Assessing fugitive emissions of CH_4 from high-pressure gas pipelines in the UK

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Abstract

Natural gas pipelines are an important source of fugitive methane emissions in lifecycle greenhouse gas assessments but limited monitoring has taken place of UK pipelines to quantify fugitive emissions. This study investigated methane emissions from the UK high-pressure pipeline system (National Transmission System - NTS) for natural gas pipelines. Mobile surveys of CH_4 emissions were conducted across four areas in the UK, with routes bisecting high-pressure pipelines (with a maximum operating pressure of 85 bar) and separate control routes away from the pipelines. A manual survey of soil gas measurements was also conducted along one of the high-pressure pipelines using a tunable diode laser. For the pipeline routes, there were 26 peaks above 2.1 ppmv CH_4 at 0.23 peaks/km, compared with 12 peaks at 0.11 peaks/km on control routes. Three distinct thermogenic emissions were identified on the basis of the isotopic signal from these elevated concentrations with a peak rate of 0.03 peaks/km. A further three thermogenic emissions on pipeline routes were associated with pipeline infrastructure. Methane fluxes from control routes were statistically significantly lower than the fluxes measured on pipeline routes, with an overall pipeline flux of 627 (241 – 1123 interquartile range) tonnes CH_4/km/yr. Soil gas CH_4 measurements indicated a total flux of 62.6 kt CH_4/yr, which equates to 2.9% of total annual greenhouse gas emissions in the UK. We recommend further monitoring of the UK natural gas pipeline network, with assessments of transmission and distribution stations, and distribution pipelines necessary.

Natural gas, transmission, greenhouse gas, mobile survey, hydrocarbons

1.0 Introduction

In the past decade, unconventional natural gas from shale deposits has been increasingly used as a source of energy, via stimulation through hydraulic fracturing. This technology has raised numerous environmental concerns, including the fugitive emission of methane (CH_4) through pre-production, production and transportation processes. Numerous studies have developed life-cycle emissions inventories to assess the impact that hydraulic fracturing has on greenhouse gas emissions (Balcombe et al., 2016; Burnham et al., 2012; Jiang et al., 2011). Incorporated within life-cycle assessments are transmission and distribution losses, including infrastructure such as pipelines and compressor stations that pressurize natural gas for transport along pipelines. Howarth et al. (2011) estimated fugitive emissions from the transmission, storage and distribution phase to total 1.4-3.6%. The figure of 1.4-3.6% has been disputed as too high (Burnham et al., 2012; Cathles et al., 2012) as the data used by Howarth et al. was based on Russian pipelines and was not applicable to the USA (Leliveld et al., 2005); and was based upon unaccounted for gas techniques (the difference between gas produced and sold) which are known to overestimate fugitive emissions (Burnham et al., 2012). Weber and Clavin (2012) downgraded the Howarth et al. (2011) loss rate to 0.8-2.2% for transmission only but cited the same concerns of the above studies; Stephenson et al. (2011) calculated fugitive emissions using facility-level factors for transmission pipeline from the 2009 API Compendium (API, 2009) and found a loss rate for transmission pipelines of 0.066% over 1440 km transportation distance. Overall, Weber and Clavin (2012) suggested transmission losses were 1.9 (1.2-2.5) g CO_2e/MJ. While life-cycle emissions inventories provide insights into fugitive emissions of CH_4 across the oil and gas sector, it is important to quantify losses based upon observations from monitoring data including components of the transmission and distribution system.

Numerous studies have reported emissions from pipeline leaks and related infrastructure. Across the gas transport system in Russia, total transmission, storage and distribution CH_4 losses were

found to be on the order of 1.4%; incorporating just the high-pressure transmission system, pipelines were estimated to contribute 999 $x10^6$ m^3 CH_4 yr^{-1}, amounting to 6531 m^3 km^{-1} yr^{-1} (Leliveld et al., 2005). A further study of leaks from pipelines in Russia estimated 381 $x10^6$ m^3 CH_4 yr^{-1} (11.3% of total emissions) and emissions from maintenance and repairs to pipelines were estimated at 17.0% of total emissions (Lechtenbohmer et al., 2007). In the USA, leaks from distribution, transmission and gathering pipelines were estimated at 1178.1 $x10^6$ m^3 CH_4 yr^{-1}, 5.7 $x10^6$ m^3 CH_4 yr^{-1} and 186.9 $x10^6$ m^3 CH_4 yr^{-1} respectively (Kirchgessner et al., 1997). A bottom-up survey of CH_4 sources in the Barnett shale region indicated that gathering and transmission pipelines contributed 940 and 230 kg CH_4 hr^{-1} (Townsend-Small et al., 2015). Peischl et al. (2013) conducted a top-down atmospheric survey of CH_4 emissions in Los Angeles and attributed 192 ± 54 Gg CH_4 yr^{-1} to natural gas, while Townsend-Small et al. (2012) confirmed fossil fuels as the major source of CH_4 in Los Angeles through isotopic analysis. Although Townsend-Small et al. (2012) and Peischl et al. (2013) indicated natural gas pipelines as a likely source of fossil fuel emissions, this was not confirmed through direct measurements from pipelines.

Natural gas pipelines include gathering, transmission and distribution pipelines that have different functions and operate at different pressures. Gathering lines transport natural gas from the wellhead to transmission lines while transmission pipelines transport natural gas from gathering, processing and storage facilities and operate at high pressure. In the UK, gas is delivered to terminals from offshore and is transported around the UK using the National Transmission System (NTS), with 23 compressor stations maintaining operating pressures of up to 85 bar (85 x 10^5 Pa). Distribution networks operate at lower pressure and include service pipelines that connect to customer's meter's or piping and mains lines that supply more than one service line. Several studies have started to quantify the scale of natural gas pipeline leaks, though the majority of research has focused on leaks in cities across the United States. Jackson et al. (2014) measured 5893 natural gas leaks, ranging from 2.5 - 88.6 ppmv CH_4, from 2400 road km traveled in Washington, DC. Emissions from four street leaks from natural gas pipelines ranged between 9200 and 38200 L CH_4/day. An average loss of 2.7% from natural gas pipelines, 2-3 times higher than the best state estimates (1.1%) was found in Boston, Massachusetts using top-down atmospheric measurements (McKain et al., 2015). Lamb et al. (2015)

measured 230 underground pipeline leaks across the USA to create emissions factors for service and mains distribution pipelines and suggested that such systems contributed 197 Gg CH_4/yr (554 CH_4 Gg/yr, 95% upper confidence limit).

The condition of pipelines is an important factor in contributing to fugitive emissions from natural gas pipelines. Although cast iron and unprotected steel pipes amounted to <10% of all pipeline length in the USA, they contributed 46% of total emissions from pipelines (Lamb et al., 2015). In a further study of fugitive emissions from cast iron mains in Boston, MA, just seven leaks were responsible for 50% of CH_4 emissions measured (Hendrick et al., 2016). The estimated emissions from Lamb et al. (2015) were lower than 2011 USEPA estimates due to the effect of pipeline repairs and replacements from 1992, increasing plastic mains (+150%) while upgrading cast iron (-38%) and unprotected steel (-22%) pipes. Gallagher et al. (2015) found that cities in the USA with pipeline replacement programmes had 90% fewer leaks per mile than cities without, while comparatively few discrete natural gas pipeline leaks were detected in Los Angeles, where cast iron mains are not present (Hopkins et al., 2016). Indianapolis was estimated to have 0.08 leaks/km compared to 0.74 leaks/km in Boston, due to protected steel or plastic mains in Indianapolis and unprotected steel and cast iron mains in Boston (Lamb et al., 2016). Leaks were small in Ithaca, NY, at <0.24 leaks/km, due to only 2.6% of mains being bare steel or cast iron (Chamberlain et al., 2016).

In the UK, the iron mains replacement programme started in 1977 and has an aim of replacing the remaining 91 000 km of iron pipes within 30 m of buildings by 2032 (Dodds and McDowall, 2013). The UK distribution networks total 280 000 km of pipeline, with 7600 km of pipes in the NTS (Dodds and McDowall, 2013). Although there has been an increasing amount of research into leaks from gas pipelines in the USA, there are a limited number of studies elsewhere. Mitchell et al. (1990) suggested that for the UK distribution system, low, medium and high leakage rates were 1.9%, 5.3% and 10.8% respectively and it was argued that leakage rates above 1.9% were more likely. When assessing fugitive emissions of CH_4 from fault zones, Boothroyd et al. (2017) identified natural gas distribution pipelines as a possible source of thermogenic (-41.2‰ $\delta^{13}C$-CH_4) CH_4, of up to 10.1 ppmv along non-faulted control routes. However, not much else has been done to monitor fugitive emissions from pipelines in the UK. Industry estimates (Nelson, 2003) have provided leak rates for

service and mains distribution pipelines in the UK, but these pipelines could be expected to have different leak rates and fugitive emissions of CH_4 than higher pressure transmission pipelines, for which no data is currently available.

Isotopic analysis of $\delta^{13}C\text{-}CH_4$ has been used to identify natural gas sources of CH_4 from pipelines and other natural gas infrastructure. Jackson et al. (2014) reported pipeline leaks across Washington, DC to have a $\delta^{13}CH_4$ isotopic value of -38.2‰, which was statistically indistinguishable from pipeline natural gas (-39‰). Although thermogenic and biogenic CH_4 have ranges of -50 to -20‰ $\delta^{13}C\text{-}CH_4$ and CH_4 -110 to -50‰ $\delta^{13}C\text{-}CH_4$ (Whiticar, 1999) respectively, the boundaries are not distinguished as factors such as oxidation and fractionation can affect $\delta^{13}CH_4$ composition. Phillips et al (2013) reported an average $\delta^{13}C\text{-}CH_4$ of -42.8‰ in Boston, reflecting a natural gas signature that had been altered by fractionation through transport in soil and mixing with background air. Similarly, Townsend-Small et al. (2016) noted the effect of natural background air on natural gas signatures while Arata et al. (2016) observed a mixture of natural gas and biogenic signatures in New Mexico. Thus, isotope analysis is an important tool to identify the source of CH_4 emissions, though source composition can be more complex than defined thermogenic and biogenic boundaries.

In this study, we investigated fugitive emissions of CH_4 from the UK high-pressure NTS. Methane concentration was detected by driving along roads crossing high-pressure gas pipelines and non-pipeline control routes. Isotope analysis of $\delta^{13}C\text{-}CH_4$ was used to identify the source of fugitive CH_4 emissions. As a follow up one high-pressure gas pipeline was selected for a survey of soil gas measurements.

2.0 Methodology

2.1 Study areas

Four high pressure gas pipeline routes were surveyed (Figure 1) in February 2015 and June 2015: the Vale of Pickering (90.7 km pipeline route, 49.8 km control route, 02/02/2015); Durham (56.7 km pipeline, 50.7 km control, 11/06/2015); Northumberland (66.3 km pipeline and 54.1 km control, 15/06/2015); and the Vale of Eden (57.7 km pipeline, 41.7 km control, 17/06/2015) – a total

of 271.4 km of pipeline and 196.3 km of control. Control surveys were undertaken on the same day in similar meteorological conditions to pipeline surveys. Control routes were surveyed to determine natural background levels of CH_4 as well as emissions in the study area that were not associated with natural gas pipeline leaks, such as from biogenic sources like farming. Control routes were selected to be in areas of similar land use to the pipeline routes, but away from the NTS. On a small number of occasions, the Northumberland control route bisected the high-pressure pipeline network where road layouts meant this was unavoidable, but CH_4 concentrations did not exceed 1.87 ppmv. Pipeline routes were longer than control routes due to taking circuits that traversed pipelines and returning back to cross pipelines as much as possible. Pipeline routes incorporated associated infrastructure to the high-pressure pipelines, such as gas sites where the high-pressure network transports gas to and from. Details of each section of pipeline that was bisected at least once are given in Table 1, with further details provided in the supplementary information.

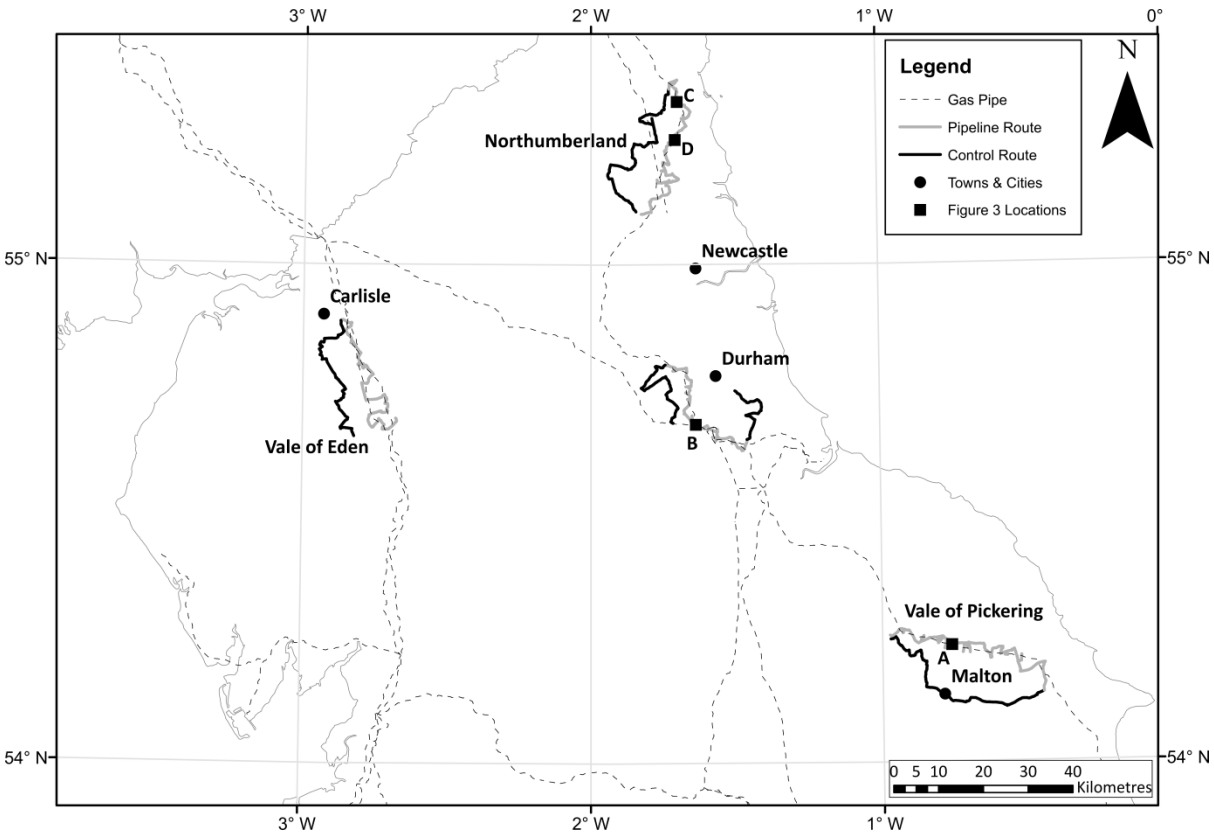

Figure 1. Map of study pipeline and control survey routes. Letters A – D refer to panels in Figure 3.

Table 1. High-pressure transmission pipeline network traversed during study. Year Comm = year commissioned. MOP = maximum operating pressure.

Area	Pipe Name	Year Comm	MOP (Bar)	Diameter (mm)	Steel Grade	Wall Thickness (mm)
Vale of Pickering	FM06 - Elton to Pickering	1972	70	750	X60	12.7
	FM06 - Pickering to Burton Agnes	1971	70	750	X60	12.7
Durham	FM13 - Cowpen Bewley to Bishop Auckland	1997	70	1050	X60	14.27
	FM13 - Corbridge to Bishop Auckland	1981	84	1050	X60	14.27
	FM13 - Bishop Auckland to Yafforth	1978	75	1050	X60	14.27
	FM07 - Bishop Auckland to Sutton Howgrave	1969	75	750	X60	12.7
	FM12 - Longtown to Bishop Auckland	1976	85	900	X60	12.7
Northumberland	FM13 - Simprim to Corbridge	1981	84	1050	X60	14.27
	FM10 - Thrunton to Saltwick	1970	70	600	X52	11.91
Vale of Eden	FM11 - Carlisle 'A' to Grayrigg	1975	85	900	X60	12.7
	FM11 - Longtown to Carlisle 'A'	1975	85	900	X60	12.7
	FM15 - Plumpton Head to Lupton	1984	85	900	X60	12.7
	FM15 - Longtown to Plumpton Head	1984	85	900	X60	12.7

2.2 Gas measurement and analysis

Methane concentration and $\delta^{13}C\text{-}CH_4$ were measured using a Picarro Surveyor P0021-S cavity ring-down spectrometer(Picarro Inc, Santa Clara, CA) whilst driving along pipeline and control routes. The spectrometer has a stated precision of 5 ppb + 0.05% of reading ^{12}C and all results are expressed as per mille relative to VPDB (Vienna PeeDee Belemnite) based upon a factory supplied calibration. Sample gas was measured at a frequency of 1 Hz through a sample line attached to the roof at the back of the survey vehicle (vertical height of sampling was 1.5 m). The Picarro software mapped wind plumes and identified source areas using wind speed (between 0-60 m/s ± 2% @ 12

m/s) and wind direction (0-359° ± 3˚) data from a 2D anemometer (WindSonic, Gill Instruments, Lymington, UK) attached to the roof the survey vehicle. Measurement location was determined using a GPS A21 (Hemisphere, Scottsdale, Arizona).

The raw concentration data was downloaded from the surveyor and converted into ArcMap (version 10) point shapefiles (Boothroyd et al., 2017). Using the point shapefiles imported into ArcMap, individual pipeline and control route lengths were calculated by converting points to polylines (i.e. connecting data points into lines to create the route) and using the measure tool to calculate the length of the polyline. A total of 467.9 km were traveled along the four pipeline and control routes. The distance between a given data point and the pipeline was calculated to the nearest meter using the Near feature in the ArcGIS toolbox. For control routes, a median line (see 2.3.1) between sections of the route traveled was mapped and the distance between it and the nearest point of measurement determined so that pipeline and control routes underwent the same treatment. Elevated CH_4 concentrations were identified as discrete peaks greater than the 99th percentile (2.1 ppmv CH_4) of all measured data. Although previous research (Boothroyd et al., 2017) used the 95th percentile to determine peak concentrations, in this study the 95th percentile was 1.94 ppmv CH_4 and so the 99th percentile was chosen to better distinguish higher concentrations of CH_4.

Pipeline and control routes were revisited the next day after the initial survey for $\delta^{13}C$-CH_4 isotopic measurements. Areas identified as having elevated CH_4 concentrations were revisited based on time constraints and allowing similar numbers of measurements between pipeline and control routes. To determine isotopic composition, real-time atmospheric measurements were conducted for ten minutes while the survey vehicle remained stationary at a given location. The isotope composition of sources was determined using Keeling plots of $\delta^{13}C$-CH_4 against the inverse of CH_4 concentration, with the intercept representing the source composition (Pataki et al., 2003). Thermogenic CH_4 was interpreted to be in the range of -50 to -20‰ $\delta^{13}C$-CH_4 and biogenic CH_4 -110 to -50‰ $\delta^{13}C$-CH_4 (Whiticar, 1999), though it is noted that mixing of CH_4 sources can occur within these ranges, as discussed in section 1.0.

2.3 Data analysis

Data were censored relative to the wind direction, any data collected whilst the wind was in opposite half-disk (outside of 90 degrees either side of the data point) from the nearest point on the pipe or control was removed and was not considered in the analysis of variance (ANOVA) and CH_4 flux determination.

For pipeline routes, isotopic data is presented for complete 10 minute analytical periods described above and data wind-resolved to the direction of the pipeline, wherein data in the wrong half-disk were removed. Isotopic data was also transformed into 30-second averages for the 10-minute analytical period to reduce natural variation from the atmospheric sampling that reduced the quality of regression. Isotopic compositions referred to in the text are from 30-second average data unless otherwise stated. All significant raw data, 30-second average and wind corrected Keeling plots are shown in Figures S1-3, with a summary comparison and locations given in Table S1. If raw data plots were not significant, 30-second average and wind corrected plots were not created. Significance was judged at the 95% probability of the gradient of the Keeling plot being different from zero. Prior to any analysis, prolonged stationary periods (primarily when changing batteries to the Picarro Surveyor, which required the machine to be turned off for a short period followed by a warm-up period) were removed from the analysis, but periods in stationary traffic were not excluded.

2.3.1 Correcting concentration for distance

As there was no fixed distance from the Target (pipeline or control line), the CH_4 concentration would be expected to decline to ambient with distance. Consequently, any difference between Areas (Vale of Pickering, Durham, Northumberland, and Vale of Eden) or Target could be ascribed to distance away from the survey line at each point of measurement. The dynamic plume approach of Hensen and Scharff (2001) was used to control for the distance away from the survey line. A 3D Gaussian plume model was applied to the data of each pipeline or control survey, where the concentration of methane (in mg CH_4/m^3) above the ambient methane concentration (typically 1.5 ppmv – 1.29 mg/m^3) at a point away from a source is given by:

$$Conc.(x,y,z) = \frac{Q}{2\pi u_x \sigma_y \sigma_z} e^{\frac{y^2}{(2\sigma_y)^2}} \left[e^{\frac{-(z-H)^2}{(2\sigma_z)^2}} + e^{\frac{(z+H)^2}{(2\sigma_z)^2}} \right] \quad \text{(i)}$$

Where: x = shortest distance from point of measurement to the pipeline (m); y = the perpendicular distance along the fault of the measurement (zero m in this study); z = the height of the detector above the ground surface (1.5 m); Q = the source strength (mg/s); u = the wind speed resolved along x (m/s); H = the height of the source (m); and σ_y and σ_z = dispersion terms in the directions y and z. The dispersion terms are approximated as $\sigma_y = I_y x$, and $\sigma_z = I_z x$ and in near surface conditions we assumed that there is no stable stratification and that therefore $I_z = I_y = 0.5$. Wind speed was resolved to the shortest distance to the target (u_x) by calculating the shortest distance (x) to the pipeline (or control line) from the point of measurement along with wind speed and direction at height z. Prior to analysis for pipeline distance, data when the wind direction was from the wrong half-disk was removed. Data, first recorded as ppmv, were converted to mg/m^3 with knowledge of the air pressure and temperature conditions on the day. No allowance for buoyant lift-off was given as methane release at the source was assumed to be passive and diffusive, wherein H = 0, meaning the measured concentration above ambient (C) could be determined having allowed for distance x and angle of the source to the measurement location. As the source location was assumed to be from a pipeline, data from the control survey was analysed using the same method, but was corrected using equation (i) to a median line rather than the pipeline. Consequently, methane concentrations corrected to the pipeline should be statistically significantly greater than those corrected to a median control line if the pipeline is a source of methane – i.e. the pipeline was hypothesized to have statistically higher concentrations of methane compared to background levels and non-pipeline sources of methane in the same study area.

Pipeline and control surveys were also corrected for distance travelled (Table 2). Periods when the survey vehicle was stationary or slow moving led to multiple measurements at one location or in close proximity and thus weighting for distance travelled removed multiple measurements from a given location.

Table 2. Sample size (n) and distance travelled (km) for distance corrected datasets.

		Distance corrected	
Basin		n	Distance
Durham	Pipeline	1327	15.7
	Control	786	34.3
Northumberland	Pipeline	1904	22.7
	Control	1635	23.5
Vale of Eden	Pipeline	1645	18.9
	Control	684	8.6
Vale of Pickering	Pipeline	3946	40.2
	Control	501	5.5
Total	Pipeline	8822	97.5
	Control	3606	71.9

2.3.2 Analysis of variance

A two factor survey design was adopted, with data assessed using analysis of variance (ANOVA). The factorial design and use of ANOVA allowed determination of whether pipelines had a significant impact upon CH_4 fluxes and whether there was variation in flux between study areas. The first factor was the area with four levels (Vale of Pickering, Durham, Northumberland and Vale of Eden), and the second factor was the nature of the source (target) which had two levels – pipeline or control. Pipeline and control were replicated across the four study areas. An interaction term between the two factors allowed assessment of significant differences between each pipeline survey and its respective control survey.

The data were Box-Cox transformed to assess for outliers and these were removed if present (Box and Cox, 1964). The data were then tested for normality using the Anderson-Darling test (Anderson and Darling, 1952) and if necessary the data were log-transformed. The Levene test was used to test for the homogeneity of variance. The Tukey test was used post hoc to assess where significant differences lay between factor levels. The proportion of variance explained by factors was assessed by the generalized ω^2.(Olejnik and Algina, 2003). To avoid type I errors all probability values were assessed as significant if the probability of difference from zero was greater than 95%, but if the probability was close to this value then it is reported. Results are expressed as least squares means as these are better estimates of the mean for that factor level (i.e. the mean for the pipeline or

control or individual mean of the four areas) having taken account of the other factors and interactions that were included in the analysis.

The flux from the pipeline and control lines were summed for each area and divided by the distance over which they were collected. Once ambient-corrected (i.e. calculate the flux of CH_4 above ambient), projected to the proposed source (calculate flux coming from direction of pipeline) and then distance corrected (distance from survey line) the fluxes were also calculated once significant sources had been identified.

2.4 Soil CH_4 measurements

A detailed, follow-up study of the Vale of Pickering pipeline mobile survey was conducted, with the mobile survey used to determine sections of the Vale of Pickering pipeline that were, *a priori*, sections where leaks had and had not been identified. Three sections were chosen, two identified as having leaks and one with no identified leak.

The approach used for surveying the sites was based on that of Boothroyd et al (2016), which measured leaks from abandoned oil and gas wells by comparing soil gas CH_4 concentrations above well pads to those from control fields. For each survey line assessed in this study, an agricultural field containing the NTS pipeline was surveyed, with a neighbouring field of identical land use and soil type used as the control field. In each of the surveyed fields, soil CH_4 measurements were made at equidistant intervals along a transect line. For the pipeline field the survey transect line was followed as close to the pipeline as possible (located by the position of gas company's own field markers). Readings were taken at an approximately 8-m spacing with locations of measurements confirmed by GPS. Due to restrictions on identical land use or crops/animals in the fields, neighbouring fields could not always be used as the control. In these cases, control lines along the far edge of the pipeline field were used, ensuring the greatest distance between the control and survey lines. In total 18 pipeline and 18 associated control fields were surveyed.

Soil CH_4 concentrations were measured in parts per million (ppmv) using an EcoTec TDL-500 portable tunable diode Laser Methane/Gas Analyser with a detection range of 0 - 10000 ppmv

290 (Geotechnical Instruments Ltd, Leamington Spa, UK). The measurements were made with a suction
291 cup, connected to the TDL, and placed onto the soil surface for up to 10 seconds – a time based upon
292 the tube delay of the instrument. Measurements were made between 09:30 and 19:30. Prior to each
293 period of data collection the detector was calibrated to a 500 ppmv standard. During soil gas
294 measurement the air temperature, air pressure, relative humidity and dew point were recorded
295 (Commeter C4141 digital Thermo-Hygro-Barometer, Comet System, the Czech Republic).

296 All data from the survey were considered relative to their control, which were considered as
297 ambient CH_4 conditions under the soil and land use for the weather conditions on the sample day.
298 Pipeline data was ratioed to the average of the CH_4 soil gas concentration for its respective control
299 field and was therefore a relative percentage of the ambient control concentration, i.e. values above
300 1.0 were interpreted as a leak.

301 The relative concentration data from the survey was considered as a two-factor ANOVA. The
302 first factor was whether the survey line was a priori considered as containing leaks or not, this factor
303 had two levels (leak or no leak). The second factor was the difference between the survey lines which
304 had 18 levels, one for each survey line measured (i.e. the 18 pipeline and control fields). Data
305 underwent the same treatment as outlined above, with Box-Cox transformation and the normality and
306 Levene tests. The ANOVA was first applied without any covariates and then the ANOVA was
307 repeated using air temperature, air pressure, relative humidity and dew point as covariates - all the
308 covariates were tested for normality and transformed as required. All results from ANOVA are
309 presented as least squares means and post-hoc analysis was performed using Tukey's pairwise
310 comparisons at 95% probability, this was taken as the detection limit within the experimental design
311 which in turn was used to estimate a determination distance, i.e. the maximum horizontal distance
312 along the soil surface for which a significant leak could have been detected.

313 To assess the magnitude of fluxes for those leaks detected from the soil gas survey the
314 diffusion modelling approach developed by Boothroyd et al (2016) was used. To model the fluxes
315 from measured leaks, Fick's first law of diffusion was applied. This first law assumes a steady state
316 diffusive flux from a region of high to low concentration proportional to the concentration gradient,
317 which in 2-dimensions can be expressed as:

$$J = -D\nabla\phi \quad \text{(ii)}$$

Where: J = the diffusive flux (mg $CH_4/m^2/s$); D = diffusion coefficient (m^2/s); and φ = the concentration of CH_4 in soil (mg CH_4/m^3). Equation (i) was solved assuming that the flux was at steady state over time in 2-dimensions using an explicit finite difference method with Δx and Δy = 0.1 m and a distance 3 m either side of the pipe was found to be sufficient to capture the variation back to an ambient concentration.: the boundary conditions were chosen such that φ was at the ambient CH_4 concentration as measured for the control field. The pipeline was located at the centre of the base of the grid and the central grid cell was given a concentration equivalent to that in the pipeline at a depth of 1.2 m below soil surface. Firstly, the model was developed fitting the observed values of φ assuming observed values for equivalent to φ at 10 cm depth; the concentration in the pipeline was taken as the maximum value observed in the field measurements; and using D as a fitting parameter. Secondly, the value of D was set based upon the approach proposed by Ridgwell et al. (1999). Initially the flux model fitted the ambient CH_4 soil concentration seen in the control field (φ); the pipeline concentration value was taken as a relative to the ambient, with the fitting parameter the diffusion coefficient (D). The approach used to set the value of D was that proposed by Ridgwell et al. (1999) using the equations:

$$D_{soil} = 0.196(1 + 0.0055T_{soil})f^{\frac{4}{3}}\left(\frac{f_{air}}{f}\right)^{1.5+\frac{3}{b}} \quad \text{(iii)}$$

$$b = 15.9f_{clay} + 2.91 \quad \text{(iv)}$$

where T_{soil} [K] is the ambient temperature (˚C), f the fractional total porosity, f_{air} the fractional air-filled porosity and f_{clay} the fraction of clay-sized particles present in the soil. The ambient temperature (T_{soil}) was taken as the average temperature measured on the sampling day by the Thermo-Hygro-Barometer. The value of f_{clay} used (0.3) was taken from Avery (1980) with the soil being a mineral loam soil, standard for the UK having a total porosity of 0.52. The concentration in the pipeline was

343 taken as 100% methane. Using equations (2) and (3) the calculated value of D_{soil} = 0.086 cm^2/s; this
344 single value was used throughout the diffusive modeling process.
345

346 # 3.0 Results

347 ## 3.1 Methane peaks and isotopes

348 Time series plots of each survey are displayed in Figure 2, showing wind corrected pipeline
349 measurements, and control measurements. The change in the control dataset following wind
350 correction to the median line is also displayed to show the effect of dataset treatment. The Vale of
351 Pickering had 15 pipeline peaks (2.13 – 2.95 ppmv CH_4) with a mean of 2.49 ± 0.07 ppmv. There
352 were four peaks on the control (2.11 – 2.91 ppmv CH_4), reduced to three when wind corrected. A peak
353 of 2.48 ppmv was recorded 28 m from the pipeline adjacent to a natural gas processing facility
354 (Figure 3A) but the isotopic analysis (Vale of Pickering – Pipeline 1, full data -63 ± 6‰ $\delta^{13}C$-CH_4,
355 Figure S1) was not from the direction of the pipeline and indicated biogenic CH_4 (Table S1). Of the
356 15 pipeline peaks, the Keeling plot regression was either insignificant in the 30-second average
357 dataset or unsampled for 10 peaks, with biogenic CH_4 at Vale of Pickering – Pipeline 2 (Figure S2),
358 applicable to five of the measured peaks. One thermogenic signature was identified on the control,
359 Vale of Pickering – Control 1 (-38 ± 3‰ $\delta^{13}C$-CH_4, Figure S2).

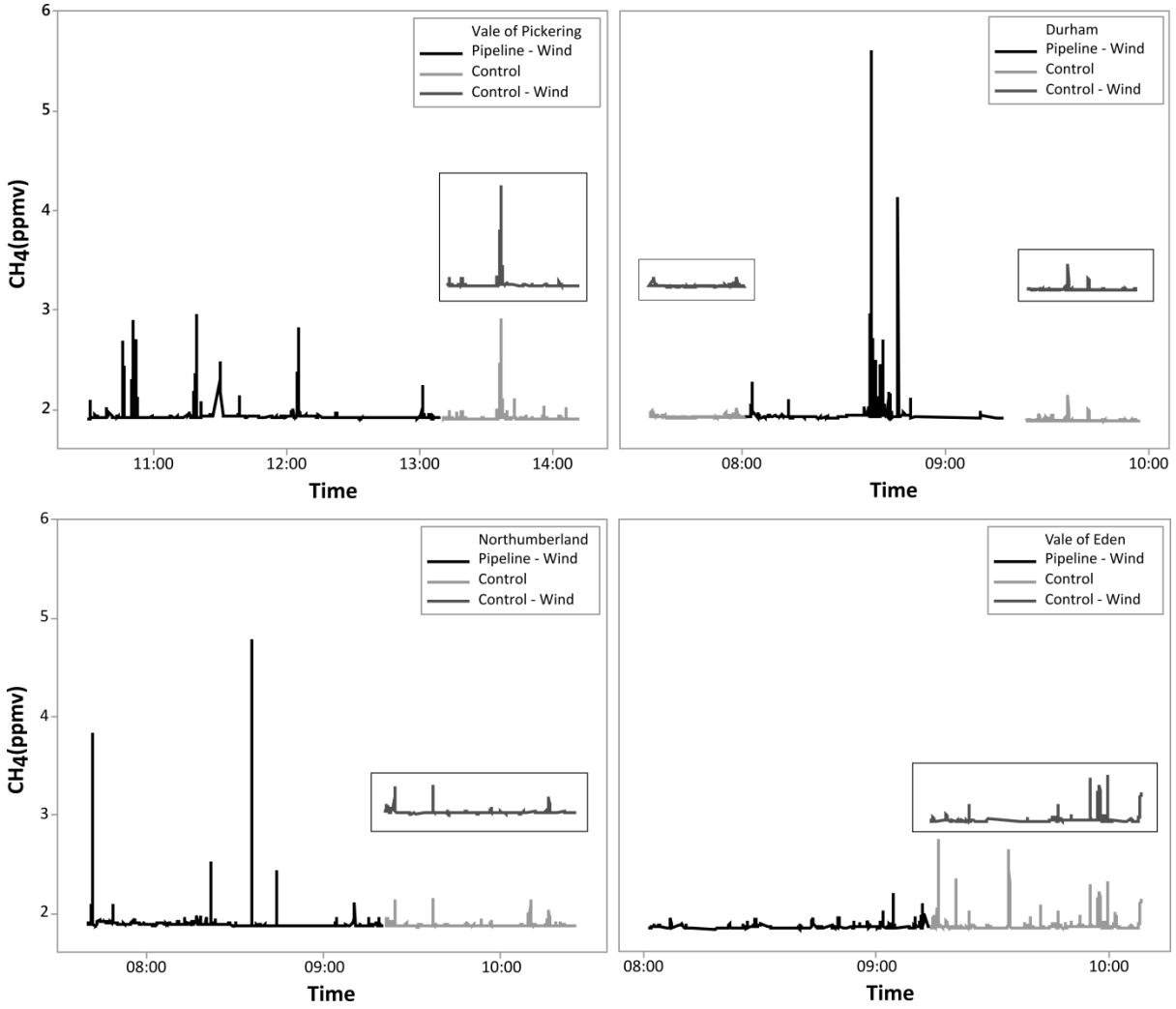

Figure 2. Time series methane concentrations for Vale of Pickering, Durham, Northumberland and Vale of Eden pipeline surveys. Wind corrected pipeline, complete control and wind corrected control surveys displayed. Inset wind corrected control plots are at the same scale as the complete control time series as way of comparison to show where data has been retained or removed. Times are GMT. Start times for each survey differ due to different travel distances on day of sampling; and Durham, Northumberland and Vale of Eden sampling was conducted during British Summer Time (GMT+1).

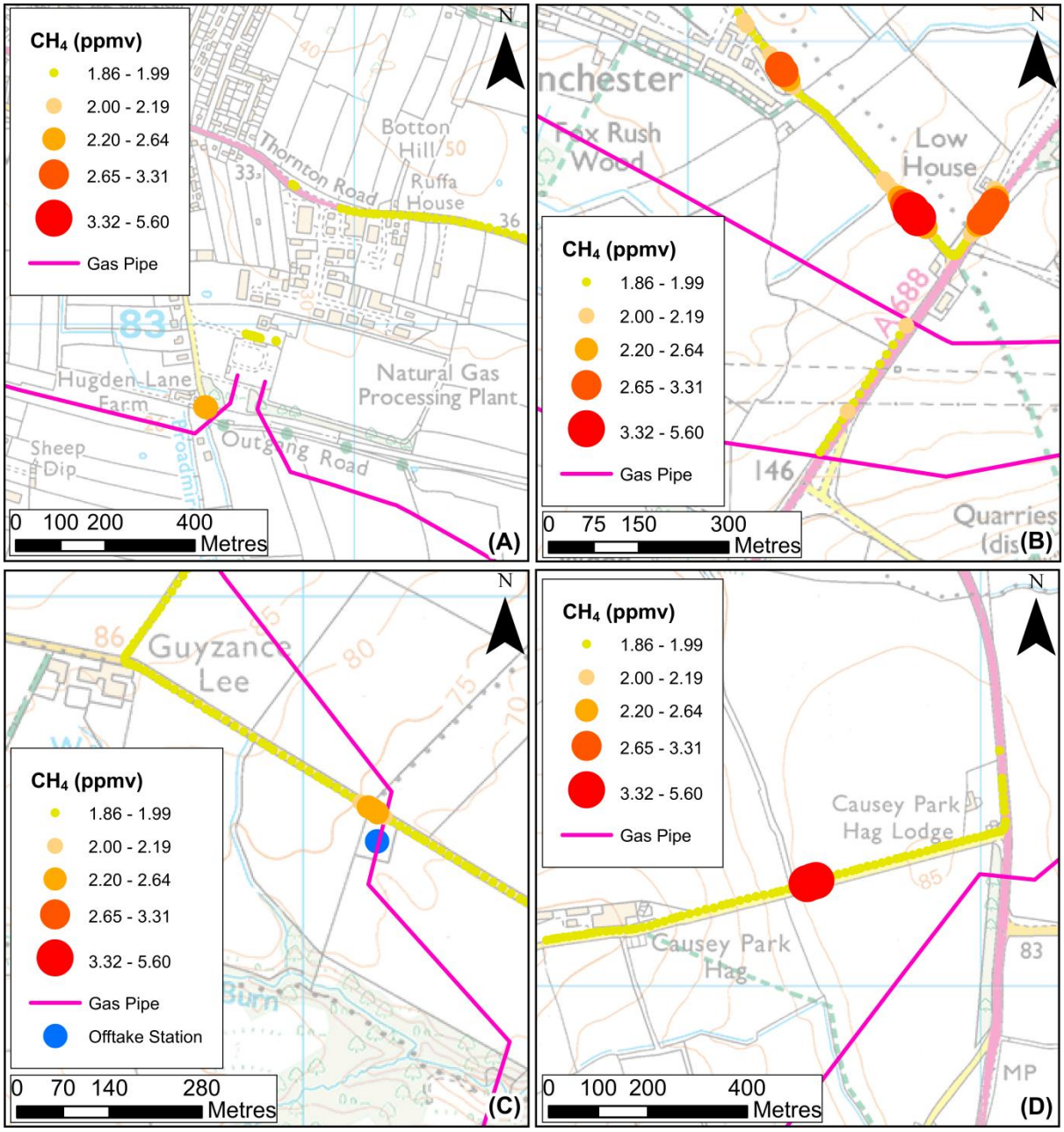

Figure 3. Methane concentrations for pipeline routes: (A) Vale of Pickering; (B) Durham; & (C) & (D) Northumberland. A, B, & D wind corrected; C not wind-corrected. Locations of panels A - D given in Figure 1. © Crown Copyright and Database Right [2016]. Ordnance Survey (Digimap Licence). Gas pipe data from National Grid (Grid, 2014).

The Durham pipeline had 15 peaks on the pipeline route, ranging from 2.12 – 5.60 ppmv CH_4 (mean 2.8 ± 0.3 ppmv CH_4). There were two peaks on the control route, 2.25 – 2.35 ppmv CH_4. Peaks of 5.60 ppmv and 2.71 ppmv (Figure 3B) were thermogenic, with isotopic compositions of -39 ± 2‰

δ^{13}C-CH_4 (Durham – Pipeline 1, Figure S2) and -38 ± 3‰ δ^{13}C-CH_4 (Durham – Pipeline 2, Figure S2). A further thermogenic source of CH_4 was identified (-37 ± 1‰ δ^{13}C-CH_4) next to a local distribution gas pipe (Durham – Pipeline 4). Three of the pipeline peaks were associated with biogenic CH_4 (Durham – Pipeline 3, two peaks, -57.2 ± 0.6‰ δ^{13}C-CH_4; Durham – Pipeline 5 -66 ± 2‰ δ^{13}C-CH_4, Figure S2). The isotopic composition for ten of the peaks was either insignificant or not sampled for isotopes.

On the Northumberland route, a 2.46 ppmv peak of CH_4 was recorded 12 m from the pipeline and although the data was not in the wind-corrected dataset, it incorporated an offtake station (Figure 3C), where the high-pressure transmission system transports gas to be redistributed to consumers. Thus, although the wind direction did not cover the high-pressure pipeline, it nonetheless incorporated infrastructure connected to it. The isotopic analysis confirmed a thermogenic CH_4 source (Northumberland – Pipeline 1, -39.1 ± 0.5‰ δ^{13}C-CH_4, Figure 4). From the wind-corrected dataset, four peaks were identified ranging from 2.43 – 4.80 ppmv CH_4 (mean 3.4 ± 0.6 ppmv CH_4.). There were three peaks on the control route (2.14 – 2.15 ppmv CH_4), reduced to two in the wind-corrected dataset. One of the pipeline peaks was biogenic but may indicate some mixing with background air (Northumberland – Pipeline 3, -53.0 ± 0.4 ‰ δ^{13}C-CH_4, Figure S2), while a 4.8 ppmv peak (Figure 3D) was thermogenic (-38.3 ± 0.6‰ δ^{13}C-CH_4, Northumberland – Pipeline 2, Figure 4). Further pipeline isotopic locations (Table S1) were from peaks not from the direction of the pipeline.

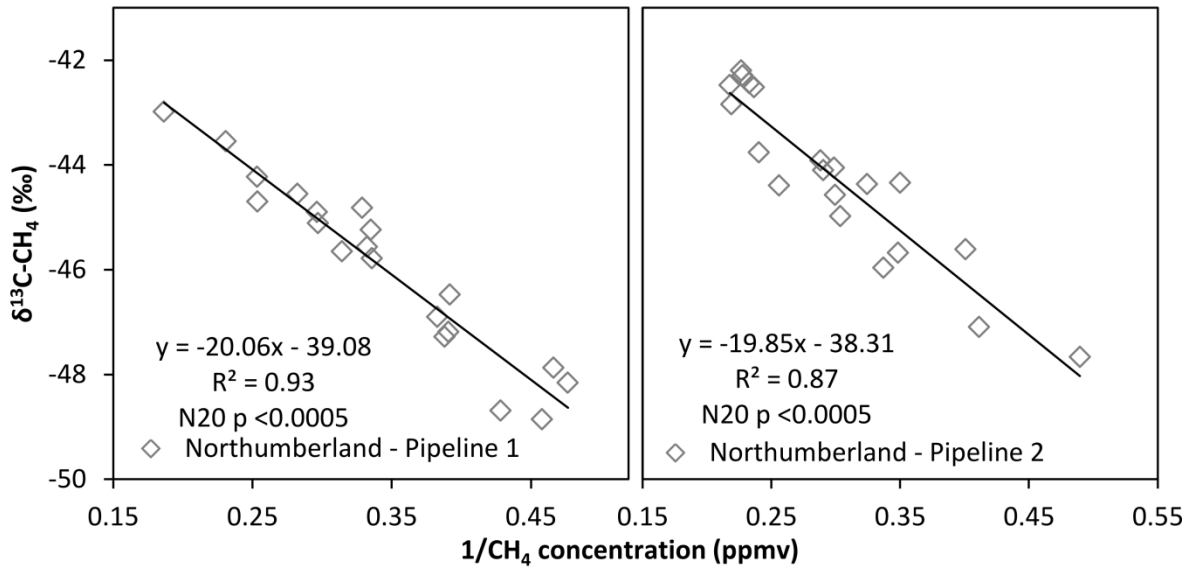

Figure 4. 30-second average Keeling plot of δ^{13}C-CH_4 from Figure 3C (Northumberland – Pipeline 2) and Figure 3D (Northumberland – Pipeline 1). Source composition is from y-intercept. N = sample size. P value refers to regression.

Only one CH_4 peak (2.20 ppmv) was above 2.1 ppmv on the Vale of Eden pipeline route, with an unsampled isotopic signature. Of the eight locations analyzed on the pipeline and control for isotopic composition, one was thermogenic (Vale of Eden – Pipeline 2, -38 ± 1‰ δ^{13}C-CH_4, Figure S2), 34 m from the pipeline. Although excluded as not from the correct wind direction on the pipeline sampling day, the location's isotope data was from the direction of the pipeline and had a maximum concentration of 10.18 ppmv CH_4 in the isotope raw data. The control route had nine peaks (2.13 – 2.76 ppmv CH4, mean 2.25 ± 0.07 ppmv), reduced to five in the wind-corrected dataset.

To summarise, six thermogenic methane sources were identified on the pipeline routes, three of which were associated with peaks above 2.1 ppmv CH_4 from the pipeline sampling data (a peak density of 0.03 thermogenic peaks/km, Table 3). One thermogenic peak was identified on control routes. Thirty-five pipeline peaks were observed at a density of 0.31 peaks/km (Table 3). Excluding peaks identified as biogenic (from farm yards and arable land) on wind corrected pipeline routes, 26 peaks were observed, at 0.23 peaks/km traveled, ranging from 0.05 peaks/km on the Vale of Eden route to 0.76 peaks/km on the Durham route (Table S2). Control routes had 0.09 peaks/km from the

full dataset and 0.11 peaks/km from the wind-corrected data. Wind-corrected control routes ranged from 0.04 peaks/km for the Durham route to 0.25 peaks/km for the Vale of Eden route, with two having a greater peak density than their respective pipeline routes. When accounting for the number of peaks observed on the control, the overall peak density from pipelines was 8 peaks at 0.07 peaks/km. Accounting for peaks from wind-corrected control data, the total number of pipeline peaks was 14 at a density of 0.12 peaks/km.

Table 3. The number of peaks >2.10 ppmv CH_4 observed from pipeline and control routes. Pipeline peaks disseminated into pipeline minus biogenic and pipeline minus biogenic & full control peaks. Note distances are different to flux calculations that remove ambient measurements.

Area	Target	Peaks	Distance (km)	Peaks/km
All	Pipeline	35	114.6	0.31
	Pipeline - Biogenic	26	114.6	0.23
	Pipeline - Biogenic & Control	8	114.6	0.07
	Full Control	18	196.3	0.09
	Wind Corrected Control	12	113.1	0.11
All	Thermogenic Pipeline	3	114.6	0.03

3.2 Flux from pipeline survey

Methane flux for each pipeline survey was scaled having accounted for the flux from its respective control survey. The greatest flux was from Northumberland pipeline and the smallest from the Vale of Eden pipeline (Table 4). For two pipelines the IQR included zero, and it may be concluded that there was no flux from these pipelines.

Table 4. Pipeline flux having accounted for control routes. IQR = inter-quartile range.

Area	Median (tonnes CH_4/km/yr)	IQR (tonnes CH_4/km/yr)
All	627	241 - 1123
Durham	206	50 - 348
Vale of Eden	121	0 - 383
Northumberland	1763	1147 - 2699
Vale of Pickering	397	0 - 707

The flux of methane from the seven sites identified with having a thermogenic methane composition was also calculated from the 10 minute isotope analytical periods. The pipeline sites had a mean of 33.2 ± 20.7 tonnes CH_4/yr with a range of 0.1-131.9 tonnes CH_4/yr (Table 5). Included within this was the Durham – Pipeline 4 thermogenic measurement, though this was likely from a mains service/distribution pipeline rather than from the high pressure network and thus the flux calculated to the nearest high pressure pipeline may be inaccurate as a consequence. The flux for the control (103.1 tonnes CH_4/yr) is greater than the mean for the pipeline fluxes and all but one of the individual measurements. The control flux was calculated to the median control line, a distance of 508 m, but was recorded on a housing estate and most likely represents a natural gas leak from a service/distribution pipeline from a much closer distance than >500 m. Thus, in reality, the control flux is likely to be much smaller than when projected to the median line. If the individual pipeline fluxes are scaled to the 97.5 km (Table 2) from distance corrected datasets, this gives a flux per km range of 1-1352 kg CH_4/km. When the flux rates are upscaled to the 7600 km of total NTS pipeline, this gives a range of 6.0 – 10278.5 tonnes CH_4/yr across the NTS, with a mean of 2588 ± 1614 tonnes CH_4/yr. Given however that the six pipeline fluxes represent all potential thermogenic CH_4 detected from the NTS during the survey, the total methane flux would be 199.2 tonnes CH_4/yr at 2043 kg CH_4/km across the 97.5 km surveyed. When applied to the entire NTS network, the annual flux from all the detected thermogenic fugitive emissions equates to 15530.4 tonnes CH_4/yr (12665.7 tonnes CH_4/yr excluding Durham – Pipeline 4). The control line applied to the same distance of 7600 km would give 10901.4 tonnes CH_4/yr but as stated, the flux is inflated by distance to the median line compared to the actual location of the CH_4 source. The flux from the control does reflect uncertainty in emissions from across the natural gas transportation sector, given it is a representation of mains and service distribution fugitive emissions.

462 Table 5. Methane flux from thermogenic CH_4 sources.

Site	Target	Distance (m)	CH_4 flux (mg/hr)	CH_4 flux (tonnes/yr)
Durham - Pipeline 1	Pipeline	154	224187	2.0
Durham - Pipeline 2	Pipeline	259	3099164	27.1
Durham - Pipeline 4	Pipeline	244	4195301	36.8
Northumberland - Pipeline 1	Pipeline	9	8831	0.1
Northumberland - Pipeline 2	Pipeline	272	15052842	131.9
Vale of Eden - Pipeline 2	Pipeline	34	163793	1.4
Vale of Pickering - Control 1	Control	508	11773219	103.1

463

464 ## 3.3 ANOVA

465 Anderson-Darling test showed that log-transformation was sufficient to normalise the data
466 and the Box-Cox transformation showed that only 5 out 12445 data were removed. The ANOVA of
467 the projected fluxes showed that both factors and the interaction term were significant. The most
468 important factor was the target with the control lines significantly lower than the pipelines, where the
469 least squares mean for pipelines was 2770 ± 84 mg $CH_4/m^3/s$ whereas for the control it was 903 ± 46
470 mg $CH_4/m^3/s$. There were significant differences between all areas with the largest least squares mean
471 being for the Vale of Pickering and the lowest being for Durham. Differences between areas can be
472 ascribed to differences between days of sampling as well as the differences in the background for each
473 area. The difference between areas does not necessarily represent the differences between the
474 pipelines but this can be estimated from the significant interaction term (Table 6).

475

476 Table 6. The least squares means of the target and area*target terms.

Area	Target	Least squares mean (mg $CH_4/m^3/s$)
Durham	Pipeline	1198±100
	Control	474±50
Northumberland	Pipeline	5778±357
	Control	811±59
Vale of Eden	Pipeline	2639±191
	Control	793±59
Vale of Pickering	Pipeline	3225±132
	Control	2190±279
Total	Pipeline	2770±84
	Control	903±46

477

478

3.4 Vale of Pickering soil CH_4

In total 1209 soil CH_4 measurements were taken, with 631 CH_4 measurements in pipeline fields and 578 in control fields. The mean value of pipeline soil gas measurements in Pickering was 1.40 ± 0.33 ppmv, with a mean of 1.43 ± 0.38 ppmv for the control fields. The relative concentrations (i.e. all 18 pipeline measurements in a field were made relative to their equivalent control measurement) of CH_4 in Pickering had a mean value of 0.985 ± 0.225, and were normally distributed. Of the relative measurements, 324 out of 631 soil gas measurements were lower than ambient with the smallest relative concentration of CH_4 as 0.341.

The ANOVA showed that all factors were significant. Of the 18 survey lines 8 were significantly greater than the sampling day ambient, 5 significantly lower and 5 with no significant difference with the greatest being 131% above ambient and the smallest value 56% lower than ambient. Using post-hoc analysis, the smallest leak detected was 3% above ambient (1.03 relative concentration). Anything smaller than 1.00 was inferred as no leak and below 1.03 (detection limit) and 1.00, analytically inferred as ambient. Assuming that the smallest detectable leak (3% above ambient) was measured directly over the point source of the leak gives an estimate for the smallest flux detectable by this experimental design in each area. For Pickering, this would be 15.6 kg CH_4/leak/yr. So as to find over what distance it would have been possible within this experimental design to measure a leak given the detection limit of the equipment it was assumed that the measurement was directly above the leak in the pipeline. Diffusion modelling given this assumption of measurement directly over the pipeline shows that there was a detectable concentration of soil CH_4 concentration up to 5 m away, therefore, the experimental design was capable of measuring a leak 2.5 metres either side of the point of measurement on the ground. Taking the determination distance into account with readings every 8 metres means 2860 m actual pipe length was surveyed. Given the number of leaks detected (i.e. measurements with relative value above 1.03) and the actual distance of pipeline surveyed (2860 m) then for this pipeline a leak was detected every 9.32 m. The average length of pipeline (between joints) is 10 metres (Institution of Gas Engineers and Managers), therefore it can be inferred that this study has detected leaks from all pipeline joints.

Figure 5 shows a linear relationship between the relative CH_4 concentration and the CH_4 flux. The average flux from soil gas CH_4 measurements was 8.24 ± 0.4 kg CH_4/km/yr. The Pickering pipeline is part of the National Transmission System (NTS) of 7600 km of pipeline; the average flux scaled up for the national pipeline estimates a flux of 62.6 ktonnes CH_4/yr.

The cross-sectional area from which CH_4 was leaking was estimated using Ramskill's non-choked mass flow equation (Ramskill et al., 1986):

$$A - Q \Big/ \left(C_{\rho A} \sqrt{\frac{2P}{\rho} \frac{k}{k-1} \left[1 - \left(\frac{P_A}{P} \right)^{(k-1)/k} \right]} \right) \qquad \text{(v)}$$

Where: Q = the mass flow rate (kg/s); C = discharge coefficient, A = discharge hole area (m^2), k = C_p/C_v with C_p and C_v $[L^2T^{-2}\theta^{-1}]$ the specific heat at constant pressure (p) and volume (v), ρ = real gas density (kg/m^3); P_A = the atmospheric pressure (Pa); and P = the absolute upstream pressure (Pa). The pressure (P) is taken as 85 bar (8.5 MPa) compared to atmospheric pressure (1 bar = 0.1 MPa).

Using the largest leak detected the cross-sectional area (assuming a uniform hole) was calculated to be 0.0582 mm^2 or 5.82 $x10^{-8}$ m^2, just larger than the area of a pixel on a modern computer display (0.055 mm^2), with a diameter of approximately 0.136 mm.

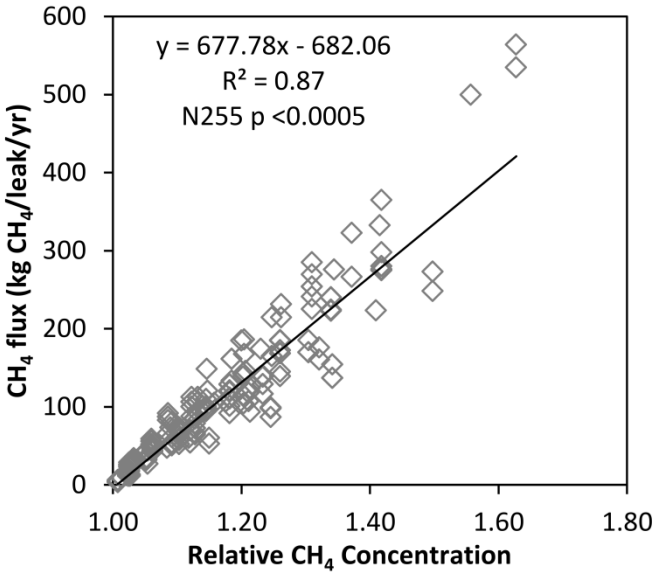

Figure 5. Pickering CH_4 flux calculations. The measured CH_4 soil gas concentration measurement relative to the its control (relative CH_4 concentration) for each leak observed in Vale of Pickering study area in comparison to the CH_4 flux for each the leak as calculated by diffusion modelling.

4.0 Discussion

The use of mobile survey equipment enabled the detection of methane leaks from high-pressure natural gas pipelines and associated infrastructure. Across four distinct areas, 26 leaks were detected from 114.6 km, having removed data from wind directions away from the pipeline and not counting confirmed biogenic sources, providing an overall leak detection rate of 0.23/km driven (range 0.05 – 0.76/km). It is not possible to compare this leak density to other studies in the UK, either of the National Transmission System or mains and service distribution networks due to an absence of research into fugitive emissions from pipelines in the UK. However, studies of mains and service distribution pipelines from the USA have reported leak densities across multiple cities: Durham, NC, 0.14 – 0.20/km; Cincinnati, OH, 0.29/km (Gallagher et al., 2015); and Ithaca, NY, 0.24/km (Chamberlain et al., 2016) were comparable to the UK NTS leak rate found in this study. Washington, DC, Boston and Manhattan had higher leak densities of 2.44 – 2.66 leaks/km (Gallagher et al., 2015; Jackson et al., 2014; Phillips et al., 2013) and consequently the leak density reported here

for the UK NTS is on the low end of those reported from US studies, with even the highest density somewhat short of leakage rates where unprotected steel and cast iron mains were monitored. Most of the leaks reported from the above US studies were classified above 2.5 ppmv CH_4, though the Ithaca study classified leaks above 1.93 ppmv; as such, the leak density for the UK NTS would be expected to rise relative to this, given that leaks were classified in this study as discrete peaks above 2.1 ppmv. Furthermore, this comparison is undertaken with available studies on leaks from pipelines but distribution pipelines in cities compared with high-pressure pipelines in predominantly rural areas must be considered to be limited as they do not operate under the same pressure. Consequently, it is difficult to place the results of this study in context for transmission systems, particularly in terms of UK emissions given that most studies focus upon USA city mains and service distribution systems that operate at lower pressure and often comprise different construction materials.

The soil gas survey of the Vale of Pickering pipeline gives a very different impression of the fluxes from pipelines. This walkover survey was, on average, able to detect a "leak" from every pipe joint. It is perhaps now better to talk not of a leak from a pipeline but that the walkover survey was measuring the in situ properties of the high pressure transmission network. It should be noted that this detection rate was only possible because of the experimental design used by the study, i.e. larger numbers of measurements and only ever judged relative to a control with covariates measured throughout. However, this more detailed and close up survey was able to give a higher estimate of the flux from the network than estimated from the drive by survey.

The 7600 km of NTS of which the Pickering pipeline is a part, is estimated to emit a fugitive CH_4 flux from the entire pipeline of 62.6 kt CH_4/yr or a CO_2 equivalent of 1570 kt CO_{2eq}/yr across the whole of the UK. The UK Greenhouse Gas inventory calculates emissions from the six direct GHGs covered under the Kyoto Protocol: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluoride (SF_6). The inventory takes into account fugitive emissions from coal mines, oil and gas upstream processing and solid fuel transformation (DECC, 2014) however does not take into account fugitive emissions from the gas transmission pipelines. The UK GHG inventory values are stated in CO_{2eq}/yr. The UK 2014 GHG emissions inventory of total GHG was 557300 kt CO_{2eq}/yr with the CH_4 contribution being 53500 kt

570 CO_{2eq}/yr (DECC, 2016). Even though the UK GHG inventory does not account for fugitive CH_4
571 emissions, the emissions calculated in this study (1570 kt CO_{2eq}/yr) represents an additional 2.9%.
572 However, this study only considered the high pressure transmission system in the UK and therefore,
573 emissions from the rest of the transmission and distribution system all the way to the customer would
574 have to be better accounted for in the future.
575

576 # 5.0 Conclusions

577 This study used two approaches to the measurement of CH_4 emissions from high pressure gas
578 pipelines (70 to 85 bar). Both approaches used demonstrated significant emissions from pipelines
579 relative to background control.

580 i) Leak rate from a mobile pipeline survey was 627 (241 – 1123 interquartile range) tonnes
581 CH_4/km/yr. The flux from thermogenic CH_4 sources was 199.2 tonnes CH_4/yr across 97.5
582 km surveyed. Scaled up to the NTS, confirmed thermogenic fluxes amount to 15.5 kt
583 CH_4/yr.
584 ii) A walkover survey of soil gas CH_4 found that it was possible to detect elevated CH_4 for
585 every pipeline joint. Scaling results for the entire UK national transmission system
586 showed a pipeline emission of 62.6 kt CH_4/yr or a CO_2 equivalent of 1570 kt CO_{2eq}/yr
587 across the whole of the UK which is 2.9% of total annual greenhouse gas emissions.
588 iii) Further research is required into the scale of fugitive emissions from pipeline
589 infrastructure in the UK. Transmission and distribution stations are known to be sources
590 of CH_4, while little research has been conducted in recent years on distribution pipeline
591 emissions, beyond industry surveys. This study has reported potential emissions from
592 transmission stations and distribution pipelines and would recommend further work to
593 better quantify their impact on GHG emissions.

594

595

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Supporting Information

Study area details; Figure S1-S3 Keeling plots; Methane peak densities.

605 Anderson, T.W., Darling, D.A., 1952. ASYMPTOTIC THEORY OF CERTAIN GOODNESS OF FIT CRITERIA
606 BASED ON STOCHASTIC PROCESSES. Annals of Mathematical Statistics, 23(2): 193-212.
607 API, 2009. Compendium of greenhouse gas emissions methodologies for the oil and natural gas
608 industry.
609 Arata, C., Rahn, T., Dubey, M.K., 2016. Methane Isotope Instrument Validation and Source
610 Identification at Four Corners, New Mexico, United States. J. Phys. Chem. A, 120(9): 1488-
611 1494.
612 Balcombe, P., Anderson, K., Speirs, J., Brandon, N.P., Hawkes, A., 2016. The natural gas supply chain:
613 the importance of methane and carbon dioxide emissions. ACS Sustainable Chemistry &
614 Engineering.
615 Boothroyd, I., Almond, S., Worrall, F., Davies, R., 2017. Assessing the fugitive emission of CH4 via
616 migration along fault zones - Comparing potential shale gas basins to non-shale basins in the
617 UK. Science of The Total Environment, 580: 412-424.
618 Boothroyd, I.M., Almond, S., Qassim, S.M., Worrall, F., Davies, R.J., 2016. Fugitive emissions of
619 methane from abandoned, decommissioned oil and gas wells. Science of the Total
620 Environment, 547: 461-469.
621 Burnham, A. et al., 2012. Life-Cycle Greenhouse Gas Emissions of Shale Gas, Natural Gas, Coal, and
622 Petroleum. Environmental Science & Technology, 46(2): 619-627.
623 Cathles, L.M., Brown, L., Taam, M., Hunter, A., 2012. A commentary on "The greenhouse-gas
624 footprint of natural gas in shale formations" by RW Howarth, R. Santoro, and Anthony
625 Ingraffea. Climatic Change, 113(2): 525-535.
626 Chamberlain, S.D., Ingraffea, A.R., Sparks, J.P., 2016. Sourcing methane and carbon dioxide emissions
627 from a small city: Influence of natural gas leakage and combustion. Environmental Pollution,
628 218: 102-110.
629 DECC, 2014. An introduction to the UK's greenhouse gas inventory. Ricardo-AEA and Department of
630 Energy & Climate Change, UK.
631 DECC, 2016. 2014 UK greenhouse gas emissions, final figures: statistical release. National Statistics,
632 Department of Energy & Climate Change, UK.
633 Dodds, P.E., McDowall, W., 2013. The future of the UK gas network. Energy Policy, 60: 305-316.
634 Gallagher, M.E. et al., 2015. Natural Gas Pipeline Replacement Programs Reduce Methane Leaks and
635 Improve Consumer Safety. Environ. Sci. Technol. Lett., 2(10): 286-291.
636 Grid, N., 2014. Gas pipe: electricity & gas transmission assets. In: Business Assurance and Systems
637 Management, E., National Grid (Ed.), Warwick, UK.
638 Hendrick, M.F., Ackley, R., Sanaie-Movahed, B., Tang, X., Phillips, N.G., 2016. Fugitive methane
639 emissions from leak-prone natural gas distribution infrastructure in urban environments.
640 Environmental pollution (Barking, Essex : 1987), 213: 710-6.
641 Hensen, A., Scharff, H., 2001. Methane emission estimates from landfills obtained with dynamic
642 plume measurements. Water, Air and Soil Pollution: Focus, 1(5-6): 455-464.
643 Hopkins, F.M. et al., 2016. Spatial patterns and source attribution of urban methane in the Los
644 Angeles Basin. J. Geophys. Res.-Atmos., 121(5): 2490-2507.
645 Howarth, R.W., Santoro, R., Ingraffea, A., 2011. Methane and the greenhouse-gas footprint of
646 natural gas from shale formations. Climatic Change, 106(4): 679-690.
647 Jackson, R.B. et al., 2014. Natural Gas Pipeline Leaks Across Washington, DC. Environmental Science
648 & Technology, 48(3): 2051-2058.
649 Jiang, M. et al., 2011. Life cycle greenhouse gas emissions of Marcellus shale gas. Environmental
650 Research Letters, 6(3): 9.
651 Kirchgessner, D.A., Lott, R.A., Cowgill, R.M., Harrison, M.R., Shires, T.M., 1997. Estimate of methane
652 emissions from the US natural gas industry. Chemosphere, 35(6): 1365-1390.
653 Lamb, B.K. et al., 2016. Direct and Indirect Measurements and Modeling of Methane Emissions in
654 Indianapolis, Indiana. Environmental Science & Technology, 50(16): 8910-U530.

Lamb, B.K. et al., 2015. Direct Measurements Show Decreasing Methane Emissions from Natural Gas Local Distribution Systems in the United States. Environmental Science & Technology, 49(8): 5161-5169.
Lechtenbohmer, S. et al., 2007. Tapping the leakages: Methane losses, mitigation options and policy issues for Russian long distance gas transmission pipelines. Int. J. Greenh. Gas Control, 1(4): 387-395.
Leliveld, J. et al., 2005. Greenhouse gases: Low methane leakage from gas pipelines. Nature, 434(7035): 841-842.
McKain, K. et al., 2015. Methane emissions from natural gas infrastructure and use in the urban region of Boston, Massachusetts. Proceedings of the National Academy of Sciences of the United States of America, 112(7): 1941-1946.
Mitchell, C., Sweet, J., Jackson, T., 1990. A STUDY OF LEAKAGE FROM THE UK NATURAL-GAS DISTRIBUTION-SYSTEM. Energy Policy, 18(9): 809-818.
Nelson, K., 2003. Asset Integrity Solutions: Report on the 2002/3 National Leakage Test Programme, Leicestershire.
Olejnik, S., Algina, J., 2003. Generalized Eta and Omega Squared Statistics: Measures of Effect Size for Some Common Research Designs. Psychological Methods, 8(4): 434-447.
Pataki, D.E. et al., 2003. The application and interpretation of Keeling plots in terrestrial carbon cycle research. Global Biogeochemical Cycles, 17(1).
Peischl, J. et al., 2013. Quantifying sources of methane using light alkanes in the Los Angeles basin, California. J. Geophys. Res.-Atmos., 118(10): 4974-4990.
Phillips, N.G. et al., 2013. Mapping urban pipeline leaks: Methane leaks across Boston. Environmental Pollution, 173: 1-4.
Ramskill, P.K., Safety, U.K.A.E.A., Directorate, R., Health, Executive, S., 1986. Discharge rate calculation methods for use in plant safety assessments. UKAEA Safety and Reliability Directorate.
Stephenson, T., Valle, J.E., Riera-Palou, X., 2011. Modeling the Relative GHG Emissions of Conventional and Shale Gas Production. Environmental Science & Technology, 45(24): 10757-10764.
Townsend-Small, A. et al., 2016. Using stable isotopes of hydrogen to quantify biogenic and thermogenic atmospheric methane sources: A case study from the Colorado Front Range. Geophysical Research Letters, 43(21): 11462-11471.
Townsend-Small, A. et al., 2015. Integrating Source Apportionment Tracers into a Bottom-up Inventory of Methane Emissions in the Barnett Shale Hydraulic Fracturing Region. Environmental Science & Technology, 49(13): 8175-8182.
Townsend-Small, A., Tyler, S.C., Pataki, D.E., Xu, X.M., Christensen, L.E., 2012. Isotopic measurements of atmospheric methane in Los Angeles, California, USA: Influence of "fugitive" fossil fuel emissions. J. Geophys. Res.-Atmos., 117.
Weber, C.L., Clavin, C., 2012. Life Cycle Carbon Footprint of Shale Gas: Review of Evidence and Implications. Environmental Science & Technology, 46(11): 5688-5695.
Whiticar, M.J., 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. Chemical Geology, 161(1): 291-314.