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**Geochemical Detection of Gas Microseepage from CO<sub>2</sub> Sequestration**

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A wide variety of techniques have been proposed for the detection of the emplaced CO<sub>2</sub> and the monitoring of lateral or vertical migration. Of particular interest is the small scale leakage or microseepage to the surface or near-surface. In this situation there could be contamination of shallow groundwater or leakage into the atmosphere. In the case of leakage to the atmosphere, the benefits of sequestration could be largely or completely negated.

An evaluation of a variety of geochemical techniques will be presented, along with published and unpublished data from research by the author and others. Although there is not a substantial amount of data from actual geologic sequestration of CO<sub>2</sub>, there is data from the migration of volatiles from oil/gas fields, and from CO<sub>2</sub>-EOR (enhanced oil recovery). These data can provide guidance about the practicality or impracticality of various proposed techniques of surface and near-surface geochemical monitoring.

Some working definitions include:

- Macroseepage (leakage) – strong odors, wet bubbly ground, abnormal snow-melt patterns, temperature anomalies at 1 meter depth.
- Miniseepage – patches of stressed or dying vegetation without evidence of disease because of flooding of soil with gas, temperature anomalies at 10 meters depth, blue-gray haze during winter inversions, saline water seepage,
- Microseepage – detection of gases at surface requires sampling and laboratory analysis or sensitive optical (IR) measurements in long open path; may be common over large areas in sedimentary basins and oil/gas fields,

Secondary effects may be present in many cases at all three levels of seepage intensity, including secondary carbonate from oxidizing carbon gases, horizontal gradient magnetic effects, abnormal bacterial consortia present, sulfate-depleted and/or bicarbonate enriched shallow ground water, radiometric anomalies, vegetation restricted to shallow-rooted grasses. Figure 1 shows a schematic that provides a visualization of the seepage process.

**Working Assumptions:**

- 1) Presume that all available techniques for locating faults/fractures have been used; remote sensing, surface geologic mapping, well logs, and 3-D seismic have been employed in the initial evaluation of an area of interest prior to any injection program.
- 2) A non-uniform seepage pattern is almost certain due to channeling of gas through faults and fractures.
- 3) A thorough understanding of the natural processes involved in production and/or consumption of an indicator gas species is necessary.
- 4) Formation overpressure will develop at acceptable injection rates unless permeability is unusually high. An overpressured, buoyant fluid at the top of the formation will tend to penetrate vertical fractures in a caprock, inducing vertical migration, which will accelerate in overlying formations of higher permeability.

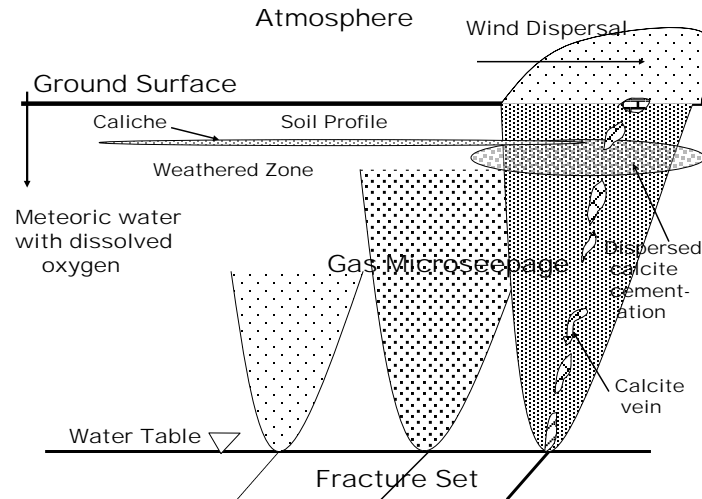


Figure 1. Schematic of gas microseepage from faults/fractures to the surface.

Parameter to Measure: Logical choice is to monitor  $\text{CO}_2$  in the atmosphere since  $\text{CO}_2$  is the gas being injected?

**Pros**

- 1) Easy to accurately measure in the atmosphere with IR spectroscopic techniques,
- 2) Continuous measurement (“monitoring”) is possible,
- 3) Large footprint (3 ha for 10-m tower); some vectoring to point source possible.

**Cons**

- 1) Atmospheric concentration is high relative of other possible tracers,
- 2) Biological consumption/production overwhelms a weak, deep, subsurface source,
- 3) Highly variable atmospheric concentration on at least two time scales (seasonal and diurnal) is partially predictable using a semi-quantitative model,
- 4) Other variables influence  $\text{CO}_2$  atmospheric concentrations in less predictable ways; ie. soil moisture and soil temperature, short-term atmospheric temperature variation, agricultural practices and fertilization,
- 5) Soluble in, and reactive with water which will substantially attenuate flows in lateral and vertical directions during migration from the injection formation,
- 6) Barometric pressure gradients influencing soil/atmosphere exchange for all gases,
- 7) Multiple sources of  $\text{CO}_2$  are present in each sample in varying proportions,
- 8) Volcanic vent/fracture flows are far too high to serve as an analog, or for purposes of development of methods.

Position (Elevation) of Measurement:

Measurement above the land surface at some convenient elevation (10 m or 1 m)

**Pros**

- 1) Mixing with the atmosphere allows potential detection of a point or linear source whose location is not precisely known initially,
- 2) Coverage of an area approximately 10+ times the elevation of measurement in an upwind direction for a tower method,
- 3) Open-path horizontal measurements change the measurement from a tower to a one-dimensional line measurement.

**Cons**

- 1) Considerable dilution of a deep source with background atmosphere makes detection of small subsurface flows difficult, particularly when superimposed on the natural variability due to biological and microbiological processes,

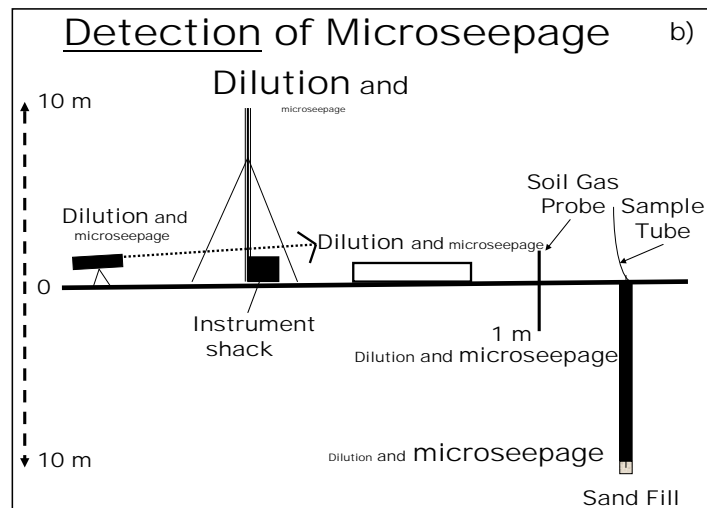
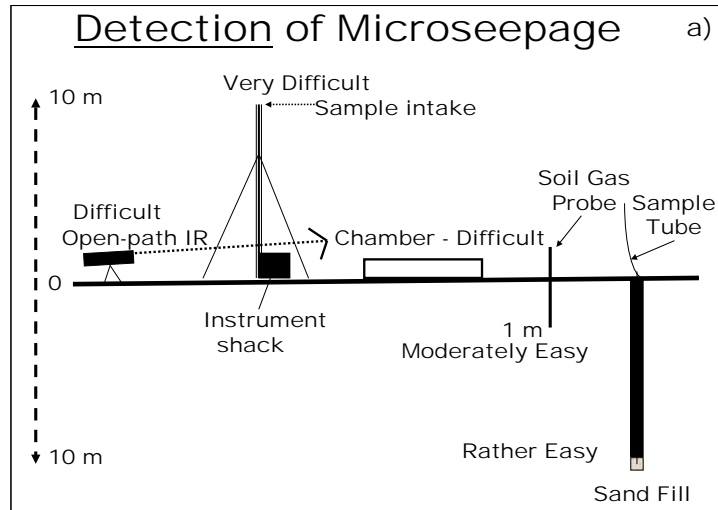


Figure 2. Detection of microseepage shown as, a) relative degree of difficulty, b) as relative strengths of "dilution" and "gas microseepage."

**Measurement below the land surface (1 m or 10 m)**

**Pros**

- 1) Diurnal and seasonal variability much less than in the atmosphere, particularly at 10 m, making a possible weak, deep source more readily detectable,
- 2) Sampling at 1 m is fast, portable, and very low cost,
- 3) Appropriate measurements of flux and 1 m soil gas allow selection of locations for 10-m holes reliable.

- 4) Anomalous soil gas perfuses through a substantial volume surrounding a fault/fracture.

**Cons**

- 1) Limited sample volume withdrawal rate may prevent continuous measurement or “monitoring,”
- 2) Discrete sampling and laboratory analysis may be required,
- 3) Subsurface volume represented by a discrete sample is quite small.

**Conclusions about Elevation of Sampling and Measurement**

- 1) Shallow soil gas (1 m) is rapid, low cost, and can establish whether the area of interest has a propensity for microseepage, even if sample(s) is/are not directly on gassy fracture,
- 2) Pre-development baseline concentrations can be established in two seasons,
- 3) Soil gas is quick and low cost for an initial characterization of sequestration site,
- 4) A single pass in the right season can allow selection of locations for 10-m holes,
- 5) Not all potential leakage locations will be found, but sampling is guided by data previously collected on faulting and fracturing,
- 6) Only large-scale seepages will be found by atmospheric measurements,
- 7) Horizontal spectroscopic measurements between a source and reflector have promise for detection and measurement of moderate-scale seepages along the path of the beam or a short distance upwind.

A review of other gaseous species or products of reactions involving gases that might be measured and potentially useful in the detection of microseepage will be presented along with illustrative data. These include methane, light alkanes (paraffins) and alkenes (olefins), stable isotopic composition of carbon dioxide and methane, carbon-14 content of carbon-containing gases, helium, neon, argon (inert indigenous tracers), injected tracers, stable carbon and oxygen isotopes in secondary carbonates, dissolved bicarbonate content of shallow ground water.

Finally, some non-geochemical detection methods, including 3-D seismic surveys, land uplift will be summarized along with a summary of how microseepage can be detected and confirmed, and how it can be missed.