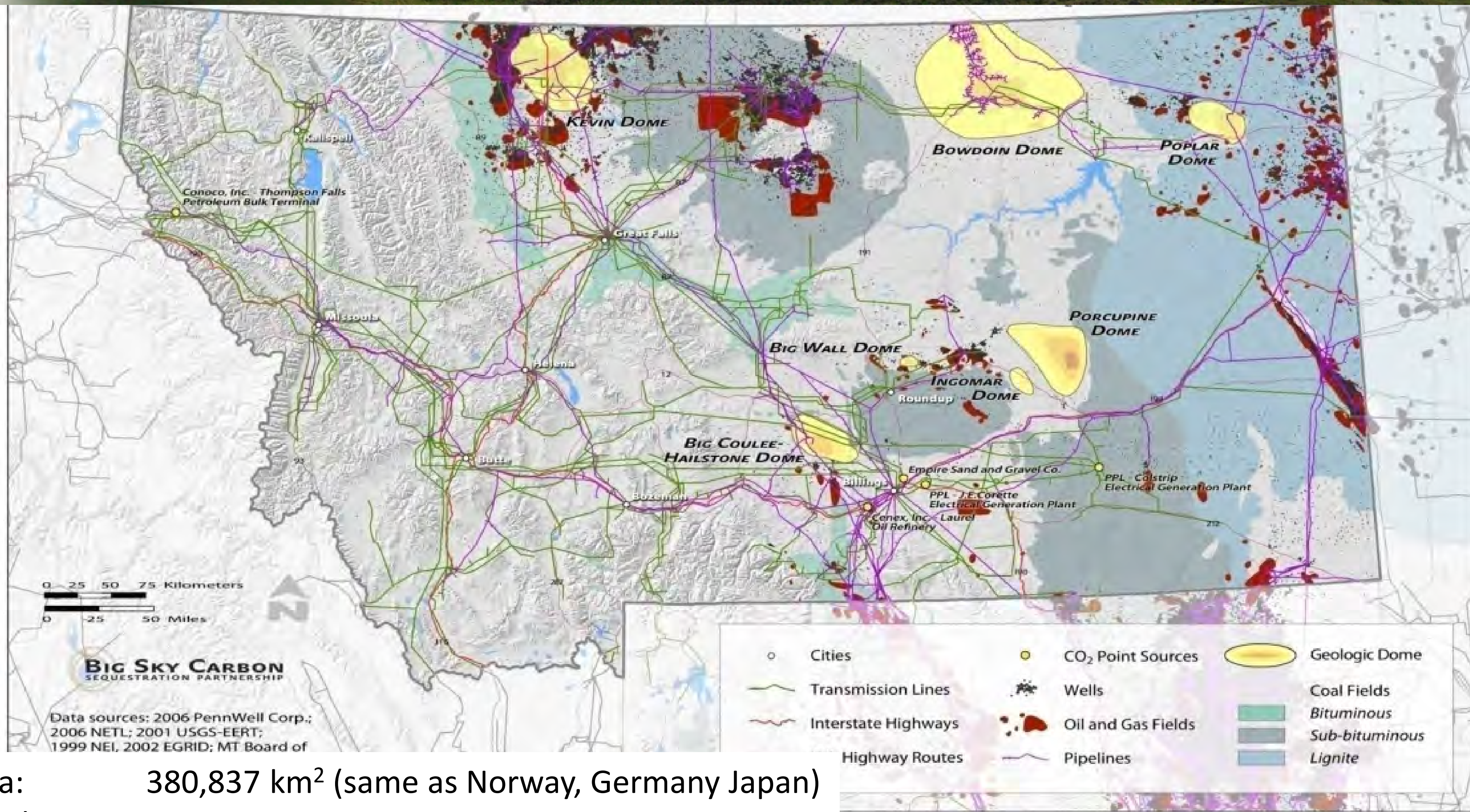
ZERT Controlled Release Facility

Montana



Area: 380,837 km^2 (same as Norway, Germany Japan)

Population **967, 440**

6% of world's coal reserves, Significant Oil & Gas

Agriculture (snowpack dep.)

Tourism (Skiing, National Parks, Fly Fishing)

MONTANA STATE UNIVERSITY

Near Surface Detection Site

Near-surface detection systems are potentially desirable for public assurance

When we built this facility, detection systems had been deployed at sequestration pilot sites

These pilot were well chosen and do not leak

They have also been used at volcanic sites – but these likely have much higher fluxes than one would see in CCS systems

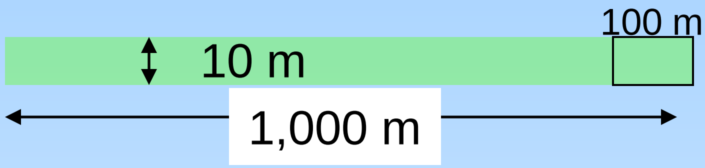
As a result, near-surface detection techniques had not been adequately tested

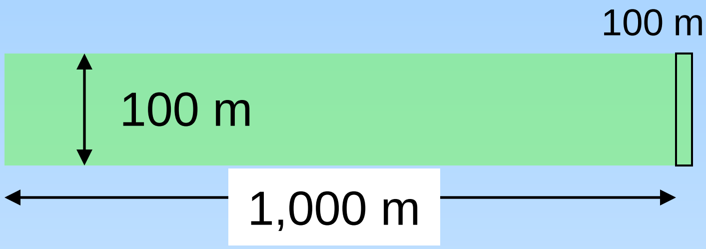
What Are Relevant Release Rates?

- 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 84 idling cars

Injection Rate

Lee Spangler
Sally Benson





What are relevant feature sizes, scaling factors?

- **Two leakage pathway concerns are Wells and Faults**
- **Envisioned faults ~1km in length and 10 – 100 m wide in surface expression**
- **A shallow horizontal well of ~100m in length could represent 10% and 1% of these cases, respectively**
- **Release between 10% to 1% of the 5.5 tonnes/day through a horizontal well ~100m in length – 0.55 – 0.06 tonnes / day**
- **Actual release rates used 0.3 – 0.1 tonnes/day (equivalent to between 5 and 1 idling cars)**

Field Test Facility

Site Soil Characteristics

Zero Emissions Research and Technology

Horizontal Well Installation

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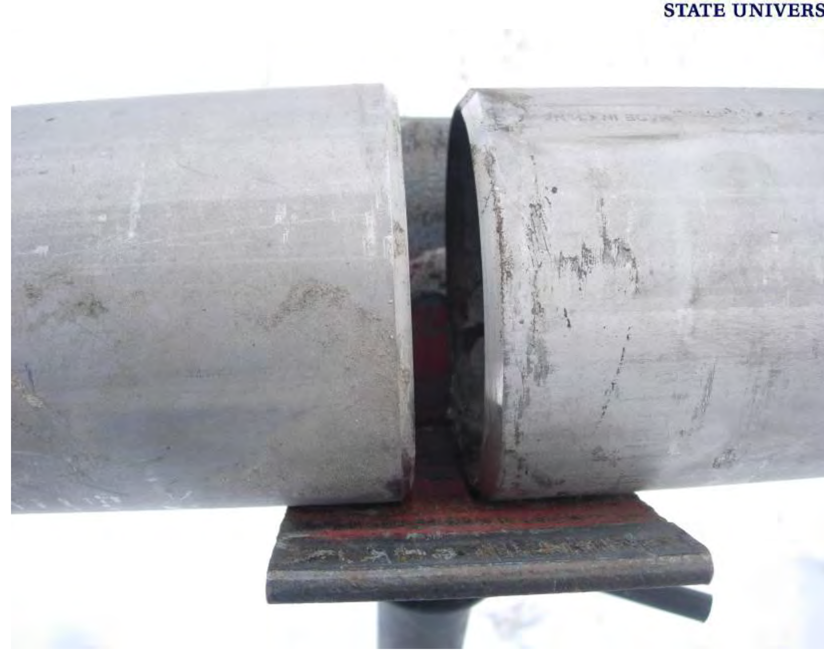
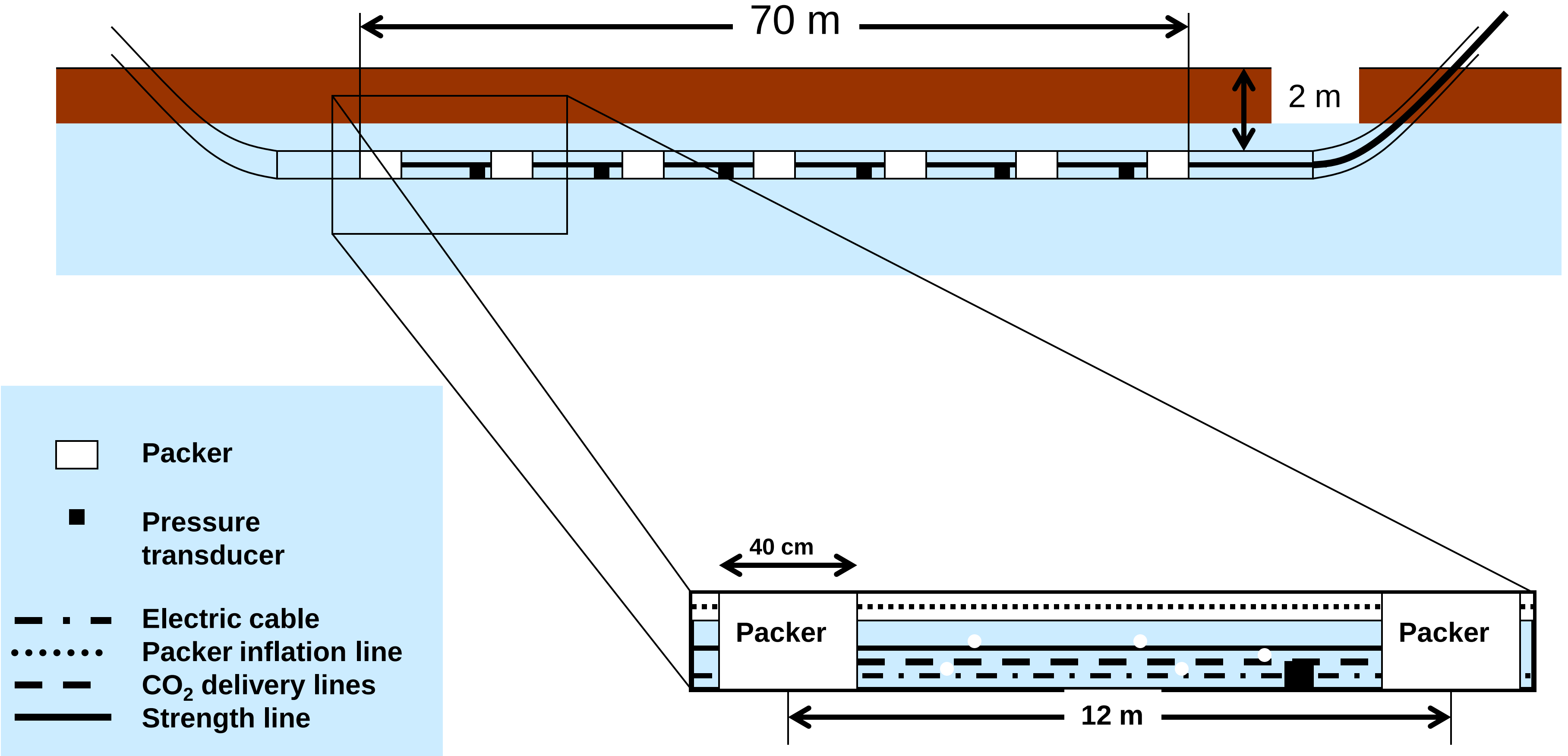
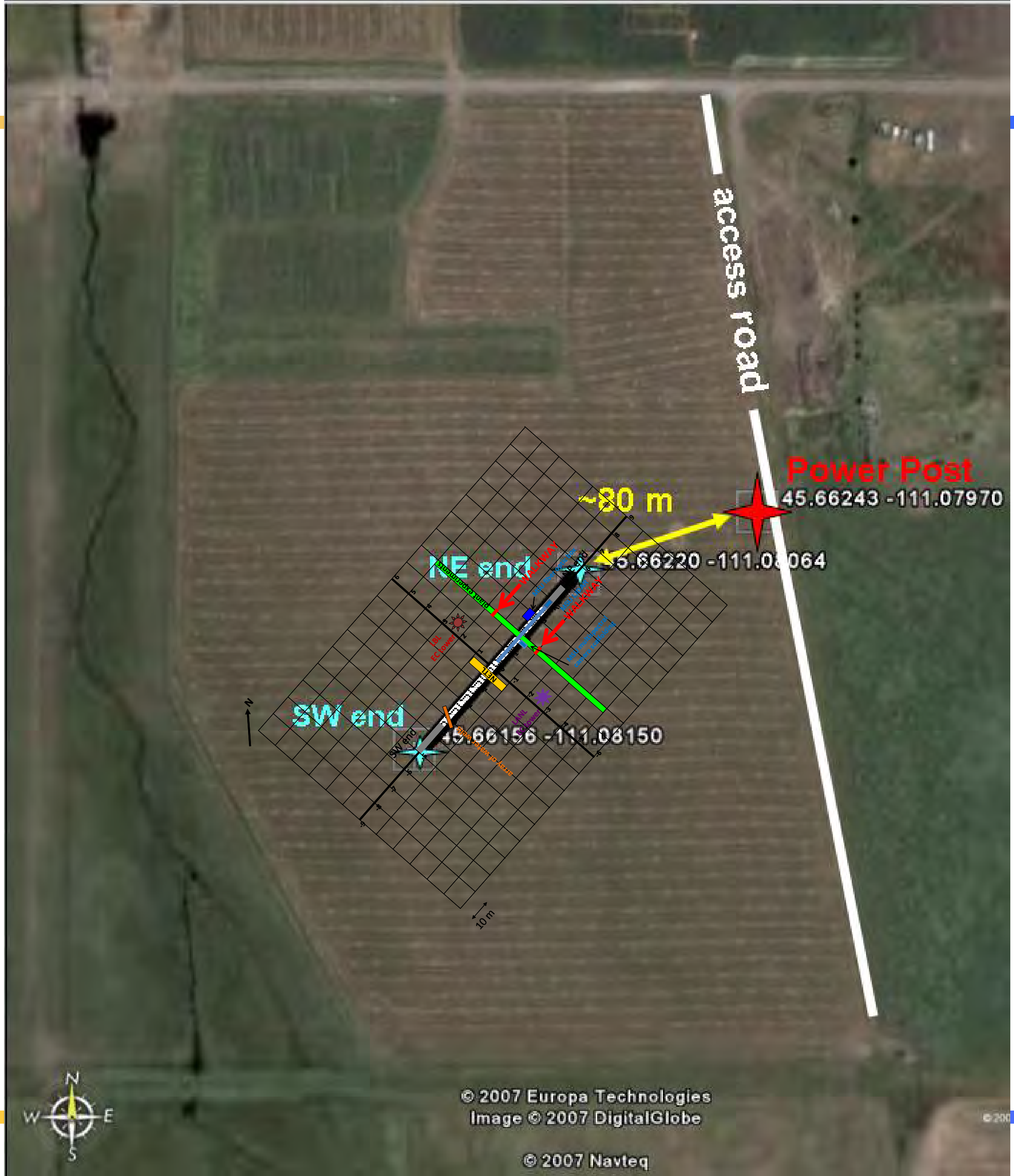


Horizontal Well Installation

Horizontal Well Installation

Ray Solbau, Sally Benson





access road
Power Post
45.66243 -111.07970
~80 m
NE end
45.66220 -111.08064
SW end
45.66156 -111.08150
10 m
N
W
E
S
© 2007 Europa Technologies
Image © 2007 DigitalGlobe
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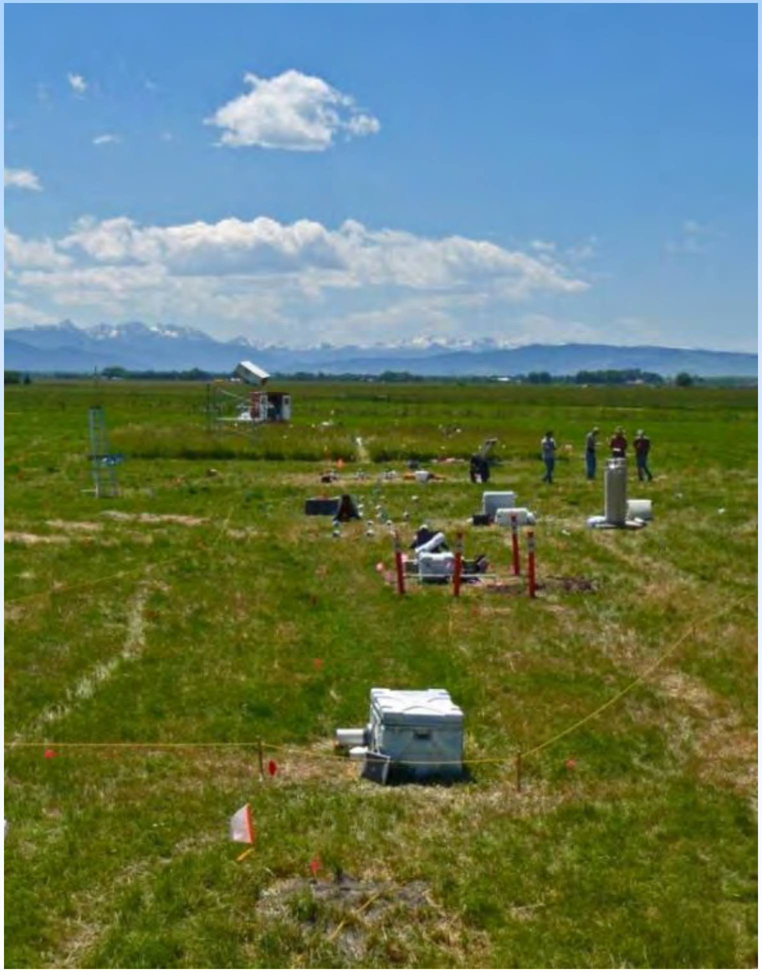
Large Number of Participants / Methods

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



Investigator	Institution	Monitoring Technology	Number of Sensors
Arthur Wells Rod Diehl Brian Strasizar	National Energy Technology Laboratory	Atmospheric tracer plume measurements	1 tower (4m) Blimp (Apogee Scientific) with 3 tether line samplers
		Bee hive monitoring for tracer with sorption tube and pollen trap	2 hives
		Automated Soil CO_2 flux system	4 chambers
William Pickles Eli Silver Erin Male	University of California- Santa Cruz	Hand held hyperspectral measurements (plant health)	1 instrument
Yousif Kharaka James ThordsenGil AmbatsSarah Beers	United States Geological Survey*	Ground water monitoring	1 EC and temperature probe, Dissolved oxygen probe, lab analysis of water samples
Henry Rauch	West Virginia University	Water monitoring well headspace gas sampling	1 sensor
Lucian Wielopolski Sudeep Mitra	Brookhaven National Laboratory*	Ineleastic neutron scattering (total soil carbon)	1 instrument
Martha Apple Xiaobing Zhou Venkata Lakkaraju Bablu Sharma +2 students	Montana Tech*	Soil moisture, temp. Chlorophyll Content Meter , Fluorescence Meter , LI-COR 2000 to measure leaf area index Leaf Porometer to measure stomatal conductance	5 sensors
		Infrared radiometry (plant health)	2 instruments
		Atmospheric humidity and temperature, accumulated rainfall	1 sensor each
		Plant root imaging	1 camera
		Soil conductivity	1 sensor
		Handheld hyperspectral measurements (plant health)	1 instrument
William Holben Sergio Morales	University of Montana*	Microbial studies	Lab analysis

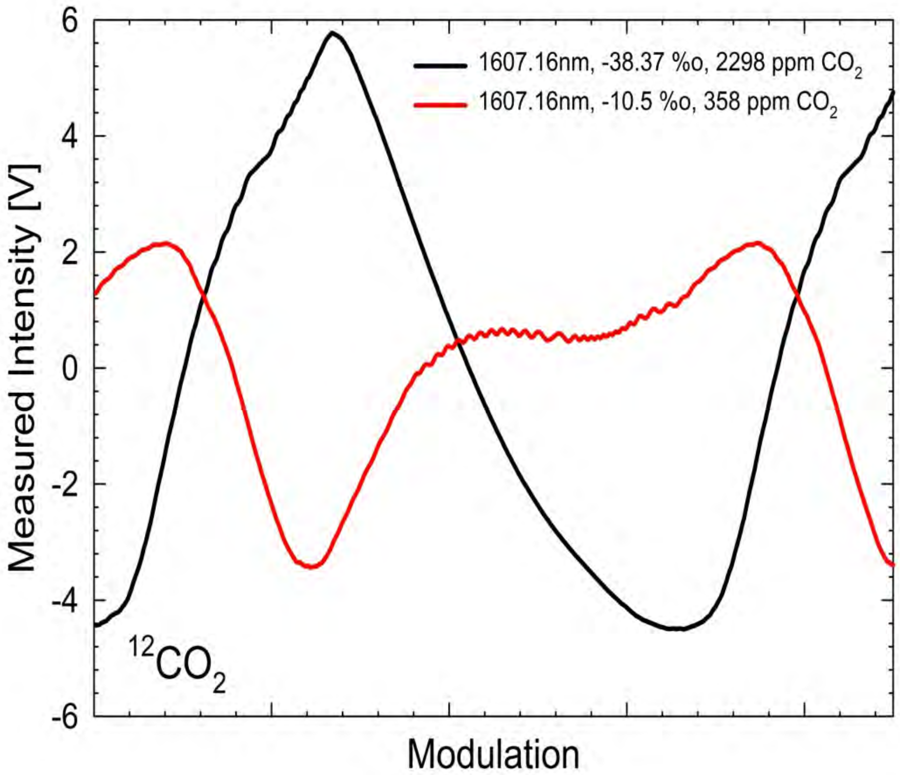
ZERT Zero Emissions Research and Technology

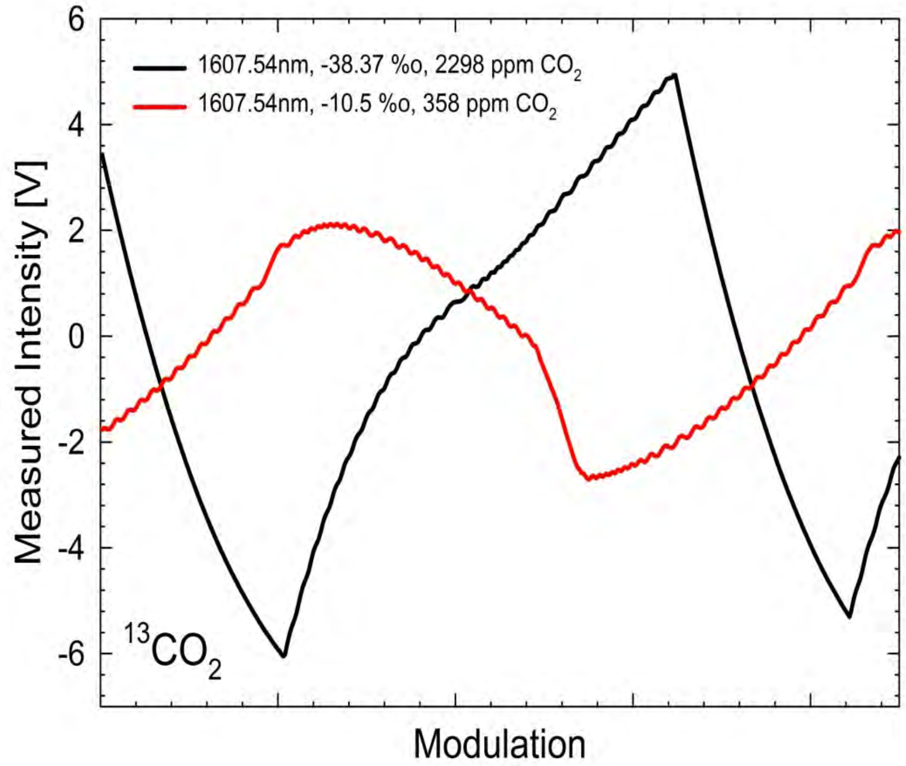
Large Number of Participants / Methods

Investigator	Institution	Monitoring Technology	Number of Sensors
Lee Spangler Laura Dobeck Kadie Gullickson	Montana State University	Water content reflectometers (soil moisture)	15 sensors
		Automated soil CO_2 flux system	5 long term chambers, 1 portable survey chamber
		CO_2 soil gas concentration	6 sensors
Kevin Repasky (PI) Jamie Barr	Montana State University	Underground fiber sensor array (CO_2 soil gas concentration)	4 sensors
Rand Swanson	Resonon*	Flight based hyperspectral imaging system	1instrument
Joseph Shaw (PI) Justin Hogan Nathan Kaufman	Montana State University	Multi-spectral imaging system (plant health)	1instrument
		Meteorological measurements	1 tower
Julianna Fessenden +3 students	Los Alamos National Laboratory	In situ (closed path) stable carbon isotope detection system	1 instrument
		Flask sampling for in situ isotope detection	Lab analysis
Sam Clegg Seth Humphries	Los Alamos National Laboratory	Frequency-modulated spectroscopy (FMS) open-air path	1 instrument
Thom Rahn	Los Alamos National Laboratory	Eddy covariance	1 tower
James Amonette Jon Barr	Pacific Northwest National Laboratory	Soil CO_2 flux (steady-state)	27 chambers
Sally Benson (PI) Sam Krevor Jean-Christophe Perin Ariel Esposito Chris Rella (Picarro)	Stanford University* / Picarro Instruments*	Commercial cavity ringdown real-time measurements of $\delta^{13}C$ and CO_2 in air	1 instrument
Greg Rau Ian McAlexander (LGR)	Lawrence Livermore National Laboratory /Los Gatos Research*	Commercial cavity ringdown real-time measurements of $\delta^{13}C$ and CO_2 in air	1 instrument
Jennifer Lewicki	Lawrence Berkeley National Laboratory	CO_2 soil gas concentration	8 sensors
		CO_2 atmospheric concentration	2 sensors
		Chamber soil CO_2 flux measurements	1 instrument
		Meteorological	1 tower

In Situ Laser Isotope Measurements

Seth Humphries, Samuel M. Clegg,
Thom A. Rahn, Julianna E. Fessenden

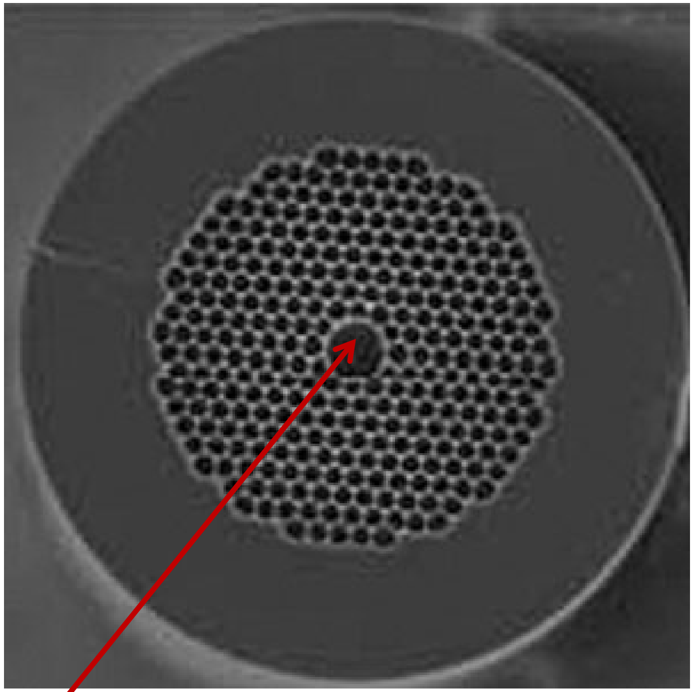




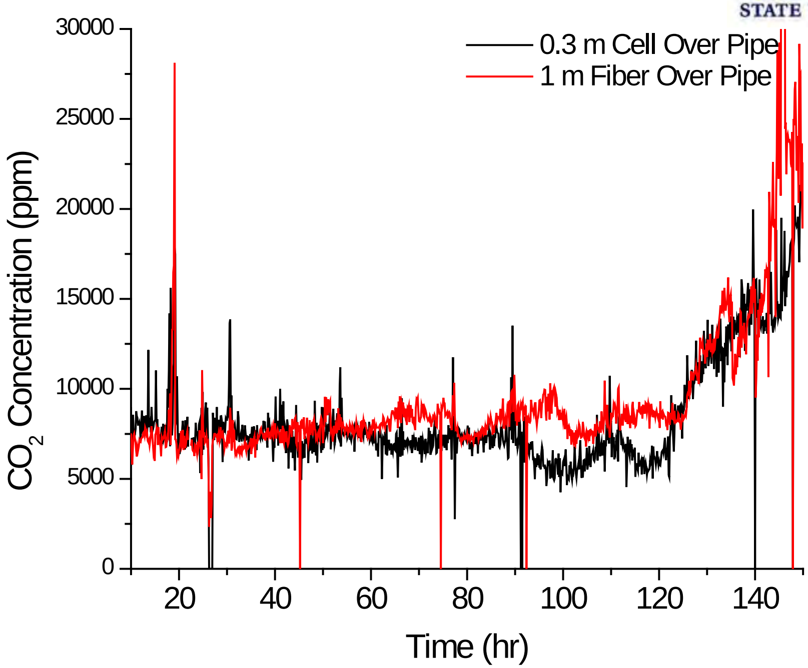
Signature of $^{12}CO_2$ and $^{13}CO_2$ over the pipe (black) and away from the pipe (red). Note that due to the high concentration of CO2 over the pipe the FMS response is in saturated conditions

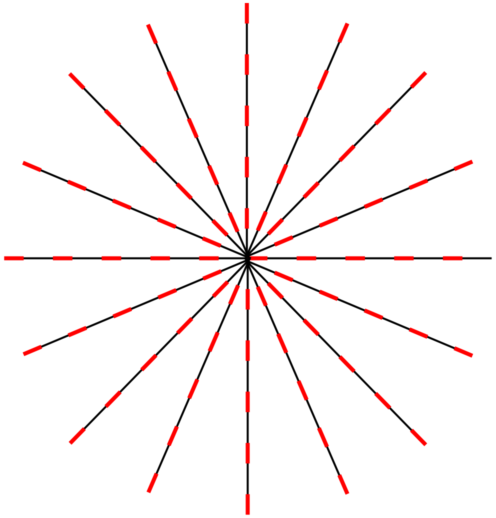
Underground Fiber Sensor

Jamie Barr
Kevin Repasky
MONTANA STATE UNIVERSITY



Hollow core where the light interacts with the carbon dioxide



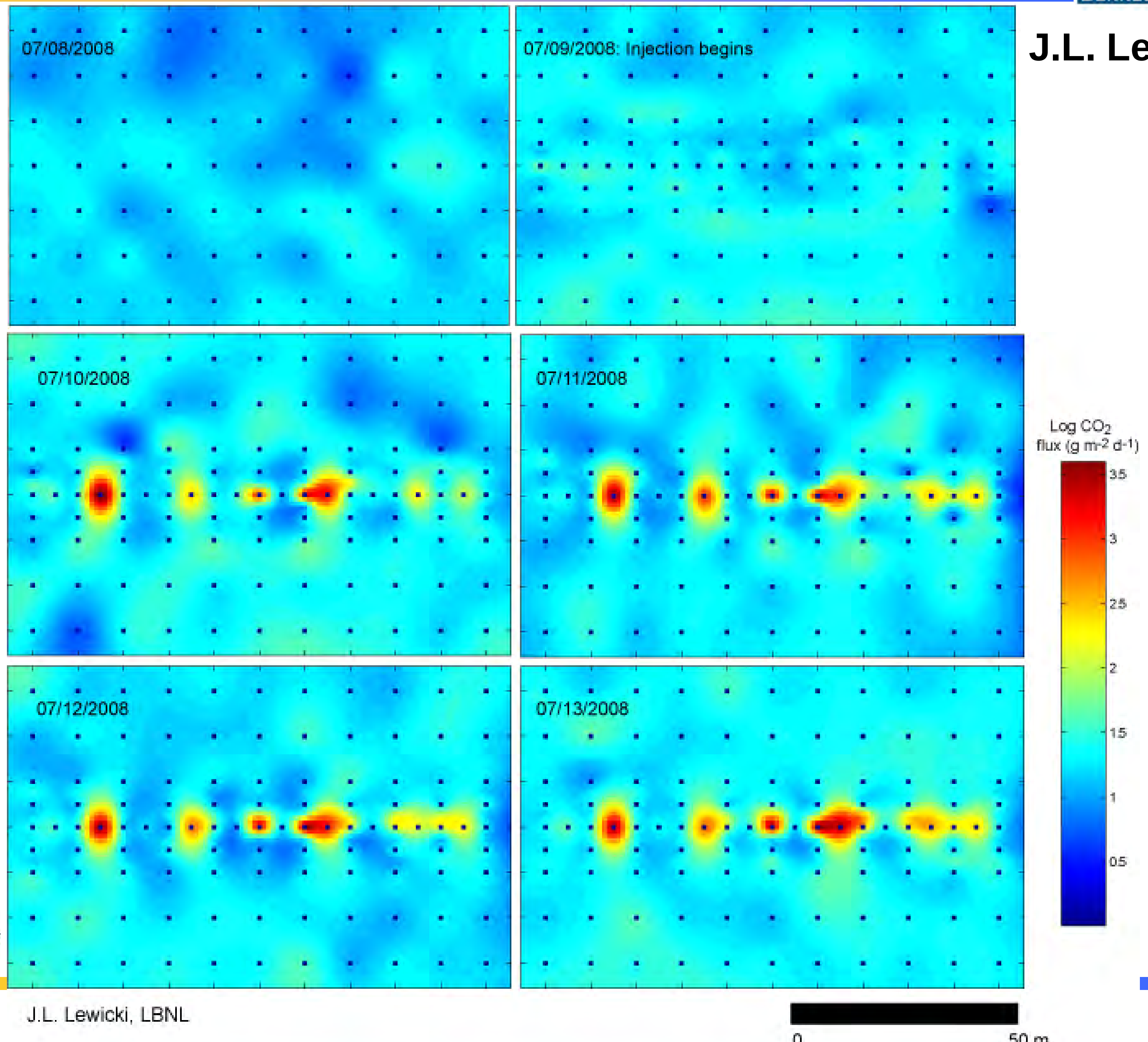


Envisioned Deployment

ZERT Zero Emissions Research and Technology

Flux Chamber

J.L. Lewicki

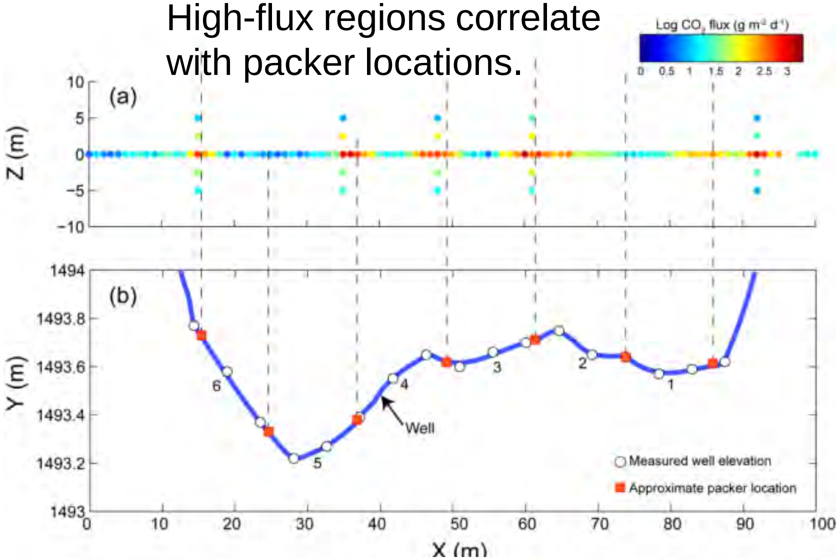


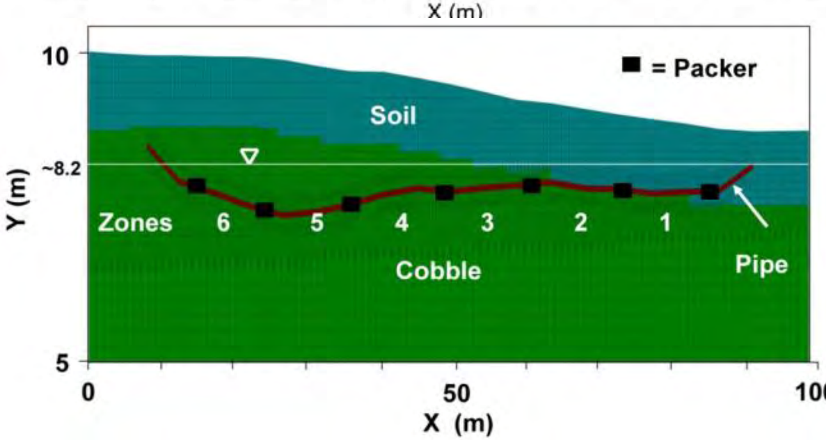
Shallow CO_2 Flow Modeling (1)

C. Oldenburg (LBNL)

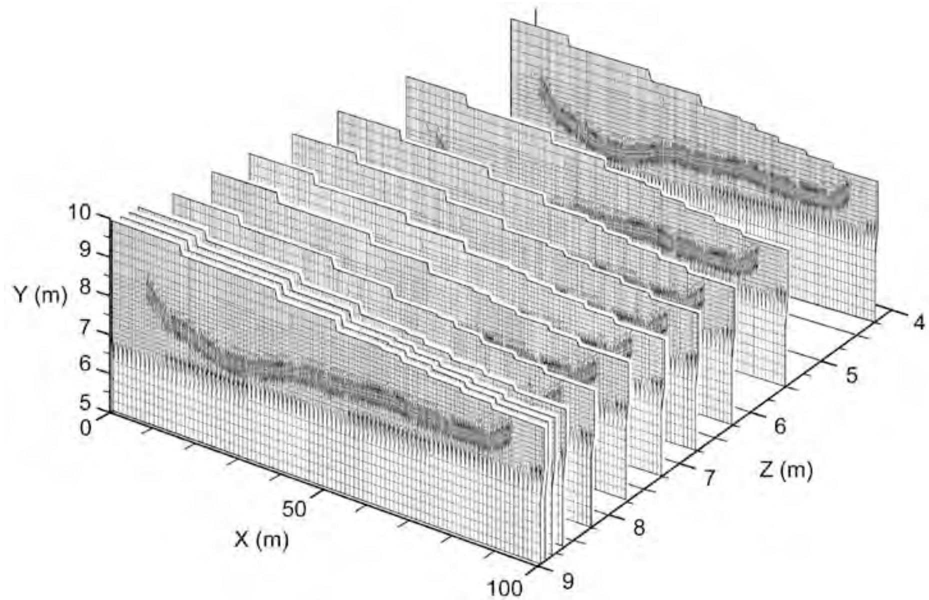
TOUGH2/EOS7CA was used to address the origin of patchy emissions at the ZERT shallow-release experiment.

High-flux regions correlate with packer locations.





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



3D longitudinal grid with 52,569 gridblocks (4779 gridblocks per XY-plane).

.

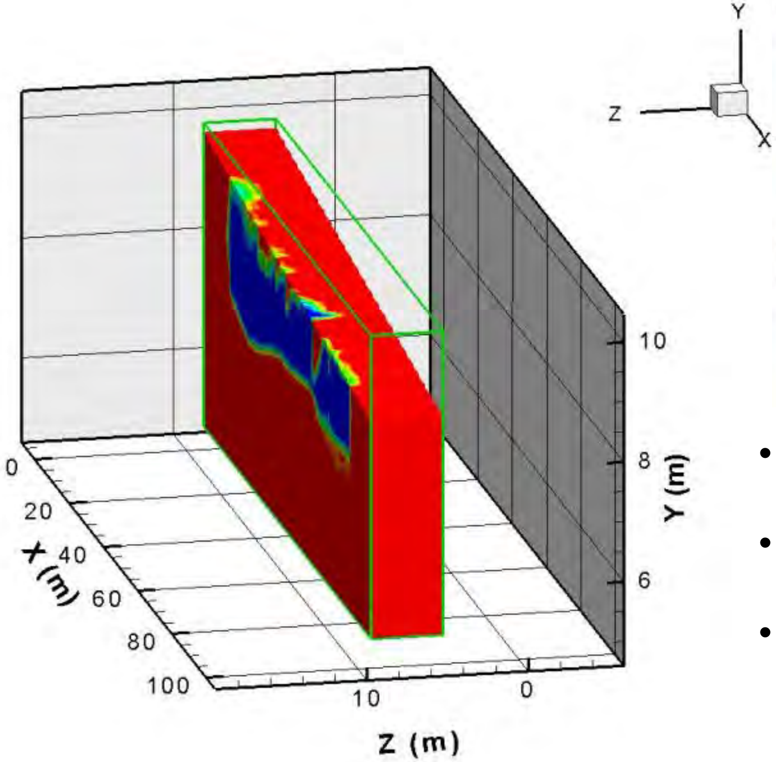
Shallow CO_2 Flow Modeling (2)

C. Oldenburg (LBNL)

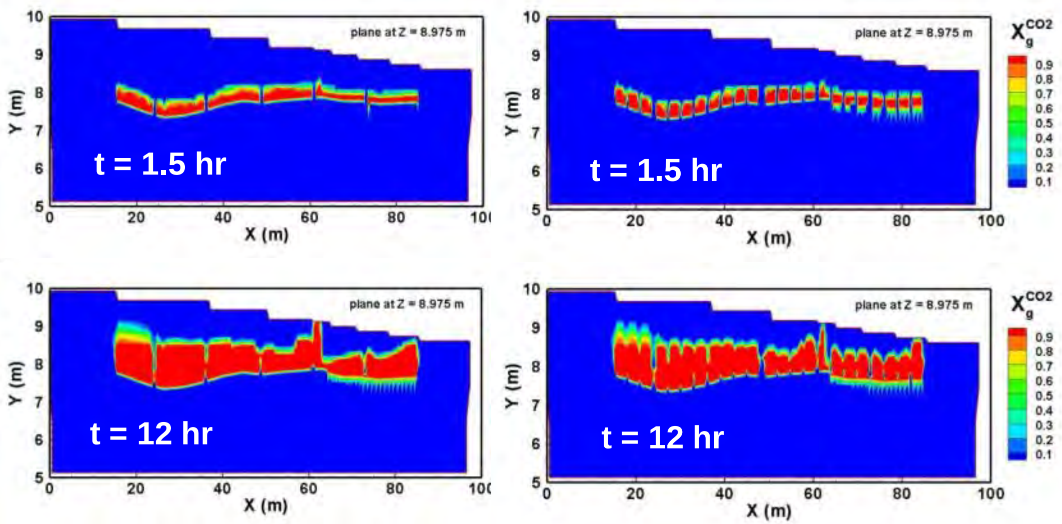
Results suggest that packer locations influence emission patterns.

q_{CO2} = 100 kg CO_2/day

Three-dimensional results of X_g^{CO2} at t = 3 days showing patchy emission pattern.



Base Case (6 zones) **Case 1 (23 zones)**

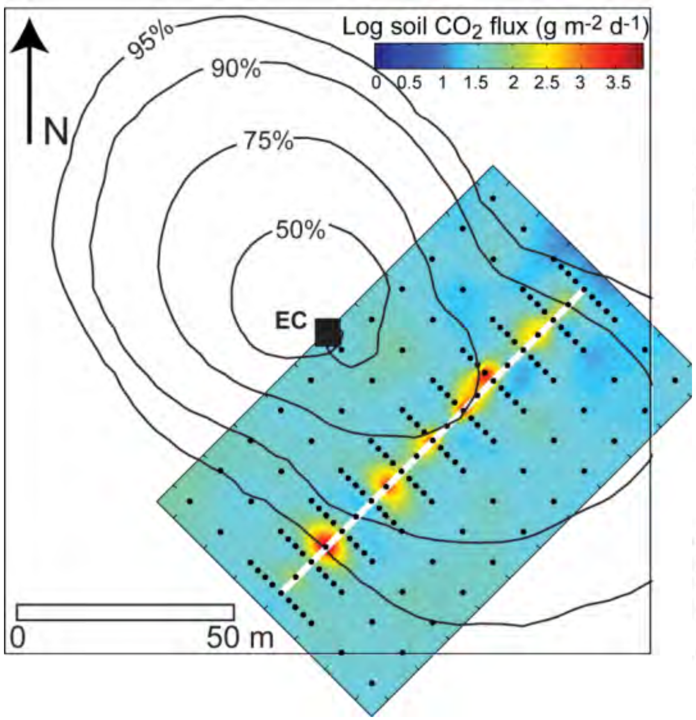


- Patches are correlated with packer locations and high-elevation regions in each zone in the soil material.
- With more packers (i.e., more zones), there are still early breakthroughs but overall emission is less patchy.
- Therefore, simulations support the hypothesis that along-pipe flow of CO_2 upwards within each zone leads to an effective point-source release that creates a persistent patchy emission.

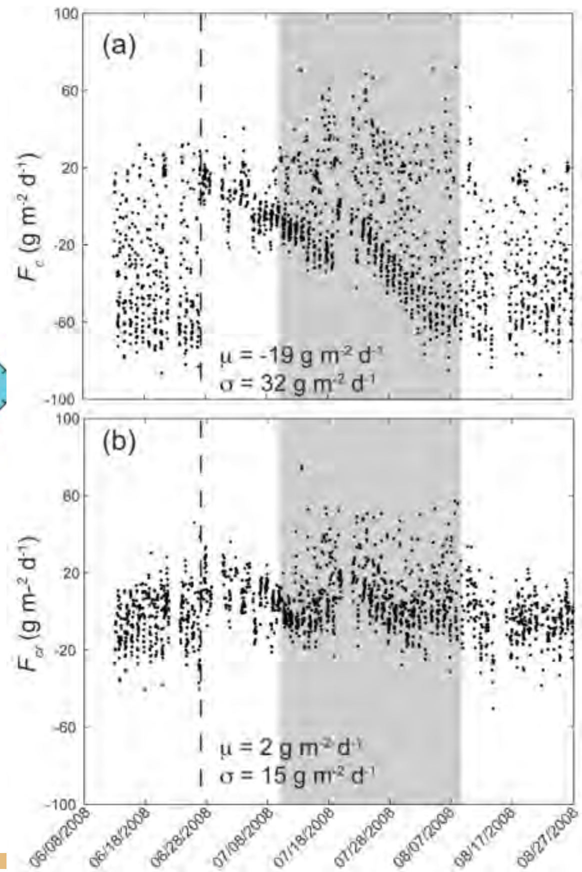
Eddy covariance net CO_2 flux monitoring

J. Lewicki (LBNL)

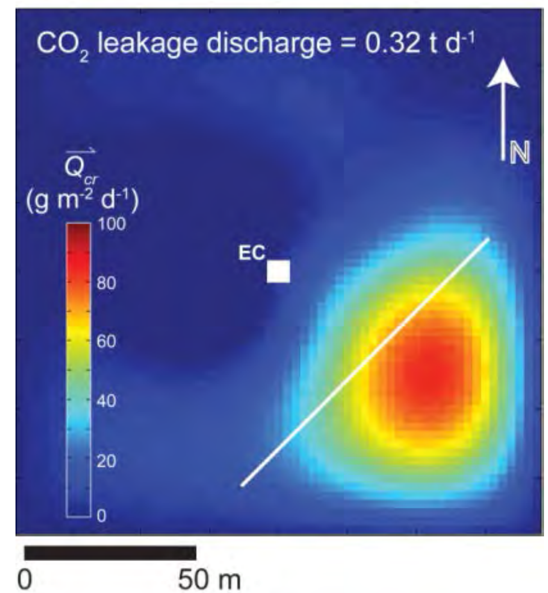
An eddy covariance (EC) station was deployed ~30 m NW of the release well in 2006, 2007, and 2008.



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.



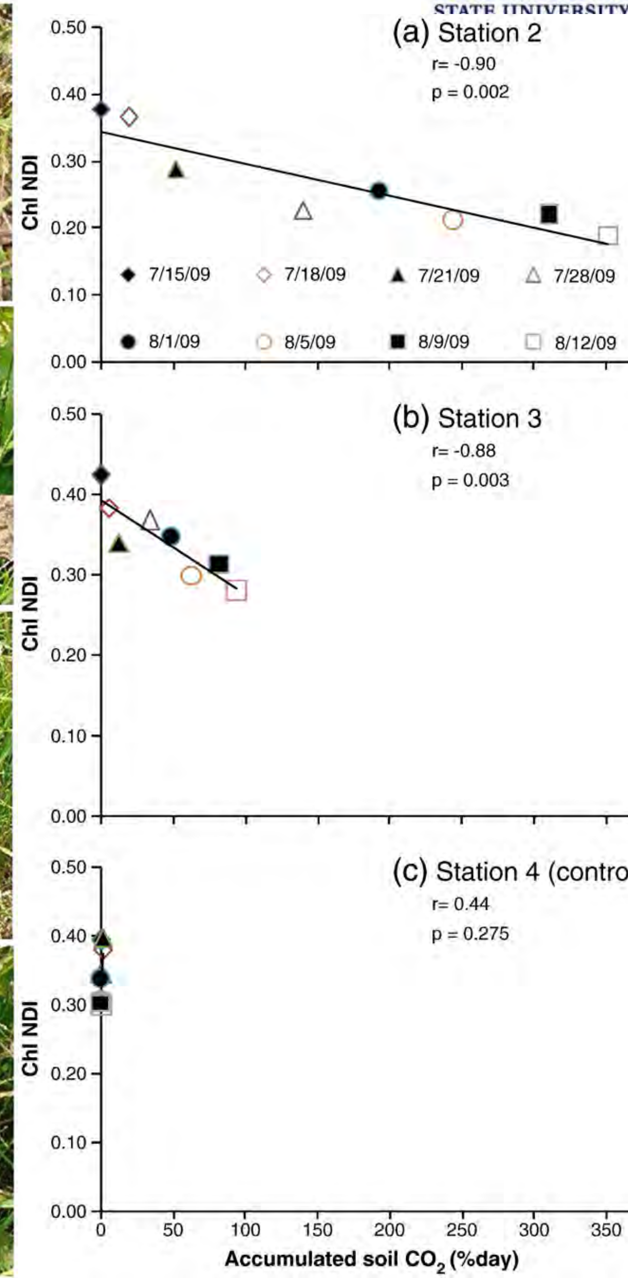
Studying the vegetation response to simulated leakage of sequestered CO2 using spectral vegetation indices

MONTANA STATE UNIVERSITY

Ecological Informatics 5 (2010) 379–389

Montana Tech

Venkata Ramana Lakkaraju, **Xiaobing Zhou, Martha E. Apple**, Al Cunningham, Laura M. Dobeck, Kadie Gullickson, Lee H. Spangler



ZERT Zero Emissions Research and Technology

Hyperspectral Imaging

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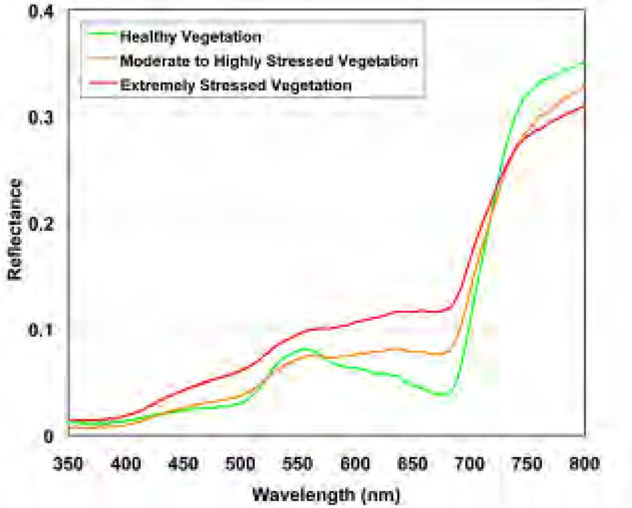
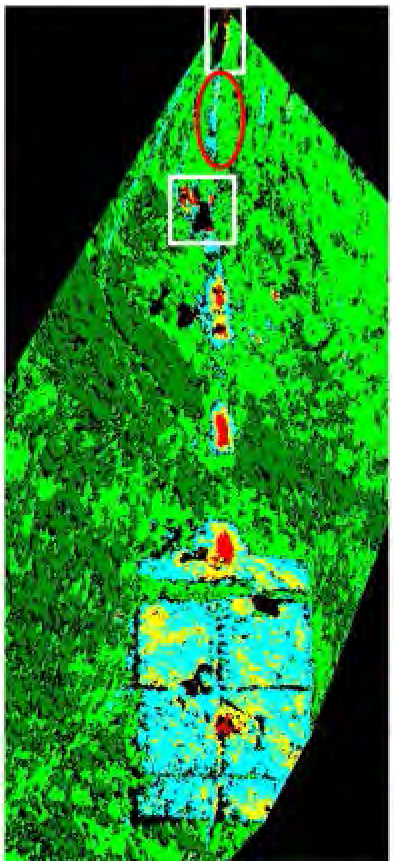
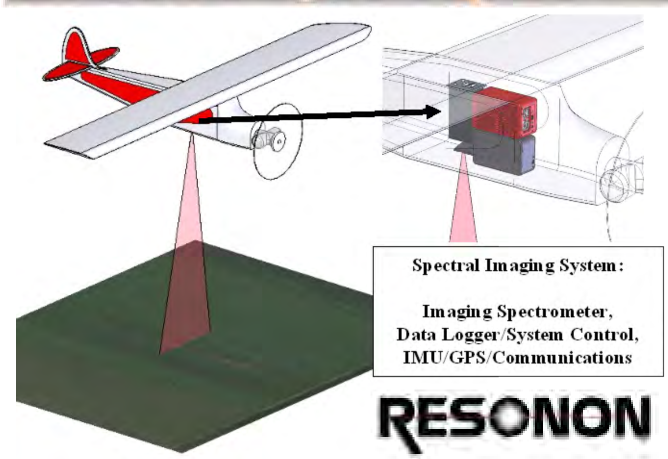


True Color

Analyzed Image

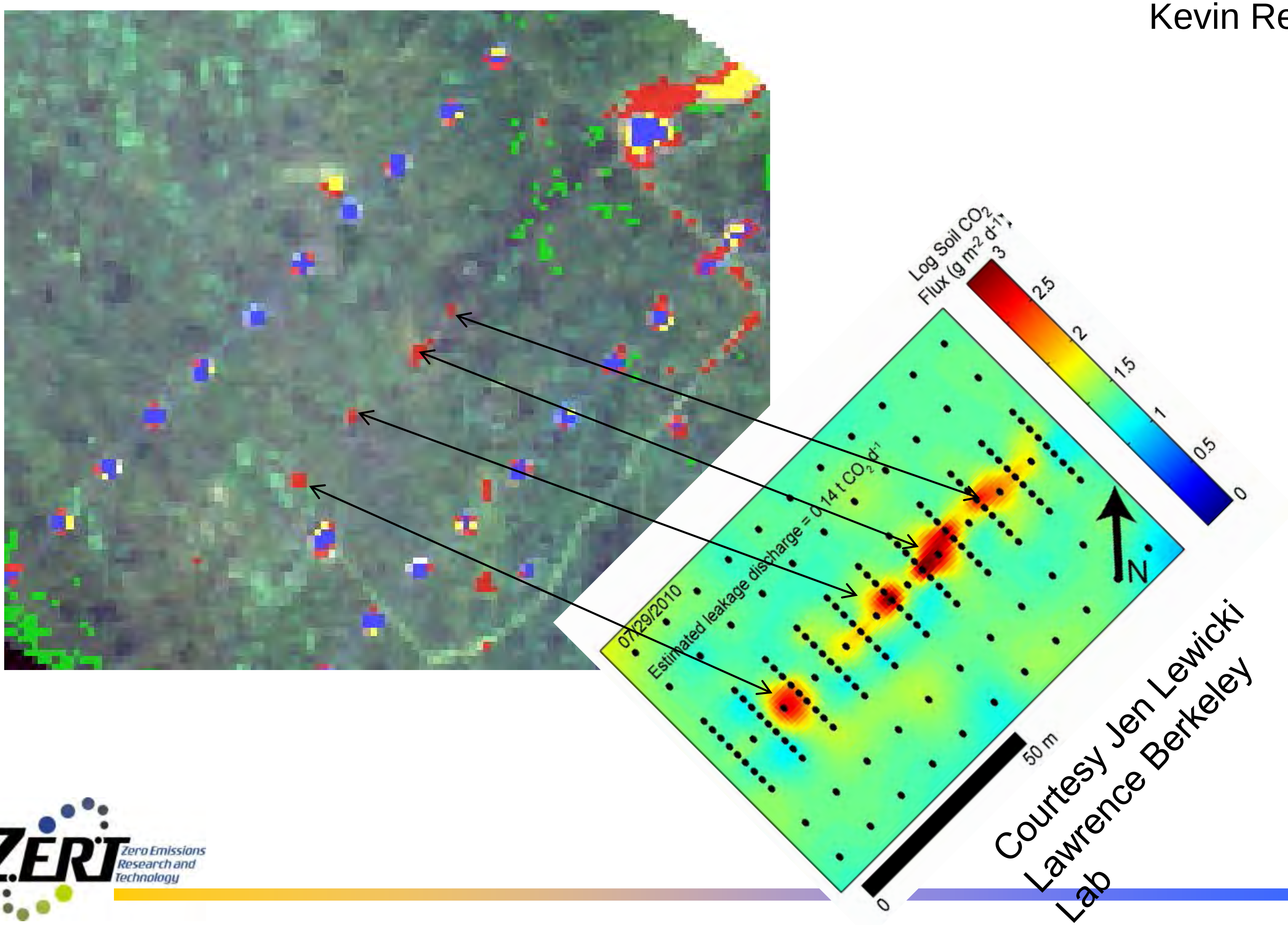


- High Stress
- Moderate Stress
- Low or Seasonal Stress
- Healthy Vegetation (Grasses)
- Healthy Vegetation (Herbaceous Legumes)
- Unclassified



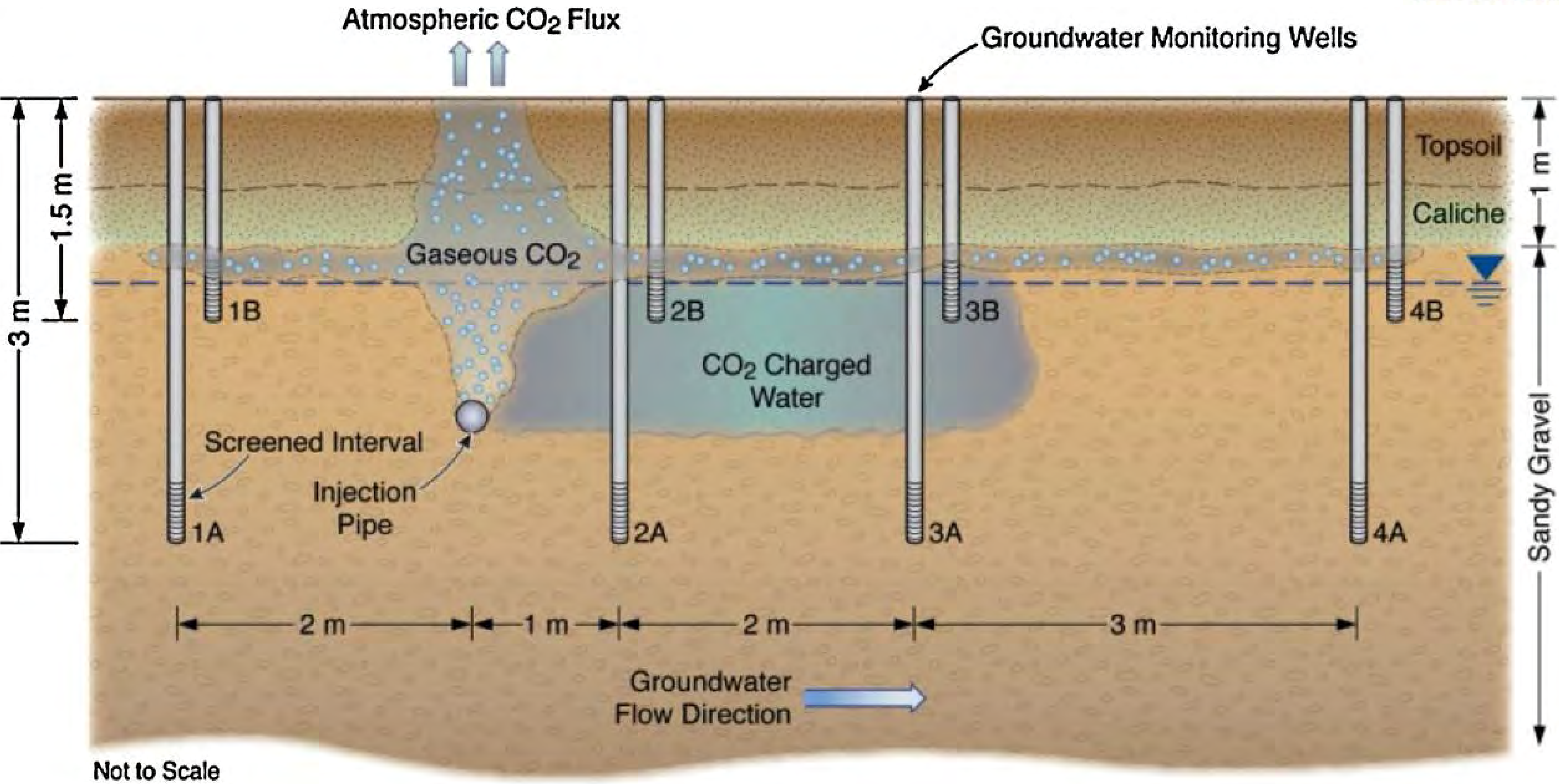
Hyperspectral Imaging Unsupervised Classification

Kevin Repasky



ZERT Zero Emissions Research and Technology

Geochemical Monitoring



USGS, LBNL, EPRI, WVU, MSU - Environ Earth Sci (2010) 60:273–284
Liange Zheng, John A. Apps, Nicolas Spycher, Jens T. Birkholzer, Yousif K. Kharaka, James Thordsen, Sarah R. Beers, William N. Herkelrath, Evangelos Kakouros, Robert C. Trautz, Henry W. Rauch Kadie S. Gullickson

Geochemical Monitoring

Environ Earth Sci (2010) 60:273–284
Int. J. Greenhouse Gas Control (2011)

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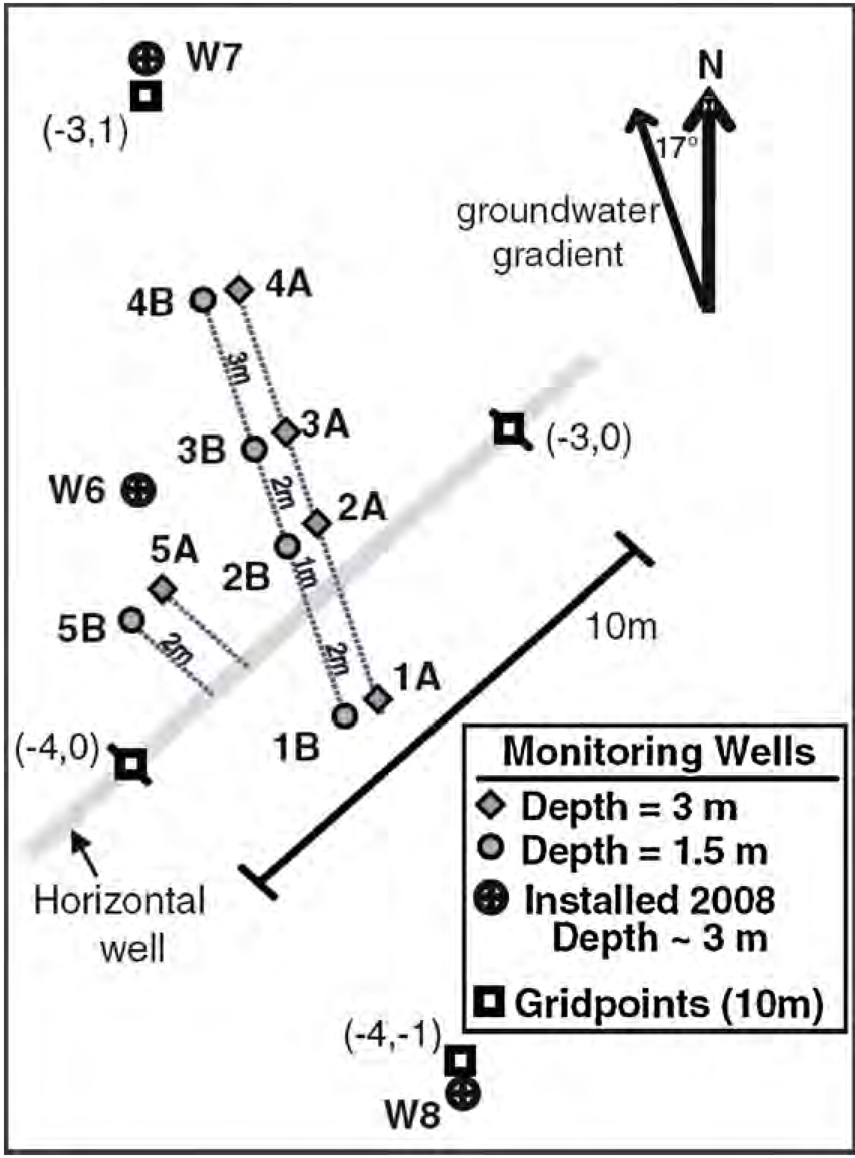
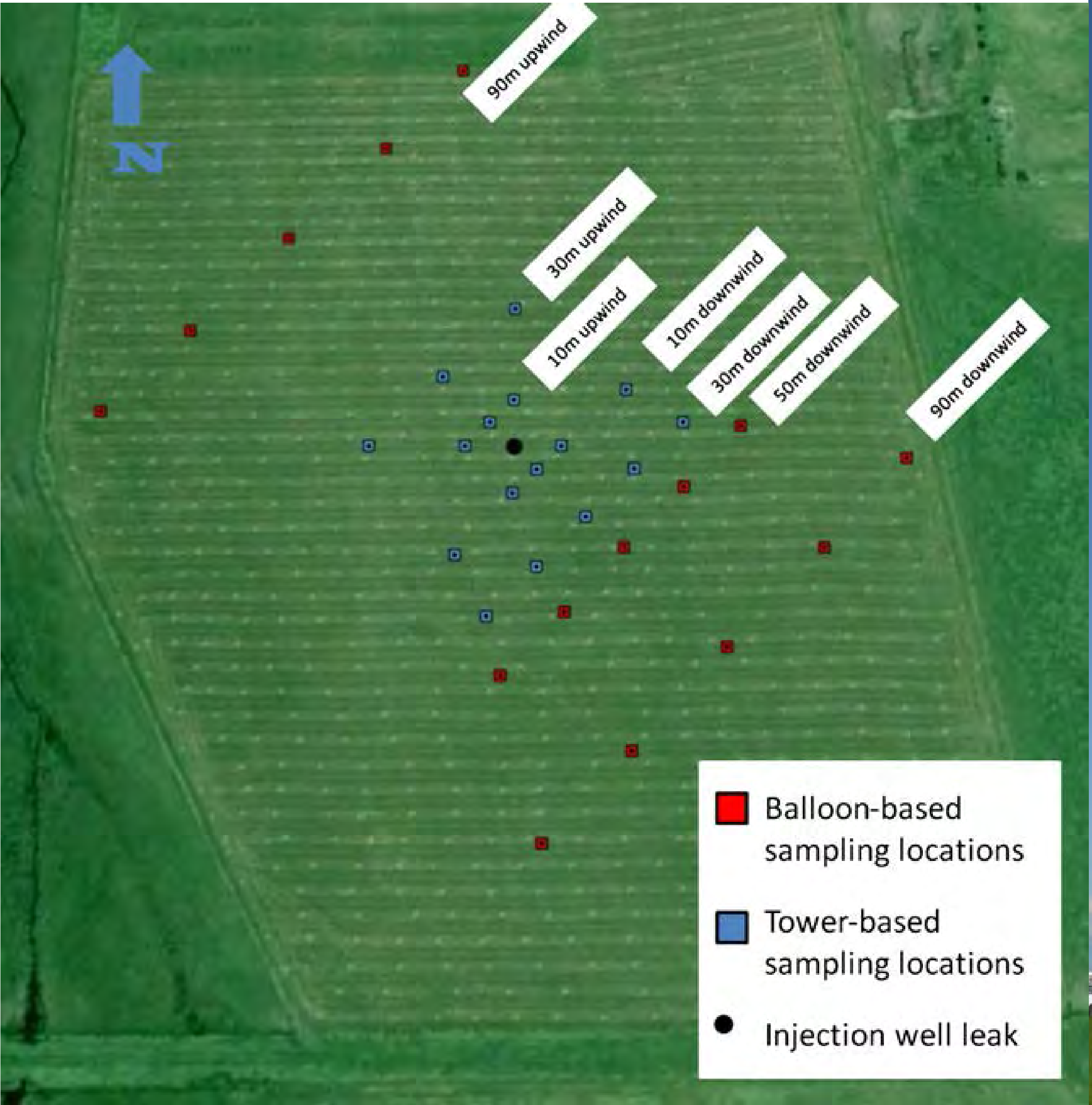
USGS, LBNL, EPRI, WVU, MSU
Liange Zheng, John A. Apps, Nicolas Spycher, Jens T. Birkholzer, Yousif K. Kharaka, James Thordsen, Sarah R. Beers, William N. Herkelrath, Evangelos Kakouros, Robert C. Trautz

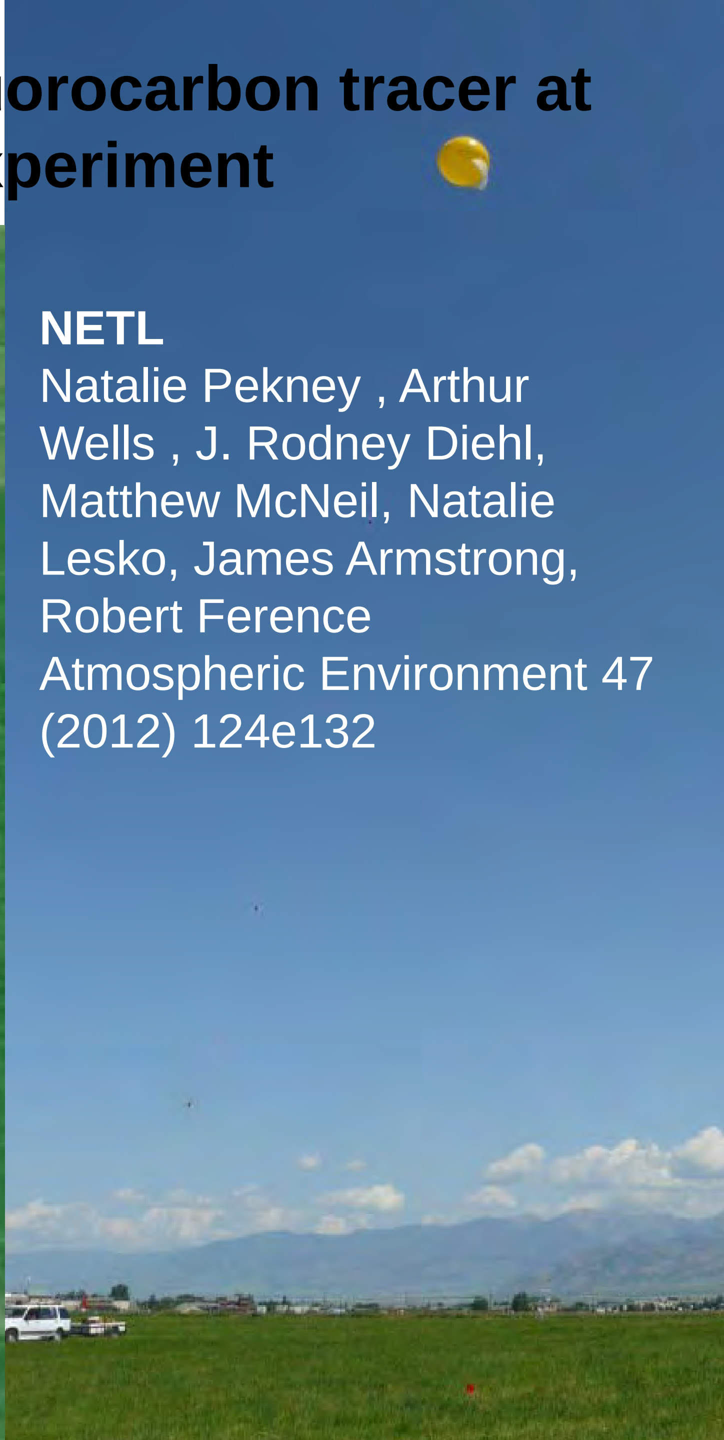
(1) calcite dissolution could be the primary process buffering pH and releasing Ca+2 in groundwater,
(2) the increase in the concentrations of major cations and trace metals except Fe could be explained by Ca+2-driven exchange reactions,
(3) the release of anions from adsorption sites due to competing 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.



ZERT Zero Emissions Research and Technology

Atmospheric monitoring of a perfluorocarbon tracer at the 2009 ZERT Center experiment



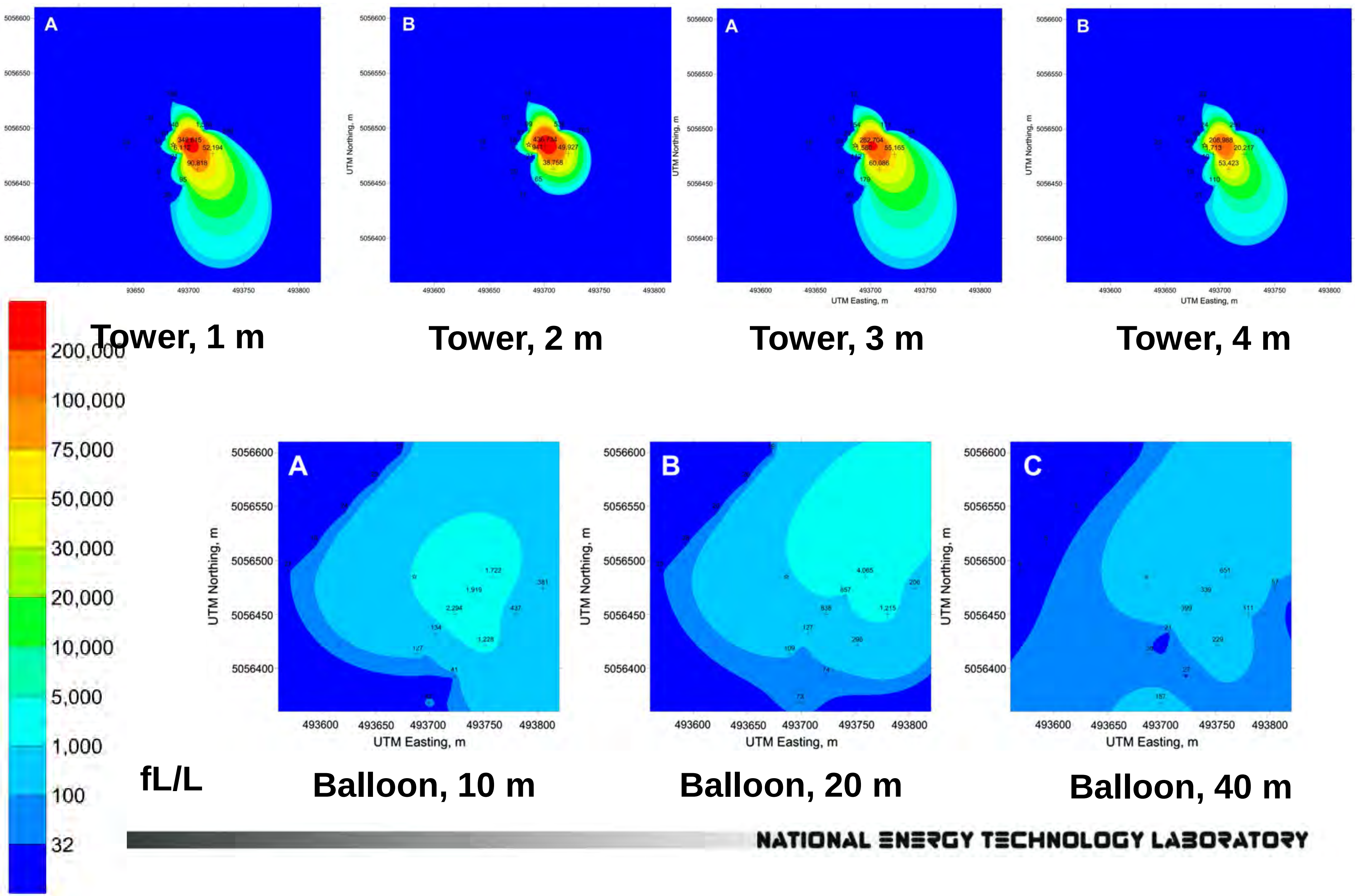


NETL

Natalie Pekney , Arthur Wells , J. Rodney Diehl, Matthew McNeil, Natalie Lesko, James Armstrong, Robert Ference

Atmospheric Environment 47 (2012) 124e132

Atmospheric monitoring of a perfluorocarbon tracer



Methods

- Soil Gas Monitoring
- In-situ soil gas probes
- Eddy Covarience
- Soil Flux chambers
- Differential Absorption LIDAR
- Cavity ring-down, other isotopic measurements
- Water chemistry
- Tracers
- Hyperspectral / mutispectral imaging
- Many more

What We Have Learned

- Many near surface methods are quantitative <u>but</u>
  - 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 site.
- Isotopes & tracers have lower detection limits than straight CO_2 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
- Will engineered systems that leak have similar properties?

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Acknowledgement

This work was carried out within the ZERT project, funded by the

Department of Energy -Fossil Energy

and the

National Energy Technology Laboratory under Award No. DE-FC26-04NT42262

Monitoring Zones

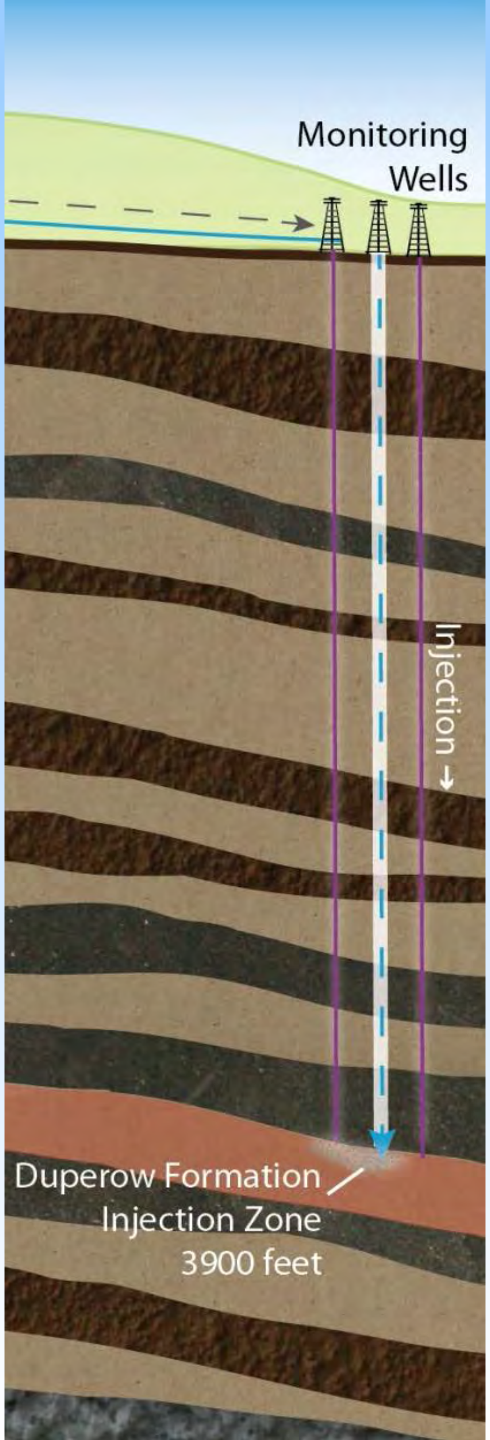
Atmosphere

Biosphere

Soil
(Vadose & Shallow
Saturated Zones

Caprock &
Deep Overburden

Injection Zone



- 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

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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%

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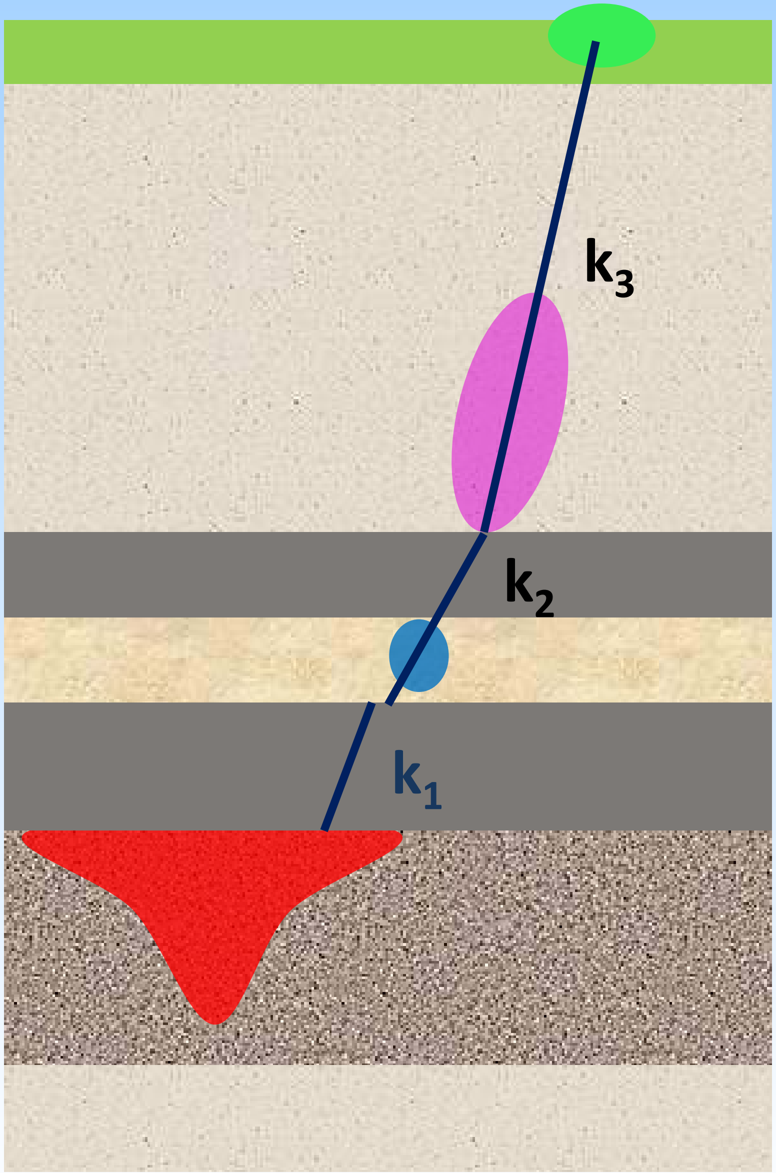
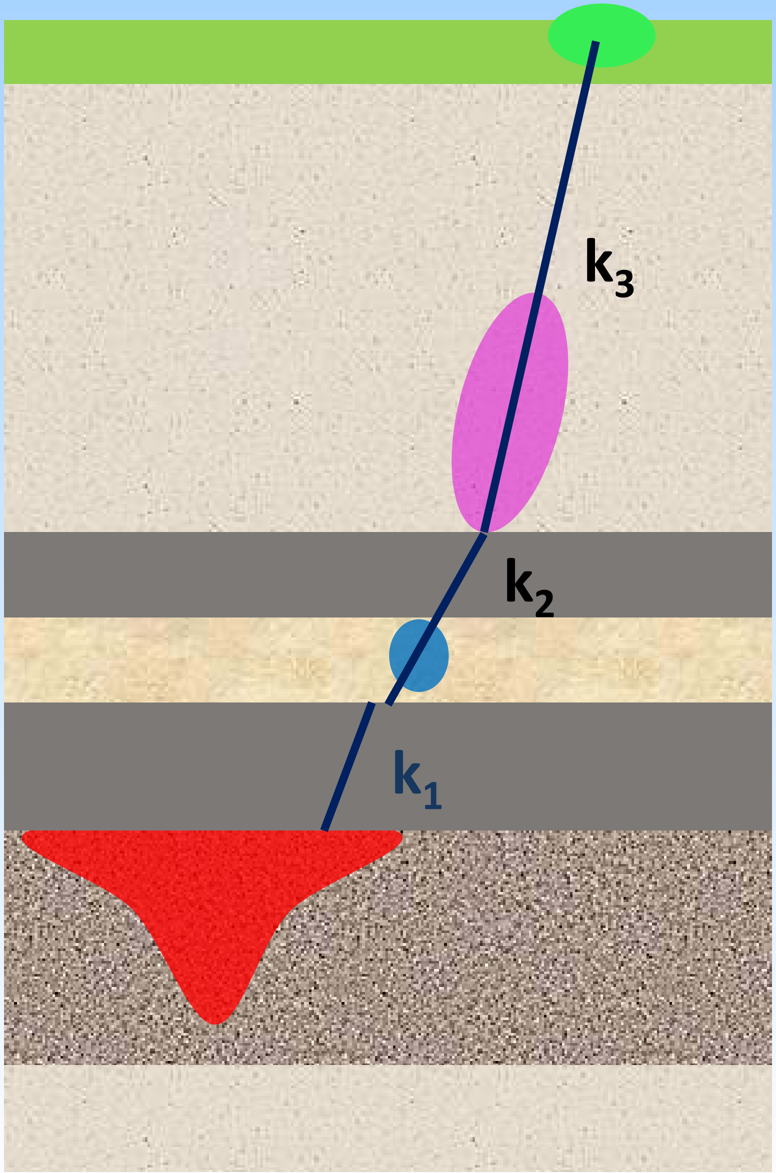
What Are Relevant Fluxes?



Mechanisms, their transport rates and relative rates will affect:

- Residence times and quantities
- Induction periods
- Flux (both area and rate)

What Are Relevant Fluxes?



- Simple model assumes 1st order rates (exp functional form) and solves three coupled differential equations.
- GHG mitigation relevant rates are used so effective time constant is very large (rates small)
- Under these conditions, most functional forms should be quasi-linear and qualitative results would be similar
- Allows support for “thought experiments” concerning induction periods, secondary accumulation, etc.

Test Case One Excellent Seal

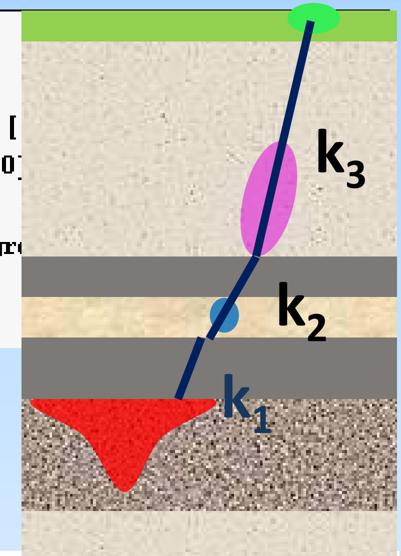
1% over 1000 yrs

Fast subsequent processes

200 Megatonnes in place

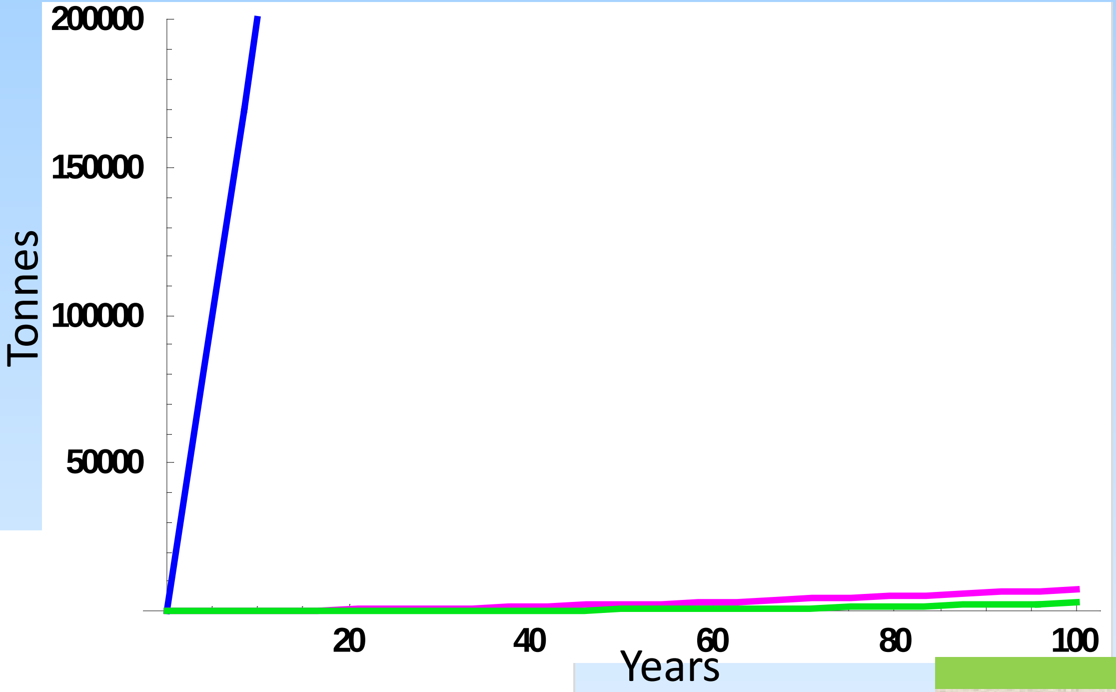
Mathematica "Intuitive Interface"

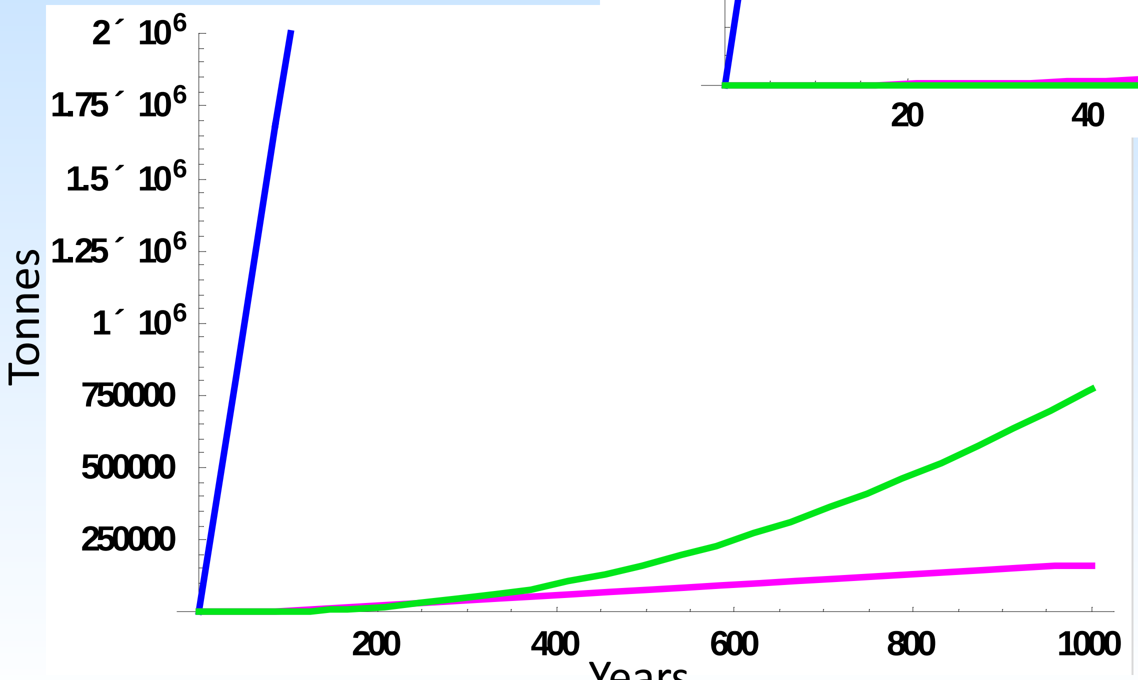
```
(* A → B → C → D *)
k1 = 0.00001; k2 = 1.0002; k3 = 1.01;
sol = NDSolve[{a'[t] == -(k1) a[t], b'[t] == (k1) a[t] - (k2) b[t], c'[t] == (k2) b[t] - (k3) c[t], d'[
   a[0] == 200000000, b[0] == 0, c[0] == 0, d[0] == 0}, {a[t], b[t], c[t], d[t]}, {t, 0.0, 10000]
$TextStyle = {FontFamily → "Ariel", FontWeight → "Bold", FontSize → 14};
Plot[Evaluate[{a[t], b[t], c[t], d[t]} /. sol], {t, 0.00, 1000}, PlotRange -> {0, 200000000}, Backgr
  PlotStyle -> {{RGBColor[1, 0, 0], AbsoluteThickness[3]}, {RGBColor[ 0, 0, 1], AbsoluteThickness[3]},
    {RGBColor[1, 0, 1], AbsoluteThickness[3]}, {RGBColor[0, .9, .1], AbsoluteThickness[3]}}];
```

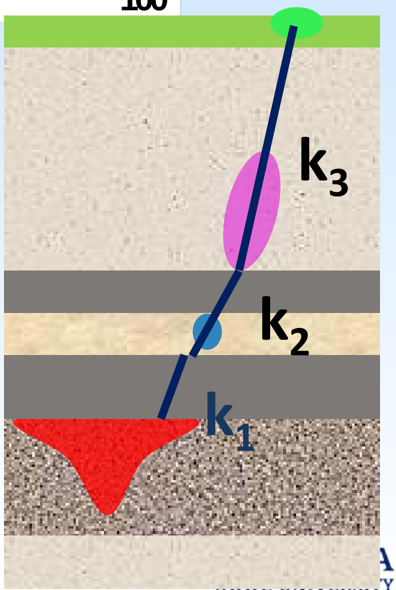


Two Good Seals

$k_1 = 0.0001$ (10 x faster than default of 1% per 1000 yrs)
$k_2 = 0.0001$ (10 x faster)
$k_3 = 0.01$

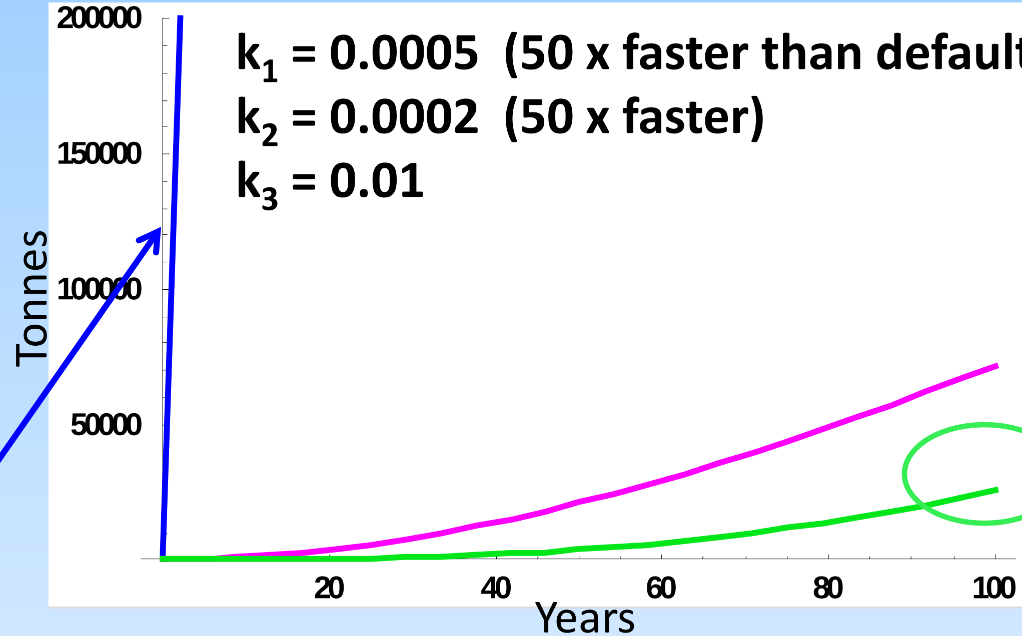






Induction Period

But there is a large and rapid accumulation under secondary seal that should be detectable



Near Surface Monitoring seems to Indicate Good Performance