FINGERPRINTING LANDFILL GAS

Richard W. Prosser, P.E.

ABSTRACT

Determining the source of methane gas occurring in soil is not always easy. There are several possible sources. The primary ones are: 1) Natural gas (pipeline gas), 2) Naturally occurring methane gas (i.e., well casing gas), 3) Landfill gas, and 4) Other biogas (swamp gas). This paper discusses tests that can be used to help determine the source of the gas.

INTRODUCTION

When measurements are made that indicate elevated methane gas concentrations in the soil, determining and correcting the source of the problem is essential. There are several techniques that can be used to help characterize the gas to determine the source. These include:

1. Looking at different constituents in the gas including:
    - Benzene
    - Hydrogen sulfide
    - Chlorinated hydrocarbons
    - All non-methane petroleum hydrocarbons (C_2+)
    - Helium
    - Hydrogen
    - Glycol
    - CO_2
    - Ethyl or methyl mercaptan
    - Organic acids
2. Determine the carbon isotope composition (expressed as $\delta^{13}C$) in the methane. Carbon is composed of a mixture of two stable isotopes, ^{12}C and ^{13}C. The ratio of $^{12}C/^{13}C$ is about 99:1. $\delta^{13}C$ is calculated as follows:

    $\delta^{13}C = [(R_s - R_r)/R_r] \times 1000\%$

    $R_s = C^{13}/C^{12}$ sample

    $R_r = C^{13}/C^{12}$ Reference (1)
3. Measuring soil vapor concentration and graphing the isograms to identify the origination of the source
4. Measuring the BTU value of the gas

Richard W. Prosser, President, GC Environmental, Inc., (714) 632-9969

DISCUSSION

Gases from different sources will tend to have different constituents present. The key constituents that each of the gases from the different sources have are:

Pipeline Gas

Typically pipeline gas may contain helium as a tracer gas (check with the local utility). It also contains an odorant (ethyl or methyl mercaptan), has low sulfur content (3.5 ppm H_2S maximum), can have benzene and other straight chain hydrocarbons, does not contain chlorinated hydrocarbons, and may have trace quantities of triethylene glycol from gas dehydration. The $\delta^{13}C$ is typically between -10 and -40[(1)].

Naturally Occurring Methane Gas

Naturally occurring methane gas may have elevated quantities of straight chain hydrocarbons, can have elevated sulfur content (H2S), no chlorinated hydrocarbons, and high benzene. There is no oxygen in the raw gas.

Landfill Gas

Probably the best tracers for LFG are the chlorinated hydrocarbons. Other characteristics include: low non-methane straight chain hydrocarbons (C_2+), low benzene, no helium, and BTU value of the gas is typically (but not always) less than 600 BTUs/Ft^3. The $\delta^{13}C$ value for LFG is not well defined. Based on other biogas sources $\delta^{13}C$ typically ranges from -50 to -90[(1)]. Biogas may have organic acids and hydrogen present.

The lack of oxygen can also be used as an indicator of the presence of LFG. Often times the soil outside a landfill has no measurable methane, but there is also no measurable oxygen. It is hypothesized that methanotrophs consume both the oxygen and methane. The remaining gases would be nitrogen, carbon dioxide and water. The tracer gases to look for in this instance would be other NMOCs and chlorinated hydrocarbons.

One complicating factor is that methanotrophs can cometabolize chlorinated hydrocarbons. This will help deplete chlorinated hydrocarbons from the soil.

Other Biogas (Swamp Gas)

No chlorinated hydrocarbons, low C_2+ hydrocarbons, mostly CO_2 and methane with some H_2S.

DATA INTERPRETATION

Interpreting analytical results is not always easy because some components are in all four gases, or can be if biodegradation occurs in the soil.

Most problems related to fingerprint gases relate to differentiating LFG from natural gas, although when two landfills are near each other it may be necessary to determine which one the gas came from.

Using the above techniques can help identify the source. **Tables 1 and 2** shows some generalized information on how to interpret some of the analytical information.

TABLE 1
GAS CHARACTERISTICS ASSOCIATED WITH VARIOUS GASES

Gas Characteristic	Pipeline Gas	Naturally Occurring Methane	Landfill Gas	Biogas
Benzene	Low to High	Low to High	<10 ppm	0
H_2S	<3 1/2 ppm	Trace to High	Typically <100 ppm	0
RCL	None	None	Numerous	None
C_2+	Numerous	Numerous	Some/Slight	Some/Slight
Helium	Yes	No	No	No
Glycol	Yes	No	No	No
CO_2	Yes	Yes	Yes	Yes
Ethyl or Methyl Mercaptan	Yes	No	No	No
$\delta^{13}C$	--	--	--	--
BTU Value BTU/Ft^3	≈1000	≈800-1500	< 600	<650

TABLE 2
VALUE RANGES OF SELECTED CARBONACEOUS MATERIALS ON THE PDB CARBON ISOTOPE SCALE (1)

Carbonaceous Materials	$\delta^{13}C$ Value Range
Inorganic Carbon	
Marine Limestones	5 to -5
Atmospheric Carbon Dioxide	-8 to -10
Diamond Carbon	0 to -10
Carbon in Living Organisms	
Marine Plants, Vertebrates & Invertebrates	-9 to -20
Marine Plankton	-17 to -30
Lipid Fraction of Marine Plants	-18 to -23
Land Plants	-8 to -19 and -21 to -30
Lipid Fraction of Land Plants	-30 to -31
Hydrocarbon Source Materials	
Organic Carbon in Recent Sediments	
Marine	-18 to -29
Non-Marine	-27 to -32
Organic Carbon Clastic Rocks	-25 to -33
Coal	-20 to -30
Hydrocarbons	
Petroleum	-21 to -35
Methane, All Sources	-15 to -90
Ethane	-25 to -47
Propane	-23 to -39
Butane	-27 to -38
Categories of Methane	
Commercial Gas Deposits	-27 to -78
Bacterial Methane Natural Sources	-50 to -90
"Shallow", Dry Gas Deposits	-60 to -79

Table 2 continued

Gas Associated with Oil Generation	-42 to -60
"Deep" Dry Gas	-25 to -42
Geothermal Methane	-25 to -31

CONCLUSION

Fingerprinting LFG usually will involve looking for chlorinated hydrocarbons. Other indicators include tracers not normally present in LFG (helium, ethyl or methyl mercaptan) or the $\delta^{13}C$ ratio. Another method is to plot the methane and/or oxygen concentration gradients in the soil to help pinpoint a source.

GAS CONSTITUENTS

Benzene -	Typically present in naturally occurring gas
H_2S -	In both biogas and naturally occurring gas
	High concentrations (>1% can occur in sour gas)
	LFG is typically less than 100 ppm
	Pipeline gas is always less than 4 ppm
RCL -	Chlorinated hydrocarbons - typical of solvents in landfill gas
C_2+ -	Wet gas (having more ethane, propane, butane, etc.) is more typical of pipeline or naturally occurring gas
Helium -	Helium is used by Southern California Gas Company as a tracer in pipeline gas
Glycol -	There may be trace residuals or tri-ethylene glycol in pipeline gas from the dehydration process
CO_2 -	Carbon Dioxide is common in all gas sources. However, pipeline or naturally occurring gas will normally have less CO_2 present. Aerobic bacteria in the soil can convert CH_4 to CO_2. If this occurs, the total oxygen from the CO_2 and the remaining air may be 21% (assuming the CO_2 does not convert to bicarbonate).
Ethyl or Methyl Mercaptan -	These sulfur compounds are used to odorize pipeline gas.

Gas Constituents continued

$\delta^{13}C$ -	This is a good test to determine if the source of the gas is biogenic (biogas) or thermogenic (natural gas). The range of ratios for the sources are as follows:
BTU Value -	Biogas is typically 55-65% methane (550 - 650 BTU/Ft^3) with the balance CO_2. Pipeline gas is usually between 1000 and 1100 BTU/Ft^3. Naturally occurring gas can vary widely. If the BTU value is high (greater than 1100 BTU/Ft^3) it is probably naturally occurring gas.
Organic Acids -	These are produced in the biodegradation process of biomass and are characteristic of biogas and LFG.

REFERENCE

1. Journal of Geochemical Exploration 7 (1977), pp. 155-188, Elseuer Scientific Publishing Co., Amsterdam, A.N. Fuex Bellaire Research Center, Shell Development Co., Houston, Texas.