Monitoring of Geological CO_2 Sequestration using Perfluorocarbon and Stable Isotope Tracers

Project Number FEAA-045

Tommy J. Phelps and David R. Cole*

Oak Ridge National Laboratory

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

Collaborators include: Barry Freifeld, Paul Cook and team at LBNL,
Susan Hovorka and team at TBEG/UT-Austin, Yousif Kharaka and team at USGS,
Juske Horita, Texas Tech

* now at The Ohio State University

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Building the Infrastructure for CO_2 Storage
August 21-23, 2012

Presentation Outline

- Benefits, Goals and Objectives

  - Fate,Transport, Interactions, and Monitoring/Verification/Accounting

- Tracer Selection and Strategy

  - Conservative/reactive natural/added

- Recent Results

  - Reveal breakthroughs, travel times, mixing, interactions, MVA

- Lessons, Accomplishments, Future Plans
  - Established methods, successful, inexpensive, Technology Transfer and collaborations

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Benefits to the Program

Program Goals addressed:

Develop technologies to demonstrate 99% CO_2 remains in zone and Conduct field tests for site characterization, operations, and for MVA

Approach and technology employed:

Use natural (isotopic) and introduced perfluorocarbon (PFT) tracers to decipher fate, transport and interactions of CO_2. Near-real-time information to optimize, calibrate and validate models for CO_2 residence time, storage capacity and mechanisms, injection scenarios and assessing potential reservoir leakage (MVA)

Results:

Provide methods to interrogate CO_2 sequestration, monitoring, calibrating models, aid interpreting geophysical data, determine breakthroughs, demonstrate the transfer of CO_2 into sedimentary units, provide cost effective innovative MVA, enhance & safety confidence with stakeholders/regulators

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Project Overview: Goals and Objectives

Our goal is to provide methods to interrogate the subsurface for improved CO_2 sequestration , developing technologies to demonstrate CO_2 remains in the zone, conduct field tests for characterization, operations, and MVA for integration into a systems model.

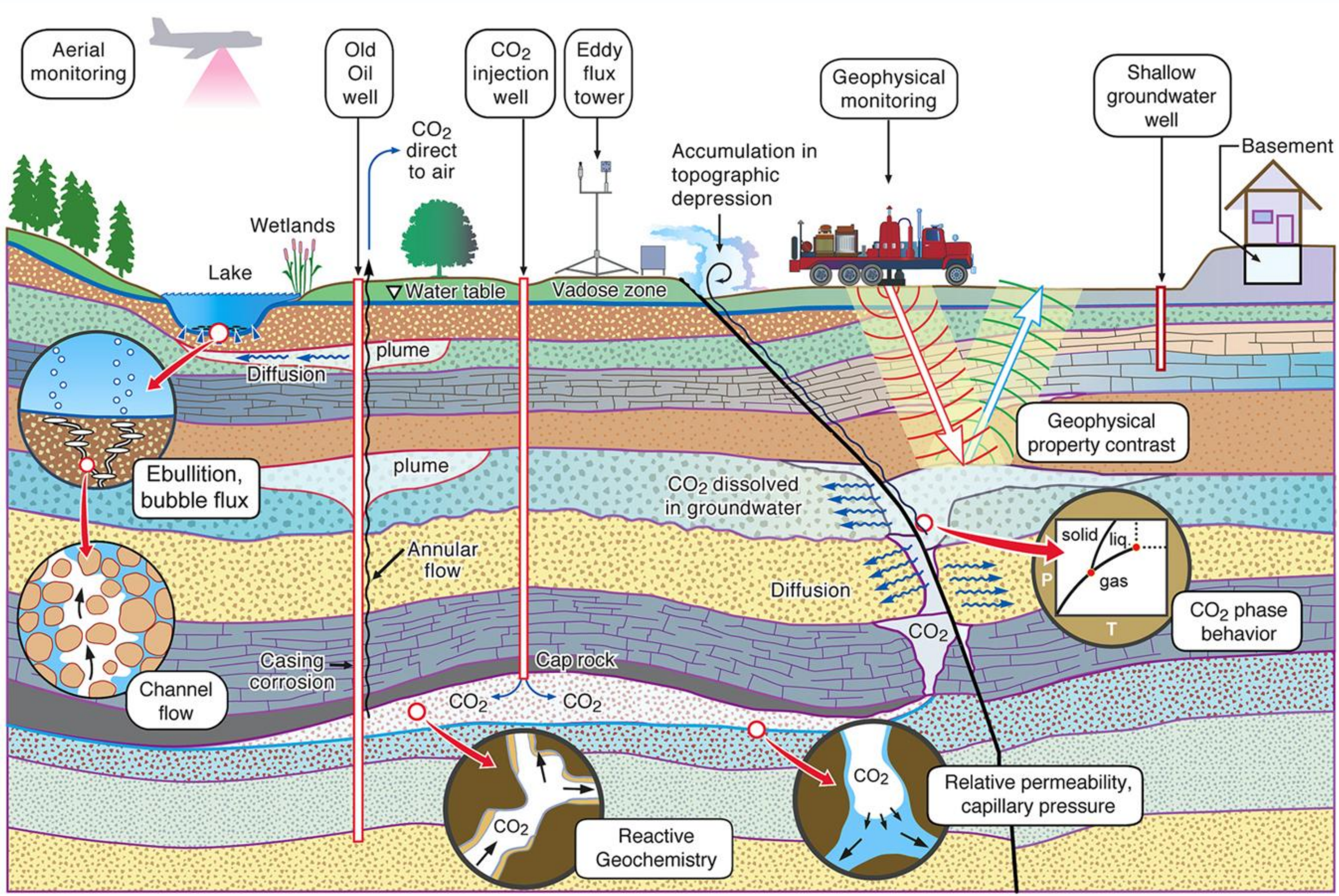
Three Objectives:

1. Assessment of injections in field. PFT gas tracers are analyzed by GC-ECD to <pg levels. GC-IRMS is used for gas chemistry and stable isotope ratios (e.g. D/H, $^{18}O/^{16}O$, and $^{13}C/^{12}C$).

2. Integrate PFT and isotopic results to assess the nature of CO_2-brine-rock interactions leading to better model understanding & MVA strategies.

3. Develop MVA strategy to decipher the fate and transport of CO_2, estimating residence time, reservoir capacity/interactions, process optimization, and assessing the potential leakage.

Monitoring Subsurface Processes and Leakage



MVA Tracer Strategy
(complementing geophysics)

Conduct base line characterization of system prior to CO_2 injection – gas, brine, & solid compositions (mineralogy)

Characterize input CO_2 for chemistry (including nobles) & isotopes

Down-hole samples preferred over well-head samples; U-Tube (LBNL) a good alternative

Deploy multiple introduced conservative gas tracers and natural isotopes

Sample prior to and during injection both at the injection well and the monitoring well(s); frequency dictated by pre-testing modeling, timing of actual breakthrough and length of injection

Continue to monitor both injection well and monitoring wells after completion of injection test.

Continue long-term monitoring to assess signal decay; leakage in well bore above primary sample horizon; leakage to environment

Candidate MVA Tracers

(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

Organic acids: acetate, formate, oxalate, etc.

Other organics: DOC; methane, CO_2, benzene, toluene

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

Ions: Br, I (*Na, K*) **Gases: 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):

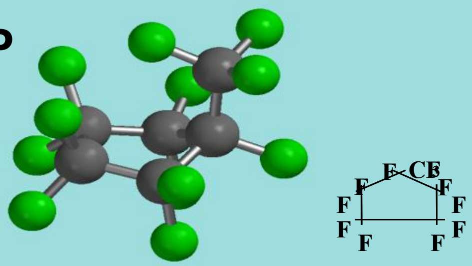
PMCP, PECH, PMCH, PDCH, PTCH (also SF_6)

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

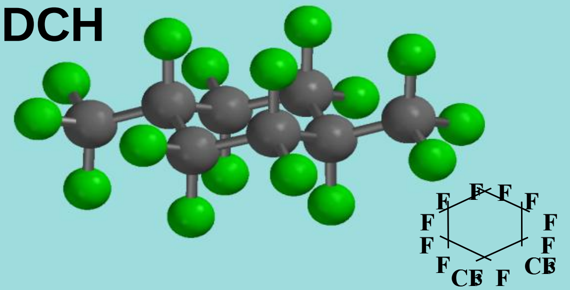
$^{13}C/^{12}C$ in CH_4, CO_2, DIC, DOC, carbonate minerals

Examples of PFTs used and sample collection

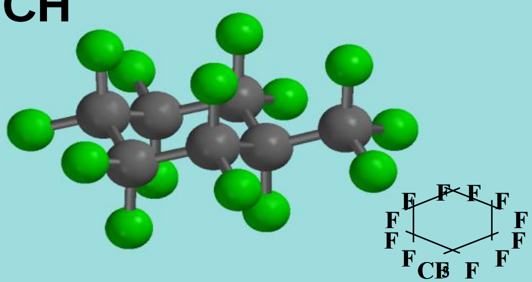
PMCP



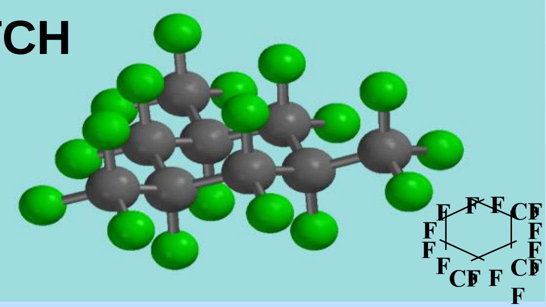
PDCH



PMCH



PTCH



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

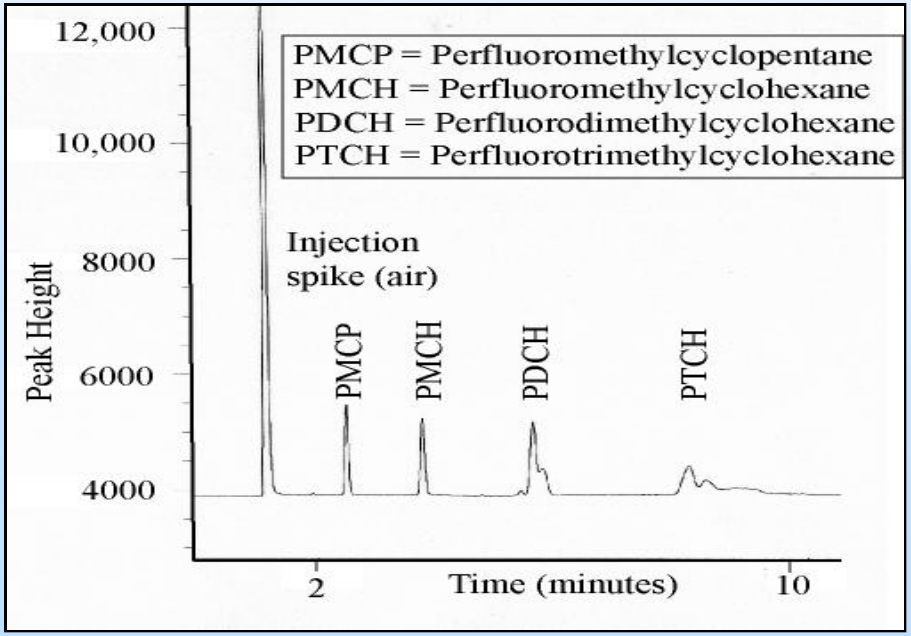
Pressure cylinders for sample collection (U-tube)

PFT Analyses performed in the field or preserved

Stable isotope analyses from pressurized samples

PFTs complement stable isotopes and geochemistry for MVA and modeling heterogeneous flow

- Conservative, Non-reactive & Non-Hazardous tracers
- PFT's sensitive at pg-fg, versus isotopes at ppt
- PFT's easy and cheap as multiple combinations or suites for multiple breakthroughs
- Complemented by geochemistry providing multiple lines of evidence for MVA, flow path assessment and modeling
- Applicable at near-surface or depth
- Scalable to thousands of samples
- Can be analyzed in the field or preserved for analysis in the lab using GC with electron capture detection
- Proven established procedures



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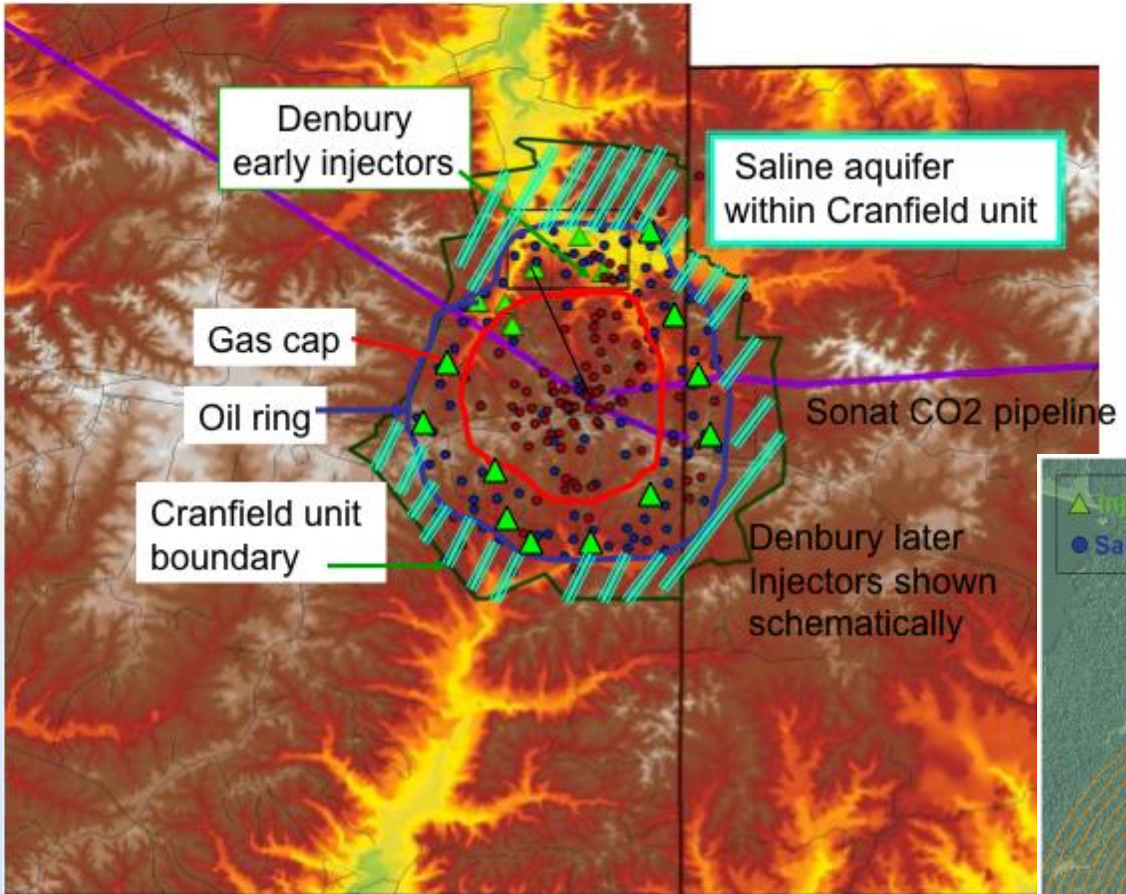
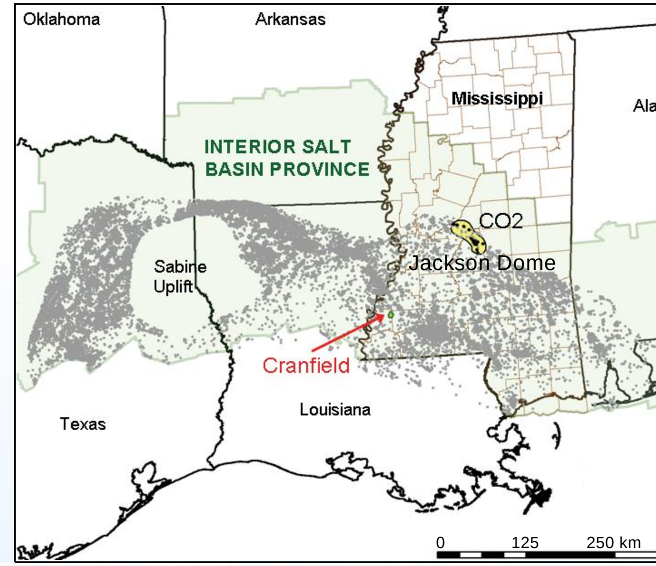
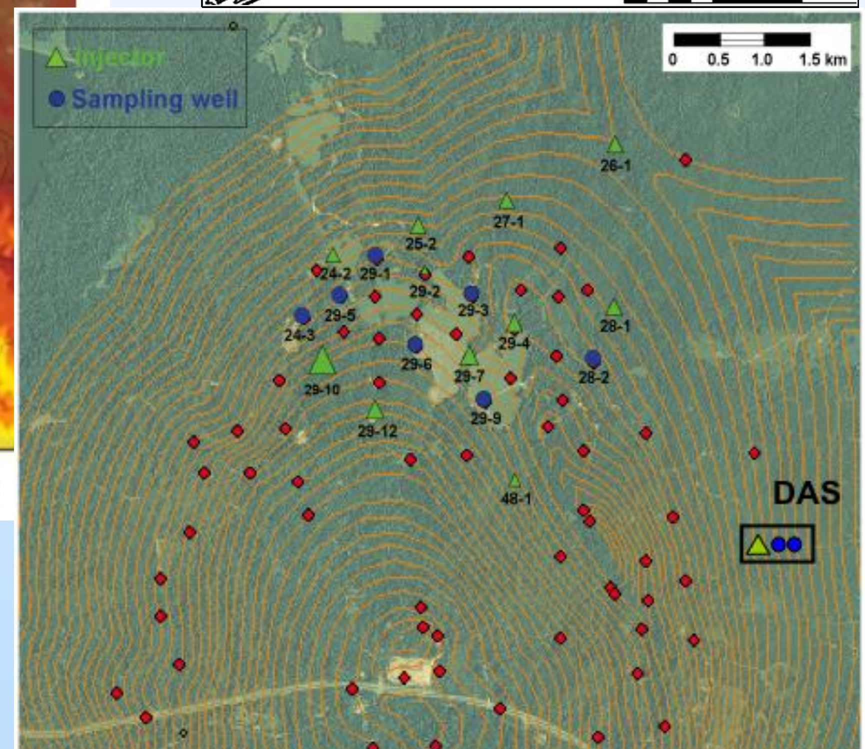
Crandfield CO_2 InjectionTest



Example Denbury Cranfield unit, MS





Injector	29-10	29-12	29-2	29-7	29-4	26-1	25-2	24-2	27-1	28-1	48-1
Injection volume by Mar/09 (10^3 metric ton)	110	62	7	69	58	52	53	48	45	56	28

Well access via Denbury Resources

First injection at DAS site - Dec 2009

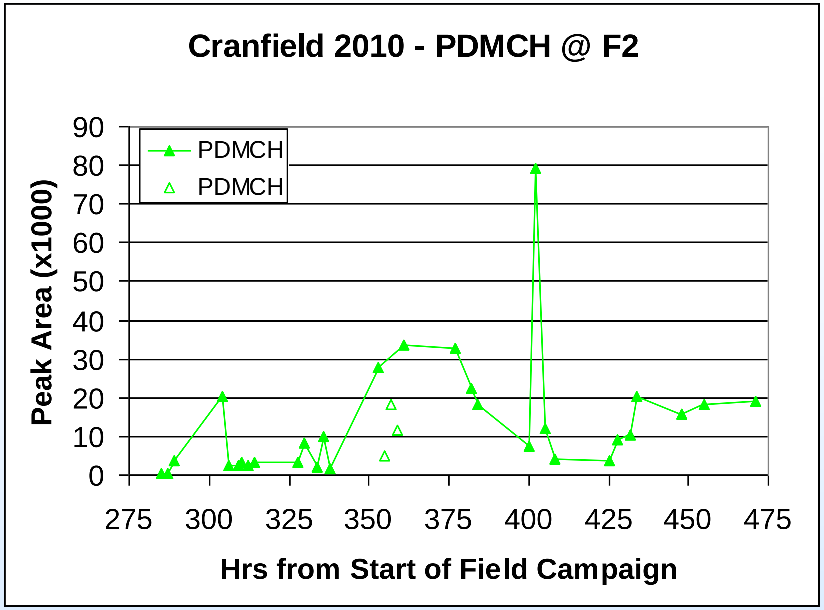
FY 2012 Preliminary Results(in progress)

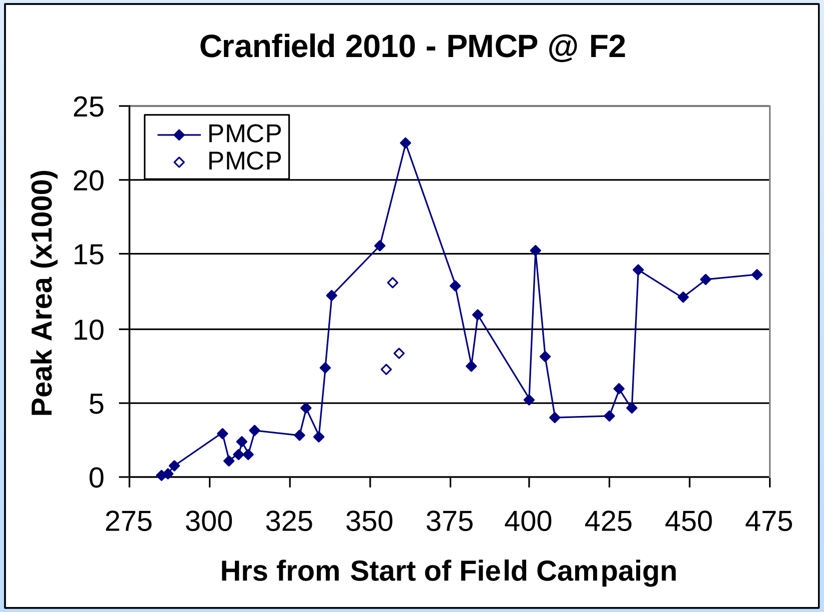
Breakthrough and developing peak of PDCH (upper figure) and PMCP (lower) from the Field Campaign of April, 2010

Pair of Perfluorocarbon tracers (PDCH & PMCP) added at t = 1hr
Initial breakthrough ~ 288hr later with maximal peak at ~ 360 hr

F2 ~ 100m from injection well
F3 ~ 200m distant

Travel times were significantly longer than the initial CO_2 injection of December, 2009.

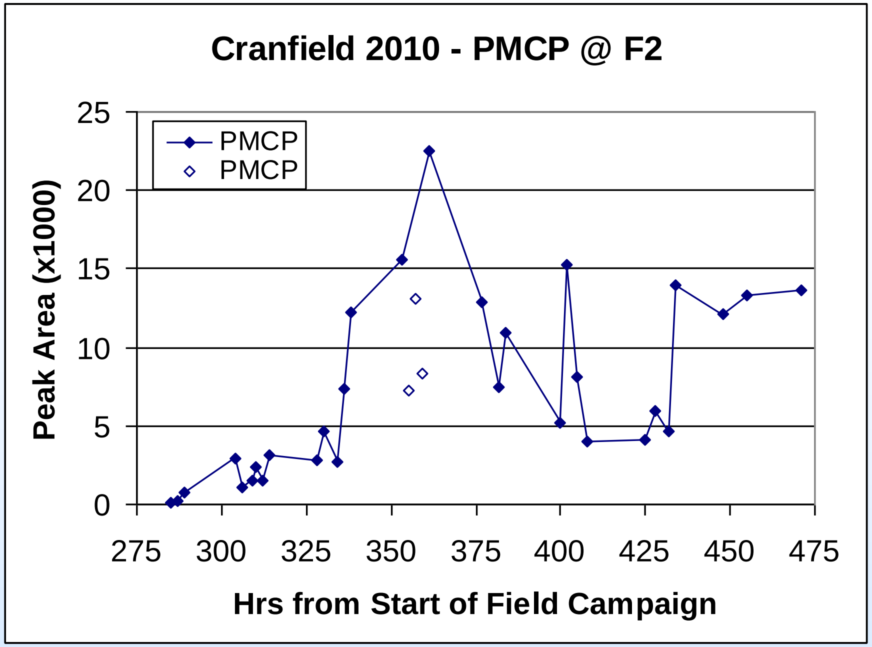




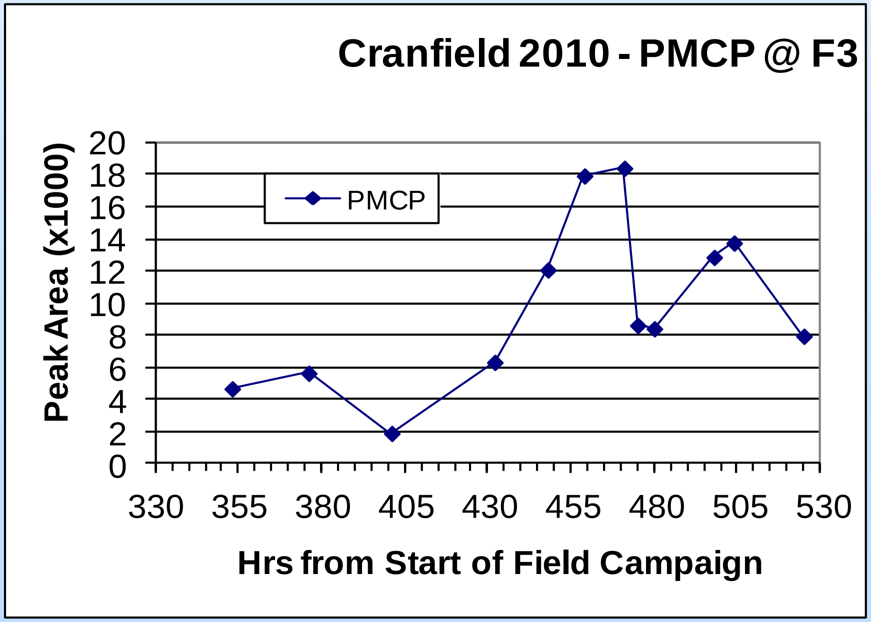
FY 2012 Preliminary Results(in progress)

Breakthrough and developing peak of PMCP at F2 and at F3 from the Field Injection Campaign of April, 2010

PMCP was added at t = 1 hr
Breakthrough and peak at F2 was 288/360hr



Breakthrough and peak at F3 is currently estimated to be approximately <355/~471/hr as data as still being analyzed



F2 was ~ 100m from injection well
F3 ~200m distant and PMCP exhibits greater travel time

Additional PFTs are also being examined

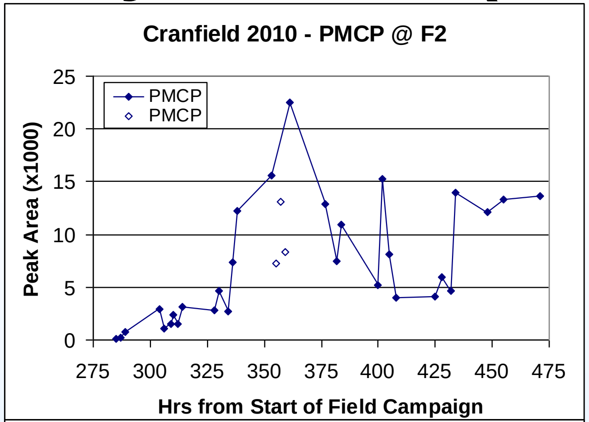
FY 2012 Preliminary Results (in progress)

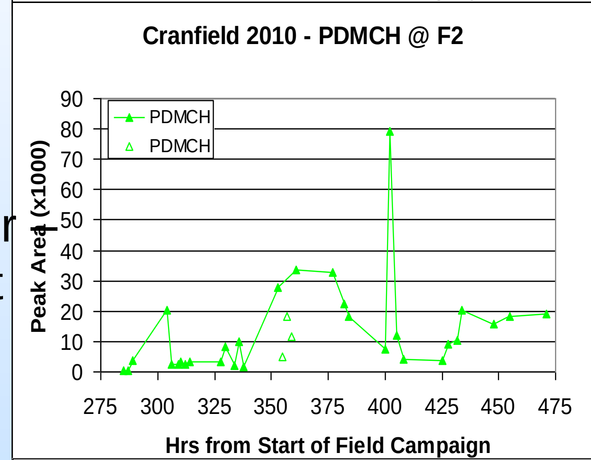
Developing peaks for PMCP, PDCH and SF_6 at F2 and F3; 04/2010

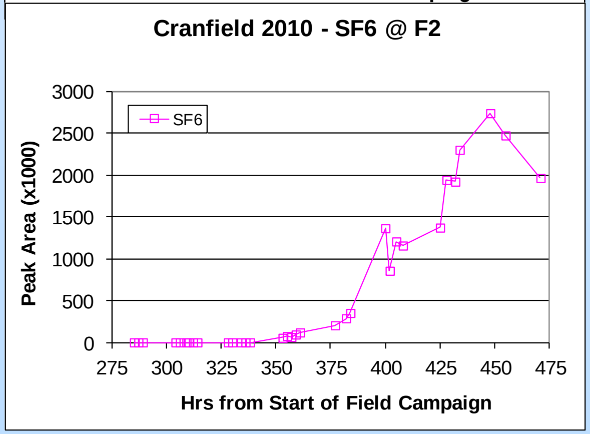
PMCP & PDCH added t =1hr
SF6 added at t = 60h

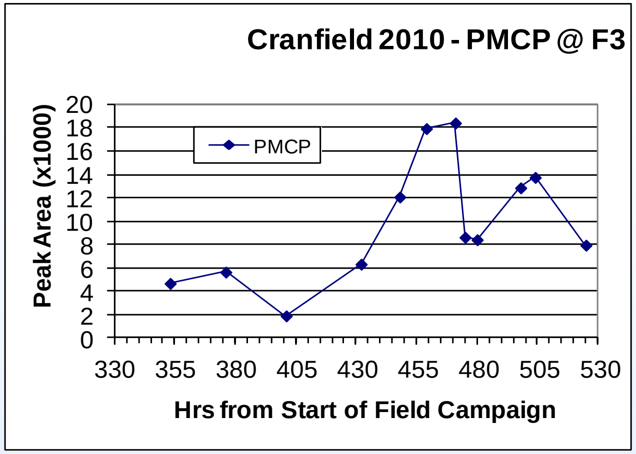
SF_6 Breakthrough travel time and peak at F2 was 275/370hr approximating the 60 hr offset *(note- considering 10 x SF6 was injected, F2 travel time is similar)*

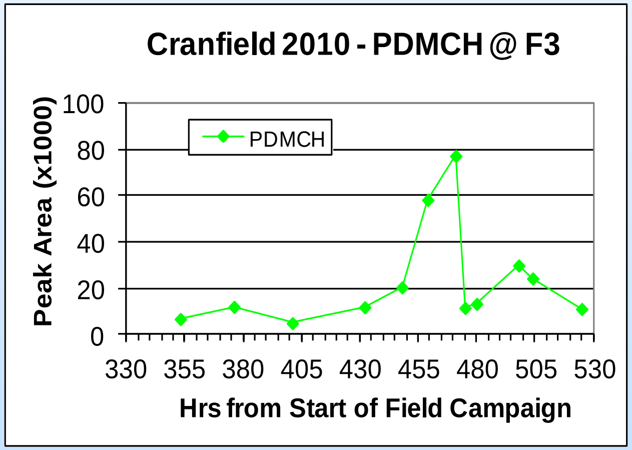
F3 samples to be analyzed
PMCH & PDCH Peaks at F3 are ~110hrs later that at F2











SF_6 arrival at F3 is yet to analyzed, likely past hr ~600

Travel Times of Initial Breakthrough and Maximum Peak

	December 2009		April 2010
	Initial Breakthrough/Maximum Peak (travel time hr)		
Monitoring Well F2			
PMCH	*/182	PMCP	288/360
PTCH	*/177	PDCH	287/359
		SF6	275/370[a]
Pressure Front	**35/38[b]**		
Monitoring Well F3			
PMCH	*/238	PMCP	? /471
PTCH	214/277	PDCH	?/470
Pressure Front	**140/158[b]**		

*Missed result due to U-tube issues

a. SF6 peak was >10-times larger so was observed earlier and longer

b. In early January 2010 CO2 flow was nearly doubled

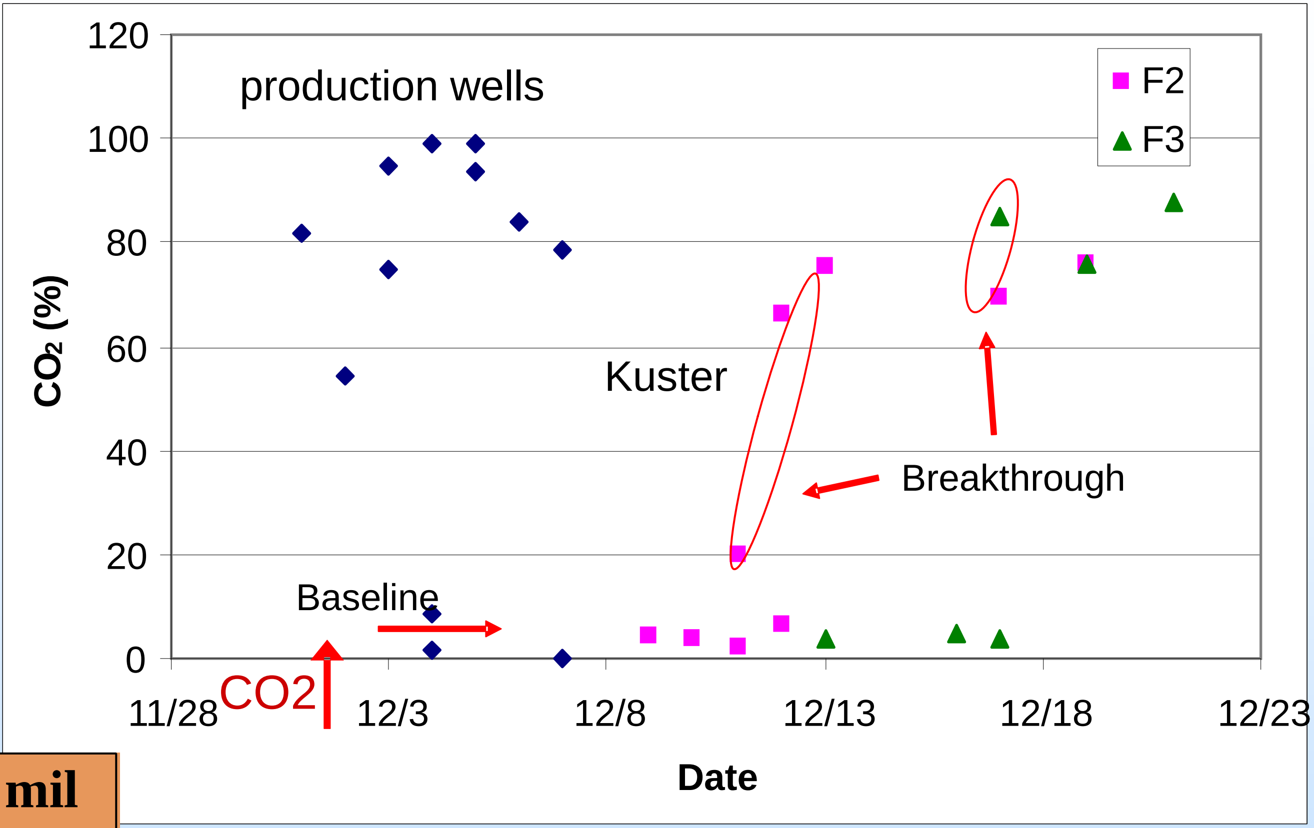
? Awaiting analysis

CO_2 Concentration Change vs Time: Production and Monitoring wells (2009 sampling)

Initial brine at DAS had high CH_4/CO_2 ratios

Breakthrough CO_2 values similar to production wells

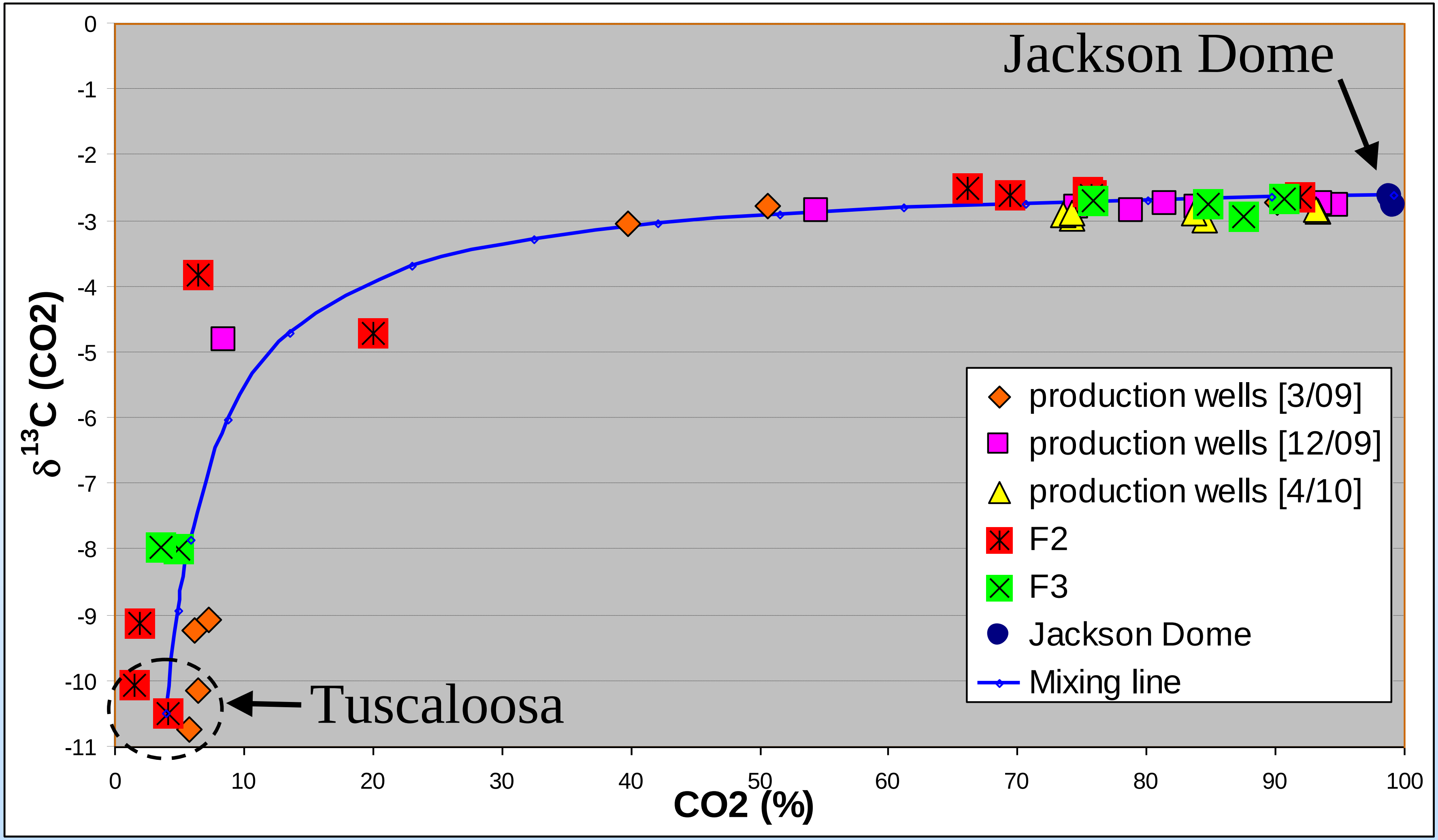
F2 well experienced CO_2 breakthrough much sooner than F3



$\delta^{13}CO_2$=-2.5 to -10.5 per mil

- **Baseline $\delta^{13}C$= -10 per mil**
- **Injection $\delta^{13}C$= -2.6 per mil w/99% CO_2 (Jackson Dome)**
- F2/F3: CO_2 (% and $^{13}C/^{12}C$) respond to injection

Carbon Isotopes ($^{13}C/^{12}C$) of Injected CO_2 Gas from Jackson Dome Show Good Mixing with Tuscaloosa CO_2



Simple two-component fluid mixing dominates at the DAS site

No evidence of CO_2 reaction with reservoir rock carbonates

December 2009 sampling: Gaseous & DIC CO_2

Dissolved inorganic carbon (DIC) $^{13}C/^{12}C$ values mimic those of CO_2 in the system

Enriched $^{13}C/^{12}C$ values indicate solubility trapping is operating

DIC C isotope values not always governed by equilibrium partitioning

- $\delta^{13}CO_2$ = -2.5 to -10.5 per mil
  - Baseline $\delta^{13}C$ = -10 per mil
  - Injection $\delta^{13}C$ = -2.9 per mil w/99% CO_2 (Jackson Dome)
  - F2/F3: CO_2 (% and $^{13}C/^{12}C$) respond to injection

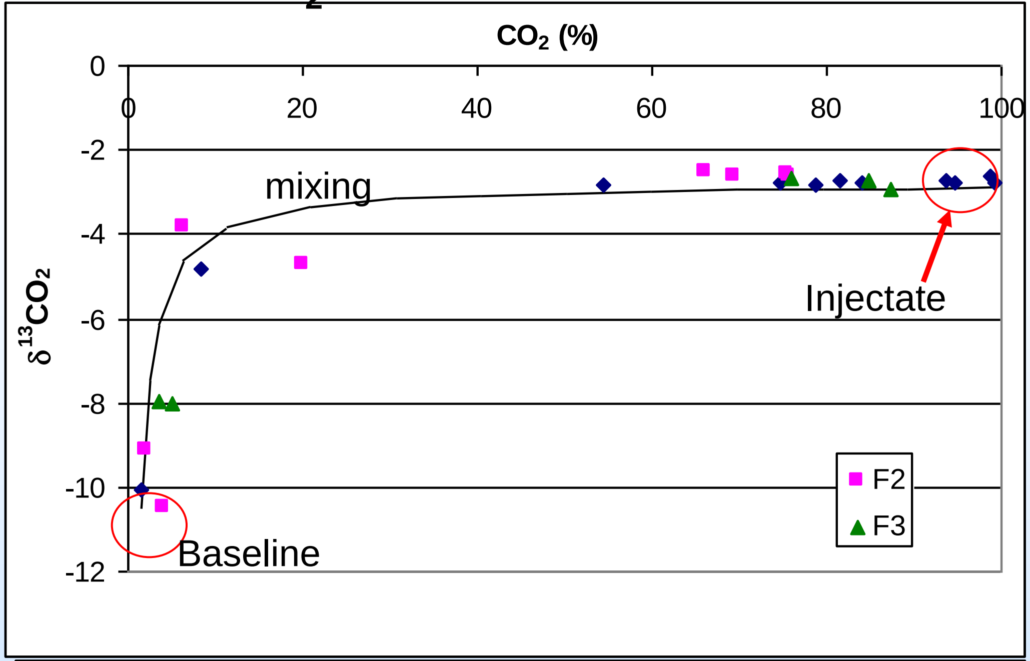
- DIC: $\delta^{13}CO_2$ = -0.6 to -9.8 per mil

  +4.4 to -1.8 per mil relative to CO_2

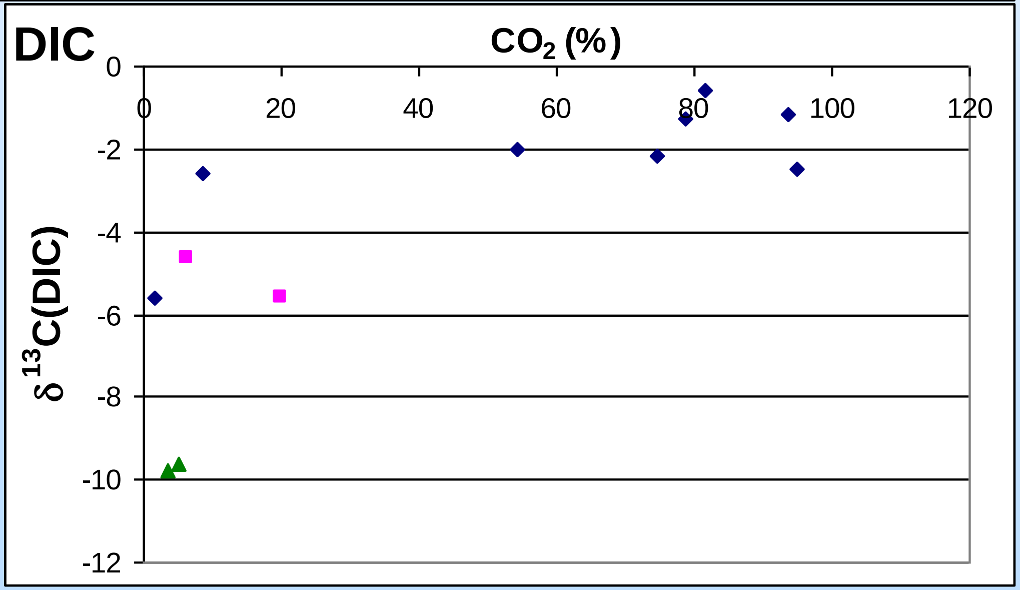
  Equilibrium (function of T) vs. kinetic process

- $\delta^{13}CH_4$ = -40 to -42 per mil

Gaseous CO_2



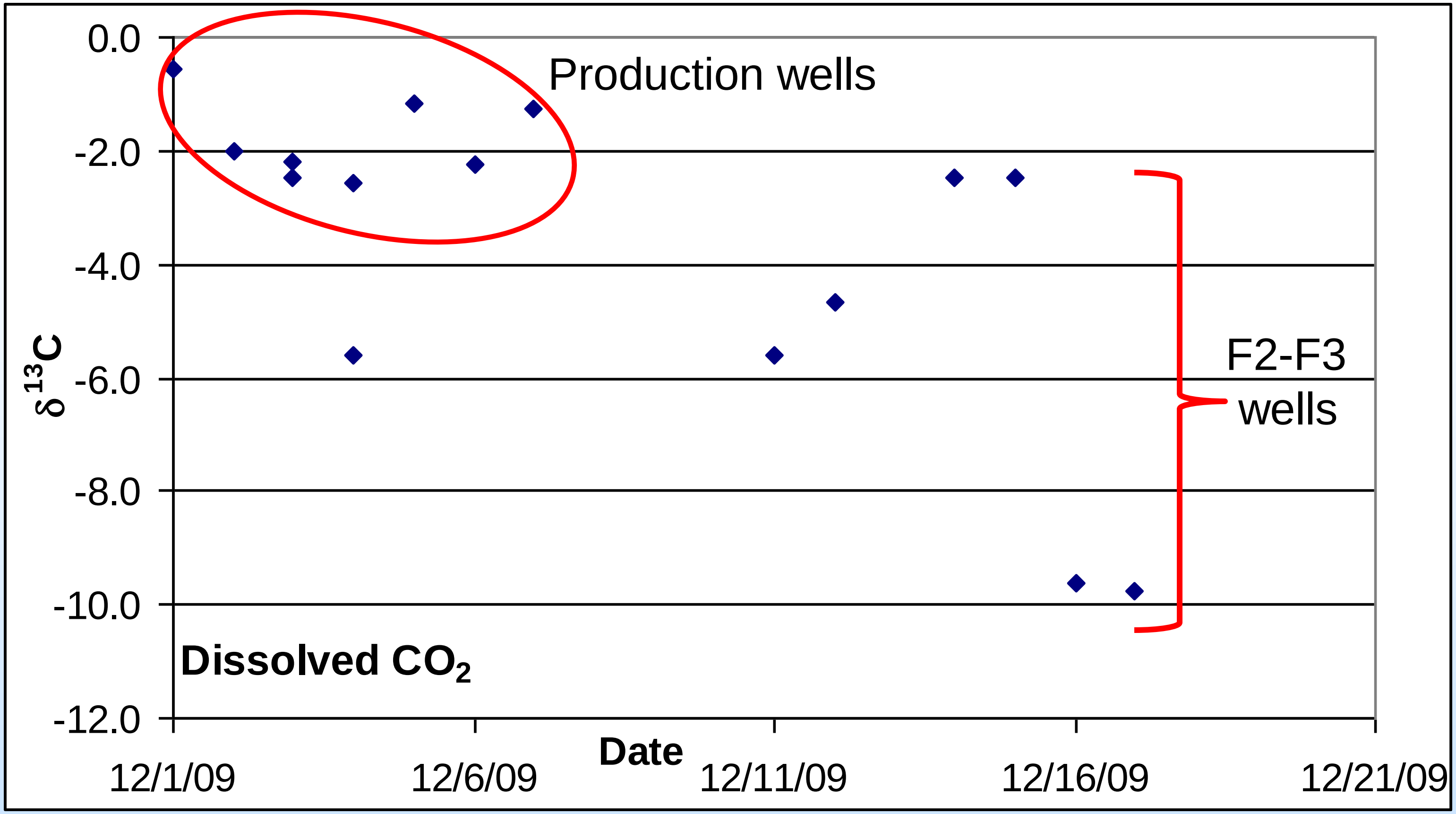
DIC



December 2009 sampling: Dissolved CO_2 (DIC)

DIC ^{13}C values respond rapidly to CO_2 injection In F2 well.

DIC 13C values In F3 well remain at background several days after detection at ell F2



- $\delta^{13}CO_2$ = -0.6 to -9.8 per mil
  +4.4 to -1.8 per mil relative to CO_2
  Equilibrium (function of T) vs. kinetic process

- Baseline $\delta^{13}C$ = -10 per mil
- Injectate $\delta^{13}C$ = -2.6 to -2.9 per mil (Jackson Dome)

Accomplishments to Date

- **Used U-tube, Kuster, site facilities and other tools to obtain water and gas samples.**
- **Determined organic and inorganic and isotopic compositions of water and gases in the baseline, during and post injection for multiple sites and campaigns.**
- **Determined behavior of perfluorocarbon tracer suites, breakthrough, maximum development of reservoir storage over time.**
- **Delineated CO_2 fronts using on-line pH probes, conductance and temperature complemented by PFT's and isotopes.**
- **Assessed water-mineral-CO_2 interactions using geochemical modeling and isotopic signatures.**
- **Investigated environmental implications of post injection**
- **Complementing efforts at other sites/partnerships**
- ***Developing procedures for tech transfer to larger carbon sequestration demonstrations for monitoring, verification and accounting (MVA)***

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Lessons Learned Leading to Technology Transfer

Conduct base line characterizations before system is perturbed

Deploy different suites of PFTs for surface and subsurface tests

Utilize multiple chemical and isotopic probes

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

Dual source of CO_2 with different isotopic values may be helpful

Obtain down-hole samples if possible during the base line studies and during test; or U-tube type design

Sample injection and monitoring wells above injection horizon to test for leakage

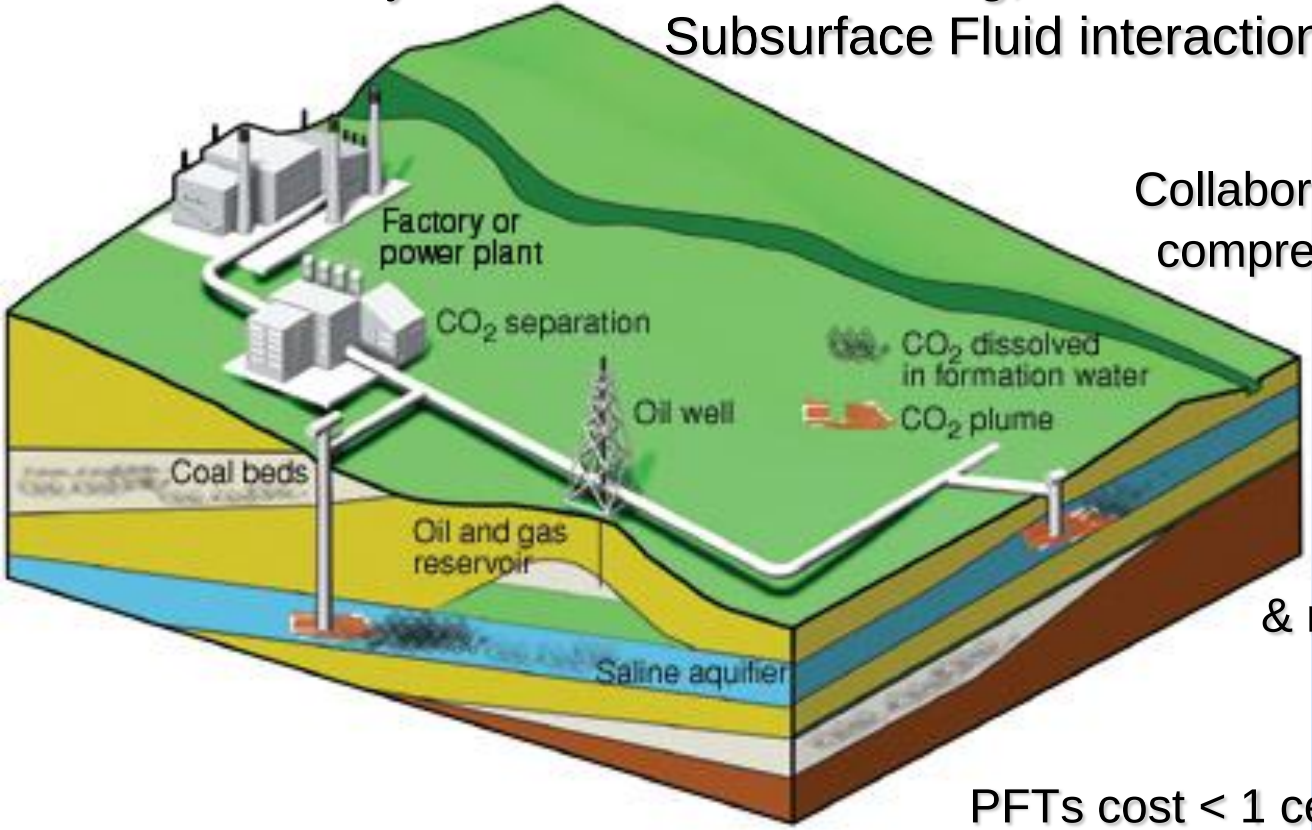
Continue to monitor both injection well and monitoring wells after completion of injection test (and above injection horizon)

Integrate results with coupled reactive-transport modeling efforts

Oak Ridge National Laboratory · The Ohio State University · USGS science for a changing world · Berkeley Lab · Bureau of Economic Geology, John A. and Katherine G. Jackson School of Geosciences

Future Plans: Technology Transfer/Collaborative Assistance

Geochemistry and PFT's for Monitoring, Verification and Accounting of Subsurface Fluid interactions



Collaborations toward developing comprehensive MVA strategies

Geochemistry, PFT's
Stable isotopes are
Established, Inexpensive
& make good Univ. projects

PFTs cost < 1 cent per ton injectate

Geochemistry and isotope analyses are readily available at universities /labs

Geochemistry, isotopes and PFT's can monitor plume movement, leakage to aquifers or surface appropriate for CO2 sequestration, oil gas/wells or others.

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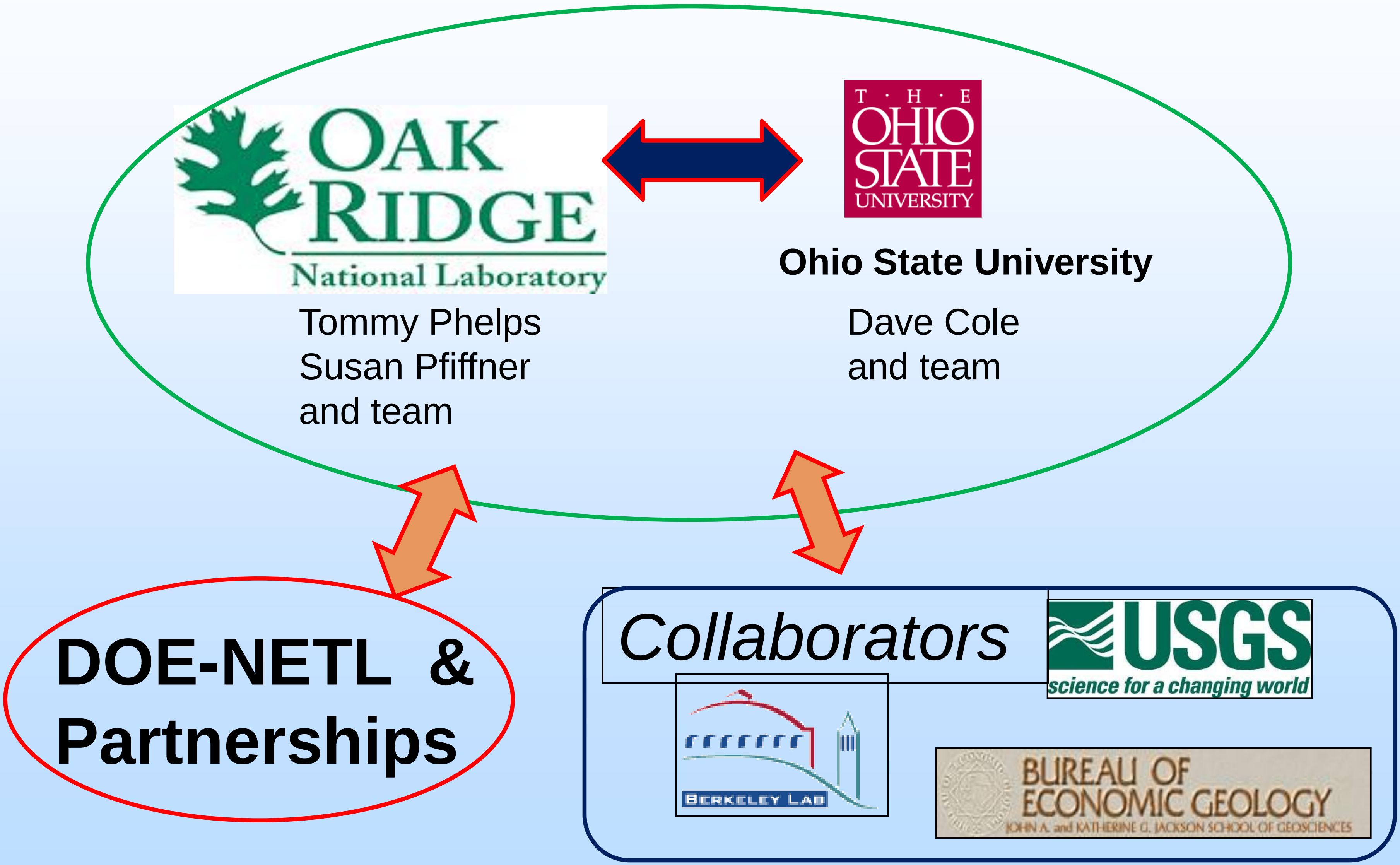
Appendix: Organization Chart



Appendix: Gantt Chart

Task	Task Description	Start : 10/1/2010 End: 9/30/2015										
		2012				2013						
		Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12			
1.1	Task 1 Program management and planning (PMP)			75								
1.2	Analysis (injection/post injection samples) Cranfield **Milestone 6-2013*			80								
1.2.1	Injection and post-injection analysis											
1.2.2	Compare evolving changes: pre- and post injection			80								
1.3	Integration of PFT/isotope results			40								
1.4	Develop PFT/isotope MVA strategy **Milestone update report 09/14*											

Appendix: Bibliography

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Since 2006 there have been:

8 proceedings papers, plus 6 abst. presentations (national international meetings)

7 peer reviewed journal papers; one in prep

3 book chapters

More papers are planned.