

DEFENDING LANDFILLS ACCUSED OF LANDFILL GAS IMPACTS ON NEIGHBORING PROPERTIES

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ABSTRACT

Landfill gas (LFG) migration impacting neighboring properties is not a new concept. However, increasingly we are seeing lawsuits filed by neighboring land owners claiming a variety of health, safety, and/or environmental impacts resulting from their alleged exposure to LFG and its constituents. These lawsuits can create significant liability for the landfill owners due to potential litigation awards and settlements, regulatory action, and negative public opinion that can damage efforts for future landfill projects like expansions or new operations. Even when cases are won, significant monies can be spent in defense against the lawsuit.

BACKGROUND

Defending landfills against these lawsuits can be expensive and complex. It is well-known that LFG migration and its impacts on the environment are difficult to quantify. However, through several legal cases and projects, specific quantitative and semi-quantitative tools for evaluating off-site LFG migration and impacts have been developed. One of these tools includes "fingerprinting" LFG for the purposes of comparing it to detected gaseous impacts in the subsurface and tracking those impacts back to the landfill. The fingerprinting technique can also be used to trace the source of methane (the primary component of LFG) to its source, which can include LFG but also natural (thermogenic) gas, petrogenic (petroleum-derived) gas, or other sources of biogas (e.g., swamp gas). Another technique includes "tracer" studies, which are used to confirm the existence of releases of LFG, as well as to quantify the resulting off-site impacts. Traditional chemical release, air dispersion modeling, and risk assessment techniques have also been used.

In some cases, it can be shown that the off-site detections of methane and other "typical" constituents in LFG are not from LFG but from other industrial, commercial, residential, or institutional sources, which can cause similar contamination containing one or more of the constituents in LFG.

This paper provides details regarding each of the noted methodologies for assessing off-site LFG migration, as well as summaries of case studies where these tools were used. Each is a landfill in California that was faced with litigation or regulatory action due to suspected off-site impacts of LFG. In each case, the landfill was able to defend itself using the noted tools to show that the impacts were not from LFG, and/or that the impacts were not as significant as the plaintiffs had alleged. Details on tracer gas applications for landfills are also provided herein.

REGULATORY REQUIREMENTS

There are very limited regulatory requirements that apply to subsurface migration of LFG, and these requirements are focused on the potential fire or explosion hazard resulting from the methane in LFG. Under federal landfill regulations contained within Resource Conservation and Recovery Act (RCRA) Subtitle D, LFG migration is limited to less than 5% methane at the landfill's permitted facility boundary. Monitoring is required to assess compliance using subsurface gas monitoring probes installed at the point of compliance around the landfill.

Methane is potentially explosive in the range of 5%, which is the lower explosive limit (LEL), to 15%, so limiting off-site impacts to less than 5% is intended to ensure that concentrations in the explosive range are never allowed to leave the landfill facility. Within the landfill facility, methane is limited to less than 1.25% in on-site structures, which provides an additional margin of safety by setting the compliance level at 25% of the LEL.

The compounds that make up LFG, including many toxic organic chemicals, are not specifically regulated in terms of subsurface LFG migration. Airborne releases of LFG are regulated by federal, state, or local air agencies, some with the ability to limit health risk caused by these toxins. Odor or nuisance caused by airborne releases of LFG can also be regulated by air agencies, solid waste agencies, or by other local ordinances. However, the only case when subsurface migration is directly regulated pertains to the aforementioned methane limitations or when LFG impacts groundwater and causes chemical concentrations to exceed

regulatory action levels for groundwater impacts. Due to this lack of specific regulation, suspected subsurface LFG impacts on neighboring properties have sometimes been handled through legal action, which can be a very cumbersome and expensive way to address the issue.

EXAMPLE PROJECTS

Provided below are summaries of several projects where the alleged subsurface migration of LFG resulted in litigation or major regulatory action. As part of each case study, the techniques used to assess and quantify the LFG migration and to determine the source of the impacts are also explained.

Highway 59 Landfill

The Highway 59 Landfill, located in the County of Merced, California, has been in operation since 1973. It was previously operated by the County of Merced, and the incorporated cities within the County, as a regional waste management authority. It is now managed under a Joint Powers Authority. The site is approximately 609 acres and includes four unlined units (89 acres); one composite-lined unit (23 acres); a 200-acre expansion area; a lined leachate management pond; several unlined storm water management ponds; and a wetland preserve (168 acres). The landfill accepts an average waste stream of about 450 tons per day. Groundwater monitoring began at the site in 1988 with 31 wells in the system (some are no longer in service), and LFG monitoring began in 1998 with 24 multi-zone gas probes (SCS Engineers, 2011).

In June 2008, a local family that had lived in the County for several generations which had land holdings in the thousands of acres, including large tracks of undeveloped land across the highway from the landfill, filed a complaint against the County claiming (among other things) diminution of property values due to contamination beneath their property, caused by the landfill. At the time the initial complaint was filed, the plaintiffs had collected no data on their property to support their position, but based the claim on documents available through the public record, including the historic monitoring data for the landfill. Between August 2008 and August 2010, the plaintiffs' environmental consultant collected a few samples of soil gas and groundwater from underneath the plaintiffs' property, which is located across the highway from the landfill, using various methods.

Using the few sample results obtained from their property, and the large historic set of monitoring data from the landfill, the plaintiffs argued that their data showed environmental impairment caused by the landfill. The case was tried in United States District Court, Eastern District of California, in January 2011. The decision was rendered by the Court in February 2011. This case is used as an example of how publicly-available monitoring data from a

landfill can be used by a plaintiff to claim environmental impairment, and how the validity of environmental data can be questioned in court, and have a significant influence on the court's decision.

The plaintiffs argued that sampling conducted on their property showed environmental impacts to groundwater and soil gas under their property, resulting in diminution of property value; however, they collected only a few samples; their sample collection methods were questionable; sample collection was not done in compliance with their documented standard operating procedures; and their quality assurance/quality control (QA/QC) samples were not appropriate and/or failed QA/QC tests. The plaintiffs dropped the claim of groundwater impact after their own data were unresponsive of that claim.

The plaintiffs continued to press their case based primarily on soil gas data from four soil gas samples, collected on two occasions, separated by almost two years, and collected using different methods. Much of the data they collected did not correlate between sampling events, but the plaintiffs claimed they detected low concentrations of some volatile organic compounds (VOCs) in soil gas, mostly compounds that are commonly petroleum-related (e.g., benzene, toluene, ethylbenzene, xylenes [BTEX]) compounds. The plaintiffs argued that since these were detected on their property, and that some of these VOCs had also been detected in LFG at some time, the impacts must be caused by the landfill.

This argument ultimately failed for several reasons including: (1) the plaintiffs' data collection methods for soil gas were inappropriate, including high volume sampling of a soil gas probe through a cemented polyvinyl chloride (PVC) sampling train (i.e., PVC cement contains certain VOCs); (2) their QA/QC data were incomplete and the duplicate sample data did not provide reproducible, and thus defensible, data; (3) they failed to test soil gas for the most important and predominant components of LFG – methane and carbon dioxide; and (4) the VOCs they claimed to have been detected did not match the predominant species of VOCs known to be present in LFG, such as the chlorofluorocarbons (CFCs or Freons), and other chlorinated hydrocarbons.

The defendant's expert witness was able to show that a "fingerprint" of VOCs that the plaintiffs claimed to have detected on their property did not match any LFG fingerprints obtained from the large set of historic LFG data. This fingerprinting showed that the mix and concentration of VOC compounds found in LFG at the landfill did not match the fingerprint of VOCs the plaintiffs alleged were under their property, especially given that none of the primary components known to be in

LFG were detected on their property. The fact that the VOCs alleged to be detected on the plaintiffs' property were primarily BTEX compounds, which are not the only or most common components in LFG, and in some cases were detected at higher concentrations offsite than detected in LFG, suggested that the VOCs were from another source, either a fuel release or sampling cross-contamination.

In the Memorandum of Decision rendered by the court in February 2011, the judge stated, "Defense expert [name], a geologist for SCS Engineers, testified at length regarding problems with the testing performed in Lot 1 [Plaintiffs' property]. He concluded that the tests performed by the plaintiffs were "indefensible" and could not be relied upon. His testimony on the subject was unimpeached." The court also found, "According to (defense witness name), there was no "fingerprint match" between the chemicals found in the landfill and those found in Lot 1. This makes it much less likely that the chemicals in Lot 1 came from the landfill. Migration from a landfill would almost certainly contain methane, carbon dioxide, and freons. Freons were found in the landfill but not in Lot 1, and the plaintiffs failed to test for methane and carbon dioxide." (U.S. District Court, 2011).

The plaintiffs' inability to show a match to the known LFG fingerprint, as well as the indefensibility of the plaintiffs' data, played a significant part in the court's decision. Without applicable and defensible environmental data to support their case, the plaintiffs were unable to prove their case based on a preponderance of the evidence. The court found in favor of the County (defendant) and further found the case to be frivolous regarding damages. The case has been appealed.

Even though the landfill operator was successful in its defense, the cost of the defense was approximately \$500,000, including in-house counsel and retained expert witnesses. The court has since awarded recovery of attorney fees to the defendant, and a motion has been made to recover other associated costs of defense. However, recovery of legal and expert fees is uncommon, and in most cases, a prevailing defendant still bears the brunt of its own cost of defense.

Closed Landfill in Central California

A similar case occurred at a closed landfill in Central California. The site is a Class III landfill, and it accepted municipal and non-hazardous industrial solid waste, mostly originating from fruit, vegetable, and nut canneries in the area. The landfill was operated, and is currently maintained, by a municipality, and accepted waste from November 1970 until July 1990. The site occupies approximately 168 acres adjacent to a river. The land use surrounding the landfill site is predominately agricultural.

Orchards exist adjacent to the landfill on three sides, and a vineyard is present on another side, across a road.

There are three residences adjacent to the landfill. One is a single family home near the landfill's northwest corner (Family No. 1), a second single family home to the south, and a mobile home park to the east of the landfill.

A groundwater extraction and treatment system was installed in 1991. This system filters the water to remove sediment and VOCs and then returns it to the groundwater aquifer. A LFG collection and control system (GCCS) was installed in two phases beginning in 1992 and concluding in 1995. The Landfill was capped in 1995 with a geomembrane top deck and clay on the side slopes. Operation and maintenance of the GCCS has been conducted by the municipality, with consultation from several privately contracted firms. The landfill is currently in a corrective action phase due to non-compliance with the site's Waste Discharge Requirements (WDRs), resulting from groundwater impacts from LFG and leachate.

Family No. 1 first took residence on the property adjacent to the northwest corner of the landfill in 1989. Various members of Family No. 1 had resided on the property for different durations. Family No. 1 had been in contact with the municipality regarding concerns about landfill contamination since April 2000. The family operates one domestic well on its property. This well has supplied domestic and drinking water to the residence on the property except at times when bottled drinking water was supplied by the municipality.

In this case, there was no doubt that the impacts on the neighboring property were from LFG, and the municipality has acknowledged this. However, a lawsuit was filed seeking damages for various health impacts caused by this contamination. Therefore, the issue at hand related to what level of health risk the LFG contamination represented.

To assess this risk and the likelihood of family members having health impacts related to the LFG contamination, a human health risk assessment (HRA) was conducted. The HRA was used in defense of the municipality as part of a litigation filed by the family. The objective of the HRA was to provide upper-bound health conservative estimates of the potential human health impacts that may have been attributable to chemicals originating from the landfill. Specifically, this assessment evaluated risks as they applied to members of Family No. 1, who resided on the property adjacent to the landfill from the time of their initial occupation in 1989 to the time of the lawsuit.

The HRA evaluated all possible exposure pathways for completeness based on the chemicals of concern identified through a review and evaluation of site-specific and industry default contamination data. Non-carcinogenic and carcinogenic risk levels for chemicals with complete exposure pathways were calculated for each receptor (i.e., member of Family No. 1).

A variety of techniques were used in the HRA. These included: (1) vapor intrusion modeling using the Johnson and Ettinger model to assess the migration of VOCs from the subsurface into indoor living spaces; (2) chemical release models to assess the impacts in outdoor air resulting from subsurface contamination, as well as landfill surface emissions; and (3) air dispersion modeling. The results of the modeling techniques were used within the construct of a formal HRA conducted in accordance with federal and state risk assessment guidance.

Based on the results of the HRA, the following conclusions were made. The hazard indices for all known contaminants in groundwater and all known and suspected contaminants in LFG that potentially originated from the landfill were calculated on a per annum basis for an adult and child resident of Family No. 1:

- For a child resident, calculations of hazard indices for each individual year from 1989 through 2002 resulted in values below the U.S. Environmental Protection Agency (U.S. EPA) threshold value of 1.0, indicating that the chances of adverse human health effects are not significantly increased by the potential presence of the investigated contaminants at the determined concentrations.
- For an adult resident, calculations of hazard indices for each individual year from 1989 through 2002 resulted in values below the U.S. EPA threshold value of 1.0, indicating that the chances of adverse human health effects are not significantly increased by the potential presence of the investigated contaminants at the determined concentrations.
- For a child resident, calculation of the hazard index for an exposure duration of 14 years from 1989 through 2002 resulted in a value below the U.S. EPA threshold value of 1.0, indicating that the chances of adverse human health effects are not significantly increased by the potential presence of the investigated contaminants at the determined concentrations.
- For an adult resident, calculation of the hazard index for an exposure duration of 14 years from 1989 through 2002 resulted in values below the U.S. EPA threshold value of 1.0, indicating that the chances of adverse human health effects are

not significantly increased by the potential presence of the investigated contaminants at the determined concentrations.

- For an adult and/or child resident, calculations of carcinogenic risk for each individual year from 1989 through 2002 resulted in values below the U.S. EPA accepted value of 1.0×10^{-6} , indicating that the chances are less than 1 in one million of contracting cancer due to the potential presence of the investigated contaminants at the determined concentrations.
- For an adult and/or child resident, calculation of carcinogenic risk for an exposure duration of 14 years from 1989 through 2002 resulted in values below the U.S. EPA accepted value of 1.0×10^{-6} , indicating that the chances are less than 1 in one million of contracting cancer due to the potential presence of the investigated contaminants at the determined concentrations.

The results of the HRA were used during expert testimony to assist in the defense of the municipality. Although the defendant felt its case was strong, they chose instead to purchase Family No. 1's property at its appraised value, as part of a settlement. This settlement decision was made both to eliminate the monetary risk of a large jury award, and to avoid future conflict with Family No. 1. Despite the settlement, the jury was polled to see what their award would have been had the case continued. The jury was planning to rule in the favor of the defendant and award Family No. 1 with no monetary award but only a requirement for the municipality to continue to provide potable water to the family at no cost to them. All told, the municipality paid over \$750,000 in legal costs, including the purchase of the plaintiff's property.

OII Landfill

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 U.S. EPA (Pierce and LaFountain, 2000).

Technical Background: LFG 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 LFG. This presumption can result in compliance problems for the landfill owner. If the methane is actually from a non-landfill source, there is virtually no possibility that the

LFG control system can reduce the observed methane concentration to a 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, regulatory scrutiny, and other liability in attempting to solve an unsolvable problem.

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 is what is commonly referred to as “natural gas”; it 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.

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

- LFG 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 parts per million by volume (ppmv). Reduced sulfur compounds, principally hydrogen sulfide, are also present. As LFG

moves away from the landfill, it is diluted by soil pore gas, which is generally ambient air. The starting point concentrations of methane, carbon dioxide, and other LFG 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 glaciations, 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 materials or waste buried outside the landfill perimeter. Petroleum hydrocarbons may be present from leaking tanks or abandoned oil wells.

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. This type of elemental analysis assesses the presence of other chemicals which are present with the methane in order to assist in determining the source of the methane.

Helium

LFG contains virtually no helium; however, 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, 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.

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, since carbon dioxide can be removed from a biogenic gas through dissolution into water, thereby increasing in 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 concentrations 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.

VOCs

LFG contains low concentrations of high molecular weight VOCs such as xylene, toluene, benzene, and vinyl chloride. 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 some of these compounds. Further, 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 researches have shown that VOCs can be biologically and/or physically removed from LFG as it moves through 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 VOCs. The starting point concentration for VOCs may be very low at a particular landfill, further complicating detection. In summary, the following statements can be made with respect to VOCs:

1. The presence of chlorinated VOC compounds is a very strong indicator that LFG is present in a sample;
2. The presence of non-chlorinated VOCs does not provide conclusive evidence that LFG is present, since it can come from other sources (e.g., petroleum); and
3. The lack of chlorinated or non-chlorinated VOCs 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. LFG at its source generally has a higher concentration of hydrogen sulfide. Landfills containing large quantities of sulfur-containing wastes, such as wallboard (which contains gypsum or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), 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, 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 LFG, 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. They use sulfur compounds (such as thiophene) which are not commonly found in LFG. 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. 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 LFG; 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. LFG 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). LFG 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.

Table 1 (Pierce and La Fountain, 2000) contains a summary of conclusions that can be drawn from chemical analysis and comparison of the above constituents in the gas (so-called “elemental analysis”). Further, the gas samples can be subjected to an additional isotopic analysis to provide better gas fingerprinting as described below.

Use of Isotopes of Carbon and Hydrogen

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 (1994) 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 referred 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 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 (^1H or protium) and 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.

Stable Isotopes: 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 $\delta^{13}\text{C}$. Similarly, δD is the ratio of ^2H and ^1H as compared to an international reference standard. The δ value in either instance is the difference, expressed in parts per thousand or per million ($^0/_{00}$), 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 $\delta^{13}\text{C}$ of methane versus δD of methane for a sample gas against a plot of typical values for methane from known sources. Coleman (1994) provides a plot (reproduced here as Figure 1) of typical $\delta^{13}\text{C}$ of methane versus δD of methane 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 in 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 LFG).

The envelopes in Figure 1 cover the typical ranges of $\delta^{13}\text{C}$ of methane and δD of methane 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 methane of -200 and a $\delta^{13}\text{C}$ of methane of -40, it would plot in the thermogenic range, and one would conclude that the methane was thermogenic rather than being one of the other two sources of gas.

There are many advantages of the use of the stable isotopic analysis, but the four most important are:

1. It allows one to differentiate between thermogenic gas and LFG 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 $\delta^{13}\text{C}$ of methane and δD of methane can be compared to the sample gas's $\delta^{13}\text{C}$ and δD of methane; and
4. In some cases, thermogenic gas may be mixed with LFG at a monitoring point. If control samples of the LFG thermogenic gas are collected, it is possible to roughly determine the blend between LFG and thermogenic gas in a gas sample. This is possible since the ratio of the gases is not affected by dilution.

Radiogenic Isotopes: A second isotopic tool that can be used in gas characterization is the use of radiogenic isotopes. The methane in LFG is produced from water and carbon dioxide originating from the recent atmosphere. Atmospheric carbon and hydrogen have elevated radiogenic isotope levels due to the affect of cosmic rays, as well as to atmospheric testing of radioactive explosive devices. The hydrogen and carbon in the methane in LFG will have higher levels of the radiogenic isotopes than the levels found in the 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. LFG has pMC values in the range of 115 to 150 percent. Thermogenic gases have pMC values near zero. Coleman (1994) 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 2 (Pierce and LaFountain, 2000) provides a summary of conclusions that can be drawn from isotopic analyses.

Case Study: The former OII Landfill was faced with regulatory action due to methane detected above 5% in facility LFG monitoring probes (Pierce and La Fountain, 2000). This situation was exacerbated by the fact that the landfill was a Superfund site. In compliance with U.S. EPA requirements, NCI maintains a network of gas monitoring probes (GPs) around the perimeter of the landfill. The purpose of the GPs is to detect migration of LFG 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 network consists of 38 GPs ranging in depth from 50 feet to 200 feet. The depths are based on the depth of the waste in the vicinity of the individual GPs. Each probe location 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.

Several 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 feet to 100 feet, and have from one to three screened sections.

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

1. Methane concentrations in a few GPs sometimes exceeded 60% 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. (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:

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

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

- Carbon Monoxide
- Oxygen
- Ethane
- Pentane
- Helium
- Carbon Dioxide
- Ethylene
- Hexane
- Hydrogen
- Nitrogen
- Propane
- Argon
- Methane
- Butane

A total of 20 samples were subjected to radiogenic isotopic analysis, including ^{14}C of methane, ^{14}C of CO_2 , and ^3H of methane. These samples were collected in canisters because of the larger quantity of gas needed to support the analysis. The clear difference between LFG and thermogenic gas was seen from the raw analytical data from selected samples:

- Both the imported and the indigenous thermogenic gas (Montebello Reservoir and Montebello Oil Field) had pMCs below 1 while the raw LFG (at the flare station) had a pMC of 117;

- The tritium levels of the thermogenic gas were much lower (<20 TV versus 1,390 TU) for the LFG;
- Ethane (C2) propane (C3), butane (C4) and pentane (C5) were much higher in the thermogenic gas than in the LFG;
- Helium was non-detect (<20 ppmv) in the LFG, 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 had relatively low δD of methane values (greater than -200) while the value for LFG was less than -280.

The former OII Landfill lies in a location that is 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-LFG. 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. It allowed a regulatory exemption to be granted for the detected methane in the gas probes.

Since the OII project, the same fingerprinting techniques have been used on numerous landfills to either confirm the source as LFG or to demonstrate that some or all of the detected methane at a particular site was from a non-LFG source. Regulatory action has been avoided in each case where it was successful, and could also be used as a tool in litigation if off-site methane from LFG became the cause of legal action.

CHEMICAL TRACER APPLICATIONS

Introduction

Beyond the techniques identified above, various chemical tracer techniques are finding application in the landfill world. Thorough study of the transport and fate of chemical vapors has become necessary to fully understand the effects of these chemicals on human health and the environment. In circumstances where chemical species of interest cannot be directly measured (such as when the source no longer exists or is difficult to quantify such as LFG subsurface migration or surface emissions) or must be simulated (prior to constructing a landfill or landfill expansion, for example) chemical surrogates known as

tracers are employed to simulate movement in the environment. Tracers are also utilized to verify that a particular impact is actually caused by a particular source, and to determine the impact of a single existing source where multiple sources may exist.

Ideally, a suitable tracer would be a chemical species that does not normally occur or is minimally present in the environment to be characterized. It should exhibit physical characteristics similar enough to the chemical(s) of interest to behave as a faithful transport surrogate. Further, an ideal tracer would possess no negative health or environmental characteristics. In addition to its uniqueness in the environment, it should be amenable to unequivocal identification and quantification by accepted analytical practice. Typically, sulfur hexafluoride and several cyclic perfluorocarbon species are employed with detection limits to the parts per quadrillion concentration level.

Uses for Chemical Tracers

One of the first uses of gaseous tracers was to investigate the flow of air in buildings and the atmosphere, to aid in determining the transport and fate of chemicals in the environment. Subsequently, they have been employed as markers or surrogates in many investigations of atmospheric transport and pollutant movement:

- Determining the movement of a parcel of air over distances of hundreds of feet to hundreds of miles;
- Quantifying the fugitive emission rate from a closed building or process area (leak rate determination);
- Confirming that odors from a given source are, in fact, the cause of odor complaints (source-receptor definition);
- Determining the relative contribution of each of several potential odor sources in a facility or operation; and
- Quantifying the source strength of an odor source based on field measurement of tracer concentration and odor concentration from dilution to threshold.

Tracers have also been applied to the measurement of flows in underground formations such as oil shale retorts and petroleum reservoirs, and are currently being investigated as a tool to characterize subsurface LFG flows in and outside of landfills. Tracers are also being used to quantify the rate of emissions of LFG constituents through the surface of the landfill, which are extremely difficult to measure with any accuracy. Further use of tracers to assess subsurface migration of LFG in the vadose zone is also being investigated. This would aid landfill operators in confirming that off-site migration is really occurring,

and to what degree, as well as in adjusting GCCS operation to better control off-site migration.

Typical Components of a Tracer Study

There are generally two components to a tracer study: field operations and sample analysis/data processing. Field operations consist of tracer dissemination and sample acquisition activities. In determining environmental transport, these activities require a somewhat different approach than most monitoring exercises. The challenge begins in the experimental design phase, such that the mass of tracer to be released is properly estimated. This determination may need the assistance of a numerical model, but experience often plays a substantial role. A second challenge arises in designing a receptor network or sampling protocol that adequately intercepts the tracer plume to provide appropriate data density within the targeted concentration range. Once samples are acquired, they are transported to the laboratory for analysis by a specialized gas chromatographic technique. The data from the laboratory analysis are then compiled and subjected to quality assurance review before being included in a final report to the client.

Application of Tracers to Landfill Operations

Several potential tracer applications exist above and below the surface of landfills. Tracers may be applied to:

- Surface emissions of LFG;
- Subsurface LFG migration within the refuse, as well as in the vadose zone outside of the landfill;
- Methane well efficiency determination and configuration optimization;
- Accurate and low-cost mass flow determination for LFG flow rates in GCCS piping; and
- Investigation of off-site odor problems.

It is expected that tracer studies will play a more important role in LFG investigations in the future, and will provide an additional tool for defending landfills in legal and regulatory situations where LFG is the suspected cause.

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**TABLE 1. SUMMARY OF CONCLUSIONS WHICH CAN BE DRAWN
FROM ELEMENTARY CHARACTERIZATION INDICATORS**

Compound	Criteria	Type of Gas		
		Landfill	Thermo2ellic	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 ₂ S absent	Inconclusive	Inconclusive	Inconclusive
	H ₂ S present	Very possible	Not pipeline but may be indigenous	Possible depending on source
NMOC (C ₂ -C ₆)	High concentration of C ₂	No	Yes Inconclusive	No
	Moderate concentration of C ₂	Inconclusive		No
	Low or absent C ₂	Possible	Possible	Possible

From Pierce and LaFountain, 2000

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

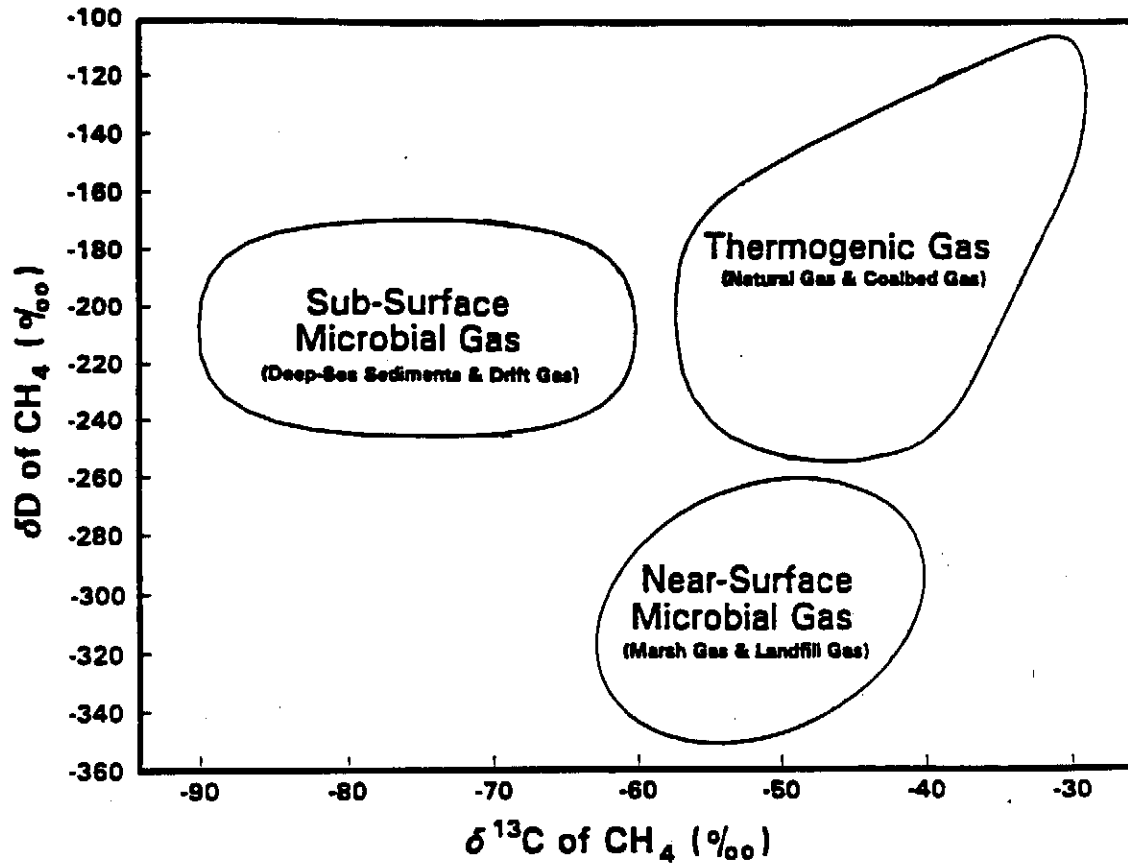
Compound	Criteria	Type of Gas			
		Landfill	Thermogenic	Drift	Swamp
Stable C and H Isotopes	$\delta^{13}\text{C}$ of CH_4	-40 to -62	-30 to -58	-60 to -90	-40to-62
	$\delta^{13}\text{C}$ of CH_4	-265 to -350	-110 to -245	-170 to-240	-260 to-350
Radiogenic C and H Isotopes	Percent Modern Carbon (pMC)	115 to 150%	Near 0%	< 300/0	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 LFG, can best be established by comparing sample results to the results from samples of known gases. A $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ of CH_4 which can indicate a mixture of these gases is generally much greater.

From Pierce and LaFountain, 2000.

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).