Role of Geochemical Monitoring in Geologic Sequestration

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Conclusions

- Monitoring approach depends on phase of deployment
  - Dense monitoring in research phase to increase confidence
  - Parsimonious monitoring in commercial phase
- Parsimonious (but effective) monitoring will work well only with upfront thorough site characterization and process understanding
- Geochemical monitoring plays a major role in providing that understanding

Purposes of Monitoring

- Ensure HSE of public and workers
  - injection wells, pipeline – operational phase
  - seismicity, environment, ground water quality
- Verify CO_2 storage (mass balance)
- Confirm predictions of CO_2 migration (plume movement, migration rates, but also pressure distribution)
- Early warnings of storage failure

From IPCC, 2005

Other Purposes of Monitoring

- Establish **baseline** (reservoir and injection fluids, aquifer composition, soil gas composition, rock mineralogy, etc.) – characterization vs. monitoring
- Learn about subsurface processes
- Evaluate and quantify subsurface trapping mechanisms (capillary and solution trapping)
- Provide data for numerical model calibration (history matching) and subsequent updates
- Compare different monitoring methods and approaches

Types of Monitoring

- Indirect / non-intrusive or direct / intrusive
- Hydrological / Engineering (P&T, flow rate)
- Geochemical (composition of fluids)
- Geomechanical (deformation)
- Geophysical (seismic, electric, EM)
- CO_2-rich phase saturation / CO_2 concentrations in other phases

Reasons for Undertaking Geochemical Sampling

- **Direct detection of CO_2**
  - Validation of geophysical techniques
  - Higher sensitivity than most (all?) other techniques
  - Unique identification of injected CO_2
- **Assess distribution and migration of CO_2**
  - Gas or dense phase vs. dissolved
  - Hydrologic use of tracers
- **Develop and validate modeling or prediction**
  - Rock/brine/gas interaction, mineralization, etc.
  - Detect leak paths CO_2 and/or associated gasses
- **Detect corrosion of natural and engineered systems**

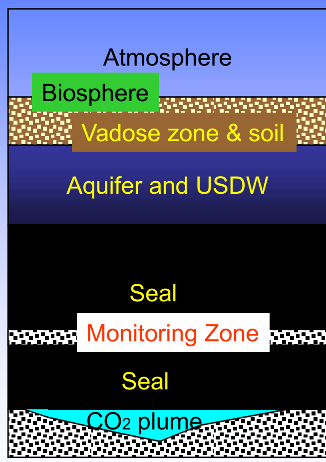
Types of Geochemical Measurements 1/2

- **Direct measurement of immiscible CO_2**
  - gas or dense phases
- **Measurement of dissolved CO_2**
  - Total inorganic carbon, bicarbonate
- **Indirect measurement of dissolved CO_2**
  - pH, alkalinity
- **Major and minor element composition**
  - Rock - mineralogy, organics
  - Water & oil
  - Gases – O_2, N_2, CO_2, H_2S, CH_4 or other hydrocarbons, noble gases;

Types of Geochemical Measurements 2/2

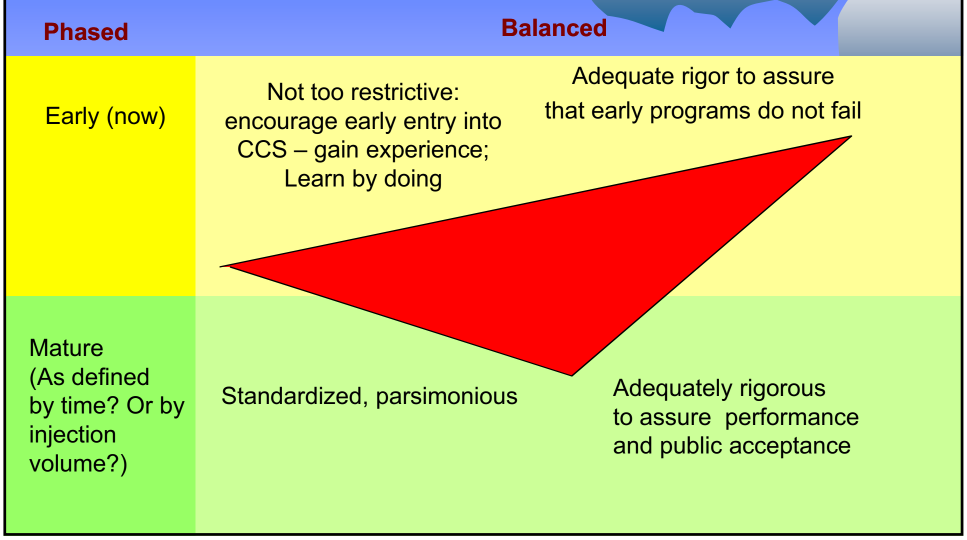
- **Isotopic compositions of any of above**
  - e.g., $^{12/13}C$; ^{14}C; ^{18}O, $^{3/4}He$, ^{2}H (natural tracers)
- **Introduced tracers**
  - SF_6, perfluorocarbons*
  - Gas soluble, water soluble
  - Conservative or interactive with various phases
- Integrator / cumulative

Location of Geochemical Sampling



- **Low pressure, lower cost**
  - Atmosphere (dynamic)
  - Soil gas (dynamic – cumul.)
  - Aquifer (cumul.)
- **Downhole / wellhead – high pressure, higher cost**
  - Above zone (first indicator)
  - Seal
  - In plume
  - Outside plume

A Balanced and Phased Approach to Permitting and Monitoring



Need for Parsimonious Monitoring Program in a Mature Industry

- Standardized, dependable, durable instrumentation, reportable measurements
- Possibility of above-background detection:
  - Need for a follow-up testing program to assure both public acceptance and safe operation
- Hierarchical approach:

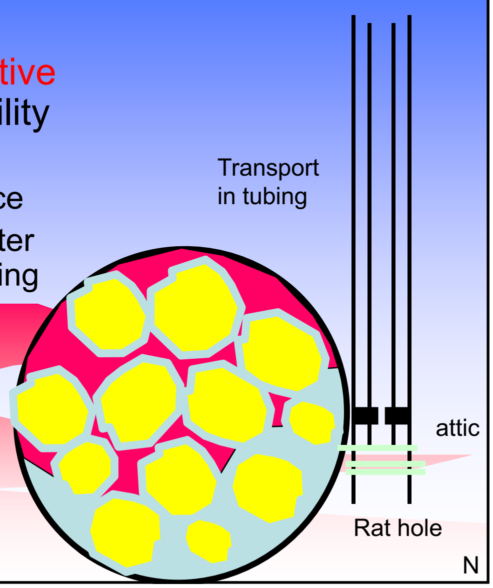
Parameter A → Not within acceptable limits: test → Parameter B → Not within acceptable limits: → Stop & mitigate

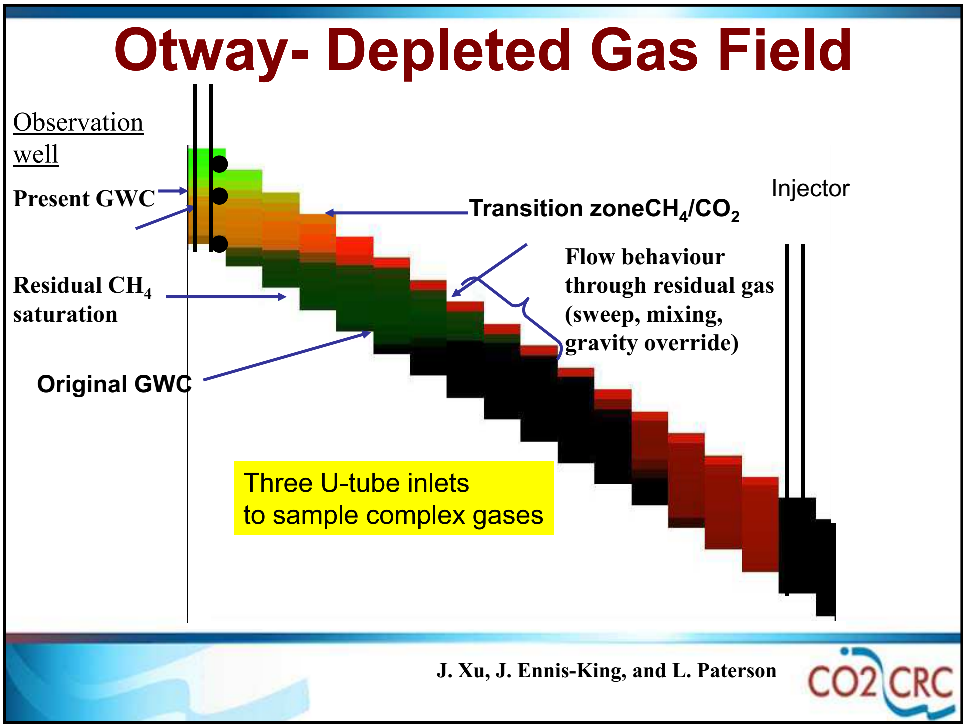
Parameter A ↓ Within acceptable limits: continue

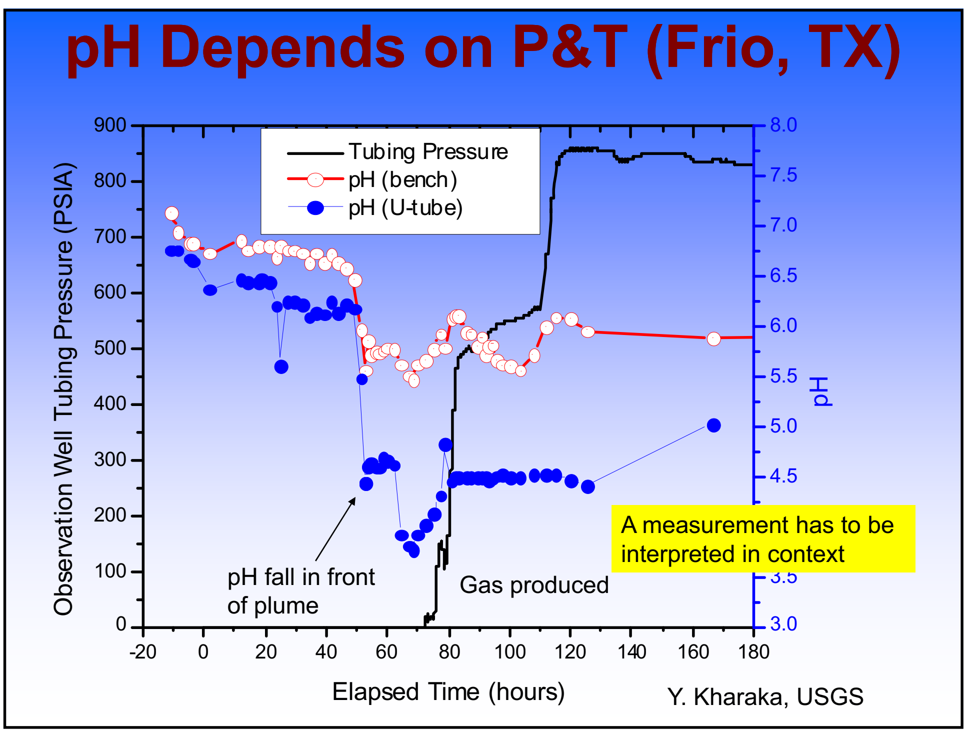
Parameter B ↓ Within acceptable limits: continue

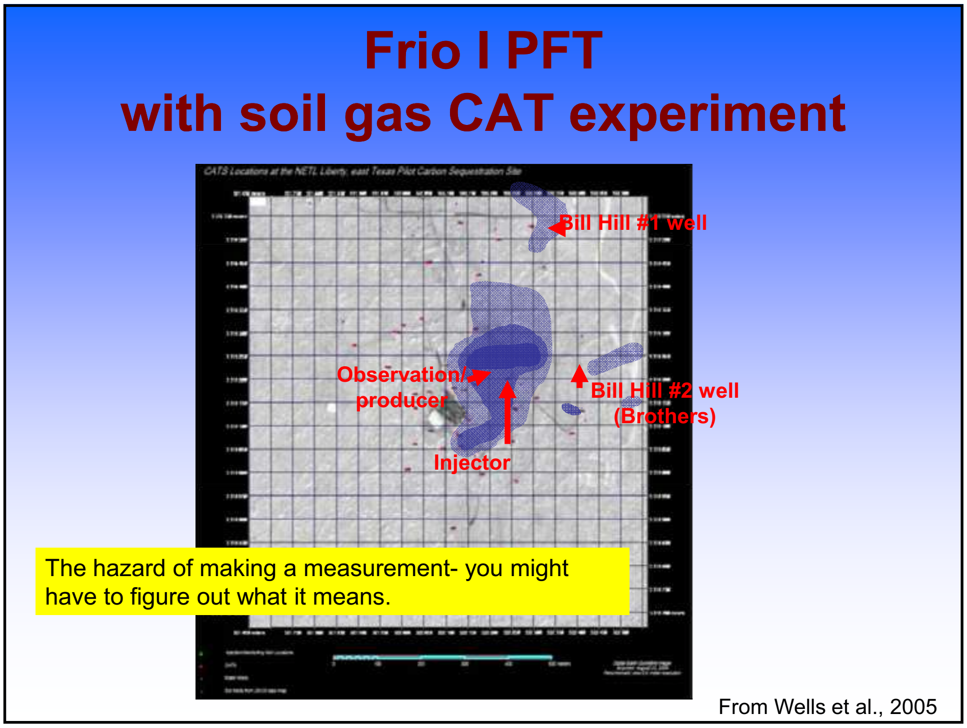
Issues and Limits of Geochemical Techniques

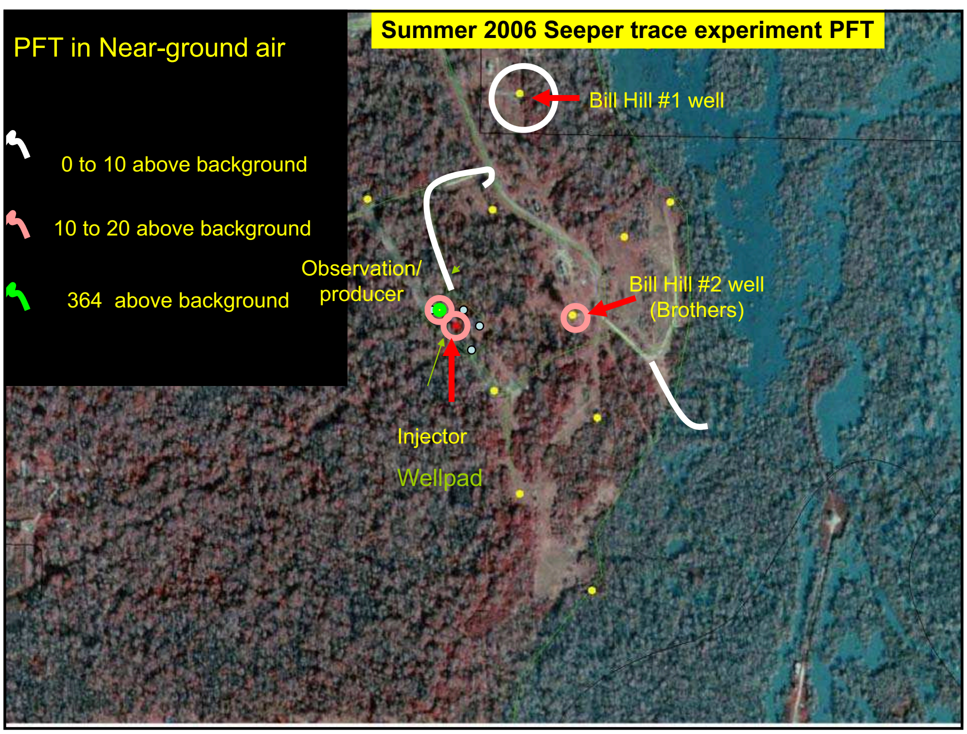
- Downhole samples are possibly non-representative because of relative mobility +buoyancy +mixing
  - Complexities in subsurface
  - Fractionation as fluids enter the well, move up the tubing
  - Pressure change=
    - Change solubility of CO_2
    - temperature change as CO_2 changes to gas




Otway- Depleted Gas Field
Observation well
Present GWC
Residual CH_4 saturation
Original GWC
Transition zoneCH_4/CO_2
Injector
Flow behaviour through residual gas (sweep, mixing, gravity override)
Three U-tube inlets to sample complex gases
J. Xu, J. Ennis-King, and L. Paterson
CO2CRC


pH Depends on P&T (Frio, TX)
Tubing Pressure
pH (bench)
pH (U-tube)
Observation Well Tubing Pressure (PSIA)
pH
Elapsed Time (hours)
pH fall in front of plume
Gas produced
A measurement has to be interpreted in context
Y. Kharaka, USGS


Frio I PFT
with soil gas CAT experiment
Bill Hill #1 well
Observation/
producer
Bill Hill #2 well
(Brothers)
Injector
The hazard of making a measurement- you might have to figure out what it means.
From Wells et al., 2005


PFT in Near-ground air
0 to 10 above background
10 to 20 above background
364 above background
Summer 2006 Seeper trace experiment PFT
Bill Hill #1 well
Observation/
producer
Bill Hill #2 well
(Brothers)
Injector
Wellpad

Return 2007 Seeper Trace PFT

- No detect except at wellhead plumbing – sorbed on grease pack in well head
- Need for experiments on performance of tracers in complex – rock fluid systems

Separation Rock-CO_2 - Water Reaction from Pipe-CO_2 - Water Reaction

$CO_{2\,(gas)} + H_2O \Leftrightarrow H_2CO_3^o$ — CO_2 dissolves into brine

$H_2CO_3^o \Leftrightarrow HCO_3^- + H^+$

$CO_{2\,(gas)} + H_2O + CaCO_3 \Leftrightarrow Ca^{++} + 2HCO_3^-$

$H^+ + CaCO_3 \Leftrightarrow Ca^{++} + HCO_3^-$

Samples are always contaminated with something – Drilling or workover fluids, cement, sampling device. How can you use them anyway?

$H^+ + FeCO_3 \Leftrightarrow Fe^{++} + HCO_3$ — CO_2 dissolves siderite

$4Fe(OH)_3 + 8H_2CO_3 \Leftrightarrow 4Fe^{++} + 8HCO_3^- + 10H_2O + O_2$ — CO2 dissolves

$2Fe(OH)_3 + 4H_2CO_3 + H_2 \Leftrightarrow 2Fe^{++} + 4HCO_3^- + 6H_2O$ — limonite

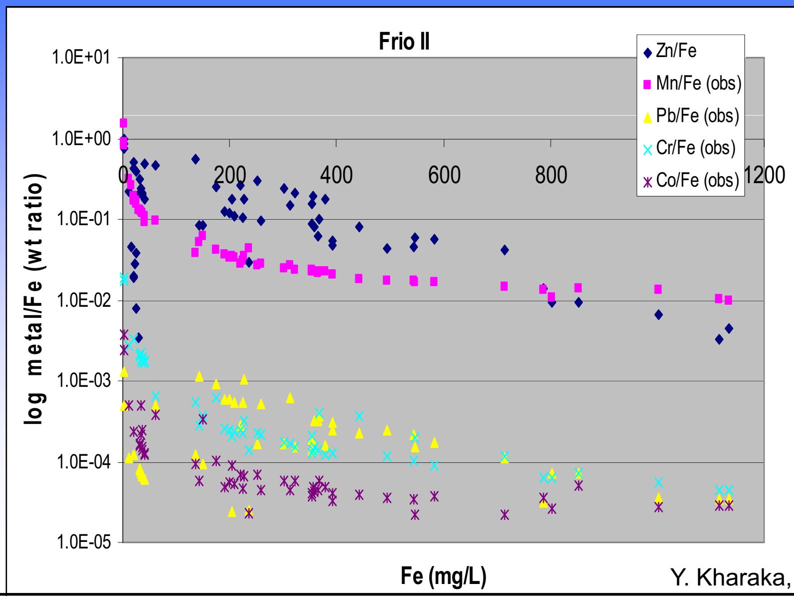
$Fe^o + 2H_2CO_3 \Leftrightarrow Fe^{++} + 2HCO_3^- + H_2$ — CO_2 dissolves steel

$2H^+ + CaMg(CO_3)_2 \Leftrightarrow Ca^{++} + Mg^{++} + 2HCO_3^-$ — CO_2 dissolves dolomite

$0.4H^+ + Ca_{.2}Na_{.8}Al_{1.2}Si_{2.8}O_8 + 0.8CO_2 + 1.2H_2O \Leftrightarrow$ — CO_2 dissolves feldspar

$.2Ca{+}{+} + .8NaAlCO_3(OH)_2 + 0.4Al(OH)_3 + 2.8SiO_2$

Other Trace Metals - Contamination from Casing and Tubing?

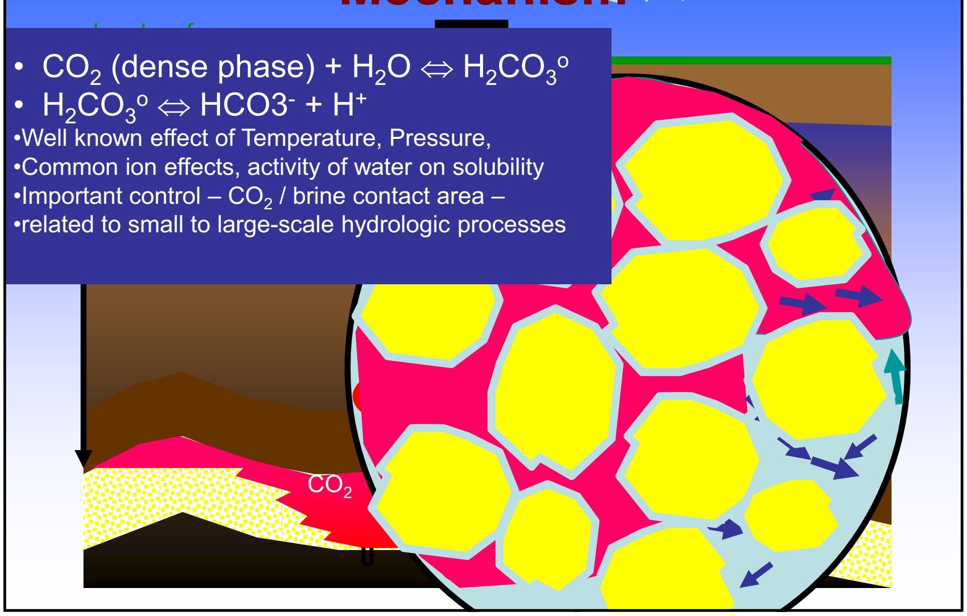


Y. Kharaka, USGS

Dissolution into Brine Trapping Mechanism

- CO_2 (dense phase) + $H_2O \Leftrightarrow H_2CO_3^o$
- $H_2CO_3^o \Leftrightarrow HCO3^- + H^+$

•Well known effect of Temperature, Pressure,
•Common ion effects, activity of water on solubility
•Important control – CO_2 / brine contact area –
•related to small to large-scale hydrologic processes



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