Obtaining Representative Field Information for Vapor Intrusion Assessments: What Do You Need to Know?

National Tanks Conference, St. Louis, MO, Monday , March 19, 1:00 - 3:00 PM

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U.S. EPA/ORD/NRMRL

The rate and extent of biodegradation a contaminant of concern [such as benzene] in soil gas is controlled by the supply of molecular oxygen.

The supply of oxygen is limited by the competing demands for oxygen to support the biodegradation of methane and total petroleum hydrocarbons in soil gas.

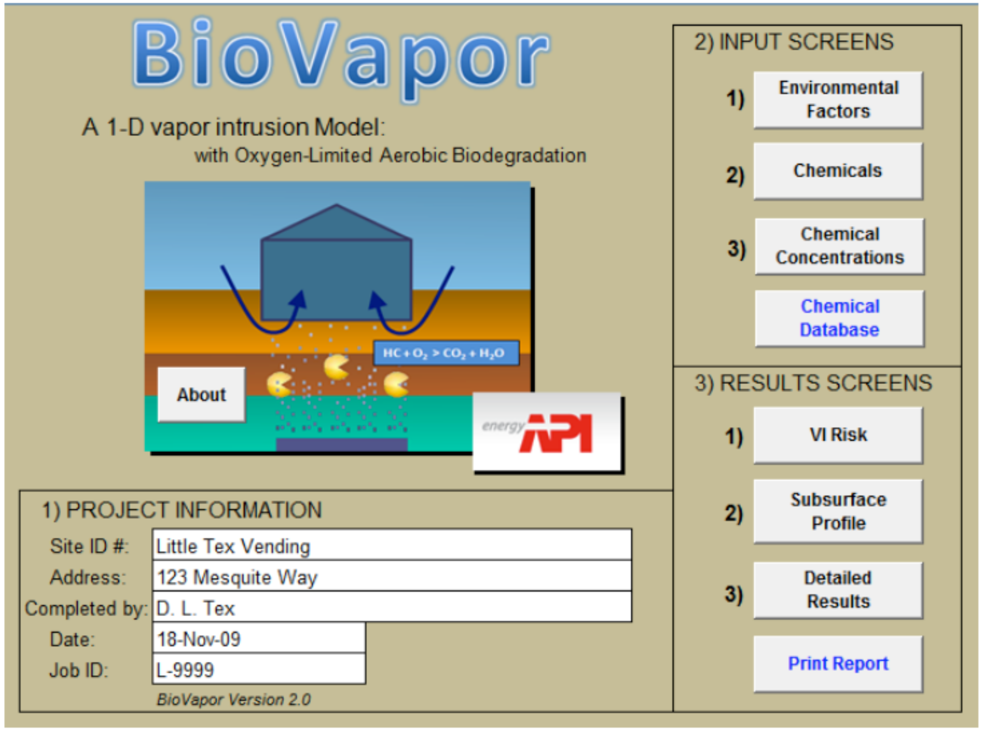
You must know the oxygen demand of methane and total petroleum hydrocarbons in soil gas to be able to predict the biodegradation of a contaminant of concern.

New approaches are coming forth that describe the behavior of petroleum constituents in a comprehensive biogeochemical and spatial context.

These new approaches offer a path forward for risk management of petroleum vapor intrusion.

BioVapor

A 1-D Vapor Intrusion Model with Oxygen-Limited Aerobic Biodegradation



Abreu, L.D.V., R. Ettinger, and T. McAlary. 2009.

Simulated soil vapor intrusion attenuation factors including biodegradation for petroleum hydrocarbons.

Ground Water Monitoring and Remediation 29, no. 1: 105-117.

Abreu et al. (2009) conducted 3-D computer simulations of the behavior of benzene in soil gas. In their simulations, the hydrocarbons originated from contaminated ground water or a deep layer of NAPL, and oxygen originated from the atmosphere.

Their simulations were done for various concentrations of hydrocarbons in soil gas (expressed as an equivalent concentration of benzene) and for various vertical separation distances between the source of vapors and the receptor.

Figure 10 of Abreu et al. (2009) can be used to estimate a value for α based on the concentration of hydrocarbons at the source and the length (L) which is the vertical separation distance between the source and the receptor.

The concentrations of hydrocarbons are expressed as a concentration of benzene (mg/L air) with a BOD equivalent to the BOD of the mix of hydrocarbons.

In the example in the next slide, if the vertical separation distance is 2 meters and the source concentration is 10 mg/L, the attenuation factor is 1 E-07, or 0.0000001.

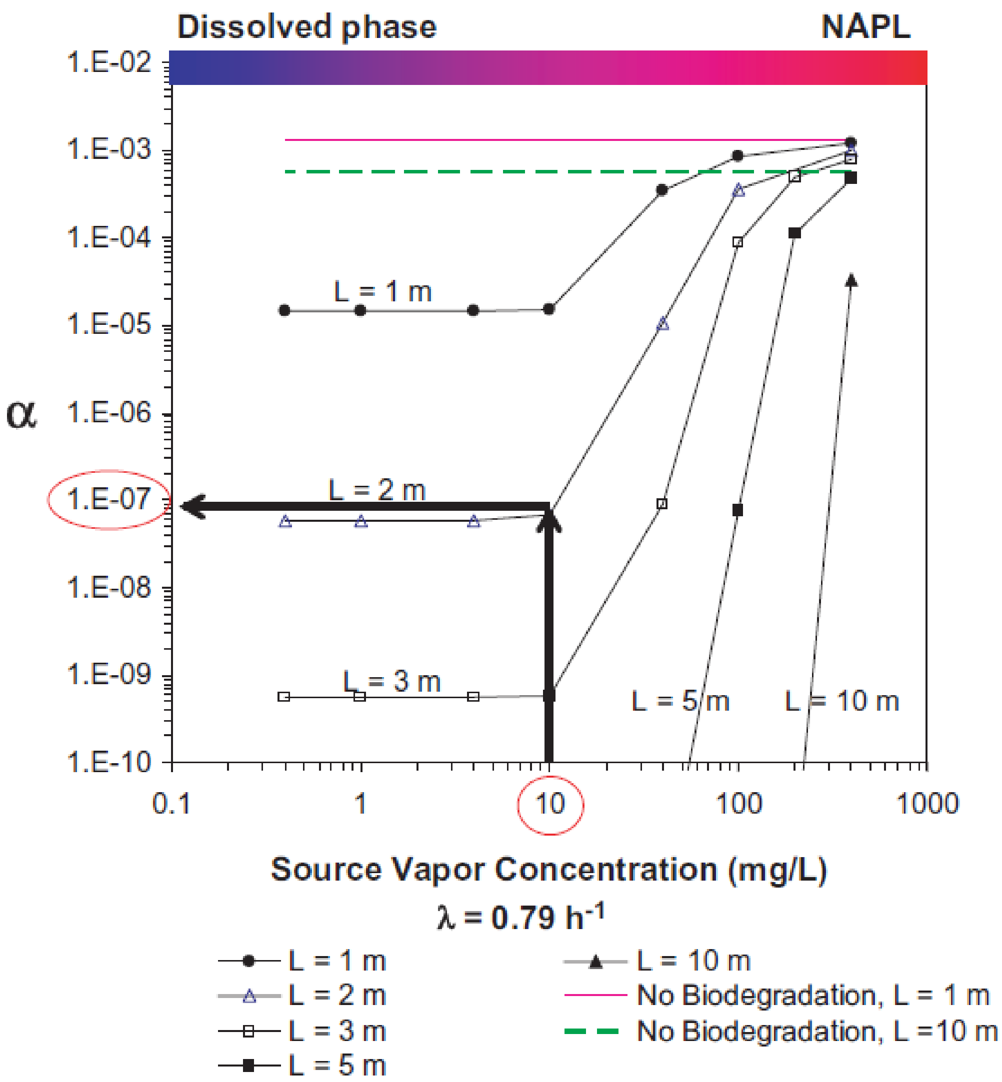


Figure 10. Use of the chart to select a semi-site-specific attenuation factor. For a source concentration of 10,000 μg/L and a source-building separation of 2 m, the attenuation factor would be about 1E-7.

BioVapor requires a concentration of benzene or other hydrocarbons in units of µg/m^3.

Figure 10 in Abreu et al. (2009) requires a concentration of benzene (in units of mg/L) that has the same oxygen demand as the sum of all the biodegradable vapors in the soil gas.

Concentrations of gases are conventionally reported as percent or part per million on a volume basis.

To use the field data, it is necessary to convert % or ppm to mg/m^3 or µg/L.

Assume the meter is calibrated to methane (CH_4), and the meter reads 4.7%. To use **BioVapor** we need a concentration in $\mu g/m^3$.

To express the equivalent concentration of methane in $\mu g/m^3$ soil gas, divide the concentration in % by 100, then multiply by the vapor density of methane (0.56, air = 1), then multiply by the density of air (1,200,000,000 $\mu g/m^3$).

$$4.7\% = [4.7/100] * 0.56 * 1,200,000,000$$
$$= 31,000,000\ \mu g/m^3$$
$$= 3.1E+07\ \mu g/m^3$$

Where to get information on vapor density of ----?

1) Google *vapor density of ----.*

2) Divide the molecular weight of ---- by 28.8 (mean molecular weight of dry air).

   As an example, the vapor density of benzene would be 78.1 / 28.8 = 2.7 where air = 1.0.

Assume the meter is calibrated to methane, and the meter reads 4.7%.

To use Figure 10 of Abreu et al. (2009) we need a concentration in total combustible gases in equivalent concentrations of benzene in mg/L.

The stoichiometry of aerobic biodegradation can be used to calculate the concentration of molecular oxygen that would be needed to degrade the measured concentrations of ----.

Consider the biodegradation of benzene:

$$C_6H_6 + 7.5\ O_2 \rightarrow 6\ CO_2 + 3\ H_2O$$

The theoretical oxygen demand is 7.5 to 1.0.

If the concentration of benzene in soil gas were 100 ppm, the estimated concentration of molecular oxygen required to degrade the benzene would be 750 ppm.

The general formula is as follows:

Volume O_2 required for 1.0 volume of Hydrocarbon

= (2*number carbon atoms+0.5* number hydrogen atoms)/2

Analyte	Carbon Atoms	Hydrogen Atoms	Stoichiometric O_2 Demand (v/v) O_2/Hydrocarbon
Benzene C_6H_6	6	6	7.5
Methane	1	4	2.0
Hexane C_6H_{14}	6	14	9.5

To calculate the concentration of benzene mg/L that is equivalent to 4.7% methane in soil gas, first multiply the concentration of methane % by the theoretical oxygen demand of methane, then divide by the theoretical oxygen demand of benzene.

4.7% methane * 2.0 / 7.5 = 1.25% benzene

Then divide the concentration benzene in % by 100, then multiply by the vapor density of benzene (2.7, air = 1), and then multiply by the density of air (1,200 mg/L).

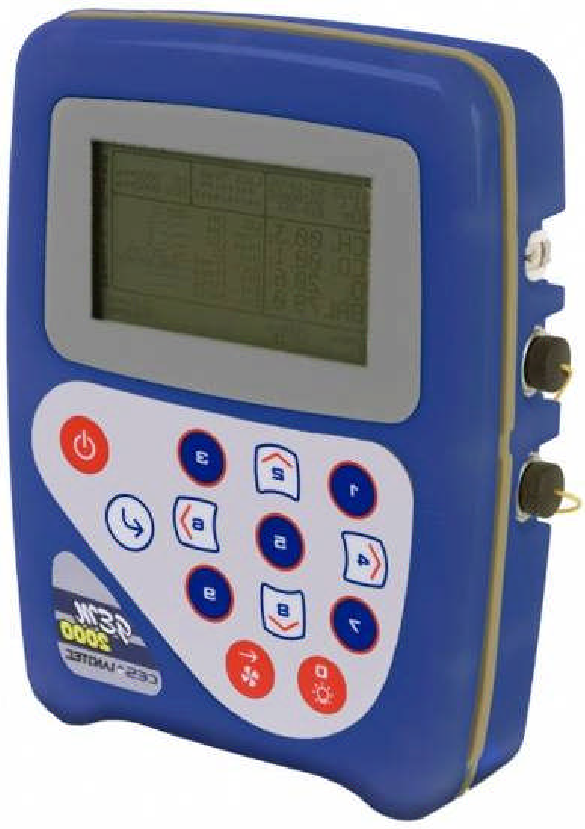
1.25% benzene=[1.25/100]*2.7 *1,200 = 41 mg/L benzene

4.7% methane = 41 mg/L benzene

How to get information on the concentrations of methane and gasoline hydrocarbons?

LandTec GEM 2000/ 2000 Plus

- Original design for measuring gases from landfill sites
- Dual wavelength infrared cell with reference channel (CH_4, CO_2)
- Electrochemical cells (O_2, H_2S, CO)
- Data logging for download to PC



LandTec GEM 2000/ 2000 Plus (~$10K)

GAS	RANGE
CH_4	0 – 100%
CO_2	0 – 100%
O_2	0 – 25%
H_2S (Plus)	0 – 500 ppmv
CO (Plus)	0 – 2000 ppmv

Accuracy

GAS	0-5% volume	5-15% volume	15%-Full Scale
CH_4	± 0.3 %	± 1.0 %	± 3.0 %
CO_2	± 0.3 %	± 1.0 %	± 3.0 %
O_2	± 1.0 %	± 1.0 %	± 1.0 %
H_2S (Plus)	± 10 %	± 10 %	± 10 %
CO (Plus)	± 10 %	± 10 %	± 10 %

LandTec GEM 2000/ 2000 Plus

QC

Operation Check	Acceptance Limits
Method Blank	0% for O_2, CH_4, and CO_2 0 ppm for H_2S, and CO
Check Standards/ Second Source Standards	± 1% for O_2, CH_4, and CO_2 ± 10% for H_2S, and CO

LandTec GEM 2000/ 2000 Plus

INTERFERENCES
RF Interference: Radio waves from devices such as cell phones can cause gas readings to fluctuate. Cell phones should be off or keep a distance of ~ 20 ft distance in active use.
Cross-Gas Effects: •If other hydrocarbons are present, CH_4 readings will be higher than the actual CH_4 concentration being monitored. A non-linear effect. •CO_2 readings are not usually affected by other gases •CO reading is potentially susceptible to interference by H_2 and H_2S.

TVA-1000B Toxic Vapor Analyzer

- FID measures organic compounds by utilizing a flame produced by the combustion of hydrogen and air in sample

$$RH + O \rightarrow RHO^{+} + e^{-} \rightarrow H_2O + CO_2$$

- Ions migrate towards collector electrode and produce current proportional to concentration

TVA-1000B Toxic Vapor Analyzer

- Uses both a Flame ionization detector (FID) and a photoionization detector (PID)

- Data logging for download to PC

TVA-1000B Toxic Vapor Analyzer

- PID uses an ultraviolet (UV) lamp of a specific energy and an ionization chamber. Compounds are excited by photon of UV energy from the lamp

$$R + h\nu \rightarrow R^{+} + e^{-}$$

- Detection depends upon energy required to remove an electron from the compound (ionization potential)
- Ions migrate towards collector electrode and produce current proportional to concentration

TVA-1000B Toxic Vapor Analyzer

FID Benefits

- High sensitivity to most hydrocarbons
- Stable and repeatable response
- Ability to measure methane
- Unaffected by CO, CO_2, and water vapor

PID Benefits

- High sensitivity to aromatics, unsaturated hydrocarbons, and chlorinated hydrocarbons
- Some inorganic gases
- Non-destructive detector allows sample to be recovered

TVA-1000B Toxic Vapor Analyzer (~$14K)

DETECTOR	DYNAMIC RANGE	LINEAR RANGE	ACCURACY
FID	0 – 50,000 ppmv	1.0 – 10,000 ppmv	±25% or ±2.5 ppm, whichever is greater, from 1.0 to 10,000 ppm
PID	0 – 2,000 ppmv	0.5 – 500 ppmv	±25% or ±2.5 ppm, whichever is greater, from 0.5 to 500 ppmv

TVA-1000B Toxic Vapor Analyzer

Detector	Calibration Check Standards
FID	90 – 110% of known value
PID	80 – 120% of known value

INTERFERENCES
Moisture at the FID flame arrestor
Water contamination in the PID detector chamber
Low oxygen levels can affect the hydrogen flame causing readings to be artificially elevated and can potentially extinguish the flame. Generally need greater than 16% oxygen to support flame.

Bascom-Turner Gas Rover (~$5K)

No H source, reads methane using thermal conductivity detector and combustion catalytic sensor

GAS	RANGES
CH_4	0 - 40,000 ppmv
	0 - 100% by volume
CO	0 - 2000 ppmv
O_2	0 – 40% by volume

Gas	Accuracy
CH_4	2% of reading ± 20 ppm ±0.1% to 5%; ±2.0% to 100 vol %
CO	± 5% of reading ± 10 ppm
O_2	± 0.2% vol %

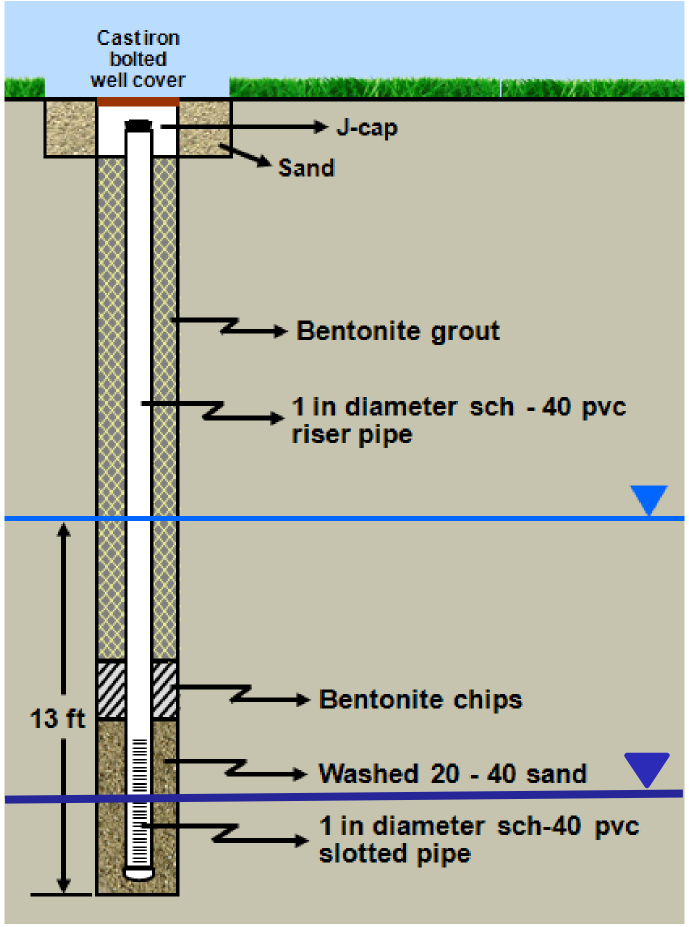
Bascom-Turner Gas Rover

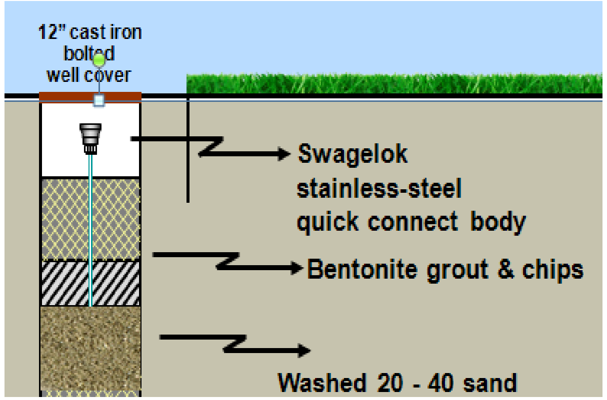
INTERFERENCES
• Substances that can combust on the catalytic combustion filament may interfere with methane detection (e.g. ethane, propane, ethylene, propylene, octane, etc.) and substances that differ in thermal conductivity from air may also interfere with methane readings (e.g. hydrogen, helium, carbon dioxide, etc.)
• Substances that can be electrochemically oxidized or reduced on the electrode of the electrochemical sensor can interfere with CO detection (e.g. hydrogen, hydrogen sulfide, oxides of nitrogen, alcohols, and unsaturated hydrocarbon.

- Stainless-steel soil vapor sampling screen
- Polyethylene tubing to ground surface

(UDEQ direct buried vapor probes)

Monitoring Wells or Vapor Probes?





If the water table is within the screened interval, a monitoring wells looks like a big vapor probe, with a lot more dead volume.

A New Screening Method for Methane in Soil Gas Using Existing Groundwater Monitoring Wells.

Kenneth P. Jewell and John T. Wilson.

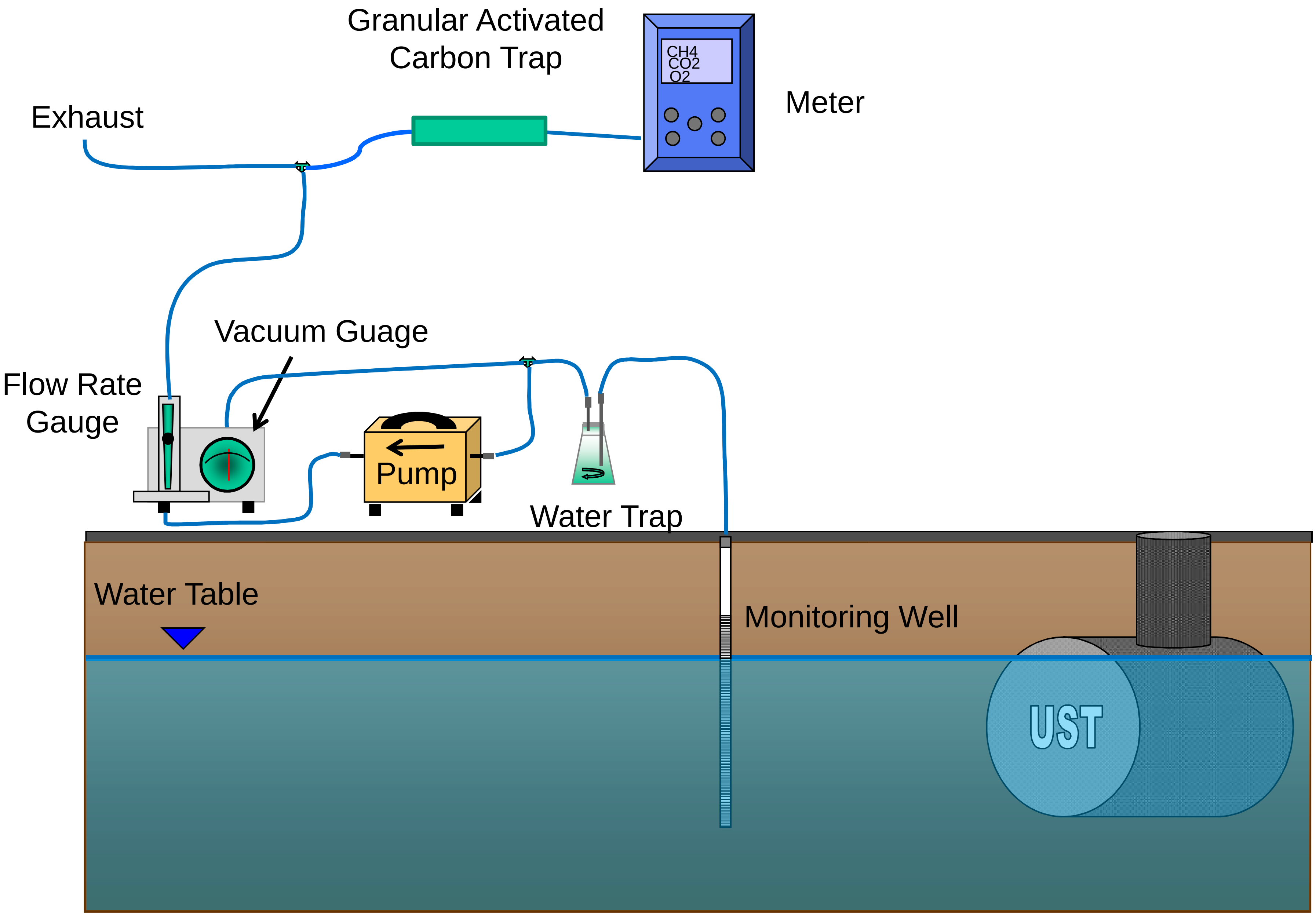
Ground Water Monitoring & Remediation 31(3): 22–94 (2011).

http://www.epa.gov/nrmrl/gwerd/pubs/methane_screening_soil_gas.pdf

Collecting Soil Gas from Water Monitoring Wells

(*Basic Requirements*)

- **Well Screened Across the Water Table**
- **Well Construction Log** (*Driller's well log notebook*)
- **Water Level Meter**
- **Well Cap That Allows for Sample Collection**
- **Vacuum Pump @10 L/min** (*pump tubing, etc.*)
- **Sample Container** (*serum bottle, foil gas sample bag*)
- **Rotameter** (*flow rate is established and monitored*)
- **Vacuum Gauge** (*Magnehelic® differential pressure gauge*)
- **Water trap** (*protects the system from water pulled to surface*)

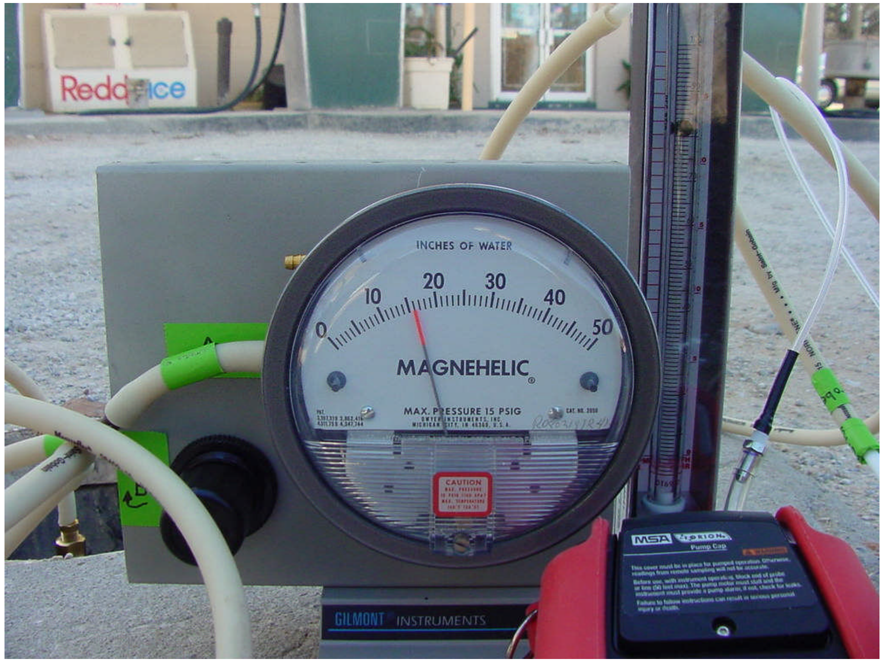

Granular Activated
Carbon Trap
CH4
CO2
O2
Meter
Exhaust
Vacuum Guage
Flow Rate
Gauge
Pump
Water Trap
Water Table
Monitoring Well
UST

Monitoring Vacuum

•Stable vacuum necessary for leak testing sampling system.

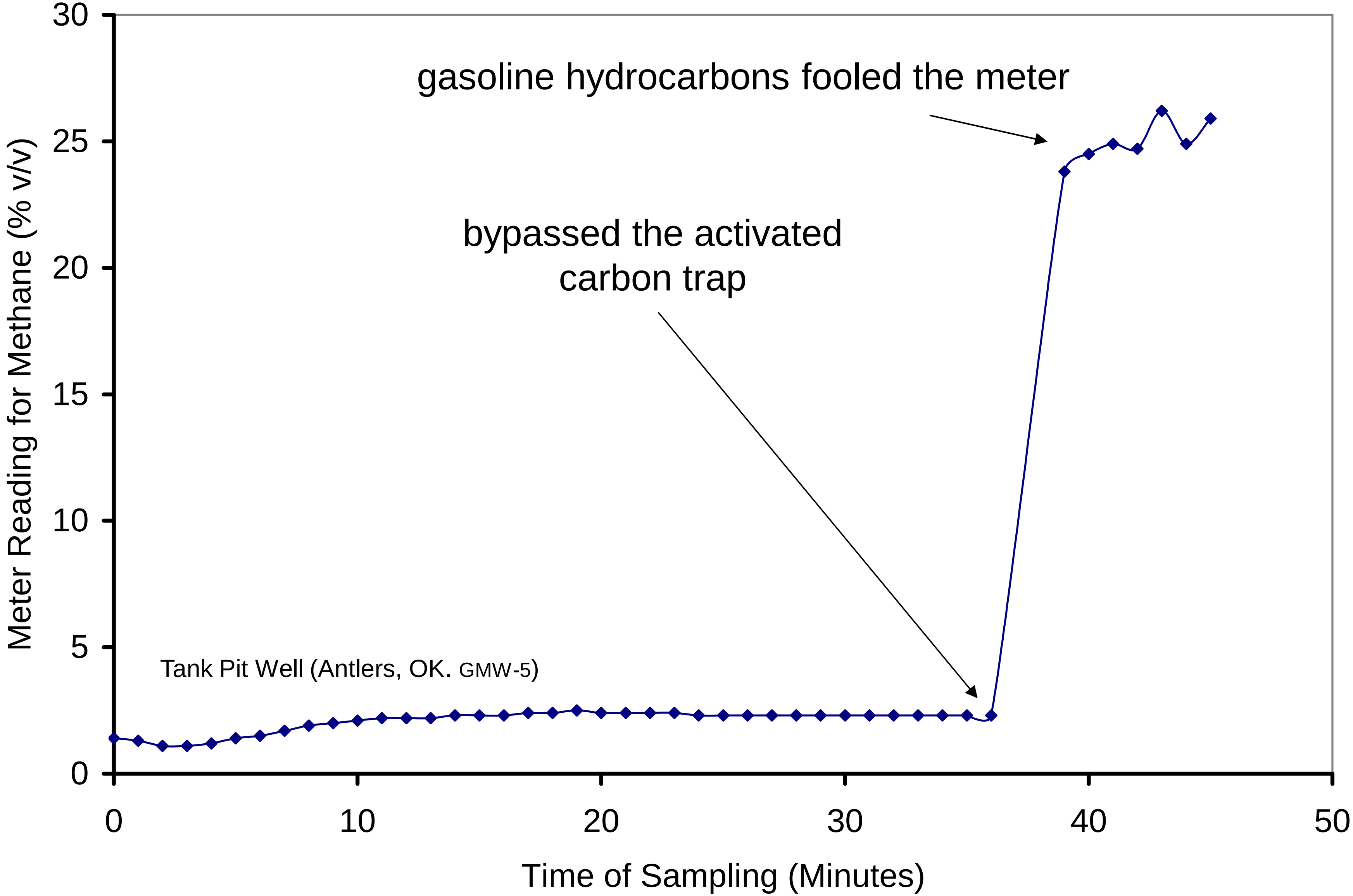
•Vacuum measurement (inches) often is an indication of the rise of water in the well (in inches).

•Knowing vacuum is useful when setting flow rate, so flow rate does not produce so much vacuum that it pulls water up inside the well and inundates the screened interval.



Construction of GAC Trap

Need for a Carbon Trap in front of the IR of the Field Meter



Well	GC at Lab	Landtec	Orion
Meters protected by GAC trap	Methane (% v/v)		
Antlers-MW-2-A	44.8	61.4	27.2
Henryetta NW-TP-1	10.0	18.4	9.9
Pauls Valley VPW-3	4.0	5.1	3.5
Pauls Valley VPW-3 10N	3.6	4.5	3.2
MW-1-Wapanuka-A	2.5	4.3	4.6
OKC S.E. 29th Street	1.3	2.3	1.8
Antlers GMW-5	0.8	1.9	1.6
Henryetta NW-TP-1E	0.5	0.7	0.8
Oklahoma City TMW-3-A	0.1	0.1	0.1
OKC N.E. 23rd Street TMW-1-A	0.1	0.0	0.1
Maysville N.E. Well	0.0	0.0	0.0
OKC N.E. 23rd Street TMW-2-A	0.0	0.0	0.0
Pickett-MW-2-4"	0.0	0.6	0.6

After the Meter Readings Stabilize

- Soil gas samples are collected in 160ml serum bottles.

- Sample bottles are filled with DI water.

- Bottle is inverted in water, and soil gas displaces the water

- Bottles are capped and later analyzed using an Agilent 3000 micro GC.

Sample Collected in Foil Bag

Hydrocarbons and Major Fixed Gases ONLY (N_2, CO_2 O_2+Ar)

3000 Micro GC

Hydrocarbons	
Methane	CH_4
Ethane	C_2H_6
Ethylene	C_2H_4
Propane	C_3H_8
Propylene	C_3H_6
Isobutane	iC_4H_{10}
Normal Butane	nC_4H_{10}
Isopentane	iC_5H_{12}
Normal Pentane	nC_5H_{12}
Hexanes Plus	C_6+

Expected Turnaround Time and Cost:			
Standard Service	3	business days	$66
Rush Service	1	business days	$132
*Advance arrangements required for RUSH SERVICE			

To calculate the concentration of benzene % that is equivalent to 4.7% methane in soil gas, first multiply the concentration of methane % by the theoretical oxygen demand of methane, then divide by the theoretical oxygen demand of benzene.

4.7% methane * 2.0 / 7.5 = 1.25% benzene

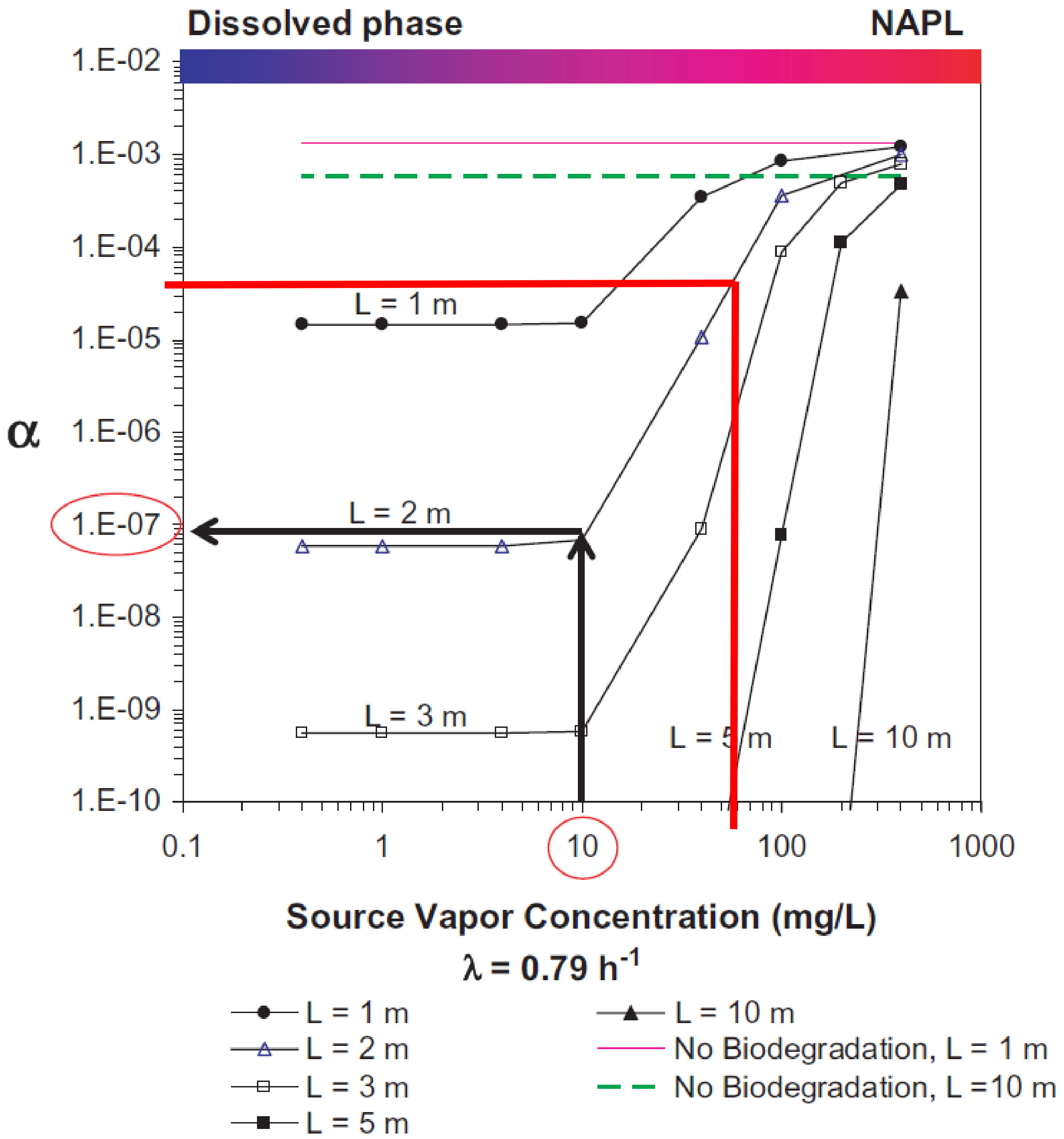
Analytes	Stoichiometric O_2 Demand	Vapor Concentration ppm (v/v)	Equivalent Benzene Concentration ppm (v/v)
Methane	2	60000	16000
Ethane	3.5	548	256
Ethylene	3	ND	0
Propane	5	220	147
Propylene	4.5	19	11
i-Butane	6.5	198	172
n-Butane	6.5	718	622
i-Pentane	8	1330	1419
n-Pentane	8	68	73
C6+	12.5	912	1520
Total			20219

Divide the equivalent concentration benzene in ppm by 1,000,000 and then multiply by the vapor density of benzene (2.7, air = 1), and then multiply by the density of air (1,200 mg/L).

20219 ppm benzene

=[20219/1000,000]*2.7 *1,200

= 66 mg/L benzene


Dissolved phase
NAPL
α
1.E-02
1.E-03
1.E-04
1.E-05
1.E-06
1.E-07
1.E-08
1.E-09
1.E-10
L = 1 m
L = 2 m
L = 3 m
L = 5 m
L = 10 m
0.1
1
10
100
1000
Source Vapor Concentration (mg/L)
λ = 0.79 h-1
L = 1 m
L = 2 m
L = 3 m
L = 5 m
L = 10 m
No Biodegradation, L = 1 m
No Biodegradation, L =10 m

Conclusions About Using Existing Water Monitoring Wells for Sampling Soil Gas

Conventional monitoring wells were useful as a vapor probe

for sampling soil gas. Field meters provide convenient and affordable ***screening tool*** *for collection soil gas, with the following advice:*

- *Use a carbon trap to separate methane from other hydrocarbons.*
- *Must watch for leaks in the sampling system.*
- *Collect duplicate samples for analysis only after meter readings stabilize.*