Department of Civil and Environmental Engineering

University of Strathclyde

Air quality implications of developing the United Kingdom's unconventional petroleum resources, with a focus on geological drilling and other analogous environments.

By

SAMUEL. T. GRAINGER

A thesis submitted in fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2021.

I. Declaration of Authenticity.

This dissertation is being submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy (PhD) from the Department of Civil and Environmental Engineering – University of Strathclyde.

Declaration of Authenticity and Author's Rights

This thesis is the result of the author's original research. It has been composed by the author and has not been previously submitted for examination which has led to the award of a degree.

Signed:

Date: 1st December 2020.

II. Abstract:

Background & Aims: There are grave concerns that Unconventional Natural Gas (UNG) developments may severely impact air quality in the UK. To address these concerns, the thesis researches the two most significant risk-assessed hazards (i.e. drilling mud and combustion-related activities) by developing methods to identify physical phenomenon and source characteristics of key air pollutants - Particulate Matter (PM), Black Carbon (BC) and Nitrogen Oxides (NO_X).

Methods: The methods include personal air quality monitoring and statistical computing, including two pilot methods tested in Glasgow, before statistical computing is tested on data from the Preston New Road UNG site.

Results: Statistical computing allows for long-term averaging and spatial-temporal evaluation of industrial sites such as the Preston New Road drilling site, and when ratios (e.g. BC: NO_X) are used, can detect discrete industrial and vehicular sources. Lastly, a review of PM on drilling rigs indicated high occupational exposures, which could cause respiratory disease, the chemicals within oil-based mad formulations were also found to pose a significant respiratory hazard.

Conclusions: Air pollution from UNG at the Preston New Road site was less significant than conjecture and was less impactful than a nearby dairy farm. However, drilling mud exposures may present a high-risk occupational respiratory hazard to workers on modern onshore drilling rigs both from the quantity of airborne PM and from hazardous chemical dust. The developed methods also offer improved and cost-effective methods for source evaluation studies which could be implemented within most air pollution microenvironments.

III. Acknowledgements:

Dedication and Acknowledgements.

DEDICATION.

I would like to dedicate this Thesis to my Parents, and my Family for their constant Love and Support.

ACKNOWLEDGEMENTS.

It is not easy to put into words the sincere thanks and heartfelt appreciation that I have for those who have assisted me in my research both emotionally, and in substance, for without these key people this thesis would not have been possible.

My largest thanks go to my parents for their boundless love and support, my diligent proof-reader Janet Cole, and my friend Nicholas Evans. Janet worked tirelessly through the thesis numerous times, helping me to iron out onerous sentences and weeding out the spelling and grammar mistakes. I feel this thesis would not be nearly as clear and dare I say 'concise' as it would be without both Janet and Nicholas's immense help. I also wish to thank my supervisor Professor Vernon Phoenix for his aid with, and supervision of the later stages of my PhD project.

I want to say thank you to several other people who kept me sane through these long research years. Firstly, to my ever-faithful parents Mrs Nicola Grainger and Mr Karl Grainger, thank for your constant love and support. I offer a sincere thank you to my grandparents – the late Avril and John Grainger (may they rest in peace), Silvia and Paul Rees, and Sandra and Graham Thompson, as well as the rest of my family – thank you.

To everyone else, thank you for helping and supporting me. I thank you from the bottom of my heart for your help and support during this thesis.

- Samuel T. Grainger (01/12/2021)

IV. List of Authors Contributions:

List relevant accomplishments during the PhD program.

1. Contribution to Published Works:

Fernandes, K.J. (2019) *'Integrated personal exposure monitoring of traffic related air pollutants – spatial averaging and evaluation of the global positioning system (GPS)'.* MSc Thesis. University of Strathclyde.

Godfrey, H. (2019) *'The Release of Black Carbon During Fracking, and the Impacts on Human Health'.* MSc Thesis. University of Strathclyde.

Masey, N., Sutherland, F., Grainger, S.T., Hamilton, S., Heal, M.R. and Beverland, I.J. (2018) 'Minimising the impact of wind-speed effects on NO_2 passive diffusion samplers through sampler modifications', in Development *and evaluation of portable passive and real-time measurement systems, and dispersion models, to estimate exposure to traffic-related air pollutants.* PhD Thesis chapter. University of Strathclyde.

Paton, K. (2018) *'Are Bus Shelters Effective in Reducing Commuter Exposure to Air Pollution: A Study of Hope Street, Glasgow, UK?'.* MSc Thesis. University of Strathclyde.

Eide, D. (2017) *'What is the human health repercussions of air pollutants associated with unconventional natural gas extraction?'.* MSc Thesis. University of Strathclyde.

2. List of Presentations:

Grainger, S. (2017) 'Assessment of Personal Exposure to Black Carbon (BC) and Nitrogen Dioxide (NO_2) in Contrasting Urban and Industrial settings', *Transatlantic Knowledge Sharing Conference on Unconventional Hydrocarbons: Resources, Risks, Impact and Research Needs.* Amsterdam, Netherlands, 20 – 21st June 2017. Available at: TinyURL.com/ y6jzzcy6 (Accessed: 28th August 2020).

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3. List of RoundTable discussions:

Federation of Small Businesses (2018). 'Cardiff Transport and Clean Air Roundtable Event', *FSB Wales RoundTable Event on Cardiff Transport and Clean Air.* Cardiff, Wales, 13th June 2018.

RTI (2020). 'COVID-19 - Scientific Panel Discussion', *Research Triangle Professionals,* 23rd https://www.youtube.com/watch?v=8d5d_HXGeMAApril 2020.

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Chemical Sciences Roundtable (2020). 'The U.S. Chemical Supply Chain: Vulnerabilities Highlighted by COVID-19', *Chemical Sciences Roundtable of the National Academies of Sciences, Engineering, and Medicine*, 2nd July 2020, Washington, D.C.

TÜV SÜD National Engineering Laboratory (2020). *'Online Focus Group Meeting of the 26th August'.* Aberdeen, Scotland. 26th August 2020.

4. List of Awards:

2016 Early Career Geologist Award – South Wales Geological Society.

2017 Winner of the University of Strathclyde: Engineering the Future Scholarship.

Category Winner of the Ocean, Air, and Space, Images in Research Competition.

2018 Highly Nominated in the category of Ocean, Air, and Space, Images in Research Competition.

Emerging Professional – Guest of Honour at the 2018 Chartered Institute of Highways Technology (CIHT) Annual Dinner and seminar.

5. Professional Memberships:

ACSM	Associate of the Camborne School of Mines.
CABE	Graduate Member of the Chartered Association of Building Engineering.
CIWEM	Graduate Member of the Chartered Institute of Water and Environmental Management.
FGS	Fellow of the Geological Society.
IOSH	Associate of the Institute of Occupational Safety and Health.

V. Table of Contents:

FRONT MATTER.

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VI. List of Figures:

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NOTE: Unless otherwise stated, the author is the copyright holder of the images, attribution is noted where appropriate. Where an author or licensing permissions have been granted, they are noted in subscript beneath the figure description.

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- No Figures are contained within this chapter.

Chapter 2 - Key air pollutants and their major human health ramifications following acute, chronic, and occupational exposures.

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VII. List of Tables:

List of tables which are distributed throughout this thesis.

Chapter 1 - An Introduction to the PhD Thesis.

- No Tables are contained within this chapter.

Chapter 2 - Key air pollutants and their major human health ramifications following acute, chronic, and occupational exposures.

Chapter 3 - The Legislative Context Surrounding Air Quality Assurance within the United Kingdom.

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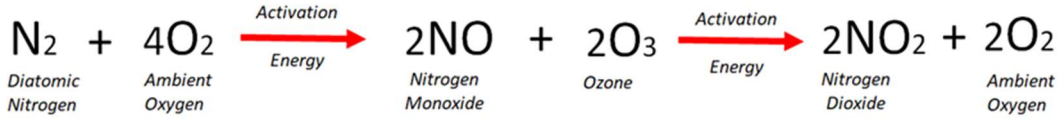
VIII. List of Equations:

Featured in this thesis.

Equation 2.1.



Equation 5.1.

$$RR = C \times Ed \times Pe$$

Risk Rating — *Consequence of Exposure* — *Exposure Duration* — *Probability of Exposure*

Equation 6.A.1.

$$BC = [BC]_0 \ (0.88\,Tr + 0.12) - 1$$

Where,

BC0 = ***Optimised Noise Algorithm,***

TR = ***Exp (−ATN100)***

ATN = ***100 ×ln⁡I/I0= −100 ×ln (T)***

I0 = ***Light Intensity through Unloaded Filter,***

I = ***Light Intensity through Loaded Filter,***

T = ***Transmission.***

Equation 6.A.1.

$$F = D\frac{(\pi d\text{^}2)}{4l}$$

Where,

F ***= the sampling rate (m3/sec),***

D ***= the diffusion coefficient of NO2 in air (cm3/sec),***

d ***= the diameter of the sampling device (cm),***

l ***= the length of the sampling device (cm).***

Equation 6.B.I.

$$C = \frac{QL}{DAt}$$

When,

C = Ambient air concentration (ng/ cm^3),

Q = Mass of nitrate measured, based on the calibration curve (ng),

L = The length of the sampling device, i.e. 7.1 cm.

D = The Diffusion Co-efficient of NO_2 in ambient air, i.e. cm^2 per second.

A = The cross-sectional area of the sampling device, i.e. 0.916 cm^2.

t = The exposure duration of the PDT tube in the field.

Equation 8.1.

$$Nc = 3 + N + N^{\frac{3}{2}}$$

Corrected $PM_{2.5}$ Value.

(N) Average 1 Minute Concentration of $PM_{2.5}$

Equation 8.2.

$$P(B|A) = \frac{P(A + B)}{P(A)}$$

When,

P is the probability (e.g. High Concentrations),

A and B are certain events (i.e. Wind Direction and Wind Speed),

End of Equations.

IX. List of Units:

List of Units and the SI Equivalent used in this PhD.

	Units	Full Name of Unit	SI Equivalent
Distance	nm	Nanometre	0.000000001 Metres
	µm	Micrometre	0.000001 Metres
	mm	Millimetres	0.001 Metres
	cm	Centimetres	0.01 Metres
	m	Metres	1 Metres
	km	Kilometres	1,000 Metres
	miles	Miles	1,609.34 Metres
Volume	litre	Litres	0.001 Cubic Metres
	m^3	Cubic Metres	1 Cubic Metre
	pH	Power of hydrogen	-
Speed	mps	Meters per second	1 Metre per Second
	m/sec	Meters per second	1 Metre per Second
	kmh	Kilometres per Hour	0.277... Metres per Second
	mph	Miles per hour	0.44704 Metres per second
Time	sec	Seconds (Clock Minute)	1 Second
	min	Minute (Clock Minute)	60 Seconds
	hour	Hour (Clock Hour)	3,600 Seconds
	day	Day (Midnight to Midnight)	86,400 Seconds
	month	Month (Calandar Month)	2,592,000 Seconds
	year	Year (Calander Year)	31,536,000 Seconds
Mass	µg	Microgrammes	0.000000001 Kilogrammes
	mg	Milligrammes	0.000001 Kilogrammes
	g	Grammes	0.001 Kilogrammes
	kg	Kilogrammes	1 Kilogrammes
Mass - Density	$\mu g/m^3$	Microgrammes per Cubic Metre	0.000000001 Kg/m^3
	mg/m^3	Milligram per Cubic Metre	0.000001 Kg/m^3

X. List of Abreviations and Acronyms:

List relevant common abbreviations and acronyms used in this thesis.

1. List of Abbreviations:

A8	-	The A8 is a major road which connects Edinburgh to Greenock.
AADF	-	Annual Average Daily Flow.
AQEG	-	Air Quality Expert Group.
AURN	-	Automatic Urban and Rural Network.
BSI	-	British Standards Institute.
CAFE	-	Clean Air For Europe Directive.
CEDA	-	Centre for Environmental Data Analysis (and corresponding archives).
COMEAP	-	Committee on the Medical Effects of Air Pollutants.
COPD	-	Chronic Obstructive Pulmonary Disease.
COSHH	-	The Control of Substances Hazardous to Health Regulations.
CPF	-	Conditional Probability Function.
DAQI	-	Daily Air Quality Index.
DEFRA	-	Department for Farming and Rural Affairs.
DoT	-	Department of Transport.
EA	-	Environment Agency (England).
EC	-	European Commission.
EU	-	European Union.
FOI	-	Freedom of Information.
GHS	-	Globally Harmonized System of Classification and Labelling of Chemicals.
GMT	-	Greenwich Mean Time.
HGV	-	Heavy Goods Vehicles (e.g. any truck with a gross combination mass (GCM) of over 3,500 kg (7,716 lb).
HRA	-	Health Risk Assessment.
HSE	-	Health and Safety Executive.
ICE	-	Internal Combustion Engines.

J15	-	Junction 15 of the M8 Motorway - Townhead Interchange connecting the M8 motorway with Glasgow Cathedral, Glasgow Cross, Kirkintilloch, and Glasgow Cross.
LED	-	Light Emitting Diode.
LGV	-	Light Goods Vehicles (e.g. a commercial carrier vehicle with a gross vehicle weight of no more than 3.5 metric tons [tonnes]).
LTOBM	-	Low Toxicity Oil Based Mud.
M8	-	M8, the busiest motorway in Scotland connecting Edinburgh to Glasgow.
MCS	-	Mud Circulation System.
MSDS	-	Material Safety Data Sheet.
NIOSH	-	United States - National Institute for Occupational Safety and Health.
NRMM	-	Non-Road Mobile Machinery.
NRW	-	Natural Resources Wales.
OBM	-	Oil Bearing Mud.
PDT	-	Palmes Diffusion Tubes.
PNR	-	Preston New Road (the UNG Development site near Blackpool).
PPE	-	Personal Protective Equipment.
R2	-	R-Squared result.
RIDDOR	-	Reporting of Injuries, Diseases and Dangerous Occurrences Regulations.
SEPA	-	Scottish Environmental Protection Agency.
STOP	-	Stop Principle (i.e. Substitution, Technical, Organisation, Personal).
UK	-	United Kingdom of Great Britain and Northern Ireland.
UNG	-	Unconventional Natural Gas (Reserve).
USA	-	United States of America.
WBM	-	Water Based Drilling Mud.
WEL	-	Workplace Exposure Limits.

WHO - World Health Organisation, a specialized agency of the United Nations responsible for international public health.

2. List of Chemical Abbreviations:

BC - Black Carbon.

NO - Nitrogen Monoxide or Nitric Oxide.

NO_2 - Nitrogen Dioxide.

NO_X - Oxides of Nitrogen.

PAH - Poly-Aromatic Hydrocarbons.

PM - Particulate Matter.

$PM_{2.5}$ - PM with an Aerodynamic Diameter of less than or equal to 2.5 Microns.

PM_{10} - PM with an Aerodynamic Diameter of less than or equal to 10 Microns.

PTFE - Polytetrafluoroethylene.

PVC - Polyvinyl chloride.

TEA - Triethylamine.

TOC - Total Organic Carbon.

VOC - Volatile Organic Compound.

CHAPTER 1

An Introduction to the PhD Thesis.

"Be it known to all within the sound of my voice,
whoever shall be found guilty of burning coal
shall suffer the loss of his head".
King Edward II (1239-1307)

► 1.1) Introduction.

Air consists primarily of three gases; nitrogen, oxygen, and argon, which comprise ~99.9% of air's volume (ISO 1975). The remaining ~0.1% contains a multitude of gases, several of which the World Health Organisation (WHO) and UK Government consider as "air pollutants" (WHO 2016; COMEAP 2019). One such air pollutant is nitrogen dioxide, which comprises only around 0.000002% of the atmosphere, (ISO 1975).

Civilisations have attempted to control the emission of air pollutants since antiquity (as per quote 1), (King Edward I of England 1307). Since the Industrial Revolution, humanity has been burning increasingly large volumes of fossil fuels (e.g. petroleum hydrocarbons) which have significantly reduced local air quality (WHO 2016). Annually, seven million premature deaths are attributed by the WHO to poor quality air, and of these deaths - 40,000 are in the UK (WHO 2016; COMEAP 2019). Consequently, exposure to poor quality air is one of the WHO's and UK Government's key environmental health priorities (WHO 2016; COMEAP 2019).

Sources of air pollution are diverse in the UK, ranging from agriculture through to industrial facilities (Defra 2019). However, one of the most contentious of these industrial sources is Unconventional Natural Gas (UNG), (Scottish Government 2014).

Much of the acrimony surrounding UNG stems from American 'horror stories' of fracking, showcased in amateur documentaries such as 'Gasland' (Fox 2011). Whilst hydraulic fracturing is now banned throughout the UK, due in part to the poor public perception of the industry, the conventional extraction of unconventional resources is still permitted (Ambrose 2019).

Conventional oil and gas developments share many sources of air pollution with UNG projects (ROENG 2012). Some of these shared sources include diesel emissions (including generators and vehicles) and the dispersion of particles during the drilling stage (i.e. from arisings and drilling mud), (ROENG 2012; ARUP Group 2014; Ezani et al. 2018). The definition of UNG throughout the remainder of this PhD, therefore, focusses on the exploitation of unconventional resources rather than from the perspective of unconventional techniques, i.e., hydraulic fracturing 'fracking'.

While the international picture of UNG exploration is important, the UK has some of the most stringent environmental laws and controls on mineral exploitation worldwide (ROENG 2012). Standard UNG practices in the USA are forbidden in the UK, e.g. using undisclosed chemical additives, (Scottish Government 2014). Given the UK's strict environmental controls, there is a dire need to identify the key occupational and environmental health aspects surrounding the UK's onshore UNG exploration even considering the recent ban on such activities (ROENG 2012).

Nationally the local air pollutants of concern are; Nitrogen Oxides (Nitric Oxide - NO, Nitrogen Dioxide - NO_2, and Oxides of Nitrogen - NO_X), Black Carbon (BC) and Particulate Matter (PM with an aerodynamic diameter of less than 2.5 and 10 µm, i.e. $PM_{2.5}$ and PM_{10}), (Defra 2019). While other air pollutants also occur, such as ozone and carbon monoxide, they are not considered in this thesis.

► 1.2) Purpose of this chapter.

This chapter forms the founding document of this thesis, outlining the fundamental principles of what is to be actively researched throughout the remainder of this work. This section summarises the aims and objectives of the research before remarking on the overall structure of the document.

♦ 1.2.1) Aim.

The thesis aims to;

> "Identify the primary sources of combustion and particulate-related air pollution (i.e. particulates and nitrogen oxides) within proximity to onshore UNG development sites, to develop methods for quantifying exposure to these air pollutants and to help determine their occupational and environmental health impacts".

♦ 1.2.2) Objectives of the Thesis.

The specific objectives of this research are;

A. To develop a human health risk assessment of key sources of air pollution on active onshore UK UNG operations.

   The review was focussed around:

   I. Synthesis of scientific research into the health effects of air pollution on the human respiratory system.

   II. Review of UK onshore UNG development stages using planning documentation and Environmental Impact Assessments.

   III. Evaluation of the key stages of air pollution, which could cause a significant hazard to human health, assessing the consequences and likelihood of exposure from identified onshore UNG sources.

IV. The remainder of the thesis is focussed around the two most substantial hazards identified in the risk assessment.

B. To develop measurement systems to characterise occupational and environmental exposure to particulate air pollutants within complex environments, which could be used at UNG developments, including:

I. Personal monitoring of air quality upwind and downwind of Internal Combustion Engines (ICEs).

C. To adapt statistical programming methods to characterise occupational and environmental exposures to combustion and particulate-related air pollutants within UNG development sites and similar complex environments.

I. Use of Open Access (OA) data from air quality monitoring stations to determine spatial-temporal trends within UNG and other complex environments.

II. Understanding and estimating potential chemical hazards to human health during the drilling stage of the UNG development process.

► 1.3) Outline of the Thesis:

The thesis comprises fourteen chapters; each chapter was written to fulfil at least one major objective. The structure of the thesis can be divided into parts, as outlined below;

INTRODUCTION:

An Introduction to the PhD Thesis.

Chapter 1. Introduces the reader to this PhD thesis and presents the research aims, objectives and structure of the work.

THEME 1:

Literature Review, Preliminary Risk Assessment, and Methods.

Chapter 2. Discusses the key air pollutants; 'Particulate Matter' and 'Oxides of Nitrogen' and the effects of exposure on human health.

Chapter 3. Explores the legal context of air pollution, explaining the different guidelines and lawful limits of the key air pollutants.

Chapter 4. Summarises the UK's petroleum reserves before outlining the stages of UNG development as a case study; Preston New Road.

Chapter 5. Uses Chapters 2 to 4 to evaluate key risks to human health in UNG development, to guide the PhD research focus areas.

Chapter 6. Discusses the techniques, methods, and equipment used in this PhD thesis; including primary and secondary data collection.

THEME 2:

Effects of Onshore Drilling Muds on Human Respiratory Health.

Chapter 7. Investigates the concentration of 'drilling mud' related PM during petroleum development, and inherent risks to respiratory health and uses the disclosed UK onshore chemical formulae of

‘drilling mud’, to evaluate employees’ respiratory health risks via the UN Globally Harmonised System ‘GHS’

THEME 4:

Novel ways to assess air pollution on complex multi-faceted environments.

Chapter 8. Focusses on two experiments, Experiment I studies a series of bus stop microenvironments along Hope Street (Glasgow), supplementing the air quality investigation with OEFM. Experiment II. uses OpenAir and AURN data to suggest that the ratio of BC: NO may indicate combustion-related activity in Glasgow.

Chapter 9. Outlines the contribution of the PNR development to nitrogen and particulate air pollution at the Little Plumpton monitoring station.

CONCLUSION:

Updated Risk Assessment and Thesis Conclusions.

Chapter 10. Uses the findings of the thesis to update the preliminary risk assessment and to conclude on the findings of this work.

► 1.4) References.

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END OF REFERENCES

Explainatory Note:

Literature Review, Preliminary Risk Assessment, and Methods.

This first theme entitled “Literature Review, Preliminary Risk Assessment, and Methods” begins in Chapter 2 by performing a literature review of the key air pollutants, (i.e. fine particulate matter, black carbon, oxides of nitrogen), and their respiratory health effects. The major risks of these air pollutants are subdivided into three major categories, short-term high exposure effects (i.e. asphyxiation), long-term effects (e.g. rhinitis), and long-term, long latency diseases such as pneumoconiosis.

The next chapter, Chapter 3, evaluates the pollutants legislative context. There are also various legislative limits which apply to air pollutants, in ambient air, and highly specific air pollutants encountered in occupational settings which are outlined in this chapter. The air quality limits are dependent on where the receptor is located i.e. in the workplace or in ambient settlings (where there are stricter limits on air quality). Following on from this, Chapter 4 outlines the United Kingdom’s onshore petroleum resources and phases of exploiting these resources by using the Preston New Road Unconventional Natural Gas development site as a case study of the UK onshore petroleum environment.

Chapter 5 undertakes a comprehensive evaluation of the hazards encountered during the exploitation of petroleum resources to focus research efforts into the two-most serious risks to environmental and occupational health around these developments. The environmental and occupational health risks were estimated by following the Risk = Consequence X Likelihood equation as outlined in CIRIA C552 (Rudland et al., 2001). The two-most significant hazards were emissions from combustion-related sources, and drilling mud (including arisings and well fluids).

Several other hazards were targeted as part of this risk assessment, but not further evaluated in this thesis, these sources included; soil and aggregate and proppant, flares, hydraulic fracturing chemicals, escape of gas or asphyxiant, Volatile Organic Carbon (VOC) release and catastrophic explosion.

With the two-most significant hazards identified, Chapter 6 outlines the adopted research and analytical techniques used to target the research chapters in the remainder of the thesis. These methods include both qualitative and quantitative research methods. The primary data collection in this thesis focussed on the microscopic analysis of filters, which was able to identify key particulates with Optical Environmental Forensic Microscopy. However, secondary data analysis was instrumental to the research chapters, here statistical computing was used to perform complex spatial-temporal research on air pollution trends. This was undertaken by not only routine Spreadsheet-Based Modelling and also by advanced programming tools i.e. R Studio's OpenAir application.

CHAPTER 2

Key air pollutants and their major human health ramifications following acute, chronic, and occupational exposures.

"The health effects of air pollution, imperil human lives. This fact is well-documented".

Eddie B. Johnson (1935 - Present)

Chapter 2 introduces the key selected air pollutants; particulate matter, black carbon, and oxides of nitrogen, to the reader. A literature review then augments this introduction by outlining the principal effects of these pollutants on human health following acute and chronic exposures.

► 2.0) Criteria Air Pollutants.

The Oxford English Dictionary defines 'air pollution' as any process which contaminates the air with harmful or dangerous substances. The UK's Department of Farming and Rural Affairs (Defra), is especially concerned with combustion-related air pollutants because of their suspected adverse health effects (Defra 2019a, b). These combustion-related air pollutants include; particulate matter (PM), black carbon (BC) and oxides of nitrogen (NO_x), i.e. comprising nitrogen monoxide (NO) and nitrogen dioxide (NO_2), (COMEAP 2011; Defra 2019a, b).

♦ 2.0.1) Particulate Matter.

Fine PM comprises a diverse range of solid and [or] liquid particles finer than 100 µm, (UK AQEG 2012). Primary particles can be released directly from their source to the atmosphere (e.g. silica sand from the Sahara desert), (Sakhamuri and Cummings 2019). Alternatively, PM can be created by secondary processes, i.e. through chemical reactions in ambient air (Calzolai *et al.* 2015).

Although aeolian processes can transport PM, the chemistry, and size of the PM affect its aerodynamic characteristics). Both $PM_{2.5}$ and PM_{10} (particles with a mean aerodynamic diameter of, or less than, 2.5 and 10 micrometres) are the most common metrics used to assess PM in the UK's ambient air, (UK AQEG 2012; Defra 2019a). Figure 2.1 shows a size analogy for the three types of PM.

Sources of PM are diverse and include both natural and anthropogenic phenomena, as shown in Figure 2.2 (Defra. 2019b). Natural causes of PM include volcanic activity, geologic dust, and forest fires (Defra 2019a). Major anthropogenic sources of PM include biomass combustion, vehicular exhaust, and industrial activities (Defra 2019a, b).

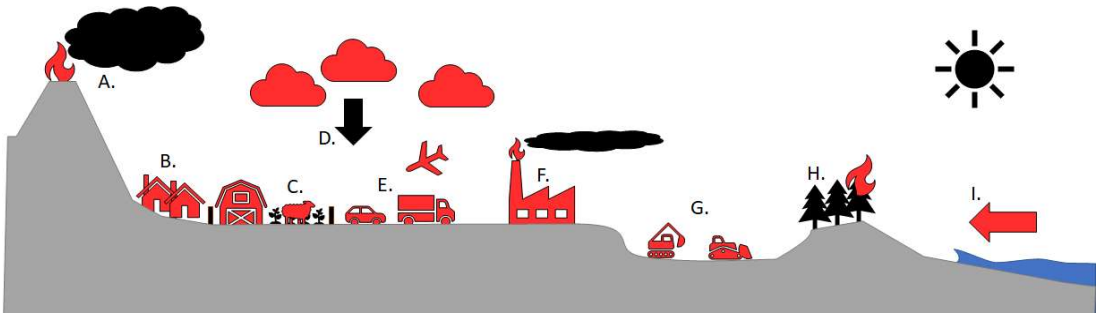

Figure 2.1. A diagram showing key sources of Particulate matter within a conceptual model landscape. **A.** Volcanic Eruption, **B.** Wood Burning and Heating within homes, **C.** Agricultural Land and Animal Pasture, **D.** Geological Deposition from Natural Processes such as Space Dust or Saharan Dust, **E.** Transportation, **F.** Industrial Processes and Power Generation, **G.** Non-Road Mobile Machinery, construction, demolition, mining and waste management, **H.** Fire such as Forest Fire, **I.** Sea Salt.

Source; Author – Grainger (2020)

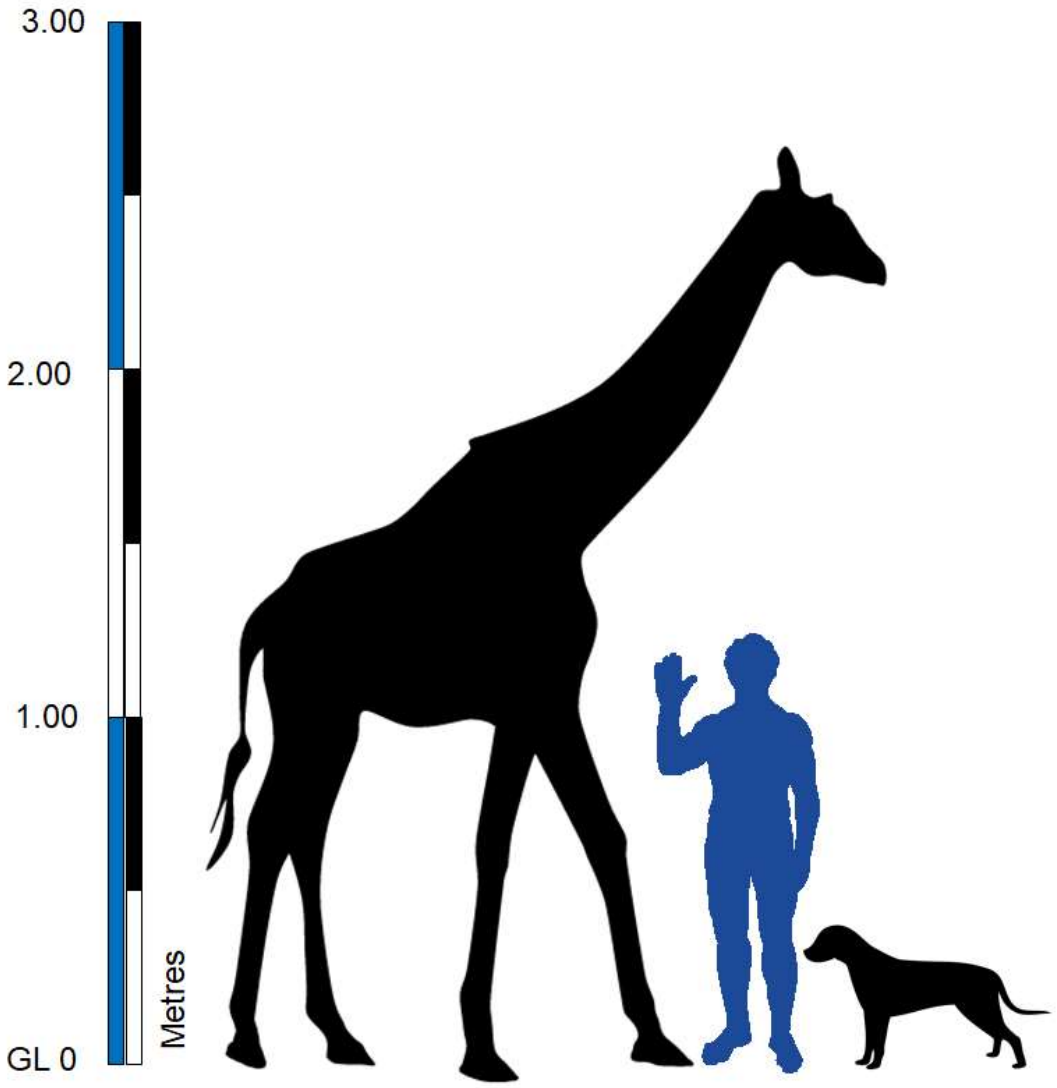

Figure 2.2; Shows a size analogy of $PM_{2.5}$ and PM_{10}, and the limit of observation with the naked eye i.e. PM_{100}. A female giraffe is ~10x the size of a human male (and signifies the size one can see with the naked eye ~100 µm). A standard human (NASA Pioneer 1) is 10x smaller than a giraffe and is equivalent to PM_{10}. A medium sized dog (border collie) is 0.25x the size of a human and is equivalent to $PM_{2.5}$. On this scale, the width of a human hair is equivalent of ten giraffes stacked on top of each other.

Source; OpenClipart (2015, 2018); NASA (1972) **(adapted).**

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♦ 2.0.2) Black Carbon (BC).

BC is a subcategory of PM comprising amorphous elemental carbon coated by poly-aromatic hydrocarbons (PAH) as illustrated in Figure 2.3, (BC can account for a significant proportion of $PM_{2.5}$ or PM_{10} emissions from fires and vehicular exhaust (Becerril-Valle *et al.* 2017).

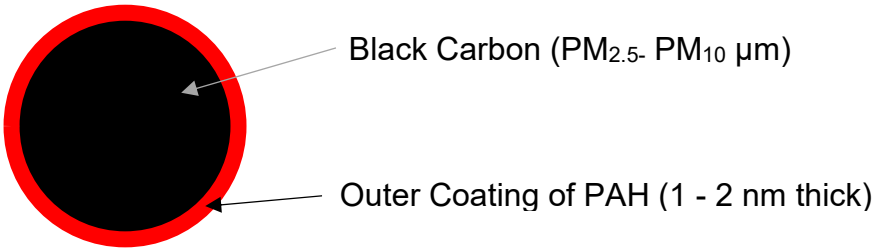


Figure 2.3. A diagram showing the outer coating of PAH which may form additional health hazards accreted to the outer surface of a BC particle.
Source; Author – Grainger (2020)

♦ 2.0.3) Nitrogen Oxides.

Nitrogen accounts for 80% of the air we breathe and is inert in standard conditions (ISO 1975). There are a variety of nitrogen compounds which can be generated through a variety of processes; however, most UK regulations on air quality focus on NO_x and its subcomponents; NO and NO_2 (molecules are shown in Figure 2.4.A and B), (Defra 2019a, b).

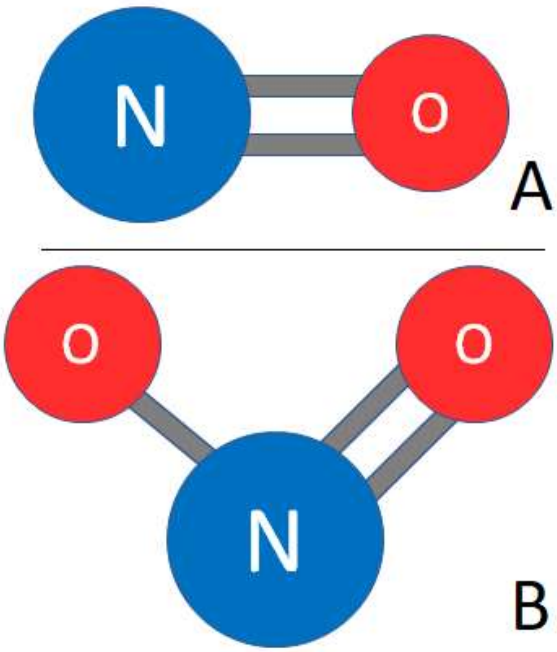
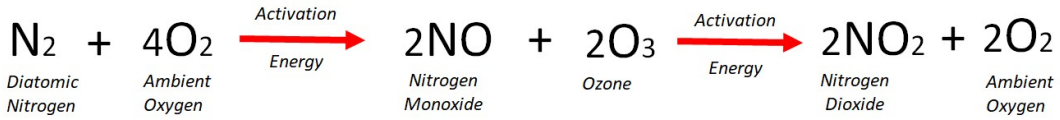


Figure 2.4. In nitrogen monoxide molecules, nitrogen atoms form a double bond with oxygen atoms whilst in nitrogen dioxide they form an additional single bond with a second oxygen atom.
Source; Author – Grainger (2020)

The formation of NO_x is complex. When diatomic nitrogen N_2 is subjected to high activation energies in ambient air, such as the heat within ICEs (Internal Combustion Engines), diatomic nitrogen (N_2) and oxygen (O_3) react forming NO as shown in Figure 2.4 and Equation 2.1 (WHO 2013; Vallero 2014). NO_2 can be formed through various mechanisms with the most common method shown in Equation 2.1 as the oxidation of NO by O_3 (Vallero 2014).



Equation 2.1. An equation showing the chemical formula illustrating the reaction between diatomic nitrogen and ambient oxygen with activation (heat) forming nitrogen monoxide and ozone, followed by a reversible reaction whereby nitrogen monoxide can further react to form nitrogen dioxide and ambient oxygen. **Source;** Author – Grainger (2020)

Figure 2.5 illustrates the sources of NO_X. Some natural processes generate NO_X such as thunderstorms, volcanic eruptions, forest-fires and nitrification (Vallero 2014). However, most NO_X is formed through anthropogenic activities rather than natural processes (WHO 2006, 2013). The dominant sources of NO_X are road transport, fossil fuel power stations, combustion of natural gas (e.g. for domestic heating and cooking) and agricultural activities (Defra 2019a).

Road emissions, according to the National Atmospheric Emissions Inventory (NAEI), are the predominant source of NO_X in the UK and Europe (UK NAEI 2018). Many busy roads and urban centres have NO_2 concentrations exceeding 40 $\mu g/m^3$ (Defra 2019a; PHE 2019). This exceedance is attributable in some respect to the failings of the European classification of engines' failure to achieve laboratory emissions in real-world conditions (Defra 2019a).

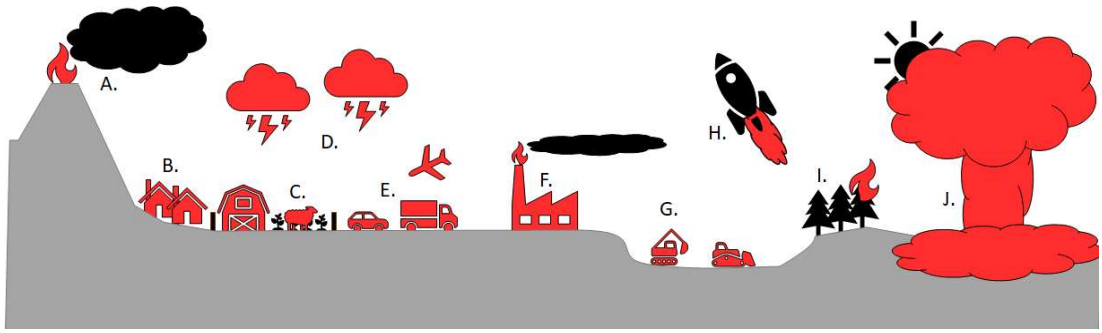


Figure 2.5. A diagram showing key sources of Nitrogen Oxides within a conceptual model landscape. **A.** Volcanic Eruption, **B.** Heating, Cooking and Recreational Burning (Candles and Smoking), **C.** Agriculture, Run-off and Fertilisers, **D.** Thunder Storms, **E.** Motor Vehicles, **F.** Industrial Processes and Energy Production, **G.** Non-Road Mobile Machinery, **H.** Rockets and Rocket Fuel, **I.** Forest Fire, **J.** Nuclear Testing.
Source; Author – Grainger (2020)

► 2.1) Effects on Human Health.

Air pollution could be considered the most serious environmental risk to human health worldwide and is increasingly present in the public consciousness (COMEAP 2018, 2019). Air pollution often generates an emotive response as vulnerable groups are at an increased risk of developing adverse health effects (COMEAP 2011). There seems to be an inexhaustible range of diseases exacerbated by acute and chronic exposure to air pollution (Simoni *et al.* 2019).

Epidemiological research, however, has found differences in the effects of acute and chronic exposure to poor air quality. The acute effects of air pollution are best seen in major pollution episodes such as the 1952 London Smog, a 5-day pollution episode which caused a morbidity upsurge of 5,000 patients, (Bell and Davis 2001; Davis *et al.* 2002). A more recent pollution episode in 1991 may have caused a 10% increase in mortality in London (Connor, 1994).

Chronic exposure to air pollution often coincides with ill health throughout the systems of the human body (WHO 2013; Valacchi *et al.* 2020). The effects of poor air quality are not only physical but often also cause societal and economic effects (Defra 2019a; PHE 2018, 2020). For instance: Public Health England has estimated that a $PM_{2.5}$ reduction of only 1 $\mu g/m^3$ could save England approximately £2.3 million between 2015 and 2035, with a similar £600,000 reduction for NO_2 per 1 $\mu g/m^3$ (PHE 2018).

♦ 2.1.1) Particulates and Black Carbon.

PM is defined conventionally as small nongaseous particles with an aerodynamic diameter of less than 100 µm, which can settle slowly under the influence of gravity (Defra 2019a, b). The aerodynamic diameter of fine PM classifies it into three major groups: PM_{10}, $PM_{2.5}$, and ultrafine particles or $PM_{0.1}$, (with the sub-scripted number indicating the aerodynamic diameter in microns of the particles). Lower size classifications such as $PM_{2.5}$ are included in PM_{10}.

The size and chemistry of PM significantly affect its human health impacts (Silva *et al.* 2019). The chemistry can include; mineral dust (e.g. crystalline silica), organic dust (e.g. house dust) or even biohazards (e.g. fungal spores), (McCrone 2020).

■ A) Penetration and Deposition of Particles.

The aerodynamic diameter of the particles broadly corresponds with the deposition location within the lungs (Figure 2.6), and to its corresponding health effects (Ohsaki *et al.* 2019). Larger PM sizes such as PM_{10}, and larger, are eliminated in the upper respiratory system (i.e. the nasopharyngeal zone and larynx, e.g. the nose and throat), (Bourke and Burns 2015).

Particles can irritate and corrode the sensitive areas of the respiratory tract such as the epithelium (via oxidisation and radicalisation of some PM particles), (Butt *et al.* 2016). Injury of the epithelium leads to a productive cough (with sputum) and sneezing (Bourke and Burns 2015). However, these particles are eliminated via sedimentation and interception with sticky mucous laden tissues (Munkholm and Mortensen 2014).

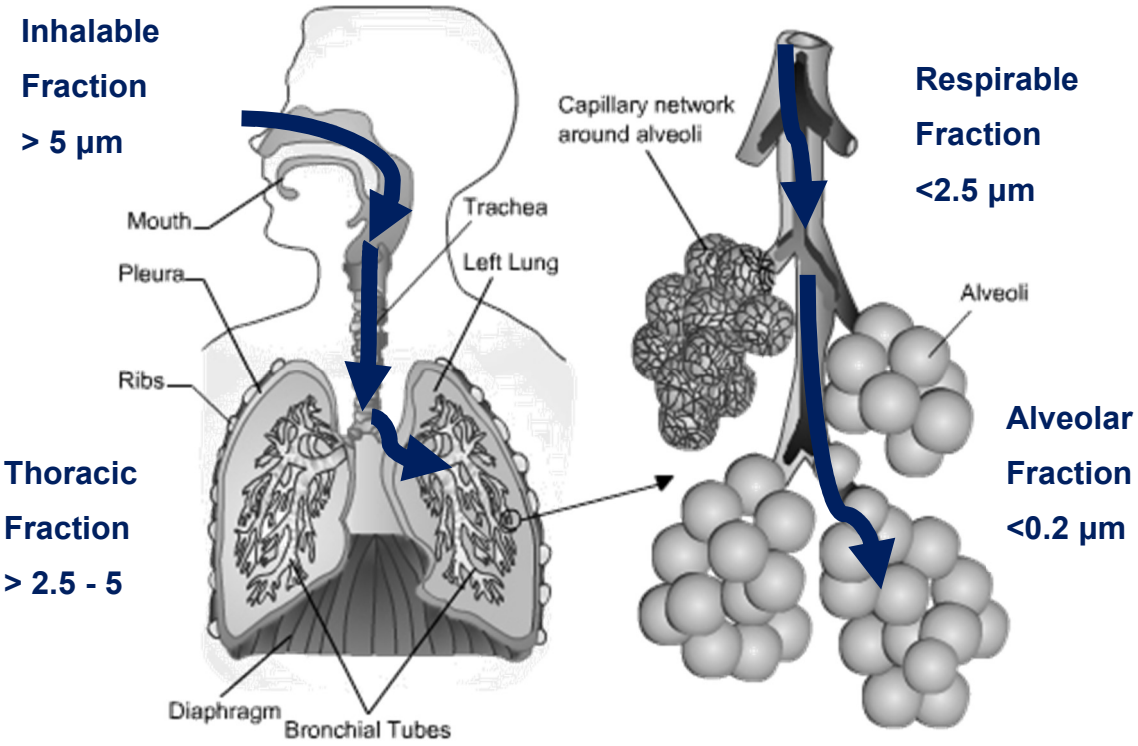


Figure 2.6. Diagram illustrating the main deposition locations for different fractions of Particulate Matter PM_1 to PM_{10}, which correspond to the inhalable, thoracic, respirable and alveolar fractions.

Source; Toxlearn (2013) **(Adapted)**

Reproduced courtesy of the U.S. National Library of Medicine.

Particles in the $PM_{2.5}$-PM_{10} range can be deposited in the primary part of the bronchial tree (Ohsaki *et al.* 2019). These particles can be swept out of the lungs and into the throat via the mucociliary elevator (Bourke and Burns 2015).

The mucociliary elevator comprises tissue coated by cilia (hairs) which beat rhythmically at around 1000 beats per minute (Munkholm and Mortensen 2014). Particles around $PM_{2.5\text{-}3}$ can reach the bronchi and alveoli, where some particles settle (Munkholm and Mortensen 2014). In the finer structures of the lung, mobile phagocytic cells (macrophages) engulf particles and attempt to move them towards the mucociliary elevator, (Munkholm and Mortensen 2014; Bourke and Burns 2015). Particles often prove toxic to macrophages, which die off, liberating the particles, and allowing the particles to be re-engulfed into the lungs (Bourke and Burns 2015).

■ B) Risks of Particulate Matter to Human Health.

◊ I). Acute Exposure of $PM_{2.5}$ and PM_{10}.

Short-term exposure to $PM_{2.5}$ to PM_{10} particles aggravates and causes a wide range of symptoms (COMEAP 2019). The most common of these symptoms in otherwise healthy people is an influenza-like ailment (1.37% and 0.74% for $PM_{2.5}$ and PM_{10} with 95% confidence), (Su *et al.* 2019). Symptoms of PM exposure include, but are not limited to, a dry chesty cough, sore throat, fatigue, tiredness and at high concentrations dust-laden sputum (Bourke and Burns 2015; Su *et al.* 2019). The resulting malaise can lead to increases in school and workplace absenteeism rates (e.g. a 2.4% ±1.2% increase per 10 $\mu g/m^3$ of PM_{10}), (Marcon *et al.* 2014). People with comorbidities exposed to PM can be more severely affected by daily fluctuations in air quality (COMEAP 2011). Those with asthma, are more likely to become symptomatic (1.1% per increase of 10 $\mu g/m^3$ of PM_{10}, confidence 95%) and seek medical attention for their asthma (1.5% for adults and 3.6% for children exposed to a $PM_{2.5}$ increase of 10 $\mu g/m^3$), (Atkinson *et al.* 2001; Fan *et al.* 2016).

Those with existing respiratory conditions are more susceptible to infection and a worsening of their comorbid symptoms, potentially requiring hospitalisation (1.4% ±0.8% daily exposure >20 μg/m^3, confidence 95%) (Martuzzi *et al.* 2006). Beyond respiratory health, the incidence of myocardial infarction and arrhythmias is increased (0.7% ±0.3%, confidence 95% daily exposure >20 μg/m^3) as is the risk of cerebrovascular accidents (CVA) (0.4% ±0.4%, confidence 95% per 10 μg/m^3 increase in exposure) (Martuzzi *et al.* 2006; Yu *et al.* 2014).

The symptoms of PM exposure are often accompanied by an underlying increase in premature death in the infirm and elderly via all-cause mortality (1.5% daily exposure >20 μg/m^3), as well as mortality associated with the respiratory (3.1% daily exposure >20 μg/m^3), cardiovascular (2.1% daily exposure >20 μg/m^3) and cerebrovascular causes (3.3% daily exposure >20 μg/m^3), (Martuzzi *et al.* 2006). The morbidity for conditions such as lung cancer and myocardial infarction are especially high at 11.9% and 19.8% respectively (Martuzzi *et al.* 2006).

◊ II). Chronic exposure to $PM_{2.5}$ and PM_{10}.

Exposure to air pollution can impact human health over a person's lifetime, from the "cradle to grave" with PM exposure affecting nearly every organ of the human body (Holgate 2017; COMEAP 2019). Three of the most prominent systems of the human body affected by PM are:

- **Respiratory –** Long term exposure to poor ambient air quality impairs lung function (COMEAP 2019). This seems to affect children and adults equally, though the mechanism appears to be different (COMEAP 2019).
  In children, poor air quality may inhibit lung capacity development, for example, Kulkarni *et al.* (2006) found that a 1 μg/m^3 increase in BC encumbrance within macrophages can lead to a 17% decrease in FEV (Forced Expiratory Volume) within school children (HEI Collaborative 2012).
  In adults, PM exposure may lead to increased ageing of the lungs associated with a decline in lung function (COMEAP 2019).

Several studies have specifically found that exposure to vehicular air pollution, including BC, has a more detrimental impact on FEV than otherwise expected, (Rice *et al.* 2015). Long term exposure to PM is also a causative factor in the development of asthma in childhood and beyond (Khreis *et al.* 2017). The risk of developing asthma in children over six years old was considered especially high with a 48% (±25%) increase in cases of asthma per 10 μg/m^3 increase in $PM_{2.5}$ exposure (Khreis *et al.* 2017). Likewise, adult exposures to PM are more likely to cause new-onset asthma, with a 16% increase in incidence per 10 μg/m^3 of $PM_{2.5}$ (Anderson *et al.* 2013).

The risk of developing Chronic Obstructive Pulmonary Disease (COPD) increases by approximately 32% per 10 μg/m^3 exposure to $PM_{10,}$ and mortality by 0.2–0.6% (Cai *et al.* 2014; Hooper *et al.* 2018).

- **Circulatory –** Approximately 2.3 million people in the UK suffer from a disease of the cardiovascular system (heart and blood vessels), with ischaemic heart disease (congestion of the coronary arteries with fatty material) being the main cause of death in the UK (BHF 2019).
  Air pollution is an established cause of a range of cardiovascular complications in adults, including; myocardial infractions (+5% per 10 μg/m^3 of $PM_{2.5}$), heart failure (+2.12% and 1.63% per 10 μg/m^3 of $PM_{2.5}$ and PM_{10}), arrhythmia (0.56% per 10 μg/m^3 of PM_{10}), and hypertension (2.8/2.7 mmHg increase per 10.5 μg/m^3 increase in $PM_{2.5}$) (Shah *et al.* 2013; Zhao *et al.* 2014; Zhang *et al.* 2016). Electrochemical responses occur following irritation of lung tissues via the sympathetic nervous system (Valacchi *et al.* 2020). These can cause multi-system oxidative stress and increase the likelihood of coagulation and thrombosis - prominent factors in circulatory and neurological morbidity (Dermarin *et al.* 2019; COMEAP 2019; Valacchi *et al.* 2020). Cardiopulmonary mortality is also predicted to increase to 6–13% per 10 μg/m^3 of $PM_{2.5,}$ (WHO 2013).

- **Neurological –** There is robust evidence that PM exposure is a cerebrovascular risk factor, although the neurodegenerative effects of PM have only recently been realised (COMEAP 2019). A meta-analysis of CVA events in 20 studies assessing 200,000 people was carried out by Scheer's *et al.* 2015, they found the overall risk of stroke around 6.1%, though the study had an incidence of stroke anywhere between 2 to 21% per 10 μg/m^3 of PM_{10} (Scheers *et al.* 2015). Mortality from cerebrovascular accidents increased markedly per 10 μg/m^3 of PM_{10}, with an elevated risk of 8.0% (Scheers *et al.* 2015). Nasal epithelial cell irritation and the cytokine response could be a contributory factor in cerebrovascular accidents via excess inflammation (intracranial pressure and cerebral oedema via the olfactory bulb), (COMEAP 2019; Valacchi *et al.* 2020). Besides stroke, there is evidence that PM is associated with other neurological diseases such as dementia, Alzheimer's disease, Autism Spectrum Disorder, Parkinson's disease, and cognitive impairment (Fu *et al.* 2019, COMEAP 2019). A study by Roux *et al.* 2017 found that in the winter, when air pollution is highest, multiple sclerosis had an increased relapse rate of 40%, whilst, Hooper *et al.* 2018 found that Alzheimer's disease, along with vascular dementia, had a 4.17% increased risk per 10 μg/m^3 rise in PM_{10}. Meanwhile, childhood exposure to PM_{10} was found to increase the risk of Attention Deficit Hyperactivity Disorder (ADHD) by 18% per 10 μg/m^3 (Min and Min 2017).

Figure 2.7 outlines several additional systems of the human body affected by adverse PM exposure.

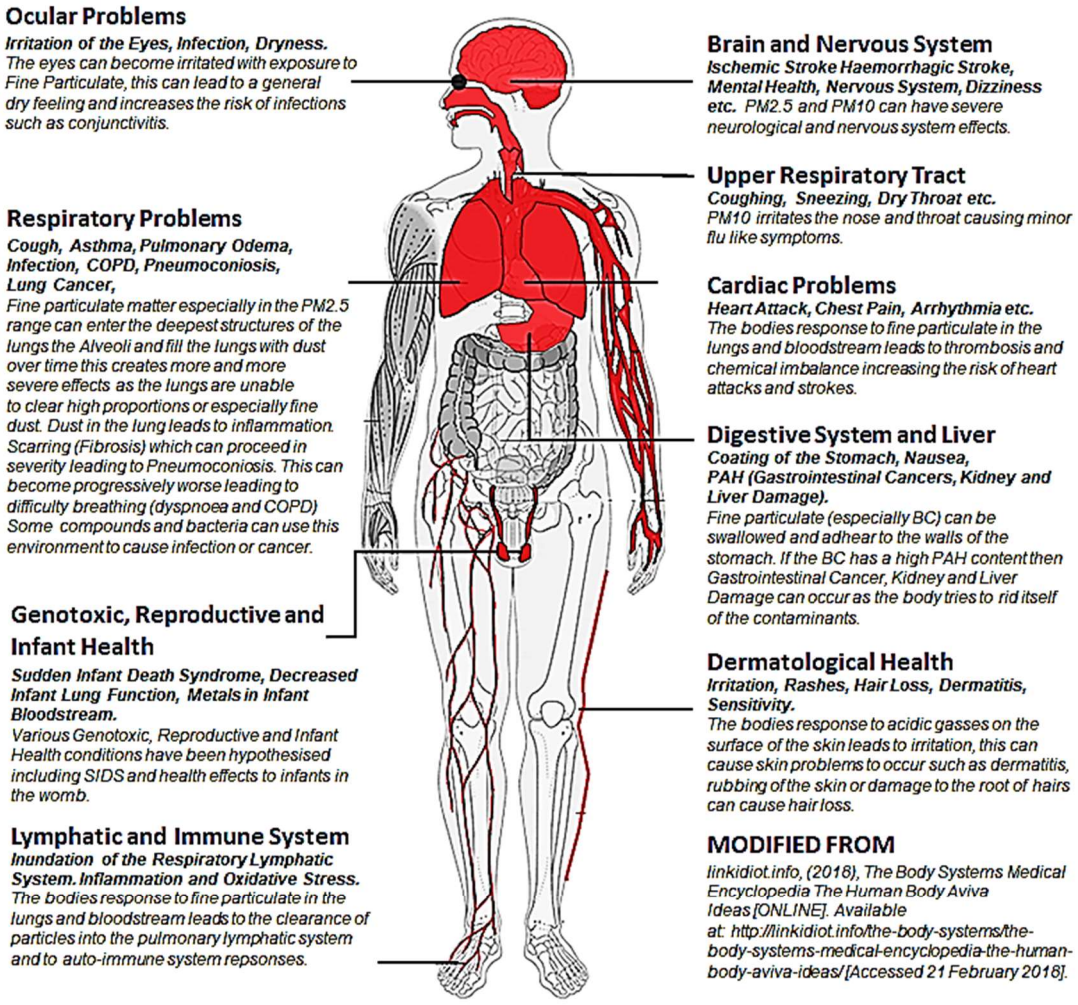


Figure 2.7. An illustration showing the human body and the main systems impacted by PM_{10} and $PM_{2.5}$ exposure.

Source; Arriva Ideas (2018) **(Adapted)**

◊ III). Particulate related occupational disease.

In the UK, there are an estimated 18,000 new cases of self-reported "breathing or lung problems" caused or exacerbated by work (HSE 2019a). The effects of occupational exposure to PM depends upon the particle's size, physical characteristics, toxicity, individual sensitivity, and duration (Bourke and Burns 2015).

- **Occupational asthma –** Occupational asthma is the most common form of occupational respiratory disease in the developed world, accounting for 20% of all new cases of asthma (Bernstein 2016). People with asthma have chronically inflamed narrow bronchi (Ralston *et al.* 2018). On exposure to air pollutants such as PM_{10} the bronchi contract and produce excessive sputum, further compromising the ability to breathe Balogun *et al.* 2018; HSE 2019b). If this inflammation is not controlled, then repeated acute asthma attacks may lead to fibrosis and narrowing of the air passages (HSE 2019b). During acute asthma attacks, the patient may present with symptoms including; wheezing, breathlessness, a tight chest, and coughing, (Bourke and Burns 2015). Occupational asthma can be caused, or made worse, by contact with many substances known as respiratory sensitisers (Balogun *et al.* 2018). These respiratory agents are either "allergenic" or "irritating" (HSE 2019b). Allergenic asthma has a lengthy lag time between exposure and symptom onset, whereas exposure to irritants can lead to symptoms within a few hours of exposure (Ralston *et al.* 2018; HSE 2019b).
- **Allergenic Rhinitis –** Rhinitis is a disorder arising from the irritation and inflammation of the mucosal membrane of the nasal passages by allergenic reaction (Balogun *et al.* 2018; HSE 2019c). Symptoms may include a blocked or runny nose, sneezing, and nasal irritation, but notably should not include a fever (Bourke and Burns 2015; Ralston *et al.* 2018; HSE 2019c).

The most common form of allergenic rhinitis is hay fever; however, a wide range of other agents can also lead to rhinitis (HSE 2019c). The development of allergenic rhinitis can be comorbid with occupational asthma (HSE 2019c).

- **Work-related Chronic Obstructive Pulmonary Disease –** COPD is the collective name used to describe a progressive and irreversible limitation of pulmonary airflow (Bourke and Burns 2015). The major symptoms are breathlessness, a chesty cough, chest infections and persistent wheezing. Two of the main phenotypes of COPD are;

◊ *Chronic bronchitis.* Chronic inflammation and stenosis of the bronchi with bronchial hypersecretion (Bourke and Burns 2015; HSE 2019d).

◊ *Pulmonary emphysema.* A permanent enlargement of the alveoli with a loss of pulmonary elasticity accompanying the destruction of alveolar walls (Bourke and Burns 2015; HSE 2019d).

COPD is considered to be a long latency disease, occurring months or years post-exposure, commonly from mid-life onwards (due mainly to attrition related damage to the lungs), (Ralston *et al.* 2018; HSE 2019d). Whilst non-occupational exposure to tobacco smoke is a dominant causative agent, occupational exposure to chemicals or dust, accompanied by an underlying genetic susceptibility, can be significant factors in COPD morbidity (Bourke and Burns 2015; HSE 2019d). The main PM chemical species associated with COPD are: coal dust, silica, PAH, organic dust, and fibres (Ralston *et al.* 2018; HSE 2019d). The HSE estimated in October 2019 that 4,000 deaths per year were likely due to occupational PM exposure (HSE 2019d).

- **Pneumoconiosis –** Pneumoconiosis is an umbrella term used to describe lung fibrosis resulting from the inhalation of inorganic dust (Bourke and Burns 2015). It is estimated that 19% of the working population has suffered some pneumoconiosis, usually from inhaling "dust from stone, cement, brick, or concrete" (HSE 2019e). A diagnosis of pneumoconiosis can be made following adverse changes in lung function coupled with the discovery of discrete nodule shadows on chest x-rays as shown in Figure 2.8 (Pattel *et al.* 2013; Bourke and Burns 2015). Pneumoconiosis can either be simple, (i.e. a benign condition without significant physiological signs or impairment), or can occur in the form of Progressive Massive Fibrosis (PMF) which is significantly more harmful (Bourke and Burns 2015; Ralston *et al.* 2018).

  Pneumoconiosis can also be sub-categorised based on the chemistry of the dust (Donaldson and Seaton 2012; Thillai *et al.* 2017). The most common form of pneumoconiosis is silicosis (exposure to silica dust) which is "the most prevalent occupational disease in the world" (Chen *et al.* 2012). Other common dust species feature a range of inorganic particles, including soot (anthracosis), silica (silicosis), and asbestos (asbestosis and potentially mesothelioma), (Donaldson and Seaton 2012).

  The risk of the development of pneumoconiosis has been well studied both in the UK and internationally (Donaldson and Seaton 2012). The UK' Health and Safety Executive (2002) created a crucial chart used to predict the risk of Scottish coal miners developing silicosis 15 years post-exposure which is shown in Table 2.1 overleaf (HSE 2002).

◊ **Simple pneumoconiosis–** When fine dust, i.e. $PM_{2.5}$ is inhaled into the lungs, the particulate becomes enveloped in pulmonary macrophages. As the dust is chemically resistant, the dust proves pneumotoxic to the macrophages, and they are unable to remove the dust from the lungs (Donaldson and Seaton 2012).

The irritation of the lungs by the particles leads to a cytokine response, which prompts collagenous fibrosis (scarring) (Donaldson and Seaton 2012; McGee *et al.* 2015). With sufficient exposure, the PM can infill various pulmonary spaces (such as the alveoli and lymph nodes) calcifying and forming discrete pulmonary nodules (Donaldson and Seaton 2012;Thillai *et al.* 2017). Initially, if the nodules are less than 5 mm in diameter (ILO score of 2/1), then they may be asymptotic, but still present a distinguishable X-ray phenomenon (Table 2.1 and Figure 2.8), (HSE 2002; Bourke and Burns 2015).

Table 2.1: Predicted risks of developing silicosis based on Scottish coal miners. **Source:** UK HSE 2002.

15 years of exposure To crystalline silica (8-hour TWA) mg/m^3	Equivalent cumulative Exposure Mg/m^3 in years	Risk of developing silicosis 15 years post-exposure as indicated by ILO score 2/1+
0.02	0.3	0.25%
0.04	0.6	0.5%
0.1	1.5	2.5%
0.3	4.5	20%

*ILO score 2/1 means international labour organisation score of pneumoconiosis from silica exposure in Scottish coal miners in the UK. The ILO score 2/1 relates to notable nodules of silica dust visible under an x-ray. An ILO score of 2/1 may be associated with notable respiratory symptoms and decline, including flu-like symptoms and chest infections such as pneumonia. TWA stands for Time Weighted Exposure.

◊ **Progressive Massive Pneumoconiosis (PMF) –** In some people, pneumoconiosis can lead to a terminal diagnosis, when fibrosis migrates outward from old injuries into surrounding tissue, progressively damaging the lungs and forming concretions of necrotic scar tissue as shown in Figure 2.9, (Seaton *et al.* 1981; Ralston *et al.* 2018).

In PMF, breathlessness and respiratory deficit become progressively more significant, creating further morbidity including; pulmonary dysfunction, pulmonary hypertension, chronic bronchitis, emphysema and infection, eventually leading towards mortality, (CDC 2012; Thillai et al. 2017). The reason for PMF developing in some people and not in others is contentious (Seaton et al. 1981). However, the development of PMF may be due to obscure reticuloendothelial functionality or genetic differences, or potentially some paternal hereditary component (Scott 1922; Beer et al. 2017;).

● **Extrinsic allergenic alveolitis (EAA) –** is an immunological disease in which exposure of an antigen to sensitised people leads to a hypersensitivity response (Bourke and Burns 2015). The pathologic mechanisms behind EEA are poorly understood, but it is believed that the disease is related to a Type III Arthus Reaction, (Bourke and Burns 2015; Ralston *et al.* 2018). EAA is similar to pneumoconiosis, but unlike pneumoconiosis, the disease is due to organic dust, e.g. hay, oil mist, or bird droppings (Ralston *et al.* 2018). The disease has two prominent forms. The first is characterised following acute exposure to antigens. The patient may become symptomatic around 4-8 hours post-exposure and may report influenza-like symptoms, malaise, pain, dry cough and breathlessness (without a discernible wheeze), (Bourke and Burns 2015; Ralston *et al.* 2018). The second is chronic EAA. In this form, the disease becomes more “insidious”, with the development of irreversible pulmonary fibrosis, dyspnoea, alveolitis, and granuloma formation, (Bourke and Burns 2015; Ralston *et al.* 2018).

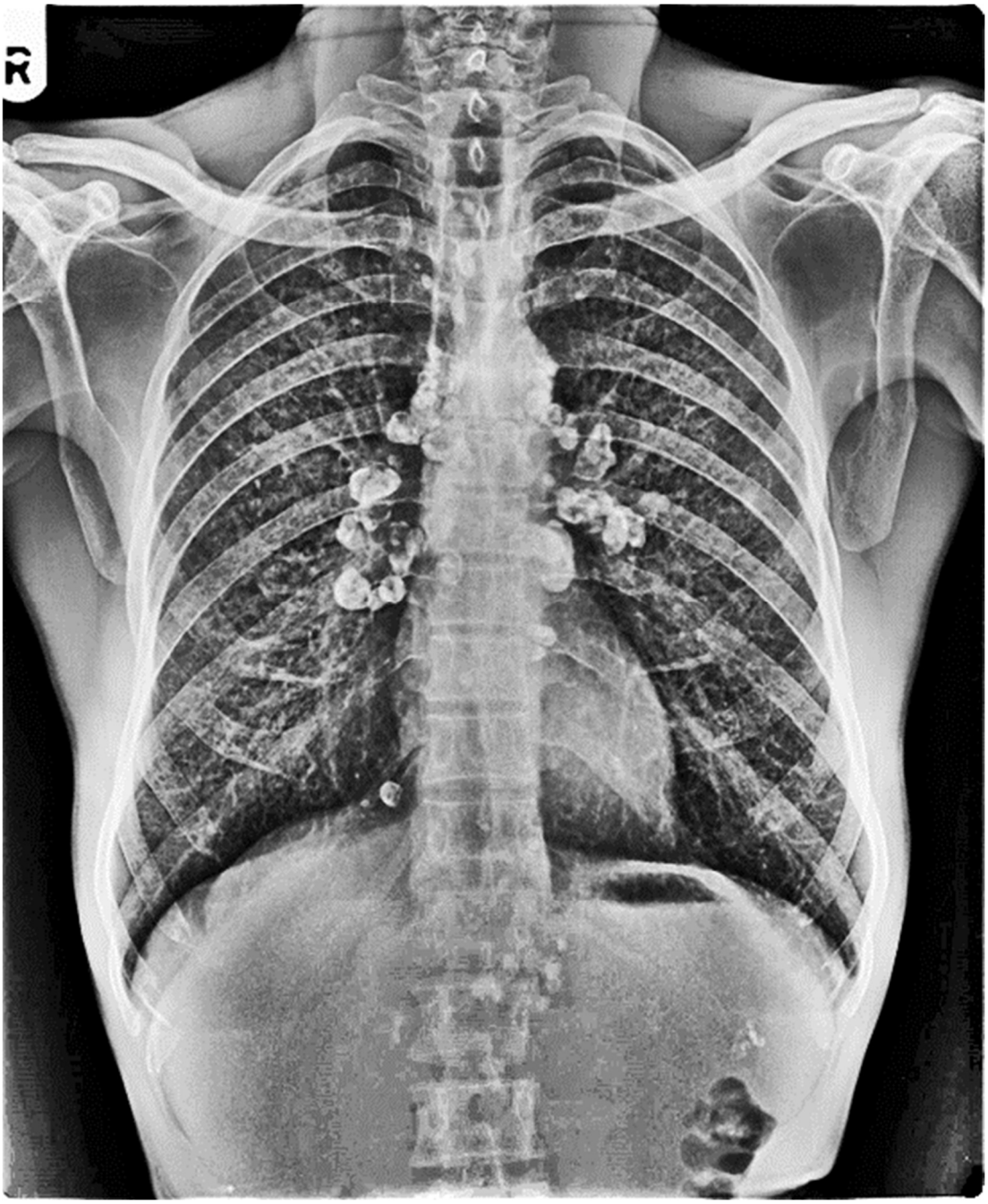


Figure 2.8. A high definition Plain X-ray of the posteroanterior view of the upper torso showing “bilateral hilar adenopathy with eggshell calcification”, Patell *et al.* 2013. The lymph nodes appeared calcified with other subtle reticulonodular opacities in the lung’s upper lobes. The patient was an occupational gemstone cutter and had been for at least 20 years, he was asymptomatic with normal lung volume and with no history of tuberculosis. The patient was diagnosed with Simple Pneumoconiosis - Silicosis.

Source; Patell *et al. (2013)* **(Adapted)**

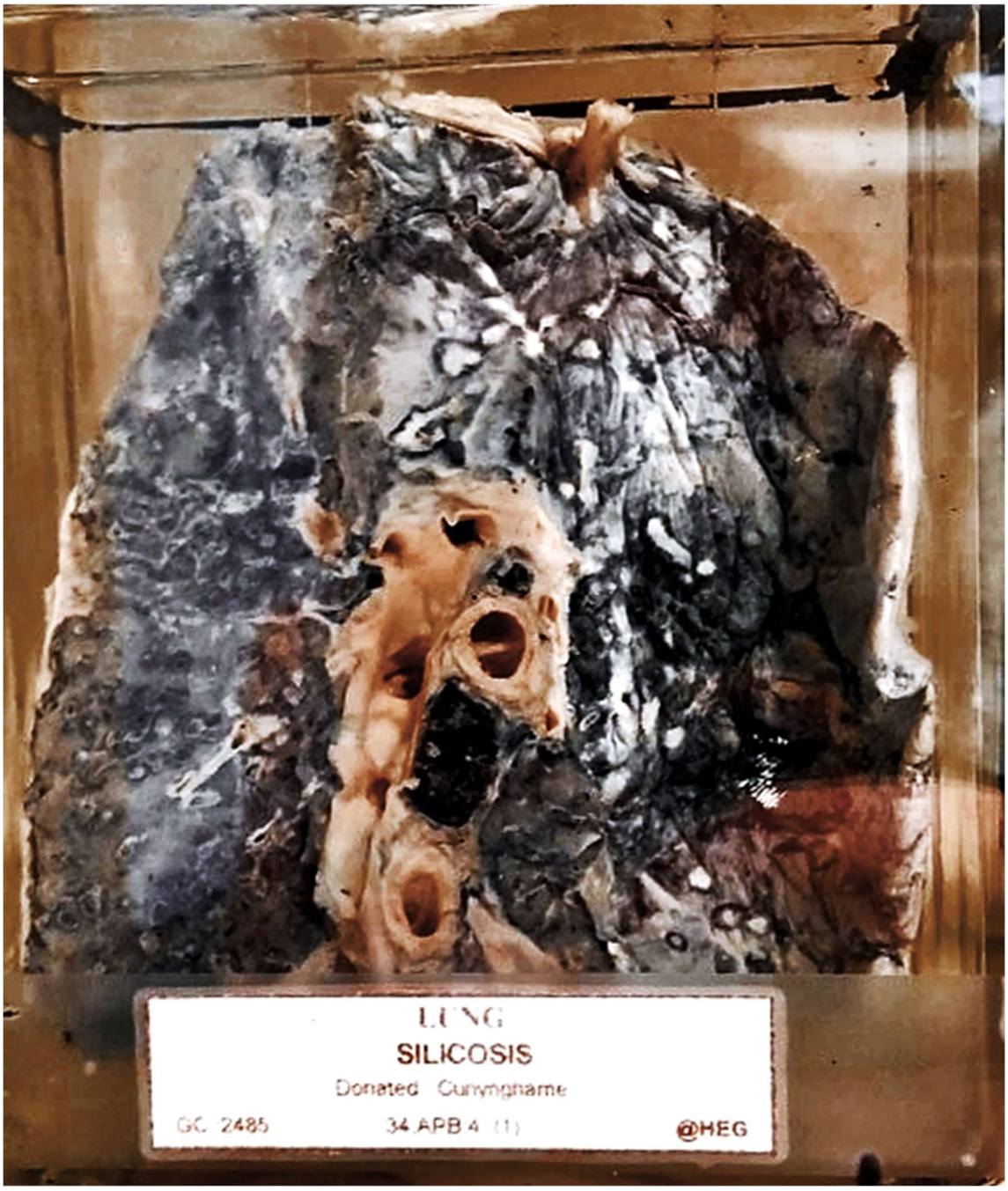


Figure 2.9. Demonstrating the effect of Silicosis on a Scottish Stone Mason. The Lungs are discoloured with black (carbon) pigmentation and grey silica filled nodules. "Microscopically the central part of the nodules is composed of concentrically arranged dense fibrous tissue containing in its spaces minute particles of stone." Note that normal lungs do not show greyness or nodules, lungs usually remain pink even after preservation.

Source: The Royal College of Surgeons (2020) **(Adapted).**

Reproduced under Licence: Surgeons' Hall Museums, The Royal College of Surgeons of Edinburgh.

♦ 2.1.2) Oxides of Nitrogen.

■ A) Penetration of NO_X into the human respiratory tract.

As part of respiration, nitrogen dioxide is inhaled deep into the lungs evading the protective properties of the respiratory tract mucosa (COMEAP 2019). Nitrogen gas eventually reaches the bronchioles; from there, it can access the finest portions (alveolus) of the human respiratory tract (US EPA 1977, 2018). When inhaled the gaseous oxides of nitrogen (NO and NO_2) react with water within the respiratory system to form nitric acid (HNO_2), (Amaza and Kreidy 2019). Once it reaches the lungs, HNO_2 erodes the lining of the lungs and dissociates to nitrates and nitrites (Amaza and Kreidy 2019).

The reaction between lung tissue and HNO_2 precipitates an extensive local and systematic auto-immune response, tissue irritation, inflammation (bronchitis), and damage (Amaza and Kreidy 2019). Inflammation following injury, which obstructs the small airways, decreases the barrier function of the epithelial cells and increases airway reactivity (Amaza and Kreidy 2019). Approximately 70-90% of the NO_2 which enters the lungs is absorbed into the bloodstream, where it reacts with haemoglobin to form methaemoglobin (an inefficient oxygen carrier) leading to hypoxia (WHO 2000; Amaza and Kreidy 2019). Metachronal rhythm (beating of the cilia) is affected by NOx exposure, reducing the respiratory tract's ability to clear sputum, showing a synergistic link between PM and NO_x (Dockery and Pope 1994; WHO 2013).

■ B) Risks of nitrogen gases to human health.

It is often difficult for researchers to isolate the effect of NO_x from PM as the two air pollutants often co-exist (Vallero 2014). Adjustment for PM and BC exposure, with nitrogen, still indicates that NO_x is a major air pollutant with dramatic effects on human health (Mills *et al.* 2015*;* Sorensen *et al.* 2017*)*. The effects of NO_X are variable and driven by characteristics such as age (the young and elderly) and vulnerability to respiratory conditions (e.g. asthma, stroke, or COPD), (Schikowski *et al.* 2014; Simoni *et al.* 2015).

◊ I). Acute exposure to nitrogen oxides

Short-term exposure to NO_x and its oxides NO and NO_2 are known to aggravate and cause a wide range of symptoms, with the most common of these being; upper respiratory reflex, i.e. rhinorrhoea, sneezing, coughing, shortness of breath, nausea, sore eyes, stuffy nose, and an itchy throat, (COMEAP 2015; ATSDR 2019). Wiwatanadate 2015 found that there was a 2.4 - 22.9% increase in “nosebleed, ‘larynx’ symptoms, dry cough, lower lung symptoms, ‘heart’ symptoms, and eye irritation” following exposure to NO_2 from a nearby forest fire (after other pollutants had been screened out).

Like with PM exposure, those with underlying health conditions can be more severely affected by daily fluctuations in NO_x air quality (COMEAP 2011). Similarly, those who have asthma are likely to have more frequent and severe episodes and even asthma-related mortality (i.e. an 1.11% increase in asthma mortality per 10 $\mu g/m^3$ of NO_2 exposure), (WHO 2000; COMEAP 2011). Those who suffer from respiratory and cardiovascular conditions may have worsening symptoms following exposure to NO_2, with daily hospitalisation rates increasing by 0.57% for respiratory and 0.66% for cardiovascular diseases per 10 $\mu g/m^3$ of NO_2 (Mills *et al.* 2015). Mortality increases markedly in elderly or ill patients due to the physiological burden of NO_x exposure.

These mortality increases include; all-cause mortality (0.71% per acute NO_2 exposure of 10 µg/m^3), respiratory (0.88% per acute NO_2 exposure of 10 µg/m^3) and cardiovascular mortality (1.09% per acute NO_2 exposure of 10 µg/m^3), (COMEAP 2015; Mills *et al.* 2015; Khaniabadi *et al.* 2017).

◊ II). Chronic exposure to oxides of nitrogen

Exposure to NO_x related air pollution (NO + NO_2) is arguably just as detrimental to human health as PM exposure, (COMEAP 2018). Like exposure to PM, NO_x impacts the morbidity and mortality of humans from the "cradle to grave" (Holgate 2017). Outlined below are three of the most prominent systems of the human body affected by NO_x exposure;

- **Respiratory –** Like PM, exposure to NO_2 is likely to lead to the inhibited development of lung capacity (FEV) in infants, even in utero, (Morales *et al.* 2015). High exposure to NO_2 was associated with low lung function and reduced FEV at 4.5 years of age as early as the second trimester (Morales *et al.* 2015). In older children, exposure to high levels of NO_2 was associated with the development of wheezing and the onset of asthma, (; Alotaibi *et al.* 2019). Khreis *et al.* 2016 found that chronic exposure to NO_2 in children under six years old produced an increased risk of asthma of 8% per 10 µg/m^3 increase in NO_2 (Khreis *et al.* 2017; PHE 2019). Older children (> 6 years old) had an elevated risk of asthma of 3% per 10 µg/m^3 increase in NO_2 exposure (Khreis *et al.* 2017; PHE 2019). New-onset asthma was also associated with high levels of NO_2 exposure, with increased morbidity of 4% per 10 µg/m^3 increase in NO_2 exposure (Khreis *et al.* 2017; PHE 2019). Due to the combined effects of NO_2 on the human body, respiratory and pneumonia mortality is predicted to increase by 5% and 27.5% respectively per 20 µg/m^3 increase in NO_2 (Eum *et al.* 2019).

- **Cardiovascular –** Multisystem oxidative stress is again a significant factor in NO_x exposures, alongside the likelihood of coagulation and thrombosis (Dermarin *et al.* 2019; COMEAP 2019; Valacchi *et al.* 2020). Exposure to NO_x causes a range of cardiovascular complications in adults with emerging evidence of impacts on children (COMEAP 2018). Nitrogen oxides have an established causative relationship with; heart failure (+7.00% per 10 µg/m^3 of NO_2), arrhythmia (2.90% per 10 µg/m^3 of NO_2), cardiovascular disease (13% per 20 µg/m^3 in NO_2) and ischemic heart disease (22.1% per 20 µg/m^3 in NO_2) (Zhao *et al.* 2014; Sørensen *et al.* 2017; Eum *et al.* 2019). During pregnancy, NO_2 exposure appears to be a risk factor in the development of pre-eclampsia and pregnancy-related hypersensitive disorders, with an increased risk of 7% and 8% per 10 µg/m^3 respectively (Pedersen *et al.* 2017; Choe *et al.* 2018).

- **Neurological –** The effects of NO_x exposure on the human body are likely to depend on the life stage of the individual (COMEAP 2019). In children, there is evidence that NO_2 impairs the neurodevelopment of sensory, motor and psychomotor functions (Clifford *et al.* 2016). Exposure to NO_x during childhood can lead to poor academic achievement in older children (-0.695%) (-4.192%), with exposure in adulthood associated with accelerated cognitive decline (Ham *et al.* 2014). Cho (2019) found that an additional three years of brain ageing was present per 20 µg/m^3 increase in NO_2 (Cho and Noh 2019). Expose to NO_x has been linked to an increased risk of dementia by 1% per 10 µg/m^3 of chronic exposure to NO_2 (Oudin *et al.* 2016; PHE 2019).

In addition to these effects, a diagram in Figure 2.10 outlines several other systems of the human body affected by NO_X exposure.

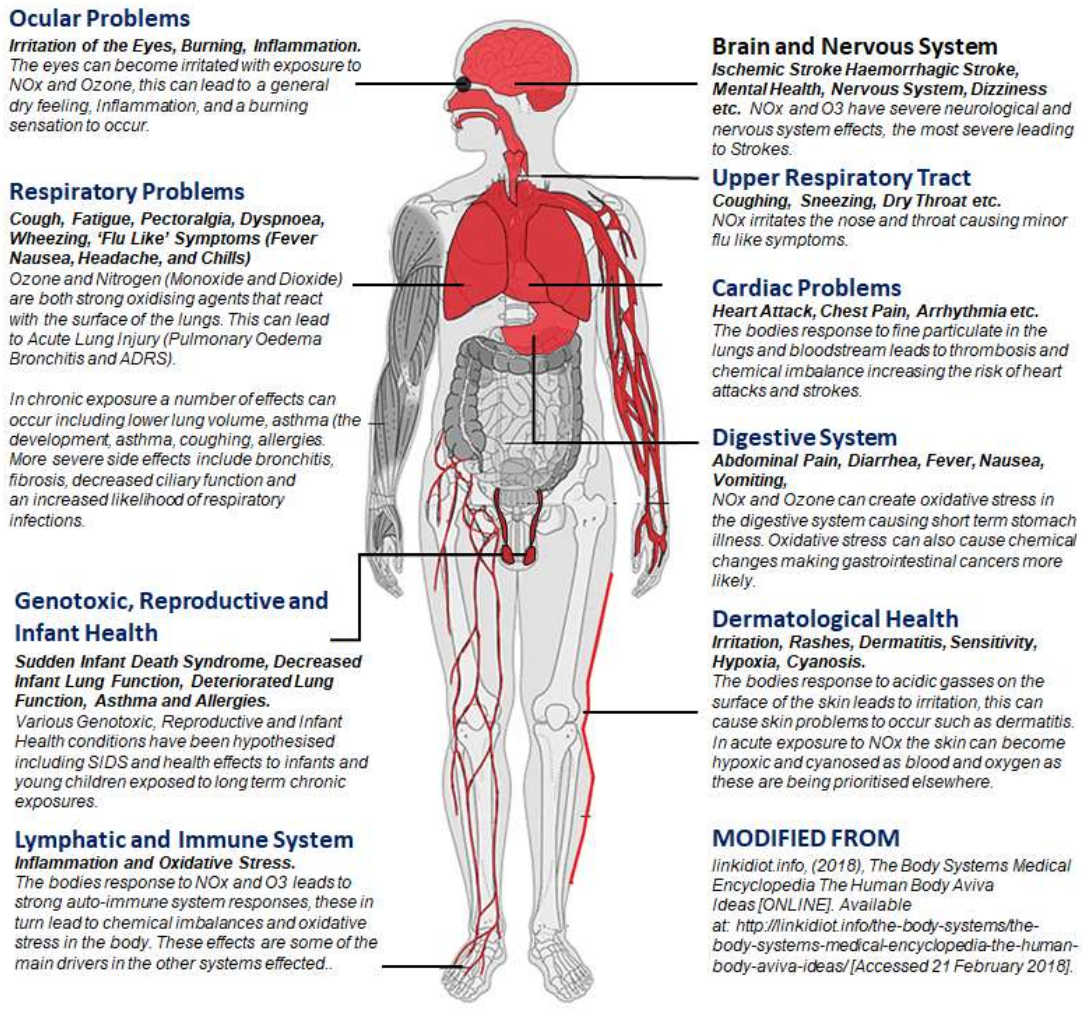


Figure 2.10. An illustration showing the human body and the main systems impacted by NO_x exposure.

Source; Arriva Ideas (2018) **(Adapted)**

◊ III). Nitrogen gas-related occupational disease.

Much of the occupational respiratory health burden from high NO_X exposures is comorbid with PM exposure (HSE 2019a). Nevertheless, there are two major diseases affected by NO_X exposure alone; these are:

- **Acute Respiratory Distress Syndrome (ARDS) –** ARDS is a form of acute respiratory failure, which arises from the inhalation of toxic gases such as NO_2 and causes diffuse pulmonary inflammation, endothelial damage, and pulmonary oedema (Ralston *et al.* 2018). One of the most classic examples of ARDS is dichloroethylsulphide poisoning, (commonly known as 'mustard gas' inhalation as shown in Figure 2.11 on 40 (Malaviya *et al.* 2020).

- **Silo fillers disease –** Is a form of ARDS which results from high NO_X exposures (Butt *et al.* 2016; Amaza and Kreidy 2019). High concentrations of NO_x exposure may initially cause mild shortness of breath and a non-productive cough or be entirely asymptomatic (ATSDR 2019; Amaza and Kreidy 2019). Those who have been exposed may notice a strong bleach-like odour (at 0.44 mg/m^3) or see a reddish vapour (at 143.44 mg/m^3). Whilst the patient would initially (or at admission) look deceptively well, over the next few hours or days (1-3), the patient may develop pulmonary oedema and bronchospasm at exposures over 900 mg/m^3 as shown in Table 2.2 on page 39, (ATSDR 2019).

  The symptoms in order of development are usually the; irritation of the eyes and upper respiratory tract, non-productive cough, fatigue, dyspnoea, wheezing, 'flu-like' symptoms (fever, nausea, headache, and chills) and in severe cases, hypoxia, and cyanosis (ATSDR 2019; Amaza and Kreidy 2019).

Clinically a victim of NO_x exposure may suffer from bronchitis and bronchopneumonia, pneumonitis, bronchiolitis fibrosa obliterans (with or without organised pneumonia) and then acute pulmonary oedema (US EPA 1977). From exposures of 286.88 mg/m^3, the patient may also suffer from more classical ARDS symptoms (US EPA 1977; Amaza and Kreidy 2019). These features are significant on x-rays, as shown in Figures 2.11 and 2.12 on pages 40 and 41, respectively. Inhalation of high concentrations of NO_2 is likely to cause burns, spasms, and swelling of the tissues of the throat leading to airway obstruction and sudden death (ATSDR 2019).

► 2.2) Conclusions.

Combustion-related air pollutants and fine particulates cause significant illness and human disease. Many of the health effects from NO_x and PM exposure arise from damage to the respiratory system via oxidation. Oxidation within the lungs can cause multi-system oxidative stress within the pneumo-lymphatic, neurological and circulatory systems which can exploit pre-existing anatomical and clinical weaknesses. Additionally, 70-90% of inhaled NO_X enters the bloodstream where it reacts with haemoglobin to form methaemoglobin (an inefficient oxygen carrier) leading to hypoxia putting even more stress on the human body.

The diverse array of human illness caused by the air pollutants can be grouped into three distinct categories depending on their exposure duration, these groups are; acute exposure, chronic exposure and long-term occupational exposures which cause an array of clinical symptomologies and diseases.

Table 2.2. Effects of acute exposure to high concentrations of nitrogen dioxide.

Effect on the human respiratory system	Exposure concentsration		The time between exposure and termination of effect
	PPM	Mg/m^3	
Odour threshold	0.23	0.44	Immediate
Airway resistance	1.5 to 2.0	2.87 3.83	Within 15 to 45 minutes.
Reversible bronchitis and bronchopneumonia	25	47.81	Within 48 hours
Focal pneumonitis	50	95.63	2-10 days
Visibility threshold	75	143.44	Immediate
Bronchiolitis fibrosa obliterans (Figure 2.12)	150	286.88	3-5 weeks
Bronchopneumonia (fatal in 2 to 10 days)	300	573.75	6-8 weeks
Fatal acute pulmonary oedema (fatal within 48 hours)	500	956.25	6-8 weeks

*The Table has been reproduced from data from the source material, contained within Table 10-19 and Table 10-20 of the medical and biologic effects of environmental pollutants: nitrogen oxides.

Source: US EPA (1997).

Figure 2.11. An example of Acute Lung Injury in a portion of the right lung from a soldier gassed by dichlorethyl sulphide commonly known as mustard gas in France during WW1 (19th December 1915). The surgeon who incised the lung indicated that; *"The lung is congested and of a purple colour, oedematous and consolidated, and the lumina of the bronchi are constricted by oedema of the submucosa. A few recent fibrinous adhesions are present between the lobes and on the pleural surface".*

Source and Caption: The Royal College of Surgeons (2020) **(Adapted).**

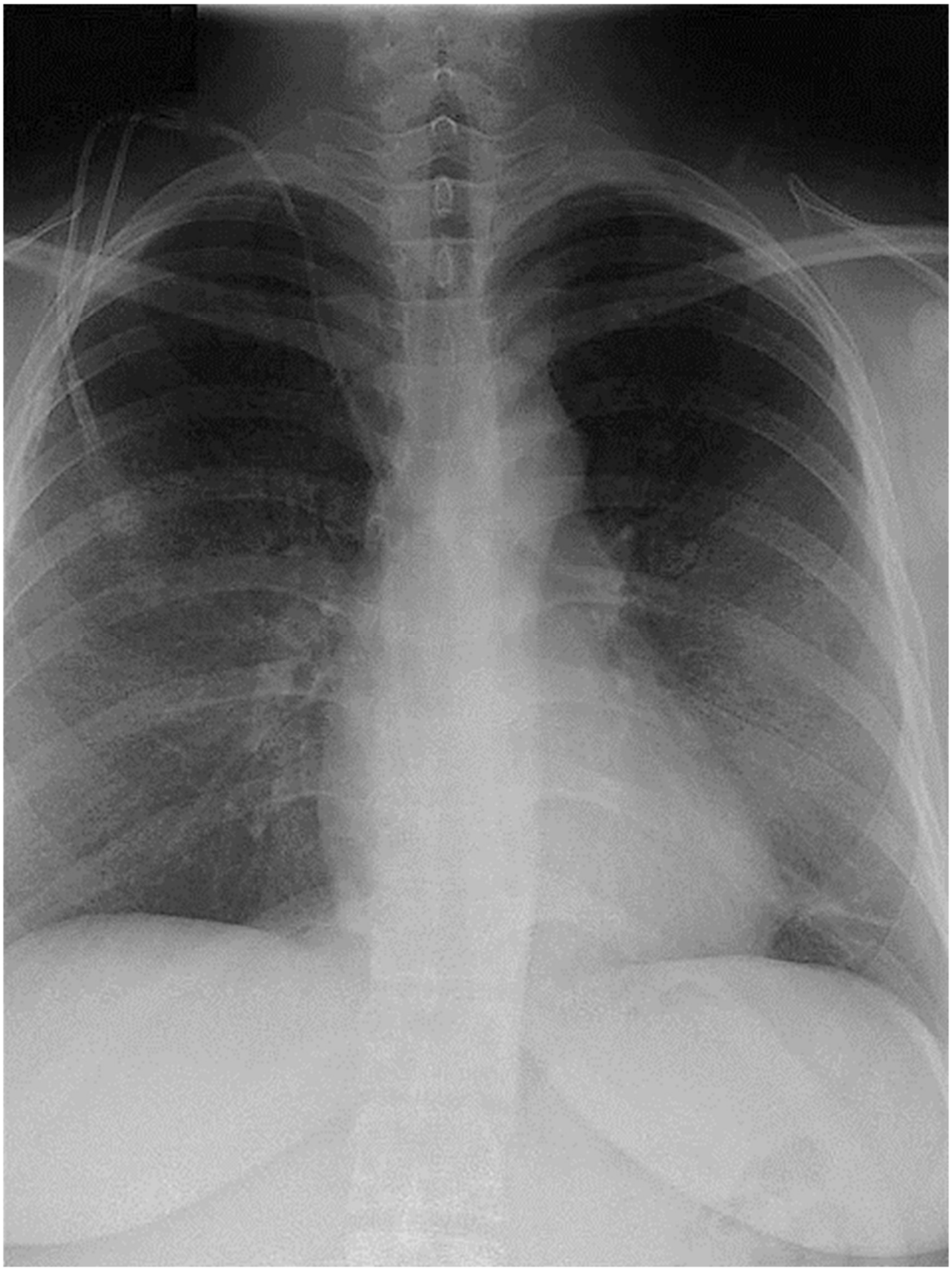


Figure 2.12. A Plain X-ray of the posteroanterior view of the upper torso showing Non-cardiogenic pulmonary oedema. There are subtle opacities in the lower lobes of the lung showing soft reticulonodular infiltrates. The X-Ray shows a patient who had been exposed to a high dose of Nitrogen Dioxide following an agricultural accident (Silo Fillers Disease).

Source; Leung (2017) **(Adapted).**

Reproduced courtesy of Professor Ann Leung, Department of Radiology, Stanford University Medical Centre.

► 2.3) References.

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► 2.4) Image References;

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CHAPTER 3

The Legislative Context Surrounding Air Quality Assurance within the United Kingdom.

"There's so much pollution in the air now,
that if it weren't for our lungs, there'd
be no place to put it all".
Robert Orben (1927 - Present)

Chapter 3 studies the legislative context surrounding air quality assurance, both legislatively, and within best practice guidelines, outlining the primary safety limits on air quality in ambient and workplace air. The legislative context of air pollution is vital for the quantification of harm to receptors, as different environments and legislative regimes allow for variable legal limits on air quality exposure.

► 3.1) Regulatory Framework.

The air quality regulatory framework imposes a national strategy on all local authorities throughout the UK (Defra 2019a). Air quality management was subject to European Union (EU) legislation, although this will almost certainly change given the UK's divergence with the EU on 31st January 2020 (Heyvaert *et al.* 2018). Currently, the Secretary of State for Environment, Food and Rural Affairs handles breaches, coordination, assessment and air quality management plans (Defra 2019a, b).

The main regulatory authorities for air quality are the UK's regional environmental protection agencies; Scottish Environmental Protection Agency (SEPA), National Resources Wales (NRW), Environment Agency (EA), and Northern Irish Environmental Agency (Defra 2019b).

♦ 3.1.1) European Union Level.

The management and improvement of air quality are driven by EU legislation; due to the primacy of EU legislation within member states - as it applies to competence held at EU level (Council Directive 2008/50/EC; Vincent *et al.* 2010).

The most important of the EU legislative changes to the control of air quality was the Ambient Air Quality and Cleaner Air for Europe (CAFE) Directive (2008/50/EC) which set legally binding limits on the concentration of ambient (outdoor) air quality of major air pollutants (*Council Directive 2008/50/EC*). The pollutants under the CAFE directive had been identified as having a substantial effect on public health in Europe (*Council Directive 2008/50/EC*; Vincent *et al.* 2010). Outdoor areas are even more strictly regulated in ecologically sensitive environments (*Council Directive 2008/50/EC*; Vincent *et al.* 2010). These air pollutants include; Particulate Matter (PM_{10} to $PM_{2.5}$), Nitrogen Dioxide (NO_2), Ozone, Sulphur Dioxide, and Carbon Monoxide (*Council Directive 2008/50/EC*; Vincent *et al.* 2010). This directive had a substantial effect on air quality in the UK as it revised most of the EU's prior air quality legislation (*Council Directive 2008/50/EC*; Vincent *et al.* 2010; Defra 2019c). The 4th Air Quality Daughter Directive (2004/107/EC), which set targets for ambient concentrations of toxic heavy metals and Polycyclic Aromatic Hydrocarbons (PAH), was incorporated into UK law through the "Air Quality Standards Regulations 2010" (*Council Directive 2004/107/EC*; *The Air Quality Standards Regulations*).

In contrast to general outdoor air quality, workplace air quality is legislated for in the Chemical Agents Directive (98/24/EC) – "Risks related to chemical agents at work" (*Council Directive 98/24/EC*). This legislation created minimum requirements for employers to protect workers from chemical risks to their safety and health (*Council Directive 98/24/EC*; HSE 2013a). As part of this directive, the EU has set-up several EU Wide (collective) chemical guidelines for protecting workers (HSE 2013a).

Member states may choose to transpose these values into their guidance or impose stricter limits (*Council Directive 98/24/EC*; HSE 2013a). The list of chemicals has had five rounds of drafting and new chemicals are added on each occasion, with new directives issued in 1998, 2000, 2006, 2009, 2017, and 2020 (HSE 2020). The Chemical Agents Directive (98/24/EC) was incorporated into UK law in 2002 as the Control of Substances Hazardous to Health (COSHH) Regulations (*The Control of Substances Hazardous to Health Regulations 2002,* HSE 2013a).

Before the Chemical Agents Directive (98/24/EC), the EU released the OSH (Occupational Safety and Health) Framework Directive (89/391/EEC), which introduced measures to encourage improvements in the safety and health at work (*Council Directive 89/391/EEC*; HSE 2018). This directive outlined the drafting of a risk assessment by a competent person (HSE 2018, 2020). Together with the Chemical Agents Directive, the legislation prescribed a "hierarchy of measures to prevent or reduce the exposure of workers to dangerous substances" which is otherwise known as the STOP principle (*Council Directive 89/391/EEC*, HSE 2018).

The Stop Principle is an abbreviation which stands for;

S = Substitution, *using a different product with less harmful health effects.*
T = Technological, *using technology to reduce exposure to employees.*
O = Organisational, *e.g. rotation of employees to reduce high exposures.*
P = Personal, *such as Personal Protective Equipment (PPE).*

♦ 3.1.2) UK National Level and Local Authorities.

The UK has an extensive history of Clean Air Legislation, with the first documented proclamation in the 13th century under the reign of King Edward 1st (Edward 1307). Later legislation was passed as a result of the catastrophic effects of the 1952 smog, which included the Clean Air Acts of 1956, 1968 and 1993, (Vincent *et al.* 2010; Defra 2018b). However, since 1995, air quality legislation has been within the competence of the European Union (Vincent *et al.* 2010; Defra 2018b). The Environment Act 1995, Part IV, requires the UK, and the devolved governments within the UK, to produce air quality strategies on a regional and national level, including upholding the Ambient Air Quality Directive (2008/50/EC) and Environment Act 1995; Defra 2018b). As an EU member state, the UK was required to incorporate European Union directives into UK Law. As a result, the Ambient Air Quality Directive (2008/50/EC) and the 4th Air Quality Daughter Directive (2004/107/EC) were transposed into UK law through the "Air Quality Standards Regulations 2010" (*The Air Quality Standards Regulations 2010*; Vincent *et al.* 2010). The main regulatory duties of the regional environmental protection agencies in Wales (National Resources Wales, NRW), England (Environment Agency, EA), Scotland (Scottish Environmental Protection Agency, SEPA) and Northern Ireland (Environmental Protection Agency, EPA) regarding air quality is to uphold the Air Quality Standards Regulations 2010, (The Air Quality Standards Regulations 2010).

Regional governments delegate the monitoring and control of breach areas to local authorities who monitor and create an action plan for the reduction of air pollution of their area through Air Quality Management Area (AQMA) restrictions (Defra 2018a). The Environmental Protection Act (1990) – amended by the 2010 regulations – granted legal powers to local authorities to mitigate and undertake abatement actions against statutory nuisances including but not limited to dust pollution (*The Environmental Permitting (England and Wales) Regulations 2010*; Defra 2018a).

The devolved administrations are also permitted to, at their discretion, enact stricter environmental standards than the Directive (2008/50/EC), (Defra 2010; Ricardo AEA 2019). Consequently, in 2016 SEPA decided to promote more stringent air quality standards in Scotland by adopting the World Health Organisation guideline values (SPICe 2016). The resulting guidelines for air quality in the United Kingdom are outlined in Section 3.2.1; Ambient Air Standards (*The Air Quality Standards (Scotland) Regulations 2010*; SPICe 2016).

Besides ambient air standards, the Chemical Agents Directive (98/24/EC) was incorporated into UK law in 2002 as the Control of Substances Hazardous to Health (COSHH) Regulations (*The Control of Substances Hazardous to Health Regulations 2002)*. The COSHH regulations restrict the chemical exposure of workers (HSE 2012, 2013a, b, 2017). The UK releases a list of Workplace Exposure Limits (WELs) through the Health and Safety Executive, which oversees the control of health and safety in the workplace (HSE 2020). The WELs are published in the document EH/40 and were last updated in 2020 to include the latest (2019) EU Indicative Occupational Exposure Limit Values (IOELV), (HSE 2020). Nitrogen Dioxide and Nitrogen Monoxide were added into the WEL guidelines as recently as 2018 (HSE 2020). However, regulation 6 of the COSHH Regulations (2002), underlines the fact that the absence of a limit value does not mean that the material is safe, (*The Control of Substances Hazardous to Health Regulations 2002*). Employers should determine their control standards if no UK or EU limit is available (HSE 2013a, b, 2017).

► 3.2) Guidelines and Standards of Air Quality.

In line with the legislative context, the guidelines, and standards of acceptable air quality within the UK's ambient and workplace environments are outlined in the following sections.

♦ 3.2.1) Ambient Air Standards.

Table 3.1 shows various target values for protecting human health, vegetation, and ecosystems for the key selected air pollutants of $PM_{2.5}$ and PM_{10} and NO_2 (Council Directive 2008/50/EC; Defra 2010, 2011). The ambient air standards recommended by the World Health Organisation (WHO) are also outlined for context (WHO 2000, 2006). The values set by the European Directive limit, as incorporated into UK law are denoted by the letter 'L' (for legislation), those based on guidance are labelled 'G' (for guidance) (Council Directive 2008/50/EC). There is no guideline for Black Carbon (BC) in ambient air; however, there is a guideline limiting Benzo[A]Pyrene (BaP), (Council Directive 2004/107/EC).

Total Carbon as an analogy for BC was measured by Siudek in 2018, who found a median concentration of 8.9% of the Total Particulate Matter was Total Carbon. Following Feng *et al.* (2019), the BC to Total Carbon ratio was estimated to be around 26.6%. Of the BC, a median of 0.22% was BaP (Siudek 2018). Therefore, the concentration of BaP as Total Carbon (0.22%) was divided by the BaP limit value of 8.80 $\mu g/m^3$ (Siudek 2018). This limit was further divided by 26.6% to give a BaP as a BC limit value of 33.08 $\mu g/m^3$ (Feng *et al.* 2019).

Table 3.1: UK ambient guidelines for selected combustion-related air pollutants.

Air pollutant	Duration and guideline [a]	GV µg/m^3	Exceedances
Particulate Matter $PM_{2.5}$	L. 1 Year (ENGLAND & WALES)	25	-
	L. 1 Year (SCOTLAND)	10	-
	G. 1 Year (WHO-AQG).	10	-
	G. 24 Hours (WHO-AQG)	25	-
	G. 20% Reduction (UK)	-	Within 10 Years.
Particulate Matter PM_{10}	L. 1 Year (ENGLAND & WALES)	40	-
	L. 1 Year (SCOTLAND)	18	-
	L. 24 Hours (England and Wales)	50	<35 Exceedances
	L. 24 Hours (Scotland)	50	<7 Exceedances
	G. 1 Year (WHO-AQG)		-
	G. 15% Reduction (UK)		Within 10 Years.
Nitrogen Dioxide NO_2	L. 24 HOURS (UK & WHO-AQG)	200	<18 Exceedances
	L. 1 Year (UK & WHO-AQG)	40	-
Oxides of Nitrogen NO_x	L. 1 Year (UK)*ECOLOGICAL AREAS	30	-
Benzo[a]Pyrene BaP	L. 1 Year (UK)	0.00025	-
*Black Carbon (BC) (*0.05852% as BaP)*	*G. 1 Year (UK)*	33.08	*Equivalent Value based on assumptions* *

* Guideline value based on 0.22% BaP composition of Total Carbon, and 26.6% of Total Carbon in Black Carbon following Siudek 2018 and Feng *et al.* 2019, respectively.

♦ 3.2.2) Occupational Standards.

Many workers are exposed to substances at work, which can sometimes harm their health. In the UK, 12,000 people are estimated to die each year due to historical occupational exposures to air pollutants, with 18,000 new annual cases of self-reported breathing or lung problems due to work (HSE 2019). Following the Chemical Agents Directive (98/24/EC), the European Commission, through the Scientific Committee for Occupational Exposure Limits (SCOEL), recommend EU community-wide Indicative Occupational Exposure Limit Values (IOELVs) (HSE 2020). In UK health and safety practice, these IOELVs are known as Workplace Exposure Limits (WELs) (HSE 2020). Employees are required to Control Substances Hazardous to Health through the COSHH regulations (2002), (HSE 2012).

The UK WELs, are issued over two major time-periods;

- **TWA:** 'Time Weighted Average' outlines the maximum average level a human should be exposed to over 8 hours (HSE 2020).
- **STEL:** 'Short Term Exposure Limits' outlines the maximum average level a human should be exposed to over 15 minutes (HSE 2020).

The UK HSE has recently defined WELs for Nitrogen Monoxide (Nitric Oxide) and Nitrogen Dioxide in the newest revision of the standards (2018), (HSE 2020). The air pollutants $PM_{2.5}$ and PM_{10} are approximately equivalent to the respirable and inhalable fraction, respectively (HSE 2019).

The US National Institute for Occupational Safety and Health (NIOSH) defines the IDLH as "values for levels of airborne contaminants likely to be; Immediately Dangerous to Life or Health". The IDLH is used to understand the upper toxic threshold of the selected air pollutants (US NIOSH 2014). In IDLH, this upper toxic threshold is "likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment" (US NIOSH 2014).

The WELs and the IDLH for the selected air pollutants are shown in Table 3.2. Besides the selected air pollutants of PM, NO, NO_2, several additional chemicals became relevant to this thesis in Chapters 10 and 11, though these chemicals are outlined in Table 3.3 for reference.

Table 3.2: WEL and IDLH guidelines for a range of air pollutants.

Air pollutant	Duration and guideline [a]	Guideline value, mg/m^3
"Respirable Dust" $PM_{2.5}$	L. 8 Hour -TWA (UK)	4.50
"Inhalable Dust" PM_{10}	L. 8 Hour -TWA (UK)	10.00
Nitrogen Monoxide NO_2	L. 8 Hour -TWA (UK) G. IDLH (US NIOSH)	2.50 24.50
Nitrogen Dioxide NO_2	L. 15 Minute -TWA (UK) L. 8 Hour -TWA (UK)	1.91 0.96

Table 3.3: WEL and IDLH guidelines for additional chemical hazards.

Air pollutant	Duration and guideline [a]	Guideline value, mg/m^3
Carbon Black	L. 15 Minute -TWA (UK)	7.00
	L. 8 Hour -TWA (UK)	3.50
	G. IDLH (US NIOSH)	1,750.00
Crystalline Silica	L. 8 Hour -TWA (UK)	0.10
"Respirable Dust"	G. IDLH (US NIOSH)	50.00
Amorphous Silica	L. 8 Hour -TWA (UK)	6.00
"Inhalable Dust"	G. IDLH (US NIOSH)	3,000
Barium Sulphate	L. 8 Hour -TWA (UK)	10.00
"Inhalable Dust"	L. 8 Hour -TWA (UK)	4.00
"Respirable Dust"	G. IDLH (US NIOSH)	50.00
Oil Mist	G. IDLH (US NIOSH)	2,500

♦ 3.2.3) RIDDOR Regulations 2002 +2013 amendments.

The Reporting of Injuries, Diseases and Dangerous Occurrences Regulations (RIDDOR) 2002 (as amended in 2013), outlines the events which are reportable to the Health and Safety Executive for further investigation, (HSE 2013c). RIDDOR only applies to an identifiable cause of physical injury which was work-related and is listed under the regulations "Types of reportable Injuries", (HSE 2013c). These investigative events can range from the incidence of occupational diseases such as asthma, through to a catastrophic explosion, (HSE 2013c).

Some of the key events which are reportable to RIDDOR include;

■ A. Reportable injury (Regulations 8 and 9 of RIDDOR).

- Deaths of workers and non-workers, if they arise from a work-related accident.
- Serious burns (including scalding) which cover more than 10% of the body or cause significant damage to the eyes, respiratory system, or other vital organs.
- Accidents, where they result in an employee absence or inability to perform normal work duties for more than seven days.
- Any loss of consciousness caused by head injury or asphyxia.
- A health care practitioner newly diagnosed an occupational respiratory disease.
- Incidence of occupational asthma.

■ **B. Dangerous occurrences (Schedule 2 of RIDDOR).**

- The malfunction of breathing apparatus.
- Release of flammable liquids and gases.
- Hazardous escapes of substances.
- Release of petroleum hydrocarbon.
- The evacuation of an offshore installation.

♦ 3.2.4) Daily Air Quality Index (DAQI).

Air Quality Indexes (AQI) are a common way to communicate information to the public about the daily, real-time and forecasted levels of ambient air pollution in the community (US EPA 2018). The forecasting of air quality information allows for advanced warning to the public about potentially health-damaging air pollution events and allows sensitive receptors to change their behaviour to reduce the severity of their symptoms (COMEAP 2011; Defra 2018c). A copy of the UK Air; Air Pollution forecast with the DAQI bandings is shown in Figure 3.1 (on page 73).

While many AQI's exist internationally, the UK uses the DAQI Daily Air Quality Index, developed by the Committee on Medical Effects of Air Pollutants (COMEAP) based on the health evidence of acute exposure to air pollution in the UK (COMEAP 2011; Defra 2018c). The COMEAP has modelled six air pollutants these include Ozone (O_3), Nitrogen Dioxide (NO_2), Sulphur Dioxide (SO_2), Particulate Matter ($PM_{2.5}$ and PM_{10}) and Carbon Monoxide (CO), (COMEAP 2011; Defra 2018c). However, the DAQI scale was redesigned in 2011 to include a ten-point scale of air pollution exposure, retire Carbon Monoxide AQI measurements and replace it with the measurement of $PM_{2.5}$, (COMEAP 2011).

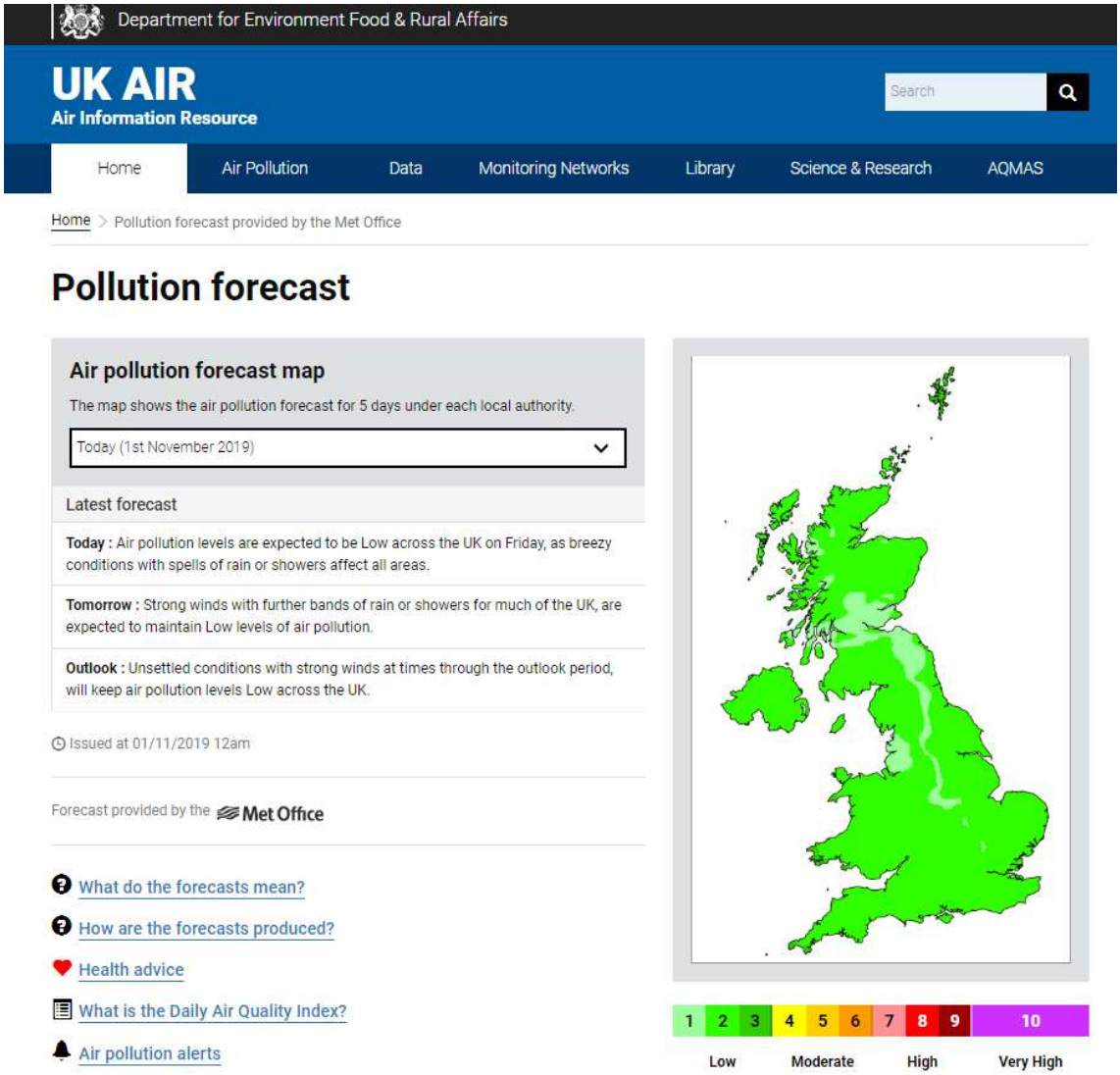

Figure 3.1: A screenshot of the UK Air Pollution Forecast provided on the UK Air: Air Information Resource of Defra as forecasted by the MET office.

Source; Defra, (2019).

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The DAQI index is simple and mimics the Sun and Pollen Indexes, (COMEAP 2011; Defra 2018c). The new DAQI ten-point scale (1-10) is resolved into four bands; Low (1-3), Moderate (4-6), High (7-9) and Very High (10+) which classify the quality of ambient air, as shown in Tables 3.4 to 3.6 on Pages 75 to 77).

The DAQI offers advice on the level of air quality and distinguishes between the general population and those who are vulnerable to the effects of air pollution (such as those who are very young or elderly, as well as people suffering from cardiovascular and [or] respiratory disease), (COMEAP 2011). As people are exposed to greater exposures of air pollution, the risk of people developing adverse health effects increases. Exposure only represents the statistical chance that someone may fall ill. Individually, even those who are especially sensitive to high concentrations of air pollution may not suffer from ill effect from an episode of exposure (Defra 2017).

Some people, such as asthmatics may become aware of the effects air pollution has on their health as they may need to use their inhaler more often (COMEAP 2011). At very high concentrations, the general population may experience soreness or a dry sensation of the throat or eyes, or cough, (COMEAP 2011). The COMEAP (2011) health bandings from ‘Low’ to ‘Very High’ have been reproduced below in Table 3.4 and 3.6 (on pages 75 to 77).

Table 3.4. COMEAP definitions of the air pollution exposures.

Source: COMEAP (2011).

Exposure Band	Description
Low	Acute exposures at this concentration are unlikely to affect anyone. Including, people who are especially susceptible to the effects of air pollution, e.g. people with underlying cardiovascular or respiratory conditions.
Moderate	Acute exposure is likely to bring “Small Effects” on people who are already susceptible to poor air quality.
High	Acute exposure is likely to bring “Significant Effects” on people who are already susceptible to poor air quality.
Very High	Acute exposure is likely to affect even healthy individuals adversely.

Table 3.5. Air Pollution Bandings by COMEAP.

Source: COMEAP (2011).

DAQI Index	Air Pollution Rating	$PM_{2.5}$ ($\mu g/m^3$)	PM_{10} ($\mu g/m^3$)	Nitrogen Dioxide ($\mu g/m^3$)
1		0 – 11	0 – 16	0 – 67
2		12 - 23	17 – 33	68 – 134
3	**LOW**	24 - 35	34 – 50	135 – 200
4		36 - 41	51 – 58	201 – 267
5		42 - 47	59 – 66	268 – 334
6	**MODERATE**	48 - 53	67 – 75	335 – 400
7		54 - 58	76 – 83	401 – 467
8		59 - 64	84 – 91	468 – 534
9	**HIGH**	65 - 70	92 – 100	535 – 600
10	**VERY HIGH**	71 or more	101 or more	> 601

Table 3.6. Recommended Actions and Health Advice.

Source: COMEAP (2011).

Air Pollution Banding	Value	Accompanying health messages for at-risk individuals*	Accompanying health messages for the general population
LOW	1-3	Enjoy your usual outdoor activities.	Enjoy your usual outdoor activities.
MODERATE	4-6	Adults and children with lung problems, and adults with heart problems, who experience symptoms, should consider reducing strenuous physical activity, particularly outdoors.	Enjoy your usual outdoor activities.
HIGH	7-9	Adults and children with lung problems and adults with heart problems should reduce strenuous physical exertion, particularly outdoors, and particularly if they experience symptoms. People with asthma may find they need to use their reliever inhaler more often. Older people should also reduce physical exertion.	Anyone experiences discomforts such as sore eyes, cough, or sore throat should consider reducing activity, particularly outdoors.
VERY HIGH	10	Adults and children with lung problems, adults with heart problems, and older people, should avoid strenuous physical activity. People with asthma may find they need to use their reliever inhaler more often.	Reduce physical exertion, particularly outdoors, especially if you experience symptoms such as cough or sore throat.

*Adults and children with heart or lung problems are at greater risk of symptoms. Follow your doctor's usual advice about exercising and managing your condition. Very sensitive individuals may experience health effects, even on Low air pollution days.

► 3.3) Conclusions.

This review of the legislative environment of the key air pollutants in the UK has shown that the place in which the exposure occurs, triggers various items of legislation. Should exposure to air pollutants be found in the workplace, then Health and Safety legislation is likely to be triggered, while exposure in the community triggers ambient air legislation. However, exposure limits in ambient air are a magnitude stricter than industrial 'work-related' exposures.

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► 3.5) Figure References

Figure 3.1. Defra. (2019) *Pollution Forecast.* London, England: Department of Environment, Farming, and Rural Affairs. Available at: TinyURL.com/y3hrukr9 (Accessed: 2nd November 2019).

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CHAPTER 4

An Introduction to the UK's Unconventional Natural Gas Industry (UNG).

"A century ago, petroleum - what we call oil - was just an obscure commodity; today it is almost as vital to human existence as water".

Rt. Hon. James Buchan (1954 – present) [1]

Chapter 4 outlines the UK oil and gas industry, briefly discussing the historical context, and various onshore hydrocarbon reserves. With this brief understanding of the geological setting, the main phases of the UK's Unconventional Natural Gas (UNG) developments are explained. An understanding of the geological context and phases of the development is vital for the risk assessment in Chapter 5, but a foundational knowledge of these topics is important in understanding the later works of this thesis.

► 4.0) Introduction.

Petroleum engineering is the field responsible for the design and extraction of hydrocarbons. It was developed in North America, the Middle East, British Isles, and the North Sea from the 1850s onwards, (Dean 2018). Before the 1850s, oil was an obscure commodity of little economic importance (Dean 2018).

In 1853, the first large-scale commercial exploitation of oil shale began in the West Lothians in Scotland (Louw and Addison 1985; MSOISI 2018). Within ten years of the West Lothian discovery, the first conventional oil well was sunk in Pennsylvania (USA) sparking the American oil rush (Dean 2018).

In the UK, the petroleum mining industry remained small with only the West Lothians and UK coalfields actively working oil shale (MSOISI 2018). The oil shale industry reached its peak around 1900 and declined, eventually ceasing production by the 1960s (Louw and Addison 1985; MSOISI 2018). One of the primary causes of the decline of the West Lothian oil shale was an occupational disease known as "mule spinners cancer" or "paraffin cancer" which befell workers who worked with oil shale and its distillates (Scott 1922). The 'last straw' for the onshore industry was the discovery of large petroleum reserves offshore within the UK's waters. This discovery marked the beginning of the UK's profitable offshore petroleum developments, though production has declined since the turn of the millennium, due to the depletion of oil and gas resources (OGA 2014; MSOISI 2018).

The decline in UK production offshore, coupled with the USA successfully harnessing their onshore reserves, has led to a shifting focus back to UK onshore reserves (Houses of Parliament 2013; Loomis and Haefele 2017). The UK public perception presents a significant barrier to extraction, due to poor perceived environmental practices in other parts of the world (e.g. The USA and Australia), (Luke *et al.* 2018). Without public support, the use of hydraulic fracturing onshore has either been banned or indefinitely suspended. However, the conventional extraction of unconventional resources is still permitted, and even some unconventional techniques are still allowed (such as directional drilling).

► 4.1) UK's extractive industries and air pollution.

The extractive industry involves the 'winning' of raw materials from the earth (e.g. the mining of aggregate, mineral, and fossil fuel resources). The extractive industries can be subdivided into three major categories;

1. Mining; this sector has an extensive history of working with bituminous materials in the UK.
2. Offshore petroleum: the sector practices modern contemporary HSE procedures according to UK legislation. HSE offshore may mirror good operational practice onshore.
3. Onshore petroleum: the sector in which this research is based.

♦ 4.1.1) Mining.

Approximately 2,000 mines and quarries were active in the UK in 2013 (shown in Figure 4.1). In 2013, the mining and quarrying sector accounted for 0.014% of UK GDP (Gross Domestic Product), (Cameron *et al.* 2013). This is a dramatic reduction from the mining industry's peak in 1913, when coal mining, alone, accounted for 13% of UK GDP (Williams 1989; Cameron *et al.* 2013).

The UK's coal legacy is important as cannel coal (the 3rd most historically worked type of coal) is a terrestrial form of oil shale, (Dean 2018). The mining of "lamosite" oil shale is the most interesting from this thesis's perspective, as considerable deposits of this oil shale are found throughout the UK (Gallois 1979; Dean 2018). Arguably, the best example of mining of lamosite is from the Strathclyde Group, a series of geological formations in the West Lothians of Scotland (Louw and Addison 1985; Dean 2018).

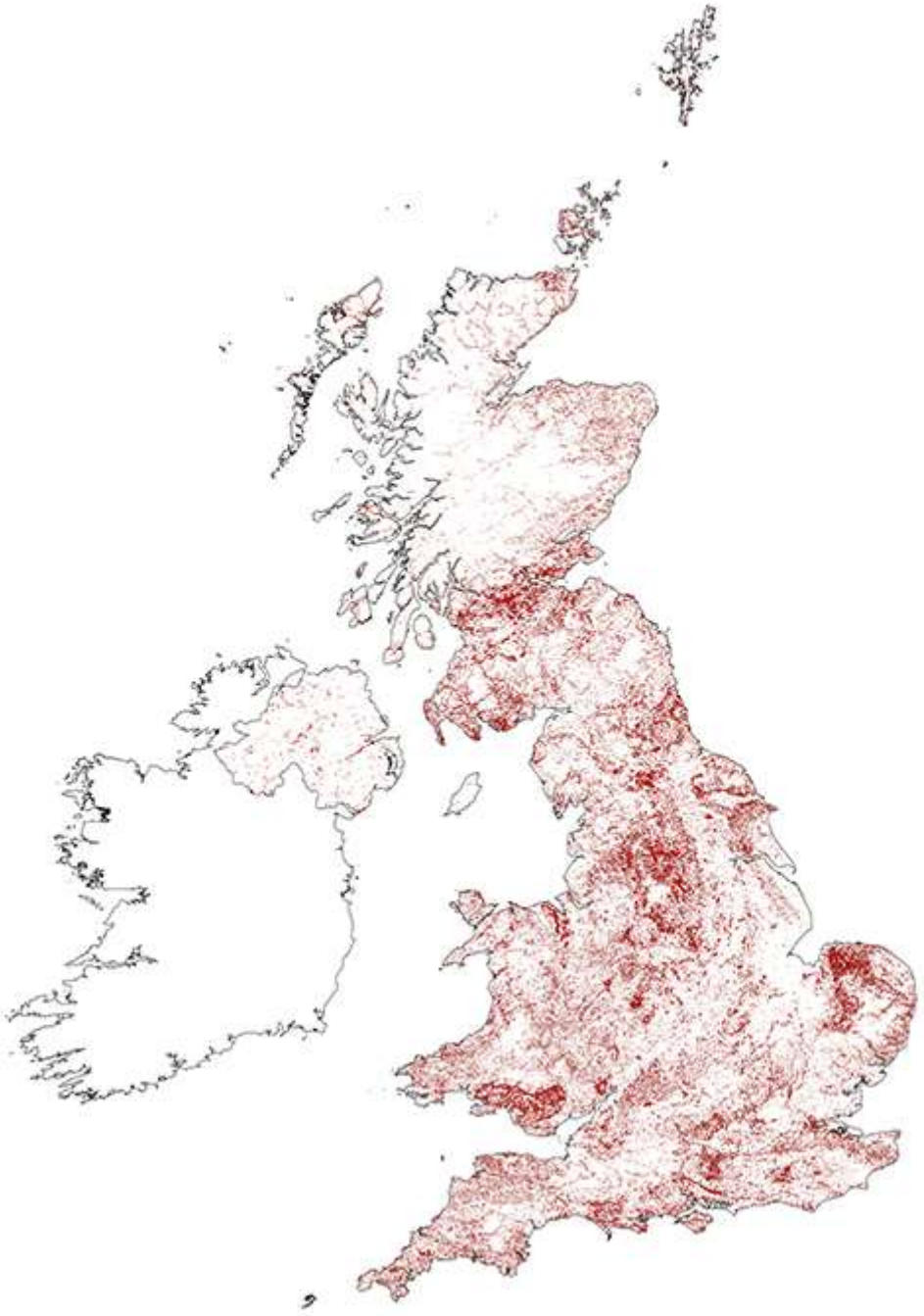

Figure 4.1. A map showing the BGS British Pits Coverage Map of the United Kingdom. The former UK coalfields are some of the most worked areas in the UK, and include South Wales, the Central Belt of Scotland and the South Pennines.

Source: BGS (2018).

The West Lothians hosted the first prominent oil shale mining industry worldwide (Gallois 1979). At its peak, there were over 42 mines which employed thousands of workers to extract and refine oil shale (a mine and refinery are shown in Figure 4.2), (Gallois 1979; LDean 2018). The industry lasted until 1962, when it ceased production because of fierce competition from North Sea oil production (Dean 2018).

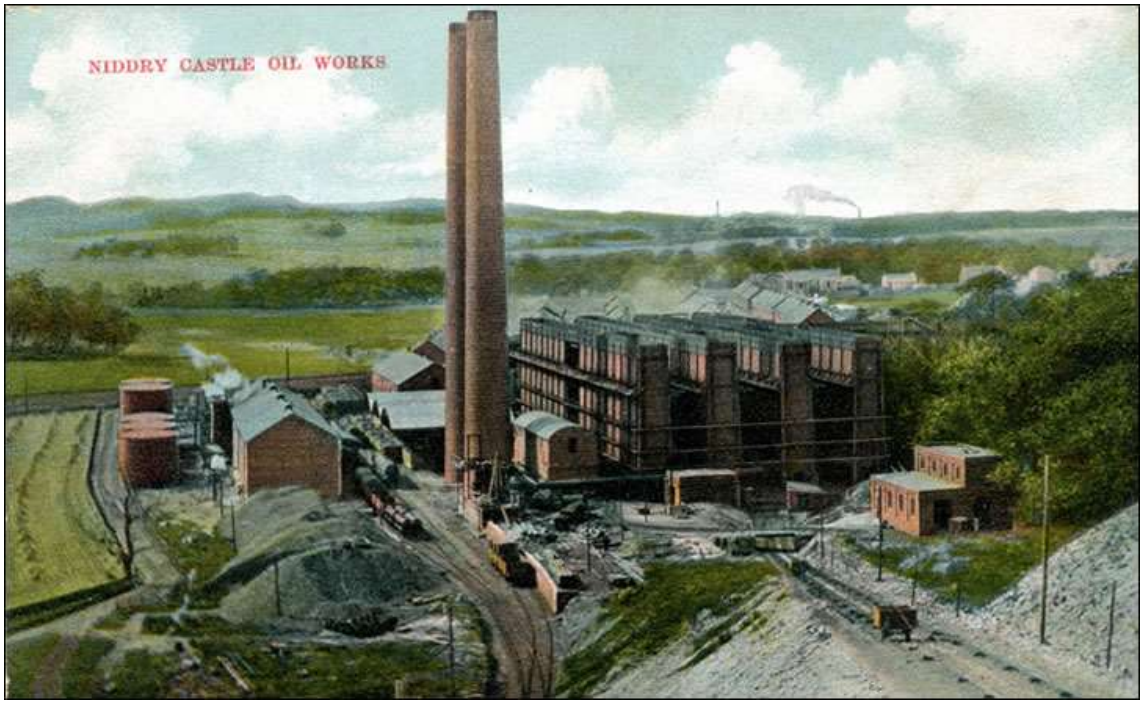

Figure 4.2: A postcard showing the Niddry Castle Oil Works in Kirkliston in the 1920's. The Niddry Castle Oil Works was one of the longest active oil works in the West Lothians lasting from 1902 through to 1959. To the right is the quarry where the oil shale was worked from the face which extended out toward the viewer.

Source: Almond Valley Heritage Trust (2018).

Reproduced courtesy of the Almond Valley Heritage Trust.

The dangers of working with the West Lothian oil shales were well known locally, with several occupational health studies being undertaken on workers (Scott 1922). In 1922 Scott found that there was a high incidence rate of carcinoma in workers, "paraffin cancer", not unlike the renowned "chimney sweepers" cancer (a squamous cell carcinoma of the scrotum), (Scott 1922). Scot also found that the disease affected even low exposure personnel, such as office workers (Scott 1922; Louw *et al.* 1985). A Home Office inquiry in 1926 found that "mule spinners cancer" (a significant occupational disease in textile mills and a synonymous disease to "paraffin cancer") was caused by shale oil distillates used to lubricate machinery (Home Office, 1926).

In modernity, whilst DEFRA does not consider that the mining sector is a major source of NO_X emissions, it is speculated that mines and quarries may produce up to 5% of the UK's particulate matter (PM) emissions (Defra 2011).

♦ 4.1.2). Offshore petroleum.

The UK is the 10th largest producer of natural gas in the world, with most of the UK's hydrocarbon reserves in the North Sea (as shown in Figure 4.3), (OGA 2013a). In 2018 there were 184 offshore petroleum drilling rigs in UK waters (Sönnichsen 2020). Whilst no UK site emissions inventories were found in the public domain, an offshore oil rig in Cyprus reported that drilling for 120 days was found to emit 10.67 tons of PM_{10} and 366 tons of NO_X (CSA International 2011). The major sources of air pollution on the rigs include marine support vessels, flaring of formation gases and onboard power generation (CSA International 2011; Lee *et al.* 2015).

Based on the Cypriot emission rates, UK offshore rigs may emit around 1,963 tons of PM_{10} and 67,344 tons of NO_X (CSA International 2011; Lee *et al.* 2015). This correlates with the UK inventory for 2015, which suggested that the North Sea accounted for around 5% of the UK's NO_X emissions (Defra 2011). There were no estimates for PM_{10}; however, based on the EIA emission rates, the North Sea may account for ~1.9% of total UK PM_{10} emissions (Defra 2011).

♦ 4.1.3). Onshore petroleum.

There are significant nationwide onshore hydrocarbon resources within the organic-rich Carboniferous and Jurassic shales (see Figure 4.3), (OGA 2013a, b). The UK has an extensive history of conventional onshore extraction, including the largest onshore oil field in Europe at Wytch Farm along with around 120 other operational wells, OGA 2013a).

UNG has precipitated much controversy from the public leading to UK-wide effective bans on UNG development, (Leadstrom 2019). Of the 200 applications for UNG wells, only two were granted permission - Preston New Road and Kirkby Misperton (MercoPress 2016; Cuadrilla Resources 2018).

Since October 2018, six seismic events passed the "pause limit" on hydraulic fracturing induced earthquake activity, (OGA 2019). Hydraulic Fracturing caused site activities to be suspended at the Preston New Road site, near Blackpool on 26th August 2019 due to a magnitude 2.9 ML earthquake event during hydraulic fracturing (OGA 2019). These activities had allegedly caused minor structural damage at the surface, for which the operator Cuadrilla was prepared to make without prejudice *ex gratia* payments (Chorley 2019).

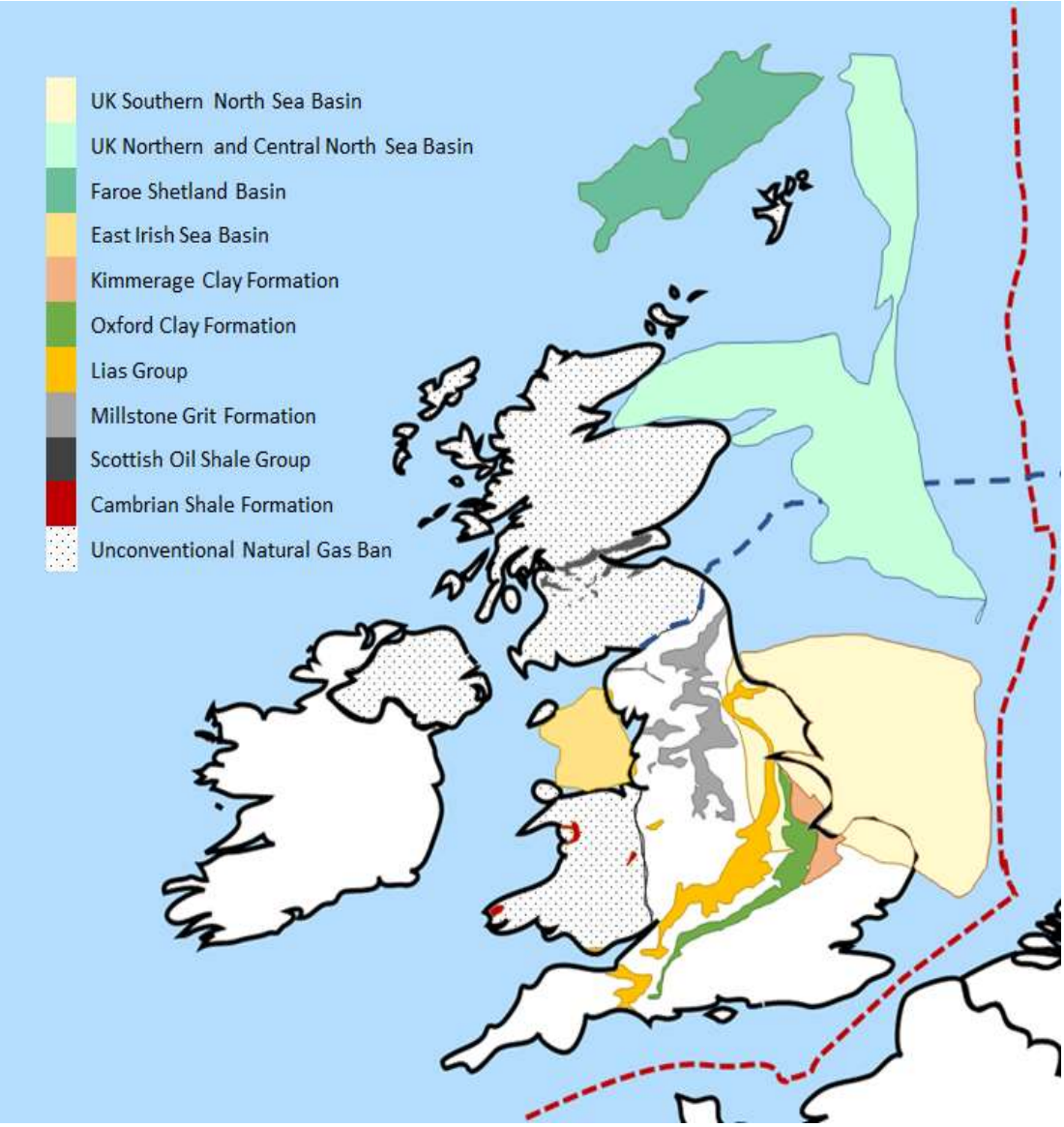

Figure 4.3: A map showing the British onshore and offshore reserves of oil and gas. Scotland, Wales and Northern Ireland are shaded as they have banned unconventional onshore oil and gas development.

Source; Dlouhý, (2006). **(Adapted)**

As of 2nd November 2019, the UK government has suspended hydraulic fracturing in England due to concerns with the potential of such activities to cause further seismic events (Leadsom 2019). Andrea Leadsom MP in her role as the Secretary of State for Business, Energy, and Industrial Strategy - announced the UK's strategy on shale gas exploration in a statement;

> *"The government is putting a moratorium on any further exploration, for the foreseeable future. The reason for that is because we have advice from the oil and gas authority… that tells us that we can no longer be certain of the safety of shale gas exploration… Shale gas offers a huge opportunity provided it can be fractured, explored safely and, in following the science, what we have been advised by the Oil and Gas Authority is that there cannot be that certainty. So, it is not a ban, but the moratorium means that we will not be permitting any other planning applications involving shale exploration to come forward successfully".*
>
> *-Leadsom 2019.*

Despite this challenge, Cuadrilla Bowland Ltd has progressed to flow testing its second shale well at their Unconventional Natural (Shale) Gas well at Preston New Road, (Cuadrilla Resources Limited 2019). A conventional natural gas well is also being drilled at the West Newton wellsite, in Yorkshire, as of 2020 (Morgan 2020).

► 4.2) Geology of petroleum deposits.

Hydrocarbons are formed when organic debris, mud, and silt settles on the ocean floor over millions of years (Zou 2017). Over time, with pressure and heat, the organic material alters into crude oil and natural gas (Zou 2017). These organic sedimentary layers are known as a source rock (Zou 2017).

♦ 4.2.1) Conventional reserves.

Eventually, oil and gas produced within the source rock may migrate closer to the surface through permeable rocks and fractures (Zou 2017). The upward migration of oil and gas may eventually lead to it becoming trapped by impervious "cap rocks" such as shale (Zou 2017). Oil and gas can settle below these cap rocks under high-pressure (Bjørlykke 2015).

Once a wellbore is drilled through the caprock, petroleum flows easily to the surface, historically forming tremendous oil fountains. These reserves are amongst the most lucrative petroleum reservoirs and include the Weald Basin in South West England (Figure 4.4) (Zou 2017).

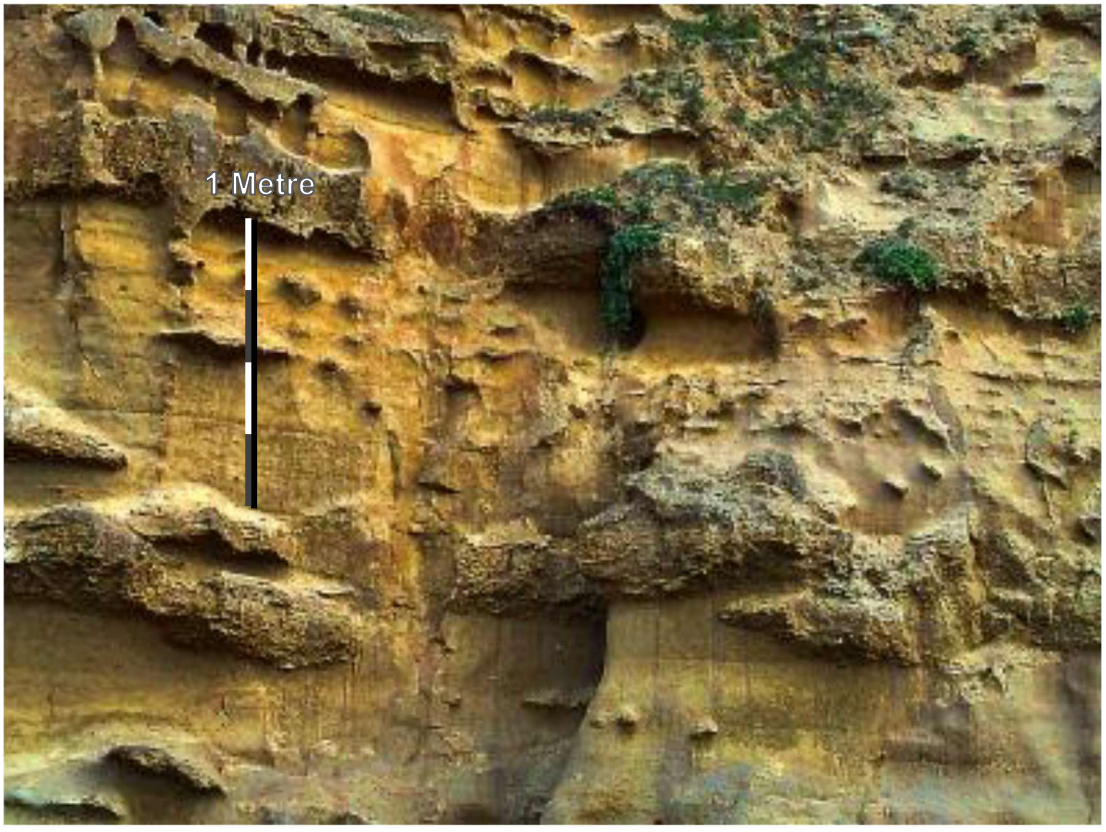

Figure 4.4: Shows a photograph of exposure of the Bridport Sandstone Formation at East Cliff, Bridport looking North. The Bridport Sandstone Formation is a traditional conventional gas reserve in the UK. The formation represents very fine-grained weathered yellow sandstone. There are lenses of calcified beds which are more weather resistant.

Source; Author – Grainger (2020)

♦ 4.2.2) Unconventional reserves.

Unconventional deposits were often discovered long ago, though, in the past commercial extraction was not feasible due to technological limitations and the high cost of extraction (ROENG 2012). As a result of technological advancement, coupled with the high price of petroleum, UNG extraction has become a viable economic concern (Houses of Parliament 2013; Loomis and Haefele 2017). UNG resources include coalbed methane, tight sands, and oil shale, (Zou 2017).

An explanation of UNG reserve types is provided below for simplification:

- **Coalbed methane;** the UK has an extensive coal mining history (Figures 4.1, 4.2 and 4.6) and coalbed methane could provide a lucrative source of gas within the UK, (OGA 2013). Historically, methane has been one of the most dangerous mine gases, having caused many deaths through asphyxiation and explosions (Brune *et al.* 2016). Methane forms once coal seams are exposed to air (Figure 4.5) and consequently coal mines are required to have advanced ventilation methods to ensure that such gases do not build-up to disastrous levels (Brune *et al.* 2016). Coalbed methane extraction taps into these coal seams and extracts the methane from the mine tunnels and [or] unworked coal seams.
- **Tight sands;** describes petroleum trapped within rocks without interconnecting pores and fissures, (similar to Figure 4.6). As petroleum is trapped within isolated pores, the well requires stimulation (hydraulic fracturing) to create artificial fractures to allow the petroleum to flow into the well, (Zou 2017; Olson 2017).

Figure 4.5: Shows a photograph of an underground exposure of "Coal" in Pwll Mawr (Big Pit) Welsh National Coal Mining Museum in Blaenavon, Gwent. The coal seam is representative of the Horn Coal Seam (NCB Name: Upper-Nine-Feet) and is a 1.2-meter-thick anthracite seam. In the roof of the seam are fine grained rootlets. The photograph was taken close to the main entrance of an underground exhibition area.
Source; Author – Grainger (2020)

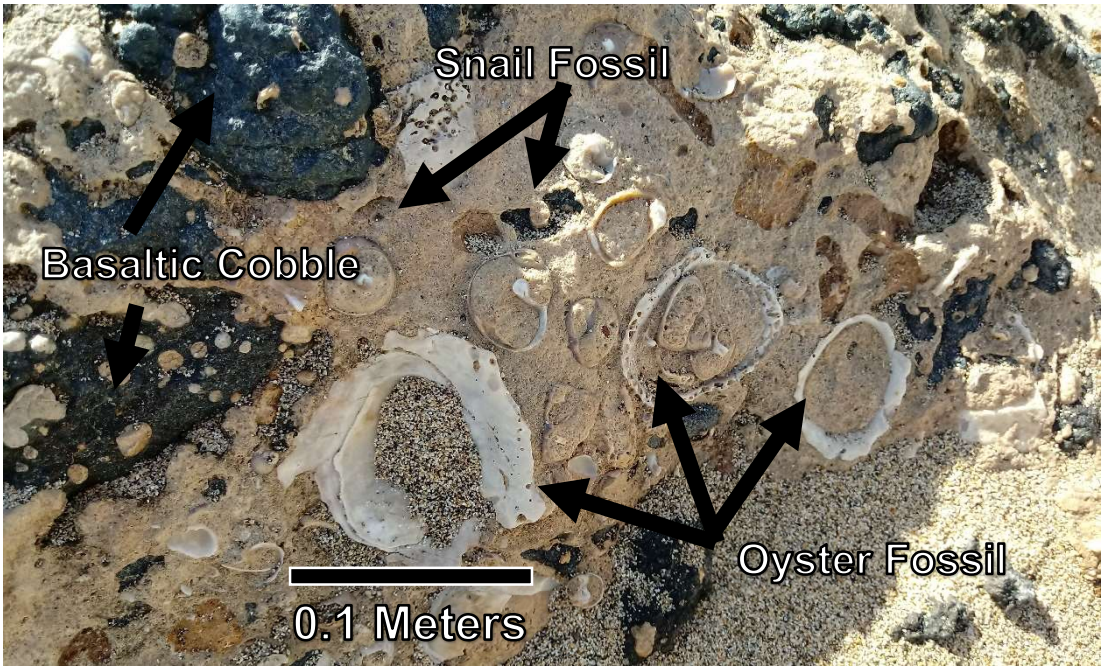

Figure 4.6: Shows a photograph of an exposure of a reasonably competent Holocene sandstone exposed at Playa Del Reducto, Arrecife, Lanzarote. The sediments are comprised of fine-grained quartzite sand with common shell fragments and whole shells of Oysters and Snails, alongside gravel to cobble sized basalt from the Volcanic Island Chain of the Canaries. The photograph is taken looking North. Such deposits contain the gasses from the breakdown of organic shell and coral materials. Exploration has been undertaken offshore in these rocks but they were found not to contain an economical natural gas reserve.
Source; Author – Grainger (2020)

- **Oil shales:** are often the highly organic source rock of petroleum found in more conventional reserves (Zou 2017). Oil shale formations comprise fine-grained laminated rocks with structures similar to the pages of a book, as shown in Figure 4.7, (Zou 2017). Petroleum often becomes trapped within microscopic pores and the individual laminations of the formation (Olson 2017). As with tight sands, the formation requires stimulation (hydraulic fracturing) to create migration pathways for the hydrocarbons and [or] natural gas to be extracted (Zou 2017).

Figure 4.7: Shows a photograph of exposure of the West Lothian Oil Shale Formation, and more specifically the Dalmeny Oil Shale Seam. The exposure was located 200 m, south of the Forth Bridge and looks towards the South. The oil shales are organic (kerogen) rich, carbonaceous fine-grained sedimentary rocks which are finely laminated. These oil shales are approximately 20% organic. In the West Lothians a series of seams are present which are extremely closely laminated like the pages of a book, these contain much greater compositions of organics, to approximately 60-80%. The seam is greatly weathered here but is still highly malodorous of sulphur.

Source; Author – Grainger (2020)

► 4.3) Development of UNG: oil shale reserves.

Developing an UNG site (oil shale reserve) is complicated, with eight common steps outlined within planning applications on both the unsuccessful applications and in the two successful applications for UNG exploration. The best developed of these sites is the Preston New Road (PNR) UNG development site near Blackpool.

The stages of the exploration and production at the PNR site have followed the steps outlined below:

♦ 4.3.1) Non-intrusive study.

A prospector should research an area using available desk study information (e.g. from the British Geological Survey) to determine if there is likely to be an uncompromised petroleum reservoir beneath the site. A company should consider, based on this information, whether they should bid to extract minerals under licence from the Crown through a Petroleum Exploration and Development Licence (PEDL), (ARUP 2014).

♦ 4.3.2) Exploration.

Should the 'non-intrusive study' indicate an economic reserve and a PEDL Licence is acquired, then planning permission would need to be granted in the usual way (though subject to strict planning permissions and environmental permitting), (Short and Szolucha 2016). The proposals may include an environmental impact assessment (including development impacts on air quality, noise, and transport), (ARUP 2014; Short and Szolucha 2016).

To help with applications; planning permissions are often broken down into several segments as partial approval is more promising for developers than an outright refusal of terms (Howe 2020).

In most cases, the drilling and hydraulic fracturing scheme are included in a planning proposal, with roadworks and gas production covered under

separate proposals, (Lancashire County Council 2014; Short and Szolucha 2016). It may take several years of drafting to gain full planning permission, with some planning applications outright refused and subject to lengthy litigation, as per the PNR development (Short and Szolucha 2016).

♦ 4.3.3) Preparation and construction of the site.

Groundworks can begin once planning permission has been successful. A contractor may start by creating a temporary access road and clearing the land of vegetation (ARUP 2014; Sanders *et al.* 2015). Excavation then removes the topsoil and subsoils over the "pad" (foundation) area and stockpiles soils in mounds (bunds) along the margins of a site, (ARUP 2014; Cuadrilla Resources 2014a). The excavation plant includes backhoe excavators, mini-excavators, and tipper trucks, as seen in Figure 4.8.A-C (Cuadrilla Resources 2017a). This process can last for several months, for example, the construction stage at the Preston New Road site began in January 2017 and finished in July 2017.

At the base of the excavations, a drainage layer (fine gravel) is laid down, (ARUP 2014; Cuadrilla Resources 2017a). Above the drainage layer are several layers of geotextiles, one of which is an impermeable HDPE barrier (High-Density Poly-Ethylene), (ARUP 2014; Cuadrilla Resources 2017a). The HDPE helps prevent the mobilisation of chemicals to the subsurface and is common on landfills. Over the geotextile layer is another drainage layer which prevents the pooling of water. Above this is a layer of fine (20 mm) gravel (often limestone) which is levelled and compressed with a series of rollers, (ARUP 2014; Cuadrilla Resources 2017a).

Contractors bring aggregate onto the site with tipper trucks protected with a canvas screen (to prevent dust migration en-route), (ARUP 2014; Cuadrilla Resources 2017a). The truck delivers aggregate to the site where an excavator moves the aggregate into piles (Figure 4.8.b). Some aggregates are screened with a T-belt assembly.

Much of the gravel is moved into place by mini-dumpers, backhoes, mini-excavators, and levelled using large rollers. Once the site is levelled a series of welfare cabins and stores are placed onto the site.

A concrete cell is constructed to house drilling safety equipment at the wellbore position, (ARUP 2014; Cuadrilla Resources 2017a). A temporary work-over rig is brought onto the site which drills a guide hole through the cell and into the soil at the marked location (ARUP 2014).

Daily HGV (Heavy Goods Vehicles) traffic flow is required to support UNG operations (Johnson *et al.* 2018). As UNG operations often precipitate strongly held views amongst members of the public, this can disrupt site operations, requiring a police presence, and a consequent reduction in local road speeds for public safety (Jackson *et al.* 2019). Police protection brings additional road traffic, with decreased speeds causing significant increases in vehicular emissions (Gkatzoflias *et al.* 2012; Outapa *et al.* 2016). For example, the COPERT model for "Road Vehicle NO_X Emission Factors" shows that a 40-ton Euro VI artic lorry travelling at 50 mph (80 kph) would yield 296% fewer emissions than the same vehicle travelling at 20 mph (32 kph), (Gkatzoflias *et al.* 2012).

Figure 4.8.A: A Backhoe excavator moving aggregate over two Geotextile Layers. The black layer is a HDPE liner laid down to protect against surface water intrusion whilst the white layer is a protective layer to prevent damage to the HDPE liner.

Figure 4.8.B: A Backhoe excavator moving aggregate away from a 20-tonne tipper truck. In the background right is the excavator, whilst in the foreground is a small diesel engine providing electricity to a compressor and lighting (out of frame).

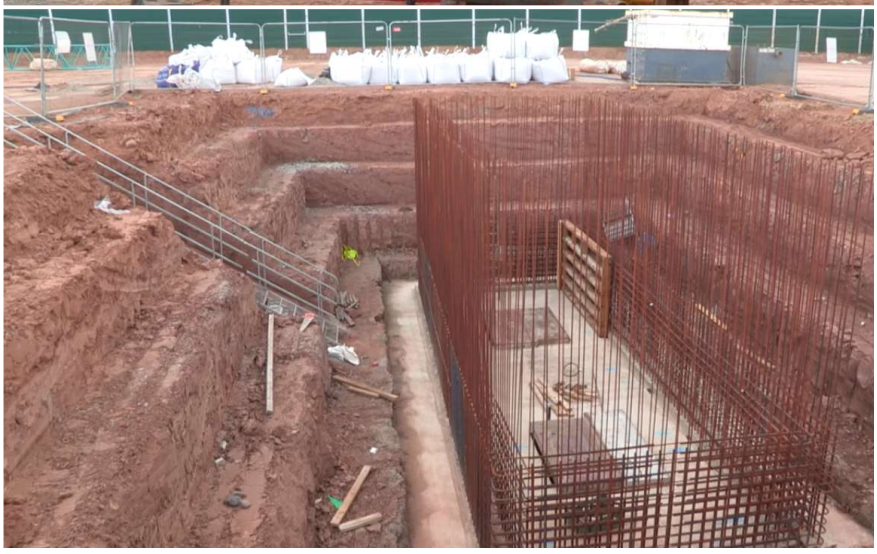

Figure 4.8.C: A Figure showing the construction of the concrete cell where the BOP and other safety equipment will be located. The excavation will later be filled with concrete.

Source (A-C)*:* Cuadrilla (2017a)

Reproduced with kind permission of Cuadrilla Resources Ltd.

♦ 4.3.4) Drilling of the petroleum formation.

Once the HGV carrying the drilling rig and munitions, the drilling rig is erected using a series of hydraulic motors on the drilling rig, cherry pickers, and a crawler crane, (ARUP 2014). During this time, the site may resemble the configuration of the PNR site shown in Figure 4.9 (on Page 103). The PNR site was drilled between July 2017 and August 2018.

The wellbore (borehole) is drilled around 2 to 3 km deep and secured with steel casing, which is later cemented into place, (ARUP 2014). The horizontal section of the well extends for around 2,000 metres away from the vertical component, as shown in Figure 4.10. (ARUP 2014; Cuadrilla Resources 2018). Several horizontal Sections can be sunk to a range of depths and directions, creating a production or "Christmas" tree pattern (Zou *et al.* 2017).

The drilling rig includes six key operating systems which include:

■ A) Rig power system:

High voltage electricity is required to power the drilling rig systems; this is usually supplied by several large marine/industrial backup diesel generators, similar to those shown housed in Figure 4.11, (ARUP 2014; Pavković *et al.* 2016). Preston New Road and Kirby Misperton both had three large CAT C-13 engines were housed within shipping containers with 3-metre tall exhausts, (ARUP 2014; MercoPress 2016).

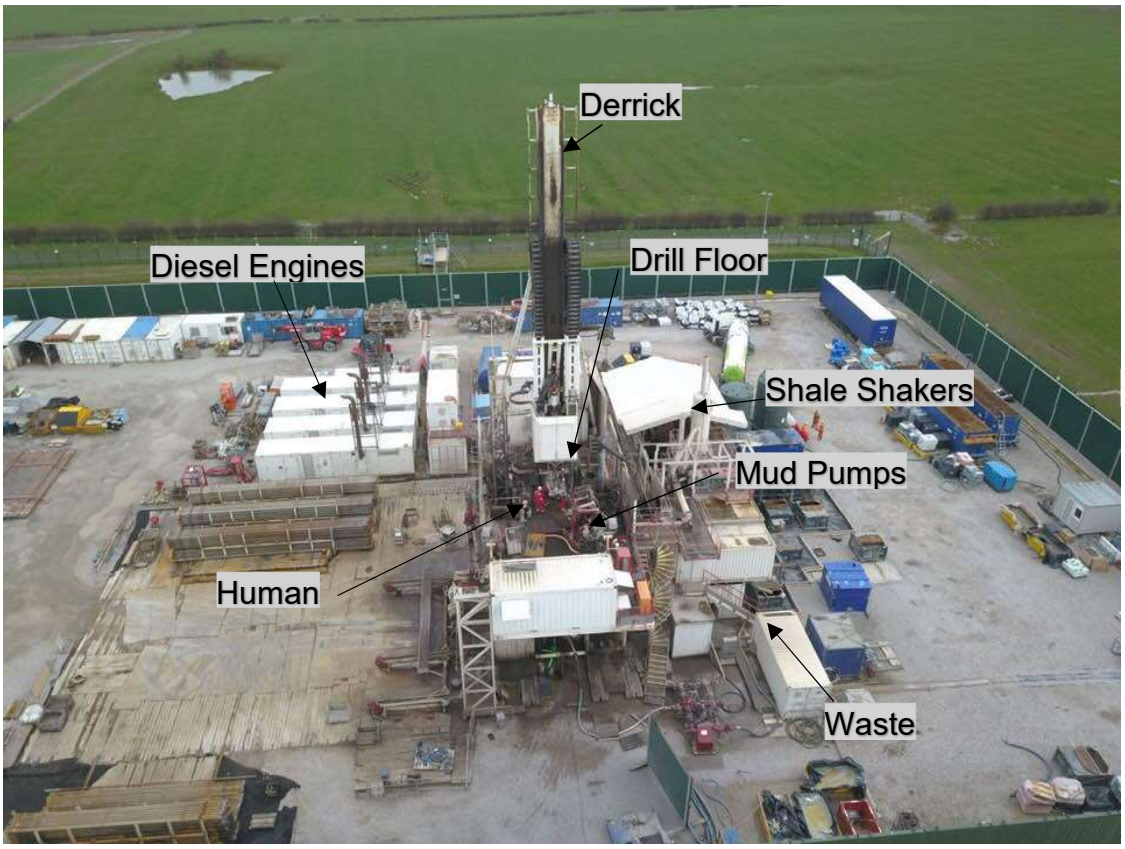

Figure 4.9. A drone photograph showing the HH-220 drilling rig at Preston New Road, Blackpool, the only currently active UNG development site in the UK. The photograph was taken by a drone by protestors in June of 2017. The view looks West at the drilling rig from a height of approximately 100 meters. Labelled are various features of the drilling rig.

Source: Steveo (2017).

Figure 4.10. A photograph with the three diesel engines displayed. The diesel engines are C12's housed within shipping containers. The exhaust from the engines are extended vertically from the container 3 meters in the air.

Source: Cuadrilla (2017b). Reproduced with kind permission of Cuadrilla Resources Ltd.

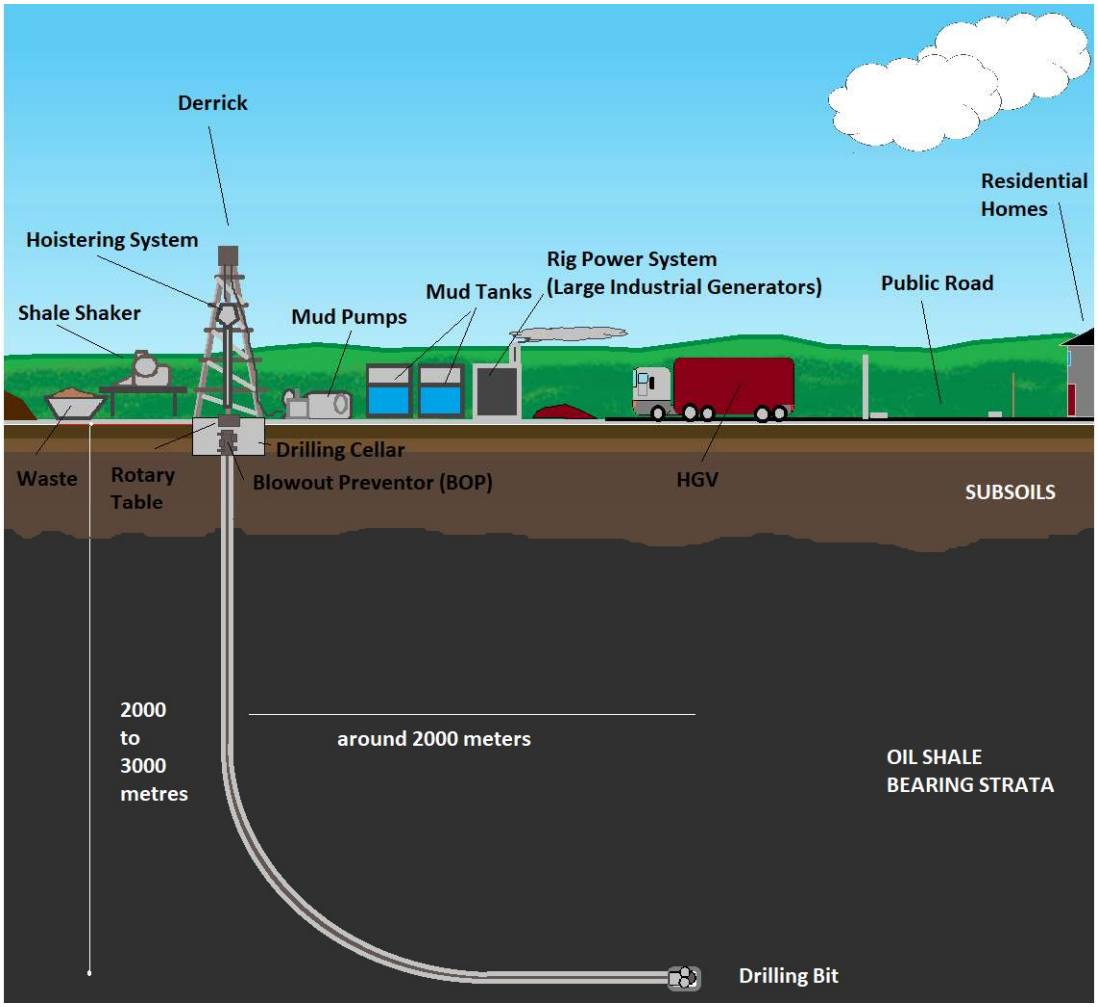

Figure 4.11. A conceptual site plan showing many of the main elements of a UK Conventional/Unconventional oil and gas exploratory site during the drilling stage. As shown the drilling bit is several thousand meters deep and has a significant horizontal component. The oil shale bearing strata is representative of the Carboniferous and Jurassic Oil shales found nationwide in the UK. Several rig systems and processes are also annotated above ground.

Source; Author – Grainger (2020)

■ B) Mud circulation system:

The system follows a continuous path where 'drilling mud' (a liquid slurry with an oil or water base) is pumped down the wellbore, returned to the surface, cleaned, and recycled (Guo and Liu 2011; Cuadrilla Resources 2017b; Fink 2020). The system starts at the blending plant where chemical additives are added to a water or oil base fluid (Figure 4.12.A), (Guo and Liu 2011; Cuadrilla Resources 2017b). The chemical mixture is then mixed in a series of 'mud' tanks (Figure 4.12.b) before it encounters the main rig pumps (powered by the rig power system), as shown in Figure 4.12, (Guo and Liu 2011). The muds are pumped through piping to the rig floor where the fluid emerges from the rotary hose. The hose is disconnected every time a length of casing (steel pipe) is added to the borehole (i.e. once per every 10 m drilled), causing leakage of the mud over workers and the rig floor, (Ormerod *et al.* 1998; Broni-Bediako and Amorin 2010; Guo and Liu 2011). When connected the drilling mud flows through the rotary hose down the wellbore (borehole) where eventually it reaches the bottom of the well and sprays out of the drill bit at high-pressure. The mud helps to spin the drill bit, and clears rock cuttings from the end of the wellbore, (Zou 2017; El Boubsi and Andresen 2017). Once used, the mud flows back up to the surface under pressure through the annular space (space between the wellbore's casing and the surrounding rock), (Zou 2017).

Once returned to the surface, the mud is passed through a vibrating screen called a shale shaker (Figure 4.12.d). The mud passes through a series of other cleaning equipment (i.e. desander, desilter and degasser), before returning to the mud tanks where it is reused (Guo and Liu 2011; El Boubsi and Andresen 2017). Waste products during cleaning are discarded into tanks, with waste gases being burned and [or] vented, and the solid waste is removed from the site using HGVs (Guo and Liu 2011; El Boubsi and Andresen 2017).

Figure 4.12.A: Showing the connection from the chemical additive mixing tank to a gutter leading to the mud tanks. The reddish colour of this mud is due to small impurities in the drilling mud and the natural reddish colour of the bedrock.

Figure 4.12.B: A photograph of the mud tanks under a walkway in between the chemical additive station and the mud pumps. The muds are circulated by a series of fans within these containers. The mud level is about 2 metres.

Figure 4.12.C: A view down the stairs from the mud tanks to one of the three mud pumps at the PNR site. These mud pumps provide the hydraulic pressure for the rotation and turning of the drill bit at the bottom of the borehole.

Figure 4.12.D: A photograph of the shale shaker, a vibrating metal screen which separates out drilling mud from more coarse drill cuttings. Some of the drill cuttings can be seen on the screen.

Source (A-D):

Cuadrilla (2017b). Reproduced with kind permission of Cuadrilla Resources Ltd.

■ C) Hoisting system:

The hoisting system (see Figure 4.13) features the derrick (a large tower) which works like a crane with a hook (travelling block), a drill string spool (crown block), and a motorised lift (draw works). The hoisting system allows for the casing and drilling pipe to be lowered or raised into the wellbore, (Zou 2017).

Figure 4.13: A photograph of the derrick on the HH220 Rig at PNR. The Rotary Table is being lifted by the hoist as well as a swivel hook on the far right.

Source: Cuadrilla (2017b). Reproduced with kind permission of Cuadrilla Resources Ltd.

■ D) Rotary System:

The system comprises a piece of rotating equipment (Kelly or a top-drive) held above the rig drilling floor via the hoisting system (Figure 4.14). The drill string is held in place with a rotary table which rotates and supports the weight of the drill string and ultimately the drill bit (Dalvi 2015).

Figure 4.14: A closeup of the rotary Table on the derrick of the HH220 Rig at PNR. This device is responsible for the rotary action of the pipe at the top of the borehole.

Source: Cuadrilla (2017b). Reproduced with kind permission of Cuadrilla Resources Ltd.

■ E) Blowout prevention system (BOP):

The BOP, as shown in Figure 4.15, is perhaps one of the most critical pieces of equipment on the rig as it helps prevent the rising of formational gases and drilling mud up the wellbore, (Zou 2017). An unexpected, but controlled, release of fluids or gases to the surface is known as a kick. If a kick cannot be brought under control, then it may develop into a blowout (Grace *et al.* 2017). A blowout is an uncontrolled release of liquids or gases at the surface, presenting significant asphyxiating, explosive and environmental hazards (Grace *et al.* 2017). Blowouts may cause catastrophic effects to the local environment (Nance *et al.* 2016; Beyer *et al.* 2016). For example, the 2008 'Deep Water Horizon' incident caused substantial environmental damage in the Gulf of Mexico (Nance *et al.* 2016; Beyer *et al.* 2016).

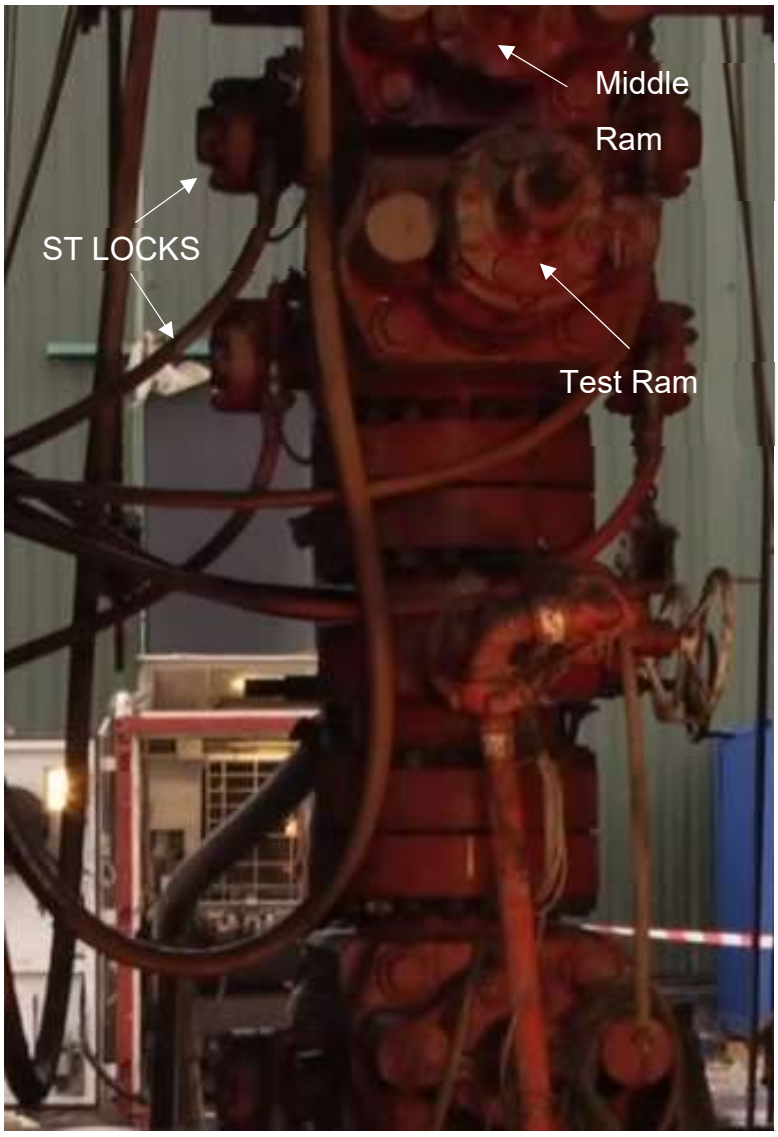

Figure 4.15: A photograph of the blowout preventer on the PNR drilling site. This device is responsible for the prevention of kicks and blowouts at the PNR site. The device operates through employing several mechanical clamps (rams) which can break the borehole several thousand meters below ground level as well as forcing the borehole closed through a steel plate clamping shut various parts of the well. Displayed in the photograph are the Lower Test Ram and the Middle Ram. The outside ends are ST locks which hold the ram preventors closed in case of a loss of pressure

Source: Cuadrilla (2017c). Reproduced with kind permission of Cuadrilla Resources Ltd.

♦ 4.3.5) Stimulation of the wellbore (hydraulic fracturing).

Stimulation of unconventional wells is required to bring the well into production, as unlike in conventional reserves, there would be only minimal petroleum flow (Zou 2017; Fink 2020).

At this stage, the information which has been collected from the drilling stage would be collated to appropriately design the stimulation (fracturing) process (shown in Figures 4.16 and 17). In the USA, it is common for stimulation fluids to comprise 30% chemicals and 70% water, with over a hundred chemicals (undisclosed) in the mix, (Speight 2016; Spellman 2017). Compared with the US EPA, Defra is much stricter with which chemicals it allows to be pumped into the ground (ARUP 2014). Typically, Defra allows no more than 0.05% additives to 96.95% water and 3% aggregate (sand), (ARUP 2014). The specific components of the 0.05% mixture depend on the well. One site in the UK (Cuadrilla Resources) has used around ten common household chemicals in its mixture, whilst another operator (IGas Energy) wanted to use only one (friction reducer), (ARUP 2014; Cuadrilla Resources 2014a). The PNR site was hydraulically fracked between August 2018 and September 2019. However, the hydraulic fracturing process was abandoned due to seismic activity (BGS, 2019). High voltage power is required for the hydraulic fracturing process which is supplied by another 3 to 4 diesel generators similar to those used in the drilling stage, (ARUP 2014).

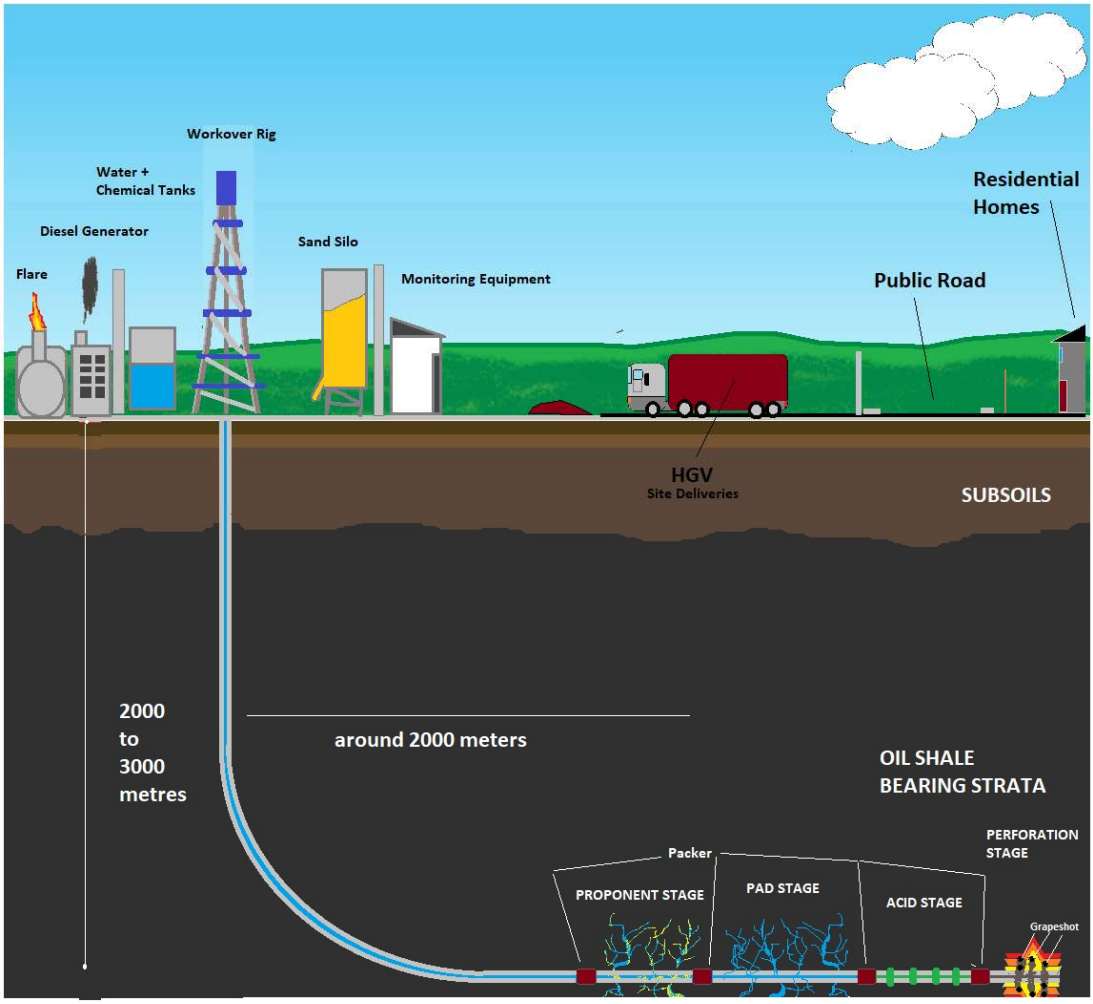

Figure 4.16. A conceptual site plan showing many of the main elements of a UK Unconventional Hydraulically Fractured oil and gas site. As shown the well is several thousand meters deep and long and has undergone a series of processes. These well processes begin with the perforation stage in this case from explosives. Followed by an acid clearing stage where acid is used to clean the wellbore. The pad stage where water is pumped down the well at high pressure creating fractures. Followed by the Proponent Stage wherein aggregate such as sand is introduced to the fractures holding them open. Above ground are a series of site plant such as flares, diesel generators and sand silos.

Source; Author – Grainger (2020)

Figure 4.17.a, and 17.b: A drone photograph showing the site layout of the hydraulic fracturing site at Preston New Road (PNR), Blackpool. Figure 4.17.a. shows a more zoomed out aerial oblique photograph of the site showing the sites complexity. The fenced area in the centre of the image is where most of the interest takes place. The white silo's contain sand as proppant for the Hydraulic fracturing stages, the blue boxes behind are diesel engines which provide energy for the rig systems. The tower to the right of these engines is the workover rig. To the bottom right of the site are two ground level flares for burning of excess gasses. Figure 4.17.B provides an alternative angle of a similar part of the site, the caravan which can be seen below the workover rig is where the hydraulic data is monitored and the hydrofracturing job carefully controlled.

Source: Thornton (2018).

Reproduced courtesy of Mr Eddie Thornton.

There are usually three stages of well stimulation; these are outlined below in further detail:

■ A) Perforation stage:

Many wells have a retractable casing. However, retractable casing is not reliable, and often explosive charges are required on at least some sections of the casing, (Guo *et al.* 2013; Speight 2016). When explosive charges are necessary, a temporary drilling rig can be brought onto the site, which lowers the explosive charge down the wellbore, (Guo *et al.* 2013; Speight 2016). Inside the explosive charge are several grapeshot (10 cm diameter). When the explosive is detonated at depth, grapeshot is fired out of the charge at high speeds (Zou *et al.* 2017). The grapeshot punctures through the steel casing, as shown in Figure 4.18, and embeds itself within the local formation (He *et al.* 2019).

Figure 4.18: A photograph of a section of steel casing on display at the SPE 2017 Aberdeen Conference, which has been fired by an explosive charge through standard drilling steel casing. In this example the grapeshot fired out from the explosive shot pierced the surrounding sand bags by up to 3 meters after passing the steel casing.

Source*:* Grainger (2017).

■ B) "Acid" stage:

The acidification stage cleans the well and clears debris before hydraulic fracturing (Guo *et al.* 2013; Speight 2016). A 10-metre section of the wellbore is isolated using several inflatable bags (packers). Once isolated, several thousand cubic metres of 'fluid' is pumped down the well (ARUP 2014; Cuadrilla Resources 2014a). This 'fluid' is predominantly water, mixed with a minor proportion of hydrochloric acid along with friction reducers (0.06%), (Cuadrilla Resources 2014a). Much of the water is taken from the mains water supply and brought onto the site on HGVs towing water bowsers, (ARUP 2014).

■ C) Pad stage:

During the pad stage, a mixture of 99.5% water and no more than 0.5% of chemicals is pumped into the wellbore under pressure using a series of hydraulic pumps. This pressure hydraulically creates and opens existing fractures within the formation (Guo *et al.* 2013; Speight 2016).

■ D) Proponent stage:

In the proponent stage, 2 mm diameter sand (e.g. silica sand, glass beads, or ceramics) and water is pumped down the wellbore (Speight 2016; Fink 2020). The sand accesses the hydraulically expanded fractures and becomes stuck (Fink 2020). When the hydraulic pressure is removed, the sand particles hold the fractures open (Fink 2020).

■ E) Flushing stage:

In the last stage, the wellbore is flushed with freshwater, or brine, to remove excess sand and chemicals from the formation (Spellman 2017).

♦ 4.3.6) Well testing stage.

The testing stage determines whether the well is economical for long-term production (ARUP 2014). During this stage, flowback fluid (i.e. excess water from the stimulation process containing stimulation and geologic chemicals) returns to the surface (He *et al.* 2017). The flowback fluid is removed from the site in tanker trucks and sent to a hazardous water treatment facility, (Cuadrilla Resources 2014a, c).

Following the flowback to the surface is natural gas, though, during the initial testing phase, the gas is burned within ground-level flares (Figure 4.19), (Cuadrilla Resources 2014a). Once flowback fluids have stopped, the extended test begins, refining the gas into its useful components in a processing station and recording the economical natural gas supplied to the UK's gas network (ARUP 2014).

Figure 4.19: This drone photograph shows an aerial oblique photograph of the ground level flares which would be active during gas flowback after the hydraulic fracturing job. Additionally, there are a series of tanks where chemical additives are stored prior to their use, and/or removal from the site. The cordoned off area shows the gas lines which stem from the well to the flares.

Source: Thornton (2018). Reproduced courtesy of Mr Eddie Thornton.

♦ 4.3.7) Production stage.

Where there are economic volumes of gas entering the system, additional planning permission is sought to bring the well into full production, including having permanent equipment on site (Figure 4.20), (ARUP 2014; Short and Szolucha 2016). If successful, the well should enter into the production stage, which may last 20 to 30 years, (ARUP 2014). Initially, the well should produce gas at a high rate, though this should decline with time (ARUP 2014). The gas is usually supplied to the natural gas grid by the infrastructure created for the well testing stage (ARUP 2014).

Figure 4.20. A photograph showing the surface oil equipment at the Singleton Well, first drilled in the 1980's and continues to produce around 500 barrels of oil a day.

Source: IGas Energy (2018). Reproduced with kind permission of IGas Energy.

♦ 4.3.8) Reclamation stage.

After the natural gas reservoir is exhausted, i.e. it is no longer economical to extract hydrocarbons, the well is decommissioned or repurposed (ARUP 2014). There are many uses for repurposed petroleum wells, including carbon capture and sequestration, as well as nuclear waste disposal (NDA 2010). Assuming that the decommissioned well is to be fully remediated, the wellbore is capped several metres below ground-level, and the site is restored for agricultural/development purposes (ARUP 2014). Helpfully, financing for the remediation of sites is withheld in an escrow account before the project can be developed, which ensures sufficient funds for restoration (ARUP 2014).

► 4.4) Other uses of Hydraulic Fracturing.

Whilst the primary use of hydraulic fracturing and deep borehole drilling is focused towards the oil and gas environment, there are several other scientific, safety and geotechnical applications for the technology (Krietsch *et al.* 2019).

One of the most promising green applications of hydraulic fracturing is in EGS, or Enhanced Geothermal Systems, which provides a method for generating geothermal heat and electricity without naturally permeable formations (Olasolo *et al.* 2016). Most geothermal resources are within "hot dry rocks" within igneous rocks like granite or basalt (Watson *et al.* 2019). Iceland has a longstanding relationship with EGS, with 90% of Iceland's domestic power being provided by Geothermal power-plants (Ma *et al.* 2020). Similarly, groundwater resources can be fractured in low permeability environments to enhance and recharge the aquifers (UNEP, 1997). However, in Scotland, a future involving enhanced borehole technology seems to be somewhat in doubt.

The author questioned Paul Wheelhouse MSP about the Scottish ban on hydraulic fracturing at the CARES conference in 2018, where he confirmed

that EGS was included in the ban on hydraulic fracturing in Scotland, though an exception could be granted depending on circumstances (Morris and Wheelhouse 2018). Not-with-standing the British Geological Survey did not expect that hydraulic fracturing legislation would affect other geological applications (Campbell 2019).

The author is concerned that the moratorium on hydraulic fracturing in England might impact research programs such as the Historic Hot Dry Rocks program of Rosemanowes Quarry (Penryn), (Watson *et al.* 2019). Other applications of hydraulic fracturing include; increasing fractures for the geological sequestration of CO_2, inducing cave-ins in mines, and for induced fracture measurement of geological stress regimes (He *et al.* 2016; Krietsch *et al.* 2019; Chen *et al.* 2020).

► 4.5) Conclusions.

With petroleum reserves steadily declining in the North Sea, it seems likely that if there is to be any notable future of the UK's petroleum industry, the focus may have to shift to onshore deposits (OGA 2014; Hughes *et al.* 2017). Due to the UK's complex geology, most of the UK's deposits lie within UNG reserves, including; coal gas, tight sands, and oil shales (OGA 2013a, b; Hughes *et al.* 2017). Of these, the UK is rich in organic-rich shales and coal reserves (Hughes *et al.* 2017). However, due to a poor social licence, driven by overseas experiences in the USA and Australia, UNG and hydraulic fracturing have now been banned throughout the UK, (Scottish Government 2014; Leadstrom 2018).

The development of UNG reserves is complex, starting with the planning and environmental permitting, where most applications fail (Short and Szolucha 2016). Those that are successful, progress to the site clearance and construction stage where the site is cleared and underlain by an impermeable liner with drainage gravel to surface (ARUP 2014).

When a rig is brought to the site, thousands of cubic metres of drilling mud are pumped down the well using mud pumps whose power is provided by large diesel industrial generators, (ARUP 2014). More diesel generators are brought to the site to power the well stimulation or 'frac job' (ARUP 2014; Speight 2016).

In a frac job, a mixture of chemicals, including fine sand, are pumped down the well at very high pressures, fracturing the rock at depth. The sand and chemicals are required to clean and maintain fractures in the formation after the frac job is completed, (Speight 2016; Fink 2020).

After the well has been hydraulically fractured, water, chemicals, and gas make their way up the wellbore, (He *et al.* 2017). The liquids are sent for disposal via tanker trucks, while the gases are burned in ground-level flares, (ARUP 2014). When the liquids have stopped emerging, the well is ready for its penultimate stage, whereby the natural gas is cleaned and sent to the National Grid, (ARUP 2014). If the well is economical, it is brought into the production stage, which could see the prolonged extraction of natural gas for up to 20 years, (ARUP 2014). When uneconomical, the site is restored and returned to its former land usage (often agricultural pasture), (ARUP 2014).

► 4.6) References.

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► 4.7) Figure References

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CHAPTER 5:

Preliminary risk assessment of airborne pollution from the United Kingdom's onshore unconventional natural oil and gas developments.

"The extraction of oil, coal, and minerals brought, and still brings, a cost to the environment".

P. D. Hewson - "Bono" (1960 - present) [1]

This chapter performs a preliminary risk assessment with the findings of Chapters 1 to 4 in collaboration with an extended literature review in Chapter 5: Supplemental A [1]. All the non-trivial hazards are outlined within this chapter to provide context, and the risk assessment performs a semi-quantitative assessment of each of these hazards. The two most hazardous environments outlined in the assessment drive this doctoral research forwards throughout the remaining chapters of this thesis.

► 5.1) Introduction: Identifying the research gaps.

The UK is relatively virgin ground for the onshore working of unconventional natural reserves (ROENG 2012; Scottish Government 2014). As there are only two active Unconventional Natural Gas (UNG) sites in the UK, little information has been published about the potential health effects generated from this industry on occupational and environmental health (ROENG 2012; Scottish Government 2014). Health and safety features prominently in the petroleum industry in UK waters (offshore), with the UK having one of the most demanding environmental and occupational standards internationally (ROENG 2012; Scottish Government 2014).

The environmental regime offshore is lax compared to similar situations onshore (HSE 2010). Similarly, the international experience, for instance in the USA and Australia, may not correlate well with environmental and public health effects of onshore UNG development in the UK (ROENG 2012; Scottish Government 2014).

A review of the available literature discovered that no relevant occupational respiratory health study within the UK onshore UNG environment has yet been undertaken for the targeted air pollutants (oxides of nitrogen or particulate matter), (Saunders *et al.* 2016). Studies which assessed the respiratory health of UK-based petroleum workers were scarce, even offshore, because of remoteness, security, and public relations sensitivity, (Broni-Bediako and Amorin 2010; El Boubsi and Andresen 2017).

As there is insufficient published information on airborne environmental and public health effects from UNG, many avenues of research could "contribute to scientific understanding and knowledge", (Saunders *et al.* 2016). It was, therefore, necessary to identify which sources of air pollution may pose the greatest risk to employees from key air pollutants (oxides of nitrogen and particulate matter, etc.). The US National Institute for Occupational Safety and Health (NIOSH) suggests that research into UNG should be conducted on hazards which have the most significant potential for harm (i.e. burdens, impacts, and needs), (Felkor *et al.* 2019). One of the best ways to identify the levels of harm which may befall a receptor is to undertake a preliminary Health Risk Assessment (HRA).

► 5.2) Health Risk Assessment.

An HRA is a systematic evaluation of workplace hazards, which assess the harms which can befall a human receptor from the proposed development (ICMM 2016; IPIECA-IOGP 2015). In this case, the HRA is focussed on the UK-based onshore UNG development. Whilst HRAs can consider the wider socio-economic consequences of developments, this thesis only considers the primary effects (disease) to the human respiratory system from inhalation of selected air pollutants, following the Source-Pathway-Receptor Model (ICMM 2016; Thunis *et al.* 2019).

There are several desk study materials which can be used to evaluate hazards as part of a preliminary HRA, these include;

- Previous HRAs.
- Occupational health or industrial hygiene studies.
- Occupational illness and injury reports.
- Sickness absence reports.
- Material safety data sheets.
- Health surveillance reports.
- Academic work published in peer-reviewed journals.
- Environmental impact assessments.

A selected bibliography of the top 100 references is presented in the Supplemental 5.A. Though in reality, the bibliographic materials used in this review spanned over 1,400 academic and industry works. Social media (i.e. YouTube and Facebook) was also important to identify hazards, as it allowed a virtual site walkover of many oil and gas development sites.

The review also relied on industrial experience within environmental consultancy and risk assessment experience in the contaminated land sector. Experiences with presentations and networking at over 30 conferences and seminars were also important. These experiences are outlined in an Appendix at the end of the thesis.

♦ 5.2.1) Model Conceptualisation.

The 'Source-Pathway-Receptor' Model is useful for evaluating potential hazards. The model follows a source of contamination, through a mode of transport (i.e. pathway) to a receptor (e.g. a person), (Hyland 2017; Waldschlager *et al.* 2020). The source of the hazard must be feasible; a pathway must exist for a receptor to come to harm and, a human receptor must be present to form a potential hazard (Rodrigues *et al.* 2009; Hyland 2017; Thunis 2019). If the linkage between the source, pathway, or receptor is broken, then a hazard could not occur as per Figure 5.1.

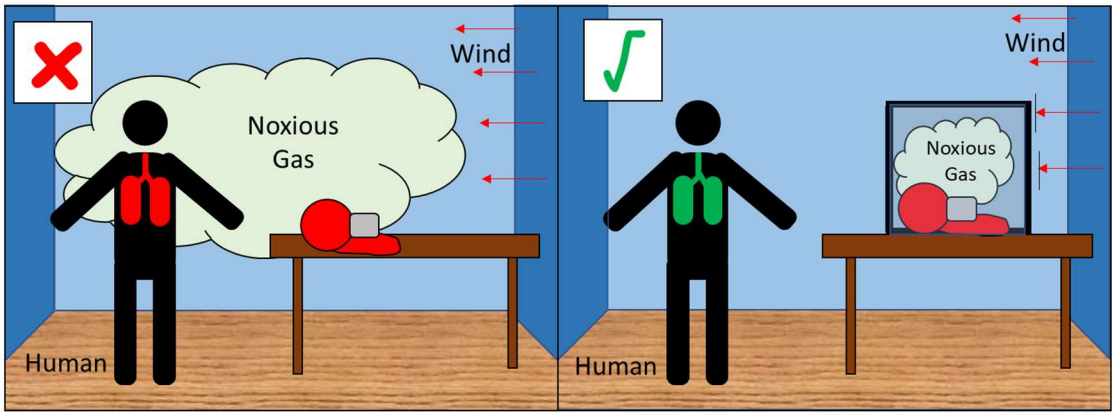

Figure 5.1. A common example of the Source-Pathway-Receptor model is shown above. In the Figure 5.1 on the left, a source of a noxious gas has leaked from its container, with ambient airflow (pathway) in the room the wind is directed toward a human receptor who inhales the noxious gas and becomes ill as a result. A similar case is presented on the right where, there is still a human in the room, the wind flow remains relatively the same but, in this case, the noxious gas is contained within a glass box. Because the noxious gas is contained, it cannot reach the human receptor who therefore would suffer no physical effect from the noxious gas as it had no access to them.

Source; Author – Grainger (2020)

► 5.3) Scope of this Preliminary HRA.

To clarify, the scoping criteria in this preliminary HRA must include:

i. A source or release of contamination or pollution.
ii. A conceivable source following the current UK legislative framework.
iii. A transport mechanism through an aeolian (windblown) mode of transport.
iv. An air pollutant which is either particulate matter ($PM_{2.5}$- PM_{10} and its associated chemical species, e.g. black carbon) or nitrogen oxides (nitrogen monoxide and nitrogen dioxide).
v. An area affected by the release of air pollution where either a human receptor or offsite air quality could be exposed.
vi. A degree of harm which must have a more than a subtle impact on a receptor, i.e. the exposure must cause an accountable symptom or decline in air quality.

► 5.4) Source-Pathway-Receptor Model.

♦ 5.4.1. Sources.

UNG sites are complex workplaces with an extensive range of activities which may generate air pollution (ROENG 2012; Ezani *et al.* 2018). Some of these industrial procedures include conventional construction activities, deep geologic drilling operations, and high-capacity pumping of chemical additives (ROENG 2012; Scottish Government 2014). Additionally, many site activities are reliant on equipment delivered by Heavy Goods Vehicles (HGVs), which generate vehicular emissions (Goodman *et al.* 2016). Some of the equipment includes dry powders, which could also generate dust (e.g. drilling muds and gravel).

Other sources of air pollution include combustion-related emissions from the burning of fossil fuels either for the generation of power in diesel engines, or from the use of flaring for safety purposes (Ezani *et al.* 2018). A more thorough explanation of activities within each stage of the UNG development is provided in Chapter 4 of this thesis.

The key processes of UNG developments were outlined in Chapter 4, but they are considered below in light of their pollutive potential in particular reference to the Preston New Road UNG site.

■ A) Vehicular emissions.

Significant levels of air pollution could be generated from vehicular emissions, particularly from diesel-powered HGVs (Goodman *et al.* 2016). Such emissions are prevalent throughout all stages of UNG developments (ARUP, 2014; Goodman *et al.* 2016). According to the Environmental Impact Assessment (EIA) and reported statistics through the 'Cuadrilla Resources Portal', vehicular emissions were at their peak during the construction, drilling, hydraulic fracturing, and well-testing phases of the PNR UNG project (ARUP Group 2014; Cuadrilla Resources 2019).

The construction and drilling stages' planning permission at PNR allowed up to 62 two-way HGV movements per day (ARUP Group 2014; Cuadrilla Resources 2019). Some researchers believe that NO_X emissions from the HGVs during peak flow could be over 30% more than original traffic emissions (Goodman *et al.* 2016). At the Preston New Road (PNR) UNG site, protestors have often posed a public safety hazard causing road closure (see Figure 5.2), a robust traffic plan and a significant police presence (Jackson *et al.* 2018). In particular, the A583 'Preston New Road' outside of the main PNR UNG site has seen two significant traffic management plans (Grainger 2019). The traffic management plans have led to slower vehicle speeds and congestion along the road (Jones 2018; Llew 2018).

Reductions in vehicular speeds can generate additional vehicular emissions (Outpa *et al.* 2016).

Figure 5.2.A Shows a view of the Preston New Road development site with heavy UNG traffic due to protestors along the margins of the road. The police are attempting to keep the peace but, a protestor had managed to "lorry surf" (climb on top of a lorry), preventing the HGV from entering the site. Figure 5.2.**B** Shows a convoy with police escort driving to the PNR facility and access road seen to the bottom right-hand corner.

Source: (A). McEwan (2017). *Reproduced courtesy of Mr Janes McEwan.*

Source: (B) Cuadrilla Resources (2019). Reproduced with kind permission of Cuadrilla Resources Ltd.

Also, in terms of police presence, as of March 2018, £7 million of extra policing was used to keep the peace around the PNR UNG development site. To protect the peace, as many as 30 police officers were stationed outside of the UNG site (Lancashire Constabulary 2018; Jones 2019). Vehicles were required to transport the police officers and to keep them supplied with equipment (Lancashire Constabulary 2018).

■ B) Non-vehicular emissions.

Non-vehicular emissions are the most prevalent during the construction through well stimulation and reclamation phases of the UNG development. Sources of non-vehicular emissions stem from the burning of diesel;

- **Primary Emissions**; sources include primary generators for use in drilling and hydraulic fracturing as well as Non-Road Mobile Machinery (NRMM) such as excavators, forklifts, cranes (etc.) which are also likely to contribute to overall (non-vehicular) emissions (ICEs), (Ezani *et al.* 2018*;* Johnson *et al.* 2018).

- **Secondary Emissions;** sources include, secondary or backup generators for lighting, welfare cabins, compressors, etc.).

■ C) Mobilised soil and aggregate.

Common construction and remediation activities such as ploughing, excavating, and stockpiling of soils and aggregate, release and mobilise soil and aggregate dust (HSE CONIAC 2015; Gálvez-Martos *et al.* 2018). Aggregate (gravel dust) emissions are associated with laying down of site cover, i.e. from the importation, sizing, and the levelling of aggregate over the site as shown in Figure 5.3 (Defra 2009; IAQM 2016;). During remediation, these soils, and aggregates are sized and reclaimed/exported; this is due to the UK's strict waste policy on un-reclaimed site materials (Heads of Planning Scotland 2018).

Figure 5.3. Showing a tipper truck and a 10-tonne excavator working gravel on the Preston New Road Unconventional oil and gas development site. The limestone in this case came from a local source of Devensian Limestone which had been pre-sized. However, some of the gravel was screened onsite for specific uses such as screed materials.

Source: Cuadrilla Resources (2017a). Reproduced with kind permission of Cuadrilla Resources Ltd.

■ D) Combustion air pollutants.

Combustion-related emissions stem from the burning of hydrocarbon vapours arising from flowback fluid after hydraulic fracturing. Flaring is especially prevalent during the initial well testing of the UNG reserve when all recovered natural gas from the formation is burned (ARUP Group 2014). The flares at the PNR facility (Figure 5.4) are designed to reduce emissions and the visual impact of the flaring activity (ARUP Group 2014).

Figure 5.4. Showing the two ground level flares at the Preston New Road Unconventional Development Site.

Source: Cuadrilla Resources (2018). Reproduced with kind permission of Cuadrilla Resources Ltd.

■ E) Drilling mud and arisings.

Parts of the well circulation system generate significant quantities of airborne drilling muds and arisings which can be blown over many parts of the UNG drilling rig (Steinsvag *et al.* 2009; Bratviet *et al.* 2009; Broni-Bediako and Amorin 2010). The main "dirty" processes involving drilling mud include; working with the rotary hose and drill pipe on the rig floor, screening of arisings, mixing of the drilling mud components and the repair of the rig circulatory systems (where mud may have dried), (Hansen *et al.* 1991; Steinsvag *et al.* 2009; Bratviet *et al.* 2009; Broni-Bediako and Amorin 2010). Other sources of dust, include; the handling and storage of chemical additives, the mixing of mud drilling additives and parts of the mixing process, (Hansen *et al.* 1991; Steinsvag *et al.* 2009; Bratviet *et al.* 2009; Broni-Bediako and Amorin 2010; HSE 2011a, b; Kaden and Rose 2016).

Figure 5.5. A photograph of the shale shaker present at Preston New Road Unconventional oil and gas development site. The two tubular features are vibrating motors which power the vibratory action of the shale shaker.

Source: Cuadrilla Resources (2017b). Reproduced with kind permission of Cuadrilla Resources Ltd.

Once the mud has been pumped down to the bottom of the borehole, it is sprayed out of the drill bit at high pressure, which washes away rock cuttings from the bottom of the borehole and carries them back up to the surface via the annular space (ARUP 2014). At the surface, the drilling mud is passed through a shale shaker (vibrating steel mesh filter shown in Figure 5.5), de-sander (hydrocyclone), desilter (hydrocyclone) and an optional dryer (centrifuge), (HSE 2011b). The cleaning equipment releases aerosolised dust into the atmosphere around the machinery (Hansen *et al.* 1991; Bratveit *et al.* 2009; HSE 2011b). Additionally, laboratory staff and the mud engineer may come into contact with arisings when sampling and examining the drill cuttings (Miller 2010).

■ F) Significant release of gases and explosions.

During the drilling stage, a kick (unplanned release of liquids or gases from the borehole) can lead to an explosion (blowout) if not brought under control by the Blowout Preventer (BOP), (Nance *et al.* 2016; Mason 2020). The last blowout in UK waters occurred in 1988 during the Piper Alpha disaster, during which 14,400 m^3/hour of natural gas was burned, which was the equivalent to the entire UK's hourly domestic consumption at the time, (Macleod and Richardson 2018). Using the US EPA's AP-42 conversions, it can be estimated that around 24.5 million tons of NO_X, 85 million tons of PM_{10} and 70 million tons of $PM_{2.5}$ were released from the disaster, (US EPA 2018).

■ G) Well stimulation.

Well stimulation sources of air pollution mostly involve above the ground contact with the thousands of tons of sand used in the proppant stage of the well stimulation process (ARUP Group 2014; Kaden and Rose 2016). The proponent is key to the well stimulation procedure as the sand “props up” fractures within the formation, (ARUP Group 2014; Kaden and Rose 2016). Sources of exposure include the stockpiling, sizing of, and moving of sand, (Cecala *et al.* 2012; ARUP Group 2014; Kaden and Rose 2016). While contact with other chemicals is possible, well stimulation chemicals are subject to very strict existing health and safety practices which overall limit exposures to site personnel (Kaden and Rose 2016; HSE 2017).

♦ 5.4.2) Summary of sources of emissions.

A summary of the key sources of the criteria air pollutants is outlined in Table 5.1:

Table 5.1: Summary of sources of emissions outlined within Sections 3 & 4.

Sources of grouped airborne contamination	Stages	Online of individual sources of airborne contamination.
Vehicle emissions:	I – VIII	Off-road vehicles, traffic management, increased HGV traffic, police presence, staff access.
Non-vehicle emissions:	I-III, VII	Drilling rig power system, hydraulic fracture power system, camp generators.
Mobilised soil and aggregate:	I, VII	Ploughing of topsoil, excavations, working and importation of aggregate, sizing of aggregate, temporary road access, construction drilling, stockpiling of soils, removal of temporary surfaces, dismantling of structures, reworking and reclamation of aggregate, reworking and levelling soil.
Drilling mud and arisings	II	Storage of dried powders, mixing of drilling mud, spillage, and drying of drilling mud, handling of drilling mud and muddy equipment/apparel, leaking rotary hose, contact with the: shale shaker, de-sander, desilter, dryer, handling of arisings, testing of rocks, arisings, and drilling mud.
Significant release of gases and catastrophic explosion:	II	An unplanned release of asphyxiating gases or the resurgence of drilling mud to the surface. Failure of the BOP leading to kick, failure of BOP leading to a blowout.
Combustion air pollutants:	II-VI	Burning hydrocarbon vapours in flowback, initial flow test flaring in flare stacks, safety flaring during production.
Well stimulation:	III	The working of proppant during the hydraulic fracture stage (moving, storage, and sizing of sand).

Many stages of the UNG development generate emissions of key air pollutants. Given the importance of understanding the specific types of the airborne pollutants associated with each stage of the UNG project, Table 5.2 qualitatively assesses the most likely air pollutants within each of the sources.

Table 5.2. Table 5 identifies the major air pollutant types associated with each stage of a UNG project.

Sources of air pollution.	Particulate matter ($PM_{2.5}$ – PM_{10})			*Oxides of Nitrogen (NO_X)*	Score
	Inert (soil)	*Additives*	*Black carb*		
STAGE I: Construction	√ (1)	X	~ (0.5)	√√ (2)	3.5
STAGE II: Drilling	X	√√√ (3)	√√ (2)	√√ (2)	7
STAGE III: Hydraulic Fracture	X	√ (1)	√√√ (3)	√√√ (3)	7
STAGE IV: Initial Flow Testing	X	√ (1)	√√ (2)	√√ (2)	5
STAGE V: Flow Testing	X	X	~ (0.5)	~ (0.5)	1
STAGE VI: Production	X	X	~ (0.5)	~ (0.5)	1
STAGE VII: Remediation	√ (1)	X	~ (0.5)	√√ (2)	3.5
	2	5	9	12	
	16				

► 5.5) Receptors and Pathways.

♦ 5.5.1) Receptors.

Exposure to the selected air pollutants (PM and NO_X) can cause a wide range of symptoms and human disease (as outlined within Chapter 2). Exposure to air pollutants may damage the respiratory system, with other health effects affecting the neurological and pneumo-circulatory systems, (Bouke and Burns 2015; Ralston *et al.* 2018; Amaza and Kreidy 2019). Human illness can have significant offset times between exposure and manifestation and the progression of symptoms and diseases (Hiriani 2019).

This HRA subdivides human harm into three main conventional categories routinely used in HRAs, these categories are;

- **Acute health effects:** the effects felt within hours of exposure, which are commonly relatively minor (e.g. sneezing, wheezing or coughing). Although in extreme cases, life-threatening diseases can befall receptors (e.g. High exposure to NO_X causing Silo Fillers Disease, Acute Lung Injury), (Bouke and Burns 2015; Ralston *et al.* 2018; Amaza and Kreidy 2019).

- **Chronic health effects:** these symptoms manifest over long exposure durations, commonly over many months or years. Such chronic effects may stem from long-term respiratory tract irritation and include diseases such as rhinitis, pneumonia, and simple pneumoconiosis, (Bouke and Burns 2015; Ralston *et al.* 2018; Amaza and Kreidy 2019).

- **Long latency effects:** these are usually only felt many years post-exposure, often during old age. Such symptoms and diseases follow a career-long exposure to air pollution. Such long latency lung diseases include COPD (Chronic Obstructive Pulmonary Disease) and PMF (Progressive Massive Fibrosis), (Bouke and Burns 2015; Ralston *et al.* 2018; Amaza and Kreidy 2019).

♦ 5.5.2) Exposure pathways.

An exposure pathway indicates how a receptor came into contact with a pollutant (Waldschlager *et al.* 2020). However, the only mode of transport evaluated in this HRA is through aeolian processes transporting gases and particulate through the air to near-site ambient air or the human respiratory tract of nearby site workers. In order for a pathway to exist, the link must be realistic, i.e. there is a causal link between a source of selected air pollutants, in a place where humans are present, who may encounter the contaminated air frequently enough, or to such a degree, that a noticeable effect takes place.

► 5.6) Conceptual risk assessment framework.

A literature review was carried out following a conceptual understanding of the risks associated with the potential hazards in the UNG industry and in general accordance with best practice guidance on HRAs, (ICMM 2016; IPIECA-IOGP 2019; Robinson 2019). Once the exposures were assessed, the potential health risks and the significance of these hazards were categorised following a risk rating assessment matrix (ICMM 2016; IPIECA-IOGP 2019; Robinson 2019). The risk rating was calculated through a multistage process whereby the health consequence (C) of each of the health hazards was assessed, alongside the duration of exposure (ED), the Consequence (C) and Exposure (Ed) factors were multiplied by a probability function (Pe), i.e. the likelihood of this exposure. Note that exposure duration was not taken into account for ambient air, as the consequence of exposure (C) already addresses the impacts on air quality in terms of days of the breach of the ambient air standards and/or the percentage change to local air quality (IPIECA-IOGP 2019).

The equation used to estimate a qualitative risk rating for each of the hazards is shown in Equation 5.1.

Equation 5.1. Risk rating calculation.

$$RR = C \times Ed \times Pe$$

Risk Rating = *Consequence of Exposure* × *Exposure Duration* × *Probability of Exposure*

► 5.6.1) Consequence of exposure.

The potential consequences of contamination occurring at UNG development site are classified based on whether they could breach:

- The UK's air quality guidelines (UK AAG). The UK's AAG governs the legislative limits of air quality found outdoors (Vincent *et al.* 2010). The guidelines for the AAG are different in England than in Scotland (SPICe 2016). Nether-the-less the AAGs are outlined in Section 3.2.1. within Table 3.1.
- The UK's Daily Air Quality Index (DAQI). The DAQI is a measure of the daily air quality of ambient air on a ten-point scale (COMEAP 2011). The air pollutants used in the DAQI include $PM_{2.5}$, PM_{10} and NO_2. The DAQIs are outlined in Section 3.2.4. Tables 3.4, 3.5, and 3.6.
- The UK's workplace exposure limits (UK WELs). The UK WELs govern the legislative limits of air quality in the workplace (HSE 2018). While the precise chemical composition of the airborne dust and gases is important, the UK WELs also outline levels of respirable and thoracic particles, NO, and NO_2 (HSE 2018). The WELs are outlined in Section 3.2.2. and within Tables 3.2 and 3.3 (on pages 71 and 72).

- *Reporting of Injuries, Diseases, and Dangerous Occurrences Regulations (RIDDOR).* RIDDOR governs the incidence of reporting in the event of an accident or the occurrence of occupational disease. The regulations come into effect when; a worker becomes ill, suffers a workplace accident, develops an occupational disease, or becomes involved in a workplace explosion (HSE 2013). The RIDDOR regulations are outlined in further detail in Section 3.2.3. (Subsections A and B).

It is clear then that there is a division in consequence between the effects on workers' health and ambient air quality. Therefore, a two-factor approach was necessary to evaluate the degree of harm to both the local air quality and to the occupational health of employees.

■ A. Consequences to Ambient Air quality.

For ambient air, there are three main mechanisms which address the severity of the change of the development on the local air quality. These mechanisms are; increases in the mean air pollutant concentration as a result of the development (Table 5.3), increases in the number of days which have breached the air quality regulations (Table 5.4), and the number of days or severity of the DAQI health bandings (Table 5.5.). If one or more of the tables is indicated, the highest consequence value is taken as the critical consequence (C) value for the risk assessment.

Table 5.3. The classification of the consequence of a hazard being realised in Ambient Air annually.

Magnitude of Change		Increase in Annual Mean of Air Pollutant
Very High	300	>15%
High	80	10-15%
Moderate	32	5-10%
Minor	16	1-5%
Negligible	8	<1%

Table 5.4. The classification of the consequence of a hazard being realised in Ambient Air annually – Magnitude of Change.

Magnitude of Change		Increase in Days of PM_{10} > 50 µg/m^3	
		England and Wales:	Scotland:
Very High	300	15> Days	>4 Days
High	80	10-15 Days	3-4 Days
Moderate	32	5-10 Days	2-3 Days
Minor	16	1-5 Days	1-2 Days
Negligible	8	<1 Day	0-1 Days

Table 5.5. The classification of the consequence of a hazard being realised in Ambient Air annually - DAQI.

Magnitude of Change		Conditions of DAQI Score against impact.	
		DAQI Days Range	Maximum DAQI Score as a result of the Development
Very High	300	15> Days >3	> 9
High	80	10-15 Days >3	6 – 9
Moderate	32	5-10 Days >3	> 6
Minor	16	1-5 Days >3	3 – 6
Negligible	8	All DAQI ⩽3	Max of 3

■ B. Consequences to Occupational Health.

For the workplace, there are two main mechanisms which address the severity of the air quality's effects on occupational health, and these are; breaches of the RIDDOR regulations (Table 5.6 on page 158) and the concentration of an air pollutant above the WELs (as per EH40), (as shown in Table 5.7 on page 159).

Breaches of the RIDDOR regulations have been given increased weight in the risk assessment as the sudden death of workers, and large hazardous escapes of substances, is a scale of magnitude above occupational disease. Indeed, sudden death through toxic exposure also falls under the RIDDOR regulations. If one or more of the tables is indicated, the highest consequence is taken as the critical consequence (C) value for the risk assessment.

Table 5.6. The classification of the consequence of a hazard being realised in Workplace Air annually in mg/m^3.

The severity of an event occurring.		Event example	Description of the Event
Very High	400.	Death of workers, an event requiring Evacuation, Release of flammable liquids and gases, Hazardous escapes of substances etc.	A significant release of poor-quality air likely to severely affect the workforce, or the bringing into effect emergency procedures such as the evacuation of an area or site, this includes “near miss” events where an event was narrowly avoided. Still, if it had occurred, the effects would have been grave.
High	80.	Incidence of Occupational Disease: e.g. Pneumoconiosis.	Adverse health effects are likely in most workers exposed to these high levels of air pollution. These health effects may be permanent and could lead to a significant decline in the quality of life or life expectancy. Ongoing exposure is likely to lead to permanent long-term chronic occupational disease, e.g. pneumoconiosis.
Moderate	32.	Incidence of Occupational Disease: e.g. Asthma	Adverse health effects may occur, causing permanent harm to sensitive employees. While symptoms may limit a person; the condition would most likely not affect the quality of life or longevity of the individual affected, though a change in occupation and lifestyle may be necessary.
Minor	16.	Short tern harm: e.g. cough and sneezing.	Non-permanent effects to sensitive employees. Any effects which do occur are readily and fully reversible shortly following exposure.
Negligible	8.	Asymptomatic to no physiological change.	This level is likely to cause little or no effects on those who are not significantly predisposed to poor air quality.

► 5.6.2) Exposure Duration.

In this risk assessment, exposure duration can only be applied to increases in air quality above the WELs. The exposure duration found in Table 5.7 shows a range of durations between once a year to the continuously over the shift. The reason why the exposure function only belongs to WELs is that a sole breach of an accident-related RIDDOR event is enough to trigger the risk. Likewise, ambient air quality has self-described numbers of days needed to ascend through the consequence tiers. For this reason, the magnitude of change has already been applied to the RIDDOR regulations, and for ambient air quality.

Table 5.7. The classification of the exposure period of the hazard.

Duration class [A]	Definition [B]	Risk rating value
Rare	Maybe once per year or less.	1
Infrequent	A few times a year, e.g. Quarterly.	2
Uncommon	Fifteen minutes a few times per month.	4
Intermittent	Occurs maybe once per shift.	8
Regularly	Occurs multiple times per shift	10
Continuously	Continuously over the shift.	12

[A] Characterises the exposure class of each of the types of duration timescales, [B] Designates the exposure class of each of the types of hazard assuming an event occurred. With for example a catastrophic explosion, this may happen for a brief period of time or once in that year. For more routine activities, say equipment handlers coming into contact with drilling mud, this exposure may be fairly continuous over their shift.

► 5.6.3) Probability of Exposure.

The probability of exposure is based on information from the extended literature review; it ranges from a Non-Zero chance through to a very high likelihood of occurrence. The probability of exposure is applied in all of the risk calculations identically, following Equation 5.1. The probability risk table is found in Table 5.8 overleaf.

Table 5.8. The definitions of the probability of a hazard occurring.

Probability class [A]	Band rating [B]	Definition	Risk rating value [C]
Non-Zero Chance	≥ 1 in 1,000,000 chance.	The chance of a hazard occurring approaches impossibility, but still there remains a non-zero chance of an event occurring.	1
Unlikely	≥ 1 in 100,000 chance.	There are elements under which a hazard could occur. However, it is improbable that an event would occur even in the long-term.	4
Low Likelihood	≥ 1 in 1,000 chance.	All the elements are possible under which a hazard could occur. A hazard is not likely to occur even in the longer term and less likely in the short-term.	16
Moderate Likelihood	≥ 1 in 100 chance.	All the elements are present for a hazard to occur, while the event is not inevitable; it is improbable in the short-term.	64
High Likelihood	≥ 1 in 10 chance.	The hazard could occur in the short-term, and an event is nearly inevitable over the long-term, or there is already evidence to suggest harm.	256
Very High Likelihood	≥ 1 in 2 chance.	There is evidence to support that the hazard already exists, or the hazard is inevitable in the short-term.	1,024

[A] Defined the definitions of the probability of a hazard occurring. [B] This table defines the probability bracket, starting with a minimum of a 1 in 1,000,000 chance and increasing through to an even chance and above. For a least 'unlikely' chance, there needs to be at least some elements under which a hazard could occur. The more elements present for an event to occur, the greater the degrees of chance where an event could occur. [C] A value is attributed to each of the hazards used within the risk assessment to determine the total risk rating. [D] The highest risk threshold which applies to the hazard is taken as the critical consequence value.

► 5.6.4) Risk Rating.

The risk rating applied to the preliminary risk assessment is based around the attributable threshold bandings which apply to each category. The risks were trailed on a series of real-world and well-risk assessed scenarios, and adjusted accordingly. The jump in values between Moderate and High risk is due to the likelihood values increasing by a factor of four to reflect the significance of harm increase between 'low risk' hazards and those which are 'moderate' and above.

Table 5.9. Screening criteria for research impact of studying certain hazards on the understanding of various risks.

Risk rating	Value threshold	Descriptions	Actions
Negligible	325	Either the risk of an event occurring is remote, or the consequence of exposure is so minor that harm is unlikely to befall a receptor even if exposed.	These hazards have been scoped out of the PhD, as they are of low risk to occupational respiratory health.
Low	600		
Moderate	5,000	The consequences, exposure, and probability are moderate. But the risk rating is not as high as other identified hazards which could occur at the site.	These hazards have been screened out of the thesis's research. Although these hazards can pose a moderate hazard to workers, the risk is not as pressing as other hazards in the risk assessment.
High	40,000	All the elements under which the hazard could take place are present, and consequences, exposure, and probability are all relatively high and potentially life-altering, especially following chronic exposure.	These hazards may pose a major hazard to occupational or environmental health. These hazards are scoped into this PhD research.
Critical	190,000		

► 5.7) Preliminary risk assessment.

The preliminary risk assessment is in two parts, Table 5.10 addresses these same hazards from an ambient environmental air quality perspective, whilst Table 5.11 addresses the risk to occupational health from hazards on oil and gas sites. In both cases, the risk assessment is based on a factual assessment of information from the extended literature review and the risk assessment methodology outlined in Section 5.7.

Table 5.10 The risk of harm to the ambient air quality environment (i.e. community-wide impacts) from UNG development sites.

Category and the major sources of pollutants [A]		Risk factors [B]		Risk values and labels [C]	
Category	Source	Consequence	Likelihood	Sum risk score	Risk
Use of chemical additives	Drilling mud, arisings and well fluids.	300	1024	307,200	Critical
Combustion-related air pollution	Power generation	300	1024	307,200	Critical
	Site transport	80	1024	81,920	High
	Flares	300	256	76,800	High
Well stimulation chemicals		300	4	1,200	Low
Construction & remediation	Soil and aggregate and proppant	16	64	1,024	Negligible
Disaster-Related Emissions	Escape of gas or asphyxiant.	300	1	300	Negligible
	VOC release	300	1	300	Negligible
	Catastrophic explosion.	300	1	300	Negligible

[A] Characterises the exposure class of each of the types of hazard, assuming an event where all factors which led to the event occurring were in place, and the associated source of the exposure. [B] Table 5.11 goes on to show the likelihood, consequence, and exposure duration based on Tables 5. (3, 5 ,9 and 10). [C] The last column shows the risk value based on the numerical multiplicity of the three risk factors and compares them against the threshold stated in Table 5.10.

Table 5.11 The risk of harm to the occupational health (i.e. workers) of Unconventional development sites.

Category	Source	Consequence [A]	Exposure duration [B]	Likelihood [B]	Sum risk score [C]	
Use of chemical additives	Drilling mud, arisings and well fluids.	24	12	1,024	295,488	Critical
Combustion-related air pollution	Power generation	16	12	1,024	196,992	Critical
Construction & remediation	Soil and aggregate and proppant	16	12	64	40,960	High
Combustion-related air pollution	Flares	16	8	64	32,768	Moderate
	Site transport	4	10	64	12,288	Moderate
Hydraulic Fracturing Chemicals		300	4	16	19,200	Moderate
Disaster-Related Emissions	Escape of gas or asphyxiant.	300	1	1	300	Negligible
	VOC release	300	1	1	300	Negligible
	Catastrophic explosion.	300	1	1	300	Negligible

[A] Characterises the exposure class of each of the types of hazard, assuming an event where all factors which led to the event occurring were in place, and the associated source of the exposure. [B] Table 5.12 goes on to show the likelihood, consequence, and exposure duration based on Tables 5. (6, 7, 8, 9 and 10). [C] The last column shows the risk value based on the numerical multiplicity of the three risk factors and compares them against the threshold stated in Table 5.10.

It is recommended that the second most significant hazard, Power Generation be grouped into a larger category 'combustion-related air pollution', as it would be difficult and fruitless to differentiate between different 'combustion-related air pollution' sources from UNG sites. Therefore, the risk values found in Tables 5.10 and 5.11 have been grouped in Table 5.12 based on their overarching source categories.

Table 5.12: Combined Risks on the Environment and Occupational Health.

Source categories. [A]	Individual sources. [B]	Risk scores. [C]	Risk.
Combustion-related air pollution	Power generation, Flares and Site transport	353,984	Critical
Drilling Chemicals	Drilling mud, arisings and well fluids.	301,344	Critical
Construction & remediation	Soil and aggregate and proppant	20,992	Moderate
Hydraulic Fracturing Chemicals		10,200	Moderate
Disaster-Related Emissions	Escape of gas or asphyxiant, VOC release and Catastrophic explosion.	900	Low

[A] Defines the exposure category of each of the major categories of hazard, e.g. Combustion-related air pollution. [B] The source of each activity is shown to provide a sign of which hazards have been grouped into which category. [C] The total of all the hazards under each category is then specified regarding the risk scores in Table 5.10 and 5.11.

► 5.8) Discussion.

The preliminary risk assessment indicates that both site workers and ambient levels of air quality are at very high risk of exposure to air pollutants. These air pollutants may cause a wide range of acute, chronic, or long-long legacy health conditions as discussed within Chapter 2 of this thesis.

- **Drilling Mud;** The single most hazardous activity identified within this review to both ambient and workplace air quality was the use of drilling mud additives during the drilling stage. Drilling mud is essentially a PM (particulate matter) hazard, incorporating both liquid droplets (oil mists) and solid PM from rock cuttings, and chemical additives (Broni-Bediako and Amorin 2010; US EPA 2015). The literature review suggests drilling mud can be found on most parts of the drilling rig, with some of the dirtiest processes involving the; addition, handling, connection and removal of drilling mud in the mud circulatory system, i.e. around mud tanks, the drill floor, and shale shakers (Steinsvag *et al.* 2009; Bratviet *et al.* 2009; Broni-Bediako and Amorin 2010). Additionally, many authors have suggested that drilling mud can disperse and cover a wide area (encompassing most areas of offshore drilling rigs), so it is conceivable that large plumes of PM-related drilling mud may escape from onshore drilling muds and affect the local community (Steinsvag *et al.* 2009; Bratviet *et al.* 2009; Broni-Bediako and Amorin 2010). There is already evidence of community harm from onshore oil and gas exploration in the United States, and such a possibility may exist in the United Kingdom at sites such as PNR (US GAO 2012, ROENG 2012, Scottish Government 2014, Kaden and Rose 2016; Saunders *et al. 2016*). Researchers have, however, found that the airborne concentration of PM does not coincide with the community effects. One possible reason for this is due to the fact that chemical components have a much more damaging effect on community health than the total concentration of PM would otherwise indicate (Garcia-Gonzales *et al.* 2019).

This combined hazard has been screened into the PhD research following the criteria outlined in Table 5.12.

- **Combustion Related Air Pollution;** Consequently, the largest grouped category of air pollution which could cause a hazard to site workers and ambient air quality were; Internal combustion engine (ICE) emissions including the burning of diesel from HGV and NRMMs, safety flaring (during the initial flow testing stage), and on-site power generation. Combustion related air pollutants are well known to cause an array of health conditions on the respiratory, circulatory, and neurological systems (as per Chapter 2). There is also evidence that harm is already occurring in other similar industries and overseas within the petroleum industry (Goodman *et al.* 2016; Kaden and Rose 2016; Ezani *et al.* 2018; Franklin *et al.* 2019). This combined hazard has been screened into the PhD research following the criteria outlined in Table 5.12.

- **Soil and aggregate dust emissions**; These have similar effects on the human respiratory system to drilling mud; however, the consequence of exposure was reduced as these emissions are relatively heterogeneous compared to the drilling mud, which contains many chemical compounds (either leached from the formation or deliberately added to the drilling mud). The exposure duration and the probability of exposure to aggregate dust were also reduced as the construction and remediation phases only contributed to outdoor air pollution, whereas during the drilling stage, dirty processes are sometimes housed within semi-enclosed areas, which could trap and increase concentrations of air pollutants, which could further risk employees' health. Contrastingly, aggregate dust formed a moderate hazard throughout the construction, demolition, and extraction stages as in large concentrations it can cause silicosis (a subtype of pneumoconiosis), (Miller 2010; HSE CONIAC 2015). However, this hazard has been screened out of the PhD research for this thesis following the criteria outlined in Table 5.9.

- **Hydraulic Fracturing Chemicals;** The risk of harm from exposure to hydraulic fracturing chemicals is quite high. However, the UK's steadfast and demanding health and safety policy makes occupational exposure to these harsh chemicals unlikely in the workplace environment and even less likely to affect ambient air quality (ROENG 2012; ARUP Group 2014). The only actual exposure risk is that of a workplace accident which would fall under disaster-related emissions in any event. As such, this hazard has been screened out of this PhD research.

- **Disaster-Related Emissions;** Despite these accident-related air pollutants having major consequences on employees and ambient air, should they come to occur, they thankfully have an extremely low incidence rate. The last significant accident related event in UK waters was the Piper Alpha disaster in 1988, with no major comparable events occurring in the intervening 30 years (Pitblabo 2014; MacLeod 2018). While the exposure duration would be short, acute lung injury (ALI) could affect workers, leading to severe or even fatal symptoms (Bourke and Burns 2015). Due to the extremely low probability of this hazard, these "accident-related air pollutants" have been screened out of this PhD research.

► 5.9) Conclusions.

This HRA identified the key sources of selected air pollutants ($PM_{2.5}$-PM_{10}, NO, NO_2, and NO_x), which may pose a risk to ambient and workplace air on UNG development sites. The two-most significant hazards were;

1. **Drilling mud.** It was found that drilling mud related dust is likely to be comprised of fine PM, which can have significant chronic effects on workers' health and the environment. Given that drilling mud is present on modern deep drilling rigs, exposure may be expected over much of a worker's shift, increasing the hazard rating. Chemicals added to drilling mud may exacerbate symptoms due to chemical sensitivity or corrosion to sensitive tissues and could potentially lead to community health effects.
2. **Combustion-related emissions.** Major sources of key air pollutants on the UNG development were combustion-related emissions from sources including, vehicles, power generation, and ground-level flares. When combined, these three sources created the most significant risk to occupational workers and ambient air quality. Diesel particulate matter is an increasing concern to occupational health worldwide, and it seems UNG developments are not exempt from this hazard.

The other hazards, construction and remediation, and disaster-related emissions were deemed to be of a less significant risk to site workers and ambient air quality and have been screened out of this PhD research.

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Supplemental 5.A:

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■ INTRODUCTION.

In undertaking this thesis, over 1,500 information sources were used to mould the research chapters. Of these 1,500 information sources, 820 were used as references within this thesis. This bibliography features the top 100 resources (industry materials, academic journals, photo/video-graphic materials, and conference proceedings) which were instrumental for this thesis. The Bibliographic materials are grouped by category for ease of reference. A series of Freedom of Information (FOI) requests were issued during this thesis, which included over 200 communications. The successful FOI Requests of this thesis are included in Appendix C at the end of the thesis.

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CHAPTER 6:

A discussion of the techniques, methods, and equipment used in this PhD thesis.

"The 7 Ps: Proper Preparation and Planning, Prevents Prohibitively Poor Performance".
The British Army (1660 – Present)

This chapter outlines the principals of primary and secondary research used in this thesis. Primary research involves the onsite collection of air quality measurements using a series of active and passive devices. Secondary research, however, relies on open-access data to analyse and model the data in new and creative ways. Regardless of which data collection method is used, data analysis can be optimised with statistical computing.

► 6.0) Introduction:

Air quality science has benefited from technological progression and increased public consciousness, which together have focused the market toward a diverse range of air quality monitoring equipment (Stacey 2019). Lightweight battery-powered personal sampling devices have become increasingly popular relative to more traditional stationary equipment (Steinle *et al.* 2015; McKercher *et al.* 2017; Stacey 2019). The popularity of personal sampling may be due-in-part to its cost-effectiveness and greater field flexibility (Steinle *et al.* 2015; McKercher *et al.* 2017; Stacey 2019).

Despite many potential fieldwork opportunities being available to researchers, sometimes, a scientist cannot access a site directly due to; logistical difficulties, safety concerns, and industry reluctance. In these situations, appropriate modelling, and scientific appraisal of publicly available data may be the best alternative to primary data collection (fieldwork).

This chapter discusses field measurement equipment and techniques, as well as sources of secondary data from various open-access and [or] publicly available datasets. The chapter continues by discussing computation and modelling possibilities of both primary and secondary data, and its utility in air quality research. This chapter forms the method philosophy for the remainder of the PhD thesis.

► 6.1) Qualitative Research

A “Desk Study” or “Literature Review” analyses online and [or] archival information was conducted to better understand the underlying principles and characteristics of a potential emission source or location (Strange *et al.* 2016). Desk studies can assess the level of health risk beyond an initial Health Risk Assessment (HRA) and move towards the creation of mitigation strategies following the hierarchy of control (HSE 2000; ICMM 2009; HSE CONIAC 2015). Hypotheses formed during qualitative research should be tested by quantitative research, or if necessary by secondary data analysis (ICMM 2009; BSI Group 2015).

► 6.2) Quantitative Research.

Quantitative research uses mathematical/numerical investigative strategies to study phenomenon. This thesis uses two main branches of data collection methods, these are;

- **Primary Data.** Data collected by the researcher as direct intrusive investigations, with a specific project being the driving force behind the research.
- **Secondary Data.** Data collected by others for other purposes (e.g. environmental permitting or regulation).

► 6.3) Primary Data.

♦ 6.3.1) Primary Air Quality Sampling Campaigns

Historically, air sampling equipment was of considerable weight and bulk, which restricted air quality research, (Steinle *et al.* 2015; Lin *et al.* 2017; McKercher *et al.* 2017).

However, since the 1990s, technological improvement has led to the development of less cumbersome equipment, which rivals the accuracy and precision standards of historical static equipment (Steinle *et al.* 2015; Lin *et al.* 2017; McKercher *et al.* 2017). Mobile real-time equipment is sometimes not on par with contemporary static equipment (such as the UK's Automated Urban and Rural Network, i.e. AURN), being in part inaccurate, imprecise (i.e. inter-instrumental precision) and unreliable (i.e. failure to operate, record or save data), (Lin *et al.* 2017; Ezani *et al.* 2018; Stacey 2019). Given these issues, mobile air quality instrumentation is used alongside more steadfast technologies such as AURN stations and accredited static devices such as the Osiris by Turnkey Instruments (Deary *et al.* 2016; Ezani *et al.* 2018).

♦ 6.3.2) Upwind-Downwind Exposure Studies.

Upwind-downwind exposure studies are a common method in air quality research (Khaniabadi *et al.* 2018; Huertas and Prato 2019). By using this method, the levels of air quality are measured;

- Upwind of the source to gain an understanding of the background levels of air quality before site emissions, as shown in Figure 6.1.
- Near to the source, to sample peak emissions from the source of emissions.
- Downwind of the source where poor-quality air mixes with ambient air. The degree of mixing from emissions is highly variable and can create long plumes of air pollution extending far from the source (Donets *et al.* 2018). The plume is usually how human and environmental receptors are affected by the pollution, sometimes at a substantial distance from the source, (e.g. metres to kilometres).

Upwind-Source-Downwind monitoring campaigns are easily accomplished with small mobile real-time instruments due to users being able to move between Upwind-Source-Downwind areas, (Steinle *et al.* 2015; Lin *et al.* 2017; McKercher *et al.* 2017).

The lower cost of mobile equipment (compared to static devices) may allow for duplicate sets of equipment sampling at two or three locations, which may provide a greater understanding of the upwind, source, and downwind concentrations of air pollutants in real-time, (McKercher *et al.* 2017; Stacey 2019).

♦ 6.3.3) Air Pollution Monitoring Equipment.

The author is conscious of the limited use of primary data within the thesis. Whilst the author is of the opinion that primary air quality equipment provides a distinct opportunity for research of air quality phenomenon, the availability of access to the equipment, combined with the reluctance of third-party stakeholders to permit primary monitoring have unfortunately precluded its extensive use in this research. Fortunately, given the substantial volume and exceptional quality of secondary data, the author is not unduly concerned that this has had an adverse impact on the overall outcome of this thesis.

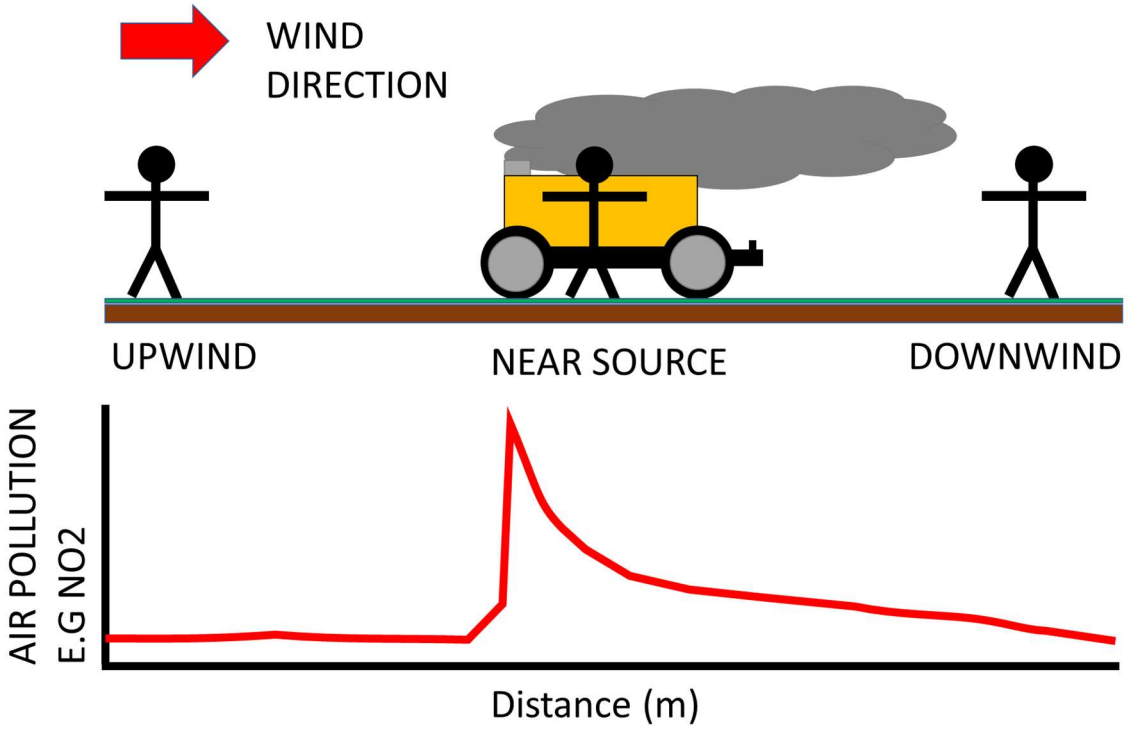

Figure 6.1. Showing the upwind, near source and downwind monitoring positions from a source of air pollution (in this case a Non-Road Diesel engine). The graph below the diagram shows air pollution e.g. "NO_2 levels" upwind, near source and downwind of the source of air pollution.

Source; Author – Grainger (2020)

The primary data analysis of air quality devices used in this thesis is principally found in Chapter 9, this equipment includes;

- MicroPEM™ $PM_{2.5}$ to PM_{10} Personal Exposure Monitor:
- MicroAetheleometer AE51 – Black Carbon Monitor:
- Palmes Diffusion Tubes (PDT's):

Further information on the air quality monitoring equipment used in primary research can be found in Supplementals 6.A and 6.B, appended to this chapter.

► 6.4) Secondary Data.

The secondary data used in this thesis provided a robust dataset for scholarly research and was analysed within several sections of the thesis. The secondary data sources outlined below are the most significant resources of data outside of peer-reviewed scientific journals.

♦ 6.4.1) Defra's UK Automatic Urban and Rural Network.

The AURN network (148 automatic urban and rural air quality monitoring stations) is used to determine compliance with the UK's Ambient Air Quality Directives, as shown in Figure 6.2 (Ricardo AEA, 2012).

Figure 6.2. The figure shows the locations of the AURN network operating systems and the level of the DAQI index (UK Air pollution health banding) from across the United Kingdom on the 12th December 2019.

Source: Defra (2019), Google Earth (2018).

Only three monitoring stations were used in the AURN network during this research; these stations were: Glasgow Townhead, High Street, and Hope Street, which took readings of Nitrogen Oxides and its compounds (NO, NO_2, and NO_X), Particulate Matter ($PM_{2.5}$, PM_{10} and Black Carbon i.e. BC) and various meteorological data (Pressure, Temperature, Wind Speed, and Direction), (Ricardo AEA, 2012). All AURN data was available with a one-hour resolution under an open-access; creative commons licence. The data was downloaded from the Defra air quality website (https://uk-air.Defra.gov.uk/interactive-map). AURN data was used in Chapters 9 and 12.

♦ 6.4.2) Centre for Environmental Data Analysis Repository.

The Centre for Environmental Data Analysis (CEDA) data archive relates to a monitoring station for air quality and meteorological observations, approximately 350 metres to the west of the Preston New Road Unconventional Development Site. Chapter 13 analyses this data to deduce whether there were changes to the source of air pollution during the UNG development. The data resolution was at one-minute intervals and was available from the early months of 2016 to December 2018.

The monitoring station was specifically located to allow a comparative environmental baseline one year before the UNG development, and for ongoing research into the air quality during various stages of the UNG development, i.e. through construction, drilling, hydraulic fracking and (in the future) during well testing and production.

The specific datasets which were used as part of this thesis were from the Little Plumpton Monitoring Station (Purvis 2018), and included;

- **Surface meteorological measurements;** from the 27th January 2016,
- **Air quality measurements;** from the 1st February 2016,

The data is subject to an open-access licence, subject to the following citation;

> *"These data were produced by the Universities of Manchester and York (National Centre for Atmospheric Science) in collaboration with the British Geological Survey and partners from the Universities of Birmingham, Bristol, and Liverpool and Public Health England, undertaking a project grant-funded by the Department for Energy & Climate Change (DECC), 2015-2016. Science-based environmental baseline monitoring associated with shale gas development in the Vale of Pickering, Yorkshire (including supplementary air quality monitoring in Lancashire)", led by the British Geological Survey"*
> **Source** - Purvis (2018, 2019).

♦ 6.4.3) UK Planning & Environmental Permitting Documents.

In the UK, onshore oil and gas developments are subject to strict environmental permitting and planning requirements (ARUP Group 2014; Short and Szolucha 2016). Fulfilling such requirements generates volumes of literary material and targeted investigative reports (ARUP Group 2014; Cuadrilla Resources 2014a; Lancashire CC 2019).

Of particular relevance to this thesis were;

■ A). Environmental Impact Assessments (EIA).

An EIA analyses the environmental consequences of a project on the built, social and natural environment (Carroll *et al.* 2019). A detailed EIA was undertaken on the Preston New Road Unconventional Natural Gas Development Site in 2014 (ARUP Group 2014). The body of the EIA was a relatively summative description for a non-specialist reader Carroll *et al.* 2019). Within the EIA's Appendices were a series of detailed investigation reports, which included; Appendices A (Figures/Plans), F (Air Quality), and R (Traffic) (ARUP Group 2014).

■ B). Waste Management Plans.

The UK has strict legislation surrounding waste management (Jones and Comfort, 2018; Gálvez-Martos *et al.* 2018). A waste management plan is required on most industrial sites (Gálvez-Martos 2018). Waste management plans contain detailed information on the type, quantities, environmental and human health aspects of each chemical and compound, which is anticipated to become waste (Cuadrilla Bowland Limited 2014a, b, c, Island Gas Energy PLC 2014, 2016a, b; Horse Hill Developments Ltd 2017; Kimmeridge Oil and Gas Ltd 2017). These plans need to be agreed upon by Defra and are consequently made publicly available from the Environment Agency (Jones and Comfort 2018; Gálvez-Martos *et al.* 2018).

■ C). Department Vehicle Licencing Agency (DVLA).

The DVLA holds over 48 million records for vehicles in the UK and EU and forms the ANPR database (i.e. UK's Police Service's Automatic Number Plate Recognition dataset) (UK DVLA 2019). However, many of these records are also available to the general public under 'Regulation 27 of the Road Vehicle (Registration and Licencing) Regulations 2002' (UK DfT 2002). Under these regulations, a data series of 30 anonymised fields are available from the DVLA to the general public upon request (UK DVLA 2019). The released data allows for a number plate search of any UK registered vehicle, including the; make, model, fuel type, engine, and registration year (UK DVLA 2019). Estimation of the vehicle's emission standards is possible with a comparison of the model registration year against the UK rollout of the European Emission Standards, (NAEI 2018; McInally 2019).

►6.5) Computer Modelling.

Computer modelling was devised during the Second World War and has been a staple of scientific research ever since (US DOE LANL 2017). Computer modelling involves a series of functions entered into a computer program forming a mathematical model which runs computations accordingly. These simulations can be run on desktop computers (as per this research), networks or super-computers, (Schmitz *et al.* 2019). Should enough calculations be performed, a complex simulation can be created. Such models can help explore and gain new insights by estimating conditions which may be prohibitively complex or expensive to conduct in the real-world, (Lee *et al.* 2017).

♦ 6.5.1) Spreadsheet-Based Modelling.

An entry-level but useful application for computer analysis is a spreadsheet, which allows for simple 'number crunching' of mathematical information. Much of this PhD research featured the spreadsheet application Microsoft Excel 2016 (version 16.0.6769.2017). As of 2017, Microsoft Excel comes with a range of 474 inbuilt functions, which can be extended through macroinstructions (Macro's) inside of the program, (Microsoft 2016). The limits of Excel, however, lie in some of its strengths, in that the program is constrained to 1,048,576 rows by 16,384 columns and only allows for relatively simple mathematical-statistical analysis (Microsoft 2016).

♦ 6.5.2) Programming (R Studio and Tools, i.e. OpenAir).

The researcher used statistical computing where advanced data analysis was necessary to analyse the data statistically and graphically. The programming language in this thesis was "R", which was developed by the 'R Foundation for Statistical Computing' and was released under a Public Release Licence (Freeware). The R environment was accessed through "R Studio" (a computer interface) which allowed for a graphical representation of data.

The software edition used in this thesis was the "Great Truth" (version 3.5.3 released on the 11th March 2019), as this was the most contemporary edition available at the time of data analysis for Chapters 12 and 13. In addition to the R environment, a range of packages (collection of data analysis tools and pre-built program scripts) was available for download through the program. The main programming package used in this thesis was OpenAir.

Openair provides a series of “open-source tools for the analysis of air pollution”, including the capacity to generate complex graphical representations of the atmospheric environment (Carslaw and Ropkins 2012). Specifically, the tools include a wide range of increasingly complex algorithms and techniques including wind direction, temporal normalisation of data, pollution roses, polar projections of air pollutants, (Carslaw and Ropkins 2012). Each of the algorithms used in this thesis are discussed in the corresponding chapter they are used in. Further information on the OpenAir Project can be found from Carslaw and Ropkins (2012) as well as the project’s website; https://davidcarslaw.github.io/openair.

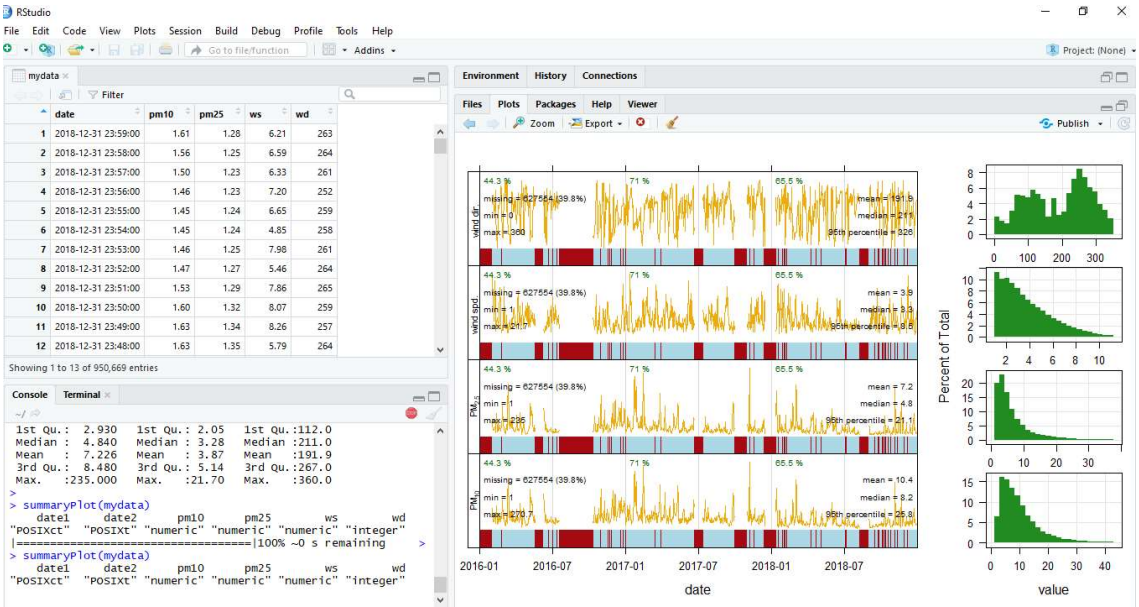

Figure 6.3. Shows a print screen of the RStudio program with the OpenAir toolset installed. Shown in the graphs are PM_{10}, $PM_{2.5}$, Wind Speed and Direction information from an air pollution monitoring station between 2016 and the end of 2018.

Source; Author – Grainger (2020)

Modified From: R Studio (2019) and Carslaw *et al.* (2019).

► 6.6) Conclusion.

Many methods are used in this thesis to produce a contribution to air quality research. The initial starting point for research should begin with a thorough "Desk Study" appraisal and review of available data. Research into these hazards can then be performed using one of two types of data analysis;

- **Primary Data;** focusing on real-time mobile monitoring of air pollutants with reference to more sophisticated static sites. This method arguably provides an estimation of receptor exposure and provides flexibility on the monitoring campaign, which is useful in industrial settings. Passive monitoring techniques through PDT tubes are also useful for longer-term deployment.

- **Secondary data:** when primary data cannot be gathered directly by the researcher (for whatever reason). Accessible data can allow researchers to make quantitative assessments of the air pollution anticipated under certain environmental conditions. A series of relevant publicly available databases were found, which included; open-access targeted monitoring station data, government databases and regulatory/planning documentation.

Whichever data strategy is used, there are many benefits of analysing this data through computer analysis. An investigation may begin with simple numerical analysis using spreadsheets and, where needed, leads to more complex techniques such as R Studio's OpenAir Package. By using such programming tools, researchers can create striking graphical representations of the data. It is often said "a picture is worth 1,000 words" and this seems to hold true with air quality research.

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6.8 Figure References

Figure 6.2. DEFRA. (2018) *Daily Air Quality Limits for the 26th December 2018* [overlain on Google Earth view of the United Kingdom].

Figure 6.3. Grainger, S. (2020) 'Screenshot of the authors RStudio Setup'. Incorporating the programs, "R" by R Foundation, "R Studio Version 1.2.5001)" by RStudio Inc, and "OpenAir" by Carslaw (2013).

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Supplemental 6.A:

Primary data collection equipment.

■ A) Air Sampling Backpack.

During air quality campaigns, mobile sampling equipment was securely housed within medium-sized (20 litres) backpacks, as shown in Figure 6.A.I. Connecting the monitoring equipment to the outside air was a single-walled Poly-Vinyl Chloride (PVC) tube. The tubes were coiled to provide a smooth (unobstructed) flow of air into the monitoring devices. A rain cowl was placed over the end of the PVC tube to help prevent macroscopic dust, debris, and moisture from entering the equipment.

The PVC tubes were secured with PVC tape to the backpack's straps to allow for more secure monitoring inside of the breathing range of the operator (within 30 cm of the operator's mouth).

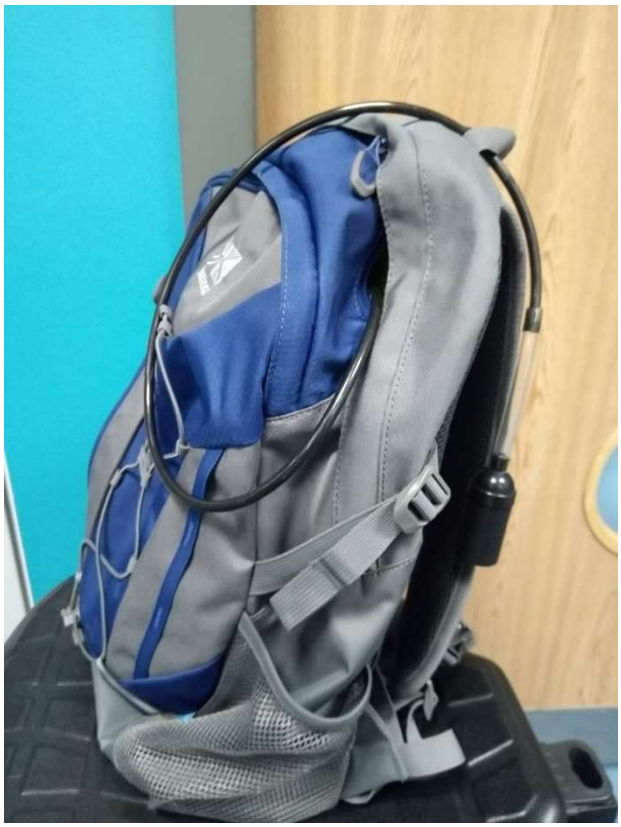

Figure 6.A.I Showing a medium sized backpack housing air quality equipment. In this case the equipment is MicroAethelometers, which monitored levels of black carbon. The inlets are fixed so that they are around the user's shoulder which is used to approximate the user's breathing zone. Inside the backpack are two 'bubble wrap' envelopes, which protect the air quality equipment from being mishandled, dropped or bashed together during air quality sampling.

Source; Author – Grainger (2020)

■ B) MicroPEM™ $PM_{2.5}$ to PM_{10} Personal Exposure Monitor.

The Research Triangle Institute's (RTI) "MicroPEM™ Personal Exposure Monitor" samples Particulate Matter (PM) in real-time (Figures 6.A.II and III). The MicroPEM can sample either $PM_{2.5}$ or PM_{10} (i.e. 2.5–10 μm in aerodynamic diameter) depending on which inlet is installed on the device (RTI International 2016; Zhang *et al.* 2018).

The device is lightweight and has many useful functions, including;

- **An inbuilt pump,** which is fully programmable and allows the user to specify and calibrate the pump rate of air through the instrument.
- **A nephelometer,** which performs laser scatter readings of air quality on a ten-second resolution, and deposits the particulate onto a filter within an internal filter cassette (RTI International 2016).
- **Internal filter cassette.** The PM laden filter allows for comparison against reference methods such as gravimetric analysis (RTI International 2016; Sloan *et al.* 2017).

According to RTI, the device has a precision and accuracy of greater than 90%, with a detection range of 1 to 10,000 mg/m^3, (RTI International 2016; Sloan *et al.* 2016; Lin *et al.* 2017). The author notes, however, significant discrepancies in the operational performance of MicroPEMs, which were also experienced by other researchers within the research group, on other projects. This problem particularly affected the inter-equipment precision (Relative Standard Deviation = 66.19% ±22%; based on four instruments) and accuracy (R_2 = 76.77% compared with a collocated TEOM at the AURN Glasgow Townhead Monitoring Station), (Sutherland and Grainger 2017; Sutherland *et al.* 2018). The author concurs with others who have identified a significant zero offset between 0 and 6 $\mu g/m^3$ at low concentrations, (Ezani 2017; Sutherland *et al.* 2018; Zhang *et al.* 2018).

Figure 6.A.II. Shows the MicroPEM when it has been fully prepared and is ready for monitoring of air quality. Note the black tape is used to secure it to the backpack seen in Figure 6.A.I.

Source; Author – Grainger (2020)

◊ I). Quality Control.

New alkaline batteries were placed into the MicroPEMs before each day of field monitoring to ensure that the devices had sufficient power for the study. Depending on the campaign's demands, a new PTFE (3 µm) particulate filter was placed inside of the MicroPEM's filter cassette (either daily or weekly) to prevent clogging of the filter and to allow subsequent analysis. The MicroPEM must be programmed before every campaign using the software 'MicroPEM Docking Station 2.0'. The program helps to calibrate the flow rate and nephelometer with the aid of external instruments.

These instruments include;

- A Mesa Labs Defender 530; personal air sampling pump calibrator which is shown in Figure 6.A.IV. The device measures the primary volumetric gas flow with a 99% certainty (5 ml/min), (MESA Labs 2007). The device undertook continuous flow rate measurements during the program cycle. The average flow rate set for the instrument was 0.50 l/min (average flow), with a designed maximum range of ±0.05 l/min. In field conditions, the MicroPEM's flow variation was around -0.03 ±0.04 l/min based on 17 days of monitoring (Sutherland and Grainger 2017; Sutherland *et al.* 2018). The instrument's flow rate was measured, shortly before and after the MicroPEM undertook field monitoring, by taking readings in the continuous mode, with an average of three cycles of the flow taken as the true flow rate.

Figure 6.A.III. Shows the Defender 530 flow calibration monitor. The yellow leak caps are removed during monitoring, and the devices inlet is placed at the top via AC tubing, whilst a Whatman filter is placed at the bottom of the device. The device is turned on for approximately 2 minutes, which allows for multiple readings to be taken. Two readings are taken of the flow rate, if they are not within around 0.001 litres/minute then further action is required.

Source; Author – Grainger (2020)

- A Whatman 3 µm HEPA (High-Efficiency Particulate Air) filter cassette was attached to the instrument's inlet valve. The filter should have eliminated much of the particulate in the incoming air, allowing the user to calibrate the device in a "clean" atmosphere. The nephelometer was offset by 2.9 µg/m^3 following the works of Lin 2017. Even with these corrections, the MicroPEM's reported level of accuracy was not always maintained as it suffers from 'baseline drift' at low concentrations (Lin *et al.* 2017; Zhang *et al.* 2018). The 'baseline drift' is a zero offset error wherein the instrument reads 3 to 6 µg/m^3 , even with no air passing through the HEPA filter, (Lin *et al.* 2017; Zhang *et al.* 2018). To correct for this error; the MicroPEMs were corrected by zeroing the instruments for at least 5 minutes before and after field deployment, with the HEPA filter cassette securely attached to the inlet of the MicroPEM. This calibrated zero allowed for the identification of the data offset, and for a correction factor (average offset value) to be applied. The correction factor allowed the background error to sum to around zero when this was subtracted from the results.

◊ II). Post-Processing.

The data was downloaded after each day of monitoring. The data was averaged using pivot tables within Microsoft Excel. The RSD or Relative Standard Deviation of duplicate devices was calculated to understand their variation. The RSD was plotted on a scatter graph and a linear trendline drawn to determine an R_2 value. However, the R_2 value only accounts for deviation on the Y-axis. Hence, the correction does not account for larger variations in either the X- or Y-axis (Masey 2018). Therefore, a method known as a Reduced Major Axis (RMA) regression was used during data analysis to correct for data errors on both the X- and Y-axis (Gillespie *et al.* 2017; Lin *et al.* 2017; Ezani *et al.* 2018). RMA correction improved the RSD of the data by ~7% (ranging from -2% to 22%); however, post-processing around 27% of the $PM_{2.5}$ and PM_{10} data became erroneously negative (Sutherland and Grainger 2017; Grainger *et al.* 2019).

■ C) MicroAetheleometer AE51 – BC Monitor.

The AethLabs MicroAetheleometer "MicroAeth" model AE51 (Figure 6.A.V) measures black carbon aerosol in real-time, (Cai *et al.* 2014; AethLabs 2016a, b; Good *et al.* 2017). This device operates an inbuilt pump which deposits aerosol onto a quartz membrane filter. The MicroAeth measures the absorption of the transmitted light through the filter (Ferrero *et al.* 2011; AethLabs 2016a; Good *et al.* 2017). The thicker and darker the deposit on the filter, the less opacity the filter has. A greater opacity increases the light's absorption and decreases the light reflectance. The decrease in reflectance of light returning from the filter is proportional to the BC deposited on the filter, and therefore the BC concentration (when the volumetric flow is considered), (Ferrero *et al.* 2011; AethLabs 2016a; Good *et al.* 2017).

The MicroAeth has a precision of around ±0.1 µg and an effective detection range between 0-1,000 BC µg/m^3, according to AethLabs (AethLabs 2016a, b). The instrument has a maximum resolution of 10 seconds, though a 1-minute resolution is a default, (Ferrero *et al.* 2011; AethLabs 2016a; Good *et al.* 2017).

The experiences of the author and their 'research group' suggest a good intra-instrument precision, but limited short-term accuracy vs reference analysers. The MicroAetheleometer inter-instrumental precision (2 devices over six studies for 28 days of monitoring) returned an average R_2 value of 0.87 (Masey 2018; Sutherland *et al.* 2018; Grainger *et al.* 2019). The MicroAeths also returned good hourly correlations (R_2 = 0.83 ±0.12) with reference analysers (Glasgow Townhead AURN), but this decreased with shorter time increments, e.g. the 5-minute accuracy (R_2) was 0.50 ±0.20 (Masey 2018; Grainger *et al.* 2019).

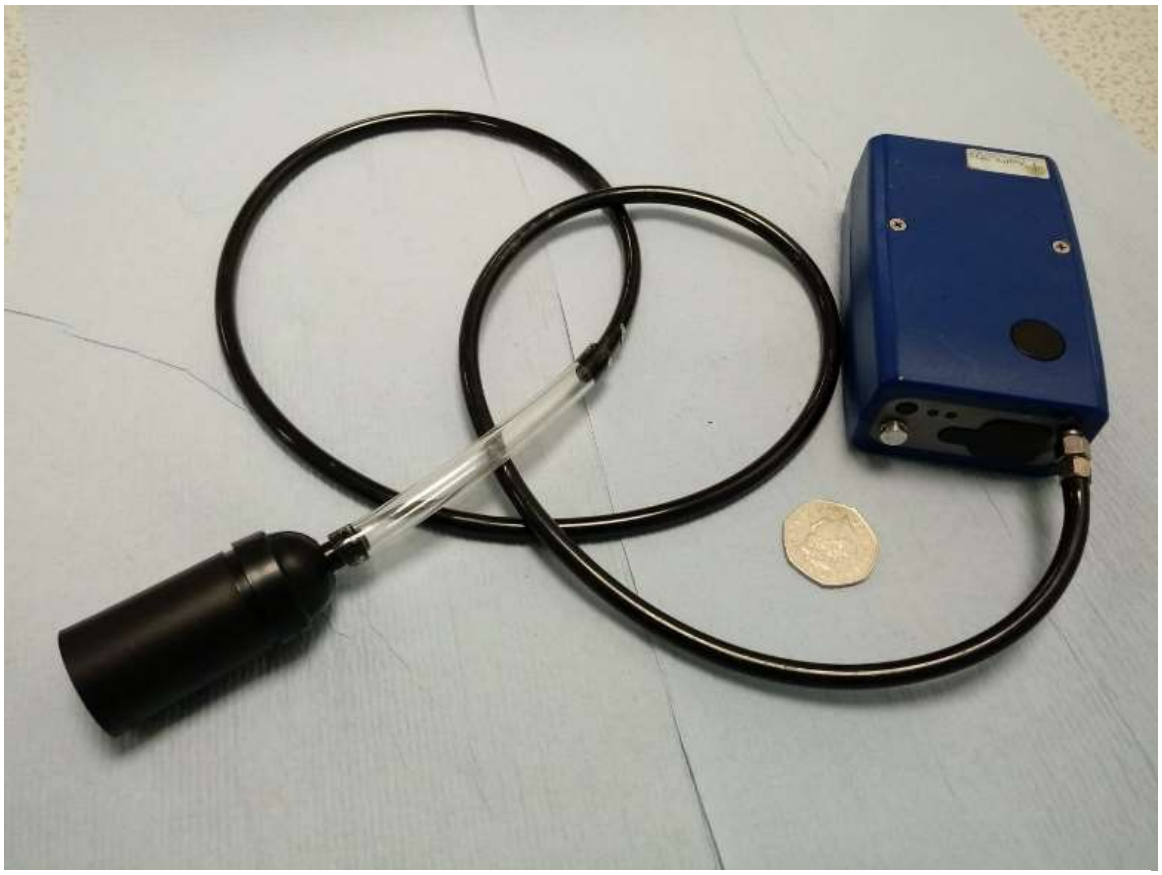

Figure 6.A.IV. Shows a MicroAeth unit which is ready to sample, with a rain cowl over the end of the tubing to help protect from macroscopic dust and unforeseen rainfall events.

Source; Author – Grainger (2020)

◊ I). Quality Control.

The MicroAeth's batteries were charged after each day of field monitoring. The device was calibrated, both in terms of its flow rate and offset. The calibration was performed as per the MicroPEM (i.e. using a Whatman filter and a Defender 530 personal air sampling pump calibrator, before and after each field deployment). The flow rate was very stable with 1 out of every 20 field sessions having a maximum variation of 0.01 l/m (though this could be because of other factors than the flow rate of the MicroAeth).

◊ II). Processing.

The data was downloaded at the end of each day of fieldwork through the MiceoAethCOM software (Figure 6.A.VI). The BC data, however, required post-processing to smooth and minimise a series of negative values within the dataset via an Optimised Noise Algorithm ONA (using the manufacture's software, i.e. AethLabs software), (Hagler *et al.* 2011; US EPA 2012; Cheng and Lin 2013). The ONA used the following equation:

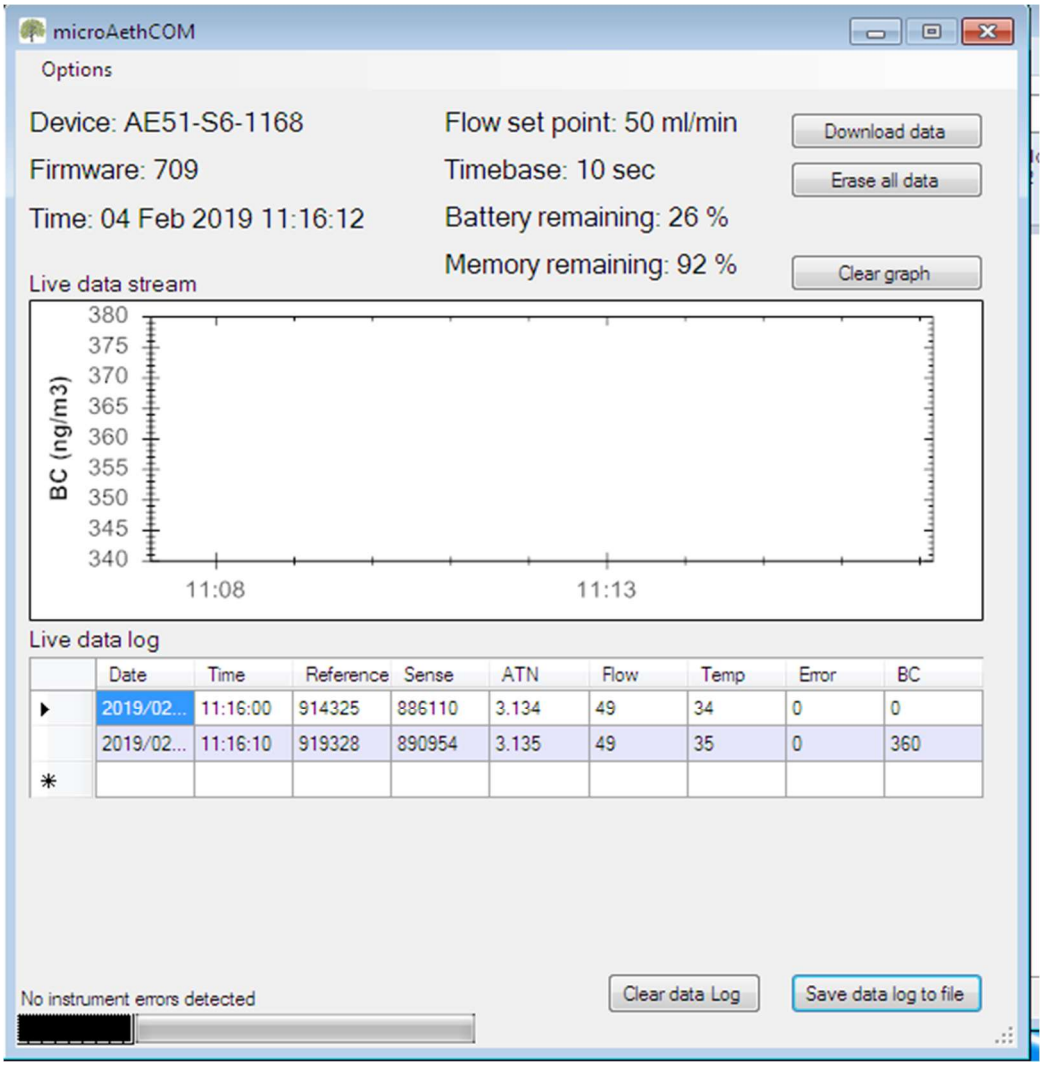

Figure 6.A.V. Shows the MiceoAethCOM program in operation with a blank MicroAeth device (AE51-S6-1168) attached. The program graphs the data for the analysist and allows for modification of the timebase and flow of the instrument.

Source: Grainger (2019), Aethlabs (2019).

Equation 6.A.I

$$\mathbf{BC} = \mathbf{BC_0}\ (\mathbf{0.88\ Tr} + \mathbf{0.12}) - \mathbf{1}$$

Where,

BC_0 = Optimised Noise Algorithm,

TR = $\mathrm{Exp}\ (-\frac{\mathrm{ATN}}{100})$

ATN = $100\ \times \ln\left(\frac{I}{I_0}\right) = -100\ \times \ln\ (T)$

I_0 = Light Intensity through Unloaded Filter,

I = Light Intensity through Loaded Filter,

T = Transmission.

Adjustment via the ONA method usually had only a minimal effect on hourly averaged data, but increased the 5-minute accuracy error (R_2) value between 3 to 5% (Masey 2018; Grainger *et al.* 2019).

■ D) Static Palmes Type Passive Diffusion Tubes

From the 1970s onwards, chemical passive (diffusive) samplers have been used for sampling NO_2 concentrations, (West 1978; Hauck 2010; Suchara, I Sucharová and Holá 2017). Passive sampling relies on unassisted (non-pumped) molecular diffusion of a target gas species through a diffusive material and onto/into an adsorbent chemical surface. While diffusive samplers were originally designed for occupational exposure, they have been used to monitor ambient air quality across the UK for over twenty years, (Campbell *et al.* 1994; Ricardo-AEA 2008; Martin *et al.* 2014; Masey *et al.* 2017; Defra 2018a).

The rate of diffusion of the target gas species (nitrogen dioxide), onto the diffuse surface, is controlled by Fick's Law, as per Equation 6.2 (Webb and Pruess 2003; AQEG 2004; Gilbert-Kawai and Wittenberg 2014).

Equation 6.A.II

$$F = D\frac{\pi d^2}{4l}$$

Where,

F = the sampling rate (m^3/sec),

D = the diffusion coefficient of NO_2 in air (cm^3/sec),

d = the diameter of the sampling device (cm),

l = the length of the sampling device (cm).

The most common passive sampler in the UK is the Palmes Diffusion Tube (PDT) which is approved for Local Air Quality Management (LAQM) by local authorities, (Ricardo-AEA 2003, 2006, 2008; Defra 2018b).

The PDT comprises a 7 cm long hollow plastic tube, which is initially capped at both ends, one end in grey and the other in white (as per Figure 6.A.VII and 6.A.VII). Within the grey end cap, there are three steel-mesh grids which are coated in TEA, i.e. Triethanolamine (an NO_2 sorbent chemical). The TEA can theoretically react with 100% of the ambient NO_2 in the tube, forming a Triethanolamine-nitrite complex. When an end cap is removed, ambient air can access the steel meshes coated in sorbent chemicals; this process stops when the cap is added at the end of the sampling campaign, (Ricardo-AEA 2003, 2006, 2008; AQEG 2004).

Figure 6.A.VI. Showing a photograph of the Glasgow High Street Monitoring Station's Palmes diffusion tubes during a wider 2017 study of Nitrogen Concentrations across Glasgow. The mural in the background was painted on the side of a series of terrace houses.

Source: Author, 2017. As premiered at the Images in Research Competition 2017.

Upon analysis, the TEA-Nitrite complex is dissolved in water and reacted with an azo-dye; N-(1-Naphthyl)ethylenediamine-sulphanilamide). The azo-dye reacts with the TEA-Nitrite complex with increasingly darker shades with higher concentrations of NO_2. A spectrophotometer analyses the colour of the sample. The samples are compared against a reference set (of a known NO_2 concentration), which enhances the accuracy of the test. The research method used to prepare, sample, and analyse the Palmes Tubes is featured in Supplement 6.B. However, the method is in general accordance with the UK NO_2 Diffusion Tube Network Instruction Manual.

In the experience of this author and their 'research group', the replicate precision error of Palmes tubes (field samples) is usually around 3%, although in one case this was erroneously poor at 29.48%, (Massey *et al.* 2018; Sutherland *et al.* 2018; Grainger *et al.* 2019). The accuracy of the Palmes tubes was compared with reference analysers at Glasgow Townhead and Glasgow Highstreet as part of ongoing research with the University of Strathclyde's 'air quality research group'. The accuracy of the Palmes tubes compared with samples from a Teledyne-API 200A NOx chemiluminescent analyser (over 50 samples) produced an R_2 value of between 20 and 64%.

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■ F) Figure References.

Figure 6.A.VI. MicroAethCOM. (2019) *A screenshot of the MicroAethCOM software which was developed by AethLabs.*

Figure 6.A.VII. Grainger, S. (2018) *A photograph of Palmes diffusion tubes with the St Mungo Mural photographed behind.* Glasgow, Scotland. Available at: TinyURL.com/y4r85jvz (Accessed: 28th August 2020). Note: Photo won the University of Strathclyde, Images in Research Competition for Air and Space in 2017.

END OF REFERENCES

Supplemental 6.B:

Standard operation of PDTs- Palmes Diffusion Tubes.

■ A) Preparation of Palmes Diffusion Tubes.

Diffusion tubes are passive sampling devices which comprise small tubes, containing a chemical reagent to absorb a target pollutant from the air, (Palmes *et al.* 1976; ADEME 2002; Ricardo-AEA 2003, 2006, 2008; BSI 2008, 2013). Here, the target chemical is NO_2, for which a triethanolamine (TEA) chemical compound is used as the sorbent chemical of NO_2, (ADEME 2002; Ricardo-AEA 2008; BSI 2013). In this research, a 1:1 solution of Acetone to TEA solution was mixed in a sterile laboratory-grade, volumetric glass flask (Ricardo-AEA 2008; BSI 2008, 2013). The solution was then poured into a glass beaker, where fine stainless steel meshes were placed into the Acetone-TEA solution, where they are thoroughly coated, (ADEME 2002; Ricardo-AEA 2008; BSI 2013). Once coated, the meshes were removed and allowed to dry before 2 of the meshes were placed into an opaque, dark grey rubber end cap, (ADEME 2002; Ricardo-AEA 2008; BSI 2013). A transparent 7 cm long tube was pushed onto the end cap to ensure a tight seal, and a light grey end cap was placed onto the other end of the tube, (Ricardo-AEA 2008; BSI 2013).

The assembled PDT tubes were placed into a polythene bag and sealed before being placed into a sealable plastic box, (ADEME 2002; Ricardo-AEA 2003, 2006, 2008; BSI 2013). The PDT tubes were then placed into a laboratory refrigerator along with QA/QC blanks, (ADEME 2002; Ricardo-AEA 2008; BSI 2013). This practice is in general accordance with the dipping method outlined within Box 2-1 of Defra's Diffusion Tubes for Ambient NO_2 Monitoring: Practical Guidance by Ricardo-AEA (2008) and in BS EN 16339:2013.

■ B) Deployment of Passive Sampling Devices.

The PDT tubes were deployed within kerbside environments (within 1 metre of the kerb), (Ricardo-AEA 2003, 2006, 2008; BSI 2008, 2013). PDT tubes were secured to street furniture with plastic cable ties; these PDT tubes were backed with foam. The PDT tubes were taped with electrical tape to help prevent accidental movement and vandalism. The foam also allowed the PDT tubes to be extended out from the structure. The devices were secured such that the cap with the meshes faced upwards, and efforts were made to make sure these tubes were not placed at an angle, (ADEME 2002; Ricardo-AEA 2008; BSI 2008, 2013). For quality assurance reasons, all PDT tubes were deployed in duplicate, i.e. two tubes were simultaneously exposed at each location (as per the Air Pollution Research Group Policy), (ADEME 2002; Ricardo-AEA 2008; BSI 2008, 2013).

The precise time when the temporary end cap was removed from the device was recorded, to the nearest second, using a cellular phone. The time when the end cap was placed back onto the device was also recorded, (ADEME 2002; Ricardo-AEA 2008; BSI 2008, 2013). The PDT tubes were placed back inside a plastic bag, which itself was placed inside a plastic sealable container (BSI 2013). Transport blanks were always taken into the field whenever the PDT tubes were brought to, or came back from, the field (ADEME 2002; Ricardo-AEA 2008; BSI 2008, 2013).

The PDT tubes were brought back from the field and placed in the refrigerator until analysis could be performed, (ADEME 2002; Ricardo-AEA 2008; BSI 2008, 2013).

■ C) Analysis of Passive Sampling Devices.

The method used in this research was colourimetry by the manual method, outlined within BS EN 16339; 2013 and Defra's Diffusion Tubes for Ambient NO_2 Monitoring: Practical Guidance, (ADEME 2002; Ricardo-AEA 2008; BSI 2013). This method extracts the TEA-Nitrate compounds into deionised water as free nitrate ions.

The method calls for two solutions, a sulphanilamide and a NEDA based solution, to be added to the sample, which reacts with the nitrate ions to form a pink azo-dye with a peak absorbance on a spectrophotometer at 540 nm, (ADEME 2002; Ricardo-AEA 2008; BSI 2013).

The intensity of the colour of the dye is linearly related to the mass of nitrate in the sample, (ADEME 2002; Ricardo-AEA 2008; Masey *et al.* 2017; BSI 2013). When compared to test solutions, the differences can be calculated between the calibration samples of a known nitrate concentration and the field measurements, (ADEME 2002; Ricardo-AEA 2008; BSI 2013).

The first step in the analysis, i.e. preparing the PDT tubes, creates a set of stock standards, according to boxes 4-3 and 4-6 of the Defra guidance, (ADEME 2002; Ricardo-AEA 2008; BSI 2013).

These stock standards include;

- A sodium nitrate stock standard made from 1 g/l sodium nitrate in deionised water.
- A sulphanilamide: water: phosphoric acid solution, with a 1-part sulphanilamide to 30 parts deionised water and 2.5 parts of phosphoric acid, with the solution being placed into a dark glass vessel.
- N-(1-naphthyl) ethylenediamine dihydrochloride (NEDA): Water solution, with a concentration of 1-part NEDA to 43 parts deionised water.

With a stock standard prepared, a series of 6 nitrate calibration standards were prepared, (ADEME 2002; Ricardo-AEA 2008; BSI 2013). These standard solutions contain between 0 and 120 ul of the sodium nitrate solution, which corresponds to between 0 and 6 ug of nitrate as shown in table 1, (ADEME 2002; Ricardo-AEA 2008; BSI 2013). Lastly, 10 ml of water was added to the calibration standards at the same time as the PDT meshes, (ADEME 2002; Ricardo-AEA 2008; BSI 2013).

Table 6.B.I. Shows the sodium nitrate concentrations in µL per calibration standard vs the concentration of nitrate in each calibration standard based on the concentration of sodium in sodium nitrate.

Sodium Nitrate Solution		Nitrate Concentration in µg
ID.	Concentration of solution to water in µL.	
A	120	6.00
B	90	4.50
C	60	3.00
D	30	1.50
E	15	0.75
F	0	0.00

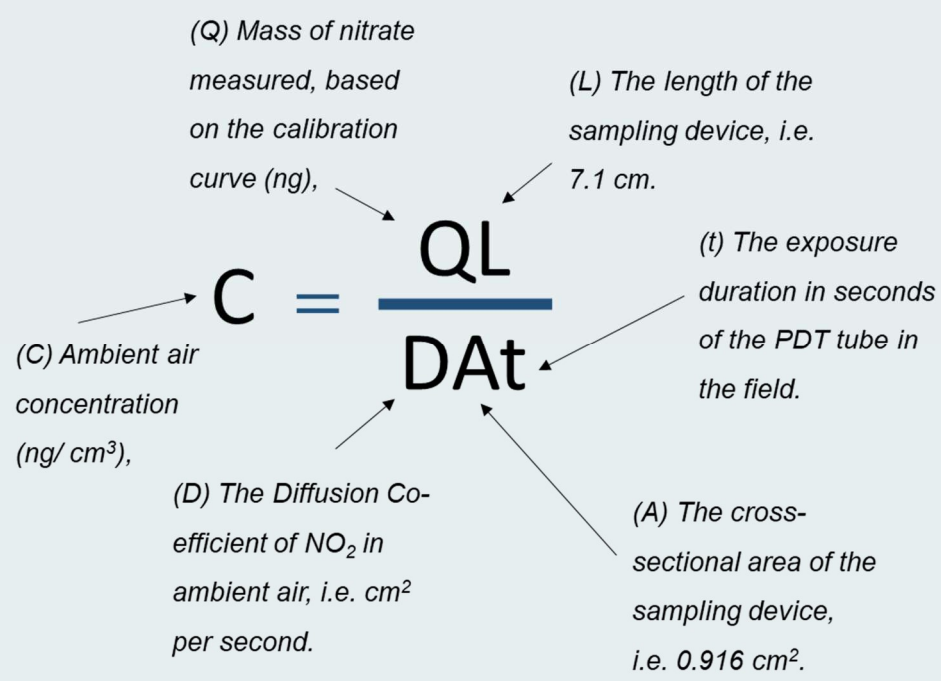
Any signs of foreign contamination, such as spiders' webs, were carefully removed from the Palmes tubes before analysis, and a note was taken of the affected tubes, (ADEME 2002; Ricardo-AEA 2008; BSI 2013).
The PDT tubes were disassembled, and the TEA meshes were placed into small glass vials. Sterile ultrapure water (1.5 ml) was added to the vials, and the vials were sealed and shaken for 3 minutes, before being left to sit for a further 27 minutes (in-house method). At the end of this 30 minutes, 1.5 ml of Sulphanilamide solution was added to the vials, followed by 0.15 ml of NEDA solution, (ADEME 2002; Ricardo-AEA 2008; BSI 2013).

After the solutions had been added to the sample, the samples were briefly shaken and left for 30 minutes to allow the solutions to develop a strong pink colour (an azo-dye), (ADEME 2002; Ricardo-AEA 2008; BSI 2013). After the 30 minutes, the dye was transferred into cuvettes for analysis with a spectrophotometer. The standard equivalent to around 0.00 µg Nitrate, was placed into the blank space of a dual-beam spectrophotometer (ensuring that the sample had not taken on any colour), (ADEME 2002; Ricardo-AEA 2008; BSI 2013; Masey *et al.* 2017).

The absorbance of all the samples, including the blanks and calibrations, was taken with a wavelength of 540 nm, (AASQA Working Group 2002; AEA Energy and Environment 2008; Masey *et al.* 2017; BSI 2013). The absorbance value of the samples was noted. Once all samples had been recorded, the samples were tested a second time. Where they differed, a third reading was taken. An average of the three readings was calculated as the determinant (BSI 2013; Masey *et al.* 2017).

A calibration curve of the average readings of the calibration standards B-F was plotted on a calibration graph, from which the ambient concentration of NO_2 was measured using Equation 6.B.I, (ADEME 2002; Ricardo-AEA 2003, 2006, 2008; BSI 2013; Masey *et al.* 2017)

Equation 6.B.1.



Where,

C = ambient air concentration (ng/ cm^3),

Q = mass of nitrate measured, based on the calibration curve (ng),

L = the length of the sampling device, i.e. 7.1 cm.

D = the Diffusion Co-efficient of NO_2 in ambient air, i.e. cm^2 per second.

A = the cross-sectional area of the sampling device, i.e. 0.916 cm^2.

t = the exposure duration of the PDT tube in the field.

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CHAPTER 7:

Exposure to Drilling Mud as PM_{10} to personnel on Petroleum Drilling Rigs in the UK.

"Drilling is risky because finding oil is only half the job.
The real challenge is finding the money to pump the oil".

Tahl Raz (1947 to Present)

Abstract: Drilling muds are liquid slurries circulated through a wellbore to remove rock cuttings from the borehole. These fluids are used throughout the exploration drilling stage, principally within the petroleum drilling industry. Drilling muds are essential to modern drilling processes. During drilling, a significant volume of fluid is pumped underground into the well and returned to the surface and cleaned through a series of open and enclosed systems (Mud Circulation System). There is a significant potential for petroleum workers to become exposed and potentially suffer health effects because of drilling mud exposure. This study aims to find the major sources of PM_{10} on petroleum wells and quantify the levels of exposure and health hazard associated with drilling mud on petroleum rigs. A literature search was performed, which included all available materials which contained static or mobile concentrations of PM_{10} or oil mist within the UK or international petroleum drilling sites. The study predicts the total PM_{10} by estimating the combined impact of both solid PM and oil mist, by assuming that the liquid phase is inert it is also possible to estimate PM_{10} concentrations when using water-based muds. Using this information, the study also identifies the setting of the main drilling mud exposure areas on an onshore oil and gas rig. The GHS (Globally Harmonised System) is used to determine the level of respiratory hazard from mixtures and individual chemicals on the known chemical formulations of drilling muds, onshore within the United Kingdom. The study finds that the risk to employees is lower than expected. Although many mud classifications used in water-based drilling muds are labelled as Category 2 (moderate) hazards, several are unclassified mixtures. Unsurprisingly all the oil-based drilling muds' chemical mixtures used in drilling mud in the UK are classified as a Category 1 (serious) hazard to the respiratory system. Silica exposure may also pose a risk to employees exposed to oil-based muds.

► 7.0) Introduction.

Particulate Matter (PM) is a major occupational health hazard with 652 people dying annually in the UK from pneumoconiosis alone (a type of disease related to the infilling of the lung structures by fine particulate), (Barber and Fishwick 2020). Exposure to airborne PM can lead to a wide range of other occupational respiratory diseases, including Chronic Obstructive Pulmonary Disease (COPD), asthma and lung cancer (HSE 2019). While occupational diseases often take years to develop, some diseases can present acutely following considerable exposures to air pollutants (such as PM), (Barber and Fishwick 2020).

Drilling muds are vital to modern drilling operations (Bridges and Robertson 2020). The earliest systems used water to remove cuttings. Drilling mud engineers soon found that chemicals added to the water enhanced drilling performance (Bridges and Robertson 2020). Today, drilling muds serve a much more complex role than simple hole cleaning. In the UK offshore, around 20 different chemicals are needed to make effective drilling mud (HSE 1999). Modern onshore drilling muds are expected to fulfil a variety of tasks, these include:

- The removal and suspension of drill cuttings.
- Cooling of the drill bit and drill string.
- Delivering the hydraulic rotary power to the drill string.
- Forming a barrier for the well control system (preventing the filtration to, damage to, or pressure loss inside: the formation).
- Constant geophysical properties (for logging of the well).

The approximate chemistry of drilling mud is formulated in the initial planning stages of the well development (ARUP 2014; Bridges and Robertson 2020). Importantly, there are two primary types of drilling muds within the UK petroleum industry; these are Water-Based Muds (WBM) and Oil-Based Muds (OBM). These two types of drilling mud are outlined below;

- WBM; or 'Water-based Mud' has a water-based "carrier" and "wetting phase", (Bridges and Robinson 2020). The water can be freshwater, saltwater, seawater, or mineral-enhanced water (e.g. lime or potassium-rich), (Bridges and Robinson 2020). Several other additives are added to the base to enhance its properties, such as sodium hydroxide, (HSE 1999; Bridges and Robinson 2020).

- OBM; or 'Oil-Based Muds' have a synthetic fluid base (Bridges and Robinson 2020). There are three subtypes of oil-based mud: Group 1 muds high in total aromatic hydrocarbons (5 to 35%) such as diesel fuel base mud; Group 2 known as an LTOBM, i.e. 'Low Toxicity Oil Based Muds' (0.5 to 5% total aromatics) and Group 3 (highly refined) mineral oil with total aromatics below 0.5%, (HSE 1999). Several other additives are also added to OBM such as lignites, barites, acids, and alkalis, (HSE 1999).

In the UK, WBMs are typically used for the first several hundred metres of drilling and around sensitive aquifers, after which the muds are swapped out with LTOBMs (ARUP 2014). Corrections are made to the drilling mud to maintain the specification, or when encountering unexpected ground conditions (Bridges and Robertson 2020). Drilling operations require complex infrastructure in which mud is stored, prepared, pumped, cleaned, and hoses added and disconnected from drill-pipes (Bridges and Robertson 2020). One of the fundamental activities on a drilling rig includes the running in and breaking out of drill pipes from the wellbore (Bridges and Robertson 2020).

Safety should be the highest priority in the selection of drilling muds, as the failure of companies not to appreciate chemical hazards in petroleum

workers has resulted in the loss of life and limb, (White 2018). In the UK, the onshore UNG (Unconventional Natural Gas) environment appears to place a greater emphasis on protecting the environment over all other objectives e.g., the protection of occupational health, which is in stark contrast to the offshore regime (Cuadrilla Resources 2014a).

Drilling engineers and health and safety officers conduct comprehensive risk assessments of drilling muds continually over the drilling stage (White et al. 2019). However, the chemical hazard assessment is often just a qualitative assessment where the most damaging SDS (Material Safety Data Sheet) in the blend, is the overriding concern (White 2019). This assessment, however, is only valid when the chemical is in isolation, such as during the storage of the additive, and may prove dangerously inaccurate when considering the interaction of the drilling mud additives with other materials, especially when mixed and subjected to both heat and pressure (Broni-Bediako and Amorin 2010; HSE 2012).

♦ 7.0.1) Aim of this work.

This study aims to find the major sources of PM_{10} (Particulate Matter with an aerodynamic diameter of ≤10 μm) at UK based petroleum well sites and quantify the levels of exposure and health risks associated with drilling mud in these areas. A literature search was performed to determine area exposures of air pollution on the drilling rig, which included all the relevant material relating to PM_{10} or oil mist exposure concentrations to workers on petroleum sites worldwide.

Only 11 academic papers were found, which presented concentrations of PM_{10} on petroleum sites. Of these studies, most focused on a subcomponent of PM_{10} - "oil mists" (liquid oil droplets less than ten microns in aerodynamic diameter). However, 'oil mist' lacks comprehensive epidemiological health toxicity data. Given the lack of epidemiological research on oil mist exposure, very little is known about the health effects of oil mist, whereas PM_{10} has been intensively studied (Google 2020a, 2020b).

Given the lack of health data, this paper therefore estimates the total level of $PM_{10,}$ including oil mists on petroleum drilling sites from LTOBM by adding the solid and liquid fraction of PM_{10} together to form a total PM_{10} value (which has longstanding robust toxicological and epidemiological data).

There was also a lack of exposure data on drilling sites using Water Based Drilling Mud (WBM), and this was estimated by using the solid PM_{10} fraction as a substitute value for the predicted PM_{10} concentration. The oil mist (liquid) fraction was discarded as WBM steam would be comprised of water (with dissolved solids). A major contaminant in WBM additives is silica, which can cause silicosis (pneumoconiosis) in workers chronically exposed to airborne PM, (Hansen *et al.* 1991). By multiplying the area exposure by the estimated concentration of silica in the air, it was possible to compare the risk of developing silicosis with coal miners' (a well-researched) occupation, to determine a quantitative indication of risk, (HSE 2002).

Using this information it was possible to assess chemical hazards associated with the drilling muds following the United Nations: Globally Harmonised System of Classification and Labelling of Chemicals (GHS) (UNECE 2019). This scheme is a United Nations method, which allows for the quantitative classification of the damage potential of materials into the human respiratory system. Though designed for shipping, the scheme is especially useful as it relies on the information held within publicly available Material Safety Data Sheets (SDS). In the UK the Environment Agency insists that all chemicals used in oil and gas are disclosed within environmental disclosures. The drilling mud disclosures, allow for the composition (recipe) of drilling muds to be determined. Using the composition of the UK onshore drilling muds and the associated SDS information, it is possible to quantify the level of risk according to the GHS.

A discussion of the potential human health implications of the respiratory hazards is also performed. It was found that LTOBM (Low Toxicity Oil Based Muds) are highly toxic to the human respiratory system, presenting a GHS Class 1; Aspiration and Respiratory sensitisation, while, WBM (Water-Based Muds) were inherently less toxic, posing a Class 2 hazard.

► 7.1) Mud Circulation System.

The Mud Circulation System (MCS) is one of the major operating systems of a drilling rig (Bridges and Robinson 2020). Figure 7.1 shows the key parts of a drilling rig's MCS, including the mud tanks, rotary hose, shale shakers, and various mud cleaning equipment as described in Chapter 4 of this thesis.

The MCS begins by adding a base OBM or WBM and other additives to supply the necessary ingredients for the mud specification via a chemical mixing room above the mud tanks (Bridges and Robinson 2020). The mud and additives are mixed using agitators with the base fluid in mud tanks. Once the drilling mud is thoroughly mixed, it travels from the mud tanks to a

mud pump, where the mud is pumped at high-pressure into the rotary hose (Bridges and Robinson 2020). The high-pressure mud enters the wellbore through the rotary hose and follows the drill string through to the drill bit. The mud emerges at high-pressure from a nozzle in the drill bit, causing hydraulic rotation of the drill bit and removing rock fragments.

The mud and rock fragments return to the surface under pressure in a gap within the wellbore, between the casing and the drill string, i.e. the annular space. Once the mud (laden with cuttings) returns to the surface, it passes through cleaning equipment, including, a shale shaker (a vibrating screen where larger rock fragments are removed) and a series of cyclones / centrifuges, which remove gas, sand, and silt (Bridges and Robinson 2020). The rock fragments, sand, and silt are discarded in open-topped waste containers and are disposed of as a hazardous waste (ARUP 2014). The cleaned mud re-enters the mud tank where it is reused. The mud is checked by the mud engineer throughout the process to ensure it continues to meet the mud specification (Bridges and Robinson 2020).

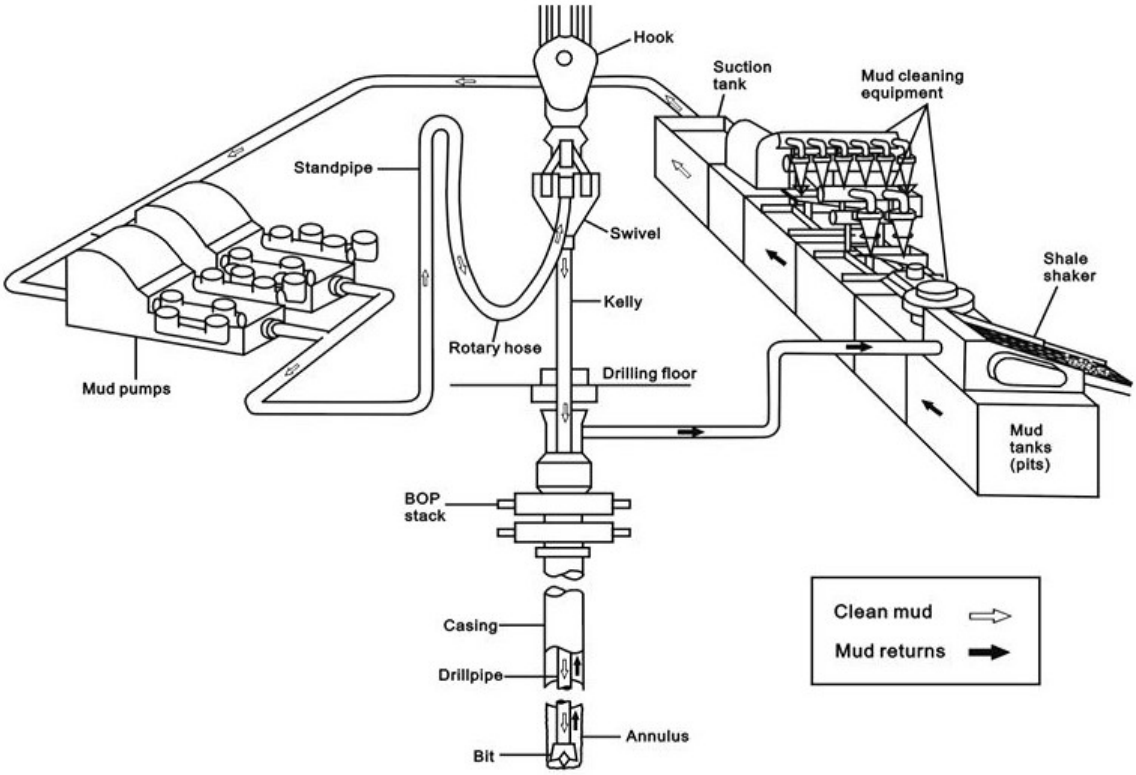


Figure 7.1. A Figure showing the main parts of the well circulatory system, showing the process from the mud tanks through the mud pump and down the wellbore via the rotary hose and drill pipe. Following the drill pipe, the mud returns through a series of cleaning apparatus including, the shale shaker and other mud cleaning equipment i.e. degassers, desander and desilter.

Source: EXLOG, 1993.

► 7.2) Drilling Mud - Pathway.

Drilling muds are exposed to elevated temperatures and pressures when the muds are used, agitated, and recycled, (Candler *et al.* 1996; Broni-Bediako and Amorin 2010). As drilling mud is circulated, it can generate vapours, aerosols, and dust through mechanical agitation (Broni-Bediako and Amorin 2010).

Steam is generated when 'warm' muds (heated via the geothermal gradient) return to the surface and contact 'cold' surface temperatures (Candler *et al.* 1996; Broni-Bediako and Amorin 2010). While airborne WBM particles only include dissolved chemicals and particles held in suspension, OBM steam is likely to comprise oil mist (fine Aromatic and Poly-Aromatic Hydrocarbons [PAH] spray), vapours and suspended particles (Candler *et al.* 1996; Broni-Bediako and Amorin 2010). LTOBMs have a low aromatic content. The chemicals can still be volatile and readily evaporate (Broni-Bediako and Amorin 2010). LTOBMs evaporate faster than more traditional 'Group One' OBMs (HSE 1999). The elevated temperatures and pressures found at depth may cause some organic compounds to break down and form more dangerous substances (HSE 1999; Broni-Bediako and Amorin 2010). OBMs are likely to metamorphose (via increased temperatures and pressures) and possibly generate dangerous substances such as PAH and benzene (Candler *et al.* 1996; Gardner 2003). The product Carbo-drill, for example, is a commonly used additive used in LTOBM formulations, which under metamorphosis may produce dangerous by-products including; sulphur oxides, halogenated compounds and metal oxides, (BHGE 2013).

► 7.3) Industrial Hygiene Standards.

There is no internationally recognised industrial hygiene standard for 'drilling mud' or even a consensus on which air pollutant should be monitored (HSE 2012, 2013). Environmental health monitoring for these substances is divided into two air pollutants. These are;

- PM_{10}, which is the traditional metric used within occupational health monitoring for airborne particulate matter.
- Oil mist, which is a hydrocarbon subcomponent of PM_{10}, which may cause health concerns at much lower concentrations than other PM_{10} species.

The exposure guidelines for both PM_{10} and oil mist are explored below in further detail with specific reference to the UK's health and safety policy.

♦ 7.3.1) Particulate Matter (PM_{10}).

In the UK, workplace exposure to PM_{10} falls under the Control of Substances Harmful to Health (COSHH) legislation and guidelines, (HSE 2012, 2013). Under COSHH, various chemicals and compounds have been assigned specific Workplace Exposure Limits (WEL). The UK's HSE has set an exposure limit on PM_{10} (inhalable dust) at 10 mg/m³ averaged over eight hours (HSE 2018), as outlined in Chapter 3.

♦ 7.3.2) Oil Mist.

Oil mist is a subcomponent of PM_{10} and is defined as aerosolised oil droplets in the size range 1-10 µm (HSE 2006, 2015). Incidence of occupational disease from oil mist has been recorded at concentrations less than 1 mg/m³. At such low concentrations, health interventions from oil mist exposure rarely succeed (HSE 2015; US NIOSH 2005). The UK's WEL has changed from 5 mg/m³ in the 1960s down to 3 mg/m³ in 2002, and recently to 1 mg/m^3, (HSE 2015). However, even the latest guideline has been withdrawn because of health effects being experienced under these concentrations (Schwarz *et al.* 2015). The HSE considers clean environments as having oil mist concentrations below 0.1 mg/m^3 (HSE 2015).

► 7.4) Respiratory Health Effects.

The most common health effects related to exposure to drilling muds are skin irritation and dermatitis. Skin conditions are the largest reported health impact of drilling mud exposure. However, it should be noted that 28.2% of all offshore petroleum sickbay consultations in the North Sea were associated with chronic and flu-like respiratory problems (HSE 2005). Some of this symptomology may be synonymous with heavy dust exposure (Barber and Fishwick 2020).

Many of the diseases related to occupational exposures of Particulate Matter are explored in-depth in Chapter 2 of this thesis.

♦ 7.4.1 Dust Exposure.

Chronic occupational exposure to PM_{10} may lead to the development of occupational asthma, allergenic rhinitis, work-related Chronic Obstructive Pulmonary Disease (COPD), chronic bronchitis, and pulmonary emphysema, even at low concentrations (Park 2019, HSE 2020). At higher concentrations, an occupational disease known as pneumoconiosis can occur. The disease is characterised by inflammation, pulmonary fibrosis, pleural thickening, pigmentation, and a range of other physiological changes (Thillai *et al.* 2017; Barber and Fishwick 2020). Pneumoconiosis can be caused by chronic exposure to asbestos (asbestosis), silica (silicosis), coal dust (coal miners lung) or even oil-shale (shalosis), (Barber and Fishwick 2020). A table showing the incidence of pneumoconiosis from exposure to silica 15 years post-exposure is found in Table 2.1 (Chapter 2).

In some people, the fibrosis can migrate into healthy tissues and continue post-exposure, causing a disease known as Progressive Massive Fibrosis (PMF). Further details about Pneumoconiosis and Progressive Massive Fibrosis can be found in Chapter 2; Subsection 1.1.B.III.

Concentrations of PM_{10} on oil rigs are undertaken either through monitoring personal exposure or from settled dust samples. Personal sampling, however, is far more important in workplace exposure, as certain tasks may be of low duration, but cause a potentially high exposure which may not necessarily increase static areawide concentrations, (Broni-Bediako and Amorin 2010). These high exposures, even if of low duration, are an important factor in ‘respiratory decline’, (Park 2019; Cormier and Lemière 2020).

7.4.2 Oil Mist Exposure

Oil mists and vapours are inherently toxic and can produce explosive vapours (HSE 1999, 2014B). However, the health effects associated with oil mist are largely unknown (US NRC 2008; HSE 2014B).

Oil mist exposure is also known to cause extrinsic allergic alveolitis (Thillai *et al* 2017; Ralston *et al.* 2018). The pathologic mechanisms behind extrinsic allergic alveolitis are poorly understood, but it is believed that the disease is related to continuous sensitisation processes (Type III Arthus reaction), (Miller *et al.* 2018; Ralston *et al.* 2018). In sensitised individuals, inhaled particles of oil mist may produce an allergic inflammatory response Thillai *et al.* 2017). The decline in respiratory health begins with influenza-like symptoms, malaise, pain, dry cough and breathlessness (without an audible wheeze), (Thillai *et al.* 2017). If exposure is not stopped, it can lead to irreversible pulmonary fibrosis, (Barber and Fishwick 2020). The development of occupational asthma and bronchitis have also been linked with oil mist exposure (Park 2019).

Oil mists can also be difficult to measure, as common techniques such as gravimetric analysis may be inaccurate due to oil mist volatilising on filters between sampling and analysis, (Broni-Bediako and Amorin 2010). As oil mist exposures are a subcomponent of $PM_{10,}$ and given oil mist's uncertain epidemiological profile, the author suggests that oil mist's exposure should only be a subcomponent of PM monitoring and should not be undertaken in isolation.

Because of this, this work will attempt to determine bulk PM_{10} concentrations using the available literature for oil mists and solid PM_{10} on petroleum development sites.

► 7.5) Exposure Sources of Drilling Mud.

Industrial hygiene measures can benefit from understanding the key locations and personnel who may be exposed to high levels of $PM_{7.}$ Exposure to dust is likely to be widespread across the drilling rig due to its ability to travel through the air from one area of a rig to another, (Broni-Bediako and Amorin 2010; Schwarz *et al.* 2015).

The highest PM_{10} concentrations are likely to be near dust sources, or where there are poor housekeeping practices (USCSB 2006). A review of the available literature and video graphic evidence from petroleum development rigs, indicates that the key sources of dust may include;

- Chemical Mixing and Storage Areas,
- Mud Tanks,
- Hydraulic Mud Pumps,
- Drilling Floor,
- Shale Shakers,
- Fine Drilling Mud Cleaning Apparatus (the desilter and de-sander),
- Waste Areas,
- Geological Laboratories.

These areas have been selected for a thorough literature review, which attempts to find and discuss (with a bias toward North Sea Operations) all known published works on PM_{10} and oil mist exposure concentrations.

♦ 7.5.1) Chemical Mixing and Storage.

Chemical mixing and storage are a source of dust and vapours across the manufacturing and petrochemical industries (Abbassi and Keshavarzi 2019). Workers can be exposed to chemicals through direct contact during handling

and mixing procedures (Figure 7.2.A and 2.B) or through the breakage of containers within storerooms (HSE 1996). Without regular housekeeping, fine dust can accumulate and become resuspended with draughts or vibration (USCSB 2006). The HSE recommend both respiratory protective equipment and Local Exhaust Ventilation (LEV) as good operational practice, as LEV can significantly reduce levels of dust within indoor areas and PPE protects workers who remain exposed (Gardener 2003; HSE 2011a, 2017)

Several authorities (e.g. Steinsvåg and Bratveit) reason that PM_{10} exposure within the sack room (storeroom for dry powders) may be around 7.5 - 15.0 mg/m^3 (5-10 times the WEL for Barium Sulphate). Steinsvåg confirms Gardener and Bratveit's suspicions, as his study found PM_{10} concentrations of up to 9.60, 0.74 and 0.18 mg/m^3 (Steinsvåg *et al.* 2006). Steinvåg also researched over 300 chemical mixing areas in the North Sea and gave an average PM_{10} exposure level of 2.8 mg/m^3, with the highest concentration reaching 27 mg/m^3, (Steinsvåg *et al.* 2006). Bratveit also recorded a total particulate concentration of 8.9 mg/m^3 during chemical mixing, with an estimated solid PM_{10} concentration of 0.18 mg/m^3 (Bratveit *et al.* 2009).

Four oil mist exposure studies found a median exposure of 3.89 mg/m^3, which ranged between 0.39 mg/m^3 to 21 mg/m^3, (Astleford *et al.* 1982; Gardner 2003; Steinsvåg *et al.* 2006; Bratveit *et al.* 2009). Additionally, several studies investigated personal exposure for staff working within the chemical mixing area, with average personal exposures to oil mist of 1.95 mg/m^3, which ranged between 1.0 mg/m^3 (detection limit) and 4.4 mg/m^3, (Astleford *et al.* 1982; Gardner 2003; Steinsvåg *et al.* 2006; Bratveit *et al.* 2009).

Figure 7.2.A and B: Shows American roughnecks (labourers) emptying sacks of Sodium Polyacrylate into the chemical mixer. Neither operator is using the appropriate personal protective equipment mandated in the SDS sheet for the product i.e. a respirator and gloves. The clouds which emerge from the bags during the opening and emptying of the chemicals may pose a respiratory (and dermal) hazard to workers.

Sources: **A.** Energy Training Resources, 2012 **B.** Patriot Energy and Royalties, 2015

(A) Reproduced courtesy of Energy Training Resources.

As part of this work, a number of drilling companies were contacted for information regarding drilling mud related HSE practices, Cuadrilla Resources issued the following statement in reply:

> *"The drilling mud was mainly pre-prepared by the supplier in the mud plant (remote from the site) and sent to the site as a whole mixed fluid in fully enclosed tankers. This removes the requirement for mixing on the wellsite. In the occasions where powdered chemicals were mixed on site, then appropriate PPE including goggles, masks and respirators were worn by the crew, depending on the chemicals utilised and the relevant COSHH assessments. Most of the chemicals added in this way were inert (e.g. calcium carbonate) and posed a low risk but the requirements of the SDS and COSHH assessments were in all cases followed scrupulously".*
> – Cuadrilla Resources (2020).

It is likely then that exposure to personnel might be much lower on Cuadrilla's Preston New Road site, and HSE practices may be much more effective given the non-routine nature of the tasks. That drilling mud is pre-mixed offsite is a novel concept in the petroleum industry and one which is quite advantageous to onsite HSE practices.

♦ 7.5.2) Mud Tanks.

Mud tanks store, agitate and prepare drilling mud for use, (Bridges and Robinson 2020). If chemicals are inappropriately mixed, then the drilling mud can undergo a violent and explosive reaction. These explosions may generate vapours and aerosolised spray, endangering employees (such as mud engineers and derrickhands), (HSE 2011b). Four papers studied stationary oil mist exposure around mud tanks and presented 11 "average" oil mist concentrations (Hansen *et al.* 1991; Simpson 2006; Steinsvåg *et al.* 2006; Murray *et al.* 2009).

The average oil mist exposure of these studies was 3.5 mg/m³ (ranging between 0.07 to 7.30 mg/m³). Three of these studies also used personal exposure monitoring for oil mists around the mud tanks, which gave concentrations of; 0.7, 0.7 and 2.15 mg/m³, (Simpson 2006; Steinsvåg *et al.* 2006; Murray *et al.* 2009). Hansen *et al.* (1991) also analysed total PM and found levels between 0.4 and 3.22 mg/m³ for an average of 0.89 mg/m³.

♦ 7.5.3) Hydraulic Mud Pumps.

Mud pumps (Figure 7.3) force drilling mud down the wellbore at high-pressure, turning the drill bit and eventually the mud makes its way back up to the surface through the annular space (Bridges and Robinson 2020). A series of chemical lines attach the mud tanks to the mud pumps and to the drill floor via the rotary hose. Disconnection of these hoses may cause leakage, which is anticipated to be a local source of airborne dust. Steinsvåg *et al.* 2006, undertook a study of oil mist levels on a North Sea rig and found concentrations of 1.46 mg/m^3 around the mud pumps.

Figure 7.3. Shows the location of a mud pump within a shipping container. Whilst shipping containers can contain mud pumps most of the mud pumps in the UK are open to the elements. However, should a mud pump be located inside a shelter, then there may be increased levels of air pollution, due to the pollutants becoming trapped. The mud pump is the lime green apparatus in the centre of the photograph.

Source: Predator Drilling LLC, 2016

♦ 7.5.4) Drilling Floor.

One of the most vital activities on the drilling rig floor is the adding and removal of casing (drill pipe). During drilling, as many as 12,000 metres of casing may need to be sunk at 10m intervals, (Bridges and Robinson 2020). Sometimes, the whole assembly needs to be removed and replaced at 10-metre intervals for the maintenance or replacement of the drill head Bridges and Robinson 2020).

The drill string and rotary hose are disconnected when adding or removing casing, which douses workers in a spray of drilling mud, as shown in Figure 7.4.A, (Broni-Bediako and Amorin 2010). Workers, by necessity, become muddy on the drill floor, which can saturate the rig operator's clothes (Broni-Bediako and Amorin 2010). Because the drill floor becomes so dirty, the floor must be routinely washed down by hoses as shown in Figure 7.4.B, which can spray fine particulate away from the rig floor, which can dry out and become resuspended.

Three studies investigated oil mist concentrations around the drill floor and had a combined average concentration of 24 mg/m³ ranging from 0.5 to 240 mg/m^3, (Davidson *et al.* 1998; Bratveit *et al.* 2009; Kirkhus *et al.* 2015). Individually, these studies had average readings of between 10 and 37 mg/m³, with maximum concentrations ranging from 200 to 240 mg/m³ (Davidson *et al.* 1998; Bratveit *et al.* 2009; Kirkhus *et al.* 2015).

Additionally, Davidson 1998, took five readings of Calcium and Iron on the drill floor from an airborne particulate filter. The levels of Calcium and Iron were 67 and 220 µg/m^3 on average, with maximum concentrations of 1100 mg/m^3 for calcium and 540 mg/m^3 for iron (Davidson *et al.* 1998). Davidson also suggests that clean mud comprises around 4.5% Iron and 1% Calcium, which may indicate average levels of PM_{10} dust of between 4.9 and 6.7 mg/m^3 (Davidson et *al.* 1998).

Figure 7.4.A. Shows several American petroleum drillers on the drill floor during the disconnection of the rotary hose with the drill string. There is an influx of drilling mud down onto the floor, splashing workers from the rotary hose. **Figure 7.4.B.** Shows a similar scene several minutes later following the re-connection of the drill pipe and workers are proceeding to spray down the rig. The drillers are covered in drilling mud i.e. their white T-shirts are dirtied, they do not have any respiratory protection, and only wear PPE to protect their heads, hands, and feet.

Source; Calculated Risk Films (2014).

Reproduced courtesy of Mr Reed Merschat owner of Calculated Risk Films.

♦ 7.5.5) Shale Shaker.

When connected to the rotary hose, the mud is pumped down the wellbore where it hydraulically rotates the drill bit, collecting and suspending drill cuttings before returning them to the surface. Once at the surface, the 'dirty mud' is passed through a vibrating mechanical screen known as a shale shaker (Figure 7.5), (Bridges and Robinson 2020). The shale shaker separates the drilling mud from the drill cuttings by allowing the fine mud to fall through a series of holes, while the larger particles are caught and slide down the screen into a chute which connects to a waste tank, (Bridges and Robinson 2020).

Frequent checks are undertaken at the shale shaker by the mud engineer, derrickhand, and geologist to ensure that the system is operating efficiently (Bridges and Robinson 2020). The shale shaker also requires cleaning with high-pressure water, monthly maintenance and replacement of mechanical parts by a mechanical engineer (motorman) (HSE 2011b).

The shale shaker vibrations can promote airborne sprays, mists, and vapours, (Broni-Bediako and Amorin 2010; HSE 2011b). These airborne particles can dirty the walls of the shale shaker housing (Cuadrilla Resources, 2017). The temperature difference between the geothermally heated mud and the colder surface (mid-latitude climate) temperatures, promotes the formation of mists and vapours, as seen in Figure 7.5 (Candler *et al.* 1996; Steinsvåg *et al.* 2006; Bratveit *et al.* 2009;). Seven studies (29 readings) were found which measured static oil mist exposures around shale shakers, (Astleford *et al.* 1982; Simpson 2006; Bratveit *et al.* 2009; Murray *et al.* 2009; Cubility US Ltd 2013; James *et al.* 2013; Kirkhus *et al.* 2015). The average oil mist concentrations around shale shakers were 1.26 mg/m^3 (ranging from 0.03 to 5.52 mg/m^3) though the median value was 0.51 mg/m^3, showing that the concentrations are highly variable from rig to rig.

Figure 7.5. Shows steam because of the contact of warm drilling mud in contact with cold (around freezing) outside air. The equipment in the foreground is a series of desanders as part of the drilling mud cleaning process. Remarkably similar equipment and practices are used in the UK. Usually, with higher temperatures steam is produced much less from this equipment, however this case was a notable contrast to the work undertaken by James *et al.* 2013.

Source: Madhouse116.

Two studies also undertook personal exposure monitoring to oil mist. giving an average personal exposure of 0.13 mg/m^3 (ranging from 0.05 to 0.40 mg/m^3) (Simpson 2006; Bratveit *et al.* 2009). Two other studies investigated solid PM_{10} concentrations, with average levels of 0.89 mg/m^3, ranging from 0.69 to 1.08 mg/m^3 (Hansen *et al.* 1991; Kirkhus *et al.* 2015).

♦ 7.5.6) Desilter and Desander.

UK drilling muds are recirculated several times for environmental reasons,which incidentally increases the particles held in suspension. These particles can be rich in heavy metals and radioactive isotopes (ARUP 2014; Bridges and Robinson 2020). The de-sander and the desilter are hydro-cyclones, responsible for removing and discarding silt and sand-sized particles into the waste stream (Cuadrilla 2017; Bridges and Robinson 2020).

James *et al.* 2013 was the only study which undertook oil mist monitoring around the cleaning apparatus. The study found average static readings of 0.05 mg/m^3, corresponding to low personal exposures of 0.04 and 0.05 mg/m^3 (James *et al.* 2013). However, the steam clouds in Figure 7.5 may indicate high variable concentrations of oil mist above their findings.

♦ 7.5.7) Removal of Drilling Mud (Waste Stream).

The waste from the mud cleaning systems is emptied into a gravity-fed waste tank (Caenn 2016; Bridges and Robinson 2020). These tanks are regularly left open, allowing volatiles to vent to atmosphere. Videos show that sometimes these waste tanks are emptied by labourers, or by mechanical excavators, generating contaminated dust clouds (Stirton 2011).

Waste is unlikely to be a significant source of dust offshore as operators pump the waste slurry into sealed containers on ships, and even historically they simply discharged the waste into cuttings piles on the seabed, (Siddique *et al.* 2017). Steinsvåg *et al.* 2006 undertook a study on an unusual offshore rig, which was not permitted to discharge slurry waste to the seabed or to ships. Steinsvåg found an oil mist concentration of 6.8 mg/m³ (N=81) for static exposure, with high personal exposures around 5.7 mg/m³ (N=161), (Steinsvåg *et al.* 2006).

Figure 7.6 A and B. Shows a worker levelling off the drill cuttings from the waste chute of the shale shaker, whilst the shale shaker was expelling cuttings. Figure 7.6.B shows an excavator removing fine wet drill cuttings from a waste tank and placing them inside of a tanker truck (off frame) to be disposed of.

Source: A. Madhouse116 (2011) **B.** M&O Partners (2014)
(B) Reproduced courtesy of Cubility on behalf of M&O Partners.

♦ 7.5.8) Geological and Laboratory Services.

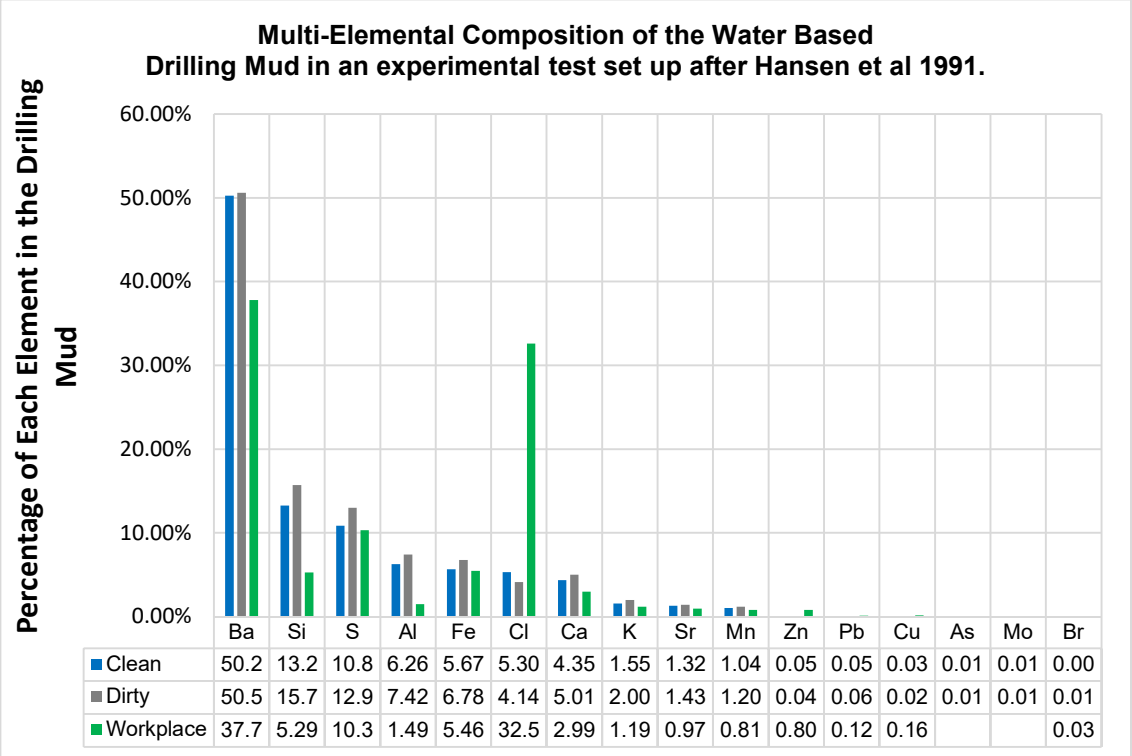
Samples of rock, drilling mud, and cuttings need to be taken for mud specification and geological appraisal (Bridges and Robinson 2020). However, the samples can become impregnated with drilling mud which can remain inside the rock even when cleaned (Bridges and Robertson 2020). Rock cuttings often need to be dried in the oven before the samples can be tested, which cause vapours and other trapped gases to escape into the logging and laboratory areas exposing personnel (Candler *et al.* 1996; Miller 2010). Compounding these hazards is that laboratory staff often do not use comprehensive forms of PPE to protect themselves as technicians often become complacent given the routine nature of the tasks and lack of immediate hazards in both Miller (2010) and the author's experience.

Steinsvåg *et al.* 2006, undertook four days of monitoring around an offshore petroleum laboratory and found oil mist levels of 1.31 mg/m^3. Miller 2010 also performed monitoring in four onshore geotechnical laboratories (N=51), wherein the concentrations ranged between 0.22 to 1.61 mg/m³, with 8-hour time-weighted personal monitoring results ranging between 0.28 to 2.11 mg/m³.

♦ 7.5.9) Elemental Composition of PM_{10} in WBM.

Hansen *et al.* 1991 undertook an elemental breakdown of the composition of the drilling mud during an experimental test setup. Hansen analysed the composition of alkane water-based drilling mud, when it was clean, dirty and in workplace conditions (near an air inlet) with a PIXE multi-element analyser (N=16), as shown in Figure 7.7.

Figure 7.7 shows that barium (most likely barium sulphate) contributed around 50% of the mass of airborne dust in both clean and dirty WBMs. However, near an air inlet (which provided fresh air) the contribution was reduced down to 38%. The second-most abundant element was silica, accounting for an airborne concentration of 13% when clean and 15% when dirty. However, near the inlet the concentration was reduced to 5%, potentially due to the density of silica in the air. Sulphur represented approximately 10% of the airborne dust by weight. Sulphur may have formed from sulphur dioxide in ambient air or within the pump. Other elements including aluminium, iron, chlorine, and calcium had an average composition between 5-7%.



	Ba	Si	S	Al	Fe	Cl	Ca	K	Sr	Mn	Zn	Pb	Cu	As	Mo	Br
Clean	50.2	13.2	10.8	6.26	5.67	5.30	4.35	1.55	1.32	1.04	0.05	0.05	0.03	0.01	0.01	0.00
Dirty	50.5	15.7	12.9	7.42	6.78	4.14	5.01	2.00	1.43	1.20	0.04	0.06	0.02	0.01	0.01	0.01
Workplace	37.7	5.29	10.3	1.49	5.46	32.5	2.99	1.19	0.97	0.81	0.80	0.12	0.16			0.03

Figure 7.7. Shows the elemental concentrations of clean, dirty and workplace drilling mud within the air of an active UNG site in the North Sea. These concentrations are in weight percent. The concentrations show that the drilling muds are high in Barium, Silica, Sulphur, Aluminium, Iron, Chlorine and Calcium. Chlorine has a very high concentration in workplace exposures. This is likely due to contamination by workplace cleaning products rich in Chlorine. **Source;** Author – Grainger (2020) **Data Source:** Hansen *et al.* 1991

► 7.6) Workers Potentially Exposed.

It is clear from the review that employees may be exposed to significant levels of air pollution from drilling mud (PM and oil mist) around petroleum development sites. The personnel considered to be at an especially high risk from occupational exposures are outlined in Table 7.1.

Table 7.1. Lists job roles which may be at a significant risk of exposure to drilling mud related PM and oil mists.

Occupation	Activities
Derrick hands	• Handling and mix chemicals in the sack room • Maintaining the specification of drilling muds • Performing specification testing on the drilling mud • Collecting mud samples • Involved with the handling of drilling pipe during the removal or addition of pipe into the wellbore
Mud Engineers	• Maintaining the specification of drilling muds • Performing specification testing on the drilling mud • Collecting mud samples • Monitor hydraulic pumps
Roughnecks	• Make pipe connections • Removal or addition of pipe to the wellbore • Conduct the majority of the activities on the rig floor • Collect core and cutting samples for the laboratories • Perform general housekeeping activities
Motormen	• Responsible for mechanical equipment • Change screens on the shale shakers • General maintenance and housekeeping of various parts of the rig.
Laboratory Workers	• Responsible for checking additives • Handle arisings and core • Perform geochemical and geotechnical testing on the samples.

♦ 7.6.1) PM_{10} Concentrations (Oil Mists and Solid PM).

After numerous discussions with health practitioners at several conferences, the author felt that an estimation of the PM_{10} hazard might prove useful in quantifying airborne hazards on drilling sites. Therefore, this section aims to predict the solid and liquid fraction of PM_{10} exposure on petroleum drilling sites using a correlation between PM and oil mist from the literature.

This correlation was required as a measure of air pollution at oil and gas sites for two prominent reasons;

- Little is known about the health impacts of oil mist exposure, with no clear occupational guideline or toxicological standard governing exposure (HSE 2014B). Contrastingly, the health ramifications of exposure to PM_{10} are well known (Google 2020a, 2020b).
- Very little is known about oil rigs which use WBM instead of LTOBM, but experts consider that exposure to WBM dust may pose a repertory hazard (Hansen *et al.* 1991).

Given the absence of data, it was felt that an approximation of the risk of pneumoconiosis to workers was an improvement over the limited existent knowledge. Approximation of the hazard could lead to increased awareness of airborne drilling mud hazards and potentially to future monitoring campaigns.

An estimation of WBM concentrations from LTOBMs is possible as the PM_{10} bulk composition of both LTOBM and WBM mud comprises a liquid and a solid fraction. Both water and oil are efficient carriers of particulate matter (Bridges and Robertson 2020). The liquid fraction of LTOBM's PM_{10} comprises Oil Mist and a minor proportion of liquid additives. However, for WBMs the liquid fraction is probably just water (which does not contribute to the PM_{10} concentration). Both WBMs and LTOBMs have a solid component, i.e. fine rock cuttings and powder additives, (Bridges and Robinson 2020).

The muds also have comparable concentrations of powered additives, undergoing similar processes and entraining arisings in the drilling mud (Bridges and Robertson 2020). Any discrepancy is likely to be comparable to the variable rig conditions, recirculation frequency and inter-project drilling mud composition.

Hansen *et al.* 1991 and Steinsvåg *et al.* 2006 undertook co-located solid PM_{10} and oil mist testing on clean and dirty LTOBMs (N=8). While two studies are insufficient to characterise hazards fully, it is possible to use these values as an approximation of PM_{10} levels on petroleum drilling rigs. The concentrations of solid PM_{10} vs Oil Mist were plotted on a scatter graph (Figure 7.8) for both dirty and clean LTOBMs. These studies had good agreement with an R_2 of 0.87 (polynomial) for clean mud and an R_2 of 0.96 (linear) for dirty mud. Given this high R_2 value, the relationship between solid PM_{10} and Oil Mist can be used to estimate the concentration of solid PM_{10} in the air.

The concentrations of oil mist (X-axis) found in the literature review were multiplied by either the clean, or dirty, drilling mud factor to calculate the solid PM_{10} fraction. Figure 7.8 shows that clean muds had a factor of $0.2378x^{0.87797}$; while dirty muds had a factor of 0.7886x+0.1372. The oil mist exposures were well researched on oil rigs, especially in contrast to PM_{10} or WBM exposures. By using the ratio of oil mist to solid $PM_{10,}$ it is possible to predict the solid PM_{10} component of LTOBMs, which is likely to be similar to the concentration of PM_{10} in WBM. However, oil mist exposure to personnel is poorly understood with very little research undertaken into the pollutant, with only 179 academic records from 2016 to 2020, according to Google Scholar (Google 2020a). However, PM_{10} has been intensely studied with 15,000 studies recorded in the same period (Google 2020b).

The average oil mist reading from each area of the drilling rig was calculated and used as the representative exposure value. The average oil mist concentration was multiplied by the dirty or clean mud ratio to determine the solid PM_{10} value. The solid PM_{10} for LTOBMs was added to the oil mist concentration to determine the total PM_{10} concentration for WBMs. The airborne PM_{10} concentration was equal to the solid PM_{10} fraction.

The concentration of each area of the drilling rig is estimated in Table 7.2 and illustrated in Figure 7.8 (A/B).

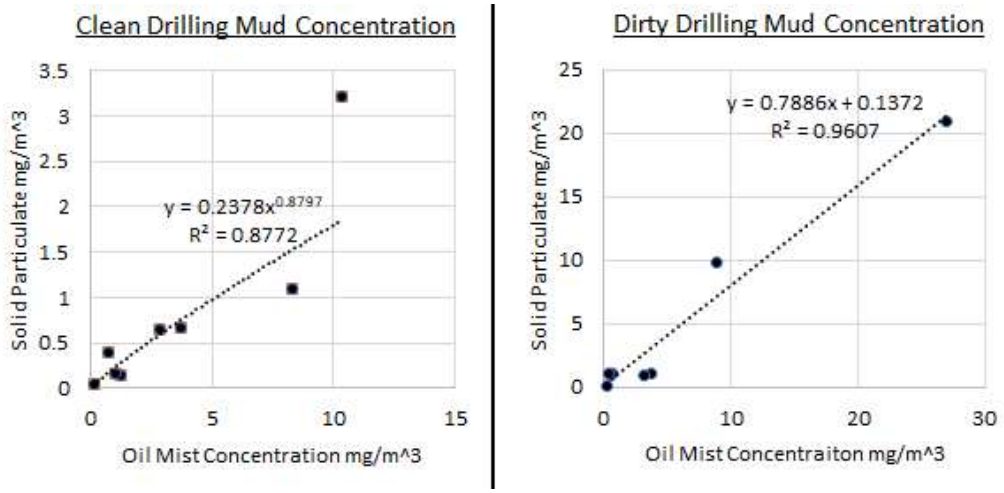


Figure 7.8.A Showing the clean drilling mud concentrations and **Figure 7.8.B**. the dirty drilling mud compositions, based on two studies which collected both Solid Particulate PM_{10} and oil mist. These initial graphs show a generally linear agreement between an increase in solid particulate and of oil mist exposures. Following these graphs, it is possible to estimate that 87.7% of clean drilling mud is comprised of oil mist and for dirty drilling mud this increases markedly to 96.1%. Therefore 12.3 and 3.9% of the drilling mud of the PM_{10} by weight might be oil mist.
Source; Author – Grainger (2020) and **Data Source:** Hansen, (1991); Steinsvåg, (2006).

Table 7.2. Shows the hypothesised water-based total PM_{10} from OBM and WBM using the literature and the estimates provided in Figure 7.8.

Drilling Mud type	Area	Hypothesised Water-based Total PM_{10} in mg/m^3		Hypothesised Oil-based Total PM_{10} in mg/m^3	
		Area	Personal	Area	Personal
Clean	Sack Room	0.51	0.70	2.46	3.50
	Mud Tanks	0.85	0.33	4.35	1.51
	Hydraulic Pumps	0.39	-	1.85	-
	Drilling Floor	4.63	-	28.63	-
Dirty	Shale Shakers	0.35	0.05	1.61	0.18
	Desilter and Desander	0.15	0.14	0.65	0.59
	Waste Areas	1.53	1.31	8.33	7.01

* This table shows the approximate PM_{10} in each of the main areas of the drilling rig following the studies outlined above. The Oil-based PM_{10} is taken as an average of the works outlined in the literature review. The Water Based PM_{10}, however, is equated from the graphs shown in Figure 7.9A and B. The water-based PM_{10} does not include that percentage which comprises solid particulate, as the oil mist proportion would be replaced with water steam.

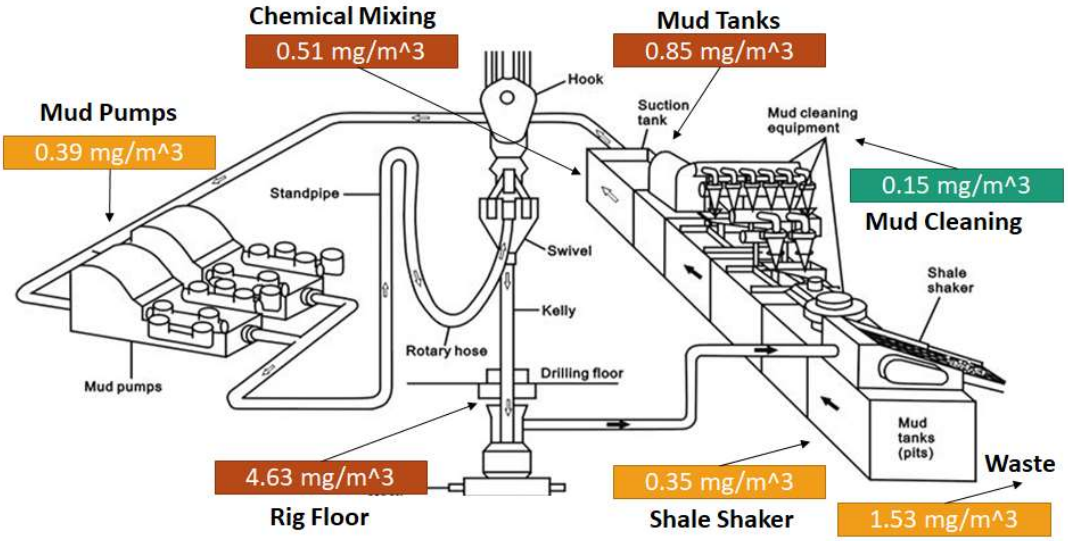


Figure 7.9.A. Shows the main areas of the well circulation system and the abundance of PM10 around the well system on a rig using water-based drilling mud WBM. The area with the highest area of exposure is on the Rig Floor, however a much smaller, though still significant concentration, is found at the mud tanks and chemical mixing stations. The mud cleaning, desiliter and desander are perhaps the cleanest areas of the drilling rig according to the literature.

Source: EXLOG, 1993.

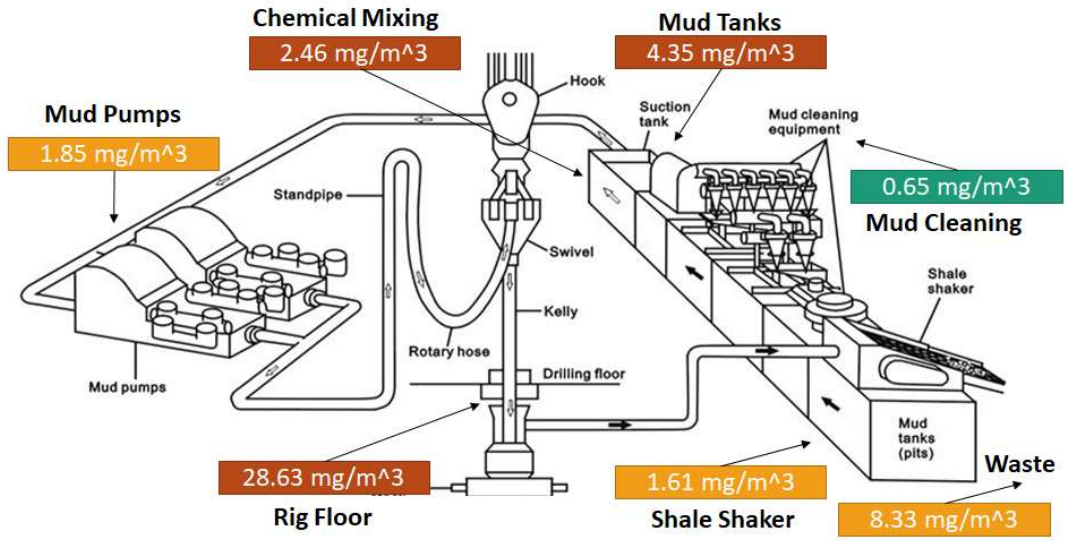


Figure 7.9.B. Shows the main areas of the well circulation system and the abundance of PM_{10} around the well system on a rig using Oil-based drilling mud OBM. The area with the highest area of exposure is on the Rig Floor, well in excess of occupational workplace limits. However a much smaller, though still significant, concentration is found at the mud tanks and chemical mixing stations. The mud cleaning, desiliter and desander are perhaps the cleanest areas of the drilling rig, with only 0.65 mg/m^3 of exposure.

Source: EXLOG, 1993.

► 7.7) Workplace Hazards.

♦ 7.7.1). WBM Potential Health Effects.

WBMs comprise a mix of water and additives, which are mixed with fine suspended arisings when the mud is used or recycled. The additives, added to the drilling mud, and suspended arisings, contain a minor proportion of silica as a contaminant. Silica is an important occupational air pollutant, as exposure is known to cause a subtype of pneumoconiosis called silicosis. The risk of developing silicosis is well studied and can be used to assess employee exposure hazards quantitively.

In order to calculate the risk to employees, several factors are required. These are:

- The estimated concentration of PM_{10} for WBM in the air. This is based on the work outlined in Section 7.6.1, with the values taken from Table 7.2.
- An estimated percentage for silica in WBM, see Figure 7.7.
- The area exposure of Silica in WBM $PM_{7.}$ This was estimated by multiplying the predicted area exposure by the silica concentration.
- The risk of developing adverse health effects has been scrutinised by the Health and Safety Executive (HSE). The HSE have released a classification table (Table 2.1) which estimates the proportion of the workforce who may develop radiological change, i.e. early diagnosis of pneumoconiosis, 15 years post-exposure, based on former occupational workers from the Scottish Coal Mines (HSE 2002).

This work, however, was subject to several assumptions, which include;

- That Hansen's results (in *1991),* is representative of average silica concentrations.
- The estimations found by this literature review are accurate and representative of modern UK onshore drilling rigs.

If these assumptions are true, then the estimated elemental concentration on drilling rigs can be multiplied by the concentration of silica in the air from Hansen, 1991, as shown in Table 7.3.

Table 7.3: The estimated risk of developing silicosis 15 years post-exposure based on estimated concentrations of WBM as silica vs the ILO score of developing class 2-1 silicosis.

Drilling Mud Type. [1]		Estimated Concentration of WBM in the air in mg/m^3. [2]	Estimated Concentration of Silica in WBM. [3]	Estimated Concentration of WBM as Silica in Air in mg/m^3. [4]	Risk of developing silicosis 15 years post-exposure as indicated by ILO score. [5]
Chemical Mixing	Clean	0.51	13%	0.07	**1.20%**
Mud Tanks	Clean	0.85		0.11	**2.98%**
Mud Pumps	Clean	0.39		0.05	0.77%
Rig Floor	Clean	4.63		0.60	**78.50%**
Shale Shaker	Dirty	0.35	15%	0.05	0.82%
Waste	Dirty	1.53		0.23	**11.89%**
Mud Cleaning	Dirty	0.15		0.02	0.25%

1,3 Based on the clean and dirty chemical compositions from Hansen *et al.,* 1991 from 16 PIXIE results on an alkane water-based drilling mud. 2 Based on the identified study averages as part of this PhD thesis. 4 If the area exposure is multiplied by the PIXIE elemental results for silica, then this would yield the silica proportion in the air at each of the locations. 5 Shows the risk of developing silicosis 15 years post-exposure, as indicated by ILO score 2/1 from each of the activities based on the HSE estimation of silicosis found in Scottish Coal Miners.

■ A) WBM: Pneumoconiosis risk.

The drill floor had the highest estimated exposures of airborne PM_{10} sized silica dust. The drill floor is also the busiest area of the drilling rig, with up to six personnel working in proximity to dust sources (Crittell and Baker 2015). These exposures led to a very significant risk of drill floor workers developing silicosis. These workers had a 78.50% risk of developing silicosis assuming a 'clean' drilling mud. However in the UK, drilling mud is recycled several times, which increases the concentration of silica in drilling mud. If dirty drilling mud concentrations of silica were used, then the probability of developing silicosis would rise to 90%.

The next most significant risk to workers was the waste area. While this is a little accessed area of the drilling rig, workers occasionally need to access these areas, sometimes without PPE (Figures 7.A and 7.B). Personnel working in these areas may face an 11% risk of developing silicosis.

Much lower risk of silicosis was found for the chemical mixing (2.98%) and mud tanks (1.20%). Other than silica, the other elements found by Hansen *et al.* 1991 were less of a concern to human health. However, exposure to barium sulphate would likely contribute to the development of pneumoconiosis, shifting potential diagnosis of pneumoconiosis to a mixed type (silica and barite).

♦ 7.7.2) LTOBM: Oil mist and Total PM.

Oil mist accounts for much of the PM_{10} composition when rigs use LTOBM. These oil mist exposures may lead to a significant risk of developing adverse respiratory health effects. No study identified in the literature review assessed the quantitative health ramifications of exposure to oil mist on drilling rigs. However, studies have found health effects at variable concentrations, which ranged from <1 mg/m^3 through to over 20 mg/m^3 (US NRC 2008; HSE 2014B). The US Navy in a study of oil mist affecting sailors, suspected that the mist was only a carrier for an agent causing adverse health effects (US NRC 2008). The US Emergency exposure guidance Level (EEGL) for hourly exposure was 20 mg/m^3/hour, based on 8-hours of exposure (US NRC 2008). The EEGL provided emergency guidelines for military operations where there was not yet any robust regulatory standard.

The EEGL was created as a conservative estimate of exceptional exposure hazards under short-term emergency conditions, and exposures at the EEGL level for a prolonged period may cause health issues in the long term (US NRC 2008). Notably, even the EEGL exposure guidelines may be breached on the drilling floor. The exposure around the fine waste area may also breach the 24-hour EEGL, especially given that a 12-hour shift is a common practice on petroleum drilling operations. The physiological effects of oil mist exposure above the EEGL in the long term, may include the development of extrinsic allergic alveolitis and occupational asthma (US NRC 2008; HSE 2014B).

♦ 7.7.3) Inadequacy of COSHH in drilling risk assessment.

Most drilling companies are aware of the decline of respiratory function of their workers, which is why medicals (including spirometry and health questionnaires) are mandatory throughout the industry and have been for decades (Whyte 1984; White et al. 2019).

Workplace chemical assessment is legislated in the UK under the Control of Substances Hazardous to Health (COSHH) Regulations (2002). COSHH assessments are used in the petroleum industry as the main prompt to take action on chemical hazards, actions which are not always effective. Often a COSHH assessment is not a proper replacement for toxicological analysis, or even quantitative analysis, when materials are combined into novel mixtures (Broni-Bediako and Amorin 2010; Sutton 2012).

The COSHH assessments can, and have been, misused; for example, in 2003, the Health and Safety Executive (HSE) found that there were “a large number of examples of inadequate industry risk assessments” (HSE 2003). One of the main problems with the COSHH assessment is that it is relatively common practice that more hazardous chemicals are given priority over less hazardous chemical components. These less hazardous components are often then relegated to a by-line on the COSHH form (Butler and Mitchells 2016; Chemwatch 2018). These less-hazardous components may, however, have additional features which can increase the overall risk of the mixture (Rustemeyer et al. 2019). The protection of workers from chemical hazards has only marginally improved over the last few decades, according to discussions with industry leaders at several international conferences (Chemwatch 2018; Dingle 2019).

An archetypal example of the weaker style of COSSH assessment was highlighted within a public health and safety manual. This manual outlined, that if a substance comprised 93% water, 5% sodium hydroxide and 2% crystalline silica, assessors may consider the chemical “sodium hydroxide” to be the most pressing concern as it presents strong corrosion and irritation hazards, i.e., following a Worst Chemical approach (Mitchells & Butlers 2016). However, addressing the worst, or most abundant chemical, might not thoroughly protect against the 2% of the mixture which comprises other chemicals, which may cause occupational disease (in this case–silicosis), over the long-term, (Barber and Fishwick 2020).

Given that the companies in the UK keep their HSE records confidential, it is difficult to highlight a public literary example, especially in the petroleum industry, where access to information is particularly restricted. Discussions with industry professionals at several conferences including the 'SPE Offshore Europe Conferences' in 2017 and 2019, highlighted that this continued to be a hazard in the petroleum industry. Some company HSE assessors at the conference from Schlumberger and BP, conceded that while this was a problem in the North Sea during the 1990s, they argued that steps have now been put in place to protect workers' health offshore.

Given that the onshore industry is relatively new, HSE practices may not be as robust as those found offshore, and legacy issues may remain in older workers. Documented examples of this phenomenon are difficult to prove and efforts made to contact occupational health experts providing expertise to the offshore industry were essentially stonewalled. The outbreak of occupational disease is reportable to the Health and Safety Executive under the RIDDOR regulations (Reporting of Injuries, Diseases, and Dangerous Occurrences Regulations, as amended in 2015). Details containing the specific details of occupational disease are kept confidential. However, the HSE report noted that "Respiratory Disease" is one of the most significant of the offshore diseases reported in offshore petroleum workers.

► 7.8) Method of identifying chemical composition.

♦ 7.8.1). Calculating Hazardous Mixture Risks.

■ A. Reported Mixtures

A search of the EA's Online Consultation Hub was undertaken, searching for oil and gas development sites within the UK. The search found 28 sites across England, which the EA had consulted on. Of these 28 sites, only 13 drilling sites had a disclosure of the drilling base muds and additives. These sites included: Broadford Bridge, Ellesmere Port, Holmwood, Horse Hill, Irlam Wellsite, Kirkby Misperton, Marishes, Preston New Road, Roseacre Woods, Springs Road 1 and 2, Stockbridge Oilfield, Tinker Lane, and the West Newton B Wellsite.

All the drilling mud compositions were disclosed within Waste Management Plans (IGas Energy 2013, 2014, 2016b, a, 2018; Cuadrilla Resources 2014b, c; UK Third Energy Gas Ltd 2014a, b; Rathlin Energy UK Ltd 2015; Horse Hill Developments Ltd 2017; KOGL 2017; Europe Oil and Gas 2018). The reported mixtures from the drilling sites can be found in Supplementals 7.A and D. As an example of the disclosure, the Waste Management Plan for the Primary Drilling Additives in Water Based Mud at the Springs Road 1 & 2 Wellsite is outlined in Table 7.4.

Table 7.4: The disclosed drilling mud composition for Springs Road.

Product Name	Average Quantity for SR01 well
Water	1020 m^3
Xanthan Gum	1650 kg
PAC	5.5 tonnes
Bentonite	44 tonnes
Soda Ash	330 kg
Caustic Soda	330 kg
Sodium Bicarbonate	330 kg
KCL	66 tonnes
Barite	5.5 tonnes

* Terms as found on the waste management plan and were not defined. PAC is Polyanionic Cellulose, and KCL is Potassium Chloride. Other common additive abbreviations include proprietary blends such as DF1.

■ B. Chemical Breakdown of the Reported Mixtures

In most cases, the disclosure only revealed the brand name or generic name of the product, e.g. “DF-1 base-oil” or “caustic soda”. However, contained within these disclosures were a series of SDS (Material Safety Data Sheets) which gave exact details on each additive (other than proprietary information) in terms of their chemical composition. Where possible, the chemistry of the drilling mud has been dissected as much as possible, to discuss trace chemicals found within the primary additives, e.g. a ‘bentonite powder additive’ containing 95% bentonite and 5% crystalline silica.

The volume of chemicals was calculated by calculating the total weight (tonnage) of the drilling mud and dividing by the subcomponents. Most of the drilling mud additives were given in either cubic metres (for water) or as kilograms, or tons. Helpfully, one cubic metre of water and one thousand kilograms are equivalent to one metric ton. A full breakdown of the chemistry of each of the drilling muds is available both within the company’s disclosure, and the chemical breakdown of the reported mixtures within Supplementals 7.A and 7.D.

An example, of the chemical breakdown for the Springs Road 1 & 2 Wellsite can be found below in Table 7.5 (as reproduced from Table E in Supplemental 7.B).

Table 7.5: The chemical ingredients in WBM used at the Springs Road drilling site.

Product Name	The concentration of a chemical in Mixture in Percent
Water	89.17%
Barium Sulphate	0.48%
Xanthan Gum	0.14%
Crystalline Silica	0.19%
Polyanionic Cellulose	0.48%
Bentonite	3.67%
Sodium Hydroxide	0.03%
Sodium Carbonate	0.03%
Sodium Bicarbonate	0.03%
Potassium Chloride	5.77%

■ C. Compiling chemicals in each drilling mud class.

Once all the drilling mud additives from the individual sites were identified, they were listed in an excel file, and the duplicate entries were deleted giving a list of 20 chemicals for WBM and 18 for LTOBM drilling muds. A full list of the chemicals identified within the main drilling mud compositions in the UK can be found within Supplemental 7.B for WBM and Supplemental 7.E for LTOBM.

■ D. Sources of Information for Chemical Safety.

This method makes use of Material Safety Data Sheets revealed by online data searches on Google (Google 2020). Safety data sheets are a commonly used system for displaying chemical hazards, storage, and disposal rather chemical ingredients and mixtures (ScienceLab.com 2018).

The GHS (Globally Harmonized System of Classification and Labelling of Chemicals) is the standard specification for the outline of safety data sheets, (UNECE 2019).

In the EU, the specification of SDS (Safety Data Sheets, as opposed to the now outdated MSDS) is governed by the European Chemical Agency (ECHA 2015). SDS sheets provide a robust and scientific appraisal of hazards to the respiratory (and other) systems, (HSE 2013c, d, 2017). On searching for appropriate SDS sheets, the user utilised Boolean accelerators within Google to enhance the quality of searches, i.e. using “speech marks” and ‘AND/OR’ operators. For example, if the user desired to search for an SDS about concentrated sulphuric acid, then the user would type ‘Concentrated “Sulphuric Acid” AND “SDS” AND “PDF”’ into the google search to return searches with these exact phrases “Sulphuric Acid”, “SDS” and in the “PDF” file format.

Most of the data sources came from the chemical wholesaler “ScienceLab” (ScienceLab.com 2018). However, several of these sources were cross-referenced with Fisher Scientific, Central Drug House Ltd, GALAB Laboratories (galab.de), Eastman, Spectrum Chemical Ltd, Lab Chem Inc and Agency for Toxic Substances and Disease Registry (ATSDR).

■ E. GHS Classification of Chemical Hazards.

In this assessment, the classification of the respiratory hazards was undertaken following the method outlined in the GHS. This classification system outlines a tiered approach to the estimation of hazards from mixtures and ascribes their likely health consequences following exposure (UNECE 2019).

The classification categories used within the GHS range between permanent injury (Category 1), transient injury (Classes 2 and 3) and unclassified. Each of these classes can be defined as follows:

■ **Category 1 –** Corrosive to the eyes and skin, causing major damage, known to cause an aspiration hazard or contain carcinogenic or highly acidic/alkaline components based primarily on epidemiological studies. The level of damage here is severe and typically over relatively acute exposure (within 24-72 hours), (UNECE 2019).

■ **Category 2 –** Irritation to the eyes and skin, thought to cause an aspiration hazard and/or suspected of having a carcinogenic hazard-based primarily on animal testing. The irritation to the eyes and skin is, however, reversible in the moderate term (i.e. within 21 days of acute exposure), (UNECE 2019).

■ **Category 3 –** This category does not include any chemicals which pose an aspiration or carcinogenic hazard. Therefore this category was classed as "unclassified in this study" (UNECE 2019).

■ **Unclassified –** Less severe and not falling into any other category, although contact may cause temporary minor irritation (UNECE 2019). Chemicals in this class are discounted in this research.

■ F. Chemical Hazards according to the GHS.

The modifiers used in the SDS sheet were used to identify the level of harm which may befall a receptor. These modifiers were hypothesised to denote the classification of chemical injury. Several of these keywords are denoted in Table 7.6.

Table 7.6. Modifiers used to denote the classes of harm.

Classes of Harm	Keyword Modifiers
■ **Category One**	Very Hazardous, Hazardous, Irritant, Corrosive, Permeator, burns, severe, cancerous, blistering, toxic, Serious, Strong Acid, Strong Alkali, pH extremes, death, violent, etc.
■ **Category Two**	Cough, Minor, redness, watering, itching, inflammation, Slightly Hazardous, Over-Exposure, etc.
■ **Unclassified**	Non-corrosive, None-known, N/A, etc.

The hazards, according to the GHS, can be found in Supplemental 7.C and Supplemental 7.F for WBMs and LTOBMs respectively. The GHS system takes into account the pH of substances so that a substance with a pH below 2.0 and above 14.0 is classified as a Category 1 Substance (UNECE 2019). While the GHS has been defined here, it remains a highly complex system, and it is recommended that the reader familiarise themselves with this framework.

■ G. GHS Cut-off Values for Chemical Harm.

A chemical is only ascribed to cause a certain health effect if there is enough of the chemical to pose a hazard (UNECE 2019). The GHS has outlined a series of cut-off values for chemical hazards, so as not to include such a trivial ingredient that harm would be almost impossible to occur. These GHS cut-off values are outlined in Table 7.7.

Table 7.7. Cut-off values for different chemical hazards.

Hazard	Classes of Harm	Concentration*	Description.
Respiratory Sensitiser	One	>1%: Category 1	May cause allergy or asthma symptoms or breathing difficulties if inhaled
Carcinogen	One	>0.1% Category 1	May cause Cancer
	Two	>1% Category 2	Suspected of Causing Cancer
Respiratory Irritation	One	>5%: Category 1	Causes Severe Burns and Eye Damage
	Two	> 1%, But <5%: Category 1 > 10%: Category 2 > 10%: (10x Category 1) + 2	Causes Respiratory Irritation.
Corrosivity	One	>1%: Acid. (pH <2) >1%: Base (pH >11.5)	Causes Severe Burns and Eye Damage

■ H. Calculating the Risk of Site-Specific Drilling Muds.

The last step is to multiply the percentage of the chemical ingredient found 7.2.2.B, by the hazard posed by the ingredient 7.2.2.F. Then it can be determined whether there was a sufficient concentration Category hazard to be labelled as a Category 1 or 2 hazard, or that the chemical hazard is unclassified.

For example, at the Springs Road Drilling Site, Barium Sulphate accounts for 0.48% of the drilling mud composition. Barium Sulphate is a Category 2 respiratory irritant. Therefore, if the Springs Road Drilling Site only contained 99.52% water and 0.48% barium sulphate, then the mixture would only contain less than half a per cent of irritating substances, which, according to

the GHS, is less than the 10% requirement for Category 2 hazards, and therefore would be an unclassified mixture.

■ I. A Step-by-step explanation of methods.

I. Understanding the drilling mud composition

a. The disclosure of drilling mud to the Environment Agency is scrutinised for chemicals used in the drilling mud at a specific drilling location as outlined in 7.2.2.A., i.e. Drilling Mud Alpha contains 920 m^3 of water, 3600 kg of ingredient A and 4.4 tonnes of ingredient B.

b. The volume of drilling mud is determined by estimating the total tonnage weight of chemicals within the formulation. One tonne of water is equal to one cubic metre; likewise, kilograms and tons are the default units for drilling mud, so chemicals are easily converted into the same units. This step allows for the total percentage of the ingredients within the drilling mud mixture to be calculated. As per step 7.2.2.B., i.e. Drilling Mud Alpha contains 92% water,
3.6% Ingredient A and 4.4% Ingredient B.

c. The individual chemicals within the drilling mud formulation are identified for further review of the chemical hazards the chemical presents. i.e. in this case, Ingredients A and B, as per step 7.2.2.C.

II. Chemical Hazards according to the Material Safety Data Sheet (SDS)

a. Each of the chemicals from the list (Step 1.C, i.e. ingredients A and B) are searched on a reputable Material Safety Data Sheet provider. As per Step 7.2.2.C.

b. The common contaminants within the SDS sheet are added to the chemical ingredients of the drilling mud, with the ingredient divided by each of its composite parts, as per step 7.2.2.D. In the example, Ingredient A makes up 3.6% of the mixture; however only 75% of the ingredient was A, with a contaminant of 25% ingredient C. Therefore, the chemical ingredients were 2.7% Ingredient A and 0.9% Ingredient C.

c. To approximate the chemical hazard posed by the individual ingredient, the word tags are reviewed as detailed in Table 7.6 and ascribed to the classes of harm according to the GHS as found in Table 7.5., as per steps, 7.2.2.E and F.

d. There is harm under the GHS as outlined in Table 7.7, as per 7.2.2.E and F., Each of the chemical constituents are reviewed for the harm according to their type. i.e. Ingredient C is only irritating (type 2). The harm is multiplied by the ingredient composition. I.e. Ingredient C is 0.9% irritating but 0% carcinogenic, 0% corrosive or 0% sensitising.

III. Determining the harm in each drilling mud classification.

a. The chemical hazards from each of the ingredients are totalled, to reveal harm from each type of hazard, as per 7.2.2.H. II.

For example;

i. Ingredient A (2.7%) is both Irritating and Corrosive,
Ingredient B (4.4%) is Irritating, Corrosive and Carcinogenic,
Ingredient C (0.9%) is Irritating, Carcinogenic and Sensitising,
Water Ingredient D (92%) is Unclassified

Therefore, Drilling Mud Alpha comprises;

ii. Irritating > 2.7% + 4.4% + 0.9% = Total: 8.0%
Corrosive > 2.7% + 4.4 = Total: 7.1%
Sensitising > 0.9% = Total: 0.9%
Carcinogenic > 4.4 + 0.9% = 5.3%

b. The concentration of the chemical hazard is contrasted against the chemical cut-off values of harm, and should they be above these cut-off values, then the hazard is deemed significant enough to make up harm.

In this Example;

i. Irritating substances were below a 10% hazard (Classification 2), and therefore the mixture was unclassified for irritation hazards.
ii. Sensitising agents were below 1% and therefore deemed to be an unclassified ingredient.
iii. Corrosive agents comprised over 1% of the liquid and were therefore deemed to pose a category one corrosive hazard.
iv. Carcinogenic hazards comprised over 0.1% of the mixture, and therefore the mixture is deemed to be carcinogenic.

IV. Given the high concentration of corrosive and carcinogenic hazards, the exemplar drilling mud was deemed a Class 1 Carcinogen and Corrosive agent but presented

as an unclassified (minimal) hazard from sensitising and irritating hazards.

♦ 7.8.2). Hazards, according to the UK WEL framework.

■ A. Workplace Exposure Limits (WEL's)

In the United Kingdom, the quality of workplace air is legislated in the Chemical Agents Directive (66/24/EC) and the Control of Substances Hazardous to Health (COSHH) Regulations 2002. This legislation makes employers responsible for on-site levels of air quality according to European and United Kingdom industrial hygiene standards (ECHA 2015).

The most relevant UK standard controlling workplace air is the guidance document: EH40/2005 Workplace Exposure Limits (WELs), (HSE 2020). This document contains a "list of workplace exposure limits for use with the Control of Substances Hazardous to Health Regulations 2002 (as amended)" (HSE 2018). This list contains entries for several hundred chemical species (HSE 2018). However, the absence of a limit value does not mean that the material is safe, and a supplemental value must be deduced (HSE 2018).

■ B. The concentration of the Ingredient in Ambient Air.

Chapter 10 of this thesis investigated the literature surrounding total airborne concentrations of PM_{10} in occupational settings on petroleum drilling sites. Table 7.6 shows that many areas of the drilling rig experience high levels of particulate matter between 0.15 and 4.63 $\mu g/m^3$ when using WBMs and 0.65 to 28.63 $\mu g/m^3$ when using LTOBMs. The difference in these levels may be because steam coming from warm drilling muds is likely to be principally composed of water in WBMs while Oil-Based Muds are likely to contain a significant proportion of dissolved oil, i.e. oil mist (Jones and Nicas 2006; Steinsvåg *et al.* 2006).

Table 7.8. Showing the chemical composition, UK WELs and their uses in different formulations of drilling mud. **Source:** HSE (2018).

Chemical Composition	United Kingdom Guidelines (WEL)	Use in WBM systems	Use in LTOMB systems
Crystalline Silica	0.10 mg/m^3	✔	✔
Barium Sulphate (Barite)	0.50 mg/m^3	✔	✔
Calcium Carbonate	4.00 mg/m^3	✔	✔
Magnesium Oxide	4.00 mg/m^3	✔	✔
Polyanionic Cellulose	4.00 mg/m^3	✔	✔
Sulphonated Asphalt	5.00 mg/m^3	✔	✔
Ammonia	18.00 mg/m^3		✔
Calcium Hydroxide	1.00 mg/m^3		✔
Ethylene / Diethylene Glycol	7.00 mg/m^3		✔
General Dusts and Chemicals with no prescribed WEL Limits	4.00 mg/m^3		✔

The drilling floor is selected as being the most critical to the health of petroleum workers as it is, both one of the most heavily trafficked and worked areas of the drilling rig, and it had the highest concentration of airborne particulate matter. Therefore, an airborne concentration of 4.63 µg/m^3 and 28.63 µg/m^3 was selected for WBM and LTOBM drilling muds, respectively. These estimated airborne concentrations (Table 7.8) were multiplied by the ingredient of interest for the WELs (e.g. Crystalline Silica) to calculate the concentration of the ingredients in ambient air. These were then compared against the UK WEL to determine whether the concentration in workplace air was above the level proscribed in the HSE Workplace Exposure Limits (WELs), (HSE 2018).

Table 7.9. Showing the major areas of the drilling mud,

Area Of An Drilling Rig	Description	Estimated Concentrations of PM_{10} in µg/m^3			
		Water-Based Total PM_{10}		Oil-Based Total PM_{10}	
		Area	*Personal*	*Area*	*Personal*
Sack Room	The place in which the drilling mud additives are added to the drilling mud.	0.51	0.70	2.46	3.50
Mud Tanks	Containers where the muds are mixed and stored before being pumped down the wellbore.	0.85	0.33	4.35	1.51
Hydraulic Pumps	Pumps which hydraulically force mud down the wellbore under pressure.	0.39	-	1.85	-
Drilling Floor	An area where the drill pipe is added and removed along with a variety of other processes. This area is one of the dirtiest areas of the drilling rig.	4.63	-	28.63	-
Shale Shakers	A vibrating screen whereby gravel-sized particles of rock are removed from the dirty drilling mud.	0.35	0.05	1.61	0.18
Desilter and Desander	A series of cyclones which separate sand and silt from the dirty drilling mud.	0.15	0.14	0.65	0.59
Waste Stream	The place in which the dirty drilling mud is discharged ready for off-site removal.	1.53	1.31	8.33	7.01

* A brief description of these areas and estimated levels of PM_{10} based on 11 studies undertaken on static and personal monitoring around drilling sites worldwide, using the literature and the estimates provided in Chapter 10 of this PhD thesis.

♦ 7.8.3) Discussion of the consequences of exposure.

Respiratory hazards are a recognised risk on drilling sites, with 28.2% of all offshore illness being attributed to workers' respiratory conditions (HSE 2005). Respiratory irritants and sensitisers include many of the base fluids and additives used in the petroleum drilling industry (Gardner 2003; Broni-Bediako and Amorin 2010). This is important, as substances which may cause inflammation and irritation to the respiratory system can create or exacerbate respiratory conditions (Heinrich and Schikowski 2018).

Respiratory sensitisers are substances or chemicals which have the potential to trigger an irreversible allergic reaction in the respiratory system (Cormier and Lemière 2020). Once this allergic reaction has taken place, further exposure to the substance, even if of short duration, produces symptoms (Cormier and Lemière 2020). Sensitisation usually requires many repeated exposures over months or years for any allergenic response to develop (Cormier and Lemière 2020). Following sensitisation, the symptoms of exposure begin with rhinitis (hay-fever) and become increasingly more severe, becoming asthma and ultimately progressing to anaphylaxis (Cormier and Lemière 2020).

Besides allergenic responses, the breathing in of fine particulate matter can have physio-chemical responses as it accesses progressively finer parts of the lungs. Particles larger than 10 μm are usually constrained to the nasopharynx while particles passing 3-10 μm can gain access to the trachea and bronchi. Particles fine enough to pass 3 μm may access the alveoli (Thillai *et al.* 2017; Barber and Fishwick 2020). Many of the key occupational respiratory diseases and symptoms are explained in Chapter 2 and include; Flu-like symptoms, Chronic Obstructive Pulmonary Disease (COPD), rhinitis, asthma, and pneumoconiosis (Thillai *et al.* 2017; Barber and Fishwick 2020).

■ A. Worked Example; WEL's at Site Specific Locations.

I. The list of chemicals' additives within the drilling mud compositions was determined as per 7.2.2, step H.I.C and H.II.B.

II. The list of chemical ingredients in all the UK drilling mud compositions was compared to the Health and Safety Executive list of chemicals with ascribed workplace exposure limits (WELs) as per EH40/2005, which contains "the list of workplace exposure limits for use with the Control of Substances Hazardous to Health Regulations 2002 (as amended)". As per step 7.2.3.A. For example, Crystalline silica is a common incidental ingredient in drilling mud compositions.

III. The chemicals, their use in the drilling mud and the Workplace Exposure Limits for the restricted (EH40) chemicals is found in Table 7.5, (HSE 2020). For example; the WEL for Silica is 0.10 mg/m^3, and it can be found in Water-Based Drilling Muds and Oil-Based Muds.

IV. The volume of chemical in the site-specific drilling mud formulation is determined following 7.2.2.H., E.g. 5% of an exemplar drilling mud comprised crystalline silica.

V. Chapter 10 of this thesis determined the composition of drilling mud in ambient air on drilling rigs. The highest concentrations of WBM and LTOBM were found on the drilling rig floor, where WBM had a concentration of 4.63 mg/m^3 and LTOBM had a concentration of 28.63 mg/m^3.

VI. The concentration of the agent on the EH40 breakdown at a specific drilling site, e.g. Crystalline Silica at 5%, was multiplied by the concentration on the drilling floor using that mud type, e.g. 4.63 mg/m^3, (HSE 2020).

a. Here, 5% x 4.63 mg/m^3 = 0.2315 mg/m^3 Crystalline Silica in ambient air at the exemplar drilling mud site.

VII. This result was then compared with the EH40 WEL value to determine whether it was greater than or less than the ascribed value, (HSE 2020).
   a. Here, 0.2315 mg/m^3 Crystalline Silica is more than the EH40 WEL value, and therefore there was a risk of adverse health outcomes, (HSE 2020).

VIII. As an extra step with crystalline silica, the risk of developing silicosis as found by the HSE, was multiplied by the percentage of silicosis in the drilling mud (HSE 2002).
   a. Here, the 0.2315 mg/m^3 value was multiplied by the risk polynomial factor of Silicosis Risk (2.3352 X^2 + 0.0129 X + 0.0002), where Exposure = X.
   b. In this example, the risk of developing silicosis is 12.83% which was contrasted against the control WEL risk of 2.5%. The risk of developing silicosis was considerably higher than prescribed by the WEL.

► 7.9) Results.

♦ 7.9.1) Water-Based Drilling mud.

■ A) Water-Based Drilling Mud Additives.

Water-based drilling muds (WBM) comprise 80-98% water by weight, with water acting as the main carrier solution for the muds. While water is a minor irritant to the respiratory system, and increased humidity can exacerbate underlying medical conditions such as COPD, water is unlikely to present a major hazard to the respiratory system (Davis *et al.* 2016). Water is a carrier solution as it can easily uptake additives, and it is these 2-20% (by weight) additives which are the primary concern for respiratory health (Schwatz 2015).

Twenty additives were found within this review of WBM drilling muds, the details of which can be found in Supplementals 11 A-C. Altogether, sixteen of the nineteen substances required respiratory protection. The PPE for twelve of these substances required dust protection while three others were deemed volatile enough to require vapour protection. These volatiles included fatty acids, polysaccharides, and ethylenediaminetetraacetic acid. Fatty acids and polysaccharides have a vapour potential at 25°c of 0.002 and 0.13 MPa respectfully, while ethylenediaminetetraacetic acid had a vapour potential of 260 MPa at the same temperature. The amount of the acid in the drilling mud was so minor (0.04%) so as not to pose a vapour risk, other than during the chemical mixing stage.

■ B) Water-Based Drilling Mud Mixtures.

The additives outlined in the waste disclosures were computed to determine the percentage concentration of the drilling mud, as outlined in 7.2.2. Based on this framework, eight of the thirteen WBM mixtures at UK onshore UNG sites were classifiable as Category 2 mixtures. These were the drilling muds from; Springs Road 1 and 2, Marishes Wellsite, Kirkby Misperton, Tinker Lane, Broadford Bridge, Preston New Road, Roseacre Woods, and Horse Hill.

These mixtures were classified because of their use of irritating substances. These irritating chemicals included bentonite, barium sulphate, potassium chloride, sodium chloride, and calcium carbonate. The remaining five drilling sites were identified as having unclassified mixtures, as these mixtures did not have a sufficient hazard potential of Category 1 or Category 2 according to the GHS. Overall, despite some additives having a high or low pH, the drilling mud mixtures had a relatively neutral pH of between 7 and 7.5.

Most of the respiratory hazards associated with WBMs stem from contact with the raw drilling mud additives during the mixing stage. Many of these are mixtures of low-risk (unclassified), with only two sites presenting a Category 2 hazard. Exposure to the chemical mixing of sodium hydroxide may cause a viable hazard to workers if proper precautions are not in place (US NIOSH 2005). The US OSHA has placed a 2 mg/m^3 ceiling limit on exposure to sodium hydroxide over an 8-hour shift, however, even at this low-level, sodium hydroxide has been associated with irritation of the throat and airways (US NIOSH 2005). Exposure to higher levels can produce swelling and spasm of the upper airway leading to obstruction, oedema (inflammation and swelling) and pleural effusion (fluid in the lungs) potentially leading to death (US NIOSH 2005).

Table 7.10: Hazard assessment of the UK WBM drilling mud additives by chemical exposure risk types according to the UN framework and the chemicals SDS sheets.

Hazard.	Description.
Corrosivity	Two chemicals (Ethylenediaminetetraacetic acid and Sodium Hydroxide) posed a Category one corrosive substance and Magnesium Oxide posed a Category two corrosivity hazard.
Permeation	Two chemicals (Polyglycol Ether and Sulphonated Asphalt) posed a Category two permeation potential.
Irritation	One chemical (Sodium Hydroxide) was a Category one irritant and 15 posed a Category 2 hazard. These were; Barium Sulphate, Bentonite Calcium Carbonate, Calcium Stearate, Crystalline Silica, Ethylenediaminetetraacetic acid, Polyglycol Ether, Magnesium Oxide, Polyanionic Cellulose, Polysaccharide, Potassium Chloride, Sodium Bicarbonate, Sodium Carbonate, Sodium Chloride, and Sulphonated Asphalt. Four chemicals were unclassified. These were; Carbohydrate, Fatty Acids, Freshwater, and Xanthan Gum
Sensitising	Four chemicals posed a Category two hazard of sensitisation; these were Fatty Acids, Polyglycol Ether, Polysaccharide, and Sodium Hydroxide
Aspiration	No chemicals were deemed to pose an aspiration risk.
pH	Most chemicals were centred around neutral, though Ethylenediaminetetraacetic acid had a pH of 2.5 and Sodium Hydroxide had a pH of 14.
IARC Hazard Group	The IARC reports one additive (Crystalline Silica) as posing a carcinogenic risk to humans

The Category 2 substances fall into two main health outcomes for chronic overexposure. These are physical pneumoconiosis (Bentonite, Sodium Carbonate, and Calcium Stearate), or chemical, i.e. allergenic responses, poisoning, and mutagenesis (from chemicals such as polyanionic cellulose, polysaccharides, fatty acids, and lubricants). Sensitising agents were used sparingly within WBM additive formulations, with an average concentration of about 0.19%, with a maximum value of 1.40%. Even at 0.19%, it should be remembered that in many occupational respiratory conditions, repeated short-term exposure even to trace amounts of sensitisers can lead to an allergic response in highly sensitive individuals, (Cormier and Lemière 2020).

Ten of the thirteen WBM formations contain trace amounts of crystalline silica as a contaminant within geologic materials (outlined in Table 7.8). Crystalline silica is commonly found within calcium carbonate, bentonite, and barium sulphate at a concentration of around 5%. Crystalline silica is not only carcinogenic according to the IARC, but also carries a significant risk of developing pneumoconiosis; Silicosis. After taking into account the contribution of these geologic materials to the overall mixtures, there is an average crystalline silica concentration of around 0.33%, ranging between 0.01% and 1.40%. The risk of silica inhalation to human health is addressed in further detail in subsection 7.3.1.C.

Table 7.11. Shows the hypothesised water-based total PM_{10} from OBM and WBM using the literature and the estimates provided in Chapter 10 of this PhD

Drilling Sites; Water Based Drilling Mud Compositions	Corrosivity	Permeating	Irritating	Sensitising	Category (GHS)		pH	IARC Group	
					1	2			
Stockbridge Oilfield	0.00%	0.70%	4.00%	1.40%	0.00%	4.90%	7.06	0.14%	Cat. 1
Holmwood Exploratory Borehole	0.00%	0.00%	2.00%	0.39%	0.00%	2.00%	7.03	0.01%	Unclassified
West Newton B	0.08%	0.00%	3.00%	0.03%	0.07%	4.10%	7.05	0.14%	Cat. 1
Irlam Wellsite	0.07%	0.00%	7.00%	0.09%	0.09%	7.26%	7.11	0.31%	Cat. 1
Ellesmere Port	0.09%	0.00%	8.00%	0.09%	0.09%	8.60%	7.11	0.26%	Cat. 1
Springs Road 1 and 2	0.03%	0.00%	7.00%	0.03%	0.03%	7.39%	7.07	0.20%	Cat. 1
Marishes Wellsite	0.04%	0.10%	20.00%	0.04%	0.04%	19.90%	7.13	0.50%	Cat. 1
Kirkby Misperton	0.09%	0.00%	19.00%	0.09%	0.09%	19.49%	7.14	0.20%	Cat. 1
Tinker Lane.	0.04%	0.10%	20.00%	0.04%	0.04%	19.90%	7.13	0.50%	Cat. 1
Broadford Bridge	0.00%	0.00%	30.00%	0.10%	0.01%	30.92%	6.98	1.40%	Cat. 1
Preston New Road	0.05%	0.00%	32.00%	0.05%	0.05%	31.90%	7.03	0.02%	Unclassified
Roseacre Woods	0.05%	0.00%	32.00%	0.05%	0.05%	31.90%	7.03	0.02%	Unclassified
Horse Hill	0.12%	0.00%	44.00%	0.03%	0.03%	44.33%	7.26	0.60%	Cat. 1

■ C) WBM Crystalline Silica Risk.

Silicosis is a serious occupational disease and is a subtype of pneumoconiosis (US NIOSH 1992). The risk of developing silicosis can be determined by using the percentage of crystalline silica in the drilling muds (IARC rating for these mixtures), multiplied by the concentration of airborne particulate matter (PM_{10}) on the drilling floor as presented in Table 7.6 and Chapter 10 of this thesis. The UK HSE WEL for crystalline silica is 0.1 mg/m^3, which according to a cohort occupational study from the UK Coal Mines, may carry a risk of pneumoconiosis of around 2.5% (HSE 2002). Given this is the guideline value to which airborne exposure at, or below, this concentration is legal in the workplace in the UK, this chapter considers this risk as acceptable, and risks above this value correspond to the threshold of harm.

Table 7.9 shows that all the UK drilling rig WBM formulations contained a minor proportion of crystalline silica. The overall estimated concentration in the air was less than the UK WEL, and this carried a risk of silicosis less severe than allowed under the UK WEL guidelines EH40, (HSE 2020). The most prominent WBM which carried the most risk of developing silicosis, was on the Broadford Bridge site, with a 1.03% risk after 15 years of exposure (KOGL 2017). Drilling sites are of short duration, with significant rest breaks and differences in mud concentrations, which would most likely diminish this hazard substantially (ARUP 2014).

Table 7.12: The concentration of crystalline silica (8-hour TWA) mg/m^3 estimated by the percentage of silica from Table 7.2 of this chapter, and the estimated concentration of solid PM_{10} from Chapter 10 of this thesis. This is considered against the UK HSE's Risk of developing silicosis 15 years post-exposure as indicated by ILO score 2/1+.

UNG Drilling sites and the UK WEL Guidelines	Crystalline Silica (8-hour TWA) in mg/m^3	Risk of developing silicosis 15 years post-exposure as indicated by ILO score 2/1+
United Kingdom Guidelines (WEL)	0.1000	2.50%
Broadford Bridge	0.0632	1.03%
Horse Hill	0.0255	0.21%
Marishes Wellsite	0.0232	0.18%
Tinker Lane.	0.0232	0.18%
Irlam Wellsite	0.0145	0.09%
Ellesmere Port	0.0122	0.07%
Springs Road 1 and 2	0.0089	0.04%
Kirkby Misperton	0.0089	0.04%
West Newton B	0.0063	0.03%
Stockbridge Oilfield	0.0006	<0.01%
Holmwood Exploratory Borehole	0.0006	<0.01%
Preston New Road	0.0011	<0.01%
Roseacre Woods	0.0011	<0.01%

■ D) Water-Based Drilling Mud Workplace Exposure Limits.

Similarly to crystalline silica, the percentage of notable air pollutants from WBM mixtures were assessed against the HSE WELs (HSE 2020). The percentage of the relevant additive in drilling mud mixtures was multiplied by the concentration of airborne particulate matter (PM_{10}) on the drilling rig floor as presented in Table 7.6 and Chapter 10 of this thesis. In this analysis, the UK HSE WELs for crystalline silica, barium sulphate, calcium carbonate, magnesium oxide, polyanionic cellulose, and sulphonated asphalt (HSE 2020).

In twelve of the thirteen cases, the concentration of the additives was less than that of the UK WEL regulation value, as shown in Table 7.10 (HSE 2020). The exception was from the Broadford Bridge site where the concentration of barium sulphate was above the WEL screening value of 0.5 mg/m^3, with a drill floor value of 1.27 mg/m^3 - assuming an airborne concentration of 4.63 mg/m^3 (HSE, 2020). Given that the predicted drill floor concentration of barium sulphate is above the screening value, then a subtype of pneumoconiosis called baritosis may afflict workers (Doig 1976). Fortuitously, most times, baritosis is both non-fibrotic (not producing scarring) and can resolve over several years following removal from the contaminated environment (Doig 1976).

Alas, many of the chemical mixtures do not have a WEL, but frameworks specify that should a be unavailable then the organisation should implement its own screening values to determine risks their employees (HSE 2020). Here, the respirable hazard for unclassified dust is 4 mg/m^3. With a drill floor concentration of 4.63 mg/m^3, the drill floor may be in breach of the UK general particulate WEL (HSE 2020).

Table 7.13. Shows the hypothesised water-based total PM_{10} chemical species.

	Crystalline Silica	Barium Sulphate	Calcium Carbonate	Magnesium Oxide	Polyanionic Cellulose	Sulphonated Asphalt
United Kingdom Guidelines (WEL)	0.100	0.500	4.000	4.000	4.000	5.000
Stockbridge Oilfield	0.001	0.000	0.000	0.000	0.000	0.000
Holmwood Exploratory Borehole	0.001	-	-	-	-	-
West Newton B	0.006	-	-	-	0.013	-
Irlam Wellsite	0.014	-	0.130	-	0.025	-
Ellesmere Port	0.012	0.068	-	-	0.072	-
Springs Road 1 and 2	0.009	-	-	-	0.022	-
Marishes Wellsite	0.023	0.232	-	-	0.023	0.005
Kirkby Misperton	0.009	-	-	-	0.022	-
Tinker Lane.	0.023	0.232	-	-	0.023	0.005
Broadford Bridge	0.063	1.271	-	-	0.047	-
Preston New Road	0.001	-	0.047	-	0.009	-
Roseacre Woods	0.001	-	0.047	-	0.009	-
Horse Hill	0.026	0.227	0.270	0.006	0.000	0.000

♦ 7.9.2) Low Toxicity Oil Based Drilling Mud Additives.

Low Toxicity Oil-Based Muds (LTOBM) occupy around 60% of the LTOBM by weight, with oil forming the main carrier solution. Oil, by its inherent nature, is more toxic to the respiratory system than water (US NIOSH 2005). The UK LTOBMs rely upon a base-oil composed of around 72% C11 - C14, with the remaining proportions comprising equal parts n-alkanes, isoalkanes, and cyclic hydrocarbons with an aromatic hydrocarbon content of less than 2%. The inherent toxicity of the base mud means that the LTOBM base mud is a Category 1 substance concerning the respiratory system, with most of the base being irritating to the respiratory system and a further 7% being permeating and/or sensitising. This toxicity is concerning as the product is inherently harmful to human respiratory health according to the methods used in this study.

Within this review of LTOBM drilling muds, 18 additives were found as outlined in Supplementals 7. D-F. The chemical hazards posed by these additives were split into seven classifications which may cause harm to workers. As outlined in Table 7.11 (and Supplemental 7.F), six of the eighteen additives pose a Category 1 hazard to the respiratory system. Another 11 of these additives were regarded as a Category 2 Hazard.

Table 7.14: Hazard assessment of the UK LTOBM drilling mud additives by chemical exposure risk types according to the UN framework and the chemicals SDS sheets.

Hazard.	Description.
Corrosivity	Four chemicals (2-methoxymethyl proponal, ammonium compounds, Calcium chloride, and calcium hydroxide) posed a Category one corrosive hazard.
Permeation	One chemical sulphonated asphalt posed a Category two permeation potential.
Irritation	Four chemicals (2 Methoxymethyl Proponal, Ammonium Compounds, and Aromatic Hydrocarbons (Benzo[A]Pyrene) posed a Category one irritant and 10 posed a Category 2 hazard. These were; Barium Sulphate, Bentonite, Calcium Carbonate, Calcium Hydroxide, Crystalline Silica, Gilsonite, Hydrocarbons C11-C14, Polymer (Polysaccharide), Sodium Carbonate and Sulphonated Asphalt
Sensitising	Two chemicals posed a Category two hazard of sensitisation; these were Fatty Acids and Polymer (Polysaccharide)
Aspiration	Two chemicals were deemed to pose an aspiration risk. Light Distillates, e.g. Kerosene is a Category one aspiration hazard, and Hydrocarbons present a Category two aspiration hazard.
pH	Most chemicals were centred around neutral, though 2 Methoxymethyl Proponal and Fatty Acids were acidic (pH 4-5) and Ammonium Compounds, Calcium Chloride, and Calcium Hydroxide were basic with a pH between 10 and 12.
IARC Hazard Group	The IARC reports two additives, Crystalline Silica, and Aromatic Hydrocarbons (Benzo[A]Pyrene) as posing a carcinogenic risk to humans

These volatile additives and base-oils combine into LTOBM mixtures that may have a significant vapour risk, with the highest vapour pressure being 1.56 KPa, as shown in Table 7.12. This vapour pressure shows that the LTOBM combinations may have a moderate to high steam and vapour potential and could be volatile when exposed to increased temperatures. The addition of heat is especially a concern as; the geothermal heat gradient is around 25-130°C per km for a well perhaps 2.5 km deep (Younger *et al.* 2012). Therefore, the temperature differential between the surface and bottom of the borehole may be as high as 156.1°C (Younger *et al.* 2012). This leads to great amounts of steam emanating from parts of the well circulation system, (Jones and Nicas 2006; Bratveit *et al.* 2009). The steam is known as oil mist in the industry, which if inhaled, can cause morbidity and mortality (Bratveit *et al.* 2009; Park 2019).

Table 7.15: A list of drilling mud additives and examples and their vapour pressure in KPa against their volatility and vapour potential according to the UN framework. Several exemplar chemicals are given for comparison.

	Drilling mud	Vapour pressure in KPa	Volatility and vapour potential
Example	Permethrin	2.9 E-9	LOW
	Chlorpyrifos	2.5 E-6	MEDIUM
	Kerosene	0.7	HIGH
	Water	2.3	
	Broadford Bridge	0.10	
	Rose Acre Woods	0.52	
	Springs Road	0.64	
	Tinker Lane	1.56	
	Holmwood	0.59	
	Kirkby Misperton	0.83	
	Ellesmere Port	0.28	
	Stockbridge	0.74	
	Irlem Wellsite	0.23	

The drilling mud formulations may, however, be subject to vapour pressure lowering, where non-vapour generating substances may reduce the volatility of the whole mixture (UNECE 2019). Nonetheless, these chemicals can be considered to be highly volatile, and present a considerable vapour risk (UNECE 2019). Subjectively, the chemical mixtures used on the Tinker Lane, Kirby Misperton, and Stockbridge well sites may have given rise to an even more significant vapour risk. These three well sites may have had drilling mud formulations, which were more volatile than kerosene, while Tinker Lane may have been as volatile as butyl acetate (US NIOSH 2005). According to the HMIS PPE requirements, the base LTOBM comprises substances, which present a dust risk of 25% (25% of the substances require a dust mask as a basic PPE measure).

■ A) LTOBM-Based Drilling Mud Mixtures.

The method used for the WBM was repeated for LTOBM mixtures. This resulted in the additive component hazard classifications, which were added together to determine the chemical hazard classifications for the entire mixture. The results of the chemical hazard classification for ten drilling mud sites throughout the UK onshore UNG industry were gained. As Table 7.13 shows, eight of the WBM mixtures at UNG sites were classifiable as Category 1 mixtures (UNECE 2019). These mixtures were classified because of their use of corrosive and irritating substances. Some of the most common irritating chemicals were hydrocarbon base oils, barium sulphate, calcium carbonate, and calcium chloride. There were high concentrations of Category 1 irritating additives at the Roseacre Woods, Preston New Road, Stockbridge, and Irlem Wellsites above the UN framework threshold for Category 1 respiratory irritants. The remaining sites all had a respiratory irritation risk of Category 2 or higher, with an average Category 2 irritation hazard content of 86.18%. Besides irritating substances, corrosiveness was a major hazard at all the drilling sites and was regarded as a Category 2 hazard. This was because of the common use of corrosive agents, which include, two methoxymethyl proponal, calcium hydroxide, ammonium compounds, calcium chloride and calcium chloride. A permeating hazard was also present at the Irlem Wellsite because of the use of sulphonated asphalt.

Table 7.16. The hypothesised chemical hazards from the WBM according to the GHS.

Drilling Sites; WBM	Corrosivity	Permeating	Sensitising	Irritating		pH	
				1	2		
Broadford Bridge	19.47%	0.00%	0.00%	0.00%	97.37%	7.68	1.91%
Roseacre Woods	11.81%	0.00%	0.00%	11.81%	80.99%	7.44	0.92%
Preston New Road	11.81%	0.00%	0.00%	11.81%	80.99%	7.44	0.92%
Springs Road	7.18%	0.00%	0.00%	6.12%	82.65%	7.16	2.31%
Tinker Lane	1.09%	0.17%	0.00%	2.34%	77.02%	7.03	1.46%
Holmwood	8.05%	0.00%	0.00%	5.58%	80.93%	8.02	0.82%
Kirkby Misperton	1.63%	0.23%	0.00%	1.41%	76.05%	7.05	1.49%
Ellesmere Port	7.83%	0.00%	0.00%	7.47%	94.81%	7.33	0.96%
Stockbridge	12.94%	0.00%	0.00%	12.94%	97.89%	7.38	1.10%
Irlem Wellsite	18.06%	2.26%	0.00%	18.06%	93.13%	7.71	2.20%

■ B) LTOBM Crystalline Silica Risk.

The same method of silicosis risk for WBM mixtures was used to quantify the risks from LTOBM drilling mixtures. Table 7.14 shows that the LTOBM formulations had a low crystalline silica content, and overall estimated concentration in the air, less than the UK WEL. Therefore, LTOBMs carried a risk of the development of silicosis less than allowed under the UK HSE guidelines (HSE 2020). There was, however, a minor risk of developing silicosis on the Ellesmere Port and Irlem Wellsite, with a 1.59% and 1.24% risk after 15 years exposure, though the mitigating factor of the short-lived duration of drilling, with significant rest breaks and differences in mud concentrations would most likely diminish this hazard substantially (Doig 1976).

Table 7.17: The concentration of crystalline silica (8-hour TWA) mg/m^3 estimated by the percentage of silica from Table 2.1, and the estimated concentration of solid PM_{10} from Chapter 10 of this thesis.

UNG Drilling sites and the UK WEL Guidelines	Crystalline Silica (8-hour TWA) in mg/m^3	Risk of developing silicosis 15 years post-exposure as indicated by ILO score 2/1+
Workplace Exposure Limit	0.10	2.50%
Ellesmere Port	0.08	1.59%
Irlem Wellsite	0.07	1.24%
Holmwood	0.06	0.94%
Broadford Bridge	0.05	0.67%
Roseacre Woods	0.05	0.67%
Preston New Road	0.05	0.67%
Springs Road	0.05	0.67%
Tinker Lane	0.00	<0.01%
Kirkby Misperton	0.00	<0.01%
Stockbridge	0.00	<0.01%

■ C) LTOBM WEL's.

Similarly to crystalline silica and for the WBM muds, the percentage of the notable air pollutants from WBM mixtures were assessed against the HSE WELs (HSE 2020). The percentage of the relevant additive in drilling mud mixtures was multiplied by the concentration of airborne particulate matter (PM_{10}) on the drilling rig floor as presented in Chapter 10 of this thesis. In this analysis, the UK HSE WELs for ammonia, barium sulphate, calcium carbonate, calcium hydroxide, crystalline silica, ethylene/diethylene glycol and sulphonated asphalt were used as they were legislated for in the WELs.

Table 7.15 shows that six of the seven additives with an HSE WEL, had a concentration less than that of the UK WEL regulation value. The exception was from the barium sulphate, which was expected to be above the WEL screening value of 0.5 mg/m^3 at 5 of the 10 UK drilling sites. These sites were; Broadford Bridge, Roseacre Woods, Preston New Road, Ellesmere Port, and Irlem Wellsite, with barium sulphate concentrations between 1.01 and 1.26 mg/m^3. The other five sites had a very low concentration of barium sulphate (barite) between trace (nil) and 0.18 mg/m^3; based on an estimated solid particulate value of 4.63 mg/m^3 on the drill floor, given that the predicted drill floor concentration of barium sulphate, a subtype of pneumoconiosis called baritosis may afflict workers (Doig, 1976). Again, this may be resolved over several years following removal from the contaminated environment (Doig, 1976).

However, the concentration of total PM recorded in the literature on the drill floor was 28.63 mg/m^3, much of which was oil mist. Nevertheless, if one assumed the higher concentration of 28.63 mg/m^3 rather than 4.63 mg/m^3, the concentration of both calcium carbonate and silica would increase to above the HSE WEL (HSE 2020).

Table 7.18. The hypothesised chemical hazards from the LTOBM according to the GHS.

	Ammonia	Barium Sulphate	Calcium Carbonate	Calcium Hydroxide	Crystlaine Silica	Ethylene / Diethylene Glycol	Sulphonated Asphalt
United Kingdom Guidelines (WEL)	18.00	0.50	4.00	1.00	0.10	7.00	5.00
Broadford Bridge	0.00	1.26	0.00	0.09	0.05	0.01	0.00
Roseacre Woods	0.00	1.07	0.00	0.05	0.05	0.00	0.00
Preston New Road	0.00	1.07	0.00	0.05	0.05	0.00	0.00
Springs Road	0.00	0.18	0.00	0.03	0.05	0.00	0.00
Tinker Lane	0.01	0.04	0.00	0.01	0.00	0.00	0.01
Holmwood	0.00	0.00	1.28	0.12	0.06	0.00	0.00
Kirkby Misperton	0.01	0.05	0.00	0.01	0.00	0.00	0.01
Ellesmere Port	0.00	1.01	0.08	0.03	0.08	0.04	0.00
Stockbridge	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Irlem Wellsite	0.00	1.25	0.10	0.00	0.07	0.00	0.10

The calcium carbonate estimated concentration was above the screening value at the Holmwood wellsite (HSE 2020). However, crystalline silica was the most concerning contaminant, with seven of the ten sites having a silica concentration above 0.10 mg/m^3, with concentrations varying between 0.28 and 0.52 mg/m^3.

Alas, many of the chemical mixtures do not have a WEL, but the UK HSE, under the COSHH assessment and WEL framework, specify that a screening value should determine risks to the employee. Here, the respirable hazard for unclassified dust and volatilities is 4 mg/m^3. With a drill floor concentration of 28.63 mg/m^3, the drill floor would most likely be in breach of the UK general particulate WEL by 715%.

♦ 7.9.3) LTOBM: Health Effects.

Based on the high-risk classification of the drilling muds (Category 1), adverse respiratory health reactions from unmitigated exposure to LTOBMs are likely to take place within the working population. These reactions may fall under physio-chemical or allergenic responses, with some pre-disposed workers possibly suffering both effects.

■ A) Physio-chemical.

Relatively short-term exposures to the LTOBM dust and vapours may lead to flu-like symptoms including; tiredness, sore throat, and productive cough with perhaps darkly pigmented sputum (with entrained LTOBM particles), (Kirkhus *et al.* 2015; Barber and Fishwick 2020). If inhaled into the lungs, then the LTOBM, because of its inherent irritability, may further irritate the lungs, while the corrosive properties would likely further enhance inflammation (Kirkhus *et al.* 2015; Barber and Fishwick 2020). The highly irritating nature of the drilling muds may exacerbate chest infections, COPD and pneumoconiosis (simple and progressive), following chronic exposure, (Heinrich and Schikowski 2018; Barber and Fishwick 2020).

■ B) Allergenic.

Many of the LTOBMs have the potential to trigger an irreversible allergenic response to the substances within the drilling mud and miscellaneous sensitisers encountered in day-to-day life (such as flour, animal dander and cleaning products), (Carder *et al.* 2019; Cormier and Lemière 2020). Once an allergic reaction occurs, the person becomes increasingly more sensitive to the substances, leading to flu-like symptoms, asthma and eventually, if not prevented, this may lead to anaphylaxis, (Cormier and Lemière 2020). Allergic alveolitis (an allergic inflammatory response in the alveoli region of the lungs) have also been reported by some workers who are exposed to oil mists over the long-term, (Steinsvåg *et al.* 2006; Park 2019; Barber *et al.* 2020).

► 7.10) Industrial Hygiene in Respiratory Health.

Aspiration hazards are reasonably well respected across the UK with excellent PPE practices, employee awareness, and training (Sutton 2012; Kirkhus *et al.* 2015). In many occupations, including the oil and gas industry, routine medical surveillance and pre-hiring medicals are used to mitigate against the adverse health effects of working in the industry (Whyte 1985; HSE 2005, 2012). The excellent medical surveillance used in the UK offshore is likely to be similar to that onshore, with three main health assessments conducted as part of the hiring and ongoing support of the workforce (HSE 2005, 2013b).

A medical is conducted with the individual as a condition of hiring to assess whether they have any underlying health conditions, including allergies, which would put them at risk of developing adverse medical conditions because of being exposed to chemicals on the drilling rig (James *et al.* 2007).

Specialist medical units are used in the hiring process to get a baseline condition of the lungs by using spirometry and x-rays, before the operator goes onto the site for the first time (HSE 2005; James *et al.* 2007).

Secondly, workers are to fill in medical evaluations periodically (between 6 months and a year) which note changes to the health of the employee (HSE 2005; James *et al.* 2007). A repeat of spirometry and x-rays may be conducted anywhere between 1 and 3 years, to ensure that the health of the workers has not changed (HSE 2005; James *et al.* 2007). Anyone unsuitable medically cannot work in the industry (HSE 2005; James *et al.* 2007). The development of any medical conditions including respiratory, gastric, and dermatitis is reportable to the HSE via the RIDDOR (Reporting Incidents, Diseases, and Dangerous Occurrences Regulations of 2013), (HSE 2013b; White 2018).

Workers who have developed minor medical conditions are reintroduced into the general populous (HSE 2005; James *et al.* 2007; Broni-Bediako and Amorin 2010). Unlike the UK's former coal mining industry, workers who show respiratory decline, but perhaps no adverse symptomology, are barred from working in the field environs of the petroleum industry (HSE 2005; James *et al.* 2007; Broni-Bediako and Amorin 2010). This is good in some respects and bad in others, as this may lead to a small amount of harm to a great number of workers, rather than much harm to a smaller number of workers. For example, a coal miner of the past may have worked for 50+ years in the mining industry, only retiring because of old age or ill health. With such chronic exposures, pneumoconiosis is much more likely (Barber and Fishwick 2020). Whereas, petroleum workers are barred from the profession at an early stage of respiratory decline and replaced with fresh personnel, (Whyte 1984; (HSE 2005; James *et al.* 2007; Broni-Bediako and Amorin 2010).

This replacement may subject a broader array of workers to an early stage of respiratory decline, contrasted against a profession with a lower turnover rate where the employees may have more advanced respiratory decline. Signs of respiratory decline are typically present on spirographs and radiology long before the disease progresses even to the onset of symptoms, or simple pneumoconiosis (HSE 2005; James *et al.* 2007). These low thresholds may bar employees from field positions and result in their removal from the industry, but in return, the most serious of consequences of chronic exposure is avoided.

► 7.11) Preventative Measures.

A reduction in risk to the lowest level possible is sought in industrial hygiene. The best method for preventing occupational hazards is to remove the hazards from the workplace. However, due to drilling mud being essential to modern drilling techniques, it is not possible to eliminate drilling mud. In order to reduce the risk, a series of preventative measures should be used following the STOP principle, (EU-OSHA, 1998). The STOP principle outlines four preventative steps (in order of importance); these are systematic (S), technical (T), organisational (O), and personal (P) measures.

Systematic (S); includes the design, maintenance, and hygiene standards of plant and equipment, (EU-OSHA 2019). Arguably the most efficient, systematic measure which could be conducted on the well circulation system would be the preference of WBM over LTOBM. LTOBMs should only be used by necessity and not as the default drilling mud from a health standpoint. Housekeeping is also a vital measure to minimise dust resuspension.

Technical (T); these measures involve adding or modifying equipment to reduce the levels of drilling mud dust and oil mists (EU-OSHA 2019). One noticeable measure which could reduce dust emissions could be the shielding of equipment, as providing cover systems over mud tanks

and other areas may prevent suspension of PM_{10} and oil mists especially by steam, (HSE 1996, 2018).

LEV could also be used in areas where there are potentially high concentrations of oil mist or dust, such as around enclosed or partially exposed places, such as the shale shakers, (HSE 2011b). Workers should also avoid manual handling of drilling mud additives where possible, using equipment such as automated lifts and mixers. (HSE 2011a, b).

Organisational (O); These measures outline company policy, which can be used to reduce hazards, (Cox and Cheyne 2000). An important organisational measure already used on petroleum rigs is employee training in safe working habits (such as wearing appropriate PPE). Medical surveillance includes; check-ups, exposure monitoring, and record-keeping, which may indicate workers who may be developing occupational diseases, (Cox and Cheyne 2000; HSE 2005). Procedural good practice also falls under organisational methods, such as the use and disposal of materials, and the proper labelling of drilling mud additives.

The basis of preventative measures for PM_{10} in the petroleum industry at present relies heavily on an occupational hygienist and occupational health worker. The goal of medical surveillance in the petroleum industry, through lung function monitoring (most commonly spirometry and radiography) and through allergy tests (skin prick test and measurement of specific antibodies) is to prevent an adverse health outcome (Broni-Bediako and Amorin 2010).

Questionnaires are also used before, during and after workers come onto the rig to supplement direct medical surveillance. (Whyte 1984; Oil and Gas UK 2008). In the UK, these questionnaires fall under the 'Oil & Gas UK ERT Medical Examination'. One of the functions of these questionnaires is to determine persons who are sensitive, or have

become sensitised, to drilling mud additives (Whyte 1984; HSE 1996; Oil and Gas UK 2008). Employees who are sensitive to drilling mud additives are unsuitable to work in the sector and are dismissed. Until recently, there was no legal recourse to these employees. However, a recent Supreme Court Decision, i.e., Dryden vs Johnson Matthey Plc (2018) was won in favour of the sensitised.

Personal (P); Focuses on the provision of Personal Protective Equipment (PPE), such as the use of gloves, goggles, and respirators, to reduce exposure, (Cox and Cheyne 2000; HSE 2005). PPE should be used as the last resort, where eliminating or reducing the level of risk to an employee is not otherwise possible. PPE is widely used in the petroleum industry, and the UK's HSE has outlined excellent PPE practices in documents such as UK HSE 2011a and b.

► 7.12) Conclusions

There are several areas of a modern petroleum drilling rig where exposure to PM may pose a respiratory hazard for personnel who work there. The most concerning area of the petroleum rig is the Drilling Floor, where exposures of PM_{10} are likely to be as high as 28 mg/m^3 (or over 2.8 times the recommended guideline value). Even when using a WBM, there may be a high risk of workers developing pneumoconiosis (71 to 90%). LTOBMs may add to this risk by introducing oil mist, which can cause extrinsic allergenic alveolitis. The waste processing areas were also an area of concern, though these areas were uncommonly accessed. Other areas of the rig had lower levels of risk.

The study has found that WBMs present a minor chemical hazard to respiratory health. The WBM is an unclassified substance, unlikely to cause problems within the respiratory system of most personnel in all but two sites. The latter two sites have a relatively mild (Category 2) risk to the respiratory system. However, the dust has a limited sensitisation potential which may

lead to highly sensitive workers developing allergenic responses. Some agents contained within the drilling muds have the potential to permeate PPE and clothing; therefore, despite having a low-risk rating, the exposure could degrade or permeate PPE, leading to higher exposures.

In contrast to WBMs, the LTOBMs were all Category One respiratory toxicants. It is likely then that LTOBMs have the potential to damage employee health even over the short-term if the proper health and safety recommendations are not followed. Because the LTOBM is highly irritable and moderately corrosive, contact with this material could lead to allergenic responses in sensitive individuals, even over relatively short exposures. The irritating character of the LTOBM may lead to irritation and inflammation in the lungs, potentially leading to the development of pneumoconiosis over the long-term. These issues could also lead to a range of physio-allergenic responses in the workforce if not properly protected from airborne LTOBM.

The high degree of LTOBM volatilisation coupled with its irritation and "corrosivity" may require advanced PPE procedures to control the risks of hazards to workers fully. Aspiration hazards are well known and respected within the petroleum industry, and routine medical surveillance is likely to minimise harm in workers. Employees suffering the early stages of respiratory decline are screened out in medical examinations and replaced. A worker would be unlikely to develop chronic conditions such as pneumoconiosis between screenings, but may develop acute - moderate-term conditions, though not necessarily with clinical symptoms. It is a philosophical question whether a small amount of harm to a great number of people, or a great amount of harm to some people is more ethically appropriate. Overall, there seems a high risk of workers developing occupational respiratory diseases where the workers' respiratory health is not thoroughly protected following the hierarchy of Control (STOP principle).

► 7.13) References

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► 7.14) Figure References.

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Figure 7.7. Grainger, S (2019) '*A graph showing solid PM_{10} concentrations vs oil mist concentrations from investigations undertaken by Hansen, 1991 and Steinsvåg, 2006'.*

END OF REFERENCES

Supplemental 7.A:

Supplementary information on drilling mud additives used in onshore WBM petroleum drilling campaigns.

A. Broadford Bridge - Water Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Freshwater	376.5	67.48%
Barium Sulphate	215.2	27.45%
Carbohydrate	11.7	1.50%
Crystalline Silica	10.7	1.37%
Xanthan Gum	7.9	1.01%
Polyanionic Cellulose	7.9	1.01%
Sodium Carbonate	0.8	0.10%
Sodium Hydroxide	0.8	0.10%

B. Horse Hill – Water Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Water	227.03	56%
Sodium Hydroxide	0.13	0%
Sodium Carbonate	0.13	0%
Bentonite	19.00	5%
Barium Sulphate	20.00	5%
Salt	110.00	27%
Potassium Chloride	5.00	1%
Magnesium Oxide	0.50	0%
Crystalline Silica	2.25	1%
Calcium Carbonate	23.81	6%

C. Roseacre Woods – Water Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Water	805.10	67.09%
Sodium Hydroxide	0.59	0.05%
Sodium Carbonate	0.59	0.05%
Bentonite	5.92	0.49%
Crystalline Silica	0.30	0.02%
Xanthan Gum	3.64	0.30%
Drilling Starch	12.10	1.01%
Polyanionic Cellulose	2.21	0.18%
Sodium Chloride	206.21	17.18%
Lubricant (Ester)	139.19	11.60%
Potassium Chloride	12.36	1.03%
Calcium Carbonate	12.10	1.01%

*The Preston New Road site uses the identical fluid composition.

D. Dart Energy – Water Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Water	961.80	80.15%
Bentonite	60.00	5.00%
Crystalline Silica	6.00	0.50%
Sodium Carbonate	1.20	0.10%
Sodium Hydroxide	4.80	0.40%
Polyanionic Cellulose	6.00	0.50%
Barium Sulphide	60.00	5.00%
Potassium Chloride	96.00	8.00%
Xanthan Gum	1.80	0.15%
Sulphonated Asphalt	1.20	0.10%
Calcium Stearate	1.20	0.10%

E. Springs Road 1 & 2 – Water Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Water	963.07	89.17%
Barium Sulphate	5.19	0.48%
Xanthan Gum	1.56	0.14%
Crystalline Silica	2.08	0.19%
Polyanionic Cellulose	5.19	0.48%
Bentonite	39.66	3.67%
Sodium Hydroxide	0.31	0.03%
Sodium Carbonate	0.31	0.03%
Sodium Bicarbonate	0.31	0.03%
Potassium Chloride	62.32	5.77%

F. Holmwood – Water Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Water	1763.87	97.99%
Polysaccaride	7.05	0.39%
Sodium Carbonate	2.64	0.15%
Bentonite	26.20	1.46%
Crystalline Silica	0.25	0.01%

G. Kirby Misperton – Water Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Water	1006.26	80.50%
Bentonite	78.26	6.26%
Sodium Carbonate	11.18	0.89%
Sodium Hydroxide	1.12	0.09%
Polyanionic Cellulose	4.47	0.36%
Calcium Stearate	1.12	0.09%
Barium Sulphate	53.11	4.25%
Crystalline Silica	2.80	0.22%
Potassium Chloride	89.45	7.16%
Xanthan	2.24	0.18%

H. West Newton – Water Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Water	1152.40	96.03%
Sodium Carbonate	0.49	0.04%
Sodium Hydroxide	0.41	0.03%
Polyanionic Cellulose	3.42	0.29%
Drilling Starch	10.27	0.86%
Bentonite	32.52	2.71%
Ethylenediaminetetraacetic acid	0.49	0.04%
Crystalline Silica	1.63	0.14%

I. Ellesmere Port – Water Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Water	1132.94	91.37%
Sodium Carbonate	1.12	0.09%
Sodium Hydroxide	1.12	0.09%
Xanthan Gum	2.25	0.18%
Polyanionic Cellulose	19.27	1.55%
Bentonite	65.19	5.26%
Barium Sulphate	18.11	1.46%
Crystalline Silica	3.26	0.26%

J. Stockbridge Oilfield– Water Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Water	1901.98	95.10%
Sodium Carbonate	1.36	0.07%
Xanthan Gum	2.71	0.14%
Polyglycol Ether	13.55	0.68%
Fatty Acids	13.55	0.68%
Polyanionic Cellulose	10.84	0.54%
Calcium Carbonate	56.00	2.80%

K. Irlem Oilfield– Water Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Water	1854.75	92.74%
Sodium Hydroxide	1.84	0.09%
Sodium Carbonate	1.84	0.09%
Xanthan Gum	1.84	0.09%
Polyanionic Cellulose	14.53	0.73%
Bentonite	104.76	5.24%
Barium Sulphate	14.19	0.71%
Crystalline Silica	6.26	0.31%

END.

Supplemental 7.B:

Supplementary information;

List of WBM chemicals.

A list of chemicals identified within the literature review which have been used in Water Based Drilling Muds approved by the Environment Agency (England).

- Barium Sulphate
- Bentonite
- Calcium Carbonate
- Calcium Stearate
- Carbohydrate
- Crystalline Silica
- Ethylenediaminetetraacetic acid
- Fatty Acids
- Freshwater
- Polyglycol Ether
- Magnesium Oxide
- Polyanionic Cellulose
- Polysaccaride
- Potassium Chloride
- Sodium Bicarbonate
- Sodium Carbonate
- Sodium Chloride
- Sodium Hydroxide
- Sulphonated Asphalt
- Xanthan Gum

END.

Supplemental 7.C:

Supplementary information; drilling mud chemical hazards used in WBM onshore petroleum drilling campaign chemicals.

Chemicals	Corrosivity	Permeating	Irritating	Sensitising		Health Effects	Aspiration	pH	IARC Group	PPE
Barium Sulphate	0	0	2	0	2	Pneumoconiois	0	7	0	Dust
Bentonite	0	0	2	0	2	Pneumoconiois	0	9	0	Dust
Calcium Carbonate	0	0	2	0	2	Pneumoconiois	0	9.91	0	Dust
Calcium Stearate	0	0	2	0	2	-	0	7.9	0	Dust
Carbohydrate	0	0	0	0	0	-	0	6	0	-
Crystlaine Silica	0	0	2	0	2	Pneumoconiois	0	7	1	Dust
Ethylenediaminetetraacetic acid	1	0	2	0	1	Lung Injury/Allergic	0	2.5	0	Vapour
Fatty Acids	0	0	0	2	2	Allergic	0	4.96	0	Dust
Freshwater	0	0	0	0	0	-	0	7	0	-
Polyglycol Ether	0	2	2	2	2	Allergic/Cough	0	7	0	Vapour
Magnesium Oxide	2	0	2	0	2	Cough	0	10.5	0	Dust
Polyanionic Cellulose	0	0	2	0	2	Allergic/Cough	0	6.25	0	Dust
Polysaccaride	0	0	2	2	2	Allergic	0	7	0	Vapour
Potassium Chloride	0	0	2	0	2	Cough	0	7	0	Dust
Sodium Bicarbonate	0	0	2	0	2	Cough	0	8.3	0	Dust
Sodium Carbonate	0	0	2	0	2	Cough	0	8.27	0	Dust
Sodium Chloride	0	0	2	0	2	Cough	0	7	0	Dust
Sodium Hydroxide	1	0	1	2	1	Lung Injury	0	14	0	Vapour
Sulphonated Asphalt	0	2	2	0	2	Cough	0	7	0	Dust
Xanthan Gum	0	0	0	0	2	Allergic	0	7	0	Dust

Supplemental 7.D:

Supplementary information: LTOBM drilling mud chemical additives used in LTOBM onshore petroleum drilling onshore in the United Kingdom.

A. Broadford Bridge – Oil Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Diethylene Glycol		0.10%
Ethylene Glycol		0.10%
Crystalline Silica		0.97%
Light Petroleum		0.97%
Polymer Emulsion		0.97%
Fatty Acid		1.46%
Calcium Hydroxide		1.95%
Calcium Chloride		19.47%
Barium Sulphate		27.26%
Hydrocarbons C11-C14		46.74%

B. Roseacre Woods – Oil Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Hydrocarbons C11-C14	263.24	39.90%
Water	124.00	18.80%
Calcium Chloride	77.00	11.67%
Primary Emulsifier	7.38	1.12%
Secondary Emulsifier	7.38	1.12%
Lime	7.38	1.12%
Organophilic Clay	7.38	1.12%
Fluid Loss Control	7.38	1.12%
Barium Sulphate	151.00	22.89%

C. Spring Road 1&2 – Oil Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Hydrocarbons C11-C14	129.87	63.28%
Water	43.29	22.10%
Calcium Chloride	11.50	5.70%
Fatty Acids	1.80	0.89%
Light Petroleum	0.30	0.15%
Methyl-Proponal	0.90	0.45%
Calcium Hydroxide	1.50	0.74%
Bentonite	1.62	0.80%
Crystalline Silica	2.13	1.05%
Fluid Loss Control	1.70	0.84%
Barium Sulphate	8.08	4.00%

D. Tinker Lane – Oil Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Hydrocarbons C11/14	126.00	70.92%
Aromatic Hydrocarbons	2.52	1.42%
Gilsonite	0.30	0.17%
Calcium Chloride	1.20	0.68%
Water	44.80	25.22%
Sulphonated Asphalt	0.30	0.17%
Ammonium Compounds	0.34	0.19%
Crystalline Silica	0.08	0.05%
Fatty Acids	0.18	0.10%
Methyl-Proponal	0.09	0.05%
Low Distillates	0.03	0.02%
Calcium Hydroxide	0.30	0.17%
Barium Sulphate	1.52	0.86%

E. Holmwood – Oil Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Hydrocarbons C11-C14		39.59%
Calcium Chloride		5.04%
Calcium Carbonate		27.67%
Calcium Hydroxide		2.51%
Fatty Acids		3.01%
Proponal		0.50%
Aromatics		0.04%
Bentonite		0.00%
Water		21.64%

F. Kirby Misperton – Oil Based Drilling Mud

Additive	Volume of Chemicals	Percentage
DF95		51.02%
Water		26.41%
Calcium Chloride		12.04%
Versaclean VB		3.01%
Fatty Acids		1.81%
Proponal		0.90%
Light Petroleum		0.30%
Sodium Carbonate		1.50%
Bentonite		1.50%
Mineral Oil (White)		1.50%

G. Ellesmere Port – Oil Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Hydrocarbons (C11-18)		43.52%
Water		10.88%
Calcium Chloride		1.81%
Calcium Carbonate		1.81%
Crystalline Silica		1.81%
Calcium Hydroxide		0.36%
Diethylene Glycol		0.79%
Calcium Chloride		5.66%
Fatty Acids		0.85%
Light Distillates		0.14%
Lime		0.71%
Organophilic Clay		0.71%
Sulphonated Asphalt		0.71%
Barite		30.24%

H. Stockbridge Oilfield – Oil Based Drilling Mud.

Additive	Volume of Chemicals	Percentage
DF95		51.02%
Water		26.41%
Calcium Chloride		12.04%
Versaclean VB		3.01%
Fatty Acids		1.81%
Proponal		0.90%
Light Petroleum		0.30%
Sodium Carbonate		1.50%
Bentonite		1.50%
Mineral Oil (White)		1.50%

I. Irlem Wellsite – Oil Based Drilling Mud

Additive	Volume of Chemicals	Percentage
Calcium Chloride		18.06%
Primary Emulsifier		3.61%
Secondary Emulsifier		0.90%
Lime		2.26%
Organophilic Clay		2.26%
Sulphonated Asphalt		2.26%
Barite		27.09%
DF1 Base Oil		36.69%
Water		6.87%

END.

Supplemental 7.E:

Supplementary information; List of LTOBM chemicals.

A list of chemicals identified within the literature review which have been used in LTOBM Based Drilling Muds approved by the Environment Agency (England).

- 2 Methoxymethyl Proponal
- Ammonium Compounds
- Aromatic Hydrocarbons (Benzo[A]Pyrene)
- Barium Sulphate
- Bentonite
- Calcium Carbonate
- Calcium Chloride
- Calcium Hydroxide
- Crystalline Silica
- Ethylene / Diethylene Glycol
- Fatty Acids
- Gilsonite
- Hydrocarbons C11-C14
- Light Distillates (Kerosene)
- Polymer (Polysaccaride)
- Sodium Carbonate
- Sulphonated Asphalt
- Freshwater

END.

Supplemental 7.F:

Supplementary information; Drilling mud chemical hazards used in LTOBM onshore petroleum drilling campaigns.

Chemicals	Corrosivity	Permeating	Irritating	Sensitising	Health Effects	Aspiration	pH	IARC Group
2 Methoxymethyl Proponal	1	0	1	0	1	0	4.00	0
Ammonium Compounds	1	0	1	0	1	0	11.63	0
Aromatic Hydrocarbons (Benzo[A]Pyrene)	0	0	1	0	1	0	7.00	1
Barium Sulphate	0	0	2	0	2	0	7.00	0
Bentonite	0	0	2	0	2	0	9.00	0
Calcium Carbonate	0	0	2	0	2	0	9.91	0
Calcium Chloride	1	0	1	0	1	0	10.00	0
Calcium Hydroxide	1	0	2	0	1	0	12.40	0
Crystalline Silica	0	0	2	0	2	0	7.00	1
Ethylene / Diethylene Glycol	0	0	0	0	0	0	6.50	0
Fatty Acids	0	0	0	2	2	0	4.96	0
Gilsonite	0	0	2	0	2	0	9.00	0
Hydrocarbons C11-C14	0	0	2	0	2	2	7.00	0
Light Distillates (Kerosene)	0	0	0	0	0	1	9.00	0
Polymer (Polysaccaride)	0	0	2	2	2	0	7.00	0
Sodium Carbonate	0	0	2	0	2	0	8.27	0
Sulphonated Asphalt	0	2	2	0	0	0	7.00	0
Freshwater	0	0	0	0	0	0	7.00	0

END.

CHAPTER 8:

Pilot Methods of Assessing Air Pollution in Complex Microenvironments, for field development in the metropolitan setting.

Abstract: This work tests two pilot methods that show promise in the industrial air quality monitoring around UNG development sites. The field methods were tested in the City of Glasgow. In metropolitan areas, daily personal exposure to air pollutants such as fine particulate matter and nitrogen oxides, is directly or indirectly caused by vehicular emissions. Experiment I compared the exposure of selected air pollutants (PM2.5, Black Carbon and Oxides of Nitrogen) at three bus stop shelters; fully enclosed, rear panel and stop pole only, along Hope Street, Glasgow. The shelters were monitored with two sets of air quality monitoring equipment (MicroPEM, MicroAeth, and Palmes Diffusion Tubes) during the morning and evening rush hours. The analysts moved to the south, inside, and north of the bus shelters to understand the concentrations of air pollution in its microenvironmental setting. In Experiment II two notable Monitoring Stations in Glasgow are at High Street and Townhead were analysed through R' Studio's 'Openair' Toolset which allowed for the analysis of the spatial characteristics of the sources relies on a series of bivariate polar plots, which help to discriminate the sources of pollutants based on their meteorological profile (wind direction and speed). Besides pollutant specific polar plots, ratios of BC to nitrogen were used to find vehicular sources (high in nitrogen vs BC). Also, Conditional Probability Function (CPF) polar plots helped to gain an understanding of the consistency of the source, given certain meteorological conditions. This analysis was useful in identifying minor sources of air pollution at these Monitoring Stations, with several unknown sources of air pollution identified. Both experiments were found to have deeply profound and important measurement indicators for air pollution and would likely have larger implications for industrial air quality monitoring especially at UNG development sites.

► 8.0). Introduction.

Exposure to air pollution adversely affects the longevity and quality of human life (Gautam and Bolia, 2020;). The World Health Organisation (WHO) has declared that air pollution is a public health emergency, and considers air pollution to be the "greatest environmental risk to health" (WHO 2016, 2019). These public health concerns have permeated through to the public consciousness through intense media scrutiny and public awareness campaigns (Huang *et al.* 2018). The city of Glasgow has not escaped from media or public scrutiny, with the highest national concentrations of air pollution within the city centre (Keane 2019).

In urban environments, most air pollution stems from exhaust gases from motor vehicles' Internal Combustion Engines (ICEs). These ICE exhaust gases include Oxides of Nitrogen (NO_X) such as Nitric Oxide (NO) and Nitrogen Dioxide (NO_2) and Particulate Matter (PM), (McInally 2019). PM is interesting as, not only does the size of the particle play a crucial role in adverse human health effects, but so does the chemistry of the particles (WHO 2016; Abbas *et al.* 2018). An important chemical subspecies of PM is Black Carbon (BC). This comprises carbon coated in Poly-Aromatic Hydrocarbons (PAH), a substance which has well-known respiratory and carcinogenic risks (WHO 2016; Abbas *et al.* 2018). Particle shape and chemistry can also affect the rate of resuspension of PM (Zheng and Li 2019; Jida *et al.* 2020).

Environmental factors greatly influence oxides of nitrogen as they can degrade or undergo chemical reactions in ambient air such as NO via its alteration to NO_2 in the presence of sunlight, (Vallero 2014). This reaction is further enhanced by turbulent conditions such as wind speed and wind-flow obstructions (Wolf *et al.* 2020).

Further field deployment methods are needed in order to be able to fully characterise complex air pollution sources within inner city locations. It is not a coincidence that the complicated array of problems befalling the inner-city air pollution expert are analogous to the complications of measuring dynamic multi-source emissions from industrial development sites (such as UNG) within the UK.

Afterall, monitoring stations, even those deployed to measure air pollution from a single source are often occluded from direct line of site. Certainly, no real-world example would stand in isolation as the sole source of air pollution as there are always complex micro-environments to consider whether this be natural phenomenon such as sea salt and sand entrained in coastal winds, agricultural emissions such as the ploughing of fields, through to phenomenon such as nearby industry and ICE emissions. All sources should be understood and characterised uniquely preferably through background air monitoring, or certainly in the discussion of hotspots and their trigger or source mechanism. An unknown natural phenomenon should absolutely not be mis-interpreted as an industrial emission especially where such emissions are large and problematic from a regulatory standpoint.

It is felt that an understanding in the real time temporal spatial analysis would offer such a focussed method to be able to observe the passing of traffic and thereby allow for a rather straightforward model of source-pathway-receptor. To complicate matters, it was decided to evaluate the role of Black Carbon Ratios to that of Nitrogen Gasses. Both pollutants afterall are given off by internal combustion engines and therefore may hold some further insight into the cycles of motion of heavy plant and large road vehicles. It was also thought that micro-environments would play a significant role in the siting of structures as is common for air pollution monitoring stations. As these structures both bear a striking similarity to the roadside bus shelters along the A565 Preston New Road and structures on the site, it was felt that this would offer a strong research focus.

Secondly, with the wealth of information generated on the Preston New Road site over years of its conceptualisation and realisation, much work has been done in terms of monitoring. However, as a proof of concept it was felt that air pollution assessment via statistical computing power was vital to understand the spatial-temporal variations on the ever-changing and complicated environment of inner-city Glasgow. If the methods held up in such a complex and unique environment, there theoretically should be a much easier dynamic in rural Brittan with much fewer pollution interactions and interferences.

Overall, both research methods were engineered to make use of the tools at the analysis arsenal from different field methods within an easily accessible location in the heart of Glasgow. Its accessibility however, did not take away from the complex workings of Glasgow and if anything, having such a resource only proved to be an opportunity far too rewarding to avoid.

♦ 8.0.1) Rationale for the field methods trialled.

A. Experimental Design I: Air Pollution Concentrations at Bus Stop Structures along a Street Canyon in the City of Glasgow.

In Scotland, around 10% of urban commuters rely on public bus services as their primary form of commute (Hoy 2019). Significant variations in commuters' exposure to air pollution are found between different transport modes (cycling, walking, private or public transport etc.), (Moore *et al.* 2012; Dons *et al.* 2012; Namdeo *et al.* 2014). Walking may have the greatest risk of exposure, as pedestrians often share polluted air with busy roads during rush hour (Morales-Betancourt *et al.* 2017).

It is conjectured that bus patrons may be exposed low concentrations of air pollution as they wait for an average of five minutes at bus stops (in Scotland), often much closer to the road than pedestrians (bus stops are

sited within 110mm of the kerb), (Morales-Betancourt *et al.* 2017). Roadside exposure is often discounted during commuter air pollution assessments, even though exposure to waiting bus patrons is speculated to be a significant source of air pollution (Scottish Government 2009;).

This field method was trialled to expand the researcher's knowledge and abilities in field analytical development within air pollution sciences. The bus stop investigation in evaluates the role of busses (analogous to HGV) emissions and the significance of increased traffic flows on major roads. HGV traffic is thought to be a major pollutant arising from the development of petroleum resources, and bus diesel engines are not dissimilar from HGV engines in terms of their size of emissions profile. The structures encountered bore a striking resemblance to the crudely built protestor shelters along the A583 - Preston New Road (PNR).

B. Experimental Design II: Black Carbon and Nitrogen Ratios at Two Governmental Air Quality Monitoring Stations Using Computer Modelling.

This field method was trialled to expand the researcher's knowledge and abilities in statistical computing using the OpenAir toolset written by Carslaw *et al.* (Carslaw *et al.* 2006, 2012; 2014, 2015a, b). Such a technique could be used on Unconventional Natural Gas (UNG) developments and other complex environments where NO_X and BC are measured along with meteorological data. The ratio between NO_X and BC (used in this experiment), has the potential to be a highly useful and influential metric for air quality investigations. This paper introduces a method of identification of hotspots, which are otherwise indistinguishable from background concentrations even when using statistical modelling tools.

This experiment suggests various new potential hotspots of air pollution, from the well-researched Glasgow Townhead and High Street Monitoring Stations (Ezani 2017; Masey 2018). This experiment may also be of interest for research undertaken on the local air quality in the eastern part of the city of Glasgow. One of these findings shows a linkage between the M8 J15 Townhead Interchange and the Townhead Monitoring Station, a linkage which has long been hypothesised but not proven (McInally 2019).

Other findings suggest hotspots at road junctions, which is unsurprising given the existing research. This method could present a useful metric in intervention and city-wide air pollution policies in complex hotspot environments, where Monitoring Stations are located close to road junctions in busy built-up areas (Sharma *et al.* 2019). An intervention reducing ICE emissions is likely to increase the relative BC ratio higher than NO_X, as nitrogen is likely to dissipate into the air while BC can stay suspended (Wang *et al.* 2011; Defra 2019). BC can become resuspended or even be brought in from air settling regionally much easier than NO_X, which may mix with ambient air and degrade (Wang *et al.* 2011; Defra 2019).

It should also be mentioned that the ratio between BC and Oxides of Nitrogen has never been explored in ambient air monitoring as far as the author is aware. The author, therefore, considers that the technique, in its own right, is novel and a contribution to scientific knowledge.

This experiment also offers an insight into the hotspot sources of BC and Oxides of Nitrogen within the eastern part of the city of Glasgow. This ratio technique offers added benefits to scholarly research and opportunities to study these potential hotspots in further depth with personal or mobile sampling methods.

► 8.1. Experimental Design 1: Experimental Design I: Air Pollution Concentrations at Bus Stop Structures along a Street Canyon in the City of Glasgow.

♦ 8.1.1. Experiment I - Introduction.

Glasgow City Council is implementing a clean air zone within the city centre to reduce levels of vehicular emissions on Glasgow's most polluted streets, (Transport Scotland 2017; McInally 2019). The most notoriously polluted street in Glasgow is Hope Street, which is an arterial road and transport nexus for the city (Transport Scotland 2017; McInally 2019). Hope Street provides access to Glasgow Central Train Station, a taxi rank and many important bus services (McInally 2019). The city's traffic emissions model shows that buses and taxis account for 90% of all NO_2 emissions along Hope Street (McInally 2019). Hope Street is flanked by buildings several (4-8 stories tall) which form a 'street canyon' (Karra *et al.* 2017). Street canyons are an important factor in urban air pollution assessment, as canyons channel and push air pollution to the sides of the road, and when wind speeds are low, air pollution can build-up, reaching harmful concentrations (Karra *et al.* 2017).

Historically, roadside exposure assessment has relied on the Automated Urban and Rural Network (AURN), which is a system of fixed monitoring stations at selected points across the UK (Lin *et al.* 2017; McKercher *et al.* 2017). Technological development and a drive to understand air pollution microenvironments have led to the development of personal monitoring equipment (Lin *et al.* 2017; McKercher *et al.* 2017). Studies have shown that AURN-like stations can underestimate air pollution in microenvironments (such as bus shelters), (Namdeo *et al.* 2014; Lin *et al.* 2017).

Personal monitoring equipment has been used on most commuting modes, including walking, buses and private transportation, (Morales-Betancourt *et*

al. 2017). Diesel buses have been intensely scrutinised as they are one of the most prevalent forms of public transportation globally (Morales-Betancourt *et al.* 2019). Studies assessing public transportation have found high levels of air pollution; one study in Newcastle (UK) found an average PM_{10} concentration of 72 µg/m^3 (>150% of the UK ambient air standard), (Namdeo *et al.* 2014). Air quality monitoring campaigns on buses rarely account for exposure on the wait for the bus or the patron's waiting location, despite the design of bus stops being the most important factor in the design of an effective transit system (Moore *et al.* 2012; TfL 2017).

Two studies have assessed the air quality inside and outside of bus shelters (when discounting studies assessing bus terminals, depots, and stations). These two studies considered roadside bus stop exposure in the USA (Moore *et al.* 2012; Dons *et al.* 2012).

A study by Moore *et al.* (2012) found that:

- The time of day, waiting for location and patrons' smoking habits had a significant effect on $PM_{2.5}$ concentrations (Moore *et al.* 2012).
- $PM_{2.5}$ concentrations of 16.24 µg/m^3 (inside) and 14.72 µg/m^3 (outside) were registered.
- Rush hour concentrations were higher in the morning than in the afternoon.

A different study by Dons *et al.* 2012 found that:

- $PM_{2.5}$ concentrations ranging between 18.37 to 24.07 µg/m^3 (inside) vs 13.61 to 30.51 µg/m^3 (outside) occurred.

No studies were found which systematically analysed BC or NO_2 inside or outside of bus shelters.

The working hypothesis for this study is that 'Bus commuters may be exposed to high levels of air pollution ($PM_{2.5}$, BC and NO_2) while waiting for buses, which accounts for a high proportion of their daily exposure'. A

literature review found that little research had been undertaken on the positioning, design and exposure to air pollution at bus stops, despite this being integral to an efficient bus service, (Moore *et al.* 2012; Dons *et al.* 2012; TfL 2017). This experiment tests this hypothesis to better understand patron exposure and how different bus shelter designs can assist with reducing personal exposure during the commute.

► 8.2) Data Collection and Experimental Design.

♦ 8.2.1) Commuting Overview.

Glasgow serves as a national and international transport nexus (Stout, 2018). Sixty thousand residents commute by buses daily, many of whom transit through Buchanan Bus Station (40,000 daily commuters), (Hoy 2019). There has been a modest decline in bus usage in Glasgow due to, amongst other things, congestion, increasing waiting times, and from the rising cost of bus fares, (Namdeo *et al.* 2014; Hoy 2019).

Besides a busy bus service, Glasgow has an important rail and subway service. Glasgow Central Train Station, which adjoins Hope Street, serves ~100,000 commuters daily, with another 40,000 commuters using the interconnected subway system, (SPT 2018; ORR 2020).

♦ 8.2.2) Monitoring Area - Hope Street.

Hope Street is a north-south, 0.965 km long, one-way (northbound) A road in Glasgow's City Centre (HSA Retail 2017). The primary land uses along Hope Street are multi-level commercial buildings and apartment complexes, which are usually around four to six levels with occasional buildings up to 10 levels. At road level, the buildings function as reception areas, café's, bars and retail outlets (HSA Retail 2017).

There are 15 bus stops along Hope Street, which consist of four main styles of bus shelters. These are; a stop pole and flag only, a single cantilever panel with no perch seats, a semi-enclosed bus shelter with perch seats, which is rear-facing (away from traffic) or the same design forwards facing (toward traffic). According to the Glasgow Traffic Management Plan, Hope Street has an Annual Average Daily Flow (AADF) of about 25,000 vehicles (Glasgow City Council 2015), notwithstanding significant access restrictions being in place (Glasgow City Council 2015).

Hope Street becomes a public highway north of the intersection with Gordon Street. The high traffic flow has led to Hope Street reportedly having the worst air quality in Scotland (Thompson 2020). Emissions modelling along Hope Street indicates that approximately 65% of all NO_2 emissions come from buses, with taxis accounting for an additional 15%, as shown in Figure 8.1 (Glasgow City Council 2015, 2018; McInally 2019). Private cars only had a 12% share of emissions and the remaining 8% included LGV (Light Goods Vehicles) and HGV (Heavy Goods Vehicles), (Glasgow City Council 2015, 2018; McInally 2019).

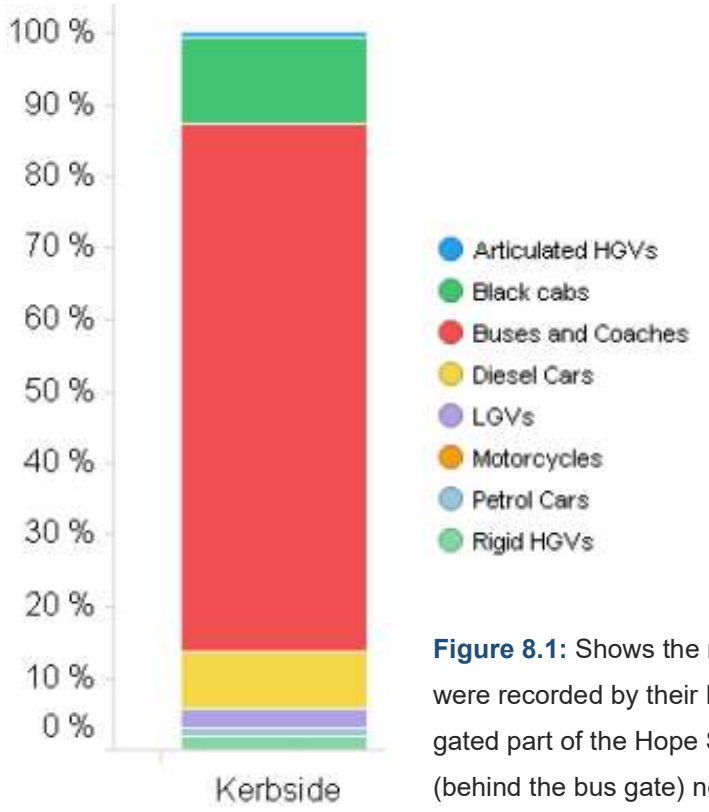


Figure 8.1: Shows the number of vehicles which were recorded by their NO_2 emissions within the gated part of the Hope Street monitoring area (behind the bus gate) near to bus stop 1. The model is part of the City of Glasgow's drive toward clean air vision.

Source: SEPA (2018).

♦ 8.2.3) Monitoring Sites.

Three of the fifteen bus shelters along Hope Street were chosen for monitoring over two weeks from the 5th June to the 19th June 2018. An 84-minute monitoring period was sampled at each bus stop during the morning (08:00–09:24) and afternoon (17:00–18:24) rush hours over the two weeks.

The morning rush hour from 08:00 to 09:24 GMT was sampled during the second week of fieldwork and the afternoon rush hour from 17:00 to 18:24 GMT was sampled during the first week of fieldwork. The bus stops were chosen at representative locations along the road, incorporating three styles of the bus shelter. Figure 8.2 shows the location of the shelters, and Table 8.1 documents information about the bus stops' monitoring localities.

Table 8.1: A description of the three bus stops chosen for monitoring.

	'Bus Stop One'	*'Bus Stop Two'*	*'Bus Stop Three'*
Facing Direction (i.e. towards the road).	Forwards (Roadside)	Backwards (Building-side)	N/A (Stop Pole Only)
Structure Type	Three Panels with two offset openings, a bench and a slanted roof.	A single panel with a cantilever roof. Commuters are behind a panel.	A stop pole with the bus timetable and a flag.
Distance to Kerb	1 metre,	1 metre	0.2 metres
Distance to an Intersection	15 metres north, or 26 metres south	19 metres north, or 20 metres south	40 metres north, or 30 metres south
Built Environment Behind Bus Shelter	Multi-storey (6 levels) building, with retail stores. Buildings set 10 metres back from the bus stop.	Multi-level (5 levels) building with a ground-level restaurant. Setback 2 metres from the bus stop.	A three levels office building, next to West Regent Lane. Buildings set 2 metres back from the bus stop.
Immediate Surroundings	Located close to Glasgow Central Railway Station.	The stop is between the busy streets of St Vincent and St George Streets	Nothing of note.
Notable Features	Taxis join the road from Gordon Street. The location is behind bus gates and is only for public vehicles and pedal bikes.	This station is at the bottom of a gentle incline with a slope of approximately 3 degrees.	A continuation of the slope, although the gradient rises slightly perhaps to 5 degrees.
Pedestrians	Busy but mostly comprising commuters. Lots of room behind as in a plaza area.	Quite Narrow and lots of pedestrians squeezing past during peak hours. Cannot fit people four abreast.	A quieter section of Hope Street. Still as narrow and busy as *'Bus Stop Two'* during peak hours.

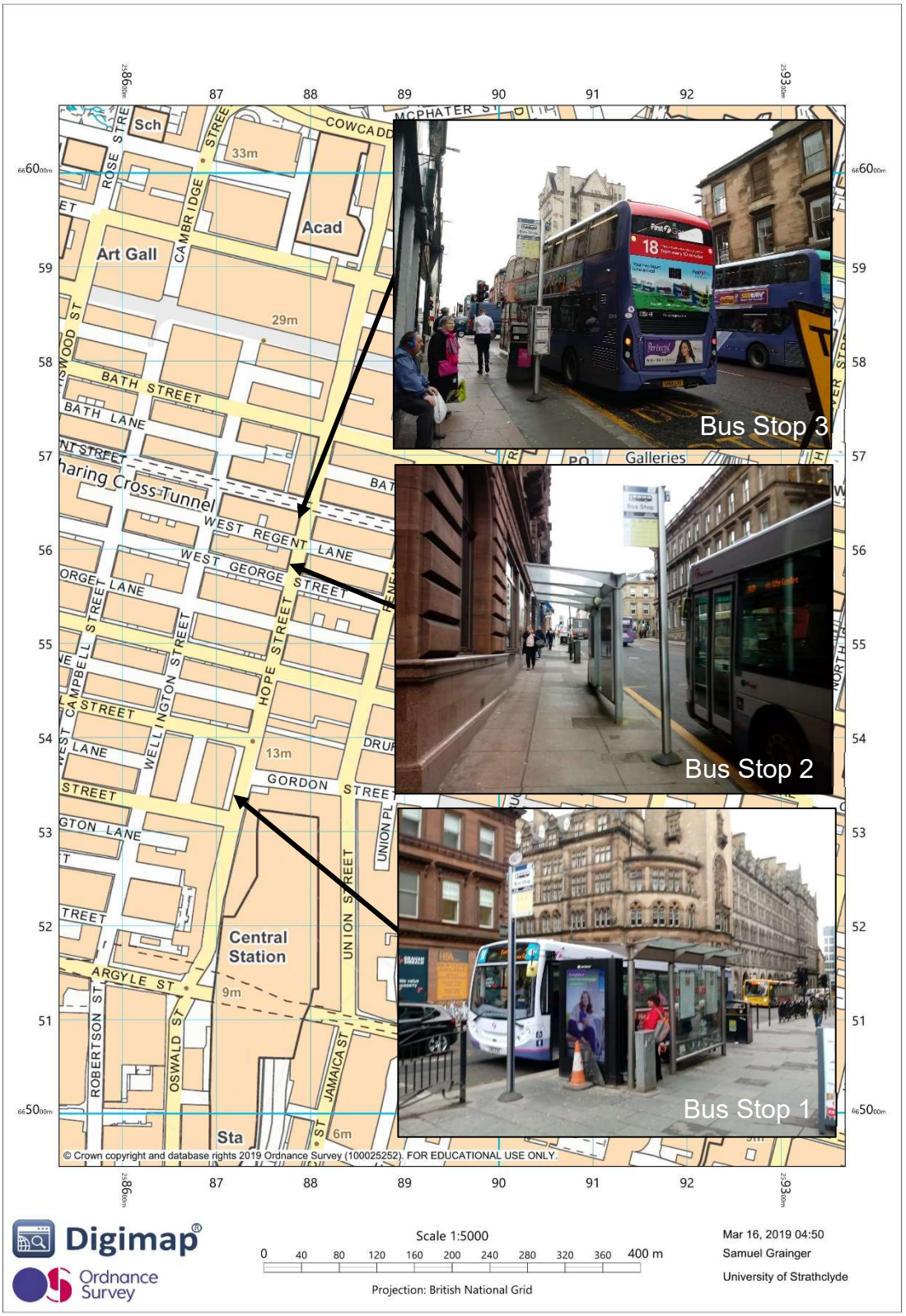


Figure 8.2: Shows a series of photographs of the bus stops 1 through 3 and their positions along Hope Street, Glasgow.

Source: Photographs - Grainger (2019), Base map - Digimap and Ordnance Survey (2019).

Contains Ordnance Survey data. © Crown copyright and database right 2010. Data provided by Digimap OpenStream, an EDINA, University of Edinburgh Service.

♦ 8.2.4) Sampling and Instrumentation.

The research was performed in two key stages:

- **STAGE 1:** During the first stage of the analysis, all the instruments are located separately, with one user remaining inside of the bus shelter and the other moving between the 'South' (down-road and before) and 'North' (up-road and after) positions. Each phase of monitoring lasted for 10 minutes.
- **STAGE 2:** During the second stage, all the instruments are combined into one backpack. The user continues to stay inside/next to the bus stop for 10 minutes, and the other user handles the combined instruments.

This strategy leads to 30 minutes of 'South' readings per bus stop, 60 minutes of inside bus stop readings, and 20 minutes outside for each of the rush hour sessions. This time was doubled over both rush hour periods to allow for 60 minutes of 'South', 120 minutes of inside and 40 minutes of north bus stop readings. There is a bias toward inside measurements, with 20 more minutes of data collection than outside measurements.

Table 8.2: A timetable of the monitoring times for the morning and afternoon rush hour periods.

Morning Rush Hour: (11th to 15th June 2018)		
Time	Backpack	
	1	2
Instruments	MicroPEM 764 and Aeth-1303	MicroPEM 765 and Aeth-1204
08:00	Inside	South
08:10	Inside	North
08:20	Inside	South
08:30	Co-Located	
08:34	Inside	
08:44	South	
08:54	Inside	
09:04	North	
09:14	Inside	
09.24	End	

Afternoon Rush Hour: (5th to 8th June 2018)		
Time	Backpack	
	1	2
Instruments	MicroPEM 764 and Aeth-1303	MicroPEM 765 and Aeth-1204
17:00	Inside	South
17:10	Inside	North
17:20	Inside	South
17:30	Co-Located	
17:34	Inside	
17:44	South	
17:54	Inside	
18:04	North	
18:14	Inside	
18:24	End	

Table 8.3. Total monitoring periods at each of the bus stops and the time taken at each of the three chosen positions.

	South (South)	Inside	North (North)
Time at each locality per fieldwork session.	30 Minutes	60 Minutes	20 minutes
North both fieldwork sessions.	60 Minutes	120 Minutes	40 Minutes

♦ 8.2.5) Black Carbon (BC) Concentrations.

Black Carbon was measured using two AethLabs: AE51 Micro-Aethalometers, commonly known as MicroAeth's (serial numbers AE51-1303 and AE51-1204), (AethLabs 2016a, b). During sampling, particulate is deposited on a PTFE coated glass fibre strip and a laser is shone onto the deposit; the attenuation of the laser light is proportional to the BC concentration, with a resolution of one nanogram, (AethLabs 2016a, b). Additional information about the AE51 can be found in Experiment 6: Supplemental A. During monitoring the AE54 is secured inside a backpack, with a one-metre long section of coiled AC tubing connecting the device to outside air, specifically the tube is secured to the user's shoulder (with adhesive tape) to allow sampling within the user's breathing zone (Ezani *et al.* 2018). A rain hood is affixed to the end of the tubing to help prevent foreign objects and water ingress into the instrument, (Ezani *et al.* 2018).

During this experiment, the MicroAeth recorded data once every 10 seconds, with an average flow rate of 100 ml/min, though this was averaged over one minute (AethLabs 2016a, b). At the beginning and end of each field-day, the instruments underwent a zero-calibration, i.e. a HEPA filter was attached to the end of the instrument for 10 minutes, as per Zhang *et al.* 2018. The baseline average for this period was subtracted from the average result to zero the device effectively.

A flow test was carried out before and after fieldwork to ensure that the flow rate remained constant (within 5%), no problems were encountered, (Lin *et al.* 2017; Ezani *et al.* 2018). Both methods of calibration are outlined further in Experiment 6: Supplemental A.

At the end of each field-day, the data was downloaded from the device using the MicroAethCOM software (Version 2.2.4.0), (AethLabs 2016a, b). The data was processed following the manufacturer's procedure and software, i.e. via an Optimised Noise Algorithm (ONA) method with a ΔATN value of 0.01, as per Experiment 6: Supplemental A (AethLabs 2016a, b).

♦ 8.2.6) Fine Particulate Matter ($PM_{2.5}$) concentrations.

$PM_{2.5}$ was measured by two RTI International: MicroPEM's (serial numbers MicroPEM-764 and MicroPEM-765), (RTI International 2016). The instrument contains both a nephelometer for real-time data collection and also an internal filter cassette allowing for the potential for gravimetric or microscopic investigation, (RTI International 2016). The MicroPEM operates by directing laser light into an incoming stream of suspended particulate, and detecting the attenuation of the laser light in real-time, (RTI International 2016). Like with the Aethalometer, a 1 m length of tubing is secured to the user's shoulder with a rain hood to help protect the instrument, (Ezani *et al.* 2018). Further details on the instrument are available in Experiment 6: Supplemental A.

The MicroPEM had a resolution of 1 reading per second, with an average flow rate of 500 ml/minute, (RTI International 2016). Like the MicroAeth, the MicroPEM was subjected to a zero-calibration and flow testing at the start and end of each field-day, (Zhang *et al.* 2018). The data was downloaded from the device using the MicroPEM Docking Station software (Version 2.0), at the end of each field-day (RTI International 2014). The data was processed using RMA (Reduced Major Axis) regression (Ezani *et al.* 2018). Further details about zero-calibration, flow testing, and RMA are discussed in Experiment 6. Supplemental A.

♦ 8.2.7) Palmes Diffusion Tubes (NO_2 Samplers).

Palmes Diffusion Tubes (PDT's) were prepared, used and analysed as per best practice as outlined in Experiment 6: Supplemental A; Subsection D and Supplemental B, (Ricardo-AEA 2006, 2008). Though, to summarise, the PDTs were prepared by the 'dipping method' using a 1:1 solution of Triethanolamine (TEA) to Acetone, (Ricardo-AEA 2006, 2008). Thirty-Six samplers were prepared simultaneously for both weeks of investigation, i.e. a set of 18 with duplicates (3 per bus stop per week). These samples were stored within sealed bags inside an air-tight plastic container within a laboratory refrigerator. A similar set-up was used to preserve samples before analysis. A set of three duplicate laboratory blanks were also prepared and stored in the refrigerator.

The PDT's were analysed in 2 concurrent batches of 8 samples. Nitrate collected from the PDT's meshes was extracted into an aqueous solution using water, and then by adding an azo-dye solution (sulphanilamide and NEDD [N-(1-Naphthyl) ethylenediamine]). Details of the chemical process and laboratory procedure are outlined in Experiment 6: Supplemental B. Essentially, the azo-dye reacted with the nitrate, turning the solution pink. The reacted solution was then analysed by colorimetric absorption at 540 nm (Ricardo-AEA 2006, 2008). The laboratory blank PDT tubes were analysed at the same time as the field samples, and the average mass of nitrite within the blanks was subtracted from the samplers, effectively performing a zero calibration. The nitrite mass of the PDT tubes was calculated into the ambient concentration using a diffusion coefficient for NO_2 in ambient air, the length and cross-sectional area of the PDT tube and the total exposure time, as per Experiment 6: Supplemental B. (Ricardo-AEA 2006, 2008).

♦ 8.2.8) Traffic Counting.

Traffic counting was performed using manual counting on seven classes of vehicles. These vehicle classes were; Motorcycles, Cars, Taxis, LGV, Rigid HGV, and Articulated HGV. As manual counting can be inaccurate, the results are an indicative measurement of vehicular flow, (Pal'o *et al.* 2019). To help counter the inaccuracies, both operators performed manual traffic counting. As there was a variance of ±10% between each surveyor's records, the author's records have been used for the first week of analysis and the assistant's records were used for the second week.

► 8.3) Results and Analysis.

♦ 8.3.1) Quality Assurance and Quality Control.

MicroPEM-764 returned an average Zero-correction of -6.03 µg/m^3 (5.01 to 7.78) and MicroPEM-765 had an average correction of -5.55 µg/m^3 (-3.19 to -7.64 µg/m^3). There was a moderate agreement between both MicroPEM's RMA and Zero-correction of around 68% (46 - 90%) for week one (afternoon), and 53% (3.4 - 84%) for week two (morning). While this would initially seem problematic, the relative standard deviation was only 18%, albeit ranging between 8 - 44%. The flow rate of the MicroPEM's was 0.49 ± 0.04 l/min for MicroPEM 764, and 0.50 ± 0.02 l/min for MicroPEM 765.

The Micro-Aethalometers did not operate correctly during the first week of analysis and had to be repeated. Before ONA correction, the correlation between devices during RMA and Zero-correction was 88.55% (62.75–98.76%) over both weeks. The flow rate of the MicroAeth's was 0.05 l/min with a maximum variation in one case of 0.10 l/min for MicroAeth AE51-1204, whereas MicroAeth AE51-1303 kept a constant flow rate of 0.05 l/min.

♦ 8.3.2) Air Quality at Glasgow Townhead.

The Glasgow Townhead AURN Station, located around 2 km to the North East of Hope Street, was the closest monitoring station to the sampling area,

sampling BC and NO_2. The Townhead station shows that background air quality during the monitoring period was relatively low with an average $PM_{2.5}$ concentration of 6.33 µg/m^3 and NO_2 concentrations of 14.73 µg/m^3, with no declared regional air pollution events in Scotland (Defra 2019b).

The Scottish Fire and Rescue Service replied to a series of Freedom of Information Requests, which outlined that while several incidents were reported during monitoring, none were of significance, spatially, temporally, or by severity, as to be an overwhelming source of air pollution during the study (Scottish Fire and Rescue Service, 2020a-k).

The normalised plot of NO_2 and $PM_{2.5}$ concentrations show a significant peak during the morning rush hour in Townhead (Figure 8.3A), although the distribution of $PM_{2.5}$ was more constant than NO_2. The afternoon rush hour resulted in a minor peak in $PM_{2.5}$, but there was no significant change to an already positive trend of NO_2.

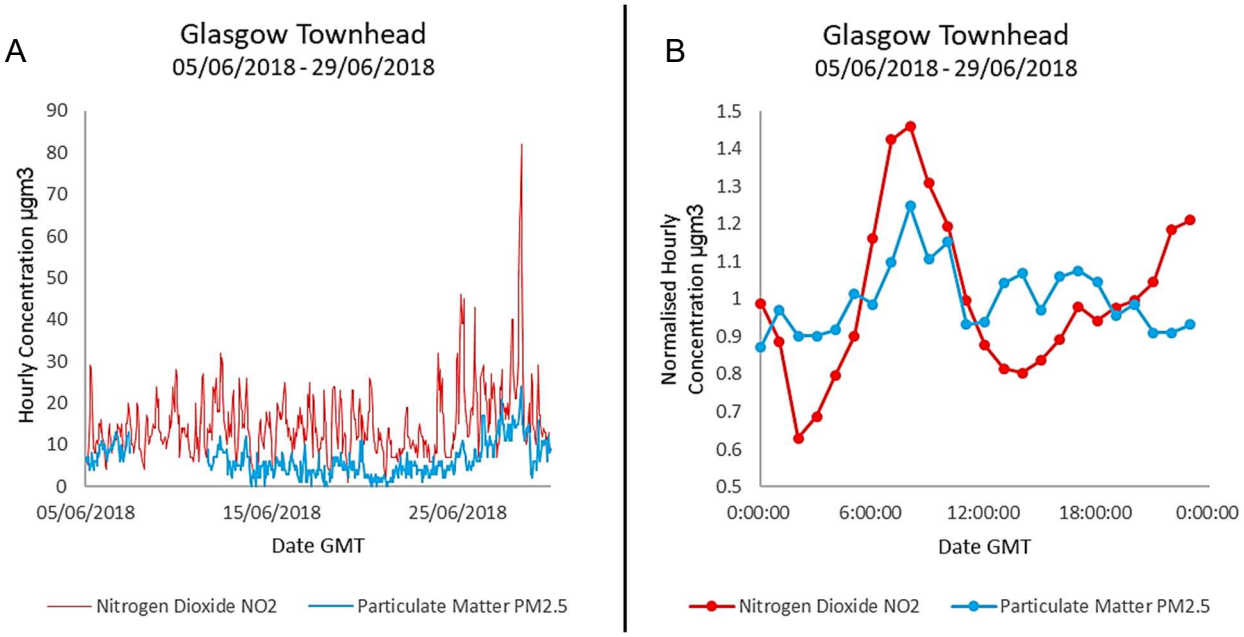


Figure 8.3.A. Shows a time plot of the levels of Nitrogen Dioxide and $PM_{2.5}$ over the whole monitoring period. There was a break in $PM_{2.5}$ monitoring from 10 am on the 7th June to 1 PM on the 11th June. **B.** The normalised levels show a bimodal distribution of NO_2 with higher concentrations in the morning and twilight hours. The $PM_{2.5}$ levels peaked both during the morning and the afternoon rush hours.

Source: Grainger (2019) using data produced by SEPA (2018).

♦ 8.3.3) Air Quality along Hope Street Bus Stops.

■ A) Phase One – Independent Measurement Devices.

Phase One of the monitoring strategy involved the separation of the MicroPEM's and MicroAeth's into two separate backpacks. Figures 9.4 A-F show the time-series concentrations of $PM_{2.5}$ at all three bus stops during both weeks of fieldwork (morning and afternoon). Similarly, Figures 9.5 A-F show the time-series BC concentrations. In this phase, one user remained inside the bus shelter or next to the stop pole, while another analyst moved between the 'south' (counter traffic flow) and 'north' (with traffic flow).

◊ I). 'Bus Stop One'.

During the morning rush hour, the mean $PM_{2.5}$ concentrations inside the bus shelter were 14.77 ± 3.45 µg/m^3 and 16.06 ± 4.91 µg/m^3 outside (Figure 8.4). No significant $PM_{2.5}$ concentrations were observed at either to the south (15.95 - 16.31 µg/m^3) or north positions (15.83 µg/m^3). Two discrete peaks occurred between 08:00:50 to 08:00:10 (at the south position) peaking at 48 µg/m^3 while the inside value remained at ~12 µg/m^3. BC was similar to $PM_{2.5}$ but with a lower average BC concentration of 4.24 ± 2.45 µg/m^3 inside and 5.34 ± 6.05 µg/m^3 outside (Figure 8.5). There was a substantial increase in BC concentration at 08:06 with an outside concentration at 34.91 µg/m^3, while the inside remained fairly constant.

During the afternoon rush hour at *'Bus Stop One'*, the concentrations of $PM_{2.5}$ had more variation than the morning, but with a similar mean $PM_{2.5}$ concentration of 14.87 ± 4.96 µg/m^3 inside and 15.36 ± 9.08 µg/m^3 outside. There were no significant $PM_{2.5}$ concentration differences at either the 'south' (average between 14.61 – 16.26 µg/m^3) or northern positions (average 14.90 µg/m^3). There were 5 peaks above 40 ug/m^3 at 17:00:30, 17:09:40, 17:12:40, 17:23:40 and 17:24:10.

Some peaks were shared between indoor and outdoor levels, such as the highest peak at 17:12:40 which had a concentration of 75 µg/m^3 of $PM_{2.5}$ outdoors while the indoor concentration rose to 39 µg/m^3. For the BC concentration, there were more pronounced peaks in the afternoon than for the morning. The average inside concentration was 6.57 ± 5.55 µgm^3 while the outside reached 8.48 ± 10.57 µgm^3. The differences in the mean concentration and the standard deviation are illustrative of the significance of the peaks during the afternoon rush hour. The most significant peaks were at 17:10 and 17:13 during the south position, which increased both the outside and inside concentration of BC. The largest BC peak recorded inside at 17:10 had a concentration of 49.76 µgm^3 with 24.75 µg/m^3.

◊ II). 'Bus Stop Two'.

The concentrations of $PM_{2.5}$ were variable in the morning and dominated by a series of peaks, as there were 40 readings which peaked above the UK $PM_{2.5}$ guidance (24 hours) value of 25 µg/m^3. The most significant of these peaks had a maximum value of 131.00 µg/m^3 at 08:07:00, the indoors values increased about 20 seconds after this significant peak with a mean one-minute concentration of 48.29 (max 70.00) µg/m^3 (Figure 8.4). The mean $PM_{2.5}$ concentration was 18.10 ± 11.09 µg/m^3 (inside) and 21.01 ± 16.97 µg/m^3 (outside). Nethertheless, there were no significant $PM_{2.5}$ concentration differences to either the south (18.31 - 26.16 µg/m^3) or north positions (19.36 µg/m^3). In the morning session at bus stop two, there was a mean BC concentration of 15.61 ± 20.18 µg/m^3 (inside) and 17.90 ± 11.95 µg/m^3 (outside) as shown in Figure 8.5. There was a high standard deviation due to a BC peak at 08:29 with an outdoor value of 136.29 and inside of 102.57 µg/m^3. If the assumed BC (24 hours) guidance value of 33.08 µg/m^3 is used, as suggested in Experiment 3, then four minutes were above the guideline during the morning, with concentrations between 36.99 and 136.29 µg/m^3 outdoors and 43.27 and 102.57 µg/m^3 indoors.

In the afternoon, there was a problem with the $PM_{2.5}$ outdoors instrument (only), which led to abnormally low concentrations after 17:05 - however, the data still showed variance. The data after 17:05:00 was modified to show an indicative value. The correcting factor is shown in Equation 9.1, this estimate was speculative and used without credence for the sole reason of estimative comparison of the two data entries graphically, the result appeared somewhat accurate but woefully imprecise.

Equation 8.1.

$$Nc = 3 + N + N^{\frac{3}{2}}$$

Corrected $PM_{2.5}$ Value.

(N) Average 1 Minute Concentration of $PM_{2.5}$

The average $PM_{2.5}$ concentration for the fully working inside monitor was 11.20 ± 7.07 µg/m^3, while the corrected $PM_{2.5}$ concentration outdoors had a value of around 12 µg/m^3. This is similar to the morning, where the concentrations of $PM_{2.5}$ were higher outside than inside. Eight data entries were over the $PM_{2.5}$ guidance value (25 µg/m^3) for the inside locality, which accounted for $PM_{2.5}$ concentration of between 29 and 64 µg/m^3. The outside BC monitoring device was again not working for the afternoon session, though the inside monitor had an average BC concentration of 14.95 ± 11.95 µg/m^3 similar to the morning session. There were three values over the BC (24 hours) guidance value, which reached maximum concentrations between 42.74, and 46.12 µg/m^3.

◊ III). 'Bus Stop Three'.

The concentrations of $PM_{2.5}$ at bus stop 3 were unlike the other monitoring positions in that the inside concentration was higher than outside. However, this inside position is just next to the stop pole and flag, with no other structure to protect the patrons.

The inside mean concentration was 17.70 ± 22.51 µg/m^3 inside with an outdoors concentration of 16.72 ± 23.01 µg/m^3 in the morning (Figure 8.4). The data variation was greater outdoors than 'indoors'. There were no significant $PM_{2.5}$ differences between the south (12.72 – 22.11 µg/m^3) or northern positions (15.44 µg/m^3). Twenty-two indoor and outdoor readings peaked above 25 µg/m^3. The highest peak within the data series was shared between the inside and outside positions at 08:26:10, peaking at 287 µg/m^3 inside and 259 µg/m^3 outside.

The average BC concentration was 22.35 ± 39.41 µg/m^3 inside and 25.39 ± 45.54 µg/m^3 outside. The high standard deviation was due to the impact of a peak BC value at 08:26 (shared with the $PM_{2.5}$ concentration) with an outdoor value of 250.44 and inside of 213.73 µg/m^3 (Figure 8.5). With this peak removed, the standard deviation was more than halved, and the mean brought down by 7 µg/m^3. The suggested guideline value (33 µg/m^3) is breached six times during the morning, with concentrations varying inside between 48.32 to 213.73 µg/m^3 and outside between 47.24 to 250.44 µg/m^3.

During the afternoon rush hour at Bus Stop Three, there was an average concentration of 12.26 ± 6.03 µg/m^3 (inside) and 13.21 ± 8.12 µg/m^3 (outside). There was a minor $PM_{2.5}$ variance between the southern position (11.48 - 12.30 µg/m^3) and the north (at 15.91 µg/m^3). There were eleven peaks above 25 µg/m^3 outside and nine inside, six of these peaks were shared between monitoring positions (within 10 seconds). The highest $PM_{2.5}$ peak, at 17:12:20, had a concentration of 73 µg/m^3 outdoors, while the indoor concentration rose to 46 µg/m^3. Only the inside monitor was functioning. This device had an average BC concentration of 10.40 ± 10.83 µg/m^3, which was about half of the morning session. There were two values over the BC (24 hours) guidance value at 17:18 and 17:20, which peaked at 47.89 and 44.19 µg/m^3, though these datapoints were not associated with any major peak in the $PM_{2.5}$ data.

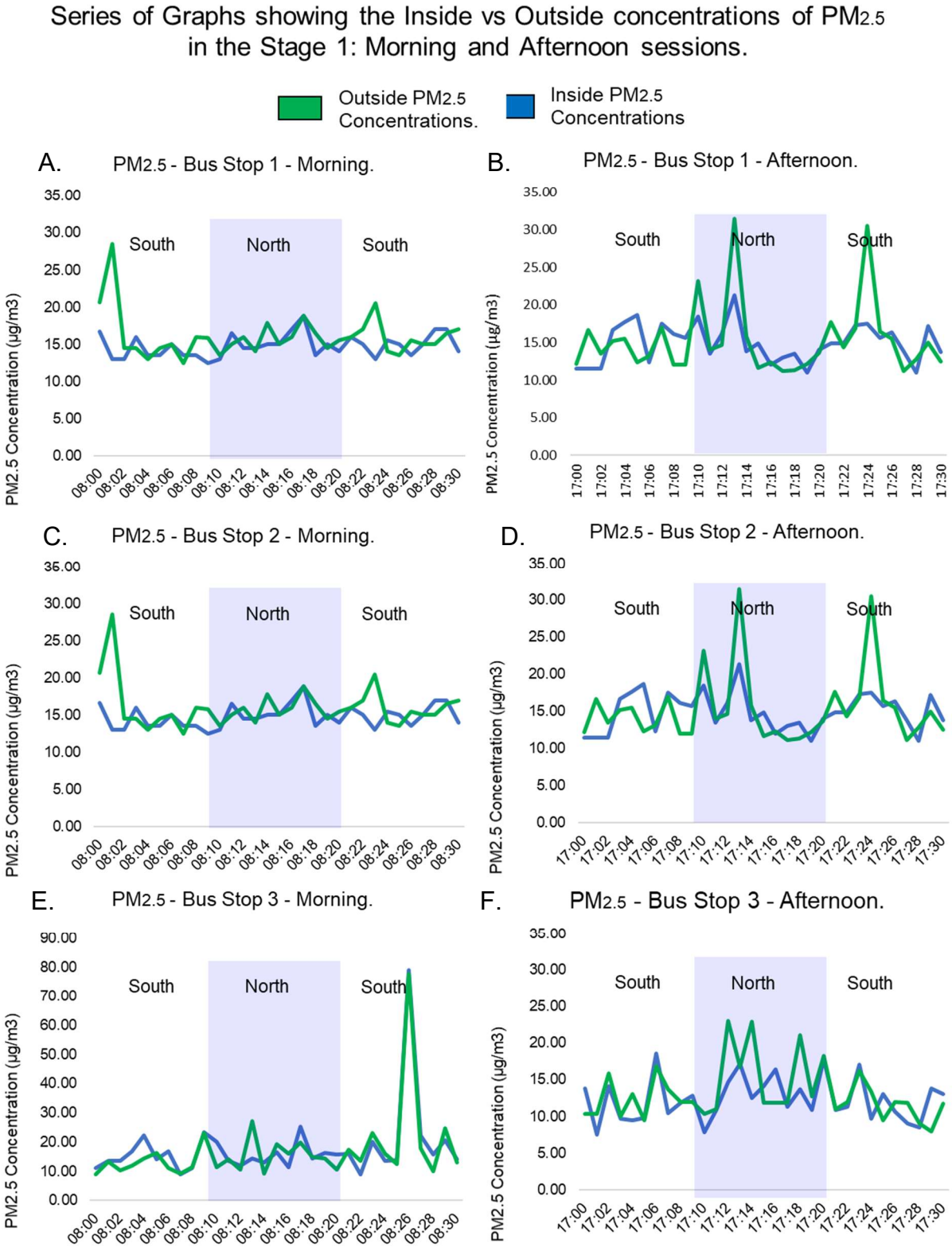


Figure 8.4. Shows a time plot of the levels of $PM_{2.5}$ over the first phase of the monitoring investigation at all bus stop localities, the graphs on the left show the morning rush hour, and those on the right show the afternoon rush hour. The green line shows the concentrations of the outside MicroPEM device for which the grey pattern applies, the blue line was taken continuously indoors and the grey positions indicated are void as the sample position was indoors.

Source; Author – Grainger (2020)

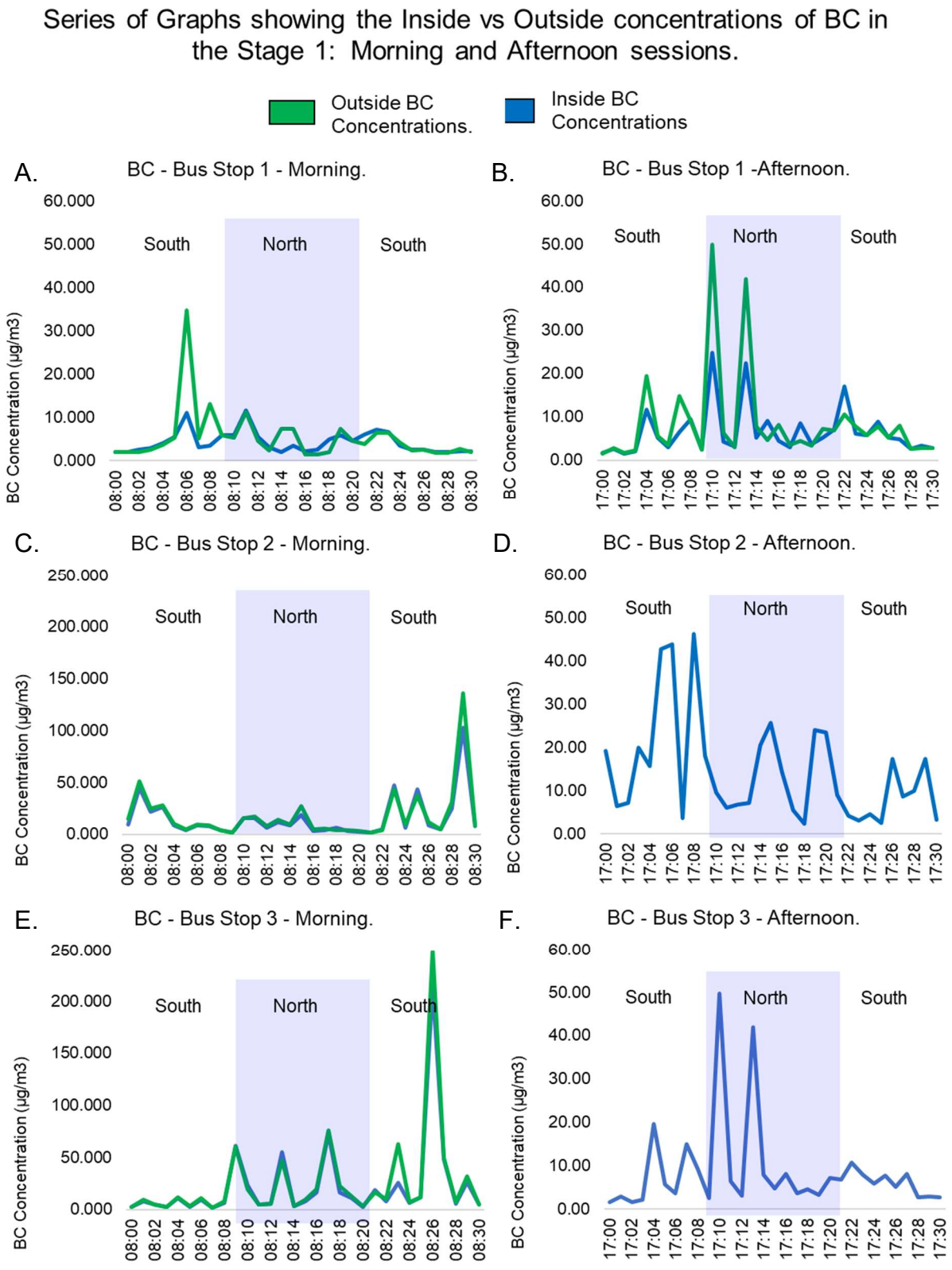


Figure 8.5. Shows a time plot of the levels of BC over the first phase of the monitoring investigation at all bus stop localities, the graphs on the left show the morning rush hour, and those on the right show the afternoon rush hour. The green line shows the concentrations of the outside MicroAeth device for which the grey pattern applies, the blue line was taken continuously indoors and the grey positions indicated are void as the sample position was indoors.

Source: Author – Grainger (2020)

■ B) Phase Two – Co-Located Measurement Devices.

Phase two of the monitoring strategy involved the co-location of both MicroPEM's and MicroAeth's within the same backpack for half an hour, moving to the south, middle (inside) and north positions. Figures 9.6 A-F show the time-series concentrations of $PM_{2.5}$ at all three-bus stops, and similarly Figures 9.7 A-F show the time-series BC concentrations.

◊ I). *'Bus Stop One'.*

During the second phase of the morning rush hour at *''Bus Stop One"*, the $PM_{2.5}$ measurement was consistent with the first phase, with a mean $PM_{2.5}$ concentration of 15.81 ± 2.45 µg/m^3 (inside) and 16.14 ± 4.27 µg/m^3 (outside) as per Figure 8.6. There was a noticeable difference between the North and South positions, between 17.92 ± 3.31 µg/m^3 to the south and 14.47 ± 1.14 µg/m^3 to the north. There were 23 readings above the screening value of 25 µg/m^3, although this resolved into eight averaged readings on both instruments. The highest of these readings happened at 09:23:50 inside the bus shelter at a concentration of 67 µg/m^3. When resolved over a minute none of the readings had a value of over 25 µg/m^3, the highest minute reading being 23.75 µg/m^3 (at 08:58).

The BC distribution was slightly higher than the first phase with an average inside BC concentration of 7.38 ± 8.58 µg/m^3 (including 2.98, 8.68 and 10.49 µg/m^3), The average outside concentration was 7.57 ± 10.11 µg/m^3 (with 8.66 µg/m^3 to the south and 6.48 µg/m^3 to the north) as per Figure 8.7. Three minutes of data were above the BC screening value. There were differences between the North and South positions with average BC concentrations of 8.66 ± 14.84 and 6.48 ± 5.38 µg/m^3. This difference may be significant as the inside concentrations were rising during this time from 2.98 to 6.48 µg/m^3.

During the second phase of the afternoon rush hour, the $PM_{2.5}$ concentration was noticeably lower than phase one, with an average concentration of 11.38 ± 2.39 µg/m^3 (inside) and 12.46 ± 1.09 µg/m^3 (outside). The difference between the North and South positions was notable with 10.95 ± 0.78 µg/m^3 to the south and 13.51 ± 1.40 µg/m^3 to the north. Altogether 15 readings were above the screening value of 25 µg/m^3, although this resolved into five averaged readings. The highest of these readings happened at 18:21:10 inside the bus shelter at a concentration of 39 µg/m^3. When resolved over a minute, none of the readings was over 25 µg/m^3, the highest minute reading being 24.25 µg/m^3 (at 18:21). The BC distribution was almost half the morning session, with an average inside BC concentration of 3.12 ± 3.32 µg/m^3 (with 10-minute averages of 3.81, 2.72, and 4.41 µg/m^3) and an average outside concentration of 3.10 ± 2.31 µg/m^3 (with a 10-minute average of 1.78 µg/m^3 to the south and 4.41 µg/m^3 to the north). No readings were above the 33 µg/m^3 guideline value. Again, there was a subtle difference between the North and South positions, with average BC concentrations of 4.41 µg/m^3 to the north and 1.78 ± 0.70 µg/m^3 to the south.

◊ II). *'Bus Stop Two'*.

During the second phase of morning rush hour at *'Bus Stop Two*, there was a mean $PM_{2.5}$ concentration of 14.63 ± 15.65 µg/m^3 (inside) and 15.38 ± 14.58 µg/m^3 (outside). There was a noticeable difference between the North and South positions, with 15.74 ± 1.83 µg/m^3 to the south and 13.42 ± 0.84 µg/m^3 to the north. There were 27 readings above the screening value of 25 µg/m^3, although this resolved into 13 averaged readings on both instruments above the screening values. The highest of these readings occurred at 09:15:50 at 43 µg/m^3, though only inside the shelter. When resolved over a minute, none of the readings was over 25 µg/m^3, the highest being 22.50 µg/m^3 (at 08:38).

The BC distribution was higher than the first phase, with an average inside BC concentration of 17.25 ± 20.04 µg/m^3 (with 10-minute averages of 8.64, 11.21 and 31.90 µg/m^3) and an average outside concentration of 15.72 ± 11.76 µg/m^3 (with a 10-minute average of 20.97 µg/m^3 to the south and 10.47 µg/m^3 to the north). Nine readings were above the 33 µg/m^3 guideline value, which resolved into 5 minutes above the guideline. The last peak at 09:19 corresponded to the highest BC value throughout the survey at 170.20 µg/m^3. There was a significant difference between the North and South, positions with an average BC concentration of 10.47 ± 7.16 µg/m^3 to the north and 20.97 ± 16.36 µg/m^3 to the south. This was likely significant due to the difference and due to the inside measurements rising within the same periods. During the second phase of afternoon rush hour, the $PM_{2.5}$ concentration was noticeably lower than phase one, with an average inside the concentration of 11.38 ± 2.39 µg/m^3 (inside) and 12.46 ± 1.09 µg/m^3 (outside). There was a noticeable difference between the North and South positions, between 10.95 ± 0.78 µg/m^3 to the south and 13.51 ± 1.40 µg/m^3 to the north, consistent with the second phase of the morning readings. Altogether 15 readings were above the screening value of 25 µg/m^3, although this resolved into five averaged readings. The highest of these readings occurred at 18:21:10, inside the bus shelter at 39 µg/m^3. When averaged over a minute, none of the readings was over 25 µg/m^3, the highest minute reading being 24.25 µg/m^3 (at 18:21).

The BC distribution was slightly higher than per Phase 1, with an average inside BC concentration of 10.55 ± 7.70 µg/m^3 (10-minute averages of 3.76, 12.43, and 15.46 µg/m^3) and an average outside concentration of 8.06 ± 5.06 µg/m^3 (a 10-minute average of 8.38 µg/m^3 - south and 7.74 µg/m^3 - north). Two minutes (from the working instrument) were above the guideline value with readings at 36.04 and 42.14 µg/m^3. There was an insignificant difference between the North and South positions with average BC concentrations of 7.74 ± 4.36 to the north and 8.38 ± 5.77 µg/m^3 to the south.

◊ III). *'Bus Stop Three'*.

The $PM_{2.5}$ at Bus Stop 3 was relatively consistent with the Phase 1 measurements, with a mean $PM_{2.5}$ concentration of 24.19 ± 15.33 µg/m^3 (inside) and 13.33 ± 18.79 µg/m^3 (outside). There was a noticeable difference between the North and South positions, between 16.55 ± 4.96 µg/m^3 to the south and 21.03 ± 8.58 µg/m^3 to the north. There were 108 readings above the screening value of 25 µg/m^3, although this resolved into 37 averaged readings on both instruments above the screening values. The highest of these readings happened at 09:12:10 to the north, with a concentration of 57 µg/m^3. Seven minutes were over the screening value, the highest of which was at 09:12 at 33.25 µg/m^3.

The BC distribution was higher than the first phase, with an average inside BC concentration of 19.58 ± 12.89 µg/m^3 (with averages of 11.49, 13.52, and 14.72 µg/m^3) and an average outside concentration of 11.84 ± 5.92 µg/m^3 (with an average of 12.20 µg/m^3 to the south and 11.49 µg/m^3 to the north). Twelve readings resolved into 4 minutes above the BC guideline value. There were no significant differences between the North and South positions with average BC concentrations of 11.49 ± 4.68 µg/m^3 and 12.20 ± 7.17 µg/m^3, respectively. During the second phase of the afternoon rush hour, there was an average inside (adjacent to the stop pole) concentration of 20.67 ± 16.64 µg/m^3 (inside) and a low outside value of 9.42 ± 9.17 µg/m^3. There was no significant difference between the North and South positions, with an average of 15.74 ± 1.83 µg/m^3 to the south and 13.42 ± 0.84 µg/m^3 to the north. Altogether 45 readings were above the $PM_{2.5}$ screening value, although this resolved into 36 averaged readings. The highest of these readings occurred at 18:19:10, inside the bus shelter, at a concentration of 60 µg/m^3. These readings corresponded to four minutes over the guideline value, the highest minute reading being 27.83 µg/m^3 (at 18:19).

The BC had an average inside BC concentration at bus stop 3 of 5.96 ± 6.45 $\mu g/m^3$ (with 10-minute averages of 3.99, 6.74, and 7.15 $\mu g/m^3$) and an average outside concentration of 6.02 ± 7.44 $\mu g/m^3$ (with a 10-minute average of 4.07 $\mu g/m^3$ to the south and 7.97 $\mu g/m^3$ to the north). No readings were above the 33 $\mu g/m^3$, the highest being 31.84 $\mu g/m^3$. There was a minor concentration difference between the North and South positions, with average BC concentrations of 7.97 ± 8.81 $\mu g/m^3$ to the north and 4.07 ± 5.04 $\mu g/m^3$ to the south, though this difference was within half of the standard deviation.

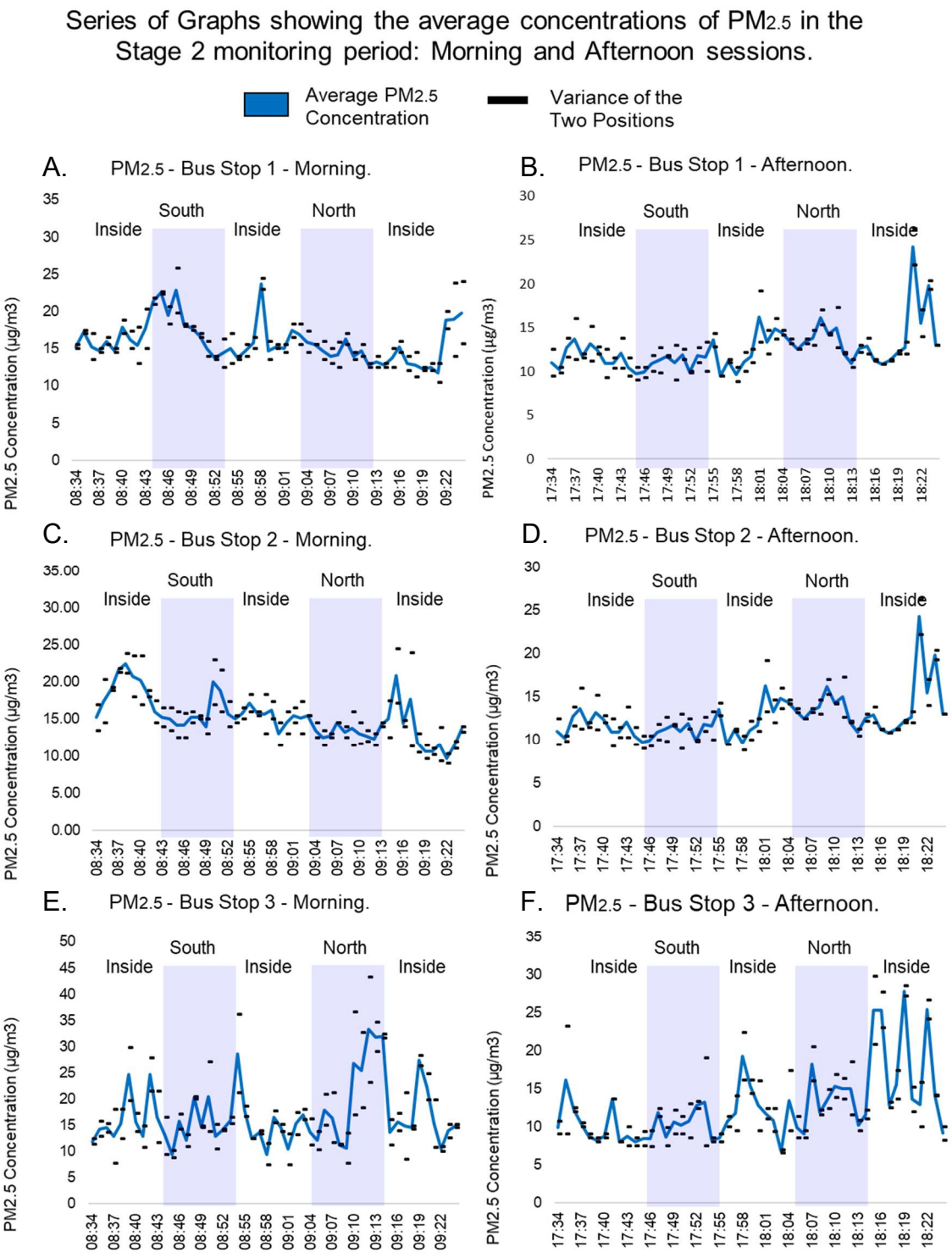


Figure 8.6. Shows a time plot of the levels of $PM_{2.5}$ over the second phase of the monitoring investigation at all bus stop localities, the graphs on the left show the morning rush hour, and those on the right show the afternoon rush hour. The blue line shows the average of the co-located devices with the grey bands showing the position of the devices. The dots indicate the devices actual results and are shown to demonstrate the inter-instrument variance.

Source; Author – Grainger (2020)

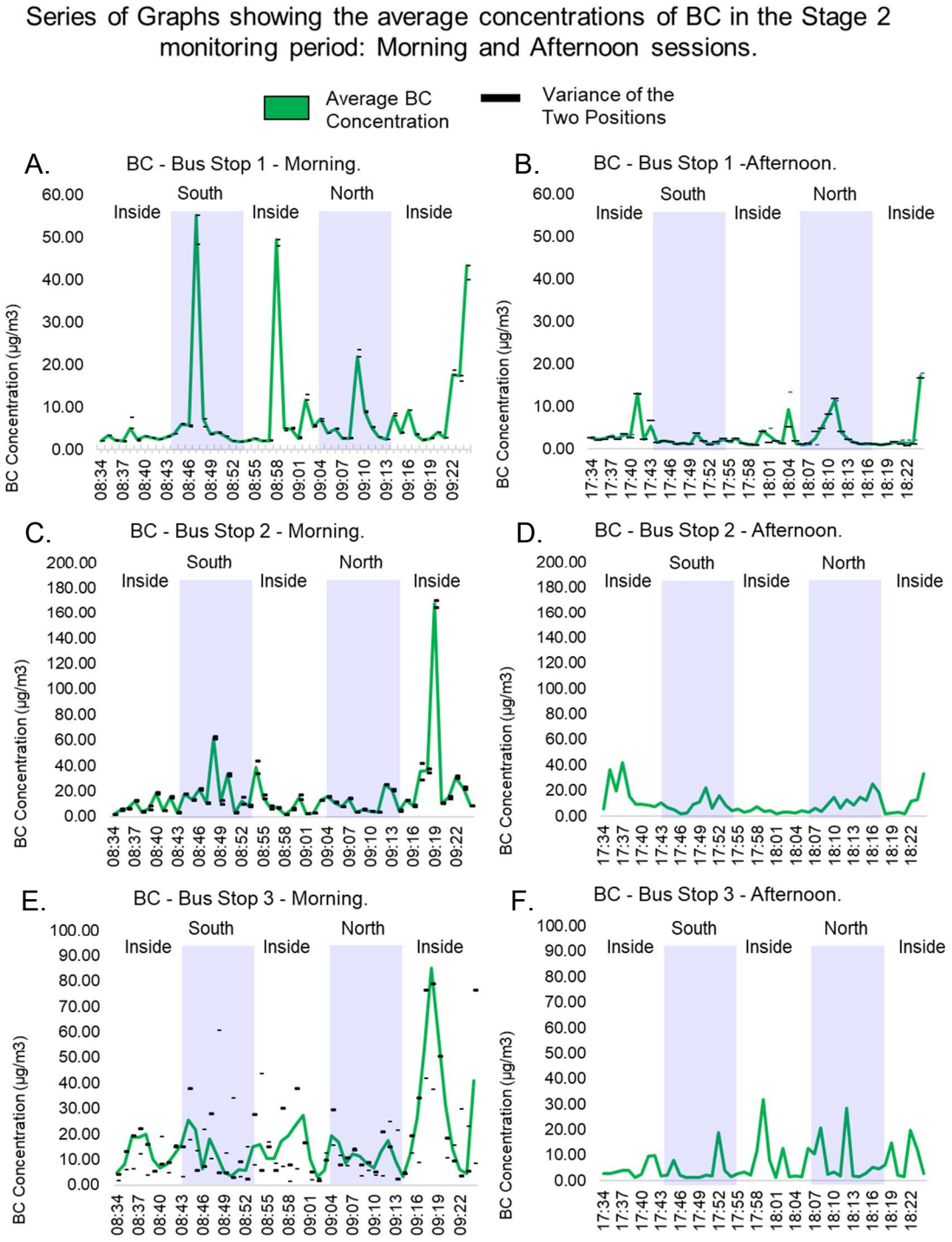


Figure 8.7. Shows a time plot of the levels of BC over the second phase of the monitoring investigation at all bus stop localities, the graphs on the left show the morning rush hour, and those on the right show the afternoon rush hour. The green line shows the average of the co-located devices with the grey bands showing the position of the devices. The dots indicate the devices actual results and are shown to demonstrate the inter-instrument variance.

Source; Author – Grainger (2020)

■ C) Nitrogen Dioxide Passive Monitoring.

A set of PDT tubes were installed at the start of each week of monitoring. The results showed high concentrations of NO_2 above the annual mean guidance value of 40 µg/m^3 at all the monitoring locations. All NO_2 results were above 72.08 µg/m^3, with the highest concentrations reaching 111.78 µg/m^3. Concentrations were lower inside the bus shelter than outside the bus shelter. At all locations, the 'south' position was higher than the 'north' position by several micrograms (bar Week 2- Bus Shelter 2).

The NO_2 concentration in *'Bus Stop One'* averaged 74.12 µg/m^3 inside (between 72.08–76.15 µg/m^3) and was nearly double the annual guideline value. NO_2 concentrations were higher by 14 µg/m^3 outdoors, i.e. 88 µg/m^3 to the south and 82 µg/m^3 to the north.

Table 8.4: The results of the PDT Palmes Diffusion Tubes in the associated bus stops, during the two weeks of analysis.

	Type	Sample Location	Week 1		Week 2	
			Dates	Concentration Mean (µg/m^3)	Dates	Concentration Mean (µg/m^3)
Location 1- Three Panel Bus Shelter	NO_2 Via PDT Tubes	South	04/06/18 to 11/06/18	86.24	11/06/18 to 18/06/18	89.53
		Inside		72.08		76.15
		North		79.50		80.48
Location 2- Single Panel Bus Shelter		South		104.65		91.99
		Inside		-		88.93
		North		95.39		95.39
Location 3 – Stop Pole and Flag.		South		106.33		111.78
		Inside		-		-
		North		105.79		105.79

Bus Stop Two had a similarly high concentration inside, of 88.03 µg/m^3 (one

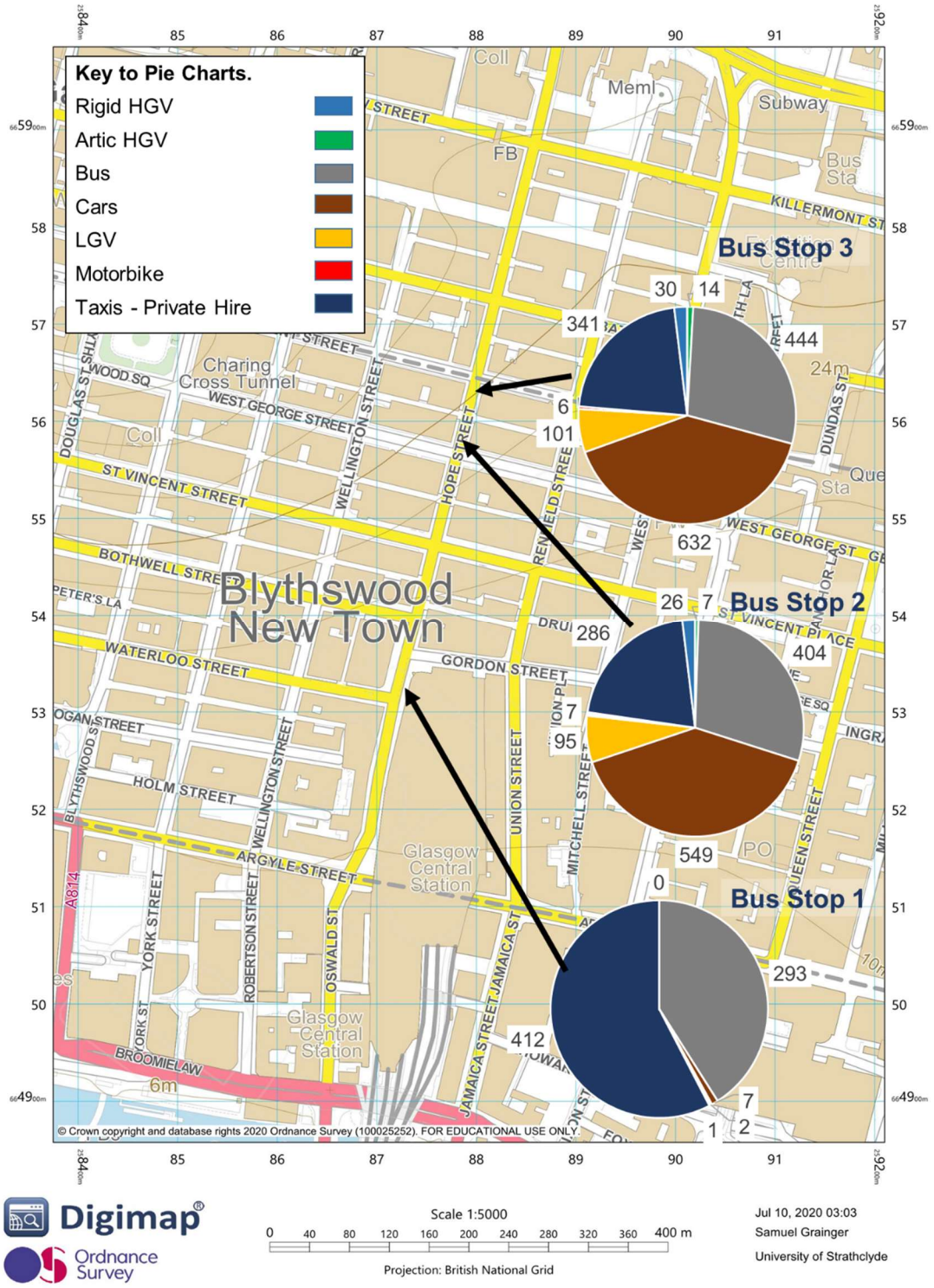
* There were problems with vandalised or broken PDT tubes during both weeks of analysis, which caused a loss of data. This majorly affected bus stop 3, where the PDT tubes were broken on both weeks, where they were placed on the bus stop pole.

set of PDT tubes were destroyed in situ). Concentrations to the north and south were about 10 µg/m^3 higher, like with the BC and $PM_{2.5}$ concentrations, the south (91.99 µg/m^3) was higher than the north (95.39 µg/m^3). Unfortunately, the inside position on the stop pole at Bus Stop Three was destroyed during both weeks of the analysis. The north position was lower than the south position during each week of analysis by between 0.54 and 5.99 µg/m^3, which followed the trend of BC and $PM_{2.5}$.

■ D) Traffic Flow.

Indicative traffic flow data was collected by manual counting; a graphical representation of the number, type, and location of vehicles is shown in Figure 8.8. Bus Stop One was located in a traffic controlled area, allowing only public vehicles. Altogether, 792 vehicles were counted, which included 208 taxis (private hire vehicles) and 128 buses. These two sources accounted for 98.8% of all vehicles; the remaining 1.2% comprised cars (0.9%) and LGV (0.3%). On the public highway, Bus Stops Two and Three were closely located and thus had similar vehicular flow. Altogether, ~1,530 vehicles were counted at Bus Stop Two and ~1,790 vehicles were counted at 'Bus Stop Three' further to the north. Along this section of Hope Street, cars (privately owned) accounted for 40% of road users. Buses and taxis accounted for the second and third most common-road vehicle (~28.2% for buses and~20.7% for taxis). LGV represented around 6.6% of the road users, while HGV vehicles represented only 2.45% of road users (divided between rigid HGV at 1.8% and articulated vehicles at 0.7%).

Traffic Flow at the three bus stop localities.



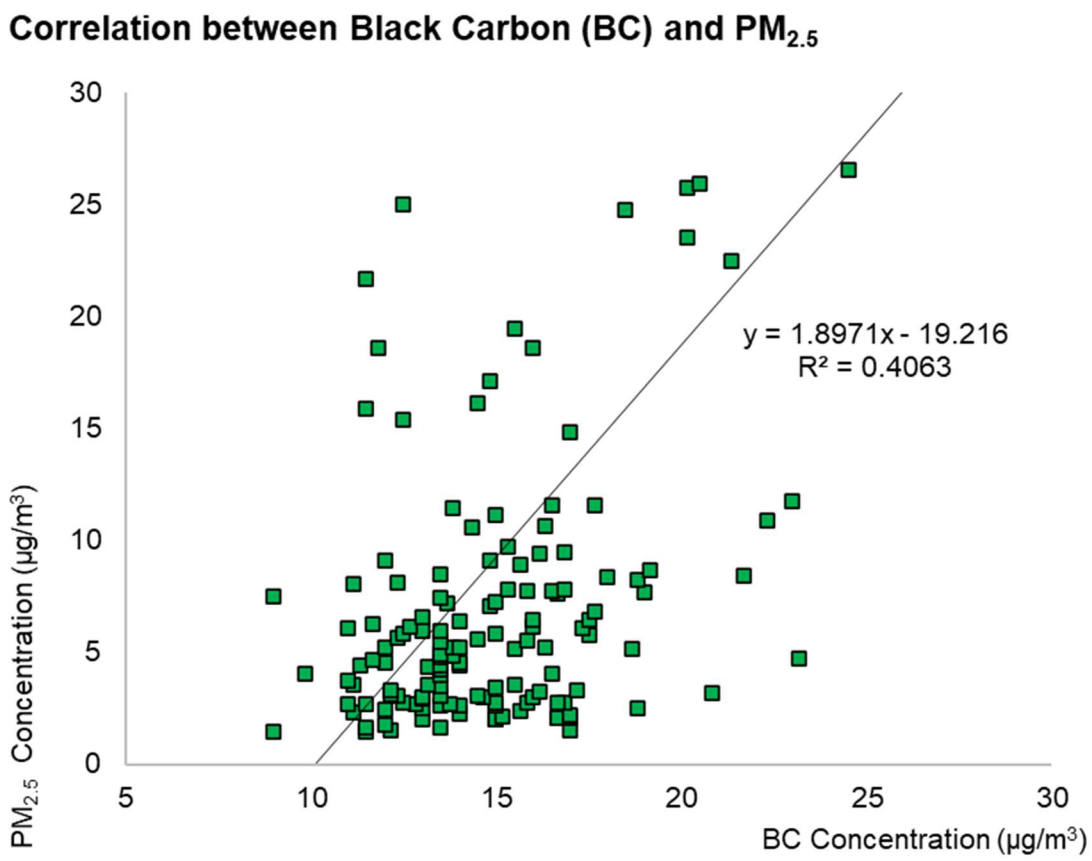
Figures 8.8 A-D, Figure A showing the area around Glasgow where the monitoring is taking place. The Arrows point to the locations of monitoring, i.e. bus stops 1-3. The pie charts display the type of vehicles which were found in the traffic counting. Bus stop one was dominated by buses and taxis whilst bus stops two and three were similar with buses, cars and taxis contributing large percentages of the motor vehicle fleet at these localities.

Source: Graphs - Grainger (2019), Base map - Digimap and Ordnance Survey (2019).

Contains Ordnance Survey data. © Crown copyright and database right 2010. Data provided by Digimap OpenStream, an EDINA, University of Edinburgh Service.

■ E) Air Pollutant Ratios and Correlations.

There is a positive correlation between BC and $PM_{2.5}$ along Hope Street, which has a weak R^2 of ~0.40. There is a steep slope on the BC vs $PM_{2.5}$ graphs which has an X-axis intercept at 10 µg/m^3, the R^2 of 0.4 indicates a possible but weak correlation between BC and $PM_{2.5}$. At concentrations below 4 µg/m^3, BC only accounts for roughly 18.52% of $PM_{2.5}$. Between 4 and 15 µg/m^3, BC accounts for roughly half of the $PM_{2.5}$ concentration (47.18%). However, concentrations above 15% are unusual in that there are higher concentrations of BC than $PM_{2.5}$ in the sample, i.e. there is, on average, 207.57% more BC than $PM_{2.5}$. This trend is troubling, as BC is considered to be a sub-category of $PM_{2.5}$.



Figures 8.9. Shows an X-Y graph showing the correlation between the BC concentration in Micrograms per cubic metres vs the $PM_{2.5}$ concentration. The correlation has a moderate agreement with a linear trendline, with an R^2 value of 40.63%. There is an intercept of the X axis at about 10 µg/m^3. **Source;** Author – Grainger (2020)

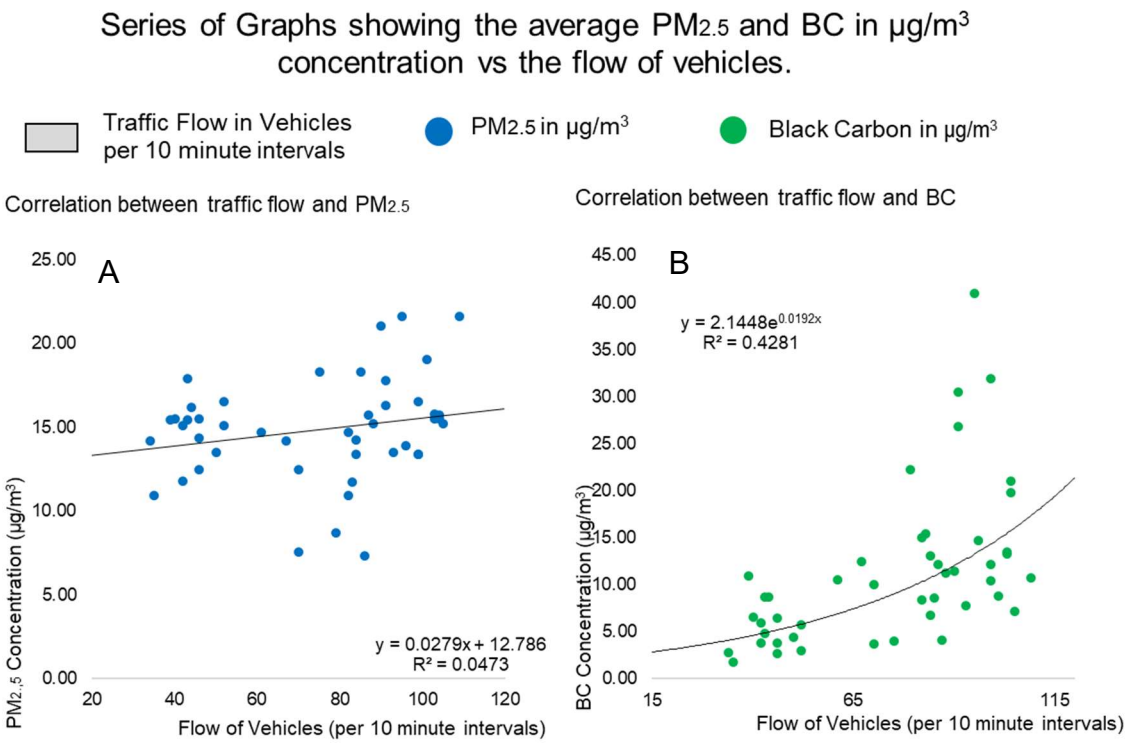
■ F) Traffic Flow vs Air Pollution.

This investigation found *Paton et al* 2018 assessment of flow vs air pollution was possibly incorrect, as the data reported here illustrates a weak but slightly positive correlation between $PM_{2.5}$ and flow of vehicles, as opposed to the negative relationship between $PM_{2.5}$ and the flow of vehicles proposed by Patton et al., 2018 (Figure 8.10). The 10-minute intervals of $PM_{2.5}$ vs traffic flow followed a weak positive relationship between $PM_{2.5}$ and BC. This relationship shows that an increase in vehicular flow potentially led to an increase in $PM_{2.5}$. The trend had a very low R^2 of 9.86 % using a polynomial (order 2) trendline and 4.73% using a linear trendline. Following a linear trendline, the $PM_{2.5}$ concentration increases by 0.02511 $\mu g/m^3$ per vehicle, with an intercept at 12.786 $\mu g/m^3$ (with 0 vehicles), likely indicating legacy $PM_{2.5}$ contamination.

The BC vs Traffic of Paton *et al. 2018* was correct, with an exponential increase in the concentration of BC along Hope Street with increased traffic flow, with a fit of the data (R^2 of 42.81%). An exponential trendline best fits the data. Following a linear trendline, the BC concentration increases by 0.18820 $\mu g/m^3$ per vehicle, with an intercept at around 15 vehicles, showing that BC is low in low traffic environments with little legacy contamination.

■ G) Temporal: Air Pollution vs Vehicular Flow.

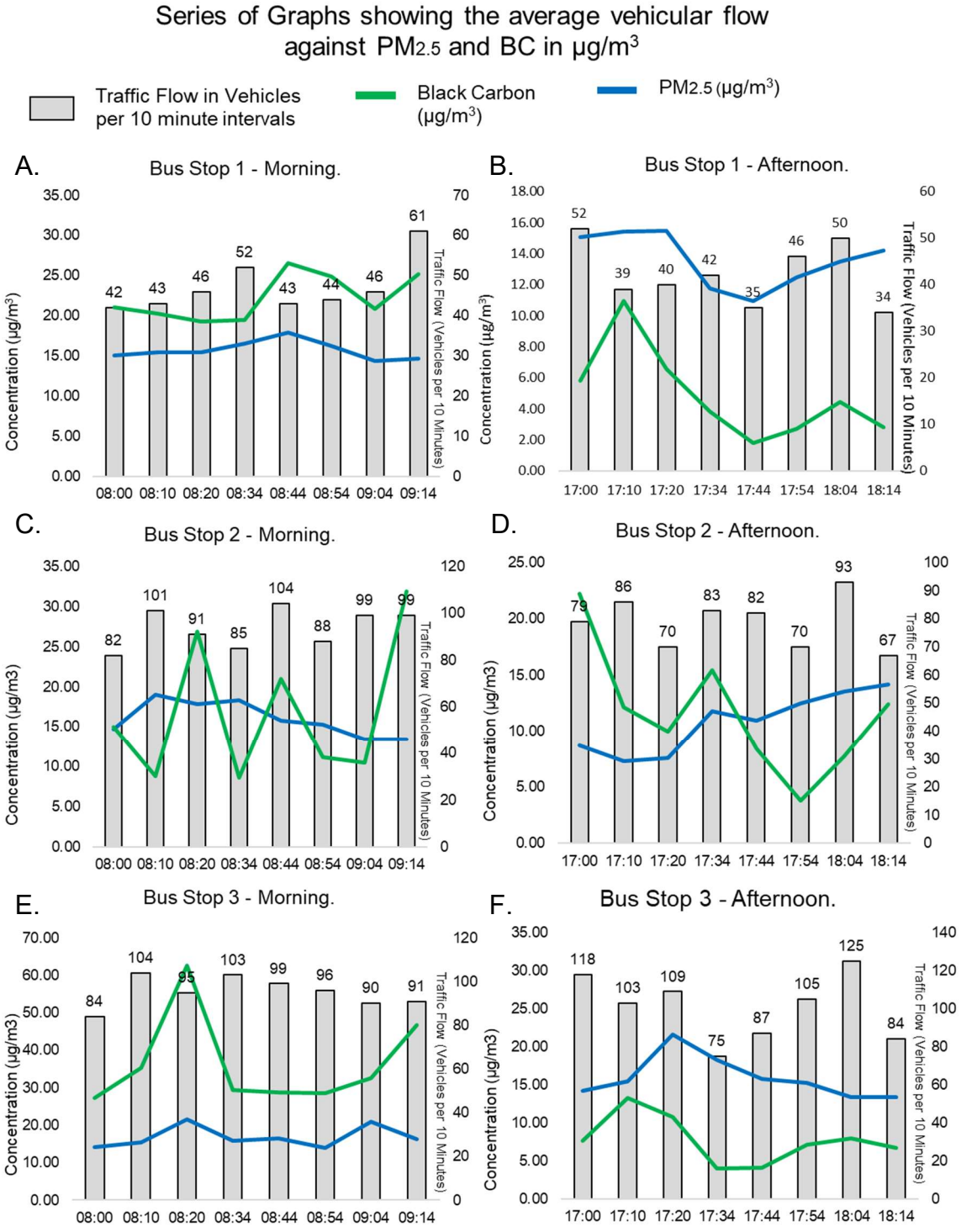
The correlation between air pollution and vehicular flow was much more difficult to resolve at 10-minute intervals. Increases in the vehicular flow did not lead to an immediate, or obvious, increase in air pollution. Rather high concentrations of air pollution occurred somewhat randomly vs the vehicular flow at this resolution. However, visually there are increases in both BC and $PM_{2.5}$ vs the traffic flow, as shown in Figure 8.10 An interesting finding was that $PM_{2.5}$ was higher in the morning vs the afternoon, while the opposite trend was found in the morning.



Figures 8.10 (A-B). Shows two X-Y graphs showing the correlation between the $PM_{2.5}$ and BC concentration vs traffic flow. (A) The correlation between traffic and $PM_{2.5}$ is quite low with an R2 of 4.83%. (B) However, has a much better correlation between traffic and BC with an R^2 of 42.81% with an exponential trendline. **Source;** Author – Grainger (2020)

There is some correlation between an increase in $PM_{2.5}$ and BC, for example, at 08:44 at Bus Stop One. Similarly, there is a decline shared between BC and $PM_{2.5}$ between 17:10 and 17:44, before gradually rising (see Figure 8.11). At Bus Stop Two this trend deviates, in that the morning session was characterised by a series of increases in the BC that were not shared by the $PM_{2.5}$ concentration, which remained relatively stable throughout the monitoring period. The BC concentrations, however, jumped between high and low, the highest point was at 09:14 at 31.90 µg/m^3 of BC when the $PM_{2.5}$ concentration was at its lowest (13.38 µg/m^3).

In the afternoon, the BC concentration gradually fell, with an intercept with the $PM_{2.5}$ concentration between 17:34 and 17:44, after which the BC concentration fell before rising, whereas the $PM_{2.5}$ concentration shallowly rose. Lastly, at Bus Stop Three there was a similar distribution between $PM_{2.5}$ and BC, though the $PM_{2.5}$ concentration was much more muted. A spike between the $PM_{2.5}$ and BC concentration was found at 08:20 (with a PM2.5 concentration of 21 $\mu g/m^3$ and a BC concentration of 40.95 $\mu g/m^3$). In the afternoon though, the $PM_{2.5}$ concentration was at least 2 $\mu g/m^3$ higher, though between 17:34 and 17:44 the difference was ~11 $\mu g/m^3$. The trend between BC and $PM_{2.5}$ is deeply confusing and unhelpful at this resolution.



Figures 8.11 (A-F). Shows the correlation plots of $PM_{2.5}$ and BC vs the average 10-minute vehicle count for all three bus stops and the monitoring period in the study. The results show a subtly positive relationship between vehicular flow with BC and a negative correlation with $PM_{2.5}$, though the many exceptions to this general trend make it quite difficult to identify with a 10-minute resolution. **Source;** Author – Grainger (2020)

► 8.4) Discussion.

♦ 8.4.1) Air Pollution Spikes: Hope Street.

Large spikes of air pollution (BC and $PM_{2.5}$) often occurred within one minute of the buses arriving at the bus stop. This peak was noticed more with out-of-town buses such as the SimpliCITY 2 bus route,where one bus led to a $PM_{2.5}$ spike of 180 $\mu g/m^3$, and not all buses (especially inner-city bus lines) led to peaks in the air pollution trend. The difference between highly and lowly polluting buses is likely to be a factor of age; the non-Glasgow fleet is older and is, therefore, more likely to correspond to an older Eurocode Classification (emissions class), (Dickson 2018; McInally 2019). Because of various government initiatives and the city of Glasgow's drive towards a clean air zone, much of the bus fleet has received subsidies to be refreshed with newer models, low emissions buses or with retrofit operations (Dickson 2018; McInally 2019). As of 2019, much of the SimpliCITY 2 line has been retrofitted to Euro 6 standards (McInally 2019).

A series of more discrete and scattered spikes at bus stops may include stop-start emissions from changes in traffic lights from red, where the road would become quiet for several minutes, to green where an influx of 20 or more vehicles, including buses, would emerge onto Hope Street. Though 'Bus Stop One' was protected from these traffic fluxes as it was located within a restricted traffic area (with only bus and taxi vehicles).

Other factors may have impacted the air quality, but were otherwise not apparent to the analysts. First was the impact of pedestrian tobacco smokers. Unlike Moore *et al.* 2012, the smokers stood further back from the bus shelter and had a much less noticeable impact on air quality. Though pedestrian smokers may have walked past the analysts while they were counting traffic, the smokers who stayed near the bus shelter did not have a noticeable impact on either the BC or $PM_{2.5}$ concentration in the study. Crosswinds from buses and pedestrians in otherwise calm wind conditions

were likely the most significant reason for resuspension of particulate along Hope Street (Karra *et al.* 2017).

♦ 8.4.2) Variably high BC to $PM_{2.5}$ concentrations.

BC concentrations were higher than $PM_{2.5}$ for 26 minutes of the 156 minutes of monitoring (16.67%). The higher concentration of BC was a curious finding as BC is classically defined as a subcomponent of $PM_{2.5}$. Though over the entire study, BC only comprised 71% (11.45 $\mu g/m^3$) of $PM_{2.5}$ (16.16 $\mu g/m^3$). The reason for occasionally high BC concentrations may be due to either; a mechanical error with one device leading to a misleading measurement, or the BC agglomerating into larger particles above $PM_{2.5}$, which were screened out of the MicroPEM measurements.

While the former consideration is more likely historically, there is evidence in this study to support that there may be speciation of BC into larger agglomerations. In some circumstances, the BC can aggregate into larger masses because the BC is lightly statically charged, coated with a sticky layer of VOC's (Volatile Organic Carbons) or even bound within hydrocarbon complexes (oil mists) (Charan *et al.* 2018; Lakshmanan *et al.* 2019). The AE51 was not fitted with a size-selective inlet, and therefore, particulate of any size was sampled. The MicroPEM's $PM_{2.5}$ size selector would have screened out larger material, but without a size selector in the AE51, larger masses of BC material could access the equipment and be measured.

♦ 8.4.3) Nitrogen Dioxide: Protection in the Bus Shelters.

There was a notable reduction in NO_2 inside the shelters at Bus Stops One and Two. The lower concentrations of NO_2 inside compared with outside readings can be explained as the result of introducing barriers to the transmission of air into the shelters. These barriers would have led to turbulent mixing and air being dissuaded from entering the bus shelters. This phenomenon may have been the case with the first bus shelter which had a 12% reduction in NO_2 inside the shelter compared to outside, while the single panel bus shelter (Bus Stop 2) offered roadside protection, leading to an 8% reduction. Unfortunately, the control samples at the third bus stop, the stop pole, were destroyed during the fieldwork campaigns.

Concentrations of NO_2 were higher to the south than the north; this was likely due to the stopping position of buses, i.e. the exhaust of buses would have been positioned due south of the bus stop close to where the southern PDT tube was located. This was the opposite trend in Bus Stop 3 mainly because buses pulled forwards to the start of the junction, meaning that the exhaust was much closer to the Northern PDT sample location than the Southern PDT.

♦ 8.4.4) Particulate: Protection in the Bus Shelters.

■ A) *'Bus Stop One'*.

Bus Stop One was a three-panel bus shelter with panels to the north, east, and south. This shelter had a 5% lower $PM_{2.5}$ concentration than the surrounding ambient environment, while BC was lower by 13%, as shown in Table 8.6. The minor $PM_{2.5}$ concentration difference between 'inside' and 'outside' was unexpected as it offered significant ameliorations of BC and NO_2. BC and NO_2 were likely reduced due to the south panel blocking the flow of contaminated air (increasing turbulent mixing) from the exhaust pipe of serving buses located to the south of the bus shelter.

The protection offered by the shelter may have promoted the settling of $PM_{2.5}$ sized dust inside the shelter. $PM_{2.5}$ inside the shelter was poorer in BC than outside particulate. Particles settle not only due to their size but also their density, for instance; BC has a density of about 1.77 g/cm^3, whereas quartz has a higher density of 2.65 g/cm^3 (Deer *et al.* 2013). The heavier particles may have remained in the shelter, whereas the lighter particles may have been excised as a result of turbulent airflow movements secondary to vehicular movements (Harrison *et al.* 2012; Amato *et al.* 2013; Jida *et al.* 2020). Because the shelter contains more structural features (like seats) than the other stop designs, $PM_{2.5}$ can settle in the corners and joints of the structure. Due to the bus stop's design and architectural features, it is inherently more difficult for street workers to clean effectively, while the seating areas may provide pedestrians the opportunity to spend more time at that position in relative comfort, eating and smoking whilst protected from the elements.

Table 8.5: Shows the averaged 'south' and 'north' readings, averaged over both monitoring periods in the afternoon and the morning rush hours.

			South	North	Av Out	Inside	I vs O
Bus Stop 1	Morning	$PM_{2.5}$	17.03	15.15	16.09	15.29	95%
		BC	8.66	6.48	7.57	5.81	77%
	Afternoon	$PM_{2.5}$	13.20	14.21	13.70	13.13	96%
		BC	6.37	8.96	7.66	7.25	97%
	Average	$PM_{2.5}$	15.11	14.68	14.89	14.21	95%
		BC	7.51	7.72	7.62	6.53	87%
		NO_2	87.89	79.99	83.94	74.12	88%
Bus Stop 2	Morning	$PM_{2.5}$	18.99	16.39	17.69	16.37	94%
		BC	20.97	10.47	15.72	17.25	110%
	Afternoon	$PM_{2.5}$	10.95	13.51	12.23	11.38	93%
		BC	8.38	7.74	8.06	10.55	131%
	Average	$PM_{2.5}$	14.97	14.95	14.96	13.87	93%
		BC	14.68	9.11	11.89	13.90	120%
		NO_2	98.32	95.39	96.86	88.93	92%
Bus Stop 3	Morning	$PM_{2.5}$	16.55	21.03	18.79	18.76	100%
		BC	12.20	11.49	11.85	19.58	165%
	Afternoon	$PM_{2.5}$	15.74	13.42	14.58	20.67	142%
		BC	4.07	7.97	6.02	5.96	99%
	Average	$PM_{2.5}$	16.15	17.23	16.69	19.72	121%
		BC	8.14	9.73	8.93	12.77	132%
		NO_2	109.06	105.79	107.42	-	-

* These are also averaged to form the corresponding average outside variable. The inside variable is the averaged morning and afternoon concentration. The percentage difference between inside and outside is reported, and that is taken as outside variable / inside variable.

The area to the south of the bus shelter had a higher mean concentration of both $PM_{2.5}$ and NO_2, with a similar BC concentration. The reason for this more polluted southern area was due to bus exhaust, i.e. as buses stopped and lined up with the bus shelter, the buses' rear ends projected several metres to the southern position. The buses' position may have led to some $PM_{2.5}$ and BC peaks. However, the bus shelter was sited within a restricted vehicle area and adjacent to a dedicated bus lane, which may have reduced the relative concentration of air pollution (when a bus was not pulled into the lane).

■ B) 'Bus Stop Two'.

Bus Stop Two comprised a cantilever single panelled bus stop, with a non-seated waiting area positioned away from the roadside. The pavement was especially narrow at the shelter, with patrons and other pedestrians jostling for space.

This position had an average concentration of $PM_{2.5}$ around 7% lower than outside and NO_2 lower by 8%, while BC was higher by 20%. The lack of side panels, and the much busier section of pavement, led to an increased ability for particles to be eliminated from the microenvironment, meaning that rarer particle forms were likely eliminated from the micro-environment before they could build-up. Foot traffic may have led to particles being more easily resuspended and transported out of the bus shelter, either from pedestrian crosswinds or adherence to footwear. Street sweepers could also more readily sweep the floor at this location to remove detritus, such as dropped food items and cigarette butts which may have contributed to a cleaner environment. BC, however, accounts for approximately 50% of diesel exhaust and therefore was a much more common particle type (Reşitoğlu *et al.* 2015). Because of its continual generation, BC could enter through the unprotected sides much more easily than it could in Bus Stop One.

Although the street canyon effect may have also contributed to the increased BC concentrations, as BC is a relatively light particle, it can be pushed to the edges of the street canyon by crosswinds and metrological effects (Amato *et al.* 2013). Heavier particles such as road materials (quartz) and metal particles (iron oxide) are of higher density and may settle quickly and be difficult to resuspend (Harrison *et al.* 2012; Amato *et al.* 2013). According to the street canyon theory, NO_2 should also have been enriched within the shelter. Pedestrian crosswinds may have been important during rush hours because of the narrowness of the pavement and busy pedestrian traffic (Buonanno *et al.* 2011; Karra *et al.* 2017).

The southern position (2 metres south of the shelter) had a higher concentration of BC than the north, but less $PM_{2.5}$ and NO_2. The buses stopped more forward than they did at the first bus stop so that the end of the bus was almost level with the 'south' position. The increased abundance of NO_2 and PM_{10} at the southern position was likely due to exhaust emissions being emitted away from the north position. Stop-Start emissions are higher in soot including BC and so when a bus pulls off, the BC rich gas is expelled from the exhaust, roughly where the North position was located. The author noted this phenomenon during monitoring.

■ C) *'Bus Stop Three'*.

'Bus Stop Three' comprises a stop pole and flag, and offers no protection from the elements. This location is characterised by the highest concentrations of $PM_{2.5}$ and NO_2 and the second-highest BC concentration. This stop was close to a junction between West George Street and Hope Street, which may have been responsible for a small local increase in air pollution concentrations. The lack of structure meant that there was an unobstructed flow of air pollution directly from source (i.e. vehicles) to 'receptors' at the bus stop.

The buses pulled so far forwards that the exhaust was level with the stop pole and directed engine emissions directly into the patron waiting area. The exhaust most likely led to the very high BC and $PM_{2.5}$ concentrations observed at the “inside” position.

Overall, $PM_{2.5}$ and BC were higher to the north, most likely as they are relatively durable in the environment (at least when compared to NO_2). The northern increase in PM-related particulate was likely due to attrition and exhaust- emissions sourced from the road junction with West George Street. Due to increased vehicular flow, attrition related emissions are higher at road junctions due to an increase in road, brake, and tyre wear (Amato *et al.* 2013; Khan and Strand 2018; Jida *et al.* 2020). Nitrogen Dioxide, however, was higher to the south than to the north. NO_2 has relatively low durability owing to the sun’s ability to convert it into ozone (not measured in the investigation), so there may have been NO_2 converted into ozone on the warm summer days of the investigation. NO_2 is relatively short-lived compared with many particles, e.g. quartz which could last in the environment for millions of years. Lastly, the northern position was further away from direct sources of NO_2, such as the exhaust of serving buses.

► 8.5) Experiement I - Conclusions.

The key air pollutants: $PM_{2.5}$, BC and NO_2, were monitored at three bus stops along Hope Street, Glasgow during the afternoon and morning rush hours. The study used two backpacks containing air quality equipment to determine the levels of air pollution inside, ‘south’ and ‘north’ of these bus stops. The structure and the waiting location at each bus stop plays a significant role in air pollution concentrations at each location.

Three-panelled bus stops offered decent protection from all air pollutants, though there is the potential for human-borne particles to accumulate within the shelter. A single panel bus shelter offers sub-optimal protection from road-borne emissions, with lower concentrations of $PM_{2.5}$ and NO_2.

However, Black Carbon is locally increased within such shelters and should this pollutant be a graver concern, then an outdoors waiting area could offer better protection. Lastly, an unprotected stop-pole offers no reprieve from air pollution, and there is a much higher risk of air pollution exposure. For one panelled and stop-flag bus stops, patrons should attempt to back away from the kerb as far as possible to help avoid adverse exposures. The research showed promising results and a strong link between bus shelter design and exposure to air pollution, though further research is required to understand the distribution of air quality around these structures fully.

A problem which emerges with this work however, is that the subtle difference seen within the shelter could be due to variation over time. i.e. there may be increases in air pollution around the monitoring position generally not associated with the position of the analyst. Whilst the probability of such an occurrence is particularly low, three separate monitoring backpacks would aid considerably with eliminating this small risk of general variability co-existing with inside monitoring periods.

8.6. Experimental Design II: Black Carbon and Nitrogen Ratios at Two Governmental Air Quality Monitoring Stations Using Computer Modelling.

8.6.1. Synopsis

Exposure to air pollution adversely affects the longevity and quality of human life (Gautam and Bolia, 2020;). The World Health Organisation (WHO) has declared that air pollution is a public health emergency, and considers air pollution to be the "greatest environmental risk to health" (WHO 2016, 2019). These public health concerns have permeated through to the public consciousness through intense media scrutiny and public awareness campaigns (Huang *et al.* 2018). The city of Glasgow has not escaped from media or public scrutiny, with the highest national concentrations of air pollution within the city centre (Keane 2019).

In urban environments, most air pollution stems from exhaust gases from motor vehicles' Internal Combustion Engines (ICEs). These ICE exhaust gases include Oxides of Nitrogen (NO_X) such as Nitric Oxide (NO) and Nitrogen Dioxide (NO_2) and Particulate Matter (PM), (McInally 2019). PM is interesting as, not only does the size of the particle play a crucial role in adverse human health effects, but so does the chemistry of the particles (WHO 2016; Abbas *et al.* 2018). An important chemical subspecies of PM is Black Carbon (BC). This comprises carbon coated in Poly-Aromatic Hydrocarbons (PAH), a substance which has well-known respiratory and carcinogenic risks (WHO 2016; Abbas *et al.* 2018). Particle shape and chemistry can also affect the rate of resuspension of PM (Zheng and Li 2019; Jida *et al.* 2020).

Environmental factors greatly influence oxides of nitrogen as they can degrade or undergo chemical reactions in ambient air such as NO via its alteration to NO_2 in the presence of sunlight, (Vallero 2014). This reaction is

further enhanced by turbulent conditions such as wind speed and wind-flow obstructions (Vallero 2014; Wolf *et al.* 2020).

The Department of farming and rural affairs (Defra) with regional environmental agencies (i.e. Wales' NRW, Scotland's; SEPA and England's EA) have set-up a series of automatic reference analysers to monitor the concentrations of air pollution throughout the UK (Defra 2017, 2018). These analysers form the Automated Urban and Rural Network (AURN). The AURN is installed and maintained to rigorous accuracy and precision standards following various international standards including the British Standards (BS), International Organisation for Standardisation (ISO) and American Society for Testing and Materials (ASTM), (AEA Technology 2010; Ricardo-AEA 2012).

Following an appraisal of site-specific spatial and temporal factors, this experiment aims to discover the major contributors of BC and NO_X to the Glasgow High Street and Townhead Monitoring Stations. The work relies on a new and interesting ratio between BC and Nitrogen Oxides, which is conjectured to signify the air pollution age. The program Openair, hosted on an open-access statistical platform called 'RStudio', was key to the development of spatial analysis, which allows for back-trajectory analysis (Carslaw and Ropkins 2012; Carslaw 2014, 2015a). This work suggests several new key sources of air pollutants at the Glasgow High Street and Townhead Monitoring Stations, including a range of intersections and industrial premises.

♦ 8.6.2) Rationale for Research Experiment.

This experiment was written to expand the researcher's knowledge and abilities in statistical computing using the OpenAir toolset written by Carslaw *et al.* (Carslaw *et al.* 2006, 2012; 2014, 2015a, b). Using statistical programming to characterise environmental exposures was an objective of this thesis (Objective C.I). This objective (C.I) stated that the thesis should

use *"Open-Access (OA) data from air quality Monitoring Stations to decide spatial-temporal trends within UNG and other complex environments".*

Also, the experiment fulfils part of the aim of the thesis, i.e. "… to develop methods for quantifying exposure to these air pollutants…"

Such a technique could be used on Unconventional Natural Gas (UNG) developments and other complex environments where NO_X and BC are measured along with meteorological data. The ratio between NO_X and BC (used in this experiment), has the potential to be a highly useful and influential metric for air quality investigations. This paper introduces a method of identification of hotspots, which are otherwise indistinguishable from background concentrations even when using statistical modelling tools.

This experiment suggests various new potential hotspots of air pollution, from the well-researched Glasgow Townhead and High Street Monitoring Stations (Ezani 2017; Masey 2018). This experiment may also be of interest for research undertaken on the local air quality in the eastern part of the city of Glasgow. One of these findings shows a linkage between the M8 J15 Townhead Interchange and the Townhead Monitoring Station, a linkage which has long been hypothesised but not proven (McInally 2019).

Other findings suggest hotspots at road junctions, which is unsurprising given the existing research. This method could present a useful metric in intervention and city-wide air pollution policies in complex hotspot environments, where Monitoring Stations are located close to road junctions in busy built-up areas (Sharma *et al.* 2019). An intervention reducing ICE emissions is likely to increase the relative BC ratio higher than NO_X, as nitrogen is likely to dissipate into the air while BC can stay suspended (Wang *et al.* 2011; Defra 2019). BC can become resuspended or even be brought in from air settling regionally much easier than NO_X, which may mix with ambient air and degrade (Wang *et al.* 2011; Defra 2019).

It should also be mentioned that the ratio between BC and Oxides of Nitrogen has never been explored in ambient air monitoring as far as the author is aware. The author, therefore, considers that the technique, in its own right, is novel and a contribution to scientific knowledge.

This experiment also offers an insight into the hotspot sources of BC and Oxides of Nitrogen within the eastern part of the city of Glasgow. This ratio technique offers added benefits to scholarly research and opportunities to study these potential hotspots in further depth with personal or mobile sampling methods.

► 8.7). Methods.

♦ 8.7.1) 'RStudio's 'Openair' Toolset.

This experiment uses an open-ware statistical computing platform called 'RStudio' in conjunction with the air pollution toolset 'Openair'. This platform was used to produce graphs of the temporal and the spatial contribution of Oxides of Nitrogen (including NO, NO_2, and NO_X) and BC, (Carslaw and Ropkins 2012; Ropkins and Carslaw 2012). This experiment used the most recent software edition at the time of analysis (April 2019), called "Planting A Tree" (version 3.6.0, released on the 26th April 2019). The "R" programming language is one of the most popular coding methods in scientific research and is used throughout industry and academia (Carslaw and Ropkins 2012; Masey 2018).

The 'Openair' toolset works similarly to functions in spreadsheets so that calculations are performed on the user's data without having to code "from scratch". Further information, including a toolset manual, can be found on the project's website at; 'davidcarslaw.github.io/openair/'.

There are key individual tools which have been used within the 'Openair' package 'toolset':

- **Normalised Temporal Distribution Graphs.** Normalised graphs show the temporal variation over various scales, including hours, days, and months.

- **Bivariate Polar Plots**. Subdivides the air pollution data into a series of hexagonal coordinates based on the prominent meteorological conditions (wind speed and direction). The average data in each bin is plotted, and a colour gradient is used to illustrate the concentration of air pollution (or ratios).

- **Conditional Probability Function (CPF) Polar Plots**. The CPF polar plots use the bivariate method, but with the addition of CPF analysis. CPF analysis tests the probability of an event occurring if other conditions are met. Here, these conditions are the probability of high ratios of air pollution under certain meteorological conditions (wind speed and direction).

The CPF can be given as;

Equation 8.2.

$$P(B|A) = \frac{P(A + B)}{P(A)}$$

Where,

P is the probability (e.g. High Concentrations),

A and B are certain events (i.e. Wind Direction and Wind Speed),

♦ 8.7.2) Air Pollution Data Collection.

Two sites; Glasgow Townhead (located at 55.860936, -4.238214) and High Street (located at 55.865782, -4.243631) were chosen for analysis from the AURN and BC Networks, the locations for which are shown in Figure 8.10. The hourly data from 07/10/2012 through to the 01/03/2019 (the first day of analysis) was downloaded from Defra's UK Air Data Selector (uk-air.Defra.gov.uk/data/data_selector).

The Townhead and High Street Monitoring Stations measure a suite of chemical and particulate pollutants, including various analyses for PM and oxidising gases (Defra 2017). The Monitoring Stations rely on Tapered Element Oscillating Microbalance-Filter Dynamics Measurement System (TEOM-FDMS) to take readings of particulate air pollutants, including BC, (Defra 2017). Chemiluminescence was used to monitor the concentration of Oxides of Nitrogen (Defra 2017). A more advanced explanation on the site locations and instrument details can be found at https://uk-air.Defra.gov.uk/.

Both datasets were filtered according to a series of criteria:

1. The entry must contain a complete record of wind direction, wind speed, air pollutant data for NO, NO_2, and NO_X and BC. Where a data entry does not have a full a set of recordings, the entire record was screened out of the analysis.
2. Only 'verified' data was permitted. Partial (no data), provisional and unverified data entries were screened out of the analysis.

Figure 8.12. A location map of the City of Glasgow showing the locations of (A) Glasgow in the United Kingdom, (B) the location of the Monitoring Stations within the Greater Glasgow area and (C) the location of the Glasgow Townhead and High Street Monitoring Stations within the eastern part of the city centre of Glasgow.

Source: Base map - Digimap and Ordinance Survey (2019). **(Adapted)**

Contains Ordnance Survey data. © Crown copyright and database right 2010. Data provided by Digimap OpenStream, an EDINA, University of Edinburgh Service.

The number of screened out data entries are included in Table 12.1.

Table 8.6: Filtered Data from the Data Series

Filtering Criteria	Townhead	Glasgow High Street
Original Data Size	47,211	47,211
No Data	3,126	22,550
Provisional	1,438	4,050
Not Verified	120	379
Filtered Data size	42,527	20,232

Table 12.1. The table shows the filtering criteria (no data, provisional and unratified data, and non-verified data) from the Townhead and High Street Monitoring Stations. The number of fields removed for each stage of the filtering process, as well as the initial number of data records collected and post filtering.

Of the two AURN stations, High Street had more data entries screened out of the dataset. The higher number of screened values for High Street was because:

- High Street (27/01/2015) was installed later than Townhead (07/10/2012).
- High Street has been prone to mechanical breakdown since installation.

Screening of the data led to almost 20,232 rows of data being screened out from High Street AURN compared with Townhead where only 4,684 rows of data were screened out, with 14 data loss periods lasting an average of 5.5 days, as shown in Figure 8.11. At Glasgow High Street, the Monitoring Station had a data loss (after screening) of around 14%. These came from roughly 14 data loss periods which accounted for an average data loss session of around 9.6 days. However, there was a major data loss between the 30th October 2015 and the 12th January 2016, which accounted for 74 days of data loss, as shown in Figure 8.12.

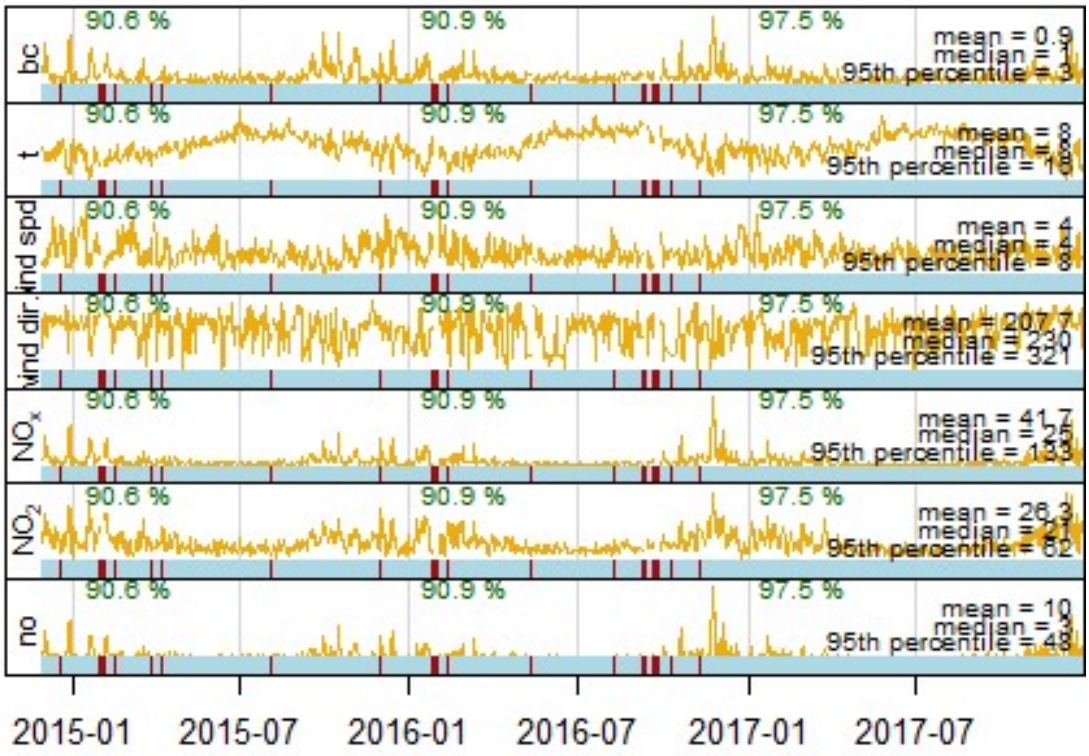


Figure 8.13. Shows a summary plot of the data for Glasgow Townhead using OpenAir. The concentration of the air pollutants and other meteorological conditions are added for context. The red spaces to the base of the concentration line graph are related to missing data errors following filtering of missing data series.

Source: Grainger (2019).

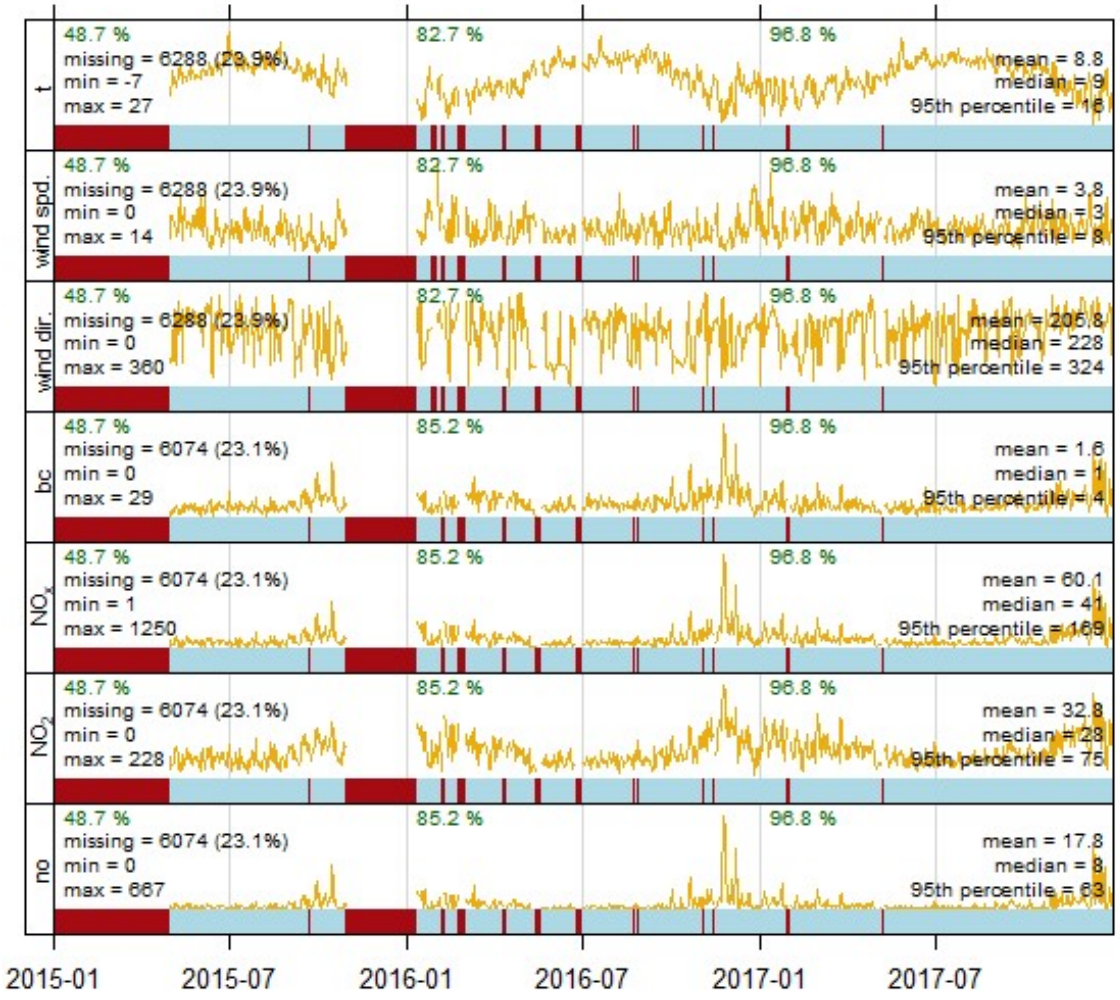


Figure 8.14. Shows a summary plot of the data for Glasgow High Street using OpenAir. It should be noted that the first missing data error is due to the Monitoring Station turning on halfway through 2015. The remaining red spaces are related to missing data errors following filtering of missing data series. The concentration of the air pollutants and other meteorological conditions are added for context.

Source: Grainger (2019).

♦ 8.7.3) Air Pollution Modelling By Others.

Following a 'Freedom Of Information' (FOI) request to Glasgow City Council (EIR 7300674), a report was made available to the researcher (Glasgow City Council 2018). This report contains information about the modelling of air pollution over the city of Glasgow for the Glasgow City: Clean Air Zone policy. The results in the report are normalised, and the whole technical report containing the actual modelled values was withheld from the FOI request (Glasgow City Council 2018).

The graph shows that at High Street, the most prominent vehicular source of NO_X is cars with a 42.3% share (2.9% Cabs, 5.2% Petrol and 34.2% Diesel) (Glasgow City Council 2018). The next prominent source is Goods Vehicles with a 39.8% share divided between Articulated HGV (4.6%), Rigid HGV (23.5%), and LGV (11.6%), (Glasgow City Council 2018). Like much of the city, buses are a prominent source with 22.5% (Glasgow City Council 2018). Townhead is similar, but with a larger impact of buses (35.3% share) and less impact of goods vehicles (25.6% - 4.2% Artic, 8% Rigid and 13.5% LGV), though most of this was due to less rigid HGV vehicles (Glasgow City Council 2018). The impact of cars was comparable when normalised with a share of 39.2% (3.9% Cabs, 4.4% Petrol, 30.8% Diesel), (Glasgow City Council 2018

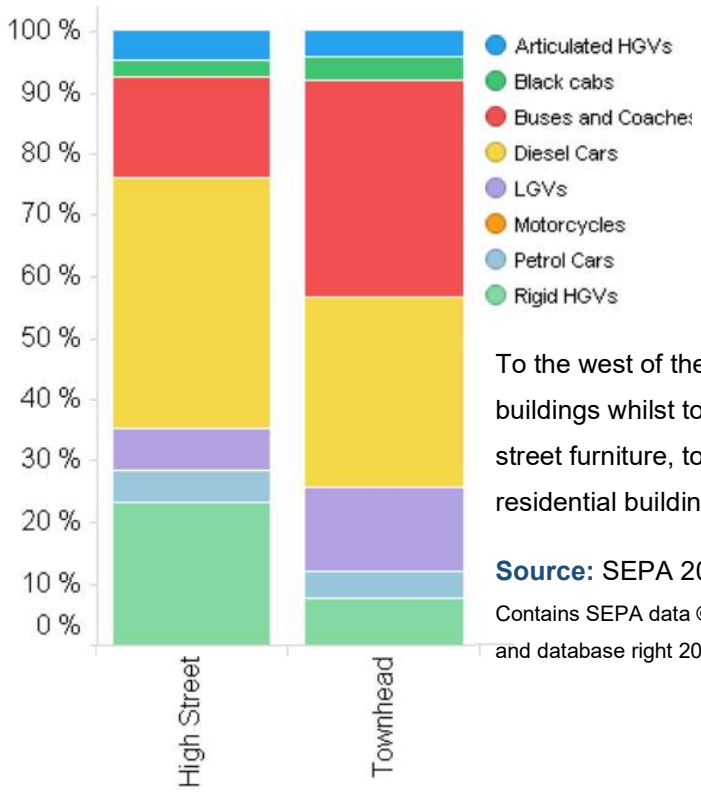


Figure 8.15. The figure shows the Glasgow High Street Monitoring Station in its environmental context. In the foreground is the A8 High Street which gives the station its name. To the west of the station is a row of tenement buildings whilst to the east is greenspace and street furniture, to the north and south are residential buildings.

Source: SEPA 2018.

► 8.8). Results and Discussion.

♦ 8.8.1). High Street (BC, NO, NO_2, and NO_X).

High Street is an urban roadside Monitoring Station, set five metres back from the A-Class' arterial corridor 'A8 High Street', as shown in Figure 8.13. High Street is one of the oldest streets in Glasgow and forms the north-south route between Glasgow Cathedral and Glasgow Cross (SCOTS 2017). A nearby Department of Transport (DoT) Monitoring Station (station 10,821), is sited 10 metres to the south and has an Annual Average Daily Flow (AADF) of 15,715 vehicles (DoT 2020a).

Figure 8.16. The figure shows the Glasgow High Street Monitoring Station in its environmental context. In the foreground is the A8 High Street which gives the station its name. To the west of the station is a row of tenement buildings whilst to the east is greenspace and street furniture, to the north and south are residential buildings.

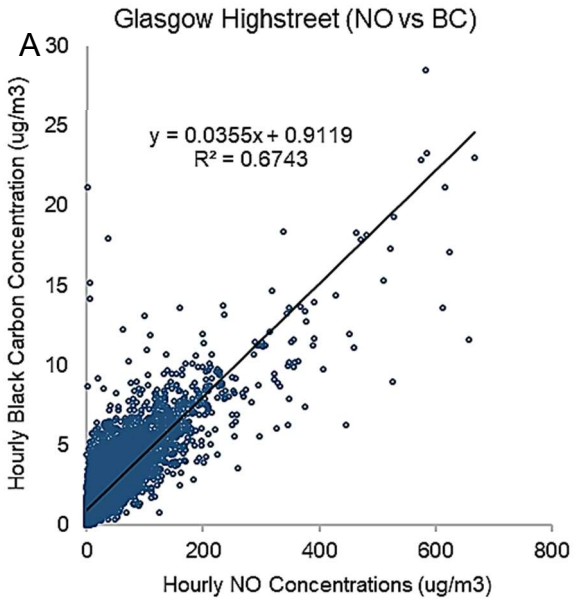
Source: Grainger (2019).

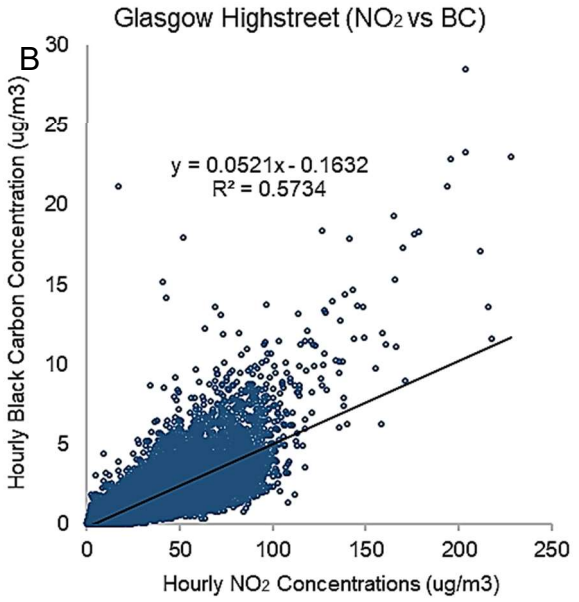
BC is only a subcomponent of PM, and therefore the concentration of BC along High Street should be much less than the PM concentration. Experiment 9 undertook personal monitoring along Hope Street at 3 bus stops, some 2 km away from the High Street AURN. The BC to PM ratio was quite variable along Hope Street at about 60.78% ±17.60% accounting for all three bus stops and waiting locations. The ratio between BC and NO_2 was much lower, at 10.57% ±1.86%. Likewise, commercial diesel engines from UNG activity in Poland had a NO_2/BC ratio of around 10:1 (~10%), (Grainger 2017; Ezani *et al.* 2018). Given the high percentage of NO_2 near ICEs, areas with raised concentrations of BC, but lower concentrations of NO_X may indicate a lack of generation activity, or an activity which produces more BC, such as uncontrolled combustion (Dumka *et al.* 2018; Li *et al.* 2019).

BC is expected to be less degradable than NO_X, as while BC can settle with distance, it can later become resuspended. Oxides of Nitrogen, however, disperse over time and lost gases can only be replaced by a new generation (Carslaw *et al.* 2006; Harrison *et al.* 2012a). At High Street, the A8 is likely to be the major source of BC and Nitrogen Species. However, local (Glasgow-borne) and longer-range emissions sources may have an underlying impact on these concentrations (Defra 2019).

■ A. High Street Ratio Comparison.

The relationship between BC, NO, NO_2, and NO_X, are shown in Figure 12.6 A-C). These plots show the ratio between the pollutants, coefficient of determination (R-Squared R^2) and slope of the graph. All the scatter graphs show a strong positive linear relationship between Nitrogen (NO, NO_2, NO_X) and BC (R^2 of 0.57 to 0.72). The best correlations were found between BC, NO, and NO_X (R^2 of 0.67 and 0.72) with a poorer correlation for NO_2 (R^2 of 0.57). The mean ratio was lower between NO_X and BC at 0.0181 per 1 $\mu g/m^3$ of NO_X. The correlation between NO and BC was three times higher than NO_X at 0.0355 $\mu g/m^3$ per 1 $\mu g/m^3$ of NO. The highest ratio was between NO_2 and BC, with a ratio of 0.0521 $\mu g/m^3$ per 1 $\mu g/m^3$ of NO_2.





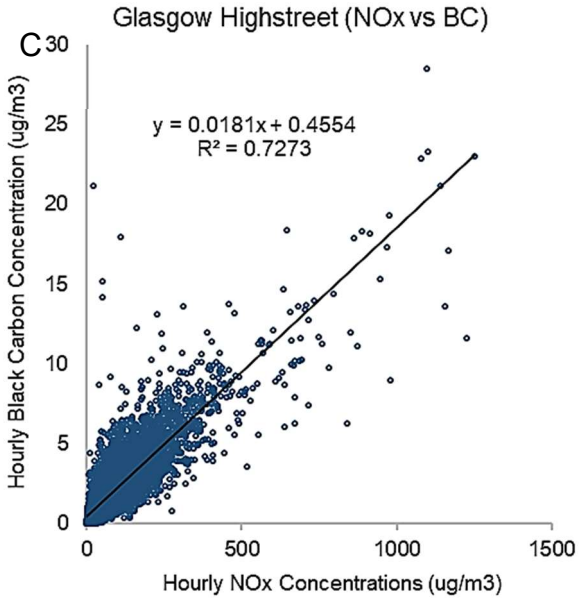


Figure 8.17.A Scatter graphs showing the strong linear relationship between Hourly Black Carbon Concentrations and Hourly Nitrogen Monoxide Concentrations at Glasgow High Street AURN Monitoring Station after QA/QC correction. There is a moderately strong R^2 value of 0.67, with most BC values averaging in the 0-10 µg/m^3 region. Although the highest recorded sample was at around 23 µg/m^3 there was a curious offset of +0.91 µg/m^3 Black Carbon, possibly indicating the presence of BC within ambient environments.

Figure 8.17.B, shows another strong positive linear relationship between Hourly Black Carbon Concentrations and Hourly Nitrogen Dioxide Concentrations at Glasgow High Street AURN Monitoring Station (post-processing). There was a less strong R^2 value of 0.57, with a less steep gradient, the BC results were also more equally spread with a higher projected trend at higher NO_2 concentrations projected (dashed line).

Figure 8.17.C, shows the strongest positive linear relationship between Hourly Black Carbon Concentrations and Hourly Nitrogen (Oxide of Nitrogen) Concentrations of the NO_X species, at Glasgow High Street AURN Monitoring Station (post-processing). There was a very strong R^2 value of 0.72, with a relatively steep gradient. Although the BC results were more equally spread than NO, this seemed to persevere to higher projected concentrations of NO_X. Indicating that it might be more reliable under most conditions.

■ B. Glasgow High Street; Temporal Variation - Results.

A series of normalised concentration plots of BC and Oxides of Nitrogen (NO, NO_2, and NO_X) averaged over hours, days, weekdays, and months are shown in Figure 12.7. The graphs show that on an average UK workday (Monday to Friday), the peak concentrations of air pollutants occur during the morning hours between 06:00 -10:00 and afternoon hours 16:00–20:00. The lowest concentrations of air pollution are recorded between 03:00 and 05:00.

During the day, air pollution concentrations began low with BC concentrations at around 0.8 µg/m^3 and NO, NO_2, and NO_X concentrations at 10, 20 and 30 µg/m^3. Though, by 08:00 during the peak of the 'morning rush hour', the air pollutants had risen to the daily highest concentrations with 2.1 µg/m^3 of BC and 30, 40 and 90 µg/m^3 for NO, NO_2, and NO_X. In the post rush hour period from 10:00 to 16:00, the concentrations slowly declined from the morning rush hour. A second, minor peak lasted from 16:00 to 18:00 corresponding to the afternoon rush hour, with air pollutants reaching 20, 40 and 70 µg/m^3 for NO, NO_2, and NO_X and 1.7 µg/m^3 for BC.

Although most days were similar, Monday had especially high concentrations of all air pollutants (1.6 µg/m^3 for BC and 20, 35 and 62 µg/m^3 for NO, NO_2, and NO_X). Saturday and Sunday (weekend) contrasted against workdays as there was an even distribution of air pollutants. The concentration during the weekend was around 1.3 µg/m^3 for BC and 12, 28 and 45 µg/m^3 for NO, NO_2, and NO_X. The concentrations of air pollution also varied seasonally, with a distinct increase in air pollution from May through to August and the peak concentrations of air pollution in November and December. The summer months (May to July) had low concentrations.

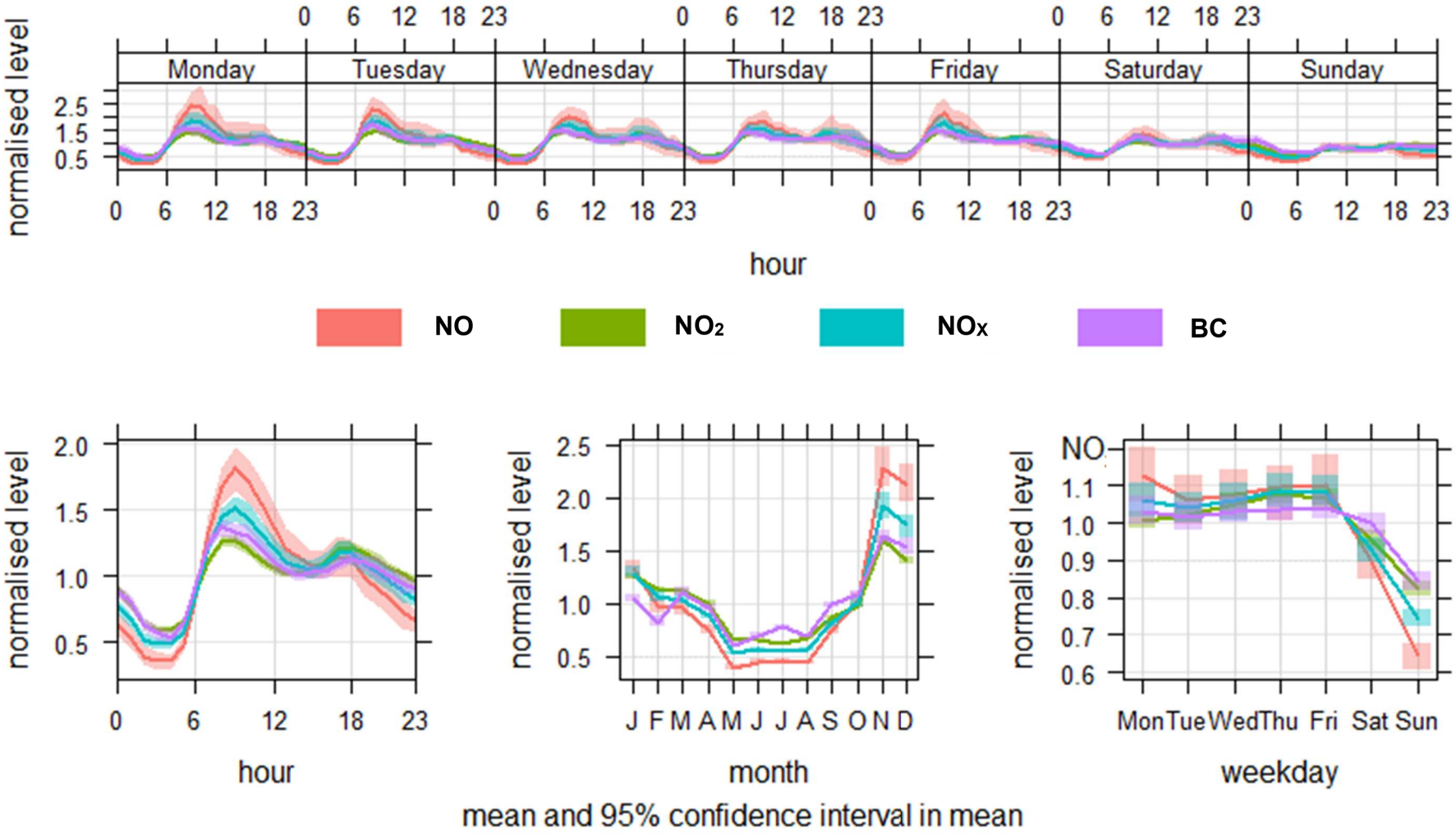


Figure 8.18 The graph shows four normalised figures at the High Street AURN Monitoring Station, Glasgow, **A.** Shows the normalised concentration of selected air pollutants (NO, NO_2 and NO_X) over the course of a working week from Monday 00:00 to Sunday 23:00. **B.** Shows the same normalised plot resolved over a 24-hour period, **C.** Shows the normalised air pollutants over the course of the months of a year. **D.** Shows the normalised air pollutants over the days of the week, averaged for each day as opposed to A which shows averaging over hourly timescales.

■ C. Glasgow High Street; Temporal– Interpretation.

Much of the rise in air pollution concentrations were because of increased vehicular activity, i.e. the morning and afternoon rush hour (Singh *et al.* 2018). Monday and Friday mark the start and end of the working week and have the highest concentrations of air pollution (Nicholson and Griffin 2017). A less significant peak occurred on a Saturday, with no peaks on Sundays. This weekend trend may be due to commuters heading to work on a Saturday, while Sunday is usually a day off (Bryce 2019).

There are relatively higher concentrations of BC on a Saturday and during the early morning and late afternoon hours. This pattern may be because of:

1. A low generation potential of Nitrogen Species during the early morning and nocturnal hours, because of a reduction in vehicular flow,
2. Continued or increased rates of resuspension of BC during nocturnal hours, possibly because of fewer obstructions (parked cars), (Jida *et al.* 2020).
3. Lower ambient temperatures between sunrise and sunset corresponding to less activation energy for NO and NO_2, (Vallero 2014 Defra 2018).
4. An increase in relative humidity in the evenings and early mornings, (Defra 2018).

As for the seasonal variation, there are four principal reasons NO_X and BC may be higher in the wintertime than during the summer months. These are:

- Meteorological effects such as inversion events (warm layers of air between layers of colder air at ground concentration and above the cloud layer), which can trap pollutants at ground level (Defra 2019).
- Colder temperatures, during which many people spend more time indoors, and when most of the domestic heating takes place. This activity can lead to increased demands on energy production (Defra 2019).

- Colder temperatures lead to increasing cold start emissions and long idling time, as people turn on their cars to de-ice their motor vehicles, (Evans 2019).

The above reasons are not specific to Glasgow and can be found worldwide during winter conditions. They are significant contributors to seasonal local and regional air quality concentrations (Defra 2019).

■ D. High Street Spatial Comparison.

A bivariate polar plot of the air pollutants at the High Street AURN was used to understand the spatial variation of air pollutants better, using the OpenAir toolset as outlined in Section 12.1.1. The corresponding polar plots for BC, NO, NO_2, and NO_X are presented in Figure 12.8.

■ E. High Street Spatial Comparison: Results.

The highest concentrations of screened air pollutants were recorded when wind speeds were low (below ~2 m/sec) and blew from the north. An elliptical increase in concentrations of NO, NO_X, and BC was present when winds blew from the north-east, at wind speeds up to about 6-8 m/sec. All pollutants had lower concentrations at high wind speeds. NO_2 concentrations varied more than the other air pollutants under similar meteorological conditions. High concentrations of NO_2 are accomplished at low wind speeds, unlike with the other pollutants. NO_2 from moderate to high-speed northerly winds also caused high concentrations. Within the high concentration areas are a series of minor hotspots. One hotspot is shared between BC and NO_2, suggesting faint sources of BC and NO_2.

Further analysis was necessary to expose faint sources of air pollution. This analysis used a ratio of Nitrogen to BC (Nitrogen compound divided by BC) bivariate polar plot to help find where concentrations of BC were high and low, relative to concentrations of Nitrogen Species, as it is conjectured that high NO_X represents local pollution sources such as vehicles. BC may have greater background concentrations.

A CPF was used to decide the robustness of the source, though the certainty of an event occurring was kept low (75th percentile) to discover more diffuse, faint, or variable sources of air pollution. These graphs are presented in Figures 12.9 A-F.

There were four major features of note on the Ratio Polar Plots, which were significant on the CPF plots; these were:

1. Northerly winds (especially from the north-east) that brought high ratios of Nitrogen to BC, with a probability approaching 100%. These winds led to concentrations of 25, 70 and 120 for NO /NO_2 / NO_X, per microgram of BC.

2. A more moderate source of NO_2 and NO_X (0.70% probability), came from south-south-aasterly winds at high wind speeds (above 4 m/sec). These winds led to concentrations of 50 and 80 µg/m^3 NO_2 / NO_X, per microgram of BC. There was no increase in the NO to BC ratio.

3. A weak hotspot (50% probability) emerges at moderate wind speeds from the west only for NO (and the resulting impact on joint NO_X). The trend is weak with NO (60% probability) and accounts for a moderate ratio between NO_2 and BC with a ratio of (15:1 µg/m^3 of NO_2 to BC).

Besides 'hotspots,' there are also two 'coldspots', where concentrations of BC were high compared to Nitrogen Species. These areas had a probability of high ratios (75th percentile) approaching 0%.

4. East-south-aast at high wind speeds. These winds led to concentrations of 5, 20 and 25 µg/m^3 for NO /NO_2 / NO_X, per microgram of BC.

5. South-west at high wind speeds. These winds led to concentrations of 3, 10 and 18 µg/m^3 for NO /NO_2 / NO_X, per microgram of BC.

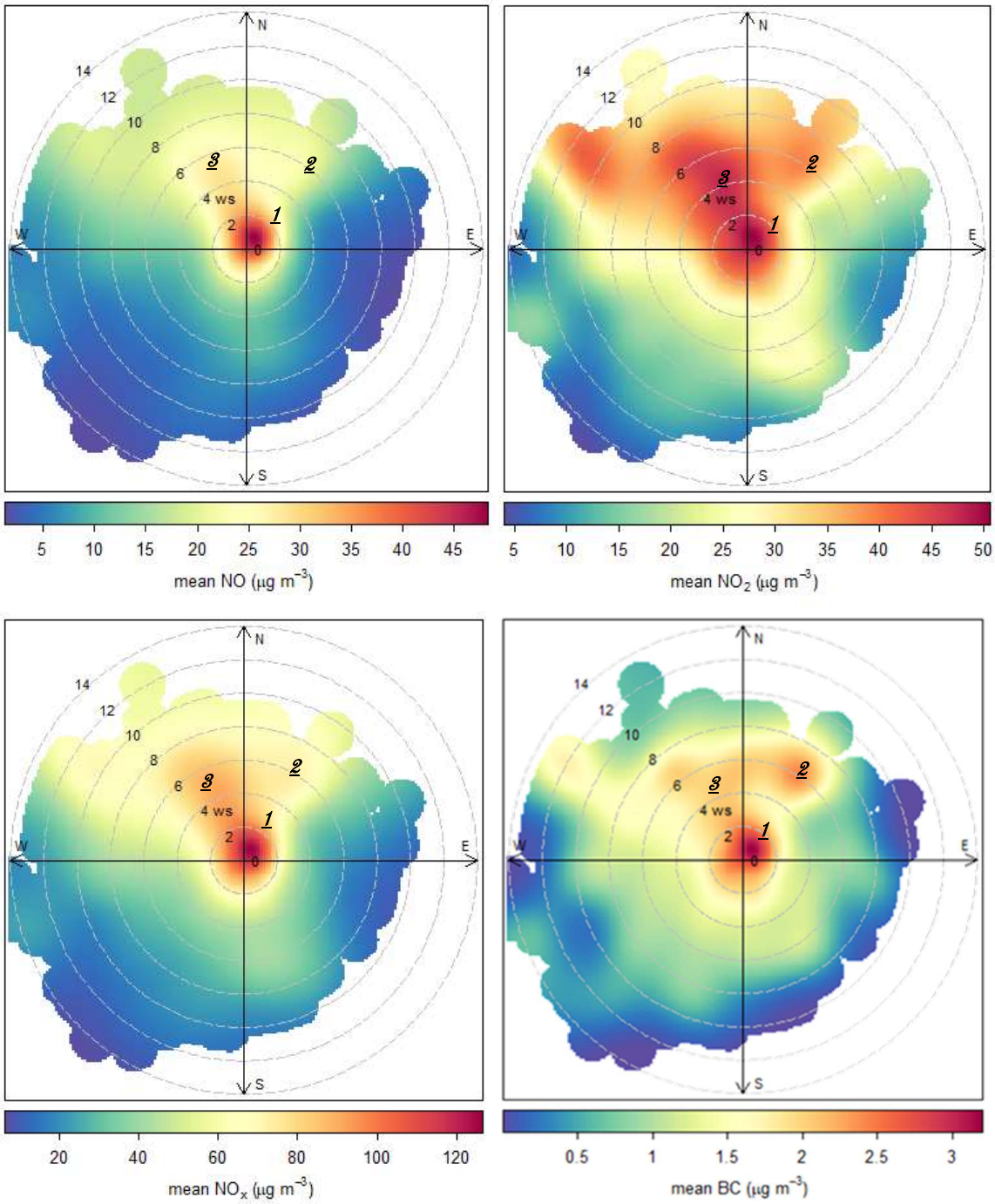


Figure 8.19. Figure A shows a ratio plot of NO concentrations under certain meteorological conditions, each meteorological condition has its own pixel. If enough data is contained within each pixel, then the average of all of the numerical values of that type are plotted. Figure **B** shows Nitrogen Dioxide, **C.** Oxides of Nitrogen as Nitrogen Dioxide and **D**. Black Carbon. All meteorological units are in metres per second whilst concentrations are in micrograms per cubic meter (µg/m^3).

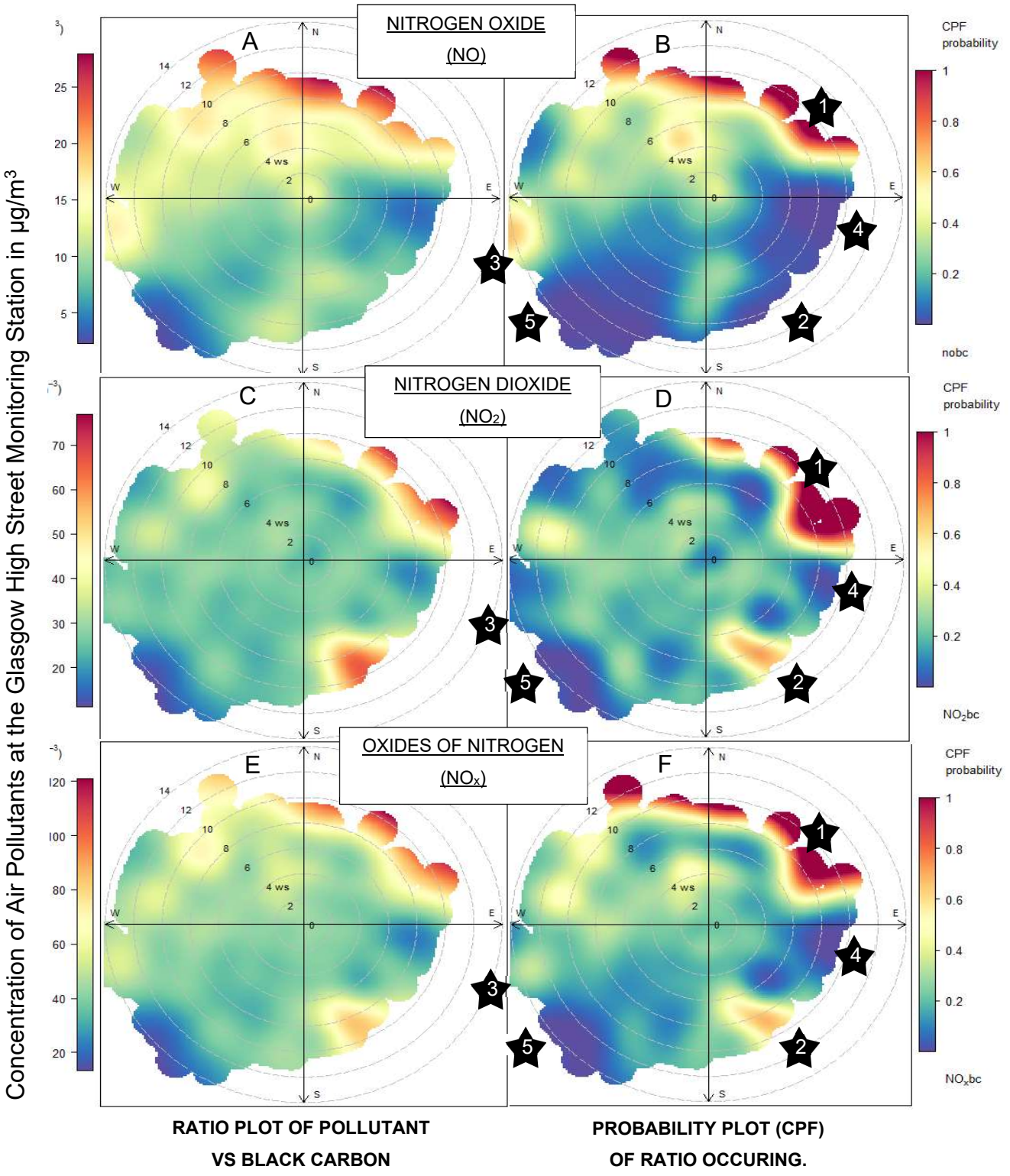


Figure 8.20. Shows a series of Ratio Plots between Black Carbon, and **A.** Nitrogen Oxide (NO), **C.** Nitrogen Dioxide, and **E.** Oxides of Nitrogen at the Glasgow High Street Monitoring Station. Alongside the ratio plots are CPF plots of the three criteria air pollutants. Labelled are a series of high and low correlation features which are further mentioned within the text.

Elsewhere within the polar and CPF plots (other than the coldspots and hotspots), there were low concentrations of either BC rich or NO_X species-rich air. These trends had a ratio of 10-12:1 NO: BC, 25-30:1 NO_2: BC and 35-45:1 for NO_X: BC.

■ F. High Street: Spatial Comparison – Interpretation.

◊ I. High Street: Single-Pollutant Polar Plots – Interpretation.

Four charts showing the concentration (non-ratio) polar plots are shown in Figure 12.8. Near-source emissions supplied high concentrations of all the pollutants to the site. These near-source concentrations are likely because of vehicular emissions from the A8; High Street. All four air pollutants (NO, NO_2, NO_X, and BC) are heavily increased from a northern source of wind. This source was likely because of air turbulence pushing air pollutants outwards from the centre of the road, into the area of low-lying landscaping to the north of the Monitoring Station. Corresponding to this theory, is that NO_2 has an increase at higher wind speeds from this direction which may signify a high degree of turbulent mixing, contributing to the conversion of NO to NO_2 (Wang *et al.* 2011; Vallero 2014).

The second feature on the non-ratio polar plots is an indicative BC hotspot from the north-east. This source may be because of legacy contamination from a busy intersection between Cathedral Street and Castle Street. Nitrogen gases may be eliminated from the system by obstructions between the Monitoring Station and the intersection, including trees and a large former church. BC, however, is free to resuspend and makes its gradual way down the A8 highway via resuspension.

The third feature on the non-ratio polar plots (single element) is a higher concentration of all pollutants from the north-north-west, though this was high for NO_2. It is speculated that the source was the intersection between Cathedral Street and Stirling Road, situated 275 metres away, with contributions from the student buildings on campus, including Murray Hall, James Goold Hall, Birkbeck Court, Garnett Hall, and Lord Todd. The student buildings likely emitted BC and Nitrogen emissions from heating and cooking activities (Zhao and Zhao, 2018; Defra 2019). Given the complexity of the topographic and building obstructions, a high degree of turbulent mixing is likely from that direction, as indicated by the NO_2 concentration (Wang *et al.* 2011; Vallero 2014).

◊ II. High Street: Polluant Ratio Polar Plots– Interpretation.

The ratio plots allow for back-trajectory analysis of sources, which might influence the High Street Monitoring Station (Figure 8.15). These sources are subjective, as they are based on a series of assumptions:

- The source of BC or Nitrogen follows the Source-Pathway-Receptor model.
- The source is identified on back-trajectory analysis alone, without the robust estimation of mitigating factors, i.e. air pollution 'decline' modelling.
- Discrete unforeseen sources (e.g. BBQ's) have been discounted.

Hotspot 1: The hotspot has a curious distribution with high ratios only occurring at high wind speeds. The source has a high CPF probability for all three NO_X species in the study. Though NO was high throughout the north, NO_2 and NO_X notably increased more from the north-east. The higher the wind speed, the greater the Nitrogen to BC profile; this may indicate a high degree of turbulent mixing, or that high wind speed overcame obstacles between the source and the receptor. Given that the source is both high in NO and NO_2, the source is likely to be extensive or is proximal to the Monitoring Station.

The ratio between NO_2 and BC was much less than expected, with the BC comprising about 1.42 to 2.00% of the NO_2 fraction, as opposed to the 10% found in other experiments (Ezani *et al.* 2018). The Monitoring Stations' height (>2.50 m) and distance from the road (5.50 m from the kerb) may have reduced the concentration of BC relative to NO_2 because of the compound's density; i.e. BC 2.26 g/m^3 and NO_2 of 1.45 g/m^3 and height distance from the road (Masey 2018). Likewise, vegetation such as trees and landscaping, can capture BC and play a mitigative role (Zheng and Li 2019).

There are four main explanations for the high concentration of Nitrogen (NO, NO_2, and NO_X) vs BC, found to the north and north-east of the Monitoring Station:

- Traffic emissions from A8 High Street.
- Traffic emissions directly next to the Monitoring Station.
- Traffic from the intersection between Cathedral Street and Stirling Road
- Traffic from the motorway (i.e. M8 J15 Townhead Interchange).

The most obvious source of air pollution at hotspot one is from heavy traffic along the A8 High Street (Figure 8.16 A and B) as noted in the council's modelling report (Glasgow City Council 2018). In the morning, traffic can be backed up to a small building to the north of the Monitoring Station, and queuing cars can be significant sources of BC and NO_X (Glasgow City Council 2018). The nitrogen gases may have been blown across the landscaping at high speeds to the Monitoring Station, while the BC particles became stuck within foliage (Zheng and Li 2019). Leading on from the first hypothesis are parking spaces and a bus stop next to the Monitoring Station. The two parking spaces and bus stops are toward the most concentrated area of NO_2, 5 and 35 metres to the north-east of the Monitoring Station. Older buses and cold start emissions can produce increased emissions of nitrogen gases.

While BC is emitted far less often than nitrogen, there is still an unusually low ratio between BC and NO_2 than one would expect from such a proximal source.

A busy intersection between the A8 (Castle Street) and Cathedral Street is present 250 metres to the north-north-east (Figure 8.16 D). The direction is further to the north than the highest concentration of NO_2 indicated on the polar plot. However, there are buildings, including Barony Hall and the St Mungo Museum, which are likely to channel wind through the area. The source is busy during most times of the day, and extensive traffic delays on this junction often back up to the Monitoring Station. Queuing cars at the intersection could emit high concentrations of air pollution (Glasgow City Council 2018). The junction is bounded by landscaping and bushes, which might have helped to trap PM, including BC (Chen *et al.* 2017; Fan *et al.* 2017). During the site walkover, much of the foliage next to the intersection was coated by PM, and several leaves showed evidence of ozone poisoning. This source would explain the lower concentration of BC relative to nitrogen gases, and the degree of turbulent mixing over the intervening distance may explain why NO_2 was higher than NO. While the ratio between BC and Nitrogen is the highest from this direction, there is a smaller increase in BC and NO_2 from this direction at more moderate wind speeds. The increase in BC alone may be due to resuspension of BC rich PM making its way down the road from the intersection, and from detritus left behind from queuing vehicles.

Lastly, there is a busy motorway interchange (M8 J15) in this direction, some 1,435 metres north of the Monitoring Station. This source is likely too far away to be a key source, as a more local source of BC is indicated on the single element plot, and a high concentration of NO is present. Albeit this may have regressed from NO_2 during turbulent mixing, it is more likely that the emissions would have become so mixed as to be unobservable.

Hotspot 2: The south-eastern source with high BC to Nitrogen ratios is most likely explained by the seven-storey Duke Street car park, situated 140 metres to the south-east (Hien and Foo 2011; Mohammed *et al.* 2014). The car park is within the 'Collegeland Development' and has space for 1170 cars. Wind can escape from the car park because of its large open bay windows which circulate air throughout the building (Hien and Foo 2011). The car park has an indirect line of sight to the Hope Street Monitoring Station, via Burrels Lane, which emerges opposite the Monitoring Station, and via landscaping at the western end of 294 High Street.

Hotspot 3: A southwestern source with high NO to BC ratios from high-speed winds. There are few sources of emissions in this direction, but the most likely source of NO was a car park situated 95 metres to the south-west of the Monitoring Station (Hien and Foo 2011; Mohammed *et al.* 2014). An extensive area of landscaping is present further in this direction, combined with a large building (the University of Strathclyde's Technology and Innovation Centre), which most likely acted as a high-rise windbreak helping to reduce local sources of air pollution from the city beyond (Harrison *et al.* 2012b; Karra *et al.* 2017). The car park provided 40 permanent marked spaces, with an overflow capacity of around 45 spaces. The air pollutants from this car park migrated in the landscaped areas between the High Street properties around 259 High Street and the student accommodation, which was on a plateau above. Cold start emissions combined with vegetation's efficiency of capturing particles may explain the low BC concentrations relative to Nitrogen emissions found at this hotspot.

There were two coldspots (features 4 and 5) identified on the ratio plots, which were low in NO_X but high in BC. There are two dominant theories for the emergence of a cold spot of nitrogen:

- A BC source which emits higher ratios of BC to Nitrogen,
- A lack of NO_X generating activities with the resuspension of BC (either local from detritus, or regional sources), leading to higher ratios of BC than usual.

There seems to be an example of both cases at this Monitoring Station.

Coldspot 4: Was likely influenced by the Well Park Brewery, 380 metres to the west of the Monitoring Station (Figure 8.16 C). The brewery is reportable to SEPA under the Scottish Pollutant Release Inventory (SPRI) for emissions to air (SEPA 2018). While the brewery is under the reporting limit for NO_x, 100 tons/annum, it emits 1,910 metric tons of Total Organic Carbon (TOC) every year (SEPA 2018). The correlation between BC and TOC is quite understudied, but in marine sediments, the ratio is approximately 65% (Glaser *et al.* 2005). Using the Glaser *et al.* 2005 correlation, as much as 1,242 metric tons of BC may have been emitted from the brewery over the year (Glaser *et al.* 2005). The smell of hops and malt can be scented in this area; odours are formed from very fine or gaseous emissions, which may hint at underlying small-scale exposures of suspended PM, (Raresdn 2018; Olajire 2020).

Coldspot 5: A back-trajectory shows a distinct lack of air pollution generating activities, with the large Greyfriars Garden and wasteland area on one side of the road, and an extensive modern student building on the other (Llaguno-Munitxa *et al.* 2017; Karra *et al.* 2017). The lack of air pollution generation likely made resuspended BC the most prominent source of air pollution from this coldspot area. Directly next to the Monitoring Station is the High Street Canyon, though if this was a major factor in the air pollution activity, then nitrogen gases should have also greatly increased.

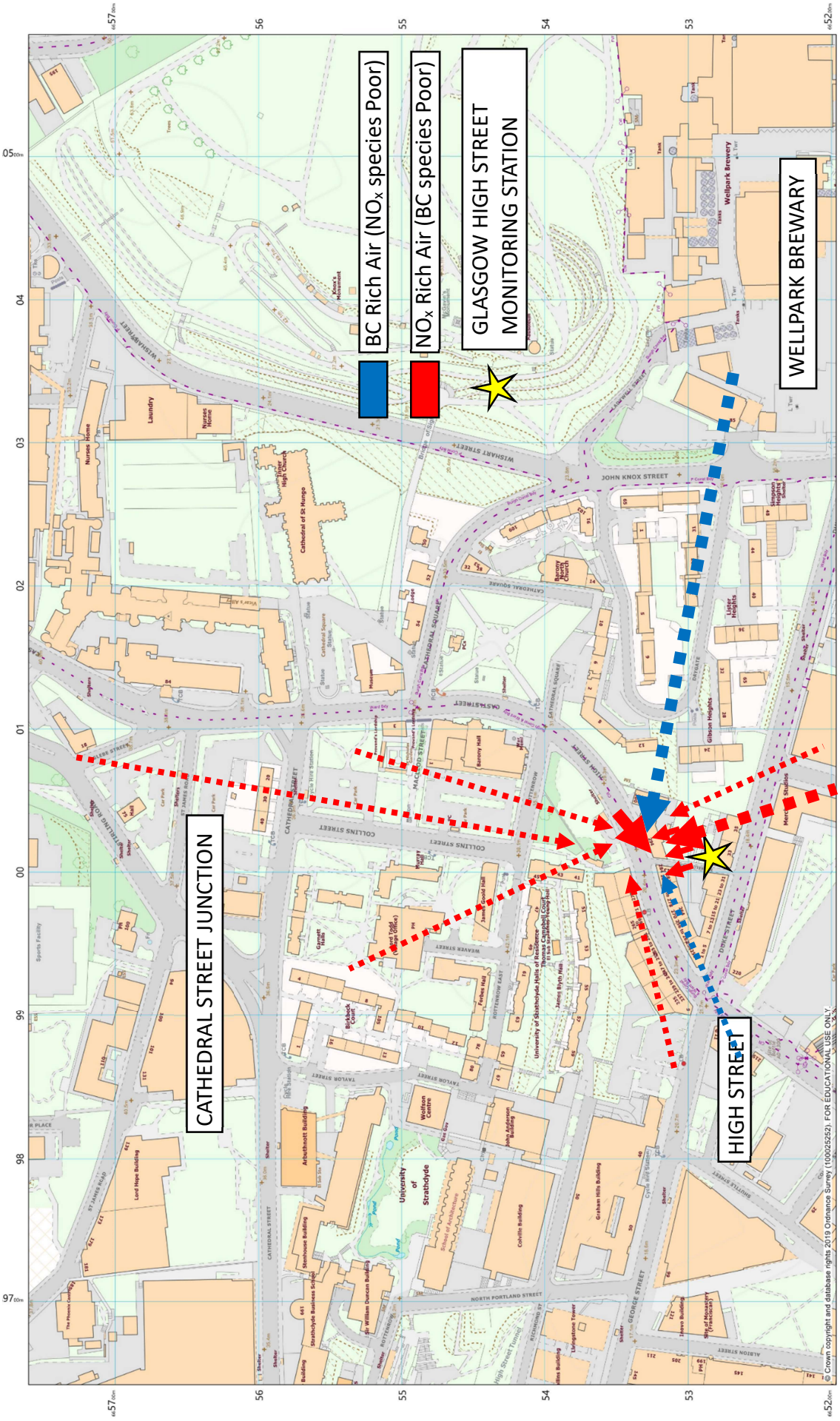


Figure 8.21 A map showing a back-trajectory analysis of BC rich air and NO_X rich air from various sources including Wellpark Brewery, The Cathedral Street Junction, and the A8 High Street. **Source:** Base map - Digimap and Ordinance Survey (2019). **(Adapted)**

Contains Ordnance Survey data. © Crown copyright and database right 2010. Data provided by Digimap OpenStream, an EDINA, University of Edinburgh Service.

Figure 8.22. A. Shows the monitoring site (circled in white) with the tenement buildings slightly to the south potentially yielding a street canyon. **B.** Shows a view of the Monitoring Station (circled in white) facing North, with the landscaping and derelict building to the North. **C.** Shows the Well Park Brewery facing south from Glasgow Necropolis, showing steam emitting from part of the brewery process. **D.** Shows parts of the road junction with Cathedral Street to the north of the Monitoring Station. **Source:** Grainger (2018).

♦ 8.8.2) High Street Summary.

To summarise, there were considerable temporal and spatial variations in the air pollution concentrations (BC, NO, NO_2, and NO_X), ratio concentrations and spatial sources at the High Street Monitoring Station. Like much of the UK, concentrations of air pollution are higher during the winter months than during the summer because of the increased energy consumption (for heating and an extended indoor time), and meteorological phenomenon (such as increased humidity, decreased temperature and inversion events).

UK rush hours also increase the concentration of air pollution over the day, especially on Monday and Friday.

A series of ratio plots revealed interesting spatial patterns, indicating key sources of air pollution from vehicular emissions, major road junctions and localised sources, such as two car parking spots and a bus stop. However, these sources were quite discrete, and a ratio plot of BC to NO_X was used to indicate the proximity of the sources as it was conjectured that near-source emissions would be high in nitrogen relative to BC. Five features were noted on the ratio of polar plots, three of these had a high relative concentration of BC to NO_X, while the other two had low concentrations of BC to Nitrogen. By using back-trajectory analysis, several sources were identified. These features included:

1. **Hotspot 1,** was likely sourced from the impact of local air pollution from the A8 High Street combined with heavy traffic located at the intersection between the A8 and Cathedral Street. The reason for the low relative BC concentration was conjectured to be due to the mitigative role of vegetation reducing PM emissions, but introducing turbulent mixing allowing for NO to converting to NO_2.

2. **Hotspot 2,** may have been sourced from the busy Duke Street multi-storey car park (1170 cars), as the building had large portal openings with an indirect line of sight to the Monitoring Station via an alleyway or landscaping.

3. **Hotspot 3,** may have been sourced from a 40-space car park less than 100 metres away. With not much generation activity beyond, wind may access the Monitoring Station via landscaped areas to the rear of the properties along the A8 High Street. These landscaped areas likely reduced the BC concentrations in the air, while leaving NO_X relatively intact (other than turbulent mixing).

4. **Coldspot 4,** was a coldspot with a high relative BC concentration to NO_X this was likely because of a BC rich source. The conjectured source of this BC rich air was the Well Park Brewery, which may emit as much as 1,242 tons of BC annually (Glaser *et al.* 2005; SEPA 2018). Odorous pollution is also an anecdotal brewery-related pollutant in the area (Raresdn 2018).

5. **Coldspot 5,** was likely a low generation area with resuspended BC contributing much of the air pollution from this relatively clean area of the city.

► 8.9). Townhead AURN.

Unlike Glasgow High Street, the Townhead Monitoring Site (Figure 8.17) is an urban background Monitoring Station and set within an urban landscaped area. In every direction from the Monitoring Station are areas of landscaped grassland, followed by car parking and housing; apart from directly to the north where there is a cluster of shops (Figure 8.18). The shops are renowned because of them appearing on the TV series 'Taggart', and to the west of the shops is a car park with a minor road, Dobbies Loan Place, linking the shops to Kennedy Place.

♦ 8.9.1). Townhead Ratio Comparison.

The relationship between BC and NO, NO_2, and NO_X is shown in Figure 8.23 A-C. These graphs (Figure 8.25) show a scatter plot between the pollutants, slope of the graph and R^2. All the scatter graphs show a strong positive linear relationship between Nitrogen (NO, NO_2, NO_X) and BC. Similar to High Street, there was a moderate to the high correlation between the pollutants with an R^2 between 57 and 79%. The best correlations were found between BC, NO, and NO_X (R^2 of 0.73 and 0.79), which were higher than High Street; and there was a comparably poor correlation for NO_2 (R^2 of 0.57).

Figure 8.23. Shows the Glasgow Townhead AURN Monitoring Station in a brick building in the foreground, with a northerly photograph showing the range of structures and environments around the Monitoring Station.

Source: Grainger (2019).

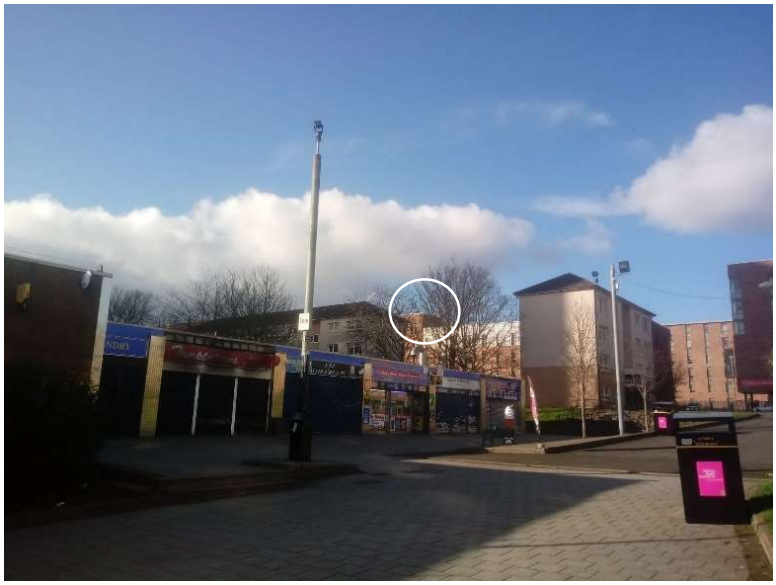


Figure 8.24. Shows the nearby Dobbies Loan shops (a locality featured in the TV show Taggart). The Tandoori restaurant is the shop at the end of the row, and has a large extractor fan on its roof and is circled in white.

Source: Grainger (2019).

The ratio between NO_X and BC was 63% higher than at High Street at 0.0295 per 1 µg/m^3 increase in BC, 20% less than at High Street between NO and BC (0.0295 per 1 µg/m^3 BC), and 20% less for BC (at 0.0434 per 1 µg/m^3 per BC). Similarly, to High Street, the best correlations were found between BC, NO, and NO_X (R^2 of 0.83 and 0.85) with a poorer correlation for NO_2 (R^2 of 0.63).

♦ 8.9.2). Townhead; Temporal Variation - Results.

A series of graphs, in Figure 8.25, plot various temporal scales (hours, days, weekdays, and months) against the normalised concentrations of BC and Nitrogen Compounds (monoxide, dioxide, and oxides of nitrogen).

The temporal variation was similar to High Street, with peak concentrations of air pollutants occurring both in the morning (06:00 -10:00) and afternoon (16:00–20:00) rush hours. The lowest concentrations were in the early hours (between 03:00 and 05:00). The morning peak was more Leptokurtic than per High Street and skewed to the left (earlier morning). Nitrogen dioxide is the most abundant air pollutant between 03:00 and 05:00 while NO and NO_X are low until about 06:00.

There were much lower concentrations of NO during the weekend than during weekdays. In terms of seasonal variation, there were peak concentrations during the winter months (November and December), with the summer months having much lower concentrations, which is/was very similar to High Street.

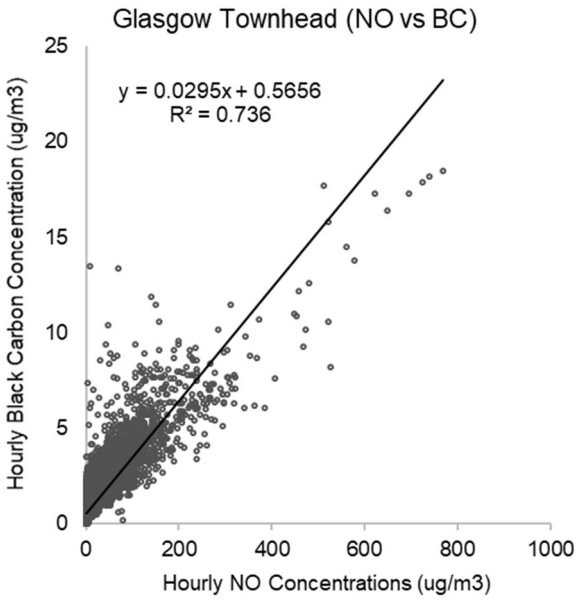


Figure 8.25.A Scatter graph showing the strong linear relationship between Hourly Black Carbon Concentrations and Hourly Nitrogen Monoxide Concentrations at Glasgow Townhead AURN Monitoring Station after QA/QC correction. There is a moderately strong R^2 value of 0.73, with most BC values averaging in the 0-10 µg/m^3 region, although the highest (95th percentile) recorded sample was at around 48 µg/m^3. There was a curious offset of +0.56 µg/m^3 Black Carbon, possibly indicating the presence of BC within ambient environments.

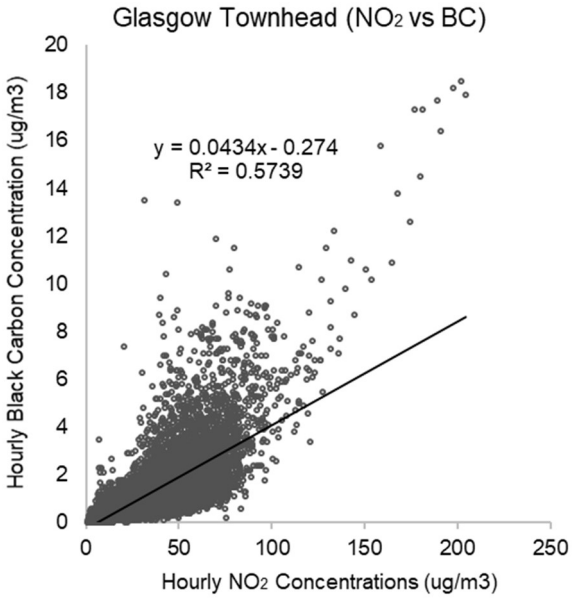


Figure 8.25.B, shows another strong positive linear relationship between Hourly Black Carbon Concentrations and Hourly Nitrogen Dioxide Concentrations at Glasgow Townhead AURN Monitoring Station (post-processing). There was a less strong R^2 value of 0.57, with a less steep gradient, the BC results were also more equally spread with a higher projected trend at higher NO_2 concentrations projected (dashed line).

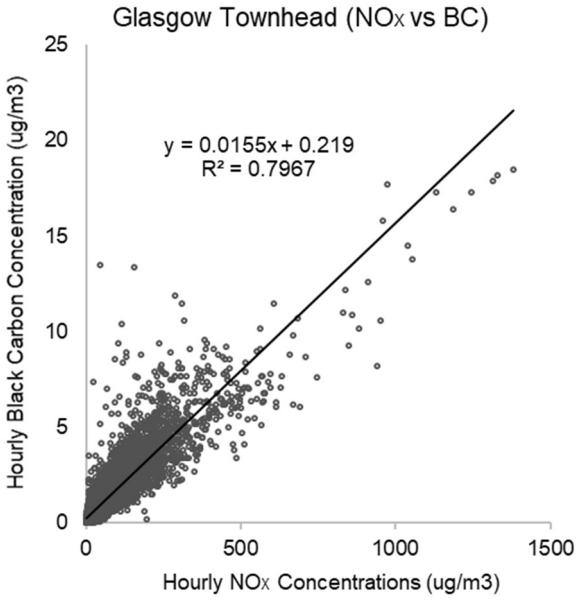


Figure 8.25.C, shows the strongest positive linear relationship between Hourly Black Carbon Concentrations and Hourly Nitrogen (Oxide of Nitrogen) Concentrations of the NO_X species, at Glasgow Townhead AURN Monitoring Station (post-processing). There was a very strong R^2 value of 0.79, with a relatively steep gradient. Although the BC results were more equally spread than NO, this seemed to persevere to higher projected concentrations of NO_X, indicating that it might be more reliable under most conditions.

Source: Grainger (2019).

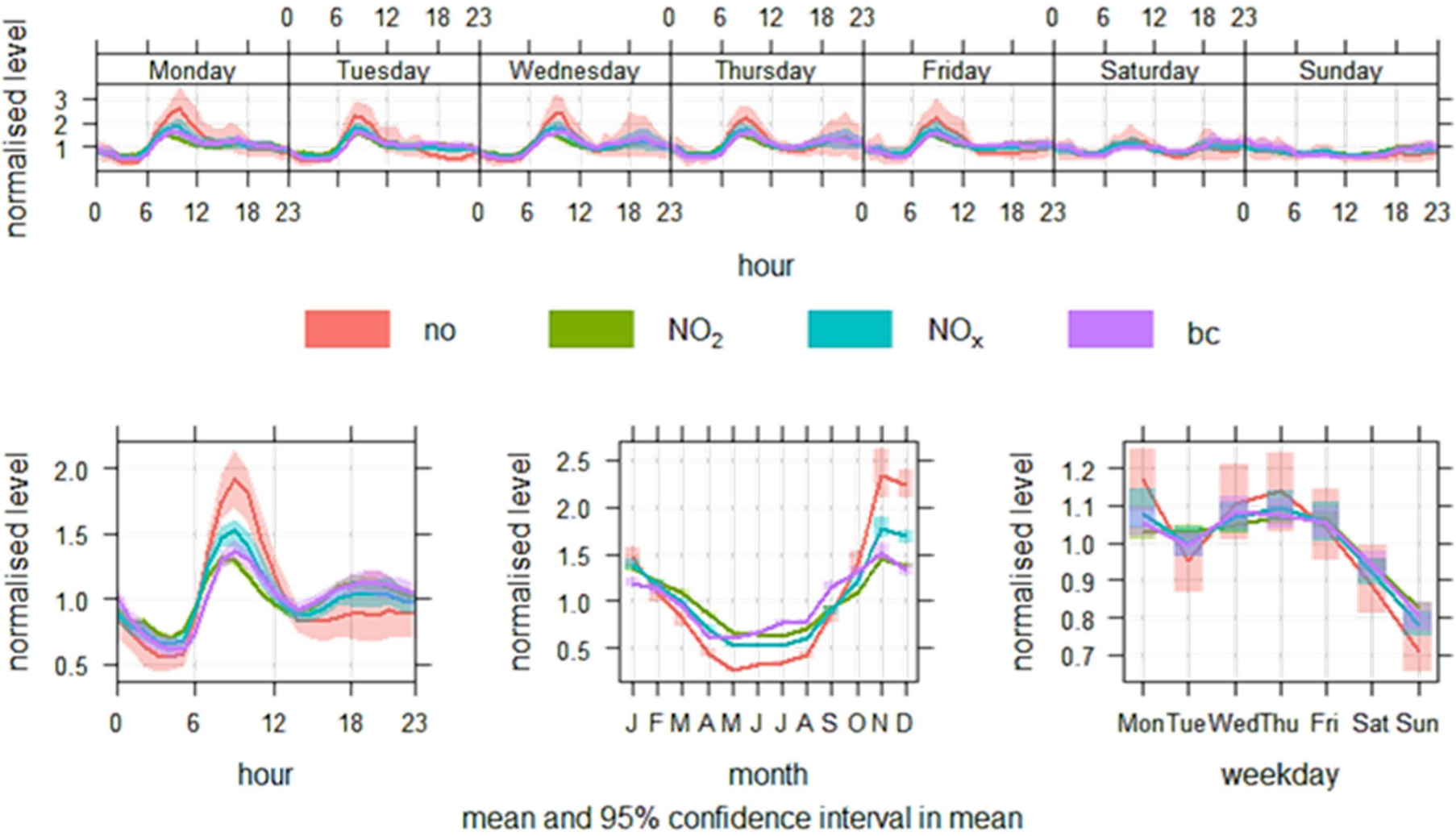


Figure 8.26 The (openair) graph shows four normalised figures at the Townhead AURN Monitoring Station, Glasgow, **A.** Shows the normalised concentration of selected air pollutants (NO, NO_2 and NO_X) over the course of a working week from Monday 00:00 to Sunday 23:00. **B.** Shows the same normalised plot resolved over a 24-hour period, **C.** Shows the normalised air pollutants over the course of the months of a year. **D.** Shows the normalised air pollutants over the days of the week, averaged for each day as opposed to A which shows averaging over hourly timescales. **Source:** Grainger (2019).

♦ 8.9.3). Glasgow Townhead; Temporal– Interpretation.

The daily peak concentrations of air pollution correspond to the hours of peak traffic volume, i.e. the morning and afternoon rush hour, as per the High Street AURN (Singh *et al.* 2018). Unlike at High Street, the concentrations of BC and Nitrogen (NO, NO_2, and NO_X) reduced from Friday over the weekend. The most likely reason for this was because of Townhead being less affected by recreational commuters heading into the city centre during the weekend. The major traffic jams seen during weekdays were more uncommon here, with traffic more uniform over the day. In particular, NO emissions were much lower during the weekend, again likely because of increased volumes of NO mixing in ambient air and converting to NO_2, without the major traffic activity bringing fresh sources of NO into the environment (Vallero 2014; Singh 2018; Defra 2019).

Seasonal variations were similar to High Street, and symptomatic of a regional phenomenon with meteorological conditions (including temperature and inversion events) and anthropogenic activity (more time indoors and additional heating-related emissions) likely causing the higher winter concentrations (Defra 2019; Evans 2019).

♦ 8.9.4). Townhead Spatial Comparison.

To better understand the spatial variation of air pollutants at the Townhead AURN, polar plots of air pollutants, (single-compound) concentrations of BC, NO, NO_2, and NO_X, were graphed. These plots are presented in Figure 8.27.

■ A. Townhead Spatial Comparison: Results.

The polar plots show that the highest concentration of air pollutants (BC, NO, NO_2, and NO_X) at Townhead was found at very low wind speeds (below ~2 m/sec), similar to the High Street AURN station.

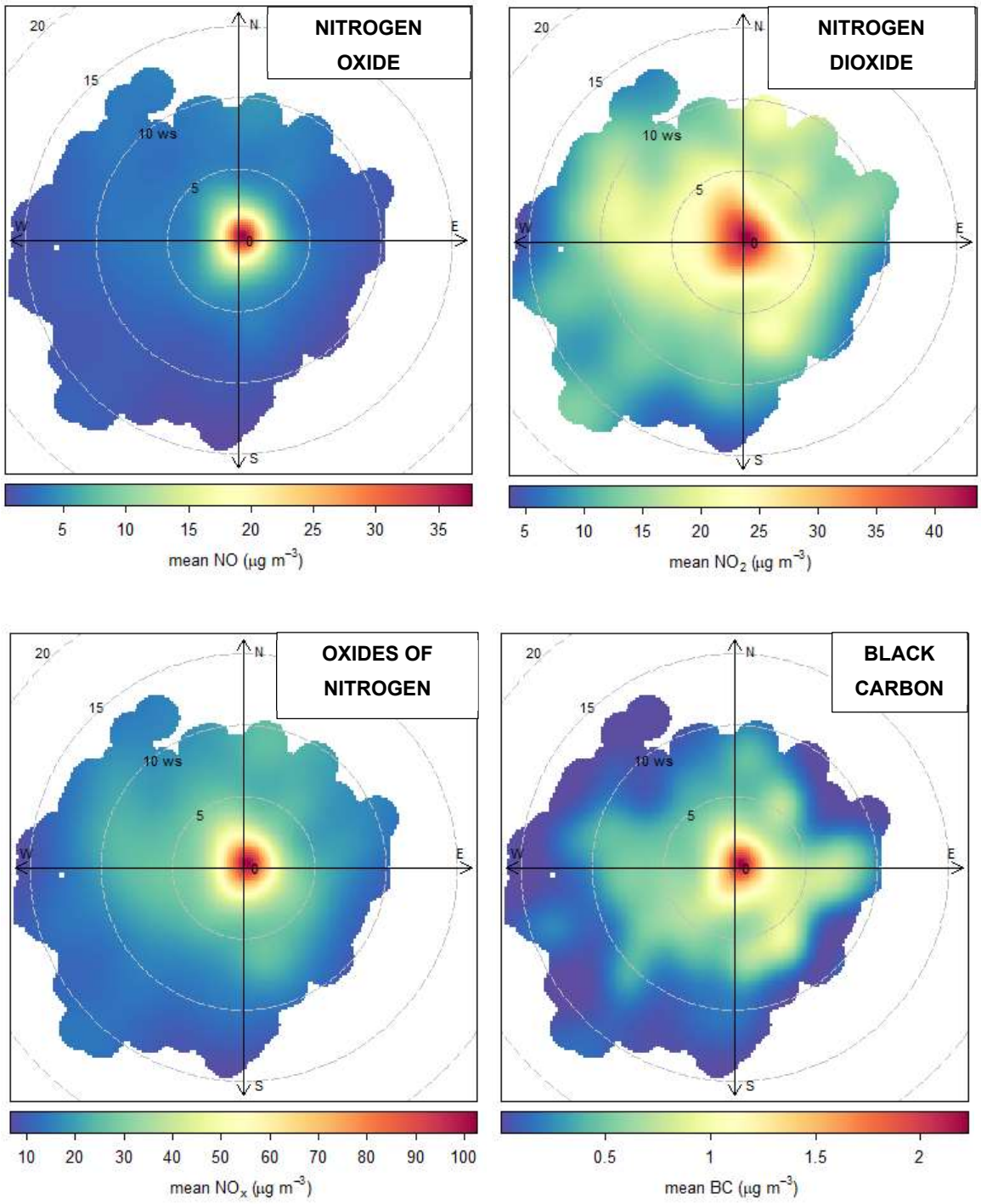


Figure 8.27. Figure A shows a ratio plot of NO concentrations under certain meteorological conditions. Each meteorological condition has its own pixel if it contains enough data within each pixel, then the average of all the numerical values of that type are plotted. Figure **B** shows Nitrogen Dioxide, **C**, Oxides of Nitrogen as Nitrogen Dioxide and **D.** Black Carbon. All meteorological units are in metres per second, whilst concentrations are in micrograms per cubic meter.

Source: Grainger (2019).

The NO concentrations, in particular, had a 'bull's eye' distribution with moderate to high concentrations (up to 35 µg/m^3) in most wind directions below 2 m/sec; no concentrations over 10 µg/m^3 were present over 5 m/sec. Outside of the central hotspot, the concentrations were about 5 µg/m^3 with minor increases (<1 µg/m^3) echoing NO_2 trend.

For NO_2 the concentration was much more varied, with concentrations as high as 15-20 µg/m^3 of NO_2 extending from a central hotspot through to 10 m/sec. The highest concentrations of NO_2 (30 µg/m^3) occurred when wind speeds were low (<2.5 m/sec), although the hotspot was pear-shaped and projected out from north-westerly sourced winds. Beyond the central hotspot, the moderate (15-20 µg/m^3) NO_2 concentrations followed a spiral-shaped projection through to around 12 m/sec. South-westerly air led to low concentrations of NO_2, compared to other wind directions, as did high wind speeds from the west and south-east. The NO_X was heavily influenced by the bull's-eye distribution of NO with a central hotspot (below 3 m/sec and peaking at 100 µg/m^3), with only minor concentrations (30 µg/m^3) of NO_X following the trend of the NO_2 distribution.

The distribution of BC was similar to NO, in that the highest concentrations (2 µg/m^3) were found below 3 m/sec, but similar to NO_2 with more minor concentrations (<1 µg/m^3) following a cruder echo of the same pattern. High wind speeds (>10 m/sec) led to a more drastic decline in BC concentrations, leading to a BC concentration less than 0.5 µg/m^3.

Again, it was felt that a series of BC to Nitrogen ratio plots with CPF analysis would be helpful to gain a better understanding of the proximity of these features. The resulting plots are displayed in Figures 12.17 A-F.

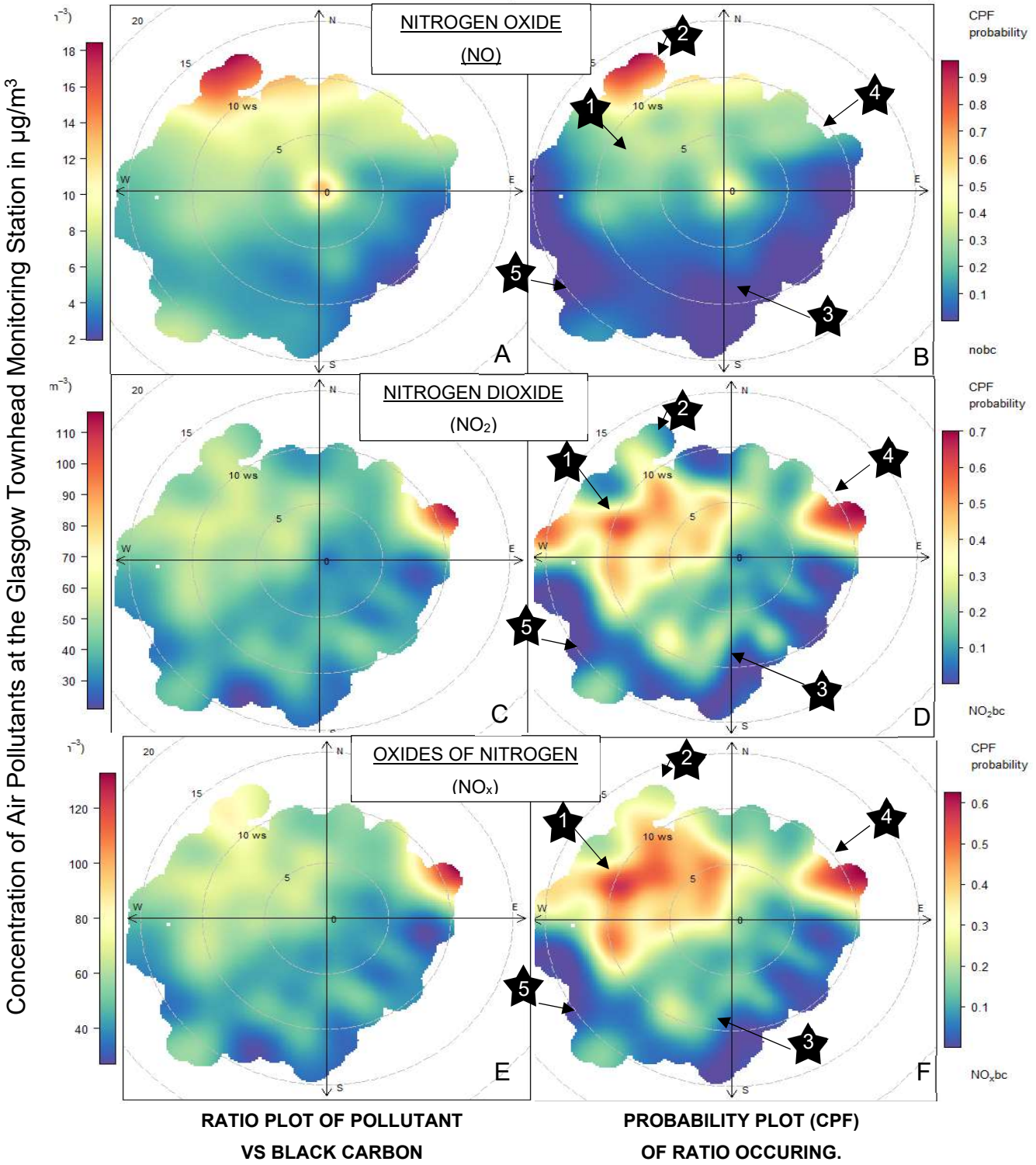


Figure 8.28. Shows a series of Ratio Plots between Black Carbon, and **A.** Nitrogen Oxide (NO), **C.** Nitrogen Dioxide, and **E.** Oxides of Nitrogen as Nitrogen Dioxide at the Glasgow Townhead Monitoring Station. Alongside the ratio plots are CPF or Conditional Probability Function plots of the three criteria air pollutants. Labelled are a series of high and low correlation features which are further mentioned within the text. **Source:** Grainger (2019).

The ratio and polar probability projections are plotted in Figure 8.28 (A-F). The similarities between the air pollutants are clearer than with the single-pollutant plot alone, and new potential sources of air pollution could be identified. There were five major features of note on the CPF and Ratio Polar Plots:

1. **Hotspot 1:** comes from north-westerly winds rich in NO_2 and NO_X at most wind speeds, with a CPF probability of >60%. The pattern is enhanced with CPF and shows a 'triskelion' shape. BC comprised 1.6% of the NO_2 concentration, with a 60-70% probability. There is only a very slight increase in the NO ratio from this direction (8:1) with CPF of ~30%.
2. **Hotspot 2:** from the north-east at very high wind speeds (~17 m/sec), though the only pollutant affected was NO. The hotspot produces a BC spike comprised 5.55% of NO (18:1) with a 90% CPF probability.
3. **Hotspot 3:** A Z shaped feature appeared on the NO_2 and NOx plots, but the resolution improved with CPF. The Z shaped feature extends into an F shape with winds from the south-east to south-west. The pattern is discernible on the NO_2 and NO_X ratio plot, with BC comprising about 2% of the NO_2 concentration. No pattern is apparent within the NO plot. There are a series of coldspots associated with this hotspot, with ratios as low as 30-40:1 BC.
4. **Hotspot 4:** There is a NO_2 and NO_X rich anomaly to the east-north-east at high wind speeds above 5 m/sec. The anomaly was especially rich in NO_2 and NO_X with BC co-existent with only 0.91% of the NO_2 concentration; the feature also had a high (70%) CPF probability.
5. **Coldspot 5:** An independent coldspot from the south-west at high wind speeds with a CPF probability below 10% (showing a consistent source of nitrogen-poor and BC rich air).

Elsewhere within the polar and CPF plots (other than the coldspots and hotspots), there were low concentrations of either BC rich or NO_X species-rich air. These trends had a ratio of 4:1 NO: BC, 40:1 NO_2: BC and 45:1 for NO_X: BC.

■ B. Townhead: Spatial Comparison- Interpretation.

◊ I. Townhead: Single-Pollutant Polar Plots- Interpretation.

The concentration (non-ratio) polar plots show that near-source emissions supplied much of the air pollution to the site, similar to the High Street Monitoring Station (Figure 8.10). There were, however, diffuse concentrations of NO_2 and BC in most wind directions which diminished at greater wind speeds. The distributed pattern of NO_2 and BC was conjectured to be due to diffuse distant sources of air pollution in the wider community. However, discrete sources of air pollution cannot be found by using the single-pollutant polar plots alone, and polar ratio plots were used to assist with source identification.

◊ II. Townhead: Ratio Polar Plots- Interpretation.

The ratio plot allows for more complex analysis of the sources which might influence the site. Five discrete features were found using polar plots of the ratio between BC and various Oxides of Nitrogen (NO, NO_2, and NO_X).

These sources are interpreted in greater depth below:

Hotspot One: The first hotspot had a triskelion shape stretching from the west-south-west to the north, with subtle ratios of NO_2 and NO_X with strong CPF plots. The source of the first hotspot appears to be traffic along North Hanover Street and Cowcaddens Road, to busy major A-roads within 100 metres of the Monitoring Station (Figure 8.19 B). The southerly projection of the shape could be North Hanover Street and its intersection with Cowcaddens Road, with the former due east of the station.

As with the intersection between Cathedral Street and the A8 at High Street, intersections have higher concentrations of air pollution than uninterrupted sections of road, due to idling and the source remaining static for a longer period (Sharma *et al.* 2019).

From the conjectured intersection between North Hanover Street and Cowcaddens Road, the feature trends towards the north where there is a CPF hotspot. This feature is expected to be the continuation and intersection of North Hanover Street with the A804 - Dobbies Loan.

The intersection 300 metres to the west-north-west of the monitoring station may account for the hotspot, though the intersection was observed to be very busy during the site walkover. From this intersection, the CPF trends towards the north-east following Kyle Street (A804) before having a hotspot. The back-trajectory analysis has shown that the hotspot could have several discrete sources:

- The traffic-light intersection between North Wallace Street and Baird Street (A804), as photographed in Figure 8.19 C. Given the intersection theme of the CPF hotspots in this anomaly, the most likely emissions source is the traffic-light intersection between North Wallace Street and Baird Street. A traffic Monitoring Station further to the north of the intersection had an AADF of 9,177 vehicles per day (DoT 2020b).
- Parking and commercial activity associated with local businesses within the Inner City Trading Estate, including: the HM Passport Office, Royal Mail Distribution Centre, Mercedes-Benz Garages and student accommodation (Mohammed *et al.* 2014). This rationale is a less likely explanation i.e. that industrial activities associated with the distribution centres are supplying high concentrations of nitrogen-rich gases to the Monitoring Station. However, the supportive role of these industrial sources cannot be discounted.

- Traffic emissions from the M8 Motorway to the north of the Royal Mail Distribution Centre. The last theory is that NO_2 and NO_X are being supplied to the Monitoring Station from the M8 motorway some 400 metres due north, following the north-south aligned with North Wallace Street. Though the M8 motorway could be a source, there is a steep vegetated slope with trees separating the motorway from the Royal Mail Distribution Centre and A804 beyond (Chen *et al.* 2017; Fan *et al.* 2017). However, there may be a linkage between this source and Hotspot 2, which will need to be explored further.

Hotspot Two: Supplies NO rich (BC poor) air to the Monitoring Station from strong north-westerly winds (>10 m/sec). There are three potential reasons for the lack of NO_2 and NO_X rich air also in this direction:

- The Tandoori Restaurant is probably the source of the NO emissions (Figure 8.17 and 12.18 D). Cooking emissions are known to be high in NO emissions. The restaurant, operating under the name Tandoori Plus, sold £41,260 of take-way food in 2014 equivalent to 13,986 set meals and thus is quite a busy restaurant (John Wilson Ltd 2014; Tandoori Plus 2015).

  Significant concentrations of cook smoke emissions could be produced by cooking with natural gas on an industrial scale (Zhao and Zhao 2018). The emissions from these cookstoves are emitted from the roof, at the same chimney height as the Monitoring Station, which may allow for a direct linkage between direct emissions of NO and the Monitoring Station at high wind speeds. The restaurant serves evening meals and is open between 15:30 and 23:35. It is worth mentioning that NO requires sunlight to convert into NO_2, and many of the business' operating hours are after sunset (Tandoori Plus 2015; Solipsys Ltd 2020).

- The M8 Motorway is in this direction, and there is a potential linkage between the Monitoring Station and the motorway via North Wallace Street. However, there is a considerable distance between the Monitoring Station and the motorway (about 400 metres). High wind speeds would have likely reduced the concentration of NO via turbulent mixing, facilitating its conversion into NO_2. However, neither NO_2 nor NO_X show evidence of a hotspot, indicating that the source is closer to the Monitoring Station than the motorway.

- There is a car park directly to the north of the Monitoring Station. These vehicles use the car park to visit the adjacent Townhead shops illicitly, and many of the emissions are likely to stem from cold start emissions and idling; consequently, BC was equal to 10% of the NO air pollution. However, the mixing height between ground level and the Monitoring Station (about 3 metres) should have introduced turbulent mixing and therefore NO_2.

Hotspot Three: The faint linear Z and F shape feature to the south-east of the Monitoring Station likely reflects two 60 space car parks associated with residential units (33-34 St Mungo Avenue) which are located to the south of the Monitoring Station. There are also potentially some impacts from the intersection between St Mungo Avenue and St James Road. There is a clear line of sight between these car parks, and anecdotally when visiting the Monitoring Station, the car parks are most often full. Many of these cars are of advanced age, with several examples of early 1990s vehicles in the car parks.

Hotspot Four: Produced NO_2 and NO_X rich air from the north-east at wind speeds above 5 m/sec. The immediate land uses include residential homes, small car parking areas, playing fields and a primary school. Behind the playing fields is the 'Townhead Interchange,' i.e. Junction 15 of the M8 motorway. The Townhead interchange comprises the M8, A8, and A803 roads. These are all major roads for the city of Glasgow. The AADF on the A803 (North) is 18,049 vehicles, A803 (South) is 7,138 vehicles, A8 (Castle Street) is 15,729 vehicles, and the M8 is 156,897 with a total daily estimated AADF of 197,813 vehicles (DoT 2020c-f).

Significant generation of BC and Oxides of Nitrogen is likely given the very high number of vehicles on this stretch of road. However, the intervening distance and the ground roughness (buildings and slopes) may have allowed the NO to convert to NO_2 and NO_X. The M8 is elevated at the Townhead Junction, and this likely led to increased mixing and turbidity, enhancing the conversion of NO to NO_2. Increased NO to NO_2 conversion was likely exacerbated by the morning and afternoon rush hours falling within sunlight hours for much of the year (Solipsys Ltd 2020). A high concentration of BC should, theoretically, have also been present from this source, which would have reduced the NO_2 to BC concentration. However, entrapment within landscaping, especially along the margins of the A803 and in the wider Townhead urban area, likely had a mitigative impact on BC concentrations (Chen *et al.* 2017; Fan *et al.* 2017).

Hotspot Five: Is a 'coldspot' with BC rich and nitrogen-poor air, coming from further west than the feature identified as the intersection of Cowcaddens Road and North Hanover Street, and likely because of Buchanan Bus Station (Figure 8.19 A). The bus station is a large transport hub which operates over 1,700 buses daily from midnight to midnight (SPT 2020). It was conjectured that much of the BC concentration was because of resuspended legacy contamination from 43 years of bus operation (opened in 1977), (SPT 2020).

While NO_X was also produced, it readily degrades in the environment, whereas there is always the potential for resuspension of legacy BC pollution. The number of years of operation during each European's emissions class was multiplied by 1700 (the contemporary buses which use the station), and by the speed-related function from the COPERT emissions model (NAEI 2020). This estimate found that as much as 4,500 tonnes of fine PM was released in diesel exhaust over the site's history (NAEI 2020). While the COPERT model also indicated that 4.55 grammes of PM and 574 grammes of NO_X should be emitted daily. It is conjectured that during high wind speed events (>12 m/sec), these NO_X emissions were overshadowed by resuspended BC particles from the bus station (NAEI 2020).

► 8.9.5). Townhead Summary.

To summarise, like at High Street, there were considerable temporal and spatial variations in the air pollution concentrations (BC, NO, NO_2, and NO_X), ratio concentrations and spatial sources at the Townhead Monitoring Station. Similarly, to High Street, the concentrations of air pollution are higher during rush hours (morning and afternoon); even when sited further away from major roads. Also, just like High Street, and much of the UK, air pollution is higher in the winter months than during the summer.

Figure 8.29. **A.** The Buchanan Bus station pictured from the western side along North Hannover Street **B.** Taken facing north, In the foreground is North Hannover Street, in the background is the junction between Dobbie's Loan and North Hanover Street. **C.** Figure taken north east, shows the corner of Baird Street looking towards the east and the road ramp over the M8 Motorway. With the Royal Mail Distribution centre being the building on the left, and the other distribution centre opposite on the right. **D.** Shows the Glasgow Townhead Monitoring Station set in the landscaped urban environment, part of the car park in the foreground and the Townhead Shops in the background. The Tandoori take away is the last of these buildings on the left. Figure taken toward the south east. **Source:** Grainger (2019).

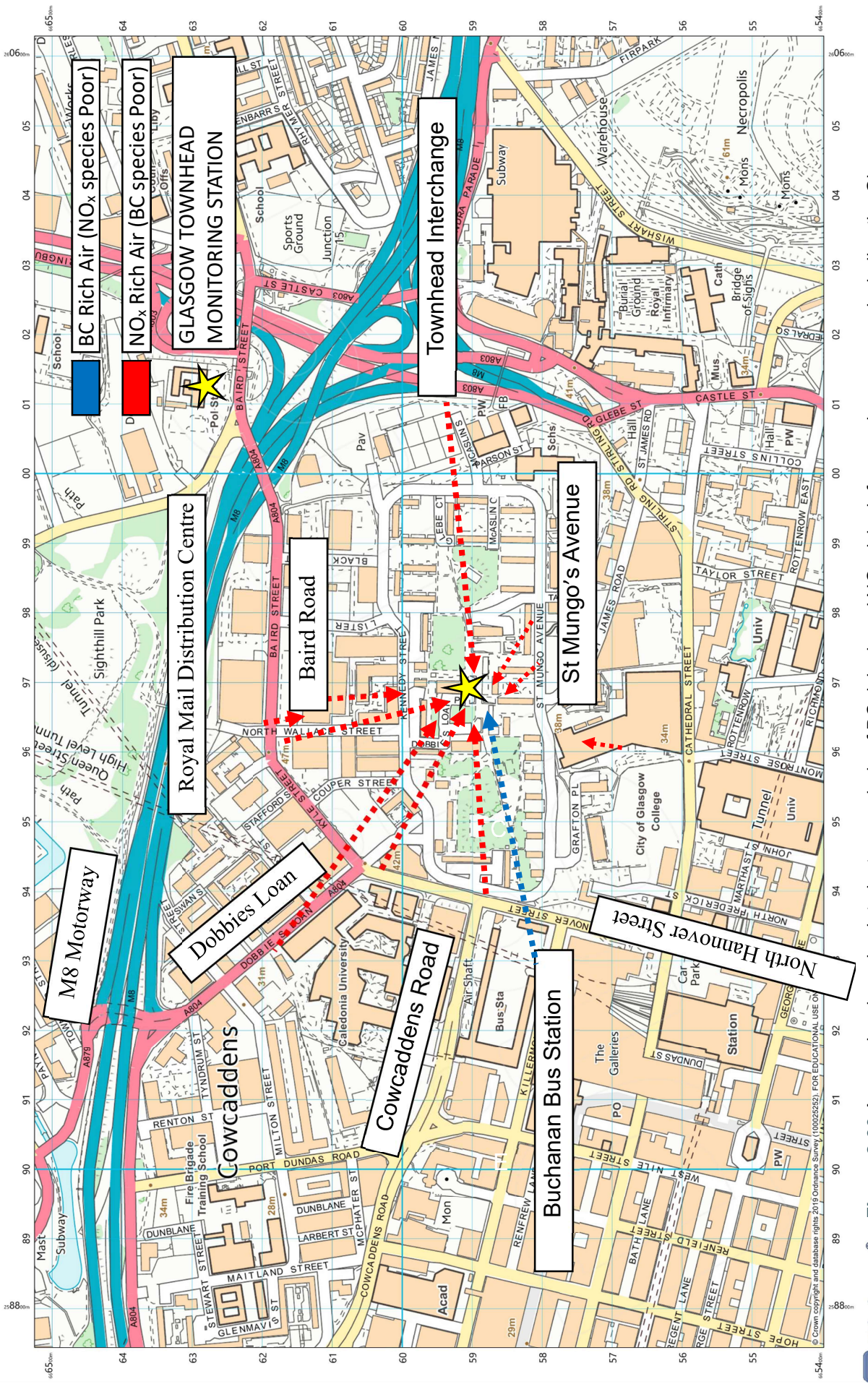


Figure 8.30 A map showing a back-trajectory analysis of BC rich air and NO_X rich air from various sources including the Glasgow Townhead Interchange, M8 Motorway, St Mungo's Avenue, Distribution Centres, Baird Road, Cowcaddens Road, Dobbie's Loan, Buchanan Bus Station and North Hanover Street. **Source:** Digimap and Ordinance Survey (2020) **(Adapted)**. *Contains Ordnance Survey data. © Crown copyright and database right 2010. Data provided by Digimap OpenStream, an EDINA, University of Edinburgh Service.*

Ratio plots were of limited use, but polar ratio plots revealed interesting spatial patterns, indicating key sources of air pollution mainly from vehicular emissions and major road junctions. Five features were noted on the ratio of polar plots; four of these had a high relative concentration of BC to NO_X. The sources were identified using back-trajectory analysis. These features included:

1. **Hotspot 1** was likely sourced from the impact of several major roads including North Hanover Street, Cowcaddens Road, and the A804 (i.e. Baird, and Kyle Streets) and their intersections. Potentially there was a minor contribution from industrial activity, and the motorway to the north of the Monitoring Station.

2. **Hotspot 2** was likely because of local pollution directly from the Tandoori Plus Restaurant, though car parking may have augmented this source. The proximity of the Monitoring Station and nocturnal hours likely repressed NO's ability to convert to NO_2, thus making the air relatively NO rich.

3. **Hotspot 3** was probably associated with car parking along St Mungo's Avenue and its busy 60 space cul-de-sac car parks.

4. **Hotspot 4** had a more complicated source with high NO_2 and NO_X ratios but low with a low NO ratio. This hotspot was resolved to the impact of the vehicles using the Townhead Interchange, the high degree of turbulent mixing, and rush hour traffic mostly occurring within sunlight hours, facilitating NO's conversion to NO_2.

5. **Coldspot 5** was a BC rich feature from the west of the lower part of Hotspot 1; the feature was probably because of Buchanan Bus Station. The BC rich character was likely a result of high wind speeds resuspending legacy BC deposits, overshadowing contemporary NO_X emissions.

► 8.10) Experiment II - Conclusions.

This paper suggests that the ratio pollutant concentrations between BC and Oxides of Nitrogen are highly useful for source identification studies. Conditional Probability Functions (CPF) also help to create a clearer understanding of the meteorological impact and underlying variability of the source. While Carslaw, in papers from 2006 to 2019, focuses on the ratio of PM to Oxides of Nitrogen, the BC plot is perhaps even more useful, as high BC environments are likely to show combustion-related emissions, both historically (resuspended hotspots) and from more soot-rich contemporary sources. In contrast, nitrogen-rich areas may show relatively recent combustion sources such as vehicular emissions.

New and previously undiscovered sources of air pollution were identified at the well-studied Glasgow High Street and Townhead Monitoring Stations. The sources of nitrogen supply at the High Street Monitoring Station involve the A8 High Street, road junctions, car parking facilities, and Wellpark Brewery (a previously unknown source of BC). The Townhead Monitoring Station had similar sources of nitrogen-rich air from nearby roads, including the A804, North Hanover Street, St Mungo Avenue, and importantly, the Townhead Interchange (J15 M8). Before this work, it was conjectured that the Townhead Interchange contributed air pollution to the Townhead AURN, but little evidence was ever presented. Also, concerningly, a local pollution source from the adjacent Tandoori restaurant seems to have a large impact on the NO concentrations at Townhead.

The methods used in this experiment could enhance source identification at air quality Monitoring Stations where BC and Nitrogen are provided. Such methods are likely to benefit air pollution analysis as characteristic shape profiles are produced, which can represent real-world linear features. Lastly, this analysis can help inform the analyst of the age, cleanliness, or industrial profile of the BC and Nitrogen-related pollution.

► 8.11) Field Methods Utility to UNG Monitoring.

Over the course of these field studies much has been discovered about the inner-city microenvironments found in Glasgow. However, the focus of this thesis is not on the environmental air quality of Glasgow but on UNG operations. It should not be forgotten that these are pilot methods which were envisaged to be used to understand and quantify deeper linkages within UNG operations. In Particular:

- **Experiment I -** focussed on the use of near source upwind-downwind air monitoring methods to evaluate air pollution microenvironments. These techniques can be used in a wide variety of settings to address pre and post emission air pollution trends. This experiment tested near source ICE emissions from vehicular traffic in particular bus emissions on narrow street canyons within the city of Glasgow. Future research may well find that this analysis could help inform the analyst of the age, cleanliness, or industrial profile of PM, BC and Nitrogen-related pollution over distance, in addition to helping to prove the emissions could not be found upwind. Its use on UNG sites however may be in the role of minor emissions in workplace air quality and industrial hygiene such as from large scale diesel generators and fugitive emissions i.e., dust escaping from aggregates. Sadly, due to access difficulties and the greater implications of COVID-19 field testing this method was not possible at the Preston New Road facility where it had been envisaged to be deployed and it shall remain up to other researchers to continue this research forward to industrial settings.

- **Experiment II -** focussed on the use of statistical computing methods to evaluate air pollution microenvironments. These techniques can be used in a wide variety of settings to address the temporal-spatial trends in voluminous air quality data containing meteorological and air pollution data. Dr David Carslaw developed the data analysis methods, with Dr Karl Ropkins on the R Studio integrated development environment. This

experiment tested the statistical computing methods called OpenAir at the Townhead and High Street within the city of Glasgow. This was to ensure that the program was sufficiently well equipped to evaluate the significance of the Preston New Road Unconventional Natural Gas Development's local air quality via a nearby monitoring station. It was found that as per Carslaw's work these methods are likely to benefit air pollution analysis as characteristic shape profiles are produced, which can represent real-world features. Future research may well find that this analysis could help inform the analyst of the age, cleanliness, or industrial profile of the BC and Nitrogen-related pollution. However, for this research it was found that the method was sufficiently well equipped to deal with complex micro-environments and consequently the next chapter adapts these methods to the Preston New Road UNG development site.

► 8.12) References.

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Figure 8.2. Grainger, S. (2020) '*Glasgow Hope Street'*, PDF map, Scale 1:500, OS MasterMap, June 2019, Ordnance Survey, using Digimap Ordnance Survey Collection, Available at:

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Figure 8.8. Grainger, S. (2020) '*Glasgow Hope Street 2'*, PDF map, Scale 1:500, OS VectorMap, June 2019, Ordnance Survey, using Digimap Ordnance Survey Collection, Available at: TinyURL.com/wp5x7y8, (Accessed: 17th July 2020).

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Figure 8.12; Grainger, S (2019) *A summary plot of the filtered dataset at Defra's High Street AURN Monitoring Station, using the Openair Toolset of R Studio.*

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Figure 8.14; Grainger, S (2019). *A photo was facing north from the Southside of the A8- High Street toward the High Street AURN Monitoring Station. Glasgow, Scotland.*

Figure 8.15; Grainger, S (2019). *A collage of four photos at various focal points around the High Street Monitoring Station. Glasgow, Scotland.*

Figure 8.16; Grainger, S (2019). *A map showing the local sources of air pollution around the High Street Monitoring Station, with the background map being a neighbourhood map of the area around*

Glasgow High Street. Modified After; Ordnance Survey and Provided by Edina Digimap. Southampton, England.

Figure 8.17; Grainger, S (2019). *Photograph of the Townhead Monitoring Station facing north.* Glasgow, Scotland.

Figure 8.18; Grainger, S (2019). *Photograph of the Townhead shops as seen in "Taggart".* Glasgow, Scotland.

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Figure 8.20; Grainger, S (2019). *A map showing the local sources of air pollution around Townhead.* Modified After; Ordnance Survey and Provided by Edina Digimap. Southampton, England.

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CHAPTER 9:

Source Apportionment Study of PM and NO_X at an UNG Development Site: Preston New Road.

"They look to the United States where fracking takes place
There have been... families [made] sick with air pollution...
we need not put our families at risk with this".

Naga Munchetty (1975 to Present)

Abstract: This study aimed to assess whether and to what extent the Preston New Road UNG Development site affected the particulate ($PM_{2.5}$ to PM_{10}) and nitrogen oxide gas (NO, NO_2, and NO_X) concentrations at the Little Plumpton monitoring station by analysing the concentrations of air quality on a wide range of spatiotemporal scales. The analysis was completed using RStudio's OpenAir statistical programming platform and package.

Nitrogen oxides: while there was an annual reduction in the levels of nitrogen throughout the year, there were significant effects from an anomaly to the west of the monitoring station conjectured to be the UNG facility. With an increase in the proportion of NO_2 provided by the western hotspot rising from 2% of emissions to 12% and 22% in 2017/2018. Peak levels of NO_2 were found in 2018 when as much as 20 $\mu g/m^3$ were provided to the site. The increases in nitrogen dioxide levels were, however, below the legislative and daily air quality standards.

Particulate Matter: Despite prevailing winds from the west (the direction of the UNG site) concentrations of $PM_{2.5}$ and PM_{10} did not increase between 2016 and 2018 in either hourly, monthly, seasonal, or annual terms. The predominant source of particulate at the monitoring station came from a dairy farm west of the monitoring station, which correlated well with temporal variations based on an understanding of dairy farmers' normal patterns of behaviour throughout the farming year. A diffuse source of PM was also observed which came from the Atlantic Ocean or from air pollution associated with Blackpool town centre.

► 9.0) Introduction.

One of the UK's most economically viable Unconventional Natural Gas (UNG) resources is found underneath Blackpool, Lancashire (OGA 2013). To bring UNG resources into production requires a range of non-traditional extraction methods (e.g. horizontal drilling and hydraulic fracture), (Kaden and Rose 2015). The development of UNG has led to improvements in American energy security, cost, and domestic supply, (Obadi and Gardoňová 2019). However, there are concerns that UNG development may release harmful concentrations of air pollution, including; Particulate Matter (PM) and oxides of nitrogen (NO_X) into the environment (Kaden and Rose 2015; HPS 2016; Ezani *et al.* 2018).

Both PM and NO_X are considered by the UK's Department of the Environment, Food and Rural Affairs (Defra) and the World Health Organisation (WHO) to pose significant risks to public and environmental health (UK AQEG 2004; WHO 2016; Defra 2019a). PM comprises airborne solid and liquid particles from natural or anthropogenic sources (UK AQEG 2012). Most PM research has focussed on PM_{10} (PM with an aerodynamic size of ≤10 μm) and $PM_{2.5}$ (PM with an aerodynamic size of ≤2.5 μm, (i.e. the alveolar PM fraction), (UK AQEG 2012). Nitrogen oxides, however, comprise three main subgroups, nitrogen monoxide (NO), nitrogen dioxide (NO_2) and oxides of nitrogen (NO + NO_2), (Defra 2018a). NO_X, unlike PM, are combustion-related gases driven primarily by anthropogenic sources, (UK AQEG 2004; COMEAP 2018).

There are growing concerns in the USA and Australia that emissions from UNG may cause local environmental health effects (Marlin-Tackie and Smith 2020). Most public health evidence is limited to the US and Australia, with very little research in the EU (HPS 2016; Brunt and Kibble 2018).

The mitigative impact of the EU's stricter environmental laws together with a lack of EU-level UNG research has created uncertainty regarding the community-level effects of UK UNG, (Gough *et al.* 2018). Such uncertainty

leads to anxiety in local communities, which has driven conservative UK policy decisions, with Scotland, Northern Ireland, and Wales precluding UNG development, citing public opinion and the inadequacy UNG health risk analysis, especially epidemiological evidence, (Wheelhouse 2017; Brunt and Kibble 2018; Gough *et al.* 2018).

To better understand the air pollution near UK UNG developments, the NERC funded an air quality and meteorological research monitoring station at Little Plumpton near to the Preston New Road (PNR) UNG development site (Cuadrilla Resources 2018). The monitoring station records data from February 2016 to December 2018, (Purvis 2018). The data was Open-Source and downloaded via 'The Natural Environment Research Council's Data Repository for Atmospheric Science and Earth Observation,' i.e. the CEDA archive (Archive.CEDA.ac.uk/). The purpose of this monitoring station was to make sure that community concentrations around the PNR development would not be detrimental to the wider community and that the concentrations of air quality conformed to ambient air quality regulatory standards (Purvis 2018).

This study performs a comprehensive analysis of the concentrations of PM and NO_X from 2016 to 2018, at the Little Plumpton monitoring station using techniques within RStudio's 'OpenAir Package'. OpenAir was introduced and used to significant effect by Carslaw in various air pollution environments (Carslaw and Ropkins 2012; Carslaw 2014, 2015a, b). Using the OpenAir statistical-computing techniques, it is possible to estimate the temporal and spatial impact of the PNR Development site at the Little Plumpton Monitoring Station. This work mostly intends to determine the significance of supply changes in the predominant air pollutions (PM or NO_X) to the site.

► 9.1) Literature Review.

♦ 9.1.1) Site Information and History.

In February 2013, Cuadrilla Bowland Ltd, a company specialising in "activities for petroleum and natural gas extraction" announced that it intended to drill for UNG at PNR, near Blackpool, Lancashire (Figure 9.1) (Cuadrilla Resources 2013, 2014, 2019). The development sits alongside the A583 - Preston New Road, from where the development takes its name, (Ordnance Survey 2019).

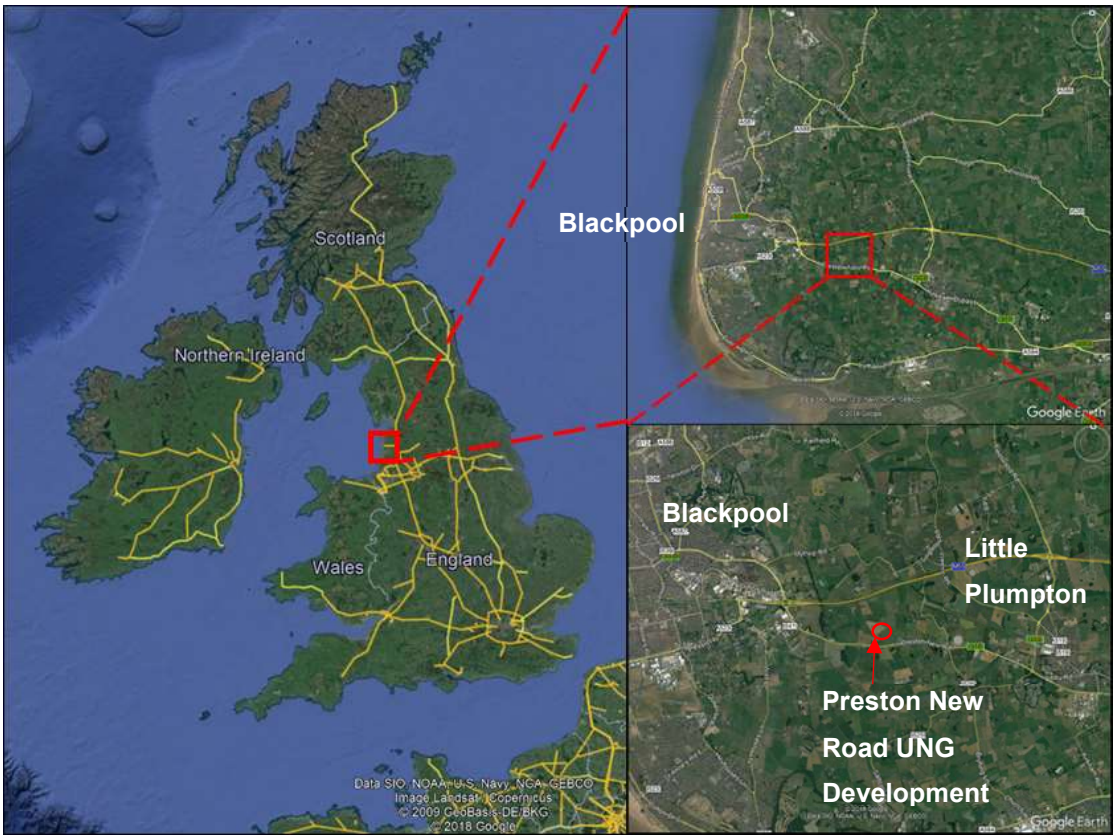

Figure 9.1. A map showing the position of A. Blackpool in the UK. B. The Fylde Peninsular, C. The location of The Preston New Road site, Blackpool and Little Plumpton in a blown-up map of the Fylde Peninsular.

Source: Map Data: SIO, NOAA, U.S. Navy, NGS, GEBCO, Google, (2020).

PNR is within the civil parish of Westby-with-Plumpton's and next to the town of Blackpool (Ordnance Survey 2019). The PNR development lies in the centre of the parish, at the western edge of the hamlet of Little Plumpton which is 8 km south east of Blackpool Tower. The Westby parish has a total population of 1,205 distributed over several small villages, including Little Plumpton (Swan 2011). Table 9.1, Figures 9.2 and 9.3 offer a description and illustration of the area around the PNR development site.

Table 9.1. A description of the site and the surrounding landscape at set distances.

Distance	Description
On-site	The site is in an area of improved grassland belonging to Plumpton Hall Farm, which supports dairy cattle. The land is low-lying with slopes rising to a height of 30 metres above sea level. The area enjoys environmental stewardship grants for farming and migrating birds. The A583 is located 50-100 metres to the south of the site.
Within 500 metres	The grassland continues and is joined by areas of deciduous woodland with a stream; the Carr Brook, to the north. Residential properties; Staining Wood Farm and a series of Cottages are located 450 metres to the west of the PNR site. Also immediately to the south, is the A583 Preston New Road which runs approximately east west.
Within 1000 metres	The rural parish of Westby on Plumpton's continues, with the village of Great Plumpton at the extreme north-eastern edge of this buffer. An important farm called Plumpton Hall Farm is located around 750 metres east of the development site. The farm is an active dairy farm operated by T H Wensley & Sons which also supports a modest plant hire business (Dave Hensley Plant Hire). The farm had expanded by 2018 to include extra over winter barns. Beyond the farm was the village of Little Plumpton which includes several small residential properties, a tractor sales business at Plumpton Lodge, a church, and a short-let holiday apartment. To the south-west, at around 725 metres is the woodland of the Staining Wood. To the west by around 1000 metres, is the town of Peel Hill, although only a light commercial garden centre building was included within the buffer zone. North-west at 1,000 metres distance is a house and caravan site at Moss House Farm. The A583 – Preston New Road continues along its east-west trajectory for the full 1000 metre radius.

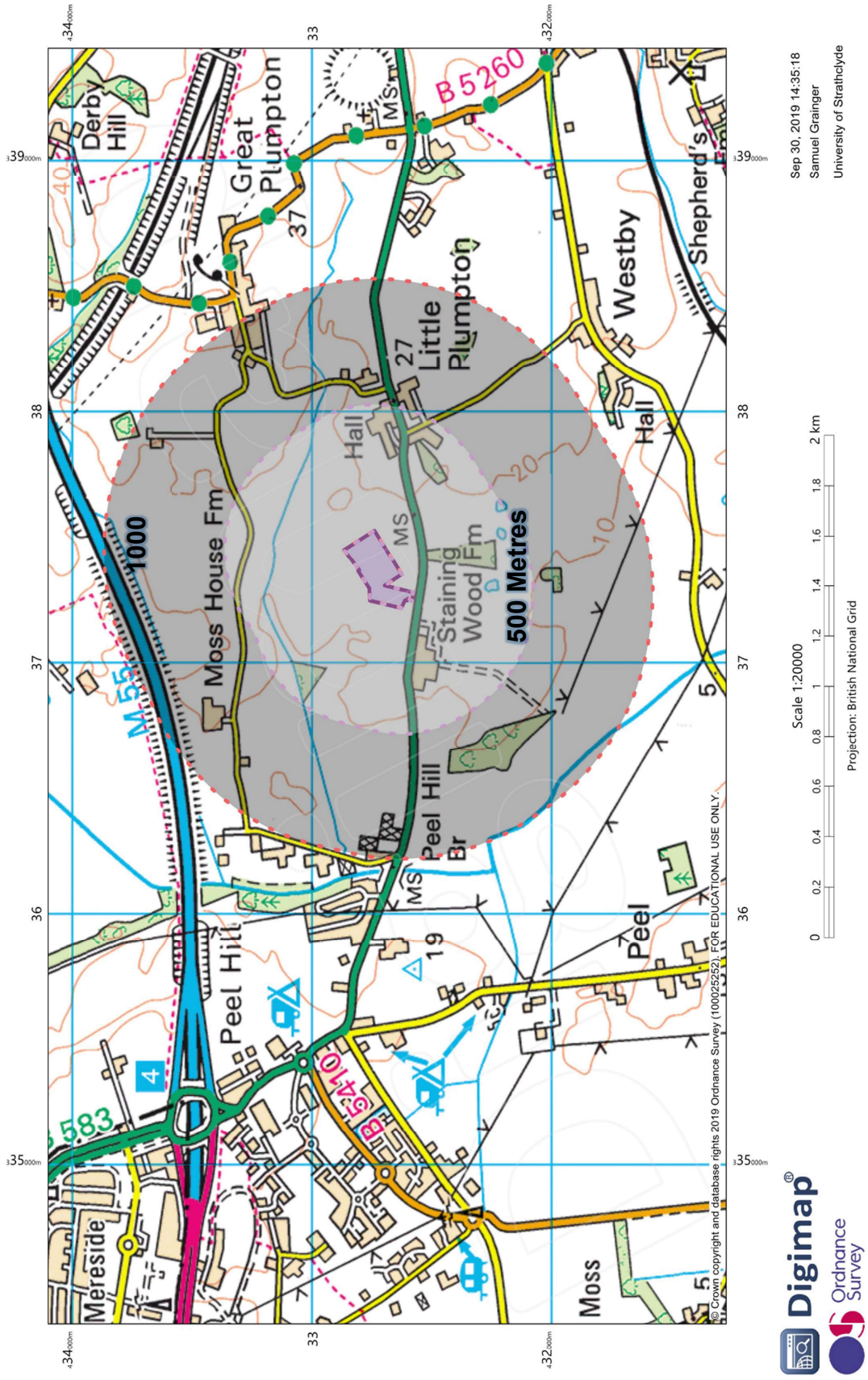

Figure 9.2. A map showing the area around the UNG development site at set buffer distances of 500 m and 1000 m.

Source: Digimap and Ordinance Survey **(Adapted).**

Contains Ordnance Survey data. © Crown copyright and database right 2010. Data provided by Digimap OpenStream, an EDINA, University of Edinburgh Service.

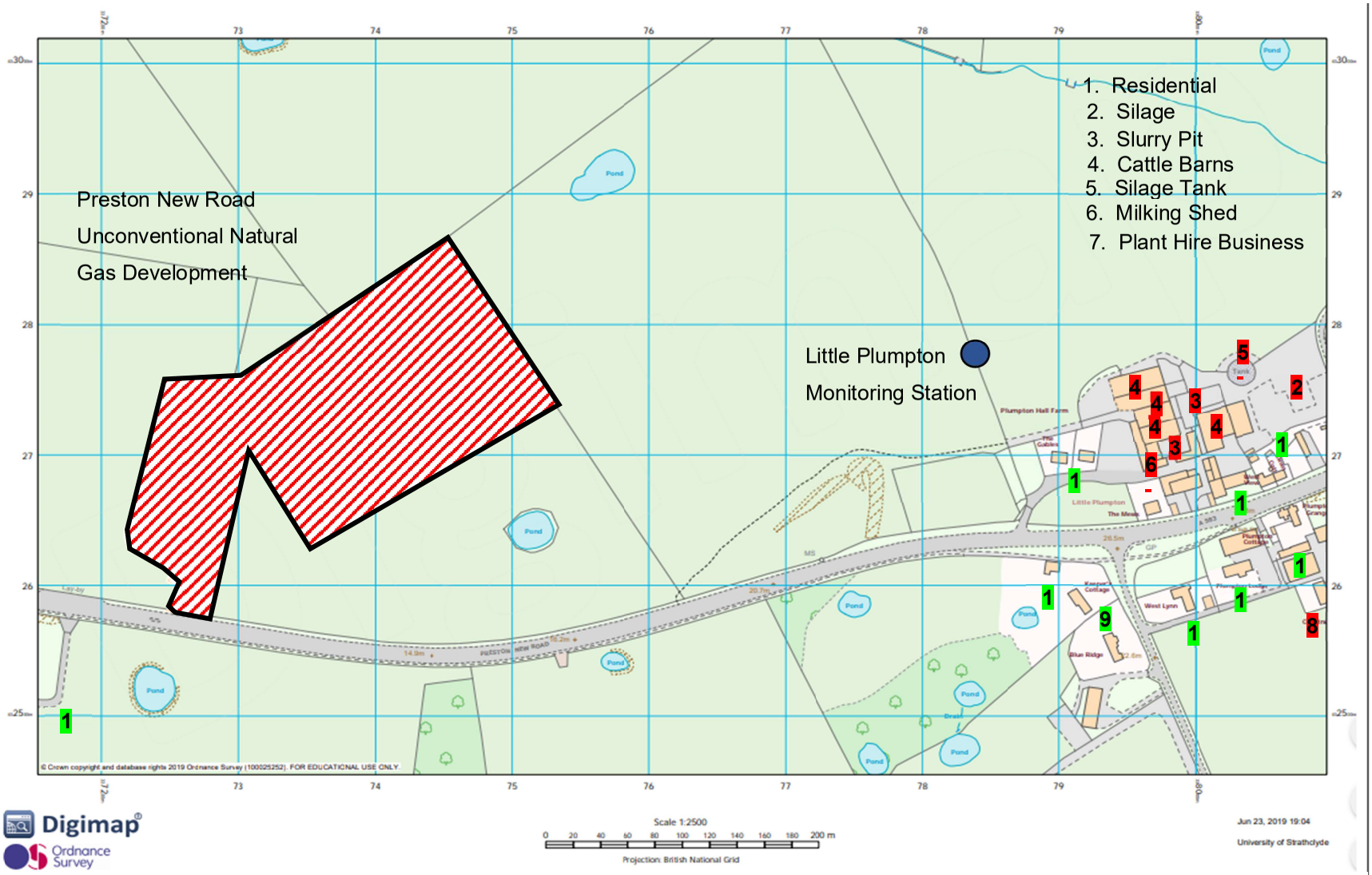

Figure 9.3. A map of the Preston New Road development site, village of Little Plumpton and the location of the monitoring station. Annotated are a series of key features. **Source:** Digimap and Ordinance Survey **(Adapted).**

Contains Ordnance Survey data. © Crown copyright and database right 2010. Data provided by Digimap OpenStream, an EDINA, University of Edinburgh Service.

♦ 9.1.2) Stages of the PNR UNG Development.

The PNR site was developed through three primary stages; construction, hydraulic fracturing and the production stage (Arup Group 2014; Kaden and Rose 2015). The timeline for these stages of the PNR development is provided below in Table 9.2.

Table 9.2. Stages of the Development of the PNR UNG development site.

Phases of Development	Duration in Months	Months involved
Background monitoring	11	February to December 2016
Construction	7	January to July 2017
Drilling	12	August 2017 to July 2018
Hydraulic Fracturing	15	July 2018 to September 2019

► 9.2) Air Quality Standards and Legislation.

♦ 9.2.1) Annual Air Quality Legislation.

There is a range of legislation and regulations which govern the acceptable levels of air quality in the UK, (Defra 2010; WHO 2016; HSE 2020). These concepts are covered in further depth in Chapter 3 of this thesis. However, for convenience, the relevant guideline values for UK ambient air quality have been reproduced in Table 9.3 and 13.4 overleaf.

Table 9.3. A table showing the UK ambient air guidelines for $PM_{2.5}$ and PM_{10} for all UK authorities and for Scotland.

Standard	Authority	Concentrations		Exceedance
		$PM_{2.5}$	PM_{10}	
Annual average concentration.	All UK authorities	25 µg/m^3	40 µg/m^3	35 Days per annum
	Scotland	10 µg/m^3	18 µg/m^3	7 Days per annum
24-Hour Daily Maximum Concentration.	All UK authorities	*	Up to 50 µg/m^3	Only permitted for 35 days or less.

Table 9.4. A table showing the UK ambient air guidelines for NO, NO_2 and NO_X for all UK authorities and for Scotland.

Standard	Guideline	Nitrogen Species	Conc. (mg/m^3)	Exceedance
Annual	All UK Authorities	NO_2	40	
	Ecological Protection	NO_X	30	
1 Hour Mean	All UK Authorities	NO_2	200	18 Times a Year

♦ 9.2.2) Daily Air Quality Index (DAQI) Legislation

In the UK, the COMEAP (Committee on Medical Effects of Air Pollutants) have created a ten-point index called the DAQI or Daily Air Quality Index. The DAQI is used to communicate the level of harm to the public from air pollution and is divided into four bands; Low', 'Moderate', 'High' and 'Very High', mimicking the Sun and Pollen indexes (COMEAP 2011; Defra 2018b).

While the COMEAP has modelled six air pollutants, only the concentrations of PM ($PM_{2.5}$ and PM_{10}) and Nitrogen Dioxide (NO_2) are of relevance to this work. The COMEAP's DAQI is outlined in further detail in Chapter 3 of this thesis; however, this is reproduced in Table 9.5 for convenience.

Table 9.5. COMEAP definitions of the air pollution exposures, from their review of the DAQI in 2011 (COMEAP 2011). *Reproduced from Table 3.4–Chapter 3.*

Exposure Band	Description
Low	Acute exposures at this concentration are unlikely to affect anyone. Including, people who are especially susceptible to the effects of air pollution, e.g. people with underlying cardiovascular or respiratory conditions.
Moderate	Acute exposure is likely to bring "Small Effects" on people who are already susceptible to poor air quality.
High	Acute exposure is likely to bring "Significant Effects" on people who are already susceptible to poor air quality.
Very High	Acute exposure is likely to affect even healthy individuals adversely.

Table 9.6. Recommended Actions and Health Advice, reproduced from the COMEAP. *Reproduced from Table 3.5–Chapter 3.* © Crown 2020 copyright Defra via uk-air.defra.gov.uk, licenced under the Open Government Licence (OGL).

DAQI Index	Air Pollution Rating	$PM_{2.5}$ (µg/m³)	PM_{10} (µg/m³)	Nitrogen Dioxide (µg/m³)
1		0 – 11	0 – 16	0 – 67
2	**LOW**	12 - 23	17 – 33	68 – 134
3		24 - 35	34 – 50	135 – 200
4		36 - 41	51 – 58	201 – 267
5	**MODERATE**	42 - 47	59 – 66	268 – 334
6		48 - 53	67 – 75	335 – 400
7		54 - 58	76 – 83	401 – 467
8	**HIGH**	59 - 64	84 – 91	468 – 534
9		65 - 70	92 – 100	535 – 600
10	**VERY HIGH**	71 or more	101 or more	> 601

► 9.3) Methods.

♦ 9.3.1) Air Quality Monitoring Station.

The Little Plumpton monitoring station undertook "Science-based environmental baseline [and project-wide] monitoring associated with shale gas development… in Lancashire" (Purvis 2018). The monitoring station is located due east of the PNR UNG site. The station is within arable farmland a short distance from Plumpton Hall Farm (Dairy Cattle Farm) operated by T H Wensley & Sons, (Purvis 2018). The station was installed independently of, and alongside, monitoring carried out by the regulatory authorities and by Cuadrilla's environmental consultants, (Purvis 2018, 2019).

The background year (2016) monitors the pre-existing concentrations of air pollution, including diffuse regional sources such as urban pollution from Blackpool and the Atlantic coast (Purvis 2018). The data was available on an Open Source licence through the 'The CEDA Archive' Data Repository for Natural Environment Research Council's Atmospheric Science and Earth Observation data, within the sub-folders:

- *"Environmental Baseline Project: Surface meteorological measurements from Kirby Misperton and Little Plumpton"* (Purvis 2018, 2019). The data hosts measurements of wind speed, wind direction, pressure, temperature, and humidity (Purvis 2019).

- *"Environmental Baseline Project: Air quality, greenhouse gas, Volatile Organic Compounds (VOCs)",* (Purvis 2018, 2019). The data hosts real-time (minute resolved) measurements of NO, NO_2, NO_X, $PM_{2.5}$, PM_{10} amongst several other air pollutants.

This data can be found on the following link:
Data.CEDA.ac.uk/BADC/Env Baseline/data/LittlePlumpton.

There is a stipulation within the CEDA Archive which states that the following authorship information must be displayed when using the Open Source data;

> *" These data were produced by the Universities of Manchester and York (National Centre for Atmospheric Science) in collaboration with the British Geological Survey and partners from the Universities of Birmingham, Bristol, and Liverpool and Public Health England, undertaking a project grant-funded by the Department for Energy & Climate Change (DECC), 2015-2016".*

A photograph of the monitoring station is reproduced in Figure 9.4 from the British Geological Survey (BGS), as the station was housed on private land (belonging to Plumpton Hall Farm) with restricted public access.

Figure 9.4: The figure shows the Little Plumpton Monitoring Station a short distance from Plumpton Hall Farm, facing due east toward the intended location of the Preston New Road UNG site prior to its construction in 2016. The wooden fence was erected to prevent cattle from interfering with the equipment. The smaller box contains the greenhouse gas monitoring equipment. The larger box however contains both the meteorological device (WS600-UMB Smart Weather Sensor) and the air quality monitoring devices including the Palas FIDAS 200. **Source:** BGS (2016).

♦ 9.3.2) PM Monitoring Equipment.

This report analyses $PM_{2.5}$ and PM_{10}, though other PM species monitored at the Little Plumpton site included: PM_1, PM_4, and TSP (total PM). The other PM species were discounted from this investigation because of the screening parameters in Chapter 1 of this thesis (Purvis 2018).

The PM monitoring device at Little Plumpton was a Palas Fidas 200 particle counter (aerosol spectrometer) which uses a high intensity LED light source (dp_{min} = 180 nm) to take PM concentration measurements (Palas GmbH 2012, 2013; Purvis 2016). The Fidas has a real-time (1 second) resolution with a default flow rate of 4.8 l/min, (Palas GmbH 2012, 2013; Purvis 2016).

The device was equipped with a Sigma-2 sampling head which allowed for PM measurement even in powerful winds (Palas GmbH 2012, 2013; Purvis 2016). Once the particulate was inside the Fidas, a drying system: IADS (Intelligent Aerosol Drying System) helped to prevent measurement inaccuracies by reducing condensation at high humidity (Palas GmbH 2013). The instrument was biannually field calibrated with a monodisperse test powder (CalDust), (Palas GmbH 2013; Ward *et al.* 2018). Overall, the Fidas 200 provides accountably accurate results, which fully complies with MCERTS, and UK DEFRA PM climate specifications, (Palas GmbH 2012, 2013; Purvis 2016).

♦ 9.3.3) Nitrogen Gas Monitoring Equipment.

This report also analyses Nitrogen Monoxide (NO), Nitrogen Dioxide (NO_2) and Oxides of Nitrogen (NO_X). The nitrogen monitoring device is a Teledyne API T200U Trace-Level chemiluminescence analyser coupled with a T200P high-efficiency photolytic converter (Purvis 2016; Teledyne API 2017, 2018). The photolytic converter houses a Blue LED light which provides the activation energy for NO_2 to be converted into NO with negligible interference from other gases (Purvis 2016; Bautista 2018).

The gas is directed from the photolytic converter into the reaction cell where NO reacts with Ozone (O_3) to form NO_2, emitting infrared energy, which is measured by an in-built photosensitive sensor (Teledyne API 2018). The newly generated NO_2 reacts with a heated molybdenum chip (315°C) converting back to NO. The re-converted NO is recirculated through the instrument's reaction cell when the NO_2 concentration is then taken as the difference between the NO and NO_X concentration (Teledyne API 2018). This innovative sampling method allows the T200 to have a default sampling resolution of 20 seconds with a flow rate of 1 l/min or 0.06 m^3/hour (Teledyne API 2018).

Field calibration is performed on the instrument annually via calibration cylinders from the National Physical Laboratory, along with monthly checks of the analyser accuracy and precision converter efficiency. The dataset is self-corrected by the T200 performing an auto-zero and QA/QC procedure through a computer program 'NumaView', (Teledyne API 2018). The results are reported in Parts Per Billion (PPB) on the CEDA archive; however they are converted in this paper to micrograms per cubic metre (µg/m^3), using a conversion ratio of 1.9125 µg/m^3 (DEFRA and Ricardo-AEA 2014).

The T200 is an automated reference method and fully complies with the MCERTS, EN 13211 and EN 15267 regulations, making it a scientifically robust monitor for this assessment (Purvis 2016; Teledyne API 2017, 2018).

♦ 9.3.4) Meteorological Equipment.

A Lufft: WS600-UMB Smart Weather Sensor provided the meteorological information at the Little Plumpton Monitoring Station (Purvis 2016; Lufft 2019). The WS600 allows for the simultaneous measurement of temperature, relative humidity, air pressure, wind (direction and speed), and precipitation (intensity, quantity, and type) at a 1-minute resolution. (Lufft 2019).

The WS00 is periodically calibrated by the University of York, though the sensor is advertised as a maintenance-free device (Purvis 2016, 2018; Lufft 2019). The sub-modules of the weather station are shown in Table 9.5. Many of the wind speeds have been converted empirically to the Beaufort Scale, i.e. breezes and gusts for ease of reading (Met Office 2018).

Table 9.7. A table showing the method of analysis for various meteorological items recorded by the Little Plumpton Site and its accuracy and range.

Meteorological Information	Measurement Method	Monitoring Range	Accuracy
Temperature	Negative Temperature Coefficient (NTC) Thermistor	50 to 60 °C	±0.2 °C (20 to 50 °C), or ±0.5 °C (> 30 °C)
Relative Humidity	Capacitive Humidity Sensor	0 to 100% RH	±2% RH
Air Pressure	Microelectromechanical systems (MEMS) Capacitive Accelerometer	300 to 1200 hPa	±0.5 hPa (0 to 40 °C)
Wind Direction	Ultrasonic Wind Sensor	0 to 359.9 °	< 3 ° (RMSE) > 1.0 m/s * Root Mean Square Error
Wind Type		0 to 75 m/s	±0.3 m/s or ±3% (0 to 35 m/s) ±5% (>35 m/s) RMS * Root Mean Square Error
Precipitation Intensity	24 GHz Doppler radar	0.9 to 15.5 m/s	20% under laboratory conditions
Quantity		0.5 to 30 mm/h	
Type		Rain/Snow	

♦ 9.3.5) Data Validation and Filtering.

Statistical analysis was required to make sure that the raw CEDA dataset was scientifically robust. A data screening method was used to improve the accuracy of the raw data files.

In-built into the CEDA data files were columns which displayed whether there were adverse data attributes, i.e. 'Flags', as shown in Table 9.6 (Purvis 2018, 2019). For this filtering process, it was decided that only records which returned good data for the air quality (flag '1' and flag '2') and meteorological data (flag '0') entries were kept for the analysis, any deviations were screened out of the analysis as is good practice. This screening method led to the deletion of all bad data entries, reducing data bias from errors or bad data (Meyers *et al.* 2016).

Only 1.1 million data entries were valid out of the possible 1.6 million entries (Table 9.7). The year 2016 had significant data losses, which resulted in data retention of under 75%. Many of the errors were due to lengthy periods of deviation from the calibration, high-zero value or data not being recorded. Despite this, the remaining readings should accurately represent site conditions.

Table 9.8: Data Flags and their meanings in the CEDA deposited data.

Data Description	Data Description Flag	
	Air Quality File	Meteorological File
Retained Data:	1 Good data	0 Good data
Deleted Data Entries	2 Reduced quality data. 3 Missing Data / Calibration / Zero 4 Bad Data	1 Local influence 2 Out of detection limit 3 Calibration/zero 4 Bad/missing data

Table 9.9. Showing the number of missing and deleted data entries and the coverage of the year as a percentage of the total minutes in the year.

Year	Number of Missing or Deleted Data Entries	Coverage of the Year
2016	264,477 / 525,600	50.32%
2017	422,263 / 525,600	80.34%
2018	422,424 / 525,600	80.37%
Total	1,109,164/1,576,800	70.34%

The PM_{10} data was not subjected to the King's College London (KCL) Volatile Correction Model (VCM). The VCM would have helped to correct volatility losses from the TEOM, but as there was no validated correction factor for $PM_{2.5}$ the VCM was not used as this would have biased the ratio of $PM_{2.5}$ to PM_{10} (Green *et al.* 2008).

♦ 9.3.6) R Statistical Programming and OpenAir.

This research uses the RStudio package 'OpenAir' to analyse spatial and temporal contributions of PM and NO_X at the Little Plumpton Monitoring Station (Carslaw *et al.* 2013; Carslaw 2014, 2015a, b). RStudio is a computer interface which relies on the programming language 'R', combined they provide a freeware environment with a graphic display for statistical analysis (R Core Team 2019).

Packages in RStudio (like OpenAir), perform pre-set calculations based on the user's data and chosen attributes, without having to code the command "from scratch", similarly to a Macro in Excel (Carslaw and Ropkins 2012; Ropkins and Carslaw 2012). OpenAir was developed by the NERC and DEFRA, to create an "open-source tool[s] for the analysis of air pollution",(Carslaw and Ropkins 2012). Further information, including a manual, can be found on the project's main website at; 'https://davidcarslaw.github.io/OpenAir/'.

However, the main analyses were;50

● **Bivariate Polar Plots.** Which subdivides the air pollution data into a series of hexagonal coordinates based on the prominent meteorological conditions (wind speed and direction), (Carslaw *et al.* 2006, 2013; Carslaw and Ropkins 2012; Grange *et al.* 2016). The average data in each of these bins are plotted, and a colour gradient is used to illustrate the concentration of the air pollutant (or ratio) (Carslaw and Ropkins 2012).

● **Conditional Probability Function (CPF) Polar Plots**. The CPF polar plots use the same method as bivariate polar plots, but use CPF statistical analysis rather than pollutant concentrations, (Lewis 1976; Carslaw 2014). CPF analysis tests the probability of an event occurring if other conditions are met; here, the probability of high air pollution (or ratio) under certain meteorological conditions (Lewis 1976; Carslaw 2014).

The equation for CPF (as reproduced from Figure 9.1) can be given as:

Equation 8.2. ***(Reproduced here for convenience)***

$$P(B|A) = \frac{P(A + B)}{P(A)}$$

When,

P is the probability (e.g. High Concentrations),

A and B are certain events (i.e. Wind Direction and Wind Speed),

► 9.4) Results.

♦ 9.4.1) Meteorological Information.

Figures 9.5 and 13.6 display the meteorological conditions at the Little Plumpton station from the 1st February 2016 to the 31st December 2018.

Westerly winds were the most dominant wind direction (~35%), which is consistent with UK-wide air currents (Ward *et al.* 2018). This wind direction also provided the strongest wind speeds, with gales of up to 22 metres per second (mps), this was likely due to storms following the mid-Atlantic storm track, though milder wind speeds below 6 mps were more common (Ward *et al.* 2018). This author does not agree with Ward *et al.* 2018 who suggests that only *"well-mixed and background air masses"* is sourced from this direction as air must first pass through the town of Blackpool, a tourist destination with a resident population of 139,300 and could be a significant local source of air pollution (Swan 2011; Ward *et al.* 2018). *However,* this dominant wind direction benefits the Little Plumpton Monitoring station in the identification of changes from the PNR site, as this is only located 300 metres to the west of the monitoring station (Ward *et al.* 2018).

Winds from the East and South-East were also relatively frequent (~28% over the entire monitoring period), the winds speeds were mild with a light to gentle breeze (0-4 mps). This wind direction would have spent "significant time in dynamic contact with the surface of the UK mainland and may also represent air that has passed over Western Europe" (Ward *et al.* 2018). Hence, there are likely to be greater air pollution influences from the UK and European emissions such as from the Town of Preston (25 km to the South-East), Manchester (70km South-East), Leeds (120 KM South-East), London (330km South-East) and the European Continent during regional pollution episodes (Over 450 km South-East). Such distant pollution sources could be problematic to resolve (Ward *et al.* 2018*).*

Though, wind sources from due east are easier to resolve as although Preston (25 km SSE), the Bradford-Leeds metropolitan area (100km East) and Hull (175 km East) are situated to the east, the North Atlantic is only 200km east with Denmark and Northern Germany which rarely produce significant regional air pollution episodes (Defra 2018, 2019).

Temporally, the average wind speed in 2016 was 4.2 mps during the winter, which reduced to 3.4 mps in the spring. Wind speeds increased in 2017 with average wind speeds around 4 mps and remained similar in 2018. The strongest wind speeds appear to be generated with passaging mid-latitude cyclones over the UK mainland. The temperature at the Little Plumpton Monitoring station was cyclical, with the summer months (northern hemisphere) having the highest temperature measurements with an inverse relationship against relative humidity. The pressure lagged in temperature, suggesting that the relationship was partially due to the progress of the normal passage of mid-latitude weather fronts.

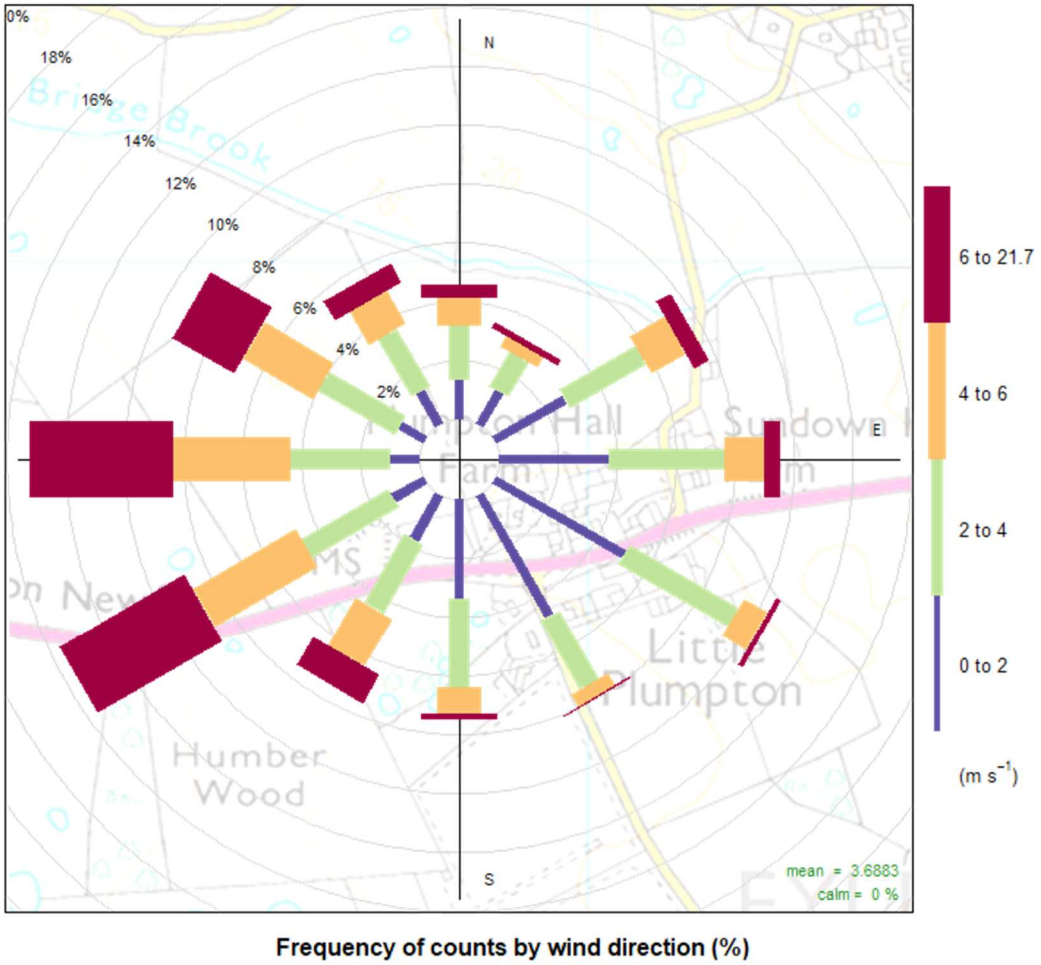

Figure 9.5. A plot is showing the frequency counts of wind direction and wind speeds. **Source:** Grainger (2019) **Source:** Digimap and Ordinance Survey **(Adapted).**

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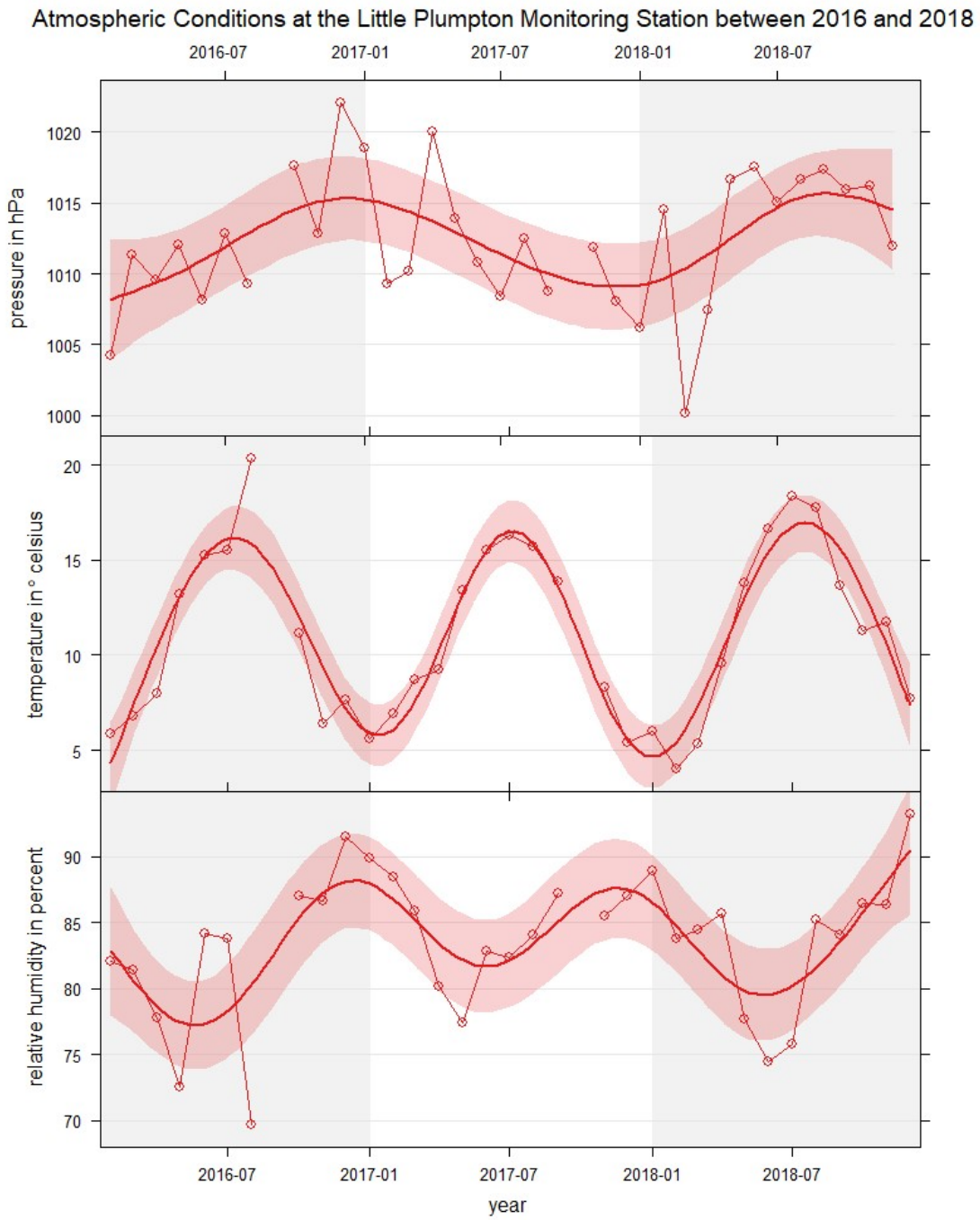


Figure 9.6. A figure was showing the temporal variation in temperature in degrees Celsius, pressure in hPa and% Humidity throughout the monitoring period from January 2016 to December 2018. Humidity and temperature have an inverse relationship. The pressure is more stable, though it is dissimilar to either the humidity or temperature trends. **Source:** Grainger (2019)

♦ 9.4.2) Particulate Matter.

A. Annual Concentrations of Particulate Matter

Figure 9.7 shows the mean $PM_{2.5}$ and PM_{10} concentrations for the Little Plumpton monitoring station. These averages were calculated based on calendar month averages (negating any data losses). The concentrations of $PM_{2.5}$ and PM_{10} reduced from 2016 to 2018, with a reduction of around 5.3% for 2017 and 21% for 2018. A smaller reduction was observed between 2017 and 2018 for PM_{10}, with a reduction of 5.3% for 2017 and a much larger reduction of 38.4% for 2018.

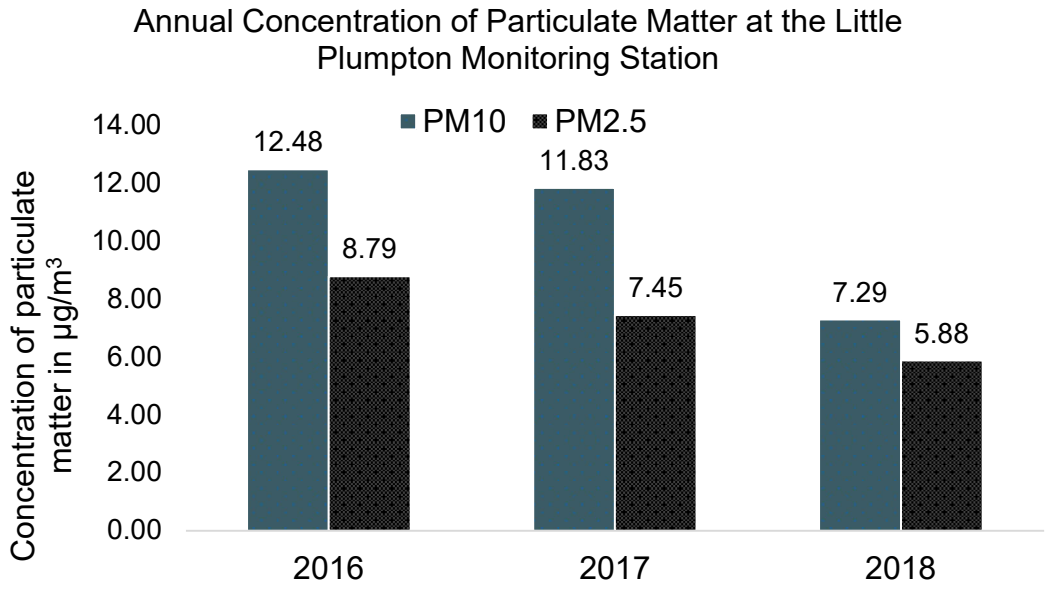


Figure 9.7. A bar graph showing the concentration of PM_{10} and $PM_{2.5}$, during the monitoring years 2016, 2017 and 2018. The graph shows that the concentration of PM fell from 2016 to 2018 at the Little Plumpton Monitoring Station. **Source:** Grainger (2019)

B. Monthly Concentrations of Particulate Matter.

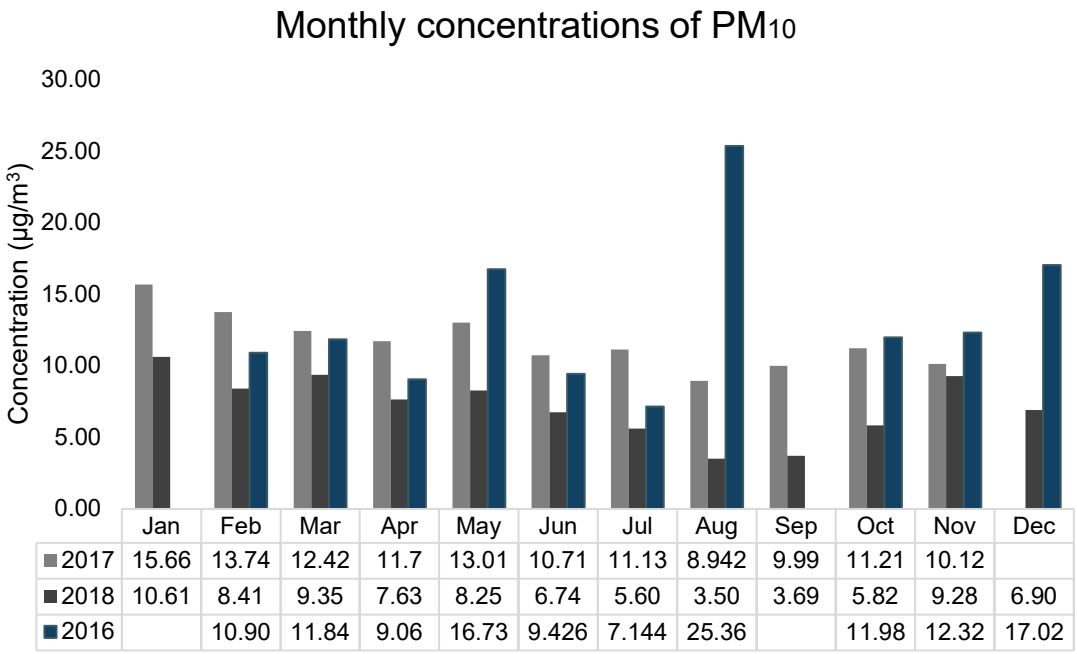
I. Results.

The mean monthly $PM_{2.5}$ and PM_{10} concentrations were calculated based on the calendar month averages (from midnight to midnight). All three years have similarities with a general decline in concentrations of PM through to the winter months (November onwards) and a minor increase in May. The concentrations were consistent with a variance of around 5 µg/m^3 averaged over the year. PM concentrations were higher in the background year than either 2016 or 2017. In terms of ratios, $PM_{2.5}$ accounted for 68% ±17%, of PM_{10}, though this reached heights of 95% during January and February 2018.

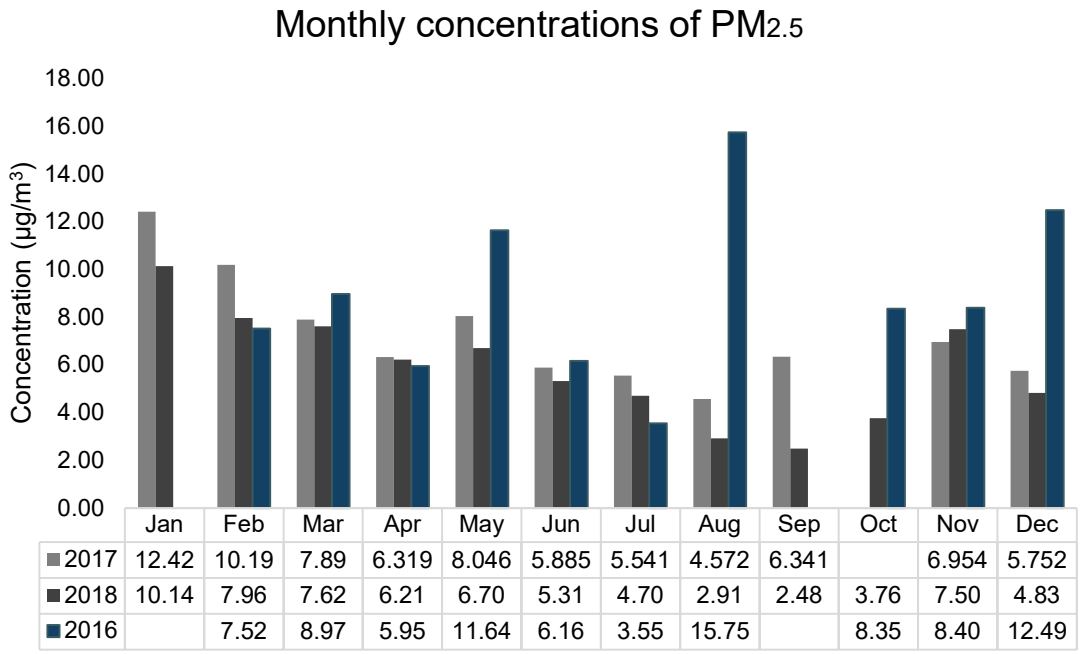
II. Discussion.

Like the general trend of $PM_{2.5}$ and PM_{10} over the year, the highest concentration of anthropogenic air pollution occurs over the winter and spring months (Defra 2020a). This trend is explained as householders using domestic heating and cooking sources such as LPG, wood, and coal to heat homes during the winter months, where more time is spent indoors (Defra 2019c, 2020).

Air pollution is low in May and remains low to the colder months of any one year (Defra 2020a). So, the peak in air pollution in May each year is likely to differ from national concentrations of PM. This trend might suggest that local sources of air pollution may have a significant impact on local sources of air pollution during May. Though the pollution episodes from European air pollution sources from south-easterly winds might have caused an increase in air pollution at the monitoring station (Defra 2017). The elevated PM concentration in August 2016 appears to be unique to this monitoring station, and there is no simple explanation for the rise in air quality during this month as no air pollution event was recorded (Defra, 2017, 2020).



	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2017	15.66	13.74	12.42	11.7	13.01	10.71	11.13	8.942	9.99	11.21	10.12	
2018	10.61	8.41	9.35	7.63	8.25	6.74	5.60	3.50	3.69	5.82	9.28	6.90
2016		10.90	11.84	9.06	16.73	9.426	7.144	25.36		11.98	12.32	17.02



	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2017	12.42	10.19	7.89	6.319	8.046	5.885	5.541	4.572	6.341		6.954	5.752
2018	10.14	7.96	7.62	6.21	6.70	5.31	4.70	2.91	2.48	3.76	7.50	4.83
2016		7.52	8.97	5.95	11.64	6.16	3.55	15.75		8.35	8.40	12.49

Figure 9.8. a b. Shows the calendar month midnight-midnight average concentrations of $PM_{2.5}$ and PM_{10} from the Little Plumpton Monitoring Station near Blackpool, Lancashire. **Source:** Grainger (2019)

C. Daily Concentrations of Particulate Matter.

I. Monitoring Year – 2016: Results.

During 2016 the average concentration of PM_{10} was 12.48 ±9.47 μg/m^3 with a maximum daily concentration of 40.69 μg/m^3 PM_{10}. Hence, there were no days in 2016 which were above the 50 μg/m^3 UK allowance for PM_{10}. If the stricter Scottish guidelines were enforced, then 39 days would have breached the guidelines. Annually, the $PM_{2.5}$ concentration was 8.79 ±8.27 μg/m^3 with a maximum daily concentration of 36.98 μg/m^3 $PM_{2.5}$. As the guideline for $PM_{2.5}$ was half of that allowed for PM_{10}, four days were in breach of the 25 μg/m^3 guideline. These days were the; 12th and 13th March, 31st October, and 6th December. If the stricter Scottish guidelines were enforced, then 58 days would have breached the guidelines.

II. Monitoring Year – 2016: Discussion.

Included within the monitoring period year of 2016 there were a series of pollution episodes. These were the;

- "Mid-March" episode, which resulted from breezy south-easterly winds bringing air from the industrialised parts of northern Europe (Germany and the Netherlands) and causing high PM concentrations nationally (Defra 2017).
- "Early May 2016" episode, from similarly sourced air (Defra 2017).
- "Bonfire Night Particulate Pollution Event", associated with firework festivals and bonfires nationally and lasted from the 29th October to the 9th November (Defra 2017).
- "Late November and December", this episode was due to meteorological conditions (light winds, fog, low temperatures) allowing local pollutant emissions to build up. These local emissions were combined with south-easterly winds on the 5th and 6th December, bringing industrial European (French) emissions to the UK (Defra 2017).

III. Monitoring Year – 2017: Results.

During 2017 the average concentration of PM_{10} was 11.83 ±9.68 µg/m^3 with a maximum daily concentration of 56.10 µg/m^3 PM_{10}. This resulted in two days above the 50 µg/m^3 guideline; these were 13th February and the 6th November. However, the 22nd to the 23rd of January and the 13th of February were above the 40 µg/m^3 standard for PM_{10}. Should the stricter Scottish guidelines be enforced, 35 days would have breached the guidelines.

Annually, the $PM_{2.5}$ concentration was 7.45 ±8.63 µg/m^3 with a maximum daily concentration of 50.75 µg/m^3 $PM_{2.5}$. As the guideline for $PM_{2.5}$ was half of that allowed for PM_{10}, eight days were in breach of the 25 µg/m^3 guideline. These days included the aforementioned dates plus the 25th and 26th January and the 28th March. Though if the stricter Scottish guidelines were enforced, then 53 days would have breached the guidelines.

IV. Monitoring Year – 2017: Discussion.

Included within the monitoring period were a series of pollution episodes. Several pollution episodes can be identified in 2016; these were the;

- "Particulate Pollution Episode (21st–28th January)" caused by "*a spell of* cold *frosty weather"* allowing local PM sources to accumulate (Defra 2018).
- "Particulate Pollution Episode (12th–15th February)" caused by mild and dry air with low wind speeds allowing air pollution to accumulate (Defra 2018). The air may have originally been sourced from industrial emissions over central and eastern Europe.
- St. Valentine's Day fireworks may have been a local source of PM emissions locally (Defra 2018; Singh and Srivastava 2019).

- "Bonfire Night Particulate Pollution Episode 5th–6th November 2017", this final episode was due to fireworks and bonfires across the country combined with calm weather, but bracketed by showery weather reducing the annual air pollution episode (Pope *et al.* 2016, Singh *et al.* 2019, Defra 2018c, 2019b).

V. Monitoring Year – 2018: Results.

During 2018 the average concentration of PM_{10} was 7.29±7.00 µg/m^3 with a maximum daily concentration of 40.42 µg/m_3 PM_{10}. These low PM_{10} values led to no days above the 50 µg/m^3 guideline; and only one day (the 3rd March breaching the 40 µg/m^3 standard for PM_{10}. Even with the Scottish guidelines, only six days would breach the 25 µg/m^3 standard for $PM_{2.5}$.

Annually, the $PM_{2.5}$ concentration was 5.88 ±6.77 µg/m^3 with a maximum daily concentration of 36.71 µg/m^3 $PM_{2.5}$. As the guideline for $PM_{2.5}$ was half of that allowed for PM_{10}, eight days were in breach of the 25 µg/m^3 guideline. These days included the aforementioned dates plus the 6th November.

VI. Monitoring Year – 2018: Discussion.

Included within the monitoring period were a series of pollution episodes. The pollution episodes which can be identified in 2018, these were the;

- "Beast from the East (26th February–28th January)" PM concentrations increased especially over the weekend of the 3rd - 4th March in the cold still air from the 2018 "Beast from the East" event.
- "Bonfire Night Particulate Pollution Episode (5th–6th November)" again led to firework and bonfire PM sources which were noted at the monitoring station.
- No significant increases were noted from the North-west England Moorland Wildfires, 60 km to the east of the monitoring station, of whose fires burned from the 24th June to the 18th July.

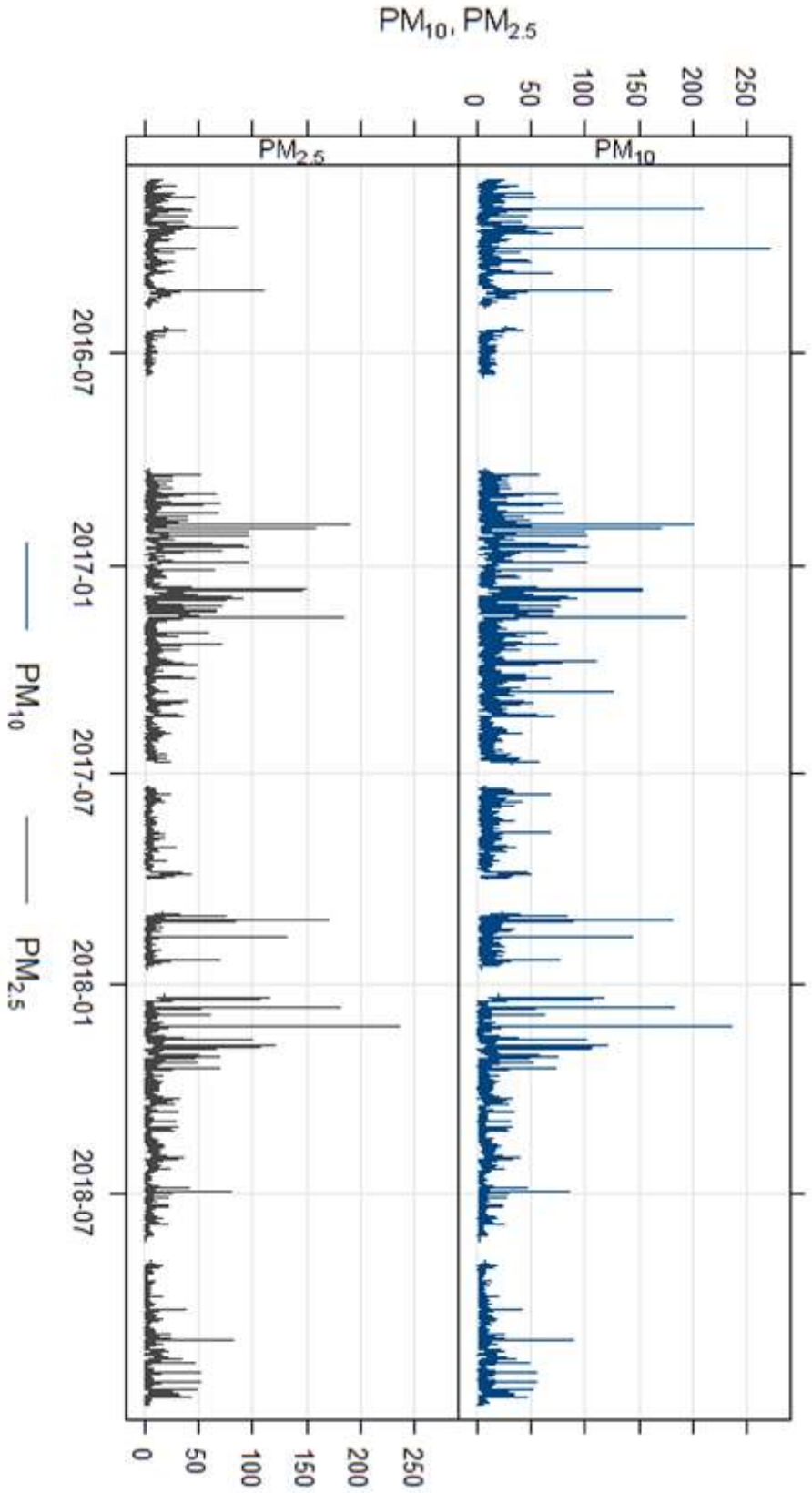


Figure 9.9. Shows the average daily plot of PM from the Little Plumpton monitoring station near Blackpool. Each day of monitoring was resolved into a 24-hour average and displayed as a bar on the bar graph. **Source:** Grainger (2019)

D. Daily Air Quality Index Plot from Little Plumpton.

When the daily air quality results are considered against the DAQI, the results show that most days had low air pollution (DAQI Score 1-3) as shown in Table 9.10 and Figures 9.10 and 13.11. The DAQI index score for $PM_{2.5}$ was higher, with only 97.67% of days being low. For $PM_{2.5}$ 20 days achieved a DAQI score of moderate (4-6) with no high days (7-10). The DAQI moderate days occurred over the three years. The breakdown of the annual number of days which achieved each DAQI are shown in Table 9.8 below;

Table 9.10: A table of the number of days passing each DAQI category.

Daily Air Quality Index Classification and Number of Days										
		1	2	3	4	5	6	7	8	9	10
2016	$PM_{2.5}$	285	23	1	5						
	PM_{10}	312	17	1							
2017	$PM_{2.5}$	241	20	3	3	2	1				
	PM_{10}	255	40	2							
2018	$PM_{2.5}$	178	45	4	4						
	PM_{10}	188	42	1							
TOTAL	$PM_{2.5}$	704	88	8	12	2	1				
	PM_{10}	755	99	4							

Whilst high DAQI scores can have damaging effects on human health in the long-term, the low incidence, and low concentration of $PM_{2.5}$, (even when these concentrations are 'moderate') are expected to have had an intangible effect on human health (COMEAP 2011, 2019).

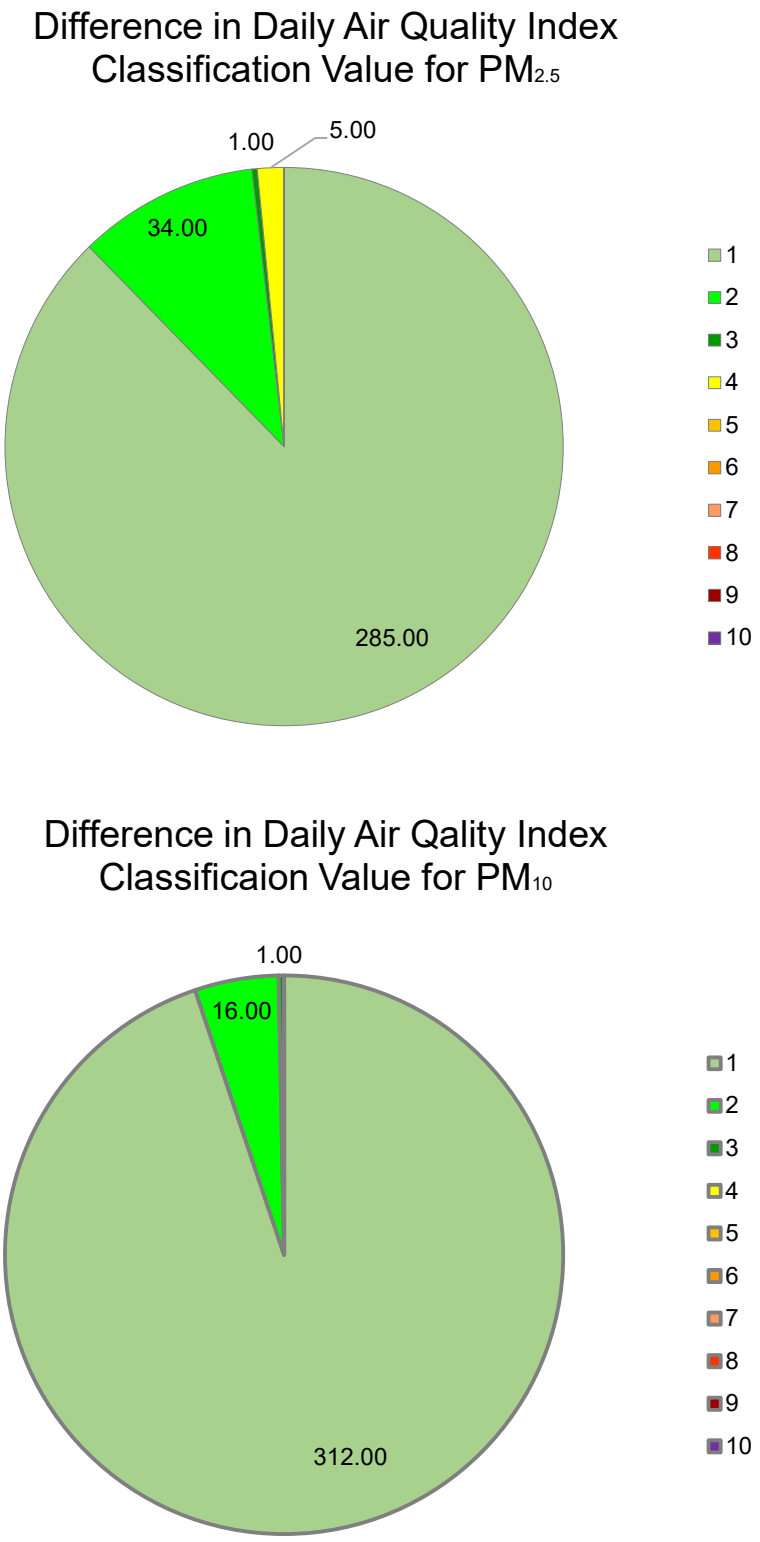


Figure 9.10 a – b: A figure showing the DAQI scores at the Little Plumpton monitoring station for 2016 to 2018 for both $PM_{2.5}$ and PM_{10}.

Source: Grainger (2019)

Difference in Daily Air Quality Index Levels resolved annually between 2016 to 2018.

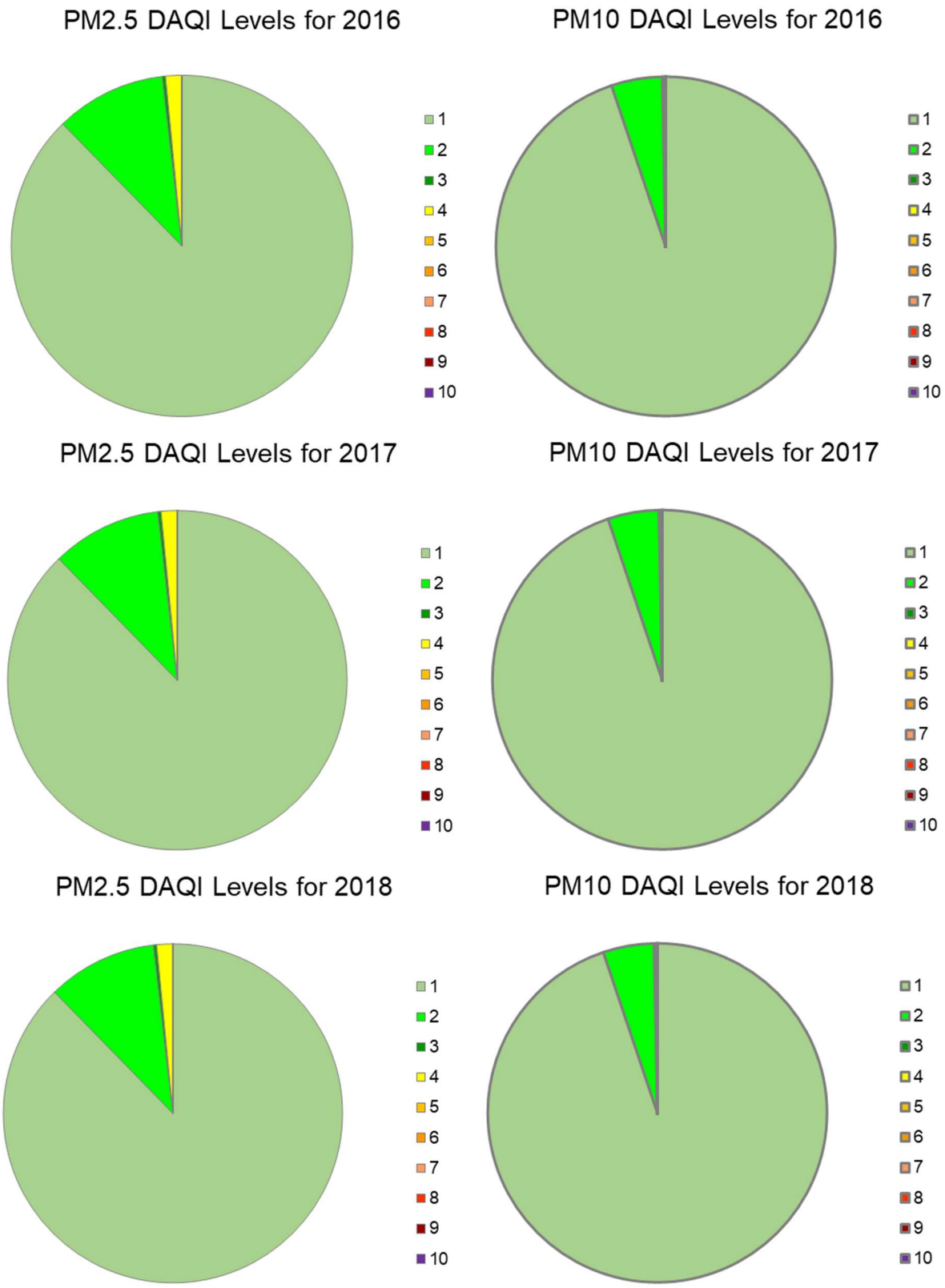


Figure 9.11. A-F: A figure showing the DAQI scores at the Little Plumpton monitoring station for 2016, 2017 and 2018 for both $PM_{2.5}$ and PM_{10}.

Source: Grainger (2019)

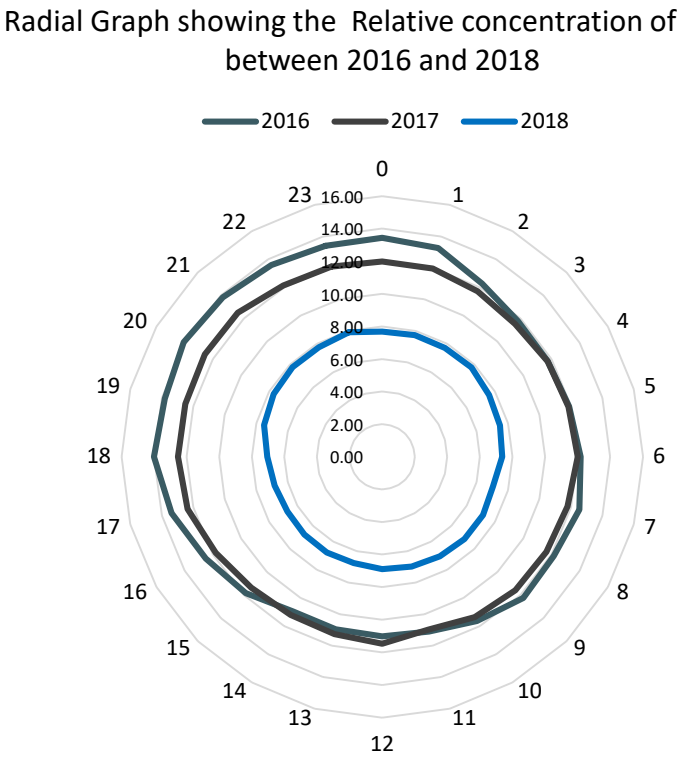
E. Hourly Summaries of Particulate Matter.

I. Results.

The hourly concentrations of $PM_{2.5}$ and PM_{10} are similar and are mostly consistent throughout much of the day, as shown in Figure 9.12. Concentrations of PM_{10} and $PM_{2.5}$ are highest at dusk, increasing from around 16:00 hours through to 02:00. From the early morning, it decreases, plateauing in the morning but increasing through to noon before decreasing until around 15:00. The years 2017 and 2018 had lower or comparable concentrations to 2016. Concentrations of $PM_{2.5}$ and PM_{10} were always at least 1 µg/m^3 lower for $PM_{2.5}$ in 2018 vs 2016/17 and 5 µg/m^3 for PM_{10} in 2018 vs 2016/17. This however reflects national improvements in air quality, and the drive towards clean and sustainable energy futures.

II. Discussion.

The diurnal distribution at the Little Plumpton monitoring station is heavily affected by road transport emissions, most likely from the nearby A583 'Preston New Road', the M55 Motorway and town of Blackpool. Rush hour is defined in the UK as between 07:00 to 10:00 and 16:00 to 19:00, (Ben-Elia and Ettema 2011). However, commuter traffic earlier in the morning and later in the afternoon is a common sight on arterial corridors. Secondary deposition of particles formed in the air, from surface loss of gases, and particle settling could also explain some PM generation (Defra 2018). Lastly, Blackpool's profile as a tourist town may have augmented nocturnal concentrations due to "social" traffic and evening events – including the 'illuminations', which are frequently on display between September and December (Bourdeau *et al.* 2015).



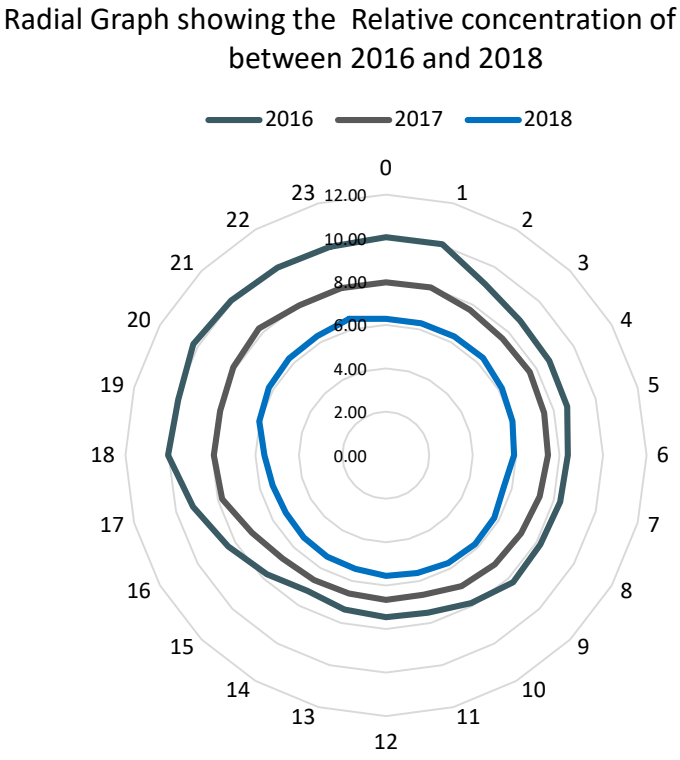


Figure 9.12. a-b; Showing the hourly concentration of $PM_{2.5}$ and PM_{10} at the Little Plumpton Monitoring site on radial graphs with 24 divisions for the years 2016 to 2018.
Source: Grainger (2019)

F. Spatial Distribution.

The PM was subjected to spatial analysis via a bivariate polar plot through the RStudio package OpenAir. This analysis plotted the concentration of $PM_{2.5}$ and PM_{10} against the wind direction and wind speed on a polar plot, as shown in Figure 9.13. The polar plot for $PM_{2.5}$ and PM_{10} at the Little Plumpton Monitoring station shows low background PM concentrations apart from two prominent hotspots these were;

- An eastern hotspot which peaked at 7 to 9 mps from a due easterly wind direction at 20 µg/m^3 for PM_{10} and 18 µg/m^3 for $PM_{2.5}$. Though traces from the eastern hotspot was found at most wind speeds from light air (>0.8 mps) to breezes and gales.

A western hotspot which had a diffuse geometry and a wide geometrical pattern from the northeast through to south-west at wind speeds above 5 mps. While the $PM_{2.5}$ and PM_{10} had a similar distribution, the concentration of PM_{10} was much higher than $PM_{2.5}$. The highest western concentrations come from the south-west and north-west, with concentrations of around 13 µg/m^3 for PM_{10} and about 8 µg/m^3 for $PM_{2.5}$.

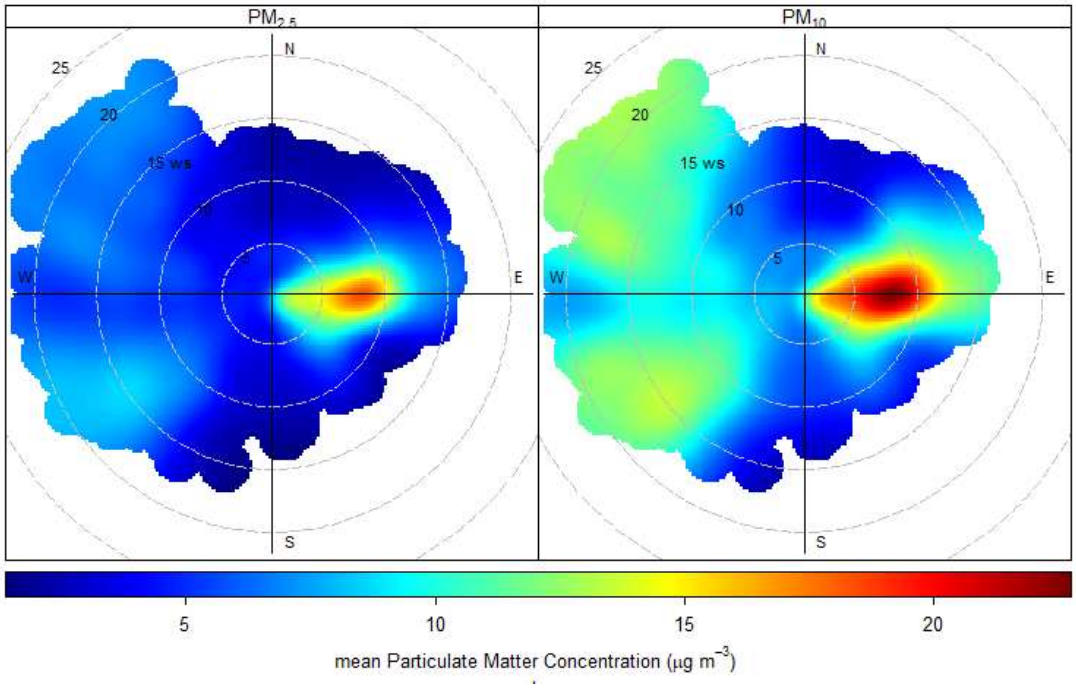


Figure 9.13: A polar plot conditional probability function showing the concentrations of $PM_{2.5}$ and PM_{10}. WS indicates Wind Speed in mps. **Source:** Grainger (2019)

The probability of high PM concentrations was tested against wind measurements using a conditional probability function to determine the significance (90th percentile of certainty) of the PM measurements.

As shown in Figure 9.14, only the eastern Hotspot was statistically significant. The eastern hotspot had a CPF probability of ~45% while the western hotspot had a very low CPF of between 5-20%. It is conjectured that the western source of PM, must have had variable conditions in the long-term, perhaps with higher concentration periods contributing to PM_{10} concentrations while the eastern hotspot remained relatively constant. However, the eastern hotspot had two more PM constant areas to the East and South-East at about 15 mps.

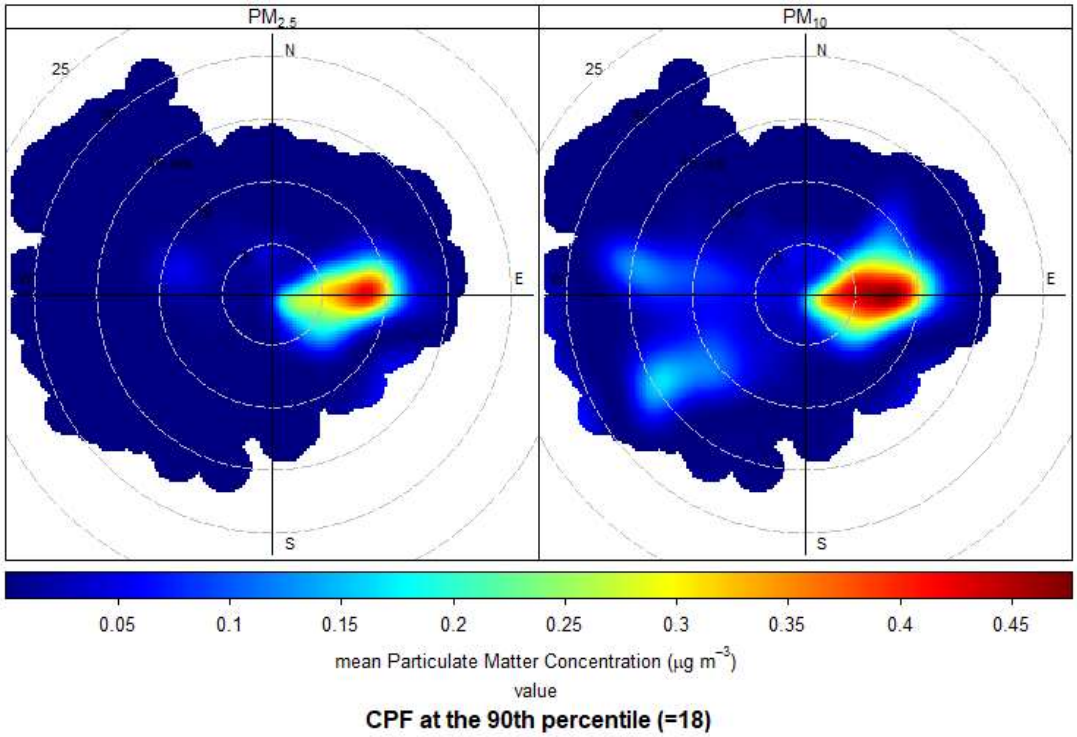


Figure 9.14: A polar plot conditional probability function showing the concentrations of $PM_{2.5}$ and PM_{10} according to the CPF function. **Source:** Grainger (2019)

G. Monthly and Seasonal Variation in Spatial Distribution.

I. Monitoring Year – 2016: Results.

There were two major hotspots of $PM_{2.5}$ and PM_{10} in the spring of 2016 which came from the east and the south-south-west. The eastern hotspot began in February and March before becoming much more substantial in April and May with wind speeds above 10 mps. The eastern hotspot disappeared through to the summer months until December 2016 when it became prominent. A southwestern hotspot was present in March 2016, which led to higher relative $PM_{2.5}$ concentrations. The south-eastern source of air pollution only occurred with wind speeds over 5 mps, but the highest concentrations were found at high wind speeds above 20 mps. Both the eastern and south-eastern hotspots had a PM_{10} concentration of about ~30 $\mu g/m^3$ during the day, which reduced to 25 $\mu g/m^3$ during the night. The diffuse western hotspot concentrations remained fairly constant with low-to-moderate PM_{10} concentrations up to about 15 $\mu g/m^3$ at wind speeds above 5 to 10 mps.

II. Monitoring Year – 2017: Results.

The eastern hotspot had the highest concentrations of $PM_{2.5}$ and PM_{10} in 2017, with easterly winds providing ~40 $\mu g/m^3$ for $PM_{2.5}$ and PM_{10}. The levels of PM were highest during the winter (January and December) and spring (February). This hotspot was present at most wind speeds, though annual statistics show that higher wind speeds caused higher concentrations of PM. There were noticeable peaks from this easterly hotspot in February, April, May, June, and September. The western hotspot was comparable to 2016.

III. Monitoring Year – 2018: Results.

There was a similar distribution of PM during 2018 though the concentrations were less than half of the year prior (annual peak concentration of 16 µg/m^3). The concentrations of PM were highest during the first few months of the year and declined through the summer into September before peaking in November. The western hotspot had about half the PM concentration of 2016-2017 (about 7 µg/m^3).

H. Discussion of the Spatial-Temporal trends of Particulate Matter ($PM_{2.5}$ and PM_{10}) at Little Plumpton.

The hourly trend offered no significant hints as to the origin of the air pollution other than PM followed a subtle diurnal rhythm and nocturnal emissions possibly associated with overnight settling of fine particulate and secondary PM generation. Annually, the level of PM reduced year on year from 2016 to 2018, though this was in line with national air quality trends (Defra 2020a). The monthly distribution of air pollution revealed that the monitoring station had been affected by regional air pollution events, which translated to most days above, or close to the PM guideline values. In terms of spatial analysis, two hotspots were found one to the east and another the west. A discussion on the likely sources of these hotspots is outlined below.

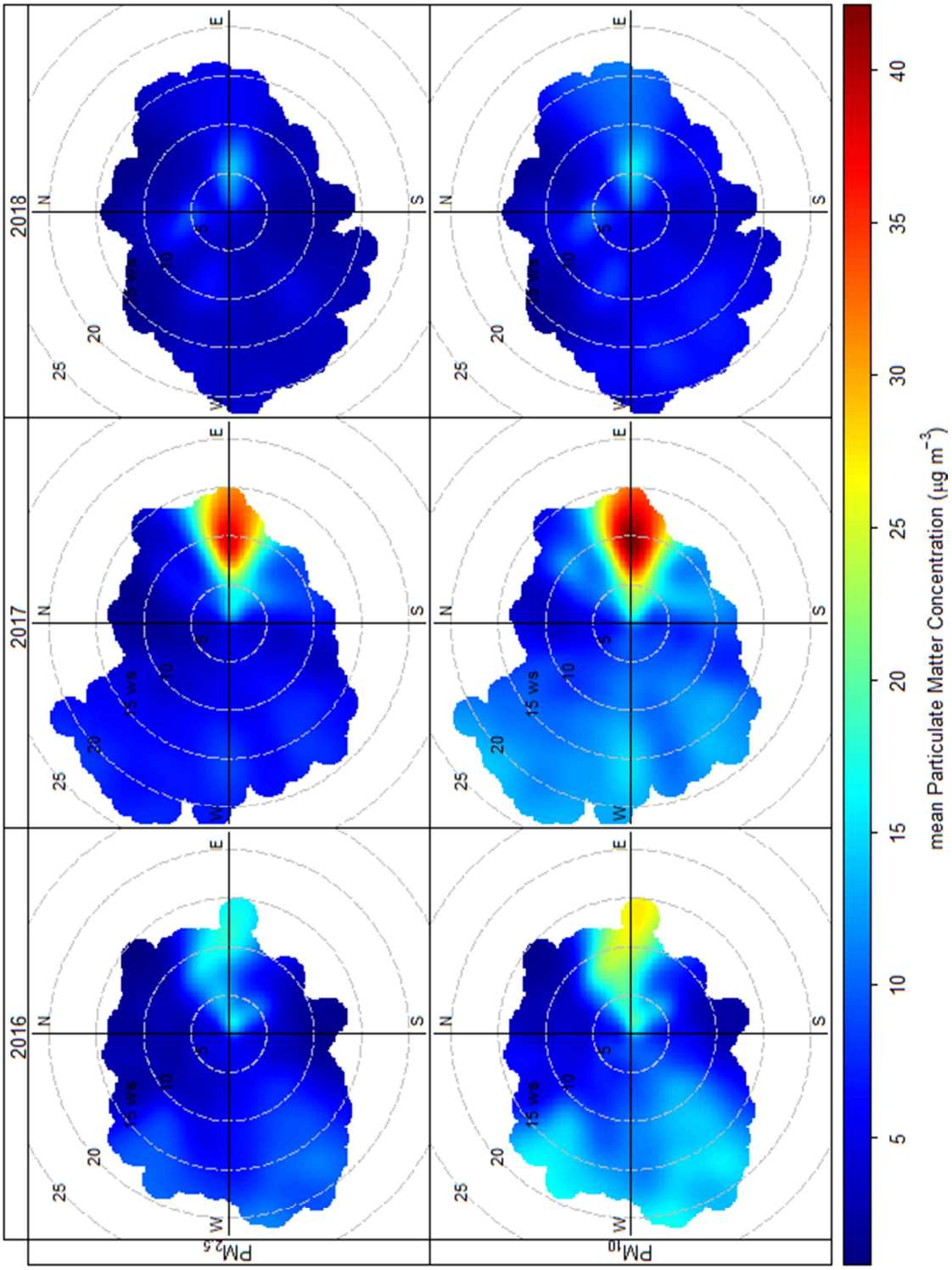


Figure 9.15. The figure shows the annual spatial-temporal plot of $PM_{2.5}$ and PM_{10} from the Little Plumpton monitoring station for 2016, 2017 and 2018 in terms of average readings vs wind measurements from those calendar month years. **Source:** Grainger (2019)

I. Eastern Hotspot.

A significant and reliable eastern source of PM was present at most wind speeds. Concentrations of PM_{10} were also elevated at night compared to during the day from this hotspot, with the highest concentrations in the spring and winter months reducing to near background levels during the summer.

In the preliminary assessment of the air quality of air pollution at the Little Plumpton monitoring station, the source of this easterly air was conjectured to stem from industrial emissions from the UK and regional pollution episodes (Ward *et al.* 2018). The author considers this regional source to be supplementary to a more prominent local source given that the CPF probability of PM from this wind direction was so high (45%). Given the indications of a local source of air pollution and the lack of nearby point sources, a thorough search of point sources was undertaken on maps and building listings.

The most significant source of air pollution to the monitoring station may have been Plumpton Hall farm, a working dairy farm 100 metres to the east of the monitoring station. The farm is operated by T.H. Wensley and sons, and includes several overwinter barns, a slurry pit, storage areas, and milking areas (Google 2019; Grainger 2019; Ordnance Survey 2019).

The seasonal concentrations in PM correlated well with dust-generating activities during the farming year (Custard 2017; Custard 2017). Dairy cattle are free to graze throughout the summer on pastureland, though from September onwards they are led into overwintering barns to help protect them against the cold weather and for barn feeding during winter conditions (Custard 2017; Mali *et al.* 2013; Walker 2020). After winter conditions have passed (February to March), the cows may be led into the pastureland (Custard 2017; Walker 2020). As a dairy farm, the cows are led to the milking sheds and milked twice or thrice daily year-round (Custard 2017; Campbell and Marshall 2016; Walker 2020).

Agricultural sources of PM comprise 40% of the UK's fine particulate emissions (UK AQEG 2012, 2018). Primary sources of PM from cattle are highest when they are indoors as; hoof action on dry manure, suspension of animal feed and soil, or feed grinding can build up in enclosed barns (Custard 2017; Joo *et al.* 2013; Mali *et al.* 2013). Significant secondary sources are generated from ammonia, manure, animal feed, and urine reacting with atmospheric nitric and sulphuric acids to form PM sized sulphate and nitrate crystals (Havlikova *et al.* 2008; UK AQEG 2018). Cooler temperatures exacerbate the secondary PM generation as colder conditions retard ammonium nitrates ability to sublimate into ammonia and nitric acid (Havlikova *et al.* 2008; UK AQEG 2018). Meteoric inversion events during winter can also trap air pollution at ground level (Defra 2019;).

The month of May also had a spike of PM. This month followed the Spring calving season when the cows were on pasture (Custard 2017; Walker 2020). Some farmers perform maintenance on the farm in May (when the overwinter barns are empty) which might agitate and liberate dry materials creating clouds of dust and movement of ammonium and nitrate-rich substrates, which may cause the increased secondary generation of PM (Havlikova *et al.* 2008; UK AQEG 2018; Walker 2020). Farmers spread this dusty material on their fields as it is a good fertiliser for potatoes, cereal, and legume crops, albeit to 'NVZ Regulations' (Havlikova *et al.* 2008, Maguire 2019; Walker 2020).

II. Western Hotspot.

There was a diffuse source of PM during gale-force winds from the west. While the PNR development site was to the west of the monitoring station, this was not the source as this hotspot was already present in 2016 before the PNR development began work. There is no discernible source of PM from the UNG development site at the Little Plumpton monitoring station. The PM generated at PNR did not cause an appreciable long-term increase in PM concentrations at the monitoring station. Any PM produced at source

seems to have dispersed in the 300 metres intervening distance between the UNG site and the monitoring station suggesting a very low PM source.

The western diffuse source of PM was likely due to sea mist and blown fine to medium “silt” grains from the Irish Sea (7 km away) perhaps augmented by urban pollution from the town of Blackpool which is immediately upwind of the monitoring station (Deacon and Smallbone 2002; UK AQEG 2012). Within the CPF plot of the western hotspot, were two higher probability areas. The source to the WSW likely came from the wind blowing from the dunes at St Anne blowing over the runways of the Blackpool Airport towards the monitoring station during gales. The airport functions as a flight school and transport hub for offshore oil rigs, with limited services undertaken at high wind speeds. However, at one end of the runway were extensive dunes which were likely a source of PM at the monitoring station. Whereas, the source from the WNW pointed roughly towards Blackpool South Pier, and most likely resulted from wind currents from the relatively open stretch of beach between Blackpool South Pier and Central Pier. Potentially with the impact of Fireworks displays and other phenomena at the Blackpool Pleasure Beach near to the South Tower.

I. Summary and Conclusions of PM at Little Plumpton.

The work found that the PM concentration at the Little Plumpton Monitoring Station reduced between 2016 and 2018, with 99.7% of daily monitoring results indicating good to moderate air quality (with low DAQI scores). The remaining 0.3% of high days were because of nationwide air pollution episodes.

Two hotspots were identified from the spatial distribution of the hotspots at the Little Plumpton monitoring station; these were from;

- **Easterly winds:** this source of PM was conjectured to be due to agricultural emissions related to a nearby dairy farm. The increases in PM from the hotspot correlated well against busy periods of the farming year, such as sheltering dairy cattle in indoors barns overwinter, maintenance and mucking out of these barns and spreading slurry during the spring (May). PM likely came from direct PM agricultural emissions and secondary nitrate and ammonium generation of PM during colder winter months.

- **Westerly winds:** this source of PM was conjectured to be due to prevailing strong winds bringing sea mist and beach sand from the coast to the monitoring station. Two sources had higher probability; these were likely due to unimpeded level access to the monitoring station via Blackpool Airport and from the beaches between the South Pier and Central Pier along the Blackpool Promenade.

It was found that despite a prevailing wind direction from the west, there was no discernible impact of the PNR UNG site on the concentration of Particulate Matter at the Little Plumpton monitoring station.

♦ 9.4.3) Nitrogen Gases.

A. Annual Concentrations of nitrogen oxides.

I. Results.

The mean NO, NO_2, and NO_X concentrations were calculated based on calendar month year averages (discounting periods of data loss). The annual concentrations of NO, NO_2, and NO_X at the Little Plumpton AURN were low. The NO_2 concentration fell from 11.59 ±12.36 µg/m^3 in 2016, to 8.40 ±9.70 µg/m^3 in 2017 before increasing to 14.62 ±17.63 µg/m^3 in 2018 with NO and NO_X having a very similar trend as shown in Figure 9.16.

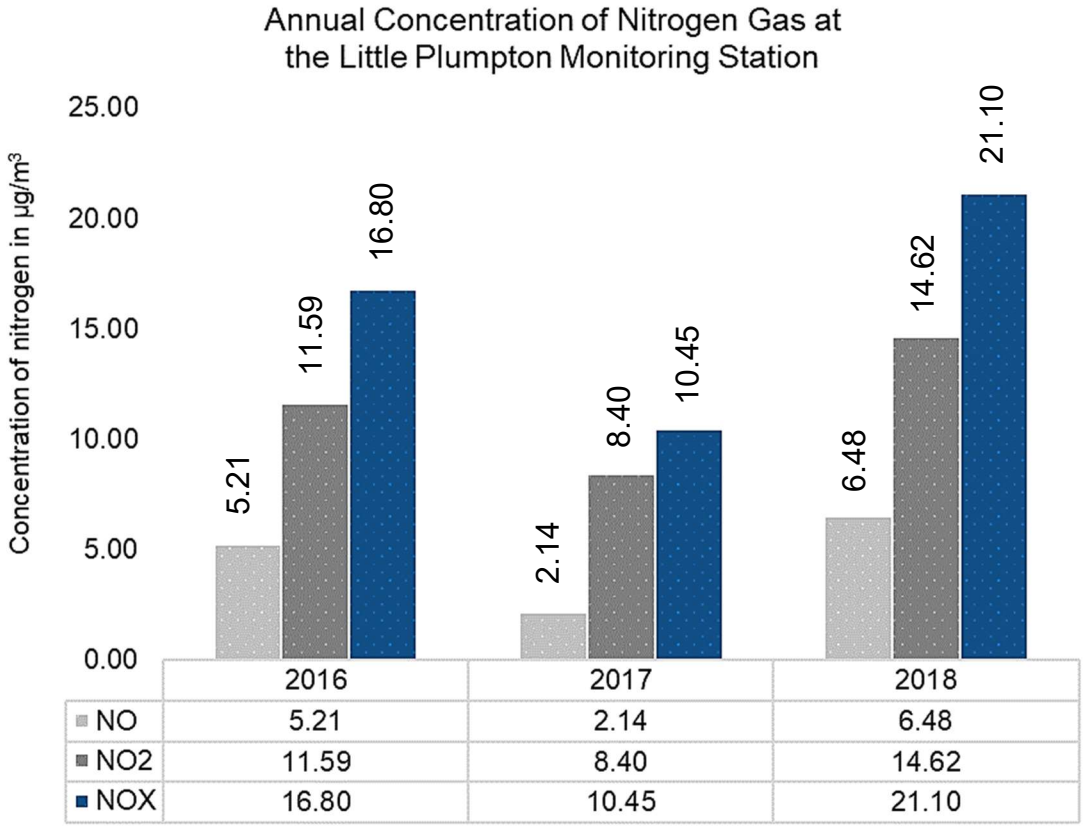


Figure 9.16. A graph showing the annual concentration of NO, NO_2, and NO_X at the Little Plumpton Monitoring Station between 2016 and 2018. **Source:** Grainger (2019)

II. Discussion.

The graph of Nitrogen Gases over time is different to the national trend of nitrogen over the UK, as the national trend reduced year on year from 2016 to 2018 is the lowest year on record for all monitoring station locations in the 1990 to 2019 monitoring period (Defra 2020b). The national trend for urban background sites reduced 1 µg/m^3 nationally (Defra 2020b). The improvement of NO_2 and other nitrogen gases over the country and wider EU was due to newer road vehicles moving towards stricter emissions controls, i.e. progressively newer European Emissions years and power generation away from coal-fired power plants (Defra 2020b). As the increase in air pollution in 2018 does not correlate with the national trend, there may be a local or regional source affecting the monitoring station (Defra 2020b).

B. Monthly Concentrations of Nitrogen Oxides.

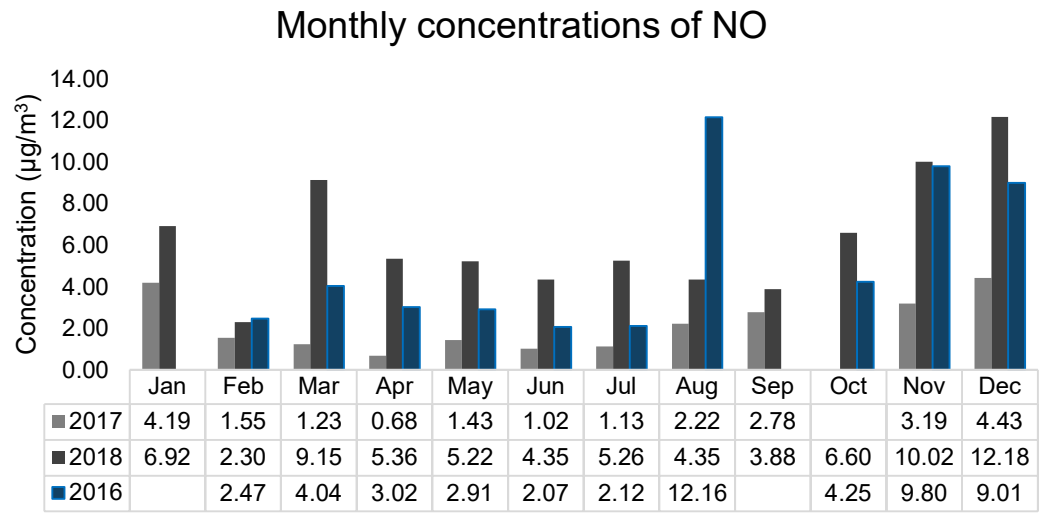
I. Seasonal and Monthly NO_2: Results.

The mean monthly NO, NO_2, and NO_X concentrations were calculated based on the calendar month average from midnight to midnight (negating any periods of data loss). Figures 9.19 A-C suggest that concentrations of NO, NO_2, and NO_X had a significant variance during all three years of monitoring. Nitrogen dioxide decreased sharply between 2016 and 2017 in most months. The concentrations of NO_2 rose again during 2018 to higher values than in 2016 for most months of the year (March to August).

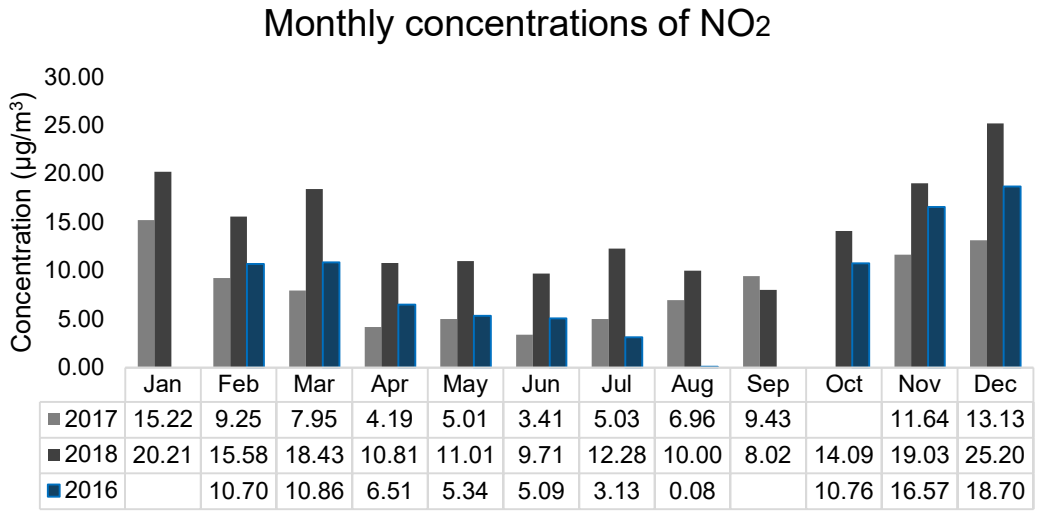
Nitrogen dioxide shows a high concentration during the first few months in both 2017 and 2018 of about 15.22 and 20.21 µg/m^3, though this reduced through to the summer months with concentrations of 3.31 and 9.71 µg/m^3. There was an increase in NO_2 from July to December, rising to 18.70 µg/m^3 in 2016, with lower values of 13.13 and 25.20 µg/m^3 in 2017 and 2018. The concentration of nitrogen oxide (NO) had the highest concentrations in 2018. The levels of NO were uniformly lower in 2017 than in 2016 or 2018.

II. Seasonal and Monthly NO_X: Discussion.

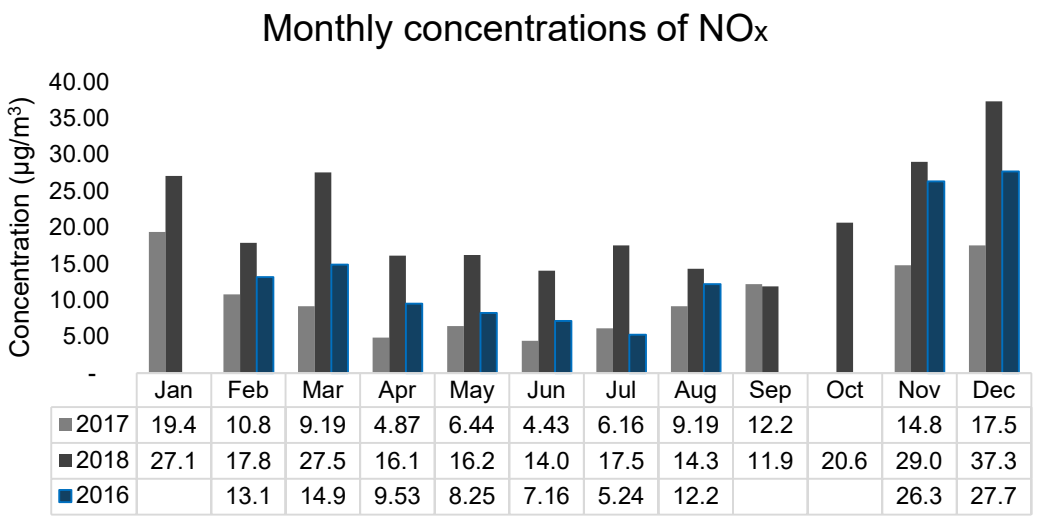
Like the general trend of $PM_{2.5}$ and PM_{10} over the year, the highest concentration of anthropogenic air pollution occurs over the winter months (Defra 2020a). This trend is very similar to the national trend, especially within rural areas where agricultural activity (e.g. overwintering livestock within barns, and the fermentation of silage) and regional air pollution episodes are significant sources during the winter (Defra 2017, 2018c, 2019b; UK AQEG 2018). The high NO readings taken in August 2016 did not translate to NO_2 or NO_X air pollution, suggesting that these readings were an error in the data set. Otherwise, the summer had the lowest concentrations of nitrogen gases annually, increasing from September to January when the concentration declines.



	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2017	4.19	1.55	1.23	0.68	1.43	1.02	1.13	2.22	2.78		3.19	4.43
2018	6.92	2.30	9.15	5.36	5.22	4.35	5.26	4.35	3.88	6.60	10.02	12.18
2016		2.47	4.04	3.02	2.91	2.07	2.12	12.16		4.25	9.80	9.01



	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2017	15.22	9.25	7.95	4.19	5.01	3.41	5.03	6.96	9.43		11.64	13.13
2018	20.21	15.58	18.43	10.81	11.01	9.71	12.28	10.00	8.02	14.09	19.03	25.20
2016		10.70	10.86	6.51	5.34	5.09	3.13	0.08		10.76	16.57	18.70



	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2017	19.4	10.8	9.19	4.87	6.44	4.43	6.16	9.19	12.2		14.8	17.5
2018	27.1	17.8	27.5	16.1	16.2	14.0	17.5	14.3	11.9	20.6	29.0	37.3
2016		13.1	14.9	9.53	8.25	7.16	5.24	12.2			26.3	27.7

Figure 9.17. a c. A graph showing the monthly concentration of NO, NO_2, and NO_X at the Little Plumpton Monitoring Station between 2016 and 2018. **Source:** Grainger (2019)

C. Daily Concentrations of Nitrogen Oxides.

I. Monitoring Year – 2016: Results.

During 2016 the average concentration of NO at 4.73 ±7.61 µg/m^3 and NO_2 at 10.20 ±9.09 µg/m^3 in 2016. While much of the year had good air quality (<DAQI 3), fifteen days had a concentration above an actionable screening value of 30 µg/m^3 in 2016 (>75% of the mandated 40 µg/m^3 concentration). These days we are in the winter months, 12th February, 8th, 11th and 12th March, 8th and 19th November and the 2nd, 5th, 6th, 18th, 19th, 28th and 29th of December. Though should the site have been of ecological importance and the NO_X screening value adopted, then 41 days would have breached these guidelines. No hours were in breach of the hourly screening threshold of 150 µg/m^3 (i.e. the planning threshold set at 25% of the NO_2 standard of 200 µg/m^3). Altogether only 5 minutes of data from 2016 was above these thresholds which occurred on high air pollution days.

II. Monitoring Year – 2016: Discussion.

Included within the monitoring period were a series of pollution episodes, some of which occurred at the same time as particulate pollution episodes. The pollution episodes which can be identified in 2016, these were the;

- "Mid-March" episode (11th–13th March) which caused NO_2 and PM high days, from low wind speeds rich in European industrial pollution (Defra 2017).
- "Bonfire Night Particulate Pollution Event" (29th October - 9th November) which caused NO_2 and PM high days, from low wind speeds, cold weather, and nationwide firework and bonfire events (Defra 2017).
- "Late November and December" (25th November–31st December), which caused NO_2 and PM high days, from low wind speeds, cold weather, and European industrial pollution (Defra 2017).

With these dates accounted for, the remaining dates not associated with national air pollution episodes were the 12th February, 8th March, and 19th November. No reasonable explanations could be found in local phenomena such as firework displays, or major fire, suggesting local phenomenon may have caused the poor air quality (Lancashire Fire and Rescue 2019).

III. Monitoring Year – 2017: Results.

In 2017, when construction and drilling began on the PNR site, the average daily level of NO and NO_2 was 2.12 ±3.27 and 8.29 ±6.56 µg/m^3. There were five days above a screening value of 30 µg/m^3. These days were the 5th, 23rd, 24th, 27th of January and the 12th December. The adoption of NO_X screening value for important ecological sites would have led to 26 days in breach of the guidelines. No hour was above the 150 µg/m^3 screening value, however,
8 minutes of NO_2 readings were higher than this concentration.

IV. Monitoring Year – 2017: Discussion.

Only one air pollution episode for NO_2 occurred on NO_2 high days, and this was the; Particulate Pollution" episode (21st–28th January) which caused NO_2 and PM high days, from cold frosty weather (Defra 2018).

The remaining days on the 5th January and 12th December were not related to any known national air pollution event (Defra 2018). Further investigation, indicates that these events were not due to any known fireworks events or major fires in the area (Lancashire Fire and Rescue 2019). Both days, however, were frigidly cold and local air pollution may have built up in the region due to inversion layering, but not necessarily on a national scale.

V. Monitoring Year – 2018: Results.

In 2018, the average daily level of NO and NO_2 was 6.26 ±4.96 and 13.27 ±11.04 µg/m^3. There were 26 days which had a level above a screening value of 30 µg/m^3. These days were the 11th, 12th, 20th, and 26th January, 5th and 7th of February, 4th, 5th, 15th March, 18th and 31st October, 5th, 16th, 20th, 21st, 22nd, 23rd and 25th November and the 4th, 5th, 19th, 20th, 22nd, 23rd and 25th December. The adoption of NO_X screening value for important ecological sites would have led to 61 days in breach of the guidelines. No hour was above the 150 µg/m^3 screening value; however, 24 minutes of NO_2 readings were higher than this concentration.

VI. Monitoring Year – 2018: Discussion.

It is worth mentioning that the 2018 monitoring year had more days, minutes, and ecological guidance breaches than the monitoring years 2016 and 2017 added together. This trend did not correlate with national trends or the unfortunate impact of regional pollution episodes as only three of the twenty-six days above the NO_2 guidance occurred during regional air pollution events. These regional air pollution events were;

- "Beast from the East" episode (26th February–4th March) which caused NO_2 and PM high days, from the UK cold wave of 2018. While national levels of NO_2 reduced around the country from these emissions, given the sites rural profile, domestic heating may have led to significant NO_2 increases rurally through to the 5th March when the weather improved (Defra 2017).
- "Bonfire Night" episode (5th–6th November) which caused NO_2 and PM high days, from the annual fireworks and burning festivities, however, the air pollution was short-lived due to unsettled weather (Defra 2017).

The remaining high days in January. February, March, October, November, and December were not related to any known national air pollution event (Defra 2018). Further investigation indicates that these events were not due to any known fireworks events or major fires in the area (Lancashire Fire and Rescue 2019).

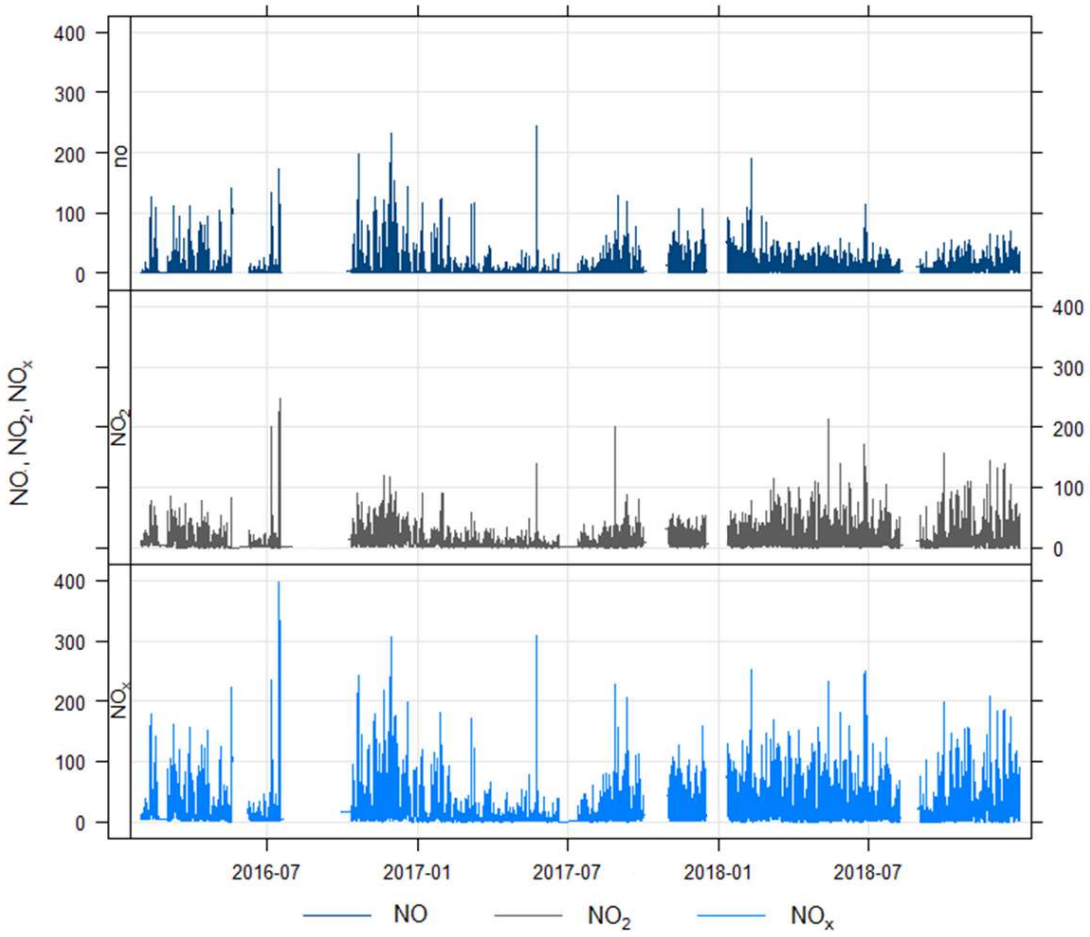


Figure 9.18. Showing the readings of NO, NO_2, and NO_X between February 2016 and December 2018 resolved onto a three-year horizontal scale. Vertical represents concentration peak readings on a minute timescale.

Source: Grainger (2019)

D. Daily Air Quality Index Plot of Nitrogen Oxides.

The DAQI only screens for Nitrogen Dioxide (NO_2) and unlike PM, the NO_2 concentration on an hourly, not daily basis. The monitoring period was marked by a "Low" NO_2 DAQI score between 1 and 3. In 2016 and 2017 only 1 hour, which achieved an hourly DAQI score of over 1 (>68 µg/m^3). However, the air quality declined in 2018, which led to 98 days having a DAQI score over 1. These higher DAQI days included 79 days of DAQI 2 and 19 days of DAQI 3. None of the hours was significant enough to breach the guideline limit of 200 µg/m^3 for NO_2, even considering the planning threshold at 75% the guideline value (150 µg/m^3).

E. Hourly Plot of Nitrogen Oxides.

I. Results.

The concentration of nitrogen gases follows a rhythmic cycle beginning from low concentrations at 3 am, though NO and NO_2 produce subtly different graphs (as shown in Figure 9.19). NO_2 peaks at 7 to 8 am 18.86 µg/m^3 before declining into the afternoon between 5 and 11 µg/m^3. NO_2 declines into the afternoon, when there is another peak between 1 pm to 7 pm, after which NO_2 decreases through to the early morning.

Nitrogen oxide has a similar distribution to NO_2; however, the trend is much less smooth. In 2017 and 2016 the morning and afternoon peaks are seen between 7, and 8 am and 5 to 7 pm with lower noon and overnight concentrations. There are significant differences in these peaks. Oddly, 2017 did not have an afternoon peak, it declined from the morning rush hour, through to the end of the day.

II. Discussion.

Like with the PM concentrations, the diurnal distribution at the Little Plumpton monitoring station is heavily affected by road transport emissions from nearby roads during rush hours in the morning (07:00 to 10:00) and afternoon (16:00 to 19:00), (Ben-Elia and Ettema 2011). However, Blackpool's status as a tourist destination may lead to commuter traffic earlier in the morning and later in the afternoon on arterial corridors. There are two key observations which can be drawn from the NO vs NO_2 concentration:

- NO was much more variable than the NO_2 concentration. This trend may have been due to NO being a primary pollutant, and so the nearby A583 may have had a greater local impact on air quality than NO_2.
- NO_2, despite being a secondary reaction product of NO, more than doubles the primary NO concentration indicating a source which had travelled some distance and could turbulently mix in the presence of sunlight.
- Noon concentrations of NO_X can be converted more readily into ozone when the suns intensity is at its maximum, i.e. around noon (Valero 2014).
- There was no rationale for the absence of an afternoon peak in 2017.

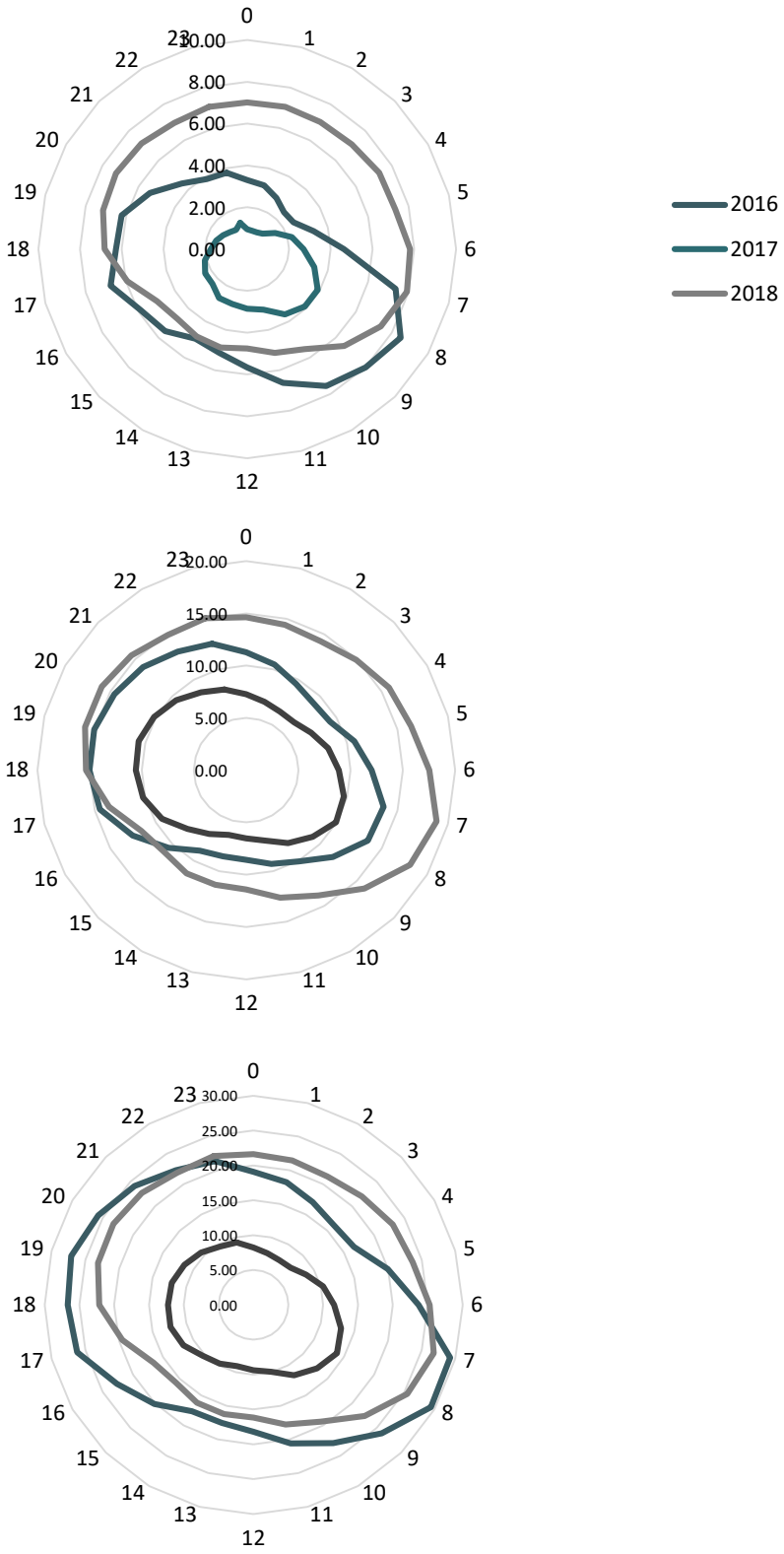


Figure 9.19. Showing the readings of NO, NO_2, and NO_X from 2016 to 2018 resolved onto a radial graph. The outer reading represents the time of day, i.e. each hour represents 30°. The extension from the centre origin point to the outside of the graph represents the concentration in µg/m^3. **Source:** Grainger (2019)

F. Spatial Distribution of Nitrogen Oxides.

The spatial distribution shows that there are two prominent hotspots, one coming from the east at low wind speeds and another coming from the west at higher wind speeds (as shown in Figure 9.20). CPF analysis was also used to determine whether the differences in the levels of NO, NO_2, and NO_X were statistically significant (to a 90% certainty). The background probability of high nitrogen oxide episodes' ranges from about 0 to 10% probability (as shown in Figure 9.21). These two hotspots are outlined in greater detail below;

- **Eastern Hotspot;** The hotspot was strongest from winds from the east and south-east at wind speeds less than 5 mps. The source of the hotspot was rich in NO, NO_2, and NO_X, which when averaged over the three years led to concentrations of 7, 23 and 30 $\mu g/m^3$, as shown in Figure 9.20. The hotspot appears to be similar to the eastern hotspot noted in the PM spatial information. The eastern source was more intense in 2016 and 2018 than in 2017. There were also minor changes to the NO concentration noted in any of the years from this eastern source. The hotspot had a high CPF probability of about 25%, with lower probabilities at wind speeds over 3 mps. The CPF chart helped to constrain the hotspot to a region between due east to the south-east at low-to-moderate wind speeds (0 to 8 mps).

- **Western Hotspot:** The second hotspot begins at around 5 mps from the west and persists through to 20 mps. The peak air pollution of NO_2 is about 10 mps, with maximum concentrations of NO, NO_2, and NO_X at 6, 8 and 13 $\mu g/m^3$. Much of the pollution from this hotspot is from NO_2 emissions, though the pollution creates similar geometric patterns with comparable relative concentrations. The hotspot was not present in 2016, remained weak in 2017 but became moderate in 2018. Though overall this hotspot had half of the NO_2 concentrations of the Eastern Hotspot. Unlike the eastern hotspot, this hotspot was not indicated on the PM charts in the first half of this chapter.

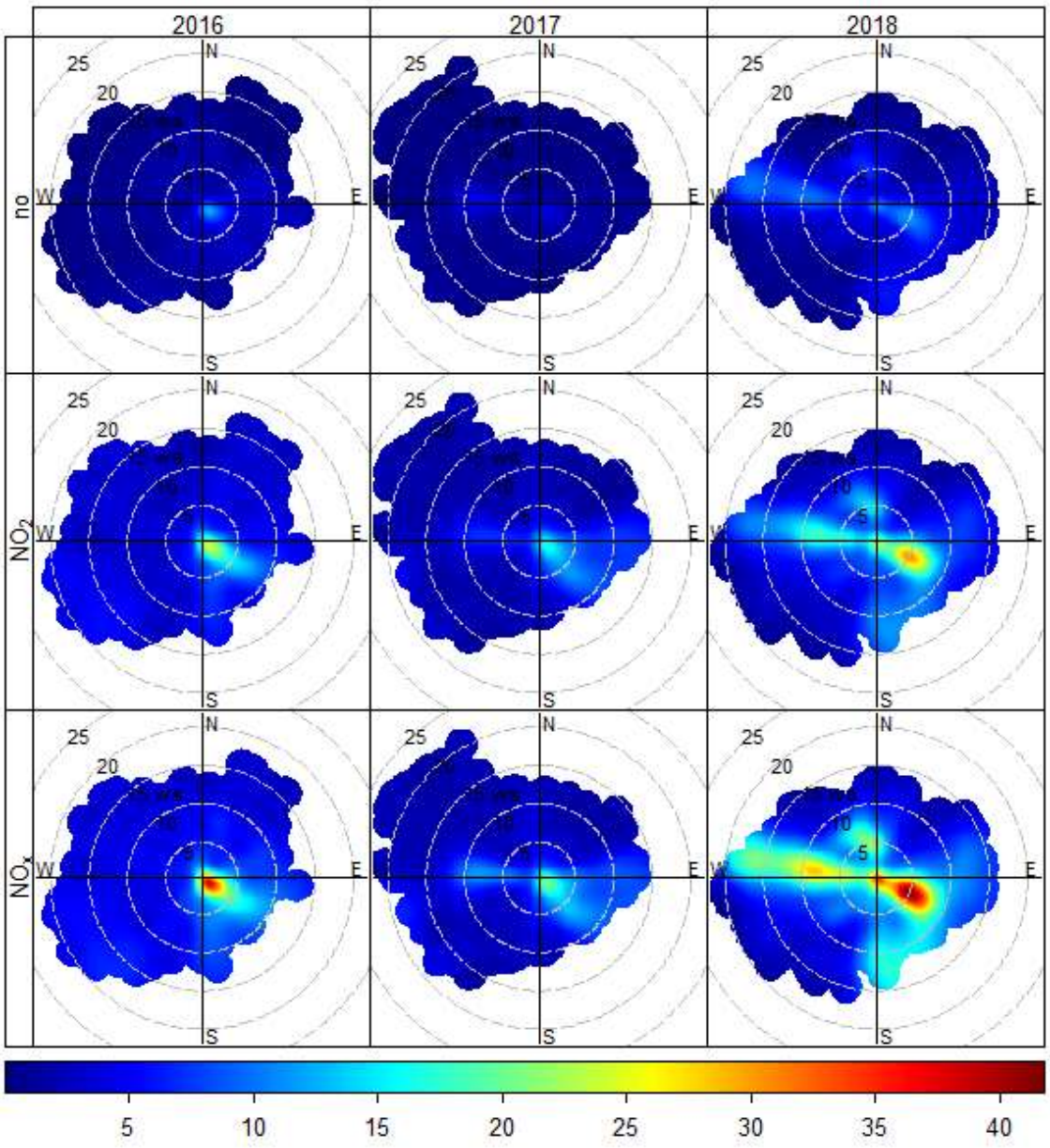


Figure 9.20. A Figure is showing the concentration of various nitrogen oxide gases in separate year periods between 2016 and 2018. The scale is in µg/m^3.

Source: Grainger (2019)

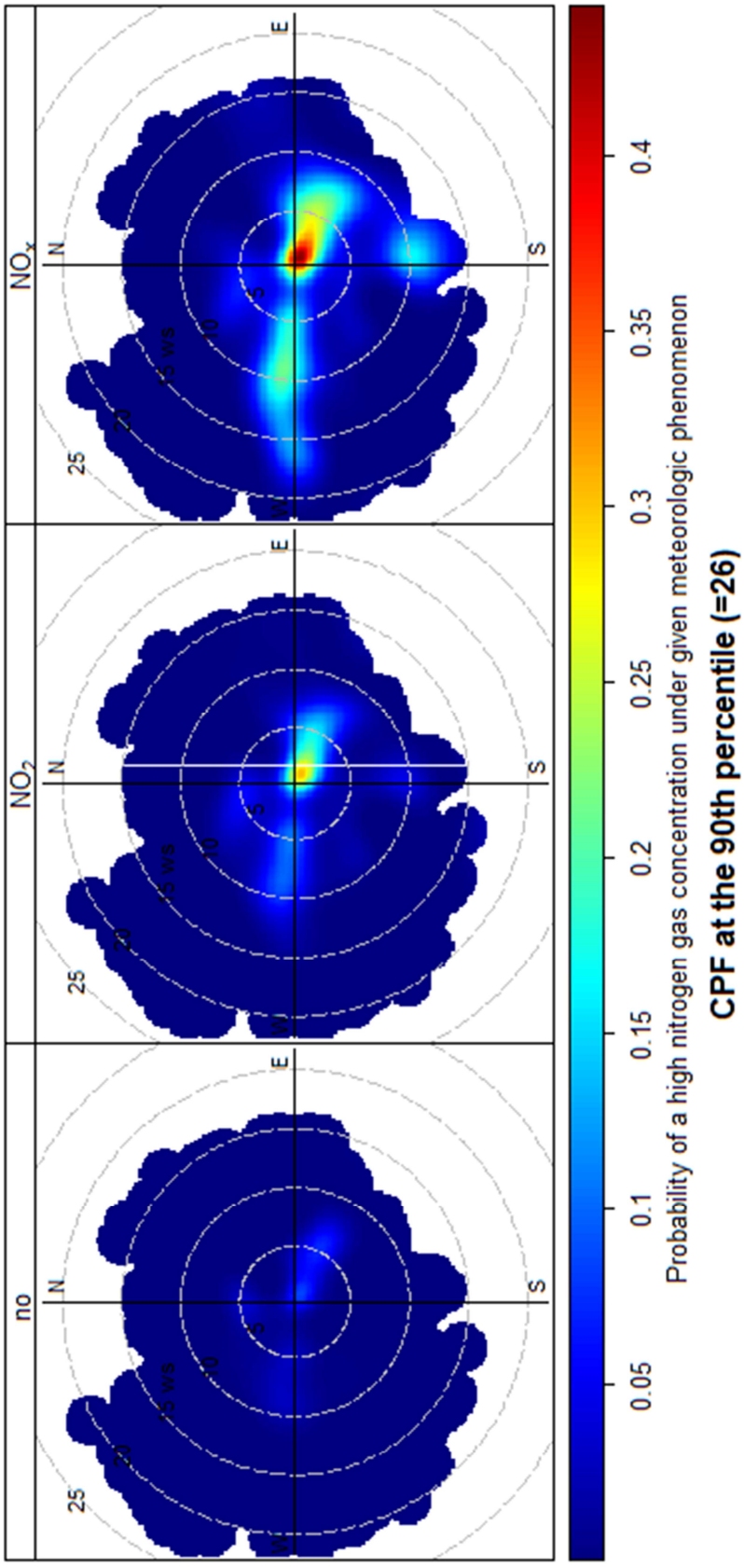


Figure 9.21. Showing the probability of a high nitrogen oxide event coinciding with certain meteorological events. **Source:** Grainger (2019)

G. Seasonal Variation of Nitrogen Compounds.

The concentrations of nitrogen gas change naturally due to climatic variations, and so the seasonal and monthly distribution was likely to be affected through natural and artificial processes. To help understand these variances, each month of monitoring was analysed with bivariate polar plot analysis (Figures 9.24 to 13.26). The results of seasonal variation within each monitoring year are detailed below;

- **Background Monitoring, 2016:** The polar plots show a prominent source of Nitrogen gas from only the eastern source, with no underlying western source. The hotspot was only present during the winter months, which included February, November, and December. A subtle increase in nitrogen gas, particularly NO_2, was noted for most months. The maximum source concentration of NO_X was detected in November with concentrations of 70 µg/m^3, a 1:1 ratio of NO and NO_2. However, there was a declining ratio with a 1:2 ratio of NO to NO_2 by December and 1:1.6 in February.

- **Site Construction and Drilling, 2017:** The eastern hotspot continued in 2017 with high nitrogen gas concentrations during the winter months from January to March, November, and December. The highest concentrations were in December and January with high NO_2 concentrations of 30 to 40 µg/m^3. A new hotspot began during August 2017, not present in 2016. The hotspot increased through to November with maximum NO and NO_2 concentrations of 15 and 20 µg/m^3 at 5 to 20 mps and only subtly reducing in December.

- **Drilling and Hydraulic Fracturing, 2018:** Again, the hotspot persisted into 2018, though at even greater concentrations than in previous years with NO_2 concentrations at 60 µg/m^3 in December. The most substantial concentrations of NO and NO_2 were November, December, January, and March. During these months the concentrations of NO_2 ranged between 40 and 60 µg/m^3. The NO concentrations ranged between 20 and 30 µg/m^3. The western hotspot became more prominent, especially in January to May, October, and November where maximum concentrations reached 25 and 40 µg/m^3. In April and November especially, the hotspot follows a pinpoint hotspot distribution of NO_X indicating a clear local source of nitrogen.

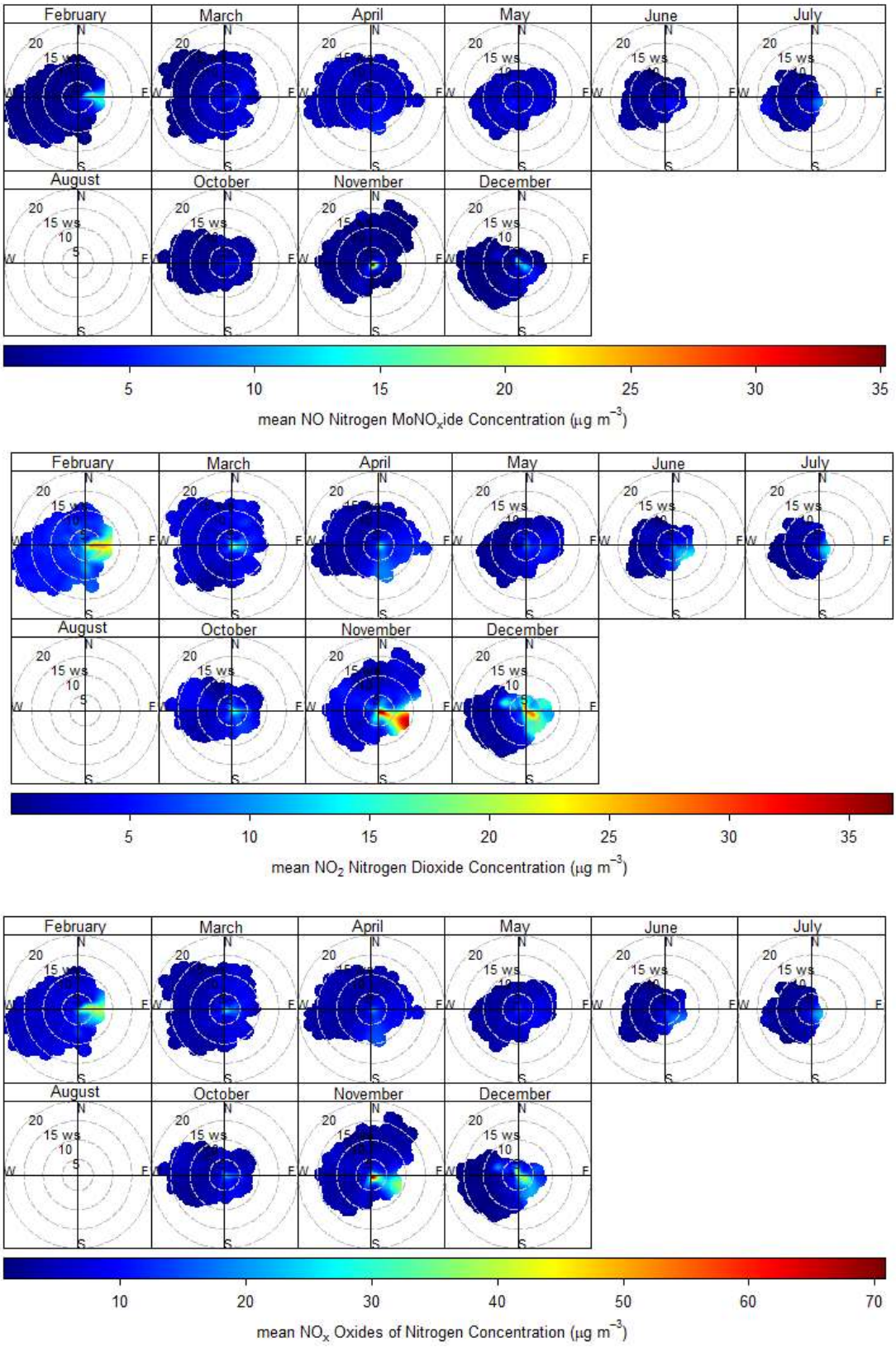


Figure 9.22. Showing bivariate polar plots of the concentration of NO, NO_2, and NO_X on a monthly plot during the years 2016. **Source:** Grainger (2019)

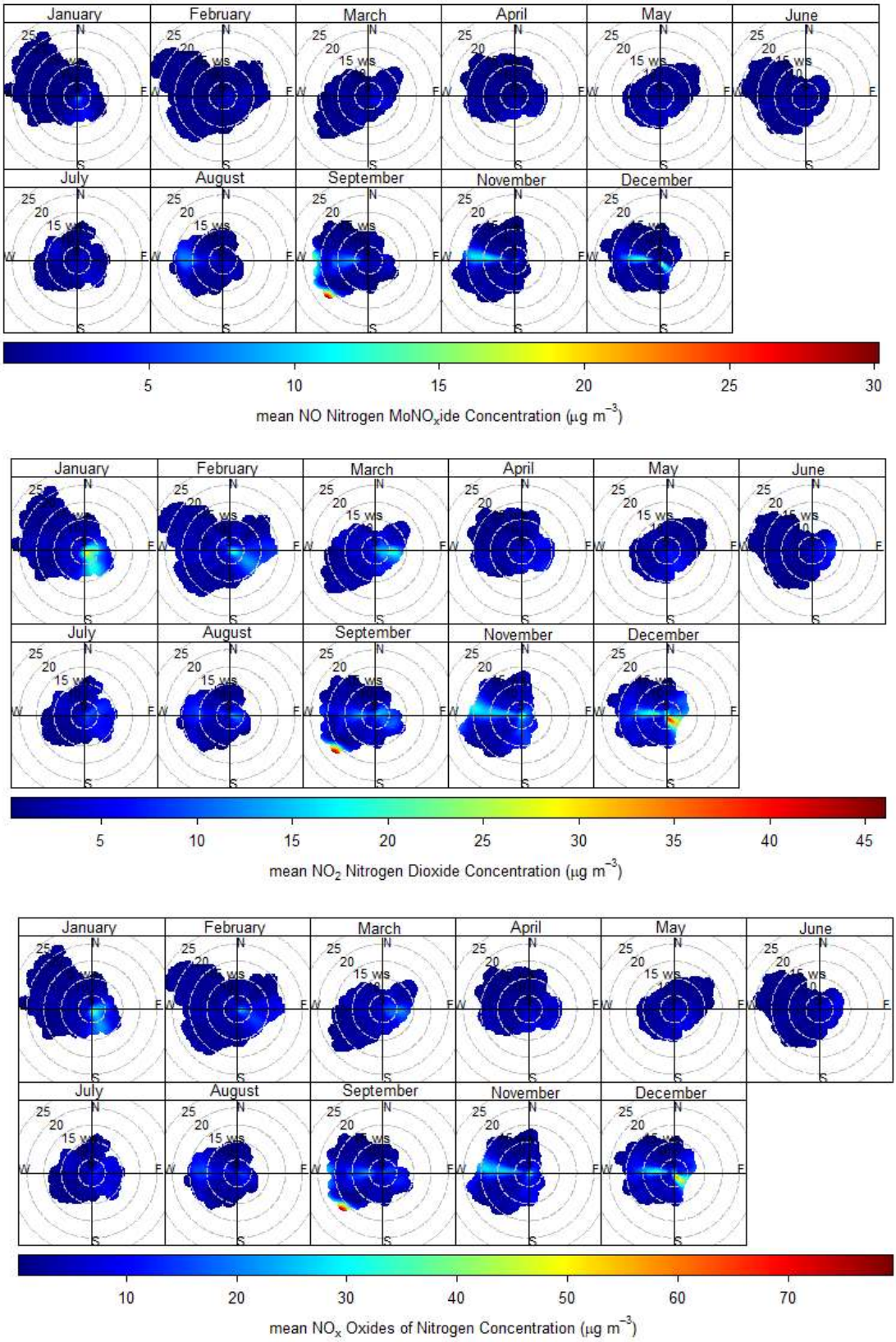


Figure 9.23. Showing bivariate polar plots of the concentration of NO, NO_2, and NO_X on a monthly plot during the year of 2017. **Source:** Grainger (2019)

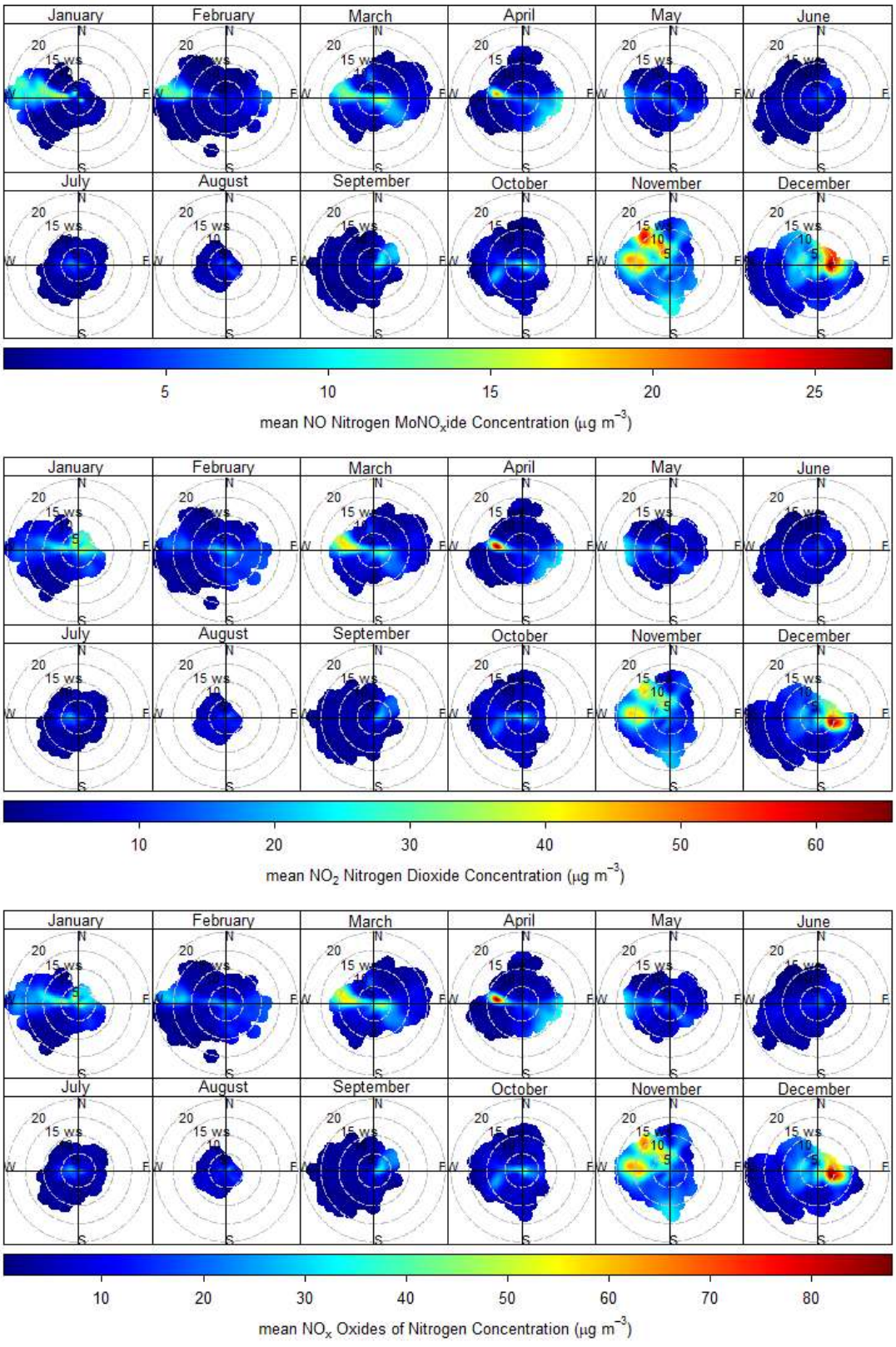


Figure 9.24. Showing bivariate polar plots of the concentration of NO, NO_2, and NO_X on a monthly plot during the year of 2018. **Source:** Grainger (2019)

H. Discussion of Spatial-Temporal Variations in Nitrogen Compounds at the Little Plumpton UNG site.

The NO_2 and NO_X concentrations were well below the hourly, daily, and the annual UK and Scottish air quality standards. However, while nitrogen gas pollution was not in breach of the air quality standards, there are major spatial and temporal variations in nitrogen gases at the monitoring station.

These spatial variations mainly came from two hotspot sources, these were;

I. Eastern Source.

There were major seasonal differences in the concentration of nitrogen gas from the east, throughout all three years of analysis. However, the most significant year on analysis was 2018 suggesting a change to the supply of nitrogen gas in that year. The source of Nitrogen gas was conjectured to be the same source as per PM, i.e. the Plumpton Hall dairy farm, and hence from sources related to agricultural (dairy-related) emissions.

There are three main agricultural sources of nitrogen which are likely to have a combined effect on the nitrogen pollution from the farm, these sources are;

- **Animal Feed.** Dairy farmers typically feed animals higher concentrations of crude protein (CP) than the animals require, maximising the yield from these animals(Reynolds *et al.* 2017). These feeds are nitrogen-rich and can become pulverised and mixed with animal wastes, where they produce nitrogen emissions (Havlikova *et al.* 2008; Mali *et al.* 2013).

- **Animal Waste.** Around 75% of the nitrogen in dairy cattle feed is excreted as manure (Mali *et al.* 2013; Reynolds *et al.* 2017). Each dairy cow produces ~40.50 grams and 135.75 grams of nitrogen from urine and a further 1.56 kg of nitrogen from manure (Havlikova *et al.* 2008; Campbell and Marshall 2016). Indeed, out-gassing from manure can lead to deadly concentration of NO_2 within cattle barns (Verhoeff *et al.* 2017). Several cattle barns and an animal waste pit are found at Plumpton Hall Farm.

- **Silage Gas.** A silo of silage was observed on Plumpton Hall Farm (Grainger 2019; Ordnance Survey 2019). Silage comprises grass or other green fodder compacted and stored in silos. The material is collected in August, and nitrogen gases are formed after they are ensiled due to fermentation and breakdown by bacteria and fungi, (Verhoeff *et al.* 2017; Driehuis *et al.* 2018). As the silage becomes increasingly deprived of oxygen, nitrophilous bacteria feed on the nitrate in the material and expel nitrogen monoxide, (Driehuis *et al.* 2018). As NO leaves the silo, it reacts in ambient air to form NO_2. Peak concentrations of NO form after five days; however, concentrations continue to be produced for up to 2 months after being ensiled (Driehuis *et al.* 2018). Concentrations of nitrogen oxide within silos can reach concentrations of between 250 to 2500 $\mu g/m^3$ and be inherently toxic (Verhoeff *et al.* 2017; Amaza and Kreidy 2019).

II. Western Source.

In 2017 and 2018, a second prominent source of nitrogen gas becomes significant. This source is present from the west at moderate wind speeds. Because of the spatial and temporal parameters of this source, the hotspot was likely from emissions at the PNR UNG development site. There were low concentrations of nitrogen from this direction through to the summer of 2017. However, the concentration of nitrogen rose in June before becoming a substantial source during the autumn. The background year of 2016 showed that there were low concentrations of nitrogen dioxide from this direction. Construction activities began at the PNR site in January 2017 and were completed in July 2017. During this period, many mobile construction vehicles and generators emitted nitrogen dioxide. However, these emissions were insufficient and not detected at the monitoring station.

In August 2017 drilling began at the PNR site, which required high voltage power 24 hours a day which was supplied via a series of diesel-electric generators (Arup Group 2015). These generators likely emitted substantial quantities of nitrogen to the atmosphere each day; however, the emissions were not significant enough to be registered by the National Atmospheric Emissions Inventory, (Arup Group 2014; NAEI 2017). While the rig power system was a constant emitter of nitrogen, emissions may have been greater due to vehicular emissions providing materials to the site. In 2018, the annual spatial concentrations of NO and NO_2 from the western Hotspot doubled and source characteristics changed most notably in November. From July 2018 to September 2019, the PNR site was hydraulically fractured and additional power and flaring activities may have led to some increase noticed at the monitoring station and have been a source of air pollution.

Overall, it is conjectured that the Western hotspot was caused by the Preston New Road UNG development site, likely from the following sources:

- **Generators.** The rig power generators used during the drilling stage were replaced with eight generators. However, the other support generators used in the drilling stage continued to supply power to the site. These diesel generators were 6x Caterpillar 3512C engines and 2 x Caterpillar C13 engines (ARUP Group, 2015). Only one of the C13 engines constantly ran, with the remaining engines only running for around 12 hours a day during hydraulic fracturing (Arup Group 2015).

- **Ground Level Flares.** The flaring of methane at the PNR site was only permitted for safety reasons (Arup Group 2014; UK EA 2019). In January 2019 alone, there were three occasions where flaring was required (UK EA 2019). However, the UK Environment Agency contests that the resulting level of air pollution was at worst on par with local dairy farm emissions (UK EA 2019). This research is however unable to comment as methane was not an assessed air pollutant of this thesis.

When active the flares Nitrogen oxides emission rate is approximately 7.6 grams per second, which would be a significant local pollutor when the flare is active (ARUP 2016).

I. Nitrogen Directional Contribution to the Mean.

As only the nitrogen gases (and not PM) were visibility effected by a second discrete hotspot to the west. An assessment of the annual contributions from the eastern and western hotspots was calculated using a "Proportion to the Mean" pollution rose (Figure 9.25) using 2016 as the background year.

a. Directional Proportion to the Mean in 2016.

Average concentrations of NO only comprised less than 5% of the total mean from any wind direction. Large concentrations of NO were responsible for most of the contribution to the mean. Most of the NO came from the south-east comprising around 57% of the NO contribution; though the proportion to the mean from the west was about 10% for NO.

East and south-east winds accounted for around 52% of the NO_2 and NO_X while concentrations from the west contributed little to the NO_2 or NO_X, with no wind direction accounting for over 5%. This western contribution was mainly due to low but persistent nitrogen concentrations below the average.

b. Directional Proportion to the Mean in 2017.

In 2017, the eastern hotspot remained a key source of nitrogen Gases. However, there was a secondary source from the west. The western source contributed the second-largest single wind direction source of air pollution at around 23% of the NO_2 and 37% from the cardinal direction, 18-32% more than per 2016. The eastern source of nitrogen continued to contribute about 42-46% of the total NO and NO_2 concentrations, 10% less than in 2016.

c. Directional Proportion to the Mean in 2018.

In 2018, the east and western hotspots contributed much of the nitrogen species present at the monitoring station. The eastern hotspot provided

around 40% of the total NO and NO_2 concentrations. The western hotspot also provided around 40% of the NO and NO_2 concentrations which was a 35% increase over background levels in 2016.

Pollution roses showing the elemental breakdown of Nitrogen Oxides between 2016 and 2018.

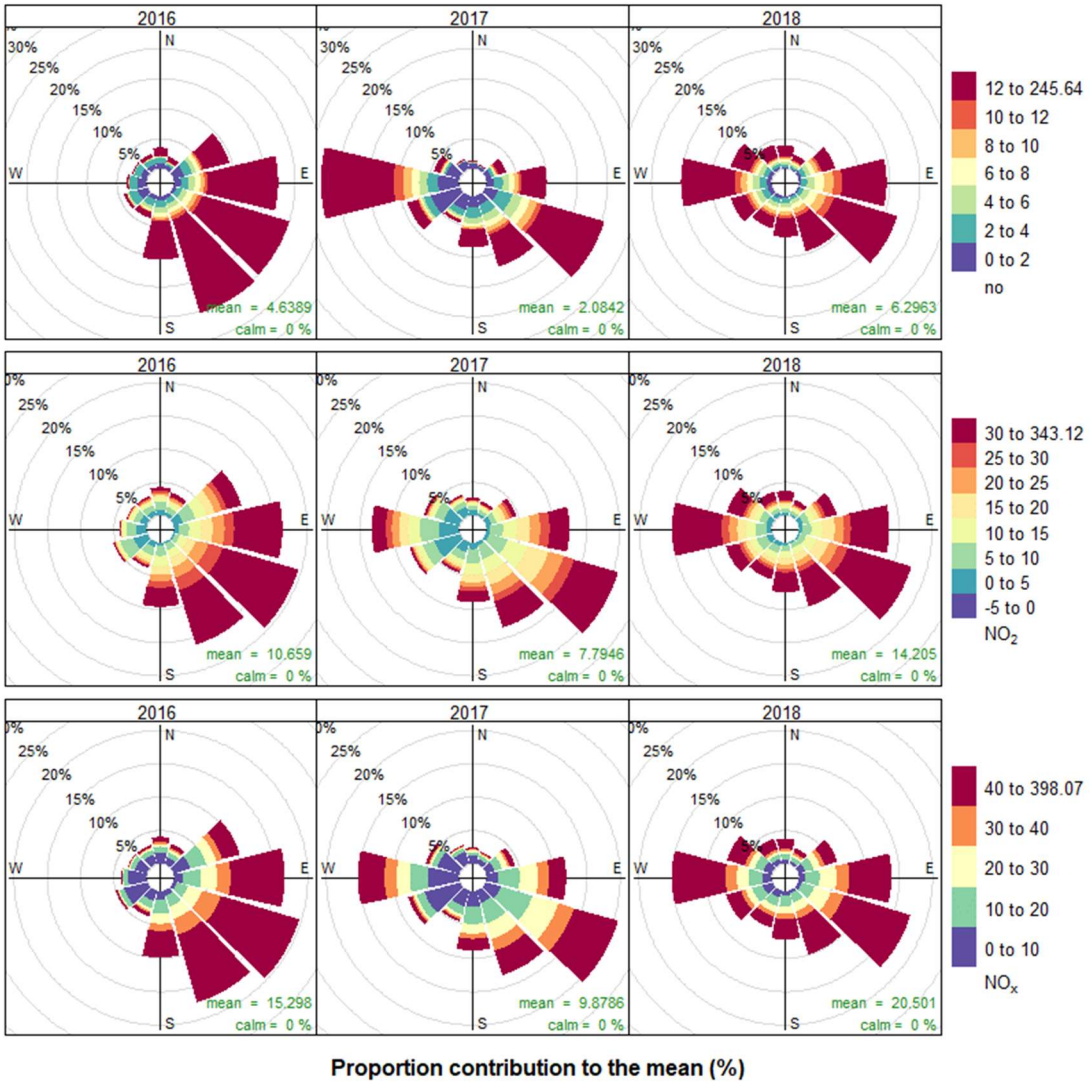


Figure 9.25. A series of pollution roses providing a directional graph of the proportion contribution of the three main nitrogen oxide gases (NO, NO_2, and NO_X) during 2016. 2017 and 2018. The colour scale shows the concentration categories with the top category representing unusually high readings.

Source: Grainger (2019)

J. Summary and Conclusions of NO_X at Little Plumpton.

The second half of this chapter investigated whether there were local influences from the PNR development site between 2016 and 2018 from namely NO, NO_2, and NO_X. However, given the DEFRA's concerns over nitrogen dioxide, NO_2 was the main pollutant used to reflect site-based exposures.

Temporarily concentrations of nitrogen dioxide reduced between 2016 and 2017 with concentrations of NO_2 falling from 11.59 to 8.32 µg/m^3. However, in 2018 the NO_2 concentration rose substantially to 13.62 µg/m^3. This trend was similarly shared with NO, which began at concentrations of 5.21 µg/m^3, falling to 2.13 µg/m^3 and rising again in 2018 to 6.48 µg/m^3. There were subtle seasonal variations with the concentrations of nitrogen oxides falling from the winter months through to the height of summer in July where concentrations again rose throughout the autumn and into winter. However, in terms of the UK ambient air legislation and guidance, all three years were well below even the strictest UK ambient air legislation (Scottish Guidelines). The annual average NO_2 concentrations were about half of the planning thresholds of 30 µg/m^3. While the concentrations were low, the PNR site seemed to have a moderate effect on the concentration of NO, NO_2, and NO_X concentrations between 2017 and 2018. As a westerly source of air pollution was found to the west of the monitoring station, which was not present in the background year (2016). In 2017 and 2018 however, this source contributed between 18-40% of NO_2 and other nitrogen gases to the monitoring station. However, UNG development was not the foremost source of nitrogen air pollution at the Little Plumpton Monitoring Station. Like with the PM distribution, the most significant source was agricultural emissions associated with dairy farming at Plumpton Hall Farm. As with the PM emissions, the levels of nitrogen closely followed the pattern of activity for dairy farmers throughout the year. Overall, this source was responsible for between 40-52% of Nitrogen Dioxide and other nitrogen gases at the monitoring station.

► 9.5) Conclusions of the Spatial-Temporal Variation of PM and NO_X at the Little Plumpton UNG Site.

This study was undertaken to determine whether they were local influences to the Little Plumpton Monitoring Station, from the PNR development site between 2016 and 2018 from selected air pollutants. These air pollutants were oxides of nitrogen (NO, NO_2, and NO_X) and Particulate Matter ($PM_{2.5}$ to PM_{10}). The air quality for both PM and nitrogen was well within even the strictest standards for air quality in the UK. However, while the air quality was good, there were two hotspots of air pollution at the monitoring station when the air quality data was analysed spatially, these sources were;

- **The eastern Hotspot (Dairy Farm):** which led to high PM and Nitrogen gas concentrations. These concentrations were conjectured to have an agricultural source related to the nearby Plumpton Hall dairy farm operated by T.H Wensley and sons. The increases in both nitrogen and PM concentrations closely follow the changes in a typical dairy farming year, with the highest periods of PM and NO_X in the winter and spring from; overwintering cattle, silage, manure clearance and muck spreading.

- **The western Hotspot (PNR UNG site):** was only significant for nitrogen gases at the Little Plumpton Monitoring Station with negligible effects to the PM concentration. These concentrations notably changed between 2016 and 2017/18 and so were attributed to the development of the nearby PNR Development site 500 metres to the west of the monitoring station. The spatial contribution of this source was about 32% in 2017 and 35% in 2018.

Overall, there were no significant effects on the ambient air quality for PM and Nitrogen at the Little Plumpton Monitoring station. Even when spatially resolved, the effects of the UNG monitoring station were less than nearby agricultural activities.

The UNG site had no significant effect on the PM concentration at the Little Plumpton monitoring station. While nitrogen gases were affected by UNG activity, these were well below the regulatory standards and less significant than agricultural emissions from Plumpton Hall Farm.

► 9.6) References.

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► 9.7 Figure References.

Figure 9.1.a GeoBasis-DE/BKG. (2015) Landsat image of the UK, 7th edn. Google, London, England

Figure 9.1.b Google. (2020) Landsat image of Blackpool.

Figure 9.1.c Infoterra Ltd & Bluesky. (2020) Landsat image of Blackpool, Getmapping PLC, Fleet Hampshire, England.

Figure 9.2 Map showing the area around the UNG development site at set buffer distances of 500 m and 1000 m" [PDF map], Scale 1:20000, 1:25 000 Scale Colour Raster [NTF geospatial data], Updated: 2019, Ordnance Survey (GB)Using: EDINA Digimap Ordnance Survey Service, <http://digimap.edina.ac.uk/>, Created: September 2019

Figure 9.3 A map of the PNR development site, the village of Little Plumpton and the location of the monitoring station. Annotated is a series of key features. [PDF map], Scale 1:20000, 1:25 000 Scale Colour Raster [NTF geospatial data], Updated: 2019, Ordnance Survey (GB)Using: EDINA Digimap Ordnance Survey Service, <http://digimap.edina.ac.uk/>, Created: September 2019

Figure 9.4 British Geological Survey. (2020) Air quality monitoring equipment at the Lancashire site. In: Atmospheric composition in Lancashire. *Reproduced with the permission of the British Geological Survey ©UKRI. All rights Reserved*. TinyURL.com/y7qvqo77. Accessed 8 May 2020.

END OF REFERENCES.

Supplemental 9.A:

A list of codes used in RStudio's OpenAir Package.

Loading The software package:

```
mydata <- read.csv(file.choose(), header=TRUE)

install.packages("openair")

library(openair)

mydata$date <- as.POSIXct(strptime(mydata$date, format =
"%d/%m/%Y %H:%M", tz = "GMT"))

summary(mydata)
```

Creating a Summary Plot:

```
summaryPlot(mydata)
```

Creating a Wind Rose:

```
windRose(mydata)
```

Creating a Normalised Graph:

```
timeVariation(mydata, pollutant = c("pollutant 1", " pollutant 2", "
pollutant 3", "pollutant 4"), normalise = TRUE)
```

Creating a Polar Plot:

```
polarPlot(mydata, pollutant = " pollutant 1", key.position =
"bottom", key.header = "axis title", key.footer = NULL)
```

Creating a CPF Ratio Polar Plot:

polarPlot(mydata, pollutant = "pollutant 1", statistic = "cpf", percentile = 90)

Creating a Proportion to Mean Polar Plot:

pollutionRose(mydata, pollutant = "nox", statistic = "prop.mean")

Smoothed Monthly Data:

```
smoothTrend(mydata, pollutant = "NOX", ylab =
"concentration (mg/m^3)", main = "monthly mean NOX")
```

END.

CHAPTER 10:

Updated Human Risk Assessment and Thesis Conclusions.

"When we come full circle there is a feeling that
we have come to a familiar place, but
we are somehow different".
M. Pope [Author], 1965 - Present

► 10.0) Aims and Objectives of this thesis.

At the start of this thesis, a series of aims and objectives outlined the direction of the PhD. However, the aims and objectives cast an intentionally wide net to further concentrate the focus of the thesis into activities which were of high-risk to occupational and environmental health. The preliminary risk assessment was, however, constrained by the overarching aim of the thesis; this aim was to;

> *"Identify the primary sources of combustion and particulate-related air pollution (i.e. particulates and nitrogen gas) proximal to onshore UNG development sites, to develop methods for quantifying exposure to these air pollutants, and to help determine their occupational and environmental health effects".*

The key air pollutants were fine particulate matter ($PM_{2.5}$, PM_{10} and black carbon) together with several nitrogen compounds (nitrogen monoxide [NO], dioxide [NO_2] and oxides of nitrogen [NO_X]). The thesis objectives had minor adjustments following the preliminary risk assessment, so that there was continuity between the sections. The key objectives and sub-objectives were resolved into three parts, which are outlined overleaf;

A. To develop an occupational and environmental health risk assessment of key sources of air pollution on active onshore UK UNG operations. The risk assessment was to review; the health effects of air pollution together with the UNG development stages in the UK. The principal objective was to create a risk assessment and targeted investigation strategy for the two most significant hazards. These hazards were ultimately found to be air pollution from ICE (Internal Combustion Engine) emissions and occupational exposure to drilling mud.

B. To develop measurement systems to characterise occupational and environmental exposure to particulate air pollutants within complex environments, which could be used at UNG developments i.e. the use of novel personal air sampling methods.

C. To use statistical computing to characterise air pollution near to UNG development sites and similar complex environments. These methods most often relied upon open access data from a myriad of governmental sources. The principal sources identified in the risk assessment (objective A) were investigated in part with statistical computing.

► 10.1) What We Have Learned.

The objectives which were outlined in the introduction (Section 1.2) formed the main drive of the thesis, and each of the learning outcomes of this work have contributed in some way to the driving forward of these research goals.

♦ 10.1.1) Objective 1: Preliminary Risk Assessment.

As outlined in Section 1.2.a and summarised in 10.0, the first objective was implemented to develop a comprehensive environmental and human health risk assessment which serves as the rationale for the direction of the thesis. This objective was undertaken in four parts in Chapters: 2, 3, 4, and 5. Chapters 2 to 4 provide the background information for the preliminary risk

assessment in Chapter 5. Outlined below is a summary of the main findings related to Objective A:

- Chapter 2 addresses the key air pollutants and their main human health ramifications following acute, chronic, and occupational exposures. This chapter outlines the damage which can befall a receptor, following adverse exposures to the criteria air pollutants used in the risk assessment.
  The physiological effects of these air pollutants affect almost every system of the human body, but were most severe within the respiratory, nervous, and cardiovascular systems (WHO 2013; Khreis *et al.* 2017; Cosford 2019; COMEAP 2019; PHE 2019; Valacchi *et al.* 2020).
  In the short-term, PM can lead to a range of influenza-like symptoms, an increase in asthma incidence, hospital admissions, and mortality (Khreis *et al.* 2017; COMEAP 2019; Valacchi et al. 2020). In occupational settings and in the longer term, PM exposure can lead to pneumoconiosis, which if it develops into Progressive Massive Fibrosis (PMF) can be fatal (Donaldson and Seaton 2012; McIvor and Johnston 2016; Amaza and Kreidy 2019). Less severe occupational diseases can manifest in a number of ways, such as occupational asthma, allergenic rhinitis, and COPD (Chronic Obstructive Pulmonary Disease) (Bernstein 2016; Balogun et al. 2018; HSE 2019). Meanwhile, Nitrogen in the short-term, causes a similar range of symptoms as per PM (COMEAP 2015; CBI 2018; ATSDR 2019). Distinctly though, nitrogen oxides lead to asphyxiation, silo filler's disease and ARDS (Acute Respiratory Distress Syndrome) at moderate to high concentrations (Chang and Frendl 2015; Nordgren and Bailey 2016; ATSDR 2019).
- Chapter 3 addresses the legislative context of air quality assurance within the UK. The regulation of air quality is governed by the European Union (EU), which issue directives to member states, who then implement these into legislation within the member state (Defra 2018; Heyvaert *et al.* 2018).

There are three main legal structures in air pollution legislation in the UK; these are;

- The Air Quality Standards Regulations 2010, which established the UK ambient air standards,
- Control of Substances Hazardous to Health Regulations 2002, which established the UK Workplace Exposure Limits (WEL)
- Reporting of Injuries, Diseases, and Dangerous Occurrences Regulations (RIDDOR) - 2013.

The UK's Daily Air Quality Index (DAQI) was used for determining adverse health outcomes in the general population (COMEAP 2011; Defra 2018). The DAQI was used where low concentrations of air pollution were expected. The legal framework (WEL and RIDDOR) indicates that the "quality of air" can be a receptor, meaning that adverse air quality outside of a work-site can be "harmed" even if there is no human interaction (Hyland 2017; Thunis 2019; Waldschlager *et al.* 2020).

- Chapter 4 introduces the UK's onshore Unconventional Natural Gas (UNG) industry in both current and historical petroleum extractive industries including mining, offshore production, and onshore reserves (Scott 1922; CSA International 2011; ROENG 2012; Dean 2018). The chapter sets UNG into its geological context, discussing both conventional and unconventional reserves (e.g. coalbed methane, tight sand, and oil shale), (ROENG 2012; OGA 2013).
- Chapter 4 then discusses the development of onshore UNG, based on the experience at Preston New Road (PNR), (ARUP Group 2014), allowing for a more in-depth assessment of airborne hazards likely to be encountered at UNG development sites. An explanation of UNG was critical to a robust preliminary risk assessment in Chapter 5.

- Chapter 5 forms a preliminary Health Risk Assessment (HRA) of airborne pollution from the UK's onshore UNG developments based on the source-pathway-receptor model and the conceptual understanding from chapters two to four (Hyland 2017; Thunis 2019; Waldschlager *et al.* 2020). A series of key sources were identified from an extended literature review. The key sources included; vehicular ICE emissions, non-vehicular ICE emissions (generators), mobilised soil and aggregate dust, drilling mud (including arisings), accidents (releases of gas and explosions), combustion-related air pollutants (flaring) and well stimulation (Broni-Bediako and Amorin 2010; ARUP Group 2014; US CONIAC 2015; Goodman *et al.* 2016; Kaden and Rose 2016; Ezani *et al.* 2018; Mason 2020).

  A preliminary risk assessment was undertaken to set the likelihood, consequence, and exposure duration of the sources into a semi-quantitative risk threshold, based on the findings of Chapters 2, 3 and 4 (ICMM 2016; IPIECA-IOGP 2019; Robinson 2019). The two most significant risks identified from the risk assessment were the foci of the PhD research. The use of chemical additives during the drilling stage presented the highest individual hazard within the UNG operation to human health, seconded by 'power generation'.
- When the hazards were grouped into their source categories in Chapter 5, "combustion-related air pollutants" (from power generation, flaring and site transport) became the most significant source. Consequently, drilling mud and combustion-related air pollution were the main research themes of the thesis.

♦ 10.1.2) Objective 2: Methodology Development.

As outlined in section 1.2.B and summarised in 10.0.B, the second objective was implemented to develop measurement systems to characterise occupational and environmental exposure to particulate air pollutants within complex environments, which could then be used at UNG developments.

The main technique were developed within the PhD thesis, these were:

- Personal monitoring of air quality upwind and downwind of ICE (Internal Combustion Engine) sources; in this case, vehicles.

Access to equipment limited the use of personal monitoring techniques in the thesis but some personal monitoring solutions were developed in Chapter 8.

- Chapter 8 utilised personal monitoring devices upwind, downwind and inside of three different bus shelter microenvironments. The monitoring strategy was novel and included one analyst who remained inside the bus shelter. Another analyst migrated up-road and down-road (an analogy for upwind and downwind). The monitoring strategy made it possible to perform continuous monitoring of the source while being able to understand the air quality upwind and downwind. Such useful measurement systems could be used with a significant effect on UNG development sites as per Ezani *et al.* 2018. This monitoring technique could focus on air pollution studies on UNG related generator emissions, drilling mud sources and vehicular emissions.

♦ 10.1.3) Objective 3: Characterisation of UNG Exposures.

As outlined in section 1.2.C and summarised in 10.C, the third objective intended to adapt statistical programming methods to characterise occupational and environmental exposures to combustion and particulate-related air pollutants from UNG development sites and similar complex environments.

Three main sub-objectives were specified within this objective, these were:

I. “Understanding and estimating potential chemical hazards to human health during the drilling stage of the UNG development process”.

This sub-objective was established in two chapters.

- Chapter 7 outlines the drilling mud types and processes required for modern geological drilling techniques at UNG sites (El Boubsi and Andresen 2017). The chapter outlines the concentrations of airborne PM found in different process areas of the drilling rig from an extended literature review.

The review found that solid PM and oil mist are commonly used air pollutants in health and safety monitoring at UNG sites (Simpson 2006; Steinsvåg *et al.* 2006; Bratveit *et al.* 2009; Murray *et al.* 2009; HSE 2014; Kirkhus *et al.* 2019). Little is known about the adverse risks of oil mist exposure, and outside of the military, petroleum, and motor industries - oil mist is considered a minor pollutant grouped under PM (as this comprises both solid and liquid particles), (US NRC 2008; HSE 2014; Google 2020). Notwithstanding, it was decided that PM_{10} would offer a better metric to compare occupational health risks to the known hazards of particulate matter.

A crude ratio between oil mist and PM_{10} was created from a limited set of data from the literature. From this ratio, the concentration of total PM_{10} was estimated at representative locations over UNG drilling rigs, which further allowed for an estimation of the liquid (oil mist) and solid PM fraction, which allowed the back-calculation of PM_{10} when oil mist would not be a pollutant, i.e. when using Water Based [drilling] Muds (WBM).

In addition to the raw concentration data, Hansen (1991) also estimated the silica, barite, and other chemicals in the air from both clean and dirty aerosolised drilling mud. Extrapolating from the substantive findings of Hansen's research, it was possible to calculate the concentration of silica in ambient air and consequently assess the risk of silicosis (ILO score 2/1) to workers in various work zones of the UNG site using both WBM and LTOBM (Low Toxicity Oil Bearing Muds), (Hansen *et al.* 1991; HSE 2002, 2019).

This paper is the first known work to approximate the ratio of solid PM to 'liquid' oil mist.

Lastly, the chapter found that several work zones were especially at high-risk of silicosis with the model estimating risk to rig floor workers (e.g. roughnecks) at 78.50% following almost continuous exposure over 15 years. The risk of silicosis was found to be especially high, and in the light of this risk, it was decided that another chapter should assess drilling mud via an internationally recognised chemical risk assessment.

- Chapter 7 is a chemical-based human risk assessment of drilling mud mixtures proposed at UK onshore petroleum extraction sites. The risk assessment method uses the United Nations Globally Harmonised System of Classification and Labelling of Chemicals Framework, i.e. GHS (UNECE 2019). The study found that WBM present either an unclassified (negligible) or low risk to respiratory health in the short-term. However, chronic exposures might result in an increased risk of sensitisation and cancer. The occupational health risks of WBM were minimal compared to using LTOBM. In contrast to the WBM Muds – LTOBM's were found to be highly irritable and corrosive to the respiratory system. All the LTOBM mixtures presented class one (major) respiratory and carcinogenic risks, with a significant respiratory sensitisation potential. Chronic exposure to LTOBM drilling muds are likely to cause either pneumoconiosis or allergenic alveolitis in, at least, sensitive employees (Donaldson and Seaton 2012; Ralston *et al.* 2018; Barber *et al.* 2020).

  Should a receptor become sensitised and exposure continues, then anaphylaxis may result (Davidson *et al.* 1998; Ralston *et al.* 2018). Until *Dryden v Johnson Matthey* (2018) before the UK Supreme Court, employees had no legal recourse for occupational sensitisation in this jurisdiction, and should they develop adverse sensitivity symptoms, employees were liable to be removed from the industry without legal recourse *(Dryden v Johnson Matthey* [2018] UKSC 18).

This chapter was the first research to address UK drilling mud chemical mixtures, rather than focusing on only the additive components in isolation (HSE 1999). The method allows for a much more accurate assessment of the chemical harms of the whole mixture on the human respiratory system, rather than previous methodologies which use the single 'worst chemical approach' (Mitchells & Butlers 2016).

II. The second sub-objective provided an "estimation of key vehicular emissions of air pollution to assess potential respiratory hazards to roadside receptors at a UK UNG development site". To help deduce the effects of roadside air pollution, Chapter 8 assessed human exposure to Black Carbon, $PM_{2.5}$ and Nitrogen Dioxide at a series of bus shelters along Hope Street, Glasgow.

The findings of the chapter are summarised below;

- Chapter 8 highlights the potential of vehicle emissions to affect the health of roadside receptors. Whilst the study focussed on bus stops along Hope Street, the buses (which use a similar engine to Heavy Goods Vehicles [HGV]) and general road vehicles are analogous to the roadside environment at the A583 Preston New Road (ARUP 2014). The study found that three panelled bus stops lead to higher levels of $PM_{2.5}$ relative to less enclosed bus stops. Though, other pollutants, including black carbon and nitrogen dioxide, increase with less enclosure of the structure. This exposure pattern should be similar at sites like Preston New Road, where there are semi-enclosed shelters (such as site security entrances and protestor-built shelters).
- As far as the author is aware, the work is the first to study bus shelter microenvironments using either a mobile sampling approach. This research is the first to suggest that bus shelter design could be important in reducing kerbside exposures of air pollution during commutes using public bus transport. Currently, air pollution is not considered when selecting a bus stop design, despite these designs potentially substantially decreasing

commuter exposure using public transport (DoT 2020; Transport Scotland 2020; TFL 2020).

III. Use of Open Access (OA) data from air quality monitoring stations to determine spatial-temporal trends within UNG and other complex environments. This sub-objective was accomplished in two chapters.

- Chapter 8 (Experiment II) explored a pollutant ratio between Black Carbon to Nitrogen Gasses (NO, NO_2, and NO_X) via OpenAir which could determine the proximity of combustion-related air pollutants in complex settings (i.e. within an inner-city environment) (Carslaw and Ropkins 2012; Carslaw 2015). BC (Black Carbon) is likely to persist longer in the environment than NO_X, and therefore should indicate the proximity of combustion-related emissions (Carslaw *et al.* 2006; Wang et al. 2011; Defra 2019). The experiment focusses on the High Street and Townhead monitoring stations in Glasgow. At these monitoring stations, the ratio offered hints at hotspot sources which are otherwise overshadowed by the local phenomenon (vehicular emissions). The sources of nitrogen-rich air at the High Street Monitoring Station include the nearby road, busy A-road junctions, car parking facilities, and the Wellpark Brewery. Whilst at the Townhead Monitoring Station, the ratio suggests impacts from Nitrogen-rich air from nearby roads, including the A804, North Hannover Street, St Mungo Avenue, and the Townhead Interchange (M8). The ratio between BC and NO_X offers great promise in the evaluation of air pollution apportionment studies as a sign of the sources of local air pollution, even in inner-city environments. This analysis is the first work to use the ratio of BC to nitrogen compounds in the investigation of ambient air environments to find sources of combustion-related phenomenon (as far as the author is aware).

- Chapter 9 analyses the data from the Little Plumpton Monitoring Station (near to the PNR UNG development site) between 2016 and 2018 using RStudio's OpenAir package. The monitoring station measures oxides of nitrogen (NO, NO_2, and NO_X), particulate matter ($PM_{2.5}$ to PM_{10}) and meteorological information to determine whether there were any changes in the air quality coinciding with the construction and drilling-related activities at the PNR UNG site (ARUP Group 2014).

  The analysis found that two major sources contributed to air pollution at the monitoring station; these sources came from an eastern and a western hotspot. The eastern hotspot was associated with agricultural emissions from a nearby dairy farm (i.e. Plumpton Hall Farm) whereas the western hotspot was, likely, due to the Preston New Road UNG site some 500 metres to the west of the station. The western hotspot was only statistically (and graphically) significant for nitrogen oxides at the Little Plumpton Monitoring Station, with little effect on PM-related air quality. Whilst the UNG site was present on the OpenAir bivariate polar plots, the effects of this air pollution were negligible at the Little Plumpton Monitoring Station and well within current regulatory limits. The dairy farm posed a much more significant risk to local air quality in terms of PM and NO_X air pollutants.

  This study is the first to look at the air quality data from the Little Plumpton Monitoring Station, assessing the impact of PNR on the local air quality. Whilst this author did not contribute to the collection of data at the PNR development site (the field monitoring was undertaken by the Universities of York and Manchester exclusively) the data was publicly available with the proviso that the data collectors are properly cited.

The data was graciously published in an open access repository. The author would like to thank these researchers for their public service and the advocation of free and open data, by citing an acknowledgement here;

> *"These data were produced by the universities of Manchester and York (National Centre for Atmospheric Science) in collaboration with the British geological survey and partners from the Universities of Birmingham, Bristol, and Liverpool and Public Health England, undertaking a project grant-funded by the Department for Energy & Climate Change (DECC), 2015-2016 ". – CEDA Archive (2020).*

Chapter 9 was illuminating to the controversy of UNG developments; as there is a division in the scientific literature between those who speculate that UNG exploration leads to a wide range of health consequences and those that dispute these hypotheses (ROENG 2012; Scottish Government 2014; Priestly 2018; Welsh Government 2018). This study is the first to add weight to this argument, using monitoring data from a UK UNG development site. According to this research, the effects of UNG on local air pollution are likely to be minor from discrete UNG sites (i.e. similar to the PNR site) and easily overshadowed by other more common local sources such as agricultural buildings.

► 10.2) Updated Human Health Risk Assessment.

The substance of the preliminary risk assessment in Chapter 5 can, on the basis of this thesis, be revised to include the classification of the consequence, likelihood and overall categorised risk profile.

The information acquired through the thesis relates to: -

- **Drilling mud, arisings and well fluids** (Chapter 7).
- **Site transport** (Chapters 8 and 9).
- **Soil, aggregate, and proppant** (Chapter 9).
- **Power generation** (Chapter 9).
- **Flares** (Chapter 9).

♦ 10.2.1) Drilling Mud, Arisings and Well Fluids.

Drilling mud was found to be as consequential to human health as predicted in the preliminary risk assessment. Whilst WBM was relatively low risk, LTOBM was found to pose a class one (major) hazard to the respiratory health of workers, according to the GHS framework (UNECE 2019).

Substantial adverse health consequences could affect employees who work with drilling mud, especially in the long-term with chronic exposure where diseases such as Pneumoconiosis could present a significant long-term risk (HSE 2002; Barber and Fishwick 2020). Rig floor workers, such as roughnecks, are likely to be at an increased risk as they are exposed almost continuously over their shift due to the nature of the tasks they undertake (i.e. disconnecting the drill pipe and handling dirty equipment), (Ormerod *et al.* 1998; Bratveit *et al.* 2009; Steinsvåg *et al.* 2006; Kirkhus *et al.* 2015). Given that there are clear source-pathway-receptor linkages outlined in the literature, together with the impact these exposures are likely to have on the respiratory health of workers, the high-risk profile of the preliminary risk assessment is upheld as significant within occupational settings (Bratveit *et al.* 2009; Steinsvåg *et al.* 2006; Kirkhus *et al.* 2015).

In terms of risk characterisation: adverse exposure to dust is likely to lead to occupational diseases such as pneumoconiosis in the long-term (80), with exposure likely to occur continuously over an employee's shift on the drill floor (12), with evidence in the literature and this assessment to suggest that not only is harm already taking place, but also to suggest that such exposure is practicably inevitable to rig floor workers (1,024).

In terms of ambient air quality, Chapter 9, which assessed the concentration of air pollution from the PNR UNG development site, failed to detect any notable increases in fine dust ($PM_{2.5}$ to PM_{10}) concentrations offsite during the drilling stage. The lack of hotspot was found, despite a complimentary wind direction, good air pollution equipment and data to detect changes to the ambient PM concentration from pre-development to the completion of geological drilling. This assessment shows that such dust emissions were not significant enough to noticeably affect the local air quality at the nearby village of Little Plumpton. The absence of such air pollution is correlated well with other work undertaken in Poland which also found that dust emissions away from UNG sites were nugatory (Jarosławsky 2017; Ezani *et al.* 2018).

This chapter, therefore, serves to decrease the likelihood of the risk of drilling mud in the wider community to a low likelihood (16) instead of previous likelihood score of "very high likelihood" (1,024) as characterised by Table 5.9. The consequence of these exposures would likely lead to only negligible increases in ambient air pollution at worst (Score 8).

♦ 10.2.2) Site Transport.

Site transport was another item of the risk assessment. Though this item was only limitedly discussed in the thesis; Chapter 9 could screen for significant sources of PM and NO_X related air pollution near to the Preston New Road development site and the A583. The basic physiological consequences of exposure to ICE-related emissions are well known and were covered in-depth in Chapter 2. Consequently, the classification of hazards are upheld in this risk assessment (PHE 2018; COMEAP 2019; Cosford 2019).

Protestors and police officers spend many hours on the pavement next to the highway where they are likely exposed to high concentrations of ICE-related emissions, especially during large HGV convoys, which can occur several times a day (Jackson and Monk 2014; Mcewan 2017; Dann *et al.* 2018; Marshall 2018). Whilst these concentrations were not detected at the nearby Little Plumpton Monitoring Station (in Chapter 9), the results of Chapter 8 suggest that there may still be very high concentrations immediately next to major arterial roads such as A-Roads. Though, apparently, these effects may be immediately local (within metres of the road). It is difficult to identify the effects of the hazard to the local air quality in the wider community, however, given the lack of any clear increase in the air quality at the Little Plumpton Monitoring Station from the development, it is conjectured that any increase in air pollution is likely to be minor at worst (score 16). However, the increase in road use from police and HGV using the site, together with a decrease in vehicle speed, has led to local air pollution.

However, the full effects of these vehicular sources would have to be determined quantitively with bespoke computer modelling in subsequent work. Occupational workers situated at the roadside include police officers, who stand near the guttering, and site security, who stand further back from the roadside behind a site access gate. Both receptors are almost certainly exposed to traffic emissions; hence the probability of an ailment befalling a receptor remained Moderate (64). The exposure duration shall be increased to 12 as exposure is likely to persist over an officer's entire shift which is 10 to 12 hours (Lancashire Constabulary 2018). The consequences of this exposure from 2017 to 2020, may have led to adverse health outcomes increasing the risk score to "moderate" (32) (Kaur 2005; Sørensen 2017; COMEAP 2019). Lastly, whilst air pollution was assessed by the Lancashire Constabulary, it was deemed that *"No issues from any assessment have been raised and no controls or RPE is required".* These findings were based off monitoring station data several hundred metres away from the road.

♦ 10.2.3) Protestor Shelter.

During the thesis, the protestors constructed a new microenvironment with an additional source of air pollution. This microenvironment was a small, poorly constructed shelter next to the A583 Preston New Road slightly north of the site entrance to the PNR development. Within the shelter there is a small woodstove which offers the protestors heat, the ability to boil water, and cook food (as shown in Figure 10.1 and noted on a field walkover undertaken on the 23rd September 2019). The stove is fed by kindling scavenged from the nearby woods and pallet wood of indeterminate provenance. Coincidentally roadside semi-enclosed microenvironments were researched by this thesis, and this allowed for an evaluation of risk both from cookstoves and to persons being exposed to ice emissions due to the shelter microenvironment.

Figure 10.1 a photo of the ill-constructed shelter used by protestors at the PNR site. Note that the chimney feeds into a cookstove, which has been used for both heating and cooking purposes. A small supply of firewood rests at the protestor's feet; the wood was scavenged from the nearby woods, pallets alongside the shelter were also used for firewood.

Source: Google (2020) **Adapted.**

This study is highly relevant to exposures within roadside shelters as it was found that road-borne and human-related particulate matter can become trapped within bus shelters. The study also was performed along a major arterial road analogous to the A583.

Given this research; the protestor-built shelter cannot be dismissed as a source and exposure location of air pollution as it may present a notable exposure location and source of air pollution to protestors at the PNR site. This assessment finds that the consequence of such exposures is likely to cause harm to sensitive receptors, and contribute to any underlying air pollution sensitive co-morbidities such as cardiological, neurological or respiratory conditions (e.g. Asthma, COPD, pulmonary hypertension, etc.) especially in the long-term giving the hazard a consequence score of 32 (Rice *et al.* 2015; Simoni *et al.* 2015; COMEAP 2016, 2019).

Given the northern climate in Lancashire, it is likely that the protestors may often be exposed continually over their protest to either road-borne emissions or from cook-smoke (Score 12).

The probability score is tricky; there are anecdotal reports from a protestor (who asked to remain anonymous) at the PNR site of complaints with their respiratory health when they spend too much time at the roadside. The likelihood of at least partial exposure is almost guaranteed given the structure and its proximity to the roadway, (Kaur *et al.* 2005; Buonanno *et al.* 2011; Morales Betancourt *et al.* 2017). Therefore, given the roadside location, significant biomass release from the woodstove, together with the anecdotal reports, the probability is set at a “High Likelihood” (Score 256). However, outside of the shelter, the effects of the cook-smoke and trapped particulate are likely presenting a non-zero likelihood (Score 1) and lead to negligible effects in air quality (Score 8).

♦ 10.2.4) Power Generation.

The potential risks of power generation were only touched upon during this thesis, mostly in Chapter 9 of this thesis. The chapter investigated the PM and nitrogen oxide sources of air pollution at the Little Plumpton Monitoring Station. The study found a negligible change in PM from the direction of the UNG development, but a significant source of Nitrogen Dioxide. Given that the air pollution was relatively clean, and that there were few entrained particles within the air pollution (or they did not travel far) it was hypothesised that the source of air pollution came from diesel generators used to supply power during the drilling and later hydraulic fracturing stage of the UNG project at PNR. Additionally, the author presented research to the EU-JRC and was involved with an investigation on-site diesel-related generator emissions from a UNG test site in Poland (Grainger 2017; Ezani *et al.* 2018). This study supported the hypothesis that diesel generators are a key occupational respiratory hazard on UNG development sites (Grainger 2017; Ezani *et al.* 2018).

Based on these findings this risk assessment finds that the risk profile to occupational air pollution from power generating sources shall stay the same, with continuous exposures to workers (score 12) likely to bring minor harm (score 16); with convincing evidence in Poland and the UK to suggest that the hazard already exists or may be inevitable in the long-term (score 1,024). In terms of risks to ambient air, the magnitude of change was minor from the PNR development and may foreseeably make up about a 5-10% increase in NO_2 concentrations at the site in a worst-case scenario (score 32). The likelihood of such an event is very high (score 1,024) with evidence to support changes of this magnitude in Chapter 9.

♦ 10.2.5) Flares.

Following a review of nitrogen related air pollution at the UNG development site; the impact of flares was less of a risk than originally expected. Chapter 8 (Experiment II) and Chapter 9 conjectured that ICE emissions are much cleaner than uncontrolled combustion or stack emissions from general industrial sources. The chapter continued to exemplify this hypothesis by showing that ICE emissions were rich in nitrogen oxides compared with a subsect of particulate matter (Black Carbon). In Chapter 8 (Experiment II), nearby industrial emissions produced by the Wellpark Brewery were especially rich in fine particulate matter (Black Carbon). It, therefore, follows that emissions from the UNG site from flares should have provided a strong PM to NO_2 ratio; however, the ratios at the Little Plumpton site were unremarkable and such ratios did not produce any significant spatial trend. Neither were there suspended PM concentrations, congruent with burning, detected within Chapter 9 of this thesis. It was therefore found that such emissions were likely due to much cleaner diesel combustion processes within generators.

It is now felt that the hazard profile of flares can be substantially reduced with these findings. The findings now suggest that air pollution is only likely to lead to negligible increases in the air quality at short distances from UNG developments (though not necessarily at the boundary), i.e. a consequence score of 8. These sources are unlikely to present any meaningful increase above this level, i.e. showing a score of 4. In terms of occupational hazards, whilst all elements are present for a hazard to occur it is not likely to occur even in the longer term (score 16). When this occurs, exposures are likely to only occur roughly once per shift at peak times (score 8), and the consequence of such exposure would only cause mild symptoms such as coughing (score 16).

♦ 10.2.6) Soil, Aggregate, and Proppant.

Chapter 9 found that there were no significant increases in PM-related emissions from the direction of the PNR site, which would have been consistent with fugitive emissions of soil, aggregate, or proppant released during the construction, drilling or early fracking stages. The lack of a PM source from the west in Chapter 9 led to the reduction of the hazard profile of this activity to negligible harm (consequence score 8) despite there being some elements under which a hazard could occur (probability score 4).

Despite this, there is emerging evidence of high on-site concentrations of PM during the construction phase of the development. Notably, on promotional material released by the operators at PNR, notable clouds of dust were seen when soil and aggregate were moved around the site (Cuadrilla Resources 2017a). It is, in the author's opinion, that the duration and likelihood of occupational exposure at the PNR site cannot be downgraded. The risks of PM inhalation (especially for silica) became better known during this thesis. In hindsight, the consequence of PM exposure from aggregates may be significant enough to cause occupational disease such as pneumoconiosis over the long-term (score 80) where workers are not properly protected by PPE (HSE 2002; Barber and Fishwick 2020).

♦ 10.2.7) Hazards not Further Assessed.

It should be mentioned that no further comments were made on Hydraulic Fracturing Chemicals or Disaster-Related Emissions (including; Escape of gas or asphyxiant, VOC release, or Catastrophic explosion) as these were not directly or indirectly investigated in this thesis. These hazards have been removed from the updated risk assessment; however, the hazard profile of these activities is the same as the preliminary risk assessment as no subsequent work was taken to investigate the risk profile, and no contradictory work was discovered during the course of this research.

► 10.2) Updated risk assessment.

Given the findings outlined above, the preliminary risk assessment found in Chapter 5 has been updated with the conclusions of the research chapters in this thesis. Similar to the preliminary risk assessment, this updated risk assessment uses Equation 5.1 and Tables 5.3 to 5.7 to come to establish the hazard profile. The findings of the updated risk assessment are shown in Tables 10.1 and 10.2.

Table 10.1 The risk of harm to the ambient air quality environment (i.e. community-wide effects) from UNG development sites.

Category	Source	Consequence	Likelihood	Sum risk score	
Combustion-related air pollution	Power generation	32	1,024	32,768	Moderate ↓
	Site Transport	16	1,024	16,384	Moderate ↓
	Protestor-Built Shelter and Firewood Smoke.	8	16	128	Negligible -
	Flares	8	4	32	Negligible ↓
Use of chemical additives	Drilling mud, arisings and well fluids.	8	16	128	Negligible ↓
Construction & remediation	Soil and aggregate and proppant	8	4	32	Negligible ↓

[A] Characterises the exposure class of each of the hazard, assuming an event where all factors which led to the event occurring were in place, and the associated source of the exposure.
[B] Table 5.11 shows the likelihood, consequence, and exposure duration based on Tables 5. (3, 5 ,9 and 10). [C] The last column shows the risk value based on the numerical multiplicity of the three risk factors and compares them against the threshold stated in Table 5.10.

Table 10.2 The risk of harm to the occupational health (i.e. workers) of Unconventional development sites.

Category	Source	Consequence	Exposure duration	Likelihood	Sum risk score	
Use of chemical additives	Drilling mud, arisings and well fluids.	32	12	256	98,304	High -
	Power generation	16	12	64	12,288	Moderate -
Combustion-related air pollution	Protestor-Built Shelter and Firewood Smoke.	32	12	256	98,304	High -
	Site Transport	16	12	64	12,288	Moderate -
	Flares	16	8	16	2,048	Low ↓
Construction & remediation	Soil and aggregate and proppant	80	12	64	61,440	High ↑

[A] Characterises the exposure class of each of the hazard, assuming an event where all factors which led to the event occurring were in place, and the associated source of the exposure.
[B] Table 5.12 shows the likelihood, consequence, and exposure duration based on Tables 5. (6, 7, 8, 9 and 10). [C] The last column shows the risk value based on the numerical multiplicity of the three risk factors and compares them against the threshold stated in Table 5.10.

► 10.3) Findings of the Risk Assessment.

The risk assessment was updated with the findings of the thesis, as outlined in section 10.2. The results of these updated risk factors led to a similar category of risk as found in the preliminary risk assessment, although the risk value has, in many cases, increased. The findings are outlined graphically in Tables 10.1 and 10.2, but are explained in some further depth here;

- **Ambient Air Quality (Negligible):** There was much lower risk than expected for several items on the ambient air quality risk assessment. Several items had such minor effects as to present a negligible hazard to ambient air quality at short distances away from the development site - such that harm is unlikely to befall a receptor. The items which achieved negligible hazards were the protestor-built shelter and firewood smoke, flares, drilling mud, arisings, and soil and aggregate and proppant.
- **Ambient Air Quality (Moderate):** Even these more moderate hazards have a considerably reduced risk profile. Power generation was seen to have a minor impact on local air quality at the Little Plumpton Monitoring Station within Chapter 9, and this was likely much more significant at the site's boundary line. Likewise, whilst the A583 road was not detected at the Little Plumpton Monitoring Station, there logically must have been some impact on immediately local air quality given the reduced vehicular speed and increased traffic flow from HGV and police vehicles following the COPERT Emissions model.
- **Occupational Air Quality Risks (General):** In terms of the occupational risk of the UNG development site, the updated risk assessment finds in favour of the preliminary risk assessment with drilling mud and power generation remaining the two-most significant hazards in the risk assessment. Whilst site transport and soil emissions remain a moderate risk - the risks from flaring were found to be substantially less than first hypothesised.

- **Occupational Hazards (High):** Drilling mud, arisings and well fluids and power generation were found to present a critical hazard to occupational workers on UK UNG development sites.
    - Whilst power generation was only limitedly discussed during this thesis in Chapter 7, there was evidence to suggest NO_2 emissions as far as 300 metres away from the PNR UNG development site, and these emissions were likely much more substantive closer to the site. The author was also involved with work undertaken in Poland, investigating PM and NO_2 emissions from diesel generators during simulated well activities (Grainger 2017; Ezani *et al.* 2018).
    - Drilling mud was considered to pose a significant hazard to long-term drilling crew on the rig floor such that the incidence of pneumoconiosis or extrinsic allergenic alveolitis (hypersensitivity pneumonitis) would be a likely result of a career spent on these oil rigs. The formulations of drilling mud, especially from LTOBM, were found to pose a Class 1 (Major) risk to human health from irritation and cancerogenic risks.
    - In both cases, however, the petroleum industry undertakes routine health screening of workers which may substantially reduce the risk of significant harm to workers. The risks of developing the occupational disease may be well defended against in terms of proactive medical intervention and litigation protections. Until 2018 in Dryden & Ors v Johnson Matthey plc [2018] UKSC 18, there was no restitution for personnel who became sensitised to chemical compounds. Workers who develop an occupational disease are ineligible to work in the industry, and with medical surveillance before and after each project, workers who develop medical conditions are likely to be barred from the profession.

- This policy would lead to much higher turnover rates of petroleum workers with asymptomatic to minor medical conditions. It remains an ethical argument whether a small amount of harm to a great number of people (oil and gas workers – barred from a profession for minor asymptomatic X-ray phenomenon), is the better than, a large amount of harm to a smaller number of people presenting with life-limiting or terminal diagnosis (such as coal miners – who develop asthma, pneumoconiosis, or progressive massive fibrosis).

- **Occupational Hazards (High):** Two hazards were found to have a high hazard threshold these hazards were:
    - Soil and Aggregate fugitive dust emissions: - Whilst no research was directly undertaken on these dust emissions it was considered that based on documentary film released by the PNR operators Cuadrilla; that the risks to respiratory health from this dust is likely to lead to pneumoconiosis over the long-term, especially where employees are exposed to such heavy dust-producing procedures as released by the working of aggregate during the construction phase of the investigation. However, should adequate site workers use PPE procedures, then this hazard could be minimalised. However, anecdotally, the author has a dim view on the use of PPE by construction teams, as compliance with PPE site policy is a very challenging issue in the construction industry.

- **Occupational Hazards (Moderate to Low):** Whilst the hazard from vehicular emissions (site transport) to occupational workers rose because of the updated risk assessment, the risk from flares was lowered to a low hazard profile.
    - The hazard profile of site transport emissions was raised, not due to any of the specific findings of this thesis. However, due to the undoubtedly pollutive effects of decreased vehicular road speeds away from vehicles' optimum emissions speed (50 mph roads reduced to 20 mph), the increased volume of Heavy Goods Vehicles needed to service the site, and from an increase in total vehicular flow with police officers and site users both accessing the site and contributing to local emissions. The effects of this pollution were mostly immediately local as no obvious pattern was clear at the Little Plumpton Monitoring Station 130 metres to the south-east (as established in Chapter 9).

- Whilst, this impact is unlikely to be a significant health risk to residents given the sites rural location, police officers, and protestors at the side of the road may be exposed substantially to vehicular emissions and would endure any increase in these emissions. As they would be exposed continually throughout their service at the side of the road, health ramifications may be possible in the long-term, though these are likely to be relatively minor even to sensitive employees.
- The hazard profile of flares was substantially reduced considering the absence of such emissions being detected at the Little Plumpton Monitoring Station some 300 metres to the east of the PNR development site. Any effects which occur may be minor, of limited duration (15 minutes perhaps once per shift), and whilst all the elements are present to present a hazard; such a hazard may not lead to harm even in the long-term. Save for an accidental release or kick from the development site this risk is unlikely to lead to even a moderate risk of harm to occupational receptors.

► 10.4) Points of Interest for Future Work.

The work of a scholar is never done; there is always something that can be studied to expand the realm of human knowledge further. Alas, there comes a time when we must leave the work to others, to continue to adapt as we make the slow and winding path towards progress. This author speculates that there are several interesting advances in this thesis, which could benefit from further research as they show great promise for air pollution and UNG related research outputs.

These key points are outlined in chronological order, below;

- The siting of bus shelters is an essential part of the public transport system. Chapter 8 (Experiment I) suggests that while the enclosure of bus shelters protects receptors from BC and NO_X emissions, it traps and increases PM inside the shelter (Moore *et al.* 2012). This work opens the dialogue on the role of bus shelter design for the protection of human health. Further research would need to examine the relationship of bus shelter design with reductions in air quality more conclusively, i.e. which styles of bus shelters best protect commuters from poor quality air. With additional research, it may be possible to establish a cost-to-benefit appraisal of different styles of bus shelters. The findings of this and further work could help augment national planning policy around bus shelter design which currently does not account for air quality when choosing bus shelter styles (TFL 2020; DFT 2020; Glasgow City Council 2020).

- Drilling mud was found to be an understudied but high-risk source of PM, presenting unique occupational respiratory health risks which include sensation and physical degradation of the lungs, (Ormerod *et al.* 1998; Steinsvåg *et al.* 2006). Chapters 7 of this PhD theses use the existent literature to assess the risk of airborne exposures. However, these studies are quite old and come from several international sources. Much of the literature is dated, being around 10 to 20 years old (at the time of writing) with little contributory contemporary research. Therefore, to clarify the risks, a contemporary intrusive investigation into onshore UNG drilling mud environments would be required to assess the risks more comprehensively and to determine the level of protection offered by modern drilling tools such as the use of an iron roughneck. However, the chemical composition of the drilling mud is contemporary with the publication of this thesis, and the presence of this mixture has the potential to present highly toxic concentrations of airborne PM to workers.

Of course, the concentration workers are exposed to would need to be categorised, in order to address the harms of these mixtures on workers' health.

- Air quality assessment on petroleum sites often relies on oil mist monitoring. There seems to be only a limited benefit to only focussing on the small PM subspecies - oil mist, as oil mist is a very understudied and poorly appreciated air pollutant, which contrasts strongly against the wealth of information available for adverse fine PM exposures (HSE 2014; Park 2019). It is widely postulated that vapour emissions from the filter membrane are the primary reason for oil mist monitoring over PM, as conventionally filters would have to be weighed before exposure could be calculated. This view is outdated, based on modern air quality equipment's ability to undertake measurement using real-time light attenuation on incoming streams of air without an opportunity for significant volatilisation (RTI International 2016). Therefore, future studies assessing the occupational respiratory health of oil and gas workers may best be undertaken with fine PM exposures or co-monitoring of fine PM (i.e. $PM_{2.5}$ or PM_{10}) rather than oil mist in isolation.

- The OpenAir toolset of R is a fantastic package, offering a diverse suite of air quality statistical computing opportunities. Chapter 9 shows the ratio between black carbon and nitrogen compounds. This ratio is expected to indicate unclean industrial activities, especially with near-source combustion-related activities. Whilst Chapter 9 shows promise in using ratios, further analysis over several unique areas where the sources of BC and NO_X are known would be of significant benefit to determine the reliability of the ratio between BC and NO_X. Further research is needed to determine the utility of the ratio in air quality assessments definitively.

- The ramifications of UNG development sites on local air quality were assessed in Chapter 9. The study correlated with other studies which showed that the community effects of UNG development were relatively low from site generated PM and NO_X emissions (Kaden and Rose 2015; Long 2016; Jarosławsky 2017). The study used the OpenAir toolset of RStudio to analyse the raw data further. The resulting OpenAir graphs show that nitrogen emissions from the PNR UNG site were responsible for a minor contribution to the nitrogen supply at the monitoring station with no discernible contributions from PM. Further research could continue with a similar analysis for the period 2018 - 2020 at the PNR site, incorporating hydraulic fracturing, a brief period of abandonment (following the seismic activity) and well testing phases. The hydraulic fracturing process may theoretically lead to much greater concentrations of process-related PM and NO_X emissions than the drilling mud operations.

► 10.5) Conclusions.

The major sources of combustion-related emissions, particularly Particulate Matter ($PM_{2.5}$ to PM_{10}) and oxides of Nitrogen (NO, NO_2 and NO_X) were evaluated at UNG development sites in a preliminary risk assessment which formed the rationale for this work with the UNG site at Preston New Road, Blackpool as the case study model.

This thesis has helped to evaluate the human health implications of the local air quality from the PNR UNG site as well as discuss the occupational risks of drilling mud used in both unconventional and conventional oil drilling sites across the UK mainland. These studies found that; UNG related emissions are unlikely to pose a considerable risk to human health at a distance from the development. However, sensitive receptors close to pollution sources such as occupational receptors may be at risk from poor air quality at UNG sites.

Indeed, air pollution sources on UNG sites can present major occupational respiratory health risks to people associated with specific UNG activities such as working with drilling mud. The occupational risks of drilling mud could be quite severe and lead to the manifestation of symptoms and consequent removal from the industry.

Other Chapters in this thesis, focussed on quantification techniques which can be used to augment complex industrial emissions, such that could be used on UNG development sites. These methods involved; the use of statistical programming via the OpenAir (RStudio) toolset. Both methods show immense promise in characterising air pollutant sources, as they are both low-cost techniques, albeit they must have a high degree of technical expertise to utilise fully.

► 10.6) References.

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► 10.7) Figure References.

Figure 10.1. Google LLC. (2019) *Google Maps: Street View: Protestor-built shelter along the A583 – Preston New Road.*

END OF REFERENCES

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Appendix

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Appendix A:

Data Associated with Chapter 8 - Air Pollution Concentrations at Bus Stop Structures along a Street Canyon in the City of Glasgow.

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0 - Bus Stop Chapter (9) - README.txt (Text File).

This read me file in a standard text format contains text art to help resolve the spatial scale of the document to the original scale. This file also contains an explanation of the contents of each file associated with this chapter's data, i.e. spreadsheets 1 through 5 and any attribution which is ascribed to these documents.

The readme file can be found here:
https://strathcloud.sharefile.eu/d-s67a62d8256af483282137c9aa276e4ff

1 - Townhead Data.xlsx (Microsoft Excel Open XML Spreadsheet).

The sheet shows the air quality monitoring data at the Townhead Monitoring Station between the Measurement Period of 05/06/2018 at 01:00:00 to the 29/06/2018 at 24:00:00. The air pollutants of interest were NO_2 and $PM_{2.5}$. There were data flags under the column P/R which signify the status of the data at the time of download.

The readme file can be found here:
https://strathcloud.sharefile.eu/d-s6674caf2941b4225980e018a6ce57109

2 - Traffic Monitoring.xlsx (Microsoft Excel Open XML Spreadsheet).

The data shows the number of various classes of vehicles which passed by the area of the street the manual counter was positioned. The number of vehicles was initially taken in field records, but has been transcribed onto an Excel file from the original information. Discrepancy of the authors field counting of the vehicle count were resolved by averaging the two results on this sheet, but otherwise the sheet reflects the as taken data recording from field notebooks. The air quality data per ten-minute segment during the morning and afternoon segments at each of the bus stops was averaged to give 10-minute concentration information. The total $PM_{2.5}$ over these 10-minute timings was divided by the concentration of BC at the same temporal scale to generate a ratio of $PM_{2.5}$ to BC. The air quality data per

ten-minute segment during the morning and afternoon segments at each of the bus stops was averaged to give 10-minute concentration information and presented alongside the traffic monitoring information.

The data file can be found here:
https://strathcloud.sharefile.eu/d-sa6d5ee5d25c4461b9361f77d81e68301

3 - Bus Stop 1 Data.xlsx (Microsoft Excel Open XML Spreadsheet).

This data was undertaken in the first and second week of analysis in the afternoon undertaking BC monitoring with a MicroAethelometer, at the first bus stop at the bottom of Hope Street, Glasgow. The true air quality measurement is preserved in the final right column, this data has been corrected with ONA correction and is divided by the raw-uncorrected data by a vertical line. Unfortunately, due to problems with the machines during this session this data reflects the abandoned experimental data, and is included here solely for prosperity. The true air quality measurement is preserved in the final right column, this data has been corrected with ONA correction and is divided by the raw-uncorrected data by a vertical line. The later sheets of this document contain the data from the MicroPEM $PM_{2.5}$ monitor undertaken at the same locations. The true air quality measurement is preserved in the column RH-Corrected Nephelometer, this data has been corrected in regards to the Relative Humidity.

The data file can be found here:
https://strathcloud.sharefile.eu/d-s0b6574d0b5424b968b4fd40f643281c8

4 - Bus Stop 2 Data.xlsx (Microsoft Excel Open XML Spreadsheet).

This data was undertaken in the first and second week of analysis in the afternoon undertaking BC monitoring with a MicroAethelometer, at the second bus stop in the middle of Hope Street, Glasgow. The true air quality measurement is preserved in the final right column, this data has been corrected with ONA correction and is divided by the raw-uncorrected data by a vertical line. Unfortunately, due to problems with the machines during this session this data reflects the abandoned experimental data, and is included here solely for posterity. The true air quality measurement is preserved in the final right column, this data has been corrected with ONA correction and is divided by the raw-uncorrected data by a vertical line. The later sheets of this document contain the data from the MicroPEM $PM_{2.5}$ monitor undertaken at the same locations. The true air quality measurement is preserved in the column RH-Corrected Nephelometer, this data has been corrected in regards to the Relative Humidity.

The readme file can be found here:
https://strathcloud.sharefile.eu/d-sc1a1de5ecdba44449ae8594e96d0bdd3

5 - Bus Stop 3 Data.xlsx (Microsoft Excel Open XML Spreadsheet).

This data was undertaken in the first and second week of analysis in the afternoon undertaking BC monitoring with a MicroAethelometer, at the third bus stop at the top of Hope Street, Glasgow. The true air quality measurement is preserved in the final right column, this data has been corrected with ONA correction and is divided by the raw-uncorrected data by a vertical line. Unfortunately, due to problems with the machines during this session this data reflects the abandoned experimental data, and is included here solely for posterity. The true air quality measurement is preserved in the final right column, this data has been corrected with ONA correction and is divided by the raw-uncorrected data by a vertical line. The later sheets of this document contain the data from the MicroPEM $PM_{2.5}$ monitor undertaken at the same locations. The true air quality measurement is preserved in the column RH-Corrected Nephelometer, this data has been corrected in regards to the Relative Humidity.

The readme file can be found here:
https://strathcloud.sharefile.eu/d-sa20499b3149a4dd8ad86521809552905

END.

Appendix B:

Data Associated with Chapter 8B - Black Carbon and Nitrogen Ratios at Two Governmental Air Quality Monitoring Stations Using Computer Modelling.

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0 - 0 - NOx BC RATIO (12) - README

This read me file which is in a standard text format and contains text art to help resolve the spatial scale of the document to the original scale. This file also contains an explanation of the contents of each file associated with this chapter's data, i.e. spreadsheet 1 and any attribution which is ascribed to these documents.

The readme file can be found here:
https://strathcloud.sharefile.eu/d-s656856a224584f03af13dc5d8587e66a

1 - Townhead Raw Data (Microsoft Excel Open XML Spreadsheet).

This spreadsheet contains the raw data from the High Street and Townhead Monitoring Station, in Glasgow for the field of study. It was downloaded from the DEFRA website on the 25th February 2019. The data has only been stylistically modified initially, which was sent from DEFRA directly to Sam Grainger University Email Address. The original file format was CSV; however, it is included here as an XLS file. The later sheets show filtered data for the High Street and Townhead Monitoring Station. The filtering process eliminated all of the files which contained unverified data for any of the measurement types and also where no data was recorded for any of the monitoring periods. The file also contains the ratio of Black Carbon to the Nitrogen Species, and vice versa. The last sheet provided details of the coding for the OpenAir Program (As of 15th March 2019) used in this analysis. The code is required with the OpenAir toolset in order to create several graphs and projections, which has been used extensively within this academic work.

The readme file can be found here:
https://strathcloud.sharefile.eu/d-sea054467c500425e8b370c2c7af7972f

END.

Appendix C:

Data Associated with Chapter 9 - Source Apportionment Study of PM and NO_X at an UNG Development Site Preston New Road.

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0 - PNR Source Apportionment (13) - README

This read me file in a standard text format contains text art to help resolve the spatial scale of the document to the original scale. This file also contains an explanation of the contents of each file associated with this chapter's data, i.e. spreadsheet 1 and any attribution which is ascribed to these documents.

The readme file can be found here:
https://strathcloud.sharefile.eu/d-see48ae6a19a9460a992e03ac8baafc62

1 - Little Plumpton Source Apportionment (Microsoft Excel Open XML Spreadsheet).

The spreadsheet's first sheet contains the filtered Little Plumpton Monitoring Station atmospheric dataset shows the wind speed (m/s), wind direction (degrees), air pressure (hPa), temperature (degrees C) and humidity for the entire dataset from 2016 to 2018. The filter has been subject to filtering which is outlined within the screening parameters mentioned within Chapter 13. Following on from this, the spreadsheet displays the data for 2016, 2017 and 2018 which has subject to filtering parameters mentioned within Chapter 13. The nitrogen oxides were corrected in light of the units used in the CEDA archive being PPB and the units used throughout this thesis were $\mu g/m^3$. The data extends from the 1st February 2016 to the 31st December 2016, not-with-standing periods of data loss.

The readme file can be found here:
https://strathcloud.sharefile.eu/d-sce174609d33746daa47cdd74c11aea1d

END.

Appendix D:

Freedom of Information Requests and Inquiries for Information collected during the PhD.

0 - Information Requests (D) - README

This read me file in a standard text format contains text art to help resolve the spatial scale of the document to the original scale. This file also contains an explanation of the contents of each file associated with this data, i.e. 63 .PDF (Portable Document Format) documents.

The readme file can be found here:
https://strathcloud.sharefile.eu/d-s7aaa2533dad645f4970090acbd5e849e

1 - Freedom of Information Requests and Enquiries.zip – PDF Documents.

This archive folder includes 63 PDF documents which were used as supplemental and bibliographic information in this thesis (unless otherwise stated). The file format explains a little about what the document includes, the first part of the filename identifies whether the document is a Freedom of Information Request (2000), or an enquiry to an information holder. The second part of the file name explains what the topic of the correspondence was, whilst the third part of the filename indicates the corresponding entity.

The readme file can be found here:
https://strathcloud.sharefile.eu/d-sae075ef6373941a491001bed47cd0d28

END.