



Study of Ambient Air Quality at Ryton 16 January 2020 and 7 Sep 2020

Date: October 2020

Report No: AAM/TR2020/15

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Executive Summary

This report provides the results of a study to investigate ambient air quality in the vicinity of Blaydon Quarry landfill site, in Ryton, Gateshead. The study was carried out by the Environment Agency's Ambient Air Monitoring (AAM) Team, on behalf of the North East area.

The study involved a monitoring campaign carried out between the 16 January 2020 and 7 September 2020 (236 days). A mobile monitoring facility (MMF) was deployed, containing equipment capable of measuring concentrations of hydrogen sulphide (H_2S) and methane (CH_4). Wind speed and wind direction measurements were also collected.

Comparing the collected data from the monitoring at Ryton with the World Health Organisation (WHO) guidelines showed that H_2S concentrations were well within health limits and were above the odour annoyance limit for 0.01% of the monitoring period.

Directional analysis showed that the highest H_2S and CH_4 concentrations came from the direction of Blaydon Quarry landfill site. Consideration of the H_2S data did suggest that there was an additional source between $190^\circ - 270^\circ$ that was not apparent in the CH_4 data. Elevations in H_2S concentrations could also be seen in the daytime, but this was not apparent for CH_4 .

Diurnal analysis showed that concentrations were higher overnight from the direction of Blaydon Quarry landfill site, when wind speeds and temperatures are lower, H_2S concentrations were also elevated during the day time from this direction.

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1 Introduction

This report provides the results of a study to investigate ambient air quality in the vicinity of Blaydon Quarry landfill site, in Ryton, Gateshead. The study was carried out by the Environment Agency's Ambient Air Monitoring (AAM) Team, on behalf of the North East area.

The study involved a monitoring campaign carried out between the 16 January 2020 and 7 September 2020 (236 days). A mobile monitoring facility (MMF) was deployed, containing equipment capable of measuring concentrations of hydrogen sulphide (H_2S) and methane (CH_4). Wind speed and wind direction measurements were also collected.

The overall objective of the study was to identify the local sources of air pollution and to quantify the environmental impact of the emissions from these sources on the surrounding area and the local community. Within this objective, the following individual aims were identified:

- To assess the general air quality of the area and compare measured H_2S concentrations against relevant WHO air quality guidelines
- To quantify the impact of surrounding pollution sources on local air quality
- To identify specific sources causing an appreciable impact on air quality
- To identify and understand the conditions that give rise to episodes of poor air quality

2 Monitoring Location

The Ambient Air Monitoring team deployed its mobile monitoring facility (MMF 4) on Stargate industrial estate, as shown in Figure 2.1. A number of landfill sites are located in the area, Table 2.1 notes the bearing of these landfill sites from the monitoring location.

With the exception of Blaydon Quarry the landfill sites were not active during the study (with the landfills being capped) and therefore they were unlikely to be sources of odour. Figure 2.2 shows a wider map of the area. A photo of the monitoring location is shown in Figure 2.3.

Figure 2.1: Map of monitoring location and nearby landfill sites

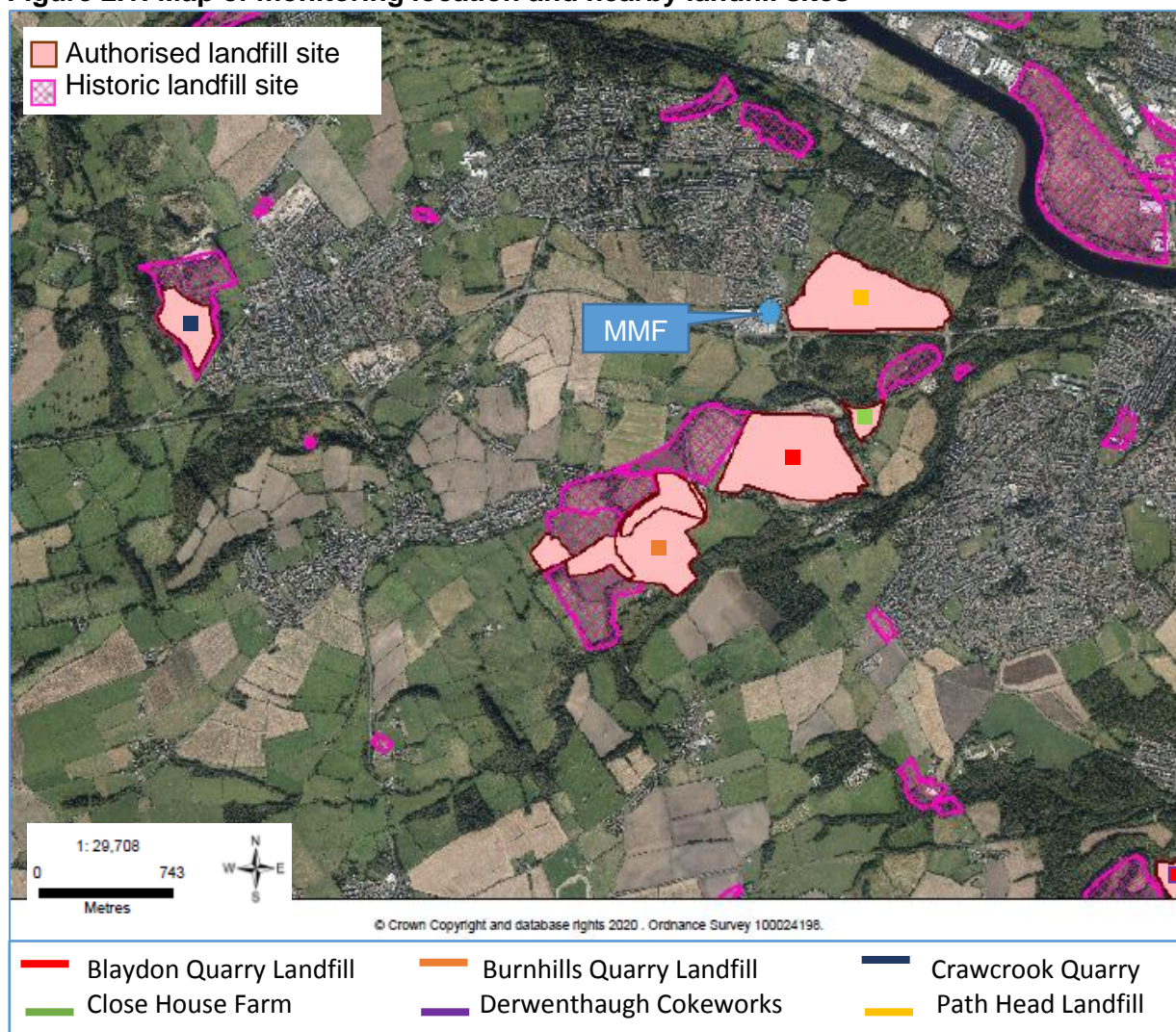


Table 2.1: Bearing of local landfill sites from the monitoring location

Site	Direction from MMF
Path Head Landfill	50° – 120°
Derwenthaugh Cokeworks	110° – 150°
Close House Farm	130° – 145°
Blaydon Quarry Landfill	150° – 200°
Burnhills Quarry Landfill	195° – 225°
Crawcrook Quarry	165° – 275°

Figure 2.2: Map of monitoring location and surrounding area

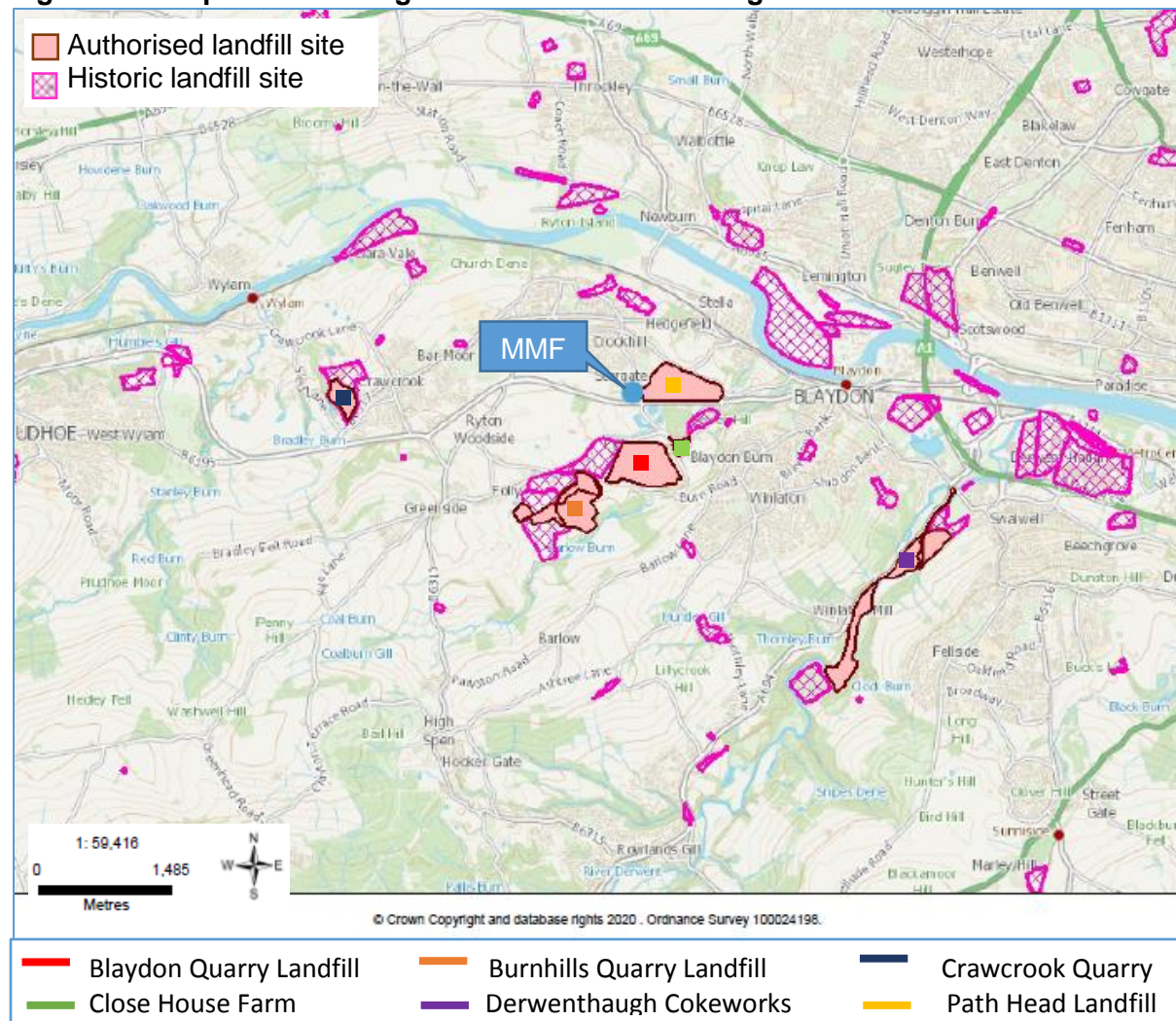


Figure 2.3 Location of MMF on site



3 Monitoring Results

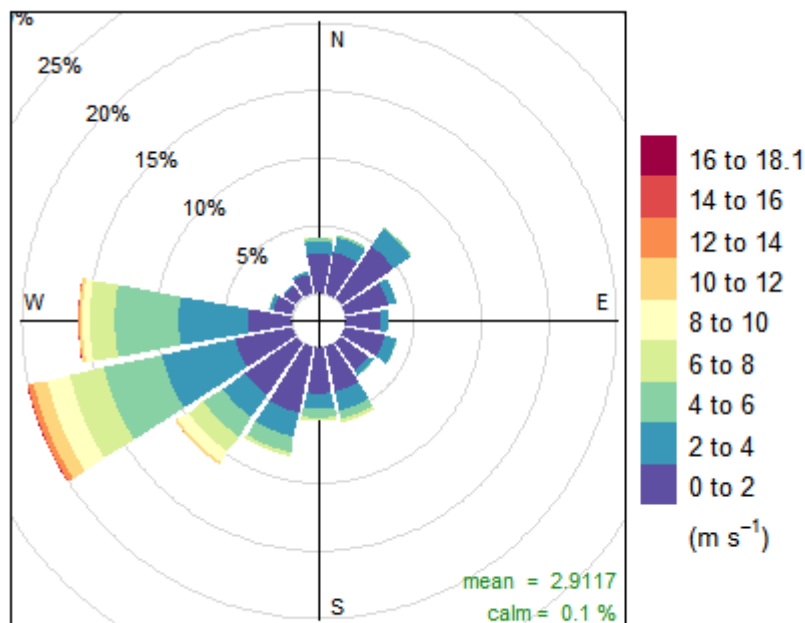
3.1 Meteorology

Wind speed and direction measurements were collected at the MMF site during the study between the 16 January 2020 and 7 September 2020 (236 days). The sensor was mounted on a mast extending 6m from the top of the MMF trailer giving an overall height above ground of 8m. Where possible MMFs are located over 100m from any buildings of greater or comparable height, so as to reduce any influence that surrounding buildings may have on the wind distribution. In this instance, the MMF was located within 100m of buildings of comparable height to the west and south. There were also trees surrounding the boundary of the monitoring location.

When setting up the instrument measuring wind direction at the beginning of the study, the mast was rotated such that the vane pointed in a known direction and this was used as datum from which other directions were determined by the sensor. An uncertainty of $\pm 5^\circ$ on the wind direction is introduced which affects all readings by the same amount.

The frequency distribution of wind direction between 16 January 2020 and 7 September 2020 (236 days) is shown in Figure 3.1.1. The wind rose shows that there were winds received for all directions at the monitoring location although they were less frequent for sector $270^\circ - 360^\circ$. Over the monitoring period the dominant wind direction was between $190^\circ - 280^\circ$, with wind coming from this sector for 57% of the time.

Figure 3.1.1: Wind rose (%) based on 5-minute means



Frequency of counts by wind direction (%)

Figure 3.1.2 shows that the most prevalent wind speeds were between 2 - 7 m.s⁻¹ between $255^\circ - 265^\circ$. The wind speed frequencies for all wind directions are summarised in Table 3.1.1.

Figure 3.1.2: Polar plot of wind frequency and speed for 10° sectors (from 5-minute means)

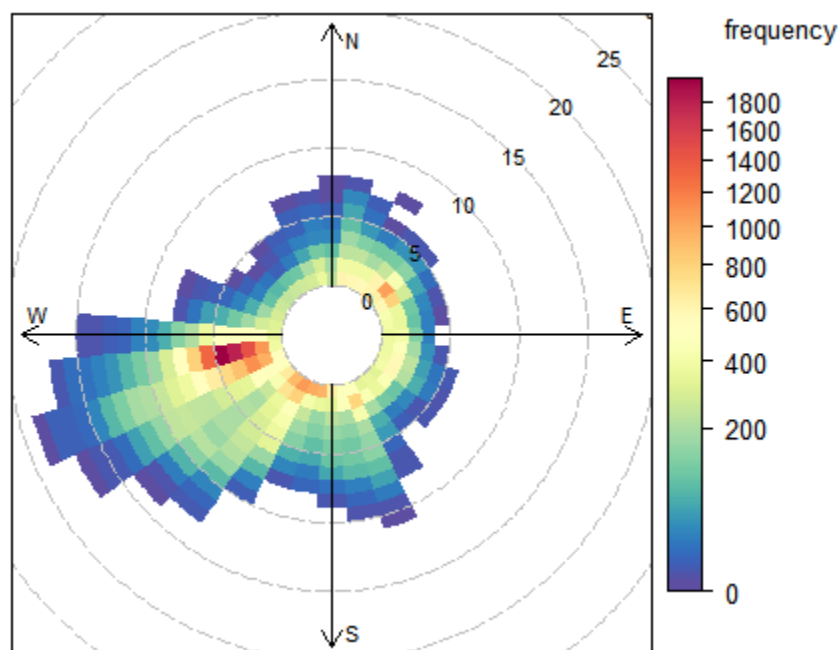


Table 3.1.1: Summary of wind speed frequencies

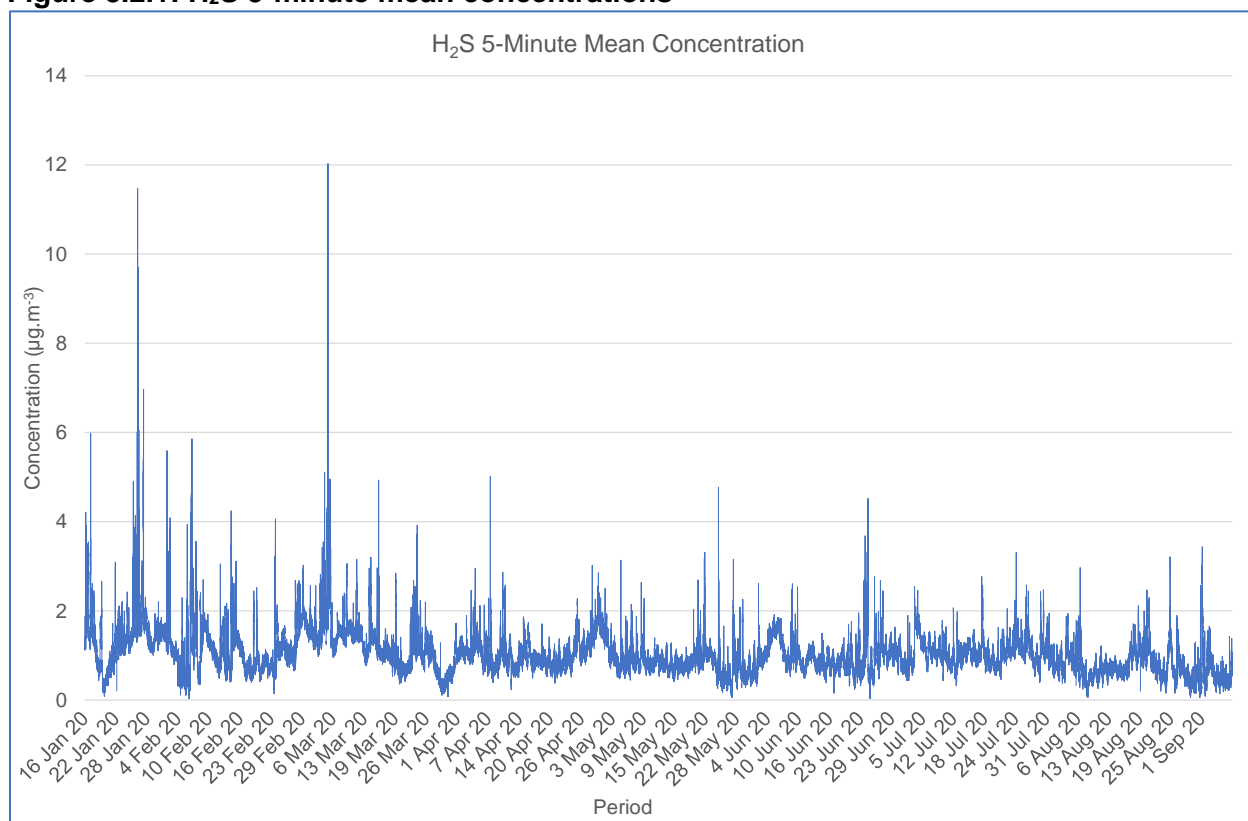
Wind Speed (m.s ⁻¹)	Frequency of wind speed (%)
<0.2	0.8
0.2 - 0.5	6.9
0.5 - 1	15.2
1 - 2	25.4
2 - 3	14.7
3 - 5	18.3
>5	18.7
Total	100

3.2 Hydrogen Sulphide (H₂S)

Between 16 January 2020 and 7 September 2020 (236 days) airborne H₂S concentrations were measured at a height of 2m above ground. Details of the instrumentation and methodology are given in Appendix C. Successful data collection for the monitoring period was 99%.

A time series plot of 5-minute mean concentrations of H₂S over the monitoring period is shown in Figure 3.2.1. The mean concentration over the monitoring period was 1.0µg.m⁻³ (0.67ppb). The maximum 5-minute mean concentration was 12.0µg.m⁻³ (8ppb).

Figure 3.2.1: H₂S 5-minute mean concentrations

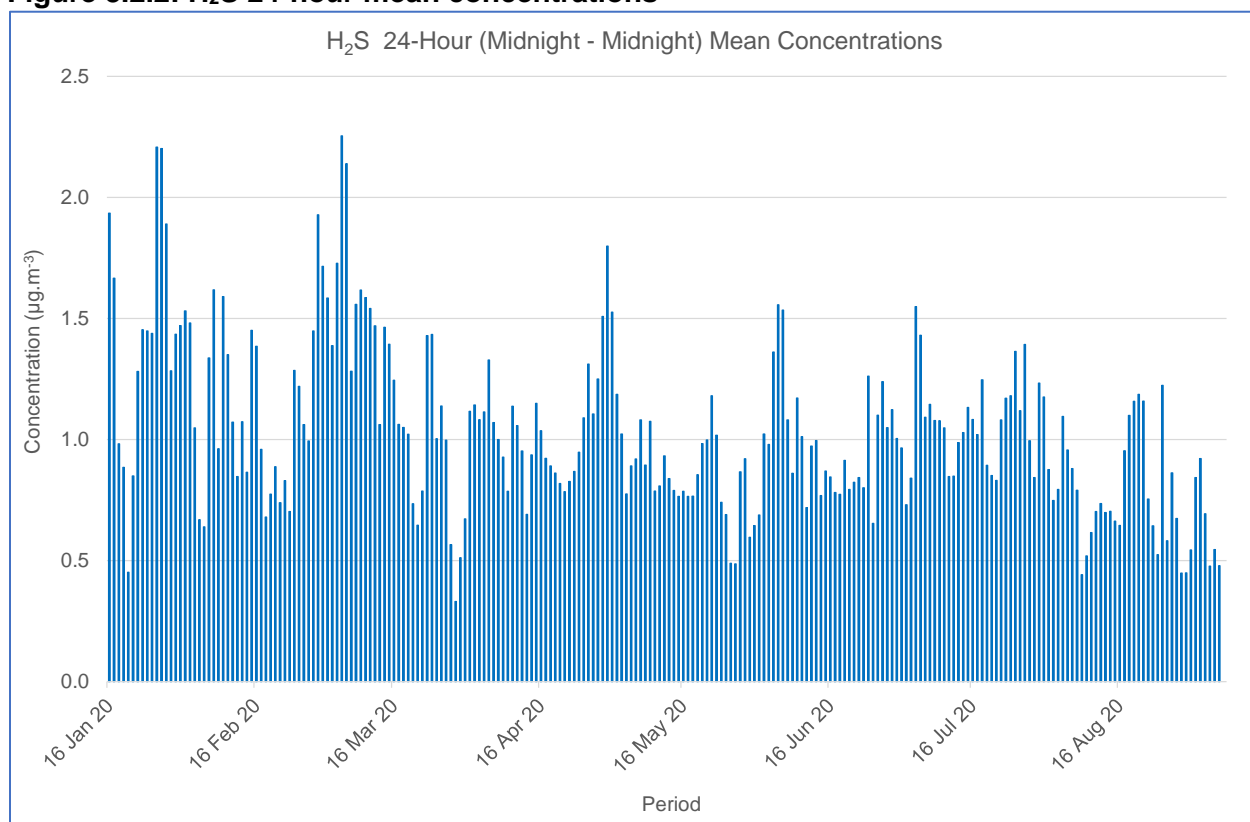


3.2.1 Comparison with WHO Guidelines

The World Health Organisation (WHO) guidelines for Europe (2000) have set a 24-hour guidance limit of 150µg.m⁻³ for H₂S in the context of human health.

A time series plot of 24-hour mean H₂S concentrations at the monitoring site is shown in Figure 3.2.2. The highest recorded 24-hour mean was 2.3µg.m⁻³, which is considerably lower than the 150µg.m⁻³ guideline.

Figure 3.2.2: H₂S 24-hour mean concentrations



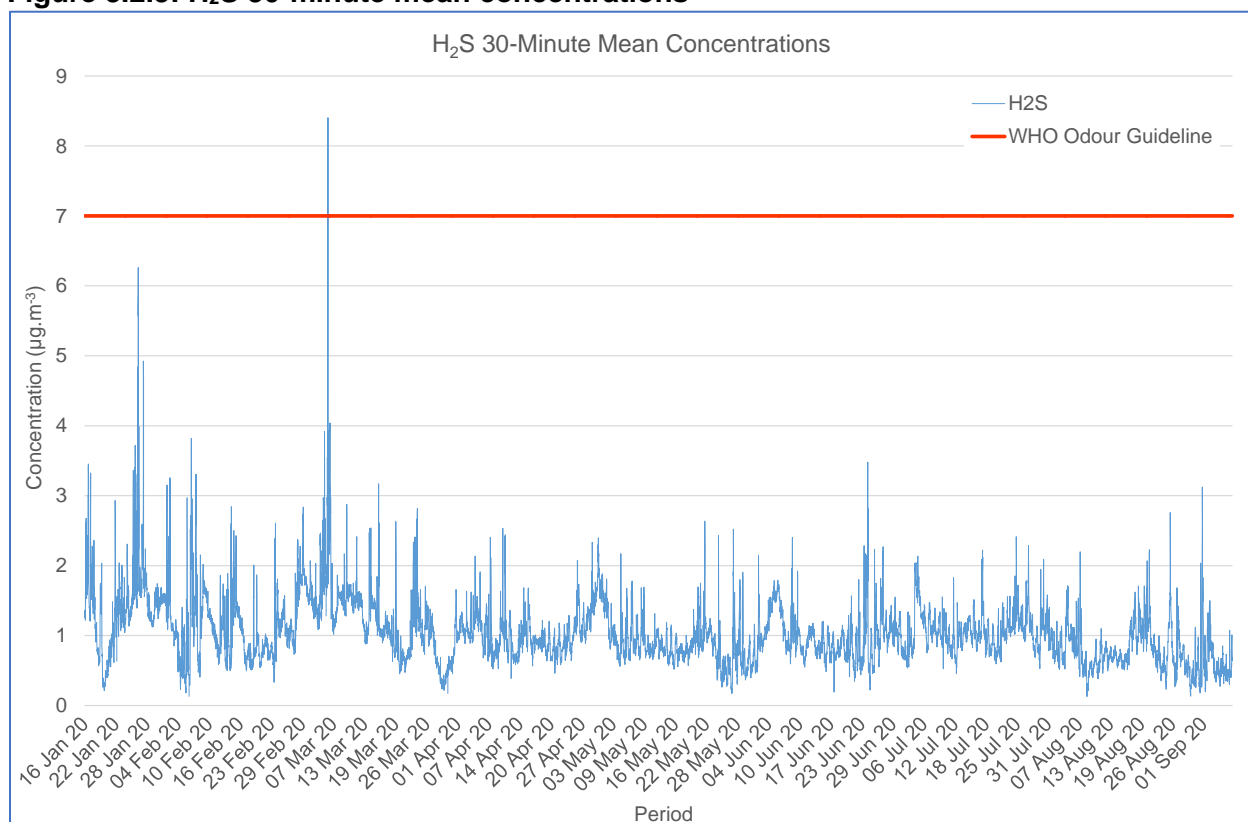
The WHO guidelines have also set a 30-minute mean H₂S guide level of 7µg.m⁻³ above which substantial complaints about odour annoyance can be expected.

A time series plot of 30-minute mean H₂S concentrations measured over the period is shown in Figure 3.2.3.

The highest recorded 30-minute mean during the monitoring period was 8.4µg.m⁻³. This was the only occasion during the monitoring period, where a 30-minute mean value exceeded the WHO guide level of 7µg.m⁻³.

Based on the WHO guideline alone, substantial complaints due to odour nuisance from H₂S could be expected for 0.01% of the total monitoring period, however this does not take in to account the subjective nature of odour complaints.

Figure 3.2.3: H₂S 30-minute mean concentrations



3.2.2 Directional Analysis

A polar frequency plot showing the mean H₂S concentrations for varying wind speeds and wind directions over the monitoring period is shown in Figure 3.2.4. The plot shows that the highest mean H₂S concentrations are seen for directions 165° – 185° for all wind speeds, from the direction of Blaydon Quarry landfill site.

A radial plot of mean H₂S concentrations (µg.m⁻³) against wind direction are shown in Figure 3.2.5. The plot shows higher H₂S concentrations in the wind direction between 160° - 190°, where mean concentrations were >1.2µg/m³.

An array of plots showing the contribution to H₂S loading (µg.m⁻³) at the monitoring site for different percentiles are shown in Figure 3.2.6. An explanation of percentile analysis is given in Appendix E.

The plot shows elevated concentrations in the lower and higher percentiles for sector 160° - 200°, again suggesting a relatively continuous source(s) when the wind comes from these wind directions.

Figure 3.2.4: H₂S polar frequency plot for 10° sectors (from 5-minute means)

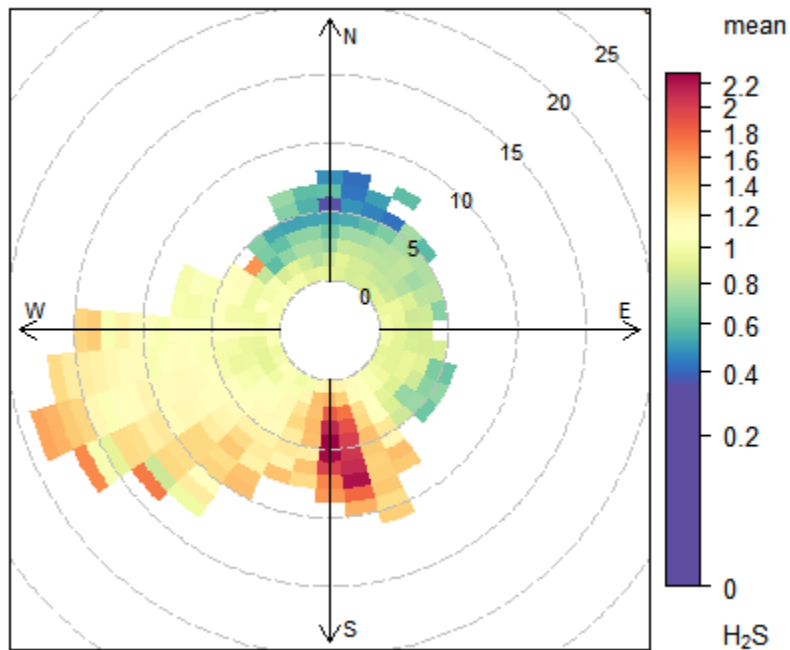


Figure 3.2.5: H₂S mean pollution rose (μg.m⁻³)

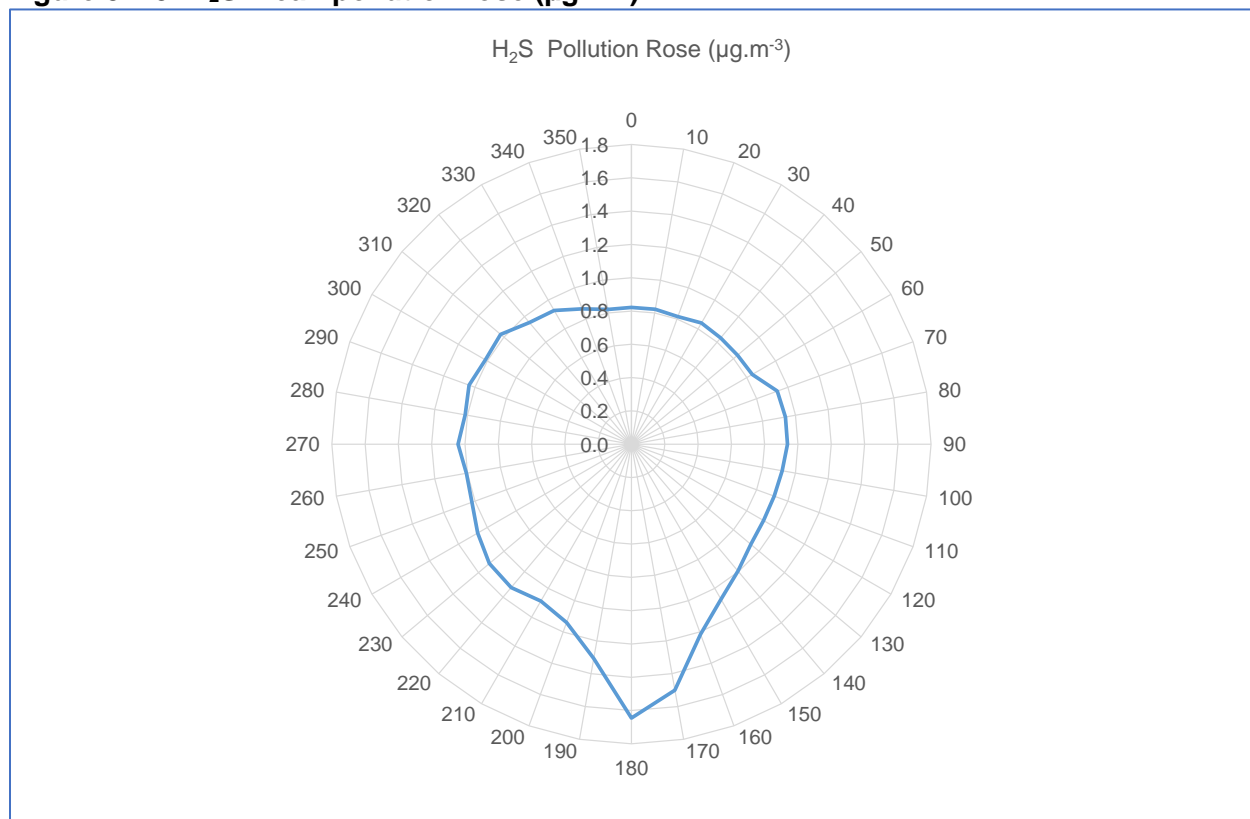


Figure 3.2.6: H₂S percentile rose ($\mu\text{g.m}^{-3}$)

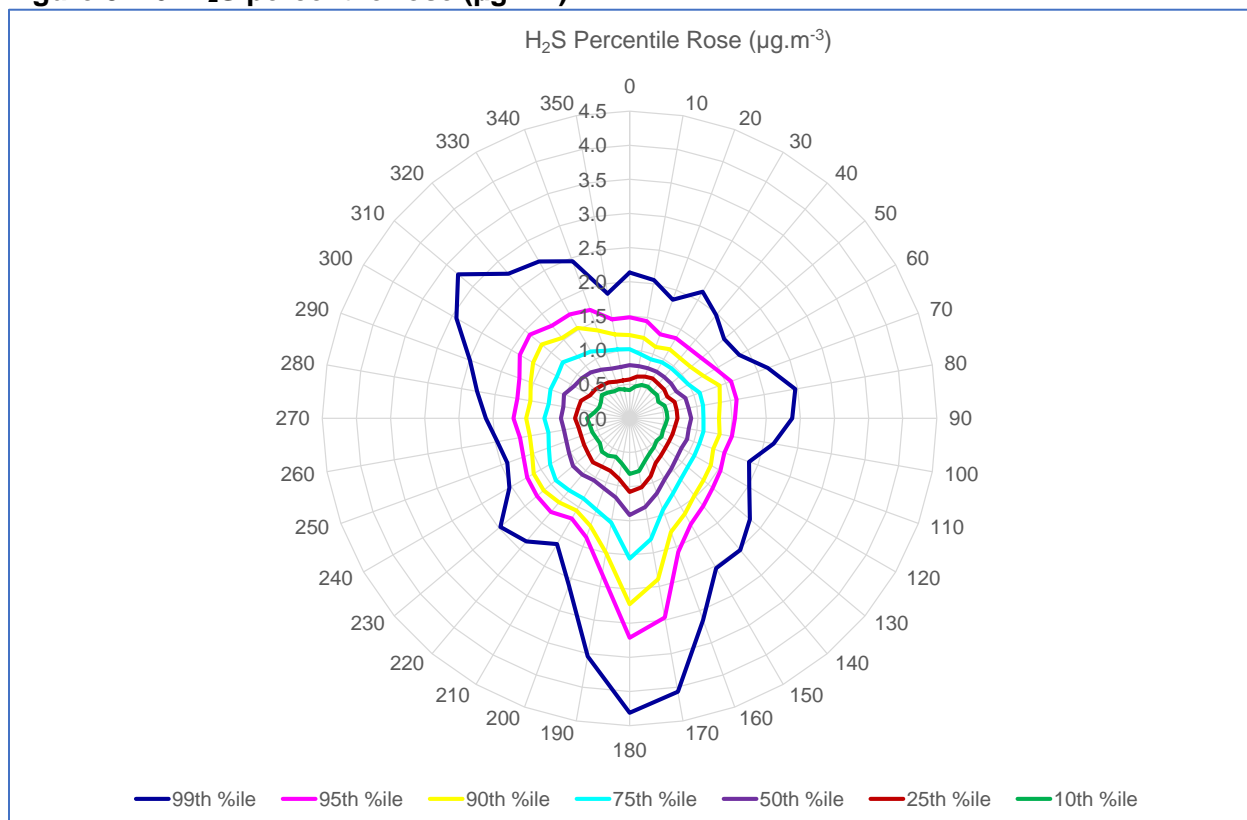
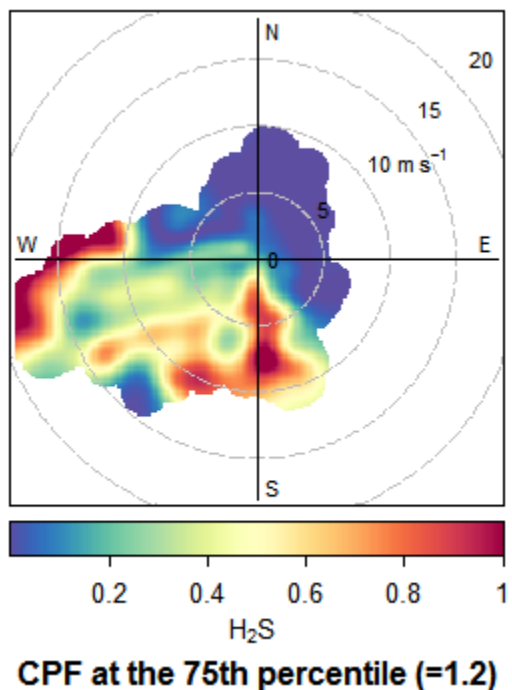


Figure 3.2.7 shows a conditional probability function plot for H₂S concentrations >75th percentile. The plot calculates the probability that H₂S concentrations would be greater than the 75th percentile value ($1.3 \mu\text{g.m}^{-3}$) for a particular wind speed and wind direction. Further information about this method can be found in Appendix F.

Figure 3.2.7 shows that high concentrations (greater than the 75th percentile of all observations) are more likely to occur between $150^\circ - 280^\circ$, with lower conditional probabilities of these concentrations being experienced for other wind directions. The higher conditional probabilities for directions $150^\circ - 190^\circ$ from the direction of Blaydon Quarry landfill site, is apparent for a range of wind speeds. The higher probability for directions $240^\circ - 280^\circ$ is seen for higher wind speeds, suggesting that there is a source from this direction that can contribute to elevations in H₂S concentrations.

Figure 3.2.7: H₂S conditional probability function plot for concentrations >75th percentile (1.3 µg.m⁻³)



3.2.3 Diurnal Analysis

Figure 3.2.8 shows the diurnal variation of mean H₂S concentrations for different wind directions at the MMF.

Figure 3.2.8 H₂S diurnal polar plot

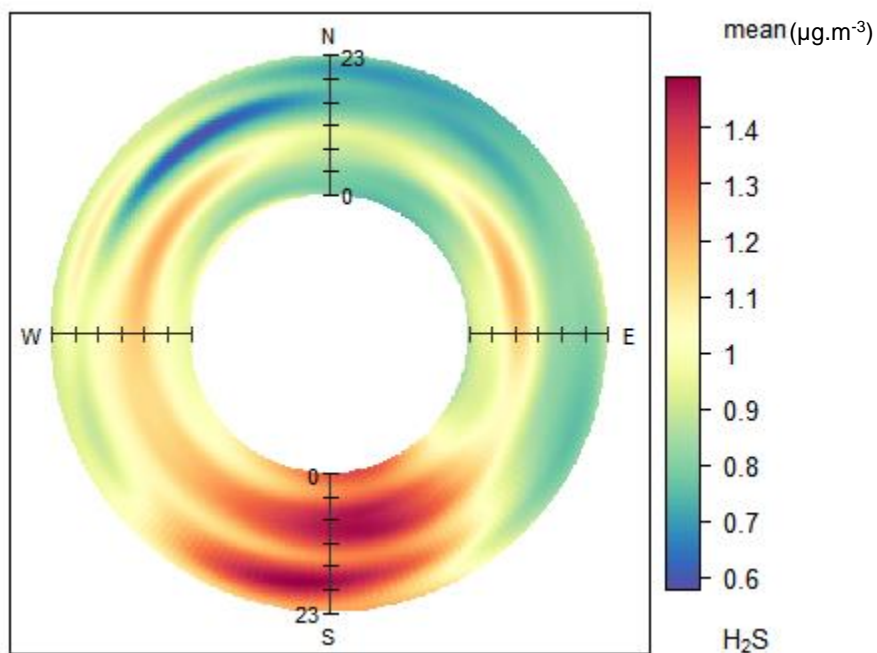


Figure 3.2.8 shows that H₂S concentrations can be elevated overnight and also during the day for sector 130° – 220°. Higher daytime concentrations are also seen for other wind directions suggesting that there is an additional source of H₂S from these directions that has contributed to an elevation in H₂S concentrations during the day.

3.2.4 Conclusion

Comparison of the H₂S data with the WHO guidelines for human health of 150µg.m⁻³, as 24-hour mean concentrations, indicated that the air quality at the monitoring site was within these guidelines.

Comparison of the H₂S data with the WHO guidelines for odour annoyance of 7µg.m⁻³, as 30-minute mean concentrations, indicated that the air quality at the monitoring site exceeded this guideline for around 0.01% of the monitoring period. The mean H₂S concentration over the monitoring period was 1.0µg.m⁻³.

Comparison of the H₂S data against wind speed showed that an elevated H₂S source was seen for wind sector 165° – 185° at high and low wind speeds.

Directional analysis indicated that the highest mean H₂S concentrations were measured from sectors 160° – 190° and that this was a relatively continuous source.

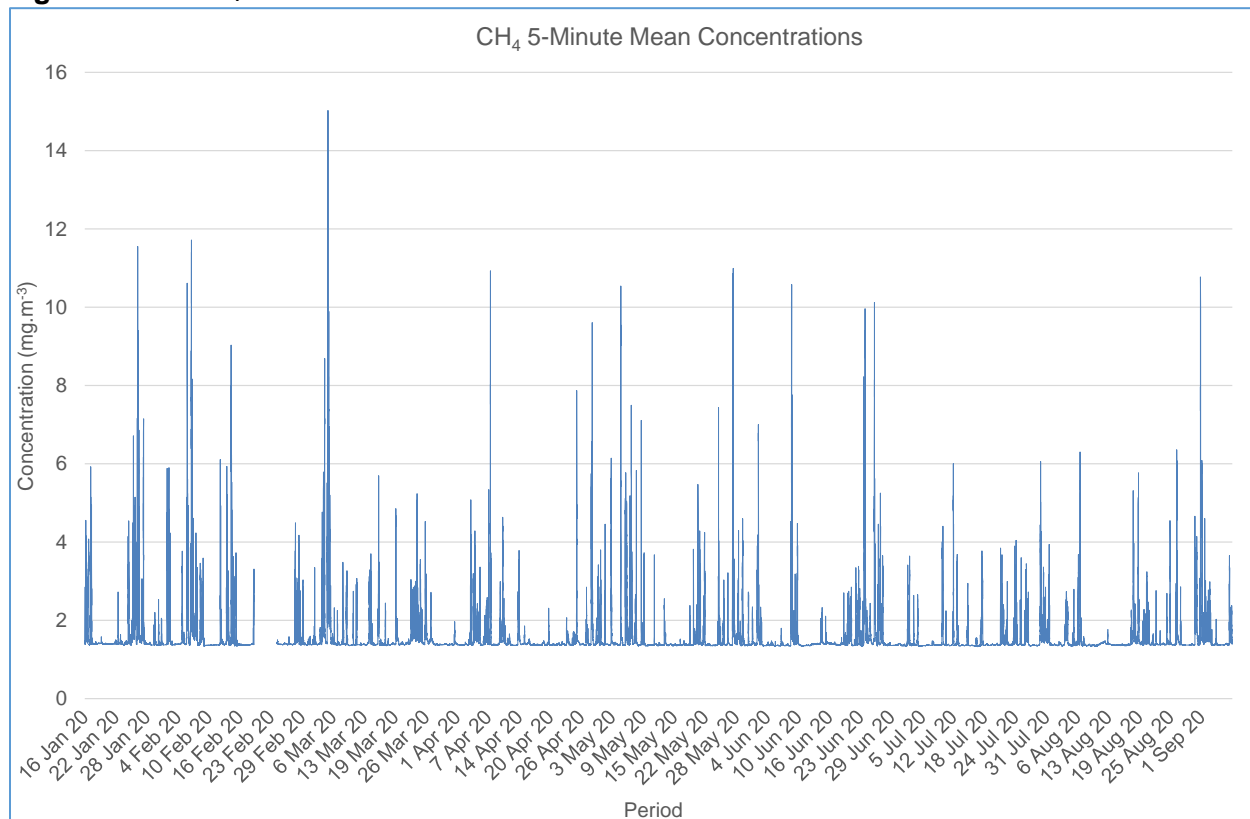
The probability of measuring higher H₂S concentrations (greater than the 75th percentile of all observations) was greater from direction 150° – 280°.

Diurnal analysis showed that H₂S concentrations were elevated during the day and overnight from directions 130° – 220°. There also appeared to be higher concentrations during the daytime from other directions.

3.3 Methane (CH₄)

Between 16 January 2020 and 7 September 2020 (236 days) airborne CH₄ concentrations were measured at a height of 2m above ground. Successful data collection over the monitoring period was 98%. Details of the instrumentation and methodology are given in Appendix D. A time series plot of 5-minute CH₄ concentrations (mg.m⁻³) over the monitoring period is shown in Figure 3.3.1.

Figure 3.3.1: CH₄ 5-minute mean concentrations

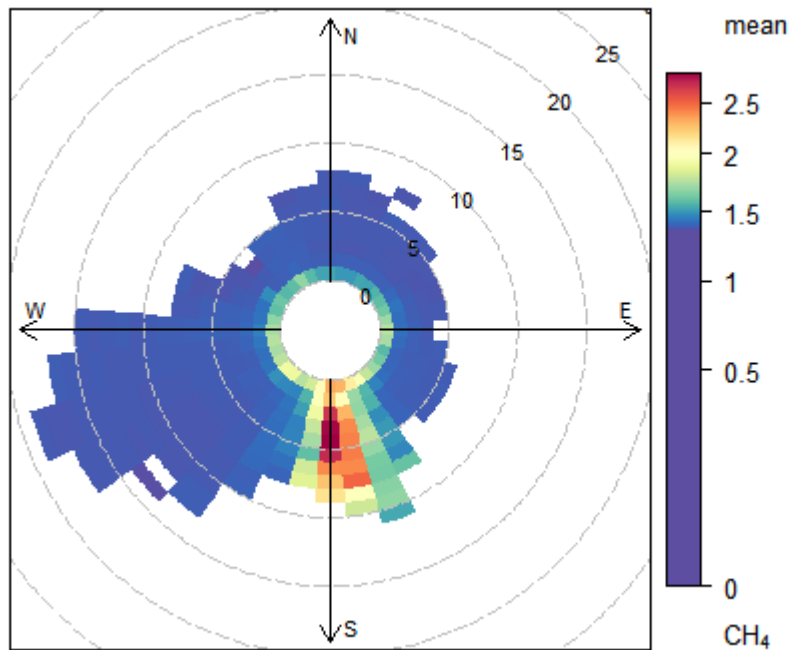


Methane does not have any associated impacts on human health, with the exception of explosive risk at very high concentrations, its main environmental impact is from its relatively high potential for global warming. The mean concentration over the period was 1.53mg.m⁻³, which is higher than the northern hemisphere background concentration of around 1.30mg.m⁻³, suggesting the potential of a localised source.

3.3.1 Directional Analysis

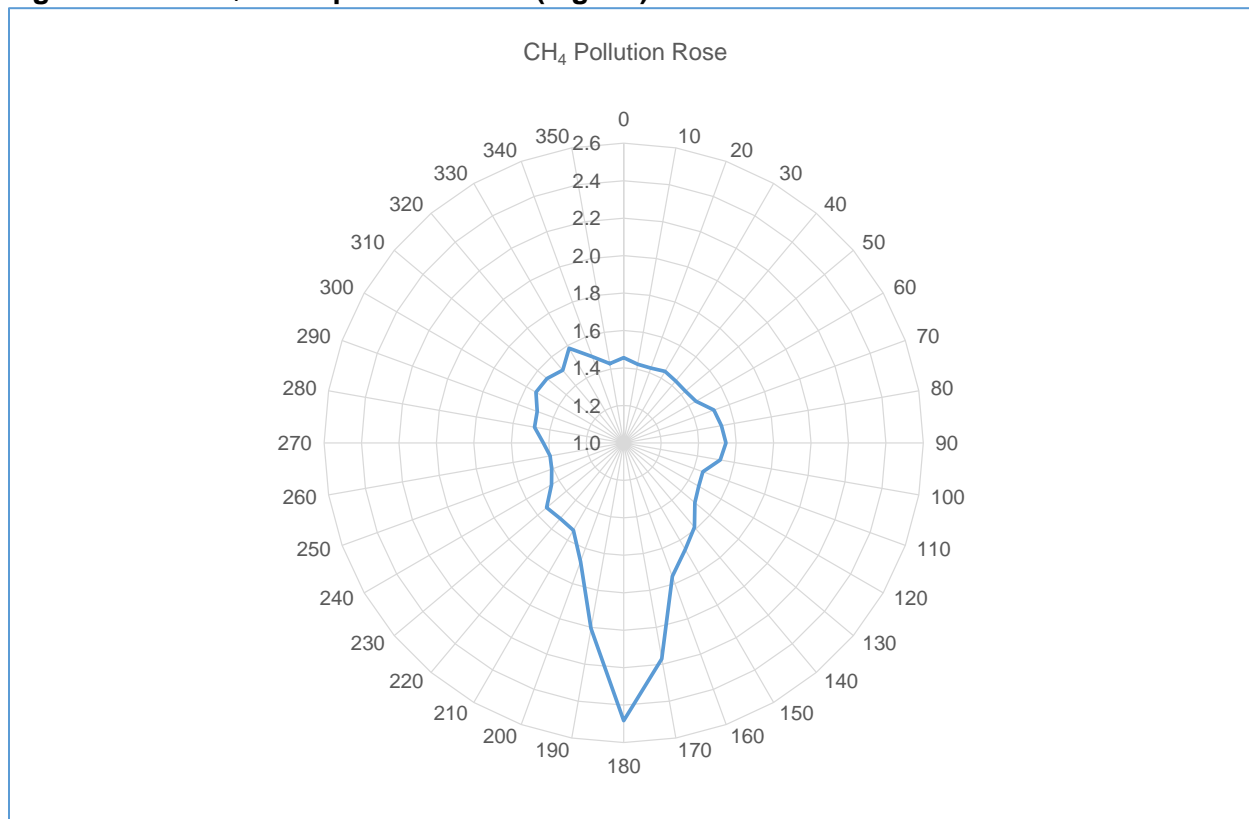
A polar frequency plot showing the mean CH₄ concentrations for varying wind speeds and wind directions over the monitoring period is shown in figure 3.3.2. The plot shows that for wind speeds up to 1m.s⁻¹, higher CH₄ concentrations can be seen for all wind directions. This suggests that at lower wind speeds, where there is less mixing of air, that there is a build-up of CH₄ concentration for all wind directions. Higher mean CH₄ concentrations are seen for wind directions 155° – 195° for all wind speeds, from the direction of Blaydon Quarry landfill site. This southerly source is also seen in the H₂S data.

Figure 3.3.2: CH₄ polar frequency plot for 10° sectors (from 5-minute means)



A radial plot of mean CH₄ concentrations (mg.m⁻³) against wind direction is shown in Figure 3.3.3.

Figure 3.3.3: CH₄ mean pollution rose (mg.m⁻³)



The plot shows that the highest mean concentrations were seen for directions $140^{\circ} - 200^{\circ}$ with concentrations $>1.6\text{mg.m}^{-3}$. Similar directional sources were also apparent in the H_2S data.

A plot showing the contribution to CH_4 loading (mg.m^{-3}) at the monitoring site for different percentiles is shown in Figures 3.3.4.

Figure 3.3.4: CH_4 percentile rose (mg.m^{-3})

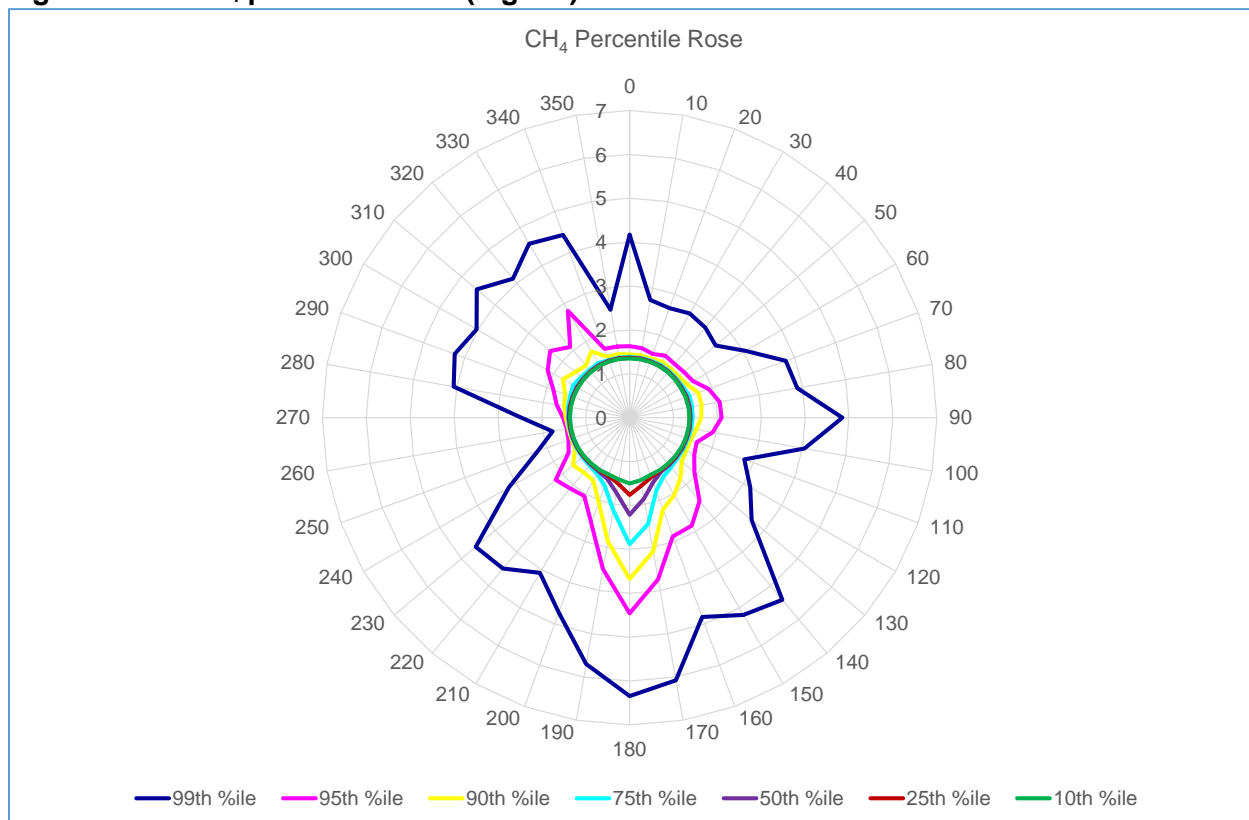
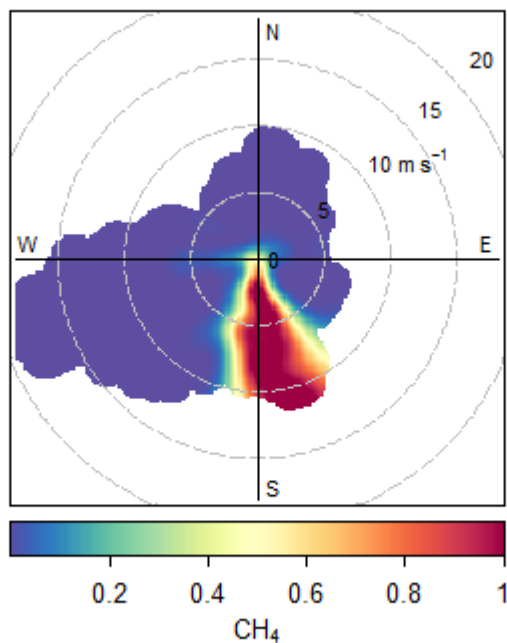


Figure 3.3.4 shows that for CH_4 , the contribution from the source(s) at $160^{\circ} - 190^{\circ}$ affect the higher and lower percentiles, contributing to a relatively continuous elevation in CH_4 concentrations at the monitoring location. This indicates a continuous source from this direction. Elevations appear in the higher percentiles for other wind directions, but Figure 3.3.2 shows that these concentrations occurred at very low wind speeds $<1\text{m.s}^{-1}$, where there is poor dispersion and a build-up of CH_4 , and you can have less confidence that the measured wind direction shows the true direction of the source.

Figure 3.3.5 shows a conditional probability function plot for CH_4 concentrations >75 th percentile. The plot calculates the probability that CH_4 concentrations would be greater than the 75th percentile value (1.4mg.m^{-3}) for a particular wind speed and wind direction. Further information about this method can be found in Appendix F.

Figure 3.3.5 shows that high concentrations (greater than the 75th percentile of all observations) are more likely to occur between $140^{\circ} - 200^{\circ}$ from the direction of Blaydon Quarry landfill site, with very low probabilities of these concentrations being experienced for other wind directions.

Figure 3.3.5: CH₄ conditional probability function plot for concentrations >75th percentile (1.4 mg.m⁻³)

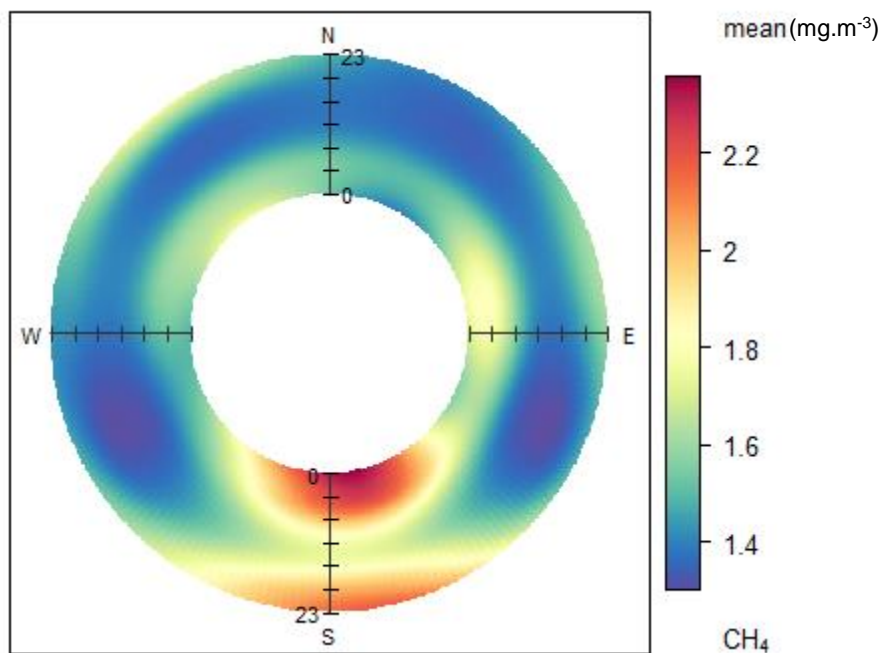


CPF at the 75th percentile (=1.4)

3.3.2 Diurnal Analysis

Figure 3.3.6 shows the diurnal variation of mean CH₄ concentrations for different wind directions at the MMF.

Figure 3.3.6 CH₄ diurnal polar plot



The plot shows that for sector 140° – 210° CH₄ concentrations were higher overnight suggesting that is likely to have coincided with lower temperatures and stiller wind conditions.

3.3.3 Conclusion

The mean CH₄ concentration over the period was 1.53mg.m⁻³, which is higher than the northern hemisphere background concentration of around 1.30mg.m⁻³, suggesting there is a localised source.

Consideration of meteorological conditions suggest that at low wind speeds <1m.s⁻¹ there is poor dispersion and a build-up of CH₄ concentrations seen for all wind directions. Higher mean CH₄ concentrations are seen for directions 155° – 195° for all wind speeds, from the direction of Blaydon quarry landfill site.

Directional analysis indicated that the highest mean CH₄ concentrations were measured from sectors 140° – 200° and that this was a relatively continuous source.

The probability of measuring higher CH₄ concentrations (greater than the 75th percentile of all observations) was greater from direction 140° – 200°.

Diurnal analysis showed that the highest CH₄ concentrations were seen overnight from directions 140° – 210°.

4 Conclusion

In the absence of any Air Quality Strategy (AQS) objectives, the hydrogen sulphide (H₂S) was compared with the World Health Organisation (WHO) guidelines for both human health and odour annoyance (Table 4.1). Comparing the collected data from the monitoring at Ryton with the World Health Organisation (WHO) guidelines showed that H₂S was well within health limits and was above the odour annoyance limit for 0.01% of the monitoring period.

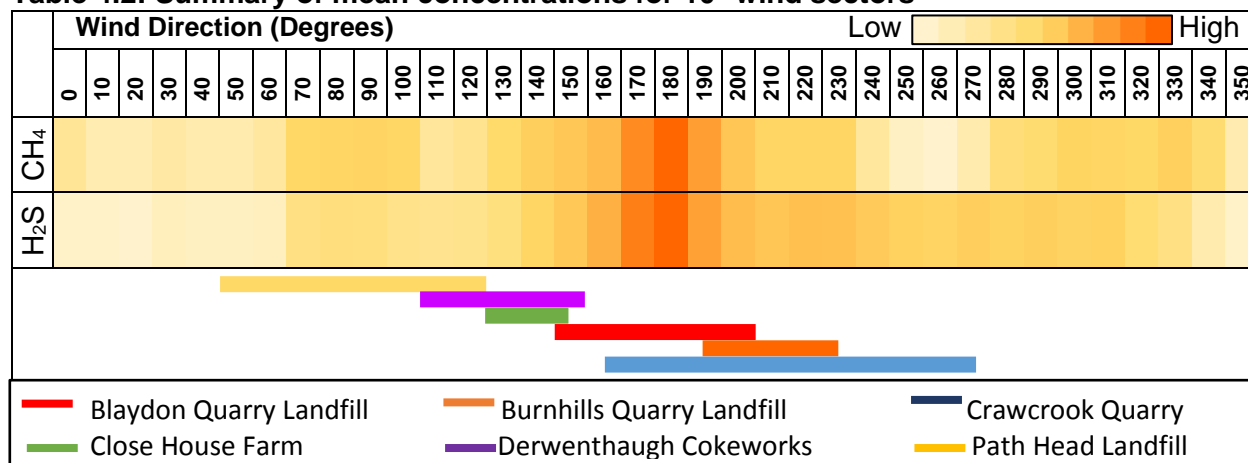
Table 4.1 Impact summary of H₂S compliance with the WHO guidelines for Europe 2000.

Pollutant	Averaging Time	Guidance Limit	Percentage of Time Exceeding the Guidance Limit
H ₂ S	24hr (midnight- midnight)	150µg.m ⁻³	0
	30-Minute	7µg.m ⁻³	0.01

Table 4.2 summarises the results of the mean pollution concentrations at the MMF monitoring location for 10° wind sectors, for all wind speeds. The bearing of the landfill sites in relation to the MMF have been highlighted. The cells are shaded proportionally to their value, from minimum value (lightest colour), to maximum value (darkest colour).

Directional analysis showed that the highest H₂S and CH₄ concentrations came from the direction of Blaydon Quarry landfill site. Consideration of the H₂S data did suggest that there was an additional source between 190° – 270° that was not apparent in the CH₄ data. Elevations in H₂S concentrations could also be seen in the daytime, but this was not apparent for CH₄.

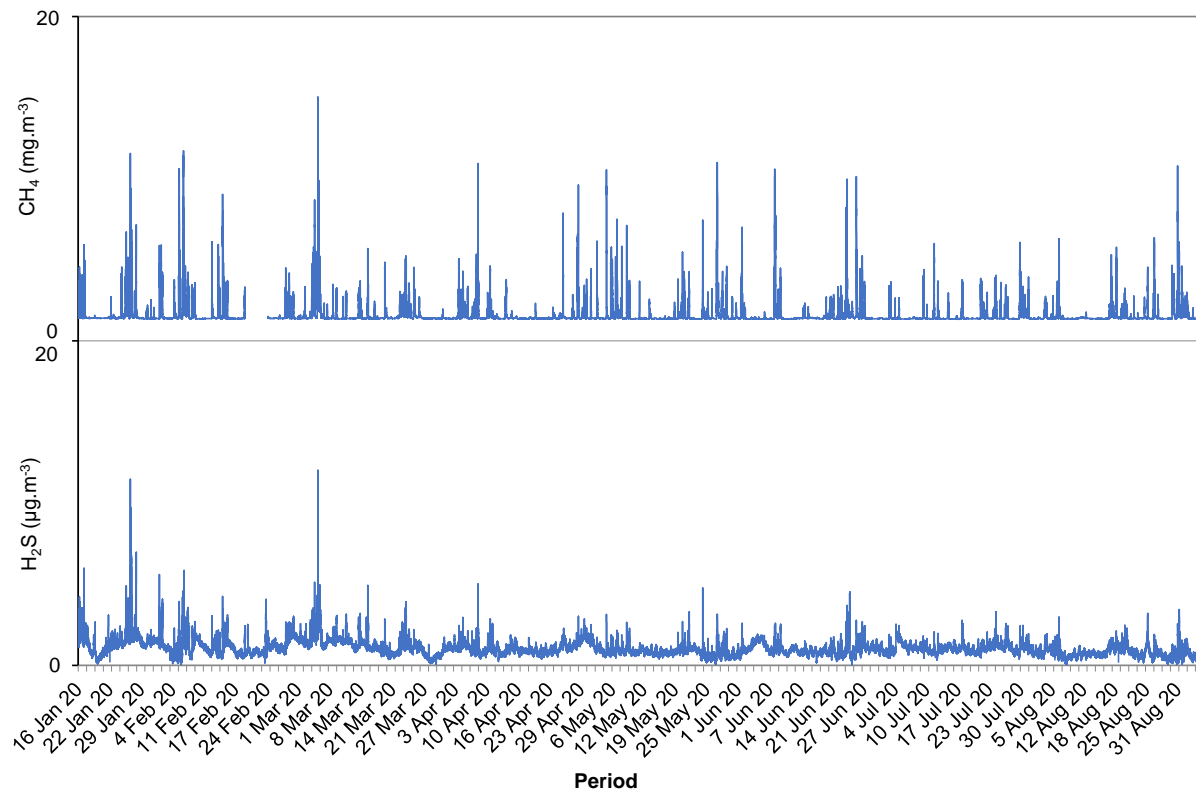
Table 4.2: Summary of mean concentrations for 10° wind sectors



Diurnal analysis showed that concentrations were higher overnight when wind speeds and temperatures are lower from the direction of Blaydon Quarry landfill site, H₂S concentrations were also elevated during the day time from this direction.

A time series plot for the pollutants monitored is shown in Figure 4.1. It is possible to see that there are periods where both elevations in CH₄ and H₂S coincide and that this is more prominent over the winter months, suggesting that these events are caused by the same source.

Figure 4.1 time series for the monitoring site in Ryton (based on 5-minute mean concentrations)



5 References

1. Carslaw, D.C. (2015). The openair manual — open-source tools for analysing air pollution data. Manual for version 1.1-4, King's College London.
2. World Health Organisation (2000), WHO Air Quality Guidelines for Europe

Appendix A Mobile Monitoring Facility

National Monitoring Services carries out ambient air monitoring on behalf of Environment Agency regions using Mobile Monitoring Facilities (MMFs). These facilities allow us to carry out flexible, short-term studies examining the impact of specific EPR permitted installations on local communities. The facilities contain a number of analysers designed to sample the atmosphere for a selection of pollutants commonly associated with industrial emissions. The equipment is contained within a trailer that can conveniently be towed. This allows it to be strategically sited at temporary locations with the intention of quantifying pollution loadings and determining sources. The MMF used in the Ryton study was MMF3. The pollutants measured using MMF3 were:

- hydrogen sulphide (H₂S)
- methane (CH₄)

Meteorological Instruments

In addition to analysers measuring the concentration of pollutants in the air the facility contains equipment that can measure meteorological conditions. This provides the opportunity to consider measured pollutant levels relative to the prevailing meteorological situation. This can supply important information allowing a more detailed understanding of the pollutants' dispersion in the atmosphere and consequently a more accurate assessment of their origins. The meteorological parameters that can be measured are:

- wind direction,
- wind speed,

Wind direction and wind speed measurements are taken at an elevation of 8m above the ground and from positions where the wind approach was unobstructed. The temporal resolution of the data is 5 minutes.

Wind direction is an important consideration as it provides direct information about the orientation of any source relative to the monitoring site. It must be noted, however, that pollutants will be carried along a wind's trajectory that may, over distances of several kilometres, be curved so that in these cases the wind direction will not simply 'point' to the source's direction. Wind speed and temperature both have a significant influence on the amount of mixing within the atmosphere, having profound effects on the vertical distribution of pollutants through the atmospheric boundary layer. Relative humidity is important because the level of moisture within the air affects the rates of reaction and removal of some air pollutants.

Appendix B Quality Assurance and Quality Control

Quality assurance covers practices that are undertaken prior to data collection in order to ensure that the sampling arrangements and analysers are capable of providing reliable measurements. Quality Control covers practices applied after data collection in order to ensure that the measurements obtained are repeatable and traceable.

In order to ensure that data from the MMF are representative of pollutant concentrations and meet appropriate standards of quality, a number of QA and QC procedures are routinely implemented in the monitoring facility's execution.

Quality assurance included:

- | | |
|--------------------|---|
| Training | - all personnel involved with the running of the facility have received appropriate training in the execution of the tasks they are expected to undertake. This training has been recorded in the personal training log of the individuals concerned. |
| Procedures | - all routine activities undertaken in the operation of the facility are clearly and unambiguously laid out in a documented set of procedures. |
| Analyser selection | - careful consideration has been given to the choice of analysers, ensuring that they meet the required standards of accuracy and precision. Also that they can be relied on to be robust and flexible enough to present the data in a suitable format. |
| Trailer Location | - attention is given to how representative the location of the facility is when compared against the objectives of the study. |

Quality control included:

- | | |
|----------------------|---|
| Routine calibration | - calibrations are performed every two weeks, using traceable gas standards and any adjustments made to the analysers documented. |
| Routine maintenance | - undertaking of stipulated checks and changes of filters. |
| Periodic maintenance | - employment of a qualified engineer to service the analysers twice a year. |
| Instrument history | - all invasive work carried out on analysers is documented and recorded. |
| Data review | - all data is checked to ensure correct scaling, rejecting negative or out-of-range readings, questioning rapid excursions, generally considering the integrity of recorded levels. |

- | | |
|--------------------|---|
| Data handling | - following recognised procedures to ensure that data capture is maximised. The data is analysed frequently so that measurements affected by instrument fault are recognised quickly. |
| Data comparison | - comparing the collected data sets with data sets from other monitoring studies that are carried out in close enough proximity to be relevant. Consideration of the relationship between different pollutants i.e. some pollutant levels will be expected to rise and fall together. |
| Data rectification | - the adjustment of data to minimise the effects of analyser |

Appendix C Hydrogen Sulphide (H₂S)

Hydrogen sulphide (H₂S) is a colourless, toxic and flammable gas, with a characteristic odour of 'rotten eggs'.

Sources

Hydrogen sulphide is produced naturally in the environment by emissions from volcanoes and geothermal activity, microbial decomposition of organic material in the absence of oxygen (anaerobic digestion) in swamps and saltmarshes and is an important participant in the natural sulphur cycle. Natural sources account for 90% of the global H₂S emissions, whilst the other 10% is emitted from anthropogenic sources such as oil refineries, coke ovens, tanneries, paper mills (using the Kraft process (sulphate process), wastewater treatment plants, viscose rayon textile production, landfills and farm manure storage facilities, to name but a few.

Human Health and Standards

'Although it is unlikely that the general population will be exposed to a level of H₂S high enough to cause adverse health effects' ⁽¹⁾, levels around some industrial sources can cause a nuisance due to the unpleasant odour associated with the hydrogen sulphide. The odour threshold (point above which an odour can be perceived by 50% of a human panel) for H₂S is between 0.2 – 2ug.m⁻³ depending on the purity. However, at these levels the human nose can only detect that an odour is present, the characteristic 'rotten egg' odour is not perceptible until 3-4 times this threshold level.

The World Health Organisation (WHO) has set two guidelines for H₂S, a health standard and an odour threshold above which substantial complaints with regard to odour nuisance should be expected.

Health guideline: 150ug.m⁻³ as a 24-hour mean

Odour guideline: 7µg.m⁻³ as a 30-minute mean

The health guideline is based on the lowest level of H₂S to cause an adverse effect, which is 15mg.m⁻³ (15,000µg.m⁻³), where it has been shown to cause eye irritation. A high protection (safety) factor of 100 is then applied and the guideline of 0.15mg.m⁻³ (150µg.m⁻³) over a 24-hour averaging time is the result.

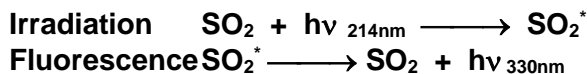
The high protection factor applied to create the guideline for health is a result of the marked toxicity of H₂S with increasing concentration above the first observable adverse effect.

H₂S analyser

The analyser used to measure hydrogen sulphide is an API T101 analyser. Gas entering the analyser first passes through a selective scrubber to remove sulphur dioxide, then enters a catalytic converter, where hydrogen sulphide is oxidised to form sulphur dioxide. This secondary gas stream of sulphur dioxide is then sampled and analysed.

The operation of the sulphur dioxide analysers is based on the measurement of fluorescence from SO₂ due to absorption of UV energy. An ultraviolet (UV) lamp emits radiation that passes through a filter admitting only light with a wavelength of 214nm. This radiation excites SO₂ molecules in the sampling air. These excited SO₂ molecules quickly return to their ground state

by emitting a photon at a longer wavelength (330nm) and this fluorescence can then be measured by a PMT with a secondary UV filter. The equations describing the reactions are:



The UV light at any point in the system is given by:

$$I_a = I_o[1 - \exp(-ax(\text{SO}_2))]$$

where I_o is the UV light intensity, a the absorption coefficient of SO_2 , x the path length, and (SO_2) the concentration of SO_2 . When the SO_2 concentration is relatively low and the path length of excited light short, the fluorescence radiation impinging upon the PMT can be considered directly proportional to the concentration of SO_2 . The PMT transfers the light energy into an electrical signal, which is directly proportional to the light energy in the sample stream being analysed. An UV detector measures the UV light. Software calculates the ratio of the PMT output and the UV detector in order to compensate for variations in the UV light energy.

References

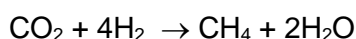
1. 'Hydrogen Sulphide: General Information', Public Health England, Toxicology Department, CRCE, PHE 2009 (version 1)
2. World Health Organisation (2000), *WHO Air Quality Guidelines for Europe*
3. 'Model T101 UV Fluorescence H_2S Analyser', User Manual, Teledyne Advanced Pollution Instrumentation, August 2016

Appendix D Methane (CH₄)

Methane, commonly known as marsh gas, is a colourless, odourless gas with a melting point of -184°C and boiling point -164°C. Its main environmental impact is from its relatively high potential for global warming. It affects the radiation balance of the Earth by absorbing infrared radiation and converting it to heat, therefore increased methane concentrations lead to increased surface temperatures.

Sources

Methane is produced by anaerobic bacterial fermentation processes in water that contains substantial organic matter, such as swamps, marshes, rice fields and lakes. This microbial degradation of organic matter may be written:



Methane is also produced by enteric fermentation in mammals and other species. The major emitting sources in 2018 were enteric fermentation from agriculture (41%), landfilling of wastes (37%), and leakage from the gas distribution system (10%)⁽³⁾.

The Northern Hemisphere background concentration is currently around 1.92ppm⁽²⁾. There has been a small increase in methane background concentrations over the last 30 years, this is mainly due to an increase in the emissions from primary sources. However the reduction in environmental levels of the hydroxide radical [OH] brought about by the increased levels of carbon monoxide (CO) also plays a part.

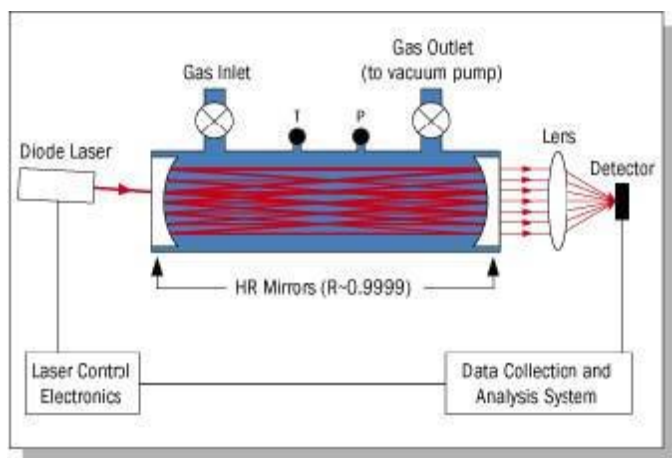
CH₄ Analysers

The analyser used for the study was a Los Gatos CH₄ analyser, which uses Off Axis Integrated Cavity Output Spectroscopy (OA-ICOS).

‘Until recently, high-sensitivity trace-gas measurements have been possible only by using expensive lasers (e.g., lead-salt or quantum-cascade) or broadband lamps that operate in the mid-infrared region where absorption features are strong. Los Gatos Research’s advances in cavity-enhanced absorption-spectroscopy techniques provide dramatic increases in the optical path length and as a result, enable ultrasensitive trace-gas measurements using robust, reliable, room-temperature diode lasers that operate in the near infrared.

Off-Axis ICOS utilizes a high-finesse optical cavity as an absorption cell as shown in Figure 8. Unlike conventional multi-pass arrangements, which are typically limited to path lengths less than two-hundred meters, an Off-Axis ICOS absorption cell effectively traps the laser photon so that, on average, they make thousands of passes before leaving the cell. As a result, the effective optical path length may be several thousands of meters using high-reflectivity mirrors and thus the measured absorption of light after it passes through the optical cavity is significantly enhanced. For example, for a cell composed of two 99.99% reflectivity mirrors spaced by 25 cm, the effective optical path length is 2500 meters.

Figure 1: Schematic diagram of an Off-Axis ICOS Instrument



Because the path length depends only on optical losses in the cavity and not on a unique beam trajectory (like conventional multipass cells or cavity-ring-down systems), the optical alignment is very robust allowing for reliable operation in the field. The effective optical path length is determined routinely by simply switching the laser off and measuring the necessary time for light to leave the cavity (typically tens of microseconds).

As with conventional tunable-laser absorption-spectroscopy methods, the wavelength of the laser is turned over a selected absorption feature of the target species. The measured absorption spectra is recorded and combined with measured gas temperature and pressure in the cell, effective path length, and known line strength, used to determine a quantitative measurement of mixing ratio directly and without external calibration.'

References

1. Department for Business, Energy and Industrial Strategy. 2019. *Long-Term Atmospheric Measurement and Interpretation of Radiatively Active Trace Gases, Annual Report (Sept 2018 – Sept 2019)*. Retrieved from <https://www.gov.uk/government/publications/uk-greenhouse-gas-emissions-monitoring-and-verification>.
2. Los Gatos Economical Ammonia Analyser User Manual.
3. Department for Environment, Food and Rural Affairs. 2020. National Statistics. [online] Available from: https://naei.beis.gov.uk/overview/pollutants?pollutant_id=3
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Appendix E Percentile Analysis

Percentile analysis provides a method of looking at the distribution of concentrations within a data set.

Excel calculates percentiles by first sorting the concentrations into ascending order and then ranking each concentration. It then uses the following formula's

$$r = 1 + \left[\frac{P(n-1)}{100} \right] I + D$$

P = the percentile you want
n = the total number of values
I = the integer part of the ranking
D = the decimal part of the ranking
r = rank

$$p = Y_I + D(Y_{I+1} - Y_I)$$

Y_I = value corresponding to the rank I
p = Value of the required percentile

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to interpolate the value of a particular percentile from the calculated ranking. i.e. it calculates the concentration below which a certain percentage of concentrations fall. For example, at the 95th percentile, 95% of the data will lie below this value and 5% of the data will lie above it.

In order to produce radial percentile roses, the data is first divided into the required wind sectors and then the data in each sector undergoes separate percentile analysis. By calculating the concentration of a pollutant at different percentiles for different wind sectors, you are able to visually examine the distribution of pollutant concentrations at a particular monitoring site. This in turn will provide information on the source that may be influencing levels at the monitoring site.

By separating the data into various wind sectors, it allows you to assess which wind directions are having the greatest influence on pollutant concentrations at the monitoring site. By calculating the mean concentration for every wind sector you can produce a 'mean pollution rose', where the influence on pollutant concentrations from a particular wind sector is seen as a bias on a radial plot. This type of analysis is very effective at visually highlighting the wind sectors where there are significant sources of a given pollutant. By breaking each wind sector down into a number of different percentiles it can be seen whether biases are present in all of the percentiles or just certain ones, which can tell you whether a source is affecting the monitoring site relatively continuously or just intermittently. For example, a bias that is observed in all of the percentiles (Figure 1) suggests that the source in that particular wind sector is emitting relatively continuously as it is influencing a large percentage of the data. Whilst a bias that is only observed in the higher percentiles (Figure 2) suggests that the source is intermittent as it only affects a small percentage of the data, i.e. it doesn't affect concentrations at the

monitoring site every time the wind is coming from this direction. Occasionally, a bias is observed in the lower percentiles that is not evident in the higher percentiles (Figure 3). This suggests that the source is relatively continuous, as it is affecting a large percentage of the data, but it also tells you that the source is not causing appreciably high concentrations at the monitoring site.

Figure 1. shows a bias between 280° – 300° that is evident in all of the percentiles.

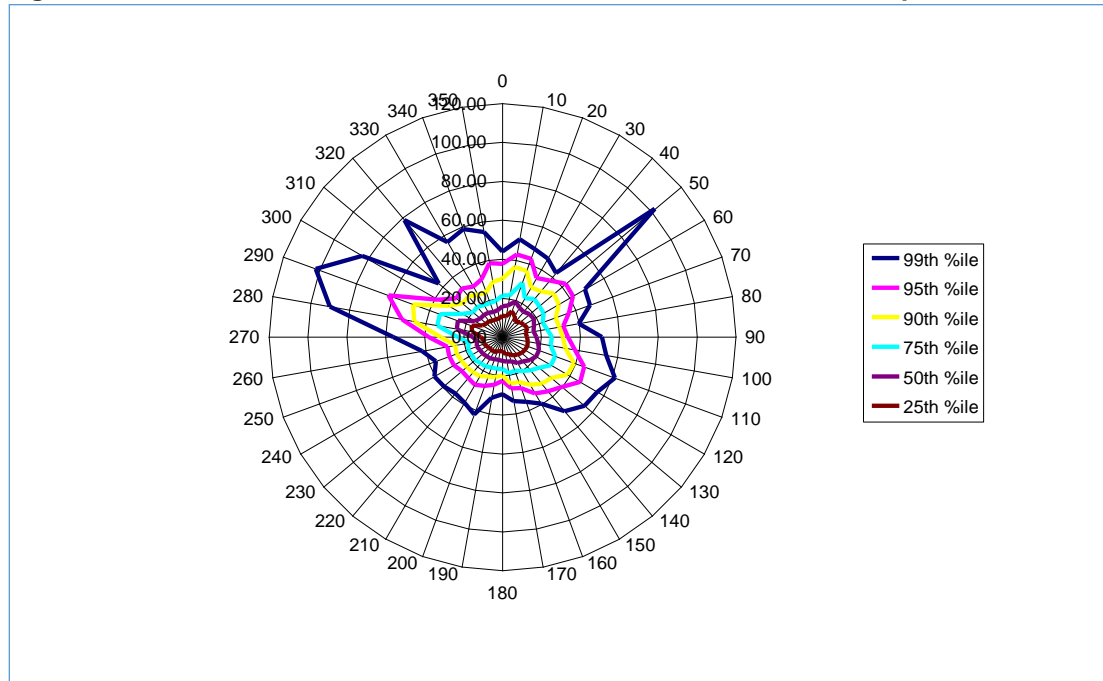


Figure 2. Shows a bias at 260° that is only evident in the 99th percentile.

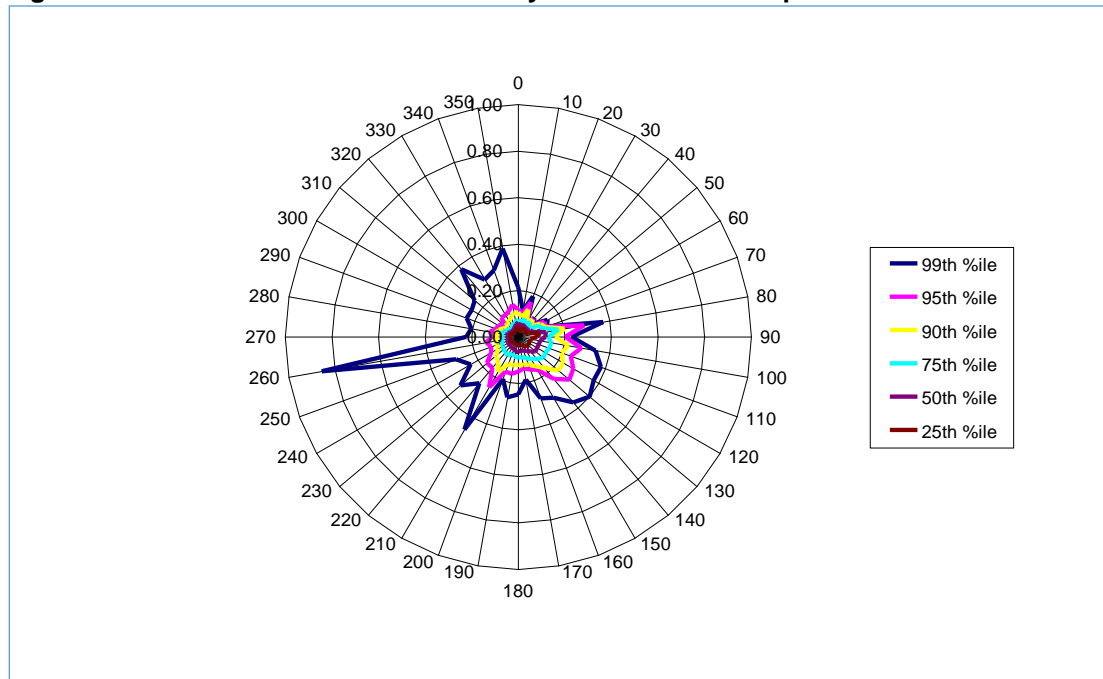
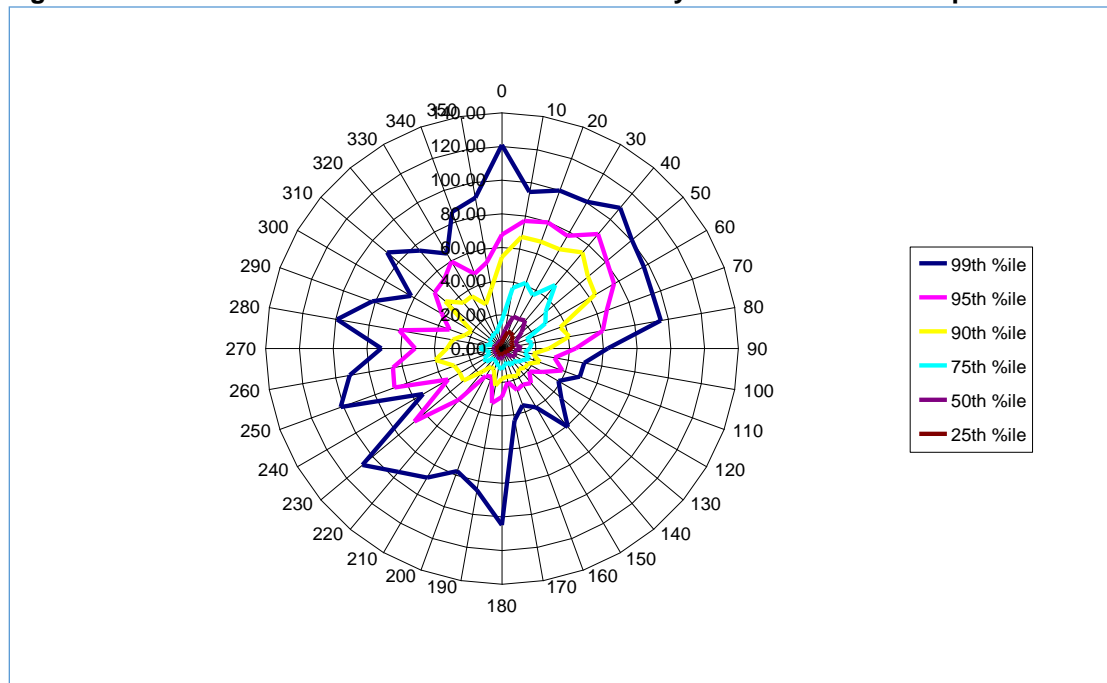


Figure 3. Shows a bias between 20° – 50° that is only evident in the lower percentiles.



Appendix F Conditional Probability Function (CPF) plots in Openair

Conditional Probability Function (CPF) plots have been used in this report, using the Openair software package in R, to help identify the wind direction and wind speeds from which the most prominent pollutant sources are likely to occur.

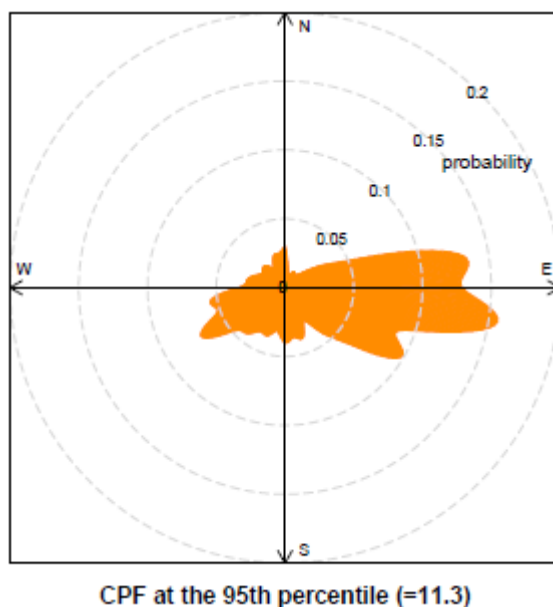
The Conditional Probability Function calculates the probability that in a particular wind sector the concentration of a species is greater than some specified value. The value specified is usually expressed as a high percentile of the species of interest e.g. the 75th or 90th percentile. CPF analysis is very useful for showing which wind directions are dominated by high concentrations and give the probability of doing so (example in Figure 1).

The CPF is defined as

$$CPF_{\Delta\theta} = m_{\Delta\theta} | C \geq x / n_{\Delta\theta}$$

Where $m_{\Delta\theta}$ is the number of samples in the wind sector θ having concentration C is greater than or equal to a threshold value x , and $n_{\Delta\theta}$ is the total number of samples from wind sector $\Delta\theta$. Thus, CPF indicates the potential for a source region to contribute to high air pollution concentrations. Conventionally, x represents a high percentile of concentration e.g. the 75th or 90th percentile. Therefore where you have experienced a high number of data points with values greater than your chosen threshold value, for a particular wind direction, you will have a higher probability value for that wind direction.

Figure 1: CPF plot of SO₂ concentrations at Marlybone Road



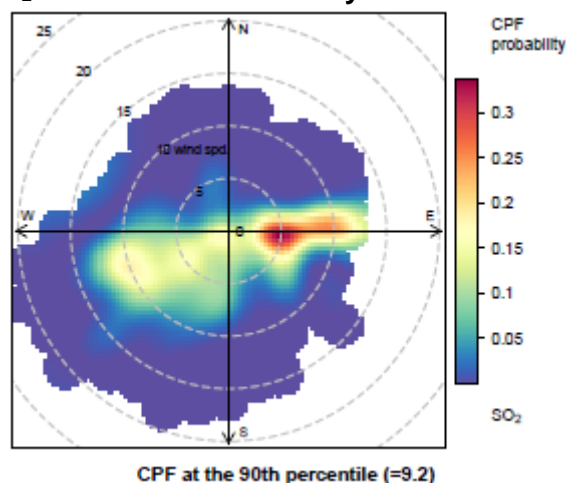
The conditional bivariate probability function (CBPF) couples ordinary CPF with wind speed as a third variable, allocating the observed pollutant concentration to cells defined by ranges of wind direction and wind speed rather than to only wind direction sectors (example in Figure 2).

It can be defined as:

$$CBPF_{\Delta\theta, \Delta u} = m_{\Delta\theta, \Delta u} | C \geq x / n_{\Delta\theta, \Delta u}$$

Where $m\Delta\theta, \Delta u$ is the number of samples in the wind sector $\Delta\theta$ with wind speed interval Δu having concentration C greater than a threshold value x , $n\Delta\theta, \Delta u$ is the total number of samples in that wind direction-speed interval.

Figure 2: Polar plot of SO_2 concentrations at Marylebone Road based on the CPF function



Therefore where you have experienced a high number of data points with values greater than your chosen threshold value, for a particular wind direction and wind speed, you will have a higher probability value for that wind direction and speed.

The extension to the bivariate case provides more information on the nature of the sources because different source types can have different wind speed dependencies. The use of a third variable can therefore provide more information on the type of source in question. It should be noted that the third variable plotted on the radial axis does not need to be wind speed, it could for example be temperature. The key issue is that the third variable allows some sort of discrimination between source types due to the way they disperse.

The scale of a CPF plots ranges from 0 – 1, from lowest to highest probability.

References

1. Carslaw, D.C. (2015). The openair manual — open-source tools for analysing air pollution data. Manual for version 1.1-4, King's College London.
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