ZERT Controlled Release Experiment

Lee H. Spangler
Director, ZERT and The Energy Research Institute
Montana State University
Zero Emissions Research & Technology

A collaborative involving Universities and DOE National Labs

- Montana State University - Lead Institution
- Los Alamos National Laboratory
- Pacific Northwest National Laboratory
- West Virginia University
- Lawrence Berkeley National Laboratory
- National Energy Technology Laboratory
- Lawrence Livermore National Laboratory
Montana - A Brief Comparison

**Japan**
Area: 377,930 km²
Population: 127,078,680

**Germany**
Area: 357,021 km²
Population: 82,282,988
0.7% of world’s coal reserves

**Norway**
Area: 384,802 km²
Population: 4,660,539
3rd largest oil exporter

**Montana**
Area: 380,837 km²
Population: 967,440
6% of world’s coal reserves
Significant Oil & Gas
Near – Surface Monitoring Zones

• Atmosphere
  – Ultimate Integrator
  – Dynamic
  – Monitoring & Modeling

• Biosphere
  – dynamic
  – requires protection
  – opportunity for wide area monitoring but indirect methods

• Soil
  – Integrates
  – dynamic

• Aquifers
  – Integrates
  – Requires protection
Motivation (2006)

The situation in 2006 when we started planning the work:

- Near-surface detectors were considered highly desirable for public assurance
- They had been deployed at sequestration pilot sites
- These pilot sites were well chosen and do not leak
- Thus, the near-surface detection techniques had not been adequately tested under realistic conditions
- The primary initial purpose was detection verification
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
Scaling

Imagine a realistic feature that might result in leakage

We chose to mimic a fault which might be on the order of 1 km long with a surface expression of 10m – 100m in width.

A 100m horizontal well would be 10% of the first case and 1% of the second case.

Scaling by a factor of 10 – 100 is a reasonable extrapolation

Sally Benson  Lee Spangler
What Are Relevant Release Rates?

- 4 Mt/year injection from 500 MW power plant
- 50 years injection - Total of 200 Mt Injected
- Consider maximum leakage rates discussed to mitigate climate change
  - 1% over 100 years = 0.01% / year = 0.0001
  - 1% over 1000 years = 0.001% / year = 0.00001
- 200,000,000 x 0.00001 = 2,000 Tonnes / yr
- 5.5 Tonnes / Day
- This is the equivalent of about 85 idling cars
Injection Rate

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

We used a 0.15 Tonne / Day rate

An idling car generates about 0.04545 kg CO$_2$ / min or 64.5 kg CO$_2$ / day. Our injection rate is about equal to 2.3 idling cars
Field Test Facility

Experiment Site
MSU Agricultural lands
Route
Experiment Site
MSU Agricultural lands
Route

Field Test Facility

Experiment Site
MSU Agricultural lands
Route
Experiment Site
MSU Agricultural lands
Route
Methods

• Soil Gas Monitoring
• In-situ soil gas probes
• Eddy Covariance
• Soil Flux chambers
• Differential Absorption LIDAR
• Cavity ring-down, other isotopic measurements
• Water chemistry
• Tracers
• Hyperspectral / multispectral imaging
• Many more
CO₂ Background is Highly Variable

Affected by sunlight, precipitation, wind, etc. Red line shows diurnal variation, but there are also short term and much longer term variations
## Large Number of Participants / Methods

**47 investigators**  
**31 instruments / sensor arrays**  
**5 univ. 6 DOE labs, 4 companies**

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Institution</th>
<th>Monitoring Technology</th>
<th>Number of Sensors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arthur Wells</td>
<td>National Energy Technology Laboratory</td>
<td>Atmospheric tracer plume measurements</td>
<td>1 tower (4m) Blimp (Apogee Scientific) with 3 tether line samplers</td>
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<tr>
<td>Rod Diehl</td>
<td></td>
<td>Bee hive monitoring for tracer with sorption tube and pollen trap</td>
<td>2 hives</td>
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<tr>
<td>Brian Strasizar</td>
<td></td>
<td>Automated Soil CO(_2) flux system</td>
<td>4 chambers</td>
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<tr>
<td>William Pickles</td>
<td>University of California- Santa Cruz</td>
<td>Hand held hyperspectral measurements (plant health)</td>
<td>1 instrument</td>
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<tr>
<td>Eli Silver</td>
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<tr>
<td>Erin Male</td>
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<tr>
<td>Yousif Kharaka</td>
<td>United States Geological Survey*</td>
<td>Ground water monitoring</td>
<td>1 EC and temperature probe, Dissolved oxygen probe, lab analysis of water samples</td>
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<tr>
<td>James ThordsenGil Ambats</td>
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<tr>
<td>Sarah Beers</td>
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<tr>
<td>Henry Rauch</td>
<td>West Virginia University</td>
<td>Water monitoring well headspace gas sampling</td>
<td>1 sensor</td>
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<tr>
<td>Lucian Wielopolski</td>
<td>Brookhaven National Laboratory*</td>
<td>Inelastic neutron scattering (total soil carbon)</td>
<td>1 instrument</td>
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<tr>
<td>Sudeep Mitra</td>
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<tr>
<td>Martha Apple</td>
<td>Montana Tech*</td>
<td>Soil moisture, temp. Chlorophyll Content Meter, Fluorescence Meter, LI-COR 2000 to measure leaf area index Leaf Porometer to measure stomatal conductance</td>
<td>5 sensors</td>
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<tr>
<td>Xiaobing Zhou</td>
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<tr>
<td>Venkata Lakkaraju</td>
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<tr>
<td>Bablu Sharma</td>
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<tr>
<td>+2 students</td>
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<td>Infrared radiometry (plant health)</td>
<td>2 instruments</td>
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<td>Atmospheric humidity and temperature, accumulated rainfall</td>
<td>1 sensor each</td>
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<td>Plant root imaging</td>
<td>1 camera</td>
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<td>Soil conductivity</td>
<td>1 sensor</td>
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<td>Handheld hyperspectral measurements (plant health)</td>
<td>1 instrument</td>
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<tr>
<td>William Holben</td>
<td>University of Montana*</td>
<td>Microbial studies</td>
<td>Lab analysis</td>
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<td>Sergio Morales</td>
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<tr>
<td>Lee Spangler, Laura Dobek, Kadie Gullickson</td>
<td>Montana State University</td>
<td>Water content reflectometers (soil moisture)</td>
<td>15 sensors</td>
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<td>Automated soil CO₂ flux system</td>
<td>5 long term chambers, 1 portable survey chamber</td>
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<td>CO₂ soil gas concentration</td>
<td>6 sensors</td>
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<tr>
<td>Kevin Repasky (PI), Jamie Barr</td>
<td>Montana State University</td>
<td>Underground fiber sensor array (CO₂ soil gas concentration)</td>
<td>4 sensors</td>
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<td>Flight based hyperspectral imaging system</td>
<td>1 instrument</td>
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<tr>
<td>Rand Swanson</td>
<td>Resonon*</td>
<td>Multi-spectral imaging system (plant health)</td>
<td>1 instrument</td>
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<td>Meteorological measurements</td>
<td>1 tower</td>
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<tr>
<td>Joseph Shaw (PI), Justin Hogan, Nathan Kaufman</td>
<td>Montana State University</td>
<td>In situ (closed path) stable carbon isotope detection system</td>
<td>1 instrument</td>
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<tr>
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<td></td>
<td>Flask sampling for in situ isotope detection</td>
<td>Lab analysis</td>
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<tr>
<td>Julianna Fessenden +3 students</td>
<td>Los Alamos National Laboratory</td>
<td>Frequency-modulated spectroscopy (FMS) open-air path</td>
<td>1 instrument</td>
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<td>Eddy covariance</td>
<td>1 tower</td>
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<tr>
<td>Sam Clegg, Seth Humphries</td>
<td>Los Alamos National Laboratory</td>
<td>Soil CO₂ flux (steady-state)</td>
<td>27 chambers</td>
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<tr>
<td>James Amonette, Jon Barr</td>
<td>Pacific Northwest National Laboratory</td>
<td>Chamber soil CO₂ flux measurements</td>
<td>1 instrument</td>
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<tr>
<td>Sally Benson (PI), Sam Krevor, Jean-Christophe Perin, Ariel Esposito, Chris Rella (Picarro)</td>
<td>Stanford University* / Picarro Instruments*</td>
<td>Commercial cavity ringdown real-time measurements of δ¹³C and CO₂ in air</td>
<td>1 instrument</td>
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<tr>
<td>Thom Rahn</td>
<td>Los Alamos National Laboratory</td>
<td>CO₂ soil gas concentration</td>
<td>8 sensors</td>
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<td></td>
<td></td>
<td>CO₂ atmospheric concentration</td>
<td>2 sensors</td>
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<tr>
<td></td>
<td></td>
<td>Chamber soil CO₂ flux measurements</td>
<td>1 instrument</td>
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<tr>
<td>Jennifer Lewicki</td>
<td>Lawrence Berkeley National Laboratory</td>
<td>Meteorological measurements</td>
<td>1 tower</td>
</tr>
<tr>
<td>Greg Rau, Ian McAlexander (LGR)</td>
<td>Lawrence Livermore National Laboratory /Los Gatos Research*</td>
<td>Commercial cavity ringdown real-time measurements of δ¹³C and CO₂ in air</td>
<td>1 instrument</td>
</tr>
</tbody>
</table>
Flux Chamber

07/08/2008

07/09/2008: Injection begins

07/10/2008

07/11/2008

07/12/2008

07/13/2008

Log CO₂ flux (g m⁻² d⁻¹)

J.L. Lewicki, LBNL
An eddy covariance (EC) station was deployed ~30 m NW of the release well in 2006, 2007, and 2008.

In 2008 (0.3 t CO$_2$ d$^{-1}$ for 1 month) leakage signal was detected in raw EC CO$_2$ flux ($F_c$) data. Ecosystem CO$_2$ fluxes were modeled and removed from $F_c$ to improve signal detection in residual flux ($F_{cr}$) data.

A least-squares inversion of measured residual CO$_2$ fluxes and corresponding modeled footprint functions during the 2008 release modeled the distribution of surface CO$_2$ fluxes, allowing us to locate and quantify (to within 7%) the leakage signal.
TOUGH2/EOS7CA was used to address the origin of patchy emissions at the ZERT shallow-release experiment.

A three-dimensional grid (3D) was developed that captures the changes in elevation of the pipe.

High-flux regions correlate with packer locations.

3D longitudinal grid with 52,569 gridblocks (4779 gridblocks per XY-plane).
Results suggest that packer locations influence emission patterns.

\[ q_{\text{CO}_2} = 100 \text{ kg CO}_2/\text{day} \]

Three-dimensional results of \( X_g^{\text{CO}_2} \) at \( t = 3 \) days showing patchy emission pattern.

- Patches are correlated with packer locations and high-elevation regions in each zone in the soil material.
- With more packers (i.e., more zones), there are still early breakthroughs but overall emission is less patchy.
- Therefore, simulations support the hypothesis that along-pipe flow of \( \text{CO}_2 \) upwards within each zone leads to an effective point-source release that creates a persistent patchy emission.
Hyperspectral Imaging

True Color Analyzed Image

Spectral Imaging System:
Imaging Spectrometer, Data Logger/System Control, IMU/GPS/Communications
Hyperspectral Imaging Unsupervised Classification

Kevin Repasky

[Image of a map with color-coded areas and text annotations]

05/30/2017

Estimated leakage discharge = 0.144 kg CO₂·d⁻¹

50 m

50 m

Courtesy Jen Lewicki
Lawrence Berkeley Lab
Multispectral imagers used to detect plant stress caused by CO\textsubscript{2} leaking from underground.

Time-series plot showing that the CO\textsubscript{2}-affected plant health decays faster over time than the control region. This plot shows Normalized Difference Vegetation Index (NDVI), found from NIR and red reflectances as \((\text{NIR-red})/(\text{NIR+red})\)
Compact, ultra-low-cost multispectral imager designed for deployment on tethered balloon.
Studying the vegetation response to simulated leakage of sequestered CO2 using spectral vegetation indices


Montana Tech

Venkata Ramana Lakkaraju, Xiaobing Zhou, Martha E. Apple, Al Cunningham, Laura M. Dobeck, Kadie Gullickson, Lee H. Spangler
calcite dissolution could be the primary process buffering pH and releasing Ca+2 in groundwater,
(2) the increase in the concentrations of major cations and trace metals except Fe could be explained by Ca+2-driven exchange reactions,
(3) the release of anions from adsorption sites due to competing adsorption of bicarbonate could explain the concentration trends of most anions, and
(4) the dissolution of reactive Fe minerals (such as fougerite) could explain the increase in total Fe concentration.
Atmospheric monitoring of a perfluorocarbon tracer at the 2009 ZERT Center experiment

NETL
Atmospheric Environment 47 (2012) 124e132
Atmospheric monitoring of a perfluorocarbon tracer

Tower, 1 m  Tower, 2 m  Tower, 3 m  Tower, 4 m

Balloon, 10 m  Balloon, 20 m  Balloon, 40 m
The inline fiber sensor uses a series of segmented photonic bandgap (PBG) fiber in series to form an inline fiber sensor array.

Each segment is addressed using time of flight of the laser pulse.

CO$_2$ diffuses into the PBG fiber to allow spectroscopic measurements of CO$_2$ concentration.

**Challenge:** PBG fiber is larger diameter than SMF and conventional splicing collapses hollow core.

Initial un-normalized CO$_2$ measurements made using one segment of the inline fiber sensor.
Cavity Ring Down Spectrometer Survey

Rapid surface detection of CO₂ leaks from geologic sequestration sites

Dylan Moriarty, Laura Dobeck, Sally Benson

*Sandia National Laboratories, 1515 Ehbank SE, Albuquerque, NM 87123, USA
†Montana State University, Montana State University, Bozeman, MT 59717, USA
‡Stanford University, 450 Serra Mall, Stanford, CA 94305, USA

Fig. 6. Detection percentage using static threshold method for $^{12}$CO₂ (left), $^{13}$CO₂ (center), and $\delta^{13}$C (right).
Process-based soil gas leakage assessment at the Kerr Farm: Comparison of results to leakage proxies at ZERT and Mt. Etna

Katherine D. Romanak\textsuperscript{a,}\textsuperscript{*}, Brad Wolaver\textsuperscript{a}, Changbing Yang\textsuperscript{a}, George William Sherk\textsuperscript{b}, Janis Dale\textsuperscript{c}, Laura M. Dobeck\textsuperscript{d}, Lee H. Spangler\textsuperscript{d}

\textsuperscript{a} Gulf Coast Carbon Center, Bureau of Economic Geology, The University of Texas at Austin, Austin, TX 78713, USA
\textsuperscript{b} Clifton Associates Ltd, 340 Maxwell Cres. Regina, SK S4N 5V5, Canada
\textsuperscript{c} Department of Geology, University of Regina, Regina, Saskatchewan S4S 0A2, Canada
\textsuperscript{d} Energy Research Institute, Montana State University, Bozeman, MT 59717, USA

A) 25

\begin{align*}
\text{O}_2 (\text{volume }\%) &= 20 \\
\text{CH}_2\text{O} + \text{O}_2 &\rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{Oxidation of CH}_4 &\rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{CO}_2 &\rightarrow \text{Mixture} \\
\text{CO}_2 \text{dissolution} &\rightarrow \text{Exogenous addition of CO}_2
\end{align*}

\text{B) ZERT}
What We Have Learned

• Many near surface methods are quantitative but
  – Diurnal, seasonal, annual variations in ecosystem background flux affect detection limits
  – Appropriate area integrated, mass balance is a challenge

• Nearly all methods could detect 0.15 tonnes/day release at ZERT
  Atmospheric signals drop rapidly away from the ground surface

• Isotopes & tracers have lower detection limits than straight CO₂ flux or concentration

• Scaling, 6 tonnes per day would be detectable over an area 40 times as large

• Surface expression was “patchy” – 6 areas of ~5m radius

• Natural analogs also seem to have “patchy” surface expression

• By comparing multiple controlled release sites we see that different ecosystems respond somewhat differently
Why is the Surface Expression “Patchy”

If the horizontal permeability is significantly less than the vertical permeability, CO$_2$ will spread laterally until it hits a lower permeability vertical path. It can then desiccate that path creating a “chimney”
If CO$_2$ Escapes the Reservoir

Many processes could prevent it from reaching the surface including:

1. Trapping under a secondary seal
2. Geochemical conversion of CO$_2$
3. Dissolution

If it does reach the surface:

1. The surface flux will not necessarily be the same as the flux leaving the reservoir
2. The surface expression could be some distance from the storage reservoir
Monitoring – A Multi-Step Process

• **Initial Detection** (Finding anomalies in a large area.)
  – Wide Area – Hyperspectral Imaging, Atmospheric tomography
  – Moderate Area – Lidar, Fiber sensors, Resistivity

• **Confirmation** (Is anomaly due to elevated CO₂ flux?)
  – CO₂ flux and / or concentration measurements, water measurements

• **Attribution** (Is elevated flux due to leakage?)
  – Isotopic measurements
  – Process based measurements (relationships between multiple gases, Romanack)

• **Mapping and Quantification**
  – Flux chamber
  – Concentration measurements in a survey mode

• **Impact Measurement** – Dependent on the receptor
What Is the Monitoring Purpose?

• Climate change mitigation?
  – 1% over 1000 yrs – climate models?

• Retention in the reservoir?
  – Subsurface techniques typically do not measure properties directly proportional to concentration / quantity

• Overall storage security?

• HSE, Resource protection (USDW)?
  – Measure to ensure levels are below impact levels

• Public assurance?

• Verification and accounting?
  – Mass flow meters only accurate to ~1%

If this is the primary focus, this could reduce need for wide – area monitoring.
How We Have Learned

Natural Analogs
- Mammoth Mountain
- Laacher See
- Latera
- Soda Springs, ID
- Crystal Geyser, UT
- More

How analogous is the analog?
Flow through significant overburden
Fluxes may be much higher than leaky engineered system

Controlled Releases
- ASGARD (Nottingham)
- ZERT (Montana State)
- Australia
- Norway
- More

Source term known
Ability to establish detection limits
Relatively little overburden
Acknowledgement

U.S. Department of Energy

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