



Study of Ambient Air Quality at Cannock

3 February 2020 – 17 June 2020

Report – AAM/TR/2020/10

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Executive summary

This report provides the results from the study of ambient air quality in the vicinity of Poplars Landfill Site, in Cannock. The Environment Agency's Ambient Air Monitoring Team (in National Permitting Services) carried out the study on behalf of the Environment Agency's West Midlands Area.

This report presents the measured levels of hydrogen sulphide (H_2S) and methane (CH_4). The levels of hydrogen sulphide are compared to the World Health Organisation (WHO) air quality guidelines.

Comparing the collected data from the monitoring at Cannock with the WHO guidelines showed that H_2S was well within health limits and was above the odour annoyance limit for 0.1% of the monitoring period (four occasions on the 5 February 2020). Looking at the period prior to the remediation work (3rd February - 12th February), levels of H_2S were above $7\mu\text{g}/\text{m}^3$ for 0.9% of the period.

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1 Introduction

The Environment Agency's Ambient Air Monitoring Team (AAM Team), on behalf of the Environment Agency's West Midlands area, carried out a study in the vicinity of the Poplars Landfill Site, in Cannock.

The study involves a programme of monitoring carried out between 3 February 2020 and 17 June 2020 (136 days).

The Ambient Air Monitoring Team's Mobile Monitoring Facility (MMF 6) was used to measure the ambient concentrations of pollutants. The reported pollutants are H₂S and CH₄.

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 H₂S 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 Location

The Ambient Air Monitoring team deployed its mobile monitoring facility (MMF 6) in the car park of the Newhall Farm Pub in Cannock (Figure 2.1). Poplars Landfill Site was at a bearing of $\sim 180^\circ$ - 260° from the monitoring site. There was also an anaerobic digester located on site at a bearing of $\sim 235^\circ$ from the monitoring site.

Figure 2.1: Aerial Photograph showing MMF monitoring location



A suitable monitoring site was required that:

- Allowed for the measurement of ambient concentrations that were representative of those experienced in the residential area where complaints had been received.
- Was located close to the site of interest, ideally in a direction downwind of the site and the prevailing wind direction, with no other sources in between or in line with the main site of interest.
- Was in an open location, away from tall buildings, so that representative wind speed and direction measurements could be collected.
- Offered an easily accessible location on a hard standing surface with access to mains power for deployment the MMF.

The monitoring site at Newhall Farm pub was chosen as it was within a residential area where complaints had been received and it met the requirements of a suitable monitoring location.

3 Monitoring Results

3.1 Meteorology

Wind speed and direction measurements were collected at the MMF site during the study. The sensor was mounted on a mast extending 8m from the top of the MMF trailer giving an overall height above ground of 10m. 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.

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. For the production of rose plots the wind direction data are resolved into 10° sectors for analysis and interpretation, therefore the uncertainty of each sector is $\pm 5^\circ$.

The frequency distribution of wind direction between 3 February 2020 and 17 June 2020 (136 days) is shown in Figure 3.1.1. The plot shows that over the period the dominant wind directions were from between 10° - 110° and 190° - 320° , with wind coming from these wind sectors 39% and 47% of the time respectively. The wind blew from the direction of Poplars landfill site (180° - 260°) 33% of the time. The wind speed frequencies are summarised in Table 3.1.1.

Figure 3.1.1: Wind rose (%)

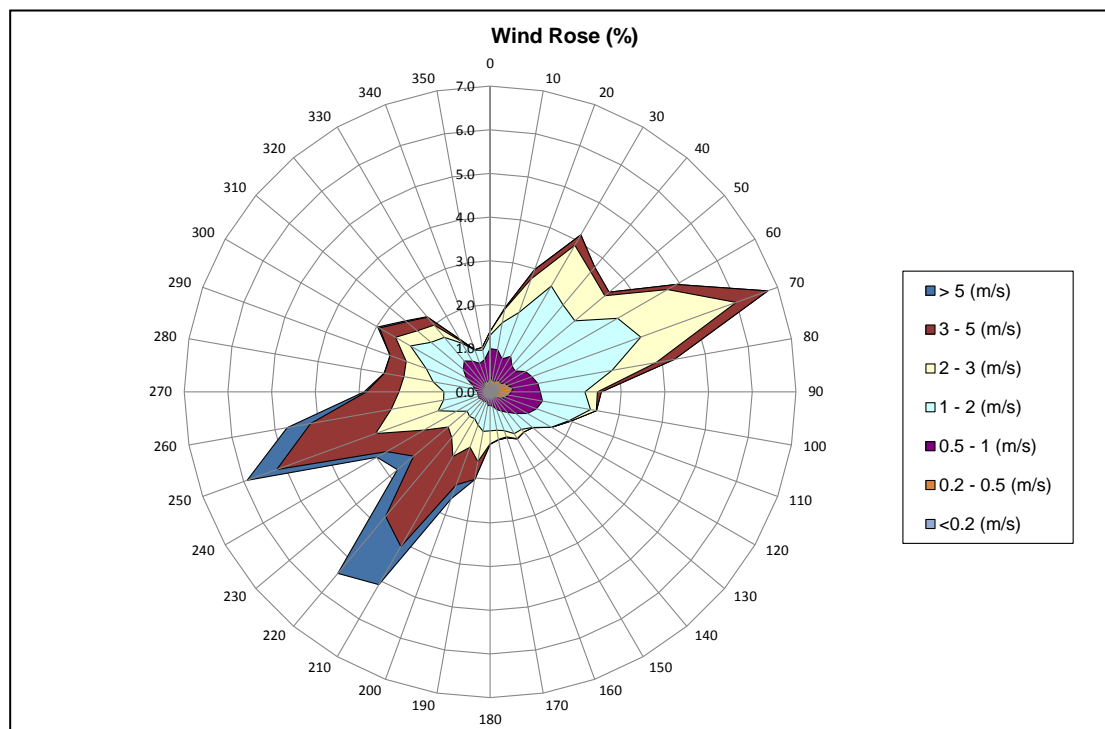
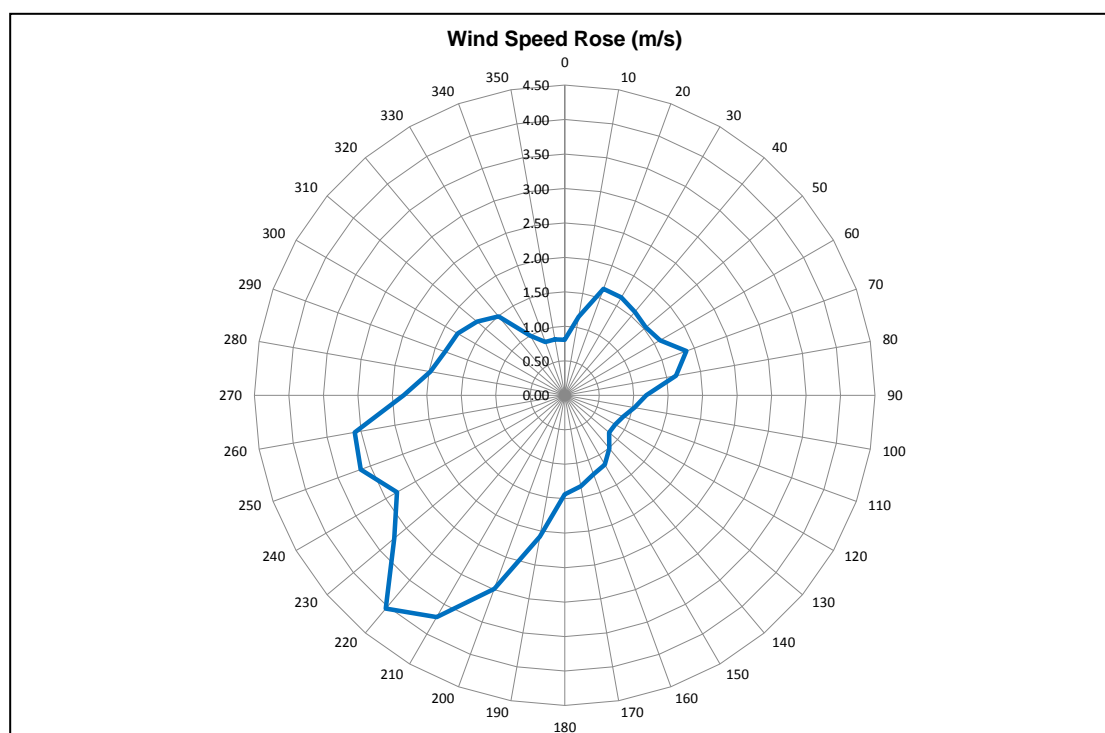


Table 3.1.1 Summary of wind speed frequencies.

Wind Speed (m/s)	Frequency of wind speed (%)
<0.2	0.82
0.2 – 0.5	7.06
0.5 - 1	15.7
1 - 2	33.1
2 - 3	20.7
3 - 5	17.4
>5	5.23
Total	100.00

A plot of mean wind speed against wind direction is shown in Figure 3.1.2. It can be seen that the highest average wind speed was greater than 3m/s and came from the wind direction 210° - 220°.

Figure 3.1.2: Wind speed rose



3.2 Hydrogen Sulphide (H₂S)

Between 3 February 2020 and 17 June 2020 (136 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%.

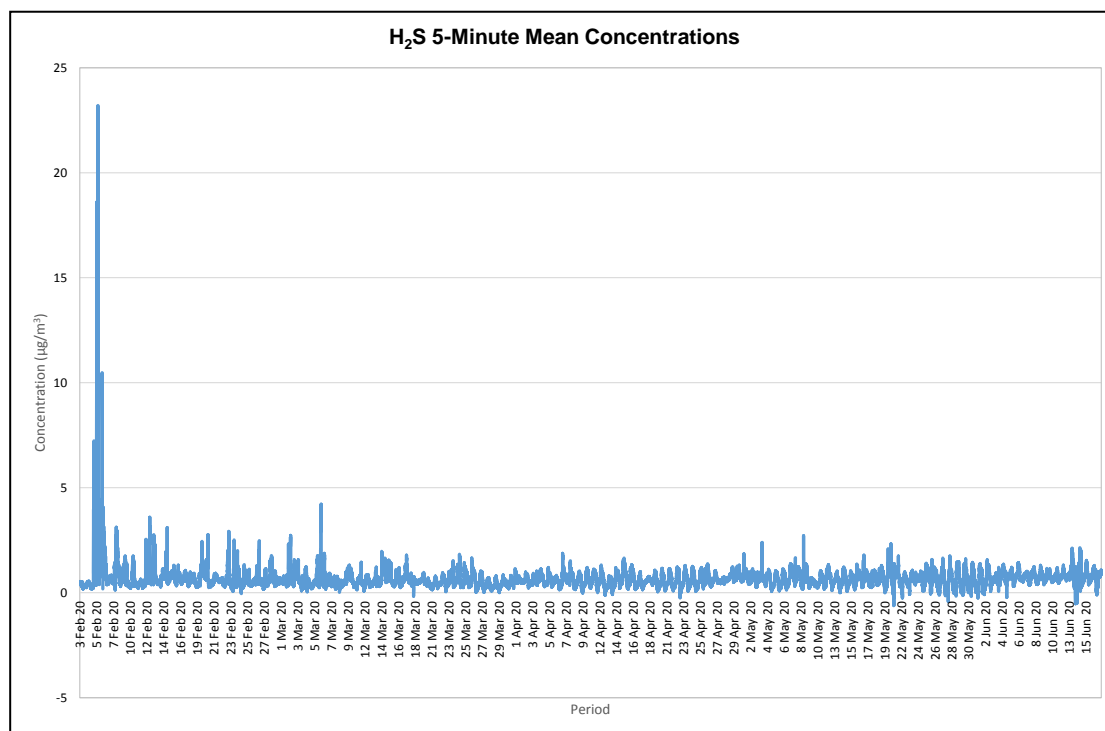
A time series plot of 5-minute mean concentrations of H₂S over the monitoring period is shown in Figure 3.2.1. The plot shows that levels were highest at the beginning of February, prior to the temporary geomembrane capping of the current tipping slopes of the landfill (completed on 13th/14th February). H₂S levels remained low after this period.

The slight undulation of the baseline between March – June 2020 is the result of increased temperature within the MMF due to the hot weather experienced during this period. This encompasses the period of lockdown for Covid19, where calibrations could not take place. However, calibrations resumed at the beginning of June and the analyser responded appropriately to the calibration and the data was deemed acceptable.

However, the low levels of H₂S and the undulation of the baseline due to temperature restricts the type of analysis that can be carried out on this data set, as data patterns are lost within the noise of the undulation. Therefore only pollution rose and percentile rose analysis of the H₂S data has been included in this report.

The average concentration over the monitoring period was 0.66µg/m³ and the maximum 5-minute mean concentration was 23.2µg/m³.

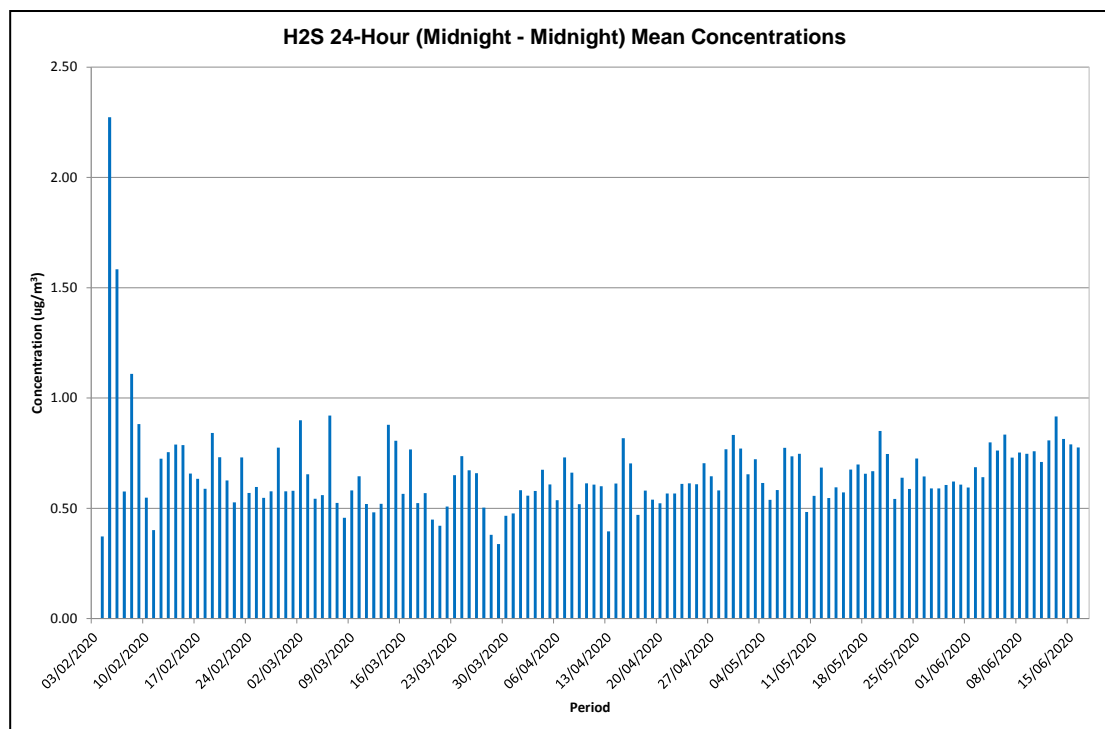
Figure 3.2.1: H₂S 5-minute mean concentrations at the monitoring site.



3.2.1 Comparison with WHO Guidelines

A time series plot of 24-hour mean H_2S concentrations at the monitoring site is shown in Figure 3.2.2. This data can be compared directly with the relevant WHO Guideline for Europe 2000. The highest recorded 24-hour mean was $2.27\mu\text{g}/\text{m}^3$, which is much lower than the $150\mu\text{g}/\text{m}^3$ limit set as a guideline by WHO, in the context of human health.

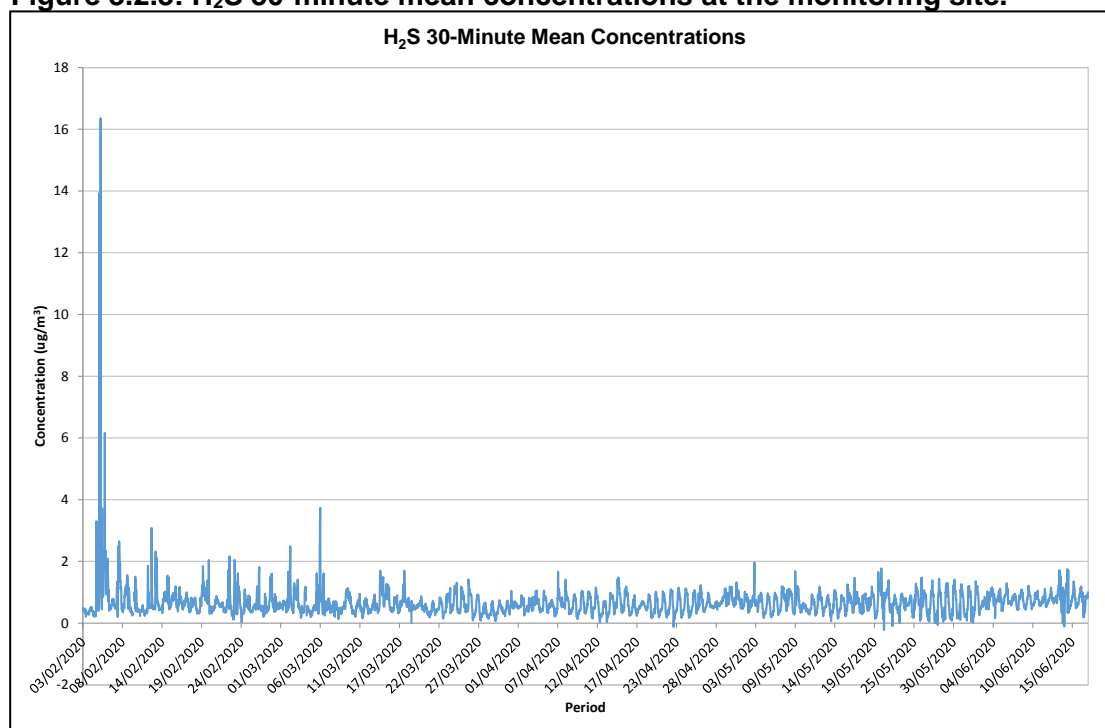
Figure 3.2.2: H_2S 24-hour (midnight – midnight) mean concentrations at the monitoring site.



A time series plot of 30-minute average H_2S concentrations measured over the period is shown in Figure 3.2.3. This data allows direct comparison with the WHO Guidelines for Europe 1987, which have set a guide level of $7\mu\text{g}/\text{m}^3$ above which substantial complaints about odour annoyance can be expected. Levels of H_2S were above $7\mu\text{g}/\text{m}^3$ for 0.1% of the monitoring period, on four occasions on the 5 February 2020, with the highest 30-minute mean being $16.4\mu\text{g}/\text{m}^3$.

Looking at the period prior to the remediation work (3rd February - 12th February), levels of H_2S were above $7\mu\text{g}/\text{m}^3$ for 0.9% of the period.

Figure 3.2.3: H₂S 30-minute mean concentrations at the monitoring site.



3.2.2 Directional Analysis

A radial plot of mean H₂S concentrations (µg/m³) against wind direction is shown in Figure 3.2.4. The plot shows that the highest concentrations of H₂S came from the wind directions between 200° - 210°, with average concentrations >1.0µg/m³. A likely source in this sector is the Poplar Landfill Site.

Figure 3.2.4: H₂S Pollution Rose, scale: 1.2µg/m³



An array of plots showing the contribution to H₂S loading at the monitoring site for different percentiles is shown in Figures 3.2.5. An explanation of percentile analysis is given in appendix E.

The plot shows that the contribution from the source between 200° - 210° (the direction of the landfill site) affects all the percentiles, which indicates that the source is relatively continuous and commonly affects H₂S concentrations at the monitoring site. Contribution from the source at 170° is only evident in the 99th percentile, which suggests that it is likely to have been a one off event.

The contribution from the source(s) between 90° – 110° is more evident in the lower percentiles, suggesting that the source(s) in this sector is relatively continuous, but does not cause appreciably high concentrations of H₂S at the monitoring site. This source can be seen more clearly in the conditional probability plot in Figure 3.2.6.

Figure 3.2.5: H₂S Percentile Rose

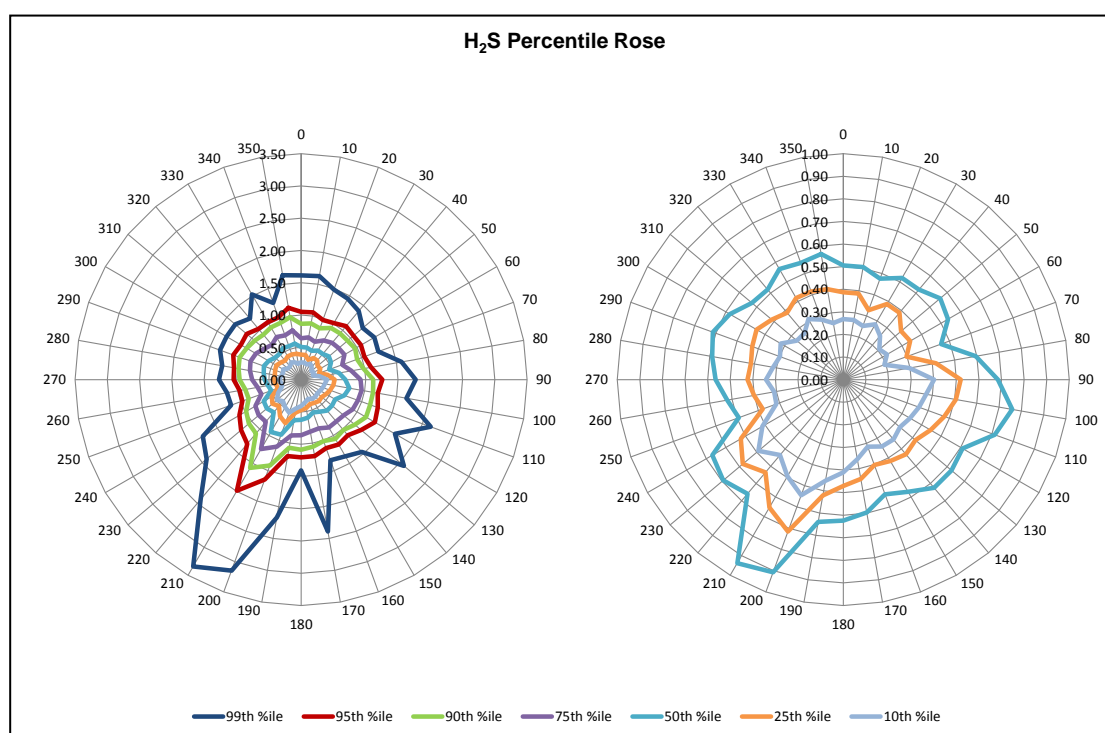
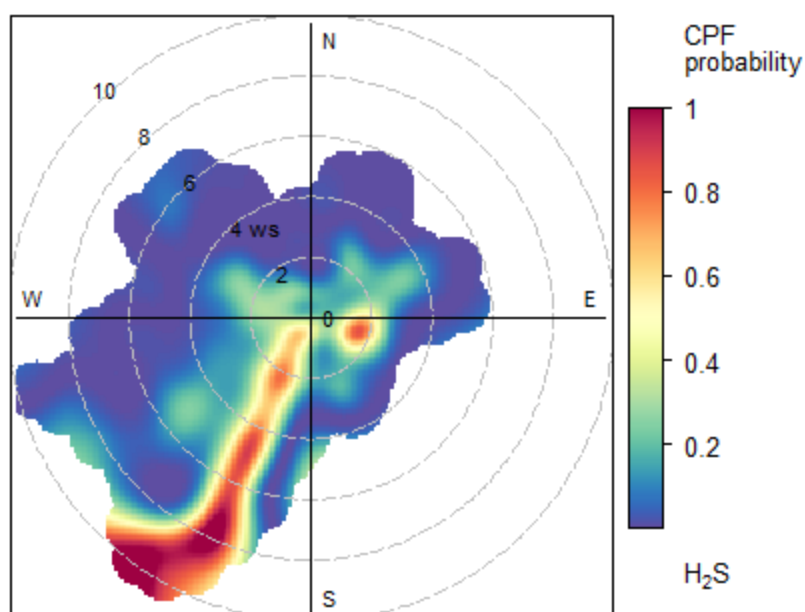


Figure 3.2.6 shows a conditional probability function plot for H₂S concentrations >75th percentile. The plot calculates the probability that H₂S concentrations would be greater than the 75th percentile value (0.82µg/m³) for a particular wind speed and wind direction. Further information about this method can be found in Appendix F.

Figure 3.2.6 shows that high concentrations (greater than the 75th percentile of all observations) are more likely to occur between 200° – 225° from the direction of the landfill site, but there is also a source between 85° – 125° at wind speeds ~1-2m/s.

Figure 3.2.6: H₂S conditional probability function plot for concentrations >75th percentile (0.82 µg.m⁻³)



CPF at the 75th percentile (=0.82)

3.2.3 Conclusions

Comparison of the H₂S data with the WHO guidelines for human health of 150µg/m³, as 24-hour mean concentrations, indicated that the air quality at the monitoring site was well within this guideline.

Comparison of the H₂S data with the WHO guideline for odour annoyance of 7µg/m³ (as 30-minute mean concentrations) indicated that the air quality at the monitoring site exceeded this guideline on 0.1% of the monitoring period (four occasions on the 5 February 2020) and therefore odour nuisance complaints could be expected during this period.

Pollution rose analysis indicates that the highest average H₂S concentrations measured at the monitoring site were seen when the wind was coming from between 200° - 210°. A likely source in this sector is the Poplars Landfill Site.

Percentile rose analysis suggested that the monitoring site was affected by both relatively continuous and intermittent sources of H₂S emissions.

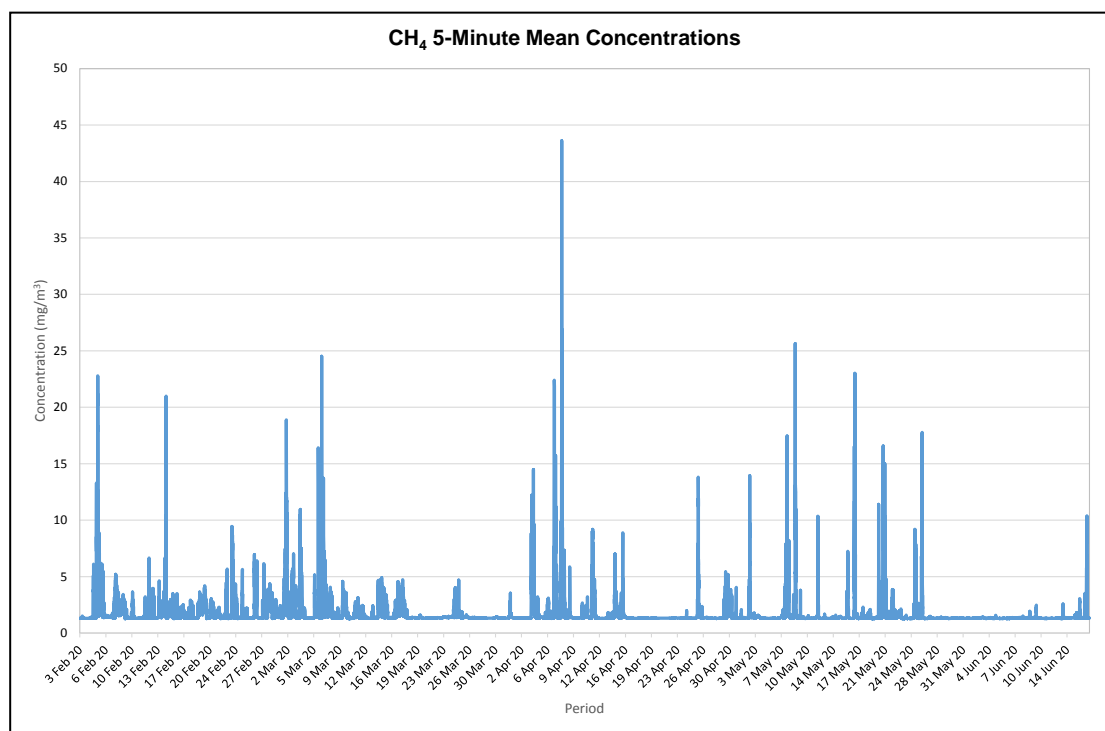
The probability of measuring higher H₂S concentrations (greater than the 75th percentile of all observations) was much more probable from wind directions 200° – 225° from the direction of the landfill site and 85° – 125°.

3.3 Methane (CH₄)

Between 3 February 2020 and 17 June 2020 (136 days) airborne CH₄ concentrations were measured at a height of 2m above ground. Details of the instrumentation and methodology are given in Appendix D. Successful data collection over the monitoring period was 99%.

The time series plot of 5-minute mean CH₄ concentrations (mg/m³) over the period is shown in Figure 3.3.1.

Figure 3.3.1: CH₄ 5-minute mean concentrations at the monitoring site



The average concentration over the period was 1.65mg/m³, which is slightly higher than the northern hemisphere background concentration of around 1.21mg/m³.

3.3.1 Directional Analysis

A radial plot of mean CH₄ concentrations against wind direction is shown in Figure 3.3.2. The highest average CH₄ concentration are seen for wind sectors 190° - 210°, with average concentrations >2.50mg/m³. A likely source in this sector is the Poplar Landfill Site.

An array of plots showing the contribution to CH₄ loading at the monitoring site for different percentiles are shown in Figure 3.3.3. The plot shows that the contribution from the source between 180° - 230° (the direction of the landfill site) affects all the percentiles, which indicates that the source is relatively continuous and commonly affects CH₄ concentrations at the monitoring site.

Contribution from the sources between 0° - 10°, 80° - 140°, 160°, 230° and 330°, are more evident in the higher percentiles. This suggests that there are intermittent

sources in these sectors that lead to elevated CH₄ concentrations. However, further analysis suggests that these additional sources may be the result of CH₄ concentrations building up under low wind speed, stable conditions. Figure 3.3.4 shows percentile plots for data where the wind speed was above 1m/s and below 1m/s.

Figure 3.3.2: CH₄ Pollution Rose, scale: 0 – 3.5 mg/m³

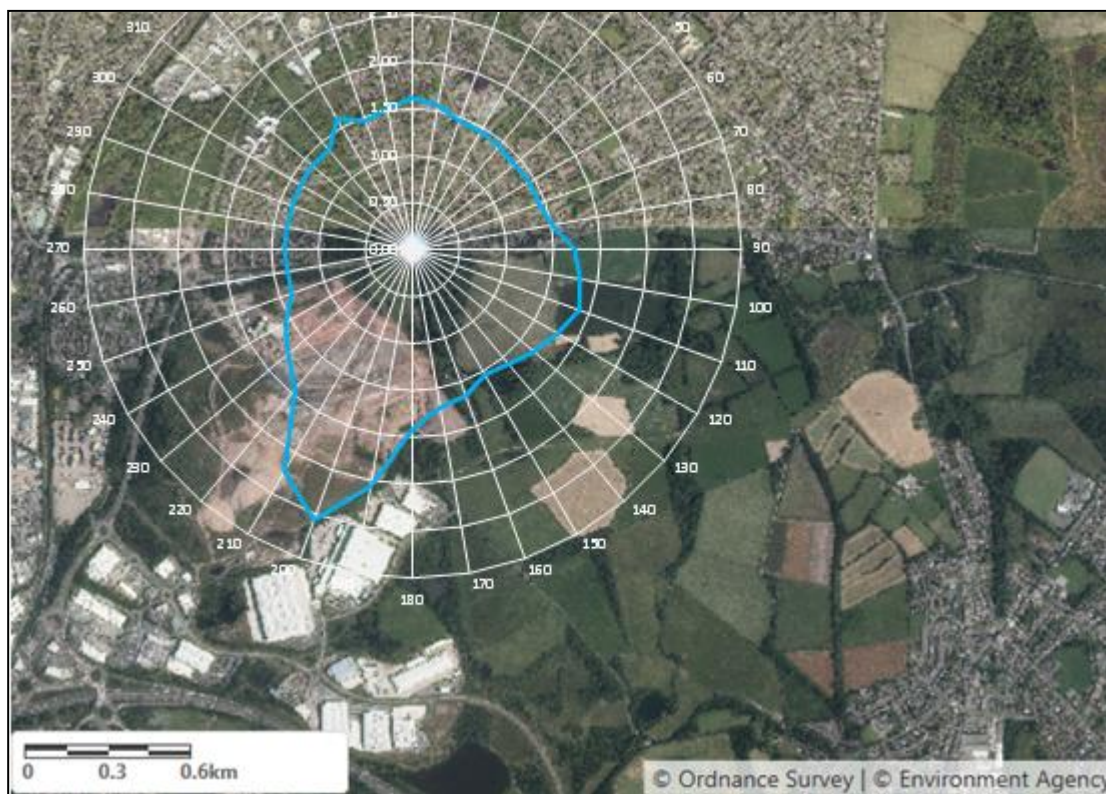
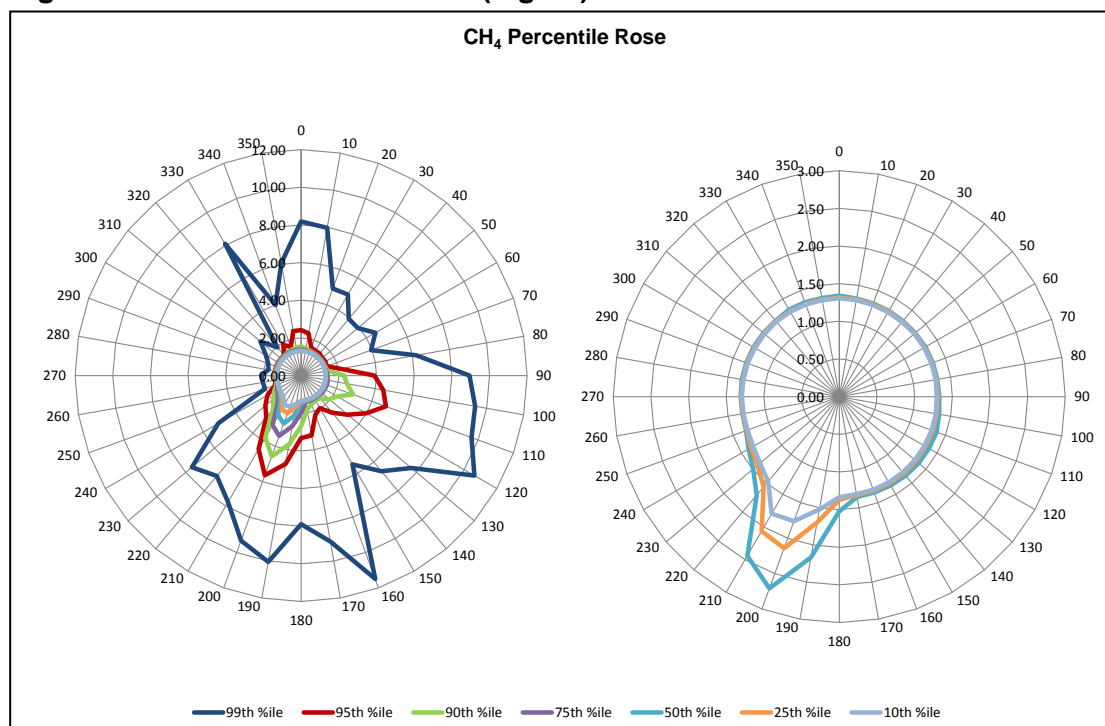


Figure 3.3.3: CH₄ Percentile Rose (mg/m³)



The plots show that the highest concentrations of CH₄ are seen at low wind speeds, when levels build up due to poor dispersion. The effect of poor dispersion is that it is harder to establish the direction of the original source of the CH₄, as high levels appear to come from a wide range of wind directions. When a source is only visible in data associated with low wind speeds it calls into question whether it is indeed a source or a figment of poor dispersion. The signal for the landfill site is evident in both data sets, but clearest in data with wind speeds above 1m/s. Therefore, it is possible that emissions from the landfill that build up under poor dispersion conditions are responsible for the bias in the higher percentiles of Figure 3.3.3 and that they are not the result of additional sources. This can be further examined by looking at the conditional probability plot in Figure 3.3.5.

Figure 3.3.4: CH₄ Percentile Rose (mg/m³)

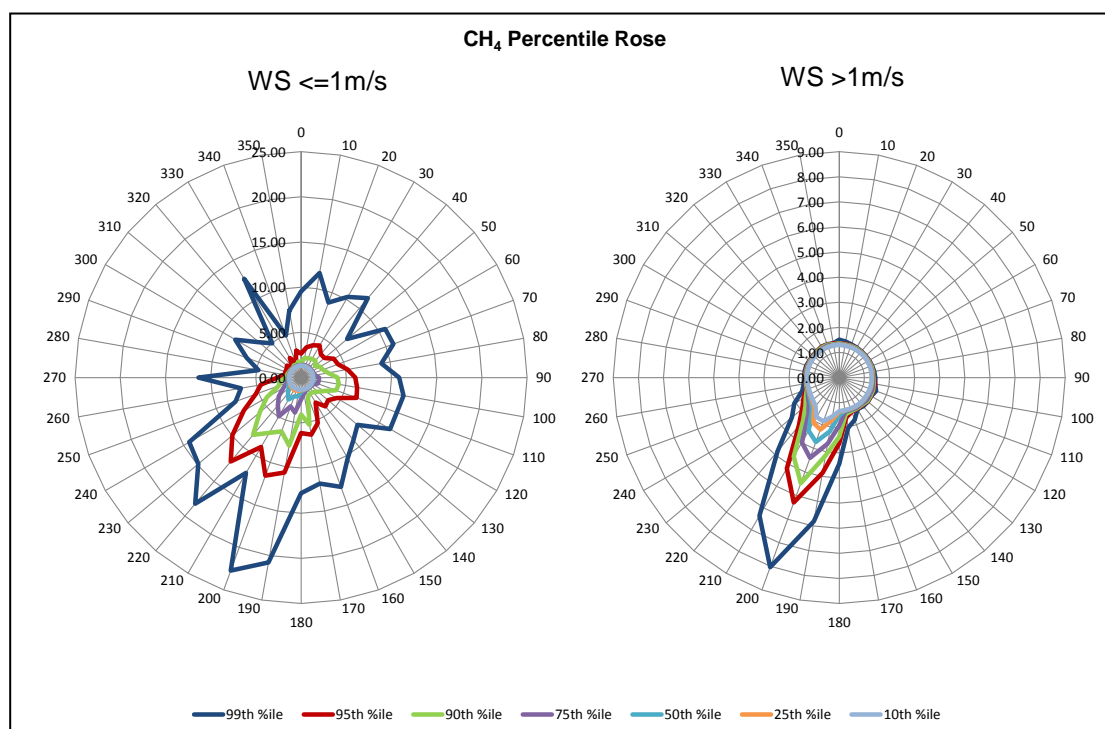
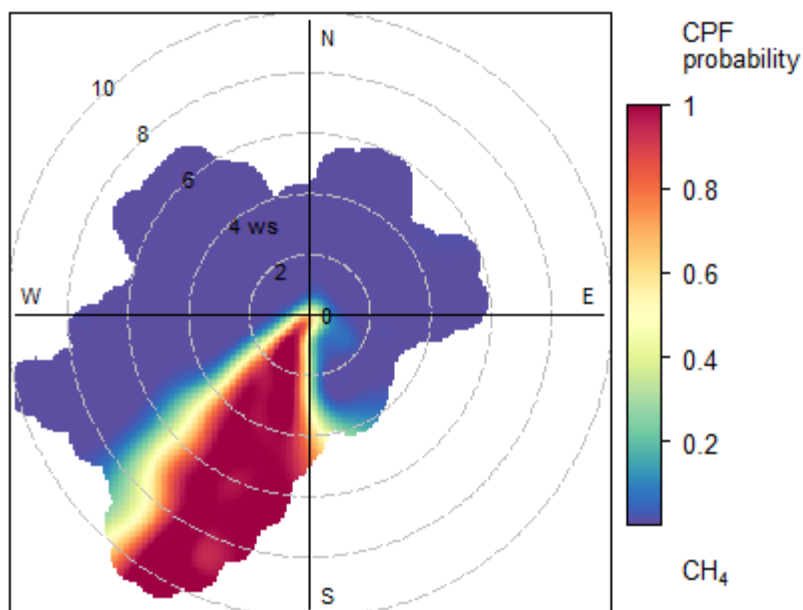


Figure 3.3.5 shows a conditional probability function plot for CH₄ concentrations >75th percentile. The plot calculates the probability that CH₄ concentrations would be greater than the 75th percentile value (1.4mg.m⁻³) for a particular wind speed and wind direction.

Figure 3.3.5 shows that high concentrations (greater than the 75th percentile of all observations) are more likely to occur between 175° – 230° from the direction of the Poplars landfill site, with very low probabilities of these concentrations being experienced for other wind directions. This suggests that the landfill site is the dominant source of CH₄ emissions at the monition site.

Figure 3.3.5: CH₄ conditional probability function plot for concentrations >75th percentile (1.4 mg/m³)



CPF at the 75th percentile (=1.4)

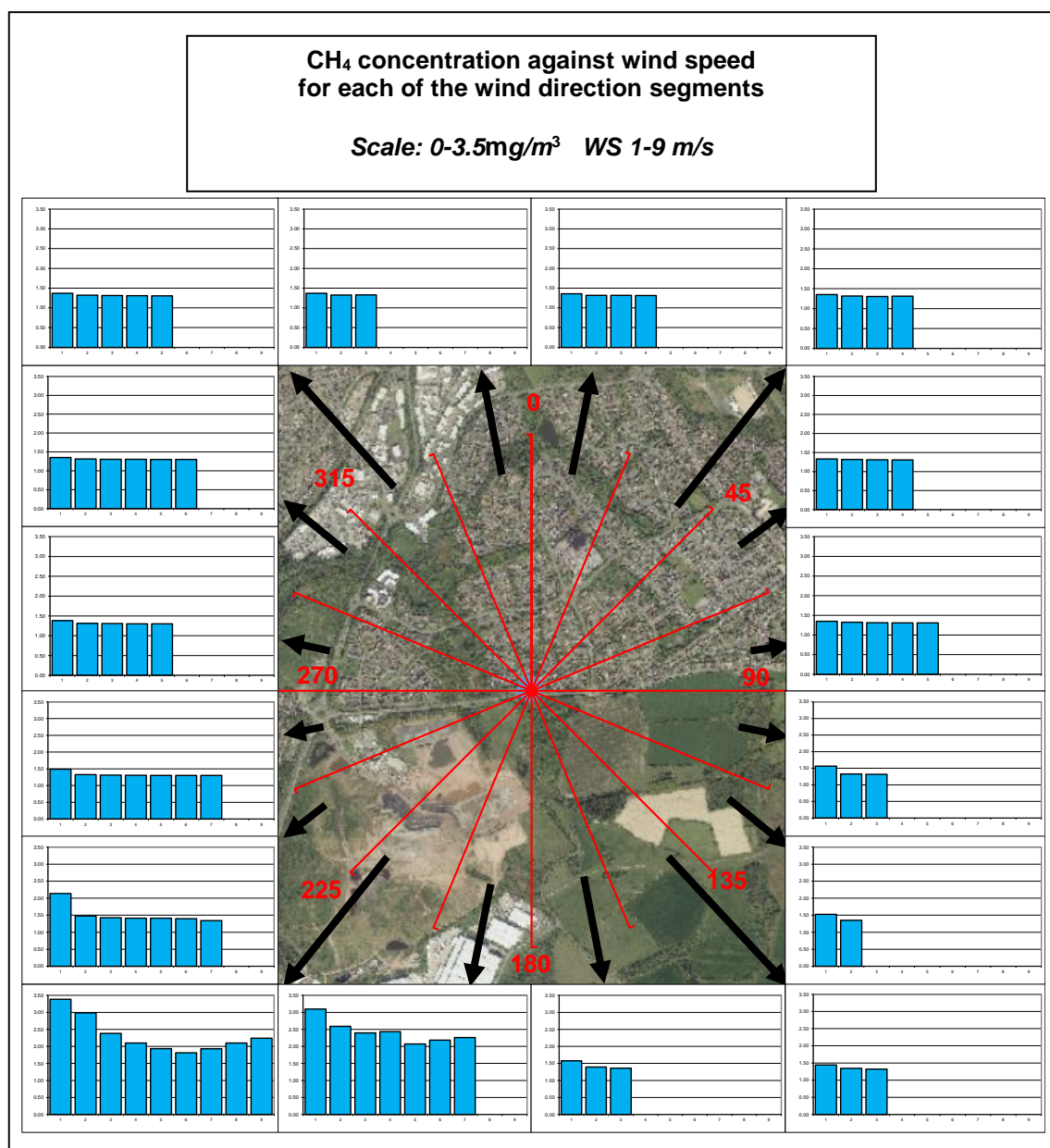
3.3.2 Wind Speed Variation

Wind speed plays an important role in the dispersion of air pollutants. Higher wind speeds generate more mechanical turbulence, which has the effect of distributing emissions more rapidly through the mixed boundary layer of the atmosphere. The relative concentrations measured at different wind speeds can provide insight to the nature of contributing sources.

Figure 3.3.6 shows the variation in CH₄ concentrations (mg/m³) with wind speed, for each 22.5° wind direction sector at the monitoring location.

The highest levels of CH₄ are seen in the sector 180° – 225°, with concentrations greatest at low wind speed, during poor dispersion conditions.

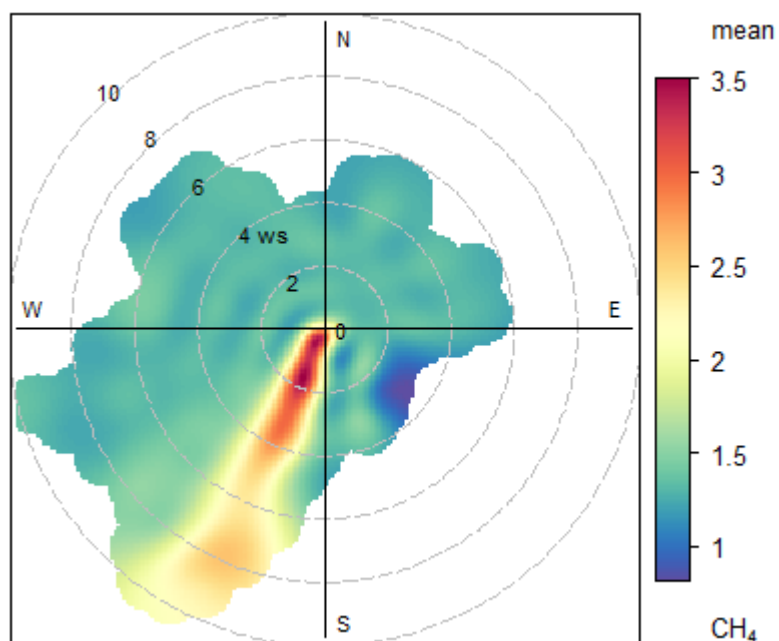
Figure 3.3.6: CH₄ Wind Speed Dependency Plots



Further information can sometimes be seen by plotting the data using Openair polar plots (Figure 3.3.7).

The plot shows a hot spot of CH₄ concentrations at the monitoring site at low wind speeds, suggesting that the highest levels are seen at relatively low wind speeds from the direction of the landfill site.

Figure 3.3.7: CH₄ Openair Wind Speed Dependency Plot (mg/m³)



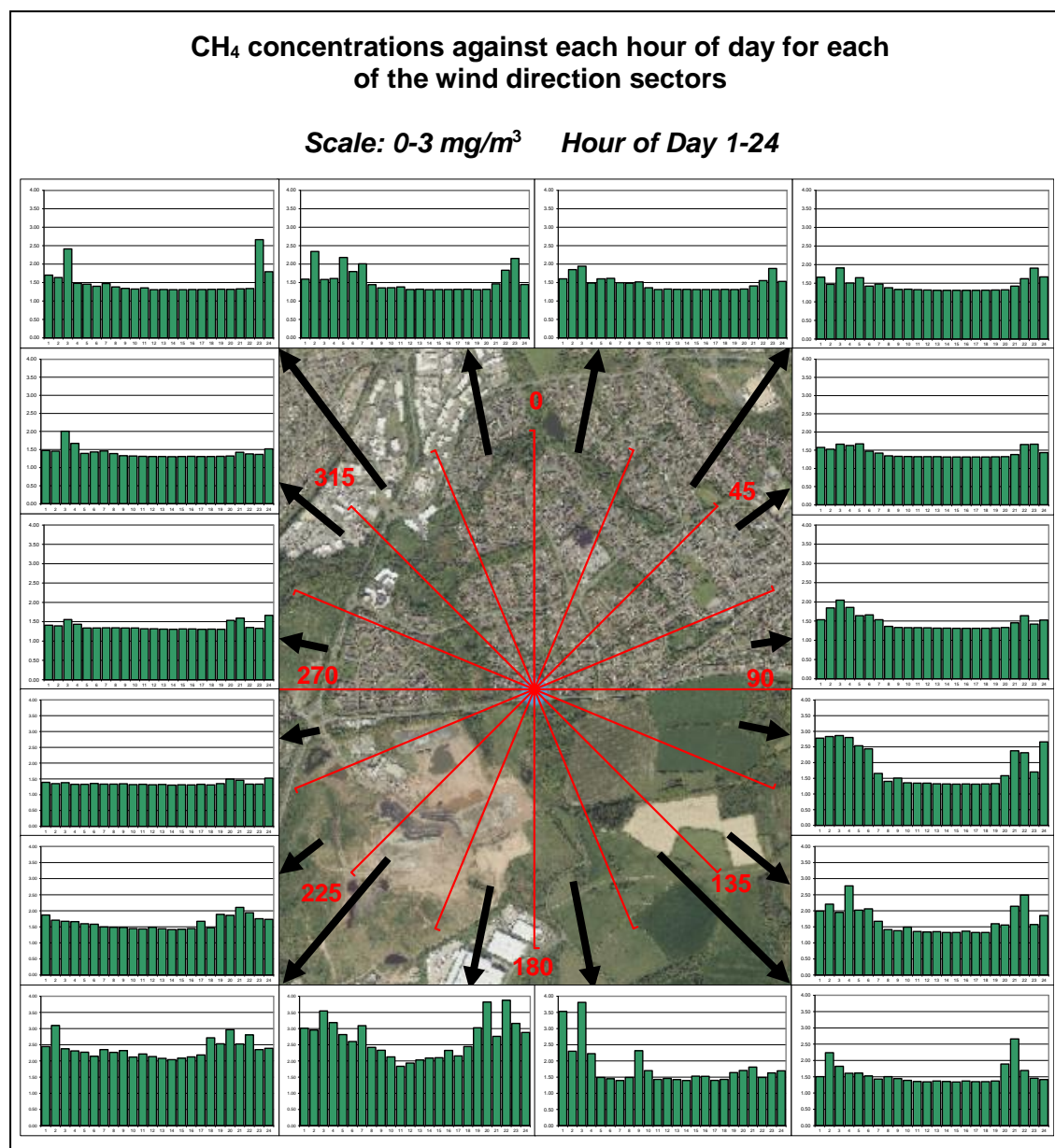
3.3.3 Diurnal Analysis

Consideration of the diurnal distribution of concentration levels can provide further useful information about the sources contributing to the ambient levels in each sector.

Figure 3.3.8 shows diurnal variation of average CH₄ concentrations (mg/m³) for each 22.5° wind direction sector.

The highest levels of CH₄ are seen in the plot for the wind sector 180° – 202.5°, the direction of the landfill site. The plot in this wind sector shows a rise in CH₄ concentration the early hours of the morning and at night. This is likely to be the result of poor dispersion resulting from stable conditions caused by nocturnal inversion layers trapping fugitive emissions close to the ground.

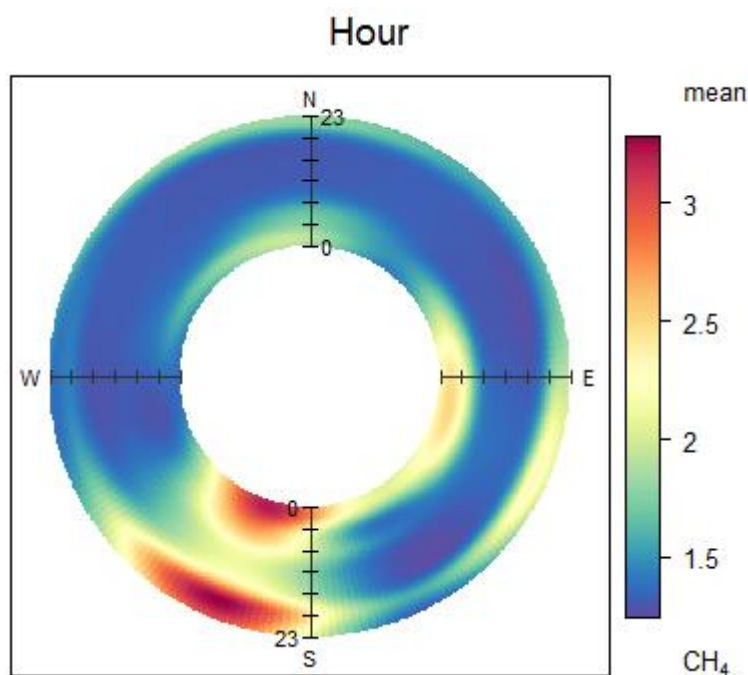
Figure 3.3.8 CH₄ diurnal plot



Diurnal Openair plots for CH₄ at the monitoring site are shown in Figure 3.3.9.

The CH₄ diurnal plot shows that the highest levels are observed during the evening and early morning between 175° – 225°, the direction of the landfill site.

Figure 3.3.9 CH₄ Openair Diurnal and Weekday Annulus Plots (mg/m³)



3.3.4 Conclusions

The mean CH₄ concentration over the monitoring period was 1.65mg/m³.

The directional analysis indicated that the highest average CH₄ concentrations were recorded at the monitoring site when the wind direction was from between 180° - 230°, the direction of the landfill site.

Percentile rose analysis suggested that the monitoring site was affected by a relatively continuous source of CH₄ emissions.

The probability of measuring higher CH₄ concentrations (greater than the 75th percentile of all observations) was much more probable from wind directions 175° – 230°, from the direction of the landfill site. This suggests that the landfill site is the dominant source of CH₄ emissions at the monition site.

Wind speed analysis suggests that the levels were highest at low wind speeds in the direction of the Poplars landfill site.

Consideration of the diurnal variation of CH₄ concentrations showed that the highest CH₄ concentrations were elevated overnight in the direction of the Poplars landfill site.

4 Conclusions

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 1.1).

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	24-hr (midnight- midnight)	150µg/m ³	0
	30-min	7µg/m ³	0.1

Comparing the collected data from the monitoring at Cannock with the World Health Organisation (WHO) guidelines showed that H₂S was well within health limits and was only above the odour annoyance limit for 0.1% of the monitoring period (four occasions on the 5 February 2020). Looking at the period prior to the remediation work (3rd February - 12th February), levels of H₂S were above 7µg/m³ for 0.9% of the period.

Table 4.2 summarises the average concentration for each 10° wind sector, colour coded from the lowest (dark green) to the highest (red) average concentration. This highlights the wind directions with the highest averages for each pollutant, but also emphasises correlations between the individual pollutants showing the wind directions of common sources.

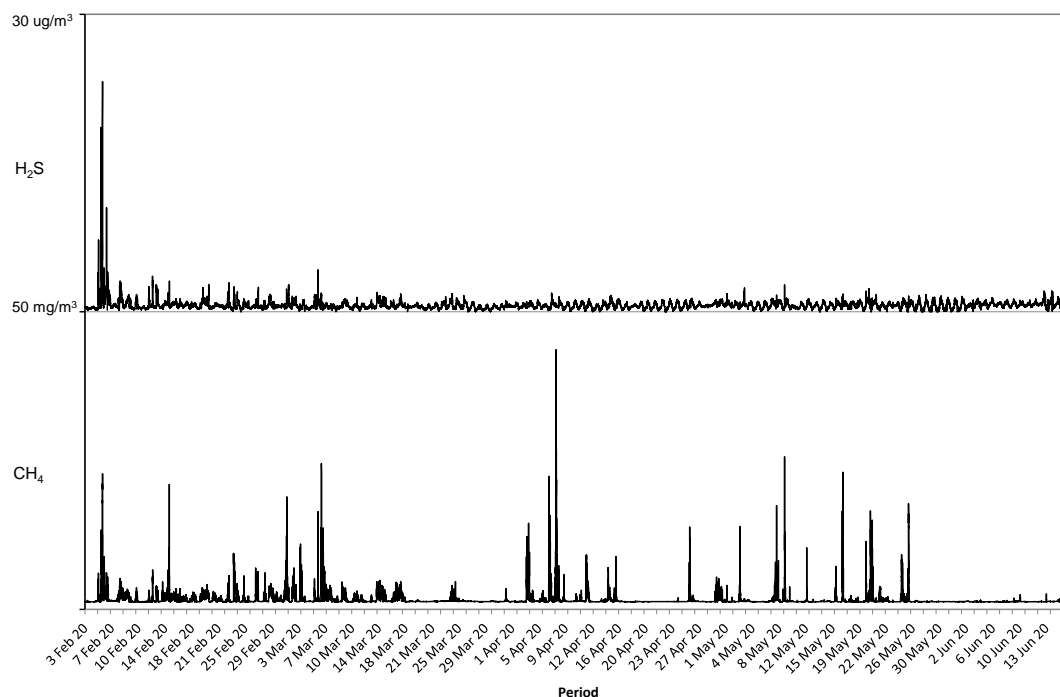
A time series plot for the pollutants monitored is shown in Figure 4.1.

Table 4.2 Summary of mean pollution roses.

<div>Low</div> <div>High</div>	Wind Direction (degrees)																	
	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180
H ₂ S																		
CH ₄																		

<div>Low</div> <div>High</div>	Wind Direction (degrees)																	
	190	200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360
H ₂ S																		
CH ₄																		

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



5 References

1. Department for Environment, Food and Rural Affairs (July 2007), *The Air Quality Strategy for England, Scotland, Wales and Northern Ireland*, (HMSO)

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 Cannock study was MMF6. The pollutants that can be measured using MMF6 are:

- hydrogen sulphide
- methane

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
- ambient air temperature
- relative humidity

All meteorological measurements are taken at an elevation of 8m above the ground and from positions where the wind approach was unobstructed. The temporal resolution of all logged meteorological 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 drift. |

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/m³ 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/m³ as a 24-hour average

Odour guideline: 7µg/m³ as a 30-minute average

The health guideline is based on the lowest level of H₂S to cause an adverse effect, which is 15mg/m³ (15,000µg/m³), 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/m³ (150µg/m³) over a 24-hour averaging time is the result.

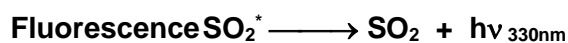
The high protection factor applied to create the guideline for health is a result of the marked toxicity of H₂S with increasing concentration above the first observable adverse effect.

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 is the absorption coefficient of SO₂, x is the path length, and (SO_2) the concentration of SO₂. When the SO₂ 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 SO₂. The PMT transfers the light energy into an electrical signal, which is directly proportional to the light energy in the sample stream being analysed.

A 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

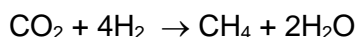
1. 'Hydrogen Sulphide: General Information', Public Health England, Toxicology Department, CRCE, PHE 2009 (version 1)
2. World Health Organisation (2000), *WHO Air Quality Guidelines for Europe*
3. 'Model T101 UV Fluorescence H₂S Analyser', User Manual, Teledyne Advanced Pollution Instrumentation, August 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, lakes and landfills. This microbial degradation of organic matter may be written:



Methane is also produced by enteric fermentation in mammals and other species.

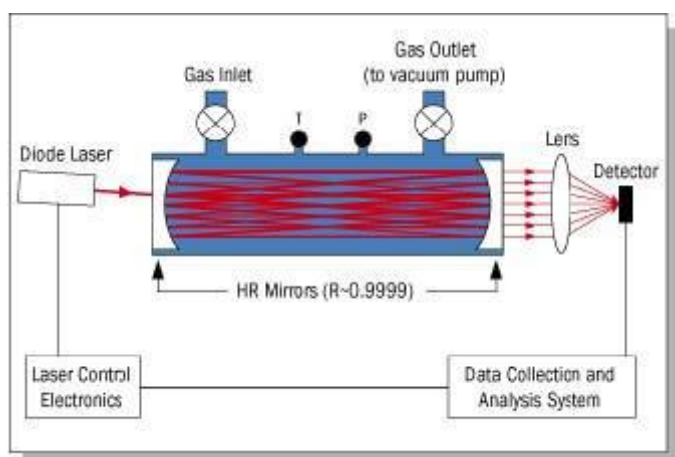
Until the late 1970s, it was accepted that the background concentration of methane was in the range of 1.4 – 1.6 ppm, since then ambient levels have risen to a background norm of approximately 1.8ppm. The increase in methane background concentrations is mainly due to an increase in the emissions from 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 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. LGR’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. Los Gatos Economical Ammonia Analyser User Manual.

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 formulas,

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

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 average 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.

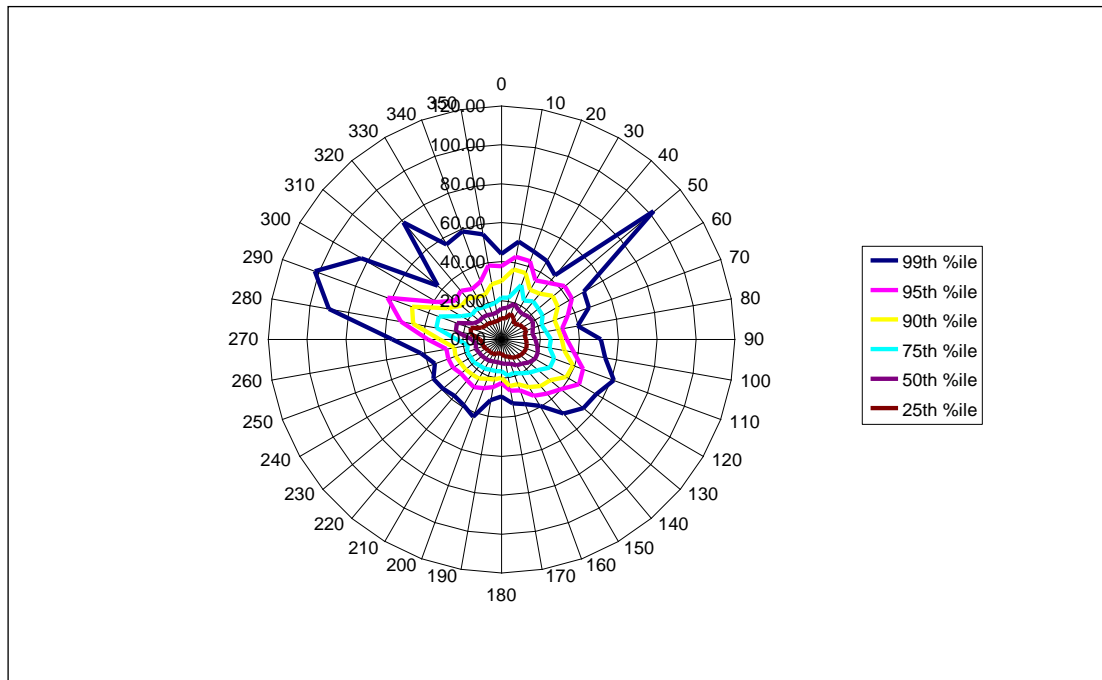


Figure 2 - shows a bias at 260° that is only evident in the 99th percentile.

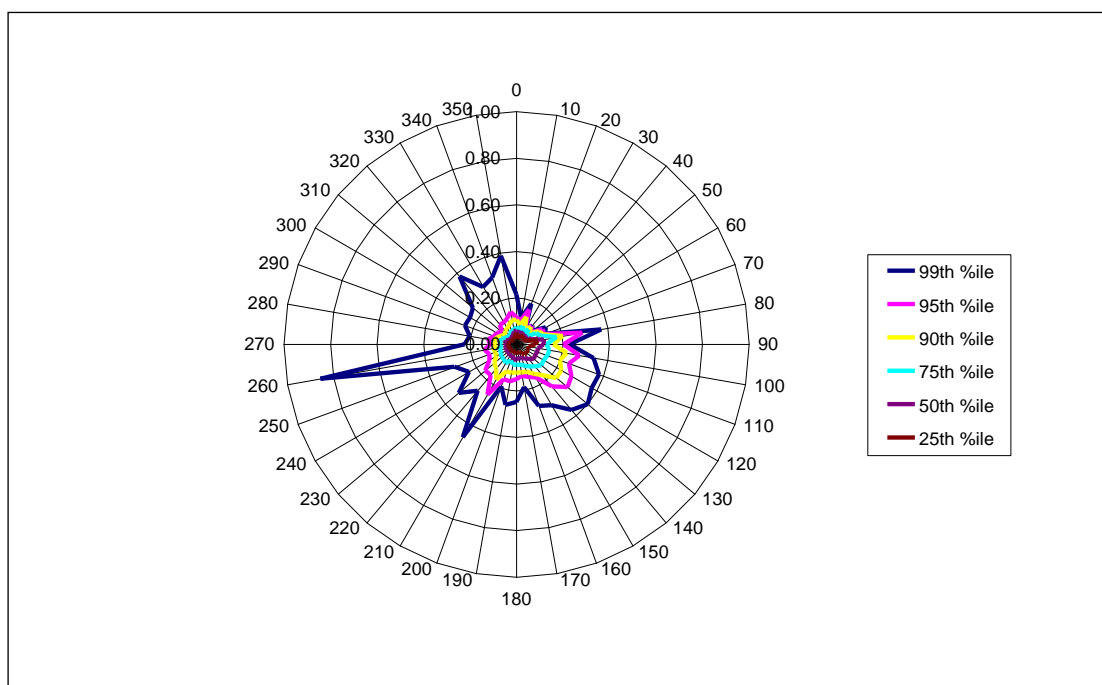
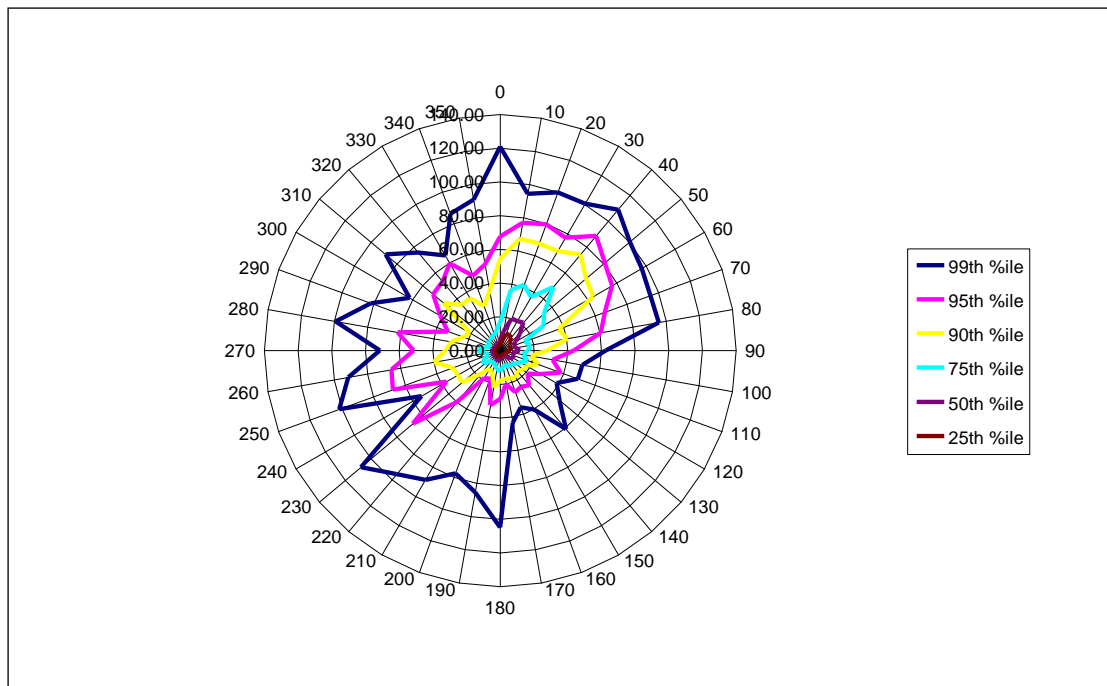


Figure 3 - shows a bias between 20° – 50° that is only evident in the lower percentiles.



Appendix F Conditional Probability Function (CPF) plots

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).

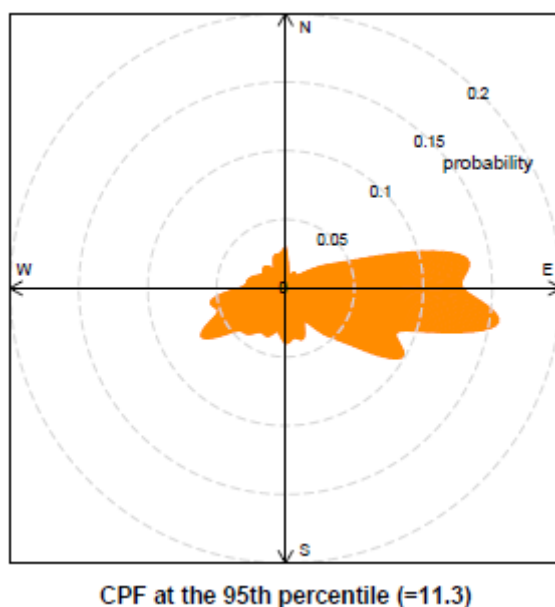
The CPF is defined as

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

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



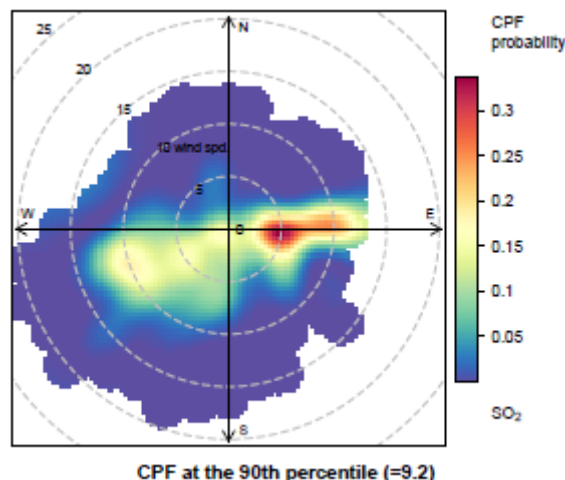
The conditional bivariate probability function (CBPF) couples ordinary CPF with wind speed as a third variable, allocating the observed pollutant concentration to cells defined by ranges of wind direction and wind speed rather than to only wind direction sectors (example in Figure 2).

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 SO₂ 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.
2. Uria-Tellaetxe, I. and D. C. Carslaw (2014). "Conditional bivariate probability function for source identification". In: *Environmental Modelling & Software* 59, pp. 1–9. DOI: 10.1016/j.envsoft.2014.05.002 (cit. on pp. 125, 135, 136).

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