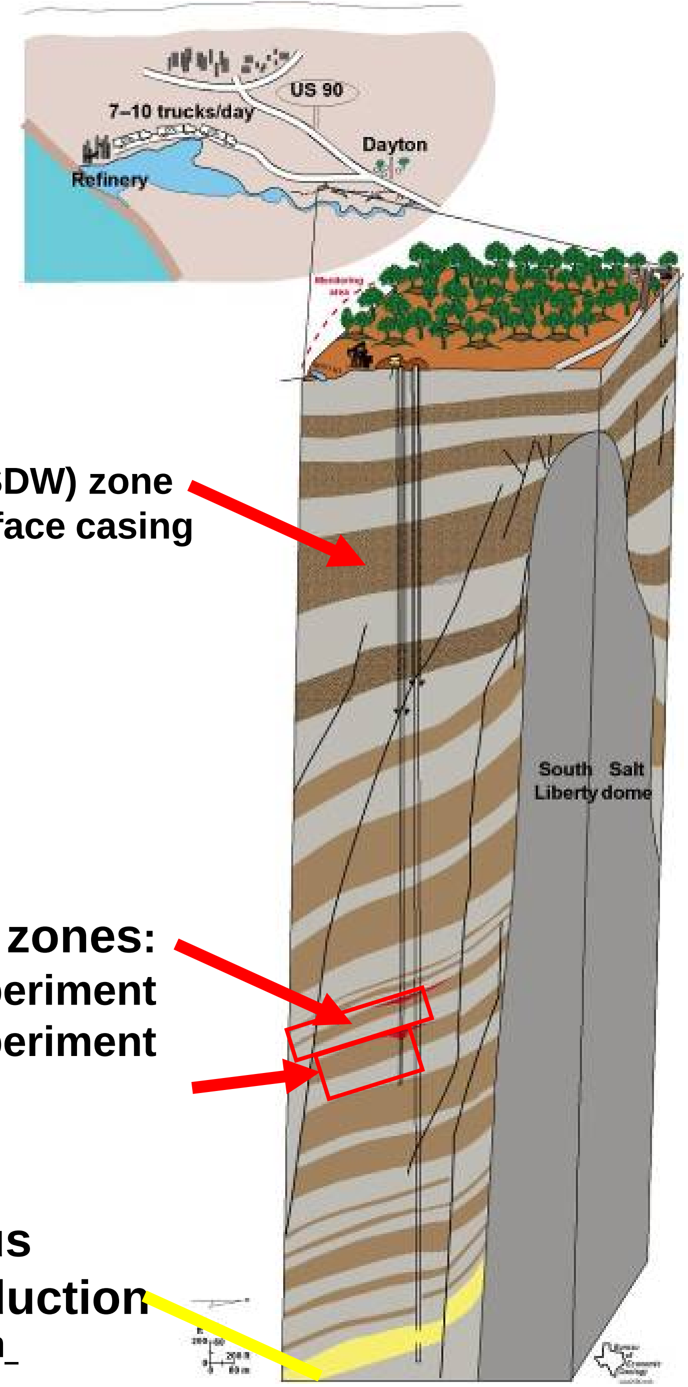
Deploy multiple-tracer suites (others available)
Different molecular weights, solubilities, and structure may enable chromatographic separation in reservoirs

Pressure cylinders for sample collection (U-tube) or use of serum vials that are inverted for storage

PFT Analyses performed in the field or preserved

Stable isotope analyses from pressurized samples

Brine Pilot Site



Fresh water (USDW) zone protected by surface casing

Injection zones:
2004 experiment
2006 experiment

Previous oil production

Injection intervals: Oligocene fluvial and reworked sandstones:

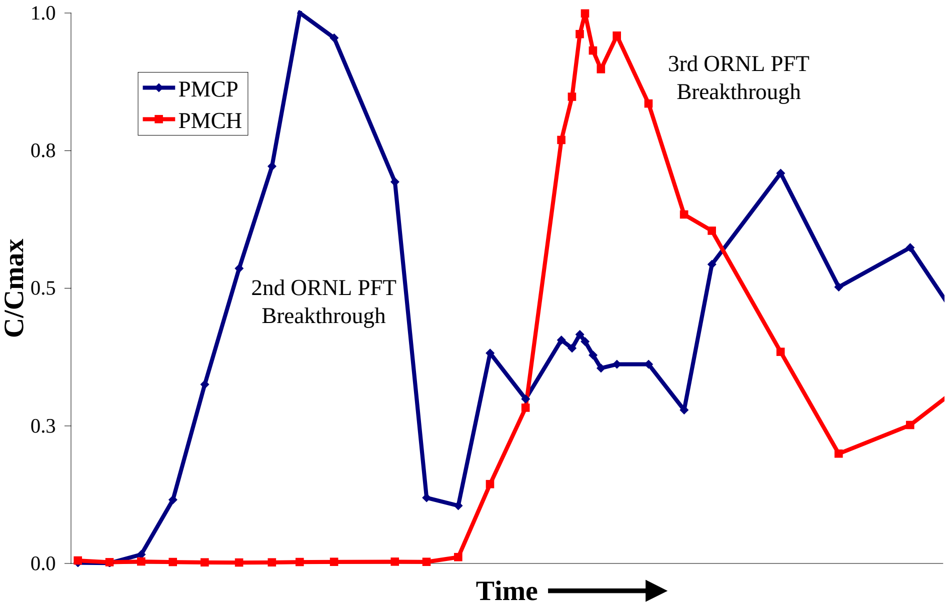
- Porosity 34-24%,
- Permeability 4.4-2.5 Darcys,
- Steeply dipping 11 to 16º ,
- Seals – several thick shales,
- Depth 1,500 and 1,657 m,
- Brine-rock system150 and 165 bar
- Temperature 53 -60°C,
- Supercritical CO_2.

Presentation_

PFT injection results

PFT Travel Time

- **Travel time nearly constant (50 ±1.6 hr)**
- **Well developed CO_2 flow path**



Peaks Broadened with time implying;

PFTs were dispersing in the CO_2 throughout the experiment

Flow paths continued to develop as the CO_2 injection progressed

Injection #	Injection time (hours after CO_2 start)	Injection Duration (hours)	Peak Arrival Time (hours)	PFT Travel Time (hours) (GC)	PFT Travel Time (hours) (MS)	PFT Peak Broadness (hours) (GC and MS)
#1 PMCH/PTCH	2	4	54	50	49	14
#2 PMCP/PDCH	103	0.6	157	52	49	20
#3 PMCH/PTCH	120	0.5	173	51	53	24

Travel Times of Tracer Breakthroughs and Major Peaks *(2nd site)*

December		April	
Breakthrough/Maximum Peak		**Breakthrough /** Major Peaks**, Maximum**	

(Travel time in hr after injection)

Monitoring Well ~ 50m

PMCH	-/ **182**	PMCP	288/ 360, **530,** 861
PTCH	-/ **177**	PDCH	288/ 359, **497**, 861
Increased flow front 35/ 38[b]		PECH	284/ 357, **423,** 446,810
		SF6	284/ 370[a], **405,** 426, 841
		PTCH/PMCH	>150/ *

Monitoring Well ~100m

PMCH	-/ **238**	PMCP	240/ 313, 470, **808**
PTCH	214/ **277**	PDCH	262/ 327, 477, **793**
Icreased flow front 140/ 158[b]		PECH	262/ **419,** 787, **880**
		SF6	299/ 402, **803**
		PTCH/PMCH	169/ 197 *

In April 2010 tracers were added at the following hours: PMCP & PDCH = hr 1; PECH = hr 52; SF6 = hr 54; PTCH & PMCH = hr 693

Missed result due to U-tube issues.*. Experiment ended at hr 906. SF6 peak was >10 times larger exhibiting larger and longer peaks.

b. After 30 days the flow into the formation was nearly doubled.

Lessons Learned for Technology Transfer

Conduct base line characterizations before system is perturbed

Utilize multiple chemical and isotopic probes and different suites of PFTs

Deploy on-site analysis methods – e.g. pH, alkalinity

Continue to monitor after test completion (surface and at depth)

Integrate results with geophysics and coupled reactive-transport modeling

PFTs cost < 1 cent per ton injectate (~ 0.1-1 ppm of fluid)

Summary:
PFTs are Low cost, Non-toxic, Scalable, Sensitive *(pg-fg;*10^{-12-15} quantities)

Geochemistry, Isotopes and PFT's complement Geophysics to monitor and verify plume movement, leakage to shallow aquifers or surface

PFTs: another tool available for potential leakage assessments

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