APPLICATION OF ADVANCED CHARACTERIZATION TECHNIQUES FOR IDENTIFICATION OF THERMOGENIC AND BIOGENIC GASES

Presented by:

Jeffrey L. Pierce, P.E.
Vice President
SCS Engineers
3711 Long Beach Boulevard
Suite 900
Long Beach, California 90807-3315
(562) 426-9544
FAX: (562) 427-0805
jpierce@scseng.com

Lester J. LaFountain, Ph. D., R.G.
Site Manager
New Cure, Inc.
2550 Greenwood Avenue
Monterey Park, California 91755
(323) 727-5576
FAX: (323) 720-9905
leslaf@deltanet.com

March, 2000

APPLICATION OF ADVANCED CHARACTERIZATION TECHNIQUES FOR IDENTIFICATION OF THERMOGENIC AND BIOGENIC GASES

Jeffrey L. Pierce, P.E.
Vice President
SCS Engineers
Long Beach, California

Lester J. LaFountain, Ph. D., R.G.
Site Manager
New Cure, Inc.
Monterey Park, California

INTRODUCTION

Federal and state regulations require that landfill gas with a methane concentration exceeding 5% be prevented from migrating beyond the property boundary of a municipal solid waste landfill. Because the lower explosive limit of methane in air is 5%, subsurface migration of landfill gas can lead to the accumulation of explosive concentrations of methane in off-site structures including buildings, water meter boxes, and storm sewers.

Multi-depth subsurface monitoring probes are installed at the perimeter of a landfill to monitor for compliance with the 5% methane standard. In addition to perimeter monitoring, off-site monitoring is sometimes undertaken, often utilizing subsurface monitoring probes and water meter boxes.

Landfill gas is one of many sources of methane in the natural environment. If methane is found when monitoring near landfills, it is generally presumed that the source of the methane must be landfill gas. This presumption can result in compliance problems for the landfill owner. If the methane is actually from a non-landfill source, then there is virtually no possibility that the landfill gas control system can reduce the observed methane concentration to the 5% methane standard. If the methane is of non-landfill origin, it is necessary to conclusively determine this to be the case in order to secure regulatory exemption for the non-compliant monitoring locations. If this determination is not made, the landfill owner will incur costs and regulatory scrutiny in attempting to solve an unsolvable problem.

In the paragraphs that follow, this paper will:

- Discuss typical sources and characteristics of methane in the natural environment;
- Discuss methods of discriminating between differing sources of methane; and
- Present a case study where advanced characterization techniques were used to successfully discriminate between landfill and non-landfill sources of methane.

SOURCES OF METHANE

All methane can be divided into two categories -- thermogenic gas and biogenic gas. Thermogenic gas is derived from the thermal decomposition of deeply buried organic material as a result of geologic processes and time frames. However, biogenic gas is derived from the microbial decomposition of organic material.

Thermogenic Gas

Thermogenic gas is what is commonly referred to as natural gas and can be indigenous or it can be imported into an area by pipeline. Because thermogenic deposits are deeply buried, when thermogenic gas is found near the surface it is generally present due to:

- Indigenous gas from improperly abandoned gas or oil wells; or
- Imported gas from leaking low-pressure local gas distribution piping, leaking higher-pressure gas transmission piping, and leaking subsurface storage reservoirs.

Leaking pipes, including the individual service lines to homes, are the most common sources of imported gas. Subsurface storage reservoirs are formations which previously held indigenous gas, but are now used for temporary gas storage. They employ deep injection systems to store gas to satisfy peak, winter demands. Although it is possible for storage gas to leak directly to the surface, it is more likely that the leakage would occur at abandoned gas wells that originally served the formation or at the storage facility's gas injection/extraction wells.

Thermogenic gas is produced from organic material that was buried over millions of years ago. At its source, this gas often contains large fractions of carbon dioxide and hydrogen sulfide that must be removed to beneficiate the gas to pipeline quality. As-delivered natural gas is typically 97% to 98% methane with the balance of the gas consisting of higher molecular weight gases (e.g., ethane and propane), plus carbon dioxide, water vapor, nitrogen and oxygen. It is virtually free of hydrogen sulfide; however, trace amounts of a sulfur-containing odorant is added to give natural gas its characteristic odor.

Biogenic Gas

Biogenic gas can originate from a number of sources, including landfill gas, drift gas, swamp gas, marine sediment gas, and gas produced from anaerobic decomposition of any organic material. Important biogenic gases are discussed below:

- Landfill gas is produced from organic material that was only recently buried, typically less than 40 to 50 years, and is a mixture of methane (55% to 60%) and carbon dioxide (40% to 45%). It contains low concentrations of various non-methane organic compounds (NMOCs), typically in the range of 500 to 2,000 ppmv. Reduced sulfur compounds, principally hydrogen sulfide, are also present. As landfill gas moves away from the landfill, it is diluted by soil pore gas, which is generally air. The starting point concentrations of methane, carbon dioxide, and other landfill gas compounds are reduced through mixing with the soil pore gas.
- Drift gas is produced from organic material left behind by glacial activity. Obviously, this source is limited to areas previously covered by glaciation, and its presence can often be ruled out by geography. The organic deposits are relatively shallow and are 10,000 to one million years old. Like all biogenic gas, it consists at its point of formation of a mixture of methane and carbon dioxide.
- Swamp gas is a generic term that applies to methane produced in anoxic wet zones such as marshes, rice fields, and wetlands. The methane in swamp gas is produced from fairly recently submerged organic material.

Miscellaneous sources of biogenic methane can include methane originating from anaerobic decomposition of petroleum or waste buried outside the landfill perimeter. Petroleum hydrocarbons may be present from leaking tanks or abandoned oil wells. Waste buried outside the landfill perimeter can include municipal waste or green waste.

ELEMENTARY CHARACTERIZATION TECHNIQUES

All methane is chemically the same and consists of one carbon atom and four hydrogen atoms. Most methane characterization techniques rely on the occurrence or the lack of occurrence of other compounds with methane in a gas sample. The techniques do not examine the methane molecule itself, and as will be explained below, this causes some uncertainty in the conclusions that can be drawn. Characterization methodologies that employ evaluations on the atomic level are discussed in the section entitled "Advanced Characterization Techniques."

Helium

Landfill gas contains virtually no helium but thermogenic gas may contain helium, depending on the geological province from which the gas is derived. Most notably, thermogenic gas from the Amarillo-Wichita Uplift in northwestern Texas is well known for its helium content. Helium in the atmosphere is present in the range of 5 to 10 ppmv but when helium is present in thermogenic gas, it is typically present at concentrations in the range of 200 to 300 ppmv.

Because of the nature of the occurrence of helium, the following statements can be made:

1. If helium is present in concentrations above atmospheric level, then it is very likely that the source of the methane is thermogenic. In some situations, however, soil pore gas helium levels can naturally be as high as 100 ppmv; and
2. If helium is not present, it is not possible to rule out the presence of thermogenic gas because the:
    - Indigenous or imported thermogenic gas may not contain helium;
    - Helium may have been diluted by soil pore gas to below the level of detection; or
    - Helium may have separated from the methane during movement through the soil.

An added complication in using helium as an indicator is that laboratories often use helium as a purge gas in gas chromatographs. Strict quality control is necessary to avoid sample contamination. Most laboratories are not commonly concerned with determining the presence of helium.

Carbon Dioxide

Pipeline natural gas contains less than 2% carbon dioxide. If an undiluted gas sample has a relatively low carbon dioxide level, as indicated by a methane percentage over 60%, or there is a very high ratio of methane to carbon dioxide in a dilute sample, this is an indication that thermogenic gas may be present in the sample. The lack of carbon dioxide or low levels of carbon dioxide is not conclusive evidence that the gas is thermogenic because carbon dioxide can be removed from a biogenic gas through dissolution into water, thereby increasing its apparent methane percentage.

On the other hand, the presence of carbon dioxide in significant quantities does not rule out thermogenic gas. Indigenous thermogenic methane is sometimes coincident with carbon dioxide (at as high as 40%). Carbon dioxide can also be produced from methane as a result of aerobic decomposition, as the methane moves through the soil.

Therefore, the following statements can be made with respect to carbon dioxide:

1. High methane percentages and high-methane-to-carbon-dioxide ratios are an indication that thermogenic gas may be present, but do not conclusively demonstrate that thermogenic gas is present; and
2. The presence of carbon dioxide does not prove that the methane is of biogenic origin.

Volatile Organic Compounds

Landfill gas contains low concentrations of high molecular weight volatile organic compounds such as xylene, toluene, benzene, and vinyl chloride (Table 1). The presence of such compounds in a gas sample is often considered to be solid evidence that the gas is from a landfill, but this conclusion is not always correct. A biogenic gas that has a petroleum waste source may contain most of these compounds. Natural gas will contain at least some of the non-chlorinated compounds.

More importantly, from the perspective of developing a defensible case to present to regulators, the lack of these compounds in a gas does not rule out the presence of landfill gas. Several researchers have shown that volatile organic compounds can be biologically and/or physically removed from landfill gas as landfill gas moves through the soil. The compounds have been shown to be biologically consumed at a rate much faster than methane. This mechanism, plus dilution, can significantly reduce the starting point concentration of volatile organic compounds. The starting point concentration for volatile organic compounds may be very low at a particular landfill -- further complicating detection. In addition, research has shown that volatile organic compound concentrations in landfill gas have been decreasing in recent years at both open and closed landfills. It is believed that this phenomenon is due to lower absolute quantities of these materials reaching landfills (due to hazardous waste controls) and due to the long-term stripping of these compounds from waste in place.

In summary, the following statements can be made with respect to volatile organic compounds:

1. The presence of chlorinated volatile organic compounds is a very strong indicator that landfill gas is present in a sample;
2. The presence of non-chlorinated volatile organic compounds does not provide conclusive evidence that landfill gas is present; and
3. The lack of chlorinated or non-chlorinated volatile organic compounds in a sample provides the inference, not conclusive evidence, that the gas is from a non-landfill, biogenic source.

Sulfur Compounds

Pipeline natural gas, by specification, contains less than 4 ppmv hydrogen sulfide. Landfill gas at its source generally has a higher concentration of hydrogen sulfide. In the landfill gas database summarized on Table 1, the concentration of hydrogen sulfide averaged 26 ppmv and varied from 41 ppbv to more than 60 ppmv. Landfills containing large quantities of sulfur-containing wastes, such as wallboard (which contains gypsum or $CaSO_4 \bullet 2H_2O$), can have much higher hydrogen sulfide levels.

The presence of hydrogen sulfide in a gas sample in levels above that of pipeline gas is a good indication that the gas is not pipeline gas. An elevated hydrogen sulfide level does not rule out the possibility that the gas is an indigenous thermogenic gas or that the gas is biogenic gas from a non-landfill source. More importantly, however, from the perspective of developing a defensible case to present to regulators, low levels of hydrogen sulfide do not rule out the possibility that the gas is from a landfill. The lack of hydrogen sulfide can be explained by:

1. Low hydrogen sulfide levels in the landfill gas, in general, or in the area of the landfill near the monitoring points in particular;
2. Dilution of hydrogen sulfide to below the level of detection by soil pore gas; and
3. Removal of hydrogen sulfide by biological or physical methods as the gas passes through the soil.

Gas transmission companies put a strong odorant in their gas to aid in detecting and locating gas leaks. The compounds are sulfur compounds, such as thiophene, and such compounds are not commonly found in landfill gas. If such a compound is present, this almost certainly indicates the presence of pipeline gas. If such a compound is not present, pipeline gas cannot be absolutely ruled out because the compound could be biologically or physically removed during its movement through the soil or the compound could have been diluted below its limits of detection. The lack of such a compound does not rule out the possibility of indigenous thermogenic gas, because the compound is a tracer added to thermogenic gas by the gas company.

In summary:

1. If a tracer compound, such as thiophene is present, then pipeline gas is present in the sample;

2. If a tracer compound is not present, this does not rule out the possibility of pipeline gas and offers no insight into the presence or absence of indigenous thermogenic gas;
3. The lack of hydrogen sulfide does not rule out the presence of landfill gas; and
4. The presence of hydrogen sulfide does not prove that the gas is of landfill origin. Hydrogen sulfide can be present in an indigenous thermogenic gas or in a non-landfill biogenic gas.

Low Molecular Weight NMOCs

Thermogenic gas always contains some ethane, propane, butane, pentane, and hexane. These compounds consist entirely of carbon and hydrogen. Although methane has one carbon molecule, these molecules have two, three, four, five, and six carbon molecules, respectively. Landfill gas is not devoid of these compounds, but they are generally present in lower concentrations. A typical thermogenic gas would, for example, have an ethane concentration of over 20,000 ppmv (undiluted). Landfill gas is unlikely to have an undiluted ethane concentration of more than 2,000 ppmv, and the concentration is more commonly <100 ppmv.

Therefore, in dealing with these compounds:

1. High concentrations of low molecular weight NMOCs are fairly conclusive evidence that thermogenic gas is present;
2. The presence of relatively low concentrations of these compounds is not absolutely conclusive that the gas is of landfill origin; and
3. The complete lack of these compounds infers, but does not confirm, that the sample represents a non-landfill, biogenic source.

Summary

The landfill owner must conclusively demonstrate that the methane at the compliance monitoring point is not landfill gas. Under certain circumstances, one or more of the above-discussed techniques can allow this determination to be made. Note however that many of the determinations are not either/or determinations. For example, if helium is present it is almost certain that the gas is partially or wholly thermogenic, but if helium is not present, the gas may or may not be thermogenic.

Some of the above techniques provide good circumstantial evidence, but the conclusions drawn from the evidence are arguable. If volatile organic compounds are not present in a sample, the landfill owner can argue that this demonstrates that the gas is of non-landfill origin. The regulators can argue that the determination is not conclusive, pointing out the possibility of volatile organic compound degradation or absorption as the gas moves through the soil.

Table 2 provides a summary of the conclusions which can be drawn from the elementary characterization indicators discussed above. Table 2 is a simplistic summary which is intended to show the general strengths and weaknesses of each indicator, and is not a substitute for a thorough evaluation of actual concentrations of the compounds and of what is known about the landfill and the area surrounding the landfill.

Another approach that can be employed to attempt to reduce ambiguity is to collect and analyze "control" samples of pipeline gas, landfill gas, storage gas, indigenous thermogenic gas or other gases in the vicinity of the landfill. The samples can then be cross analyzed for key parameters. The natural gas industry commonly checks their gas for helium and low molecular weight compounds but not for volatile organic compounds. The landfill industry commonly analyzes for volatile organic compounds, but not for helium or low molecular weight compounds. File information will generally not provide the data that is required to establish control samples.

All of the above-discussed techniques rely on analysis of compounds that travel coincident with the methane in the sample. The methods do not address whether the methane from different sources is actually different. All of the above-discussed techniques operate on the molecular level. The following paragraphs discuss techniques that are employed on an atomic level. The techniques look at the differences that exist in atoms of the methane molecule itself and these techniques are much less ambiguous.

ADVANCED CHARACTERIZATION TECHNIQUES

Overview

Carbon and hydrogen isotopic analyses can be employed to distinguish between various sources of methane. Both the stable isotopes and the radiogenic isotopes can be used for methane characterization. Coleman[1] discusses the theory and application of isotopic analyses in identifying the source of methane. The paragraphs that follow summarize the theory and application of isotopic analyses. However, the reader is deferred to Coleman's paper for a more thorough discussion.

Carbon and hydrogen each have three naturally occurring isotopes. Two isotopes are stable and one is radioactive. Carbon-12 (^{12}C) and Carbon-13 (^{13}C) are the stable isotopes of carbon. On the average, ^{12}C is 100 times more common in nature than ^{13}C. Carbon-14 (^{14}C) is carbon's radioactive isotope. By comparison to ^{12}C and ^{13}C, ^{14}C is extremely rare. Hydrogen-1 (^{1}H or protium) and

---

[1] Coleman, D.D. 1994. Advances in the Use of Geochemical Fingerprinting for Gas Identification. American Gas Association Operations Conference, San Francisco, CA. May 9-11.

Hydrogen-2 (^2H or deuterium) are the stable isotopes of hydrogen with ^1H being the common stable isotope. Hydrogen-3 (^3H or tritium) is hydrogen's radioactive isotope.

Use of Stable Isotopes of Carbon and Hydrogen

The ratio of the stable isotopes in a sample is expressed using a δ (delta) notation. The ratio of ^{13}C to ^{12}C as compared to an international reference standard is designated as $\delta^{13}C$. Similarly, δD is the ratio of ^2H to ^1H as compared to an international reference standard. The δ value in either instance is the difference, expressed in parts per thousand or per mil (‰), between the isotopic ratio of the sample and that of an internationally accepted standard. Negative numbers mean that the sample is enriched in the lighter isotope relative to the standard, and positive numbers mean that the sample is enriched in the heavier isotope relative to the standard.

Stable isotopes can be used to establish the source of a gas by comparing the plotted position of $\delta^{13}C$ of CH_4 versus δD of CH_4 for a sample gas against a plot of typical values for methane from known sources. Coleman[1] provides a plot (reproduced here as Figure 1) of typical $\delta^{13}C$ of CH_4 versus δD of CH_4 values for methane from various known sources. Coleman's research shows that methane produced in different ways has differing ratios of the stable isotopes of carbon and hydrogen. As can be seen on Figure 1, Coleman divides all of the methane data he has collected into three categories:

- Subsurface microbial gas (deep-sea sediment and drift gas);
- Thermogenic gas (natural gas and coal bed gas); and
- Near-surface microbial gas (marsh gas and landfill gas).

The envelopes on Figure 1 cover the typical ranges of $\delta^{13}C$ of CH_4 and δD of CH_4 Coleman found for actual methane samples from sources of known origin. As a result, Figure 1 can be used to determine the source of a methane sample of unknown origin. If, for example, a methane sample from an unknown origin has a δD of CH_4 of -200 and a $\delta^{13}C$ of CH_4 of -40, it would plot in the thermogenic range, and one would conclude that the methane was thermogenic rather than being from one of the other two sources of gas.

The advantages of the use of the stable isotopic analysis are several, but the four most important are:

1. It allows one to differentiate between thermogenic gas and landfill gas without being concerned about the presence or absence of coincident compounds. It eliminates all arguments about biological and physical phenomena which may or may not cause changes to the coincident compounds;
2. It is possible to divide biogenic gas into at least two broad categories (near-surface biogenic gas and subsurface biogenic gas);
3. It is sometimes possible to determine whether the source of the thermogenic gas is indigenous versus imported because thermogenic gases from different regions often have different stable isotopic ratios. If a control sample of pipeline or storage gas is taken, the control sample's $\delta^{13}C$ of CH_4 and δD of CH_4 can be compared to the sample gas's $\delta^{13}C$ and δD of CH_4; and
4. In some cases, thermogenic gas may be mixed with landfill gas at a monitoring point. If control samples of the landfill gas thermogenic gas are collected, it is possible to roughly determine the blend between landfill gas and thermogenic gas in a gas sample. This is possible since the ratio of the gases is not affected by dilution.

Use of Radiogenic Isotopes of Carbon and Hydrogen

A second isotopic tool that can be used in gas characterization is the use of radiogenic isotopes. The methane in landfill gas is produced from water and carbon dioxide originating from the recent atmosphere. Atmospheric carbon and hydrogen have elevated radiogenic isotope levels due to the effect of cosmic rays and due to atmospheric testing of radioactive explosive devices. The hydrogen and carbon in the methane in landfill gas will have higher levels of the radiogenic isotopes than the levels found in methane from older geologic sources (i.e., "natural gas" associated with petroleum deposits having an age in excess of tens of millions of years). Pure natural gas has virtually no ^{14}C or ^3H. The half-life for ^{14}C is about 5,700 years, and the half-life for ^3H is about 12 years.

A metric known as percent modern carbon (pMC) is used to measure the presence of ^{14}C. The ratio of ^{14}C in a sample to the pre-1950 atmospheric ^{14}C level is the pMC of the sample. Landfill gas has pMC values in the range of 115 to 150 percent. Thermogenic gases have pMC values near zero. Coleman[1] also reports that glacial drift gas has pMCs ranging from 0 to 30, and that swamp and marsh gas are generally in the range of 85 to 125.

The ^3H levels in natural gas are expressed through a metric known as tritium units (TU). TU levels in natural gas are near zero. The TU levels in landfill gas are in the range of 1,000 to 20,000. Swamp gas has lower TU levels than landfill gas, since the hydrogen in swamp gas methane is exclusively from very recent rainfall. Current atmospheric TU levels are very low and are in the range of 5 to 10 TU.

Table 3 summarizes the conclusions which can be drawn with respect to gas origin based on isotopic testing.

OII LANDFILL CASE STUDY

Overview

The former Operating Industries, Inc. (OII) Landfill is a closed refuse disposal site located in Monterey Park, California. The OII Landfill accepted about 30 million tons of municipal solid waste and 300 million gallons of industrial waste between 1948 and 1984. OII was designated as a Superfund Site in 1986, and remediation work at the landfill is currently being performed by New Cure, Inc. (NCI) under the supervision of the United States Environmental Protection Agency (USEPA). In compliance with USEPA requirements, NCI maintains a network of gas monitoring probes (GPs) around the perimeter of the OII Landfill. The purpose of the GPs is to detect migration of landfill gas away from the landfill. In addition to the perimeter GPs, a number of off-site GPs and water meter boxes are currently being monitored.

The perimeter GP network consists of 38 GPs ranging in depth from 50 ft to 200 ft. The depths vary, based on the depth of the waste in the vicinity of the individual GPs. Each probe location (Figure 2) consists of a multiple completion containing up to six screened sections at different depths, allowing for the separate measurement of gas characteristics at different depths. The individual screened sections are designated P1 through P6, with the deepest screened section designated P6.

Several gas probes are located off the landfill property in the residential and commercial areas to the south and east of the landfill. They vary in depth from 25 ft to 100 ft and have from one to three screened sections. The off-site probes are also located on Figure 2.

Approximately 50 water meter boxes are monitored on a quarterly basis. The boxes are located adjacent to the street curb and consist of water company-installed, in-ground water meters enclosed in small, vented concrete vaults. The meter boxes monitored by OII are located in a residential area along the south perimeter of the landfill. The water meter boxes are not part of the OII compliance monitoring system but are monitored to provide additional data.

The perimeter GPs represent OII's long-term landfill gas compliance monitoring network and it is of critical importance that these GPs measure landfill gas alone. If other sources of methane contribute to the methane found in these GPs, then these GPs would give false high readings from a landfill gas compliance perspective. The presence of even small quantities of methane from non-landfill sources could easily cause the landfill gas compliance limit of 5 percent methane to be exceeded.

It was suspected that not all of the methane detected in some of the monitoring points at the OII Landfill was of landfill origin. Factors that lead to these suspicions included:

1. Methane concentrations in a few GPs sometimes exceeded 60% (GP-3 through GP-6, GP-11, GP-12, GP-14, and GP-15), and were sometimes coupled with high gas pressures (20 inches of water column [in w.c.], or above);
2. The detection of methane at off-site monitoring points when no methane was detected at monitoring points between the landfill and the measured location;
3. The location of a natural gas compression/subsurface storage facility adjacent to the western boundary of the landfill; and
4. The existence of a former operating oil field close to or within the current landfill footprint as well as a currently operating oil wells as close as 1,000 feet from the landfill. There are a number of abandoned oil wells in the area.

A comprehensive sampling and analysis program was undertaken between July 1998 and March 1999 that focused on suspicious GPs. Both stable isotopic and radiogenic isotopic analyses were employed. Stable isotopic analysis is less expensive and was applied to all samples. Radiogenic isotopic analysis is more expensive and was used to confirm the stable isotopic analyses, and to clarify a few ambiguities left by the stable isotopic analyses. Stable isotopic analyses were run on 65 gas samples and included the determination of:

- $\delta^{13}C$ of CH_4 (isotopic ratio of ^{13}C to ^{12}C);
- δD of CH_4 (isotopic ratio of ^{2}H to ^{1}H); and
- $\delta^{13}C$ of CO_2.

The gas composition was also analyzed in each of these samples, including the following elements and compounds:

- oxygen
- helium
- nitrogen
- argon
- carbon monoxide
- carbon dioxide
- hydrogen
- methane
- ethane
- ethylene
- propane
- butane
- pentane
- hexane

Samples were drawn into aluminized Cali-5 Bond bags and were analyzed by ISOTECH Laboratories of Champaign, IL.

A total of 20 samples were subjected to radiogenic isotopic analysis, including ^{14}C of CH_4, ^{14}C of CO_2, and ^{3}H of CH_4. These samples were collected in canisters because of the larger quantity of gas needed to support the analysis. ISOTECH also performed these analyses.

The data from several of the most interesting samples will be discussed in the following paragraphs.

Control Samples

$\delta^{13}C$ of CH_4 versus the δD of CH_4 from gas samples of known origin at the OII Landfill were plotted (Figure 3) for evaluation. The envelopes for thermogenic gas and landfill gas are the envelopes developed by Coleman (see Figure 1). Several control samples were taken, analyzed and plotted:

- A sample of landfill gas taken at the landfill flare station was known to be virtually 100% landfill gas. As expected, it plotted within the landfill gas envelope;
- The sample designated Montebello Reservoir was a sample of gas provided by the Southern California Gas Company (Gas Company) from the underground storage reservoir adjacent to OII;
- The sample of gas designated Montebello Oil Field was provided by an oil/gas production company operating wells adjacent to the landfill; and
- The sample designated 829 Ashiya was a sample drawn from a water meter box in the residential area south of the landfill. The gas at 829 Ashiya was originally tested because it was suspected that the gas was from a non-landfill source. The Gas Company then found a pipeline gas leak at this location. Upon repair of the leak, the methane in the meter box disappeared and did not return. The absolute confirmation that 829 Ashiya was thermogenic gas allowed us to consider 829 Ashiya to be a control sample.

All three samples of thermogenic gas lie within the thermogenic gas envelope. It is interesting to note that the samples from the Montebello Reservoir and 829 Ashiya (both being imported thermogenic gas) clustered near the same location, and that the sample from the Montebello Oil Field (an indigenous thermogenic gas) plotted away from these samples. This indicates that the imported thermogenic gases (Montebello Reservoir and Ashiya) are not the same as the local Montebello Oil Field. However, all three samples of themogenic gas fall within the area of thermogenic gas defined by the envelope in Figure 3.

Discussion of Isotopic Data from Specific Samples

The clear difference between landfill gas and thermogenic gas can be seen from the raw analytical data from selected samples (Table 4):

- Both the imported and the indigenous thermogenic gas (Montebello Reservoir and Montebello Oil Field) have pMCs below 1 while the landfill gas (Flare Station) has a pMC of 117;
- The tritium levels of the thermogenic gas are much lower (<20 TU versus 1,390 TU) for the landfill gas;
- It can also be seen that ethane (C2) propane (C3), butane (C4) and pentane (C5) are much higher in the thermogenic gas than in the landfill gas;
- Helium was non-detect (<20 ppmv) in the landfill gas and the indigenous thermogenic gas, but it was 190 ppmv in the imported gas. The Montebello Reservoir is supplied with helium-bearing gas from Texas; and
- The thermogenic gases all have relatively low δD of CH_4 values (greater than -200) while the value for landfill gas is less than -280. The relative differences between the δD of CH_4 and $\delta^{13}C$ of CH_4 of the samples can be seen graphically on Figure 3.

The following discussion presents examples of representative interpretations of data from specific monitoring probe sampled at OII. Stable isotope evaluations were conducted using a diagram (Figure 4) derived from Coleman's work.

GP-4 (P5) is an example of a GP screen section containing virtually 100% indigenous thermogenic gas:

- The pMC is 2.5, the tritium level is less than 20 TU; and
- It has elevated C2 through C6 levels.

The stable isotopic data for GP-4 (P5) puts it well within the thermogenic range as shown by the plotted positions (Figure 4) of the δD of CH_4 and $\delta^{13}C$ of CH_4. It is interesting to note that the methane content of GP-4 (P5) was only 65% (despite its being 100% thermogenic) and that helium was a non-detect.

GP-4 (P2) is a good example of a difficult to characterize sample. At first view, it appears to be 100% landfill gas because the methane content is only 45% and the carbon dioxide content is 26%. The C2 through C5 levels are elevated, but the C2 level is certainly much lower than that which would be expected from thermogenic gas (even after dilution is considered). The pMC level of 101 clearly indicates, however, that this sample is either not landfill gas or that it is landfill gas blended with a much older type of gas. The stable isotopic data (Figure 4) clearly support the conclusion that this gas is a blend of thermogenic gas and landfill gas because it plots at the edge of the landfill gas envelope.

GP-6 (P4) is an example of a sample that is virtually 100% landfill gas. The sample's δD of CH_4 and $\delta^{13}C$ of CH_4 plots within the landfill gas envelope, close to the flare station data point, and it has a very high pMC of 133.

MW 9-B is a sample that could easily be mistaken for landfill gas if isotopic analysis was not employed. MW 9-B is an off-site probe that was sampled in 1998 and about 10 months later in 1999. Both samples (Table 4) have carbon dioxide present, low or non-detect levels of C2 through C5, and non-detect levels of helium. Despite the above indications, the 1999 sample plots clearly within the thermogenic envelope (Figure 4). It has a somewhat elevated pMC of 9.6 (i.e., higher than the near zero of thermogenic gas). It is concluded that this sample is almost 100% thermogenic gas. The 1998 sample had a much lower methane content (2.5% versus 21.6%), and had a moderate pMC of 52.8. The pMC level implies a blend of thermogenic gas and a newer gas. The plot of the stable isotopes puts the sample just to the left of the thermogenic envelope. The conclusion, based on Coleman's diagram, (Figure 1), is that this sample is a blend of thermogenic gas and a non-landfill biogenic gas. It can also be concluded that the amount of thermogenic gas varies over time – as does its methane content.

Off-Site Probe 3D (10') is an example of the fact that it is not always possible to rely on stable isotopic analyses alone. The stable isotopic ratios plot (Figure 4) between the thermogenic envelope and the landfill gas envelope based on the strength of its δD of CH_4 of 252. The implication is that the sample is a blend of thermogenic gas and landfill gas. The sample shows two suspicious characteristics. First, there is a severe oxygen deficiency with respect to nitrogen and argon. The nitrogen and argon levels indicate that oxygen should be about 20%, rather than less than 2%. The uptake of oxygen implies biological activity, and the possible conversion of some of the methane to carbon dioxide. The high negative value for $\delta^{13}C$ of CO_2 of -37.43 also implies biological activity.

Biological activity will change the stable isotopic ratios in the methane left behind. Biological oxidation of methane preferentially consumes lighter isotopes. As a result of this biofractionation, the unoxidized methane that remains in a sample appears to be enriched with respect to the heavier isotopes. The product CO_2 in a sample is enriched with the lighter isotopes. This causes a methane to have lower absolute negative δD of CH_4 and $\delta^{13}C$ of CH_4 values thereby moving a methane from the landfill gas envelope toward the thermogenic envelope. It also causes the $\delta^{13}C$ of CO_2 of a methane sample to decrease.

GP-11 (P4) is a more dramatic illustration of the problem of methane oxidation. Samples were taken from GP-11 (P4) in 1998 and 1999. The 1999 sample shows an oxygen deficiency while the 1998 sample does not. The 1998 stable isotopic plot puts GP-11 (P4) in the landfill gas envelope based on its δD of CH_4 of –281. The 1999 sample plots in the thermogenic range based on its δD of CH_4 of –207. The 1999 sample was subjected to a pMC analysis after the 1999 stable isotopic results provided contradictory information. The pMC of 137 proves beyond a doubt that this sample is landfill gas. The stable isotope shift in the 1999 sample was due to oxidation. Where contradictory information is seen, the pMC analysis eliminates the confusion.

Commentary on Isotopic Testing

Radiogenic isotopic testing is significantly more expensive than stable isotopic testing. It is suggested, if time allows, that stable isotopic testing be used to screen suspicious samples, and that radiogenic tests then be used to provide final confirmation between landfill gas and thermogenic gas -- the radiogenic isotopic testing is certainly necessary if any indication of methane oxidation exists.

Tritium is an interesting indicator and may be of use on other investigations. It was of limited use at the OII investigation. The thermogenic samples, as expected, had very low tritium levels and this was helpful in corroborating the ^{14}C of CH_4 test results. The ^{14}C of CH_4 test is, however, absolutely definitive, and corroboration of its results was not really necessary.

The TU level at the flare station was 50 to 100 times higher than the level found in the gas known to be of thermogenic origin, as would be expected. However, the TU levels at the monitoring points should have been similar to the flare station, but they were generally one fifth to one tenth of the levels seen at the flare station. The variations were not explainable by air dilution or another decipherable factor. Tritium's relatively short half-life and the rapidly declining tritium levels in the atmosphere (since suspension of hydrogen bomb testing) adds to the complexity of the interpretation of TU data.

Until more work is done with tritium, it is suggested that tritium be given secondary consideration in characterization investigations. An exception to this statement is that tritium can and should be used as an aid to differentiate between landfill gas and swamp gas. This differentiation cannot always clearly be made using pMC alone.

CONCLUSIONS

The former OII Landfill lies in a location adjacent to a natural gas deep injection storage facility along with abandoned oil wells and an active oil field that would lead one to suspect that some of the monitoring probes might be influenced by non-landfill gas. Isotopic analyses, of both stable and radiogenic isotopes, were used successfully at OII to demonstrate that some of the perimeter and off-site monitoring locations were impacted by methane from non-landfill sources. Without the use of isotopic analysis, it would have been difficult to identify indigenous thermogenic gas as the source of much of this gas. In addition, the use of isotopic analysis countered the perception that the lack of helium ruled out thermogenic gas. Isotopic analysis removed ambiguities that would have remained using only elementary characterization techniques.

TABLE 1.
CONCENTRATIONS OF VOCs and H_2S
IN LANDFILL GAS AT 27 SOUTHERN CALIFORNIA LANDFILLS (in ppb)

Compounds	Average	Minimum	Maximum
Acetonitrile	1,906	27	13,925
Benzene	2,549	432	16,638
Benzyl Chloride	201	10	2,500
Chlorobenzene	569	54	5,143
Dichlorobenzenes	1,354	335	5,427
1,1-Dichloroethane	2,138	100	13,478
1,2-Dichloroethane	264	10	3,407
1,1-Dichloroethene	181	11	958
Dichloromethane	9,733	14	49,975
Hydrogen sulfide	26,312	41	63,624
Tetrachloroethylene	2,934	54	28,200
Tetrachloromethane	41	1	335
Toluene	26,873	7,822	60,025
1,1,1-Trichloroethane	541	35	5,993
Trichloroethylene	1,457	42	13,600
Trichloromethane	50	2	335
Vinyl chloride	1,802	218	15,754
Xylenes	19,190	6,394	47,733

TABLE 2. SUMMARY OF CONCLUSIONS WHICH CAN BE DRAWN FROM ELEMENTARY CHARACTERIZATION INDICATORS

		Type of Gas		
Compound	**Criteria**	**Landfill**	**Thermogenic**	**Biogenic**
Helium	Present at >100 ppmv	No	Yes	No
	Absent	Inconclusive	Inconclusive	Inconclusive
CO_2	Present	Inconclusive	Inconclusive	Inconclusive
	High CH_4% or high CH_4/CO_2 ratio	Fair indicator of absence or only partial presence	Fair indicator of presence	Fair indicator of absence or only partial presence
	Absent	Very unlikely	Extremely likely	Very unlikely
VOC	Chlorinated are present	Very Likely	Extremely unlikely	Very unlikely
	Chlorinated are absent	Inconclusive	Inconclusive	Inconclusive
	Non-chlorinated present	Generally inconclusive	Generally inconclusive	Generally conclusive of absence
	Non-chlorinated are absent	Inconclusive	Inconclusive	Inconclusive
Sulfur Compounds	Tracer present	No	Yes	No
	Tracer not present	Inconclusive	Inconclusive	Inconclusive
	H_2S absent	Inconclusive	Inconclusive	Inconclusive
	H_2S present	Very possible	Not pipeline but may be indigenous	Possible depending on source
NMOC (C2-C6)	High concentration of C2	No	Yes	No
	Moderate concentration of C2	Inconclusive	Inconclusive	No
	Low or absent C2 concentration	Possible	Possible	Possible

TABLE 3. SUMMARY OF CONCLUSIONS WHICH CAN BE DRAWN FROM ISOTOPIC CHARACTERIZATION INDICATORS

		Type of Gas			
Compound	**Criteria**	**Landfill**	**Thermogenic**	**Drift**	**Swamp**
Stable C and H Isotopes	δ ^{13}C of CH_4	-40 to -62	-30 to -58	-60 to -90	-40 to -62
	δ ^{13}C of of CH_4	-265 to -350	-110 to -245	-170 to -240	-260 to -350
Radiogenic C and H Isotopes	Percent Modern Carbon (pMC)	115 to 150%	Near 0%	< 30%	85 to 125%
	Tritium Units (TU)	1,000 to 20,000	Very low (<10)	Very low (<10)	Very low (<20)

Note: Mixtures of gases, such as thermogenic gas and landfill gas, can best be established by comparing sample results to the results from samples of known gases. A δ ^{13}C of CH_4, between -245 to -265 almost certainly indicates a mixture of thermogenic gas and landfill gas (or swamp gas); however, the band of δ ^{13}C of CH_4 which can indicate a mixture of these gases is generally much greater.

TABLE 4. OII LANDFILL: SELECTED DATA FROM ISOTOPIC ANALYSES

SAMPLE LOCATION	He (ppm)	Ar (%)	O_2 (%)	CO_2 (%)	N_2 (%)	CH_4 (%)	C2 (ppm)	C3 (ppm)	C4 (ppm)	C5 (ppm)	C6+ (ppm)	$\delta^{13}C$ of CO_2 (o/oo)	$\delta^{13}C$ of CH_4 (o/oo)	δD of CH_4 (o/oo)	^{14}C of CH_4 (pMC)	Tritium of CH_4 (TU)
Flare Station	ND	0.64	9.30	19.30	49.59	20.95	27	ND	ND	ND	220	9.16	-57.30	-283.8	117	1390
GP-4 (P2)	ND	0.29	4.41	26.2	22.98	45.25	4300	2200	940	264	600	3.06	-54.94	-265.6	101	153
GP-4 (P3)	ND	0.27	4.63	25.6	20.62	45.96	15400	8200	3700	990	470	-23.28	-44.91	-196.9		
GP-4 (P5)	ND	0.28	5.72	1.7	22.09	65.00	25900	15100	6800	2430	1900	6.28	-42.59	-179.1	2.5	18.8
GP-5 (P6)	ND	0.97	20.24	0.12	75.06	3.35	1400	760	320	97	72		-42.46	-181.2		
GP-6 (P4)	ND	ND	ND	36.5	0.43	63.05	97	ND	ND	ND	360	15.28	-56.16	-278.4	133	196
GP-11 (P4) (1998)		0.36	6.59	17.2	27.00	48.80	120	54	ND	ND	68	1.98	-54.90	-281.4		
GP-11 (P4) (1999)	ND	0.92	10.25	12.9	74.78	1.17	20	ND	ND	ND	23	-3.14	-37.27	-207.5	137	
3D (10')		0.98	1.62	13.20	76.65	7.55	ND	ND	ND	ND	ND	-37.43	-52.07	-252.5		
MW 9-B (1998)	ND	1.11	0.20	8.31	87.91	2.47	ND	ND	ND	ND	ND	-36.42	-59.57	-166.1	52.8	164
MW 9-B (1999)	ND	0.86	0.16	8.94	68.42	21.61	98	ND	ND	ND	39	-45.32	-48.45	-194.2	9.6	57.2
829 Ashiya		0.97	21.81	0.07	75.74	1.38	240	38	ND	ND	ND		-42.56	-185.9		
Montebello Oil Field	ND	0.02	0.32	0.88	1.52	94.29	19700	6000	1840	400	1600	10.13	-50.12	-190.9	0.7	<13.1
Montebello Reservoir	190	0.01	0.06	0.82	1.33	94.15	28900	4800	1380	460	540	10.62	-43.50	-190.1	0.6	<20.1

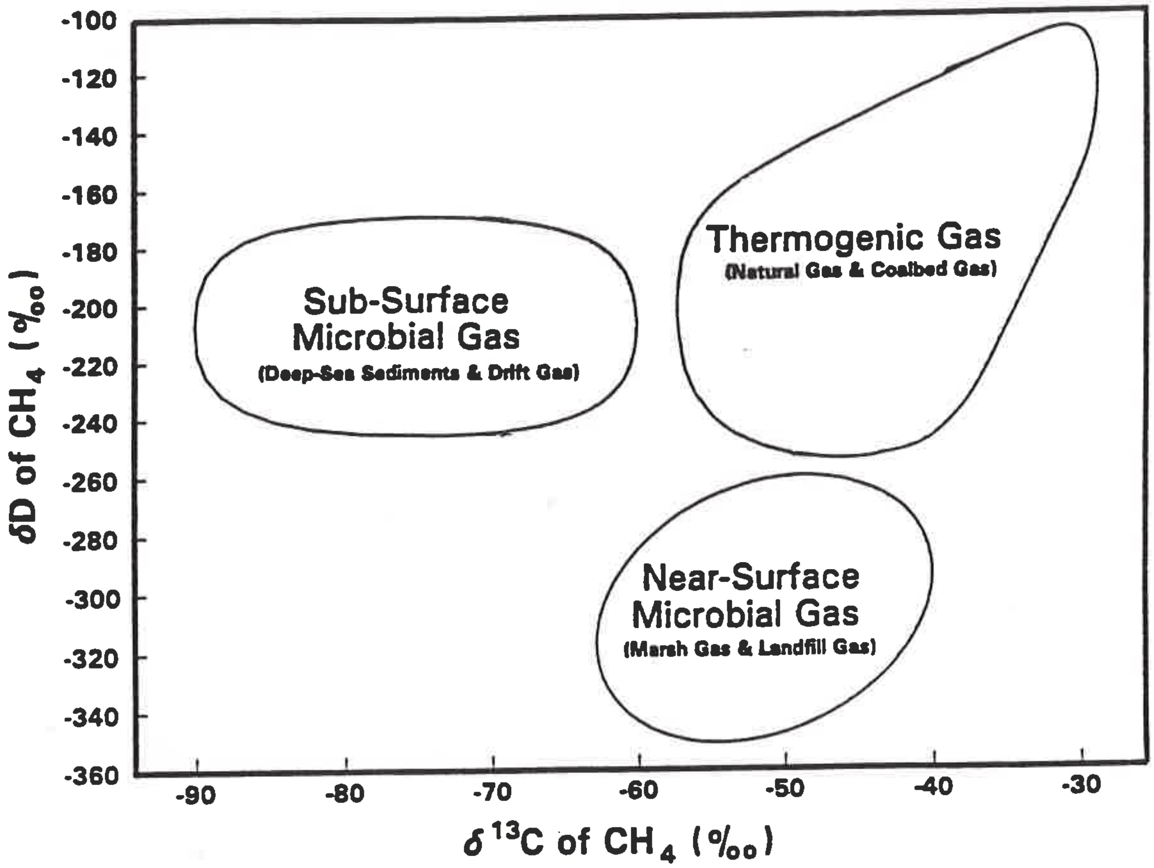
Notes:

ND=below non-detect level

Blank=no analysis to report

FIGURE 1.

CARBON AND HYDROGEN ISOTOPIC COMPOSITIONAL TYPICAL RANGES OF METHANE FROM DIFFERENT SOURCES



Source: "Advances in the Use of Geochemical Fingerprinting for Gas Identification," Coleman (1994).

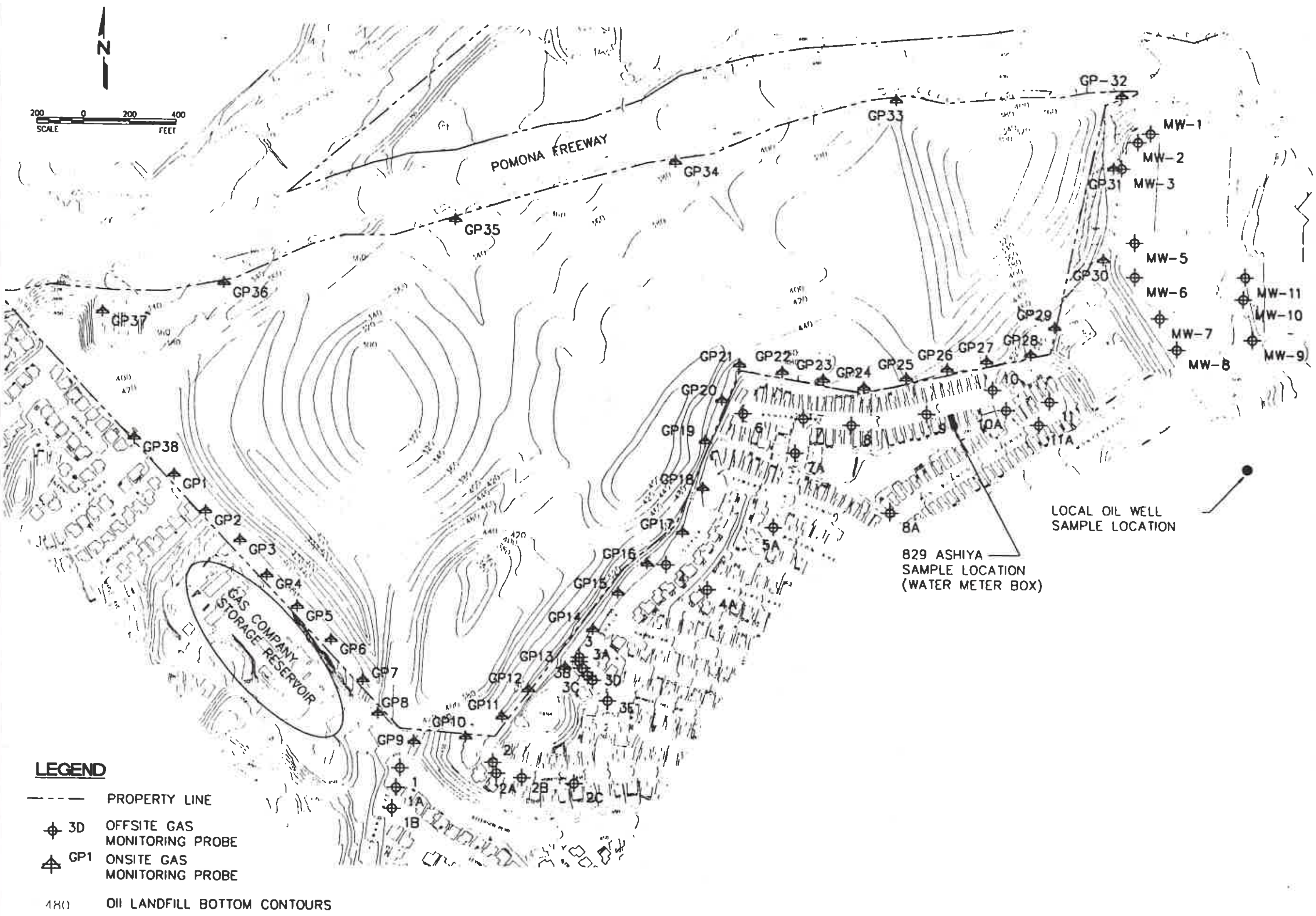
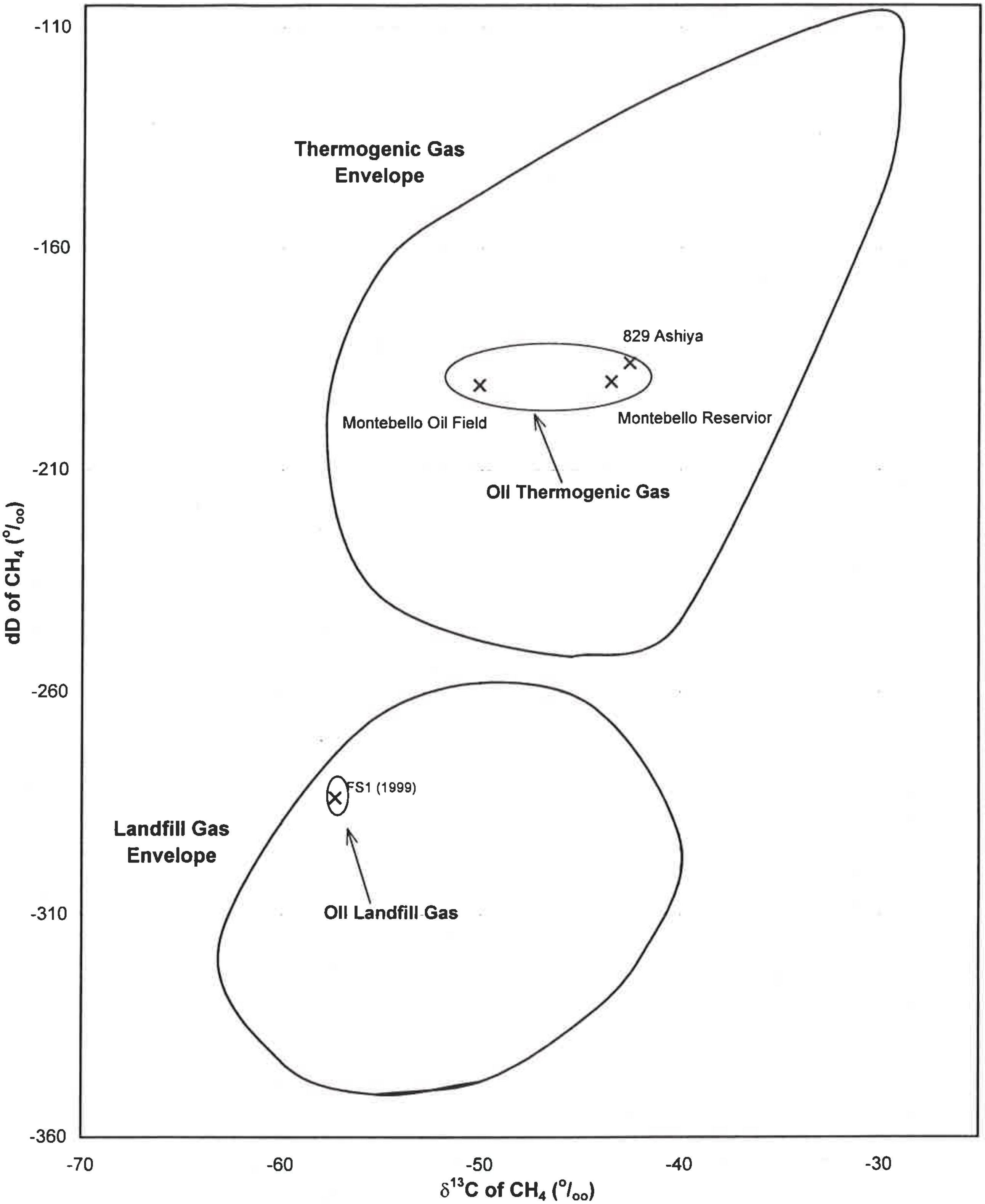


FIGURE 2 - OII LANDFILL MONITORING LOCATIONS

FIGURE 3. RESULTS OF STABLE ISOTOPIC ANALYSIS OF GAS SAMPLES OF KNOWN ORIGIN AT OII



NOTE: Envelopes are based on Coleman (see Figure 1). 1/17/00

FIGURE 4. RESULTS OF STABLE ISOTOPIC ANALYSIS OF OII GAS MONITORING PROBES