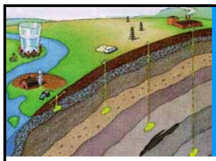
GWPC/EPA CO2 MMV Workshop

USEPA Opening Remarks on MMV

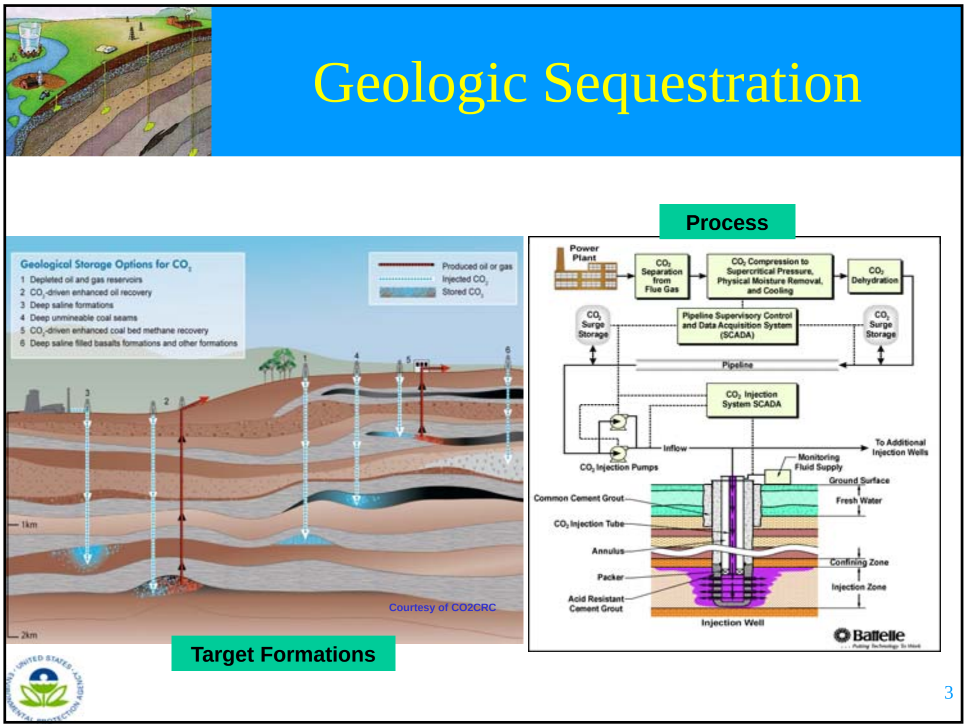
Bruce J. Kobelski
U.S. Environmental Protection Agency
Office of Ground Water and Drinking Water

Ground Water Protection Council UIC Annual Meeting
New Orleans, LA
January 14-16, 2008



Overview

- Carbon Capture and Storage (CCS) is a key climate change mitigation technology.
- DOE leads US efforts to advance sequestration technologies including fundamental R&D, FutureGen and Regional Sequestration Partnerships.
- EPA works closely DOE, with a focus on risk assessment/management and to ensure R&D supports regulatory development.
- Deployment of sequestration technologies will need support from a broad range of stakeholders.
- EPA has technical & regulatory expertise and experience working with key stakeholders and the public.

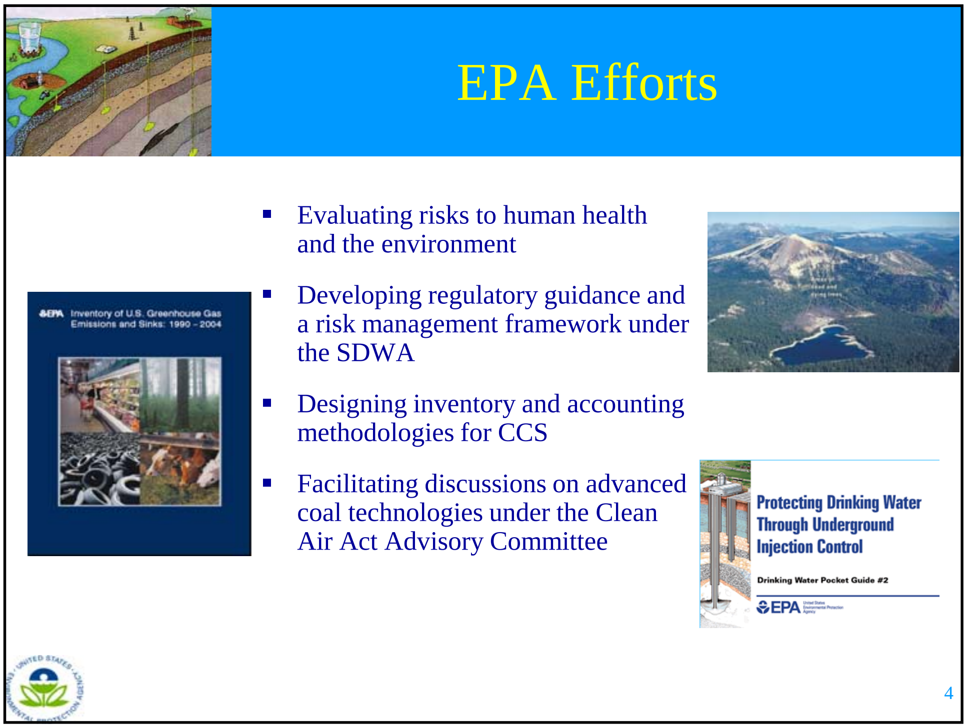


Geologic Sequestration

Process

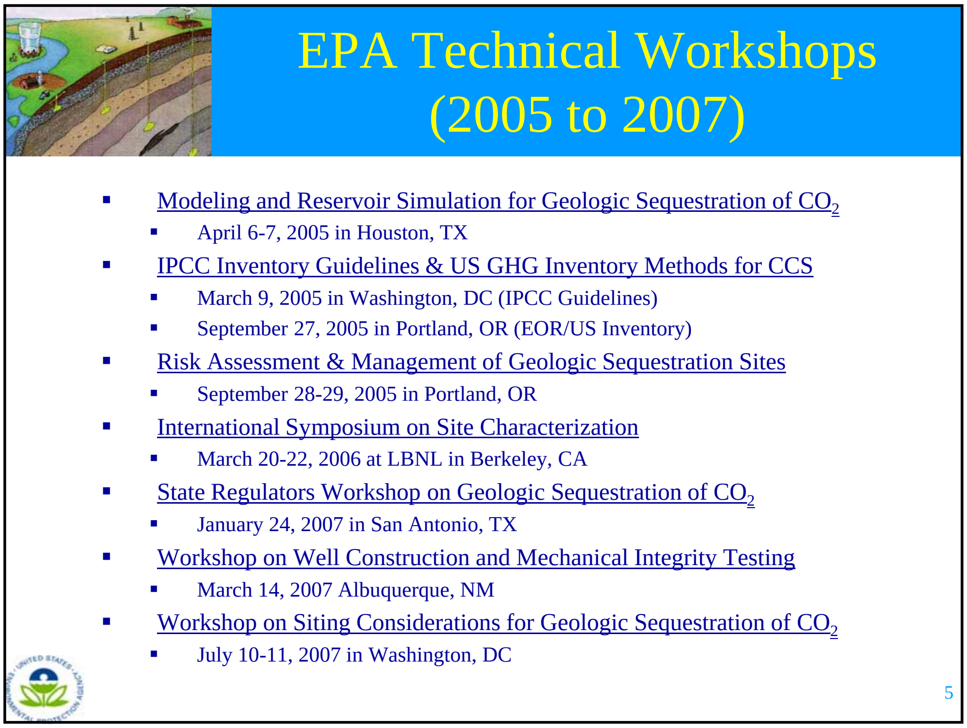
Target Formations

Courtesy of CO2CRC



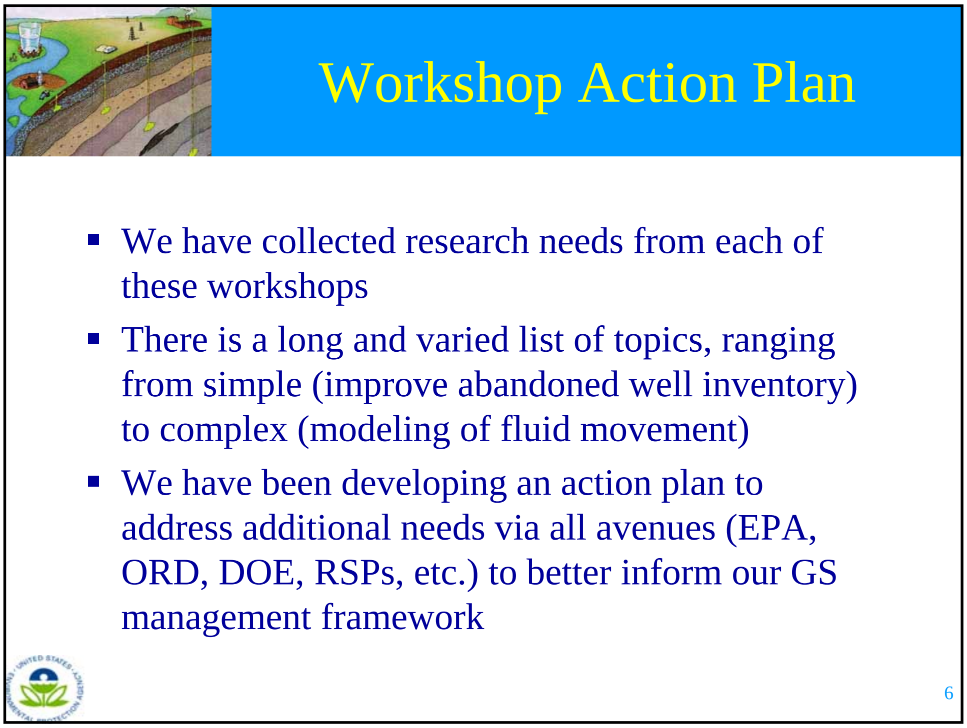
EPA Efforts

- Evaluating risks to human health and the environment
- Developing regulatory guidance and a risk management framework under the SDWA
- Designing inventory and accounting methodologies for CCS
- Facilitating discussions on advanced coal technologies under the Clean Air Act Advisory Committee



EPA Technical Workshops (2005 to 2007)

- Modeling and Reservoir Simulation for Geologic Sequestration of CO_2
    - April 6-7, 2005 in Houston, TX
- IPCC Inventory Guidelines & US GHG Inventory Methods for CCS
    - March 9, 2005 in Washington, DC (IPCC Guidelines)
    - September 27, 2005 in Portland, OR (EOR/US Inventory)
- Risk Assessment & Management of Geologic Sequestration Sites
    - September 28-29, 2005 in Portland, OR
- International Symposium on Site Characterization
    - March 20-22, 2006 at LBNL in Berkeley, CA
- State Regulators Workshop on Geologic Sequestration of CO_2
    - January 24, 2007 in San Antonio, TX
- Workshop on Well Construction and Mechanical Integrity Testing
    - March 14, 2007 Albuquerque, NM
- Workshop on Siting Considerations for Geologic Sequestration of CO_2
    - July 10-11, 2007 in Washington, DC



Workshop Action Plan

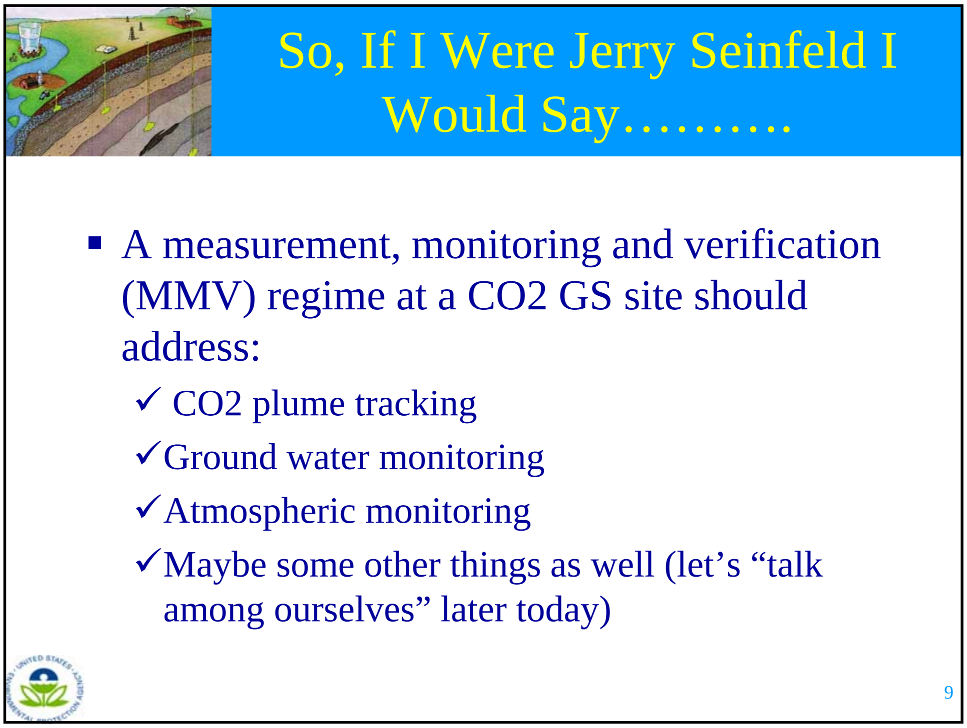
- We have collected research needs from each of these workshops
- There is a long and varied list of topics, ranging from simple (improve abandoned well inventory) to complex (modeling of fluid movement)
- We have been developing an action plan to address additional needs via all avenues (EPA, ORD, DOE, RSPs, etc.) to better inform our GS management framework

Next Workshops

- Monitoring, Measurement and Verification Workshop- January 16, 2008 at GWPC Annual UIC Meeting, New Orleans, LA
- Financial Responsibility and Risk Analysis Workshop – Pending proposed GS rule development schedule

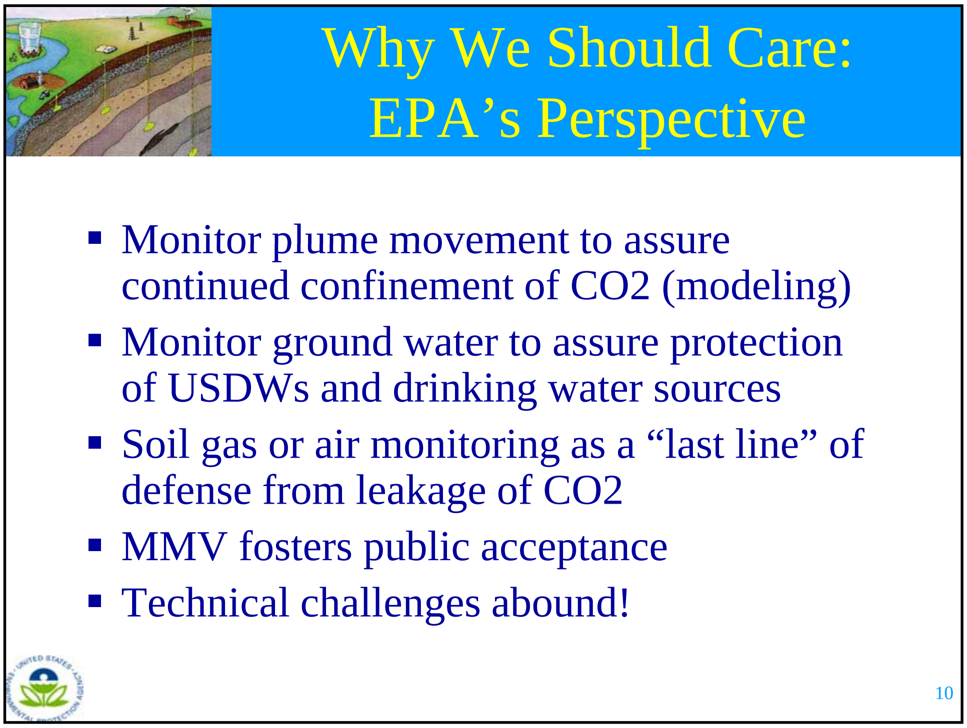
Recent CO2 GS MMV Workshops of Particular Note

- 4th Int’l. Energy Assoc. (IEA) Monitoring Network – Nov. 7-9, 2007 (Edmonton)
- Amer. Geophys. Union (AGU): *Session on Monitoring and Modeling* – Dec. 10, 2007 (San Francisco)
- DOE/NETL RCSP 2007 Annual Meeting: *MMV Special Session*- December 14, 2008



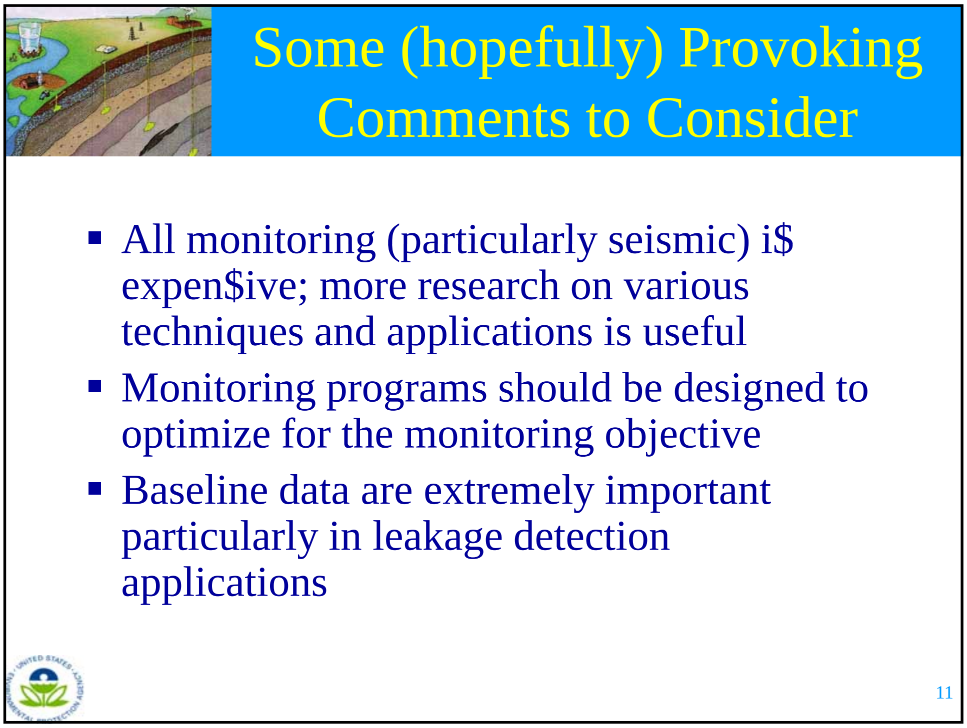
So, If I Were Jerry Seinfeld I Would Say……….

- A measurement, monitoring and verification (MMV) regime at a CO2 GS site should address:
  - ✓ CO2 plume tracking
  - ✓ Ground water monitoring
  - ✓ Atmospheric monitoring
  - ✓ Maybe some other things as well (let’s “talk among ourselves” later today)



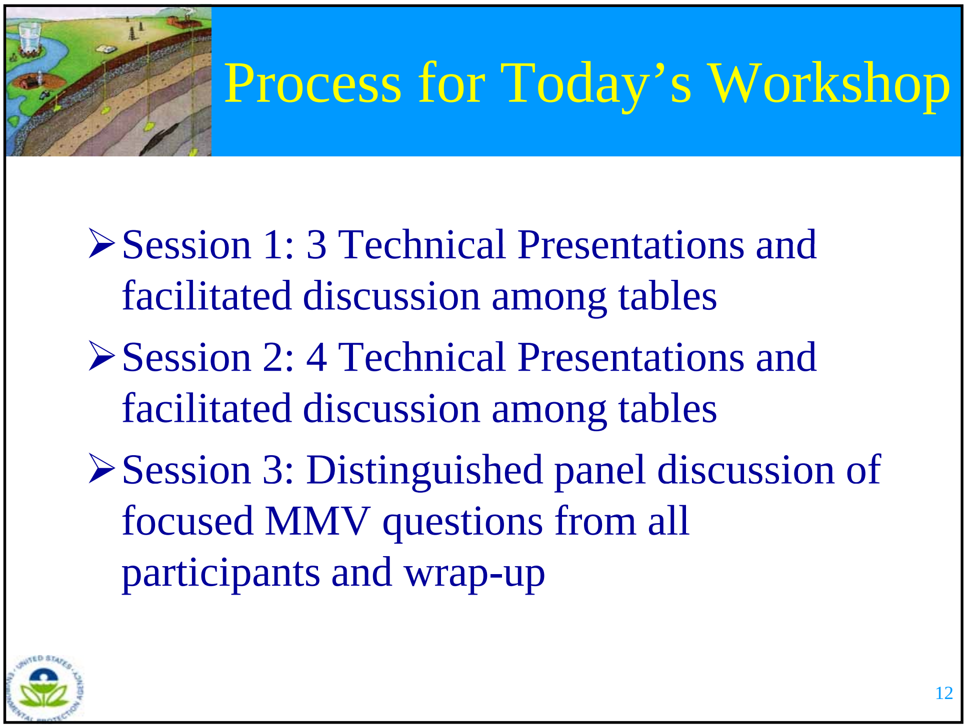
Why We Should Care: EPA’s Perspective

- Monitor plume movement to assure continued confinement of CO2 (modeling)
- Monitor ground water to assure protection of USDWs and drinking water sources
- Soil gas or air monitoring as a “last line” of defense from leakage of CO2
- MMV fosters public acceptance
- Technical challenges abound!



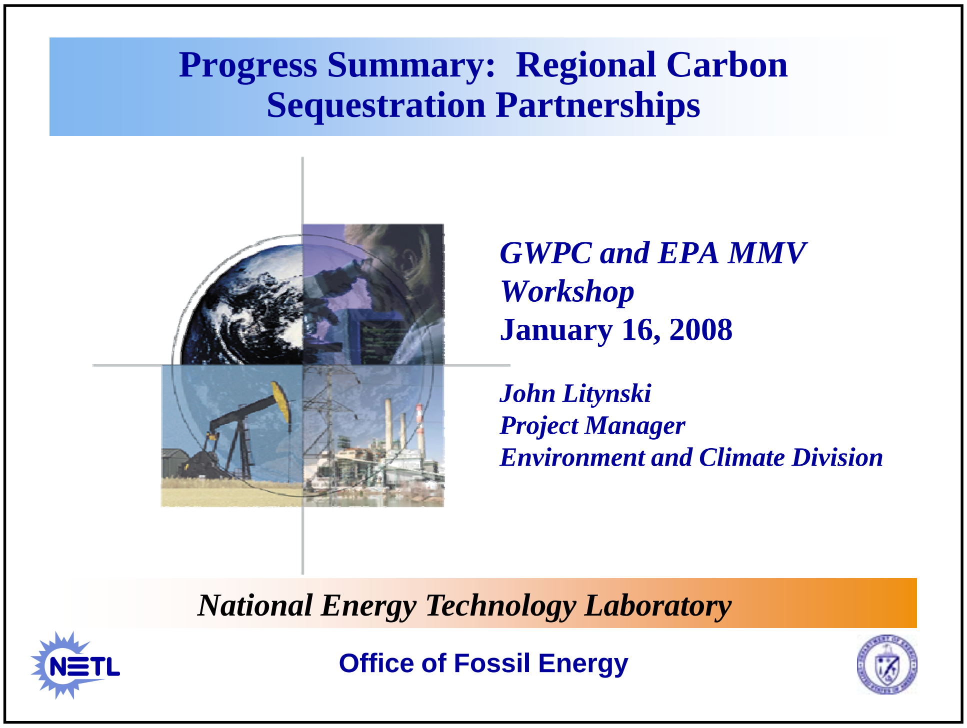
Some (hopefully) Provoking Comments to Consider

- All monitoring (particularly seismic) i$ expen$ive; more research on various techniques and applications is useful
- Monitoring programs should be designed to optimize for the monitoring objective
- Baseline data are extremely important particularly in leakage detection applications



Process for Today’s Workshop

- Session 1: 3 Technical Presentations and facilitated discussion among tables
- Session 2: 4 Technical Presentations and facilitated discussion among tables
- Session 3: Distinguished panel discussion of focused MMV questions from all participants and wrap-up



Progress Summary: Regional Carbon Sequestration Partnerships

GWPC and EPA MMV Workshop
January 16, 2008

John Litynski
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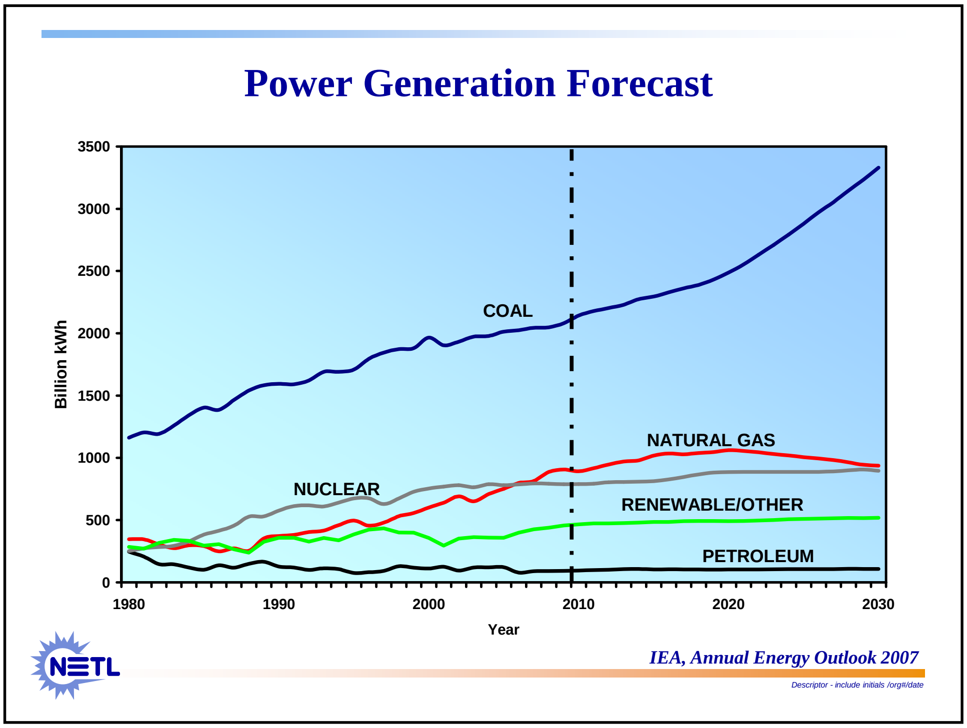
Environment and Climate Division

National Energy Technology Laboratory

Office of Fossil Energy



Power Generation Forecast

IEA, Annual Energy Outlook 2007

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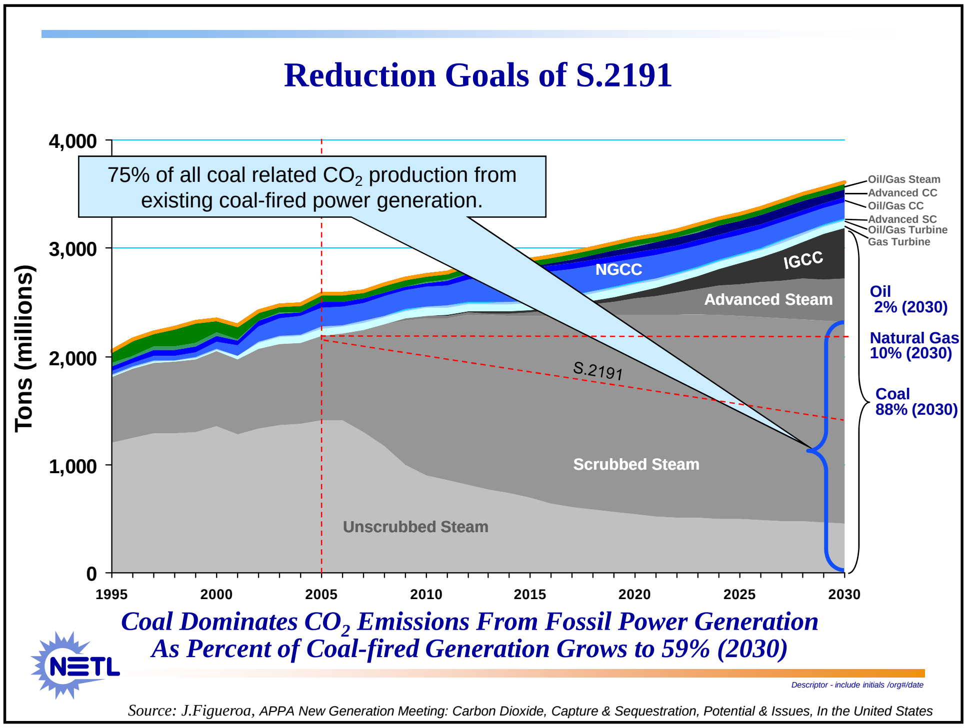

Reduction Goals of S.2191

Coal Dominates CO_2 Emissions From Fossil Power Generation
As Percent of Coal-fired Generation Grows to 59% (2030)

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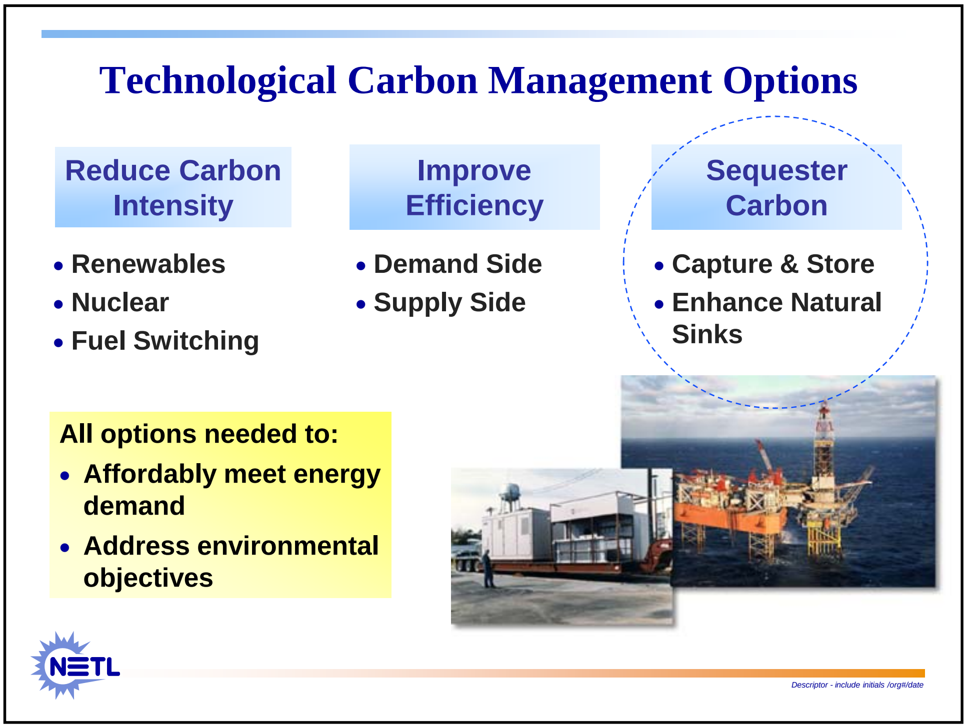
Source: J.Figueroa, *APPA New Generation Meeting: Carbon Dioxide, Capture & Sequestration, Potential & Issues, In the United States*



Technological Carbon Management Options

Reduce Carbon Intensity
- Renewables
- Nuclear
- Fuel Switching

Improve Efficiency
- Demand Side
- Supply Side

Sequester Carbon
- Capture & Store
- Enhance Natural Sinks

All options needed to:
- **Affordably meet energy demand**
- **Address environmental objectives**

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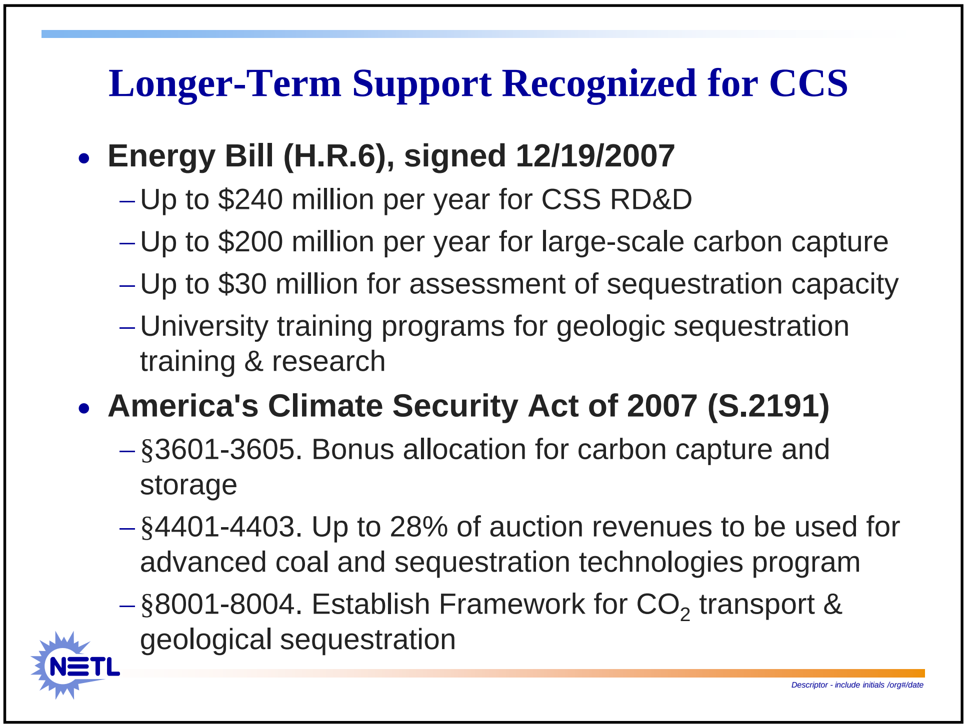

Longer-Term Support Recognized for CCS

- **Energy Bill (H.R.6), signed 12/19/2007**
  - Up to $240 million per year for CSS RD&D
  - Up to $200 million per year for large-scale carbon capture
  - Up to $30 million for assessment of sequestration capacity
  - University training programs for geologic sequestration training & research
- **America's Climate Security Act of 2007 (S.2191)**
  - §3601-3605. Bonus allocation for carbon capture and storage
  - §4401-4403. Up to 28% of auction revenues to be used for advanced coal and sequestration technologies program
  - §8001-8004. Establish Framework for CO_2 transport & geological sequestration

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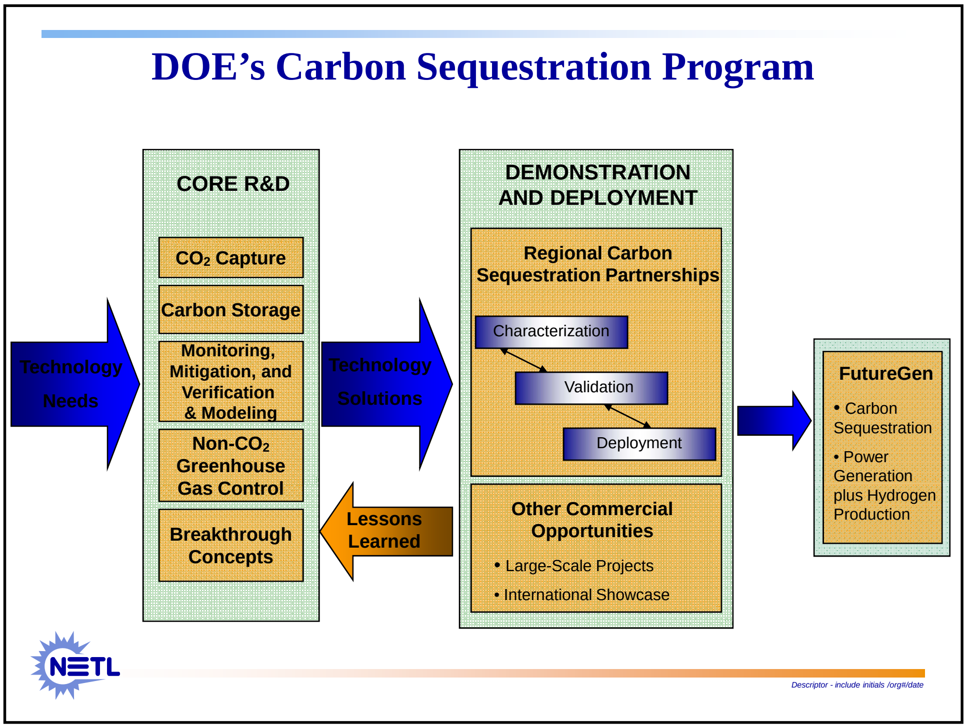

DOE’s Carbon Sequestration Program

Technology Needs

CORE R&D

- CO_2 Capture
- Carbon Storage
- Monitoring, Mitigation, and Verification & Modeling
- Non-CO_2 Greenhouse Gas Control
- Breakthrough Concepts

Technology Solutions

Lessons Learned

DEMONSTRATION AND DEPLOYMENT

Regional Carbon Sequestration Partnerships

Characterization

Validation

Deployment

Other Commercial Opportunities

- Large-Scale Projects
- International Showcase

FutureGen

- Carbon Sequestration
- Power Generation plus Hydrogen Production

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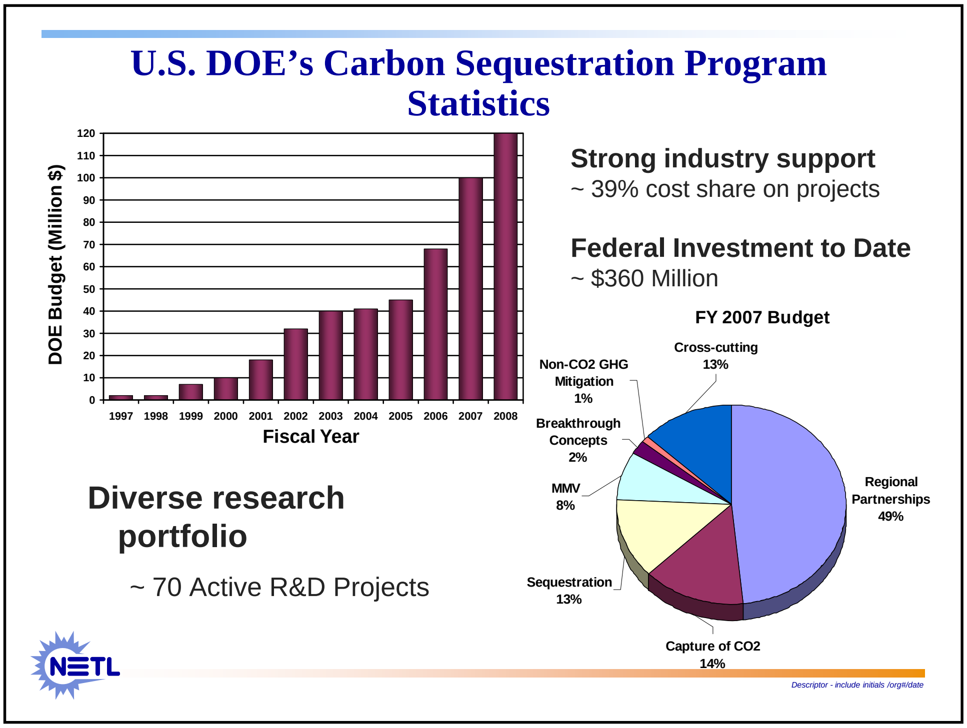

U.S. DOE's Carbon Sequestration Program Statistics

Strong industry support

~ 39% cost share on projects

Federal Investment to Date

~ $360 Million

FY 2007 Budget

Diverse research portfolio

~ 70 Active R&D Projects

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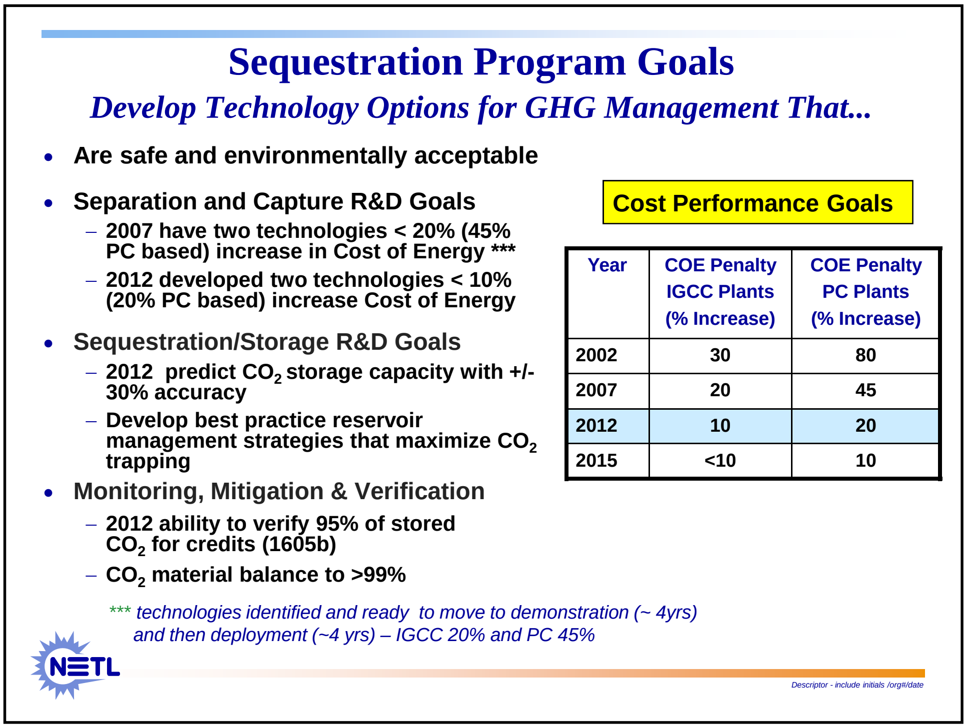

Sequestration Program Goals

Develop Technology Options for GHG Management That...

- **Are safe and environmentally acceptable**
- **Separation and Capture R&D Goals**
  - **2007 have two technologies < 20% (45% PC based) increase in Cost of Energy *****
  - **2012 developed two technologies < 10% (20% PC based) increase Cost of Energy**
- **Sequestration/Storage R&D Goals**
  - **2012 predict CO_2 storage capacity with +/- 30% accuracy**
  - **Develop best practice reservoir management strategies that maximize CO_2 trapping**
- **Monitoring, Mitigation & Verification**
  - **2012 ability to verify 95% of stored CO_2 for credits (1605b)**
  - **CO_2 material balance to >99%**

Cost Performance Goals

Year	COE Penalty IGCC Plants (% Increase)	COE Penalty PC Plants (% Increase)
2002	30	80
2007	20	45
2012	10	20
2015	<10	10

**** technologies identified and ready to move to demonstration (~ 4yrs) and then deployment (~4 yrs) – IGCC 20% and PC 45%*

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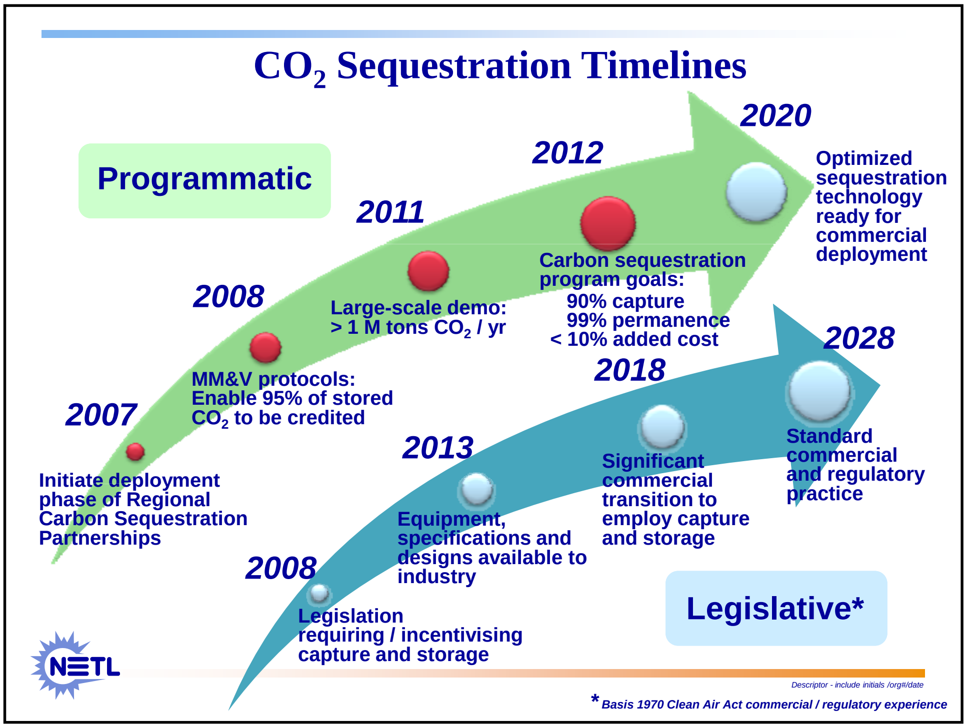


CO_2 Sequestration Timelines

Programmatic

2007 Initiate deployment phase of Regional Carbon Sequestration Partnerships

2008 MM&V protocols: Enable 95% of stored CO_2 to be credited

2011 Large-scale demo: > 1 M tons CO_2 / yr

2012 Carbon sequestration program goals:
90% capture
99% permanence
< 10% added cost

2020 Optimized sequestration technology ready for commercial deployment

Legislative*

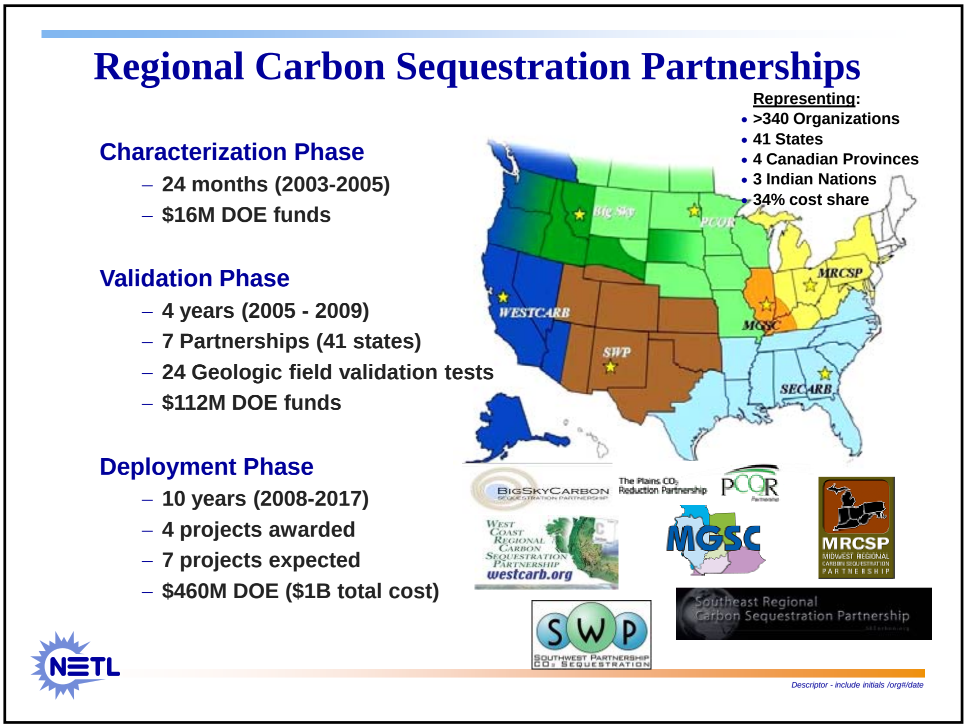
2008 Legislation requiring / incentivising capture and storage

2013 Equipment, specifications and designs available to industry

2018 Significant commercial transition to employ capture and storage

2028 Standard commercial and regulatory practice

* Basis 1970 Clean Air Act commercial / regulatory experience



Regional Carbon Sequestration Partnerships

Characterization Phase
- 24 months (2003-2005)
- $16M DOE funds

Validation Phase
- 4 years (2005 - 2009)
- 7 Partnerships (41 states)
- 24 Geologic field validation tests
- $112M DOE funds

Deployment Phase
- 10 years (2008-2017)
- 4 projects awarded
- 7 projects expected
- $460M DOE ($1B total cost)

Representing:
- >340 Organizations
- 41 States
- 4 Canadian Provinces
- 3 Indian Nations
- 34% cost share

National Atlas Resource Assessment

CO_2 Sources (Giga Tons)

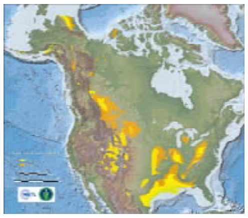
	CO_2 Emission	Number of Facilities
CO_2 Sources	3.8	4,365

North American CO_2 Storage Potential (Giga Tons)

Sink Type	Low	High
Saline Formations	1,014	3,724
Unmineable Coal Seams	173	203
Oil and Gas Fields	90	90

Saline Formations

Unmineable Coal Seams



Oil and Gas Fields

Available for download at http://www.netl.doe.gov/publications/carbon_seq/refshelf.html

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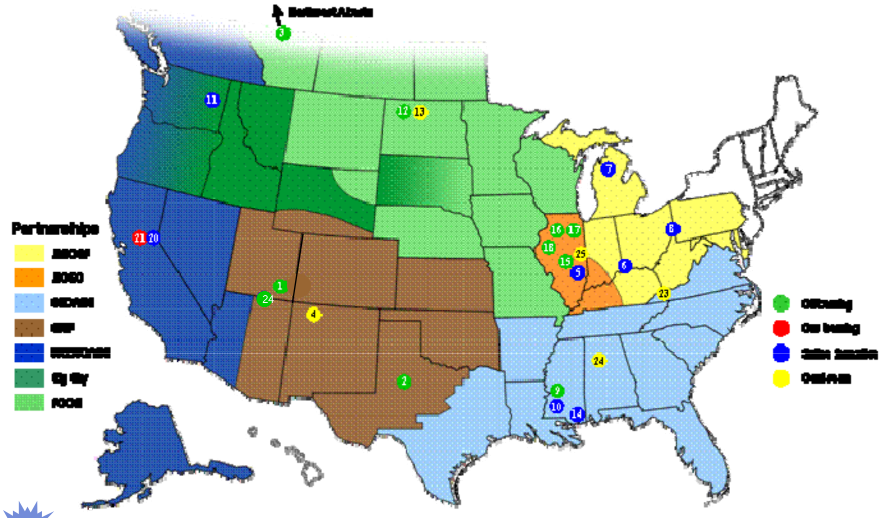
Field Validation Tests
Phase II Field Validation Tests



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Regional Carbon Sequestration Partnerships Phase II Projects

- **Twenty-four Active projects**
  - – Variety of Federal and State Agencies Involved
    - Reflect Diversity of Project Types
    - Reflect Differences in Primacy
- **Permitting Agency**
  - – State – 19
  - – Federal – 4
  - – Joint – 1
- **UIC Class**
  - – Class I – 1 *(activities being merged with Phase III)*
  - – Class II – 15 *(300 – 900,000 tons of CO_2)*
  - – Class V – 7 *(1,000 – 30,000 tons CO_2)*
  - – Other – 1 (Acid Gas In Canada) *(90,000 tons CO_2)*

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Phase II: Coal Seam Projects Summary

Project	Target Formation	Target Depth	Injection Total	2007 Project Highlights	2008 Plans
SWP – San Juan Basin	Upper Createaceous Fruitland Coals	3,200 feet	82,700 tons CO_2	•Baseline Complete •Injection Began 12/2007 •3D Reservoir Modeling	•Complete Injection 12/2008 •Post Injection MMV
SECARB – Black Warrior	Pennsylvanian-age Pottsville Shale Formation	2,500 feet	1,000 tons CO_2	•Test Site Selected •Pre-injection Monitoring •Technology Transfer Outreach	•Drilling Begins: Q2-2008 •Injection Begins: Q3-2008 •Injection MMV
SECARB – Central Appalachian	Pocahontas and Lee Sandstone	1,850 feet	1,000 tons CO_2	•Reservoir Modeling (Prelim) •Test Site Selected •Technology Transfer Outreach	•Drilling Begins: 3/2008 •Install monitoring tools •Injection Begins: 7/2008
PCOR – Williston Basin	Lignite Coal in Williston Basin	1,200 feet	1,0000 tons CO_2	•Well Drilling and Logging •Canister Tests Underway •Models (geologic & numerical)	•Injection Begin: 9/2008 •MMV Events Begin
MGSC – Illinois Basin	Pennsylvanian Carbondale Coal Seam Formation	900 feet	700 tons CO_2	•Two Wells Complete: 2/2007 •Site MMV Activities	•Core & Well Testing •Injection Begins: 5/2008

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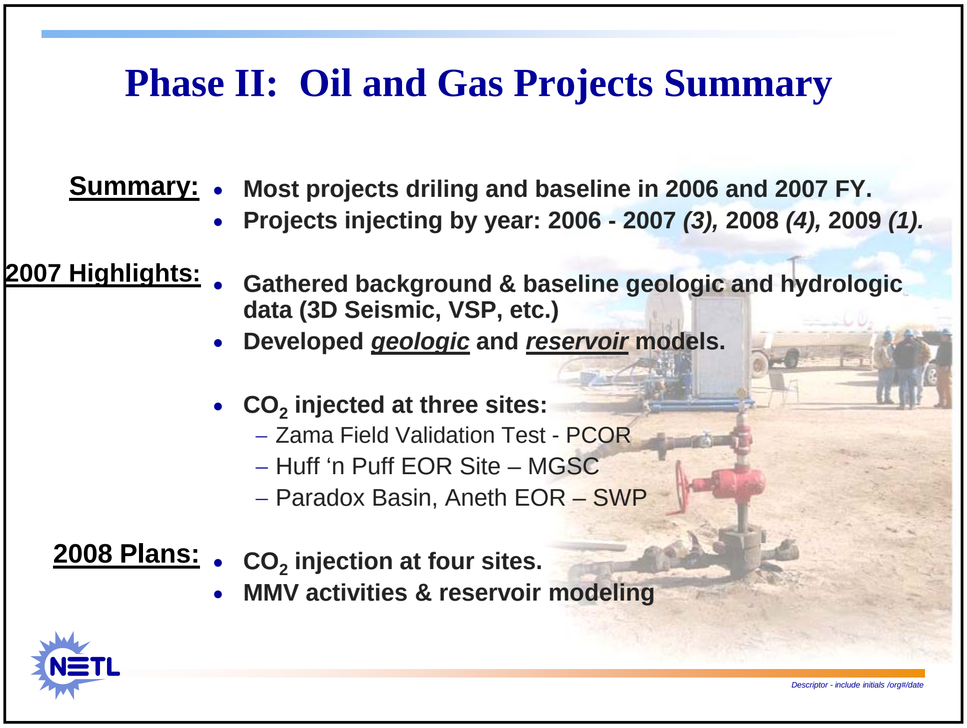

Phase II: Oil and Gas Projects Summary

Summary:
- **Most projects driling and baseline in 2006 and 2007 FY.**
- **Projects injecting by year: 2006 - 2007 *(3)*, 2008 *(4)*, 2009 *(1)*.**

2007 Highlights:
- **Gathered background & baseline geologic and hydrologic data (3D Seismic, VSP, etc.)**
- **Developed *geologic* and *reservoir* models.**
- **CO_2 injected at three sites:**
  - Zama Field Validation Test - PCOR
  - Huff 'n Puff EOR Site – MGSC
  - Paradox Basin, Aneth EOR – SWP

2008 Plans:
- **CO_2 injection at four sites.**
- **MMV activities & reservoir modeling**

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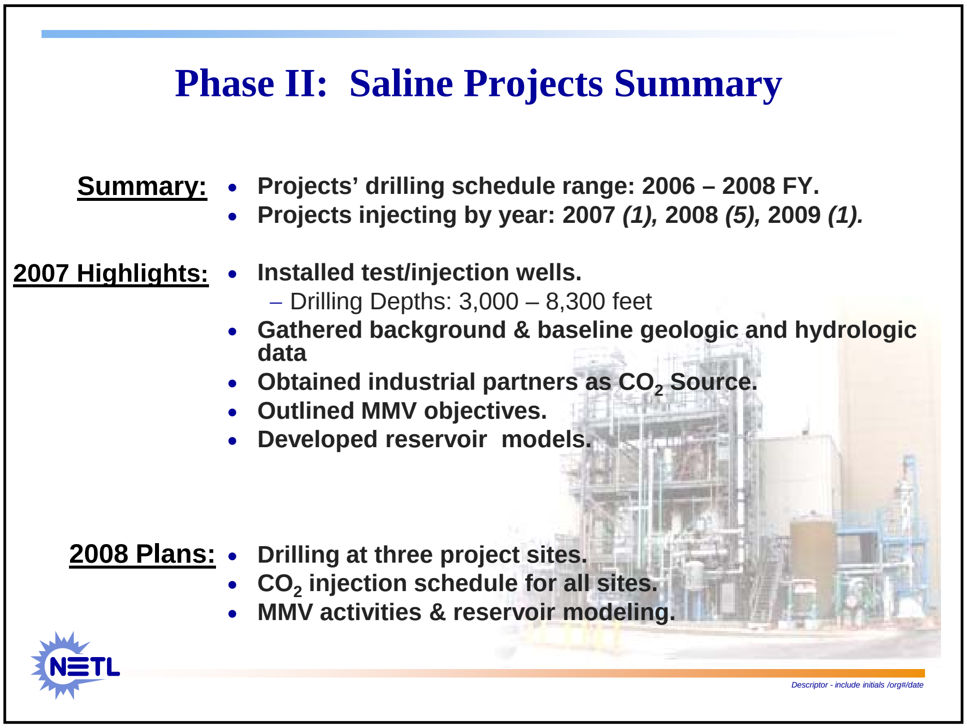

Phase II: Saline Projects Summary

Summary:
- **Projects' drilling schedule range: 2006 – 2008 FY.**
- **Projects injecting by year: 2007 *(1)*, 2008 *(5)*, 2009 *(1)*.**

2007 Highlights:
- **Installed test/injection wells.**
  - Drilling Depths: 3,000 – 8,300 feet
- **Gathered background & baseline geologic and hydrologic data**
- **Obtained industrial partners as CO_2 Source.**
- **Outlined MMV objectives.**
- **Developed reservoir models.**

2008 Plans:
- **Drilling at three project sites.**
- **CO_2 injection schedule for all sites.**
- **MMV activities & reservoir modeling.**

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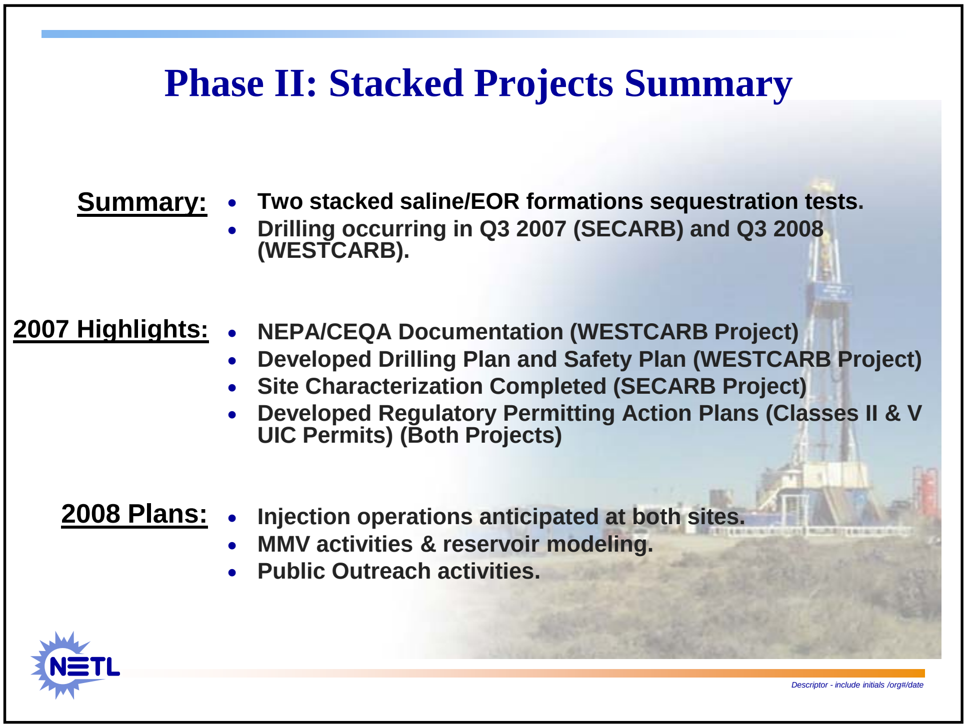

Phase II: Stacked Projects Summary

Summary:

- Two stacked saline/EOR formations sequestration tests.
- Drilling occurring in Q3 2007 (SECARB) and Q3 2008 (WESTCARB).

2007 Highlights:

- NEPA/CEQA Documentation (WESTCARB Project)
- Developed Drilling Plan and Safety Plan (WESTCARB Project)
- Site Characterization Completed (SECARB Project)
- Developed Regulatory Permitting Action Plans (Classes II & V UIC Permits) (Both Projects)

2008 Plans:

- Injection operations anticipated at both sites.
- MMV activities & reservoir modeling.
- Public Outreach activities.

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Phase III Overview

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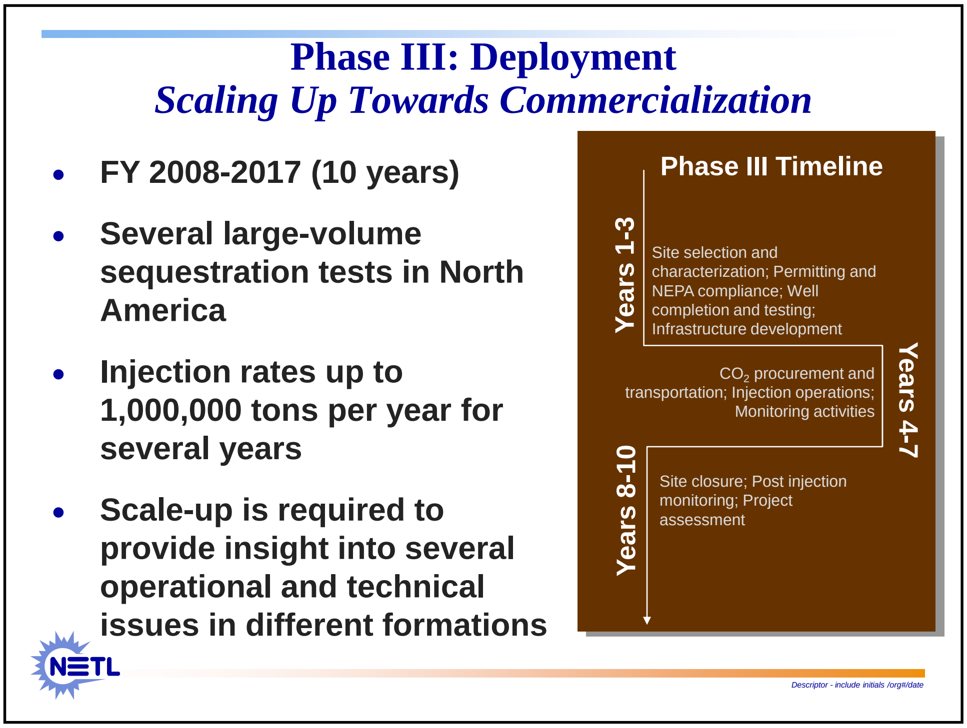

Phase III: Deployment
Scaling Up Towards Commercialization

- **FY 2008-2017 (10 years)**
- **Several large-volume sequestration tests in North America**
- **Injection rates up to 1,000,000 tons per year for several years**
- **Scale-up is required to provide insight into several operational and technical issues in different formations**

Phase III Timeline

Years 1-3
Site selection and characterization; Permitting and NEPA compliance; Well completion and testing; Infrastructure development

Years 4-7
CO_2 procurement and transportation; Injection operations; Monitoring activities

Years 8-10
Site closure; Post injection monitoring; Project assessment

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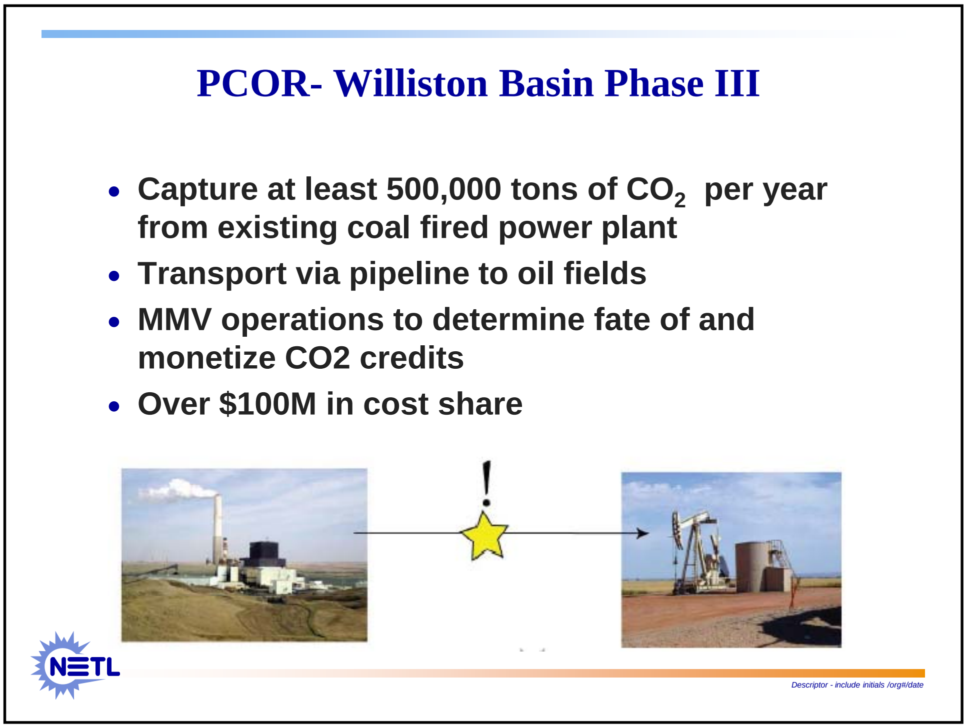

PCOR- Williston Basin Phase III

- **Capture at least 500,000 tons of CO_2 per year from existing coal fired power plant**
- **Transport via pipeline to oil fields**
- **MMV operations to determine fate of and monetize CO2 credits**
- **Over $100M in cost share**

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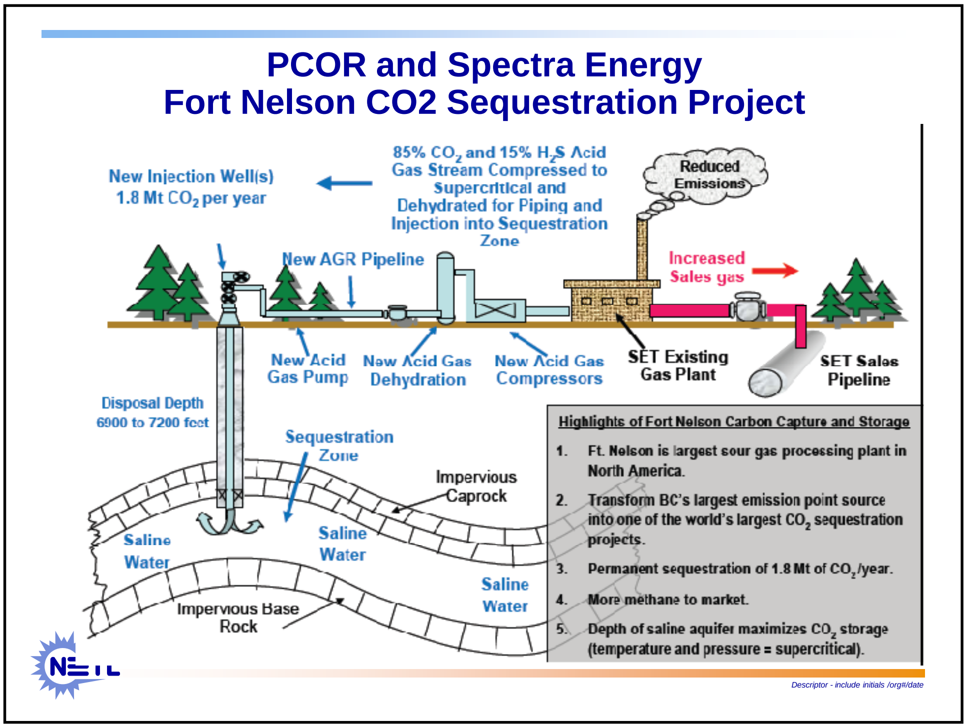

PCOR and Spectra Energy
Fort Nelson CO2 Sequestration Project

Highlights of Fort Nelson Carbon Capture and Storage

1. Ft. Nelson is largest sour gas processing plant in North America.
2. Transform BC's largest emission point source into one of the world's largest CO_2 sequestration projects.
3. Permanent sequestration of 1.8 Mt of CO_2/year.
4. More methane to market.
5. Depth of saline aquifer maximizes CO_2 storage (temperature and pressure = supercritical).

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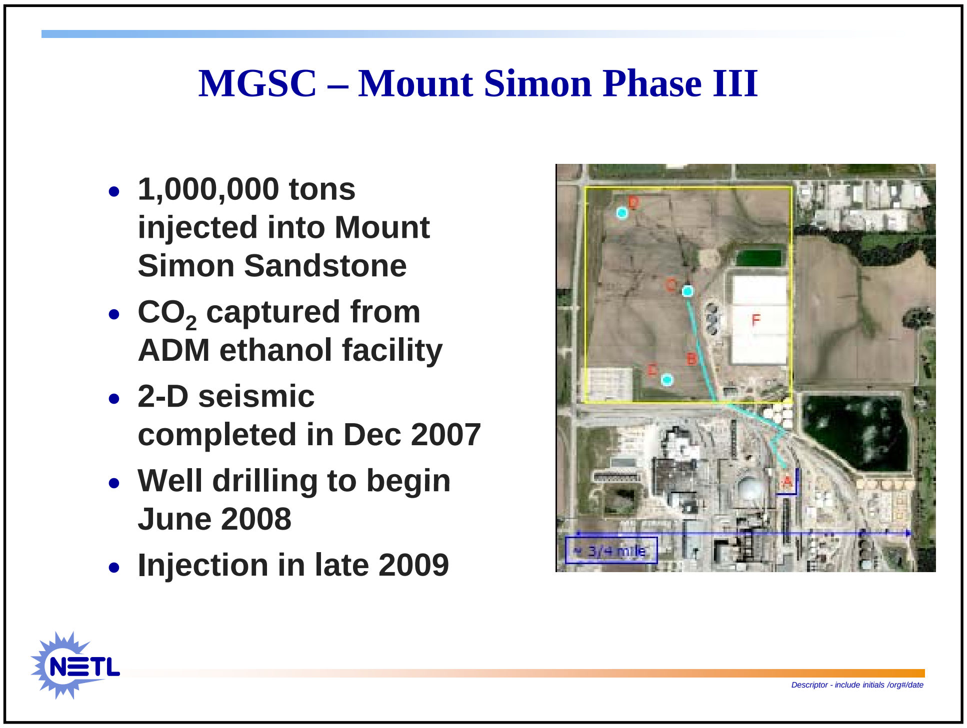

MGSC – Mount Simon Phase III

- 1,000,000 tons injected into Mount Simon Sandstone
- CO_2 captured from ADM ethanol facility
- 2-D seismic completed in Dec 2007
- Well drilling to begin June 2008
- Injection in late 2009

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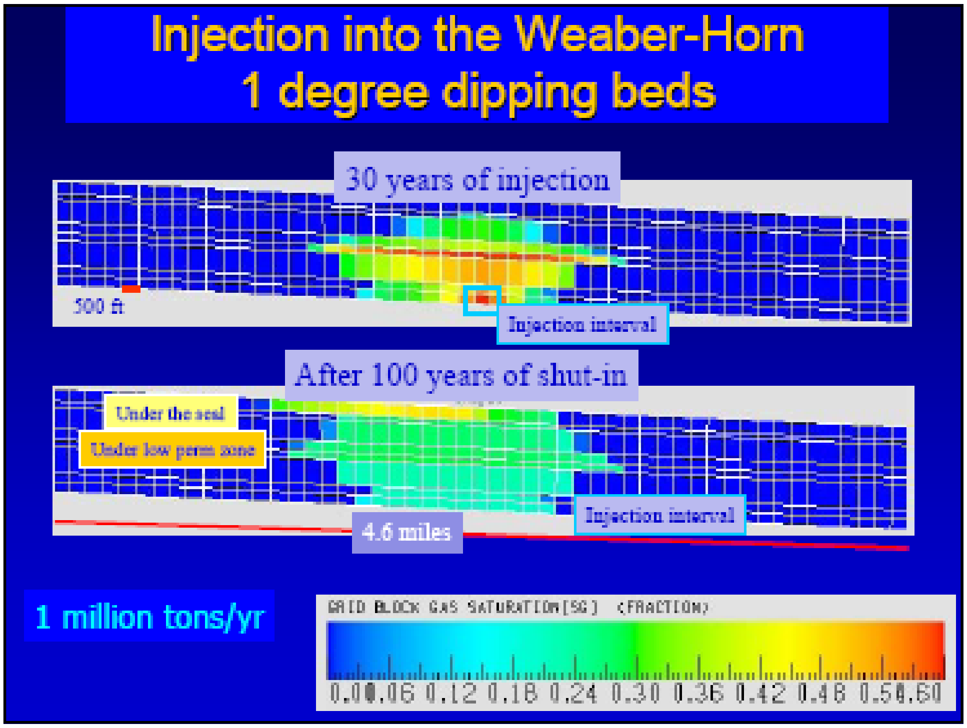
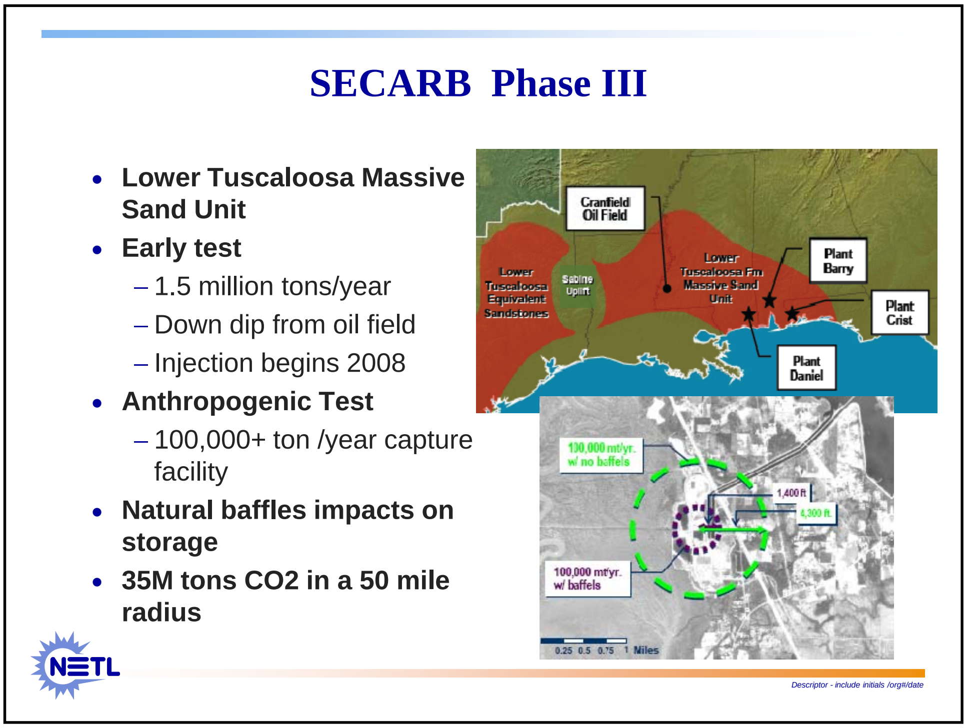


Injection into the Weaber-Horn 1 degree dipping beds

1 million tons/yr



SECARB Phase III

- **Lower Tuscaloosa Massive Sand Unit**
- **Early test**
  - 1.5 million tons/year
  - Down dip from oil field
  - Injection begins 2008
- **Anthropogenic Test**
  - 100,000+ ton /year capture facility
- **Natural baffles impacts on storage**
- **35M tons CO2 in a 50 mile radius**

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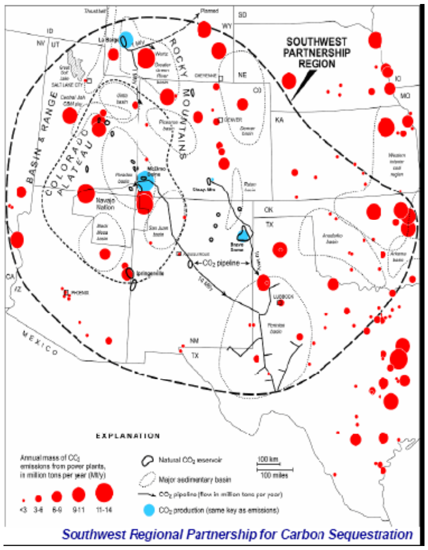
Southwest Partnership Phase III

- Evaluate Jurassic-Triassic Sandstones in the region
- Up to 1 million tons per year for 4 years
- Transition to Commercial IGCC facility at last stage of project
- Injection to begin in early 2009



Southwest Regional Partnership for Carbon Sequestration

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Partnerships

BIGSKYCARBON SEQUESTRATION PARTNERSHIP	Montana State University http://www.bigskyco2.org/
MGSC	University of Illinois, Illinois State Geological Survey http://www.sequestration.org/
MRCSP	Battelle Memorial Institute http://www.mrcsp.org
EERC Plains CO_2 Reduction Partnership	University of North Dakota, Energy & Environmental Research Center http://www.undeerc.org/pcor/
Southeast Regional Carbon Sequestration Partnership	Southern States Energy Board http://www.secarbon.org/
Southwest Regional Partnership on Carbon Sequestration	New Mexico Institute of Mining and Technology http://www.southwestcarbonpartnership.org/
West Coast Regional Carbon Sequestration Partnership westcarb.org	California Energy Commission http://www.westcarb.org/

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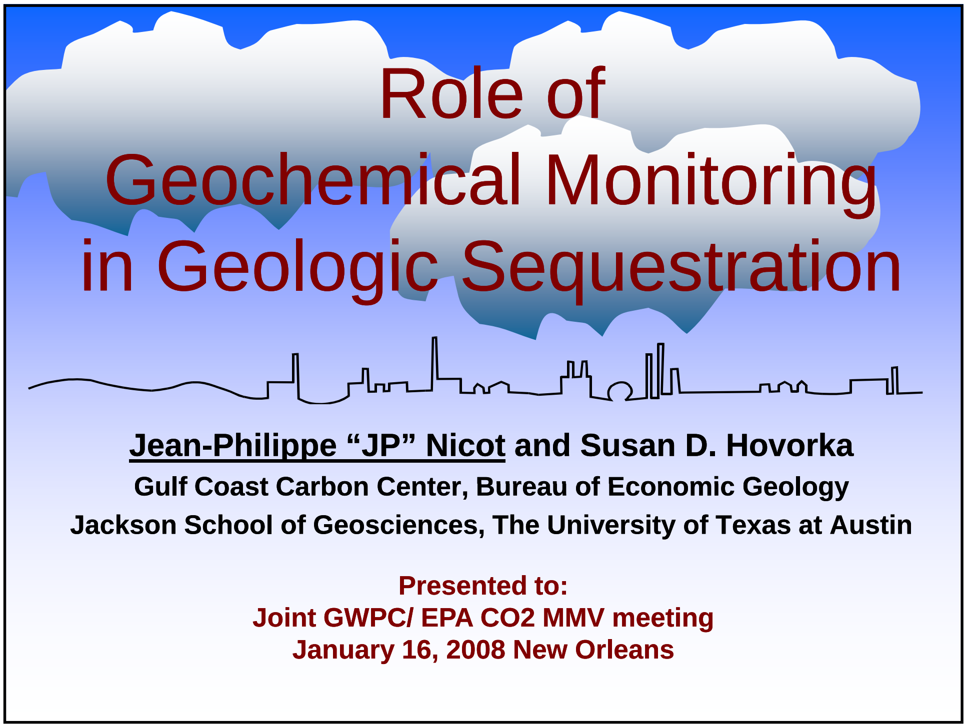

Role of Geochemical Monitoring in Geologic Sequestration

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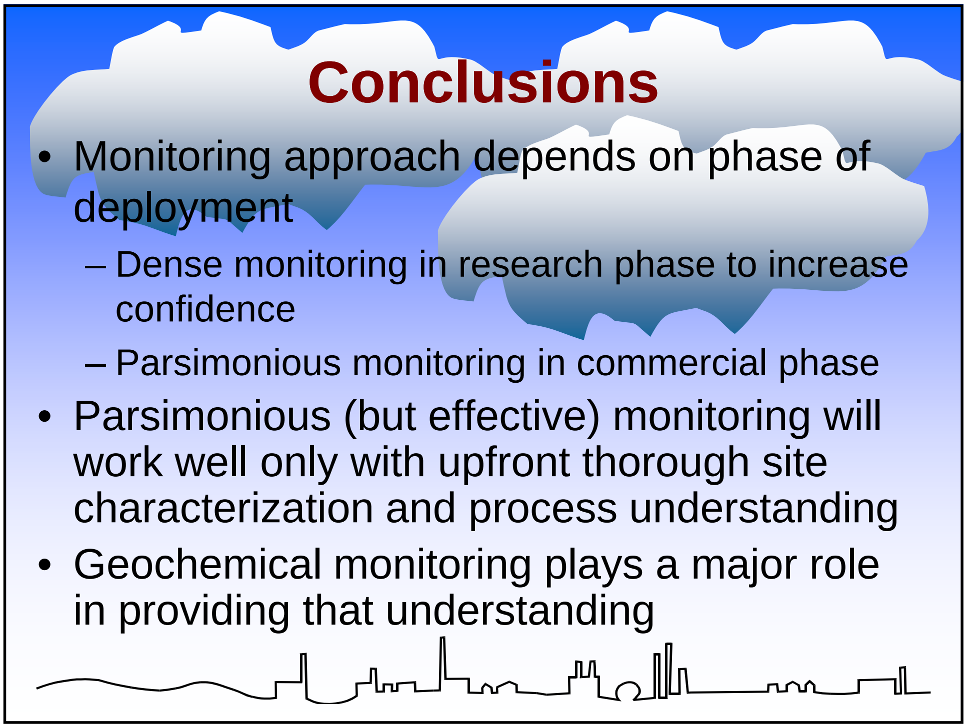
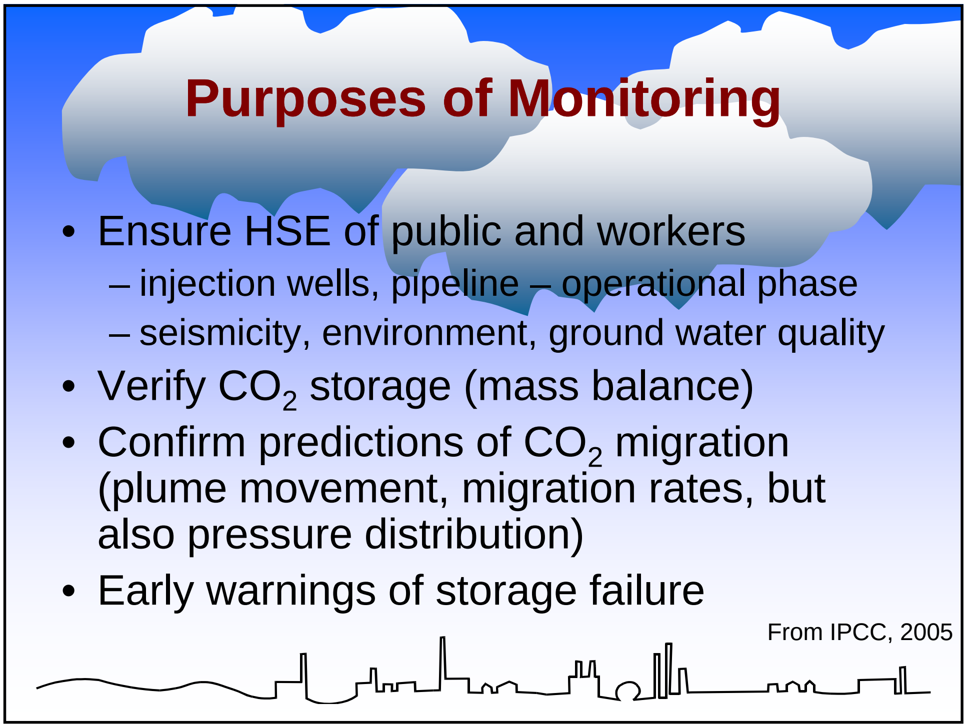
Presented to:
Joint GWPC/ EPA CO2 MMV meeting
January 16, 2008 New Orleans



Conclusions

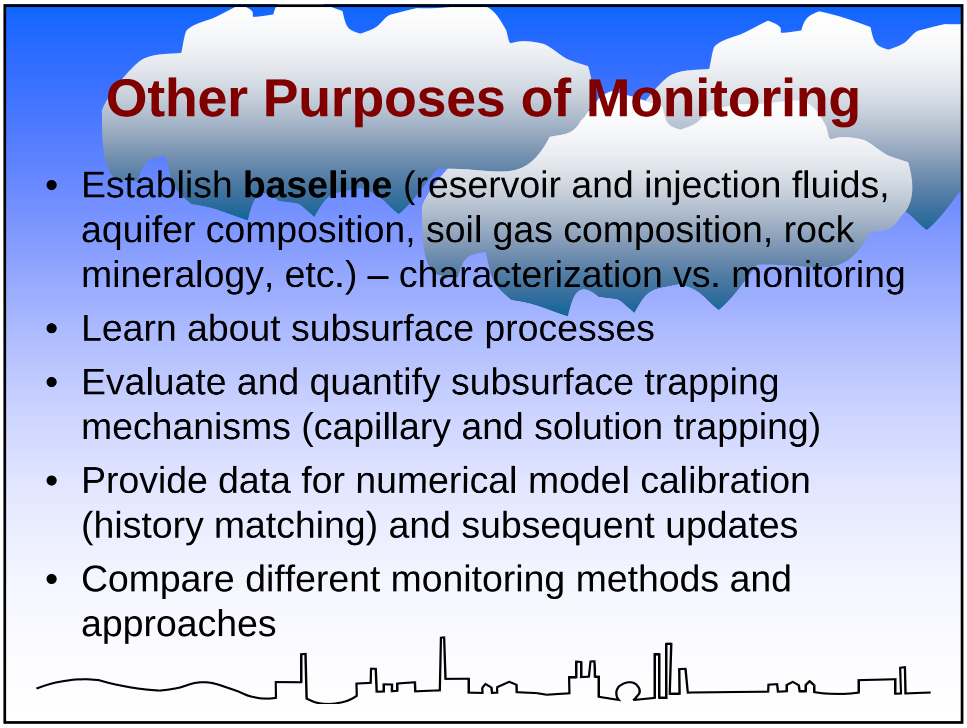
- Monitoring approach depends on phase of deployment
  - Dense monitoring in research phase to increase confidence
  - Parsimonious monitoring in commercial phase
- Parsimonious (but effective) monitoring will work well only with upfront thorough site characterization and process understanding
- Geochemical monitoring plays a major role in providing that understanding



Purposes of Monitoring

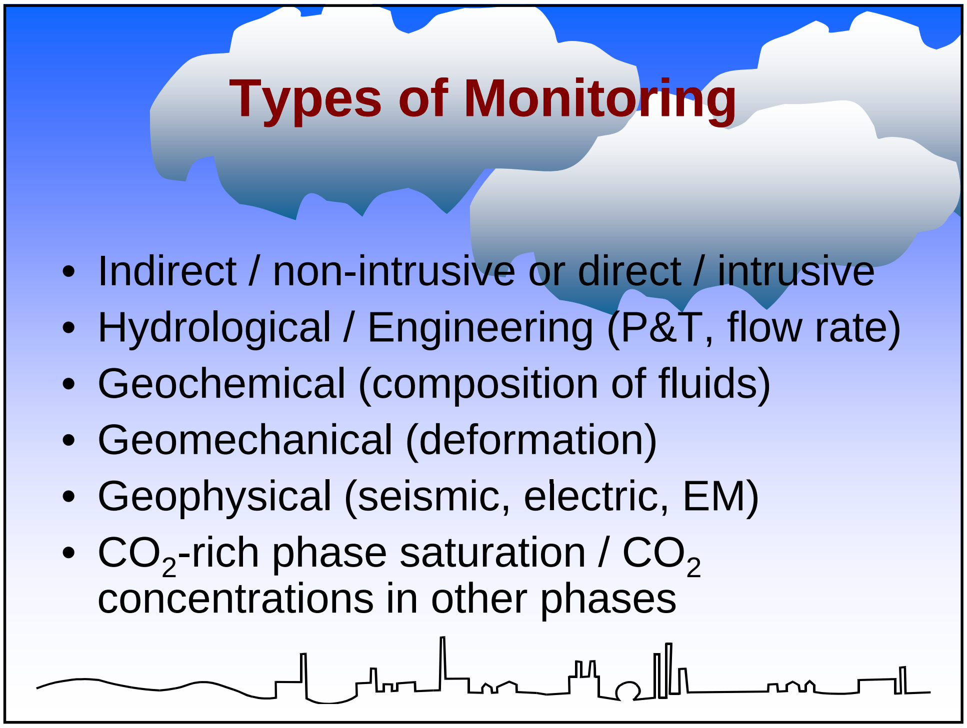
- Ensure HSE of public and workers
  - – injection wells, pipeline – operational phase
  - – seismicity, environment, ground water quality
- Verify CO_2 storage (mass balance)
- Confirm predictions of CO_2 migration (plume movement, migration rates, but also pressure distribution)
- Early warnings of storage failure

From IPCC, 2005



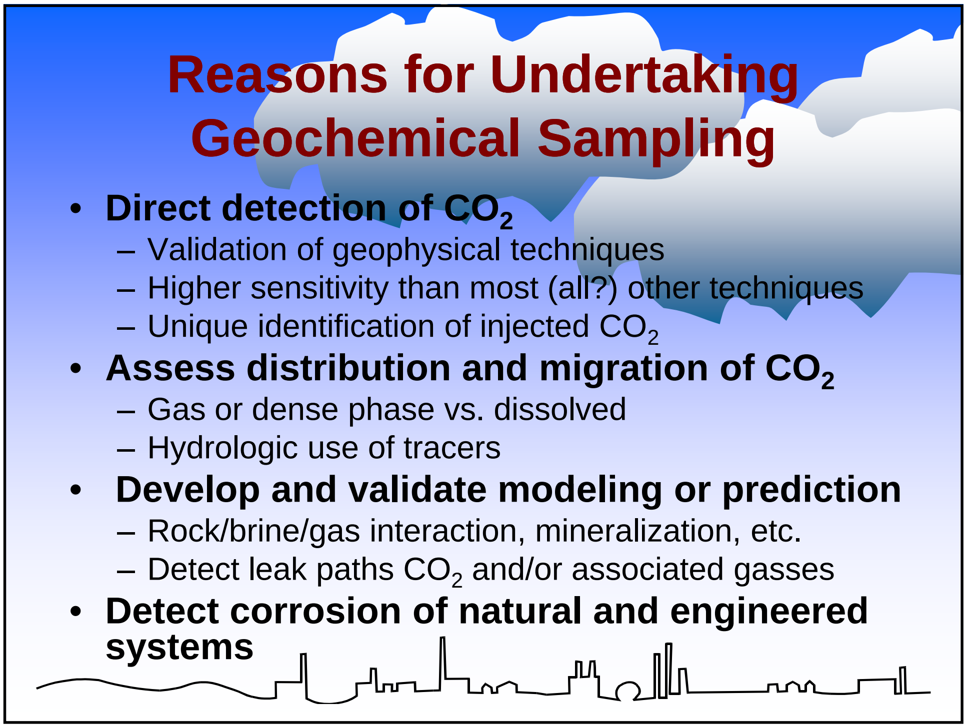
Other Purposes of Monitoring

- Establish **baseline** (reservoir and injection fluids, aquifer composition, soil gas composition, rock mineralogy, etc.) – characterization vs. monitoring
- Learn about subsurface processes
- Evaluate and quantify subsurface trapping mechanisms (capillary and solution trapping)
- Provide data for numerical model calibration (history matching) and subsequent updates
- Compare different monitoring methods and approaches



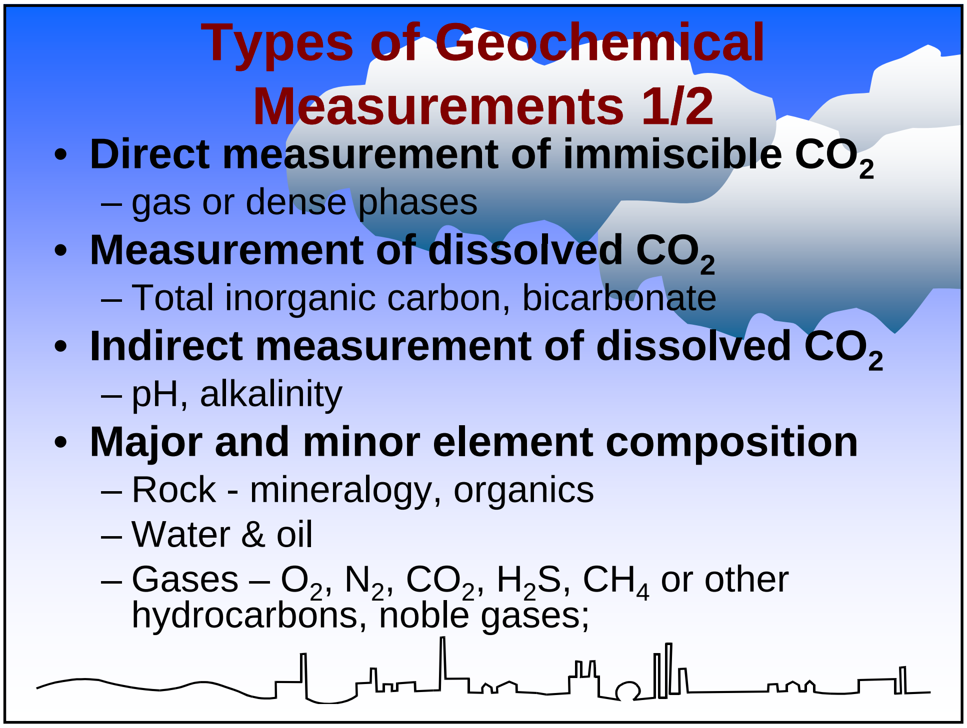
Types of Monitoring

- Indirect / non-intrusive or direct / intrusive
- Hydrological / Engineering (P&T, flow rate)
- Geochemical (composition of fluids)
- Geomechanical (deformation)
- Geophysical (seismic, electric, EM)
- CO_2-rich phase saturation / CO_2 concentrations in other phases



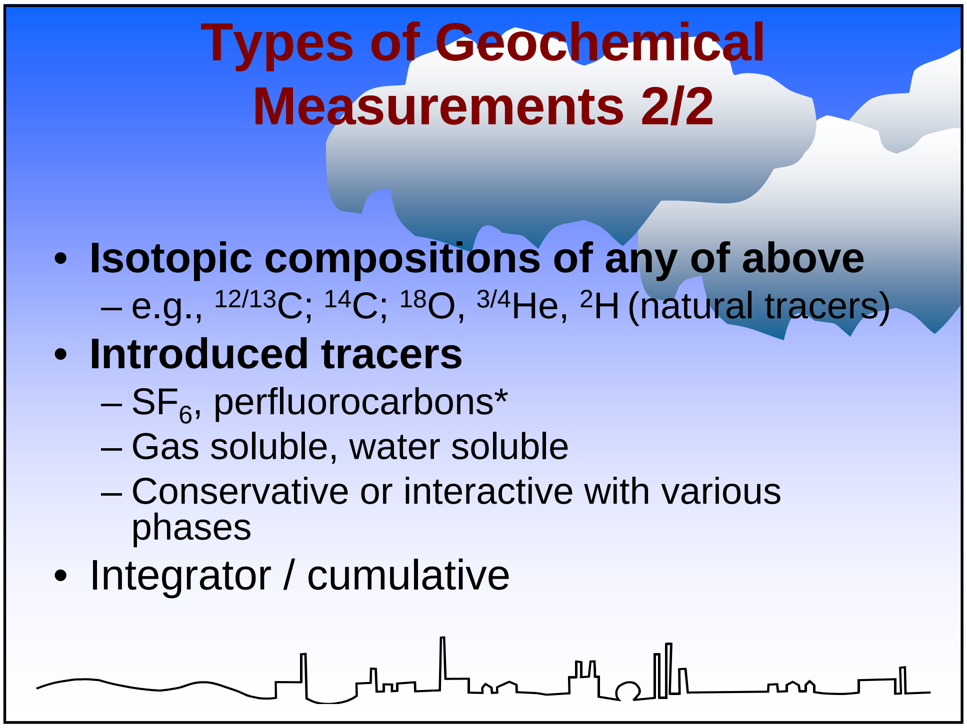
Reasons for Undertaking Geochemical Sampling

- **Direct detection of CO_2**
  - Validation of geophysical techniques
  - Higher sensitivity than most (all?) other techniques
  - Unique identification of injected CO_2
- **Assess distribution and migration of CO_2**
  - Gas or dense phase vs. dissolved
  - Hydrologic use of tracers
- **Develop and validate modeling or prediction**
  - Rock/brine/gas interaction, mineralization, etc.
  - Detect leak paths CO_2 and/or associated gasses
- **Detect corrosion of natural and engineered systems**



Types of Geochemical Measurements 1/2

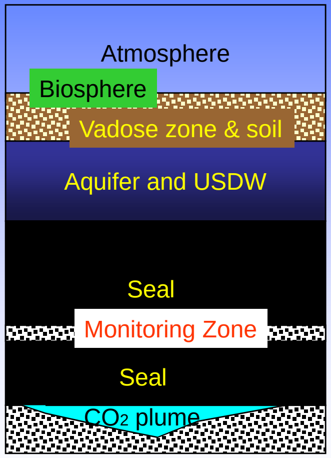
- **Direct measurement of immiscible CO_2**
  - gas or dense phases
- **Measurement of dissolved CO_2**
  - Total inorganic carbon, bicarbonate
- **Indirect measurement of dissolved CO_2**
  - pH, alkalinity
- **Major and minor element composition**
  - Rock - mineralogy, organics
  - Water & oil
  - Gases – O_2, N_2, CO_2, H_2S, CH_4 or other hydrocarbons, noble gases;



Types of Geochemical Measurements 2/2

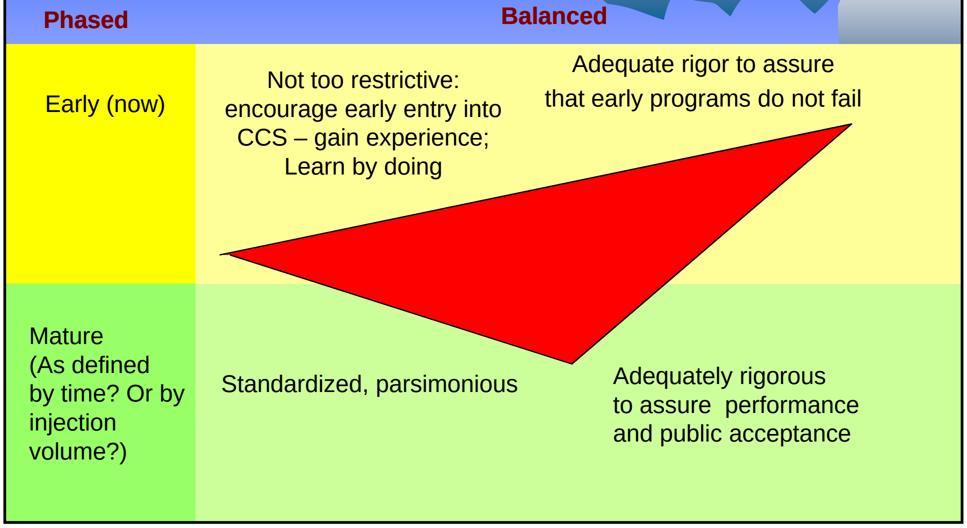
- **Isotopic compositions of any of above**
  - e.g., $^{12/13}C$; ^{14}C; ^{18}O, $^{3/4}He$, ^{2}H (natural tracers)
- **Introduced tracers**
  - SF_6, perfluorocarbons*
  - Gas soluble, water soluble
  - Conservative or interactive with various phases
- Integrator / cumulative

Location of Geochemical Sampling

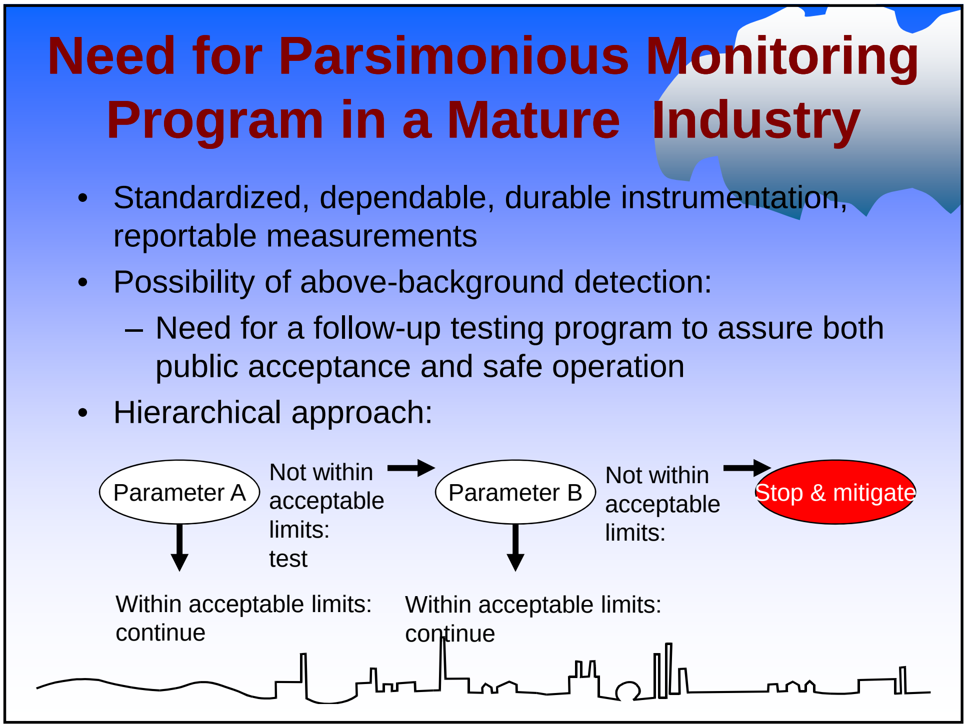


- **Low pressure, lower cost**
  - Atmosphere (dynamic)
  - Soil gas (dynamic – cumul.)
  - Aquifer (cumul.)
- **Downhole / wellhead – high pressure, higher cost**
  - Above zone (first indicator)
  - Seal
  - In plume
  - Outside plume

A Balanced and Phased Approach to Permitting and Monitoring



Phased	Balanced	
Early (now)	Not too restrictive: encourage early entry into CCS – gain experience; Learn by doing	Adequate rigor to assure that early programs do not fail
Mature (As defined by time? Or by injection volume?)	Standardized, parsimonious	Adequately rigorous to assure performance and public acceptance



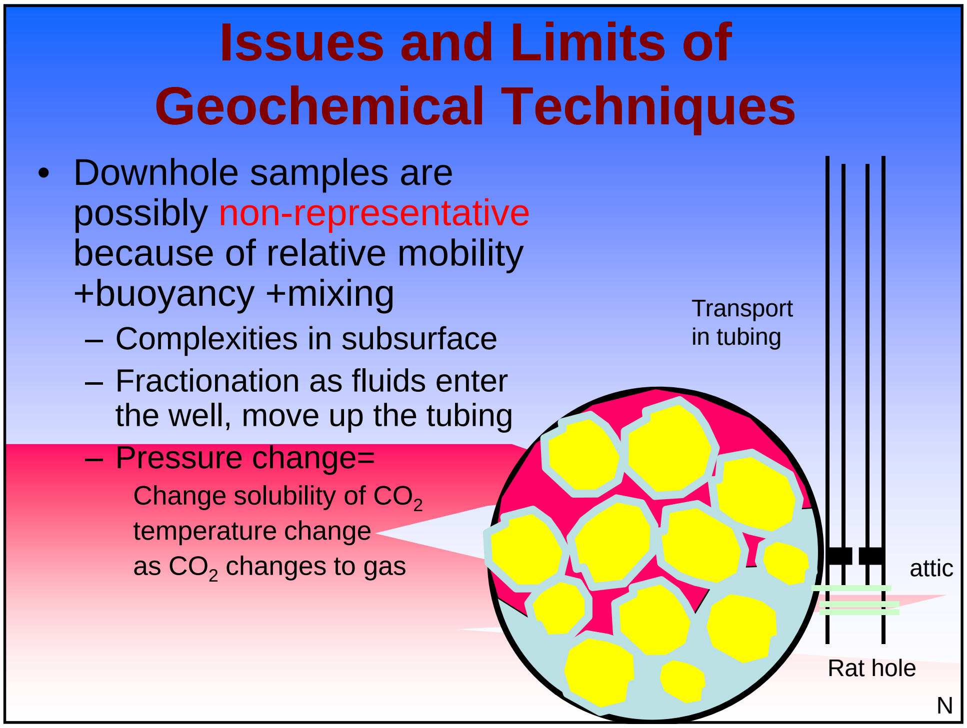
Need for Parsimonious Monitoring Program in a Mature Industry

- Standardized, dependable, durable instrumentation, reportable measurements
- Possibility of above-background detection:
  - Need for a follow-up testing program to assure both public acceptance and safe operation
- Hierarchical approach:

Parameter A → Not within acceptable limits: test → Parameter B → Not within acceptable limits: → Stop & mitigate

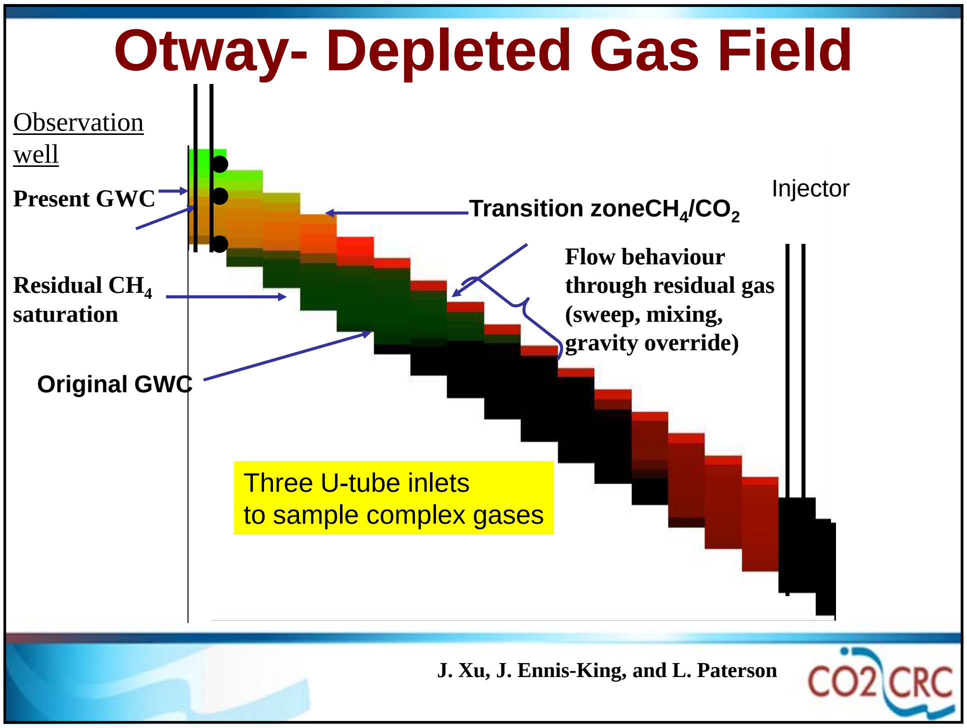
Parameter A ↓ Within acceptable limits: continue

Parameter B ↓ Within acceptable limits: continue



Issues and Limits of Geochemical Techniques

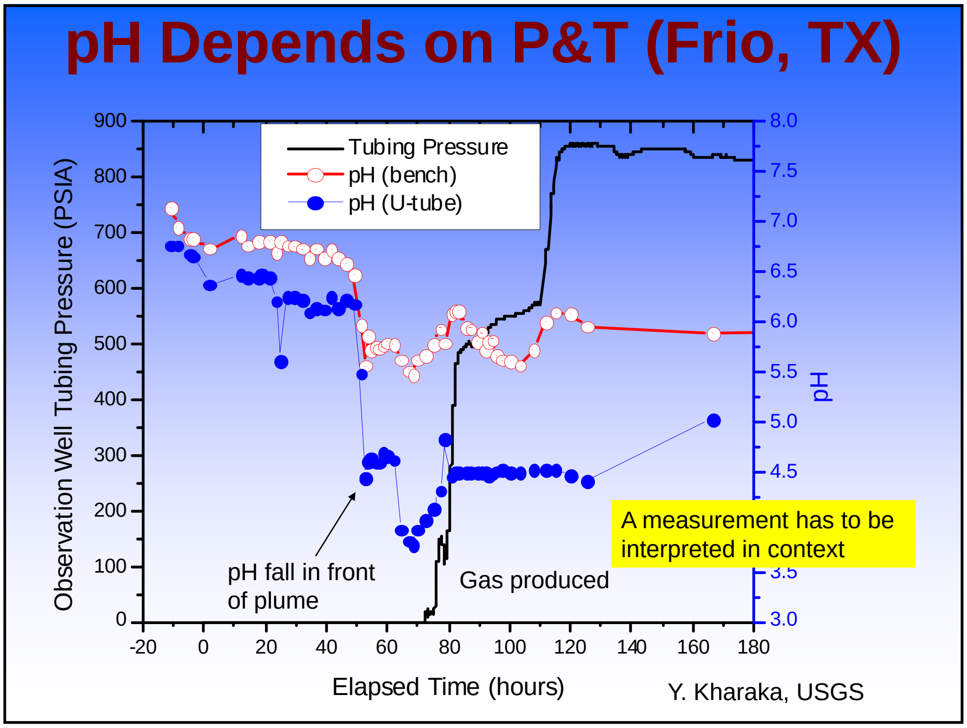
- Downhole samples are possibly non-representative because of relative mobility +buoyancy +mixing
  - Complexities in subsurface
  - Fractionation as fluids enter the well, move up the tubing
  - Pressure change=
    Change solubility of CO_2
    temperature change
    as CO_2 changes to gas



Otway- Depleted Gas Field

Three U-tube inlets to sample complex gases

J. Xu, J. Ennis-King, and L. Paterson



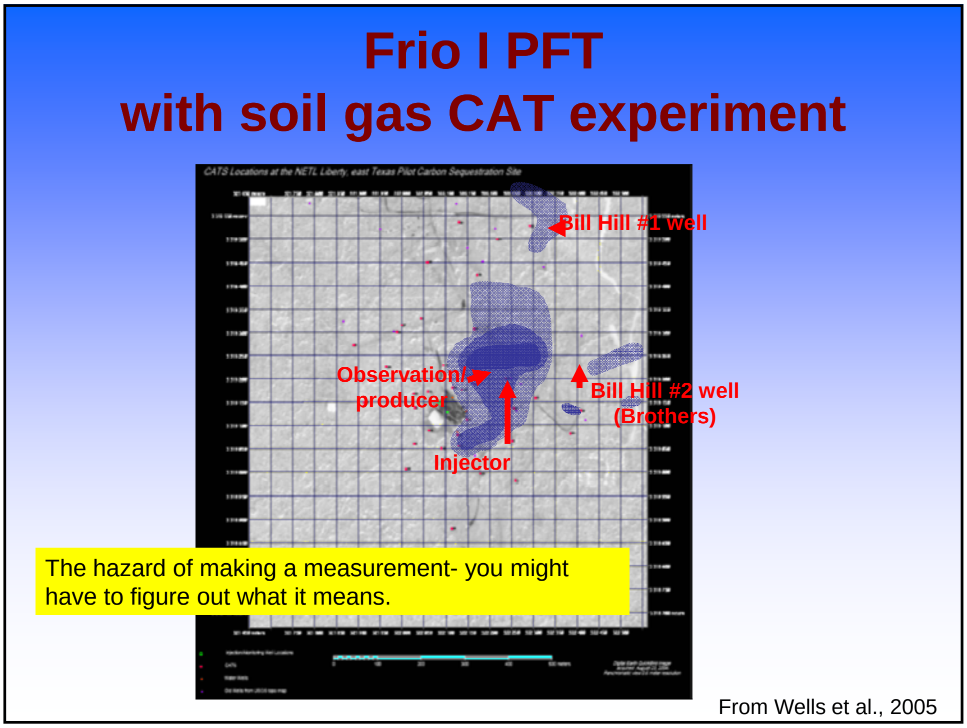
pH Depends on P&T (Frio, TX)

pH fall in front of plume

Gas produced

A measurement has to be interpreted in context

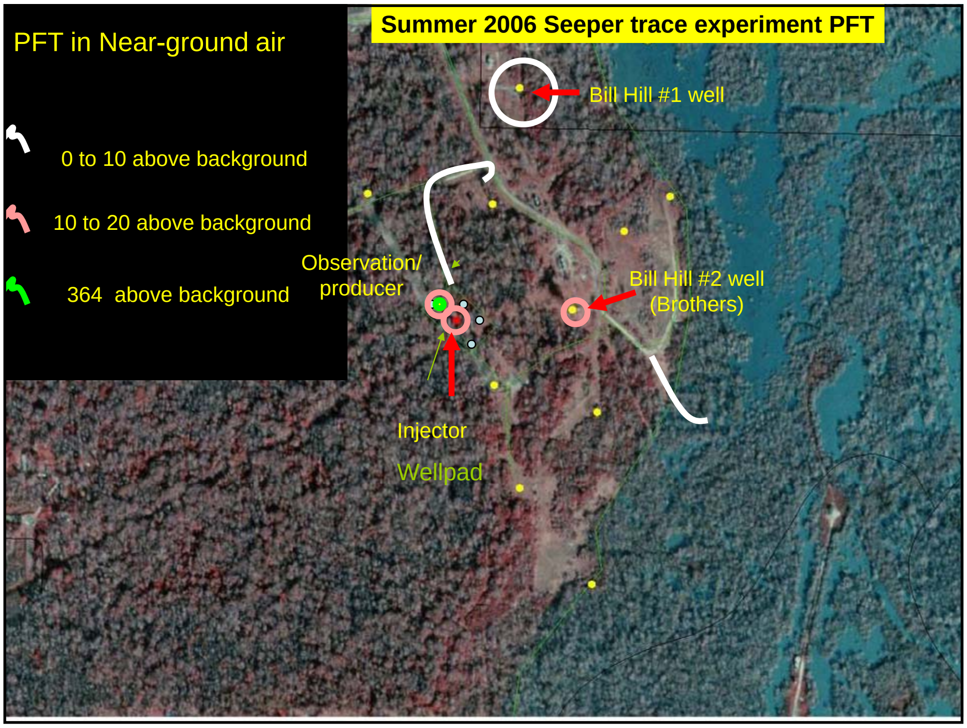
Y. Kharaka, USGS



Frio I PFT with soil gas CAT experiment

The hazard of making a measurement- you might have to figure out what it means.

From Wells et al., 2005



PFT in Near-ground air

- 0 to 10 above background
- 10 to 20 above background
- 364 above background

Summer 2006 Seeper trace experiment PFT

Return 2007 Seeper Trace PFT

- No detect except at wellhead plumbing – sorbed on grease pack in well head
- Need for experiments on performance of tracers in complex – rock fluid systems

Separation Rock-CO_2 - Water Reaction from Pipe-CO_2 - Water Reaction

$CO_{2\,(gas)} + H_2O \Leftrightarrow H_2CO_3^o$ CO_2 dissolves into brine

$H_2CO_3^o \Leftrightarrow HCO_3^- + H^+$

$CO_{2\,(gas)} + H_2O + CaCO_3 \Leftrightarrow Ca^{++} + 2HCO_3^-$

$H^+ + CaCO_3 \Leftrightarrow Ca^{++} + HCO_3^-$

Samples are always contaminated with something – Drilling or workover fluids, cement, sampling device. How can you use them anyway?

$H^+ + FeCO_3 \Leftrightarrow Fe^{++} + HCO_3$ CO_2 dissolves siderite

$4Fe(OH)_3 + 8H_2CO_3 \Leftrightarrow 4Fe^{++} + 8HCO_3^- + 10H_2O + O_2$ CO2 dissolves

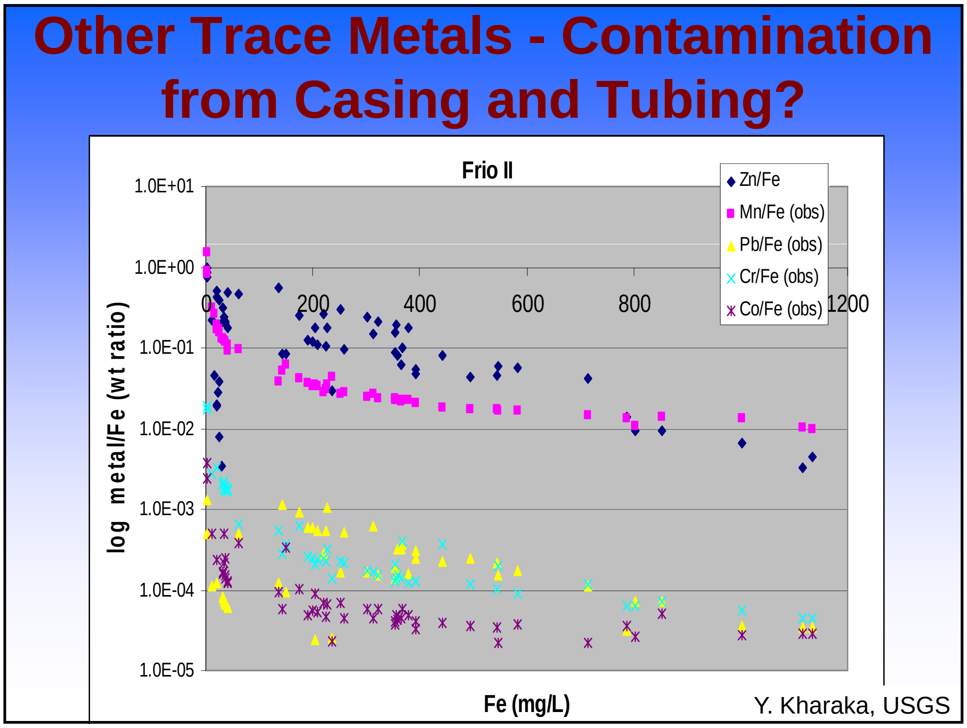
$2Fe(OH)_3 + 4H_2CO_3 + H_2 \Leftrightarrow 2Fe^{++} + 4HCO_3^- + 6H_2O$ limonite

$Fe^o + 2H_2CO_3 \Leftrightarrow Fe^{++} + 2HCO_3^- + H_2$ CO_2 dissolves steel

$2H^+ + CaMg(CO_3)_2 \Leftrightarrow Ca^{++} + Mg^{++} + 2HCO_3^-$ CO_2 dissolves dolomite

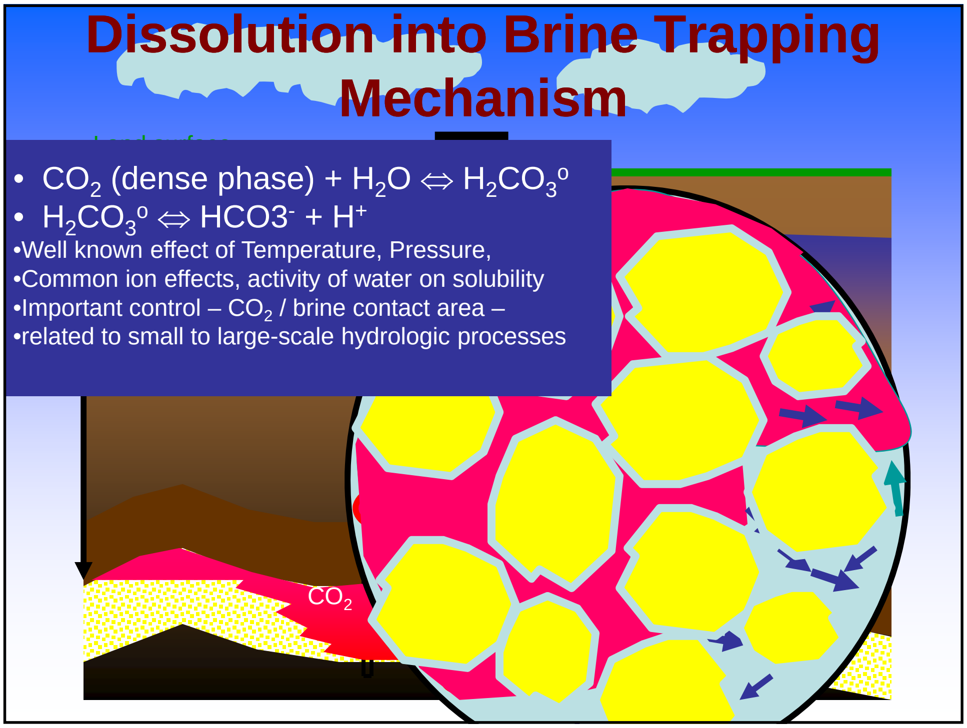
$0.4H^+ + Ca_{.2}Na_{.8}Al_{1.2}Si_{2.8}O_8 + 0.8CO_2 + 1.2H_2O \Leftrightarrow$ CO_2 dissolves feldspar

$.2Ca{+}{+} + .8NaAlCO_3(OH)_2 + 0.4Al(OH)_3 + 2.8SiO_2$



Other Trace Metals - Contamination from Casing and Tubing?

Y. Kharaka, USGS



Dissolution into Brine Trapping Mechanism

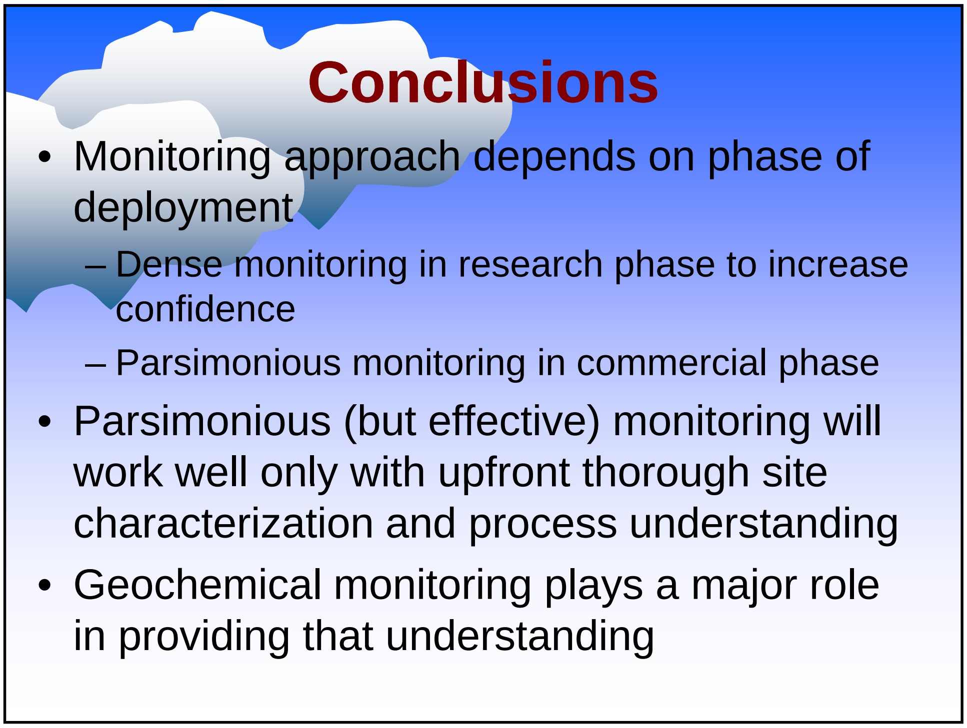
- CO_2 (dense phase) + $H_2O \Leftrightarrow H_2CO_3^o$
- $H_2CO_3^o \Leftrightarrow HCO3^- + H^+$

•Well known effect of Temperature, Pressure,

•Common ion effects, activity of water on solubility

•Important control – CO_2 / brine contact area –

•related to small to large-scale hydrologic processes



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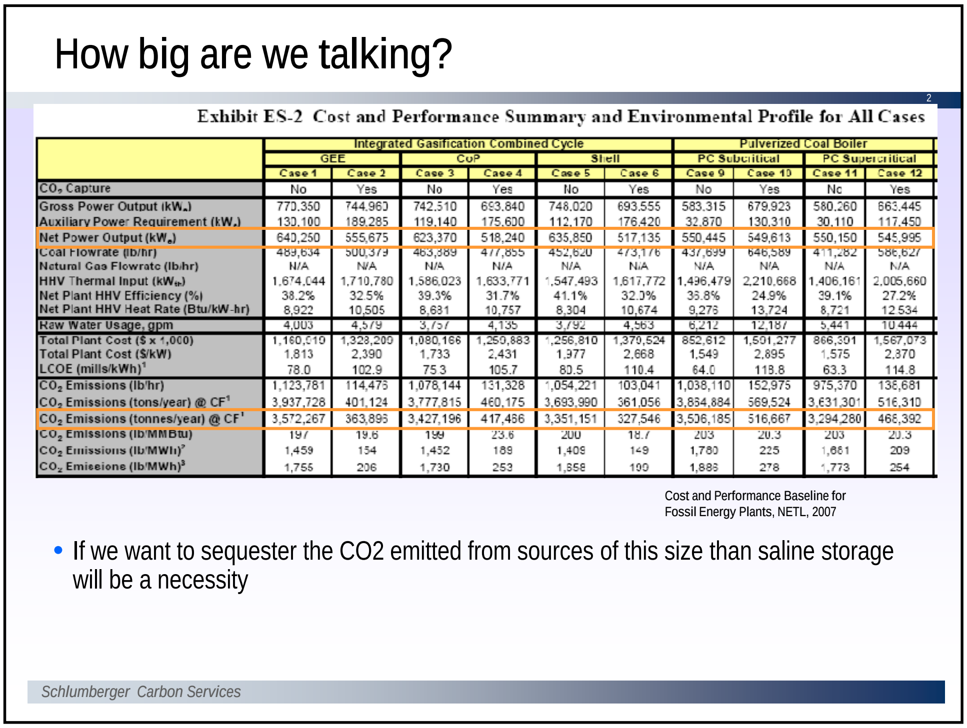
MMV Technologies for Effective and Efficient Monitoring of Geologic Carbon Capture and Storage Projects

GWPC/US EPA CO_2 MMV Workshop

Andrew Duguid
Marcia Couëslan
John Tombari
January 16, 2007

Schlumberger



How big are we talking?

2

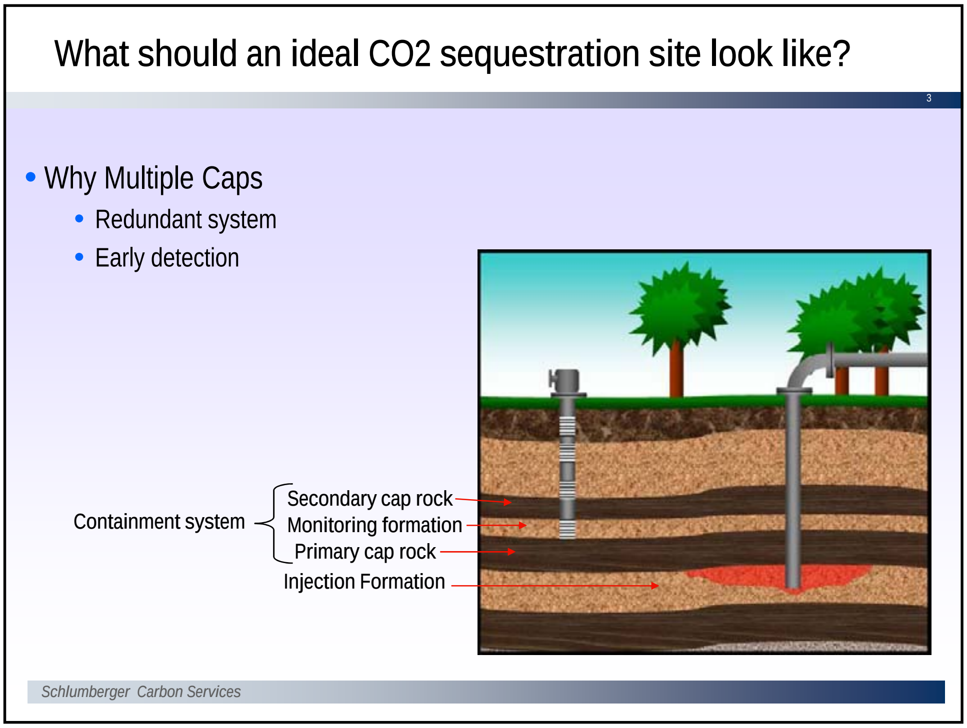
Exhibit ES-2 Cost and Performance Summary and Environmental Profile for All Cases

	Integrated Gasification Combined Cycle						Pulverized Coal Boiler			
	GEE		CoP		Shell		PC Subcritical		PC Supercritical	
	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 9	Case 10	Case 11	Case 12
CO_2 Capture	No	Yes	No	Yes	No	Yes	No	Yes	No	Yes
Gross Power Output (kW_e)	770,350	744,960	742,510	693,840	748,020	693,555	583,315	679,923	580,260	663,445
Auxiliary Power Requirement (kW_e)	130,100	189,285	119,140	175,600	112,170	176,420	32,870	130,310	30,110	117,450
Net Power Output (kW_e)	640,250	555,675	623,370	518,240	635,850	517,135	550,445	549,613	550,150	545,995
Coal Flowrate (lb/hr)	489,634	500,379	463,389	477,855	452,620	473,176	437,699	646,589	411,282	586,627
Natural Gas Flowrate (lb/hr)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
HHV Thermal Input (kW_{th})	1,674,044	1,710,780	1,586,023	1,633,771	1,547,493	1,617,772	1,496,479	2,210,668	1,406,161	2,005,660
Net Plant HHV Efficiency (%)	38.2%	32.5%	39.3%	31.7%	41.1%	32.0%	36.8%	24.9%	39.1%	27.2%
Net Plant HHV Heat Rate (Btu/kW-hr)	8,922	10,505	8,681	10,757	8,304	10,674	9,276	13,724	8,721	12,534
Raw Water Usage, gpm	4,003	4,579	3,757	4,135	3,792	4,563	6,212	12,187	5,441	10,444
Total Plant Cost ($ x 1,000)	1,160,919	1,328,209	1,080,166	1,250,883	1,256,810	1,370,524	852,612	1,501,277	866,391	1,567,073
Total Plant Cost ($/kW)	1,813	2,390	1,733	2,431	1,977	2,668	1,549	2,895	1,575	2,870
LCOE (mills/kWh)[1]	78.0	102.9	75.3	105.7	80.5	110.4	64.0	118.8	63.3	114.8
CO_2 Emissions (lb/hr)	1,123,781	114,476	1,078,144	131,328	1,054,221	103,041	1,038,110	152,975	975,370	136,681
CO_2 Emissions (tons/year) @ CF[1]	3,937,728	401,124	3,777,815	460,175	3,693,990	361,056	3,864,884	569,524	3,631,301	516,310
CO_2 Emissions (tonnes/year) @ CF[1]	3,572,267	363,896	3,427,196	417,466	3,351,151	327,546	3,506,185	516,667	3,294,280	468,392
CO_2 Emissions (lb/MMBtu)	197	19.6	199	23.6	200	18.7	203	20.3	203	20.3
CO_2 Emissions (lb/MWh)[2]	1,459	154	1,452	189	1,409	149	1,780	225	1,661	209
CO_2 Emissions (lb/MWh)[3]	1,755	206	1,730	253	1,658	199	1,886	278	1,773	254

Cost and Performance Baseline for
Fossil Energy Plants, NETL, 2007

- If we want to sequester the CO2 emitted from sources of this size than saline storage will be a necessity

Schlumberger Carbon Services



What should an ideal CO2 sequestration site look like?

- Why Multiple Caps
  - Redundant system
  - Early detection

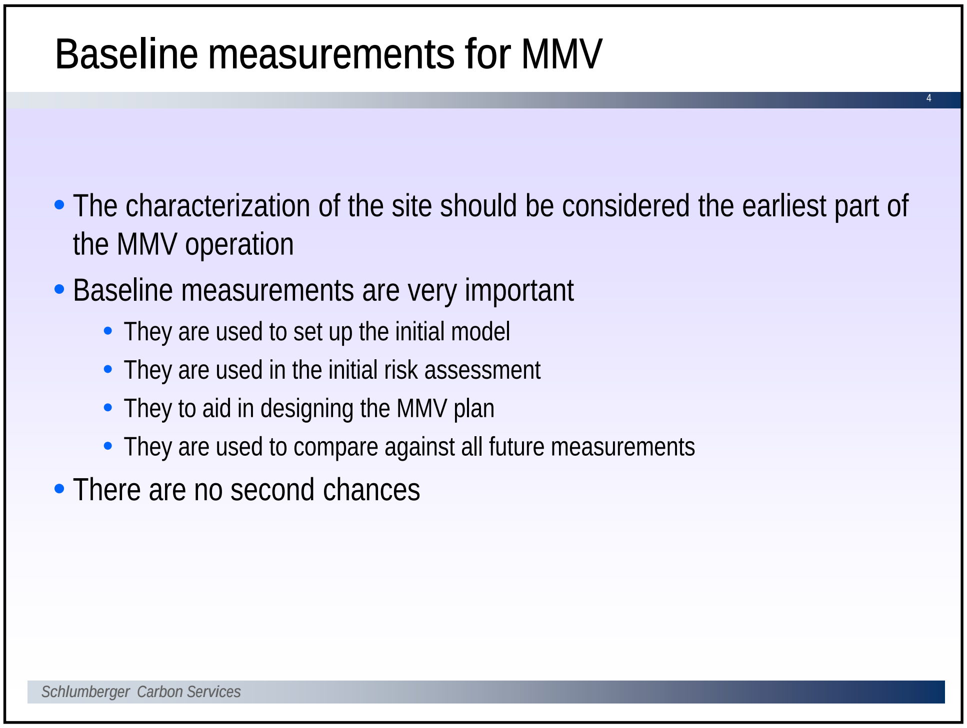
Containment system

Secondary cap rock

Monitoring formation

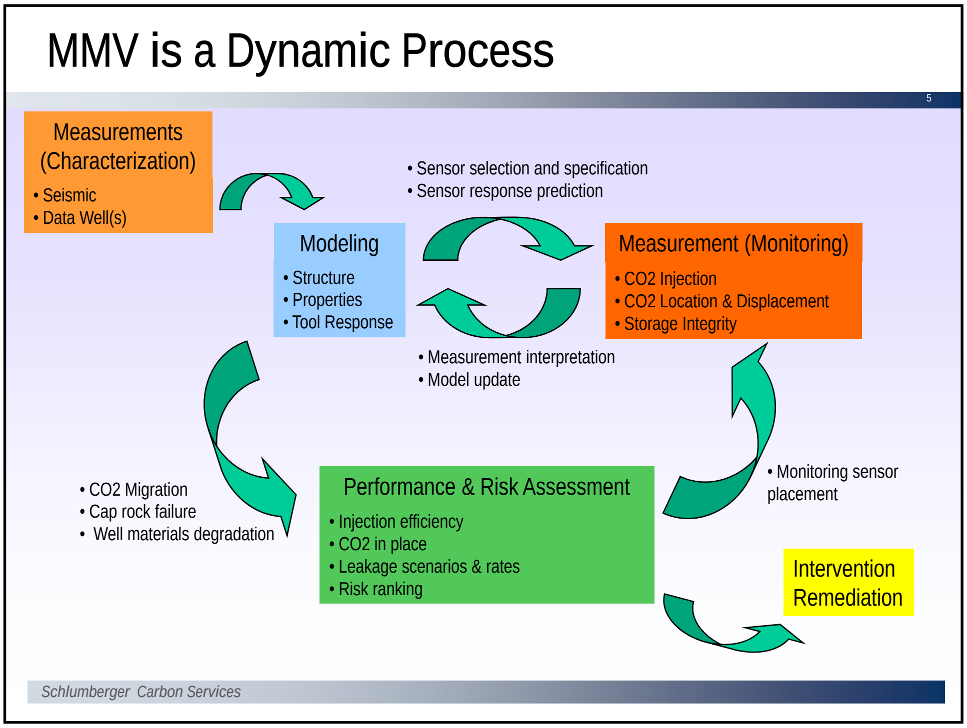
Primary cap rock

Injection Formation



Baseline measurements for MMV

- The characterization of the site should be considered the earliest part of the MMV operation
- Baseline measurements are very important
  - They are used to set up the initial model
  - They are used in the initial risk assessment
  - They to aid in designing the MMV plan
  - They are used to compare against all future measurements
- There are no second chances



MMV is a Dynamic Process

Measurements (Characterization)
- Seismic
- Data Well(s)

Modeling
- Structure
- Properties
- Tool Response

- Sensor selection and specification
- Sensor response prediction

Measurement (Monitoring)
- CO2 Injection
- CO2 Location & Displacement
- Storage Integrity

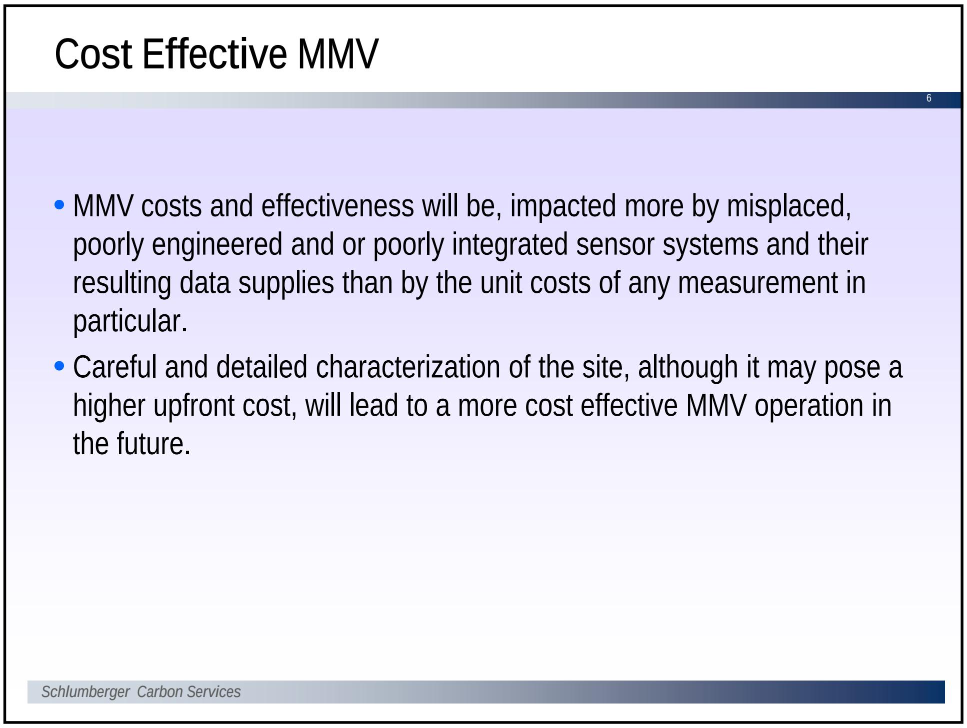
- Measurement interpretation
- Model update

- CO2 Migration
- Cap rock failure
- Well materials degradation

Performance & Risk Assessment
- Injection efficiency
- CO2 in place
- Leakage scenarios & rates
- Risk ranking

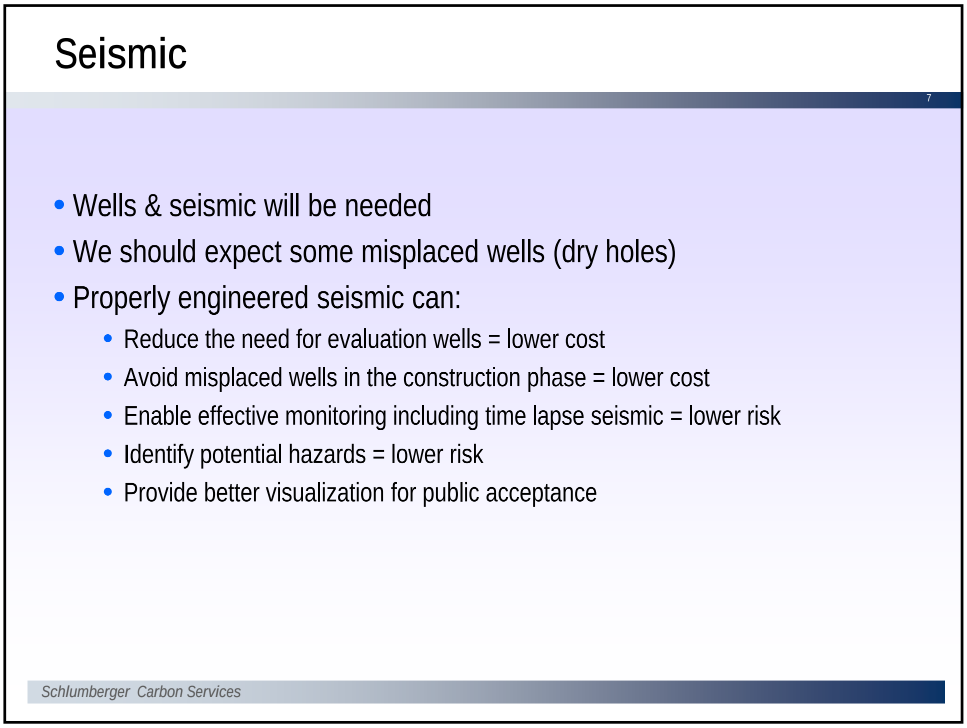
- Monitoring sensor placement

Intervention Remediation



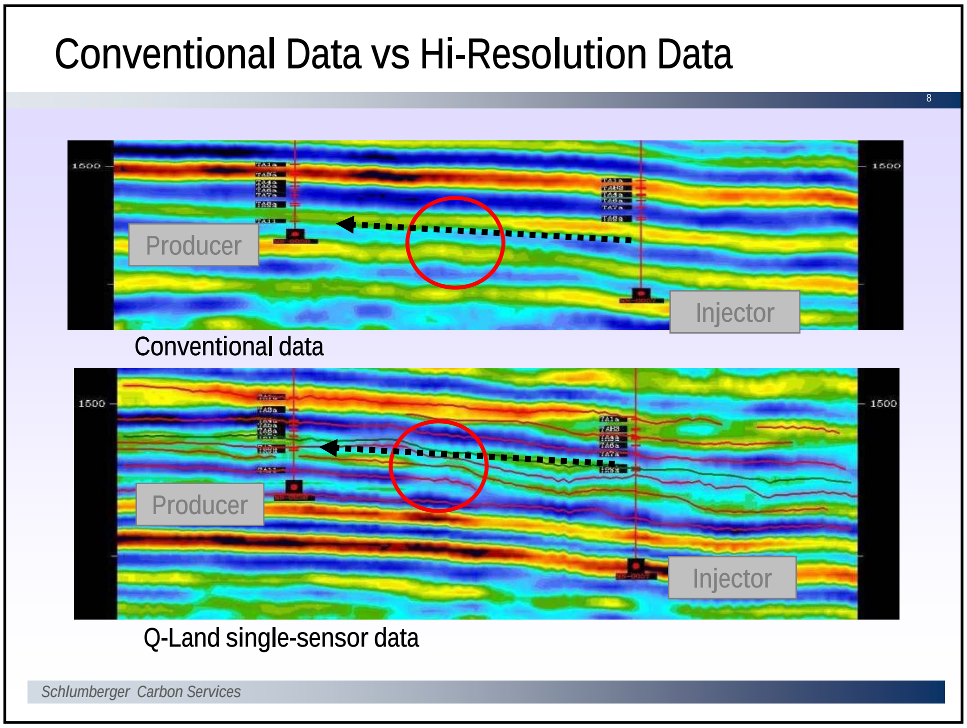
Cost Effective MMV

- MMV costs and effectiveness will be, impacted more by misplaced, poorly engineered and or poorly integrated sensor systems and their resulting data supplies than by the unit costs of any measurement in particular.
- Careful and detailed characterization of the site, although it may pose a higher upfront cost, will lead to a more cost effective MMV operation in the future.



Seismic

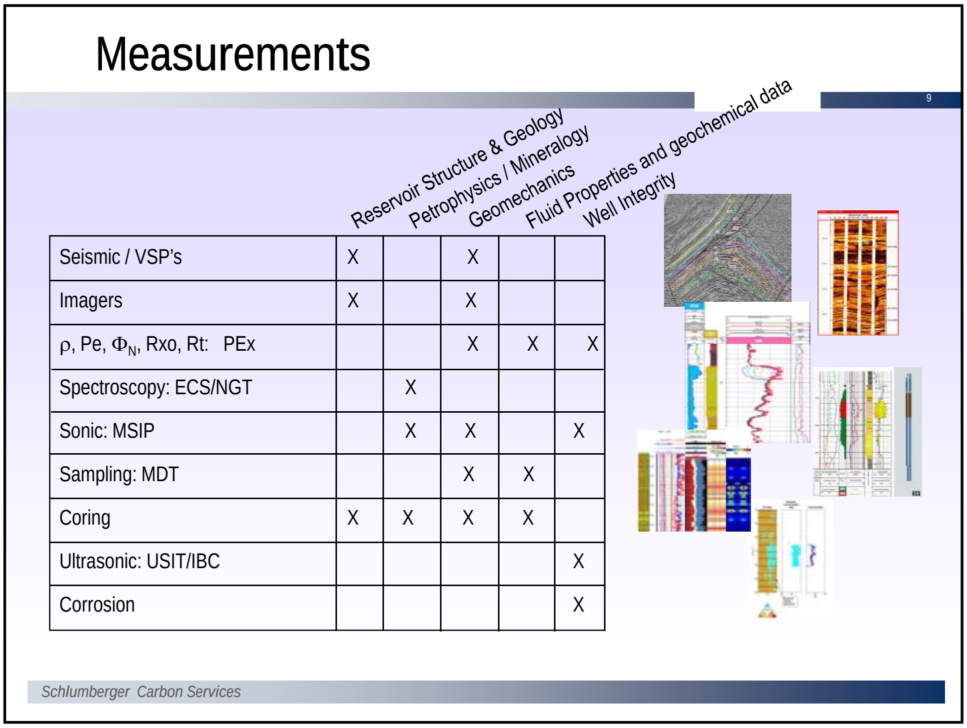
- Wells & seismic will be needed
- We should expect some misplaced wells (dry holes)
- Properly engineered seismic can:
  - Reduce the need for evaluation wells = lower cost
  - Avoid misplaced wells in the construction phase = lower cost
  - Enable effective monitoring including time lapse seismic = lower risk
  - Identify potential hazards = lower risk
  - Provide better visualization for public acceptance



Conventional Data vs Hi-Resolution Data

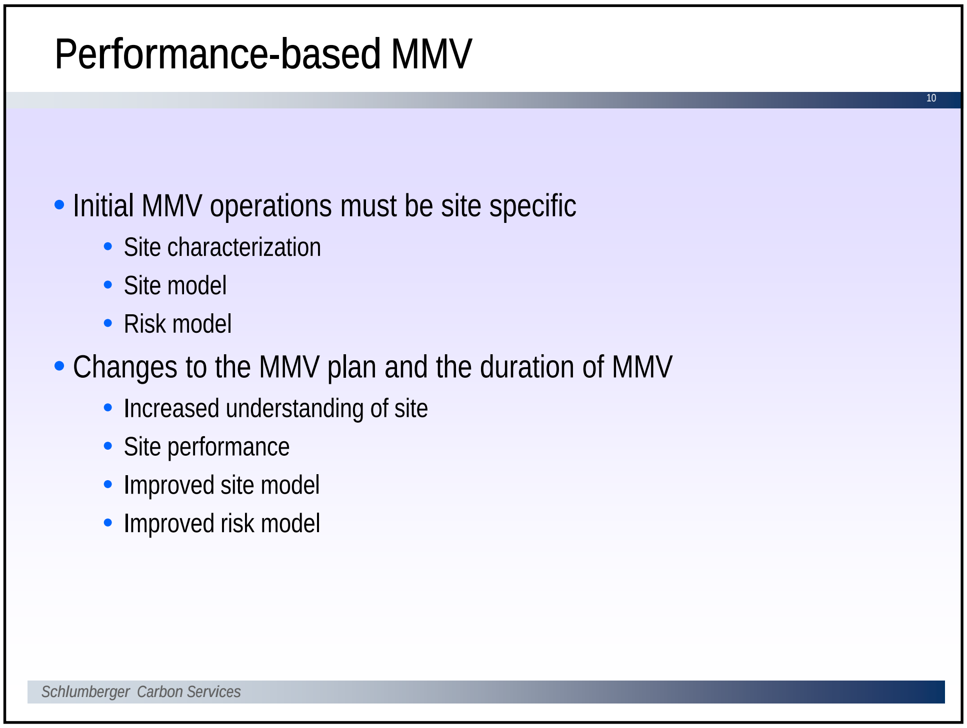
Conventional data

Q-Land single-sensor data



Measurements

	Reservoir Structure & Geology	Petrophysics / Mineralogy	Geomechanics	Fluid Properties and geochemical data	Well Integrity
Seismic / VSP's	X		X		
Imagers	X		X		
ρ, Pe, Φ_N, Rxo, Rt: PEx			X	X	X
Spectroscopy: ECS/NGT		X			
Sonic: MSIP		X	X		X
Sampling: MDT			X	X	
Coring	X	X	X	X	
Ultrasonic: USIT/IBC					X
Corrosion					X



Performance-based MMV

- Initial MMV operations must be site specific
  - Site characterization
  - Site model
  - Risk model
- Changes to the MMV plan and the duration of MMV
  - Increased understanding of site
  - Site performance
  - Improved site model
  - Improved risk model

Summary

- Ideally CCS sites should have redundant caps
- The success of the baseline survey will have an impact on all future MMV operations
- Overall cost effectiveness will be gained through careful and detailed characterization
- MMV is site specific
- Models will help identify needs for MMV
- All phases of MMV operations should be based on performance criteria

Questions

- Thank you

Development of a New Facility for Testing Near Surface CO$_2$ Detection

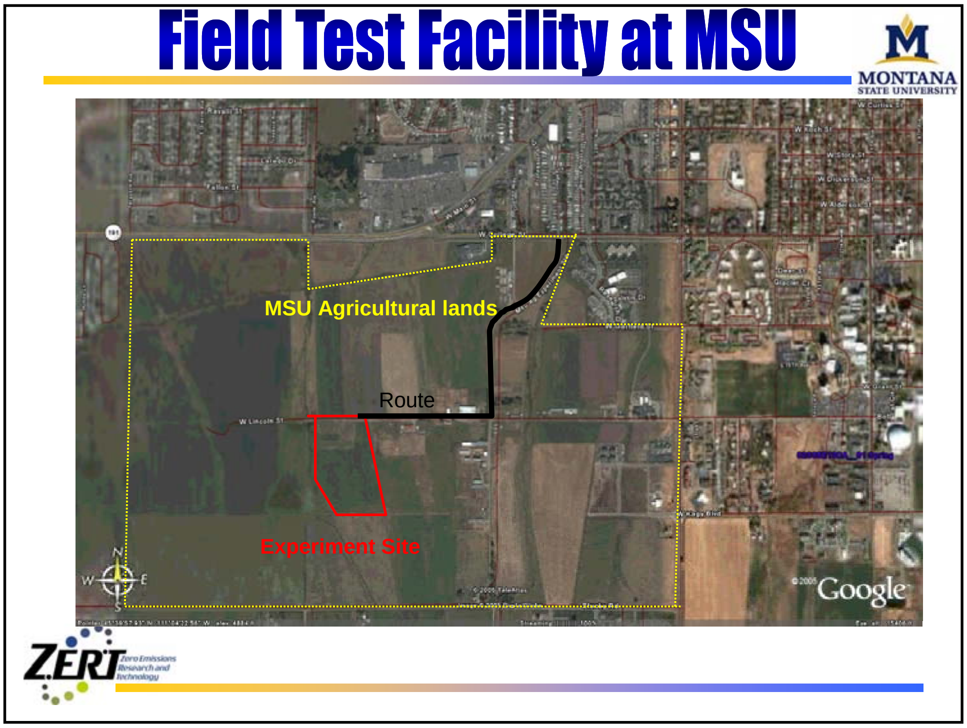
Lee H. Spangler, Director
The Zero Emissions Research and Technology Collaborative
Montana State University, Bozeman, MT

Laura Dobeck, Tim Holley, Cole S. Peebles, Kyle Scarr, Al Cunningham, Kevin Repasky, Seth Humphries, Bob Mokwa – Montana State Universty, Jennifer Lewicki, Curt Oldenburg, Sally Benson - LBNL, Brian Strazisar, Rick Hammack, Garret Veloski, Art Wells, Rod Diehl, Dave Wildman – NETL, Julianna Fessenden - LANL, Bill Pickles, Frank Gouveia – LLNL, Jim Amonette, Charlotte Sullivan – PNNL

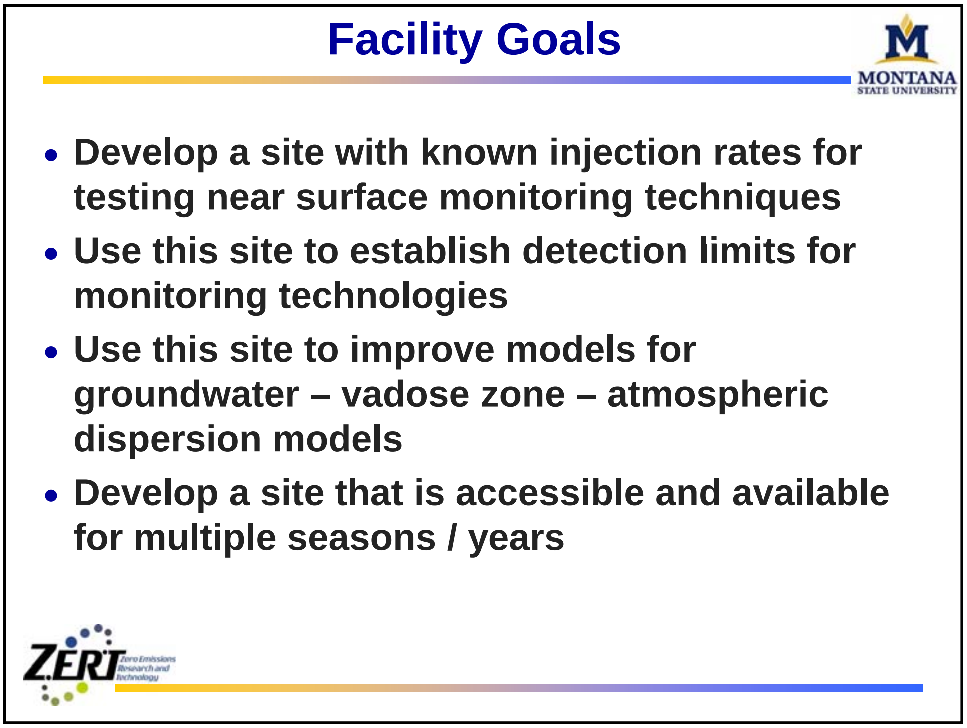
Zero-Emission Research & Technology Center

A collaborative involving Universities and DOE National Labs

- Montana State University
- Los Alamos National Laboratory
- Pacific Northwest National Laboratory
- West Virginia University
- Lawrence Berkeley National Laboratory
- National Energy Technology Laboratory
- Lawrence Livermore National Laboratory

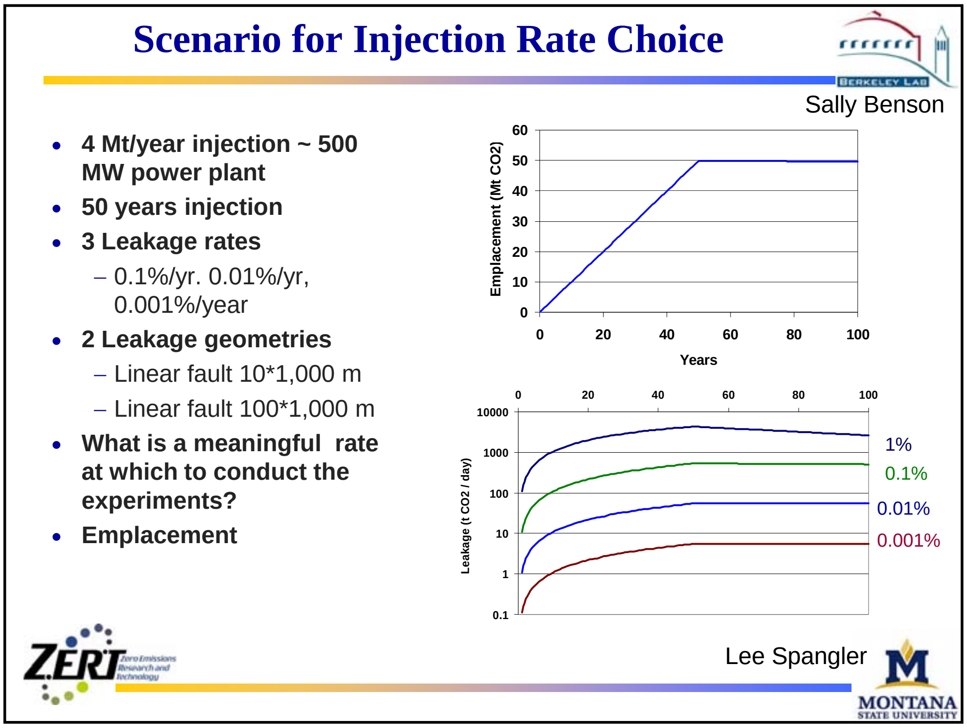


Field Test Facility at MSU



Facility Goals

- Develop a site with known injection rates for testing near surface monitoring techniques
- Use this site to establish detection limits for monitoring technologies
- Use this site to improve models for groundwater – vadose zone – atmospheric dispersion models
- Develop a site that is accessible and available for multiple seasons / years

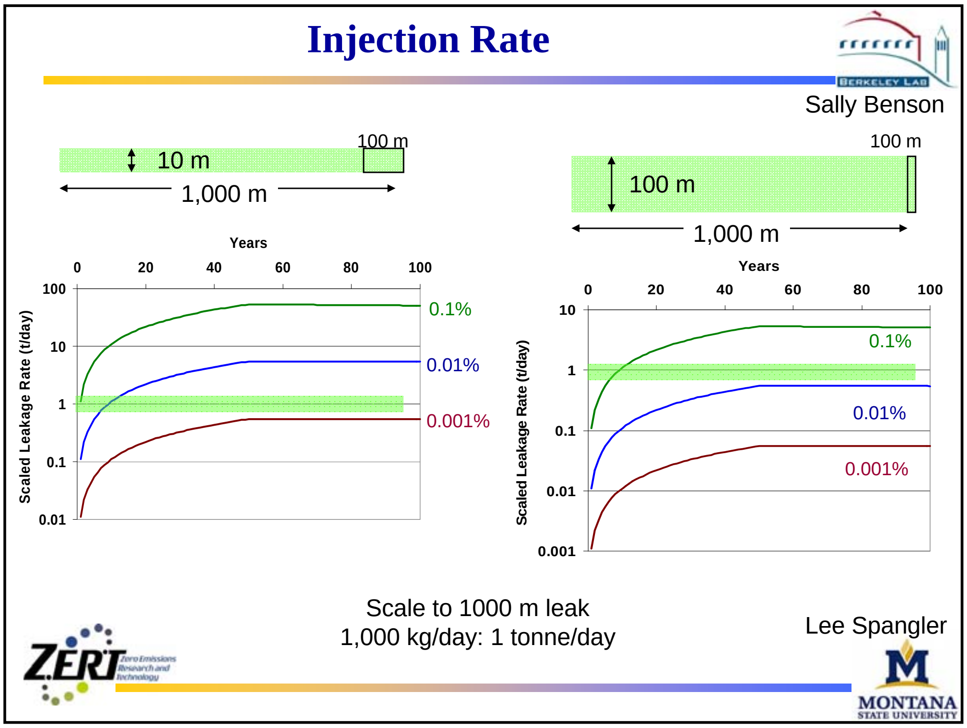


Scenario for Injection Rate Choice

Sally Benson

- **4 Mt/year injection ~ 500 MW power plant**
- **50 years injection**
- **3 Leakage rates**
  - 0.1%/yr. 0.01%/yr, 0.001%/year
- **2 Leakage geometries**
  - Linear fault 10*1,000 m
  - Linear fault 100*1,000 m
- **What is a meaningful rate at which to conduct the experiments?**
- **Emplacement**

Lee Spangler

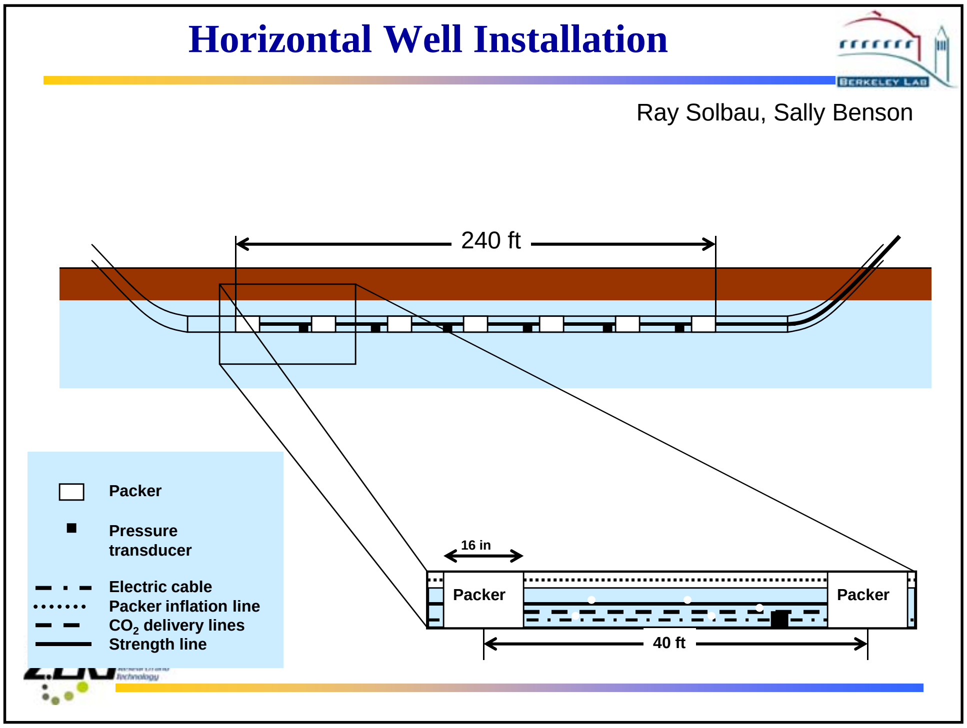


Injection Rate

Sally Benson

Scale to 1000 m leak
1,000 kg/day: 1 tonne/day

Lee Spangler



Horizontal Well Installation

Ray Solbau, Sally Benson

240 ft

16 in

Packer

Packer

40 ft

□ Packer

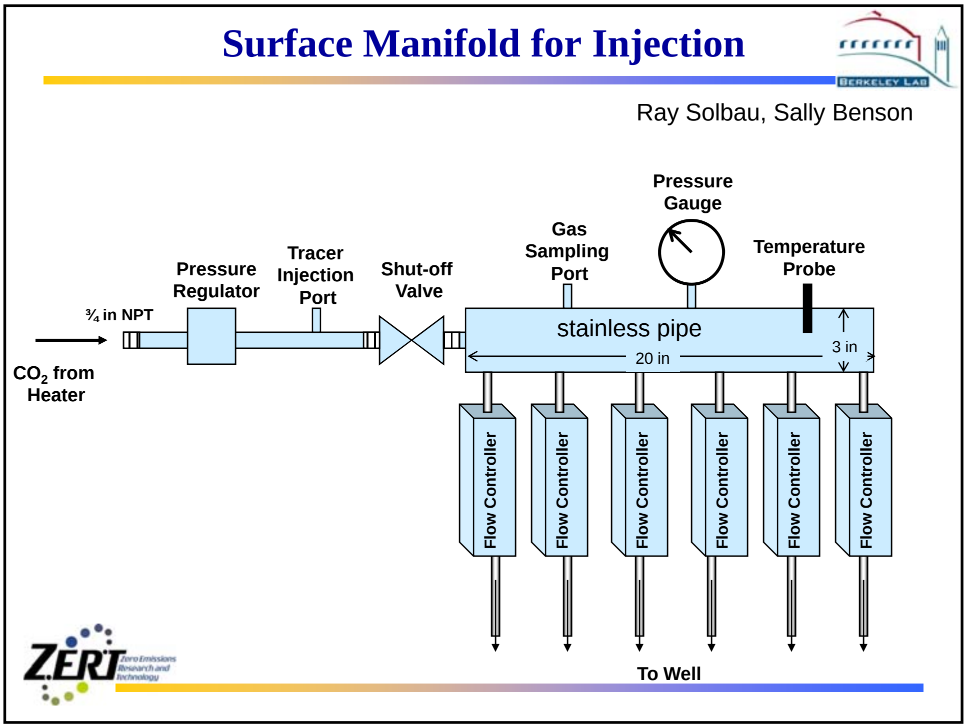
■ Pressure transducer

Electric cable

Packer inflation line

CO_2 delivery lines

Strength line



Surface Manifold for Injection

Ray Solbau, Sally Benson

Pressure Gauge

Gas Sampling Port

Temperature Probe

Tracer Injection Port

Shut-off Valve

Pressure Regulator

¾ in NPT

CO_2 from Heater

stainless pipe

20 in

3 in

Flow Controller

Flow Controller

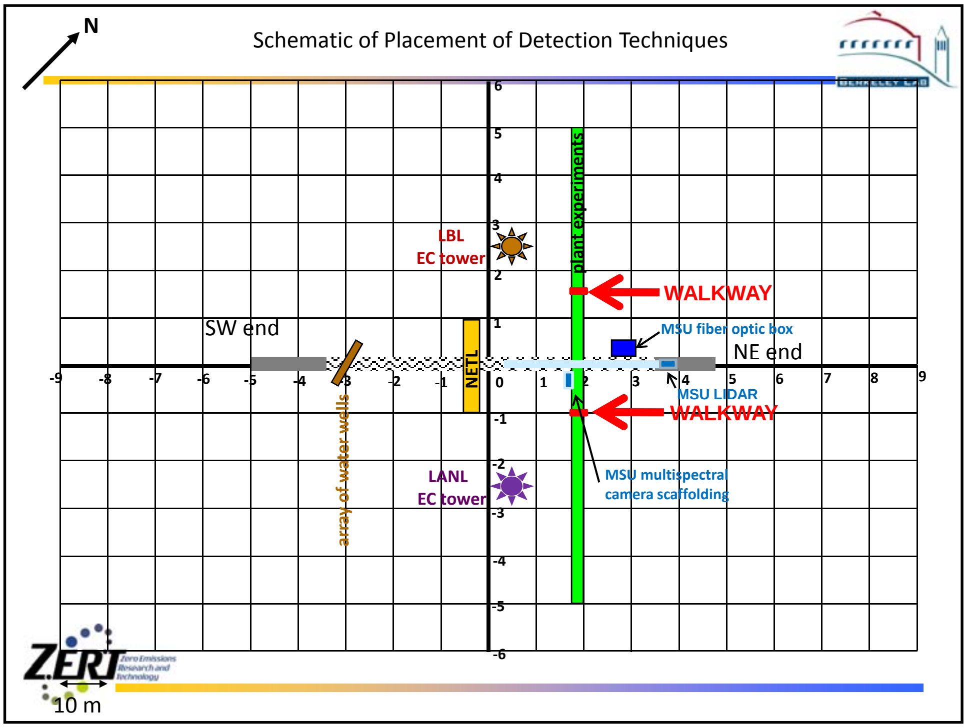
Flow Controller

Flow Controller

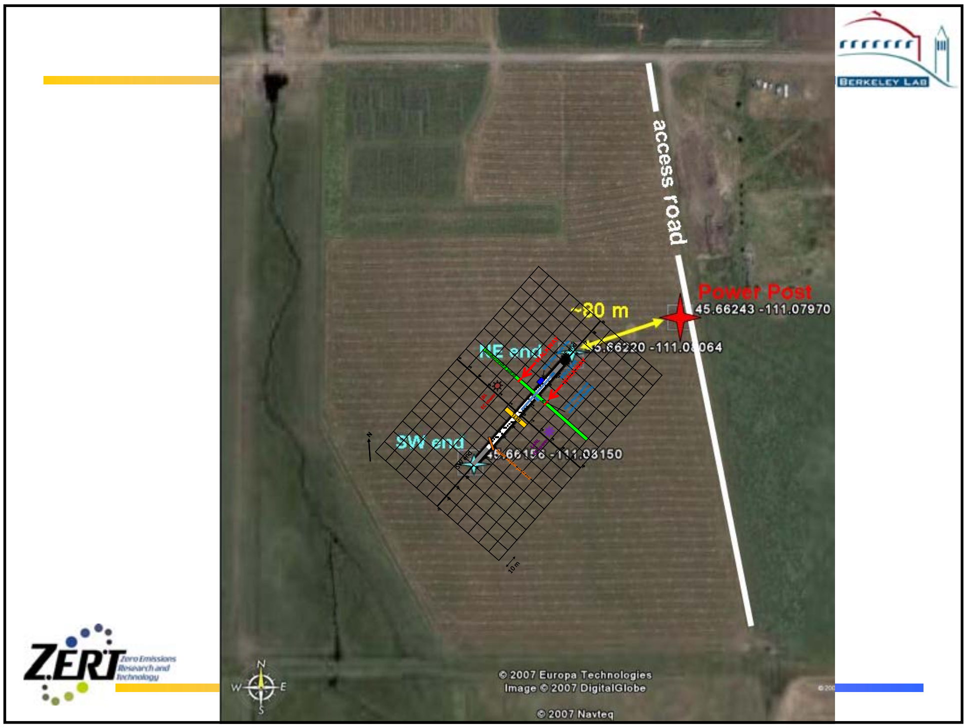
Flow Controller

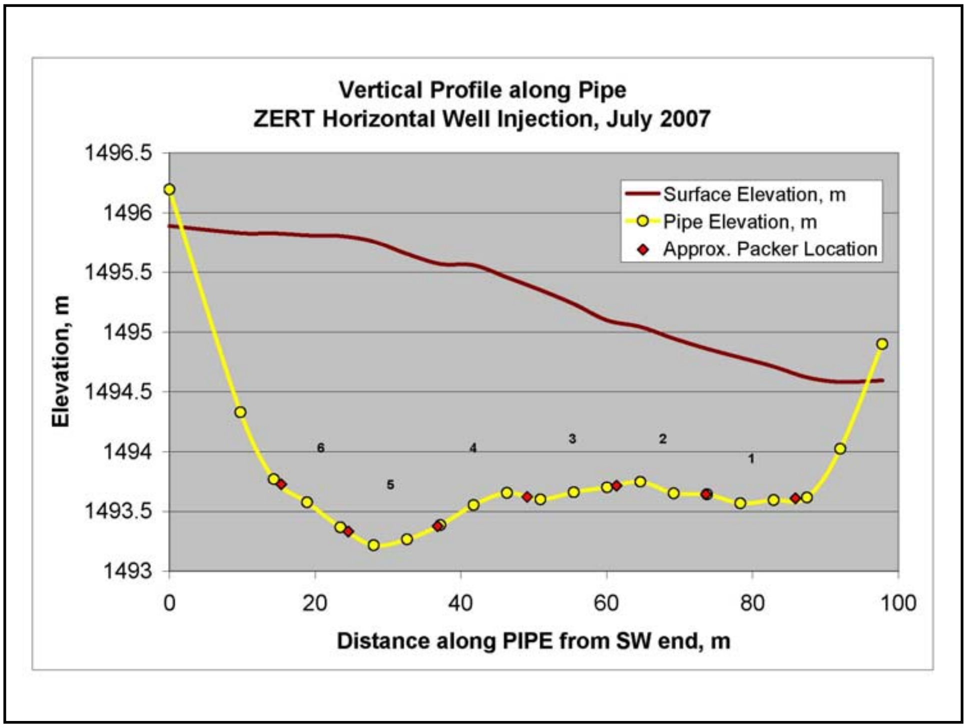
Flow Controller

To Well

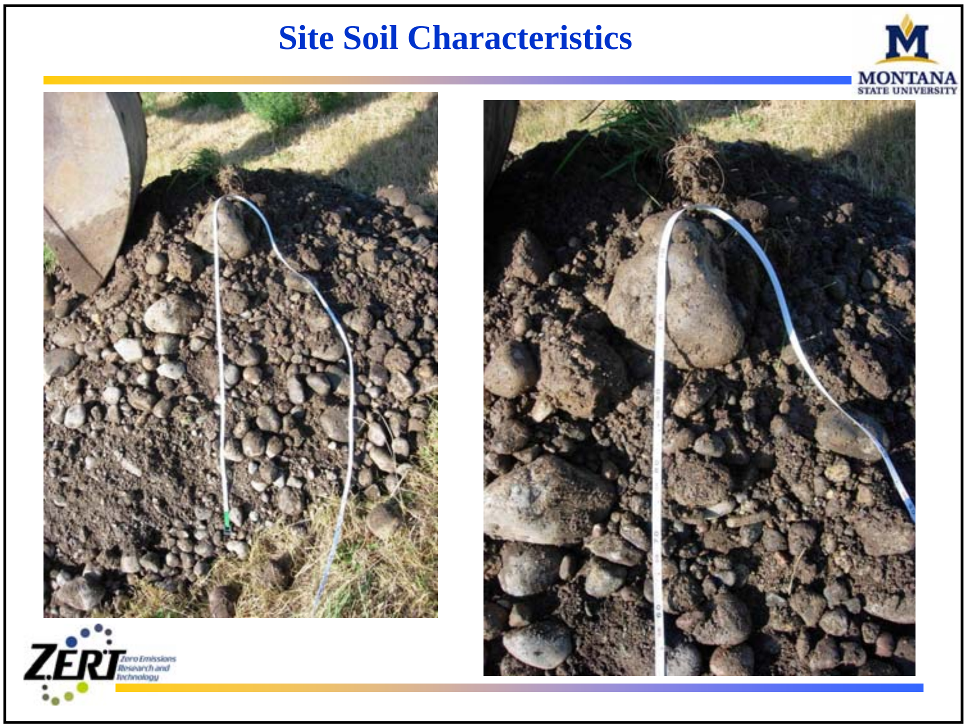


Schematic of Placement of Detection Techniques

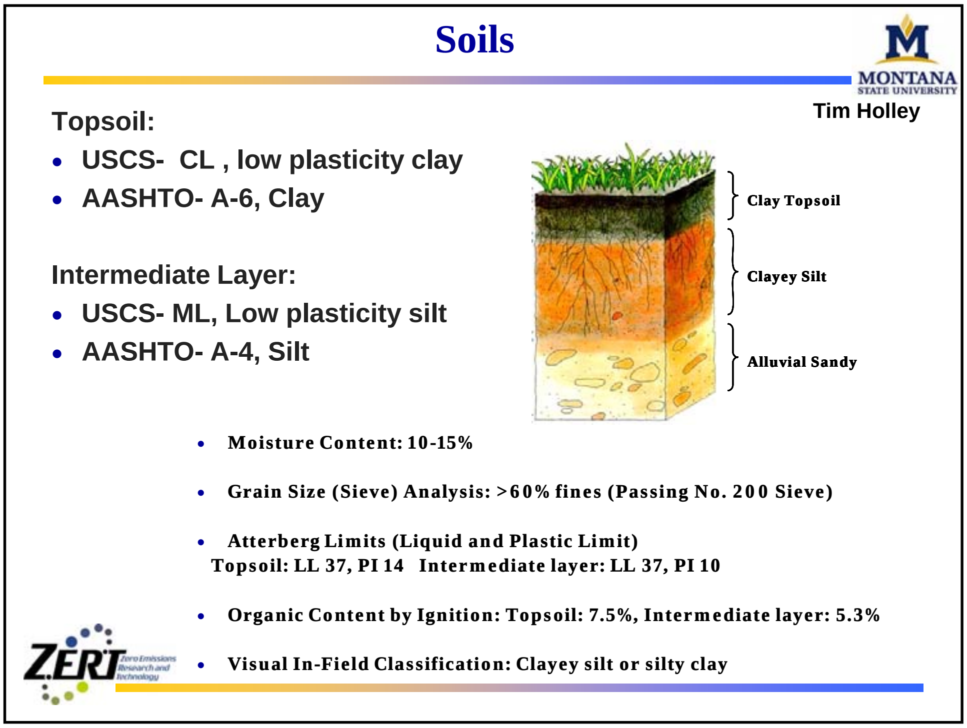




Vertical Profile along Pipe
ZERT Horizontal Well Injection, July 2007



Site Soil Characteristics



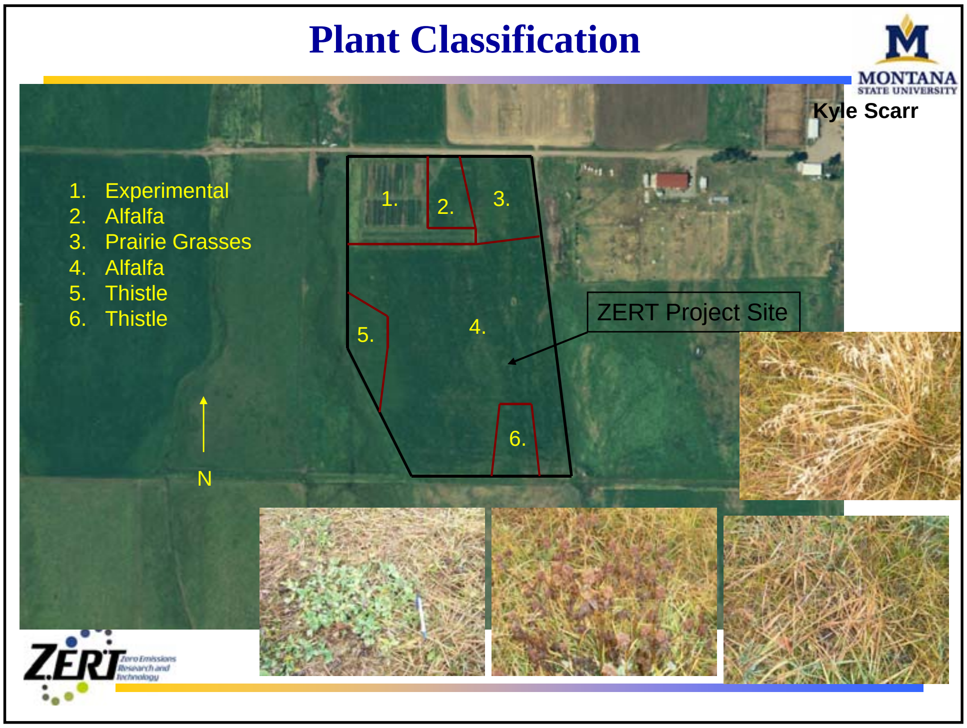
Soils

Tim Holley

Topsoil:
- USCS- CL , low plasticity clay
- AASHTO- A-6, Clay

Intermediate Layer:
- USCS- ML, Low plasticity silt
- AASHTO- A-4, Silt

- Moisture Content: 10-15%
- Grain Size (Sieve) Analysis: >60% fines (Passing No. 200 Sieve)
- Atterberg Limits (Liquid and Plastic Limit)
  Topsoil: LL 37, PI 14 Intermediate layer: LL 37, PI 10
- Organic Content by Ignition: Topsoil: 7.5%, Intermediate layer: 5.3%
- Visual In-Field Classification: Clayey silt or silty clay



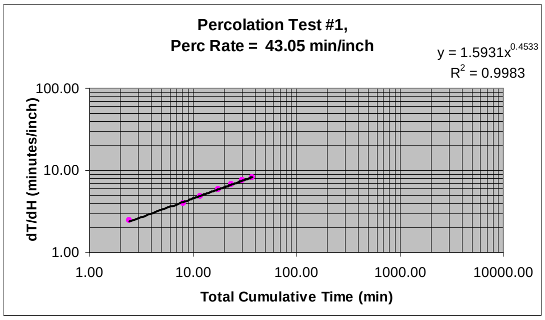
Plant Classification

Kyle Scarr

1. Experimental
2. Alfalfa
3. Prairie Grasses
4. Alfalfa
5. Thistle
6. Thistle

Percolation Testing: Results

Cole S. Peebles



Typically only represent horizontal hydraulic conductivity.
- **Upper Silty Topsoil: k = 2.79 ft/day.**
- **Clayey Silt Zone: k = 2.18 ft/day.**
- **Silt/Sandy Gravel Interface: k = 4.70 ft/day.**
- Average Conductivity: k = 3.22 ft/day.

** This is between 2 and 3 orders of magnitude less than alluvial gravels.

Geology of the Gallatin Valley

Localized ZERT Ground Water Gradient 17° East of North

Gradient = 0.0143 ft/ft

Relative SWL El. = -9.30 ft

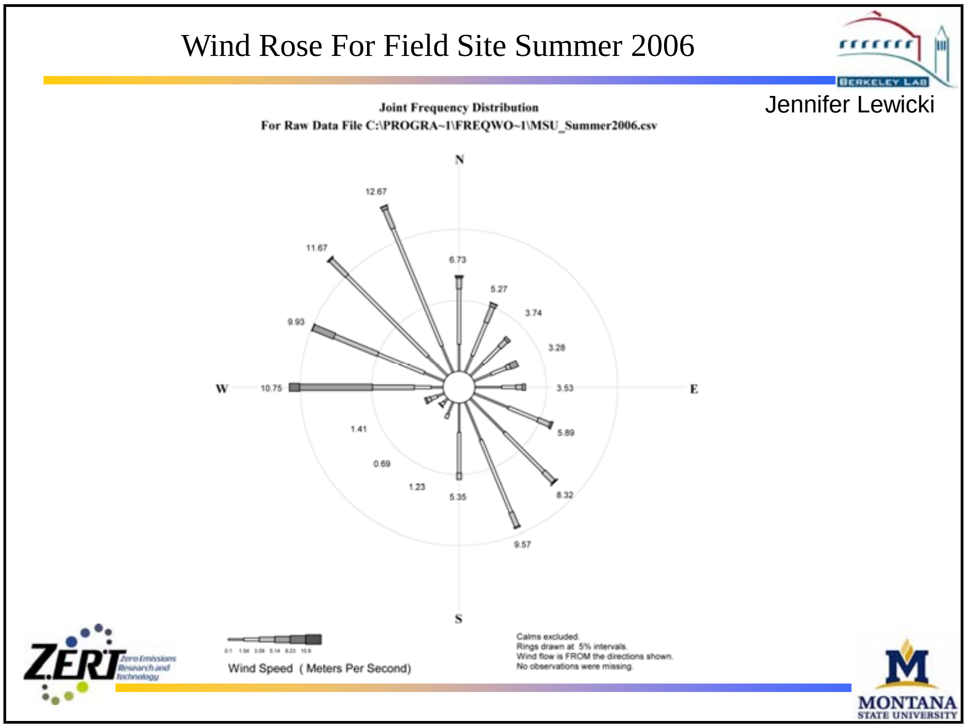
Triangulation of Static Water Level Elevations for MW-1,3,4

Relative SWL El. = -7.47 ft

Actual Direction of Ground Water Gradient

Length of this bar = 100 ft

Relative SWL El. = -5.56 ft

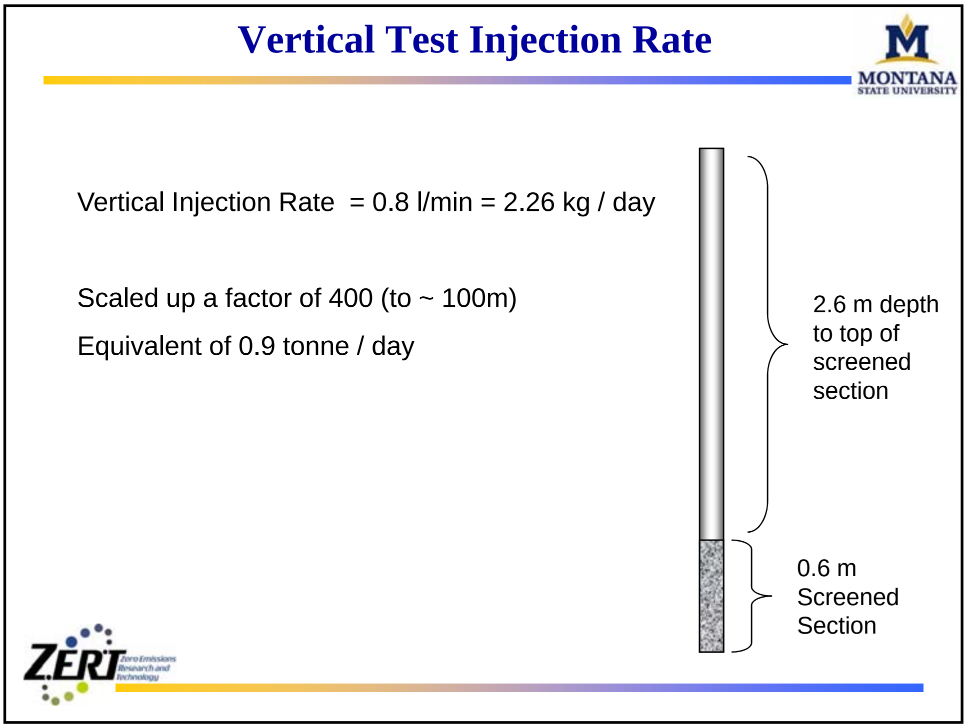


Wind Rose For Field Site Summer 2006

Jennifer Lewicki

Joint Frequency Distribution
For Raw Data File C:\PROGRA~1\FREQWO~1\MSU_Summer2006.csv

Calms excluded.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.



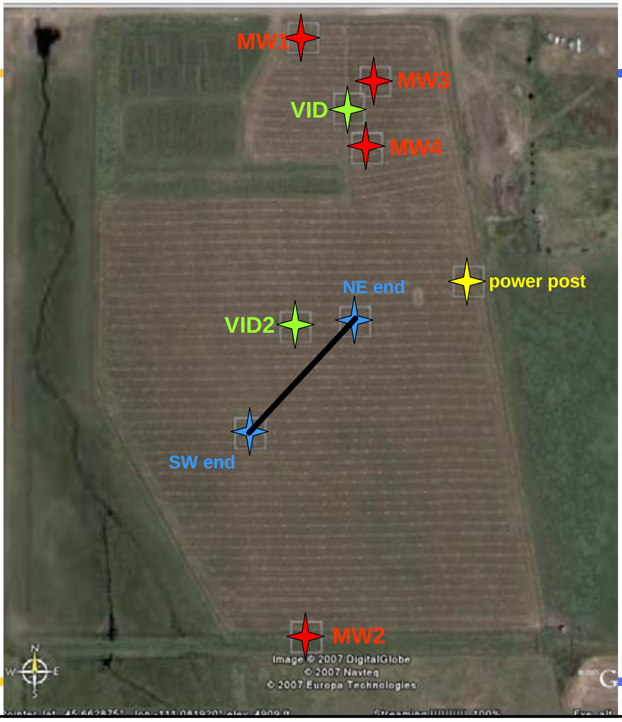
Vertical Test Injection Rate

Vertical Injection Rate = 0.8 l/min = 2.26 kg / day

Scaled up a factor of 400 (to ~ 100m)

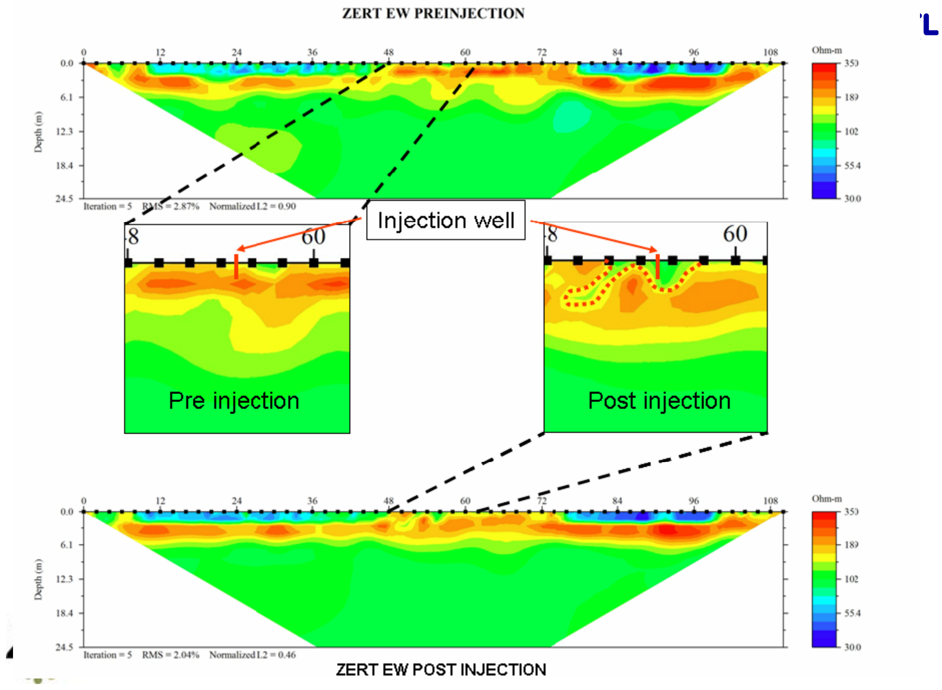
Equivalent of 0.9 tonne / day

Vertical Injection Site



Large Number of Participants / Methods

- **MSU – Geotechnical, O2, CO2 (isotope) Lidar, soil microbes.**
- **LBNL – Eddy Covariance, Soil Gas Chamber, Modeling**
- **LANL – EC, Stable Isotopes Gas & Water**
- **PNNL – Soil & Hydrology, Tracers**
- **LLNL – Gas Stable Isotope, Soil Microbes, Hyperspectral,**
- **NETL – Background Charaterization, Tracers (sorption tubes)**
- **WVU – Water Chemistry**

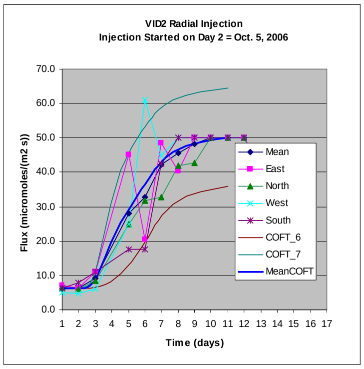


TOUGH2/EOS7CA Model was Calibrated on Initial Vertical Well Injection Test

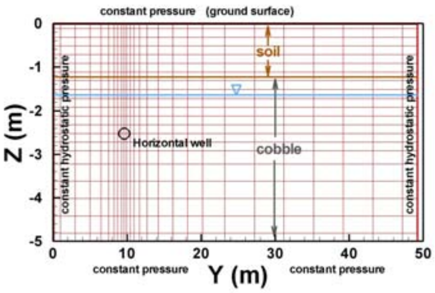
Curtis M. Oldenburg

Accumulation Chamber measurements (points) with model fits (lines)

(Data collected by Laura Dobeck)



A two-layer model (soil and cobble) transverse to the horizontal well was used for predictive modeling.

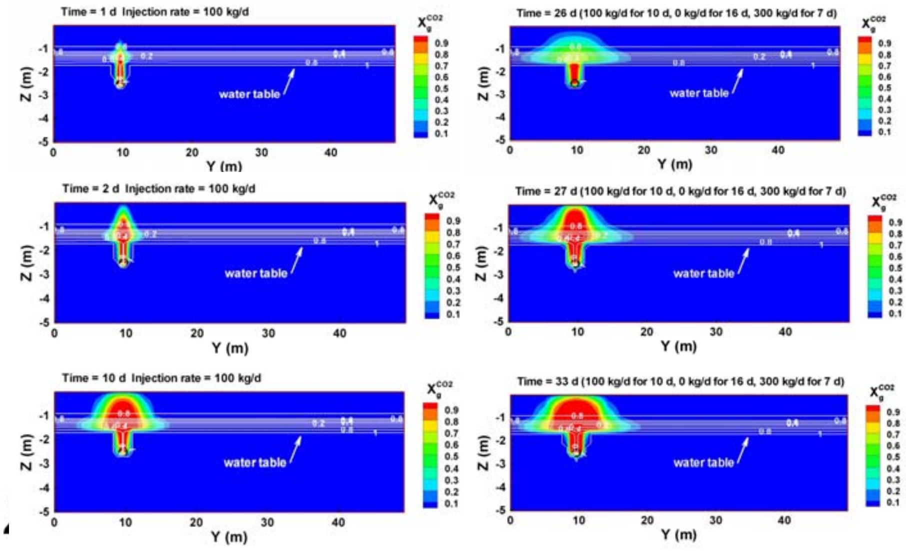


Two-layer model manual fit:
$k_{soil} = 5 \times 10^{-11}\ m^2$
$k_{cobble} = 3.2 \times 10^{-12}\ m^2$
$\phi = 0.35$

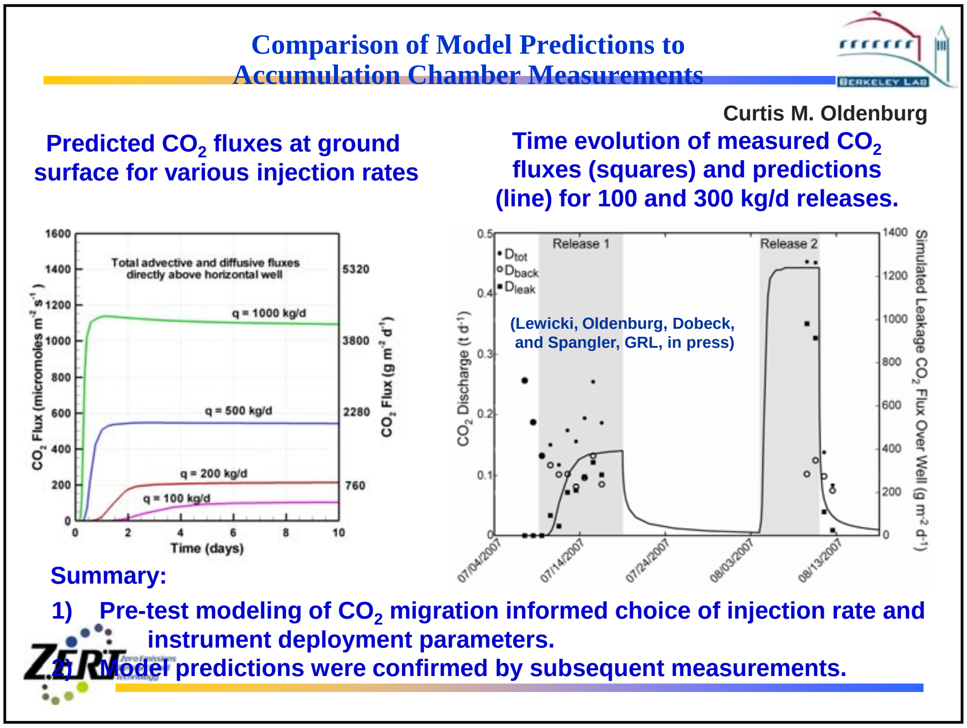
Large soil permeability is attributed to macropores (e.g., root casts, cracks)

TOUGH2/EOS7CA Model Results of CO_2 Release for Experiment Design

Curtis M. Oldenburg


Release 1 (100 kg/d)

Release 2 (300 kg/d)



Comparison of Model Predictions to Accumulation Chamber Measurements

Curtis M. Oldenburg

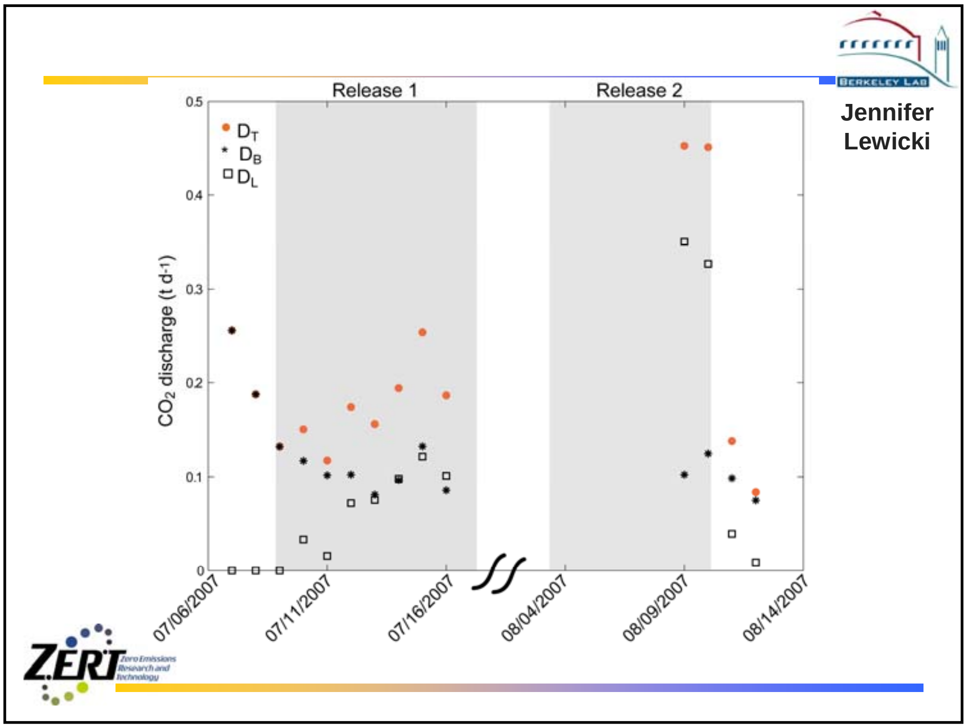
Predicted CO_2 fluxes at ground surface for various injection rates

Time evolution of measured CO_2 fluxes (squares) and predictions (line) for 100 and 300 kg/d releases.

(Lewicki, Oldenburg, Dobeck, and Spangler, GRL, in press)

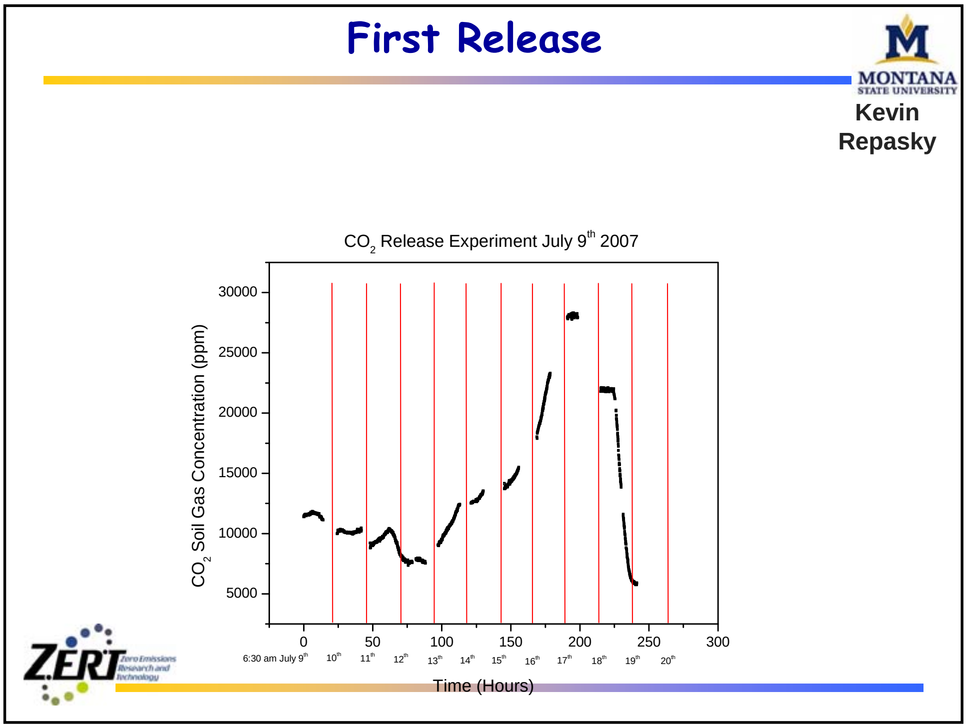
Summary:

1) Pre-test modeling of CO_2 migration informed choice of injection rate and instrument deployment parameters.
2) Model predictions were confirmed by subsequent measurements.



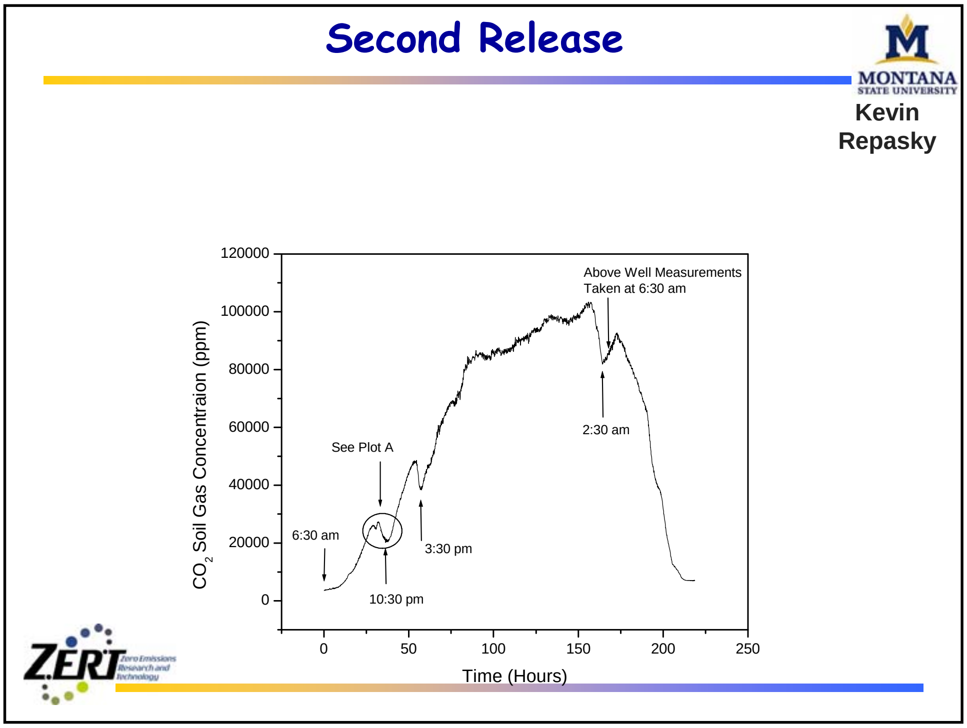
Jennifer Lewicki

Below Ground Instrument



First Release

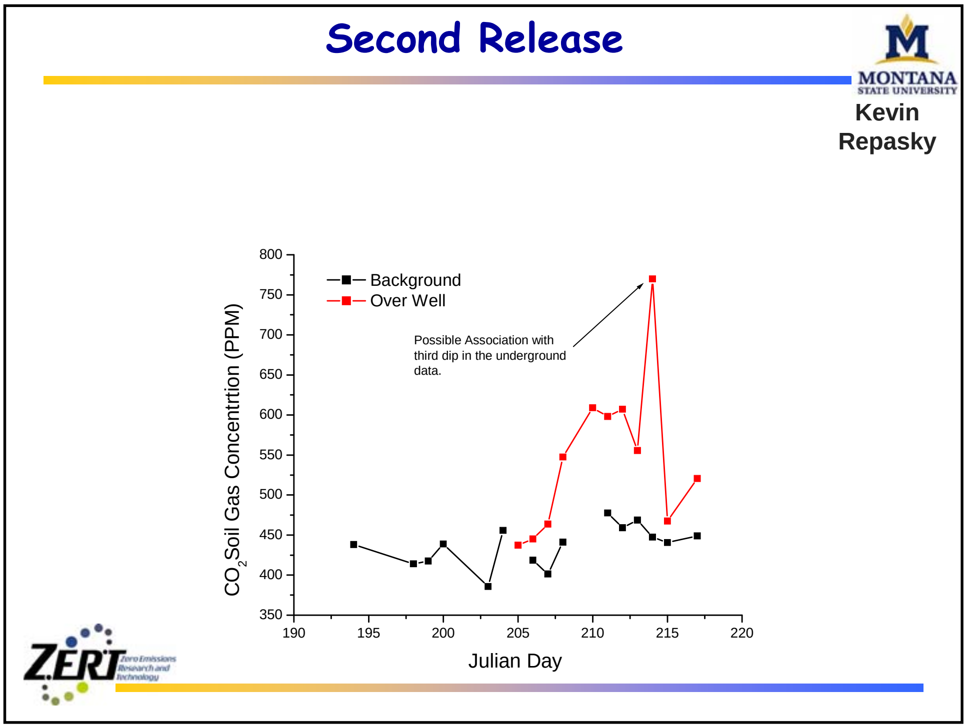
Kevin Repasky



Second Release

MONTANA STATE UNIVERSITY

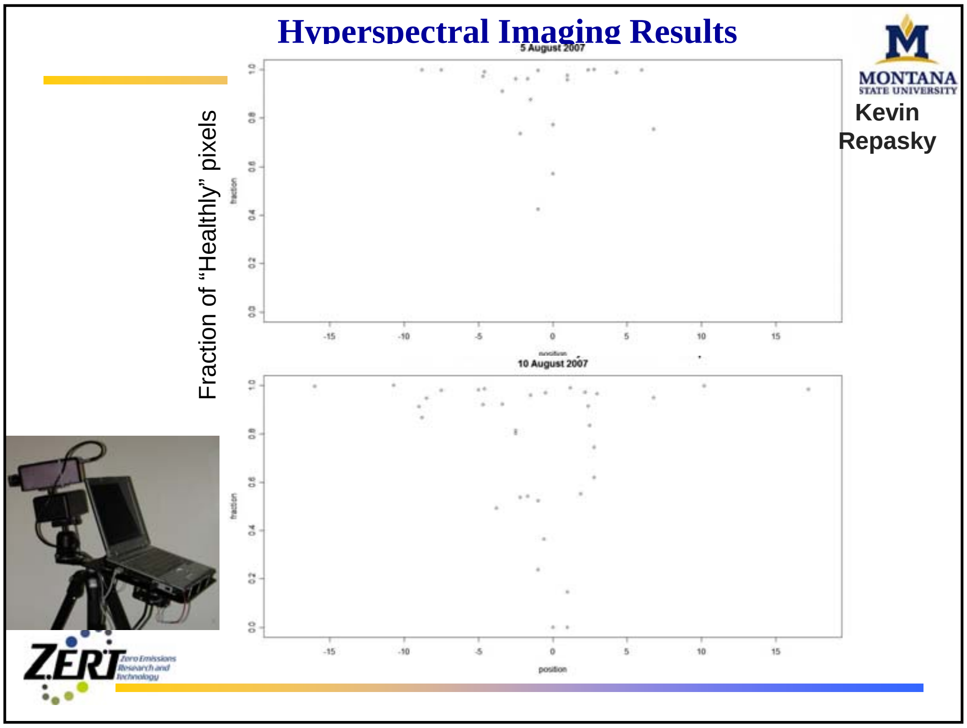
Kevin Repasky



Second Release

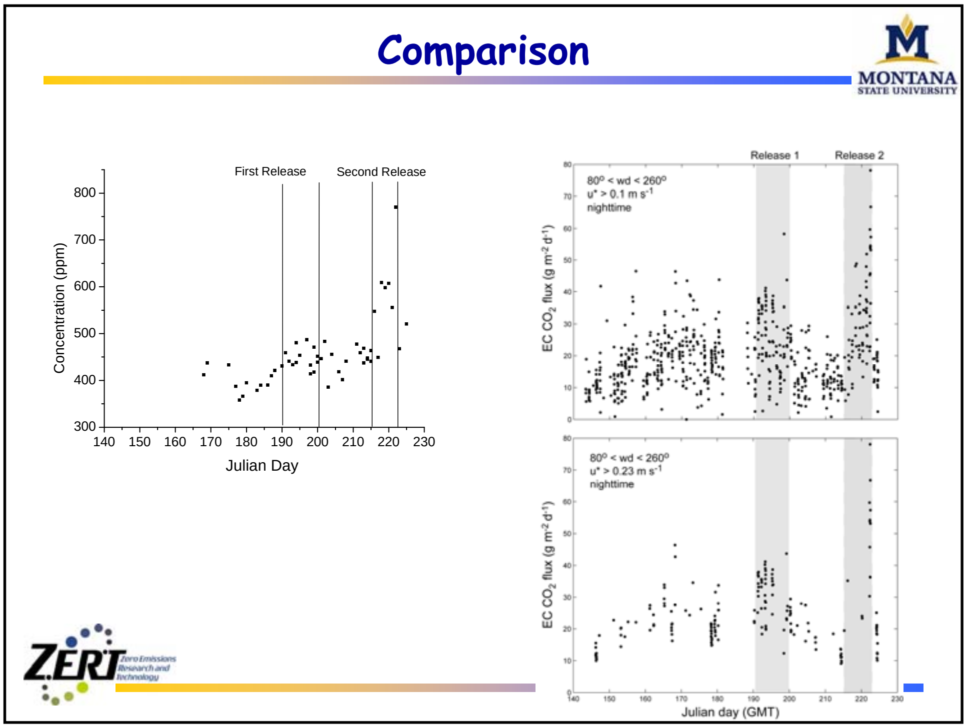
MONTANA STATE UNIVERSITY

Kevin Repasky

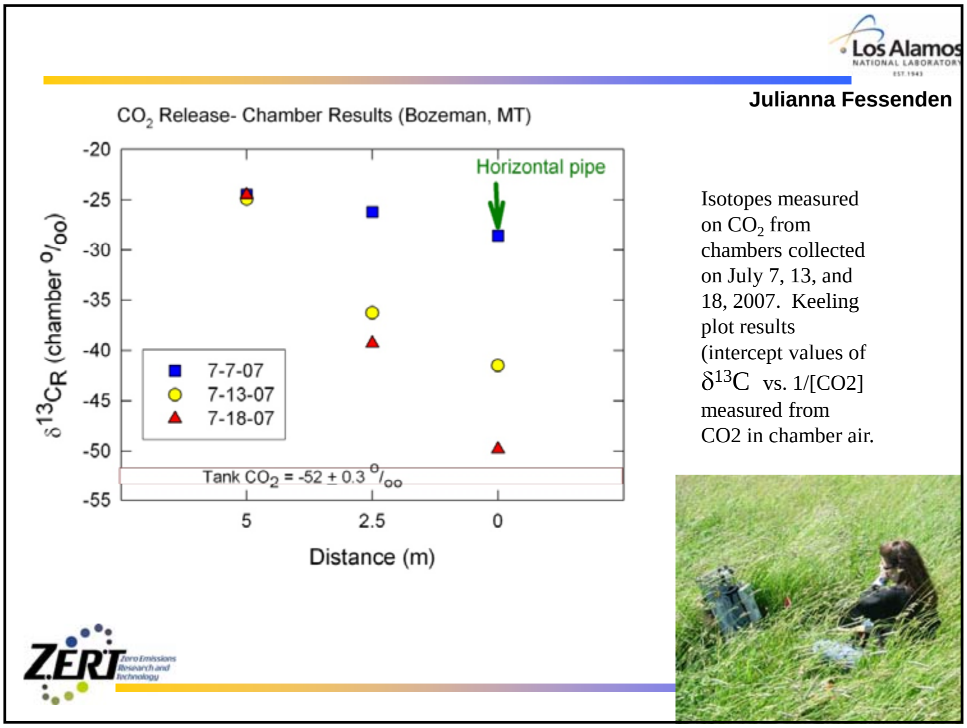


Hyperspectral Imaging Results

Kevin Repasky

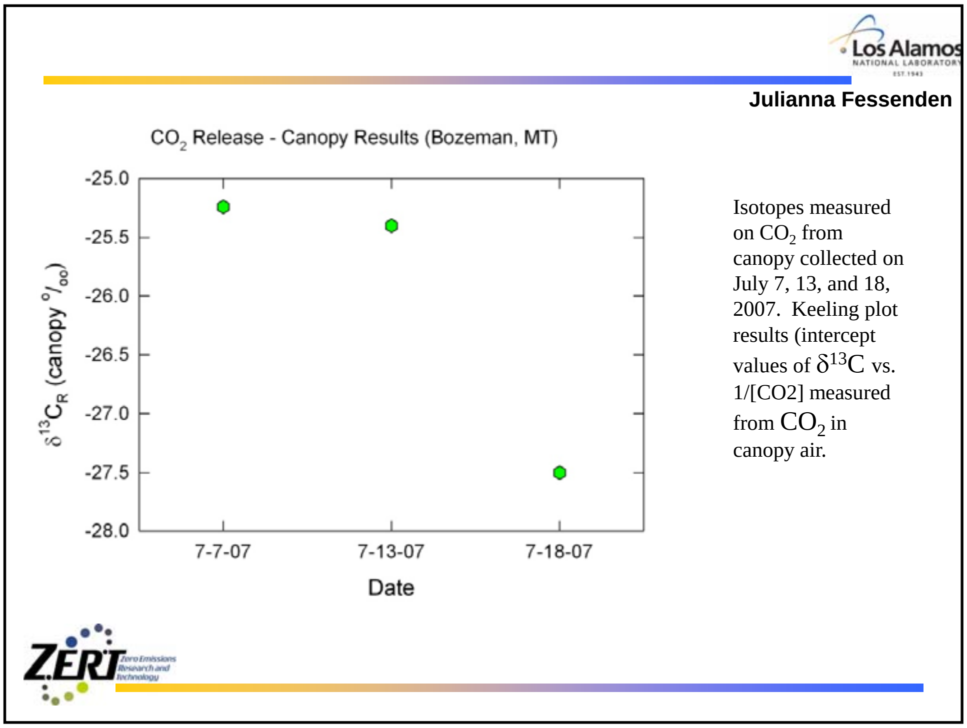


Comparison



Julianna Fessenden

Isotopes measured on CO$_2$ from chambers collected on July 7, 13, and 18, 2007. Keeling plot results (intercept values of $\delta^{13}C$ vs. 1/[CO2] measured from CO2 in chamber air.



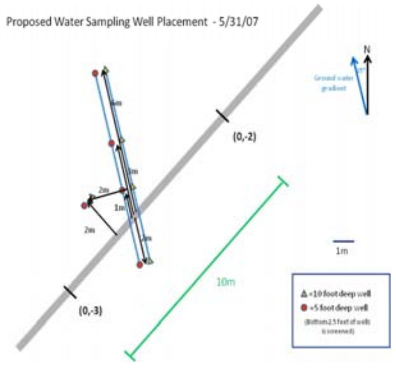
Julianna Fessenden

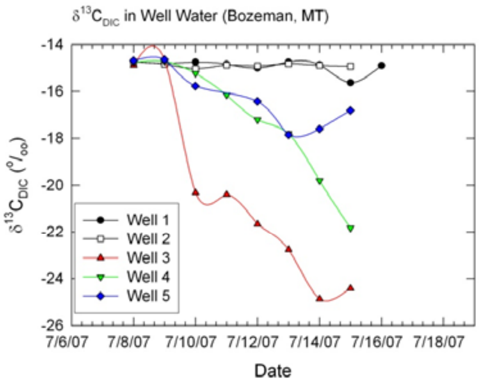
Isotopes measured on CO$_2$ from canopy collected on July 7, 13, and 18, 2007. Keeling plot results (intercept values of $\delta^{13}C$ vs. 1/[CO2] measured from CO$_2$ in canopy air.

Isotopes In Water

Julianna Fessenden

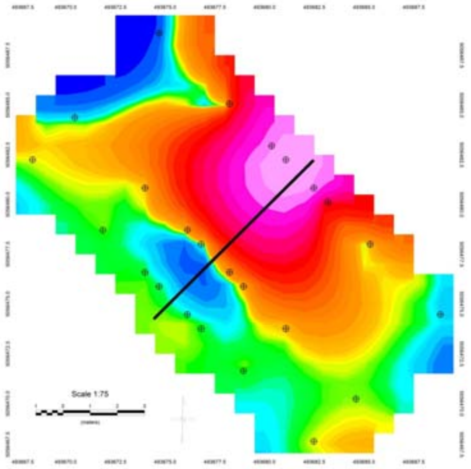
Isotopes measured on dissolved inorganic carbon (DIC) in the groundwater

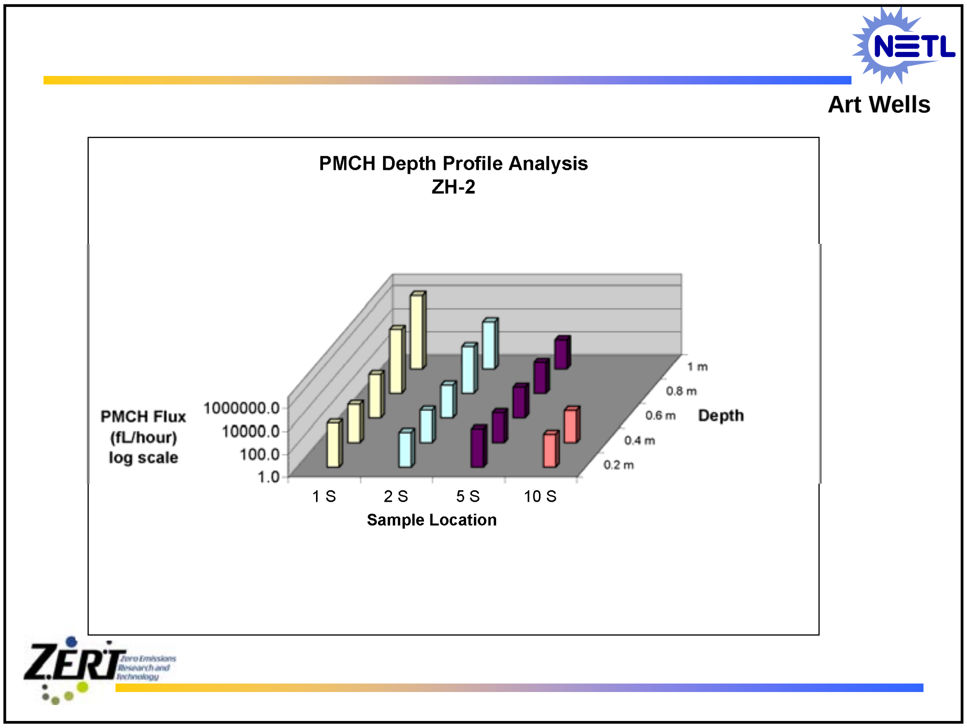




ZERT Horizontal Well Tracer Concentrations

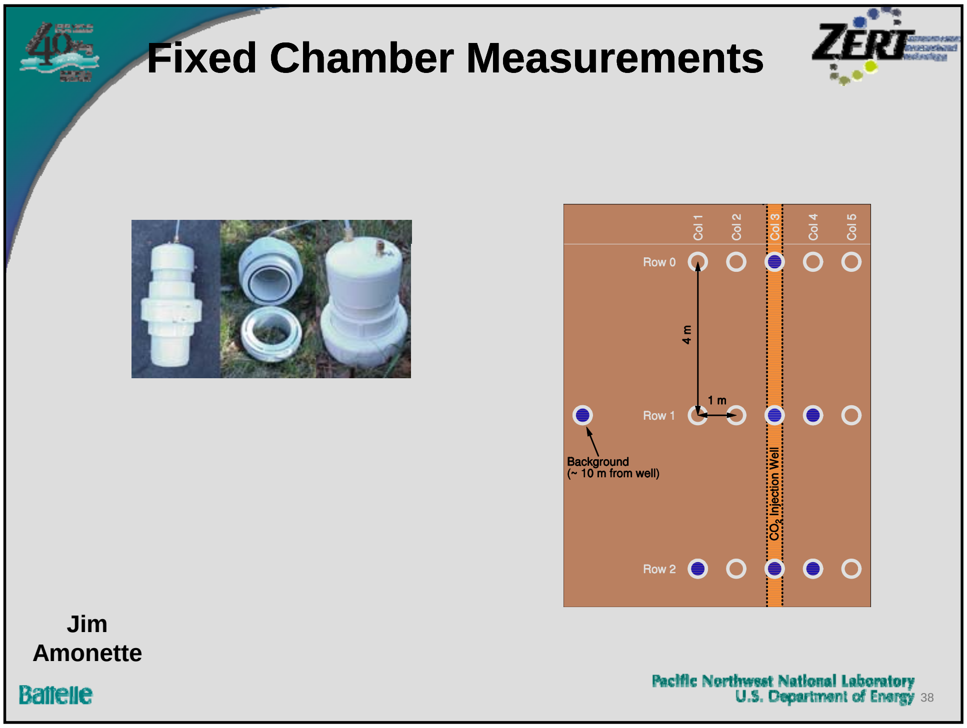
Art Wells





Art Wells

PMCH Depth Profile Analysis
ZH-2

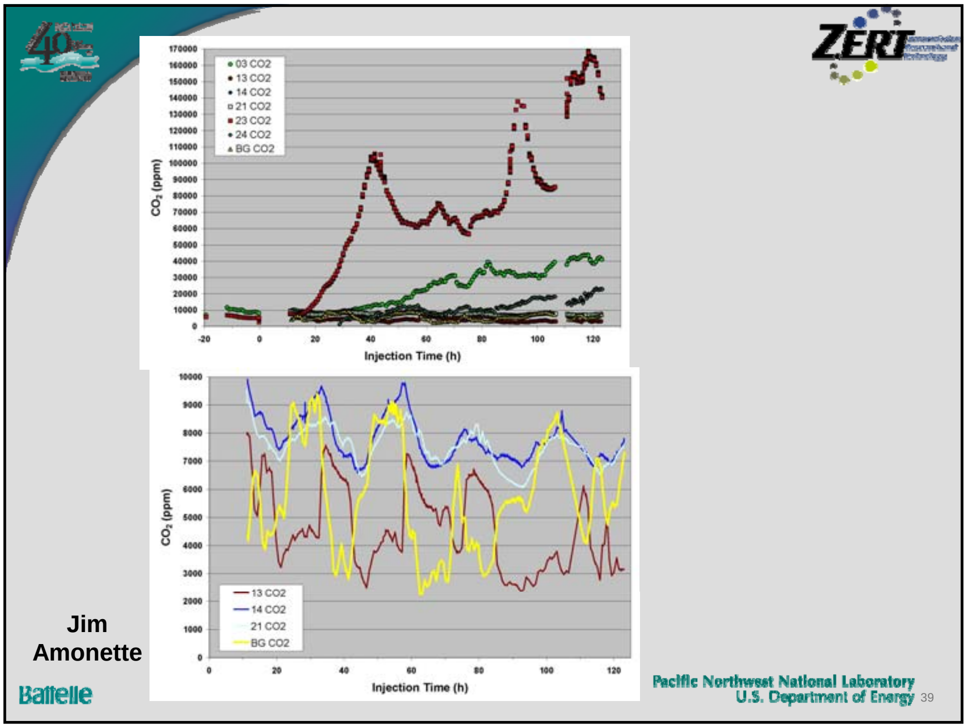


Fixed Chamber Measurements

Jim Amonette

Battelle

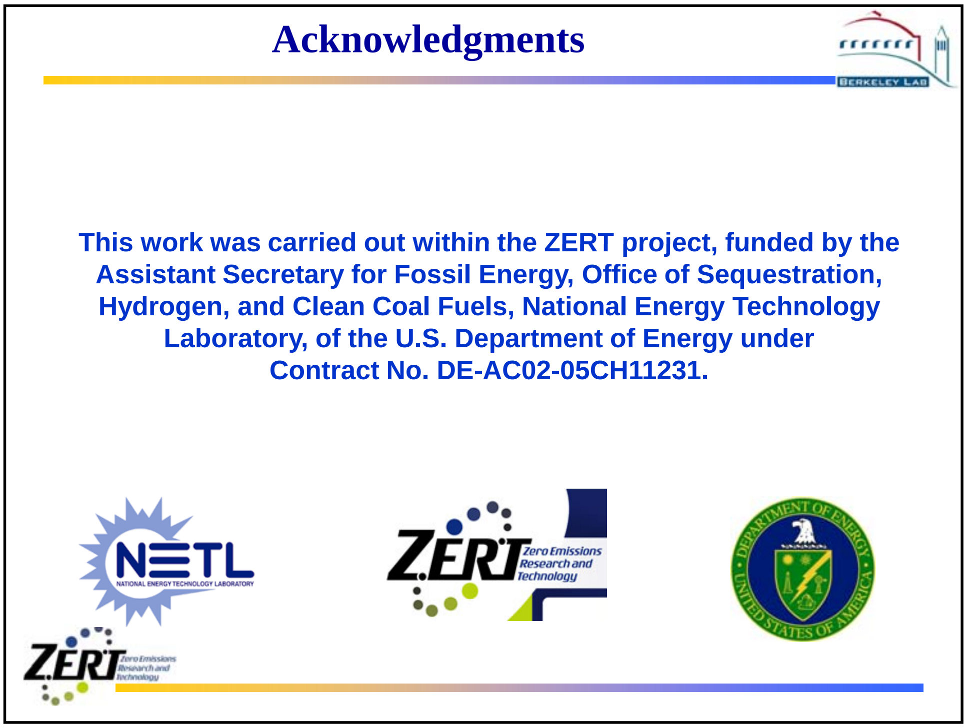
Pacific Northwest National Laboratory
U.S. Department of Energy 38



Jim Amonette

Battelle

Pacific Northwest National Laboratory
U.S. Department of Energy



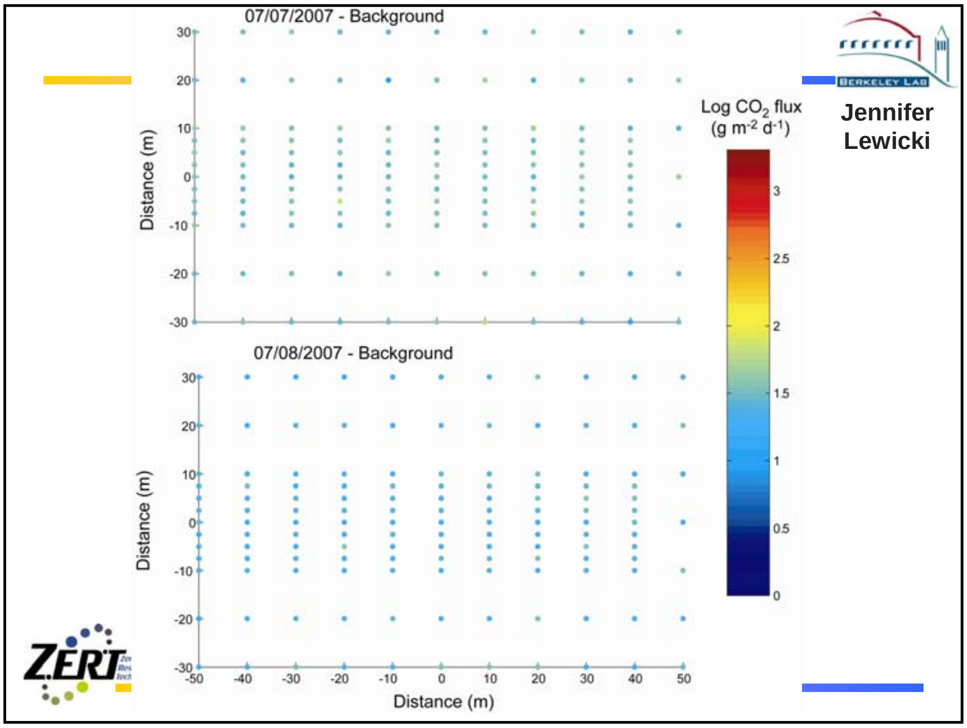
Acknowledgments

This work was carried out within the ZERT project, funded by the Assistant Secretary for Fossil Energy, Office of Sequestration, Hydrogen, and Clean Coal Fuels, National Energy Technology Laboratory, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

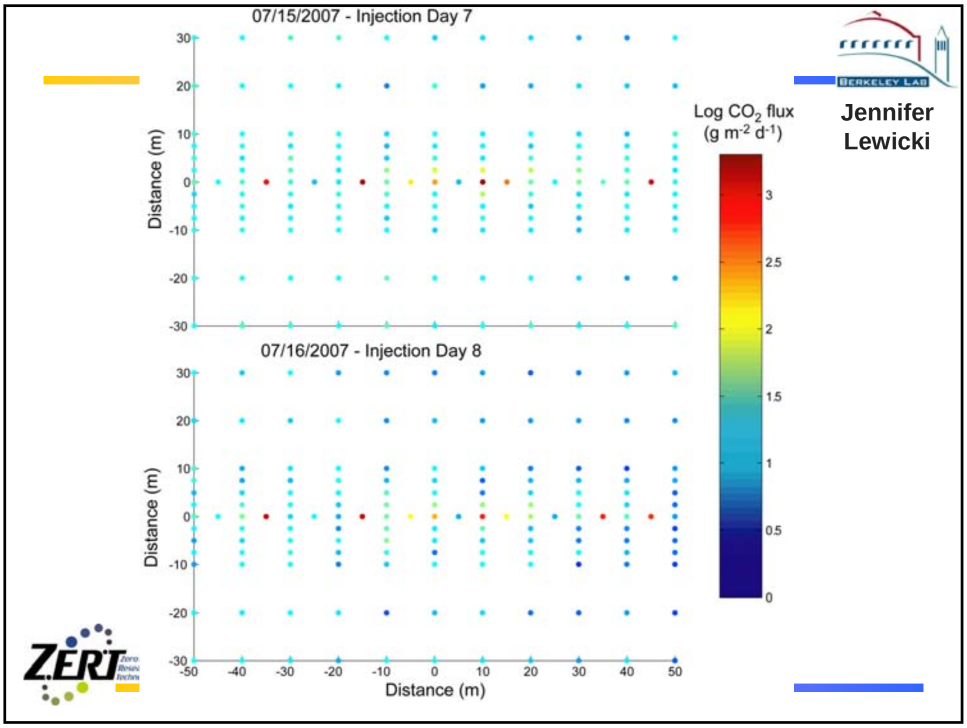
NETL NATIONAL ENERGY TECHNOLOGY LABORATORY

ZERT Zero Emissions Research and Technology

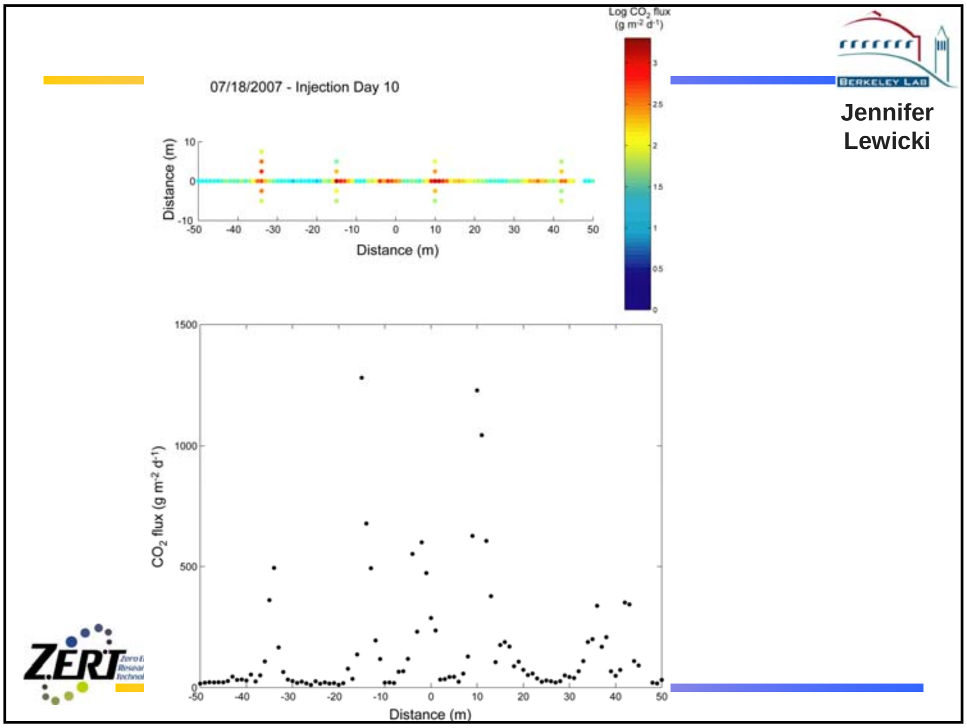
DEPARTMENT OF ENERGY UNITED STATES OF AMERICA



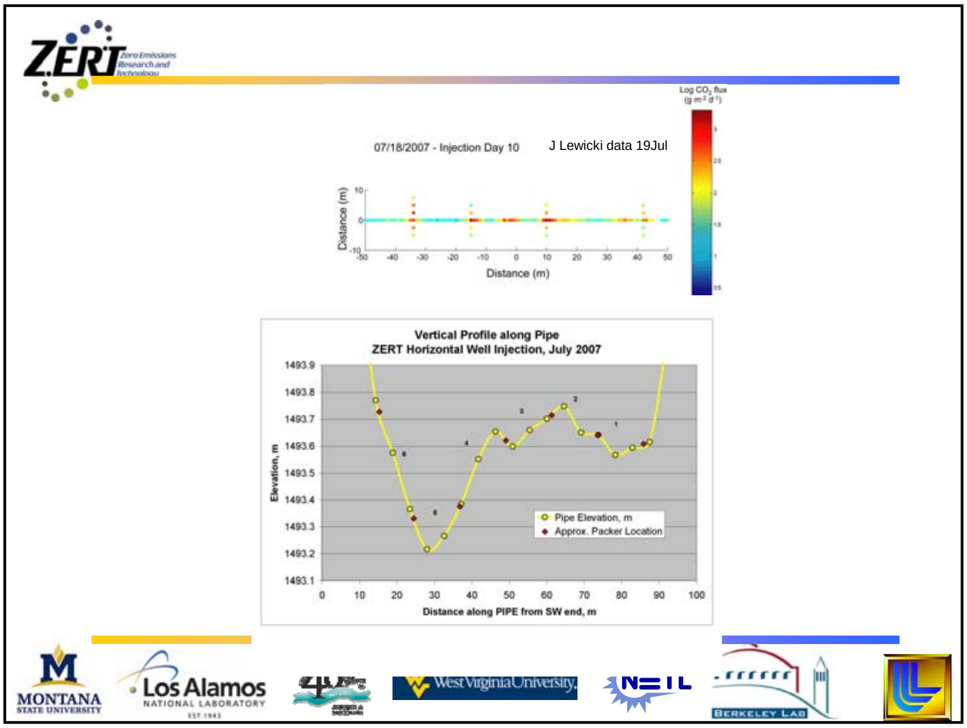
Jennifer Lewicki



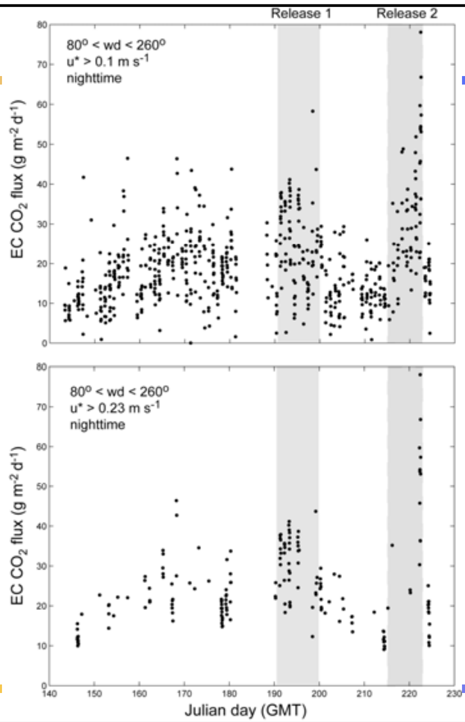
Jennifer Lewicki



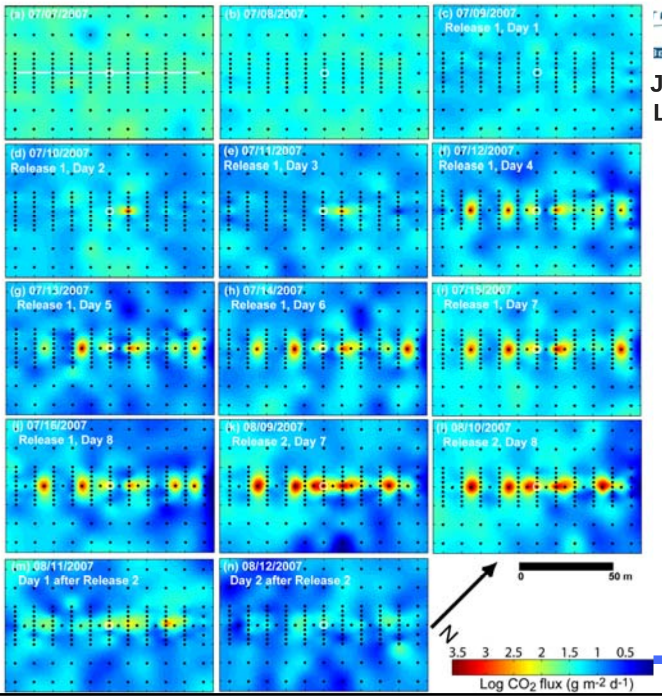
Jennifer Lewicki



J Lewicki data 19Jul



Jennifer Lewicki



Jennifer Lewicki

Statistical Techniques For Incorporating Near-Surface Monitoring and Modeling

Ya-Mei Yang and Mitchell J. Small
Carnegie Mellon University & NETL

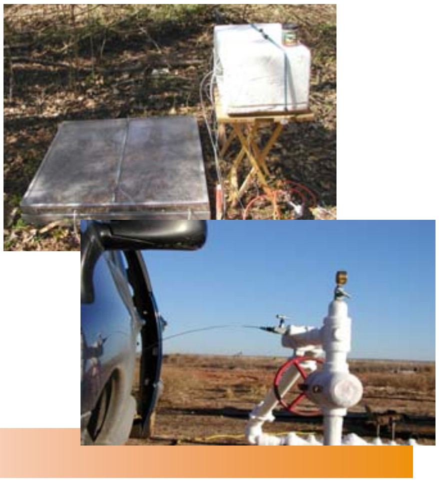
Egemen O. Ogretim and Donald D. Gray
West Virginia University & NETL

Grant S. Bromhal
DOE, National Energy Technology Laboratory

GWPC Meeting
New Orleans, LA
January 15, 2008

Cheap effective monitoring of sequestration sites is necessary for success.

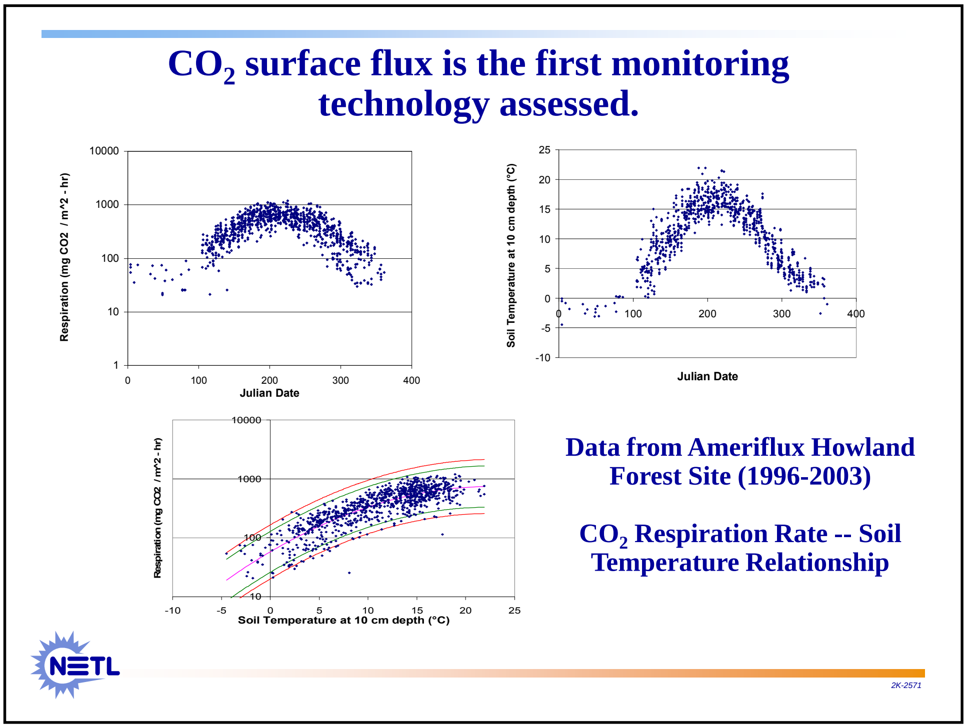
- Focus on near-surface detection technologies
- Combine modeling and monitoring
- Integrate multiple monitoring technologies in a statistically valid way
- Obtain and use actual data, as possible



The project goals and objectives are:

- Implement CO_2 transport model to predict migration from different possible leakage events at a site.
- Determine performance characteristics of leak detection technologies for simulated leak events.
- Combine evidence from multiple detection systems to infer probability that a leak of a given size will be detected.
- Reduce the likelihood of false positive and false negative leak detections.

2K-2571

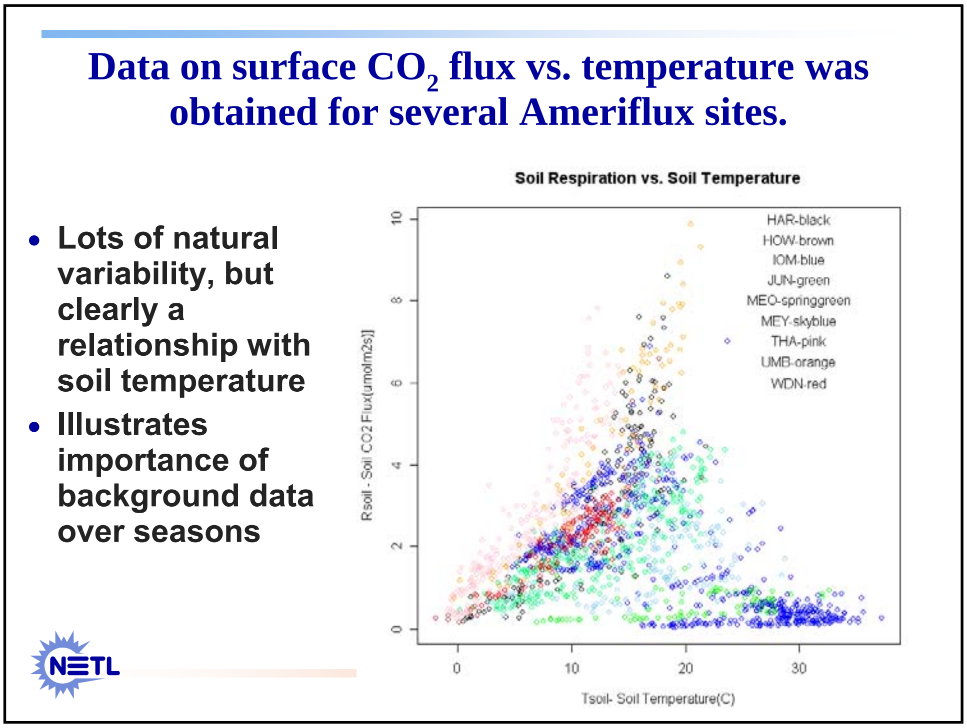


CO_2 surface flux is the first monitoring technology assessed.

Data from Ameriflux Howland Forest Site (1996-2003)

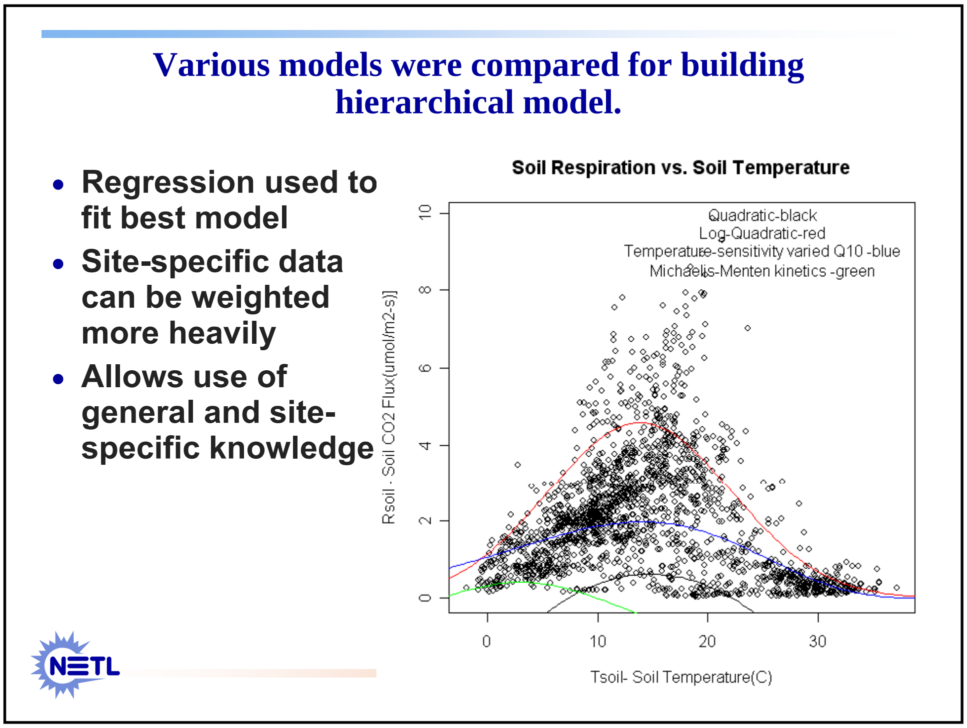
CO_2 Respiration Rate -- Soil Temperature Relationship

2K-2571



Data on surface CO_2 flux vs. temperature was obtained for several Ameriflux sites.

- Lots of natural variability, but clearly a relationship with soil temperature
- Illustrates importance of background data over seasons



Various models were compared for building hierarchical model.

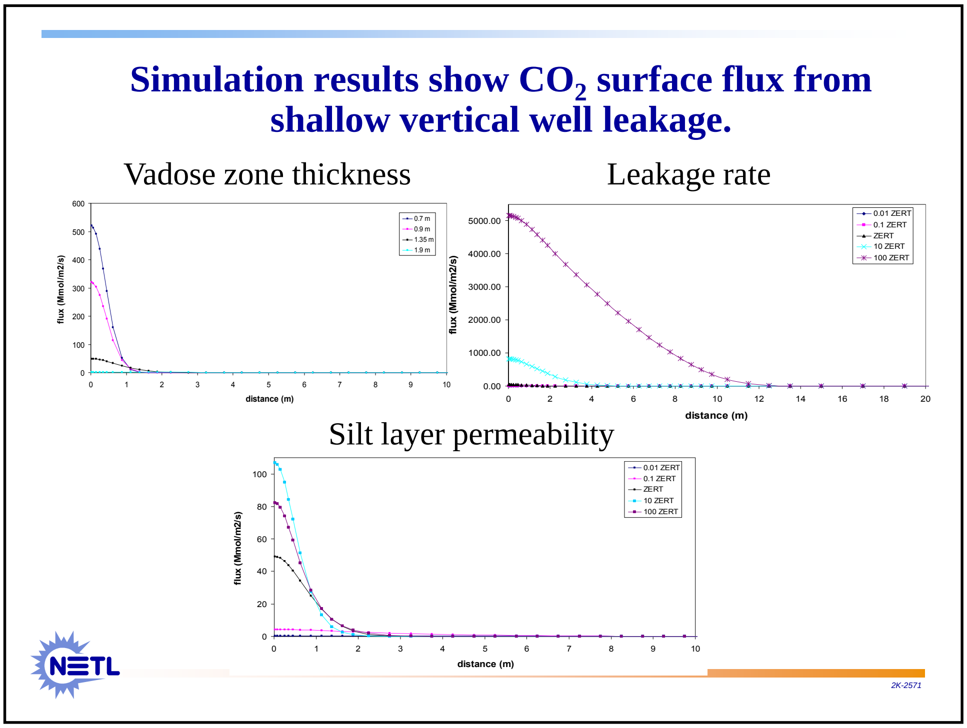
- Regression used to fit best model
- Site-specific data can be weighted more heavily
- Allows use of general and site-specific knowledge

Leakage around vertical well was simulated based on ZERT site data.

- **TOUGH2 used for simulations**
- **Two soil layers simulated:**
  - silt layer (ρ=1700 kg/m^3, Φ=0.47, k=1.5^{-12} m^2)
  - sand layer (ρ=2000 kg/m^3, Φ=0.35, k=1.0^{-9} m^2)
- **Domain: 40m wide, 5m deep**
- **Divide between layers: 1.35m below surface**
- **Leakage simulated at 2.9m below surface**
- **Leakage rate: 2.26kg/d**
- **Parametric studies of the following parameters were done:**
  - permeability, porosity, injection rate, injection depth, leakage rate.

NETL

2K-2571

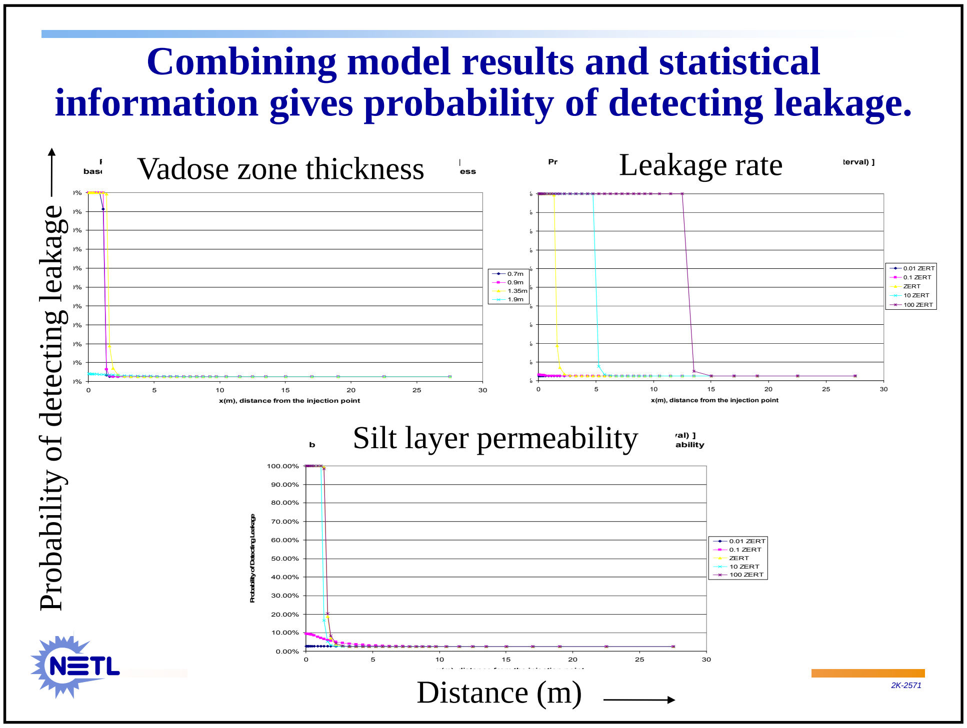


Simulation results show CO_2 surface flux from shallow vertical well leakage.

Vadose zone thickness

Leakage rate

Silt layer permeability



Combining model results and statistical information gives probability of detecting leakage.

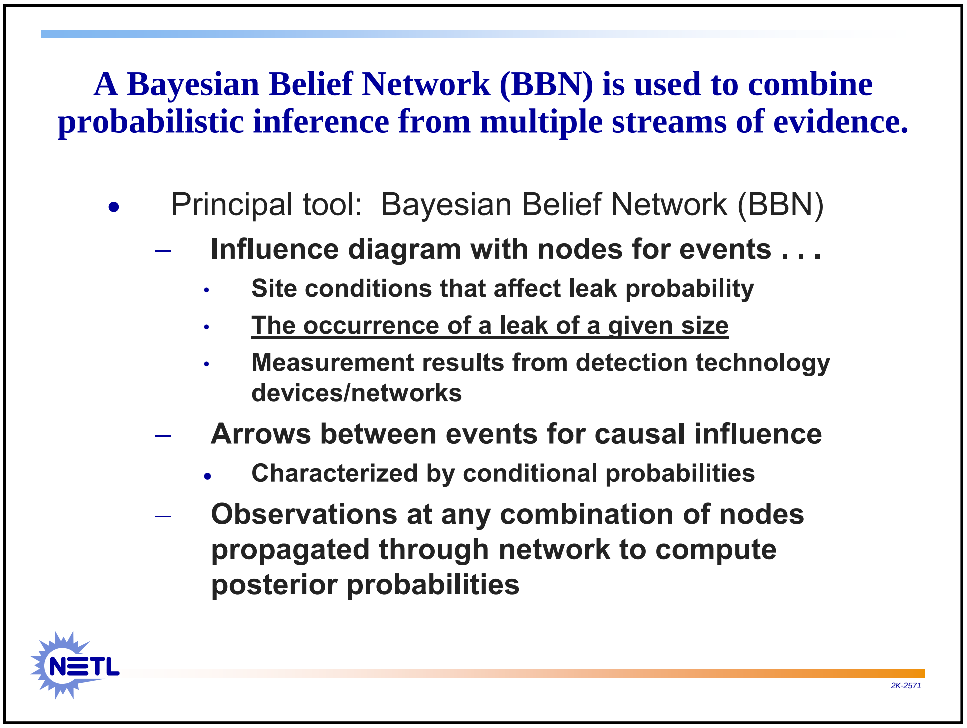
Vadose zone thickness

Leakage rate

Silt layer permeability

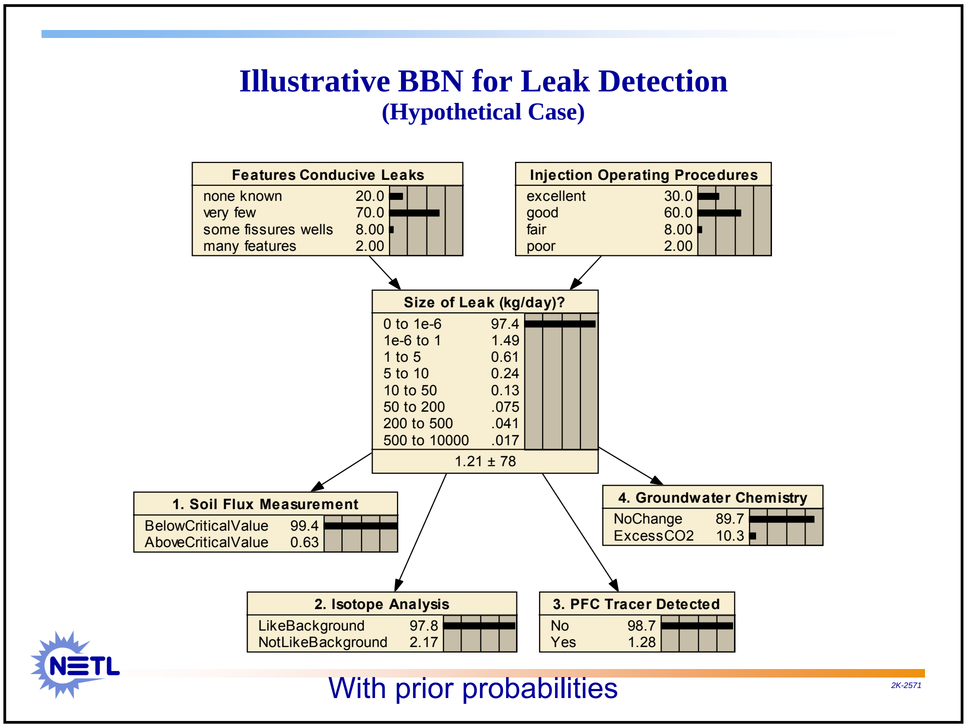
Probability of detecting leakage

Distance (m)



A Bayesian Belief Network (BBN) is used to combine probabilistic inference from multiple streams of evidence.

- Principal tool: Bayesian Belief Network (BBN)
  - **Influence diagram with nodes for events . . .**
    - **Site conditions that affect leak probability**
    - **<u>The occurrence of a leak of a given size</u>**
    - **Measurement results from detection technology devices/networks**
  - **Arrows between events for causal influence**
    - **Characterized by conditional probabilities**
  - **Observations at any combination of nodes propagated through network to compute posterior probabilities**



Illustrative BBN for Leak Detection

(Hypothetical Case)

Features Conducive Leaks	
none known	20.0
very few	70.0
some fissures wells	8.00
many features	2.00

Injection Operating Procedures	
excellent	30.0
good	60.0
fair	8.00
poor	2.00

Size of Leak (kg/day)?	
0 to 1e-6	97.4
1e-6 to 1	1.49
1 to 5	0.61
5 to 10	0.24
10 to 50	0.13
50 to 200	.075
200 to 500	.041
500 to 10000	.017

1.21 ± 78

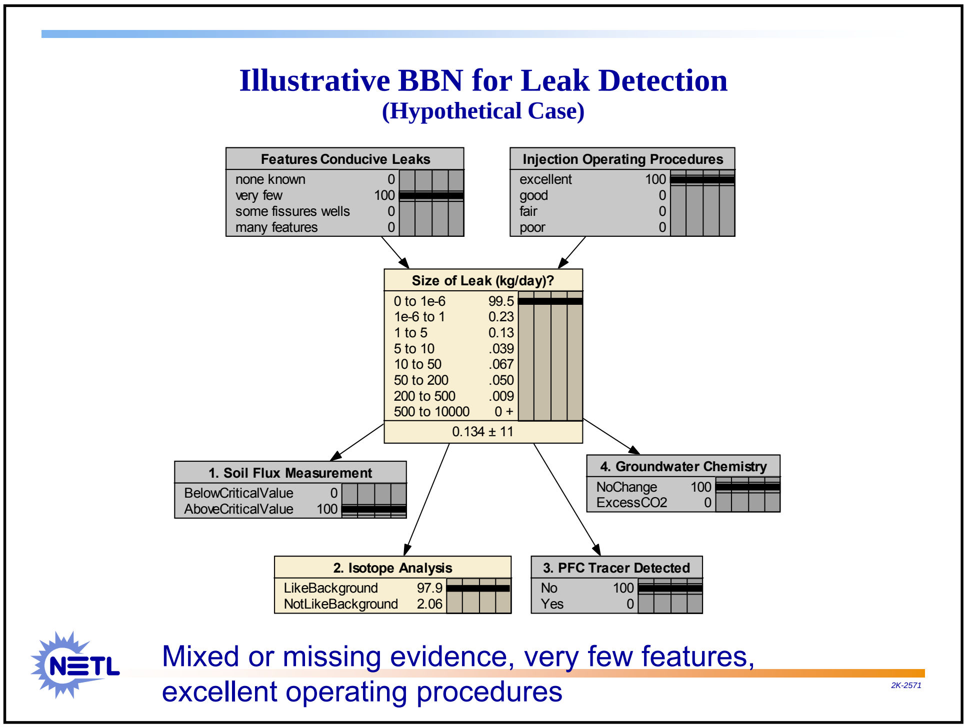
1. Soil Flux Measurement	
BelowCriticalValue	99.4
AboveCriticalValue	0.63

4. Groundwater Chemistry	
NoChange	89.7
ExcessCO2	10.3

2. Isotope Analysis	
LikeBackground	97.8
NotLikeBackground	2.17

3. PFC Tracer Detected	
No	98.7
Yes	1.28

With prior probabilities



Illustrative BBN for Leak Detection

(Hypothetical Case)

Features Conducive Leaks	
none known	0
very few	100
some fissures wells	0
many features	0

Injection Operating Procedures	
excellent	100
good	0
fair	0
poor	0

Size of Leak (kg/day)?	
0 to 1e-6	99.5
1e-6 to 1	0.23
1 to 5	0.13
5 to 10	.039
10 to 50	.067
50 to 200	.050
200 to 500	.009
500 to 10000	0 +

0.134 ± 11

1. Soil Flux Measurement	
BelowCriticalValue	0
AboveCriticalValue	100

4. Groundwater Chemistry	
NoChange	100
ExcessCO2	0

2. Isotope Analysis	
LikeBackground	97.9
NotLikeBackground	2.06

3. PFC Tracer Detected	
No	100
Yes	0

Mixed or missing evidence, very few features, excellent operating procedures

Future work involves incorporating multiple monitoring technologies.

1. Soil Flux Measurement
2. PFC Tracer
3. Isotope Analysis
4. Ground Water Chemistry
5. Others? (can be added with this methodology)

Future plans also include incorporating flux data from the ZERT site and incorporating this data at the San Juan Basin Regional Partnership site.

2K-2571

Thank You!

- Questions?

2K-2571

Compare Simulated CO_2 Flux Rates with those Detectable (high power)

- **Generate CO_2 flux measurements using TOUGH2 for a hypothetical, idealized site**
  - As a function of fugitive injection (leakage) rate
  - As a function of radial distance from leakage point; and
  - As a function of depth of release

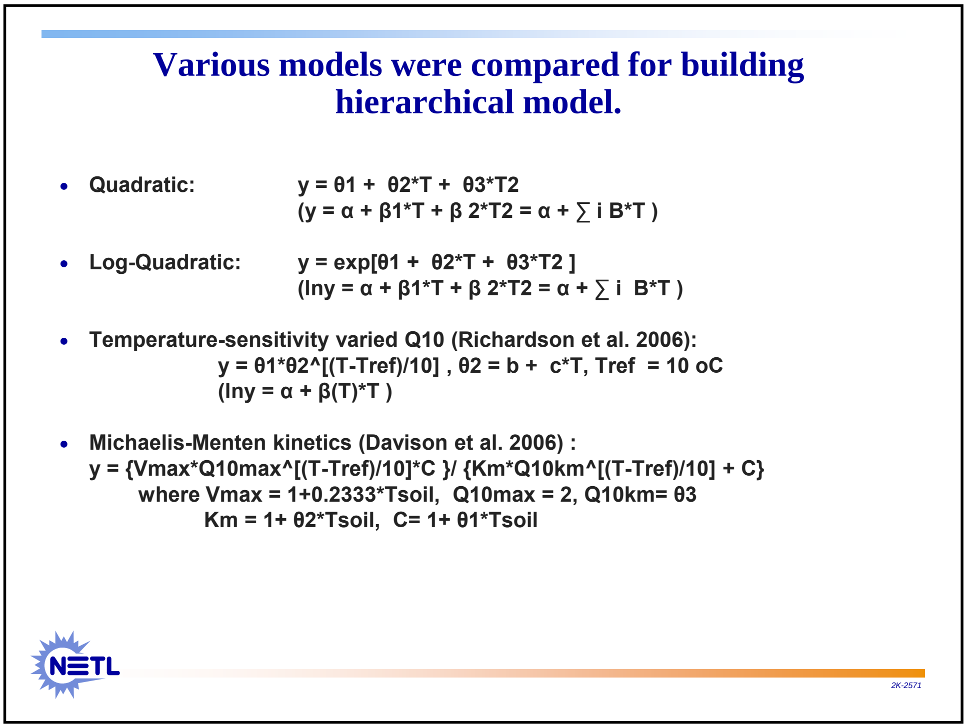
2K-2571

Data on surface CO_2 flux vs. temperature was obtained for several Ameriflux sites.

Site	Location	Country/ State	Climate	MAT (°C)	Rs Submitted
Evergreen Needleleaf Forest (ENF)					
HOW	45.2 N 68.7 W	USA-- ME	Temperate, continental	5.69	1997-2001
MEO	44.5W 121.62 N	USA-- OR	Temperate	8.5	96,97,99-01
MEY	44.5W 121.57N	USA-- OR	Temperate	7.25	1999-2001
THA	50.96 N 13.75 E	Germany -- Tharandt	Temperate, continental	7.6	2000-02
WDN	50.09 N 11.52 E	Germany -- Weidenbrunnen	Temperate, oceanic	6	1999
Mixed Deciduous/Evergreen Forest (MXD)					
UMB	45.56 N 84.71 W	USA-- MI	Temperate, northern	6.2	1998-00
HAR	42.54 N 72.17 W	USA-- MA	Temperate	7.85	1995-2001
Woodland/Savanna (WSV)					
JUN	44.27N 121.38 W	USA-- OR	Temperate	NA	19,972,002
Grassland (GRS)					
IOM	38.4 N 120.95 W	USA-- CA	Mediterranean	21.4	2000-01

source: AmeriFlux (http://public.ornl.gov/ameriflux/index.html)

2K-2571



Various models were compared for building hierarchical model.

- **Quadratic:** $y = \theta1 + \theta2*T + \theta3*T2$
  ($y = \alpha + \beta1*T + \beta\ 2*T2 = \alpha + \sum i\ B*T$)
- **Log-Quadratic:** $y = \exp[\theta1 + \theta2*T + \theta3*T2\ ]$
  ($\ln y = \alpha + \beta1*T + \beta\ 2*T2 = \alpha + \sum i\ B*T$)
- **Temperature-sensitivity varied Q10 (Richardson et al. 2006):**
  $y = \theta1*\theta2\verb|^|[(T-Tref)/10]$, $\theta2 = b + c*T$, $Tref = 10$ oC
  ($\ln y = \alpha + \beta(T)*T$)
- **Michaelis-Menten kinetics (Davison et al. 2006) :**
  $y = \{Vmax*Q10max\verb|^|[(T-Tref)/10]*C\ \}/\ \{Km*Q10km\verb|^|[(T-Tref)/10] + C\}$
  where $Vmax = 1+0.2333*Tsoil$, $Q10max = 2$, $Q10km= \theta3$
  $Km = 1+ \theta2*Tsoil$, $C= 1+ \theta1*Tsoil$

Monitoring Surface CO_2 Fluxes During Two Shallow Subsurface CO_2 Releases

Jennifer L. Lewicki and Marc L. Fischer
(Lawrence Berkeley National Laboratory)

Laura Dobeck and Lee Spangler
(Montana State University)

Additional Participants

- Sally Benson (**Stanford U, LBNL**)
- Curt Oldenburg, Ray Solbau, Paul Cook (**LBNL**)
- Kevin Repasky, Joe Shaw, Kadie Gullickson, Amin Nehrir, Seth Humphries, Al Cunningham, Josh Rouse, Charlie Keith (**Montana State U**)
- Bill Pickles, James Jacobson (**UC Santa Cruz**)
- James Amonette, Jon Barr (**PNNL**)
- Julianna Fessenden, Thom Rahn (**LANL**)
- Henry Rauch (**West Virginia U**)
- Dennis Stanko, Art Wells, Rodney Diehl, Grant Bromhal, Brian Strasizar, Rick Hammack, Garret Veloski (**NETL**)

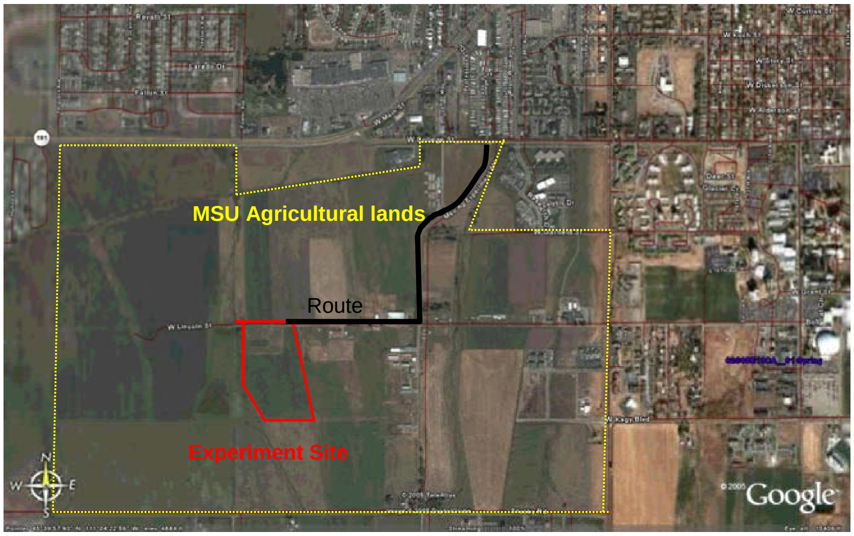
Motivation

- Importance of near-surface monitoring of CO_2 storage sites
- Test the ability of two different, yet complementary techniques to detect (+/- locate and quantify) surface CO_2 leakage
- Under the scenarios investigated:
  - What are the strengths and weaknesses of the techniques?
  - How can they be used in a complementary fashion?

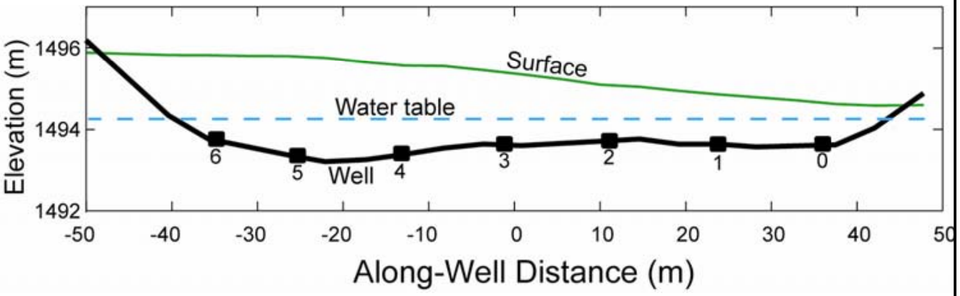
Outline

- Overview of field site and CO_2 release experiments (Summer 2007)
- Chamber measurements of surface CO_2 fluxes [Lewicki et al., *Geophys. Res. Lett*., 2007]
- Eddy covariance measurements of surface CO_2 fluxes
- Discussion of strengths and weaknesses and recommendations for CO_2 storage monitoring

Field Site



Horizontal Well



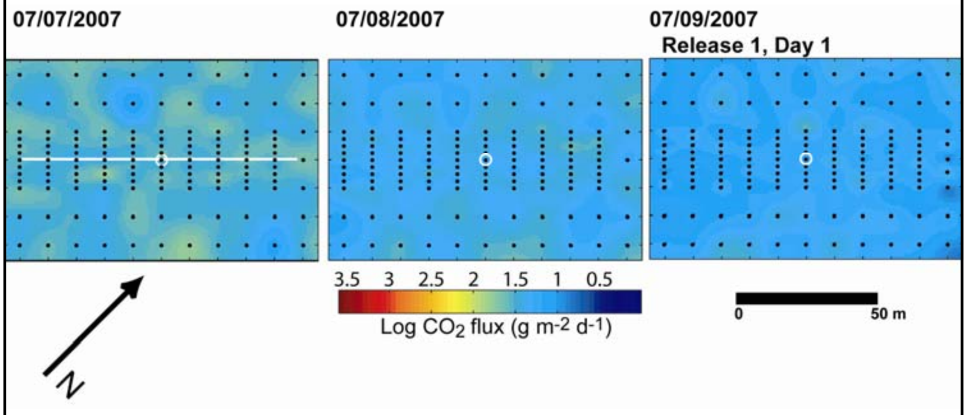
-~30 cm-thick clay topsoil overlies a ~20 cm-thick clayey silt layer, which overlies an alluvial sandy cobble with 10-25 cm diameter cobbles.

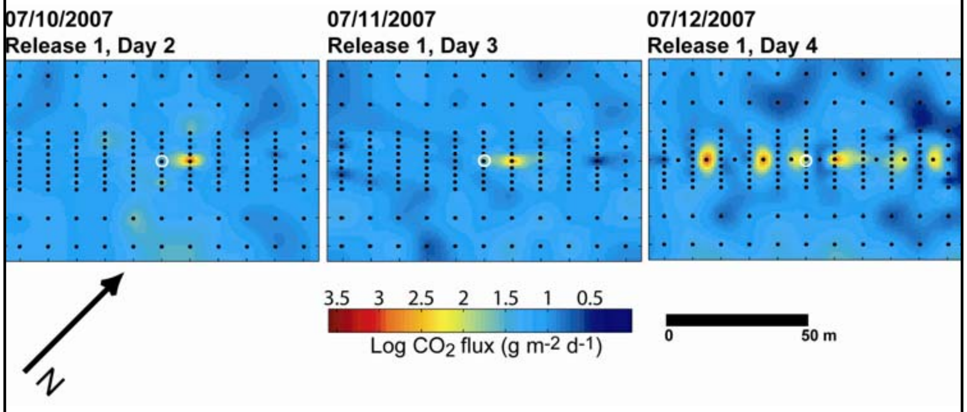
- Slotted section located in sandy cobble, sub-water table.

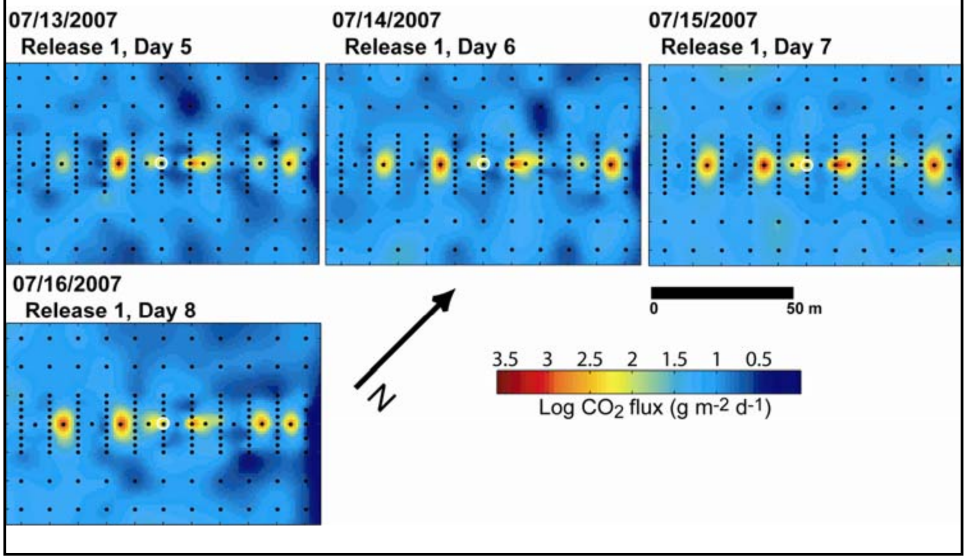
Summer 2007 CO_2 Releases

- **Release 1**: 9-18 July, injection at 0.1 t CO_2 d^{-1}
  - chosen based on numerical simulations to provide a challenging detection problem while still ensuring CO_2 would reach surface
- **Release 2**: 3-10 August, injection at 0.3 t CO_2 d^{-1}
  - Chosen to obtain a larger surface flux for demonstration purposes

Chamber Soil CO_2 Fluxes


07/07/2007
07/08/2007
07/09/2007
Release 1, Day 1
3.5 3 2.5 2 1.5 1 0.5
Log CO2 flux (g m-2 d-1)
0
50 m
N

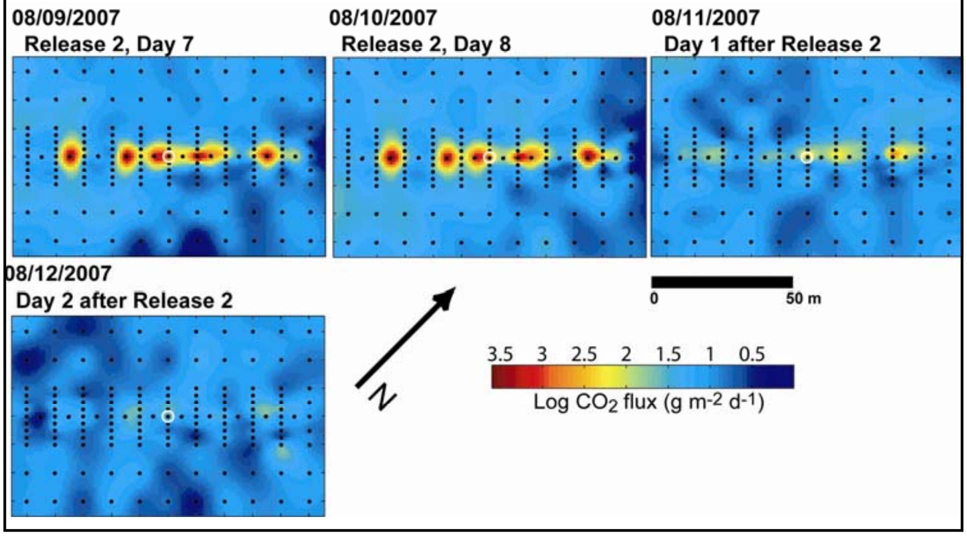

07/10/2007
Release 1, Day 2
07/11/2007
Release 1, Day 3
07/12/2007
Release 1, Day 4
3.5 3 2.5 2 1.5 1 0.5
Log CO2 flux (g m-2 d-1)
0
50 m
N


07/13/2007 Release 1, Day 5

07/14/2007 Release 1, Day 6

07/15/2007 Release 1, Day 7

07/16/2007 Release 1, Day 8


08/09/2007 Release 2, Day 7

08/10/2007 Release 2, Day 8

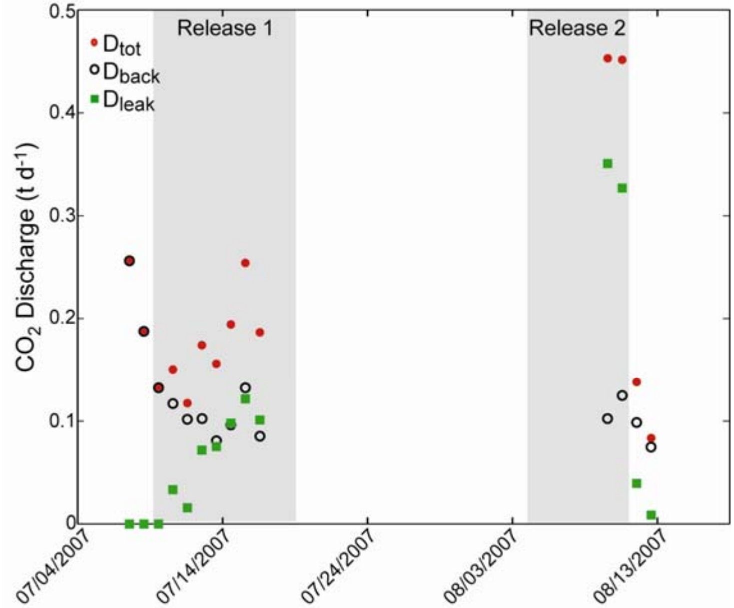
08/11/2007 Day 1 after Release 2

08/12/2007 Day 2 after Release 2

Dtot = declustered mean CO_2 flux x 7700 m^2

Dback = mean CO_2 flux at 10-30 m from well x 7700 m^2

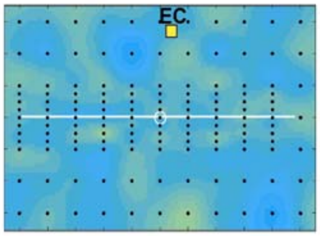
Dleak = Dtot - Dback

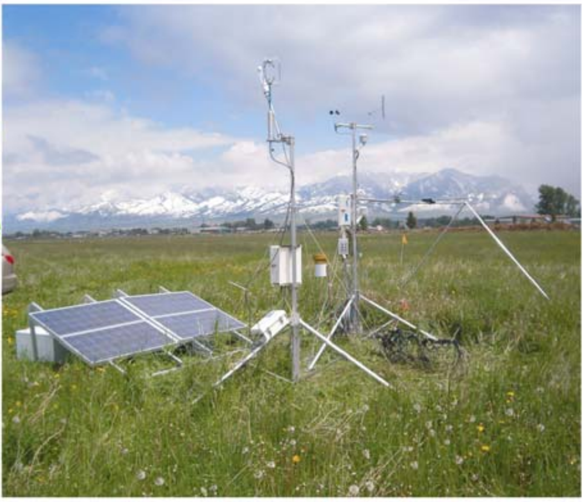


Eddy Covariance Measurements of Net CO_2 Flux

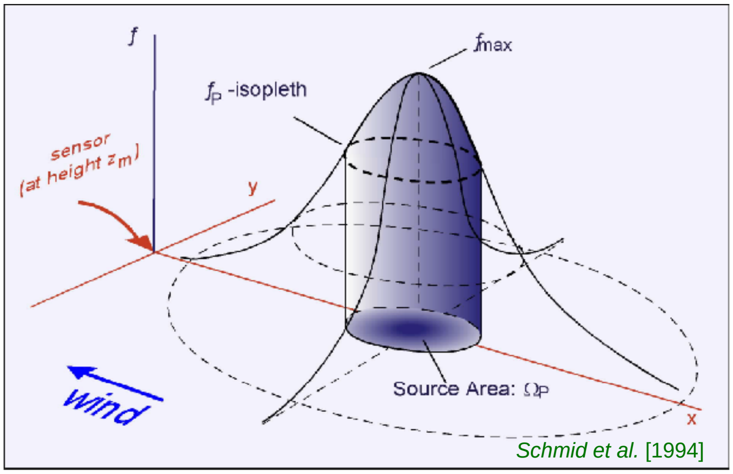
$F_c = \overline{w'c'}$

- Requires sufficiently long averaging time, assumes steady-state conditions, homogeneous surface



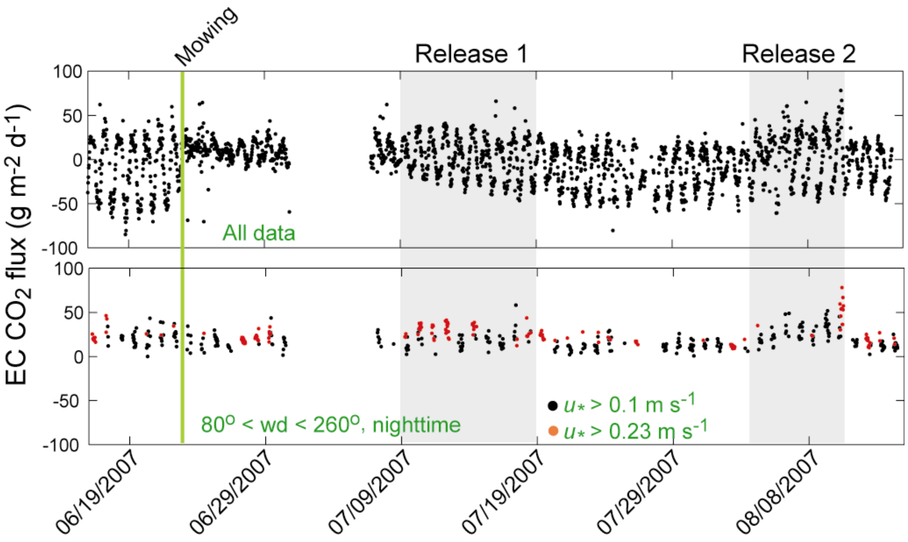


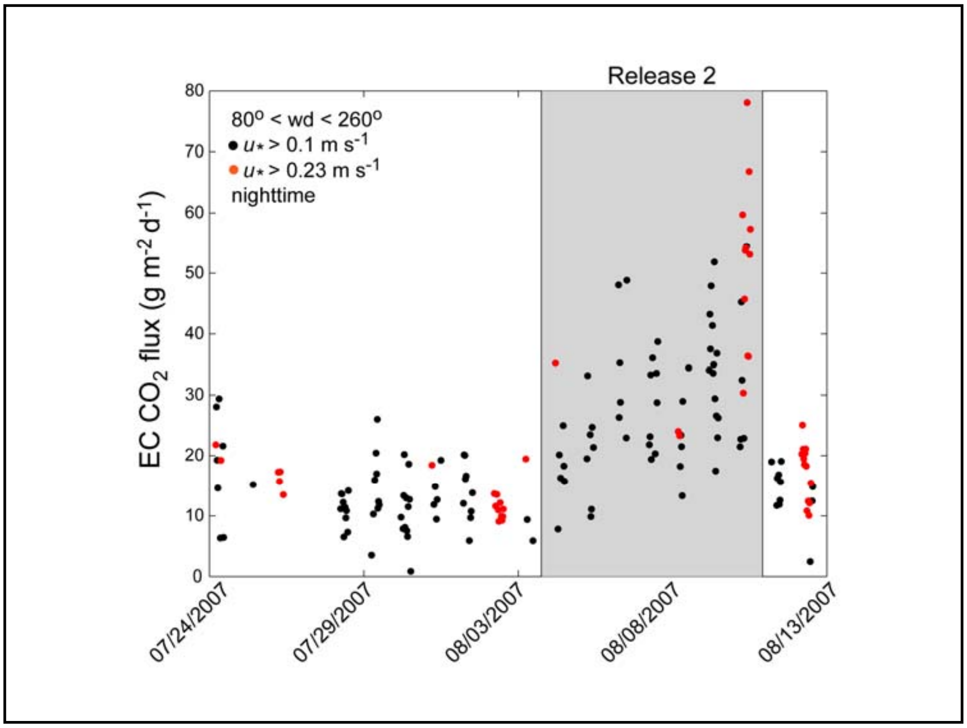
Eddy Covariance Footprint

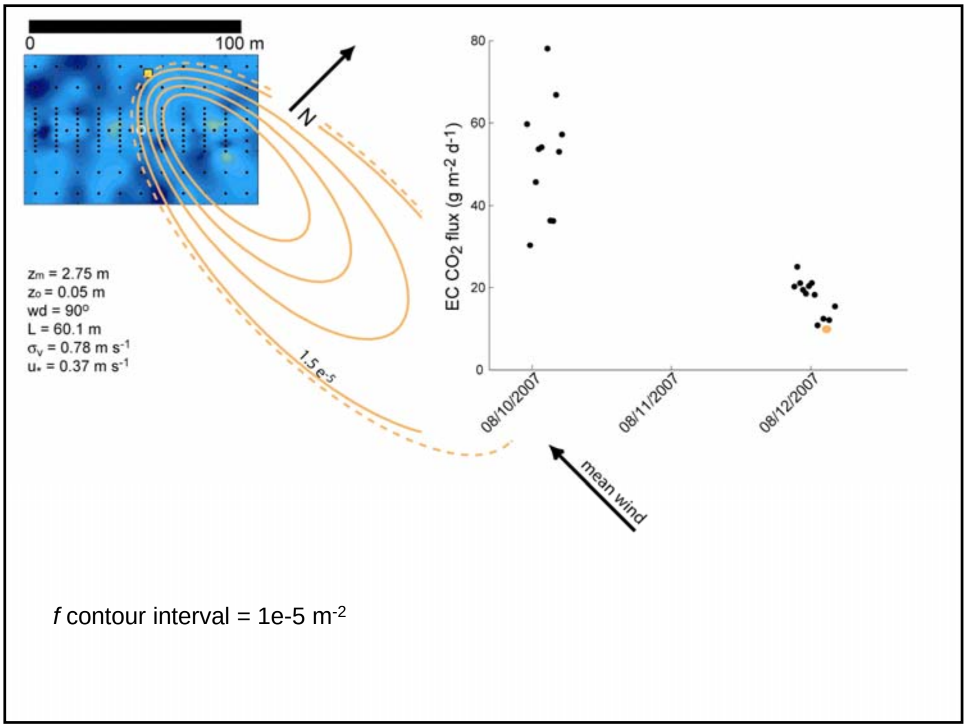


Schmid et al. [1994]

$$F_C(x_m,y_m,z_m)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} Q_C(x',y',z'=z_0)\cdot f(x_m-x',y_m-y',z_m-z_0)\cdot dx'dy'$$







z_m = 2.75 m
z_0 = 0.05 m
wd = 90°
L = 60.1 m
σ_v = 0.78 m s^{-1}
u_* = 0.37 m s^{-1}

f contour interval = 1e-5 m^{-2}

Summary

- Chamber measurements mapped the spatio-temporal evolution of surface CO_2 leakage.
- Chamber measurements were close to and away from the well, allowing us to quantify CO_2 emissions from background soil respiration separately from leakage.
- Releases 1 and 2 resulted in high leakage relative to background CO_2 fluxes, but leakage areas were small relative to the total study area.

Summary

- Since eddy covariance averages over a large area, temporal trends in background fluxes masked leakage during Release 1. Drop in background fluxes and increase in leakage fluxes during Release 2 allowed for leakage detection.
- Location and height of EC station, atmospheric conditions, and background flux variability influence ability to detect leakage.

Summary

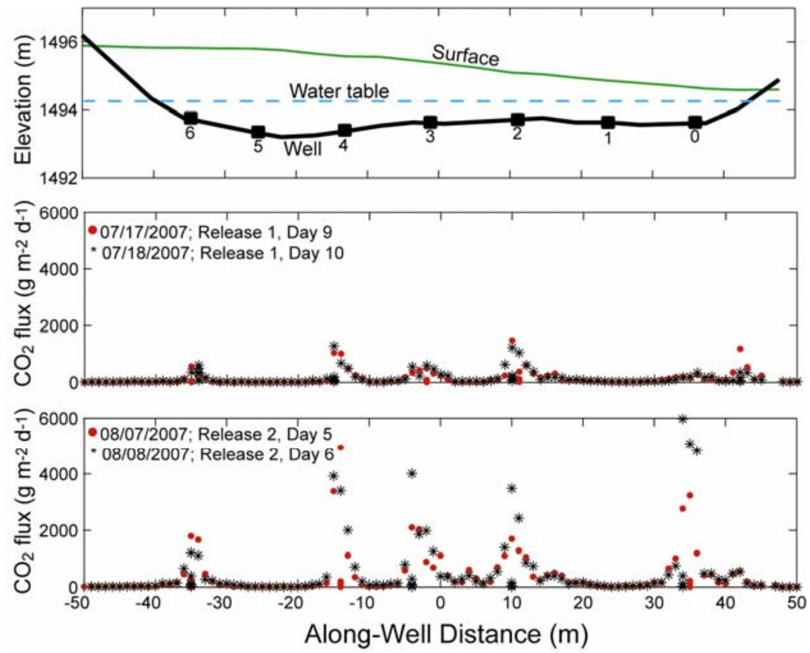
- Chamber method
  - Point measurement
  - Map spatio-temporal variation of leakage + background
  - Detect, locate, quantify leakage
  - Laborious; measurements over limited area in given time
- Eddy covariance
  - Spatially and temporally averaged measurement
  - Automated; low effort
  - Large spatial scale convenient yet background large influence
  - Assumes homogeneous surface conditions
  - Detect leakage; need multiple stations to locate and quantify (or many footprints sampling stable leak)

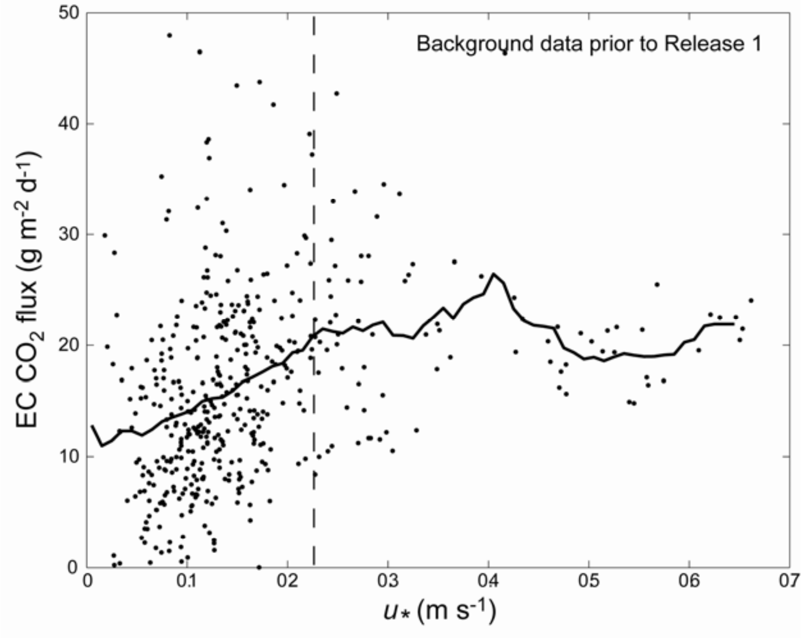
Summary

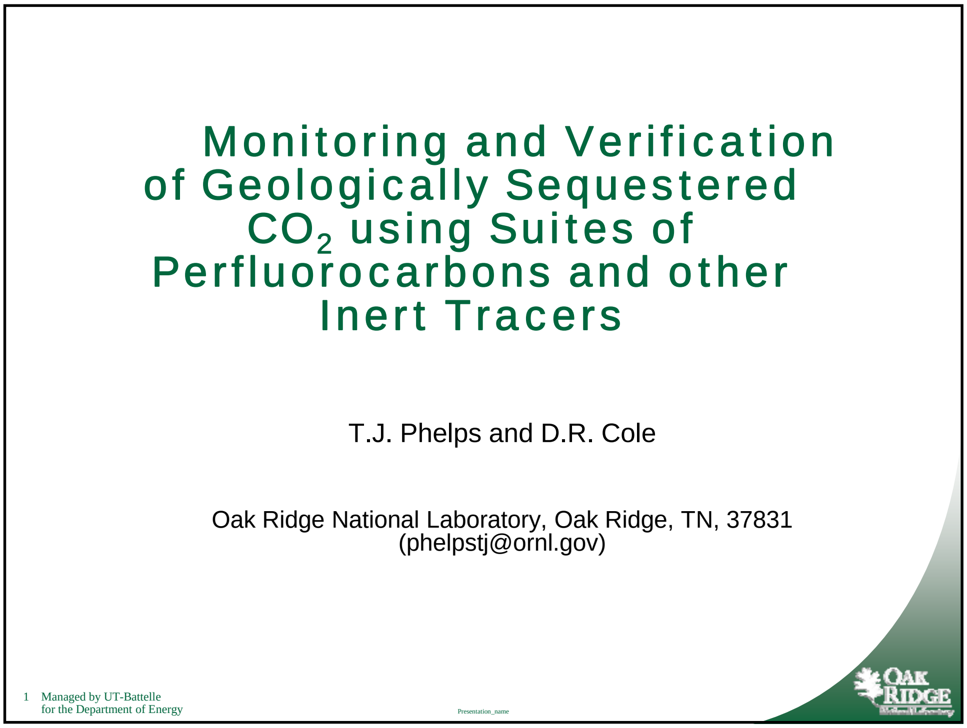
- Important to:
  - characterize background CO_2 variability prior to CO_2 injection
  - limit area of investigation by focus on features most susceptible to leakage based on site characterization
  - use a variety of complementary measurement techniques, statistical methods
- New ZERT CO_2 release facility provides an excellent opportunity to develop integrated field methodologies to detect and quantify potential CO_2 leakage from geologic storage sites.

Thank you

- Entire ZERT team for making experiment a success
- This work was funded by the Assistant Secretary for Fossil Energy, Office of Sequestration, Hydrogen, and Clean Coal Fuels, NETL, of the U.S. Dept. of Energy under Contract No. DE-AC02-05CH11231




Background data prior to Release 1
EC CO2 flux (g m-2 d-1)
u* (m s-1)
0
10
20
30
40
50
0
01
02
03
04
05
06
07



Monitoring and Verification of Geologically Sequestered CO_2 using Suites of Perfluorocarbons and other Inert Tracers

T.J. Phelps and D.R. Cole

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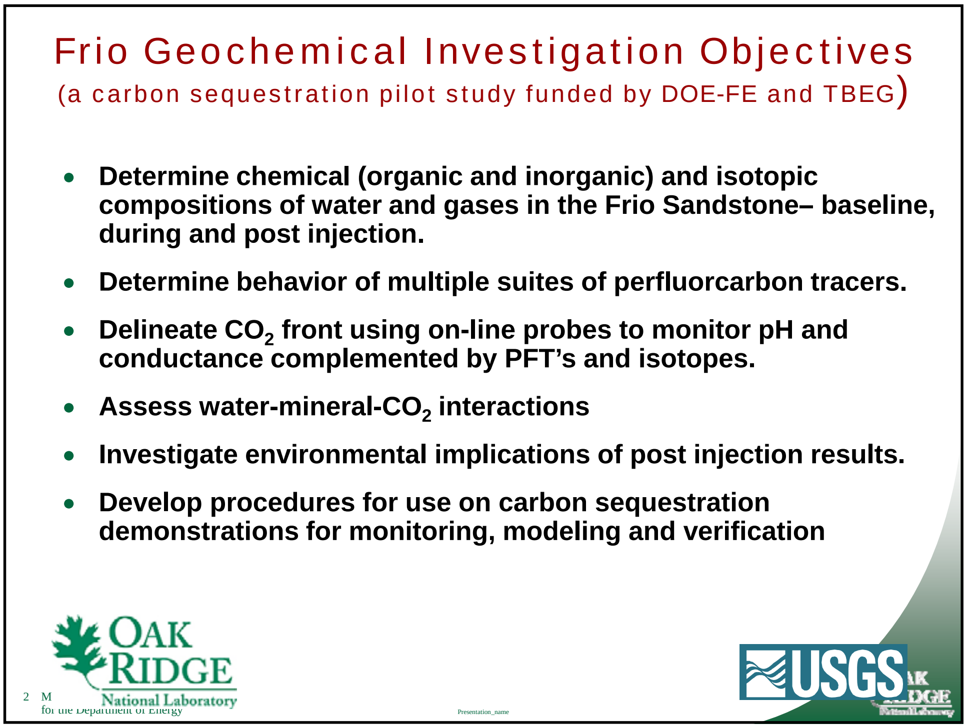
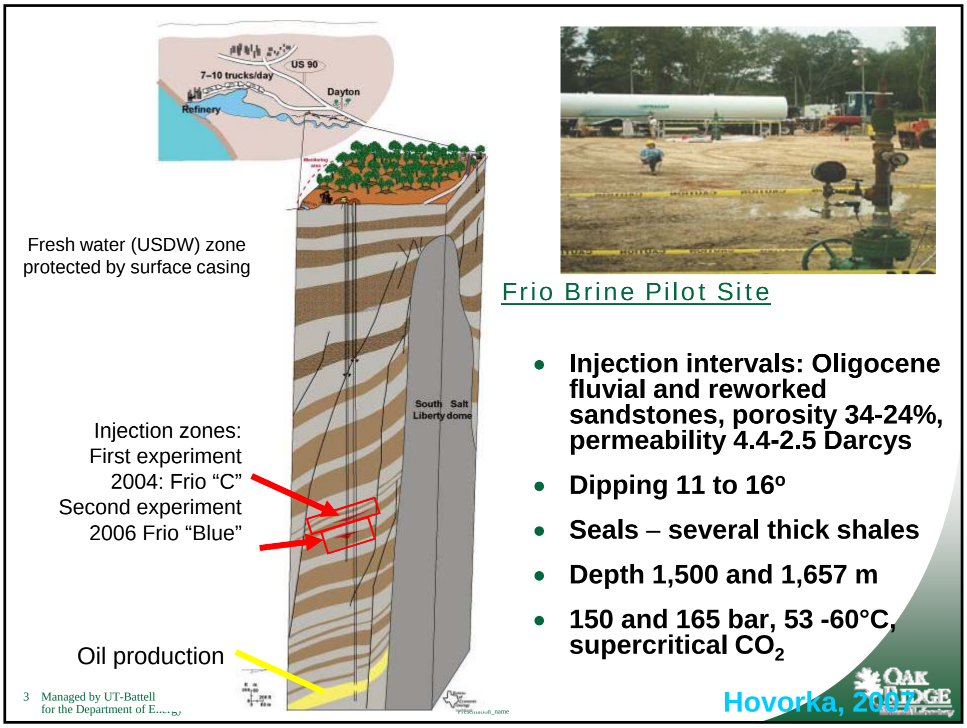
(phelpstj@ornl.gov)



Frio Geochemical Investigation Objectives

(a carbon sequestration pilot study funded by DOE-FE and TBEG)

- **Determine chemical (organic and inorganic) and isotopic compositions of water and gases in the Frio Sandstone– baseline, during and post injection.**
- **Determine behavior of multiple suites of perfluorcarbon tracers.**
- **Delineate CO_2 front using on-line probes to monitor pH and conductance complemented by PFT's and isotopes.**
- **Assess water-mineral-CO_2 interactions**
- **Investigate environmental implications of post injection results.**
- **Develop procedures for use on carbon sequestration demonstrations for monitoring, modeling and verification**



Fresh water (USDW) zone protected by surface casing

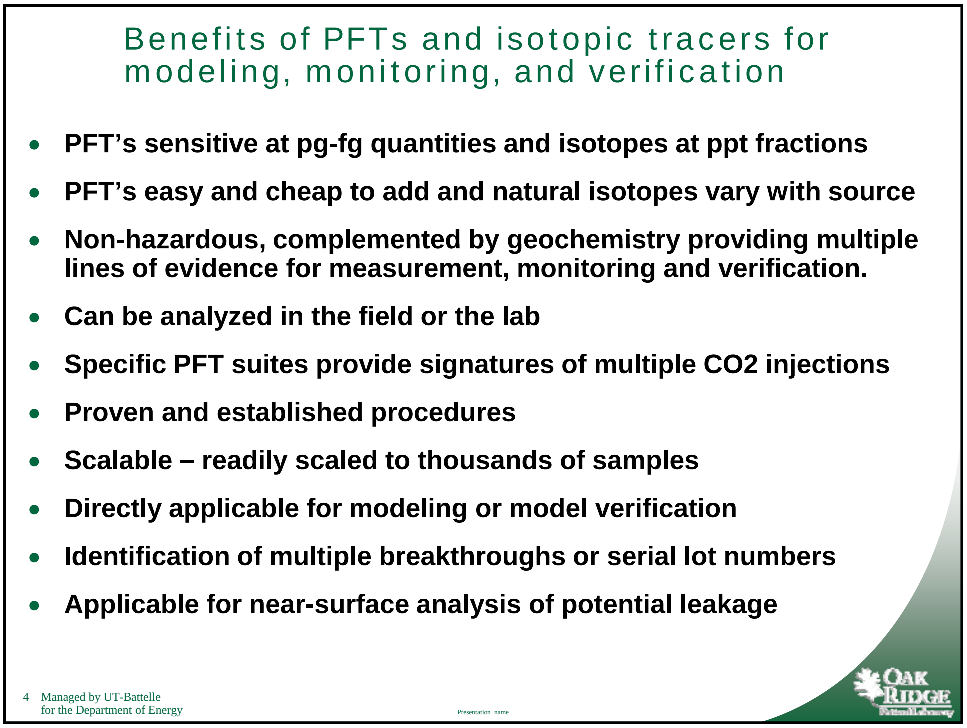
Injection zones:
First experiment
2004: Frio “C”
Second experiment
2006 Frio “Blue”

Oil production

Frio Brine Pilot Site

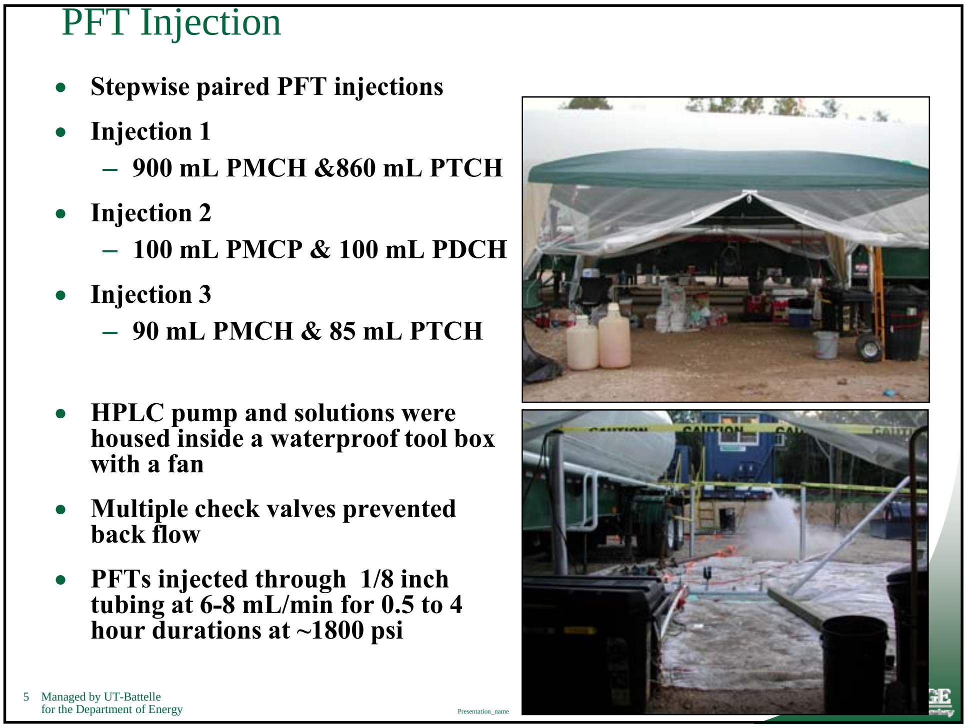
- **Injection intervals: Oligocene fluvial and reworked sandstones, porosity 34-24%, permeability 4.4-2.5 Darcys**
- **Dipping 11 to 16º**
- **Seals – several thick shales**
- **Depth 1,500 and 1,657 m**
- **150 and 165 bar, 53 -60°C, supercritical CO_2**

Hovorka, 2007



Benefits of PFTs and isotopic tracers for modeling, monitoring, and verification

- **PFT’s sensitive at pg-fg quantities and isotopes at ppt fractions**
- **PFT’s easy and cheap to add and natural isotopes vary with source**
- **Non-hazardous, complemented by geochemistry providing multiple lines of evidence for measurement, monitoring and verification.**
- **Can be analyzed in the field or the lab**
- **Specific PFT suites provide signatures of multiple CO2 injections**
- **Proven and established procedures**
- **Scalable – readily scaled to thousands of samples**
- **Directly applicable for modeling or model verification**
- **Identification of multiple breakthroughs or serial lot numbers**
- **Applicable for near-surface analysis of potential leakage**



PFT Injection

- **Stepwise paired PFT injections**
- **Injection 1**
  - **900 mL PMCH &860 mL PTCH**
- **Injection 2**
  - **100 mL PMCP & 100 mL PDCH**
- **Injection 3**
  - **90 mL PMCH & 85 mL PTCH**
- **HPLC pump and solutions were housed inside a waterproof tool box with a fan**
- **Multiple check valves prevented back flow**
- **PFTs injected through 1/8 inch tubing at 6-8 mL/min for 0.5 to 4 hour durations at ~1800 psi**

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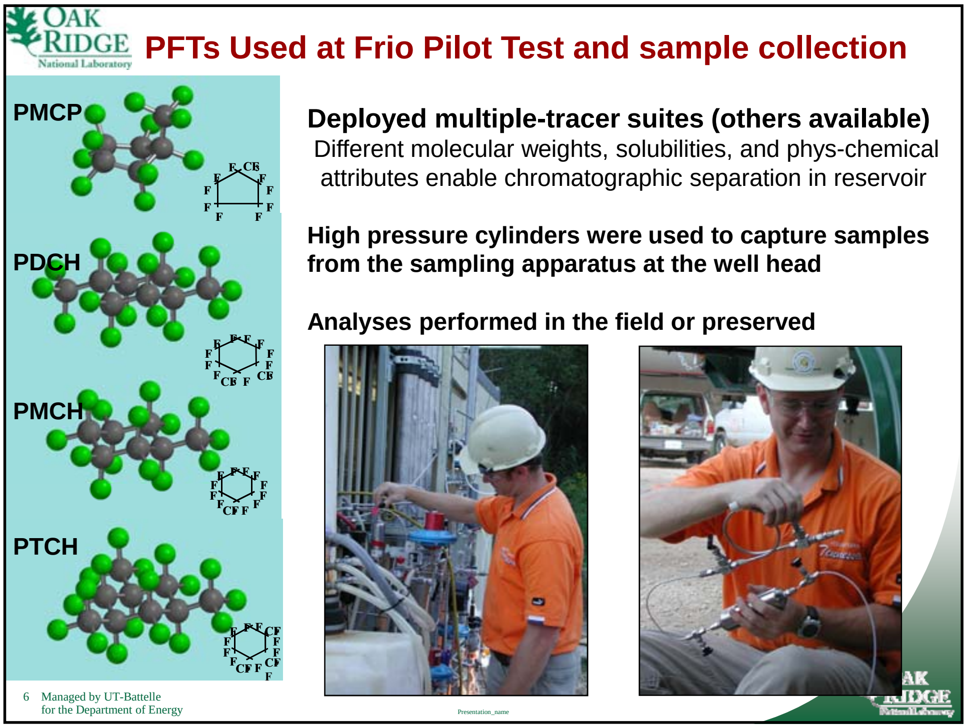
Presentation_name



PFTs Used at Frio Pilot Test and sample collection

Deployed multiple-tracer suites (others available)
Different molecular weights, solubilities, and phys-chemical attributes enable chromatographic separation in reservoir

High pressure cylinders were used to capture samples from the sampling apparatus at the well head

Analyses performed in the field or preserved

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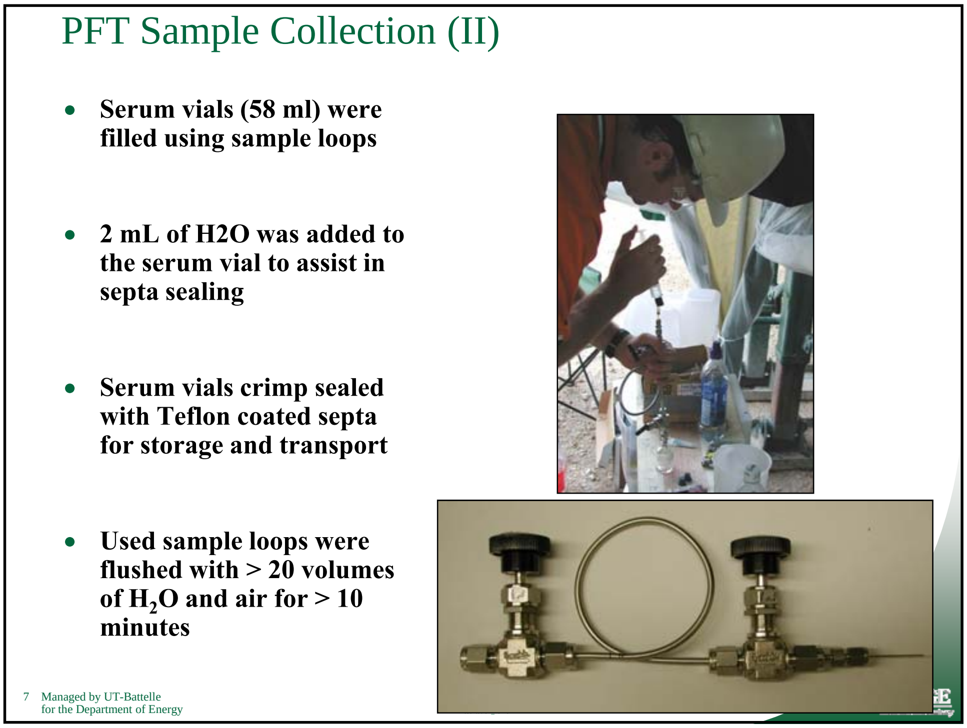
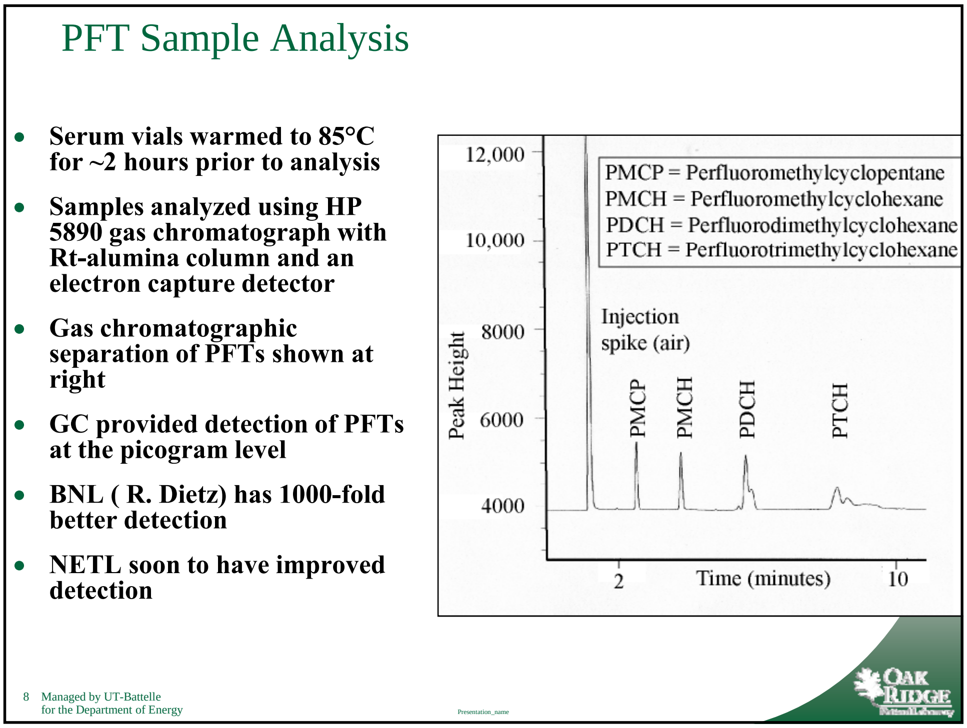


PFT Sample Collection (II)

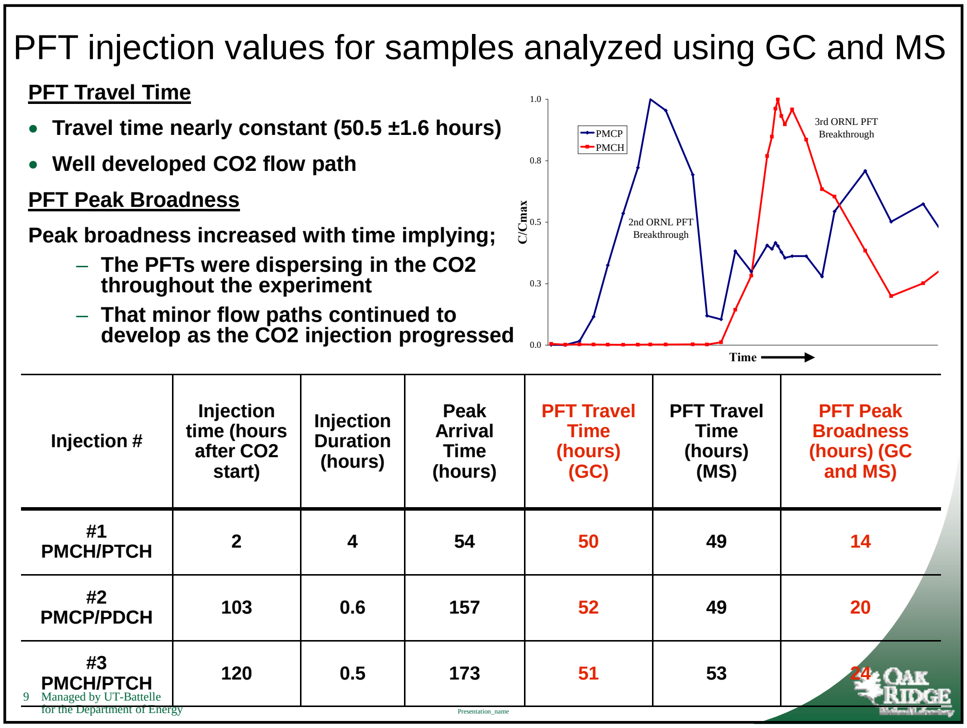
- Serum vials (58 ml) were filled using sample loops
- 2 mL of H2O was added to the serum vial to assist in septa sealing
- Serum vials crimp sealed with Teflon coated septa for storage and transport
- Used sample loops were flushed with > 20 volumes of H_2O and air for > 10 minutes



PFT Sample Analysis

- Serum vials warmed to 85°C for ~2 hours prior to analysis
- Samples analyzed using HP 5890 gas chromatograph with Rt-alumina column and an electron capture detector
- Gas chromatographic separation of PFTs shown at right
- GC provided detection of PFTs at the picogram level
- BNL (R. Dietz) has 1000-fold better detection
- NETL soon to have improved detection

PMCP = Perfluoromethylcyclopentane
PMCH = Perfluoromethylcyclohexane
PDCH = Perfluorodimethylcyclohexane
PTCH = Perfluorotrimethylcyclohexane



PFT injection values for samples analyzed using GC and MS

PFT Travel Time

- Travel time nearly constant (50.5 ±1.6 hours)
- Well developed CO2 flow path

PFT Peak Broadness

Peak broadness increased with time implying;

- The PFTs were dispersing in the CO2 throughout the experiment
- That minor flow paths continued to develop as the CO2 injection progressed

Injection #	Injection time (hours after CO2 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

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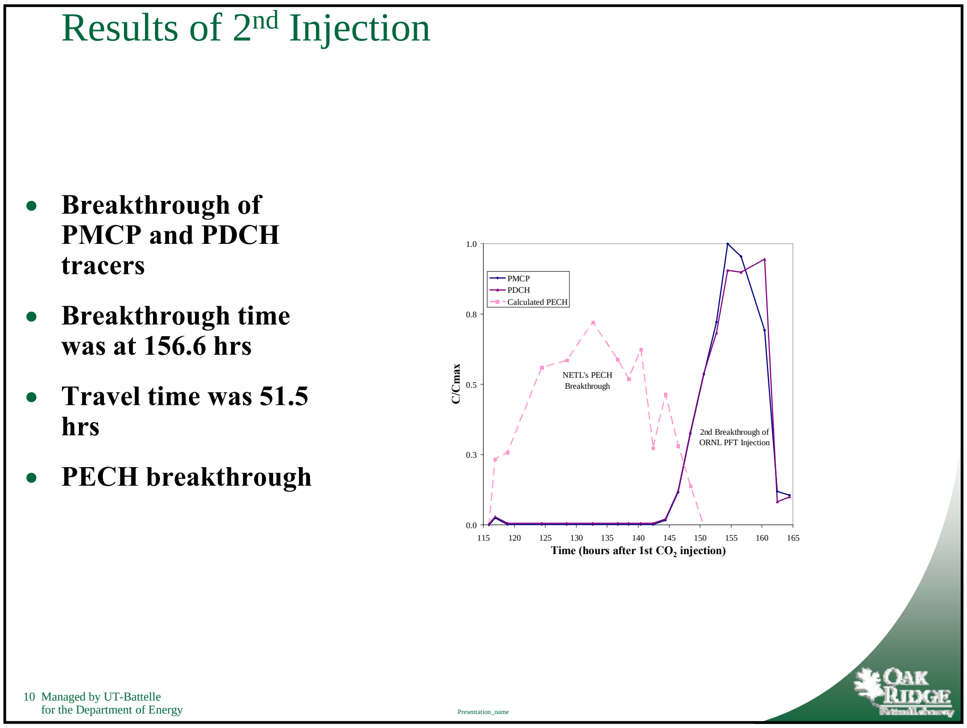

Results of 2nd Injection

- Breakthrough of PMCP and PDCH tracers
- Breakthrough time was at 156.6 hrs
- Travel time was 51.5 hrs
- PECH breakthrough

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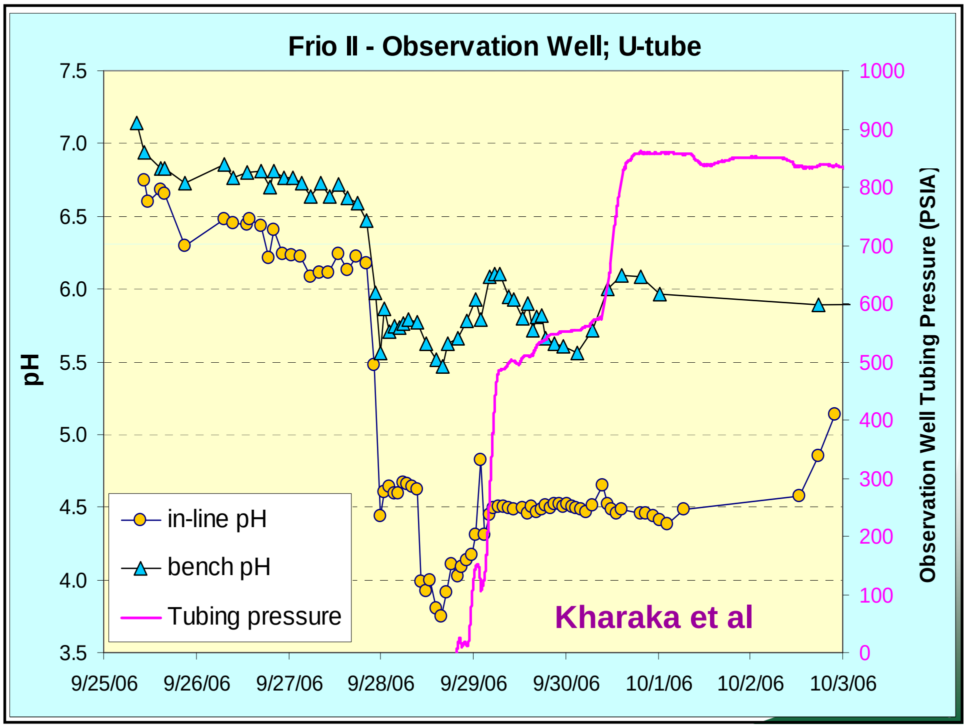
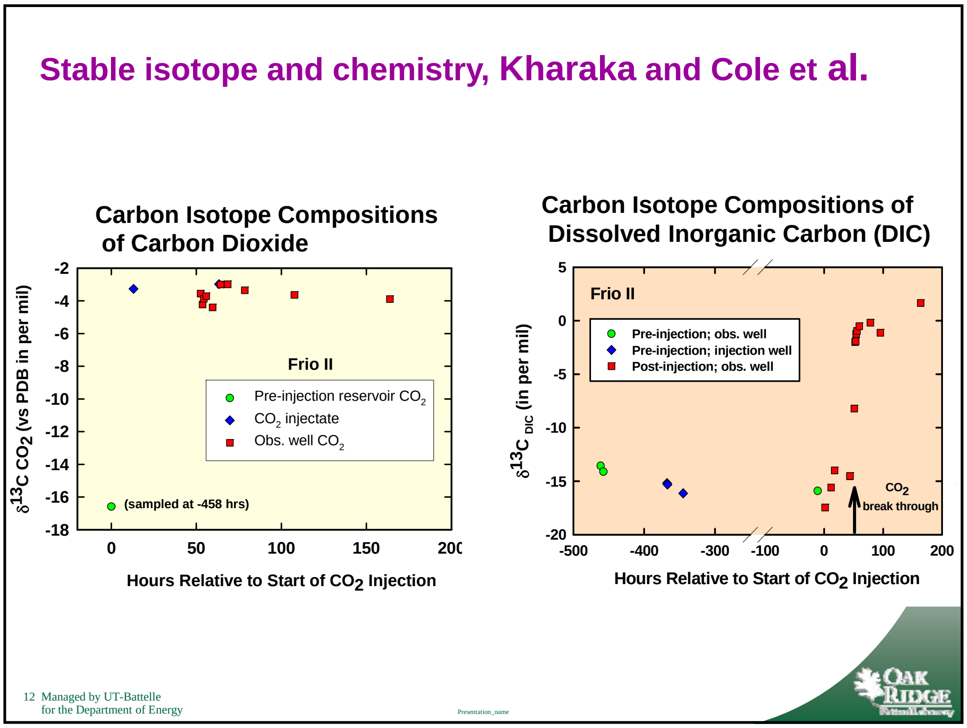
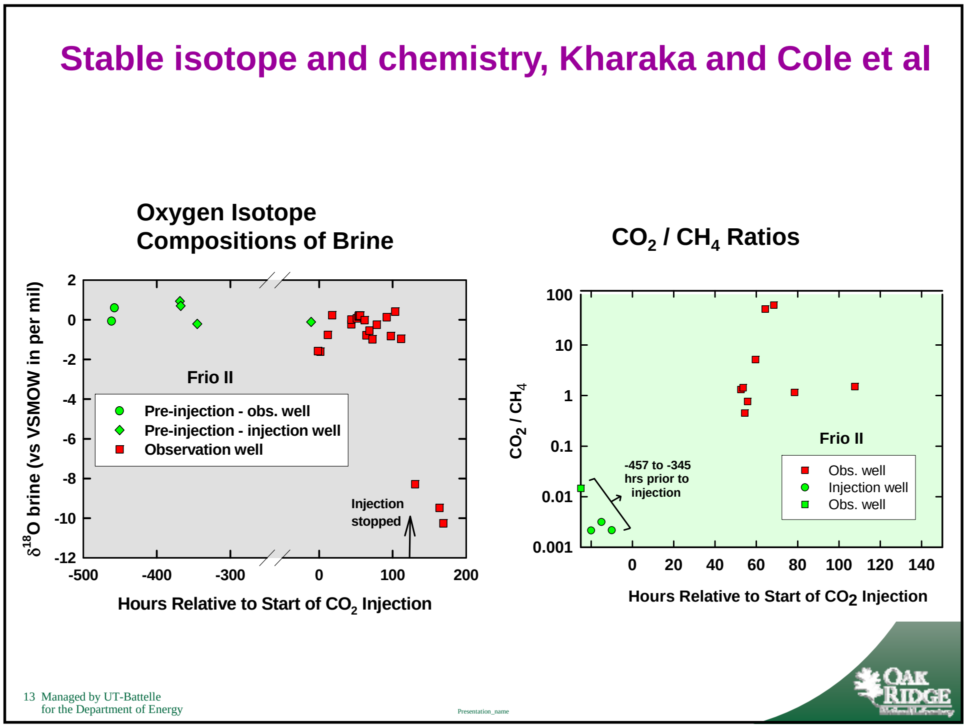




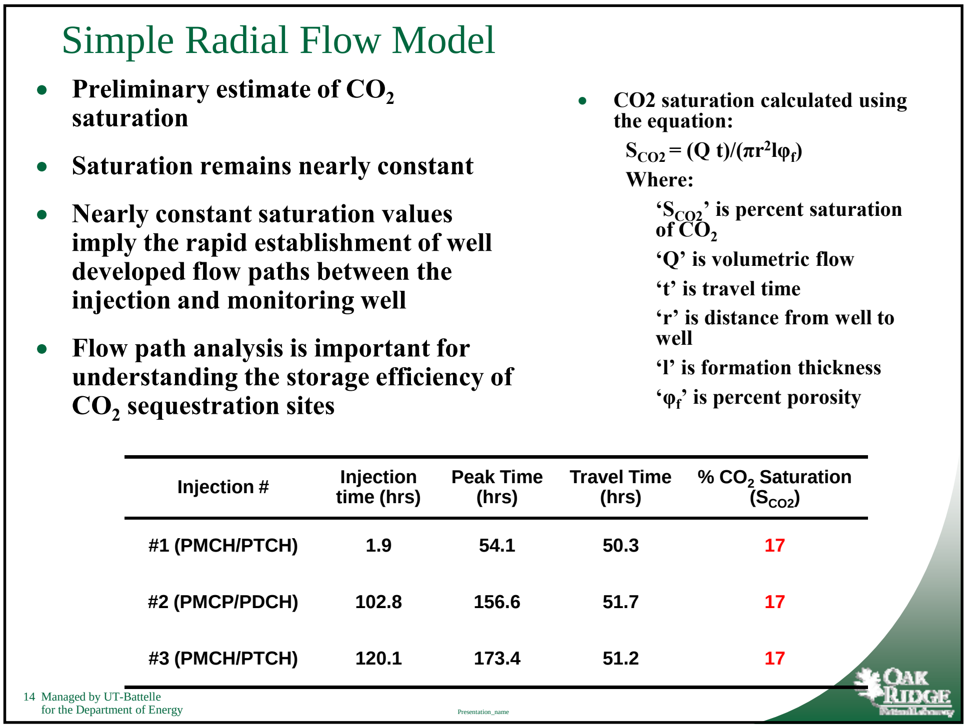
Stable isotope and chemistry, Kharaka and Cole et al.



Stable isotope and chemistry, Kharaka and Cole et al

Oxygen Isotope Compositions of Brine

CO_2 / CH_4 Ratios



Simple Radial Flow Model

- **Preliminary estimate of CO_2 saturation**
- **Saturation remains nearly constant**
- **Nearly constant saturation values imply the rapid establishment of well developed flow paths between the injection and monitoring well**
- **Flow path analysis is important for understanding the storage efficiency of CO_2 sequestration sites**

- **CO2 saturation calculated using the equation:**

$S_{CO2} = (Q\ t)/(\pi r^2 l \varphi_f)$

Where:

'S_{CO2}' is percent saturation of CO_2

'Q' is volumetric flow

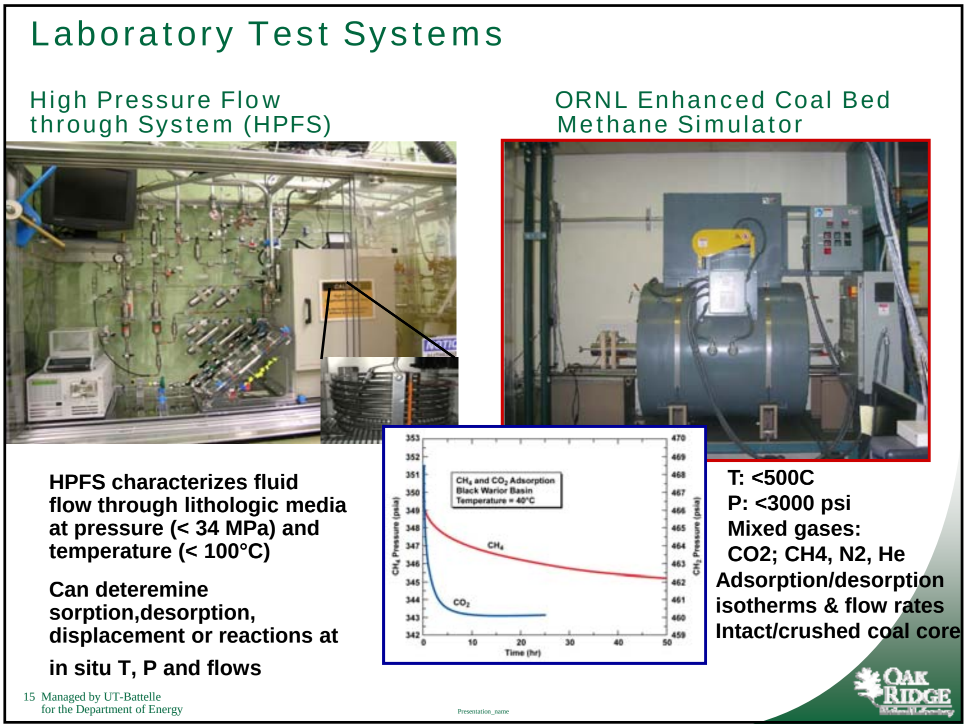
't' is travel time

'r' is distance from well to well

'l' is formation thickness

'φ_f' is percent porosity

Injection #	Injection time (hrs)	Peak Time (hrs)	Travel Time (hrs)	% CO_2 Saturation (S_{CO2})
#1 (PMCH/PTCH)	1.9	54.1	50.3	17
#2 (PMCP/PDCH)	102.8	156.6	51.7	17
#3 (PMCH/PTCH)	120.1	173.4	51.2	17



Laboratory Test Systems

High Pressure Flow through System (HPFS)

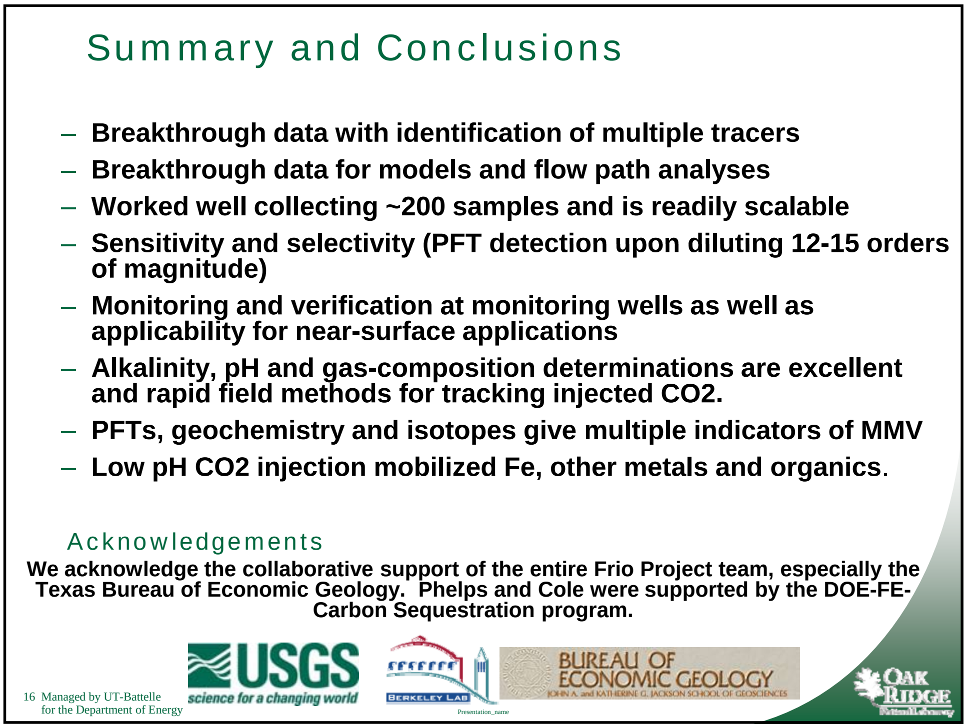
ORNL Enhanced Coal Bed Methane Simulator

HPFS characterizes fluid flow through lithologic media at pressure (< 34 MPa) and temperature (< 100°C)

Can deteremine sorption,desorption, displacement or reactions at

in situ T, P and flows

T: <500C
P: <3000 psi
Mixed gases:
CO2; CH4, N2, He
Adsorption/desorption isotherms & flow rates
Intact/crushed coal core



Summary and Conclusions

- **Breakthrough data with identification of multiple tracers**
- **Breakthrough data for models and flow path analyses**
- **Worked well collecting ~200 samples and is readily scalable**
- **Sensitivity and selectivity (PFT detection upon diluting 12-15 orders of magnitude)**
- **Monitoring and verification at monitoring wells as well as applicability for near-surface applications**
- **Alkalinity, pH and gas-composition determinations are excellent and rapid field methods for tracking injected CO2.**
- **PFTs, geochemistry and isotopes give multiple indicators of MMV**
- **Low pH CO2 injection mobilized Fe, other metals and organics**.

Acknowledgements

We acknowledge the collaborative support of the entire Frio Project team, especially the Texas Bureau of Economic Geology. Phelps and Cole were supported by the DOE-FE-Carbon Sequestration program.