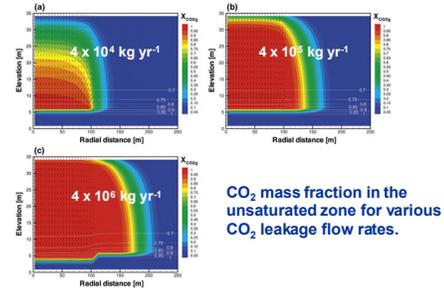


Expected Concentrations and Fluxes

- Case-studies of geologic CO₂ sequestration leakage are lacking.
- Therefore, we turn to modeling to predict expected behavior.
 - (1) CO₂ attenuation in the unsaturated (aka vadose) zone.
 - (2) Atmospheric dispersion of CO₂ in the surface layer.
- Leakage can lead to high CO₂ concentrations in the subsurface.
- Atmospheric dispersion is effective at dispersing seeping gases.
- However, CO₂ concentrations may be higher in stagnant (low-wind) areas.
- CO₂ concentrations can also be higher for higher fluxes.

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CO₂ Migration Through 30 m of Unsaturated Zone with Infiltration 10 cm yr⁻¹

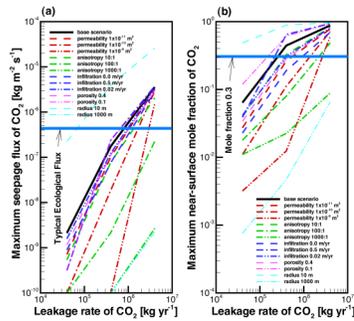


CO₂ mass fraction in the unsaturated zone for various CO₂ leakage flow rates.

(Oldenburg and Unger, *Vadose Zone Journal*, 2, 287–296, 2003)

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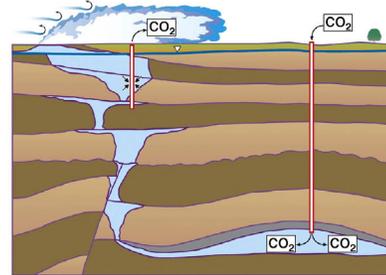
Sensitivity of CO₂ Seepage and Soil Gas Concentration to Various UZ Properties



(Oldenburg and Unger, *Vadose Zone Journal*, 2, 287–296, 2003)

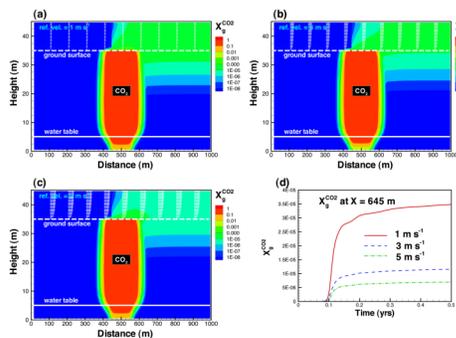
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CO₂ Leakage, Seepage, and Dispersion



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X_g^{CO2} in Subsurface and Surface Layer

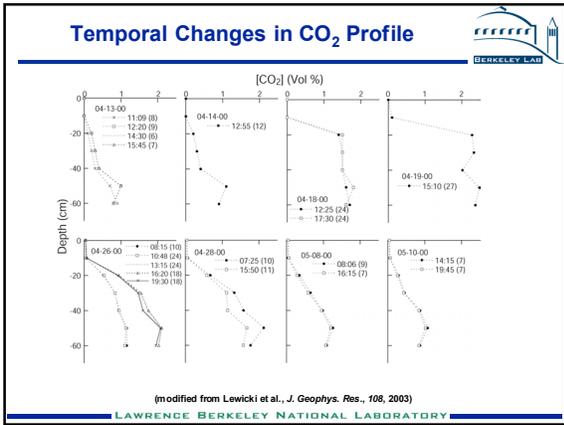
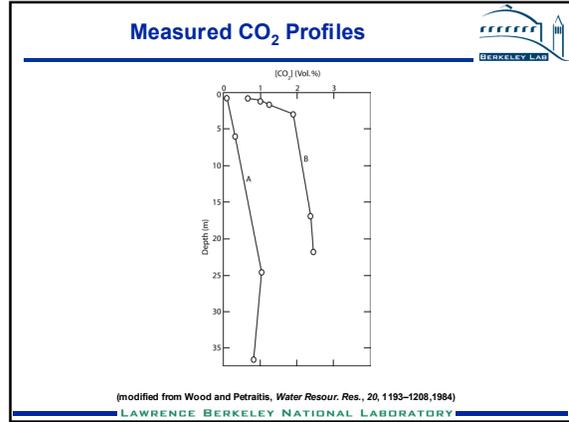
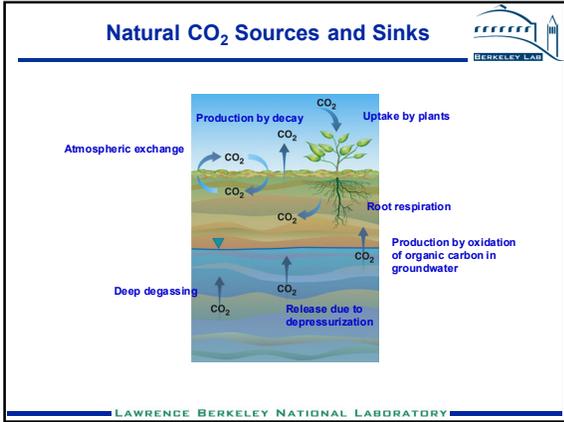


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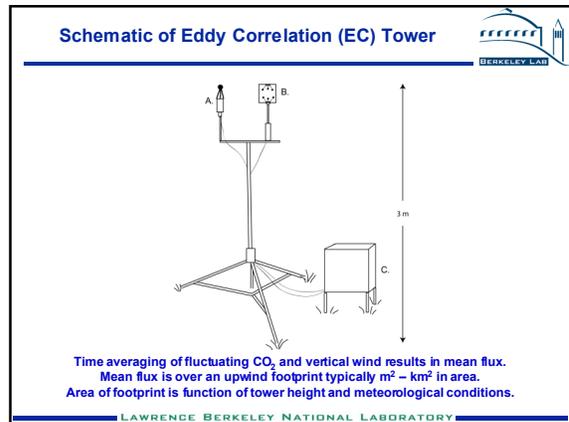
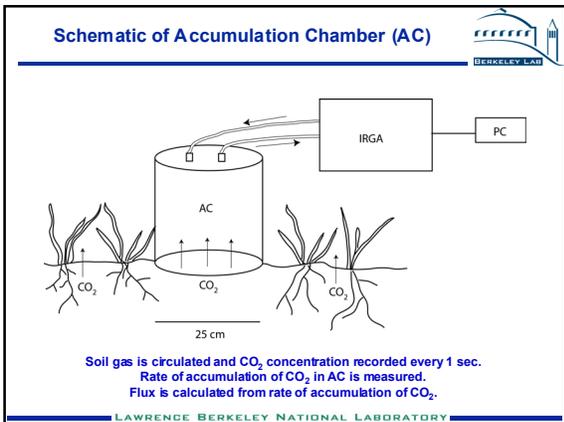
Modeling Summary

- Even for small leakage fluxes, subsurface CO₂ concentrations can be high.
- Diffuse seepage leads to passive dispersion in the surface layer.
- Atmospheric dispersion is effective at dispersing seeping gases, subject to caveats, among which are:
 - CO₂ concentrations will be higher in stagnant (low-wind) areas.
 - CO₂ concentrations will be larger for higher fluxes.
 - CO₂ concentrations may be higher periodically.
- Result is small LOSS in surface layer.
- Larger LOSS in the subsurface.

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- ### Overview of Approaches for Monitoring
- Conventional CO₂ Monitoring Technologies:
 - IRGA (infrared gas analyzer) for point measurements of CO₂ in gas.
 - Absorption at 4.26 μm .
 - Frequency 1-10 Hz.
 - Typically 0-3000 ppmv detection range, also up to 100% CO₂.
 - Precision +/- 0.2 ppmv at 350 ppmv.
 - \$5-30k.
 - Transportable.
 - Although point measurement, can be combined with other instrumentation to measure fluxes over small (accumulation chamber) and large (eddy correlation) areas.
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Schematic of Truck-Mounted LIDAR

LIDAR = Light Detection And Ranging.
Raman LIDAR = detecting wavelength shifts due to Raman scattering.
DIAL = Differential Absorption LIDAR = tunable laser to create backscatter ratios.
 Rapidly developing, good areal coverage.
 Concentration integrated over path length.

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Strategies for Storage Verification

- Subsurface gas geochemistry.
 - Carbon isotopes.
 - Bulk soil gas composition.
 - Trends with depth. Spatial trends.
- Surface CO₂ concentration and flux monitoring.
 - EC good for large areas and average flux measurements.
 - AC good for small features and delineating spatial trends.
- Water chemistry.
 - pH. Gas bubbles. Dissolved Inorganic Carbon.
- Integrated sampling strategy
 - Baseline monitoring and modeling.
 - Long-term monitoring.

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Chemical and Isotopic Signatures

CO ₂ source	$\delta^{13}C_{CO_2}$ ‰	$\Delta^{14}C_{CO_2}$ ‰	Near-surface CO ₂ conc.	CO ₂ conc. profile with depth	O ₂ conc. profile with depth
Atmosphere	-7	-70	Low	-	-
Plant root respiration and oxidative decay of young soil organic matter	C ₃ : -24 to -38 C ₄ : -6 to -19	≥ -70	Low to moderate	Increasing through soil zone	Decreasing through soil zone
Oxidative decay of ancient organic matter	C ₃ : -24 to -38 Aquatic C ₃ : -6 to -19 Also age dependent	Highly depleted to absent, depending on age	Low	Increasing potentially through vadose zone	Decreasing potentially through vadose zone
Marine carbonate rocks	0 ± 4	absent	Low	Increasing through vadose zone	No effect
Fossil fuel	Average: -27	absent	Moderate to high	Increasing through vadose zone	No effect

Conc., C₃ and C₄ refer to concentration, C₃ plants, and C₄ plants. All near-surface concentrations given are general estimates; these concentrations will be strongly dependent on the magnitude of the CO₂ flux.

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Integrated Sampling Strategy

- Baseline monitoring and modeling.
 - Characterize spatial and temporal variability
 - Soil, parent material, vegetation, hydrology, topography, surface water, ...
 - Flow modeling (TOUGH2) and ecological modeling (LSM).
- Surface CO₂ concentration and flux monitoring (AC and EC).
- Soil gas sampling and analysis. Fixed sites over time.
- Soil moisture and temperature.
- Goal is to understand the natural ecological system prior to injection.

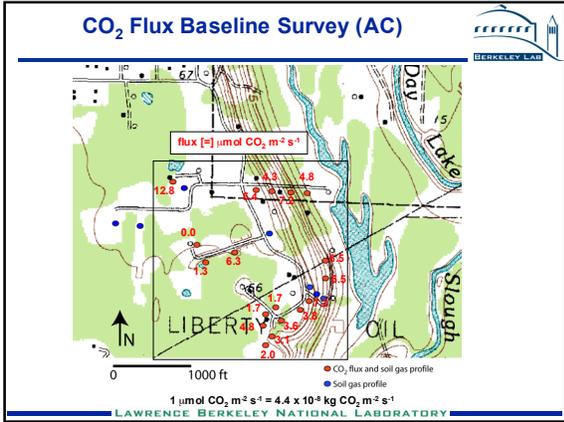
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Potential Activities and Schedule

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South Liberty Site (Frio Pilot Study)

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- ### Summary
- Extensive knowledge exists about behavior, properties, detection, and monitoring of CO₂.
 - Modeling provides plausible expectations of CO₂ seepage flux and concentration.
 - Nevertheless, discerning small CO₂ LOSS from natural background variation will be challenging.
 - Strategy we propose involves comprehensive baseline monitoring and modeling to develop understanding of natural system.
 - Program of multiple and integrated measurement and monitoring can be applied during and after injection.
 - Measurements in conflict with expectations of the natural system would be investigated thoroughly by more detailed studies.
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