Environmental Field Studies Topic 3: Real-world leakage assessment

Katherine Romanak







Funders and Collaborators

The authors wish to acknowledge financial assistance provided through Australian National Low Emissions Coal Research and Development (ANLEC R&D). ANLEC R&D is supported by COAL21 Ltd and the Australian Government through the Clean Energy Initiative.

Nick Hudson and Rob Heath- CTSCo Paul Jensen - ALS Geochemistry JP Nicot – Bureau of Economic Geology David Bomse - Mesa Photonics Gulf Coast Carbon Center



COAL21 Low Emissions Coal Australia

CTSCO Carbon Transport and Storage Company





Proposed CTSCo Surat CCS Demonstration Project

- Total of 180,000 tonnes CO₂ captured from the Millmerran Power Station in southeastern Queensland.
- Stored over 3 years in the low salinity groundwater of the Precipice Sandstone
- Storage site 21 km SW of Wandoan, Queensland at Glenhaven





Environmental Monitoring Infrastructure

- 5 monitoring stations
 - 1 weather station
 - 4 soil gas stations (1- & 5-m depths)
 - 4 groundwater stations (10- & 20-m depths)







Siller et al., 2018, Applied Geochemistry Volume 96, Pages 191-203

BEG's Process-Based Approach

- 4 simple coexisting soil gases: CO₂, O₂, CH₄, N₂
- Stoichiometry of reactions to identify key processes.
- No need for years of background CO₂ measurements and weather data
- Universal leakage threshold
- Stakeholder friendly, simple, immediate







Romanak et al., 2014, International Journal of Greenhouse Gas Control, 30, 42-57 Romanak et al., 2012, Geophysical Research Letters, 39 (15).

Two Related Field Studies for Advancing a Process-based Approach

- 1. Optimizing a process-based approach for near-surface leakage assessment
- 2. Isotopic characterization of source CO₂ and naturally occurring CO₂, Glenhaven







Two Parts to a Process Based Approach

- Most assessments will indicate no anomaly (on or left of the respiration trend)
- #2
 In the case where the respiration threshold is exceeded more assessment will be needed.





#1

Problem Statement and Objectives

Increase the ease and accuracy of environmental M&V to support the successful industrial deployment of CCS

- Avoid false positives for leakage
- Respond to stakeholders concerns (e.g. Kerr Claim)
- Easily comply with regulation (e.g. Low Carbon Fuel Standard)



*Second affiliation, Address, City and Postsode, Country



First Project- 3 Main Deliverables

Optimizing a process-based approach for near-surface leakage assessment

- **1.** Attribution:
 - Refine the process-based matrix for methane-rich sites. Current matrix fields are not rigorously tested in methane-rich soils.

2. Quantification:

- A methodology for separating background surface emissions from leakage emissions will be tested.
- 3. Sensing:
 - Techno-economic assessment of currently available sensors and recommendations for advancements in real-time sensing.

Updated Process-Based Matrix

- No methane in soil gas at Glenhaven site
- Mined data from literature + numerical modelling
- Anaerobic processes
- Acetoclastic methanogenesis : $CH_3COOH \rightarrow CH_4 + CO_2$

When significant methane is present or when anaerobic process is indicated





Process-Based Matrix Conclusions

- It is important to accurately measure CH₄
- Low O₂ environments signal natural processes of methanogenesis
- Including a second set of PB ratios with CO₂+CH₄ in the place of CO₂ will help distinguish and correctly attribute unexpected signals





Deliverable 2 : Integrating PB with Quantification -Theoretical approach



EPA Flux chamber method

 $EF_i = (C_i)(Q)$

EF_i = emission rate of species i in ug/m²min

C_i = measured concertation of species i in vol% converted to ug/m³

Q = sweep air flow rate in m³/min

A = exposed surface area in m²

Eklund, B. 1992. Practical Guidance for Flux Chamber Measurements of Fugitive Volatile Organic Emission Rates. *J. Air Waste Mange Assoc* 42:1583-1591.



Deliverable 2 : Integrating PB with Quantification - Theoretical approach

• Assuming 100% CO₂ is being approached

GEOLOGY

- Regressions of trends calculated from various data point configurations all give accurate results for real background CO₂ of 3.43%
- Suggests assumption is valid and leakage could be separated accurately from background with minimal information.



Quantification Conclusions

- Process-based methods shows promise for integration with flux
- Assumption that leakage trends towards 100% CO₂ appears valid
- At the ZERT site, one early or one late leakage data point combined with 100% leakage gave background $\rm CO_2$ concentration within 0.01% absolute error
- Analysis of field test results are ongoing





Sensor Testing

Sensor Type	Range	Accuracy	Respo Tim	nse Environmental e Limits	Technology	Manufacture	
CO2							
CMD 351	0.40 20%	+0.2.%	. 1	-40°C to +60°C	NDID	Vaisala	
GIVIP 251	0 to 20%	±0.2 %	< 1 m	0 to 100% RH	NDIK		
CMD 242	0 to 2%		40.00	-40°C to +60°C	NDID	Vaicala	
GIVIP 343	343 0 to 2% ± 3 ppm 40 secs		0 to 100% RH	NDIK	valsala		
O ₂							
SO 210	0% to	6 to		-40 to 60 C; 0 to 100%	Electro-	Ano	
	100%	±0.2%	secs	RH	chemical	Apogee	
CH₄							
MSH2-	0 to 100%	±10%	<10	-20 to 50°C	NDIR	Dunament	
LP/HC/NC	0 10 100%	absolute	secs	0 to 95% RH	NDIK	Dynament	





Romanak, Womack, Bomse,

- Sensors installed by CTSCo
- Maintained by ALS Geochemistry
- 3 years of process-based data collection
- Technical and economic assessment of sensing systems





Nick Hudson, Rob Heath, Paul Jensen,

Un-useable Data

Un-useable data defined as error.

0.7 % error is acceptable

site (hans	Total Entring	CO2#of		12.# of NANo		O2#of values	O2 % unuseable with NANs and out	propagated error CO2	
site / bore	Total Entries	NANS	COZ % NANS	Z # OF MAINS	UZ % INAINS	out of range	or range	+02	
2SV1	126,359	5,309	4.20	75	0.06	8	0.07	4.20	
2SV5	126,359	5,409	4.28	1664	1.32	3788	4.31	6.08	
3SV1	140,508	25,537	18.17	1814	1.29	9207	7.84	19.80	
3SV5	140,508	25,491	18.14	146	0.10	16807	12.07	21.79	
4SV1	153,484	14,575	9.50	557	0.36	9313	6.43	11.47	
4SV5	153,484	4,746	3.09	220	0.14	3357	2.33	3.87	
5SV1	122,346	7,702	6.30	204	0.17	16265	13.46	14.86	
5SV5	122,346	41,568	33.98	34881	28.51	4015	31.79	46.53	

- The percentage of data that are useable is variable between sensors and among locations
- Because both sensors are required to function at the same time for PB analysis, the propagated "error"
- increases the number of un-useable results

False positives

- The percentage of data that are useable (95 to 40%) is variable between sensors and among locations
- Because both sensors are required to function at the same time for PB analysis, the propagated "error" increases the number of unuseable results
- Much of the data represent false positives for leakage
- CO₂ sensor looses accuracy at high concentrations and O₂ at lower concentrations.





Paul Jensen maintains the sensors

Potential for Raman?

- Raman spectra show simultaneous detection of all four gases.
- Raman shows good linear response to changes in N₂ and O₂ at constant pressures





Figure 2 - HC-PCF Raman spectrum of a fourcomponent mixture demonstrating simultaneous detection of CO₂, O₂, N₃, and CH₄ using only 1 second of signal averaging.



David Bomse, Mesa Photonics



Figure 2 - ERGS linear response to changing proportions of N₂ and O₂ at constant head pressure.

Conclusions Sensor Data

- Much of the data are unusable with a loss of accuracy over certain ranges
- Artifacts result in data slopes that give the potential for false positives.
- Effort intensive- Need to calibrate multiple sensors often
- Cost of ownership low up front high on the back end.
 Sensor fits budget but then you have to maintain it.
- Recommendations for Raman development



Characterization Results

- Focus on ¹⁴C versus δ^{13} C of CO₂
- Which aquifers have enough gas to impact a signal?
- Assess the CO₂ formed by CH₄ oxidation
- Look for isotopic overlap

	$\delta^{13}CO_2$		δ ¹⁸ CO ₂		¹⁴ CO ₂		δ ¹³ C ₁		δDC1		¹⁴ C ₁	
	max	min	max	min	max	min	max	min	max	min	max	min
Site Soil gas	-10.9	-18.1	7.0	5.5	104.7	77.3	none	none	none	none	none	none
GW-10 (Alluvium)	-20.9	-23.4	6.2	5.4	108.3	101.7	-62.6	-77.9	-219.4	-347.1	23.0	13.8
GW-20 (Westbourne Formation)	-23.2	-29.4	6.4	5.8	23.1	13.8	-61.4	-75.3	-161.2	-223.3	13.6	2.6
Walloon Coal Measures (literature values)	res (literature values) 7.7 -2.5 no data no da		no data	near 0		-45.3	-58.0	-202.0	-238.0	near 0		
Pecos Bore (Hutton Formation)	-6.8	-8.5	no data	no data	too low	/ CO2 %	-51.1	-51.1	-211.2	-213.1	0.0	0.0
Town Bore (Precipice Sandstone)	-17.7	-17.8	4.3	4.2	too low	too low CO2 %		-47.8	-219.0	-219.0	10.4	1.3
Flue gas CO2	-23.8	-23.84	-6.90	-6.90	nea	ar O	none	none	none	none	none	none



Potential for ¹⁴C versus δ^{13} C of CO₂ to be useful at Glenhaven

- Gas from CSG will not be confused with CO₂ injectate.
- Influx from the Springbok
 Formation may be mistaken for a leakage signal
- Helium may be diagnostic





Conclusions Characterization

- A new data set represents the first full pre-project characterization for a process-based attribution method.
- It is important to have an attribution plan before a project starts to avoid stakeholder doubt (e.g. Kerr leakage claim at Weyburn).
- Assessing gas concentrations, aquifer permeability and interconnectivity can be used to simplify attribution by excluding certain aquifers as potential signals.
- Covariation of ¹⁴C versus δ¹³C of CO₂ shows promise for the second stage of process-based assessment.





Katherine Romanak Gulf Coast Carbon Center Bureau of Economic Geology The University of Texas at Austin

katherine.romanak@beg.utexas.edu

http://www.beg.utexas.edu/gccc/







CTSCO Carbon Transport and Storage Company

