Discriminating Methane Sources in Ground Gas Emissions in North-West England

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ABSTRACT

The identification of the source of methane (CH₄) and carbon dioxide (CO₂) in gases within unconsolidated deposits outside municipal landfill sites, where there are multiple potential contributing gas inputs, is important for regulation and to inform gas management policy. Stable isotope analysis was applied to ground gas samples from boreholes close to but external to landfill cells, and landfill gas, to differentiate CH₄ from biological and abiological geological sources at sites in NW England. Landfill flare gas and landfill without external gas inputs were biogenic references. Ground gases adjacent to one landfill had potential external CH₄ inputs from underlying Coal Measures. Mineshaft vent gas and commercially-supplied North Sea Gas were used as non-biological, thermogenic, source references. Ground gas samples were subjected to Compound-Specific Isotope Ratio Mass Spectrometry (GC-IRMS) and conventional IRMS examination. $\delta^{13}\text{C}_{\text{CH}_4}$ values for landfill flare gas and landfill site 1 were -65.0‰ and -61.0‰, and $\delta\text{D}_{\text{CH}_4}$ values were -319‰ and -298‰ respectively, consistent with a wholly biogenic origin. $\delta^{13}\text{C}_{\text{CH}_4}$ values for site 2 landfill were -55‰ to -48‰, and $\delta\text{D}_{\text{CH}_4}$ values were -173 to +55‰. Mineshaft vent gas and North Sea Gas CH₄ $\delta^{13}\text{C}_{\text{CH}_4}$ values were -46.2‰ and -43.5‰, and $\delta\text{D}_{\text{CH}_4}$ values were -214‰ and -203‰, respectively. Given their similarity to these data, gases in the vicinity of site 2 landfill are considered to have a thermogenic CH₄ contribution, due to ¹³C and D enrichment in CH₄.

KEYWORDS

methane, carbon dioxide, biogenic gas, geogenic gas, thermogenic gas, ground gas, stable isotopes, IRMS

1 INTRODUCTION

Biological decomposition of organic waste at municipal landfill sites generates landfill gas, typically 60% v/v methane (CH₄) and 40% v/v carbon dioxide (CO₂) (Farquhar & Rovers, 1973; Hooker & Bannon 1993; Kjeldsen *et al.*, 2002; Wilson *et al.*, 2006). Additional components include hydrogen sulphide (H₂S), carbon monoxide (CO), and volatile organic compounds (VOCs). Landfill, natural wetlands, rice production, ruminant animals, termites, wastewater treatment, fossil fuel production and consumption, and biomass burning all constitute terrestrial CH₄ sources with different origins. Collectively, the non-wetlands sources account for more than half of the annual atmospheric input of 450–550 Tg CH₄ (Bogner & Matthews, 2003). Khalil (2000) estimated that landfill accounts for 17% of all artificial CH₄ emissions. The production of landfill gas may last 30 years or longer, until most organic substrate has been exhausted (Kjeldsen *et al.*, 2002). In unconsolidated media, such as fill or natural soils, sediments and rocks adjacent to a landfill, CH₄ and CO₂ gases may migrate as a result of pressure or concentration gradients resulting in emissions to atmosphere or into structures (Kerfoot *et al.*, 2013; Röwer *et al.*, 2011; Teasdale *et al.*, 2014). CH₄ originating from underlying coal-bearing strata, such as the UK's Coal Measures, may enter the landfill system and so mix with landfill gas following migration through faults, fractures, fissures and porous strata in the bedrock. In the context of landfill gas monitoring, it is important not only to be able to measure the amounts of CH₄ that may be emitted, but also to identify the source of the gas, so that appropriate management of emissions can be designed.

A key concept in the use of stable isotopes to determine gas source is that CH₄ formed biochemically in landfills (biogenic) is generally depleted in the heavier ¹³C and ²H (D) isotopes as microbes discriminate against these isotopes (i.e. lower, or more negative $\delta^{13}\text{C}$ and δD) compared with geogenic CH₄ (Kerfoot *et al.*, 2013). Biogenic gas sources such as landfill tend to have more negative $\delta^{13}\text{C}_{\text{CH}_4}$ values and are isotopically depleted in the heavier ¹³C isotope (values generally -60‰ (Hitchman *et al.*, 1989)). Correspondingly, CO₂ evolved from landfill gas is enriched in ¹³C. Values of $\delta^{13}\text{C}_{\text{CO}_2}$ are higher than (more positive than) $\delta^{13}\text{C}_{\text{CH}_4}$. Hitchman *et al.* (1989) reported $\delta^{13}\text{C}_{\text{CO}_2}$ values from landfill in the range -12.8 to +12.0‰.

In contrast, geological sources of CH₄ that lack microbiological inputs are relatively enriched isotopically in ¹³C and have more positive $\delta^{13}\text{C}_{\text{CH}_4}$ values. For closed collieries in Nottinghamshire, UK, Zazzeri *et al.* (2015) observed $\delta^{13}\text{C}_{\text{CH}_4}$ values in the range $-33.3 \pm 1.8\text{‰}$ to $-30.9 \pm 1.4\text{‰}$. Similarly, Ni *et al.* (2014) reported geologically-produced CH₄ from the Hongtai Gas Field, Turpan-Harmi Basin, China with $\delta^{13}\text{C}_{\text{CH}_4}$ values in the range -39.0 to -37.7‰.

Also used to identify gas source is D in CH₄. Like ¹³C_{CH₄} from biogenic sources such as landfill, there is a depletion in D in CH₄. For example, Raco *et al.* (2014) reported $\delta\text{D}_{\text{CH}_4}$ from biogenic sources in the range -329 to -291‰. Geological sources such as coal gas are relatively enriched isotopically in D in CH₄ and consequently have higher (or more positive) $\delta\text{D}_{\text{CH}_4}$ values than biogenic sources. Kerfoot

et al. (2013) observed δD_{CH_4} values in the range -197.4 to -193.7‰. Ni *et al.* (2014) reported δD_{CH_4} values in the range -257 to -250‰ while Dai *et al.* (2012) recorded δD_{CH_4} values in the range -173 to -155‰. Unfortunately, Zazzeri *et al.* (2015) did not give δD values for samples from UK collieries. While a broad range of δD_{CH_4} values are reported in the literature, most data consistently show that δD_{CH_4} values for CH_4 with a deep geological origin are greater than δD_{CH_4} values for biogenic CH_4 . Therefore, using the $\delta^{13}C_{CH_4}$, $\delta^{13}C_{CO_2}$ and δD_{CH_4} values it is possible to differentiate biogenic CH_4 from that with a deep geological origin, as both sources have distinct signatures.

Identification of gas origin is crucial for regulation. In the case of the Loscoe Explosion in Derbyshire in March 1986, radiocarbon dating of gas samples yielded ^{14}C 125 pMC (Williams & Aitkenhead, 1991). This clarified that the CH_4 was modern (i.e. was not a fossil source) and proved that the explosion had been caused by landfill gas migrating 70 m from the nearby municipal landfill via the adjacent permeable sandstone beds. However, radiocarbon dating is relatively expensive, and not widely used to distinguish gas sources.

2 HISTORIC GAS MONITORING DATA

Two locations are used in this study to demonstrate the likely presence of a previously unrecognized contribution of deep geological methane to shallow ground gas. Described more fully in Teasdale *et al.* (2014), they are referred to as Sites 1 and 2. Site 1, situated in unconsolidated Quaternary deposits, (Middle Sands Formation) (Evans, 1968)) has no known gas source other than the municipal landfill. It overlies a thick Triassic sedimentary sequence, dominated by mudstones (Keuper marl), with no known underlying faults. Site 2 is situated in a thick layer of glacial till consisting of clay with occasional sand lenses and overlies a major fault. Underlying the Quaternary material is both (because of faulting) Permo-Triassic sandstone and Carboniferous (Westphalian) Coal Measures. At Site 2 there is potential for coal-derived CH_4 to mix with landfill (biogenic) CH_4 via the fault and the weathered (pre-Quaternary) top-surface of the Permo-Triassic sandstone. Perimeter monitoring wells at both sites are located **outside** the landfill cells and are screened to permit gas sampling from the unsaturated zone in the adjacent strata. In accordance with regulatory requirements, they have been monitored using (prior to 2012) a GA2000 landfill gas monitor (http://www.keison.co.uk/geotechnical_ga2000.shtml) and after 2012 a GFM435 landfill gas analyser (<http://www.gasdata.co.uk/products/landfill-gas-analyser/> since updated to GFM436).

Borehole gas composition data were compared (Teasdale *et al.*, 2014) in ternary plots in terms of the measured CH_4 , CO_2 and O_2 normalised to N_2 (assuming N_2 to be the balance, i.e. $100 - (CH_4 + CO_2 + O_2)$). This allows the relative proportions of CH_4 and CO_2 to be compared irrespective of any dilution by air, the O_2/N_2 ratio indicating whether this has occurred and the extent to which O_2 has been removed, as N_2 can be regarded as non-reactive (Bergmaschi & Harris, 1995). Figure 1 shows the historic gas compositions for landfill Sites 1 and 2

Site 1 Monitoring Wells

Site 2 Monitoring Wells and Flare Gas

Figure 1. Historic Gas Compositions Measured at Sites 1 (2004–2015) and 2 (1998–2015) by Hand-Held Gas Monitors GA2000 and GFM435

Throughout the monitoring period 2004–2015, Site 1 BH 03/4 gas composition was either landfill gas (~70% CH_4/N_2 and 30% CO_2/N_2) or air (100% O_2/N_2). Mixing of gases between these end members was observed on few occasions. With increasing distance from the landfill perimeter (BH 06/14), the cluster of data points around the landfill gas ratio became more diffuse and at 100 m only air was recorded (BH 06/17).

In contrast, perimeter monitoring wells at Site 2 showed more complex mixing patterns. When compared with the flared gas at the site, BH 04 gas was predominantly richer in CH_4 during the monitoring period 1998–2015. End member CH_4/N_2 was approached on multiple occasions. Mixing of CH_4 with air was indicated by data points along the join between 100% CH_4/N_2 and 100% O_2/N_2 . The CH_4 -rich gas compositions observed for BH 04 suggest, but do not prove, a geological gas origin. Similarly, externally-sourced methane may have mixed with landfill gas in two other perimeter boreholes, BHs 12 and 14. In these, gas with the ratio 70:30 $\text{CH}_4/\text{N}_2:\text{CO}_2/\text{N}_2$ was observed along with gas approaching end member CH_4/N_2 . Mixing between CO_2 and air (100% CO_2/N_2 to 100% O_2/N_2) was also observed in BHs 12 and 14. This mixing pattern was absent from BH 04.

The CH_4 -rich gas compositions observed in the external monitoring boreholes suggest that a component originating from coal seams underlying the landfill needs to be considered, alongside other possible sources. Site 2 flare and cell gases were used as references for biogenic CH_4 while abandoned coal mineshaft vents at the former Parkside Colliery in the Lancashire Coal Field (Westphalian; 29 km WNW of Site 2) and commercially-supplied North Sea Gas (Newcastle upon Tyne; May 2016) were used as references for geologically-derived CH_4 .

3 METHODOLOGY

3.1 Atmospheric and Meteorological Conditions

Landfill gas samples were collected from Sites 1 and 2 between 10:00 and 14:00 on 8th February 2016. The sampling was timed to coincide with rapidly falling atmospheric pressure to ensure positive borehole flow conditions to allow collection of samples that represent ground gas. On the day of the sample collection, the UK was impacted by 'Storm Imogen' as part of the 2015–16 UK and Ireland Windstorm Season (lowest pressure of 962 mbar; (Met Office, 2016). Local conditions at Sites 1 and 2 were windy with heavy rain. Peak wind gusts were recorded at Manchester Airport (12.3 km from Site 1; 6.5 km from Site 2) at 107.3 km/hr and low pressure at 973 mbar (Figure 2).

Figure 2. Atmospheric Pressure Preceding and During Landfill Gas Sampling (06/02/2016–10/02/2016)

Significantly, before Storm Imogen, there was a steep decrease in atmospheric pressure between 00:00–18:30 on 6th February 2016, from 1004 mbar to 980 mbar, equivalent to an average rate of 1.3 mbar/hr. This decrease in atmospheric pressure coupled with a further drop of 16 mbar over 18 hours (average 0.89 mbar/hr) during Storm Imogen would have induced positive borehole pressure in the boreholes.

3.2 Landfill Gas Sampling

Gas samples were collected in 1 l SKC FlexFoil sample bags with stainless steel fittings (Product Code 263–01). Prior to sample collection on 8th February 2016, the bags were cleaned by flushing three times with N₂.

Boreholes were selected for gas sampling based upon historic composition of gas. At Site 1, boreholes 03/4, 03/6 and 03/7 and at Site 2 boreholes 04, 08 and 12 were selected. Additionally the flared gas and gas from within the landfill waste were directly sampled at Site 2 as a reference for 'pure' landfill gas.

The following parameters were measured using the handheld landfill gas monitor (GFM436; Gas Data Ltd): CH₄ (%), CO₂ (%), O₂ (%), CO (ppm), H₂S (ppm), Atmospheric Pressure (mbar), Differential Pressure (mbar) and Flow (l/hr). A dip meter was used to measure the groundwater depth at Site 1. The recorded atmospheric pressure was corrected to sea level.

Following the measurement of gases using the GFM436, a sample bag was attached to the borehole valve via a hand pump. Gas was pumped into the sample bag using the hand pump over a period of 30 s (the large flows recorded aided the inflation of the sample bags). Once the sample was acquired, the flexfoil bag valve was securely closed. Using a 10 ml syringe, four 10 ml samples were aliquoted into 12 ml exetainers for storage prior to analysis.

The atmospheric and ground conditions on 8th February 2016 are recorded in [Table 1](#). The differential pressure of the flared gas at Site 2 was above the certified calibration range of the instrument. Groundwater depths are not routinely recorded at Site 2 as part of the gas monitoring regime and were not measured on the day of the sample collection.

3.3 Coal Gas Sampling

Gas samples were taken from the two former mineshaft vents at Parkside Colliery (53.447854 °N, 2.604223 °W (SJ599947 OS grid reference); 53.447913 °N, 2.603292 °W (SJ600947 OS grid reference) on 16th March 2016. The sampling process was the same as for landfill gas sampling.

For all sites, atmospheric and ground conditions are summarised in Table 1.

Table 1. Atmospheric and Ground Conditions Measured During Sampling by GFM436

Sample ID	Atmospheric Pressure (mbar)	Differential Pressure (mbar)	Peak Flow (l/hr)	Steady Flow (l/hr)	Groundwater Depth (m)	Ambient Temp. (°C)
<i>Site 1 (08/02/2016)</i>						
BH 03/4	973	13.58	72.6	72.6	Dry	7
BH 03/6	973	-0.31	0.2	-3.2	18.32	7
BH 03/7	976	1.42	14.8	14.7	Dry	7
<i>Site 2 (08/02/2016)</i>						
BH 04	974	-0.17	0.8	-2.1	NM	7
BH 08	974	1.04	23.6	10.4	NM	7
BH 12	975	-0.05	-0.9	-0.9	NM	7
Flare Gas	975	>>	110.3	110.3	NM	7
Cell Gas	973	10.39	60.6	59.5	NM	7
<i>Mineshaft Vents (16/03/2016)</i>						
Mineshaft 1	1027	0.0	0.0	0.0	NM	10
Mineshaft 2	1027	0.0	0.0	0.0	NM	10

>> indicates that the sample was above the calibration range of the instrument.

3.4 GC-MS Analysis

Gas compositions were determined using a Fisons 8060 GC with split injection (150°C) linked to a Fisons MD800 MS (electron voltage 70 eV, filament current 4 A, source current 800 µA, source temperature 200°C, multiplier voltage 500 V, interface temperature 150°C). Data acquisition was

controlled by a Compaq Deskpro computer using Xcalibur software, in full scan mode (1-150 amu/scdwell 10 ms/amu) or in SIM mode 10 ions (dwell 100 ms/ion) for greater sensitivity. Separation was performed on a HP-PLOT-Q capillary column (30 m x 0.32 mm i.d.) packed with 20 µm Q phase. The GC was held isothermally at 35°C with He as the carrier gas (flow 1 ml/min, pressure 65 kPa, split at 100 ml/min. The chromatograms of the separated gases (CH₄ and CO₂) were integrated and quantified. The acquired data were stored on DVD for any further data processing, integration and printing.

3.5 Stable Isotope Analysis

Stable isotope analysis was carried out at Newcastle University using compound-specific GC-IR-MS analysis. Bulk samples were also analysed on a commercial basis by IRMS at the University of California, according to the method prescribed by UC Davis Stable Isotope Facility (2016) and Yarnes (2013). Full details of the methodologies may be found in the Appendix.

IRMS limits of quantification for the bulk gas analysis are summarised in Table 2.

Table 2. IRMS Limits of Quantification (from (UC Davis Stable Isotope Facility, 2016))

Analysis	Limit of Quantification (nmol)	Long-term Standard Deviation (‰)
¹³ C CH ₄	0.8	0.2
D CH ₄	2.0	2.0
¹³ C CO ₂	150	0.1

4 RESULTS

4.1 Absolute Gas Concentrations

Gas concentrations measured using the GFM436 landfill gas analyser of CH₄ (%), CO₂ (%), O₂ (%), CO (ppm) and H₂S (ppm) (Table 3) were normalised to N₂ (Figure 3). Where the concentration of these gases was below the detection limit (<0.1%), the concentration was assumed to be 0.0%.

The samples show a range of CH₄ and CO₂ compositions. 'Site 2: Flare' and 'Site 2: Landfill Cell' samples show a ratio of approximately 60:40 CH₄:CO₂ corresponding to the landfill gas ratio. Likewise, the proportion of CH₄ to CO₂ in 'Site 1: BH 03/4' is 60:40 which is also indicative of landfill gas. 'Site 1 BH: 03/7' also shows a landfill gas signature but in a slightly greater CH₄ proportion to CO₂ (70:30). Of all the landfill boreholes sampled, 'Site 2: BH 04' contained the greatest proportion of CH₄ at 80% compared with 20% CO₂. Importantly, the relative quantities of CH₄, CO₂ and O₂ measured in these samples are consistent with those measured historically by point measurement and by high temporal frequency sampling (Teasdale *et al.*, 2014).

Borehole 12, Site 2, demonstrated a mixing of CH₄, CO₂ and O₂ in the relative proportions CH₄/N₂ 23.3%, CO₂/N₂ 65.1 and O₂/N₂ 11.6%. The differential pressure and flow rate were both slightly negative (-0.05 mbar and -0.9 l/hr respectively) despite the large drop in atmospheric pressure that had induced very large flows elsewhere on Site 2 (23.6 l/hr peak flow BH 08 and 60.6 l/hr peak flow LFC).

Similarly, BH 04 recorded a weak negative differential pressure (-0.17 mbar) and a weak peak flow of 0.8 l/hr. However, steady flow was weakly negative (-2.1 l/hr). Despite this CH₄ and CO₂ were present in the ratio CH₄/N₂:CO₂/N₂ 80:20.

At Site 1, BH 03/6 was the only borehole to record a negative differential pressure (-0.31 mbar) and flow rate (-3.2 l/hr (steady)). Considering BH 03/4 and BH 03/7 recorded differential pressures of 13.58 and 1.42 mbar respectively and steady flow rates of 72.6 l/hr and 14.7 l/hr respectively, BH 03/6 seems to be anomalous in the context of the site and proximity to the landfill waste. It could be that this borehole does not have an air-tight seal thereby diluting the CH₄ and CO₂ concentrations. Additionally, the concentrations of CH₄, CO₂ and O₂ are such that the balance (i.e. N₂) was 97.7% which is an unlikely scenario. This could be attributed to instrument error or other extraneous gases not quantified by the instrument. However, as will be seen with the GC-MS data, the concentration of CO₂ was in reasonable agreement with the GFM436.

Figure 3. Measured Gas Compositions for Landfill and Mineshaft Vent Samples

The mineshaft vents showed very different relative proportions of CH₄ and CO₂. Mineshaft 1 approached 100% CH₄/N₂ while Mineshaft 2 gas was in the ratio 75:25 CH₄/N₂:O₂/N₂. These gas compositions were consistent with CH₄-rich gas derived from underlying Carboniferous Coal Measures. Additionally, on numerous occasions Site 2 BH 04 also approached 100% CH₄/N₂ throughout the 17-year historic monitoring period (1998–2015).

In most cases, the GC-MS data were in reasonable agreement with the GFM436 data (Table 3). Measured concentrations of CH₄ by GC-MS were within $\pm 11.4\%$ and CO₂ were within $\pm 7.8\%$. Notable exceptions included Site 1 BH 03/4 where the concentration of CH₄ and CO₂ was two orders

of magnitude lower than that measured by the GFM436. It was assumed that ingress of air had occurred during sampling. Likewise, the concentration of CH₄ and CO₂ measured in the landfill cell by GC-MS was one order of magnitude lower than that measured by the GFM436, again indicating ingress of air.

For the purposes of IR-MS analysis, all samples were above the limits of quantification (Table 3). Although an order of magnitude less than measured by the GFM436, the concentration of CH₄ and CO₂ measured in the landfill cell by GC-MS approximately equated to the expected 60:40 CH₄:CO₂ landfill gas ratio. When calculating concentrations by peak area from the GC-MS chromatogram, there is a scaling error beyond the calibration curve limits. This would account for some of the deviations observed between concentration measured by GC-MS and GFM436.

Table 3. Gas Concentrations Measured by GC-MS Compared against GFM436 Data

Sample ID	GFM436 Data			GC-MS Data		
	CH ₄ (%)	CO ₂ (%)	CH ₄ / CO ₂	CH ₄ (%)	CO ₂ (%)	CH ₄ / CO ₂
Site 1 BH 03/4	15.8	9.0	1.76	0.4	0.2	2.00
Site 1 BH 03/6	<0.1	0.5	0.200	0.0	0.2	0
Site 1 BH 03/7	19.2	7.1	2.70	17.9	6.1	2.93
Site 2 BH 04	22.1	5.6	3.95	20.4	4.0	5.10
Site 2 BH 08	<0.1	5.2	0.0192	NM	NM	NM
Site 2 BH 12	2.0	5.6	0.357	2.1	5.0	0.420
Site 2 Flare Gas	41.7	25.5	1.64	53.1	17.7	3.00
Site 2 Cell Gas	39.3	24.2	1.62	5.9	3.4	1.74
Mineshaft 1	98.8	0.8	124	NM	NM	NM
Mineshaft 2	35.0	0.6	58.3	NM	NM	NM

4.2 Stable Isotope Data

4.2.1 Comparison of Data Sets

Data produced at Newcastle University and the University of California Davis Stable Isotope Facility (UC Davis SIF) are compared in Tables 4 and 5. The average difference between data sets is 1.80‰ with a standard deviation of 1.23‰ for δ¹³C_{CH₄} values. Similarly, the δ¹³C_{CO₂} values show a low dispersion with an average difference of 1.06‰ between the two data sets. A slightly larger standard deviation of 3.33‰ was derived for δ¹³C_{CO₂} values owing to the large difference of 35.59‰ between Newcastle University and UC Davis SIF data for Site 1, BH 03/6. The data for Site 1, BH 03/6 represents the only significant deviation in δ¹³C values.

The average difference between δD_{CH₄} values calculated at Newcastle University and UC Davis SIF was 9.81‰ with a standard deviation of 14.13‰. Similarly to δ¹³C values, the greatest difference between data sets was recorded at 35.67‰ for Site 2, BH 08 for δD_{CH₄}. This value is approximately the same maximum deviation as was recorded for δ¹³C_{CO₂} values.

Table 4. Stable Isotope Ratios Measured at Newcastle University and UC Davis Stable Isotope Facility

Sample ID	Newcastle University Data			UC Davis SIF Data		
	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰)	$\delta\text{D}_{\text{CH}_4}$ (‰)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰)	$\delta\text{D}_{\text{CH}_4}$ (‰)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)
Site 1 BH 03/4	-58.2	-298	-55.6	-54.07	-307.1	-46.74
Site 1 BH 03/6	N/A	N/A	-13.3	N/A	N/A	-48.92
Site 1 BH 03/7	-61.0	-253	-51.0	-60.60	-238.1	-50.48
Site 2 BH 04	-55.6	-172	-47.0	-53.77	-158.2	-46.74
Site 2 BH 08	-55.0	-173	-37.0	-53.80	-137.3	-28.10
Site 2 BH 12	-48.0	+55	-32.8	-47.06	+74.0	-32.79
Site 2 Flare Gas	-65.0	-319	+5.0	-63.58	-309.8	+6.96
Site 2 Cell Gas	-64.5	-316	+5.5	-62.12	-326.3	+6.50
Mineshaft 1	-46.2	-214	-10.9	-43.05	-202.6	-9.21
Mineshaft 2	-50.5	-208	-46.1	-49.85	-204.2	-48.81

As the difference between data sets for $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ values was so little, there is a good degree of confidence that the values reported are close to the true values for the samples. The only exception was the $\delta^{13}\text{C}_{\text{CO}_2}$ value for Site 1 BH 03/6, for which the true value is uncertain. The $\delta^{13}\text{C}_{\text{CH}_4}$ values demonstrated a greater average difference between the two data sets. The standard deviation was only 14.13‰ and the maximum difference was 35.67‰ (Site 2, BH 08), a similar discrepancy to the maximum $\delta^{13}\text{C}_{\text{CO}_2}$ difference value that was recorded for Site 1, BH 03/6. Owing to the greater dispersal of the data, there is perhaps less confidence in the $\delta\text{D}_{\text{CH}_4}$ values. However, the discrepancies between the data sets was not large enough to be a major concern.

Table 5. Difference between Stable Isotope Ratios Measured at Newcastle University and UC Davis Stable Isotope Facility

Sample ID	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰)	$\delta\text{D}_{\text{CH}_4}$ (‰)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)	$\delta^{13}\text{C}_{\text{CH}_4}$ (% Diff)	$\delta\text{D}_{\text{CH}_4}$ (% Diff)	$\delta^{13}\text{C}_{\text{CO}_2}$ (% Diff)
Site 1 BH 03/4	4.12	9.12	2.05	7.4	-3.0	17.3
Site 1 BH 03/6	N/A	N/A	35.6	N/A	N/A	N/A
Site 1 BH 03/7	0.40	14.9	0.52	0.7	6.1	1.0
Site 2 BH 04	1.80	13.8	0.26	3.3	8.4	0.6
Site 2 BH 08	1.20	35.7	8.90	2.2	23.0	27.3
Site 2 BH 12	0.94	19.0	0.03	2.0	-29.5	0.0
Site 2 Flare Gas	1.42	9.21	1.96	2.2	2.9	-32.8
Site 2 Cell Gas	2.43	10.3	0.95	3.8	-3.2	-16.7
Mineshaft 1	3.16	11.4	1.72	7.1	5.5	16.8
Mineshaft 2	0.70	3.77	2.71	1.3	1.8	-5.7
Average	1.80	9.81	1.51	3.32	1.33	0.88
Standard Deviation	1.23	14.1	12.6	2.40	13.9	18.4

5 DISCUSSION

5.1 Determination of Gas Source using $\delta^{13}\text{C}_{\text{CH}_4}$ versus $\delta^{13}\text{C}_{\text{CO}_2}$

The $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ data show substantial difference between the landfill gas samples and mineshaft vent sample. Landfill gas samples have $\delta^{13}\text{C}_{\text{CH}_4}$ -65.0‰, $\delta^{13}\text{C}_{\text{CO}_2}$ +5.0‰ for Site 2 Flare and $\delta^{13}\text{C}_{\text{CH}_4}$ -

64.5‰, $\delta^{13}\text{C}_{\text{CO}_2}$ +5.5‰ for the landfill cell. With reference to these values, the perimeter boreholes at Site 1 and Site 2 (along with the mineshaft vents and North Sea Gas samples) are all relatively depleted in ^{13}C . Values recorded for $\delta^{13}\text{C}_{\text{CO}_2}$ at Site 1 landfill were -55.6‰ and -51.0‰ for BH 03/4 and BH 03/7 respectively, while Site 2 landfill perimeter boreholes were slightly more enriched in ^{13}C with more positive $\delta^{13}\text{C}_{\text{CO}_2}$ values of -47.0‰, -37.0‰ and -32.8‰ measured for BH 04, BH 08 and BH 12 respectively. These data indicate that the perimeter boreholes at both sites are isotopically enriched in ^{13}C with respect to Site 2 Landfill Flare and Landfill Cell gases. This observed discrepancy could be due to several factors including the age of the waste and the composition of the waste material.

In contrast, Mineshaft Vent 1 and North Sea Gas samples show a slight enrichment in ^{13}C by comparison with the landfill perimeter borehole gas samples. The values recorded for $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ were -46.2‰ and -10.9‰ respectively for Mineshaft 1 and -43.5‰ and -15.5‰ respectively for North Sea Gas. This was consistent with older, geological gas sources being enriched in ^{13}C and ^{12}C . Mineshaft Vent 2 showed an isotope signature ($\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ were -50.5‰ and -46.1‰ respectively) that was similar to the landfill perimeter boreholes, particularly at Site 2. This demonstrated an overlap with Site 2 landfill perimeter boreholes. This could be attributed to air leaking into this mineshaft vent (the gas contained 11.4% O_2).

5.2 Determination of Gas Source using $\delta^{13}\text{C}_{\text{CH}_4}$ versus $\delta\text{D}_{\text{CH}_4}$

Figure 4 clearly demonstrates a spectrum of stable isotope signatures ranging from biogenic gas source to non-bacterial gas source. Using Site 2 Landfill Flare and Landfill Cell gas samples as a reference, the $\delta^{13}\text{C}_{\text{CH}_4}$ values were measured at -65.0‰ and -64.5‰ respectively while $\delta\text{D}_{\text{CH}_4}$ values were measured at -319‰ and -316‰ respectively. Site 2 Landfill Flare Gas and Landfill Cell Gas samples demonstrated depletion in ^{13}C and D in CH_4 . All other samples were isotopically enriched in ^{13}C and D in CH_4 in comparison to Site 2 Landfill Flare Gas and Landfill Cell gases.

Figure 4. $\delta^{13}\text{C}_{\text{CH}_4}$ Ratio versus $\delta\text{D}_{\text{CH}_4}$ Ratio for Gases from Landfills and Geological Sources

Site 1 landfill monitoring wells recorded $\delta^{13}\text{C}_{\text{CH}_4}$ values of -58.2‰ and -61.0‰ (BH 03/4 and BH 03/7 respectively) and $\delta\text{D}_{\text{CH}_4}$ values of -298‰ and -253‰ (BH 03/4 and BH 03/7 respectively). The $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta\text{D}_{\text{CH}_4}$ ratios for Site 1 BH 03/4 and BH 03/7 also indicate a biogenic gas source as the values were similar to the pure landfill gas samples from Site 2 and biogenic sources generally yield $\delta^{13}\text{C}_{\text{CH}_4}$ values <-60‰ (Hitchman *et al.*, 1989).

Site 2 perimeter boreholes (BH 04, BH 08 and BH 12) diverge significantly from the Site 2 Flare and Landfill Cell gas stable isotope ratios. The stable isotope ratios acquired for $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta\text{D}_{\text{CH}_4}$ demonstrated enrichment in both ^{13}C and D in CH_4 . As BH 12 recorded a larger CO_2 component relative to CH_4 it is possible that some of the biogenic CH_4 from the landfill was oxidised to CO_2 during migration to the borehole. This would account for the enrichment in both ^{13}C and D observed in the isotope data. It is less reasonable to attribute the gases in BH 12 as derived from the underlying Carboniferous Coal Measures owing to the $\delta\text{D}_{\text{CH}_4}$ value of +55‰ which suggests CH_4 oxidation. The $\delta^{13}\text{C}_{\text{CH}_4}$ ratios measured for BH 04, BH 08 and BH 12 were -55.6, -55.0 and -48.0‰ respectively. Borehole 12 in particular shows a significant enrichment in $\delta^{13}\text{C}_{\text{CH}_4}$ with respect to the Flare and Landfill Cell gases which were ~-65.0‰. Using the Hitchman *et al.* (1989) rule that non-bacterial gas sources generally yield $\delta^{13}\text{C}_{\text{CH}_4}$ values >-60‰, this would suggest that at least Site 2 BH 04 perimeter monitoring well contains a geological gas input component that has mixed with the landfill gas.

In contrast, the $\delta^{13}\text{C}_{\text{CH}_4}$ values for known deep geological gas sources were -46.2, -50.5 and -43.5‰ for Mineshaft Vent 1, Mineshaft Vent 2 gas samples and North Sea Gas (reference gas). The Site 2 perimeter borehole gas samples overlap this range of $\delta^{13}\text{C}_{\text{CH}_4}$ ratios and provide evidence that they contain a geological, not landfill, gas source contribution.

Perhaps the most surprising results were the $\delta\text{D}_{\text{CH}_4}$ ratios for the Site 2 perimeter boreholes which all yielded values greater than the mineshaft vents and North Sea Gas reference, at -172, -173 and +55‰ for BH 04, 08 and 12 respectively. These data indicate D enrichment compared with Mineshaft 1 and Mineshaft 2 which produced $\delta\text{D}_{\text{CH}_4}$ values of -214 and -208‰ respectively. As Site 2 perimeter boreholes show $\delta^{13}\text{C}_{\text{CH}_4}$ ratios similar to the mineshaft vent samples and $\delta\text{D}_{\text{CH}_4}$ ratios greater than the mineshaft vents, in this context, it provides evidence that Site 2 boreholes contain gas from a deep geological source.

The $\delta\text{D}_{\text{CH}_4}$ result for BH 12 stands out from all the other samples. The positive value of +55‰, corroborated by the UC Davis SIF figure of +74.0‰ implies an enrichment of deuterium in BH 12 CH_4 . As residual CH_4 in landfills is expected to be depleted in the heavier isotopes of carbon (^{13}C) and hydrogen (D), the data indicate that the origin of CH_4 in this particular borehole is different from BHs 04 and 08. Bacterial oxidation of CH_4 enriches residual CH_4 in both ^{13}C and D with changes in $\delta\text{D}_{\text{CH}_4}$ values typically ~ 8 to 14 times greater than $\delta^{13}\text{C}_{\text{CH}_4}$ (Aelion *et al.*, 2009; Coleman *et al.*, 1981). Given that the gas composition of BH 12 as shown in [Figure 3](#) was (relatively) ~ 23% CH_4 , 65% CO_2 , 12% O_2 , it could have experienced CH_4 oxidation to CO_2 in an oxic environment. However, it was not possible to obtain comparable $\delta\text{D}_{\text{CH}_4}$ values from the literature. If this hypothesis is correct, the gas present in Site 2 BH 12 could be of biogenic origin. This would also agree with the historic gas monitoring data for this borehole ([Figure 1](#)) which predominantly showed a landfill gas composition between 1998 and 2015.

To put the data into context, they were plotted with data from other studies ([Figure 5](#)). Data compiled by Golding *et al.* (2013) include stable isotope ratios resulting from acetoclastic reactions (biogenic gas sources) and geological sources from Australia (Bowen Basin and Surat Basin) and the USA (Antrim Shale, Michigan Basin; New Albany Shale, Illinois Basin; and Appalachian Shales, Northern Appalachian Basin). Site 2, BH 12 is not shown in [Figure 5](#) owing to its high $\delta\text{D}_{\text{CH}_4}$ value lying far outside the common range for stable isotopes reported in the literature.

Figure 5. $\delta^{13}\text{C}_{\text{CH}_4}$ (‰) against $\delta\text{D}_{\text{CH}_4}$ (‰) compared with Golding *et al.* (2013). (Bowen and Surat Basins Coal Bed and Coal Mine CH_4 (Kinnon *et al.*, 2010); Gas Samples from the Powder River Basin (Bates *et al.*, 2011; Flores *et al.*, 2008); Gas Samples from the Antrim and New Albany Shales (Martini *et al.*, 1998; McIntosh *et al.*, 2002); and Gas Samples from Organic-Rich Shales of the Northern Appalachian Basin (Osborn & McIntosh, 2010)

Figure 5 provides a useful reference for the determination of gas sources at Site 1 and Site 2 landfills. Both Site 2 Flare and Landfill Cell gases, and Site 1 BH 03/4 and BH 03/7 gases are shown to be in the acetoclastic reaction (biogenic gas) range. For landfill gas, Raco *et al.* (2014) reported $\delta^{13}\text{C}_{\text{CH}_4}$ values in the range -66.3 to -46.1‰ and $\delta\text{D}_{\text{CH}_4}$ values in the range -329 to -291‰. Similarly, Kerfoot *et al.* (2013) reported $\delta^{13}\text{C}_{\text{CH}_4}$ values in the range -63.2 to -47.2‰ and $\delta\text{D}_{\text{CH}_4}$ values in the range -299.6 to -253.7‰. Site 2 Flare and Landfill Cell gases are shown to be at the lower end of the ranges outlined by Raco *et al.* (2014) indicating the greatest isotopic depletion in ^{13}C in CH_4 .

At Site 1 where there is no known input of CH_4 and CO_2 except from the landfill, the values recorded for the perimeter boreholes BH 03/4 and BH 03/7 were -58.2‰ $\delta^{13}\text{C}_{\text{CH}_4}$, -298‰ $\delta\text{D}_{\text{CH}_4}$ and -61.0‰ $\delta^{13}\text{C}_{\text{CH}_4}$, -253‰ $\delta\text{D}_{\text{CH}_4}$ respectively. These values also agree with those reported by Raco *et al.* (2014) and Kerfoot *et al.* (2013) and clearly plot in the biogenic range in Figure 5. The $\delta\text{D}_{\text{CH}_4}$ value of -253‰ recorded for Site 1 BH 03/7 is on the cusp of the biogenic gas source range when compared with data from the literature.

Site 2 BH 04 and BH 08 indicate $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta\text{D}_{\text{CH}_4}$ values outside the biogenic range despite being perimeter monitoring wells for the landfill. While the $\delta^{13}\text{C}_{\text{CH}_4}$ ratios recorded for BH 04 and 08 (-55.6 and -55.0‰ respectively) were not atypical of biogenic source according to Raco *et al.* (2014), the $\delta\text{D}_{\text{CH}_4}$ ratios (-172 and -173‰ respectively) were outside the biogenic range. These boreholes showed an enrichment of $^{13}\text{C}_{\text{CH}_4}$ that is more typical of geological gas sources. These figures compared to Dai *et al.* (2012) who reported a $\delta\text{D}_{\text{CH}_4}$ range of values between -173 and -155‰ for natural gases in the Xujiahe Formation, Sichuan Basin, China. As residual CH_4 in landfill gas is expected to be isotopically

depleted in ^{13}C and D, the evidence suggests that the gas captured in Site 2 BH 04 and BH 08 contains methane derived from a deep geological source.

In the context of other published data, the mineshaft vent gas samples and North Sea Gas samples show a depletion in ^{13}C and D with respect to the natural gas samples reported by Kerfoot *et al.* (2013) and Dai *et al.* (2012). For California, USA, Kerfoot *et al.* (2013) reported a range of stable isotope ratios between -36.46 and -29.91‰ $\delta^{13}\text{C}_{\text{CH}_4}$, and -197.4 and -193.7‰ $\delta\text{D}_{\text{CH}_4}$. Similarly, for natural gas samples originating from Sichuan Province, China, Dai *et al.* (2012) detailed a range of stable isotope ratios between -36.9 and -30.8‰ $\delta^{13}\text{C}_{\text{CH}_4}$, and -173 and -155‰ $\delta\text{D}_{\text{CH}_4}$. With respect to these data, the mineshaft vent samples and North Sea Gas are isotopically depleted in both ^{13}C and D. Some variation is anticipated in natural gas samples depending on the origin of the gas, the geology, and mixing from external sources. Using both the mineshaft vent gas samples, North Sea Gas and the literature data, the evidence strongly supports the conclusion that Site 2 landfill perimeter borehole gas has a deep geological component. It is interesting to note that Site 2 perimeter borehole gases are isotopically enriched in D with respect to the mineshaft vent gas samples and North Sea Gas.

All gas samples discussed by Golding *et al.* (2013) were derived from natural environments and none were from anthropogenic environments. Samples procured from the Powder River Basin, USA, by Bates *et al.* (2011) indicate a microbial influence on stable isotope ratios. The presence of active methanogenic communities in coal bed CH_4 coupled with fresh nutrient recharge from the Powder River Basin margins has been hypothesised to encourage microbial growth, specifically favouring CH_4 generation via acetate fermentation (Flores *et al.*, 2008). Acetoclastic methanogenesis described by Bates *et al.* (2011) and Flores *et al.* (2008) in the Powder River Basin, USA, is the same process that occurs in anaerobic conditions in municipal landfills forming CH_4 .

In the context of Golding *et al.* (2013), Site 2 Landfill Flare and Landfill Cell gases along with Site 1 BH 03/4 plot in the 'acetoclastic reactions' range of [Figure 5](#). Site 1 BH 03/7 plots on the boundary between 'mixing' gases and 'microbial CH_4 '. As previously discussed, Site 2 BH 04 and BH 08 gases are different in nature from landfill gases as they plot in the 'mixing' region of [Figure 5](#). Mineshaft Vent 1 gas and North Sea Gas plot in the 'thermogenic CH_4 ' region of the plot while Mineshaft Vent 2 gas lies on the boundary between thermogenic and mixed gases.

While stable isotope ratios go a long way to differentiating the source of ground gases, it is clearly not the whole picture as there is an overlap demonstrated in the ratios shown here. Coupled with radiocarbon dating (not within the scope of this study) it would be possible to fully differentiate gas sources. Owing to the relatively short half-life of ^{14}C (5,730 years), geological sources of gases are totally depleted in ^{14}C by virtue of their age while modern biogenic sources contain ^{14}C that reflects contemporary atmospheric ^{14}C levels (Fellner & Rechberger, 2009; Muir *et al.*, 2015). Williams and Aitkenhead (1991) were able to prove the biogenic source of the CH_4 and CO_2 from a nearby landfill that caused the Loscoe explosion in 1986 using radiocarbon dating in conjunction with stable isotope ratios. In the case of Site 2 landfill perimeter boreholes, this approach could provide conclusive evidence for the mixing of landfill gas with coal bed gas from the underlying strata that the stable isotope ratios indicate.

It is possible that the isotopic characteristics of the Site 2 boreholes are influenced by methanotrophic microbial processes. While this cannot be ruled out, the geological setting of the boreholes at both Sites 1 and 2 are similar, between and within sites. Further work would be needed to clearly demonstrate the presence or absence of methanotrophy in the subsurface, which can only take place under oxic conditions.

5.3 Gas Emissions from Drift-Covered Coal-Bearing Sequences

Building on from the work of Teasdale *et al.* (2014), a conceptual model of the ground gas regime is presented in [Figure 6](#)~~Figure 6~~. High temporal frequency gas monitoring of Site 1 showed a correlation between falls in atmospheric pressure and gas emissions. During atmospheric pressure increases, air was forced into the monitoring wells. The composition of gas measured was cycled between landfill gas and air in response to atmospheric pressure change.

Figure 6. Conceptual Model of the Ground Gas Regime

Stable isotope ratios can be used to differentiate gas sources. Owing to the physiology of landfill microbial communities, ^{12}C is preferentially consumed in acetoclastic reactions. Consequently, residual CH_4 is isotopically depleted in ^{13}C . Also, CH_4 is isotopically depleted in deuterium (^2H or D). Hitchman *et al.* (1989) proposed a guideline for gas source as $\delta^{13}\text{C}_{\text{CH}_4} > -60\text{‰}$ generally indicates a deep geological source and $\delta^{13}\text{C}_{\text{CH}_4} < -60\text{‰}$ generally a biogenic source.

However, the data presented here from landfill and literature data from biogenic sources often showed that the $\delta^{13}\text{C}_{\text{CH}_4}$ value can be as high as -50‰ . The maximum $\delta^{13}\text{C}_{\text{CH}_4}$ value obtained in this research for a non-landfill gas source was -50.5‰ . Likewise, data reported in the literature rarely show the $\delta^{13}\text{C}_{\text{CH}_4}$ value exceeding -55‰ . As a slight adjustment to Hitchman *et al.* (1989), it is proposed that biogenic gas sources will generally produce a $\delta^{13}\text{C}_{\text{CH}_4} < -55\text{‰}$ while thermogenic gas sources will

generally produce a $\delta^{13}\text{C}_{\text{CH}_4} > -55\text{‰}$. The data reported here and data from the literature suggest a general trend for biogenic sources to have $\delta\text{D}_{\text{CH}_4}$ values $< -250\text{‰}$ and deep geological sources to have $\delta\text{D}_{\text{CH}_4}$ values $> -250\text{‰}$. Caution should be exercised with these figures as the data also indicate overlap of stable isotope ratios between gas sources.

The Conceptual Model shown in [Figure 6](#) includes the determination of gas source according to stable isotope ratios. This should be treated as a guide only. The more negative the $\delta^{13}\text{C}_{\text{CH}_4}$ and the $\delta\text{D}_{\text{CH}_4}$ values, the more isotopically depleted the CH_4 in ^{13}C and D such as biogenic gases originating from landfills.

However, where stable isotope ratios indicate a mixed gas source as for perimeter boreholes at Site 2, it may be necessary to perform radiocarbon dating on samples to conclusively determine gas source. Modern CH_4 reflects contemporary atmospheric concentrations of ^{14}C (currently ~ 104 pMC) while older, geologic sources are completely depleted in ^{14}C owing to the relatively short half-life of ^{14}C (5,730 years). It is anticipated that in the case of Site 2 landfill perimeter boreholes (BH 04, BH 08 and BH 12), the CH_4 present in these boreholes would be ~ 0 pMC if a non-bacterial gas input from the underlying Coal Measures is present as hypothesised in this paper.

This study is restricted to just two sites, and the data presented here would justify a more extensive investigation. We have shown, from a regulatory perspective, that stable isotopes (ideally in conjunction with radiocarbon dating) could be used to determine gas source, in a two stage process. Routine stable isotope analysis will allow biogenic gases to be determined with confidence. The use of two laboratories with different instrumental approaches and sample shipping requirements gave similar results, suggesting that for regulatory purposes the logistics of sample analysis need not have a significant effect. For samples where stable isotope ratios, especially $\delta\text{D}_{\text{CH}_4}$ indicate a possible deep geological origin, it may be necessary to use ^{14}C dating to unambiguously confirm the source. While stable isotopes should be enough to differentiate gas sources in most cases, in the case of Site 2, it was unclear where the gas source had originated from. For examples such as Site 2, radiocarbon dating may be needed to fully clarify gas sources.

6 CONCLUSION

Historic gas monitoring records of two landfills situated in similar drift deposits in NW England, UK, showed potential differing sources. Site 2, known to overlie Coal Measures, historically showed a CH_4 -rich gas composition in at least three monitoring wells. Stable isotope analysis of C and H from gas samples was used to determine the origin of the gases present on the two landfills. Site 1 with no known external CH_4 input showed depleted ^{13}C signatures indicative of biogenic gas origin. Conversely, Site 2 showed enriched ^{13}C signatures indicative of a deep geological gas origin, likely from the underlying Coal Measures. The use of carbon and hydrogen stable isotopes identifies biogenic CH_4 with confidence, allowing inputs deep geological sources to be recognised. Where justified on grounds of cost, deep sources can be confirmed using radiocarbon dating.

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8 APPENDIX

The geological setting of the sites investigated is summarised in this section.

8.1 Site 1

Figure A1 shows the layout of Site 1.

Figure A1. Site 1 Map Showing the Locations of Monitoring Wells and nearby Premises

A former sand quarry, the site was progressively filled with inert waste from 1968. Over half of the quarry void was filled by 1991. In order to allow reclamation of the quarry and to raise the level to the surrounding land, tipping of solid non-biodegradable wastes (e.g. soils, sands, clay, clean brick and stone) commenced in 1998. By 2002, landfilling operations had ceased. The adjacent land is generally undulating in nature and slopes downward gently towards the north. To the north and east, the site is bounded by pasture, while the south and west boundaries are bordered by residential dwellings and gardens.

Figure A2. Sketch Cross Sections of Site 1 Showing Geological Relationships

Figure A2 shows a schematic geological cross-section of the site. The underlying solid geology consists of the Permo-Triassic Tarporley Siltstone Formation, which dips in a westerly direction and is overlain by a substantial thickness of glacial drift deposits. Immediately overlying the Tarporley Siltstone Formation is a layer of Lower Boulder Clay that varies in thickness with the rock-head approximately 30 m below ground level. Generally in excess of 15.2 m thick, the Middle Sands overlie the Lower Boulder Clay. During operations of the quarry, the Middle Sands were excavated. Capping the Middle Sands is an upper layer of Boulder Clay which is between 0.9 m and 3.6 m thick.

The Environment Agency classes the Middle Sands groundwater as a minor aquifer. The geological memoir (Evans, 1968) suggests that the groundwater level limited the quarry base, which at the time was 12.2 m below the original ground surface. A number of springs, all occurring around 163 m A.O.D., can be identified from local maps within the vicinity of the site. This spring line occurs where the topography drops below the interface between the Lower Boulder Clay and the Middle Sands. The underlying Permo-Triassic strata are classed as a major aquifer with a groundwater level of approximately 95–100 m A.O.D.

The monitoring well installations are approximately between 30 m and 35 m in depth. Up to the top 3.6 m is plain pipe, while the middle 15 m of the installations is slotted pipe. All boreholes have at least a 1 m bentonite seal. Therefore, the response zones of the installations are from the porous Middle Sands. All gas measured in these wells is assumed to originate from the Middle Sands.

8.2 Site 2

Figure A3 shows the layout of Site 2.

Figure A3. Site 2 Map Showing the Location of Monitoring Wells and nearby Premises

Site 2 is a fully engineered containment landfill facility that was constructed in phases within the footprint of a former clay brick quarry. The site occupies just over 6 hectares, is dome-shaped in relief, stands a maximum 75m A.O.D. and is approximately 350 m long by 150 m wide. Household, commercial, construction and industrial wastes were permitted to be deposited during operation.

Landfill construction was in four phases (1A, 1B, 2A and 3). After installation of a composite liner, landfilling would commence in that area and construction of the next phase would begin. Each phase was separated by an engineered bund, designed to minimise the movement of any leachate produced at the site. Landfilling took place over a 5 year period from July 1998 to October 2003. In total, around 900,000 tons of waste was deposited in the quarry void. The landfill cap specification features a 1.0 mm high-density polyethylene (HDPE) flexible membrane liner on a clay regulating layer and a 1.0 m thick layer of restoration soils.

To the north east of the site is a former landfill area operated by a different authority. It is understood that this site was not constructed with formal containment engineering. Instead, it relies on

the natural clays to attenuate potentially polluting emissions. This site is older having obtained its licence for the tipping of domestic and commercial waste in a former clay pit in 1979. By 1989, high levels of methane emissions were recorded. An active ventilation system was installed to mitigate against this. In 1995 landfill gas barriers were installed along the perimeter of this secondary landfill site. However, the specification of these installations is unknown.

Figure A4. Sketch Cross Sections of Site 2 Showing Geological Relationships

In a regional geological context, Site 2 is located on the northern boundary of the Cheshire Basin. Permo-Triassic deposits overly Westphalian (Carboniferous) Coal Measures at depth. Faults in this area tend to be orientated north-south, affecting both the Permo-Triassic and Carboniferous deposits. The whole area is overlain by Glacial Till. Borehole logs indicate that the Glacial Till across the site is composed of a firm to stiff, dark brown silty clay with occasional sand and gravel and occasional lenses of fine sand. The depth of this clay is between 5.5 and 19.0 m.

Site 2 immediately overlies sandstones of the Permo-Triassic Sherwood Sandstone Formation. Aligned below the western portion of the site and running NNW-SSE, the Cheadle Heath Fault has downthrown the Wilmslow Sandstone to the east of the fault, alongside rocks of the older Pebble Beds Group to the west. The beds dip slightly in a westerly direction.

The Sherwood Sandstone Formation is classified as a major aquifer by the Environment Agency (EA). However, the site is not located within the Source Protection Zones (SPZ) of any major abstractions (Environment Agency, 2010). Regional groundwater flow is shown to be from SSE to NNW and the piezometric surface at the site is approximately 57.0 m A.O.D. according to British Geological Survey (BGS) records (Allen *et al.*, 1997). Groundwater flow is thought to be in hydraulic continuity with a water course to the west of the site. Within the sand and gravel unit at the base of the superficial deposits, groundwater strikes were made at approximately 45.0 m A.O.D. during site investigations. In addition, some minor groundwater strikes were encountered within sand layers in the Boulder Clay.

Generally, groundwater levels are higher in boreholes to the north-east of the site (boreholes 1, 4 and 7) than those to the south-west (boreholes 11, 13 and 16). This appears to confirm that groundwater flow is towards the water course to the west of the site. The boundary shown in Figure A3 is that of the permit boundary. In reality the boreholes are not located within the landfill waste but are in the adjacent strata.

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8.3 Stable Isotope Analysis Methodologies

At Newcastle University, compound-specific GC-IR-MS was conducted on a Thermo Trace Ultra GC using a splitless injector (150°C) via a Combustion III Interface linked to a Thermo Delta V+ IR-MS (HT voltage 3-5 kV, trap current 0.75 mA, box current 0.7 mA). The acquisition was controlled by a Dell computer using Thermo Isodat software. The Thermo Delta V+ GC-IR-MS instrument was initially set in carbon mode monitoring the $\text{CO}_2^{44/45}$ $\delta\text{C}^{12/13}$ ratio. The sample (1-100 μl) was injected manually with the split open at 500:1. The GC column was kept at 35°C for the entire run with He as the carrier gas (flow 1 ml/min, at a pressure of 80 kPa, split at 500 ml/min). Chromatographic separation of the mixture of gases was performed on a fused silica capillary column (30 m x 0.32 mm i.d.) filled with 20 μm PLOT-Q powder phase.

The reference gas was pulsed into the mass spectrometer and after 5 minutes the back flush valve directed the split sample from the end of the GC column via the combustion furnace (940°C) and reduction furnace (650°C), oxidising CH_4 to CO_2 . The reference gas was introduced into the mass spectrometer through a micro capillary isolation valve into the source where the gas was ionised. The resulting ions separated in a magnetic field to 3 cup detectors for masses 44, 45, 46 to give an isotopic ratio value determined from a pulsed reference gas (CO_2) calibrated from a reference 15 alkane (A4) or 8 flame (F8) mixture with peak specific known isotopic values for carbon (Arndt Schimmelmann, Indiana University, USA, Certificate of Analysis.)

The Thermo Delta V+ GC-IR-MS instrument was then set in hydrogen mode monitoring the $\text{H}_2^{2/3}$ $\delta\text{H}^{2/3}$ ratio. The hydrogen reference gas was pulsed into the mass spectrometer and after 5 minutes the back flush valve directed the split sample from the end of the GC column via the combustion furnace (1400°C) only. H_2 was introduced into the mass spectrometer through a micro capillary isolation

valve into the source where the gas was ionised and the resulting ions separated in a magnetic field to 2 cup detectors for masses 2, 3. An isotope ratio value was determined from a pulsed reference gas (H_2) calibrated from a reference 15 alkane (A5) or 8 flame (F8) mixture with peak specific known isotopic values for H_2 (Arndt Schimmelmann, Indiana University, USA, Certificate of Analysis.)

The resulting isotope ratios were determined using the Thermo Isodat dynamic background integration Workspace software to give the peak retention times and isotope ratios as $\delta^3\text{H}$ and $\delta^{13}\text{C}$ values. The data were also stored on DVD for any further data processing, integration or printing.

Bulk samples were also analysed on a commercial basis by IRMS at the University of California, according to the method prescribed by UC Davis Stable Isotope Facility (2016) and Yarnes (2013). Stable isotope ratios of $\delta^{13}\text{C}$ and δD in CH_4 were measured using a ThermoScientific PreCon concentration system interfaced to a ThermoScientific Delta V Plus IRMS (ThermoScientific, Bremen, DE). Gas samples were purged from vials through a double-needle sampler into a He carrier stream (20 ml/min), which was passed through a $\text{H}_2\text{O}/\text{CO}_2$ scrubber ($\text{Mg}(\text{ClO}_4)_2$, Ascarite) and a cold trap cooled by liquid N_2 .

The CH_4 was separated from residual gases by a Rt-Q-BOND GC column (30 m x 0.32 mm x 10 μm , 30°C, 1.5 ml/min). After the CH_4 was eluted from the separation column, CH_4 was either oxidised to CO_2 by reaction with nickel (II) oxide (NiO) at 1,000 °C ($\delta^{13}\text{C}$), or pyrolysed in an empty alumina tube heated to 1,350°C (δD). Subsequently the sample was transferred to the isotope ratio mass spectrometer.

A pure reference gas (CO_2 or H_2) was used to calculate provisional δ -values for the sample peak. Final δ -values were obtained after adjusting the provisional values for changes in linearity and instrumental drift so that correct δ -values for laboratory standards were obtained. Laboratory standards were commercially prepared CH_4 gas diluted in He or air and were calibrated against National Institute of Standards and Technology (NIST) reference materials (SRM) 8559 (Natural gas/coal origin), 8560 (Natural gas/petroleum origin), and 8561 (Natural gas/biogenic).

Stable isotope ratios of $\delta^{13}\text{C}$ in CO_2 were measured using a ThermoScientific PreCon-GasBench system interfaced to a ThermoScientific Delta V Plus IRMS (ThermoScientific, Bremen, DE). CO_2 was sampled by a six-port rotary valve (Valco, Houston TX) with a 100 μl loop programmed to switch at the maximum CO_2 concentration in the He carrier gas. The CO_2 was subsequently separated from N_2O and other residual gases by a Poroplot Q GC column (25 m x 0.32 mm i.d., 45°C, 2.5 ml/min).

A pure reference gas (CO_2) was used to calculate provisional δ -values of the sample peak. Final $\delta^{13}\text{C}$ values were obtained after adjusting the provisional values so that correct $\delta^{13}\text{C}$ values for laboratory standards were obtained. Two laboratory standards were analysed with every 10 samples. NIST SRM 8545 (LSVEC/C, O, and Li isotopes in Li_2CO_3) was used to directly calibrate laboratory standards.

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