



Carbon isotopic characterisation and oxidation of UK landfill methane emissions by atmospheric measurements

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ARTICLE INFO

Keywords:

Carbon isotopic signature
Landfill methane emissions
Gas well isotopic signature
Oxidised proportion estimation

ABSTRACT

Biological oxidation of methane in landfill cover material can be calculated from the carbon isotopic signature ($\delta^{13}\text{C}_{\text{CH}_4}$) of emitted CH_4 . Enhanced microbial consumption of methane in the aerobic portion of the landfill cover is indicated by a shift to heavier (less depleted) isotopic values in the residual methane emitted to air. This study was conducted at four landfill sites in southwest England. Measurement of CH_4 using a mobile vehicle mounted instrument at the four sites was coupled with Flexfoil bag sampling of ambient air for high-precision isotope analysis. Gas well collection systems were sampled to estimate landfill oxidised proportion. Closed or active status, seasonal variation, cap stripping and site closure impact on landfill isotopic signature were also assessed. The $\delta^{13}\text{C}_{\text{CH}_4}$ values ranged from -60 to -54‰ , with an average value of $-57 \pm 2\text{‰}$. Methane emissions from active cells are more depleted in ^{13}C than closed sites. Methane oxidation, estimated from the isotope fractionation, ranged from 2.6 to 38.2%, with mean values of 9.5% for active and 16.2% for closed landfills, indicating that oxidised proportion is highly site specific.

1. Introduction

Methane (CH_4) and its indirect impacts account for at least 25% of the anthropogenic radiative forcing since industrialisation (Ganesan et al., 2019). The past decade has seen sharp growth in atmospheric methane (Nisbet et al., 2019). In 2020 the global averaged dry mole fraction of methane in the air was 1873 ppb, with growth in excess of 15 ppb in 2019 (NOAA, 2021). The CH_4 is the second most potent anthropogenic greenhouse gas (GHG) after carbon dioxide (CO_2) in radiative forcing, with a global warming potential 32 times greater than CO_2 over a 100-year timespan (Etminan et al., 2016).

Given methane's importance, there is strong need to mitigate emissions (Nisbet et al., 2020). Between 2008 and 2017, global CH_4 emissions from landfills and waste are estimated to have ranged from 60 to 69 Tg CH_4 yr⁻¹, approximately 12% of global anthropogenic emissions (Saunois et al., 2020). Landfills make up around 3.2% of total UK GHG emissions, 28% of total CH_4 emissions and 76% of waste CH_4 emissions. CH_4 emissions from landfills decreased by 76% between 1990 and 2018 (NAEI, 2021).

Landfill gas (LFG) consists mainly of CH_4 (35–65% v/v) and CO_2 (15–50% v/v) (IEA Bioenergy, 2006), produced by degradation of

organic waste. Conventionally, LFG systems are managed with a landfill cover system, a landfill gas collection system or a combination of the two. Gas extraction systems within the waste collect the CH_4 , which is then flared or used for energy generation. Impermeable clay caps, geomembrane liners (usually high-density polyethylene) and soil cover systems cap the landfill to minimise LFG fugitive emissions and leachate generation (Sadasivam and Reddy, 2014). CH_4 escapes from landfill into the atmosphere directly from uncovered operational areas, in transport through the top layer of cover soil, through cracks or fissures in soil caps and leaking boreholes, and via leaks or vents around gas collection systems (Innocenti et al., 2013, 2015). Methanotrophic bacteria in aerobic uppermost parts of the landfill cover system consume methane that has been produced by methanogens in the anaerobic deeper parts of the landfill, and they may even consume methane drawn from the atmosphere during high atmospheric pressure events (Innocenti et al., 2013).

Each organic source has a distinct signature range of stable isotopic ratios ($^{13}\text{C}/^{12}\text{C}$, expressed relative to the Vienna Pee Dee Belemnite, or VPDB, standard as $\delta^{13}\text{C}_{\text{CH}_4}$ (Craig, 1957). Similarly, removal of CH_4 is isotopically fractionating and leads to a change in atmospheric isotopic ratio. Since 2007, the $\delta^{13}\text{C}_{\text{CH}_4}$ of atmospheric methane has shifted to

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<https://doi.org/10.1016/j.wasman.2021.07.012>

Received 19 January 2021; Received in revised form 15 June 2021; Accepted 11 July 2021

Available online 2 August 2021

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more negative values by about -0.03‰ per year (Nisbet et al., 2016). There are various hypotheses to explain this shift, including a possible marked increase in biogenic methane emissions (Nisbet et al., 2019; Rigby et al., 2017; Turner et al., 2019).

Methane produced from the decay of the organic matter by methanogens in anaerobic conditions is strongly depleted in ^{13}C with respect to the degraded organic matter. Methanogens preferentially utilize the molecules with the lower isotopic mass because of their faster diffusion and reaction rate compared to the isotopically heavier species (Aghdam et al., 2018; Chanton et al., 2011). Biogenic CH_4 is formed from two main pathways, formation of acetate and reduction of CO_2 with H_2 . Typically, $\delta^{13}\text{C}_{\text{CH}_4}$ values in methane from acetate fermentation is less depleted in ^{13}C than methane from CO_2 reduction (Chanton et al., 2011).

During oxidation of methane under aerobic conditions by methanotrophs in landfills, ^{12}C is preferentially utilised biologically, and the residual CH_4 is thus more enriched with ^{13}C (Chanton and Liptay, 2000). Therefore, emitted CH_4 becomes more ^{13}C -enriched as it passes upwards through landfill cover soils into the atmosphere. The degree of preference for $^{12}\text{CH}_4$, α_{ox} , expresses the constant ratio of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$:

$$\alpha_{\text{ox}} = k_{12}/k_{13} \quad (1)$$

where k_{12} and k_{13} are the first-rate constants of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$, respectively. Both the underlying anaerobic methanogenic processes and the overlying aerobic methanotrophic pathways determine the actual fractionation factor in the emitted methane (Aghdam et al., 2018; Chanton et al., 2011). Thus, the isotopic signature and CH_4 composition can be used to identify the underlying methanogenic substrates.

Previous studies report α_{ox} values from 1.005 to 1.049 (see Table 1). This fractionation factor varies with type of soil and temperature, and probably also with microbial community population and type, cell density, moisture, nutrient amount, CH_4/O_2 ratio, presence of inorganic nitrogen, inhibiting chemical agents and acidity (Chanton et al., 2008a; Sadasivam and Reddy, 2014; Templeton et al., 2006).

Several studies (Börjesson et al., 2001; Chanton and Liptay, 2000; Scheutz et al., 2011) indicate that microbial CH_4 oxidation in top cover soil is efficient in controlling CH_4 emissions from landfill sites. The main gas transport mechanism in landfill likely varies according to local site-specific designs and working practices. Chanton et al., (2008a) and Liptay et al., (1998) suggested that advection is the dominant mechanism for CH_4 transportation, whereas De Visscher et al., (2004) thought molecular diffusion may be a significant gas transport mechanism. Likely, both processes occur in different parts of each landfill. Diffusive fractionation clearly increases the oxidised proportion in comparison with the advection transport mechanism. According to Börjesson et al., (2007), there is no method of allocating the ratio of advection to diffusion in the overall CH_4 transportation mechanism and that molecular diffusion fractionation may be negligible because of wind causing advective transport and pressure inside the landfills.

In the United Kingdom, landfills are the second highest contributor to anthropogenic CH_4 emissions (NAEI, 2021). UK landfill emissions came down sharply for a decade (NAEI, 2021), but now it is getting tougher to reduce the remaining emissions. Thus, it is important to assess $\delta^{13}\text{C}_{\text{CH}_4}$ to obtain better source attribution and to understand characteristic methane emission pathways. Although stable carbon isotopic analyses have been widely used to quantify the CH_4 oxidised proportion in landfill emissions (see Table 1), there are few studies which have focused on estimating oxidised proportions at UK landfill sites (Innocenti et al., 2013, 2015). In estimates made by the Intergovernmental Panel on Climate Change (Buendia et al., 2019) and by the UK National Atmospheric Emissions Inventory (NAEI, 2021), the CH_4 oxidised proportion for covered and well-managed landfill is assumed to be 10% for all site types. This study examines the validity of this default value and whether it is appropriate for determining the oxidation ratios of different landfills.

Published isotopic values for atmospheric CH_4 emissions, such as

from flux chamber measurements, and from anoxic zones, using samples of the gas well collection system, the oxidation and fraction rates are presented in Table 1. The global landfill $\delta^{13}\text{C}_{\text{CH}_4}$ isotopic signature has been reported as -56‰ over the period 1995–2013 (Sherwood et al., 2017). Monteil et al., (2011) estimate the $\delta^{13}\text{C}_{\text{CH}_4}$ signature of landfill and wastewater treatment at -55‰ for the year 2000. Typical $\delta^{13}\text{C}_{\text{CH}_4}$ signatures of landfill gas emitted to the atmosphere range from -69.6 to -50.0‰ for measurements in six countries in Europe and North America (Table 1). The characteristics of microbial methanogenesis from organic waste, the concentration of organic matter and the age of landfills all influence the $\delta^{13}\text{C}_{\text{CH}_4}$ signatures of emitted methane (Nozhevnikov et al., 1993). The proportion of CH_4 emitted into the atmosphere differs between active and closed landfills (Table 1) due to cover soil and oxidation effectiveness.

Recently, landfill practice in the UK has changed significantly. With the UK government commitment to achieving “Net-Zero” emissions by 2050, all biodegradable waste will be eliminated from landfill by 2025, with separation of food waste from inorganic waste collections (CCC, 2019). These rapid changes in the composition of new waste inputs to landfills are changing the generation of landfill gas, thus affecting the methane production rate and isotopic signature of emitted CH_4 from UK landfills. This work was designed to assess the impact on carbon isotopic signature and oxidised proportion as landfills have evolved in recent years. While the isotopic method is considered to represent a minimum oxidation proportion (Bourn et al., 2019) and can give highly variable results for small chamber studies, the usefulness of this technique to provide better consistency of oxidised proportions using plumes downwind of cells and to distinguish closed from active landfill cells will be discussed.

In this study, the reasons for variation in methane mole fraction and $\delta^{13}\text{C}_{\text{CH}_4}$ signature across four southwest UK landfills, including impacts of factors such as seasonality, landfill status (closed/active), cap stripping and closure, were assessed to characterise typical UK landfill emissions using $\delta^{13}\text{C}_{\text{CH}_4}$ analyses, and to estimate oxidised proportions. The validity of using flux chambers for oxidation calculations is questionable because individually they are not representative of whole cells. Methane captured by small-area flux chambers can represent widely-varying oxidised proportions depending on positioning of the chamber. The ambient air isotopic signature has a 13.5‰ range, while flux chambers have a 33‰ range (Table 1). IPCC (2006) advise that CH_4 flux measurements should not be used directly because they are likely to overestimate the oxidation rate. Additionally, ambient air sampling is cheaper, quicker in terms of measurement duration, more site representative and a more practical solution for sampling, compared for example with big chambers, especially as the main emission could be a fugitive pipeline leak on a cell flank without any oxidation. Therefore, in this study the isotopic values were measured a) in gas well samples of methane produced in the anoxic zone, and b) determined *in-air*, by sampling downwind plumes of methane emitted from the sites, to give oxidised proportions averaged at the scale of the cell.

2. Material and methods

2.1. Sampling sites

The selected four landfill sites in southwest England are designated by letters owing to a necessary confidentiality agreement with site managership. Twelve measurement campaigns were carried out between July 2018 and February 2020. Air samples were collected in downwind emission plumes and upwind for background, and landfill gas was collected directly from gas well pipes across two separate surveys for each site. Details of the landfill sites are given in Table 2. All sites have similar gas collection systems.

Landfill A has both a closed area covered with topsoil and vegetation, and an active landfill area being filled with freshly placed waste. It also has a composting area and a leachate pond. It was selected to assess

Table 1
Overview of publications on landfill $\delta^{13}\text{C}-\text{CH}_4$ measurements and oxidation calculations for various site emissions in chronological order.

Location	Source	Method	Ambient Air (excess plume), $\delta^{13}\text{C}-\text{CH}_4$, ‰	Anoxic Zone, $\delta^{13}\text{C}-\text{CH}_4$, ‰	Flux Chamber, $\delta^{13}\text{C}-\text{CH}_4$, ‰	Probe ¹ , $\delta^{13}\text{C}-\text{CH}_4$, ‰	Uncovered areas, $\delta^{13}\text{C}-\text{CH}_4$, ‰	Fractionation, α_{ox}	Oxidised proportion (%)	References
Moscow region	Several landfills	GC-MS		-60 to -50						Nozhevnikova et al., (1993)
Moscow region	Kuchino big old landfill (closed)	GC-MS		-60 to -58					70 for summer, 50 for annually	Nozhevnikova et al., (1993)
Moscow region	Ramenki, spontaneous dump	GC-MS		-55 to -50						Nozhevnikova et al., (1993)
Germany	Landfill	GC-MS			-52	-62.9 ± 4.6				Levin et al., (1993)
Germany	Active landfill	TDLAS		-62.3 to -55.3				1.008 ± 0.003		Bergamaschi and Harris (1995)
Germany and the Netherlands	4 landfill sites	TDLAS and IRMS	-55.4 ± 1.4	-59 ± 2.2	-64 to -31	-72 to -16	-55.1 ± 5.2	1.005-1.009	70-97	Bergamaschi et al., (1998)
US	6 different landfills	IRMS	-50.4 to -48.1	-55.9 to -56.2				1.022 ± 0.008	24-35	Liptay et al., (1998)
US	Nashua landfill (active)	GCC - IRMS	-54.3 to -49.4	-56.7 to -53.8					0-23.6	Chanton et al., (1999)
US	PLF-A Massachusetts	GCC - IRMS	-58.1 to -52.2	-57.2 to -56.3					0-14	Chanton et al., (1999)
Sweden	Leon country Landfill (closed)	GC - IRMS		-56 to -54	-54 to -40			1.025-1.049 ³	3-55 (20 ± 3)	Chanton and Liptay (2000)
Sweden	Falkoping landfill (recently closed)	GCC - IRMS		-54.3 ± 0.05 -53.6 ± 1.7	-56.6 to -43			1.023-1.038	23-49	Börjesson et al., (2001)
Sweden	Hokhuvud Landfill (older)	GCC - IRMS		-58.6 ± 1.4 -43.4 ± 0.04	-61 to -32.3				20-94	Börjesson et al., (2001)
UK	4 landfills	GC-IRMS	-51.4 to -50.8	-52.6 to -51.7						Lowry et al., (2001)
US	Leon country landfill	GCC-IRMS		-55.4	-55.4 to -34.5				0-63.9 (22.1)	Abichou et al., (2006)
Sweden	2 closed landfills	GCC - IRMS	-52.2 to -50.3	-61.1 to -58.3				1.0204-1.0358	38-43	Börjesson et al., (2007)
Sweden	4 active landfills	GCC - IRMS	-58.1 to -52.9	-60.2 to -56					6-25	Börjesson et al., (2007)
US & Sweden	17 different landfill soils in lab experiment	GCC- IRMS						1.013-1.031	32-77	Chanton et al., (2008a)
US	1 closed landfill	GCC- IRMS	-56.5 to -43.0	-56.6 to -52.8		-46 to -32		1.024	23-38	Chanton et al., (2008b)
US	2 landfills	GCC-IRMS							0 to 100	Chanton et al., (2011)
Canada	Closed Landfill	GC-C- IRMS			-59.6 to -42.4	-59.5 to -35.8			0.0 to 89.7	Cabral et al. (2010)
Denmark	Fakse Landfill	GCC- IRMS	-57.6 to -51.7	-62.3 to -56.8				1.026 ± 0.002	15.7- 41.1	Scheutz et al. (2011)
Canada	Closed Landfill	GC-C- IRMS		-57.5 to -56.8	-56.9 to -26.8			1.0258 ⁴	1.7 to 94.9	Capanema and Cabral (2012)
US	Los Angeles Country closed landfill	CF-IRMS		-61.9 to -61.5						Townsend-Small et al., (2012)
France	Landfill with two distinct sections	GC-C/TC- IRMS		-60 to -46.7	-56.3 to -33.0			1.0245 ⁵	15-110	Widory et al., (2012)
UK	3 active landfills	GC-IRMS	-58.7 to -55.9	-60.7 to -57.8					5.3-12.8	Innocenti et al., (2013)
UK	6 closed landfills	GC-IRMS	-59.9 to -52.8	-64.7 to -56					12.8 -23.7	Innocenti et al., (2013)
UK	2 active sites	GC-IRMS	-58.7 to -53.2	-61.4 to -60.4					6.9-12	Innocenti et al., (2015)
UK	2 covered areas	GC-IRMS	-59.8 to -53.9	-62.6 to -55.5					12.2-32	Innocenti et al., (2015)
UK	2 Closed landfills	GC-IRMS	-56.1 to -55.2							Zazzeri et al., (2015)

(continued on next page)

Table 1 (continued)

Location	Source	Method	Ambient Air (excess plume), $\delta^{13}\text{C-CH}_4$, ‰	Anoxic Zone, $\delta^{13}\text{C-CH}_4$, ‰	Flux Chamber, $\delta^{13}\text{C-CH}_4$, ‰	Probe ¹ , $\delta^{13}\text{C-CH}_4$, ‰	Uncovered areas, $\delta^{13}\text{C-CH}_4$, ‰	Fractionation, ϵ_{ox}	Oxidised proportion (%)	References
UK	7 Active landfills	GC-IRMS	-60.2 to -57.3							Zazzeri et al., (2015)
US	Colorado active landfill	CF-IRMS	-58.1 ± 1.4							Townsend-Small et al., (2016)
Canada	Active Edmonton landfill	CRDS	-55.3 ± 0.2							Lopez et al., (2017)
Denmark	Odense Nord (active)	GCC- IRMS	-62.5 to -57.6	-69.6 to -66.8					17–37	Aghdam et al., (2018)
Denmark	Stige Ø (closed)	GCC- IRMS	-56 to -52.7	-57.2 to -54.4				1.015–1.024	6–9	Aghdam et al., (2018)
Australia	Closed landfill with. Two sites	GC-C-IRMS			-67.4 to -49.7	-59.5 to -55.4		1.030–1.034	1.6–8.6	Obersky et al., (2018)
Germany	Sinsheim landfill (closed)	CRDS	-62.2 to -54.2	-59.5 ± 0.1	-69.3 to -59.1					Hoheisel et al., (2019)
France	6 active landfills	IRMS	-63.7 ± 0.3 to -58.2 ± 0.3							Xueref-Remy et al., (2020)
US	7 landfills	GCC-IRMS	-55.4 to -45	-58.8 to -51.6	-55.9 to -43.8 ²	-55.7 to -37.2			0–43 ⁵	Sparrow et al., (2019)
US	7 landfills	CF-GC-IRMS	-65.5 to -54.4							Yang et al., (2019)
UK	4 closed landfills	GC-IRMS	-57.9 to -54.3							Lowry et al., (2020)
UK	2 active landfills	GC-IRMS	-61.4 to -57.8							Lowry et al., (2020)

Notes: CF-GC-IRMS: continuous flow gas chromatography and isotopic ratio mass spectrometer; GCC-IRMS: Hewlett-Packard gas chromatograph coupled via a combustion interface to a Thermo-Finnigan Delta V isotope ratio mass spectrometer; GC-C-IRMS: Isoprime/Agilent Gas Chromatography-combustion-isotope ratio mass spectrometer; GC-C/TC-IRMS: Trace GC Ultra coupled to a Delta Plus XP; Thermo; TDLAS: tunable diode laser absorption spectrometer; CRDS: cavity ring down spectrometer; ¹soil air sample; ² transects of air samples from 5 to 10 cm above the landfill surface; ³for at 8 °C, 20 °C; ⁴for soils at 25 °C; ⁵Fraction of methane oxidised based on atmospheric plume isotopic signature.

seasonal variation in $\delta^{13}\text{C}_{\text{CH}_4}$ due to accessibility and having both active and closed area. It was surveyed in summer 2019, autumn 2019 and winter 2020. A total of 27 landfill gas samples were collected from Landfill A's gas collection system: 12 from the closed area and 15 from the active area. Landfill A is a shallow landfill, with a maximum gas well temperature of 40 °C.

Landfill B was closed during the period of the first two surveys and was then partially uncapped for placement of new waste in August 2019. A cap of topsoil and vegetation previously covering old waste was partially removed to allow overfilling with fresh waste. It was evaluated to assess the impact of partial cap stripping on CH_4 and $\delta^{13}\text{C}_{\text{CH}_4}$. Twenty-six landfill gas wells were sampled from uniformly distributed branches of the gas well collection system in the landfill area during July and August 2019. Landfill B's gas collection system was always hotter than the other landfills, up to 58 °C.

Landfill C is the smallest and deepest landfill. It was still in use during the first campaign in August 2019 and closed in November 2019. It was surveyed after closure to analyse the impact of closure on CH_4 and $\delta^{13}\text{C}_{\text{CH}_4}$. Nineteen landfill gas samples were collected from different branches of the gas collection. Gas temperatures ranged between 40 and 50 °C.

Landfill D comprises a closed and an active site, a food waste biogas plant, a composting area and a leachate treatment plant, surveyed in August 2019. Twenty landfill gas samples were collected from the gas wells, with 10 from the closed area and 10 from the active area. Landfill D is shallow, similar to Landfill A, with a maximum landfill gas temperature of 43 °C.

2.2. Mobile campaigns and sampling methodology

CH_4 was measured in plumes downwind of the landfills, most likely including CH_4 emitted from various sources: gas wells or pipeline leaks, from cracks and fissures, by diffusion in the soil cap, or directly from uncovered, active sites with only daily cover. The details of the Royal Holloway, University of London, mobile measurement vehicle set-up and air sampling methods are explained in Lowry et al., 2020 and Zazzeri et al., 2015. Prior to campaigns, the Picarro analyser was calibrated to the WMO X2004A CH_4 scale (NOAA, 2015), against three cylinders calibrated by NOAA and MPI-Jena Gaslab.

During mobile surveys, the vehicle was driven on accessible routes around the landfill sites, typically at 10–30 km/h inside the landfill area. After completing a circuit of a landfill site and detecting the location of CH_4 plumes, the vehicle was driven back through the plumes to collect air samples at different locations within the CH_4 plumes.

Plumes were intersected perpendicular to the prevailing wind direction, allowing the best Gaussian peak shape to be mapped. Multiple points in the plume with a range of CH_4 excesses over ambient background levels were sampled to obtain more precise characterisations of the isotopic signatures. Background samples were collected upwind of the landfills, providing background data for isotopic source characterisation using the Keeling plot technique (Pataki et al., 2003).

Landfill gas samples were collected on-foot, from take-off points of gas wells that were currently in use for gas collection. Gas wells were selected across the sites. One- or three-litre Tedlar bags were used, filled for two to three minutes each, using the exhaust outlet of a portable GEM 2000 Plus gas analyser. The instrument was flushed with sample gas for two minutes before collecting samples.

2.3. Laboratory analysis

Air samples were measured in RHUL's greenhouse gas laboratory using a Picarro 1301 CRDS calibrated weekly to the WMO X2004A CH_4 scale. Precision for CH_4 was ±0.2 ppb (600s) for standards and ±0.4 ppb for the air bag samples.

Isotopic analysis in the RHUL laboratory uses continuous-flow gas chromatography/isotope-ratio mass spectrometry (CF-GC/IRMS) with a

Table 2
Overview of landfill characteristics.

Landfill Name	Receiving waste since	Status (active/closed)	Waste type	Total waste (million tonnes)	Total surface area (m ²)	Number of gas wells	Waste depth (m)	Landfill temperature range (°C)	Atm. temperature(°C) and pressure(mb) during the survey day	Survey dates
A	1967	Both	46.5% Dom, 40% I/C, 6% Cont. Soil, 5% Cover, 2% Diff, 0.5% SS	4.6	500,000	260	7–25	max 40	23 °C & 1021 mb 10 °C & 999 mb 9 °C & 1010 mb	9–10 Jul. 2019 5 Nov. 2019 17 Feb. 2020
B	1986, suspended in 2016 and reopened in August 2019	Open	53% Dom, 32.6% I/C, 13% Cover, 0.8% Diff, 0.5% Cont. Soil, 0.1% SS	9.4	480,000	260	10–35	up to 58	20 °C & 1018 mb 18 °C & 1019 mb 22 °C & 1025 mb	5 Jul. 2018 16–17 Jul. 2019
C	1998, closed in November 2019	Closed	48% Dom, 37% I/C, 13% Cover, 1.4% Cont. Soil, 0.6% Diff,	3.3	10,500	137	20–50	40 to 50	22 °C & 1016 mb 7 °C & 1013 mb	20 Aug. 2019 23 Jul. 2019
D	1988	Both	44% I/C, 24% Dom, 15% Cover, 13% Cont. Soil, 3.8% Diff, 0.2% SS	5.5	650,000	220	7–25	40 to 43	20 °C & 1007 mb	17 Feb. 2020 6–7 Aug. 2019

Notes: Atm: atmospheric; Cont.: contaminated; Cover: soil used to fill the landfill; Diff: difficult waste; Dom: domestic waste; I/C: industrial and commercial; mb: millibar; SS: sludge and sewage. Type of soil is sand and gravel quarry for all landfill sites.

modified Isoprime Trace Gas system (Fisher et al., 2006), giving $\delta^{13}\text{C}$ analysis of CH_4 with repeatability of 0.05‰.

Samples were measured at least three times to attain $\delta^{13}\text{C}_{\text{CH}_4}$ precision to better than $\pm 0.1\text{‰}$, averaging $\pm 0.04\text{‰}$. Samples with mole fractions higher than 7 ppm CH_4 , including all landfill gas well samples, were diluted with high-purity N_2 so that they were in the linear range of the mass spectrometer for isotopic analysis (Fisher et al., 2006).

2.4. Data processing of mobile measurements and isotopic analysis

Raw mobile Picarro data for each survey were corrected using calibration standards and for inlet time delay, to match measured CH_4 plumes to their correct GPS locations. Background CH_4 was determined as the second lowest percentile of a ± 10 -min moving average, considering variations in background time and space conditions across the survey route (Lowry et al., 2020). The background value was then subtracted from the corrected and calibrated data, to obtain the “excess methane above background”. The moving background needs to be calculated to remove any influence from regional sources contributing to the build-up of CH_4 under inversion conditions that may persist during morning survey, particularly in the winter months. The remaining peaks represent emission plumes from the site under investigation.

Keeling plots were used to characterise $\delta^{13}\text{C}_{\text{CH}_4}$ for each emission source assuming a constant background (Keeling, 1958; Pataki et al., 2003). Keeling-plot analysis uses sampled $\delta^{13}\text{C}_{\text{CH}_4}$ and the associated inverse of atmospheric CH_4 mole fraction. The intercept of the linear regression line between these two variables constitutes the isotopic signature of the source inputs being added to the background (Pataki et al., 2003). The source signature error given is the one standard deviation (1SD) fitting error, calculated using a bivariate correlated errors and intrinsic scatter (BCES) estimator (Akritas and Bershad, 1996), which accommodates correlated errors in both variables and accounts for the error on the slope and intercept of the best interpolation line (for details, see Zazzeri et al., 2015 and supplementary information S1, S2, S3 and S4 for Keeling plots).

2.5. Estimates of fractionation factors and methane oxidation

The extent of methane oxidation is a major uncertainty in estimating landfill methane emissions. Bogner et al., (1995) observed slower diffusive flux to cover in landfills with pumped gas recovery systems. Gas collection systems were actively used at all our surveyed landfill sites. These reduce gas pressure inside the landfills. Therefore, we assumed that diffusive transport ($\alpha_{\text{trans}} = 1$) was negligible, and that the dominant CH_4 transportation mechanism was advection (Börjesson et al., 2007; Capanema and Cabral, 2012; Liptay et al., 1998). Although some studies have demonstrated that neglecting the diffusive flux can underestimate oxidation rate by a factor of 2–4 (De Visscher et al., 2004; Gebert et al., 2011), this study aimed to obtain an average oxidised proportion for closed and active areas and to assess seasonal and process variations across different landfills, that can be used to refine the default factor of 10% used for modelling of landfill oxidation (NAEI, 2021).

Samples in our study were collected in downwind plumes to calculate bulk oxidised proportions per landfill cell, or large point source. Previous studies in the UK used flux chamber measurements in addition to plume measurements (Innocenti et al., 2013, 2015), but these proved to be highly variable for sites with gas extraction, even including methane uptake, so for Innocenti et al. (2013, 2015) all calculations were based on downwind plumes.

The amount of CH_4 oxidation in a landfill can be determined by comparing $\delta^{13}\text{C}_{\text{CH}_4}$ of methane from the anoxic zone with that of methane emitted into the atmosphere. To calculate the fraction oxidised, it is assumed that CH_4 is well mixed in the porous soil media, f_0 (Börjesson et al., 2007; Chanton et al., 1999):

$$f_o = \frac{\delta_E - \delta_A}{(\alpha_{ox} - \alpha_{trans})1000} \quad (2)$$

The $\delta^{13}\text{C}$ of methane emitted from the landfill (δ_E) and the methane in the anoxic zone (δ_A) are known, so the fraction of methane oxidised (f_o) can be calculated using Eq. (2) (Chanton and Liptay, 2000; De Visscher et al., 2004; Liptay et al., 1998). This equation assumes methane is transported advectively through the cover soil. α_{ox} is a fractionation factor that depends on temperature and soil type. It is determined mainly by the incubation of soil cover samples. The fractionation factor, α_{ox} in Eq. (3) was taken from that derived by Borjesson et al., (2009) from measurements in a Swedish landfill site, and additionally utilised by Innocenti et al. (2013, 2015). They evaluated 13 UK landfills, which are assumed to have similar temperature range, cover soil, moisture content and waste characteristics with the landfills assessed in this study; therefore, it was appropriate to use the same equation to estimate α_{ox} in this study.

$$\alpha_{ox} = 1.0251 - 0.000313T \quad (3)$$

where T (°C) is the mean soil temperature measured. Although detailed defence of this method of calculating the oxidised proportion is beyond the scope of this paper, we consider that our results illustrate the lower limit of CH_4 oxidation. We performed the same plume measurement and oxidised proportion estimation technique as described previously by Innocenti et al. (2013, 2015). Capanema and Cabral (2012) observed only 0.5% variation in α_{ox} values. The calculated values from Eq. (3) were reassessed by considering this important dispersion in oxidation efficiencies (Capanema and Cabral, 2012).

The isotopic composition of anoxic methane was taken from the operational gas wells. The interquartile range (IQR) was calculated for the collected gas well samples for each site and the 1.5 IQR was applied to allow the identification of potential operational problems or stagnation in the gas well. The gas well samples containing oxygen concentration (>0.5%) were eliminated as unrepresentative of the anaerobic conditions in the gas wells. The averaged site/cell isotopic signatures of gas well samples are reported in Tables 3–5.

3. Results and discussion

3.1. Seasonal variation in landfill A

Mobile CH_4 measurement and air and gas-well sampling for $\delta^{13}\text{C}_{\text{CH}_4}$ analysis of Landfill A were carried out between summer 2019 and winter

Table 3

Seasonal variations in $\delta^{13}\text{C}_{\text{CH}_4}$ measurement for downwind plumes of Landfill A with $\delta^{13}\text{C}_{\text{CH}_4}$ of mean gas well samples and oxidised proportion estimate. The errors are given as one standard deviation.

$\delta^{13}\text{C}_{\text{CH}_4}$ (‰)	Site 1 (closed)	Site 1 oxidised proportion ³	Site 2 (active)	Site 2 oxidised proportion ³
Summer 2019 ¹	-53.9 ± 0.6	11.6 ± 1.3% (9.6–18.8) ⁴	-59.6 ± 0.1	4.1 ± 0.5% (3.1–5.7) ⁴
Autumn 2019 ¹	-53.6 ± 0.3	11.3 ± 1.2% (9.6–16.8) ⁴	-58.7 ± 0.1	7.8 ± 0.5% (6.7–11.6) ⁴
Winter 2019 ¹	-54.6 ± 0.02	6 ± 1.2% (4.8–7.8) ⁴	-59.6 ± 0.04	3.2 ± 0.5% (2.6–4.1) ⁴
Gas well samples ²	-55.9 ± 1.2(10)	-	-60.3 ± 0.5(10)	-

Notes: ¹Ambient air samples collected from downwind of Sites 1 and 2. ²It was assumed that gas well $\delta^{13}\text{C}_{\text{CH}_4}$ signatures showed no seasonal variation at anoxic zone temperatures (Chanton et al., 1999) owing to a constant temperature, waste composition and age in the anaerobic zone across the six-month survey duration. Number of gas well samples in parentheses. ³The temperatures were taken to be 25 °C, 15 °C and 10 °C for summer, autumn and winter surveys, respectively, to estimate the fractionation factor in Eq. (3), and the oxidised proportion was estimated from Eq. (2). ⁴A small 0.5% change in α_{ox} value is considered (Capanema and Cabral, 2012).

Table 4

Ambient air samples, gas well samples and estimated oxidised proportion at 25 °C for Landfill D. Errors are calculated as standard deviations.

Landfill D	Site 1 (closed)	Site 2 (active)
Ambient air, $\delta^{13}\text{C}_{\text{CH}_4}$ (‰)	-55.1 ± 0.1	-57.8 ± 0.3
Gas well samples, $\delta^{13}\text{C}_{\text{CH}_4}$ (‰) ¹	-57.8 ± 1.3 (7)	-59.0 ± 0.7 (7)
Oxidised proportion (%)	15.4 (11.9–21.9) ²	7.0 (5.4–9.9) ²

Notes: ¹Number of gas well samples in parentheses. ²A small 0.5% change in α_{ox} value is considered (Capanema and Cabral, 2012).

Table 5

Summary of average ambient air signature, gas well isotopic signature and estimated oxidised proportion of overall landfill sites. The errors are calculated as standard deviations.

Site Name	Range of ambient air isotopic signature, $\delta^{13}\text{C}_{\text{CH}_4}$ (‰)	Average gas well isotopic signature, $\delta^{13}\text{C}_{\text{CH}_4}$ (‰)	Range of estimated oxidised proportion (%)	Emissions in 2018 NAEI (tonnes yr ⁻¹ , NAEI, 2021)
Landfill A – active	-59.6 to -58.7	-60.3 ± 0.5 (10)	2.6–11.6	0.07
Landfill A – closed	-54.6 to -53.6	-55.9 ± 1.2 (10)	4.8–18.8	-
Landfill B	-57.3 to -55.7	-60.1 ± 1.1 (18)	13–38.2	0.14
Landfill C	-57.5 to -55.9	-59.7 ± 1.1 (15)	9.7–22.3	-
Landfill D – active	-57.8 ± 0.3	-59.0 ± 0.7 (7)	5.4–9.9	0.05
Landfill D – closed	-55.1 ± 0.1	-57.8 ± 1.3 (7)	11.9–21.9	-
Active cells of Landfills A, D and C while active: -59.6 to -57.5‰ and 3.2–12.5%				
Closed cells of Landfills A, D, B and C while closed: -57.3 to -53.6‰ and 6–26.6%				

Notes: The number of gas wells are given in the brackets.

2020. A more detailed mobile survey could only be performed during dry July 2019, owing to restricted vehicle access on the muddy soil during autumn and winter surveys. The excess CH_4 mole fraction over the background is colour coded in Fig. 1, and a summary of seasonal surveys at Landfill A is provided in Table 3.

Plots of excess CH_4 above background demonstrate a seasonal trend, with slightly lower values in autumn. In addition to changes in prevailing wind direction and temperature, rainfall in autumn and winter fills the pores of the gas exchange medium, which is likely to cause lower emissions. Even though the autumn survey was performed under lower barometric pressure (Table 2), the surveyed downwind areas did not show higher CH_4 than summer and winter. Maximum excess CH_4 (around 29 ppm) was recorded during the winter survey on the active site and east side of Landfill A, in an area downwind of a closed (historical) site where a leaking gas well was identified (Fig. 1c). Due to operations on the active site during the autumn and winter measurements, we were unable to survey the Site 2 road as during summer.

Following the winter survey, the higher excess CH_4 above the background was assessed during the summer survey. In particular, in summer, active, uncovered areas produced more excess CH_4 than other areas of the landfill, apart from leaking or leachate gas wells. The high CH_4 mole fraction to the far west of the landfill, representing the upwind edge of the active site, probably reflects changing wind direction from NW-NE during the survey, and samples emissions from the flank of the active cell rather than site perimeter emissions. There was strong underlying variation in $\delta^{13}\text{C}_{\text{CH}_4}$ signatures calculated for downwind plumes between the closed and active sites at Landfill A, with a minimum $\delta^{13}\text{C}_{\text{CH}_4}$ emission value of -59.6‰ in summer active site and a

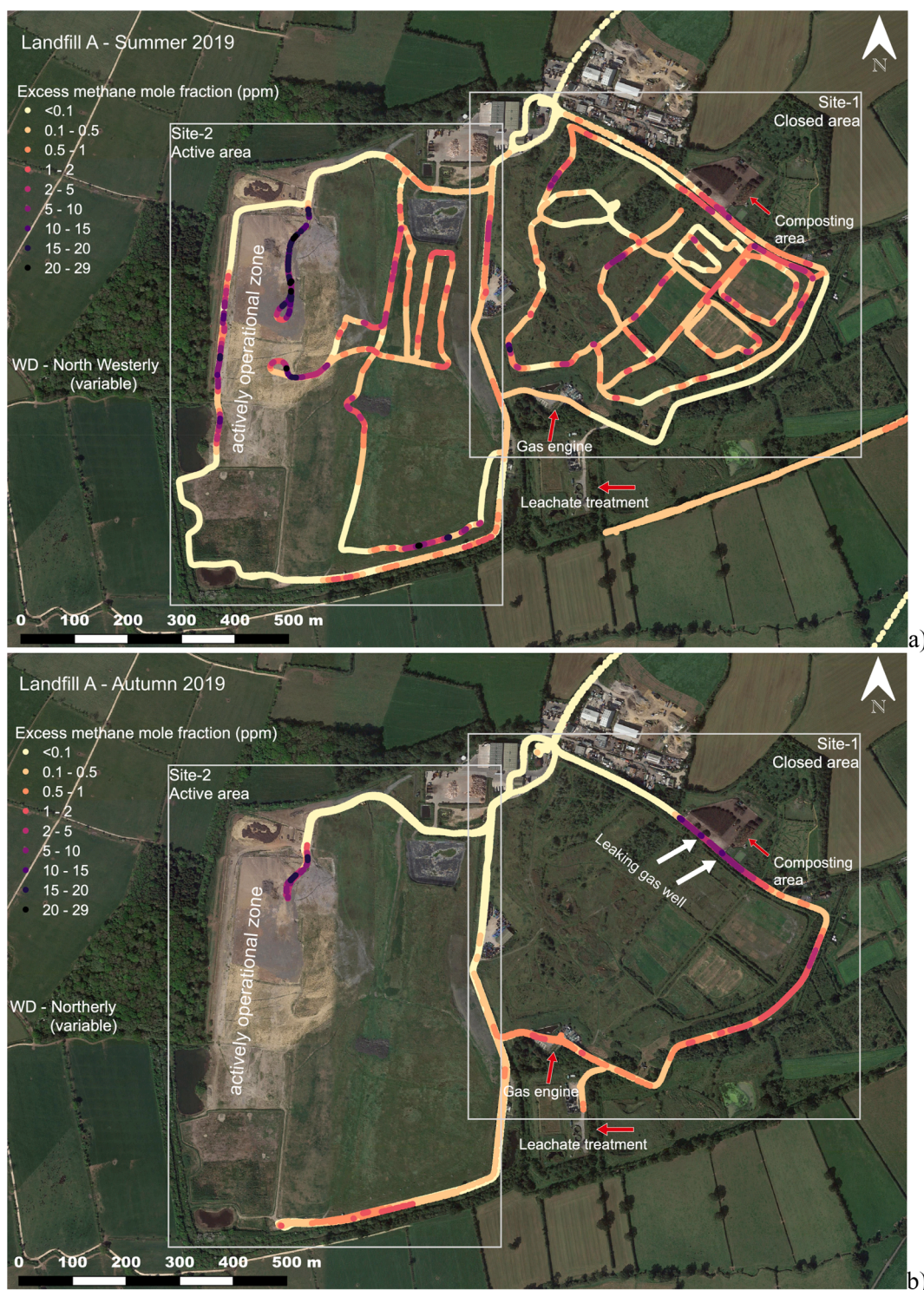


Fig. 1. QGIS map of excess CH_4 mole fraction above background in ppm at Landfill A (QGIS Development Team, 2021). Maps Data: Google, ©2019. Notes: the recorded wind speed was (a) around 3–8 m/s on 9 July 2019 for the summer survey; 5–6 m/s on 5 November 2019 for the autumn survey; and (c) and 7–10 m/s on 17 February 2020 for the winter survey. Red arrows represent the different sites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

maximum $\delta^{13}\text{C}_{\text{CH}_4}$ emission value of -53.6% in autumn in the closed site (Table 3). High precision isotopic measurements found a maximum 1‰ difference between seasonal emission signatures. Similarly, Hoheisel et al., (2019) also observed no seasonal variation in the isotopic signature of a closed landfill.

The mean $\delta^{13}\text{C}_{\text{CH}_4}$ of methane emitted into the atmosphere ranged

from $-59.3 \pm 0.5\%$ in the active part of the site to $-54.0 \pm 0.5\%$ in the closed part of the landfill. CH_4 emissions from older, closed sites were characteristically more enriched in $\delta^{13}\text{C}$ than emissions from active sites. Isotopic signatures of landfill emissions from covered areas have been shown to differ from those in uncapped active tipping areas, owing to oxidation mediated by methanotrophic bacteria in the cover soil

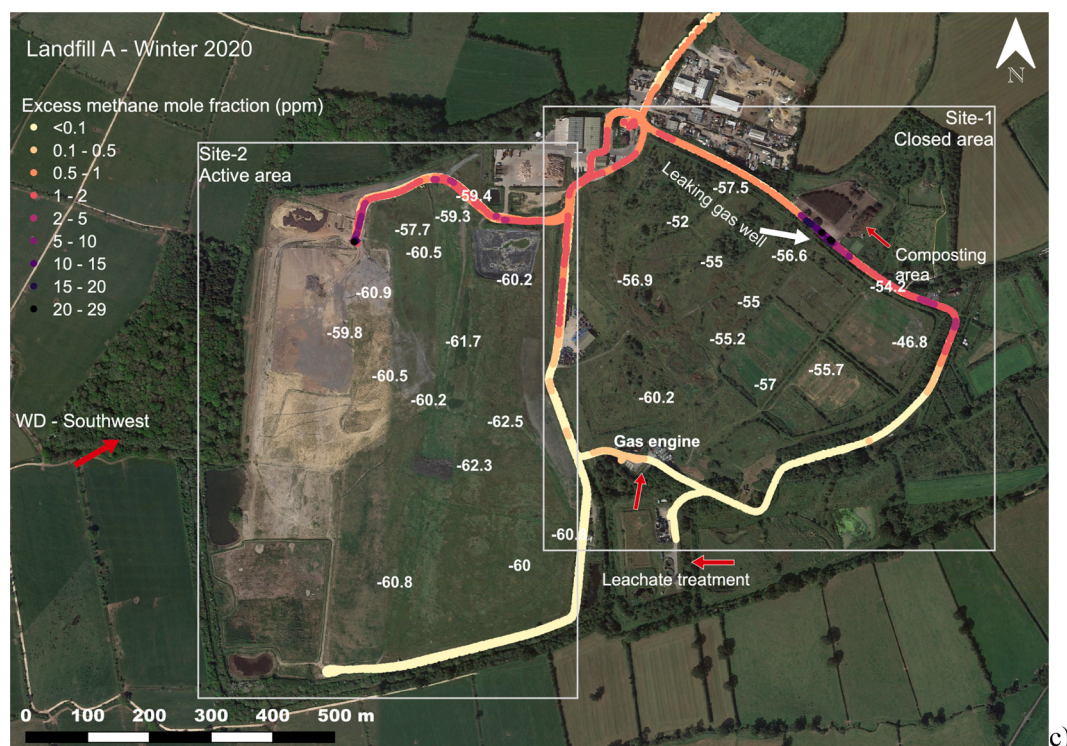


Fig. 1. (continued).

(Bergamaschi et al., 1998). Bergamaschi et al., (1998) obtained highly enriched values ($-45.9 \pm 8\%$) in covered areas compared with samples from uncovered areas ($-55.1 \pm 5.2\%$).

A similar trend was observed for the isotopic signatures for the anoxic zone gas wells of both active and closed sites. Closed site isotopic signatures were more enriched in ^{13}C than active sites, presumably because they were older and further along the methane generation curve, so residual methane might be more enriched. Older waste may produce methane that is more ^{13}C -enriched because the easier-to-decompose ^{12}C has already been preferentially used by methanogens in earlier decomposition soon after waste deposition and the residual organic fraction in mature waste is resistant to biodegradation. Another reason might be that waste composition changed as it evolved and matured over time, which might produce a higher proportion of degradable organic matter in the older waste and variation in methanogenic communities. Also, over time there may have been variation in composition of the input waste mixture in various parts of the landfill.

The oxidised proportion was higher in the closed part of the site than in the active site in all seasons. During winter, a more depleted isotopic signature and lower oxidised proportion were observed from the closed cell, probably because of decreased oxidizing ability of methanotrophs in soil cover during cold weather (Nazhavenriko et al., 1993). Summer produced the highest oxidised proportions of 11.6 % (9.6 to 18.8%) for the closed area and autumn showed the highest oxidised proportion of 7.8% (6.7 to 11.6%) for the active area of Landfill A, respectively. Chanton et al., (1999) found the highest oxidised proportion in autumn ($21 \pm 2.7\%$) and summer ($15.9 \pm 4.5\%$). These results are also consistent with Czepiel et al.'s (1996) finding of less oxidation in winter owing to increased precipitation and soil moisture, which limits the rate of CH_4 delivery to methanogens. In summary, the annual oxidised proportion at Landfill A was approximately $8.4 \pm 5.1\%$, being $11.1 \pm 5.2\%$ for the closed site, and $5.6 \pm 3.3\%$ at the active site.

3.2. Impact of partial cap-stripping on Landfill B

Landfill B was opened in 1986, suspended in 2016, and partially

reopened in August 2019. It was surveyed three times between July 2018 and August 2019. It was assessed to understand the impact of cap-stripping on CH_4 emissions and $\delta^{13}\text{C}_{\text{CH}_4}$. Keeling plots of each survey are provided in the Supplementary information Fig. S2.

The widest plume and highest mole fraction of methane were recorded from Landfill B during the July 2019 survey (Fig. 2). The recorded maximum excess methane over background on site was 3.5 ppm, 10 ppm and 6.5 ppm for July 2018, July 2019 and August 2019 surveys, respectively. Hot spots were mostly downwind of leaking gas wells and the landfill gas engine area.

Landfill B calculated $\delta^{13}\text{C}_{\text{CH}_4}$ emission signatures are $-56.8 \pm 0.1\%$, $-55.7 \pm 0.1\%$ and $-57.3 \pm 0.2\%$ for July 2018, July 2019 and August 2019, respectively (Supplementary information Fig. S3 for Keeling plots). In general, July 2019 survey results revealed a higher CH_4 mole fraction with emitted methane being more enriched in ^{13}C . Isotopic signatures of emitted plumes at different parts of the site were similar even after the partial cap-stripping process, probably because placement of fresh waste in the few weeks after stripping would not yet have been producing much CH_4 under the higher atmospheric pressure and ambient temperature (Table 2). Downwind of cap-stripping areas, we did not observe any methane plumes. Thus, removal of the topsoil did not result in high emissions during the time of the survey because new waste did not have time to decay before the final survey.

The average $\delta^{13}\text{C}_{\text{CH}_4}$ of 18 gas well isotopic samples was $-60.1 \pm 1.1\%$, with oxidised proportions of 26.6% (20.3–38.2%) in July and 16.9% (13.0–24.4%) in August 2019. Because all gas wells were sampled in 2019, the oxidised proportion for 2018 was not estimated. Landfill B, with the hottest landfill temperature, gave the highest oxidised proportion of the sites studied. Innocenti et al. (2013) also suggested increased temperature represents more intense enzymatic activity of methanotrophs.

3.3. Impact of closure on Landfill C

Landfill C was surveyed in July 2019 and February 2020. There was freshly placed waste during the first survey, and there was a significant

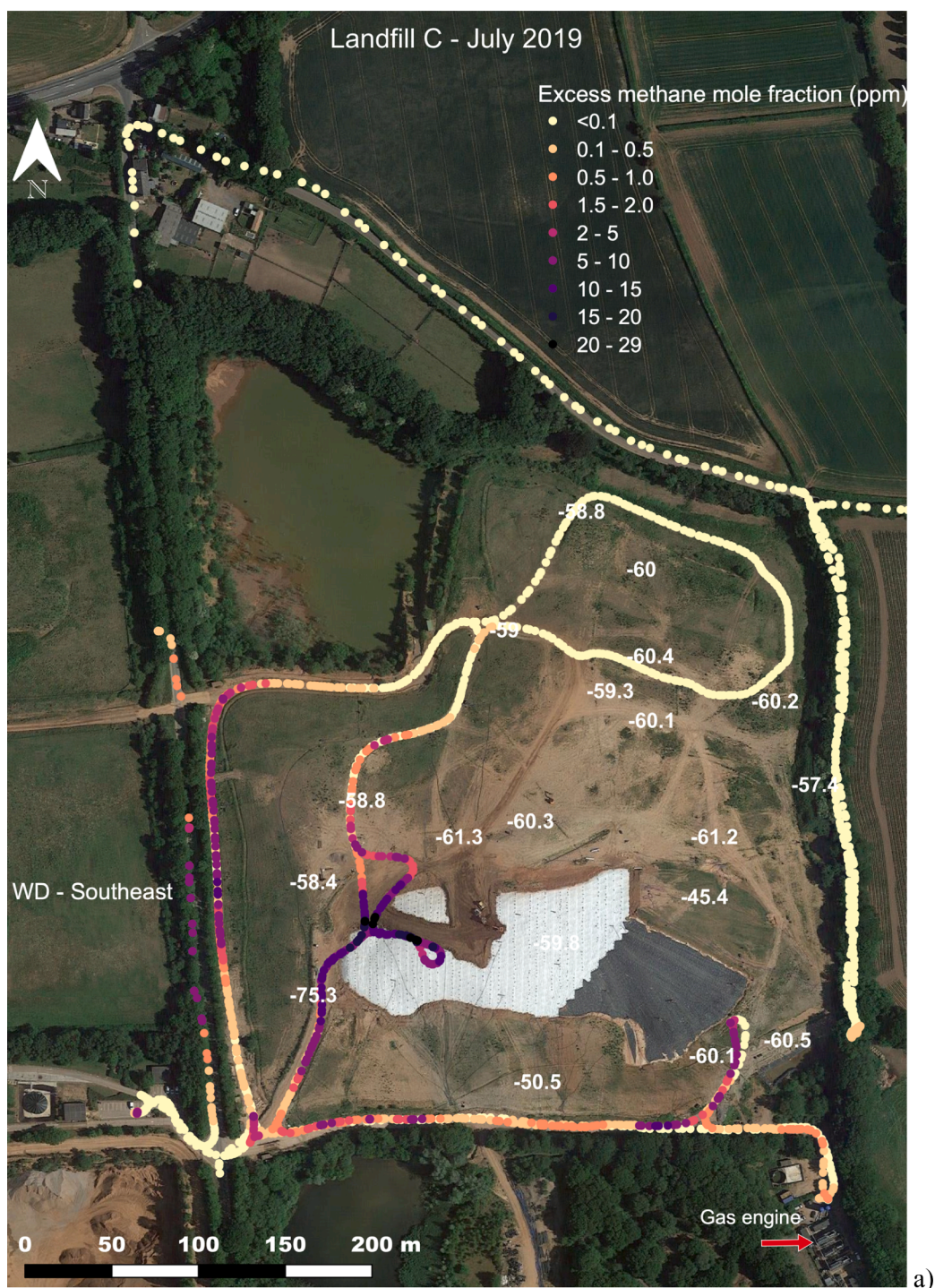


Fig. 2. QGIS map of CH_4 excess mole fraction in ppm at Landfill C (QGIS Development Team, 2021). Maps Data: Google, ©2019. Notes: recorded wind speeds were (a) 12 m/s on 23 July 2019 while waste was being actively placed; and (b) 10 m/s on 17 February 2020 after cell closure and coverage with topsoil.

(almost 18.7 times) observable difference between measured CH_4 mole fraction in the downstream plume when active, compared to after closure. As shown in Fig. 3a, excess CH_4 above the background was up to 28 ppm while it was active, owing to direct CH_4 emissions into the atmosphere from uncapped active areas that have not yet had gas extraction system installed and connected. After closure, excess CH_4 above the background dropped dramatically to 1.5 ppm (Fig. 3b). In winter weather conditions, accessible roads to drive around the landfill site were limited. In previous studies of sources, methane emissions in

plumes can be still measured up to 4–5 km downwind of the largest landfill sites (Lowry et al., 2020; Zazzeri et al., 2015), but in this case a wide plume was not detected at ~600 m downwind of Landfill C during the winter survey. The small plume measured around the gas engine site where the methane was converted to electricity was due to gas engine work during the survey.

$\delta^{13}\text{C}_{\text{CH}_4}$ signatures of CH_4 emissions from Landfill C were found to be between -57.5 ± 0.2 and $-55.9 \pm 0.02\text{‰}$ (see Fig. 3 for Keeling plots), more depleted in ^{13}C while the site was still active, and 1.6‰ more



Fig. 2. (continued).

enriched after closure. The average $\delta^{13}\text{C}_{\text{CH}_4}$ signature of the 15 gas well samples was $-59.7 \pm 1.1\text{‰}$. Oxidised proportions were estimated at 12.5% (9.7–17.8%) while waste was actively being placed, and 17.1% (13.9–22.3%) after the site was closed from Eq. (2), an increase of 4.6%. A build-up of surface vegetation, with an increase in soil microorganisms is likely to lead to increased organic decomposition and microbial competition (Czepiel et al., 1996). The increase in oxidised proportion after closure could also be due to this increase in CH_4 retention time in the topsoil layer.

3.4. Landfill D site

Landfill D is similar to Landfill A with respect to waste depth, number of gas wells and cover soil type (Table 2). They have also both active and closed sites. Therefore, the comparison of the two landfills can clearly show how waste type and age affects the isotopic signature of methane.

$\delta^{13}\text{C}_{\text{CH}_4}$ isotopic signatures of downwind plume observed for Landfill D (Table 4) are $-57.8 \pm 0.3\text{‰}$ for active and $-55.1 \pm 0.1\text{‰}$ for closed sites. In the closed parts of Landfills A and D, $\delta^{13}\text{C}_{\text{CH}_4}$ ranged from $-55.1 \pm 0.1\text{‰}$ to $-53.9 \pm 0.6\text{‰}$, indicating greater enrichment in ^{13}C than in active parts, where values varied between $-59.6 \pm 0.1\text{‰}$ and

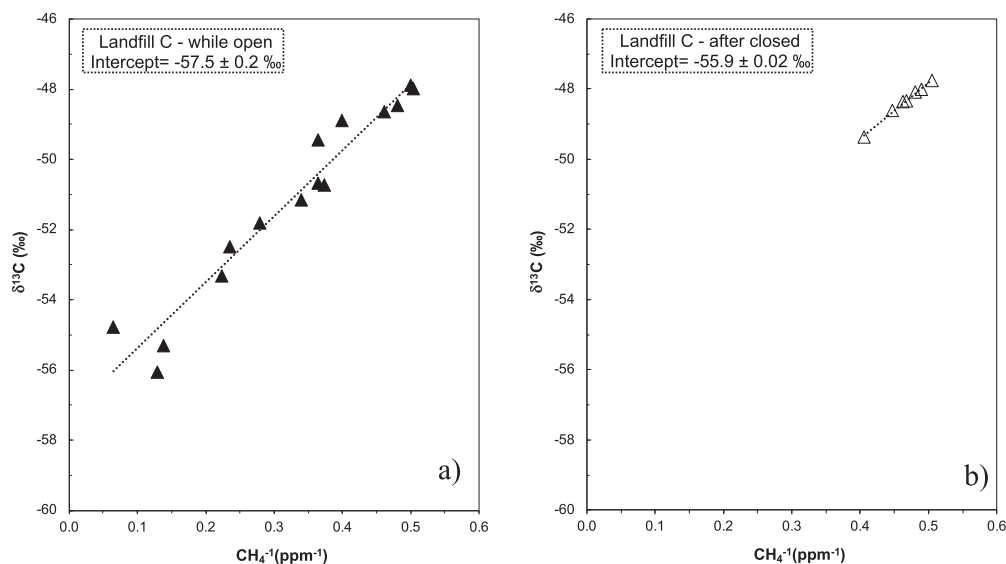


Fig. 3. Keeling plots of Landfill C. (a) while waste was actively placed; (b) after covered with topsoil. Error bars are not shown because they are smaller than the displayed symbol.

$-57.8 \pm 0.3\text{‰}$. These results are comparable with those of Lowry et al., (2020) and Zazzeri et al., (2015).

The closed area of Landfill D was more depleted in ^{13}C relative to atmospheric background compared to the closed area of Landfill A. The difference between Landfill D and Landfill A may be due to differences in methanogenic communities, temperatures and/or the age and composition of waste. Because the closed area of Landfill D is younger than the closed area of Landfill A, methanogenesis in landfill D may have generated more-depleted, isotopically lighter CH_4 in the presence of excess substrate. Because the methanogens preferentially utilise ^{12}C , the CH_4 from fresher waste would be more depleted in ^{13}C (Nozhevnikova et al., 1993). The CH_4 is then gradually enriched in ^{13}C as the substrate concentration in the waste decreases over the time. On the other hand, methane from the active site of Landfill A was more depleted in ^{13}C in comparison to Landfill D active site, possibly because it had a higher ratio of domestic waste compared to industrial and commercial waste (Table 2).

In general, at Landfills A and D, the fraction of methane oxidised at closed sites, as identified in the plumes, were higher (average $11.1 \pm 3.9\%$) than at active areas (average $5.4 \pm 2.2\%$), and much of the methane emitted into the atmosphere from the active sites was from operational areas with a daily cover only. However, it is possible that some oxidation may also occur in areas with temporary caps, but very little oxidation was observed in active zones of Landfills A and D as they only had thin daily cover.

A detailed survey map and Keeling plots for Landfill D are provided in supplementary information Figs. S4 and S5, respectively.

3.5. Discussion of all site results

Table 5 provides a summary of atmospheric signatures, gas well samples and estimated oxidised proportions at the four landfill sites (see the Supplementary information for corresponding Keeling plots).

$\delta^{13}\text{C}_{\text{CH}_4}$ in methane emitted at active sites ranged from -59.6 to -57.5‰ , with an averaged value of $-58.6 \pm 1.0\text{‰}$. In closed sites $\delta^{13}\text{C}_{\text{CH}_4}$ varied from -57.3 to -53.6‰ , with an average of $-55.4 \pm 1.3\text{‰}$ indicating more enrichment in ^{13}C compared to active sites (Table 5). These trends are in line with findings of Börjesson et al., (2007) and Lowry et al., (2020). Anoxic zone samples were also more depleted in ^{13}C than the emissions to the atmosphere at all sites. Methane from anoxic zones of the older closed parts of Landfills A and D was less depleted in ^{13}C than $\delta^{13}\text{C}_{\text{CH}_4}$ in anoxic zones of active sites. This

result is similar to findings of earlier studies (Innocenti et al., 2013). This is likely to be attributable to several factors, including changes through maturation of waste composition, variations in decomposition rates for different types of waste, depth of burial, and the temperature and moisture content of the soil (Innocenti et al., 2013).

Oxidised proportions for these four landfills varied across active and closed sites (Tables 3 and 4), as well as between different landfills (Table 5). The oxidised proportions were estimated at 2.6–24.4% for active sites and 4.8–38.2% for closed sites. The oxidised proportion may have been lower for active, uncapped areas because most methane escaped directly into the atmosphere. These estimates of oxidised proportions for active sites are slightly higher than previous studies in the UK using the isotopic signature technique: Innocenti et al.'s (2013) results ranged from 5.3 to 12.8% for the total amount of CH_4 oxidation at active landfill sites.

The highest oxidised proportions were measured in the closed sites of Landfills A and D. This is attributed to the well-vegetated soil cover and capping of the waste, similar to Abichou et al.'s (2006) finding of the lowest oxidation values from a thin intermediate daily cover area compared to a thick intermediate well-vegetated soil cover in the landfill. This applied to the active parts of Landfills A and D, and to Landfill C while it was being actively used during summer 2019.

The default oxidised proportion assumed for UK landfills is 10% (NAEI, 2021). This compares with oxidised proportions for the four landfills studied, which varied between 2.6 and 38.2%, with an average of 9.5% for active and 16.3% for closed sites. Thus, we agree with Chanton et al., (2011) that the percentage oxidised proportion should not be considered to be constant, as it depends highly on the activity of the landfill site. Therefore, we recommend using site-specific oxidised proportions rather than a default value.

It should be noted that the stable carbon isotope technique yields a minimum estimate of CH_4 oxidation (Bourn et al., 2019). Moreover, Gebert et al., (2011) suggest that the reliability of this technique depends significantly on the isotopic fractionation mechanism. For example, flux chamber methods yield highly variable results because of the local fractionations in the topsoil zone (Table 1). In this work, we measured atmospheric methane plumes "in air" that integrated emissions from several cells and possibly point sources, thus the average of a statistically significant number of gas wells was used to estimate oxidised proportion.

In earlier studies, the isotopic signatures of average landfill sources ranged between -55 and -51‰ (Bergamaschi et al., 1998; Levin et al.,

1993; Wahlen, 1993), whereas our results ranged from -60 to -54% , with an average of $-57 \pm 2\%$. These suggest a shift to more negative values in recent years influenced by the introduction of gas extraction systems and the changes in composition of waste being sent to landfills. The gas extraction systems in closed-cell areas are highly efficient, leading to an increase in the proportion of CH_4 emitted from the active cells as emissions from covered areas have declined. In addition, the diversion of food and garden waste from landfills to biogas plants in recent years may result in a more depleted $\delta^{13}\text{C}_{\text{CH}_4}$ signature. Bakkaloglu (2021) reported that biogas plants fed with food waste are in general more enriched in ^{13}C than active landfills. Although landfill methane emissions have decreased since 1990, these observed changes in the isotopic signature of landfill emissions with improved landfill practice may also make a small contribution to the more negative $\delta^{13}\text{C}_{\text{CH}_4}$ values observed globally over the 2007–2017 period.

3.6. Evaluation of the effects of the α_{ox} estimation and the $\alpha_{\text{trans}} = 1$ assumption

We performed a sensitivity analysis of the oxidised proportion (f_{o}) values in Table 5 to evaluate 0.5% variation in α_{ox} values as suggested by Capanema and Cabral (2012). The range of results presented in Table 5 demonstrate that the increase in the α_{ox} by 0.5% decreases oxidised proportion by an average of 21%, while decrease in the α_{ox} by 0.5% increases the oxidised proportion by an average of 38%. In summary, this analysis suggests that small changes in the isotopic fractionation factor have a measurable effect on the CH_4 oxidised proportion.

The value of $\alpha_{\text{trans}} = 1$ indicates pure advective transport and $\alpha_{\text{trans}} > 1$ demonstrates some degree of diffuse transport, which results in isotopically fractionated CH_4 . Taking into account the diffusive fractionation clearly could increase the oxidised proportion. For instance, only 1% increase in α_{trans} value ($\alpha_{\text{trans}} = 1.01$) could lead to 1.8–2.4-fold increase in the oxidised proportion of CH_4 . There is, however, no method to distinguish between advection and diffusion transport of CH_4 in the landfill. With an oxidised proportion up to 38.2% a factor of 2 to 4 increase (as suggested by De Visscher et al., 2004) is hardly appropriate to our results. In this study, similar to Börjesson et al., (2007), the wind was responsible for the advective transport (3–12 m/s during surveys) and pressure inside the landfill. We believe that our findings represent a lower range of oxidised proportion of CH_4 and are applicable to evaluate default oxidation rates.

4. Conclusions

Methane oxidation, estimated using stable isotope methods, ranged from 2.6 to 38.2%, with mean values of 9.5% and 16.3% for active and closed landfills, respectively. $\delta^{13}\text{C}_{\text{CH}_4}$ signatures of methane emissions to the atmosphere from four UK landfills ranged between -59.6 and -53.6% . Samples taken from gas collected within the anoxic zone of the landfills had $\delta^{13}\text{C}_{\text{CH}_4}$ signatures that varied from -60.3 to -55.9% . Methane emissions from older, closed sites were characteristically more enriched in ^{13}C than those from active sites, having lower emissions and higher oxidised proportions. Gas well isotopic signatures revealed more ^{13}C depletion than emission plume samples and methane was oxidized to some degree during the transportation through the cover at all sites. $\delta^{13}\text{C}_{\text{CH}_4}$ signatures of emitted methane did not show seasonal variation, but lower methane mole fractions and higher oxidised proportions were observed in the autumn compared to summer surveys. There was no plume observed from a partial cap stripping process to assess changes in $\delta^{13}\text{C}_{\text{CH}_4}$ signatures of emitted methane. In addition, closure and topsoil cover of landfills with productive gas extraction systems resulted in dramatic decreases in CH_4 emissions, leading to more enrichment in ^{13}C due to increased oxidised proportions of the residual fugitive methane.

The United Kingdom has a ‘Net Zero’ emission goal by 2050 (CCC, 2019). Although UK landfill emissions have been reducing for well over a decade, addressing the core problem is becoming increasingly difficult.

Better understanding of the landfill emissions is needed to achieve net zero emission goal, by assisting in formulation of controls and regulations. This study helps to identify targets for further mitigation of landfill emission. This work also shows that $\delta^{13}\text{C}_{\text{CH}_4}$ signatures of the ambient air and anoxic zone samples can be used to understand overall budget and emission pathways for methane from landfills, and that site and process-specific analysis can contribute to process-based modelling studies, as well as mitigation strategies. Some limitations to this study are worth noting. Elimination of organic waste deposition in landfills will not terminate methane emissions instantly, as older landfill sites continue to mature, but a gradual decrease in emissions from closed sites would be expected.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We thank the collaborating landfill company for granting us access to the sites. We are obliged to them for their support during landfill surveys. This study is funded by Methane goes MOBILE: MEasurement and MOdeling (MEMO²) project from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 722479, and also supported by U.K. Natural Environment Research Council grants NE/P019641/1, New methodologies for removal of methane, and NE/N016238/1 The Global Methane Budget. Landfill site isotopic data is available via the MEMO² isotopic database at: <https://doi.org/10.5281/zenodo.3975543>. We are grateful to Jerry Morris for maintenance of the survey vehicle, and Mathias Lanoisellé for help with driving the vehicle for surveys. Special thanks go to colleagues in the Greenhouse Gas Research Group for supporting this study. Google Satellite ©2019 is used to create base maps for the figures.

Appendix A

Supplementary information to this article can be found online at <https://doi.org/10.1016/j.wasman.2021.07.012>.

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