# VI Issues: Lessons Learned- Including Methane

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# VI Issues Encountered, con't.

- **Consultant Issues**:

- Using RBSLs for soil gas for sub-slab or vice-versa.
- Using screening levels as clean-up criteria
- Calculating wrong screening levels (wrong alpha or model values)
- Using non-cancer screening levels for carcinogens
- Using wrong exposure times
- Proposing indoor air sampling before evaluating if the VI pathway is complete
- Incorrect construction of soil gas sampling points

- **Unit Confusion**:

- Assuming ug/L equivalent to ppbv
- Assuming ug/m3 equivalent to ppbv
- Not knowing how to go from ug/m3 to ug/L

# "Top Ten" List of VI Issues Encountered

- **Reviewer/Agency Issues**:

- Requiring soil gas data be acquired even though soil and groundwater is clean enough to screen out site
- Requiring all soil gas samples to be collected in Summa canisters and analyzed by TO-15 when TO-14, 8260 or 8021 ok.
- Using guidance for petroleum hydrocarbon issue that was written for chlorinated hydrocarbons.
- Setting inconsistent clean up levels
- Not permitting SVE systems to be shut off prior to collecting soil gas samples
- Unfamiliar with science/reason for setting reasonable screening out criteria
- Requiring deep soil gas samples

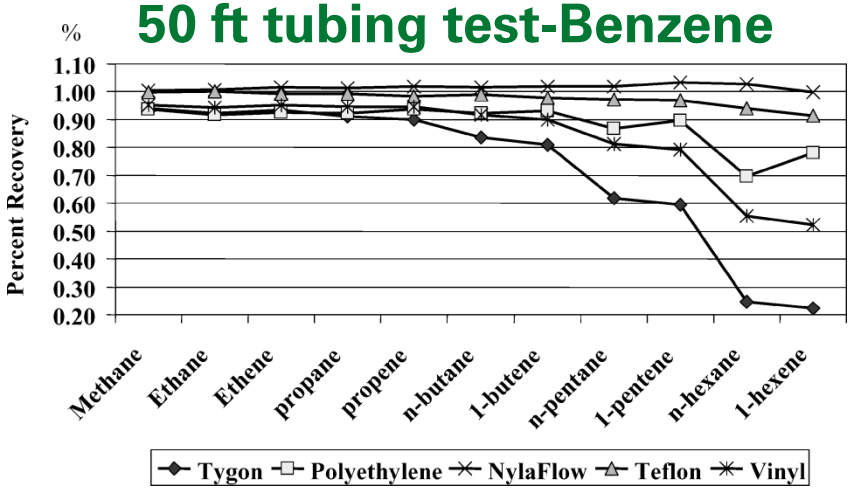
# VI Issues Encountered, con't.

- **Work Plan Issues**:

- Work plans submitted for VI work not needed
- Too many samples recommended for what is needed
- Not specifying collection of samples in upper part of vadose zone (e.g., 5' bgs) to demonstrate bioattenuation
- Analyzing compounds that were never used at the site.
- Not analyzing for fixed air gases
- Not using correct analytical method to achieve needed detection limits

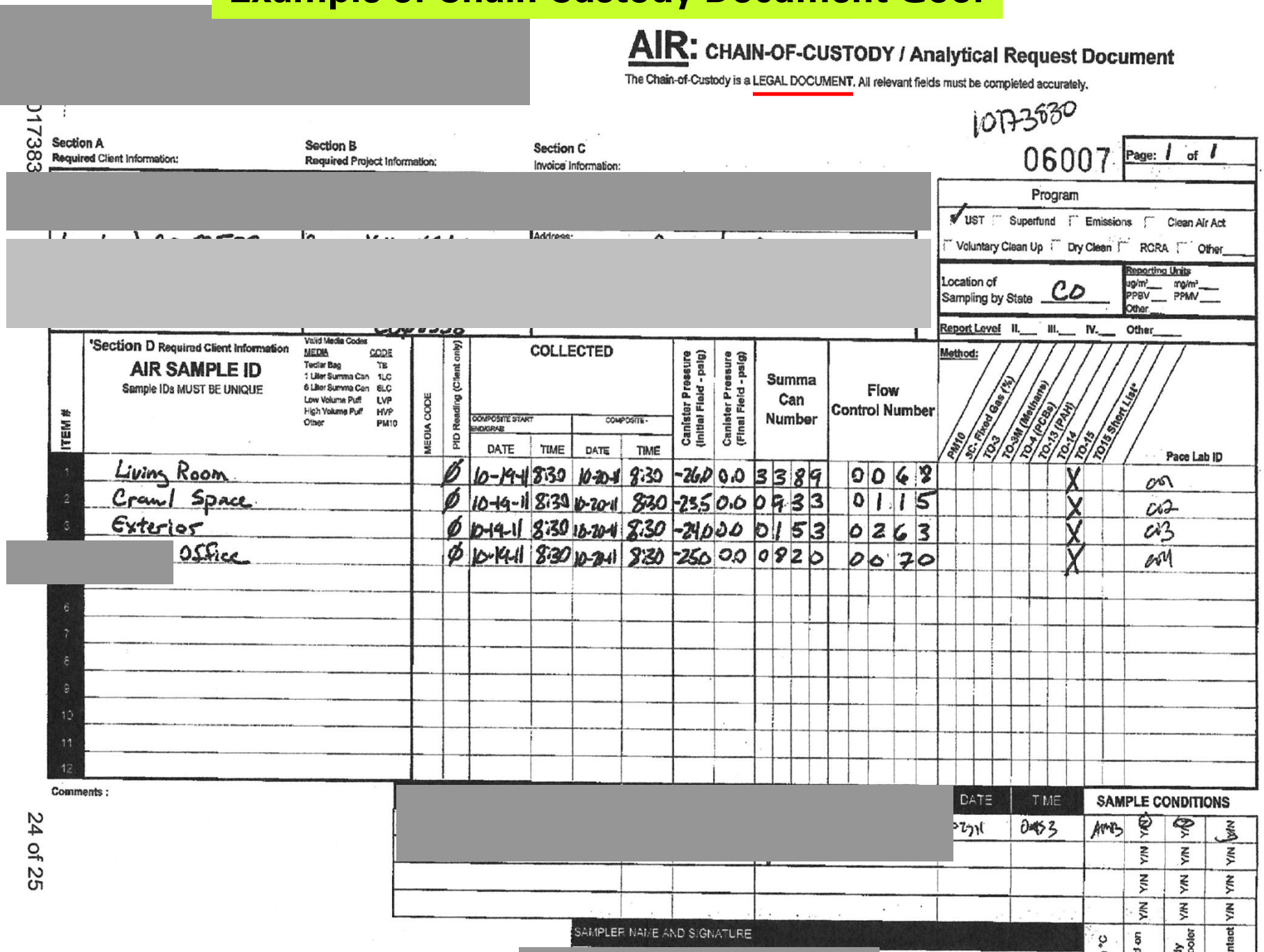
# VI Issues Encountered, con't.

- **Soil Gas Probe Installation Issues**:
  - Using wrong tubing type
  - Pinching off tubes incorrect completion
  - Not collecting an equipment blank




- **Consultant Field Sampling Issues**:
  - Not opening Summa canisters or Tedlar bags
  - No experience with swagelok connectors
  - Applying too much liquid tracer
  - Returning Summa canisters with 0 pressure
  - Lack of attention to chain of custody details

# Example of Chain Custody Document Goof



**AIR: CHAIN-OF-CUSTODY / Analytical Request Document**

The Chain-of-Custody is a LEGAL DOCUMENT. All relevant fields must be completed accurately.

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Page: 1 of 1

Section A Required Client Information:

Section B Required Project Information:

Section C Invoice Information:

Program: ✓ UST ☐ Superfund ☐ Emissions ☐ Clean Air Act ☐ Voluntary Clean Up ☐ Dry Clean ☐ RCRA ☐ Other

Location of Sampling by State: CO

Reporting Units: ug/m³ ___ ng/m³ ___ PPBV ___ PPMV ___ Other ___

Report Level: II. ___ III. ___ IV. ___ Other ___

| ITEM # | Section D Required Client Information: AIR SAMPLE ID (Sample IDs MUST BE UNIQUE) | MEDIA CODE | PID Reading (Client only) | COLLECTED: COMPOSITE START / END/GRAB DATE | COLLECTED: COMPOSITE START / END/GRAB TIME | COLLECTED: COMPOSITE END/GRAB DATE | COLLECTED: COMPOSITE END/GRAB TIME | Canister Pressure (Initial Field - psig) | Canister Pressure (Final Field - psig) | Summa Can Number | Flow Control Number | Method: PM10 | SC: Fixed Gas (%) | TO-3 | TO-3M (Methane) | TO-4 (PCBs) | TO-13 (PAH) | TO-14 | TO-15 | TO15 Short List* | Pace Lab ID |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Living Room | | Ø | 10-19-11 | 8:30 | 10-20-11 | 8:30 | -26.0 | 0.0 | 3389 | 0068 | | | | | | | X | | | 001 |
| 2 | Crawl Space | | Ø | 10-19-11 | 8:30 | 10-20-11 | 8:30 | -23.5 | 0.0 | 0733 | 0115 | | | | | | | X | | | 002 |
| 3 | Exterior | | Ø | 10-19-11 | 8:30 | 10-20-11 | 8:30 | -24.0 | 0.0 | 0153 | 0263 | | | | | | | X | | | 003 |
| 4 | Office | | Ø | 10-19-11 | 8:30 | 10-20-11 | 8:30 | -25.0 | 0.0 | 0820 | 0070 | | | | | | | X | | | 004 |
| 5 | | | | | | | | | | | | | | | | | | | | | |
| 6 | | | | | | | | | | | | | | | | | | | | | |
| 7 | | | | | | | | | | | | | | | | | | | | | |
| 8 | | | | | | | | | | | | | | | | | | | | | |
| 9 | | | | | | | | | | | | | | | | | | | | | |
| 10 | | | | | | | | | | | | | | | | | | | | | |
| 11 | | | | | | | | | | | | | | | | | | | | | |
| 12 | | | | | | | | | | | | | | | | | | | | | |

Valid Media Codes: MEDIA / CODE — Tedlar Bag TB; 1 Liter Summa Can 1LC; 6 Liter Summa Can 6LC; Low Volume Puff LVP; High Volume Puff HVP; Other PM10

Comments:

| DATE | TIME | SAMPLE CONDITIONS |
|---|---|---|
| 10-21-11 | 0853 | Amb N/A N/A N/A |

SAMPLER NAME AND SIGNATURE

Reported: 04/15/2011 15:13

# Results for Office Indoor Air

| CAT No. | Analysis Name | CAS Number | As Received Final Result | | MDL | As Rece Final Re |
|---|---|---|---|---|---|---|
| **Volatiles in Air** | **ASTM D1946** | | % | | % | |
| 00034 | Oxygen | 7782-44-7 | 7.5 | | 0.060 | $O_2$= |
| **Volatiles in Air** | **EPA 18 modified** | | mg/m3 | | mg/m3 | ppm(v) |
| 11687 | Butane | 106-97-8 | < 3.6 | | 3.6 | < 1.5 |
| 07056 | Methane | 74-82-8 | 85 | | 3.9 | 130 |
| **Volatiles in Air** | **EPA TO-15** | | ug/m3 | | ug/m3 | ppb(v) |
| 05298 | Acetone | 67-64-1 | 68 | | 12 | 29 |
| 05298 | Acetonitrile | 75-05-8 | 22 | J | 8.4 | 13 |
| 05298 | Acrolein | 107-02-8 | < 11 | | 11 | < 5.0 |
| 05298 | Acrylonitrile | 107-13-1 | < 11 | | 11 | < 5.0 |
| 05298 | Benzene | 71-43-2 | < 6.4 | | 6.4 | < 2.0 |
| 05298 | Bromobenzene | 108-86-1 | < 13 | | 13 | < 2.0 |
| 05298 | Bromoethene | 593-60-2 | < 22 | | 22 | < 5.0 |
| 05298 | Bromoform | 75-25-2 | < 21 | | 21 | < 2.0 |
| 05298 | Bromomethane | 74-83-9 | < 7.8 | | 7.8 | < 2.0 |
| 05298 | 1,3-Butadiene | 106-99-0 | < 11 | | 11 | < 5.0 |
| 05298 | 2-Butanone | 78-93-3 | < 15 | | 15 | < 5.0 |
| 05298 | tert-Butyl Alcohol | 75-65-0 | < 15 | | 15 | < 5.0 |
| 05298 | n-Butylbenzene | 104-51-8 | < 11 | | 11 | < 2.0 |
| 05298 | sec-Butylbenzene | 135-98-8 | < 11 | | 11 | < 2.0 |
| 05298 | tert-Butylbenzene | 98-06-6 | < 11 | | 11 | < 2.0 |
| 05298 | Carbon Disulfide | 75-15-0 | < 6.2 | | 6.2 | < 2.0 |
| 05298 | Carbon Tetrachloride | 56-23-5 | < 13 | | 13 | < 2.0 |
| 05298 | Chlorobenzene | 108-90-7 | < 9.2 | | 9.2 | < 2.0 |
| 05298 | Chlorodifluoromethane | 75-45-6 | < 7.1 | | 7.1 | < 2.0 |
| 05298 | Chloroethane | 75-00-3 | < 5.3 | | 5.3 | < 2.0 |
| 05298 | Chloroform | 67-66-3 | < 9.8 | | 9.8 | < 2.0 |
| 05298 | Chloromethane | 74-87-3 | < 4.1 | | 4.1 | < 2.0 |

| Location | Near DWSS | to VP-1 | VP-4 | fence post | corner | garage | DWSS |
|---|---|---|---|---|---|---|---|
| Summa size (litres) | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
| Summa ID | 832/4505 | 109 | 535/1291 | 822/4548 | 198 | 114 | 107 |
| Flow Controller ID | 7329537 | 7336786 | 7301041 | 7252153 | 7234843 | 7336758 | 7336759 |
| Summa Flow regulator setting (time) | 24hr intake | 24hr intake | 24hr intake | 24hr intake | 24hr intake | 24hr intake | 24hr intake |
| | | | | | | | |
| Total single implant volume (litres) | 0.191 | NA | NA | NA | NA | NA | NA |
| Purge Time Start | 11:12 | NA | NA | NA | NA | NA | NA |
| Purge Time Stop | 11:17 | NA | NA | NA | NA | NA | NA |
| Total purge time (mins.) | 5 | NA | NA | NA | NA | NA | NA |
| Volume purged (litres) | 1 | NA | NA | NA | NA | NA | NA |
| | | | | | | | |
| Tracer Gas Reading - Initial (%) | 0.6400% | NA | NA | NA | NA | NA | NA |
| Pressure gauge pre-sample (inches Hg) | -29 | >-30 | -30 | >-30 | -29 | >-30 | -28.5 |
| Sample start time | 13:57 | 14:34 | 14:26 | 14:22 | 14:10 | 13:55 | 13:56 |
| Sample end time | 10:12 | 12:58 | 11:41 | 11:16 | 11:55 | 10:40 | 10:15 |
| Elapsed sample time (mins.) | 1215 | 1344 | 1275 | 1254 | 1305 | 1245 | 1219 |
| Pressure gauge post-sample (inches Hg) | -12 | -10 | -12 | -21 | -9 | -21 | -11 |
| Tracer gas reading - Final | 0.5000% | NA | NA | NA | NA | NA | NA |
| PID reading (ppm) | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

**Note Negative Vacuums: The cans only filled partially!**

# VI Issues Encountered, con't.

- Probe installation:  ground disturbance issues mean no direct push methods can be used
- Avoid air knife
- Sampling open bore holes

# VI Issues Encountered, con't.

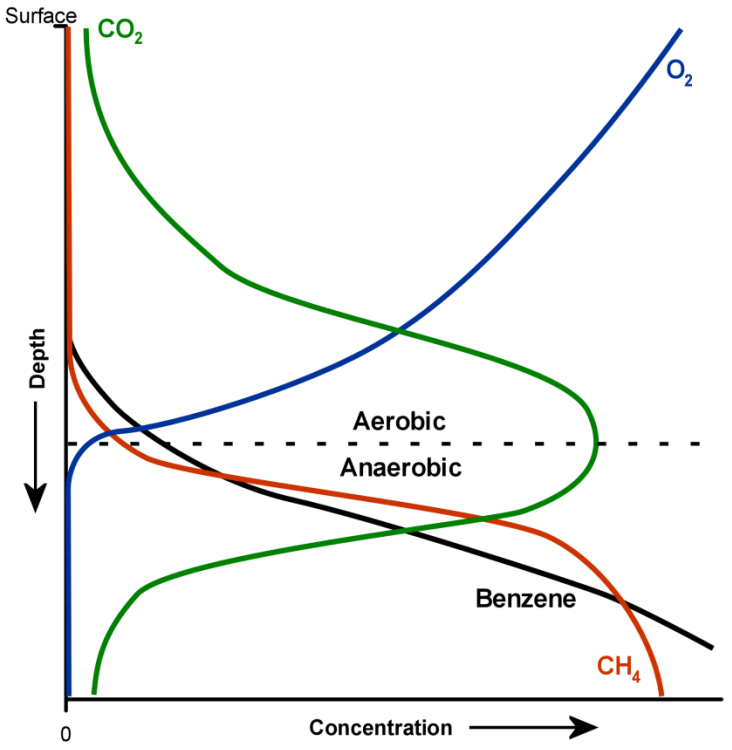
- Smaller samples are better; including Summa canisters
- Flow rate can easily be monitored using hand held syringe
- Tedlar bags have maximum holding time of about 3 days for benzene and 2 days for TEX

# Methane: Potential Safety Hazard

- Colorless-odorless gas: CH4
- Ubiquitous
- Value in Air: 1.8 ppmv
- Lower Explosive Limit: 50,000 ppmv
- Upper Explosive Limit: 150,000 ppmv
- Main component of natural gas
- Most abundant organic compound on Earth
- Methanogenesis: $CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O$
- Fermentation: Biogas from biodegradable organic matter: Landfills
- Global Warming: Current Biology publication suggests flatulence from dinosaurs may have warmed the Earth!

# Methane: Site Data Required to Assess Hazard and Determine if Action is Needed

- Source concentration
- Volume
- Pressure
- Transport/Preferential Pathways
- Dilution
- Bio-attenuation




**The presence of methane in soil gas does not mean there is a hazard**

**Modified from J. Sepich, 2012**

# Good Example of Unexpected Source of Methane/Benzene in Residential Area

| Analyte | BBQ | Garage | Patio | Garage #2 | Closet |
|---|---|---|---|---|---|
| methane | 40% | 90% | 100% | nd (0.1%) | nd (0.1% |
| | ug/m3 | ug/m3 | ug/m3 | ug/m3 | ug/m3 |
| n-hexane | 1700 | 2000 | 10000 | nd (15) | nd (15) |
| cy-hexane | 750 | 5500 | 12000 | nd (20) | 21 |
| n-heptane | 460 | 710 | 3100 | nd (50) | nd (50) |
| benzene | 270 | 340 | 1900 | 6.5 | 7.9 |
| toluene | 150 | 110 | 120 | 44 | 62 |
| xylenes | 40 | 105 | 177 | 113 | 33 |
| tri-methyl benzene | 3 | 85 | 25 | 110 | nd (10) |
| tri-methyl pentane | nd (200) | 300 | nd (200) | nd (20) | nd (20) |

**Homeowner had to be reminded twice to call gas company**

**Regulators ignored the issue**

# What Homeowners and Companies Do NOT Want

# Soil Gas Sampling Results

**Site 1**

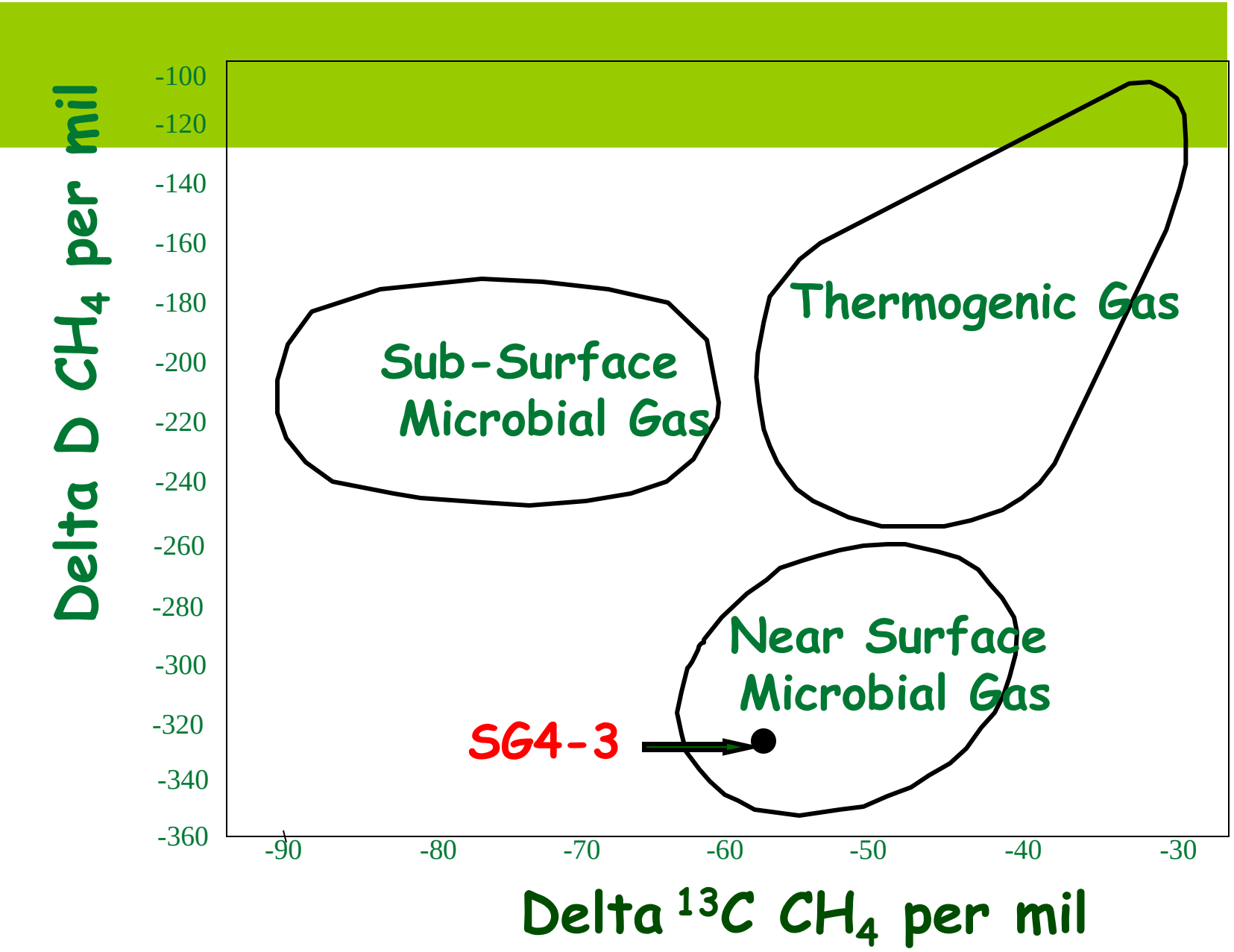
| Sample depth | Methane (ppmv) |
|---|---|
| 1. Subslab 0.5 ft | 12 |
| 2. Subslab 3 ft | 8,300 |
| 3. Outside 1ft | 1,700 |
| 4. Outside 3ft | 180,000 |

**Site 2**

| Sample depth | Methane (ppmv) |
|---|---|
| 1. Subslab 0.5 ft | <10 |
| 2. Subslab 3 ft | 11,000 |
| 3. Outside 1ft | 45 |
| 4. Outside 5ft | 120,000 |

# Isotech Gas Data: High $CH_4$ Sample

- $O_2$ = 2.54%
- $CO_2$ = 35.19%
- $N_2$ = 38.9%
- C1 = 22.9%
- C2 through C6+ = 0%
- Delta $^{13}$C1 = -57.18 per mil
- Delta DC1 = -328.4 per mil
- $^{14}$C pMC = 109%

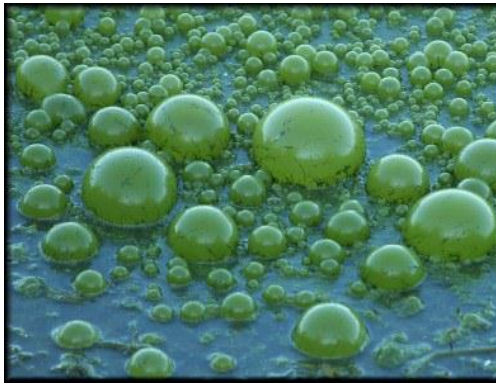



Sources of gases as defined in Coleman (1994)

# Sources of Methane in the Subsurface

- **Methane from biodegradation of petroleum is characterized by**:
  - Lack of significant concentrations of ethane and propane
  - CO2 / methane ratios between 0.3 and 0.6
  - Relationship between carbon isotope ratio of CO2 and
  - methane concentration
  - C14 age > 50,000 years old

- **'Swamp' gas of poorly identified source can also be distinguished by C-14 age**
- **Thermogenic methane can be distinguished by molecular composition**
  - Geologic considerations and stable isotope ratios may be needed



**Modified from R.E. Sweeney, 2011**