Geochemical and VOC-constraints on landfill gas age and attenuation characteristics: A case study from a waste disposal facility in Southern California

Benjamin Hagedorn a,⇑, Henry B. Kerfoot b, Mark Verwiel c, Bruce Matlock d

a Department of Geological Sciences, California State University, Long Beach, CA 90840, USA
b Civil & Environmental Consultants, Inc., Phoenix, AZ 85028, USA
c Waste Management, Inc., Novato, CA 94948, USA
d Waste Management, Inc., Simi Valley, CA 93065, USA

Article history:
Received 8 July 2015
Revised 24 September 2015
Accepted 29 October 2015
Available online xxxx

Keywords:
Monitored natural attenuation
Environmental forensics
Methane source tracing
Landfill gas dating
VOCs

A B S T R A C T

In this study, a multi-tracer approach was applied to a complex, methane-impacted site in Southern California to (1) distinguish between natural gas and landfill gas (LFG)-derived methane impacts at site perimeter gas probes, (2) estimate the relative age of the LFG at these probes, and (3) document natural attenuation trends during a 3-year monitoring period. Relationships between methane and ethane values suggest that at the majority of probes, methane is from LFG and not from natural gas and that the relative contribution of LFG methane at these probes has increased over the monitoring period. To evaluate whether LFG is attenuating in the subsurface, the relative age of LFG was estimated by comparing readily degraded VOCs that are major constituents in LFG (toluene in this case) with those resistant to degradation (Freons). Time-series data trends are consistent with several probes being impacted by fresh LFG from recent releases that occurred after the update of the local LFG collection and control system (LFGCCS). Data further indicate some probes to be only affected by legacy LFG from a past release that occurred prior to the LFGCCS update and that, because of a lack of oxygen in the subsurface, had not been fully degraded. The outlined attenuation evaluation methodology is potentially applicable to other sites or even groundwater contaminants; however, the assessment is limited by the degree of homogeneity of the LFG source composition and non-LFG-derived toluene inputs to the analyzed samples.

1. Introduction

Municipal solid waste landfills generate landfill gas (LFG) as a result of volatization and fermentation of organic matter. In addition to its major constituents methane and carbon dioxide, LFG can contain numerous volatile organic compounds (VOCs) including halogenated hydrocarbons and aromatic compounds, of which many are toxic and/or contribute to the greenhouse effect (Habib et al., 2013; Scheutz et al., 2004). Pressure and concentration gradients in the subsurface can cause LFG migration away from the waste through the most permeable soil portions (Amini et al., 2012; Christopherson and Kjeldson, 2001; Sepich, 2008). This can result in (1) LFG entering closed spaces in structures and potentially creating explosive conditions, (2) LFG interaction with and contamination of groundwater, and (3) LFG off-gassing into the atmosphere (Barlaz et al., 2004; Castañeda et al., 2011; Ettinger and Kerfoot, 2012; Kerfoot et al., 2004; Thomsen et al., 2012). LFG migration away from landfills is controlled by numerous measures including biologically active soil covers, which shield waste and LFG from the atmosphere while promoting destruction of methane and VOCs. In addition, LFG collection and control systems (LFGCCS) are used to withdraw gas from the waste and to control pressures, thereby reducing emissions and subsurface migration, and also using LFG combustion as a source of energy.

Because the production of LFG continues until the majority of the organic material in the waste has been degraded, which can take several decades (Scheutz, 2002), landfills need to be managed for prolonged periods during the active phase and after closure to assure long-term environmental compatibility (Laner et al., 2012). This management includes the monitoring of LFG migration away from the waste via monitoring probes installed at multiple depths at the facility property perimeter. In the United States, the regulatory action level for LFG impact at a perimeter monitoring probe is

* Corresponding author.
E-mail address: Klaus.Hagedorn@csulb.edu (B. Hagedorn).

http://dx.doi.org/10.1016/j.wasman.2015.10.033
0956-053X/Published by Elsevier Ltd.
set by a simple criterion; a methane concentration of 5% (volumetric ratio; v:v) which is the lower explosive limit (USEPA, 2012). While this criterion can provide useful information about whether methane impact at a probe occurs or not, it is limited in view of evaluating long-term environmental risks associated with LFG migration. This is especially the case at sites where additional sources of methane such as swamp gas or natural gas may contribute to probe methane detections. In such settings, other LFG-specific tracers such as low molecular-weight hydrocarbons (i.e., ethane or propane) or synthetic VOCs (i.e., Freons) as well as ²H and ¹³C isotopes can shed more light on LFG impact (Coleman et al., 1995; Hackley et al., 1996). Another problem with the 5% methane compliance criterion is that it provides limited quantitative information on LFG transport which is needed to design appropriate remediation measures (Spokas et al., 2006). Clearly, a methane detection of a finite volume of residual or legacy LFG that originated from an isolated release in the past and that has stayed in place and attenuated for years can be considered to pose less of a risk than a methane detection stemming from fresh LFG of an ongoing release (Fig. 1). Fresh LFG implies mobile LFG is continuously migrating to the sample location and potentially onward to receptors. If the migration is more rapid than oxygen transport from aeration, accumulation of LFG can potentially result in a hazard.

In this study, we present a multi-tracer approach to (1) evaluate landfill gas age patterns at perimeter gas monitoring probes, and (2) distinguish lower-risk perimeter probes affected by legacy LFG from higher-risk probes affected by fresh LFG. This method is generally applicable to facilities experiencing LFG impacts at perimeter monitoring probes and provides valuable quantitative information about site-scale degradation rates of VOCs such as toluene and the dynamic characteristics of LFG migration at local (i.e., gas probe) scales.

2. Case study – local setting and previous evaluations

This study focuses on a class III (non-hazardous) municipal solid waste (MSW) landfill and recycling facility located in Southern California, USA (Fig. 2). The site began disposal operations in 1970 as an unlined facility accepting MSW, industrial waste and selected solid and liquid hazardous waste; the latter being permitted until 1983 and restricted to 30 acres along the northern half of the facility. In 1988, a compacted clay layer was constructed to separate MSW from underlying hazardous waste. Later expansions of the landfill occurred over multiple phases since the early 1990s increasing the permitted landfill property boundary from approximately 233 acres to 877 acres and the permitted refuse footprint from approximately 83 acres to 368 acres (CH2MHILL, 2015). Areas that are equipped with liner systems at the landfill are illustrated in Fig. 2. Cell A (4.3 acres) was lined in January 1990 with a 60 mm high density polyethylene (HDPE) geomembrane placed in direct and uniform contact over a >30 cm thick compacted clay base liner. Subsequently, Cell B (25.1 acres, 1994–2000) and Cell D (26.0 acres, 2004–2006) were installed with comparable liners. All lined areas are covered by geocomposite leachate drainage layers and about 60 cm of protective soil.

Construction of a LFGCCS was initiated in 1988 and has been expanded periodically (most recently in 2010). The system consists of a network of vertical gas extraction wells, horizontal extraction trenches, collection header pipes, and a flare system which destroys LFG through combustion. The waste footprint is surrounded by numerous, evenly spaced perimeter gas monitoring probes (Fig. 2). Each of these contains up to four individual probes (shallow, intermediate, deep 1 and deep 2) which are monitored monthly to evaluate the performance of the LFGCCS in controlling offsite gas migration.

The site is located in the Transverse Ranges geomorphic province, which is characterized by an east–west–trending sequence of ridges and valleys underlain by a similarly arranged sequence of folds and faults (Yerkes and Campbell, 1995a,b). Two distinct water-bearing units and potential LFG migration pathways have been identified beneath the facility: a shallow alluvial zone and a series of transmissive sandstone beds within the Sespe Formation (collectively known as the Sespe sandstone beds). The alluvial deposits generally are limited to the axis of the main canyon that originally traversed the site from north to south. They consist of an up to 7 m thick sequence of mixed gravels, sands, silts, and clays with hydraulic conductivity values in the range of 1 × 10⁻² to 1 × 10⁻⁶ cm/s (RUST, 1998). The Sespe Formation comprises a series of alternating sandstone and claystone units that dip at 25–30° to the northwest. Hydraulic conductivity of these units is reported as 1 × 10⁻³ cm/s and 1 × 10⁻⁷ cm/s for the sandstones and clays, respectively (RUST, 1998). All landfill perimeter monitoring probes considered herein are screened within the Sespe Formation (Fig. 2). Because of the extremely low permeability of the intervening claystone beds, groundwater (and potentially gas) within each of the Sespe sandstone beds is effectively isolated from its surroundings. This is evidenced in adjacent beds exhibiting distinctly different groundwater levels and chemistries (CH2MHILL, 2015). Some hydrologic continuity exists between the alluvial groundwater zone and those portions of the Sespe Formation that it traverses; however, because of the lower permeability of the Sespe Formation, groundwater within the alluvial deposits is thought to flow primarily southward following topography down the canyon.

(a) Fresh LFG from an ongoing release

(b) Legacy LFG from a past release

Fig. 1. Conceptual model of emplacement of fresh LFG (a) vs. legacy LFG (b) at a perimeter gas probe. Note that in this instance, the updated LFGCCS in (b) draws in fresh LFG and isolates legacy LFG at the probe from the source.

Please cite this article in press as: Hagedorn, B., et al. Geochemical and VOC-constraints on landfill gas age and attenuation characteristics: A case study from a waste disposal facility in Southern California. Waste Management (2015), http://dx.doi.org/10.1016/j.wasman.2015.10.033
Fig. 2. Site location and cross-section (A–A') of the case study landfill in Southern California (modified from Kerfoot et al., 2013). Probes with continuous methane exceedances and considered in this study are highlighted in red. Blue arrows indicate groundwater flow direction. Note that the shaded area shows the lined portion of waste. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Seasonal fluctuations in water levels at the site are relatively muted (generally < 1 m with highest values in late winter/early autumn); however, over the time period 2013–2015, groundwater elevations have declined as a result of prolonged drought conditions in Southern California.

The site is underlain by a reservoir of crude oil and natural gas and impacts from associated brines on local groundwater have been documented since the early 1990s. Natural gas methane associated with petroleum seeps has been the basis for variances in probe monitoring at the site since 1992; specifically for probes GP-9, GP-3 and GP-14R (Geosyntec, 2010). In 2009, new gas probes (GP-6R and GP-7R), which monitor four depth intervals, were installed along the eastern side of the waste prism to comply with the new California Code of Regulations (Title 27 CCR Sections 20919–20939) regulations. Monthly readings from these probes exceeded the regulatory threshold of 5% methane on several occasions following their installation. However, in those instances, methane was considered to be primarily LFG-derived based on VOC source end-members GP-3R2D1 (as a natural gas end-member) and because natural gas impact has been the reason for monitoring the site since installation with maximum values as high as 75.7% (v/v) at GP-7RM on 12/20/2013 (Fig. 3a–h). Despite these trends, nearby all probes reveal some short-term fluctuations with several methane troughs associated with concurrent oxygen peaks (e.g., Fig. 3a). These signals are attributed to oxidation events induced by aeration. The exact cause for these aeration events is not clear. On some occasions, such as on 02/19/2010 or 01/26/2011 for GP-6RS (Fig. 3a) methane troughs coincide with consistently stable nitrogen to oxygen ratios (<10). The methane oxidation and aeration in these deeper samples does not seem consistent with an atmospheric oxygen source expected to affect deep probes in a sedimentary basin as oxygen in deeper soil horizons is preferentially utilized for breakdown of organic compounds. An abundance of fractures (and air migration pathways) present in the subsurface or caused during probe installation could have sustained localized methane oxidation.

### 4. Results and discussion

#### 4.1. Methane and oxygen patterns

The analyzed probes exhibit methane readings that consistently exceed 5% with mean values (ranked from lowest to highest) of: 10.1% (GP-3R2D1), 13.5% (GP-7RD2), 17.8% (GP-7RD1), 30.4% (GP-6RD2), 41.6% (GP-6RD1), 41.9% (GP-6RS), 42.2% (GP-7RS), 43.1% (GP-6RM) and 50.6% (GP-7RM). With the exception of GP-3R2D1, which shows highly variable methane concentrations, all probes display consistently increasing methane concentration patterns since installation with maximum values as high as 75.7% (v/v) at GP-7RM on 12/20/2013 (Fig. 3a–h). Despite these trends, nearly all probes reveal some short-term fluctuations with several methane troughs associated with concurrent oxygen peaks (e.g., Fig. 3a). These signals are attributed to oxidation events induced by aeration. The exact cause for these aeration events is not clear. On some occasions, such as on 02/19/2010 or 01/26/2011 for GP-6RS (Fig. 3a) methane troughs coincide with consistently stable nitrogen to oxygen ratios (<10). The methane oxidation and aeration in these deeper samples does not seem consistent with an atmospheric oxygen source expected to affect deep probes in a sedimentary basin as oxygen in deeper soil horizons is preferentially utilized for breakdown of organic compounds. An abundance of fractures (and air migration pathways) present in the subsurface or caused during probe installation could have sustained localized methane oxidation.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Depth intervals (in m bgs) sampled by probes in this study.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Probe</td>
<td>Label</td>
</tr>
<tr>
<td>GP-R6</td>
<td>S</td>
</tr>
<tr>
<td>M</td>
<td>5.4 17</td>
</tr>
<tr>
<td>D1</td>
<td>20 34</td>
</tr>
<tr>
<td>D2</td>
<td>36 49</td>
</tr>
<tr>
<td>GP-R7</td>
<td>S</td>
</tr>
<tr>
<td>M</td>
<td>5.7 18</td>
</tr>
<tr>
<td>D1</td>
<td>20 34</td>
</tr>
<tr>
<td>D2</td>
<td>36 49</td>
</tr>
<tr>
<td>GP-3R2</td>
<td>S</td>
</tr>
<tr>
<td>M</td>
<td>6.1 21</td>
</tr>
<tr>
<td>D1</td>
<td>24 39</td>
</tr>
<tr>
<td>D2</td>
<td>41 57</td>
</tr>
</tbody>
</table>

Please cite this article in press as: Hagedorn, B., et al. Geochemical and VOC-constraints on landfill gas age and attenuation characteristics: A case study from a waste disposal facility in Southern California. Waste Management (2015), http://dx.doi.org/10.1016/j.wasman.2015.10.033
The presence of aerobic and anaerobic zones in the area can be evaluated by comparing time-series methane vs. oxygen data of monitoring probes with those measured at the flare inlet (Fig. 5a–e). Probe data generally align within a ternary domain that is defined by three processes: methanogenesis, dilution and oxidation. Methanogenesis (via CO₂ reduction) and dilution under

**Fig. 3.** Time-series trends of methane and oxygen at GP-6RS (a), M (b), D1 (c) and the Flare Inlet (d), and GP-7RS (e), M (f), D1 (g) and GP-3R2D1 (h). Data for GP-6R and 7R D2 probes resemble those of D1 probes and are not shown for brevity purposes. Note the increasing methane trends since the update of the LFGCCS (vertical line). Also note the inverse correlation between methane and oxygen values which is consistent with isolated oxidation events.

Please cite this article in press as: Hagedorn, B., et al. Geochemical and VOC-constraints on landfill gas age and attenuation characteristics: A case study from a waste disposal facility in Southern California. Waste Management (2015), http://dx.doi.org/10.1016/j.wasman.2015.10.033
anaerobic conditions affect methane concentrations (increase relative to the flare inlet for methanogenesis, and decrease relative to the flare inlet for dilution) without influencing oxygen levels (remain at <1.5%). Methanogenesis is particularly evident at GP-7RM where >90% of all oxygen levels were lower than those at the flare inlet and 65% of all methane readings were higher than those at the flare inlet (Fig. 5b). The presence of oxygen in more aerobic zones facilitates methane degradation which, in turn, decreases methane at a rate controlled by the oxygen supply. This process is well illustrated at GP-3R2D1 (Fig. 5e) where a strong positive linear correlation ($r^2 = 0.99, n = 23$) between methane and oxygen concentrations indicates a stable methane source and a continuous (i.e., atmospheric) oxygen supply. The overall scatter of the data at the other probes, however, reveals the dynamic characteristics of methanogenesis, dilution and oxidation processes which can be subject to pronounced spatial and temporal variations. Based on the data considered herein, it appears that all probes are, to some degree, affected by oxidation of methane that has undergone various degrees of enrichment or dilution relative to LFG at the flare inlet. At GP-7R (particularly at GP-7RS and GP-7RM), however, conditions appear to be nearly consistently anaerobic.

4.2. Natural gas vs. LFG tracing using methane to ethane ratios

Time-series methane trends are useful for delineating impacted probes at the site, but do not provide conclusive evidence regarding a pure LFG methane source as thermogenic (natural gas-derived) methane could theoretically display the same characteristics. Ethane can be used as a tracer of natural gas methane at gas probes as it is not a significant fermentation product at landfills. Lower methane/ethane ratios reflect a natural gas origin, whereas high ratios are more consistent with a LFG source. GP-3R2D1 samples show relatively low methane/ethane ratios (mean value: 63) along with a strong positive linear correlation trend ($r^2 = 0.98, n = 18$) which is consistent with a natural gas origin (Fig. 6). The fact that methane at GP-3R2D1 also has a very low $^{14}$C value of <0.2 percent modern carbon (pmc; Appendix A), indicative for an ancient (and not a modern, LFG-derived) $^{14}$C source (Coleman et al., 1995), is consistent with that hypothesis. By contrast, GP-7R samples are characterized by very high methane to ethane ratios (mean value: 17,741) which suggest a dominant impact from LFG methane. GP-6R samples exhibit somewhat intermediate ratios (mean value: 927) which indicate mixing between natural gas and LFG methane.

A comparison of methane to ethane ratios allows a quantitative assessment of LFG vs. natural gas derived methane inputs as:

$$m_{M/E \ probe} = x m_{M/E \ NG} + y m_{M/E \ LFG}$$

where $m_{M/E \ probe}$ is the slope of the linear methane vs. ethane regression at a perimeter probe and $m_{M/E \ NG}$ and $m_{M/E \ LFG}$ correspond to the slope of the linear methane vs. ethane regression of the natural gas end-member GP-3R2D1 (170) and the flare inlet LFG end-member (0), respectively. $x$ and $y$ are the contribution fractions of natural gas and LFG, respectively, assuming $x + y = 100\%$. Eq. (1) assumes that only fermentation (i.e., LFG)-derived and natural gas-derived methane and ethane contribute to probe detections and that no significant methane/ethane fractionation occurs during oxidation and/or interaction with pore- or groundwater. It is furthermore assumed that advective flow largely outweighs diffusive flow and that the differences in the methane and ethane diffusivities do not cause significant fractionation. This is considered valid given the fact that high diffusivity compounds such as methane have been detected concurrent with and not prior to low diffusivity compounds (e.g., Freon-12; Appendix A) at the monitoring probes. Diffusive transport would also not be consistent with the pronounced short-term fluctuations in the data and the fact that methane and ethane patterns track each other at probes were natural gas impact is significant (Fig. 7). Aside from GP-3R2D1, GP-6RS displayed the strongest methane vs. ethane correlation coefficient ($r^2 = 0.6, n = 23$) and the steepest linear regression slope (13.1; Fig. 6), which, according to Eq. (1), corresponds to a LFG input of about 88.8%. This value is considered a lower limit for LFG impact at the site and differs from that deduced from $^{14}$C data collected in 2010 which indicated a LFG contribution of 46.8% of only 60% (Kerfoot et al., 2013). The observation that methane to ethane ratios at GP-6R (particularly in the S and M probes) have increased since early 2011 (Fig. 7) is consistent with these data and suggests that the relative input of LFG-derived methane at the probes has increased as well.

4.3. Methane to carbon dioxide ratios

An important indicator for LFG impact and attenuation is LFG age. The older the LFG at a probe, the more it will interact with its surroundings and be affected by degradation in the subsurface. Past studies have utilized methane to carbon dioxide concentration ratios as indirect indicators for LFG age assuming that the degree of partitioning of the more soluble carbon dioxide into the pore water phase, commonly referred to as water “washing” or “weathering”, increases steadily with time (e.g., Coleman et al., 1995). Even though methane to carbon dioxide ratios of the analyzed probes show some spatial trends, which are generally increasing ratios (suggesting older LFG age) with probe screen depth, the application of this method is considered of limited value for temporal LFG age assessments in this study. This is mainly because of the local geologic setting with laterally continuous siltstone layers effectively isolating sandstone beds and inhibiting vertical gas and water flow. Moreover, the degree of carbon dioxide dissolution should vary with time as a function of seasonally changing soil water infiltration rates and groundwater table fluctuations within the individual zones screened by the probes. The uncertainty in the GP-6R and 7R methane/carbon dioxide vs. depth patterns illustrates these issues (Fig. 8a and b). GP-6R reveals an exponential soil gas aging trend with depth, although at high uncertainty given the large range of methane/carbon dioxide ratios particularly in the deeper D1 and D2 probes. This aging trend suggests an increasing degree of carbon dioxide dissolution with depth and distance away from the LFG source. At GP-7R, this aging pattern is not as clear. GP-7RM, for instance, exhibits a relatively high mean methane/carbon dioxide ratio (46.8) that could be due to a relatively high rate of $^{14}$CO$_2$ dissolution into pore waters, or methanogenesis via carbon dioxide reduction. GP-7R2D1, on the other hand, is characterized by a relatively low methane/carbon dioxide ratio (mean value: 4.57) which may be the result of methane oxidation, reduced water washing, or impact of fresh LFG. Because it is not possible to
exactly quantify the degree of carbon dioxide dissolution, carbon dioxide reduction or methane oxidation at the probe scale and because the relative importance of these processes can vary over time, observed methane/carbon dioxide ratios should – if at all – only be used as cursory proxies for LFG age.

4.4. Tracing LFG release(s) from toluene vs. Freon-12 ratios

Comparing time-series patterns of readily degraded VOCs that are major constituents in LFG, such as toluene, with those resistant to degradation, such as Freon-12, can provide valuable constraints on the timing of LFG release(s) so that fresh LFG can be distinguished from legacy LFG. Using the toluene/Freon-12 ratio instead of toluene concentrations alone accounts for the effect of soil gas dilution in the subsurface. Fresh LFG is assumed to be continuously replenished to a gas probe by the source (the landfill), whereas legacy LFG is assumed to be cut-off and effectively isolated from the source (Fig. 1). Given the distinct biogeochemical characteristics of toluene and Freon-12, probes impacted by fresh (and homogeneous) LFG should exhibit uniform toluene vs. Freon-12 ratios over time at steady state (when the VOC supply from the landfill is balanced by the VOC degradation at the probe). Ratios could even increase over time if the inflow of fresh LFG exceeds the rate of LFG degradation, or decrease if LFG degradation exceeds the inflow of fresh LFG. Probes only impacted by legacy LFG should be characterized by a decreasing toluene vs. Freon-12 trend defined by the first order reaction constant of toluene.

Several limitations need to be considered for the application of toluene and Freon-12 as LFG tracers. Unlike methane, which serves as a proxy for the LFG fraction derived from fermentation, toluene and Freon-12 data should only be considered proxies for the LFG fraction produced from evaporation and direct volatization of organic compounds (e.g., solvents) in the waste. For toluene and Freon-12 to be appropriate proxies, they should be present at (1)
detectable concentrations at the probes, and (2) constant levels in the source (i.e., flare inlet) throughout the monitoring period, which is the case here (Appendix A). It is furthermore assumed that toluene to Freon-12 ratios are not significantly fractionated due to their difference in diffusivities. We consider this assumption valid because of the dominance of pressure-driven (advective) flow over diffusive flow at the landfill perimeter (Ettinger and Kerfoot, 2012; Sepich, 2008). If diffusive transport were important, characteristic diffusive flow at the landfill perimeter (Ettinger and Kerfoot, 2012; because of the dominance of pressure-driven (advective) flow over their difference in diffusivities such as methane being detected prior to low diffusivity compounds such as Freon-12. This is clearly not the case here (see Appendix A) as both compounds have been detected at monitoring probes since their installation. In addition, toluene and Freon-12 exhibit similar diffusion constants that translate only into minor differences in diffusive migration velocities. Using Fick’s Law combined with Marshall’s (1959) approach for estimating effective soil gas diffusivity at a total porosity of ~30% (characteristic for sandy soils) and a migration distance of 20 m (i.e., the shortest lateral distance from the permitted waste boundary to the monitoring probes) yields 1-dimensional diffusion velocities for toluene and Freon-12 of 6.8 mm/d and 7.7 mm/d, respectively. Clearly, these estimates are conservative given, e.g., the effect of legacy LFG and/or pore waters in the subsurface (and the related non-representativeness of effective diffusivity constants). Given the fact that the landfill has been in operation for over 40 years, the differences in diffusion velocities of toluene and Freon-12 are considered too small to cause significant toluene/Freon-12 fractionation at the landfill perimeter during the monitoring period (2011–2014). As such, we consider the system to be effectively at diffusional steady state and short-term fluctuations of toluene/Freon-12 ratios to be primarily related to advective transport. However, because toluene exhibits a higher solubility than Freon-12, the potential lack of conservativeness of toluene, particularly over long migration distances, serves to cause age estimates to be lower limits. Another limitation relevant to this particular setting is natural gas (i.e., thermogenic toluene) impact on the toluene vs. Freon-12 trend. Even though methane/ethane ratios mitigate against major contributions from natural gas at probes GP-6R/7R and even though toluene concentrations at the natural gas end-member probe GP-3R2D1 are generally low (<6 ppb v/v compared to >20 ppb v/v at GP-6R/7R; Appendix A), the effect of thermogenic influences on observed toluene/Freon-12 ratios is accounted for by including concurrently obtained methane/ethane ratio data (Fig. 7) in the evaluation.

Data collected at GP-6R suggest some degree of fresh LFG impact as indicated by relatively flat and sometimes even increasing toluene/Freon-12 trends (Fig. 9a and c). This whole process is well illustrated at GP-6RD2 for which numerous data points (with both toluene and Freon-12 detections) are available (Fig. 9c). First, toluene/Freon-12 ratios decrease from 0.66 in January 2010 to 0.16 in February 2010. This trend is accompanied by a concurrent decrease (760–473) in methane/ethane ratios (Fig. 7d). These observations suggest both rapid LFG degradation and increasing natural gas (and potentially thermogenic toluene) impact, although the effect of the former appears to largely outweigh that of the latter given the observed toluene/Freon-12 ratio decrease. Next, there is a toluene/Freon-12 “rebound” to higher than pre-degradation values until May 2010 with a maximum value of 1.60. This trend is coupled with a methane/ethane increase to a value of 590. These patterns are consistent with increasing inflow of fresh LFG coupled with decreasing contributions of natural gas (and thermogenic toluene). From May 2010 to April 2011, toluene/Freon-12 ratios decrease again over multiple sampling events to a minimum value of 0.17. Over this time period, methane/ethane ratios continue to rise to values >1,000 (Fig. 7d). Collectively, these trends suggest that the released LFG and any residual natural gas have stayed in place and degraded over time. In fact, toluene/Freon-12 ratios exhibit a pseudo first-order decay trend (see the dashed line in Fig. 9c) characteristic for a half-life of ~100 days. This half-life fits within the observed ranges determined for anaerobic toluene decay in other site studies (Bruce et al., 2010; Lawrence, 2006; Thierrin, 1993). The apparent LFG release date can be calculated by extrapolating the probe decay trend until it intercepts the toluene/Freon-12 ratio at the source (i.e., flare inlet). Using the measured flare inlet data range to express uncertainty in the source ratio yields an apparent LFG release time frame of 03/15/2009 to 06/01/2009 which was prior to the updates of the LFGCCS (September of 2009). The data are therefore consistent with impact from legacy LFG. There are only a few carbon dioxide detections at GP-6RD2 (Fig. 9e) which

![Fig. 6. Relationship between ethane and methane concentrations. Probe data align in-between the natural gas end-member (GP-3R2D1) and the LFG end-member (flare inlet samples).](image-url)
Fig. 7. Time-series trends of methane and ethane at GP-6RS (a), M (b), D1 (c), D2 (d) and the Flare Inlet (e), and GP-7RS (f), M (g), D1 (h), D2 (i) and GP-3R2D1 (j). Note the arrows indicating increasing methane to ethane ratios at several probes consistent with increasing LFG input (see flare inlet data). GP-3R2D1 exhibits low ratios typical for natural gas.
prohibits a detailed comparison of the data. Still, from March 2010 until April 2011, methane/carbon dioxide ratios are increasing and peak at ~322 which, assuming methane/carbon dioxide ratios are only affected by water washing, further supports the hypothesis that LFG at GP-6RD2 reaches its greatest age by April 2011. From that point onwards, toluene/Freon-12, methane/ethane and methane/carbon dioxide ratios stabilize at uniform values of 0.2, 1.200 and 40, respectively, which is consistent with impact of fresh LFG at more or less steady state conditions. Interestingly, this inflow of fresh LFG, starting April 2011, is also supported by toluene/Freon-12 data at GP-6RM and D1 (Fig. 9a). However, more refined time series data is needed to further reconstruct the LFG release event(s) at these particular probes.

Toluene/Freon-12 patterns at GP-7R are less variable than those at GP-6R and exhibit characteristic declining trends (Fig. 9b and d) consistent with degradation of legacy LFG in the subsurface. In the case of GP-7RM, for which more than 2 data points are available, toluene/Freon-12 ratios decline by about one order of magnitude from 0.08 in March 2010 to 0.008 in late December 2010, the last sampling event with both toluene and Freon-12 detections. The fact that toluene levels at that probe have remained below detection limits since then militates against any “recent” inflow of fresh LFG such as documented since April 2011 for GP-6R. The legacy LFG degradation trend at GP-7RM is consistent with increasing methane/ethane ratios (6.102 – 9.278; Fig. 7g) which suggest that residual natural gas has stayed in place and degraded as well. The toluene/Freon-12 trend at GP-7RM, again, indicates a half-life of 100 days which in light of the relatively low oxygen levels (Fig. 5b) and relatively high methane to carbon dioxide ratios (Fig. 6b) suggest that decay occurs anaerobically. Unlike at GP-6RD2, where decreasing toluene/Freon-12 ratios are associated with increasing methane/carbon dioxide values and vice versa, methane/carbon dioxide ratios at GP-7RM exhibit a decreasing trend from a value of 103 to 25.6 (Fig. 9f). This is surprising given that progressive CO₂ dissolution over time should increase methane/carbon dioxide ratios as the gas gets older. We do not believe that methane oxidation is a likely cause for the methane/carbon dioxide ratio decline because of the relatively low oxygen levels and the overall increasing methane levels (Fig. 3f). Also, inflow of fresh LFG (with a methane/carbon dioxide ratio of ~1.25) is not considered to be the cause for the decline given that toluene concentrations decreased from 38 ppb (v:v) to 5.4 ppb (v:v) over the monitoring time-span (Appendix A). A temporary reduction in soil water infiltration rates and therefore a reduction in CO₂ dissolution into pore waters could be a plausible explanation for the decreasing methane/carbon dioxide ratios. As could be a reduced degree of methanogenesis via CO₂ reduction over this time period. Detailed data on hydrological parameters (precipitation, evapotranspiration and groundwater recharge rates) and methane δd and δ¹³C isotopes are necessary to further test these hypotheses.

Extrapolating the toluene/Freon-12 decay trend at GP-7RM back in time to the point at which the toluene/Freon-12 ratio intercepts the source ratios yields an apparent LFG release date range of 11/28/2007 to 02/12/2008. Again, this pre-dates the local LFGCCS update and indicates legacy LFG impact. At GP-7RS the decay trend (based on only 2 data points) suggests a very long half-life of 510 days and a significantly older apparent release date range of 10/03/1998 to 11/05/1999. Whether this implies a reduced degradation rate or simple mixing between legacy and fresh LFG needs to be evaluated with more time-series data.

The absence of detectable toluene at GP-7RD1 and D2, and Freon-12 at GP-3RD1 prohibits further LFG evaluations for these probes. In the case of GP-7RD1 and D2, the relatively high oxygen contents likely facilitate rapid toluene degradation at a rate higher than the inflow of any fresh LFG. The lack of Freons at GP-3RD1 reflects the dominant impact of natural gas which does not contain detectable Freons.

5. Conclusions and implications

Analysis of geochemical data from a municipal solid waste disposal landfill in Southern California revealed highly variable soil gas chemistries characteristic for a complex setting where multiple sources contribute to methane detections at monitoring probes and where attenuation from biodegradation is subject to pronounced temporal and spatial variations. Based on time-series methane vs. ethane ratios, the methane in probe GP-3RD1 is mainly from natural gas while that in the remaining impacted probes GP-6R (S, M, D1, D2) and 7R (S, M, D1, D2) is predominantly from LFG. Data from GP-3RD2 and GP-7RD1 and D2 are consistent with ongoing aerobic methane degradation as implied by the absence of degradable VOCs (e.g., toluene) as well as the relatively low methane and relatively high oxygen levels. The other considered probes are only affected by isolated (short-term) oxidation events that do not appear to significantly attenuate overall LFG impacts. Time-series toluene/Freon-12 ratios suggest GP-6R to be impacted, to some degree, by fresh LFG from a release that occurred after the update of the LFGCCS (late 2009). Data further indicate GP-7RS and M samples to be more influenced by legacy LFG from a past release that occurred prior to the LFGCCS update and that, because of the lack of oxygen at the probes, has not yet been fully degraded. In this case, locally-executed short-duration remediation measures that facilitate aeration in the deeper zones may provide the desired attenuation effect. However, additional
data are required to refine and further test these assumptions. This is particularly the case for the probes for which only few toluene/Freon-12 data points are available.

Further research should also address the mechanism of LFG transport using, e.g., gas pressure and flow data. Recent studies have noted that advective (i.e., pressure-driven) flow of LFG creates significantly greater LFG flux than diffusional (i.e., concentration gradient-driven) flow (Ettinger and Kerfoot, 2012; Sepich, 2008). This suggests that probes affected by a soil gas pressure gradient are likely to pose higher risks to LFG contamination than those only affected by a concentration gradient. A combination of LFG age information (as provided in this study) and LFG flow information (as provided through pressure data) can potentially benefit LFG contamination risk evaluations because it could highlight preferential migration pathways for high fluxes of fresh LFG.

Acknowledgements

Funding for this study was provided by Waste Management, Inc. (contract number: 402914-01502). The authors would like to thank the staff at the site for their help with sample collection and the geochemical analyses. We would also like to thank A.R. Cabral, A.J. Sarubbi and three anonymous reviewers for their helpful comments and suggestions that greatly improved the quality of this paper.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.wasman.2015.10.033.

References


Fig. 9. Time series trends of toluene/Freon-12 ratios at GP-6RS, M, D1 (a), GP-7RM (b), GP-6RD2 (c) and GP-7RM (d) and methane/carbon dioxide ratios at GP-6RD2 (e) and GP-7RM (f). Arrows indicate the presence of fresh LFG (flat or positive slope) and legacy LFG (negative slope). Dashed lines illustrate anaerobic toluene decay trend which is superimposed on measured GP-6RD2, and GP-7RM data.


