

Methane emissions from natural gas extraction and distribution.

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Abstract

CH₄ has come under increased scrutiny in recent years following the creation of the Global Methane Pledge (GMP), which requires signatory countries to reduce their 2020 CH₄ emissions by 30 % by 2030. In order to aid reduction efforts in sectors like the oil and gas (O&G) industry, legislation such as the Oil and Gas Methane Partnership 2.0 (OGMP 2.0) has been brought into effect. This requires O&G operators to report emissions through measurement based techniques. This thesis focuses on improving mobile measurement methodologies responsible for the detection of CH₄ emissions, firstly from domestic natural gas distribution and secondly from offshore O&G platform flaring. Methodologies used in the detection of fugitive emissions from natural gas distribution were adapted based on instrumental limitations, to allow the detection of smaller emissions at a higher spatial resolution. Additionally, source assignment was included as a core part of the methodology to avoid CH₄ emissions from other sources being associated with natural gas emissions. The deployment of this methodology within the cities of York and New York City showed that there were many very small fugitive emissions as opposed to a few large emissions, additionally, other sources, namely domestic pyrogenic emissions, were shown to provide a large contribution to city-wide CH₄ emissions. Detection of CH₄ from offshore flaring has become increasingly difficult as flares become more efficient. The final part of this thesis proposes a new approach to detect and quantify emissions from a highly efficient flare using a large research aircraft. Platform emissions may be modelled through dispersion modelling software before sources are assigned to enhancements using NO_x : CO₂ enhancement ratios. Additional work within this section compared the emissions of other flares within the same region to demonstrate how much of a reduction in CH₄ emissions a highly efficient flare results in.

For Carole and Chris Moore

Contents

Abstract	i
List of abbreviations and acronyms	viii
List of figures	xi
List of tables	xviii
Acknowledgements	xxi
Author's declaration	xxiii
1 Introduction	1
1.1 A brief introduction to climate change	1
1.2 Carbon dioxide (CO ₂)	4
1.3 Methane (CH ₄)	5
1.3.1 CH ₄ emissions	7
1.3.1.1 Anthropogenic emissions	7
1.3.1.2 Natural and indirect anthropogenic sources .	8
1.3.1.3 Methane sinks and lifetimes	9
1.3.2 Formation of tropospheric ozone	9
1.4 The oil and gas industry	13
1.4.1 Oil usage in the UK	16
1.4.2 Natural gas usage in the UK	16
1.4.3 Natural gas distribution in the UK	17
1.5 Methane emissions legislation	18
1.6 Atmospheric emissions inventories	18
1.7 Scope of this thesis	19

2	Development of a domestic natural gas detection algorithm	21
2.1	Introduction to natural gas detection algorithms and definition of terms	21
2.2	Methodology	24
2.3	Algorithm Development	27
2.3.1	CH ₄ enhancement parameter	27
2.3.2	SIFT-MS	30
2.3.3	TILDAS	32
2.3.4	Time clustering parameters	36
2.3.5	Source identification	39
2.3.6	Controlled release experiment	40
2.3.6.1	Quantification equation	43
2.3.6.2	TILDAS lag time	45
2.4	Resulting algorithms	47
3	Methane emissions in York and Bradford	50
3.1	Introduction	50
3.2	Methodology	51
3.2.1	INGENIOUS campaigns	52
3.2.2	York 2024 campaign	53
3.2.3	Meteorological data	56
3.3	Results	59
3.3.1	INGENIOUS	59
3.3.1.1	Bradford INGENIOUS February 2023	59
3.3.1.2	Bradford INGENIOUS June 2023	60
3.3.1.3	York INGENIOUS February 2023	60
3.3.1.4	York INGENIOUS September 2023	60
3.3.1.5	Bradford vs York INGENIOUS comparison	61
3.3.2	York 2024 Campaign	62
3.3.2.1	City wide route	62

3.3.2.2	Neighbourhood route	65
3.3.2.3	City-wide vs. neighbourhood route comparison	67
3.3.3	Comparison of York 2024 campaign algorithm to previous methodologies	68
3.3.4	Industry applicability of York 2024 campaign algorithm	70
3.3.5	Comparison of different quantification equations for the York 2024 campaign	73
3.4	Conclusions	77
4	Methane emissions in New York City	80
4.1	Introduction	80
4.2	Methodology	82
4.2.1	Instrumentation	82
4.2.2	Leak detection	84
4.2.3	Route planning	86
4.2.4	Meteorological data	88
4.2.5	Inventory data	89
4.3	Results	91
4.3.1	Winter	91
4.3.1.1	Leak detection parameters and instrument selection	91
4.3.1.2	Source types detected per drive	97
4.3.1.3	Comparison of quantification equations . . .	99
4.3.1.4	Neighbourhood comparison	102
4.3.2	Summer	103
4.3.2.1	Source types detected per drive	104
4.3.2.2	Neighbourhood comparison	107
4.3.3	Summer vs Winter	108
4.4	Conclusions	115

5	Offshore flaring emissions	119
5.1	Introduction	119
5.2	Methodology	122
5.2.1	Instrumentation	122
5.2.2	Flight plans	123
5.2.2.1	Site 1 flight tracks	125
5.2.2.2	Site 2 flight tracks	129
5.2.2.3	Site 3 flight tracks	129
5.2.3	Detecting flaring enhancements	130
5.2.4	Emission ratio calculation	131
5.2.5	Flaring efficiency calculation	131
5.2.6	Flux Calculation	132
5.2.7	Dispersion Modelling	135
5.2.8	Global Fuel Exploitation Inventory	136
5.3	Results	138
5.3.1	Site 1	138
5.3.1.1	March 2019 (C148)	138
5.3.1.2	October 2023 (C359)	140
5.3.1.3	October 2023 (C360)	141
5.3.1.4	October 2023 (C361)	143
5.3.2	Site 2	144
5.3.3	Site 3	147
5.3.4	Comparison of Sites	154
5.3.5	Environmental impact of flaring vs. venting	160
5.4	Conclusions	160
6	Summary and conclusions	162
6.0.1	Thesis summary	163
6.0.2	Recommendations for future work	167

List of abbreviations and acronyms

BTU - British Thermal Unit

ConEd - Consolidated Edison company of New York

COP26 - The 2021 meeting of the United Nations Climate Change Conference

DRE - Destruction Removal Efficiency

FAAM - Facility for Airborne Atmospheric Measurement

FGGA - Fast Greenhouse Gas Analyser

FPSO - Floating Production, Storage and Offloading unit

GDN - Gas Distribution Network

GFEI - Global Fuel Exploitation Inventory

GMP - Global Methane Pledge

GWP - Global Warming Potential

ICAD - Iterative CAvity enhanced Differential optical absorption spectrometer

INGENIOUS - UnderstandiNG the sourcEs, traNsformations and fates of IndOor air pollUtantS

LI - Leak Indication

LPM - Litres Per Minute

MGGA - Microportable Greenhouse Gas Analyser

NOAA - National Oceanic and Atmospheric Administration

NSTA - North Sea Transition Authority

NTS - National Transmission System

NYAAQ - New York Atmospheric composition and Air Quality

NYC - New York City

O&G - Oil and Gas

OGMP 2.0 - Oil and Gas Methane Partnership 2.0

OP - Observed Peak

SIFT-MS - Selected-Ion Flow-Tube Mass Spectrometry

SLPM - Standard Litres Per Minute

TILDAS - Tuneable Infrared Laser Direct Absorption Spectrometer

UK - United Kingdom

UNEP - United Nations Environment Programme

VOC - Volatile Organic Compound

WASP - WACL Air Sampling Platform

List of figures

1.1	An excerpt from (<i>Judd et al., 2024</i>) [1] showing the estimated temperature of Earth’s surface across the last 485 million years, based on integrated geological data and climate model simulations.	2
1.2	“Climate stripes” illustrating the global average temperature anomaly from 1850 - 2024 relative to a 1961 - 2010 reference period adapted from (<i>Hawkins, #ShowYourStripes</i>)[3] with an overlaid time series of the same anomaly plotted with data from a collaboration between the Met Office Hadley Centre and the Climatic Research UniT at the University of East Anglia (HadCRUT5) [4]	3
1.3	Average monthly atmospheric CO ₂ concentration / ppm, measured at Mauna Loa Observatory, adapted from (<i>Friedlingstein et al., 2025</i>)[7]	4
1.4	Globally averaged monthly CH ₄ concentrations (ppb) between 1983 and 2023, measured using NOAA’s Earth System Research Laboratory adapted from (<i>Saunio et al., 2025</i>)[13].	6
1.5	2023 annual emissions of CH ₄ in the UK from four major emission sources. Data taken from the NAEI, UK Emissions Data Selector [25]	9

1.6	Example O_3 isopleth, taken from (<i>Nelson et al., 2021</i>) [31], showing mean modelled results of O_3 production ($P(O_3)$) with varying VOC and NO_x concentrations are shown, with a red diamond representing the study's modelled $P(O_3)$ at observed VOC and NO_x concentrations.	12
1.7	Change in the number of platforms in the North Sea between 1966 and 2016 where fixed platforms are purple and floating platforms are yellow. Taken from (<i>Martins et al., 2023</i>) [38]. .	15
2.1	Diagram of the WASP and its core instrumentation based on (<i>Wagner et al., 2021</i>) [62].	25
2.2	Measurements made of CH_4 during an in-lab variance experiment, a calculated background and enhancement threshold are also included.	28
2.3	The updated enhancement threshold applied to a 2024 mobile survey using the WASP.	30
2.4	A CH_4 enhancement measured via the MGGA on a mobile survey with the associated SIFT-MS measurements of C_3H_8 and C_4H_{10}	32
2.5	Simplified diagram of the three TILDAS valve configurations.	34
2.6	C_2H_6 calibration plot from a mobile survey with the associated calibration equation.	36
2.7	Example response transition of TILDAS from high concentration to ambient, annotated are the 90 % and 10 % transition values of the high standards concentration.	38
2.8	Relationship between CH_4 and C_2H_6 for three OPs of different source types located during the sampling campaign. Equations are derived using a linear regression model of C_2H_6 to CH_4 measurements across a 10 s window centred on the plume maximum.	40

2.9	Density plot of number of detected enhancements against distance from release point	42
2.10	Density plot of number of detected enhancements against distance from release point (Limited to 0 – 30 m)	43
2.11	Plot of the ln of the maximum detected CH ₄ enhancement against the ln of the known CH ₄ release rate.	44
2.12	Density plot of time lag of the maximum C ₂ H ₆ measurement from the maximum CH ₄ measurement.	46
2.13	Density plot of time lag of the maximum C ₂ H ₆ measurement from the maximum CH ₄ measurement (Only including C ₂ H ₆ measurements that precede the CH ₄)	47
3.1	Colour map of CH ₄ concentration from one of the Bradford INGENIOUS route mobile surveys.	52
3.2	Colour map of CH ₄ concentration from one of the York INGENIOUS route mobile surveys.	53
3.3	Colour map of CH ₄ concentration from one of the York city-wide route mobile surveys.	54
3.4	Colour map of CH ₄ concentration from one of the York neighbourhood route mobile surveys.	55
3.5	Map showing both routes taken during the York mobile survey campaigns, coloured by specific route.	55
3.6	Wind rose and air temperature time series of both Bradford campaigns. The air temperature time series have been shaded to illustrate when mobile surveys took place.	56
3.7	Wind rose and air temperature time series of both York campaigns. The air temperature time series have been shaded to illustrate when mobile surveys took place.	57

3.8	Wind rose and air temperature time series of the York 2024 campaign. The air temperature time series has been shaded to illustrate when mobile surveys took place.	58
3.9	Total number of enhancements from each source type for each of the mobile surveys on the city-wide route.	65
3.10	Total number of enhancements from each source type for each of the mobile surveys on the neighbourhood route	66
3.11	Total number of enhancements from each source type for each of the mobile surveys on the both routes (City-wide: 1-8 & 17-26, Neighbourhood: 9-16).	67
3.12	Bar charts showing the varying detected leak rate categories for each methodology.	70
3.13	Mean resultant length and number of OPs per thermogenic leak indication.	71
3.14	Pie charts of each LI showing number of mobile surveys they were detected vs not.	72
3.15	Box plots illustrating the calculated leak rates of each LI detected in the York 2024 campaign, using three different quantification equations, with the York and (<i>Weller at al., 2019</i>) [54] equations using maximum of all enhancements. .	75
3.16	Box plots illustrating the calculated leak rates of each LI detected in the York 2024 campaign, using three different quantification equations, with the York and (<i>Weller at al., 2019</i>) [54] equations using mean of all enhancements.	76
4.1	Route map of a NYC mobile survey, coloured by CH ₄ concentration, with an inset to show the route's position within the island of Manhattan.	87
4.2	Overview of the area covered in mobile surveys, coloured and labelled by neighbourhood and supply type.	88

4.3	Wind rose and air temperature time series of both campaigns. The air temperature time series have been shaded to illustrate when mobile surveys took place.	89
4.4	Grid squares showing CH ₄ emissions from natural gas distribution, according to GFEI v3 [21].	90
4.5	Number of enhancements detected during the winter campaign using various enhancement parameters.	91
4.6	Time series of a CH ₄ enhancement measured by both the LI- COR and the Aeris.	94
4.7	Location of LIs detected during winter campaign, coloured by which instrument they were detected by.	96
4.8	Number of enhancements detected per drive in the winter campaign, coloured by source type.	97
4.9	Number of enhancements of each source type detected per drive in winter, with daily average temperature overlaid. . . .	98
4.10	Box-plots illustrating each LI's leak rate calculated with the three main leak quantification equations.	101
4.11	LIs detected during the winter campaign, coloured by leak rate overlaid on polygons coloured by neighbourhood.	102
4.12	Number of enhancements detected per drive in the summer campaign, coloured by source type.	104
4.13	Number of enhancements of each source type detected per drive in summer, with daily average temperature overlaid. . .	106
4.14	LIs detected during the summer campaign, coloured by leak rate overlaid on polygons coloured by neighbourhood.	107
4.15	Frequency of detection of OPs by source type for Winter (Drives 1-5) and Summer (Drives 6-10) campaigns plotted against the mean temperature observed during the drives. . .	111

4.16	Frequency of detection of OPs by source type for Winter (Drives 1-5) and Summer (Drives 6-10) campaigns plotted against the median wind speed observed during the drives. .	112
4.17	Location of LIs detected across both campaigns, coloured by the campaign they were detected during.	113
5.1	Flaring emissions of CH ₄ from natural gas and oil production in the UK, data taken from GFEI v3 [21]	121
5.2	Plots showing mean altitude of runs, wind rose and flight track of site 1 sampling, March 2019 C148.	126
5.3	Plots showing mean altitude of runs, wind rose and flight track of site 1 sampling, October 2023 C359.	127
5.4	Plots showing mean altitude of runs, wind rose and flight track of site 1 sampling, October 2023 C360.	128
5.5	Plots showing mean altitude of runs, wind rose and flight track of site 1 sampling, October 2023 C361.	128
5.6	Flight track of site 2 sampling, C363.	129
5.7	Plots showing mean altitude of runs, wind rose and flight track of site 3 sampling C362.	130
5.8	Diagrams showing how the parameters of the flux calculation are derived, the altitude plot shows hypothetical sampling runs at various altitudes, while the gaussian curve shows the pollutant enhancement of Run B.	134
5.9	Time series of species mixing ratios measured during 2019 site 1 sampling C148.	138
5.10	Time series of species mixing ratios measured during October 2023 sampling of site 1 C359.	140
5.11	Time series of species mixing ratios measured during October 2023 sampling of site 1 C360.	141

5.12	Time series of species mixing ratios measured during October 2023 sampling of site 1 C361.	143
5.13	Time series of species mixing ratios measured during site 2 sampling, C363.	144
5.14	Location of detected flaring enhancements (triangles) coloured by their respective run number, in relation to platforms (circles) at site 2 C363.	146
5.15	Time series of species mixing ratios measured during sampling of site 3 C362.	147
5.16	Technical diagram of the flaring platform.	148
5.17	Prediction of vertical plume dispersion from the two platform sources, modelled with ADMS, compared to flight height above flare.	151
5.18	C362 power generation CO ₂ flux against altitude of run, modelled as a gaussian curve.	153
5.19	Comparison of NO _x : CO ₂ emission ratios from each site, coloured by flight number, with shape indicating methodology used.	155
5.20	Comparison of C ₂ H ₆ : CH ₄ emission ratios from each site, coloured by flight number, with shape indicating methodology used.	157

List of tables

2.1	Mobile sampling campaigns where the WASP was deployed for natural gas detection.	26
2.2	Instrumentation used within the WASP on all natural gas sampling campaigns.	27
2.3	Mean, minimum and maximum percentages of CH ₄ , N ₂ , C ₂ H ₆ , CO ₂ , C ₃ H ₈ and C ₄ H ₁₀ in the UK's natural gas mixture, (<i>Bains et al.</i> , 2016) [66].	31
2.4	Parameters associated with the natural gas detection algorithm depending on instrumentation used.	49
3.1	Comparison in the number of OPs and LIs detected in each campaign depending on if the SIFT-MS is included in the algorithm.	61
3.2	Mean number of each source type detected on a drive-by-drive basis for both campaigns.	68
3.3	Number of detected OPs and LIs in the York 2024 city-wide route, depending on changing algorithm parameters.	69
4.1	Instrumentation used aboard NYAAQ mobile platform during natural gas sampling surveys	83
4.2	Number of leak indications detected on each instrument using all thermogenic assignment criteria.	95
4.3	Number of each source type detected per drive in the winter campaign.	99

4.4	Number of each source type detected per drive in the summer campaign.	104
4.5	Median number of each OP source type detected in summer vs winter campaigns.	109
4.6	Number of LIs in each neighbourhood and the campaign they were detected during.	114
4.7	Number of LIs in each leak rate bin for each neighbourhood and for each campaign.	115
5.1	Instrumentation aboard the FAAM BAe-136 atmospheric research aircraft.	124
5.2	List of flight numbers with their associated dates and sampling site.	125
5.3	Each site's annual CH ₄ emissions as a result of flaring as reported in the GFEI v3[21].	137
5.4	NO _x : CO ₂ and C ₂ H ₆ : CH ₄ emission ratios of enhancements located during C148	139
5.5	NO _x : CO ₂ and C ₂ H ₆ : CH ₄ emission ratios of enhancements located during C359.	141
5.6	NO _x : CO ₂ and C ₂ H ₆ : CH ₄ emission ratios of enhancements located during C360	142
5.7	NO _x : CO ₂ and C ₂ H ₆ : CH ₄ emission ratios of enhancements located during C361	144
5.8	NO _x : CO ₂ and C ₂ H ₆ : CH ₄ emission ratios of enhancements located during C363	145
5.9	NO _x : CO ₂ and C ₂ H ₆ : CH ₄ emission ratios of enhancements located during C362	149
5.10	Maximum vertical dispersion of CO ₂ from ADMS models using a range of temperatures and source types	150

5.11	NO _x : CO ₂ and C ₂ H ₆ : CH ₄ emission ratios of enhancements located during C362 that fall within the ADMS modelled vertical dispersion of the flaring plume.	152
5.12	Species emission ratios from each flight with operator's comments where available.	158
5.13	CH ₄ , CO ₂ and C ₂ H ₆ fluxes from each flight's flaring emissions	159

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Author's declaration

I declare that this thesis is a presentation of original work and I am the sole author. This work has not previously been presented for a degree or other qualification at this University or elsewhere. All sources are acknowledged as references. *Chapter 2* and *Chapter 3* include work from a publication currently under peer-review, of which I am the lead author. Details are provided below.

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Chapter 1

Introduction

1.1 A brief introduction to climate change

The terms “climate change” and “global warming” are often interlinked despite the two having differing definitions. Global warming specifically refers to the increase in temperature across the Earth since the early 20th century, mainly due to the increased use of fossil fuels following the industrial revolution but also caused by additional human activities such as deforestation, intensive farming and waste transportation or disposal. Climate change however, encompasses the idea of global warming but also includes other changes related to this, including, sea level rise, retreating ice sheets, shifts in plant behaviour and extreme weather events. Global temperatures have changed constantly over the course of the Earth’s history, influenced by a range of factors, including the evolution of flora and fauna, plate tectonics, all in addition to the chemistry of the Earth’s atmosphere and oceans [1]. *Figure 1.1* shows this variation in the estimated temperature of Earth based on geological data integrated with climate model simulations.

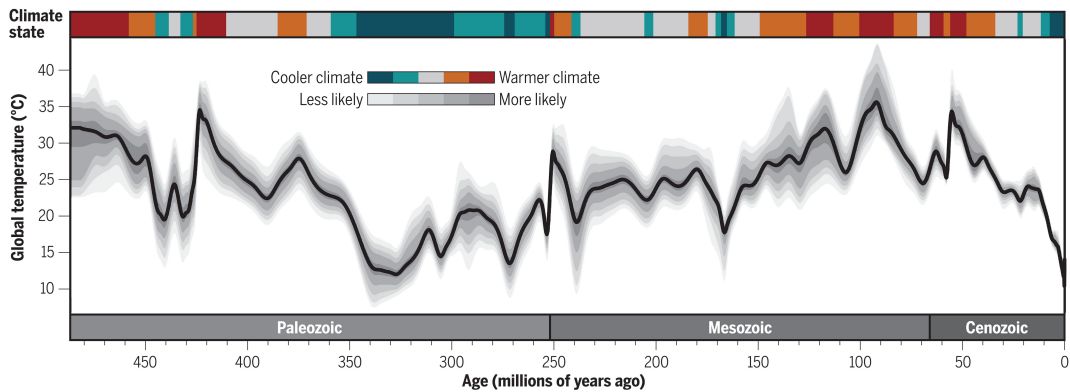


Figure 1.1: An excerpt from (Judd *et al.*, 2024) [1] showing the estimated temperature of Earth’s surface across the last 485 million years, based on integrated geological data and climate model simulations.

Natural climate change however, is slow, with these changes occurring over millions of years. 2024 was noted as the warmest year since global meteorological records began in 1850, with the average global surface temperature reaching 1.29 degrees Celsius above the 20th century average [2]. The changing global temperature is perhaps best visually represented through “climate stripes”, where each stripe represents the average global temperature of that year coloured to represent its difference in reference to a 30 year average between 1971 and 2000. This creates a visual representation of years that were colder than the reference period (shaded blue) and the years that were warmer than the reference period (shaded red). These climate stripes are displayed in **Figure 1.2** and show that there has been a rapid increase in global temperatures since 1850, a rate far beyond that capable of natural means alone.

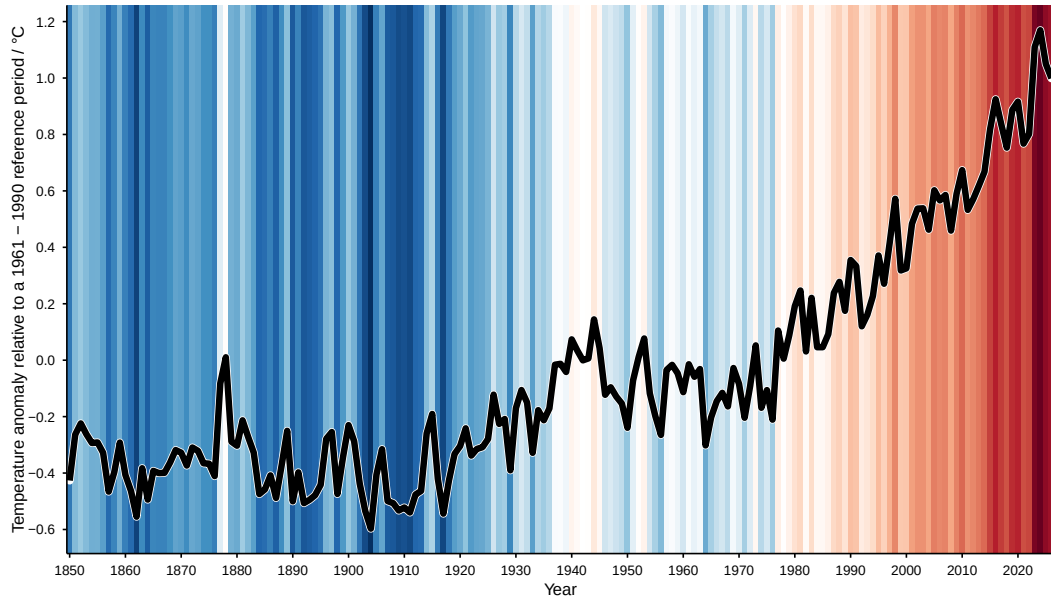


Figure 1.2: “Climate stripes” illustrating the global average temperature anomaly from 1850 - 2024 relative to a 1961 - 2010 reference period adapted from (Hawkins, #ShowYourStripes)[3] with an overlaid time series of the same anomaly plotted with data from a collaboration between the Met Office **Had**ley Centre and the **Climatic Research UniT** at the University of East Anglia (HadCRUT5) [4]

The main driver of this temperature increase is due to the increased use of fossil fuels since the industrial revolution and subsequently the increased release of greenhouse gases to the atmosphere [5, 6]. Greenhouse gases warm the planet by absorbing and re-emitting heat radiated from the Earth’s surface, resulting in heat being “trapped” within the Earth’s atmosphere. This effect is necessary to some extent as without the Earth’s naturally occurring greenhouse gases, the average surface temperature would drop below 0 °C. However, increased concentrations of greenhouse gases in the atmosphere following the industrial revolution have increased this effect, resulting in an imbalance in the Earth’s energy budget and therefore resulting in additional heat being trapped and the Earth’s average surface temperature increasing.

1.2 Carbon dioxide (CO₂)

CO₂ is the most abundant human-emitted greenhouse gas in the Earth's atmosphere and therefore has garnered the majority of attention when it comes to climate change. CO₂ has increased from a concentration (where concentration refers to a dry air mole fraction of approximately 278 ppm in 1750 (the beginning of the industrial era) to 419.3 ppm as of 2023 [7]. This is shown below in *Figure 1.3*.

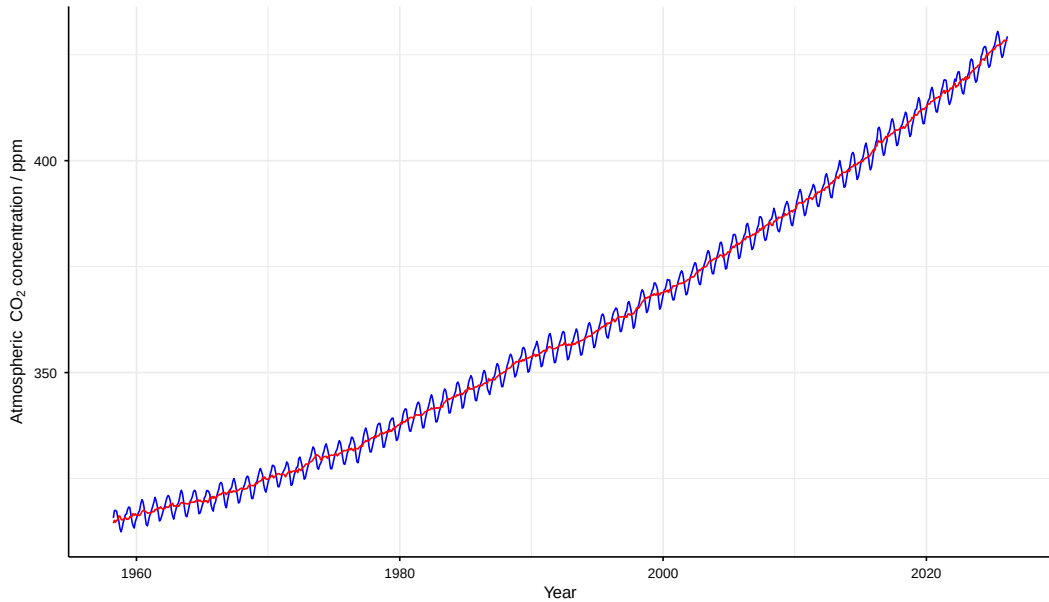


Figure 1.3: Average monthly atmospheric CO₂ concentration / ppm, measured at Mauna Loa Observatory, adapted from (*Friedlingstein et al., 2025*)[7]

For the decade of 2014 - 2023, CO₂ emissions reached an average of $10.8 \pm 0.9 \text{ GtC year}^{-1}$ [7]. Only 45 % of CO₂ that is emitted remains in the atmosphere [8]. Around 25 % of CO₂ emissions are absorbed by the ocean [7, 9], the remainder ($\sim 30 \%$) [7, 10] are absorbed by land ecosystems via processes such as photosynthesis. However, CO₂ has an atmospheric lifetime in the range of hundreds of years, this means that CO₂'s warming effects act over large timespans and the reduction of CO₂ emissions would

not have a visible impact on the atmosphere until many years in the future. This has led to shorter lived climate forcers coming under increased scrutiny.

1.3 Methane (CH₄)

In recent years there has been increasing concern over the potency of CH₄ as a greenhouse gas. Although CH₄ has a much shorter lifetime in the atmosphere than CO₂, approximately 9 years [11], it is much more efficient at absorbing heat compared to the equivalent weight of CO₂, due to a greater number of infra-red active vibrational states in CH₄ compared to CO₂ allowing it to absorb heat across a wider range of wavelengths than CO₂. Additionally, CH₄ is a precursor to CO₂ as well as O₃, another greenhouse gas. This results in CH₄ having a higher global warming potential (GWP), 28 times greater than CO₂ over a 100-year timescale and 84 times higher over a 20-year timescale [12]. GWP is defined as the measure of how much energy the emission of 1 tonne of a gas will absorb over a given period of time, relative to the emission of 1 tonne of CO₂. The Earth's CH₄ emissions have been steadily increasing since the industrial revolution, although yearly CH₄ growth rate is variable, there has been a consistent growth rate of > 5 ppb year⁻¹ since 2007, with 2021 and 2022 seeing growth rates of 17.8 ppb year⁻¹ and 14 ppb year⁻¹ respectively [13]. The total annual emissions for the most recent decade (2010 - 2019) reached an average of 575 Tg CH₄ year⁻¹ for top-down estimates and 669 Tg CH₄ year⁻¹ for bottom-up estimates [13]. The Earth's average atmospheric CH₄ concentration reached 1912 ppm in 2022, a value 2.6 times higher than estimated pre-industrial values [13]. *Figure 1.4* illustrates the growth of CH₄ concentrations between 1983 and 2022.

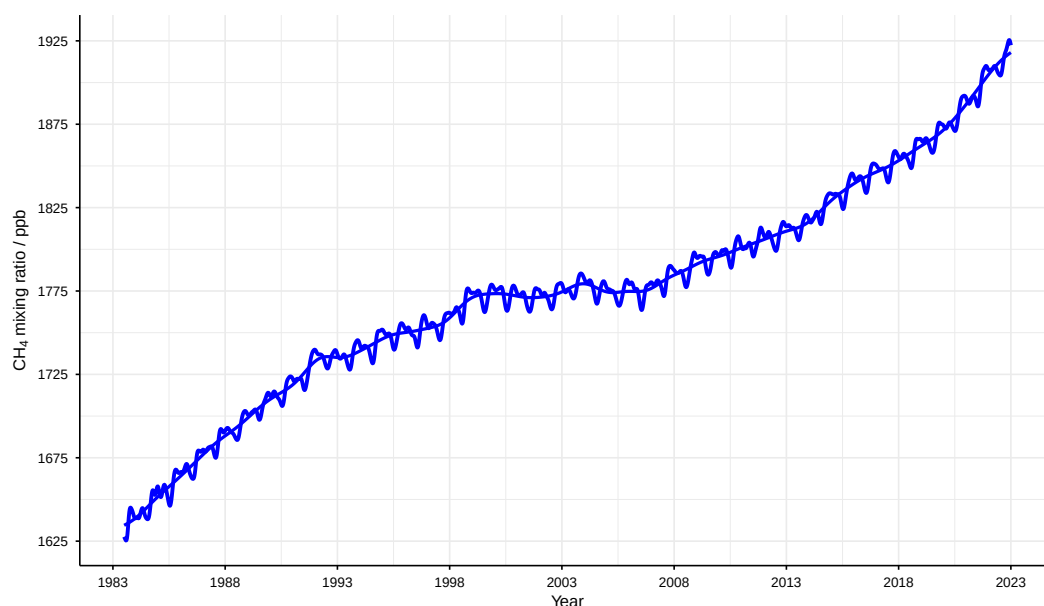


Figure 1.4: Globally averaged monthly CH₄ concentrations (ppb) between 1983 and 2023, measured using NOAA’s Earth System Research Laboratory adapted from (Saunio *et al.*, 2025)[13].

Figure 1.4 also illustrates the seasonal variation seen in atmospheric CH₄ concentrations. This is due in part to seasonal variations in several CH₄ sources (wetlands, rice cultivation, manure and fires) as well as sinks (loss through oxidation to the hydroxyl radical (OH) and uptake to soil) [14]. **Figure 1.4** also shows a stabilisation in CH₄ concentrations in the early 2000s. There has been much debate as to the cause of this stabilisation, with studies suggesting a range of explanations from a reduction in microbial emissions of CH₄ [15] to a reduction in fossil fuel sources [16, 17]. Although these are both reasonable explanations for a stabilisation, there is also strong evidence to suggest that OH concentrations changed across this period, resulting in a greater sink for CH₄ in the early 2000s [18, 19]. Understanding the overall increase in CH₄ concentrations requires an understanding of the varied sources of CH₄, both natural and anthropogenic. But more importance is placed on anthropogenic emissions due to them comprising 65 % of the total CH₄

emissions worldwide [13].

1.3.1 CH₄ emissions

1.3.1.1 Anthropogenic emissions

The fossil fuel sector accounts for an average of 34 % of global anthropogenic CH₄ emissions for the decade 2010 - 2019 [13]. The majority of these emissions are a result of coal, oil and natural gas exploitation, transportation and usage. A small contribution is made to this sector from industrial processes, including production of chemicals and metals as well as fossil fuel fires. Global coal consumption has been decreasing since 2014 but as of 2020, 35 % of the world's electricity was still produced from coal [20]. Emissions can occur at all points of the oil and gas (O&G) supply chain, including the drilling of wells, extraction, transportation, storage, distribution, end use and incomplete combustion of gas flares. Between 2010 and 2019 CH₄ emissions from the O&G sector were estimated to represent 56 % of total fossil fuel CH₄ emissions [13]. This sector is of particular importance to the UK which is the 19th largest country emitter of CH₄ from the natural gas industry [21].

The agriculture and waste sector is responsible for around 40 % of global anthropogenic CH₄ emissions, with the largest contribution coming from livestock production (enteric fermentation in ruminants and manure management), followed by waste handling, rice cultivation with a minor source relating to the burning of agricultural residue [13]. Emissions from livestock is mainly comprised of emissions from ruminant livestock such as cattle, buffalo, sheep, goats and camels that may emit CH₄ due to enteric fermentation; the anaerobic microbial activity that takes place within a ruminant digestive system as a by-product of the digestion of plant matter. The majority (90 %) of emissions from the ruminant then take place via release from the mouth [22]. Manure handling of livestock is an additional

important source of CH_4 , anaerobic decomposition of manure occurs when manure is handled as a liquid and results in release of CH_4 , however, when handled as a solid manure tends to decompose aerobically, which leads to less CH_4 release, but an increase in nitrous oxide (N_2O) emissions, another greenhouse gas [13]. Although there are certain ways to reduce emissions from this sector, notably through the changing of feedstock for cattle, for example grass to maize silage [23], there is still a requirement for social change and land management change as well as education of those working within this sector all of which is difficult to implement by a 2030 deadline. Emissions from rice cultivation are mainly influenced by the water management systems, in particular flooding which is used to cultivate the rice [13, 24]. Between 30 and 50 % of emissions from rice cultivation are found in Asia, however, globally, it is estimated to only contribute 8 % to global anthropogenic CH_4 emissions [13]. 12 % of global anthropogenic CH_4 emissions are a result of waste management, which may include emissions from landfills and wastewater handling [13]. Finally, 5 % of global anthropogenic CH_4 emissions occur as a result of biomass burning while 3 % may be attributed to biofuel burning [13].

1.3.1.2 Natural and indirect anthropogenic sources

~25 % of the total (natural plus indirect anthropogenic) global CH_4 emissions are a result of emissions from wetlands. Other natural sources of CH_4 include; inland freshwater ecosystems (lakes, ponds, reservoirs, streams, rivers), geological sources (hydrocarbon formation in sedimentary basins, natural seeps, volcanic activity), termites, wild animals, coastal and oceanic sources (including from gas hydrates), terrestrial permafrost and vegetation [13].

An overview of CH_4 emissions in 2023 specific to the UK's four major emission sectors is shown in *Figure 1.5*, this matches the global overview,

showing that agriculture and waste dominate CH_4 emissions within the UK, with the energy sector being the next largest.

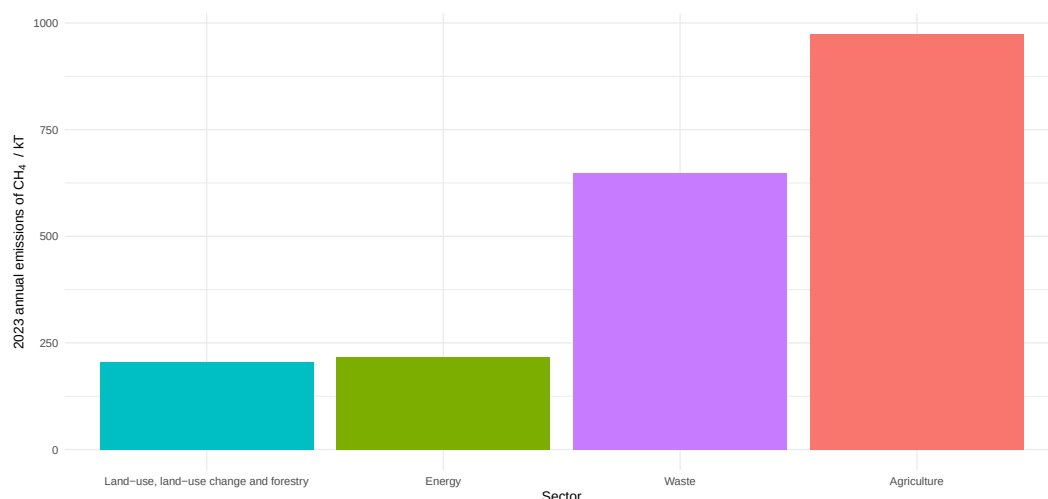


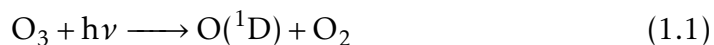
Figure 1.5: 2023 annual emissions of CH_4 in the UK from four major emission sources. Data taken from the NAEI, UK Emissions Data Selector [25]

1.3.1.3 Methane sinks and lifetimes

90 % of the total atmospheric sink of CH_4 is as a result of oxidation with the hydroxyl radical in the troposphere [13], this loss is covered in 1.3.2. Additional losses of CH_4 include; losses via photochemistry in the stratosphere, including reactions with atomic chlorine (Cl) and excited atomic oxygen $\text{O}(^1\text{D})$ [26]; photochemistry in the marine boundary layer [27, 28] and uptake into soils via methanotrophic bacteria [29, 30].

1.3.2 Formation of tropospheric ozone

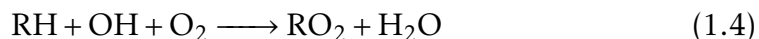
The primary mechanism of removal of CH_4 from the atmosphere is via reaction with the OH radical. The major formation mechanism of OH is from the photolysis of O_3 to form excited $\text{O}(^1\text{D})$ atoms (*Equation 1.1*) which subsequently react with H_2O to form the OH radical (*Equation 1.2*).



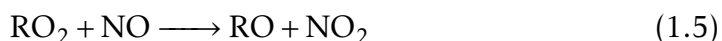
Additional formation of OH has been documented in polluted environments via the photolysis of nitrous acid (HONO) (*Equation 1.3*).



CH₄ and other volatile organic compounds (VOCs) may then react with the newly formed OH through a series of reactions that ultimately promote the formation of tropospheric O₃. These VOCs may be represented by the generalised formula RH. Initially RH and OH react in the presence of O₂ to form RO₂ (peroxy radicals) (*Equation 1.4*).

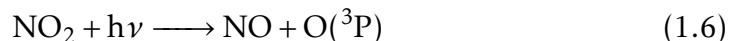
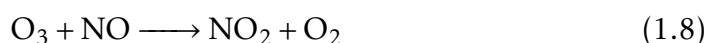


NO may then be oxidised to NO₂ by the newly formed RO₂ radicals (*Equation 1.5*).



O₃ is typically formed via the photodissociation of NO₂ to NO and O(³P), and subsequent reaction of O(³P) with O₂ and a co-reactant (M). O₃ is then also destroyed by the subsequent reaction of O₃ with NO to reform NO₂, (*Equations 1.6, 1.7 and 1.8*). This creates a scheme in clean air environments that results in a net zero in respect to O₃ formation, this may also be referred to as the photostationary steady state. However, the formation of RO₂ radicals via hydrogen abstraction of RH species with OH and then subsequent reaction of RO₂ with NO to form NO₂, creates a new pathway of NO₂ formation that does not require destruction of O₃. This

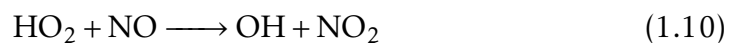
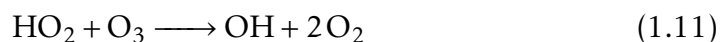
creates a net production of O_3 as the NO_2 formed in this way still undergoes the reactions to form O_3 via its own photodissociation.



The oxidation of NO to NO_2 with the RO_2 radical also results in the formation of an alkoxy radical RO . This may in turn react with O_2 to form a carbonyl ($RCHO$) as well as HO_2 (**Equation 1.9**).



In environments with an excess of NO_x , often referred to as “polluted”, a subsequent reaction of HO_2 with NO can occur to reform the OH radical as well as more NO_2 (**Equation 1.10**). In a low NO_x environment however HO_2 is more likely to react with O_3 , resulting in its destruction and formation of the OH radical and O_2 (**Equation 1.11**).



Again this highlights the concern that oxidation of VOCs in a NO_x rich environment results in the net production of tropospheric O_3 . However, in certain environments described as “VOC limited”, where NO_x is in much more abundance than VOCs, this can lead to reaction of OH with NO_2 to form nitric acid (HNO_3) creating a sink for both OH and NO_x (**Equation 1.12**).



The balance between net O_3 photochemical production and destruction is therefore shown to be highly dependent on concentrations of NO_x and VOCs in the same environment. This dependence can be visualised with the use of O_3 isopleth diagrams. Isopleths show the production of O_3 on the z -axis with an environment's VOC and NO_x concentrations on the x and y axes respectively.

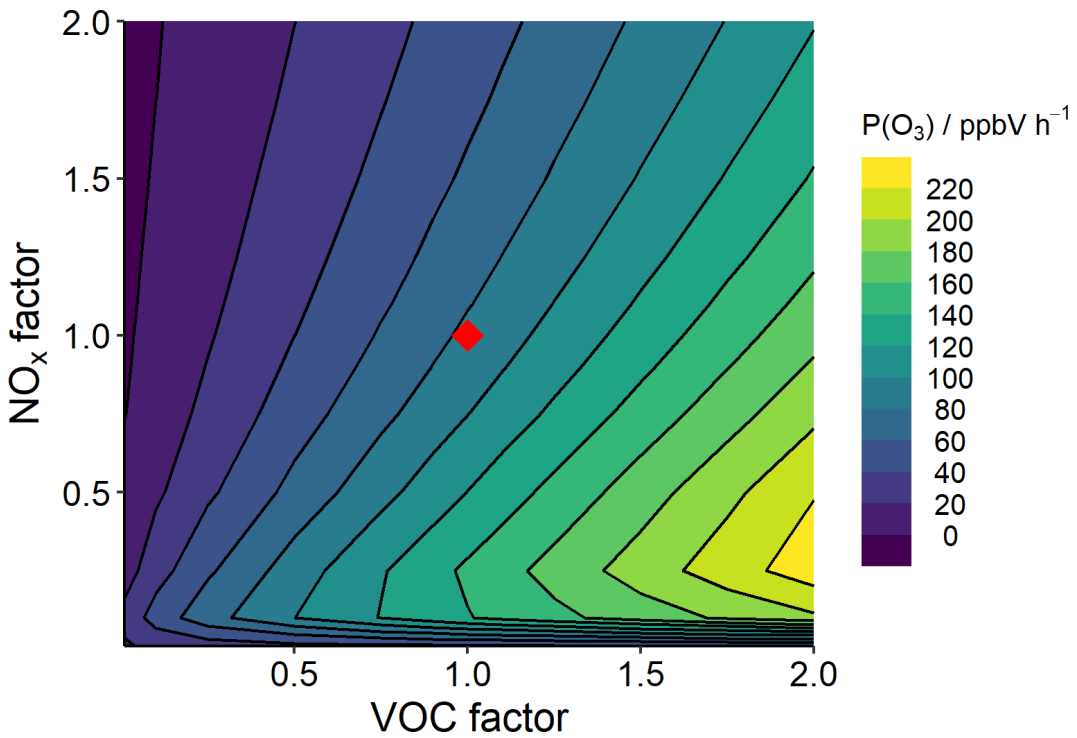


Figure 1.6: Example O_3 isopleth, taken from (Nelson *et al.*, 2021) [31], showing mean modelled results of O_3 production ($P(\text{O}_3)$) with varying VOC and NO_x concentrations are shown, with a red diamond representing the study's modelled $P(\text{O}_3)$ at observed VOC and NO_x concentrations.

Figure 1.6 shows that there are two regimes that may be considered, “VOC limited” which is to the left of the ridge line and “ NO_x limited” to the right of the ridge line. In a VOC limited regime, which is often

representative of polluted urban environments, reducing VOC concentrations whilst maintaining a constant NO_x concentration will result in lower peak O_3 concentrations. Conversely, in this regime, lowering NO_x concentration whilst maintaining constant VOC concentration will result in a higher peak O_3 until a ridgeline is met. This is because in this environment, the NO_2 is in competition with VOCs to react with OH, when concentrations are high it will outcompete the VOCs and follow (*Equation 1.12*) to form HNO_3 and create a sink for OH resulting in a lower RO_2 production and therefore reducing the net O_3 production. However, when NO_x is reduced this frees OH to react with the VOCs and instead follow (*Equation 1.4*), forming more of the RO_2 radical and increasing the net O_3 production. In a NO_x limited regime however, an environment more typical of rural and suburban areas, reducing VOC concentration at constant NO_x has no effect on the peak O_3 concentration, but reducing the NO_x concentration at constant VOC concentration will lead to a reduction in O_3 production. This is because this environment has an abundance of RO_2 radicals from the VOCs reacting with OH, but the photolysis of NO_2 is still a source of O_3 production in these environments and so reducing NO_x affects this process. This net production of O_3 poses many issues as tropospheric O_3 is known to have a negative effect on human health, in particular it raises the risk of a population suffering chronic obstructive pulmonary disease [32]. Additionally, O_3 has negative effects on plant health, reducing their activity and reducing their ability to act as a sink for CO_2 [33, 34]. It is also known to act as a greenhouse gas [35] and greatly impacts air quality [36].

1.4 The oil and gas industry

Fossil fuels (coal, oil and natural gas) have been the driving force and primary fuel for the industrial revolution, with a world consumption that

was insignificant at the turn of the 1800s, to a consumption of 517.7 Exajoules (greater than 12,000 million tonnes of oil equivalents) as of 2025.[37].

This increase in Oil and Gas (O&G) production has coincided with an increase in activity in O&G fields around the world. The UK is home to many O&G reserves, mainly in the North Sea. Growth in the number of platforms has increased in this region from < 10 in 1966 to a peak of > 600 in 2016 [38]. **Figure 1.7** shows the changing number of fixed O&G platforms in the North Sea from 1966 to 2016.

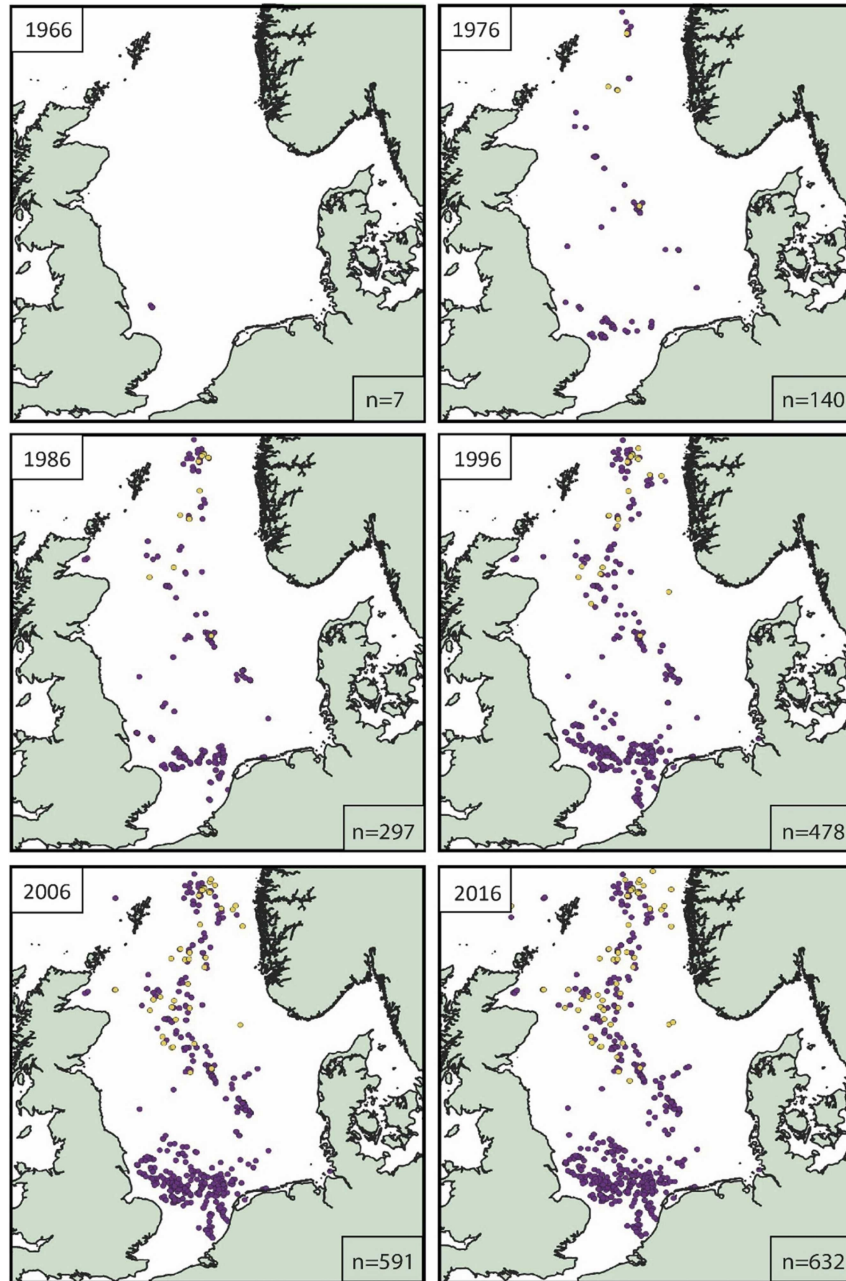


Figure 1.7: Change in the number of platforms in the North Sea between 1966 and 2016 where fixed platforms are purple and floating platforms are yellow. Taken from (Martins *et al.*, 2023) [38].

This increase has been seen in both types of O&G platforms, fixed and floating. Floating platforms exhibit an upward trend until 1999, after which year by year has seen both increases and decreases. For fixed platforms the

upwards trend was seen until 2009, followed by a stability between 2009 and 2017 as new platform creation matched old platform decommissioning. Post 2017 has seen an overall decrease in the number of platforms active in this region [38].

These trends are then reflected in the UK's production of O&G, with natural gas production peaking in 2000 at a value of 1,260,138 TWh and subsequently reaching the lowest level since 1973 in 2024 of 343,722 TWh [39]. Oil production also followed this trend, peaking in 1999 at a value of 137 million tonnes, while 2024 reached a record low of 31 million tonnes [40].

1.4.1 Oil usage in the UK

Transport is the largest demand sector for petroleum products in the United Kingdom, accounting for three quarters of total demand with over 70 % of this being used in road fuels. Following transport, the domestic and industry sector has the next largest demand, with the energy sector and non-energy splitting the remaining demand [40].

1.4.2 Natural gas usage in the UK

The United Kingdom consumed 63.5 billion cubic metres of natural gas in 2023 [41]. 65 % of the UK's natural gas is imported into the UK, with the major supplier of this being Norway [42], this is used in a range of applications including; industrial use, electricity generation and domestic use. 37 % of the UK's natural gas consumption is from the domestic sector [39], with 73.8 % of households in England and Wales using mains gas for either heating or cooking purposes [43]. The electricity sector has the second largest demand for natural gas but is decreasing rapidly, with 2024 being the lowest demand since 1992 [39].

1.4.3 Natural gas distribution in the UK

In the UK once natural gas has been refined, it can be transported across the country. Initially, this takes place through the use of National Gas' National Transmission System (NTS), a network of over 5,000 miles of high-pressure steel pipes and more than 500 above ground installations that allows the transport of natural gas across mainland UK to one of the 8 Gas Distribution Networks (GDNs). These are managed by 4 companies that then deal with the pre-meter distribution of natural gas to homes and businesses within each of their jurisdictions. Each GDN is responsible for supplying natural gas to millions of households and businesses using tens of thousands of kilometres of pipework before being handled by the post meter gas supplier companies. With such an extensive network taking natural gas from extraction in its raw form all the way to its eventual use by domestic or industrial customers, there are many stages at which CH_4 may be emitted into the atmosphere. One such emission of natural gas to the atmosphere is via fugitive emissions, where a fugitive emission may be classed as an unexpected or unwanted emission of gas from a pressurised network that is not detected by standard means [44]. This can include intentional operations such as flaring of natural gas (and the inherent slip of non-combusted CH_4) or it may refer to a more unintentional emission from pipelines, the latter is colloquially referred to as a "gas leak", although there is a certain stigma surrounding this term both from industrial operators and the public. Additionally, fugitive emissions from natural gas distribution may occur at other facilities, including compressor stations, off-take stations, gas governors, compressor stations, above ground installations and storage facilities. In the UK in 2023, the NAEI estimated 109.8 kt of CH_4 was emitted as fugitive emissions of natural gas from gas distribution alone [45].

1.5 Methane emissions legislation

Following the 2021 United Nations Climate Change Conference (COP26) there has been an increased scrutiny surrounding CH₄ and its role in the atmosphere. At COP26 the Global Methane Pledge (GMP) came into effect, the signatories of the pledge stated that they will reduce their 2020 CH₄ emissions by at least 30 % by 2030 [46]. This has led to the formation of initiatives such as the Oil & Gas Methane Partnership 2.0 (OGMP 2.0), the United Nations Environment Programme's (UNEP) oil and gas reporting programme. OGMP 2.0 requires operators to report emissions through measurement based methods, which has placed increased importance on research surrounding these methodologies in recent years.

1.6 Atmospheric emissions inventories

Throughout this thesis, atmospheric emissions inventories, such as the UK's National Atmospheric Emissions Inventory (NAEI) and the Global Fuel Exploitation Inventory v3 (GFEI) [21] are used to provide comparison between predicted emissions and those measured during sampling campaigns.

The NAEI is the UK's specific atmospheric inventory that encompasses a range of atmospheric pollutants, it reports emission estimates that are calculated by applying emission factors to an appropriate activity statistic [47]. A simplified equation is shown in *Equation 1.13*

$$\text{Emission} = \text{Emission Factor} \times \text{Activity Data} \quad (1.13)$$

An example of an emission factor would be the amount of NO_x emitted from a car per kilometre driven, while activity data would then encompass statistics on the average driving statistics of the UK car fleet. Data for the NAEI is provided from a range of governmental statistical sources,

regulators and industry reporting.

The GFEI however is a global gridded inventory for CH₄ at a $0.1^{\circ} \times 0.1^{\circ}$ resolution. Data is collected from country's national emission inventories that are reported to the United Nations Framework Convention on Climate Change (UNFCCC). These emissions are divided into activity related to either oil, natural or coal exploitation and are then spatially allocated based on geospatial data on the locations of facilities, along with infrastructure and population density per grid cell.

1.7 Scope of this thesis

The work in this thesis intends to explore the development of methodologies surrounding the detection and quantification of CH₄ emissions associated with natural gas. As previously mentioned, fugitive emissions of natural gas are a large contributor to the oil and gas industry's overall CH₄ emissions, but are often hard to monitor due to the unpredictable nature of where they occur. **Chapter 2** explores the development of a mobile sampling methodology designed to detect fugitive emissions from the domestic natural gas network. This work takes existing methodologies and investigates the limitations of the instruments used in order to adapt the parameters to detect smaller fugitive emissions. The resulting instrument specific algorithms were then deployed on multiple campaigns in two separate UK cities, detailed in **Chapter 3**, allowing for an overview and inter-comparison of each city's CH₄ emissions from natural gas. **Chapter 4** takes the prior work and applies it in New York city. This chapter discusses the adaptations required for a new mobile platform as well as the challenges of detecting natural gas in a mega-city with emissions greatly different to UK cities. Additionally, this section explores the effects of Manhattan's district steam heating on the frequency and magnitude of natural gas emissions by comparing

neighbourhoods supplied by this steam heat to those that aren't. Finally, **Chapter 5** explores a different aspect of emissions in the oil and gas sector, namely emissions from offshore oil and gas flaring in the North Sea. This chapter examines the effectiveness of existing flaring detection methodologies as flares become more efficient, in addition to proposing different detection methods that may provide more confidence in the detection of CH₄ from flaring.

Chapter 2

Development of a domestic natural gas detection algorithm

2.1 Introduction to natural gas detection algorithms and definition of terms

As mentioned in *Section 1.4.3*, the UK has an extensive natural gas supply network, with fugitive emissions possible at all parts of the supply chain. Fugitive emissions from GDNs are particularly difficult to measure, due to the scale of the operation as well as being surrounded by other potential CH₄ emissions due to their placement within cities, leading many previous studies to implement mobile sampling platforms. Mobile measurements of CH₄ via car or van allows for direct sampling of potential fugitive emissions within a city. However, due to the nature of on-road measurements there can be a varying factors that affect the measurements, including emissions from road traffic or other single day emission sources (particularly combustion sources), platform speed and varying meteorological conditions. Due to these factors there is a requirement for mobile sampling across multiple days to reduce their influence. Additionally, there is difficulty in converting measured CH₄

Chapter 2. Development of a domestic natural gas detection algorithm

concentrations associated with a natural gas fugitive emission into an emission rate. This is due to the unknown locations of the fugitive emissions, dispersion of the plume to the van, can be affected by distance, speed of platform in addition to wind speed and direction. In order to aid with this conversion of concentration to emission rate, controlled release experiments are often implemented in order to understand the relationship between known emission rates and measured concentrations aboard the sampling platform. There have been many different approaches to designing an algorithm to detect fugitive emissions of natural gas, all of which utilise detection of an enhancement in CH₄ concentrations, the major component of natural gas. These algorithms define an enhancement based on whether CH₄ mixing ratios are higher than a certain value [48], are above a certain percentile in measured readings [49, 50], or by using an outlier detection model [51]. The paper upon which the methodology in this thesis is based defines Observed Peaks (OPs) as CH₄ enhancements > 110 % of a 5-minute rolling background of the mean CH₄ concentrations (2.5 minutes before and after each measured point), and that they occur over less than 160 m (*von Fischer et al., 2017*) [52]. Enhancements occurring within 5 seconds of each other are then grouped together, meaning that if two enhancements occur within 5 seconds, they are considered part of the same OP. Surveys should be repeated at least 5 - 8 times over separate days in order to capture > 90 % of emissions [53]. OPs from all surveys that occur within 20 m of one another are then grouped into clusters. Clusters that contain OPs from at least 2 separate surveys are labelled as Leak Indications (LIs). The LIs are then quantified into emission rates, in L min⁻¹, using an equation derived from the results from a controlled release experiment (*Equation 2.1*).

Chapter 2. Development of a domestic natural gas detection algorithm

$$\text{Release rate (L min}^{-1}\text{)} = 0.1178 + (0.08267 \times M) - (0.005175 \times A) + (0.08626 \times K) \quad (2.1)$$

Where:

- M is the maximum CH_4 reading in ppm
- A is the peak area in ppm·meters
- K is the ratio of ppm·meters to maximum CH_4

This methodology was then further developed in (Weller *et al.*, 2019) [54], this changed the baseline such that it was the median CH_4 value over the 5 minute background, the spatial grouping of OPs to LIs changed from 20 m to 30 m and the quantification equation was also changed (**Equation 2.2**).

$$\ln(\text{excess CH}_4/\text{ppm}) = -0.988 + 0.817 \times \ln(\text{emission rate} / \text{L min}^{-1}) \quad (2.2)$$

Where the excess CH_4 is a mean of all CH_4 enhancements from each OP within an LI cluster. Although many subsequent studies apply the Weller *et al.*, 2019 [54] equation to their own surveys, there is concern about applying this without some acknowledgement of the potential inaccuracies. The Weller *et al.*, 2019 [54] equation was designed from the results of a controlled release experiment and quantifies based on the peak height of CH_4 measured by a specific instrument. Firstly, applying this equation to a different platform will lead to errors due to different manifold lengths and flow rates through the manifold of platforms that can contribute to changes in the measured peak shape of a CH_4 enhancement, a slower flow rate through a longer manifold may lead to a shorter but wider CH_4 peak which would result in a lower calculated emission rate than if sampled with the original platform. Secondly, the

Chapter 2. Development of a domestic natural gas detection algorithm

instrument used to measure CH_4 concentrations can affect the quantification, different instruments may have differing measurement frequency, flow rate, sample cell volume and sample cell flush rates, all of which again can influence the shape of a peak which will result in errors when quantifying based on a peak height equation designed for a specific instrument. Therefore, if the Weller et al., 2019 [54] equation is applied to different platforms or on different instruments, there must be acknowledgement of the potential errors that will arise from doing so.

In (Maazallahi et al., 2020) [55], it was proposed that the existing methodology categorised certain burning emissions as fugitive emissions, to counter this an additional stage using CO_2 ratios with CH_4 was introduced to filter burning emissions out of the analysis. Source attribution was also used in (Fernandez et al., 2022) [56], using isotopic measurements of CH_4 in addition to C_2H_6 : CH_4 ratios. Variations of this algorithm has been used in many major cities across the US and Canada [57, 58] as well as European cities [56, 59–61].

2.2 Methodology

For the UK natural gas mobile sampling surveys, all campaigns used the WACL Air Sampling Platform (WASP), detailed fully in (Wagner et al., 2021) [62]. The WASP is a Nissan NV400SE L3H2, a van with interior dimensions of length 3450 mm, width 1650 mm and height of 1750 mm. The walls and floor of the van are overlaid with 50 mm of insulation and an air-conditioning system was fitted in the rear of the van and controlled from the drivers cab. Instruments are mounted on aircraft-style L-tracks built into the floor and ceiling. Power is supplied from two 12 VDC 230Ah batteries that are charged while driving by a 240 VAC inverter, it is also charged when stationary by an external main power point. The battery can run core instruments for a full day of driving, but with more energy

Chapter 2. Development of a domestic natural gas detection algorithm

intensive instruments, such as a SIFT-MS there is a total battery life of 2 hours. Air is sampled through a front facing inlet 2.25 m above the ground, made from 6 m length of PTFE (Teflon) tubing with a diameter of 12.5 mm. Air is drawn through the manifold with a pump located in the rear of the WASP with a flow rate of 40 SLPM. Location is monitored with a Quark-Elec QK-AS07-0183 GPS and heading sensor, wind speed and direction were recorded with a Gill 2D ultrasonic wind sensor. An overview of the core suite of instruments in the WASP is shown in **Figure 2.1**.

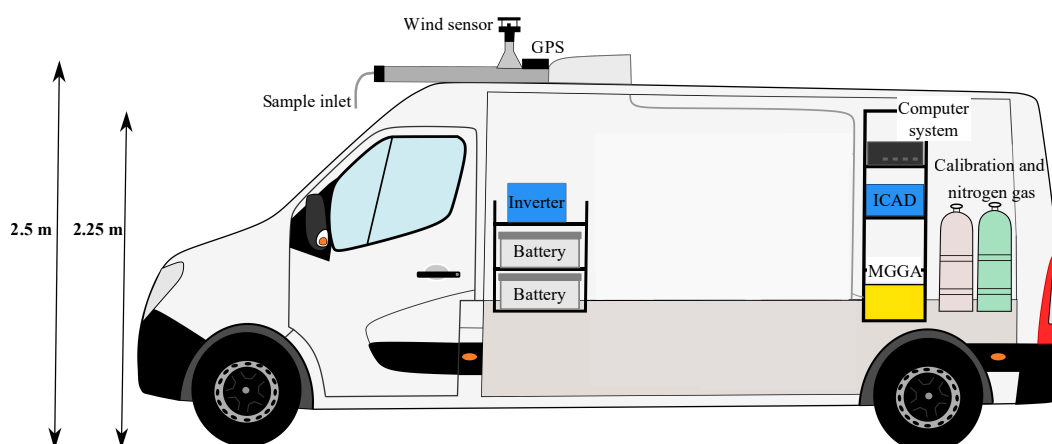


Figure 2.1: Diagram of the WASP and its core instrumentation based on (Wagner *et al.*, 2021) [62].

For measurements of CH_4 and CO_2 , the WASP implemented a Los Gatos Microportable Greenhouse Gas Analyser (MGGA). The MGGA uses laser absorption spectroscopy, specifically off-axis integrated cavity output spectroscopy, where the optical absorption of the species is measured when irradiated with a light beam. As described previously, several methodologies use measurements of secondary compounds to confirm the source of CH_4 [55, 56]. The WASP was used in two separate campaigns, detailed in **Table 2.1**, where natural gas emissions were detected and each campaign used a different instrument for this source identification stage.

Chapter 2. Development of a domestic natural gas detection algorithm

Campaign	Dates	Instrumentation
INGENIOUS Bradford	February & June 2023	MGGA, ICAD, SIFT-MS
INGENIOUS York	February & September 2023	MGGA, ICAD, SIFT-MS
York 2024 Campaign	May & June 2024	MGGA, ICAD, TILDAS

Table 2.1: Mobile sampling campaigns where the WASP was deployed for natural gas detection.

The first two campaigns were a collaboration with the INGENIOUS (UnderstandING the sourcEs, traNsformations and fates of IndOor air pollUtantS) campaign [63] and used a selected-ion flow-tube mass spectrometer (SIFT-MS, Voice200 Ultra, Syft Technologies). The SIFT-MS has a multi-port sample inlet that switches between sample, zero and calibrant gases in addition to fast reagent ion switching between H_3O^+ , NO^+ and O_2^+ , which are generated with a microwave plasma ion source. The reagent ions are then able to selectively ionise target analytes and the resultant product ions flow through a quadrupole mass filter and secondary electron multiplier detector, where ions are separated by mass to charge ratios and the ion counts are measured. For the INGENIOUS campaigns, there was a 100 ms dwell time, scanning 72 masses, resulting in a total measurement time of 7.2 s per cycle. Two of the species the SIFT-MS was measuring during the INGENIOUS campaigns that were of interest to natural gas detection, were C_3H_8 and C_4H_{10} .

The final campaign, the York 2024 campaign, was devoted to solely detecting natural gas emissions and used an Aerodyne Tuneable Infrared Laser Direct Absorption Spectrometer (TILDAS) measuring C_2H_6 . The principle of TILDAS measurements is based on infrared absorption spectroscopy; sample air is pumped into the TILDAS cell into which a laser beam is directed, the laser makes multiple passes across the cell before exiting onto a photodetector. Laser frequency is then tuned across a C_2H_6 absorption line and the depths of which are used to determine C_2H_6 mole

Chapter 2. Development of a domestic natural gas detection algorithm

fraction. Additionally, the WASP was equipped with an Iterative CAVity enhanced Differential optical absorption spectrometer (ICAD), developed by Airyx, for measurements of NO_x ($\text{NO}_2 + \text{NO}$). The instrument provides direct measurements of NO_2 , measured in the spectral range between 430 and 465 nm. NO is transformed to NO_2 using an internal converter based on gas phase titration with a NO_x -free O_3 source, allowing for a measurement of total NO_x . An overview of all instruments used within the WASP across all campaigns and the species measured are shown in **Table 2.2**.

Instrument	Measurement Technique	Measured Species	Precision
MGGA	Off-axis integrated cavity output spectroscopy	CH_4 , CO_2	CH_4 (1 Hz, 1 σ): 0.9 ppb; CO_2 (1 Hz, 1 σ): 0.35 ppm
ICAD	Iterative cavity enhanced differential absorption spectroscopy	NO_x ($\text{NO} + \text{NO}_2$)	(1 σ at 30 s): 0.15 ppb
SIFT-MS	Selected-ion flow-tube mass spectrometer	C_3H_8 , C_4H_{10}	$\pm 35\%$ of measurement for uncalibrated species
TILDAS	Infrared absorption spectroscopy	C_2H_6	Mounted to a mobile platform (1 σ at 1 s): 210 ppt [64]

Table 2.2: Instrumentation used within the WASP on all natural gas sampling campaigns.

Calibration of the SIFT-MS was performed for 12 VOCs and alkanes on the days sampling using multipoint standards covering the expected concentration range and is explained in further detail in *Budisulistiorini et al., 2026* [65]. TILDAS calibration took place during sampling campaigns using a 3-point calibration described in further detail in **Section 2.3.3**. Both the ICAD and MGGA were calibrated using a similar 3-point calibration of a low concentration, target concentration and high concentration, these calibrations were conducted by FAAM before the deployment of the instruments.

2.3 Algorithm Development

2.3.1 CH_4 enhancement parameter

Previous algorithms define an enhancement as being higher than 1.1 times than a 5 minute rolling median background. This work seeks to

Chapter 2. Development of a domestic natural gas detection algorithm

understand if this parameter holds true for the specific instrumentation used in the mobile surveys. To understand what this parameter may be, a variance experiment was undertaken. For 2 hours compressed air flowed through the Los Gatos MGGA, measured at a median CH_4 value of 7.2 ppm, the standard deviation of these results was found to be 0.006 ppm. An enhancement criteria was proposed as 5 times this standard deviation divided by the median baseline, resulting in an enhancement criteria of 1.002 times the baseline. The results of this in-situ variance experiment can be found in *Figure 2.2*.

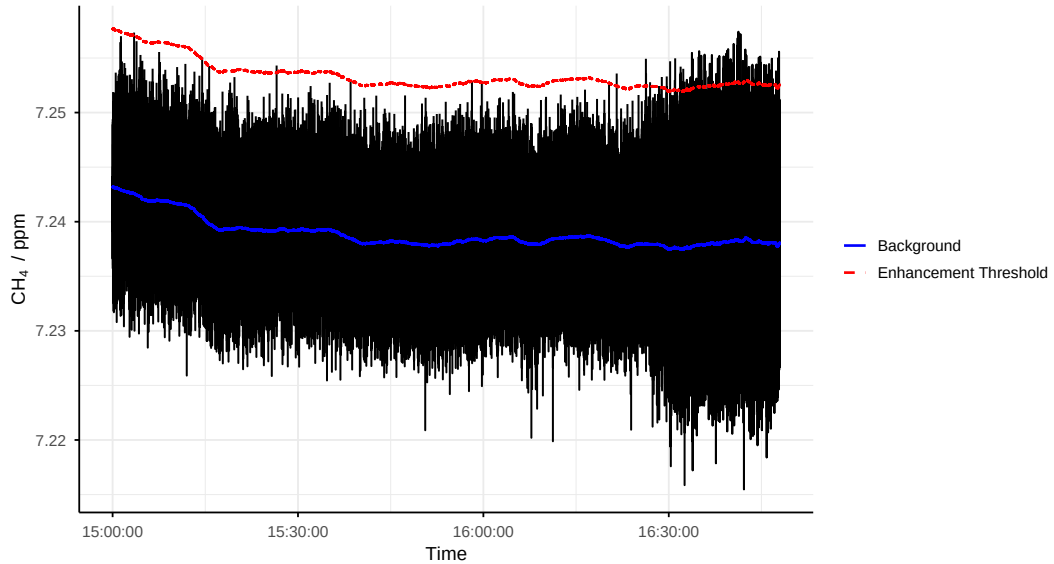


Figure 2.2: Measurements made of CH_4 during an in-lab variance experiment, a calculated background and enhancement threshold are also included.

As can be seen in *Figure 2.2*, this enhancement parameter would still categorise some noise within the MGGA as a CH_4 enhancement and so is therefore too low to be used within the mobile surveys. Additionally, this approach assumes a stable baseline that is replicated in the field. In reality, when applying this enhancement criteria it leads to the detection of enhancements that are too small to be reliably quantified. Instead, the CH_4

Chapter 2. Development of a domestic natural gas detection algorithm

mixing ratios measured during each mobile survey, were collated and the standard deviation was calculated for each mobile survey. Again enhancement criteria was calculated as anything larger than 5 times the standard deviation divided by the median of CH₄ mixing ratios, this was done for each mobile survey and resulted in a median enhancement criteria of 1.01 times the baseline. This would result in detection of enhancements that would be very small, diffuse, or from enhancements that occurred far from the roads and therefore harder to quantify as true natural gas emissions, and so a larger enhancement criteria of 1.05 times the background was selected. The application of this updated enhancement threshold is shown in **Figure 2.3**. This ensured there was still a large difference from the original methodologies criteria, while still remaining within the instrumentation's known variation.

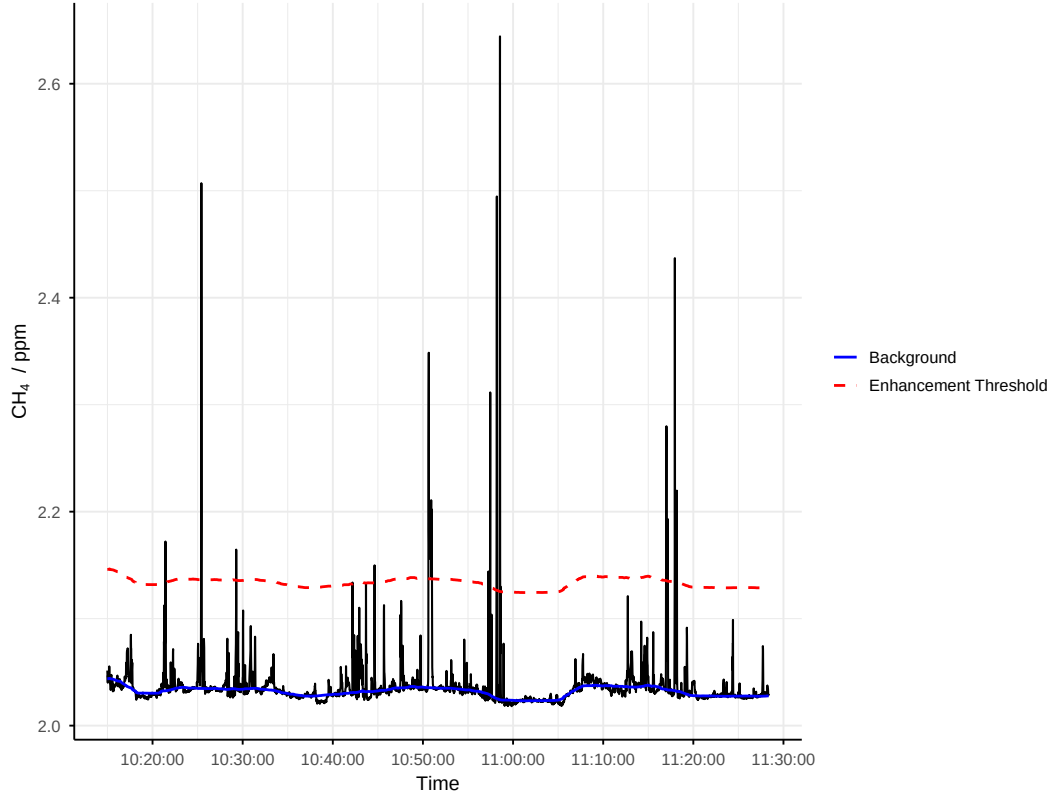


Figure 2.3: The updated enhancement threshold applied to a 2024 mobile survey using the WASP.

2.3.2 SIFT-MS

As previously stated, during INGENIOUS mobile survey campaigns, a SIFT-MS was deployed for use in source identification stages. This was done by measuring other VOCs present within the UK's natural gas mixture and ensuring the ratios were within the range of what was known for the UK's natural gas composition [66]. A simplified overview of the percentages of major components in the UK's natural gas mixture are shown in *Table 2.3*.

Chapter 2. Development of a domestic natural gas detection algorithm

	CH ₄ / %	N ₂ / %	C ₂ H ₆ / %	CO ₂ / %	C ₃ H ₈ / %	C ₄ H ₁₀ / %
Mean	92.42	3.67	3.02	0.78	0.59	0.14
Minimum	90.84	2.44	2.93	0.32	0.53	0.11
Maximum	94.42	4.84	3.14	1.35	0.67	0.16

Table 2.3: Mean, minimum and maximum percentages of CH₄, N₂, C₂H₆, CO₂, C₃H₈ and C₄H₁₀ in the UK's natural gas mixture, (*Bains et al., 2016*) [66].

Data from *Bains et al., 2016*[66] features the analysis of 119 samples of natural gas collected across 2 days. Although composition may vary over time and location depending on supply, this dataset provides one of the few insights into the UK's natural gas mixture and is therefore used to inform compound ratios to aid with natural gas identification with a SIFT-MS. During sampling campaigns with the SIFT-MS, the two VOCs of interest to natural gas were C₃H₈ and C₄H₁₀. This resulted in three separate ratios that could be used to confirm the presence of natural gas; CH₄ : C₃H₈ (138.58 to 178.15), CH₄ : C₄H₁₀ (567.75 to 858.36) or C₃H₈ : C₄H₁₀ (3.31 to 6.09). As stated previously, the SIFT-MS operates on a total scan time of 7.2 s per cycle, with each ion dwelled on for 100 ms, this results in C₃H₈ and C₄H₁₀ being measured, 5.40 and 5.58 s into the scans respectively. In order to avoid data gaps in the SIFT-MS, C₃H₈ and C₄H₁₀ measurements were converted to 1 Hz, where the measured C₃H₈ and C₄H₁₀ concentrations were repeated over the total cycle time. Because of this, the time lag between the measured CH₄ and C₃H₈ or C₄H₁₀ was inconsistent. Therefore, it was deemed that only C₃H₈ : C₄H₁₀ ratios were able to be used in the source identification stage. An example of how a time series of CH₄, C₃H₈ and C₄H₁₀ concentrations appear within a CH₄ enhancement, is shown in *Figure 2.4*.

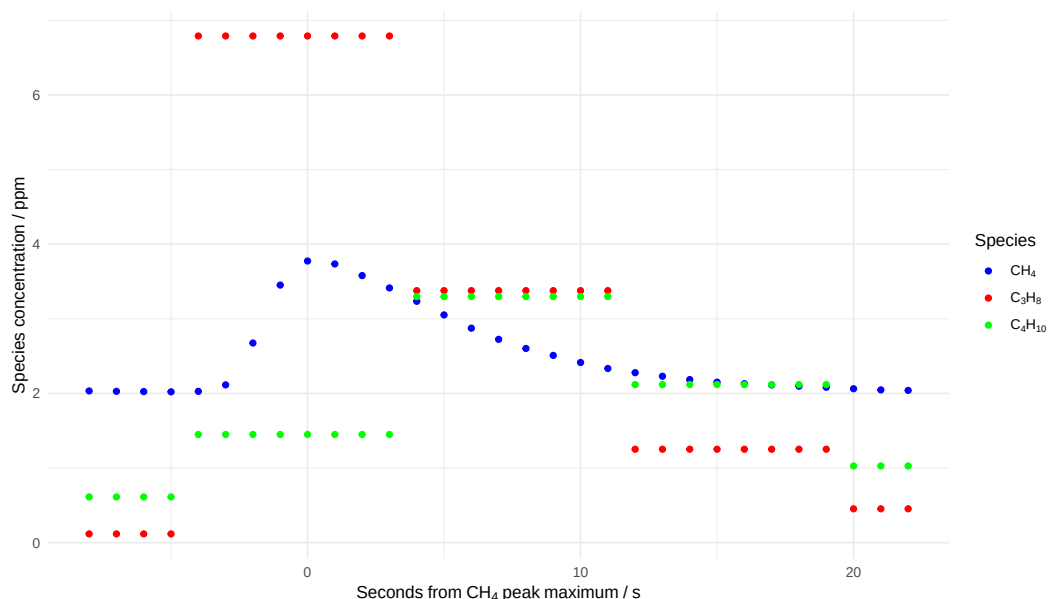


Figure 2.4: A CH₄ enhancement measured via the MGGA on a mobile survey with the associated SIFT-MS measurements of C₃H₈ and C₄H₁₀.

2.3.3 TILDAS

During the 2024 gas leak detection campaign, the SIFT-MS was replaced with a TILDAS. This change was implemented in order to correct the issues with sampling time found with using the SIFT-MS. As opposed to the measurement of C₃H₈ and C₄H₁₀, the TILDAS measures C₂H₆, allowing for C₂H₆ : CH₄ ratios to be used for source identification. The TILDAS is capable of data acquisition at 10 Hz, however, for this to be a true representation of 10 Hz data, it requires the measurement cell to be flushed at a 10 Hz rate as well. The measurement cell has a volume of 0.5 L, therefore requiring a flow rate of 300 LPM. The measurement cell is required to be held at a constant pressure of 70 Torr (93 mbar), with atmospheric pressure being close to 1,000 mbar, this would require a flow rate of roughly 30 SLPM to achieve the 10 Hz flush rate, this meant adapting the TILDAS' inlet to handle a greater flow of air. The initial configuration of the TILDAS inlet was a filter, followed by two valves in

Chapter 2. Development of a domestic natural gas detection algorithm

series, a stainless steel integral bonnet needle valve, 0.37 Cv, 1/4 in. #SS-1RS4 and an electronic upstream flow control valve, 10,000 sccm, 0.25 in. tube, viton seal #0248A-10000SV which allows small changes to maintain the internal pressure at 70 Torr. This initial configuration could achieve a flow rate of 11.1 SLPM, less than half of the target flow rate. It was determined that the pin valve was restricting the flow before the solenoid, the next configuration removed the pin valve to only have the solenoid between the filter and instrument inlet. This second configuration achieved a flow rate 17.15 SLPM, but the cell could not stabilise at 70 Torr. A third configuration was tested where the pin valve was in parallel to the solenoid, this configuration achieved a 16 SLPM flush rate but importantly kept the cell at a constant 70 Torr. The limiting factor was now determined to be the pump itself and so although the TILDAS could acquire data at a 10 Hz rate, the actual flush rate of the instrument was expected to be closer to 5 Hz. **Figure 2.5** shows a simplified overview of each of the three tested TILDAS configurations, with configuration 3 being the configuration used in future measurements.

Chapter 2. Development of a domestic natural gas detection algorithm

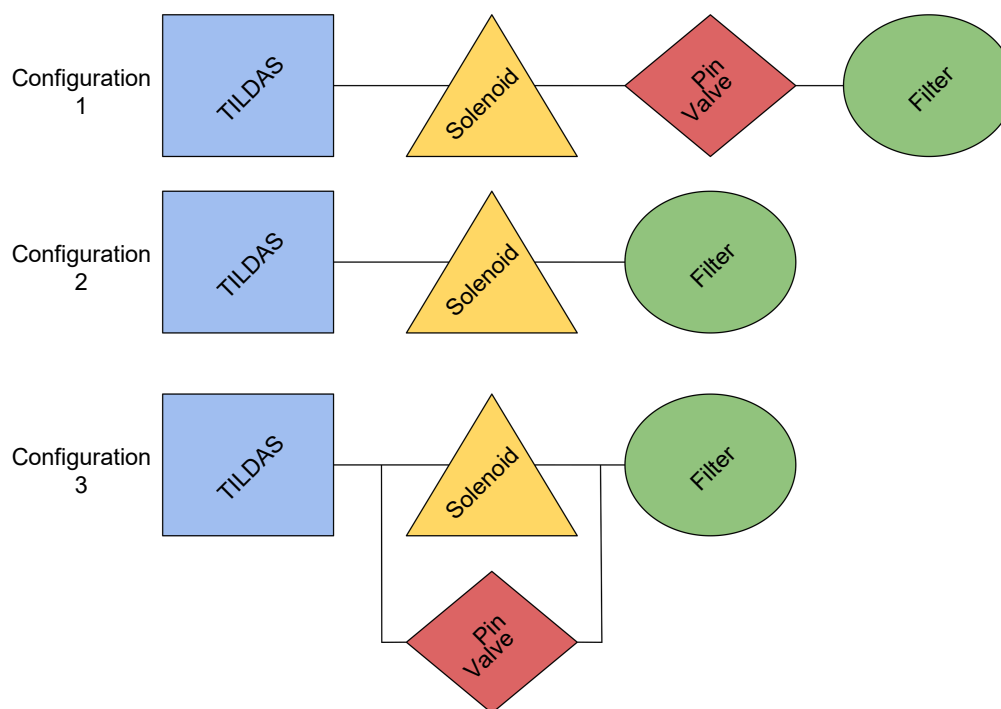


Figure 2.5: Simplified diagram of the three TILDAS valve configurations.

Calibration of the TILDAS took place using a 3-step calibration. This utilised a high concentration of C_2H_6 (~20 ppb), a low concentration of C_2H_6 (~2.5 ppb) and a zero of nitrogen. Calibration gases had their concentrations confirmed via gas chromatography. Once installed in the WASP, it was noticed that during calibrations of the TILDAS, when measurements of the low concentration standard were made, the TILDAS reported higher concentrations, conversely when measurements were made of the high concentration standard, the TILDAS reported lower concentrations. This meant that during calibrations of the TILDAS the range of concentrations reported were lower than the range of concentrations of the standards used, creating a "squashing" effect. This was able to be corrected with the calibrations, but with a requirement for more frequent calibrations. For mobile sampling, this meant a calibration was conducted before and after every drive and an average was taken

Chapter 2. Development of a domestic natural gas detection algorithm

between the two calculated calibration equations. The 3-step calibration was performed before and after each mobile survey and a linear regression of instrument response vs known calibration concentration allowed a calibration equation to be calculated for C_2H_6 measurements made during that mobile survey. **Figure 2.6** shows an example calibration of one mobile survey and the resulting calibration equation. Additionally, as can be seen in **Figure 2.6**, there is a noticeable drift between calibrations, with that particular calibration set reporting lower instrument response for all standards after the mobile survey as opposed to the calibration that was run before the survey. This effect however, was not consistent, with the lower response alternating between the post and pre drive calibrations. As calibrations during the drives would require disruption to the survey, this highlights the need to calibrate pre and post survey with the mean reflecting the instrumental drift during the survey.

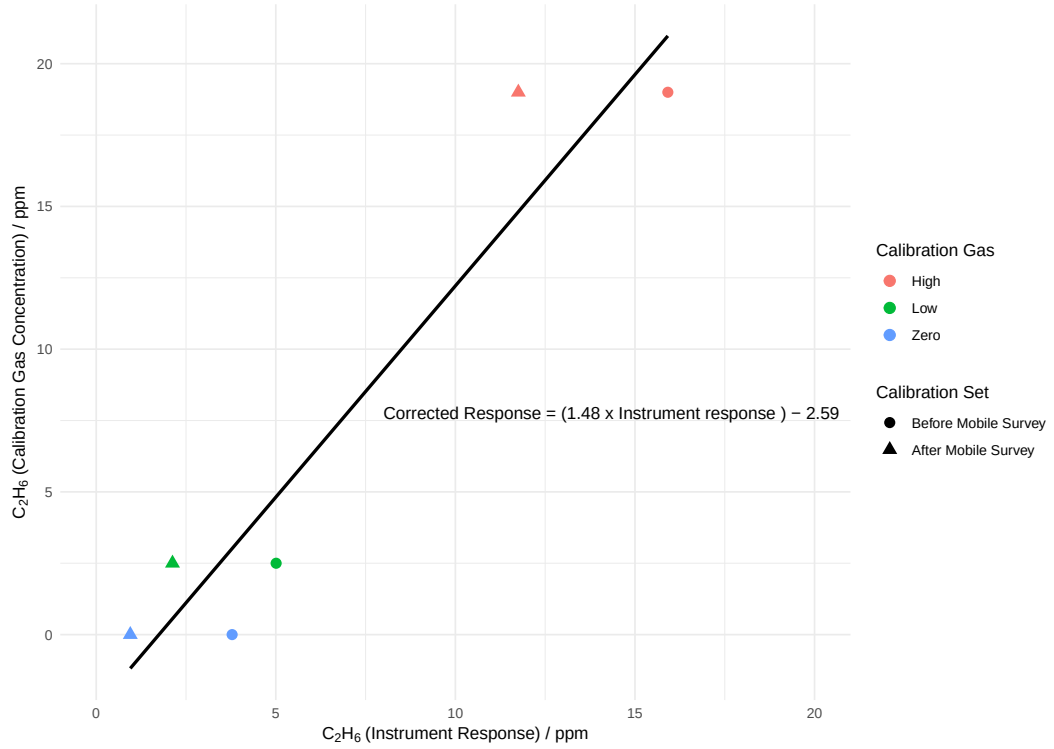


Figure 2.6: C₂H₆ calibration plot from a mobile survey with the associated calibration equation.

2.3.4 Time clustering parameters

The time clustering parameter of the natural gas detection algorithm is used as a means of determining the minimum time over which one CH₄ enhancement could be distinguished from another. For example, in (*von Fischer et al., 2017; Weller et al., 2019*) [52, 54], the time clustering parameter was set at 5 seconds, meaning enhancements that occur within 5 seconds of each other could not be reliably separated and therefore must be considered as part of the same enhancement. The time clustering parameter is therefore based on the flush rate of the instruments, a faster flush rate would mean that the time clustering parameter could be lowered therefore allowing enhancements that occur closer temporally to be separated. For these previous methodologies, the time clustering only

Chapter 2. Development of a domestic natural gas detection algorithm

takes into account the instrument measuring CH_4 . For the WASP based studies with the SIFT-MS and the TILDAS, measurements of secondary pollutants were used in source identification, they become a core stage of the detection algorithm and therefore they too must also be considered in the time clustering parameter. Response time of the MGGGA is reported as < 0.5 s from the manufacturer's specification [67]. For the SIFT-MS a response time would have to be associated with the length of the sampling cycle, therefore cannot be lower than 7.2 s. For the TILDAS, after being adapted to the configuration that resulted in the fastest flow rate, it was thought that the TILDAS had the ability to achieve a response rate close to 5 Hz. An experiment was undertaken to find a more accurate response rate of the TILDAS. A high concentration of C_2H_6 (17.630 ± 0.715 ppb, measured via GC-MS) was flowed through the TILDAS and switched to ambient air 10 times on 2 separate valve setups for a total of 20 repeats of low-high-low transitions in the concentration of C_2H_6 , an example of a high to low transition is shown in **Figure 2.7**. The transition times were located by eye and then the time taken to go from 90 % of the maximum value to 10 % of the maximum value was calculated (T_{90-10}). The transition time on the first valve ranged from 0.7 – 1.1 s with a mean value of 0.9 s, the second valve having responses ranging from 0.7 – 1.4 s also with a mean response of 0.9 s. Giving confidence in a sub 1 s response rate from the TILDAS. The data was still averaged to 1 s with a 1 s clustering time due to the data now being limited by the data acquisition rate of the WASP's GPS.

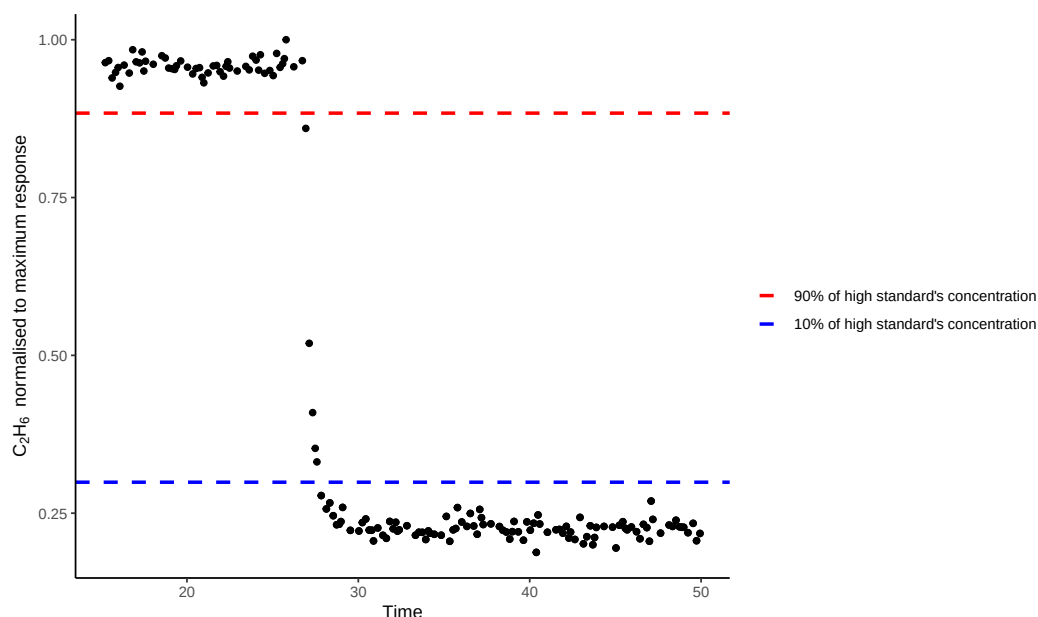


Figure 2.7: Example response transition of TILDAS from high concentration to ambient, annotated are the 90 % and 10 % transition values of the high standards concentration.

This therefore results in two separate time clustering parameters, for the campaigns using a SIFT-MS the time clustering parameter must be set at the cycle time of the SIFT-MS, 7.2 s, however due to using 1 Hz data, this must be set at 8 s, in order to include the complete cycle time. For the work using a TILDAS there is high confidence that the time clustering parameter can be set to 1 s. In terms of spatial separation that this allows for, if an average speed of the platform during a sampling survey is 20 miles hour⁻¹, the original time clustering parameter of 5 s requires enhancements to occur 44.7 m apart in order for them to be separated. At 1 second clustering this reduces to 8.9 m. But, for the 8 s clustering this would be 71.5 m. As fugitive emission identification requires high spatial resolution, this shows how limiting the SIFT-MS is for this methodology. However, the improvement to 1 s time clustering in the TILDAS campaign has a large effect on the spatial resolution of sampling campaigns using this

instrument.

2.3.5 Source identification

For measurement campaigns using the SIFT-MS, ratios using C_3H_8 and C_4H_{10} were used to confirm the presence of natural gas. As previously mentioned, $C_3H_8 : C_4H_{10}$ could be considered thermogenic if between 3.31 and 6.09. With the sampling time of the SIFT-MS being 7.2 s and with C_3H_8 and C_4H_{10} analysis occurring late into this cycle, it was deemed necessary to include the cycle previous and the cycle following in order to have the highest probability of capturing the same packet of air the CH_4 emission originates from. This requires setting a 16 second window surrounding the time of the maximum CH_4 and using the maximum $C_3H_8 : C_4H_{10}$ ratio to assign the source type. This creates a large distance over which the $C_3H_8 : C_4H_{10}$ ratio is measured (143 m, assuming a 20 miles hour⁻¹ average speed), with also no guarantee that the $C_3H_8 : C_4H_{10}$ ratio reported is from the same packet of air as the CH_4 enhancement. The unreliability of this method is expanded on in *Chapter 3*.

Source determination using $C_2H_6 : CH_4$ ratios has been shown to be effective, due to C_2H_6 being present in measurable quantities in thermogenic gas but not biogenic gas [56], $C_2H_6 : CH_4$ ratios can be used in order to determine the source of a CH_4 emission. Demonstrated in (Fernandez et al., 2022; Defratyka et al., 2021; Lowry et al., 2020; Yacovitch et al., 2014) [56, 59, 64, 68], $C_2H_6 : CH_4 < 0.005$ is associated with biogenic sources, > 0.005 to < 0.09 are thermogenic and > 0.1 are considered pyrogenic or combustion. Where thermogenic relates to a fugitive natural gas emission, biogenic, an emission from a natural source and pyrogenic a combustion source. *Figure 2.8* shows examples on how each of the three source types are assigned based on $C_2H_6 : CH_4$ ratios. To complete this, time alignment of CH_4 and C_2H_6 values needs to be undertaken due to

them being measured on separate instruments, the criterion for aligning these times is based on the results from **Section 2.3.6**. Additionally enhancements are removed where the R^2 of $\text{CO}_2 : \text{CH}_4$ is greater than 0.9 to ensure no combustion sources are wrongly assigned as thermogenic.

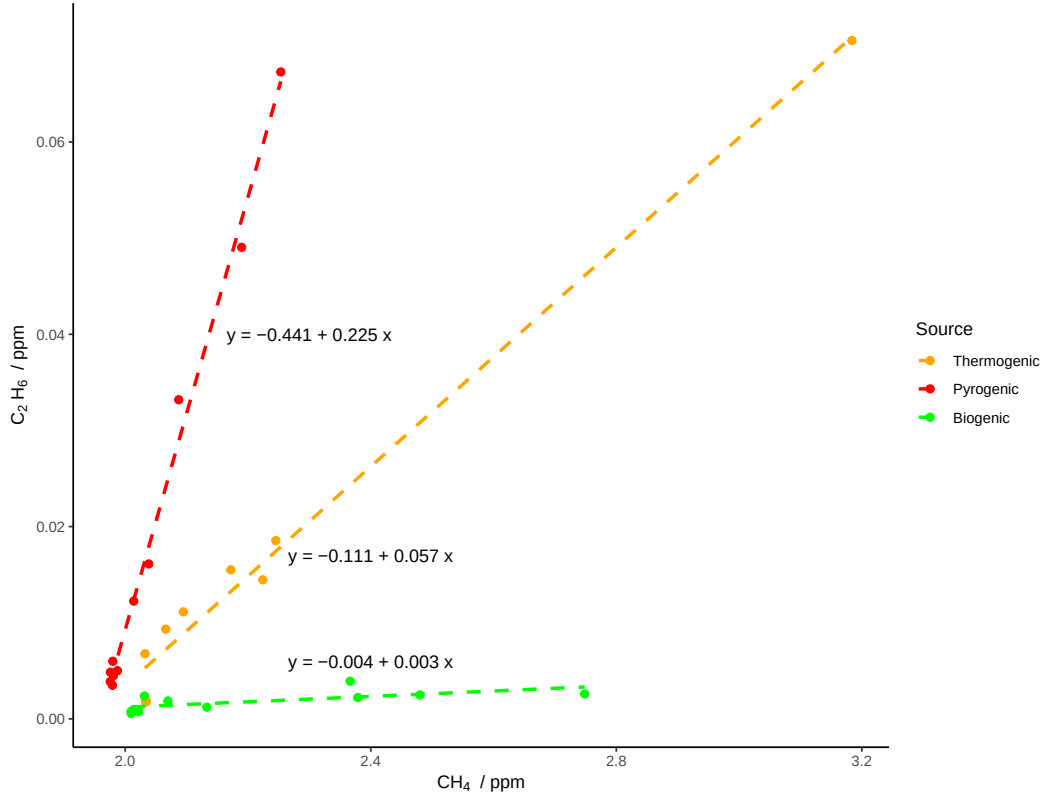


Figure 2.8: Relationship between CH_4 and C_2H_6 for three OPs of different source types located during the sampling campaign. Equations are derived using a linear regression model of C_2H_6 to CH_4 measurements across a 10 s window centred on the plume maximum.

2.3.6 Controlled release experiment

To attain a quantification equation specific to the equipment used at York, a controlled release experiment was conducted at the Bedford Aerodrome. The controlled release took place over the course of 5 days and included 41 releases lasting an average of 30 minutes each. Releases consisted of

Chapter 2. Development of a domestic natural gas detection algorithm

varying amounts of CH_4 ($0.2 - 70.48 \text{ L min}^{-1}$), C_2H_6 ($0 - 7.01 \text{ L min}^{-1}$) and NH_3 ($0 - 7.87 \text{ L min}^{-1}$) to reflect a range of CH_4 sources, including natural gas and farm emissions. Releases occurred at various heights from ground level to 3 m above ground. During each release, the van made multiple passes at various distances from the release point. However, as the data from the controlled release was intended to be used in quantifying sub-road and near-road fugitive emissions of natural gas, a maximum distance of 30 m from the controlled release point was applied due to this reflecting the maximum road widths typically found within a city like York [69]. Of the 41 releases conducted in the controlled release, only 26 releases were able to be used for processing data, as some releases did not have detectable enhancements. Within these 26 releases, 3525 CH_4 enhancements were detected over distances between 5.8 m and 382.1 m from the release point. When this was filtered to include enhancements from only 30 m from the release point this resulted in including 1226 enhancements from 23 drives. Density plots of the number of detected enhancements against distance from source are shown in **Figure 2.9** for all detected enhancements and **Figure 2.10** for enhancements detected within 30 m from the source.

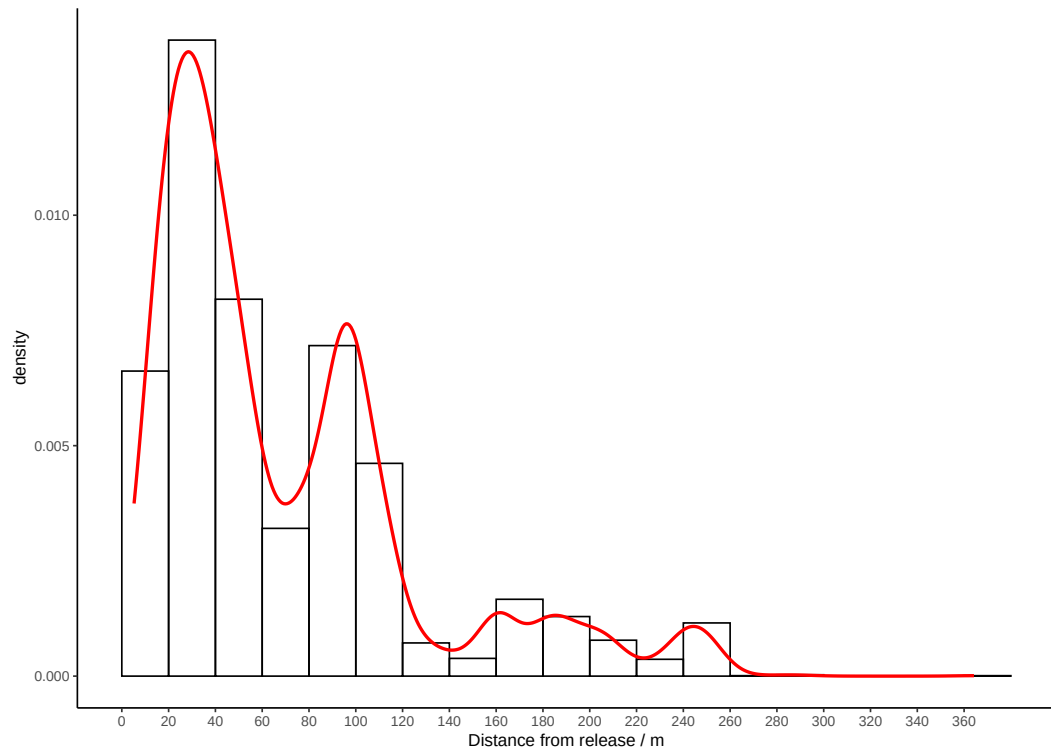


Figure 2.9: Density plot of number of detected enhancements against distance from release point

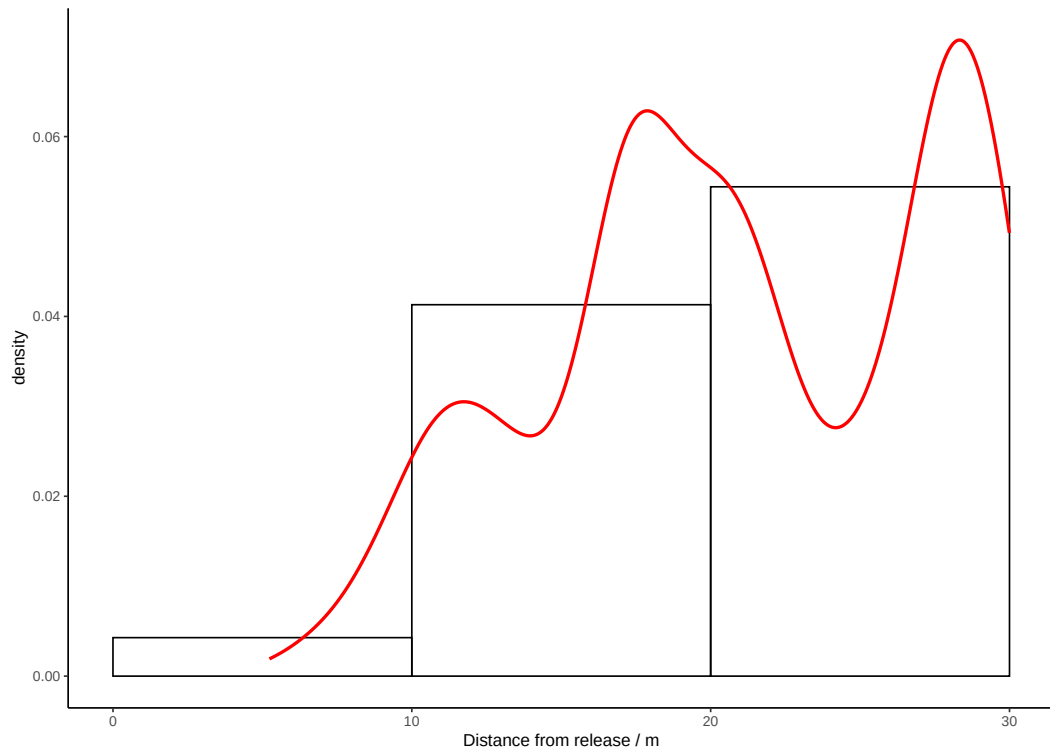


Figure 2.10: Density plot of number of detected enhancements against distance from release point (Limited to 0 – 30 m)

2.3.6.1 Quantification equation

A quantification equation to calculate emission rate from CH_4 measurements could be calculated using enhancements that were detected within 30 m of the controlled release emission point, to better reflect the enhancements likely to be detected from under-road natural gas emissions. By first using the CH_4 detection algorithm a linear regression model could then be used to find a relationship between the release rate and the maximum enhancement. 1226 enhancements were detected from 23 separate releases that were within 30 m of the emission point. These enhancements were determined from CH_4 releases ranging from 0.49 to 70.48 L min^{-1} . A linear regression was then performed using *Equation 2.3*:

$$\ln(\text{max excess CH}_4 / \text{ppm}) = b_0 + b_1 \times \ln(\text{emission rate} / \text{L min}^{-1}) + \epsilon, \epsilon \sim^{iid} N(0, \sigma^2) \quad (2.3)$$

Figure 2.11 shows the plot of this linear regression.

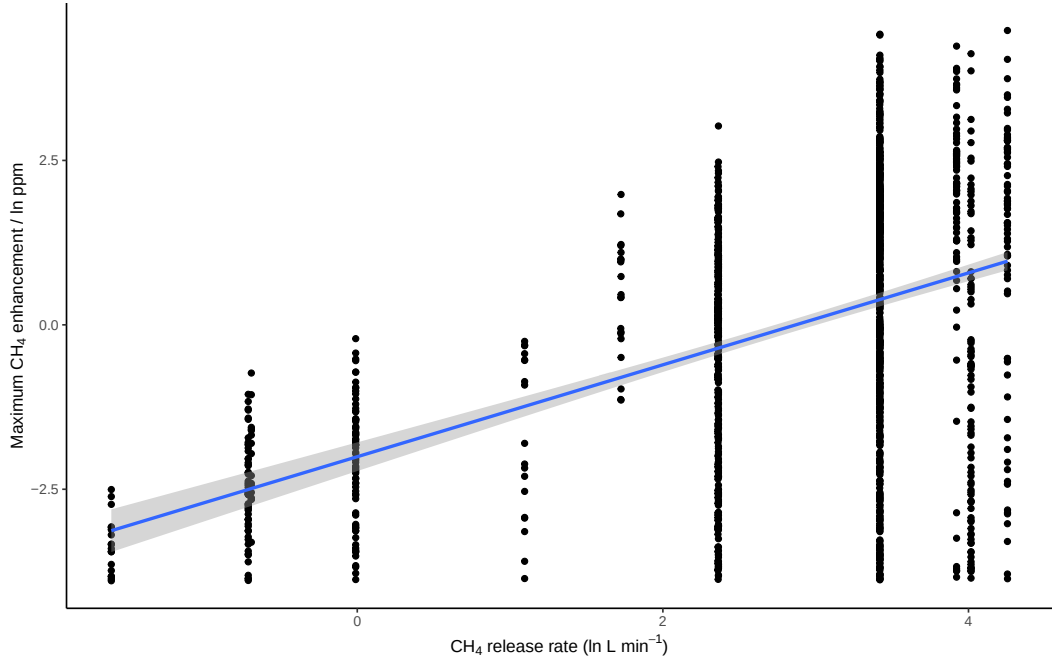


Figure 2.11: Plot of the $\ln$ of the maximum detected CH_4 enhancement against the $\ln$ of the known CH_4 release rate.

This resulted in the quantification equation shown in *Equation 2.4*

$$\ln(\text{max excess CH}_4 / \text{ppm}) = -1.2668 + 0.6323 \times \ln(\text{emission rate} / \text{L min}^{-1}) \quad (2.4)$$

It is important to note that as the instrument setup used during INGENIOUS campaigns was not used within the controlled release experiment. Due to altering the instrumental setup as well as the position of instruments themselves along the sampling manifold, it was deemed that the resulting quantification equation would not accurately reflect

measurements made by this iteration of the platform and therefore would be less reliable during these campaigns. Instead, the quantification equation used in (Weller *et al.*, 2019) [54] was used, due to this having been used in a greater number of prior published studies. Therefore this new quantification methodology was only used in the York 2024 campaign.

2.3.6.2 TILDAS lag time

For each of the releases, the lag time between detecting a C_2H_6 enhancement and a CH_4 enhancement was calculated. As a packet of air sampled by the WASP will take a different amount of time to flow through the manifold to each instrument, it was deemed necessary to calculate the lag time between the instruments. To find the lag time of the instruments, the maximum CH_4 enhancement for each pass was found, following this the maximum C_2H_6 enhancement was found (that occurred within 5 seconds of the CH_4 maximum). The 5 second window was selected as on transects of the controlled release the van travelled at roughly 20 miles $hour^{-1}$. Over the course of 10 s (5 s either side of the CH_4 maximum) this would mean 85 m covered in the van, the average length of a transect being 180 m. The time lag between C_2H_6 and CH_4 showed that in most cases (88.1 %), maximum C_2H_6 concentration preceded maximum CH_4 concentration with a mean lag of 2.7 s before and a median of 3.8 s before. Observing a window of time of maximum CH_4 to 5 s before maximum CH_4 resulted in a mean lag of 3.3 s from C_2H_6 to CH_4 and a median lag of 3.9 s. This helped inform the detection algorithm to look for maximum C_2H_6 within a window only up to 5s before the maximum CH_4 . Density plots showing the time lag of maximum C_2H_6 from maximum CH_4 are shown in *Figure 2.12* for the full 10 second time window and *Figure 2.13* for up to 5 seconds before the time of maximum measured CH_4 .

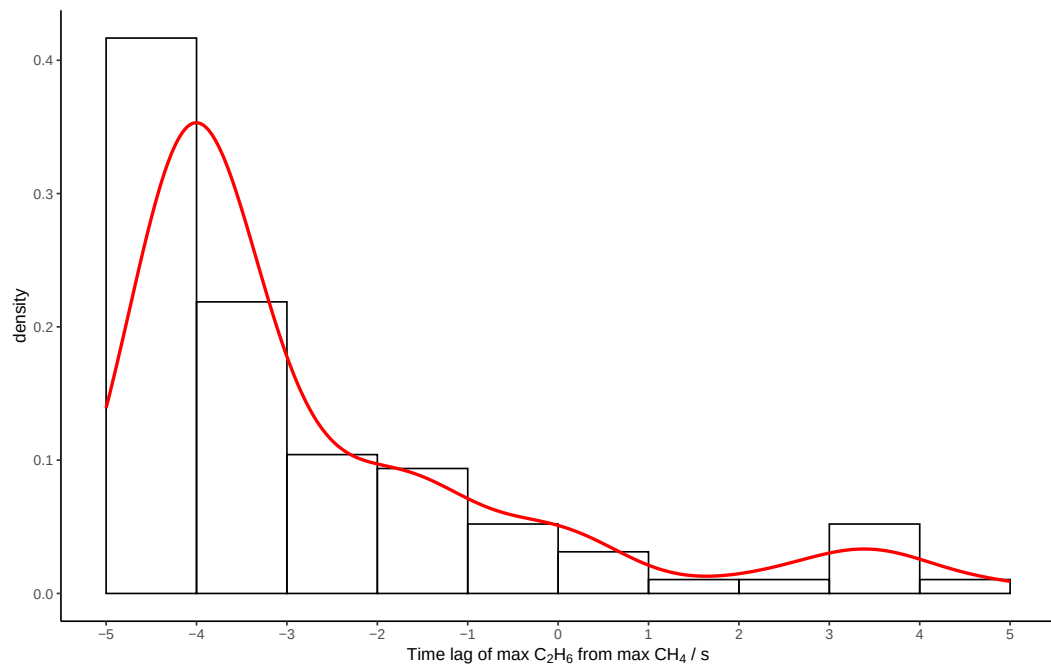


Figure 2.12: Density plot of time lag of the maximum C₂H₆ measurement from the maximum CH₄ measurement.

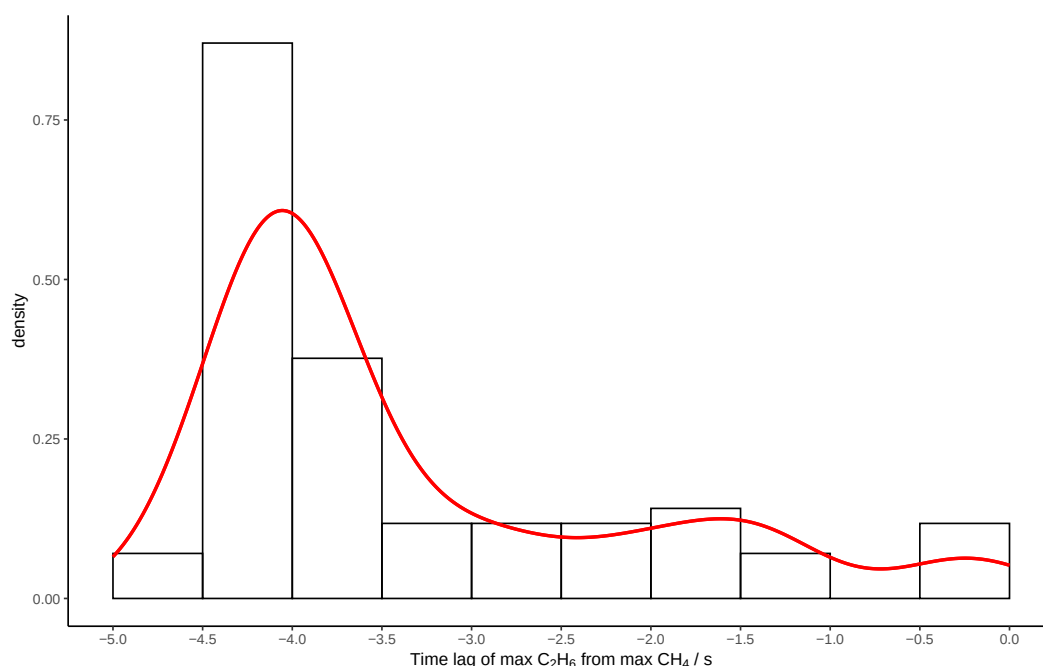


Figure 2.13: Density plot of time lag of the maximum C_2H_6 measurement from the maximum CH_4 measurement (Only including C_2H_6 measurements that precede the CH_4)

2.4 Resulting algorithms

These prior findings result in separate detection algorithms depending on if the SIFT-MS or TILDAS was used in the deployment. For the SIFT-MS, this algorithm also changes depending on if the SIFT-MS identification is used as a core part of the algorithm. **Table 2.4** shows a breakdown of the 3 possible algorithms for OP determination. All algorithms use the same background calculation of the median concentration of a rolling 5 minute window and the same enhancement criteria of $1.05 \times$ background as discussed in **Section 2.3.1**. Time clustering changed depending on response time of instruments involved in the sampling, core instrumentation was capable of a sub 1 s response time and therefore this could be used in the majority of situations, however, for the SIFT-MS, with

Chapter 2. Development of a domestic natural gas detection algorithm

a cycle time of 7.2 s, the time clustering had to be set at 8 s. For the methodologies that included source identification, this meant filtering out any enhancements that did not fall into the thermogenic assignment, with the SIFT-MS this required $C_3H_8 : C_4H_{10}$ between 3.31 to 6.09 and for the TILDAS $C_2H_6 : CH_4$ between 0.005 and 0.09. Finally, the quantification equation differed for the TILDAS, as this instrumental setup participated in the controlled release, it was not able to use the quantification equation present in **Section 2.3.6.1**, as the SIFT-MS instrument setup was not present in the controlled release, quantification followed the equation present in (Weller *et al.*, 2019) [54].

Once OPs had been located all algorithms followed the same LI identification. All OPs from each of a campaign's mobile surveys were clustered using a 30 m clustering parameter. Each cluster was then filtered such that only clusters containing enhancements from more than 1 different mobile survey were kept (in order to keep emissions that were persistent). Finally, the resulting LIs emission rate was determined as the maximum leak rate of the OPs within the cluster, in order to provide a "worst case scenario" of the potential leak rates. To avoid overconfidence in the quantification of leak rates, the LIs leak rate was placed into one of 4 bins. Very small ($< 2 \text{ L min}^{-1}$), small ($2 - 6 \text{ L min}^{-1}$), medium ($6 - 40 \text{ L min}^{-1}$) and large ($> 40 \text{ L min}^{-1}$). In order to ensure the lowest of these leak rate categories was reasonable, the minimum possible leak rate detectable using the quantification equation derived from the controlled release was calculated. Assuming a background CH_4 concentration of 2 ppm, the minimum detectable enhancement using the detection algorithm would be 0.1 ppm, which would result in a leak rate of 0.19 L min^{-1} . In surveys, the algorithm was implemented using a code written in the R statistical programming language which was subsequently made publicly available in an online repository [70].

Instrumentation	Background calculation	Enhancement criteria	Time clustering parameter	Source identification	Quantification equation	Campaign
MGGA (CH ₄ , CO ₂) ICAD (NO, NO ₂) SIFT-MS (VOCs)	Rolling 5 minute median	1.05 x background	8 s	C ₃ H ₈ : C ₄ H ₁₀ (3.31 - 6.09)	(Weller <i>et al.</i> , 2019)[54]	INGENIOUS York and Bradford
MGGA (CH ₄ , CO ₂) ICAD (NO, NO ₂)	Rolling 5 minute median	1.05 x background	1 s	NA	(Weller <i>et al.</i> , 2019)[54]	INGENIOUS York and Bradford
MGGA (CH ₄ , CO ₂) ICAD (NO, NO ₂) TILDAS (C ₂ H ₆)	Rolling 5 minute median	1.05 x background	1 s	C ₂ H ₆ : CH ₄ (0.005 - 0.09)	Section 2.3.6.1	York 2024 campaign

Table 2.4: Parameters associated with the natural gas detection algorithm depending on instrumentation used.

Chapter 3

Methane emissions in York and Bradford

3.1 Introduction

As mentioned in *Chapter 2*, the York WASP was deployed on multiple campaigns to two UK cities; Bradford and York. Bradford is a city in West Yorkshire with a population of over 500,000, while York is a city in North Yorkshire with a population over 200,000. Both cities are supplied by the same Gas Distribution Network (GDN), which covers the entirety of the north-east of England and northern Cumbria, covering the pre-meter distribution of natural gas to 2.7 million homes and businesses via the use of tens of thousands of kilometres of pipework, leading to a great area over which fugitive emissions could occur. Several campaigns took place in both cities, resulting in two Bradford campaigns using the SIFT-MS within the platform and three York campaigns, two with the SIFT-MS and one with the TILDAS. This chapter aims to investigate how suitable each instrument is for its use within a fugitive CH₄ emissions detection survey. Additionally, this chapter will explore how the changes made to the CH₄ detection algorithm in *Chapter 2* affect the size and quantity of detected

fugitive emissions.

The Global Fuel Exploitation Inventory (GFEI) v3 [21] provides gridded inventory data from CH₄ emissions at a $0.1^\circ \times 0.1^\circ$ resolution for the year 2020. Data is allocated to emissions from various fuel types and processes, data relating to natural gas distribution is taken for York and Bradford in order to provide a comparison for the expected CH₄ emissions from fugitive emissions for each city. The GFEI reports York as having CH₄ emissions from natural gas distribution totalling 390.12 Mg annum⁻¹ while Bradford had emissions totalling 842.54 Mg annum⁻¹. The local GDN aims to aid in reducing these emissions through their efforts of replacing the existing pipe network with a modernised polyethylene pipe network, this however is time consuming and therefore the potential benefits of mobile surveys to find the “leakiest” sections of pipe to replace first can help these GDNs reduce their CH₄ emissions in line with the timescale set by the GMP. Additionally, although these UK cities may not have as high emissions as larger cities within the UK, this presents the opportunity to deploy this type of measurement campaign in small to medium sized cities, as previous studies tended to focus on major cities across the US and Canada [52, 57, 58] as well as European cities [55, 56, 59–61] and Japan [71, 72].

3.2 Methodology

Through 2023 and 2024, 5 mobile sampling campaigns took place in York and Bradford. The first four were in collaboration with the INGENIOUS campaign work package 3, which aims to identify and quantify the impact of different indoor air sources on outdoor air quality [63]. These campaigns therefore required the deployment of a SIFT-MS. The final campaign in York was purely devoted to natural gas detection, therefore a TILDAS was deployed on this campaign. For each campaign an effort was made to drive

the route at least 5 - 8 times over separate days in order to capture > 90 % of emissions [53].

3.2.1 INGENIOUS campaigns

Of the 4 INGENIOUS sampling campaigns, 2 took place in York and 2 took place in Bradford. The first York campaign featured 8 mobile sampling surveys over the course of 7 days in February of 2023. The second York campaign featured 8 surveys over 4 days in September of 2023. The initial Bradford campaign featured 10 surveys over the course of 5 days in February of 2023 and the second Bradford campaign featured 11 surveys over the course of 6 days in June of 2023. The routes of each city's sampling campaign are shown in *Figure 3.1* and *Figure 3.2*.

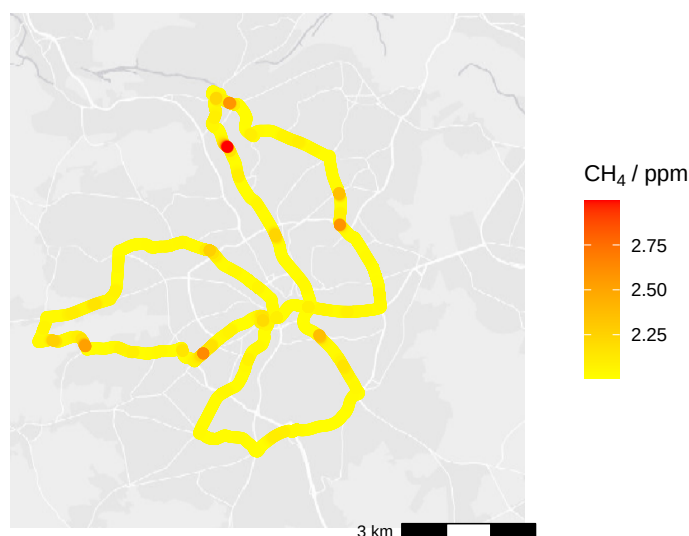


Figure 3.1: Colour map of CH₄ concentration from one of the Bradford INGENIOUS route mobile surveys.

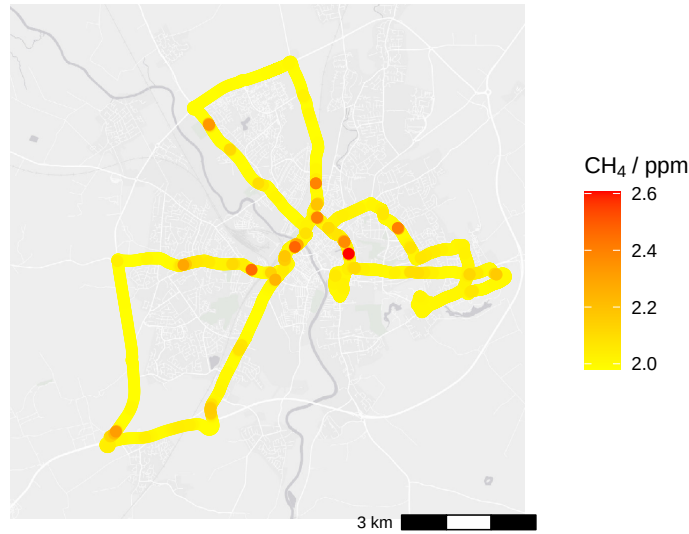


Figure 3.2: Colour map of CH₄ concentration from one of the York INGENIOUS route mobile surveys.

3.2.2 York 2024 campaign

The York 2024 campaign was based around 2 separate routes, the first route, referred to as the city-wide route, was chosen as it covers the majority of the city of York, but was not intended to be used to compare measurements to the cities emissions inventory as it only covers a small fraction of the total miles of road within the York urban area, 27 miles of a total 507 administered by the local authority [73]. This route allowed for the updated TILDAS algorithm to be tested on the mobile platform and allows for a direct comparison to the INGENIOUS route. This first route took place over two separate weeks in May and June of 2024 resulting in 18 mobile surveys of a “flower petal” route. An overview of this route is shown in *Figure 3.3*.



Figure 3.3: Colour map of CH₄ concentration from one of the York city-wide route mobile surveys.

A second route driven during this campaign took place on a separate week in May of 2024. This route, referred to as the neighbourhood route, featured the sampling of 3 neighbourhoods in York that are directly next to one another. During this campaign a more intensive approach was taken with a higher number of roads sampled in this survey area. The main limitation of this survey route was that not all of the roads could be sampled by the WASP due to them not being wide enough or having dead-ends that would lead to high difficulty in manoeuvring the vehicle. This route was designed in order to more closely relate to the areas covered by emissions inventories, but also allowed to see the effect that smaller roads have on the number of leak indications in a city. The neighbourhood route featured 8 drives on 5 days, however due to instrument failure, only 5 drives across 4 days contained usable data. An overview of the route is shown in *Figure 3.4* While *Figure 3.5 shows both routes displayed together*.

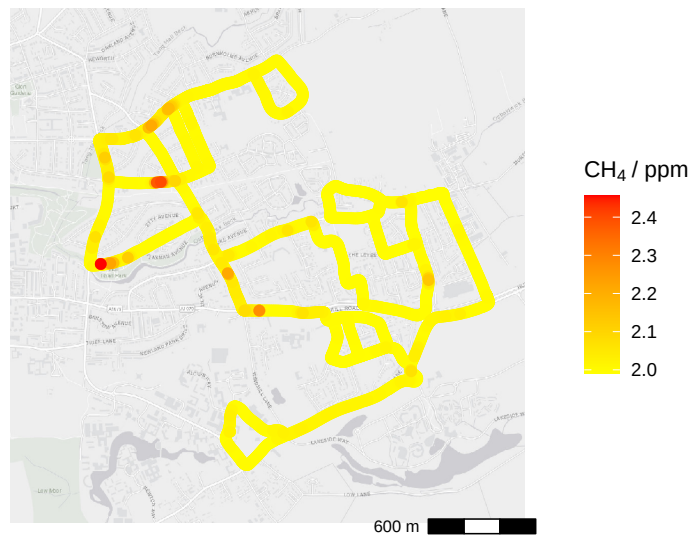


Figure 3.4: Colour map of CH₄ concentration from one of the York neighbourhood route mobile surveys.

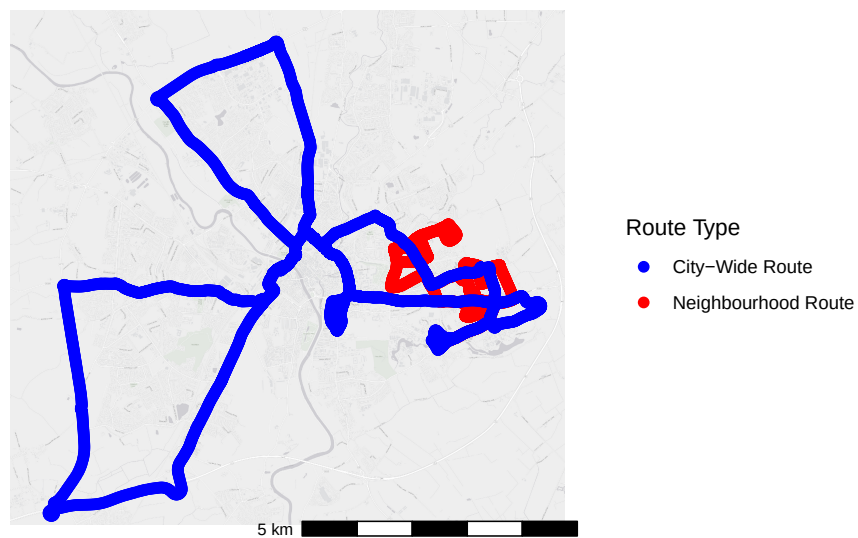


Figure 3.5: Map showing both routes taken during the York mobile survey campaigns, coloured by specific route.

3.2.3 Meteorological data

Synoptic meteorological data for all campaigns was taken from Leeds Bradford airport's weather monitoring station. Wind data was filtered to times during which a sampling campaign was being conducted. For the Bradford February campaign, wind speed averaged 4.25 m s^{-1} with calm conditions (where calm refers to times when wind speed was 0 m s^{-1}) 0 % of the time, during the June campaign, the average wind was higher at 6.48 m s^{-1} with calm conditions again at 0 % of the time. Average air temperature during the February campaign was 5°C , ranging between 3.5°C and 6.5°C while in the June campaign, average air temperature was 16.9°C , ranging between 14°C and 21°C . A wind rose and air temperature series for each campaign is shown in *Figure 3.6*.

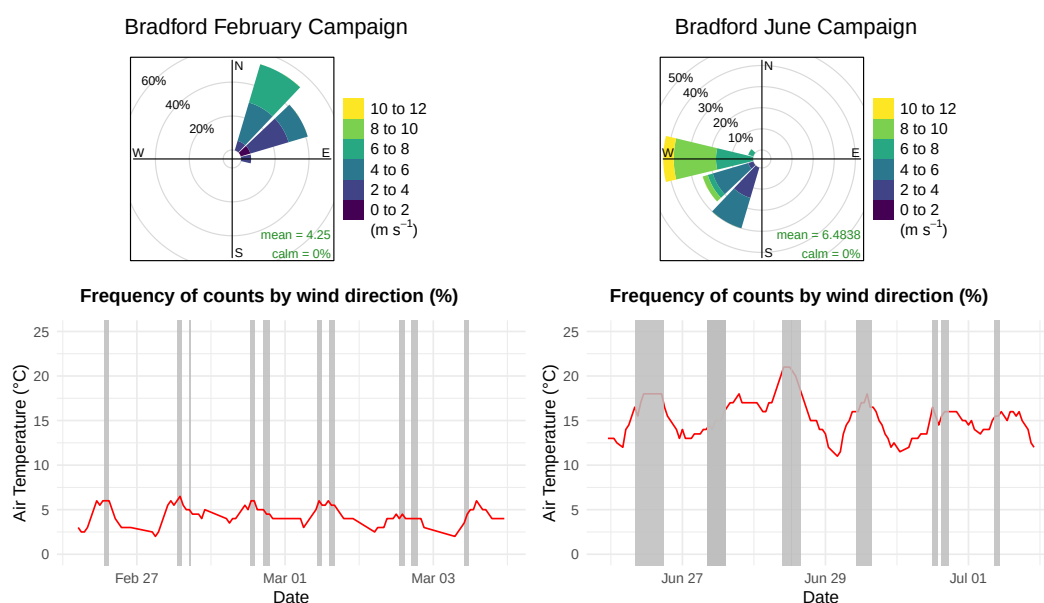


Figure 3.6: Wind rose and air temperature time series of both Bradford campaigns. The air temperature time series have been shaded to illustrate when mobile surveys took place.

For the York February campaign, wind speed averaged 4.53 m s^{-1} with calm conditions 0 % of the time, during the September campaign, the

Chapter 3. Methane emissions in York and Bradford

average wind was higher at 3.41 m s^{-1} with calm conditions again at 0 % of the time. Average air temperature during the February campaign was 5.9°C , ranging between 3.0°C and 9.0°C while in the September campaign, average air temperature was 14.4°C , ranging between 10.5°C and 18°C . A wind rose and air temperature series for each campaign is shown in **Figure 3.7**.

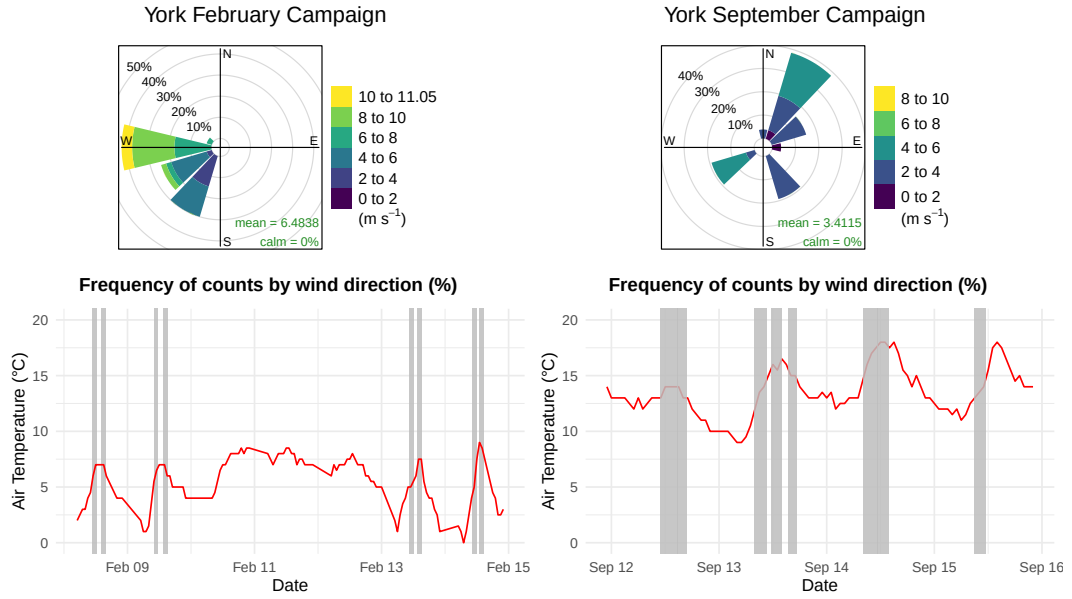


Figure 3.7: Wind rose and air temperature time series of both York campaigns. The air temperature time series have been shaded to illustrate when mobile surveys took place.

For the York 2024 campaign, wind speed averaged 6.76 m s^{-1} with calm conditions 0 % of the time. Average air temperature during the 2024 campaign was 13.3°C , ranging between 11.5°C and 17.0°C . A wind rose and air temperature series for the campaign is shown in **Figure 3.8**.

Chapter 3. Methane emissions in York and Bradford

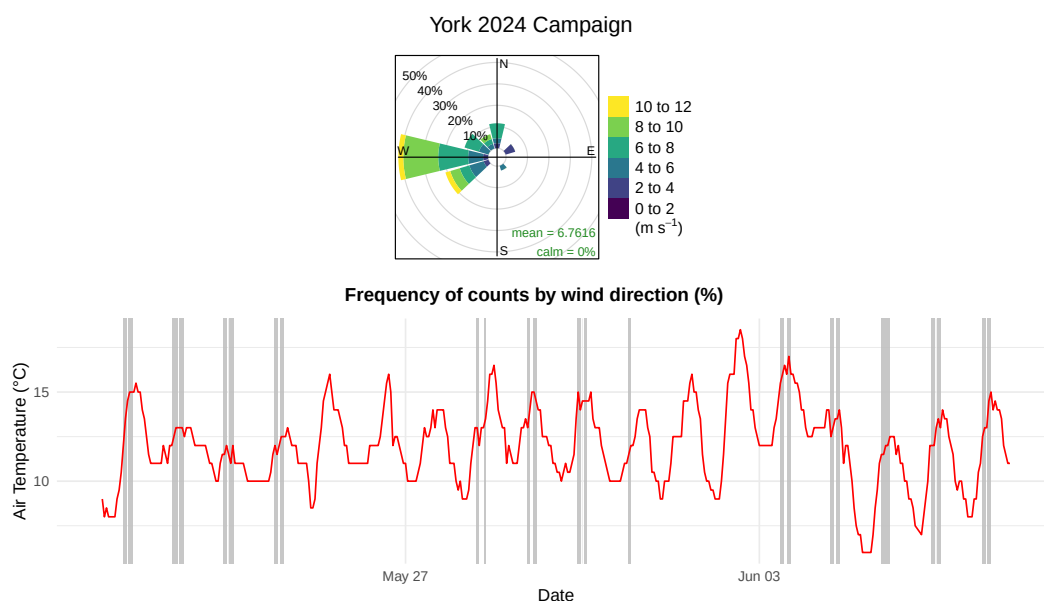


Figure 3.8: Wind rose and air temperature time series of the York 2024 campaign. The air temperature time series has been shaded to illustrate when mobile surveys took place.

Although wind data was available from this monitoring site and gives some insight into regional changes across the campaigns, it was determined that any wind analysis associated with the WASP's sampling, would be conducted using the WASP's measurements of wind, in order to use winds that are local to point of detection. The WASP's raw wind measurements are affected by the speed and direction of travel of the platform, in order to calculate corrected wind speed and direction, measured wind and platform speed were converted into two dimensional vectors, true wind vector was calculated using vector addition of the two components and the magnitude of this vector informed the true wind speed. Wind direction was calculated as the arctangent of vector components.

3.3 Results

3.3.1 INGENIOUS

As discussed in *Chapter 2*, the inclusion of the SIFT-MS in the INGENIOUS campaigns, although allowing source identification, has an impact on the time clustering parameter for the algorithm. In this section the results of 2 separate algorithms will be discussed. The first using the SIFT-MS in a core source identification step in the algorithm, which forces time clustering to be set at 8 s. In the second, this stage is omitted, allowing time clustering to be set at 1 s, but removing the certainty that detected LIs are definitively thermogenic in nature. Due to this iteration of the WASP not participating in the controlled release experiment, quantification followed the equation present in (Weller *et al.*, 2019) [54] as this has been more widely used across previous literature.

3.3.1.1 Bradford INGENIOUS February 2023

Deploying the SIFT-MS source filtering algorithm, resulted in the detection of 175 OPs over the course of the 10 mobile surveys, $C_3H_8 : C_4H_{10}$ source assignment resulted in 22 (12.6 %) of these being assigned as thermogenic. LI spatial clustering and filtering resulted in the detection of only 3 LIs in this campaign which, when quantified, resulted in 2 being assigned to the very small ($0 - 2 \text{ L min}^{-1}$) leak rate bin and 1 being assigned to the small ($2 - 6 \text{ L min}^{-1}$) leak rate bin. In comparison, when the non SIFT-MS algorithm was used, 298 OPs were detected across the 10 mobile surveys, as there was no source filtering, all these OPs underwent the LI spatial clustering and filtering, resulting in 41 LIs from this campaign. After quantification, the LIs were assigned to the quantification bins such that 5 were medium ($6 - 40 \text{ L min}^{-1}$), 4 were small ($2 - 6 \text{ L min}^{-1}$) and 32 were very small ($0 - 2 \text{ L min}^{-1}$).

3.3.1.2 Bradford INGENIOUS June 2023

The SIFT-MS source filtering algorithm resulted in the detection of 94 OPs, $C_3H_8 : C_4H_{10}$ source assignment resulted in 0 being assigned as thermogenic and as such none could be assigned as LIs using this algorithm. The non SIFT-MS approach resulted in the detection of 123 OPs and subsequently 24 LIs. After quantification, this resulted in the LIs being assigned to the following leak rate bins; 1 medium ($6 - 40 \text{ L min}^{-1}$), 1 small ($2 - 6 \text{ L min}^{-1}$) and 22 very small ($0 - 2 \text{ L min}^{-1}$).

3.3.1.3 York INGENIOUS February 2023

The SIFT-MS version of the algorithm resulted in the detection of 133 OPs over the course of 8 mobile surveys, $C_3H_8 : C_4H_{10}$ source assignment resulted in 20 (15.0 %) assigned as thermogenic. LI spatial clustering and filtering resulted in 3 LIs being detected in this campaign, all 3 of which were assigned to the very small ($0 - 2 \text{ L min}^{-1}$) leak rate bin. The non SIFT-MS algorithm detected 182 OPs, again, as no source filtering took place with this approach all OPs underwent the LI spatial clustering and filtering, resulting in 33 LIs from the campaign. After quantification, 2 were assigned as small ($2 - 6 \text{ L min}^{-1}$) and 31 were assigned as very small ($0 - 2 \text{ L min}^{-1}$).

3.3.1.4 York INGENIOUS September 2023

The SIFT-MS version of the algorithm resulted in the detection of 71 OPs, but once again the $C_3H_8 : C_4H_{10}$ assignment resulted in none being assigned as thermogenic and therefore once again, none could be assigned as LIs. The non SIFT-MS version of the algorithm detected 86 OPs and subsequently 16 LIs which were then assigned to the following leak rate bins; 1 high ($> 40 \text{ L min}^{-1}$), 2 small ($2 - 6 \text{ L min}^{-1}$) and 13 very small ($0 - 2 \text{ L min}^{-1}$).

3.3.1.5 Bradford vs York INGENIOUS comparison

The results of all INGENIOUS campaigns show that although the SIFT-MS allows the ability to confirm enhancements as being from thermogenic sources, the effect it has on time clustering parameters, due to the sampling cycle, results in far less enhancements being detected than when a smaller time clustering parameter is used. The alternative however, is to omit the source identification stage, changing the time clustering parameter from 8 s to 1 s. This results in much higher detection of both the OPs and of the LIs. An overview of each campaign's OP and LI count based on the algorithm used can be found in *Table 3.1*.

Campaign	OP count (SIFT-MS included)	OP count (SIFT-MS not included)	LI count (SIFT-MS included)	LI count (SIFT-MS not included)
Bradford February 2023	175	298	3	41
Bradford June 2023	94	123	0	24
York February 2023	133	182	3	33
York September 2023	71	86	0	16

Table 3.1: Comparison in the number of OPs and LIs detected in each campaign depending on if the SIFT-MS is included in the algorithm.

Table 3.1 illustrates that the OP count is far lower when using the 8 s time clustering parameter than when the 1 s time clustering parameter is used. This suggests that CH₄ enhancements within the two cities often occur spatially close to one another, requiring instruments with high temporal resolution in order to ensure that the time clustering parameter can be set as low as possible. LI count also drops when the SIFT-MS is used, this suggests that either the SIFT-MS assignment criteria is too strict and results in very few OPs being assigned as thermogenic, which would therefore mean less would be available to be attributed to LIs, or, the alternative, that because of the sampling time of the SIFT-MS, there is a low chance that the air sampled by the SIFT-MS is the same parcel of air that the CH₄ enhancement is detected from. Additionally, the LI count

from the methodology not undergoing source assignment with the SIFT-MS, is likely an over-prediction, due to all CH₄ enhancements being included in the LI analysis and not just the thermogenic enhancements. It is expected that not all of the CH₄ emissions found within a city will be thermogenic, as CH₄ will be emitted from a range of sources. The York route, for example, passes by a waste water treatment plant as well as farmland, rivers and landfills all of which have a potential to emit CH₄ and must be omitted from any thermogenic specific analysis. However, not all of a city's CH₄ sources will have known locations, these may include emissions from sewers or emissions associated with combustion, therefore highlighting the need for fast CH₄ source assignment within the detection algorithm. This informs future campaigns that the platform needs to be able to have all instrumentation operate with at least a 1 s response time and that source assignment in an algorithm to detect fugitive natural gas emissions is not realistically feasible with a SIFT-MS.

3.3.2 York 2024 Campaign

3.3.2.1 City wide route

18 mobile surveys were conducted across the city wide route of York, the raw data was taken from 10 Hz files for CH₄ (MGGA) and C₂H₆ (TILDAS) and time averaged to 1 Hz data to be of the same response time as the WASP's other internal components (e.g. GPS). The data was then processed to remove data taken when speeds were 0 or > 40 miles hour⁻¹ as well as removing data within the area of Wolfson Atmospheric Chemistry Laboratories due to this also being the location within which calibrations and other instrument tests were conducted. A rolling 5-minute median background of CH₄ was then applied and enhancements were determined as any CH₄ measurement taken that was greater than 1.05 times the calculated background, the enhanced readings were then clustered such

Chapter 3. Methane emissions in York and Bradford

that any elevated reading within one second of another were assumed to correspond to the same enhancement. These enhancements were then spatially averaged such that 468 OPs were detected over the course of the 18 mobile surveys.

For each of these OPs the maximum C_2H_6 value was found from the time of maximum CH_4 to 5 seconds prior. The two instruments' data were then aligned for each OP such that time of maximum CH_4 measurement was equal to time of maximum C_2H_6 measurement. A linear regression was then taken of values from 5 seconds prior to the maximum CH_4 measurement to 5 seconds after and a source type was assigned such that $C_2H_6 : CH_4 < 0.005$ is associated with biogenic sources, > 0.005 to < 0.09 are thermogenic and > 0.1 are considered pyrogenic or combustion.

This meant that of the 468 OPs, 177 (37.8 %) were found to be thermogenic in origin. Each thermogenic OP was then clustered to find others within 30 m of one another and filtered to ensure that clusters contained OPs occurring on at least two separate mobile surveys, to remove any OPs occurring from an event happening on only one drive. The remaining clusters were then averaged into LIs such that the CH_4 enhancement was the maximum from the OPs and the latitude and longitude were a weighted spatial average, resulting in 24 thermogenic LIs from the 177 thermogenic OPs. As described in *Chapter 2* leak rate was determined for each OP and the LI leak rate was determined as the maximum of all OP leak rates within the LI cluster. The smallest leak rate was determined to be 0.26 L min^{-1} and the largest being 16.04 L min^{-1} , when assigned to bins 3 LIs were categorised as medium ($6 - 40 \text{ L min}^{-1}$), 4 were small ($2 - 6 \text{ L min}^{-1}$) and 17 were very small ($0 - 2 \text{ L min}^{-1}$). When the source type filter is omitted, this results in 58 LIs with leak rates ranging from 0.24 to 23.10 L min^{-1} , when assigned to bins 9 were medium ($6 - 40 \text{ L min}^{-1}$), 11 were small ($2 - 6 \text{ L min}^{-1}$) and 38 were very small ($0 - 2 \text{ L min}^{-1}$).

Chapter 3. Methane emissions in York and Bradford

While 177 of the 468 OPs were determined to be thermogenic, 39 were assigned as biogenic (8.3 %), 199 were pyrogenic (42.5 %) and 53 were not able to be assigned a source type. NO_x : CO_2 ratios were investigated for the pyrogenic OPs using the same methodology used for the CH_4 : C_2H_6 source assignment. 115 of the 199 pyrogenic OPs were able to be analysed in this way, 87 of these 115 OPs (75.7 %) had a NO_x : CO_2 ratio $< 0.88 \times 10^{-3}$, this fraction was assigned to combustion associated with domestic combustion, following the results of (Cliff *et al.*, 2025), which compiled inventory estimates on the NO_x : CO_2 ratios from vehicle and domestic boiler exhausts to calculate the 0.88×10^{-3} NO_x : CO_2 divide between domestic combustion and other combustion sources. This implied that the majority of pyrogenic emissions did not originate from traffic but more likely emissions from domestic heat and power generation (such as emissions from domestic boilers). This study found that 42.5 % of all CH_4 enhancements were pyrogenic in nature, while (Maazallahi *et al.*, 2020 [55] reported 8 % of LIs were pyrogenic and (Fernandez *et al.*, 2022 [56] found 5 % of LIs were pyrogenic. Initially it may seem that this study detects many more pyrogenic emissions than previously, however, it is important to note that these previous studies identify the sources at the LI stage (i.e. only permanent CH_4 emissions undergo source identification). The York study identifies the source at the OP stage, this is an important distinction and an important change to previous methodologies as it shows that pyrogenics are unlikely to be a source that is repeatedly detected but also that at the OP stage there is a wide range of CH_4 sources detected which must be differentiated before doing further LI analysis.

Emissions from pyrogenic and biogenic sources are compared to thermogenic source emissions at the OP stage on a drive by drive basis due to the high unlikelihood of pyrogenics and biogenics being persistent emission sources, the number of times each source type was detected per drive is shown in **Figure 3.9**.

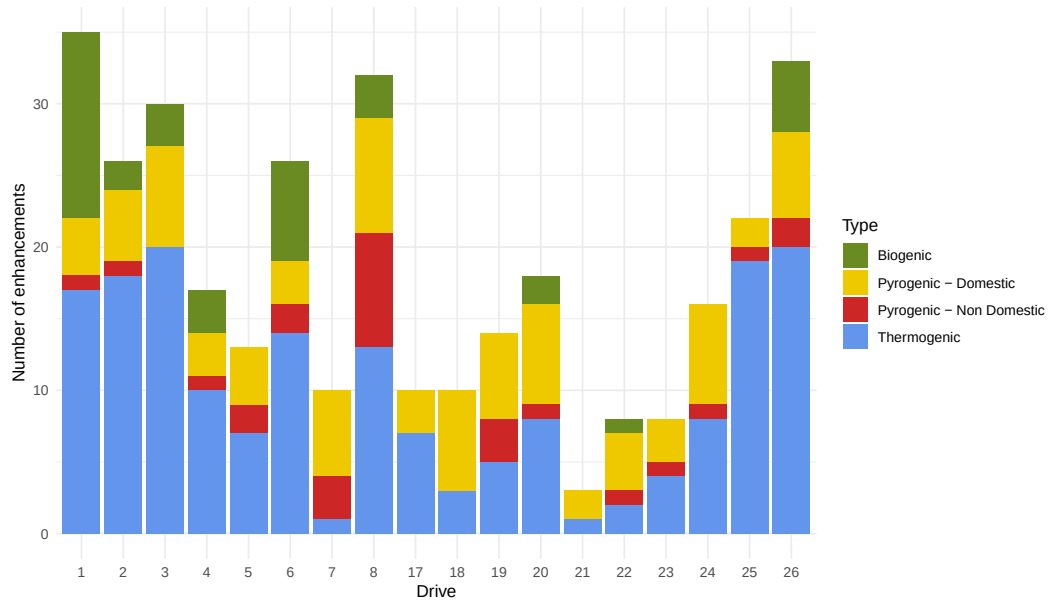


Figure 3.9: Total number of enhancements from each source type for each of the mobile surveys on the city-wide route.

Thermogenics were the most frequently located source type on 13 of the 18 surveys, with drives 7, 18, 19, 21 and 22, finding pyrogenic emissions related to heating and cooking were the most frequently occurring source type.

3.3.2.2 Neighbourhood route

Of the 5 drives with usable data, the same initial data processing as the city-wide route first took place. A rolling 5-minute median background of CH_4 was again applied and CH_4 enhancements greater than 1.05 times the calculated background were located and clustered such that others occurring within 1 second were treated as the same enhancement. This resulted in only 49 OPs from the 5 drives. Source determination again took place using $\text{C}_2\text{H}_6 : \text{CH}_4$ ratios, this resulted in 14 of the 49 OPs (28.6 %) being assigned as thermogenic in origin. LI spatial averaging and filtering took place again, resulting in 3 LIs detected on this sampling campaign.

Leak rate was again calculated using the same quantification equation used in the mobile surveys city-wide route and were assigned using the same bin-sizes, this resulted in 1 of the LIs being assigned as medium ($6 - 40 \text{ L min}^{-1}$) and 2 assigned as very small ($0 - 2 \text{ L min}^{-1}$). While 49 OPs were assigned as thermogenic, 2 were assigned as biogenic (4.1 %), 25 were assigned as pyrogenic (51.0 %) and 8 were not able to be assigned. Again $\text{NO}_x : \text{CO}_2$ ratios were used to assign the pyrogenic enhancements into domestic and non-domestic sub-sources. Of the 25 pyrogenic OPs, 16 were able to be assigned to sub-sources using this methodology, 11 of the 16 (68.75 %) were assigned as domestic pyrogenics while 5 of the 16 (31.25 %) were assigned to non-domestic pyrogenics. The number of each source type detected on a drive by drive basis is shown in **Figure 3.10**.

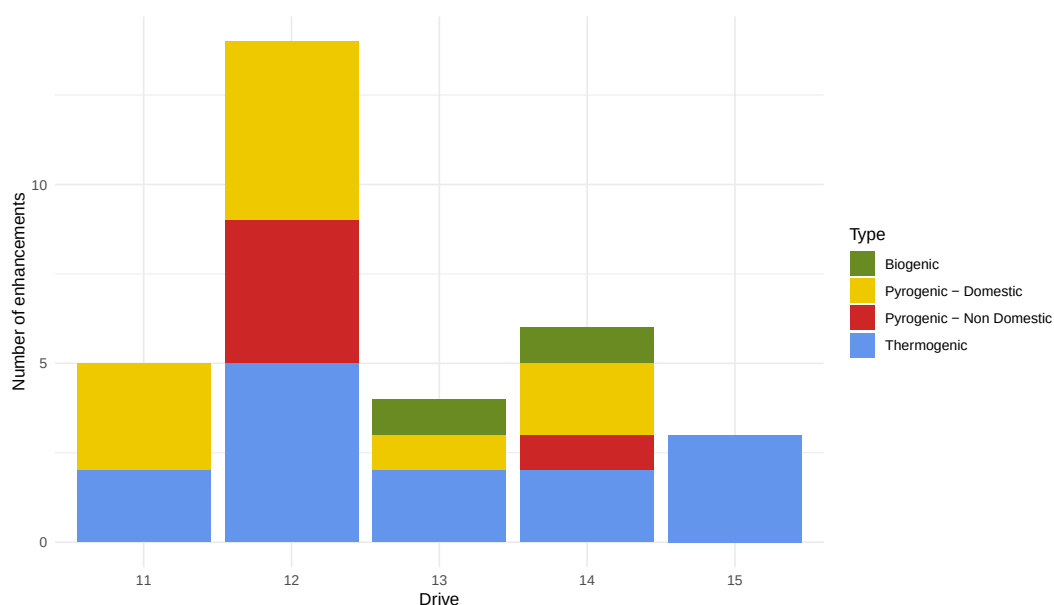


Figure 3.10: Total number of enhancements from each source type for each of the mobile surveys on the neighbourhood route .

Domestic pyrogenics were shown to be the most frequently located source during surveys of the neighbourhoods route, with thermogenics still being a large secondary contributor. The dominance of the domestic

pyrogenics during this route may be easily explained due to sampling much closer to residential properties.

3.3.2.3 City-wide vs. neighbourhood route comparison

As described in the previous sections, during the city-wide route sampling, there was a clear dominance in the number of thermogenic enhancements detected per drive, with domestic pyrogenics being a large secondary source along this route. Detection of thermogenics on a drive by drive basis were much lower during the neighbourhood route sampling, with domestic pyrogenics being the most dominant source along this route. **Figure 3.11** shows a comparison of the source contribution on a drive by drive basis, where drives 1 - 8 and 17 - 26 were the city-wide route and 9 - 16 were the neighbourhood route, drives 9, 10 and 16 show no enhancements due to these being the 3 drives with poor sampling from several key instruments.

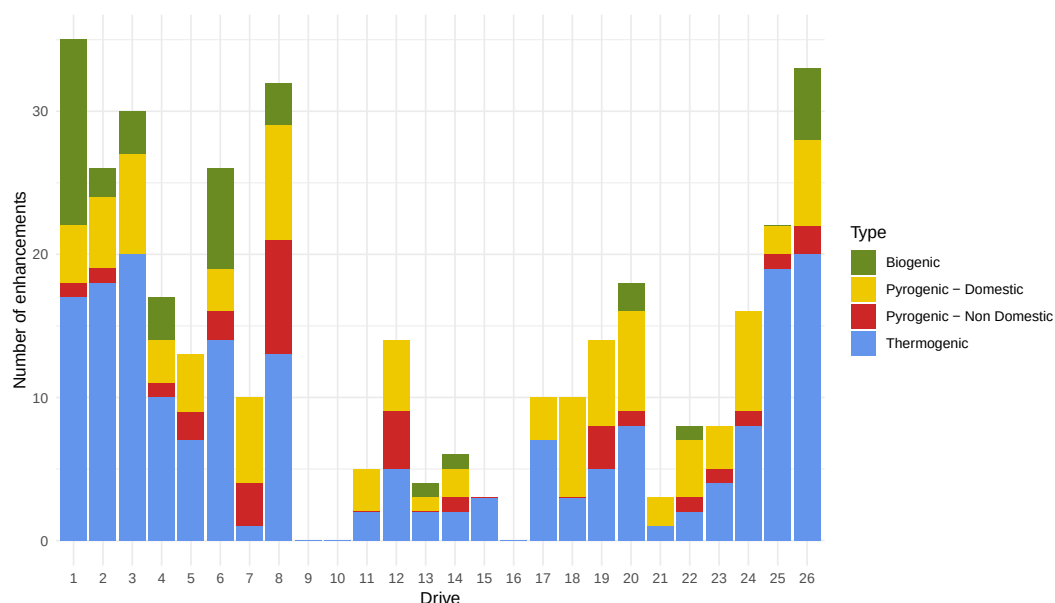


Figure 3.11: Total number of enhancements from each source type for each of the mobile surveys on the both routes (City-wide: 1-8 & 17-26, Neighbourhood: 9-16).

As can be seen in **Figure 3.11** and **Table 3.2** the neighbourhood route detects fewer enhancements, on average, regardless of source type. This is most noticeable in the thermogenic fraction, which **Table 3.2** shows to have the largest reduction in mean number detected in the campaign. This suggests that natural gas fugitive emissions may occur more frequently on major roads as opposed to the smaller residential roads, this holds true when LI km^{-1} is calculated for each route, the city-wide route detected 24 LIs over a 47 km route resulting in 0.51 LI km^{-1} while the neighbourhood route detected only 3 LIs over a 34 km route resulting in 0.09 LI km^{-1} .

Route	Mean no. of thermogenics detected	Mean no. of biogenics detected	Mean no. of domestic pyrogenics detected	Mean no. of non-domestic pyrogenics detected
City-wide	10	4	5	2
Neighbourhood	3	1	3	2

Table 3.2: Mean number of each source type detected on a drive-by-drive basis for both campaigns.

3.3.3 Comparison of York 2024 campaign algorithm to previous methodologies

The main alterations to the methodology used in the York 2024 campaign from that present in (Weller *et al.*, 2019) [54] (and other studies that were based off this method), were that enhancement criteria was changed from 1.1 times the baseline to 1.05 times the baseline, clustering by time was changed such that emissions within 1 s of each other were clustered instead of within 5 s. Finally, a source determination stage was added as a core step in the algorithm as opposed to previous iterations that either had no source determination stage or one that came later in the analysis. **Table 3.3** shows the effect that all of these changes to the methodology make on the resulting detection of OPs and LIs for the York 2024 campaign's city-wide route.

Chapter 3. Methane emissions in York and Bradford

Enhancement Criteria	Time Clustering Criteria / s	Source Determination Included?	Number of OPs	Number of LIs
110% of baseline	5	No	179	27
		Yes	66	6
	1	No	216	29
		Yes	79	7
105% of baseline	5	No	357	58
		Yes	144	23
	1	No	468	58
		Yes	177	24

Table 3.3: Number of detected OPs and LIs in the York 2024 city-wide route, depending on changing algorithm parameters.

This shows the new methodology could locate more LIs. Additionally, when the predicted leak rates were compared from the non-source filtered LIs it showed that in addition to being able to locate more LIs, the changes to enhancement criteria and time clustering have also led to the ability to locate LIs of a greater range of leak rates. For the (Weller *et al.*, 2019) [54] methodology the 27 detected LIs range in leak rate between 0.70 and 23.10 L min⁻¹, with a mean Leak Rate of 4.53 L min⁻¹. Binning into the leak rate categories of very small (0 - 2 L min⁻¹), small (2 - 6 L min⁻¹), medium (6 - 40 L min⁻¹) and high (> 40 L min⁻¹) showed that of the 24 LIs in the new source filtered methodology, 3 were medium, 4 were small and 17 were very small. For the 58 LIs of the new non filtered methodology, 9 were medium, 11 were small and 38 were very small. For 27 LIs from the (Weller *et al.*, 2019) [54] non-filtered methodology 5 were medium, 11 were small and 11 were very small. Finally the 6 LIs from the (Weller *et al.*, 2019) [54] source filtered methodology, 1 was medium, 4 were small and 1 was very small. This shows the (Weller *et al.*, 2019) [54] methodology, requiring an enhancement of 1.1 times the baseline with 5 s time clustering, misses a large proportion of LIs that the newer methodology, requiring an enhancement of 1.05 times the baseline with 1 s time clustering, detects. A large proportion of these missed LIs occur in the very small category as expected with a smaller enhancement criteria, however, some are within

the larger categories of small and medium. Source filtering shows that regardless of criteria used, less LIs will be detected with this method, this suggests that previous methodologies that do not use this stage may be mischaracterising some thermogenic enhancements as being permanent, instead, they may be detecting CH₄ enhancements of differing source types that occur within the same vicinity of one another. **Figure 3.12** shows how the LIs detected within each methodology are distributed across leak rate categories.

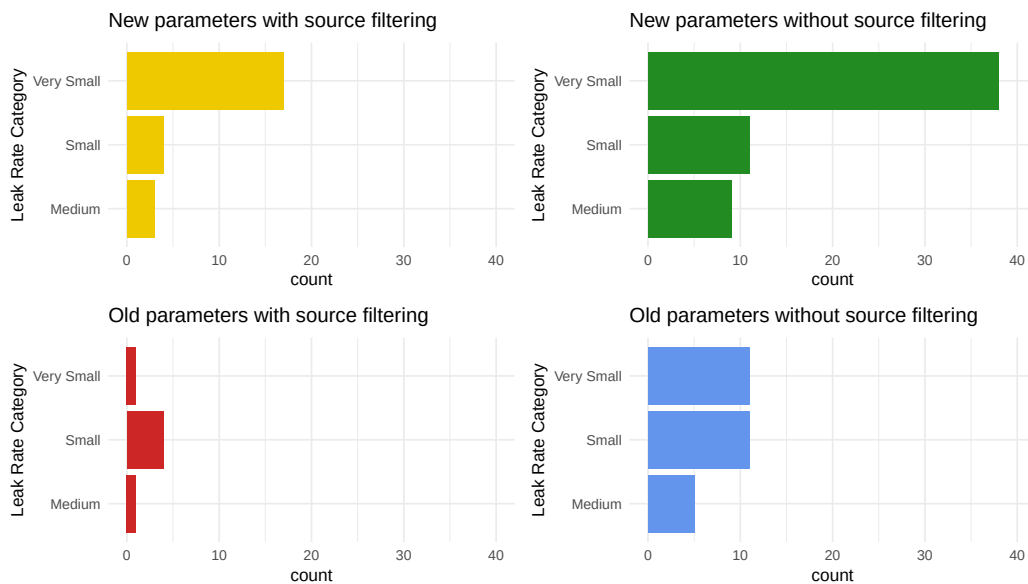


Figure 3.12: Bar charts showing the varying detected leak rate categories for each methodology.

3.3.4 Industry applicability of York 2024 campaign algorithm

As many gas distribution companies have signed up to voluntary emission reporting programmes, such as the Oil and Gas Methane Partnership (OGMP) 2.0, they are now obligated to report emissions through measurement based methods. One of the most popular methods for such a

reporting programme is through comprehensive, repeated vehicle based measurement surveys of an operator's gas network. In the York 2024 campaign, city-wide route, we have a repeated route of measurements where thermogenic emissions have been reported at certain locations throughout the campaign. It is therefore interesting from a mitigation perspective to investigate how many times each of those thermogenic emissions were identified over the course of the campaign.

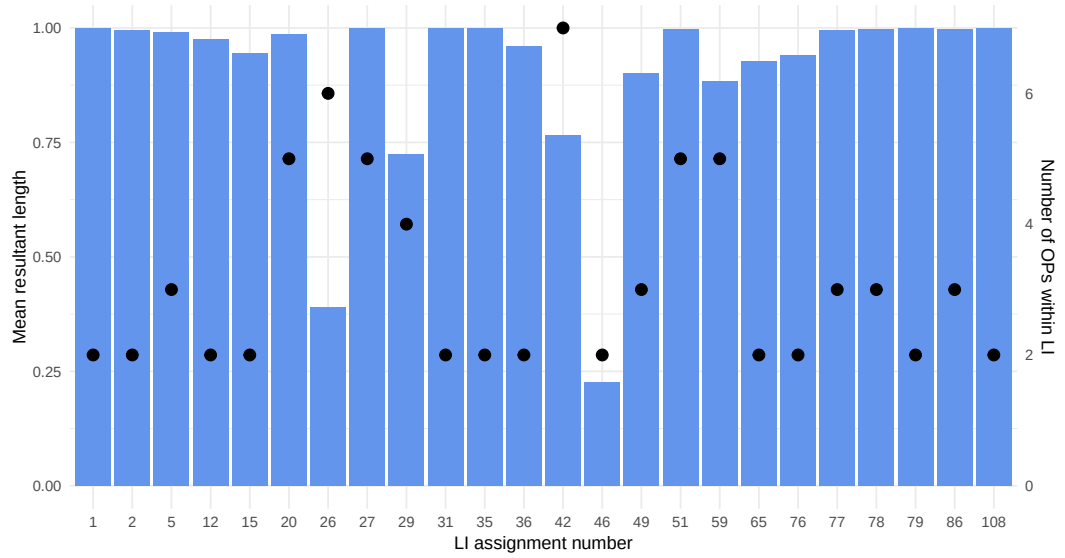


Figure 3.13: Mean resultant length and number of OPs per thermogenic leak indication.

The effect of wind on detection of LIs was initially investigated by calculating the mean resultant length of wind directions when a thermogenic OP was detected. This was calculated using *Equation 3.1*.

$$\rho = \sqrt{\left(\sum_{i=1}^n \cos \theta_i\right)^2 + \left(\sum_{i=1}^n \sin \theta_i\right)^2} \quad (3.1)$$

Where:

- ρ is the mean resultant length
- n is the number of data points

- θ_i is the angle of the wind direction, from north, in radians

For this analysis ρ is close to 1 when the wind directions are concentrated (similar) and close to 0 when more dispersed. **Figure 3.13** shows that for the majority of LIs detected in this campaign ρ is close to 1, suggesting that most LIs occur away from the road and require correct wind direction in order to detect them. For LIs where ρ is lower suggests that the LIs may occur closer to the mobile platform therefore not needing a specific direction of wind in order to detect them.

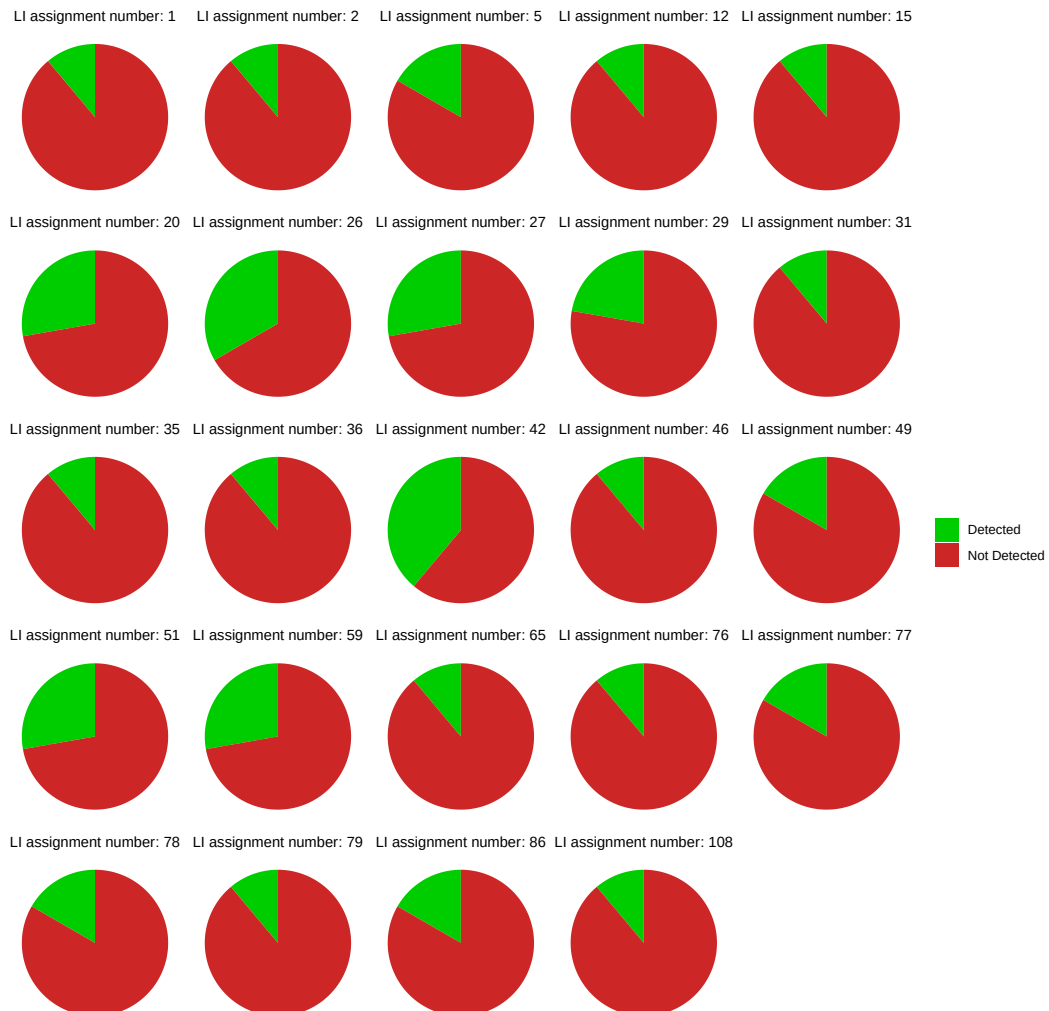


Figure 3.14: Pie charts of each LI showing number of mobile surveys they were detected vs not.

The number of mobile surveys is a large factor in the probability of detecting an LI. Each LI requires the enhancement to be detected on at least 2 separate mobile surveys, for the 24 LIs detected over the course of this campaign 12 LIs were detected on 2 mobile surveys, 6 were detected on 3 mobile surveys, 4 on 5 mobile surveys and 2 on 7, this meant that the average probability of detection was 0.18, detection versus non detection for each LI is demonstrated in **Figure 3.14**. This low probability of detection highlights the need for surveys with multiple passes. These result, along with the results of the wind direction analysis, suggest that detection of LIs are likely influenced by external factors such as wind or platform speed, this also starts to raise questions surrounding the reliability of a quantification equation relying on peak height, as peaks are likely to occur in differing shapes as external conditions change.

3.3.5 Comparison of different quantification equations for the York 2024 campaign

Throughout this work, two quantification equations have been used, the one present in (Weller *et al.*, 2019) [54] and the one derived from the controlled release experiment discussed in **Chapter 2**. Both these quantification equations rely on the peak height of an enhancement being used. An alternative quantification equation used in (Tettenborn *et al.*, 2025) [74] is proposed that uses peak area for quantification, the thought behind this is that through various factors including dispersion of an enhancement due to wind, different sampling speeds of mobile surveys and the use of different instruments, peak height of a CH₄ enhancement may not be consistent and therefore the peak area is a more suitable metric to be used for future measurements. The resulting quantification equation is shown in **Equation 3.2**.

$$\text{emission rate} / L \min^{-1} = \exp(1.292 \times \ln(\text{CH}_4 \text{ area}) - 2.377) \quad (3.2)$$

Where $\ln(\text{CH}_4 \text{ area})$ is the average of all calculated $\ln(\text{CH}_4 \text{ area})$ for each OP within the same LI assignment. And CH_4 area is calculated using **Equation 3.3**.

$$[\text{CH}_4]_{\text{area}} = \sum_{i=0}^n \Delta t \times c(t_{i+1}) \times \overline{v_{\text{peak}}} \quad (3.3)$$

Where a CH_4 enhancement at time t_{i+1} ($c(t_{i+1})$) in ppm was multiplied by the measurement time step (Δt) and the average speed of the platform across the plume ($\overline{v_{\text{peak}}}$) to give the spatial peak area in ppm · m. Results from the York 2024 city-wide route, were re-quantified using all three quantification equations to see the effects of changing the quantification equation on the LI leak rates. **Figure 3.15** shows box-plots of each LI in the campaign quantified using each of the three quantification equations. The (Weller *et al.*, 2019) [54] equation was adapted for this comparison such that the excess CH_4 term was determined from the maximum of all CH_4 enhancements of OPs within an LI cluster, so that it followed the York 2024 campaign approach more closely.

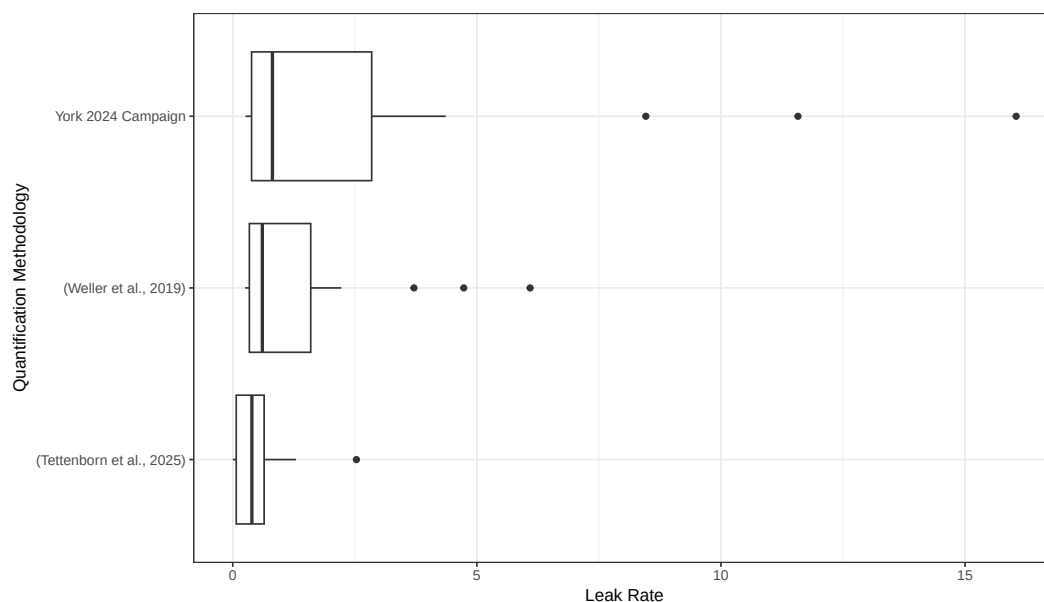


Figure 3.15: Box plots illustrating the calculated leak rates of each LI detected in the York 2024 campaign, using three different quantification equations, with the York and (Weller *et al.*, 2019) [54] equations using maximum of all enhancements.

The York 2024 campaign has the largest range of leak rates, with the equation present in (Weller *et al.*, 2019) [54] resulting in a smaller range and again, using the equation in (Tettenborn *et al.*, 2025) [74], LIs have an even smaller leak rate range. It can also be seen that the leak rates are weighted lower using the (Weller *et al.*, 2019) [54] equation compared to the York 2024 campaign equation and are weighted even lower when using the (Tettenborn *et al.*, 2025) [74] equation. This is partly due to the York and (Weller *et al.*, 2019) [54] equations using the maximum values of CH₄ enhancements in an LI cluster, while the equation in (Tettenborn *et al.*, 2025) [74] uses the mean of $\ln(\text{CH}_4 \text{ area})$ in the LI cluster to calculate leak rate. In order to remove this higher weighted bias, leak rates are again reprocessed using the York campaign quantification equation and (Weller *et al.*, 2019) [54] equation, this time determining the leak rate from the mean of CH₄ enhancements (as was the approach in the original (Weller *et al.*, 2019) [54] manuscript).

These results are again shown in a box-plot in *Figure 3.16*.

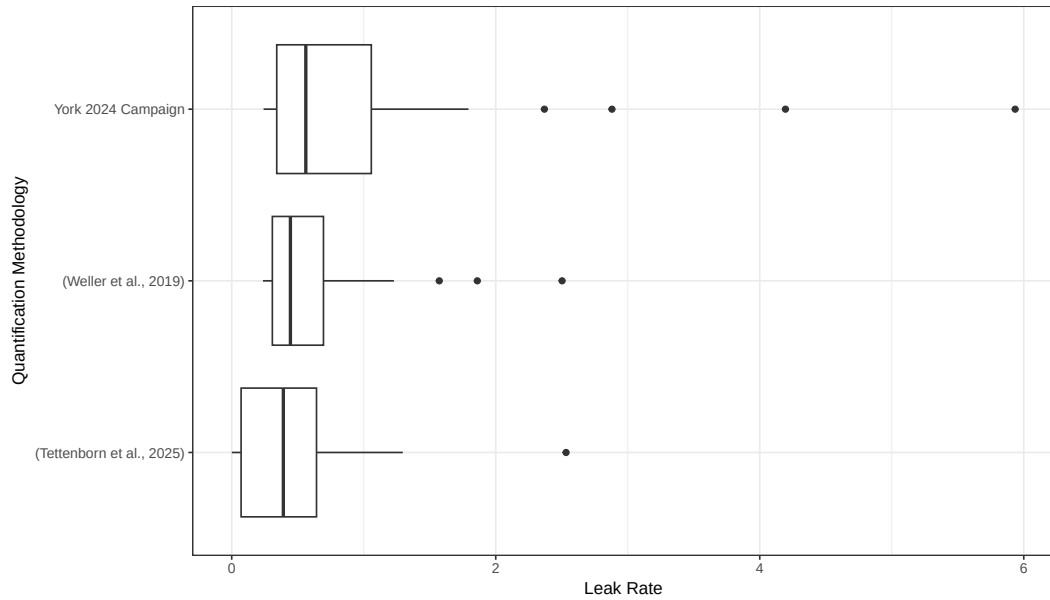


Figure 3.16: Box plots illustrating the calculated leak rates of each LI detected in the York 2024 campaign, using three different quantification equations, with the York and (Weller *et al.*, 2019) [54] equations using mean of all enhancements.

Using this approach to quantification, there is still the same trends in terms of range of leak rates quantified with these equations as well as leak rates being weighted lower in the order of the York 2024 campaign equation to the (Weller *et al.*, 2019) [54] equation to the (Tettenborn *et al.*, 2025) [74] equation. However, this approach does not result in any LIs being quantified $> 6 \text{ L min}^{-1}$ which would result in no LIs being placed in the medium leak rate bin ($6 - 40 \text{ L min}^{-1}$). This comparison shows firstly, that leak rate quantification using the York 2024 campaign equation or the (Weller *et al.*, 2019) [54] equation is heavily affected by outliers. This comparison does however start to raise doubts in the reliability of using a quantification equation based on peak height, with high variability in multiple factors surrounding the sampling on mobile surveys (including; vehicle speed, wind speed, wind direction), it is likely to have a large effect

on the measured peak height, this uncertainty leads to the peak area quantification being the most reliable approach going forward. This comparison between quantification equations is repeated in *Chapter 4* where a secondary platform that participated in none of the controlled releases was used in another natural gas emission sampling campaign.

3.4 Conclusions

The mobile survey campaigns in both York and Bradford illustrate the difficulty in locating and quantifying fugitive emissions of natural gas. The INGENIOUS campaign illustrates the importance of high time resolution in all instruments used in this style of campaign, the implementation of the SIFT-MS, although allowing a basic form of source identification, affects the platforms time clustering parameter in a way that greatly reduces the number of enhancements detected. This could be seen in the INGENIOUS campaigns when the SIFT-MS source assignment stage was removed, allowing to reduce the time clustering parameter from 8 s to 1 s which results in an increase in the number of OPs and LIs detected in all campaigns. This resulted in the changes made to the York 2024 campaign, where the platform was designed to measure at as high a time resolution as possible for all instruments included. The final York campaign was able to reduce time clustering to 1 s, from previous studies 5 s and reduced the required enhancement to 1.05 times the median background, from previous studies 1.1 times the median background. These changes were explored in the city-wide route surveys and show previous methodologies would result in detection of 27 LIs compared to the 58 LIs using updated parameters (53.5 % less), the parameter change has also shown the ability to detect more LIs in all leak rate categories, but in particular, the very small ($0 - 2 \text{ L min}^{-1}$) category, where 11 of 27 LIs were located in the previous methodology, but 38 of the 58 were located in the new

methodology.

Source appointment proved to be a useful tool for predicting emissions directly related to natural gas, when source filtering was introduced at the OP stage of detection, it resulted in only 41.4 % of LIs still being detected as opposed to the non-source filtered method. Additionally, source filtering has helped to highlight that although thermogenic emissions from natural gas are the highest contributor to CH₄ emissions, pyrogenic emissions related to domestic heat and power generation also provide a high but often overlooked contribution to a city's CH₄ emissions which is often not included within atmospheric emissions inventories.

The surveys conducted on the neighbourhood route again illustrate the prevalence of domestic pyrogenics within York. However, this route resulted in the detection of far less thermogenic emissions, suggesting that within the city fugitive emissions of natural gas are more likely to be detected on major roads, which can be used to inform future route design for similar campaigns within the UK.

Wind is shown to be an important factor in the detection of LIs within York on the city-wide route. LIs themselves are often not detected on the majority of sampling surveys, and analysis of the detected OPs within each LI show a high consistency between the wind direction when each OP was detected. This wind direction dependence and the variability of factors such as wind speed and vehicle speed between mobile surveys, leads to concern over using quantification equations that rely on peak height. A comparison of existing quantification equations to one that relies on peak area, shows that quantification equations that rely on peak height often have high variability in the calculated leak rates and often result in the calculated leak rates being weighted higher than when peak area is used in quantification.

Comparison of the results in these studies to previous studies is difficult due to the differences in instrumentation used and differing algorithms. In

order to effectively compare the results of different studies, a standardised algorithm needs to first be accepted. Additionally, as demonstrated in this study the peak height approach to quantification leads to a large amount of variability in calculated leak rates, previous studies would require re-quantification using the peak area approach in order to reduce the effect of differing instrumentation and platforms. Ultimately these types of survey should be used to provide verification to emissions inventories, however, for an accurate comparison to inventory data, a greater number of roads must be covered than were in this study in order to more accurately reflect the roads within an inventory's grid squares.

Chapter 4

Methane emissions in New York City

4.1 Introduction

New York City (NYC) is the most populous and most densely populated city within the United States of America and one of the most populous cities within the world, with an estimated population of 8.5 million and a population density of $11,314 \text{ km}^{-2}$. This means that in terms of complying with the GMP, the fugitive emissions of natural gas from domestic distribution in NYC is of much more importance globally than the cities of York and Bradford discussed in *Chapter 2* and *Chapter 3*. CH_4 emissions in NYC have been shown to be underestimated within inventories [75, 76], showing the need for further measurements within the city. Additionally, due to the structure of the city, emissions can occur at multiple heights (from street-level to rooftop). Although rooftop and tower measurements will capture emissions emitted from a range of heights, street-level monitoring campaigns are still required to understand how much street-level emissions contribute to the overall picture of city-wide emissions.

Chapter 4. Methane emissions in New York City

New York also offers another difference, not commonly seen outside of the USA and especially not on the scale seen within NYC, that being the district heating and cooling systems. The district heating and cooling system in Manhattan is a steam distribution system operated by Consolidated Edison Company of New York (ConEd). Steam is created by heating treated water in a boiler and, in some cases, is sent through a turbine for steam-electric co-generation. ConEd's steam distribution in Manhattan has been in operation for over 100 years. Between the 1960s and 1970s ConEd's generating stations were updated from coal powered to oil powered. In the 1980s to the 2010s gas-firing capability was added to stations. Currently, ConEd operates 105 miles of steam mains and six generating stations primarily using natural gas for production, with about 60 % of produced steam coming from steam-electric co-generation. As of 2020 total capacity of steam system generating plants had a capacity of 11,425 Mlb hour⁻¹, higher than the existing peak demand of 8,356 Mlb hour⁻¹ [77].

(Shiferl *et al.*, 2025) [78] shows that although inventories expect landfills, wastewater and natural gas distribution to be the largest contributors to CH₄ in the NYC metropolitan area, their tall tower study found that a large contribution to CH₄ emissions came from combustion sources. However, as this study was based on measurements from a tall tower, there is still uncertainty as to how much street-level emissions and rooftop emissions each contribute to the overall city's CH₄ emissions, highlighting the need for a mobile study to quantify solely the street-level CH₄ emissions of the city.

4.2 Methodology

4.2.1 Instrumentation

Mobile surveys took place aboard the New York Atmospheric composition and Air Quality (NYAAQ) program's mobile laboratory. The NYAAQ mobile platform is equipped with a LI-COR 7810 to measure CH₄, CO₂ and H₂O, an Aeris MIRA Ultra Leak Detection System to measure CH₄, C₂H₆ and H₂O and a second Aeris MIRA Ultra to measure N₂O, CO and H₂O. Manufacturer specifications report the LI-COR 7810 as having a response time ($T_{10} - T_{90}$, 0 - 2 ppm) of ≤ 2 s, CH₄ precision (1σ) of 0.60 ppb at 2 ppm with 1 second averaging, CO₂ precision (1σ) of 3.50 ppm at 400 ppm and H₂O precision (1σ) of 45 ppm at 10,000 ppm with 1 second averaging [79]. The Aeris MIRA Ultra CH₄ / C₂H₆ is reported by the manufacturer as having a response time ($1/e$) of ≤ 1 s, CH₄ sensitivity of < 1 ppb s⁻¹ and C₂H₆ sensitivity of < 500 ppt s⁻¹ [80], however, in lab testing of this instrument has shown sensitivity to be lower for CH₄ at 0.14 ppbv over 100 s and C₂H₆ at 0.02 ppbv over 100 s [81]. Finally the manufacturer states the Aeris MIRA Ultra N₂O / CO as having a sensitivity of 500 ppt s⁻¹ for both CO and N₂O [82]. An overview of all instrumentation used aboard the NYAAQ mobile platform is shown in *Table ??*.

The NYAAQ mobile platform samples air from an inlet mounted at the top of the vehicle 1.8 m above ground. Calibrations were made before and after each sampling survey, using the WMO-X2004A standard for CH₄, WMO-X2019 standard for CO₂, WMO-X2014A standard for CO and the NOAA-2006A standard for N₂O. C₂H₆ is calibrated using the internal NOAA calibration scale from 2012 [83]. Internal clock times for each instrument were compared to GPS time before and after each mobile survey to determine any instrumental time drift. During the winter campaign internal clocks of the Aeris MIRA Ultra CH₄ / C₂H₆ and the

Instrument	Species measured	Precision / sensitivity	Measurement frequency	Flow rate
LI-COR 7810	CH ₄ , CO ₂ , H ₂ O	CH ₄ precision (1 σ): 0.60 ppb at 2 ppm CO ₂ precision (1 σ): 3.50 ppm at 400 ppm H ₂ O precision (1 σ): 45 ppm at 10,000 ppm	1 Hz	0.25 L min ⁻¹ in standard configuration
Aeris MIRA Ultra Leak Detection System	CH ₄ , C ₂ H ₆	CH ₄ sensitivity: 0.14 ppbv over 100 s C ₂ H ₆ sensitivity: 0.02 ppbv over 100 s	1 Hz or 10 Hz	0.2 - 0.7 L min ⁻¹
Aeris MIRA Ultra	N ₂ O, CO	N ₂ O and CO sensitivity: 500 ppt s ⁻¹	1 Hz	0.2 - 0.7 L min ⁻¹

Table 4.1: Instrumentation used aboard NYAAQ mobile platform during natural gas sampling surveys

LI-COR 7810 drifted by up to 3 s relative to one another. Drift was corrected using a methodology whereby plumes containing CH₄ enhancements were located, followed by varying the time offset of both enhancements recorded by each instrument across a 7 second window to find the time of best peak correlation. The resulting time corrections were manually checked for consistency and applied to the original data. The drift seen between instruments in the winter campaign was not present for the summer campaign as all instruments were logged on a single computer as opposed to data being taken separately from each instrument.

4.2.2 Leak detection

The gas leak detection algorithm used within NYC again follows the algorithms used in (von Fischer *et al.*, 2017; Weller *et al.*, 2019; Moore *et al.*, 2025) [52, 54, 84] with the adaptations added for the York survey detailed in **Chapter 2**. Backgrounds were determined as a rolling 5 minute median and an enhancement was defined as when the measured concentration of CH₄ was equal to or exceeded a specific multiple over the relevant background, enhancements were detected using both the LI-COR and the Aeris. Enhancement parameters in previous work were set as being greater than 1.1 times the background [54], while the York work in **Chapter 2** and **Chapter 3** showed this parameter could be reduced to 1.05 times over the background, both these enhancement parameters were tested during the NYC sampling surveys. Enhancements that occurred within 1 second of each other were clustered together and considered as the same enhancement. A 10 s window was then placed around the maximum of each enhancement and the ratio and R² of C₂H₆ : CH₄ were calculated using a linear regression, in order to assign each enhancement as biogenic, pyrogenic or thermogenic. Ratios and R² were calculated only using the Aeris instrument due to both C₂H₆ and CH₄ being measured on this

Chapter 4. Methane emissions in New York City

instrument while there is no C₂H₆ measurement associated with the LI-COR, thus removing the need to calculate C₂H₆ to CH₄ lag as was done in **Chapter 2** and **Chapter 3**. Thermogenic enhancements that occur within 30 m of one another were then clustered together and clusters that contained enhancements from more than one drive were considered leak indications (LIs).

As the NYAAQ mobile platform had not undergone a controlled release, as was done with the York WASP platform in **Chapter 2**, there was not a platform specific means of determining leak rates from measurements of CH₄. Although it would be possible to calculate estimates of leak rates in NYC by using York's quantification equation regardless of not being optimised for the NYAAQ platform, it was deemed better to use a different quantification approach. The method used in (Tettenborn *et al.*, 2025) [74], previously described in **Chapter 3**, was employed for this campaign, this uses a quantification approach where leak rates were calculated via peak areas, this quantification equation is re-iterated in **Equation 4.1**.

$$emission\ rate / L\ min^{-1} = exp(1.292 \times \ln(CH_4\ area) - 2.377) \quad (4.1)$$

Where the $\ln(CH_4\ peak\ area)$ is a mean of all enhancements associated with the same leak indication. This approach removes the need to use quantification equations that require the use of peak height, which varies between different instruments, often leading to the need for controlled releases to determine instrument specific quantification equations, or using a different study's quantification equation, which will often lead to inherent error due to not being designed for that platform. Quantification equations used in (Weller *et al.*, 2019) [54] and in **Chapter 2** and **Chapter 3** were also used to allow further comparison for the (Tettenborn *et al.*, 2025) [74] quantification approach. As in **Chapter 2** and **Chapter 3**, leak rates are

not taken as definitive quantifications of a LI's leak rate, but instead informs which one of four bins it lies within: Very small ($< 2 \text{ L min}^{-1}$), small ($2 - 6 \text{ L min}^{-1}$), medium ($6 - 40 \text{ L min}^{-1}$) and large ($> 40 \text{ L min}^{-1}$).

4.2.3 Route planning

The route implemented in the NYC campaigns took place within the boundaries of 111th street and 72nd street to the north and south and 5th avenue and 1st avenue to the west and east. During the campaign each avenue was driven, and there was an attempt to drive every third cross road. Due to temporary road closures, not all roads were accessible on each mobile survey, where a cross road was not available on earlier mobile surveys the next available cross road was sampled and this replacement cross road was sampled on future surveys. In other cases, where only a block of the desired road was closed or inaccessible during a survey, the survey was rerouted in order to then sample the rest of the desired road. A plot showing the route of one of these surveys, coloured by concentration of CH_4 is shown in *Figure 4.1*.

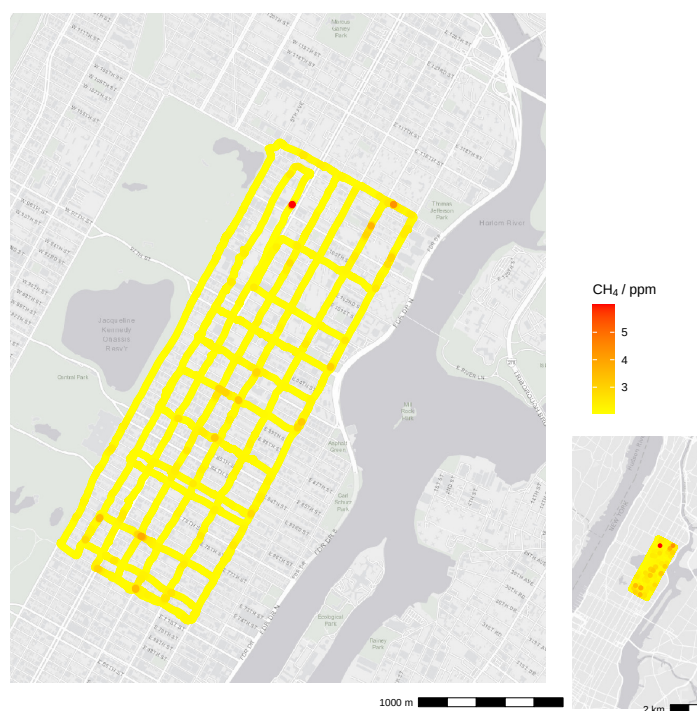


Figure 4.1: Route map of a NYC mobile survey, coloured by CH₄ concentration, with an inset to show the route's position within the island of Manhattan.

The choice of route meant that two neighbourhoods in Manhattan were covered; The Upper East Side and East Harlem. The total area encompasses a population of 173,000 spread across 94,000 housing units; a population of 48,505 in 21,248 housing units in East Harlem (an average of 2.3 per housing unit) and a population of 124,467 in 73,227 housing units in The Upper East Side (an average of 1.7 per housing unit). The two neighbourhoods also differ in terms of median household income, with the Upper East Side having a median household income of \$157,509 while East Harlem's is \$45,031 [85].

5 mobile surveys were undertaken in the winter sampling campaign between the 27th of January and 31st of January 2025 and 5 mobile surveys in the summer sampling campaign between the 2nd of March and

6th of March 2025. The Upper East Side was split into the area under ConEd's district steam supply and the area without. A full overview of each area covered within the mobile survey is shown in **Figure 4.2**.



Figure 4.2: Overview of the area covered in mobile surveys, coloured and labelled by neighbourhood and supply type.

4.2.4 Meteorological data

Meteorological data for the two campaigns was taken from the NOAA Central Park monitoring station. Wind data were filtered to times during which a sampling campaign was being conducted. Over the course of the mobile surveys of the winter campaign, wind speed averaged 3.0 m s^{-1} with calm conditions only occurring 21.4 % of the time. In comparison, during the summer surveys, the wind was much calmer with an average speed of 1.5 m s^{-1} and calm conditions 72.2 % of the time. Average air

temperature during the winter campaign was 4.9 °C, ranging between 1.1 and 10 °C while in summer, average air temperature was 24.8 °C with the temperature ranging between 18.9 and 29.4 °C. A wind rose for each campaign as well as a time series of air temperature is shown in **Figure 4.3**.

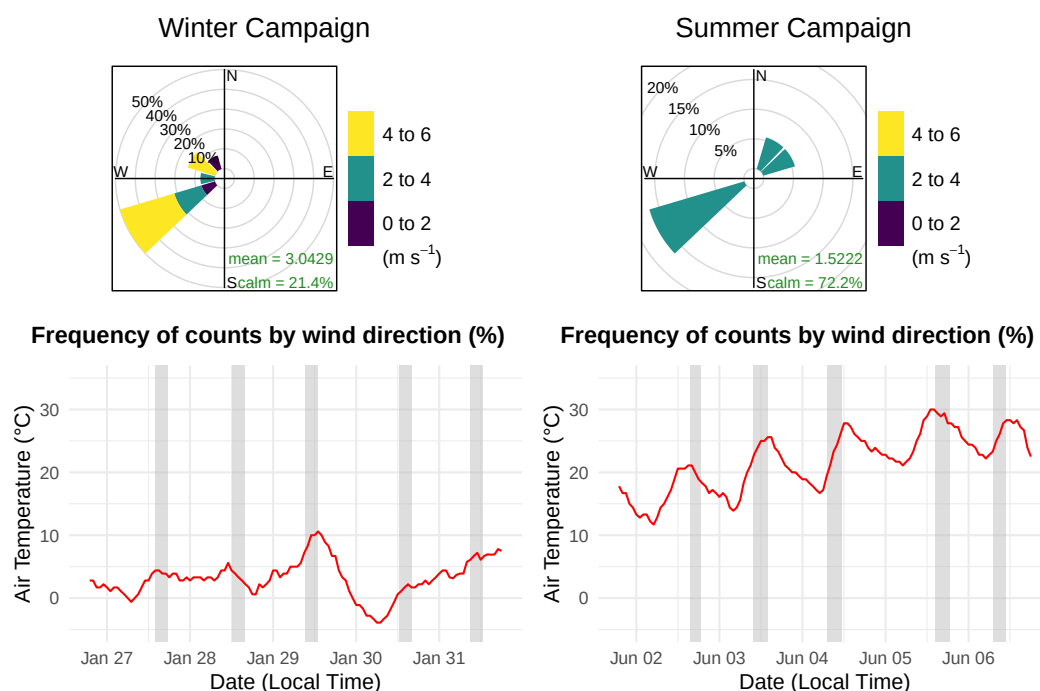


Figure 4.3: Wind rose and air temperature time series of both campaigns. The air temperature time series have been shaded to illustrate when mobile surveys took place.

4.2.5 Inventory data

Inventory data for NYC is taken from the Global Fuel Exploitation Inventory (GFEI) v3 [21], a global 0.1° x 0.1° resolution gridded inventory of CH₄ emissions from oil, gas and coal exploitation. Within the GFEI, data is split into emissions from each fuel type as well as the individual process, for this work, data is taken from the natural gas distribution dataset. 6 grid squares were chosen from the GFEI to provide coverage of the island of Manhattan and the immediate surrounding area, the data set provides emissions in

$\text{Mg year}^{-1} \text{ km}^{-2}$, these are converted into Mg year^{-1} based on the relative size of the grid squares. The GFEI shows that emissions from natural gas distribution were higher in areas of higher population density and the grid cell of interest to the NYC campaigns was predicted to have emissions of $22.38 \text{ Mg year}^{-1}$. A visualisation of the GFEI is shown in **Figure 4.4**, where emission rates have undergone a $\log_{10}$ transformation.

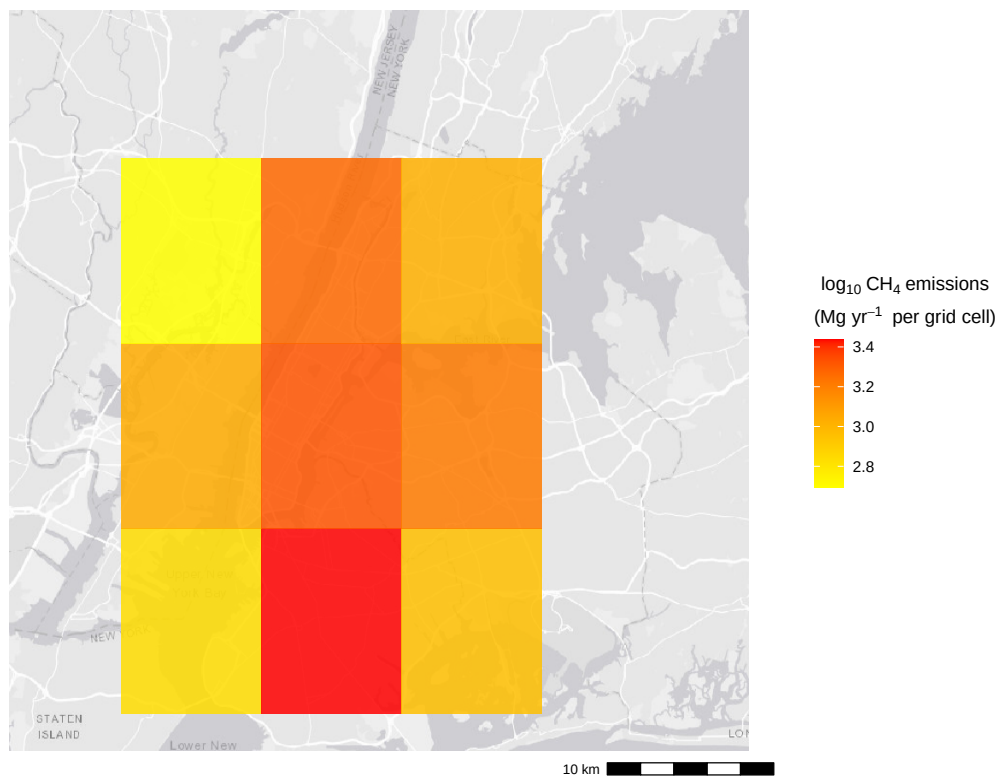


Figure 4.4: Grid squares showing CH₄ emissions from natural gas distribution, according to GFEI v3 [21].

4.3 Results

4.3.1 Winter

4.3.1.1 Leak detection parameters and instrument selection

CH₄ enhancements were detected on both the LI-COR and Aeris instruments. Due to quantification requiring a peak area to be calculated, peaks containing only a singular enhancement point or, not being observed over a measurable distance were omitted. Enhancement parameters of 1.1 times the background and 1.05 times the background were both used and the number of enhancements detected by each were compared, both with and without the distance filter (enhancements must occur over a measurable distance), **Figure 4.5** shows number of enhancements detected on the winter campaign for all iterations of the detection algorithm.

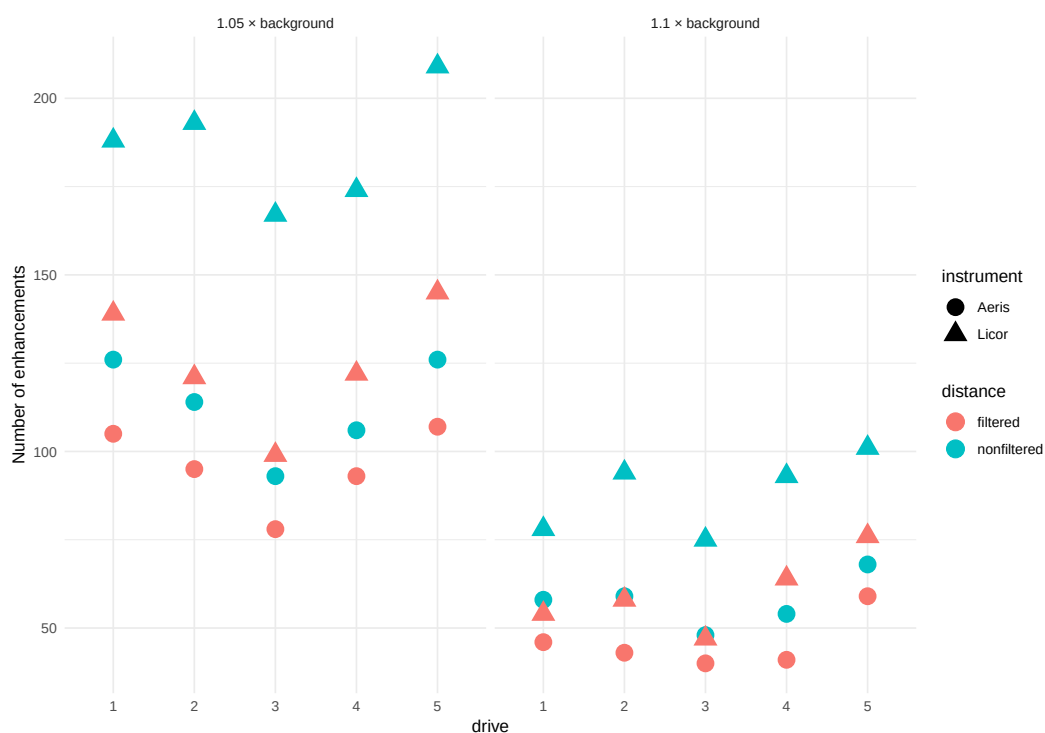


Figure 4.5: Number of enhancements detected during the winter campaign using various enhancement parameters.

Chapter 4. Methane emissions in New York City

In the case of the enhancement parameter being 1.1 times the background, the LI-COR detected more enhancements than the Aeris over all the drives, once peaks were filtered to ensure they covered measurable distances, the number of enhancements reduced for both instruments. In 2 of 5 drives, the filtered LI-COR still located more enhancements than the non filtered Aeris. When the enhancement parameter was reduced to 1.05, 2 of 5 drives had a higher number of enhancements measured with the LI-COR than with the 1.1 times parameter and 4 of 5 drives in the Aeris had higher enhancements. Only 3 of 5 drives had the non filtered LI-COR enhancements higher than the Aeris enhancements and with this parameter whichever instrument had higher number of enhancements before filtering, still had higher enhancements than the other instruments non-filtered enhancement number after distance filtering. It was deemed that an enhancement criteria of 1.05 times the background would be used going forward.

Enhancements were assigned to sources depending on the ratio of $C_2H_6 : CH_4$, while previously, in *Chapter 2* and *Chapter 3*, sources had been assigned using a range of 0.005 to 0.09 for thermogenics, below this the sources were assigned as biogenic and above this pyrogenics. For the New York work, daily composition data of the natural gas composition was provided from the East Rutherford monitoring station of the Transcontinental pipeline. $C_2H_6 : CH_4$ ratios were collated from the week before, during and after the sampling surveys in order to give a representative range of the natural gas composition at that time. By applying the minimum to maximum $C_2H_6 : CH_4$ ratios observed over this time period, the thermogenic range was given as 0.0227 to 0.0387. Biogenic's were still assigned as $C_2H_6 : CH_4 < 0.005$ due to C_2H_6 not being seen in measurable quantities in biogenics [56], pyrogenics were also still assigned as $C_2H_6 : CH_4 > 0.09$ [56, 68]. This results in two new source assignment categories in this chapter, CH_4 enhancements where C_2H_6 is

measurable, but the $C_2H_6 : CH_4$ ratio is lower than the pipeline range and those where C_2H_6 is measurable but $C_2H_6 : CH_4$ is higher than the pipeline range. Thermogenic enhancements occurring within 30 m of one another were then clustered together and clusters were filtered such that they were required to contain enhancements from more than one drive. Resulting in 35 enhancements when Aeris was used to measure enhancements, 43 when the LI-COR was used to measure enhancements.

Additionally, as the $C_2H_6 : CH_4$ ratios were measured on the same instrument, thermogenic enhancements could also be categorised as when the R^2 of $C_2H_6 : CH_4$ was higher than 0.9. Resulting in 46 LIs when Aeris was used to measure enhancements, 63 when the LI-COR was used to measure enhancements. The reason for the difference in the number of LIs detected by each instrument is purely instrumental. As can be seen in **Figure 4.6**, the CH_4 enhancement is much higher and sharper when detected by the LI-COR but wider and shorter when detected by the Aeris. This increase the probability that CH_4 enhancements would fall below the enhancement criteria when measuring with the Aeris, and therefore result in a lower total number of enhancements being detected.

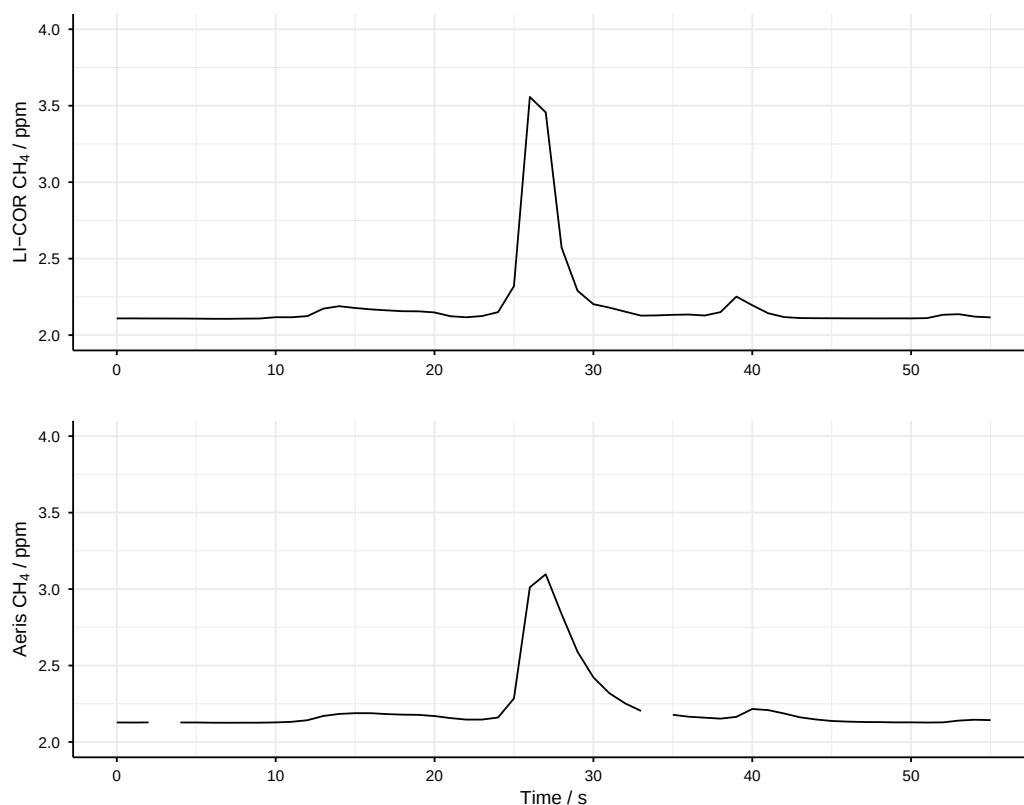


Figure 4.6: Time series of a CH₄ enhancement measured by both the LI-COR and the Aeris.

If both R^2 and ratio were used to determine thermogenic sources, 31 LIs were detected using the Aeris and 36 LIs when using the LI-COR. However, in densely populated cities like NYC, there is a high chance of multiple emissions occurring near the same location, which could potentially lead to incorrect assignments when only factoring in C_2H_6 and CH_4 ratios and their R^2 . Additional filters were added that ensured the R^2 s of $CO_2 : CH_4$, $CO : CH_4$, $C_2H_6 : CO$, $C_2H_6 : CO_2$, $CH_4 : N_2O$ and both CH_4 instrument measurements to any instrument's H_2O measurements were all lower than 0.9. This resulted in 31 LIs measured using Aeris for the enhancements, 36 LIs when LI-COR was used to determine enhancements, 2 of these LIs occur slightly outside of the neighbourhoods of interest so are included within this analysis but excluded from map

projections and neighbourhood analysis, the number of LIs for each instrument and thermogenic assignment criteria is shown in **Table 4.2**. Although there is no visible difference in the number of LIs detected using the ratio and R^2 versus using the ratio, R^2 and additional R^2 s, the latter methodology was selected going forward due to the increased confidence that other, non-thermogenic enhancements would not be associated with definitive thermogenic enhancements.

Thermogenic assignment criteria	Measurement instrument	Number of leak indications
$C_2H_6 : CH_4$ - ratio	LI-COR	43
$C_2H_6 : CH_4$ - ratio	Aeris	35
$C_2H_6 : CH_4$ - R^2	LI-COR	63
$C_2H_6 : CH_4$ - R^2	Aeris	46
$C_2H_6 : CH_4$ - R^2 and ratio	LI-COR	36
$C_2H_6 : CH_4$ - R^2 and ratio	Aeris	31
$C_2H_6 : CH_4$ - R^2 and ratio. Plus additional R^2 s	LI-COR	36
$C_2H_6 : CH_4$ - R^2 and ratio. Plus additional R^2 s	Aeris	31

Table 4.2: Number of leak indications detected on each instrument using all thermogenic assignment criteria.

In order to determine if the instruments detected the same LIs, LIs detected by each instrument were clustered based on a 30 m spatial buffer, if the cluster contained an LI from both LI-COR and Aeris detection methods, the resulting LI was labelled as being located using both detection methods, else it was labelled as the detection method from the specific instrument, the placement of these LIs are shown in **Figure 4.7**.



Figure 4.7: Location of LIs detected during winter campaign, coloured by which instrument they were detected by.

Of the 36 total LIs detected, 31 LIs were detected when either the LI-COR or AERIS was used to measure enhancements, while 5 more LIs were only detected when the LI-COR was used to measure enhancements, no enhancements were detected solely by the AERIS, showing the LI-COR was a better candidate for the detection of CH_4 emissions in cities. Of the 31 LIs detected by both the LI-COR and AERIS, their leak rate categories were investigated to determine the effect, if any, that the instrument has on quantification. Of the 31 LIs, the AERIS identifies 2 as a medium leak rate ($6 - 40 \text{ L min}^{-1}$), 6 as small ($2 - 6 \text{ L min}^{-1}$) and 23 as very small ($< 2 \text{ L min}^{-1}$). The LI-COR identified 2 as medium, 6 as small and 23 as very small. This gives confidence in using the (Tettenborn *et al.*, 2025) [74] equation as an approach for any instrument used on a mobile platform that has not undergone a controlled release, due to no difference in quantification when either instrument was used.

4.3.1.2 Source types detected per drive

Over the 5 drives 597 OPs were located in total and were assigned to various sources based on their $C_2H_6 : CH_4$ ratios, as discussed previously; 21 could not be assigned to a source type, 18 were assigned as biogenic, 12 were assigned as pyrogenic, 27 enhancements had measurable C_2H_6 but a $C_2H_6 : CH_4$ ratio that was higher than the pipeline range but not high enough to be classed as pyrogenic, 254 had a $C_2H_6 : CH_4$ lower than the pipeline range but not low enough to be classed as biogenic and 265 were assigned thermogenic. The thermogenic source type was subdivided into those that conformed with the further R^2 criteria and those that did not. 217 of the 265 thermogenics conformed to these further criteria while 48 did not. An overview of each source type seen per drive is shown below in *Figure 4.8* and *Table 4.3*.

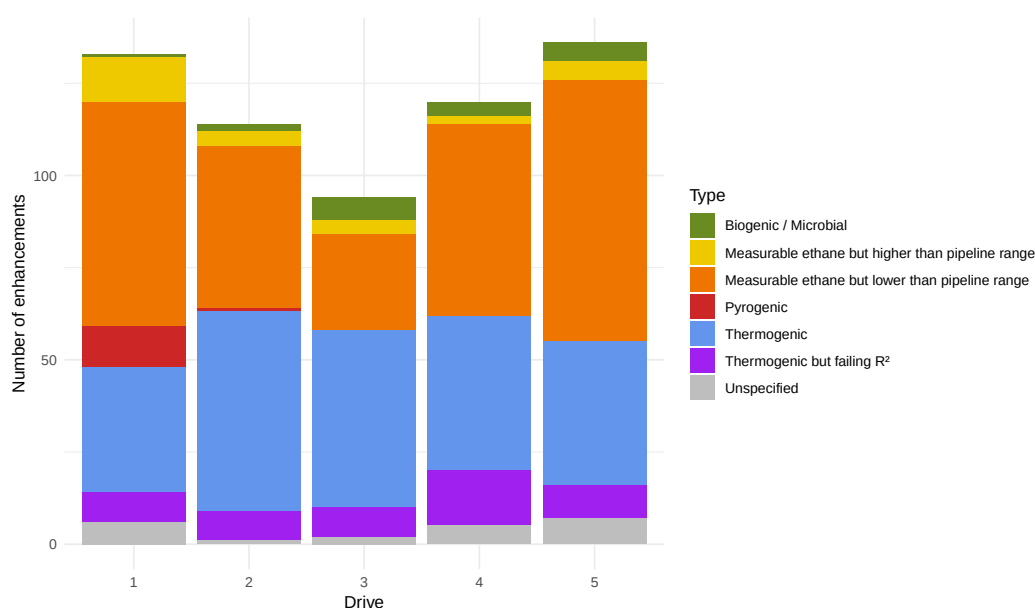


Figure 4.8: Number of enhancements detected per drive in the winter campaign, coloured by source type.

The average temperature during the mobile surveys was taken from the NOAA Central Park station and compared to the number of enhancements

of each source type per drive, shown in **Figure 4.9**. No apparent relationship between temperature and number of thermogenic or pyrogenic enhancements was visible during this analysis, there was however a slight trend noticeable in the fraction where enhancements had a measurable C_2H_6 but the ratio was lower than the pipeline range, the number of enhancements decreased between drive 1 and drive 2 along with temperature and increased between drive 4 and drive 5 along with temperature. However, this trend did not hold true for drive 3 which had the lowest number of these enhancements despite having the highest average temperature of the winter campaign, additionally, despite the relationships noted previously, the number of enhancements seen on drive 2 compared with drive 4 did not follow their associated temperatures. Overall, it could be stated that in winter, the effect of air temperature on the number of enhancements was low.

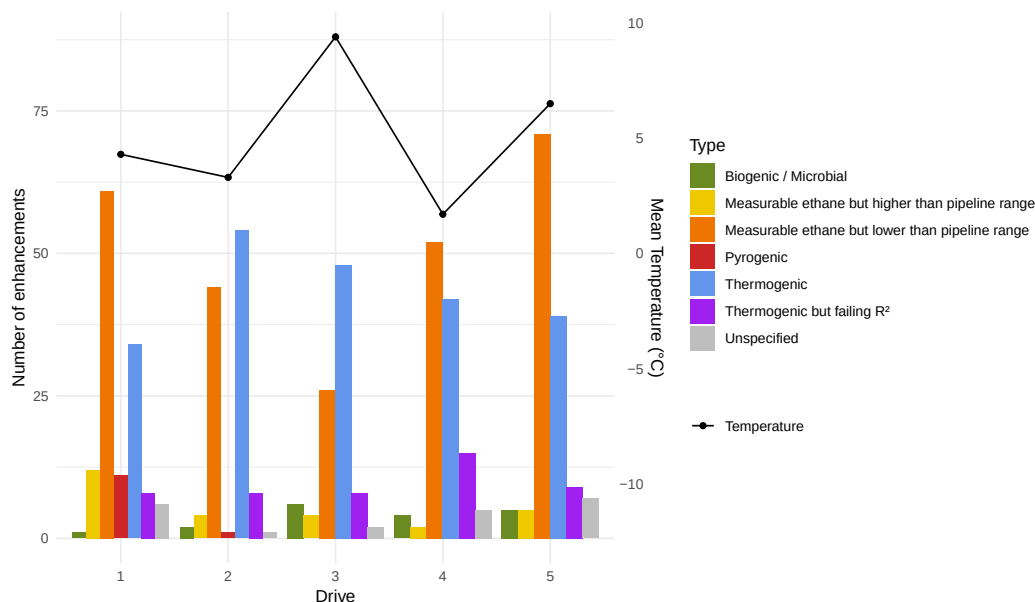


Figure 4.9: Number of enhancements of each source type detected per drive in winter, with daily average temperature overlaid.

Chapter 4. Methane emissions in New York City

Drive no.	Thermogenic	Thermogenic (failing R ²)	Biogenic / Microbial	Pyrogenic	Higher than pipeline range	Lower than pipeline range	Unspecified
1	34	8	1	11	12	61	6
2	54	8	2	1	4	44	1
3	48	8	6	0	4	26	2
4	42	15	4	0	2	52	5
5	39	9	5	0	5	71	7

Table 4.3: Number of each source type detected per drive in the winter campaign.

The drive-by-drive analysis of source types shows that the area is dominated by thermogenics, along with enhancements where there is measurable C₂H₆ but the ratio is lower than that of the pipeline range, with 2 of the 5 drives having thermogenics as the most frequently detected OP type and the remaining 3 drives having the latter as the most dominant. CH₄ emissions in this area are therefore most likely to be occurring from gas mains leaks (for the thermogenic fraction), but also the fraction where the C₂H₆ : CH₄ ratio is lower than the pipeline range.

4.3.1.3 Comparison of quantification equations

When using the LI-COR to measure enhancements and the quantification equation present in (Tettenborn *et al.*, 2025) [74], 36 LIs in total were detected, with 2 assigned as a medium leak rate (6 - 40 L min⁻¹), 6 were small (2 - 6 L min⁻¹) and 28 were very small (< 2 L min⁻¹). Previous quantification equations in (Weller *et al.*, 2019) [54] and in **Chapter 2**, reiterated in **Equation 4.2** and **Equation 4.3**, quantify based on maximums of peak heights as opposed to peak area. The quantification equation present in (Weller *et al.*, 2019) [54] has been used in a range of studies but as discussed in **Chapter 2**, it is derived as a platform specific equation, hence the need for the newer equation in **Chapter 2**, for use within a different platform.

Chapter 4. Methane emissions in New York City

$$\ln(\text{excess CH}_4/\text{ppm}) = -0.988 + 0.817 \times \ln(\text{emission rate} / \text{L min}^{-1}) \quad (4.2)$$

$$\ln(\text{max excess CH}_4 / \text{ppm}) = -1.2668 + 0.6323 \times \ln(\text{emission rate} / \text{L min}^{-1}) \quad (4.3)$$

Applying the (Weller *et al.*, 2019) [54] equation to the 36 LIs results in 3 being assigned as medium, 14 as small and 19 as very small, while the equation designed in **Chapter 2** (using mean CH₄ response to avoid bias, as discussed in **Chapter 3**), assigns 10 as medium, 18 as small and 8 as very small. As can be seen in **Figure 4.10**, the (Weller *et al.*, 2019) [54] equation quantifies a much smaller range of leak rates than the equation derived in **Chapter 2** and additionally, misses some of the smaller leak rate LIs identified with the (Tettenborn *et al.*, 2025) [74]. On the other hand the quantification equation developed for the York surveys in **Chapter 2**, results in a much larger range of leak rates, but is weighted much higher than both of the other methodologies (Weller *et al.*, 2019; Tettenborn *et al.*, 2025) [54, 74]. This shows the shortcomings of quantification equations like those present in **Chapter 2** and (Weller *et al.*, 2019) [54], because they are based on peak height for quantification and are designed as instrument and platform specific quantification equations, when a different platform attempts to use these equations, any differences can lead to large variation in predictions of leak rate, strengthening the argument to use the (Tettenborn *et al.*, 2025) [74] quantification equation for platforms that have not undergone controlled releases.

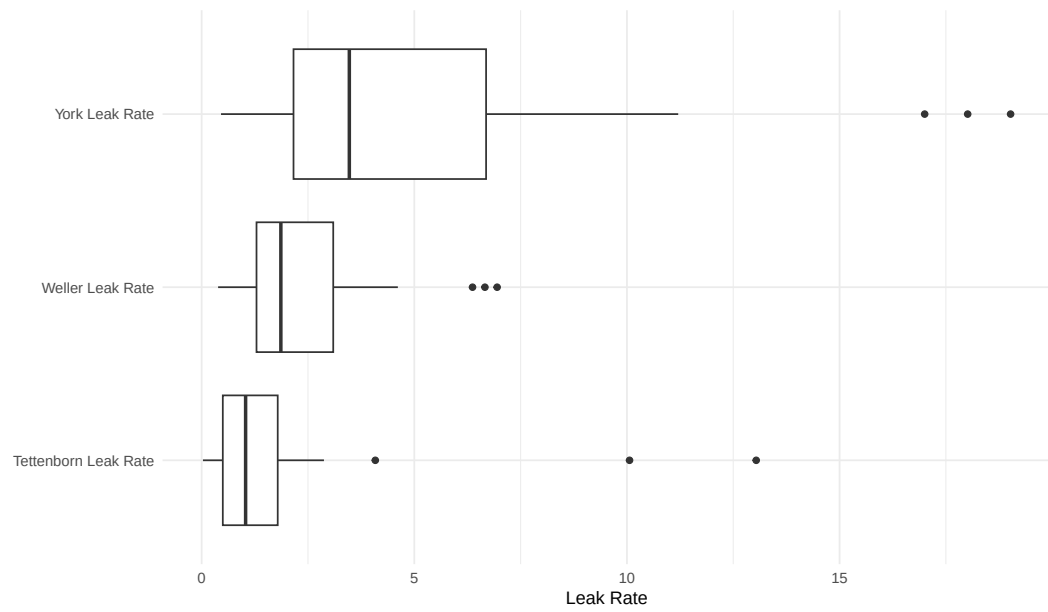


Figure 4.10: Box-plots illustrating each LI's leak rate calculated with the three main leak quantification equations.

4.3.1.4 Neighbourhood comparison

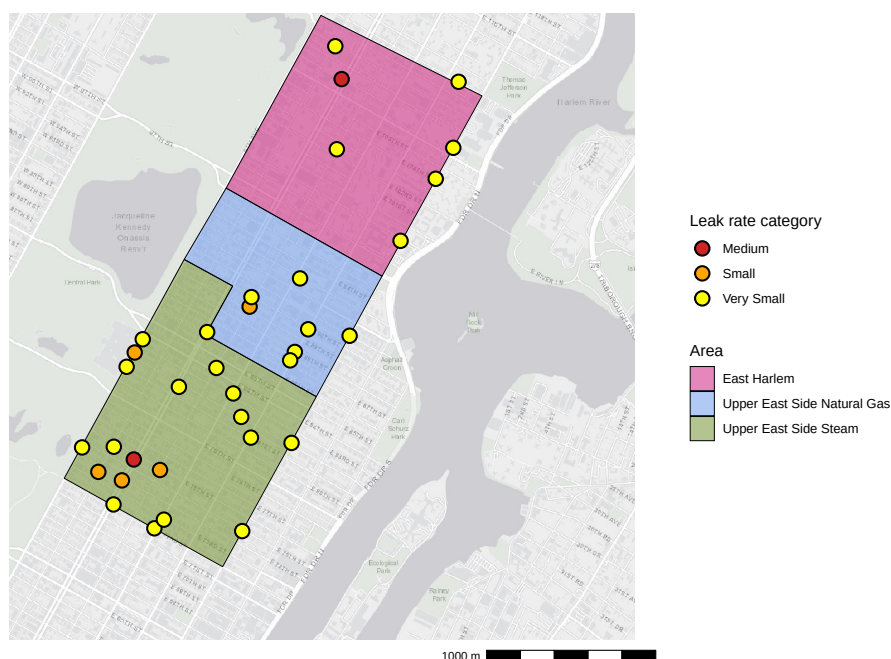


Figure 4.11: LIs detected during the winter campaign, coloured by leak rate overlaid on polygons coloured by neighbourhood.

Of the 34 LIs that were recorded within neighbourhood bounds, each was assigned to the appropriate neighbourhood or supply area in which it was detected (East Harlem with only natural gas supply, Upper East Side with only natural gas supply or Upper East Side with natural gas and steam supply). LIs that fell outside of these neighbourhood boundaries were omitted from this analysis, resulting in 7 LIs being observed in East Harlem resulting in an LI km^{-1} of 0.24, 7 were located in the Upper East Side under only natural gas supply resulting in an LI km^{-1} of 0.62 and 20 LIs were located in the Upper East Side area that had steam supply as well as natural gas supply resulting in 1.09 LI km^{-1} . Locations of the 34 LIs are shown in **Figure 4.11**. When assigned to leak rate categories, East Harlem had 6 very small and 1 medium, the Upper East Side with natural gas

supply had 6 very small and 1 small and the Upper East Side with steam supply had 15 very small, 4 small and 1 medium.

4.3.2 Summer

Mobile surveys were repeated in the summer using the methodology proven to be effective by the winter campaign, enhancements had to be 1.05 times higher than the calculated background, measured on the LI-COR, thermogenics were then assigned using the R^2 and ratios methodology discussed in the Winter, the thermogenic $C_2H_6 : CH_4$ ratio window was again calculated from the week proceeding to the week after the summer campaign, resulting in a window of 0.0188 to 0.0246, the fraction where $C_2H_6 : CH_4$ ratio was lower than pipeline range and the fraction where this ratio was higher than the pipeline range were adjusted accordingly, while biogenic and pyrogenic $C_2H_6 : CH_4$ assignments remained constant. Over the 5 mobile surveys in the summer, a total of 1010 OPs were detected, these were then assigned to their source types per drive as seen in *Figure 4.12*, with a breakdown in *Table 4.4*.

4.3.2.1 Source types detected per drive

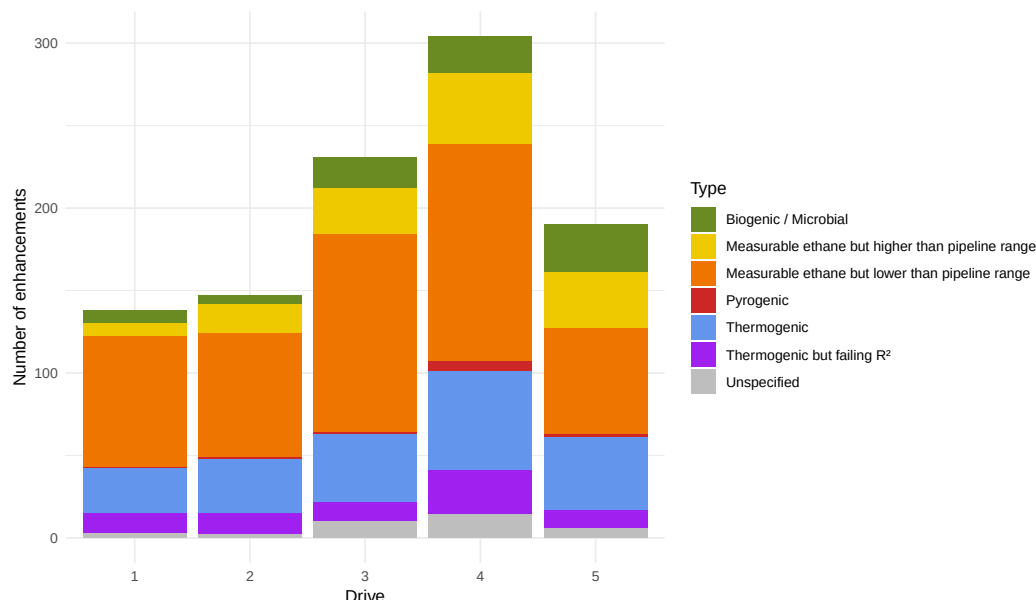


Figure 4.12: Number of enhancements detected per drive in the summer campaign, coloured by source type.

Drive no.	Thermogenic	Thermogenic (failing R ²)	Biogenic / Microbial	Pyrogenic	Higher than pipeline range	Lower than pipeline range	Unspecified
1	27	12	8	1	8	79	3
2	33	13	5	1	18	75	2
3	41	12	19	1	28	120	10
4	60	27	22	6	43	132	14
5	44	11	29	2	34	64	6

Table 4.4: Number of each source type detected per drive in the summer campaign.

Of the 1010 OPs detected over 5 drives 35 could not be assigned to a source type, 83 were assigned as biogenic, 11 were assigned as pyrogenic, 131 had measurable C₂H₆ but a higher C₂H₆ : CH₄ ratio than pipeline range, 470 had C₂H₆ : CH₄ lower than pipeline range and 280 were assigned thermogenic. The thermogenic source type was subdivided into those that conformed with the further R² criteria (as detailed in *Section 4.3.1.1*) and those that did not. 205 of the 280 thermogenics conformed to

these further criteria while 75 did not. The drive-by-drive analysis of source types shows, again, that the survey area was dominated by the fraction with measurable C_2H_6 but a $C_2H_6 : CH_4$ ratio lower than that of the pipeline range. The average temperature during the mobile surveys was again taken from the NOAA Central Park station and compared to the number of enhancements of each source type per drive, shown in **Figure 4.13**. The number of thermogenics, biogenics, enhancements with measurable C_2H_6 but $C_2H_6 : CH_4$ ratio lower than pipeline range and the fraction with $C_2H_6 : CH_4$ ratio higher than pipeline range all have a slight relationship seen between the number of each enhancement detected and the average temperature measured by the NOAA site. For thermogenics this likely reflects that increased temperature leads to an increased pressure in the pipes and therefore a larger number of emissions from leaks that would be more likely to be detected by the mobile surveys. The biogenic / microbial fraction's temperature dependence is likely caused by increased activity of microbial sources, such as sewage, with increased temperatures. The other fractions temperature dependence is hard to justify without knowledge of the specific source these originate from. Overall, unlike in winter, temperature and number of enhancements were much more closely related.

Chapter 4. Methane emissions in New York City

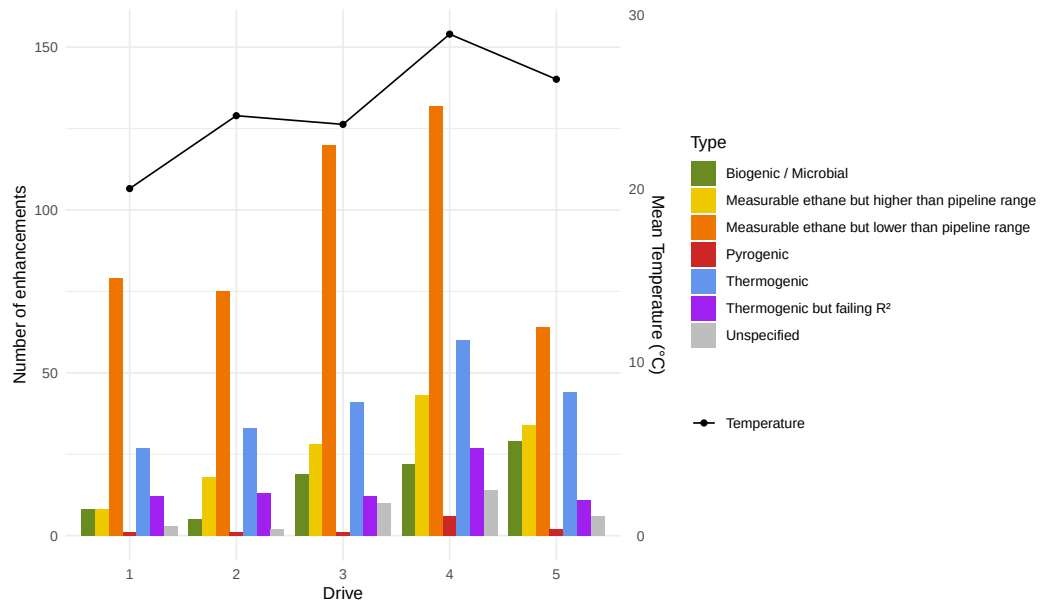


Figure 4.13: Number of enhancements of each source type detected per dive in summer, with daily average temperature overlaid.

4.3.2.2 Neighbourhood comparison



Figure 4.14: LIs detected during the summer campaign, coloured by leak rate overlaid on polygons coloured by neighbourhood.

Of the 205 thermogenic OPs detected, after clustering across 30 m and filtering those clusters to only keep those containing OPs from multiple drives, 29 LIs were detected in total. Of these 29 LIs, there were 6 LIs observed in East Harlem, with only natural gas supply, resulting in an LI km^{-1} of 0.20, 3 were located in the Upper East Side under only natural gas supply resulting in an LI km^{-1} of 0.27 and 20 LIs were located in the Upper East Side area that had steam supply as well as natural gas supply resulting in 1.09 LI km^{-1} . The locations of these LIs are shown in **Figure 4.14**. When assigned to leak rate categories, East Harlem had 3 very small, 2 small and 1 medium, the Upper East Side with natural gas supply had 1 very small and 2 small and the Upper East Side with steam supply had 6 very small, 6 small and 8 medium.

4.3.3 Summer vs Winter

In winter the median number of OPs detected was 120, with the lowest number of OPs detected on a drive being 94 and the largest being 136. In summer, the median number of OPs detected per drive was 190, with the lowest being 138 and the highest being 304. The difference between the median number of OPs detected per drive in summer compared to winter was 1.6 times higher in the summer. For thermogenics, a median of 42 OPs were detected in winter (lowest number of 34, highest of 54) and 41 in summer (lowest of 27, highest of 60). For those assigned as thermogenic but failing the R^2 tests, the median number of OPs detected in winter was 8 (lowest of 8 and highest of 15), in summer the median was 12 (lowest of 11, highest of 27). For biogenic / microbial, the winter median was 4 (lowest of 1, highest of 6) and summer median was 19 (lowest of 5, highest of 29). Pyrogenic winter median was 0 (lowest of 0, highest of 11), pyrogenic summer median was 1 (lowest of 1, highest of 6). Enhancements with measurable C_2H_6 but a $C_2H_6 : CH_4$ ratio lower than the pipeline range winter median was 52 (lowest of 26, highest of 71), summer median was 79 (lowest of 64, highest of 132). Enhancements with measurable C_2H_6 but a $C_2H_6 : CH_4$ ratio higher than the pipeline range winter median was 4 (lowest of 2, highest of 12), summer median was 28 (lowest of 8, highest of 43). Finally for the OPs unable to be assigned, in winter the median number was 5 (lowest of 1, highest of 7) and in summer the median was 6 (lowest of 2, highest of 14). An overview of the median number of OP types detected in each campaign is shown in *Table 4.5*.

Chapter 4. Methane emissions in New York City

OP type	Winter (Median number detected)	Summer (Median number detected)
Thermogenic	42	41
Thermogenic (failing R^2)	8	12
Biogenic / Microbial	4	19
Measurable C_2H_6 ($C_2H_6 : CH_4$ lower than pipeline range)	52	79
Measurable C_2H_6 ($C_2H_6 : CH_4$ higher than pipeline range)	4	28
Pyrogenic	0	1
Unspecified	5	6

Table 4.5: Median number of each OP source type detected in summer vs winter campaigns.

There is noticeable growth between summer and winter surveys in terms of the median number of OPs detected, however, this growth is small, or not seen for OPs classed as unspecified, thermogenic or the thermogenics that fail further R^2 tests and pyrogenics. For thermogenics, this lack of change is easily explainable, even if demand of natural gas is lower in summer than winter, this would not affect the amount of natural gas being distributed, the pipework would stay at pressure in both seasons leading to natural gas being emitted from leaks regardless. For the unspecified OPs, the lack of change gives confidence in the algorithms source identification, these OPs should not be influenced by external factors such as air temperature as they are instead an error brought about by the instrumentation being unable to provide usable results to compute the source analysis, therefore should be relatively constant between surveys. Growth was seen noticeably in the biogenic / microbial fractions, the fraction where C_2H_6 was detectable but the $C_2H_6 : CH_4$ ratio was higher than the pipeline range and enhancements where there is measurable C_2H_6 but a $C_2H_6 : CH_4$ ratio lower than the pipeline range. For biogenics, this is likely due to the increased air temperature as explained in *Section 4.3.2.1* the number of biogenic OPs detected is closely related to air temperature, in warmer environments the methanogenic bacteria present in sewer systems would have more activity and therefore

result in a larger off-gassing of CH_4 emissions from sewers. The fraction where C_2H_6 was measurable but the $\text{C}_2\text{H}_6 : \text{CH}_4$ ratio was higher than the pipeline range and the fraction where there is measurable C_2H_6 but a $\text{C}_2\text{H}_6 : \text{CH}_4$ ratio lower than the pipeline range are harder to explain without knowledge of the specific source of these enhancements.

Figure 4.15 and *Figure 4.16* further explore the relationship between frequency of detection of OP type with temperature and wind speed. Winter drives are now labelled 1 to 5 while summer drives are labelled 6 to 10. *Figure 4.15* shows the fractions where there is measurable C_2H_6 but a $\text{C}_2\text{H}_6 : \text{CH}_4$ ratio lower than the pipeline range and where C_2H_6 was measurable but the $\text{C}_2\text{H}_6 : \text{CH}_4$ ratio was higher than the pipeline range exhibit some correlation with increasing temperatures. However, as *Figure 4.16* shows, these days also exhibited lower wind speeds, which could potentially increase the probability of detecting certain enhancements that otherwise would have been too disperse in higher wind conditions. There is however still more work required to understand the nature of these two sources before fully understanding why these trends occur.

Chapter 4. Methane emissions in New York City

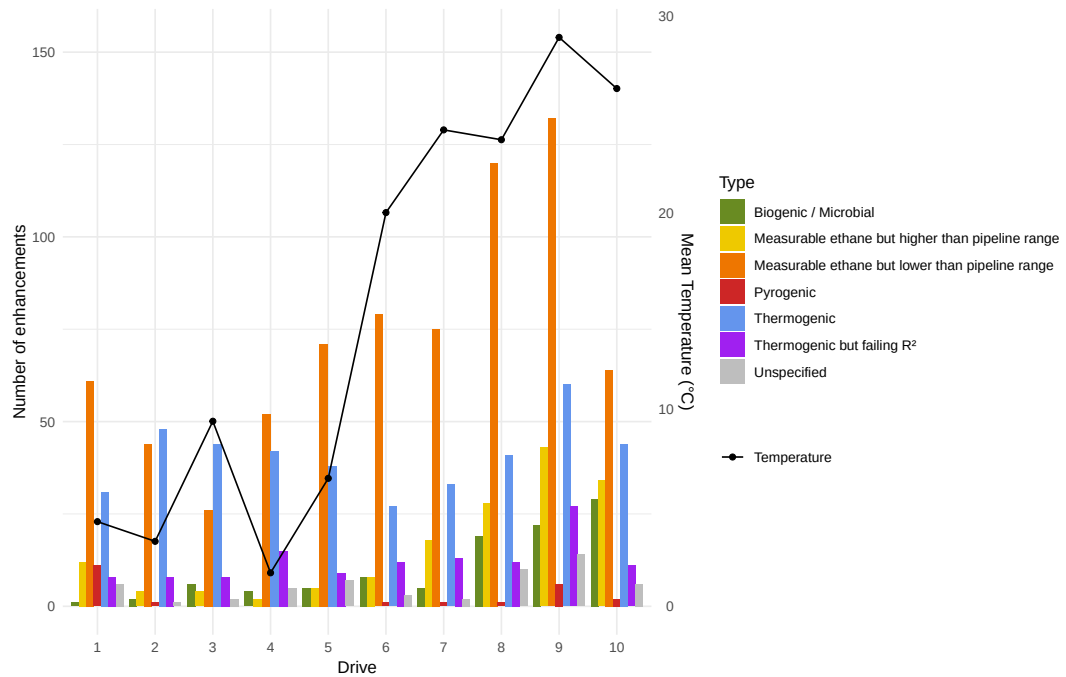


Figure 4.15: Frequency of detection of OPs by source type for Winter (Drives 1-5) and Summer (Drives 6-10) campaigns plotted against the mean temperature observed during the drives.

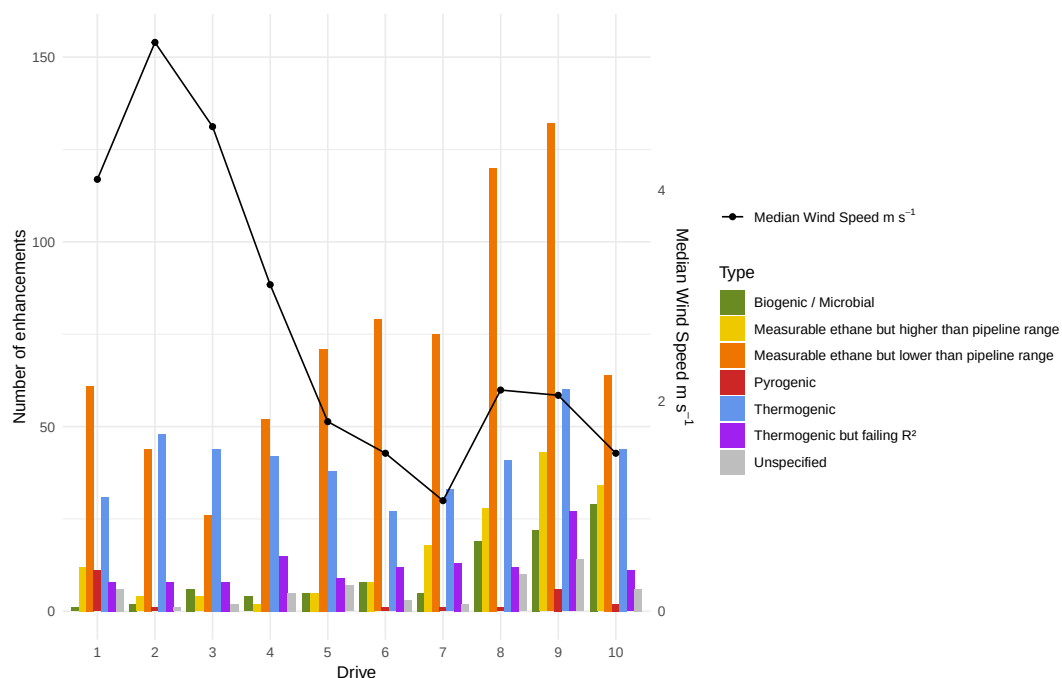


Figure 4.16: Frequency of detection of OPs by source type for Winter (Drives 1-5) and Summer (Drives 6-10) campaigns plotted against the median wind speed observed during the drives.

Although there was little difference in the number of thermogenic OPs detected in winter versus summer, when the LI identification took place, this resulted in the winter campaign detecting 34 LIs within neighbourhood bounds, while the summer campaign detected 29 LIs within the same bounds. As with the LI-COR versus Aeris comparison in *Section 4.3.1.1*, summer and winter LIs were clustered within 30 m, if a cluster contained an LI detection from both summer and winter campaigns it could be regarded as being a persistent LI that had not been repaired between the two campaigns. An LI that was only detected in winter but not summer is likely one that has been repaired in the months between, while an LI that was present in summer but not winter is likely a newly formed LI. Location of all LIs detected in summer and winter, with the respective campaign during which they were detected is shown in *Figure 4.17*.

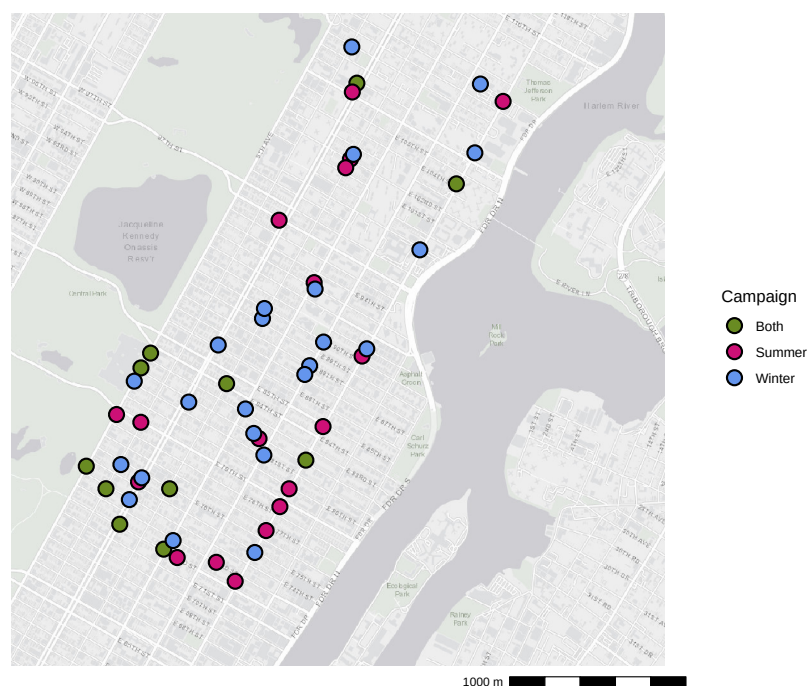


Figure 4.17: Location of LIs detected across both campaigns, coloured by the campaign they were detected during.

Between the 34 LIs detected in winter and the 29 detected in summer, 11 LIs were detected in both, 23 were winter only and 18 were summer only. The 11 persistent LIs had their leak rate categories compared to determine the effect of changing seasons on these LIs. Of the 11, 5 maintained the same leak rate category, the remaining 6 were all placed into larger leak rate bins in summer than winter, 2 LI went from very small ($< 2 \text{ L min}^{-1}$) to small ($2 - 6 \text{ L min}^{-1}$), 1 went from small to medium ($6 - 40 \text{ L min}^{-1}$) and 3 went from very small to medium. Two of these persistent LIs were located in East Harlem (one having a persistent leak rate, the other being one of the 2 that went from very small to small), all other persistent LIs were located in the Upper East Side under steam supply, no persistent LIs were situated in the Upper East Side with only natural gas supply. For winter only LIs, 4 were situated in East Harlem, 7 in the Upper East Side with natural gas and 11 in

the Upper East Side with steam supply. For summer only LIs, again 4 were situated in East Harlem, 3 in the Upper East Side with natural gas supply and 11 in the Upper East Side with steam supply. This showed that in terms of number of LIs East Harlem and the Upper East Side with steam supply stayed consistent with the number of leaks, with the Upper East Side with natural gas being the only neighbourhood where there was a net loss in LIs (more leaks repaired than new ones formed). A summary of the number of LIs in each neighbourhood, and which campaign they were detected in, is shown in **Table 4.6**.

Neighbourhood	LIs present in both campaigns	LIs present only in winter	LIs present only in summer
East Harlem	2	4	4
Upper East Side (Natural Gas)	0	7	3
Upper East Side (Steam)	9	11	11

Table 4.6: Number of LIs in each neighbourhood and the campaign they were detected during.

A comparison of summer only and winter only leak rate bins also took place, this can be seen in detail in **Table 4.7**. For East Harlem in the winter, all 4 LIs were in the very small leak rate category, while in summer, 3 were very small, 1 was small. For the Upper East side under natural gas distribution, in winter, 6 were very small, 1 was small, while in the summer, there was 1 LI in the very small category and 2 medium. For the Upper East Side with steam supply, in the winter, there were 9 very small, 1 small and 1 medium, in the summer, 4 were very small, 3 were small and 4 were medium.

Chapter 4. Methane emissions in New York City

Leak Rate Bin	East Harlem Winter	East Harlem Summer	Upper East Side (Natural Gas) Winter	Upper East Side (Natural Gas) Summer	Upper East Side (Steam) Winter	Upper East Side (Steam) Summer
Very small (< 2 L min ⁻¹)	4	3	6	1	9	4
Small (2 - 6 L min ⁻¹)	0	1	1	2	1	3
Medium (6 - 40 L min ⁻¹)	0	0	0	0	1	4
Large (> 40 L min ⁻¹)	0	0	0	0	0	0

Table 4.7: Number of LIs in each leak rate bin for each neighbourhood and for each campaign.

This shows that although the number of LIs stayed consistent in two of the neighbourhoods, both neighbourhoods total leak rates actually increased in the summer. For the Upper East Side with natural gas, the only neighbourhood with a net loss in the number of LIs, there could still be an argument made that because of the new LIs that were detected in summer being higher leak rate categories, this neighbourhood too has an increased emission of CH₄ from natural gas distribution in the summer.

4.4 Conclusions

The summer and winter mobile surveying campaigns provide an initial insight into the street level emissions of CH₄ in NYC and a start to understanding how the city's street-level emissions contribute to the overall city emissions. Enhancement parameters were set as 1.05 times the calculated rolling background after showing that this resulted in the detection of more CH₄ enhancements when either the LI-COR 7810 or Aeris MIRA Ultra CH₄ / C₂H₆ were used to detect enhancements. As in the York methodology, detailed in *Chapter 2* and *Chapter 3*. CH₄ enhancements are assigned to a source type before further LI identification steps took place, a range of assignment criteria were used, with the two strictest being, firstly when both C₂H₆ : CH₄ ratio was within the city's natural gas ratio and C₂H₆ : CH₄ R² was ≤ 0.9, secondly, when the

previous is true but also that the R^2 of $\text{CO}_2 : \text{CH}_4$, $\text{CO} : \text{CH}_4$, $\text{C}_2\text{H}_6 : \text{CO}$, $\text{C}_2\text{H}_6 : \text{CO}_2$, $\text{CH}_4 : \text{N}_2\text{O}$ and both CH_4 instrument measurements : any instrument's H_2O measurements were all lower than 0.9. Although there was no further reduction in the number of LIs detected using this criteria, compared to using only the $\text{C}_2\text{H}_6 : \text{CH}_4$ ratio and R^2 , this methodology was still selected to assign thermogenic signals, due to the complexity of emission sources that occur within a city like NYC.

LI identification using both the LI-COR and Aeris to detect CH_4 enhancements, showed that of the 36 total LIs detected, 31 were detected by both instruments, while 5 were only detected when the LI-COR was used to detect CH_4 enhancements, this determined that LI-COR would be used to calculate the CH_4 enhancements for mobile surveys.

During the Winter campaign, 597 OPs were detected across the 5 drives, with the majority of OPs being assigned to the thermogenic fraction and the fraction where C_2H_6 was measurable but the $\text{C}_2\text{H}_6 : \text{CH}_4$ ratio was lower than that of the pipeline range. Of the 36 LIs that were detected, 2 were assigned as a medium leak rate (6 - 40 L min^{-1}), 5 were small (2 - 6 L min^{-1}) and 27 were very small (< 2 L min^{-1}). 34 of the 36 LIs detected in winter were within the the bounds of the three sampled neighbourhoods, the majority of LIs, and the largest leak rate LIs were located within the Upper East Side with steam supply.

In the summer campaign, a total of 1010 OPs were detected across 5 drives, again the most dominant source type was the fraction where C_2H_6 was measurable but $\text{C}_2\text{H}_6 : \text{CH}_4$ ratio was lower than that of the pipeline range, followed by the thermogenic fraction. The summer campaign resulted in the detection of 29 LIs, 10 of which were in the very small leak rate category, 10 in the small, and 9 medium, again the majority of LIs occurred in the Upper East Side with steam supply.

Comparisons between summer and winter campaigns showed visible growth in the median number of enhancements detected per drive for the

biogenic / microbial fraction and the fraction where $C_2H_6 : CH_4$ was higher than the pipeline range, but little difference in all other source types. It is also noted that although the number of LIs, within neighbourhood bounds, decreases from winter to summer (34 to 29), the majority of these reductions occur in the Upper East Side with natural gas supply (the only neighbourhood with a net loss in the number of LIs), the other neighbourhoods had an equal number of new LIs to repaired LIs. Additionally, leak rates increased in all neighbourhoods from winter to summer, meaning that street level thermogenic emissions of CH_4 in summer months are likely to be higher than in winter months, even with a reduction in the number of LIs.

Emissions from the survey area are high as expected from the GFEI data, however, the results of the mobile campaigns shows that the distribution of these emissions is not uniform between the neighbourhoods, this again shows the requirement for on-ground mobile surveys, that can operate at a much higher spatial resolution to give much more localised information on distribution of emissions within cities. This work raises questions as to why there is an increased frequency in the number of LIs that occur within the steam heat supply region; many of these LIs occur within the same vicinity as steam vents, such as outside the MET museum. As there is a great difference between the steam supply region and non-steam supply region of the Upper East Side, notably in the $LI\ km^{-1}$ metric, it suggests that the increase in LIs is in some way related to the steam heat distribution. An argument may be made that natural gas is carried within the steam if there was a leak within the one of the natural gas turbines used to create the steam, however, if the LI was a natural gas / steam co-emission it would be expected that H_2O would be seen within the enhancements, but the H_2O filter within the thermogenic assignment would then filter these out, suggesting this hypothesis is unlikely. Another argument is that the heat from the steam pipework places increased

mechanical stress on the natural gas pipework, through increased pressure, resulting in an increase in LI formation. The results of the summer drives give confidence to this theory, after showing that the number of thermogenics detected varied in relation to daily average temperature. In order to truly assess the cause of increased LIs within the steam region, further analysis would have to take place, including direct sampling of the steam vents.

Additionally, this work highlights that although adapting source identification for thermogenics to base their $C_2H_6 : CH_4$ ratio off pipeline data and require a high R^2 between C_2H_6 and CH_4 , results in higher confidence that the assigned sources are from pipeline leaks. It does introduce three new source types not present in *Chapter 2* and *Chapter 3*. The first of these is where the $C_2H_6 : CH_4$ ratio is within the range of pipeline gas but the R^2 correlation between C_2H_6 and CH_4 is lower than required. The second, where the $C_2H_6 : CH_4$ ratio is higher than that of the biogenic / microbial fraction, therefore containing measurable quantities of C_2H_6 , but the ratio is still lower than that of the pipeline range. The final new source type is where the $C_2H_6 : CH_4$ ratio is higher than the pipeline range, but still not high enough to be confidently assigned as a pyrogenic emission. Previously, all three of these fractions would have been grouped within the thermogenic assignment, but by using an instrument that measures both C_2H_6 and CH_4 allows for the introduction of the R^2 stage of analysis and knowledge of the pipeline's exact $C_2H_6 : CH_4$ range has allowed the stricter assignment of thermogenics. The exact sources of these are still unclear and would require further analysis to determine their origin, however, their frequency of detection highlights a potential overprediction in frequency of thermogenics, that may have been present in *Chapter 2* and *Chapter 3* and a potential unexplored source of CH_4 emissions within cities.

Chapter 5

Offshore flaring emissions

5.1 Introduction

The Global Methane Pledge (GMP) brought about during COP26 requires its signatories to reduce their 2020 CH₄ emissions by 30 % by 2030 [46]. This increased effort is, in part, due to CH₄'s role as a potent greenhouse gas, with a global warming potential (GWP) 28 times greater than CO₂ over a 100-year timescale and 84 times higher over a 20-year timescale [12]. 65 % of all CH₄ emissions are thought to be anthropogenic in nature and atmospheric CH₄ has seen a consistent growth rate of > 5 ppb year⁻¹ since 2007, with 2021 and 2022 seeing growth rates of 17.8 ppb year⁻¹ and 14 ppb year⁻¹ respectively [13], therefore understanding and reducing anthropogenic CH₄ is seen as a key goal for global warming mitigation.

One of the major anthropogenic sectors contributing to CH₄ emissions is from the oil and gas industry. Among the many contributors to this sector's emissions is fugitive emissions, typically described as unwanted emissions of gas from a pressurised system [44]. In relation to the oil and gas industry, this may specifically refer to unwanted emission during transportation of product, or inefficient flaring, where CH₄ undergoes combustion to CO₂ but some of the CH₄ does not undergo combustion and instead is released

directly to the atmosphere, known as CH₄ slip. As of 2023 the oil and gas industry was responsible for 1.2 % of the UK's total CH₄ emissions, with flaring emissions representing 69 % of this sector's emissions [86].

Figure 5.1 shows onshore and offshore flaring emissions associated with natural gas and oil production in the United Kingdom and neighbouring countries. Flaring may occur for one of three reasons;

- Routine flaring, where an oil producing facility is unable to re-inject the produced gas, use it on site or sell it to market, this may occur in the absence of sufficient facilities.
- Safety flaring, where flaring ensures the safe operation of the facility. This may occur if the flared gas originates from an accident or an emergency shutdown that could lead to over-pressurisation.
- Non-routine flaring encompasses all other flaring, examples may include flaring during construction activities, maintenance or initial start up of the facility amongst others.

However, flaring is not necessarily a required part of the offshore oil and gas industry. In 2021, Norway had more than double the oil and gas production of the UK but had 81 % less flaring and venting, the major reason for this difference is attributed to Norway's economic disincentives including a carbon tax for offshore oil and gas emissions as well as joining the EU's Emissions Trading Scheme [87].

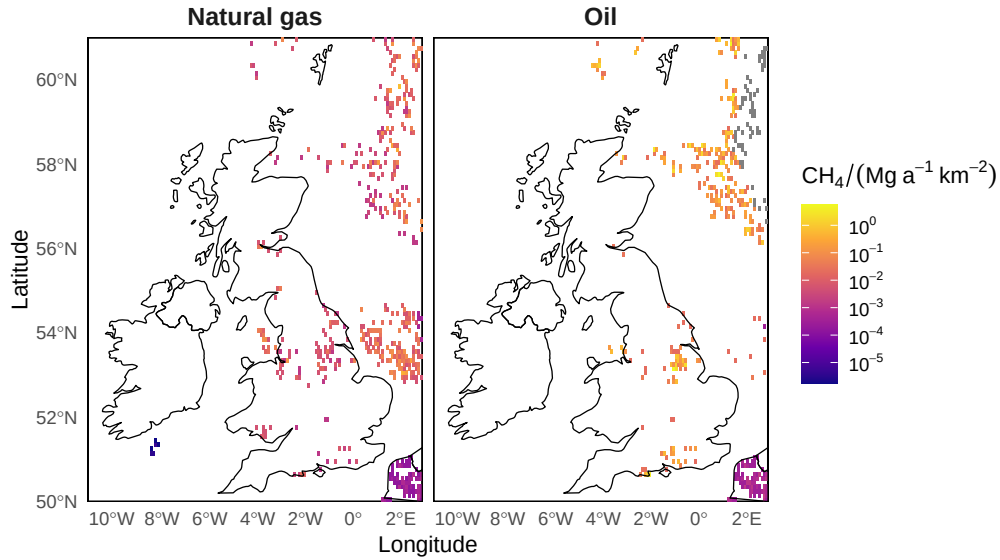


Figure 5.1: Flaring emissions of CH₄ from natural gas and oil production in the UK, data taken from GFEI v3 [21]

The North Sea is one of the most active areas in the world for oil and gas activities, with one study in 2023 estimating a total of 590 platforms in the area, 280 within the UK jurisdiction [38]. The North Sea Transition Authority (NSTA) requires all oil and gas platforms within the United Kingdom's continental shelf to report their annual emissions from flaring and venting activities. Recent attempts between 2018 and 2022 have reduced flaring activities in the North Sea by 50 %, an important step to reducing emissions in this region, as one fifth of all emissions in the North Sea related to oil and gas production activities are attributed to flaring [88]. As of 2024, the volume of natural gas flared reached its lowest recorded level of 658 million cubic metres [86]. While flaring activity continues to be reduced, in order to reach the zero flaring by 2030 target, some facilities require the continued use of flares, in these cases attempts have been made to adapt the flare itself and improve its overall efficiency to ensure that more CH₄ is converted to CO₂.

As of 2024 however, CH₄ emissions only accounted for 6 % of a total

11.8 MtCO₂e from upstream operations, with 2 % being attributed to N₂O and 92 % to CO₂ [86]. The largest source of these emissions is attributed to power generation with 7.62 MtCO₂e and flaring being the second largest with 1.55 MtCO₂e [86]. Showing that there is still a requirement for the accurate monitoring and reporting of flaring emissions even if total CH₄ emissions of upstream processes are low.

This work takes data collected from 6 flights, aboard a research aircraft measuring CH₄, at 3 different oil and gas platforms, with the aim of detecting and quantifying emissions resulting from flaring. An existing methodology for detecting flaring emissions, present in (*Shaw et al., 2023*) [89], was tested at all of the sites, but in the case of highly efficient flaring at one site, a new methodology is proposed. This new methodology is based on modelling the dispersion of plumes from different processes at the platform and subsequently calculating NO_x : CO₂ emission ratios of enhancements found during the sampling in order to determine the source of said enhancements.

5.2 Methodology

5.2.1 Instrumentation

All flights during this campaign were conducted using the UK's Facility for Airborne Atmospheric Measurement (FAAM) BAe-146 atmospheric research aircraft, with external inlets facing forward and backward to allow sampling of air via instruments within the cabin [90], a full list of instruments with their respective errors is given in *Table 5.1*. Meteorological data was measured using the core instrument suite on board. Air temperature was measured using a Rosemount 102AL sensor, with a 95 % confidence interval of ± 0.1 K. Air pressure was measured by use of pitot tubes along the aircraft with an accuracy of ± 0.5 hPa.

3-dimensional wind data was measured using a five-hole, nose mounted probe system. CH₄ and CO₂ dry mole fractions were measured with a Los Gatos Fast Greenhouse Gas Analyser (FGGA) detailed in both [91] and more recently an updated instrumental setup in [92]. The instrument uses a technique referred to as either cavity-enhanced absorption spectroscopy or off-axis integrated cavity output spectroscopy, which involves using an optical cavity and a laser that is passed through this cavity at an angle. This can generate an effective path length of several kilometres aiding in the detection of species at low concentrations. Nitrogen monoxide (NO) was measured using a custom chemiluminescence instrument and nitrogen dioxide (NO₂) was measured on a second channel by photolytic conversion to NO followed by detection by chemiluminescence [93] [94]. C₂H₆ mole fractions were measured by the use of an Aerodyne Tuneable Infrared Laser Direct Absorption Spectrometer (TILDAS) operating in the mid-infrared region ($\lambda = 3.3 \mu\text{m}$) detailed in (Yacovitch *et al.*, 2014) [64] and in *Chapter 2*.

5.2.2 Flight plans

For this work, sampling took place at 3 sites; the first being a Floating Production, Storage and Offloading unit (FPSO) situated to the West of the Shetland islands. Unlike a traditional fixed platform which extracts oil and gas and is then able to transport product directly to the mainland via permanent pipework, a FPSO instead acts as a semi-permanent platform that can extract product, but must store it onboard before offloading to a tanker vessel. Additionally, when an oil or gas field depletes, a traditional fixed platform would be decommissioned, a FPSO however is able to move to a new oil or gas field. This site was sampled on 2 separate campaigns, the first featured a single flight in March of 2019, the second was part of a campaign to monitor loading of oil from the FPSO to a tanker, which

Instrument	Measurement	Technique	Measurement frequency	Uncertainty
Rosemount 102AL	Air Temperature	Platinum resistance thermometer	1 Hz	± 0.1 K
Nose mounted five-port turbulence probe	Wind Speed, Wind Direction	5-hole probe	1 Hz	± 0.5 m s ⁻¹
Pitot tubes	Air Pressure	1 Hz		± 0.5 hPa
Los Gatos Fast Greenhouse Gas Analyzer	CH ₄ , CO ₂	Off axis-integrated cavity output spectroscopy	1 Hz (With ability to measure at 10 Hz)	± 2.86 ppb (1 Hz CH ₄ 1 σ)
				± 3.23 ppb (10 Hz CH ₄ 1 σ)
				± 0.46 ppm (1 Hz CO ₂ 1 σ)
				± 0.72 ppm (10 Hz CO ₂ 1 σ)
Air Quality Design Inc. Chemiluminescence Instrument	NO, NO ₂	Chemiluminescence	1 Hz	$\pm 4\%$ (1 Hz NO ± 31 pptv precision)
				$\pm 5\%$ (1 Hz NO ₂ ± 45 pptv precision)
Aerodyne TILDAS	C ₂ H ₆	Tunable infrared laser direct absorption spectroscopy	1 Hz (With ability to measure at 10 Hz)	± 50 ppt precision

Table 5.1: Instrumentation aboard the FAAM BAe-136 atmospheric research aircraft.

featured several flights in October of 2023. The second site was an oil field to the east of mainland Scotland within the North Sea which features 6 platforms. The final location was another oilfield to the west of the Shetland islands which features two platforms. During the work, one platform was intentionally flaring and this platform was sampled. Names of all platforms and oilfields have been omitted, at the request of operators. Details of date and location for each flight are shown in *Table 5.2*.

Flight Number	Year	Site
C148	05/03/2019	Site 1
C359	03/10/2023	Site 1
C360	03/10/2023	Site 1
C361	04/10/2023	Site 1
C362	05/10/2023	Site 3
C363	06/10/2023	Site 2

Table 5.2: List of flight numbers with their associated dates and sampling site.

5.2.2.1 Site 1 flight tracks

The first sampling of site 1 (C148) took place in March of 2019 and consisted of 20 runs past a single platform, shown in *Figure 5.2*.

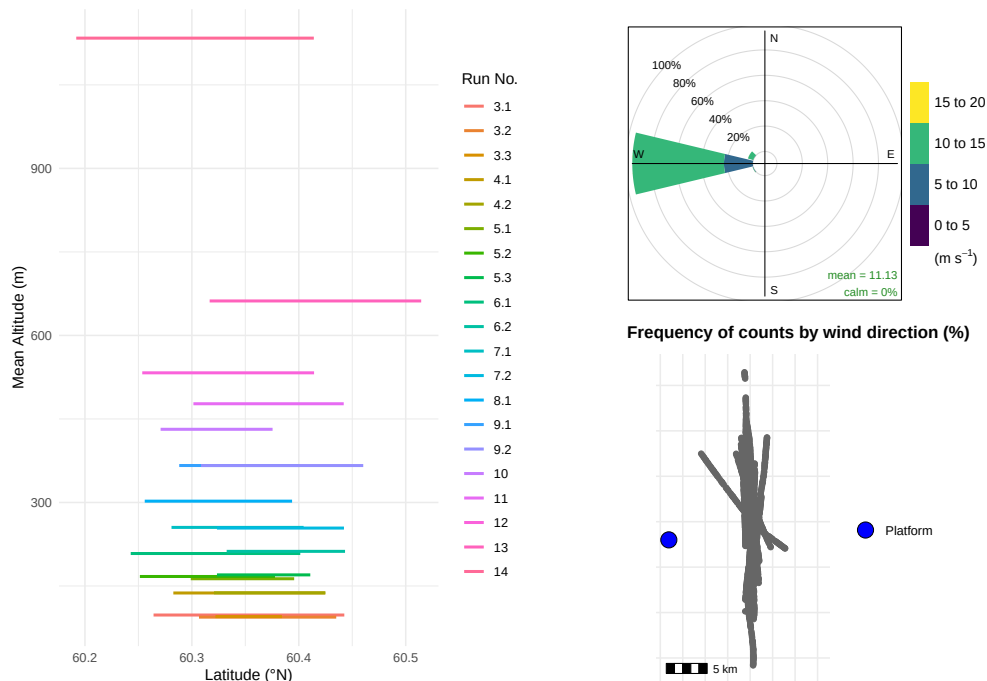


Figure 5.2: Plots showing mean altitude of runs, wind rose and flight track of site 1 sampling, March 2019 C148.

A separate campaign returned to site 1 in October of 2023 where 4 surveys over 3 days took place, only 3 surveys are included in this analysis as enhancements on the final day were not detected. For the first two surveys, data was provided from the operator that showed the platform flare was not actively flaring, but was under purge conditions (maintaining a minimum flow of gas, including N₂ to maintain a positive pressure in the flare and prevent air ingress). For the third survey, the operator confirms that the flare was active, however this survey also took place during the FPSO's offloading to a tanker. Flight 1 of the 2023 campaign (C359) featured 6 runs past the platform, shown in *Figure 5.3*. Flight 2 (C360) consisted of 8 runs, *Figure 5.4* and flight 3 (C361) had 19 runs, *Figure 5.5*.

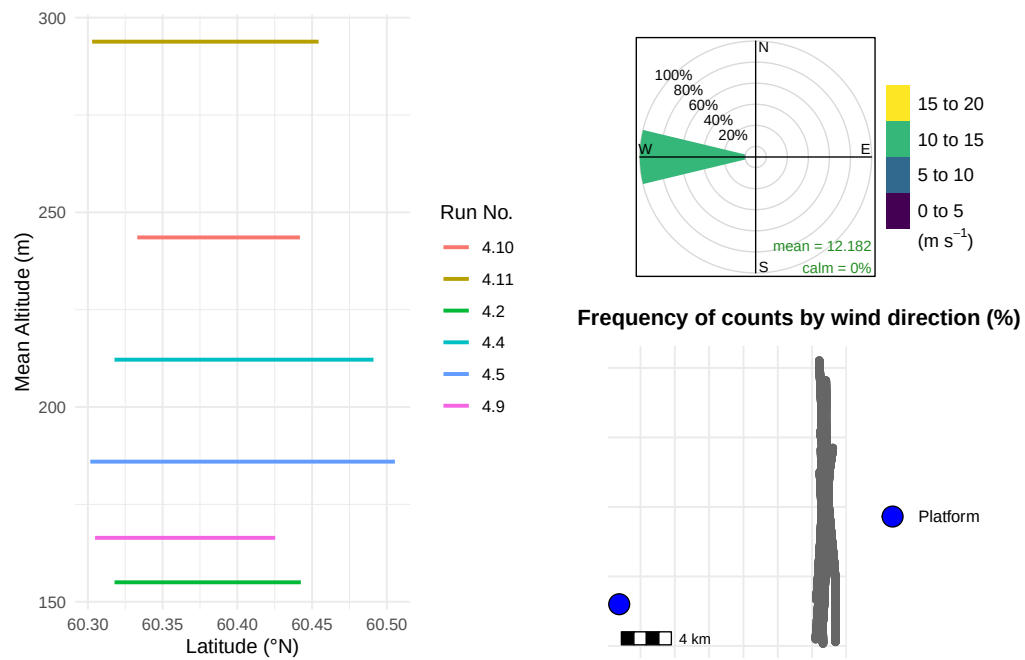


Figure 5.3: Plots showing mean altitude of runs, wind rose and flight track of site 1 sampling, October 2023 C359.

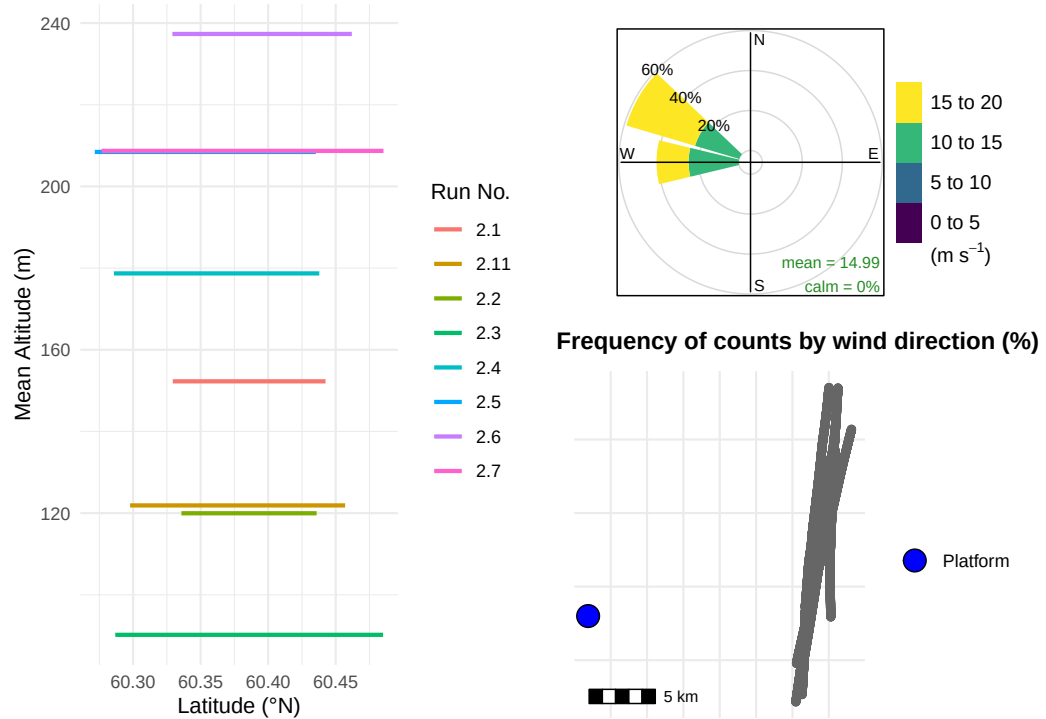


Figure 5.4: Plots showing mean altitude of runs, wind rose and flight track of site 1 sampling, October 2023 C360.

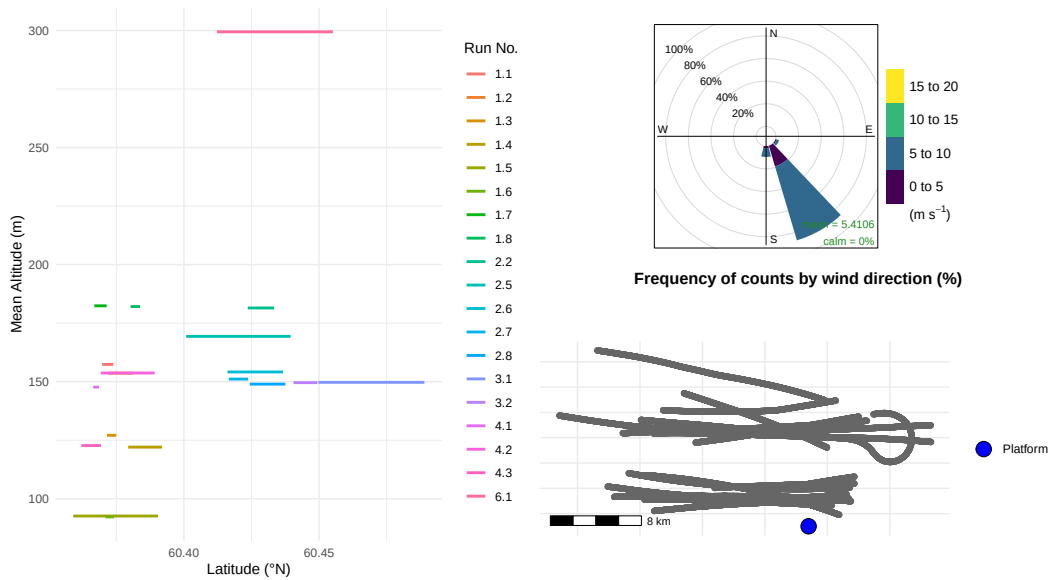


Figure 5.5: Plots showing mean altitude of runs, wind rose and flight track of site 1 sampling, October 2023 C361.

5.2.2.2 Site 2 flight tracks

Site 2 sampling took place in October of 2023 on a single flight (C363), the region features 6 platforms and 14 runs were made in varying orientations between the platforms, shown in *Figure 5.6*.

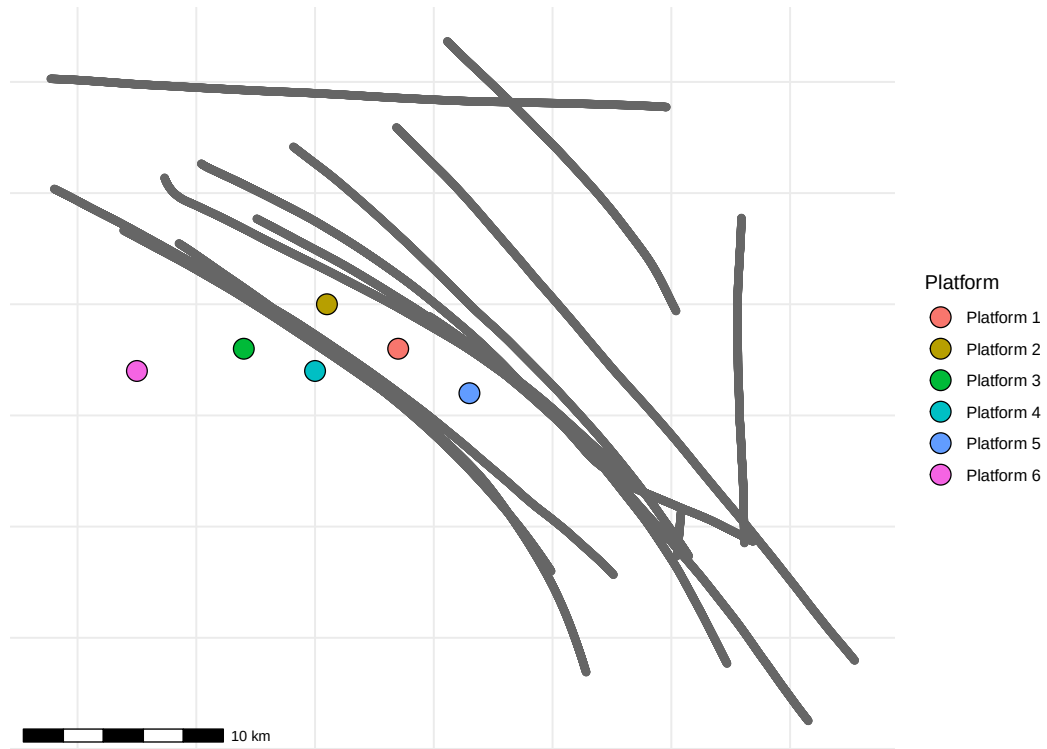


Figure 5.6: Flight track of site 2 sampling, C363.

5.2.2.3 Site 3 flight tracks

The third site had one platform (southern platform) intentionally flaring while the aircraft was on task. A single flight (C362) took place where 13 runs were made between the two platforms in order to be downwind of the flare without any interference from the northern platform; flight tracks are shown in *Figure 5.7*.

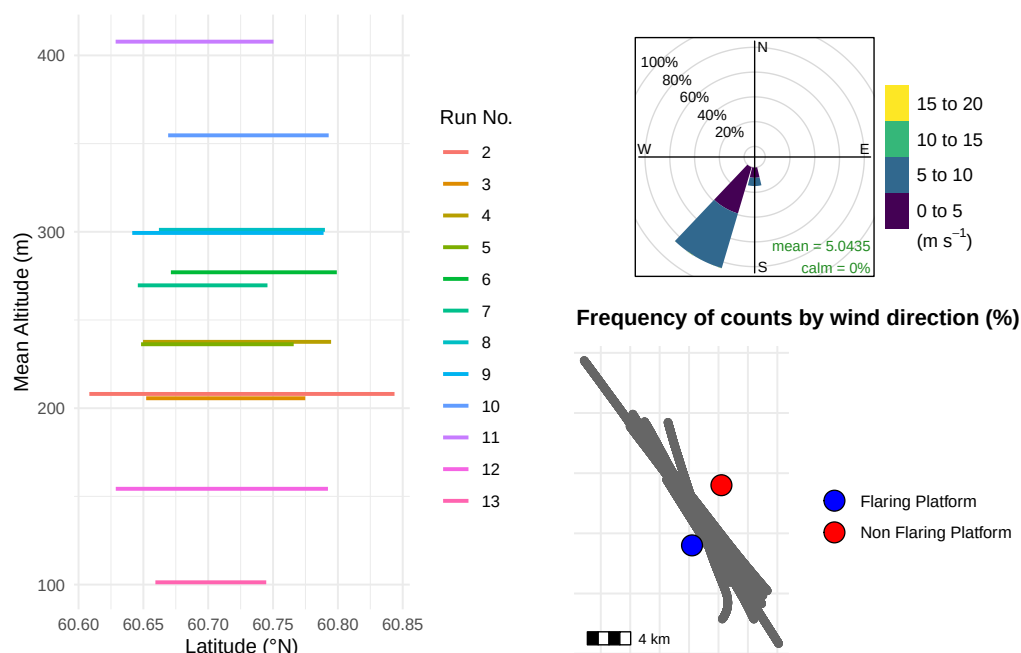


Figure 5.7: Plots showing mean altitude of runs, wind rose and flight track of site 3 sampling C362.

5.2.3 Detecting flaring enhancements

Detection of flares follows the methodology detailed in (Shaw *et al.*, 2023) [89]. Where in the absence of visual identification of a flare, plumes could be source assigned to gas flaring when enhancements in species associated with flaring of hydrocarbons were detected (CO_2 , CH_4 , C_2H_6 and NO_x). In order to be assigned as flaring, this methodology requires enhancements to be detected in all four of the species. Background concentrations were calculated using a 60 s rolling median and enhancements required mixing ratios to be greater than 2 standard deviations of the background mole fraction.

5.2.4 Emission ratio calculation

NO_x : CO₂ emission ratios and C₂H₆ : CH₄ emission ratios were calculated for each plume detected.

$$ER_{NO_x} (\text{ppm ppm}^{-1}) = \frac{NO_x (\text{ppm})}{CO_2 (\text{ppm})} \quad (5.1)$$

$$ER_{C_2H_6} (\text{ppm ppm}^{-1}) = \frac{C_2H_6 (\text{ppm})}{CH_4 (\text{ppm})} \quad (5.2)$$

5.2.5 Flaring efficiency calculation

Flaring efficiency may be calculated in several ways, the first being combustion efficiency, which is a calculation of how much of a fuel gas is converted into CO₂, where fuel gas is the unwanted or unusable natural gas ignited at the flare tip.

$$\eta [\%] = \frac{CO_2 \text{ in flared gas}}{\text{carbon in fuel gas}} \times 100\% \quad (5.3)$$

However for situations where fuel gas composition is unknown, this may not be an appropriate approach. Estimates for fuel composition cannot be used, as fuel composition varies widely from region to region and also within fields. For these scenarios combustion efficiency may be approximated by using CO₂ and CH₄ as an indication of carbon in fuel gas [95].

$$\eta [\%] = \frac{\Delta CO_2 (ppm)}{\Delta CO_2 (ppm) + \Delta CH_4 (ppm)} \times 100\% \quad (5.4)$$

This may lead to an overestimation in combustion efficiencies as it assumes that the fuel gas is composed entirely of CH₄. (Shaw *et al.*, 2023) [89] presents a third alternative for calculation of combustion efficiency, where C₂H₆ is also factored into the fuel gas composition, in order to reduce the potential overestimation from the efficiency that only factors in

CH₄ for fuel gas composition. C₂H₆ oxidises to two molar equivalents of CO₂ and is therefore accounted for twice in this equation. This will still result in some overestimation of combustion efficiency but in scenarios where measurements of larger hydrocarbons are not available at a high time resolution, this provides a more suitable alternative.

$$\eta [\%] = \frac{\Delta\text{CO}_2(\text{ppm})}{\Delta\text{CO}_2(\text{ppm}) + \Delta\text{CH}_4(\text{ppm}) + 2(\Delta\text{C}_2\text{H}_6(\text{ppm}))} \times 100\% \quad (5.5)$$

Destruction removal efficiency (DRE) calculations is an alternative approach to combustion efficiency in order to understand the efficiency of a flare. This instead is a measure of how a particular fuel gas component is oxidised within a flare [96, 97].

$$\text{DRE}_i[\%] = \left(1 - \frac{\Delta x_i}{(X_i \times \Delta\text{CO}_2) + \Delta x_i}\right) \times 100\% \quad (5.6)$$

x_i refers to the component in the fuel gas under investigation while X_i refers to that components fractional contribution towards the fuel gas composition. The drawback with the use of DRE calculations is that it requires knowledge of the fuel composition.

5.2.6 Flux Calculation

A mass balance methodology can be used in order to determine the emission rate (flux) at point of release from a mobile survey such as those conducted by the FAAM aircraft [98–101]. This methodology requires wind speeds to be consistent within the target region and assumes that the plume is well mixed in regards to the vertical plane, up to the planetary boundary layer. To reduce uncertainty in regards to this vertical mixing, multiple horizontal transects that occur at similar distances from the platform but at different altitudes are included in the calculation. This therefore creates a 2D vertical plane with layers associated with each horizontal transect. Initially the unit mass per time is calculated for each of these layers.

$$\text{Flux}_i = C_i \times \frac{p_i M}{RT_i} \times V_{\perp} \times \Delta x_i \times D_i \quad (5.7)$$

With ΔC_i representing the enhancement of the gas of interest within the plume, measured as a mole fraction. This is then converted to a mass density with the application of the ideal gas law, i.e. multiplication by p_i , the measured pressure, M , the molar mass of the gas of interest and division by R , the ideal gas constant and T_i , the measured temperature. This is all then multiplied by $V_{\perp}$, the average wind speed perpendicular to the flight track and Δx_i the width of the plume. Finally, everything is then multiplied by D_i , the depth of the mixing layer, each horizontal transect is assumed to represent a mixing layer which covers halfway to the transect above and below. In cases where plumes are still detected up to the highest horizontal transect, the maximum altitude of the vertical plane should be assumed to be at the boundary layer. Conversely, where the plume is still detected at the lowest altitude horizontal transect, the lowest altitude of the vertical plume was the height of the emission point, if known, else typical platform flare arm height was used. However, if there are horizontal transects without detection, higher or lower than the detected plume, these can be used as the minimum or maximum altitude and depth can be calculated using these. A diagram showing how these parameters are derived is shown in **Figure 5.8**. Once the flux at each transect is calculated, the total flux of the emission can be calculated as a summation across the entire 2D vertical plane:

$$\text{Flux}_{\text{total}} = \sum_i^{\text{transects}} \text{Flux}_i \quad (5.8)$$

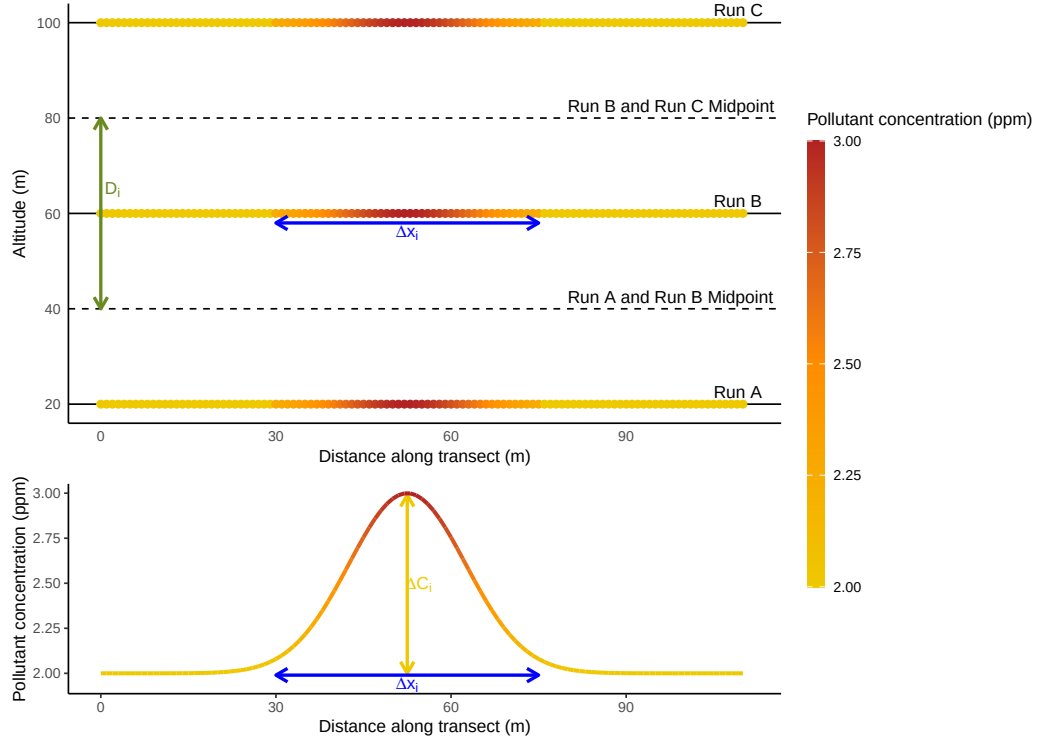


Figure 5.8: Diagrams showing how the parameters of the flux calculation are derived, the altitude plot shows hypothetical sampling runs at various altitudes, while the gaussian curve shows the pollutant enhancement of Run B.

Uncertainty is calculated during flux calculations following the methodology presented in (Pühl *et al.*, 2023) [101]. The uncertainty of flux at each measured transect ($uFlux_i$) is calculated using the uncertainties of all measured parameters (q), which includes the CH_4 enhancement (ΔC_i), wind speed ($V_{\perp}$), pressure (p_i), temperature (T_i), plume width (Δx_i) and plume depth (D_i) this calculation is shown in **Equation 5.9**. Uncertainty of the total flux ($uFlux_{total}$) is calculated as the sum of the uncertainties calculated for each transect, shown in **Equation 5.10**.

$$u(Flux_i) = Flux_i \cdot \sqrt{\sum_q^{parameters} \left(\frac{u(q)}{\bar{q}} \right)^2} \quad (5.9)$$

$$u(\text{Flux}_{\text{total}}) = \sum_i^{\text{transects}} u(\text{Flux}_i) \quad (5.10)$$

5.2.7 Dispersion Modelling

As work on flaring at site 3 was in partnership with the operator, greater access to information surrounding the flare was available. Due to this, dispersion modelling using ADMS 5.2.2 [102] was implemented in order to better understand the vertical spread of both the flaring plume and power generation plume. The power generation was modelled as a point source while the flare was modelled as a jet and although there was slight difference in the position of each source, both were assigned as 0,0 in coordinates with respect to the x,y plane. The flare was positioned at $z = 93.9$ m, and based on information provided by the platforms management, the flare tip had an effective diameter of 0.185 m, a flow rate of $500 \text{ m}^3 \text{ hour}^{-1}$ with individual emissions of $0.39 \text{ kg s}^{-1} \text{ CO}_2$ and 0.0001 kg s^{-1} of CH_4 and a net heating value of $1000 \text{ BTU (standard cubic foot)}^{-1}$ but no recorded temperature of the flare. During ADMS modelling, the flare was modelled as having temperatures of 100°C , 1000°C , 1950°C (the typical temperature of a natural gas flame in air) and 3000°C to determine if changing temperature affected the maximum vertical dispersion of the plume. Changing the temperature showed to have no effect on vertical plume dispersion, therefore for the model a temperature of 1950°C was used, the typical temperature of a natural gas flame in air. Platform management also provided information related to the power generation exhaust, the exhaust was positioned at $z = 93.0$ m, at the time of sampling two exhausts were running, each with a diameter of 2.5 m, modelled as an effective diameter of 5 m, a temperature of 368°C and a mass flux of 48 kg s^{-1} (3 kg s^{-1} of which were CO_2). Meteorology for the model was taken as the average of what was measured on the aircraft during sampling, this

meant a wind speed of 5 m s^{-1} originating at an angle of 201 degrees from North (South South Westerly) and a surface temperature of 10.4°C . Due to the sampling occurring over sea surface roughness was assigned as 0.0001 m. Finally both sources were modelled over a grid where each integer coordinate represented 1 m, the x plane was modelled between -3000 to 3000 with 121 total points (every 50 m), the y plane was modelled between 0 and 10000 with 201 points (every 50 m) and the z plane was modelled between 90 and 500 with 22 points (every 19.5 m). CO_2 concentrations were modelled in the short term and averaged over 1 hour.

5.2.8 Global Fuel Exploitation Inventory

The Global Fuel Exploitation Inventory (GFEI) v3 [21] is a global $0.1^\circ \times 0.1^\circ$ resolution gridded inventory of CH_4 emissions from oil, gas and coal exploitation; this edition updates the inventory with national emissions up to 2020. GFEI v3 is divided into separate processes, for this work the data inventories of interest are flaring associated with oil production and flaring assigned to gas production, these are combined to give total CH_4 area emissions as a result of flaring. GFEI data for flaring at site 1 reported CH_4 emissions associated with natural gas production as $9.80 \times 10^{-3} \text{ Mg km}^{-2} \text{ annum}^{-1}$ while oil production flaring was $3.49 \text{ Mg km}^{-2} \text{ annum}^{-1}$ giving site 1 total flaring emissions of $3.50 \text{ Mg km}^{-2} \text{ annum}^{-1}$ from the 1 platform. GFEI data for flaring at site 2 showed CH_4 emission associated with flaring from natural gas production was $0.02 \text{ Mg km}^{-2} \text{ annum}^{-1}$, while oil production flaring was $7.87 \text{ Mg km}^{-2} \text{ annum}^{-1}$ for a total CH_4 flaring emission in this region of $7.89 \text{ Mg km}^{-2} \text{ annum}^{-1}$. The GFEI reports site 3 as having CH_4 emissions from flaring associated with natural gas production as $4.96 \times 10^{-3} \text{ Mg km}^{-2} \text{ annum}^{-1}$, oil production flaring was $1.05 \text{ Mg km}^{-2} \text{ annum}^{-1}$ this gives the region a total of $1.06 \text{ Mg km}^{-2} \text{ annum}^{-1}$ between 2 platforms. CH_4 flaring emissions from each site are

shown below in **Table 5.3**.

Site	Number of platforms	CH ₄ flaring emissions / Mg km ⁻² annum ⁻¹
Site 1	1	3.50
Site 2	6	7.89
Site 3	2	1.06

Table 5.3: Each site's annual CH₄ emissions as a result of flaring as reported in the GFEI v3[21].

Predicted emissions vary greatly between the NAEI and the GFEI, mainly due to the NAEI reporting emissions from all sources while the GFEI is able to report source specific emissions. However both inventories report site 2 as having the highest overall emissions, the inventories then differ with NAEI reporting site 3 as having the second highest, while GFEI reports Site 1 as the second highest emission site. Throughout GFEI in all cases emissions from flaring associated with oil production is higher than that associated with gas production.

5.3 Results

5.3.1 Site 1

5.3.1.1 March 2019 (C148)

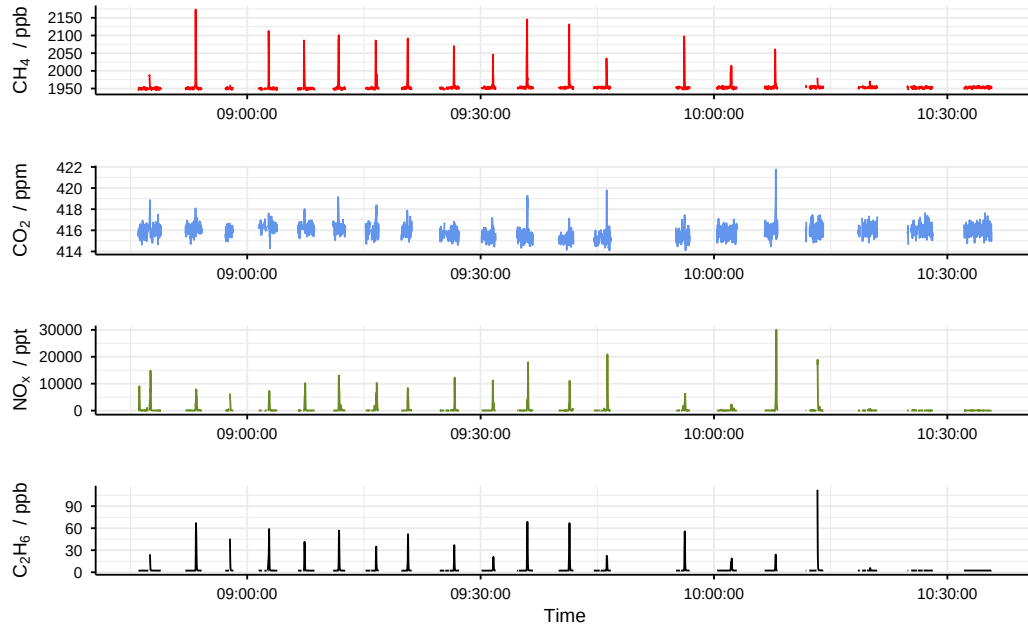


Figure 5.9: Time series of species mixing ratios measured during 2019 site 1 sampling C148.

The time series from sampling at site 1 **Figure 5.9** showed that flares were detectable using methodology present in (*Shaw et al., 2023*) [89] as enhancements were detectable in all of CH_4 , CO_2 , NO_x and C_2H_6 . Emission ratios for the flaring were calculated and resulted in an average $\text{NO}_x : \text{CO}_2$ emission ratio of $0.005 \text{ ppm ppm}^{-1}$ and a $\text{C}_2\text{H}_6 : \text{CH}_4$ emission ratio of $0.271 \text{ ppm ppm}^{-1}$. Individual $\text{NO}_x : \text{CO}_2$ and $\text{C}_2\text{H}_6 : \text{CH}_4$ emission ratios for each enhancement are detailed in **Table 5.4**. Flux was then calculated, as there were runs above and below the highest and lowest runs that detected flaring, these were used as boundaries for the 2D vertical plane. CO_2 flux was calculated as $4.15 \pm 1.93 \text{ kg s}^{-1}$, CH_4 flux was $0.29 \pm$

0.18 kg s^{-1} and C_2H_6 was $0.13 \pm 0.09 \text{ kg s}^{-1}$. Combustion efficiency was calculated for each flaring plume to give a mean efficiency of 91.58 %.

Run Number	$\text{NO}_x : \text{CO}_2$ Emission Ratio	$\text{C}_2\text{H}_6 : \text{CH}_4$ Emission Ratio
3.1	0.0048	0.2196
3.2	0.0035	0.2792
4.2	0.0056	0.2847
5.1	0.0040	0.3532
5.2	0.0038	0.2408
6.2	0.0060	0.1850
7.1	0.0046	0.3321
7.2	0.0056	0.3484
10.0	0.0050	0.1967

Table 5.4: $\text{NO}_x : \text{CO}_2$ and $\text{C}_2\text{H}_6 : \text{CH}_4$ emission ratios of enhancements located during C148

5.3.1.2 October 2023 (C359)

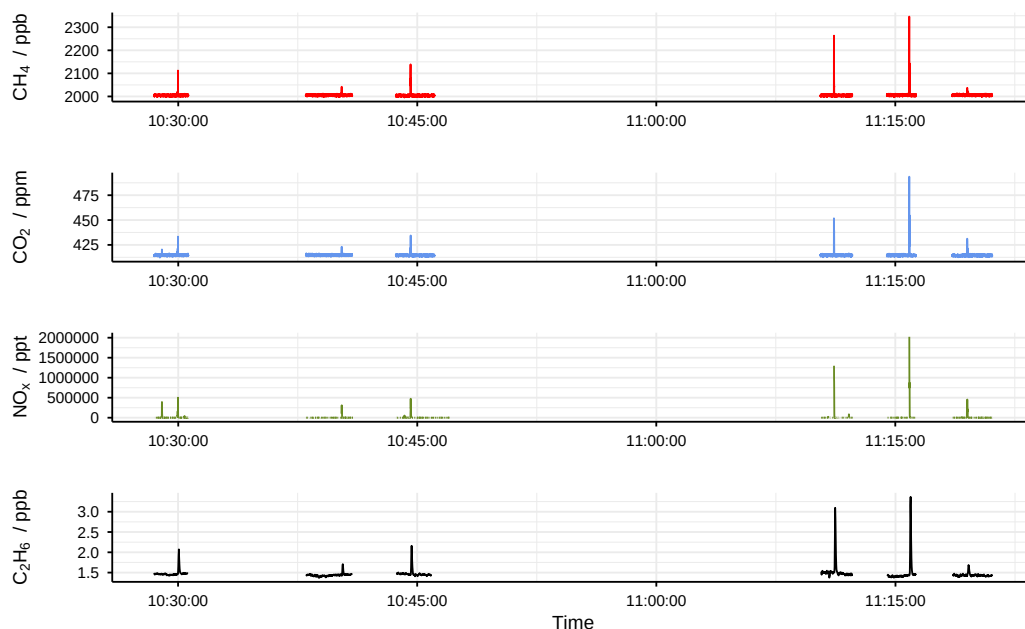


Figure 5.10: Time series of species mixing ratios measured during October 2023 sampling of site 1 C359.

C359 again implemented the methodology of requiring enhancements in all of CH_4 , CO_2 , C_2H_6 and NO_x due to these being visible in the time series of **Figure 5.10**. This methodology found 4 enhancements in 4 of the 6 runs. Emission ratios were again calculated resulting in a mean $\text{NO}_x : \text{CO}_2$ emission ratio of $0.030 \text{ ppm ppm}^{-1}$ and a mean $\text{C}_2\text{H}_6 : \text{CH}_4$ emission ratio of $0.006 \text{ ppm ppm}^{-1}$. Individual $\text{NO}_x : \text{CO}_2$ and $\text{C}_2\text{H}_6 : \text{CH}_4$ emission ratios for enhancements are detailed in **Table 5.5**. CO_2 flux was calculated as $1.55 \pm 0.50 \text{ kg s}^{-1}$, CH_4 flux was $1.27 \times 10^{-3} \pm 1.13 \times 10^{-3} \text{ kg s}^{-1}$ and C_2H_6 was $3.21 \times 10^{-5} \pm 2.75 \times 10^{-5} \text{ kg s}^{-1}$. Combustion efficiency was calculated for each flaring plume to give a mean efficiency of 99.52 %.

Run Number	NO _x : CO ₂ Emission Ratio	C ₂ H ₆ : CH ₄ Emission Ratio
4.2	0.0262	0.0054
4.4	0.0356	0.0067
4.9	0.0337	0.0059
4.11	0.0251	0.0075

Table 5.5: NO_x : CO₂ and C₂H₆ : CH₄ emission ratios of enhancements located during C359.

5.3.1.3 October 2023 (C360)

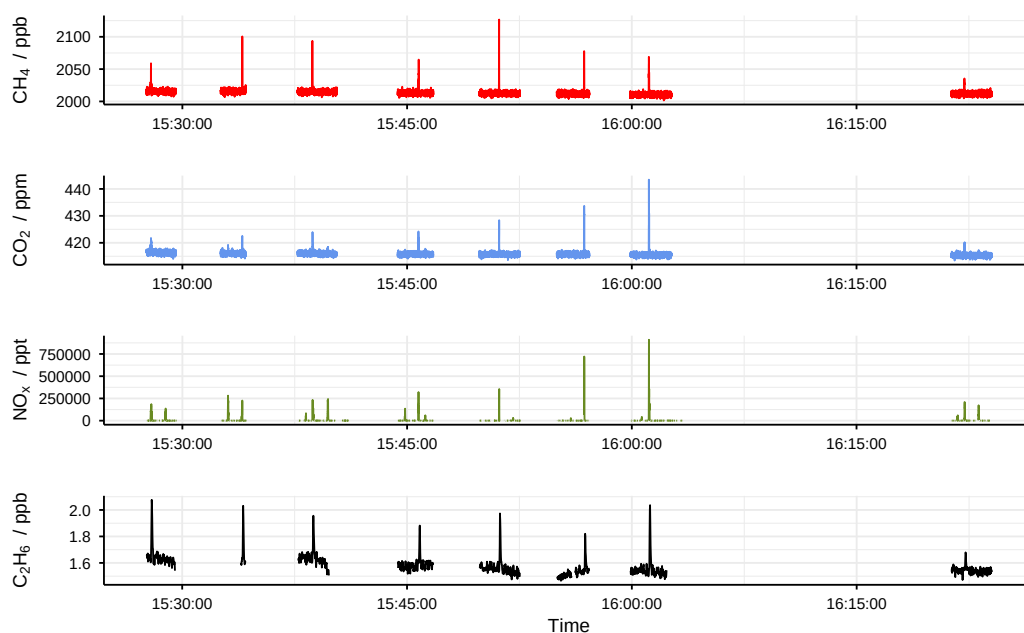


Figure 5.11: Time series of species mixing ratios measured during October 2023 sampling of site 1 C360.

Flight C360 also shows enhancements in all species **Figure 5.11** and found 8 enhancements, one in each of the 8 runs using the (Shaw *et al.*, 2023) [89] methodology. Mean NO_x : CO₂ emission ratio was calculated as 0.032 ppm ppm⁻¹ and mean C₂H₆ : CH₄ emission ratio as 0.006 ppm ppm⁻¹. Individual NO_x : CO₂ and C₂H₆ : CH₄ emission ratios are shown in **Table**

5.6. CO₂ flux was calculated as $3.83 \pm 0.47 \text{ kg s}^{-1}$, CH₄ flux was $4.21 \times 10^{-3} \pm 1.18 \times 10^{-3} \text{ kg s}^{-1}$ and C₂H₆ flux was calculated as $1.13 \times 10^{-4} \pm 0.36 \times 10^{-4} \text{ kg s}^{-1}$. Combustion efficiency was calculated for each flaring plume to give a mean efficiency of 99.29 %.

Run Number	NO _x : CO ₂ Emission Ratio	C ₂ H ₆ : CH ₄ Emission Ratio
2.10	0.0307	0.0095
2.11	0.0390	0.0054
2.20	0.0319	0.0042
2.30	0.0263	0.0039
2.40	0.0360	0.0055
2.50	0.0270	0.0034
2.60	0.0376	0.0039
2.70	0.0309	0.0082

Table 5.6: NO_x : CO₂ and C₂H₆ : CH₄ emission ratios of enhancements located during C360

5.3.1.4 October 2023 (C361)

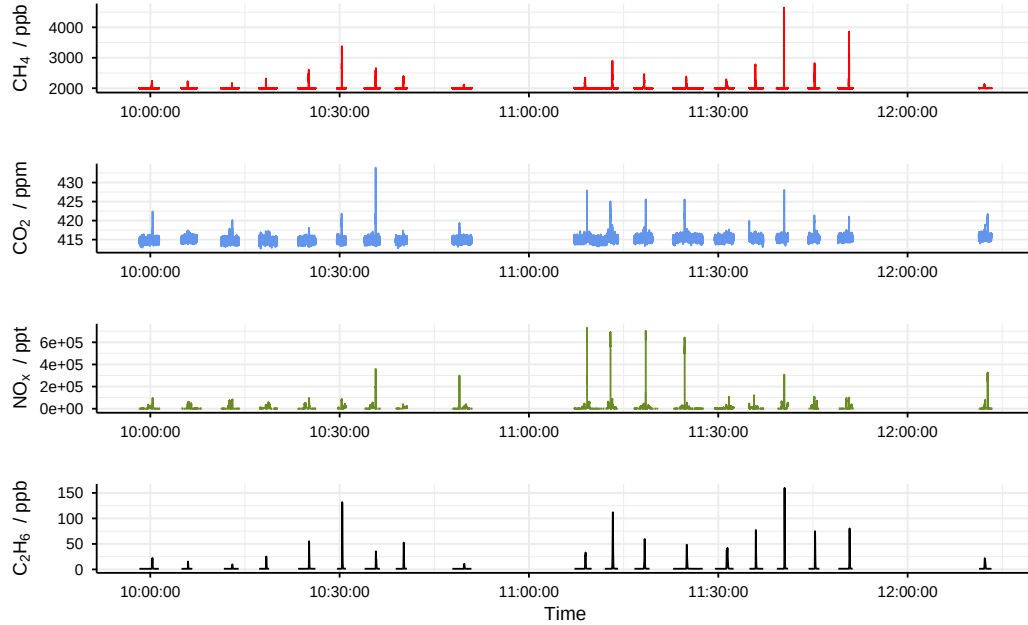


Figure 5.12: Time series of species mixing ratios measured during October 2023 sampling of site 1 C361.

The time series of C361 **Figure 5.12** once again showed that enhancements were present in all 4 species allowing the (Shaw *et al.*, 2023) [89] methodology to be used again. C361 located 8 enhancements across 8 of the 19 runs. Mean NO_x : CO_2 emission ratio was $0.017 \text{ ppm ppm}^{-1}$ and mean C_2H_6 : CH_4 emission ratio was $0.068 \text{ ppm ppm}^{-1}$. Individual NO_x : CO_2 and C_2H_6 : CH_4 emission ratios are shown in **Table 5.7**. CO_2 flux was calculated as $0.84 \pm 0.15 \text{ kg s}^{-1}$, CH_4 flux was $4.90 \times 10^{-2} \pm 1.82 \times 10^{-2} \text{ kg s}^{-1}$ and C_2H_6 flux was $1.08 \times 10^{-2} \pm 0.45 \times 10^{-2} \text{ kg s}^{-1}$. Combustion efficiency was calculated for each flaring plume to give a mean efficiency of 86.71 %.

Run Number	NO _x : CO ₂ Emission Ratio	C ₂ H ₆ : CH ₄ Emission Ratio
1.1	0.0118	0.0840
1.3	0.0129	0.0460
1.5	0.0264	0.0850
1.6	0.0112	0.0906
1.7	0.0179	0.0542
4.1	0.0235	0.0570
4.2	0.0164	0.0855
4.3	0.0159	0.0402

Table 5.7: NO_x : CO₂ and C₂H₆ : CH₄ emission ratios of enhancements located during C361

5.3.2 Site 2

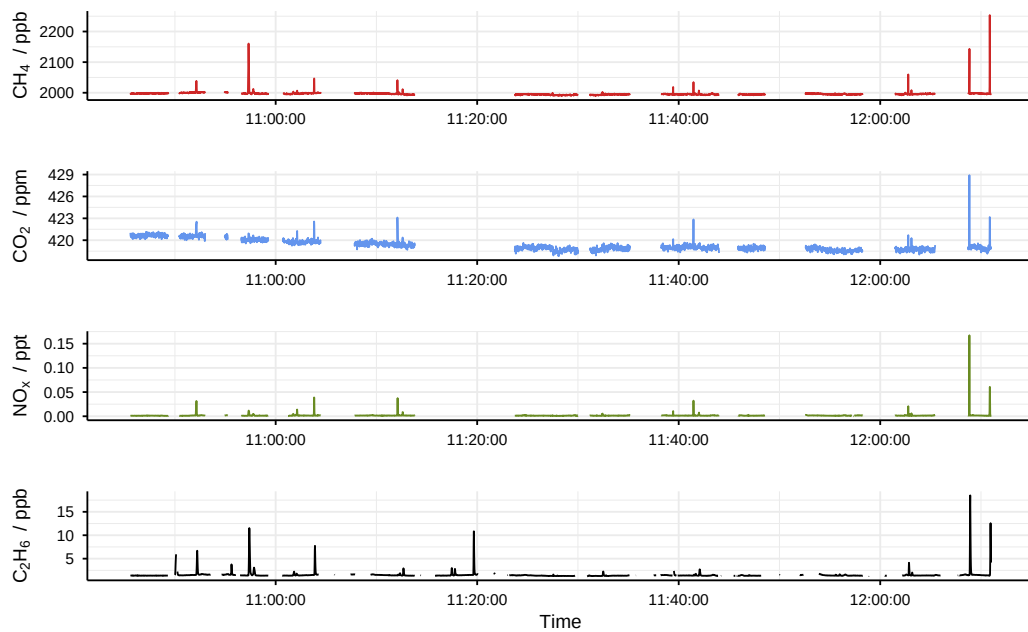


Figure 5.13: Time series of species mixing ratios measured during site 2 sampling, C363.

Site 2 again had enhancements present in all of CH₄, CO₂, NO_x and C₂H₆, shown in **Figure 5.13**, allowing the method present in (Shaw *et al.*, 2023) [89] to be used again and resulted in 9 flaring emissions from 7 runs. Emission ratios were calculated once again, resulting in a mean NO_x : CO₂ emission ratio of 0.012 ppm ppm⁻¹ and a C₂H₆ : CH₄ emission ratio of 0.082 ppm ppm⁻¹. Individual NO_x : CO₂ and C₂H₆ : CH₄ emission ratios are detailed in **Table 5.8**. Although it was noted that the emission ratios at this site varied greatly, likely because this was averaged over the field as a whole and not per individual platform.

Run Number	NO _x : CO ₂ Emission Ratio	C ₂ H ₆ : CH ₄ Emission Ratio
2.0	0.0155	0.1323
4.0	0.0121	0.0596
5.0	0.0135	0.1249
6.0	0.0065	0.0883
10.1	0.0080	0.0383
10.2	0.0103	0.0948
13.0	0.0097	0.0393
14.1	0.0169	0.1162
14.2	0.0134	0.0403

Table 5.8: NO_x : CO₂ and C₂H₆ : CH₄ emission ratios of enhancements located during C363

Flux from these sites and efficiency of flaring was not calculated for this site due to each platform's flare rarely being seen more than once, locations of these detections relative to platform location are shown in **Figure 5.14**.

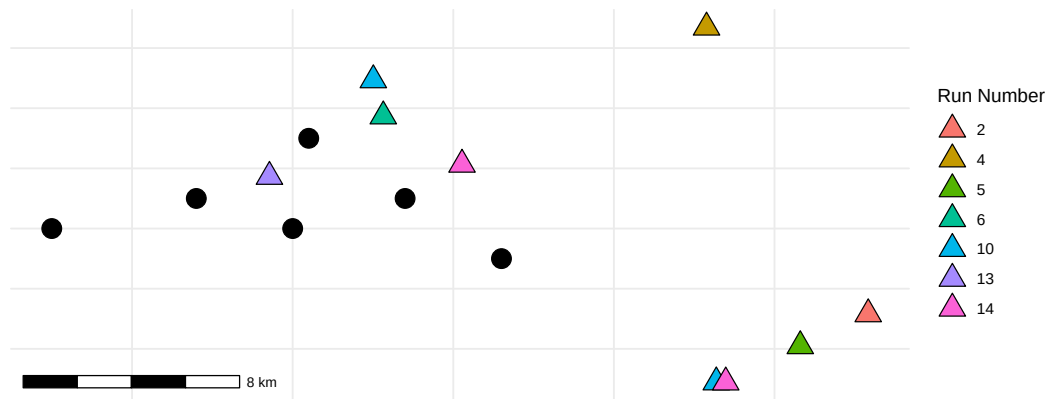


Figure 5.14: Location of detected flaring enhancements (triangles) coloured by their respective run number, in relation to platforms (circles) at site 2 C363.

5.3.3 Site 3

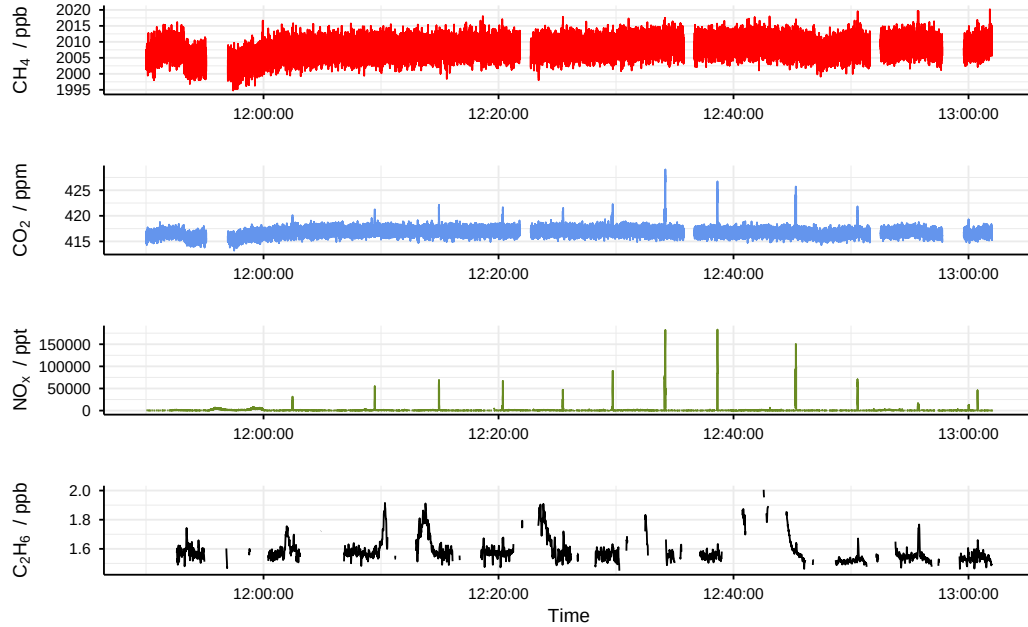


Figure 5.15: Time series of species mixing ratios measured during sampling of site 3 C362.

Sampling of the southern platform at site 3, had very few enhancements in CH_4 and intermittent coverage in C_2H_6 , shown in **Figure 5.15**, meaning that the methodology used in (Shaw *et al.*, 2023) [89] was not possible for this site. Instead enhancements were defined as an enhancement greater than 2 standard deviations in CO_2 and NO_x only, using this approach enhancements were detected in 12 of the 13 runs, with several runs detecting multiple enhancements.

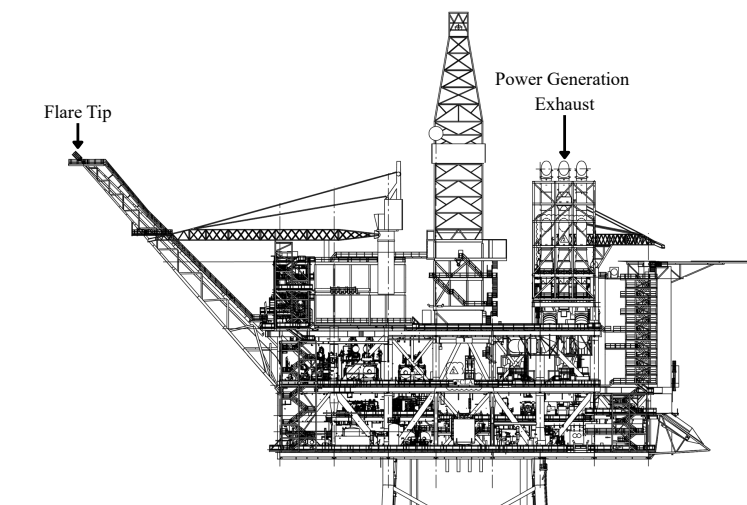


Figure 5.16: Technical diagram of the flaring platform.

The reasoning for the multiple enhancements was thought to be related to the processes present on the platform, although the flare is active and enhancements in CO_2 and NO_x would be detected, these same species would also be detectable from other processes on the platform, most notably from the exhaust associated with power generation. A diagram of the platform is shown in *Figure 5.16*, which shows the flare tip and exhaust are situated at a similar height. It was predicted that the runs featuring multiple enhancements may include enhancements from each source and therefore a method of identifying the source of each plume was required.

Results from (*Shaw et al., 2023*) [89] found that $\text{NO}_x : \text{CO}_2$ emission ratios associated with flaring in the North Sea were on average $0.004 \text{ ppm ppm}^{-1}$, it was determined that it was likely to be able to identify the two separate sources based on their emission ratio. The $\text{NO}_x : \text{CO}_2$ and $\text{C}_2\text{H}_6 : \text{CH}_4$ emission ratios for each enhancement were calculated and are detailed in *Table 5.9*.

Run Number	NO _x :CO ₂ Emission Ratio	C ₂ H ₆ :CH ₄ Emission Ratio
2.0	0.0092	NA
3.0	0.0129	NA
4.0	0.0131	NA
5.0	0.0140	NA
6.0	0.0101	0.0154
7.0	0.0168	0.0135
8.0	0.0140	NA
9.0	0.0178	NA
10.0	0.0112	NA
10.0	0.0157	NA
11.0	0.0151	NA
11.0	0.0125	NA
12.0	0.0114	NA
12.0	0.0071	0.0201
13.0	0.0383	0.0138
13.0	0.0039	0.0099
13.0	0.0040	NA

Table 5.9: NO_x : CO₂ and C₂H₆ : CH₄ emission ratios of enhancements located during C362

17 separate enhancements were detected over 12 runs. 4 runs had multiple enhancements detected on the run, these being; Run 10 which had 2 enhancements, Run 11 with 2, Run 12 with 2 and Run 13 with 3. This led to several hypotheses, flaring could be associated to enhancements where the NO_x : CO₂ emission ratio was within the same order of magnitude as the results from (Shaw *et al.*, 2023) [89] i.e. 1×10^{-3} to 1×10^{-2} , this would include the enhancement in Run 12 and 2 of the enhancements in Run 13. A second potential route to assign the flare would be to take the lower NO_x : CO₂ emission ratio of runs with multiple

enhancements, this would include; Run 10, Run 11, Run 12 and Run 13. Due to the uncertainty in how to separate the flare's plume and power generation plume, as well as uncertainty in the likelihood either were detected, it was deemed necessary to model the two sources using dispersion modelling software, specifically ADMS. As discussed in *Section 5.2.7*, the exact temperature of the flare was unknown, although a flare temperature of 1950 °C was selected for the final model, a range of temperatures were initially used in the model, in addition to modelling the flare as both a point source and as a jet, where the jet model allows the angle of the flare arm to be factored in. *Table 5.10* presents a range of model parameters and the resulting maximum vertical dispersion of CO₂. This showed that temperature had little effect on the vertical dispersion of CO₂, however whether the flare was modelled as a point or as a jet did have a small effect on the maximum vertical dispersion, with jet models predicting a dispersion 19 m higher. Therefore the jet was used in the final model.

Source	Temperature / °C	Angle	Maximum CO ₂ vertical dispersion
Point	100	NA	324
Point	1000	NA	324
Point	1950	NA	324
Point	3000	NA	324
Jet	100	45°	343
Jet	1000	45°	343
Jet	1950	45°	343
Jet	3000	45°	343

Table 5.10: Maximum vertical dispersion of CO₂ from ADMS models using a range of temperatures and source types

The maximum vertical spread was found to be 343 m for the flare and 402 m for power generation, shown in *Figure 5.17*. When this was

compared to sampling heights, it suggested that flaring would be detectable in runs 3, 12 and 13 with runs 2 and 5 lying close to the modelled flaring plume. It is important to note that ADMS visibly under-predicts the vertical dispersion of plumes, this is most noticeable with the power generation plume, which when modelled through ADMS, does not extend to the height of Run 11 despite the fact that enhancements were seen within this sampling run, it is however more likely that flaring would be detected at lower altitude sampling runs than the higher altitude ones.

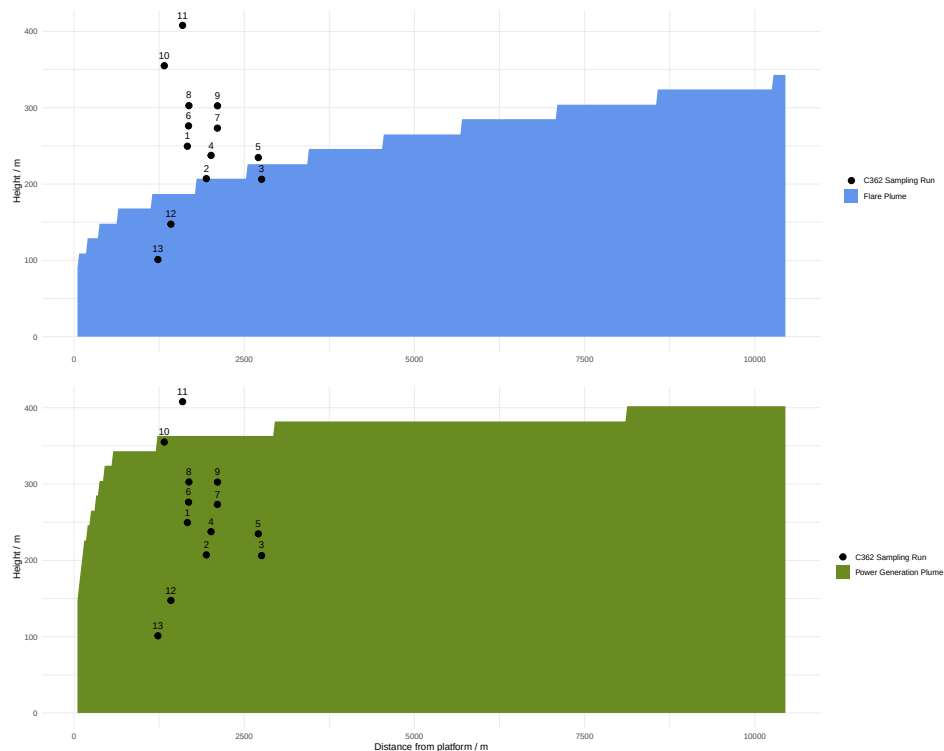


Figure 5.17: Prediction of vertical plume dispersion from the two platform sources, modelled with ADMS, compared to flight height above flare.

Runs 12 and 13 are therefore the most likely candidates to contain flaring enhancements. Firstly, they occur at lower altitudes, within the modelled ADMS dispersion of the flaring plume. Secondly, they contain multiple enhancements within their sampling runs, this gives high

confidence that there is separation between the flaring plume and power generation plume and finally these runs contain enhancements with $\text{NO}_x : \text{CO}_2$ emission ratios within the same order of magnitude as those in (Shaw *et al.*, 2023) [89]. 5 enhancements were detected across Run 12 and Run 13, in Run 12, there were two enhancements, 0.011 ppm ppm⁻¹ and 0.007 ppm ppm⁻¹ and in Run 13, 3 enhancements one of 0.038 ppm ppm⁻¹ and the other two both 0.004 ppm ppm⁻¹. The lowest three enhancements from the two runs were likely to be associated with the flare, however the second enhancement of Run 13 featured no enhancements in CH_4 or C_2H_6 so was omitted from calculations of flux and efficiency. Of the other runs that featured multiple enhancements, it was deemed that the reason for separate enhancements was likely due to separation in plumes from the two separate exhausts. This resulted in a mean $\text{NO}_x : \text{CO}_2$ emission ratio of 0.005 ppm ppm⁻¹ and mean $\text{C}_2\text{H}_6 : \text{CH}_4$ emission ratio of 0.015 ppm ppm⁻¹ for flaring and a mean $\text{NO}_x : \text{CO}_2$ emission ratio of 0.015 ppm ppm⁻¹ for power generation. All emission ratios of enhancements within the extent of the flaring plume are detailed in **Table 5.11**.

Run Number	$\text{NO}_x : \text{CO}_2$ Emission Ratio	$\text{C}_2\text{H}_6 : \text{CH}_4$ Emission Ratio
12.0	0.0114	NA
12.0	0.0071	0.0201
13.0	0.0383	0.0138
13.0	0.0039	0.0099
13.0	0.0040	NA

Table 5.11: $\text{NO}_x : \text{CO}_2$ and $\text{C}_2\text{H}_6 : \text{CH}_4$ emission ratios of enhancements located during C362 that fall within the ADMS modelled vertical dispersion of the flaring plume.

Flux was calculated for this site for both the flare and the power generation exhaust as a means of determining the viability of using aircraft

measurements to detect highly efficient platform flares in the future. The power generation extended to the highest altitude run, therefore for calculating the depths of each run, the maximum altitude for the mass balance calculation was taken as the absolute maximum altitude covered by the aircraft on this run, while lowest altitude was calculated as the height of the power generation exhaust. CO₂ flux was calculated as $2.59 \pm 0.54 \text{ kg s}^{-1}$. However, as the plume extended to the maximum height of the survey it was assumed that the entirety of the plume may not have been sampled, sampling at higher altitude was not possible as this would have extended into the cloud base. In order to know how much of the plume had been sampled, the flux was plotted against run altitude and modelled as a gaussian distribution, shown in **Figure 5.18**. This allowed a scaling factor to be calculated to estimate the total CO₂ flux of the power generation.

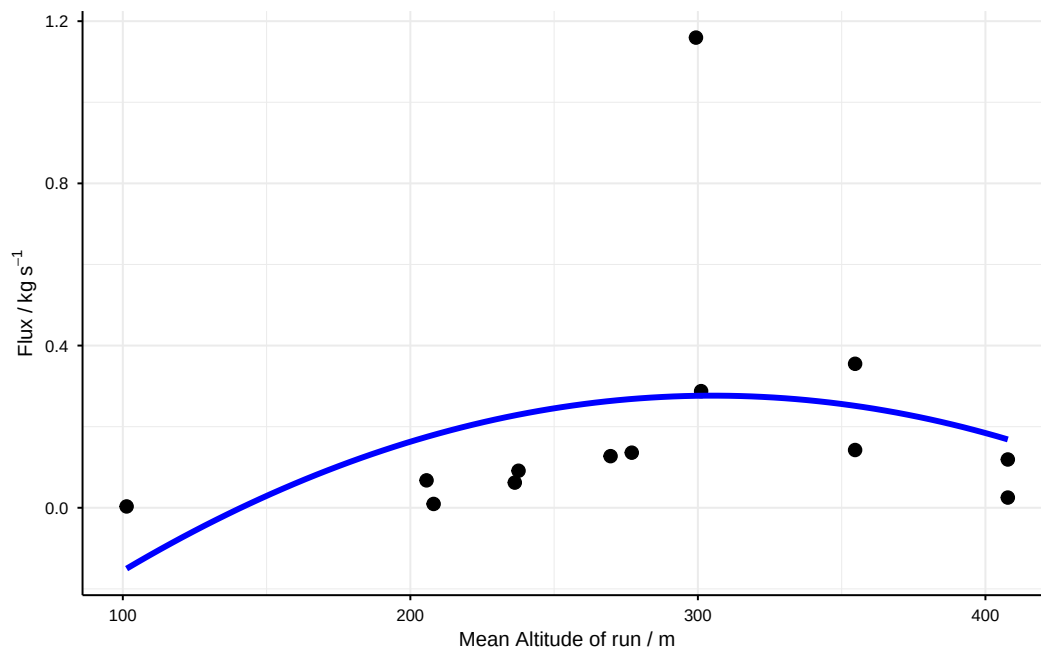


Figure 5.18: C362 power generation CO₂ flux against altitude of run, modelled as a gaussian curve.

This predicted a total estimated CO₂ flux of $3.47 \pm 0.73 \text{ kg s}^{-1}$ compared

to the operator's prediction of 3 kg s^{-1} . For the flare, flux of CO_2 , CH_4 and C_2H_6 was calculated, again the lowest altitude was the height of the flare tip while the highest altitude was the mean altitude of the first run where flaring was not detected. This gave a calculated CO_2 flux of $1.26 \pm 0.33 \text{ kg s}^{-1}$, a CH_4 flux of $2.66 \times 10^{-5} \pm 0.87 \times 10^{-5} \text{ kg s}^{-1}$ and a C_2H_6 flux of $1.38 \times 10^{-5} \pm 0.49 \times 10^{-5} \text{ kg s}^{-1}$, where again the operator predicted fluxes of 0.39 kg s^{-1} for CO_2 and $2 \times 10^{-5} \text{ kg s}^{-1}$ for CH_4 . The over-prediction of fluxes was likely due to a large depth for the upper flaring signal, which was necessitated by no runs occurring between the highest run where flaring was found and the next run where flaring was not detected. Again efficiency was calculated from each of the flaring plumes to give a mean efficiency of 99.60 %.

5.3.4 Comparison of Sites

Although the methodology present in (Shaw *et al.*, 2023) [89] does possess the ability to detect flaring emissions, the flights of C359 and C360, which had operator verification that flaring did not take place, show that this methodology alone can falsely identify some enhancements as flares.

NO_x : CO_2 emission ratios vary greatly between points but give some insight into the source of an enhancement, the ADMS modelling gives high confidence that flaring was detected on the site 3 survey. This gives a NO_x : CO_2 emission ratio figure of $0.005 \text{ ppm ppm}^{-1}$ for flaring. This figure in turn gives confidence that flight C148 solely detects a flaring plume due to it also possessing a NO_x : CO_2 emission ratio of $0.005 \text{ ppm ppm}^{-1}$. For the second survey of site 1 in 2023, it is possible to see that the NO_x : CO_2 emission ratio varied in accordance with platform activity, as previously discussed, although flaring was not occurring during flights C359 and C360, flaring was still assigned as enhancements were detected in all of the target species, when flaring did occur during flight C361 the

NO_x : CO_2 emission ratio dropped accordingly, as would be expected as flaring would increase the amount of CO_2 emitted from the platform as a whole. However, the NO_x : CO_2 emission ratio is still higher than that of the site 3 flare, but also the flaring detected at this platform 4 years previously. This suggests that although the plumes detected at site 1 in 2023 are influenced by flaring, they may also comprise emissions from other sources, which is likely as this campaign was monitoring the platform during its tanker offloading operations. NO_x : CO_2 emission ratios from all sites and using all methodologies are shown below in **Figure 5.19**.

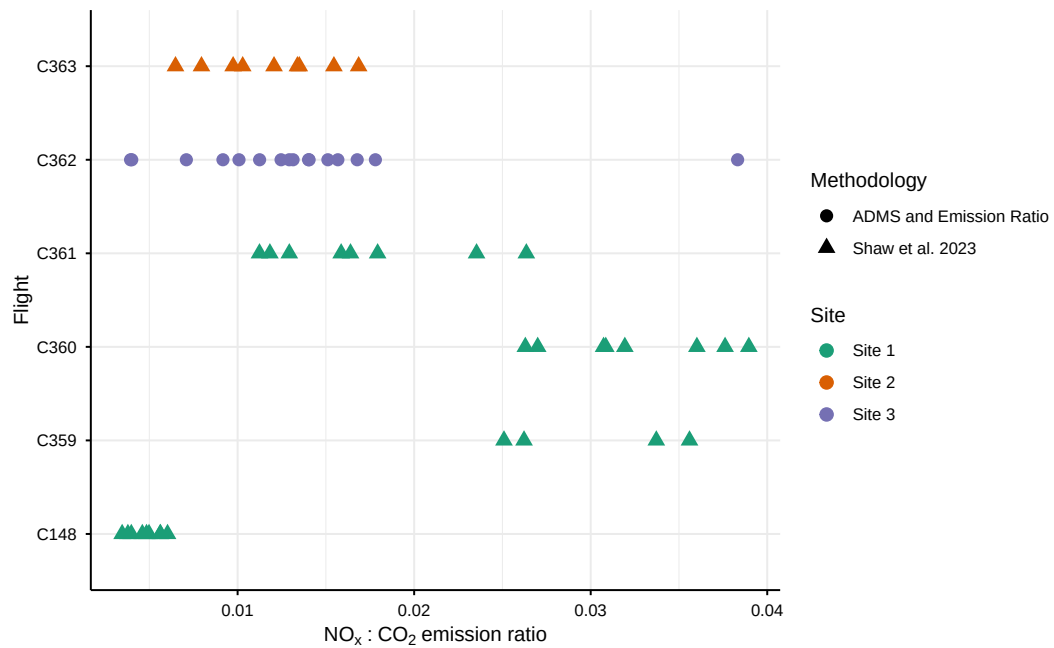


Figure 5.19: Comparison of NO_x : CO_2 emission ratios from each site, coloured by flight number, with shape indicating methodology used.

C_2H_6 : CH_4 emission ratios also vary depending on platform and platform behaviour. The flaring at site 3 gave a figure of $0.015 \text{ ppm ppm}^{-1}$ while the likely flaring at site 1 during C148 gave a much higher figure of $0.271 \text{ ppm ppm}^{-1}$, potential differences may be due to the different efficiencies in the flaring resulting in more emission of C_2H_6 and CH_4 from

site 1, or may be a result of the differing fuel compositions at the site. During the 2023 sampling of site 1, $C_2H_6 : CH_4$ emission ratios were much lower during the purging conditions of C359 and C360 with $C_2H_6 : CH_4$ emission ratios of $0.006 \text{ ppm ppm}^{-1}$ for both flights. When flaring did occur on C361, $C_2H_6 : CH_4$ emission ratios increased to $0.068 \text{ ppm ppm}^{-1}$. As with $NO_x : CO_2$ emission ratios, this shows that there is a visible change at site 1 between purging conditions and active flaring but for $C_2H_6 : CH_4$ emissions ratios this results in an increase in emission ratio as opposed to the decrease seen in $NO_x : CO_2$ emission ratios. The increase is likely due to an increase in the flow of gas through the flare during the flaring as opposed to purging which only requires a very small flow rate. The difference in $C_2H_6 : CH_4$ emission ratios between C361 and C148 is likely due to the influence of the tanker offloading, which results in a larger emission of CH_4 from the platform [103]. This would therefore reduce the $C_2H_6 : CH_4$ emission ratio if the flaring plume is mixed with the offloading plume. All $C_2H_6 : CH_4$ emission ratios, from all sites using all methodologies are shown below in **Figure 5.20**.

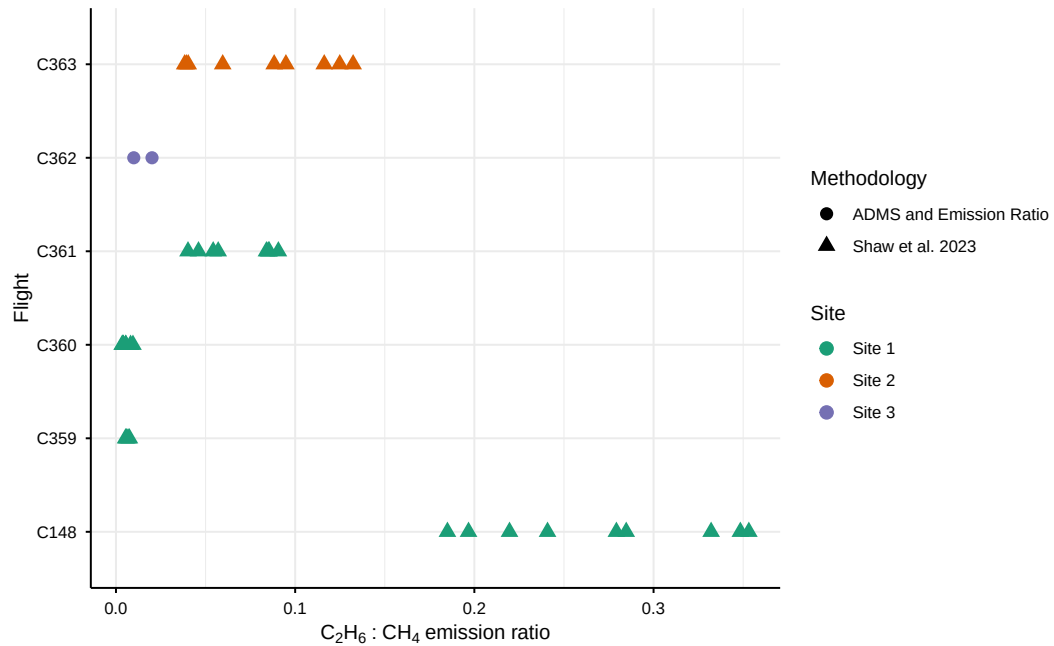


Figure 5.20: Comparison of $C_2H_6 : CH_4$ emission ratios from each site, coloured by flight number, with shape indicating methodology used.

Comparisons to site 2 are difficult due to the site not featuring data associated with a single platform but instead was sampled as a whole site of 6 platforms. $C_2H_6 : CH_4$ emission ratio was found to be $0.082 \text{ ppm ppm}^{-1}$, higher than the $NO_x : CO_2$ emission ratio of $0.012 \text{ ppm ppm}^{-1}$, this is consistent with behaviour seen in known flaring of C362 and C361 as well as likely flaring of C148. The $NO_x : CO_2$ emission ratio was higher than that seen during C362 and C148 which suggests that the plume is mixed with other emissions much like that during the 2023 sampling of site 1. A full comparison of the mean emission ratios calculated for each flight, along with operator's comments where given is shown in **Table 5.12**.

Chapter 5. Offshore flaring emissions

Site	Flight	Mean NO _x : CO ₂ Emission Ratio	Mean C ₂ H ₆ : CH ₄ Emission Ratio	Operator's Comments
Site1	C148	0.005	0.271	NA
Site1	C359	0.030	0.006	Purge Conditions
Site1	C360	0.032	0.006	Purge Conditions
Site1	C361	0.017	0.068	Flaring and Tanker loading
Site2	C363	0.012	0.082	NA
Site 3 Flare Separated	C362	0.005	0.015	Active Flaring
Site 3 Power Generation Separated	C362	0.015	NA	Active Flaring

Table 5.12: Species emission ratios from each flight with operator's comments where available.

Fluxes of all species for all flights are shown in **Table 5.13**. Site 1 has a large variation in its calculated flaring efficiencies, however, this will partly be due to the inability to separate flaring emissions from emissions associated with other sources. This is most noticeable in the efficiency drop from the purge condition runs of C359 and C360 to the flaring and tanker loading run of C361. Although an efficiency drop would be expected during flaring with a larger volume of gas passing through the flare resulting in more slip of CH₄ and C₂H₆, an efficiency drop to this scale is likely due to the added influence of emissions from the offloading of oil to the tanker vessel, which were not separated using this methodology. C148 again shows a different efficiency from the flights of C359 and C360, but, without operator's comments on whether the flare was active during sampling, it is not possible to know if this efficiency change is due to improved efficiency on the platform between 2019 and 2023, or if this is the step-down in efficiency resulting in the platform going from purge conditions on the flare to active flaring. As such, the only flare that can be commented on in regards to global flaring emissions is that of C362, due to the higher confidence from the multiple source attribution stages in its methodology.

Flight	Process	CH ₄ flux / kg s ⁻¹	CH ₄ flux in CO ₂ equivalents / kg s ⁻¹	CO ₂ flux / kg s ⁻¹	C ₂ H ₆ flux / kg s ⁻¹	Mean Flaring Efficiency	Operator comments
Cl48 (Site 1)	Flaring (Shaw et al., 2023)	0.25 ± 0.14	7.45 ± 4.17	2.98 ± 1.38	0.10 ± 0.87	91.58 %	NA
C359 (Site 1)	Flaring (Shaw et al., 2023)	(1.27 ± 1.13) × 10 ⁻³	(3.78 ± 3.37) × 10 ⁻²	1.55 ± 0.50	(3.21 ± 2.75) × 10 ⁻⁵	99.52 %	Purge Conditions
C360 (Site 1)	Flaring (Shaw et al., 2023)	(4.21 ± 1.18) × 10 ⁻³	(1.25 ± 0.35) × 10 ⁻¹	3.83 ± 0.47	(1.13 ± 0.36) × 10 ⁻⁴	99.29 %	Purge Conditions
C361 (Site 1)	Flaring (Shaw et al., 2023)	(4.90 ± 1.82) × 10 ⁻²	(1.46 ± 0.54) × 10 ⁻¹	0.84 ± 0.15	(1.08 ± 0.45) × 10 ⁻²	86.71 %	Flaring and Tanker loading
C362 (Site 2 Flaring)	Flaring (Shaw et al., 2023 with ADMS confirmation)	(2.66 ± 0.87) × 10 ⁻⁵	(7.93 ± 2.59) × 10 ⁻⁴	1.26 ± 0.33	(1.38 ± 0.49) × 10 ⁻⁵	99.60 %	Active Flaring

Table 5.13: CH₄, CO₂ and C₂H₆ fluxes from each flight's flaring emissions

5.3.5 Environmental impact of flaring vs. venting

As *Table 5.13* showed, emissions as a result of flaring at site 3 were; $2.66 \times 10^{-5} \pm 0.87 \times 10^{-5} \text{ kg s}^{-1}$ for CH_4 , $1.26 \pm 0.33 \text{ kg s}^{-1}$ for CO_2 and $1.38 \times 10^{-5} \pm 0.49 \times 10^{-5} \text{ kg s}^{-1}$ with a mean efficiency over the sampling period of 99.60 %. Although the CO_2 produced by flaring is a result of the combustion of CH_4 , C_2H_6 and other hydrocarbons, for a simplified estimation of CH_4 released if the fuel gas was vented, we will assume that all CO_2 is formed as a result of ideal combustion of solely CH_4 . This would mean that the 1.26 kg s^{-1} of CO_2 released by the flare would originate from a release of an equivalent 0.46 kg s^{-1} of CH_4 plus the non combusted $2.66 \times 10^{-5} \text{ kg s}^{-1}$. As CH_4 from fossil fuels has a GWP of 29.8, the venting in CO_2 equivalents ($\text{CO}_2 \text{ e}$) would be 13.65 kg s^{-1} showing that the efficient flaring results in 10.8 times smaller emissions of CO_2 equivalents.

5.4 Conclusions

Flaring continues to be an important contributor to CH_4 emissions from the oil and gas industry and an even more important target to reduce in order to comply with the Global Methane Pledge. Countries like Norway have shown that flaring need not scale in line with oil and gas production and that as a process it can largely be reduced. The incentive to reduce flaring in the UK has increased since the introduction of the NSTA's zero flaring by 2030 policy, but the issue still persists in accurate reporting of operational flares. This work has shown that previous methodologies that rely on flare identification solely from detecting enhancements in all target species may not necessarily be viable for reasons that a flare may be too efficient to detect large enough enhancements of CH_4 or C_2H_6 such as the flaring at Site 3 during C362. Additionally this method may not be viable for platforms when increased processes take place, such as during the 2023

sampling of Site 1 which featured an FPSO preparing for and subsequently offloading oil to a tanker and likely an over prediction of emissions resulting from flaring. In the first instance, this work has shown a promising method when working with operators, the vertical spread of the plume can be understood by using dispersion modelling such as ADMS and subsequent source identification using $\text{NO}_x : \text{CO}_2$ emission ratios can then be used to correctly identify flaring emissions. Emission ratios have also shown to react to changing conditions on a platform, $\text{NO}_x : \text{CO}_2$ emission ratios at site 1 were 1.8 times smaller during C361 compared to the average of the C359 and C360 where the flare was not active but under purge conditions. Conversely, $\text{C}_2\text{H}_6 : \text{CH}_4$ emission ratios were over 10 times higher when the platform was actively flaring compared to purge conditions. These emission ratios are also an indication of other sources mixing with the flaring plume as $\text{NO}_x : \text{CO}_2$ emission ratios of C361 were 3.4 times higher than those detected on C148, the likely isolated flare at the same platform. While $\text{C}_2\text{H}_6 : \text{CH}_4$ emission ratios were 4 times lower, likely due to the increased CH_4 emission from tanker loading during C361. Ultimately this work shows that for future flare sampling, blind surveys become increasingly difficult as both flaring efficiency increases and as more FPSO's are used, increasing the number of different sources. Instead, working with operators to accurately model plume dispersion and inform flight plans beforehand, while using emission ratios after the survey to split different sources, is the recommended approach.

Chapter 6

Summary and conclusions

The introduction of the Global Methane Pledge (GMP) in 2021 has led to an increased importance in the accurate monitoring and reporting of CH₄ emissions by signatory countries. With these signatory countries required to reduce their 2020 CH₄ emissions by 30 % by 2030, this has put a strict time limit on the implementation of this more accurate monitoring. One particular sector that has come under increased focus as a result of the introduction of the GMP, is the oil and gas (O&G) sector, with the Oil and Gas Methane Partnership 2.0 (OGMP 2.0) being introduced which requires operators to report emissions based on measurement based methodologies.

Fugitive emissions are one of the key areas under scrutiny for the O&G sector, they are often unwanted emissions from pressurised pipework, colloquially referred to as gas leaks. But can occur, seemingly randomly at any point in a distribution company's pipework, that in the UK, often covers tens of thousands of kilometres. This creates difficulty in both locating and quantifying these emissions, resulting in difficulty for these companies to comply with OGMP 2.0. Mobile surveys provide a means to locate these emissions as a single survey with a mobile platform can cover a large area of a city, allowing for the monitoring of multiple kilometres of pipework per survey.

Another sector of the O&G industry that is of particular challenge for companies complying with the OGMP 2.0 in the UK is a result of offshore flaring. Although there are directives in place for zero flaring in the North Sea, the reporting of flaring emissions is becoming increasingly difficult in the meantime. Unlike fugitive emissions, flaring emissions occur at a known location, allowing for a targeted survey from a mobile sampling platform. However, as flaring technologies become increasingly efficient, CH₄ undergoes more complete combustion within the flare, resulting in less CH₄ emitted from the flare and therefore a lower chance of being detected by a mobile platform. This leads to difficulty in separating flaring emissions from other processes that occur on an O&G platform.

6.0.1 Thesis summary

The work within this thesis focuses on the development and implementation of mobile measurement methodologies for both the detection of CH₄ from fugitive emissions of domestic natural gas distribution, as well as from offshore O&G flaring.

Chapter 2 discusses adapting existing methodologies for the detection of CH₄ from domestic natural gas networks using mobile platforms. Previous studies have applied the same algorithm with very little adaptation to each study's instrumentation. This chapter takes an existing algorithm but adapts the parameters based on limitations of the survey equipment. The CH₄ enhancement parameter is reduced from previous iterations after exploring the variance of the instrument measuring CH₄, both in laboratory and when situated in the sampling platform, resulting in the enhancement parameter reducing from 1.1 times the calculated background to 1.05 times the calculated background, allowing for the detection of much smaller fugitive emissions. The time clustering parameter was also changed from previous methodologies after response

times of the platforms instrumentations were determined. For campaigns involving the SIFT-MS, this resulted in an increased time clustering parameter (from 5 s to 8 s), however, for surveys where the SIFT-MS was omitted or where the platform used a TILDAS in its place, the time clustering parameter reduced from the previous algorithm (from 5 s to 1 s), this allowed for a greater spatial resolution for gas leak detection surveys, as enhancements that occurred close together could now be reliably differentiated. Finally, a controlled release experiment allowed iterations of the mobile platform using a TILDAS to use an updated quantification equation and explore the lag time that occurs between the separate measurement instruments on the platform.

Chapter 3 features the results of applying *Chapter 2*'s methodology in two UK cities; Bradford and York. The two cities were both initially surveyed during the INGENIOUS campaigns, allowing for the testing of a SIFT-MS for source identification, before revisiting York, with a TILDAS replacing the SIFT-MS. The use of the SIFT-MS was shown to be ineffective within the mobile sampling campaigns, its long measurement time leads to the algorithm's time clustering parameter having to be increased. This leads to far fewer OPs being detected due to a lack of spatial resolution that a lower time clustering parameter allows. Additionally, because the SIFT-MS does not necessarily measure the same parcel of air as the CH₄ enhancement, this leads to very few enhancements being assigned as thermogenic. This is most noticeable in the summer INGENIOUS surveys where 0 LIs are detected due to very few OPs being assigned as thermogenic. The TILDAS however proves to be much more effective for use within a mobile survey to measure fugitive emissions, the shorter response time allows the time clustering parameter to be lowered to 1 s, allowing for greater spatial resolution of the survey and subsequently resulting in the detection of far more OPs than with the SIFT-MS or with algorithms using a 5 s time clustering parameter. Results from the York

2024 surveys showed that natural gas emissions occurred more frequently on major roadways than on smaller neighbourhood roads, as noted in the difference in LI km^{-1} detected on the city wide route as opposed to the neighbourhood route. The source assignment using $\text{C}_2\text{H}_6 : \text{CH}_4$ ratios also gave insight that within cities, pyrogenic emissions provide a large contribution to a city's CH_4 emissions. This pyrogenic fraction was further divided by observing the $\text{NO}_x : \text{CO}_2$ ratios within each peak, this stage allowed pyrogenics to be separated into those originating from domestic combustion and those that didn't. This analysis was new for this type of study, but showed that in York, domestic pyrogenics were a frequently located source of CH_4 , but they have previously received much less attention. Frequency of detection of LIs was found to be low, reinforcing the belief that surveys should be conducted a large number of times in order to detect the fugitive emissions. LIs that were detected, were found to often have a high consistency in prevailing wind direction when detected, suggesting that many fugitive emissions do not occur directly under the centre of the road's surface but rather towards the sides of roads, as this would require wind to blow towards the sampling platform in order to increase the likelihood of detection. Finally, this chapter explores the concerns surrounding the quantification of leak rates from fugitive emissions using peak heights within the quantification equation, an alternative method using peak area was investigated, this approach led to a lower variation in calculated leak rates of LIs across the city, suggesting that the peak height approach is likely highly susceptible to interference from external factors such as wind direction, wind speed and driving speed.

Chapter 4 tests the same methodology within New York City (NYC), exploring how an increased population density affects the number and magnitude of fugitive emissions within a city. The methodology used within NYC expands on the methodology used in York in 2024, source

assignment became stricter due to availability of data surrounding pipeline composition in addition to deploying an instrument that measured both C_2H_6 and CH_4 allowing for an R^2 filter to be applied to the thermogenic assignments. This stricter assignment led to a lower number of OPs being assigned as thermogenic, suggesting that previous assignment parameters may result in an overprediction of thermogenic emissions. Neighbourhood comparisons within NYC showed a large discrepancy in the number of LIs occurring within one specific region of the survey area, the part that was supplied by district steam heating. One of the likely reasons for this increase is the mechanical stress a heated steam pipe may put on surrounding natural gas pipework. Finally, a comparison of emissions in summer vs winter shows that in only one neighbourhood did the number of LIs decrease from winter to summer. The remaining two neighbourhoods had a consistent number of LIs in both seasons, however, all neighbourhoods showed that the leak size of LIs increased from winter to summer.

Finally, *Chapter 5* explores the difficulties with using mobile airborne sampling to detect CH_4 emissions from highly efficient flares on offshore O&G platforms. Previously, flares could be identified by eye or by locating plumes that had enhancements in all of CH_4 , C_2H_6 , CO_2 and NO_x . The highly efficient flare in this study showed little to no enhancements in CH_4 and C_2H_6 , despite knowledge that the flare was active during sampling flights. The source of plumes with NO_x and CO_2 enhancements therefore had to be determined as either originating from the flare or from other processes aboard the platform, such as power generation exhausts. It was found that by using ADMS dispersion modelling, the maximum heights of the flaring plume and power generation plume could be predicted, and enhancements that occur within the height that both sources emit to could then be separated based on $NO_x : CO_2$ emission ratios. This approach allowed emissions from the efficient flare to be detected and quantified

and additionally be compared to other historical flights within the region in order to assess the differing efficiencies and fluxes of platforms in this region.

6.0.2 Recommendations for future work

As the end goal of the GMP comes closer, technology involved in the extraction, refinement and distribution of O&G products containing CH₄ is becoming increasingly efficient and less susceptible to CH₄ loss to the atmosphere through fugitive emission. OGMP 2.0 still requires operators to report their emissions through measurement based methods, but as the emissions get smaller and less frequent, there should be concern in the efficacy of existing methods in order to comply with this.

For surveys surrounding domestic natural gas distribution, this thesis has shown that detected LIs are most often binned within the smallest of leak rate categories ($< 2 \text{ L min}^{-1}$), it is therefore important for future studies that mobile platforms are fitted with instrumentation capable of detecting the smallest possible CH₄ enhancements. While this thesis showed that it was possible to reduce the algorithm's enhancement parameter from 1.1 times the background to 1.05 times the background, future work should aim to reduce this further, to more completely understand the contribution that the smallest leak rate LIs provide to a city's overall CH₄ emissions from natural gas distribution.

Quantification of LIs received a great deal of attention over the course of this thesis, when quantifying via peak height, it has been shown that the quantification equation should be unique to the sampling platform, this can be achieved via a controlled release experiment. However, controlled releases are often expensive and time consuming and peak height quantification is still susceptible to change from external factors such as wind and platform speed. This thesis has shown that peak area

quantification is not only more robust to these external factors, but can easily be applied to platforms that have not undergone a controlled release experiment, allowing for a standardised approach to quantification and therefore more reliable comparisons between different studies.

Source identification was introduced within this thesis as a core step within the LI detection algorithm, the work within York and later NYC shows that without this stage, there are often CH₄ enhancements from other sources that are grouped with thermogenics leading to an over prediction of the number of LIs within a survey area. Additionally, this stage showed that there are several CH₄ emission sources that occur within cities that previously have not received as much attention as emissions from natural gas distribution. For York, this was most notably emissions from domestic pyrogenics, such as from stoves and boilers powered by natural gas; this presents a new avenue for future studies to pursue, to observe the indoor to outdoor exchange of CH₄ from natural gas usage within homes, as well as investigating the efficiencies of said appliances that use natural gas. For NYC, the unidentified fractions were where C₂H₆ : CH₄ ratios exceeded the known natural gas range, but were not so high as to be assigned as pyrogenic; C₂H₆ : CH₄ ratios were lower than the known natural gas range but were not so low as to be assigned biogenic; C₂H₆ : CH₄ ratios were within the known natural gas range but C₂H₆ : CH₄ R² correlation was too low. Greater work needs to be done within NYC to categorise not only these emissions, but to further understand the emission profiles from steam within the city to increase the understanding in the relationship between steam and its effect on a city's CH₄ emissions.

Finally, this thesis attempted to observe seasonal changes in fugitive natural gas emissions, most notably in the NYC work. Although in this instance, there was little change to the number of detected LIs, there was shown to be an effect on the magnitude of LIs, it would therefore be recommended for future studies to attempt to include seasonal

comparisons in this type of survey, to avoid the seasonal effect that may apply to quantification of LIs.

For detection of CH₄ from offshore O&G platform flaring, this thesis has shown that existing methods applied by large research aircraft have become increasingly difficult. For flares which are highly efficient, there is very little CH₄ slip, almost all of the flares fuel gas is converted to CO₂. The little CH₄ that is emitted is often too dispersed to detect at the distance a large research aircraft is required to operate. Although this thesis has shown a methodology whereby working with the operator to produce a more targeted sampling survey can be conducted after modelling plume behaviour with ADMS and subsequently assigning detected enhancements to sources using NO_x : CO₂ emission ratios, the question remains as to whether large research aircraft are the best tools for this type of survey. The solution to this problem where CH₄ is too well dispersed at these distances, may be to employ different measurement platforms, such as drones, which can operate much closer to the platform and potentially overcome the problem that research aircraft face.

In conclusion, although the number of signatories and progress of the GMP provides some optimism in reducing global CH₄ emissions, it also introduces challenges in the monitoring and reporting of these same emissions, particularly from O&G activities. With OGMP 2.0 requiring operators to report emissions through measurement based methods, the future challenges will be accurate reporting, as the emissions become smaller and therefore harder to detect, in order to ensure that not only do operators reach their targets in reduction of CH₄ emissions, but that they can maintain these reductions.

Bibliography

- [1] Judd, E. J., Tierney, J. E., Lunt, D. J., Montañez, I. P., Huber, B. T., Wing, S. L., and Valdes, P. J. A 485-million-year history of Earth's surface temperature. *Science* 385.6715 (2024). doi: 10.1126/science.adk3705.
- [2] NOAA National Centers for Environmental Information. *Monthly Global Climate Report for Annual 2024*. Accessed June 2026. 2025. URL: <https://www.ncei.noaa.gov/access/monitoring/monthly-report/global/202413>.
- [3] Hawkins, E. #ShowYourStripes. <https://showyourstripes.info/>. Accessed: March 2026.
- [4] Morice, C. P., Kennedy, J. J., Rayner, N. A., Winn, J. P., Hogan, E., Killick, R. E., Dunn, R. J. H., Osborn, T. J., Jones, P. D., and Simpson, I. R. An Updated Assessment of Near-Surface Temperature Change From 1850: The HadCRUT5 Data Set. *Journal of Geophysical Research: Atmospheres* 126.3 (2021). doi: 10.1029/2019jd032361.
- [5] Hansen, J. E., Sato, M., Simons, L., Nazarenko, L. S., Sangha, I., Kharecha, P., Zachos, J. C., Schuckmann, K. von, Loeb, N. G., Osman, M. B., Jin, Q., Tselioudis, G., Jeong, E., Lacis, A., Ruedy, R., Russell, G., Cao, J., and Li, J. Global warming in the pipeline. *Oxford Open Climate Change* 3.1 (2023). doi: 10.1093/oxfclm/kgad008. URL: <http://dx.doi.org/10.1093/oxfclm/kgad008>.
- [6] Bilgili, M., Tumse, S., and Nar, S. Comprehensive Overview on the Present State and Evolution of Global Warming, Climate Change, Greenhouse Gasses and Renewable Energy. *Arabian Journal for Science and Engineering*

- 49.11 (2024), pp. 14503–14531. doi: 10.1007/s13369-024-09390-y. URL: <http://dx.doi.org/10.1007/s13369-024-09390-y>.
- [7] Friedlingstein, P. et al. Global Carbon Budget 2024. *Earth System Science Data* 17.3 (2025), pp. 965–1039. doi: 10.5194/essd-17-965-2025.
 - [8] Filonchyk, M., Peterson, M. P., Zhang, L., Hurynovich, V., and He, Y. Greenhouse gases emissions and global climate change: Examining the influence of CO₂, CH₄, and N₂O. *Science of The Total Environment* 935 (2024), p. 173359. doi: 10.1016/j.scitotenv.2024.173359.
 - [9] Watson, A. J., Schuster, U., Shutler, J. D., Holding, T., Ashton, I. G. C., Landschützer, P., Woolf, D. K., and Goddijn-Murphy, L. Revised estimates of ocean-atmosphere CO₂ flux are consistent with ocean carbon inventory. *Nature Communications* 11.1 (2020). doi: 10.1038/s41467-020-18203-3.
 - [10] Duffy, K. A., Schwalm, C. R., Arcus, V. L., Koch, G. W., Liang, L. L., and Schipper, L. A. How close are we to the temperature tipping point of the terrestrial biosphere? *Science Advances* 7.3 (2021). doi: 10.1126/sciadv.aay1052.
 - [11] Prather, M. J., Holmes, C. D., and Hsu, J. Reactive greenhouse gas scenarios: Systematic exploration of uncertainties and the role of atmospheric chemistry. *Geophysical Research Letters* 39.9 (2012). doi: 10.1029/2012gl051440.
 - [12] Intergovernmental Panel on Climate Change (IPCC). *Climate Change 2021 – The Physical Science Basis: Working Group I Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, 2021. doi: 10.1017/9781009157896.
 - [13] Saunio, M., Martinez, A., Poulter, B., Zhang, Z., Raymond, P. A., Regnier, P., Canadell, J. G., Jackson, R. B., Patra, P. K., Bousquet, P., Ciais, P., Dlugokencky, E. J., Lan, X., Allen, G. H., Bastviken, D., Beerling, D. J., Belikov, D. A., Blake, D. R., Castaldi, S., Crippa, M., Deemer, B. R., Dennison, F., Etiope, G., Gedney, N., Höglund-Isaksson, L., Holgersson, M. A., Hopcroft, P. O., Hugelius, G., Ito, A., Jain, A. K.,

- Janardanan, R., Johnson, M. S., Kleinen, T., Krummel, P. B., Lauerwald, R., Li, T., Liu, X., McDonald, K. C., Melton, J. R., Mühle, J., Müller, J., Murguia-Flores, F., Niwa, Y., Noce, S., Pan, S., Parker, R. J., Peng, C., Ramonet, M., Riley, W. J., Rocher-Ros, G., Rosentreter, J. A., Sasakawa, M., Segers, A., Smith, S. J., Stanley, E. H., Thanwerdas, J., Tian, H., Tsuruta, A., Tubiello, F. N., Weber, T. S., Werf, G. R. van der, Worthy, D. E. J., Xi, Y., Yoshida, Y., Zhang, W., Zheng, B., Zhu, Q., Zhu, Q., and Zhuang, Q. Global Methane Budget 2000–2020. *Earth System Science Data* 17.5 (2025), pp. 1873–1958. doi: 10.5194/essd-17-1873-2025.
- [14] East, J. D., Jacob, D. J., Balasus, N., Bloom, A. A., Bruhwiler, L., Chen, Z., Kaplan, J. O., Mickley, L. J., Mooring, T. A., Penn, E., Poulter, B., Sulprizio, M. P., Worden, J. R., Yantosca, R. M., and Zhang, Z. Interpreting the Seasonality of Atmospheric Methane. *Geophysical Research Letters* 51.10 (2024). doi: 10.1029/2024gl108494.
- [15] Kai, F. M., Tyler, S. C., Randerson, J. T., and Blake, D. R. Reduced methane growth rate explained by decreased Northern Hemisphere microbial sources. *Nature* 476.7359 (2011), pp. 194–197. doi: 10.1038/nature10259. URL: <http://dx.doi.org/10.1038/nature10259>.
- [16] Aydin, M., Verhulst, K. R., Saltzman, E. S., Battle, M. O., Montzka, S. A., Blake, D. R., Tang, Q., and Prather, M. J. Recent decreases in fossil-fuel emissions of ethane and methane derived from firn air. *Nature* 476.7359 (2011), pp. 198–201. doi: 10.1038/nature10352. URL: <http://dx.doi.org/10.1038/nature10352>.
- [17] Simpson, I. J., Sulbaek Andersen, M. P., Meinardi, S., Bruhwiler, L., Blake, N. J., Helmig, D., Rowland, F. S., and Blake, D. R. Long-term decline of global atmospheric ethane concentrations and implications for methane. *Nature* 488.7412 (2012), pp. 490–494. doi: 10.1038/nature11342. URL: <http://dx.doi.org/10.1038/nature11342>.
- [18] McNorton, J., Chipperfield, M. P., Gloor, M., Wilson, C., Feng, W., Hayman, G. D., Rigby, M., Krummel, P. B., O'Doherty, S., Prinn, R. G., Weiss, R. F., Young, D., Dlugokencky, E., and Montzka, S. A. Role of OH

- variability in the stalling of the global atmospheric CH₄ growth rate from 1999 to 2006. *Atmospheric Chemistry and Physics* 16.12 (2016), pp. 7943–7956. doi: 10.5194/acp-16-7943-2016. URL: <http://dx.doi.org/10.5194/acp-16-7943-2016>.
- [19] Turner, A. J., Frankenberg, C., Wennberg, P. O., and Jacob, D. J. Ambiguity in the causes for decadal trends in atmospheric methane and hydroxyl. *Proceedings of the National Academy of Sciences* 114.21 (2017), pp. 5367–5372. doi: 10.1073/pnas.1616020114. URL: <http://dx.doi.org/10.1073/pnas.1616020114>.
- [20] International Energy Agency (IEA). *Energy Statistics Data Browser: Total Energy Supply by Source*. <https://www.iea.org/data-and-statistics/data-tools/energy-statistics-data-browser?country=WORLD&fuel=Energy%20supply&indicator=TESbySource>. Accessed: March 2026. International Energy Agency, 2025.
- [21] Scarpelli, T. R., Roy, E., Jacob, D. J., Sulprizio, M. P., Tate, R. D., and Cusworth, D. H. Using new geospatial data and 2020 fossil fuel methane emissions for the Global Fuel Exploitation Inventory (GFEI) v3. *Earth System Science Data* 17.12 (2025), pp. 7019–7033. doi: 10.5194/essd-17-7019-2025.
- [22] Hill, J., McSweeney, C., Wright, A.-D. G., Bishop-Hurley, G., and Kalantar-zadeh, K. Measuring Methane Production from Ruminants. *Trends in Biotechnology* 34.1 (2016), pp. 26–35. doi: 10.1016/j.tibtech.2015.10.004.
- [23] Bačėninaitė, D., Džermeikaitė, K., and Antanaitis, R. Global Warming and Dairy Cattle: How to Control and Reduce Methane Emission. *Animals* 12.19 (2022), p. 2687. doi: 10.3390/ani12192687.
- [24] Zhang, B., Tian, H., Ren, W., Tao, B., Lu, C., Yang, J., Banger, K., and Pan, S. Methane emissions from global rice fields: Magnitude, spatiotemporal patterns, and environmental controls. *Global Biogeochemical Cycles* 30.9

- (2016), pp. 1246–1263. doi: 10.1002/2016gb005381. URL: <http://dx.doi.org/10.1002/2016GB005381>.
- [25] National Atmospheric Emissions Inventory (NAEI). *UK Emissions Data Selector. Selected emissions data for the year 2023, all sectors*. Accessed: March 2026. National Atmospheric Emissions Inventory (NAEI). URL: <https://naei.energysecurity.gov.uk/data/data-selector>.
- [26] Texier, H. le, Solomon, S., and Garcia, R. R. The role of molecular hydrogen and methane oxidation in the water vapour budget of the stratosphere. *Quarterly Journal of the Royal Meteorological Society* 114.480 (1988), pp. 281–295. doi: 10.1002/qj.49711448002.
- [27] Allan, W., Struthers, H., and Lowe, D. C. Methane carbon isotope effects caused by atomic chlorine in the marine boundary layer: Global model results compared with Southern Hemisphere measurements. *Journal of Geophysical Research: Atmospheres* 112.D4 (2007). doi: 10.1029/2006jd007369.
- [28] Thornton, J. A., Kercher, J. P., Riedel, T. P., Wagner, N. L., Cozic, J., Holloway, J. S., Dubé, W. P., Wolfe, G. M., Quinn, P. K., Middlebrook, A. M., Alexander, B., and Brown, S. S. A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. *Nature* 464.7286 (2010), pp. 271–274. doi: 10.1038/nature08905.
- [29] Curry, C. L. Modeling the soil consumption of atmospheric methane at the global scale. *Global Biogeochemical Cycles* 21.4 (2007). doi: 10.1029/2006gb002818.
- [30] Dutaur, L. and Verchot, L. V. A global inventory of the soil CH₄ sink. *Global Biogeochemical Cycles* 21.4 (2007). doi: 10.1029/2006gb002734.
- [31] Nelson, B. S., Stewart, G. J., Drysdale, W. S., Newland, M. J., Vaughan, A. R., Dunmore, R. E., Edwards, P. M., Lewis, A. C., Hamilton, J. F., Acton, W. J., Hewitt, C. N., Crilley, L. R., Alam, M. S., Şahin, Ü. A., Beddows, D. C. S., Bloss, W. J., Slater, E., Whalley, L. K., Heard, D. E., Cash, J. M., Langford, B., Nemitz, E., Sommariva, R., Cox, S., Gadi, R., Gurjar, B. R., Hopkins, J. R.,

- Rickard, A. R., and Lee, J. D. In situ ozone production is highly sensitive to volatile organic compounds in Delhi, India. *Atmospheric Chemistry and Physics* 21.17 (2021), pp. 13609–13630. doi: 10.5194/acp-21-13609-2021.
- [32] Lim, S. S. et al. A comparative risk assessment of burden of disease and injury attributable to 67 risk factors and risk factor clusters in 21 regions, 1990–2010: a systematic analysis for the Global Burden of Disease Study 2010. *The Lancet* 380.9859 (2012), pp. 2224–2260. doi: 10.1016/S0140-6736(12)61766-8.
- [33] Sitch, S., Cox, P. M., Collins, W. J., and Huntingford, C. Indirect radiative forcing of climate change through ozone effects on the land-carbon sink. *Nature* 448.7155 (2007), pp. 791–794. doi: 10.1038/nature06059.
- [34] Fowler, D., Pilegaard, K., Sutton, M., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H., Fuzzi, S., Schjoerring, J., Granier, C., Neftel, A., Isaksen, I., Laj, P., Maione, M., Monks, P., Burkhardt, J., Daemmgen, U., Neirynck, J., Personne, E., Wichink-Kruit, R., Butterbach-Bahl, K., Flechard, C., Tuovinen, J., Coyle, M., Gerosa, G., Loubet, B., Altimir, N., Gruenhage, L., Ammann, C., Cieslik, S., Paoletti, E., Mikkelsen, T., Ro-Poulsen, H., Cellier, P., Cape, J., Horváth, L., Loreto, F., Niinemets, Ü., Palmer, P., Rinne, J., Misztal, P., Nemitz, E., Nilsson, D., Pryor, S., Gallagher, M., Vesala, T., Skiba, U., Brüggemann, N., Zechmeister-Boltenstern, S., Williams, J., O'Dowd, C., Facchini, M., Leeuw, G. de, Flossman, A., Chaumerliac, N., and Erisman, J. Atmospheric composition change: Ecosystems–Atmosphere interactions. *Atmospheric Environment* 43.33 (2009), pp. 5193–5267. doi: 10.1016/j.atmosenv.2009.07.068.
- [35] Stevenson, D. S., Young, P. J., Naik, V., Lamarque, J.-F., Shindell, D. T., Voulgarakis, A., Skeie, R. B., Dalsoren, S. B., Myhre, G., Berntsen, T. K., Folberth, G. A., Rumbold, S. T., Collins, W. J., MacKenzie, I. A., Doherty, R. M., Zeng, G., Noije, T. P. C. van, Strunk, A., Bergmann, D., Cameron-Smith, P., Plummer, D. A., Strode, S. A., Horowitz, L., Lee, Y. H., Szopa, S., Sudo, K., Nagashima, T., Josse, B., Cionni, I., Righi, M.,

- Eyring, V., Conley, A., Bowman, K. W., Wild, O., and Archibald, A. Tropospheric ozone changes, radiative forcing and attribution to emissions in the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP). *Atmospheric Chemistry and Physics* 13.6 (2013), pp. 3063–3085. doi: 10.5194/acp-13-3063-2013.
- [36] Shindell, D., Kuylensstierna, J. C. I., Vignati, E., Dingenen, R. van, Amann, M., Klimont, Z., Anenberg, S. C., Muller, N., Janssens-Maenhout, G., Raes, F., Schwartz, J., Faluvegi, G., Pozzoli, L., Kupiainen, K., Höglund-Isaksson, L., Emberson, L., Streets, D., Ramanathan, V., Hicks, K., Oanh, N. T. K., Milly, G., Williams, M., Demkine, V., and Fowler, D. Simultaneously Mitigating Near-Term Climate Change and Improving Human Health and Food Security. *Science* 335.6065 (2012), pp. 183–189. doi: 10.1126/science.1210026.
- [37] Energy Institute. *Statistical Review of World Energy*. Accessed: July 2026. Energy Institute. 2026. URL: <https://www.energyinst.org/statistical-review>.
- [38] Martins, M. C. I., Carter, M. I., Rouse, S., and Russell, D. J. Offshore Energy Structures in the North Sea: Past, Present and Future. *Marine Policy* 152 (2023), p. 105629. doi: 10.1016/j.marpol.2023.105629.
- [39] Department for Energy Security and Net Zero (DESNZ). *Digest of UK Energy Statistics (DUKES): Natural Gas, DUKES 2025 Chapter 4: Natural Gas*. Accessed: March 2026. Department for Energy Security and Net Zero (DESNZ). 2025. URL: <https://www.gov.uk/government/statistics/natural-gas-chapter-4-digest-of-united-kingdom-energy-statistics-dukes>.
- [40] Department for Energy Security and Net Zero (DESNZ). *Digest of UK Energy Statistics (DUKES): Petroleum, DUKES 2025 Chapter 3: Oil and Oil Products*. Accessed: March 2026. Department for Energy Security and Net Zero (DESNZ). 2025. URL: <https://www.gov.uk/government/statistics/petroleum-chapter-3-digest-of-united-kingdom-energy-statistics-dukes>.

- [41] Energy Institute. *Statistical Review of World Energy: Natural gas consumption in the United Kingdom (UK) from 2003 to 2023 (in billion cubic meters)*. Accessed: December 2024. Energy Institute. 2023. URL: https://www.energyinst.org/__data/assets/pdf_file/0004/1055542/EI_Stat_Review_PDF_single_3.pdf.
- [42] Department for Energy Security and Net Zero (DESNZ). *Energy Trends: UK gas; Natural gas supply and consumption ET 4.1 - quarterly*. Accessed: July 2026. Department for Energy Security and Net Zero (DESNZ). 2026. URL: <https://www.gov.uk/government/statistics/gas-section-4-energy-trends>.
- [43] Stewart, I. and Bolton, P. *Households off the gas-grid and prices for alternative fuels*. Accessed December 2024. House of Commons Library. 2024. URL: <https://researchbriefings.files.parliament.uk/documents/CBP-9838/CBP-9838.pdf>.
- [44] Sotoodeh, K. Why packing adjustment cannot stop leakage: Case study of a ball valve failing to seal after packing adjustment during fugitive emission as per ISO 15848-1. *Engineering Failure Analysis* 130 (2021), p. 105751. DOI: 10.1016/j.engfailanal.2021.105751.
- [45] National Atmospheric Emissions Inventory (NAEI). *UK Emissions Data Selector. Selected emissions data for the year 2023, methane emissions related to gas leakage from gas distribution 1B2bv*. Accessed: March 2026. National Atmospheric Emissions Inventory (NAEI). URL: <https://naei.energysecurity.gov.uk/data/data-selector>.
- [46] European Commission and United States of America. *Global Methane Pledge*. <https://www.ccacoalition.org/sites/default/files/resources/Global-Methane-Pledge.pdf> (accessed July 2025). 2021.
- [47] Tsagatakis, I., Richardson, J., Evangelides, C., Hows, S.-M., Hamilton, N., Richmond, B., Pearson, B., Passant, N., Pommier, M., Pizzolato, M., and Otto, A. *UK Spatial Emissions Methodology: A report of the National*

- Atmospheric Emission Inventory* 2022. 2024. URL: https://uk-air.defra.gov.uk/assets/documents/reports/cat05/2501171412_UK_Spatial_Emissions_Methodology_for_NAEI_2022.pdf.
- [48] Phillips, N. G., Ackley, R., Crosson, E. R., Down, A., Hutyra, L. R., Brondfield, M., Karr, J. D., Zhao, K., and Jackson, R. B. Mapping urban pipeline leaks: Methane leaks across Boston. *Environmental Pollution* 173 (2013), pp. 1–4. doi: 10.1016/j.envpol.2012.11.003.
 - [49] Chamberlain, S. D., Ingraffea, A. R., and Sparks, J. P. Sourcing methane and carbon dioxide emissions from a small city: Influence of natural gas leakage and combustion. *Environmental Pollution* 218 (2016), pp. 102–110. doi: 10.1016/j.envpol.2016.08.036.
 - [50] Hopkins, F. M., Kort, E. A., Bush, S. E., Ehleringer, J. R., Lai, C.-T., Blake, D. R., and Randerson, J. T. Spatial patterns and source attribution of urban methane in the Los Angeles Basin. *Journal of Geophysical Research: Atmospheres* 121.5 (2016), pp. 2490–2507. doi: 10.1002/2015jd024429.
 - [51] Keyes, T., Ridge, G., Klein, M., Phillips, N., Ackley, R., and Yang, Y. An enhanced procedure for urban mobile methane leak detection. *Heliyon* 6.10 (2020), e04876. doi: 10.1016/j.heliyon.2020.e04876.
 - [52] Fischer, J. C. von, Cooley, D., Chamberlain, S., Gaylord, A., Griebenow, C. J., Hamburg, S. P., Salo, J., Schumacher, R., Theobald, D., and Ham, J. Rapid, Vehicle-Based Identification of Location and Magnitude of Urban Natural Gas Pipeline Leaks. *Environmental Science & Technology* 51.7 (2017), pp. 4091–4099. doi: 10.1021/acs.est.6b06095.
 - [53] Luetschwager, E., Fischer, J. C. von, and Weller, Z. D. Characterizing detection probabilities of advanced mobile leak surveys. *Elementa: Science of the Anthropocene* 9.1 (2021). doi: 10.1525/elementa.2020.00143.
 - [54] Weller, Z. D., Yang, D. K., and Fischer, J. C. von. An open source algorithm to detect natural gas leaks from mobile methane survey data. *PLOS ONE* 14.2 (2019). Ed. by M. Mauder, e0212287. doi: 10.1371/journal.pone.0212287.

- [55] Maazallahi, H., Fernandez, J. M., Menoud, M., Zavala-Araiza, D., Weller, Z. D., Schwietzke, S., Fischer, J. C. von, Denier van der Gon, H., and Röckmann, T. Methane mapping, emission quantification, and attribution in two European cities: Utrecht (NL) and Hamburg (DE). *Atmospheric Chemistry and Physics* 20.23 (2020), pp. 14717–14740. doi: 10.5194/acp-20-14717-2020.
- [56] Fernandez, J., Maazallahi, H., France, J., Menoud, M., Corbu, M., Ardelean, M., Calcan, A., Townsend-Small, A., Veen, C. van der, Fisher, R., Lowry, D., Nisbet, E., and Röckmann, T. Street-level methane emissions of Bucharest, Romania and the dominance of urban wastewater. *Atmospheric Environment: X* 13 (2022), p. 100153. doi: 10.1016/j.aeaoa.2022.100153.
- [57] Ars, S., Vogel, F., Arrowsmith, C., Heerah, S., Knuckey, E., Lavoie, J., Lee, C., Pak, N. M., Phillips, J. L., and Wunch, D. Investigation of the Spatial Distribution of Methane Sources in the Greater Toronto Area Using Mobile Gas Monitoring Systems. *Environmental Science & Technology* 54.24 (2020), pp. 15671–15679. doi: 10.1021/acs.est.0c05386.
- [58] Weller, Z. D., Im, S., Palacios, V., Stuchiner, E., and Fischer, J. C. von. Environmental Injustices of Leaks from Urban Natural Gas Distribution Systems: Patterns among and within 13 U.S. Metro Areas. *Environmental Science & Technology* 56.12 (2022), pp. 8599–8609. doi: 10.1021/acs.est.2c00097.
- [59] Defratyka, S. M., Paris, J.-D., Yver-Kwok, C., Fernandez, J. M., Korben, P., and Bousquet, P. Mapping Urban Methane Sources in Paris, France. *Environmental Science & Technology* 55.13 (2021), pp. 8583–8591. doi: 10.1021/acs.est.1c00859.
- [60] Wietzel, J. B. and Schmidt, M. Methane emission mapping and quantification in two medium-sized cities in Germany: Heidelberg and Schwetzingen. *Atmospheric Environment: X* 20 (2023), p. 100228. doi: 10.1016/j.aeaoa.2023.100228.

- [61] Vogel, F., Ars, S., Wunch, D., Lavoie, J., Gillespie, L., Maazallahi, H., Röckmann, T., Nęcki, J., Bartyzel, J., Jagoda, P., Lowry, D., France, J., Fernandez, J., Bakkaloglu, S., Fisher, R., Lanoiselle, M., Chen, H., Oudshoorn, M., Yver-Kwok, C., Defratyka, S., Morgui, J. A., Estruch, C., Curcoll, R., Grossi, C., Chen, J., Dietrich, F., Forstmaier, A., Denier van der Gon, H. A. C., Dellaert, S. N. C., Salo, J., Corbu, M., Iancu, S. S., Tudor, A. S., Scarlat, A. I., and Calcan, A. Ground-Based Mobile Measurements to Track Urban Methane Emissions from Natural Gas in 12 Cities across Eight Countries. *Environmental Science & Technology* 58.5 (2024), pp. 2271–2281. doi: 10.1021/acs.est.3c03160.
- [62] Wagner, R. L., Farren, N. J., Davison, J., Young, S., Hopkins, J. R., Lewis, A. C., Carslaw, D. C., and Shaw, M. D. Application of a mobile laboratory using a selected-ion flow-tube mass spectrometer (SIFT-MS) for characterisation of volatile organic compounds and atmospheric trace gases. *Atmospheric Measurement Techniques* 14.9 (2021), pp. 6083–6100. doi: 10.5194/amt-14-6083-2021.
- [63] Carslaw, N., Aghaji, J., Budisulistiorini, S. H., Carslaw, D. C., Chatzidiakou, L., Cheung, R. W., Dillon, T. J., Edwards, P., Genes, D., Giorio, C., Hamilton, J. F., Ikeda, E., Jones, R. L., Lee, J., Lewis, A. C., Kumar, A., McEachan, R., McFiggans, G., Murrels, T., Pleace, N., Ruangkanit, A., Shao, Y., O'Meara, S. P., Shaw, D. R., Shaw, M., Waiblinger, D., Warburton, T., West, S., Wood, C., and Yang, T. The INGENIOUS project: towards understanding air pollution in homes. *Environmental Science: Processes & Impacts* 27.2 (2025), pp. 355–372. doi: 10.1039/d4em00634h.
- [64] Yacovitch, T. I., Herndon, S. C., Roscioli, J. R., Floerchinger, C., McGovern, R. M., Agnese, M., Pétron, G., Kofler, J., Sweeney, C., Karion, A., Conley, S. A., Kort, E. A., Nöhle, L., Fischer, M., Hildebrandt, L., Koeth, J., McManus, J. B., Nelson, D. D., Zahniser, M. S., and Kolb, C. E. Demonstration of an Ethane Spectrometer for Methane

- Source Identification. *Environmental Science & Technology* 48.14 (2014), pp. 8028–8034. DOI: 10.1021/es501475q.
- [65] Budisulistiorini, S. H., Moore, T. C., Shaw, M. D., Drysdale, W. S., Lee, J. D., and Carslaw, D. C. Toward Linking Indoor Commercial Source Emissions to Outdoor Volatile Organic Compounds Using Mobile Measurements. *ACS ES&T Air* 3.5 (2026), pp. 1191–1203. DOI: 10.1021/acsestair.5c00290. URL: <http://dx.doi.org/10.1021/acsestair.5c00290>.
- [66] Bains, M., Hill, L., and Rossington, P. *Material comparators for end-of-waste decisions, Fuels: natural Gas*. Report: SC130040/R15. Accessed: March 2026. Environment Agency, 2016. URL: https://assets.publishing.service.gov.uk/media/5a80f4b9ed915d74e6231655/Material_comparators_for_fuels_-_natural_gas.pdf.
- [67] ABB. *Microportable Gas Analyzers GLA131 Series*. <https://new.abb.com/products/measurement-products/analytical/laser-gas-analyzers/laser-analyzers/lgr-icos-portable-analyzers/lgr-icos-microportable-analyzers-gla131-series>. Accessed: March 2026. n.d.
- [68] Lowry, D., Fisher, R. E., France, J. L., Coleman, M., Lanoisellé, M., Zazzeri, G., Nisbet, E. G., Shaw, J. T., Allen, G., Pitt, J., and Ward, R. S. Environmental baseline monitoring for shale gas development in the UK: Identification and geochemical characterisation of local source emissions of methane to atmosphere. *Science of The Total Environment* 708 (2020), p. 134600. DOI: 10.1016/j.scitotenv.2019.134600.
- [69] Association, E. P. O. *The Essex Design Guide: Design Details, 2018 Edition, V3*. Accessed December 2024. 2018. URL: <https://www.essexdesignguide.co.uk/media/2402/design-details-v3.pdf>.
- [70] Moore, T. *tcm515/Fugitive-natural-gas-emissions-York-code: WACL fugitive emission detection*. 2026. DOI: 10.5281/ZENODO.20411639. URL: <https://zenodo.org/doi/10.5281/zenodo.20411639>.

- [71] Ueyama, M., Umezawa, T., Terao, Y., Lunt, M., and France, J. L. Evaluating urban methane emissions and their attributes in a megacity, Osaka, Japan, via mobile and eddy covariance measurements. *Atmospheric Chemistry and Physics* 25.19 (2025), pp. 12513–12534. doi: 10.5194/acp-25-12513-2025.
- [72] Umezawa, T., Terao, Y., Ueyama, M., Kameyama, S., Lunt, M., and France, J. L. Measurement report: Mobile measurements to estimate urban methane emissions in Tokyo. *Atmospheric Chemistry and Physics* 25.23 (2025), pp. 18015–18029. doi: 10.5194/acp-25-18015-2025.
- [73] Department for Transport. *Road Length Statistics, RDL0102: Road length (miles) by road type and local authority in Great Britain*. Accessed April 2025. 2025. URL: <https://www.gov.uk/government/statistical-data-sets/road-length-statistics-rdl>.
- [74] Tettenborn, J., Zavala-Araiza, D., Stroeken, D., Maazallahi, H., Veen, C. van der, Hensen, A., Velzeboer, I., Bulk, P. van den, Vogel, F., Gillespie, L., Ars, S., France, J., Lowry, D., Fisher, R., and Röckmann, T. Improving consistency in methane emission quantification from the natural gas distribution systems across measurement devices. *Atmospheric Measurement Techniques* 18.14 (2025), pp. 3569–3584. doi: 10.5194/amt-18-3569-2025.
- [75] Pitt, J. R., Lopez-Coto, I., Hajny, K. D., Tomlin, J., Kaeser, R., Jayarathne, T., Stirm, B. H., Floerchinger, C. R., Loughner, C. P., Gately, C. K., Hutyra, L. R., Gurney, K. R., Roest, G. S., Liang, J., Gourdji, S., Karion, A., Whetstone, J. R., and Shepson, P. B. New York City greenhouse gas emissions estimated with inverse modeling of aircraft measurements. *Elementa: Science of the Anthropocene* 10.1 (2022). doi: 10.1525/elementa.2021.00082.
- [76] Pitt, J. R., Lopez-Coto, I., Karion, A., Hajny, K. D., Tomlin, J., Kaeser, R., Jayarathne, T., Stirm, B. H., Floerchinger, C. R., Loughner, C. P., Commane, R., Gately, C. K., Hutyra, L. R., Gurney, K. R., Roest, G. S., Liang, J., Gourdji, S., Mueller, K. L., Whetstone, J. R., and Shepson, P. B. Underestimation of Thermogenic Methane Emissions in New York City. *Environmental Science*

- & Technology* 58.21 (2024), pp. 9147–9157. doi: 10.1021/acs.est.3c10307.
- [77] Con Edison, Inc. *Long-Range Plan: Our District Steam System*. Accessed February 2026. 2021. URL: <https://www.coned.com/-/media/files/coned/documents/our-energy-future/our-energy-vision/long-range-plans/steam-long-range-plan.pdf>.
- [78] Schiferl, L. D., Hallward-Driemeier, A., Zhao, Y., Toledo-Crow, R., and Commane, R. Missing wintertime methane emissions from New York City related to combustion. *Atmospheric Chemistry and Physics* 25.22 (2025), pp. 15683–15700. doi: 10.5194/acp-25-15683-2025. URL: <http://dx.doi.org/10.5194/acp-25-15683-2025>.
- [79] LI-COR. *LI-7810 CH₄/CO₂/H₂O Trace Gas Analyzer: Real-time methane measurements*. Accessed February 2026. n.d. URL: <https://www.licor.com/products/trace-gas/LI-7810#specs>.
- [80] Aeris Technologies. *MIRA Ultra Mobile LDS: CH₄/C₂H₆ Natural Gas Leak Detection System with GPS*. Accessed February 2026. n.d. URL: https://aerissensors.com/wp-content/uploads/2021/12/MIRA-Ultra-LDS-Rackmount_211208.pdf.
- [81] Commane, R., Hallward-Driemeier, A., and Murray, L. T. Intercomparison of commercial analyzers for atmospheric ethane and methane observations. *Atmospheric Measurement Techniques* 16.5 (2023), pp. 1431–1441. doi: 10.5194/amt-16-1431-2023.
- [82] Aeris Technologies. *MIRA Ultra N₂O/CO: High Accuracy N₂O/CO Analyzer*. Accessed February 2026. n.d. URL: https://thomsongroup.com.au/wp-content/uploads/2024/09/MIRA-Ultra_N2O_CO_191207_FINAL_quartz.pdf.
- [83] National Oceanic and Atmospheric Administration (NOAA). *NOAA Calibration Scales for Various Trace Gases*. Accessed March 2026. URL: <https://gml.noaa.gov/ccl/scales.html>.

- [84] Moore, T. C., Hopkins, J. R., Drysdale, W. S., Young, S., Budisulistiorini, S. H., Shaw, M. D., France, J. L., Lowry, D., and Lee, J. D. Fugitive emissions of natural gas in York, United Kingdom: Adapting existing algorithm parameters to be based on instrument specifications. *EGUsphere (preprint)* (2025). doi: 10.5194/egusphere-2025-5348.
- [85] NYC Department of City Planning. *NYC Population Fact Finder*. Data source: American Community Survey (ACS) 2019–2023; Upper East Side and East Harlem census tracts. Accessed February 2026. n.d. URL: <https://popfactfinder.planning.nyc.gov/#13.94/40.78565/-73.94552>.
- [86] North Sea Transition Authority. *Emissions Monitoring Report 2025*. Accessed October 2025. 2025. URL: <https://storymaps.arcgis.com/stories/0d057da0fdd84f8ea7f7889a918b1903>.
- [87] Reid, A. and Flora, A. *UK Offshore Flaring and Venting*. Accessed October 2025. 2023. URL: https://ieefa.org/sites/default/files/2023-03/UK-Offshore-Flaring-and-Venting_March-2023-0.pdf.
- [88] North Sea Transition Authority. *UK North Sea flaring halved in just four years*. Accessed July 2025. 2023. URL: <https://www.nstauthority.co.uk/news-publications/uk-north-sea-flaring-halved-in-just-four-years/>.
- [89] Shaw, J. T., Foulds, A., Wilde, S., Barker, P., Squires, F. A., Lee, J., Purvis, R., Burton, R., Colfescu, I., Mobbs, S., Cliff, S., Bauguitte, S. J.-B., Young, S., Schwietzke, S., and Allen, G. Flaring efficiencies and NO_x emission ratios measured for offshore oil and gas facilities in the North Sea. *Atmospheric Chemistry and Physics* 23.2 (2023), pp. 1491–1509. doi: 10.5194/acp-23-1491-2023.
- [90] Palmer, P. I., O'Doherty, S., Allen, G., Bower, K., Bösch, H., Chipperfield, M. P., Connors, S., Dhomse, S., Feng, L., Finch, D. P., Gallagher, M. W., Gloor, E., Gonzi, S., Harris, N. R. P., Helfter, C., Humpage, N., Kerridge, B., Knappett, D., Jones, R. L., Le Breton, M., Lunt, M. F., Manning, A. J., Matthiesen, S., Muller, J. B. A., Mullinger, N.,

- Nemitz, E., O'Shea, S., Parker, R. J., Percival, C. J., Pitt, J., Riddick, S. N., Rigby, M., Sembhi, H., Siddans, R., Skelton, R. L., Smith, P., Sonderfeld, H., Stanley, K., Stavert, A. R., Wenger, A., White, E., Wilson, C., and Young, D. A measurement-based verification framework for UK greenhouse gas emissions: an overview of the Greenhouse gAs Uk and Global Emissions (GAUGE) project. *Atmospheric Chemistry and Physics* 18.16 (2018), pp. 11753–11777. doi: 10.5194/acp-18-11753-2018.
- [91] O'Shea, S. J., Bauguitte, S. J.-B., Gallagher, M. W., Lowry, D., and Percival, C. J. Development of a cavity-enhanced absorption spectrometer for airborne measurements of CH₄ and CO₂. *Atmospheric Measurement Techniques* 6.5 (2013), pp. 1095–1109. doi: 10.5194/amt-6-1095-2013.
- [92] Shaw, J. T., Allen, G., Barker, P., Pitt, J. R., Pasternak, D., Bauguitte, S. J.-B., Lee, J., Bower, K. N., Daly, M. C., Lunt, M. F., Ganesan, A. L., Vaughan, A. R., Chibesakunda, F., Lambakasa, M., Fisher, R. E., France, J. L., Lowry, D., Palmer, P. I., Metzger, S., Parker, R. J., Gedney, N., Bateson, P., Cain, M., Lorente, A., Borsdorff, T., and Nisbet, E. G. Large Methane Emission Fluxes Observed From Tropical Wetlands in Zambia. *Global Biogeochemical Cycles* 36.6 (2022). doi: 10.1029/2021gb007261.
- [93] Lee, J. D., Moller, S. J., Read, K. A., Lewis, A. C., Mendes, L., and Carpenter, L. J. Year-round measurements of nitrogen oxides and ozone in the tropical North Atlantic marine boundary layer. *Journal of Geophysical Research: Atmospheres* 114.D21 (2009). doi: 10.1029/2009jd011878.
- [94] Graham, A. M., Pope, R. J., McQuaid, J. B., Pringle, K. P., Arnold, S. R., Bruno, A. G., Moore, D. P., Harrison, J. J., Chipperfield, M. P., Rigby, R., Sanchez-Marroquin, A., Lee, J., Wilde, S., Siddans, R., Kerridge, B. J., Ventress, L. J., and Latter, B. G. Impact of the June 2018 Saddleworth Moor wildfires on air quality in northern England. *Environmental Research Communications* 2.3 (2020), p. 031001. doi: 10.1088/2515-7620/ab7b92.
- [95] Nara, H., Tanimoto, H., Tohjima, Y., Mukai, H., Nojiri, Y., and Machida, T. Emissions of methane from offshore oil and gas platforms in Southeast Asia. *Scientific Reports* 4.1 (2014). doi: 10.1038/srep06503.

- [96] Caulton, D. R., Shepson, P. B., Cambaliza, M. O. L., McCabe, D., Baum, E., and Stirm, B. H. Methane Destruction Efficiency of Natural Gas Flares Associated with Shale Formation Wells. *Environmental Science & Technology* 48.16 (2014), pp. 9548–9554. doi: 10.1021/es500511w.
- [97] Corbin, D. J. and Johnson, M. R. Detailed Expressions and Methodologies for Measuring Flare Combustion Efficiency, Species Emission Rates, and Associated Uncertainties. *Industrial & Engineering Chemistry Research* 53.49 (2014), pp. 19359–19369. doi: 10.1021/ie502914k.
- [98] O’Shea, S. J., Allen, G., Gallagher, M. W., Bower, K., Illingworth, S. M., Muller, J. B. A., Jones, B. T., Percival, C. J., Bauguitte, S. J.-B., Cain, M., Warwick, N., Quiquet, A., Skiba, U., Drewer, J., Dinsmore, K., Nisbet, E. G., Lowry, D., Fisher, R. E., France, J. L., Aurela, M., Lohila, A., Hayman, G., George, C., Clark, D. B., Manning, A. J., Friend, A. D., and Pyle, J. Methane and carbon dioxide fluxes and their regional scalability for the European Arctic wetlands during the MAMM project in summer 2012. *Atmospheric Chemistry and Physics* 14.23 (2014), pp. 13159–13174. doi: 10.5194/acp-14-13159-2014.
- [99] Pitt, J. R., Allen, G., Bauguitte, S. J.-B., Gallagher, M. W., Lee, J. D., Drysdale, W., Nelson, B., Manning, A. J., and Palmer, P. I. Assessing London CO₂, CH₄ and CO emissions using aircraft measurements and dispersion modelling. *Atmospheric Chemistry and Physics* 19.13 (2019), pp. 8931–8945. doi: 10.5194/acp-19-8931-2019.
- [100] Klausner, T., Mertens, M., Huntrieser, H., Galkowski, M., Kuhlmann, G., Baumann, R., Fiehn, A., Jöckel, P., Pühl, M., and Roiger, A. Urban greenhouse gas emissions from the Berlin area: A case study using airborne CO₂ and CH₄ in situ observations in summer 2018. *Elem Sci Anth* 8 (2020). Ed. by D. Helmig and L. Bruhwiler. doi: 10.1525/elementa.411.
- [101] Pühl, M., Roiger, A., Fiehn, A., Gorchov Negron, A. M., Kort, E. A., Schwietzke, S., Pisso, I., Foulds, A., Lee, J., France, J. L., Jones, A. E., Lowry, D., Fisher, R. E., Huang, L., Shaw, J., Bateson, P., Andrews, S., Young, S., Dominutti, P., Lachlan-Cope, T., Weiss, A., and Allen, G.

Aircraft-based mass balance estimate of methane emissions from offshore gas facilities in the southern North Sea. *Atmospheric Chemistry and Physics* 24.2 (2024), pp. 1005–1024. doi: 10.5194/acp-24-1005-2024.

- [102] Cambridge Environmental Research Consultants, Ltd. *Atmospheric Dispersion Modelling System (ADMS) Version 5.2*. 2016. URL: <https://www.cerc.co.uk>.
- [103] Purvis, R. M., Burton, R., Allen, G., Dawson, K., Drysdale, W. S., France, J., Hopkins, J. R., Lee, J. D., Lewis, A. C., Mobbs, S., Moore, T. C., Thistlethwaite, G., and Young, S. Methane emission from shuttle tankers during standard operations on an oil platform during oil loading. *Environmental Science: Processes & Impacts* (2026). doi: 10.1039/d5em00768b.