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Gas Fingerprinting to Determine Sources of Offsite Gases

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The findings of gas fingerprinting studies can continue to serve a purpose in the future as they help narrow investigations and focus on similar scenarios that may occur later. It is all about being proactive in making informed decisions.

By Patrick Sullivan, BCES, CPP, REPA

In recent years, there has been a steady uptick in redevelopment adjacent to active landfills and closed disposal sites that still produce landfill gas (LFG). These projects are driving greater regulatory scrutiny and risk for litigation, with plaintiffs claiming potential health, environmental, and safety impacts due to allegedly migrating LFG. If neighboring property owners detect gaseous chemicals on their sites, they immediately assume the landfill is responsible, even though LFG is just one of many sources of methane and other gases in the natural environment. Regulators often make the same initial conclusion when detecting methane in LFG monitoring probes at the landfill property boundary.

Increasingly, landfill operators are responding to these assumptions by leveraging an evidence-based line of defense known as gas fingerprinting. This tool is a series of scientific methods that compare the landfill fingerprint (or LFG profile) to the gas fingerprint at the offsite or landfill perimeter location where gas was detected to determine if it is LFG from the landfill—or if another source is responsible.

Fingerprinting is instrumental in providing science-based data to avoid regulatory action and to defend against litigation involving offsite gases that could derive from landfills. Gases include methane—the most common constituent in LFG—but also various other chemicals evolving from landfill and non-landfill sources.

Under federal regulations [Resource Conservation and Recovery Act (RCRA) Subtitle D] or state equivalents, landfill owners and operators must prevent LFG with methane concentrations above 5 percent from migrating beyond the property boundaries of municipal solid waste landfills. Landfill operators monitor routinely and operate the landfill and LFG collection system to avoid exceedances whenever possible. But should an exceedance be confirmed, we look to determine if it requires further investigation to identify and, if possible, isolate the source, beginning with the first of several gas fingerprinting phases that may be employed.

Phase 1: Comparing Methane and Carbon Dioxide (CO2) Ratios and Concentrations

If we confirm that anomalous readings (for example, greater than 50 percent methane) in a gas monitoring probe warrant further investigation, or we suspect that there could be another source of methane, we first compare methane and CO2 ratios and concentrations.

Methane and CO2 have certain concentrations typical in raw LFG—about 45 to 55 percent methane, with the remainder being CO2. However, as the gas migrates from the landfill, it dilutes because it mixes with air in the pore spaces of the soil. Not only do concentrations decrease, but the ratio of methane and CO2 changes, partly because methane can oxidize into CO2, and CO2 can dissolve in soil moisture. By examining concentrations and ratios, we get good intelligence to begin the vetting process and identify anomalies that might suggest another source of methane. Phase 1 will not definitively conclude whether LFG is the source of offsite gases, but it tells us if additional investigation is warranted.

Let's take a scenario where we determine a gas probe outside the landfill perimeter has 85 percent methane, or, perhaps, we encounter a scenario where the gas detected offsite contains significantly more CO2 than methane. Both scenarios have occurred in real-world situations where LFG was the assumed source and represented large discrepancies. Still, sometimes indicators are more subtle, such as finding methane in a probe or offsite in an unexpected location, or cases where another possible source (e.g., natural gas pipeline) is in the same area. We conduct Phase 1 as part of the standard data review after detecting an exceedance or when methane has been detected offsite.

Phase 2: Speciating Gas for Different Constituents, then Comparing Samples

When we suspect gas detected offsite is from a source other than a landfill, we move to Phase 2 gas fingerprinting, where we look for constituents beyond methane and CO2 to pinpoint the source. We speciate the gas for various volatile organic compounds (VOCs), sulfur compounds, and other constituents common in LFG. We test samples from the perimeter probe or offsite location for the same constituents. We then compare the gas profile from offsite samples with samples and/or LFG data from known landfill locations to determine if the two fingerprints match.

Typically, we are looking for fuel-related constituents, chlorinated solvents, and chlorofluoro hydrocarbons (CFCs or freons). If we, for instance, only find fuel-related constituents (common constituents found in soil vapor) in the perimeter or offsite sample, we can confirm LFG is unlikely the source, although elevated VOCs are present in LFG. LFG contains numerous other VOC species, including CFCs/freons and some chlorinated solvents, which would be present if LFG was nearby.

Similarly, LFG commonly contains high concentrations of hydrogen sulfide (H2S), which would be present if LFG is the source. The absence of H2S suggests that LFG is not the source. In the example noted, the two profiles did not align. We provided testimony in a litigation case in this very scenario and won resoundingly because we could say decisively, LFG was not the source because many of the common constituents of LFG were not found. The Phase 2 findings are not always as definitive as they were in this case. Sometimes, we may detect a handful of chemicals that could come from LFG; if so, we investigate further to determine if they are from LFG.

• Application of Advanced Characterization Techniques for Identification of Thermogenic and Biogenic Gases discusses sources and characteristics of methane, methods to discriminate between sources, and a case study using advanced characterization techniques to discriminate between landfill and non-landfill methane sources. (www.scsengineers.com/scs-white-papers/application-of-adanced-characterization-techniques-for-identification-of-thermogenic-and-biogenic-gases)

• Defending Landfills Accused of LFG Impacts on Neighboring Properties provides additional insight on gas fingerprinting and defending landfills accused of LFG impacts on neighboring properties. (www.scsengineers.com/scs-white-papers/defending-landfills-accused-of-lfg-impacts-on-neighboring-properties)

• Fingerprinting and Forensic Techniques for Landfill Gas Geochemical Assessment is a presentation prepared by California state regulators providing insight on identifying and correlating methane releases to their sources, including leveraging gas fingerprinting. Provides a case study. (https://dokumen.tips/documents/1-fingerprinting-and-forensic-techniques-for-landfill-gas-geochemical-assessment.html?page=1)

Phase 3: Isotopic Analysis Further Delineates the Methane Source

In Phase 3, we complete an isotopic analysis of stable and/or radioactive isotopes of carbon and hydrogen that are present in methane to determine the source and nature of methane gas. Similarly, when we look for VOCs, a known sample of LFG is compared to the sample(s) in question at the perimeter or offsite location.

We may conduct Phases 2 and 3 together for more comprehensive information; for instance, if our findings from Phase 1 indicate that Phase 2 data may not provide a definitive conclusion.

Isotopes are different "versions" of carbon or hydrogen molecules (for example, carbon13 or tritium), and by studying isotopes in carbon or hydrogen, we can accomplish two goals.

We can date the carbon to determine if it is biologic in nature (microbial decomposition of organics), a very recent carbon, or if it is petrogenic in nature (thermal decomposition of organics due to geological processes), which is much older. If it is petrogenic, we know that LFG is not the contributor. This carbon is from geologic material present for many thousands of years and is likely related to petroleum sources, such as a leaky natural gas pipeline. We confirm whether the source is petrogenic or biologic by studying isotopes in carbon—essentially conducting carbon dating.

Suppose we know that the alternative source is also biologic in nature, like LFG. In that case, we need further delineation to determine whether the gas is from the landfill or another biologic source. Other sources could be swamp gas or buried organic material not associated with the landfill. This closer study is needed because distinguishing between varied biologic sources is often subtle. We differentiate by looking at radioactive isotopes.

With isotopic studies, we collect samples at a location known to have LFG and compare them to the offsite or perimeter location where methane was detected. We may collect a sample directly from the alternative source if identified already. We get a reading of carbon and/or hydrogen isotopes, then plot those sample results against the isotopic values in the known LFG sample. It is when offsite/perimeter samples and LFG at landfill plot the same in a stable isotope analysis that we perform a radiological isotopic analysis to pinpoint the exact biologic source.

We usually suggest doing both stable and radiologic isotopic analyses simultaneously. Although this increases analytical costs, you have already invested the time and money to collect the samples and having both stable and radiological isotopic data provides for a more complete analysis.

About 85 percent of gas fingerprinting cases end with isotopic analyses. After this phase, you normally have sufficient data to confirm whether the landfill contributes to any of the offsite or perimeter gas—or can be absolved as a source of the methane.

Phase 4: Testing Soil for Total Organic Carbon (TOC)

We would move to this additional phase of study if we are reasonably certain that the methane detected offsite is not from LFG, but we still need to confirm the actual source for further evidence to support our position.

We may have already concluded that the methane is plotting as a biologic-driven gas similar to LFG, but it does not look exactly the same. Through this study, we can directly identify the source, which provides an additional line of evidence in a legal or regulatory case.

We begin by testing the soil for the presence of TOC because when organic material in the soil breaks down underground in anaerobic conditions, it generates methane. This generation is common if there is a source of moisture to facilitate anaerobic degradation of organic materials—just as is the case with organics buried in landfills.

In addition to testing the soil for TOC, we take samples of methane from soil vapor at the same location. Then, we look for a correlation between concentrations of TOC in the soil and methane concentrations in the soil vapor. Suppose we find the highest TOC and methane levels at the same location. In that case, the soil is likely the emitting source, whether from woody debris, fill material containing organics, or whether the carbon was always in the soil. These results enable us to further narrow and identify the methane source.

Phase 5: Tracer Studies

Tracer studies entail injecting a known amount of tracer gases into the landfill and/or at an alternative source at a location that could potentially be a migration source to the perimeter or the detected gas offsite point. Tracer chemicals are very stable, non-soluble, and non-reactive VOCs in the environment, so they are expected to migrate without reaction or transformation. Once the tracer is released, we look to see if it appears at the location in question and at what concentrations. We continually test the monitoring probe over time to confirm whether gas is migrating from the landfill and determine how far and fast it moves.

We use this method in special circumstances: usually to provide regulatory agencies with more data to determine compliance or to verify during litigation that the landfill is not responsible for the offsite gas emissions.1 Tracer studies have helped absolve landfill operators when their LFG is not the offsite source, and they are instrumental in proactively identifying potential gas issues to plan for control installations at the most appropriate locations.

Fingerprinting—Not Only for Mitigation

In many cases, gas fingerprinting can be key to avoiding regulatory action and has proven useful in litigation settings when parties point to landfills as the alleged source of offsite methane and/or VOCs, and more comprehensive data is needed to support your position. These tools also provide data that enables us to discontinue additional monitoring and know where and how to clean up migrating LFG to prevent potential issues and later costly remediation.

The findings of gas fingerprinting studies can continue to serve a purpose in the future as they help narrow investigations and focus on similar scenarios that may occur later. It is all about being proactive in making informed decisions for maintaining landfill health, proving compliance, and having a good defense if you are not the source of gas found offsite or in LFG monitoring probes. | WA

A Case Study in Southern California

A Southern California property owner took a neighboring landfill owner to court, alleging that the landfill was responsible for methane and volatile organic compounds (VOCs) detected on its property. But a comprehensive series of analyses involving several gas fingerprinting methods helped the landfill owner defend itself in legal proceedings. The gas fingerprinting methodologies included:

- Methane concentration and plume analyses
- VOC analysis
- Total Organic Carbon (TOC) analysis

Methane Concentration Evaluation

Methane concentrations found at monitoring probes on the plaintiff's property were compared with concentrations at perimeter gas probes on the landfill. This comparison confirmed the scattered detections of offsite methane did not originate at the landfill, as the methane was not present in the landfill's gas probes at corresponding locations. In fact, the highest methane concentrations on the plaintiff's property were at locations farther away from the landfill, in the center of the plaintiff's property, and not along the boundary with the landfill, strongly indicating it did not originate at the landfill. This finding did not match how a methane plume would look if it originated from the landfill; there would be decreasing concentrations as the gas mixes with air in the soil as it travels.

Further, the methane was where deeper fill soil was present, not matching elevations where methane is on the landfill. These soils often contain organic carbon underground in anaerobic conditions, where they can generate methane. As confirmed by regulatory agencies, the concentrations detected were below action levels; therefore, no remediation was required regardless of the source.

VOC analysis

Various monitoring events detected individual VOCs in the soil gas on the plaintiff's property. While these compounds are also in LFG, the offsite sample fingerprint did not match the LFG profile at the landfill. The comparisons, based on VOC data from raw LFG data as compared to soil gas samples from the plaintiff's property, provide strong evidence that the VOCs detected on the plaintiff's property are not from LFG but are likely from a petroleum-based source. Among specific findings:

- There were various VOCs present on the plaintiff's property but not found in LFG at the landfill.
- Various VOCs, including certain CFC/freons, were present in LFG at the landfill. These VOCs were either not found in soil gas on several lots on the plaintiff's property or in the landfill's perimeter gas probe or found in a pattern that did not match migration from the landfill,

confirming there was likely no migration from the landfill at these locations. Freons are commonly the leading edge of migrating LFG plumes, and their absence strongly indicates that LFG is not present.

Total Organic Carbon analysis (TOC)

The plaintiff's property contained engineered fill materials, which are a known potential source of methane if they contain TOC. TOC produces methane [and carbon dioxide (CO2)] when it breaks down underground in anaerobic conditions, especially during grading or when adding water to the soil; both activities occurred on the plaintiff's property.

To determine if the engineered fill soil on the plaintiff's property could be the source of the gases, we ran correlations of the TOC concentrations found in those soils to methane concentrations detected at the same locations in soil vapor. This fingerprinting analysis confirmed that the highest methane concentrations were in the areas with the highest TOC, indicating that the methane came from engineered fill soils or native soils under the engineered fill—not the landfill.

Isotopic Analysis

This analysis confirms that the methane detected on the plaintiff's property is biogenic in nature, meaning it could come from landfills or other biogenic sources. The analysis goes on to isolate the specific biogenic source. The study entailed comparing a specific carbon isotope from a sample from a soil gas probe on the plaintiff's property to LFG extraction well isotopic data. This step confirms that the CO2, a common constituent of LFG, is from a different source than the CO2 on the plaintiff's property.

The next step entailed plotting specific carbon and hydrogen isotopes and comparing isotopic data from LFG wells at the landfill to soil gas samples on the plaintiff's property. As was true with the CO2 analysis, this comparison clearly shows that the methane from LFG is from a different biological source than the soil gas at the plaintiff's property. The isotopic data from the plaintiff's property are consistent with degrading organic material present in soils on that property.

In summary, the overall conclusions of this case study were:

- There was no evidence to support the claim that LFG from the landfill migrated to, or impacted, the plaintiff's property.
- Rather, data supports that the produced methane migrated from engineered fill or native materials buried on the plaintiff's property during site development.
- VOCs at the plaintiff's property are not indicative of LFG migration but characteristic of petroleum contamination from a non-landfill source.
- VOCs and methane at the plaintiff's property are not present in concentrations requiring remediation, in accordance with regulatory thresholds.

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Notes

An SCS Engineers' specialty group conducts tracer studies, and we bring this expertise to the table in compliance and legal cases, supplying robust science-based evidence supporting our client's position.