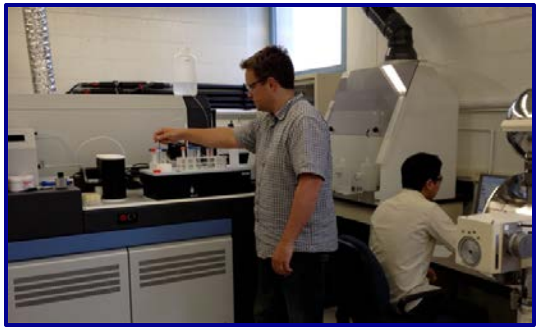
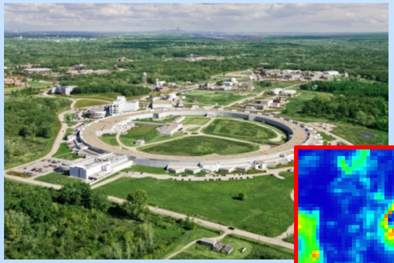


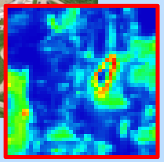
Natural Geochemical Signals for Monitoring Groundwater Impacts

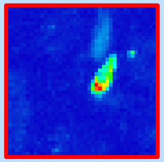
Christina L. Lopano

US DOE – NETL ORD

1022403 (Task 3)







U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Infrastructure for CCS
August 12-14, 2014

Presentation Outline

- Project Goals and Benefits
- Project Overview and Breakdown:
  - Lab, Field, Isotope/sensor development
  - 5 subtasks
- Technical Status: In-situ CO_2 measurements
- Accomplishments
- Summary and Future Direction

Benefit to the Program

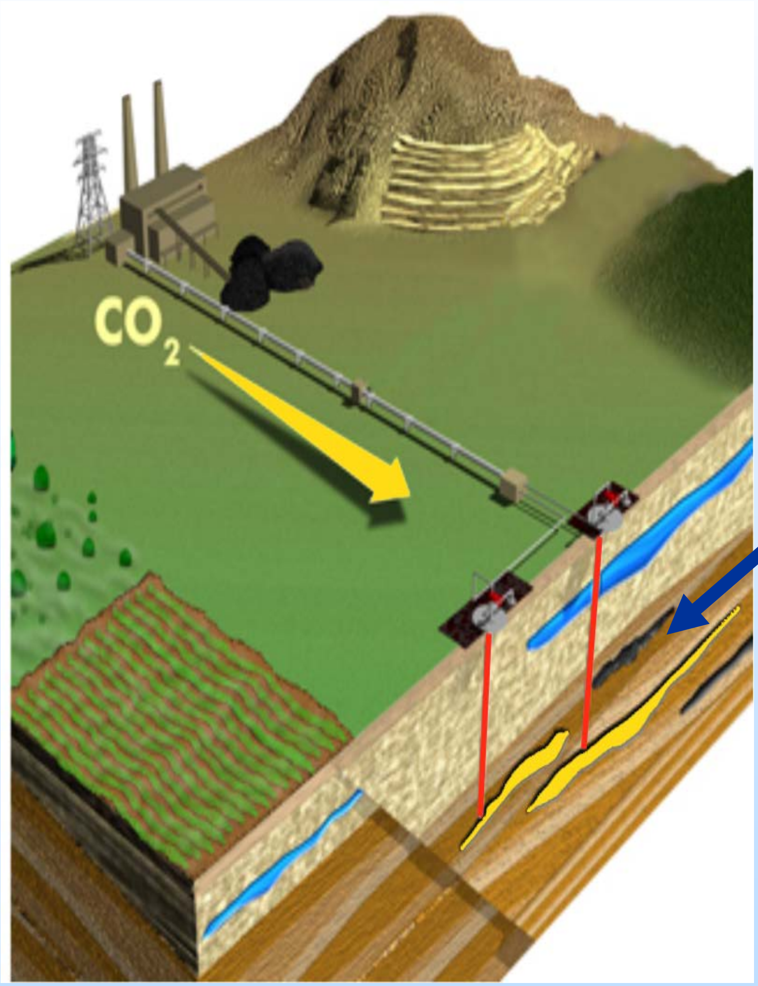
- Program Goals:
  - Validate/ensure 99% storage permanence.
  - Develop Best Practice Manuals for monitoring, verification, accounting, and assessment; site screening, selection and initial characterization…
- Project benefits:
  - *There is a need to be able to quantify leakage of* CO_2 *to the near surface and identify potential groundwater impacts. This project works to develop a suite of complementary monitoring techniques to identify leakage of* CO_2 *or brine to USDW's and to quantify impact.*

Project Overview:
Goals and Objectives

Monitoring Groundwater Impacts – What suite of measurements can be made in groundwater to detect CO_2 and/or brine leakage and to evaluate the impact?

- Establish the utility of stable isotopes to track migration of a CO_2 plume
- Develop and apply metal isotope tracers for QMVA
- Test and validate the use of CO_2 monitoring devices under field conditions
- Understand natural variability in background
- Develop a better understanding of physical-chemical parameters to determine viability of using trace metals and/or organic compounds for geochemical tracers

Project Overview: Background



Natural geochemical signals

Migration into Shallow Aquifers

Migration into other Deep Formations

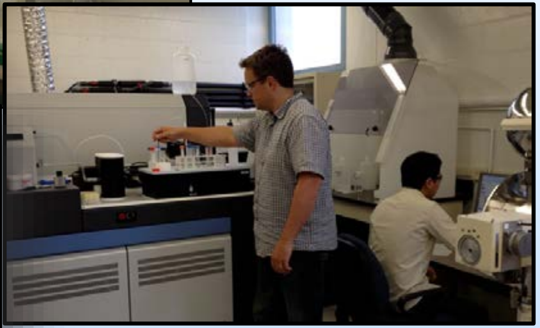
Develop natural tracers that can be used for

- **Detecting (1) CO_2 or (2) brine leakage from storage formations**
- **Understanding potential impacts to shallow environments (groundwater aquifers, vadose zone)**

Natural geochemical signals to monitor leakage to groundwater

FY 2014 Team

- Christina Lopano, NETL-ORD
- Hank Edenborn, NETL-ORD
- J. Rod Diehl, NETL-ORD
- Sheila Hedges, NETL-ORD
- Denny Stanko, NETL-ORD
- Karl Schroeder, NETL-ORD
- Rosemary Capo, Pitt
- Brian Stewart, Pitt
- Shikha Sharma, WVU
- Dorothy Vesper, WVU
- Athanasios Karamalidis, CMU
- Andrew Wall, ORISE NETL
- Thai Phan, Pitt
- Gwen Macpherson, KU
- host of supporting analysts, graduate students and undergraduate students



Technical approach employs a multidisciplinary team (chemists, geologists, microbiologists, environmental scientists) in both laboratory and field work

Natural geochemical signals to monitor leakage to groundwater

Natural Geochemical Signals

- **CO_2 stable isotope indicators** (WVU, NETL)
  e.g. C, H, O, S
- **Metal Isotope Tracers** (Pitt, NETL)
  e.g. Sr, Li, U, Cu, Fe
- **Field CO_2 Monitoring** (NETL, WVU)
  Carbonation meter
- **Organic compounds to track CO_2 migration**
  (CMU) Volatile organic carbon
- **Trace Metal Trends: Potential Impacts** (NETL,CMU)
  As, caprock

All subtasks consist of various proportions of lab development, field collection & measurements, and experimental studies into fundamental components

1. Stable Isotope Indicators

Dr. Shikha Sharma & Bethany Meier WVU;
J. Rodney Diehl, Dennis Stanko, NETL

CURRENT RESEARCH

- C & O isotopes are excellent natural tracers – track CO_2 molecule itself.
- If there is isotope distinction between different end members, then use to:
  - ➢ Trace movement of CO_2 plume in injected formation
  - ➢ Monitor leakage of CO_2 into overlying formations
- Ongoing research projects utilize isotopic signatures of waters and gases in injected formation, overlying aquifers and shallow soil to understand the movement of CO_2 within
  - ➢ Natural high CO_2 analogue sites- springs and mine portals
  - ➢ Enhanced Oil Recovery (EOR) Systems
  - ➢ Enhanced Coal Bed Methane Recovery Systems

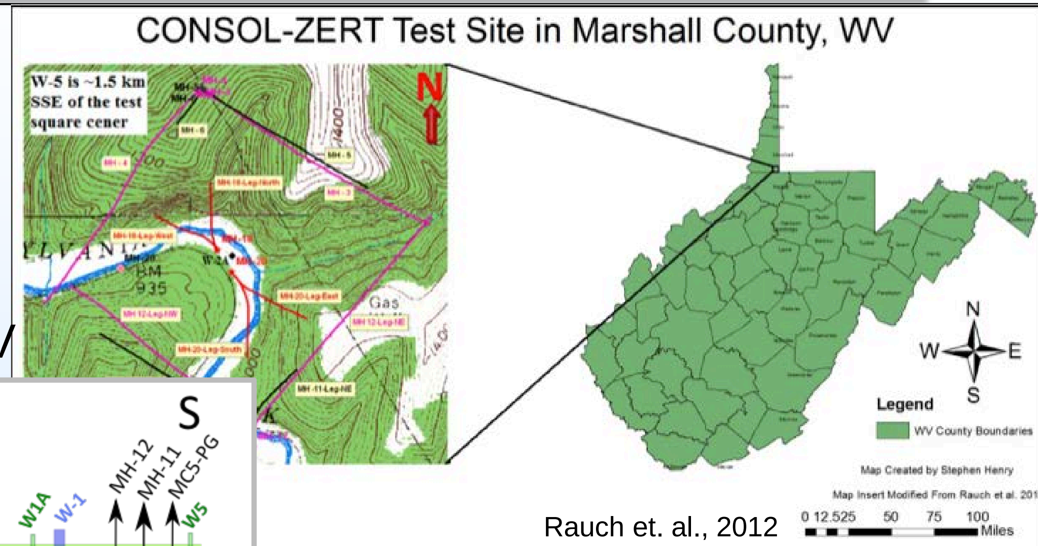
TECHNIQUES

Isotopic signatures monitored at different sites:

- Shallow Soil Vadose Gas ($\delta^{13}C$)
- Overlying Groundwater aquifers ($\delta^{18}O$, δD, $\delta^{13}C$)
- Produced Natural Gas from well heads in injected and overlying formations ($\delta^{13}C$, δD)
- Produced Waters from well heads in injected and overlying formations($\delta^{13}C$, δD)

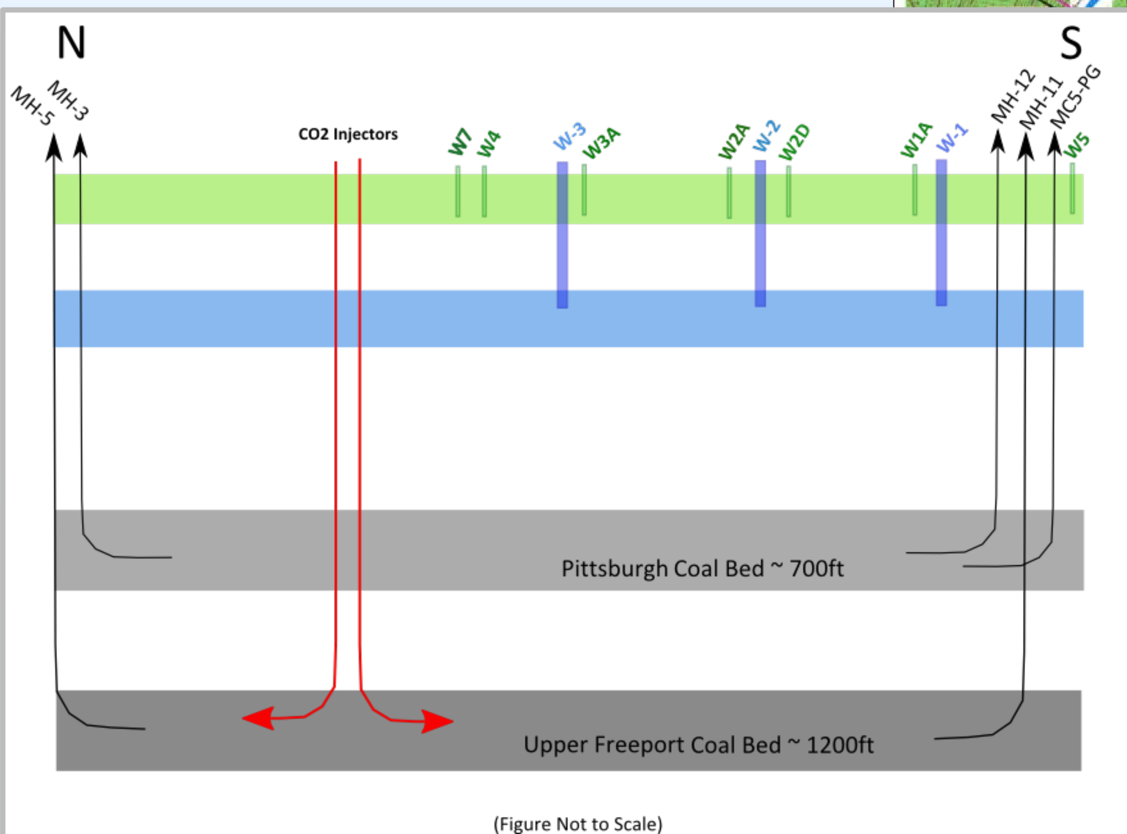
1. Stable Isotope Indicators

Ex. Marshall County, WV Pilot CO_2 Sequestration Site - Isotopes



Rauch et. al., 2012

Schematic cross section of sampling wells at the Consol-ZERT test site in WV

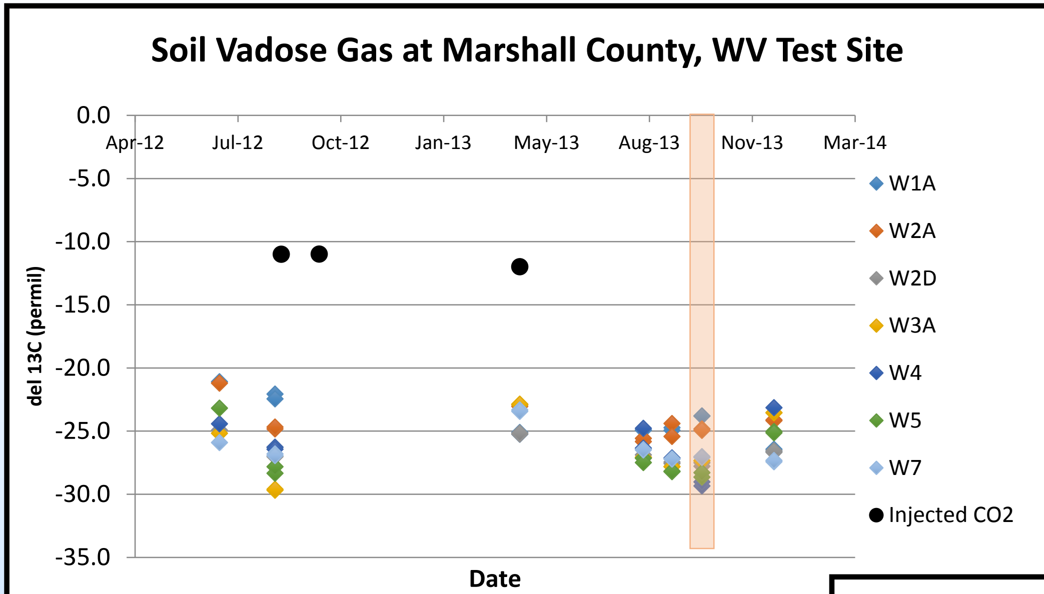


- Enhanced coal bed methane (ECBM) recovery site
- Consol Energy Inc. CO_2 seq pilot test site

Mod from Meier et al. 2013 GSA

1. Stable Isotope Indicators

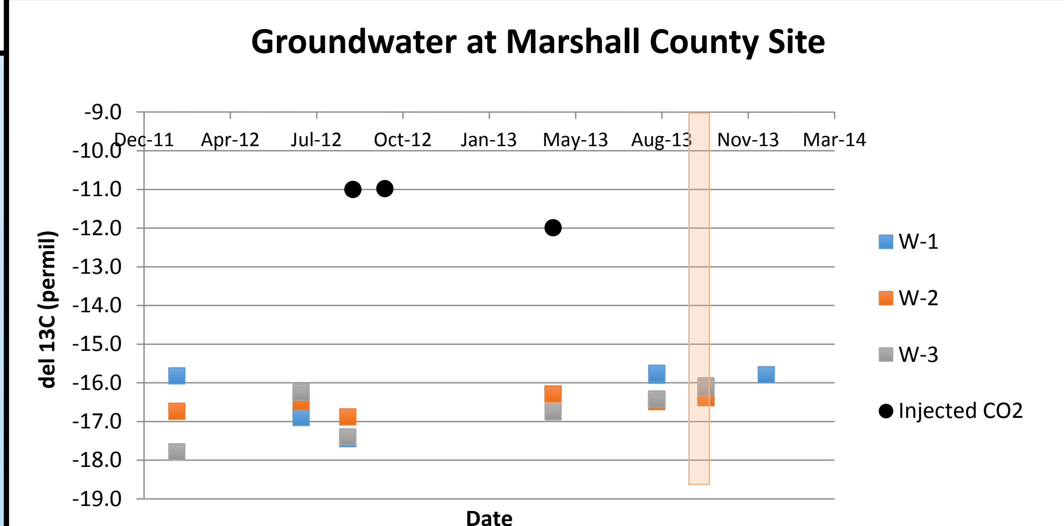
Marshall County, WV Pilot CO_2 Sequestration Site - Isotopes



Injected CO_2 $\delta^{13}C_{CO2}$ of -11 $\pm$ 1 ‰ VPDB

- The highlighted date is September of 2013 when high CO_2 %'s (10-28%) were recorded at the *injection wells.*
- $\delta^{13}C_{CO2}$ of soil vadose is consistently between -23.9 and -27‰ VPDB during the time of sampling.
- No significant changes in the isotope values of soil CO_2 after the high inj. CO_2 %s were recorded.
- No evidence of leakage from the Upper Freeport Coal Seam to the soil vadose zone.

- The $\delta^{13}C_{DIC}$ of groundwaters consistently range from -16.1 to -17.8 ‰ VPDB.
- No significant changes in the isotope values of the groundwater at the site during the time of sampling.
- No evidence for leakage to groundwater

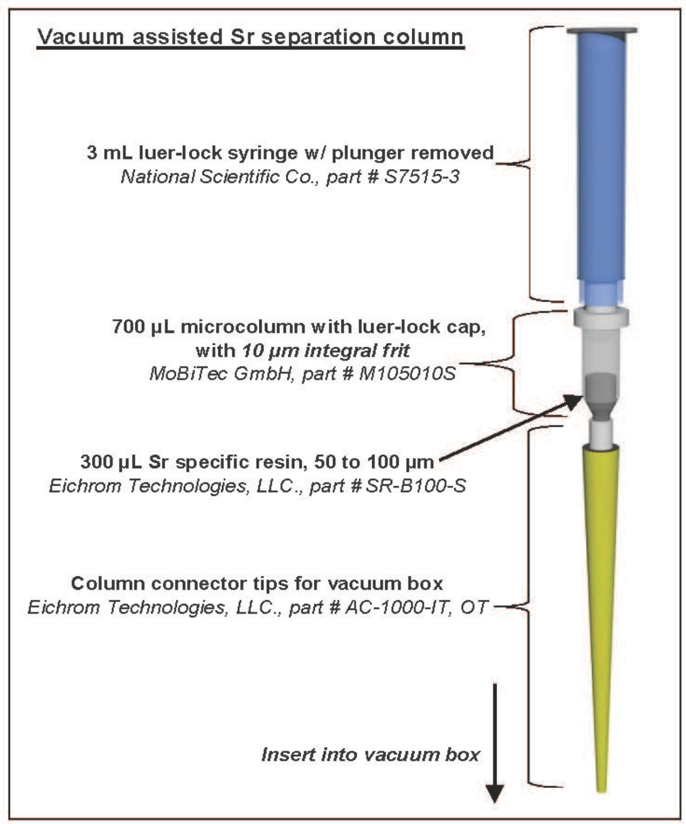


Injected CO_2 $\delta^{13}C_{CO2}$ of -11 $\pm$ 1 ‰ VPDB

2. Metal Isotope Tracers

Method Development & Application to Complex Field Samples

Wall, A. J.; Capo, R. C.; Stewart, B. W.; Phan, T. T.; Jain, J. C.; Hakala, J. A.; Guthrie, G. D. High-Throughput Method for Strontium Isotope Analysis by Multi-Collector-Inductively Coupled Plasma-Mass Spectrometer; J. Anal. At. Spectrom. 28, 1338-1344



Sr separation column assembly for vacuum extraction (Wall et al., 2013)

Expanded detail in an 80 page NETL Technical report: NETL-TRS-X-2014

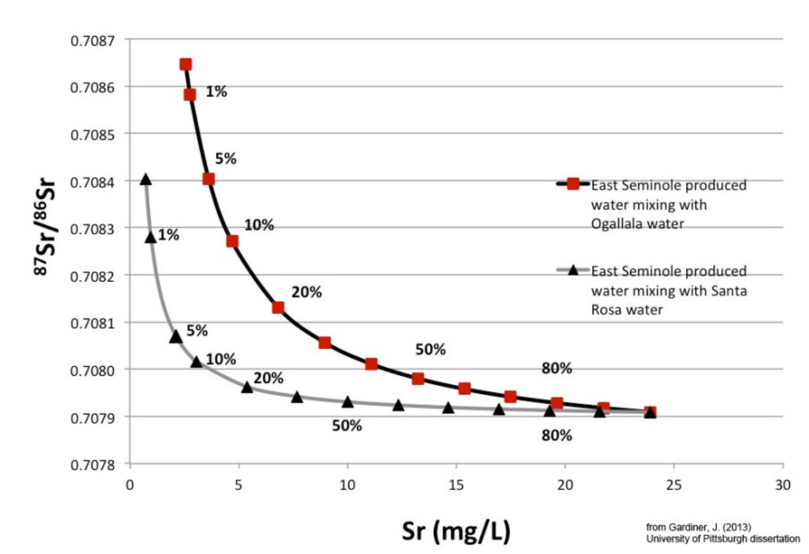
NETL's Thermo Scientific NEPTUNE PLUS MC-ICP-MS at the University of Pittsburgh, Dept. of Geology and Planetary Science.

2. Metal Isotope Tracers

Dr. Rosemary Capo, Dr. Brian Stewart, James Gardiner and Samantha Pfister (PITT)
Dr. Gwen Macpherson (KU), Dr. Andy Wall (ORISE-NETL)

Preliminary analysis & Ongoing Work:

- Sample injection fluids, produced water, and overlying groundwater aquifer wells at a new EOR site
- Baseline Sr isotope analysis of pre-injection waters:
  - $^{87}Sr/^{86}Sr$ signatures are sensitive indicators of produced water-fresh water mixing: Kolesar Kohl, CA, Capo RC, Stewart BW, Wall AJ, Schroeder KT, Hammack RW, Guthrie GD (2014) *Env. Sci. Technol.*
  - . . . and reservoir rock reaction: Newell DL, Larson T, Perkins G, Pugh JD, Stewart BW, Capo RC, Trautz RC (2014 in press) *Int. J. Greenhouse Gas Contr.*
- Li isotope analyses in progress for water-CO_2-reservoir rock interaction
  - *Pfister et al. Dec 2014 AGU Conference*



Theoretical Sr isotope mixing curve for injected waters with two overlying aquifers (*Gardiner, J. 2013 PhD dissertation – Univ. Pittsburgh*)

Future plans:

- Collection & Analysis of post-injection samples

3. Field CO_2 Monitoring

Dr. Hank Edenborn, NETL, Dr. Dorothy Vesper, WVU, Jill Riddell, WVU & Chris Nicholson, WVU

CURRENT RESEARCH

- Pioneered the use of instrumentation (CarboQC) utilized by carbonation industry to measure dissolved CO_2 in natural waters
    - Testing in groundwaters
    - Applying to more complex systems
- Testing probes for direct CO_2 real-time analysis
    - Successful in freshwater to-date

TECHNIQUES

Two primary methods are being explored:

- CarboQC – measure CO_2 via Volumetric Expansion
- NDIR – non-dispersive infrared – real time analysis

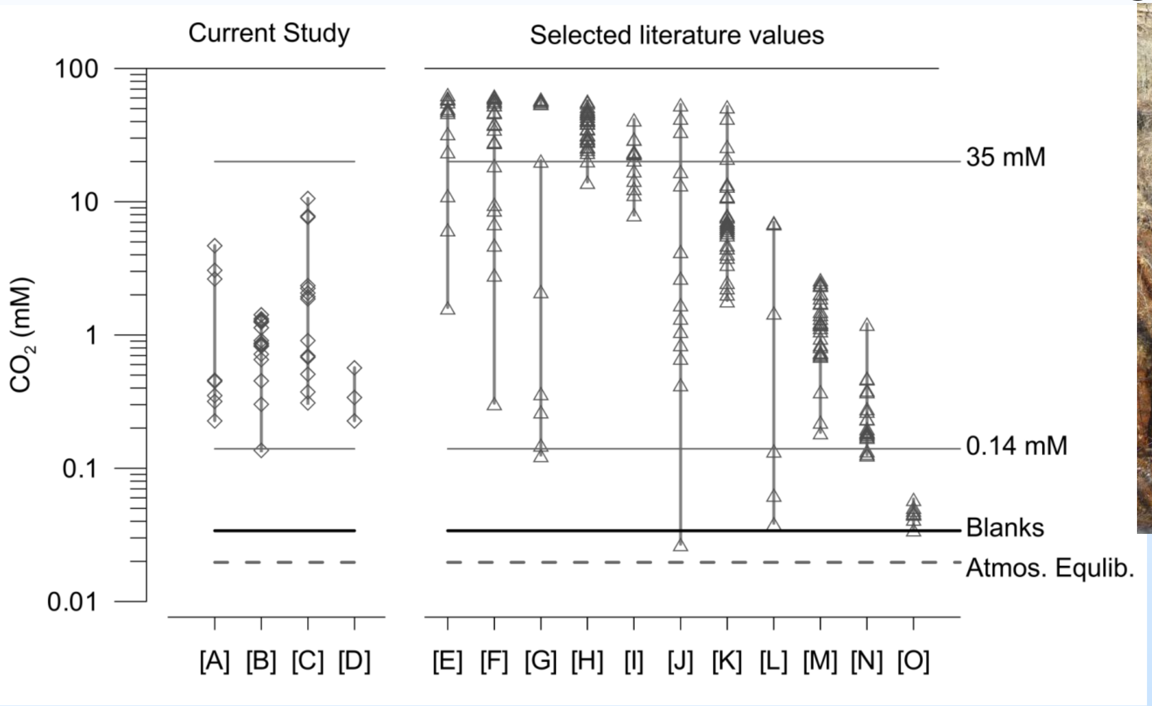
3. Field CO_2 Monitoring

CarboQC Analysis of CO_2 by Volumetric Expansion

- Volumetric expansion
  - Anton Paar
  - Expands a sealed volume of water twice and measures the resulting change in T & P to determine the quantity of dissolved CO_2
  - Not influenced by N_2 or O_2
- Surface waters can be measured direct injection
- Pressure filling device allows for sampling in the field in soda pop bottles
  - Measure back in the lab
  - Prevents gas loss

3. Field CO_2 Monitoring

Testing in Natural Surface Systems with High CO_2



Coal mine drainage

Tufa springs

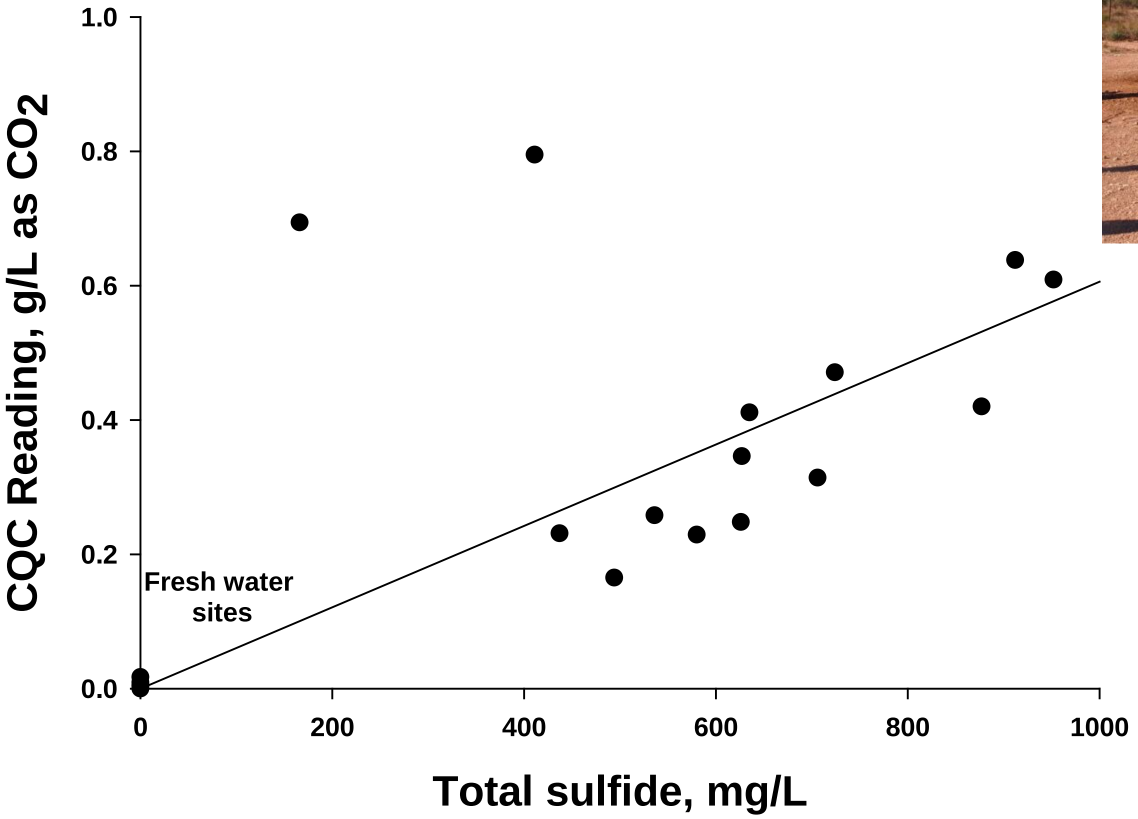
Thermal springs

- Concentrations measured quickly using direct injection method under field conditions
- Measurements ranged from the minimum detectable level of CO_2 (ca. 10 mg/L) to values consistent with other studies.

3. Field CO_2 Monitoring

Testing in Complex EOR settings

- H_2S concentrations in EOR are not uncommon
- H_2S and CO_2 solubility in water is similar
- EOR waters are often high in both



- Samples collected in field in “soda-pop” bottles
- strong correlation between dissolved sulfide and the apparent CO_2 in field samples, as shown here.
- Outliers in this graph may be especially high in CO_2.

3. Field CO_2 Monitoring

Testing in Complex EOR settings: Troubleshooting

- EOR waters are often high in both H_2S and CO_2 (Similar solubility in water)
- How to account for interferences?
  - Selectively remove the sulfide component ($CuSO_4$)
  - Record differences in the total gas readings
- Laboratory studies are also underway with well defined chemical solutions to test the practical applications and limitations of this approach
  - Determine impacts of lowering pH
  - Geochemical equilibria for sulfide and TIC in solution

- **Take duplicate samples with and w/o added $CuSO_4$**
- **Precipitate sulfide as CuS and measure CO_2 by difference**

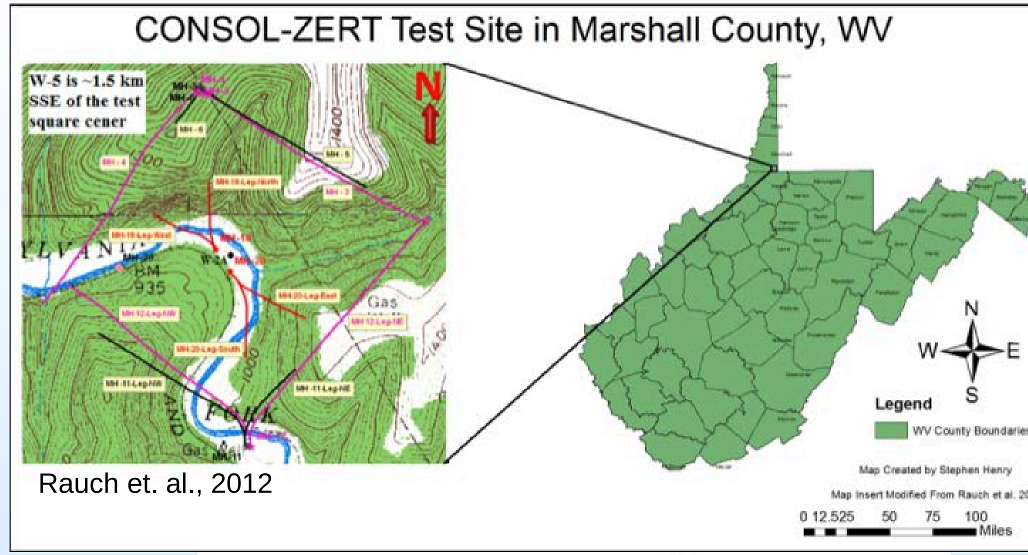
3. Field CO_2 Monitoring

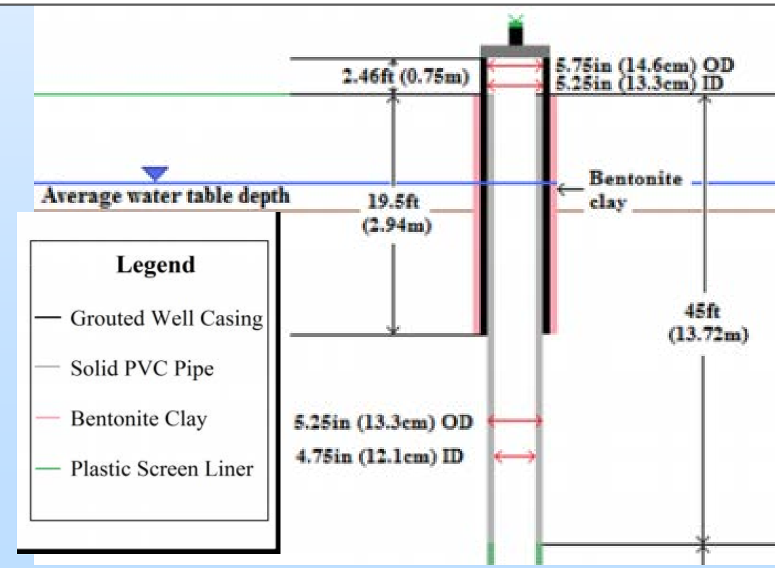
In-situ testing – direct CO_2 measurements

Additional Testing Methods:

- NDIR – non-dispersive infrared – real time analysis
  - Successful in freshwater to-date
  - Difficulties in AMD water test (potential clogging of membrane) – slow equilibration

- ONGOING: working to deploy the NDIR sensor in shallow groundwater monitoring well at Marshall County, WV test site





Mod from Meier et al. 2013 GSA

4. Organic Compounds as Tracers

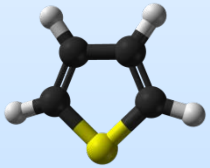
Dr. Athanasios Karamalidis and Aniela Burant (CMU); Dr. Ale Hakala (NETL)

CURRENT RESEARCH

Work during FY 2014 has focused on developing a better understanding of the physical-chemical parameters and interactions necessary to determine the viability of using organic compounds as natural geochemical tracers.

CHALLENGES:

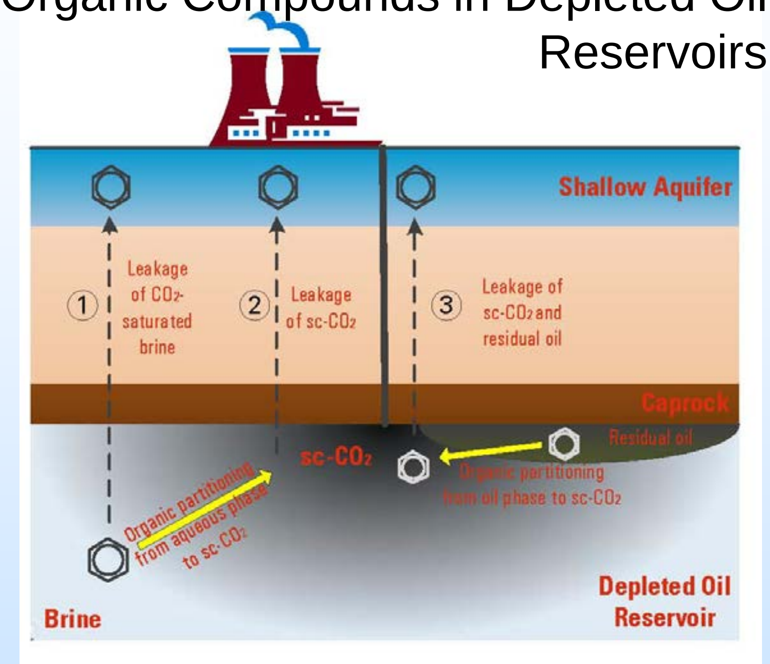
- High salt concentrations + levels of dissolved petroleum hydrocarbons



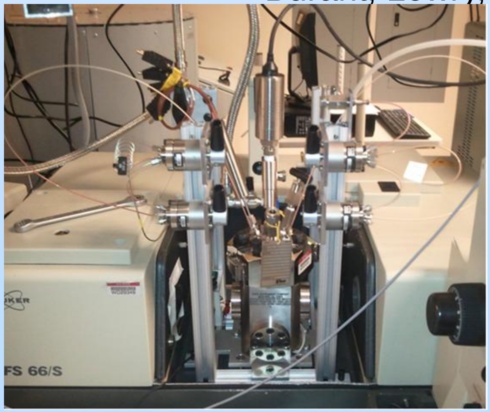
Unknown: High salinity effect on solubility

Unknown: Organic partitioning to sc-CO_2 from water or residual oil

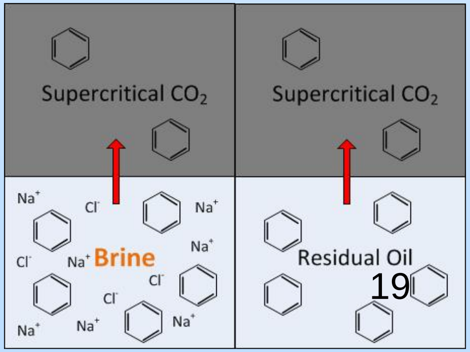
Organic Compounds in Depleted Oil Reservoirs



Burant, Lowry, Karamalidis, (2013) *ES&T*, 47(1)



CO_2 Phase:
Bruker IFS 66/S FTIR spectrometer
PNNL/EMSL



5. Trace Metals Trends & Impacts

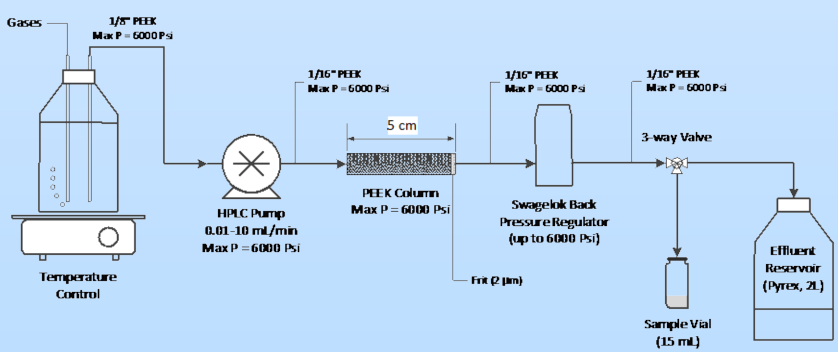
Dr. Christina Lopano, Dr. Mengling Stuckman, Dr. Alexandra Hakala (NETL)
Dr. Athanasios Karamalidis and Hari Parthasarathy(CMU)

CURRENT RESEARCH

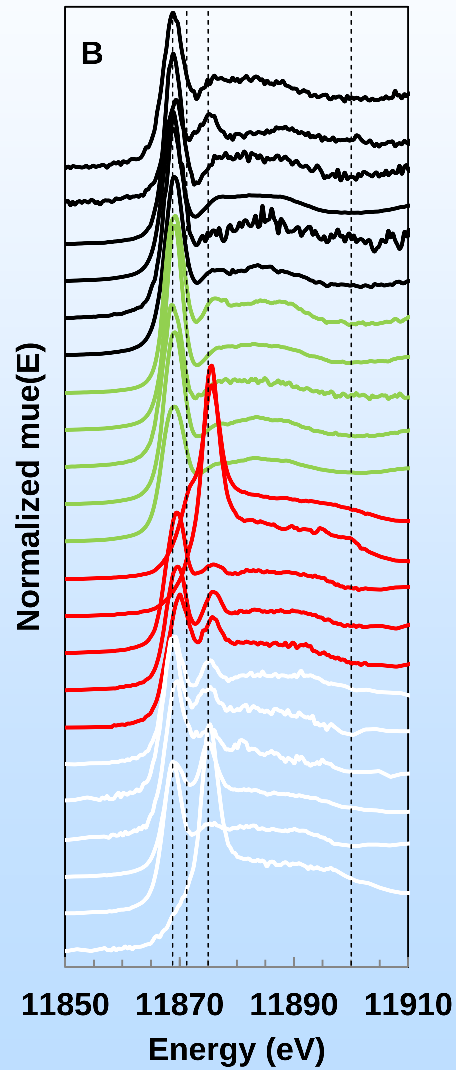
This work addresses the lack of knowledge about potential for mobilization of metal species such as arsenic in brines under CO_2 storage conditions, and will improve ability to predict arsenic retention and release from reservoir and caprocks and impacts to GW.

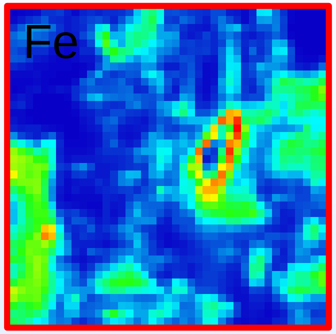
APPROACH:

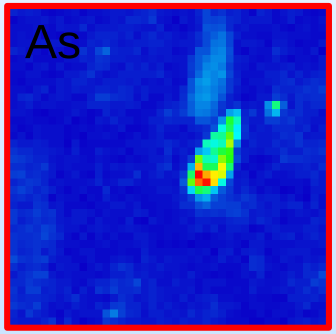
Laboratory experiments coupled with detailed spectroscopic analysis of the rock materials before and after brine contact to gain a better understanding of arsenic mobilization in CO_2 storage conditions.



Parthasarathy H. et al. (2013) Chemical Geology, 354, 65-72







Lopano et al. in prep

Accomplishments to Date (FY2014)

- Team developed a methodology for high through-put Sr isotope measurements in complex sample matrices using a MC ICPMS
- Team has successfully utilized stable isotopes for monitoring a coal-bed CO_2 sequestration site (GW and Soil Gas)
- Arrangements at an EOR site have been made and preliminary sampling has commenced (background)
- Team has employed a novel in-situ CO_2 field measurement technique at surface conditions and is exploring in-situ downhole measurements
- Team has identified potential interferences with measurements of CO_2 at EOR sites and is working towards ways to rectify interferences

Summary

- Key Findings: Stable Isotope, metal isotope and CO_2 field measurements show a lot of promise for monitoring CO_2 GW impacts in the field
- Lessons Learned: Real world field conditions may present a lot of natural interferences
  - Multiple measurement techniques are key
  - Fundamental research helps deconvolute interferences
- Future Plans:
  - Focus measurement techniques under real world site conditions (e.g. EOR, Coal Bed Methane, Regional Partnerships)
  - Establish baseline GW and storage formation water chemistries

Acknowledgements

- Consol Energy
- Blue Strategies, LLC
- PNNL/EMSL

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Appendix

Organization Chart

3.1 Natural Geochemical Signals

- **3.1.1 Metal Isotope Tracers** (Pitt, NETL)
  Method Dev., Field Measurements & Validation
  e.g. Sr, Li, U, Cu, Fe
- **3.1.2 CO_2 stable isotope indicators** (WVU, NETL)
  Field Measurements & Validation
  e.g. C, H, O, S
- **3.1.3 Field CO_2 Monitoring** (NETL, WVU)
  Method Dev., Field Measurements & Validation
  e.g. Carbonation meter, NDIR sensor
- **3.1.4 Organic compounds & CO_2 migration** (CMU)
  Lab Experimentation, Method Dev.
  Volatile organic carbon
- **3.1.5 Trace Metal Trends: Potential Impacts** (NETL,CMU)
  Lab Experimentation, Method Dev.
  As, caprock

Gantt Chart

Carbon Storage
FWP Number Car Stor_FY14
Schedule and Milestones

U.S. DEPARTMENT OF ENERGY

Task No.	Activity Name (Task/Sub-task)	Start	Finish	FY14 (Q1: O N D; Q2: J F M; Q3: A M J; Q4: J A S)
1.0	**Project Management**	**10/1/13**	**9/30/14**	
1.1	Project Management	10/1/13	9/30/14	
2.0	**Reservoir and Seal Performance**	**10/1/13**	**9/30/14**	M1.14.2.A
2.1	Impact of CO_2-Brine-Rock Chemistry on Storage Formations and Seals	10/1/13	9/30/14	
2.2	Impact of Microbial Processes on Storage Formations and Seals	10/1/13	9/30/14	
2.3	Impact of CO_2 on Shale Formations as Seals	10/1/13	9/30/14	
2.4	Characterization of Reservoir and Seal Material Performance	10/1/13	9/30/14	
2.5	Understanding of Multiphase Flow for Improved Injectivity and Trapping	10/1/13	9/30/14	
2.6	Geochemical Model Sensitivity at Caprock Interfaces	10/1/13	9/30/14	
3.0	**Monitoring Groundwater Impacts**	**10/1/13**	**9/30/14**	M1.14.3.A
3.1	Natural Geochemical Signals for Monitoring Groundwater Impacts	10/1/13	9/30/14	
4.0	**Resource Assessments and Geospatial Resource**	**10/1/13**	**9/30/14**	M1.14.4.A
4.1	Resource Assessments	10/1/13	9/30/14	
4.2	Geospatial Data Management	10/1/13	9/30/14	
5.0	**Monitoring CO_2 and Pressure Plume**	**10/1/13**	**9/30/14**	M1.14.5.A
5.1	Development of Technology to Monitor CO_2 and Pressure Plume	10/1/13	9/30/14	
6.0	**Catalytic Conversion of CO_2 to Industrial Chemicals**	**10/1/13**	**9/30/14**	M1.14.6.A
6.1	Catalytic Conversion of CO_2 to Industrial Chemicals	10/1/13	9/30/14	

◇ Milestone — Summary — Page 1 of 1

Task 3.0 Monitoring Groundwater Impacts			
M1.14.3.A	Coordinate experiments at PNNL/EMSL about in-situ, on-line and simultaneous measurements of organics in both sc-CO_2 and brine phases to determine partitioning coefficients.	12/31/13	Experimental Plan - COMPLETED

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- Burant, A.S., Lowry, G.V., Hakala, A.J., and Karamalidis, A.K. (2014) "The Validation of the Setschenow Equation for Selected Petroleum Hydrocarbons in Hypersaline Solutions," presented at the Goldschmidt Conference, Sacramento, CA, June 8–13, 2014.
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